

Excited States of Butadiene to Chemical Accuracy: Reconciling Theory and Experiment

Mark A. Watson* and Garnet Kin-Lic Chan

Department of Chemistry, Princeton University, Princeton, New Jersey, 08544

S Supporting Information

ABSTRACT: We obtain the vertical excitation energies of the notoriously challenging lowest-lying dark and bright excitations of *trans*-butadiene to chemical accuracy using high-order equation-of-motion coupled-cluster theory. Convergence is demonstrated in both the one-particle basis set (up to augmented quintuple-zeta quality) and the coupled-cluster expansion (including up to connected quadruple excitations) within an incremental scheme. Our best estimates for the bright $1^1B_u^+$ and dark $2^1A_g^-$ vertical transitions are 6.21 ± 0.02 eV and 6.39 ± 0.07 eV, respectively, establishing definitively that the vertical $1^1B_u^+$ transition lies below the $2^1A_g^-$ transition. Our $1^1B_u^+$ excitation energy remains significantly higher than the generally cited experimental value of 5.92 eV. To rationalize this difference, we have computed the zero-point vibrational energy corrections, which reduce the theoretical $1^1B_u^+$ excitation energy to 6.11 eV. We also correct for nonverticality in the experimental value by recomputing the transition as the weighted intensity average of the electron impact energy loss spectra, which gives the range 5.96–6.05 eV. The corrected best theoretical and experimental $1^1B_u^+$ excitation energies are then in good agreement, resolving a long-standing discrepancy.

The photochemistry of conjugated organic molecules is central to many processes, ranging from animal vision and light-harvesting in biology to light-emission and the photovoltaic effect in organic materials. As the simplest conjugated molecule, butadiene's photochemistry is important as a starting point to better understand such phenomena.¹ The two lowest singlet excited states of butadiene have very different electronic character. There is an experimentally "bright", dipole-allowed $1^1B_u^+$ state with single-excitation character and a "dark", dipole-forbidden $2^1A_g^-$ state with substantial double-excitation character. Historically, the relative ordering of these states in theory and experiment has been a matter of some debate.^{2–6} Obtaining accurate theoretical excitation energies for these states is a long-standing challenge, and quantitative agreement between different theoretical methods, let alone theory and experiment, remains elusive. The goals of the present study are twofold: (1) to use high-order coupled cluster theory to obtain well-converged theoretical excitation energies and (2) to use these converged benchmarks to better understand and resolve the disagreement between theory and experiment.

Experimentally, the bright $1^1B_u^+$ state is observable through several techniques such as UV absorption spectroscopy and electron impact energy loss spectroscopy.^{5,20,21} The widely quoted experimental value for the $1^1B_u^+$ vertical excitation is 5.92 eV, corresponding to the intensity maximum in the energy loss spectrum.⁵ It has proved difficult, however, to reproduce this value using theory. A representative set of theoretical $1^1B_u^+$ excitation energies from the literature is given in Table 1, and their spread (relative to the $2^1A_g^-$ state) is shown in Figure 1. Qualitatively, the $1^1B_u^+$ state is a one-electron $\pi-\pi^*$ HOMO–LUMO transition; thus we expect that the state is described well by single-reference theoretical methods. Single-reference equation-of-motion coupled-cluster (EOM-CC) and the related symmetry adapted cluster configuration interaction (SAC–CI)

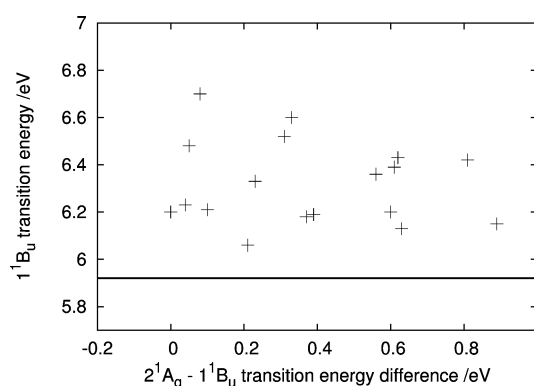


Figure 1. Scatter plot of selected theoretical literature values for the $1^1B_u^+$ and $2^1A_g^-$ transition energies, plotted as $1^1B_u^+$ versus the energy difference. The solid line represents the $1^1B_u^+$ experimentally derived vertical transition energy of 5.92 eV.

