

Prediction of Spectroscopic Constants for Diatomic Molecules in the Ground and Excited States Using Time-Dependent Density Functional Theory

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Received 29 April 2005; Accepted 15 June 2005

DOI 10.1002/jcc.20330

Published online in Wiley InterScience (www.interscience.wiley.com).

Abstract: Spectroscopic constants of the ground and next seven low-lying excited states of diatomic molecules CO, N₂, P₂, and ScF were computed using the density functional theory SAOP/ATZP model, in conjunction with time-dependent density functional theory (TD-DFT) and a recently developed Slater type basis set, ATZP. Spectroscopic constants, including the equilibrium distances r_e , harmonic vibrational frequency ω_e , vibrational anharmonicity $\omega_e x_e$, rotational constant B_e , centrifugal distortion constant D_e , the vibration–rotation interaction constant α_e , and the vibrational zero-point energy E_n^0 were generated in an effort to establish a reliable database for electron spectroscopy. By comparison with experimental values and a similar model with an established larger Slater-type basis set, et-QZ3P-xD, it was found that this model provides reliably accurate results at reduced computational costs, for both the ground and excited states of the molecules. The over all errors of all eight lowest lying electronic states of the molecules under study using the effective basis set are r_e ($\pm 4\%$), ω_e ($\pm 5\%$ mostly without exceeding $\pm 20\%$), $\omega_e x_e$ ($\pm 5\%$ mostly without exceeding 20%, much more accurate than a previous study on this constant of $\pm 30\%$), B_e ($\pm 8\%$), D_e ($\pm 10\%$), α_e ($\pm 10\%$), and E_n^0 ($\pm 10\%$). The accuracy obtained using the ATZP basis set is very competitive to the larger et-QZ3P-xD basis set in particular in the ground electronic states. The overall errors in r_e , $\omega_e x_e$, and α_e in the ground states were given by ± 0.7 , ± 10.1 , and $\pm 8.4\%$, respectively, using the efficient ATZP basis set, which is competitive to the errors of ± 0.5 , ± 9.2 , and $\pm 9.1\%$, respectively for those constants using the larger et-QZ3P-xD basis set. The latter basis set, however, needs approximately four times of the CPU time on the National Supercomputing Facilities (Australia). Due to the efficiency of the model (TD-DFT, SAOP and ATZP), it will be readily applied to study larger molecular systems.

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Key words: spectroscopic constants; diatomic molecules; ground state; excited states; Density Function Theory

Introduction

In recent years spectroscopy has played a particularly important role in many scientific disciplines, such as chemistry. It offers direct extraction of information from the curvature of the potential energy surface near the equilibrium in which a molecule resides.¹ An understanding of molecular spectroscopy is therefore dependent upon the accuracy of prediction of the molecular states in question for both the ground, and excited electronic states. In comparison to ground states, molecular excited states are less investigated, often with incomplete information available.^{2–4} Prediction and interpretation of the discrete spectrum therefore presents numerous challenges for molecular electron spectroscopy,

particularly for medium to larger sized molecules. Undoubtedly, theoretical procedures for solution of the rotational–vibrational Schrödinger equation directly using a fully coupled and anharmonic basis are ideal for any sized molecule;^{5,6} however, this method is currently limited to smaller molecules.

Alternatively, with a fairly good accuracy, one can predict the spectroscopic constants of molecules, such as diatomic molecules, by fitting their potential energy curves from the electronic states.¹ Prediction of spectra therefore depends upon the accuracy of the spectroscopic constants, which in turn, are employed as a bench-

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mark to assess new theoretical methods, such as the electron correlation effects, basis set effects, and the quality of new basis sets.^{7–9} Moreover, spectroscopic constants of diatomic molecules are useful for yet experimentally unknown or poorly characterized electronic states,⁷ in particular, excited states. Therefore, an accurate but inexpensive method for the prediction of spectroscopic constants of diatomic molecules systematically for several low-lying electronic states can be very useful. This is the aim of the present study.

The quality of quantum mechanical calculations is determined by the description of the N -electron space (wave function model) and the one-electron space (basis set). The Density Functional Theory (DFT)¹⁰ has been proven successful in wide-ranging applications for computing a variety of ground-state properties with a high degree of accuracy.^{11–16} DFT methods rectify many problems associated with the Hartree–Fock (HF) approximation at a comparable computational cost. Accordingly, DFT methods are rapidly replacing traditionally correlated *ab initio* methods for use in many chemical applications.⁷ Moreover, the development of DFT can be considered as the need for more accurate exchange–correlation potentials V_{xc} , which can exhibit the correct asymptotic behavior to give accurate predictions of higher excited states.^{3–8} On the other hand, the practical formulation of the time-dependent density functional response theory (TD-DFT) in recent years^{17–19} has been quickly applied to compute molecular excitation energies and transition probabilities.⁹ It is undoubtedly motivated by the fact that the option of selecting TD-DFT is now available in several computer program packages.

In quantum chemical calculations, one often requires a smaller number of Slater-type basis functions (STO) than Gaussian-type basis functions (GTO), to obtain the same accuracy.²⁰ As a result, STO basis sets have been developed, assessed, and incorporated into computational chemistry programs such as the Amsterdam Density Functional (ADF) 2002.03.^{21–25} Some important and established Slater basis sets with different types available have been assessed recently.²⁰ However, to improve the accuracy and reduce computational costs for application with larger molecules, more efficient basis sets have been developed to provide an efficient prediction of molecular excitation spectra.⁹ For example, Chong⁹ developed a procedure of generating diffuse functions that were, in turn, added to standard Slater-type orbital basis sets for atoms that lie between hydrogen and krypton. Such new basis sets are (albeit approximate) augmented basis sets, and are called augmented DZP (ADZP) and augmented TZP (ATZP), respectively. In this study, the newly developed ATZP basis set is compared with a larger basis set, et-QZ3P-xD,^{26,27} which is an established basis set available in the databases of the ADF program. Therefore, it may be assumed that such a basis set could provide a reliable assessment for the quality of the new ATZP basis set.

The extraction of spectroscopic constants for any molecular system requires the location of accurate potential energy curves. In view of their simplicity, diatomic molecules offer an important ground for such an investigation. Spectroscopic constants of the ground electronic state and the next seven lowest lying excited states of a group of representative hetero- and homo-nuclear diatomic molecules are formed by atoms in the periodic table from hydrogen to krypton, such as CO and ScF, N₂, and P₂. In this investigation, the SAOP/ATZP model and TD-DFT were utilized

in a move to access larger molecules for the database. The results are then compared with the data obtained using the more established TD-DFT(SAOP)/et-QZ3P-xD model. Here, the SAOP functional is a recently developed DFT functional known as statistical averaging of orbital potentials.²⁸

Excitation of the isoelectronic molecules, carbon monoxide (CO), and molecular nitrogen (N₂) are important in the estimation of electron energy deposition in the atmospheres of the Earth, Mars, and Venus.²⁹ Carbon monoxide is one of the most abundant molecules in the universe and, for many years, it has been the subject of extensive spectroscopic investigations.^{2–4,30} In the present work, the heteronuclear diatomic CO molecule will be studied as the benchmark for the two models employed. As the major component of air (78%), the homonuclear diatomic molecule, N₂, has attracted intensive research interest in recent years due to the possible existence in the interstellar medium.²⁹ The unique triply bonded electronic structure with a very stable electronic ground state has been very attractive to structural chemistry. More recently, its highest occupied molecular orbital (HOMO) has been experimentally observed in a three-dimensional structure by high harmonics from intense femtosecond laser pulsed on aligned molecules,³¹ which stimulates our research interest in this diatomic molecule. However, the excited electronic states of N₂ still present a major challenge.²⁹ There is also considerable interest in the bonding and spectroscopic properties of diatomic molecules that contain atoms consisting of the 3d metal atoms, such as ScF. The interaction with transition metals is of fundamental importance, because the open-shell nature of the majority of such molecules leads to a large number of low-lying configurations and electronic states.³² This also leads to considerable difficulties in the computational study of their electronic structure and bonding with results varying with the methods applied.^{33–35} Spectroscopic information for the electronic excited states of P₂ is still incomplete.³ Although a considerable amount of spectroscopic data has been reported for these molecules, a systematic study of their electronic excited states is still a demanding task.

