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On the Vertical and Adiabatic Excitation Energies of the 2^1A_g State of *trans*-1,3-Butadiene

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The excitation energy to the 2^1A_g state of *trans*-1,3-butadiene is examined using a variety of ab initio electronic structure techniques. While analogous states have been shown to be the lowest singlet excited states for all longer polyenes, for butadiene the position of the 2^1A_g state relative to the HOMO → LUMO excitation (1^1B_u) has been difficult to establish theoretically. We employ a variety of methods (CASSCF, CASPT2, MRSDCI, QDVPT) to examine both the vertical and adiabatic excitation energies for this state. At the ground-state geometry, the vertical excitation energies obtained by CASPT2 and Davidson-corrected MRSDCI for the 2^1A_g state differ by approximately 0.15 eV, but all of the methods predict that the 2^1A_g state has a lower 0−0 excitation energy than the 1^1B_u state. Possible reasons for the discrepancies between the various methods for the vertical excitation energy are discussed.

I. Introduction

Since the pioneering work of Hudson and Kohler which demonstrated that the lowest singlet excited state in α,ω-diphenyloctatetraene is not of HOMO → LUMO character (1^1B_u in C_{2h} symmetry), but is rather of "doubly excited" character (2^1A_g in C_{2h} symmetry),[1−3] there has been intense experimental and theoretical interest in determining the ordering and positions of these two states in other polyenes.[4] The results of this work have shown that, for all polyenes longer than butadiene (straight chain as well as substituted), the 2^1A_g state is indeed the lowest singlet state, and is the state out of which fluorescence occurs.[5] Oddly, however, it is butadiene which has posed the most significant challenge to theorists and has been the most elusive species for experimental determination of the position of the 2^1A_g state.

A vast amount of experimental data has been gathered on the electronically excited states of butadiene[6−16] using absorption, fluorescence, electron energy loss (EEL), and resonance Raman spectroscopies. A variety of Rydberg series have been identified, and the position of the 1^1B_u state, which absorbs strongly in a transition from the ground state, is known to be 5.92 eV (vertical) and 5.74 eV (adiabatic). The earliest experimental assignment of the position of the 2^1A_g was to a broad, structureless feature in the region of 7.3 eV in the EEL spectrum of butadiene.[9,10] Later resonance Raman data[12,15] provided evidence for the state at significantly lower energies, in the region of 5.4−5.8 eV. In neither case is there direct evidence for whether the observed transition is vertical, adiabatic, or intermediate between the two extremes, although indirect evidence in the case of the resonance Raman data suggests the lower value should be near the adiabatic transition energy.

The complications associated with location of the 2^1A_g state in absorption spectroscopy arise from the "doubly forbiddenness" of this state, stemming from the one-photon symmetry-forbiddenness as well as the strong doubly excited character of the state (see below). In longer polyenes, this complication is overcome by measuring fluorescence, but in the case of butadiene, no fluorescence is observed, making the detection of the state significantly more difficult.

Butadiene has also been treated theoretically[17−34] using a host of methods, and has served as a proving ground for newly developed methods for the description of electronically excited states. The early work of Shih et al.[20] and Nascimento and Goddard[21] was particularly successful in identifying various Rydberg series for butadiene, with other later calculations largely supporting these assignments.[22,23,26−28] The 1^1B_u state has presented somewhat of a challenge to ab initio calculations (while its assignment and position have never been in doubt experimentally) for much the same reasons that the $\pi \rightarrow \pi^*$ state in ethylene has been a difficult problem for theorists.[35,36] That is, the butadiene 1^1B_u state has large contributions from "ionic" valence bond configurations (see Nascimento and Goddard[21] for an excellent discussion of the valence bond description of the various low-lying states). Computationally, the consequence of ionic character is to drive up the zeroth-order energy of such states relative to covalent or Rydberg-like states. Since butadiene has a series of $\pi \rightarrow$ np Rydberg states of ^1B_u symmetry, Rydberg configurations can mix with the valence-like $\pi \rightarrow \pi^*$ state, and only upon inclusion of extensive electron correlation is a largely valence-like 1^1B_u state recovered.[24]

The 2^1A_g state, on the other hand, is not expected to present such complications. An MO theory description of the state clearly indicates it is multiconfigurational at zeroth-order, thus mandating an MCSCF description of the state. However, as Nascimento and Goddard showed, the 2^1A_g state can be described as two triplet ethylenes coupled to an overall singlet in valence bond terms. This description is dominated by covalent valence bond configurations, as is that of the ground state, thus one might expect that a simple π-electron CASSCF calculation would yield a reasonable description of the 2^1A_g state and its excitation energy from the ground state. Nevertheless, the range of excitation energies obtained for this state is quite dramatic, as shown in Table 1. The higher estimates of the excitation energy (above 7 eV) are almost certainly due to limited correlation treatments or to correlation treatments that are based on a single reference configuration (e.g., CIS). In addition, the

