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A Comparison of the Electronic Transition Energies for Ethene, Isobutene, Formaldehyde, and Acetone Calculated Using RPA, TDDFT, and EOM-CCSD. Effect of Basis Sets

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The effect of basis sets on the calculated transition energies for ethene, formaldehyde, acetone, and isobutene has been studied at the RPA, TDDFT, and EOM-CCSD theoretical levels. Polarization functions beyond the (d,p) level have little effect on the calculated energies. However, diffuse functions have a major effect on the calculated energies. Using 6-311(2+,2+)G(d,p) which has two sets of diffuse functions, EOM-CCSD gave very good agreement with the available experimental data in most cases. Another set of diffuse functions led to lower transition energies in a few cases. The RPA calculations for ethene are in fairly good agreement with the first 10 experimental transition energies, and TDDFT is less satisfactory. On the other hand, for formaldehyde and acetone, TDDFT gives fairly good agreement with experiment for the first states, and RPA is quite unsatisfactory. The use of global diffuse functions instead of additional atom-centered diffuse functions was examined. They proved to be quite satisfactory for the compounds in this investigation and serve to reduce the time required for the calculations.

1. Introduction

An understanding of electronically excited states is important in a variety of photochemical and photophysical processes. With most molecules, only a limited amount of information is available from experimental studies, and they must be supplemented by computational studies. It is important to determine what level of theory and basis set is needed, and this will be the subject of this report.

Theoretical approaches to treating excited states can be divided into single and multireference methods. In many ways, these approaches are complementary. Single reference approaches are straightforward to apply and their quality is easy to assess; however, the use of a single reference can result in an unbalanced treatment of the ground and exited states. Normally, quantitative results are limited to states that can be described as a single excitation from the ground state. Multireference methods are capable of describing each state with equal quality and methods such as CASPT2[1] and MRD-CI[2] that have had considerable success. Excited states that are double excitations from the ground state, conical intersections, and regions of the potential energy surface involving bond formation/breaking are best treated by multireference methods. The drawback of the multireference approaches is that they can be ambiguous to apply and therefore their quality is difficult to assess.

In this study, we examine the excited state analogues of three very common and widely used single reference ground-state methods: Hartree−Fock, density functional, and coupled-cluster theories. A single reference method is completely defined given the level of theory and the basis set. For excitation energies, the level of theory should be chosen to provide a balanced treatment of both the ground and excited state including an adequate description of electron correlation for both. Determining which excited state method to apply can seem daunting, although many of the theoretical formalisms are equivalent or closely related for excitation energies. In fact, a hierarchy of methods for excited states has been proposed analogous to that available for ground states.[3]

To provide an overview of the methods we employ, it is useful to review the simplest excited-state method beyond Koopman's theorem, Configuration Interaction Singles (CIS)[4] also known as the Tamm−Dancoff approximation (TDA). In this approach, the excited state is a linear combination of singly excited determinants formed by replacing an occupied spin−orbital with a virtual spin−orbital in the Hartree−Fock reference determinant. Despite the name, CIS does not include any electron correlation because single excitations do not mix with the Hartree−Fock reference. CIS has been described as an adequate zeroth-order treatment[4] performing qualitatively much like Hartree−Fock Theory for ground states. The quantitative performance is poor with CIS frequently yielding errors of 1 eV or more.[5]

One way of improving CIS is to consider it as the zeroth-order wave function in a perturbative approach. This gives rise to an approximation known as CIS(D).[6] Another is to include selected doubly excited determinants to CIS, which gives rise to the familiar Random Phase Approximation (RPA)[7] also known as Time-Dependent Hartree−Fock (TDHF). Thus, CIS and RPA share the same treatment of the ground state and differ only in the description of the excited state. This improved description generally results in better quantitative agreement compared with CIS, but RPA can also suffer from numerical instabilities resulting in complex excitation energies. Both CIS and RPA can only describe systems for which the ground and excited states are well represented by a single determinant.[8]

Recently, the RPA approach has been extended to density functional theory. Time-dependent density-functional theory (TDDFT)[9,10] within the adiabatic approximation employs the

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TABLE 1: Ethene Transition Energies Calculated Using EOM-CCSD