Methods and Computational Details

As indicated in the introduction, the quality of the calculations is determined by the description of the wave function model (theory) and basis set. In the present work, the TD-DFT (with V_{xc} = SAOP) approach was employed to model the N -electron space for the ground and excited states. The most recently developed ATZP basis set⁹ was used for the basis set in this model. The generation of the spectroscopic constants of the set of diatomic molecule consists of three steps: (1) generation of the potential energy surfaces (PES). The discrete potential energy curves for each of the eight lowest lying electronic states, in conjunction with the TD-DFT method, are generated using the TD-DFT(SAOP)/ATZP model and TD-DFT(SAOP)/et-QZ3P-xD models, respectively; (2) PES fitting. The obtained discrete PES of the states were individually fitted to power series expansions for their analytical functional forms; and (3) spectroscopic constants production. Based on the fitted analytical PES, the spectroscopic constants of all the states are obtained.

Under the Born–Oppenheimer approximation, nuclear motion can be separated from electronic motion in a diatomic molecule. The solution of vibration–rotation energy levels requires a particular potential energy function $U_n(\rho)$ for a given electronic state. However, the electronic states of real molecules are not presented by any known analytical potential functions, although many ingenious approximate functions^{30,36,37} have been created. A power series expansion therefore can represent any potential on a given interval to arbitrary precision³⁸ such as

$$U_n(\rho) = \sum_{i=1}^6 c_i \rho^i \quad (1)$$

where $\rho = r - r_e$ and $N = 0, 1, 2, \dots, 7$; where n represents the level in question (ground = 0). The potential energy curves in eq. (1) were generated for each state as follows. For every individual electronic state investigated in this study (including the ground states), a parallel series of single point calculations were performed using the TD-DFT(SAOP)/ATZP and TD-DFT(SAOP)/et-QZ3P-xD models at internuclear separations ranging over $[r_e^o - 0.25, r_e^o + 0.30]$ Å, with intervals of 0.05 Å (here, r_e^o was initially taken from available experimental data.³ A guess of r_e^o was made from various sources such as the r_e^o s of other states if the experimental r_e is not available). All electronic state calculations were performed using the ADF program package,^{21–25} with the exchange–correlation functional, $V_{xc} = \text{SAOP}$,²⁸ in conjunction with TD-DFT. To avoid numerical errors, the integration accuracy parameter has been set to 12 in all calculations. The potential energy curves, which were calculated discretely for the ground electronic states and then applied TD-DFT for the electronic excited states of diatomic molecules CO, N₂, P₂, and ScF, respectively, were fitted to eq. (1) for their analytical functions.

Two basis sets were examined in this study. For clarity in this article, they are labelled as “large” and “efficient” basis sets; the large basis set is the established et-QZ3P-xD [^{26, 27, 39, 40}], where $x = 2$ for all atoms from B to Ne and $x = 1$ for H to Kr. The efficient basis set is known as augx-TZP (or ATZP), with $x = 1$ (B to Ne) and $x = 0$ for H to Kr.⁹ When $x = 1$, that is aug1-TZP, the fit set was copied from et-QZ3P-1D, while the aug0-TZP fit set was from et-QZ3P-0D.⁹ This set was derived from QZ3P with the even-tempered parameter equal to 1.7²⁷ by the addition of n ($n = 1$ or 2) diffuse functions in the same even-tempered manner. The efficient basis set is the replacement of the even-tempered set by the inclusion of additional augmenting diffuse basis functions to the standard Slater-type basis set, TZP. The latter basis set was designed to improve excitation energies and polarizabilities and to reduce computational costs.⁹

Theoretical equilibrium bond length r_e , adiabatic excitation energy (term value) of the state relative to the ground state T_e , harmonic vibrational frequency ω_e , vibrational anharmonicity $\omega_e x_e$, rotational constant B_e , centrifugal distortion constant D_e , the vibration–rotation interaction constant α_e , and the vibrational zero-point energy E_n^0 have been determined for each of the eight lowest electronic states of the diatomic molecules of CO, N₂, P₂, and ScF accordingly. The individual power series potential energy curves can be derived using Herzberg’s energy level expressions as follows,

$$G(\nu) = \frac{E_n(\nu)}{hc} = \omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right)^2 + \dots \quad (2)$$

where the fundamental harmonic vibrational frequency, ω_e , and the vibrational anharmonicity, $\omega_e x_e$, relate to vibrational zero-point energy (ZPE)

$$E_n(\nu = 0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e \quad (3)$$

and the rovibrational energy term is

$$F_\nu(J) = \frac{E_\nu(J)}{hc} = B_\nu J(J+1) - D_\nu J^2(J+1)^2 + \dots \quad (4)$$

where the rotational constant at the ν th vibrational state is given by

$$B_\nu = B_e - \alpha_e \left(\nu + \frac{1}{2} \right) + \dots \quad (5)$$

Here, B_e is the equilibrium rotational constant, and α_e is the vibration–rotation interaction constant. The centrifugal distortion constant can be estimated via

$$D_\nu = D_e - \beta_e \left(\nu + \frac{1}{2} \right) + \dots \quad (6)$$

For a given electronic state (note that nonsinglet cases can be considerably more complicated), labeled by n , the total energy $E_{n\nu J}$ for a given electronic rovibrational state $|n\nu J\rangle$ is given by³⁸

$$E_{n\nu J} = T_e(n) + G(\nu) + F(J). \quad (7)$$

Here, $T_e(n)$ is the adiabatic excitation energy of a specific electronic excited state. The spectroscopic constants including the theoretical equilibrium bond length were then obtained from iteration using a least-squares fit from the calculated potential energy functions individually, in a program called VIBROT.⁴¹

Results and Discussion

Spectroscopic constants including zero-point energy (ZPE) predicted by the two parallel basis sets, that is, ATZP and et-QZ3P-xD, for the eight lowest lying electronic states of CO, N₂, P₂, and ScF, together with available experimental data, are presented in Tables 1–4. Errors (in percentage) of these electronic states for each molecule have been presented based on individual spectroscopic constants, that is, r_e , ω_e , $\omega_e x_e$, B_e , D_e , α_e , and E_n^0 , which are given in Figures 1–7, respectively. To assess the accuracy and efficiency of the ATZP basis set, the spectroscopic constants generated using the large (et-QZ3P-xD) and efficient (ATZP) sets were compared in parallel for the constants in Figures 8 and 9.

