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Abstract

The reliability of density functional theory and other electronic structure methods is examined for anharmonicities and spectroscopic constants of low-lying valence electronic excited states. The equilibrium bond length $r_e$, harmonic vibrational frequency $\omega_e$, rotational constant $B_e$, centrifugal distortion constant $D_e$, and vibration-rotation interaction constant $\epsilon_e$, have been determined for low-lying singlet excited states of BF, CO, N\textsubscript{2}, CH\textsuperscript{+}, and NO\textsuperscript{+}. Predictions using configuration interaction singles, equation-of-motion coupled-cluster singles and doubles, and various time-dependent density functional methods have been made using the 6-31G*, aug-cc-pVDZ, and aug-cc-pVTZ basis sets and compared to experimental values. Time-dependent density functional theory compares favorably to equation-of-motion coupled-cluster theory for the properties considered, but errors are substantially larger for excited states than for ground states.

Keywords: Density Functional Theory; Anharmonicity; Coupled-Cluster Theory; Spectroscopic constants; Diatomic molecules.

Introduction

Over the past decade, a variety of electronic structure methods have been developed for electronic excited states. The reliability of some of these methods [including configuration interaction singles, CIS\textsuperscript{[1]}, and equation-of-motion EOM-CCSD\textsuperscript{[2]} for equilibrium geometries and harmonic vibrational frequencies of low-lying excited states has been investigated by Stanton, Gauss, Ishikawa, and Head-Gordon\textsuperscript{[3]}, who examined several diatomic molecules as well as ammonia, formaldehyde, and acetylene. Approximate versions of EOM-CCSD were investigated for these molecules by Gwaltney and Bartlett\textsuperscript{[4, 5]}. The present paper extends the benchmarking of excited state property predictions to the recently developed time-dependent density functional theory (TDDFT)\textsuperscript{[6-9]}. Preliminary investigations by Caillie and Amos\textsuperscript{[10, 11]} who implemented analytic TDDFT gradients, suggest that TDDFT seems to give fairly good predictions of excited state geometries. Here we consider TDDFT predictions of valence excited state geometries and frequencies for several of the molecules considered by Stanton and coworkers\textsuperscript{[3]}. Various functionals have been used, and

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results are compared to experiment as well as to CIS and EOM-CCSD predictions. Three different Gaussian basis sets are considered to examine the basis set dependence of the excited state properties.

We extend previous work on the reliability of excited state properties by analyzing the behavior of a spectroscopic constant that rely on higher derivatives of the potential energy surface, namely the vibration-rotation interaction constants \( \alpha_e \) (depending on third derivatives). The constant \( \alpha_e \) is necessary to relate zero-point averaged bond lengths \( r_0 \) to equilibrium bond lengths \( r_e \). Such anharmonic spectroscopic constants are sometimes predicted for excited states \(^{12, 13}\) using sophisticated multi-reference CI methods \(^{14}\), however, to our knowledge, the reliability of excited state methods for these constants is unknown at present.

**Theoretical Approach**

The vibrational term values \( G(\nu) \) of a diatomic molecule are

\[
G(\nu) = \omega_e \left( \nu + \frac{1}{2} \right) - \omega_e x_e \left( \nu + \frac{1}{2} \right)^2 + \ldots \tag{1}
\]

While the rotational term values \( F_\nu(J) \) are given by

\[
F_\nu(J) = B_e J(J + 1) - D_e J^2 (J + 1)^2 + \ldots \tag{2}
\]

The effective rotational constant \( B_\nu \) depends on the equilibrium rotational constant \( B_e \) and the vibration-rotation interaction terms \( \alpha_e \) via

\[
B_\nu = B_e - \alpha_e \left( \nu + \frac{1}{2} \right) + \ldots \tag{3}
\]

Fundamental frequencies are thus related to harmonic vibrational frequencies via \( \nu = \omega_e - 2 \omega_e x_e + \ldots \).

Using the INTDIF module of the PSI electronic structure package \(^{15}\) we determined the equilibrium bond length \( r_e \), harmonic vibrational frequency \( \omega_e \), rotational constant \( B_e \), centrifugal distortion constant \( D_e \), and the vibration-rotation coupling constant \( \alpha_e \) for the lowest singlet excited states of BF, CO, \( \text{N}_2 \) and \( \text{CH}^+ \). For \( \text{NO}^+ \), we considered the third \( (\tilde{A}^1\Pi) \) excited singlet state, for which better experimental data exists than for the lower-lying excited singlets.

