J. Phys. Chem. A **2001,** *105,* 4953−4962

Time-Dependent Density Functional Theory Calculations of Photoabsorption Spectra in the Vacuum Ultraviolet Region

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Received: October 19, 2000; In Final Form: February 8, 2001

The results of time-dependent density functional theory (TD-DFT) calculations of the transition energies and oscillator strengths of the excited states of formaldehyde, benzene, ethylene, and methane are reported. The local DFT (LDFT) transition energies tend to be smaller than experimental values by 0.1−1.3 eV. Inclusion of nonlocal (NLDFT) (gradient corrected) effects made the calculated energies larger than the LDFT values and thus made the energies closer to the experimental values for formaldehyde, ethylene, and methane. For benzene, no significant change in the calculated transition energies due to the addition of nonlocal effects was observed. The TD-DFT oscillator strengths are much better than those found at the configuration interaction singles (CIS) level. The agreement between the calculated TD-DFT values and the experimental values for the oscillator strengths is quite good, at least semiquantitative at both the LDFT and NLDFT levels.

Introduction

Electronic structure theory is rapidly becoming an effective and powerful tool for use in the design of molecules which have specific, required properties. One of the main reasons for the acceleration of the use of electronic structure theory in materials design has been the development of density functional theory (DFT), especially for molecular systems.[1−3] An important reason as to why DFT is becoming so popular for such studies is its lower computational cost, formally scaling as N^3 where N is the number of basis functions (when charge fitting is done), and including the effects of electron correlation at some reasonable level. In contrast, conventional ab initio MO theory formally scales as N^4 at the HF (Hartree−Fock) level and the effects of electron correlation are not included.[1−3] The combination of low computational cost with reasonable accuracy has led to the successful application of the DFT method to the prediction of a broad range of properties of molecules in the ground state.[4] Although time-dependent density functional theory (TD-DFT) was first proposed more than 20 years ago for treating excited-state properties,[5−7] it has only recently been applied to molecules.[8,9]

Our present interest in molecular design is the prediction of the photoabsorption of molecules in the vacuum ultraviolet region. It is critical in semiconductor processing to have molecules whose absorption spectra are transparent in the wavelength region of the laser being used in the patterning process. The region of interest to the industry is wavelengths near 157 nm (the F_2 laser), and new photoresist materials are required for the manufacture of the next-generation of semiconductor devices.[10] In this wavelength region, Rydberg transitions appear in addition to transitions between bonding and antibonding valence orbitals. We thus decided to benchmark the TD-DFT method for predicting such transitions by using reasonable sized basis sets augmented with Rydberg functions. We are specifically interested in predicting the photoabsorption spectrum, i.e., both transition energy and oscillator strength.

There have been a number of other recent studies where the TD-DFT method was used for the prediction of photoabsorption. Casida et al.[9,11,12] have calculated transition energies and polarizabilities of the N_2, CO, H_2CO, and C_2H_4 molecules with the Sadlej basis set[13] augmented with additional diffuse functions (Sadlej+). Bauernschmitt et al.[8,14] have investigated transition energies of the N_2, C_2H_4, H_2CO, $C_{10}H_8$, benzene, pyridine, and porphine molecules with the Sadlej+, SVP, and TZVP basis sets. Further calculations for the transition energy and ionization potential of CO, H_2CO, Me_2CO, CH_4, benzene, pyridine, and naphthalene with the Sadlej+ and 6-311++G(d,p) basis set,[15] the transition energy of H_2CO, acetaldehyde and acetone with the 6-311++G(d,p) basis set,[16] the transition energy of benzene, porphine, and C_{70} with basis sets ranging from DZ to cc-pVTZ + diffuse,[17] the transition energy and static polarizability of CO, N_2, CH_2O, C_2H_4, and benzene with the 6-31G* and TZ2P basis set,[18,19] and the transition energy and polarizability of N_2, C_2H_4, and C_5H_5N with the Sadlej basis set [20] have been reported. In these studies, the calculated transition energies were compared to experimental values, and it was found that better agreement could be obtained with the TD-DFT method as compared to the configuration interaction singles (CIS)[21] method. However,

10.1021/jp003937v CCC: $20.00

TABLE 1: Calculated Transition Energies (eV) of Formaldehyde[a]

	CIS		SVWN				B3LYP						
transition	DZ[b]	cc-pVTZ[c]	TZVP[c]	TZVP (+H)[c]	cc- pVTZ[c]	cc-pVTZ (+H)[c]	DZ[d]	DZP[d]	DZVP[d]	TZV[d]	TZVP[d]	cc-pVTZ [c]	expt
$^1A_2$ $n \rightarrow \pi^*$	4.39	4.58	3.67	3.66	3.70	3.68	3.87	4.00	4.05	3.89	3.98	3.94	4.2,[56−59] 3.49[60]
$^1B_2$ $n \rightarrow 3s$	8.59	8.59	5.93	5.93	5.91	5.91	6.42	6.39	6.50	6.48	6.48	6.47	7.10,[56] 7.08,[61] 7.10,[62] 7.09[63]
$^1B_2$ $n \rightarrow 3p_z$	9.43	9.38	6.76	6.75	6.71	6.70	7.24	7.18	7.30	7.27	7.29	7.27	7.97,[56] 7.97,[61] 8.00,[62] 8.13[63]
$^1A_1$ $n \rightarrow 3p_y$	9.53	9.51	6.78	6.67	6.66	6.63	7.18	7.15	7.30	7.25	7.26	7.27	8.14,[61] 8.13,[62] 7.98[63]
$^1A_2$ $n \rightarrow 3p_x$	9.74	9.76	6.97	6.99	6.96	6.97	7.46	7.43	7.57	7.54	7.55	7.57	
$^1B_1$ $5a_1(\sigma) \rightarrow \pi^*$	9.72	9.80	8.76	8.74	8.77	8.73	8.98	9.11	9.18	9.03	9.10	8.98	9.0,[56] ~9.0[61]
$^1A_2$ $1b_2(\sigma) \rightarrow \pi^*$	11.69	11.31	9.66	9.64	9.66	9.63	10.33	10.16	10.23	10.31	10.15	10.10	
$^1B_1$ $\pi \rightarrow 3s$	11.53	11.14	9.96	9.96	9.91	9.91	10.25	10.02	10.12	10.27	10.11	9.96	10.7[64,65]
$^1A_1$ $\pi \rightarrow \pi^*$	10.24	9.76	9.70	9.86	9.49	9.76	10.06	9.86	9.87	9.77	9.81	9.34	10.7[64,65]
$^1B_1$ $\pi \rightarrow 3p_z$	12.39	11.95	10.79	10.79	10.73	10.72	11.13	10.84	10.98	11.13	10.97	10.80	11.6−11.9[64,65]

[a] All basis sets are augmented with Dunning-Hay Rydberg functions. [b] Geometry optimization done at the HF/6-31G* level. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] Geometry optimization done at the B3LYP/6-311G* level.

in the above studies, in general, oscillator strengths were not reported. In addition to the above studies, calculations on other molecules have been reported including the band-gap and transition energy of alkanes,[22] the excited-state potentials of the H_2 molecule,[23] the transition energy, ground-state dipole moment and polarizability of He, Be and Ne,[24] the excited-state geometry of H_2CO and C_2H_4,[25] and the transition energies of various metal atoms.[26,27]

Although no extensive benchmark studies of the calculation of oscillator strengths at the TD-DFT level have been done, a number of calculated oscillator strengths at the TD-DFT level have been reported including those of MnO_4^-, $Ni(CO)_4$ and $Mn_2(CO)_{10}$,[28] triazines,[29] anthracene, pyrene and perylene,[30] free-base porphin,[31] chlorophyll a,[32] and fullerenes.[33] In these studies, some comparisons between calculated and experimental oscillator strength were reported. However we believe that benchmarking the TD-DFT method for the prediction of oscillator strengths is useful if we are to use this method for the design of new materials for the development of future semiconductor manufacturing processes. We have calculated the oscillator strengths and transition energies of the CH_2O, CH_4, C_2H_4, C_2H_6, and benzene molecules with a variety of basis sets including the addition of Rydberg functions. Our study is focused on the oscillator strength of absorption peaks in the vacuum ultraviolet region, and where appropriate, we compare our calculated transition energies to previously reported TD-DFT values.