The quality of the present model on ground electronic states of CO and N₂ has been compared with other recent theoretical calculations, such as the CCSD(T)/aug-cc-pVTZ and B3LYP/aug-

Table 1. Theoretical and Experimental Spectroscopic Constants for the Eight Lowest Lying Electronic States of CO.^a

State	Method	T_e (cm ⁻¹)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (cm ⁻¹)	α_e (cm ⁻¹)	E° (cm ⁻¹)
CO									
$X \ ^1\Sigma^+$	et-QZ3P-2D	0.0	1.1333	2134	13.7	1.914	6.16e-06	0.0182	1063.6
	ATZP	0.0	1.1375	2214	13.5	1.900	6.08e-06	0.0179	1103.6
	Expt ^b	0.0	1.1282	2170	13.3	1.931	6.12e-06	0.0175	1081.7
$a \ ^3\Pi$	et-QZ3P-2D	48652.1	1.2016	1766	15.1	1.703	6.33e-06	0.0196	879.2
	ATZP	48471.0	1.2062	1759	15.1	1.690	6.23e-06	0.0194	875.7
	Expt	48686.7	1.2057	1743	14.4	1.691	6.36e-06	0.0190	867.9
$a' \ ^3\Sigma^+$	et-QZ3P-2D	54372.2	1.3857	1110	16.9	1.280	6.82e-06	0.0207	550.8
	ATZP	53704.9	1.3903	1098	16.9	1.272	6.83e-06	0.0210	544.8
	Expt	55825.4	1.3523	1229	10.5	1.345	6.41e-06	0.0189	611.9
$d \ ^3\Delta$	et-QZ3P-2D	60619.6	1.3773	1166	12.7	1.296	6.41e-06	0.0174	579.8
	ATZP	60079.0	1.3813	1158	12.7	1.288	6.38e-06	0.0176	575.8
	Expt	61120.1	1.3696	1172	10.6	1.311	6.59e-06	0.0178	583.4
$e \ ^3\Sigma^-$	et-QZ3P-2D	65665.0	1.3782	1162	11.8	1.294	6.42e-06	0.0170	578.1
	ATZP	65346.4	1.3821	1155	11.9	1.287	6.39e-06	0.0173	574.5
	Expt	64230.2	1.3840	1118	10.7	1.284	6.77e-06	0.0175	556.3
$A \ ^1\Pi$	et-QZ3P-2D	65587.8	1.2342	1506	19.3	1.614	7.42e-06	0.0174	748.2
	ATZP	65546.1	1.2399	1497	19.8	1.599	7.30e-06	0.0282	743.6
	Expt	65075.7	1.2353	1518	19.4	1.612	7.33e-06	0.0232	754.2
$I \ ^1\Sigma^-$	et-QZ3P-2D	65912.6	1.3782	1162	11.8	1.294	6.42e-06	0.0170	578.1
	ATZP	65346.4	1.3821	1155	11.9	1.287	6.39e-06	0.0173	574.5
	Expt	65084.4	1.3911	1092	10.7	1.271	—	0.0170	543.3
$D \ ^1\Delta$	et-QZ3P-2D	69503.2	1.3786	1157	11.7	1.294	6.47e-06	0.0174	575.6
	ATZP	69066.5	1.3826	1149	11.8	1.286	6.44e-06	0.0173	571.6
	Expt	65928.0	1.3990	1094	10.2	1.257	—	0.0170	544.5

^aExperimental values are taken from Huber and Herzberg³ unless otherwise stated.^bExperimental values from George et al.⁴⁹

cc-pVTZ models⁷ for the same constants. The Slater-type (STO) ATZP is close to the Gaussian type (GTO) basis set of aug-cc-pVTZ of Dunning^{9,42–45} in quality. Finally, the efficiency comparison (accuracy—ground and excited states—and computational costs) between the two sets are presented in Figures 8–10.

Accurately Predicted Properties— r_e and B_e

Equilibrium bond lengths r_e and rotational constants B_e are generally well predicted spectroscopic constants in the present models across the states studied. The errors in equilibrium internuclear distances r_e predicted by the TD-DFT(SAOP)/ATZP model as shown in Figure 1 are well within the band of $\pm 4\%$ for all states. This is consistent with previous studies on this property in the ground electronic states of diatomic molecules.⁷ The equilibrium rotational constants, B_e , which are closely related to the equilibrium bond lengths r_e via

$$B_e = \frac{\hbar}{4\pi\mu r_e^2}$$

are expected to have similar variations as the bond lengths but in a reciprocal manner. That is, if the errors in r_e are located

above (overestimation) the x-axis, such as the ground electronic states of CO and N₂ in Figure 1, the errors associated with the B_e constants in the same states are located below the x-axis (underestimation), as indicated in Figure 2. They are, however, enlarged due to the inverse relationship between the two constants. Therefore, if the errors in r_e are small, the errors in B_e should not be significantly larger for the same state of the molecule. The errors in B_e are approximately within the band of $\pm 8\%$ for all states in Figure 2.

The equilibrium bond length r_e of the fifth excited state of ScF is apparently underestimated by the present models. However, the efficient basis set yields a bond length of 1.84 Å, which is competitive in accuracy compared to the larger basis set, which yields a value of 1.81 Å; the experimental value for this constant is 1.92 Å (see Table 4). The better quality prediction of the equilibrium bond length r_e for this state results in a more accurate determination of the equilibrium rotational constants B_e ; the efficient and larger basis sets determined values of 0.372 and 0.376 cm⁻¹, respectively, compared with the value of 0.343 cm⁻¹ from the experiment.³ Thus, the efficient basis set not only needs less time for computing, but also can produce the spectroscopic constants as accurate as the larger basis set.

Table 2. Theoretical and Experimental Spectroscopic Constants for the Eight Lowest Lying Electronic States of N₂.^a

State	Method	T_e (cm ⁻¹)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (cm ⁻¹)	α_e (cm ⁻¹)	E° (cm ⁻¹)
N ₂									
X ¹ Σ _g ⁺	et-QZ3P-2D	0.0	1.1012	2356	14.3	1.986	5.64e-06	0.0170	1174.4
	ATZP	0.0	1.1045	2346	13.3	1.974	5.59e-06	0.0168	1169.7
	Expt	0.0	1.0977	2359	14.3	1.998	5.76e-06	0.0173	1175.9
A ³ Σ _u ⁺	et-QZ3P-2D	48904.8	1.3157	1281	30.1	1.391	6.56e-06	0.0257	633.0
	ATZP	48451.2	1.3178	1261	31.7	1.387	6.71e-06	0.0263	622.6
	Expt ^b	49755.0	1.2866	1461	13.9	1.455	6.10e-06	0.0180	727.0
B ³ Π _g	et-QZ3P-2D	57664.0	1.2120	1728	12.7	1.640	5.91e-06	0.0183	860.8
	ATZP	57410.2	1.2149	1726	12.2	1.632	5.84e-06	0.0183	860.0
	Expt ^b	59307.0	1.2126	1733	14.1	1.637	5.90e-06	0.0179	863.0
W ³ Δ _u	et-QZ3P-2D	57682.3	1.2932	1450	10.5	1.440	5.68e-06	0.0172	722.3
	ATZP	57447.5	1.2951	1451	12.2	1.436	5.63e-06	0.0282	722.5
	Expt ^b	59080.0	1.2797	1506	12.5	—	—	—	749.9
B' ³ Σ _u ⁻	et-QZ3P-2D	65043.1	1.2887	1476	10.9	1.450	5.60e-06	0.0164	735.3
	ATZP	64578.2	1.2906	1471	11.1	1.446	5.59e-06	0.0166	735.7
	Expt	66272.4	1.2784	1517	12.2	1.473	5.56e-06	0.0166	755.5
a' ¹ Σ _u ⁻	et-QZ3P-2D	64968.9	1.2887	1468	9.71	1.450	5.66e-06	0.0162	731.6
	ATZP	64578.2	1.2906	1471	11.1	1.446	5.59e-06	0.0166	732.7
	Expt	68152.7	1.2755	1530	12.1	1.480	5.55e-06	0.0166	762.0
a ¹ Π _g	et-QZ3P-2D	69078.0	1.2236	1648	12.4	1.609	6.13e-06	0.0185	820.9
	ATZP	68910.6	1.2264	1647	14.0	1.601	6.05e-06	0.0195	820.0
	Expt	69283.1	1.2203	1694	13.9	1.617	5.89e-06	0.0179	843.5
w ¹ Δ _u	et-QZ3P-2D	69797.3	1.2859	1480	11.3	1.456	5.64e-06	0.0166	734.2
	ATZP	69540.5	1.2879	1475	11.4	1.452	5.63e-06	0.0168	734.7
	Expt	72097.4	1.2680	1559	11.6	1.498	—	0.0167	776.6