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TABLE 1: Previous Theoretical Estimates of the Vertical Excitation Energy for the 2^1A_g State of *trans*-1,3-Butadiene[a]

method	basis	$2^1A_g\ \Delta E$(eV)	$2^1A_g\ \langle x^2\rangle$
CIS[17]	TZPR	7.19	Rydberg
π CISD[18]	DZ	7.71	
$\sigma\pi$ CI	DZR	6.73	Valence
π CASSCF[31]	5s4p2dR/3s2p	6.58	24.4
$\sigma\pi$ RASSCF[31]	5s4p2dR/3s2p	6.79	23.7
π CI[24]	5s3p1dR/3s	6.77	23.5
MRSDCI[57]	DZR	7.02	
GVB−CI[21]	DZ	7.0	
MRSDCI[22]	DZPR	6.53	
MRSDCI[34]	DZPR	6.78	
MRSDCI[24]	5s3p1dR/3s	6.24	23.3
SAC−CI[23]	DZPR	7.05	
CASSCF[26]	6s3p1dR/2s1p	6.64	23.2
CASPT2[26]	6s3p1dR/2s1p	6.27	
EOM-CCSD(T)[27]	6s3p1dR/2s1p	6.76	36.1
H_v[28,29]	4s3p1dR/2s1p	6.19[28]	25.0
	5s3p1dR/2s1p	6.01[29]	
RPA[32]	5s3p2d	7.2	

[a] See the cited references for details of the various calculations. Basis denotes the approximate size of the one-electron basis set used for the given calculation; the appendage "R" to the C basis indicates diffuse functions were used in the calculation.

EOM-CCSD(T) and SAC-CI methods are best applied to states of largely singly excited character,[37] and their relatively high excitation energy estimates and/or somewhat diffuse character are explicable on the basis of the significant doubly excited character of the 2^1A_g state at zeroth-order. However, neglecting these high-energy values still leaves one with a spread of almost 0.8 eV for the vertical excitation energy of the 2^1A_g state. In addition, the 2^1A_g state is known to have significantly more relaxation energy than the 1^1B_u state.[30,33,34,38] Thus, should the vertical transition energies of the two states be nearly equal, there is no doubt that the 2^1A_g state is lower in the adiabatic sense for butadiene. On the other hand, if they are well-separated at the ground-state geometry, it may be that the 1^1B_u state is lowest in the adiabatic sense as well, which would have important implications for understanding the lack of fluorescence from butadiene.

There is some organization to the lower excitation energy values (6.0−6.8 eV), largely dividing along the lines of whether the estimate is based on perturbation theory, tending toward lower energy values (CASPT2,[26] H_v,[28,29] or perturbation theory-selected MRSDCI [24]), or whether the estimate is from a CI, which tend to be in the higher energy range. Given the lack of size-consistency in CI, one might naturally suspect the CI values, but the similar correlation energies for the ground and 2^1A_g states argue that size inconsistency is not expected to play a large role in determining the CI excitation energy.[39] Alternatively, it may be that low-order perturbation theory is somewhat less accurate in the case of a strongly multireference state such as the 2^1A_g.[26] The purpose of the present article is to address these questions using perturbation theory-selected multireference singles and doubles configuration interaction (MRSDCI), quasidegenerate variational perturbation theory (QDVPT),[40] CASSCF, and CASPT2.[41,42] In particular, we (a) extend the PT-selected MRSDCI calculations to significantly larger configuration spaces, (b) use larger basis sets than have been previously used in CI calculations on this system, (c) examine size-inconsistency effects using Davidson-corrected MRSDCI and QDVPT, and (d) calibrate the various methods using the vertical excitation energy for the 1^3B_{1u} state of ethylene.

The remainder of the article is organized as follows. In section II, we discuss the various theoretical methods and basis sets used in the present study. In section III, results are presented, and they are discussed in section IV. Conclusions are presented in section V.

II. Theoretical Methods

a. Geometries. The ground-state equilibrium geometry for butadiene was taken from the experimental geometry.[43] The planar 2^1A_g excited-state geometry (in C_{2h} symmetry) was taken from a four-electron/four-orbital CASSCF calculation in the 6-31G(d,p) basis.[44] A frequency analysis showed this geometry was not a minimum, but instead had four imaginary frequencies, as was also found by Zerbetto and Zgierski in a smaller basis set.[30] In their work, several lower symmetry, nonplaner minima were found to lie within approximately 0.2 eV of the C_{2h} stationary point. To assess the accuracy of this energy lowering, we optimized to a C_2 stationary point for the 2^1A_g state again using a 4/4 CASSCF wave function in the 6-31G(d,p) basis, followed by a CASPT2 calculation identical to that used for the planar structures examined below. Our CASPT2 energy lowering relative to the planar 2^1A_g stationary point is 0.14 eV, quite similar to that of Zerbetto and Zgierski. Thus, to estimate relaxation effects for the 2^1A_g state we use energies obtained at our planar C_{2h} stationary point, and correct them with the small energy lowering (i.e., 0.14 eV) obtained from our CASPT2 results in proceeding to the nonplanar minima. Our geometry optimizations were performed using Gaussian 94.[45]

