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

CHANTAL T. FALZON,1 DELANO P. CHONG,2 FENG WANG1
1Centre for Molecular Simulation, Swinburne University of Technology, P.O. Box 218, Hawthorn, Melbourne, Australia, 3122
2Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, B.C., Canada, V6T 1Z1

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 \( \omega_v \), vibrational anharmonicity \( \omega_v \Delta \), rotational constant \( B_0 \), centrifugal distortion constant \( D_0 \), the vibration–rotation interaction constant \( \alpha_e \), and the vibrational zero-point energy \( E_0^v \) 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 \( r_e (\pm 4\%) \), \( \omega_v (\pm 5\% \text{ mostly without exceeding } \pm 20\%) \), \( \omega_v \Delta (\pm 5\% \text{ mostly without exceeding } 20\%) \), much more accurate than a previous study on this constant of \( \pm 30\%) \), \( B_0 (\pm 8\%) \), \( D_0 (\pm 10\%) \), \( \alpha_e (\pm 10\%) \), and \( E_0^v (\pm 10\%) \). 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 \( r_e \), \( \omega_v \Delta \), and \( \alpha_e \) in the ground states were given by \( \pm 0.7, \pm 10.1, \text{ and } \pm 8.4\% \), respectively, using the efficient ATZP basis set, which is competitive to the errors of \( \pm 0.5, \pm 9.2, \text{ and } \pm 9.1\% \), 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.


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

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-
mark to assess new theoretical methods, such as the electron correlation effects, basis set effects, and the quality of new basis sets. Moreover, spectroscopic constants of diatomic molecules are useful for yet experimentally unknown or poorly characterized electronic states, 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) has been proven successful in wide-ranging applications for computing a variety of ground-state properties with a high degree of accuracy. 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. Moreover, the development of DFT can be considered as the need for more accurate exchange–correlation potentials , which can exhibit the correct asymptotic behavior to give accurate predictions of higher excited states. On the other hand, the practical formulation of the time-dependent density functional response theory (TD-DFT) in recent years has been quickly applied to compute molecular excitation energies and transition probabilities. 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. As a result, STO basis sets have been developed, assessed, and incorporated into computational chemistry programs such as the Amsterdam Density Functional (ADF) 2002. Some important and established Slater basis sets with different types available have been assessed recently. 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. For example, Chong 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) augmenting 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, 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. 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. 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. 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. 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 pulses on aligned molecules, which stimulates our research interest in this diatomic molecule. However, the excited electronic states of N₂ still present a major challenge. 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. This also leads to considerable difficulties in the computational study of their electronic structure and bonding with results varying with the methods applied. Spectroscopic information for the electronic excited states of P₂ is still incomplete. 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 ) approach was employed to model the N-electron space for the ground and excited states. The most recently developed ATZP basis set 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.

Journal of Computational Chemistry DOI 10.1002/jcc
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 energy function \( U_n(p) \) 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 have been created. A power series expansion can represent any potential on a given interval to arbitrary precision such as

\[
U_n(p) = \sum_{i=1}^{6} c_i p^i
\]

where \( p = r - r_e \) and \( N = 0, 1, 2, \ldots, 7 \); where \( n \) represents the level in question (ground state). 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 \( [r'_e - 0.25, r'_e + 0.30] \) Å, with intervals of 0.05 Å (here, \( r'_e \) was initially taken from available experimental data). A guess of \( r'_e \) was made from various sources such as the \( r'_e \) of other states if the experimental \( r_e \) is not available. All electronic state calculations were performed using the ADF program package 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, N\(_2\), P\(_2\), 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), \( x = 1 \) (B to Ne) and \( x = 0 \) for H to Kr. This basis set was copied from et-QZ3P-1D, while the aug0-TZP fit set was from et-QZ3P-0D. This basis was derived from QZ3P with the even-tempered parameter equal to 1.27 by the addition of \( n = 1 \) 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.

