



Theoretical calculations with spin orbit effects of the diatomic molecules YS, YN, ZrS, ZrN

Ayman Farhat

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TITRE :

**Calculs théoriques avec le couplage spin orbitales pour les molécules diatomiques YS, YN, ZrS,
et ZrN**

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I would like to dedicate this thesis to my loving parents ...

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

Theoretical Calculations with Spin Orbit Effects of the Diatomic Molecules

YS, YN, ZrS, ZrN

Abstract

This dissertation is dedicated to the *ab initio* study of the electronic structures of the polar diatomic molecules YN, YS, ZrN, and ZrS. The identification of these molecules in the spectra of stars as well as the lack in literature on the electronic structures of these molecules motivated the present study. Theoretical calculations are useful in this respect since they can provide important data for the properties of the ground and excited electronic states that are not available from experimental means. In the present work the *ab initio* calculations were performed at the complete active space self-consistent field method (CASSCF) followed by multireference single and double configuration interaction method (MRSDCI). The Davidson correction noted as (MRSDCI+Q) was then invoked in order to account for unlinked quadruple clusters. The calculations were performed on two stages in the first spin orbit effects were neglected while in the second type of calculations spin orbit effects were included by the method of effective core potentials. All of the calculations were done by using the computational physical chemistry program MOLPRO and by taking advantage of the graphical user interface Gabedit. In the present work potential energy curves were constructed and spectroscopic constants computed, along with permanent electric dipole moments, internal molecular electric fields, and vibrational-rotational energy structures. We detected in the ZrS molecule several degenerate vibrational energy levels which can be used to search for possible variations of the fine structure constant α and the electron to proton mass ratio μ in three S-type stars, named Rand, RCas, and χ Cyg. A comparison with experimental and theoretical data for most of the calculated constants demonstrated a good accuracy for our predictions giving a percentage relative difference that ranged between 0.1% and 10%. Finally, we expect that the results of the present work should invoke further experimental investigations for these molecules.

Key Words

Ab initio Calculations, multireference configuration interaction, diatomic molecules, spin orbit effects, spectroscopic constants, fine structure constant, electric dipole moment of the electron.

Calculs théoriques avec le couplage spin orbitales pour les molécules diatomiques YN, YN, ZrS, et ZrN

Abstrait

Cette thèse est consacrée à l'étude *ab initio* des structures électroniques des molécules diatomiques polaires YN, YS, ZrN, et ZrS. Cette étude est motivé par le manque d'informations dans la littérature sur la structure électronique de ces molécules, alors qu'elles ont clairement été identifiées dans le spectre de certaines étoiles. Des calculs théoriques sont ainsi nécessaire puis qu'ils peuvent fournir d'importantes informations quant aux propriétés des états électroniques fondamentaux et excités qui ne sont pas accessibles expérimentalement. Dans ce travail les calculs *ab initio* ont été effectués par la méthode du champ auto-cohérent de l'espace actif complet (CASSCF), suivie par l'interaction de configuration multiréférence (MRSDCI). La correction de Davidson, notée (MRSDCI+ Q), a ensuite été appliquée pour rendre compte de clusters ou agrégats quadruples non liés. Les calculs ont été effectués selon deux schémas. Dans le premier les effets spin-orbite ont été négligés alors que dans le second les effets spin-orbite ont été inclus par la méthode des potentiels de noyau efficaces. Tous les calculs ont été effectués en utilisant le programme de calcul de chimie physique MOLPRO et en tirant parti de l'interface graphique Gabedit. Les courbes d'énergie potentielle ont été construites et des constantes spectroscopiques calculées, ainsi que les moments dipolaires électriques permanent, les champs électriques moléculaire intenses et les structures énergétiques de vibration-rotation. Nous avons détecté dans la molécule ZrS plusieurs niveaux vibrationnels dégénérés ceux-ci peuvent être utilisés pour rechercher les variantes possibles de la constante de structure fine α et du rapport de masse μ de l'électron par rapport au proton dans trois étoiles de type S, du nom de Rand, les RCas, et χ Cyg. La comparaison des données expérimentales et théoriques pour la plupart des constantes calculées a montré une bonne précision pour nos prédictions avec une différence relative (en pourcentage) qui varie entre 0,1% et 10%. Ces résultats devraient ainsi mener à des études expérimentales plus poussées pour ces molécules.

Mots-Cles

Ab initio Calculations, Multireference configuration interaction, Diatomic molecules, Spin orbit effects, Spectroscopic constants, Fine structure constant, Electric dipole moment of the electron.

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Introduction

In recent years, there has been a growing interest in the electronic structure of polar diatomic molecules, particularly due to their importance in astrophysics [1], ultra cold interactions [2], chemistry [3], quantum computing [4-6], precision measurements [7] and metallurgy [3]. The recent advancements in computational sciences, have lead to the surge of interest in using molecules for experimental precision measurements, especially where they offer new properties that are not available from atoms and atomic ions. Indeed, several diatomic molecules have been suggested as model systems to test one of the fundamental physical concepts of the standard model (SM), the constancy of physical laws and the structure of fundamental interactions. Diatomic molecules such as Cs_2 [8], CaH , MgH , CaH^+ [9, 10], Cl_2^+ , IrC , HfF^+ , SiBr , LaS , and LuO [11], that have a near cancellation between the hyperfine structure and rotational intervals or between the fine structure and vibrational intervals have been proposed as model systems to test any spatial and temporal variations in two fundamental constants of the standard model, the fine structure constant α and the electron to proton mass ratio μ . Other polar diatomic molecules such as HfF^+ [12], HI^+ [13], YbF [14], PbO [15], ThO [16], ThF [16], and BaF [17] have been also suggested as laboratory candidates to search for the electric dipole moment of the electron (eEDM). A fundamental property, whose existence, shall provide an evidence of CP-violation (charge conjugation and parity) in lepton particles, with deep implications for our understanding of particle physics and cosmology [18, 20]. In this regard, diatomic molecules are very promising, particularly due to their large internal electric field $E_{\text{mol}} \approx 10^9$ V/cm, which is 4 to 5 orders of magnitude larger than any typical laboratory field in an EDM experiment [19]. In quantum computing, the use of polar arrays of trapped diatomic molecules as qubits looks very promising, particularly due to the feasibility by which such

simple systems may be scaled up to form large networks of coupled qubits [20-33]. Many linear molecules that have a variety of long lived internal electronic states have been proposed as a mean to address and manipulate qubit states $|0\rangle, |1\rangle$ [34]. Another promising new approach for realizing a quantum computer is based on using the vibrational states of molecules to represent qubits [35]. In this approach, quantum logic operations are performed to induce the desired vibrational transitions [36], where by using more vibrational states it may be possible to represent quantum information units having more than two qubit states (i.e. $|0\rangle, |1\rangle, |2\rangle, |3\rangle \dots$) [36]. In spectroscopic studies, the electronic structure of transition metal diatomic molecules should form a viable tool to test for the abundance of transition metal diatomics in the spectra of stars [37, 42]. Many transition metal diatomic oxides, sulfides and nitrides have been detected in the spectra of S and M type stars [43, 44]. Precise spectroscopic data are necessary for a meaningful search for these molecules in complex stellar spectra. In industrial processes such as catalysis and organometallic chemistry, Transition metal nitrides are important in the fixation of nitrogen in industrial, inorganic and biological systems [45, 46]. In high temperature material applications, within the group of refractory metal nitrides (Ti, Zr, Hf, Nb) titanium and zirconium nitrides are the most promising hardening additives, which are used for raising the high-temperature strength of sintered molybdenum and provide high enough ductility parameters at a temperature up to 2000°C [47]. In ultra-cold interactions the recent experimental achievements in producing an ultra-cold sample of the heteronuclear diatomic molecule SrF by researchers at Yale [48] offers a new possibility for producing ultra-cold samples of several heteronuclear diatomics as the transition metal diatomics of interest in the present work. Such achievements in ultracold techniques on new molecules are hindered by the lack in the spectroscopic studies of their electronic structures. In these respects, theoretical investigations for the spectroscopic properties of heteronuclear diatomic molecules are extremely useful in any future production of ultracold samples of heteronuclear diatomic molecules. Transition metal diatomics represent simple metal systems where d electrons participate in the bonding [49]. These molecules provide models for understanding the bonding and reactivity in transition metal systems [50]. The spectroscopic study of transition metal diatomics is difficult particularly due to the high density of low-lying electronic states associated with partially occupied d orbitals [51, 52].

Having seen that the electronic structure of heavy transition metal polar diatomic molecules is an active area of research with many applications in several areas of science, we decided in the present work to investigate the electronic structure of the mono-nitrides and mono-sulfides of the transition metals of group III and IV, Yttrium and Zirconium. Owing to their unfilled 4d shells the transition metals of group III and IV have a complex electronic structure. Their spectra is less daunting than other transition metals towards the middle of the periodic table. The metal atom often has many unpaired electrons that can produce a large number of low-lying electronic states with high values of spin multiplicity and orbital angular momentum, as well as large spin orbit interactions. These electronic states may perturb one other, thereby complicating their spectra and making the experimental analysis very difficult. Theoretical calculations are plagued with similar problems as it is hard to predict the energy order and properties of the low-lying electronic states. Electronic correlation effects become important when there are many unpaired electrons and so these molecules provide a challenge for *ab initio* calculations. Despite these difficulties, most of the 4d transition metal monoxides and monocarbides have been well studied partly due to their importance in astrophysics and as models in understanding the chemical bonding in simple metal systems. In contrast, little data are available for the corresponding transition metal nitrides and sulfides (MN, MS).

In this work, we perform *ab initio* calculations for the electronic structure of the mono-nitrides and mono-sulfides of Yttrium and Zirconium (YS, YN, ZrN, and ZrS). Relativistic spin orbit effects were included by the method of effective core potentials (ECP). The potential energy curves (PEC) for the ground and excited electronic states were constructed as a function of the internuclear distance R . Then by fitting the calculated potential energy curves in to a polynomial in R several spectroscopic constants were calculated, such as the transition energy T_e relative to the ground state, the harmonic vibrational frequencies ω_e , the equilibrium internuclear distances R_e , and the rotational constants B_e and D_e . Then based on the calculated PECs vibro-rotational calculations were performed for the vibrational and rotational energy levels of each molecule. Various physical properties were also computed, such as the permanent electric dipole moment, and the internal molecular electric field. The bonding nature in each of the investigated molecules was also analyzed in terms of molecular orbital configurations. A comparison is made between the calculated values of the present work for the bond distances, vibrational frequencies

and dipole moments to the remaining series of 4d transition metal mono-nitrides (ZrN, NbN, ..., CdN) and mono-sulfides (ZrS, NbS, ..., CdS). The comparison between the different species of transition metal mono-nitrides (MN) and mono-sulfides (MS) should give an idea on the variation of molecular properties across the series of 4d transition metals in the periodic table.

Throughout this thesis, we try to validate our theoretical results by comparing the calculated values of the present work to the experimental and theoretical values in literature. The comparison between the values of the present work to the experimental and theoretical results shows a very good agreement. The small percentage relative error, of less than 10% reported in our calculations for all of the molecular constants, reflects the nearly exact representation of the true physical system by the wave functions used in our calculations. The extensive results in the present work on the electronic structures with relativistic spin orbit effects of the molecules YN, ZrN, YS, and ZrS are presented here for the first time in literature. A preprint for the results of the present work has been requested by an experimental research group working at Yale under the supervision of Prof. David Demille.

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Chapter One

Many Body Problems in Atoms and Molecules

Computational physical chemistry is primarily concerned with the properties of single molecules and with their arrangement in periodic trends, homologous series, functional groups, and crystals. Theoretical calculations have emerged as an important tool for investigating a wide range of problems in Molecular Physics, Material Science and Chemistry. Within the recent development of computational methods and more powerful computers, it has become possible to solve physical and chemical problems that only a few years ago seemed far beyond the reach of a rigorous quantum-mechanical treatment.

In this section, we turn our attention to the development of approximations which are more accurate than the independent particle model and can take account of electron correlation effects. The Hartree-Fock theory followed by the methods of Complete Active Space Self Consistent Field (CASSCF) and Multi-reference Configuration Interaction (MRCI) play a pivotal role in the development of approximate treatments of correlation effects. A key feature of these calculations is the use of the method of second quantization. We therefore start by introducing the second quantization formalism in quantum mechanics.

I. Second Quantization and Many Body Problems

Second quantization forms the basis of a very powerful technique for developing a theoretical description of many-body systems. Many-particle physics is formulated in the second quantization representation, which is also known by the occupation number representation. In the second quantization formalism theoretical expressions are written in terms of matrix elements of

operators in a given basis and are manipulated using the algebra of creation and annihilation operators.

In this section, we briefly describe the second quantization formalism giving sufficient details for the application which we describe. First, let us observe that the Schrödinger equation can be easily written down for an atom or, more particularly, a molecule of arbitrary complexity. The difficulty is usually said to lie not in writing down the appropriate eigenvalue problem but in the development of accurate approximations to the solutions of this molecular Schrödinger equation. However, the Schrödinger equation for a system of arbitrary complexity has another problem associated with it, namely, it applies to a fixed number of particles. In other words the Schrödinger equation applies to systems in which the number of particles is conserved. However, in many physical processes the number of particles is not conserved and particles can be created or destroyed. Then there arises the need for a new approach in quantum mechanics, namely the second quantization approach, which allows for the creation and destruction of particles.

Let us digress and turn our attention to the equations of motion in relativistic quantum mechanics. In particular, if following Dirac we write down the eigen-problem for the hydrogen atom, we find a very different set of solutions to those found in the non-relativistic (Schrödinger) case. Solutions of the Dirac equation for the hydrogen atom lead to a spectrum which is divided into two branches a positive energy branch and a negative energy branch. The Dirac spectrum for the hydrogen atom is shown schematically in Figure 1.

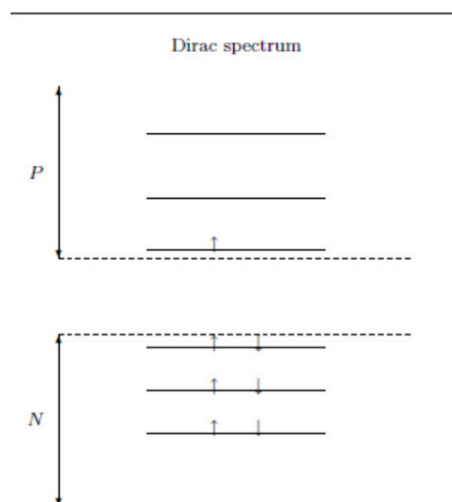


Fig.1. The Dirac spectrum for the ground state of the hydrogen atom consists of a positive energy branch P and a negative energy branch N . A single electron occupies the lowest energy level in the positive energy branch. The negative energy branch N is assumed to be full of positrons in the ground state.

In the non-relativistic formalism, the ground state of the hydrogen atom consists of a single electron occupying the lowest energy level in the spectrum. In the relativistic formalism, the ground state of the hydrogen atom consists of a single electron occupying the lowest energy level in the positive energy branch of the Dirac spectrum. Dirac famously conjectured that this electron is prevented from decaying into one of the negative energy states because these states are themselves filled with electrons. A consequence of this conjecture is that even the simple hydrogenic atom is an infinity many bodied problem. The electrons filling the negative branch of the Dirac spectrum are not directly observable. They are positrons. A direct consequence of the Dirac picture is that the number of electrons in a relativistic system is not conserved. A single excitation can lead to the formation of an electron-positron pair. In the Dirac picture, it is the total charge of the system which is conserved. Therefore the use of second quantization is mandatory in the description of many body problems.

The development of quantum electrodynamics saw the introduction of diagrammatic techniques. In particular, Feynman [1] in a paper entitled “Space Time approach to Quantum Electrodynamics”, introduced diagrams which provide not only a pictorial representation of the microscopic processes but also a precise graphical algebra which is entirely equivalent to other formulations. It is thus not surprising that second quantization and diagrammatic formulations emerged as a powerful approach to the quantum many-body problem in non-relativistic quantum mechanics. Having seen that the second quantization approach to quantum mechanics is extremely useful in many body problems, we now turn our attention to the mathematical formalism of second quantization.

II. Ladder Operators in the Simple Harmonic Oscillator

The basic idea behind the second quantization formalism is to rewrite quantum mechanics in terms of the creation and annihilation operators, which allow for particle creation and destruction.

It is therefore useful to first review the use of ladder operators in the simple harmonic oscillator. First we consider the Hamiltonian for the simple harmonic oscillator

$$H = \frac{1}{2m} p^2 + \frac{1}{2} Kx^2. \quad (1)$$

In this section only let us scale the variables so that $m = 1$, $K = 1$, and also $\hbar = 1$, to save writing, so the Hamiltonian is

$$H = \frac{1}{2}p^2 + \frac{1}{2}x^2, \quad (2)$$

and using $p = -i\partial/\partial x$ in the Schrödinger's equation $H\Psi = E\Psi$, with the given eigenstates Ψ_n and eigenvalues ε_n , we get

$$-\frac{1}{2}\frac{d^2}{dx^2}\Psi_n(x) + \frac{1}{2}x^2\Psi_n(x) = \varepsilon_n\Psi_n(x). \quad (3)$$

This differential equation can be solved with all the techniques of partial differential equations in order to find its eigenvalues $\varepsilon_n = n + \frac{1}{2}$. Instead, we can also solve the eigenvalue problem algebraically by introducing the creation and annihilation operators a^+ and a , as

$$a = \frac{1}{\sqrt{2}}(p - ix), \quad (4)$$

$$a^+ = \frac{1}{\sqrt{2}}(p + ix), \quad (5)$$

where the $+$ superscript denotes that a^+ is the Hermitian conjugate of a . We also know the commutator

$$[x, p] = xp - px = i, \quad (6)$$

which follows from the Heisenberg uncertainty principle, and so it is natural to look at the commutation properties of a and a^+

$$[a, a^+] = \frac{1}{2}[p - ix, p + ix] = -i[x, p] = 1. \quad (7)$$

Then the Hamiltonian for the simple harmonic oscillator can be written in terms of the creation and annihilation operators

$$H = a^+a + \frac{1}{2}, \quad (8)$$

where also the following commutation relations apply

$$[a, a^+a] = aa^+a - a^+aa = [a, a^+]a = a, \quad (9)$$

and

$$[a^+, a^+ a] = a^+ a^+ a - a^+ a a^+ = -a^+ [a^+, a] = -a^+, \quad (10)$$

collecting the results, we get

$$[a, a^+] = 1, \quad [a, a^+ a] = a, \quad [a^+, a^+ a] = -a^+. \quad (11)$$

Then the Hamiltonian H has the lowest eigenvalue ε_0 with the corresponding normalized eigenfunction Ψ_0 . Now let us consider the state $a\Psi_0$ and ask how the Hamiltonian acts on this state by using the commutation rules to transfer the action of H onto Ψ_0

$$H(a\Psi_0) = \left(a^+ a + \frac{1}{2}\right) a\Psi_0 = \left[a\left(a^+ a + \frac{1}{2}\right) - a\right]\Psi_0 = (\varepsilon_0 - 1)(a\Psi_0). \quad (12)$$

This suggest that $a\Psi_0$ is an eigenfunction with energy $\varepsilon_0 - 1$, but since ε_0 was defined as the lowest energy, then this is not possible, and the only way out is to set $a\Psi_0 = 0$. Thus the ground state eigenfunction is defined by the action of the down ladder operator a , giving a zero eigenvalue. Similarly

$$H(a^+\Psi_0) = (\varepsilon_0 + 1)(a^+\Psi_0), \quad (13)$$

so that $(a^+\Psi_0)$ is an eigen function with energy $\varepsilon_0 + 1$. Continuing in this way we find a ladder of eigenstates

$$\Psi_n = (a^+)^n \Psi_0 \text{ with energies } \varepsilon_n = n + \frac{1}{2}. \quad (14)$$

Having seen the importance of the creation and annihilation operators in the simplest case of the harmonic oscillator, we now focus on the use of the creation and annihilation operators in N-body problems of quantum mechanics.

III. The Fock Space in Quantum Theory

Consider the N-particle Hamiltonian operator of particles

$$H = \sum_{k=1}^N T(x_k) + \frac{1}{2} \sum_{k \neq l, l=1}^N V(x_k, x_l), \quad (15)$$

with T being the one electron operator term, and V is the two electron contribution to the total energy. This Hamiltonian operator generates the dynamics of the system through the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi. \quad (16)$$

For systems with a variable number of particles the explicit dependence on the particle number is inconvenient. Evolution of the quantum system may be represented in a form independent of the particle number in a Fock space with the operators written in their second quantized forms.

It is usually convenient to express wave functions of many particle systems as linear combinations of one particle wave function products of the form

$$\Psi(x_1, \dots, x_n) = \sum_n C(1, \dots, N) \Phi_1(x_1) \Phi_2(x_2) \dots \Phi_N(x_N). \quad (17)$$

Thus, if Ψ is symmetric under an arbitrary exchange $x_i \leftrightarrow x_k$, the coefficients $C(n_1, \dots, n_N)$ must be symmetric under the exchange $n_j \leftrightarrow n_k$. A set of N particle basis states with well defined permutation symmetry is the properly symmetrized tensor product

$$|\Psi_1, \dots, \Psi_N\rangle = |\Psi_1\rangle \times |\Psi_2\rangle \times \dots \times |\Psi_N\rangle = \frac{1}{\sqrt{N!}} \sum_P \xi^P |\Psi_{P(1)}\rangle \times \dots \times |\Psi_{P(N)}\rangle, \quad (18)$$

where the sum runs over the set of all possible permutations P . The weight factor ξ is +1 for bosons and -1 for an odd permutation of fermions. The inner product of two N -particle states is

$$\begin{aligned} \langle \Phi_1, \dots, \Phi_N | \Psi_1, \dots, \Psi_N \rangle &= \frac{1}{N!} \sum_{PQ} \xi^{P+Q} \langle \Phi_{Q(1)} | \Psi_{P(1)} \rangle \dots \langle \Phi_{Q(N)} | \Psi_{P(N)} \rangle \\ &= \frac{1}{N!} \sum_{P'} \xi^{P'} \langle \Phi_{Q(1)} | \Psi_{P(1)} \rangle \dots \langle \Phi_N | \Psi_{P(N)} \rangle, \end{aligned} \quad (19)$$

where $P'=P+Q$ denotes the permutation resulting from the composition of the permutations P and Q . Since P and Q are arbitrary permutations, P' spans the space of all possible permutations as well. It is easy to see that Eq (19) is nothing but the familiar inner product or Slater determinant

$$\langle \Phi_1, \dots, \Phi_N | \Psi_1, \dots, \Psi_N \rangle = \begin{vmatrix} \langle \Phi_1 | \Psi_1 \rangle & \dots & \langle \Phi_1 | \Psi_N \rangle \\ \vdots & & \vdots \\ \langle \Phi_N | \Psi_1 \rangle & \dots & \langle \Phi_N | \Psi_N \rangle \end{vmatrix}. \quad (20)$$

Note that the interchange of the coordinates of two electrons corresponds to interchanging two rows in the Slater determinant which changes the sign of the determinant, thus satisfying the antisymmetry condition. In addition, having two electrons occupying the same spin orbital corresponds to having two identical columns in the determinant, which makes it zero, as required by the Pauli principal. Let us denote by $|\alpha\rangle$ a complete set of orthonormal one particle states, which satisfy

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta} \quad \sum_{\alpha} |\alpha\rangle \langle \alpha| = 1. \quad (21)$$

N-particle states can then be constructed $|\alpha_1, \dots, \alpha_N\rangle$. The N-particle states for a system of fermions are complete and orthonormal

$$\frac{1}{N!} \sum_{\alpha_1, \dots, \alpha_N} |\alpha_1, \dots, \alpha_N\rangle \langle \alpha_1, \dots, \alpha_N| = \hat{I}, \quad (22)$$

where the sum runs over all the α 's and the operator I is the identity operator in the space of N-particle states.

We will now consider the more general problem in which the number of particles N is not fixed. Rather, we will consider an enlarged space of states in which the number of particles is allowed to fluctuate. Thus let us denote by H_0 the Hilbert space with no particles, H_1 the Hilbert space with only one particle, and in general H_N the Hilbert space for N-particles. The direct sum of these spaces H , gives

$$H = H_0 \oplus H_1 \oplus \dots \oplus H_N, \quad (23)$$

which is usually called the Fock space.

An arbitrary state $|\Psi\rangle$ in Fock space is the sum over the subspaces H_N .

The subspace with no particles is a one dimensional space spanned by the vector $|\nu ac\rangle$ which is the vacuum state. The subspaces with well-defined number of particles are defined to be orthogonal to each other in the sense that the inner product in Fock space

$$\langle \Phi | \Psi \rangle = \sum_{j=0}^{\infty} \langle \Phi^{(j)} | \Psi^{(j)} \rangle, \quad (24)$$

vanishes if $|\Phi\rangle$ and $|\Psi\rangle$ belong to different subspaces.

IV. N-particle wave functions

Let us consider now the problem of a system of N non-relativistic particles. The wave function for this system is $\Psi(x_1, x_2, \dots, x_N)$. If the particles are identical then the probability density $|\Psi(x_1, x_2, \dots, x_N)|^2$ must be invariant under arbitrary exchanges of the labels that we use to identify the particles. In quantum mechanics, however, the particles do not have well defined trajectories. Only the states of a physical system are well defined. Thus even though at some initial time t_0 the N particles may be found around a set of positions $x_1, \dots, x_N$, they will become delocalized as the system evolves. Furthermore the Hamiltonian itself is invariant under

permutation of the particles and the probability density of any eigenstate must remain invariant under any exchange of particle pairs. If we denote by P_{ij} the operator that exchanges the labels of particles i and j , then the wave function must change under the action of P_{ij} , at most by a phase factor $e^{i\theta}$. Hence we must require that

$$P_{ij}\Psi(x_1, \dots, x_N) = e^{i\theta}\Psi(x_1, \dots, x_N), \quad (25)$$

under a further exchange operation, the particles return to their initial labels and we recover the original state. This sample argument requires that $\theta = 0$, or π . We then conclude that there are two possibilities, either Ψ is even under particle-permutations, or odd. Systems of identical particles which have even (symmetric) wave functions relative to a pair wise permutations of the particles are called bosons. On the other hand systems of identical particles with odd (antisymmetric) wave functions with respect to pair permutations of particles are called Fermions. The Hamiltonian operator H for an N -electron system is invariant relative to the exchange of any two electrons (fermions). So, if P_{ij} is an operator which permutes the electron indices i and j , then

$$[H, P_{ij}] = 0, \quad (26)$$

so that the exact wave function, Ψ , is a solution of the Schrödinger equation

$$H\Psi = E\Psi, \quad (27)$$

and $P_{ij}\Psi$ is also a solution since

$$HP_{ij}\Psi = P_{ij}H\Psi = E P_{ij}\Psi. \quad (28)$$

From the indistinguishability of particles follows that if two coordinates in an N -particle state are interchanged. The same physical state results and the corresponding state function can at most differ from the original one by a simple factor λ

$$P_{ij}\Psi = \lambda\Psi. \quad (29)$$

If the same two coordinates are interchanged a second time we end with the exact same state function. Applying P_{ij} to this equation from the left we get

$$\left(P_{ij}\right)^2\Psi = \lambda^2\Psi = \Psi, \quad (30)$$

so that $\lambda^2 = 1$ or $\lambda = \pm 1$, and we conclude that only two species of particles are thus possible in quantum mechanics, the so called bosons ($\lambda=1$) symmetric under particle exchange and fermions ($\lambda=-1$) antisymmetric under particle exchange

$$P_{ij}\Psi = \pm\Psi. \quad (31)$$

For fermions, the antisymmetry requirement of the N particle wavefunction immediately leads to the Pauli Exclusion Principle stating that two fermions cannot occupy the same state. It thus explains the periodic table of elements.

In the first quantization approach to quantum mechanics, N -particle wave functions are written as a single Slater determinant or as a linear combination of Slater determinants which are convenient for constructing many-electron wave functions that are antisymmetric with respect to the exchange of any two electrons. These N -electron wave functions $|\Phi\rangle$ are written as

$$|\Phi\rangle = (N!)^{-\frac{1}{2}} \begin{vmatrix} \varphi_{A_1}(x_{A_1}) & \varphi_{A_2}(x_{A_1}) & \cdots & \varphi_{A_N}(x_{A_1}) \\ \varphi_{A_1}(x_{A_2}) & \varphi_{A_2}(x_{A_2}) & \cdots & \varphi_{A_N}(x_{A_2}) \\ \vdots & \vdots & & \vdots \\ \varphi_{A_1}(x_{A_N}) & \varphi_{A_2}(x_{A_N}) & \cdots & \varphi_{A_N}(x_{A_N}) \end{vmatrix}, \quad (32)$$

or more compactly as

$$|\Phi\rangle = \frac{1}{(N!)^{1/2}} \sum_P (-1)^P P \prod_{i=1}^N \varphi_{A_i}(x_{A_i}), \quad (33)$$

where $\varphi_{A_i}(x_{A_i})$ represents spin-orbitals and x represents the electronic space and spin coordinates.

In second quantization, however, N -particle wave functions are written in the occupation number representation, which is a definition entirely equivalent to Slater determinants. We can completely specify a Slater determinant by recording which of the spin-orbitals φ_{A_i} from a given set occur in the Slater determinant and which do not. This may be expressed by an occupation state vector $|k\rangle$

$$|k\rangle = |n_1, n_2, \dots, n_m\rangle, \quad (34)$$

where the indices n_i can have the value 0 or 1 depending on whether the spin-orbital φ_{A_i} is occupied or unoccupied, that is whether it occurs in the Slater determinant or not. Eventually, each spin orbital could only hold one electron. This is mainly due to restrictions imposed by the Pauli Exclusion Principle, that no two electrons could have the same four quantum numbers.

The numbers n_i are called occupation numbers and their representation of Slater determinants is accordingly called the occupation number representation.

Slater Determinant	On-Vectors	Number of electrons
$\Phi_3(1)$	$ 0,0,1,0\rangle$	1
$\frac{1}{2!} \begin{vmatrix} \Phi_1(1) & \Phi_2(1) \\ \Phi_1(2) & \Phi_2(2) \end{vmatrix}$	$ 1,1,0,0\rangle$	2
$\frac{1}{3!} \begin{vmatrix} \Phi_1(1) & \Phi_3(1) & \Phi_4(1) \\ \Phi_1(2) & \Phi_3(2) & \Phi_4(2) \\ \Phi_1(3) & \Phi_3(3) & \Phi_4(3) \end{vmatrix}$	$ 1,0,1,1\rangle$	3

Fig.2 A comparison between the conventional notation used in first quantization (Slater Determinants) and its Second Quantization analogue (On-Vectors).

The Slater determinant wave functions represented above can be written in the occupation number representation as a product of creation operators acting on the vacuum state $|vac\rangle$

$$a_p^+ a_q^+ \dots a_N^+ |vac\rangle \leftrightarrow (N!)^{-1/2} \det |\Phi_p \Phi_q \dots \Phi_N|. \quad (35)$$

The Fermi statistics presented in such wave functions can be expressed either in terms of a sign change arising upon permuting columns of the determinant, or in terms of the fundamental anticommutation relations among the creation operators

$$[a_i^+, a_j^+]_+ = a_i^+ a_j^+ + a_j^+ a_i^+ = 0. \quad (36)$$

It is evident that since an unoccupied state cannot contain the same spin orbital twice (Pauli Exclusion Principle), then we must demand that $a_i^+ |\dots, 1_i, \dots\rangle = 0$.

The Fermion annihilation operator a_p , which is the adjoint of the creation operator a_p^+ can be thought of as annihilating an electron in Φ_p and is defined to yield zero when operating on the vacuum state.

N-particle states can be written by the action of a product of creation operators on the vacuum state

$$|n_1, \dots, n_N\rangle = \prod_{j=1}^N \frac{(a_j^+)^{n_j}}{\sqrt{n_j!}} |0, \dots, 0\rangle. \quad (37)$$

Othonormality restrictions must also apply on the ON vectors, in other words, the ON vectors must also satisfy the following relations

$$\langle k_i | k_j \rangle = \delta_{ij}, \quad (38)$$

with the Kronecker delta δ_{ij} defined by

$$\delta_{ij} = \begin{cases} 1 & \text{when } i = j \\ 0 & \text{when } i \neq j \end{cases}. \quad (39)$$

V. The Creation and Annihilation Operators in Second Quantization

In second quantization, all operators and states can be constructed from a set of elementary creation and annihilation operators. In this section we introduce these operators and explore their basic algebraic properties. In general, the effect of the creation and annihilation operators (a_i^+, a_i) on each spin-orbital, can be summarized by

$$\begin{aligned} a_i^+ |n_1, \dots, 0_i, \dots, n_m\rangle &= \Gamma(n)_i |n_1, \dots, 1_i, \dots, n_m\rangle \\ a_i^+ |n_1, \dots, 1_i, \dots, n_m\rangle &= 0 \\ \Gamma(n)_i &= (-1)^{\sum_{j=1}^{i-1} n_j}, \end{aligned} \quad (40)$$

and

$$\begin{aligned} a_i |\dots 1_i \dots\rangle &= \Gamma(n)_i |\dots 0_i \dots\rangle \\ a_i |\dots 0_i \dots\rangle &= 0, \end{aligned} \quad (41)$$

where the phase-factor $\Gamma(n)$ depends on the number of electrons found before the created or the annihilated electron: $\Gamma(n) = 1$ for an even number of electrons and $\Gamma(n) = -1$ for an odd number of electrons.

Sometimes in quantum mechanics, the need of transformations between position space (x, y, z) and momentum space (p_x, p_y, p_z) , arises. Then the Fourier transform that changes position space into momentum space can be written as

$$|\vec{p}\rangle = \int d^d x |\vec{x}\rangle e^{i\vec{p} \cdot \vec{x}}, \quad (42)$$

and conversely

$$|\vec{x}\rangle = \int \frac{d^d p}{(2\pi)^d} |\vec{p}\rangle e^{i\vec{p}\cdot\vec{x}}. \quad (43)$$

Then the creation and annihilation operators themselves obey

$$a^+(\vec{p}) = \int d^d x a^+(\vec{x}) e^{i\vec{p}\cdot\vec{x}}, \quad a^+(\vec{x}) = \int \frac{d^d p}{(2\pi)^d} a^+(\vec{p}) e^{-i\vec{p}\cdot\vec{x}}, \quad (44)$$

$$a(\vec{p}) = \int d^d x a(\vec{x}) e^{-i\vec{p}\cdot\vec{x}}, \quad a(\vec{x}) = \int \frac{d^d p}{(2\pi)^d} a(\vec{p}) e^{i\vec{p}\cdot\vec{x}}. \quad (45)$$

V. 1. Products of Creation and Annihilation Operators

The creation and annihilation operators introduced earlier change the number of particles in a state and therefore couple ON vectors belonging to different subspaces. We now turn to focus on the products of creation and annihilation operators a_i^+ and a_j^+ which are usually written as

$$i = j \quad a_i^+ a_i^+ |\dots, 0_i, \dots\rangle = \Gamma(n)_i a_i^+ |\dots, 1_i, \dots\rangle = 0 \quad (46)$$

$$i < j \quad a_i^+ a_j^+ |\dots, 0_i, \dots, 0_j, \dots\rangle = \Gamma(n)_i \Gamma(n)_j |\dots, 1_i, \dots, 1_j, \dots\rangle = 0, \quad (47)$$

with the anticommutator relations given by

$$[a_i^+, a_j^+]_+ = a_i^+ a_j^+ + a_j^+ a_i^+ = 0 \quad (48)$$

$$[a_i^+, a_j]_+ = a_i^+ a_j + a_j a_i^+ = \delta_{ij}. \quad (49)$$

Then by conjugating the last expression, we get the anticommutation relations

$$[a_i^+, a_j^+]_+^* = a_i a_j + a_j a_i = 0. \quad (50)$$

These anticommutation rules (48)-(50) are very important in second quantization, particularly since all other operators in quantum mechanics can be constructed from a simple product of these operators. For example, the number operator (N), which counts the number of electrons, can be written as a simple product of a creation and an annihilation operator

$$N_P = a_P^+ a_P \quad (51)$$

$$N_P |k\rangle = a_P^+ a_P |k\rangle = \delta_{kp} |k\rangle = k_P |k\rangle, \quad (52)$$

or as a product of these operators

$$NP = \sum_{p=1}^M a_p^+ a_p, \quad (53)$$

which would simply count the number of particles.

VI. Configuration State Functions

In the first quantization formalism of quantum mechanics, N-particle fermion wave functions were expressed by using the conventional notation of Slater determinants. Slater determinants however are eigen functions of the projected spin operator S_z , only. The exact nonrelativistic wave function of the Schrödinger equation is an eigen function of the total and projected spins (S_z, S^2). Such spin adapted functions are called configuration state functions (CSF), which can be constructed from a linear combination of Slater determinants as

$$|CSF\rangle = \sum_i C_i |i\rangle, \quad (54)$$

where the $|i\rangle$ s represent Slater determinants, with coefficients C_i fixed by the spin symmetry of the wave function. In order to distinguish between orbitals of different occupancies, we use the following conventions: orbitals that are doubly occupied in all determinants are called inactive and are labeled by i, j, k. Partially occupied orbitals are known as active and are distinguished by the labels v, w, x, y, z. For the virtual orbitals, which are unoccupied in all determinants, we use the indices a, b, c, d. Within the occupation number representation, each determinant $|i\rangle$ in (54) is written as a product of creation operators working on the vacuum state, and (54) reads

$$|CSF\rangle = \prod_i a_{i\alpha}^+ a_{i\beta}^+ |vac\rangle = A_c^+ |vac\rangle, \quad (55)$$

where we used the core creation operator

$$A_c^+ = \prod_i a_{i\alpha}^+ a_{i\beta}^+. \quad (56)$$

Other CSFs of different multiplicities and occupancies can be constructed

$$|CSF\rangle^{S, M_s} = Q_{vw}^{S, M_s} A_c^+ |vac\rangle = (a_{i\sigma}^+ a_{i\tau}^+)^{S, M_s} A_c^+ |vac\rangle \quad (57)$$

where Q_{vw}^{S, M_s} represents the excitation operator, and S and M_s represent the total and projected spins of the wave function, respectively. For example the following CSF

$$|CSF\rangle^{1,1} = Q_{vw}^{1,1} A_c^+ |vac\rangle = \hat{a}_{v\alpha}^+ \hat{a}_{w\alpha}^+ \left(\prod_i \hat{a}_{i\alpha}^+ \hat{a}_{i\beta}^+ \right) |vac\rangle \quad (58)$$

represents a triplet state with two alpha unpaired electrons, giving a total spin of $S = 1$, a projected spin of $M_s = 1$ and a multiplicity of $2S+1=3$.

VII. The Representation of One and Two Electron Operators

Expectation values correspond to observables and should therefore be independent of the representation given to the operators and states. Then we require that the second quantization representation of one and two electron operators must be equivalent to its counterpart in first quantization. An operator in the Fock space can be thus constructed in second quantization by requiring its matrix elements between ON vectors to be equal to the corresponding matrix elements between Slater determinants of the first quantization operator.

In first quantization one electron operators (kinetic energy) are written as

$$f^c = \sum_{i=1}^N f^c(x_i), \quad (59)$$

where the summation runs over all N electrons of the system. The superscript c indicates that we are working in the coordinate representation of first quantization. The second quantization analogue of (59) is

$$\hat{f} = \sum_{PQ} f_{PQ} a_P^+ a_Q, \quad (60)$$

where the operators $a_P^+ a_Q$ shift a single electron from the orbital Φ_Q in to orbital Φ_P . Eventually, the summation in (60) runs over all pairs of occupied spin orbitals. The term f_{PQ} in second quantization could be linked to the first quantization f^c operator by the relation

$$f_{PQ} = \int \Phi_P^*(x) f^c(x) \Phi_Q(x) dx. \quad (61)$$

Therefore, the recipe for constructing a second quantization representation of one electron operators is to use equations (60) with (61). That is by adding to the first quantization kinetic and electron-nuclear interaction operators the term $a_P^+ a_Q$.

On the other hand, two electron operators such as the electron-electron repulsion and the electron-electron spin orbit operators have a different representation in second quantization. In first quantization these operators were written as

$$g^c = \frac{1}{2} \sum_{i \neq j} g^c(x_i, x_j), \quad (62)$$

where the $\frac{1}{2}$ term avoids counting the electron-electron interactions twice. In a manner similar to

the arguments above, the second quantization representation of a two electron operator can then be written as

$$g = \frac{1}{2} \sum_{PQRS} g_{PQRS} a_P^+ a_R^+ a_S a_Q. \quad (63)$$

The annihilation operators in the above expression must appear to the right of the creation operators in order to ensure a zero eigen value, especially when g acts on an ON vector with less than two electrons.

The expectation values of the parameters g_{PQRS} may be determined by evaluating the matrix element of g between two ON vectors and setting the result equal to the matrix elements corresponding to Slater determinants in first quantization. Then the two electron operator g may act between two:

1. Identical ON vectors

$$\langle k | g | k \rangle = \frac{1}{2} \sum_{PQRS} g_{PQRS} \langle k | a_P^+ a_R^+ a_S a_Q | k \rangle = \frac{1}{2} \sum_{PR} k_P k_R (g_{PPRR} - g_{RRPP}). \quad (64)$$

2. ON vectors differing in one pair of occupation numbers

$$|k_1\rangle = |k_1, \dots, 0_I, \dots, 1_J, \dots, k_M\rangle, \quad |k_2\rangle = |k_1, \dots, 1_I, \dots, 0_J, \dots, k_M\rangle \quad (65)$$

$$\langle k_2 | g | k_1 \rangle = \Gamma_I^{k_2} \Gamma_J^{k_1} \sum_R k_R (g_{IJRR} - g_{RRJI}). \quad (66)$$

3. ON vectors differing in two pairs of occupation numbers

$$|k_1\rangle = |k_1, \dots, 0_I, \dots, 0_J, \dots, 1_K, \dots, 1_L, \dots, k_M\rangle, \quad |k_2\rangle = |k_1, \dots, 1_I, \dots, 1_J, \dots, 0_K, \dots, 0_L, \dots, k_M\rangle \quad (67)$$

$$\langle k_2 | g | k_1 \rangle = \Gamma_I^{k_2} \Gamma_J^{k_1} \Gamma_K^{k_1} \Gamma_L^{k_1} (g_{IKJL} - g_{LJKI}), \quad (68)$$

where $I < J$, and $K < L$.

4. ON vectors differing in more than two pairs of occupation numbers

$$\langle k_2 | g | k_1 \rangle = 0. \quad (69)$$

Our aim in this section is to construct a representation of two electron operators in second quantization, and this is only possible when g_{PQRS} becomes identical to the corresponding first quantization two electron operator g^c

$$g_{PQRS} = \iint \Phi_P^*(x_1) \Phi_R^*(x_2) g^c(x_1, x_2) \Phi_Q(x_1) \Phi_S(x_2) dx_1 dx_2. \quad (70)$$

Then the recipe for constructing a two electron second quantization operator is therefore given by expressions (63) and (70). This construction renders $g^c(x_1, x_2)$ symmetric with respect to the exchange of any two electrons. It should be noted that the order of the creation and annihilation operators appearing in Eq (63) must be presented in order to guarantee that the proper sign will result when expectation values of such operators are evaluated. These spin orbitals Φ_R , appearing in Eq (70), are in most practical applications obtained as linear combinations of atomic orbital basis functions

$$\Phi_R = \sum_a^{\alpha\beta} C_{Ra} \chi_a, \quad (71)$$

where the summation runs over all spins α and β . The χ_a are usually taken to be Slater type orbitals or contracted Gaussian atomic orbitals, and the C_{Ra} are the linear orbital expansion coefficients.

VIII. The Molecular Electronic Hamiltonian

Combining the previous results of section VII we may now construct the full second quantization representation of the electronic Hamiltonian operator in the Born-Oppenheimer approximation. In the absence of external fields the second quantization nonrelativistic and spin free molecular Hamiltonian is given by

$$H = \sum_{PQ} h_{PQ} a_P^+ a_Q + \frac{1}{2} \sum_{PQRS} g_{PQRS} a_P^+ a_R^+ a_S a_Q + h_{nucl} \quad (72)$$

$$h_{PQ} = \int_0^x \Phi_P^*(x) \left(-\frac{1}{2} \nabla^2 - \sum_l \frac{Z_l}{r_l} \right) \Phi_Q(x) dx, \quad (73)$$

where in atomic units

$$g_{PQRS} = \iint \frac{\Phi_P^*(x_1) \Phi_R^*(x_2) \Phi_Q(x_1) \Phi_S(x_2) dx_1 dx_2}{r_{12}} \quad (74)$$

$$h_{nucl} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{R_{IJ}}. \quad (75)$$

Here the Z_I 's represent the nuclear charges, r_i , r_{12} , and R_{IJ} represent the electron-nuclear, the electron-electron, and the internuclear separations. The scalar term in (72) represents the nuclear

repulsion energy and it is simply added to the Hamiltonian and gives the same contribution to the Hamiltonian as in first quantization.

Acting on the vacuum state the second quantization Hamiltonian (72) produces a linear combination of the original state with states generated by single ($a_p^+ a_Q$) and double electron excitations ($a_p^+ a_R^+ a_S a_Q$). With each of these excitations there is an associated amplitude h_{PQ} or g_{PQRS} , which represents the probability for one and two electron interactions. These probabilities are best calculated from the spin-orbitals and the one and two electron operators, according to equations (73) and (74).

VIII. 1. The Hamiltonian of a Two Body Interaction

As an example of the electronic Hamiltonian discussed in the previous section we shall consider the example of a two body interaction whose Hamiltonian operator can be written as a summation of one and two electron operators

$$H = \sum_{i=1}^2 \frac{p^2}{2m} + V(\vec{x} - \vec{y}), \quad (76)$$

where the two electron interaction operator V is written as

$$V = \frac{1}{2} \int d^3x \int d^3y a^+(\vec{x}) a(\vec{y}) a^+(\vec{y}) a(\vec{x}) V(\vec{x} - \vec{y}). \quad (77)$$

Transforming the above expression into momentum space gives

$$\begin{aligned} V &= \sum_{k_1 k_2 k_3 k_4} a^+(k_4) a(k_2) a^+(k_3) a(k_1) \int d^3x \int d^3y e^{i\vec{k}_2 \cdot \vec{y}} e^{-i\vec{k}_3 \cdot \vec{y}} e^{-i\vec{k}_4 \cdot \vec{x}} e^{i\vec{k}_1 \cdot \vec{x}} V(\vec{x} - \vec{y}) \\ V &= \sum_{k_1 k_2 k_3 k_4} a^+(k_4) a(k_2) a^+(k_3) a(k_1) \int d^3x \int d^3y e^{i(\vec{k}_2 - \vec{k}_3) \cdot \vec{y}} e^{i(\vec{k}_1 - \vec{k}_4) \cdot \vec{x}} V(\vec{x} - \vec{y}). \end{aligned} \quad (78)$$

Change the variables $\vec{r} = \vec{x} - \vec{y}$, so that $\vec{x} = \vec{y} + \vec{r}$

$$V = \sum_{k_1 k_2 k_3 k_4} a^+(k_4) a(k_2) a^+(k_3) a(k_1) \int d^3y e^{i(\vec{k}_2 - \vec{k}_3 + \vec{k}_1 - \vec{k}_4) \cdot \vec{y}} \int d^3r e^{i(\vec{k}_1 - \vec{k}_4) \cdot \vec{r}} V(\vec{r}). \quad (79)$$

The first integral to the right gives

$$\int d^3y e^{i(\vec{k}_2 - \vec{k}_3 + \vec{k}_1 - \vec{k}_4) \cdot \vec{y}} = \int d^3y e^{i(0) \cdot \vec{y}} = 1. \quad (80)$$

This is due to the law of momentum conservation which according to Fig 2 gives

$$\vec{k}_2 - \vec{k}_3 + \vec{k}_1 - \vec{k}_4 = 0. \quad (81)$$

This means that if two particles interact the total momentum in the system cannot change. Finally, we change the variables again to $\vec{q} = \vec{k}_1 - \vec{k}_4$ which with (81) leads to the final form of the two term interaction

$$V = \sum_{k_1 k_2 q} a^\dagger(\vec{k}_1 - \vec{q}) a(\vec{k}_2) V(\vec{q}) a^\dagger(\vec{k}_2 + \vec{q}) a(\vec{k}_1), \quad (82)$$

with

$$V(\vec{q}) = \int d^3r V(\vec{r}) e^{i\vec{q} \cdot \vec{r}}, \quad (83)$$

being the Fourier transform of the interaction potential $V(r)$. One can think of this as one particle with initial momentum $\vec{k}_1$ interacting with another particle with initial momentum $\vec{k}_2$ by exchanging a virtual particle with momentum $\vec{q}$, finally giving two particles with momenta $\vec{k}_1 - \vec{q}$ and $\vec{k}_2 + \vec{q}$. Actually, this is the Coulomb interaction occurring between two electrons with $V(k)$ representing the Coulomb two electron operator. The whole process could be visualized with the aid of the Feynman diagram shown in Figure 2.

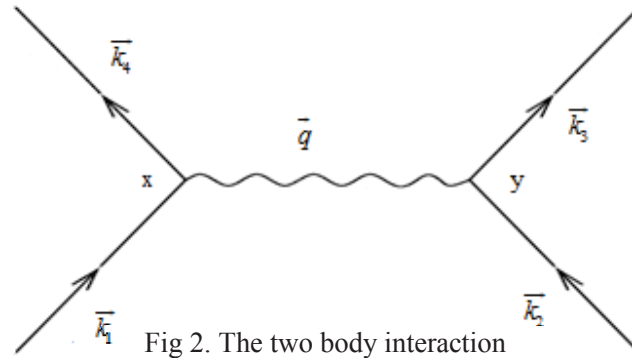


Fig 2. The two body interaction

IX. Spin in Second Quantization

In quantum mechanics and particle physics, spin is a fundamental characteristic property of elementary particles. All elementary particles of a given kind, Fermions let us say, have a spin quantum number which forms an important part of a particle's quantum state. When combined with the antisymmetry requirement of the fermionic wave functions the spin of electrons result in the Pauli Exclusion Principle which in turn underlies the periodic table of chemical elements.

Thus the spin of a particle is an important intrinsic degree of freedom. In the formalism of second quantization presented so far there were no reference to electron spin. In the present section we develop the theory of second quantization so as to allow for an explicit description of electron spin.

IX. 1. Spin Functions

The spin coordinate of an electron can take only two values $m_s = 1/2$ and $m_s = -1/2$, representing the two allowed values of the projected spin angular momentum S_z of the electron. The spin space is accordingly spanned by two functions, which are taken to be the eigen functions $\alpha(m_s)$ and $\beta(m_s)$ of the projected spin angular momentum operator S_z

$$S_z^C \alpha(m_s) = \frac{1}{2} \alpha(m_s), \quad S_z^C \beta(m_s) = -\frac{1}{2} \beta(m_s). \quad (84)$$

These spin functions, which we will denote by σ , τ , μ , and ν , are usually eigen functions of the total spin angular momentum operator S^2

$$(S^C)^2 \sigma(m_s) = s(s+1) \sigma(m_s) = \frac{3}{4} \sigma(m_s). \quad (85)$$

In addition, these spin eigen functions form an orthonormal set, which is in accordance with the general theory of angular momentum in quantum mechanics. In general, the functional form of the spin functions is given by the following equations

$$\alpha\left(\frac{1}{2}\right)=1, \quad \alpha\left(-\frac{1}{2}\right)=0, \quad \beta\left(\frac{1}{2}\right)=0, \quad \beta\left(-\frac{1}{2}\right)=1, \quad (86)$$

where the completeness of the spin functions leads to the following identity

$$\sum_{\sigma} \sigma^*(m_s) \sigma(m_{s'}) = \delta_{m_s m_{s'}}. \quad (87)$$

In describing N-electron systems, it is more convenient to write the electronic wave function as a product of an orbital part and a spin part. Such spin orbitals are written as

$$\Phi_{p\sigma}(r, m_s) = \Phi_p(r) \sigma(m_s), \quad (88)$$

so that a given spin orbital consists of an orbital function multiplied by a spin function. This simple product is acceptable since the nonrelativistic Hamiltonian operator does not involve spin and thus cannot couple the spatial and spin parts of the spin orbitals. With this notation, the creation and annihilation operators $a_{p\sigma}^+$ and $a_{q\tau}$ are defined to act on an electron with orbital functions Φ_p , Φ_q and spin eigenfunctions σ and τ .

IX. 2. Spin Operators

Our previous definition of one and two electron operators neglected the effect of electronic spin. However, spin is an important physical property that must be included in the definition of one and two electron operators. First let us consider one electron operators of the form

$$f^c = \sum_{i=1}^N f^c(r_i), \quad (89)$$

which may be written in the spin orbital basis as

$$f = \sum_{p\sigma q\tau} f_{p\sigma,q\tau} a_{p\sigma}^+ a_{q\tau}. \quad (90)$$

The integrals entering the second quantization operator f vanish for opposite spins. First due to that the spin eigenfunctions are orthogonal and second due to that the first quantization operator f^c is spin free

$$\begin{aligned} f_{p\sigma,q\tau} &= \int \Phi_P^*(r) \sigma^*(m_s) f^c(r) \Phi_q(r) \tau(m_s) dr dm_s \\ &= \delta_{\sigma\tau} \int \Phi_P^*(r) f^c(r) \Phi_q(r) dr = f_{pq} \delta_{\sigma\tau}, \end{aligned} \quad (91)$$

with the notation

$$f_{pq} = \int \Phi_P^*(r) f^c(r) \Phi_q(r) dr. \quad (92)$$

The second quantization representation for the spin free one electron operator now becomes

$$f = \sum_{pq} f_{pq} E_{pq}, \quad (93)$$

with the singlet excitation operator

$$E_{pq} = a_{p\sigma}^+ a_{q\sigma} + a_{p\tau}^+ a_{q\tau}. \quad (94)$$

Similarly two electron operators can be written as

$$g = \frac{1}{2} \sum_{pqrs} g_{p\sigma,q\tau,r\mu,s\nu} a_{p\sigma}^+ a_{r\mu}^+ a_{s\nu} a_{q\tau}. \quad (95)$$

$\sigma\tau\mu\nu$

Most of the terms in the two electron operator vanish because of the orthogonality of the spin functions

$$\begin{aligned} g_{p\sigma,q\tau,r\mu,s\nu} &= \int \int \Phi_p^*(r_1) \sigma^*(m_1) \Phi_r^*(r_2) \mu^*(m_2) g^c(r_1, r_2) \Phi_q(r_1) \tau(m_1) \Phi_s(r_2) \nu(m_2) dr_1 dm_1 dr_2 dm_2 \\ &= g_{pqrs} \delta_{\sigma\tau} \delta_{\mu\nu}, \end{aligned} \quad (96)$$

with g_{pqrs} given by

$$g_{pqrs} = \iint \Phi_p^*(r_1) \Phi_r^*(r_2) g^c(r_1, r_2) \Phi_q(r_1) \Phi_s(r_2) dr_1 dr_2. \quad (97)$$

Inserting the integrals in (96) into (97), the second quantization representation of a two electron operator with the inclusion of spin gives

$$\begin{aligned} g &= \frac{1}{2} \sum_{pqrs} g_{pqrs} \sum_{\sigma\tau} a_{p\sigma}^+ a_{r\tau}^+ a_{s\tau} a_{q\sigma} = -\frac{1}{2} \sum_{pqrs} g_{pqrs} \sum_{\sigma\tau} a_{p\sigma}^+ a_{r\tau}^+ a_{q\sigma} a_{s\tau} = \\ &= -\frac{1}{2} \sum_{pqrs} g_{pqrs} \left(\sum_{\sigma\tau} a_{p\sigma}^+ (-a_{q\sigma} a_{r\tau}^+ + \delta_{qr} \delta_{\sigma\tau}) a_{s\tau} \right) = \frac{1}{2} \sum_{pqrs} g_{pqrs} \left(\sum_{\sigma\tau} a_{p\sigma}^+ a_{q\sigma} a_{r\tau}^+ a_{s\tau} - \delta_{qr} \delta_{\sigma\tau} a_{p\sigma}^+ a_{s\tau} \right) \\ &= \frac{1}{2} \sum_{pqrs} g_{pqrs} (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \end{aligned} \quad (98)$$

where for convenience we have introduced the two electron excitation operator

$$e_{pqrs} = E_{pq} E_{rs} - \delta_{qr} E_{ps} = \sum_{\sigma\tau} a_{p\sigma}^+ a_{r\tau}^+ a_{s\tau} a_{q\sigma}. \quad (99)$$

Finally, the second quantization representation of the nonrelativistic molecular electronic Hamiltonian in the spin-orbital basis takes the form

$$H = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} e_{pqrs} + h_{nucl}, \quad (100)$$

where the one and two electron integrals are given by

$$h_{pq} = \int \Phi_p^*(r) \left(-\frac{1}{2} \nabla^2 - \sum_l \frac{Z_l}{r_l} \right) \Phi_q(r) dr \quad (101)$$

$$g_{pqrs} = \iint \Phi_p^*(r_1) \Phi_q^*(r_2) \Phi_q(r_1) \Phi_s(r_2) dr_1 dr_2. \quad (102)$$

The expression of the molecular Hamiltonian given in Eq (100) is different from the spin free Hamiltonian operator given in equation (72) by its dependence on the single and double excitation operators (E_{pq} , e_{pqrs}), which in turn depend on the spin through the operators $a_{p\sigma}^+ a_{q\sigma}$ $a_{p\tau}^+ a_{q\tau}$ appearing in expression (94) and (99).

IX. 3. Spin Orbit Fine Structure Operator

The phenomenon of spin orbit coupling (SOC) arises from the interaction of the intrinsic magnetic moment of an electron with its orbital angular momentum. The best known example of this is that spin orbit interactions cause energy shifts in electronic states interacting with magnetic fields which is mainly detectable by a splitting of spectral lines.

Using some semiclassical electrodynamics and non relativistic quantum mechanics, we derive a relatively simple and quantitative description of the spin orbit operator for an electron bound to a nucleus. In general, the energy of a magnetic moment in a magnetic field is given by

$$V_{so} = -\mu.B, \quad (103)$$

where μ is the magnetic moment of the particle and B is the magnetic field it experiences. Even if there is no magnetic field in the rest frame of the nucleus, there is a magnetic field in the rest frame of the electron

$$B = -\frac{\mathbf{v} \times \mathbf{E}}{c^2}, \quad (104)$$

where v is the velocity of the electron, E is the electric field that it experiences and c is the speed of light in vacuum. But E is radial so we can rewrite $E = \left| \frac{E}{r} \right| \vec{r}$ and the momentum of the electron p is written as $p = m_e v$. Substitute this into (104) to get

$$B = -\frac{p}{m_e c^2} \times \left| \frac{E}{r} \right| \vec{r} = \frac{r \times p}{m_e c^2} \left| \frac{E}{r} \right|. \quad (105)$$

Next, we express the electric field as the gradient of the electric potential $E = -\frac{\partial V}{\partial r}$ (assuming spherical symmetry), and by noting that the angular momentum of a particle from classical mechanics is $L = p \times r$. Putting it all together in (105) we get

$$B = \frac{1}{m_e c^2} \frac{1}{r} \frac{\partial V}{\partial r} L, \quad (106)$$

but the magnetic moment of the electron is given by $\mu = -g_s \mu_B S / \hbar = -2\mu_B S / \hbar$. Therefore the spin orbit interaction Hamiltonian given in (103) reads

$$V_{so} = \frac{2\mu_B}{\hbar m_e c^2} \frac{1}{r} \frac{\partial V}{\partial r} L.S. \quad (107)$$

However, μ_B the Bohr magneton, which is a physical constant used to express the electron magnetic dipole moment is given by $\mu_B = \frac{e\hbar}{2m_e}$ and the electric potential V is related to the electric potential energy U by $V = U/e$. Inserting these last expressions of μ_B and V in to (107)

we get

$$V_{so}^c = -\frac{1}{m_e^2 c^2} \frac{1}{r} \frac{\partial U}{\partial r} L.S = \xi(r) L.S, \quad (108)$$

with $\xi(r) = \frac{1}{m_e^2 c^2 r} \frac{\partial U}{\partial r}$, and L and S represent the angular momentum and spin operators in the first quantization formalism of quantum mechanics.

Finally, the effective spin orbit interaction operator derived in Eq (108) can be written in its second quantization analogue as

$$V_{so} = \sum_{pq} \int \Phi_p^*(r) \sigma^*(m_s) V_{so}^c \Phi_q(r) \tau(m_s) dr dm_s a_p^\dagger \sigma a_{q\tau}, \quad (109)$$

This term added to the electronic Hamiltonian allows for the inclusion of spin orbit effects in the electronic structure calculations.

X. The Variation Principle

Having established the general form of the wave function, still we need to test its quality. In this section we will discuss an important theorem, called the variation principle, which is a simple iterative procedure used to test the validity of the given wave function.

First, let us choose a normalized function Φ that satisfies the appropriate boundary conditions

$$\langle \Phi | \Phi \rangle = 1. \quad (110)$$

The variation principle states that the expectation value of the Hamiltonian is an upper bound to the exact ground state energy

$$\langle \Phi | H | \Phi \rangle \geq \epsilon_0, \quad (111)$$

where ϵ_0 is the exact ground state energy. The above equality holds (left side = right side) only when the wave function Φ is identical to the true exact wave function of the system. The variation principle for the ground state informs us that the energy of the approximate wave function is always high. Thus one can measure the quality of a wave function, by referring to its energy. The lower the energy the better is the wave function. This is the main idea behind the variation theorem in which we take a normalized trial wave function that depends on certain coefficients that can be varied until the energy expectation value reaches a minimum.

The process of energy minimization can be greatly simplified if we write the wave function as a linear combination of trial basis functions [2]

$$|\Phi\rangle = \sum_{i=1}^N c_i |\Psi_i\rangle, \quad (112)$$

where $|\Psi_i\rangle$ is a fixed set of N real and orthonormal basis functions, and the coefficients (c_i) represent the contribution of the corresponding basis function in $|\Phi\rangle$. The expectation value of the Hamiltonian can now be written as a function of the expansion coefficients

$$\langle\Phi|H|\Phi\rangle = \sum_{ij} c_i c_j \langle\Psi_i|H|\Psi_j\rangle = \sum_{ij} c_i c_j H_{ij}. \quad (113)$$

Then the problem of energy minimization, reduces to finding the optimum set of coefficients (c_i) for which Eq(113) is a minimum i.e.

$$\frac{\partial}{\partial c_k} \langle\Phi|H|\Phi\rangle = 0 \quad k = 1, 2, \dots, N. \quad (114)$$

But, the coefficients (N -parameters) are not independent, and are related by the normalization condition $\sum_i c_i^2 = 1$. The process of minimizing a set of parameters subject to a constraint could be solved by the Lagrange method of undetermined multipliers. First, let us construct the function

$$\begin{aligned} L(c_1, c_2, \dots, c_N, E) &= \langle\Phi_i|H|\Phi_j\rangle - E(\langle\Phi_i|\Phi_j\rangle - 1) \\ &= \sum_{ij} c_i c_j H_{ij} - E\left(\sum_i S_{ij} c_i^2 - 1\right) \end{aligned} \quad (115)$$

Since the trial function is normalized we have merely added zero to Eq(113), and so the minimum of L and H occurs at the same values of the coefficients. To proceed further, we need to minimize the Lagrange function with respect to the c_k coefficients i.e.

$$\begin{aligned} \frac{\partial L}{\partial c_k} &= 0 \\ \text{but } \frac{\partial L}{\partial c_k} &= \sum_j c_j H_{kj} + \sum_i c_i H_{ik} - 2ES_{ij}c_k = 0, \end{aligned} \quad (116)$$

and since $H_{ij}=H_{ji}$, then we have

$$2\sum_j H_{ij}c_j - 2Ec_i S_{ij} = 0 \Rightarrow \sum_j H_{ij}c_j - ES_{ij}c_i = 0, \quad (117)$$

and finally, we can write the secular equation in matrix notation, as

$$Hc = ES c, \quad (118)$$

where S is an identity matrix that represents the overlap integral $\langle\Phi_i|\Phi_j\rangle$.

XI. The Underlying Theoretical Basis – The Born Oppenheimer Approximation

The task of solving the electronic Schrödinger equation for a N particle system is very complicated, so that the task of finding a solution for larger molecules becomes impossible. To overcome this difficulty we must adopt the Born-Oppenheimer approximation [3], which separates the electronic from nuclear motions in the Schrödinger equation.

In view of the fact that, the nuclei are much heavier than the electrons and their speeds are slower, Born and Oppenheimer showed in 1927 [3] that molecular problems could be much simplified by treating the electrons as moving in the field of fixed nuclei. Within this approximation the kinetic energy of the nuclei can be neglected while the nuclear repulsion terms appearing in the Schrödinger equation can be considered constant. Any constant added to an operator only adds to the operator's eigenvalues and has no effect on the operator's eigenfunctions. Thus the electronic Hamiltonian describing the motion of N electrons in the field of M fixed nuclei can be written as

$$H_{elec} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}. \quad (119)$$

By the virtue of this approximation, it is possible to decouple electronic from nuclear motion in the Schrödinger equation [4,5]. This indicates that the molecular Hamiltonian can be written as

$$H_T = H_{elec} + H_{nucl}, \quad (120)$$

where H_{elec} and H_{nucl} are the electronic and nuclear Hamiltonians respectively. It is because of the validity of this approximation that we may concentrate on solving the electronic Schrödinger equation

$$H_{elec} \Phi_{elec} = \epsilon_{elec} \Phi_{elec}, \quad (121)$$

where the electronic wave function

$$\Phi_{elec} = \Phi_{elec}(r_i, [R_A]), \quad (122)$$

depends parametrically on the nuclear coordinates (R_A) and explicitly on the electronic coordinates (r_i). By a parametric dependence we mean that, for different nuclear arrangements, Φ_{elec} is a different function.

After calculating the electronic energy eigen values (ϵ_{elec}), we should include the constant nuclear repulsion term in the expression of the total molecular energy ϵ_{tot} ,

$$\varepsilon_{tot} = \varepsilon_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (123)$$

In fact, the total molecular energy $\varepsilon_{tot}(\mathbf{R})$ calculated above provides a potential energy curve (PEC) for molecular vibrations and rotations Fig. 2.

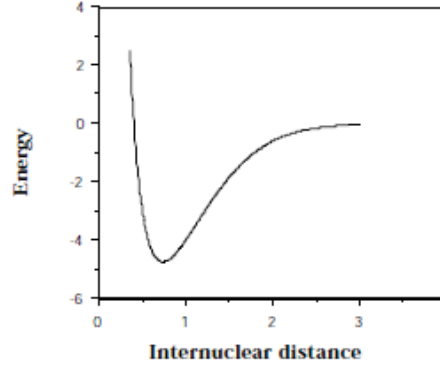


Fig 2. Energy as a function of internuclear distance for a typical bound diatomic molecule.

Where in order to describe nuclear vibrations and rotations, we should solve the nuclear Schrödinger equation

$$H_{nucl} \Phi_{nucl} = \varepsilon \Phi_{nucl}, \quad (124)$$

whose Hamiltonian is given by

$$\begin{aligned} H_{nucl} &= -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \varepsilon_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \\ &= -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \varepsilon_{tot}. \end{aligned} \quad (125)$$

The solutions of the above nuclear equation give the eigen functions and eigen values of the vibrational and rotational energy levels of a molecule.

XII. The Hartree Fock Approximation

The simplest kind of *ab-initio* calculations is a Hartree-Fock (HF) calculation. It was first proposed by Hartree in 1928 [6] to solve atomic problems, then it was latter generalized to tackle molecular geometries. The problem that Hartree addressed arises from the fact that an exact solution to the Schrödinger equation for molecules with more than one electron is not possible, basically because of the electron-electron interaction terms. The expectation value of the energy operator H is the energy of the molecule (or atom). Of course this energy will be the exact true energy only if the wave function Ψ and the Hamiltonian are an exact representation of the true

physical system. The variational theorem discussed in the previous section states that the energy calculated from the equation $E = \langle \Psi | H | \Psi \rangle$ must be greater or equal to the true ground-state energy of the molecule Eq(111). In practice, any molecular wave function we use is always only an approximation to the true wave function of the system, therefore the variationally calculated molecular energy will always be greater than the true energy. In general the Hartree Fock (HF) method is variational, so the correct energy always lies below any calculated energy by HF method, then the better the wave function is the lower is the energy.

In the Hartree Fock approximation the electronic wave function is approximated by a single configuration of spin orbitals (i.e. by a single Slater determinant) and the energy is optimized with respect to variations of these spin orbitals. In this method the ground state wave function can then be written as

$$|\Psi_{HF}\rangle = a_1^+ a_2^+ \dots a_N^+ |0\rangle \quad \text{or} \quad |\Psi_{HF}\rangle = \prod_{i=1}^N a_i^+ |0\rangle. \quad (126)$$

The optimization of the Hartree Fock wave function must be done to arrive at the optimal determinant that may be found by solving a set of effective one electron Schrödinger equations called the Hartree Fock equations and their associated Hamiltonian operator is called the Fock operator

$$F = H^{core} (1) + \sum_{j=1}^n (2J_j (1) - K_j (1)), \quad (127)$$

with

$$\begin{aligned} H^{core} &= -\frac{1}{2} \nabla_i^2 - \sum_{all \mu} \frac{Z_\mu}{r_{\mu l}} \\ J_i (1) &= \int \frac{\Phi_p^* (r_1) \Phi_p (r_1) \Phi_i^* (r_2) \Phi_i (r_2)}{r_{12}} dr_1 dr_2 \\ K_i (1) &= \int \frac{\Phi_p^* (r_1) \Phi_i (r_1) \Phi_i^* (r_2) \Phi_p (r_2)}{r_{12}} dr_1 dr_2 \end{aligned} \quad (128)$$

In the Fock operator the one-electron part of the true Hamiltonian H^{core} is retained. The two electron part J_i is the regular Coulomb repulsion term while the 3rd part K_i is called the exchange term which is a correction to the two Coulomb interaction that arises from the antisymmetry of the wave function. The Hartree Fock eigenvalue equation is then written as

$$f |\Psi_{HF}\rangle = \varepsilon_p |\Psi_{HF}\rangle, \quad (129)$$

with eigen values

$$\begin{aligned} \varepsilon_P = \int \Phi_P(r_1) \left(-\frac{1}{2} \nabla^2 - \sum_K \frac{Z_K}{r_{1K}} \right) \Phi_P(r_1) dr_1 + 2 \sum_i \iint \frac{\Phi_P^*(r_1) \Phi_P(r_1) \Phi_i^*(r_2) \Phi_i(r_2)}{r_{12}} dr_1 dr_2 \\ - \sum_i \iint \frac{\Phi_P^*(r_1) \Phi_i(r_1) \Phi_i^*(r_2) \Phi_P(r_2)}{r_{12}} dr_1 dr_2. \end{aligned} \quad (130)$$

An electron in Φ_p thus experiences a classical electrostatic Coulomb potential (the 2nd term in the above equation), generated by the nuclear framework and by the charge distribution of the remaining electrons, as well as a nonclassical exchange potential (the 3rd term in the above equation), which corrects the classical repulsion energy for Fermi correlation. The exchange integral arises from Slater determinant expansion terms that differ only in the exchange of electrons. It is said to have no simple physical meaning [7], but we can regard the exchange term as a kind of correction to the Coulomb integral, reducing its effect. This reduction arises because particles with opposite spins cannot occupy the same spatial orbital. In other words two electrons of the same spin avoid each other more than expected in the columbic repulsion.

XIII. The Roothaan-Hall Self Consistent Field Equation

In this section we present the Roothaan-Hall formulation of the Hartree Fock theory, in which the molecular orbitals (MOs) are expanded in a set of atomic orbitals (AOs) whose expansion coefficients are used as the variational parameters [7, 8].

In most applications of Hartree Fock theory to molecular systems, the MOs Φ_p are expanded in a set of Gaussian type AOs (χ_μ), with coefficients $C_{\mu p}$

$$\Phi_p = \sum_{\mu} C_{\mu p} \chi_{\mu}. \quad (131)$$

In this case, we are expanding the molecular orbital (MO) Φ in terms of a set of basis functions. Usually, these basis functions are located on atoms, and thus could be regarded as atomic orbitals. Therefore, one could write the MOs as a linear combination of atomic orbitals (LCAO), and the set of basis functions is called a basis set.

Conventionally, there is no upper limit to the size of a basis set and the number of basis functions m in the expansion can be much bigger than the number n of electron pairs in the molecule [10]. However, only the n occupied orbitals are used to construct the Slater determinant, which represents the HF wave functions.

Now, if we substitute the expansion (131) in to the HF Equation (129) we get

$$f_1 \Psi_a(1) = \varepsilon_a \Psi_a(1) \rightarrow \sum_{s=1}^m c_{sa} f_1 \Phi_s = \varepsilon_a \sum_{s=1}^m c_{sa} \Phi_s, \quad (132)$$

where, f_1 is the Fock operator for the 1st electron in Ψ_a .

Then multiply equation (132) by the basis function $\Phi_j^*(1)$ from the left and integrate,

$$\sum_{s=1}^m c_{sa} \int \Phi_j^*(1) f_1 \Phi_s(1) d\tau_1 = \varepsilon_a \sum_{s=1}^m c_{sa} \int \Phi_j^*(1) \Phi_s(1) d\tau_1, \quad (133)$$

where by identifying the following terms:

$$\begin{aligned} S_{js} &= \int \Phi_j^*(1) \Phi_s(1) d\tau_1 \\ f_{js} &= \int \Phi_j^*(1) f_1 \Phi_s(1) d\tau_1, \end{aligned} \quad (134)$$

we could rewrite equation (133), as

$$\sum_{s=1}^m f_{js} c_{sa} = \varepsilon_a \sum_{s=1}^m S_{js} c_{sa}, \quad (135)$$

or in matrix notation, as

$$\mathbf{F}\mathbf{c} = \mathbf{S}\mathbf{c}\varepsilon, \quad (136)$$

where $\mathbf{c}$ is an $m \times m$ matrix (m basis functions) and ε is an $m \times m$ diagonal matrix of the orbital energies.

XIV. Post Hartree Fock Calculations

The Hartree Fock method relies on averages [11], it does not consider the instantaneous electrostatic interaction between the electrons nor does it take into account the quantum mechanical effects on electron distributions. This is because the effect of the $n-1$ electrons on an electron of interest is treated in an average way. In fact, the HF method overestimates the electron-electron repulsion and so gives higher electronic energies than the correct ones, even with the largest basis sets. In brief, we summarize these deficiencies by saying that the HF method ignores electron correlation [10].

Actually, the HF method allows for some electron correlation, two electrons of the same spin cannot be in the same place because their spatial and spin coordinates would then be the same and the Slater determinant (32) representing the molecular wave function would vanish, since a determinant with two identical rows or columns is zero. This is a consequence of the Pauli exclusion principal, where in the neighborhood of each electron there would still be a region

unfriendly to other electrons of the same spin. This region is called a Fermi hole and the HF method overestimates the size of a Fermi hole [12].

XIV. 1. Multi Configuration Self Consistent Field Theory MCSCF

The first step in post Hartree Fock quantum mechanical calculations is the Multi Configuration Self Consistent Field (MCSCF) method, which involves a generalization of the Hartree Fock wave function to systems dominated by more than one electronic configuration. This model is useful in describing the electronic structure of bonded molecular systems, and in particular excited states [13].

In MCSCF theory, the wave function is written as a linear combination of determinants or configuration state functions CSFs, whose expansion coefficients are optimized simultaneously with the MOs according to the variational principle. Thus the MCSCF wave functions may be written as

$$|\Psi\rangle = \sum_i C_i |i\rangle, \quad (137)$$

where the C_i s are the configuration expansion coefficients (normalized to unity). Then the problem of finding the ground state MCSCF optimum wave function can be obtained by minimizing the energy with respect to the variational parameters

$$E_{MC} = \min \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (138)$$

This method allows for a highly flexible description of the electronic system, where both the one and N-electron functions, MOs and CSFs, may adapt to the physical situation. Usually, the greatest difficulty faced in setting up an MCSCF calculation is the selection of configuration space which contributes appreciable to the wave function. Indeed, even for small systems, it is often impossible to generate an MCSCF configuration space sufficiently flexible to describe the physical process and yet sufficiently small to be computationally tractable.

The selection of MCSCF configurations is usually not carried out by inspection of the individual configurations. Instead, whole classes of configurations are simultaneously selected and classified into three sets:

1. A set of inactive orbitals composed of the lowest energy spin orbitals which are doubly occupied in all determinants.

2. A set of virtual orbitals composed of very high energy spin orbitals which are unoccupied in all determinants.
3. A set of active orbitals which are energetically intermediate between the inactive and virtual orbitals.

The active electrons are those that are not in the doubly occupied inactive orbitals, but rather to which excitations are allowed. The single, double, and triple, etc., excited determinants are those that arise from all possible ways of distributing the active electrons over all the active orbitals. This method is known as the complete active space self consistent method CASSCF [13,14].

XIV.2. Configuration Interaction

The configuration interaction (CI) wave function consists of a linear combination of Slater determinants, the expansion coefficients of which are variationally determined. Owing to the simple structure of the wave function, the CI method has been extensively and successfully applied in quantum mechanical calculations [15]. The method is flexible and can give highly accurate wave functions for small closed and open shell molecular systems with electron correlation and it may be used to describe complex electronic structure problems such as bond breakings and excited states. The principle shortcomings of the CI method is that it is difficult to implement for large molecules because of the rapid growth in the number of configurations needed to recover a substantial part of the correlation energy for larger systems.

In the treatment of electron correlations it is important to distinguish between static and dynamical correlations. Static correlation effects are best treated in the complete active space self-consistent field method CASSCF, by retaining in the CAS reference space the configurations arising from the distribution of valence electrons in all possible ways among the active orbitals, while keeping the core orbitals doubly occupied in all configurations. Dynamic correlations, on the other hand, are subsequently treated by including in the wave function expansion all configurations generated from the reference space by carrying out excitations up to a given excitation level.