b. Orbitals. The orbitals used for butadiene were, in most cases, optimized for the state of interest based on a four-electron/eight-orbital CASSCF (denoted 4/8-CASSCF) calculation, the eight orbitals being four a_u and four b_g π orbitals. In the results of Table 7, we have used RHF orbitals for the ground state and either ground state RHF or 4/4-CASSCF orbitals for the excited state. For ethylene, we used RHF/ROHF orbitals for the CI and CCSD calculations and 2/4-CASSCF orbitals for the CASPT2 calculations. Except where noted, the s component of the d functions was not deleted.

c. Correlation Approaches. All correlated results do not include correlation of the C 1s electrons. In a test calculation on ethylene this was found to have no effect on the calculated excitation energies.

PT-Selected MRSDCI. Reference spaces were constructed from smaller prior CI calculations, using the most important single and double excitations (based on the size of the CI coefficients in the final CI expansion) relative to the dominant configuration for the given state. From this set of reference configurations all single and double excitations were generated. The Hamiltonian is then diagonalized over the zeroth-order (reference) configurations and the *n*th eigenvalue taken as the zeroth-order energy of the *n*th state of interest. Multireference second-order Rayleigh−Schrödinger perturbation theory[46] (MR-RSPT) was used to scan the single and double excitations, using an energy threshold (E_{thresh}) to determine whether a given configuration was included in the variational portion of the calculation. For the 1^1A_g or 1^3A_g states of butadiene configurations were selected only on the basis of their contribution to the given state, whereas in calculations on the 2^1A_g state selection was based on the contribution to either the 1^1A_g or 2^1A_g states to achieve a balanced description of both states in the final CI. All included configurations were then treated variationally, and a linear expression[46] was used to extrapolate the energy to that expected were all configurations included. Results based on this approach are denoted PT-MRSDCI below. All results for butadiene are based on use of thresholds in the range of 10^{-6} to 10^{-7} hartrees. Finally, to correct PT-MRSDCI

total energies for size inconsistency we used the Davidson correction[49] (results denoted DC-MRSDCI below). This "later generation" of the Davidson correction tends to be more stable as the number of electrons increases. The CI calculations were performed using MELDF.[49]

QDVPT. Quasidegenerate variational perturbation theory was developed as a size-consistent analogue of MRSDCI, and possesses similarity to variants of multireference coupled cluster theory[50−52] and averaged coupled-pair functional theory.[53] Identical selection procedures and reference spaces to those of the PT-MRSDCI results were used so that the only difference between the results from the two types of calculations is that either QDVPT or MRSDCI was applied. Extrapolation to approximately include the effects of those configurations not treated to infinite-order was performed using a simple linear scheme published previously.[54] The QDVPT calculations were performed using MELDF.[49]

CASPT2. The single-reference, multiconfigurational, nondiagonal variant of CASPT2 due to Anderson, Malmqvist, and Roos was used for all results reported here.[42] MOLCAS3 was used to perform the CASSCF and CASPT2 calculations.[55]

CCSD, CCSD(T). All CCSD calculations were based on RHF (ground state) and ROHF (excited state) SCF wave functions. These calculations were performed using ACES2.[56]

d. Basis Sets. *ANO Basis Sets.* The largest basis sets used were taken from the ANO family of basis sets of Widmark et al.;[57] the ANO basis for C is based on a (14s,9p,4d,2f) primitive set. In most cases, we used the (4s3p2d) contraction, but in test calculations on ethylene a larger contracted set was used, (5s4p3d,2f). For H, the (8s,4p,3d) basis was contracted to (3s2p) or (4s3p2d).

DZP Basis Sets. A series of test calculations were run for ethylene and butadiene with a smaller DZP basis (the Dunning Hay[58] (9s,5p,1d/4s,2p,1d) basis for C and the (4s,1p/2s,1p) basis for H). These calculations were intended to assess the excitation energy sensitivity to PT-selection energy threshold and reference space expansion, and two basis sets were constructed based on this set. The basis designated DZP is the Dunning Hay set, except that the C d polarization function had an exponent of 0.51, rather than the standard value of 0.75. Basis set DZPR was composed of the DZP basis with the addition of a set of p Rydberg functions on C (0.021).

