Towards an accurate molecular orbital theory for excited states: Ethene, butadiene, and hexatriene

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A newly proposed quantum chemical approach for *ab initio* calculations of electronic spectra of molecular systems is applied to the molecules ethene, *trans*-1,3-butadiene, and *trans-trans*-1,3,5-hexatriene. The method has the aim of being accurate to better than 0.5 eV for excitation energies and is expected to provide structural and physical data for the excited states with good reliability. The approach is based on the complete active space (CAS) SCF method, which gives a proper description of the major features in the electronic structure of the excited state, independent of its complexity, accounts for all near degeneracy effects, and includes full orbital relaxation. Remaining dynamic electron correlation effects are in a subsequent step added using second order perturbation theory with the CASSCF wave function as the reference state. The approach is here tested in a calculation of the valence and Rydberg excited singlet and triplet states of the title molecules, using extended atomic natural orbital (ANO) basis sets. The ethene calculations comprised the two valence states plus all singlet and triplet Rydberg states of 3*s*, 3*p*, and 3*d* character, with errors in computed excitation energies smaller than 0.13 eV in all cases except the *V* state, for which the vertical excitation energy was about 0.4 eV too large. The two lowest triplet states and nine singlet states were studied in butadiene. The largest error (0.37 eV) was found for the 2 ^1B_u state. The two lowest triplet and seven lowest singlet states in hexatriene had excitation energies in error with less than 0.17 eV.

I. INTRODUCTION

The understanding, both qualitatively and quantitatively, of the excited states of the short polyenes has remained a challenge for quantum chemistry ever since the first *ab initio* calculations were performed. Much of the discussions have centered around the problem of the nature of the lowest excited singlet state in butadiene and hexatriene. It is known that for the longer polyenes, starting with octatetraene, the lowest singlet transition corresponds to an electronic state of the same symmetry as the ground state (2 ^1A_g).[1] Transition to this state is one-photon forbidden and the vertical excitation energy is difficult to establish from experiment. There has been an ongoing discussion whether 2 ^1A_g is also the lowest excited singlet state in the shorter polyenes, butadiene and hexatriene. The first *ab initio* study of *trans*-butadiene[2] showed 2 ^1A_g to be located 2.5 eV below the strongly allowed 1 ^1B_u state. It was, however, shown in a later communication,[3] that this results was due to the use of a too restrictive basis set and a too limited account of correlation. The new calculations placed 1 ^1B_u below 2 ^1A_g. The same ordering has been obtained in all later theoretical studies. The issue should thus be settled. However, one problem with most of the *ab initio* studies is that they overestimate the excitation energy for the 1 ^1B_u with several tenths of an eV. Only a very recent study by Graham and Freed,[4] gives an excitation energy for this state in reasonable agreement with experiment [6.14 eV compared

to an experimental value for the band maximum of 5.92 eV (Refs. 5–8)]. Their value for the vertical excitation energy of 2 ^1A_g is 6.19 eV, which places the two bands on top of each other. The issue was further confused when a resonance Raman scattering experiment[9,10] indicated that the 2 ^1A_g state should be located about 0.25 eV below the 1 ^1B_u state, apparently in conflict with the all theoretical data. The situation is complicated by the fact that both states are sensitive to geometry relaxation.

The difficulties in predicting the excitation energies of the two lowest valence excited states in butadiene is only one example of a situation, which is very common for the valence excited states of the short polyenes. A similar situation obtains in hexatriene, and the problems related to the exact determination (experimentally and theoretically) of the vertical excitation energy for the *V* state in ethene is well documented.

There are several reasons why it has been difficult to compute the vertical excitation energies of valence excited states in conjugated π-electron systems using *ab initio* quantum chemical methods. As we see it, there are three major sources for these difficulties:

(1) Extended basis sets are needed in order to account for the diffuse character of some of the excited states and to account for differential correlation effects. Some of the very large errors obtained in the early studies are most certainly due to the limited basis sets, that could be afforded.

(2) Electron correlation effects play a crucial role for

the excitation energies. Especially important is the dynamic polarization of the σ orbitals in excited states, which are dominated by ionic valence structures. Typical examples are the V state in ethene[11] and the E_{1u} state in benzene.[12,13] Inability to fully account for these differential correlation effects is the reason for most deviations between calculated and experimental excitation energies for some valence excited singlet and triplet states. When configuration interaction (CI) based methods are used it is in practice impossible to include the dynamic polarization effects fully for larger molecules, due to the size bottleneck inherent in this approach, as a recent study of the valence excited states in pyrimidine illustrates.[14]

(3) While the effect of dynamic correlation can be large on some valence excited states, it is usually rather small for excited states of the Rydberg type. Because of the different correlation effects, the reference wave function for a valence excited state often has an energy larger than one or several Rydberg states. This may in some cases give rise to an erroneous and too strong interaction between the valence state and a Rydberg state, which makes the orbitals of the former state too diffuse. The electron density is then not well described at this level of the calculation, and it may be very difficult to correct this in a subsequent CI calculation. A well known example is the V state in planar ethene, where the SCF orbitals are much too diffuse due to a too strong interaction with a Rydberg state. It was shown in a recent study,[15] that it is virtually impossible to converge the calculation with respect to the diffuseness of the electron density (measured as the expectation value of z^2), by increasing the reference space in a multireference (MR) CI calculation. In the present study we compute the dynamic correlation effects using second order perturbation theory. It is clear that such an approach will not be able to correct an electron density, which is strongly affected by electron correlation. Thus we can expect some errors in cases where the reference function is mixed in an erratic way with Rydberg states. This situation obtains in ethene and also for the ^1B_u states in butadiene. The resulting errors are of the order of 0.3 eV, which is considerably larger than the errors obtained for states where such a mixing of Rydberg and valence states do not occur (the error in the excitation energy for the ^1B_u state in hexatriene is only 0.06 eV, as will be shown below).

For some time, we have attempted to gain some insight into the correlation among spectral and structural features of aromatic systems through *ab initio* quantum chemical calculations on the electronic spectra of small and medium size (up to 20 first row atoms) molecules. Recently, we reported on the π-π^* singly excited states of benzene[13] as an illustration of a novel approach that has the aim of being accurate to better than 0.5 eV. We have also reported results for the π-π^* and n-π^* singly excited states of pyridine, pyrimidine, pyrazine, pyridazine, and s-triazine using the same approach.[16] In all these cases were the excitation energies computed with an accuracy much higher than the proposed aim. The largest error among all the valence excited states in benzene occurred for the $^3E_{1u}$ state and was 0.26 eV. The same type of accuracy will be re-

ported in the present study, where we extend the number of examples of the new approach to include vertical excitation energies in the molecules ethene, *trans*-butadiene, and *trans-trans*-hexatriene. We also extend the treatment to include not only valence excited states, but also some Rydberg states, thus covering all types of excited states up to about 9 eV for ethene, 8 eV for butadiene and about 6.5 eV for hexatriene.