^aExperimental values are taken from Huber and Herzberg³ unless otherwise stated.^bExperimental values from Zumofen et al.⁵⁰

Fairly Accurately Predicted Constants— ω_e and D_e

Although the prediction of the equilibrium bond lengths is relatively easy to achieve a high accuracy in quantum-chemical computational calculations, the prediction of the harmonic constants requires the accuracy up to the second derivatives of the potential energy curves. As a consequence, serious sacrifices in the quality of the first derivatives (related to structure) and the energies themselves (thermochemistry) usually occurs.¹ Figure 3 provides an assessment on the accuracy of the theoretically calculated harmonic vibrational frequency ω_e with (1) the TD-DFT(SAOP)/ATZP model, and (2) the TD-DFT(SAOP)/et-QZ3P-xD model. It can be seen that the majority of the errors occur in ω_e are well within the band of $\pm 5\%$, while the overall errors for this constant do not exceed $\pm 20\%$. The accuracy of our theoretically generated vibrational constants (ω_e) in the ground electronic states is very competitive to other recent calculations. For example, the errors associated with ω_e predicted for CO and N₂ diverge no more than 44 cm⁻¹ (CO) and -13.0 cm⁻¹ (N₂) (see Tables 1 and 2) in the present study. In comparison, this pair was given by 53 and 101 cm⁻¹ from the most recent DFT calculations¹ using the DFT-EDF2/cc-pVTZ model, by 38 and 89 cm⁻¹ from the B3LYP/aug-cc-pVTZ model and 3 and -11 cm⁻¹ from the CCSD(T)/aug-cc-pVTZ model,⁷ respectively. It should also be noted that the present models have also been applied to other excited electronic states,

whereas the DFT calculations of both refs 1 and 7 were applied to only ground electronic states of the molecules.

The spectroscopic constants, that is, harmonic vibrational frequencies ω_e and centrifugal distortion constants D_e , are found as a pair, which exhibits fairly accurate agreement with experiment. The latter accounts for the stretch of the bond with larger angular momentum J and has a relationship with the rotational constants B_e and vibrational harmonic frequencies, ω_e as

$$D_e = \frac{4B_e^3}{\omega_e^2}.$$

Hence, the accuracy of this constant D_e will be affected by the accuracy from both of the equilibrium rotational constants B_e and harmonic vibrational frequencies ω_e . That is, the errors in the centrifugal constants D_e would not be large if the errors in the rotational constants B_e are very small (as was found in the previous section), and the errors of vibrational harmonic frequencies ω_e are not very large. Figure 5 indicates that the errors of the centrifugal constants D_e for most states of the molecules under this study are in fact within ca. $\pm 10\%$. As seen, the errors in this constants (D_e) are a result of a balanced compensation between the equilibrium rotational constants B_e and harmonic vibrational frequencies ω_e .

Table 3. Theoretical and Experimental Spectroscopic Constants for the Eight Lowest Lying Electronic States of P₂.^a

State	Method	T_e (cm ⁻¹)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (cm ⁻¹)	α_e (cm ⁻¹)	E° (cm ⁻¹)
P ₂									
X ¹ Σ _g ⁺	et-QZ3P-1D	0.0	1.9017	788	2.9	0.301	1.76e-07	0.0014	393.3
	ATZP	0.0	1.9066	782	2.9	0.299	1.75e-07	0.0014	390.3
	Expt	0.0	1.8934	781	2.9 ^a	0.304	1.88e-07	0.0015	389.8
a ³ Σ _u ⁺	et-QZ3P-1D	18165.9	2.1122	505	5.8	0.244	2.28e-07	0.0023	251.1
	ATZP	17990.3	2.1234	505	4.6	0.241	2.20e-07	0.0014	251.4
	Expt ^b	18794.5	2.0782	565	2.8	0.252	—	0.0015	281.8
³ Δ _u	et-QZ3P-1D	22401.8	2.0824	574	2.01	0.251	1.92e-07	0.0013	286.5
	ATZP	22446.0	2.0898	562	0.4	0.249	1.96e-07	0.0012	280.9
	Expt	—	—	—	—	—	—	—	—
b ³ Π _g	et-QZ3P-1D	26462.1	1.9801	643	3.6	0.277	2.06e-07	0.0018	320.6
	ATZP	26675.0	1.9864	632	3.3	0.276	2.11e-07	0.0018	315.2
	Expt	28068.9	1.9700	645	3.2	0.281	2.00e-07	0.0018	321.7
b' ³ Σ _u ⁻	et-QZ3P-1D	26267.0	2.0736	586	2.2	0.253	1.89e-07	0.0014	292.5
	ATZP	26148.2	2.0810	579	2.2	0.251	1.89e-07	0.0014	289.0
	Expt	28503.0	2.0520	604	2.2	0.258	1.70e-07	0.0014	301.5
¹ Σ _u ⁻	et-QZ3P-1D	26266.7	2.0736	586	2.2	0.253	1.89e-07	0.0014	292.5
	ATZP	26165.8	2.0808	575	2.0	0.251	1.91e-07	0.0014	287.0
	Expt	—	—	—	—	—	—	—	—
¹ Δ _u ⁻	et-QZ3P-1D	29212.0	2.0679	590	2.2	0.254	1.88e-07	0.0014	294.5
	ATZP	29269.1	2.0753	582	2.2	0.253	1.91e-07	0.0014	290.5
	Expt	—	—	—	—	—	—	—	—
A ¹ Π _g	et-QZ3P-1D	33016.0	2.0026	606	3.4	0.271	2.17e-07	0.0018	302.2
	ATZP	33327.2	2.0100	591	2.7	0.269	2.23e-07	0.0019	294.8
	Expt	34515.3	1.9887	618	3.0	0.275	2.20e-07	0.0017	308.3

^aExperimental values are taken from Huber and Herzberg³ unless otherwise stated.