Spectroscopic constants were determined using the INTDIF module of the PSI electronic structure package \(^{15}\), which performs a linear least-squares regression fit of a fifth order polynomial to five tightly converged \( \sim 10^{-11} \) hartrees) energy points uniformly spaced around \( r_e \) with some constraints on the quintic force constant \(^{16, 17}\). Basis set effects were estimated by using three basis sets up to the triple-\( \zeta \) quality: (a) Pople’s 6-31G* double-\( \zeta \) basis including polarized \( d \)-functions for first row elements, \(^{18, 19}\) (b) the augmented correlation-consistent polarized valence double-\( \zeta \)
basis set of Dunning and coworkers [20] denoted aug-cc-pVDZ and (c) their corresponding triple-ζ basis set, aug-cc-pVTZ. In (a) we use six Cartesian d-type functions while the polarization functions on (b) and (c) are pure angular momentum functions (5 d-type and 7 f-type functions).

A variety of excited state methods were employed in this work: configuration iteration singles (CIS) [1], equation of motion coupled-cluster theory including both single and double excitations (EOM-CCSD) [2], and time-dependent density functional theory (TDDFT) [5-9]. To gauge the dependence of TDDFT calculations on the choice of exchange-correlation functional, we used the Slater exchange functional [21] paired with the correlation functional of Vosko, Wilk, and Nusair [22] denoted here as SVWN, and Becke’s 1988 exchange functional [23] with the correlation functional of Lee, Yang, and Parr [24] referred to as BLYP, and Becke’s 3 parameter exchange functional paired with LYP correlation denoted B3LYP [25, 26]. CIS calculations were carried out using the Q-Chem package [27] while the ACES II electronic structure program [28] was used for the EOM-CCSD calculations. We have used the TDDFT implementation of Hirata and Head-Gordon [9] as found in the Q-chem package [27], which also includes a Tamm-Dancoff approximation variant denoted TDDFT/TDA. Geometries were optimized with analytic gradient for CIS [1] and EOM-CCSD [29] methods; however, geometry optimization for DFT excited state methods were carried out numerically using finite differences of energies. As has been shown by Hassanzedeh and Irikura [30], a large grid size for DFT calculation is essential for convergence of spectroscopic constants studied here. In light of this, we have employed a 100-302 Lebedev grid for all the TDDFT calculations. Finally, all electrons including the core were correlated.

We had difficulty obtaining energies converged tightly enough (around 10^{-11} hartrees) to make higher-order derivatives numerically stable for some of the TDDFT computations, most frequently for the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

It would seem reasonable to ascribe these convergence problems to the use of finite integration grids, although similar problems (i.e., instability with respect to step size) were not apparent in our study of the ground electronic states [32]. A ground state study by Hassanzedeh and Irikura [30] notes that DFT estimates of anharmonic constants that need higher-order force constants can change significantly with respect to integration grid, which we also observed in the present study. The numerical stability of anharmonic constants with respect to displacement size and their convergence with respect to the integration grid are both important issues for those interested in making DFT computations of anharmonic constants routine.
Results and Discussion

Total electronic energies and spectroscopic constants are presented in Tables I (\( \tilde{A}^1\Pi\) BF), II (\( \tilde{A}^1\Pi\) CO), III (\( \tilde{a}^1\Sigma^+\) N\(_2\)), IV (\( \tilde{A}^1\Pi\) CH\(^+\)) and V (\( \tilde{A}^1\Pi\) NO\(^+\)).

Errors vs. experimental values from Huber and Herzberg\(^{[31]}\) are displayed in Figures 1 (\( T_e \)), 2 (\( r_e \)), 3 (\( B_e \)), 4 (\( \omega_e \)), 5 (\( D_e \)), and 6 (\( \alpha_e \)). Table VI summarizes the average absolute relative errors for the spectroscopic constants at each level of theory.

A. Adiabatic excitation energies

Figure 1 displays errors in the theoretically predicted adiabatic excitation energies from the ground electronic states to the excited states considered. Experimental values were taken from Huber and Herzberg\(^{[31]}\). As it is well known\(^{[1, 3, 4]}\), CIS performs poorly, with errors sometimes exceeding one electron-volt. EOM-CCSD offers a tremendous improvement, with most predictions being within 0.2 eV of experiment; the much larger error (around 2 eV) for 6-31G* is due to the absence of polarization functions for hydrogen in that basis.