Due to its inherent flexibility, the complete active space (CAS) SCF approximation[17] has proven to be particularly suited to cope with situations where the electronic structure varies strongly, e.g., in the close vicinity of transition states or in excitation processes. In this approach the wave function is constructed by distributing the active electrons among the active orbitals in all possible ways whereas the inactive orbitals are kept doubly occupied in all configurations. The strong configurational mixing, common to many excited states, is then automatically included in the wave function already at this level of approximation. Such an approach is a necessary prerequisite for a balanced treatment of the dynamic correlation effects. Both the inactive and the active orbitals are optimized. Thus the static response of the core orbitals is accounted for in addition to correlation effects involving the valence orbitals.

A convenient alternative to an usual MRCI calculation is a second order perturbation treatment where the CASSCF wave function is taken as the reference function.[18,19] This method has a much larger range of applicability. The second order perturbation approach, called the CASPT2 approximation, has been shown in the studies of the benzene[13] and the azabenzenes[16] to yield accurate results for relative energies and other properties of excited states. The simplicity of the CASPT2 method makes it possible to use larger basis sets and thus to a larger extent avoid contamination of the results due to basis set deficiencies. The development of direct methods and gradient techniques will further extend the range of molecules, which can be treated with the present approach, and will allow geometry optimization for excited states and transition states for photochemical reactions.

Details about the approach and the calculations are described in the next section. A discussion of the results for each of the molecules then follows and is finally summarized in the last section, which also includes a discussion of the features common to all three molecules.

II. METHODS AND COMPUTATIONAL DETAILS

A. Basis sets

Generally contracted basis sets of the atomic natural orbital (ANO) type[20,21] are used. They have been obtained from $(14s,9p,4d)$ and $(8s,4p)$ primitive sets for carbon and hydrogen, respectively. These basis sets are constructed to optimally treat correlation and polarization effects and should be large enough to describe the electronic structure of the valence excited states within the desired accuracy. The contraction scheme used is different for the three molecules and the details are presented in Table I. Since the aim here is to describe both valence excited states and

TABLE I. Geometries, basis sets, and active spaces for ethene, butadiene, and hexatriene.

Geometry (Å, deg)[a]	Basis set[b]	Active space
1. Ethene ($H_2C_aC_bH_2$)	C($4s3p2d$), H($3s2p$)	Symmetry D_{2h} ($\sigma:a_gb_{3u}b_{2u}b_{1g}$
$r(C_aC_b)=1.339$	+C($2s$) exp: 0.012 138, 0.004 248 2	$\pi:b_{1u}b_{2g}b_{3g}a_u$).
$r(HC_a)=1.086$	+C($2p$) exp: 0.008 015 0, 0.002 805 2	all states: (31112210)
$\angle HC_aC_b$ 117.6	+C($2d$) exp: 0.028 512	2 active electrons
2. Butadiene ($H_2C_aC_bHC_bHC_aH_2$)		Symmetry C_{2h} ($a_gb_ua_ub_g$)
$r(C_aC_b)=1.343$, $r(C_bC_b)=1.467$,	C($6s3p1d$), H($2s1p$)	$\pi-\pi^*$ states: (0044)
$r(CH)=1.094$,	+C($2p$) exp: 0.008 01, 0.002 81	$\pi-\sigma^*$ states: (2222)
$\angle HC_aC_b=119.5$ $\angle C_aC_bC_b=122.8$		4 active electrons
3. Hexatriene ($H_2C_aC_bHC_cHC_cHC_bHC_aH_2$)		Symmetry C_{2h} ($a_gb_ua_ub_g$)
$r(C_aC_b)=1.337$, $r(C_bC_c)=1.457$,	C($6s3p1d$), H($2s1p$)	$\pi-\pi^*$ states: (0044)
$r(C_cC_c)=1.367$, $r(CH)=1.103$,	+C($2p$) exp: 0.008 01, 0.002 81	$\pi-\sigma^*$ states: (2244)
$\angle HC_aC_b=120.5$ $\angle C_aC_bH=117.0$		6 active electrons
$\angle HC_cC_c=115.0$ $\angle C_aC_bC_c=122.4$		

[a]References: ethene, Refs. 39 and 40; butadiene and hexatriene, Ref. 41.
[b]The primitive set is always of the ANO type (Ref. 21) constructed from the primitive set: C($14s9p4d$), H($8s4p$).

Rydberg states, the original basis sets have been supplemented with diffuse functions.

B. The CASSCF and the CASSI methods

Initially, multiconfigurational wave functions are determined at the CASSCF level of approximation. Only the π electrons were active, with all σ electrons inactive. The carbon $1s$ electrons were kept frozen in the form determined by the ground state SCF wave function and were not included in the calculation of the correlation energy.

Thus the excitations treated are of the types $\pi-\pi^*$ and $\pi-\sigma^*$, while no excitations out of the σ orbitals are considered. The choice of the active orbital space is different in the two cases. In the case of $\pi-\pi^*$ excitations eight active π orbitals were used in butadiene and hexatriene (ethene was treated differently as will be discussed below). Tests using smaller active spaces showed that this size is necessary in order to obtain converged results for all the Rydberg states included in the study. Even larger active spaces were also tested, for example, 12 active π orbitals, but were not found to lead to any sizeable modifications of the results. The active space used in the calculations for the $\pi-\sigma^*$ states comprised in addition to the π orbitals four σ orbitals.

The wave functions have been optimized for each state individually. However, in some cases near degeneracy between different states leads to convergence problems in the orbital optimization. In such cases it has proven useful to optimize a set of "average" orbitals, i.e., a single set of orbitals is determined which span a common MO basis for several excited states. In a few cases both methods have been used with very similar results for the excitation energies, ensuring that the state average approach is accurate enough. Details of the active spaces chosen for the three molecules are given in Table I.

The wave functions obtained by optimizing individual states are not mutually orthogonal. The CASSCF state interaction (CASSI) method[22] has been developed to compute transition properties from nonorthogonal state functions and is used here to compute the oscillator strength. In the formula for the oscillator strength we used the energy differences corrected for by the second order perturbation method (PT2F). Such a mixed approach may seem inconsistent, but is based on the knowledge, that the excitation energies are grossly affected by dynamic electron correlation, while this is not the case for transition densities. The approach is by now well documented in a number of applications and has in a recent study of the pyrimidine molecule been shown to give results similar to those obtained with the multireference CI method.[14]

C. The CASPT2 method

The CASPT2 method[18,19] computes the first order wave function and the second order energy in the full CI space without any further approximation with a CASSCF wave function constituting the reference function. The zeroth order Hamiltonian is defined as a Fock type one electron operator and is constructed such that a Möller–Plesset type perturbation theory is obtained in the closed shell single determinant case. Two different formulations of the zeroth order Hamiltonian are possible: one which utilizes only the diagonal part of the Fock matrix (called PT2D) and one, which includes also the nondiagonal elements (PT2F). The first choice is computationally simpler and leads in most cases to results not very different from PT2F, as illustrated, for example, in the study of the electronic spectrum of the benzene molecule.[13] It should be emphasized, however, that it is only the nondiagonal approach, which is invariant to rotations of the molecular orbitals. The full approach must therefore be used in cases, where such invariance is important, for example, in calculations of potential surfaces. An additional example is given in the present work, where it is shown that the difference between PT2D and PT2F can be substantial for excited states of the Rydberg type. As will be shown below this is especially evident in the ethene case, while the effect is smaller for butadiene and almost nonexistent for hexatriene. When the difference between the two formulations is large, PT2F is in almost all cases more accurate.