methods yield excitation energies in the range of 6.1–6.4 eV, depending on the one-particle basis set and precise details of the correlation treatment. Multireference methods, such as multireference perturbation theory and configuration interaction methods, have also been used for this state. However, standard multireference singles and doubles configuration interaction (MR-CISD) calculations, for example, are well-known to suffer from an artificial mixing of the valence $1^1B_u^+$ state and the Rydberg-like $2^1B_u^+(3p_\pi)$ state. The problem arises from the lack of dynamic correlation in the reference space. Dynamic correlation is generally less important for diffuse Rydberg states, and this differential correlation effect means that the valence $1^1B_u^+$ state is artificially raised closer in energy

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to the $2^1B_u^+$ state in the reference space and the states mix strongly. As a result, the $1^1B_u^+$ state becomes too diffuse, and the excitation energy is generally overestimated, sometimes by 1 eV or more. This is exemplified in the worst case by the complete active space self-consistent field method (CASSCF), which includes essentially no dynamic correlation and gives a value of 8.54 eV for the $1^1B_u^+$ excitation energy.¹¹ The related RASSCF method (restricted active space SCF) can give more balanced results if the active spaces are chosen appropriately,¹³ and in general the situation can also be ameliorated by using carefully optimized molecular orbitals in the reference wave function.¹⁹ Remarkably, a low-order perturbation treatment on top of a CASSCF wave function (CASPT2) can also yield much better energies. Thus, we find that multireference perturbation theories yield excitation energies in the range of 6.1–6.5 eV, while multireference configuration interaction calculations using appropriate orbitals can yield similar excitation energies of approximately 6.2 eV.¹⁹ However, we see that all calculations in the literature, regardless of methodology, consistently overestimate the $1^1B_u^+$ excitation energy by at least 0.2 eV compared with the experimental value of 5.92 eV.

Table 1. Some Representative Theoretical Literature Values for the $1^1B_u^+$ and $2^1A_g^-$ Vertical Transition Energies in eV at Different Levels of Theory

method	$1^1B_u^+$	$2^1A_g^-$	reference
EOM-CCSD	6.42	7.23	7
EOM-CCSD(T)	6.13–6.36	6.76–6.92	7
CC2	6.15	7.04	8
CC3	6.19	6.58	8
SAC-CI	6.43	7.05	9
SAC-CI	6.39	7.00	9
SAC-CI	6.33	6.56	10
CASSCF	8.54	6.64	11
CASSCF	7.73	6.67	12
RASSCF	6.60	6.93	13
CASPT2	6.23	6.27	11
CASPT2	6.06	6.27	14
MROPT	6.52	6.83	15
MRMP	6.21	6.31	12
MR-CISD	6.70	6.78	16
MR-CISD	6.2	6.2	17
MR-CCCI-PS	6.48	6.53	18
MR-AQCC	6.18	6.55	19
this work	6.21	6.41	

Unlike the $1^1B_u^+$ state, the $2^1A_g^-$ state is not directly accessible to one-photon techniques. Also, unlike in longer polyenes, no fluorescence from this state is observed in butadiene. Early electron energy loss spectra assigned the $2^1A_g^-$ state to a broad feature at about 7.3 eV, while later resonance Raman studies estimated the state to lie in the region of 5.4–5.8 eV. It is not known whether these measurements reflect vertical transitions. Overall, we do not consider these measurements to be reliable estimates of the $2^1A_g^-$ vertical transition energy. The $2^1A_g^-$ state has substantial multireference and double-excitation character, dominated by three configurations: (1) doubly excited $b_g \rightarrow a_u^*$ (HOMO→LUMO), (2) singly excited $b_g \rightarrow b_g^*$ (HOMO→LUMO+1), and (3) singly excited $a_u \rightarrow a_u^*$ (HOMO–1→

