J. Phys. Chem. A **2001,** *105,* 451−458

Excitation Energies from Time-Dependent Density Functional Theory for Linear Polyene Oligomers: Butadiene to Decapentaene

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Received: July 6, 2000; In Final Form: October 19, 2000

Time-dependent density functional theory (TDDFT) is applied to calculate vertical excitation energies of *trans*-1,3-butadiene, *trans*−*trans*-1,3,5-hexatriene, all-*trans*-1,3,5,7-octatetraene, and all-*trans*-1,3,5,7,9-decapentaene. Attachment and detachment densities for transitions in butadiene and decapentaene from the ground state to the 2 ^1A_g and 1 ^1B_u excited states are also calculated and analyzed. Based on comparisons with experimental results and high level ab initio calculations in the literature, significant improvement over configuration−interaction singles is observed for the 2 ^1A_g state of the polyenes, which has been known to have significant double excitation character. For the 1 ^1B_u state, TDDFT underestimates the excitation energy by 0.4−0.7 eV. In this case we have observed a significant difference between the results for TDDFT and TDDFT within the Tamm−Dancoff approximation, both in excitation energies and, at least for butadiene, in the character of the excited state.

1. Introduction

All-trans polyene molecules have been an interesting class of systems for both experimental and theoretical reasons. Their photochemistry is related to many important biochemical functions. The structure and state ordering of the lowest singlet excited state have been interesting topics in photochemistry and in electronic structure theory. At the Hückel level of theory, it was believed that the lowest singlet excited state for polyenes was of B_u symmetry (in the C_{2h} point group). This B_u state is essentially a single excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in a configuration interaction (CI) picture. However, later experiments and theoretical calculation showed that for polyenes longer than three double bonds, the lowest singlet excited state is a one-photon forbidden state, 2 ^1A_g, instead of the dipole-allowed 1 ^1B_u state.[1−3] The major configurations for the 2 ^1A_g state are a double excitation from HOMO to LUMO and two other single excitations.[4] Semiempirical calculations showed that the high degree of electron−electron correlation made the forbidden 2 ^1A_g state lower in energy than the strongly allowed 1 ^1B_u state.[4,5,6]

Accurate ab initio calculations on the electronic structure of moderate-sized polyenes have become feasible in the past decade. Calculations using the complete active space self-consistent-field (CASSCF) method plus a second-order perturbation correction (CASPT2) suggested that the vertical transition to the 2 ^1A_g state is above the 1 ^1B_u state for *trans*-butadiene and hexatriene, and for octatetraene this ordering is reversed.[7,8] A multireference Møller−Plesset (MRMP) study[9] obtained similar results, except that for hexatriene the two states are virtually degenerate at the ground state geometry. The state ordering of 2 ^1A_g and 1 ^1B_u for polyenes is still a rather challenging problem in electronic structure calculations. As noted by Nakayama et al.,[9] a correct treatment of the 1 ^1B_u state includes a $\sigma-\pi$ dynamic polarization effect which is not as significant for the 2 ^1A_g state of polyenes. In ref 7, the authors pointed out that the 1 ^1B_u state appears to have some (artificial) valence-Rydberg mixing in the CASSCF reference function, leading to difficulty in calculating its excitation energy with perturbation methods. In light of these considerations, it appears that these two contrasting excited states of polyenes have offered a challenging test for time-dependent density functional theory (TDDFT), a recently developed tool for calculating excitation energies.

TDDFT has been developed and formulated for a variety of purposes.[10−13] For calculating excitation energies,[14−18] the computational cost and complexity of TDDFT is roughly comparable to single excitation theories based on a Hartree−Fock ground state, such as single excitation CI (CIS) or the random phase approximation (RPA). At the same time, excitation energies to valence excited states are considerably improved,[15−18] and there is even significant improvement for excitation energies of excited states that, when treated by wave function-based methods, have appreciable double-excitation character.[19,20]

In the present work, we report excitation energies for the low lying excited states for *trans*-1,3-butadiene (butadiene), *trans*-*trans*-1,3,5-hexatriene (hexatriene), all-*trans*-1,3,5,7-octatetraene (octatetraene), and all-*trans*-1,3,5,7,9-decapentaene (decapentaene) using TDDFT. Our work explores the validity of applying TDDFT, with standard exchange-correlation functionals, to the study of these states of polyenes and related molecules.

2. Calculations

The fundamental theorems of TDDFT were developed in 1984.[10] The time-dependent density-functional response theory (TD-DFRT) was later formulated and offers a formally exact theory for calculating excitation energies.[12,14] The detailed formalism for TDDFT excitation energies can be found in refs

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10.1021/jp0024367 CCC: \$20.00

TABLE 1: Basis Set Dependence of Vertical Excitation Energies (in eV) of *trans*-Butadiene Calculated by TDDFT/TDA and TDDFT Using the BLYP Functional at the B3LYP/6-311(2+,2+)G Optimized Ground State Geometry**

	TDDFT/TDA/BLYP					TDDFT/BLYP				
state	6-31G	6-31G**	6-31++G**	6-311++G**	6−311(2+,2+)G**	6-31G	6-31G**	6-31++G**	6-311++G**	6-311(2+,2+)G**
					Triplet States					
1 ^3B_u	3.26	3.23	3.20	3.22	3.22	3.07	3.03	3.02	3.04	3.04
1 ^3A_g	5.41	5.33	5.21	5.21	5.21	5.26	5.17	5.07	5.07	5.07
					Singlet States					
2 ^1A_g	6.62	6.56	6.11	6.12	6.02	6.61	6.54	6.10	6.11	6.01
3 ^1A_g	9.61	9.43	7.58	7.61	6.39	8.91	8.75	7.37	7.39	6.39
4 ^1A_g	11.02	10.99	8.03	8.06	6.60	11.00	10.97	8.02	8.05	6.59
1 ^1A_u	6.96	6.89	5.58	5.67	5.50	6.96	6.88	5.58	5.67	5.50
2 ^1A_u	7.80	7.80	5.63	5.71	5.51	7.80	7.80	5.63	5.71	5.51
1 ^1B_g	8.02	7.91	5.33	5.41	5.26	8.01	7.91	5.33	5.41	5.25
2 ^1B_g	8.13	8.11	6.47	6.53	6.03	8.13	8.10	6.47	6.53	6.03
1 ^1B_u	6.63	6.53	5.83	5.86	5.64	5.96	5.86	5.42	5.43	5.37
2 ^1B_u	10.69	10.52	7.52	7.47	6.36	10.34	10.17	7.34	7.31	6.12
3 ^1B_u	11.03	10.98	8.29	8.32	6.85	10.97	10.93	8.28	8.32	6.85

