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Theoretical study of the electronic spectra of *cis*-1,3,5-hexatriene and *cis*-1,3-butadiene

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Summary. The electronic spectra for *cis*-1,3-butadiene and *cis*-1,3,5-hexatriene have been studied using multiconfiguration second-order perturbation theory (CASPT2) and extended ANO basis sets. The calculations comprise all singlet valence excited states below 8.0 eV, the first 3*s*, 3*p*, 3*d* Rydberg states, and the second 3*s* state. The four lowest triplet states were also studied. The resulting excitation energies for *cis*-hexatriene have been used in an assignment of the experimental spectrum, leading to a maximum deviation of 0.13 eV for the vertical transition energies. The calculations place the 1^1B_2 state 0.04 eV below the 2^1A_1 state. 16 excited states were studied in *cis*-butadiene, using a CASPT2 optimized ground state geometry. The 1^1B_2 state was located at 5.58 eV, 0.46 eV below the 2^1A_1 state and 0.09 eV above the experimental value. No experimental assignments are available for the 15 other transitions.

Key words: *Cis*-1,3-butadiene – *Cis*-1,3,5-hexatriene – CASPT2 – Electronic spectra

1 Introduction

The main features of the gas phase ultraviolet absorption spectrum of hexatriene are known from early experimental studies [1], but it was only with the more detailed studies of Gavin et al. [2] that a large number of transitions could be identified and it became possible to differentiate between the two isomers of the molecule. The most intense peak was obtained at 4.93 eV in the *trans*- and at 4.92 eV in the *cis*-isomer. A large number of features at higher energies were also found, although without further assignments. Electron impact spectroscopy has also been used [3–6], although without enough resolution to be able to distinguish between the two isomers. Multi-photon ionization [7] and two-photon absorption spectroscopy [8] has focused mainly on the *trans*-isomer. The two isomers of

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hexatriene have in recent years been the subject of a large number of experimental studies. McDiarmid et al. have, for example, used electron energy loss and multi-photon ionization spectroscopies to accurately assign the lower Rydberg states of *trans* [9, 10] and *cis* [9, 11]-hexatriene.

The two systems have been invoked in the wide discussion about the order of the two lowest valence states that have plagued the spectroscopy of the polyenes [12]. No evidence of the 2^1A_1 (2^1A_g for the C_{2h} *trans*-isomer) valence state under the lowest optically allowed 1^1B_2 (1^1B_u for *trans*) has been found in earlier studies, as in butadiene [12]. Recently however, Buma et al. [13] and Petek et al. [14] using multi-photon ionization spectroscopy and fluorescence excitation, reported the presence of the 0–0 transition for the 2^1A_1 state of *cis*-1,3,5-hexatriene[1] (hereafter *cis*-hexatriene) at 4.26 eV, more than 0.6 eV under the 1^1B_2 state. Buma et al. [13] estimated the vertical transition to be located around 4.57 eV. However, a two-photon absorption study by Fujii et al. [15] showed, that the maximum of this band in both the *trans*- and the *cis*-isomers was above the first optical allowed state, and they suggested a vertical transition energy for the 2^1A_g state in *trans*-1,3,5-hexatriene (hereafter *trans*-hexatriene) around 5.21 eV and for the 2^1A_1 state in the *cis*-isomer around 5.37 eV. The discussion is then still open.

For *cis*-1,3-butadiene (hereafter *cis*-butadiene) only the UV spectrum has been reported [16] with enough accuracy to differentiate between the transitions corresponding to this minor conformer of butadiene. The edge of the discussion has been focused on the *gauche* or planar conformation of the ground state of the molecule [17]. However, there are many experimental studies of the excited states of the trans isomer (see for instance [18] and references therein).

In hexatriene, the theoretical studies for the excited states are limited to two *ab initio* CI calculations by Nascimento et al. [19] and Cave et al. [20] and our own CASPT2 study [18] on the *trans*-isomer, while only semi-empirical calculations [2, 21] have been performed for the *cis* form. Therefore, to our knowledge, the present work is the first *ab initio* calculation reported for the excited states of *cis*-hexatriene.

In butadiene, a large number of *ab initio* calculations have appeared for the *trans* molecule (see [18] and references therein), and Buenker et al. [22], Cave et al. [23] and Kitao et al. [24] have reported *ab initio* CI calculations on the *cis* isomer. Also in this system, the problem of the ordering of the two low-lying valence states has been discussed. All theoretical studies show a 1^1B_2 state under the 2^1A_1 state, in agreement with the theoretical findings for *trans*-butadiene.

We have used the Complete Active Space (CAS) SCF approximation [25], which is able to describe the most important correlation effects in a balanced way for all states by including in the wavefunction all configuration state functions (CSFs) mixing the π-electrons among the valence π-orbitals. To obtain quantitatively correct results for the excitation energies, dynamic correlation effects have also to be considered. These effects are dominated by the dynamic polarization of the σ-electrons, which is described by configurations involving simultaneous σ–σ^* and π–π^* excitations, and can differ substantially for states of different character. The large dynamic correlation effects are added in a subsequent step, where the CASSCF wave function serves as the reference function in a second-order

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[1] Although *cis*-1,3,5-hexatriene and *trans*-1,3,5-hexatriene are the widely used names for the two stable isomers of 1,3,5-hexatriene, their unambiguous and systematic names would be: 2,4,5 *s-trans*, 3 *cis*-1,3,5-hexatriene and 2,3,4,5 *s-trans*-1,3,5-hexatriene, respectively.

perturbation calculation of the correlation energy. The approach has been recently presented as the CASPT2 method [26, 27], and its validity on calculating the differential correlation effects on excitation energies has been demonstrated in earlier applications [18, 28, 29].

2 Methods and computational details

2.1 Basis sets and geometries

Generally contracted basis sets of the atomic natural orbital (ANO) type [30, 31] are used, which are obtained from C (14*s*9*p*4*d*)/H(8*s*4*p*) primitive sets. 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 with the desired accuracy. The contraction used in the present work is C [4*s*3*p*1*d*]/H[2*s*1*p*]. Since the aim is to describe both valence excited states and Rydberg excited states, the original basis sets have been supplemented with 2*s*2*p*2*d* diffuse functions in the average charge centroid for the $^2B_1$ and $^2A_2$ states of the cation. The procedure was explained in a previous work [29]. We have used the same exponents as we used for the cyclopentadiene molecule [29].