TDDFT methods also show substantial improvement over CIS for the low-lying valence excited states considered in this study; Rydberg excited states are considerably more difficult for TDDFT\(^{[9]}\). In general, the TDDFT predictions are almost as good as EMO-CCSD, with most errors within 0.3 eV of the reference experimental values. Adiabatic excitation energies do not consistently improve when the larger aug-cc-pVTZ basis is employed. The TDA approximation\(^{[9]}\) to TDDFT performs better for the S-VWN and BLYP functionals, while it does not make much difference for the B3LYP functional except in the case of BF, where it results in significantly larger errors.

B. Equilibrium bond lengths and rotational constants

Errors in excited state equilibrium bond lengths are presented in figure 2. With all basis sets used, CIS bond lengths are always underestimated (except for BF 6-31G* and aug-cc-pVDZ where they are slightly overestimated), with an average absolute errors of 0.03 Å. This value is about the same as that found for a similar set of molecules studied by Stanton et al.\(^{[3]}\) and by Gwaltney and Bartlett\(^{[4, 5]}\) using CIS. The underestimated of excited state bond lengths by CIS is consistent with the underestimation of ground state bond lengths by Hartree-Fock. For the 6-31G* basis set, EOM-CCSD studies improve upon CIS with an average absolute error of 0.014 Å. For the present cases, we do not observe a significant improvement for EOM-CCSD on going to the larger basis. For the double-\( \zeta \) basis sets, S-VWN, B3LYP, and B3LYP/TDA usually improve over CIS. With the aug-cc-pVTZ basis, TDDFT and TDDFT/TDA predictions are generally much better than CIS. B3LYP performs the best of the three functionals, with bond lengths that are reasonable even with the smaller basis sets (6-31G* and aug-cc-pVDZ) and an average absolute error (0.007 Å for aug-cc-pVTZ) even smaller than for EOM-CCSD.
The equilibrium rotational constants $B_e$ are simply related to the equilibrium bond length via $B_e = \frac{\hbar}{(8\pi^2 \mu r_e)^2}$. Hence we expect the general trends observed for bond length error to persist for $B_e$ errors, with underestimates of bond lengths leading to overestimates of $B_e$ and vice versa. Consistent with this, the $B_e$ errors in figure 3 qualitatively mirror (through zero error) the bond length errors in figure 2. Most errors in $B_e$ are within ±7% with very few points above ±10%. CIS typically overestimates, while other methods considered here typically underestimate experiment. As with many bond lengths, TDDFT predictions of $B_e$ frequently (but not uniformly) improve over CIS. Our best results are obtained with aug-cc-pVTZ B3LYP/TDA, with an average absolute error of only 0.9%. With the largest basis set used (aug-cc-pVTZ), EOM-CCSD performs better than BLYP/TDA and S-VWN/TDA, with an average absolute error of 2.7%, as compared with 2.9% for BLYP/TDA and 3.2% for S-VWN/TDA. TDDFT B3LYP and B3LYP/TDA have smaller average absolute errors than EOM-CCSD for all basis sets used.
Figure 1: Errors in theoretically predicted adiabatic excitation energies for excited electronic states.
Figure 2: Errors in theoretically predicted bond lengths $r_e$ for excited electronic states.
Figure 3: Relative errors in theoretically predicted rotational constants $B_e$ for excited electronic states.
C. Harmonic vibrational frequencies

Figure 4 displays the relative errors in harmonic vibrational frequencies $\omega_e$. CIS overestimates $\omega_e$ by 1-20% in most cases, which is consistent with bond length underestimation. EOM-CCSD frequencies are substantially improved, with most errors within 10%, usually underestimating experiment. The TDDFT methods are better than CIS and generally perform as well as or better than EOM-CCSD for the diatomics studied, with most errors within 10% for S-VWN and BLYP, and 7% for B3LYP. BLYP tends to underestimate, while B3LYP mostly overestimates harmonic frequencies. The TDA approximation typically lowers predicted frequencies slightly, usually giving poorer agreement with experiment (except for B3LYP). Basis set effects are usually minor and using the largest basis set is not always an improvement. Of all the methods studied, TDDFT B3LYP/TDA method with the aug-cc-pVTZ basis has the smallest average absolute error for $\omega_e$, at 1.5%.