TABLE 2: Calculated and Observed Vertical Excitation Energies (in eV) and Oscillator Strengths (in parentheses) for *trans*-Butadiene[n]

states	B3LYP′[a]	B3LYP	BLYP′	BLYP	SVWN′	SVWN	CIS	CASPT2[b]	MRMP[c]	EOM-CCSD($\tilde{T}$)[d]	expt
						Triplet States					
1 ^3B_u	3.18	2.83	3.22	3.04	3.39	3.30	2.65	3.20	3.20		3.22[e]
1 ^3A_g	5.12	4.89	5.21	5.07	5.45	5.37	4.35	4.89	4.87		4.91[e]
						Singlet States					
2 ^1A_g V[f]	6.48	6.46	6.02	6.01	6.19	6.18	7.23	6.27	6.31	6.76	
3 ^1A_g R	6.83	6.83	6.39	6.39	6.90	6.89	7.49	7.47		7.53	7.48[g,h]
4 ^1A_g R	7.12	7.10	6.60	6.59	7.01	6.99	8.31			7.50	
1 ^1A_u R	5.88	5.88	5.50	5.50	5.95	5.95	6.49	6.56		6.41	6.66[g,i]
2 ^1A_u R	5.94	5.94	5.51	5.51	6.00	6.00	6.65	6.69		6.56	6.80[g,i]
1 ^1B_g R	5.63	5.63	5.26	5.25	5.72	5.71	6.16	6.29		6.19	6.27[g]
2 ^1B_g R	6.49	6.49	6.03	6.03	6.50	6.50	7.26	7.30		7.27	7.28,[g] 7.33[j]
1 ^1B_u V	5.90	5.59	5.64	5.37	5.92	5.51	6.22	6.23	6.21	6.13	5.92[g]
	(0.623)	(0.593)	(0.426)	(0.511)	(0.667)	(0.592)	(0.899)	(0.686)[k]	(0.803)	(0.651)[l]	(0.4)[m]
2 ^1B_u R	6.63	6.47	6.36	6.12	6.70	6.55	7.02	6.70		7.03	7.07[g]
	(0.365)	(0.084)	(0.496)	(0.496)	(0.119)	(0.258)	(0.046)	(0.080)		(0.113)	
3 ^1B_u R	7.31	7.30	6.85	6.85	7.37	7.37	8.10	7.79		7.87	8.00[g]

[a] The prime on the functional acronym indicates the use of the Tamm−Dancoff approximation. [b] Reference 7. [c] Reference 9. [d] Reference 41. [e] References 42, 43, 44. [f] V (or R) indicates that the excited states are principally valence (Rydberg) character, following the assignments in ref 7. [g] Reference 36. [h] References 45, 46. [i] Reference 47. [j] Ref 44. [k] CASSI results reported in ref 7. [l] EOM-CCSD results reported in ref 41. [m] Reference 48. [n] The CIS, TDDFT, and TDDFT/TDA calculations are performed using the 6-311(2+,2+)G** basis set at the B3LYP/6-311(2+,2+)G** optimized geometry at the ground state.

12, 14, 16, 18, so it is not repeated here. In the present work, we use the acronym "TDDFT" to represent results obtained by solving for the poles of the density−density response function (eq 1) of ref 20, for example. Our current work involves the adiabatic approximation (e.g., 12, 16) and the use of approximate exchange-correlation functionals.

The Tamm−Dancoff approximation to TDDFT (TDDFT/TDA)[21] is also employed in the present study. The use of the this method is indicated in tables by primes on the acronyms for the exchange-correlation functionals. The TDA was proposed as a simple approximation to TDDFT by realizing that within TDDFT, most of the excitation processes were simple transitions of an electron from an occupied orbital to an unoccupied orbital. This suggested that the so-called B matrix in the TDDFT formulas played a very minor role in the final excitation energies. This observation may be a pragmatic justification for the use of this approximation, as we can expect that it will not change the excitation energies significantly from the original TDDFT values. This is generally true, as has already been demonstrated.[21] As will be shown shortly, TDDFT and TDDFT/TDA excitation energies for the polyene oligomers studied here also usually agree with each other to within a small fraction of an electronvolt. There are occasional rare exceptions where the differences are larger. The only one of significance here, as will be discussed in detail later, is the optically allowed valence 1 ^1B_u state.

All of the calculations were performed with a development version of the Q-Chem quantum chemistry program[22] running on IBM RS/6000 workstations. All ground-state molecular geometries used in our calculations were optimized at the B3LYP/6-31G** (or larger basis set), assuming C_{2h} symmetry. The basis set dependence of excitation energies was studied for butadiene using TDDFT and TDDFT/TDA and the BLYP functional. The basis sets compared include 6-31G, 6-31G**, 6-31++G**, 6-311++G**, and 6−311(2+,2+)G**. The results are listed in Table 1. Comparison of the vertical excitation energies and the oscillator strengths calculated with the CIS, TDDFT, and TDDFT/TDA methods (with Slater−Vosko−Wilk−Nusair (SVWN),[23,24] Becke−Lee−Yang−Parr (BLYP)[25,26] and Becke3−Lee−Yang−Parr (B3LYP)[27] exchange-correlation functionals) are listed in Table 2, using a large basis set (6−311(2+,2+)G**). To quantify the spatial extent of the excited states of butadiene, the values of $\langle z^2 \rangle$, where z is the coordinate perpendicular to the molecular plane, are listed in Table 3, and they are discussed in the following section. For hexatriene, octatetraene, and decapentaene, only the 6-31++G**