Calculations

The calculations were performed by using the program Gaussian 98.[34] Geometry optimizations were done at the second-order perturbation Møller−Plesset (MP-2) level[35] with the cc-pVTZ basis set,[36−39] or at the nonlocal density functional level (B3LYP)[40,41] with the 6-311G*[42,43] basis set.[44] Our calculations on the transition energy and oscillator strength were performed at the time-dependent density functional theory (TD-DFT) level[8,9] and, in some cases at the CIS level,[21,45−47] the latter for comparison purposes. The TD-DFT calculations were performed both at the local (LDFT) and gradient-corrected nonlocal (NLDFT) levels. For the LDFT calculations, the Slater type exchange functional[1,2] and Vosko-Wilk-Nusair correlation functional[48] was used (SVWN), and for the NLDFT calculations, Becke's three parameter functional[40] and the Lee−Yang−Parr functional[41] were used (B3LYP). A variety of basis sets were used for the calculations of the photoabsorption properties: DZ,[49] DZP,[49] DZVP (DFT-derived),[50] TZV,[51,52] TZVP (DFT-derived),[50] and cc-pVTZ[36−39] basis sets with Dunning and Hay's[53] Rydberg functions added to these basis sets for the carbon and oxygen atom.[54] In addition to the Rydberg basis set, in some cases, we further added a set of diffuse s and p functions[55] to the cc-pVTZ and TZVP basis set for the hydrogen atom, and we denote this basis set as cc-pVTZ(+H) and TZVP(+H), respectively. All the calculations were performed on a Cray J916/12−4016, a 48-node IBM SP (Power2 SuperChip), or an SGI computer.

Results and Discussion

Formaldehyde. Formaldehyde is often used as a benchmark for the calculation of the phototransition energy and oscillator strength. Our calculated values of the transition energy are summarized in Table 1 together with experimental values.[56−65] In Table 2, we compare our calculated values to previously calculated TD-DFT values.[9,11,14−16,19] Due to the difficulties in measuring high excitation energies, we also include values from calculations at the highly correlated EOM-CC level in Table 2.[66] We performed a linear fit between the calculated and experimental values; the linear equations and the linear correlation coefficients are listed in Table 3.

Consistent with previous results,[67−69] our calculated CIS values tend to be higher than the experimental values. The only exception is the transition energy for the $\pi \rightarrow \pi^*$ transition where the calculated values are actually lower than the experimental values. At the LDFT level, the calculated TD-DFT values tend to be smaller than the experimental values by 0.6−1.0 eV, consistent with previous work (see Table 2).[8,19] Furthermore, this difference of 0.6−1.0 eV between the calculated and experimental values becomes slightly larger when the transition energy exceeds ~9 eV. This effect can be clearly seen from the fits in Table 3. The value of the slope multiplying the calculated transition energy is greater than 1.0 showing that the differences increase with increasing transition energies.

The NLDFT values with the B3LYP potential are larger than the LDFT values, but smaller than the CIS values, so that the B3LYP TD-DFT values give the best agreement with experiment. This is again in consistent with previous work (see Table 2),[8,19] where it has been shown that the use of gradient-corrected noncontinuum functionals such as B3LYP improves the calculated transition energy as compared to the use of local functionals, whereas the application of gradient-corrected continuum functionals do not lead to any significant improvement.[19] For the low-lying states with energies less than ~9.0 eV, there is a good agreement between the calculated and

TABLE 2: Comparison of Present Calculated[a] Transition Energies (eV) for Formaldehyde with Other Calculated Values

transition		SVWN/ cc-pVTZ (+H)[c]	B3LYP/ DZ[d]	B3LYP/ pVTZ[c]	LDA/ Sadlej+ (ref 9)	LB94/ Sadlej+ (ref 9)	BP/ aug-Sadlej (ref 14)	B3LYP/ Sadlej+ (ref 15)	PBE0/ Sadlej+ (ref 15)	B3P86/ 6-311++G** (ref 16)	B3LYP/ Sadlej+ (ref 19)	HCTH(AC)/ Sadlej+[b] (ref 19)	AC-LDA/ Sadlej+ (ref 11)	EOM-CC[e] (ref 66)
$^1A_2$	$n \to \pi^*$	3.68	3.87	3.94	3.65	3.48	3.80	3.92	3.96	3.95	3.92	3.93		3.98
$^1B_2$	$n \to 3s$	5.91	6.42	6.47	5.83	6.97	5.96	6.27	6.66	6.98	6.38	6.77		6.99
$^1B_2$	$n \to 3p_z$	6.70	7.24	7.27				7.13	7.69	7.93	7.13	7.67		7.93
$^1A_1$	$n \to 3p_y$	6.63	7.18	7.27			6.74	7.10	7.37	8.09	7.10	7.87	8.02	7.99
$^1A_2$	$n \to 3p_x$	6.97	7.46	7.57						8.81	7.34	8.12		8.45
$^1B_1$	$5a_1(\sigma) \to \pi^*$	8.73	8.98	8.98			8.79			9.23				9.33
$^1A_2$	$1b_2(\sigma) \to \pi^*$	9.63	10.33	10.10										10.38
$^1B_1$	$\pi \to 3s$	9.91	10.25	9.96										
$^1A_1$	$\pi \to \pi^*$	9.76	10.06	9.34									9.48	9.47
$^1B_1$	$\pi \to 3p_z$	10.72	11.13	10.80										

[a] All basis sets are augmented with Dunning-Hay Rydberg functions. [b] AC: asymptotically corrected. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] Geometry optimization done at the B3LYP/6-311G* level. [e] EOM-CC: equation of motion coupled cluster; basis set is [5s3p2d/3s2p].

TABLE 3: Linear Fits between the Calculated and Experimental Values for the Transition Energies[a]