sym.	basis set 1	2	3	4	5	6	7	obs
$1B_{3u}$	10.73	11.57	10.80	7.30	7.35	7.39	7.30	7.11
$1B_{1u}$	8.60	8.39	8.26	8.00	8.15	8.05	8.13	7.65
$1B_{1g}$	8.85	8.74	8.62	7.98	8.05	8.10	7.94	7.80
$1B_{2g}$	10.19	9.66	9.50	8.01	8.08	8.13	7.98	8.01
$2A_g$	14.58	11.94	11.92	8.78	9.11	9.16	8.33	8.28
$2B_{1g}$	11.86	10.57	10.31	8.57	8.71	8.61	8.69	
$2B_{3u}$	13.95	11.89	11.52	9.07	9.52	9.50	8.85	8.62
$1A_u$	11.77	11.67	11.57	9.20	9.29	9.34	9.00	
$2B_{1u}$	14.77	13.32	13.07	10.34	10.54	10.57	9.42	9.33
$2B_{2g}$	10.77	10.20	10.10	10.02	10.14	10.07	9.44	
$1B_{3g}$	13.42	13.91	13.22	9.67	9.78	9.79	9.86	9.51
$2A_u$	15.12	12.39	12.20	11.16	11.53	11.50	9.95	
$1B_{2u}$	13.19	12.13	11.91	9.97	10.50	10.52	10.38	
$3A_g$	15.21	15.33	15.02	11.60	11.83	11.87	10.59	
$2B_{3g}$	15.90	14.46	13.86	11.43	11.90	11.86	11.27	
$2B_{2u}$	15.98	14.89	14.59	10.38	12.32	12.35	11.90	
time (sec)	181	379	1238	1185	646	1961	1224	
E (−78.)	.38471	.41157	.43567	.39032	.41692	.43761	.41707	

exchange-correlation functionals of time-independent DFT. This approach appears to work well for low-lying valence excitations. The advantage of TDDFT over RPA is the inclusion of additional electron correlation effects though the exchange-correlation potential for both the ground and excited states. At this point of development, hybrid density functionals seem to provide the best results.[11] In theory, TDDFT is expected to significantly improve quantitative results over CIS and RPA. Whereas TDDFT gives more satisfactory transition energies for carbonyl compound than does RPA,[12] the opposite is true for small alkenes.[13] This variation is most likely attributable to the choice of functional employed as the exact functional is unknown.

CIS, RPA, and TDDFT are very cost-effective and applicable to very large systems via modern direct methods.[4,14,15] Yet, our investigations demonstrate the need to go beyond these approximations to obtain more uniform accuracy for a variety of molecules. Coupled-cluster (CC) theory has been proven to be highly accurate for ground states, and there is increasing evidence that similar accuracy can be expected for its application to excited states. This is achieved by the equation of motion formalism[16] which gives rise to the equation of motion coupled-cluster (EOM-CC)[17] approach (EOM-CC may also be expressed in the linear response formalism (LR−CC);[18] likewise, symmetry adapted cluster configuration interaction (SAC−CI)[19] may be though of as an approximate EOM-CC method).

EOM-CC is exact in theory but in practice is limited to some level of approximation, and several intriguing methods have been developed on the basis of the EOM formalism.[20] An analogue of the CCSD approximation for the ground state which truncates the wave operators to singly and doubly substituted determinants is known as the EOM-CCSD approximation. The choice of wave operator is nonlinear giving rise to the inclusion of certain types of higher order excitations.[20c] Because both the ground and excited states are fairly well balanced and include a high degree of electron correlation, there is typically good agreement with full CI and a dramatic improvement over singles and double CI (CISD).[8] EOM-CCSD excitation energies for excited states that can be characterized as single excitations from the ground states are reported to be accurate to within 0.2−0.3 eV.[3,21] While considerably more computationally intensive than the other methods we have described, this level of truncation provides a method that is uniformly accurate. The asymptotic scaling for EOM-CCSD is the same as for CCSD for ground states meaning that EOM-CCSD excited states are practical for any system where CCSD can be used to study the ground state.

To gain more information about the applicability of these theoretical methods, we have examined some small representative organic molecules. Ethene and isobutene have a few valence transitions (mainly $\pi \rightarrow \pi^*$) along with many Rydberg transitions, some of which have lower energies than the valence transitions.[22] Formaldehyde and acetone provide examples of carbonyl compounds that have $n \rightarrow \pi^*$ transitions along with many Rydberg transitions. These compounds were chosen since the transition energies have been examined experimentally. In addition, they have symmetry and experimental band assignments so that a clear comparison between experiment and theory may be made. In most of the calculations of the vertical transition energies, the MP2/6-311+G** optimized geometries for the ground states were used. The EOM-CCSD calculations, except for columns 1−6 in Table 1, made use of the geometries optimized at the corresponding theoretical level.

The basis set used for the calculations plays an important role in determining how well the calculations reproduce the experimental data. Since most of the states are Rydberg in nature, diffuse functions are needed to properly describe them. Thus, a series of basis sets of increasing size were examined. As will be shown, additional polarization functions have little effect on the calculated energies, and special attention will be directed toward the diffuse functions.