The geometry used to perform all the calculations in *cis*-hexatriene has been that reported by Traetteberg [32] from electron diffraction measurements. However, this author presented a non-planar geometry for the ground state of *cis*-hexatriene. A torsional angle around the central double bond of 10 degrees seemed to fit better with the obtained data, although the same author recognized a slight uncertainty in this measurement. In spite of earlier discussions about the suggested non-planarity of the ground state, later experimental [33] and theoretical [34] studies appear to agree with a planar geometry for the ground state of *cis*-hexatriene, as for the *trans* isomer. We have selected a planar conformation on the basis of this evidence.

There is no experimental geometry described for *cis*-butadiene. The best theoretical geometry we have found in the literature is that Rice et al. [35] obtained at the MP2 level with a TZ2P basis set, which seem to be of higher quality than the MCSCF determination (DZ basis set) by Feller et al. [36] or the estimation by Buenker et al. [22]. We decided to redetermine the most important geometry parameters using the CASPT2 scheme, which is known to yield accurate values for bond distances [27b]. The planar geometry by Rice et al. [35] was chosen as the initial point for a pointwise optimization of three degree of freedom (the C–C central bond, the *y* co-ordinate, and the *z* co-ordinate of the terminal C atom). Ten points were distributed on a tetrahedron with a sidelength of 0.05 au, one in each corner and one at the midpoint of each side plus one extra point in the centre. The basis set used in the optimization was an ANO contraction C[4*s*3*p*1*d*]/H[2*s*1*p*]. The four π-electrons were distributed among 8 active orbitals of π-symmetry. The molecule was assumed to have C_{2v} symmetry. Only the carbon skeleton was re-optimized at the CASPT2 level. Table 1 shows the optimized geometries for the ground state of *cis*-butadiene in the C_{2v} symmetry point group. The calculated bond distances are very similar to those obtained by Rice et al. at the MP2/TZ2P level, with the exception of the CC double bond, which here was determined to be 0.014 Å longer. The present value, 1.351 Å is slightly longer than the experimental distance measured for *trans*-butadiene: 1.343 Å.

Table 1. Optimized geometries for the ground state of the *syn*-*cis*-1,3-butadiene

Variable	Geometry (Å, deg)				
	PT2F[a]	SCF/TZ2P[b]	CPF/DZP[b]	MP2/TZ2P[b]	MCSCF/DZ[c]
$r(C_b{-}C_b)$	1.469	1.478	1.483	1.466	1.503
$r(C_b{=}C_a)$	1.351	1.318	1.354	1.337	1.377
$r(C_b{-}H_b)$	1.080	1.074	1.092	1.080	1.074
$r(C_b{-}H_{a1})$	1.076	1.072	1.089	1.076	1.072
$r(C_b{-}H_{a2})$	1.078	1.072	1.089	1.078	1.073
$<(C_b{-}C_b{-}C_a)$	126.0	127.1	126.6	126.2	126.0
$<(C_b{-}C_b{-}H_b)$	115.9	114.9	115.5	115.9	115.0
$<(C_b{-}C_a{-}H_{a1})$	122.0	122.7	122.3	122.0	122.0
$<(C_b{-}C_a{-}H_{a2})$	120.7	120.7	120.7	120.7	121.0

[a] This work: only the carbon skeleton was optimized. See text
[b] Ref. [35]
[c] Ref. [36]

The selection of a planar geometry for the ground state of *cis*-butadiene is not obvious. It has been widely discussed whether the most stable conformer of *cis*-butadiene is the *syn* (planar) or *gauche* (non-planar) form. While some experimental evidence [37] suggest that the *cis* conformer is *gauche*, the most recent measurements [16, 17, 38, 39] have been interpreted as requiring a planar *syn-cis* structure. From the theory there is evidence of a more stable *gauche* conformer from SCF/MP2 calculations [35], while MCSCF calculations [36] give a planar *cis* conformer. Anyway, it is well established that the energetic difference between the two forms is only around 1 kcal/mol, and the twist angle has been estimated to be between 0 and 15 degrees [16, 39]. Following the most recent experiments [16, 17, 38, 39] we have selected the planar *syn* form.

The placement of the two reflection planes in molecules of C_{2v} symmetry remains ambiguous. We have followed the old recommendation by Mulliken [40] that the x-axis should be perpendicular to the molecular plane, that is, in our case, the yz plane. Furthermore, the C_2 axis will be our z-axis. The result is that in some references [11] the labels of the B_2 and B_1 states are found interchanged with respect to our notation, although without further consequences.

2.2 CASSCF and CASSI calculations

Initially, multiconfigurational wavefunctions are determined at the CASSCF level of approximation. Only the π-electrons were active, with all σ-electrons inactive. The carbon 1*s* electrons were kept frozen in the form determined by the ground-state SCF wavefunction and were not included in the calculation of the correlation energy. Thus the excitations treated are of the types π–π^* and π–σ^*, while no excitations out of the σ-orbitals are considered at this stage in the calculations. The choice of the active orbital space is determined by the type of excited states to be studied, in this case valence excited states and in addition Rydberg excitations to the 3*s*, 3*p* and 3*d* orbitals. The way of selecting systematically the active space for each type of state has been explained in detail in [29].

For hexatriene, the six π-electrons were considered active. If we label the orbitals within the C_{2v} point group in order a_1, b_1, b_2, and a_2, we obtain for the

π–π^* excited states a space with 10 π orbitals (b_1 and a_2 symmetries) named (0604), because only external π-orbitals will be occupied in the CASSCF wavefunctions of A_1 and B_2 symmetries. The six valence π-orbitals plus the $3p_x$, $3d_{xy}$, and $3d_{xz}$ orbitals give nine active orbitals. One more orbital of b_1 symmetry has been added to minimize the effect of intruder states in the CASPT2 calculations. It is not necessary to occupy the π-type Rydberg orbitals in calculations on π–σ^* Rydberg states (B_1 and A_2), and, if with the inclusion of σ-type Rydberg orbitals, we need a minimum space of 11 orbitals (4323). If the active space is not so small, that intruder states appear in the CASPT2 function [28, 29], the results are not very sensitive to the size of the active space, as long as the minimum space is covered. Of course, the energy of each excited state has been referred to the corresponding ground state, 1^1A_1, which was computed both for the (0604) and the (4323) spaces. Note, however, that the two ground state total energies (PT2F) differ from each other with only 0.04 eV both for butadiene and hexatriene (cf. Tables 3 and 5), which illustrates the insensitivity of the CASPT2 energy to the detailed choice of the active space.