method	linear equation	linear correlation coefficient
Formaldehyde		
CIS/DZ + Rydberg	$E_{expt} = 1.02 \cdot E_{calc} - 1.00$	0.967 (8)
CIS/cc-pVTZ + Rydberg	$E_{expt} = 1.09 \cdot E_{calc} - 1.52$	0.950 (8)
SVWN/TZVP + Rydberg	$E_{expt} = 1.02 \cdot E_{calc} + 0.68$	0.984 (8)
SVWN/TZVP(+H) + Rydberg	$E_{expt} = 1.01 \cdot E_{calc} + 0.74$	0.984 (8)
SVWN/cc-pVTZ + Rydberg	$E_{expt} = 1.04 \cdot E_{calc} + 1.04$	0.982 (8)
SVWN/cc-pVTZ(+H) + Rydberg	$E_{expt} = 1.02 \cdot E_{calc} + 0.70$	0.983 (8)
B3LYP/DZ + Rydberg	$E_{expt} = 1.04 \cdot E_{calc} + 0.22$	0.991 (8)
B3LYP/DZP + Rydberg	$E_{expt} = 1.08 \cdot E_{calc} - 0.07$	0.987 (8)
B3LYP/DZVP + Rydberg	$E_{expt} = 1.08 \cdot E_{calc} - 0.21$	0.989 (8)
B3LYP/TZV + Rydberg	$E_{expt} = 0.93 \cdot E_{calc} + 0.07$	0.990 (8)
B3LYP/TZVP + Rydberg	$E_{expt} = 1.08 \cdot E_{calc} - 0.13$	0.989 (8)
B3LYP/cc-pVTZ + Rydberg	$E_{expt} = 1.12 \cdot E_{calc} - 0.34$	0.988 (8)
Benzene		
CIS/cc-pVTZ + Rydberg	$E_{expt} = 0.52 \cdot E_{calc} + 2.99$	0.804 (10)
SVWN/cc-pVTZ + Rydberg	$E_{expt} = 1.05 \cdot E_{calc} - 0.15$	0.934 (10)
B3LYP/DZ + Rydberg	$E_{expt} = 0.86 \cdot E_{calc} + 1.04$	0.858 (10)
B3LYP/TZVP + Rydberg	$E_{expt} = 1.01 \cdot E_{calc} + 0.01$	0.933 (10)
B3LYP/cc-pVTZ + Rydberg	$E_{expt} = 1.41 \cdot E_{calc} - 2.45$	0.979 (8)
Ethylene		
SVWN/TZVP + Rydberg	$E_{expt} = 1.49 \cdot E_{calc} - 2.90$	0.975 (9)
SVWN/cc-pVTZ + Rydberg	$E_{expt} = 1.49 \cdot E_{calc} - 2.94$	0.977 (9)
SVWN/cc-pVTZ(+H) + Rydberg	$E_{expt} = 1.54 \cdot E_{calc} - 3.25$	0.973 (9)
B3LYP/DZ + Rydberg	$E_{expt} = 1.39 \cdot E_{calc} - 2.14$	0.975 (9)
B3LYP/TZVP + Rydberg	$E_{expt} = 1.35 \cdot E_{calc} - 1.90$	0.985 (9)
B3LYP/cc-pVTZ + Rydberg	$E_{expt} = 1.39 \cdot E_{calc} - 2.23$	0.982 (9)
All Peaks for Formaldehyde, Benzene, and Ethylene		
SVWN/cc-pVTZ + Rydberg	$E_{expt} = 0.80 \cdot E_{calc} + 1.82$	0.790 (25)
B3LYP/DZ + Rydberg	$E_{expt} = 1.04 \cdot E_{calc} + 0.10$	0.946 (27)
B3LYP/TZVP + Rydberg	$E_{expt} = 1.11 \cdot E_{calc} - 0.35$	0.971 (27)
B3LYP/cc-pVTZ + Rydberg	$E_{expt} = 1.19 \cdot E_{calc} - 0.83$	0.984 (25)

[a] For transitions with several experimental values, we used an average of the experimental values for the linear fits. Values in parentheses are the number of data used for the linear fit. For the $\pi \to 3p_x$, $3p_y$, and $\pi \to 3d$ transitions of benzene, the average of the calculated values is used for the fit.

experimental values at the NLDFT level (see Table 1 and II),[8,19] when the appropriate functional is used. For our results, the difference between the calculated and experimental values are less than ~0.5 eV with the calculated values being smaller than the experimental values. For transitions whose energy is higher than ~9.0 eV (i.e., $\pi \to 3s$, $\pi \to \pi^*$, and $\pi \to 3p_z$ transitions), the same conclusion can be reached and the agreement between the NLDFT and the experimental values is excellent with the former being slightly smaller than the latter. For these transitions, the difference between the calculated and experimental values are slightly larger as compared to those for the low-lying states, in part due to the experimental values being less well-established, and also in part, due to the wrong asymptotic behavior of the exchange-correlation potential as shown by Casida et al.,[9] which leads to the energy of the highest occupied molecular orbital (HOMO) being too small.

The basis set dependence of the calculated transition energies is not as pronounced as compared to the effect of the exchange-correlation functional. For example, at the LDFT level, the maximum differences of the calculated transition energies is less than 0.15 eV for all of the calculated transitions except for the $\pi \to \pi^*$ transition, where a difference of 0.37 eV is found. However, the presence of these slight differences does not necessarily mean that the use of a larger basis set leads to a better value. For example, for the $n \to 3p_y$ transition, the cc-pVTZ(+H) + Rydberg and TZVP + Rydberg values are 6.63 and 6.78 eV, respectively, whereas the experimental values are 7.98−8.14 eV, so that the latter value is slightly closer to experiment as compared to the former. At the NLDFT level, a similar trend is found. Except for the $\pi \rightarrow \pi^*$ transition, the differences are less than 0.33 eV, and no pronounced improvement of the calculated values can be seen even when the size of the basis set is increased from the DZ + Rydberg to the cc-pVTZ + Rydberg basis set. At this level of calculation, a larger difference of 0.72 eV is found for the valence-to-valence (V−V) $\pi \rightarrow \pi^*$ transition. This is not surprising as we used the same Rydberg basis functions for all of the calculations and only the basis set for valence orbitals are altered.

Our value at the B3LYP/cc-pVTZ + Rydberg level is essentially the same as the B3LYP/Sadlej+ value[15,19] for the $n \rightarrow \pi^*$ transition, whereas for the $n \rightarrow$ 3s and $n \rightarrow$ 3p transitions, our values are larger by 0.1 to 0.2 eV, and are closer to the experimental values. The LB94[70]/Sadlej+[9] and BP[71,72]/aug-Sadlej[14] values tend to be smaller than our values by 0.2 to 0.5 eV except for the $n \rightarrow$ 3s transition value at the LB94/Sadlej+ level, so that our values again tend to be closer to experiment. Slightly better agreement with experiment as compared to our values was obtained at the PBE0[73]/Sadlej+,[15] B3P86[40,72]/6-311++G**,[16] HCTH(AC)[74]/Sadlej+,[19] and AC-LDA/Sadlej+[11] DFT levels as well as at the EOM-CC[66] level. For many of the transition energies, our values are in reasonable agreement with the high level EOM-CC results. The values at these levels are larger than our values by up to 1.3 eV, and are slightly closer to experiment when such comparisons can be made. However, for the transitions with the largest differences in the calculations, experimental results are not available.

The values of the linear correlation coefficient in Table 3 can be used to summarize the above discussions. The coefficients at the LDFT level are closer to unity than those at the CIS level. At the LDFT level, the coefficients do not depend on the basis set. Actually, the coefficients for the TZVP + Rydberg basis set are slightly closer to unity than those for the cc-pVTZ(+H) + Rydberg basis set. The coefficients at the NLDFT level are closer to unity than those at the LDFT level, suggesting that the NLDFT level is giving better results as compared to the LDFT level. The coefficients at the NLDFT level differ slightly, but, again, these differences do not exhibit a trend that the coefficient becomes closer to unity with increasing size of the basis set. For example, the coefficient for the DZ + Rydberg basis set is closer to unity than that for the cc-pVTZ + Rydberg basis set, although the difference in the coefficients is very small.

Next, we discuss the calculated oscillator strengths for formaldehyde. The calculated values are listed in Table 4 together with experimental values.[61,62,75−77] In Table 4, we also list the calculated values[66] at the EOM-CC level. In addition, TD-DFT calculated oscillator strengths have been very recently reported by Casida and Salahub[78] (this work appeared after our submission of this manuscript), and these are given in Table 4. We note that Casida and Salahub also reported oscillator strength values for CO, N_2, and C_2H_4. As found previously, the agreement between the oscillator strengths calculated at the CIS level and the experimental values is at best qualitative.[67−69] For example, for the $n \rightarrow 3p_z$ and $n \rightarrow 3p_y$ transitions, the calculated values are 0.037−0.047 and 0.072−0.150, respectively, whereas the experimental values are about 0.017−0.019 for the former and about 0.032−0.036 for the latter. Thus, the CIS values are significantly larger than the experimental values.