LUMO). The same qualitative state can also be described as arising from the singlet recoupling of two triplet ethylenes. As seen from Figure 1, theoretical excitation energies for the $2^1A_g^-$ state show a very large spread. A number of earlier EOM-CC and SAC-CI calculations^{7,9} yielded high excitation energies, 6.8 eV or greater, which is attributable to an insufficient treatment of correlations for the double excitation character of the state. Consistent with this, a more recent SAC-CI calculation, which included some quadruples, found a lower excitation energy of 6.6 eV.¹⁰ Multireference methods efficiently describe the mixed excitation character of the $2^1A_g^-$ state. Multireference perturbation theories^{11,14,15,12} generally yield excitation energies at the lower end, 6.2–6.3 eV, while multireference configuration interaction theories^{11,17,19} yield a somewhat wide range from 6.2 to 6.6 eV. Above all, the large spread in the theoretical values for both the $1^1B_u^+$ and $2^1A_g^-$ states from all methods reflects their very different electronic characters, and this spread means that their energetic ordering is still not completely resolved.

In this report, we aim to benchmark the $1^1B_u^+$ and $2^1A_g^-$ vertical excitation energies to an accuracy of 0.1 eV or better in order to resolve their order and the difference (if any) from experimental results. To achieve this accuracy, three sources of error have to be controlled: (1) the partial inclusion of *N*-particle correlations, (2) the use of an incomplete one-particle basis set, and (3) the choice of molecular geometry in the ground state, assuming verticality in the transition. There is a long discussion in the literature describing examples of the role of each of these errors, for example, see ref 19 and citations therein. Our strategy is to apply EOM-CC as the theoretical methodology.^{22–24} Using modern formulations, accuracy of the EOM-CC method can be systematically improved by including successively higher order levels in the excitation operators, thus controlling the correlation error 1 above. By brute-force treatment of high-level correlations in this manner, we can thus treat even multireference states such as the $2^1A_g^-$ state which have in the past been poorly described within EOM-CC calculations. When combined with a series of systematic one-particle basis sets with complete basis set (CBS) extrapolations, error 2 may also be controlled. In both these respects, we go significantly beyond earlier EOM-CC calculations, including bases as large as six-zeta and augmented quintuple-zeta, and excitations through connected quadruples. Finally, we estimate the effect of 3 by performing our calculations at several different ground-state geometries.

All our calculations were performed with the general coupled-cluster code MRCC of Kállay and Surjan,²⁵ the quantum chemistry suite Molpro,²⁶ and the NWChem package.^{27,28} We carried out equation-of-motion coupled cluster calculations at the doubles, triples, and quadruples levels (EOM-CCSD, EOM-CCSDT, EOM-CCSDTQ), as well as perturbative triples through the completely renormalized EOM-CC method (CR-CCSD(T)) as implemented in NWChem. The EOM-CCSDT and EOM-CCSDTQ calculations for the $1^1B_u^+$ state were carried out with MRCC, while the EOM-CCSDT and EOM-CCSDTQ for the $2^1A_g^-$ state were carried out with NWChem, as MRCC did not converge for this state. In all cases, the EOM-CC calculations used the closed-shell Hartree–Fock ground state as the reference determinant. Unless otherwise stated, we kept the four lowest-lying core orbitals frozen for all calculations reported in the tables, but a core-correlation correction was computed at the EOM-CCSD level in an augmented core and valence polarized quadruple- ζ

basis (aug-cc-pCVQZ). For the large EOM-CCSDT and EOM-CCSDTQ calculations, it was necessary to freeze more orbitals, and the effect of the remaining core correlation was estimated through extrapolation and a many-body expansion as described in detail in the Supporting Information. For our basis sets, we