TABLE 3: Calculated $\langle z^2 \rangle$ (in a.u.^{2}) for *trans*-Butadiene where z is the Coordinate Perpendicular to the Molecular Plane in Comparison with Other Results in the Literature

states	B3LYP′[a]	B3LYP	BLYP′	BLYP	SVWN′	SVWN	CIS	CASSCF[b]	EOM-CCSD[c]
ground state		21.8		21.8		22.0	22.3	21.9	22.1
triplet states									
1 ^3A_g	22.7	22.4	23.2	22.9	23.1	22.9	22.5	22.0	
1 ^3B_u	22.0	21.8	22.0	21.9	22.2	22.1	22.2	21.8	
singlet states									
2 ^1A_g	42.6	42.3	38.1	38.0	27.6	27.6	54.1	23.2	36.1
3 ^1A_g	76.8	76.5	77.1	76.8	77.8	76.8	75.2	94.8	107.1
4 ^1A_g	59.3	57.4	64.3	63.0	71.5	69.4	58.3		78.2
1 ^1A_u	32.9	32.9	34.7	34.7	33.6	33.6	32.5	36.2	32.5
2 ^1A_u	38.1	38.0	40.1	40.0	39.8	39.8	36.7	40.1	36.9
1 ^1B_g	41.9	41.9	43.7	43.8	48.0	48.0	36.8	50.6	41.4
2 ^1B_u	42.6	42.6	45.3	45.3	48.0	48.0	36.8	50.6	41.4
1 ^1B_u	40.5	28.8	50.3	32.4	36.3	26.6	32.3	40.9	31.7
2 ^1B_u	64.4	73.0	56.9	70.7	68.9	75.4	68.6	88.9	88.2

[a] The prime on the functional acronym indicates the use of the Tamm-Dancoff approximation. [b] Reference 7. [c] Reference 41.

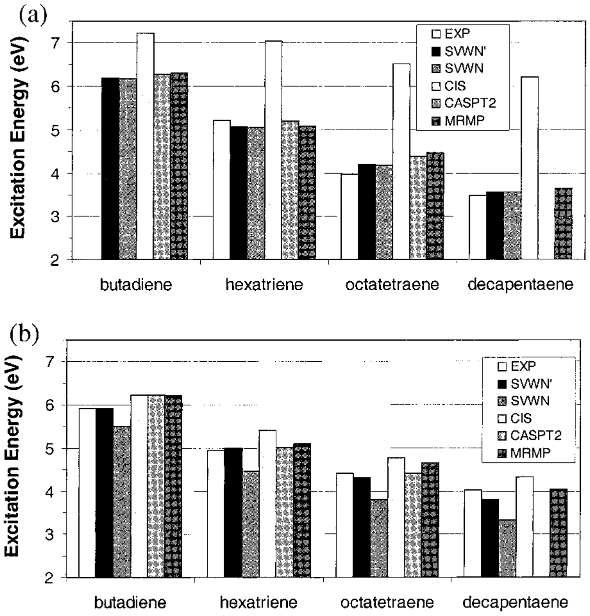


Figure 1. Excitation energies plotted against chain length for the polyenes studied in the present work. (a) results for the 2 ^1A_g state (b) 1 ^1B_u state.

basis is used, and their excitation energies are listed in Tables 4−6. In Figure 1 we summarize the excitation energies for the 2 ^1A_g and 1 ^1B_u states across the series of molecules studied here.

Attachment and detachment densities are calculated for transition from the ground state to 2 ^1A_g and 1 ^1B_u states of butadiene and decapentaene using a scheme described in ref 28. The detachment density describes the removal of charge from the initial state and the attachment density represents the added charge distribution for the new arrangement in the excited state. Such attachment and detachment densities have been shown to provide useful insights in electronic transitions of molecules.[28−31] The contour surfaces enclosing 90% of the electronic densities are plotted in Figures 2−5. In these figures, results from CIS, TDDFT/TDA, and full TDDFT calculations are plotted.

3. Results and Discussion

A large amount of work has been devoted to both experimental and theoretical studies of small polyenes. Many of them are briefly reviewed and discussed in refs 2, 7, and 9. In the following sections we will focus on comparison of our results with experiments and CASPT2, MRMP, and CCSD($\tilde{T}$) calculations.

3.1. Butadiene. In Table 1 we list the basis-set dependence of the excitation energies for butadiene using the BLYP functional. From the results we conclude that the addition of one set of diffuse functions is essential to obtain converged excitation energies for valence states (2 ^1A_g and 1 ^1B_u). There is an exception, however, for the case of 1 ^1B_u state with TDDFT/TDA, which will be discussed in section 3.1.2. For all other states, which have been assigned as Rydberg states in ref 7, the second set of diffuse functions reduced the excitation energy by about 0.2 eV to 1.5 eV. While it may be desirable to find and use a basis set that is fully converged for all of the states listed, it has been concluded that current standard functionals cannot properly treat Rydberg states, since the asymptotic behavior of the exchange-correlation potentials is not correct.[32−34] In the present work, we have used the 6−311-(2+,2+)G** basis set for butadiene to capture all of the possible (artificial) Rydberg character of the 1 ^1B_u and 2 ^1A_g states and to sketch a rather primitive and general trend of the Rydberg states. For hexatriene and larger molecules, the basis set 6-31++G** is used, and for these larger systems we limit our discussion to valence states lying below the Rydberg threshold.