The CASPT2 program also calculates the weight, ω, of

the CASSCF reference in the first order wave function. This weight is a measure of how large a fraction of the wave function is treated variationally. The relative weight of ω in different states then gives a measure of how balanced the calculation is. Normally one requires ω to be about the same for the ground and the excited states in order for the calculation to be balanced with respect to the treatment of electron correlation.

Some parts of the calculations have been performed on the IBM 9021/500-2VF computer at the university of Valencia, others on an IBM RS/6000 workstation (models 550), in all cases using the MOLCAS-2 quantum chemistry software,[23] which includes as one module the CASPT2 program. Some timing data were presented in the recent paper on the benzene molecule.[13]

III. RESULTS AND DISCUSSION

In this section we shall present and discuss the results for each molecule separately and also compare the present data with previous *ab initio* results and available experimental data.

A. Ethene

The electronic spectrum of the ethene molecules has been intensely studied, both theoretically[24–27] and experimentally.[28–38] It is dominated by the intense and broad band corresponding to the $\pi–\pi^*$ valence excitation ($N–V$). It is by now well established that the maximum of this band, which occurs at 7.66 eV[31] does not correspond to the vertical transition, but to a somewhat twisted molecule (the equilibrium geometry of the V state has a twist angle of 90°).[25,37] A number of theoretical studies of increasing accuracy has led to a final estimate of about 8.0 eV for the vertical transition energy.[25–27] At the ground state geometry the V state has a mixed valence and Rydberg character, a mixture which is strongly dependent on the level of theory used to describe it. It was shown in a recent MRCI study,[27] that the expectation value $\langle z^2 \rangle$ (with the z coordinate perpendicular to the molecular plane) decreased slowly and monotonously with the addition of more and more correlation terms to the wave function. A plot of the π^* orbital revealed an inner part of valence character combined with a diffuse Rydberg-type tail. For this reason we can expect, that it will be especially difficult to achieve a good result for the V state with second order perturbation theory. The valence–Rydberg mixing will certainly not be correctly described at the CASSCF level of theory.

The calculations were performed with the ANO basis set contracted to $4s3p2d$ functions for carbon and $3s2p$ function for hydrogen. To this set was added 2 s-type, 2 p-type, and 1 d-type primitive gaussian functions with smaller exponents (for details see Table I). Only the two π electrons were active in the CASSCF calculations and the active orbital space comprised the two valence π orbitals together with the 3s-, 3p-, and 3d-type Rydberg orbitals. This yields an active space of 11 orbitals (cf. Table I). The states considered were in addition to the ground state, the T and V state plus the singlet and triplet Rydberg states of 3s, 3p, and 3d character, in total 11 singlet and 10 triplet

states. Average CASSCF calculations were performed for the excited states of each symmetry (a separate calculation was performed for the ground state). However, only the symmetries B_{3u} and B_{1u} comprised more than one state (3 and 2, respectively). The molecule is placed in the xy plane with the x axis along the CC bond.

The results of the CASSCF and CASPT2 calculations have been collected in Table II. Before discussing these results in more details some general features of them are worth noting. The weight, ω, of the reference function in the first order perturbed function is in all cases 0.91–0.92. Thus the calculations are well balanced and there is no problem with intruder states. It is a little surprising that the same high weight is attained also for the V state, since the CASSCF wave function is not a very good reference in this case (see below). Another result is the large contributions of the nondiagonal part of the Fock matrix in the zeroth order Hamiltonian (the difference between PT2D and PT2F in Table II). In no other case have we seen such large differences between the two methods. The difference is also much smaller for butadiene and hexatriene as will be shown below. The good agreement with experiment is only achieved with the nondiagonal approximation (PT2F). This difference between PT2D and PT2F is most probably due rotations between the weakly occupied active orbitals of σ-type and inactive orbitals in the excited states.

With the exception of the V state, the errors in the present study vary between 0.00 and +0.13 eV. To this should be added, that most experimental data refer to adiabatic excitation energies. The corresponding vertical energies should be somewhat larger: The Rydberg states of ethene are in general expected to be twisted.[28,31]

In Table II we have also for comparison included results from some of the previous theoretical studies.[24–26] Most accurate is probably the multireference CI study of Petrongolo et al.[25] With the exception of the V state and the $^1B_{3u}(3d\delta)$ Rydberg state, there is good agreement between their and the present results. The CI singles approach gives reasonable excitation energies for most of the Rydberg states [with the exception of the $^3A_g(3p\pi)$ state], but fails badly for the T state. The low energy obtained for the V state is due to the use of an SCF wave function for the ground state, instead of the more natural two-configurational wave function, which includes the effect of the configuration $(\pi^*)^2$.

The T and V states. Most calculations yield a value for the $N–T$ excitation energy in agreement with the experimental value [the CI Singles (CIS) result of Foresman et al.[24] is a notable exception]. Electron impact spectroscopy[35(a)] and electron-energy loss[35(b)] studies have established the T-state excitation energy to 4.36 and 4.32 eV, respectively, which gives errors of +0.03 and +0.06 eV, respectively, for the PT2F result. The too low value obtained in the CIS study[24] is most probably due to the SCF treatment of the ground state, which neglects the important contribution from the $(\pi_u)^2 \rightarrow (\pi_g)^2$ configuration. This internal correlation effect is not present in the T state. The CIS value for the $N–V$ excitation energy is too low for the same reason.

TABLE II. CASSCF and CASPT2 excitation energies (in eV), and CASSI oscillator strengths for ethene.

