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Hanson-Heine, Magnus W.D. and George, Michael W. and Besley, Nicholas A. (2013) Calculating excited state properties using Kohn-Sham density functional theory. Journal of Chemical Physics, 138 (6). 064101/1-064101/8. ISSN 0021-9606

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Published in *J. Chem. Phys.*, **138**, 064101 (2013)
DOI: 10.1063/1.4789813

Calculating Excited State Properties Using Kohn-Sham Density Functional Theory

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The accuracy of excited states calculated with Kohn-Sham density functional theory using the maximum overlap method has been assessed for the calculation of adiabatic excitation energies, excited state structures, and excited state harmonic and anharmonic vibrational frequencies for open-shell singlet excited states. The computed Kohn-Sham adiabatic excitation energies are improved significantly by post self-consistent-field spin-purification, but remain too low compared with experiment with a larger error than time-dependent density functional theory. Excited state structures and vibrational frequencies are also improved by spin-purification. The structures show a comparable accuracy to time-dependent density functional theory, while the harmonic vibrational frequencies are found to be more accurate for the majority of vibrational modes. The computed harmonic vibrational frequencies are also further improved by perturbative anharmonic corrections, suggesting a good description of the potential energy surface. Overall, excited state Kohn-Sham density functional theory is shown to provide an efficient method for the calculation of excited state structures and vibrational frequencies in open-shell singlet systems, and provides a promising technique that can be applied to study large systems.

Introduction

Insight into the properties of electronic excited states and the reaction mechanisms that molecules undergo following photolysis is key to provide a full understanding of a wide number of processes involving the excited states of organic, transition metal and DNA/RNA related systems.[1] Theoretical calculations of molecular properties are well established, and the application of theoretical methods to describe the electronic ground state of molecules is often considered to be routine, although it can still be very demanding. The description of excited states presents a greater challenge due to problems such as the multiconfigurational nature of electronic excited states, the variety of different types of excited state, and the complexity that open shell systems with unpaired electrons can introduce.

Ideally it would be possible to treat excited states in a similar manner to the calculation of ground states. Excited states are commonly calculated using wavefunction based approaches such as complete active space self-consistent-field (CASSCF) coupled with multiconfigurational perturbation theory (CASPT2)[2] and multireference configuration interaction (MRCI)[3]. However, these wavefunction based approaches quickly become prohibitively expensive as the size of the system increases, particularly when optimizing a molecular structure within an excited state. Furthermore, the calculation of even more computationally demanding properties, such as accurate vibrational frequencies,[4-7] can also be of importance for the assignment of experimental vibrational spectra.[8, 9] This motivates the search for alternative, computationally less expensive methods, to explore potential energy surfaces within electronically excited states.

Kohn-Sham density functional theory (DFT) is computationally less expensive and can be applied to large systems. Within DFT, excited states are usually determined using time-dependent density functional theory (TDDFT), and analytical gradients and second derivatives have been reported.[10-20] Results for adiabatic excitation energies, excited state structures, and vibrational frequencies for low-lying excited states of small molecules have previously been found to be in good agreement with gas-phase experimental data when using TDDFT.[10, 12] However, it is also possible to study electronically excited states directly using Kohn-Sham DFT without the need for TDDFT. This can be achieved through applying some constraint, overlap criterion, intermediate optimization or energy penalty to prevent the variational collapse to the ground state within the SCF procedure.[21-26] One such approach, which is used in this work, is the maximum overlap method (MOM) that maintains the excited state within the Kohn-Sham calculation through an overlap analysis of the orbitals between iterations of the self-consistent field procedure.[24] Recently, a constricted variational DFT approach was introduced that overcomes problems associated with excited state Kohn-Sham DFT methods, such as cases of unavoidable variational collapse,[27, 28] and the relationship between excited state Kohn-Sham DFT and constrained (constricted) DFT has been described.[29] Van Voorhis and co-workers have explored the theoretical foundation for such approaches to computing excited states and have shown that the states obtained through solution of the Kohn-Sham equations for a non-Aufbau occupation of the molecular orbitals correspond to stationary densities of the interacting systems within the adiabatic approximation to TDDFT.[30, 31] There are several reasons why computing excited states using excited state Kohn-Sham DFT (also termed eDFT)[30] is an attractive alternative to TDDFT. TDDFT is known to be inaccurate for particular types of electronic excitation when using common approximate forms of the exchange-correlation functional. Charge transfer,[32, 33] Rydberg,[34, 35] and core excitations[36] are all treated poorly, and while the use of range corrected functionals can lead to much better agreement with experiment,[36, 37] within eDFT these types of transition require no special attention.[30] eDFT is also computationally less expensive than TDDFT. Although the cost of TDDFT and eDFT scale similarly with system size, the prefactor for TDDFT is 2-3 times larger.[19] Furthermore, unlike TDDFT, all of the functionality available for ground state DFT calculations, such as gradients, second-derivatives, and solvent modelling, are available for eDFT calculations in existing codes with little additional effort.