3.1.1. The 2 ^1A_g State. The 2 ^1A_g state of polyenes is known to have significant double excitation character and therefore cannot be properly described by single excitation theories such as CIS. It is then a challenging test of the extent to which TDDFT can describe states with bielectronic character. Our results show that TDDFT calculations give a significantly lower excitation energy, compared to CIS. For this 2 ^1A_g state, the TDDFT/TDA and TDDFT results are quite similar. The excitation energies fall between 6.01 eV to 6.48 eV as listed in Table 2. To the best of our knowledge there is not yet a reliable experimental value for the vertical excitation energy for this state. We therefore compare our results with other accurate ab intitio calculations. From Table 2, our results for the 2 ^1A_g state agree well with CASPT2[7] and MRMP[9] calculations, with <0.3 eV difference. By contrast, the CIS excitation energy deviates from other calculations by almost 1 eV.

One of the major failures of CIS for the 2 ^1A_g state of butadiene is the false Rydberg character of the excited state.[35] The CIS attachment density shown in Figure 2g is indeed diffusive and resembles an atomic *d* orbital. The same analysis for the TDDFT/TDA and TDDFT results shows a less diffusive attachment density for the new charge distribution in the excited

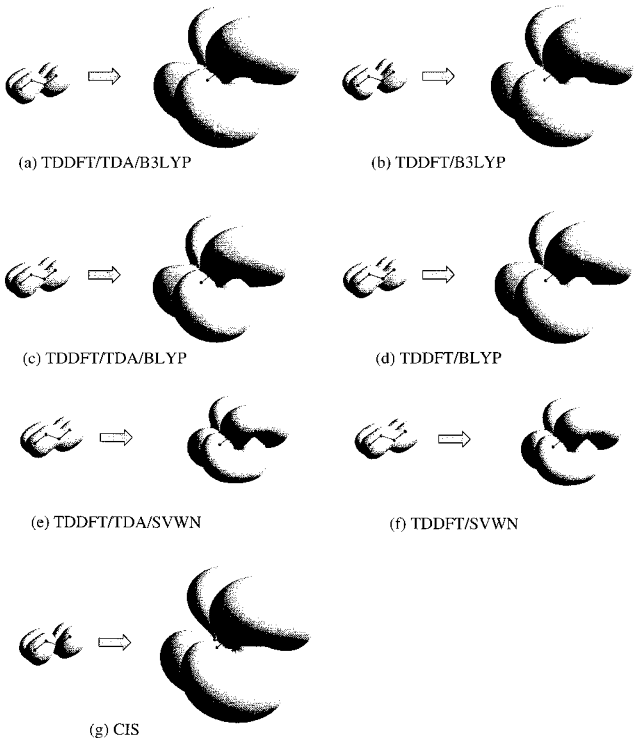

(a) TDDFT/TDA/B3LYP
(b) TDDFT/B3LYP
(c) TDDFT/TDA/BLYP
(d) TDDFT/BLYP
(e) TDDFT/TDA/SVWN
(f) TDDFT/SVWN
(g) CIS

Figure 2. The attachment and detachment densities for the transition 1 ^{1}Ag → 2 ^{1}A$_g$ of *trans*-butadiene with the following calculation methods and exchange-correlation functionals: (a) TDDFT/TDA/B3LYP, (b) TDDFT/B3LYP, (c) TDDFT/TDA/BLYP, (d) TDDFT/BLYP, (e) TDDFT/TDA/SVWN, (f) TDDFT/SVWN, (g) CIS. All excited-state calculations were performed with 6-311(2+,2+)G** basis set at the B3LYP/6−311(2+,2+)G** optimized ground-state geometry. The detachment densities are plotted to the left of the arrows and the attachment densities, to the right. All densities are plotted by contour surfaces that enclose 90% of the total densities.

state. According to the contour surfaces, this result is quite independent of the Tamm−Dancoff approximation. However, in this case we observe significant differences between the B3LYP, BLYP, and SVWN functionals. Calculations using SVWN yield the least diffusive (most valence-like) attachment densities.

We have also calculated the expectation value of z^2 for each of the excited states, where z is the distance perpendicular to the molecular plane. The quantity $\langle z^2\rangle$ can be regarded as an indication of the extent of Rydberg character of the wave function.[7] In Table 3, the $\langle z^2\rangle$ is reduced from 54.1 (atomic units) for CIS, to about 28, 38, and 42 for calculations using SVWN, BLYP and B3LYP, functionals, respectively. As observed already, TDDFT/TDA and TDDFT yield similar results. The $\langle z^2\rangle$ values of our TDDFT or TDDFT/TDA calculations with the SVWN functional are close to that of the ground state, indicating a valence state, and this result is quite close to that of CASSCF calculations.

3.1.2. The 1 ^1B_u State. The 1 ^{1}B$_u$ state has received a lot of attention in the literature. It has a large transition dipole moment so that it is easily accessible through optical excitation in experiments.

The SVWN functional with TDDFT yields an excitation energy of 5.51∼eV for the 1 ^{1}B$_u$ state. Compared to the experimental value of 5.92 eV,[36] our result underestimates the excitation energy by 0.41 eV. This error is slightly larger than is sometimes obtained using TDDFT, although it is still within error ranges reported before.[32,33] On the other hand, the results using TDDFT/TDA agree quite well with experiments. Similar disagreement is observed when TDDFT is compared to results from CASPT2 and EOM-CCSD($\tilde{\mathrm{T}}$).