The basis sets used in this study are

1. DZP
2. TZP
3. TZ2p
4. PBS
5. 6-311++G**
6. 6-311++G(2d,2p)
7. 6-311(2+,2+)G**
8. 6-311(3+,3+)G**

DZP is a Dunning−Huzenaga double-ζ basis set with polarization functions, TZP is the corresponding triple-ζ basis set, and TZ2p includes a second set of polarization functions.[23] PBS is a Sadlej basis set that is designed for calculation of excited states.[24] Basis sets 5 and 6 are standard Pople basis sets that include diffuse functions on all atoms. Basis set 6 includes a second set of polarization functions. Basis set 7 is similar to 5 but contains a second set of diffuse functions on all atoms. We have found this basis set to be particularly useful in

TABLE 2: Calculated and Observed Transition Energies for Ethene

	RPA			TDDF T			EOM- CCSD				
sym.	5	4	7	5	4	7	5	4	7	8	obs
$1B_{3u}$	7.19	7.12	7.11	7.16	7.01	7.05	7.35	7.30	7.30	7.29	7.11[a]
$1B_{1u}$	7.41	7.34	7.40	7.57	7.50	7.50	8.15	8.00	8.13	8.12	7.65[b]
$1B_{1g}$	7.82	7.74	7.70	7.77	7.67	7.59	8.05	7.98	7.94	7.94	7.80[c]
$1B_{2g}$	8.00	7.87	7.85	7.78	7.56	7.58	8.08	8.01	7.98	7.97	7.90[d]
$2A_g$	8.89	8.57	8.07	8.98	8.58	7.93	9.11	8.78	8.33	8.32	8.28[e]
$2B_{1g}$	9.22	9.16	9.08	8.05	8.01	8.03	8.71	8.57	8.69	8.70	
$2B_{3u}$	9.37	8.67	8.63	9.28	8.13	8.29	9.52	9.07	8.85	8.81	8.62[f]
$3B_{3u}$	10.19	9.18	8.93	10.04	8.94	8.44	10.41	9.59	9.20	9.07	8.90[g]
$1A_u$	9.11	9.00	8.77	8.55	8.78	8.31	9.29	9.20	9.00	8.99	
$4B_{3u}$	11.48	9.65	9.11	11.05	9.48	8.89	11.46	10.34	9.28	9.17	9.08[h]
$3B_{1g}$	11.07	10.33	9.08	10.84	10.01	8.54	11.34	10.60	9.40	9.29	9.2[i]
$2B_{1u}$	10.79	10.24	9.05	10.78	9.88	8.41	10.54	10.34	9.42	9.28	9.33[j]
$2B_{2g}$	10.20	9.08	9.18	9.59	8.28	8.54	10.14	10.02	9.44	9.31	
$1B_{3g}$	10.54	10.52	10.49	9.37	9.19	9.20	9.78	9.67	9.86	9.73	
$2A_u$	12.13	11.61	10.26	11.03	10.70	9.02	11.53	11.16	9.95	9.67	
$3B_{2g}$	10.96	10.07	10.17	10.73	9.45	9.58	11.10	10.50	9.86	9.82	
$4B_{1g}$	11.29	11.00	10.05	11.13	10.86	9.65	11.53	11.19	10.31	9.80	
$4B_{2g}$	11.64	10.67	10.41	11.27	10.42	9.87	11.76	10.76	10.19	10.13	
$5B_{3u}$			10.46		11.24	10.51	13.28	12.68	10.78	9.63	9.51[k]

[a] 7.11 eV: ref 27b, e, f, g. [b] Reference 27g. [c] 7.78 eV: ref 27f. 7.80 eV: ref 27a, b, d, g. 7.83 eV: ref 27g. [d] Reference 27a, g. [e] 8.15 eV: ref 27f. 8.28 eV: ref 27a, b. 8.26 eV: ref 27g. 8.29 eV: ref 22. [f] 8.60 eV: ref 27f. 8.62 eV: ref 27c, e, g. 8.56 eV: ref 27h. [g] Reference 27c, f, g.[h] 9.10 eV: ref 27b. 9.08 eV: ref 27h. [i] Reference 12. [j] Reference 27b, i. [k] 9.51 eV: ref 27e.

calculations of transition energies.[25] Finally, basis set 8 has a third set of diffuse functions and was used to see if any further improvement in the calculated transition energies could be achieved.

This study is concerned not only with the lower energy excited states but also with the higher energy Rydberg states. These states may be important in photophysical processes in the upper atmosphere. In addition, satisfactory calculations for these states imply that the excited configurations are well described. This is important in the study of a number of other properties such as the optical rotation of chiral molecules.[26]

2. Ethylene

Ethylene is probably the most extensively studied organic molecule, both experimentally[27] and theoretically. The large amount of data for the experimental transition energies makes it the ideal test molecule for theoretical calculations. Calculations have been reported at the CIS,[4] RPA,[28] TDDFT,[11] SD-CI,[29] MRD-CI,[30] MCSCF,[31] QDVPT,[32] SAC−CI,[33] CASPT2,[34] and EOM-CCSD[35] theoretical levels, but the basis set dependence was not fully explored.

Table 1 summarizes the result of EOM-CCSD calculations for the first two transition energies of ethylene for each symmetry group, using basis sets 1−7. The transition energies obtained using basis sets 1−3 are generally much too large. There is little difference in the values calculated using sets 2 and 3 indicating that additional polarization functions are not very helpful. The basis sets that include diffuse functions, 4−7, all give significantly lower transition energies that are in better accord with experimental data. Basis sets 5 and 6 give essentially the same values, again indicating that additional polarization function are not needed. These calculations indicate that a further examination of transition energies need only use basis sets 4, 5, and 7, and possibly 8. For the transitions in Table 1, basis sets 7 and 8 give the same transition energies.