A wide variety of applications exploiting eDFT has been reported, ranging from core excited states to photoisomerization.[31, 38-46] For excited doublet and triplet states, directly applying eDFT can provide accurate excitation energies.[24, 43] However, computed excitation energies for some excited (open-shell) singlet states are found to be significantly underestimated.[24] This failure can be attributed to the description of an open-shell singlet state with a single determinant, and the Zeigler post self-consistent field (SCF) spin-purification formula[47] provides a simple correction for this deficiency

$$E = 2E_s - E_T \tag{1}$$

where E is the energy of the true singlet state, E_S is the energy of the spin mixed (single determinant) state and E_T is the energy of the corresponding triplet state. For some states, such as core excited states and Rydberg states[24, 42] where $E_S \approx E_T$ the correction will be small. However, for typical valence excited states $E_T < E_S$, resulting in an increase in the excitation energy.

While the accuracy of vertical excitation energies using eDFT has been studied, the reliability of eDFT to reproduce the shape of excited state potential energy surfaces has not. This is addressed in this paper, wherein we assess the accuracy of spin-mixed and spin-purified eDFT calculations for adiabatic excitation energies, excited state structures and vibrational frequencies compared to TDDFT for a set of small molecules where experimental gas-phase data are available. Furthermore, anharmonic frequencies provide a good indicator of potential energy surface quality,[4] and anharmonic frequencies based on second-order vibrational perturbation theory (VPT2)[48, 49] are also assessed.

Computational Details

Constructing an extensive data set that incorporates excited state structures and vibrational frequencies is hindered by the relative scarcity of experimental gas phase data for excited states compared to the ground state, and by the variety of molecular excited states. The test set of molecules used here has been selected from those used to examine TDDFT excited state properties by Furche et al,[10, 12] and includes only the lowest singlet excitations due to their importance in experimental photochemistry, and because they constitute a problematic case for eDFT calculations. For diatomic molecules, the data uses inferred harmonic frequencies for infinitesimal amplitudes of vibration, and anharmonically corrected bond lengths determined by Huber and Herzberg.[50]

Excited state energies, optimized structures and harmonic vibrational frequencies were determined using TDDFT, spin-mixed excited state DFT, which we denote eDFT^{SM}, and spin-purified excited state DFT, which we denote eDFT^{SP}, for the B3LYP,[51, 52] B97-1,[53] and EDF1[54] exchange-correlation functionals with the 6-311+G(d,p) basis set. The B3LYP, B97-1, and EDF1 exchange-correlation functionals were chosen for this comparison, as they are known reproduce ground state experimental frequencies well using scaled harmonic,[55, 56] anharmonic,[4, 57] and harmonic techniques,[4, 58] respectively. All calculations were performed within a locally modified version of the Q-Chem software package.[59] The excited state Kohn-Sham calculations were performed using unrestricted Kohn-Sham DFT with the maximum overlap method invoked to prevent the variational collapse to the ground state to give the spin-mixed excited state.[24] The molecular orbitals of the ground state were used as an initial guess for the excited state calculation, with a β-electron moved from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In the case of HCN the LUMO+1 was occupied. This gives the spin-mixed excited state, which we denote eDFT^{SM}. Subsequently, energies, analytic gradients and Hessian matrices modified according to equation (1) were calculated to give the spin-purified state. These were calculated by combining energies, gradients and Hessian matrices obtained from separated SCF calculations on the singlet and triplet states.