For butadiene we have followed the same scheme to select the active space. Thus, 4 π-electrons are considered active, a space of 8 orbitals (0503) is used for π–π^* A_1 and B_2 states, and a space of 10 orbitals (4222) is used for σ–π^* B_1 and A_2 states.

The molecular orbitals (MOs) have been obtained from average CASSCF calculations, where the averaging is over all states of interest of a given symmetry. In agreement with earlier experience, no additional uncertainties are introduced by performing average as compared to single state calculations. For some symmetries it became necessary to include in the averaging procedure more states than desired, in order to locate the states of interest. This has been also a previous experience in the furan molecule [29]. Thus, in the $^1B_2$ symmetry of *cis*-hexatriene, five states were used in the averaged CASSCF calculation, even though there are only three states of the studied type. This was necessary in order to locate the lowest valence excited state and avoid the valence-Rydberg mixing that the absence of the higher $1a_2 \rightarrow n = 3$ Rydberg states in the averaging procedure caused. The same situation obtained in $^1B_1$ symmetry, where five states were averaged while only four were computed at the CASPT2 level. Also the calculations on *cis*-butadiene required this sort of solution for some of the singlet states.

The MOs obtained in the different CASSCF calculations are in general not the same. Also, CASSCF wavefunctions, which have been optimized for different states of the same symmetry, are not orthogonal to each other. The CASSCF state interaction (CASSI) method [41] has been developed to compute transition properties from non-orthogonal state functions and is used here to compute the transition dipole moments. In the formula for the oscillator strength we used the energy differences corrected for by the second order perturbation method (PT2F). This approach for the oscillator strength 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 multi-reference CI method [42].

2.3 *The CASPT2 method*

The CASPT2 method [26, 27] computes the first-order wavefunction and the second-order energy in the full CI space without any further approximation, with a CASSCF wavefunction 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). It is only the PT2F approach, that leaves the zeroth-order Hamiltonian invariant with respect to rotations among the molecular orbitals. Earlier studies [18] have shown that this invariance is of importance in the description of the Rydberg states and we shall therefore only present the PT2F results from the present study.

The CASPT2 program calculates the weight, ω, of the CASSCF reference in the first-order wavefunction. This weight is a measure of how large a fraction of the wavefunction is treated variationally. The relative weight of ω in different states 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. It may happen, however, that interference with nearby electronic states not included in the reference CI space, deteriorates this balance for some excited states. Normally these excited states are of the Rydberg type invoking orbitals not included in the active orbital space. Such a situation can be tolerated in cases where the interaction is very weak, and consequently the effect on the second-order energy small. In severe cases, where it is clear that the energy has been affected, two solutions are possible. If the Rydberg orbital in question can be clearly defined, it can be removed from the MO basis set, or it can included into the active space. Both approaches had been previously used to correct the calculation and were found to give identical results [28]. The first approach has been necessary for the third valence state of ${}^1A_1$ symmetry and the second valence state ${}^1B_2$ symmetry. In this case, the interfering external Rydberg orbitals were clearly defined, and after deleting them from the MO basis, the states had a final weight in agreement with the ground state.

The calculations have been performed on an IBM RS/6000 workstation (model 560) at the University of Lund, using the MOLCAS-2 quantum chemistry software [43], which includes as one module the CASPT2 program.

3 Results and discussion

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

3.1 Cis-1,3,5-hexatriene

The valence π structure of *cis*-hexatriene is composed of six π-orbitals of increasing energy: $1b_1$, $1a_2$, $2b_1$, $2a_2$, $3b_1$, and $3a_2$. In systems previously studied, as cyclopentadiene, pyrrole and furan [29], we showed the occurrence of three low-lying valence excited singlet states arising from excitation from the two highest occupied orbitals to the two lowest virtual orbitals. Two pairs of states of A_1 symmetry arise from linear combinations of the excitations $1a_2$–$2a_2$ and $2b_1$–$3b_1$:${}^1A_1^-$ with lower energy and lower intensity, and ${}^1A_1^+$ at higher energy and carrying most of the intensity. The excitation $1a_2 \rightarrow 3b_1$ give rise to an excited state of ${}^1B_2$ symmetry, while the corresponding state for the $2b_1 \rightarrow 2a_2$ excitation was found at rather high energy, as was excitations to the $3a_2$ orbital. However, two things are different in *cis*-hexatriene: first, the $2b_1$ orbital is higher in energy than the $1a_2$, and thus, the two described ${}^1B_2$ states have interchanged the dominant configurations. Secondly, the vertical ionization energies for the three occupied orbitals are: ≈ 11.9 eV, 10.4 eV and 8.32 eV [44], respectively. The ionization potential for the $1b_1$ orbital is below the equivalent IPs in pyrrole and furan, 12.6 eV and 15.2 eV, respectively [29], representing there a lone-pair orbital. Therefore, in *cis*-hexatriene, the $1b_1$ orbital is close enough to promote CSFs nearly degenerate with the other valence states. Two new valence states, one of ${}^1A_1$ symmetry and one of ${}^1B_2$ symmetry are expected to appear in the calculated spectrum. As in the other systems [18, 29], the ${}^1A_1$ states are expected to have a considerable mixing of the doubly excited configurations, mainly in the lower ${}^1A_1^-$ state. Summarizing, a valence spectrum is expected with two intense ${}^1B_2$ states, one at low and one at higher energy, and three ${}^1A_1$ valence states, the lowest with very low intensity and great diexcited character, the next one as a more intense state, and the last one at high energy. In order to illustrate these qualitative features of the valence excited spectrum we have performed a set of calculation utilizing a small (ANO-DZ) basis set. Table 2 presents the CASSCF and CASPT2 results from this set of calculations for *cis*-hexatriene, including the coefficients of the main configurations for each state in order to illustrate the main features of the electronic structure. The wavefunctions produced with the large ANO basis set are of course more complex, partly due to valence Rydberg mixing, but qualitatively they have the same structure. With the large basis set, we have in addition to the valence states calculated the Rydberg states arising from excitations out of the $2b_1$ orbital, and also the $1a_2 \rightarrow 3s$ Rydberg state. Total energies are presented in Table 3.