	CASSCF	PT2D	PT2F	Exp	Error[a]	ω[b]	$\langle z^2 \rangle$[c]	Osc. str. Calc.	Other calculations[d] CIS	MRCI	CI1
Ground state ($1\,^1A_g$)	...	...	...	...		0.92	11.8	...		...	
Singlet states											
$1\,^1B_{1u}(V)$	8.20	7.97	8.40	$\approx 8.0^e$	+0.4	0.91	44.1	0.16	7.78	7.96	7.96
$1\,^1B_{3u}(3s)$	6.82	6.62	7.17	7.11^{f-i}	+0.06	0.92	24.3	0.067	7.10	7.13	7.26
$1\,^1B_{1g}(3p\sigma)$	7.43	7.27	7.85	$7.80^{j,k}$	+0.05	0.92	17.2		7.68	7.86	7.93
$1\,^1B_{2g}(3p\sigma)$	7.51	7.37	7.95	7.90^k	+0.05	0.92	18.0		7.83	7.89	8.01
$2\,^1A_g(3p\pi)$	7.92	8.05	8.40	8.28^k	+0.12	0.91	36.3		8.10	8.21	8.36
$2\,^1B_{3u}(3d\sigma)$	8.24	8.11	8.66	$8.62^{f-h,l}$	+0.04	0.92	27.9	0.000 94	8.71	8.73	8.80
$2\,^1B_{1u}(3d\pi)$	8.94	8.88	9.31	9.33^m	−0.02	0.92	175.3	0.078	...	...	8.99
$1\,^1A_u(3d\pi)$	8.40	8.44	8.94	...	...	0.91	17.8		8.83	9.04	...
$3\,^1B_{3u}(3d\delta)$	8.51	8.49	9.03	$8.90^{f-h,n}$	+0.13	0.92	102.4	0.000 57	8.92	9.31	...
$1\,^1B_{2u}(3d\delta)$	8.69	8.73	9.18	$9.05^{f,l}$	+0.13	0.91	17.7	0.077	8.88	8.99	...
Triplet states											
$1\,^3B_{1u}(T)$	4.65	3.97	4.39	4.36^m	+0.03	0.91	11.9		3.54	4.35	...
$1\,^3B_{3u}(3s)$	6.74	6.49	7.05	6.98^g	+0.07	0.92	23.8		6.88	...	...
$1\,^3B_{1g}(3p\sigma)$	7.41	7.25	7.80	7.79^g	+0.01	0.92	17.0		7.60	...	...
$1\,^3B_{2g}(3p\sigma)$	7.47	7.31	7.90	...	...	0.92	17.7		7.72	...	...
$2\,^3A_g(3p\pi)$	7.73	7.84	8.26	8.15^g	+0.11	0.92	34.9		7.75	...	...
$2\,^3B_{3u}(3d\sigma)$	8.21	8.01	8.57	8.57^g	+0.00	0.91	28.3		8.63	...	...
$2\,^3B_{1u}(3d\pi)$	8.71	8.77	9.07	...	...	0.92	84.1		...	...	...
$1\,^3A_u(3d\pi)$	8.40	8.46	8.94	...	...	0.92	17.7		...	...	...
$1\,^3B_{2u}(3d\delta)$	8.61	8.66	9.09	...	...	0.91	17.5		...	...	...
$3\,^3B_{3u}(3d\delta)$	8.47	8.42	8.97	...	...	0.92	85.1		...	...	...

[a]Difference between the PT2F results and experiment.
[b]The weight of the CASSCF reference function in the first order wave function.
[c]Expectation value (CASSCF) of z^2 (in a.u.^{2}), where z is the coordinate perpendicular to the molecular plane.
[d]CIS results from Ref. 24; MRCI results from Ref. 25;. CI1 results from Ref. 26.
[e]Estimated vertical excitation energy from earlier theoretical work (Refs. 25–27).
[f]Reference 28.
[g]Reference 29.
[h]Reference 30.
[i]Reference 31.
[j]Reference 32.
[k]Reference 33.
[l]Reference 34.
[m]Reference 35.
[n]Reference 36.

The situation is very different for the V state. The vertical excitation energy has been estimated to be around 8.0 eV.[25–27] A recent extensive multireference (MR) CI study gave the value 7.94 eV,[27] which should be rather accurate. The value for $\langle z^2 \rangle$ was in that study computed to be 16.8 a.u.^{2} The present CASSCF value is 44.1 a.u.^{2} This value is much too large, even if the basis set used here includes more diffuse function. There is thus an erroneous valence–Rydberg mixing in the CASSCF reference function. We actually searched among the lower excited states to see if we could find a state with a more valence like character. However, no such state could be found below 10.0 eV. It seems that the valencelike state is completely submerged among the Rydberg states at this level of theory. The CASPT2 calculation does not lead to an improvement of the excitation energy: the error is about 0.4 eV, which is the largest deviation from experiment found for any of the molecules in the present study. It is, however, still within the proposed error limit of the CASSCF/CASPT2 approach: 0.5 eV.

In order to monitor in more detail the importance of more contracted orbitals in the reference function for the

dynamic correlation calculation we have performed CASSCF/CASPT2 and MRCI calculations on the N and V states with an applied perturbation, $\lambda \langle r^2 \rangle$, where r is the distance from the center of the molecule. This perturbation can be considered as a penalty function for the Rydberg states, and should thus provide a more compact reference function for the CASPT2 and MRCI calculations. A slightly different set of diffuse functions was used in the AO basis set: 2 p-type and 2 d-type functions with exponents 0.0229, 0.0081 (p) and 0.0815, 0.0285 (d), respectively.

CASSCF calculations were first performed with the two valence π orbitals active. The MRCI calculation used as reference configurations $(\pi)^2$ and $(\pi^*)^2$ for the N state and $(\pi\pi^*)_S$ for the V state. The perturbing field was removed in the MRCI calculations. The excitation energies for CASSCF and CASPT2 were obtained with the expectation value of the perturbation removed from the respective energies.

The results of these calculations are shown in Table III. We first notice, that the CASSCF value of $\langle r^2 \rangle$ decreases sharply with the strength of the applied perturba-

TABLE III. CASSCF/CASPT2 and MRCI excitation energies and $\langle r^2 \rangle$ expectation values as a function of an external perturbation $V = \lambda \langle r^2 \rangle$.

λ (a.u.)	Excitation energies (eV)			$\langle r^2 \rangle$ (a.u.^{2}) for the V state	
	CASSCF	PT2F	MRCI	CASSCF	PT2F
0.0000	8.17	8.43	8.45	154.9	76.2
0.0005	8.69	8.37	8.26	106.9	78.2
0.0010	8.96	8.33	8.24	98.2	79.8
0.0015	9.15	8.31	8.25	93.5	81.1

tion. The PT2F value is smaller for all field strengths, but the two values approach each other, when the field strength increases. Even without the field ($\lambda = 0.0000$) the size of the CASPT2 wave function is valence like. Actually it is more compressed than the N state, for which the value of $\langle r^2 \rangle$ is 82.7 (82.4) a.u.^{2} at the PT2F (CASSCF) level. The first order wave function thus overcorrects the diffuse character of the CASSCF reference function.

We can use λ as a variational parameter in the MRCI calculation and determine the minimum value of the V-state energy as a function of λ. The optimum value is 0.0011, corresponding to an excitation energy of 8.24 eV, an improvement of 0.21 eV compared to the zero field results. Since the CASPT2 method is nonvariational, the same technique cannot be used here. We note, however, that the PT2F and MRCI excitation energies behave the same way as functions of the applied field. The CASPT2 result at the field strength 0.0011 is 8.32 eV, only 0.08 eV above the MRCI results. We conclude that the original error in the excitation energy (0.4 eV) is not an artifact of the CASPT2 approach, but is due to the diffuse character of the CASSCF reference function. The same erratic mixing of valence and Rydberg configurations in the reference function occurs also for the ^1B_u state in butadiene, but there to a smaller extent.

The 3s Rydberg states. The singlet π–3s excitation is dipole allowed and is assumed to be the source of the 2R band. The transition has been studied by uv spectroscopy,[31] one-photon absorption spectroscopy,[30] and electron energy loss spectroscopy,[29] establishing the excitation energy to 7.11 eV. The resonance Raman spectroscopy study by Sension and Hudson[37] yields the value 7.10 eV, while a low-energy electron impact measurement[35(a)] gives 7.12 eV. The singlet–triplet splitting has been determined with electron loss spectroscopy to be 0.13 eV.[29] These results can be compared to the present energies of 7.17 and 7.05 eV for the singlet and the triplet state, respectively. The theoretical energies are thus slightly too large (0.06 eV), but the computed singlet–triplet splitting is in excellent agreement with experiment.