^bExperimental values from Brion.⁵¹

^cExperimental values from Malicet et al.⁵²

Predicted Spectroscopic Constants with Varied Accuracies— $\omega_e x_e$ and α_e

The theoretical prediction of the anharmonic vibrational constants $\omega_e x_e$ has its significance in high accuracy predictions of experimentally observed fundamental vibrational frequencies. The vibrational–rotational constant α_e and vibrational anharmonic constants $\omega_e x_e$ depend upon the third and up to fourth derivatives of the potential energy curves, respectively. In the past, accurate prediction of these constants challenged many theoretical models. For example, even for the ground electronic states, the estimated errors for the prediction of $\omega_e x_e$ are only good to about 30%.⁷ However, these errors are the result from only a couple of the lowest-lying excited states (first and second excited states). The present models estimate these constants in ground states are basically within $\pm 5\%$. In other excited electronic states, the errors are, in fact, well within the $\pm 20\%$ envelop, except for ScF in its fifth excited state. Figure 5 clearly indicates such trends.

The equilibrium vibration–rotational constants α_e is related to other spectroscopic constants via

$$\alpha_e = \frac{6\sqrt{\omega_e x_e B_e^3} - 6B_e^2}{\omega_e}$$

This constant depends upon anharmonic vibrational constants $\omega_e x_e$, which can be poorly predicted, harmonic vibrational constants ω_e , which can be evaluated fairly accurately, as demonstrated in the previous section and equilibrium rotational constants B_e , which usually can be well predicted but the errors can be enlarged as α_e depends on the square of B_e . For this constant, the performance of the effective set is very competitive to that of the larger set. Although the effective set reproduces almost the overall quality of the larger set, as shown in Figure 6, it also significantly improves the accuracy in the first electronic excited states of P₂ and ScF (Fig. 6a and b). This finding demonstrates again that the efficient basis set is capable of sufficient accuracy in producing spectroscopic constants for molecules including transition metals.

Prediction of Zero-Point Energies and Adiabatic Excitation Energies— E_n^0 and T_e

Zero-point energy (ZPE), which has been considered as a quantum effect, plays a causal role in some important fundamental processes. For normal molecules, the ZPE, which is the energy at ($v = 0$), can be very small as shown in the tables. However, for weakly bound systems, such as van der Waals complexes^{46–48} the ZPE is significantly large, and therefore must be considered when order-

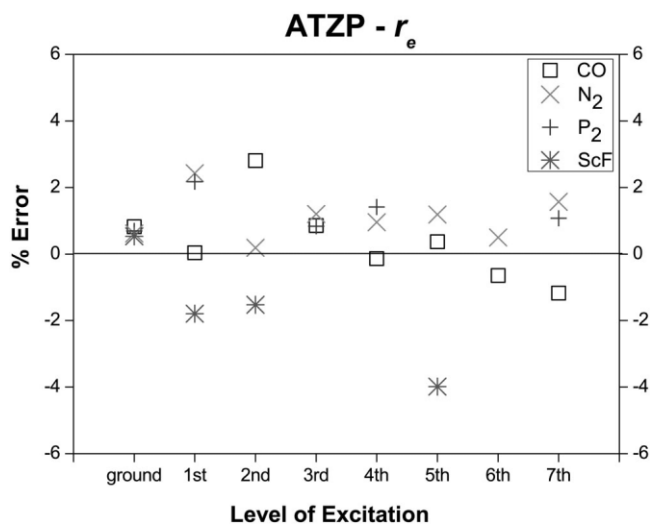
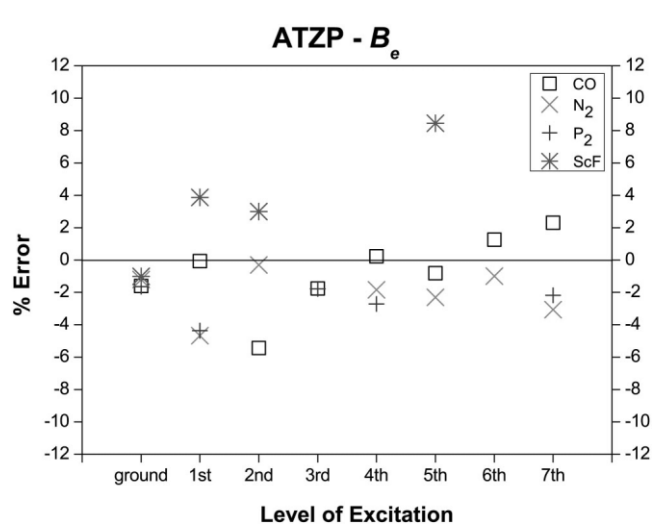
Table 4. Theoretical and Experimental Spectroscopic Constants for the Eight Lowest Lying Electronic States of ScF₂.^a

State	Method	T_e (cm ⁻¹)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (cm ⁻¹)	α_e (cm ⁻¹)	E° (cm ⁻¹)
ScF									
$X^1\Sigma^+$	et-QZ3P-xD	0	1.7857	717	3.7	0.396	4.80e-07	0.0028	357.6
	ATZP	0	1.7965	714	3.7	0.391	4.69e-07	0.0028	356.1
	Expt	0	1.7870	736	3.8	0.395	—	0.0027	367.1
$a^3\Delta$	et-QZ3P-xD	3017.8	1.8245	659	4.2	0.379	5.01e-07	0.0030	328.5
	ATZP	3368.9	1.8326	678	4.8	0.376	4.63e-07	0.0026	337.8
	Expt	—	1.8660	649	3.0	0.362	—	0.0025	323.8
$^3\Pi$	et-QZ3P-xD	10225.3	1.8154	696	2.7	0.383	4.64e-07	0.0024	347.3
	ATZP	10418.5	1.8237	695	3.7	0.379	4.51e-07	0.0026	346.6
	Expt	—	1.8520	—	—	0.368	—	—	—
$^1\Delta$	et-QZ3P-xD	10282.4	1.8003	712	3.5	0.389	4.64e-07	0.0026	355.1
	ATZP	10596.2	1.8117	707	3.5	0.385	4.57e-07	0.0026	352.6
	Expt	—	—	—	—	—	—	—	—
$^3\Sigma^+$	et-QZ3P-xD	13082.9	1.8568	627	3.3	0.366	4.99e-07	0.0027	312.7
	ATZP	13056.5	1.8644	627	3.4	0.363	4.87e-07	0.0028	312.7
	Expt	—	—	—	—	—	—	—	—
$B^1\Pi$	et-QZ3P-xD	15255.7	1.8232	697	3.0	0.376	4.38e-07	0.0023	347.8
	ATZP	15538.8	1.8417	690	2.9	0.372	4.33e-07	0.0024	344.3
	Expt	10735.4	1.9181	586	2.0	0.343	—	0.0026	292.5
$2^3\Pi$	et-QZ3P-xD	21629.2	1.8023	724	4.0	0.388	4.46e-07	0.0029	361.0
	ATZP	22114.3	1.7990	650	3.4	0.390	5.62e-07	0.0045	324.2
	Expt	—	—	—	—	—	—	—	—
$2^1\Sigma^+$	et-QZ3P-xD	22066.0	1.8408	658	5.2	0.372	4.76e-07	0.0027	327.7
	ATZP	22147.2	1.8509	649	3.2	0.368	4.73e-07	0.0026	323.7
	Expt	—	—	—	—	—	—	—	—

^aExperimental values are taken from Huber and Herzberg.³

ing the stability of the minimum structures of the species.⁴⁸ For this reason, we also produced the ZPE as a “spectroscopic constant” in this study. As seen in Figure 7, the errors of the prediction

using the current model are within $\pm 10\%$ for the majority and only a few exceed the $\pm 10\%$ band. As the ZPE is dependent upon the vibrational harmonic frequencies ω_e and the vibrational anhar-

**Figure 1.** Error in bond lengths (r_e) predicted by the TD-DFT(SAOP)/ATZP model.**Figure 2.** Error in equilibrium rotational constants (B_e) predicted by the TD-DFT(SAOP)/ATZP model.