This table also gives CASSCF values for the dipole moments (quadrupole moments were computed, but are not presented here) and the expectation value of x^2, which is used to identify the states as valence or Rydberg in character. Included in the table is also the value of ω, the weight of the reference configuration in the first-order wavefunction. The Rydberg excited states have values of ω almost identical to that of the ground state, while those for the valence excited states are somewhat smaller. This is a reflection of the larger importance of dynamic electron correlation effects in these electronic states.

In Table 4 we present the results obtained for excitation energies and oscillator strengths. In this table we also attempt an assignment of the observed bands and

Table 2. Calculated excitation energies, oscillator strengths and CI coefficients of the main configurations of the valence singler π–π^* states of *cis*-1,3,5-hexatriene. Double zeta basis set

State	Excitation energy (eV) CASSCF	PT2F	Osc. strength	CI coefficients			
			A_1:	$2b_1 \rightarrow 3b_1$	$1a_2 \rightarrow 2a_2$	$1b_1 \rightarrow 3b_1$	diex[a]
2^1A_1	5.64	5.41	.0002	+ 0.46	+ 0.44	+ 0.14	+ 0.55
3^1A_1	9.00	7.65	.0233	+ 0.65	− 0.48	− 0.09	− 0.16
4^1A_1	8.57	8.24	.0564	− 0.30	+ 0.21	− 0.35	− 0.36
			B_2:	$2b_1 \rightarrow 2a_2$	$1a_2 \rightarrow 3b_1$	$1b_1 \rightarrow 2a_2$	diex[a]
1^1B_2	7.15	5.75	1.047	− 0.91	− 0.06	+ 0.12	− 0.20
2^1B_2	6.77	6.56	0.007	+ 0.41	< 0.05	+ 0.52	+ 0.40
3^1B_2	10.41	9.68	0.261	< 0.05	+ 0.87	< 0.05	− 0.22

[a] Highest CI coefficients for a diexcited configuration

Table 3. Total energies, dipole moments and other properties of the excited states of *cis*-1,3,5-hexatriene

State	Energy + 231 au		$\langle x^2\rangle$[a]	μ[b]	ω[c]	N_{states}[d]
	CASSCF	PT2F				
π–π^* singlet states (active space (0604)):						
1^1A_1	−0.971763	−1.728703	31.8	−0.004	0.79	1
2^1A_1	−0.751367	−1.543318	33.8	−0.097	0.75	1–6
3^1A_1	−0.730292	−1.503229	77.9	−0.192	0.76	1–6
4^1A_1	−0.711552	−1.480500	88.9	+1.189	0.78	1–6
5^1A_1	−0.654823	−1.477434	44.8	+1.084	0.71	1–6
6^1A_1	−0.640154	−1.434052	33.9	+0.156	0.67	1–6
1^1B_2	−0.683005	−1.544919	41.0	+0.421	0.70	1–5
2^1B_2	−0.700818	−1.519419	32.8	−0.043	0.70	1–5
3^1B_2	−0.722178	−1.497730	83.4	+0.426	0.77	1–5
σ–π^* singlet states (active space (4323)):						
1^1A_1	−0.972231	−1.730215	31.7	−0.006	0.79	1
1^1B_1	−0.755881	−1.521279	51.2	−2.026	0.78	1–5
2^1B_1	−0.746584	−1.512927	45.6	+2.172	0.76	1–5
3^1B_1	−0.722874	−1.483925	50.4	+0.444	0.77	1–5
4^1B_1	−0.720780	−1.479670	95.5	+0.745	0.78	1–5
1^1A_2	−0.739960	−1.505754	50.1	−0.488	0.78	1–3
2^1A_2	−0.724555	−1.486125	48.9	+1.030	0.78	1–3
3^1A_2	−0.676823	−1.455005	49.7	+3.124	0.76	1–3
π–π^* triplet states (active space (0604)):						
1^3A_1	−0.814441	−1.583901	31.9	−0.010	0.78	1
1^3B_2	−0.865432	−1.634194	31.7	+0.026	0.78	1
σ–π^* triplet states (active space (4323)):						
1^3B_1	−0.765324	−1.521923	48.4	−3.552	0.78	1
1^3A_2	−0.747169	−1.507388	49.9	−0.794	0.78	1

[a] Expectation value (CASSCF) of x^2 (in au^2), where x is the coordinate perpendicular to the molecular plane.

[b] Dipole moment in au.

[c] The weight of the CASSCF reference function in the first order wavefunction.

[d] States included in the state average CASSCF calculation.

compare the computed vertical transition energies with experiment. Below, these assignments will be discussed in more detail for each class of transitions.

Valence excited singlet states (1^1B_2, 2^1A_1, 3^1B_2, 5^1A_1, and 6^1A_1). The calculated lowest vertical excitation energy for a singlet state appears in *cis*-hexatriene at 5.00 eV as the 1^1B_2 state, with an oscillator strength of 0.617 au, in good agreement with the experimental result at 4.92 eV [2], and very close to our previous value for the equivalent 1^1B_u state in the *trans* isomer at 5.01 eV, as was expected from experiment [2]. The calculated value of the oscillator strength of the *trans* form [18], 0.85, and the present value for the *cis*-hexatriene, 0.62, is in fair agreement with the ratio 1:1 estimated from the UV absorption spectrum [2]. The size of the expectation value of x^2, 41.0 au [2] is consistent with the values computed for the *trans* polyenes [18], where a clear mixing of valence and Rydberg configurations appears. The next state, 2^1A_1, is nearly degenerate with 1^1B_2, with an energy of

Table 4. Calculated and experimental excitation energies and oscillator strengths in *cis*-1,3,5-hexatriene