The 3p Rydberg states. The singlet π–3p transitions are optically quadrupole allowed and are in the D_{2h} point group assigned to the irreducible representations $A_g(3p\pi)$, $B_{1g}(3p\sigma)$, and $B_{2g}(3p\sigma)$. The excitation energies for the B_{1g} and A_g states have been measured with multiphoton ionization spectroscopy[32] to 7.80 and 8.29 eV, respectively. Electron energy loss[29] and electron impact spectroscopy[34] both give the value 8.26 eV for the A_g state and the values

7.85 and 7.83 eV for B_{1g}. The corresponding low-energy electron impact[35(a)] values are 8.24 and 7.83 eV. A recent two-electron REMPI study[33] includes also the B_{2g} transition and yields the values 8.28(A_g), 7.80(B_{1g}), and 7.90(B_{2g}) eV. This assignment is confirmed by the PT2F transition energies: 8.40, 7.85, and 7.95 eV, respectively. The singlet–triplet splitting has been measured by electron energy loss spectroscopy[29] to be 0.11(A_g) and 0.06(B_{1g}) eV. The theoretical values are 0.14 and 0.05 eV and the theoretical prediction for the B_{2g} state is 0.05 eV. The assignment of the quadrupole-allowed transition around 7.45 eV[38] to π–3p is not supported by this study.

The 3d Rydberg states. The π–3d singlet transitions are dipole allowed and belong to the irreducible representations $B_{1u}(3d\pi)$, $B_{2u}(3d\delta)$, $B_{3u}(3d\sigma, 3d\delta)$. The only exception to this rule is the transition to $A_u(3d\pi)$, which is both dipole and quadrupole forbidden. It has not been reported in any experimental work. The PT2F result predicts the excitation energy to be 8.94 eV for both the singlet and the triplet state. The assignments are clear for the $B_{3u}(3d\sigma)$ and $B_{1u}(3d\pi)$ transition with measured transition energies of 8.62 eV for the first transition[28–30,34] and 9.33[35(a)] or 9.36 eV[28] for the second. The corresponding PT2F values are 8.66 and 9.31 eV, respectively. For the B_{2u} and $B_{3u}(3d\delta)$ transition there is some controversy in the experimental literature. The B_{3u} transition is assigned at 8.90 eV by a number of experiments[28,29,34] and the B_{2u} transition at 9.05 eV.[28,34] However, based on magnetic circular dicroism (MCD) measurements[36] Snyder et al. argue that the origins at 8.90 and 9.05 eV are each a composite of two electronic transitions: the 3R origin is assigned to a $B_{2u} + B_{3u}$ transition and the $4R'''$ origin is then assigned to a vibrational member of the same band. The same assignment had earlier been proposed by McDiarmid based on vacuum uv absorption spectroscopic measurements.[30] Although the theoretical (vertical) excitation energies are somewhat (0.13 eV) larger, the energy splitting, 0.15 eV is predicted to be almost identical to the splitting between the vibrational members of the 3R band as suggested by McDiarmid[30] and Snyder et al.[36] Hence, the present results support the conclusions of Johnson et al.,[34] who argue that the feature at 9.05 eV is due both to the $4R'''_{00}$ transition and to higher vibrational members of the 3R band [$v_3 = 1212$ cm^{-1} (0.15 eV)].

The singlet–triplet splitting for the $B_{1u}(3d\pi)$, $B_{3u}(3d\sigma)$, $B_{3u}(3d\delta)$, and $B_{2u}(3d\delta)$, states is predicted to be 0.22, 0.09, 0.06, and 0.09 eV, respectively. The only experimental singlet–triplet separation reported so far is for the $B_{3u}(3d\sigma)$ state: 0.05 eV.[29]

B. Butadiene

The electronic spectrum of the butadiene molecule has been extensively studied both experimentally[5–10,42–48] and by theory.[2–4,49–62] Much of the theoretical work is concerned with the geometry of the excited states and will not be further discussed here. Some of the older work is also of less interest, since only small basis sets were used and dynamic correlation effects were, as a consequence, not prop-

TABLE IV. CASSCF and CASPT2 excitation energies (in eV), and CASSI oscillator strengths for butadiene.

	CASSCF	PT2D	PT2F	Exp	Error[a]	ω[b]	$\langle z^2 \rangle$[c]	Osc. str. Calc.	Osc. str. Exp.	Other calculations[d] GVB-CI	SAC-CI	MRCI1	MRCI2	VSEH
Ground state ($1\,^1A_g$)	...	...	...	...		0.85	21.9	...	...					
Singlet states														
$1\,^1B_u(V)$	8.54	6.12	6.23	5.92[e-g]	+0.31	0.76	40.9	0.686	0.4[h]	6.90	6.39	7.07	6.48	6.14
$1\,^1B_g(3s)$	6.30	6.11	6.29	6.27[f]	+0.02	0.84	40.0	forbidden		6.29	...	...	...	...
$2\,^1A_g(V)$	6.64	6.23	6.27	?	?	0.80	23.2	forbidden		7.06	7.00	8.67	6.53	6.19
$1\,^1A_u(3p\sigma)$	6.49	6.38	6.56	6.66[e-g]	−0.10	0.84	36.2	0.002	...	6.61	...	...	...	...
$2\,^1A_u(3p\sigma)$	6.58	6.51	6.69	6.80[e-g]	−0.11	0.84	40.1	0.037	...	6.78	...	...	...	...
$2\,^1B_u(3p\pi)$	6.88	6.75	6.70	7.07[e-f]	−0.37	0.82	88.9	0.080	...	6.67	7.05	...	...	7.00
$2\,^1B_g(3d\delta)$	7.20	7.14	7.30	7.28[e]	+0.02	0.84	50.6	forbidden		7.29	...	...	...	...
$3\,^1A_g(3d\pi)$	7.55	7.44	7.47	7.48[f,g]	−0.01	0.84	94.8	forbidden		7.68	7.33	...	...	7.49
$3\,^1B_u(4p\pi)$	7.85	7.76	7.79	8.00[e-g]	−0.21	0.83	284.5	0.036	...	7.79	7.87	...	...	...
Triplet states														
$1\,^3B_u$	3.39	3.14	3.20	3.22[e]	−0.02	0.84	21.8			3.35	3.48	3.60	3.18	3.23
$1\,^3A_g$	5.08	4.81	4.89	4.91[e]	−0.02	0.84	22.0			5.08	5.15	5.33	4.83	4.90

[a]Difference between the PT2F results and experiment.
[b]The weight of the CASSCF reference function in the first order wave function.
[c]Expectation value (CASSCF) of z^2 (in a.u.^{2}), where z is the coordinate perpendicular to the molecular plane.
[d]GVB-CI results from Ref. 54; SAC-CI results from Ref. 58;. MRCI1 results from Ref. 56; MRCI2 results from Ref. 57. VSEH results from Ref. 4. (see the text for further details).
[e]References 5 and 6.
[f]References 7 and 42.
[g]Reference 43.
[h]Reference 66.