The transition energies for ethene calculated using these basis sets and RPA, TDDFT, and EOM-CCSD are summarized in Table 2 along with the experimental transition energies. We previously found that the B3P86 density functional was more satisfactory than B3LYP in TDDFT calculations for carbonyl compounds,[12] and the same is true for ethylene. Therefore, only the B3P86 TDDFT transition energies are given in the table.

The first 10 experimental values are well estimated using RPA and basis set 7, but the next transition energies are too large in comparison with experiments or the EOM-CCSD energies. The TDDFT calculated transition energies are less satisfactory and are generally too small.

The EOM-CCSD transition energies are in good accord with the experimental values. In many cases, the values calculated using basis sets 7 and 8 are essentially the same, but in some cases, there is a significant difference, and basis set 8 is in better accord with the experimental data. This is especially true with $5B_{3u}$ where the calculated transition energy drops by 1.1 eV on going from basis set 7 to 8, and the latter is in good agreement with the experimental value.

3. Formaldehyde

The excited states of formaldehyde have also been the subject of many experimental[36] and theoretical studies.[37,38] CIS,[5] RPA,[6] TDDFT,[12] and EOM-CCSD[6,38t] studies have been reported, as well as CASPT2[39] and MRD-CI[40] studies. The basis set dependence has not been extensively studied in any case. Table 3 reports the RPA, TDDFT, and EOM-CCSD calculated transition energies for basis sets 4−8.

Here, the RPA transition energies are not satisfactory and are generally considerably larger than the experimental values. The TDDFT values using basis set 7 are often in satisfactory agreement with the experimental values, but when additional diffuse functions are added, the calculated transition energies are generally too small.

Head-Gordon et al.[6] have compared CIS, CIS(D), and CCSD-EOM for formaldehyde using basis set 7. CIS(D) was markedly better than CIS but not as satisfactory as EOM-CCSD.

The EOM-CCSD calculated transition energies are generally in very good accord with the experimental values. The values obtained using basis set 4 are the same as those previously reported.[38t] As with ethylene, there usually is little difference between the values calculated via basis sets 7 and 8. However, in some cases, especially $3A_2$, they differ significantly, and basis set 8 gives the more satisfactory energy.

TABLE 3: Formaldehyde Excited States[a]

	RPA			TDDF T				EOM- CCSD				
	5	4	7	5	4	7	8	5	4	7	8	obs
A_1	9.21	9.18	9.19	7.92	7.70	7.62	7.63	8.18	8.00	7.98	7.98	8.14[b]
	9.76	9.57	9.55	9.44	9.18	8.43	8.13	9.74	9.48	9.27	9.13	
	11.90	11.35	10.83	10.31	9.74	8.98	8.36	10.60	10.17	9.59	9.37	9.58[c]
	12.88	12.50	11.18	11.98	10.66	9.66	8.57	12.54	11.16	10.16	9.86	
	14.33	12.78	12.05	12.47	11.97	9.94	9.04	12.99	12.27	10.75	9.93	
A_2	4.35	4.36	4.35	3.92	3.87	3.92	3.92	4.00	3.98	4.04	4.04	4.0[d]
	10.36	10.02	9.74	8.80	8.41	7.89	7.84	8.76	8.45	8.21	8.21	8.37[e]
	11.23	10.99	10.91	10.08	10.00	9.17	8.30	10.57	10.43	9.70	9.29	9.22[f]
	12.23	12.08	11.40	11.48	10.47	10.07	8.55	11.94	10.67	10.46	9.44	
	14.11	12.30	12.00	12.78	11.31	10.19	9.46	12.93	11.81	10.65	10.28	
B_1	9.52	9.56	9.52	9.03	8.99	9.03	9.03	9.34	9.35	9.43	9.43	9.0[g]
	11.21	11.14	11.12	10.53	9.75	10.45	10.45	10.87	9.84	10.89	10.89	10.60[h]
	12.12	11.35	11.93	11.67	10.44	11.25	11.25	11.92	10.81	11.79	11.78	11.70[i]
	14.32	12.06	13.05	13.54	11.97	11.75	11.56	13.83	11.79	12.91	12.77	
	15.26	13.38	13.32	13.81	12.58	12.41	11.77	14.12	12.97	13.08	12.96	
B_2	8.65	8.55	8.59	6.95	6.82	6.87	6.87	7.10	7.01	7.04	7.04	7.08[j]
	9.51	9.37	9.33	8.06	7.84	7.67	7.66	8.08	7.88	7.88	7.88	7.97[k]
	11.81	10.84	10.57	10.11	9.06	8.17	7.99	10.22	9.25	9.07	8.94	8.88[l]
	12.82	11.76	10.93	10.61	9.78	8.93	8.23	11.05	9.93	9.31	9.12	9.26[m]
	13.26	11.92	11.14	11.91	10.09	8.96	8.32	12.00	10.10	9.43	9.18	9.63[n]