State	Excitation energy (eV)				Osc. strength
	CASSCF	PT2F	exp.	deviation[a]	
Singlet states					
1^1B_2 (valence)	7.86	5.00	4.92[b]	−0.08	.6170
2^1A_1 (valence)	6.00	5.04	–[c]	–	.0008
1^1B_1 ($2b_1$–$3s$)	5.89	5.69	5.66[d]	+0.03	.0010
2^1B_2 (valence)	7.37	5.70	5.7[e]	–	.0170
2^1B_1 ($2b_1$–$3p\sigma$)	6.14	5.91	5.88[f]	+0.03	.0152
1^1A_2 ($2b_1$–$3p\sigma$)	6.32	6.11	6.08[d,g]	+0.03	forbidden
3^1A_1 ($2b_1$–$3p\pi$)	6.57	6.14	6.22[d,f]	−0.08	.0107
3^1B_2 ($2b_1$–$3d\pi$)	6.79	6.29	6.40[f]	−0.11	.0703
2^1A_2 ($2b_1$–$3d\delta$)	6.74	6.64	6.51[d,f,g]	+0.13	forbidden
3^1B_1 ($2b_1$–$3d\delta$)	6.79	6.70	6.60[f]	+0.10	.0150
4^1A_1 ($2b_1$–$3d\pi$)	7.08	6.75	6.70[f]	+0.05	.0001
4^1B_1 ($2b_1$–$3d\sigma$)	6.84	6.82	6.79[f]	+0.03	.0025
5^1A_1 (valence)	8.62	6.84	6.88[d,f,h]	−0.04	.0308
3^1A_2 ($1a_2$–$3s$)	8.04	7.49	7.40[f]	+0.09	forbidden
6^1A_1 (valence)	8.95	8.02	8.0[g,h]	–	.0362
Triplet states					
1^3B_2 (valence)	2.89	2.57	–[i]	–	
1^3A_1 (valence)	4.28	3.94	–[i]	–	
1^3B_1 ($2b_1$–$3s$)	5.63	5.67	–	–	
1^3A_2 ($2b_1$–$3p\sigma$)	6.12	6.06	–	–	

[a] Difference between the calculated (PT2F) and experimental excitation energies

[b] Optical absorption spectra, Ref. [2, 45] and electron impact spectrum, Ref. [6]

[c] Experimental estimates range from 4.57 eV, Ref. [13] to 5.37 eV, Ref. [15]. See text for discussion

[d] Multi-photon ionization spectroscopy, Ref. [11]

[e] Optical absorption spectrum, Ref. [2] and electron impact spectra, Refs. [3] and [6]

[f] Electron energy loss spectroscopy, Ref. [9]

[g] Optical absorption spectrum, Ref. [2] and electron impact spectrum, Ref. [6]

[h] Electron impact spectroscopy, Ref. [5]

[i] No value has been reported for the *cis* isomer. See text for comparison with the *trans* values.

5.04 eV. This is in agreement with Fujii et al. [15], who obtained the maximum of the two-photon spectrum above the first allowed 1^1B_2 state. The two states are closer in energy than in *trans*-hexatriene [18] where the difference was around 0.2 eV. The recent experimental evidence [13, 14] of a 2^1A_1 state at 4.26 eV, below the 1^1B_2 state, refers to the 0–0 transition. Buma et al. [13] estimate the vertical energy at 4.57 eV. Several authors [20] have pointed out the great sensibility of the excitation energy for the 2^1A_1 state of polyenes towards geometry relaxation of the excited state. Estimates made for *trans*-hexatriene [20] gives a relaxation energy of about 1.0 eV. This makes a precise location of the vertical transition energy difficult and could explain the different state orderings suggested for hexatriene and related molecules. However, the estimate of 4.57 eV as the vertical excitation energy of this state in *cis*-hexatriene [13] is not consistent with the present results. It would give a deviation of 0.47 eV from the calculated excitation energy. We have not in any of the previous studies found such large errors for a valence state where no valence-Rydberg mixing appear. The position of the 2^1A_1 state above the 1^1B_2 state is in agreement with all earlier *ab initio* calculations performed on the hexatriene molecule [18–20, 22–24].

A second valence excited state of $^1B_2$ symmetry appears at 5.70 eV. Although no valence transitions have been described at this energy, Gavin et al. [2] with UV absorption spectroscopy, and Knoop et al. [3] and Flicker et al. [6] with electron impact techniques, described a shoulder at 5.7 eV. It was assigned as a vibrational transition [6] of the more intense 1^1B_2 state, but, as has been pointed by McDiarmid et al. [9], the bands in this energy range are very difficult to analyze because of the optical conditions: they are under the intense π–π^* transition. The low oscillator strength, which is due to a cancellation of contributions from $2b_1$–$2a_2$ and $1b_1$–$2a_2$ and extensive diexcited contributions (see Table 2), makes an analysis even more difficult.

McDiarmid et al. [9,11] described a transition at 6.88 eV with anomalous behaviour. They first assigned it as a $3d$ Rydberg state by comparison with a higher Rydberg band. This peak at 6.88 eV appears very weakly in both the optical and electron impact spectra, and has not still been found by three or two photon spectroscopies due to technical difficulties [11]. We have found the valence 5^1A_1 state at 6.84 eV, with an oscillator strength of 0.031 au. Although the $3d$ Rydberg states appears very close to this transition, the peak at 6.88 eV could be suggested as a $^1A_1$ valence state. It includes some fraction of doubly excited configurations (14%), and may be found by two photon spectroscopy.

Finally, we have also computed the third valence singlet excited state of symmetry $^1A_1$ at 8.02 eV. The label six to designate this state should be considered only orientative, because of the presence of lower Rydberg states between the 5^1A_1 state and this valence $^1A_1$ state. This state is mainly composed of configurations arising from the $1b_1$ orbital, with high weights for diexcited configurations. Gavin et al. [2] and Flicker et al. [6] describe a transition around 8.0 eV without clear assignment. Although in a provisional way, we report the presence of a highly excited valence state with an oscillator strength of 0.036 au near this energy.

$2b_1 \rightarrow 3s$ (1^1B_1). The $n = 3$ Rydberg series arising from the $2b_1$ orbital in *cis*-hexatriene have been experimentally described by McDiarmid et al. [9, 11]. They found a transition at 5.66 eV that was unambiguously characterized as the 1^1B_1 state corresponding to the $2b_1 \rightarrow 3s$ Rydberg excitation. Our present result at 5.69 eV is in perfect agreement with that prediction.