Theoretical equilibrium bond length \( r_e \), adiabatic excitation energy (termed value) of the state relative to the ground state \( T_e \), harmonic vibrational frequency \( \omega_v \), rotational constant \( B_r \), centrifugal distortion constant \( D_e \), vibrational–rotation interaction constant \( \alpha_{v, r} \), and the vibrational zero-point energy \( E_{zpe} \) have been determined for each of the eight lowest electronic states of the diatomic molecules of CO, N\(_2\), P\(_2\), and ScF accordingly. The individual power series potential energy curves can be derived using Herzberg’s energy level expressions as follows,

\[
G(v) = \frac{E_v(v)}{\hbar c} = \omega_v \left( v + \frac{1}{2} \right) - \omega_{v,r} \left( v + 1 \right)^2 + \cdots
\]

where the fundamental harmonic vibrational frequency, \( \omega_v \), and the vibrational anharmonicity, \( \omega_{v,r} \), relate to vibrational zero-point energy (ZPE)

\[
E_v(v = 0) = \frac{1}{2} \omega_v - \frac{1}{4} \omega_{v,r}
\]

and the rovibrational energy term is

\[
F_v(J) = \frac{E_v(J)}{\hbar c} = B_v(J + 1) - D_v J(J + 1)^2 + \cdots
\]

where the rotational constant at the \( v \)th vibrational state is given by

\[
B_v = B_e - \alpha_v \left( v + \frac{1}{2} \right) + \cdots
\]

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

\[
D_v = D_e - \beta_v \left( v + \frac{1}{2} \right) + \cdots
\]

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

\[
E_{n,m} = T_e(n) + G(v) + F(J).
\]

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.