D. Centrifugal distortion constants

The centrifugal distortion constant, which accounts for the lengthening of the bond with higher angular momentum, is given by $D_c = 4B_c^3 / \omega_e^2$. Errors in theoretical predictions of $D_c$ are presented in Figure 5, which shows that CIS and EOM-CCSD methods almost always underestimate $D_c$, by as much as 20% or more. On average, EOM-CCSD improves significantly over CIS. The TDDFT methods also improve over CIS in estimating $D_c$, with most errors within $\pm$ 10%. S-VWN and B3LYP tend to underestimate $D_c$, whereas BLYP tends to overestimate it. Theoretical estimates of $D_c$ are sensitive to basis set used and seem to improve significantly when the larger aug-cc-pVTZ basis is used (except with BLYP). S-VWN with aug-cc-pVTZ has the smallest average absolute error, at 2%.
Figure 4: Relative errors in theoretically predicted harmonic vibrational frequencies $\omega_e$ for excited electronic states.
**Figure 5**: Relative errors in theoretically predicted centrifugal distortion constants $\overline{D_e}$ for excited electronic states.
E. Vibration-rotation interaction constants

The vibration-rotation interaction constants $\alpha_u$ depend on the third derivative of the potential energy and relate the effective rotational constant $B_\nu$ for vibrational level $\nu$ to the equilibrium rotational constant $B_e$ via equation 3. Figure 6 displays the errors in predicted values. For all methods used, theory usually underestimates $\alpha_u$, except for BF where it is usually overestimated. CIS exhibits the largest errors, underestimating $\alpha_u$, except for BF where it is usually overestimated. CIS exhibits the largest errors, underestimating $\alpha_u$ for CH$^+$ by as much as 36% (compared to a maximum Hartree-Fock error of 23% for the ground states of these molecules). EOM-CCSD is typically within 20% (except for NO$^+$); for ground states, CCSD is usually within 10% and average absolute errors for the largest basis are 6% compared to 13% here. Like EOM-CCSD, all TDDFT methods are also typically within 20% for $\alpha_u$. As for the ground state, the larger aug-cc-pVTZ basis improves the average absolute errors for most methods; from the figure, one can see that the most noticeable improvement is for BF. With the aug-cc-pVTZ basis, the average absolute errors are 21% (CIS), 13% (EOM-CCSD), 10% (S-VWN), 13% (S-VWN/TDA), 6% (BLYP), 10% (BLYP/TDA), 9% (B3LYP), and 11% (B3LYP/TDA). For the ground states, the corresponding errors for DFT were usually somewhat smaller at 4-8%.

The leading term in the difference between the (zero-point) vibrationally averaged rotational constant $B_0$ and the equilibrium rotational constant $B_e$ is $-\frac{\alpha_u}{2}$ (see equation 3). For the cases considered here, this difference is about 0.5-4.0% of $B_e$. As noted above, the smallest average absolute error for predictions of $B_e$ is 0.9% for aug-cc-pVTZ B3LYP/TDA. Given the small errors in $\alpha_u$ predictions, the difference $(B_0 - B_e)$ can be accurately estimated with any of the theoretical methods considered here. Once the $-\frac{\alpha_u}{2}$ vibrational correction is included, the majority of the error in theoretical estimates of the vibrationally averaged rotational constant $B_0$ again comes from the errors in the equilibrium constant $B_e$ itself.
Figure 6: Relative errors in theoretically predicted vibration-rotation interaction constants $\alpha_\gamma$ for excited electronic states.
Conclusions

The main purpose of this paper is to assess the performance of TDDFT methods and compare them to other excited state theoretical methods (CIS and EOM-CCSD) for the prediction of spectroscopic constants \((\rho_e, \omega_e, \alpha_e, D_e)\) of low-lying valence excited states of diatomic molecules. In general, the TDDFT predictions are fairly reliable, performing as well as (and frequently better than) EOM-CCSD. In contrast, CIS predictions are usually poor, producing shorter equilibrium bond lengths than experiment and large errors for other spectroscopic constants. Presumably this arises from the neglect of electron correlation by CIS. As is well known, CIS predictions of adiabatic excitation energies are poor. In contrast, TDDFT predictions are rather good, with most errors within 0.3 eV of experimental values, compared to ~0.2 eV for EOM-CCSD method.