III. Results

In Table 2 we present results from PT-MRSDCI, DC-MRSDCI, QDVPT, CASSCF, and CASPT2 calculations for the vertical excitation energy to the 2^1A_g state of butadiene. The results were obtained using the Widmark ANO (4s3p2d/3s2p) basis set. It is seen that, as in past calculations, the variational results yield a higher vertical excitation energy for the 2^1A_g state than do the CASPT2 results, but the DC-MRSDCI excitation energies show a steady downward trend as the reference spaces are augmented and E_{thresh} is lowered. In fact, in comparison with results using small reference spaces and small basis sets (comparable to those used previously) the overall effect is to lower the estimated excitation energy by approximately 0.25 eV, cutting the difference between CASPT2 and DC-MRSDCI excitation energies in half. In test calculations using smaller basis sets (see below) we find that QDVPT excitation energies are generally about 0.05 eV lower than the DC-MRSDCI results. Given that the Davidson correction depends on size-inconsistent input from the CI, while QDVPT optimizes the wave function coefficients using an approximately size-consistent ansatz, we suggest this indicates a small deterioration of the Davidson correction for the number of electrons correlated (22). We thus estimate the QDVPT result by subtracting 0.05 eV from the DC-MRSDCI result (Table 2). Our CASPT2 result is quite close to the original CASPT2 value of Serrano-Andres et al.[26]

TABLE 2: Results for the 1^1A_g and 2^1A_g States of *trans*-1,3-Butadiene at the Experimental Ground State Geometry[a]

method	ref	E_{thresh} (hartrees)	$E(1^1A_g)$ (hartrees)	$\Delta E(2^1A_g)$ (eV)
PT-MRSDCI[b]	9/13	10^{-6}	−155.5395	6.65
DC-MRSDCI[b]	9/13	10^{-6}	−155.6292	6.71
QDVPT[b]	9/13	10^{-6}	−155.6326	6.65
PT-MRSDCI[c]	9/13	5×10^{-7}	−155.5375	6.63
DC-MRSDCI[c]	9/13	5×10^{-7}	−155.6287	6.60
PT-MRSDCI[d]	69/38	10^{-6}	−155.5413	6.60
DC-MRSDCI[d]	69/38	10^{-6}	−155.6234	6.54
PT-MRSDCI[e]	125/93	10^{-6}	−155.5429	6.58
DC-MRSDCI[e]	125/93	10^{-6}	−155.6209	6.48
PT-MRSDCI[f]	125/93	5×10^{-7}	−155.5415	6.60
DC-MRSDCI[f]	125/93	5×10^{-7}	−155.6211	6.40
est. QDVPT[g]	125/93	5×10^{-7}		6.35
(4/8) CASSCF			−155.0402	6.63
CASPT2			−155.5710	6.25

[a] All results obtained using the 4s3p2d/3s2p basis with 4/8-CASSCF orbitals for the given state. E_{thresh} is the energy threshold used in the selection of configurations, and ref is the number of spin-adapted configurations in the reference space, denoted $(1^1A_g)/(2^1A_g)$. [b] The percentage of the second-order RSPT energy accounted for by the configurations treated variationally (%PTK) for the ground state was 92%, while for the 2^1A_g state it was 82%. [c] %PTK $(1^1A_g) = 95\%$ and %PTK $(2^1A_g) = 90\%$. [d] %PTK $(1^1A_g) = 91\%$ and %PTK $(2^1A_g) = 81\%$. [e] %PTK $(1^1A_g) = 91\%$ and %PTK $(2^1A_g) = 80\%$. [f] %PTK $(1^1A_g) = 94\%$ and %PTK $(2^1A_g) = 89\%$. [g] Estimated by subtracting 0.05 eV from the DC-MRSDCI result, as discussed in the text.

Analogous calculations for the 1^3A_g state of butadiene with $E_{thresh} = 10^{-6}$ hartrees yield a PT-MRSDCI excitation energy of 5.05 eV and a DC-MRSDCI excitation energy of 5.13 eV, based on a small reference space. Results based on a somewhat larger reference space yield 5.10 and 4.97 eV, respectively. The CASPT2 value in the same basis is 4.88 eV. The intensity maximum in the electron impact spectroscopy results for the 1^3A_g state occurs at 4.91−4.95 eV[59,60] in gas-phase EEL spectra, while it occurs at 5.1 eV in solid-phase EEL results.[61]

As noted above, we perform two-root selection in PT-MRSDCI calculations for the 2^1A_g state, but only one-root selection for the 1^1A_g state. To assess whether two-root selection is also needed for the 1^1A_g state, we repeated the $E_{thresh} = 10^{-6}$ hartrees 125 reference configuration calculation for the 1^1A_g state using two-root selection. The energy lowering, relative to that obtained using one-root selection, was 0.01 eV, yielding essentially the same excitation energy as the one-root selection result. For smaller reference spaces the difference between one- and two-root selection total energies may be as large as 0.1 eV but it appears that our largest reference space results for the ground state are converged with respect to the number of states on which PT-selection is performed.