The agreement between the calculated and experimental oscillator strengths is dramatically improved at the TD-DFT level, and as shown in Table 4, there is at least a semiquantitative agreement between the calculated and experimental values. For

TABLE 4: Calculated Oscillator Strengths of Formaldehyde[a]

	CIS		SVWN				B3LYP								
transition	DZ[b]	cc-pVTZ[c]	TZVP[c]	TZVP (+H)[c]	cc-pVTZ[c]	cc-pVTZ (+H)[c]	DZ[d]	DZP+[d]	DZVP[d]	TZV[d]	TZVP[d]	cc-pVTZ[c]	EOM-CC[e]	AC-LDA[f]	expt[g]
$^1B_2$ $n \rightarrow 3s$	0.026	0.025	0.027	0.028	0.028	0.029	0.029	0.026	0.027	0.032	0.028	0.025	0.022	0.055	0.028,[75] 0.038,[61] 0.0413,[62] 0.032[76]
$^1B_2$ $n \rightarrow 3p_z$	0.037	0.047	0.010	0.010	0.012	0.012	0.013	0.015	0.017	0.016	0.016	0.019	0.042	0.018	0.017,[75] 0.017 ± 0.002,[61] 0.0281,[62] 0.019[76]
$^1A_1$ $n \rightarrow 3p_y$	0.072	0.150	0.034	0.030	0.033	0.028	0.033	0.032	0.032	0.037	0.034	0.035	0.057	0.071	0.032,[75] 0.038 ± 0.004,[61] 0.0605,[62] 0.036[76]
$^1B_1$ $5a_1(\sigma) \rightarrow \pi^*$	0.002	0.000	0.001	0.001	0.001	0.000	0.003	0.001	0.001	0.003	0.001	0.000	0.0007		
$^1B_1$ $\pi \rightarrow 3s$	0.064	0.070	0.021	0.021	0.021	0.021	0.022	0.026	0.023	0.021	0.024	0.025		0.055	
$^1A_1$ $\pi \rightarrow \pi^*$	0.183	0.111	0.095	0.106	0.035	0.075	0.090	0.066	0.044	0.027	0.034	0.130	0.063		
$^1B_1$ $\pi \rightarrow 3p_z$	0.022	0.020	0.024	0.022	0.024	0.019	0.028	0.026	0.028	0.031	0.028	0.029			

[a] All basis sets for the present work are augmented with Dunning-Hay Rydberg functions. [b] Geometry optimization done at the HF/6-31G* level. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] Geometry optimization done at the B3LYP/6-311G* level. [e] Ref 66; EOM-CC: equation of motion coupled cluster; basis set is [5s3p2d/3s2p]. [f] Ref 78; basis set: Sadlej + diffuse. [g] Values obtained by using dipole (e,e) spectroscopy are expected to be more reliable than the other experimental values (ref 62).

the $n \rightarrow 3s$ transition, the calculated oscillator strength values are 0.025−0.032, essentially independent of the basis set and of exchange-correlation functional. The experimental values for this transition range from 0.028 to 0.041, showing reasonable agreement between the calculated and experimental values. Our calculated value is somewhat smaller than the most reliable experimental value of 0.0413 from dipole (e,e) measurements.[62] For the $n \rightarrow 3p_z$ transition, there is, again, no pronounced dependence on the basis set. For this transition, the LDFT values are 0.010−0.012, and somewhat larger values are obtained at the NLDFT level (0.013−0.019). The most reliable experimental value is 0.0281,[62] and again our calculated values are, somewhat smaller than this experimental value. A similar result is found for the $n \rightarrow 3p_y$ transition. The basis set dependence is again not significant. The LDFT and NLDFT values range from 0.028 to 0.034 and 0.032 to 0.037, respectively, whereas the most reliable experimental value is 0.0605,[62] and again, our calculated values are somewhat smaller than the experimental value.

For the other Rydberg transitions (the $\pi \rightarrow 3s$ and $\pi \rightarrow 3p_z$ transitions), the same trends hold: the effect of the basis set and functional is not significant. For the valence transition (i.e., the $\pi \rightarrow \pi^*$ transition), the situation is different, and the dependence on the basis-set and exchange-correlation functional is larger. For example, at the LDFT level, the calculated oscillator strength is 0.035 with the cc-pVTZ + Rydberg basis set and it goes to 0.075 by adding diffuse basis functions on hydrogen. In addition, the cc-pVTZ + Rydberg basis set yields an oscillator strength of 0.035 at the LDFT level, whereas it is 0.130 at the NLDFT level. This suggests that the Rydberg basis set we are using can well describe Rydberg excited states even at the local level, but for the valence excited states, we need to use a basis set at least as large as cc-pVTZ together with the use of nonlocal functionals. This is in agreement with the enhanced basis-set dependence of the calculated $\pi \rightarrow \pi^*$ transition energy shown in Table 1.

The EOM-CC method[66] predicts that the oscillator strength for the $\pi \rightarrow 3p_z$ transition is larger than that for the $\pi \rightarrow 3s$ transition, in contrast to our calculated values and to the experimental and AC-LDA values.[77] Except for the $\pi \rightarrow 3s$ and the $\pi \rightarrow \pi^*$ transitions, our calculated values tend to be smaller than the EOM-CC values, and there is overall agreement between the two sets of values within a factor of 2. The recent AC-LDA values tend to be larger than our values by about a factor of 2 except for the $\pi \rightarrow 3p_z$ transition where the values are comparable. The AC-LDA values are, in general, larger than the experimental values by an amount comparable to the amount that our values underestimate the most reliable experimental values.

Benzene. The calculated transition energies for benzene are given in Table 5 together with available experimental values.[79−84] As previously reported,[85,86] the CIS calculated values tend to be larger than the experimental values, although for the $\pi \rightarrow$ 3p and $\pi \rightarrow$ 3d transitions, the difference between the calculated and experimental values is not pronounced. The LDFT values are, again, smaller than the CIS values, and except for the $\pi \rightarrow \pi^*$ ($^1B_{2u}$) and $a_{1u} \rightarrow \pi^*$ transitions, the values also tend to be smaller than the experimental values. The difference between the LDFT and experimental values is typically about 0.1 to 0.6 eV, a somewhat smaller value than found for formaldehyde at the LDFT level (0.6 to 1.0 eV). Use of gradient-corrected functionals does not lead to any significant changes in the calculated transition energy, and the calculated values, again, tend to be smaller by 0.6 to 1.0 eV than the experimental values. This is in contrast to the case of formaldehyde where the use