Adiabatic excitation energies are calculated as the difference between the ground and excited state energies for each method. Zero point energy (ZPE) corrections were made (where stated) by subtracting the difference in harmonic vibrational ZPE between the ground and excited state from the uncorrected excitation energies. Analytical derivatives were unavailable for TDDFT with the B97-1 and EDF1 functionals, and for the aug-cc-pVQZ basis set. In these cases, numerical second derivatives of the energy with respect to nuclear displacements where evaluated from finite differences of the energies with a step size of 0.00189 a_0. Anharmonic vibrational frequencies were determined using VPT2 and the transition-optimised shifted Hermite (TOSH) method.[49] Third and fourth order derivatives of the energy with respect to nuclear displacements were calculated using finite difference schemes using analytical energies, gradients and Hessians using the default step size of 0.1 a_0,[49] the resulting derivatives were used to compute a two-mode coupled quartic force field.[49] Even for small systems, this requires a large number of energy evaluations. Within the MOM framework, it remains possible that variational collapse to the ground state can occur, and this was found to be the case for the larger molecules studied here when evaluating the anharmonic frequencies. In order to ensure that the correct excited state energy is computed for all energy evaluations, if variational collapse is detected the energy evaluation is repeated with an alternative set of starting orbitals (the ground state orbitals for the minimum energy structure) or by converging a Hartree-Fock calculation for the excited state and using these orbitals as a starting point for the DFT calculation. Linear scaling of the computed harmonic frequencies was performed for comparison with anharmonic experimental data using values established for the 6-311+G(d,p) basis set. Following the work of Merrick et al,[56] B3LYP harmonic frequencies were scaled by 0.9688, B97-1 frequencies by 0.9684, and EDF1 frequencies by 0.9858, and we assume here that scaling factors derived for the ground state can be applied to excited states without further modification. Normal mode displacement diagrams have been generated using the Visual Molecular Dynamics software package.[60]

Results and Discussion

The main focus of this work is to explore the performance of the eDFT^{SM} and eDFT^{SP} methods for open-shell singlet excitation energies, excited state structures and vibrational frequencies. However, it is necessary to use an appropriate basis set that ensures sufficient convergence with respect to basis set size. For this reason, excitation energies, geometries, and frequencies were evaluated for a selection of common basis sets using the 1 ^{1}A" state of H_2CO as a test case, and the results are shown in Table 1. The results for the quadruple-ζ aug-cc-pVQZ basis set are sufficiently close to the basis set limit.[10] This basis set is too large to apply to moderately sized molecules and it is necessary to identify a smaller basis set that can adequately reproduce the results of the larger basis set at a lower computational cost. For the 1 ^{1}A" state of H_2CO, the 6-31G(d) basis set shows large errors compared to aug-cc-pVQZ and augmentation with diffuse functions on non-hydrogen atoms is necessary for an accurate description of both energies and bond lengths. We have chosen the 6-311+G(d,p) basis set, in order to provide reasonable accuracy at a practical cost. Compared to aug-cc-pVQZ, 6-311+G(d,p) has errors of less than 0.01 eV for adiabatic excitation energies, with energies differing by as little as 0.001 eV for eDFT^{SM}, 0.007 eV for eDFT^{SP}, and 0.026 eV for

TDDFT. Vibrational frequencies for the third harmonic mode, containing a significant amount of both carbon-oxygen and carbon-hydrogen motion, differs by 4 and 5 cm^{-1} from the aug-cc-pVQZ result for the $\mathrm{eDFT}^{\mathrm{SM}}$ and $\mathrm{eDFT}^{\mathrm{SP}}$ methods, and by less than 1 cm^{-1} for TDDFT. The bond length error is roughly 0.4 pm for the carbonyl bond and 0.3 pm for the carbon-hydrogen bonds for all three methods, and while bond lengths do show some improvement for the larger basis sets, this uncertainty is at a level comparable to that of experiment.

Excitation Energies

The calculation of accurate adiabatic excitation energies represents a greater challenge than for vertical excitation energies, since both a good description of the ground and excited state equilibrium geometries is required, in addition to the relative energy difference between them. Accurate ZPE corrections are further reliant on predicting the vibrational frequencies of both ground state and the excited state. Computed adiabatic excitation energies are shown in Table 2, in addition to the values from experiment. The excitation energies from TDDFT are closest to the experimental data and the mean absolute deviation (MAD) of the calculated values from experiment shows little variation between the different functionals used, with only a 0.04 eV difference in MAD, and a maximum difference between the two hybrid functionals of only 0.08 eV. The transitions studied here all involve excitation to low-lying valence states and are described well by standard hybrid and generalized gradient approximation functionals.[61]

By contrast, for both variants of eDFT, there is a much greater dependence on the functional used. This is quite surprising given that B97-1 and B3LYP both contain a similar fraction of

Hartree-Fock exchange. It is known that excitation energies for valence excited states, like the ones considered here, have a large error when described by a single determinant. As expected, the excitation energies for eDFT^{SM} are much too low compared with experiment with MAD values of 0.82 eV for B3LYP, 0.77 eV for B97-1, and 0.93 eV for EDF1, and showing errors in excess of 1 eV for BF, BH, CO, and SiF_2. Application of the post SCF spin-purification leads to a significant reduction in the error with MAD values of 0.53, 0.38, and 0.58 eV for B3LYP, B97-1, and EDF1, respectively. Closer observation of the data shows that even for B97-1, which shows the best agreement with experiment, there is a consistent underestimation for the majority of excitation energies. This suggests that better agreement with experiment should be possible with a small modification to the functional. However, it is interesting to note that some of the largest errors in the excitation energies occur for molecules with triple bonds. Such bonding can be described poorly by DFT and as such the source of the error for these excitation energies may lie with the ground state rather than the excited state.