In the CI method, the wave function is constructed as a linear combination of determinants or configuration state functions CSFs

$$|\Phi\rangle = |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \sum_{a \prec b} \sum_{r \prec s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{a \prec b \prec c} \sum_{r \prec s \prec t} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots, \quad (139)$$

where $|\Psi_0\rangle, |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle, |\Psi_{abc}^{rst}\rangle \dots$ represent the ground state, singly excited, doubly excited, and triply excited state determinants. The weighting factors c in the above expansion determine to what extent each determinant contribute to the wave function $|\Phi\rangle$, and the summing terms ($a \prec b, r \prec s$) avoid counting similar determinants twice in the summation. If every possible determinant was included in the expansion, then the wave function Φ would be the full CI FCI wave functions. Full CI calculations are possible only for very small molecules because the promotion of electrons into virtual orbitals can generate a large number of states unless we have only a few electrons and orbitals [17, 18]. Even when CI calculations are performed for relatively moderate sized molecules, a large number of these determinants still exist. However, a significant number of them can be eliminated by exploiting the following facts:

1. There is no mixing of wave functions with different spins (i.e. $\langle \Psi_i | \mathbf{H} | \Psi_j \rangle = 0$, if $|\Psi_i\rangle$ and $|\Psi_j\rangle$ have different spins.
2. There is no coupling between the HF ground state and single, triple and quadruple excitations (i.e. $\langle \Psi_0 | \mathbf{H} | \Psi_a^r \rangle = 0$). As well, singles do not mix with quadruples. This is a consequence of the fact that the Hamiltonian between Slater determinants which differ by more than two spin orbitals is zero.

The coefficients in the CI expansion (139) are determined by a variational optimization of the expectation value of the electronic energy

$$E_{CI} = \min \frac{\langle C | \mathbf{H} | C \rangle}{\langle C | C \rangle}. \quad (140)$$

These conditions are equivalent to an eigenvalue problem, similar to equation (124), for the eigen values and energies

$$\mathbf{H}\mathbf{C} = E\mathbf{C}, \quad (141)$$

where $\mathbf{H}$ is the Hamiltonian matrix with elements

$$H_{ij} = \langle i | \mathbf{H} | j \rangle, \quad (142)$$

and $\mathbf{C}$ is a vector containing the expansion coefficients C_i . Equation (141) is a standard

Hermitian eigenvalue problem that is solved by either diagonalizing the Hamiltonian matrix or by other iterative techniques to extract the eigenvalues and eigenvectors.

Owing to its formal and conceptual simplicity, the CI method has been extensively and successfully applied in quantum chemistry. However, for even the simplest systems, it is not possible to carry out full configuration interaction FCI, particularly due to the large number of determinants included in the expansion. It then becomes necessary to truncate the CI expansion so that only a small set of the determinants is included. The truncated CI expansion should preferably recover a large part of the correlation energy and provide a uniform description of the electronic structure over the whole potential energy surface.

XIV. 3. Multireference CI Wave Function MRSDCI

The Multireference CI (MRCI) wave function is generated by including in the wave function all configurations arising from the single and double excitations from the reference space, thus resulting in the multireference singles and doubles configuration interaction (MRSDCI) wave function

$$|\Psi_{MRSDCI}\rangle = \left(1 + \sum_{AI} X_I^A + \sum_{A>B, I>J} X_{IJ}^{AB} \right) |\Psi_0\rangle, \quad (143)$$

where, the single and double excitation operators are given in second quantization by

$$X_I^A |\Psi_0\rangle = C_I^A a_A^\dagger a_I |\Psi_0\rangle, \quad X_{IJ}^{AB} |\Psi_0\rangle = C_{IJ}^{AB} a_A^\dagger a_B^\dagger a_I a_J |\Psi_0\rangle. \quad (144)$$

The construction of a multireference CI wave function begins with the generation of a set of orbitals and a reference space of configurations $|\Psi_0\rangle$, which are best generated by the CASSCF method. The CASSCF method writes the wave function as a linear combination of determinants or CSFs, whose expansion coefficients are optimized simultaneously with the MOs according to the variation principle. The fully optimized wave functions in the CASSCF method are then used as a reference state in the MRSDCI technique, in which single and double excitations are included.

XIV. 4. Davidson's Correction

Configuration interaction calculations that include single, double, triple, and quadruple excitations are designated SDTQCI. However, large basis sets involve too many determinants to be computationally practicable. As the quadruply excited determinants can be important in

computing the correlation energy, a simple formula known as the Davidson correction has been proposed for estimating the contribution of quadruply excited determinants to the correlation energy [10, 19, 20], this is given by the following relation

$$\Delta E_{Davidson} = (1 - c_0^2)(E_{DCI} - E_{SCF}) \quad (145)$$

where E_{DCI} is the correlation energy computed in CI calculation using the ground state wave function Φ_0 and all its double excitations; c_0 is the coefficient of Φ_0 for the normalized wave function. E_{SCF} is the ground state energy obtained in HF-SCF calculations. The Davidson correction can be computed without additional labor since the c_0 is already computed in DCI calculations. However, in spite of its usefulness for small molecules, the Davidson correction fails for relatively large molecules [17].

XV. Spin Orbit Effects

The nonrelativistic Schrödinger picture discussed in the previous sections is not complete and additional terms are needed to account for the intrinsic magnetic moment of the electron (spin). In atomic and molecular systems, the exact solution of the non-relativistic Schrödinger equation doesn't reproduce the real experimental energies. The difference arises from relativistic effects, which increase with the 4th power of the nuclear charge (Z^4) [21]. Relativistic effects can be neglected in most cases for lighter atoms, but have to be included when dealing with heavy elements. In non-relativistic quantum mechanics, the velocity of light can be assumed to be infinite, so that any finite velocity of particles is very small and the mass of the particle can be approximated by its rest mass. For most measurements on the lighter elements in the periodic table, non-relativistic quantum mechanics is sufficient, since the velocity of an electron is small compared to the speed of light. For the heavier elements in the periodic table the picture is entirely different. As a result for the heavy atoms, the inner electrons attain such high velocities, comparable to that of light, and non-relativistic quantum mechanics is far from adequate. We can divide relativistic effects in to several categories such as the mass-velocity correction, Darwin correction, spin-orbit correction, spin-spin interaction, and Breit interaction [21, 22].

Of all the different kinds of relativistic effects the spin-orbit interaction represented by the Breit-Pauli Hamiltonian is the most important part [21], which mainly arises from the interaction of the intrinsic magnetic moment of the electron with the magnetic moment arising from orbital motions. These effects alter the spectroscopic properties of molecules containing heavy elements to a considerable extent. Even if a molecule has a closed shell ground state the excited states may

stem from open shell electronic configurations, in which case the spin-orbit interaction not only splits the excited states, but mixes different excited states which would not mix in the absence of spin-orbit interaction. Indeed, the yellow color of gold is due to orbital mixing occurring between the $5d^{10}$ and $6s^1$ orbitals [23]. This relativistic effect allows gold to absorb light in the violet and blue regions of the spectrum while it allows for the reflection to occur in the yellow and red regions [23].

Spectroscopically, the magnitude of the spin orbit coupling Hamiltonian H_{SO} in atoms is measured as a splitting in the spectral lines of the multiplet components

$$H_{SO} = \frac{1}{2}hcA(j(j+1) - l(l+1) - s(s+1)) \quad (146)$$

where l is the orbital angular momentum quantum number and s is the spin quantum number and j is the total angular momentum $j = l + s$, and A is the magnitude of the spin-orbit coupling constant. Expanding (146), we get

$$\begin{aligned} H_{SO} &= \frac{1}{2}hcA((l+s)(l+s+1) - l(l+1) - s(s+1)) \\ &= \frac{1}{2}hcA(l^2 + s^2 + ls + sl + l + s - l^2 - l - s^2 - s) = hcAl.s. \end{aligned} \quad (149)$$

Then the magnitude of the spin orbit coupling operator can be calculated in terms of molecular parameters by the substitution

$$hcAl.s = \frac{Z\alpha^2}{2} \left\langle \frac{1}{r^3} \right\rangle l.s, \quad (150)$$

where α is the fine structure constant $\alpha = e^2 / \hbar c 4\pi\epsilon_0$ which is a dimensionless constant ($\alpha = 1/137.037$) that characterizes the strength of the electromagnetic interaction or the amplitude for an electron to emit or absorb a real photon. Z is the atomic number, representing the number of protons inside the nucleus.

In heteronuclear diatomic molecules the orbital angular momentum along the internuclear axis Λ couples to the electronic spin (S) through its projection along the internuclear axis $\Sigma = S, S-1, \dots, -S+1, -S$. Then the total electronic angular momentum about the internuclear axis, denoted by Ω , is obtained by adding the values of Λ and Σ to give the electronic states resulting from the interaction of spin and orbital angular momentums

$$\Omega = |\Lambda + \Sigma|. \quad (151)$$

As an example, consider in Fig.3 the relative orientations of the vectors Λ and Σ for a $^3\Delta$ state

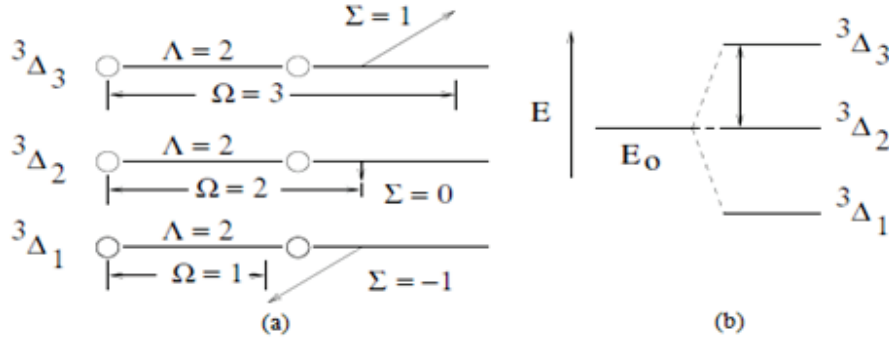


Fig 3. (a) Vector diagram and (b) Energy level diagram for the multiplet states of the $^3\Delta$ state ($\Lambda=2$, $S=1$)

The spin-orbit splitting between the Ω and $\Omega-1$ levels arising from the same term Λ is calculated by using the formula

$$E_{so} = \frac{1}{2\Lambda\Sigma} \langle \Psi_0 | H_{so} | \Psi_0 \rangle, \quad (152)$$

where the spin-orbit coupling operator H_{so} is derived from the Breit-Pauli Hamiltonian [24] defined by

$$H_{SO} = \frac{1}{2m^2c^2} \left(\sum_i \sum_I \frac{Ze^2}{r_{iI}^3} \hat{l}_{iI} \cdot \hat{s}_i - \sum_i \sum_j \frac{e^2}{r_{ij}^3} \hat{l}_{ij} \cdot (\hat{s}_i + 2\hat{s}_j) \right). \quad (153)$$

The above spin-orbit coupling operator is composed of a one and two-electron parts. The $\hat{l}$ and $\hat{s}$ operators are the orbital and spin angular momentum operators, respectively, and the summation over the index (i) refers to electrons and that over (I) refers to nuclei. Finally, the entire Breit-Pauli operator may be approximated by pseudo-effective core potential operators that are extracted from relativistic wavefunctions for atoms. The pseudopotential approximation accounts for the most important relativistic effects and decreases the computational costs of calculations involving heavy elements [25]. The pseudopotential approximation relies on the separation between core and valence electrons in the electronic Hamiltonian. In this case, the valence electrons can be treated as if they were moving in an effective potential, generated by the core electrons and the nuclei. This procedure utilizes the fact that only valence electrons take part in chemical bond formation. With this assumption, calculations can be done using the valence basis set only. The cores (inner-shell electrons and the atomic nucleus) of the individual atoms are approximated through a non-local effective potential.

Separating core and valence electrons leads to an electronic Hamiltonian which describes only the valence electrons. In contrast to all-electron calculations, within the pseudopotential

procedure only the valence electrons or the electrons (n-1)th shell, are explicitly considered. In this case the electronic Hamiltonian can be reduced to an atomic valence operator, H^{val} given by,

$$H^{val} = -\frac{1}{2} \sum_{i=1}^{N_v} \nabla_i^2 + \sum_{i=1}^{N_v} V(r_i) + \sum_{i=1}^{N_v} \sum_{j=1}^{N_v} \frac{1}{r_{ij}}, \quad (154)$$

where the indices i and j denote only valence electrons, and the $V(r_i)$ operator represents a one-component, (spin-orbit-averaged) relativistic pseudopotential [26]

$$V(r_i) = -\sum_i^N \frac{Z}{r_i} + \sum_l \sum_k A_{lk} \exp(-\alpha_{lk} r_i^2) P_l, \quad (155)$$

where P_l is the projection operator onto the subspace with angular symmetry l

$$P_l = \sum_{m_l=1}^l |Y_{l,m_l}\rangle \langle Y_{l,m_l}|. \quad (156)$$

In Eq (155) the pseudopotential parameters, the coefficients, A_{lk} and the exponential parameters, α_{lk} are adjusted to total-valence energies derived from numerical all-electron calculations. The pseudopotentials for atoms can be used for molecules containing heavy atoms. These potentials can easily be implemented in quantum mechanical programs. The pseudopotential approximation is not exact. However, its main advantage is the ease with which relativistic effects can be included in the calculations. Indeed, a significant reduction of the computational effort can be achieved by a restriction of the actual spin orbit calculations to the valence electron system and the implicit inclusion of the influence of the chemically inert atomic cores by means of suitable parameterized effective core potentials [27].

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Chapter Two

Canonical Function's Approach for Molecular Vibrations and Rotations

Much attention has recently been focused on the optimal control of quantum systems, and extensive theoretical works have been performed [1 – 10]. The research on realizing quantum computers using the molecular internal degrees of freedom (electronic, vibrational, and rotational) has only begun since the beginning of the century and the proposed chemical system has been the molecular rovibrational modes of diatomic molecules [11,12-22, 23, 24, 25]. In the present work we explore the vibrational energy structures of the diatomic molecules YN, YS, ZrN, and ZrS, by solving the vibrational Schrödinger equation within the canonical functions approach. The theoretical backgrounds of our rovibrational calculations are listed in this chapter, while the results of these calculations are shown in chapter three of this thesis.

I. Canonical Function's Approach

In view of the fact that in a molecule, the nuclei are much heavier than the electrons and their speeds are slower, Born and Oppenheimer showed in 1927 [26] that molecular problems could be much simplified by treating the electrons as moving in the field of fixed nuclei. In section XI of chapter one of this thesis we discussed the theoretical basis of the Born-Oppenheimer approximation. Within this approximation the kinetic energy of the nuclei is neglected and the nuclear repulsion energy is considered constant. This allows for decoupling the electronic and nuclear wavefunctions in the Schrödinger equation.

$$\Psi_{Total} = \Psi_{electronic} \times \Psi_{nuclear} \quad (1)$$

The vibrational-rotational wave function of a diatomic molecule is a solution of the radial Schrödinger equation [27]

$$\frac{\partial^2 \Psi_{vj}(r)}{\partial r^2} + \left[k(E_{vj} - V(r)) - \frac{J(J+1)}{r^2} \right] \Psi_{vj}(r) = 0$$

$$k = \frac{2\mu}{\hbar^2} \quad \text{and } \lambda = J(J+1), \quad (2)$$

where v and J represent respectively the vibrational and rotational quantum numbers. μ and $\hbar$ represent the reduced mass and planks constant.

The above equation could be simply written, as [27]

$$\Psi''_{\lambda}(x) = f_{\lambda}(x) \Psi_{\lambda}(x), \quad (3)$$

where $\lambda = J(J+1)$, $x = r - r_e$ (r_e being the equilibrium distance), and

$$f_{\lambda}(x) = -k[E_{\lambda} - U(x)] + \frac{\lambda}{(x + r_e)^2}. \quad (4)$$

However, equation (2) is equivalent to the Volterra integral equation [28]

$$\Psi_{\lambda}(x) = \Psi_{\lambda}(0) + x' \Psi'_{\lambda}(0) + \int_0^x (x-t) f_{\lambda}(t) \Psi_{\lambda}(t) dt, \quad (5)$$

in the sense that any solution of equation (5) is a solution to equation (2).

Within the formulation of the canonical function's approach [29, 30], one considers the canonical functions $\alpha(r)$ and $\beta(r)$ defined by

$$\Psi_v(x) = \Psi_v(0) \alpha_v(x) + \Psi'_v(0) \beta_v(x), \quad (6)$$

with

$$\begin{aligned} \alpha(0) &= 1 & \alpha'(0) &= 0 \\ \beta(0) &= 0 & \beta'(0) &= 1, \end{aligned} \quad (7)$$

and

$$\alpha(x) = \sum_{i=0}^{\infty} A_i(x) \quad \text{where } A_i = \int_0^x (x-t) f_{\lambda}(t) A_{i-1}(t) dt$$

$$\text{with } A_0(x) = 1, \quad (8)$$

$$\beta(x) = \sum_{i=0}^{\infty} B_i(x) \quad \text{where } B_i(x) = \int_0^x (x-t) f_{\lambda}(t) B_{i-1}(t) dt$$

$$\text{with } B_0(x) = r - r_0 = x. \quad (9)$$

Then the initial values of $\Psi_\lambda(0)$ and $\Psi'_\lambda(0)$ can be deduced from $\alpha(x)$ and $\beta(x)$ by using Eq(6) and by using the following boundary condition [31]

$$\lim_{\substack{\ell \\ x \rightarrow \infty \\ -r_e}} \Psi(x) \rightarrow 0, \quad (10)$$

one can find

$$\frac{\Psi'_\lambda(0)}{\Psi_\lambda(0)} = \lim_{x \rightarrow \infty} \frac{-\alpha(x)}{\beta(x)}, \quad \frac{\Psi'_\lambda(0)}{\Psi_\lambda(0)} = \lim_{x \rightarrow r_e} \frac{-\alpha(x)}{\beta(x)}. \quad (11)$$

II. The Rotational Schrödinger Equation

The vibration-rotation energies of a diatomic molecule are usually written as

$$E_\lambda = E_V + \lambda B_V - \lambda^2 D_V + \lambda^3 H_V + \dots, \quad (12)$$

where, $B_V, D_V, H_V, \dots$, represent the rotational constants. One can write [27]

$$E_\lambda = \sum_{n=0}^{\infty} e_n \lambda^n,$$

$$\text{with } e_0 = E_V, e_1 = B_V, e_2 = -D_V, \dots \text{ and } \lambda = J(J+1). \quad (13)$$

Then the energy factor $f_\lambda(x)$ given earlier in equations (3) and (4) could be expanded as [27]

$$f_\lambda(x) = \sum_{i=0}^{\infty} \varepsilon_i(x) \lambda^i, \quad (14)$$

$$\text{where } \varepsilon_0 = -k(e_0 - U(x)) \quad (15-a)$$

$$\varepsilon_1 = -ke_1 + \frac{1}{(r_0 + x)^2} \quad (15-b)$$

$$\varepsilon_n = ke_n \text{ for } (i \geq 2). \quad (15-c)$$

Now by replacing $f_\lambda(x)$ by its value in the function $A_n(r)$ in equation (8), one finds [32]

$$\begin{aligned} A_0(r) &= 1 \\ A_1(r) &= \int_{r_0}^r (r-t) \sum_{n=0}^{\infty} \varepsilon_n(t) \lambda^n dt = \sum_{i=0}^{\infty} a_i(t) \lambda^i \\ A_2(r) &= \int_{r_0}^r (r-t) \sum_{n=0}^{\infty} \varepsilon_n(t) \lambda^n \sum_{i=0}^{\infty} a_i(t) \lambda^i dt = \sum_{i=0}^{\infty} a_i^2(t) \lambda^i, \end{aligned} \quad (16)$$

and finally

$$\alpha_{\lambda}(r) = \sum_{n=0}^{\infty} G_n(r) \lambda^n. \quad (17)$$

With the same manner, one obtains

$$\beta_{\lambda}(r) = \sum_{n=0}^{\infty} H_n(r) \lambda^n. \quad (18)$$

The functions $G_n(r)$ and $H_n(r)$ play the role of the function $f_{\lambda}(x)$ and the canonical functions of pure vibration [27]

$$\alpha_0(r) = G_0(r) \text{ and } \beta_0(r) = H_0(r). \quad (19)$$

Then by taking advantage of the limits in equation (11), and by replacing $\alpha(r)$ and $\beta(r)$ by their expressions in equation (17) and (18), we get [27]

$$\Psi'(0)/\Psi(0) = \sum_{n=0}^{\infty} I_n \lambda^n, \quad (20)$$

where the coefficients I_n are deduced from the values of the coefficients G_n and H_n at the boundaries $-r$ and ∞ . The vibrational-rotational wavefunctions defined in equation (6) can be written as

$$\begin{aligned} \Psi_{\lambda}(x) &= \Psi_{\lambda}(0) \sum_{n=0}^{\infty} G_n(x) \lambda^n + \Psi_{\lambda}(0) \sum_{n=0}^{\infty} I_n \lambda^n \sum_{n=0}^{\infty} G_n(x) \lambda^n \\ &= \Psi_{\lambda}(0) G_0 \lambda^0 + \Psi_{\lambda}(0) I_0 \lambda^0 G_0(x) \lambda^0 + \Psi_{\lambda}(0) \left[\sum_{n=1}^{\infty} C_n(x) \lambda^n + \sum_{n=1}^{\infty} I_n \lambda^n \sum_{n=1}^{\infty} G_n(x) \lambda^n \right], \end{aligned} \quad (21)$$

where from Eq(13), if $n=0$ then $e_0 = E_V$, which indicates that the term with $n=0$ is a purely vibrational term. In addition, the first two terms of expression (21) are not related to the rotational quantum number J , since $\lambda^0 = 1$, and with $n=0$ these two terms could be assigned to a purely vibrational wavefunction $\varphi_0(x)$. Accordingly, the vibro-rotational wave function $\Psi_{\lambda}(x)$ given in equation (21) could be refined as

$$\Psi_{\lambda}(x) = \varphi_0(x) + \sum_{n=1}^{\infty} \varphi_n(x) \lambda^n. \quad (22)$$

The second term of the above equation is a purely rotational function $\varphi_n(x)$, since it depends directly on λ . Thus the rotational effect in the vibration-rotation wavefunction $\Psi_{\lambda}(x)$ is separated from the pure vibration wavefunction $\varphi_0(x)$ [27]. The terms $\varphi_n(x)$ in the above equation are called the rotational harmonics that depend on $C_n(x)$, $G_n(x)$, and $I_n(x)$.

Finally, by replacing the wave function's expression of equation (22) in equation (3), we find

$$\varphi_0''(r) + \sum_{n=1}^{\infty} \varphi_n''(r) \lambda^n = \left(\varepsilon_0 + \sum_{n=1}^{\infty} \varepsilon_n \lambda^n \right) \left(\varphi_0 + \sum_{n=1}^{\infty} \varphi_n \lambda^n \right), \quad (23)$$

which gives [27]

$$\varphi_0''(x) - \varepsilon_0(x) \varphi_0(x) = 0 \quad (24-a)$$

$$\varphi_1''(x) - \varepsilon_0(x) \varphi_1(x) = \varepsilon_1(x) \varphi_0(x) \quad (24-b)$$

$$\varphi_2''(x) - \varepsilon_0(x) \varphi_2(x) = \varepsilon_1(x) \varphi_1(x) + \varepsilon_2(x) \varphi_0(x) \quad (24-c)$$

$$\varphi_n''(x) - \varepsilon_0(x) \varphi_n(x) = \sum_{m=1}^n \varepsilon_m(x) \varphi_{n-m}(x). \quad (24-n)$$

The first of these equations is called the radial Schrödinger equation of pure vibration for $J = 0$. All of the other equations are called the rotational Schrödinger equations for $J > 0$ nuclear rotations. The rotational Schrödinger equations allow us to successively determine the rotational harmonics $\varphi_1, \varphi_2, \dots$, and φ_n .

III. Finding the Pure Vibrational Wavefunction

The pure vibrational Schrödinger equation was given by

$$\varphi_0''(x) - \varepsilon_0(x) \varphi_0(x) = 0, \quad (25)$$

where ε_0 represents the energy factor which corresponds to pure vibration. It is obtained by setting $\lambda = 0$ in equation (4). Equation (25) can be written in the integral form [30]

$$\varphi_0(x) = \varphi_0(r_0) + (r - r_0) \varphi_0'(r_0) + \int_{r_0}^r (r - t) \varepsilon_0(t) \varphi_0(t) dt, \quad (26)$$

where the function $\varphi_0(r)$ can be written in the form

$$\varphi_0(r) = \varphi_0(r_0) \alpha_0(r) + \varphi_0'(r_0) \beta_0(r). \quad (27)$$

The two canonical functions $\alpha(r)$ and $\beta(r)$, associated with $\varepsilon_0(r)$, are given by [29]

$$\alpha(r) = \sum_{i=0}^{\infty} A_i(r) \quad \text{where} \quad A_i = \int_0^r (r - t) \varepsilon_0(t) A_{i-1}(t) dt$$

with $A_0(r) = 1,$ (28)

$$\beta(r) = \sum_{i=0}^{\infty} B_i(r) \quad \text{where} \quad B_i(r) = \int_0^r (r - t) \varepsilon_0(t) B_{i-1}(t) dt$$

with $B_0(r) = r - r_0.$ (29)

If we take $\lambda = 0$ in equation (21), one can write $\varphi_0(r_0) = 1$ for the wave function. Then by using the conditions applicable on φ_0 at the limits (10), with the relations between φ_0 , α_0 , and β_0 and by considering the initial condition of $\varphi'_0(r_0)$ given by [27]

$$\varphi'_0(r_0) = \lim_{\substack{r \rightarrow \infty \\ r \rightarrow 0}} - \frac{\alpha_0(r)}{\beta_0(r)} \quad (30)$$

with $l_0 = \varphi'_0(r_0)$, we get

$$\varphi_0(r) = \alpha_0(r) + l_0 \beta_0(r). \quad (31)$$

In conclusion the calculations for the proper value of pure vibrational energy ε_0 and for the pure vibrational wave function φ_0 by using equation 24-a. Then by using the calculated values of ε_0 and φ_0 in equation 24-b, one can obtain the values of the rotational constant $\varepsilon_1 = B_v$ and the rotational harmonic wavefunction φ_1 . Then by using the values of ε_0 , ε_1 , φ_0 , and φ_1 in equation 24-c one can obtain the values of the centrifugal distortion constants $\varepsilon_2 = D_v$, with the values of the 2nd order rotational harmonic φ_2 . The iterative cycle can be repeated by using equation 24-n in order to obtain rotational constants as L_v , H_v , ...

The remaining part of this chapter is devoted for calculating the rotational harmonics φ_1 , φ_2 , ..., φ_n , described in Ref [27] and whose corresponding eigenvalues are ε_1 , ε_2 , ..., ε_n .

IV. Canonical Formulation for the First Rotational Harmonic

Formerly, we found a solution to the vibrational Schrödinger equation (24-a). Now, in this section we will concentrate on finding a solution to the rotational Schrödinger equation (24-b)

$$\varphi_1''(x) - \varepsilon_0(x) \varphi_1(x) = \varepsilon_1(x) \varphi_0(x). \quad (32)$$

The solution of the above equation is equivalent to the solution of the Voltera integral equation [27, 33]

$$\varphi_1(r) = \varphi_1(r_0) + \varphi_1'(0)(r - r_0) + \int_{r_0}^r (r-t) \varepsilon_0(t) \varphi_1(t) dt + \int_{r_0}^r (r-t) \varepsilon_1(t) \varphi_0(t) dt. \quad (33)$$

The solution of the above equation can be greatly simplified by following a procedure similar to that adopted in section III and by using the canonical functions α and β together with equations (8) and (9), we get

$$\varphi_1(r) = \varphi_1(r_0) \alpha_0(r) + \varphi_1'(r_0) \beta_0(r) + \sigma_1(r) \quad (34)$$

$$\text{and} \quad \sigma_1(r) = \sum_{n=0}^{\infty} K_n(r) \quad (35-a)$$

$$K_0(r) = \int_0^r (r-t) \varepsilon_1(t) \varphi_0(t) dt \quad (35-b)$$

$$K_1(r) = \int_0^r (x-t) \int_{r_0}^t (t-t_1) \varepsilon_1(t) \varphi_0(t) dt_1 dt \quad (35-c)$$

$$K_n(r) = \int_{r_0}^r (r-t) \varepsilon_1(t) K_{n-1}(t) dt, \quad (35-d)$$

with the properties below [32]:

(i) for $r = r_0$

$$K_0(r_0) = K_1(r_0) = \dots = K_n(r_0) = \dots = 0 \\ \text{giving } \sigma_1(r_0) = 0. \quad (36)$$

The derivation of the $\sigma_1(r)$

$$\sigma_1'(r) = \sum_{n=0}^{\infty} K_n'(r), \quad (37)$$

with $K_n'(r) = \int_{r_0}^r \varepsilon_1(t) K_{n-1}(t) dt$ and

$$K_0'(r_0) = K_1'(r_0) = \dots = K_n'(r_0) = \dots = 0 \\ \text{giving } \sigma_1'(r) = 0. \quad (38)$$

For the other higher order derivatives of $\sigma_1(r)$, we find

$$\sigma_1''(r) = \sum_{n=0}^{\infty} K_n''(r), \quad (39)$$

with $K_n''(r) = \varepsilon_1(r) K_{n-1}(r)$,

and $K_0''(0) \neq K_1''(0) \neq \dots \neq K_n''(0) \neq \dots \neq 0$

(ii) The rotation harmonics must vanish at the boundaries [27], i.e.

$$\lim_{\substack{x \rightarrow +\infty \\ x \rightarrow -r_e}} \varphi_n(x) = 0, n \geq 0. \quad (40)$$

Then the first rotational harmonic $\varphi_1(r)$ written in equation (34), gives

$$\varphi_1(r) = \varphi_1'(r_0) \beta_0(r) + \sigma_1(r), \quad (41)$$

with the limiting conditions (40)

$$\phi_1'(r_0) = \lim_{\substack{x \rightarrow +\infty \\ x \rightarrow -r_e}} -\frac{\sigma_1(r)}{\beta_0(r)} = l_1, \quad (42)$$

to give the rotational wave function

$$\phi_1(r) = l_1 \beta_0(r) + \sigma_1(r). \quad (43)$$

V. Numerical Methods

For a potential function given by $U(r)$, and a vibrational energy value E , the function ϕ_0 is given by [27]

$$\phi_0(r) = \alpha_0(r) + l_0 \beta_0(r), \quad (44)$$

where the functions $\alpha_0(r)$ and $\beta_0(r)$ are given by the expression (28) and (29), in terms of the functions $U(r)$ and $E = \varepsilon_0$. The study of these expressions is available independent on the form of the potential considered. For a numerical potential of type RKR [34, 35] defined by the turning points and by the polynomial interpolation of the calculated potential energy curves. Once the formulation of the potential is specified, the calculations can be carried out for the canonical functions $\alpha_0(r)$, $\beta_0(r)$, and the parameters l_0 and ϕ_0 .

Within a specified interval $[r_i, r_{i+1}]$ delimited by the abscissa of two successive points P_i, P_{i+1} . The potential function $U(r)$ is written as

$$U(x) = \sum_{n=0}^N \gamma_n x^n, \quad (45)$$

with $x = r - r_i, 0 \leq x \leq r_{i+1} - r_i$,

and the constants γ_n are the coefficients determined for the specified numerical potential energy function.

II.5.1. Calculations of the Canonical Functions $\alpha_0(r)$ and $\beta_0(r)$

The pure vibrational equation, given by equation (24-a) can be written as

$$y''(x) = \varepsilon_0(x) y(x), \quad (46)$$

with $\varepsilon_0(x) = -k(e_0 - U(x))$. The solution of this equation is written in the form [2]

$$y(r) = \sum_{n=0}^{\infty} c_n(i) (r - r_i)^n. \quad (47)$$

The functions $\alpha_0(r)$ and $\beta_0(r)$ are given by the same function $y(r)$. Then by substituting equation (47) in to equation (46), we get [27]

$$(n+2)(n+1)c_{n+2}(i) = -ke_0c_n(i) + k\sum_{m=0}^n c_m(i)\gamma_{n-m}, \quad (48)$$

with the initial values

$$c_0(i) = y(r), \quad c_1(i) = y'(r_i), \quad (49)$$

and

$$y(r_i) = \sum_{n=0}^{\infty} c_n(i-1)(r_i - r_{i-1})^n, \quad y'(r_i) = \sum_{n=1}^{\infty} nc_n(i-1)(r_i - r_{i-1})^{n-1}. \quad (50)$$

The equations (47 - 50) are sufficient for calculating $\alpha_0(r)$ and $\beta_0(r)$ at each point r of the potential energy curve. The values of y and y' at an origin r_0 are passed in between successive intervals $(r_i - r_{i-1})$, in order to calculate the values of $\alpha_0(r)$ and $\beta_0(r)$ at each point. From these we calculate the ratios

$$\alpha_0(r)/\beta_0(r), \text{ and } \alpha'_0(r)/\beta'_0(r)$$

These ratios are calculated to the right and then to the left of the equilibrium internuclear distance of the potential energy curve $r > r_0$ and $r < r_0$, as

$$\lim_{r \rightarrow \infty} -\frac{\alpha_0(r)}{\beta_0(r)} = \frac{\phi'_0(r)}{\phi_0(r)} \Big|_{r > r_0} = l_0^+(E), \quad \text{and} \quad \lim_{r \rightarrow 0} -\frac{\alpha_0(r)}{\beta_0(r)} = \frac{\phi'_0(r)}{\phi_0(r)} \Big|_{r < r_0} = l_0^-(E) \quad (51)$$

At the points $r_i > r_0$ and $r_j < r_0$ were $l_0^+(E) = l_0^-(E)$ the vibrational energy E_v for a v vibrational level is found and its value is then determined at the points r_i and r_j of the potential energy surface.

The numerical values of the pure vibrational wave function ϕ_0 are then determined by using in equation (44) the values of α_0 , β_0 and l_0 .

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Chapter Three

Results and Discussions

Metal-ligand bonding underlies the vast physical and chemical properties that a material has. The spectroscopic study of heavy polar diatomic molecules is important in such diverse fields as astrophysics [1], ultracold interactions [2], organometallic chemistry [3], quantum computing [4-6], precision measurements [7], and metallurgy [3]. The present investigation is devoted to the prediction for the electronic structures of the transition metal nitrides and sulfides of Yttrium and Zirconium. Our interest in transition metals has been investigated by the desire to understand the role played by d orbitals in bonding. The diatomic molecules composed of the transition metals of groups III and IV are the simplest of the d- block open shell molecules with the valence electronic configuration $[(n-1)d^{1,2}ns^2]$. In this chapter we list the results of our calculations for the electronic structures, spectroscopic constants, and vibrational structures of the heavy polar diatomic molecules YN, ZrN, ZrS and YS. A comparison is made, where available, between the results of the present work to the experimental and theoretical results in literature. The small relative difference of less than 10% obtained in the present calculations reflects the accuracy of our computational approach in representing the true physical systems.

I. The Computational Approach

In the present work *ab initio* investigations for the lowest lying molecular states of the molecules YN, ZrN, YS, and ZrS have been performed at the Complete Active Space Self Consistent Field (CASSCF) method followed by the Multi Reference Single and Double Excitation Configuration Interaction (MRSDCI) method. The Davidson correction, noted as MRSDCI+*Q* was then invoked in order to account for unlinked quadruple clusters. The *ab initio* MRSDCI+*Q* calculations were performed on two stages. In the first, electronic structure calculations were carried out ignoring the effect of relativistic spin orbit coupling.

While in the second type of calculations spin orbit relativistic effects were added through the inclusion of effective core potentials (ECP) in the expression of the molecular Hamiltonian. Both types of calculations were performed in the C_{2v} point group. The molecular electronic states, represented by the projection component of the orbital angular momentum ($\Lambda = 0, 1, 2, 3, 4$) on the internuclear axis, are classified into four symmetric representations of the point group C_{2v} according to $\Sigma^{\pm}$, Π , Δ , Φ , and Γ electronic states denoted as a1, a2, b1, and b2 symmetries, respectively. Further inclusion of spin orbit interactions couples the orbital angular momentum Λ with the spin angular momentum S through its projection Σ on the internuclear axis. This produces a total angular momentum along the internuclear axis $\Omega = |\Lambda \pm \Sigma|$, that characterizes the spin orbit electronic states. In this approach, spin orbit states with a well-defined quantum number $\Omega = 0, 1/2, 1, 3/2, \dots$ may arise from the spin orbit splitting in the parent $\Sigma^{\pm}$, Π , Δ , Φ , and Γ electronic states.

First we start with the CASSCF method to generate the molecular orbitals which were then used in higher level MRSDCI calculations. In all of the subsequent calculations, the CASSCF configuration space was divided into a set of inactive, active, and virtual molecular orbitals. The set of inactive molecular orbitals is composed of the lowest spin molecular orbitals which are doubly occupied in all determinants. While, the active molecular orbitals are in the energetically intermediate region, between the inactive doubly occupied orbitals and the virtual unoccupied orbitals. Then the single, and double excited determinants in MRSDCI calculations are generated from the reference CASSCF configuration by distributing the active electrons in all possible ways over all of the active molecular space. All of the calculations were done via the computational chemistry program MOLPRO [8] and by taking advantage of the graphical user interface GABEDIT [9].

The Yttrium and Zirconium species are treated in all electron schemes. The 39 electrons of the yttrium atom are considered using a contracted Gaussian basis set from literature [10, 11] for s, p, d functions and to which we have added one f function (27s 20p 17d 1f / 12s 7p 7d 1f). The exponent of this f-function was taken to be 0.26. The 40 electrons of the Zirconium atom were considered, using a contracted Gaussian basis set from literature [12, 13] for s, p, d functions (27s 20p 17d / 18s 16p 11d 1f) and to which we have added one f function with exponent 0.08, in order to facilitate the representation of the valence orbitals on Zirconium. On the other hand, the Nitrogen atom is treated, in all electron scheme, as a system of seven electrons by using the Rydberg2 (Dunning-Hay DZP + Rydberg) [14] basis set from literature (9s, 5p, 1d). The Sulfur atom is treated as a system of 16 electrons by using the Rydberg4 (Dunning-Hay DZP + Rydberg) [15-16] contracted basis set (11s, 7p / 6s, 4p).

Among the 56 electrons considered for Zirconium monosulfide ZrS, 48 electrons were frozen in subsequent calculations so that 8 valence electrons were distributed over all the active molecular orbitals. The CASSCF active configuration space contains 4σ (Zr: 5s, 4d₀, 5p_z, S: 3p_z), 3π (Zr: 4d_{±2}, 5p_{x,y}, S: 3p_{x,y}), and 1δ (Zr: 4d_{±1}) molecular orbitals. This corresponds to five *a*₁, three *b*₂, three *b*₁, and one *a*₂ orbital denoted as [5,3,3,1]. In Zirconium mononitride ZrN, the CASSCF active space included a CI space of configurations obtained by freezing 40 electrons and by distributing seven valence electrons among the active orbitals (Zr: 4d, 5s, 5p, N: 2s, 2p) in all possible ways. The CASSCF active space contains 4σ (Zr: 5s, 4d₀, 5p_z, N: 2p_z), 3π (Zr: 4d_{±2}, 5p_{x,y}, N: 2p_{x,y}), and 1δ (Y: 4d_{±1}) molecular orbitals. This corresponds to five *a*₁, three *b*₂, three *b*₁, and one *a*₂ orbital denoted as [5,3,3,1]. The CASSCF active space of Yttrium mononitride YN is obtained by distributing 6 valence electrons in all possible ways over the orbitals 3σ (Y: 5s, 4d₀, N: 2p_z), 2π (Y: 4d_{±2}, N: 2p_{x,y}), and 1δ (Y: 4d_{±1}). This corresponds to four *a*₁, two *b*₂, two *b*₁, and one *a*₂ orbital, denoted as [4,2,2,1]. Of the 55 electrons explicitly considered for Yttrium monosulfide YS, 39 electrons for Y and 16 for S, 48 inner electrons were frozen in subsequent calculations so that 7 valence electrons were explicitly treated. The active space contains 4σ (Y: 5s, 5p_z, 4d₀, S: 3p_z), 3π (Y: 5p_{x,y}, 4d_{±2}, S: 3p_{x,y}), and 1δ (Y: 4d_{±2}) orbitals in the C_{2v} symmetry, this corresponds to 8 active molecular orbitals distributed into irreducible representations *a*₁, *b*₁, *b*₂ and *a*₂ in the following way: 5*a*₁, 3*b*₁, 3*b*₂, 1*a*₂, noted [4,2,2,1], while the doubly occupied orbital 1σ (Y:4s) of Yttrium has been considered as inactive in CASSCF calculations. In the four molecules of interest the CASSCF/MRSDCI+Q calculations were performed piecewise as a function of the internuclear distance *R*, at equal steps of 0.03Å. This allows for the construction of Born-Oppenheimer potential energy curves (PEC) for the ground and low lying excited electronic states. The fitting of the drawn PECs into a polynomial in *R* allows for the determination of the equilibrium internuclear distance *R*_e and for the calculation of several spectroscopic constants as the; transition energies *T*_e, harmonic vibrational frequencies ω_e , and rotational constants *B*_e, *D*_e, and α_e .

For the most part spin orbit coupling (SO) is simply ignored for light elements. However, for intermediate weight main group elements SO interactions become significant and can actually grow to the order of a few hundreds to a few thousand of cm⁻¹ [17]. Transition metal compounds have a rich set of electronic states owing to unfilled d shells, and therefore SO effects are commonplace. In this work, the energies for the SO molecular states Ω are obtained from the treatment of the total Hamiltonian $H_t = H_e + W_{SO}$, where *H*_e is the Hamiltonian in the Born-Oppenheimer approximation for calculating the energies of the

molecular states labeled $^{2s+1}\Lambda^\pm$, and where W_{SO} is the spin orbit pseudopotential used to represent SO coupling. The semi-empirical spin orbit pseudopotential (W_{SO}^{PS}) used in our calculations was designed from Effective Core Potentials ECP to represent the spin orbit effects in Yttrium and Zirconium [18]. The impact of the SO relativistic effect on molecular properties increases with nuclear charge Z to an extent that molecules containing heavy elements cannot be described correctly even in a qualitative manner without SO effects. Owing to the relatively small charge and size of Nitrogen and Sulfur with respect to the heavy metals Yttrium and Zirconium, spin orbit effects have been neglected in sulfur and nitrogen. The energies for the molecular states Ω including the spin orbit effects have been obtained by diagonalizing the total Hamiltonian H_t in the basis of $\Lambda\Sigma$ states yielding the spin orbit electronic states $\Omega = |\Lambda\pm\Sigma| = 0^+, 0^-, 1/2, 1, 3/2, 2, \dots$

II. Electronic Structure Calculations

Studies of small units containing a non-metal atom and a transition-metal atom are of immense scientific and technological interests. With the present investigation, we begin a systematic study of the transition metal nitrides and sulfides of Yttrium and Zirconium (YN, ZrN, ZrS, YS) in order to elucidate their electronic structures and explore their bonding characteristics.

III. A. The Structure of Yttrium Nitride YN

III. A. 1. Preliminary Works on YN

Of all the transition metal nitrides, the YN molecule is the least one characterized. To the best of our knowledge only five papers have been published on the electronic structure of Yttrium mononitride. To our knowledge, experimental investigations of the Yttrium mononitride were done by three groups: First, Ram and Bernath [19] studied the vibrational structure of the electronic transition $(1)^1\Sigma^+ \leftarrow X^1\Sigma^+$, reporting several vibrational levels and spectroscopic constants. Further, rotational analysis resulted in accurate rotational constants of the six lowest vibrational levels of the $A^1\Sigma^+$ and $X^1\Sigma^+$ states. Then, Jakubek *et. al* [20] studied the electronic structure of the YN molecule by laser excitation spectroscopy, reporting several spectroscopic constants for the ground and 3 newly observed excited states (B1, C1, D1). The assignment of these states could not be done based on the preexisting *ab initio* calculations of Shim *et. al* [21]. Jakubek *et. al.* [22] then reinvestigated the YN molecule by a Laser induced fluorescence spectroscopy, for the ground $X^1\Sigma^+$ and the two excited states $(1)^1\Sigma^+$ and $(1)^3\Sigma^+$; RKR potential energy curves were constructed based on calculated

vibrational constants. To the best of our knowledge only two theoretical papers have been published, so far, on the electronic structure of YN. First Shim *et. al* [21] performed an all-electron CASSCF *ab initio* calculations for nine electronic states (singlet, triplet, and quintet) of the YN molecule. Shim *et. al* [21] results are questionable as they fail to reproduce the experimental results available in Ref [19, 20, 22]. Recently, Duo *et. al* [23] performed CASSCF/CASPT2 calculations for the low lying 14 (singlet, triplet, quintet) electronic states of the YN molecule. The calculated spectroscopic constants are in good agreement with experimental results, however, many experimentally available excited electronic states B1, C1, and D1 [20] could not be assigned clearly.

III. A. 2. Results on YN

For the first part of our calculations without spin orbit effects we draw in Figures 1 – 5 the potential energy curves for the 25 low-lying singlet, triplet, and quintet electronic states $^{2s+1}\Lambda^{(\pm)}$ of the YN molecule as a function of the internuclear distance range $1.3\text{\AA} \leq R \leq 3\text{\AA}$. In Table I we list our results for the spectroscopic constants in the ground and excited electronic states of YN, together with the theoretical and experimental results available in literature. A percentage relative difference that reflects the accuracy of our calculations with respect to other experimental and theoretical results was also evaluated in Table I.

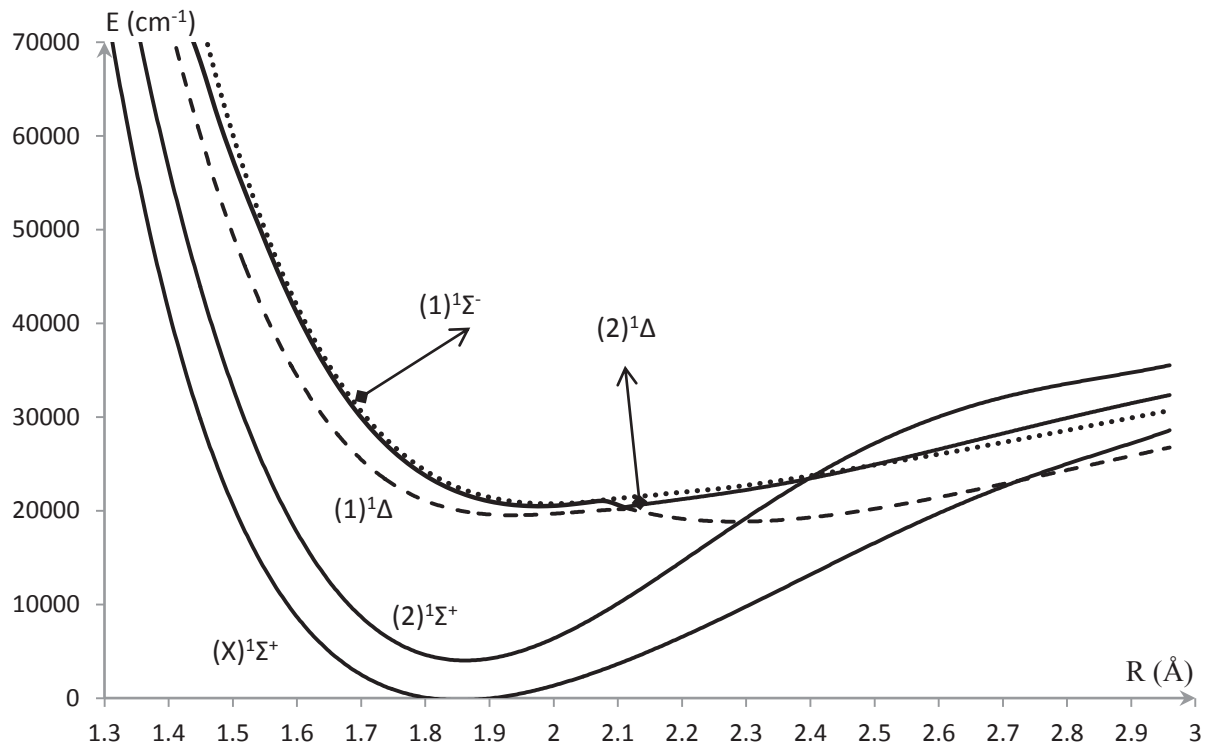


Fig. 1: Potential energy curves for the $1\Sigma^\pm$ and 1Δ states of the molecule YN.

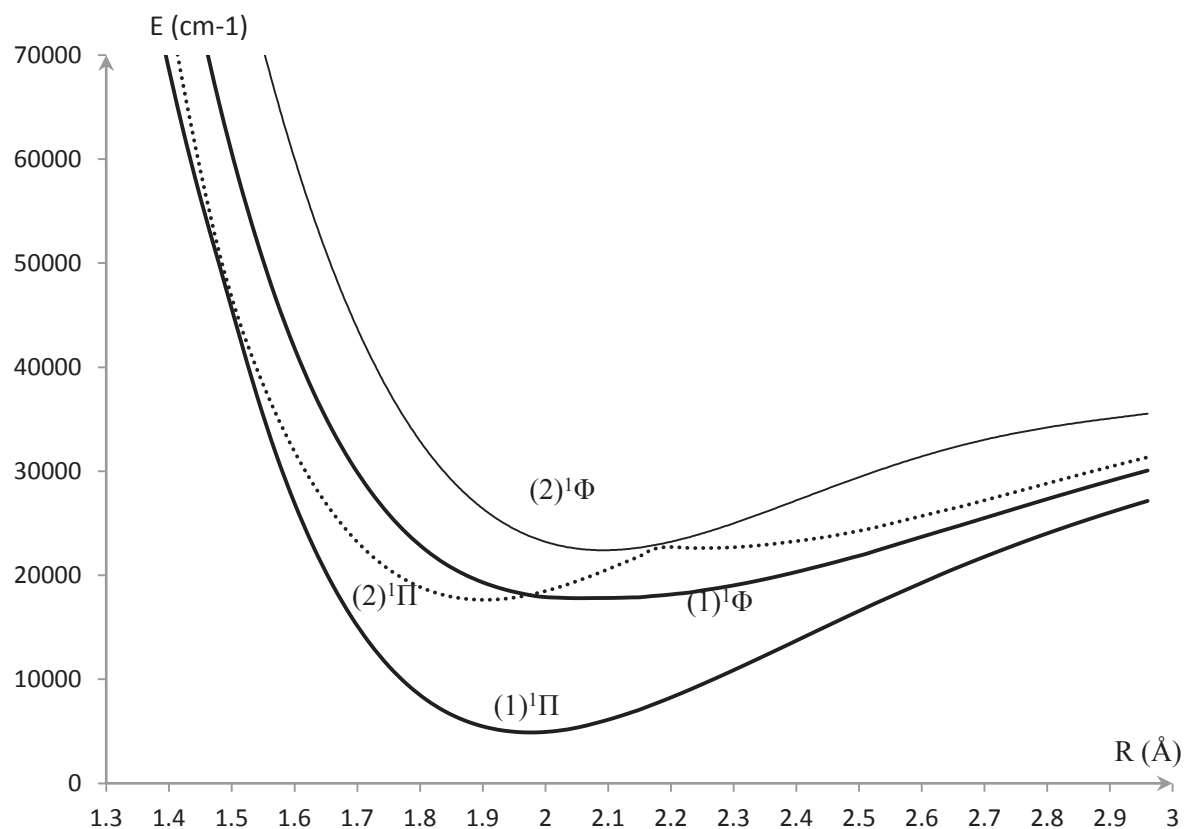


Fig. 2: Potential energy curves for the 1Π and 1Φ states of the molecule YN.

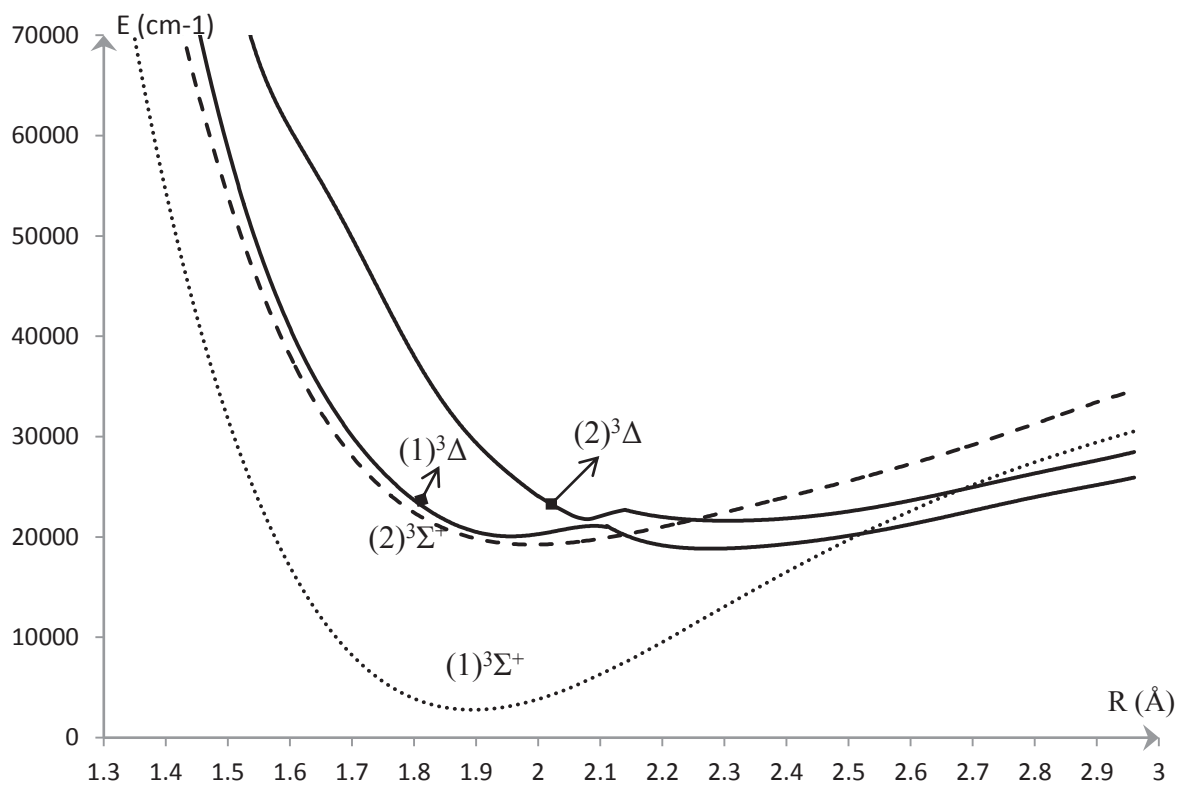


Fig. 3: Potential energy curves for the $3\Sigma^+$ and 3Δ states of the molecule YN.

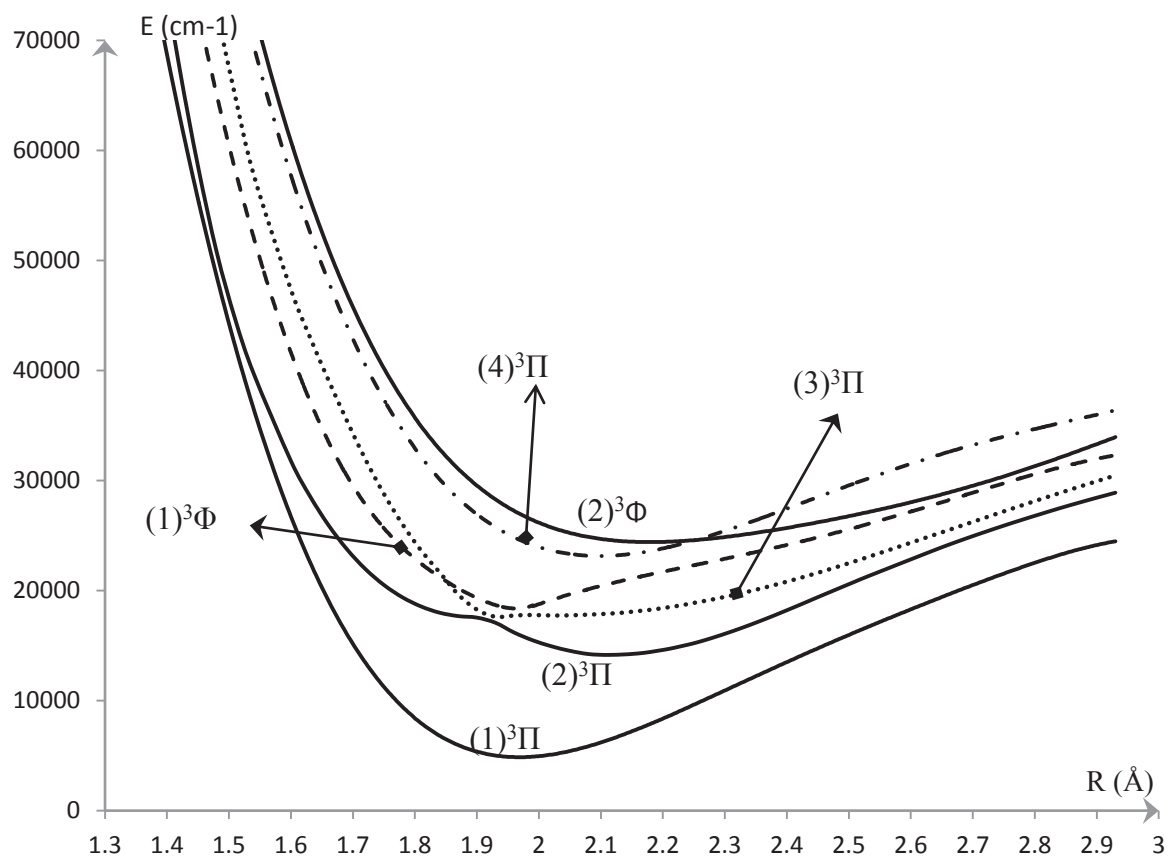


Fig. 4: Potential energy curves for the $^3\Pi$ and $^3\Phi$ states of the molecule YN.

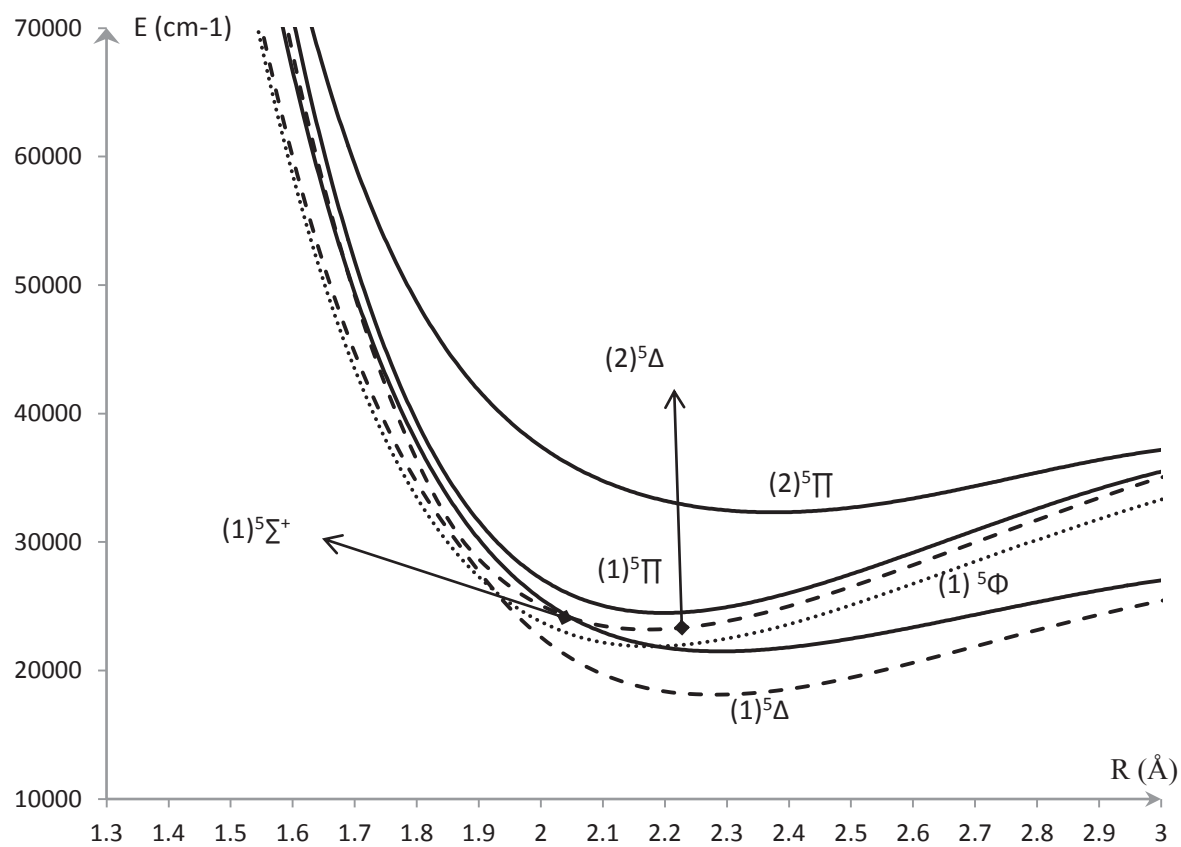


Fig. 5: Potential energy curves for the $^5\Sigma$, $^5\Delta$, $^5\Pi$ and $^5\Phi$ states of the molecule YN.

Table I:

Spectroscopic constants for the lowest lying 25 singlet, triplet and quintet electronic states of the molecule YN.

State	T_e (cm ⁻¹)	$\delta T_e/T_e$	ω_e (cm ⁻¹)	$\delta\omega_e/\omega_e$	$B_e \times 10^1$ (cm ⁻¹)	$\delta B_e/B_e$	α_e (cm ⁻¹)	$\delta\alpha_e/\alpha_e$	R_e (Å)	$\delta R_e/R_e$
$X^1\Sigma^+$	0 ^a		656.51 ^a		4.1173 ^a		0.00304 ^a		1.839 ^a	
	0 ^b		650.6 ^{Exp b}	0.9%	4.2815 ^{Exp c}	3.8%	0.00333 ^{Exp c}	8.5%		
	0 ^c		661.0 ^{Exp c}	0.6%					1.80405 ^{Exp c}	1.9%
	0 ^{Theo d}		807.0 ^{Theo d}	18.6%					1.78862 ^{Theo d}	2.8%
	0 ^{Theo e}		658 ^{Theo e}	0.2%					1.809 ^{Theo e}	1.7%
	0 ^{Exp f}		633.2 ^{Exp f}	3.7%						
$(2)^1\Sigma^+$	3850.76		970.4		4.0377		0.00173		1.857	
	3612.0 ^{Exp c}	6.6%	1200.0 ^{Exp c}	19.1%	4.2311 ^c	4.6%	0.00188 ^{Exp c}	8.3%	1.81477 ^{Exp c}	2.3%
	3670 ^{Theo e}	4.9%	979 ^{Theo e}	0.9%					1.803 ^{Theo e}	3.0%
	3700 ^{Exp f}	4.1%	1007.4 ^{Exp f}	3.6%						
$(1)^1\Delta$	18776.85		775.14		2.6938		-0.00526		2.272	
	17305 ^{Theo e}	8.5%	715 ^{Theo e}	8.4%					1.876 ^{Theo e}	21%
	30780 ^{Theo d}	39%								
$(2)^1\Delta$	20764.10		186.08		3.1718		-0.22287		2.131	
$(1)^1\Pi$	5802.90		720.53		3.6078		0.00812		1.968	
	9915 ^{Theo d}	41%	706.0 ^{Theo d}	2.05%					1.97383 ^{Theo d}	0.5%
	6482 ^{Theo e}	10.4%	755 ^{Theo e}	4.5%					1.916 ^{Theo e}	2.7%
$(1)^1\Phi$	17788.92		376.56		3.2096		0.00975		2.075	
$(2)^1\Pi$	19232.61		380.05		3.2191		0.01516		2.08646	
	19832.98 ^{v=1 Exp b}	3.0%			3.255 ^{Exp b}	1.1%				
	19232 ^{Theo e}	0.00%	562 ^{Theo e}	32%					2.057 ^{Theo e}	1.4%
$(2)^1\Phi$	22192.52		737.37		3.1428		-0.00634		2.102	
$(1)^1\Sigma^-$	20652.51		849.91		3.4703		-0.00264		2.002	
$(1)^3\Sigma^+$	2781.84		763.82		3.8773		0.00358		1.896	
	5177 ^{Theo d}	46%	771.0 ^{Theo d}	0.9%					2.09025 ^{Theo d}	9.2%
	2360 ^{Theo e}	17.8%	831 ^{Theo e}	8.1%					1.833 ^{Theo e}	3.4%
	2413 ^{Exp f}	15.3%	805.12 ^{Exp f}	5.1%					1.866 ^{Exp f}	1.6%
$(2)^3\Sigma^+$	19096.71		749.17		3.7495		0.00196		1.928	
	18661.5 ^{Exp b}	2.3%	723.5 ^b	3.5%	3.90173 ^{Exp b}	3.9%			1.919 ^{Exp b}	0.4%
$(1)^3\Delta$	18821.32		707.49		3.6319		0.00019		1.958	
	16967 ^{Theo e}	19%	777 ^{Theo e}	8.9%					1.861 ^{Theo e}	5.2%
$(2)^3\Delta$	19269.14		427.36		2.7091		0.01872		2.279	
$(1)^3\Pi$	5485.09		685.65		3.5675		-0.0000036		1.975	
	9290 ^{Theo d}	41%	711.0 ^{Theo d}	3.5%					1.96853 ^{Theo d}	0.3%
	5962 ^{Theo e}	7.9%	758 ^{Theo e}	9.5%					1.922 ^{Theo e}	2.7%
$(1)^3\Phi$	17503.14		801.52		3.5069		-0.00352		1.989	
$(2)^3\Pi$	14201.42		403.62		3.1156		0.01550		2.118	
	15380 ^{Theo e}	7.7%	692 ^{Theo e}	41%					2.034 ^{Theo e}	4.1%
$(2)^3\Phi$	18602.08		880.03		3.5676		-0.0034		1.975	
$(3)^3\Phi$	21700.96		1033.76		3.1612		-0.00421		2.099	
$(3)^3\Pi$	24536.04		605.09		3.0916		0.02057		2.116	
$(1)^5\Sigma^+$	21994.68		213.97		3.0284		0.15761		2.176	
$(1)^5\Phi$	20186.18		526.56		3.0460		-0.0019		2.184	
$(1)^5\Delta$	18559.14		476.94		2.7229		0.00610		2.266	
	20538 ^{Theo e}	9.6%	462 ^{Theo e}	3.2%					2.219 ^{Theo e}	2.1%
$(1)^5\Pi$	21200.05		842.05		2.7497		-0.0006		2.250	
	21746 ^{Theo e}	2.5%	572 ^{Theo e}	44%					2.096 ^{Theo e}	7.3%
$(2)^5\Delta$	23321.93		458.14		3.1565		0.21811		2.167	
$(2)^5\Pi$	24780.30		493.99		2.8045		0.01875		2.229	
			390 ^{Theo d}	26.6%					2.35 ^{Theo d}	5.1%

Ref: a. First entry is for the values of the present work

b. Ref [20]

c. Ref [19]

d. Ref [21]

e. Ref [23]

f. Ref [22]

Note: 19832.98^{v=1 b}, corresponds to the first vibrational energy level in the $(2)^1\Pi$ state.

The comparison between our calculated values of T_e with those obtained experimentally [19, 20, 22] shows a very good agreement with a percentage relative difference of 2.3% (Ref.[20]) $\leq \delta T_e/T_e \leq 15.3\%$ (Ref.[22]) for the states $(2)^1\Sigma^+$, $(2)^1\Pi$, $(1)^3\Sigma^+$, and $(2)^3\Sigma^+$. This agreement deteriorates by comparing our values to those calculated by Shim and Gingerich [21] with relative difference of $39\% \leq \delta T_e/T_e \leq 46\%$ for the states $(1)^1\Delta$, $(1)^1\Pi$, $(1)^3\Sigma^+$, $(1)^3\Pi$ and $(2)^5\Pi$. The comparison between the experimental energy levels obtained for YN [19, 20, 22] to those of ScN [24] shows that the electronic states $^{2s+1}\Lambda^{(\pm)}$ in YN are much lower than their counterparts in ScN. This suggests that the lowest $(1)^1\Pi$ and $(1)^3\Pi$ states of ScN must lie in a higher energy region than the $(1)^1\Pi$ and $(1)^3\Pi$ states in YN. But since the energies of the $(1)^1\Pi$ and $(1)^3\Pi$ states in ScN are 7443 cm^{-1} and 7331 cm^{-1} respectively [24], then it is unlikely to have the energies of these states in YN at a higher energy region of 9915 cm^{-1} and 9290 cm^{-1} , as it has been calculated by Shim and Gingerich [21]. Unfortunately, the positions of the low-lying excited states calculated by Shim and Gingerich [21] are approximately twice the corresponding values obtained for ScN [24]. These discrepancies in the calculated energy position are presumably due to a problem in presenting the ground state wavefunctions by Shim and Gingerich [21]. In order to confirm the accuracy of our predictions for the states $(2)^1\Sigma^+$, $(1)^1\Pi$ and $(1)^3\Pi$ we repeated the calculation of the transition energy T_e and the equilibrium internuclear distance R_e (Table II) by using different basis sets and with different active spaces. The investigated energy values confirm that the $(1)^1\Pi$ and $(1)^3\Pi$ states lie at a lower energy value of $\approx 5000\text{ cm}^{-1}$, than that originally predicted by Shim and Gingerich [21].

Table II:

Comparison between theoretical results obtained for the $(1)^1\Pi$, $(1)^3\Pi$, and $(2)^1\Sigma^+$ states by using different basis sets with different active spaces.

N- basis	State	Active space	Method	$T_e(\text{cm}^{-1})$	$R_e(\text{\AA})$
Ryd3 ^a	$(1)^1\Pi$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	4917 / 4799	1.98
	$(1)^3\Pi$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	5200 / 4900	1.96
	$(2)^1\Sigma^+$	(Y: 5s, 4d, 5p), (N: 2p)	MRCI / CASSCF	4660 / 4400	1.85
Ryd2 ^a	$(1)^1\Pi$	(Y: 5s, 4d, 5p), (N: 2p)	MRCI / CASSCF	5056 / 4620	1.98
		(Y: 5s, 4d), (N: 2p)	MRCI / CASSCF	5803 / 4910	1.97
	$(1)^3\Pi$	(Y: 5s, 4d), (N: 2p)	MRCI / CASSCF	5485 / 5200	1.98
	$(2)^1\Sigma^+$	(Y: 5s, 4d), (N: 2p)	MRCI / CASSCF	3923 / 4536	1.85
		(Y: 5s, 4d, 5p), (N: 2p)	MRCI / CASSCF	3300 / 4567	1.86
Hazinaga ^a	$(1)^1\Pi$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	4041 / 3653	2.02
	$(1)^3\Pi$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	3900 / 3137	2.03
	$(2)^1\Sigma^+$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	1556 / 1962	1.86
Roos ^a	$(1)^1\Pi$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	3800 / 3600	2.10
	$(1)^3\Pi$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	3403 / 3300	2.10
	$(2)^1\Sigma^+$	(Y: 5s, 4d), (N: 2p, 3s)	MRCI / CASSCF	4686 / 4329	1.92

a. Basis sets obtained from literature Ref [8].

The comparison between our calculated values of T_e by using the methods of CASSCF/MRDSCI+Q to those calculated by Dou *et al.* [23] by using the methods of CASSCF/CASPT2, shows a very good agreement with a percentage relative difference of $0.0\% \leq \delta T_e/T_e \leq 10.4\%$, except for the values of the two states $(1)^3\Sigma^+$ and $(1)^3\Delta$ where the relative differences are respectively, 17.8% and 19.0%. The comparison between the calculated values of the vibrational harmonic frequency ω_e in the present work with those obtained experimentally in literature shows a very good agreement with a relative difference of $0.6\% \leq \delta\omega_e/\omega_e \leq 5.1\%$ for the states $X^1\Sigma^+$, $(2)^1\Sigma^+$, $(1)^3\Sigma^+$, and $(2)^3\Sigma^+$, except for the value of ω_e in Ref [19] for the state $(2)^1\Sigma^+$ where a relative difference of $\delta\omega_e/\omega_e=19.1\%$ was obtained. The agreement is also very good by comparing our values with those calculated by Shim and Gingerich [21] and Dou *et al.* [23] with relative differences of $0.2\% \leq \delta\omega_e/\omega_e \leq 9.5\%$ except for the values given by Shim and Gingerich [21] for the states $X^1\Sigma^+$ and $(2)^5\Pi$ where the relative differences are respectively $\delta\omega_e/\omega_e = 18.6\%$ and $\delta\omega_e/\omega_e = 26.6\%$ and those given by Dou *et al.* [23] for the states $(2)^1\Pi$, $(2)^3\Pi$, $(1)^5\Pi$ where the relative differences are respectively, $\delta\omega_e/\omega_e = 32\%$, $\delta\omega_e/\omega_e = 41\%$ and $\delta\omega_e/\omega_e = 44\%$. A very good agreement is obtained by comparing the experimental values in literature for the rotational constant B_e with our calculated values with relative differences of $1.1\% \leq \delta B_e/B_e \leq 4.6\%$. The experimental and theoretical values in literature for the internuclear distance at equilibrium R_e are in good agreement with our calculated values with relative differences of $0.3\% \leq \delta R_e/R_e \leq 9.2\%$.

Upon close examination of the drawn potential energy curves in Figures (1 – 5) one observes certain regions of crossings and avoided crossings among the potential energy curves of the investigated electronic states. These are regions at which the electronic states perturb one another and are important in deciding the channel of molecular dissociation in photo dissociation dynamics [25]. In Table III we report the positions of these crossings R_c and avoided crossings R_{av} together with the energy gap separations ΔE_{av} , recorded between the different potential energy curves of the investigated electronic state in the YN molecule.

Within the investigated electronic states of YN three avoided crossings have been detected to occur between the potential energy curves of the states $(1)^1\Delta - (2)^1\Delta$, $(1)^3\Delta - (2)^3\Delta$, and $(2)^3\Pi - (3)^3\Pi$. The magnitude of the energy gap between the interacting states at these regions ranged between 550cm^{-1} and 611cm^{-1} . There are two other avoided crossings noticeably appearing in Figures 2 and 3 and occurring between the $(2)^1\Pi$ and the $(3)^1\Pi$ state at $R = 2.18\text{Å}$, and between the $(2)^3\Delta$ state and the $(3)^3\Delta$ state at $R = 2.16\text{Å}$ but unfortunately the potential

energy curve of the two excited states $(3)^1\Pi$, $(3)^3\Delta$ weren't very clear at these regions, mainly because they were mixed with higher excited electronic states.

Table III:

Positions of the crossings and avoided crossings recorded between the different electronic states of the molecule YN.

molecule 1A:					molecule 1B:					
State1	State2	Crossing R _c (Å)	Avoided crossing R _{av} (Å) ΔE _{av} (cm ⁻¹)		State1	State2	Crossing R _c (Å)	Avoided crossing R _{av} (Å) ΔE _{av} (cm ⁻¹)		
X ¹ Σ ⁺	(1) ¹ Δ	2.72			(1) ¹ Σ ⁻	(1) ¹ Π	2.14/2.28			
	(1) ¹ Π	2.50				(2) ³ Δ	2.20			
	(2) ³ Π	2.42				(2) ³ Σ ⁺	2.32			
	(1) ³ Δ	2.71				(3) ³ Π	2.25			
	(1) ⁵ Δ	2.65				(1) ⁵ Φ	2.20			
	(1) ⁵ Φ	2.80				(1) ⁵ Σ ⁺	2.19/2.40			
(2) ¹ Σ ⁺	(1) ¹ Σ ⁻	2.40			(1) ¹ Π	(1) ³ Σ ⁺	2.10			
	(2) ¹ Δ	2.40				(1) ³ Δ	2.80			
	(1) ¹ Δ	2.29				(1) ³ Π	2.0 / 2.30			
	(1) ¹ Π	1.94				(1) ⁵ Δ	2.70			
	(1) ¹ Φ	2.30			(1) ¹ Φ	(2) ³ Σ ⁺	1.80/2.30			
	(2) ¹ Π	2.40				(1) ³ Φ	1.84/1.94			
	(2) ³ Π	1.94				(3) ³ Π	2.04			
	(3) ³ Π	2.20				(1) ⁵ Δ	2.22			
	(1) ³ Φ	2.30				(1) ⁵ Φ	2.55			
	(4) ³ Π	2.42			(2) ¹ Π	(2) ³ Σ ⁺	2.04/2.30			
	(1) ³ Δ	2.30				(1) ³ Δ	2.11			
	(2) ³ Δ	2.36				(2) ³ Δ	2.18			
	(2) ³ Σ ⁺	2.42				(3) ³ Π	1.90			
	(1) ⁵ Δ	2.26				(1) ³ Φ	2.10			
	(1) ⁵ Φ	2.36				(1) ⁵ Δ	2.08			
	(1) ⁵ Σ ⁺	2.40				(1) ⁵ Σ ⁺	2.16/2.33			
	(2) ⁵ Δ	2.49			(1) ⁵ Φ	2.15				
	(1) ⁵ Π	2.51			(2) ³ Π	(2) ³ Π		1.93	552.8	
	(1) ¹ Δ	(2) ¹ Δ		2.14	550	(1) ¹ Φ	(2) ³ Δ	2.08/2.12		
		(2) ³ Σ ⁺	1.9 / 2.12				(4) ³ Π	1.80		
(3) ³ Π		1.86 / 2.25			(1) ⁵ Σ ⁺		2.11			
(1) ³ Φ		1.89 / 2.04			(2) ⁵ Δ		2.21			
(2) ³ Π		2.47			(1) ⁵ Π		2.30			
(2) ¹ Π		2.09			(1) ³ Δ	(2) ³ Δ		2.08	611.1	
(1) ¹ Φ		1.90 / 2.29								
(2) ¹ Δ	(2) ¹ Π	2.10 / 2.34								
	(1) ³ Δ	2.05 / 2.12								
	(1) ⁵ Δ	2.04								
	(1) ⁵ Φ	2.22								
	(3) ³ Π	1.82								
	(1) ³ Φ	2.10								

The inclusion of relativistic spin orbit effects in molecular electronic structure calculations greatly enhances the accuracy of nonrelativistic *ab initio* results. In heavy elements spin orbit effects may induce splittings that can reach the order of 1000 cm^{-1} . These splittings may change the shape of the potential energy curves, and could thus modify the values of the

spectroscopic constants appreciably. In Figures 6 – 13 we draw the potential energy curves for the spin orbit electronic states $\Omega=0^+$, 0^- , 1, 2, 3, 4, resulting from the interaction of the orbital angular momentum Λ with the spin angular momentum S projected along the internuclear distance Σ .