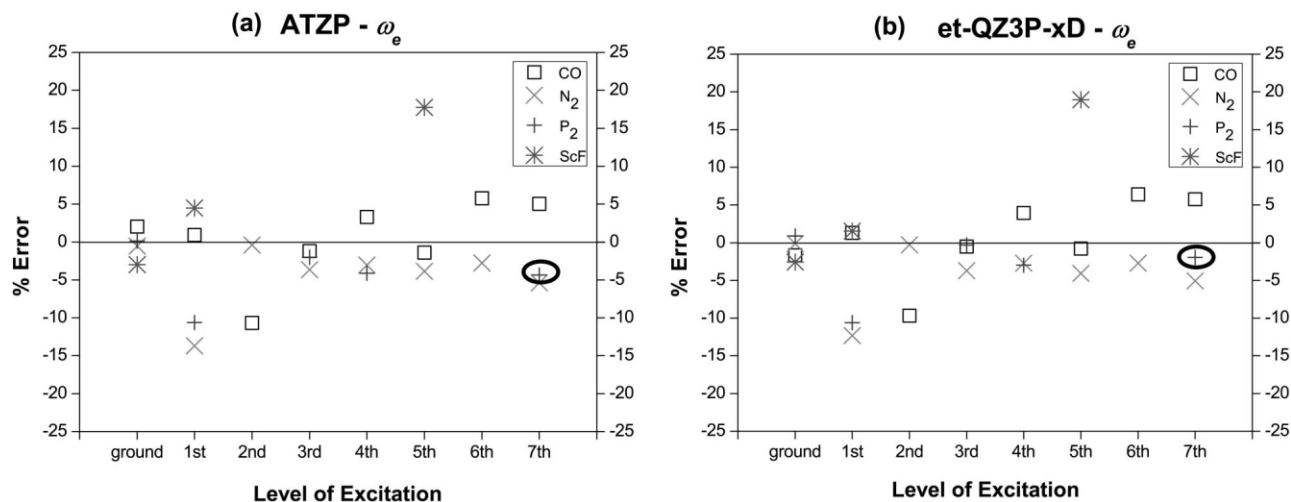


Figure 3. Errors in the harmonic vibrational frequencies (ω_e) predicted by (a) the TD-DFT(SAOP)/ATZP model, and (b) the TD-DFT(SAOP)/et-QZ3P-xD model.

monic constants $\omega_e x_e$, it is no surprise that the errors of ZPE are similar to ω_e , as the values of $\omega_e x_e$ are generally very small (second order).

Adiabatic excitation energies, $T_e(n)$, of molecules determine the transition line positions in electron spectroscopy. They are generally quite difficult to obtain experimentally⁹ as experimental data rarely provide complete excitation energy for all excited states, even for the low-lying excited states. For example, some transitions may not be observable by experimental methods as yet. This constant has therefore been discussed in ref. 9 so that it is not further discussed in this study.

Assessment of the Efficient Basis Set (ATZP)

All eight spectroscopic constants investigated in this study have been produced in parallel using the larger (et-QZ3P-xD) and

efficient (ATZP) basis sets. The overall quality of the larger set has been well reproduced by the efficient basis set as demonstrated in Tables 1–4, except for the vibration–rotational constants α_e of the fifth excited state of CO ($A^1\Pi$), as seen in Figure 6. The ATZP basis set overestimates this constant by 21.5%, whereas the large basis set et-QZ3P-xD underestimated it by -25.0% . Although a generally good agreement exists between the two basis sets, the larger set does demonstrate a better quality for a few states, such as the first excited state of ScF ($a^3\Delta$: ω_e , $\omega_e x_e$) and the seventh excited state of P₂ ($A^1\Pi_g$: ω_e), as shown by the circled data in Figures 3b and 5b. However, as witnessed above, this is not always the case. There are some examples where the efficient basis set produces better accuracy than the larger basis set. For example, the first excited states of P₂ ($a^3\Sigma_u^+$: $\omega_e x_e$, α_e) and ScF ($a^3\Delta$: α_e), and the sixth excited state of CO ($I^3\Sigma^-$: α_e), the efficient basis set predicts these constants with significantly better accuracy than the larger basis set. Please refer to the squared data in Figures 5a and 6a.

Figure 8 exhibits a direct comparison in the ground electronic state using the calculated absolute average percentage deviation (AAPD) for the diatomic spectroscopic constants. The three models in comparison are SAOP with both basis sets, as well as the B3LYP/aug-cc-pVTZ model of ref. 7. It is clear from this figure that the SAOP functional produces a generally better agreement with the experiments in the ground states. Although for the majority of the predicted constants, the B3LYP/aug-cc-pVTZ model and the TD-DFT(SAOP)/ATZP model exhibit a competitive accuracy across the spectrum. The “difficult-to-predict” constants, that is, the anharmonic $\omega_e x_e$ and the vibration–rotational constants α_e are as accurately predicted by the SAOP/ATZVP model as the B3LYP/aug-cc-pVTZ model. It is noted that the B3LYP/aug-cc-pVTZ model is based on a subset of six diatomic molecules,⁷ in which four of them are different from the set of four molecules in the present study. However, the molecules in ref. 7 are all in the first row and do not contain any transition metal atoms, whereas the four molecules in the present study include atoms from first, second, and third rows, which indicates a larger coverage in the periodic table. In the comparison of the basis sets (SAOP/ATZVP

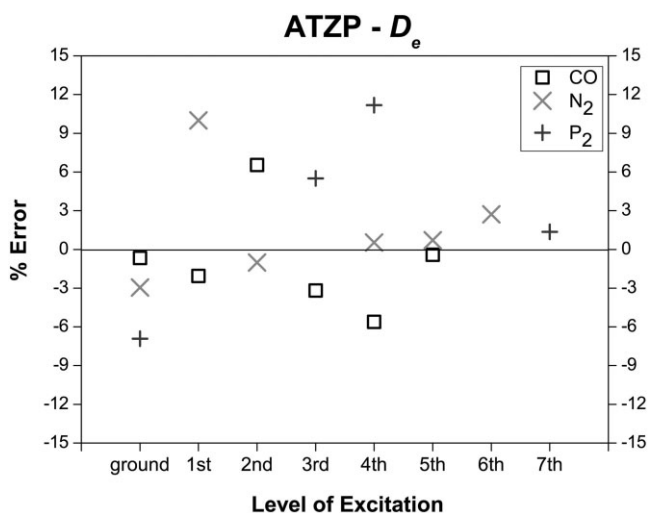


Figure 4. Error in the centrifugal distortion constants (D_e) predicted by the TD-DFT(SAOP)/ATZP model.