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, N\(_2\), P\(_2\), 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, \( r_e, \omega_v, \omega_{v,r}, B_e, D_e, \alpha_e, \) and \( E_{zpe} \) 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 N\(_2\) has been compared with other recent theoretical calculations, such as the CCSD(T)/aug-cc-pVTZ and B3LYP/aug-
cc-pVTZ models\(^7\) for the same constants. The Slater-type (STO) ATZP is close to the Gaussian type (GTO) basis set of aug-cc-pV TZ of Dunning\(^8\) 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 \(N_2\) 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 \(\text{cm}^{-1}\), respectively, compared with the value of 0.343 \(\text{cm}^{-1}\) 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>
<thead>
<tr>
<th>State</th>
<th>Method</th>
<th>(T_e) ((\text{cm}^{-1}))</th>
<th>(r_e) (Å)</th>
<th>(\omega_1) ((\text{cm}^{-1}))</th>
<th>(\omega_2) ((\text{cm}^{-1}))</th>
<th>(\omega_3) ((\text{cm}^{-1}))</th>
<th>(B_e) ((\text{cm}^{-1}))</th>
<th>(D_e) ((\text{cm}^{-1}))</th>
<th>(\alpha_e) ((\text{cm}^{-1}))</th>
<th>(E^o) ((\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>(X) (\Sigma^+)</td>
<td>et-QZ3P-2D</td>
<td>0.0</td>
<td>1.1333</td>
<td>2134</td>
<td>13.7</td>
<td>1.914</td>
<td>6.16e-06</td>
<td>0.0182</td>
<td>1063.6</td>
</tr>
<tr>
<td></td>
<td>(a) (\Pi)</td>
<td>ATZP</td>
<td>0.0</td>
<td>1.1375</td>
<td>2214</td>
<td>13.5</td>
<td>1.900</td>
<td>6.08e-06</td>
<td>0.0179</td>
<td>1103.6</td>
</tr>
<tr>
<td></td>
<td>(a) (\Pi)</td>
<td>Expt(^b)</td>
<td>0.0</td>
<td>1.1282</td>
<td>2170</td>
<td>13.3</td>
<td>1.931</td>
<td>6.12e-06</td>
<td>0.0175</td>
<td>1081.7</td>
</tr>
<tr>
<td>(\Delta) (d)</td>
<td>et-QZ3P-2D</td>
<td>48652.1</td>
<td>1.2016</td>
<td>1766</td>
<td>15.1</td>
<td>1.703</td>
<td>6.33e-06</td>
<td>0.0192</td>
<td>879.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATZP</td>
<td>48471.0</td>
<td>1.2062</td>
<td>1759</td>
<td>15.1</td>
<td>1.690</td>
<td>6.23e-06</td>
<td>0.0194</td>
<td>875.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>48686.7</td>
<td>1.2057</td>
<td>1743</td>
<td>14.4</td>
<td>1.691</td>
<td>6.36e-06</td>
<td>0.0190</td>
<td>867.9</td>
<td></td>
</tr>
<tr>
<td>(\Delta) (e)</td>
<td>et-QZ3P-2D</td>
<td>54372.2</td>
<td>1.3857</td>
<td>1110</td>
<td>16.9</td>
<td>1.280</td>
<td>6.82e-06</td>
<td>0.0207</td>
<td>550.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATZP</td>
<td>53704.9</td>
<td>1.3903</td>
<td>1098</td>
<td>16.9</td>
<td>1.272</td>
<td>6.83e-06</td>
<td>0.0210</td>
<td>544.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>55825.4</td>
<td>1.3523</td>
<td>1229</td>
<td>10.5</td>
<td>1.345</td>
<td>6.41e-06</td>
<td>0.0189</td>
<td>611.9</td>
<td></td>
</tr>
<tr>
<td>(\Delta) (e)</td>
<td>et-QZ3P-2D</td>
<td>60619.6</td>
<td>1.3773</td>
<td>1166</td>
<td>12.7</td>
<td>1.296</td>
<td>6.41e-06</td>
<td>0.0174</td>
<td>579.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATZP</td>
<td>60079.0</td>
<td>1.3813</td>
<td>1158</td>
<td>12.7</td>
<td>1.288</td>
<td>6.38e-06</td>
<td>0.0176</td>
<td>575.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>61120.1</td>
<td>1.3696</td>
<td>1172</td>
<td>10.6</td>
<td>1.311</td>
<td>6.59e-06</td>
<td>0.0178</td>
<td>583.4</td>
<td></td>
</tr>
<tr>
<td>(\Delta) (e)</td>
<td>et-QZ3P-2D</td>
<td>65665.0</td>
<td>1.3782</td>
<td>1162</td>
<td>11.8</td>
<td>1.294</td>
<td>6.42e-06</td>
<td>0.0170</td>
<td>578.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATZP</td>
<td>65346.4</td>
<td>1.3821</td>
<td>1155</td>
<td>11.9</td>
<td>1.287</td>
<td>6.39e-06</td>
<td>0.0173</td>
<td>574.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>64230.2</td>
<td>1.3840</td>
<td>1118</td>
<td>10.7</td>
<td>1.284</td>
<td>6.37e-06</td>
<td>0.0175</td>
<td>556.3</td>
<td></td>
</tr>
<tr>
<td>(\Delta) (e)</td>
<td>et-QZ3P-2D</td>
<td>65587.8</td>
<td>1.2342</td>
<td>1506</td>
<td>19.3</td>
<td>1.614</td>
<td>7.42e-06</td>
<td>0.0174</td>
<td>748.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATZP</td>
<td>65546.1</td>
<td>1.2399</td>
<td>1497</td>
<td>19.8</td>
<td>1.599</td>
<td>7.30e-06</td>
<td>0.0282</td>
<td>743.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>65075.7</td>
<td>1.2353</td>
<td>1518</td>
<td>19.4</td>
<td>1.612</td>
<td>7.33e-06</td>
<td>0.0232</td>
<td>754.2</td>
<td></td>
</tr>
<tr>
<td>(\Delta) (e)</td>
<td>et-QZ3P-2D</td>
<td>65912.6</td>
<td>1.3782</td>
<td>1162</td>
<td>11.8</td>
<td>1.294</td>
<td>6.42e-06</td>
<td>0.0170</td>
<td>578.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ATZP</td>
<td>65346.4</td>
<td>1.3821</td>
<td>1155</td>
<td>11.9</td>
<td>1.287</td>
<td>6.39e-06</td>
<td>0.0173</td>
<td>574.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt</td>
<td>65084.4</td>
<td>1.3911</td>
<td>1092</td>
<td>10.7</td>
<td>1.271 —</td>
<td>0.0170</td>
<td>543.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Experimental values are taken from Huber and Herzberg\(^3\) unless otherwise stated.