$2b_1 \rightarrow 3p$ (2^1B_1, 1^1A_2, and 3^1A_1). Several peaks are found between 5.66 eV and 6.23 eV [9]. The features at 5.88 eV [9], 6.08 eV [11] and 6.22 eV [9, 11] have been proposed as the $3p$ Rydberg states. The transition at 5.88 eV is difficult to analyze because it is under the transition to the intense 1^1B_2 state [9]. Anyway, we obtain 5.91 eV for the 2^1B_1 Rydberg state. McDiarmid et al. [9] also described a feature at 5.95 eV without assignment, that could be related to this state. The 6.08 eV transition of *cis*-hexatriene has been also assigned as a $3p$ Rydberg state on the basis of its quantum defect [11]. This transition had been previously described [2, 6] and assigned [6] as a possible valence state, but on the basis of our present result at 6.11 eV, we agree with the assignment of McDiarmid et al. [11]. Finally, more clear evidence is presented for the peak at 6.22 eV. A comparison of the intensities of the spectra obtained with circularly and linearly polarized light led to the conclusion that this is a state of $^1A_1$ symmetry [11]. This assignment is consistent with the early suggestion of a peak at 6.24 eV as an ^1A_g state in *trans*-hexatriene [7] and the confirmation of its Rydberg character [8]. Our present result at 6.14 eV agrees with these experimental conclusions.

$2b_1 \rightarrow 3d$ (2^1B_2, 2^1A_2, 3^1B_1, 4^1A_1, and 4^1B_1). The region between 6.30 eV and 7.00 eV presents a number of medium intensity bands. Earlier studies [2] have described a transition at 6.56 eV, assigned as a possible π–σ^* state [6], and has assigned another peak at 6.9 eV [6] as a vibrational band of a lower state. The analysis of McDiarmid et al. [9, 11] by optical and two and three-photon resonant multi-photon ionization spectroscopy, gave new evidence. A lower energy transition at 6.40 eV [9] had no assignment, although it was considered as an allowed transition under optical conditions with relaxed optical selection rules in an energy loss spectrum. We have calculated the 3^1B_2 state at 6.29 eV, which could be consistent with the allowed transition at 6.40 eV. The only strange feature is the rather high intensity of the state, implying that it ought to be more easy to identify the band in the spectrum. Instead it seems that the 6.22 eV transition is the most intense band near this energy. Therefore, the assignment to the feature at 6.40 eV should be taken with some caution. The transition to 6.51 eV was clearly assigned as a $3d$ $^1A_2$ Rydberg state [9, 11]. Our result at 6.64 eV for this state is close to the experimental observations. The electron-energy loss spectrum [9] showed a number of unassigned transitions at 6.60 eV, 6.70 eV and 6.76 eV. Our present results for the three Rydberg states in this energy region are: 6.70 eV for the 3^1B_1 state, 6.75 eV for the 4^1A_1 state, and 6.82 eV for the 4^1B_1 state. The highest oscillator strength is obtained for the 3^1B_1 state, while the others carry very low intensities. The assignments in Table 4 are only tentative. They were chosen to give the best agreement with the experimental evidence. The transition at 6.88 eV, proposed as a Rydberg $3d$ state [11] has been discussed together with the valence states, due to its present assignment as a possible valence $^1A_1$ state.

$1a_2 \rightarrow 3s$ (3^1A_2). We have also computed the first Rydberg state of the series arising from the $1a_2$ orbital in order to locate the start of this series within the spectrum. The label three to designate this $^1A_2$ state is only orientative, because, although it appears as the third root in the CASSCF calculation, the $2b_1 \rightarrow n = 4$ Rydberg series are expected to be below the $1a_2 \rightarrow n = 3$ series. McDiarmid et al. [11] assign the start of the $n = 4$ series at 7.07 eV, and it is possible that other states of $^1A_2$ symmetry lie under the computed $1a_2 \rightarrow 3s$ state. A more diffuse basis set is necessary in order to compute accurately the $n = 4$ series, and the reason for calculating the $1a_2 \rightarrow 3s$ state is only to give some guidance about the beginning of the $1a_2$ Rydberg series in the spectrum. The assignment of the state to the observed transition at 7.40 eV [2, 6, 9] is made in a provisional way, although this peak was assigned by McDiarmid et al. [9] as a $^1A_2$ state.

Triplet states. The first triplet state in each of the four symmetries have been studied. The lowest state is a valence excited state of $^3B_2$ symmetry. As no experimental excitation energies have been reported for the *cis*-hexatriene, we can only compare the result at 2.57 eV for the valence excited 1^3B_2 state with the 2.6 eV [3, 5, 6] found for the equivalent 1^3B_u state of the *trans* form. For the 1^3A_1 valence excited state, our computed value of 3.94 eV is about 0.2 eV below the reported value of 4.11 eV [6] for the *trans* isomer 1^3A_g valence state, which is in close correspondence with the observed lowering of the energy for the lowest singlet state of A_1 symmetry with respect to the *trans* form [18].

3.2 Cis-1,3-butadiene

The valence structure of *cis*-butadiene is similar to *cis*-hexatriene, but with only four valence *p*-orbitals ordered $1b_1$, $1a_2$, $2b_1$ and $2a_2$, where the two first orbitals are occupied. Four valence states are expected from this structure, but only two of them appear in the low-lying region of the spectrum, while the second $1A_1$ state ($^1A_1^+$) and $^1B_2$ states, appears at energies above 8.5 eV. Again, the intense valence state 1^1B_2 (with the dominant configuration $1a_2 \rightarrow 2b_1$) is expected to be lowest in energy, while the $^1A_1^-$, combination of the mono-excitations $1a_2 \rightarrow 2a_2$ and $1b_1 \rightarrow 2b_1$ and several di-excitations, as for example $(1a_2)^2 \rightarrow (2a_2)^2$, is expected to be close in energy and carry very little intensity.

We have also computed the Rydberg states arising from the highest occupied orbital, $1a_2$, to the $n = 3$ Rydberg orbitals, and the first state of the $2b_1$ $n = 3$ series in order to locate it within the spectrum. Total energies, dipole moments, $\langle x^2 \rangle$, and ω values are presented in Table 5.