TABLE 5: Calculated Transition Energies (eV) of Benzene[a]

transition		CIS/DZ[b]	CIS/cc-pVTZ[c]	SVWN/cc-pVTZ[c]	B3LYP/DZ[d]	B3LYP/TZVP[d]	B3LYP/cc-pVTZ[d]	expt
$^1B_{2u}$	$\pi \rightarrow \pi^*$	6.36	6.05	5.26	5.51	5.39	5.40	4.90[81]
$^1B_{1u}$	$\pi \rightarrow \pi^*$	6.53	6.20	6.03	6.27	6.05	6.05	6.19,[79] 6.19[81]
$^1E_{1u}$	$\pi \rightarrow \pi^*$	8.27	7.97	6.80	6.88	6.83	6.83	6.94,[79] 6.96[81]
$^1E_{2g}$	$a_{1u} \rightarrow \pi^*$	11.20	10.89	8.28	9.06	8.80		7.3,[82,83] 7.8?[84]
Rydberg transitions[e]								
$^1E_{1g}$	$\pi \rightarrow 3s$	6.74	6.56	6.03	6.02	6.01	6.01	6.33[84]
$^1E_{2u}$, $^1A_{1u}$, $^1A_{2u}$	$\pi \rightarrow 3p_x,p_y$	7.13, 7.29 × 2, 7.47	6.96, 7.13 × 2, 7.31	6.51, 6.51 × 2, 6.53	6.46, 6.49 × 2, 6.54	6.48, 6.50 × 2, 6.55	6.48, 6.50 × 2, 6.55	6.93,[80] 6.95[84]
$^1E_{1u}$	$\pi \rightarrow 3p_\pi$	7.46	7.26	7.10	7.27	7.10	7.09	7.59,[79] 7.41[80]
$^1E_{1g}$, $^1B_{1g}$, $^1B_{2g}$	$\pi \rightarrow 3d$	7.88, 7.89, 7.94 × 2	7.71, 7.72, 7.76 × 2	7.03, 7.04, 7.04 × 2	7.04 × 2, 7.04, 7.04	7.05, 7.06 × 2, 7.06	7.06, 7.06, 7.07 × 2	7.62,[80] 7.46,[84] 7.54[84]
$^1E_{2g}$, $^1A_{1g}$, $^1A_{2g}$	$\pi \rightarrow 3d$	8.00, 8.04 × 2, 8.11	7.83, 7.86, 7.94 × 2	7.32, 7.32 × 2, 7.34	7.31, 7.32 × 2, 7.36	7.32 × 2, 7.32, 7.35	7.32 × 2, 7.33, 7.36	7.98,[80] 7.81[84]
$^1A_{2u}$	$a_{2u} \rightarrow 3s$	11.63	11.40	8.81	9.14	9.12		9.41[79]
$^1E_{1g}$	$a_{2u} \rightarrow 3d$	12.65	12.43					10.47[79,f]

[a] All basis sets are augmented with Dunning-Hay Rydberg functions. [b] Geometry optimization done at the HF/6-31G* level. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] Geometry optimization done at the B3LYP/6-311G* level. [e] Values with "× 2" correspond to the transition energy for the degenerate transition. [f] In ref 79, this value is reported as 11.47 eV, a probable typographical error.

of gradient-corrected functionals led to an improvement of the calculated energies. The B3LYP/DZ values are in the worst agreement with experiment and the fit is the worst due to overestimating the valence transition energies.

Any basis set dependence of the calculated values is observed mainly for non-Rydberg transitions at the NLDFT level, similar to formaldehyde. The difference in the calculated values between the DZ + Rydberg and TZVP + Rydberg basis sets is as large as 0.22 eV, whereas the differences between the TZVP + Rydberg and cc-pVTZ + Rydberg basis sets is less than 0.01 eV. This shows that the DZ + Rydberg basis set does not have sufficient flexibility to describe the molecular orbitals of benzene for the prediction of transition energies, especially for valence excited states and that larger basis sets with polarization functions are required. The linear fits for benzene show more variation than for formaldehyde and are sensitive to the largest calculated value.

In Table 6, our calculated transition energies are compared to those reported by others at the TD-DFT level.[15,17,18] We also include values from high-level CC2 calculations[87] in Table 6. Our B3LYP/cc-pVTZ + Rydberg values are essentially the same as the previously reported B3LYP/aug-cc-pVTZ values,[17] except for the $\pi \rightarrow 3p_\pi$ transition, where the aug-cc-pVTZ value is significantly smaller than our value and also further from the experimental value. The addition of Rydberg functions seems to yield a better value than the addition of the diffuse functions used in ref 17. The calculated values at the PBE0[72]/Sadlej+[15] and HCTH(AC)[18]/6-31G*+diffuse levels tend to be larger than our values by up to 0.5 eV, and consequently, a better agreement with experiment as compared to our values is obtained at these levels, just as found for formaldehyde (Table 4). Comparison of our values to the high level CC2/aug-cc-pVTZ-CM2 results shows reasonable agreement with our values being at most 0.5 eV lower.

Next, we discuss the calculated oscillator strengths of benzene. The calculated values are listed in Table 7 together with available experimental data.[77,81,88−92] We also include the value for the $\pi \rightarrow \pi^*$ transition obtained at the EOM-CC level.[93] The oscillator strength for the $\pi \rightarrow \pi^*$ transition at the CIS level is significantly larger than the experimental values, as found previously.[67−69] Our TD-DFT values are, in general, in semiquantitative agreement with the experimental values. Excellent agreement between theory and experiment is obtained at the LDFT level with the cc-pVTZ + Rydberg basis set. A basis-set dependence is present for the NLDFT numbers, showing that the DZ + Rydberg basis set is not large enough to be used for the prediction of the oscillator strengths of benzene. The NLDFT/cc-pVTZ + Rydberg value is smaller than the corresponding LDFT value and also smaller than the experimental value. This result is consistent with the results for formaldehyde, where our TD-DFT values are smaller than the most reliable experimental values. The EOM-CC value is larger than the experimental values as well as our calculated values as found for formaldehyde.

Another experimental number available for comparison is an oscillator strength of 0.075 for all Rydberg transitions whose energy is less than 9.2 eV.[81] This value should be compared to a sum of calculated oscillator strengths for the $\pi \rightarrow 3p_x,3p_y$ and $\pi \rightarrow 3p_\pi$ transitions. This sum is 0.236 and 0.477 at the LDFT and NLDFT levels, respectively, with the cc-pVTZ + Rydberg basis set. These numbers are apparently significantly larger than the experimental value. However, the experimental number was determined by a decomposition of a measured spectrum to separate the contribution of the $\pi \rightarrow \pi^*$ transition and the

TABLE 6: Comparison of Present Calculated Transition Energies (eV) for Benzene with Other Calculated Values[a]

transition		SVWN/ cc-pVTZ + Rydberg[b]	B3LYP/ cc-pVTZ + Rydberg[c]	B3LYP/ aug-cc-pVTZ[17]	LSDA/ aug-cc-pVTZ[17]	HCTH(AC)/ 6-31G* + diffuse[18]	PEB0/ Sadlej+[15]	CC2/ aug-cc-pVTZ-CM2[87]
$^1B_{2u}$	$\pi \rightarrow \pi^*$	5.26	5.40	5.34	5.26	5.42	5.48	5.232
$^1B_{1u}$	$\pi \rightarrow \pi^*$	6.02	6.05	5.99	6.02	6.22	6.16	6.463
$^1E_{1u}$	$\pi \rightarrow \pi^*$	6.80	6.83			7.00	6.92	7.070
$^1E_{2g}$	$a_{1u} \rightarrow \pi^*$	8.80						8.909
Rydberg transitions								
$^1E_{1g}$	$\pi \rightarrow 3s$	6.03	6.01	6.01	6.19	6.10	6.32	6.452
$^1E_{2u}$, $^1A_{1u}$, $^1A_{2u}$	$\pi \rightarrow 3p_x,p_y$	6.51, 6.51 × 2, 6.53	6.48, 6.50 × 2, 6.55	6.51	6.80	6.81	6.82	6.970, 7.028 × 2, 7.120
$^1E_{1u}$	$\pi \rightarrow 3p_\pi$	7.10	7.09	6.54	6.80	7.35	7.14	7.319
$^1E_{1g}$, $^1B_{1g}$, $^1B_{2g}$	$\pi \rightarrow 3d$	7.03, 7.04, 7.04 × 2	7.06, 7.06, 7.07 × 2			7.48, 7.49, 7.49 × 2	7.48, 7.49, 7.49 × 2	7.557 × 2, 7.587, 7.600
$^1E_{2g}$, $^1A_{1g}$, $^1A_{2g}$	$\pi \rightarrow 3d$	7.32, 7.32 × 2, 7.34	7.32 × 2, 7.33, 7.36			7.66 × 2, 7.66, 7.69	7.65 × 2, 7.67, 7.70	7.798 × 2, 7.806, 7.829
$^1A_{2u}$	$a_{2u} \rightarrow 3s$	8.81						

[a] Values with "× 2" correspond to the transition energy for the degenerate transition. [b] Geometry optimization done at the MP2/cc-pVTZ level. [c] Geometry optimization done at the B3LYP/6-311G* level.