In comparison with ground state predictions in our previous paper and other papers dealing with diatomic and other small and medium-size polyatomic molecules [32-41], excited state predictions are less reliable. The errors in equilibrium bond lengths and vibration-rotation interaction constants for excited states are almost twice as large as their ground state counterparts. Errors in predicted harmonic vibrational frequencies and the centrifugal distortion constants are almost the same for both states. Although \(\alpha_e\) values are not predicted as accurately for excited states as they are for ground states, nevertheless they should be accurate enough to give fairly reliable estimates of the absolute difference between equilibrium and zero-point averaged rotational constants and between harmonic and fundamental vibrational frequencies.
Table I. Spectroscopic constants for the $\tilde{A}^1\Pi$ excited electronic state of BF.$^a$

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy</th>
<th>$T_e$</th>
<th>$r_e$</th>
<th>$\omega_e$</th>
<th>$B_e$</th>
<th>$\bar{D}_e$</th>
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$^a$ Energies in hartrees, adiabatic excitation energies in eV, bond lengths in Å, and other quantities in cm$^{-1}$. Core electrons are correlated. Experimental data are from Huber and Herzberg (31).
Table II. Spectroscopic constants for the 3\(^{1}\Pi\) excited electronic state of CO.\(^a\)

<table>
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<tr>
<th>Method</th>
<th>Energy</th>
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<th>(r_e)</th>
<th>(\omega_e)</th>
<th>(B_e)</th>
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\(^a\) Energies in hartrees, adiabatic excitation energies in eV, bond lengths in Å, and other quantities in cm\(^{-1}\). Core electrons are correlated. Experimental data are from Huber and Herzberg (31).
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* Energies in hartrees, adiabatic excitation energies in eV, bond lengths in Å, and other quantities in cm⁻¹. Core electrons are correlated. Experimental data are from Huber and Herzberg (31).
Table IV. Spectroscopic constants for the $\tilde{A}^1\Pi$ excited electronic state of CH$^+$.\textsuperscript{a}