Excited State Structures and Harmonic Frequencies

While excitation energies primarily examine the relative heights of the ground and excited state potential energy surfaces, the calculation of excited state structures and frequencies, depends on predicting the position of the energy minimum and the curvature of the potential energy surface at the minimum correctly. The predicted structures for the excited states are shown in Table 3. Previous work has shown that structures predicted from TDDFT are in good agreement with experiment.[10, 12] The results in Table 3 show that the structures for eDFT^{SM} and eDFT^{SP} are very close to the values from TDDFT. For the HCP bond angle and Li_2 bond length, there is a significant error in eDFT^{SM} that is partially corrected by spin-purification. In general, spin-purification leads to a small increase in the predicted bond lengths. There is some discrepancy with experiment for the dihedral angle (ϕ) in H_2CS. For this angle, eDFT^{SM} predicts a value that is closer to experiment than eDFT^{SP}. However, the value for eDFT^{SP} is consistent with the predictions of TDDFT raising some doubt over the experimental value. In contrast to excitation energies, the predicted structures are not strongly dependent on the choice of functional.

Unscaled harmonic frequencies are shown in Table 4. Calculated harmonic frequencies tend to overestimate their experimentally observed values for all three functionals, and indicate EDF1 to perform best due to systematic error cancellation. Frequencies calculated using the eDFT^{SM} and TDDFT methods are in poor agreement with experiment, and have MAD values around 70 cm^{-1} for B3LYP and B97-1, with the eDFT MAD falling to around 55 cm^{-1} on spin-purification. As expected, on scaling of the harmonic frequencies, shown in Table 5, the agreement with experiment is significantly improved. The scaled MAD decreases by ~10-20 cm^{-1} compared to the harmonic value, although this improvement is more modest for the EDF1 functional. The results show that scaled harmonic frequencies for eDFT^{SM} and eDFT^{SP} are closer to experiment than those from TDDFT. The results when incorporating spin-purification have the best agreement with experiment, with a MAD of 35 cm^{-1} and 36 cm^{-1} for B3LYP and B97-1, respectively.

Comparison between the calculated and experimental harmonic frequencies for the diatomic molecules, shown in Table 6, shows a similar trend to the scaled polyatomic frequencies, with eDFT^{SM} performing worst, followed by TDDFT, and with eDFT^{SP} providing the best direct match with experiment, albeit with significantly larger errors. It is likely that functionals designed to predict harmonic frequencies correctly would lead to an improvement in the values.[62] Overall comparison between experimental, harmonic and scaled frequencies indicate that the excited state methods have the following order of accuracy, $eDFT^{SP}$ > TDDFT > $eDFT^{SM}$, for calculating the vibrational frequencies of open-shell singlet states.

Excited State Normal Mode Analysis

Comparison of the harmonic normal modes of molecules containing four atoms (see Figures 1-3 in the Supplementary Material), shows that while the frequencies vary significantly, the normal mode displacement vectors calculated for the excited state vibrations of H_2CO, H_2CS and C_2H_2 using $eDFT^{SM}$ closely mirror the displacements calculated by TDDFT. The C-O stretching ν_3 mode for the excited state of H_2CO is one notable exception, and is poorly treated by both methods. Here, the difference between the eDFT and TDDFT hydrogen atom displacement leads to reordering between the ν_3 and ν_4 modes using TDDFT compared with the eDFT order. While there is no assignment for the experimental atomic displacements in the excited state, the eDFT frequencies for the ν_3 mode are in good agreement with the experimental mode at 1183 cm^{-1}, with an error of less than 35 cm^{-1} for $eDFT^{SM}$ compared to over 100 cm^{-1} for TDDFT. Reordering of the ν_3 and ν_4 modes for TDDFT modes leads to a 58 cm^{-1} reduction (from 66 to 8 cm^{-1}) in the error between the TDDFT result and experimental mode at 1293 cm^{-1}, with a corresponding increase in error for the 1183 cm^{-1} experimental mode, moving from 118 to 176 cm^{-1}. The corrected ordering of these two TDDFT modes has been used in Tables 1, 4 and 5. Despite resulting in significantly improved harmonic and scaled harmonic frequencies, the normal modes calculated using the $eDFT^{SP}$ method tend to involve the same atoms and displacement magnitudes as modes calculated using TDDFT and $eDFT^{SM}$, but with rotated directions.