TABLE 7: Calculated Oscillator Strengths of Benzene[a]

transition		CIS		SVWN	B3LYP				
		DZ[b]	cc-pVTZ[c]	cc-pVTZ[c]	DZ[d]	TZVP[d]	cc-pVTZ[d]	EOM-CC[e]	expt
$^1E_{1u}$	$\pi \rightarrow \pi^*$	1.734	1.686	0.894	0.359	0.615	0.594	1.33	1.20,[88] 0.88,[89] 0.86,[90] 0.900 or 0.953,[81] 0.900[91]
Rydberg transitions									0.075[81,f]
$^1A_{2u}$	$\pi \rightarrow 3p_x,p_y$	0.080	0.076	0.027	0.045	0.046	0.044		
$^1E_{1u}$	$\pi \rightarrow 3p_\pi$	0.205	0.252	0.209	0.721	0.433	0.433		
$^1A_{2u}$	$a_{2u} \rightarrow 3s$	0.002	0.006	0.036	0.024	0.029			

[a] All basis sets for present work are augmented with Dunning-Hay Rydberg functions. [b] Geometry optimization done at the HF/6-31G* level. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] Geometry optimization done at the B3LYP/6-311G* level. [e] Ref 93; basis set is [5s3p2d/3s2p]. [f] An approximate value for all Rydberg transitions for $E < 9.2$ eV from a truncated spectrum.

TABLE 8: Calculated Transition Energies and Oscillator Strengths of Ethylene[a,b]

transition		SVWN/ TZVP[c]	SVWN/ TZVP (+H)[c]	SVWN/ cc-pVTZ (+H)[c]	B3LYP/ DZ[d]	B3LYP/ TZVP[d]	B3LYP/ cc-pVTZ[d]	EOM[95,e]	expt[89,94]
$^1B_{3u}$	$\pi \rightarrow 3s$	6.69 (0.068)	6.68 (0.065)	6.69 (0.065)	6.63 (0.068)	6.67 (0.071)	6.67 (0.071)	7.24 (0.033)	7.11 (0.04)
$^1B_{1g}$	$\pi \rightarrow 3p_\sigma$	7.24 (0.000)	7.21 (0.000)	7.18 (0.000)	7.15 (0.000)	7.21 (0.000)	7.19 (0.000)	7.91	7.80
$^1B_{1u}$	$\pi \rightarrow \pi^*$	7.45 (0.249)	7.45 (0.252)	7.43 (0.248)	7.54 (0.224)	7.42 (0.243)	7.44 (0.241)	7.89 (0.358)	~8.0 (0.29)
$^1B_{2g}$	$\pi \rightarrow 3p_\sigma$	7.18 (0.000)	7.18 (0.000)	7.18 (0.000)	7.13 (0.000)	7.18 (0.000)	7.16 (0.000)	7.95	7.90
^1A_g	$\pi \rightarrow 3p_\pi$	7.66 (0.000)	7.66 (0.000)	7.66 (0.000)	7.60 (0.000)	7.65 (0.000)	7.64 (0.000)	8.42	8.28
$^1B_{3u}$	$\pi \rightarrow 3d$	7.89 (0.002)	7.86 (0.000)	7.88 (0.000)	7.89 (0.001)	7.98 (0.000)	7.97 (0.006)	8.75 (0.079)	8.90 or 8.62
$^1B_{3u}$	$\pi \rightarrow 3d$	7.94 (0.017)	7.91 (0.019)	7.85 (0.021)	7.90 (0.030)	8.02 (0.023)	7.94 (0.024)	9.05 (0.0007)	8.90 or 8.62
$^1B_{2u}$	$\pi \rightarrow 3d$	7.99 (0.011)	7.97 (0.018)	7.92 (0.022)	7.96 (0.016)	8.07 (0.011)	8.00 (0.018)	9.23 (0.062)	9.05
$^1B_{1u}$	$\pi \rightarrow 3d$	8.05 (0.073)	8.06 (0.067)	8.01 (0.064)	8.15 (0.087)	8.19 (0.052)	8.15 (0.045)	9.28 (0.027)	9.33

[a] All basis sets are augmented with Dunning-Hay Rydberg functions. [b] Numbers not in parentheses are transition energies (eV), and numbers in parentheses are oscillator strengths. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] Geometry optimization done at the B3LYP/6-311G* level. [e] Basis set used: C, 4s3p2d ANO basis set with 2s2p1d diffuse functions; H, 3s2p ANO basis set. Excitation energies are those calculated at the EOM-CCSDT-3 level, and oscillator strengths are at the EOM-CCSD level (ref 95).

TABLE 9: Comparison of Present Calculated Transition Energies (eV) for Ethylene to Other Calculated Values

transition		SVWN/ cc-pVTZ(+H) + Rydberg[a]	B3LYP/ cc-pVTZ + Rydberg[b]	LDA/ aug-Sadlej (ref 20)	LB94/ Sadlej+ (ref 9)	BP/ aug-Sadlej (ref 14)	B3LYP/ Sadlej (ref 8)	PEB0/ Sadlej+ (ref 15)	HCTH(AC)/ Sadlej+ (ref 19)
$^1B_{3u}$	$\pi \rightarrow 3s$	6.69	6.67	6.65	7.84	6.62	6.61	6.93	7.16
$^1B_{1g}$	$\pi \rightarrow 3p_\sigma$	7.18	7.19	7.23		7.17	7.19	7.51	7.78
$^1B_{1u}$	$\pi \rightarrow \pi^*$	7.43	7.44	7.47		7.40	7.36	7.58	7.61
$^1B_{2g}$	$\pi \rightarrow 3p_\sigma$	7.18	7.16	7.21		7.11	7.17	7.52	7.77
^1A_g	$\pi \rightarrow 3p_\pi$	7.66	7.64	8.24		8.12	8.19	8.04	8.33
$^1B_{3u}$,$^1B_{3u}$	$\pi \rightarrow 3d$	7.85, 7.88	7.94, 7.97					8.65, 8.76	8.70, 8.95
$^1B_{2u}$	$\pi \rightarrow 3d$	7.92	8.00					9.02	9.04
$^1B_{1u}$	$\pi \rightarrow 3d$	8.01	8.15					9.33	9.32

[a] Geometry optimization done at the MP2/cc-pVTZ level. [b] Geometry optimization done at the B3LYP/6-311G* level.

Rydberg transitions to the total oscillator strength. Thus, the sum of the experimental oscillator strengths for the $\pi \rightarrow \pi^*$ and the Rydberg transitions should be a more reliable number in terms of comparison to experiment. By using the experimental values in ref 78, the sum is 0.975−1.028. The sum from our calculation is 1.130 and 1.071 at the LDFT and NLDFT levels, respectively, with the cc-pVTZ + Rydberg basis set. Thus, our calculated sums are in excellent agreement with experiment with the LDFT value being slightly too large.