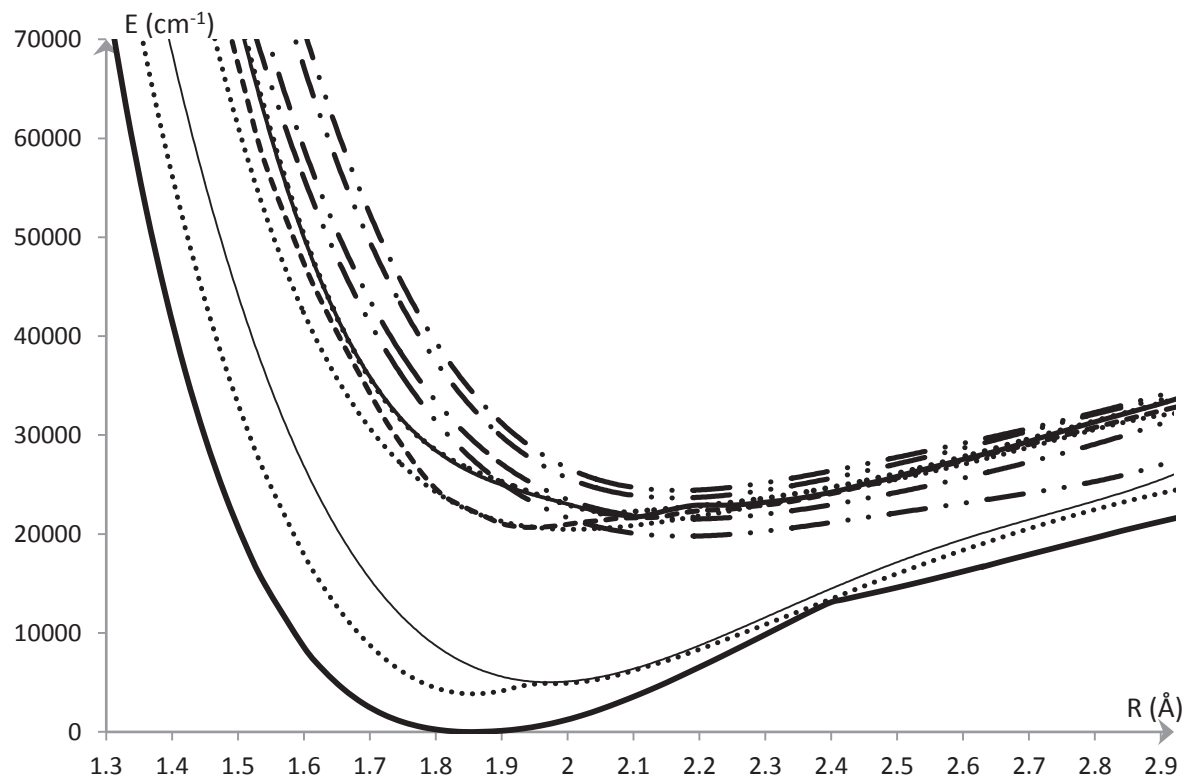


Fig. 6: Potential Energy curves of $\Omega = 0^+$ states (full and dotted lines) of the molecule YN.

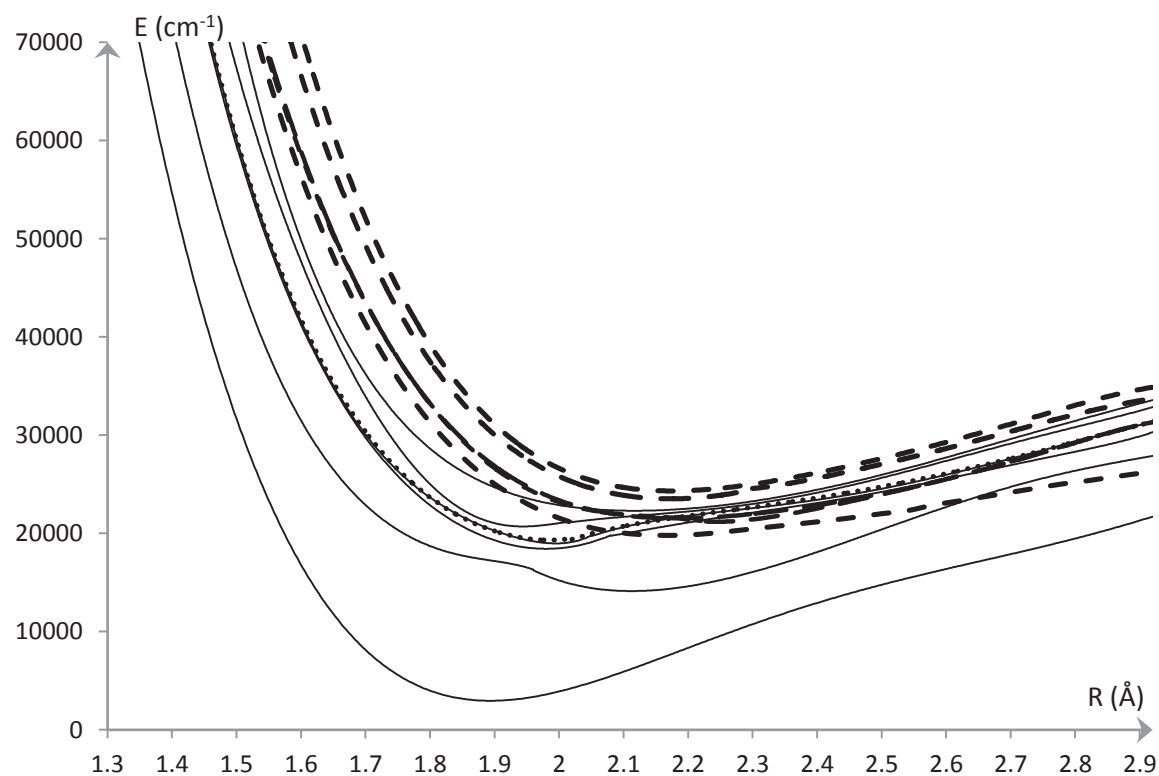


Fig. 7: Potential Energy curves of $\Omega = 0^-$ states (full and dotted lines) of the molecule YN.

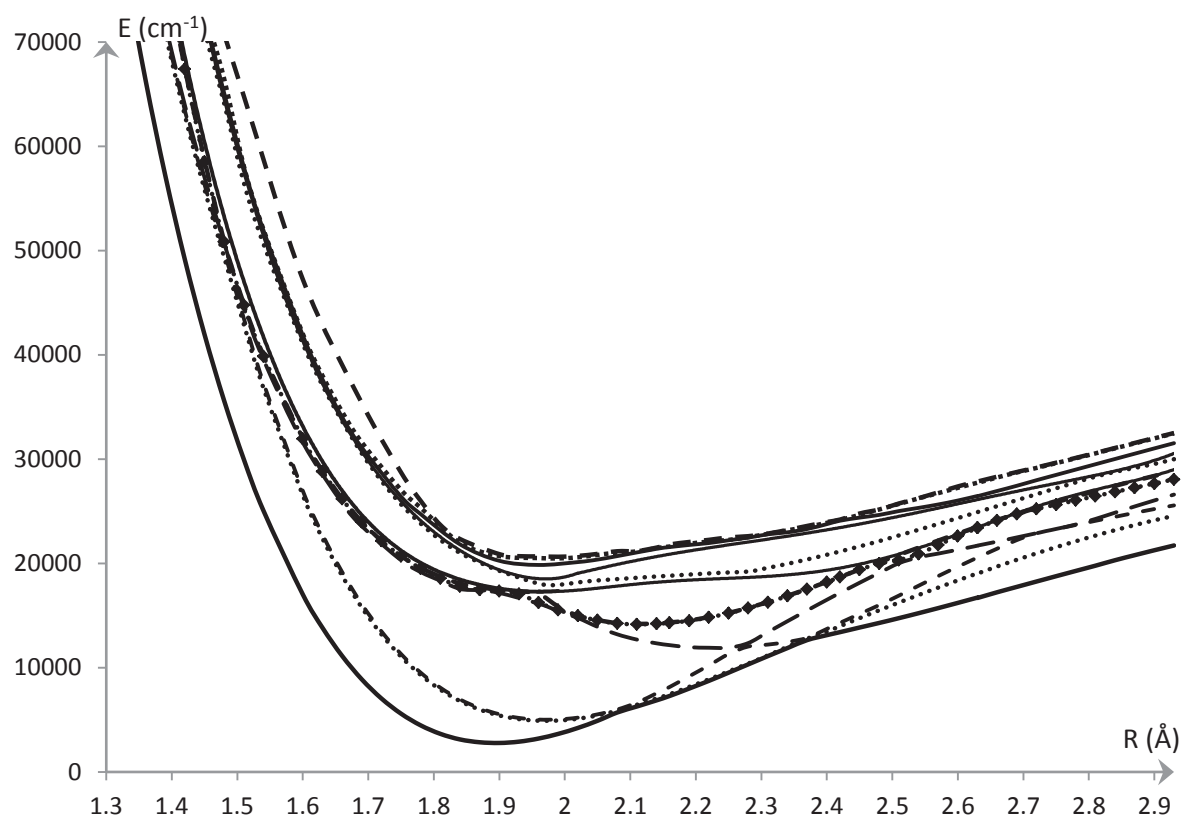


Fig. 8: Potential Energy curves of the $\Omega = 1$ states (full and dotted lines) of the molecule YN originating from singlet and triplet parent states ($^3\Sigma^+$, $^3\Delta$, $^3\Pi$, $^1\Pi$).

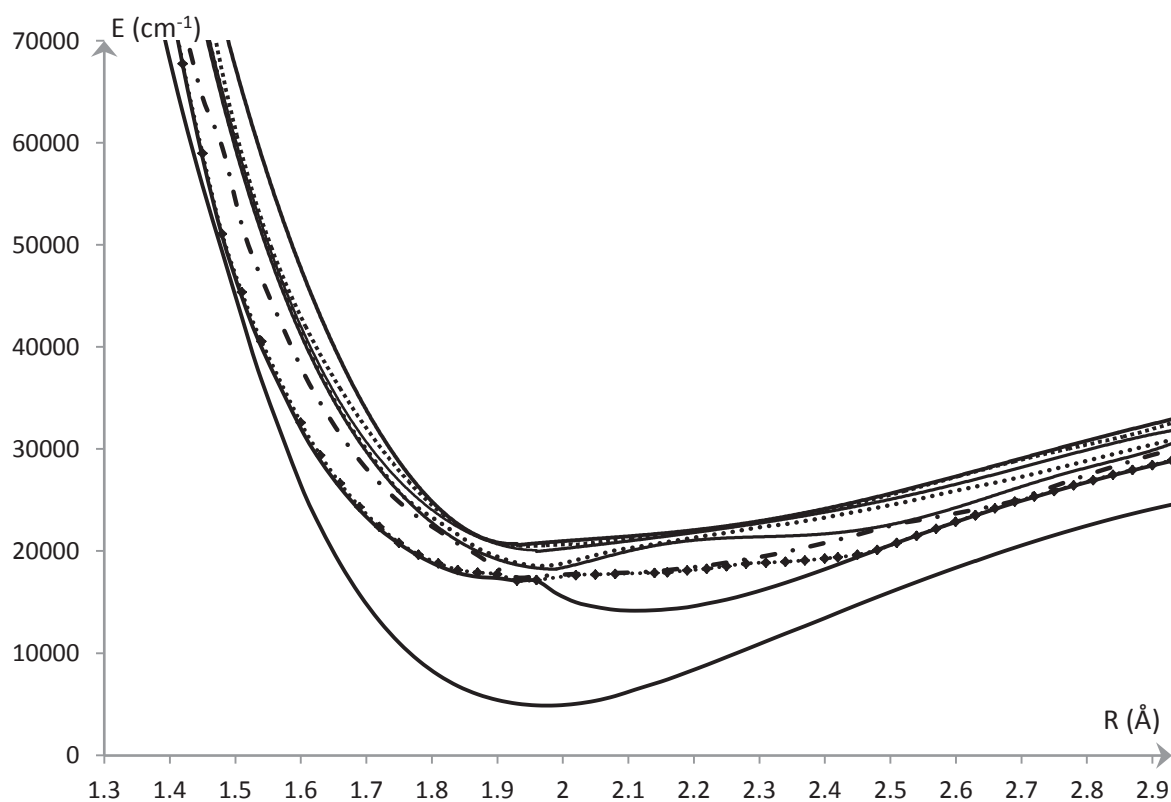


Fig. 9: Potential Energy curves of the $\Omega = 2$ states (full and dotted lines) of the molecule YN originating from singlet and triplet parent states ($^1\Pi$, $^1\Delta$, $^3\Pi$, $^3\Delta$, $^3\Phi$).

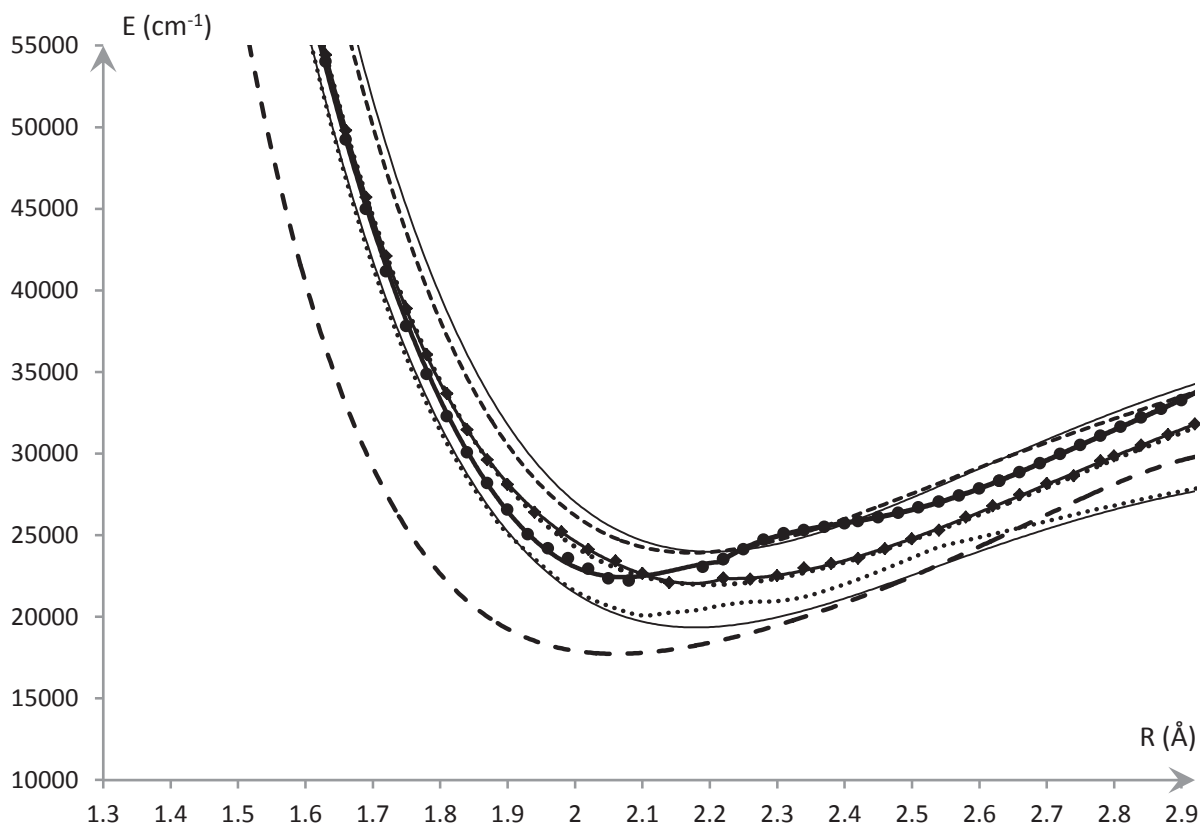


Fig. 10: Potential Energy curves of $\Omega = 3$ (full and dotted lines), $\Omega = 4$ (—♦—♦) and $\Omega = 5$ (—●—●) states of the molecule YN.

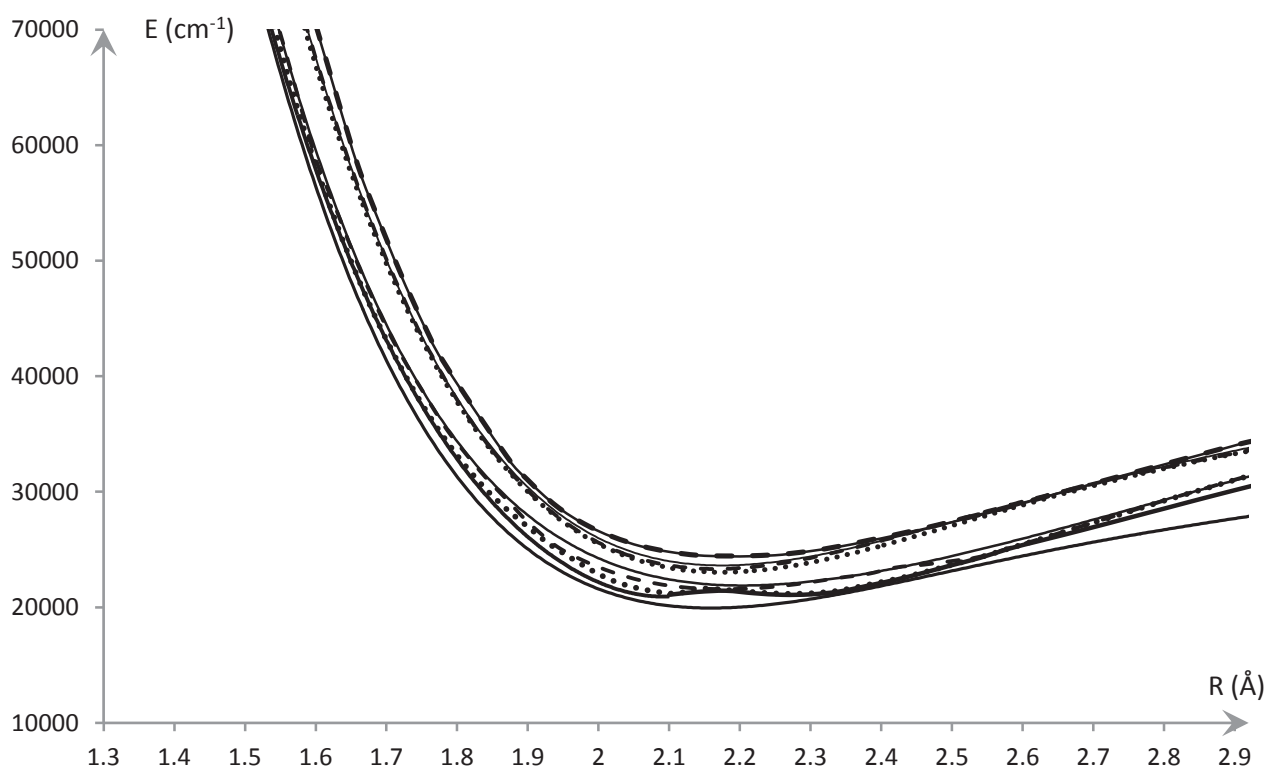


Fig. 11: Potential Energy curves of the $\Omega = 1$ (dotted lines) and $\Omega = 2$ (full lines) states of the molecule YN originating from quintet parent states ($^5\Sigma^+$, $^5\Delta$, $^5\Pi$, $^5\Phi$).

Then by fitting the calculated potential energy curves around their equilibrium into a polynomial in R several spectroscopic constants T_e , R_e , ω_e , D_e , and B_e were calculated. These results for the spin orbit electronic states Ω of YN are shown in Table IV.

Table IV:
Spectroscopic constants for the 60 low lying spin orbit electronic states of the molecule YN.

State	T_e (cm ⁻¹)	$\delta T_e / T_e$	ω_e (cm ⁻¹)	$\delta \omega_e / \omega_e$	$D_e \times 10^7$ (cm ⁻¹)	$B_e \times 10^1$ (cm ⁻¹)	$\delta B_e / B_e$	R_e (Å)	$\delta R_e / R_e$
(1) $0^+[(X)^1\Sigma^+]$	0.0		638.99 ^a		-6.4581	4.0625		1.853	
			650.6 ^{Exp b}	1.8%					
			661.0 ^{Exp c}	3.3%		4.2815 ^{Exp c}	5.1%	1.80405 ^{Exp c}	2.7%
			807.0 ^{Theo d}	21%				1.78862 ^{Theo d}	3.4%
			633.2 ^{Exp e}	0.9%					
			658 ^{Theo f}	2.8%				1.809 ^{Theo f}	2.4%
(2) $0^+[(2)^1\Sigma^+]$	3813.62		1080.56		-2.4046	4.0843		1.846	
	3612.0 ^{Exp c}	5.5%	1200.0 ^{Exp c}	9.9%		4.2311 ^{Exp c}	3.5%	1.81477 ^{Exp c}	1.7%
	3700 ^{Exp e}	3.0%	1007.4 ^{Exp e}	7.2%					
	3670 ^{Theo f}	3.9%	979 ^{Theo f}	10.3%				1.803 ^{Theo f}	2.3%
(3) $0^+[(1)^3\Pi]$	5026.52		686.75		-3.8233	3.5545		1.979	
(4) $0^+[(3)^1\Sigma^+]$	20491.97		647.17		-4.4896	3.6035		1.966	
(5) $0^+[(1)^1\Sigma^+]$	20778.05		767.43		-3.4329	3.6735		1.947	
(6) $0^+[(4)^3\Pi]$	21997.95		763.52		-2.1650	3.1463		2.104	
(7) $0^+[(4)^1\Sigma^+]$	22019.43		919.58		-1.5731	3.1940		2.088	
(8) $0^+[(1)^5\Delta]$	21666.22		755.29		-1.6347	2.8348		2.217	
(9) $0^+[(2)^5\Pi]$	23732.20		742.50		-1.8579	2.9417		2.176	
(10) $0^+[(1)^5\Pi]$	24646.88		664.23		-2.1224	2.8585		2.208	
(1) $0^-[(1)^3\Sigma^+]$	2762.26		814.36		-3.5256	3.8807		1.895	
(2) $0^-[(2)^3\Pi]$	14116.63		704.17		-2.4718	3.1383		2.107	
(3) $0^-[(2)^3\Sigma^+]$	18467.12		886.03		-2.3389	3.5760		1.974	
(4) $0^-[(3)^3\Pi]$	18933.11		980.87		-1.9022	3.5708		1.975	
(5) $0^-[(3)^3\Sigma^+]$	19310.95		864.94		-2.3998	3.5498		1.981	
(6) $0^-[(1)^3\Sigma^-]$	20868.93		698.28		-4.1031	3.6669		1.949	
(7) $0^-[(4)^3\Pi]$	22080.55		748.61		-2.2578	3.1469		2.103	
(8) $0^-[(1)^5\Phi]$	20116.15		508.02		-4.0265	2.9584		2.169	
(9) $0^-[(1)^5\Sigma^+]$	21510.96		615.53		-2.2683	2.7408		2.255	
(10) $0^-[(1)^5\Delta]$	21802.65		477.81		-3.6458	2.8293		2.216	
(11) $0^-[(2)^5\Pi]$	23711.36		754.06		-1.8019	2.9413		2.176	
(12) $0^-[(1)^5\Pi]$	24703.19		517.88		-3.6405	2.8980		2.195	
(1) $1[(1)^3\Sigma^+]$	2763.17		812.77		-3.5376	3.8799		1.895	
(2) $1[(1)^3\Pi]$	4906.21		737.55		-3.3983	3.5893		1.970	
(3) $1[(1)^1\Pi]$	5028.25		693.07		-3.7766	3.5581		1.978	
	9915 ^{Theo d}	49%	706.0 ^{Theo d}	1.8%				1.97383 ^{Theo d}	0.2%
	6482 ^{Theo f}	22.4%	755 ^{Theo f}	8.2%				1.916 ^{Theo f}	3.2%
(4) $1[(3)^1\Pi]$	11839.69		915.12		-1.1183	2.8212		2.222	
(5) $1[(2)^3\Pi]$	14142.49		702.51		-2.4421	3.1157		2.115	
(6) $1[(2)^1\Pi] B1$	17391.12		542.88		-6.8009	3.6492		1.953	
	19188.02 ^{Exp b}	9.3%				3.255 ^{Exp b}	12%		
	19232 ^{Theo f}	9.5%	562 ^{Theo f}	3.4%				2.057 ^{Theo f}	5.0%
(7) $1[(2)^3\Sigma^+] C1$	18076.00		645.27		-4.0848	3.4649		2.004	
	18615.51 ^{Exp b}	2.8%	718.3 ^{Exp b}	10%		3.873464 ^{Exp b}	10%	1.939 ^{Exp b}	3.3%
(8) $1[(3)^3\Pi]$	18614.13		827.15		-2.6573	3.5623		1.977	
(9) $1[(3)^3\Sigma^+] D1$	19921.51		706.09		-3.7525	3.6084		1.965	
	18661.53 ^{Exp b}	6.7%	723.5 ^{Exp b}	2.4%		3.90074 ^{Exp b}	7.5%	1.9194 ^{Exp b}	2.4%
(10) $1[(1)^3\Delta]$	20408.20		688.58		-4.1086	3.6414		1.956	
(11) $1[(2)^3\Delta]$	20634.19		556.64		-5.9734	3.5811		1.972	

(12) 1 [(4) ³ Π]	21936.26	758.78	-2.1765	3.1384	2.106
(13) 1 [(1) ⁵ Σ ⁺]	21474.26	525.14	-3.4952	2.8474	2.109
(14) 1 [(1) ⁵ Δ]	21849.29	565.73	-2.9558	2.8772	2.199
(15) 1 [(2) ⁵ Π]	23430.28	648.63	-2.3320	2.9057	2.189
(16) 1 [(1) ⁵ Π]	24775.33	543.67	-3.7712	2.9923	2.156
(1) 2 [(1) ³ Π]	4867.26	729.82	-3.4255	3.5728	1.974
(2) 2 [(2) ³ Π]	17610.43	380.38	-15.945	3.6589	1.949
(3) 2 [(1) ¹ Δ]	17434.63	817.39	-2.8423	3.5468	1.980
	17305 ^{Theo f}	715 ^{Theo f}			1.876 ^{Theo f}
	30780 ^{Theo d}				5.5%
	7.4%	14%			43%
(4) 2 [(1) ³ Φ]	18311.24	965.54	-1.9487	3.5635	1.977
(5) 2 [(3) ³ Π]	18563.61	1062.34	-1.6667	3.5954	1.968
(6) 2 [(1) ³ Δ]	20058.95	731.88	-3.5027	3.6030	1.966
(7) 2 [(2) ³ Δ]	20548.03	613.71	-4.9508	3.6213	1.962
	19610.18 ^{Exp b}				4.7%
(8) 2 [(2) ¹ Δ]	20821.64	691.12	-4.4393	3.6823	1.944
(9) 2 [(2) ³ Φ]	23386.80	804.63	-1.7938	2.9487	2.175
(10) 2 [(1) ⁵ Φ]	20142.59	524.32	-3.8096	2.9798	2.163
(11) 2 [(1) ⁵ Σ ⁺]	21368.02	586.19	-4.2232	3.1326	2.105
(12) 2 [(1) ⁵ Δ]	22090.18	575.98	-2.8241	2.8606	2.067
(13) 2 [(2) ⁵ Π]	23843.34	734.12	-1.9038	2.9459	2.175
(14) 2 [(1) ⁵ Π]	24703.35	500.68	-3.9560	2.9206	2.184
(1) 3 [(1) ³ Φ]	17682.26	961.44	-2.0107	3.5845	1.971
(2) 3 [(2) ³ Δ]	20668.34	692.38	-4.3783	3.6551	1.951
(3) 3 [(1) ⁵ Φ]	20122.13	522.87	-3.5636	2.9831	2.187
(4) 3 [(1) ⁵ Δ]	22140.24	579.29	-2.8252	2.8722	2.202
(5) 3 [(2) ⁵ Π]	24517.17	542.49	-3.2049	2.8705	2.202
(6) 3 [(1) ⁵ Π]	24615.90	560.96	-2.7916	2.8110	2.225
(1) 4 [(2) ³ Φ]	22077.79	838.12	-1.7747	3.1492	2.103
(1) 5 [(1) ⁵ Φ]	20538.24	586.18	-3.4610	3.0876	2.124
Ref: a. First entry is for the values of the present work b. Ref [20] c. Ref [19] d. Ref [51]					
e. Ref [22] f. Ref [23]					

The spin orbit *ab initio* results of Table IV further confirm the accuracy of our nonrelativistic findings. Truly, the comparison between the values of the present work to the experimental values available in literature shows a very good agreement for the states (1)0⁺[(X)¹Σ⁺], (2)0⁺[(2)¹Σ⁺], (6)1[(2)¹Π], (7)1[(2)³Σ⁺], (9)1[(3)³Σ⁺], and (7)2[(2)³Δ] with a percentage relative error of 2.8% (Ref [20]) ≤ δT_e/T_e ≤ 9.3% (Ref [20]), and 0.9% (Ref [22]) ≤ δω_e/ω_e ≤ 10% (Ref [20]), and 3.5% (Ref [19]) ≤ δB_e/B_e ≤ 12% (Ref [20]), and 1.7% (Ref [19]) ≤ δR_e/R_e ≤ 3.3% (Ref [20]). The agreement is also very good by comparing the values of the present work to the recent theoretical results of Duo *et. al.* [23] in literature for the singlet states (1)0⁺[(X)¹Σ⁺], (2)0⁺[(2)¹Σ⁺], (3)1[(1)¹Π], (6)1[(2)¹Π], and (3)2[(1)¹Δ], reporting the relative differences of 3.9 % ≤ δT_e/T_e ≤ 9.5%, and 2.8% ≤ δω_e/ω_e ≤ 10.3%, and 2.3% ≤ δR_e/R_e ≤ 5.5%, except for the transition energy T_e of the state (3)1[(1)¹Π] and the harmonic vibrational frequency ω_e of the state (3)2[(1)¹Δ]. A less agreement exists when we compare our results for T_e and ω_e to the *ab initio* results of Shim *et. al.* [21] for the states (3)1[(1)¹Π],

and $(3)2[(1)^1\Delta]$, reporting a relative difference of $43\% \leq \delta T_e/T_e \leq 49\%$ and $\delta\omega_e/\omega_e = 14\%$ for the state $(1)0^+[(X)^1\Sigma^+]$. The other values of R_e reported by Shim *et. al.* [21] agree with our calculated values with a percentage relative difference of $0.2\% \leq \delta R_e/R_e \leq 3.4\%$. Finally, the comparison for the other results shown in Table IV is not possible since they are given here for the first time.

A recent spectroscopic investigation of the YN molecule [20] detected three new $\Omega = 1$ (B1, C1, D1) electronic states within the energy region of $18000\text{ cm}^{-1} \rightarrow 19000\text{ cm}^{-1}$, but the exact identities of these states could not be determined based on earlier *ab initio* results. A more recent sophisticated *ab initio* investigation of the electronic structure of YN was done by Duo *et. al* [23], in which they assign the B1 state to be the $D^1\Pi$ state. However, further assignments of the unknown states C1 and D1 could not be determined. In this work we assign the newly observed B1, C1, and D1 ($\Omega = 1$) states to be the $(6)1[(2)^1\Pi]$, $(7)1[(2)^3\Sigma^+]$, and the $(9)1[(3)^3\Sigma^+]$ states, respectively, since their spectroscopic constants (T_e , ω_e , r_e) agree with our calculated values for each of the assigned states. The $(9)1[(3)^3\Sigma^+]$ state is the closest state in energy to the D1 state with a percentage relative difference of $\delta T_e/T_e = 6.7\%$, $\delta\omega_e/\omega_e = 2.4\%$, $\delta B_e/B_e = 7.5\%$, and $\delta R_e/R_e = 2.4\%$. The other spectroscopic constants for the states $(6)1[(2)^1\Pi]$ and $(7)1[(2)^3\Sigma^+]$ are in excellent agreement with those for the B1 and C1 states, with percentage relative differences of $2.8\% \leq \delta T_e/T_e \leq 9.3\%$, $\delta\omega_e/\omega_e = 10\%$, $\delta B_e/B_e \leq 12\%$, $\delta R_e/R_e = 3.3\%$. The new assignment of the states $\{(6)1[(2)^1\Pi], (7)1[(2)^3\Sigma^+], (9)1[(3)^3\Sigma^+]\}$ is logical, particularly since these states have $\Omega = 1$ in agreement with the experimental predictions provided in Ref [20].

The composition in percentage of the spin orbit Ω state-wave functions in terms of the Λ parent states, calculated at the equilibrium internuclear distance of the ground state $R = 1.85\text{ \AA}$, are presented in Table V. For each state Ω there is a predominant component Λ with a contribution larger than 80% so that a main parent $^{2s+1}\Lambda$ state may be identified. Nevertheless, there are states for which a small but significant contribution of other $^{2s+1}\Lambda$ states is obtained.

Transition metal compounds have a rich set of electronic states owing to unfilled d shells, and therefore spin orbit effects are commonplace. In Appendix I we draw the parent electronic Λ states together with their respective daughter states Ω and their energy separation. This representation allows for a clear estimation of the spin orbit splitting in the electronic states of YN.

Table V:Composition of Ω spin orbit state wave functions of the molecule YN, in terms of $^{2s+1}\Lambda$ -states (in percentage) at $R = 1.85\text{\AA}$.

Ω	% (Λ -parent)	Ω	% (Λ -parent)
(1) 0+	100% (X) $^1\Sigma^+$	(9) 1	100%(3) $^3\Sigma^+$
(2) 0+	99.97% (2) $^1\Sigma^+$, 0.03% (1) $^3\Pi$	(10) 1	84% (1) $^3\Delta$, 16% (2) $^3\Delta$
(3) 0+	99.9% (1) $^3\Pi$, 0.1% (X) $^1\Sigma^+$	(11) 1	84%(2) $^3\Delta$, 16% (1) $^3\Delta$
(4) 0+	93%(3) $^1\Sigma^+$, 6%(1) $^3\Sigma^-$	(12) 1	100% (4) $^3\Pi$
(5) 0+	100% (1) $^1\Sigma^-$	(13) 1	100% (1) $^5\Sigma^+$
(6) 0+	99%(4) $^3\Pi$, 1% (4) $^1\Sigma^+$	(14) 1	99.8% (1) $^5\Delta$
(7) 0+	100%(4) $^1\Sigma^+$	(15) 1	100% (2) $^5\Pi$
(8) 0+	100% (1) $^5\Delta$	(16) 1	100%(1) $^5\Pi$
(9) 0+	100%(2) $^5\Pi$	(1) 2	100% (1) $^3\Pi$
(10) 0+	100%(1) $^5\Pi$	(2) 2	84% (2) $^3\Pi$, 16% (1) $^1\Delta$
(1) 0-	99.98% (1) $^3\Sigma^+$, 0.02% (1) $^3\Pi$	(3) 2	100% (1) $^1\Delta$
(2) 0-	99.6% (2) $^3\Pi$, 0.4% (2) $^3\Sigma^+$	(4) 2	100% (1) $^3\Phi$
(3) 0-	89% (2) $^3\Sigma^+$, 11% (1) $^3\Phi$	(5) 2	100% (3) $^3\Pi$
(4) 0-	99.7% (3) $^3\Pi$, 0.3% (1) $^3\Sigma^-$	(6) 2	76% (1) $^3\Delta$, 22%(2) $^1\Delta$
(5) 0-	100%(3) $^3\Sigma^+$	(7) 2	97% (2) $^3\Delta$
(6) 0-	94% (1) $^3\Sigma^-$, 6% (3) $^1\Sigma^+$	(8) 2	77% (2) $^1\Delta$, 23% (1) $^3\Delta$
(7) 0-	99.84%(4) $^3\Pi$, 0.16% (2) $^3\Sigma^+$	(9) 2	100%(2) $^3\Phi$
(8) 0-	99.88% (1) $^5\Phi$	(10) 2	100% (1) $^5\Phi$
(9) 0-	100% (1) $^5\Sigma^+$	(11) 2	100% (1) $^5\Sigma^+$
(10) 0-	100% (1) $^5\Delta$	(12) 2	100% (1) $^5\Delta$
(11) 0-	99.88%(2) $^5\Pi$	(13) 2	99.9%(2) $^5\Pi$
(12) 0-	99.7%(1) $^5\Pi$	(14) 2	99.87%(1) $^5\Pi$
(1) 1	99.98%(1) $^3\Sigma^+$, 0.02% (1) $^3\Pi$	(1) 3	82% (1) $^3\Phi$
(2) 1	76% (1) $^3\Pi$, 24% (1) $^1\Pi$	(2) 3	84%(2) $^3\Delta$, 16% (1) $^3\Delta$
(3) 1	75.6% (1) $^1\Pi$, 24.4% (1) $^3\Pi$	(3) 3	100% (1) $^5\Phi$
(4) 1	100% (3) $^1\Pi$	(4) 3	100% (1) $^5\Delta$
(5) 1	100 (2) $^3\Pi$	(5) 3	100%(2) $^5\Pi$
(6) 1	100% (2) $^1\Pi$	(6) 3	100%(1) $^5\Pi$
(7) 1	85% (2) $^3\Sigma^+$	(1) 4	100%(2) $^3\Phi$
(8) 1	83% (3) $^3\Pi$, 8% (2) $^3\Sigma^+$	(1) 5	100% (1) $^5\Phi$

III. A. 3. The Nature of Bonding in Yttrium Nitride

Molecular electronic states of $^3\Delta$ symmetries arising from σ and δ molecular orbitals have been proposed to be important in the search for the electric dipole moment of the electron (eEDM). A property, whose existence along the spin axis of the electron should provide evidence of parity and time reversal invariance [27]. In this regards, molecular orbitals of σ symmetry are important since they allow for electrons to penetrate closer to the heavy atomic nucleus, a place at which relativistic effects become significant [27]. Other electronic states, such as the $^3\Delta$ state, arising from the occupation of both σ and δ molecular orbitals were also suggested to create larger electric fields sufficient to produce a measureable eEDM signal [27]. Then understanding the composition of molecular electronic states in terms of molecular orbital configurations is of significant importance.

In the present calculations, the choice of the active space allows for the determination of the bonding molecular orbitals (σ , π , δ) participating in the formation of molecular states, denoted by Σ , Π , Δ , Φ , ... In multiconfigurational quantum chemistry, a single chemical bond is described by a pair of orbitals, a bonding and an antibonding one. Usually, their occupation numbers add up to 2.0 [28]. Thus, two electrons reside in two orbitals. If the occupation number of the bonding orbital, η_b , is close to two and the corresponding antibonding orbital has a small occupation number, η_{ab} , then there is a fully developed chemical bond with a bond order equal to one. This is the situation for the chemical bonds in most normal molecules at their equilibrium geometry. However, in transition metal compounds with multiple metal-ligand bonds, one often sees occupation numbers η_b which are smaller than two. If the two occupation numbers (η_b and η_{ab}) are both close to one, then we have no chemical bond [28]. We can therefore define a quantity called the effective bond order EBO which quantifies the formation of a chemical bond [29]. The EBO for a single bond is defined by

$$\text{EBO} = (\eta_b - \eta_{ab}) / 2. \quad (1)$$

For a fully developed single bond the EBO will be close to one, while for a dissociated bond the EBO will be close to zero. In multiply bonded systems, one has to add up the individual values for each pair of bonding and antibonding orbitals to obtain the total EBO. Thus the EBO gives us a mean to quantify the bond order concept from optimized wave functions. In our multi-configurational treatment of the wave function in the ground state $X^1\Sigma^+$ we obtained the occupation numbers of the 6 valence electrons distributed over the chosen active space as $\eta_b = 1.39576$ (10σ), $\eta_b = 0.53874$ (11σ), $\eta_{ab} = 0.16036$ (12σ), $\eta_{ab} = 0.02265$ (13σ), $\eta_{ab} = 0.26255$ (3δ), $\eta_b = 3.14946$ (5π), $\eta_{ab} = 0.37884$ (6π), $\eta_{ab} = 0.09164$ (7π). Then by applying equation (1) we obtain an effective bond order (EBO) of ≈ 2 . Thus, indicating that the bond in the ground state of YN is a double bond.

The Y-N bond is formed from 3 valence electrons on nitrogen $2p^3$ and 3 valence electrons on Yttrium $5s^2$ and $4d^1$ orbitals. Thus it is not surprising that such a bond is difficult to quantify theoretically because of the strong correlation effects that occur due to the crowdedness of the electrons in the bonding region. However, our MRSDCI+Q calculations yielded accurate spectroscopic constants with experimental results. We can thus conclude that the electronic structure of YN is well described at this level of theory. In particular we can gain significant insight into the nature of the Y-N bond by analyzing the orbital compositions of electronic states $^{2s+1}\Lambda$ in terms of their molecular orbital configurations. Table VI shows the leading

configurations of the electronic states of YN. The ground state of YN has the leading configuration of $11\sigma^2 5\pi^4$ (56%), where the 11σ orbital is formed from the combination of $2p_z$ on Nitrogen and the $3d_0$ orbital on Yttrium, and the 5π orbital is formed from the combination of $3d_{\pm 1}$ on Yttrium and $2p_{x,y}$ on Nitrogen. Other combinations of molecular orbitals such as $11\sigma^1 12\sigma^1 5\pi^4$ (15%), $11\sigma^1 13\sigma^1 5\pi^4$ (13%), and $11\sigma^1 5\pi^3 6\pi^1$ (7%) participate in forming the ground state, but with smaller contributions.

Table VI:

Leading Configurations with percentage composition of the parent states $^{2s+1}\Lambda^\pm$ of the molecule YN.

Label	Leading Configurations with percentage composition
$X^1\Sigma^+$	$11\sigma^2 5\pi^4$ (56%), $11\sigma^1 12\sigma^1 5\pi^4$ (15%), $11\sigma^1 13\sigma^1 5\pi^4$ (13%), $11\sigma^1 5\pi^3 6\pi^1$ (7%)
$(2)^1\Sigma^+$	$11\sigma^1 12\sigma^1 5\pi^4$ (75%), $11\sigma^2 5\pi^4$ (13%)
$(1)^1\Delta$	$11\sigma^2 5\pi^3 6\pi^1$ (93%)
$(3)^1\Sigma^+$	$11\sigma^2 5\pi^3 6\pi^1$ (84%), $11\sigma^1 13\sigma^1 5\pi^4$ (9%)
$(4)^1\Sigma^+$	$11\sigma^1 13\sigma^1 5\pi^4$ (62%), $11\sigma^2 5\pi^4$ (4%), $11\sigma^2 5\pi^3 6\pi^1$ (5%)
$(2)^1\Delta$	$11\sigma^1 12\sigma^1 5\pi^3 6\pi^1$ (70%), $11\sigma^1 12\sigma^1 5\pi^3 6\pi^1$ (22%)
$(5)^1\Sigma^+$	$11\sigma^1 12\sigma^1 5\pi^3 6\pi^1$ (87%)
$(1)^1\Pi$	$11\sigma^2 12\sigma^1 5\pi^3$ (91%)
$(2)^1\Pi$	$11\sigma^1 5\pi^4 6\pi^1$ (91%)
$(1)^1\Phi$	$11\sigma^1 5\pi^3 6\pi^1 2\delta^1$ (91%)
$(3)^1\Pi$	$11\sigma^1 13\sigma^1 5\pi^3$ (84%), $11\sigma^1 14\sigma^1 5\pi^3$ (3%), $11\sigma^1 5\pi^3 2\delta^1$ (6%)
$(2)^1\Phi$	$11\sigma^1 12\sigma^1 5\pi^3 2\delta^1$ (90%)
$(4)^1\Pi$	$11\sigma^1 12\sigma^2 5\pi^3$ (85%)
$(1)^3\Sigma^+$	$11\sigma^1 12\sigma^1 5\pi^4$ (90%), $11\sigma^1 13\sigma^1 5\pi^4$ (2%)
$(2)^3\Sigma^+$	$11\sigma^2 5\pi^3 6\pi^1$ (47%), $11\sigma^2 5\pi^3 6\pi^1$ (40%)
$(3)^3\Sigma^+$	$11\sigma^2 5\pi^3 6\pi^1$ (43%), $11\sigma^2 5\pi^3 6\pi^1$ (50%)
$(1)^3\Delta$	$11\sigma^2 5\pi^3 6\pi^1$ (95%)
$(2)^3\Delta$	$11\sigma^1 12\sigma^1 5\pi^3 6\pi^1$ (95%)
$(1)^3\Pi$	$11\sigma^2 12\sigma^1 5\pi^3$ (92%)
$(2)^3\Pi$	$11\sigma^1 5\pi^4 6\pi^1$ (91%)
$(3)^3\Pi$	$11\sigma^1 12\sigma^2 5\pi^3$ (72%), $11\sigma^2 5\pi^3 2\delta^1$ (13%), $11\sigma^1 5\pi^3 6\pi^2$ (2%)
$(1)^3\Phi$	$11\sigma^2 5\pi^3 2\delta^1$ (76%), $11\sigma^2 13\sigma^1 5\pi^3$ (2%), $11\sigma^1 12\sigma^2 5\pi^3$ (11%)
$(4)^3\Pi$	$11\sigma^2 13\sigma^1 5\pi^3$ (87%)
$(2)^3\Phi$	$11\sigma^1 12\sigma^1 5\pi^3 2\delta^1$ (91%)
$(3)^3\Phi$	$11\sigma^1 12\sigma^1 5\pi^3 2\delta^1$ (81%), $11\sigma^1 5\pi^3 6\pi^2$ (4%), $11\sigma^1 13\sigma^1 5\pi^3 1\delta^1$ (2%)

Leading configuration with weights less than 2% have been omitted.

These results agree very well with the recent CASPT2 calculations of Duo *et. al* [23] on the ground state of YN suggesting that the ground state is formed mainly from the mixing between the two configurations $11\sigma^2 5\pi^4$ (77%) and $11\sigma^1 12\sigma^1 5\pi^4$ (10%). Other results in Ref. [20, 22] suggest that the leading configurations of the $X^1\Sigma^+$ and $(1)^1\Sigma^+$ states in YN are strongly mixed between the molecular orbital configurations $11\sigma^2 5\pi^4$ and $11\sigma^1 12\sigma^1 5\pi^4$ on Yttrium and Nitrogen in agreement with our conclusions.

The $(2)^1\Sigma^+$ and $(1)^3\Sigma^+$ states can be interpreted by analyzing their leading orbital configurations. The $(2)^1\Sigma^+$ is formed from a combination between the $11\sigma^1 12\sigma^1 5\pi^4$ (75%) and the $11\sigma^2 5\pi^4$ (13%) configurations, which mainly arise from the promotion of an electron from the 11σ orbital in the ground state configuration into the 12σ bonding orbital in the $(2)^1\Sigma^+$ state. The leading configuration $11\sigma^1 12\sigma^1 5\pi^4$ (90%) of the $(1)^3\Sigma^+$ state of YN is

similar to that of the $(2)^1\Sigma^+$ state, but with a slight difference: The $11\sigma^1$ and $12\sigma^1$ electron-spins pair in the same or in the opposite directions to produce a total spin of $S = \frac{1}{2} + \frac{1}{2} = 1$ and $S = \frac{1}{2} - \frac{1}{2} = 0$, giving a triplet and a singlet multiplicity states, the $(1)^3\Sigma^+$ and the $(2)^1\Sigma^+$ states, respectively. These predictions for the leading configurations of the $(1)^3\Sigma^+$ state are in agreement with both Jakubek *et. al* [22] and Duo *et. al* [23] results.

III. A. 4. The Vibrational Structure of Yttrium Nitride

Exploring the vibrational structures of diatomic molecules has received great attention in recent years [30]. In fundamental concepts, the search for spatial and temporal variations of the fine structure constant α and the proton to electron mass ratio $\mu = m_p/m_e$ has been proposed in transitions between nearly degenerate vibrational energy levels of diatomic molecules. Degeneracies of the order $<10\text{cm}^{-1}$ between vibrational energy levels have been proposed to enhance the measurement sensitivity of α and μ by several orders of magnitude [30]. In fact, the search for transitions between the almost degenerate vibrational energy levels in ultra-cold CaH^+ has been applied to measure variations in μ [31]. In Quantum Computing femtosecond laser induced transitions between vibrational-vibrational and vibrational-rotational energy levels in several heteronuclear diatomic molecules have been proposed to produce the quantum bits $|0\rangle$ and $|1\rangle$ [32, 33].

Thus the vibrational energy structures of heteronuclear diatomic molecules are important in several areas of research and for that we have decided in the present work to investigate the vibration-rotation energy structures of YN. These calculations are performed by solving the vibrational-rotational Schrödinger equation for nuclear motions on the previously calculated potential energy surfaces for the ground and excited electronic states. The solutions for the vibrational-rotational Schrödinger equation are obtained iteratively by following the canonical functions approach [34, 35], which allows for the determination of the vibrational energy levels E_v , the rotational constants B_v and D_v , and the coordinates of the turning points $R_{\min}$ and $R_{\max}$. In this iterative procedure, a large number of vibrational levels could be determined up to vibrational levels near dissociation. However, their number is largely determined by the amount of points to the left and to the right of the equilibrium internuclear distance of the potential energy curve. In the present work, we calculated the vibrational constants for the 25 low-lying electronic states $^{2s+1}\Lambda$ and their spin orbit component states. A part of these calculations is shown in the context of this chapter while the rest are shown in Appendix II.

In Tables VII and VIII, the vibrational calculations are performed for several low lying electronic states $X^1\Sigma^+$, $(1)^1\Pi$, $(1)^3\Pi$, $(1)^3\Sigma^+$, and $(2)^1\Sigma^+$ and are shown together with the

available experimental and theoretical values in literature. All of the vibrational energy levels E_v were calculated with respect to the zero vibrational energy level of the ground state. The zero point energy or the difference in energy between the $v = 0$ vibrational level and the transition energy at the equilibrium internuclear distance for the ground state is calculated to be 303.56 cm^{-1} , considered zero in this work.

Table VII:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v for the different vibrational levels of the $X^1\Sigma^+$, $(1)^1\Pi$, and $(1)^3\Pi$ states in YN.

X ¹ Σ ⁺										
v	E _v (cm ⁻¹)	δE _v /E _v	R _{min} (Å)	δR _{min} /R _{min}	R _{max} (Å)	δR _{max} /R _{max}	B _v ×10 ¹ (cm ⁻¹)	δB _v /B _v		
0	0 ^a		1.78 ^a		1.94 ^a		4.021 ^a			
	0 ^b		1.63 ^b	9.2%	1.87 ^{Exp b}	3.7%	4.2666 ^{Exp b}	5.7%		
1	632.05 ^a		1.75		1.97		3.991			
	650.64 ^{Exp b}	2.8%	1.64 ^{Exp b}	6.7%	1.93 ^{Exp b}	2.1%	4.23328 ^{Exp b}	5.7%		
2	1286.44		1.73		2.01		3.981			
	1319 ^{Exp c}	2.4%	1.65 ^{Exp b}	4.8%	1.96 ^{Exp b}	2.5%	4.20739 ^{Exp d}	5.4%		
3	1948.91		1.71		2.04		3.962			
	1998 ^{Exp c}	2.4%	1.67 ^{Exp b}	2.3%	1.99 ^{Exp b}	2.5%	4.18365 ^{Exp d}	5.3%		
4	2620.94		1.69		2.07		3.941			
	2688 ^{Exp c}	2.5%	1.69 ^{Exp b}	0.0%	2.02 ^{Exp b}	2.4%	4.16036 ^{Exp d}	5.2%		
5	3294.49		1.68		2.10		3.921			
	3387 ^{Exp c}	2.7%	1.74 ^{Exp b}	3.4%	2.05 ^{Exp b}	2.4%	4.13793 ^{Exp d}	5.3%		
6	3966.69		1.66		2.12		3.891			
	4090 ^{Exp c}	3.0%								
7	4638.30		1.65		2.15		3.872			
8	5307.24		1.64		2.17		3.852			
9	5975.13		1.63		2.19		3.830			
(1) ¹ Π					(1) ³ Π					
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)
0	5369.55 ^a	1.91 ^a	2.03 ^a	3.571	3.461	5261.68	1.91	2.03	3.581	3.551
1	6094.86	1.87	2.08	3.572	3.112	5978.32	1.87	2.08	3.572	3.481
2	6837.86	1.84	2.12	3.574	2.884	6694.14	1.84	2.12	3.541	3.781
3	7596.47	1.82	2.14	3.575	2.776	7394.70	1.82	2.16	3.523	3.932
4	8366.24	1.80	2.17	3.566	3.237	8080.03	1.80	2.18	3.494	3.833
5	9129.04	1.78	2.19	3.551	3.228	8756.30	1.79	2.21	3.470	3.804
6	9885.60	1.77	2.21	3.536	3.172	9425.06	1.77	2.24	3.445	4.047
7	10637.42	1.76	2.23	3.522	3.816	10082.35	1.76	2.27	3.416	4.260
8	11371.95	1.75	2.25	3.488	5.164	10727.66	1.75	2.29	3.392	3.921
9	12064.28	1.74	2.28	3.392	1.125	11365.55	1.74	2.32	3.361	4.121
10	12636.82	1.73	2.36	3.187	1.391	11994.53	1.73	2.34	3.342	3.902
11	13124.36	1.72	2.38	3.203	-5.944	12617.49	1.72	2.36	3.323	4.663
12	13693.04	1.72	2.39	3.256	3.941	13226.58	1.72	2.39	3.284	5.194
13	14268.03	1.71	2.42	3.231	2.396	13818.15	1.71	2.41	3.245	4.765
14	14851.77	1.70	2.44	3.230	3.188	14398.37	1.70	2.43	3.226	3.496
15	15437.13	1.69	2.46	3.201	5.483	14977.18	1.70	2.45	3.202	3.941
16	16007.54	1.69	2.48	3.173	2.685	15550.98	1.69	2.48	3.174	5.243

a. First entry is for the values of the present work

b. Ref [20]

c. Ref [22]

d. Ref [19]

Note: All vibrational Energy values are measured relative to the zeroth vibrational level whose $E_v = 303.56 \text{ cm}^{-1}$ relative to the transition energy at the equilibrium internuclear distance T_e for the ground state $X^1\Sigma^+$.

Exp, correspond to experimental results in literature.

Table VIII:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v for the different vibrational levels of the $(1)^3\Sigma^+$, and $(2)^1\Sigma^+$ states in YN.

$(1)^3\Sigma^+$								$(2)^1\Sigma^+$							
v	E_v (cm^{-1})	δE_v / E_v	$R_{\min}$ ($\text{\AA}$)	$\delta R_{\min}$ / $R_{\min}$	$R_{\max}$ ($\text{\AA}$)	$\delta R_{\max}$ / $R_{\max}$	$B_v \times 10^1$ (cm^{-1})	E_v (cm^{-1})	δE_v / E_v	$R_{\min}$ ($\text{\AA}$)	$\delta R_{\min}$ / $R_{\min}$	$R_{\max}$ ($\text{\AA}$)	$\delta R_{\max}$ / $R_{\max}$	$B_v \times 10^1$ (cm^{-1})	δB_v / B_v
0	2864.03 ^a 2469 ^{Exp c}	1.84 ^a 16%	1.71 ^{Exp b}	7.6%	1.96 ^a 1.92 ^{Exp b}	2.1%	3.871 ^a	4015.62 ^a 3879 ^{Exp c} 3882.8 ^{Exp d}	1.82 ^a 3.5% 3.4%	1.65 ^{Exp b}	10%	1.91 ^a 1.87 ^{Exp b}	2.1%	4.031 ^a 4.2193 ^{Exp d}	4.5%
1	3639.22 3297 ^{Exp c}	1.80 10%	1.73 ^{Exp b}	4.0%	2.01 1.97 ^{Exp b}	2.0%	3.852	4967.42 4879 ^{Exp c} 4879.6 ^{Exp d}	1.78 1.8% 1.8%	1.67 ^{Exp b}	6.6%	1.94 1.91 ^{Exp b}	1.6%	4.001 4.2047 ^{Exp d}	4.9%
2	4411.44 4102 ^{Exp c}	1.78 7.5%	1.75 ^{Exp b}	1.7%	2.04 2.01 ^{Exp b}	1.5%	3.832	5900.79 5850 ^{Exp c} 5848 ^{Exp d}	1.75 0.8% 0.9%	1.68 ^{Exp b}	4.2%	1.99 1.94 ^{Exp b}	2.6%	3.982 4.1804 ^{Exp d}	4.8%
3	5180.04 4921 ^{Exp c}	1.75 5.2%	1.77 ^{Exp b}	1.1%	2.09 2.04 ^{Exp b}	2.4%	3.811	6816.97 6813 ^{Exp c} 6797 ^{Exp d}	1.73 0.05% 0.03%	1.70 ^{Exp b}	1.7%	2.02 1.97 ^{Exp b}	2.5%	3.971 4.1626 ^{Exp d}	4.6%
4	5944.15 5762 ^{Exp c}	1.73 3.1%	1.81 ^{Exp b}	4.4%	2.10 2.06 ^{Exp b}		3.802	7724.69 7737 ^{Exp d}	1.71 0.02%	1.72 ^{Exp b}	0.5%	2.05 1.99 ^{Exp b}	3.0%	3.952 4.1598 ^{Exp d}	5.0%
5	6702.47	1.72			2.12		3.771	8624.22 8668 ^{Exp d}	1.70 0.03%	1.76 ^{Exp b}	3.4%	2.07 2.01 ^{Exp b}	3.0%	3.942 4.1427 ^{Exp d}	4.9%
6	7447.68	1.71			2.15		3.752	9512.83 9565 ^{Exp d}	1.70 0.05%			2.10		3.923	
7	8185.84	1.69			2.17		3.731	10390.94		1.67		2.11		3.901	
8	9644.52	1.68			2.22		3.693	11251.16		1.66		2.13		3.883	
9	10365.99	1.66			2.23		3.673	12101.16		1.65		2.15		3.862	
10	11077.28	1.65			2.27		3.654	12940.94		1.64		2.17		3.841	
11	11783.41	1.64			2.28		3.635	13772.18		1.64		2.18		3.824	
12	12483.01	1.64			2.29		3.601	14593.19		1.63		2.21		3.806	
13	13169.09	1.63			2.31		3.581	15402.67		1.62		2.22		3.781	
14	13849.32	1.62			2.33		3.562	16203.44		1.61		2.24		3.760	
15	14521	1.62			2.35		3.533	16995.1		1.59		2.26		3.742	
16	15184.41	1.61			2.37		3.514	17776.04		1.59		2.27		3.721	
17	15839.45	1.60			2.38		3.481	18546.93		1.58		2.29		3.691	
18	16485.25	1.60			2.40		3.460	19307.85		1.58		2.31		3.672	
19	17123.64	1.59			2.41		3.431	20057.98		1.57		2.33		3.653	
20	17751.4	1.59			2.45		3.412	20799.64		1.57		2.34		3.632	
21	18372.51	1.58			2.46		3.383	21532.02		1.56		2.36		3.601	
22	18983.33	1.58			2.48		3.351	22253.11		1.56		2.37		3.572	
23	19587.26	1.57			2.51		3.332	22965.86		1.55		2.39		3.552	
24	20181.14	1.56			2.52		3.301	23668.34		1.55		2.41		3.521	
25	20767.12	1.56			2.54		3.272	24360.45		1.54		2.42		3.503	
26	21343.9	1.55			2.57		3.241	25043.18		1.54		2.44		3.471	
27	21912.2	1.55			2.58		3.212	25714.23		1.54		2.47		3.442	
28	22471.58	1.54			2.61		3.191	26374.83		1.53		2.48		3.413	
29	23022	1.54			2.62		3.163	27024.37		1.53		2.51		3.381	
30	23563.7	1.53			2.69		3.133	27662.70		1.52		2.53		3.353	

a. First entry is for the values of the present work b. Ref [20] c. Ref [22] d. Ref [19]

Note: All vibrational Energy values are measured relative to the zeroth vibrational level $v = 0$ whose energy value is $E_v = 303.56 \text{ cm}^{-1}$ relative to the transition energy at the equilibrium internuclear distance T_e of the ground state $X^1\Sigma^+$.

Exp, corresponds to experimental results in literature.

The comparison between the values of E_v , and B_v in the present work with the experimental values available in Ref [20, 22] for the states $X^1\Sigma^+$, $(1)^3\Sigma^+$, and $(1)^1\Sigma^+$ shows a very good agreement, with a relative difference of $0.05\% \leq \delta E_v \leq 16\%$, and $\delta B_v = 5.7\%$. The values of the turning points $R_{\min}$ and $R_{\max}$ evaluated for the corresponding vibrational levels are also in

good agreement with the experimental values calculated in Ref [22], with a percentage relative difference of $0.0\% \leq \delta R_{\min} \leq 10\%$ and $1.5\% \leq \delta R_{\max} \leq 3.7\%$.

In Tables IX the vibrational energy levels are shown for the spin orbit states (6)1[(2)¹Π], (7) 1 [(2)³Σ⁺], and (9) 1 [(3)³Σ⁺], which have been respectively assigned in the present work to be the B1, C1, and D1 states experimentally reported in Ref [20].

Table IX:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v for the different vibrational levels of the (6)1[(2)¹Π], (7)1 [(2)³Σ⁺], and (9)1[(3)³Σ⁺] states in YN.

(6)1[(2) ¹ Π] B1						
v	E _v (cm ⁻¹)	δE _v /E _v	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	δB _v /B _v
0	17602.30 ^a 18974.66 ^{Exp b}	7.2%	1.92 ^a	2.01 ^a	3.591 ^a 3.8833 ^{Exp b}	7.4%
1	18068.22 19692.979 ^{Exp b}	8.2%	1.85	2.15	3.331 3.5209 ^{Exp b}	5.2%
2	18468.71		1.82	2.20	3.432	
3	18829.25		1.81	2.24	3.281	
4	19131.49		1.80	2.35	2.993	
5	19420.56		1.79	2.41	3.061	
6	19769.78		1.78	2.45	3.024	
7	20111.98		1.77	2.48	3.041	
8	20494.07		1.77	2.49	3.063	
9	20876.85		1.76	2.51	3.092	
10	21286.64		1.75	2.52	3.094	
11	21708.11		1.74	2.54	3.071	
12	22130.67		1.73	2.56	3.092	
13	22548.99		1.72	2.59	3.063	
14	22967.48		1.71	2.60	3.071	
15	23388.71		1.70	2.62	3.044	
16	23812.26		1.69	2.64	3.026	
17	24238.28		1.69	2.66	2.971	

(9) 1 [(3) ³ Σ ⁺] D1							(7) 1 [(2) ³ Σ ⁺] C1					
v	E _v (cm ⁻¹)	δE _v /E _v	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	δB _v /B _v	E _v (cm ⁻¹)	δE _v /E _v	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	δB _v /B _v
0	20203.09 ^a 19823.99 ^{Exp b}	1.9%	1.91 ^a	2.02 ^a	3.591 ^a 3.846 ^{Exp b}	6.6%	18365.24 ^a 19023.28 ^b	3.4%	1.94 ^a	2.04 ^a	3.481 ^a 3.9017 ^{Exp b}	10.7%
1	20867.74		1.87	2.09	3.519		18997.40 19746.82 ^b		1.91	2.20	3.232 3.6516 ^{Exp b}	11.3%
2	21489.60		1.85	2.14	3.431		19315.36		1.90	2.28	3.063	
3	22011.09		1.84	2.21	3.272		19701.95		1.89	2.32	3.121	
4	22464.59		1.82	2.28	3.213		20144.99		1.87	2.35	3.112	
5	23354.82		1.80	2.36	3.092		20591.03		1.85	2.38	3.090	
6	23790.50		1.79	2.40	3.081		21032.80		1.84	2.41	3.071	
7	24241.33		1.78	2.43	3.074		21482.41		1.83	2.44	3.065	
8	24680.68		1.775	2.48	2.985		21933.78		1.81	2.46	3.032	
9	25075.99		1.765	2.51	2.921		22384.78		1.80	2.49	3.013	
10	25483.13		1.76	2.54	2.940		22838.59		1.79	2.51	2.994	
11	25899.63		1.756	2.59	2.931		23291.69		1.785	2.54	2.961	
12	26318.61		1.75	2.61	2.902		23744.18		1.78	2.56	2.940	
13	26722.45		1.74	2.65	2.843		24193.21		1.77	2.59	2.921	
14							24640.13		1.76	2.61	2.909	

a. First entry is for the values of the present work

b. Ref [20]

Exp, corresponds to experimental results in literature.

The comparison between the present values for the vibrational structure in YN (Table IX) to the experimental values reported in Ref [20] for the B1, C1, and D1 states shows a very good agreement, with a percentage relative difference of $1.9\% \leq \delta E_v \leq 8.2\%$, and $5.2\% \leq \delta B_v \leq 11.3\%$. These results further confirm our previous assignments of the B1, C1, and D1 states.

The experimentally available $\{(0-0), (1-1), (2-2), (3-3), (4-4), \text{ and } (5-5)\}$ vibrational energy band transitions [19] for the $(2)^1\Sigma^+ - X^1\Sigma^+$ system are reproduced in our calculations with a very high accuracy. These results are shown in Table X, where a percentage relative difference of $0.9\% \leq \delta E_{v-v'} \leq 3.4\%$ was obtained.

Table X:

Comparison between our results of the vibrational energy bands for the $(2)^1\Sigma^+ - X^1\Sigma^+$ transition and experimental results in Ref [49] in YN.

	0 – 0 Band	1 – 1 Band	2 – 2 Band	3 – 3 Band	4 – 4 Band	5 – 5 Band
$E_{v-v'}$	4015.62 ^a	4335.37 ^a	4614.35 ^a	4868.06 ^a	5103.75 ^a	5329.73 ^a
	3882.76 ^b	4229.04 ^b	4528.65 ^b	4798.51 ^b	5049.44 ^b	5281.21 ^b
$\delta E_{v-v'} / E_{v-v'}$	3.4%	2.5%	1.9%	1.4%	1.1%	0.9%
a.	Values of the present work		b. Ref [19]			

Vibrational energy level calculations were then followed by rotational energy level calculations by using the formula: $E_J = E_v + B_v J(J+1) - D_v J^2(J+1)^2$, and the results of E_v , B_v , and D_v for the corresponding vibrational levels are obtained from the results of the present work. The rotational energy calculations have been performed for the rotational energy levels in the $v = 0$ and $v = 1$ vibrational levels of the $(2)^1\Sigma^+$ and $X^1\Sigma^+$ states. Rotational spectroscopic lines denoted by P(J) and R(J) branches, corresponding to the transitions $\Delta J = -1$ and $\Delta J = +1$, respectively, have been calculated by using the relations $E_{J+1} - E_J$ in the R(J) branch and $E_{J-1} - E_J$ in the P(J) branch. These results are shown in Table XI together with the experimental spectroscopic P(J) and R(J) branches available in Ref [19].

Table XI:

Rotational energy band transitions between the sub-rotational energy levels of the vibrational energy bands (0 – 0) and (1 – 1) of the $(2)^1\Sigma^+ - X^1\Sigma^+$ system for the YN molecule.

0 – 0 Band			1 – 1 Band	
J	R(J) branch $E_{J+1} - E_J$	P(J) branch $E_{J-1} - E_J$	R (J) branch $E_{J+1} - E_J$	P(J) branch $E_{J-1} - E_J$
2			4337.78 ^a	
			4231.55 ^b	
3			4338.58	
			4232.27	
4	4019.67 ^a	4012.42 ^a	4339.39	4332.19 ^a
	3886.88 ^b	3879.29 ^b	4233.19	4225.63 ^b
5	4020.49	4011.62	4340.20	4331.40
	3887.68	3878.39	4234.01	4224.76
6	4021.30	4010.83	4341.01	4330.61
	3888.46	3877.49	4234.81	4223.88
7	4022.12	4010.03	4341.83	4329.83
	3889.25	3876.59	4235.61	4223.00

8	4022.95	4009.24	4342.64	4329.04
	3890.01	3875.67	4236.41	4222.12
9	4023.77	4008.46	4343.46	4328.26
	3890.77		4237.19	4221.22
10	4024.60	4007.67	4344.28	4327.48
			4237.98	4220.33
11	4025.42	4006.89	4345.10	4326.70
	3892.27	3872.86	4238.76	4219.42
12	4026.25	4006.10	4345.93	4325.93
	3892.99	3871.91	4239.53	4218.51
13	4027.09	4005.32	4346.75	4325.15
	3893.72	3870.95	4240.30	
14	4027.92	4004.55	4347.58	4324.38
	3894.44		4241.06	
15	4028.76	4003.77	4348.41	4323.61
	3895.14			4215.76
16	4029.60	4003.00	4349.24	4322.84
	3895.84	3868.00		4214.84
17	4030.44	4002.23	4350.08	4322.08
	3896.53	3867.01	4243.32	4213.90
18	4031.28	4001.46	4350.91	4321.31
	3897.21	3866.00	4244.06	4212.97
19	4032.12	4000.69	4351.75	4320.55
	3897.88		4244.80	4212.02
20	4032.97	3999.92	4352.59	4319.79
	3898.55	3863.97	4245.53	4211.08
21	4033.82	3999.16	4353.43	4319.03
		3862.95	4246.26	4210.13
22	4034.67	3998.40	4354.28	4318.28
	3899.86		4246.98	4209.17
23	4035.52	3997.64	4355.12	4317.53
	3900.50	3860.87	4247.70	4208.22
24	4036.37	3996.88	4355.97	4316.77
	3901.14	3859.83	4248.41	4207.25
25	4037.23	3996.13	4356.82	4316.02
		3858.77	4249.13	4206.29
26	4038.09	3995.37	4357.68	4315.28
	3902.39	3857.77	4249.83	4205.31
27	4038.95	3994.62	4358.53	4314.53
	3903.01	3856.65	4250.53	4204.34
28	4039.81	3993.87	4359.39	4313.79
	3903.62	3855.58	4251.23	4203.36
29	4040.68	3993.13	4360.25	4313.05
			4251.93	4202.39
30	4041.55	3992.38	4361.11	4312.31
	3904.82		4252.62	4201.40
31	4042.41	3991.64	4361.97	4311.57
	3905.42		4253.30	4200.42
32	4043.29	3990.90	4362.83	4310.84
		3851.24	4253.99	4199.43
33	4044.16	3990.16	4363.70	4310.10
	3906.59	3850.14	4254.67	4197.44
34	4045.03	3989.42	4364.57	4309.37
	3907.17	3849.04	4255.35	4196.45
35	4045.91	3988.69	4365.44	4308.64
	3907.75	3847.94	4256.03	4195.45
36	4046.79	3987.95	4366.31	4307.91
	3908.31	3846.84	4256.70	4194.45
37	4047.67	3987.22	4367.19	4307.19
	3908.89	3845.73	4257.37	4193.45
a. First entry if for the values of the present work				
b. Second entry is for the values in Ref [19]				

III. A. 5. The Permanent Dipole Moment of YN

The electric dipole moment μ is the most fundamental electrostatic property of a neutral molecule. It is of great utility in the construction of the molecular orbital based models of bonding. Fermi and Teller established long ago [36] that a neutral closed shell molecule with values of μ greater than 1.625 Debye can capture an electron in its electrostatic dipole field resulting in bound electronic states for the anion. Accordingly, the description of the mobility of electrons through a polar gas relies upon knowledge of μ [37]. It has been realized for decades that the multipole moments of which μ is the leading term for electrically neutral systems, have proved useful in accounting for intermolecular forces and therefore have helped in the search for an understanding of the macroscopic properties of imperfect gases liquids and solids [38]. Recently, the availability of experimentally well determined values for μ has become increasingly more important in the assessment of *ab initio* electronic structure calculations for molecules. The dipole moment operator is among the most reliably predicted physical properties because the quantum mechanical operator is a simple sum of one-electron operators. The expectation value of this operator is sensitive to the nature of the most chemically relevant valence electrons [38]. Accordingly, a comparison of the experimental and theoretical values of μ is a sensitive test to the general predictive quality of the computational methodology. In Table XII we report the values of μ calculated at the equilibrium internuclear distance of the ground state $R=1.84\text{\AA}$ of YN.

Table XII:

Permanent dipole moments for the singlet, triplet, and quintet states of the molecule YN at $R = 1.84\text{\AA}$.

State $^{2s+1}\Lambda$	$ \mu (\text{Debye})$	$\delta\mu / \mu$	State $^{2s+1}\Lambda$	$ \mu (\text{Debye})$	$\delta\mu / \mu$
$X^1\Sigma^+$	5.186 ^a		$(1)^3\Pi$	3.840	
	8.19 ^{theo b}	36.7%		5.52 ^{theo b}	30.4%
$(1)^1\Sigma^+$	6.552		$(2)^3\Pi$	3.793	
	10.64 ^{theo b}	38.4%			
$(1)^1\Delta$	4.113		$(3)^3\Pi$	0.812	
$(2)^1\Delta$	3.466		$(1)^3\Phi$	5.835	
$(1)^1\Pi$	3.352		$(2)^3\Phi$	1.249	
	5.33 ^{theo b}	37.1%			
$(1)^1\Phi$	3.825		$(3)^3\Phi$	0.059	
$(2)^1\Pi$	7.159		$(1)^5\Delta$	3.866	
$(1)^1\Sigma^-$	3.722		$(2)^5\Delta$	0.986	
$(1)^3\Sigma^+$	3.356		$(1)^5\Pi$	1.884	
$(2)^3\Sigma^+$	3.213		$(2)^5\Pi$	0.451	
$(1)^3\Delta$	4.014		$(1)^5\Phi$	4.103	
$(2)^3\Delta$	4.014				

a. Values of the present work b. Ref [21]

Note: (theo) corresponds to theoretical results.

The results of the permanent electric dipole moment reported in the present work do not agree with the theoretical results of Shim *et. al.* [21], with a relative difference of $30.4\% \leq$

$\delta\mu \leq 38.4\%$. This is not surprising, as Shim *et. al.* [21] results fail to reproduce the experimental results in literature [19, 20, 22]. Indeed, we can assert that our results for the permanent dipole moments are much better than those reported by Shim *et. al.* [21], particularly due to that our results succeed in reproducing the experimental results for the spectroscopic constants of YN [19, 20, 22] (Tables I and IV).

The variation of the permanent electric dipole moment with molecular geometry enters into the description of light-matter interaction in resonant spectroscopy [38]. Figure 12 shows the variation of the permanent dipole moment as a function of the internuclear distance for several low lying experimentally detected electronic states in YN.

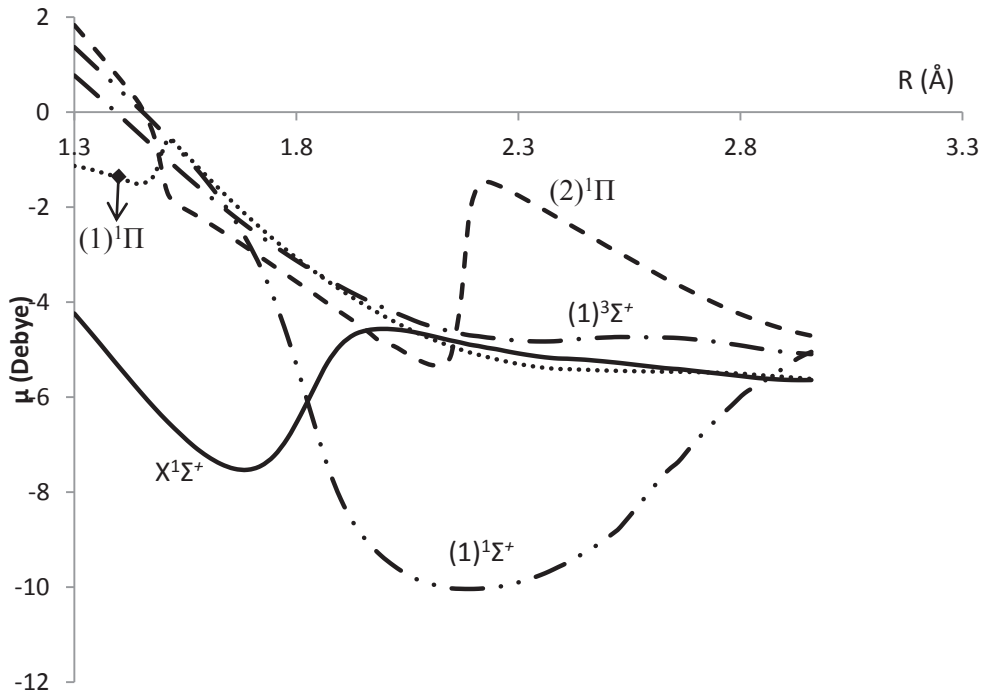


Fig. 12. Variation of the permanent dipole moment in (Debye) as a function of the internuclear distance R (Å) for the states $(X)^1\Sigma^+$, $(1)^1\Sigma^+$, $(1)^3\Sigma^+$, $(1)^1\Pi$, and $(2)^1\Pi$.