Anharmonic Vibrational Frequencies

Anharmonic frequencies evaluated using either the VPT2 or TOSH methods together with eDFT are shown in Table 7. For the majority of the vibrational modes, the computed frequencies lie close to their experimental values, suggesting that eDFT still provides a good description of the anharmonic potential energy surface around the equilibrium geometry. This is true for both the spin-mixed and spin-purified frequencies, and indicates that the eDFT^{SP} formula in equation (1) remains accurate for greater sampling of potential energy surface despite providing a different description for some of the normal modes. These calculations show small deviations from experiment of below 30 cm^{-1} for most vibrational modes, which is reflected by a median absolute error of 23 cm^{-1}. There is a closer agreement with experiment for the spin-purified compared to the spin-mixed values, with MADs for the TOSH method of 41 and 36 cm^{-1}, respectively. Improvements are also seen even in cases where the harmonic surface is poorly treated within eDFT, such as with the excited states of SiF_2 and HCP, and the lower frequency mode of HCP is found to improve by ~100 cm^{-1}. The asymmetric C-H stretching mode of the H_2CO excited state is also poorly treated. Overall, the results indicate that eDFT can provide an accurate description of both anharmonic as well as the harmonic frequencies, with the possibility of providing accuracy across a wider region of the potential energy surface.

Conclusions

In this paper the calculation of excited state properties for open-shell singlet states within excited state DFT has been investigated. Application of the spin-purification formula (eqn. (1)) leads to improved results for adiabatic excitation energies, excited state structures and vibrational frequencies compared to the spin mixed state. Spin-purification has the greatest effect on the excitation energies, which are much closer to experiment but remain consistently too low and less accurate than TDDFT. The computed excitation energies also show a greater sensitivity to the choice of exchange-correlation functional than TDDFT. The predicted structures from eDFT are of a similar accuracy to TDDFT, and spin-purification does correct the few significantly larger errors found with eDFT^{SM}. For calculated scaled and harmonic frequencies, the values from eDFT^{SP} are found to be closer to experiment than for TDDFT, although spin-purification can lead to different normal modes. Anharmonic eDFT frequencies provide accurate vibrational frequencies for the majority modes for both eDFT^{SM} and eDFT^{SP}. Consequently, eDFT represents a computationally inexpensive approach that provides an alternative to TDDFT that can be applied to study the properties and dynamics of electronically excited states of large molecules.

Acknowledgements

We would like to thank the University of Nottingham for funding. MWG gratefully acknowledges receipt of a Royal Society Wolfson Merit award.

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Table 1. Basis set dependence for some properties of the 1 ^{1}A" state of H_2CO, calculated using B3LYP at the TDDFT, eDFT^{SM}, and eDFT^{SP} levels of theory. Adiabatic excitation energies (ΔE) are given in eV, bond lengths are in pm, and vibrational frequencies for the third harmonic mode (ν_3) are in cm^{-1}.

Basis	ΔE	C-O	C-H	ν_3
TDDFT				
6-31G(d)	3.713	130.47	109.80	1392
6-311G(d)	3.716	129.70	109.74	1375
6-311G(d,p)	3.692	129.77	109.62	1369
6-311+G(d,p)	**3.672**	**129.45**	**109.58**	**1359**
6-311+G(2d,2p)	3.676	129.38	109.30	1357
6-311+G(2df,2p)	3.696	129.17	109.34	1363
aug-cc-pVTZ	3.688	129.22	109.36	1359
aug-cc-pVQZ	3.698	129.04	109.32	1360
eDFT^{SM}				
6-31G(d)	3.117	131.98	110.05	1269
6-311G(d)	3.126	131.16	110.00	1263
6-311G(d,p)	3.106	131.20	109.91	1258
6-311+G(d,p)	**3.099**	**130.96**	**109.87**	**1250**
6-311+G(2d,2p)	3.097	130.85	109.59	1248
6-311+G(2df,2p)	3.100	130.67	109.61	1255
aug-cc-pVTZ	3.090	130.76	109.61	1251
aug-cc-pVQZ	3.098	130.56	109.58	1254
eDFT^{SP}				
6-31G(d)	3.277	132.64	109.90	1236
6-311G(d)	3.292	131.82	109.82	1228
6-311G(d,p)	3.273	131.89	109.74	1224
6-311+G(d,p)	**3.259**	**131.61**	**109.71**	**1217**
6-311+G(2d,2p)	3.256	131.51	109.42	1215
6-311+G(2df,2p)	3.256	131.31	109.45	1223
aug-cc-pVTZ	3.245	131.39	109.45	1219
aug-cc-pVQZ	3.252	131.19	109.42	1222

Table 2. Calculated ZPE corrected adiabatic excitation energies compared with experiment (in eV).