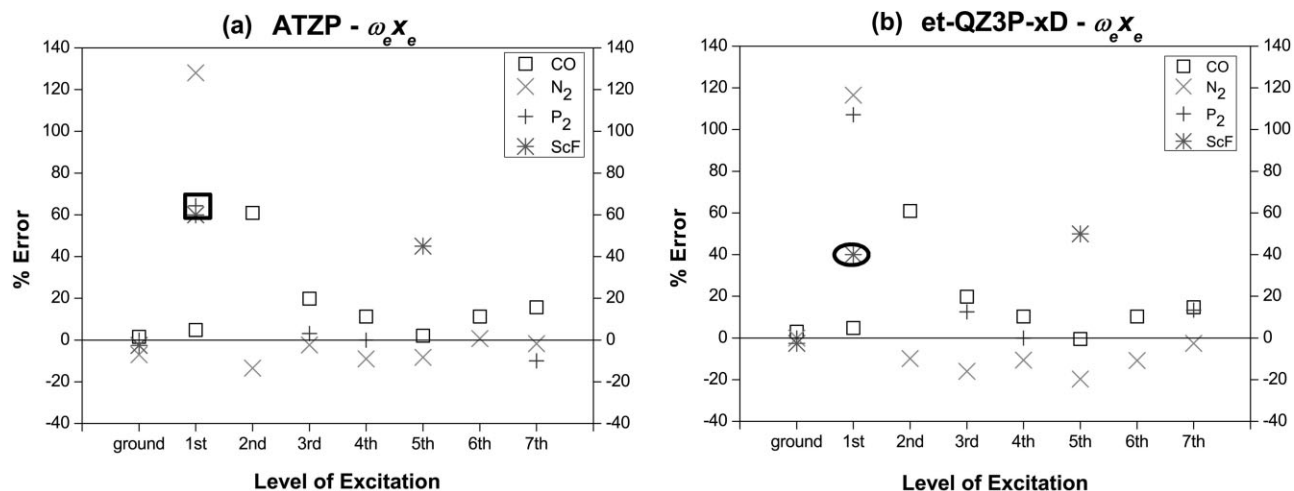


Figure 5. Errors in the anharmonic constants ($\omega_e x_e$) predicted by (a) the TD-DFT(SAOP)/ATZP model, and (b) the TD-DFT(SAOP)/et-QZ3P-xD model.

and TD-DFT(SAOP)/et-QZ3P-xD) in the ground state, the error amplitudes (average) calculated by the larger basis set for constants r_e , $\omega_e x_e$ and α_e did not exceed 0.5, 9.2, and 9.1%, respectively, compared to 0.7, 10.1, and 8.4% computed for the smaller set, respectively. This agreement is very encouraging, as it indicates that the efficient set, at least for the molecules under consideration, is an accurate alternative for the prediction of these important chemical and physical properties.

The capability of this method to predict spectroscopic constants for a wide variety of molecular systems is also reflected in the results obtained for the low-lying excited levels investigated. Figure 9 compares the AAPD errors of the spectroscopic constants of the seven lowest lying excited states using the efficient and large basis sets. Interestingly, for most of the spectroscopic properties investigated, the efficient basis set was found to generate a slightly

smaller margin of error than the larger basis set. The efficiency of the smaller basis set is highlighted in the error values predicted for $\omega_e x_e$ and α_e , where the efficient basis set yields the errors of being 3.1 and 1.7%, respectively, which is smaller than those predicted by the larger set. It is noted that the anharmonic constants $\omega_e x_e$ and the vibration rotational constants α_e are a difficult to predict pair of spectroscopic constants. This indicates that the efficient basis set may produce better higher order derivatives of the potential energy curves than the larger basis set.

The efficiency of the ATZP basis set is also highlighted in Figure 10 by the CPU time (seconds) needed in the generation of the potential energy curve of the ground electronic state of CO ($X^1\Sigma^+$) using the TD-DFT(SAOP)/ATZP and TD-DFT(SAOP)/et-QZ3P-xD models. From this figure, it is apparent that the CPU time required for the TD-DFT(SAOP)/ATZP model is only approximately 25% of that

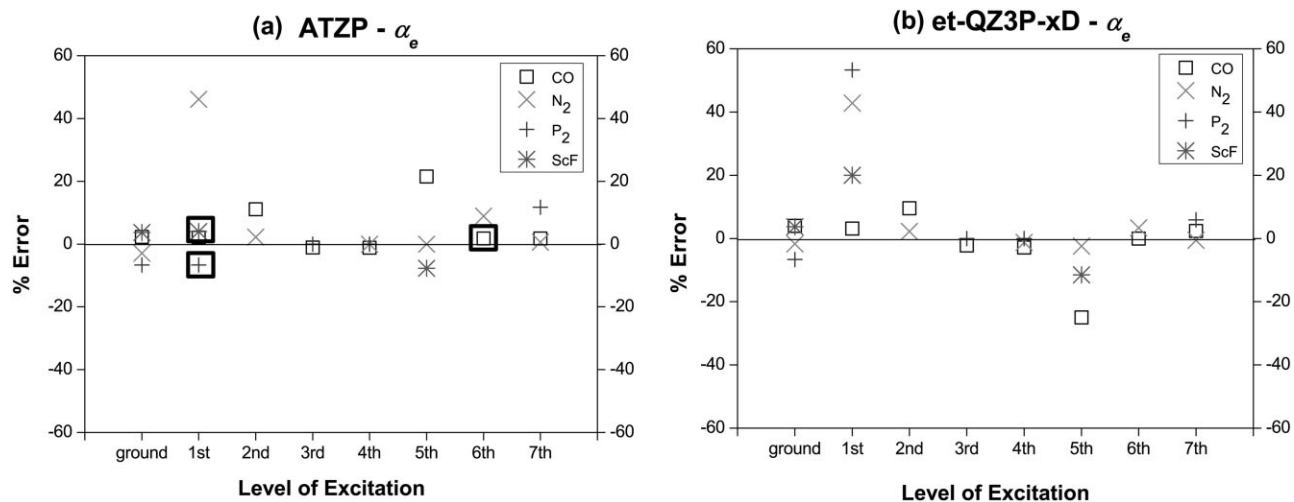


Figure 6. Errors in the vibration-rotation interaction constant (α_e) predicted by (a) the TD-DFT(SAOP)/ATZP model and (b) the TD-DFT(SAOP)/et-QZ3P-xD model.

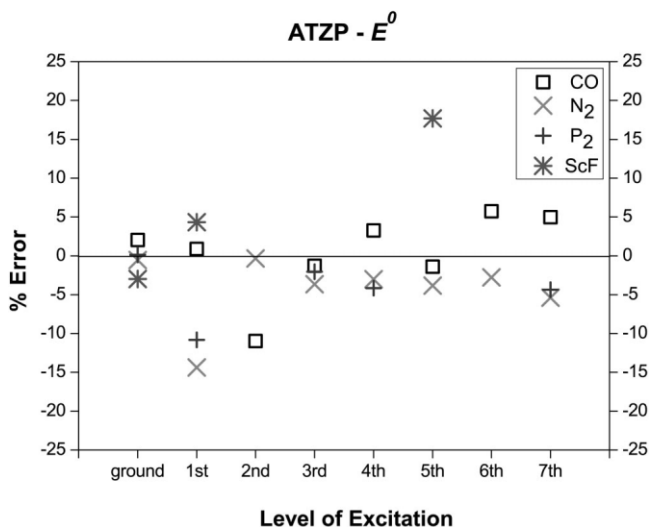


Figure 7. Error in the vibrational zero-point energy (E_n^0) predicted by the TD-DFT(SAOP)/ATZP model.

needed for the larger basis set on the Compaq SC AlphaServer Cluster National Facilities (a 126 node 504 processor (1GHz) Compaq AlphaServer SC. Web site: <http://nf.apac.edu.au/facilities/sc/hardware.php>). This indicates the potential of the current model and basis set (TD-DFT(SAOP)/ATZP) to be applied to larger molecular systems without a significant loss of accuracy.