III. A. 6. The Internal Molecular Electric Fields in YN

It has been proposed in recent years that heavy polar diatomic molecules have large internal molecular electric fields in GV/cm that are 4 to 5 times larger than any laboratory electric field [39]. These large internal electric fields are very useful in the search for the electric dipole moment of the electron eEDM. A fundamental physical property, whose measurement shall dramatically influence all the popular extensions of the standard model [27]. The measurement of an electric dipole moment of the electron d_e requires extremely large electric fields to observe the energy shift due to different alignments of d_e . The current upper limit on the electron eEDM 1.6×10^{-27} e.cm, comes from measurements in thallium atoms [40]. In this

experiment, an effective electric field is generated inside the atom. The magnitude of this electric field (on the order of 70 MV/cm) is far larger than the field that could be applied directly in the laboratory [27]. The new generation of electron eEDM experiments, employing polar diatomic molecules, is expected to reach sensitivity of $10^{-30} - 10^{-28}$ e.cm [41]. In this respect, many diatomic molecules, with $^3\Delta$ and $^{2,3}\Sigma$ molecular symmetries, have been proposed as model candidates to measure the electron's eEDM. Molecules such as, BaF [42], YbF [43, 44], HgF [45], PbF [45], PbO [46], HBr⁺ [47], HI⁺ [47], PtH⁺ [27], HfH⁺ [27] have been already proposed as a mean to measure the electron's eEDM. In these systems molecular electric fields as large as 99 GV/cm were detected in HgF [45] and as small as 0.02 GV/cm in HBr⁺ [47]. *Ab initio* calculations are very useful in this respect, particularly due to the relative ease by which internal molecular electric fields can be computed. The quality of the electric field results largely depends on the methods and the basis sets used. In the present work we have computed the internal molecular electric fields $E_{\text{molecular}}$ for the various electronic states of the molecule YN at the highest level of theory MRSDCI. The computed values for the internal molecular electric field along the internuclear axis are reported in Table XIII at the equilibrium internuclear distance of the ground state and in units of GV/cm. The values of $E_{\text{molecular}}$ for the various states of YN are reported here for the first time in literature.

Table XIII:

Internal Molecular Electric Field for the electronic states of YN at $R = 1.84\text{\AA}$.

State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} (\text{GV/cm})$	State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} (\text{GV/cm})$
$X^1\Sigma^+$	0.124	$(1)^3\Pi$	0.237
$(2)^1\Sigma^+$	0.017	$(1)^3\Phi$	0.011
$(1)^1\Delta$	0.069	$(2)^3\Pi$	0.054
$(2)^1\Delta$	0.049	$(2)^3\Phi$	0.002
$(1)^1\Sigma^-$	0.065	$(3)^3\Phi$	0.270
$(1)^1\Pi$	0.237	$(3)^3\Pi$	0.339
$(1)^1\Phi$	0.011	$(1)^5\Delta$	0.187
$(2)^1\Pi$	0.054	$(1)^5\Phi$	0.179
$(2)^1\Phi$	0.002	$(1)^5\Sigma^+$	0.184
$(1)^3\Sigma^+$	0.124	$(2)^5\Delta$	0.242
$(2)^3\Sigma^+$	0.017	$(1)^5\Pi$	0.204
$(1)^3\Delta$	0.069	$(2)^5\Pi$	0.017
$(2)^3\Delta$	0.049		

The values of the internal molecular fields are largely dependent on the charge distribution in each of the molecular orbital configurations of each state. This gives a molecular electric field in YN that varies between 0.002 GV/cm for the $(2)^1\Phi$ state and 0.339 GV/cm for the $(3)^3\Pi$ state.

III. B. The Structure of Zirconium Nitride ZrN

III. B. 1. Preliminary Works on ZrN

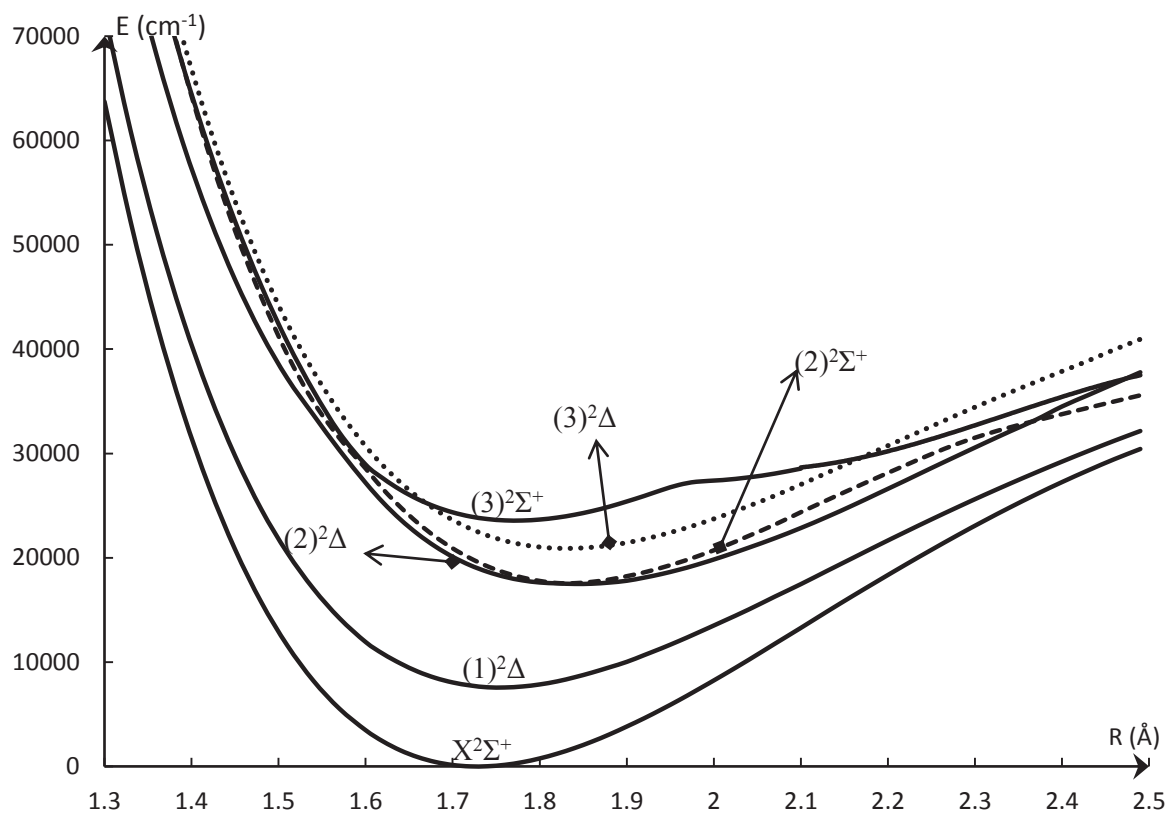
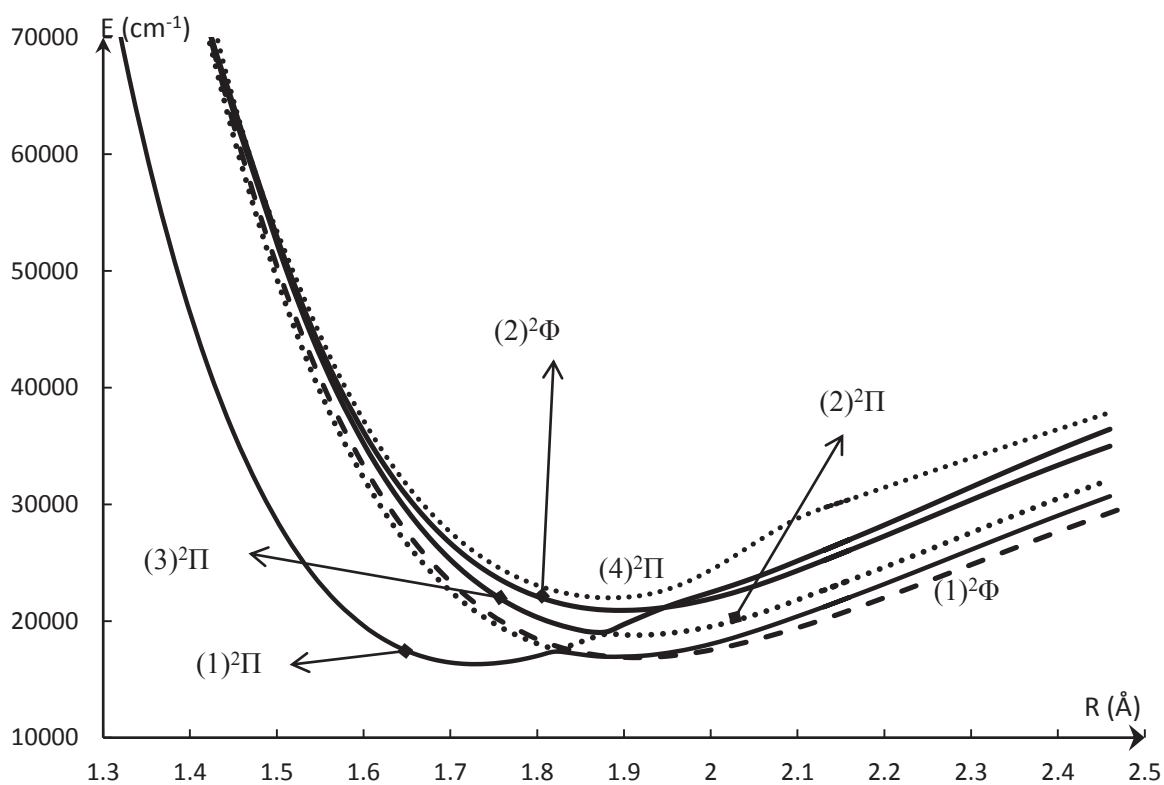
Zirconium nitride is an interesting and versatile material owing to its low electrical resistivity, good corrosion resistance, low formation energy, and high mechanical properties [48 - 50]. Typically, ZrN and TiN possessing the best mechanical properties are deposited by physical vapor deposition to coat medical devices, industrial parts, automotive, aerospace components and other parts subject to high wear and corrosive environments [51 - 54]. In high temperature material applications, within the group of refractory metal nitrides Ti, Zr, Hf, and Nb titanium and zirconium nitrides are the most promising hardening additives, which are used for raising the high-temperature strength of sintered molybdenum and provide high enough ductility parameters at a temperature up to 2000°C [55]. Understanding the formation and nature of the Zirconium-nitrogen bond is thus an active area of research with many applications in several areas of science. In astrophysics, transition metal atoms are relatively abundant in cool M- and S-type stars [56]. In fact, diatomic transition metal hydrides and oxides have been detected in the spectra of stellar atmospheres [57 - 61] and since the nitrides and oxides often have similar bond energies [62], the nitrides are also of potential astrophysical importance.

To the best of our knowledge the electronic structures and vibrational spectra of the ZrN molecule have been topics of research for a considerable period of time [63 - 71]. Bates and Dunn [63] performed a spectroscopic study for the (0,0) band in the $(1)^2\Pi - X^2\Sigma^+$ and $(2)^2\Sigma^+ - X^2\Sigma^+$ transitions. Recently, Cheung and coworkers [64 - 68] studied the (0,0), (1,1), and (2,2) vibrational bands of the $(1)^2\Pi - X^2\Sigma^+$ transition for various isotopomers of ZrN ^{90}ZrN , ^{91}ZrN , ^{92}ZrN , ^{94}ZrN , ^{96}ZrN . More recently, Chen *et. al.* [69] performed a laser spectroscopic study for the (0,0) vibrational band in the $(2)^2\Sigma^+ - X^2\Sigma^+$ system. These spectroscopic studies [69] were then followed by *ab initio* MRCI calculations on the low-lying 5 doublet states and 2 low-lying quartet states. Haiyang *et. al.* [70] studied the magnetic hyperfine structure of the $X^2\Sigma^+$ state for the isotopomer ^{91}ZrN , recording the laser induced fluorescence spectrum of the $(1)^2\Pi - X^2\Sigma^+$ vibrational transition (0 - 0). Gary *et. al.* [71] performed an infrared spectroscopic and density functional investigation for the reaction between transition metals, Ti, Zr, and Hf with nitrogen atoms. They reported the value of the harmonic constant $\omega_e = 991\text{cm}^{-1}$ in the ground state of ZrN. Devore *et. al.* [72] performed an infrared vibrational spectroscopy of the group IV transition metal gaseous nitrides TiN, ZrN, and HfN. The ground state in each of the three molecules was detected to be of $^2\Sigma$ symmetry. Infrared

spectroscopic analysis yielded vibrational frequencies and rotational P and R branches in the ground state of ZrN. A common feature exists between the different experimental studies on the ZrN molecule. It is the existence of strong severe perturbations in the experimental spectra. These perturbations could not be resolved easily and resulted in a limited partial analysis of the obtained spectrum. This is not surprising, as several perturbations have been also detected in the spectrum of the isoelectronic molecules TiN [73, 74] and ScO [75, 76], which are similar to ZrN. As the identity of the perturbing states in ZrN could not be identified, there arises the need for a high quality *ab initio* investigation for the electronic structure of the neutral ZrN molecule. Although the atomic structure of Nitrogen is relatively simple with 4S as its ground electronic state. The electronic structure of Zirconium is more complicated with 3F as the ground state. These combinations of atomic orbitals on Zr and N will result in a plenty of molecular states, which could also split due to spin orbit coupling. In the present work we try to fully explore the electronic structure of the molecule ZrN with the inclusion of relativistic spin orbit effects. The results of the present calculations yielded potential energy curves, spectroscopic constant and vibro-rotational energy levels. The comparison between the values of the present work to the experimental and theoretical results available in literature shows a very good agreement. This reflects the high accuracy by which our theoretical calculations are able to represent the bonding in ZrN. Until the work described here, no extensive theoretical study was available on ZrN.

III. B. 2. Results on ZrN

The potential energy curves for 21 low-lying electronic states $^{2s+1}\Lambda^{(\pm)}$ of the molecule ZrN have been obtained from MRSDCI +Q calculations performed at 40 internuclear distances equally distributed between 1.3 Å and 2.5 Å. Figures 13-16 show the potential energy curves of 12 low-lying doublet and 9 low-lying quartet states. The energy scale of all figures is relative to the minimum energy of the ground electronic state predicted here to be a $X^2\Sigma^+$ state. The spectroscopic constants obtained from all of these curves are given in Table XIV where R_e is the equilibrium internuclear distance, ω_e is the harmonic frequencies around the equilibrium, T_e is the transition energy relative to the ground state, B_e is the rotational constant, and D_e is the centrifugal distortion constant. The ground state of ZrN is a $X^2\Sigma^+$ state resulting from the distribution of 7 valence electrons over the active space of molecular orbitals $1\sigma^2 1\pi^4 2\sigma^1$ leading in to an orbital angular momentum $\Lambda = \Sigma \lambda_i = 0$, with one unpaired electron ($S = 1/2$), giving a doublet multiplicity $(2s+1)$ ground state $X^2\Sigma^+$.

Fig.13: Potential energy curves for the $^2\Sigma^+$ and $^2\Delta$ states of the molecule ZrN.Fig.14: Potential energy curves for the $^2\Pi$ and $^2\Phi$ states of the molecule ZrN.

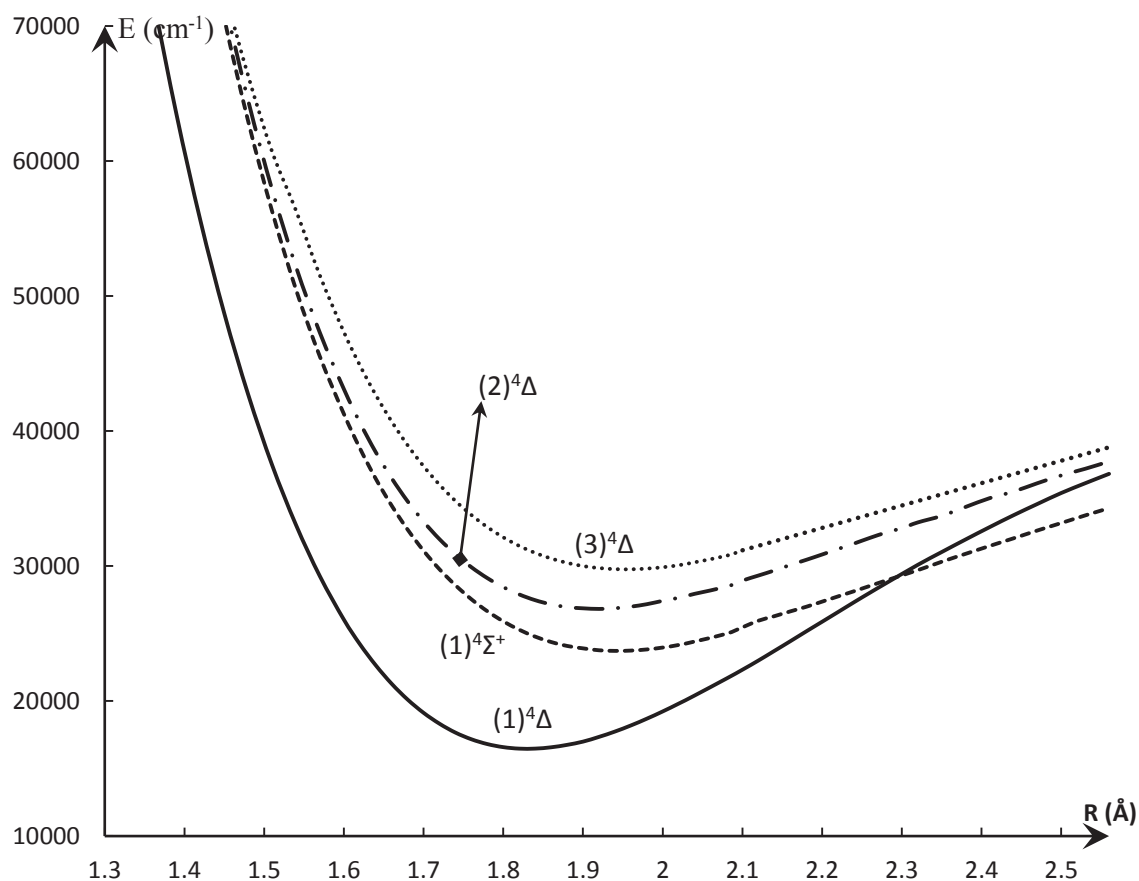


Fig.15: Potential energy curves for the $^4\Sigma^\pm$ and $^4\Delta$ states of the molecule ZrN.

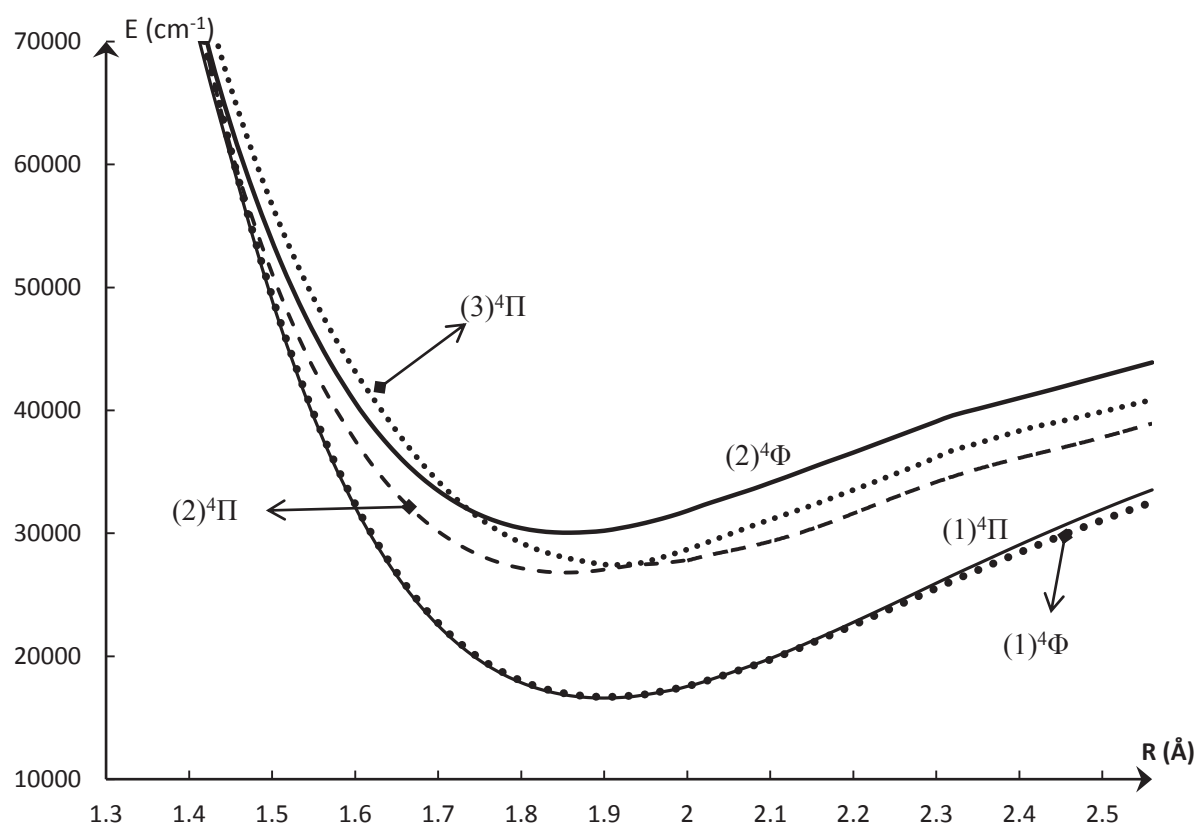


Fig.16: Potential energy curves for the $^4\Pi$ and $^4\Phi$ states of the molecule ZrN.

Table XIV:

Spectroscopic constants for the lowest lying 21 doublet and quartet states of the molecule ZrN.

State	$T_e(\text{cm}^{-1})$	$\delta T_e / T_e$	$\omega_e(\text{cm}^{-1})$	$\delta \omega_e / \omega_e$	$B_e \times 10^{-1}(\text{cm}^{-1})$	$\delta B_e / B_e$	$D_e \times 10^7(\text{cm}^{-1})$	$\delta D_e / D_e$	$R_e(\text{\AA})$	$\delta R_e / R_e$
$X^2\Sigma^+$	0 ^a 0 ^{b,c,d,e,f,g,h,i,j,k}		982.79 ^a 1015 ^{Theo b} 1002.6 ^{Exp c} 1002.2 ^{Exp d} 1030 ^{Exp d} 991 ^{Exp j}		4.626 4.7816 ^{Exp e} 4.8052 ^{Exp f} 4.7981 ^{Exp g} 4.8406 ^{Exp h} 4.83 ^{Exp i}		4.094 4.55 ^{Exp e} 4.54 ^{Exp f} 4.515 ^{Exp g} 4.53 ^{Exp h}		1.731 ^a 1.7023 ^{Exp b} 1.6943 ^{Exp e} 1.6954 ^{Exp h} 1.7 ^{Exp i}	
(1) ² Δ	7580.02 8531 ^{Theo b}		920.97 944 ^{Theo b}		4.509		4.322		1.754 1.7228 ^{Theo b}	
(2) ² Δ	17494.25		727.12		4.108		5.329		1.838	
(2) ² Σ^+	17595.15 16228 ^{Theo b}		959.83 935 ^{Theo b}		4.133 4.587 ^{Exp i}		3.060		1.833 1.7789 ^{Theo b}	
(3) ² Δ	20905.95		867.13		4.156		3.798		1.828	
(3) ² Σ^+	23604.08 25844 ^{Theo b} 24670.06 ^{Exp b} 24670 ^{Exp k}		783.84 830 ^{Theo b}		4.461 4.587 ^{Exp b}		5.781		1.767 1.7247 ^{Theo b}	
(1) ² Π	16317.00 16747 ^{Theo b} 17401 ^{Exp k} 17318.76 ^{Exp e} 16905.1 ^{Exp f}		929.20 1004 ^{Theo b} 973 ^{Exp d}		4.621 4.5870 ^{Exp b} 4.7508 ^{Exp e} 4.7601 ^{Exp f}		4.579 5.61 ^{Exp e} 5.54 ^{Exp f}		1.732 1.7000 ^{Theo b} 1.7062 ^{Exp d}	
(2) ² Π	17904.42		1415.93		4.184		1.468		1.822	
(1) ² Φ	16879.49		746.89		3.778		3.869		1.916	
(3) ² Π	19155.01		1408.58		4.009		1.313		1.861	
(2) ² Φ	20924.10		778.16		3.857		3.793		1.897	
(4) ² Π	21992.86		948.11		3.907		2.645		1.885	
(1) ⁴ Δ	16477.72 17026 ^{Theo b}		844.59 828 ^{Theo b}		4.145		3.989		1.830 1.8033 ^{Theo b}	
(1) ⁴ Σ^+	23730.45		723.81		3.697		3.732		1.939	
(2) ⁴ Δ	26833.38		764.83		3.786		3.689		1.915	
(3) ⁴ Δ	29763.96		802.67		3.712		4.126		1.931	
(1) ⁴ Π	16621.60		763.27		3.851		3.929		1.899	
(1) ⁴ Φ	16708.48		768.29		3.833		3.820		1.903	
(2) ⁴ Π	26841.14		787.26		4.056		4.406		1.849	
(3) ⁴ Π	27476.45		974.42		3.818		2.347		1.907	
(2) ⁴ Φ	30054.29		780.77		4.034		4.289		1.856	

Ref: a. First entry is for the values of the present work

b. Ref [69]

c. Ref [70]

d. Ref [66]

e. Ref [65]

f. Ref [64]

g. Ref [68]

h. Ref [67]

i. Ref [72]

j. Ref [71]

k. Ref [63]

Note: Theo and Exp represents theoretical and experimental results in references.

The comparison between the values of the present work to the theoretical results available in Ref [69] shows a very good agreement with a percentage relative difference of $2.5\% \leq \delta T_e / T_e \leq 11\%$, $2.0\% \leq \delta \omega_e / \omega_e \leq 7.4\%$, and $1.4\% \leq \delta R_e / R_e \leq 3\%$ for the states $X^2\Sigma^+$, $(1)^2\Delta$, $(2)^2\Sigma^+$, $(3)^2\Sigma^+$, $(1)^2\Pi$, $(1)^4\Delta$. The experimental results available on ZrN for the states $X^2\Sigma^+$, $(3)^2\Sigma^+$, and $(1)^2\Pi$ are reproduced in our calculations with percentage relative differences of 3.4% (Ref [64]) $\leq \delta T_e / T_e \leq 6.2\%$ (Ref [63]), 0.8% (Ref [71]) $\leq \delta \omega_e / \omega_e \leq 4.5\%$ (Ref [66]), 2.1% (Ref [72]) $\leq \delta B_e / B_e \leq 9.8\%$ (Ref [72]), and 1.5% (Ref [66]) $\leq \delta R_e / R_e \leq 2.1\%$ (Ref [67]). The

experimental values of the centrifugal distortion constant D_e are reproduced in our calculations for the ground $X^2\Sigma^+$ state with a relative difference of 9.3% (Ref [68]) $\leq \delta D_e/D_e \leq 10\%$ (Ref [65]), except for the $(1)^2\Pi$ state where a relative difference of 17% (Ref[64]) $\leq \delta D_e/D_e \leq 18.3\%$ (Ref[65]) has been obtained.

In the results of Table XIV the transition energy $T_e = 16905.1\text{cm}^{-1}$ of the experimentally detected $(1)^2\Pi$ state in Ref [64] has been estimated by using the following relation $T_e = T_v - \omega_e(v+1/2)$, where T_v is the experimentally determined vibrational energy level in Ref [64], and ω_e is the experimentally available harmonic vibrational frequency in Ref [66]. The other transition energy value (17318.76 cm^{-1}) of the $(1)^2\Pi$ state listed in table XIV has been averaged over the two spin component states $\Pi_{1/2}$ and $\Pi_{3/2}$ listed in Ref [65] by using the following relation $(T_{1/2} + T_{3/2})/2$.

A good theoretical determination of spectroscopic constants for a molecule containing heavy elements requires the inclusion of spin orbit coupling and other scalar relativistic effects in the electronic structure calculations. In this study we try to fully explore the electronic structure of the molecule ZrN with spin orbit effects, at the complete active space (CASSCF) method and Multi-reference single and double configuration interaction (MRSDCI) method, for the lowest lying 49 spin orbit states $\Omega^{(\pm)}$. We also compute the entire potential energy curves of these states and perform numerical fitting to obtain the spectroscopic constants of ZrN. Theoretical results obtained in the present work are in excellent agreement with the experimental and theoretical results available in literature. In this research, several low lying doublet and quartet states have been studied for the first time. In Figures 17 – 20 we draw the potential energy curves of 49 low-lying spin orbit electronic states ($\Omega = 1/2, 3/2, 5/2, 7/2$, and $9/2$) as a function of the internuclear distance R . Then by fitting the calculated energy curves for the different investigated electronic states in to a polynomial in R , several spectroscopic constants were calculated such as, the harmonic vibrational frequencies ω_e , the equilibrium internuclear distances R_e , the rotational constants B_e , the centrifugal distortion constants D_e and the transition energies with respect to the minimum energy of the ground states T_e . These are reported in Table XV together with the experimental and theoretical results available in literature for the spin orbit states in ZrN.

The new results calculated in the present work for the excited electronic states of ZrN are of particular interest since they are viable candidates for experimental observations by optical spectroscopy techniques. The excited electronic states $(1)^2\Pi$, $(2)^2\Pi$, $(3)^2\Pi$, $(4)^2\Pi$, $(2)^2\Sigma^+$, $(3)^2\Sigma^+$ are accessible through dipole allowed electronic transitions from the ground state, obeying the selection rules $\Delta\Lambda = 0, \pm 1$, $\Delta S = 0$, and $\Delta\Omega = 0$. Other excited electronic states

with Δ and Φ symmetries might be accessible through transitions from excited electronic states with Π and Δ symmetries.

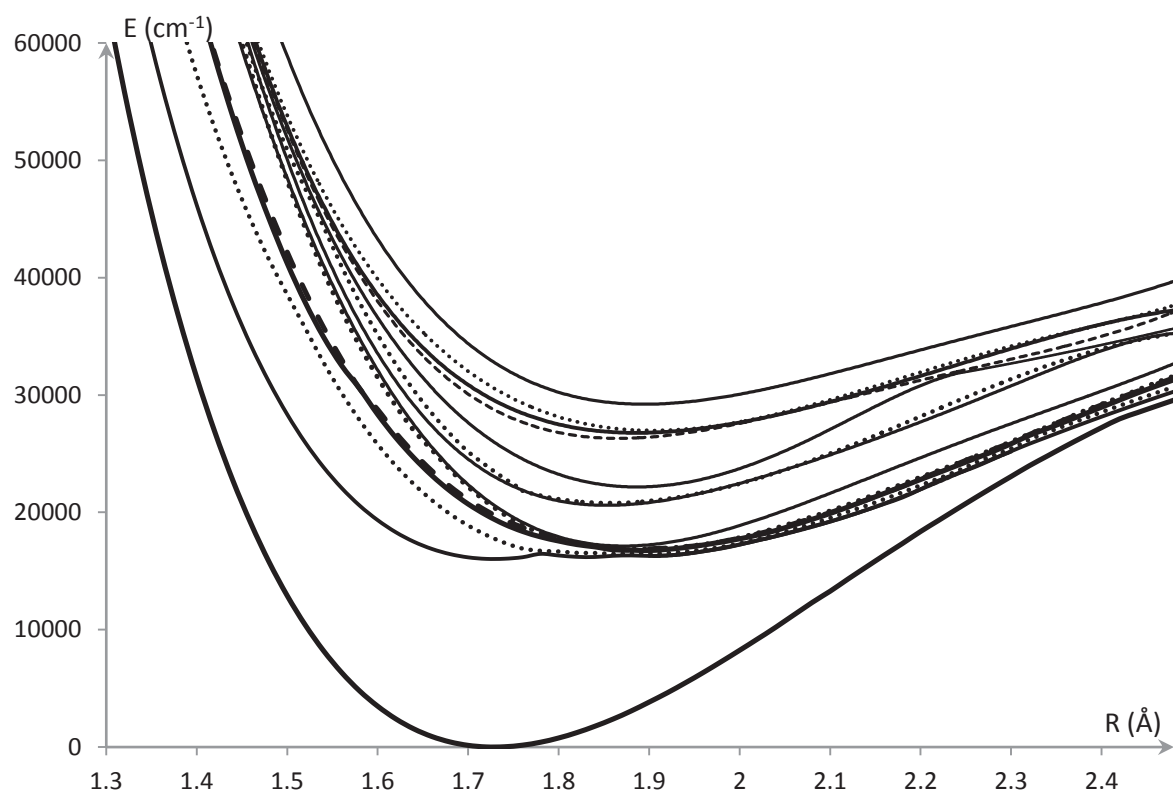


Fig. 17: Potential energy curves for 14 ($\Omega = 1/2$) states of the molecule ZrN (Full and dotted lines).

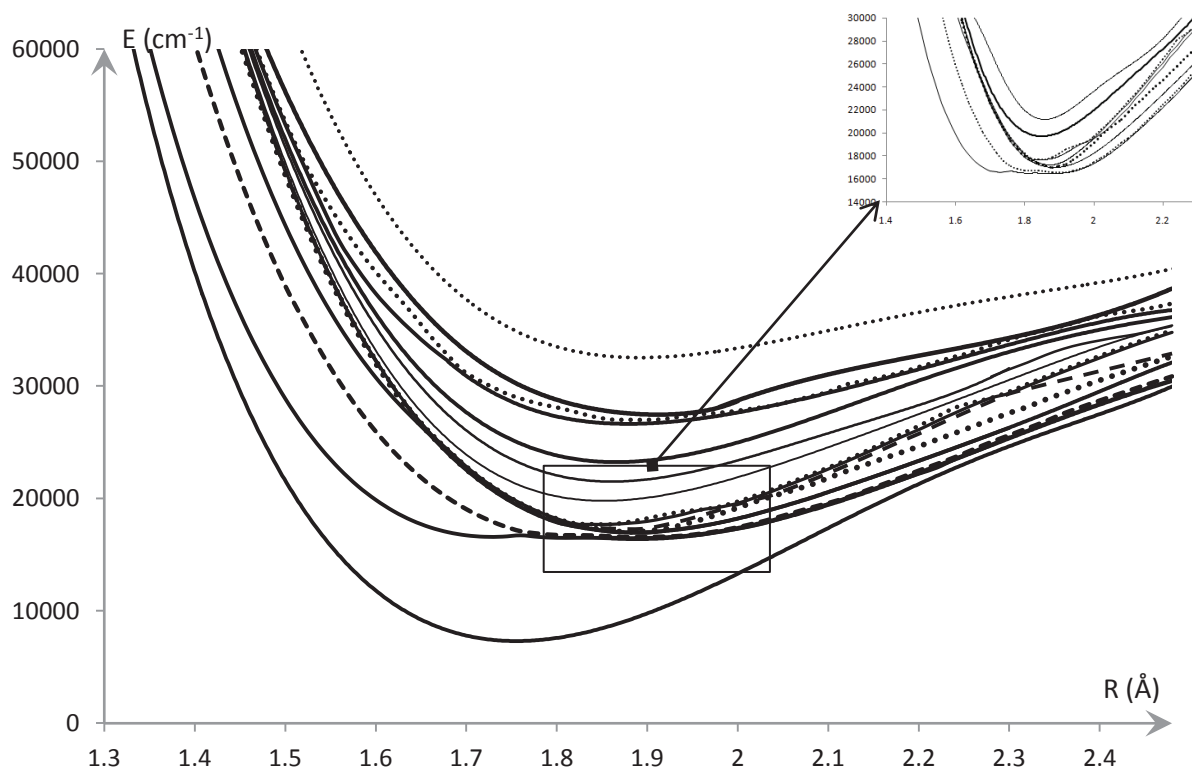


Fig. 18: Potential energy curves for 15 ($\Omega = 3/2$) states of the molecule ZrN (Full and dotted lines).

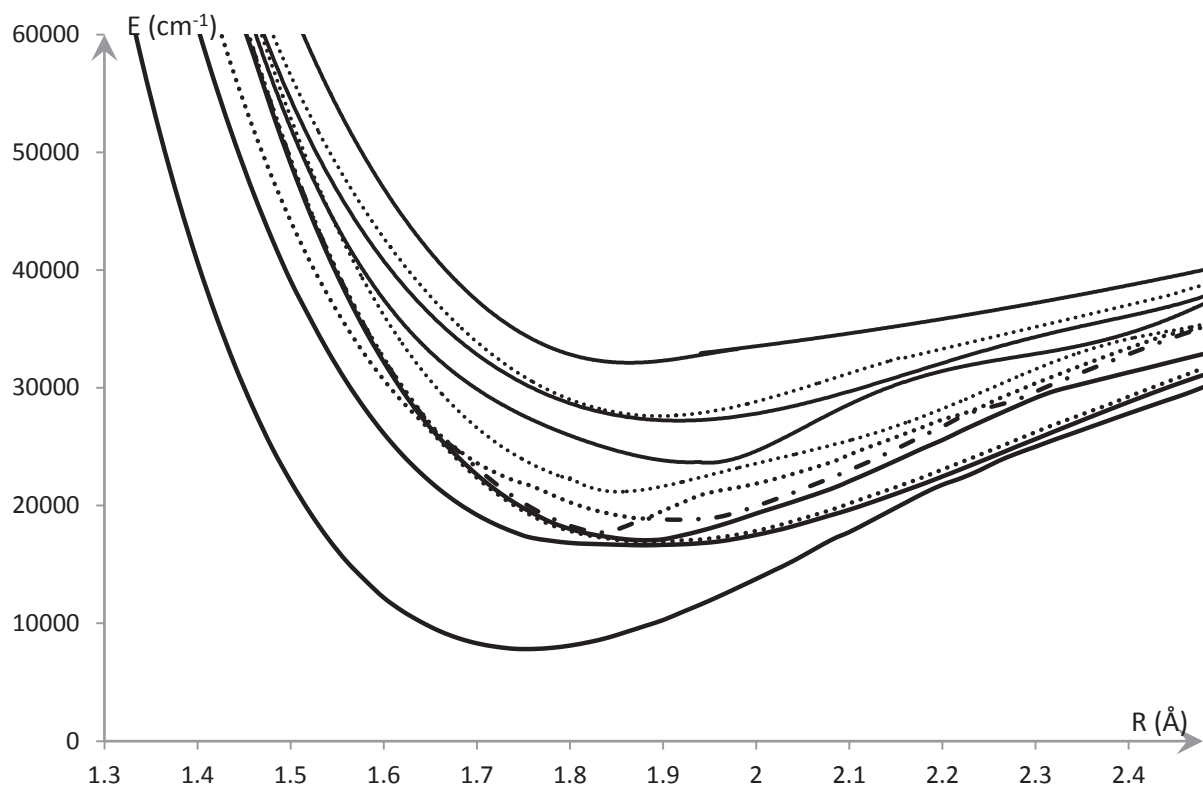


Fig. 19: Potential energy curves for 11 ($\Omega = 5/2$) states of the molecule ZrN (Full and dotted lines).

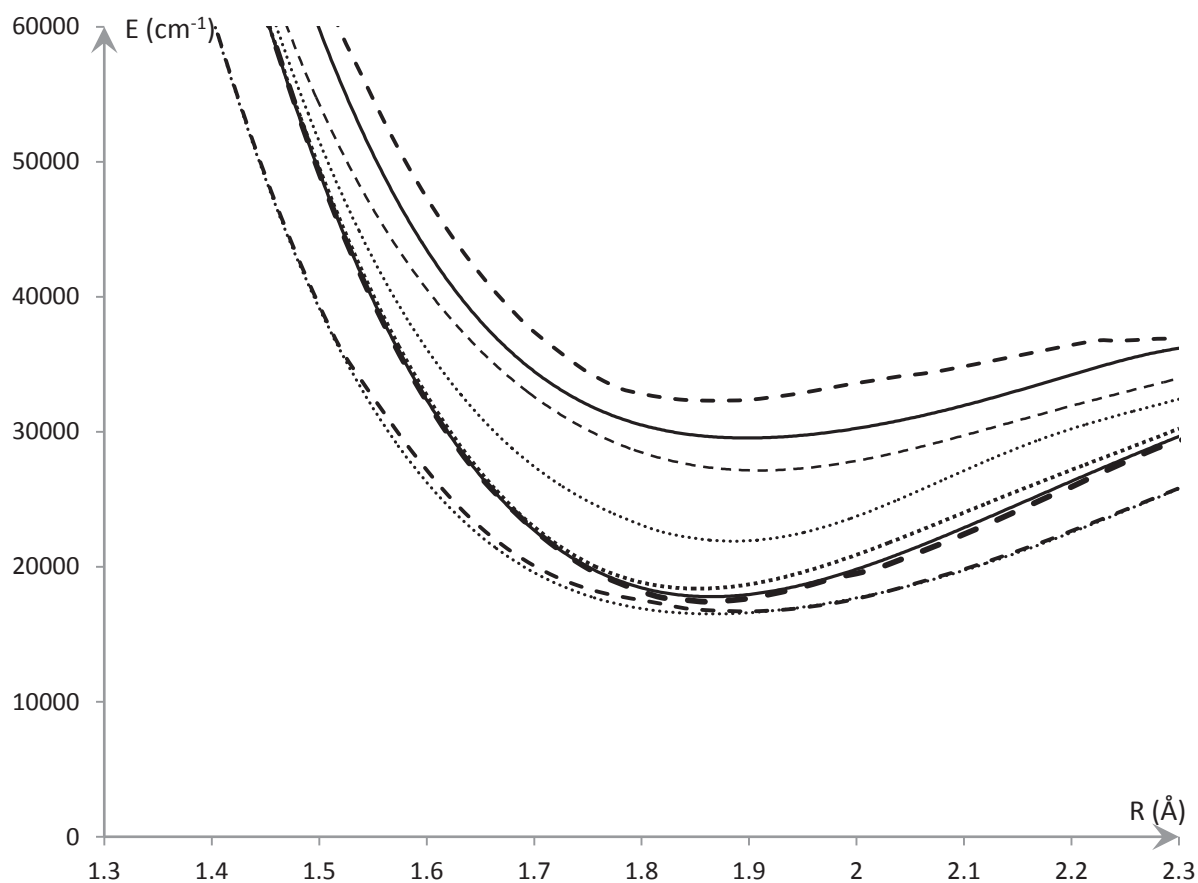


Fig. 20: Potential energy curves for 7 ($\Omega = 7/2$) (dotted lines) and 2 ($\Omega = 9/2$) (Full lines) states of the molecule ZrN.

TABLE XV:

Equilibrium internuclear distances R_e , transition energies T_e , rotational constants B_e , centrifugal distortion constants D_e and harmonic frequencies ω_e , for Ω states of the molecule ZrN.

$(n)\Omega[(k)^{2S+1}\Lambda]$	T_e (cm ⁻¹)	$\delta T_e/T_e$	ω_e (cm ⁻¹)	$\delta\omega_e/\omega_e$	R_e (Å)	$\delta R_e/R_e \times 10^1$ (cm ⁻¹)	$\delta B_e/B_e \times 10^7$ (cm ⁻¹)	$\delta D_e/D_e$
(1)1/2 [$X^2\Sigma^+$]	0.0		972.12		1.728 ^a	4.647	-4.227	
			1015 ^{Theo b}	4.2%	1.7023 ^{Theo b}	1.5%	4.7816 ^{Theo b}	2.8%
			1002.6 ^{Exp c}	3.0%	1.6943 ^{Exp e}	1.9%	4.7816 ^{Exp e}	2.8%
			995 ^{Exp d}	2.3%	1.6954 ^{Exp h}	1.9%	4.8052 ^{Exp f}	3.3%
			1030 ^{Exp d}	5.6%	1.7 ^{Exp i}	1.6%	4.7981 ^{Exp g}	3.1%
			991 ^{Exp j}	1.9%			4.8406 ^{Exp h}	4.0%
							4.83 ^{Exp i}	3.7%
(2)1/2[(1) ² Π]	16140.43		968.82		1.732	4.649	-5.282	
	17040.05 ^{Exp e}	5.2%	958 ^{Exp d}	1.1%		4.751 ^{Exp e}	2.1%	5.61 ^{Exp e}
(3)1/2[(1) ⁴ Δ]	16154.76		667.04		1.845	4.079	-6.091	
(4)1/2[(2) ² Σ ⁺]	16798.78		853.89		1.902	4.194	-3.947	
	16228 ^{Theo b}	3.5%	935 ^{Theo b}	8.6%	1.7789 ^{Theo b}	6.1%	4.587 ^{Exp i}	8.4%
(5)1/2[(2) ² Δ]	16848.38		716.79		1.891	3.883	-4.560	
(6)1/2[(1) ⁴ Π]	16894.09		689.82		1.889	3.891	-4.952	
(7)1/2[(2) ² Π]	16994.25		935.16		1.877	3.939	-2.798	
(8)1/2[(3) ² Π]	17454.86		976.13		1.861	4.006	-2.704	
(9)1/2[(3) ² Σ ⁺]	20921.51		763.76		1.859	4.225	-5.674	
	25844 ^{Theo b}	19.0%	830 ^{Theo b}	7.9%	1.7247 ^{Theo b}	7.7%	4.587 ^{Exp b}	7.8%
	24670.06 ^{Exp b}	15.2%						
	24670 ^{Exp k}	15.2%						
(10)1/2[(4) ² Π]	22120.44		943.80		1.875	3.948	-2.768	
(11)1/2[(2) ⁴ Π]	26551.16		607.14		1.843	4.102	-6.540	
(12)1/2[(1) ⁴ Σ ⁺]	26945.11		660.97		1.869	4.142	-7.146	
(13)1/2[(2) ⁴ Δ]	27146.18		685.01		1.894	4.027	-5.340	
(14)1/2[(3) ⁴ Π]	29495.28		547.10		1.888	3.902	-7.684	
(1)3/2[(1) ² Δ]	7334.31		912.30		1.755	4.508	-4.405	
(2)3/2[(1) ² Π]	16582.20		972.64		1.783	4.369	-5.589	
	17597.52 ^{Exp e}	5.7%	943 ^{Exp d}	3.1%				
(3)3/2[(1) ⁴ Δ]	16605.82		245.25		1.865	4.199	-6.392	
(4)3/2[(1) ⁴ Φ]	16973.93		803.36		1.883	3.914	-4.780	
(5)3/2[(2) ² Π]	17050.04		956.78		1.874	3.953	-2.702	
(6)3/2[(1) ⁴ Π]	17637.56		1002.63		1.855	4.034	-2.628	
(7)3/2[(3) ² Δ]	19416.51		1177.46		1.859	4.016	-1.882	
(8)3/2[(3) ² Π]	21195.56		1034.32		1.865	3.989	-2.383	
(9)3/2[(4) ² Π]	23823.43		916.41		1.815	4.198	-4.217	
(10)3/2[(2) ⁴ Π]	24869.72		1222.37		1.858	4.019	-1.749	
(11)3/2[(1) ⁴ Σ ⁺]	26803.27		579.65		1.878	3.941	-7.234	
(12)3/2[(2) ⁴ Δ]	27045.98		703.52		1.897	3.855	-4.636	
(13)3/2[(2) ⁴ Φ]	27446.06		832.92		1.897	3.857	-3.308	
(14)3/2[(3) ⁴ Π]	29320.72		660.25		1.861	4.007	-6.015	
(15)3/2[(3) ⁴ Δ]	32294.98		816.35		1.863	4.001	-3.856	
(1)5/2[(1) ² Δ]	7767.43		845.68		1.745	4.559	-5.302	
(2)5/2[(1) ⁴ Δ]	16631.23		486.85		1.861	4.026	-10.735	
(3)5/2[(1) ⁴ Π]	16929.17		709.39		1.890	3.886	-4.662	
(4)5/2[(1) ⁴ Φ]	17099.05		986.99		1.871	3.967	-2.567	
(5)5/2[(1) ² Φ]	18094.71		975.88		1.846	4.073	-2.862	
(6)5/2[(3) ² Δ]	19267.32		1163.36		1.864	3.997	-1.897	
(7)5/2[(2) ² Φ]	21306.29		1040.98		1.864	3.996	-2.361	
(8)5/2[(2) ⁴ Π]	23605.51		1056.1		1.925	3.746	-1.892	
(9)5/2[(2) ⁴ Δ]	27269.01		720.44		1.898	3.851	-4.429	

(10)5/2[(2) ⁴ Φ]	27555.51	926.39	1.904	3.828	-2.618
(11)5/2[(3) ⁴ Δ]	32258.52	792.59	1.863	4.000	-4.079
(1)7/2[(1) ⁴ Δ]	16734.96	494.84	1.879	3.929	-1.027
(2) 7/2 [(1) ² Γ]	16717.43	704.92	1.895	3.864	-4.651
(3)7/2 [(1) ⁴ Φ]	17472.76	952.63	1.863	4.001	-2.826
(4)7/2[(1) ² Φ]	18283.97	1069.80	1.849	4.059	-2.362
(5)7/2 [(2) ² Φ]	21935.57	904.86	1.882	3.920	-2.947
(6)7/2 [(2) ⁴ Δ]	27200.27	796.33	1.882	3.915	-4.061
(7)7/2 [(3) ⁴ Δ]	32312.65	722.69	1.862	4.019	-4.756
(1)9/2[(1) ⁴ Φ]	17726.03	1027.23	1.850	4.054	-2.543
(2)9/2[(2) ⁴ Φ]	29650.74	593.91	1.903	3.836	-6.399
Ref: a. First entry is for the values of the present work b. Refs [69] c. Ref [70] d. Ref [66]					
e. Ref [65] f. Ref [64] g. Ref [68] h. Ref [67] i. Ref [71] k. Ref [63]					
Note: Theo and Exp represent theoretical and experimental results, respectively.					

The comparison between the values of the present work and the results available in literature shows a very good agreement. The ground state has been predicted in ZrN to be a $\Omega = 1/2$ ($X^2\Sigma^+$) state with $\omega_e = 972 \text{ cm}^{-1}$ in agreement with previous experimental and theoretical observations [63 – 71]. Our results for the (1)1/2 [$X^2\Sigma^+$], (4)1/2[(2)² Σ^+], and (9)1/2[(3)² Σ^+] states are in excellent agreement with the theoretical calculations without spin orbit effects of the parent states $X^2\Sigma^+$, (2)² Σ^+ , and (3)² Σ^+ respectively, with relative differences of $\delta T_e/T_e = 3.5\%$ (Ref [69], $4.2\%(\text{Ref [69]}) \leq \delta\omega_e/\omega_e \leq 8.6\%(\text{Ref [69]})$, and $1.5\%(\text{Ref [69]}) \leq \delta R_e/R_e \leq 7.7\%(\text{Ref [69]})$. However, a less agreement exists between our T_e value in the (9)1/2[(3)² Σ^+] state and the T_e value of the parent state (3)² Σ^+ , reported in literature [63, 69], with a percentage relative difference of 15.2% ($\text{Ref}[63, 69]) \leq \delta T_e/T_e \leq 19\%(\text{Ref}[69])$. Actually, our result for the T_e value in the parent (3)² Σ^+ state, initially located in our calculations at 23604.08cm^{-1} , is in very good agreement with the experimental results available for this state [63, 69] (Table XIV). However, when spin orbit interactions are taken into account the (9)1/2[(3)² Σ^+] state is shifted by -2682.6cm^{-1} into a lower energy region. This places the (9)1/2[(3)² Σ^+] state at $T_e=20921.51\text{cm}^{-1}$ which creates the large difference between our T_e value for the spin orbit state (9)1/2[(3)² Σ^+] and its parent state (3)² Σ^+ reported in Table XIV. The experimental results available on the spin orbit component Ω states of ZrN are reproduced in our calculations to a very high accuracy, with a percentage relative difference of 5.2% ($\text{Ref [65]}) \leq \delta T_e/T_e \leq 5.7\%$ ($\text{Ref [65]})$, 1.1% ($\text{Ref [66]}) \leq \delta\omega_e/\omega_e \leq 5.6\%$ ($\text{Ref [66]})$, 1.6% ($\text{Ref [71]}) \leq \delta R_e/R_e \leq 1.9\%$ ($\text{Ref [65]})$, 2.1% ($\text{Ref [65]}) \leq \delta B_e/B_e \leq 8.4\%$ ($\text{Ref [71]})$, and 5.8% ($\text{Ref [65]}) \leq \delta D_e/D_e \leq 7.1\%$ ($\text{Ref [65]})$.

One of the important applications of molecular quantum chemistry is to study non-adiabatic transitions. It is quite common for ground and especially excited state potential energy curves of molecules to make a crossing or an avoided crossing. Such crossings or avoided crossings, known as conical intersections [77] can dramatically alter the stability of molecules owing to

the possibility of crossing from one state to another. Within the considered internuclear distance range several crossings and avoided crossings are recorded between the potential energy curves of the interacting states, these are displayed in Tables XVI and XVII along with the internuclear position R , and the energy gap separating the avoided crossing states ΔE_{AC} .

Table XVI: Positions of the crossing and avoided crossings between the different electronic states of the molecule ZrN.

Crossing						Avoided crossing					
State 1	State 2	(n ₁)State 1 / (n ₂)State 2	R _c (Å)	R _{av} (Å)	ΔE _{av} (cm ⁻¹)	State 1	State 2	(n ₁)State 1 / (n ₂)State 2	R _c (Å)	R _{av} (Å)	ΔE _{av} (cm ⁻¹)
² Σ ⁺	² Φ	1/1	2.43			² Π	² Π	3/2	1.66		
² Δ	² Φ	1/1	2.24			² Φ	² Φ	3/1	1.67		
	⁴ Π	1/1	2.30			² Π	² Π	3/3	1.72		
	⁴ Φ	1/1	2.28			² Φ	² Φ	3/2	1.76		
	² Σ ⁺	2/2	2.37			² Σ ⁺	² Π	3/4	1.77		
² Δ	² Φ	2/1	1.83			⁴ Σ ⁺	⁴ Σ ⁺	3/1	1.84		
	² Π	2/2	1.97			⁴ Δ	⁴ Δ	3/2	1.94		
	⁴ Δ	2/1	1.51			⁴ Π	⁴ Π	3/1	1.67		
	⁴ Π	2/1	1.80			⁴ Φ	⁴ Φ	3/1	1.68		
	⁴ Φ	2/1	1.81			² Φ	⁴ Σ ⁺	2/1	2.21		
	⁴ Π	2/2	2.49			² Φ	² Φ	1/1	1.86		
	² Φ	2/1	1.83			⁴ Δ	⁴ Δ	1/1	1.79		
	² Π	2/2	1.93			² Π	⁴ Π	1/1	1.82		
² Σ ⁺	² Φ	2/2	2.09			⁴ Φ	⁴ Φ	1/1	1.82		
	⁴ Σ ⁺	2/1	2.16			² Π	² Π	1/2		1.82	285
	⁴ Φ	2/1	1.81			² Π	² Π	2/3		1.88	186
	⁴ Π	2/1	1.81			² Π	² Φ	2/1	1.83		
	² Σ ⁺	2/3		1.6	383	⁴ Δ	⁴ Δ	2/1	2.03		
	² Σ ⁺	3/4		1.96		⁴ Π	⁴ Π	2/1	1.77		
	² Σ ⁺	3/3	1.67/2.15			² Φ	⁴ Δ	1/1	1.90		
	² Π	3/2	1.65			⁴ Π	⁴ Π	1/1	1.96		
² Δ	² Φ	3/1	1.68			⁴ Φ	⁴ Φ	1/1	1.96		
	² Π	3/3	2.76			² Π	² Φ	3/2	1.94		
	² Φ	3/2	1.87			⁴ Σ ⁺	⁴ Σ ⁺	3/1	2.12		
	² Π	3/4	2.25			⁴ Π	⁴ Π	3/2	1.56		
	⁴ Σ ⁺	3/1	2.01			⁴ Δ	⁴ Π	1/1	1.86		
	⁴ Δ	3/2	2.19			⁴ Φ	⁴ Φ	1/1	1.87		
	⁴ Δ	3/3	2.29			⁴ Π	⁴ Σ ⁺	2/1	1.73		
	⁴ Φ	3/1	1.64			⁴ Δ	⁴ Δ	2/2	1.89		
	⁴ Π	3/1	1.64			⁴ Π	⁴ Π	2/3		1.94	101
	⁴ Π	3/2	2.28			⁴ Σ ⁺	⁴ Σ ⁺	2/1	1.61		
	⁴ Π	3/3	2.42			⁴ Δ	⁴ Δ	2/2	1.69		
	⁴ Π	4/1	1.99			⁴ Δ	⁴ Δ	2/3	1.88		
	⁴ Δ	4/2	2.10			⁴ Π	⁴ Δ	3/2	1.54		
	⁴ Δ	4/3	2.33								
² Π	⁴ Σ ⁺	4/1	1.99								

Table XVII:

Positions of the avoided crossings R_{AC} and the energy difference ΔE_{AC} at these points with the corresponding crossings of Λ states for Ω states of ZrN.

Ω	$(n+1)\Omega$ $/n\Omega$	R_{AC} (Å)	ΔE_{AC} (cm ⁻¹)	Crossings of Λ states
1/2	2 / 3	1.76	369	(1) ² Π / (1) ⁴ Δ
	4/5	1.84	52	(2) ² Σ^+ / (2) ² Δ
	10 / 11	1.81	52	(3) ² Σ^+ / (4) ² Π
	10/ 12	2.28	152	(3) ² Σ^+ / (2) ⁴ Π
	11 / 12	2.28	347	(4) ² Π / (2) ⁴ Π
3/2	2 / 3	1.76	369	(1) ² Π / (1) ⁴ Δ
	4 / 5	1.86	52	(2) ² Σ^+ / (1) ⁴ Π
	6/ 7	2.36	96	(1) ⁴ Π / (1) ⁴ Φ
5/2	4 / 5	1.82	246	(1) ⁴ Φ / (1) ² Φ
	5 / 6	1.88	56	(1) ² Φ / (1) ² Δ
	8/ 9	2.24	183	(2) ⁴ Π / (2) ⁴ Δ

The composition in percentage of the Ω state-wave functions in terms of the $^{2s+1}\Lambda$ states calculated at $R = 1.72$ Å are presented in Table XVIII. For each state Ω there is a predominant component Λ with a contribution larger than 80% so that a main parent $^{2s+1}\Lambda$ may be identified. Nevertheless, there are states for which a small but significant contribution of other Λ states is obtained.

Table XVIII:

Composition of Ω -state wave functions of the molecule ZrN, in terms of Λ -states (in percentage) at $R = 1.72$ Å.

Ω	% (Λ -parent)	Ω	% (Λ -parent)
(1)1/2	100% X ² Σ^+	(12)3/2	100%(2) ⁴ Δ
(2)1/2	100% (1) ² Π	(13)3/2	88% (2) ⁴ Φ , 12% (1) ⁴ Σ^-
(3)1/2	100% (1) ⁴ Δ	(14)3/2	99.85%(3) ⁴ Π , 0.15% (2) ⁴ Δ
(4)1/2	100% (2) ² Σ^+	(15)3/2	100% (3) ⁴ Δ
(5)1/2	52% (2) ² Δ , 48% (2) ² Σ^+	(1)5/2	100% (1) ² Δ
(6)1/2	100% (1) ⁴ Π , 8%(1) ² Φ	(2) 5/2	100% (1) ⁴ Δ
(7)1/2	53% (2) ² Π , 39% (1) ⁴ Π , 8% (1) ⁴ Φ	(3)5/2	92% (1) ⁴ Π
(8)1/2	100%(3) ² Π	(4)5/2	74% (1) ⁴ Φ , 24% (1) ⁴ Π
(9)1/2	100%(3) ² Σ^+	(5)5/2	100% (1) ² Φ
(10)1/2	100%(4) ² Π	(6)5/2	100%(3) ² Δ
(11)1/2	100%(2) ⁴ Π	(7)5/2	100% (2) ² Φ
(12)1/2	95% (1) ⁴ Σ^+ , 5%(1) ⁴ Φ	(8)5/2	100%(2) ⁴ Π
(13)1/2	100%(2) ⁴ Δ	(9)5/2	53% (2) ⁴ Δ , 10%(2) ⁴ Φ , 37% (1) ⁴ Σ^-
(14)1/2	100%(3) ⁴ Π	(10)5/2	100%(2) ⁴ Φ
(15)1/2	100% (3) ⁴ Δ	(11)5/2	100%(3) ⁴ Π
(1)3/2	100% (1) ² Δ	(12)5/2	100% (3) ⁴ Δ
(2)3/2	100% (1) ² Π	(1)7/2	100% (1) ⁴ Δ
(3)3/2	100% (1) ⁴ Δ	(2)7/2	96% (1) ⁴ Φ , 4% (2) ² Π
(4)3/2	100% (1) ⁴ Φ	(3)7/2	100% (1) ² Φ
(5)3/2	87% (2) ² Π , 9%(1) ⁴ Π , 3.5% (1) ⁴ Φ , 0.5% (2) ² Δ	(4)7/2	100% (2) ² Φ
(6)3/2	85% (1) ⁴ Π , 15% (1) ⁴ Φ	(5)7/2	53% (2) ⁴ Δ , 47% (1) ⁴ Σ^-
(7)3/2	100% (1) ⁴ Π	(6)7/2	100%(2) ⁴ Φ
(8)3/2	100%(3) ² Δ	(7)7/2	100% (3) ⁴ Δ
(9)3/2	100%(3) ² Π	(1)9/2	100% (1) ⁴ Φ
(10)3/2	100%(4) ² Π	(1)9/2	100% (1) ⁴ Φ
(11)3/2	95% (1) ⁴ Σ^+ , 5%(1) ⁴ Φ		

III. B. 3. The Bonding Nature in ZrN

The complexity of transition metal-containing molecules makes the study of diatomics like ZrN ideal prototype for the better understanding of the bonding in larger molecular systems. *Ab initio* multi configuration calculations are very useful in this respect since their basic principle involves the mixing of s, p, and d atomic orbitals to form molecular σ , π , and δ orbitals. In Table XIX, we report the percentage composition of each molecular electronic state in terms of molecular orbital configurations. The percentage weights of each molecular orbital configuration are calculated as the squares of the corresponding CI coefficients. Configuration weights lower than 2% percent have been omitted from the results of Table XIX.

Table XIX:

Leading Configurations with percentage composition of the parent electronic states $^{2s+1}\Lambda^\pm$ in the molecule ZrN.

Electronic State	Weight
$X^2\Sigma^+$	89% $1\sigma^2 1\pi^4 2\sigma^1$
$(2)^2\Sigma^+$	88% $1\sigma^2 1\pi^4 3\sigma^1$
$(3)^2\Sigma^+$	95% $1\sigma^1 1\pi^4 2\sigma^1 3\sigma^1$
$(1)^2\Delta$	86% $1\sigma^2 1\pi^3 3\sigma^1 3\pi^1$
$(2)^2\Delta$	72% $1\sigma^2 1\pi^3 2\sigma^1 2\pi^1$, 12% $1\sigma^2 1\pi^3 3\sigma^1 2\pi^1$
$(1)^2\Pi$	85% $1\sigma^2 1\pi^4 2\pi^1$, 3% $1\sigma^2 1\pi^4 3\pi^1$
$(2)^2\Pi$	66% $1\sigma^2 1\pi^3 2\sigma^2$, 13% $1\sigma^2 1\pi^3 2\sigma^1 4\sigma^1$
$(1)^2\Phi$	50% $1\sigma^2 1\pi^3 2\sigma^1 4\sigma^1$, 49% $1\sigma^2 1\pi^3 2\sigma^1 1\delta^1$
$(3)^2\Pi$	41% $1\sigma^2 1\pi^3 2\sigma^1 3\sigma^1$, 40% $1\sigma^2 1\pi^3 2\sigma^1 1\delta^1$, 16% $1\sigma^2 1\pi^3 2\sigma^2$
$(2)^2\Phi$	47% $1\sigma^2 1\pi^3 2\sigma^1 3\sigma^1$, 45% $1\sigma^2 1\pi^3 2\sigma^1 1\delta^1$
$(4)^2\Pi$	41% $1\sigma^2 1\pi^3 2\sigma^1 3\sigma^1$, 44% $1\sigma^2 1\pi^3 2\sigma^1 1\delta^1$
$(1)^4\Delta$	90% $1\sigma^2 1\pi^2 2\sigma^1 3\sigma^2$
$(1)^4\Sigma^+$	84% $1\sigma^2 1\pi^3 2\sigma^1 2\pi^1$, 5% $1\sigma^2 1\pi^3 3\sigma^1 2\pi^1$, 5% $1\sigma^2 1\pi^3 2\pi^1 1\delta^1$
$(2)^4\Delta$	70% $1\sigma^2 1\pi^3 2\sigma^1 2\pi^1$, 25% $1\sigma^2 1\pi^3 3\sigma^1 2\pi^1$
$(3)^4\Delta$	50% $1\sigma^2 1\pi^3 3\sigma^1 2\pi^1$, 22% $1\sigma^2 1\pi^3 2\sigma^1 2\pi^1$, 20% $1\sigma^2 1\pi^3 2\pi^1 1\delta^1$
$(1)^4\Pi$	98% $1\sigma^2 1\pi^3 2\sigma^1 3\sigma^1$
$(1)^4\Phi$	99% $1\sigma^2 1\pi^3 2\sigma^1 3\sigma^1$
$(2)^4\Pi$	88% $1\sigma^1 1\pi^4 2\sigma^1 2\pi^1$, 9% $1\sigma^1 1\pi^4 3\sigma^1 2\pi^1$
$(3)^4\Pi$	48% $1\sigma^1 1\pi^4 3\sigma^1 2\pi^1$, 48% $1\sigma^1 1\pi^4 2\pi^1 1\delta^1$
$(2)^4\Phi$	43% $1\sigma^1 1\pi^4 3\sigma^1 2\pi^1$, 43% $1\sigma^1 1\pi^4 2\pi^1 1\delta^1$, 10% $1\sigma^1 1\pi^4 2\pi^1 1\delta^1$

Weights (in percent) are obtained from the square of the corresponding configuration interaction coefficients (CMRCI); weights lower than 2% are not reported.

The $(1)^2\Pi$ state arises from the promotion of the $2\sigma^1$ electron in the ground electronic state into a $2\pi^1$ orbital with an increase in energy of about 16317.00 cm^{-1} . The $(2)^2\Sigma^+$ state ($1\sigma^2 1\pi^4 3\sigma^1$) arises from the promotion of a $2\sigma^1$ electron in the ground state into a $3\sigma^1$ orbital with a corresponding energy increase of 17595.15 cm^{-1} . The $(3)^2\Sigma^+$ state ($1\sigma^1 1\pi^4 2\sigma^1 3\sigma^1$) arises from the promotion of the $1\sigma^1$ electron in the ground state into the $3\sigma^1$ molecular orbital with an energy increase of 23604.08 cm^{-1} . The lowest quartet state $(1)^4\Delta$ state ($1\sigma^2 1\pi^2 2\sigma^1 3\sigma^2$)

arises from the promotion of two 1π electrons in the ground state into a $3\sigma^2$ orbital with an energy change of 16477.72cm^{-1} .

In computational quantum chemistry *ab initio* calculations can be used to analyze the bonding in simple metal systems. The expansion of molecular orbital wave functions in terms of atomic orbital basis sets is very useful in understanding the bonding order in the ground state of small molecules. In the present work, the bonding order in the ground state of the ZrN molecule is analyzed in terms of the molecular orbital occupation numbers available from the CASSCF calculations and in the active space of molecular orbitals ($4\sigma 3\pi 1\delta$). The effective bond order EBO is a quantity that gives the formation of a chemical bond, and was given in equation (1) of this chapter. In our CASSCF calculations the ground state wave function in ZrN is obtained by distributing seven valence electrons over the active space of molecular orbitals $4\sigma 3\pi 1\delta$. In this treatment we obtained the occupation numbers of the bonding and anti-bonding orbitals in the following way: $\eta_b(1\sigma) = 1.61887$, $\eta_b(2\sigma) = 0.69819$, $\eta_{ab}(3\sigma) = 0.37438$, $\eta_{ab}(4\sigma) = 0.11726$, $\eta_{ab}(1\delta) = 0.38276$, $\eta_b(1\pi) = 3.33124$, $\eta_{ab}(2\pi) = 0.39012$, $\eta_{ab}(3\pi) = 0.0872$. Now by applying equation (1) for the effective bond order we obtain an $\text{EBO} = 2.148 \approx 2$, thus indicating that we have a fully developed double bond in ZrN.

III. B. 4. The Vibrational Structure of ZrN

In the past few years, the realization of elementary quantum logic gates on molecular systems have witnessed remarkable experimental achievements [80 – 84]. Due to their rich inner energy structures, that can be used to encode information, molecules offer a promising prospect for scalable quantum information processing and have attracted lots of attention. After the work of Vivie-Riedle and coworkers [85, 86], several groups have explored the possibility of encoding qubits in rovibrational states of a single diatomic molecule [87 – 97] or polyatomic molecule [98 – 108] or in two interacting diatomic molecules [109,110]. In these works, logic gate operations were driven by femtolaser pulses designed by optimal control theory or genetic algorithms or by using stimulated Raman Adiabatic passage techniques [111]. In conclusion investigating the vibrational-rotational energy structures of diatomic molecules is gaining significant importance in diverse research fields as molecular quantum computing.

In the present work we investigate the vibrational energy levels of the ZrN molecule. First we solve the time independent radial Schrödinger equation for the vibrational and rotational motions of the ZrN molecule in the vicinity of the potential energy curves obtained by

MRSDCI+Q calculations, in order to obtain the eigenvalues of energy E_v , and the rotational constants B_v and the distortion constant D_v for every vibrational level. This is mainly done by separating the vibrational and rotational motions in the radial Schrödinger equation and then following an iterative cycle, called the canonical functions approach [34, 35]. The results of our vibrational-rotational calculations are shown in Tables XX and XXI, in which we report the vibrational energy levels E_v , the constants B_v , D_v , and the turning points of each vibrational level $R_{\min}$ and $R_{\max}$ for the parent states $X^2\Sigma^+$, $(3)^2\Sigma^+$, $(1)^2\Phi$, $(1)^2\Delta$, and their spin orbit component states $(1)1/2 [X^2\Sigma^+]$, $(7)1/2 [(2)^2\Pi]$, $(5)3/2 [(2)^2\Pi]$.

Table XX :

Values of the eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, the constants B_v , D_v for the different vibrational levels of the states $X^2\Sigma^+$, $(1)^2\Phi$, $(3)^2\Sigma^+$, $(1)^2\Delta$ of the ZrN molecule.

$X^2\Sigma^+$								$(1)^2\Phi$				
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$\delta B_v/B_v$	$D_v \times 10^7$ (cm ⁻¹)	$\delta D_v/D_v$	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	474.97 ^a	1.68 ^a	1.78 ^a	4.634 ^a		4.249 ^a		17236.71	1.87	1.97	3.777	3.912
				4.8288 ^{Exp b}	4.0%	4.53 ^{Exp b}	6.2%					
				4.830 ^{Exp c}	4.0%	6.00 ^{Exp c}	29.2%					
1	1439.64	1.64	1.83	4.609		4.242		18707.04	1.79	2.06	3.727	4.033
				4.8053 ^{Exp d}	4.1%	4.54 ^{Exp d}	6.6%					
2	2397.94	1.62	1.86	4.586		4.284		19427.67	1.77	2.10	3.700	4.123
				4.7816 ^{Exp e}	4.1%	4.55 ^{Exp e}	5.8%					
3	3348.26	1.60	1.89	4.563		4.193		20137.51	1.76	2.13	3.674	4.049
4	4293.88	1.59	1.91	4.539		4.362		20839.71	1.74	2.16	3.649	4.109
5	5230.42	1.58	1.94	4.517		4.383		21533.87	1.73	2.18	3.624	4.187
6	6158.12	1.56	1.96	4.492		4.290		22219.06	1.72	2.20	3.596	4.256
7	7079.23	1.55	1.98	4.471		4.327		22894.97	1.71	2.23	3.569	4.293
8	7993.51	1.54	2.00	4.447		4.271		23561.97	1.70	2.25	3.543	4.271
9	8900.97	1.53	2.01	4.420		4.411		24220.44	1.68	2.28	3.515	4.412
10	9800.17	1.52	2.03	4.397		4.421						
11	10691.52	1.51	2.05	4.372		4.261						
12	11576.61	1.51	2.06	4.349		4.382						
13	12454.65	1.50	2.08	4.325		4.630						
14	13323.15	1.49	2.10	4.297		4.464						
15	14183.49	1.48	2.12	4.271		4.629						
16	15035.19	1.48	2.13	4.247		4.489						

$(3)^2\Sigma^+$								$(1)^2\Delta$				
v	E_v (cm ⁻¹)	$\delta E_v/E_v$	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$\delta B_v/B_v$	$D_v \times 10^7$ (cm ⁻¹)	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	23996.42 ^a		1.72 ^a	1.83 ^a	4.408 ^a		4.585 ^a	8017.98	1.70	1.81	4.499	4.424
	24670.5 ^{Exp d}	2.7%										
	24670.06 ^{Theo f}	2.7%			4.587 ^{Theo f}	3.9%						
1	24857.97		1.68	1.88	4.384		4.576	8923.06	1.67	1.86	4.478	4.731
2	25712.94		1.66	1.91	4.356		4.833	9807.00	1.64	1.89	4.456	5.155
3	26550.11		1.64	1.94	4.309		6.486	10667.87	1.62	1.92	4.441	5.885
4	27322.56		1.62	1.98	4.178		1.444	11503.90	1.61	1.94	4.455	7.137
5	27915.90		1.61	2.06	3.918		1.258	12310.25	1.59	1.96	4.474	7.159
6	28447.72		1.60	2.09	3.953		1.077	13097.54	1.58	1.99	4.466	4.038
7	29029.99		1.59	2.12	3.882		9.574	13899.58	1.57	2.01	4.446	1.642
8	29585.39		1.59	2.16	3.839		5.006	14735.93	1.56	2.03	4.431	2.626
9	30141.29		1.58	2.19	3.767		7.626	15592.02	1.55	2.05	4.417	4.506
10	30683.78		1.58	2.22	3.739		3.051	16443.88	1.54	2.07	4.377	5.887
11	31237.18		1.57	2.25	3.705		4.225	17271.69	1.53	2.10	4.298	7.406
12	31793.43		1.57	2.27	3.679		2.747	18066.54	1.53	2.11	4.262	4.956

Ref:(a). First entry is for the results of the present work. (b). Ref [67], (c). Ref [63], (d). Ref [64], (e). Ref [65],

(f). Ref [69]. Note: Exp, corresponds to experimental results whie Theo, corresponds to theoretical results.

Table XXI: Values of the eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the constants B_v , D_v for the different vibrational levels of the states $(1)1/2 [X^2\Sigma^+]$, $(7)1/2 [(2)^2\Pi]$, $(5)3/2 [(2)^2\Pi]$ of the ZrN molecule.

(1)1/2 [X ² Σ ⁺]										
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	δB _v /B _v	D _v ×10 ⁷ (cm ⁻¹)	δD _v /D _v			
0	475.09 ^a	1.68 ^a	1.78 ^a	4.634 ^a		4.244 ^a				
				4.82882 ^{Exp b}	4.0%	4.53 ^{Exp b}	6.3%			
				4.830 ^{Exp c}	4.1%	6.00 ^{Exp c}	29.3%			
1	1440.37	1.64	1.83	4.609		4.236				
				4.80529 ^{Exp d}	4.1%	4.54 ^{Exp d}	6.7%			
2	2399.37	1.62	1.86	4.586		4.306				
				4.78164 ^{Exp e}	4.1%	4.55 ^{Exp e}	5.3%			
3	3349.19	1.60	1.89	4.562		4.202				
4	4294.14	1.58	1.91	4.539		4.328				
5	5230.98	1.57	1.93	4.517		4.405				
6	6158.37	1.56	1.95	4.491		4.269				
7	7079.49	1.55	1.97	4.470		4.277				
8	7994.44	1.54	1.99	4.446		4.327				
9	8901.75	1.53	2.01	4.419		4.386				
10	9801.39	1.52	2.03	4.398		4.444				
11	10693.29	1.52	2.04	4.374		4.214				
12	11579.68	1.51	2.06	4.352		4.270				
13	12460.07	1.50	2.08	4.328		4.658				
14	13330.08	1.50	2.10	4.296		4.798				
15	14188.29	1.49	2.12	4.266		4.811				
16	15036.37	1.48	2.13	4.243		4.125				
17	15880.28	1.48	2.15	4.223		4.429				
18	16716.83	1.47	2.17	4.191		5.313				
19	17539.69	1.47	2.18	4.159		4.699				
20	18353.78	1.46	2.20	4.135		4.324				
21	19161.67	1.46	2.21	4.107		5.157				
22	19958.23	1.45	2.23	4.074		5.173				
23	20743.58	1.45	2.25	4.045		4.780				
24	21520.19	1.44	2.26	4.016		4.983				
(7)1/2 [(2) ² Π]				(5)3/2 [(2) ² Π]						
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)
0	17442.50 ^a	1.83 ^a	1.94 ^a	3.918 ^a	2.874 ^a	17512.35 ^a	1.82 ^a	1.93 ^a	3.936 ^a	2.783 ^a
1	18359.22	1.78	1.98	3.941	3.155	18449.61	1.78	1.97	3.948	3.285
2	19254.73	1.76	2.01	3.909	3.332	19344.99	1.76	2.00	3.915	3.230
3	20125.29	1.74	2.04	3.872	3.879	20218.79	1.74	2.04	3.869	4.213
4	20959.56	1.72	2.07	3.839	5.062	21041.82	1.72	2.07	3.829	4.931
5	21740.06	1.71	2.10	3.793	3.435	21817.58	1.71	2.10	3.794	3.197
6	22515.73	1.70	2.12	3.774	3.948	22596.01	1.70	2.12	3.778	4.169
7	23279.34	1.69	2.15	3.739	5.203	23357.56	1.69	2.15	3.735	5.308
8	24009.28	1.68	2.18	3.681	4.661	24084.98	1.68	2.18	3.687	4.375
9	24721.10	1.67	2.20	3.668	4.284	24797.69	1.67	2.20	3.663	4.283
10	25423.66	1.66	2.22	3.629	4.634	25500.13	1.66	2.22	3.631	4.569

Ref:(a)First entry is for the results of the present work. (b). Ref [67], (c). Ref [63], (d). Ref [64], (e). Ref [65]
Exp, corresponds to experimental results in literature.