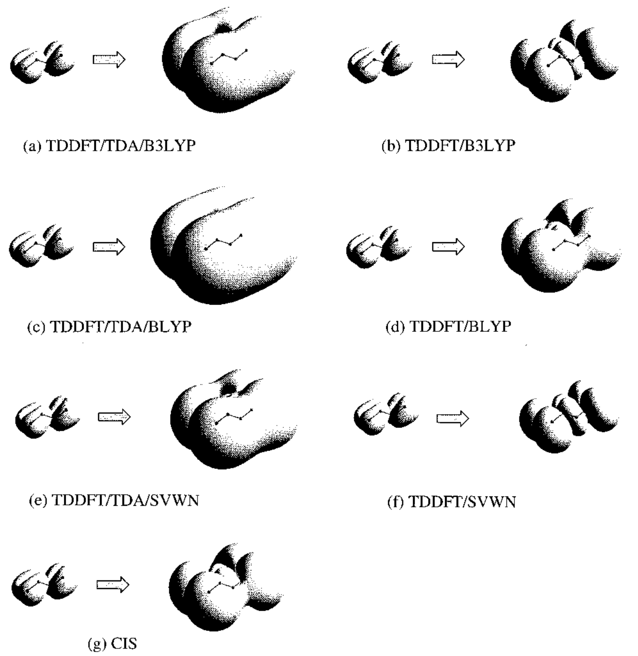

(a) TDDFT/TDA/B3LYP
(b) TDDFT/B3LYP
(c) TDDFT/TDA/BLYP
(d) TDDFT/BLYP
(e) TDDFT/TDA/SVWN
(f) TDDFT/SVWN
(g) CIS

Figure 3. The attachment and detachment densities for the transition 1 ^{1}Ag → 1 ^{1}B$_u$ of *trans*-butadiene with the following calculation methods and exchange-correlation functionals: (a) TDDFT/TDA/B3LYP, (b) TDDFT/B3LYP, (c) TDDFT/TDA/BLYP, (d) TDDFT/BLYP, (e) TDDFT/TDA/SVWN, (f) TDDFT/SVWN, (g) CIS. Other details are the same as those listed in the caption of Figure 2.

The excitation energies suggest a significant disagreement between TDDFT/TDA and the full TDDFT results. Further analysis shows that TDDFT/TDA yields a state with more Rydberg character, as indicated by a larger $\langle z^2\rangle$ and a larger attachment density contour surface in Figure 3. Calculations with the SVWN functional yield the least diffusive attachment density, and results with the BLYP functional give the most diffusive excited state charge distribution. This result is the first case we have seen where TDDFT/TDA results significantly differ from TDDFT. In addition to a larger $\langle z^2\rangle$ for the 1 ^{1}B$_u$ state with TDA/TDDFT, from Table 3 we have also observed a smaller $\langle z^2\rangle$ for the 2 ^{1}B$_u$ state with TDDFT/TDA, compared to the corresponding full TDDFT results and other calculations in the literature. This suggests that there is possibly a mixing of the valence 1 ^{1}B$_u$ and the Rydberg 2 ^{1}B$_u$ states introduced by TDA in the calculation. We may also understand the basis set dependence of calculations for the 1 ^{1}B$_u$ state listed in Table 1 with this argument. From 6 to 311++G** to 6−311(2+,2+)-G**, the second set of diffuse functions lowers the excitation energy of the 1 ^{1}B$_u$ state by 0.22 eV with TDDFT/TDA, while with TDDFT it is lowered by only 0.06 eV.

Oscillator strengths from the ground state to this 1 ^{1}B$_u$ state are also calculated and listed in Table 2. They all agree reasonably well with experimental results, at least relative to other published theoretical calculations. CIS is known to overestimate oscillator strengths in many cases, and this effect does not seem to exist with TDDFT calculations.

3.1.3. Rydberg States. The functionals used in this current study do not have the correct asymptotic behavior to describe Rydberg states properly.[32−34] However, we include the results for a number of the lowest Rydberg states in Table 2 as part of the survey of TDDFT performance and as a source to understand the unusual results for the 1 ^{1}B$_u$ state reported above. Both TDDFT/TDA and TDDFT underestimate the excitation energy

TABLE 4: Calculated and Observed Vertical Excitation Energies (in eV) and Oscillator Strengths (in parentheses) for all-*trans*-1,3,5-hexatriene

											$\langle z^2 \rangle$[d]		
states	B3LYP′[a]	B3LYP	BLYP′	BLYP	SVWN′	SVWN	CIS	CASPT2[b]	MRMP[c]	Exp	SVWN′	SVWN	CASSCF
triplet states													
1 ^3A_g	4.19	3.94	4.22	4.09	4.40	4.33	3.56	4.12	4.15	4.11[e]			
1 ^3B_u	2.47	2.10	2.47	2.32	2.61	2.53	2.08	2.55	2.40	2.61[e]			
singlet states													
2 ^1A_g	5.66	5.65	5.02	5.01	5.06	5.05	7.04	5.20	5.09	5.21[f]	32.9	32.9	31.8
1 ^1B_u	5.06	4.64	4.90	4.42	4.99	4.47	5.40	5.01	5.10	4.95[e]	34.3	33.3	40.4
	(1.61)	(1.11)	(1.53)	(1.01)	(1.56)[g]	(1.01)[g]	(1.70)	(0.85)[h]	(1.08)				

[a] The prime on the functional acronym indicates the use of the Tamm−Dancoff approximation. [b] Reference 7. [c] Multiference Møller−Plesset study corrected for the basis-set and active-space effects, from ref 9. [d] Expectation value of z^2 (in a.u.^{2}) where z is the coordinate perpendicular to molecular plane. For ground state it is 43.1 (SVWN) and 31.8 (CASSCF). The calculation was performed with 6-31++G** basis set. The $\langle z^2 \rangle$ values calculated in a larger basis (6-31(2+,2+)G**) are 33.2 for 2 ^1A_g (both SVWN′ and SVWN), 35.3 for 1 ^1B_u (SVWN′) and 33.6 (SVWN). [e] Reference 49. [f] Reference 50. [g] Oscillator strengths for 1 ^1B_u states with a larger basis (6-31(2+,2+)G**) are 1.52 (SVWN′) and 1.12 (SVWN). [h] CASSI results reported in ref 7.

by 0.6−1.3 eV, which is not surprising at all. In most cases, the results from TDDFT/TDA are very similar to those from TDDFT except for the 2 ^1B_u state.