[a] The 4.0 eV A_2 transition is n$-\pi^*$ and the 9.0 eV B_1 transition is $\pi-\pi^*$. The other exited states are best described as Rydberg states. Cf. ref 5. [b] 8.11 eV: ref 36a. 8.14 eV: ref 36b, d, f. [c] Reference 36d. [d] 3.49 eV, ref 36a. 3.84 eV: ref 36c. 4.2 eV: ref 36e. 4.07 eV: ref 36f. [e] 8.4 eV: ref 36a. 8.37 eV: ref 22. [f] Reference 36f. [g] Reference36d. [h] Reference36f. [i] Reference 36f. [j] 7.09 eV: ref 36a. 7.08 eV: ref 36bd. 7.10 eV: ref 36c. 7.11 eV: re 36f. [k] 7.96 eV: ref 36a. 7.97 eV: ref 36b, d, f. [l] Reference 36f. [m] 9.26 eV: ref 36a. 9.27 eV: ref 36b. [n] Reference 6b, d.

TABLE 4: EOM-CCSD Calculated Structures of Formaldehyde and Some of Its Excited states

state	r(C═O)	r(C−H)	∠H−C−H	a	Erel (eV)
GS[a]	1.205	1.106	116.3	0.0	0.00
n_y–π^* (A″)[b]	1.311	1.095	118.8	32.5	3.70
$n_z-\pi^*$ (A′)	1.459	1.094	119.3	47.8	8.02
$\pi-\pi^*$ ($2A_1$)	1.583	1.095	119.6	0.0	8.43
($1B_2$)	1.198	1.131	120.7	0.0	7.06
rad. cat.	1.198	1.115	120.3	0.0	

[a] Obs: r(C═O) = 1.2031(1), r(C−H) = 1.1012(2), ∠O═C−H = 116.25(4). Berry, R. J.; Harmony, M. D. *Struct. Chem*. **1990**, *1*, 49. [b] Obs.: r(C═O) = 1.323, r(C−H) = 1.098, ∠H−C−H = 118.8, a = 34°, Erel = 3.49 (ref 41).

The reported transition energy for $5B_2$ is 9.63 eV, which is considerably larger than the basis set 8 value. However, here, $4B_2$ and $5B_2$ are predicted to have essentially the same transition energies and would not be resolved in the experimental spectrum. Thus, the experimental $5B_2$ values probably should be reassigned as $6B_2$. The latter is calculated to be 9.4 eV.

4. Formaldehyde Excited State Structures

The $1A_2$ $n_y \rightarrow \pi^*$ exited state has been the subject of many studies, and its structure has been found to be bent both experimentally[41] and theoretically.[42] The geometries of some of the excited states have been calculated at the CCSD/6-311++G** level and are summarized in Table 4. The ground-state structure[43] is well reproduced. The A″ $n_y \rightarrow \pi^*$ state ($1A_2$ if planar) is found to be bent out-of-plane by 30°, in good agreement with the experimental value of 33°. The calculated adiabatic transition energy is 3.70 eV, again in good agreement with the observed value of 3.49 eV.

The other $n_z \rightarrow \pi^*$ state (A′, $1B_1$ if planar) also is bent and is more distorted than the A″ state. Both of them have significantly elongated C═O bond lengths, corresponding to the transfer of an electron into the C═O antibonding p level. The adiabatic transition energy for the A′ state is calculated to be 8.02 eV.

The $\pi-\pi^*$ level has not been observed, and previous calculations have suggested that it would dissociate.[31] The very long calculated C═O bond length is in agreement with this proposal. On the other hand, the Rydberg states have short C═O bond lengths, 1.198 Å for the $1B_2$ state. The Rydberg states are formed by taking one electron from the molecule and placing it in a diffuse orbital about the positively charged core. Thus, the molecule effectively becomes a radical cation. A calculation for this species finds bond lengths that are similar to the $1B_2$ state. The calculated energy change (ionization potential) is 10.61 eV in good agreement with the experimental value, 10.88 eV.[44]

5. Global Diffuse Functions

Basis set 8, with three sets of diffuse functions, has been found to be the more satisfactory basis for these calculations. The use of diffuse functions at each atom has the advantage of considerable flexibility in describing the excited-state wave functions. They may be combined to form higher angular momentum Rydberg diffuse functions. Thus, two out-of-phase s functions on different atoms would simulate a p function, and two out-of-phase p functions would simulate a d function. However, the use of several sets of diffuse functions adds considerably to the total number of functions and to the time required for the calculations.

Another approach is to add diffuse Rydberg orbitals centered at the center of mass. This has been successfully used by Roos and co-workers in their CASPT2 calculations.[45] We have tried a combination of the two approaches, using basis sets 5 and 7 and adding global diffuse functions.[34] Some results for calculations for ethylene are given in Table 5. With the inclusion of 3 sets of spd functions, the 6-311(2+,2+)G** and 6-311(3+,3+)-G** EOM calculated transition energies were essentially the same. Thus, there is no need for the (3+,3+) basis.