Conclusion

Time-dependent density functional theory incorporating with the exchange-correlation energy potential V_{xc} = SAOP was used to

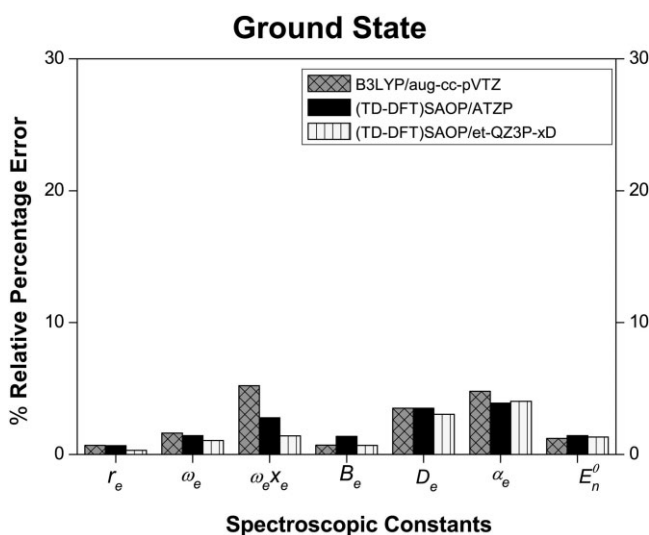


Figure 8. Comparison between the theoretical models of TD-DFT(SAOP)/ATZP, TD-DFT(SAOP)/et-QZ3P-xD (this work) and the B3LYP/aug-cc-pVTZ,⁷ in the ground electronic states.

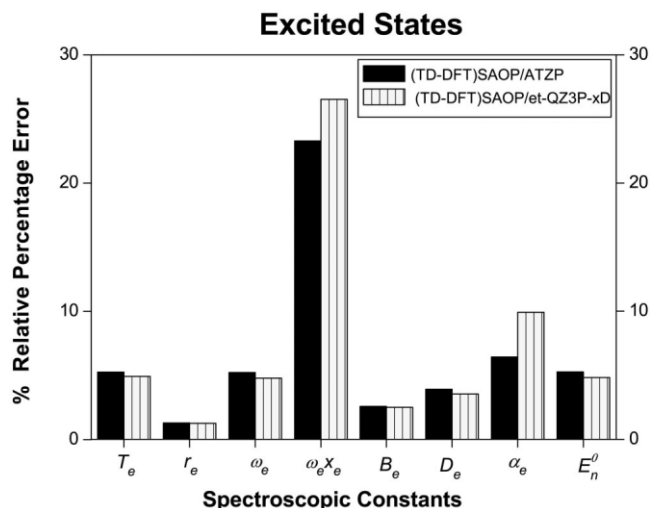


Figure 9. Comparison of the accuracy between the TD-DFT(SAOP)/ATZP and the TD-DFT(SAOP)/et-QZ3P-xD models for the spectroscopic constants of molecules CO, N₂, P₂, and ScF in their low-lying excited electronic states.

produce the eight lowest lying electronic states of a group of representative diatomic molecules of CO, N₂, P₂, and ScF systematically. The recently developed Slater type basis set, the augmented-TZP was employed in this study to generate the equilibrium spectroscopic constants, including the equilibrium distances r_e , harmonic vibrational frequency ω_e , vibrational anharmonicity $\omega_e X_e$, rotational constant B_e , centrifugal distortion constant D_e , and the vibration-rotation interaction constant α_e , and vibrational zero-point energy, E_n^0 , were extracted in an effort to establish a reliable data base for electron spectroscopy.

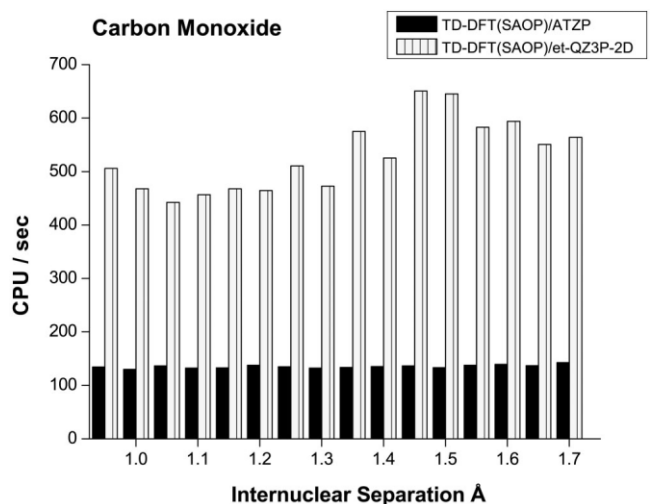


Figure 10. Comparison of the CPU time (second) for the two basis sets in the generation of energies associated with the ground state of CO ($X^1\Sigma^+$).

A parallel set of calculations for comparative purposes for these constants have been also performed using the TD-DFT(SAOP)/et-QZ3P-xD model. A very good agreement with experimental data was obtained for the electronic states studied.

Specifically, using the effective basis set, the overall errors of all eight lowest lying electronic states of the molecules under study are $r_e(\pm 4\%)$, $\omega_e(\pm 5\%$ mostly without exceeding $\pm 20\%)$, $\omega_e x_e(\pm 5\%$ mostly without exceeding 20% , this constant was estimated within the error of $\pm 30\%$ in ref. 7), $B_e(\pm 8\%)$, $D_e(\pm 10\%)$, $\alpha_e(\pm 10\%)$, and $E_n^0(\pm 10\%)$. The accuracy obtained using the ATZP basis set is very competitive to the larger et-QZ3P-xD basis set, in particular, in the ground electronic states. The overall errors in r_e , $\omega_e x_e$, and α_e in the ground states were given by ± 0.5 , ± 9.2 , and $\pm 9.1\%$, respectively, using the large and established basis set of et-QZ3P-xD, whereas the errors for these constants using the efficient basis set of ATPV increase only slightly to ± 0.7 , ± 10.1 , and $\pm 8.4\%$, respectively. The larger basis set, however, needs approximately four times of the CPU time on the National Supercomputing Facilities (a 126 node 504 processor (1GHz) Compaq AlphaServer SC. Web site: <http://nf.apac.edu.au/facilities/sc/hardware.php>). Our results have also shown that the time-dependent density functional theory in conjunction with our newly developed basis set is an effective and accurate tool for the prediction of spectroscopic constants for not only ground states but also excited state of the diatomic molecules. As the set of diatomic molecules were chosen from the periodic table from H to Kr, the results from this work has demonstrated that the combination of the SAOP/ATZP and TD-DFT methods can be applied to low-lying excited states of larger molecular systems, with reliable accuracy and minimal computational cost.

Acknowledgments

The authors, C.F. and F.W., acknowledge the Vice-Chancellor's Strategic Research Initiative Grant of Swinburne University of Technology. C.F. acknowledges the Australian Partnership for Advanced Computing for using the National Supercomputing Facilities, and D.P.C. acknowledges the Faculty of Information and Communication Technologies, Swinburne University of Technology for the Visiting Research Fellowship and NSERC (Canada) for part of the financial support.

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