From Table 1, it is seen that the 2 ^1B_u state is not yet fully converged with current basis set employed. However, as discussed above, in Table 3 we see that for the current level of calculation, there still is an increase of $\langle z^2 \rangle$ for TDDFT relative to TDDFT/TDA, for this 2 ^1B_u state, indicating a more diffusive excited-state charge distribution by TDDFT and less valence-Rydberg mixing than for TDDFT/TDA.

The oscillator strengths for excitation from the ground state to the 2 ^1B_u state are listed in Table 2. Larger oscillator strengths with TDDFT/TDA results are observed, which may indicate a better overlap with its ground state wave function, and this observation agrees with the above conclusion, namely that the (artificial) valence Rydberg mixing makes the 2 ^1B_u state less diffusive, with a better overlap with its compact ground-state wave function.

3.1.4. Triplet States. We have obtained generally good agreement for the triplet states with experimental excitation energies for both 1 ^3A_g and 1 ^3B_u states, for both TDDFT and TDDFT/TDA and most functionals. The only errors larger than 0.2 eV are for TDDFT/SVWN and TDDFT/TDA/SVWN for the 1 ^3A_g and TDDFT/B3LYP for the 1 ^3B_u state. For the B3LYP functional, excitation energies for both triplet states are somewhat different with and without the TDA. Both states are valence in their characters, indicated by the $\langle z^2 \rangle$ values that are close to the ground-state value. This result is in good agreement with CASSCF calculations.

3.2. Hexatriene. Much attention has been paid to the energy level ordering of the first two excited states of hexatriene and longer conjugated polyene molecules. Brief reviews and discussions have been presented in refs 7 and 37 and will not be repeated here. For hexatriene, we are employing a smaller (6-31++G**) basis set than for butadiene. Excitation energies to Rydberg states are affected by the lack of the second set of diffuse function, and so we restrict our discussion to the two valence states only.

In Table 4, we list the excitation energies from our calculations and some previous theoretical and experimental values. There is little difference between TDDFT and TDDFT/TDA for the 2 ^1A_g state. We obtain about 0.2 eV agreement between TDDFT calculations with SVWN and BLYP functionals. Results using the B3LYP hybrid functional overestimate the excitation energy by 0.44 eV, which is still much better than the 1.8 eV error made by CIS.

For the 1 ^1B_u state, TDDFT underestimates the excitation energy by about 0.5 eV, as it did for butadiene. Similarly, excitation energies from TDDFT/TDA agree better with experimental results, although this is likely to be fortuitous. The oscillator strengths from TDDFT, for all three functionals used in the present work, agree quite well with the values of 0.85 from the CASSCF state interaction method (CASSI)[7] and 1.08 from MRMP[9] calculations. Our TDDFT results show that the vertical transition of the 2 ^1A_g state lies above the 1 ^1B_u state, although TDDFT is clearly underestimating the value of the latter.

In Table 4 we have also listed $\langle z^2 \rangle$ for some of the calculations. For the 1 ^1B_u state it is 34.3 for TDDFT/TDA/SVWN and 33.3 for TDDFT/SVWN, and for the ground state it is 43.1. A calculation with an additional set of diffusive basis functions (6-31(2+,2+)G**) shows little changes in both oscillator strengths and $\langle z^2 \rangle$, indicating that the 1 ^1B_u state is a valence state and there is virtually no mixing of Rydberg character in our results, to the contrary of the case of butadiene. From our analysis of the 1 ^1B_u state, it is still not clear what has caused the appreciable deviation between TDDFT/TDA and TDDFT and the underestimation of excitation energy in TDDFT. In application, one should avoid relying on TDDFT to provide excited-state properties of the 1 ^1B_u state for similar molecules.

For low-lying triplet states, the agreement with experimental values is within about 0.3 eV. Employing TDA in TDDFT calculations again raises the excitation energies by 0.07−0.37 eV. Among the functionals we have examined, SVWN yields the best results for the 1 ^3B_u state while the BLYP and B3LYP functionals give better results for the 1 ^3A_g state.

3.3. Octatetraene. The state ordering of the (mainly) doubly excited 2 ^1A_g state and the 1 ^1B_u state of octatetraene has long been studied experimentally and theoretically. A detailed study of the electronic spectrum of octatetraene was performed by Serrano−Andres et al.[8] The MRMP work of Nakayama et al. has included this molecule as well.[9] Both studies placed the forbidden 2 ^1A_g state below the 1 ^1B_u state in vertical transitions.

Our calculated TDDFT results are listed in Table 5. For the 2 ^1A_g state, we again observe that the results change very little when the TDA is employed. The B3LYP functional yields excitation energies that are 0.6−0.7 eV higher than those obtained with BLYP and SVWN functionals. Results from the BLYP and SVWN functionals are both within about 0.3 eV of the best reported calculations (by the CASPT2 and MRMP methods).

For the 1 ^1B_u state we again observe a significant underestimation (between 0.5−0.7 eV) in excitation energies calculated with TDDFT. TDDFT/TDA again has a higher excitation energy for this state. From Figure 1 we can see the deviation from experimental results is slightly larger for the longer polyenes.

TABLE 5: Calculated and Observed Vertical Excitation Energies (in eV) and Oscillator Strengths (in parentheses) for all-*trans*-1,3,5,7-Octatetraene

											$\langle z^2\rangle$[d]		
states	B3LYP′[a]	B3LYP	BLYP′	BLYP	SVWN′	SVWN	CIS	CASPT2[b]	MRMP[c]	exp	SVWN′	SVWN	CASSCF
triplet states													
1 ^3A_g	3.50	3.26	3.51	3.40	3.65	3.59	2.99	3.39	3.55	3.55[e]			
1 ^3B_u	2.06	1.68	2.04	1.90	2.14	2.07	1.74	2.17	2.20	2.10[e]			
singlet states													
2 ^1A_g	4.83	4.83	4.17	4.16	4.19	4.18	6.51	4.38	4.47	3.97[f]	42.4	42.4	41.8
1 ^1B_u	4.39	3.98	4.25	3.77	4.31	3.80	4.78	4.42	4.66	4.41[g]	43.4	42.9	43.5
	(2.34)	(1.56)	(2.29)	(1.40)	(2.31)[h]	(1.40)[h]	(2.27)	(1.83)	(1.08)				