The table compares the 6-311++G** and 6-311(2+,2+)-G** EOM-CCSD calculations with no global diffuse functions and with 6 sets of spd functions. The transition energies derived from the two basis sets using 6 sets of diffuse orbitals are essentially the same, except for $4B_{2g}$ and $5B_u$ where the energy decreases by 0.3 eV on going from basis set 5 to 7. The

TABLE 5: Effect of Global Diffuse Functions on the Calculated Transition Energies for Ethene, EOM-CCSD

sym.	6-311G**	with 6spd	6-311++G **	with 6spd	6-311(2+,2 +)G**	with 6spd	obs
A_g	13.08	8.32	9.11	8.32	8.33	8.32	8.28
	14.44	9.42	11.82	9.42	10.59	9.42	
B_{1g}	8.84	7.95	8.06	7.94	7.94	7.94	7.80
	9.38	8.69	8.70	8.67	8.69	8.67	
	15.18	9.31	11.34	9.30	9.40	9.30	9.2
	21.51	9.81	11.53	9.81	10.31	9.73	
	21.96	10.13	13.16	10.11	11.72	9.82	
B_{2g}	9.62	7.99	8.09	7.98	7.98	7.98	8.01
	10.34	9.34	10.16	9.33	9.44	9.33	
	14.87	9.83	11.11	9.82	9.86	9.78	
	17.82	10.13	11.73	10.11	10.14	9.83	
	18.75	10.19	12.79	10.18	10.63	10.06	
B_{3g}	11.04	9.71	9.76	9.70	9.71	9.70	
	15.23	11.23	11.89	11.21	11.27	11.20	
A_u	11.54	9.01	9.29	9.00	9.00	9.00	
	11.89	9.69	11.52	9.69	9.95	9.69	
B_{1u}	8.74	8.13	8.16	8.10	8.13	8.10	7.65
	12.11	9.30	10.53	9.30	9.42	9.30	9.33
B_{2u}	12.12	9.03	10.48	9.03	10.38	9.03	
	13.63	9.69	12.33	9.68	11.90	9.68	
B_{3u}	8.64	7.30	7.36	7.30	7.30	7.30	7.11
	15.01	8.80	9.53	8.78	9.20	8.78	8.62
	15.63	9.00	10.42	8.98	8.85	8.98	8.90
	17.92	9.14	11.46	9.14	9.28	9.14	9.08
	19.79	9.59	13.28	9.58	10.78	9.58	9.51

TABLE 6: Effect of Global Diffuse Functions on the EOM-CCSD Transition Energies for Formaldehyde

	++			2+,2+			
	$n = 0^a$	3	6	0	3	6	obs
A1	8.17	7.97	7.97	7.98	7.97	7.98	8.14
	9.82	9.15	9.13	9.27	9.12	9.12	
	10.61	9.46	9.37	9.59	9.41	9.37	9.58
	12.58?	9.91	9.73	10.16	9.85	9.73	
	12.62	10.66	9.89	10.75	10.11	9.87	
A2	4.05	4.04	4.04	4.04	4.04	4.04	4.0
	8.75	8.19	8.20	8.21	8.19	8.19	8.37
	10.63	9.22	9.29	9.70	9.21	9.19	9.22
	12.01	9.56	9.44	10.46	9.49	9.44	
	12.91	10.61	9.85	10.65	10.33	9.81	
B1	9.43	9.12	9.10	9.43	9.12	9.26	9.0
	10.94	9.42	9.42	10.89	9.42	9.42	
	11.99	10.47	9.76	11.79	10.47	9.83	
	13.89	10.89	10.13	12.91	10.89	10.19	
	14.15	11.77	10.66	13.08	11.77	10.80	10.60
B2	7.09	7.01	7.04	7.04	7.03	7.04	7.08
	8.08	7.86	7.86	7.88	7.86	7.86	7.97
	10.22	8.89	8.89	9.07	8.88	8.90	8.88
	11.04	9.06	9.05	9.31	9.05		9.26
	11.99	9.16	9.15	9.43	9.15		

[a] Number of spd diffuse functions.

calculated energies appear to converge on final values as the level of theory is increased.

The effect of the global diffuse functions on the calculated transition energies for formaldehyde also was examined (Table 6). Again, with a modest addition of these functions, the (2+,2+) and (3+,3+) basis sets gave essentially the same calculated transition energies. The effect of global diffuse functions was much more profound with formaldehyde than with ethene. With the latter, essentially all of the excited states in Table 5 originate from the π orbital, and the high symmetry results in little mixing of Rydberg types within a given symmetry block. On the other hand with formaldehyde, the excited states may originate from the π orbital or from either of the n_x or n_y lone pairs. Since there are only four irreducible representations, each symmetry block will contain several types of Rydberg states (Table 8).