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<td>1849</td>
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<td>1.91e-03</td>
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<td>1865</td>
<td>11.898</td>
<td>2.00e-03</td>
<td>0.9414</td>
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\textsuperscript{a} Energies in hartrees, adiabatic excitation energies in eV, bond lengths in Å, and other quantities in cm$^{-1}$. Core electrons are correlated. Experimental data are from Huber and Herzberg (31).
Table V. Spectroscopic constants for the $\tilde{A} \ ^1\Pi$ excited electronic state of NO$^+$.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy</th>
<th>$T_e$</th>
<th>$r_e$</th>
<th>$\omega_e$</th>
<th>$B_e$</th>
<th>$\bar{D}_e$</th>
<th>$\alpha_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G$^*$ CIS</td>
<td>-128.548314</td>
<td>9.83</td>
<td>1.1661</td>
<td>1878</td>
<td>1.660</td>
<td>5.19e-06</td>
<td>0.0186</td>
</tr>
<tr>
<td>aug-cc-pVDZ CIS</td>
<td>-128.570776</td>
<td>9.96</td>
<td>1.1616</td>
<td>1873</td>
<td>1.673</td>
<td>5.34e-06</td>
<td>0.0187</td>
</tr>
<tr>
<td>aug-cc-pVTZ CIS</td>
<td>-128.600695</td>
<td>10.08</td>
<td>1.1567</td>
<td>1857</td>
<td>1.687</td>
<td>5.58e-06</td>
<td>0.0187</td>
</tr>
<tr>
<td>6-31G$^*$ EOM-CCSD</td>
<td>-128.901065</td>
<td>9.27</td>
<td>1.1925</td>
<td>1789</td>
<td>1.588</td>
<td>5.00e-06</td>
<td>0.0170</td>
</tr>
<tr>
<td>aug-cc-pVDZ EOM-CCSD</td>
<td>-128.937316</td>
<td>9.35</td>
<td>1.1865</td>
<td>1786</td>
<td>1.604</td>
<td>5.17e-06</td>
<td>0.0174</td>
</tr>
<tr>
<td>aug-cc-pVTZ EOM-CCSD</td>
<td>-129.052740</td>
<td>9.43</td>
<td>1.1710</td>
<td>1817</td>
<td>1.647</td>
<td>5.41e-06</td>
<td>0.0173</td>
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<tr>
<td>6-31G$^*$ S-VWN</td>
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<td>1.1883</td>
<td>1754</td>
<td>1.599</td>
<td>5.32e-06</td>
<td>0.0188</td>
</tr>
<tr>
<td>aug-cc-pVDZ S-VWN</td>
<td>-128.256918</td>
<td>8.88</td>
<td>1.1840</td>
<td>1750</td>
<td>1.610</td>
<td>5.46e-06</td>
<td>0.0189</td>
</tr>
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<td>aug-cc-pVTZ S-VWN</td>
<td>-128.291921</td>
<td>8.99</td>
<td>1.1768</td>
<td>1736</td>
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<td>5.75e-06</td>
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<tr>
<td>6-31G$^*$ S-VWN/TDA</td>
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<td>8.98</td>
<td>1.1909</td>
<td>1736</td>
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<td>5.35e-06</td>
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<td>aug-cc-pVDZ S-VWN/TDA</td>
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<td>1732</td>
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<td>aug-cc-pVTZ S-VWN/TDA</td>
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<td>1.1794</td>
<td>1717</td>
<td>1.623</td>
<td>5.80e-06</td>
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<tr>
<td>6-31G$^*$ BLYP</td>
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<td>8.64</td>
<td>1.2119</td>
<td>1597</td>
<td>1.537</td>
<td>5.70e-06</td>
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<td>aug-cc-pVDZ BLYP</td>
<td>-129.232146</td>
<td>8.72</td>
<td>1.2078</td>
<td>1592</td>
<td>1.548</td>
<td>5.85e-06</td>
<td>0.0204</td>
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<tr>
<td>aug-cc-pVTZ BLYP</td>
<td>-129.262208</td>
<td>8.83</td>
<td>1.2008</td>
<td>1576</td>
<td>1.566</td>
<td>6.18e-06</td>
<td>0.0209</td>
</tr>
<tr>
<td>6-31G$^*$ BLYP/TDA</td>
<td>-129.206802</td>
<td>8.79</td>
<td>1.2150</td>
<td>1577</td>
<td>1.529</td>
<td>5.75e-06</td>
<td>0.0205</td>
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<td>aug-cc-pVDZ BLYP/TDA</td>
<td>-129.226681</td>
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<td>1.2110</td>
<td>1572</td>
<td>1.540</td>
<td>5.91e-06</td>
<td>0.0206</td>
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<tr>
<td>aug-cc-pVTZ BLYP/TDA</td>
<td>-129.256644</td>
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<td>1.2040</td>
<td>1556</td>
<td>1.557</td>
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<td>6-31G$^*$ B3LYP</td>
<td>-129.151269</td>
<td>8.86</td>
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<td>1686</td>
<td>1.577</td>
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<td>1.588</td>
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<td>1.1857</td>
<td>1665</td>
<td>1.606</td>
<td>5.97e-06</td>
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<td>6-31G$^*$ B3LYP/TDA</td>
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<td>1677</td>
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<td>aug-cc-pVDZ B3LYP/TDA</td>
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<td>1602</td>
<td>1.586</td>
<td>5.60e-06</td>
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</table>

\textsuperscript{a} Energies in hartrees, adiabatic excitation energies in eV, bond lengths in Å, and other quantities in cm\textsuperscript{-1}. Core electrons are correlated. Experimental data are from Huber and Herzberg (31).
Table VI. Average absolute relative errors (percent) for spectroscopic constants.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Method</th>
<th>$T_e$</th>
<th>$r_e$</th>
<th>$\omega_e$</th>
<th>$B_e$</th>
<th>$D_e$</th>
<th>$\alpha_e$</th>
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<tbody>
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<td>6-31G* CIS</td>
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<td>0.59</td>
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<td>12.7</td>
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<td>10.1</td>
<td>20.7</td>
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<td>15.4</td>
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<td>aug-cc-pVVDZ EOM-CCSD</td>
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<td>12.3</td>
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<td>6-31G* S-VWN/TDA</td>
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<td>3.2</td>
<td>10.3</td>
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<td>aug-cc-pVTZ BLYP</td>
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<td>5.9</td>
<td>6.3</td>
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<td>14.9</td>
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<td>6.3</td>
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<td>3.7</td>
<td>2.2</td>
<td>8.0</td>
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<td>4.2</td>
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<td>2.1</td>
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<td>4.4</td>
<td>11.1</td>
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</table>

\textsuperscript{a} Energies in hartrees, adiabatic excitation energies in eV, bond lengths in Å, and other quantities in cm$^{-1}$.
Core electrons are correlated. Experimental data are from Huber and Herzberg (31).

P.S. Bond length errors are in Å, not percentage errors.

References