[a] The prime on the functional acronym indicates the use of the Tamm−Dancoff approximation. [b] Reference 8. [c] Multiference Møller−Plesset study corrected for the basis-set and active-space effects, from ref 9. [d] Expectation value of z^2 (in a.u.^{2}) where z is the coordinate perpendicular to molecular plane. For ground state it is 56.5 (SVWN) and 41.3 (CASSCF). The calculation was performed with 6-31++G** basis set. (The $\langle z^2\rangle$ values calculated in a larger basis (6-31(2+,2+)G**) are 42.4 for 2 ^1A_g (both SVWN′ and SVWN), 43.6 for 1 ^1B_u (SVWN′) and 42.9 (SVWN). [e] Reference 51. [f] Estimated from the fluorescence spectrum assuming the same parabolic shapes for the ground and the excited-state surfaces, ref 2. [g] Refs 52, 53. [h] Oscillator strengths for 1 ^1B_u states with a larger basis (6-31(2+,2+)G**) are 2.29 (SVWN′) and 1.52 (SVWN).

TABLE 6: Calculated and Observed Vertical Excitation Energies (in eV) and Oscillator Strengths (in parentheses) for all-*trans*-1,3,5,7,9-Decapentaene[e]

states	B3LYP′[a]	B3LYP	BLYP′	BLYP	SVWN′	SVWN	CIS	MRMP[b]	expt.
triplet states									
1 ^3A_u	3.01	2.76	3.00	2.89	3.12	3.07	2.56	2.98	
1 ^3B_u	1.78	1.40	1.75	1.62	1.83	1.77	1.52	1.89	
singlet states									
2 ^1A_g	4.22	4.21	3.55	3.55	3.57	3.56	6.21	3.65	3.48[c]
1 ^1B_u	3.90	3.52	3.76	3.30	3.80	3.32	4.33	4.05	4.02[c]
	(3.03)	(2.14)	(3.00)	(1.92)	(3.02)[d]	(1.91)[d]	(2.79)	(1.40)	

[a] The prime on the functional acronym indicates the use of the Tamm−Dancoff approximation. [b] Multiference Møller−Plesset study corrected for the basis-set and active-space effects, from ref 9. [c] Reference 38. [d] Oscillator strengths for 1 ^1B_u states with a larger basis (6−31(2+,2+)G**) are 3.01 (SVWN′) and 1.91 (SVWN). [e] The CIS, TDDFT and TDDFT/TDA calculations are performed using the 6-31++G** basis set at the B3LYP/6-31G** optimized geometry at the ground state.

This systematic underestimation of excitation energies of the 1 ^1B_u state in TDDFT apparently indicates a deficiency in the exchange-correlation functionals employed in the present study. The oscillator strengths for the 1 ^1Ag → 1 ^1B_u transition are also listed in Table 5. It is seen that our results from full TDDFT lie between those obtained from CASSCF and MRMP calculations.

For all the three functionals employed in the present study, TDDFT puts the 2 ^1A_g state above the 1 ^1B_u state, while other calculations give the reverse result. With TDDFT/TDA, the 2 ^1A_g state is placed below the 1 ^1B_u state when SVWN and BLYP functionals are used. This reflects the underestimation of the excitation energy to the 1 ^1B_u state that occurs in TDDFT.

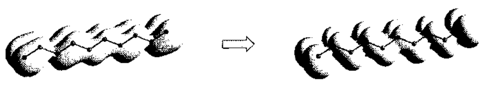
In Table 5 we have listed $\langle z^2\rangle$ for some of the calculations and from the literature. A calculation with an additional set of diffusive basis functions (6-31(2+,2+)G**) shows small changes in both oscillator strengths and $\langle z^2\rangle$, indicating that the 1 ^1B_u state is a valence state for both TDDFT/TDA and TDDFT results.

For the two triplet states calculated the agreement with experimental results is within 0.3 eV, except the one obtained for the 1 ^3B_u state with B3LYP/TDDFT.

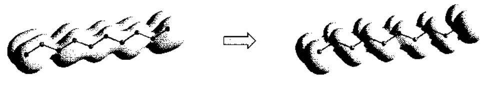
3.4. Decapentaene. Ab initio studies for excited states of decapentaene are less common than for the smaller polyenes discussed above. Nakayama et al. included this molecule in their MRMP calculations.[9] Comparison was made to experimental results by D'Amico et al.,[38] and the effective Hamiltonian method (EHM) calculation by Said et al.[39] A recent two photon absorption experiment[40] reported 3.05−3.07 eV for the 0−0 transition of the 1 ^1Ag → 2 ^1A_g transition for decapentaene in low-temperature alkane matrices. In Table 6 we report our TDDFT results. It is seen that both BLYP and SVWN yield excellent agreement (within 0.1 eV) with experiment for the 2 ^1A_g state. For the 1 ^1B_u state we find the same underestimation of excitation energies as seen above, with errors of 0.5−0.7 eV for TDDFT and 0.1−0.3 eV for TDDFT/TDA. Oscillator strengths for transitions to the 1 ^1B_u state are larger than those from MRMP.

We note that the HF ground state calculation is probably unstable. The initial guess of the self-consistent field (SCF) calculation has a large effect on the ground state calculation. If we choose to start with a superposition of atomic density (SAD) as the initial guess, the SCF calculation yields a ground state with only 4 π electrons. Subsequent CIS calculation gives negative triplet state excitation energy, indicating that it is probably UHF unstable. However, if we start with the SVWN ground-state density, the final HF−SCF ground-state energy is more than 60 Hartrees higher than that of SAD initial guess, but the electronic structure is much closer to the physical intuition: the molecule now has 10 π electrons. In Table 6 we report CIS excitation energies following the ground-state calculation with SVWN density as its initial guess. In Figures 1, 4, and 5 the results corresponding to the same CIS calculation are presented.Our TDDFT results give triplet excitation energies that agree with MRMP calculations to 0.3 eV, except TDDFT/B3LYP for the 1 ^3B_u state, which is about 0.5 eV lower than the MRMP result.