TABLE 7: Effect of Global Diffuse Functions on the B_1 Block for Formaldehyde, EOM-CCSD/6−311(2+,2+)G**

$n = 0$	1	2	3	4	5	6
9.43	9.42	9.37	9.12	9.10	9.26	9.26
10.89	10.47	9.42	9.42	9.42	9.42	9.42
11.79	10.89	10.89	10.47	9.89	9.86	9.83
12.91	11.78	11.77	10.89	10.89	10.49	10.19
13.08	12.88	12.31	11.77	11.15	10.89	10.80
13.33	13.06	12.75	12.71	11.77	11.77	10.89
13.57	13.24	13.07	12.92	12.72	12.71	11.77
13.69	13.56	13.35	13.04	12.92	12.91	12.15

TABLE 8: Symmetries for Rydberg States of Formaldehyde

state	transitions		
A_1	n_y–p_y	n_z–s	π–p_x
	n_y–d_{yz}	n_z–p_z	π–π*
A_2	n_y–p_x	n_y–π*	π–p_y
	n_y–d_{xz}		
B_1	n_z–p_x	n_z–π*	π–s
	π–p_z	n_y–d_{xy}	
B_2	n_y–s	n_y–p_z	n_z–p_y
	n_y–$d_{x^2y^2}$	n_y–d_{z^2}	

Table 7 presents the effect of global diffuse functions in more detail for the B1 block. It can be seen that some transition energies, such as 10.89 and 11.77 eV, remain as the number of diffuse functions is increased but are pushed down in the order by the appearance of new lower energy transitions. Likely, these new transitions are ones that are particularly strongly affected by diffuse functions and correspond to one or more of the possibilities in Table 8. This question will receive further study, and perhaps the present results will lead to more detailed experimental studies of the formaldehyde transitions.

6. Acetone

Acetone has received considerable study. Many transition energies have been assigned,[46] and calculations at the TDDFT,[12] EOM-CCSD,[38w] and CASPT2[34] levels have been reported. Again, there has not been an examination of the basis set effect on the calculated transition energies.

Table 9 gives the transition energies calculated using basis sets 4, 5, and 7. The RPA values are quite unsatisfactory.

TABLE 9: Acetone Excited States

	RPA			TDDFT			EOM-CCSD					
	5	4	7	5	4	7	5	4	5a	7	5b	obs
A1	9.18	9.13	8.83	7.19	7.11	6.98	7.57	7.45	7.40	7.41	7.40	7.41[a]
	9.63	9.52	9.10	8.07	7.94	7.55	8.41	8.23	8.03	8.02	8.01	7.8[b]
	10.28	10.11	9.46	8.85	8.74	7.88	9.45	9.17	8.66	8.59	8.47	
	11.30	11.12	10.41	9.47	9.20	8.20	9.92	9.53	9.37	8.80	8.70	
	11.67	11.38	10.57	10.13	9.50	8.31	10.52	9.95	9.55	8.93	8.89	
B1	9.68	9.72	9.68	8.32	8.15	7.64	8.74	8.43	8.12	8.11	8.08	8.17[c]
	10.23	10.18	9.90	8.67	8.63	8.33	9.41	9.29	9.38	8.87	8.73	
	10.63	10.30	10.16	8.96	8.94	8.66	9.45	9.33	9.41	9.31	9.10	
	11.43	11.21	10.64	9.52	9.23	8.91	9.90	9.47	9.61	9.34	9.38	
	11.74	11.34	11.07	10.30	10.15	9.04	10.84	10.47	10.40	9.62	9.41	
A2	5.00	5.03	4.50	4.38	4.37	4.38	4.52	4.53	4.52	4.47	4.52	4.43[d]
	9.40	9.19	9.05	7.40	7.28	7.09	7.59	7.40	7.30	7.31	7.29	7.36[e]
	10.40	10.18	9.85	8.32	8.28	7.81	8.94	8.44	8.05	8.08	8.03	
	10.81	10.53	10.33	8.95	8.38	7.98	9.62	9.47	8.58	8.60	8.42	
	11.07	11.01	10.50	9.86	9.44	8.32	10.36	9.68	9.27	9.13	8.69	
B2	8.33	8.27	8.25	6.23	6.21	6.19	6.46	6.38	6.41	6.42	6.41	6.36[f]
	9.53	9.31	9.16	7.63	7.39	7.16	7.78	7.50	7.38	7.39	7.37	7.49[g]
	9.99	9.84	9.61	7.85	7.64	7.38	8.15	7.93	7.80	7.82	7.80	8.09[h]
	10.69	10.32	9.86	8.50	8.29	7.65	8.84	8.54	8.09	8.10	8.07	
	11.19	11.04	10.06	9.40	8.72	7.76	9.41	8.98	8.21	8.27	8.19	

[a] Reference 46b. [b] Reference 46a. [c] Reference 46a. [d] 4.3, ref 46d, 4.37; ref 46e; 4.38, ref 46c; 4.43, ref 25. [e] Reference 46b. [f] 6.36, ref 46d; 6.35, ref 46e. [g] Reference 46b. [h] Reference 46a.