III. B. 5. The Permanent Dipole Moment of ZrN

In an approach to create a quantum computer Demille [113] suggested the use of heteronuclear diatomic molecules trapped in a 1-dimensional trap array, and controlled by an electric field gradient that allows the spectroscopic control of molecules. In this system the qubits are considered to be the electric dipole moments of diatomic molecules, which are in

principle oriented along or against the external electric field. Molecules such as KCs with a permanent electric dipole moment of $\mu = 1.92\text{D}$ [114] were proposed in Ref [113] to be suitable for control in such traps. The permanent electric dipole moments available for polar molecules provide a ready means to address and manipulate qubits encoded in rotational states through the interaction with external electric fields as well as photons [115]. Typically, the permanent dipole moments in diatomic molecules might vary between 0 D and 11 D [116]. At one extreme, a symmetrical molecule such as chlorine Cl_2 has zero dipole moment, while near the other extreme gas phase potassium bromide KBr , which is highly ionic, has a dipole moment of 10.5 D [116]. Thus the permanent electric dipole moment of a diatomic molecule is an important physical property with significant importance in several areas of research. Due to the limited theoretical and experimental studies on the permanent electric dipole moment of the ZrN molecule, we calculate in the present work the permanent electric dipole moments of the molecule ZrN in the ground and excited electronic states at the MRSDCI level of theory. To the best of our knowledge, this is the first study in literature that investigates the permanent dipole moment of ZrN . Thus a comparison between the values in the present work to other values in literature is not possible. But, the permanent electric dipole moment is a one electron operator, whose accuracy depends on the wavefunctions used, and since our results for the spectroscopic constants and vibrational-rotational energy levels of ZrN match with the theoretical and experimental values in literature, then we can claim that our results for the permanent dipole moment of the ZrN molecule are accurate enough to represent the true physical system. In Table XXII, the results for the values of the permanent electric dipole moment of the ZrN molecule are shown at the equilibrium internuclear distance of the ground state $R = 1.72\text{\AA}$.

Table XXII:

Permanent dipole moments for the electronic states of the molecule ZrN at $R = 1.72\text{\AA}$.

State $^{2s+1}\Lambda$	$ \mu (\text{Debye})$	State $^{2s+1}\Lambda$	$ \mu (\text{Debye})$
$\text{X}^2\Sigma^+$	3.190	$(4)^2\Pi$	0.983
$(1)^2\Delta$	6.489	$(1)^4\Delta$	1.954
$(2)^2\Delta$	2.063	$(1)^4\Sigma^+$	0.730
$(2)^2\Sigma^+$	0.603	$(2)^4\Delta$	1.270
$(3)^2\Sigma^+$	0.827	$(3)^4\Delta$	2.977
$(3)^2\Delta$	4.399	$(1)^4\Pi$	2.246
$(1)^2\Pi$	4.712	$(1)^4\Phi$	2.222
$(2)^2\Pi$	1.324	$(2)^4\Pi$	0.778
$(1)^2\Phi$	1.805	$(3)^4\Pi$	3.255
$(3)^2\Pi$	1.499	$(2)^4\Phi$	4.029
$(2)^2\Phi$	0.765		

The interaction of a molecule with a laser field in resonant spectroscopy largely depends on the variation of the permanent electric dipole moment with the change in molecular geometry [38]. In Figure 21 we draw the variation of the permanent dipole moment with the internuclear distance for the electronic states in ZrN. In this figure we notice that the $(1)^2\Delta$ state attains the largest dipole moment of 7.385D at $R = 1.82\text{\AA}$. These results for the permanent electric dipole moment in ZrN are reported here for the first time in literature.

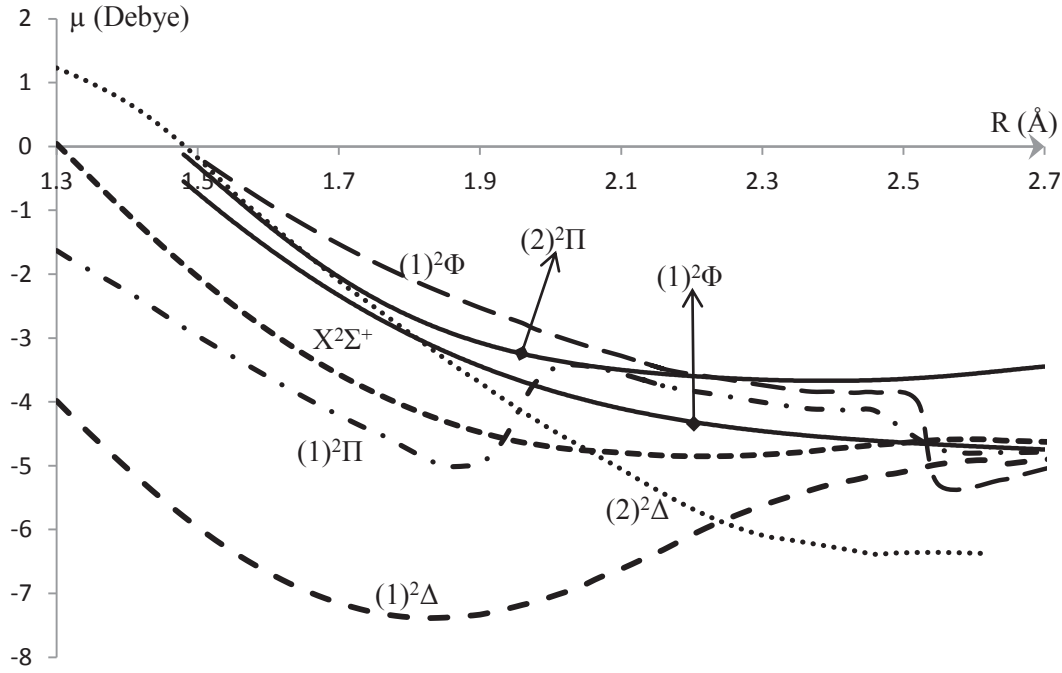


Fig. 21: Variation of the permanent dipole moment in (Debye) as a function of the internuclear distance R ($\text{\AA}$) for the states $(X)^2\Sigma^+$, $(1)^2\Pi$, $(2)^2\Pi$, $(1)^2\Delta$, $(2)^2\Delta$, $(1)^2\Phi$, and $(2)^2\Phi$.

III. B. 6. The Internal Molecular Electric Fields in ZrN

Polar molecules offer a new ideal laboratory for an eEDM search, mainly due to their large effective electric fields which might reach the orders of a few tens of GV/cm [117]. The electric fields of ground and excited electronic states in diatomic molecules are very useful in a possible observation of the electric dipole moment of the electron [117]. Mostly appealing molecular candidates are those with large values of internal electric fields. In the present work we calculate the expectation value of the internal molecular electric field in the different electric states of ZrN at the MRSDCI level of theory and at the equilibrium internuclear distance of the ground state $R = 1.72\text{\AA}$. These results are reported in units of GV/cm in Table XXIII.

The current result of the internal molecular electric field in the ground state of ZrN ($X^2\Sigma^+$) is almost 3 times larger than that previously obtained in the present work for the ground state

($X^1\Sigma^+$) of YN. The results obtained here for the internal molecular electric field in ZrN are reported here for the first time in literature.

Table XXIII:

Internal Molecular Electric Field for the electronic states of ZrN at $R = 1.72\text{\AA}$.

State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} $ (GV/cm)	State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} $ (GV/cm)
$X^2\Sigma^+$	0.310	$(1)^4\Delta$	0.304
$(1)^2\Delta$	0.119	$(1)^4\Sigma^+$	0.214
$(2)^2\Delta$	0.296	$(2)^4\Delta$	0.201
$(2)^2\Sigma^+$	0.376	$(3)^4\Delta$	0.128
$(3)^2\Delta$	0.324	$(1)^4\Pi$	0.284
$(3)^2\Sigma^+$	0.065	$(1)^4\Phi$	0.288
$(1)^2\Pi$	0.128	$(2)^4\Pi$	0.231
$(2)^2\Pi$	0.345	$(2)^4\Phi$	0.103
$(1)^2\Phi$	0.299	$(3)^4\Pi$	0.130
$(3)^2\Pi$	0.318		
$(2)^2\Phi$	0.321		
$(4)^2\Pi$	0.320		

III. C. Comparison between 4d Transition Metal Nitrides MN ($M = Y, Zr, Nb, \dots, Cd$)

Transition Metal Nitrides (TMN) are known to have extreme physical properties. They are chemically very stable with high corrosion resistance, high melting temperature and are extremely hard [118]. These TMN are widely used in the industry of information storage technology, cutting tools, high power energy industry, and optoelectronics [118, 119]. The origins of their unusual physical properties are mainly due to their bonding characteristics. In order to understand the difference in bonding between the 4d transition metals and nitrogen, we compare in the present work the spectroscopic constants R_e , ω_e , μ_e in the ground state of the transition metal nitrides of YN and ZrN to the other series of diatomic 4d transition metal nitrides MN in the periodic table, where M stands for Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd.

In literature the molecule NbN has been the subject of several experimental and theoretical investigations [120-126]. Its ground state was predicted to be a $^3\Delta$ state arising from the molecular orbital configuration $4\delta^1 5\sigma^1$ [125]. The experimental spectroscopic constants R_e , ω_e , and μ_e previously determined in the ground state of NbN are $R_e = 1.663\text{\AA}$ [123], $\omega_e = 1003\text{cm}^{-1}$ [123], and $\mu_e = 4.49$ Debye [127]. The MoN molecule has been studied experimentally by two groups Andrews *et. al.* [128] and Fletcher *et. al.* [129, 130] using a high resolution optical spectroscopic study. The ground state in neutral MoN is of $^4\Sigma^-$ symmetry, with an experimental bond length of $R_e = 1.648\text{\AA}$ [129], and harmonic vibrational frequency of $\omega_e = 1075\text{cm}^{-1}$ [129], and permanent dipole moment of $\mu_e = 3.38$ Debye [129]. The analysis for the electronic structure of the TcN molecule is limited to a theoretical study

done by A. C. Borin *et. al.* [131]. Experimental investigations for this molecule are not available, possibly due to the radioactivity character of Tc [132]. The ground state of neutral TcN has been predicted at the CASPT2 level [131] to be of $^3\Delta$ state with the following spectroscopic constants $R_e = 1.605\text{\AA}$ [131], $\omega_e = 1085\text{cm}^{-1}$ [131], and $\mu_e = 2.38$ Debye [131]. The electronic structure of the RuN molecule has been well characterized experimentally [133-135], and theoretically [136, 137]. The ground state in RuN arises from the full filling of δ orbitals in the molecular electronic configuration $5\sigma^2 2\pi^4 1\delta^4 6\sigma^1$ to give rise to a $^2\Sigma^+$ ground state [133]. The experimental spectroscopic constants determined in the ground state of RuN are respectively; $R_e = 1.574\text{\AA}$ [133], $\omega_e = 1108.32\text{ cm}^{-1}$ [134]. The ground state in the RhN molecule is of $^1\Sigma^+$ symmetry with an experimental bond distance of $R_e = 1.642\text{\AA}$ [138], and a calculated harmonic vibrational frequency of 942 cm^{-1} [132]. The permanent electric dipole moment in the ground states of RuN and RhN has been theoretically predicted to be 2.54 Debye and 2.98 Debye from B3LYP in density functional (DFT) calculations [132]. To the best of our knowledge, for the rest of the transition metal nitrides PdN, AgN, and CdN the experimental and theoretical analysis are limited in literature. Hong *et. al.* [132] used the method of B3LYP in DFT calculations to investigate the ground states of the molecules PdN, AgN, and CdN. Their results [132] predict the ground state in PdN and CdN to be of $^4\Sigma^-$ symmetry [132], while it has been predicted to be of $^3\Sigma^-$ symmetry in AgN [132]. In these calculations The equilibrium internuclear distances, harmonic vibrational frequencies, and permanent electric dipole moments have been predicted in the ground states of PdN [132] to be $R_e = 1.86\text{\AA}$, $\omega_e = 607\text{cm}^{-1}$, $\mu_e = 3.10$ Debye, and in AgN [132] to be $R_e = 2.08\text{\AA}$, $\omega_e = 425\text{cm}^{-1}$, $\mu_e = 3.14$ Debye, and in CdN [132] to be $R_e = 2.51\text{\AA}$, $\omega_e = 161\text{cm}^{-1}$, $\mu_e = 0.908$ Debye. The reported results in literature of the values of R_e , ω_e , μ_e for the molecules NbN, MoN, TcN, RuN, RhN, PdN, AgN, and CdN are shown in Table XXIV.

Table XXIV:

Variation of the values of the equilibrium internuclear distance R_e , harmonic vibrational frequency ω_e , and permanent electric dipole moment μ_e in the ground state of the series of 4d transition metal nitride molecules in the periodic table.

Metal Nitrides	R_e ($\text{\AA}$)	μ_e (Debye)	ω_e (cm^{-1})
YN	1.839 ^a	5.186 ^a	656.51 ^a
ZrN	1.731 ^a	3.190 ^a	982.79 ^a
NbN	1.663 ^b	4.49 ^c	1003 ^b
MoN	1.648 ^d	3.38 ^d	1075 ^d
TcN	1.605 ^c	2.38 ^c	1085 ^c
RuN	1.574 ^f	2.54 ^g	1108.32 ^h
RhN	1.642 ⁱ	2.98 ^g	942 ^g
PdN	1.86 ^g	3.10 ^g	607 ^g
AgN	2.08 ^g	3.14 ^g	425 ^g
CdN	2.51 ^g	0.908 ^g	161 ^g

a. values obtained from the results of the present work, b. Ref [123], c. Ref [127], d. Ref [129], e. Ref [131], f. Ref [133], g. Ref [132], h. Ref [134], i. Ref [138].

The comparisons between the values of the spectroscopic constants R_e , ω_e , and μ_e across the series of 4d transition metal nitrides are shown in Figures 22 - 24.

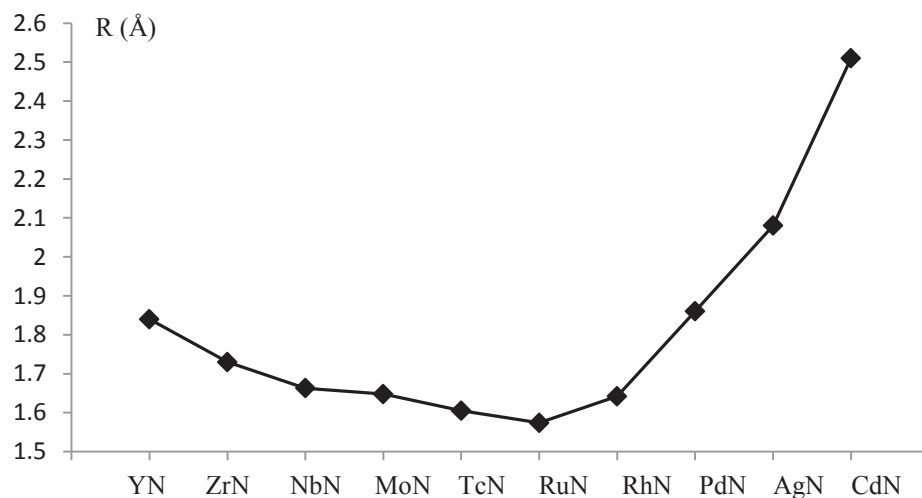


Fig. 22. Variation of the equilibrium internuclear distance in the ground state of 4d transition metal nitrides.

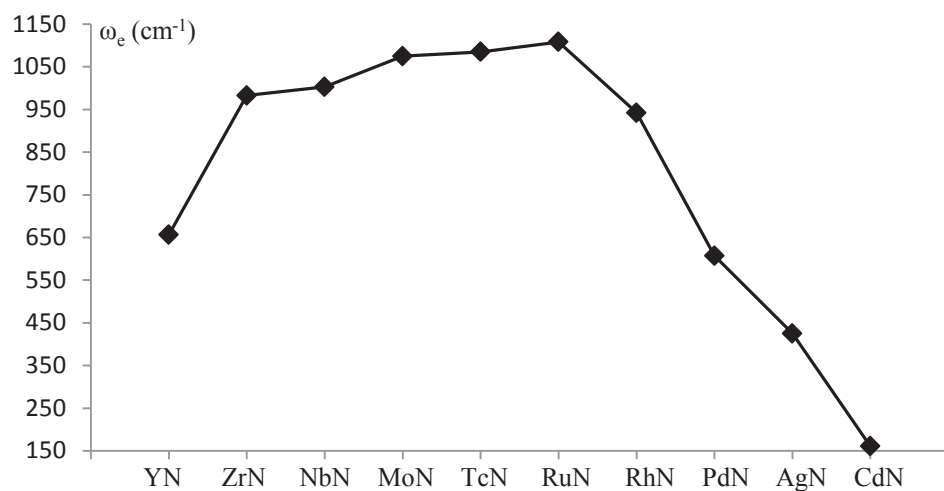


Fig. 23. Variation of the harmonic vibrational frequency ω_e in the ground state of 4d transition metal nitrides.

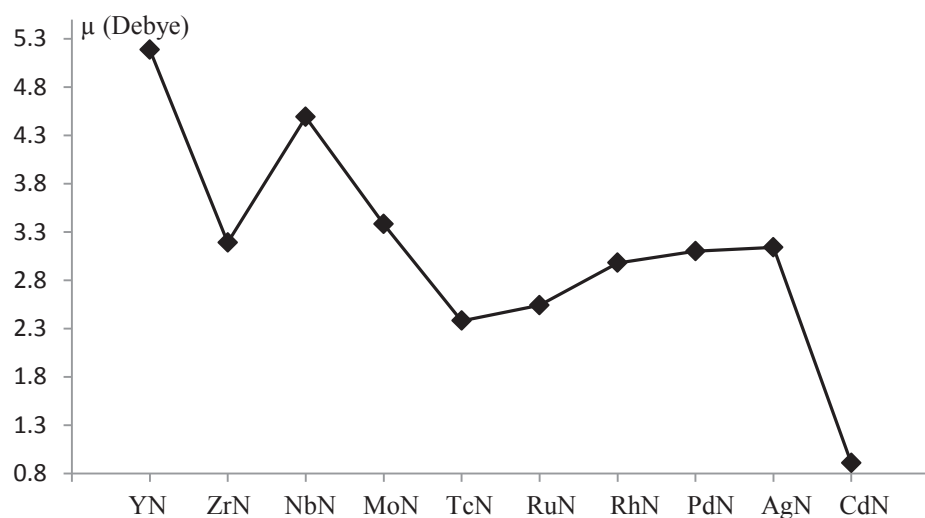


Fig. 24. Variation of the permanent dipole moment μ_e in the ground state of 4d transition metal nitrides.

Across the series of 4d transition metal nitrides from YN to CdN the equilibrium internuclear distance in the ground state (Fig. 22) decreases from 1.84Å in YN to reach a minimum at 1.574Å in RuN and then increases again to reach a value of 2.51Å in CdN. The shortest bond length attained in RuN suggests that the bonding in RuN is the strongest among the other 4d transition metal nitrides. For the harmonic vibrational frequency ω_e in the ground state of each molecule (Fig. 23) it is seen that the value of ω_e increases from 656.5cm⁻¹ in YN to 1108.32cm⁻¹ in RuN, and then decreases to reach 161cm⁻¹ in CdN. The polarity in each of the transition metal nitrides is largely determined by the value of the permanent electric dipole moment in the ground state of each molecule. The permanent electric dipole moment in Fig 24 is highest in YN, with a value of 5.186 Debye. Its variation across the series of 4d transition metals is not continuous. Rather, its value decreases from 5.186 Debye in YN to 3.19 Debye in ZrN and then it abruptly increases to reach a value of 4.49 Debye in NbN, to decrease gradually to a value of 2.38 Debye in TcN. A gradual increase in the dipole moment value is then observed between TcN and AgN. Across the series of 4d transition metals CdN has the lowest dipole moment in its ground electronic state, while the mostly polar bond is that attained in the ground state of YN. The decrease of the dipole moment is an indication for the decrease of the electronegativity difference between the metal and nitrogen atoms, and hence a decrease of ionic character across the series of 4d transition metal nitrides.

III. D. The Structure of Zirconium Sulfide ZrS

III. D. 1. Preliminary Works on ZrS

The electronic structure and the nature of the transition metal-sulfur bond is of importance in such diverse fields as industrial catalysis and biological process [139 - 141]. In Astrophysics the transition metal monosulphides, including ZrS, may be more abundant than their corresponding metal monoxides [142] {TiO [143], LaO [144]} and hydrides FeH [145]. In fact, the ZrS molecule has been reported in cool S-type stars as the carrier of the so-called Keenan bands [146]. The identification of ZrS bands in the spectra of S stars provides an opportunity to determine the abundance of sulfur in late-type stars and may give additional clues to the nuclear processes responsible for their abnormal compositions [147].

Until the work described here, no extensive theoretical study was available on ZrS, except that performed by Langhoff *et. al.* [148] on 6 low-lying excited electronic states, and that of Reddy *et. al.* [149] on the vibrational band structure of the ground electronic state $X^1\Sigma^+$. Experimentally, the first published spectroscopic study of ZrS was done by Simard *et. al* [150] on the $(5)^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition. Jonson and coworkers first studied the $(2)^3\Pi \leftarrow (1)^3\Delta$

transition [151] via microwave-induced emission spectroscopy, and then the $(2)^1\Pi-X^1\Sigma^+$, $(3)^1\Sigma^+-X^1\Sigma^+$, $(5)^1\Sigma^+-X^1\Sigma^+$ transitions [146] via high resolution emission spectroscopy. In astrophysics, the first identification of ZrS bands in stars was done by K. Hinkle [147], who analyzed the spectra obtained between 7400 and 9700 cm^{-1} of three Mira variable type stars M and S. The detected bands provide a rare opportunity to measure the sulfur abundance in the photospheres of late-type stars [147]. Recently, the electronic structures of the states $X^1\Sigma^+$ and $(1)^3\Delta$ in ZrS have received a great attention particularly due to their small energy separation. Experimentally, S. Beaton and M. Gerry [152] performed a cavity Fourier transform microwave spectroscopy on the $X^1\Sigma^+$ and $(1)^3\Delta$ bands for five isotopomers of Zr^{32}S . Theoretically, B. Laing and L. Andrews [153] computed the relative energy separation of the $^1\Sigma^+-^3\Delta$ system via density functional theory, but their results contrasts with the experimental and theoretical results available, as they predict the $^3\Delta$ to be the ground state of ZrS and the relative energy separation of the $^1\Sigma^+-^3\Delta$ system ranged in their calculations between 2937 cm^{-1} (B3LYP-calculations) and 8394 cm^{-1} (MP2-calculations). Recently, X. Sun *et. al.* [154] reinvestigated the ground state of neutral ZrS by the MP2 method in DFT calculations, their most extensive results placed the $X^1\Sigma^+$ state lower than the $(1)^3\Delta$ state by 338.75 cm^{-1} . Then by repeating the calculations with a larger basis set the $(1)^3\Delta$ state was predicted to be 556 cm^{-1} above the ground $X^1\Sigma^+$ state. Finally, and in order to understand the interaction of the ZrS molecule with light, R. Bousquet *et. al.* [155] studied the dipole moment of the ZrS molecule in the ground $X^1\Sigma^+$ and excited $(3)^1\Sigma^+$ states. Their experimentally measured values of the dipole moments are not in good agreement with the theoretical results, and thus a more elaborate theoretical *ab initio* study is required. The apparent disagreement in literature on the nature of the ground state in the ZrS molecule, surely warrants a more elaborate theoretical study for the ground and excited electronic states of this molecule at a high level of theory and with the inclusion of relativistic spin orbit effects.

In general, transition metal monosulfides have been less well characterized than the analogous monoxides. The majority of the work to date on these species has been electronic spectroscopy. However, these molecules often have complicated electronic spectra and thus provide a challenge to *ab initio* calculations. In this paper, we try to fully explore the electronic structure of the ZrS molecule, at the complete active space (CASSCF) method followed by Multi-reference Single and Double Configuration Interactions (MRSDCI) for the lowest lying 22 singlet-triplet states and their spin orbit component states.

III. D. 2. Results on ZrS

In this work, the potential energy curves of 22 low-lying electronic states in the representation $^{2s+1}\Lambda^\pm$ (neglecting spin orbit effects) have been drawn versus the internuclear distance range of 1.6 to 3.0 Å (Figures 25-28). Further sophisticated approaches including spin orbit (SO) effects were then invoked to draw the SO potential energy curves of 44 spin orbit electronic states $\Omega^\pm$ within the internuclear distance range of $1.6 \text{ Å} \leq R \leq 2.9 \text{ Å}$ in Figures 29-33.

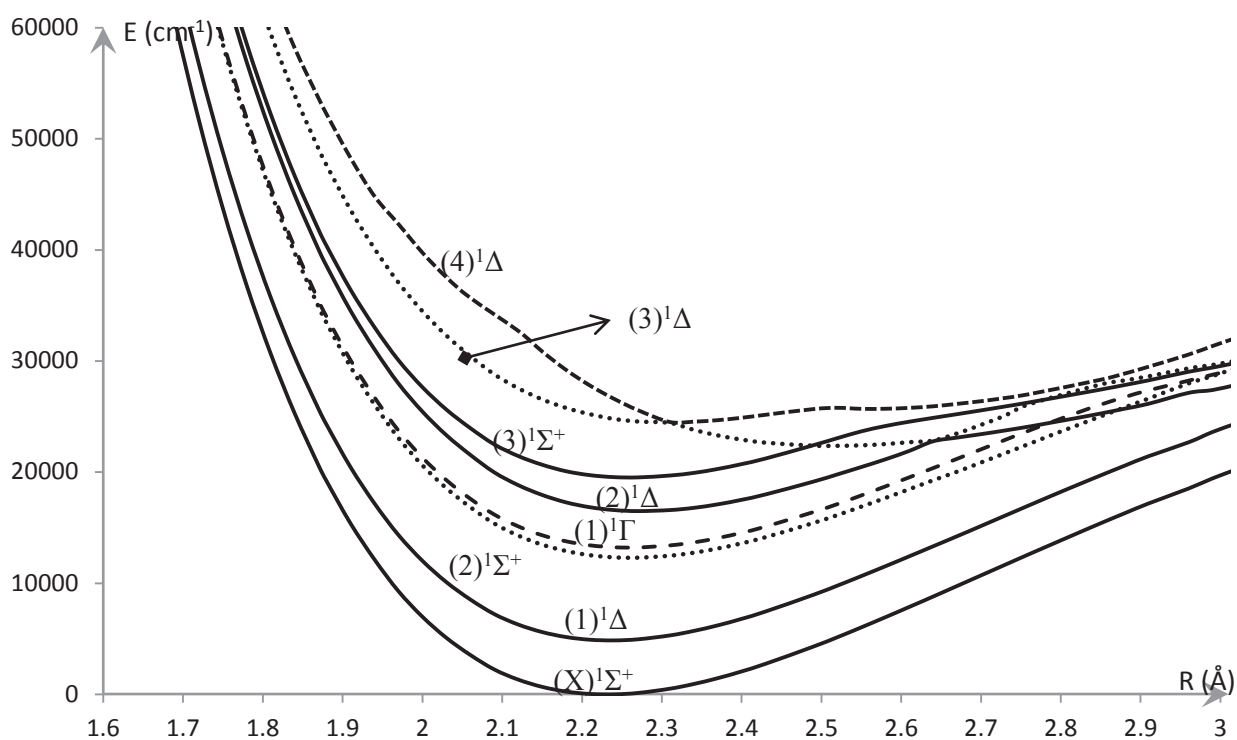


Fig. 25: Potential energy curves for the $^1\Sigma^\pm$ and $^1\Delta$ states of the molecule ZrS.

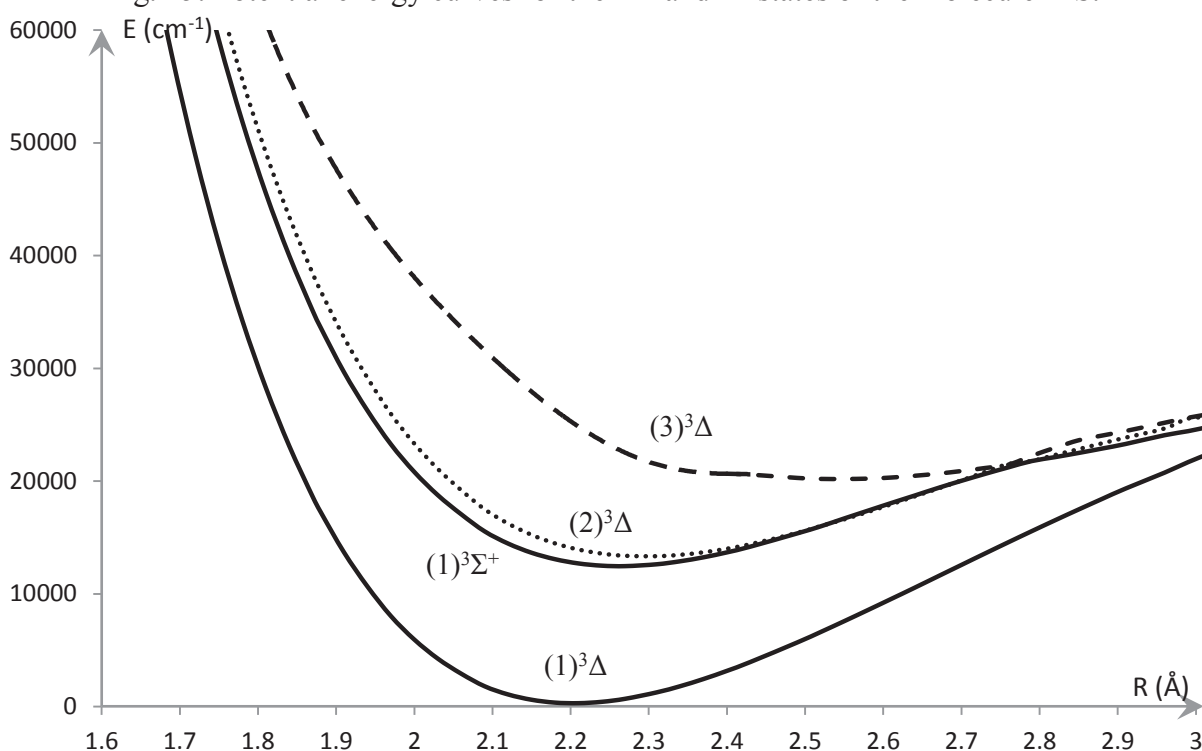


Fig. 26: Potential energy curves for the $^3\Sigma^\pm$ and $^3\Delta$ states of the molecule ZrS.

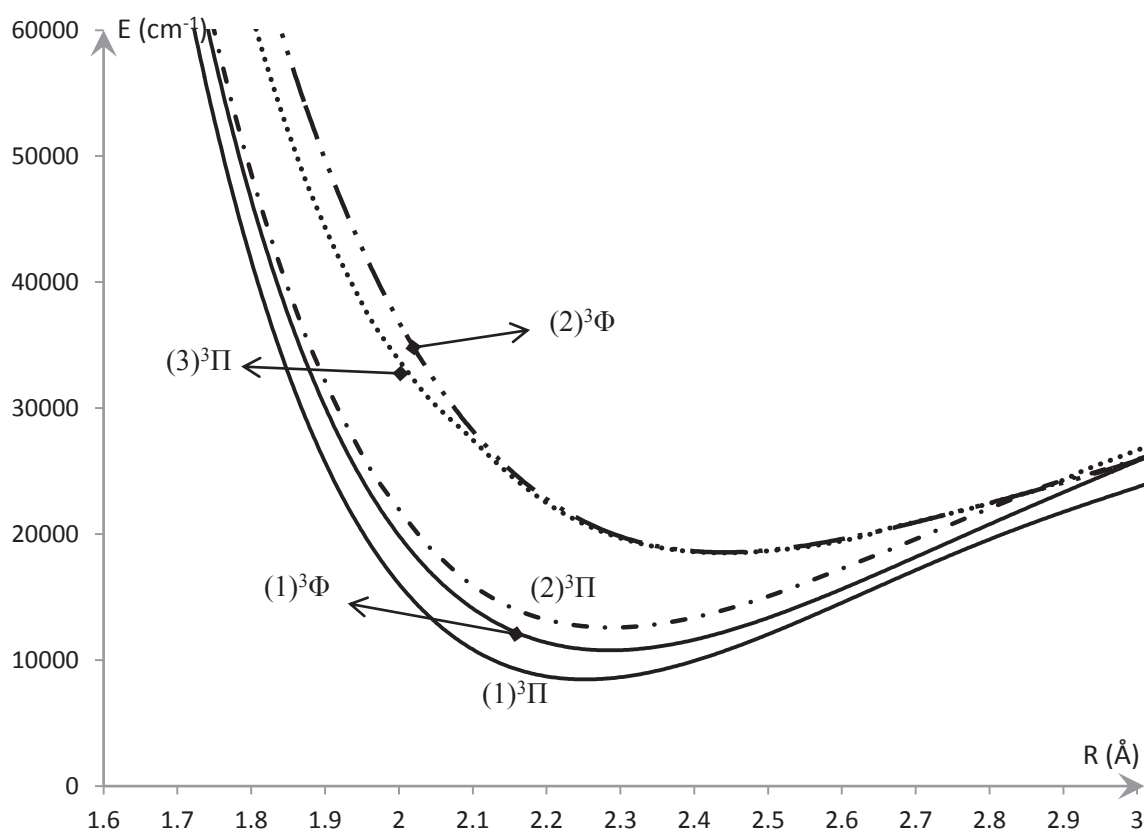


Fig. 27: Potential energy curves for the $^3\Pi$ and $^3\Phi$ states of the molecule ZrS.

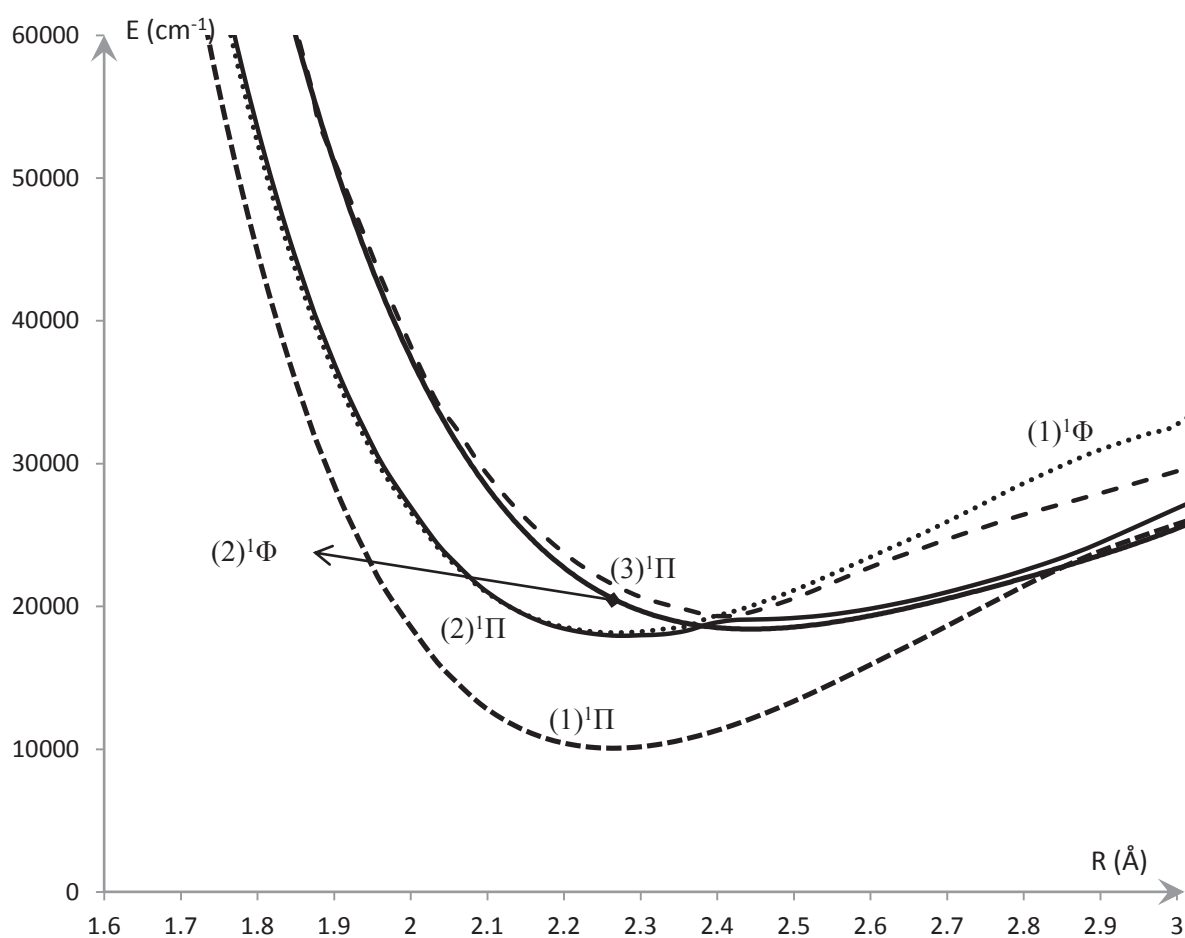


Fig. 28: Potential energy curves for the $^1\Pi$ and $^1\Phi$ states of the molecule ZrS.

The spectroscopic constants T_e , ω_e , R_e , B_e , and D_e were then calculated for the lowest lying singlet and triplet electronic states of ZrS. These values are shown in Table XXV along with the theoretical and experimental values available in literature.

Table XXV: Equilibrium internuclear distances R_e , transition energies T_e , rotational constants B_e , centrifugal distortion constant D_e , and harmonic frequencies ω_e for the $^{2s+1}\Lambda^\pm$ states of the molecule ZrS.

State	$T_e(\text{cm}^{-1})$	$\delta T_e/T_e$	$\omega_e(\text{cm}^{-1})$	$\delta\omega_e/\omega_e$	$B_e \times 10^{-1}(\text{cm}^{-1})$	$\delta B_e/B_e$	$D_e \times 10^8(\text{cm}^{-1})$	$\delta D_e/D_e$	$R_e(\text{\AA})$	$\delta R_e/R_e$
(X) $^1\Sigma^+$	0.0 ^a		532.44 ^a		1.464 ^a		4.429 ^a		2.203 ^a	
			560 ^{MRCI b}	4.9%					2.182 ^{MRCI b}	0.9%
			548.34 ^{Exp c}	2.8%	1.537 ^{Exp c}	4.7%	4.880 ^{Exp c}	9.2%	2.1566 ^{Exp c}	2.1%
			530 ^{B3LYP d}	0.4%			5.19 ^{B3LYP d}	14.6%	2.208 ^{B3LYP d}	0.2%
			597 ^{MP2 d}	10.8%			5.33 ^{MP2 d}	16.9%	2.147 ^{MP2 d}	2.6%
			548.4 ^{Exp i}	2.9%					2.156 ^{Exp g}	2.1%
			565.7 ^{B3LYP h}	5.8%					2.173 ^{B3LYP h}	1.4%
			558.3 ^{BPW91 h}	4.6%					2.175 ^{BPW91 h}	1.3%
			548.5 ^{MP2 h}	2.9%					2.167 ^{MP2 h}	1.6%
(1) $^1\Delta$	4861.87		496.78		1.421		4.661		2.236	
	5520 ^{MRCI b}	12%	516 ^{MRCI b}	3.7%					2.22 ^{MRCI b}	0.7%
(2) $^1\Sigma^+$	12312.78		462.02		1.389		5.041		2.261	
	13664.49 ^{Exp c}	9.8%	554.73 ^{Exp c}	16.7%	1.4482 ^{Exp c*}	4.1%	4.9526 ^{Exp c*}	1.8%	2.222 ^{Exp j}	1.7%
(1) $^1\Gamma$	13236.19		444.30		1.391		5.501		2.259	
(2) $^1\Delta$	16502.96		453.87		1.373		5.036		2.275	
(3) $^1\Sigma^+$	19526.77		456.08		1.390		5.175		2.261	
	20242.90 ^{Exp c}	3.5%	488.61 ^{Exp c}	6.6%	1.4625 ^{Exp c}	4.9%	5.106 ^{Exp c}	1.3%	2.211 ^{Exp c}	2.2%
	20218.90 ^{Exp i*}	3.6%	491.8 ^{Exp i}	7.3%						
(3) $^1\Delta$	24490.67		408.86		1.334		5.696		2.308	
(4) $^1\Delta$	22328.25		454.69		1.091		2.671		2.552	
(1) $^1\Pi$	10091.62		472.92		1.388		4.786		2.263	
	11076 ^{MRCI b}	8.8%	491 ^{MRCI b}	3.6%					2.25 ^{MRCI b}	0.5%
	10836.21 ^{Exp c}	6.8%	495.9 ^{Exp c}	4.6%	1.4509 ^{Exp c}	4.3%	5.0163 ^{Exp c}	4.5%	2.219 ^{Exp c}	1.9%
	10866 ^{Exp e}	6.8%	489 ^{Exp e}	3.4%						
	10836.7 ^{Exp e}	6.8%								
(1) $^1\Phi$	18154.98		464.17		1.382		4.902		2.268	
(2) $^1\Pi$	17917.22		471.35		1.367		4.609		2.279	
(2) $^1\Phi$	18461.39		351.70		1.195		4.963		2.441	
(3) $^1\Pi$	19061.41		424.07		1.175		3.623		2.458	
(1) $^3\Delta$	302.65		504.23		1.428		4.587		2.231	
	209 ^{MRCI b}	45%	522 ^{MRCI b}	3.4%					2.216 ^{MRCI b}	0.7%
	193.57 ^{MP2 d}	56%	557 ^{Exp e}	9.4%			4.7821 ^{Exp f}			
	338.75 ^{MP2 d}	10.6%	527.24 ^{Exp f}	4.4%	1.49328 ^{Exp f}	4.4%		4.0%	2.1878 ^{Exp f}	1.9%
	556.52 ^{MP2 d}	45.6%								
	2937.94 ^{B3LYP h}	89.7%	529.4 ^{B3LYP h}	4.7%					2.214 ^{B3LYP h}	0.7%
	4336.96 ^{BPW91 h}	93%	523.2 ^{BPW91 h}	3.6%					2.212 ^{BPW91 h}	0.8%
	8394.12 ^{MP2 h}	96.4%	548.5 ^{MP2 h}	8.1%					2.209 ^{MP2 h}	1.0%
(1) $^3\Sigma^+$	12464.55		470.49		1.389		4.846		2.262	
(2) $^3\Delta$	13345.50		439.39		1.351		5.102		2.293	
	15034.85 ^{Exp L}	11.2%	471.05 ^{Exp L}	6.7%	1.41326 ^{Exp L}	4.4%	5.09585 ^{Exp L}	0.1%	2.2489 ^{Exp L}	1.9%
(1) $^3\Pi$	8469.94		484.05		1.405		4.733		2.249	
	7890 ^{MRCI b}	7.3%	517 ^{MRCI b}	6.3%					2.23 ^{MRCI b}	0.8%
	8008 ^{Exp e}	5.7%	506 ^{Exp e}	4.3%						
	8024.2726 ^{Exp f}	5.5%	502.6466 ^{Exp f}	3.7%	1.46851 ^{Exp f}	4.3%	5.0125 ^{Exp f}	5.6%	2.20619 ^{Exp f}	1.9%
(1) $^3\Phi$	10787.88		455.13		1.365		4.909		2.282	
	11710 ^{MRCI b}	7.8%	436 ^{MRCI b}	4.3%					2.27 ^{MRCI b}	0.5%
	11730 ^{Exp e}	8.0%								
	11608 ^{Exp f}	7.0%			1.42067 ^{Exp L}					
	11601.79 ^{Exp L}	7.0%	472.95 ^{Exp L}	3.7%		3.9%	5.1166 ^{Exp L}	4.1%	2.243 ^{Exp L}	1.7%
(2) $^3\Pi$	12589.70		464.04		1.364		4.695		2.283	
	13324.38 ^{Exp L}	5.5%	473.245 ^{Exp L}	1.9%	1.4217 ^{Exp L}	4.0%	5.1490 ^{Exp L}	8.8%		
(3) $^3\Pi$	18511.91		369.31		1.185		4.862		2.448	

(2) ³ Φ	18688.74	363.36	1.205	5.039	2.429
(3) ³ Δ	20196.34	733.27	1.095	4.639	2.548
a. Results of the present work	b. Ref [148]	c. Ref [146]	d. Ref [154]	e. Ref [147]	
f. Ref [156]	g. Ref [152]	h. Ref [153]	i. Ref [150]	j. Ref [155]	
k. Ref [157]	L. Ref [158]				

Note:

Exp corresponds to experimental results, while theoretical results are represented by the methods used (MRCI, MP2, B3LYP, and BPW91).

c *: The values of B_v and D_v are reported in Ref [146] for the $v = 0$ vibrational level of the $(2)^1\Sigma^+$ state.

i *: The value of T_e reported in Ref [150] is that of the $v = 0$ vibrational level of the state $(3)^1\Sigma^+$.

The comparison between our values for the spectroscopic constants in neutral ZrS to the experimental values available in literature [146, 147, 150, 156, 158] shows a very good agreement with percentage relative differences of 3.5% (Ref[146]) $\leq \delta T_e/T_e \leq 11.2\%$ (Ref[158]), 1.9% (Ref[158]) $\leq \delta \omega_e/\omega_e \leq 9.4\%$ (Ref[147]), 1.7% (Ref[155, 158]) $\leq \delta R_e/R_e \leq 2.2\%$ (Ref[146]), and 0.1% (Ref[158]) $\leq \delta D_e/D_e \leq 9.2\%$ (Ref[146]) for the states $(X)^1\Sigma^+$, $(2)^1\Sigma^+$, $(3)^1\Sigma^+$, $(1)^1\Pi$, $(2)^3\Delta$, $(1)^3\Pi$, $(1)^3\Phi$, and $(2)^3\Pi$. The comparison between our theoretical results at the MRSDCI+Q level of calculations to the results obtained by Langhoff *et. al.* [148] at the MRCI level of calculations for the states $(X)^1\Sigma^+$, $(1)^1\Delta$, $(1)^3\Delta$, $(1)^1\Pi$, $(1)^3\Pi$, $(1)^3\Phi$ shows a very good agreement, with percentage relative differences of $7.3\% \leq \delta T_e/T_e \leq 12\%$, $3.4\% \leq \delta \omega_e/\omega_e \leq 4.9\%$, and $0.5\% \leq \delta R_e/R_e \leq 0.9\%$. Our *ab initio* results place the first excited $(1)^3\Delta$ state at a transition energy of $T_e = 302 \text{ cm}^{-1}$, which is only 100 cm^{-1} from the theoretical values reported in Ref [148, 154]. In spite of that the percentage relative difference calculated for the T_e value in the $(1)^3\Delta$ state is large and ranges between 10.6% (Ref[154]) $\leq \delta T_e/T_e \leq 56\%$ (Ref[154]), still our ability in the present calculations to reproduce the T_e value in the $(1)^3\Delta$ state within a 100 cm^{-1} is considered accurate, especially if we know that the energy value reported by Langhoff *et. al* [148] for the $(1)^3\Delta$ state ranged between 200 cm^{-1} and $200+500 \text{ cm}^{-1}$, with a large uncertainty. In particular, electronic states lying within the vibrational continuum of the ground state are hard to represent experimentally and theoretically since the eigenfunctions of both states might overlap in regions near to the equilibrium internuclear distance. Further enhancements for the energy positions of the $(1)^3\Delta$ state are left for our more extensive relativistic *ab initio* calculations with the inclusion of spin orbit effects. The DFT theoretical calculations performed by employing B3LYP, MP2, and BPW91 methods in Ref [153] agree with our calculated values of ω_e and R_e for the states $X^1\Sigma^+$ and $(1)^3\Delta$ with percentage relative differences of $2.9\% \leq \delta \omega_e/\omega_e \leq 8.1\%$ and $0.7\% \leq \delta R_e/R_e \leq 1.6\%$. However, a less agreement exists for the T_e values of the $X^1\Sigma^+$ and $(1)^3\Delta$ states [153]. This is mainly due to an inaccuracy in Liang *et. al.* [153] representation of the ground electronic state in ZrS which has been predicted to be a $^3\Delta$ state and at thousands of

cm^{-1} below the $^1\Sigma^+$ state. This contrasts all of the experimental and theoretical results available on ZrS in literature [146-148, 150, 154, 156, 158].

With the inclusion of relativistic spin orbit effects, great enhancements might be obtained for the potential energy curves and the spectroscopic constants. In the present work the electronic structures of the ZrS molecule have been reinvestigated with the inclusion of relativistic spin orbit effects. The spin orbit effects were then introduced for Zirconium and neglected for Sulfur via a semi-empirical spin orbit pseudopotential W_{SO}^{PS} that was designed from Effective Core Potentials (ECP) for spin orbit calculations [18]. Energy MRSDCI+Q calculations were performed piecewise at equal steps of $0.03\text{\AA}$ as a function of the internuclear distance range $1.6\text{\AA} \rightarrow 2.9\text{\AA}$. This allows for the construction of potential energy curves for the spin orbit electronic states $\Omega = 0^+, 0^-, 1, 2, 3, 4$ in Figures 29 – 33. Then by fitting the obtained potential energy curves around the equilibrium internuclear distance into a polynomial in R several spectroscopic constants were calculated such as the electronic transition energies at equilibrium T_e , the harmonic vibrational frequencies ω_e , the rotational constants B_e , the centrifugal distortion constants D_e , and the equilibrium internuclear distances R_e . These results for the spectroscopic constants of the spin orbit states Ω are reported in Table XXVI together with the experimental and theoretical results available in literature.

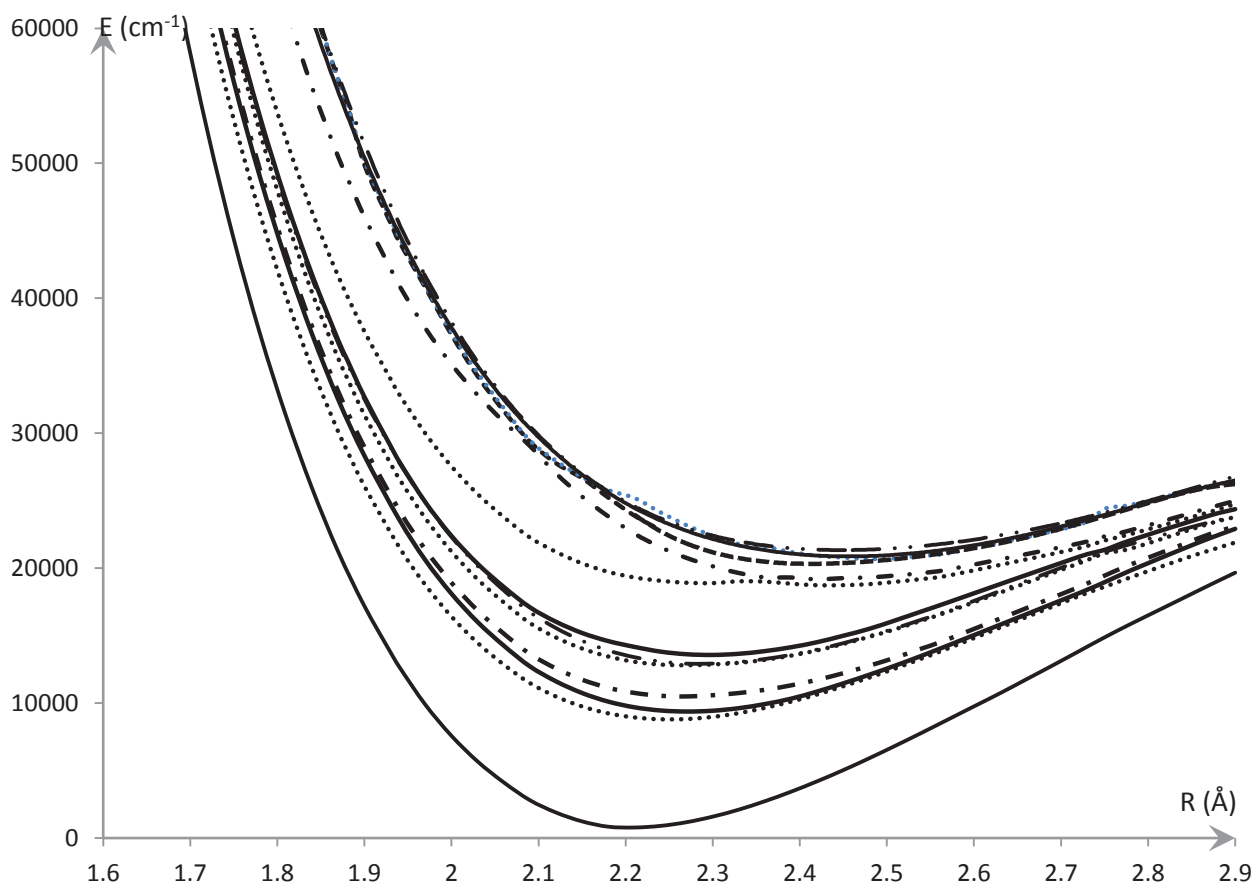


Fig. 29. Potential energy curves for 12 ($\Omega = 1$) states of the molecule ZrS [Full and dotted lines].

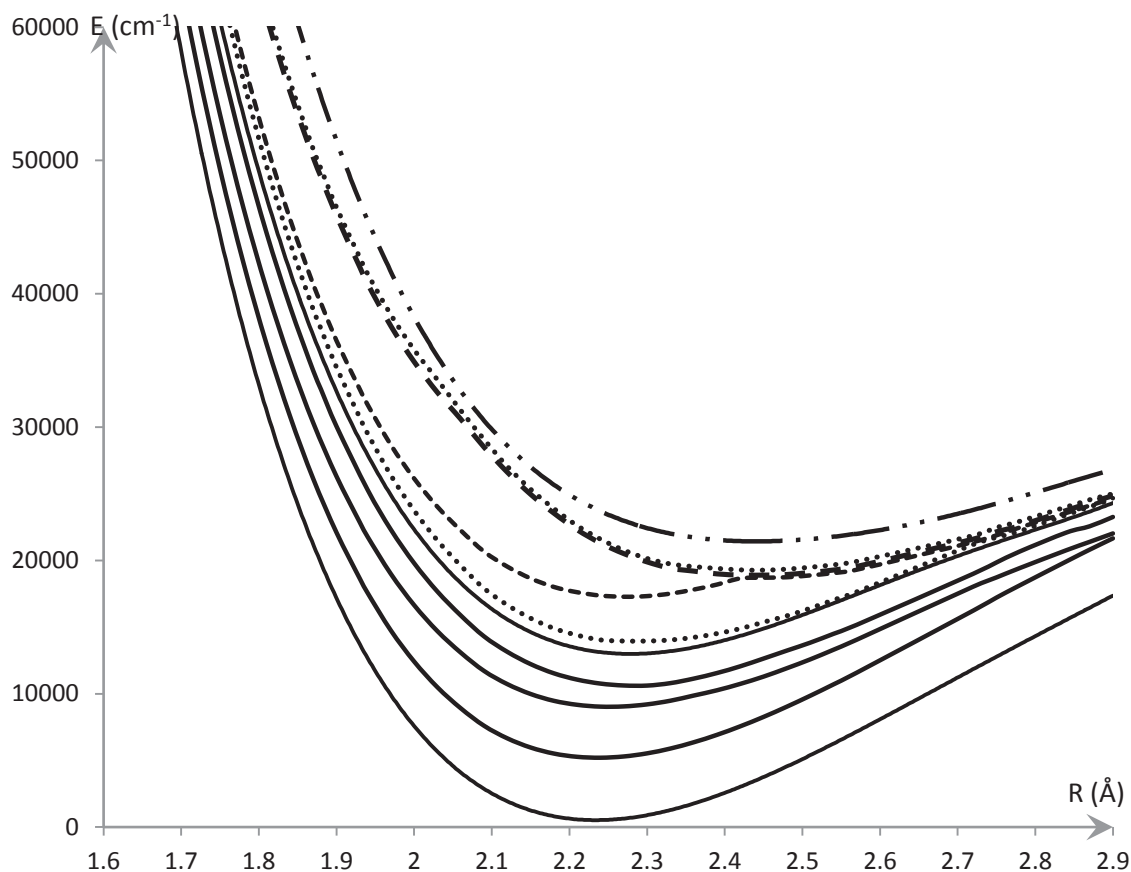


Fig. 30. Potential energy curves for 10 ($\Omega = 2$) states of the molecule ZrS [Full and dotted lines].

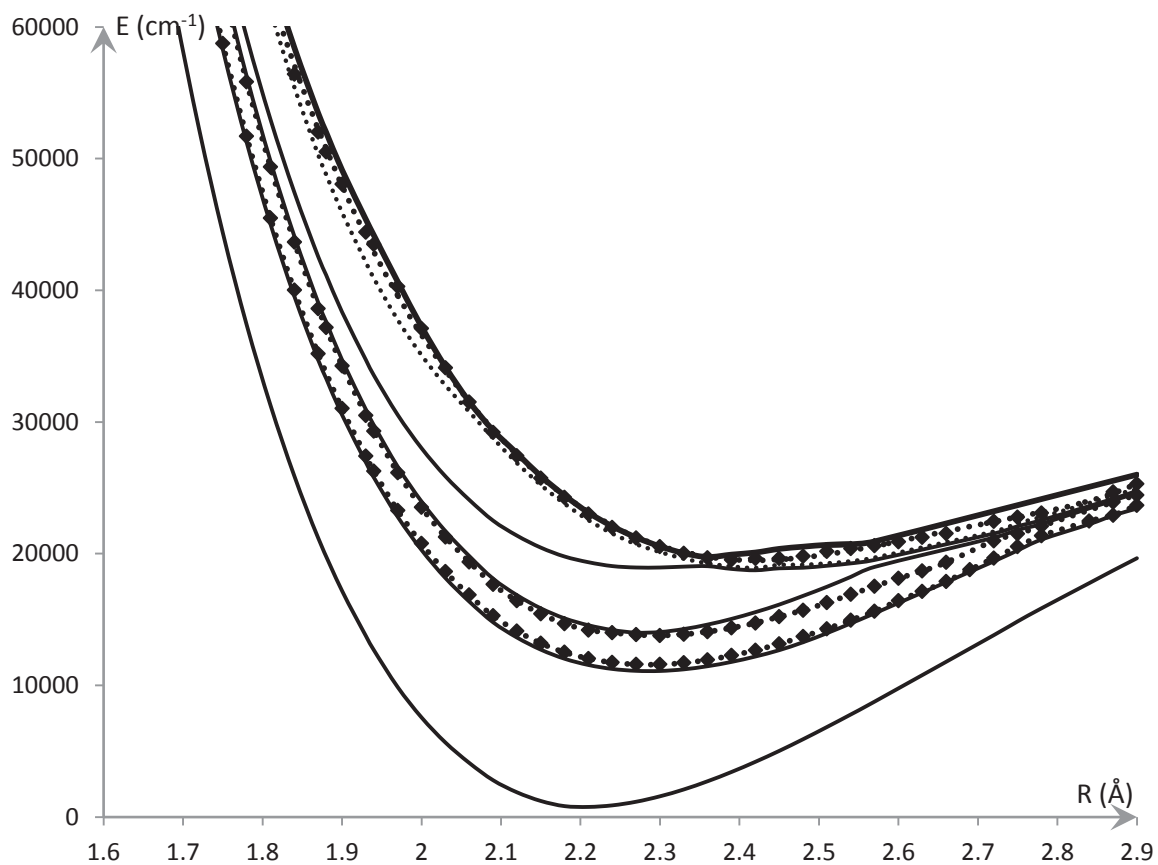


Fig. 31. Potential energy curves for 6 ($\Omega = 3$) [Full and dotted lines] and 3 ($\Omega = 4$) [◆] states of the molecule ZrS.

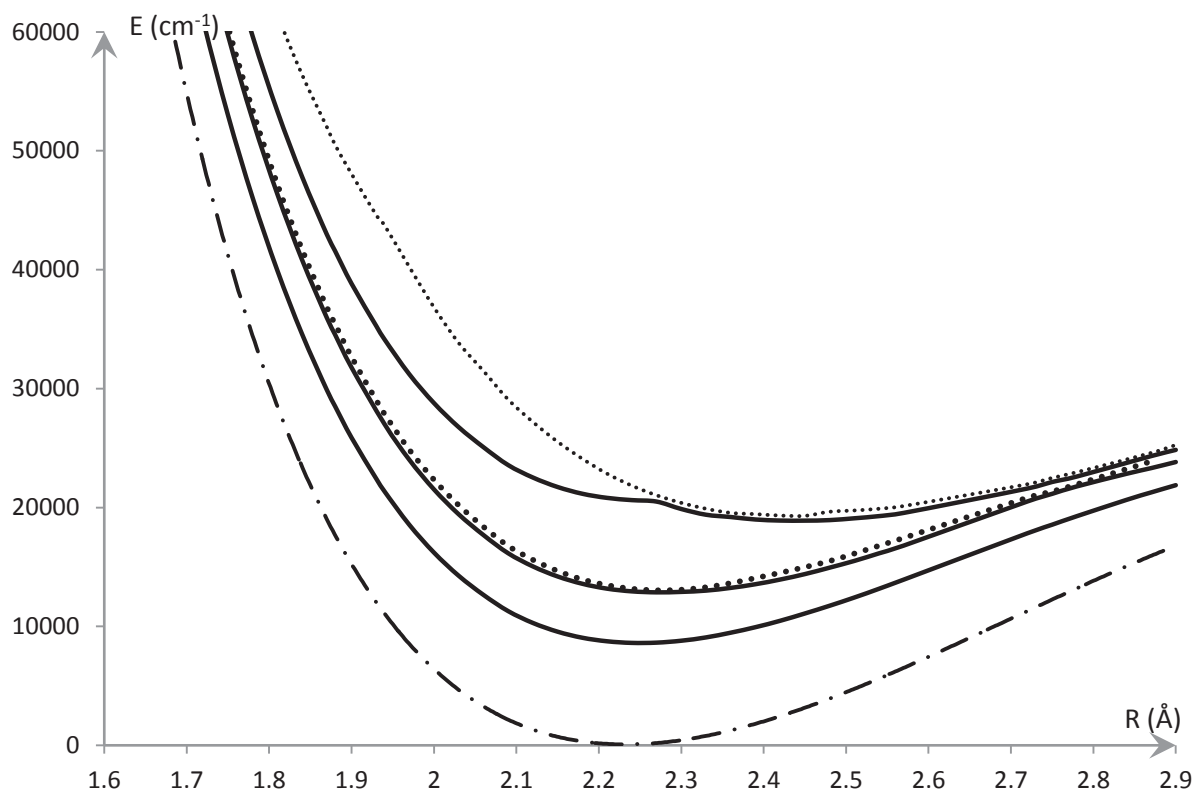


Fig. 32. Potential energy curves for $6 (\Omega = 0^+)$ [Full and dotted lines] states of the molecule ZrS .

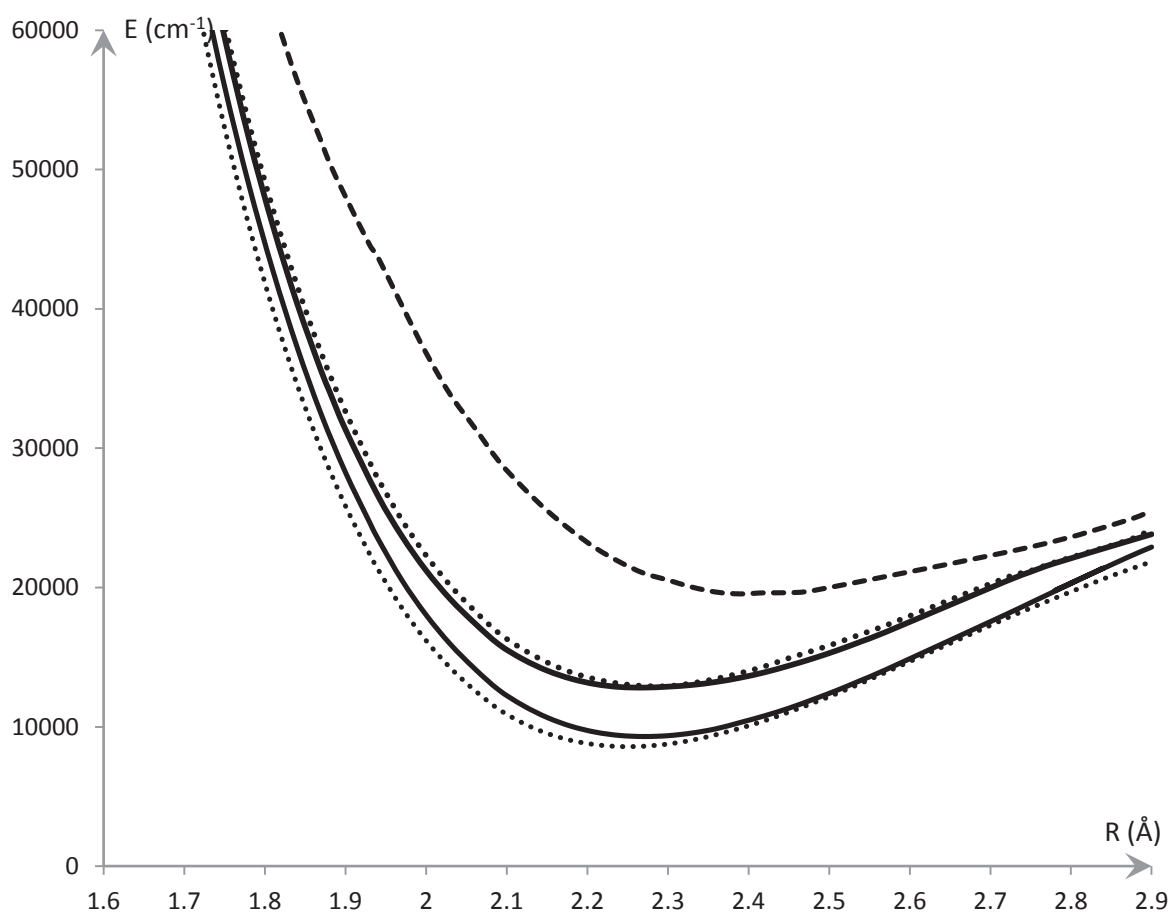


Fig. 33. Potential energy curves for $5 (\Omega = 0^-)$ [Full and dotted lines] states of the molecule ZrS .

TABLE XXVI:

Equilibrium internuclear distances R_e , transition energies T_e , rotational constants B_e , centrifugal distortion constants D_e , and harmonic frequencies ω_e , for Ω states of the molecule ZrS.

$(n)\Omega[(k)^{2S+1}\Lambda]$	T_e (cm ⁻¹)	δT_e / T_e	ω_e (cm ⁻¹)	$\delta\omega_e$ / ω_e	R_e (Å)	δR_e / R_e	$B_e \times 10^1$ (cm ⁻¹)	δB_e / B_e	$D_e \times 10^7$ (cm ⁻¹)	δD_e / D_e
(1) $0^+ [X^1\Sigma^+]$	0.0 ^a		534.01 ^a 560 ^{MRCI b} 548.34 ^{Exp c} 530 ^{B3LYP d} 597 ^{MP2 d} 548.4 ^{Exp i} 565.7 ^{B3LYP h} 558.3 ^{BPW91 h} 548.5 ^{MP2 h}		2.234 ^a 2.182 ^{MRCI b} 2.1566 ^{Exp c} 2.208 ^{B3LYP d} 2.147 ^{MP2 d} 2.156 ^{Exp g} 2.173 ^{B3LYP h} 2.175 ^{BPW91 h} 2.167 ^{MP2 h}		1.423 ^a		4.442 ^a	
(2) $0^+ [(1)^3\Pi]$	8628.96		484.16		2.247		1.407		4.748	
(3) $0^+ [(2)^1\Sigma^+]$	12889.82 13664.49 ^{Exp c}		415.29 554.73 ^{Exp c}		2.275		1.373 1.4451 ^{Exp c*}		5.199 4.9766 ^{Exp c*}	
(4) $0^+ [(2)^3\Pi]$	13078.69		491.45		2.276		1.371		4.284	
(5) $0^+ [(3)^1\Sigma^+]$	18890.20 20242.90 ^{Exp c} 20256.22 ^{Exp i*}		384.45 488.61 ^{Exp c} 491.8 ^{Exp i}		2.434 2.211 ^{Exp c}		1.199 1.4625 ^{Exp c}		4.644 5.106 ^{Exp c}	
(6) $0^+ [(3)^3\Pi]$	19374.87		424.23		2.412		1.222		4.074	
(1) $0^- [(1)^3\Pi]$	8608.96		478.15		2.249		1.404		4.851	
(2) $0^- [(1)^3\Sigma^-]$	9314.32		488.89		2.269		1.379		4.393	
(3) $0^- [(1)^3\Sigma^+]$	12831.67		425.07		2.269		1.380		5.808	
(4) $0^- [(2)^3\Pi]$	12969.35		499.20		2.275		1.373		4.152	
(5) $0^- [(3)^3\Pi]$	19578.32		463.82		2.401		1.232		3.500	
(1) $1 [(1)^3\Delta]$	772.77		523.54 527.0854 ^{Exp L}		2.215		1.445 1.49151 ^{Exp L}		4.515 4.767 ^{Exp L}	
(2) $1 [(1)^3\Pi]$	8817.85		666.34	0.6%	2.249		1.404	3.1%	4.956	5.3%
(3) $1 [(1)^3\Sigma^-]$	9403.49		459.60		2.269		1.381		4.981	
(4) $1 [(1)^1\Pi]$	10493.76 11076 ^{MRCI b} 10836.21 ^{Exp c} 10866 ^{Exp e} 10836.7 ^{Exp e}		456.65 491 ^{MRCI b} 495.9 ^{Exp c} 489 ^{Exp e}		2.268 2.25 ^{MRCI b} 2.219 ^{Exp c}		1.381 0.8% 2.2%		5.051 5.0163 ^{Exp c}	
(5) $1 [(1)^3\Sigma^+]$	12811.18		425.79		2.270		1.379		5.776	
(6) $1 [(2)^3\Pi]$	12922.49		461.77		2.286		1.359		4.716	
(7) $1 [(2)^3\Delta]$	13562.56 15043.232 ^{Exp L}		467.64 470.9596 ^{Exp L}		2.302		1.340 1.41111 ^{Exp L}		4.395 5.078 ^{Exp L}	
(8) $1 [(2)^1\Pi]$	18843.55		176.47	0.7%	2.415		1.203	5.0%	1.061	13.4%
(9) $1 [(3)^3\Pi]$	19222.71		341.49		2.419		1.214		6.052	
(10) $1 [(3)^1\Pi]$	20338.98		462.72		2.385		1.248		3.775	
(11) $1 [(3)^3\Delta]$	20759.05		515.63		2.489		1.147		2.329	
(12) $1 [(4)^3\Pi]$	20951.89		495.97		2.442		1.191		2.752	
(1) $2 [(1)^3\Delta]$	283.21		502.96 527.222 ^L		2.229		1.429 1.49329 ^{Exp L}		4.607 4.775 ^{Exp L}	
(2) $2 [(1)^1\Delta]$	5218.67 5520 ^{MRCI b}		510.55 516 ^{MRCI b}	4.6% 3.7%	2.236 2.22 ^{MRCI b}		1.421 0.7%	4.3%	4.404	3.5%
(3) $2 [(1)^3\Pi]$	9060.69		469.09		2.248		1.405		5.044	
(4) $2 [(1)^3\Phi]$	10635.01 11357.061 ^{Exp L}		492.99 474.1487 ^{Exp L}		2.276		1.371 1.41948 ^{Exp L}		4.248 5.088 ^{Exp L}	
(3) $2 [(2)^3\Pi]$	12989.29		491.70	4.0%	2.276		1.371	3.4%	4.265	16.5%
(6) $2 [(2)^3\Delta]$	13896.30 15049.4155 ^{Exp L}		471.12 471.0809 ^{Exp L}		2.291		1.354 1.41352 ^{Exp L}		4.470 5.089 ^{Exp L}	
				0.0%				4.2%		12.1%

(7) 2 [(2) ¹ Δ]	17286.69	507.35	2.263	1.387	4.165		
(8) 2 [(3) ³ Π]	18916.91	359.07	2.425	1.209	5.366		
(9) 2 [(2) ³ Φ]	19309.98	356.18	2.417	1.216	5.615		
(10) 2 [(3) ³ Δ]	20742.65	363.03	2.503	1.133	4.224		
(1) 3 [(1) ³ Δ]	569.48	498.32	2.231	1.428	4.696		
		527.3170 ^{Exp L}	5.5%	1.49512 ^{Exp L}	4.5%	4.845 ^{Exp L}	3.1%
(2) 3[(1) ³ Φ]	11100.28	457.36	2.288	1.357	4.779		
	11634.9365 ^{Exp L}	473.8174 ^{Exp L}	3.5%	1.42001 ^{Exp L}	4.4%	5.087 ^{Exp L}	6.0%
(3) 3 [(2) ³ Δ]	14048.14	532.84	2.278	1.368	3.610		
	15012.1296 ^{Exp L}	471.1004 ^{Exp L}	13.1%	1.41521 ^{Exp L}	3.3%	5.154 ^{Exp L}	30.0%
(4) 3 [(1) ¹ Φ]	18882.96	257.74	2.436	1.203	1.472		
(5) 3 [(2) ³ Φ]	19054.61	376.39	2.415	1.218	5.079		
(6) 3 [(2) ¹ Φ]	20002.13	471.95	2.372	1.262	3.645		
(1) 4 [(1) ³ Φ]	11568.46	473.04	2.290	1.354	4.439		
	11812.3539 ^{Exp L}	471.3077 ^{Exp L}	0.4%	1.42259 ^{Exp L}	4.8%	5.184 ^L	14.4%
(2) 4 [(1) ¹ Γ]	13747.29	472.17	2.294	1.349	4.408		
(3) 4 [(2) ³ Φ]	19588.40	432.30	2.416	1.216	3.857		
a. Results of the present work	b. Ref [148]	c. Ref [146]	d. Ref [154]	e. Ref [147]			
f. Ref [156]	g. Ref [152]	h. Ref [153]	i. Ref [150]	j. Ref [155]			
k. Ref [157]	L. Ref [158]						

Note: Exp corresponds to experimental results, while theoretical results are represented by the methods used (MRCI, MP2, B3LYP, and BPW91).

c *: The values of B_v and D_v are reported in Ref [146] for the $v = 0$ vibrational level of the $(2)^1\Sigma^+$ state.

i*: The value of T_e reported in Ref [150] is that of the $v = 0$ vibrational level of the state $(3)^1\Sigma^+$.

Our spin orbit results for the spectroscopic constants of the ZrS molecule further confirm the accuracy of our nonrelativistic spin orbit calculations. Indeed the comparison between the values of the spectroscopic constants T_e , ω_e , R_e , B_e , and D_e of the present work for the states (1) $0^+ [X^1\Sigma^+]$, (2) 2 [(1)¹Δ], (4) 1[(1)¹Π], (3) $0^+ [(2)^1\Sigma^+]$, (5) $0^+ [(3)^1\Sigma^+]$ to the experimental and theoretical results available in literature shows a very good agreement with a percentage relative difference of $3.2\% (\text{Ref}[147]) \leq \delta T_e/T_e \leq 6.7\% (\text{Ref}[146, 150])$, $0.7\% (\text{Ref}[154]) \leq \delta \omega_e/\omega_e \leq 10.5\% (\text{Ref}[154])$, $0.7\% (\text{Ref}[148]) \leq \delta R_e/R_e \leq 10\% (\text{Ref}[146])$, $4.8\% (\text{Ref}[146]) \leq \delta B_e/B_e \leq 7.4\% (\text{Ref}[146])$, and $0.7\% (\text{Ref}[146]) \leq \delta D_e/D_e \leq 9\% (\text{Ref}[146])$, except for the values of ω_e for the states (3) $0^+ [(2)^1\Sigma^+]$, (5) $0^+ [(3)^1\Sigma^+]$ in which a relative difference of $21.3\% (\text{Ref}[146]) \leq \delta \omega_e/\omega_e \leq 25\% (\text{Ref}[146])$, was obtained. The other D_e value for the ground state (1) $0^+ [X^1\Sigma^+]$ obtained in our MRSDCI calculations doesn't agree with the theoretical value reported in Ref [154] and obtained by MP2 and B3LYP methods in DFT calculations with a percentage relative difference of $14.4\% \leq \delta D_e/D_e \leq 14.8\%$, but it agrees with the experimental result reported in Ref [146]. The agreement is also very good by comparing our results for the spin orbit components $\Omega = 1, 2, 3, 4$ of the states $(1)^3\Delta$, $(2)^3\Delta$, and $(1)^3\Phi$ to the experimental results reported in Ref [158] with percentage relative differences of $2.1\% \leq \delta T_e/T_e \leq 9.8\%$, $0.0\% \leq \delta \omega_e/\omega_e \leq 13\%$, $3.1\% \leq \delta B_e/B_e \leq 5\%$, and $3.1\% \leq \delta D_e/D_e \leq 16.5\%$. However, a less agreement exists between our values of D_e to those reported in Ref [158] for the state (3)3[(2)³Δ] with a relative error of $\delta D_e/D_e = 30\%$.

A close look at molecular electronic spectra reveals that electronic spin multiplet states are not properly degenerate. Actually, the sublevels are separated energetically by what is called the fine structure splitting. It is often useful to draw an energy diagram representing the splitting between the parent electronic states along with their spin orbit daughter states. In Table III of Appendix I we draw the energy order of the spin orbit electronic states and their parent states. These diagrams show that splittings as small as 78.6cm^{-1} occur between the spin orbit component states of the $(2)^3\Sigma^+$ state in ZrS, and as large as 933cm^{-1} occur between the spin orbit components of the state $(1)^3\Phi$. In Table XXVII the composition in percentage of the Ω state-wave functions in terms of the Λ states, calculated at $R = 2.23 \text{ \AA}$, are presented. For each state Ω there is a predominant component Λ with a contribution larger than 80% so that a main parent SA may be identified. Nevertheless, there are states for which a small but significant contribution of other Λ states is obtained.

Table XXVII:
Composition of Ω -state wave functions of the molecule ZrS, in terms of Λ -states (in percentage) at $R = 2.23 \text{ \AA}$.