\(^b\) Experimental values from George et al.\(^49\)
Fairly Accurately Predicted Constants—ωe and De

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 themselves (thermochemistry) usually occurs. Figure 3 provides an assessment on the accuracy of the theoretically calculated harmonic vibrational frequency ωe with (1) the TD-DFT(SAO)/ATZP model, and (2) the TD-DFT(SAO)/et-QZ3P-xD model. It can be seen that the majority of the errors occur in ωe are well within the band of ±5%, while the overall errors for this constant do not exceed ±20%. The accuracy of our theoretically generated vibrational constants (ωe) in the ground electronic states is very competitive to other recent calculations. For example, the errors associated with ωe 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 calculations using the DFT-EFD2/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, 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 ωe and centrifugal distortion constants De, 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 Be and vibrational harmonic frequencies, e, as

\[
D_e = \frac{4B_e^3}{\omega_e^3}
\]

Hence, the accuracy of this constant De will be affected by the accuracy from both of the equilibrium rotational constants Be and harmonic vibrational frequencies ωe. That is, the errors in the centrifugal constants De would not be large if the errors in the rotational constants Be are very small (as was found in the previous section), and the errors of vibrational harmonic frequencies ωe are not very large. Figure 5 indicates that the errors of the centrifugal constants De for most states of the molecules under this study are in fact within ca. ±10%. As seen, the errors in this constants (De) are a result of a balanced compensation between the equilibrium rotational constants Be and harmonic vibrational frequencies ωe.
The theoretical prediction of the anharmonic vibrational constants \( \omega_e \) and vibrational anharmonic constants \( \omega_{\text{eBe}} \) 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 \( \omega_{\text{eBe}} \) are only good to about 30%. 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 ±5%.

In other excited electronic states, the errors are, in fact, well within the ±20% envelop, except for ScF in its fifth excited state. Figure 5 clearly indicates such trends. The equilibrium vibration–rotational constants \( \alpha_e \) is related to other spectroscopic constants via

\[
\alpha_e = \frac{6}{\omega_e} \frac{\omega_{\text{eBe}}B_e^2 - B_e^3}{\omega_e}.
\]

This constant depends upon anharmonic vibrational constants \( \omega_{\text{eBe}} \), which can be poorly predicted, harmonic vibrational constants \( \omega_e \), 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 \( \alpha_e \) 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 \( P_2 \) 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.

### Table 3. Theoretical and Experimental Spectroscopic Constants for the Eight Lowest Lying Electronic States of \( P_2 \)\(^a\)

<table>
<thead>
<tr>
<th>State</th>
<th>Method</th>
<th>( T_e ) (cm(^{-1}))</th>
<th>( r_e ) (Å)</th>
<th>( \omega_e ) (cm(^{-1}))</th>
<th>( \omega_{\text{eBe}} ) (cm(^{-1}))</th>
<th>( B_e ) (cm(^{-1}))</th>
<th>( D_e ) (cm(^{-1}))</th>
<th>( \alpha_e ) (cm(^{-1}))</th>
<th>( E^0 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X ) (^1\Sigma^+_g^-)</td>
<td>et-QZ3P-1D</td>
<td>0.0</td>
<td>1.9017</td>
<td>788</td>
<td>2.9</td>
<td>0.301</td>
<td>1.76e-07</td>
<td>0.0014</td>
<td>393.3</td>
</tr>
<tr>
<td>( a ) (^3\Sigma^+_g^-)</td>
<td>et-QZ3P-1D</td>
<td>18165.9</td>
<td>2.1122</td>
<td>505</td>
<td>5.8</td>
<td>0.244</td>
<td>2.28e-07</td>
<td>0.0023</td>
<td>251.1</td>
</tr>
<tr>
<td>( b ) (^3\Pi^+_g)</td>
<td>et-QZ3P-1D</td>
<td>26462.1</td>
<td>1.9801</td>
<td>643</td>
<td>3.6</td>
<td>0.277</td>
<td>2.06e-07</td>
<td>0.0018</td>
<td>320.6</td>
</tr>
<tr>
<td>( b' ) (^3\Sigma^-_g)</td>
<td>et-QZ3P-1D</td>
<td>26267.0</td>
<td>2.0736</td>
<td>586</td>
<td>2.2</td>
<td>0.253</td>
<td>1.92e-07</td>
<td>0.0013</td>
<td>286.5</td>
</tr>
</tbody>
</table>

\(^a\)Experimental values are taken from Huber and Herzberg\(^6\) unless otherwise stated.