In Table 3, results are presented for the planar C_{2h} stationary point for the 2^1A_g state. As mentioned above, this geometry was obtained from a CASSCF geometry optimization (four electrons in four π orbitals) in a 6-31G(d,p) basis and a frequency analysis reveals that it is not a true minimum (four imaginary frequencies). Nevertheless, previous results[30,33,34,38] and calculations discussed above indicate that the dominant energetic effects associated with relaxation of the 2^1A_g state geometry occur in proceeding to the planar stationary point, with smaller energy changes[30] occurring as the molecule

TABLE 3: Results at the Planar Stationary Point for the 2^1A_g State of Butadiene[a]

method	$E(1^1A_g)$ (hartrees)	$\Delta E(2^1A_g)$[b] (eV)	1^1A_g ΔE(gs-es)[c] (eV)	2^1A_g ΔE(gs-es)[c] (eV)
PT-MRSDCI[d]	−155.5084	4.38	0.85	−1.42
DC-MRSDCI[d]	−155.6018	4.44	0.75	−1.53
PT-MRSDCI[e]	−155.5045	4.42	0.90	−1.32
DC-MRSDCI[e]	−155.5992	4.41	0.80	−1.38
CASSCF	−155.0044	4.47	0.97	−1.19
CASPT2	−155.5408	4.34	0.82	−1.09

[a] All results obtained using the 4s3p2d/3s2p basis with 4/8-CASSCF orbitals for the given state. [b] Energy difference between the ground state and the 2^1A_g state at the planar stationary point for the 2^1A_g state. [c] Energy difference for the designated state between the ground-state equilibrium geometry and the planar stationary point for the 2^1A_g state. The smaller reference space data of Table 2 was used to obtain this energy difference. [d] Calculations were performed using PT selection and extrapolation, with an energy selection threshold of 1×10^{-6} h. The reference space for the 1^1A_g state consisted of 11 spin-adapted configurations, and that for the 2^1A_g state consisted of 11 spin-adapted configurations. The %PTK for the ground state was 90%, while for the 2^1A_g state it was 80%. [e] Calculations were performed using PT selection and extrapolation, with an energy selection threshold of 5×10^{-7} hartrees. The reference spaces were the same as those in footnote d. The %PTK for the ground state was 94%, while for the 2^1A_g state it was 89%.

TABLE 4: Estimated 0−0 Excitation Energies for the 2^1A_g State of *trans*-1,3-Butadiene[a]

method	$\Delta E_{0-0}(2^1A_g)$ (eV)
PT-MRSDCI[b]	5.17
DC-MRSDCI[b]	5.08
CASSCF	5.30
CASPT2	5.02

[a] Estimated as discussed in the text. All results obtained in the (4s3p2d/3s2p) basis set, and are based on the results of Tables 2 and 3. [b] On the basis of the 5×10^{-7} hartree results of Table 2 and 3. The smaller reference space results were used for the 1^1A_g energies.

becomes nonplanar and reaches one of several minima. It is seen that the CI energy change associated with the geometry relaxation to the planar stationary point is fairly large for the 2^1A_g state, in agreement with past results.[30,34,38] The CASPT2 results yield energy changes of similar magnitude to the CI results, but the ground and excited state energy changes are closer in size.

In Table 4, we present estimated 0−0 excitation energies for the 2^1A_g state, based on the results of Tables 2 and 3. For these estimates, we used the correlated energy difference between the 1^1A_g state at the ground state equilibrium geometry and the 2^1A_g state at the planar stationary point, and then subtract 0.14 eV, to account for the expected further lowering of the 2^1A_g state were it to relax to the C_2 stationary point. All methods yield 0−0 transition energies well below the experimental value for the 1^1B_u state.

Our present DC-MRSDCI 2^1A_g excitation energy differs from CASPT2 results in the same basis by 0.15 eV, while the estimated QDVPT result is approximately 0.10 eV higher than the CASPT2 result. To calibrate the methods and assess the convergence of the CI results we have done a series of test calculations. In particular, we have (1) examined the convergence of excitation energies obtained using PT-MRSDCI and DC-MRSDCI as a function of selection threshold, (2) examined the convergence of the excitation energy as a function of reference space size, and (3) compared DC-MRSDCI with QDVPT results for this system. In cases 1 and 2 our most detailed calculations were performed on ethylene, while for case 3 the results we present were obtained for butadiene, where size inconsistency should be a larger issue.