erly accounted for. Of special interest is the paper by Graham and Freed[4] (hereafter referred to as GF). The approach used is in spirit very similar to CASPT2. A valence shell effective Hamiltonian (VSEH) is constructed using partitioning technique with the resolvent truncated at third order. GF shows that the third order corrections are essential to correct for a forced orbital degeneracy in the zeroth order Hamiltonian. A comparison order by order with the present results is then not very meaningful, since such a forced degeneracy is not necessary in the CASPT2 approach. As will be illustrated below our second order results are in fact very similar to the third order results of GF. Another approach, similar to CASPT2 is the quasidegenerate variation perturbation theory (QDVPT) of Cave and Davidson,[63] which was recently applied by Cave to study size-inconsistency effect of the transition energies in ethene and butadiene.[60]

The results from the present work together with experimental data and selected results from previous calculations are collected in Table IV. The first three columns give the excitation energies obtained from the CASSCF, PT2D, and PT2F calculations. The error column refers to the difference between the experimental energies and the PT2F results, which we believe to be most accurate. ω gives the weight of the CASSCF reference function in the first order wave function (PT2F), and $\langle z^2 \rangle$ is the CASSCF expectation value of z^2 (in a.u.^{2}), where z is the coordinate perpendicular to the molecular plane. Oscillator strengths, obtained with the CASSI method are also presented in the table.

The ^1B_u states. The first state of ^1B_u symmetry represents the major feature in the electronic spectrum of butadiene. The maximum of the broad band has been well established and is assumed to be close to the vertical

excitation energy (in contrast to ethene). Most calculations find this state to be rather diffuse and it is assumed to include some Rydberg character. McDiarmid has recently tried to estimate the apparent Rydberg–valence mixing in this state from experimental data,[65] and suggests that the $3p$ contribution to the valence state is 29%, while the VSEH calculation of GF gives 17%. From the values of $\langle z^2 \rangle$ in Table II we estimate the mixing to be about 20%. This value is based on the CASSCF wave functions for the $1\,^1B_u$ and $2\,^1B_u$ states. However, the valence state is much more affected by electron correlation than the Rydberg state. As can be seen in Table I the CASSCF energies are in reversed order with the valence state above the two lowest Rydberg states. The valence–Rydberg mixing in these states may then be an artifact of the erratic energetics and is probably overestimated. As was explained in the introduction, such an artificial mixing of Rydberg and valence character in the reference function cannot be fully compensated for in a low order perturbation calculation. The errors in the computed excitation energies are also unusually large in this case (+0.31 eV for the $1\,^1B_u$ state, −0.37 eV for $2\,^1B_u$, and −0.21 for $3\,^1B_u$). The fact that the error is positive for the lowest state and negative for the two higher states indicates a too large Rydberg character of the lowest state.

Even if the errors for the ^1B_u states are somewhat larger than expected, they are still acceptable and well within the proposed accuracy (0.5 eV) of the present model. A comparison with the results of GF indicates that the VSEH approach is somewhat better suited to deal with the valence–Rydberg mixing. The difference in computed excitation energies is, however, not large (0.09 eV for the lowest state). A comparison with earlier calculations based on different versions of the CI technology[54–59] shows that

the perturbation approach recovers a larger fraction of the correlation error than most CI based methods. The QD-VPT method of Cave and Davidson yields an excitation energy of 6.39 eV for $1\,{}^1B_u$ and 7.06 eV for $2\,{}^1B_u$. The calculated oscillator strength for ${}^1B_u$ is 0.69 in fair agreement with an old experimental value of 0.4.[66]

The $2\,{}^1A_g$ state. One of the major issues concerning the electronic spectrum of butadiene has been the relative location of the $1\,{}^1B_u$ and $2\,{}^1A_g$ states. Experimental assignments range from 5.4 to 7.3 eV. The old assignment at 7.28 eV[5] can be ruled out in the light of the more recent experimental and theoretical results. Multiphoton ionization experiments shows no sign of an ${}^1A_g$ state below 6.05 eV,[67] while a recent resonance Raman scattering experiment gives indication of an ${}^1A_g$ state 0.25 eV below the $1\,{}^1B_u$ state.[10] There is, however, no indication in the paper that this difference refers to the vertical excitation energies. It is well known[61,62,64] that the two states behave differently with respect to geometry relaxation, with the consequence that the 0–0 transition of the ${}^1A_g$ state is lower than that of the $1\,{}^1B_u$ state. Most calculations place the vertical excitations energies in the reversed order (cf. Table II). The results of GF indicates that they should be very close in energy. The present calculation places this state at 6.27 eV above the ground state, 0.08 eV above the result of GF, but the relative positions are the same in both studies. The state is clearly of valence character with a $\langle z^2 \rangle$ value close to that of the ground state. We therefore expect the error in the computed excitation energy to be smaller than it is for the $1\,{}^1B_u$ state. Thus we also conclude that the vertical excitation energy for $2\,{}^1A_g$ lies above that of $1\,{}^1B_u$ and we estimate the energy difference to be 0.2–0.5 eV, based on earlier experience[13,16] for excited states of similar character. A large fraction of the CASSCF wave function for the $2\,{}^1A_g$ state can be described as doubly excited with respect to the ground state. Actually, only 58% of the wave function consists of singly excited configurations. This feature of the $2\,{}^1A_g$ state is well known. It could cause problems in more limited CI treatments, but does not constitute a problem here where the entire CASSCF wave function is used as a reference for the correlation treatment. The situation resembles that of the ${}^1E_{1g}$ state in benzene for which an excitation energy in good agreement with experiment (the error was 0.03 eV) was recently obtained using the CASSCF/CASPT2 formalism.[13]

Rydberg states. The present study also includes a number of the lowest Rydberg states (cf. Table IV). It was shown for the ethene molecule that these states can be obtained with good accuracy using the present approach. This is also the case here, maybe with the exception of the ${}^1B_u$ states for which the valence–Rydberg mixing introduces some complications, as discussed above. The positions of Rydberg states of the other symmetries (A_g, A_u, and B_g) are predicted with errors not larger than about 0.1 eV, and confirm previous assignments. Again we see that the correlation effects are small and of the reversed order compared to the valence states. A comparison is made in Table II with the GVB-CI results of Nascimento and Goddard.[54] While this approach does not seem to be able to

recover the large dynamic correlation effects of the valence states, it gives results for the Rydberg states, which are very similar to those obtained here (maybe with the exception of $3\,{}^1A_g$, where the difference is 0.2 eV).

C. *Trans*-1,3,5-hexatriene

Hexatriene has received less attention than butadiene, doubtless due to the increased size of the computations and the limited success of the CI approach in the description of the valence states of the shorter chain species. Surprisingly enough the present approach is less complicated for hexatriene than for ethene and butadiene. The molecule is larger, but not so large that it imposes further restrictions on the chosen basis set (which is the same as used for butadiene), or on the active space. On the other hand all low lying excited states are now well behaved and there is no appreciable mixing between valence and Rydberg states. The calculations then become more balanced and the CASSCF wave functions are, for all states studied, appropriate reference functions for the CASPT2 calculations. As a results we should obtain excitation energies with better accuracy than was possible for butadiene, and this is indeed the case. The largest deviation from experiment is -0.17 eV and occurs for the $1\,{}^1A_u$ Rydberg state, provided of course that the present assignment of the spectrum is correct.