Molecule	State		B3LYP			B97-1			EDF1		
		Exp.	TDDFT	eDFT^{SM}	eDFT^{SP}	TDDFT	eDFT^{SM}	eDFT^{SP}	TDDFT	eDFT^{SM}	eDFT^{SP}
BeO	1 $^1\Pi$	1.17	1.26	0.89	0.92	1.34	1.01	1.03	1.17	1.17	1.20
BF	1 $^1\Pi$	6.34	6.08	4.31	5.26	6.12	4.54	5.53	6.07	4.15	4.97
BH	1 $^1\Pi$	2.87	2.70	1.68	2.22	2.73	1.87	2.46	2.80	1.60	2.07
C_2H_2	1 ^1A_u	5.23	4.70	4.38	4.61	4.66	4.41	4.67	4.78	4.41	4.66
CCl_2	1 $^1B_1$	2.14	1.99	1.30	1.81	2.03	1.40	1.96	2.10	1.39	1.88
t-$(CHO)_2$	1 ^1A_u	2.72	2.41	2.12	2.31	2.42	2.16	2.37	2.05	1.75	1.95
CO	1 $^1\Pi$	8.07	7.95	6.60	7.37	7.98	6.72	7.54	7.85	6.39	7.11
H_2CO	1 $^1A''$	3.49	3.58	3.01	3.17	3.60	3.08	3.26	3.48	3.07	3.28
H_2CS	1 $^1A_2$	2.03	2.06	1.67	1.75	2.07	1.73	1.82	2.00	1.76	1.87
HCN	1 $^1A''$	6.48	6.00	5.63	5.90	5.97	5.69	5.99	6.12	5.72	6.03
HCP	1 $^1A''$	4.31	3.91	4.02	3.88	3.93	4.08	3.99	4.05	3.86	3.99
Li_2	1 $^1\Sigma_u^+$	1.74	1.92	1.74	1.21	1.92	1.32	1.70	1.86	0.93	0.94
N_2	1 $^1\Sigma_u^-$	8.45	7.77	7.58	7.89	7.74	7.65	7.98	8.03	7.33	7.87
SiF_2	1 $^1B_1$	5.34	5.30	3.95	4.71	5.28	3.99	4.75	5.15	3.78	4.45
MAD			0.25	0.82	0.53	0.26	0.77	0.38	0.22	0.93	0.58

Table 3. Calculated excited state structural parameters compared with experiment. Bond lengths are in pm, and angles are in degrees. Experimental diatomic bond lengths are corrected for anharmonicity.

Molecule	State			B3LYP			B97-1			EDF1		
			Exp.	TDDFT	eDFT^{SM}	eDFT^{SP}	TDDFT	eDFT^{SM}	eDFT^{SP}	TDDFT	eDFT^{SM}	eDFT^{SP}
BeO	$1\ ^1\Pi$	Be-O	146	143	147	147	144	147	147	145	148	148
BF	$1\ ^1\Pi$	B-F	130	131	132	132	131	132	132	131	133	133
BH	$1\ ^1\Pi$	B-H	122	121	120	121	122	121	122	123	121	122
C_2H_2	$1\ ^1A_u$	C-C	139	137	137	137	137	138	138	138	138	138
		∠(HCC)	120	122	122	122	122	121	122	121	121	121
CCl_2	$1\ ^1B_1$	C-Cl	165	166	169	168	166	169	169	165	169	168
		∠(ClCCl)	131	138	129	130	137	129	130	136	129	130
t-$(CHO)_2$	$1\ ^1A_u$	C-H	112	110	110	110	110	110	110	111	110	110
		C-O	125	123	123	123	123	123	123	124	124	124
		C-C	146	148	148	149	149	149	149	147	148	148
		∠(HCC)	114	114	114	114	113	114	113	114	114	114
		∠(OCC)	124	125	124	125	125	124	125	126	125	125
CO	$1\ ^1\Pi$	C-O	124	123	121	122	123	121	122	124	122	122
H_2CO	$1\ ^1A''$	C-H	110	110	110	110	110	110	110	110	111	111
		C-O	132	129	131	132	129	131	131	131	130	131
		∠(HCH)	118	117	116	117	117	115	116	116	112	114
		ϕ	34	44	43	38	36	44	40	39	47	42
H_2CS	$1\ ^1A_2$	C-H	108	108	108	108	109	109	109	109	109	109
		C-S	168	169	170	171	169	171	172	170	170	171
		∠(HCH)	121	120	120	120	120	120	120	120	120	120
		ϕ	12	0	1	0	4	10	1	4	6	0
HCN	$1\ ^1A''$	C-H	114	112	112	113	113	112	113	114	113	114
		N-C	130	130	131	130	130	131	130	130	131	131
		∠(HCN)	125	123	121	122	122	121	122	123	121	122
HCP	$1\ ^1A''$	P-C	169	170	168	171	170	168	171	171	169	172
		∠(HCP)	128	130	119	128	130	118	128	128	121	127
Li_2	$1\ ^1\Sigma_u^+$	Li-Li	311	303	269	304	305	340	318	302	326	308
N_2	$1\ ^1\Sigma_u^-$	N-N	128	128	128	128	128	128	128	129	121	122
SiO	$1\ ^1\Pi$	Si-O	162	162	161	164	162	161	164	163	161	162
SiF_2	$1\ ^1B_1$	Si-F	160	166	164	165	165	164	164	168	165	166
		∠(FSiF)	116	113	115	114	114	115	115	114	115	115
MAD (pm)				2	4	2	2	3	2	2	3	2