TABLE 5: Ethylene Ground State Total Energy and Excitation Energy to the 1^3B_{1u} State as a Function of E_{thresh} and Reference Space Size for DC-MRSDCI[a]

ref	E_{thresh} (hartrees)	%PTK	$E(1^1A_g)$ (hartrees)	ΔE (eV)
1/1	10^{-6}	99.95	−78.3558	4.56
1/1	10^{-8}	>99.99	−78.3569	4.55
1/1	10^{-10}	100	−78.3570	4.55
22/72	10^{-4}	85.7	−78.3481	4.57
22/72	10^{-6}	99.2	−78.3546	4.60
22/72	10^{-8}	99.98	−78.3614	4.61
22/72	10^{-10}	100	−78.3620	4.60
92/243	10^{-6}	97.65	−78.3506	4.58
92/243	10^{-8}	99.9	−78.3602	4.60
92/243	10^{-10}	100	−78.3619	4.60

[a] The DZP basis set was used. The geometry was the Brooks and Schaefer geometry for ethylene.[62] Other quantities defined in Table 2.

Results for ethylene (obtained at the geometry used by Brooks and Schaefer[62]) are presented in Table 5. Here we focus on the excitation energy to the 1^3B_{1u} state, i.e., the valence-like triplet $\pi \rightarrow \pi^*$ state. Calculations were performed using different reference spaces at various selection thresholds, and it is seen that the excitation energies obtained are within approximately 0.06 eV of each other. Note that, especially in the largest reference space calculations, the *total* energy does vary significantly with threshold. This is in large part due to the inadequacy of second-order PT in estimating the energy contribution of configurations with small direct interactions with the zeroth-order wave function.[47] However, the behavior is mirrored in the large reference space calculation on the excited state; thus, the excitation energies obtained are quite similar. This is different from the behavior in butadiene, where the 1^1A_g state is somewhat more sensitive to reference space expansion than is the 2^1A_g state, and the convergence of the excitation energy with respect to E_{thresh} is slower. Thus, even though butadiene and ethylene are, on the surface, quite similar problems, the behavior of the excitation energies with respect to the parameters of the calculations is somewhat different. As a result, one cannot assume that results are converged for butadiene merely because they would be for a comparable state of ethylene.

The intensity maximum in the EEL spectra for the ethylene 1^3B_{1u} state occurs at approximately 4.32−4.36 eV.[63,64] The optical absorption value is 4.60 eV,[65] although background charge-transfer absorption may contribute to this value being artificially high.[64] The values obtained in Table 5 are approximately 0.2−0.25 eV higher than the EEL values. The results of Table 5 were obtained using the DZP basis set and the Brooks and Schaefer ethylene geometry, which is slightly different from experiment. Thus, in Table 6 we compare results from a variety of methods (using a threshold and reference space size for PT- and DC-MRSDCI that was essentially converged, based on the results of Table 5) using larger basis sets and the experimental geometry for ethylene.[66] It is seen that the CASPT2 results are approximately 0.1 eV below the results from PT-MRSDCI, DC-MRSDCI, and QDVPT, which are themselves 0.04 eV below the CCSD(T) result. All methods are in good agreement (within 0.12 eV) with the EEL data. The CCSD value is quite close to the CASPT2 value, but is likely to be less accurate than the CCSD(T) value due to the significant doubly excited character in the ground state ($\pi \rightarrow \pi^*$ double excitation). Note that the extension of the basis has essentially no effect on the CCSD and CCSD(T) excitation energies. Our results for

TABLE 6: Ethylene Excitation Energies vs Method and Basis Set

method[a]	basis	$\Delta E(1^3B_{1u})$ (eV)
DC-HFSDCI	4s3p2d/3s2p	4.40
VPT(1 Ref.)	4s3p2d/3s2p	4.44
CASPT2(2/4)	4s3p2d/3s2p	4.33
DC-MRSDCI[b]	4s3p2d/3s2p	4.43
QDVPT[b]	4s3p2d/3s2p	4.43
CCSD	4s3p2d/3s2p	4.33
CCSD(T)	4s3p2d/3s2p	4.47
CCSD	5s4p3d2f/4s3p2d	4.34
CCSD(T)	5s4p3d2f/4s3p2d	4.48

[a] All SDCI and QDVPT calculations use an energy threshold for configuration selection of 10^{-6} hartrees. The configurations treated variationally account for better than 98% of the second-order RSPT energy. The geometry for ethylene was the experimental geometry.[66] [b] The reference space was comprised of 12 spin-adapted configurations for the ground state and 42 spin-adapted configurations for the excited state.

the 1^3B_{1u} state are in somewhat better agreement with the EEL data than that obtained by Pérez-Casany et al.[67] based on a size-consistent CI approach, although their result is essentially in perfect agreement with the optical value of 4.6 eV.