The calculations have been performed with one active orbital in each of the symmetries a_u and b_g in addition to the six valence shell π orbitals. Two active orbitals in each of the symmetries a_g and b_u were added for the calculation of the lowest Rydberg states of π–σ^* character. Only excitations out of the π orbitals were considered. In total we have studied six singlet states (two valence and four Rydberg states) and in addition the two triplet valence excited states. Only the PT2D approach has been used for hexatriene. The results for ethene and butadiene indicates that the difference between PT2D and PT2F decreases when the molecule gets larger. Our earlier experience on benzene[13] and the azabenzenes[16] points in the same direction. We performed two control calculations in order to test the assumption directly on hexatriene. The difference between the PT2D and PT2F results for the $2\,{}^1A_g$ and $3\,{}^1A_g$ excitation energies came out as 0.01 and 0.05 eV, respectively. We are thus confident that the PT2D results are accurate enough.

The results are presented in Table V. Comparison is made with experimental data and with two other calculations, one GVB-CI study of Nascimento and Goddard[68] and a CI study by Cave and Davidson.[62,69] In the, so-called quadruples CI(QCI) of Cave and Davidson, only the π electrons (and in one case a σ Rydberg electron) are correlated, while the more extended CI6 calculations also include $\pi\sigma$ correlation by including into the configuration space also double excitations involving at least one of the π electrons. The underlying assumptions for these CI space selections can be tested by the present approach which includes all types of correlation effects. A partitioning of the correlation energy into $\sigma\sigma$, $\sigma\pi$, and $\pi\pi$ can easily be performed. Carrying out such an analysis for all the π–π^*

TABLE V. CASSCF and CASPT2 excitation energies (in eV), and CASSI oscillator strengths for hexatriene.

	CASSCF	PT2D	Exp	Error[a]	ω[b]	$\langle z^2 \rangle$[c]	Osc. Str. Calc.	Previous[e]	Other calculations[e] GVB-CI	QCI/CI6
Ground state ($1\,^1A_g$)	...	...	...	.	0.78	31.8	...	...		
Singlet states										
$1\,^1B_u(V)$	7.36	5.01	4.95[h]	+0.06	0.70	40.4	0.85	1.24	6.56	5.14
$2\,^1A_g(V)$	5.65	5.19(5.20)[d]	5.21[j]	−0.01	0.74	31.8	forbidden		5.87	5.74
$1\,^1A_u(3s)$	5.75	5.84	5.67[k]	+0.17	0.77	69.4	0.0015	...	5.97	...
$2\,^1B_u(3d\pi)$	6.59	6.11	6.06[h]	+0.05	0.74	85.0	0.071	0.035	6.27	6.09
$1\,^1B_g(3p\sigma)$	5.87	6.12	6.20[f]	−0.08	0.78	48.0	forbidden		6.00	6.12
$3\,^1A_g(3p\pi)$	6.27	6.19(6.24)[d]	6.22[f,h,j]	+0.02	0.77	105.6	forbidden		6.26	6.51
Triplet states										
$1\,^3B_u$	2.70	2.55	2.61[h]	−0.06	0.78	31.8			2.71	2.84
$1\,^3A_g$	4.32	4.12	4.11[h]	+0.01	0.77	31.7			4.32	...

[a]Difference between the PT2D (PT2F) results and experiment.
[b]The weight of the CASSCF reference function in the first order wave function.
[c]Expectation value (CASSCF) of z^2 (in a.u.^{2}), where z is the coordinate perpendicular to the molecular plane.
[d]Values within brackets are PT2F results.
[e]GVB-CI results from Refs. 54 and 68; QCI/CI6 results (and oscillator strengths) from Refs. 62 and 69.
[f]Reference 70.
[g]Reference 71.
[h]Reference 72.
[i]Reference 66.
[j]Reference 73.
[k]Reference 74.

excited states included in the present study shows that the difference in the $\sigma\sigma$ pair correlation energies between an excited state and the ground state is never larger than 0.2 eV, while the difference for the $\sigma\pi$ correlation energy can be as large as 0.7 eV. $\sigma-\pi^*$ excitations will obviously give rise to larger modifications of the total $\sigma\sigma$ pair correlation energy.

The 1 ^1B_u state. Two states of this symmetry have been studied. The CASSCF results place them in the reversed order with the valence state higher than the Rydberg state. The valence state is, however, much less diffuse than was the case in ethene and butadiene, indicating a smaller valence–Rydberg mixing. We note, however, that the $\langle z^2 \rangle$ value is still about 30% larger than for the ground state. Cave and Davidson[69] have pointed out that it is only after inclusion of the dynamic electron correlation effects that the size of this state shrinks to that of the ground state. Our CASSCF value is therefore too large. We have not computed the $\langle z^2 \rangle$ value using the correlated CASPT2 wave function. It could have been done, using finite field techniques, but we did not find it essential enough for the interpretation of the results to perform such calculations. The conclusions of Ref. 69 are most probably correct.

The 1 ^1B_u state is well characterized experimentally, both by vacuum uv spectroscopy,[70] absorption spectroscopy of jet-cooled molecules,[71] and electron impact.[72] The maximum intensity occurs at 4.95 eV,[72] which is then taken as the vertical transition energy. The present PT2D result for the excitation energy is 5.01 eV, which is only 0.06 eV larger than the experimental value. The CI6 results of Cave and Davidson[62] is 5.14 eV. The GVB-CI[68] excitation energy is, not surprisingly, much too large, 6.56 eV. The oscillator strength computed here is 0.85 somewhat lower than the results obtained by Cave and Davidson,[69] 1.24. No experimental value has been reported.

The 2 ^1A_g state. The calculated transition energy for this state is 5.19 eV (5.20 eV with PT2F). Both the GVB-CI[68] and the CI6[62] calculations yield considerably larger excitation energies, 5.87 and 5.74 eV, respectively. All calculations place this state above the 1 ^1B_u state. Based on an empirical correction, Cave and Davidson estimate the vertical transition energy for 2 ^1A_g to be in the range 5.5–5.8 eV, thus confirming an earlier assignment of a band in the uv spectrum,[70] extending from 5.7–6.6 eV. However, this assignment was taken from semiempirical π-electron calculations, which are known not to yield very accurate results for this state in the polyenes. A recent two-photon absorption study of hexatriene[73] finds a two-photon allowed band with a maximum at 42 000 cm^{-1} (5.21 eV) in perfect agreement with the present result. The earlier assumption,[75] that the excitation energy should lie near 4.4 eV, has no support from theory or experiment,[72,73] except for the 0–0 transition in the *cis* isomer.[76] Based on the general accuracy of the present approach we conclude that the vertical excitation energy for the 2 ^1A_g state is 5.2 eV with an error bar of at most ±0.2 eV.