Table 4. Calculated excited state polyatomic harmonic frequencies compared with experiment (in cm^{-1}).

Molecule	State		B3LYP			B97-1			EDF1		
		Exp.	TDDFT	$eDFT^{SM}$	$eDFT^{SP}$	TDDFT	$eDFT^{SM}$	$eDFT^{SP}$	TDDFT	$eDFT^{SM}$	$eDFT^{SP}$
C_2H_2	$1\ ^1A_u$	1365	1435	1421	1421	1423	1407	1407	1406	1389	1393
		1048	1094	1105	1102	1098	1109	1107	1088	1092	1090
CCl_2	$1\ ^1B_1$	634	595	628	607	591	634	611	589	622	605
		303	192	301	302	191	299	299	251	300	301
t-$(CHO)_2$	$1\ ^1A_u$	2809	2970	3008	2978	2964	3006	2976	2917	2963	2930
		1391	1570	1554	1563	1588	1575	1587	1526	1521	1533
		1281	1526	1424	1403	1543	1453	1440	1499	1498	1506
		1195	1239	1242	1237	1230	1236	1230	1225	1225	1221
		1172	1197	1225	1211	1190	1219	1207	1122	1205	1198
		952	970	973	964	966	972	963	974	974	963
		735	778	770	764	775	765	752	760	752	742
		720	777	756	759	768	743	750	760	730	733
		509	519	516	517	516	513	515	514	510	512
		379	386	400	392	385	399	391	346	397	394
		233	251	242	239	251	241	238	249	238	235
H_2CO	$1\ ^1A''$	2968	3090	3050	3071	3078	3035	3055	3044	2913	2943
		2846	2992	2956	2975	2978	2940	2958	2940	2846	2873
		1293	1301	1302	1313	1297	1296	1308	1266	1288	1258
		1183	1359	1250	1217	1377	1271	1234	1295	1223	1229
		904	891	893	914	887	892	916	870	840	856
H_2CS	$1\ ^1A_2$	3081	3242	3230	3219	3231	3219	3213	3215	3180	3170
		3034	3129	3114	3103	3115	3102	3094	3097	3070	3059
		1316	1372	1351	1355	1366	1345	1349	1338	1307	1313
		820	893	830	815	889	824	807	853	839	819
		799	801	784	796	796	779	791	783	755	770
HCN	$1\ ^1A''$	1496	1532	1511	1529	1532	1510	1531	1491	1468	1487
		941	988	987	994	981	986	995	978	974	980
HCP	$1\ ^1A''$	951	951	1024	952	963	1027	962	927	1010	913
		567	696	785	763	685	788	761	717	794	758
SiF_2	$1\ ^1B_1$	598	675	748	722	676	745	718	602	721	695
		342	238	247	244	238	245	241	219	239	237
MAD			71	73	56	71	67	55	57	66	54

Table 5. Calculated excited state polyatomic scaled harmonic frequencies compared with experiment (in cm^{-1})