Ethylene. Our calculated transition energies and oscillator strength of ethylene are reported in Table 8 together with available experimental values.[77,89,92,94] In Table 8, we also list theoretical values at the highly correlated EOM-CCSDT-3 level.[95] In Table 9, our calculated values are compared to previously obtained TD-DFT values.[8,9,14,15,19,20] The LDFT and NLDFT values exhibit almost no basis set dependence with the differences being on the order of 0.1 eV. This is further supported by the values of the linear correlation coefficients shown in Table 3. The coefficients are essentially the same with respect to each other at the LDFT level. At the NLDFT level, the coefficients are essentially the same with the TZVP + Rydberg and cc-pVTZ + Rydberg basis set, whereas the coefficient at the DZ + Rydberg basis set is slightly smaller than the other two. This again shows that the DZ based basis set is probably too small for the proper description of the excited states.

The LDFT values are, again, smaller than the experimental values by 0.4 to 1.3 eV. This difference between theory and experiment increases when the transition energy becomes large. For example, for the $\pi \rightarrow 3s$ transition [$^1B_{3u}$, 7.11 eV (expt)], the difference is ~0.4 eV, whereas for the $\pi \rightarrow 3d$ transition [$^1B_{1u}$, 9.33 eV (expt)], the difference is 1.3 eV. The deterioration of the agreement between theory and experiment is due, in part, to the incorrect asymptotic behavior of exchange-correlation potential which leads to occupied orbital energies that are too low.[9] At the NLDFT level, the difference between theory and experiment is slightly reduced for the $\pi \rightarrow 3d$ transitions, whereas for the other transitions, there is essentially no difference between the LDFT and NLDFT calculated values. Consequently, the linear correlation coefficients in Table 3 for ethylene are slightly closer to unity at the NLDFT level than at the LDFT level.

Our calculated transition energies at the B3LYP/cc-pVTZ + Rydberg level are essentially the same as those obtained at the LDA/aug-Sadlej,[20] LB94[70]/Sadlej+,[9] BP[71,72]/aug-Sadlej,[14] and B3LYP/ Sadlej[8] levels except for the $\pi \rightarrow 3p_\pi$ transition. For this transition, the values calculated by others are larger than our values and are closer to the experimental value. As found

TABLE 10: Calculated Transition Energies and Oscillator Strengths of Methane[a,b]

transition		SVWN/ TZVP[c]	SVWN/ TZVP(+H)[c]	SVWN/ cc-pVTZ(+H)[c]	B3LYP/ cc-pVTZ[c]	B3LYP/ cc-pVTZ(+H)[c]	expt
$T_2 \rightarrow A_1$	$T_2 \rightarrow 3s$	9.27 (0.28)	9.22 (0.24)	9.25 (0.27)	9.67 (0.28)	9.66(0.28)	9.7 and 10.4[96,97] (0.26,[99] 0.277[100])
$T_2 \rightarrow T_2$	$T_2 \rightarrow 3p$	10.16 (0.02)	10.09 (0.01)	10.07 (0.01)	10.61 (0.02)	10.57(0.02)	10.90 ($T_2 \rightarrow 3p$)[96,d]
$T_2 \rightarrow T_2$	$T_2 \rightarrow 3p$	10.14, 10.19, 10.42 (0.00)	10.08, 10.11, 10.25 (0.00)	10.06, 10.10, 10.24 (0.00)	10.61, 10.64, 10.94 (0.00)	10.57, 10.60, 10.82(0.00)	
$T_2 \rightarrow T_2$	$T_2 \rightarrow 3d$	10.58 (0.08)	10.57 (0.04)	10.53 (0.05)	11.19 (0.08)	11.17(0.05)	12 ($T_2 \rightarrow 3d$)[96,d]
$T_2 \rightarrow T_2$	$T_2 \rightarrow 3d$	10.55, 10.56, 10.58 (0.00)	10.54, 10.55, 10.57 (0.00)	10.50, 10.50, 10.52 (0.00)	11.14, 11.17, 11.18 (0.00)	11.12, 11.14, 11.16(0.00)	
$T_2 \rightarrow E$	$T_2 \rightarrow 3d$	10.61 (0.04)	10.60 (0.07)	10.58 (0.05)	11.23 (0.07)	11.22(0.09)	
$T_2 \rightarrow T_2$		14.97 (0.46)	11.81 (0.32)	11.66 (0.26)		12.19(0.27)	
$T_2 \rightarrow A_1$		14.64 (0.23)	11.50 (0.11)	13.23 (0.15)		13.69(0.15)	
$T_2 \rightarrow T_2$		15.79 (2.08)	14.41 (0.30)	13.73 (0.13)		14.24(0.15)	
other observed peaks							11.7 ($T_2 \rightarrow 4s$), 13.7, 14.7, 16.5[96,98]

[a] All basis sets are augmented with Dunning-Hay Rydberg functions. [b] Numbers not in parentheses are transition energies (eV), and numbers in parentheses are oscillator strengths. Beyond the first few peaks, only allowed transitions are given. [c] Geometry optimization done at the MP2/cc-pVTZ level. [d] From electron impact measurements.

for the formaldehyde and benzene, the PBE0[73]/Sadlej+,[15] and HCTH(AC)[74]/Sadlej+,[19] values are, again, larger than our calculated values and are in somewhat better agreement with the experimental values. Comparison of our TD-DFT values with the EOM-CCSDT-3[95] values shows that our calculated values are too low by 0.5−1.0 eV.

For the oscillator strengths, the effect of the basis set and functional becomes more enhanced when the transition energy becomes large, i.e., for the $\pi \rightarrow 3d$ transitions. For the other transitions (i.e., the $\pi \rightarrow 3s$ and $\pi \rightarrow \pi^*$ transitions), the dependence on the basis set and functional is not pronounced. For the $\pi \rightarrow 3s$ transition, the differences due to the basis set are less than 0.003 at both the LDFT and NLDFT levels. For this transition, the NLDFT values are slightly larger than the LDFT values, although the difference between the LDFT and NLDFT levels is less than 0.006. For the $\pi \rightarrow \pi^*$ transition, the variation of the LDFT values is less than 0.003, whereas at the NLDFT level, it is 0.019. This larger variance at the NLDFT level is caused by the presence of the DZ + Rydberg calculated value. The calculated value at this level is smaller by 0.019 than that at the TZVP level, showing that the DZ basis set is again too small.

Our calculated oscillator strength for the $\pi \rightarrow \pi^*$ transition is ∼0.24 both at the LDFT and NLDFT level with the cc-pVTZ based basis set. This value is in agreement with the experimental value of 0.29 obtained by Hammond et al.,[86] and our values are slightly smaller than the experimental value. The EOM-CCSD value is 0.358, so that our calculated values are, again, smaller than the EOM value. An experimental value of 0.04 for the $\pi \rightarrow 3s$ transition can be compared to our calculated values of ∼0.07. and to an EOM-CCSD value of 0.033. The experimental values reported by Hammond et al.[86] are the oscillator strength for the $\pi \rightarrow \pi^*$ transition (0.29) and the sum of the oscillator strengths for the $\pi \rightarrow \pi^*$ and $\pi \rightarrow 3s$ transitions (0.33), as these two peaks are overlapped. Thus, an error may be present when their measured spectrum was decomposed in order to separate the two transitions and the sum should be more reliable for comparison to our calculated numbers. The sum from our calculation is 0.313 and 0.312 at the LDFT and NLDFT level, respectively, with the cc-pVTZ based basis sets, in excellent agreement with the experimental value of 0.33 as well as with the EOM-CCSDT-3 sum of 0.39. Comparing the oscillator strengths at the TD-DFT and EOM-CCSDT-3 levels for the $\pi \rightarrow 3d$ transitions shows larger differences than for the lower energy transitions and we note that there are reversals in the ordering of the various states.