Rydberg states. Four Rydberg states have been included in the present study, one in each symmetry. The first $^1A_u(3s)$ state is computed to appear at 5.84 eV. Even if the transition is dipole allowed, the computed intensity is very small, 0.0015. The corresponding GVB-CI energy is 5.97 eV.[68] Cave and Davidson did not include this state in there study. Experimental information on this state is scarce. Flicker et al.[72] do not mention it in their electron impact study. They find eight states in the region between 6.0 and 7.4 eV, but do not make any specific assignments. Gavin and Rice in their vacuum uv study[70] find a series of band at the high energy side of the 1 ^1B_u transition, but neither they dare to make an assignment. Finally, McDiarmid et al.[74] assigned a transition at 5.67 eV which ob-

served selection rules are consistent with the $1\,^1A_u(3s)$ state. We tentatively agree with this assignment even if the resulting error is somewhat large ($+0.17$ eV) for a state of Rydberg type.

The second ^1B_u state occurs next on our spectrum with an excitation energy of 6.11 eV. It is a $3d\pi$ Rydberg state with a computed oscillator strength of 0.07. We note that this state falls below the $3p$ Rydberg states, probably due to differences in the interaction with the corresponding valence states. Flicker *et al.*[72] have in their electron impact study reported a band system with peaks at 6.06 eV, which they tentatively assign to either $2\,^1A_g$, $3\,^1A_g$, or $2\,^1B_u$. The assignment to $2\,^1A_g$ can be ruled out as discussed above. $3\,^1A_g$ is not a good candidate, since an alternative assignment (see below) is more likely for this state. Gavin and Rice[70] assign the band at 6.53 to $2\,^1B_u$. However such an assignment should lead to an error in our calculated excitation energy of 0.42 eV, which is highly unlikely for a Rydberg state. The GVB-CI[68] and the CI6[69] results also indicate a much lower excitation energy (cf. Table V). We conclude that the $2\,^1B_u$ state is located near 6.1 eV, in agreement with the band at 6.06 eV found by Flicker *et al.*[72]

Two Rydberg states of $3p$ character occur next among the states considered: $1\,^1B_g(3p\sigma)$ and $3\,^1A_g(3p\pi)$ with excitation energies of 6.12 and 6.19 eV, respectively. The GVB-CI study[68] places these states at 6.00 and 6.26 eV, respectively, while Cave and Davidson report quite different results[69] (cf. Table V). The polarized two-photon studies of Parker *et al.*[48] present quite a strong case for assigning the peak at 6.22 eV to the $3\,^1A_g$ state. McDiarmid *et al.*[74] assign a peak at 5.85 eV as $3\,^1A_g$, although Flicker *et al.*[72] describe it as a vibronic band of the $1\,^1B_u$ system. They, on the other hand, suggest that the $3p$ transition should be found among the bands between 6.0 and 7.4 eV. The optical absorption spectrum also shows a weak feature around 6.2 eV, which could be interpreted as the $3p$ Rydberg states.[70] The calculated excitation energies for the two $3p$ states are very similar and both transitions are single photon dipole forbidden and of the g–g type. It is therefore highly likely that they cannot be separated in the spectrum. Our results strongly indicate that both bands are located in the spectral region around 6.2 eV.

The triplet states. The two lowest valence triplet states have also been included in the study. As was the case both for ethene and butadiene they present no computational problem and the transition energies agree well with the electron impact data.[72]

IV. DISCUSSION

This paper presents results from one more test of a novel computational method for calculating excitation energies in molecular systems. The proposed aim of the method is to achieve an accuracy of at least 0.5 eV for all excitation energies. This goal was reached in the previous studies of benzene[13] and the azabenzenes[16] for all states where an unambiguous comparison with experimental data was possible. Also in the present study of ethene, butadiene, and hexatriene are the results of the same accuracy.

The largest errors occur for the V state in ethene ($+0.4$ eV) and for the three states of ^1B_u symmetry in butadiene ($+0.31$, -0.37, and $+0.21$ eV). In these cases the lower accuracy can be attributed to an erroneous mixing of valence and Rydberg character in the CASSCF reference function, which cannot be completely accounted for by the second order perturbation treatment. The root mean square (rms) error for the 32 excitation energies is 0.13 eV. Without the states mentioned above the rms value drops to 0.08 eV, a highly satisfactory result.

One basic assumption of the current approach is that all essential electronic structure features should be covered by the CASSCF reference function. Such a condition is a prerequisite for a low order perturbation theory to be able to give reliable results. Modifications of the electron density (the strongly occupied natural orbitals) due to dynamic correlation effects is a higher order effect involving in addition single and triple (and higher) replacements with respect to the main configurations of the reference state. This situation makes it, for example, difficult to use CASPT2 to compute electron affinities for negative ions, that are not bound at the CASSCF level of approximation. In the present study of excited states we have seen, that similar problems can arise due to artificial interactions between valence excited states and Rydberg states. It was noticed for the V state in ethene, that an improved reference function can be constructed by means of a penalty function that shifts the Rydberg states to higher energies. The corresponding CASSCF reference function becomes more compact and both the CASPT2 and the MRCI excitation energies are improved. We do not believe, however, that this should be used as a general procedure, since the CASPT2 method is non-variational and there is no automatic way of choosing the perturbation parameter. An effective Hamiltonian approach, where dynamic correlation effects are included at the orbital optimization step, would probably be able to handle also these more difficult cases (see e.g., Ref. 4). Strong Rydberg–valence mixing is, however, not common for the lower excited states. It occurs mainly for small molecules, where the first valence excitation energies fall in the same region as the onset of the first Rydberg series. For hexatriene, for example, the problem disappeared, all the excited states studied are well behaved, and the a maximum error in computed relative energies is 0.17 eV.

In addition to testing a new computational scheme the present work has also provided new information about the excited states of the target molecules. Thus the full $3s$, $3p$, $3d$ singlet and triplet Rydberg series of ethene has been computed. The errors are small enough (maximum 0.13 eV) to provide unambiguous assignments for all states. The calculations confirm the earlier results, that places the vertical excitation energy of the ^1B_u state below ^1A_g in both butadiene and hexatriene. The predicted energy difference in hexatriene is 0.19 eV, which is probably a slight underestimate. The assignment of the ^1A_g state at 5.21 eV[73] would result in an energy separation of 0.26 eV. In addition assignments for four Rydberg states are also provided. The corresponding bands are seen in the experimental

spectra, but no conclusive assignment has been possible. We believe, that the present result are accurate enough for the proposed assignments to be definite.

V. SUMMARY AND CONCLUSIONS

A recently proposed[13] theoretical method for the calculation of properties of excited states in conjugated molecular systems, has been tested in calculations of the electronic spectra of ethene, butadiene, and hexatriene. The model is a two step procedure with static correlation effects included in the first step where the molecular orbitals are optimized. Remaining (dynamic) correlation effects are computed in the second step using a second order perturbation approach. The model has earlier been tested in a study of the excited states of the benzene molecule,[13] where it was shown to yield excitation energies with an accuracy of 0.25 eV or better for all valence excited singlet and triplet states. A similar accuracy is obtained in the present study, even if valence–Rydberg mixing poses special problems for two of the molecules.

Graham and Freed have recently published results for the *trans*-butadiene π–valence states obtained with an effective valence Hamiltonian method.[4] The computed excitation energies have the same accuracy as that obtained here. Even though these calculations are carried to third order in the treatment of dynamic correlation, they provide further evidence for the validity of a low order multiconfigurational perturbation approach in calculations of electronic excitation energies.

ACKNOWLEDGMENTS

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