Table 2. $1^1B_u^+$ Vertical Excitation Energies in eV with Various Basis Sets and EOM-CC Increments^a

basis	orbitals	CCSD	+CR(T)	+T	+Q
cc-pVDZ	86	6.918	−0.264	−0.124	−0.014 ^b
cc-pVTZ	204	6.660	−0.324	−0.125	
cc-pVQZ	400	6.562	−0.340		
cc-pVSZ	694	6.474			
cc-pV6Z	1106	6.428			
CBS estimate	∞	6.365	−0.352		
aug-cc-pVDZ	146	6.389	−0.250	−0.104	
aug-cc-pVTZ	322	6.365	−0.309	−0.124 ^c	
aug-cc-pVQZ	596	6.362	−0.324		
aug-cc-pVSZ	988	6.360			
CBS estimate	∞	6.357	−0.335	−0.133	
d-aug-cc-pVDZ	206	6.341	−0.235		
d-aug-cc-pVTZ	440	6.346	−0.304		
d-aug-cc-pVQZ	792	6.352			
CBS estimate	∞	6.357	−0.333		
best estimate		6.357	−0.335	−0.135	−0.014 ^b
estimated error		0.003	0.011	0.011	0.005
running total		6.36	6.02	6.22	6.21
+ core correlation ^d		6.36	6.03	6.23	6.21
+ ZPE ^e		6.26	5.92	6.12	6.11

^aColumns +CR(T), +T, and +Q denote the increment from CCSD to CR-CCSD(T), CCSD to CCSDT, and CCSDT to CCSDTQ, respectively. Exptl. = 5.92 eV. ^bEstimated with a many-body expansion (see text). ^cEstimated with nine frozen orbitals and extrapolation (see text). ^dEOM-CCSD/aug-cc-pCVQZ core correlation correction = 0.005 eV. ^eEOM-CCSD/aug-cc-pVDZ zero-point energy (ZPE) correction = −0.104 eV.

used standard correlation-consistent basis sets up to cc-pV6Z and augmented correlation-consistent basis sets up to aug-cc-pVSZ and considered the effect of double augmentation using the standard d-aug-cc-pVXZ basis sets.^{29–31} Finally, for the molecular geometries, we considered three choices: the experimental ground state geometry commonly used in previous studies³² and two theoretical geometries obtained by optimizing at the CCSD(T)/aug-cc-pVQZ and MP2/cc-pVQZ levels of theory.

Our results are summarized in Tables 2 and 3. We present our numbers in terms of an incremental decomposition of the total excitation energy, E , divided into contributions from each level of theory:

$$E^{\text{CBS}} = E^{\text{EOM-CCSD}} + (E^{\text{EOM-CCSDT}} - E^{\text{EOM-CCSD}}) + (E^{\text{EOM-CCSDTQ}} - E^{\text{EOM-CCSDT}}) + \dots$$

where a ‘best estimate’ is made for each increment as discussed case by case below. Considering the two largest basis sets in each series, the CBS estimate was obtained using an $a + b/L^3$ two-point extrapolation as advocated by Halkier et al.³³ Although originally proposed to extrapolate correlation

Table 3. $2^1A_g^-$ Vertical Excitation Energies in eV with Various Basis Sets and EOM-CC Increments^a

basis	orbitals	CCSD	+CR(T)	+T	+Q
cc-pVDZ	86	7.648	−0.499	−0.818	−0.074 ^b
cc-pVTZ	204	7.555	−0.545		
cc-pVQZ	400	7.458	−0.530		
cc-pVSZ	694	7.329			
cc-pV6Z	1106	7.250			
CBS estimate	∞	7.141	−0.520		
aug-cc-pVDZ	146	7.057	−0.307	−0.480	
aug-cc-pVTZ	322	7.093	−0.376		
aug-cc-pVQZ	596	7.103	−0.391		
aug-cc-pVSZ	988	7.100			
CBS estimate	∞	7.097	−0.403		
d-aug-cc-pVDZ	206	6.977	−0.268		
d-aug-cc-pVTZ	440	7.051	−0.353		
d-aug-cc-pVQZ	792	7.078			
CBS estimate	∞	7.098	−0.389		
best estimate		7.097	−0.403	−0.630	−0.074 ^b
estimated error		0.003	0.012	0.030	0.040
running total		7.10	6.69	6.47	6.39
+ core correlation ^c		7.12	6.71	6.49	6.41
+ ZPE ^d		6.94	6.54	6.31	6.24