Ω	% (Λ -parent)	Ω	% (Λ -parent)
(1) 0^+	100% $X^1\Sigma^+$	(11) 1	100%(3) $^3\Delta$
(2) 0^+	99.68% $(1)^3\Pi$, 0.32% $(X)^1\Sigma^+$	(12) 1	100%(4) $^3\Pi$
(3) 0^+	80%(2) $^1\Sigma^+$, 20%(2) $^3\Pi$	(1) 2	100% $(1)^3\Delta$
(4) 0^+	80.6% $(2)^3\Pi$, 19.4% $(2)^1\Sigma^+$	(2) 2	100% $(1)^1\Delta$
(5) 0^+	100%(3) $^1\Sigma^+$	(3) 2	100%(1) $^3\Pi$
(6) 0^+	100%(3) $^3\Pi$	(4) 2	100%(1) $^3\Phi$
(1) 0^-	99.12%(1) $^3\Pi$, 0.88% $(1)^3\Sigma^+$	(5) 2	88.6% $(2)^3\Pi$, 11.4% $(2)^3\Delta$
(2) 0^-	100%(1) $^3\Sigma^-$	(6) 2	88%(2) $^3\Delta$, 12%(2) $^3\Pi$
(3) 0^-	100%(1) $^3\Sigma^+$	(7) 2	100%(2) $^1\Delta$
(4) 0^-	100% $(2)^3\Pi$	(8) 2	100%(3) $^3\Pi$
(5) 0^-	100%(3) $^3\Pi$	(9) 2	100%(2) $^3\Phi$
(1) 1	99.8% $(1)^3\Delta$, 0.02% $(1)^3\Sigma^-$	(10) 2	100%(4) $^3\Pi$
(2) 1	100%(1) $^3\Pi$	(1) 3	100% $(1)^3\Delta$
(3) 1	100%(1) $^3\Sigma^-$	(2) 3	100%(1) $^3\Phi$
(4) 1	100%(1) $^1\Pi$	(3) 3	100%(2) $^3\Delta$
(5) 1	100% $(1)^3\Sigma^+$	(4) 3	100%(1) $^1\Phi$
(6) 1	78%(2) $^3\Pi$, 22%(2) $^3\Delta$	(5) 3	52%(2) $^3\Phi$, 48%(2) $^1\Phi$
(7) 1	82% $(2)^3\Delta$, 18%(2) $^3\Pi$	(6) 3	52%(2) $^1\Phi$, 48%(2) $^3\Phi$
(8) 1	100%(2) $^1\Pi$	(1) 4	100%(1) $^3\Phi$
(9) 1	96%(3) $^3\Pi$, 4%(3) $^1\Pi$	(2) 4	100% $(1)^1\Gamma$
(10) 1	100%(3) $^1\Pi$	(3) 4	100%(2) $^3\Phi$

The points of intersection/crossings and avoided crossings occurring between the potential energy curves of a diatomic molecule are important in photochemistry [159]. The avoided crossing regions are likely to be a leakage channel along which the molecules flow from the higher down to the lower potential energy surface [159]. From the potential energy curves of the present work in Figures 25 - 33 several crossings and avoided crossings have been detected between the electronic states of the molecule ZrS. These are reported in Tables

XXVIII and XXIX together with the internuclear distance R and the energy gap separation ΔE .

Table XXVIII: Positions of the avoided crossings R_{AC} and the energy differences ΔE_{AC} at R_{AC} with the corresponding crossings of parent Λ states for Ω states in ZrS.

Ω	$(n+1)\Omega / n\Omega$	$R_{AC} (\text{\AA})$	$\Delta E_{AC} (\text{cm}^{-1})$	Crossings of Λ states
1	8 / 9	2.36	317.0	$(3)^3\Pi / (2)^1\Pi$
	10 / 11	2.15	86.0	$(3)^3\Delta / (3)^1\Pi$
3	4 / 5	2.42	172.6	$(1)^1\Phi / (2)^3\Phi$
		2.54	162.2	
0^+	5 / 6	2.36	348.0	$(3)^1\Sigma^+ / (3)^3\Pi$
3	5 / 6	2.33	414.5	$(2)^3\Phi / (2)^1\Phi$

Table XXIX: Positions of the crossings and avoided crossings occurring between the parent Λ electronic states of the molecule ZrS.

		Crossing					Crossing		
State1	State2	$R_c(\text{\AA})$	$R_{av}(\text{\AA})$	$\Delta E_{av}(\text{cm}^{-1})$	State1	State2	$R_c(\text{\AA})$	$R_{av}(\text{\AA})$	$\Delta E_{av}(\text{cm}^{-1})$
$(X)^1\Sigma^+$	$(1)^3\Delta$	2.18				$(4)^1\Delta$		2.31	83.2
	$(2)^1\Delta$	2.78						2.85	424.5
$(1)^1\Gamma$	$(2)^3\Delta$	2.30			$(3)^1\Delta$	$(3)^3\Delta$	2.19		
	$(3)^3\Delta$	2.64				$(4)^3\Delta$	2.26		
	$(4)^3\Delta$	2.71				$(1)^1\Phi$	2.56		
	$(2)^1\Phi$	2.60				$(2)^1\Pi$	2.60		
	$(3)^1\Pi$	2.63				$(2)^1\Phi$	2.09		
	$(2)^3\Pi$	2.13				$(3)^1\Pi$	2.12		
	$(3)^3\Pi$	2.61				$(2)^3\Phi$	2.06		
	$(2)^3\Phi$	2.62				$(4)^3\Delta$	2.11		
	$(2)^1\Delta$	2.86				$(1)^1\Phi$	2.72		
	$(3)^3\Delta$	2.70				$(3)^1\Pi$	1.97		
$(2)^1\Sigma^+$	$(4)^3\Delta$	2.77			$(2)^3\Delta$	$(1)^3\Sigma^+$	2.54		
	$(2)^1\Phi$	2.68				$(3)^3\Delta$		2.76	60.6
	$(3)^1\Pi$	2.72				$(1)^1\Pi$	2.84		
	$(2)^3\Pi$	2.36			$(3)^3\Delta$	$(4)^3\Delta$		2.85	155.8
	$(3)^3\Pi$	2.71				$(1)^1\Phi$	2.46		
	$(2)^3\Phi$	2.70				$(2)^1\Pi$	2.49		
	$(1)^3\Sigma^+$	2.50				$(2)^1\Phi$	1.96		
	$(2)^3\Delta$	2.47				$(3)^1\Pi$	2.0/2.67		
	$(3)^1\Delta$	2.49/2.76				$(3)^3\Pi$	2.68		
	$(3)^3\Delta$	2.40				$(2)^3\Phi$	1.96/2.69		
	$(4)^3\Delta$	2.44			$(4)^3\Delta$	$(1)^1\Phi$	2.51		
	$(1)^1\Phi$	2.69				$(2)^1\Pi$	2.54		
$(3)^1\Sigma^+$	$(2)^1\Phi$	2.31			$(1)^1\Pi$	$(1)^3\Sigma^+$	2.81		
	$(3)^1\Pi$	2.35				$(3)^1\Pi$		2.42	302
	$(3)^3\Pi$	2.30			$(1)^3\Phi$	$(3)^3\Pi$	2.39		
	$(2)^3\Phi$	2.31				$(1)^3\Sigma^+$	2.88		
	$(3)^1\Delta$		2.64	67.6		$(2)^3\Delta$	2.92		
	$(3)^3\Delta$	2.54				$(3)^3\Delta$	2.98		
	$(4)^3\Delta$	2.59				$(1)^1\Pi$	2.52		
	$(2)^1\Phi$	2.45				$(2)^1\Pi$	2.89		
	$(3)^1\Pi$	2.50			$(2)^3\Pi$	$(1)^3\Sigma^+$	2.31/2.80		
	$(3)^3\Pi$	2.46				$(2)^3\Delta$	2.79		
$(2)^1\Delta$	$(2)^3\Phi$	2.47				$(2)^1\Pi$	2.80		
						$(3)^3\Pi$		2.90	26.8

III. D. 3. The Nature of Bonding in ZrS

In the present section we discuss the bonding in neutral ZrS molecule. The percentage composition of molecular electronic states in terms of molecular orbital configurations obtained from our multiconfigurational treatment of the wavefunctions in ZrS, are shown in Table XXX. The percentage weights of each molecular orbital configuration are calculated as the squares of the corresponding CI coefficients. Configuration weights lower than 2% percent have been omitted from the results of Table XXX. It is often useful to discuss the properties of molecular electronic states in terms of their molecular orbital configurations. In the sections below we discuss the properties and differences which exist between the ground state $X^1\Sigma^+$, and the low lying electronic states $^1,^3\Pi$, $^1,^3\Phi$, $^1,^3\Delta$ of ZrS.

Table XXX. Leading configurations of the $^{2s+1}\Lambda^\pm$ states of ZrS at $R = 2.23\text{\AA}$.

Electronic State	Weight
$X^1\Sigma^+$	78% $1\sigma^2 1\pi^4 2\sigma^2$, 5% $1\sigma^2 1\pi^4 3\pi^2$, 5% $1\sigma^2 1\pi^4 3\sigma^2$, 5% $1\sigma^2 1\pi^3 2\sigma^2 2\pi^1$
$(1)^1\Delta$	77% $1\sigma^2 1\pi^4 2\sigma^1 1\delta^1$, 13% $1\sigma^2 1\pi^4 3\sigma^1 1\delta^1$
$(2)^1\Sigma^+$	22% $1\sigma^2 1\pi^4 2\sigma^1 3\sigma^1$, 27% $1\sigma^2 1\pi^4 3\pi^2$, 28% $1\sigma^2 1\pi^4 1\delta^2$, 12% $1\sigma^2 1\pi^4 2\pi^2$
$(1)^1\Gamma$	100% $1\sigma^2 1\pi^4 1\delta^2$
$(2)^1\Delta$	76% $1\sigma^2 1\pi^4 3\sigma^1 1\delta^1$, 13% $1\sigma^2 1\pi^4 2\sigma^1 1\delta^1$
$(3)^1\Sigma^+$	60% $1\sigma^2 1\pi^4 2\sigma^1 3\sigma^1$, 25% $1\sigma^2 1\pi^4 1\delta^2$, 5% $1\sigma^2 1\pi^4 3\sigma^2$
$(3)^1\Delta$	56% $1\sigma^2 1\pi^3 2\sigma^2 2\pi^1$, 27% $1\sigma^2 1\pi^3 2\sigma^1 1\delta^1 2\pi^1$
$(4)^1\Delta$	86% $1\sigma^2 1\pi^4 2\pi^2$
$(1)^1\Pi$	56% $1\sigma^2 1\pi^4 2\sigma^1 2\pi^1$, 40% $1\sigma^2 1\pi^4 2\pi^1 1\delta^1$
$(1)^1\Phi$	82% $1\sigma^2 1\pi^4 2\pi^1 1\delta^1$
$(2)^1\Pi$	64% $1\sigma^2 1\pi^4 2\pi^1 1\delta^1$, 22% $1\sigma^2 1\pi^4 2\sigma^1 2\pi^1$
$(2)^1\Phi$	85% $1\sigma^2 1\pi^3 2\sigma^2 1\delta^1$
$(3)^1\Pi$	84% $1\sigma^2 1\pi^3 2\sigma^2 1\delta^1$
$(1)^3\Delta$	94% $1\sigma^2 1\pi^4 2\sigma^1 1\delta^1$
$(2)^3\Sigma^+$	98% $1\sigma^2 1\pi^4 2\sigma^1 3\sigma^1$
$(2)^3\Delta$	94% $1\sigma^2 1\pi^4 3\sigma^1 1\delta^1$
$(1)^3\Pi$	92% $1\sigma^2 1\pi^4 2\sigma^1 2\pi^1$
$(1)^3\Phi$	99% $1\sigma^2 1\pi^4 2\pi^1 1\delta^1$
$(2)^3\Pi$	93% $1\sigma^2 1\pi^4 2\pi^1 1\delta^1$
$(3)^3\Pi$	94% $1\sigma^2 1\pi^3 2\sigma^2 1\delta^1$
$(2)^3\Phi$	89% $1\sigma^2 1\pi^3 2\sigma^2 1\delta^1$

Weights (in percent) are obtained from the square of the corresponding

^a configuration interaction coefficients weights lower than 2% are not reported.

D. 3. 1. The $X^1\Sigma^+$ and $(1)^3\Delta$ states

The difference between the electronegativities of the atoms Zr and S indicates that the ZrS molecule is likely to be appreciable polar with charge transfer from the Zr to the S atom. As part of the ZrS molecule the resulting configuration of the Zr atom is presumably somewhere in between the $(4d^2 5s^2)$ of the neutral Zr atom and $(5s^2)$ of the Zr^{2+} ion. Also, the configuration of the S atom as part of the ZrS is expected to be somewhere between $3p^4$ and $3p^6$. In consequence, it appears likely that the electronic ground state of ZrS should arise from

the valence shell configuration: $1\sigma^2 1\pi^4 2\sigma^2$ (Table XXXIII). This electronic configuration ($1\sigma^2 1\pi^4 2\sigma^2$) gives rise to the singlet electronic ground state $X^1\Sigma^+$, with orbital angular momentum $\Lambda = \sum \lambda_i = 0$. Other configurations arising from the single and double excitation of electrons from the ground state configuration in to virtual molecular orbitals, forming the active space of ZrS, may lead to other electronic states $^1,^3\Sigma$, $^1,^3\Pi$, $^1,^3\Delta$, $^1,^3\Phi$, and $^1,^3\Gamma$. In ZrS the electronic energy of the $(1)^3\Delta$ state is within the vibrational interval of the ground state. Actually, the potential energy curves of the two states $(1)^3\Delta$ and $X^1\Sigma^+$ state cross at $R = 2.15\text{\AA}$. The main difference between the molecular orbital configurations of the two states $(1)^3\Delta$ and $X^1\Sigma^+$ arises from the promotion of a $2\sigma^1$ electron in the ground state in to a $1\delta^1$ orbital, thus giving the $(1)^3\Delta$ state the following molecular orbital configuration $1\sigma^2 1\pi^4 2\sigma^1 1\delta^1$.

D. 3. 2. The Low-Lying $^1,^3\Pi$ and $^1,^3\Delta$ states:

The first $(1)^3\Pi$ and $(1)^1\Pi$ states, located at 8469.94cm^{-1} and 10091.62cm^{-1} above the ground electronic state are in excellent agreement with the experimental results available in Ref [160, 161, 162]. The electronic configurations of the lowest lying $(1)^1\Pi$ and $(1)^3\Pi$ states arise from the promotion of a 2σ electron on to the virtual molecular orbital $2\pi^1$. Thus giving the two electronic states $(1)^1\Pi$ and $(1)^3\Pi$ the leading molecular orbital configurations 56% $1\sigma^2 1\pi^4 2\sigma^1 2\pi^1$, 92% $1\sigma^2 1\pi^4 2\sigma^1 2\pi^1$, respectively. The lowest lying $(1)^1\Delta$ state $1\sigma^2 1\pi^4 2\sigma^1 1\delta^1$ arises from the promotion of a metal centered (5s) $2\sigma^1$ electron in to the vacant metal ($4d_{\pm 1}$) 1δ orbital. This places the $(1)^1\Delta$ state at a transition energy of $T_e = 4861.87\text{cm}^{-1}$ relative to the ground state, in excellent agreement with previous *ab initio* calculations [139]. The second $(2)^3\Delta$ state has a configuration that differs from that of the $(1)^3\Delta$ state by the promotion of an electron from the metal (5s) $2\sigma^1$ orbital into a vacant ($4d_0$) $3\sigma^1$ orbital. This raises the $(2)^3\Delta$ state in to a higher energy region of 13345 cm^{-1} above the ground state. Additionally, the $(2)^1\Sigma^+$ state located in our calculations at 12312.78cm^{-1} arises from a combination of several orbital configurations 22% $1\sigma^2 1\pi^4 2\sigma^1 3\sigma^1$, 27% $1\sigma^2 1\pi^4 3\pi^2$, 28% $1\sigma^2 1\pi^4 1\delta^2$, 12% $1\sigma^2 1\pi^4 2\pi^2$ without a dominant molecular orbital configuration.

In order to completely describe the bonding in the ground electronic state of the neutral ZrS molecule, we calculate in the following section the effective bond order EBO, which was defined earlier in equation (1) of this chapter. A better definition of the effective bond order can be obtained by considering the occupation numbers of bonding and antibonding natural orbitals derived from multiconfigurational wave functions. In our CASSCF calculations we obtained the ground state of ZrS by distributing the 8 valence electrons over the active space of molecular orbitals. The occupation numbers of bonding molecular orbitals are given by the

number η_b and those in the antibonding molecular orbitals are given by η_{ab} . In our CASSCF treatment of the wavefunctions in ZrS we obtained the occupation numbers of the bonding and anti-bonding orbitals in the following way: $\eta_b(1\sigma)= 1.95456$, $\eta_b(2\sigma)= 0.7686$, $\eta_{ab}(3\sigma)= 0.43403$, $\eta_{ab}(4\sigma)= 0.23715$, $\eta_{ab}(1\delta)= 0.4516$, $\eta_b(1\pi)= 3.54098$, $\eta_{ab}(2\pi)= 0.54062$, $\eta_{ab}(3\pi)= 0.07246$. Then by using equation (1), we obtain an effective bond order EBO of $2.26 \approx 2$, which indicates that the bonding in neutral ZrS is a double bond.

III. D. 4. The Vibrational Structure of ZrS

We suspect in the present section that several vibrational energy levels belonging to the vibrational spectrum of the ground $(1)0^+[X^1\Sigma^+]$ and first excited states $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, $(1)3[(1)^3\Delta]$ are degenerate. For this we investigate the vibrational energy structures of ZrS by solving the vibrational-rotational Schrödinger equation within the canonical functions approach [34, 35].

The vibrational energy structures of diatomic molecules are important in the search for possible variations in the fundamental constants of the standard model, the fine structure constant α and the electron to proton mass ratios μ . In fundamental concepts the fine structure constant namely called the coupling constant characterizes the strength of the electromagnetic interaction, or the probability of an electron to capture a photon. Physicists have pondered for many years whether the fine structure constant is in fact constant and whether or not its value differs by location and time. The current value of the fine structure constant $\alpha = e^2 / \hbar c$ is $1 / 137.035999074$ [163, 164] and the current limit on variations in α obtained from atomic spectra measurements is $\Delta\alpha / \alpha = (-2.7 \pm 2.6) \times 10^{-15} \text{ years}^{-1}$ [165, 166]. Variations in α can be detected by relativistic energy level shifts in atoms and molecules [167]. If we choose close energy levels which move differently as α varies, variations in the transitions frequency would correspond to variations in α . An extreme example of this is in dysprosium. In dysprosium, there are two almost degenerate states with an energy of 19797.97 cm^{-1} . In [168] it was demonstrated that the relative change of the transition frequency between these two levels in dysprosium is orders of magnitude larger than the relative change in α [167]. An experiment is currently in progress utilizing this transition [169]. These measurements can be greatly enhanced by several orders of magnitude, in transitions occurring between the nearly degenerate fine structure vibrational energy levels in diatomic molecules. These transitions exist in the microwave frequency range, on the order of $< 20 \text{ cm}^{-1}$, and the level widths are generally very small, typically of the order of $\approx 10^{-2} \text{ Hz}$ [170]. Accurate measurements for variations in α can be done by observing transitions between nearly degenerate fine structure vibrational energy levels in diatomic

molecules. In these regards, searching for the nearly degenerate vibrational levels in diatomic molecules is important, as it might shed the light on new limits in the search for laboratory variations of α in certain diatomic molecules. Particularly interesting molecules are those identified in the spectra of stars, as laboratory tests on these molecules might be extended to search for variations of α in stars. The molecule of interest in the present work ZrS is important in this domain since it has been identified as the carrier of the Keenan bands in the spectra of cool S-type stars [147]. In ZrS, we detected a $(1)^3\Delta$ state that is only 302cm^{-1} above the ground state. We further suspect that near degeneracies of order $< 20\text{cm}^{-1}$ might exist between the vibrational energy levels of the spin orbit component states $(1)0^+[(X)^1\Sigma^+]$, $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, and $(1)3[(1)^3\Delta]$. In search for possible degeneracies between the vibrational intervals of the ground and low lying electronic states of ZrS, we have decided in the present work to investigate the vibrational structures of the spin orbit electronic states in ZrS.

In literature the first identification of the ZrS molecule in the spectra of three Mira variable stars of type S was done by K. Hinkle *et. al.* [147] and was based on the identification of the $\Delta v = -1, 0, 1$, and 2 vibrational transitions in the $^3\Pi - ^3\Delta$ band system of ZrS. Laboratory observations for the rotational structure of the ZrS molecule were done by rotational microwave spectroscopy in Ref [152] for the rotational energy transitions in the vibrational $v = 0, 1, 2$ levels of the $X^1\Sigma^+$ and $(1)^3\Delta$ states. Further spectral analysis in Ref [146, 150] yielded rotational and vibrational energy spectrums in the singlet electronic states of ZrS $\{X^1\Sigma^+, (2)^1\Sigma^+, (3)^1\Sigma^+, (1)^1\Pi\}$. Selected vibrational energy transitions were then observed in laboratory spectra for the transition $(1)^3\Delta - (1)^3\Pi$ in Ref [156] and for the transitions $(4)^3\Delta - (1)^3\Delta$, $(2)^3\Phi - (1)^3\Delta$, $(2)^1\Pi - X^1\Sigma^+$, $(3)^1\Sigma^+ - X^1\Sigma^+$ in Ref [151].

The results of our previous *ab initio* calculations on ZrS place the first $(1)^3\Delta$ state at a transition energy of $T_e = 302\text{cm}^{-1}$ above the ground state, which is in excellent agreement with the theoretical values reported in Ref [139, 154]. The ground and first excited states in ZrS are similar to those in HfF^+ , which have been suggested as a model system to study the variations in the fundamental constants α and μ [18]. In this respect, the ZrS molecule is better than the HfF^+ molecule since the $[X^1\Sigma^+] \rightarrow [(1)^3\Delta]$ transition occurs at $\approx 302\text{cm}^{-1}$ in ZrS, and at 1633cm^{-1} in HfF^+ . Which means, that close degeneracies between vibrational energy levels of the order $< 20\text{cm}^{-1}$ are more likely to occur in ZrS.

In Tables XXXI, XXXII and XXXIII we report our results for the vibrational energy values of the states $(1)0^+[X^1\Sigma^+]$, $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, $(1)3[(1)^3\Delta]$, $(4)1[(1)^1\Pi]$ obtained by solving the vibrational Schrödinger equation within the canonical functions approach.

Table XXXI:

Values of the eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the constants B_v , D_v for the different vibrational levels of the states (1) $0^+ [X^1\Sigma^+]$, (4) $1[(1)^1\Pi]$.

(1) $0^+ [X^1\Sigma^+]$										
v	$E_v(\text{cm}^{-1})$	$\delta E_v/E_v$	$R_{\min}(\text{\AA})$	$\delta R_{\min}/R_{\min}$	$R_{\max}(\text{\AA})$	$\delta R_{\max}/R_{\max}$	$B_v \times 10^1(\text{cm}^{-1})$	$D_v \times 10^8(\text{cm}^{-1})$		
0	248.80 ^a		2.181 ^a		2.287 ^a		1.423 ^a	4.473 ^a		
	273.8 ^{theo b}	9.1%	2.107 ^{theo b}	3.5%	2.209 ^{theo b}	3.5%				
1	755.34		2.146		2.330		1.418	4.446		
	819.2 ^{theo b}	7.8%	2.073 ^{theo b}	3.5%	2.250 ^{theo b}	3.5%				
2	1259.96		2.123		2.361		1.412	4.499		
	1361.6 ^{theo b}	7.5%	2.050 ^{theo b}	3.6%	2.280 ^{theo b}	3.5%				
3	1761.36		2.106		2.387		1.408	4.599		
	1901.1 ^{theo b}	7.3%	2.033 ^{theo b}	3.6%	2.305 ^{theo b}	3.6%				
4	2258.57		2.090		2.410		1.402	4.600		
	2437.7 ^{theo b}	7.3%	2.018 ^{theo b}	3.6%	2.327 ^{theo b}	3.6%				
5	2752.56		2.076		2.432		1.399	5.049		
	2971.4 ^{theo b}	7.4%	2.005 ^{theo b}	3.5%	2.348 ^{theo b}	3.6%				
6	3240.08		2.063		2.452		1.395	4.946		
	3502.0 ^{theo b}	7.5%	1.993 ^{theo b}	3.5%	2.367 ^{theo b}	3.6%				
7	3723.40		2.051		2.470		1.392	5.241		
8	4201.29		2.041		2.488		1.388	4.917		
9	4676.13		2.031		2.505		1.383	4.939		
10	5147.76		2.022		2.522		1.379	4.692		
11	5616.83		2.013		2.538		1.374	4.068		
12	6083.83		2.005		2.553		1.372	2.722		
13	6548.53		1.998		2.569		1.374	-3.982		
14	7011.22		1.991		2.584		1.359	4.811		
15	7471.46		1.983		2.599		1.354	4.820		
16	7929.19		1.977		2.613		1.349	4.794		
17	8384.44		1.971		2.628		1.343	4.861		
18	8836.96		1.965		2.642		1.338	4.805		
19	9286.83		1.960		2.656		1.332	4.861		
20	9733.86		1.954		2.671		1.327	4.937		
21	10177.84		1.949		2.685		1.321	4.947		
(4) $1[(1)^1\Pi]$										
v	$E_v(\text{cm}^{-1})$	$\delta E_v/E_v$	$R_{\min}(\text{\AA})$	$\delta R_{\min}/R_{\min}$	$R_{\max}(\text{\AA})$	$\delta R_{\max}/R_{\max}$	$B_v \times 10^1(\text{cm}^{-1})$	$\delta B_v/B_v$	$D_v \times 10^8(\text{cm}^{-1})$	$\delta D_v/D_v$
0	10712.84 ^a		2.214 ^a		2.326 ^a		1.378 ^a		5.353 ^a	
	11083.8 ^{theo b}	3.3%	2.167 ^{theo b}	2.0%	2.275 ^{theo b}	2.0%				
	11083.716 ^{Exp c}	3.3%					1.4483 ^{Exp c}	4.8%	5.0272 ^{Exp c}	6.5%
1	11152.21		2.178		2.377		1.366		5.408	
	11577.1 ^{theo b}	3.7%	2.132 ^{theo b}	2.2%	2.318 ^{theo b}	2.7%				
2	11586.46		2.156		2.411		1.361		4.771	
	12067.8 ^{theo b}	4.0%	2.108 ^{theo b}	2.5%	2.350 ^{theo b}	2.5%				
3	12026.48		2.138		2.439		1.354		4.987	
	12556.00 ^{theo b}	4.2%	2.090 ^{theo b}	2.4%	2.376 ^{theo b}	2.7%				
4	12465.75		2.123		2.464		1.348		4.770	
	13041.50 ^{theo b}	4.5%	2.074 ^{theo b}	2.2%	2.399 ^{theo b}	2.5%				
5	12905.64		2.109		2.487		1.343		5.066	
	13524.4 ^{theo b}	4.6%	2.061 ^{theo b}	2.4%	2.421 ^{theo b}	2.4%				
6	13342.94		2.097		2.509		1.338		4.846	
	14004.70 ^{theo b}	4.7%	2.048 ^{theo b}	2.5%	2.441 ^{theo b}	2.4%				
7	13778.38		2.087		2.528		1.331		4.173	
8	14213.55		2.078		2.548		1.328		2.924	
9	14648.55		2.069		2.567		1.318		4.589	
10	15081.54		2.061		2.585		1.311		5.042	
11	15510.58		2.053		2.603		1.305		4.899	
12	15937.24		2.045		2.621		1.299		5.088	
13	16361.26		2.038		2.637		1.295		5.416	
14	16781.77		2.031		2.654		1.291		5.123	
15	17199.88		2.024		2.669		1.286		4.903	
16	17616.13		2.018		2.685		1.282		4.788	

a. First entry is for the values of the present work, b. Ref [149], c. Ref [146]

Note: Exp, corresponds to experimental results.

Theo, corresponds to theoretical results.

Table XXXII:

Values of the eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the constants B_v , D_v for the different vibrational levels of the states (1) 2 $[(1)^3\Delta]$, (1) 3 $[(1)^3\Delta]$ in ZrS.

v	(1) 2 $[(1)^3\Delta]$					(1) 3 $[(1)^3\Delta]$				
	$E_v(\text{cm}^{-1})$	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm^{-1})	$D_v \times 10^8$ (cm^{-1})	$E_v(\text{cm}^{-1})$	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm^{-1})	$D_v \times 10^8$ (cm^{-1})
0	526.24	2.179	2.288	1.365	3.775	789.26	2.181	2.287	1.424	4.484
1	1042.33	2.145	2.332	1.355	4.719	1295.35	2.146	2.329	1.418	4.393
2	1524.76	2.123	2.361	1.349	2.919	1801.45	2.123	2.360	1.413	4.541
3	2033.76	2.104	2.387	1.349	4.629	2303.08	2.105	2.387	1.408	4.426
4	2526.49	2.089	2.410	1.339	3.345	2802.63	2.089	2.409	1.402	4.427
5	3024.69	2.077	2.432	1.338	3.970	3299.59	2.078	2.431	1.396	4.193
6	3519.01	2.067	2.452	1.328	3.501	3795.77	2.067	2.451	1.389	4.179
7	4013.55	2.056	2.471	1.325	3.961	4290.62	2.056	2.471	1.383	4.399
8	4504.64	2.046	2.489	1.319	4.172	4782.60	2.046	2.489	1.378	4.692
9	4991.07	2.037	2.507	1.315	4.112	5270.39	2.037	2.507	1.374	4.891
10	5474.09	2.028	2.524	1.310	4.468	5753.23	2.028	2.524	1.369	4.658
11	5951.88	2.020	2.540	1.307	3.534	6231.98	2.020	2.540	1.365	3.844
12	6429.69	2.013	2.556	1.302	3.636	6707.89	2.013	2.556	1.363	2.238
13	6907.29	2.005	2.572	1.302	2.331	7181.07	2.006	2.572	1.354	4.589
14	7391.33	1.998	2.588	1.302	8.730	7651.29	1.999	2.588	1.348	4.616
15	7888.95	1.991	2.605	1.312	2.771	8118.57	1.992	2.603	1.343	4.660
16	8402.79	1.985	2.622	1.320	-1.301	8582.92	1.986	2.617	1.338	4.704
17	8939.67	1.978	2.639	1.333	-2.785	9044.24	1.980	2.629	1.332	4.721
18	9493.51	1.971	2.654	1.343	-1.376	9502.50	1.974	2.641	1.327	4.719
19	10069.16	1.964	2.671	1.354	-1.954	9957.73	1.969	2.654	1.322	4.719
20	10657.93	1.958	2.691	1.364	-7.547	10409.89	1.964	2.677	1.316	4.738
21	11262.59	1.952	2.710	1.375	4.989	10858.94	1.959	2.696	1.310	4.758
22	11872.65	1.945	2.730	1.362	3.031	11304.81	1.953	2.707	1.304	4.773
23	12481.75	1.939	2.749	1.359	8.526	11747.46	1.949	2.718	1.298	4.788
24	13058.92	1.934	2.768	1.328	2.353	12186.85	1.945	2.730	1.292	4.776
25	13543.15	1.929	2.784	1.261	1.972	12623.08	1.940	2.745	1.286	4.725
26	13981.68	1.925	2.798	1.297	-1.800	13056.33	1.936	2.759	1.281	4.649
27	14502.69	1.920	2.815	1.337	3.943	13486.88	1.932	2.773	1.275	4.633
28	15017.22	1.916	2.831	1.290	2.581	13914.83	1.928	2.786	1.270	4.771
29	15459.43	1.912	2.846	1.252	-1.216	14339.94	1.924	2.799	1.264	5.013
30	15920.87	1.908	2.861	1.210	1.461	14761.67	1.921	2.814	1.258	5.251
31	16113.76	1.906	2.867	1.017	-1.488	15179.65	1.917	2.827	1.252	5.325
32	16539.65	1.903	2.883	1.266	1.221	15593.94	1.913	2.841	1.246	5.241
33	16979.96	1.899	2.898	1.126	1.068	16004.71	1.909	2.855	1.240	5.310
34	17206.10	1.898	2.905	1.013	-8.721	16411.97	1.906	2.868	1.235	5.043
35	17576.91	1.895	2.918	1.230	-2.289	16815.74	1.903	2.882	1.229	4.139
36	18018.93	1.891	2.933	1.064	1.145	17216.18	1.899	2.896	1.224	5.369
37	18288.93	1.889	2.942	1.154	-1.091	17613.49	1.896	2.909	1.219	2.260
38	18748.38	1.886	2.959	1.162	7.009	18007.77	1.893	2.923	1.213	-1.947
39	19072.04	1.883	2.971	1.052	-8.546	18399.09	1.890	2.936	1.209	0.132
40	19412.15	1.881	2.984	1.155	-3.756	18787.34	1.887	2.950	1.201	5.458

Table XXXIII:

Values of the eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the constants B_v , D_v for the different vibrational levels of the state $(1)1[(1)^3\Delta]$.

$(1)1[(1)^3\Delta]$					
v	$E_v(\text{cm}^{-1})$	$R_{\min}$ ($\text{\AA}$)	$R_{\max}$ ($\text{\AA}$)	$B_v \times 10^1$ (cm^{-1})	$D_v \times 10^8$ (cm^{-1})
0	1051.98	2.160	2.259	1.454	3.696
1	1625.22	2.131	2.303	1.442	3.822
2	2188.64	2.109	2.334	1.436	4.199
3	2738.49	2.091	2.361	1.431	4.220
4	3279.69	2.078	2.384	1.424	3.729
5	3820.47	2.066	2.405	1.417	4.302
6	4353.52	2.055	2.426	1.411	4.060
7	4882.99	2.044	2.445	1.405	4.599
8	5405.15	2.035	2.463	1.401	4.712
9	5920.73	2.026	2.480	1.396	4.389
10	6432.44	2.017	2.497	1.391	4.488
11	6939.72	2.009	2.513	1.386	4.278
12	7443.45	2.002	2.529	1.380	4.197
13	7943.11	1.995	2.545	1.376	3.558
14	8438.55	1.988	2.559	1.375	1.610
15	8930.38	1.982	2.575	1.364	4.631
16	9418.24	1.975	2.589	1.358	4.634
17	9902.16	1.969	2.605	1.353	4.608
18	10382.27	1.964	2.619	1.347	4.653
19	10858.61	1.959	2.634	1.341	4.526
20	11331.68	1.954	2.648	1.335	4.492
21	11801.62	1.949	2.661	1.330	4.516
22	12268.49	1.944	2.675	1.325	4.388
23	12732.66	1.939	2.689	1.319	4.361
24	13194.27	1.935	2.702	1.314	4.401
25	13653.31	1.931	2.715	1.309	4.352
26	14109.93	1.926	2.728	1.304	4.446
27	14563.94	1.923	2.741	1.299	4.689
28	15014.81	1.918	2.754	1.293	4.930
29	15461.92	1.915	2.768	1.287	5.272
30	15904.54	1.911	2.781	1.281	5.557
31	16342.25	1.907	2.795	1.274	5.566
32	16775.41	1.903	2.809	1.268	5.277
33	17204.71	1.899	2.822	1.263	5.098
34	17630.51	1.896	2.835	1.257	5.130
35	18053.01	1.893	2.849	1.251	5.390
36	18472.56	1.889	2.862	1.246	4.491
37	18889.34	1.886	2.875	1.240	6.556
38	19303.12	1.883	2.888	1.236	1.141

The comparison between the present values of E_v , $R_{\min}$, $R_{\max}$, B_v , and D_v to the values found in literature shows a very good agreement with percentage relative differences of 3.3% (Ref [146,149]) $\leq \delta E_v/E_v \leq 9.1\%$ (Ref [149]), 2% (Ref[149]) $\leq \delta R_{\min}/R_{\min} \leq 3.6\%$ (Ref[149]), 2% (Ref[149]) $\leq \delta R_{\min}/R_{\min} \leq 3.6\%$ (Ref[149]), $\delta B_v/B_v = 4.8\%$, and $\delta D_v/D_v = 6.5\%$. All of the calculated vibrational energy values are measured relative to the zeroth transition energy of the ground electronic state. Upon close examination of the investigated vibrational energy levels of the $(1)0^+[X^1\Sigma^+]$, $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, $(1)3[(1)^3\Delta]$ states we find several

degeneracies of order $\leq 16\text{cm}^{-1}$ occurring between the vibrational intervals. These are reported in Table XXXIV together with the energy separation $\Delta E_v = E_v - E_{v'}$.

Table XXXIV:

Recorded degeneracies between the vibrational energy levels of the $(1)0^+ [X^1\Sigma^+]$, $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, $(1)3[(1)^3\Delta]$ states in ZrS.

$(1)0^+ [X^1\Sigma^+]$		$(1)1[(1)^3\Delta]$		$(1)2[(1)^3\Delta]$		$(1)3[(1)^3\Delta]$		
v	$E_v(\text{cm}^{-1})$	v	$E_v(\text{cm}^{-1})$	v	$E_v(\text{cm}^{-1})$	v	$E_v(\text{cm}^{-1})$	$\Delta E_v = E_v - E_{v'} $ (cm^{-1})
5	2752.56	3	2738.49					14.07
		0	1051.98	1	1042.33			9.65
		10	6432.44	12	6429.69			2.75
		28	15014.81	28	15017.2			2.41
		29	15461.92	29	15459.4			2.49
		30	15904.54	30	15920.9			16.33
		33	17204.71	34	17206.1			1.39
				18	9493.51	18	9502.5	8.99
				24	13058.9	26	13056.3	2.59
				34	17206.1	36	17216.2	10.08

Upon close investigation of the vibrational energy levels, we can find near degeneracies of the order of $\leq 16\text{cm}^{-1}$ occurring between the vibrational intervals of the $(1)2[(1)^3\Delta]$ state and that of the $(1)1[(1)^3\Delta]$ state, particularly, between the $v = 0, 10, 28, 29, 30, 33$ levels in the state $(1)1[(1)^3\Delta]$ and the $v' = 1, 12, 28, 29, 30, 34$ levels of the state $(1)2[(1)^3\Delta]$. The smallest energy separation of 1.39cm^{-1} recorded between the $v = 33$ of the state $(1)1[(1)^3\Delta]$ and the $v = 34$ of the state $(1)3[(1)^3\Delta]$ exceeds that detected between the vibrational energy levels of the two $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states in SiBr [30] and that detected between the $v = 3$ level of the $^1\Sigma^+$ state and the $v = 1$ level of the $^3\Delta_1$ state in HfF^+ [170]. Other degeneracies have also been reported in the present work on ZrS to occur between the $v = 18, 24, 34$ levels of the $(1)2[(1)^3\Delta]$ state and the $v' = 18, 26, 36$ levels of the $(1)3[(1)^3\Delta]$ states.

To this end, it is useful to study theoretically the effects for the variation of the fundamental constants (α , μ) and the degeneracies reported between vibrational intervals in diatomic molecules. The fine structure interval ω_f depends on the nuclear charge Z and is sensitive to variations in the fine structure constant, scaling as α^2

$$\omega_f \approx Z^2 \alpha^2 E_H, \quad (2)$$

where E_H is the atomic energy unit Hartree. On the other hand, the harmonic vibrational energy quantum ω_v depends on the reduced mass and is sensitive to variations in μ , scaling as $\mu^{-1/2}$

$$\omega_{vib} \approx \mu^{-1/2} \quad (3)$$

Therefore, we obtain an equation for the lines where we can expect approximate cancellation between the fine structure and vibrational intervals:

$$\omega = \omega_f - (v+1/2)\omega_{vib} \approx 0, \quad v = 0, 1, 2, \dots \quad (4)$$

Using equations (2 – 4) we could find the relation between the variation of the transition frequency ω and the variation in the fundamental constants α and μ

$$\frac{\delta\omega}{\omega} = \frac{1}{\omega} \left(2\omega_f \frac{\delta\alpha}{\alpha} + \frac{(v+1/2)}{2} \omega_{vib} \frac{\delta\mu}{\mu} \right) \approx K \left(2 \frac{\delta\alpha}{\alpha} + \frac{1}{2} \frac{\delta\mu}{\mu} \right). \quad (5)$$

The enhancement factor $K = \omega_f / \omega$ determines the relative frequency shift for a given change in the fundamental constants. Large values of factor $K \approx 10^3 - 10^5$ hint at potentially favorable cases for making experiments, because it is usually preferable to have larger relative shifts [30]. Because the number of molecules is finite we cannot have $\omega = 0$ exactly. However, a large number of molecules have $\omega / \omega_f \ll 1$ and $|K| \gg 1$ [170]. Moreover, an additional fine tuning may be achieved by including Ω doublet and hyperfine components. Note that ω is sensitive to the variation of two most important dimensionless parameters of the Standard Model. The first parameter α , determines the strength of the electroweak interactions [171]. The second parameter, $\mu = m_p/m_e$, is related to the weak mass scale and strong interaction scale. The electron mass is proportional to the vacuum expectation value of the Higgs field which also determines the masses of all fundamental particles [171]. The proton mass is proportional to another fundamental parameter, the quantum chromodynamics scale Λ_{QCD} [171]. Therefore, we are speaking about the relative variation of a very important dimensionless fundamental parameters of the Standard Model.

The near degeneracies detected in Table XXXIV between the vibrational intervals of the $(1)0^+[X^1\Sigma^+]$, $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, and $(1)3[(1)^3\Delta]$ states can all be used to search for any variations in the fundamental constants of the Standard Model α and μ , especially those which can be observed spectroscopically. As an example we shall apply equation (4) on the $v = 0$ vibrational level of the $(1)1[(1)^3\Delta]$ state and the $v' = 1$ level of the $(1)2[(1)^3\Delta]$ state

$$\omega = T_e^{\Omega=2} + \frac{3}{2} \omega_v^{\Omega=2} - T_e^{\Omega=1} - \frac{1}{2} \omega_{v'}^{\Omega=1} \approx 0 \quad (6)$$

where $T_e^{\Omega=2}$ and $T_e^{\Omega=1}$ represent the transition energies at equilibrium of the $(1)2[(1)^3\Delta]$ and $(1)1[(1)^3\Delta]$ states relative to the zero transition energy of the ground state. The other constants $\omega_v^{\Omega=1}$ and $\omega_{v'}^{\Omega=2}$ represent the vibrational harmonic frequencies of the two states $(1)1[(1)^3\Delta]$ and $(1)2[(1)^3\Delta]$, respectively. Then by using equation (5), and by considering that the fine structure interval $\omega_f = T_e^{\Omega=2} - T_e^{\Omega=1} = 489.56 \text{ cm}^{-1}$ is the energy splitting occurring between the $v = 1$ level in the $(1)2[(1)^3\Delta]$ state and the $v = 0$ level in the $(1)1[(1)^3\Delta]$ state.

With $\omega_v = 523.54\text{cm}^{-1}$ being the vibrational harmonic frequency of the higher $(1)1[(1)^3\Delta]$ state, we get

$$\therefore \delta\omega = \left(979.12 \frac{\delta\alpha}{\alpha} \right), \quad (7)$$

then by assuming that $\delta\alpha/\alpha \approx 10^{-15}$, which is equivalent to the experimental variation of α from atomic spectra [165, 166], we obtain $\delta\omega \approx 10^{-12}\text{cm}^{-1} = 2.935 \times 10^{-2}\text{Hz}$. The estimated line widths are on the order of 10^{-2}Hz . This is comparable to the accuracy, which is necessary to reach sensitivity $\delta\alpha/\alpha \approx 10^{-15}$ of the best modern laboratory tests [167, 171]. Of course other vibrational energy level degeneracies listed in Table XXXIV can also be used to measure any variations in α , their line widths should be comparable to the line width calculated above. The natural line widths on the order of 10^{-2}Hz obtained in the present work are identical to the natural line widths calculated in Ref [171] for the molecules Cs_2 and SiBr which were suggested to be suitable for measuring α variations.

It is natural to search for any changes in α using measurements of the spin orbit splitting within a specific fine structure multiplet of atoms, and indeed this method has been applied to quasar atomic spectra by several groups [168, 173-175]. However, while this method is appealing through its simplicity, it is possible to improve on its efficiency [168]. An order of magnitude sensitivity gain can be achieved by comparing transition frequencies of heavy atoms, ions or molecules [173, 176]. Other possibilities for measuring changes in α involve studying transitions between accidentally degenerate levels in the same atom or molecule [168]. Of course, there are many more possibilities in molecules where there are vibrational and rotational structures. The relativistic corrections to the different energy levels are different and can exceed the very small frequency corresponding to the transition between degenerate states by many orders of magnitude, i.e., a tiny variation of α can change the transition frequency significantly [168]. Since α variations have been measured from spectral analysis of atoms and ions previously identified in quasar spectra, we suggest the inspection for the spectra of the ZrS molecule in laboratory experiments and in cool S-type stars as a mean to measure any possible variations of the fine structure constant. The detection of the ZrS molecule in the spectra of three Mira variable stars, named RAnd, χCyg , and RCas [147], further enhances this possibility. In fact, the vibrational band systems suggested to be suitable for measuring α variations in the present work have been previously analyzed in the Kennan bands of the three Mira variable stars [147]. We suggest the re-inspection of the Kennan bands in the spectra of the stars RAnd, χCyg , and RCas as a mean to measure possible

variations in the fine structure constant. Recently, a copy of our conclusions on ZrS has been requested by an experimental research group working at the University of Yale in the group of Prof. David Demille.

Our vibrational energy calculations were also performed for the lowest lying spin orbit electronic states in ZrS. A part of these calculations are shown in this chapter while the rest are left for Appendix III. In Table XXXV we report our results for the vibrational energy structures of the $(3)0^+[(2)^1\Sigma^+]$ state together with the values available on this state in Ref [146]. Our calculations for the values of E_v and B_v are in excellent agreement with the values in literature [146] with a percentage relative difference of $6.2\% \leq \delta E_v/E_v \leq 6.8\%$ and $5.1\% \leq \delta B_v/B_v \leq 5.6\%$. However, a less agreement exists for our values of D_v with a relative difference of $15.8\% \leq \delta D_v/D_v \leq 37.4\%$.

Table XXXV:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the constants B_v , D_v for the different vibrational levels of the state $(3)0^+[(2)^1\Sigma^+]$.

v	E_v (cm ⁻¹)	$\delta E_v / E_v$	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$\delta B_v / B_v$	$D_v \times 10^8$ (cm ⁻¹)	$\delta D_v / D_v$
0	13072.75 ^a		2.221 ^a	2.341 ^a	1.366 ^a		5.737 ^a	
	13937.793 ^{Exp b}	6.2%			1.44821 ^{Exp b}	5.6%	4.9526 ^{Exp b}	15.8%
1	13492.88		2.181	2.382	1.359		4.897	
	14460.0 ^{Exp b}	6.7%			1.43264 ^{Exp b}	5.1%	4.21 ^{Exp b}	16.3%
2	13926.43		2.162	2.423	1.353		5.323	
	14949.679 ^{Exp b}	6.8%			1.43118 ^{Exp b}	5.4%	3.875 ^{Exp b}	37.4%
3	14357.03		2.143	2.443	1.346		4.738	
4	14791.07		2.132	2.475	1.341		5.164	
5	15222.73		2.111	2.497	1.335		4.789	
6	15654.21		2.104	2.521	1.329		5.033	
7	16082.30		2.095	2.543	1.324		3.958	
8	16509.88		2.081	2.560	1.322		1.926	
9	16937.67		2.070	2.581	1.310		4.722	
10	17363.32		2.061	2.592	1.303		4.375	
11	17788.66		2.062	2.611	1.299		4.200	
12	18214.70		2.053	2.623	1.294		4.963	
13	18638.35		2.044	2.645	1.290		5.349	
14	19058.32		2.035	2.662	1.285		5.434	

a. First entry is for the values of the present work, b. Ref [146]. Note: Exp, corresponds to experimental results.

III. D. 5. The Permanent Dipole Moment of ZrS

The permanent electric dipole moment is one of the most important physical properties of a molecule. Establishing ligand-induced trends in the permanent electric dipole moments (μ) is particularly beneficial because dipole moments are the most effective measures for the ionic nature of the bond [177]. Furthermore, the dependence of μ on the displacement of the nuclei, governs the primary interaction between a molecule and light [177]. In the present work we have computed the permanent electric dipole moment in the ground and excited electronic states of the ZrS molecule at the highest level of theory MRSDCI with the inclusion of spin

orbit effects. These results for the spin orbit electronic states in ZrS are shown in Tables XXXVI and XXXVII together with the results available in literature. The comparison between the present results of the dipole moment to the results available in literature [177] for the states $(X)^1\Sigma^+$ and $(3)^1\Sigma^+$ shows a very good agreement with a percentage relative difference of $0.9\% \leq \delta\mu/\mu \leq 1.3\%$. The other results of the permanent electric dipole moment for the spin orbit electronic states of the ZrS molecule are reported here for the first time in literature.

Table XXXVI:

Permanent dipole moments for the spin orbit electronic states Ω of the molecule ZrS at $R = 2.24\text{\AA}$.

State Ω	$\mu(\text{Debye})$	State Ω	$\mu(\text{Debye})$
(1) $0^+ [X]^1\Sigma^+$	4.759 ^a	(3) $2[(2)^3\Pi]$	6.204
(1) $2 [(1)^3\Delta]$	4.753	(4) $0^+ [(2)^3\Pi]$	6.250
(1) $3 [(1)^3\Delta]$	4.759	(7) $1 [(2)^3\Delta]$	4.701
(1) $1 [(1)^3\Delta]$	3.679	(2) $4 [(1)^1\Gamma]$	8.297
(2) $2 [(1)^1\Delta]$	2.520	(6) $2[(2)^3\Delta]$	4.583
(1) $0^- [(1)^3\Pi]$	3.677	(3) $3 [(2)^3\Delta]$	4.335
(2) $0^+ [(1)^3\Pi]$	3.707	(7) $2 [(2)^1\Delta]$	6.682
(2) $1[(1)^3\Pi]$	3.689	(8) $1 [(2)^1\Pi]$	5.358
(3) $2 [(1)^3\Pi]$	3.685	(4) $3 [(1)^1\Phi]$	5.940
(2) $0^- [(1)^3\Sigma^-]$	8.046	(5) $0^+ [(3)^1\Sigma^+]$	5.811
(3) $1 [(1)^3\Sigma^-]$	8.088	(8) $2 [(3)^3\Pi]$	0.374
(4) $1[(1)^1\Pi]$	5.628	(5) $3 [(2)^3\Phi]$	0.574
(4) $2 [(1)^3\Phi]$	6.543	(9) $1 [(3)^3\Pi]$	0.447
(2) $3[(1)^3\Phi]$	6.539	(4) $2 [(1)^3\Phi]$	0.262
(1) $4 [(1)^3\Phi]$	6.575	(6) $0^+ [(3)^3\Pi]$	0.417
(5) $1 [(1)^3\Sigma^+]$	1.047	(5) $0^- [(3)^3\Pi]$	0.417
(3) $0^- [(1)^3\Sigma^+]$	0.930	(3) $4 [(2)^3\Phi]$	0.261
(3) $0^+ [(2)^1\Sigma^+]$	5.508	(6) $3 [(2)^1\Phi]$	0.507
(6) $1 [(2)^3\Pi]$	5.934	(10) $1 [(3)^1\Pi]$	1.421
(4) $0^- [(2)^3\Pi]$	6.435	(10) $2 [(3)^3\Delta]$	0.908

a. First entry is for the values of the present work.

Table XXXVII:

Permanent dipole moments for the parent electronic states Λ of the molecule ZrS at $R = 2.24\text{\AA}$.

State $^{2s+1}\Lambda$	$ \mu (\text{Debye})$	$\delta\mu/\mu$	State $^{2s+1}\Lambda$	$ \mu (\text{Debye})$
$(X)^1\Sigma^+$	3.811 ^a	1.3%	$(2)^1\Phi$	0.909
	3.86 ^b			
$(1)^1\Delta$	3.011	0.9%	$(3)^1\Pi$	1.216
$(2)^1\Sigma^+$	4.811		$(1)^3\Delta$	5.100
$(1)^1\Gamma$	7.794		$(1)^3\Sigma^+$	0.793
$(2)^1\Delta$	5.104		$(2)^3\Delta$	3.131
$(3)^1\Sigma^+$	4.664		$(3)^3\Delta$	1.738
	4.71 ^b			
$(3)^1\Delta$	1.351	0.9%	$(1)^3\Pi$	3.943
$(4)^1\Delta$	4.397		$(1)^3\Phi$	6.177
$(1)^1\Pi$	5.247		$(2)^3\Pi$	6.035
$(1)^1\Phi$	5.559		$(3)^3\Pi$	0.910
$(2)^1\Pi$	5.680		$(2)^3\Phi$	0.819

a. First entry is for the values of the present work, b. Ref [177]

The variation of the electric dipole moment with nuclear geometry is important in resonant spectroscopy [38]. In Figure 34 we draw the variation of the permanent dipole moment with the internuclear distance for several low lying electronic states in ZrS. In this figure we notice that the molecule ZrS is mostly polar in the $(1)^3\Phi$ state with a permanent dipole moment value of $-8.77D$ at $R = 2.87\text{\AA}$. These results on the permanent electric dipole moment of ZrS are reported here for the first time in literature.

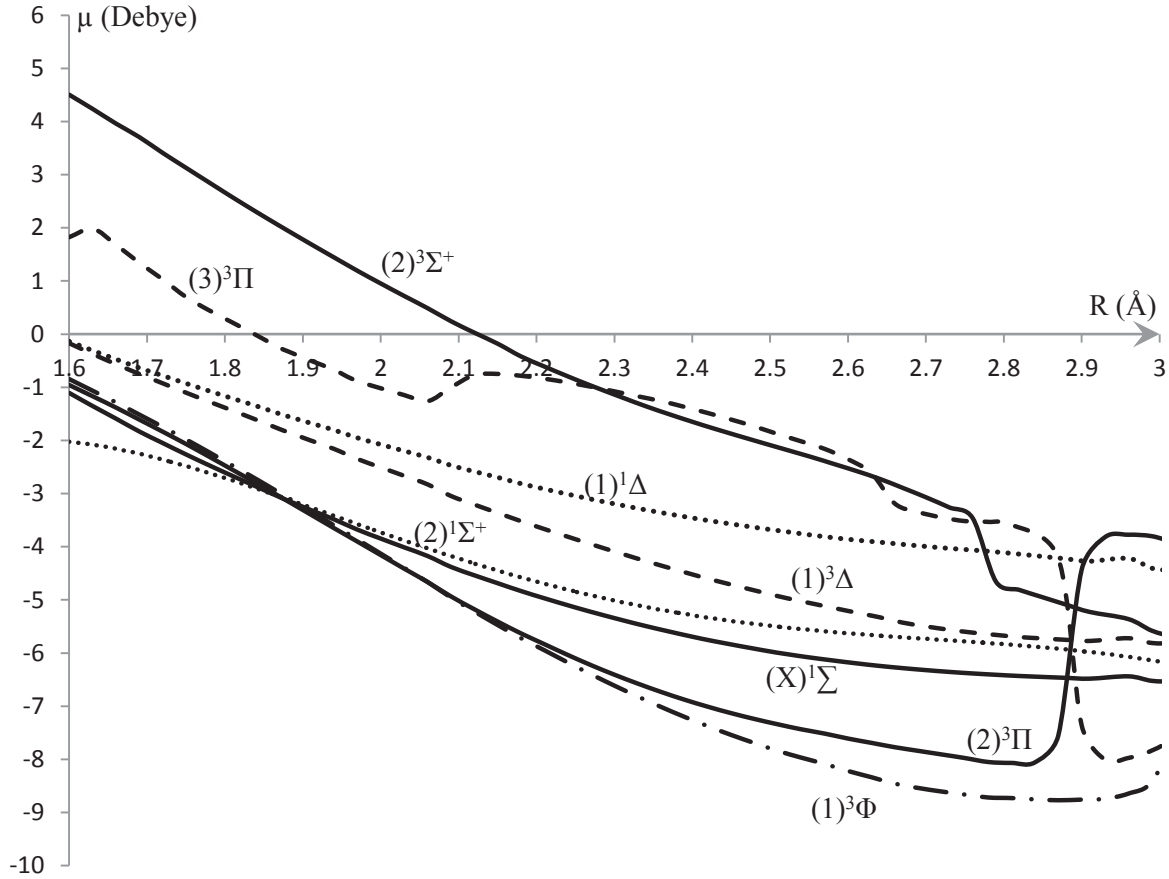


Fig. 34. Variation of the permanent dipole moment in (Debye) as a function of the internuclear distance R (Å) for the states $(X)^1\Sigma^+$, $(2)^3\Pi$, $(3)^3\Pi$, $(1)^1\Delta$, $(1)^3\Delta$, $(2)^1\Sigma^+$, $(2)^3\Sigma^+$, $(1)^3\Phi$.

III. D. 6. The Internal Molecular Electric Field in ZrS

Internal molecular electric fields are important in the search for the electric dipole moment of the electron eEDM (d_e). The longest running molecular search for d_e uses the ground $X^2\Sigma^+_{1/2}$ ($v = 0$, $N = 0$) state of ^{174}YbF at Imperial College in the group of E. Hinds [178]. At Yale Demille's group [179-181] used PbO, with an electric field value of $\epsilon_{\text{eff}} \sim 29$ GV/cm [44, 178, 182]. Molecules suitable for an eEDM experiment are preferred to have a large rotational constant, small or vanishing nuclear spin, with deeply bound molecular electronic states [183]. A possible use for the ZrS molecule in an eEDM experiment largely relies on its internal molecular electric field. Therefore, we have decided in the present work to compute

the internal molecular electric field in various electronic states of the ZrS molecule at the highest level of theory MRSDCI. These results are reported here for the first time in literature in Table XXXVIII.

Table XXXVIII:

Internal Molecular Electric Field for the electronic states of ZrS at $R = 2.23 \text{ \AA}$.

State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} $ (GV/cm)	State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} $ (GV/cm)
(X) $^1\Sigma^+$	0.239	(2) $^1\Pi$	0.023
(1) $^1\Delta$	0.253	(1) $^3\Delta$	0.189
(2) $^1\Sigma^+$	0.068	(2) $^3\Sigma^+$	0.104
(1) $^1\Gamma$	0.036	(2) $^3\Delta$	0.038
(2) $^1\Delta$	0.081	(1) $^3\Gamma$	0.113
(3) $^1\Sigma^+$	0.044	(1) $^3\Pi$	0.124
(3) $^1\Delta$	0.066	(1) $^3\Phi$	0.021
(4) $^1\Delta$	0.081	(2) $^3\Pi$	0.023
(1) $^1\Pi$	0.048	(3) $^3\Pi$	0.194
(1) $^1\Phi$	0.006	(2) $^3\Phi$	0.198

The largest value of the molecular electric field in ZrS is attained in its ground electronic state with a value of 0.239 GV/cm. This electric field is smaller than that attained in the ground state of ZrN and larger than that in the ground state of YN. The present values of the molecular electric field could be compared, for example, to the value of 1.43 GV/cm in HI^+ [184] and to the value of 26 GV/cm in YbF [43] which have been already suggested as suitable candidates for an eEDM experiment. A possible use of ZrS in an eEDM experiment cannot be guaranteed unless provided that the experimental scheme is improved to reach much better accuracies.

III. E. The Structure of Yttrium Sulfide YS

III. E. 1. Preliminary Works on YS

It has been long established that transition metals play an important role in many fields, including catalysis, organic synthesis, stellar atmospheres, and cosmochemistry [185]. Of particular interest are the 4d-row of transition metals, which have relatively large natural abundance because of their production in non-explosive nucleosynthesis [186]. Also, the 3d-orbitals of these metals have energies comparable to the 2p orbitals of oxygen, nitrogen and carbon [186]. Therefore quite interesting simple compounds of these elements possess a mixture of ionic and covalent bondings [187, 188]. In astrophysics, the presence of Yttrium mono-sulfide in stellar atmospheres is possible as a similar diatomic, Zirconium sulfide has been identified as the carrier of the Keenan bands in the spectrum of cool S-type stars [170]. These molecules are useful for examining bonding schemes in simple metal systems which

then can be generalized to bulk properties [189, 190]. Transition metal sulfides are another class of interesting 4d molecules. Unlike the oxides, these species are not well studied experimentally or theoretically.

The spectra and structure of Yttrium mono-sulfide YS has been the subject of a limited number of theoretical and experimental studies. The Experimental observations of the spectra of this molecule revealed the existence of strong perturbations leading to unobvious assignment of the perturbing states [191, 192]. In literature 5 states have been studied experimentally and theoretically without spin orbit effect [148, 193-198]. Kowalczyk *et al.* [199] performed a high resolution excitation spectrum of gaseous YS and reported the (0, 0) band of the $(1)^2\Pi_{1/2} \leftarrow X^2\Sigma^+$ transition, which was rotationally analyzed, and a set of spectroscopic constants were then given. More recently, Steimle and Virgo [192] studied the optical Stark effect in the (0, 0) vibrational band in the $(1)^2\Pi_{1/2} \leftarrow X^2\Sigma^+$ transition of YS molecule, and calculated the magnitude of the permanent dipole moment for the $(1)^2\Pi_{1/2}$ and $(1)^2\Pi_{3/2}$ states. The electronic structure of the YS molecule is thus far from complete. The present investigation is devoted to the prediction of the electronic structure of the YS molecule at the highest level of theory including the spin orbit effects.

III. E. 2. Results on YS

The calculations have been performed in the range $2.1\text{\AA} \leq R \leq 2.90\text{\AA}$ for 54 electronic states in the representation $\Omega^{(\pm)}$ (including spin orbit effects). The PECs for the symmetries $\Omega = 1/2, 3/2, 5/2, 7/2, 9/2$ are drawn respectively in figures (35-38). Within the considered internuclear distance range several crossings and avoided crossings have been recorded between the potential energy curves of different electronic states. Their positions R_{AC} , their corresponding parent states and the energy difference ΔE_{AC} between the states $(n+1)\Omega/(n)\Omega$ at the crossing/avoided-crossing points are displayed in Table XXXIX. The composition in percentage of the Ω state-wave functions in terms of the Λ states, calculated at the equilibrium internuclear distance of the ground electronic state $R = 2.32\text{\AA}$, is presented in Table XXXX. For each state Ω there is a predominant component Λ with a contribution larger than 80% so that a main parent SA may be identified. Nevertheless, there are states for which a small but significant contribution of other Λ , than the dominant one is obtained.

By fitting the calculated energy values of the different investigated electronic states into a polynomial in R around the minimum, the harmonic frequencies ω_e , the equilibrium internuclear distances R_e , the rotational constants B_e , and the transition energies with respect to the minimum energy of the ground states T_e have been calculated. These values for the

states $\Omega^{(+/)}$ are displayed in Table XXXXI along with the available experimental values in literature.

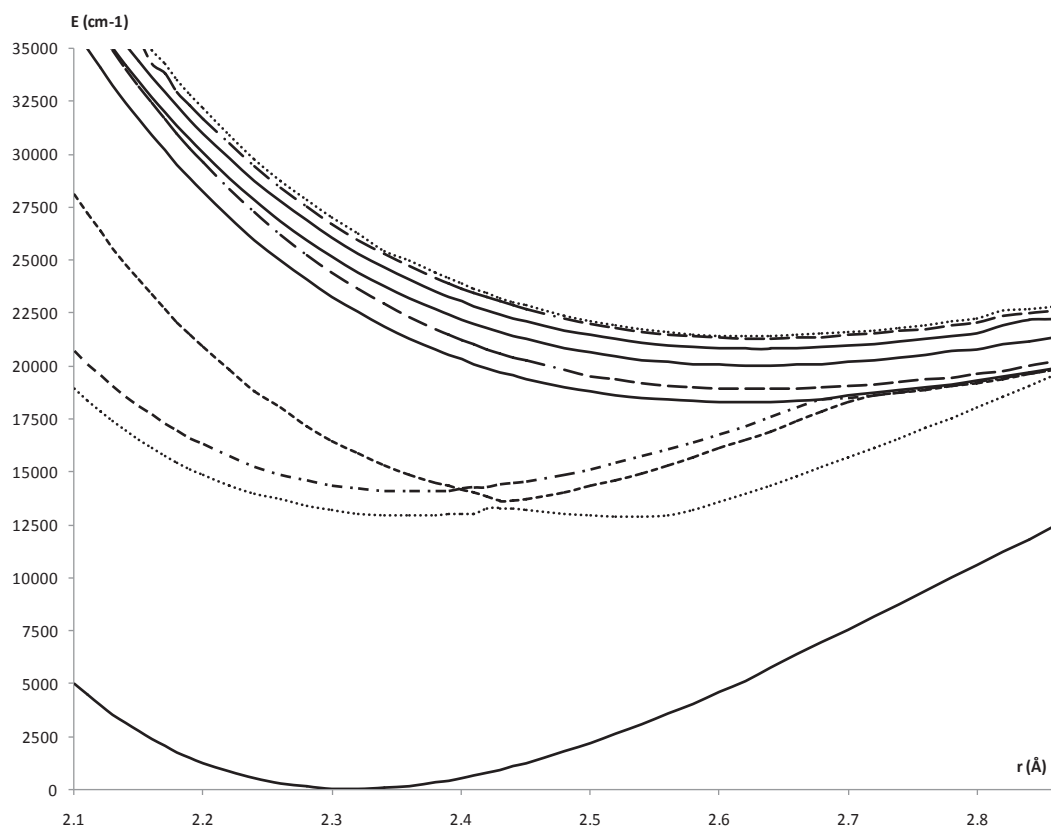


Fig. 35: Potential energy curves for 10 states $\Omega = 1/2$ of the molecule YS.

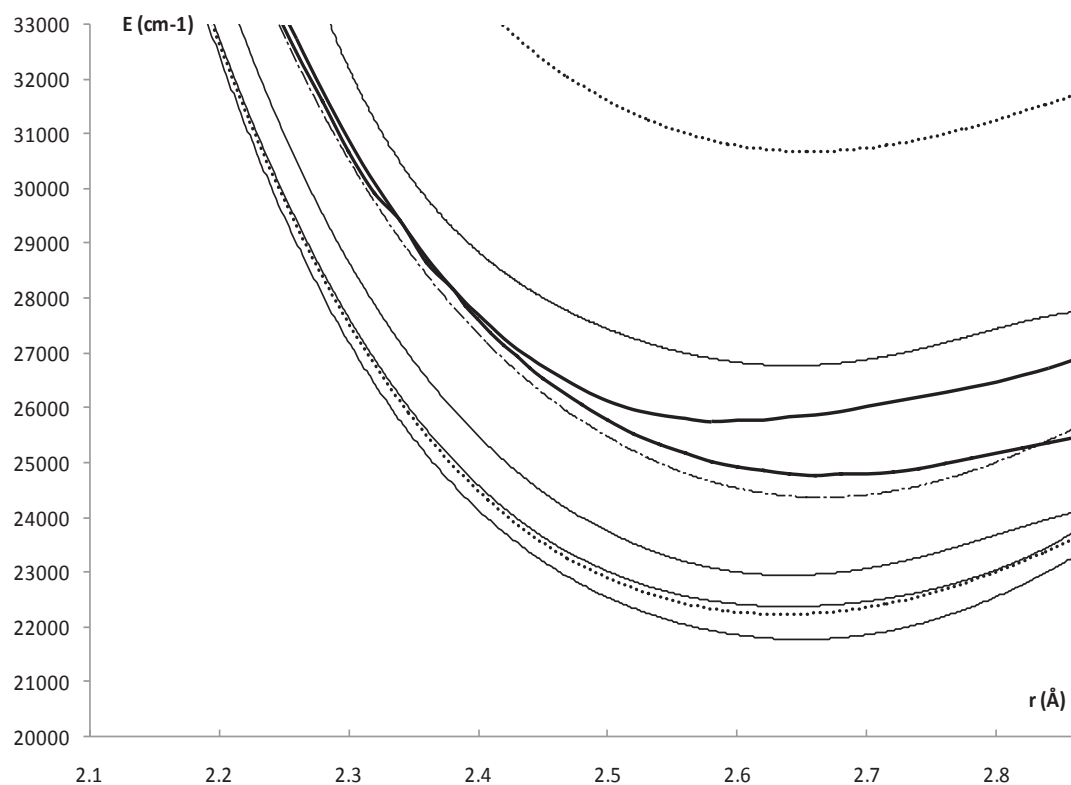


Fig. 36: Potential energy curves for 9 states $\Omega = 1/2$ of the molecule YS.

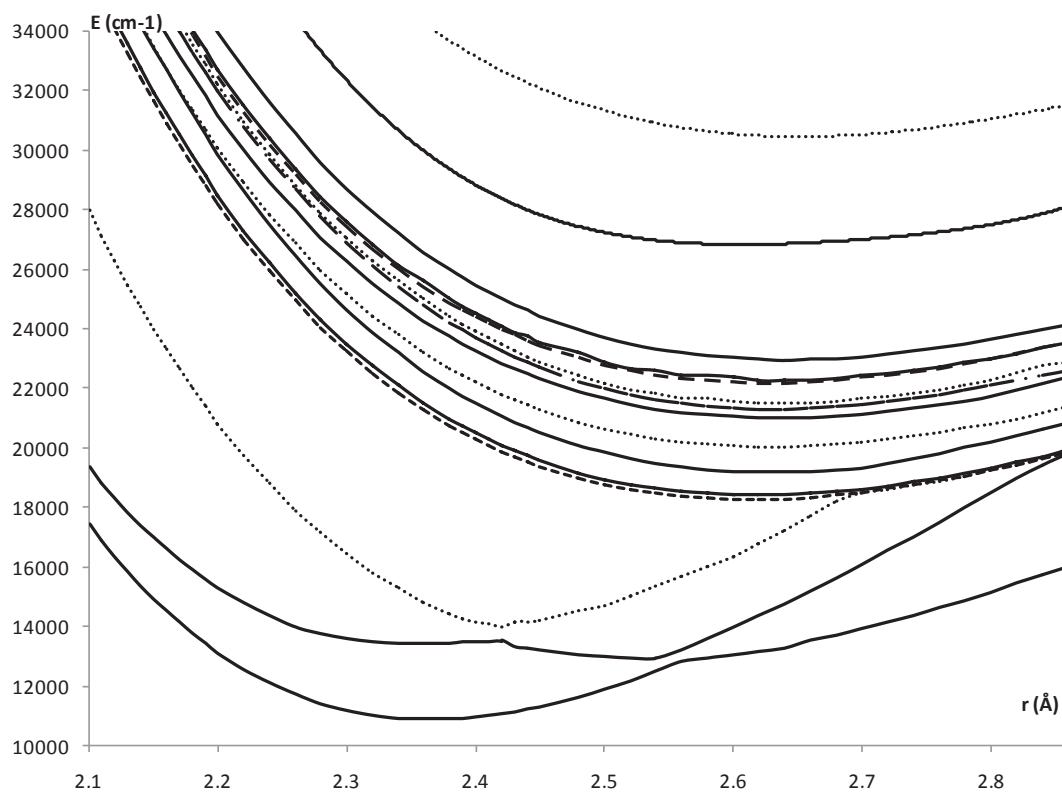


Fig. 37: Potential energy curves for 15 states $\Omega = 3/2$ of the molecule YS

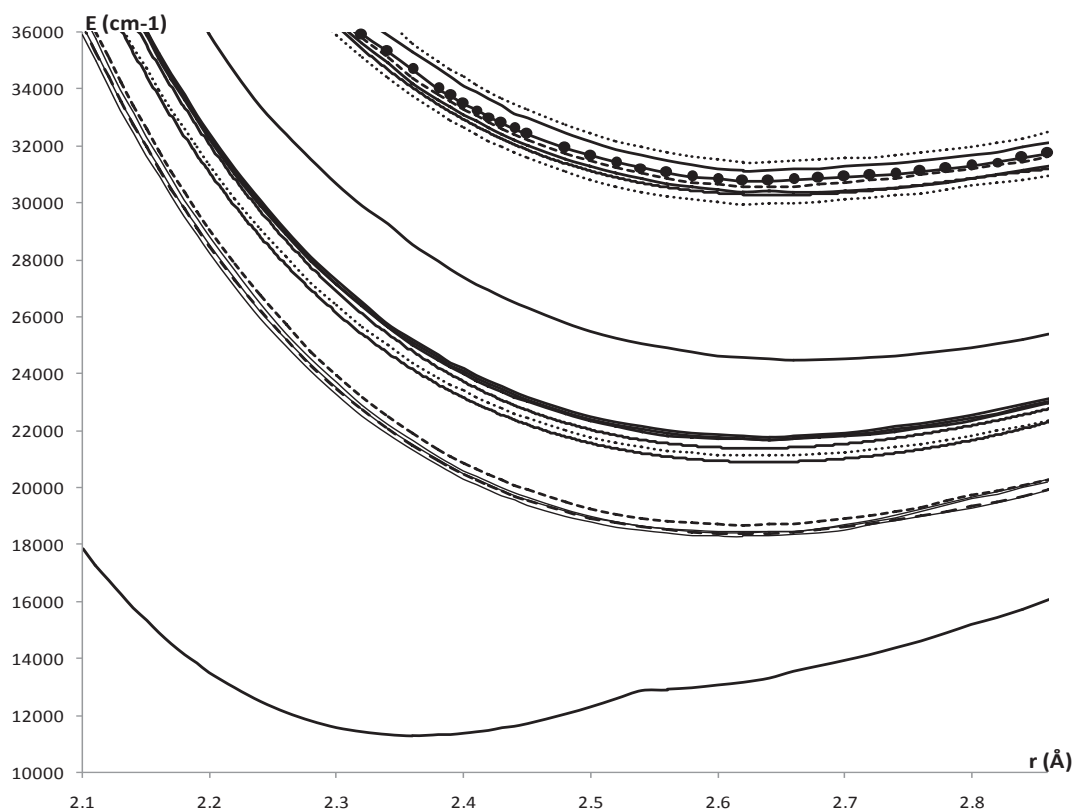


Fig. 38: Potential energy curves for the states $\Omega = 5/2$ (11-full lines), $\Omega = 7/2$ (8-dotted lines), $\Omega = 9/2$ (1 - $\bullet$ -) of the molecule YS.

Table XXXIX: Positions of the avoided crossings R_{AC} and the energy difference ΔE_{AC} at these points with the corresponding avoided crossings and crossings of Λ states for Ω states of the YS molecule.

Ω	$(n+1)\Omega/n\Omega$	$R_{AC} (\text{\AA})$	$\Delta E_{AC} (\text{cm}^{-1})$	Avoided crossing of Λ states	Crossings of Λ states
3/2	2 / 3	2.42	506.9	(1) ² Π and (2) ² Π	
	2 / 5	2.86	132.6		(2) ² Π /(1) ⁴ Φ
	3 / 5	2.71	132.8	(2) ² Π and (4) ² Π	
	1 / 2	2.56	415.4		(1) ² Δ / (1) ² Π
1/2	2 / 4	2.43	334.7	(1) ² Π and (2) ² Π	
	2 / 5	2.86	672.2		(2) ² Π /(1) ⁴ Φ
	4 / 6	2.71	527.2	(2) ² Π and(3) ² Π	
	3 / 5	2.67	548.5		(2) ² Σ^+ /(1) ⁴ Π

Table XXXX:Composition of Ω -state wave functions of the molecule YS, in terms of Λ -states (in percentage) at $R = 2.32 \text{\AA}$

Ω	% (Λ -parent)	Ω	% (Λ -parent)
(1)1/2	99.9 % $X^2\Sigma^+$	(11)3/2	62.29% (4) ² Π ; 31.34%(2) ⁴ Π ;6%(1) ⁴ Σ
(2)1/2	96.64% (1) ² Π ; 3.36 % (2) ² Σ^+	(12) 3/2	72.3%(2) ⁴ Π ; 22.25%(1) ⁴ Σ^- ; 3.2%(4) ² Π
(3)1/2	96.69% (2) ² Σ^+ ; 3.31% (1) ² Π	(13)3/2	99%(5) ² Π ; 0.61%(2) ² Δ ; 0.39%(3) ² Δ
(4)1/2	100% (2) ² Π	(14)3/2	99.84%(6) ² Π ; 0.16%(1) ⁴ Σ^+
(5)1/2	100% (1) ⁴ Π	(15)3/2	100%(2) ⁴ Δ
(6)1/2	99.08% (3) ² Π ; 0.56%(1) ⁴ Σ^+ ; 0.12(3) ² Σ^+	(1)5/2	99.99% (1) ² Δ
(7)1/2	98.87% (1) ⁴ Σ^+ ; 0.38% (1) ⁴ Π ; 0.75%(3) ² Π	(2)5/2	99.48% (1) ⁴ Π ; 0.16% (1) ⁴ Δ
(8)1/2	91.91%(1) ⁴ Δ ; 6.3%(1) ⁴ Δ ; 1.75%(2) ⁴ Π	(3)5/2	100% (1) ⁴ Φ
(9)1/2	96.42%(3) ² Σ^+ ; 1.1% (4) ² Π ; 0.53%(5) ² Π	(4)5/2	98.57%(1) ² Φ ; 1.43(2) ² Δ
(10) 1/2	75.21%(1) ⁴ Σ ; 23.24%(2) ⁴ Π ; 1.54%(1) ⁴ Δ	(5)5/2	97.56%(1) ⁴ Δ ; 0.6%(2) ² Π ; 0.06%(1) ⁴ Φ
(11)1/2	18% (3) ² Σ^+ ; 41.16% (4) ² Π ; 9.95%(2) ⁴ Π ;30%(1) ⁴ Σ^-	(6)5/2	97.7%(2) ² Δ ; 2%(2) ² Φ ; 0.3%(1) ⁴ Δ
(12) 1/2	86%(2) ⁴ Π ; 12%(1) ⁴ Σ^- ; 2%(1) ² Σ^-	(7)5/2	96.33%(2) ² Φ ; 0.92%(4) ² Π ; 1.74%(2) ² Δ
(13) 1/2	97.69% (1) ² Σ^- ; 1.59%(3) ² Σ^+ ; 0.72% (5) ² Π	(8) 5/2	100%(2) ⁴ Π
(14)1/2	98.68%(5) ² Π ; 0.92%(1) ⁴ Σ^- ; 0.4%(3) ² Σ^+	(9)5/2	99.97%(3) ² Δ ; 0.03%(3) ² Φ
(15)1/2	98.81%(2) ² Σ^- ; 0.26%(5) ² Π ; 0.93%(4) ² Σ^+	(10)5/2	97.93%(2) ⁴ Δ ; 1.69%(1) ⁴ Γ ; 0.38%(3) ² Φ
(16)1/2	98.3%(4) ² Σ^+ ; 1.7%(2) ² Σ^-	(11)5/2	97.74%(1) ⁴ Γ ; 0.4%(3) ² Φ ; 1.86%(2) ² Δ
(17)1/2	98%(2) ² Σ^- ; 1.78%(4) ² Σ^+ ; 0.22%(5) ² Π	(1)7/2	98.19% (1) ⁴ Φ ; 1.81%(1) ² Φ
(18)1/2	99.81%(6) ² Π ; 0.19(3) ² Σ^+	(2)7/2	99.29% (1) ² Φ ; 0.01% (1) ⁴ Φ
(19)1/2	100%(2) ⁴ Δ	(3)7/2	99.45%(1) ⁴ Δ ; 0.55%(2) ⁴ Π
(2)3/2	99.71% (1) ² Π ; 0.29% (2) ² Δ	(4) 7/2	99.22%(2) ² Φ ; 0.38%(1) ² Φ ; 0.4%(1) ⁴ Σ^-
(3)3/2	99.99% (2) ² Π	(5)7/2	99.62%(2) ⁴ Δ ; 0.38%(3) ² Φ
(4)3/2	99.27% (1) ⁴ Π ; 0.58% (1) ⁴ Σ^+ ; 0.15% (3) ² Π	(6)7/2	96.03%(3) ² Φ ; 3.63%(1) ⁴ Γ
(5)3/2	99.92% (1) ⁴ Φ ; 0.08%(1) ⁴ Δ	(7)7/2	96.03%(3) ² Φ ; 3.63%(1) ⁴ Γ
(6)3/2	99.71% (3) ² Π ; 0.09%(1) ⁴ Σ^+ ; 0.2%(4) ² Π	(8) 7/2	100% (3) ² Φ
(7)3/2	97.93% (1) ⁴ Σ^+ ; 0.47%(3) ² Π ; 0.94%(1) ⁴ Σ^-	(1)9/2	97.88%(1) ⁴ Γ ; 2.08%(3) ² Φ
(8)3/2	96.92%(1) ⁴ Δ ; 0.15%(1) ⁴ Σ^- ; 2.1%(2) ⁴ Π		
(9)3/2	98.56%(2) ² Δ ; 0.99%(4) ² Π ; 0.45%(5) ² Π ;		
(10)3/2	91.4%(1) ⁴ Σ^- ; 7.04%(2) ⁴ Π ; 0.79%(1) ⁴ Σ^+		

Table XXXXI:

Equilibrium internuclear distances R_e , transition energies T_e , rotational constants B_e and harmonic frequencies, ω_e , for Ω states of the molecule YS.