In Table 7, we present results for butadiene using smaller basis sets in order to compare DC-MRSDCI and QDVPT estimates for the 2^1A_g state of butadiene, as well as to test the need for Rydberg functions in the description of this state. It is seen that the excitation energies obtained from the Davidson-corrected results tend to be 0.02−0.08 eV higher than the QDVPT values. In some cases for the larger basis set we had difficulties converging QDVPT, but the uniformity of the correction in Table 7 (as well as results for test cases using the larger basis) suggests that the DC-MRSDCI 2^1A_g excitation energies should be adjusted down by approximately 0.05 eV to estimate QDVPT results as was done in Table 2 for the large reference QDVPT value.

IV. Discussion

The present PT-MRSDCI and DC-MRSDCI results represent significantly more extensive variational treatments of the ground and 2^1A_g states of butadiene than have been presented previously. Compared to our previous results, the present study utilizes a larger one-electron basis and the size of the CI treatment is at least 10-fold larger.[24] Compared to the most extensive previous CI treatment,[34] the basis set is again significantly larger, as are the reference spaces used. In this way, we address the question of whether increasing the size of the basis set and/or the CI would significantly alter the predicted excitation energy for the 2^1A_g state. Comparison of our small basis results (Table 7) with those of Table 2 which use small reference spaces suggests that the basis set is not a significant factor. However, the larger reference space results of Table 2 suggest that (i) increasing the reference space, (ii) decreasing E_{thresh}, and (iii) use of QDVPT to account for size-inconsistency effects as compared to DC-MRSDCI all have effects on the excitation energy. In combination these three factors lower the excitation more than 0.25 eV in comparison with PT-MRSDCI results using small reference spaces.

In comparison with our previous results, we find a higher vertical excitation energy (6.4−6.5 eV compared to the previous value of 6.24 eV[24]). In our previous study, the largest selected configuration space we were able to treat was on the order of 80 000 configurations, accounting for only about 77% of the RSPT second-order energy (in a smaller one-electron basis set). We suggested that this was a relatively low %PTK for high accuracy, and that the actual excitation energy might be higher were one to variationally treat a greater fraction of the configurations. In the present study, we have variationally treated up to 1.2 million configurations, accounting for nearly 90% of the second-order RSPT energy of the 2^1A_g state, and upon doing so the DC-MRSDCI excitation energy climbs to approximately 6.40 eV (estimated QDVPT, 6.35 eV). Compared to Szalay et al.[34] our most extensive MRSDCI results are about 0.2 eV lower than their MRSDCI results, while our DC-MRSDCI/QDVPT results are about another 0.2 eV lower still. Their reference spaces were smaller than those used here, which we have shown to have an effect on the excitation energy, and their results are not corrected for size consistency, which also has a nonnegligible effect. Our largest reference space PT-MRSDCI is in good agreement with the CIPSI value of Serrano-Andres et al.,[22] which yields a vertical excitation energy of 6.53 eV. (The CIPSI algorithm is also a PT-selected MRSDCI approach, but relies on larger reference spaces and treats more of the singles and doubles configuration space via second-order PT.)

Regarding the question "What is the lowest singlet excited state of butadiene?", there is unanimity in the answer based on the present results. All methods predict that the 0−0 transition energy of the 2^1A_g state is significantly below that of the 1^1B_u state and yield lower 0−0 excitation energies than those of Szalay et al.[34] and our previous results,[38] even without the 0.14 eV correction for nonplanarity. Thus, the present results lend strong support to the notion that the 2^1A_g state should be observed in the region of 5.4 eV, as found in the previous resonance Raman work[12,15] but also suggest that the state could be observed at lower energies, in the region of 5.0 eV.

However, our results have not completely reconciled the difference between second-order PT and CI-based excitation energies for the 2^1A_g state, although the difference between the CASPT2 value and our estimated QDVPT value is about 0.1 eV. The extended CI treatment presented here significantly narrowed the PT/CI gap and the question then is whether further expansion of the CI treatment would in fact yield results closer to the H_ν values (6.0−6.2 eV).

It is possible that the CASPT2 result is an artificially high estimate of the excitation energy for the 2^1A_g state and that the H_ν results are more accurate. Serrano-Andres et al.[26] noted there may be a somewhat larger inherent error in the excitation energy for a state of this type for CASPT2. It is interesting to note that the H_ν method of Freed and co-workers is actually a third-order method, and one might expect there to be some change in the excitation energy relative to CASPT2 if higher order effects are important. However, the H_ν method used for the butadiene calculation is based on forced degeneracy in the reference space, and a portion of the "work" done at third-order is to correct for the forced zeroth-order degeneracy. In some states, there is a considerable excitation energy change in proceeding from second-order to third-order results[29] and it may be that the third-order results are not fully converged for this choice of model space (i.e., higher-order results are needed). The third-order H_ν estimate for the vertical excitation energy for the 1^3B_{1u} state of ethylene is 4.22 eV,[29] somewhat low compared to the EEL maximum, so it is possible that its estimate for the 2^1A_g state is also slightly low.