Molecule	State		B3LYP			B97-1			EDF1		
		Exp.	TDDFT	eDFT^{SM}	eDFT^{SP}	TDDFT	eDFT^{SM}	eDFT^{SP}	TDDFT	eDFT^{SM}	eDFT^{SP}
C_2H_2	$1\ ^1A_u$	1365	1391	1377	1377	1378	1363	1362	1386	1369	1373
		1048	1060	1070	1068	1064	1074	1072	1073	1077	1075
CCl_2	$1\ ^1B_1$	634	576	609	588	572	614	592	581	614	596
		303	186	292	292	185	289	290	247	295	296
t-$(CHO)_2$	$1\ ^1A_u$	2809	2878	2914	2885	2870	2911	2882	2875	2921	2889
		1391	1521	1506	1515	1538	1525	1536	1504	1500	1511
		1281	1478	1380	1359	1494	1408	1394	1477	1477	1485
		1195	1200	1203	1199	1191	1197	1191	1208	1207	1203
		1172	1160	1186	1174	1152	1181	1169	1106	1188	1181
		952	940	943	934	936	941	933	961	960	949
		735	754	746	741	751	741	728	749	741	732
		720	752	733	735	743	719	727	749	720	723
		509	503	499	501	500	497	499	506	503	504
		379	374	387	379	373	386	379	341	392	388
		233	243	235	232	243	234	230	245	234	232
H_2CO	$1\ ^1A''$	2968	2993	2955	2975	2980	2939	2958	3001	2872	2901
		2846	2898	2864	2882	2884	2847	2864	2898	2806	2833
		1293	1260	1261	1272	1256	1255	1267	1248	1269	1240
		1183	1317	1211	1179	1334	1231	1195	1277	1206	1212
		904	863	865	886	859	864	887	858	828	844
H_2CS	$1\ ^1A_2$	3081	3141	3129	3119	3129	3117	3111	3170	3135	3125
		3034	3031	3017	3006	3017	3004	2996	3053	3026	3015
		1316	1329	1309	1313	1323	1303	1307	1319	1289	1295
		820	865	804	789	861	798	782	841	827	807
		799	776	759	771	771	754	766	771	744	759
HCN	$1\ ^1A''$	1496	1485	1464	1481	1483	1462	1483	1470	1447	1465
		941	957	956	963	950	955	963	964	960	966
HCP	$1\ ^1A''$	951	921	992	922	932	995	932	914	996	900
		567	675	761	740	663	763	737	707	782	748
SiF_2	$1\ ^1B_1$	598	654	725	699	655	721	696	593	711	685
		342	230	239	236	230	237	234	216	236	234
MAD			47	40	35	47	42	36	48	48	44

Table 6. Calculated excited state diatomic harmonic frequencies compared with harmonic experimental frequencies (in cm^{-1}).

System	State		B3LYP			B97-1			EDF1		
		Exp.	TDDFT	$eDFT^{SM}$	$eDFT^{SP}$	TDDFT	$eDFT^{SM}$	$eDFT^{SP}$	TDDFT	$eDFT^{SM}$	$eDFT^{SP}$
BeO	$1\ ^1\Pi$	1144	1227	1105	1113	1222	1100	1110	1182	1069	1080
BF	$1\ ^1\Pi$	1265	1229	1262	1253	1220	1249	1229	1185	1227	1217
BH	$1\ ^1\Pi$	2251	2129	2503	2398	2351	2468	2341	2213	2468	2379
CO	$1\ ^1\Pi$	1518	1534	1691	1589	1543	1693	1591	1505	1678	1622
Li_2	$1\ ^1\Sigma_u^+$	255	260	351	265	436	169	224	227	204	255
N_2	$1\ ^1\Sigma_u^-$	1530	1554	1330	1563	1544	1562	1547	1491	1771	1747
SiO	$1\ ^1B_1$	853	1024	892	820	802	899	807	1011	936	877
MAD			65	115	48	71	88	47	56	124	84

Table 7. Calculated excited state B3LYP polyatomic TOSH and VPT2 frequencies compared with experiment (in cm^{-1}).

			TOSH		VPT2	
System	State	Exp.	eDFT^{SM}	eDFT^{SP}	eDFT^{SM}	eDFT^{SP}
C_2H_2	1 ^1A_u	1365	1390	1388	1390	1388
		1048	1084	1082	1081	1078
CCl_2	1 $^1B_1$	634	629	605	623	601
		303	298	299	297	298
t-$(CHO)_2$	1 ^1A_u	2809	2831	2798	2811	2798
		1391	1529	1544	1532	1544
		1281	1405	1380	1405	1380
		1195	1212	1205	1210	1205
		1172	1190	1173	1190	1173
		952	931	924	929	924
		735	769	764	769	764
		720	754	756	754	756
		509	511	513	512	513
		379	393	385	393	385
		233	246	261	246	261
H_2CO	1 $^1A''$	2968	2833	2862	2833	2862
		2846	2821	2847	2792	2823
		1293	1269	1283	1264	1289
		1183	1234	1198	1221	1166
		904	882	896	882	896
H_2CS	1 $^1A''$	3081	3052	3048	3052	3048
		3034	3006	3000	2977	2973
		1316	1335	1338	1330	1335
		820	823	807	823	807
		799	777	789	777	789
HCN	1 $^1A''$	1496	1483	1501	1482	1500
		941	954	959	954	959
HCP	1 $^1A''$	951	928	926	928	926
		567	675	664	675	664
SiF_2	1 $^1B_1$	598	739	713	736	709
		342	244	240	243	240
MAD			41	36	42	37