^aColumns +CR(T), +T, and +Q denote the increment from CCSD to CR-CCSD(T), CCSD to CCSDT, and CCSDT to CCSDTQ, respectively. ^bEstimated with a many-body expansion (see text). ^cEOM-CCSD/aug-cc-pCVQZ core correlation correction = 0.020 eV. ^dEOM-CCSD/aug-cc-pVDZ zero-point energy (ZPE) correction = −0.175 eV.

energies, rather than total energies, we have applied it to the excitation energies directly. In the Supporting Information, we examine the quality of the fit for the EOM-CCSD and CR-CCSD(T) results and argue that this is unreasonable. All the results in Tables 2 and 3 are computed at the experimental geometry. (Results using the other geometries are given in the Supporting Information.)

Looking in detail at the $1^1B_u^+$ state first, the best estimates of each theory increment, and the corresponding errors were obtained as follows. For EOM-CCSD, we take our best estimate as 6.357 eV from the aug-cc-pV(Q,5) CBS extrapolation. We attach an error bar of 0.003 eV to this value, which is the difference between the CBS estimate and the aug-cc-pVSZ value. There is a difference of 0.008 eV between the augmented and unaugmented CBS estimates, but we assumed the augmented value was closer to the true CBS limit. To further confirm the effect of augmentation, we also completed calculations with the doubly augmented basis sets. In fact, the d-aug-cc-pV(T,Q) CBS extrapolation gives the same value of 6.357 eV. This concurs with the trends reported in ref 8, in which systematic basis set calculations were reported using the linear response CC2 method (which is an approximation to CCSD).

For the CR-CCSD(T) increment, we obtain our best estimate of −0.335 eV from the aug-cc-pV(T,Q) CBS extrapolation. We estimate an error bar of 0.011 eV by taking the difference between the CBS estimate and the aug-cc-pVQZ value. Again, we examined the effect of doubly augmented basis

sets, but it was small. For the EOM-CCSDT increment, we obtain our best estimate by combining our EOM-CCSDT data with the CR-CCSD(T) results. As explained in detail in the Supporting Information, the EOM-CCSDT/aug-cc-pVTZ increment was estimated by extrapolation of the frozen core results to be -0.124 eV. Using this value, the CBS limit was estimated from the aug-cc-pV(D,T) two-point extrapolation as -0.133 eV. As an alternative way to estimate the EOM-CCSDT basis set limit, we also note an approximate proportionality between the CR-CCSD(T) and EOM-CCSDT increments in different basis sets. Thus, by rescaling the -0.335 eV CR-CCSD(T) CBS increment by the ratio of the CR-CCSD(T) and EOM-CCSDT aug-cc-pVTZ values, we obtain an alternative estimate of the EOM-CCSDT CBS increment of -0.135 eV. We chose the latter as our 'best estimate' of the true value, but clearly a difference of 0.002 eV is immaterial here. Finally, we conservatively use the same error bar (0.011 eV) for the EOM-CCSDT increment as we estimated for the CR-CCSD(T) increment.

For the EOM-CCSDTQ increment, we used the cc-pVDZ result and made no attempt to estimate a CBS limit. It is difficult to estimate the basis set error without more data, but since the quadruples correction is an order of magnitude smaller than the triples correction, we assign a rough quadruples error of 0.005 eV, which anyway is insignificant. Our EOM-CCSDTQ calculations also demonstrate that further increments, such as quintuples, are likely to be much smaller than 0.01 eV and thus can be neglected. Combining these increments and errors (adding the absolute values), we arrive at the final best estimate for the $1^1B_u^+$ state of approximately 6.21 ± 0.02 eV.