We notice the same trends as for hexatriene. Thus the ω values for all Rydberg states are close to 0.85, the value obtained for the ground state, while those of the valence excited states are somewhat smaller. The 1^1B_2 state is clearly more diffuse than the ground state, indicating some valence-Rydberg mixing, as was also found for the *trans* form [18]. Computed excitation energies and intensities are presented in Table 6, together with corresponding results obtained for the *trans* form.

Table 5. Total energies, dipole moments and other properties of the excited states of *cis*-1,3-butadiene

State	Energy + 154 au CASSCF	PT2F	$\langle x^2 \rangle^a$	μ^b	ω^c	N_{states}^d
π–π* singlet states (active space (0503)):						
1^1A_1	– 1.030229	– 1.538779	21.7	+ 0.012	0.85	1
2^1A_1	– 0.790146	– 1.316682	22.1	+ 0.053	0.84	1–3
3^1A_1	– 0.755229	– 1.265698	80.1	+ 0.027	0.84	1–3
1^1B_2	– 0.782974	– 1.333799	37.4	+ 1.587	0.76	1–3
2^1B_2	– 0.776104	– 1.286849	62.1	– 3.404	0.84	1–3
3^1B_2	– 0.752061	– 1.268817	79.5	+ 2.492	0.84	1–3
σ–π* singlet states (active space (4222)):						
1^1A_1	– 1.031223	– 1.540114	21.7	+ 0.017	0.85	1
1^1B_1	– 0.789446	– 1.294997	36.5	– 0.560	0.84	1–4
2^1B_1	– 0.768070	– 1.271162	37.0	+ 0.743	0.85	1–4
3^1B_1	– 0.717679	– 1.230070	38.0	– 1.748	0.77	1–4
1^1A_2	– 0.807665	– 1.317801	38.3	– 0.505	0.84	1–5
2^1A_2	– 0.794084	– 1.302021	33.7	+ 0.662	0.84	1–5
3^1A_2	– 0.767027	– 1.270395	48.6	– 0.210	0.85	1–5
4^1A_2	– 0.764484	– 1.269992	71.1	+ 0.067	0.85	1–5
π–π* triplet states (active space (0503)):						
1^3A_1	– 0.849882	– 1.364634	21.6	+ 0.185	0.84	1
1^3B_2	– 0.921022	– 1.435693	22.0	+ 0.046	0.84	1
σ–π* triplet states (active space (4222)):						
1^3B_1	– 0.794613	– 1.296101	36.1	– 0.603	0.85	1
1^3A_2	– 0.814752	– 1.319829	38.0	– 0.462	0.84	1

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[a] Expectation value (CASSCF) of x^2 (in au^2), where x is the coordinate perpendicular to the molecular plane.

[b] Dipole moment in au.

[c] The weight of the CASSCF reference function in the first order wavefunction.

[d] States included in the state average CASSCF calculation.

Table 6. Calculated and experimental excitation energies and oscillator strengths in *cis*-1,3-butadiene

State	Excitation energy (eV)				*Trans*[b]	Osc. strength
	CASSCF	PT2F	exp.	Other results		
Singlet states						
1^1B_2 (valence)	6.73	5.58	5.49[c]	6.35[d], 5.65[e], 5.55[f]	6.23	.2181
2^1A_1 (valence)	6.53	6.04	–	6.66[d], 6.13[e]	6.27	.0082
1^1A_2 ($1a_2$–$3s$)	6.08	6.05	–	6.14[d]	6.29	forbidden
2^1A_2 ($1a_2$–$3p\sigma$)	6.45	6.48	–	6.55[d]	6.56	forbidden
1^1B_1 ($1a_2$–$3p\sigma$)	6.58	6.67	–	6.71[d]	6.69	.0399
2^1B_2 ($1a_2$–$3p\pi$)	6.92	6.86	–	7.11[d], 7.02[e], 6.67[f]	6.70	.0873
2^1B_1 ($1a_2$–$3d\delta$)	7.16	7.32	–	7.26[d]	7.30	.00008
3^1A_2 ($1a_2$–$3d\delta$)	7.19	7.34	–	–	–	forbidden
3^1A_1 ($1a_2$–$3d\pi$)	7.48	7.43	–	7.89[d], 7.23[f]	7.47	.0012
3^1B_2 ($1a_2$–$3d\pi$)	7.57	7.43	–	7.37[f]	–	.0028
4^1A_2 ($1a_2$–$3d\sigma$)	7.26	7.44	–	–	–	forbidden
3^1B_1 ($1b_1$–$3s$)	8.53	8.44	–	–	–	.0456
Triplet states						
1^3B_2 (valence)	2.97	2.81	–	2.95[d], 3.01[f]	3.20	
1^3A_1 (valence)	4.91	4.74	–	4.90[d], 5.06[f]	4.88	
1^3A_2 ($2b_1$–$3s$)	5.89	5.99	–	6.07[d]	–	
1^3B_1 ($1a_2$–$3p\sigma$)	6.44	6.64	–	6.65[d]	–	

[a] Difference between the calculated (PT2F) and experimental excitation energies
[b] CASPT2 excitation energies for the equivalent states in *trans*-1,3-butadiene. Ref. [18]
[c] Optical absorption spectrum, Ref. [16]
[d] π-CI results, Ref. [22]
[e] CI4 results, Ref. [23]
[f] SAC-CI results, Ref. [24]

Comparison is also made in this table to earlier theoretical results. Below we shall discuss these results in more detail.

Valence excited singlet states (1^1B_2 and 2^1A_1). As in *trans*-butadiene [18], the two lowest excited states are 1^1B_2 and 2^1A_1. The only available experimental information [16] reports a maximum in the absorption UV spectrum at 5.49 eV, near 0.4 eV below the maximum of the *trans* isomer. In the previous study [18], we found the most intense excitation in the spectrum of the *trans* form to be 1^1B_u, with an oscillator strength of 0.686. We have also obtained the maximum intensity for the 1^1B_2 state of the *cis* form, with an excitation energy of 5.58 eV, close to the experimental value, and an oscillator strength of 0.22. The experimentally estimated ratio of the extinction coefficients between the *cis* and the *trans* forms is 0.45 [16], which is in the good agreement with the relation between our computed intensities. The agreement with some of the earlier theoretical calculations [23, 24] is also satisfactory and yields further strength to the present assignment.