Methane. Our calculated transition energies and oscillator strengths for methane are given in Table 10 together with the available experimental values.[77,96−100] At the LDFT level, the calculated energies for the $T_2 \rightarrow 3s$, 3p, and 3d transitions do not depend on the basis set, whereas for other higher energy transitions, a basis-set dependence is observed. The NLDFT values are, again, larger than the LDFT values. Experimental values for methane are somewhat limited, in part due to the significant overlap of the broad absorption peaks. There are two different assignments for the two peaks located at 9.7 and 10.4 eV.[96,97] One of them is that the two broad bands at 9.7 and 10.4 eV are attributed to the two Jahn−Teller components of the $T_2 \rightarrow 3s$ transition [$T_2 \rightarrow 3s$ (C_{2v}) and $T_2 \rightarrow 3s$ (C_{3v})].[96] The other assignment is that the $T_2 \rightarrow 3s$ (C_{2v}) transition is responsible for the broad underlying continuum starting from ∼8.63 eV and the $T_2 \rightarrow 3s$ (C_{3v}) transition for the two weak undulatory peaks of 9.7 and 10.4 eV.[97] Our calculated value is closer to the lower of the two experimental values. The experimental value for the transitions of $T_2 \rightarrow 3p$ and $T_2 \rightarrow 3d$ are 10.90 and 12 eV, and again, our calculated values are too small, consistent with the above results for the other molecules that we studied. We note that the transitions for CH_4 are somewhat sensitive to the basis set and for transitions above 12 eV, significant differences in the number of allowed transitions are found if diffuse functions are not included in the basis set.

For the $T_2 \rightarrow 3s$, $T_2 \rightarrow 3p$, and $T_2 \rightarrow 3d$ Rydberg transitions, the calculated values of the oscillator strength do not depend on the basis set and functional, whereas for the other transitions, there is a significant dependence of the calculated values. The experimental value of oscillator strength is only available for the $T_2 \rightarrow 3s$ transition, and our calculated value is in good agreement with the experimental value, with our calculated values being slightly larger than the experimental values. This is somewhat different from the cases of the other molecules where our calculated values are smaller than the experimental values. We note that although no TD-DFT results have been previously reported for methane, a value of 0.129 was calculated at the MRCI+D(8,8)/aug-pVTZ level.[97] Our TD-DFT value is in better agreement with experiment.

Differences between TD-DFT and Experiment. It has been shown that the energy of the highest occupied molecular orbital (HOMO) calculated at the DFT level is usually too low as compared to the ionization potential of an atom or molecule.[101−105] This is because of the incorrect asymptotic behavior of typical exchange-correlation potentials.[19,103−105] This is the reason an asymptotically corrected functional was developed by Handy et al.,[19] and why the mixing of DFT and HF exchange and correlation was proposed by Scuseria et al. (PBE0 potential; PBE: Perdew-Burke-Erzenrhof)[15] for the accurate prediction

TABLE 11: Calculated and Experimental Ionization Potentials (eV)[a]

molecule	method	ionization potential
CH_2O	SVWN/cc-pVTZ(+H) + Rydberg	6.32
	B3LYP/cc-pVTZ + Rydberg	7.63
	expt	10.87
C_6H_6	SVWN/cc-pVTZ + Rydberg	6.53
	B3LYP/cc-pVTZ + Rydberg	7.07
	expt	9.25
C_2H_4	SVWN/cc-pVTZ(+H) + Rydberg	6.94
	B3LYP/cc-pVTZ + Rydberg	7.66
	expt	9.25
CH_4	SVWN/cc-pVTZ(+H) + Rydberg	9.48
	B3LYP/cc-pVTZ + Rydberg	10.75
	expt	12.51

[a] Calculated ionization potentials (IP) taken as the negative of the highest occupied molecular orbital (HOMO) energy. Experimental IP's from the NIST Webbook, http://webbook.nist.gov/.

of transition energies. It has been found, that if the self-interaction correction (SIC) is included, the HOMO energies are now in good agreement with Hartree−Fock orbital energies and consequently by use of Koopmanns' theorem in good agreement with experiment.[103−105] It has been shown that there is a linear relationship between the orbital energies calculated at the LDFT level and with those calculated with SIC. In addition, these studies have shown that the energy difference $\epsilon_{LUMO} - \epsilon_{HOMO} = GAP$ calculated at the DFT level is a good approximation to the first excitation energy, especially if the SIC is included.[103−105] Given the fact that the calculated HOMO energies are too low as compared to experiment as shown in Table 11, one would expect that the excited states would be compressed into too low a range consistent with the fact that the TD-DFT states are too low as compared to the experimental states. What is surprising is that the error in the calculated IP's ranges from 2.3 eV too low to 4.5 eV too low at the LDFT level and 1.6−3.2 eV too low at the NLDFT level. Yet even for the highly excited states near the region of 8−10 eV which are important for materials design, the TD-DFT method is making errors on the order of only 1 eV at the NLDFT level. The fact that the NLDFT values are in better agreement with experiment is consistent with the better orbital eigenvalues at this level.

Conclusions

Time-dependent density functional theory (TD-DFT) calculations of the transition energies and oscillator strengths of formaldehyde, benzene, ethylene, and methane molecules have been performed. The LDFT transition energies tend to be smaller than experimental values by 0.1−1.3 eV. Inclusion of nonlocal effects tends to make the calculated energies larger than the LDFT values and in better agreement with the experimental values for the formaldehyde, ethylene and methane (the difference between the NLDFT calculations and experiment is less than 1.0 eV for these molecules). For benzene, no significant change in the calculated transition energies due to the addition of nonlocal effects was observed.

To predict photoabsorption spectra for practical applications, good correlations between the calculated and experimental values are needed. A single correlation plot was made for all of the calculated peaks of formaldehyde, benzene, and ethylene, and the result is shown at the bottom of Table 3. From the linear correlation coefficients in Table 3, it can be concluded that the use of a gradient-corrected exchange-correlation functional significantly improves the correlation, whereas the use of larger basis set does not improve the correlation as much. We note that if equations such as those in Table 3 hold empirically for other molecules, then such equations can be applied to the actual prediction of photoabsorption spectra to further design materials of interest. In addition, such linear, empirical relations may exist due to the need to correct the long-range asymptotic behavior of most currently used exchange-correlation potentials.

A dramatic improvement in the predicted oscillator strengths as compared to the CIS level was found at the TD-DFT level. The agreement between our TD-DFT values and the experimental values is quantitative or at least semiquantitative at both the LDFT and NLDFT levels, although the calculated values tend to be smaller than the experimental values.

Acknowledgment. This research was performed in part under the management of the Association of Super-Advanced Electronics Technologies (ASET) as part of the Ministry of International Trade and Industry (MITI) Program of Super-Advanced Electronics Technologies supported by the New Energy and Industrial Technology Development Organization (NEDO). This research was supported in part by the U.S. Department of Energy (Office of Biological and Environmental Research, Office of Science) under Contract DE-AC06-76RLO 1830. This research was performed in part using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory. The MSCF is funded by the Office of Biological and Environmental Research in the U.S. Department of Energy. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute. Part of the calculations in this article were performed on the JRCAT (Joint Research Center for Atom Technology) supercomputer system, which is also supported by NEDO. The authors would like to thank Mr. H. Setoya (ASET), Dr. S. Okazaki (ASET), Prof. K. Tanaka [JRCAT and National Institute for Advanced Interdisciplinary Research (NAIR)], and Prof. C. G. Willson (University Texas at Austin) for their useful discussions.

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