We next consider the $2^1A_g^-$ transition. Our final best estimate for the excitation energy is 6.39 ± 0.07 eV. Examining Table 3, we see that the $2^1A_g^-$ increments converge more slowly than the $1^1B_u^+$ increments, which is unsurprising given its multireference character. Perhaps more surprising, in light of the valence nature of the state, is the relatively strong effect of diffuse functions on the excitation energy. In particular, there is a difference of 0.044 eV between the aug-cc-pVXZ and cc-pVXZ basis set limits. Again this trend concurs with the basis set studies in ref 8, and we decided that the unaugmented basis is insufficient for a good description of this excited state. Thus, we take our best EOM-CCSD estimate as the aug-cc-pV(Q,5) CBS extrapolation, and assign an error bar of 0.003 eV by taking the difference between the CBS estimate and the aug-cc-pV5Z value. As above, we examined the effect of doubly augmented basis sets, but the difference between the CBS estimates was very small (0.001 eV). For the CR-CCSD(T) increments, we obtain the best estimates and errors in the same manner as for the $1^1B_u^+$ state. For the EOM-CCSDT values, we have less data, so we use the ratio of results in the aug-cc-pVDZ basis ($0.480/0.307$) to scale up the CR-CCSD(T) best estimate to -0.630 eV. If we consider a ratio taken from the cc-pVDZ results ($0.818/0.499$) we instead obtain an estimate of -0.660 eV. Thus, we estimate an error bar of 0.030 eV, taken as the difference of these two numbers. For the EOM-CCSDTQ increment, we used the same many-body expansion as we used for the $1^1B_u^+$ state but were not able to converge it as fully, as detailed in the Supporting Information.

We now discuss our results for the $1^1B_u^+$ and $2^1A_g^-$ states. For the $1^1B_u^+$ state, our computed excitation energy lies on the lower end of prior estimates. The EOM-CC method was applied to the excited states of butadiene for the first time in 1996 by

Watts et al.⁷ Their EOM-CCSD(T) result of 6.36 eV in a modest basis set of 134 orbitals is significantly above our value of 6.21 eV. However, a more recent linear-response coupled-cluster study by Lehtonen et al.⁸ obtains an extrapolated value for the $1^1B_u^+$ excitation of 6.19 eV at the CC3 level of theory, although they used a slightly different geometry. Compared to our best estimate, the SAC-CI results^{9,10} appear to be generally too high. The CASPT2 result (6.23 eV) in ref 11 appears to be remarkably good, but the more recent result (6.06 eV) in ref 14 appears to be too low. The multireference perturbation theory result (6.21 eV) in ref 12 is also in excellent agreement with our best estimate, but a similar methodology in ref 15 gives a much higher value (6.52 eV). As discussed, multireference configuration interaction results vary widely depending on the precise details of the calculation, but the relatively recent calculation of Dallos and Lischka (6.18 eV)¹⁹ is in very good agreement with our best estimate. For the $2^1A_g^-$ state, our computed excitation energy lies significantly below previous coupled-cluster calculations, due to our inclusion of connected triples and quadruples contributions and the use of large basis sets. Previous SAC-CI results are also higher than ours. We find that the sample of values obtained using explicitly multireference based methods quoted in Table 1 spans a range spread to both sides of our best estimate of 6.39 eV, but generally within approximately 0.2 eV. Overall, our calculations indicate that the $1^1B_u^+$ and $2^1A_g^-$ states are very close in energy, with the vertical excitation to the $1^1B_u^+$ state lying slightly below that to the $2^1A_g^-$.

Our value of 6.21 eV for the $1^1B_u^+$ state remains significantly higher than the generally cited experimental value of 5.92 eV. However, we have not discussed in detail yet the choice of molecular geometry. The results in Tables 2 and 3 used the experimental ground state geometry favored by previous authors, but we also repeated some of the above calculations using two other geometries optimized at the CCSD(T)/aug-cc-pVQZ and MP2/cc-pVQZ levels of theory, as given in the Supporting Information. In summary, we found that none of the incremental EOM-CC energies we computed changed by more than 0.03 eV, and in particular, at the EOM-CCSD/aug-cc-pVQZ level, the $1^1B_u^+$ excitation energy changed by less than 0.02 eV on changing the geometry. These results indicate that the difference between theory and experiment, which is 0.29 eV, is almost certainly too large to be explained by any remaining uncertainties in the theoretical calculation of the vertical excitation energy. However, while many theoretical papers in the literature have focused on reproducing the 5.92 eV number, it should be remembered that the experimental papers cited here do not themselves describe the band maximum as a 'vertical excitation' energy. Consequently, to achieve agreement between theory and experiment, it is necessary to consider additional effects.