\(^b\)Experimental values from Brion.\(^51\)

\(^c\)Experimental values from Malicet et al.\(^52\)

---

**Predicted Spectroscopic Constants with Varied Accuracies—\( \omega_{\text{eBe}} \) and \( \alpha_e \)**

The theoretical prediction of the anharmonic vibrational constants \( \omega_{\text{eBe}} \) has its significance in high accuracy predictions of experimentally observed fundamental vibrational frequencies. The vibration–rotational constant \( \alpha_e \) and vibrational anharmonic constants \( \omega_{\text{eBe}} \) 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 \( \omega_{\text{eBe}} \) are only good to about 30%. 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 ±5%.

In other excited electronic states, the errors are, in fact, well within the ±20% envelop, except for ScF in its fifth excited state. Figure 5 clearly indicates such trends. The equilibrium vibration–rotational constants \( \alpha_e \) is related to other spectroscopic constants via

\[
\alpha_e = \frac{6}{\omega_e} \frac{\omega_{\text{eBe}}B_e^2 - B_e^3}{\omega_e}.
\]

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 \( \nu = 0 \), 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-
ing the stability of the minimum structures of the species.\(^4\) 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 ±10% for the majority and only a few exceed the ±10% band. As the ZPE is dependent upon the vibrational harmonic frequencies \(\omega_x\) and the vibrational anhar-
monic constants \( \omega_{e} \), it is no surprise that the errors of ZPE are similar to \( \omega_{e} \), as the values of \( \omega_{e} \) 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 experimentally 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 \( \alpha_e \) of the fifth excited state of CO (\( \alpha^1\Pi \)), 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 (\( \alpha^3\Sigma^+; \omega_{e}, \omega_{x} \)) and the seventh excited state of P_2 (\( \alpha^1\Pi_x; \omega_{e} \)), 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 P_2 (\( \alpha^3\Sigma^+; \omega_{e}, \omega_{x} \)) and ScF (\( \alpha^3\Sigma^+; \omega_{e} \)), and the sixth excited state of CO (\( \alpha^1\Sigma^+; \omega_{e} \)), 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 \( \omega_{e}, \omega_{x} \), and the vibration–rotational constants \( \alpha_e \) 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, 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
and TD-DFT(SAOP)/et-QZ3P-xD) in the ground state, the error amplitudes (average) calculated by the larger basis set for constants $r_e$, $\omega_x$, and $\alpha_e$ 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 $\omega_x$, and $\alpha_e$, 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 $\omega_x$ and the vibration rotational constants $\alpha_e$ 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
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 produce the eight lowest lying electronic states of a group of representative diatomic molecules of CO, N$_2$, P$_2$, 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 $\omega_e$, vibrational anharmonicity $\omega_x$, rotational constant $B_e$, centrifugal distortion constant $D_e$, and the vibration–rotation interaction constant $\alpha_e$, and vibrational zero-point energy, $E_{0}^\text{v}$, were extracted in an effort to establish a reliable data base for electron spectroscopy.

Figure 7. Error in the vibrational zero-point energy ($E_{0}^\text{v}$) predicted by the TD-DFT(SAOP)/ATZP model.

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, 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, N$_2$, P$_2$, and ScF in their low-lying excited electronic states.

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 $\pm 20\%)$, $\alpha_e(\pm 5\%$ mostly without exceeding 20%), this constant was estimated within the error of $\pm 30\%$ in ref. 7), $B_{ex}(\pm 8\%)$, $D_{ex}(\pm 10\%)$, $\alpha_{ex}(\pm 10\%)$, and $E_{ex}(\pm 10\%)$. 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 $r_e$, $\omega_e$, and $\alpha_e$ in the ground states were given by $\pm 0.5$, $\pm 9.2$, 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 ATVP increase only slightly to $\pm 0.7$, $\pm 10.1$, 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.

References

40. van Gisbergen, S. J. A. unpublished work.