Of course, one should keep in mind the intent of Anderson et al.[41,42] in proposing CASPT2. That is, the method is expected to be accurate to about 0.3 eV or better in most cases, and the disagreement with our most extensive CI/QDVPT results is less than this. However, the accuracy of the method in predicting the EEL maxima for the 1^3B_{1u} state of ethylene and the 1^3A_g

TABLE 7: Excitation Energies to the 2^1A_g State of Butadiene; Small Basis Results[a]

basis	orbs	ref	E_{thresh} (hartrees)	%PTK	ΔE_{MRSDCI}	$\Delta E_{DC-MRSDCI}$	ΔE_{QDVPT}
DZP[b]	RHF/RHF	25/17	10^{-5}	83/59	6.36	6.36	6.34
DZP[b]	RHF/RHF	25/17	10^{-6}	96/91	6.80	6.55	6.49
DZP[b]	RHF/RHF	25/17	10^{-7}	99/99	6.87	6.57	6.49
DZPR	RHF/RHF	19/23	10^{-6}	95/82	6.70	6.44	
DZPR	RHF/CAS	19/14	10^{-6}	95/91	6.50	6.62	
DZPR	RHF/CAS	19/14	10^{-7}	99/99	6.40	6.58	

[a] Basis sets and orbital spaces defined in the text, energy differences in electronvolts. All other quantities defined in Table 2. [b] The s component of the d functions was deleted.

state of butadiene suggests that similar accuracy in the case of the 2^1A_g state might not be unreasonable to expect given the qualitative similarity of these states. The data for ethylene in Table 6 indicate that the CASPT2 agreement with the EEL maximum may arise from a small fortuitous cancellation of errors, since the CCSD(T) result is higher than the CASPT2 result by about 0.15 eV, but the difference is modest, and no larger than that for the 2^1A_g state of butadiene. Since both of the triplet excited states in question are nonplanar at their equilibrium geometries, it is also possible the experimental maxima may arise from nonvertical transitions related to twisting motion and thus the CASPT2 results would actually be below the true vertical transition energy. It is interesting to note that the one solid-phase EEL spectrum for butadiene finds the 1^3A_g state at 5.11 eV,[61] but the authors attribute this higher energy maximum (relative to the gas phase) to electron−phonon scattering. In addition, the early optical studies of ethylene place the maximum for the 1^3B_{1u} state at 4.6 eV,[65] but later discussion points out the highest energy discernible peaks are at 4.42 and 4.54 eV, and that the position of the maximum may be shifted to higher energies by charge-transfer absorption.[64]

In comparison with CASPT2, our largest DC-MRSDCI results are high by about 0.15 eV, which may be about as close agreement as one can expect based on our ethylene results, but it is still of interest to ask about the origin of this difference. There is no question that the basis set used is still limited, but the CASPT2 results appear to be converged with respect to basis, and it is not obvious that the CI results should be significantly more sensitive to basis. The molecular orbitals and geometries were identical in the CI and CASPT2 calculations, and are thus not an issue. We have examined reference space expansion in the CI studies and while it does lower our excitation energies relative to previous small reference space estimates, it does not appear to completely "close the gap." We do not, however, include the entire CASSCF space in our reference space, and it may be that the configurations not included still would exert some effect. It is also possible that the PT selection procedure biases against the 2^1A_g state, since a lower fraction of the second-order energy is recovered for the 2^1A_g state and it is known that for small contributors second-order RSPT underestimates their contributions. In the smaller basis sets we were able to treat configuration spaces corresponding to greater fractions of the second-order energy, and the results of Table 7 show little change in excitation energy with selection threshold. In addition, the results of Szalay et al.[34] were unselected (albeit in a smaller basis) and their MRSDCI excitation energies are slightly higher than our small basis results, but it is possible that the effects are more significant when larger basis sets and reference spaces are used. In any event, our most extensive calculations considerably diminish the difference between the CASPT2 and DC-MRSDCI excitation energies for the 2^1A_g state and suggest that the vertical transition energy is in the range of 6.25−6.40 eV for this state. Given the accuracy of CASPT2 in other test cases it may be that the vertical excitation energy is nearer the lower end of this range.

V. Conclusion

The present study has probed a series of questions regarding differences between second-order PT and variational treatments for the vertical and nonvertical excitation energies of the 2^1A_g state of butadiene. Significantly more extensive CI results yield lower excitation energies than have been obtained previously which are still somewhat higher than those obtained using PT-based methods. All methods predict that the 0−0 transition energy of the 2^1A_g state is significantly below that of the 1^1B_u state, and thus the 2^1A_g state is predicted to be the lowest singlet excited state of butadiene.

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