TABLE 10: Isobutene Excited States

	RPA			TDDFT			EOM-CCSD					
	5	4	7	5	4	7	5	4	5a	7	5b	obs[a]
A1	6.94	6.88	6.84	6.74	6.64	6.61	7.19	7.00	6.98	6.97	6.98	~6.7
	8.18	7.97	7.74	7.73	7.59	7.28	8.18	7.97	7.87	7.83	7.85	
	9.07	8.73	8.04	8.85	8.41	7.61	9.25	8.80	8.15	8.17	8.08	
	10.61	9.82	8.52	9.73	9.25	7.94	9.87	9.63	8.66	8.52	8.43	
	10.85	10.11	8.82	9.51	9.26	8.21	9.90	9.78	9.30	8.78	8.58	
B1	6.64	6.56	6.55	6.16	6.08	6.10	6.49	6.39	6.43	6.41	6.43	6.17
	7.48	7.33	7.30	6.99	6.73	6.76	7.31	7.18	7.16	7.14	7.16	
	8.32	7.95	7.82	7.66	7.11	7.28	8.15	7.89	7.73	7.73	7.72	
	8.60	8.17	7.94	8.01	7.45	7.33	8.43	8.03	7.88	7.83	7.85	
	9.36	8.25	8.12	8.78	7.51	7.48	9.06	8.61	8.04	8.08	8.02	
A2	7.43	7.32	7.29	6.94	6.75	6.77	7.34	7.23	7.21	7.19	7.21	
	8.13	7.97	7.86	7.46	7.39	7.22	7.94	7.81	7.76	7.72	7.74	
	9.39	8.46	8.42	8.10	7.49	7.69	8.74	8.65	8.50	8.39	8.30	
	9.43	9.22	8.58	8.78	8.05	7.83	9.30	9.05	8.70	8.52	8.49	
	9.96	9.35	8.73	9.10	8.63	7.89	9.83	9.49	9.01	8.63	8.71	
B2	8.94	8.45	8.04	8.27	7.97	7.43	8.75	8.29	7.97	7.96	7.94	
	9.98	9.41	8.73	8.71	8.62	8.06	9.04	8.98	8.98	8.68	8.57	
	10.28	10.21		9.33	8.83	8.66	9.83	9.23	9.26	9.01	8.93	
	10.80	10.72		9.47	9.25		10.12	9.71	9.55	9.62	8.98	
	11.09			9.59	9.42		10.56	10.01	9.67	9.70	9.33	

[a] Reference 47.

TDDFT gives fairly satisfactory transition energies for the first few transitions of each symmetry block, but the higher transition energies are generally unsatisfactory. The EOM-CCSD values obtained using basis set 7 are in quite good accord with the experimental data.

The effect of global diffuse functions also was examined. Basis set 5a is basis set 5 plus three sets of spd diffuse functions, and set 5b is basis set 5 plus six sets of spd diffuse orbitals. Basis sets 7 and 5b give essentially the same calculated transition energies except for $5B_1$, $4A_1$, and $4A_2$ where the latter gives a somewhat smaller transition energy. Unfortunately, the experimental data are limited, and it is not possible to compare these calculated energies with experimental values.

7. Isobutene

Isobutene has high enough symmetry to allow a meaningful comparison of experiment and theory. Unfortunately, at the present there is only a limited amount of experimental data. The ultraviolet spectrum and electron transmission experiments have been reported[47] but a detailed assignment has not been made. Also, there have not been many theoretical studies of the transition energies.

Table 10 gives the transition energies calculated using RPA, TDDFT, and EOM-CCSD using basis sets 4, 5, and 7, as well as the effect of global diffuse functions on the EOM-CCSD transition energies using basis set 5a (5 with 3 sets of spd diffuse functions) and 5b (5 with 6 sets of spd diffuse functions). In most cases basis sets 5b and 7 give essentially the same calculated transition energies, although in a few cases 5b gives a significantly lower energy.

In view of the limited experimental data for this molecule, we are currently reexamining its spectrum experimentally

Summary

EOM-CCSD is the only method of those we have studied that gives calculated transition energies in good agreement with experiments. The basis set used has a large effect on the calculated values. Additional polarization functions had little effect, but diffuse functions proved to be essential in reproducing the experimental values. Both atom-centered and global diffuse functions were effective, and a combination of the two proved to be especially useful.

With these small symmetrical molecules, placing the global diffuse functions at the center of mass appears to be satisfactory. However, that may not be the case for larger or less symmetrical molecules. With a diene, such as norbornadiene, it may be necessary to use two sets of these functions, one centered at each of the double bonds. This is currently being investigated.

Calculations

Geometry optimizations for the ground states and the RPA and TDDFT calculations were carried out using Gaussian-99.[48] The EOM-CCSD calculations were carried out using ACES-2.[49]

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