One issue that can be considered is the importance of vibrational zero-point energy (ZPE) contributions. The neglect of ZPE contributions is based on the assumption that the shapes of the excited state and ground state potential energy surfaces are the same near the point of the transition, leading to cancellation of the respective ZPE. We therefore estimated the ZPEs of the ground and excited states by computing the numerical Hessian of each state at the EOM-CCSD/aug-cc-pVDZ level using Molpro, assuming the same geometry for the ground and excited states, followed by a normal mode and harmonic frequency analysis. Within this crude approximation, we found that the difference in zero-point energies between the ground and excited states is quite significant. For example, for

the $1^1B_u^+$ state it is 0.104 eV, and this reduces our estimate of the excitation energy from 6.21 to 6.11 eV, giving a value which is significantly closer to the experimental band maximum.

Further, as emphasized by Davidson and Jarzecki,³⁴ assumption of verticality in the experimental spectra requires, in particular, high vibrational excitation of the excited state, as well as the validity of the Born–Oppenheimer and Franck–Condon approximations. In cases such as ours, where these assumptions are questionable, it was suggested that a better estimate of the vertical transition could be made by taking the intensity weighted average energy of the absorption spectrum, which is not equivalent to the band maximum when the band is asymmetric. Carrying out such an averaging of the original experimental data, we arrive at a corrected experimental vertical transition energy ranging from 5.96 to 6.05 eV. (Our reanalysis of the electron impact spectra of ref 5 is described in detail in the Supporting Information.) These values agree remarkably well with our ZPE corrected $1^1B_u^+$ excitation energy, to approximately 0.1 eV.

In summary, the lowest-lying dark and bright excitations of *trans*-butadiene have been computed using high-order equation-of-motion coupled-cluster theory, obtaining convergence to better than 0.1 eV in the vertical excitation energies. Our best estimates for the bright $1^1B_u^+$ and dark $2^1A_g^-$ vertical transitions are 6.21 ± 0.02 eV and 6.39 ± 0.07 eV, respectively, establishing definitively that the vertical $1^1B_u^+$ transition lies slightly below the $2^1A_g^-$ transition. We found that other reasonable choices of ground-state geometries did not alter these values significantly. Nevertheless, this energy for the $1^1B_u^+$ state is significantly higher than the traditionally cited experimental value of 5.92 eV. To resolve this difference, we also estimated the zero-point vibrational energy corrections, which reduced the $1^1B_u^+$ theoretical excitation energy to 6.11 eV. Moreover, if we reinterpret experimental results by considering the intensity weighted average of the absorption spectrum, we obtain a higher estimate of the transition energy in the range 5.96–6.05 eV. With these factors taken into account, the theoretical and experimental excitation energies for the $1^1B_u^+$ state are found to be in good agreement, thus resolving a long-standing discrepancy.

■ ASSOCIATED CONTENT

■ Supporting Information

Frozen orbital extrapolation, many-body frozen orbital expansion, molecular geometries, basis set extrapolations, and reinterpretation of the $1^1B_u^+$ experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mark.watson@cantab.net.

Notes

The authors declare no competing financial interest.

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■ NOTE ADDED IN PROOF

It was pointed out to us [T. J. Martinez, private communication] during the proof stage of the manuscript that an alternative to the experimental electron impact spectra is to consider the weighted intensity average of the UV

absorption spectrum found in *J. Chem. Phys.* **1977**, 66, 2224. Taking a lower integration limit of 43000 cm^{-1} and an upper integration limit in the range $53000\text{--}58000\text{ cm}^{-1}$, we obtain estimates for the bright excitation energy in the range 5.97–6.06 eV, which agrees closely with the results from the electron impact spectra originally given.