We have calculated the 2^1A_1 state of the *cis*-butadiene at 6.04 eV, with a very low intensity and important contributions of doubly excited configurations. The relative energy for this state is only shifted down with 0.23 eV with respect to the *trans* form. Thus the energy difference to the 1^1B_2 state is larger in the *cis* form: 0.46 eV compared to only 0.04 eV in *trans*. There is no experimental evidence to support this difference between the two forms, but it may be noted that similar results were obtained by Cave et al. [23] in their *ab initio* CI study.

As we may conclude from the calculated position of the $1b_1$ $n = 3$ Rydberg series, the third and fourth valence excited states for this molecule ought to appear at high energies, as they also do in *trans*-butadiene [18].

$1a_2 \rightarrow 3s$ (1^1A_2). No experimental evidence have been reported for the Rydberg states of *cis*-butadiene, and thus, we can only compare our results with other theoretical calculations and with the corresponding transitions of the *trans* isomer.

We have calculated the first state of the Rydberg series at 6.05 eV. The only other *ab initio* calculation for this state placed it at 6.14 eV [22]. Experimental and theoretical evidence placed the equivalent state 1^1B_g in the *trans* form around 6.2 eV [18]. We observe a general decrease of the excitation energies for the *cis* form with respect to the *trans* isomer (with the exception of $3p\pi$ and $3d\delta$).

$1a_2 \rightarrow 3p$ (2^1A_2, 1^1B_1, and 2^1B_2). The $1a_2 \rightarrow 3p$ series offers three states, 2^1A_2, 1^1B_1, and 2^1B_2, which we have computed at 6.48 eV, 6.67 eV, and 6.86 eV, respectively. The last one has the largest oscillator strength: 0.087. This is the only state that differs substantially from those reported in earlier theoretical studies [22, 23] where in general larger excitation energies have been obtained. The present value is close to that found earlier for the *trans* form: 6.70 eV [18]. The other two $3p$ Rydberg states are also found to be close to those of the *trans* form (see Table 6) and the calculated energies differs less than 0.07 eV from the theoretical values of Buenker et al. [22]

$1a_2 \rightarrow 3d$ (3^1B_2, 2^1B_1, 3^1A_2, 3^1A_1, and 4^1A_2). The energies for the $1a_1 \rightarrow 3d$ Rydberg states fall in the range 6.86–7.44 eV. Only two Rydberg states of $3d$ type were included in our previous study of *trans*-butadiene, but we notice that the energy difference for these two states is only 0.02–0.04 eV (cf. Table 6). It is reasonable to assume that also the order $3d$ Rydberg states have similar energies in both isomers. For some of them other theoretical results are available [22, 24], which in general give excitation energies in the same range. All the $3d$ states have low intensities, as the computed oscillator strengths show.

$1b_1 \rightarrow 3s$ (3^1B_1). As we explained above, we have computed the first state of this Rydberg series to place it within the spectrum, even though a definitive assignment is not possible due to lack of experimental information in this energy range. Therefore, the label three to designate the $^1B_1$ is only formal, due to the probable presence of $1a_2 \rightarrow n = 4$ Rydberg series below this state. Anyway, the computed value of 8.44 eV indicates, that a high energy is necessary to excite an electron from this orbital, confirming the expected position for the higher valence states.

Triplet states. The first triplet state in each of the four symmetries have been studied. The lowest state is a valence excited state of $^3B_2$ symmetry. The comparison with the other *ab initio* results for the *cis* isomer [22] shows close agreement. If we compare our results of the 1^3B_2 state of *cis*-butadiene at 2.81 eV with the theoretical and experimental value for the 1^3B_u state of the *trans*-butadiene around 3.20 eV [18], we observe the same decrease in the excitation energy as for the first singlet state. The 1^3A_1 state at 4.74 eV shows a somewhat smaller decrease in energy with respect to the excitation energy of 4.88 eV obtained for the 1^3A_g state in the *trans* isomer [18]. The corresponding energy shift for the singlet state is 0.23 eV.

4 Discussion

In this contribution we have presented results for the vertical excitation energies in the *cis* forms of butadiene and hexatriene. The calculations include all valence excited states and a number of Rydberg states. We have earlier presented corresponding (although somewhat less complete) results for the *trans*-isomers [18]. For *cis*-hexatriene the experimental spectrum is fairly well known and the present investigation has been able to confirm the assignments made, or in some cases suggest alternative assignments. The largest error in computed excitation energies is, with these assignments, 0.13 eV and occurs for one of the 3*d* Rydberg states. A comparison of the *cis* and *trans* forms indicates a small down shift in the energies of the two first valence excited states. This is for the first state in agreement with experimental evidence. The location of the 2^1A_1 state in the *cis* form has been debated in the literature. The present calculation strongly favours a vertical excitation energy above 5 eV, which is in line with the results of a two-photon absorption study [15], but disagrees with the estimate, 4.57 eV, made by Buma et al. [13]. The present study places the 2^1A_1 and 1^1B_2 states at about the same energy with the latter state slightly below. However, since the energy difference is very small we cannot suggest an unambiguous ordering of the two states in the *cis* form.

For *cis*-butadiene the situation is different. Here the 1^1B_2 state falls 0.46 eV below 2^1A_1 and the ordering is clearly established. The computed energy for the 1^1B_2 state is also in good agreement with the experimental energy (the error is 0.09 eV). For *trans*-butadiene the two states are much closer in energy with a computed difference of only 0.04 eV [18]. The true splitting is, however, probably larger, since error in the computed excitation energy for 1^1B_u is 0.31 eV [18]. This larger error is *trans*-butadiene is related to a more pronounced valence-Rydberg mixing, which is not well described at the CASSCF level of treatment. The CASPT2 method is not capable of a complete correction of this error since it involves modifications of the one-electron density, and consequently higher order energy contributions. The valence-Rydberg mixing is much less pronounced in the *cis* isomer and the error in the computed excitation error is consequently smaller.

The present study gives one more illustration of the possibilities that the newly developed CASSCF/CASPT2 method gives for the calculation of electronic spectra of conjugated molecules. A CASSCF gradient program has recently been added to the MOLCAS software [46] thus now also giving the possibility to compute equilibrium geometries for the excited states. One of the first applications of this technique will involve studies of the 0–0 transitions in the linear polyenes [47].

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