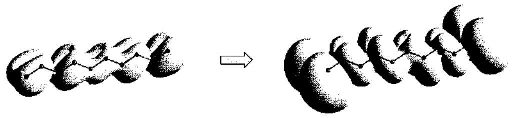
We have also performed the attachment/detachment analysis for this molecule, the longest oligomer studied in the present work, and the results are plotted in Figures 4 and 5. From such contour surfaces (enclosing 90% of electronic density), we see all of the transitions are now valence in character. For the 2 ^1A_g state, the attchment density of CIS is more diffusive in its spacial distribution. For the 1 ^1B_u state the differences among CIS, TDDFT/TDA, and TDDFT are less pronounced. The attachment density for TDDFT/TDA is slightly larger in space.



(a) TDDFT/TDA/SVWN

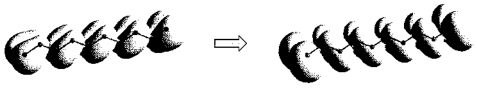


(b) TDDFT/SVWN

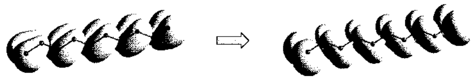


(c) CIS

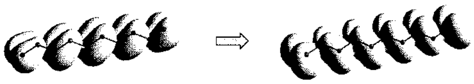
Figure 4. The attachment and detachment densities for the transition 1 ^{1}Ag → 2 ^1A_g of all *trans*-decapentaene with the following calculation methods and exchange-correlation functionals: (a) TDDFT/TDA/SVWN, (b) TDDFT/SVWN, (c) CIS. All excited-state calculations were performed with 6-31++G** basis set at the B3LYP/6-31G** optimized ground-state geometry. Other details are the same as those listed in the caption of Figure 2.



(a) TDDFT/TDA/SVWN



(b) TDDFT/SVWN



(c) CIS

Figure 5. The attachment and detachment densities for the transition 1 ^{1}Ag → 1 ^1B_u of all *trans*-decapentaene with the following calculation methods and exchange-correlation functionals: (a) TDDFT/TDA/SVWN, (b) TDDFT/SVWN, (c) CIS. All excited-state calculations were performed with 6-31++G** basis set at the B3LYP/6-31G** optimized ground-state geometry. Other details are the same as those listed in the caption of Figure 2.

TABLE 7: Negative Energies of Highest Occupied Molecular Orbitals in Units of eV

	butadiene[a]	hexatriene	octatetraene	docapentaene
B3LYP	6.53	5.90	5.58	5.36
BLYP	5.69	5.17	4.87	4.71
SWVN	6.04	5.52	5.25	5.09

[a] 6-311(2+,2+)G** basis set is used for butadiene. For all other polyene oligomers 6-31++G** is employed.

3.5. The Rydberg Threshold. One of the major approximations we have made in the current study is the use of inexact exchange-correlation functionals (which decay too fast in the asymptotic region). It has been noted that excitation energies calculated by TDDFT with asymptotically incorrect functionals tend to collapse as they approach the negative of the highest occupied orbital energies.[32,33] As we can see in Table 7, most of the TDDFT excitation energies for butadiene (Table 2) above this value seem to be too low relative to experiment and other calculations, and the 2 ^1A_g state is close to this threshold. However, the 2 ^1A_g state is very compact as shown in Figure 2 and does not sample the asymptotic region of the exchange-correlation potentials. Furthermore, as the oligomer chain length increases, the 1 ^1B_u and 1 ^1A_g excited states lie lower than the negative of the highest occupied orbital energies, and hence the incorrect asymptotic decay behavior of the approximate exchange-correlation functional should have little influence.

Conclusion

By way of summary it is interesting to examine the overall trends obtained for the excitation energies to the singlet 2 ^1A_g state and the 1 ^1B_u states for the entire series of polyenes examined here. These trends are shown in Figure 1. As has been discussed for each of the molecules individually, it is readily apparent from the figure that TDDFT has performed very well indeed in describing the excitation energies to the 2 ^1A_g state across this series of molecules. This state has been considered very difficult to describe by wave function-based methods because of its substantial double excitation character. The success of TDDFT must therefore be considered somewhat surprising, particularly because it is an explicitly one-electron description. Higher excitations are only treated implicitly by dressing the response matrix with the effects of electron correlation. This good performance is very encouraging because TDDFT can be straightforwardly applied to much larger systems, such as carotenoids, where states of similar character play a crucial role in the energy transfer associated with fundamental biochemical processes such as photosynthesis and vision.

The overall performance of TDDFT for excitation to the optically allowed 1 ^1B_u state is considerably poorer as is evident from the second part of Figure 1. This is despite the fact that this state is simpler to describe in the sense that it is much closer to a single electron excitation, and is therefore easier to treat in wave function-based methods. While there is a systematic underestimation of the excitation energy to this state by approximately 0.5−0.7 eV, the general trend of decreasing excitation energy with chain length is correctly reproduced. We see that the excitation energy to this state exhibits greater sensitivity to the choice of functional than we see for the 2 ^1A_g state. On balance the SVWN functional or the BLYP functional appear to be the best choices. Finally it is interesting to note that the Tamm−Dancoff approximation (TDA) to TDDFT actually performs considerably better for the excitation energies than TDDFT itself, as also shown in Figure 1. While it appears to yield a better balanced description of the two states than TDDFT, this must be viewed with caution because TDDFT/TDA is itself an approximation to full TDDFT.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. C.P.H. acknowledges a Fellowship from the Miller Institute for Basic Research in Science, and M.H.G. acknowledges a David and Lucile Packard Fellowship (1995−2000).

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