(n) $\Omega[(k)^{2S+1}\Lambda]$	T_e (cm ⁻¹)	δT_e / T_e	R_e (Å)	δR_e / R_e	B_e (cm ⁻¹)	δB_e / B_e	ω_e (cm ⁻¹)	$\delta \omega_e$ / ω_e
(1) 1/2 [$X^2\Sigma^+$]	0.00 ^a		2.311 ^a 2.2802 ^{(DF) b} 2.2717 ^{(Exp) b} 2.3003 ^c		0.134 ^a		500.64 ^a 461 ^{(DF) b} 492.7 ^d 508 ^c	
(2) 1/2 [(1) ² Π] 1 st Min	12907.69 13312.744 ^{(v=0) e}	3.04%	2.356	1.3% 1.4% 0.5%	0.129 0.1340093 ^b		505.55	8.5% 1.6% 1.4%
2 nd Min	12798.84		2.523		0.112		604.12	
(3) 1/2 [(2) ² Σ^+]	14104.72		2.371		0.126		440.67 449.7 ^d	2.0%
(4) 1/2 [(2) ² Π]	14332.98		2.409		0.123		656.78	
(5) 1/2 [(1) ⁴ Π]	18289.45		2.613 2.49510 ^b	4.71%	0.104		347.72 365.3 ^{cb}	4.8%
(6) 1/2 [(3) ² Π]	18899.59		2.662		0.101		475.75	
(7) 1/2 [(1) ⁴ Σ^+]	20065.50		2.609		0.105		304.50	
(8) 1/2 [(1) ⁴ Δ]	20787.11		2.619		0.104		417.08	
(9) 1/2 [(3) ² Σ^+]	21316.85		2.634		0.103		252.26	
(10) 1/2 [(1) ⁴ Σ^-]	21418.52		2.619		0.104		367.26	
(11) 1/2 [(2) ⁴ Π]	21754.82		2.646		0.102		385.60	
(12) 1/2 [(2) ⁴ Π]	22240.70		2.627		0.104		305.83	
(13) 1/2 [(1) ² Σ^-]	22369.98		2.642		0.102		408.56	
(14) 1/2 [(5) ² Π]	22905.37		2.616		0.104		473.20	
(15) 1/2 [(2) ² Σ^-]	24389.25		2.651		0.102		329.48	
(16) 1/2 [(4) ² Σ^+]	24729.93		2.754		0.094		877.48	
(17) 1/2 [(2) ² Σ^-]	25679.54		2.558		0.109		661.27	
(18) 1/2 [(6) ² Π]	26844.20		2.553		0.109		843.83	
(19) 1/2 [(2) ⁴ Δ]	30688.87		2.649		0.102		361.35	
(1) 3/2 [(1) ² Δ]	11287.94		2.361		0.128		461.66	
(2) 3/2 [(1) ² Π] 1 st Min	13388.89		2.344		0.130		523.28	
2 nd Min	12885.64		2.501		0.114		591.64	
(3) 3/2 [(2) ² Π]	14332.98		2.409		0.123		656.78	
(4) 3/2 [(1) ⁴ Π]	18269.57		2.612		0.105		343.17	
(5) 3/2 [(1) ⁴ Φ]	18373.58		2.614		0.105		429.76	
(6) 3/2 [(3) ² Π]	20088.66		2.636		0.145		285.47	
(7) 3/2 [(1) ⁴ Σ^+]	19167.98		2.645		0.102		400.45	
(8) 3/2 [(1) ⁴ Δ]	21046.75		2.636		0.103		168.26	
(9) 3/2 [(2) ² Δ]	21240.50		2.615		0.104		514.01	
(10) 3/2 [(1) ⁴ Σ^-]	21665.12		2.552		0.109		409.34	
(11) 3/2 [(4) ² Π]	22220.06		2.619		0.104		305.97	
(12) 3/2 [(2) ⁴ Π]	22253.21		2.599		0.106		510.38	
(13) 3/2 [(5) ² Π]	23072.91		2.726		0.987		76.635	
(14) 3/2 [(6) ² Π]	26701.88		2.588		0.107		575.88	
(15) 3/2 [(2) ⁴ Δ]	30535.53		2.652		0.120		642.55	
(1) 5/2 [(1) ² Δ]	12972.40		2.506		0.114		526.98	
(2) 5/2 [(1) ⁴ Π]	18275.41		2.613		0.105		364.31	
(3) 5/2 [(1) ⁴ Φ]	18418.89		2.628		0.103		336.18	
(4) 5/2 [(1) ² Φ]	18411.94		2.621		0.104		417.90	
(5) 5/2 [(1) ⁴ Δ]	20857.19		2.617		0.104		492.60	
(6) 5/2 [(2) ² Δ]	21375.56		2.616		0.104		384.13	
(7) 5/2 [(2) ² Φ]	21501.41		2.612		0.105		731.26	

(8) 5/2 [(2) ⁴ Π]	21865.52	2.661	0.101	309.40
(9) 5/2 [(3) ² Δ]	24464.19	2.649	0.102	602.96
(10) 5/2 [(2) ⁴ Δ]	30180.29	2.646	0.102	329.48
(11) 5/2 [(1) ⁴ Γ]	30305.22	2.627	0.103	324.53
(1) 7/2 [(1) ⁴ Φ]	18353.11	2.614	0.105	424.57
(2) 7/2 [(1) ² Φ]	18701.22	2.624	0.104	320.35
(3) 7/2 [(1) ⁴ Δ]	21125.70	2.626	0.104	337.05
(4) 7/2 [(2) ² Φ]	21682.70	2.626	0.104	355.96
(5) 7/2 [(2) ⁴ Δ]	30088.53	2.595	0.106	366.91
(6) 7/2 [(1) ⁴ Γ]	30388.10	2.642	0.102	332.72
(8) 7/2 [(3) ² Φ]	31501.81	2.595	0.106	615.47
(1) 9/2 [(1) ⁴ Γ]	30859.21	2.621	0.103	297.13

Ref: (a), first entry is for the values of the present work (b) Ref [191] (c)Ref [148] (d) Ref [195]

(e) Ref [199]

Note: DF(b); Density Functional calculations in Ref(b)

Exp(b); Experimental results in Ref(b)

Note: (v =0) (b) results are for the zero vibrational level in Ref b.

To the best of our knowledge, there are experimental values for the spin orbit calculations of the YS molecule for only the two states (1)²Π_{1/2} and the (1)⁴Π_{1/2} [151, 194]. The comparison between these values and those of the present work shows an excellent agreement. The transition energy T_e and the rotational constant B_e of the (1)²Π_{1/2} [151] are very close to our calculated values with relative differences of δT_e/T_e=3.04% and δB_e/B_e=3.85% respectively. The comparison of our calculated value of R_e for the (5)Ω=1/2 [(1)⁴Π] state with that of McIntyre *et al.* [192] shows an excellent agreement with a relative difference δR_e/R_e=4.71%.

III. E. 3. The Nature of Bonding in YS

In the present section we discuss the bonding in the neutral YS molecule. The percentage composition of molecular electronic states in terms of molecular orbital configurations are shown in Table XXXXII. The percentage weights of each molecular orbital configuration are calculated as the squares of the corresponding CI coefficients. Configuration weights lower than 2% percent have been omitted from the results of Table XXXXII. The ground electronic state arises from the distribution of seven valence electrons over the molecular orbital configurations 1σ²1π⁴2σ¹ and 1σ²2σ¹1π³3π¹ with percentages of 85% and 5%, respectively.

Excited molecular states arise from the promotion of electrons into the active molecular orbital space by single and double excitations. In order to completely describe the bonding in the ground electronic state of the neutral YS molecule, we calculate in the following section the effective bond order EBO, which was given earlier in equation (1) of this chapter. A better definition of the effective bond order can be obtained by considering the occupation numbers of bonding and antibonding natural orbitals derived from multiconfigurational wave functions.

Table XXXII:Leading configurations of the $^{2s+1}\Lambda^\pm$ states of YS at $R = 2.32\text{\AA}$.

Electronic State	Weight
$X^2\Sigma^+$	85% $1\sigma^2 1\pi^4 2\sigma^1$, 5% $1\sigma^2 2\sigma^1 1\pi^3 3\pi^1$
$(1)^2\Delta$	90% $1\sigma^2 1\delta^1 1\pi^4$
$(2)^2\Sigma^+$	85% $1\sigma^2 3\sigma^1 1\pi^4$, 5.5% $1\sigma^2 3\sigma^1 1\pi^3 2\pi^1$
$(2)^2\Delta$	97% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$
$(3)^2\Sigma^+$	92% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$
$(3)^2\Delta$	68% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$, 21% $1\sigma^2 1\delta^1 1\pi^3 2\pi^1$
$(4)^2\Sigma^+$	66% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$, 7% $1\sigma^2 1\pi^3 2\pi^1 1\delta^1$, 11% $1\sigma^2 2\sigma^1 1\pi^3 3\pi^1$
$(1)^2\Gamma$	97% $1\sigma^2 1\delta^1 1\pi^3 2\pi^1$
$(1)^2\Pi$	88% $1\sigma^2 2\sigma^2 1\pi^3$
$(2)^2\Pi$	85% $1\sigma^2 1\pi^4 2\pi^1$, 5% $1\sigma^2 1\pi^3 2\pi^1 3\pi^1$
$(1)^2\varphi$	99% $1\sigma^2 2\sigma^1 1\delta^1 1\pi^3$
$(3)^2\Pi$	96% $1\sigma^2 2\sigma^1 1\delta^1 1\pi^3$
$(2)^2\varphi$	72% $1\sigma^2 2\sigma^1 1\delta^1 1\pi^3$, 5% $1\sigma^2 1\delta^1 3\sigma^1 1\pi^3$
$(4)^2\Pi$	81% $1\sigma^2 2\sigma^1 1\delta^1 1\pi^3$, 4% $1\sigma^2 2\sigma^1 3\sigma^1 1\pi^3$, 6% $1\sigma^2 3\sigma^1 1\delta^1 1\pi^3$, 4% $1\sigma^2 3\sigma^2 1\pi^3$
$(5)^2\Pi$	93% $1\sigma^2 2\sigma^1 3\sigma^1 1\pi^3$
$(6)^2\Pi$	66% $1\sigma^2 2\sigma^1 3\sigma^1 1\pi^3$, 11% $1\sigma^2 3\sigma^2 1\pi^3$, 11% $1\sigma^2 1\pi^3 1\delta^2$, 7% $1\sigma^2 1\pi^3 2\pi^2$
$(3)^2\varphi$	87% $1\sigma^2 1\delta^1 3\sigma^1 1\pi^3$, 10% $1\sigma^2 1\pi^3 3\pi^1$
$(1)^4\Sigma^+$	98% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$
$(1)^4\Delta$	98% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$
$(2)^4\Delta$	98% $1\sigma^2 1\delta^1 1\pi^3 2\pi^1$
$(1)^4\Gamma$	100% $1\sigma^2 1\delta^1 1\pi^3 2\pi^1$
$(1)^4\Pi$	97% $1\sigma^2 2\sigma^1 1\delta^1 1\pi^3$, 2.5% $1\sigma^2 2\sigma^1 3\sigma^1 1\pi^3$
$(1)^4\varphi$	99% $1\sigma^2 2\sigma^1 1\delta^1 1\pi^3$
$(2)^4\Pi$	96% $1\sigma^2 2\sigma^1 3\sigma^1 1\pi^3$
$(1)^4\Sigma^-$	98% $1\sigma^2 2\sigma^1 1\pi^3 2\pi^1$

Weights (in percent) are obtained from the square of the corresponding

^a configuration interaction coefficients (CMRCI) weights lower than 2% are not reported.

In our CASSCF calculations we obtained the ground state of YS by distributing the 7 valence electrons over the active space of molecular orbitals. The occupation numbers of bonding molecular orbitals are given by the number η_b and those in the antibonding molecular orbitals are given by η_{ab} . In this treatment we obtained the occupation numbers of the bonding and anti-bonding orbitals in the following way: $\eta_b(1\sigma) = 2.0$, $\eta_b(2\sigma) = 0.69155$, $\eta_{ab}(3\sigma) = 0.21479$, $\eta_{ab}(1\delta) = 0.50744$, $\eta_{ab}(4\sigma) = 0.00289$, $\eta_b(1\pi) = 3.08152$, $\eta_{ab}(2\pi) = 0.4582$, $\eta_{ab}(3\pi) = 0.0436$. This gives an effective bond order EBO of $2.27 \approx 2$, thus indicating that the bonding in YS is a double bond.

III. E. 4. The Vibrational Structure of YS

The time independent vibrational-rotational Schrödinger equation have been solved by using the canonical functions approach [34, 35] in the vicinity of the potential energy curves obtained by MRSDCI+Q calculations for the molecule YS. A part of these results are shown in Table XXXXIII, while the rest are left for Appendix II. To the best of our knowledge there

are no results available in literature on the vibrational structure of the spin orbit electronic states in the YS molecule.

Table XXXIII:

Values of the eigenvalues E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, the rotational constants B_v and the centrifugal distortion constants D_v for the different vibrational levels of the states (1) $1/2 [X^2\Sigma^+]$, (3) $3/2 [(2)^2\Pi]$ and (4) $1/2 [(2)^2\Pi]$.

(1) $1/2 [X^2\Sigma^+]$					
v	$E_v(\text{cm}^{-1})$	$R_{\min}(\text{\AA})$	$R_{\max}(\text{\AA})$	$B_v \times 10^1(\text{cm}^{-1})$	$D_v \times 10^8(\text{cm}^{-1})$
0	237.07 ^a	2.26 ^a	2.37 ^a	1.323 ^a	4.071 ^a
1	713.24	2.22	2.42	1.319	4.081
2	1186.97	2.20	2.45	1.314	4.088
3	1658.31	2.18	2.47	1.310	4.102
4	2127.17	2.17	2.50	1.305	4.085
5	2593.86	2.16	2.52	1.301	4.145
6	3057.83	2.14	2.54	1.296	4.079
7	3519.75	2.13	2.56	1.292	4.179
8	3978.96	2.12	2.58	1.288	4.126
(3) $3/2 [(2)^2\Pi]$					
v	$E_v(\text{cm}^{-1})$	$R_{\min}(\text{\AA})$	$R_{\max}(\text{\AA})$	$B_v \times 10^1(\text{cm}^{-1})$	$D_v \times 10^8(\text{cm}^{-1})$
0	14409.47 ^a	2.38 ^a	2.46 ^a	1.207 ^a	1.827 ^a
1	15020.55	2.35	2.52	1.191	2.475
2	15578.72	2.33	2.57	1.189	3.028
3	16100.22	2.31	2.58	1.181	2.979
4	16603.55	2.30	2.61	1.175	2.993
5	17097.77	2.28	2.63	1.175	3.083
6	17584.29	2.27	2.65	1.169	3.010
7	18064.27	2.26	2.67	1.164	5.491
(4) $1/2 [(2)^2\Pi]$					
v	$E_v(\text{cm}^{-1})$	$R_{\min}(\text{\AA})$	$R_{\max}(\text{\AA})$	$B_v \times 10^1(\text{cm}^{-1})$	$D_v \times 10^8(\text{cm}^{-1})$
0	14615.05 ^a	2.37 ^a	2.45 ^a	1.218 ^a	1.657 ^a
1	15260.79	2.34	2.51	1.198	2.594
2	15825.43	2.32	2.54	1.197	3.057
3	16351.53	2.30	2.58	1.187	3.023
4	16856.67	2.29	2.60	1.179	3.295
5	17346.22	2.28	2.62	1.177	3.071
6	17828.43	2.26	2.65	1.170	3.276

a. First entry is for the values of the present work

III. E. 5. The Permanent Dipole Moment of YS

The expectation values for the permanent electric dipole moments were calculated at the highest level of MRSDCI calculations with the inclusion of spin orbit effects. The results for these calculations at the equilibrium internuclear distance of the ground electronic state are

reported in Table XXXIV. To the best of our knowledge there are no results available in literature on the permanent electric dipole moment in the spin orbit component states of the molecule YS.

Table XXXIV:

Permanent electric dipole moments for the electronic states of the molecule YS at $R = 2.32 \text{ \AA}$.

State Ω	$ \mu (\text{Debye})$	State Ω	$ \mu (\text{Debye})$
(1) 1/2 [$X^2\Sigma^+$]	6.781	(7) 3/2 [$(1)^4\Sigma^+$]	3.082
(1) 3/2 [$(1)^2\Delta$]	11.822	(7) 1/2 [$(1)^4\Sigma^+$]	0.773
(1) 5/2 [$(1)^2\Delta$]	11.835	(6) 3/2 [$(3)^2\Pi$]	0.775
(2) 1/2 [$(1)^2\Pi$]	8.197	(8) 1/2 [$(1)^4\Delta$]	0.871
(2) 3/2 [$(1)^2\Pi$]	8.054	(5) 5/2 [$(1)^4\Delta$]	0.902
(3) 1/2 [$(2)^2\Sigma^+$]	8.012	(8) 3/2 [$(1)^4\Delta$]	0.884
(3) 3/2 [$(2)^2\Pi$]	2.264	(3) 7/2 [$(1)^4\Delta$]	0.938
(4) 1/2 [$(2)^2\Pi$]	2.185	(9) 1/2 [$(3)^2\Sigma^+$]	0.780
(4) 3/2 [$(1)^4\Pi$]	5.916	(9) 3/2 [$(2)^2\Delta$]	0.375
(2) 5/2 [$(1)^4\Pi$]	5.977	(6) 5/2 [$(2)^2\Delta$]	0.463
(1) 7/2 [$(1)^4\Phi$]	6.263	(12) 1/2 [$(2)^4\Pi$]	0.922
(5) 3/2 [$(1)^4\Phi$]	6.415	(12) 3/2 [$(2)^4\Pi$]	0.717
(4) 5/2 [$(1)^2\Phi$]	3.169	(4) 7/2 [$(2)^2\Phi$]	0.462
(2) 7/2 [$(1)^2\Phi$]	3.078	(7) 5/2 [$(2)^2\Phi$]	0.857
(6) 1/2 [$(3)^2\Pi$]	3.042	(12) 3/2 [$(2)^4\Pi$]	0.726

The largest permanent electric dipole moments are those attained in the states (1) 3/2 [$(1)^2\Delta$], and (1) 5/2 [$(1)^2\Delta$]. In Figure 39 we draw the variation of the permanent electric dipole moment in some low lying electronic states of YS as a function of the internuclear distance separating Yttrium from Sulfur.

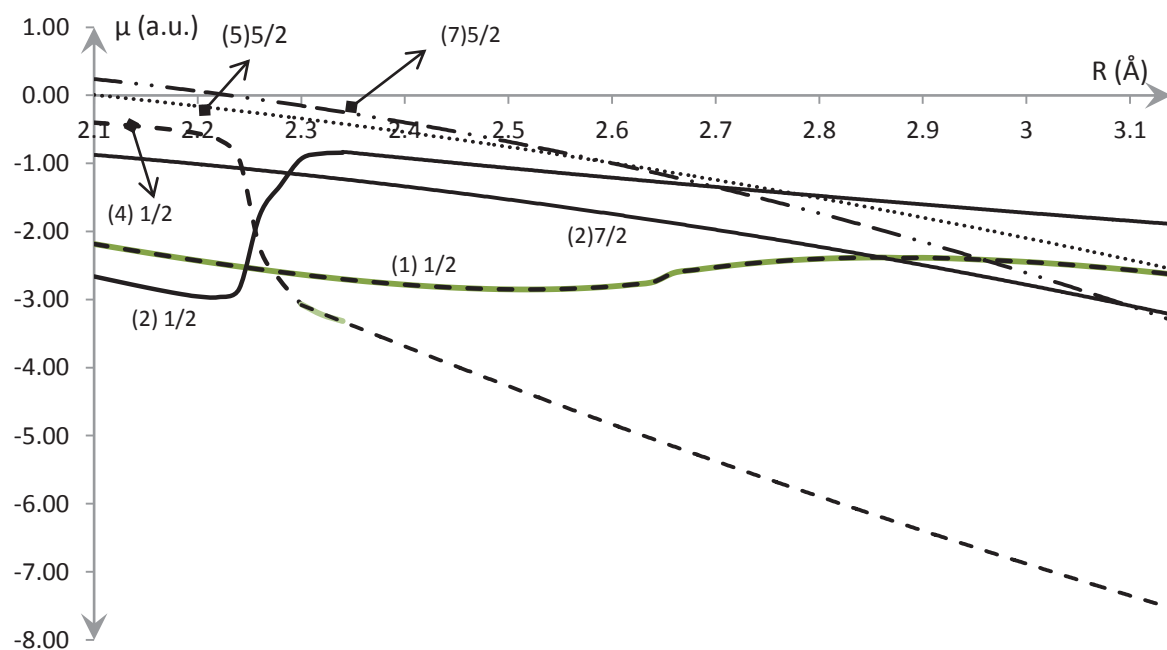


Fig. 39. Variation of the permanent dipole moment in (a.u.) as a function of the internuclear distance R ($\text{\AA}$) for several low lying states in YS.

III. E. 6. The Internal Molecular Electric Field in YS

The expectation values of the internal molecular electric fields in units of GV/cm have been calculated at the MRSDCI level calculations for the lowest lying molecular states of YS. These results are shown in Table XXXXV and reported for YS here for the first time in literature.

Table XXXXV:

Internal Molecular Electric Field for the electronic states of YS at $R = 2.32\text{\AA}$.

State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} (\text{GV/cm})$	State $^{2s+1}\Lambda^\pm$	$ E_{\text{molecular}} (\text{GV/cm})$
$X^2\Sigma^+$	0.126	$(3)^2\Pi$	0.136
$(1)^2\Delta$	0.056	$(2)^2\Phi$	0.132
$(2)^2\Sigma^+$	0.125	$(4)^2\Pi$	0.049
$(3)^2\Sigma^+$	0.077	$(5)^2\Pi$	0.027
$(3)^2\Delta$	0.076	$(1)^4\Sigma^+$	0.067
$(4)^2\Sigma^+$	0.021	$(1)^4\Delta$	0.069
$(1)^2\Gamma$	0.030	$(1)^4\Pi$	0.557
$(1)^2\Pi$	0.075	$(1)^4\Phi$	0.562
$(2)^2\Pi$	0.194	$(2)^4\Pi$	0.236
$(1)^2\Phi$	0.121		

III. F. Comparison between 4d Transition Metal Sulfides MS ($M = Y, Zr, Nb, \dots, Cd$)

Materials formed from the combination of transition metals with the chemical elements of group 16 in the periodic table, such as oxygen, sulfur, selenium, tellurium and polonium are called chalcogens. The interest in transition-metal chalcogenides evolves primarily from the numerous applications of transition metal oxides and sulfides in catalysis, lubricants, support materials, superconductors, gas sensors for pollution monitoring and control as well as electrode materials in photoelectrolysis [200]. Moreover, transition metal oxides and sulfides are found in the reaction centers of many enzymes, and metal sulfides have been postulated to be essential for the evolution of life [201, 202]. In industry, transition metal oxides are used as versatile catalysts in many applications, however for some processes their reactivity is too high and non-specific product formation occur [200]. In contrast, transition metal sulfides are less reactive and sulfur is often added as a catalyst moderator in order to improve selectivity [201]. Despite their successful application in industry and their relevance in biology, the electronic structures of transition metal sulfide molecules is far from complete. In order to gain better understanding of the similarities and differences observed for the various transition metal chalcogenides, the neutral transition metal sulfides appear to be suitable model systems. The comparison of properties such as electronic ground states, bond lengths, and bond polarity may help to elucidate the nature of the metal-sulfur interaction. This knowledge could in turn be used for the development of better catalysis [200]. In the present work we compare the values of the spectroscopic constants R_e , ω_e , μ_e in the ground state of

the transition metal sulfides of YS and ZrS to the other series of diatomic 4d transition metal sulfides MS, where M stands for Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd.

To the best of our knowledge in literature the electronic ground state in NbS has been determined to be of $X^4\Sigma^-$ symmetry [148, 203, 204], with a bond length of $R_e = 2.164\text{\AA}$ [203], harmonic vibrational frequency $\omega_e = 540\text{cm}^{-1}$ [203], and permanent electric dipole moment of $\mu = 4.007$ Debye [203]. The electronic structure of the MoS molecule has been studied by three groups in literature [205 – 207]. The ground state has been determined to be an $X^5\Pi$ state with bond lengths $R_e = 2.165\text{\AA}$ [232], harmonic vibrational frequency $\omega_e = 521\text{cm}^{-1}$ [205], and permanent electric dipole moment of $\mu = 3.474$ Debye [205]. The structure of a neutral TcS molecule is limited to the results reported in [200, 205]. In these studies the electronic ground state has been predicted to be of $X^6\Sigma^+$ symmetry with $R_e = 2.168\text{\AA}$ [205], $\omega_e = 492\text{cm}^{-1}$ [205], and $\mu = 4.045$ Debye [205]. The electronic structure in the ground electronic state of the molecules RuS, RhS, PdS, AgS, and CdS have been investigated by Knudsen-effusion mass spectrometry in Ref [200]. The spectroscopic constants in the ground state of each molecule have been determined in Ref [200] to be; $R_e = 2.176\text{\AA}$ and $\omega_e = 480\text{cm}^{-1}$ in RuS, $R_e = 2.159\text{\AA}$ and $\omega_e = 470\text{cm}^{-1}$ in RhS, $R_e = 2.259\text{\AA}$ and $\omega_e = 360\text{cm}^{-1}$ in PdS, $R_e = 2.432\text{\AA}$ and $\omega_e = 270\text{cm}^{-1}$ in AgS, and $R_e = 2.356\text{\AA}$ and $\omega_e = 331\text{cm}^{-1}$ in CdS. To the best of our knowledge, the other values for the dipole moment in the ground states of RuS, RhS, PdS, AgS and CdS aren't available. The reported results in literature for the values of the spectroscopic constants R_e , ω_e , and μ_e in the ground state of 4d transition metal sulfide molecules NbS, MoS, TcS, RuS, RhS, PdS, AgS, and CdS are shown in Table XXXXVI.

The comparisons between the our values for the spectroscopic constants R_e , ω_e , and μ_e of YS and ZrS to the other series of 4d transition metal sulfides are shown in Figures 40 - 42.

Table XXXXVI:

Variation of the values of the equilibrium internuclear distance R_e , harmonic vibrational frequency ω_e and permanent electric dipole moment μ_e in the ground state of the series of 4d transition metal sulfide molecules in the periodic table.

Metal Nitrides	$R_e (\text{\AA})$	$\mu_e (\text{Debye})$	$\omega_e (\text{cm}^{-1})$
YS	2.312 ^a	6.781 ^a	500.64 ^a
ZrS	2.203 ^a	3.811 ^a	532.40 ^a
NbS	2.164 ^b	4.007 ^b	540 ^b
MoS	2.165 ^c	3.474 ^d	521 ^c
TcS	2.168 ^d	4.045 ^d	492 ^d
RuS	2.176 ^e	—	480 ^e
RhS	2.159 ^e	—	470 ^e
PdS	2.259 ^e	—	360 ^e
AgS	2.432 ^e	—	270 ^e
CdS	2.356 ^e	—	331 ^e

a. values obtained from the results of the present work, b. Ref [203], c. Ref [232], d. Ref [205], e. Ref [200].

Note: The sign (—) indicates that to the best of our knowledge there are no results available in literature for the specific values of the permanent dipole moment in RuS, RhS, PdS, AgS, and CdS.

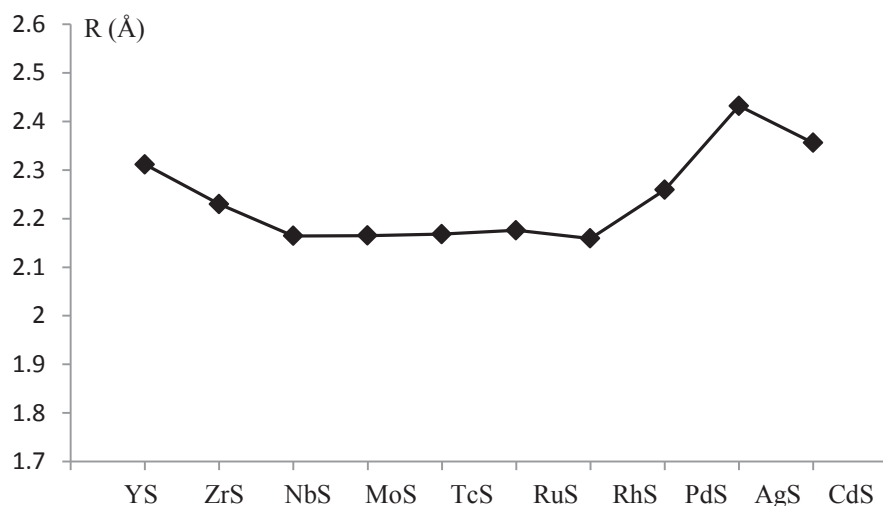


Fig. 40: Variation of the equilibrium internuclear distance in the ground state of 4d transition metal sulfides.

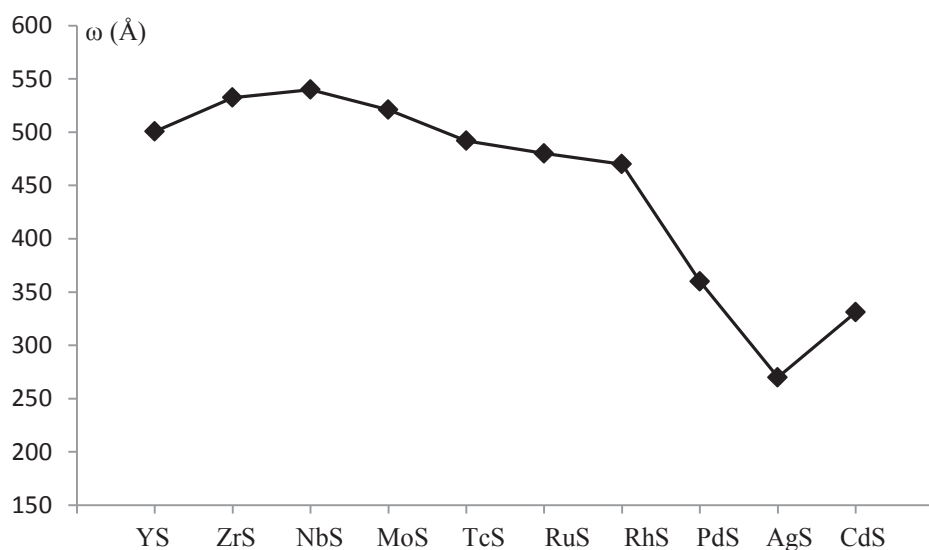


Fig. 41: Variation of the harmonic vibrational frequency in the ground state of 4d transition metal sulfides.

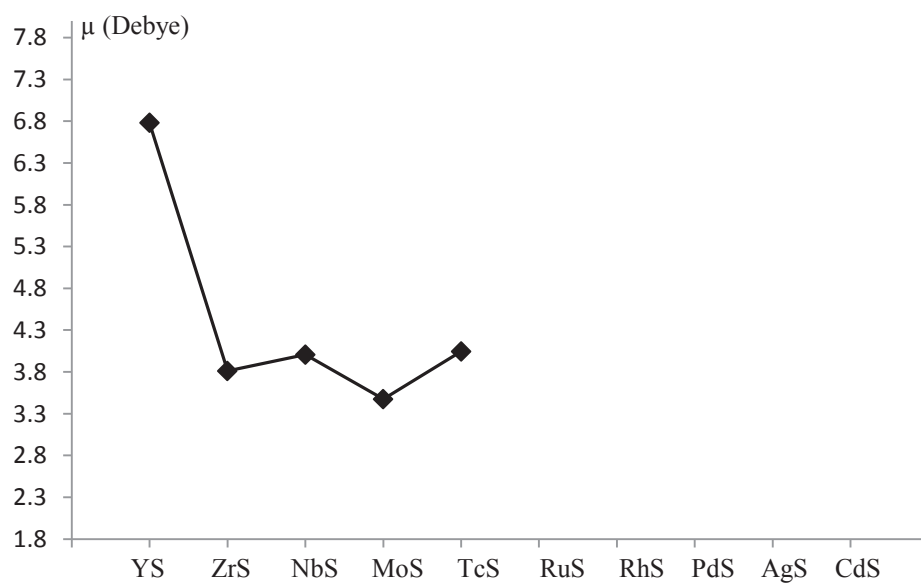


Fig. 42: Variation of the permanent electric dipole moment in the ground state of 4d transition metal sulfides.

Across the series of 4d transition metal sulfides from YS to CdS the equilibrium internuclear distance in the ground state (Fig. 40) decreases from 2.3116Å in YS to reach a minimum at 2.165Å in MoS and then increases again to reach a value of 2.432Å in AgS. The shortest bond length attained in MoS suggests that the bonding in MoS is the strongest among the other 4d transition metal sulfides. For the harmonic vibrational frequency ω_e in the ground state of each molecule (Fig. 41) it is seen that the value of ω_e is largest in NbS and MoS with a value of 540cm^{-1} , respectively. The polarity in each of the transition metal nitrides is largely determined by the value of the permanent electric dipole moment in the ground state of each molecule. In Fig 42 we compare the permanent electric dipole moment results for the molecules YS, ZrS, NbS, MoS, and TcS. These results indicate that the least polar bond is that in MoS with a permanent dipole moment of 3.474 Debye. The values of 6.78 Debye reported in YS is the largest among the other values of the permanent dipole moment across the series of transition metal sulfides ZrS, NbS, MoS, and TcS. The increase of the dipole moment is an indication for the increase in the electronegativity difference between the metal and sulfur atoms, and hence a decrease of ionic character across the series of 4d transition metal sulfides.

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Chapter 4

Summary and Outlook

Ab initio calculations provide us with a tool to describe the electronic structures and chemical properties of molecules. Computational studies can in general be carried out in order to find a starting point for laboratory experiments, or to assist in understanding experimental data. Thus computational studies can explore new properties and guide new experimental works. Heavy polar diatomic molecules form suitable candidates for computational investigations, particularly due to their rich inner electronic structures and due to their importance in several areas of science, as chemistry, astrophysics, ultracold interactions, and molecular quantum computing. Although, the electronic structures of small diatomic molecules have been well characterized, still the electronic structures of heavy polar diatomic molecules containing a transition metal atom of group III and IV is far from complete. The main objective of this thesis was to fill the gap and study the electronic structures of the transition metal nitrides and sulfides of Yttrium and Zirconium. In the present work the electronic structures of the molecules YN, YS, ZrN, and ZrS have been investigated at the multireference single and double configuration interaction method followed by spin orbit calculations implemented by the method of effective core potentials. These calculations yielded accurate spectroscopic constants along with several physical and chemical properties that are within a few percent of the experimental values. Many other properties have been also computed that weren't available in literature on the electronic structures of these molecules. We expect that the results in the present work should invoke further experimental investigations for this class of molecules. As an example, we found in the ZrS molecule several degenerate vibrational energy levels which might increase the

experimental sensitivity for measurements of small variations in the fine structure constant α in laboratory experiments and in S-type stars. A preprint for the results of this work has been requested by an experimental research group working at Yale in the group of Prof. David Demille.

In chapter 1, we present a brief overview for the theoretical backgrounds of the computational methods used in the present work. The theoretical backgrounds for the electronic structure calculations in the Hartree-Fock method, followed by Complete Active Space Calculations and Multireference Configuration Interaction methods are written within the formalism of second quantization. A brief discussion for the theoretical background of spin orbit relativistic interactions in diatomic molecules have been also incorporated within the context of the first chapter.

In chapter 2, we present the canonical function's approach for solving the vibrational and rotational Schrödinger equation in a diatomic molecule. This has allowed us to compute the vibrational energy structures and rotational constants for the ground and excited electronic states of each molecule.

In chapter 3, we list the results of our calculations for the electronic structures, with and without spin orbit effects, of the four diatomic molecules YN, YS, ZrN, and ZrS. Potential energy curves were constructed and spectroscopic constants were computed. Various other physical properties were also computed such as the permanent electric dipole moment, internal molecular electric fields, and bonding characteristics. Ro-vibrational energy calculations were performed by solving the vibrational-rotational Schrödinger equation in the ground and excited electronic states of each molecule. With the inclusion of spin orbit effects in the electronic structure calculations further enhancements in the accuracy of nonrelativistic *ab initio* results could be obtained. In the present work a large number of spin orbit electronic states have been studied for the first time in literature up to 60 states in YN, 49 states in ZrN, 44 states in ZrS, and 54 states in YS. From these results several other properties and spectroscopic constants were also studied here for the first time in literature. The accuracy of the calculated constants in the present work was measured by reporting a percentage relative difference between the present results and the experimental results, whenever available in literature. For the other values reported here for the first time in literature no comparison is made. The calculated values of the internal molecular

electric fields in these molecules are reported here for the first time in literature and might help in clarifying the structures of these molecules in a search for a possible electric dipole moment of the electron. We detected several degenerate vibrational energy levels in the ground $(1)0^+[X^1\Sigma^+]$ and first excited electronic states $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, $(1)3[(1)^3\Delta]$ of the ZrS molecule. We suggest that the reported degeneracies in ZrS, specifically between the vibrational energy levels of the $(1)1[(1)^3\Delta]$ and $(1)2[(1)^3\Delta]$ states, can be used to enhance the experimental accuracy in measurements for variations in the fine structure constant α . Finally, in an attempt to observe the variation of molecular properties across the series of 4d transition metal nitrides and sulfides, we compare the values in the present work for the equilibrium internuclear distance, permanent electric dipole moment, and harmonic vibrational frequency for the molecules YN and ZrN to the other spectroscopic values across series of 4d transition metal nitrides and sulfides: MN and MS, where M stands for Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd.

Résumé et Perspectives (French)

Les calculs *ab initio* fournissent un outil pour décrire les structures électroniques et les propriétés chimiques des molécules. Les études théoriques peuvent, en général, constituer un point de départ pour des expériences de laboratoire, ou encore aider à comprendre certaines données expérimentales. Ainsi, les études numériques représentent un moyen d'explorer de nouvelles propriétés et ainsi guider de nouvelles expériences.

Les molécules diatomiques polaires sont des candidats appropriés pour des études numériques en raison de la richesse de leur structure électronique et de leur importance dans de nombreux domaines: chimie, astrophysique, interaction à très basses températures ou encore le calcul quantique moléculaire. Les structures électroniques des petites molécules diatomiques sont à présent bien connues, cependant les structures électroniques des molécules diatomiques polaires lourdes contenant un atome de métal de transition des groupes III et IV ne sont "pas complètement comprises". L'objectif principal de cette thèse est de combler cet écart "en étudiant" les structures électroniques des nitrures de métaux de transition ainsi que les sulfures d'yttrium et le zirconium. Dans ce travail, les structures électroniques des molécules lourdes diatomiques polaires du type YN, YS, ZrN et ZrS ont été étudiées à la configuration de l'interaction multireference méthode simple et double suivies par des calculs spin-orbite mis en œuvre par la méthode des potentiels de cœurs effectifs. Ces calculs ont permis d'obtenir des constantes spectroscopiques précises ainsi que plusieurs propriétés physico-chimiques à quelques pourcent de leur valeur expérimentale. De nombreuses autres propriétés qui n'étaient pas

disponibles dans la littérature ont également été calculées sur la structure électronique de ces molécules. Nous nous attendons à ce que les résultats présentés dans cette thèse inspirent de futures études expérimentales pour cette classe de molécules. A titre d'exemple, nous avons trouvé dans la molécule ZrS plusieurs niveaux d'énergie vibratoire dégénérés, ces niveaux pourraient augmenter la sensibilité expérimentale pour les mesures de faibles variations dans la constante de structure fine α et dans les étoiles du type S. De plus, un preprint concernant les résultats de ce travail a été demandé par le groupe de recherche expérimentale dirigé par le professeur David Demille de l'Université de Yale.

Dans le chapitre 1 nous présentons un bref aperçu du cadre théorique des méthodes de calcul utilisées dans le travail actuel. Le cadre théorique pour le calcul de la structure électronique avec la méthode d'Hartree-Fock, suivi par les méthodes de calcul de l'espace actif et de l'interaction en configuration multiréférence est celui du formalisme de la seconde quantification. Une brève discussion sur la théorie de l'interaction spin-orbite pour les molécules diatomiques relativistes a également été intégrée dans le premier chapitre.

Dans le chapitre 2, nous présentons l'utilisation de la fonction canonique pour la résolution de l'équation de Schrödinger pour les modes de vibration et de rotation d'une molécule diatomique. Cela nous a permis de calculer les énergies vibrationnelles des structures et les constantes de rotation pour l'état fondamental et les états électroniques excités de chaque molécule.

Dans le chapitre 3, nous présentons les résultats de nos calculs pour les structures électroniques, avec et sans effet spin-orbite, de quatre molécules diatomiques YN, YS, ZrN et ZrS. Les courbes d'énergie potentielle ont été tracées et les constantes spectroscopiques calculées. D'autres propriétés physiques ont été calculées comme le moment dipolaire permanent, le champ électrique moléculaire interne et les caractéristiques de liaison. Les calculs d'énergie rovibrationnelle ont été effectués en résolvant l'équation de Schrödinger de rotation et de vibration pour l'état fondamental et les états excités de chaque molécule. Avec la prise en compte des effets spin-orbite dans les calculs de structure électronique, on a pu obtenir de nouvelles améliorations sur l'exactitude des résultats non relativistes et *ab initio*. De nombreux états électroniques de spin-orbite ont été étudiés pour la première fois dans la littérature lors du travail actuel jusqu'à 60 états pour YN, 49 états pour ZrN, 44 états pour ZrS et 54 états pour YS. A partir de ces résultats plusieurs autres propriétés et constantes spectroscopiques ont été étudiées

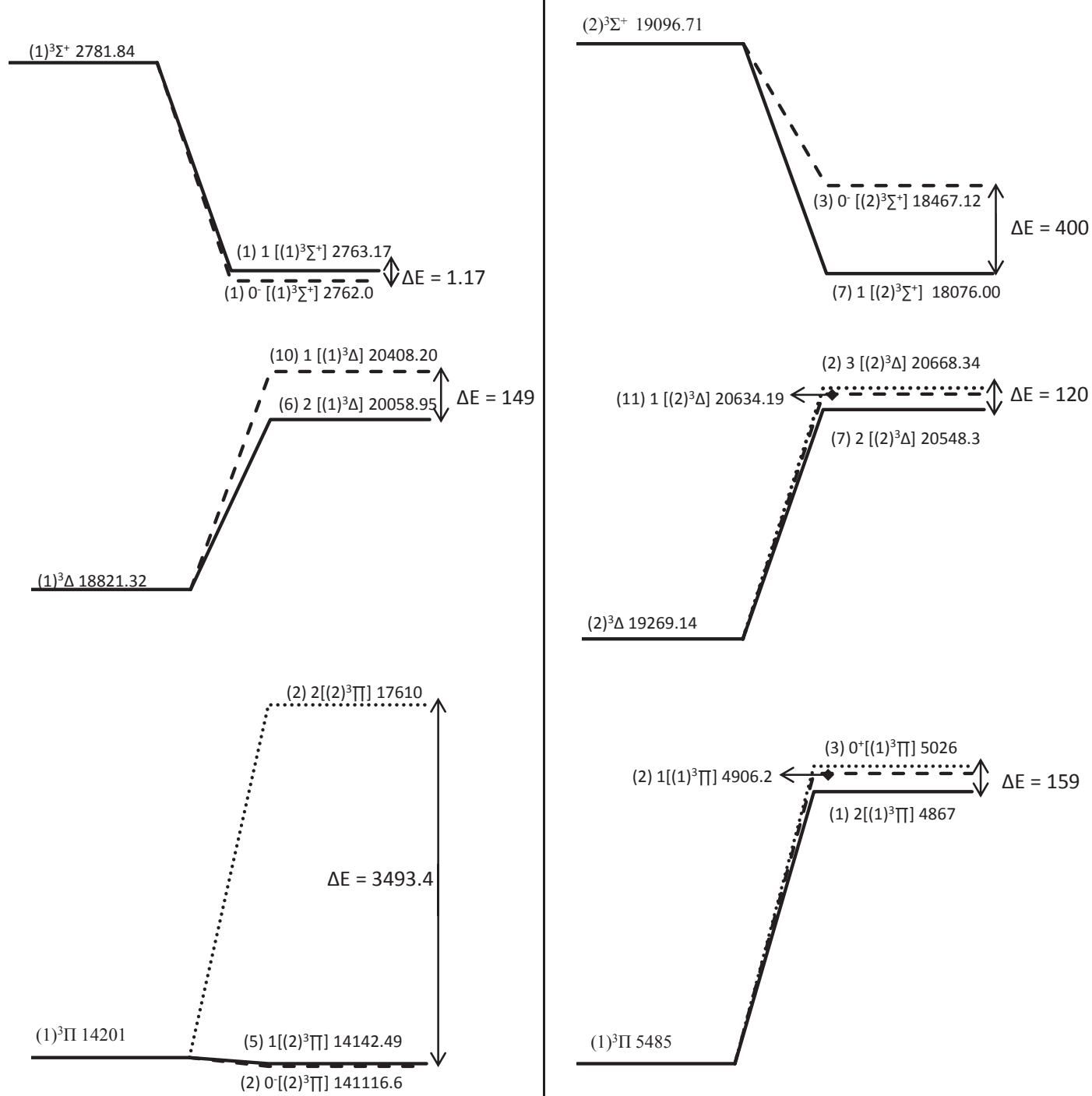
pour la première fois dans la littérature. La précision des constantes calculées dans le travail actuel a été calculé à partir de la différence relative entre les résultats et ceux des expériences, à chaque fois qu'ils s'étatisent disponibles dans la littérature. Il n'y a pas eu de comparaison faite pour les autres valeurs rapportées pour la première fois dans la littérature. Les valeurs calculées du champ électrique moléculaire interne de ces molécules sont rapportées pour la première fois dans la littérature et pourraient aider à clarifier la structure de ces molécules dans la recherche d'un éventuel moment dipolaire de l'électron. Nous avons détecté plusieurs niveaux d'énergie vibrationnelle dégénérées dans le fondamental $(1)0^+[X^1\Sigma^+]$ et les premiers états excités $(1)1[(1)^3\Delta]$, $(1)2[(1)^3\Delta]$, $(1)3[(1)^3\Delta]$ de la molécule ZrS. Nous supposons que les dégénérescences du ZrS, en particulier entre les niveaux d'énergie vibrationnelle des états $(1)1[(1)^3\Delta]$ et $(1)2[(1)^3\Delta]$ peuvent être utilisées pour améliorer la précision expérimentale des mesures de variation de la constante de structure fine α . Finalement, en tentant d'observer les variations des propriétés moléculaires pour les séries des nitrures et sulfures de métaux de transition 4d on compare les valeurs de la distance internucléaire d'équilibre, du moment dipolaire électrique permanent et de la fréquence de vibration harmonique pour les molécules YN et ZrN calculées dans ce travail aux valeurs spectroscopique pour le nitreux et sulfures de métaux de transition 4d MN (M = Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd).

Appendix I
Splitting Figures between Spin orbit electronic states

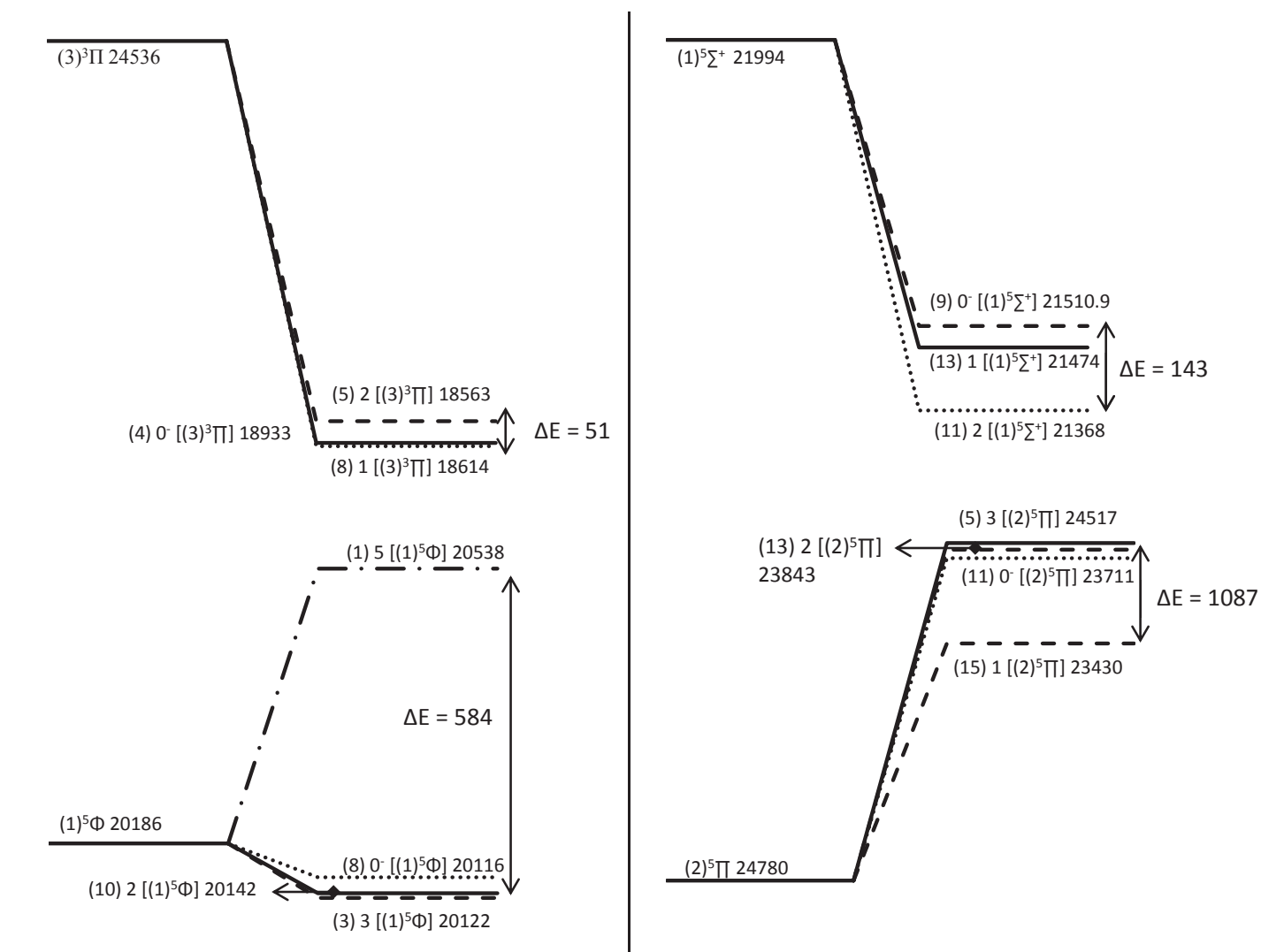
Appendix I. Splitting Figures between Spin orbit electronic states

Table I: Spin Orbit splitting occurring in the electronic states of the YN molecule.

Note: all numbers below are in cm^{-1} units of energy.



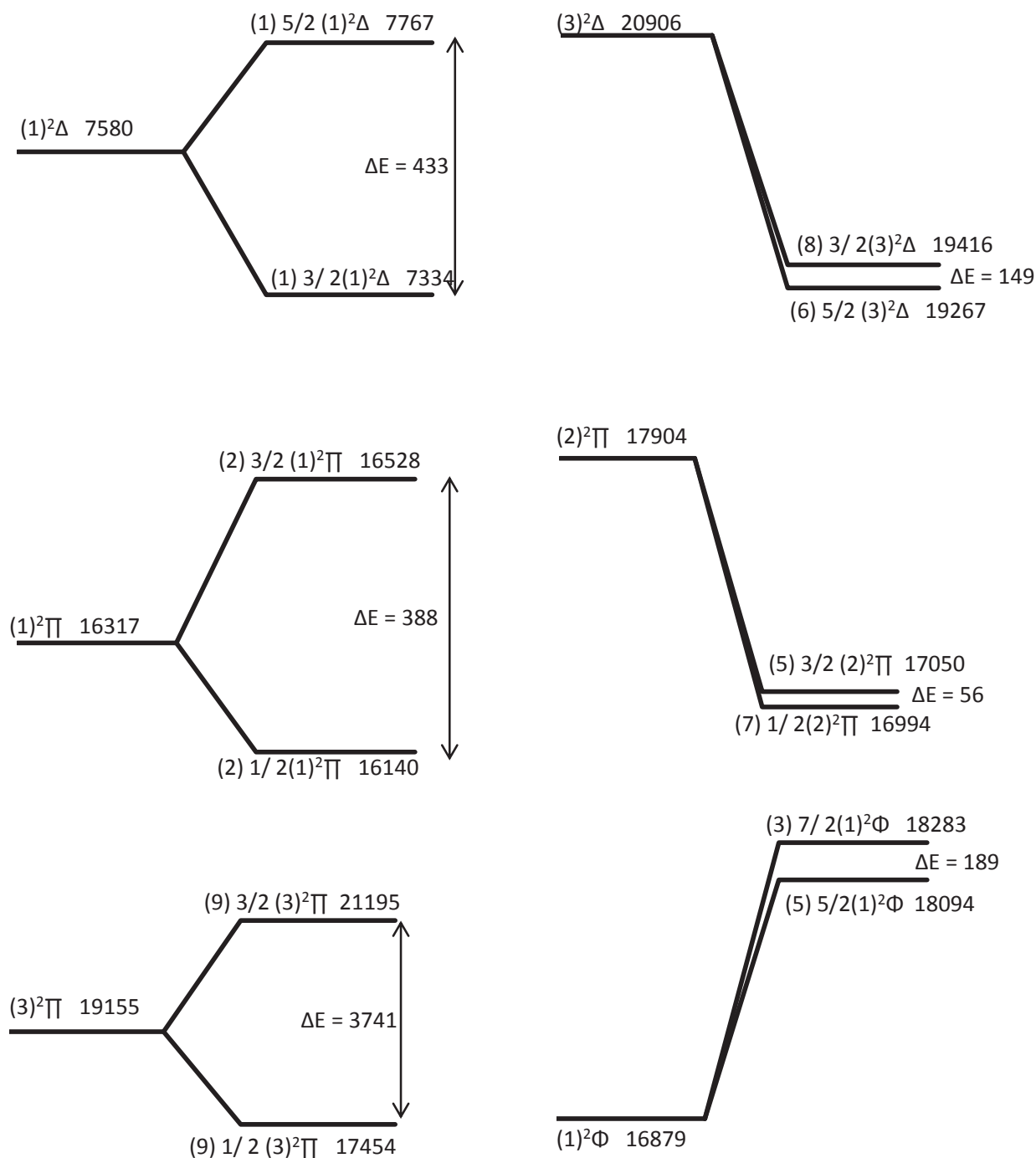
Appendix I. Splitting Figures between Spin orbit electronic states



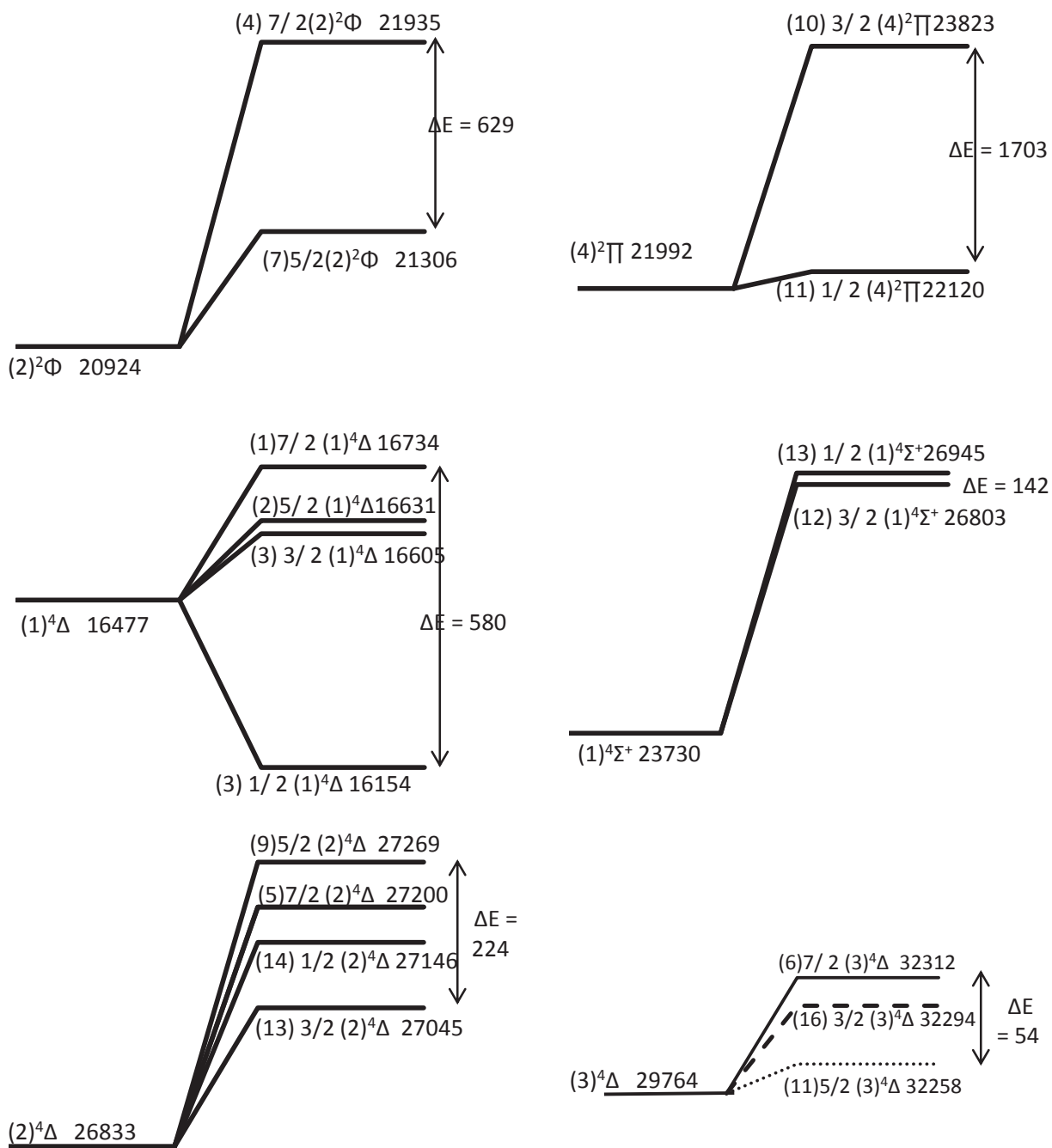
Appendix I. Splitting Figures between Spin orbit electronic states

Table II: Spin Orbit splitting occurring in the electronic states of the ZrN molecule.

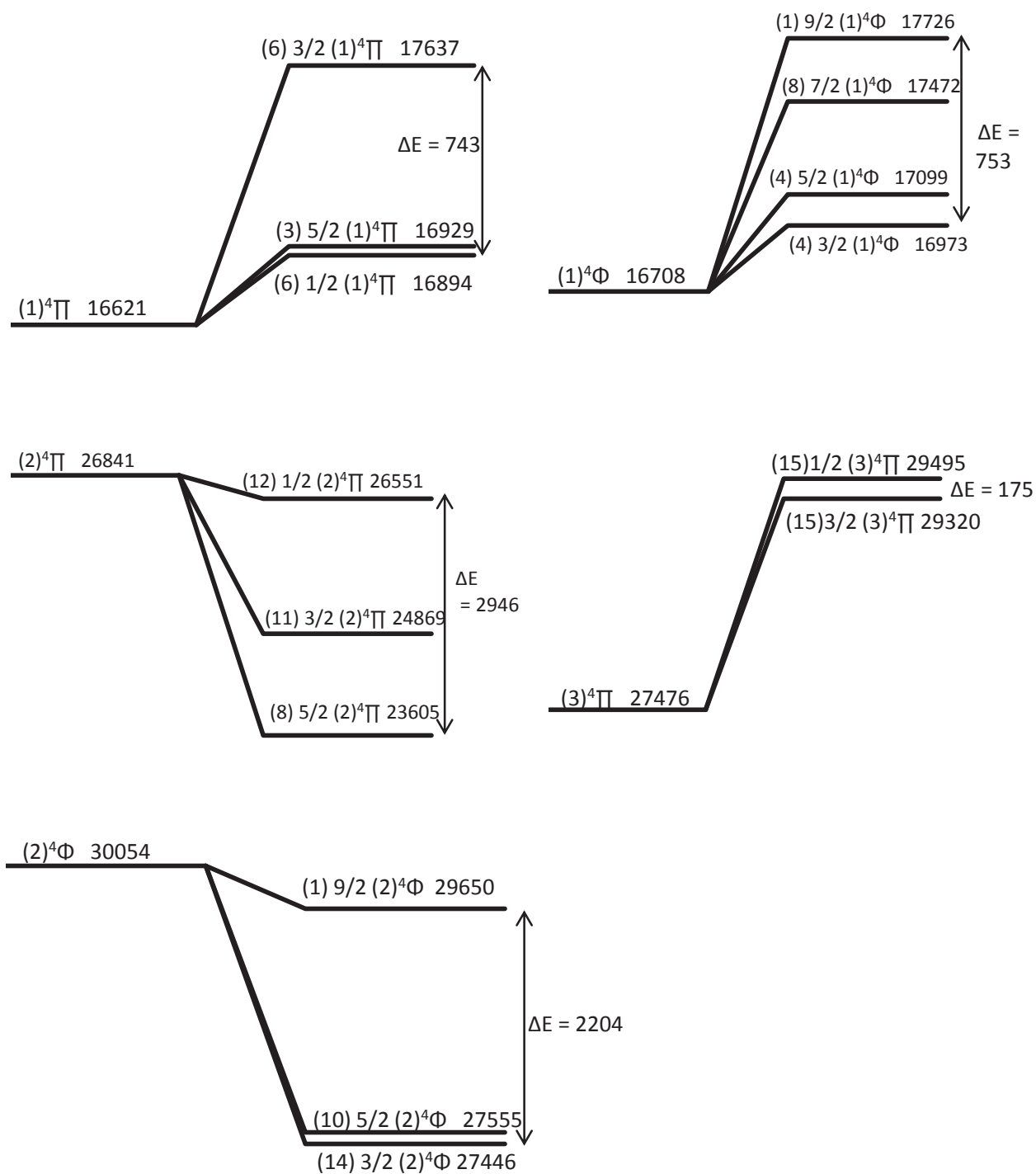
Note: all numbers below are in cm^{-1} units of energy.



Appendix I. Splitting Figures between Spin orbit electronic states



Appendix I. Splitting Figures between Spin orbit electronic states

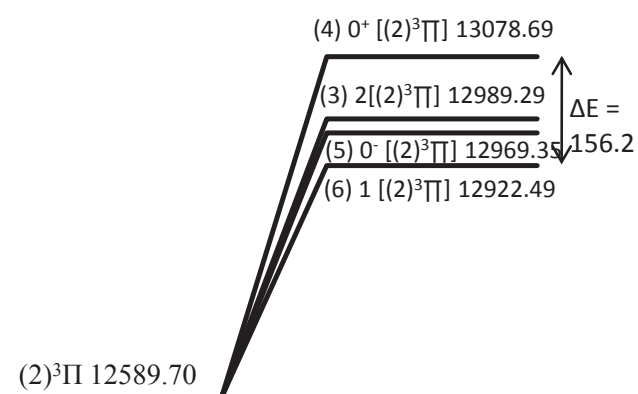
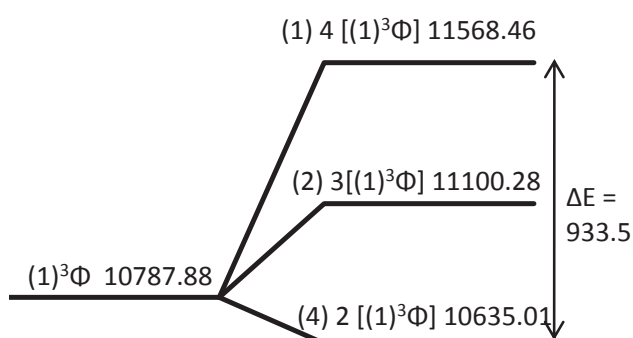
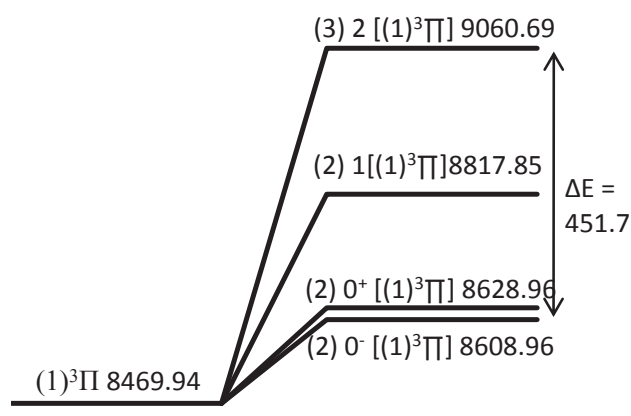
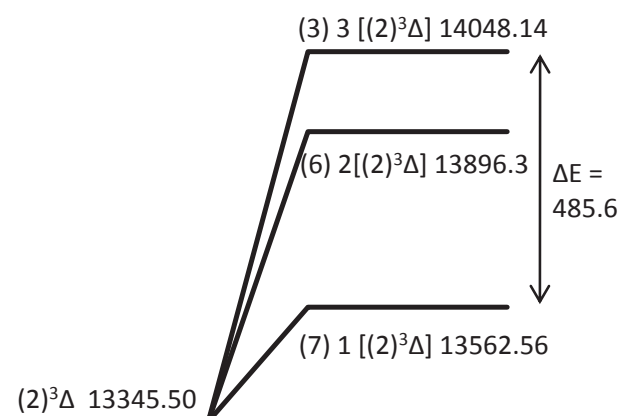
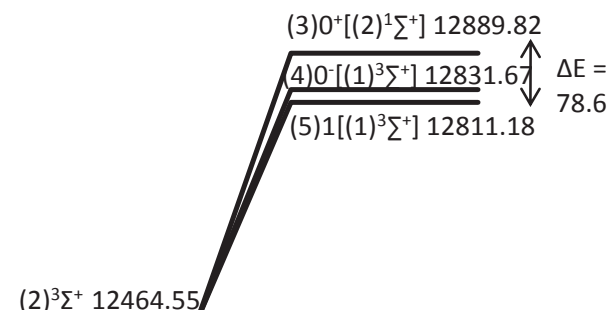
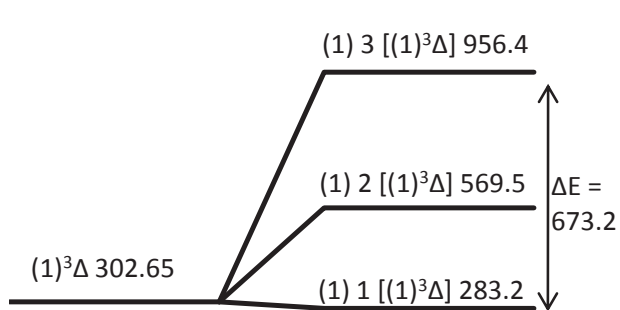


Appendix I. Splitting Figures between Spin orbit electronic states

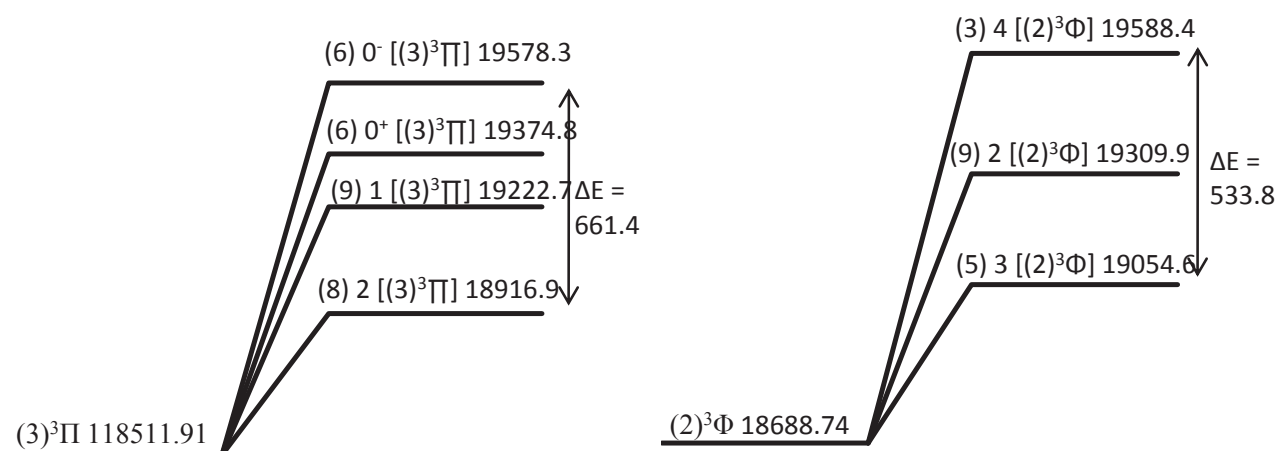
Table III:

Spin Orbit splitting occurring in the Triplet electronic states of the ZrS molecule.

Note: all numbers below are in cm^{-1} units of energy.



Appendix I. Splitting Figures between Spin orbit electronic states

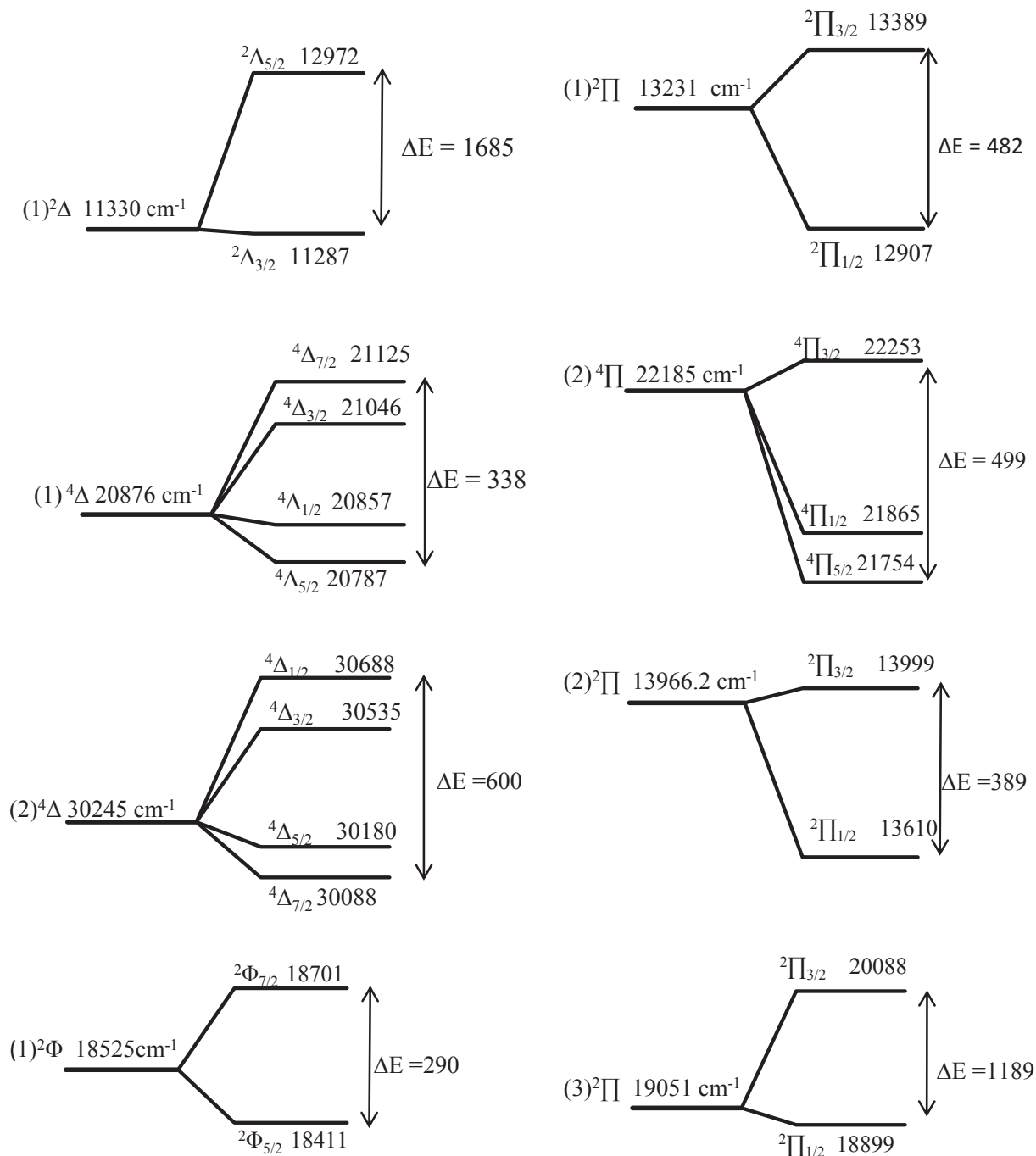


Appendix I. Splitting Figures between Spin orbit electronic states

Table IV:

Spin Orbit splitting occurring in the Triplet electronic states of the YS molecule.

Note: all numbers below are in cm^{-1} units of energy.



Appendix II

Results of Vibrational Calculations

Appendix II. Results of Vibrational Calculations

Table I:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states $(3)1/2[(1)^4\Delta]$, $(3)3/2[(1)^4\Delta]$, $(2)5/2[(1)^4\Delta]$, $(4)1/2[(2)^2\Sigma^+]$, $(7)1/2[(2)^2\Pi]$, $(5)3/2[(2)^2\Pi]$, $(5)1/2[(2)^2\Delta]$, $(3)5/2[(1)^4\Pi]$ in ZrN.

$(3)1/2[(1)^4\Delta]$						$(3)3/2[(1)^4\Delta]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	16703.84	1.78	1.94	3.979	9.510	0	16812.62	1.78	1.95	3.951	9.527
1	17218.48	1.75	1.99	3.995	4.039	1	17322.35	1.75	1.99	4.003	3.758
2	17825.58	1.72	2.02	3.949	3.736	2	17933.71	1.73	2.02	3.944	3.104
3	18474.24	1.71	2.06	3.906	3.606	3	18600.00	1.71	2.05	3.911	5.085
4	19148.22	1.69	2.08	3.882	5.652	4	19265.74	1.69	2.08	3.888	4.848
5	19811.92	1.68	2.11	3.865	4.726	5	19930.78	1.68	2.11	3.845	5.414
6	20477.04	1.67	2.14	3.837	4.890	6	20587.51	1.67	2.14	3.830	4.568
7	21137.94	1.66	2.16	3.806	3.895	7	21246.89	1.66	2.16	3.812	2.953
8	21802.02	1.64	2.18	3.774	5.302	8	21920.68	1.64	2.18	3.792	5.211
9	22458.36	1.64	2.20	3.761	4.856	9	22585.75	1.64	2.20	3.761	5.174
10	23111.37	1.62	2.22	3.736	3.936	10	23242.82	1.63	2.22	3.738	4.603
11	23764.08	1.62	2.25	3.702	4.930	11	23896.43	1.62	2.25	3.713	4.486
$(2)5/2[(1)^4\Delta]$						$(4)1/2[(2)^2\Sigma^+]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	16886.99	1.79	1.95	3.962	8.832	0	17119.44	1.83	1.94	3.883	4.597
1	17417.64	1.75	1.99	3.975	4.267	1	17832.19	1.78	2.00	3.873	5.728
2	18031.77	1.73	2.02	3.938	3.570	2	18502.34	1.76	2.04	3.862	4.726
3	18690.86	1.71	2.06	3.900	4.881	3	19179.25	1.74	2.06	3.848	3.847
4	19353.43	1.70	2.08	3.880	4.551	4	19872.73	1.72	2.10	3.826	4.581
5	20021.42	1.68	2.11	3.853	5.302	5	20563.19	1.70	2.12	3.806	4.473
6	20682.40	1.67	2.14	3.828	4.315	6	21250.53	1.69	2.14	3.778	4.064
7	21346.37	1.66	2.16	3.805	4.326	7	21938.71	1.68	2.17	3.759	5.235
8	22011.04	1.65	2.18	3.779	4.991	8	22615.08	1.67	2.19	3.734	4.501
9	22669.61	1.64	2.20	3.754	4.548	9	23284.91	1.66	2.21	3.696	4.336
10	23325.82	1.63	2.22	3.734	4.298	10	23950.36	1.64	2.24	3.679	5.608
$(7)1/2[(2)^2\Pi]$						$(5)3/2[(2)^2\Pi]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	17442.50	1.82	1.94	3.917	2.873	0	17512.35	1.82	1.93	3.935	2.782
1	18359.22	1.78	1.97	3.940	3.155	1	18449.61	1.78	1.97	3.948	3.285
2	19254.73	1.76	2.01	3.909	3.332	2	19344.99	1.76	2.00	3.915	3.230
3	20125.29	1.74	2.03	3.872	3.878	3	20218.79	1.74	2.04	3.869	4.213
4	20959.56	1.72	2.07	3.839	5.061	4	21041.82	1.72	2.07	3.829	4.931
5	21740.06	1.71	2.10	3.792	3.434	5	21817.58	1.71	2.10	3.794	3.197
6	22515.73	1.70	2.12	3.774	3.948	6	22596.01	1.70	2.12	3.778	4.168
7	23279.34	1.69	2.15	3.739	5.203	7	23357.56	1.69	2.15	3.734	5.308
8	24009.28	1.68	2.18	3.680	4.661	8	24084.98	1.68	2.18	3.687	4.375
9	24721.10	1.67	2.20	3.667	4.284	9	24797.69	1.67	2.20	3.663	4.283
$(5)1/2[(2)^2\Delta]$						$(3)5/2[(1)^4\Pi]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	17194.99	1.83	1.95	3.877	4.564	0	17275.99	1.83	1.96	3.870	4.311
1	17906.51	1.78	2.00	3.849	4.581	1	18004.58	1.79	2.00	3.834	4.068
2	18614.64	1.76	2.04	3.858	4.786	2	18738.79	1.76	2.04	3.833	3.658
3	19313.32	1.74	2.06	3.816	3.678	3	19482.87	1.74	2.07	3.788	3.403
4	20024.83	1.72	2.10	3.805	6.127	4	20232.12	1.74	2.10	3.764	4.089

Appendix II. Results of Vibrational Calculations

Table II:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states (1)7/2[(1)⁴Δ], (2) 7/2 [(1)²Γ], (4)5/2[(1)⁴Φ], (5)3/2[(2)²Π], (6)3/2[(1)⁴Π], (1)9/2[(1)⁴Φ], (5)5/2[(1)²Φ], (7)3/2[(3)²Δ] in ZrN.

(1)7/2[(1) ⁴ Δ]						(2) 7/2 [(1) ² Γ]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	16978.31	1.83	1.95	3.909	6.731	0	17052.84	1.83	1.95	3.872	4.889
1	17575.73	1.75	1.99	3.986	8.794	1	17742.79	1.79	2.01	3.880	5.508
2	18138.51	1.73	2.03	3.958	1.143	2	18414.29	1.74	2.04	3.901	6.252
(4)5/2[(1) ⁴ Φ]						(5)3/2[(2) ² Π]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	17570.27	1.82	1.92	3.950	2.626	0	17723.61	1.81	1.92	3.963	2.760
1	18539.81	1.78	1.97	3.958	3.385	1	18672.84	1.78	1.97	3.959	3.170
2	19441.23	1.76	2.00	3.915	3.369	2	19580.53	1.75	2.00	3.913	3.939
3	20312.48	1.74	2.04	3.878	4.245	3	20427.29	1.74	2.04	3.868	4.165
4	21134.31	1.72	2.06	3.836	3.896	4	21235.16	1.72	2.07	3.836	3.273
5	21936.30	1.71	2.10	3.820	3.371	5	22046.36	1.71	2.09	3.844	3.270
6	22736.96	1.70	2.12	3.803	3.363	6	22858.27	1.70	2.11	3.810	3.774
7	23534.41	1.68	2.14	3.782	3.812	7	23654.79	1.68	2.14	3.780	3.884
8	24319.86	1.68	2.16	3.754	3.872	8	24439.13	1.67	2.16	3.765	3.644
9	25093.59	1.66	2.18	3.731	4.139	9	25216.00	1.66	2.18	3.736	4.157
10	25854.79	1.65	2.20	3.710	4.375	10	25978.22	1.65	2.21	3.710	4.140
11	26601.33	1.64	2.23	3.680	3.652	11	26727.99	1.65	2.22	3.684	3.946
(6)3/2[(1) ⁴ Π]						(1)9/2[(1) ⁴ Φ]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	18119.19	1.80	1.91	4.021	3.098	0	18200.05	1.80	1.89	4.046	2.730
1	19020.47	1.77	1.96	3.949	3.359	1	19159.05	1.77	1.97	3.943	4.697
2	19877.39	1.75	2.01	3.878	4.181	2	19951.99	1.75	2.01	3.882	2.485
3	20686.98	1.74	2.04	3.884	2.687	3	20795.16	1.74	2.04	3.902	3.485
4	21526.37	1.72	2.06	3.875	3.581	4	21633.17	1.72	2.06	3.866	3.713
5	22350.40	1.70	2.09	3.826	3.785	5	22452.16	1.70	2.09	3.835	3.304
6	23158.12	1.69	2.12	3.818	3.812	6	23266.84	1.69	2.12	3.817	4.504
7	23955.16	1.68	2.14	3.790	3.921	7	24057.26	1.68	2.14	3.796	2.926
8	24739.10	1.67	2.16	3.769	3.519	8	24851.17	1.67	2.16	3.774	3.599
9	25517.13	1.66	2.18	3.743	4.789	9	25639.49	1.66	2.18	3.766	4.278
10	26275.79	1.65	2.20	3.727	4.225	10	26414.33	1.65	2.20	3.741	3.788
11	27022.26	1.64	2.22	3.692	3.769	11	27180.36	1.64	2.22	3.717	4.195
(5)5/2[(1) ² Φ]						(7)3/2[(3) ² Δ]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	18511.16	1.79	1.87	4.105	2.731	0	20108.85	1.80	1.91	4.029	2.578
1	19388.84	1.77	1.97	3.841	3.764	1	21116.33	1.76	1.94	4.038	3.843
2	20204.64	1.75	2.01	3.957	3.885	2	21997.58	1.74	2.00	3.921	6.440
3	21031.03	1.74	2.04	3.874	1.941	3	22738.23	1.72	2.03	3.897	4.150
4	21897.04	1.72	2.06	3.858	5.335	4	23485.05	1.70	2.07	3.899	5.092
5	22702.37	1.71	2.09	3.850	2.359	5	24213.59	1.69	2.09	3.861	3.055
6	23524.51	1.70	2.12	3.801	4.070	6	24957.80	1.68	2.12	3.864	2.790
7	24327.81	1.68	2.14	3.808	4.509	7	25717.19	1.67	2.13	3.835	2.484
8	25113.88	1.67	2.16	3.782	3.276	8	26487.78	1.66	2.15	3.806	5.638
9	25899.26	1.66	2.18	3.772	4.954	9	27220.79	1.65	2.19	3.717	7.125
10	26666.02	1.65	2.19	3.759	4.453	10	27898.77	1.64	2.22	3.627	5.499

Appendix II. Results of Vibrational Calculations

Table III:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states $(8)1/2[(3)^2\Pi]$, $(8)3/2[(3)^2\Pi]$, $(6)1/2[(1)^4\Pi]$, $(10)1/2[(4)^2\Pi]$, $(8)5/2[(2)^4\Pi]$, $(1)3/2[(1)^2\Delta]$, $(1)5/2[(1)^2\Delta]$ in ZrN.

(8)1/2[(3) ² Π]						(8)3/2[(3) ² Π]					
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)	v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)
0	21140.38	1.79	1.94	3.741	5.430	0	21681.44	1.81	1.91	3.990	2.398
1	21758.52	1.76	1.97	3.745	9.735	1	22705.96	1.78	1.96	3.967	3.369
2	22558.69	1.74	2.00	3.693	4.116	2	23631.25	1.75	1.99	3.935	4.255
3	23299.84	1.73	2.03	3.605	4.149	3	24477.33	1.73	2.04	3.885	6.431
4	24013.24	1.72	2.06	3.615	1.002	4	25215.65	1.72	2.08	3.795	6.544
5	24800.84	1.68	2.09	3.686	4.984	5	25897.40	1.70	2.12	3.768	5.038
6	25562.86	1.67	2.11	3.696	5.625	6	26570.46	1.69	2.14	3.744	3.987
7	26284.28	1.66	2.14	3.613	4.793	7	27246.41	1.68	2.17	3.723	2.796
8	26964.51	1.65	2.18	3.491	4.270	8	27936.95	1.67	2.19	3.711	4.342
(6)1/2[(1) ⁴ Π]						9	28623.81	1.66	2.21	3.692	3.063
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)	10	29314.72	1.65	2.23	3.658	4.359
0	17231.07			3.8713	4.4225	(10)1/2[(4) ² Π]					
1	17952.62			3.8475	4.0748	v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)
2	18684.91			3.8417	3.9949	0	22561.90	1.82	1.93	3.931	2.899
3	19418.64			3.8031	3.3418	1	23475.91	1.79	1.98	3.919	3.447
4	20160.44			3.7631	3.8471	2	24343.26	1.76	2.02	3.890	3.852
(8)5/2[(2) ⁴ Π]						3	25173.49	1.74	2.04	3.869	3.065
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)	4	26010.28	1.73	2.07	3.861	3.223
0	24149.33	1.87	1.99	3.733	2.483	5	26845.14	1.71	2.09	3.838	3.562
1	25064.63	1.83	2.01	3.801	1.983	6	27668.29	1.70	2.68	3.820	3.369
2	26046.38	1.79	2.03	3.835	2.753	7	28486.41	1.69	2.67	3.806	3.752
3	27002.94	1.77	2.06	3.836	3.793	8	29290.99	1.68	2.16	3.769	4.573
4	27900.74	1.74	2.08	3.825	4.134	9	30070.27	1.67	2.18	3.739	3.745
5	28757.07	1.72	2.10	3.833	5.772	10	30838.39	1.66	2.20	3.706	5.061
6	29554.52	1.71	2.12	3.818	6.475	(1)3/2[(1) ² Δ]					
7	30300.51	1.69	2.16	3.775	7.717	v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)
(1)5/2[(1) ² Δ]						0	7776.58	1.70	1.81	4.497	4.462
v	E _v (cm ⁻¹)	R _{min} (Å)	R _{max} (Å)	B _v ×10 ¹ (cm ⁻¹)	D _v ×10 ⁷ (cm ⁻¹)	1	8676.86	1.66	1.86	4.474	4.617
0	8275.66	1.71	1.81	4.499	4.447	2	9563.35	1.64	1.89	4.452	4.741
1	9178.12	1.66	1.85	4.477	4.611	3	10436.19	1.62	1.92	4.421	4.871
2	10066.45	1.64	1.89	4.455	4.737	4	11296.20	1.61	1.95	4.403	4.537
3	10940.89	1.62	1.92	4.424	4.899	5	12153.27	1.59	1.97	4.379	4.984
4	11801.61	1.60	1.94	4.406	4.515	6	12996.71	1.58	1.99	4.341	4.478
5	12659.95	1.59	1.97	4.382	4.989	7	13834.91	1.57	2.01	4.317	4.540
6	13504.34	1.58	1.99	4.342	4.502	8	14667.02	1.56	2.04	4.283	5.066
7	14343.00	1.57	2.01	4.320	4.496	9	15487.60	1.55	2.05	4.263	4.343
8	15176.12	1.56	2.03	4.285	5.135	10	16306.65	1.54	2.07	4.245	5.303
9	15996.90	1.55	2.05	4.264	4.347	11	17113.64	1.53	2.09	4.211	5.299
10	16816.19	1.54	2.07	4.247	5.334	12	17905.91	1.53	2.11	4.165	5.691
11	17623.17	1.54	2.09	4.212	5.312	13	18681.20	1.52	2.13	4.130	3.908
12	18415.09	1.53	2.12	4.165	5.815	14	19456.62	1.51	2.15	4.120	3.796
13	19188.83	1.52	2.13	4.128	3.982	15	20232.91	1.51	2.17	4.090	6.096
14	19962.02	1.51	2.15	4.118	3.888	16	20993.01	1.50	2.19	4.054	5.720

Appendix II. Results of Vibrational Calculations

Table IV:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states (1) $0^+[(X)^1\Sigma^+]$, (1) $0^-[(1)^3\Sigma^+]$, (2) $0^-[(2)^3\Pi]$, (8) $0^-[(1)^5\Phi]$ of the molecule YN.

(1) $0^+[(X)^1\Sigma^+]$						(1) $0^-[(1)^3\Sigma^+]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	303.49	1.79	1.93	4.024	6.470	0	3165.81	1.84	1.96	3.871	3.848
1	935.46	1.75	1.98	3.997	5.424	1	3940.25	1.80	2.00	3.853	3.818
2	1590.28	1.72	2.02	3.984	5.376	2	4710.54	1.78	2.04	3.830	3.905
3	2252.14	1.70	2.05	3.964	4.761	3	5472.29	1.76	2.07	3.808	4.402
4	2924.14	1.69	2.08	3.942	5.020	4	6211.67	1.74	2.10	3.763	5.682
5	3597.61	1.68	2.10	3.925	5.041	5	6904.58	1.72	2.14	3.692	6.296
6	4269.74	1.66	2.12	3.897	4.778	6	7557.97	1.71	2.17	3.659	3.644
7	4941.36	1.65	2.14	3.875	4.952	7	8217.41	1.69	2.19	3.642	4.877
8	5610.65	1.64	2.17	3.856	4.665	8	8866.99	1.68	2.22	3.606	4.714
9	6279.01	1.63	2.19	3.833	4.752	9	9508.33	1.68	2.25	3.584	4.580
10	6944.56	1.62	2.21	3.810	5.127	10	10143.13	1.67	2.27	3.551	4.841
11	7604.47	1.61	2.23	3.786	4.778	11	10769.41	1.66	2.30	3.529	4.753
12	8260.43	1.60	2.25	3.760	4.532	12	11387.79	1.66	2.32	3.492	5.557
13	8913.35	1.59	2.27	3.737	4.445	13	11992.60	1.65	2.34	3.460	5.296
14	9563.01	1.58	2.29	3.710	4.286	14	12585.38	1.64	2.36	3.416	7.333
15	10209.01	1.58	2.31	3.680	4.234	15	13152.82	1.64	2.40	3.345	1.031
16	10851.23	1.57	2.32	3.654	4.440	16	13678.27	1.63	2.43	3.241	1.145
17	11488.98	1.56	2.34	3.628	4.895	17	14165.02	1.62	2.47	3.187	4.317
18	12120.19	1.56	2.36	3.599	5.873	18	14649.27	1.62	2.50	3.166	7.335
19	12740.36	1.56	2.38	3.562	8.075	19	15120.69	1.61	2.53	3.108	6.906
20	13338.63	1.55	2.42	3.496	1.330	20	15581.28	1.60	2.56	3.090	4.305
21	13890.78	1.55	2.45	3.369	1.870	21	16040.39	1.60	2.59	3.052	7.555
22	14384.68	1.54	2.49	3.272	7.164	22	16488.18	1.59	2.62	3.022	4.527
23	14868.39	1.53	2.52	3.275	5.873	23	16933.14	1.59	2.64	2.994	6.625
24	15348.47	1.53	2.55	3.213	1.196						
25	15807.48	1.52	2.57	3.179	2.639						
26	16268.80	1.52	2.60	3.155	9.607						
27	16716.02	1.51	2.63	3.101	4.235						
(6) $0^-[(3)^3\Pi]$						(3) $3^-[1)^5\Phi]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	19011.34	1.92	2.01	3.592	2.165	0	20071.52	2.10	2.24	2.954	4.029
1	19921.05	1.88	2.08	3.526	4.158	1	20572.87	2.05	2.29	2.916	4.979
2	20643.26	1.85	2.14	3.435	6.918	2	21032.82	2.02	2.38	2.847	5.703
3	21227.56	1.84	2.19	3.363	3.664	3	21459.75	2.00	2.44	2.800	5.477
4	21813.59	1.83	2.24	3.299	1.456	4	21871.53	1.98	2.48	2.759	5.158
5	22254.60	1.82	2.32	3.150	-2.676	5	22273.81	1.97	2.52	2.718	5.075
6	22753.79	1.81	2.34	3.127	1.648	6	22669.06	1.96	2.56	2.691	3.596
7	23163.30	1.80	2.40	3.034	-1.087	7	23071.39	1.94	2.58	2.695	1.329
8	23604.88	1.79	2.44	3.017	9.625	8	23496.38	1.93	2.60	2.707	2.426
9	24027.01	1.78	2.46	3.006	4.971	9	23932.98	1.92	2.63	2.697	4.298
10	24451.08	1.77	2.50	2.958	1.016	10	24365.66	1.91	2.65	2.676	3.874
11	24857.22	1.76	2.52	2.958	5.764	11	24796.60	1.90	2.68	2.665	3.375
12	25265.17	1.75	2.55	2.941	2.976	12	25228.56	1.89	2.71	2.652	3.908
13	25676.82	1.74	2.58	2.900	5.244	13	25657.73	1.88	2.73	2.633	3.610

Appendix II. Results of Vibrational Calculations

Table V:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states (1) $1 [(1)^3\Sigma^+]$, (2) $0^+ [(2)^1\Sigma^+]$, (2) $0^- [(2)^3\Pi]$, (5) $1 [(2)^3\Pi]$ in YN.

(1) $1 [(1)^3\Sigma^+]$						(2) $0^+ [(2)^1\Sigma^+]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	3165.87	1.84	1.97	3.871	3.848	0	4311.84	1.81	1.91	3.890	3.366
1	3940.31	1.79	2.00	3.853	3.818	1	5095.03	1.77	2.04	3.692	1.113
2	4710.60	1.77	2.03	3.830	3.905	2	5589.31	1.76	2.07	3.627	-1.116
3	5472.36	1.75	2.07	3.808	4.402	3	6236.68	1.74	2.10	3.617	5.773
4	6211.73	1.74	2.10	3.763	5.682	4	6859.68	1.73	2.12	3.605	2.592
5	6904.63	1.72	2.13	3.692	6.296	5	7510.64	1.72	2.16	3.562	5.006
6	7558.02	1.71	2.16	3.659	3.644	6	8141.56	1.71	2.19	3.515	5.296
7	8217.46	1.70	2.19	3.642	4.877	7	8753.53	1.70	2.21	3.479	3.619
8	8867.05	1.69	2.21	3.606	4.713	8	9370.68	1.69	2.23	3.482	2.248
9	9508.38	1.68	2.25	3.584	4.580	9	10002.99	1.68	2.26	3.445	6.376
10	10143.18	1.67	2.27	3.551	4.840	10	10607.89	1.68	2.28	3.400	3.386
11	10769.47	1.66	2.30	3.529	4.753	11	11214.79	1.67	2.31	3.399	4.041
12	11387.86	1.66	2.31	3.492	5.556	12	11816.84	1.66	2.33	3.346	5.348
13	11992.69	1.65	2.34	3.460	5.298	13	12405.45	1.65	2.35	3.341	2.320
14	12585.46	1.64	2.36	3.415	7.336	14	13000.89	1.64	2.38	3.307	6.026
15	13152.89	1.63	2.39	3.345	1.030	15	13581.43	1.63	2.40	3.297	1.481
16	13678.32	1.63	2.41	3.241	1.145	16	14171.34	1.62	2.42	3.267	7.102
17	14165.07	1.62	2.47	3.187	4.319	17	14738.42	1.62	2.45	3.218	5.897
18	14649.32	1.61	2.51	3.166	7.335	18	15286.22	1.61	2.47	3.157	6.655
19	15120.74	1.61	2.52	3.108	6.905	19	15819.57	1.61	2.49	3.167	-1.061
20	15581.33	1.60	2.54	3.090	4.306	20	16373.39	1.60	2.51	3.156	6.346
21	16040.44	1.60	2.59	3.052	7.554	21	16911.49	1.60	2.53	3.098	8.045
22	16488.23	1.59	2.61	3.022	4.528	22	17427.29	1.59	2.55	3.069	-2.774
23	16933.18	1.58	2.63	2.994	6.624	23	17955.23	1.59	2.58	3.072	7.273
						24	18465.71	1.58	2.60	2.999	4.422
						25	18967.54	1.58	2.63	2.999	2.159
(2) $0^- [(2)^3\Pi]$						(5) $1 [(2)^3\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^4$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	14433.52	2.04	2.20	3.102	2.994	0	14477.89	2.05	2.18	3.189	3.248
1	15062.26	2.01	2.22	3.081	3.035	1	15106.92	2.01	2.24	3.166	3.252
2	15685.73	1.97	2.28	3.080	3.542	2	15732.56	1.98	2.27	3.166	4.032
3	16290.93	1.95	2.31	3.075	3.751	3	16334.29	1.95	2.31	3.165	4.120
4	16883.50	1.93	2.33	3.090	6.481	4	16923.94	1.94	2.33	3.179	7.102
5	17430.00	1.85	2.36	3.177	1.687	5	17468.02	1.86	2.36	3.272	1.834
6	17874.01	1.82	2.38	3.352	1.356	6	17911.69	1.83	2.38	3.447	1.360
7	18293.70	1.81	2.40	3.282	-4.977	7	18335.38	1.81	2.40	3.363	-6.382
8	18772.67	1.79	2.41	3.222	7.401	8	18822.36	1.80	2.41	3.293	6.685
9	19244.97	1.78	2.44	3.248	7.945	9	19305.60	1.78	2.44	3.307	7.972
10	19708.95	1.76	2.46	3.205	4.487	10	19780.46	1.76	2.46	3.274	6.682
11	20172.57	1.74	2.49	3.145	9.132	11	20247.78	1.76	2.49	3.215	1.000
12	20618.06	1.73	2.52	3.105	7.862	12	20695.75	1.75	2.51	3.174	1.017
13	21054.41	1.73	2.54	3.095	2.589	13	21130.53	1.74	2.54	3.174	-2.435
14	21507.51	1.72	2.56	3.108	6.575	14	21584.75	1.73	2.56	3.193	-2.628
15	21976.84	1.71	2.58	3.117	3.870	15	22058.71	1.72	2.57	3.206	4.298
16	22450.50	1.70	2.59	3.109	4.146	16	22536.57	1.71	2.59	3.193	6.590

Appendix II. Results of Vibrational Calculations

Table VI:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states (3) $0^+[(1)^3\Pi]$, (2) $1[(1)^3\Pi]$, (10) $2[(1)^5\Phi]$, (3) $1[(1)^1\Pi]$ in YN.

(3) $0^+[(1)^3\Pi]$						(2) $1[(1)^3\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	5364.51	1.92	2.24	3.575	3.519	0	5261.68	1.91	2.03	3.577	3.549
1	6084.46	1.87	2.09	3.568	3.170	1	5978.32	1.87	2.08	3.563	3.481
2	6822.08	1.84	2.11	3.571	2.894	2	6694.14	1.84	2.12	3.545	3.787
3	7577.49	1.82	2.14	3.574	2.780	3	7394.70	1.82	2.16	3.518	3.929
4	8344.86	1.80	2.16	3.564	3.325	4	8080.03	1.80	2.18	3.490	3.834
5	9103.71	1.78	2.19	3.551	3.199	5	8756.30	1.79	2.21	3.471	3.800
6	9857.86	1.77	2.21	3.537	3.204	6	9425.06	1.77	2.24	3.443	4.042
7	10607.33	1.76	2.23	3.523	3.795	7	10082.35	1.76	2.27	3.415	4.260
8	11340.49	1.75	2.24	3.486	5.088	8	10727.66	1.75	2.29	3.393	3.917
9	12033.85	1.74	2.29	3.402	1.087	9	11365.55	1.74	2.32	3.364	4.119
10	12612.15	1.72	2.34	3.191	1.494	10	11994.53	1.73	2.34	3.342	3.900
11	13097.10	1.72	2.39	3.199	-6.110	11	12617.49	1.72	2.36	3.317	4.656
12	13662.36	1.71	2.40	3.256	3.737	12	13226.58	1.72	2.39	3.277	5.190
13	14236.61	1.70	2.41	3.235	2.544	13	13818.15	1.71	2.41	3.242	4.761
14	14818.47	1.70	2.43	3.238	3.031	14	14398.37	1.70	2.43	3.219	3.486
15	15403.22	1.69	2.46	3.207	5.579	15	14977.18	1.70	2.45	3.203	3.938
16	15972.54	1.68	2.48	3.178	3.076	16	15550.98	1.69	2.48	3.173	5.237
17	16543.01	1.68	2.49	3.174	3.390	17	16111.37	1.68	2.50	3.139	4.638
18	17112.29	1.67	2.51	3.143	5.032	18	16662.66	1.68	2.53	3.116	4.015
19	17670.67	1.67	2.53	3.121	3.421	19	17208.45	1.67	2.55	3.088	5.102
20	18226.89	1.66	2.56	3.103	4.409	20	17743.52	1.67	2.57	3.057	4.640
21	18776.04	1.66	2.58	3.075	4.328	21	18270.41	1.66	2.59	3.032	4.599
22	19318.02	1.65	2.60	3.052	4.310	22	18789.36	1.66	2.61	3.000	5.105
(10) $2[(1)^5\Phi]$						(3) $1[(1)^1\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	20088.35	2.11	2.23	2.954	3.962	0	5369.55	1.91	2.03	3.575	3.464
1	20595.18	2.05	2.31	2.925	4.173	1	6094.86	1.87	2.08	3.566	3.114
2	21088.82	2.02	2.35	2.902	2.718	2	6837.86	1.84	2.12	3.566	2.887
3	21611.78	2.00	2.37	2.924	2.049	3	7596.47	1.82	2.14	3.567	2.771
4	22167.95	1.98	2.40	2.918	4.357	4	8366.24	1.80	2.17	3.560	3.232
5	22697.10	1.96	2.44	2.852	6.840	5	9129.04	1.78	2.19	3.546	3.217
6	23168.80	1.95	2.48	2.774	1.082	6	9885.60	1.77	2.21	3.531	3.167
7	23537.39	1.94	2.50	2.535	8.877	7	10637.42	1.76	2.23	3.518	3.806
8	23883.84	1.92	2.52	2.760	-15.26	8	11371.95	1.75	2.25	3.479	5.157
9	24409.83	1.91	2.58	2.876	1.040	9	12064.28	1.74	2.28	3.391	1.123
10	24964.56	1.90	2.60	2.848	9.351	10	12636.82	1.73	2.36	3.179	1.395
11	25440.13	1.89	2.64	2.592	3.241	11	13124.36	1.72	2.38	3.201	-5.943
12	25762.01	1.88	2.68	2.531	-1.804	12	13693.04	1.72	2.39	3.250	3.940
13	26174.51	1.88	2.73	2.620	1.303	13	14268.03	1.71	2.42	3.231	2.388
14	26545.47	1.87	2.76	2.456	8.315	14	14851.77	1.70	2.44	3.234	3.178
15	26892.93	1.86	2.80	2.491	-7.995	15	15437.13	1.69	2.46	3.201	5.483
16	27252.97	1.86	2.84	2.416	1.530	16	16007.54	1.69	2.48	3.175	2.682
17	27574.32	1.85	2.87	2.381	-3.169	17	16581.78	1.68	2.49	3.176	3.065
18	27909.09	1.84	2.93	2.337	1.868	18	17157.32	1.68	2.52	3.152	4.161
19	28205.69	1.84	2.96	2.285	2.571	19	17727.14	1.67	2.53	3.139	2.741
20	28500.63	1.83	3.02	2.211	1.167	20	18299.02	1.67	2.55	3.127	3.881

Appendix II. Results of Vibrational Calculations

Table VII:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states (8) 1 [(3)³Π], (6) 1[(2)¹Π], (4) 2 [(1)³Φ], (4) 1 [(3)¹Π], (12) 1 [(4)³Π], (6) 2 [(1)³Δ] in YN.

(8) 1 [(3) ³ Π]						(6) 1[(2) ¹ Π]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	19011.34	1.92	2.02	3.592	2.165	0	17602.30	1.91	2.01	3.596	6.841
1	19921.05	1.88	2.08	3.526	4.158	1	18068.22	1.85	2.15	3.335	1.132
2	20643.26	1.85	2.14	3.435	6.918	2	18468.71	1.83	2.21	3.438	1.634
3	21227.56	1.84	2.18	3.363	3.664	3	18829.25	1.81	2.25	3.280	1.470
4	21813.59	1.82	2.25	3.299	1.456	4	19131.49	1.81	2.37	2.997	1.152
5	22254.60	1.82	2.29	3.150	-2.676	5	19420.56	1.79	2.41	3.066	-5.965
6	22753.79	1.80	2.36	3.127	1.648	6	19769.78	1.79	2.45	3.026	1.037
7	23163.30	1.80	2.40	3.034	-1.087	7	20111.98	1.78	2.48	3.038	-2.688
8	23604.88	1.79	2.42	3.017	9.625	8	20494.07	1.77	2.49	3.063	8.821
9	24027.01	1.78	2.46	3.006	4.971	9	20876.85	1.77	2.51	3.091	-6.425
10	24451.08	1.76	2.50	2.958	10.165	10	21286.64	1.76	2.52	3.097	2.324
11	24857.22	1.76	2.53	2.958	5.764	11	21708.10	1.74	2.54	3.070	6.186
12	25265.17	1.75	2.55	2.941	2.976	12	22130.67	1.72	2.57	3.091	8.378
13	25676.81	1.75	2.59	2.900	5.244	13	22548.99	1.72	2.58	3.066	6.230
14	26081.04	1.74	2.62	2.857	3.180	14	22967.48	1.71	2.60	3.075	4.525
						15	23388.71	1.71	2.62	3.044	3.012
						16	23812.26	1.70	2.64	3.019	1.826
						17	24238.28	1.70	2.66	2.976	-5.465

(4) 2 [(1) ³ Φ]						(4) 1 [(3) ¹ Π]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	18723.77	1.93	2.02	3.574	2.053	0	12252.63	2.15	2.27	2.859	1.723
1	19659.63	1.89	2.07	3.538	3.450	1	12987.16	2.09	2.30	2.920	1.405
2	20437.53	1.86	2.15	3.434	7.270	2	13773.10	2.05	2.32	2.955	1.638
3	21029.03	1.84	2.19	3.344	8.890	3	14565.42	2.03	2.34	2.964	2.601
4	21482.59	1.83	2.36	2.981	4.476	4	15308.45	1.99	2.36	2.981	3.655
5	21714.39	1.82	2.40	2.990	-2.144	5	15992.91	1.97	2.38	3.027	4.904
6	22064.02	1.81	2.46	2.886	1.468	6	16622.80	1.93	2.40	3.074	6.262
7	22383.93	1.81	2.50	2.931	-1.655	7	17204.17	1.89	2.42	3.158	1.340
8	22740.79	1.80	2.51	2.917	-1.669	8	17697.64	1.83	2.44	3.303	1.461
9	23132.57	1.79	2.53	2.963	1.479	9	18148.76	1.81	2.45	3.305	4.426
10	23545.29	1.78	2.55	2.939	4.972	10	18635.38	1.80	2.46	3.249	7.108
11	23958.05	1.77	2.57	2.915	6.160	11	19147.53	1.78	2.48	3.210	4.663
12	24366.94	1.76	2.60	2.898	2.581	12	19661.65	1.76	2.49	3.211	9.103
						13	20159.73	1.75	2.51	3.209	8.894
						14	20641.77	1.74	2.54	3.145	1.041
						15	21095.61	1.73	2.58	3.026	1.308

(12) 1 [(4) ³ Π]						(6) 2 [(1) ³ Δ]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	22211.61	2.04	2.15	3.153	2.270	0	20416.61	1.91	2.04	3.546	4.336
1	22929.29	2.00	2.27	3.050	9.507	1	21051.25	1.87	2.11	3.496	4.884
2	23334.18	1.98	2.32	2.927	1.512	2	21642.22	1.86	2.16	3.389	6.355
3	23810.70	1.96	2.37	2.987	7.141	3	22164.82	1.84	2.24	3.264	1.085
						4	22598.72	1.83	2.29	3.176	3.228
						5	23051.79	1.82	2.34	3.143	7.477
						6	23487.27	1.81	2.38	3.091	3.841

Appendix II. Results of Vibrational Calculations

Table VIII:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the states (4) 1 [(3)¹Π], (1) 5 [(1)⁵Φ], (3) 0⁻ [(2)³Σ⁺], (5) 2 [(3)³Π], (6) 2 [(1)³Δ], (11) 1 [(2)³Δ] in YN.

(4) 1 [(3) ¹ Π]						(1) 5 [(1) ⁵ Φ]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	12252.63	2.14	2.27	2.859	1.723	0	20416.61	1.91	2.04	3.546	4.336
1	12987.16	2.09	2.29	2.920	1.405	1	21051.25	1.88	2.10	3.496	4.884
2	13773.10	2.05	2.32	2.955	1.638	2	21642.22	1.86	2.16	3.389	6.355
3	14565.42	2.02	2.34	2.964	2.601	3	22164.82	1.85	2.22	3.264	1.085
4	15308.45	1.99	2.36	2.981	3.655	4	22598.72	1.83	2.28	3.176	3.228
5	15992.91	1.96	2.38	3.027	4.904	5	23051.79	1.82	2.32	3.143	7.477
6	16622.80	1.93	2.40	3.074	6.262	6	23487.27	1.81	2.37	3.091	3.841
7	17204.17	1.90	2.42	3.158	1.340	7	23930.46	1.80	2.40	3.071	3.300
8	17697.63	1.83	2.44	3.303	1.461	8	24384.29	1.79	2.44	3.043	8.600
9	18148.76	1.81	2.45	3.305	4.426	9	24813.67	1.78	2.49	2.973	7.746
10	18635.38	1.80	2.46	3.249	7.108	10	25224.42	1.78	2.51	2.934	1.578
11	19147.53	1.78	2.48	3.210	4.663	11	25650.54	1.77	2.54	2.947	6.403
12	19661.65	1.76	2.49	3.211	9.103	12	26074.34	1.76	2.56	2.931	2.884
13	20159.73	1.75	2.51	3.209	8.894	13	26503.37	1.76	2.59	2.900	7.124
14	20641.77	1.74	2.54	3.145	1.041						
(3) 0 ⁻ [(2) ³ Σ ⁺]						(5) 2 [(3) ³ Π]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	18831.95	1.92	2.03	3.563	2.222	0	19072.05	1.92	2.02	3.594	2.060
1	19728.46	1.88	2.07	3.532	3.721	1	20008.48	1.88	2.07	3.537	4.313
2	20471.91	1.86	2.15	3.422	6.914	2	20721.46	1.86	2.14	3.413	6.092
3	21066.11	1.84	2.19	3.372	5.207	3	21312.83	1.85	2.20	3.335	5.438
4	21636.44	1.82	2.24	3.315	8.146	4	21860.57	1.83	2.26	3.235	7.327
5	22143.21	1.81	2.29	3.213	6.647	5	22355.51	1.82	2.30	3.170	6.418
6	22615.01	1.81	2.34	3.125	7.972	6	22827.94	1.81	2.36	3.102	9.714
7	23054.41	1.80	2.39	3.059	6.877	7	23262.55	1.80	2.39	3.057	5.984
8	23477.29	1.79	2.44	3.003	5.729	8	23698.24	1.79	2.43	3.061	6.648
9	23893.66	1.78	2.47	2.965	6.391	9	24128.89	1.78	2.47	3.009	7.912
10	24305.54	1.77	2.51	2.948	6.450	10	24546.20	1.77	2.50	2.991	5.316
11	24715.34	1.77	2.54	2.934	5.325	11	24962.86	1.76	2.53	2.959	5.713
12	25125.13	1.76	2.57	2.910	5.160	12	25375.73	1.75	2.56	2.938	3.729
13	25533.08	1.75	2.59	2.885	5.167	13	25790.53	1.75	2.59	2.905	6.217
						14	26197.27	1.74	2.62	2.869	5.053
(6) 2 [(1) ³ Δ]						(11) 1 [(2) ³ Δ]					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	20416.61	1.76	2.49	3.546	4.336	0	20896.09	1.90	2.05	3.553	6.395
1	21051.25	1.74	2.52	3.496	4.884	1	21413.61	1.87	2.13	3.463	6.322
2	21642.22	1.73	2.54	3.389	6.355	2	21909.67	1.85	2.17	3.377	3.034
3	22164.82	1.72	2.57	3.264	1.085	3	22433.60	1.84	2.24	3.269	1.444
4	22598.72	1.71	2.59	3.176	3.228	4	23271.92	1.82	2.34	3.127	6.420
5	23051.79	1.70	2.61	3.143	7.477	5	23706.16	1.81	2.38	3.135	6.698
6	23487.27	1.70	2.63	3.091	3.841	6	24166.29	1.80	2.42	3.051	6.159
						7	24612.16	1.79	2.44	3.045	2.130
						8	25072.31	1.79	2.47	3.013	2.712
						9	25536.89	1.78	2.50	2.980	3.090
						10	26001.93	1.78	2.52	2.941	4.525

Appendix II. Results of Vibrational Calculations

Table IX:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the different Vibrational levels of the state (2) $0^- [(1)^3\Pi]$, (2) $0^+ [(1)^3\Pi]$, (2) $1[(1)^3\Pi]$, (3) $2 [(1)^3\Pi]$, (3) $0^- [(1)^3\Sigma^-]$, and (3) $1 [(1)^3\Sigma^-]$ in ZrS.

(2) $0^- [(1)^3\Pi]$						(2) $0^+ [(1)^3\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	8653.82	2.19	2.31	2.734	1.803	0	8677.46	2.19	2.30	2.809	1.956
1	9325.04	2.15	2.37	2.720	1.794	1	9348.53	2.15	2.37	2.794	1.943
2	9991.77	2.12	2.41	2.703	1.856	2	10015.35	2.12	2.40	2.776	2.011
3	10649.01	2.10	2.44	2.686	1.771	3	10672.64	2.10	2.44	2.759	1.922
4	11302.71	2.08	2.47	2.670	1.813	4	11326.23	2.08	2.47	2.742	1.967
5	11950.12	2.07	2.50	2.652	1.797	5	11973.4	2.06	2.49	2.723	1.950
6	12590.12	2.06	2.52	2.633	1.710	6	12613.03	2.05	2.53	2.703	1.856
7	13227.09	2.04	2.55	2.618	1.952	7	13249.58	2.04	2.55	2.688	2.105
8	13855.89	2.03	2.58	2.604	1.963	8	13878.23	2.03	2.58	2.674	2.122
9	14477.08	2.02	2.60	2.588	1.999	9	14499.33	2.02	2.60	2.658	2.176
10	15090.48	2.01	2.62	2.574	2.068	10	15112.37	2.01	2.62	2.642	2.237
11	15695.16	2.00	2.64	2.556	1.964	11	15716.7	2.00	2.64	2.624	2.117
(2) $1[(1)^3\Pi]$						(3) $2 [(1)^3\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	8857.47	2.18	2.31	2.733	1.810	0	9092.71	2.19	2.32	2.732	1.838
1	9527.1	2.14	2.37	2.719	1.797	1	9756.13	2.15	2.38	2.715	1.917
2	10192.54	2.12	2.40	2.702	1.866	2	10405.09	2.12	2.41	2.690	2.053
3	10848.15	2.10	2.44	2.684	1.784	3	11036.65	2.10	2.44	2.671	1.735
4	11499.86	2.08	2.47	2.668	1.834	4	11671.54	2.08	2.48	2.658	1.835
5	12144.62	2.07	2.50	2.650	1.819	5	12302.57	2.07	2.51	2.640	1.717
6	12781.19	2.06	2.52	2.630	1.735	6	12930.29	2.06	2.53	2.624	1.698
7	13414.08	2.04	2.55	2.614	1.988	7	13556.43	2.05	2.56	2.606	1.893
8	14038.06	2.03	2.58	2.599	2.026	8	14176.92	2.04	2.58	2.596	1.898
9	14653.35	2.02	2.60	2.582	2.000	9	14792.42	2.02	2.60	2.581	1.984
10	15261.44	2.01	2.62	2.569	1.992	10	15401.29	2.01	2.63	2.569	1.927
(3) $0^- [(1)^3\Sigma^-]$						(3) $1 [(1)^3\Sigma^-]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^7$ (cm $^{-1}$)
0	9372.52	2.21	2.32	2.685	1.755	0	9431.55	2.21	2.33	2.684	1.774
1	10035.45	2.17	2.39	2.675	1.697	1	10090.19	2.17	2.39	2.673	1.707
2	10699.62	2.14	2.42	2.660	1.851	2	10751.24	2.14	2.42	2.661	1.660
3	11349.95	2.12	2.46	2.641	1.838	3	11413.74	2.12	2.46	2.650	1.743
4	11991.6	2.10	2.49	2.629	1.642	4	12070	2.10	2.48	2.634	1.863
5	12633.27	2.08	2.52	2.614	1.865	5	12714.45	2.08	2.51	2.617	1.726
6	13266.01	2.07	2.54	2.595	1.641	6	13354.08	2.07	2.54	2.601	1.720
7	13896.51	2.06	2.57	2.580	1.744	7	13988.48	2.06	2.56	2.583	1.724
8	14521.5	2.05	2.59	2.562	1.850	8	14617.21	2.05	2.59	2.565	1.905
9	15138.87	2.04	2.62	2.546	1.949	9	15236.61	2.04	2.61	2.547	2.067
10	15748.56	2.02	2.64	2.534	1.971	10	15845.07	2.02	2.64	2.532	2.126

Appendix II. Results of Vibrational Calculations

Table X:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the Vibrational levels of the state (4) 2 $[(1)^3\Phi]$, (2) 3 $[(1)^3\Phi]$, (1) 4 $[(1)^3\Phi]$, (5) 1 $[(1)^3\Sigma^+]$, (6) 1 $[(2)^3\Pi]$, (5) 0⁻ $[(2)^3\Pi]$, (4) 0⁺ $[(2)^3\Pi]$, (7) 1 $[(2)^3\Delta]$ in ZrS.

(4) 2 $[(1)^3\Phi]$						(2) 3 $[(1)^3\Phi]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	10681.85	2.22	2.34	2.665	1.581	0	11139.83	2.22	2.34	2.721	1.993
1	11373.66	2.17	2.39	2.663	1.712	1	11773.86	2.18	2.40	2.708	2.008
2	12048.39	2.15	2.43	2.645	1.776	2	12402.05	2.15	2.44	2.692	1.895
3	12709.19	2.12	2.46	2.633	1.783	3	13031.79	2.13	2.48	2.683	1.768
4	13359.11	2.10	2.49	2.610	2.035	4	13666.27	2.11	2.50	2.673	1.751
5	13988.36	2.09	2.52	2.592	1.917	5	14303.42	2.09	2.53	2.664	1.959
6	14607.64	2.08	2.56	2.574	1.689	6	14934.38	2.08	2.55	2.648	1.816
7	15224.17	2.07	2.58	2.557	1.935	7	15562.07	2.07	2.58	2.632	1.941
8	15831.03	2.06	2.60	2.536	1.779	8	16182.72	2.06	2.60	2.613	1.904
9	16432.31	2.04	2.62	2.521	1.829	9	16796.96	2.05	2.62	2.595	2.016
(1) 4 $[(1)^3\Phi]$						(5) 1 $[(1)^3\Sigma^+]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	11626.36	2.22	2.34	2.649	1.848	0	12826.42	2.21	2.34	2.678	2.217
1	12259.04	2.18	2.41	2.637	1.875	1	13411.12	2.17	2.40	2.653	1.859
2	12884.47	2.15	2.44	2.620	1.817	2	14014.92	2.14	2.43	2.639	1.996
3	13507.47	2.12	2.48	2.607	1.820	3	14615.89	2.12	2.48	2.623	1.853
4	14126.79	2.11	2.51	2.591	1.842	4	15217.64	2.10	2.50	2.606	1.983
5	14741.18	2.09	2.54	2.577	1.926	5	15813.51	2.09	2.53	2.587	1.807
6	15348.56	2.08	2.56	2.563	1.616	6	16407.99	2.08	2.56	2.570	1.873
7	15957.11	2.07	2.59	2.549	1.726	7	16997.8	2.06	2.58	2.548	1.935
8	16562.81	2.06	2.61	2.534	1.648	8	17580.22	2.05	2.61	2.525	1.971
(6) 1 $[(2)^3\Pi]$						(5) 0 ⁻ $[(2)^3\Pi]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	12959.35	2.22	2.34	2.647	1.845	0	13011.79	2.21	2.34	2.662	1.524
1	13590.26	2.18	2.41	2.627	1.845	1	13714.57	2.17	2.40	2.657	1.795
2	14215.62	2.16	2.44	2.613	1.872	2	14383.93	2.14	2.43	2.638	1.727
3	14834.59	2.13	2.48	2.599	1.764	3	15043.12	2.13	2.46	2.624	1.925
4	15451.06	2.11	2.51	2.580	1.908	4	15682.89	2.11	2.50	2.596	2.176
5	16060.11	2.09	2.54	2.568	1.914	5	16299.15	2.09	2.53	2.578	1.924
6	16662.78	2.08	2.57	2.552	1.782	6	16907.29	2.08	2.56	2.562	1.746
7	17261.54	2.07	2.60	2.533	1.852	7	17511.57	2.08	2.58	2.540	2.038
8	17854.69	2.06	2.62	2.519	1.618	8	18105.27	2.06	2.61	2.526	1.360
(4) 0 ⁺ $[(2)^3\Pi]$						(7) 1 $[(2)^3\Delta]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	13128.23	2.21	2.33	2.675	1.544	0	13614.29	2.23	2.36	2.699	2.022
1	13830.49	2.17	2.39	2.662	1.799	1	14236.79	2.18	2.41	2.691	2.256
2	14498.45	2.14	2.43	2.638	2.029	2	14840.29	2.15	2.46	2.687	2.212
3	15134.31	2.12	2.47	2.613	1.796	3	15438.68	2.13	2.49	2.679	1.982
4	15760.89	2.11	2.50	2.598	1.800	4	16039.14	2.11	2.51	2.663	1.861
5	16383.74	2.09	2.53	2.587	1.780	5	16643.05	2.09	2.54	2.651	2.083
6	17002.56	2.08	2.56	2.569	1.865	6	17242.14	2.08	2.56	2.634	2.191
7	17613.18	2.07	2.59	2.548	1.786	7	17832.43	2.09	2.60	2.612	1.852

Appendix II. Results of Vibrational Calculations

Table XI:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the Vibrational levels of the state (3) $2[(2)^3\Pi]$, (7) $1[(2)^3\Delta]$, (2) $2[(1)^1\Delta]$, (6) $2[(2)^3\Delta]$, (2) $4[(1)^1\Gamma]$, (7) $2[(2)^1\Delta]$, (3) $3[(2)^3\Delta]$ in ZrS.

(3) $2[(2)^3\Pi]$						(7) $1[(2)^3\Delta]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	13024.18	2.22	2.34	2.732	1.642	0	13614.29	2.23	2.36	2.699	2.022
1	13728.3	2.18	2.40	2.728	1.938	1	14236.79	2.18	2.41	2.691	2.256
2	14398.79	2.15	2.44	2.708	1.848	2	14840.29	2.15	2.46	2.687	2.212
3	15060.38	2.12	2.47	2.696	2.017	3	15438.68	2.13	2.49	2.679	1.981
4	15706.11	2.11	2.49	2.671	2.148	4	16039.14	2.11	2.51	2.663	1.861
5	16335.24	2.09	2.53	2.655	2.015	5	16643.05	2.09	2.54	2.651	2.083
6	16956.53	2.08	2.56	2.639	1.939	6	17242.14	2.08	2.56	2.634	2.191
7	17570.66	2.07	2.59	2.613	2.336	7	17832.43	2.09	2.60	2.612	1.851
8	18168.93	2.06	2.61	2.592	1.829	8	18421.24	2.06	2.62	2.597	1.913
9	18762.95	2.05	2.64	2.570	2.403						
(2) $2[(1)^1\Delta]$						(6) $2[(2)^3\Delta]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	5289.18	2.17	2.30	2.767	1.710	0	13963.06	2.22	2.36	2.644	2.014
1	5991.08	2.24	2.35	2.754	1.699	1	14564.92	2.18	2.41	2.621	1.608
2	6689.07	2.10	2.39	2.739	1.706	2	15192.55	2.16	2.45	2.601	1.897
3	7381.76	2.09	2.42	2.724	1.714	3	15809.95	2.14	2.49	2.590	1.942
4	8068.69	2.07	2.45	2.709	1.645	4	16415.82	2.12	2.52	2.565	1.660
5	8752.6	2.06	2.48	2.693	1.674	5	17022.86	2.10	2.54	2.553	1.873
6	9431.66	2.04	2.50	2.679	1.684	6	17624.19	2.09	2.58	2.537	2.095
7	10104.96	2.03	2.52	2.664	1.838	7	18213.34	2.08	2.60	2.517	1.451
8	10770.16	2.02	2.54	2.652	1.859	8	18806.23	2.07	2.62	2.507	1.558
9	11427.68	2.01	2.57	2.638	1.784						
(2) $4[(1)^1\Gamma]$						(7) $2[(2)^1\Delta]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
0	13828.05	2.22	2.36	2.708	2.252	0	17336.94	2.21	2.33	2.680	1.826
1	14421.62	2.18	2.41	2.704	2.050	1	17983.15	2.17	2.39	2.660	2.413
2	15024.11	2.16	2.45	2.678	1.611	2	18553.41	2.14	2.49	2.549	7.959
3	15645.76	2.14	2.49	2.656	2.065	3	18916.09	2.13	2.55	2.435	-4.456
4	16257.17	2.12	2.52	2.639	2.108	4	19352.97	2.12	2.59	2.470	4.233
5	16860.36	2.10	2.55	2.625	1.926						
6	17459.9	2.09	2.58	2.602	2.353						
7	18043.05	2.08	2.61	2.573	2.314						
						(3) $3[(2)^3\Delta]$					
						v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^7$ (cm ⁻¹)
						0	14125.69	2.22	2.34	2.666	1.383
						1	14863.83	2.18	2.39	2.653	1.733
						2	15554.75	2.15	2.43	2.641	1.641
						3	16234.53	2.13	2.46	2.625	1.592
						4	16908.47	2.11	2.49	2.611	1.722
						5	17571.13	2.09	2.52	2.599	1.735
						6	18224.06	2.08	2.54	2.579	1.758
						7	18865.78	2.07	2.57	2.555	2.269

Appendix II. Results of Vibrational Calculations

Table XII:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the Vibrational levels of the state (4) $3/2 [(1)^4\Pi]$, (2) $5/2 [(1)^4\Pi]$, (5) $1/2 [(1)^4\Pi]$, (6) $1/2 [(3)^2\Pi]$, (7) $3/2 [(1)^4\Sigma^+]$, (7) $1/2 [(1)^4\Sigma^+]$, (8) $1/2 [(1)^4\Delta]$, (5) $5/2 [(1)^4\Delta]$ in YS.

(4) $3/2 [(1)^4\Pi]$						(2) $5/2 [(1)^4\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	18424.82	2.55	2.68	1.038	4.550	0	18441.76	2.55	2.68	1.038	4.439
1	18738.06	2.50	2.74	1.035	4.697	1	18759.44	2.50	2.73	1.038	4.177
2	19046.82	2.47	2.78	1.029	4.746	2	19080.79	2.47	2.77	1.033	5.317
3	19352.21	2.45	2.81	1.025	4.474	3	19387.26	2.45	2.81	1.024	4.810
4	19657.51	2.43	2.84	1.021	4.613	4	19690.18	2.43	2.84	1.022	4.135
5	19961.35	2.42	2.87	1.018	4.118	5	19995.32	2.41	2.87	1.016	5.289
6	20266.64	2.40	2.89	1.014	4.738	6	20294.45	2.40	2.89	1.012	3.943
7	20569.07	2.39	2.92	1.009	5.103	7	20595.39	2.39	2.92	1.007	5.650

(5) $1/2 [(1)^4\Pi]$						(6) $1/2 [(3)^2\Pi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	18448.64	2.55	2.68	1.040	4.249	0	19070.85	2.56	2.70	1.032	3.480
1	18774.07	2.50	2.73	1.040	4.240	1	19426.62	2.51	2.72	1.042	2.381
2	19098.12	2.47	2.77	1.032	5.842	2	19817.75	2.48	2.75	1.051	2.414
3	19400.05	2.45	2.81	1.024	4.022	3	20224.30	2.45	2.76	1.052	3.414
4	19706.40	2.43	2.84	1.023	5.107	4	20620.85	2.43	2.79	1.050	4.230
5	20007.36	2.41	2.87	1.014	4.549	5	20999.75	2.41	2.82	1.044	6.367
6	20307.07	2.40	2.89	1.012	4.846	6	21342.34	2.39	2.86	1.018	8.085
7	20604.08	2.38	2.92	1.005	4.670	7	21651.92	2.38	2.88	1.015	1.361
						8	21975.12	2.37	2.91	1.008	8.648
						9	22276.29	2.36	2.94	1.005	5.241

(7) $3/2 [(1)^4\Sigma^+]$						(7) $1/2 [(1)^4\Sigma^+]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	19344.19	2.56	2.70	1.029	3.584	0	20172.96	2.56	2.70	1.027	4.685
1	19693.25	2.51	2.73	1.039	2.266	1	20476.99	2.51	2.75	1.026	4.022
2	20082.57	2.48	2.74	1.051	2.368	2	20792.38	2.48	2.79	1.028	2.996
3	20488.81	2.45	2.76	1.058	3.256	3	21126.69	2.46	2.80	1.036	2.129
4	20888.92	2.43	2.80	1.052	4.566	4	21483.79	2.44	2.81	1.043	2.397
5	21266.47	2.41	2.81	1.042	3.109	5	21854.39	2.42	2.83	1.046	3.880
6	21644.98	2.39	2.82	1.052	1.436	6	22218.72	2.40	2.86	1.034	9.262
7	22041.22	2.38	2.86	1.052	7.133	7	22535.06	2.38	2.90	1.002	9.360
8	22394.20	2.36	2.89	1.007	1.540						

(8) $1/2 [(1)^4\Delta]$						(5) $5/2 [(1)^4\Delta]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	20965.66	2.56	2.70	1.024	4.720	0	21071.47	2.56	2.70	1.023	4.769
1	21266.82	2.52	2.76	1.020	4.688	1	21370.73	2.52	2.76	1.019	4.684
2	21567.23	2.49	2.80	1.018	3.919	2	21670.13	2.49	2.80	1.018	3.942
3	21876.22	2.46	2.82	1.019	3.571	3	21977.99	2.46	2.82	1.019	3.613
4	22193.15	2.44	2.86	1.019	4.734	4	22293.49	2.44	2.86	1.018	4.780
5	22504.05	2.43	2.88	1.008	7.487	5	22603.10	2.43	2.88	1.008	6.459
6	22792.87	2.41	2.91	0.997	3.609	6	22897.91	2.41	2.90	1.003	2.125

Appendix II. Results of Vibrational Calculations

Table XIII:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the Vibrational levels of the state (9) $1/2 [(3)^2\Sigma^+]$, (10) $1/2 [(1)^4\Sigma^-]$, (1) $7/2 [(1)^4\Phi]$, (5) $3/2 [(1)^4\Phi]$, (3) $5/2 [(1)^4\Phi]$, (4) $5/2 [(1)^2\Phi]$, (2) $7/2 [(1)^2\Phi]$, (7) $3/2 [(1)^4\Sigma^+]$ in YS.

(9) $1/2 [(3)^2\Sigma^+]$						(10) $1/2 [(1)^4\Sigma^-]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	21446.53	2.56	2.67	1.024	4.436	0	21576.46	2.56	2.69	1.027	4.138
1	21756.65	2.52	2.76	1.018	4.622	1	21898.00	2.52	2.75	1.018	4.211
2	22061.49	2.49	2.80	1.014	3.824	2	22216.26	2.49	2.80	1.018	4.028
3	22373.63	2.47	2.82	1.013	4.548	3	22535.90	2.47	2.81	1.015	4.231
4	22682.17	2.45	2.86	1.008	5.855	4	22853.02	2.45	2.86	1.011	5.758
5	22976.53	2.43	2.89	9.954	6.112	5	23153.34	2.43	2.89	9.938	6.870
6	23260.33	2.42	2.92	9.939	2.456						
(1) $7/2 [(1)^4\Phi]$						(5) $3/2 [(1)^4\Phi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	18544.63	2.55	2.69	1.035	4.495	0	18567.18	2.55	2.69	1.034	4.664
1	18858.57	2.51	2.74	1.033	4.590	1	18874.83	2.51	2.74	1.031	4.568
2	19168.98	2.48	2.78	1.026	4.985	2	19182.35	2.48	2.78	1.026	4.752
3	19472.24	2.45	2.81	1.022	4.263	3	19486.56	2.45	2.82	1.022	4.278
4	19777.38	2.44	2.85	1.018	4.819	4	19792.69	2.44	2.85	1.020	3.914
5	20079.45	2.42	2.87	1.015	3.497	5	20102.85	2.42	2.87	1.020	2.933
						6	20422.57	2.40	2.88	1.022	3.168
						7	20748.09	2.39	2.91	1.021	4.494
(3) $5/2 [(1)^4\Phi]$						(4) $5/2 [(1)^2\Phi]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	18574.05	2.55	2.69	1.036	4.234	0	18603.94	2.55	2.68	1.040	3.326
1	18898.73	2.50	2.73	1.039	3.206	1	18972.08	2.50	2.70	1.051	2.579
2	19246.39	2.47	2.75	1.043	3.895	2	19366.52	2.47	2.74	1.054	4.130
3	19590.39	2.45	2.80	1.033	7.072	3	19736.67	2.44	2.77	1.042	5.652
4	19896.31	2.43	2.83	1.017	4.161	4	20074.72	2.42	2.81	1.035	4.775
5	20203.50	2.41	2.86	1.024	3.304	5	20399.13	2.41	2.85	1.017	7.841
6	20517.55	2.40	2.89	1.013	6.045	6	20697.24	2.39	2.87	1.018	3.006
7	20821.06	2.38	2.91	1.016	7.726	7	21020.58	2.38	2.90	1.015	7.776
8	21142.87	2.37	2.92	1.016	5.890	8	21325.16	2.37	2.92	1.014	-2.052
						9	21661.02	2.36	2.93	1.024	4.767
(2) $7/2 [(1)^2\Phi]$						(7) $3/2 [(1)^4\Sigma^+]$					
v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)	v	E_v (cm $^{-1}$)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm $^{-1}$)	$D_v \times 10^8$ (cm $^{-1}$)
0	18862.11	2.55	2.68	1.037	3.655	0	21162.80	2.57	2.70	1.022	4.788
1	19212.33	2.50	2.72	1.045	2.792	1	21461.22	2.52	2.76	1.019	4.555
2	19587.92	2.47	2.75	1.050	3.093	2	21762.48	2.49	2.80	1.019	3.604
3	19968.09	2.45	2.77	1.052	2.939	3	22076.24	2.47	2.81	1.022	3.220
4	20353.34	2.42	2.78	1.056	2.692	4	22400.93	2.44	2.86	1.021	5.395
5	20745.15	2.40	2.80	1.056	4.013	5	22711.14	2.43	2.88	1.002	10.15
6	21125.58	2.39	2.83	1.046	6.617	6	22984.67	2.41	2.90	9.932	-0.755
7	21471.80	2.37	2.87	1.022	9.840						
8	21777.60	2.36	2.90	1.013	1.116						

Appendix II. Results of Vibrational Calculations

Table XIV:

Values of the Eigen-values E_v , the abscissas of the turning point $R_{\min}$, $R_{\max}$, and the rotational constants B_v , D_v for the Vibrational levels of the state (3) $7/2 [(1)^4\Delta]$, (9) $3/2 [(2)^2\Delta]$, (6) $5/2 [(2)^2\Delta]$, (12) $1/2 [(2)^4\Pi]$ in YS.

(3) $7/2 [(1)^4\Delta]$						(9) $3/2 [(2)^2\Delta]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^8$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^8$ (cm ⁻¹)
0	21268.51	2.57	2.71	1.021	4.776	0	21466.41	2.56	2.70	1.024	4.452
1	21566.82	2.52	2.76	1.018	4.558	1	21776.22	2.52	2.76	1.019	4.488
2	21867.79	2.49	2.80	1.017	3.685	2	22083.92	2.49	2.80	1.017	3.718
3	22180.13	2.47	2.81	1.020	3.204	3	22400.27	2.47	2.81	1.017	3.725
4	22503.84	2.44	2.85	1.021	4.674	4	22720.57	2.45	2.86	1.013	5.934
5	22820.54	2.43	2.88	1.009	8.331	5	23021.84	2.43	2.89	9.941	8.477
6	23108.09	2.41	2.91	9.948	3.790						
(6) $5/2 [(2)^2\Delta]$						(12) $1/2 [(2)^4\Pi]$					
v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^8$ (cm ⁻¹)	v	E_v (cm ⁻¹)	$R_{\min}$ (Å)	$R_{\max}$ (Å)	$B_v \times 10^1$ (cm ⁻¹)	$D_v \times 10^8$ (cm ⁻¹)
0	21540.39	2.55	2.70	1.027	4.869	0	21576.46	2.60	2.68	1.027	4.138
1	21837.61	2.52	2.75	1.021	3.763	1	21898.00	2.53	2.75	1.018	4.211
2	22151.06	2.49	2.80	1.017	4.101	2	22216.26	2.50	2.80	1.018	4.028
3	22774.84	2.44	2.86	1.015	5.143	3	22535.90	2.47	2.81	1.015	4.231
						4	22853.01	2.45	2.86	1.011	5.758
						5	23153.34	2.43	2.88	9.938	6.870

Appendix III

Dipole Moment Results

Table I:

Permanent dipole moments for the electronic states of the molecule YN at
R= 1.84Å.

State Ω	$\mu(\text{Debye})$	State Ω	$\mu(\text{Debye})$
(1) 0 ⁻ [(1) ³ Σ^+]	-3.045	(1) 2[(1) ³ Π]	-3.426
(2) 0 ⁻ [(2) ³ Π]	-4.313	(3) 2 [(1) ¹ Δ]	-4.018
(3) 0 ⁻ [(2) ³ Σ^+]	-3.962	(4) 2 [(1) ³ Φ]	-5.688
(4) 0 ⁻ [(3) ³ Π]	1.070	(6) 2 [(1) ³ Δ]	-3.922
(5) 0 ⁻ [(3) ³ Σ^+]	-3.479	(7) 2 [(2) ³ Δ]	1.741
(6) 0 ⁻ [(1) ³ Σ^-]	-3.975	(8) 2 [(2) ¹ Δ]	-4.153
(7) 0 ⁻ [(4) ³ Π]	-2.585	(9) 2 [(2) ³ Φ]	-0.707
(8) 0 ⁻ [(1) ⁵ Φ]	-0.666	(10) 2 [(1) ⁵ Φ]	-0.668
(9) 0 ⁻ [(1) ⁵ Σ^+]	1.276	(11) 2 [(1) ⁵ Σ^+]	-1.093
(10) 0 ⁻ [(1) ⁵ Δ]	1.276	(12) 2 [(1) ⁵ Δ]	1.164
(1) 0 ⁺ [(X) ¹ Σ^+]	-2.503	(14) 2 [(1) ⁵ Π]	1.568
(2) 0 ⁺ [(2) ¹ Σ^+]	-9.180	(1) 3 [(1) ³ Φ]	-5.713
(3) 0 ⁺ [(1) ³ Π]	-3.429	(2) 3 [(2) ³ Δ]	-4.011
(4) 0 ⁺ [(3) ¹ Σ^+]	-3.942	(3) 3 [(1) ⁵ Φ]	-0.666
(6) 0 ⁺ [(4) ³ Π]	-2.559	(4) 3 [(1) ⁵ Δ]	1.156
(7) 0 ⁺ [(4) ¹ Σ^+]	-1.535	(5) 3 [(2) ⁵ Π]	1.350
(8) 0 ⁺ [(1) ⁵ Δ]	-0.668	(6) 3 [(1) ⁵ Π]	3.294
(9) 0 ⁺ [(2) ⁵ Π]	1.276	(1) 4 [(2) ³ Φ]	-0.707
(10) 0 ⁺ [(1) ⁵ Π]	3.424		
(1) 1 [(1) ³ Σ^+]	-3.045		
(2) 1 [(1) ³ Π]	-3.291		
(3) 1 [(1) ¹ Π]	-2.999		
(4) 1 [(3) ¹ Π]	-2.496		
(5) 1 [(2) ³ Π]	-4.369		
(6) 1 [(2) ¹ Π]	-4.445		
(7) 1 [(2) ³ Σ^+]	-4.100		
(8) 1 [(3) ³ Π]	-6.128		
(9) 1 [(3) ³ Σ^+]	-3.479		
(10) 1 [(1) ³ Δ]	-7.462		
(12) 1 [(4) ³ Π]	-2.590		
(13) 1 [(1) ⁵ Σ^+]	-2.524		
(14) 1 [(1) ⁵ Δ]	-0.668		
(15) 1 [(2) ⁵ Π]	1.162		

Table II:

Permanent dipole moments for the electronic states of the molecule ZrN at $R = 1.73 \text{ \AA}$.

State Ω	$\mu(\text{Debye})$	State Ω	$\mu(\text{Debye})$
(1)1/2 [$X^2\Sigma^+$]	-3.189	(11)3/2[(1) $^4\Sigma^+$]	-0.954
(2)1/2[(1) $^2\Pi$]	-4.718	(1)5/2[(1) $^2\Delta$]	-6.489
(3)1/2[(1) $^4\Delta$]	-2.637	(2)5/2[(1) $^4\Delta$]	-1.955
(4)1/2[(2) $^2\Sigma^+$]	-2.903	(3)5/2[(1) $^4\Pi$]	-2.171
(5)1/2[(2) $^2\Delta$]	-2.018	(4)5/2[(1) $^4\Phi$]	-2.211
(6)1/2[(1) $^4\Pi$]	-2.283	(5)5/2[(1) $^2\Phi$]	-1.801
(7)1/2[(2) $^2\Pi$]	-2.643	(6)5/2[(3) $^2\Delta$]	-0.863
(8)1/2[(3) $^2\Pi$]	-1.450	(7)5/2[(2) $^2\Phi$]	-0.753
(9)1/2[(3) $^2\Sigma^+$]	-4.393	(8)5/2[(2) $^4\Pi$]	-0.769
(1)3/2[(1) $^2\Delta$]	-6.490	(1)7/2[(1) $^4\Delta$]	-1.955
(2)3/2[(1) $^2\Pi$]	-4.705	(2)7/2 [(1) $^2\Gamma$]	-0.608
(3)3/2[(1) $^4\Delta$]	-1.955	(3)7/2 [(1) $^4\Phi$]	-1.824
(4)3/2[(1) $^4\Phi$]	-2.216	(4)7/2[(1) $^2\Phi$]	-0.369
(5)3/2[(2) $^2\Pi$]	-1.447	(6)7/2 [(2) $^4\Delta$]	-2.182
(6)3/2[(1) $^4\Pi$]	-1.828	(1)9/2[(1) $^4\Phi$]	-2.222
(7)3/2[(3) $^2\Delta$]	-2.242		
(8)3/2[(3) $^2\Pi$]	-2.222		
(9)3/2[(4) $^2\Pi$]	-0.804		
(10)3/2[(2) $^4\Pi$]	-1.030		

Curriculum Vitae

Ayman K. Farhat

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Target Job: Post-Doctoral Research Fellow

Education:

- September 2009 → June 2012

PhD research fellow in physics with emphasis on computational material sciences from the University of Claude Bernard – Lyon1, Laboratoire de Physique de la matière Condensée et Nanostructures, France.

- September 2006 → May 2009

M.S. in Molecular Computational Quantum physics from Beirut Arab University (GPA = 3, in first M.S. year courses, during the courses and the thesis work I obtained the first rank over all my classmates).

- September 2003 → June 2006

B.S in physics from the Lebanese International University (major courses GPA=3.2, I got the first rank over all my classmates, 10 students).

- September 2007 → June 2007

Registered in a double major program of Mechanical Engineering at the Lebanese International University (GPA = 3.5).

- June- 2003

Lebanese Baccalaureate degree - life science section.

Research Experience:

- September 2009 → June 2012

My PhD research experience includes high quality post Hartree Fock Multireference Single and Double Excitation Configuration Interaction (MRSDCI) *ab initio* calculations for the electronic structures of the transition metal nitrides and sulfides of Yttrium and Zirconium. In my PhD thesis work we studied the electronic structures of the four molecules YS, YN, ZrN, and ZrS with the inclusion of relativistic spin orbit effects. The results of these calculations yielded accurate spectroscopic constants which are in excellent agreement with the experimental and

theoretical results available in literature. Several molecular properties were also computed such as the permanent electric dipole moments, internal molecular electric fields, and diamagnetic shielding tensors. We further used a Fortran 95 code, developed by our research group, that solves the time independent Schrödinger equation within the canonical functions approach for the vibrational and rotational motions of each molecule. The implemented program yielded accurate vibrational energy levels and rotational constants that are only within 10% of experimental accuracy. I further expect to develop the code into solving the time dependent vibrational-rotational Schrödinger equation under the effect of an oscillating laser field perturbation for a selected two vibrational level transition. This should have applications in quantum computing as selected transition between vibrational levels may be followed by designing an optimal laser pulse that is sufficient to cause transition between the quantum states (qubits) of a polar diatomic molecule. The results of our relativistic *ab initio* calculations are the first of their kind on these molecules reported in literature. Finally, I searched for applications of the molecules of interest in three domains; in quantum computing on heteronuclear diatomic molecules, in the search for variations in the fundamental constants in nature such as the fine structure constant and the electron to proton mass ratio, and in the search for the electric dipole moment of the electron. I found in the ZrS molecule several degenerate vibrational energy levels of order $< 10\text{cm}^{-1}$ which can enhance the experimental sensitivity measurement to orders of 10^{-15}year^{-1} for slight variations of the fine structure constant in laboratory experiments and in S type stars. As a member of the theoretical and computational spectroscopy group of Prof. Miguel Marques I developed an excellent research experience in applying DFT calculations within the abinit code to search for different stable metallic Silicon structures which might have superconducting characteristics. This research work was performed in the past 5 months at the Theoretical and Computational Spectroscopy group of Prof. Miguel Marques at the University of Lyon 1. Please check the following website <http://www.tddft.org/bmg/index.php> for an overview of our research activities.

- September 2007 → June 2009

I gained a great research experience during my M.S. studies with my supervisor Prof. Mahmoud Korek in which I applied non-relativistic quantum mechanical calculations for the electronic structure of the diatomic gaseous molecule Yttrium monosulfides YS.

- October 2003 → June 2006

During my undergraduate studies I participated in building the Murex submarine at the Lebanese International University (LIU), weighing 5 tons the Murex submarine could submerge into a depth of 125 meters with two persons inside, it has been successfully tested several times in the Mediterranean Sea.

- Summer 2008

I won the first prize at the American University of Beirut (AUB) science fair contest for the project "Energy saving in architectural design of Buildings and concert halls", and I had a

training session in operating a geode device to investigate underground surface layers at Beirut Arab University

Work Experience:

- September 2006 → June 2009

I worked as a full time physics teacher at Omar Mokhtar educational center, (Lebanon) for the grades 8, 9, 10, 11, and 12.

- September 2007 → June 2009

I worked as a part time assistant in physics and chemistry for the first and second year science and engineering students at both the Lebanese International University and Beirut Arab University.

Research Interests:

As a PhD research fellow at the University of Claude Bernard, I developed the basic skills and techniques that allow me to pursue a research career in computational sciences. I believe that my experience in DFT calculations as well as MRSDCI relativistic calculations developed at the Theoretical and Computational Spectroscopy Group of Dr. Miguel Marques and at the group of Molecular physics of Prof. Mahmoud Korek at Beirut Arab University is very beneficial in launching my research career in higher education. I am currently interested in expanding my research experience towards other research domains.

Publications:

As a result of my M.S. and PhD thesis I wrote the following papers:

- 1- A. Farhat, M. Korek, S. Abdul-Al, M. A. L. Marques., Enhanced Sensitivity to the Time Variation of the Fine-Structure Constant and m_p/m_e in Zirconium Mono-Sulfide. (In preparation)
- 2- A. Farhat, M. Korek, S. Abdul-Al, M. A. L. Marques., All-electron *ab initio* calculations of the ground and excited states of the YN molecule including vibro-rotational calculations. (In preparation).
- 3- M. Korek, A. Farhat, S. Abdul-Al., Theoretical Calculations of the Low-Lying Electronic States of the Molecule YS., JTCC, 9, 757 (2010).
- 4- A. Farhat, M. Korek, S. Abdul-Al, M. A. L. Marques., All-electron *ab initio* calculations of the low-lying electronic states of the molecule ZrN. (Submitted to the Canadian Journal of Chemistry).
- 5- A. Farhat, M. Korek, S. Abdul-Al, M. A. L. Marques., All-electron *ab initio* calculations of the ground and excited electronic states of the ZrS molecule without spin-orbit effects. (submitted to the Journal of Chemical Physics).
- 6- A. Farhat, M. Korek, S. Abdul-Al, M. A. L. Marques., All-electron *ab initio* calculations of the ground and excited states of the ZrN molecule including spin-orbit effects. (In Preparation).
- 7- A. Farhat, M. Korek, S. Abdul-Al, M. A. L. Marques., All-electron *ab initio* calculations of the ground and excited states of the YS molecule including spin-orbit effects. (In Preparation).

Conferences invited to / attended:

1. One of my research papers “Ab initio Calculation of Molecular States of Compounds of the Lanthanum and Yttrium Molecules”, was accepted and I was invited to present my work at the ICCMSE seventh International Conference of Computational Methods in Sciences and Engineering, Rhodes, Greece September 2009
2. I was invited to present my research achievements at the 16th International Lebanese Scientific Conference (LAAS), at Beirut Arab University, Beirut - Lebanon November 2009.
3. I participated with an oral presentation in the 17th International Lebanese Scientific Conference (LAAS), at the Université Saint Esprit de Kaslik (USEK), Beirut - Lebanon, November 2010.

Honors and Awards:

- PhD research fellow at the University of Claude Bernard, Lyon 1, 2011 – 2012.
- I was honored for participating in building the Murex submarine, and I gave a speech on behalf of the participating students in the project.

Scientific Research Groups:

- I am a member of the Theoretical and Computational Spectroscopy Group of **Prof. Miguel A. L. Marques** at the Lab. de Physique de la Matière Condensée et Nanostructure; Université Lyon 1.
- I am a member of the molecular spectroscopy group of **Prof. Mahmoud Korek** at Beirut Arab University.

Presentations:

- “Einstein’s general theory of relativity and Black holes” (B.S. seminar).
- Theoretical calculations with spin orbit effect of the molecule Yttrium monosulfide YS” (M.S Thesis.
- “Electron Beam lithography and it applications to nanotechnology” (performed at Beirut Arab University).
- “X – Ray emission, a Theoretical investigation” (performed at Beirut Arab University).
- “Uranium enrichment in heavy water nuclear reactors” (performed at Beirut Arab University).
- “Theoretical Calculation with spin-orbit effect of Yttrium sulfide” (performed at Université Saint Joseph de Kaslik, Liban).
- “Carbon nanotubes, discovery and current applications” (performed at Beirut Arab University).
- “New Prospects of Molecular Quantum Computing on the Vibrational States of Heteronuclear Diatomic Molecules” (Seminar expected to be performed at the University of Lyon 1 on the 14th of February 2012).

Languages:

- Fluent in Arabic and English, my TOEFL IBT test score is 90/120.

- Intermediate in French, my level is B1.
- My GRE test scores are:
Math Quantitative Reasoning: 730/800 English Verbal Reasoning: 480/800.

Recently read books (in the past 14 months):

1. Quantum (A Guide for the Perplexed) by Jim Al-Khalili 2003. (Finished)
2. Entanglement (The Spooky action of a distance) by Amir D. Aczel 2002.(Finished)
3. Many Body Problems and Quantum Field Theory, An Introduction by Philippe Marin and François Rothen. (Finished)
4. Concepts of Nuclear Physics by Bernard L Cohen 1997. (Finished)
5. The Self-Aware Universe by Goswami and Amit. (Finished)
6. Quantum electrodynamics (The Strange Theory of Light and Matter) by Richard Feynman. (Finished)
7. The Universe in a Nutshell by Stephan Hawking. (Finished)
8. The Conceptual Basis of Quantum Field Theory by Gerard 't Hooft (Institute of Theoretical Physics, Utrecht University the Netherlands)., Elsevier 2004. (Finished)
9. Molecular Electronic Structure Theory by Trygve Helgaker, Poul Jorgensen, and Jeppe Olsen. (Finished)
10. Essentials of Computational Chemistry, Theories and Models by Christopher Cramer. (Finished)
11. Quantum Field Theory In a Nutshell by A. Zee. (I finished the first 120 pages).

Community Services:

I am former volunteer/member at the Lebanese Red Cross organization.

Computer Skills:

Experienced user of Linux commands, **Molpro** and **Abinit** computational Physics programs and their applications to material science and physical chemistry research.

I am an active user of the computational nanotechnology resources available online (www.nanohub.org) by the university of Purdue/USA.

I know C++ programming language.

I am a professional user of the AutoCAD program.

I am a professional user of the Microsoft office programs (Word, Excel, and PowerPoint).

I also master dealing with windows vista, windows 7, and XP.