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Ab initio quantum study of UV absorption spectra of *cis*- and *trans*-hexatriene

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ABSTRACT

The vibronic structure of the UV-absorption spectra of *cis*- and *trans*-hexatriene is revisited in a comparative theoretical investigation. The multidimensional potential energy surfaces of the relevant $^1A_1$ (^1A_g) and $^1B_2$ (^1B_u) electronic states are obtained from CASPT2 and MRCI ab initio calculations using carefully chosen CAS-spaces. These provide the basis for subsequent wavepacket dynamical calculations for the coupled electronic states carried out with the multiconfiguration time-dependent Hartree scheme. The experimental spectra in the ~5 eV energy range are well reproduced for both isomers. The influence of the various degrees of freedom is assessed by comparing the results for different dimensionalities of the calculations. The implications of these findings for the photophysical properties (fluorescence dynamics) are discussed.

1. Introduction

The hexatriene isomers are important representatives of short polyenes and therefore of immediate interest in view of the broad importance of polyenes in different fields (see for example Refs. [1–6]). They are among the smallest systems displaying *cis-trans* isomerization around a double bond, which plays a crucial role, for example in the process of vision [6–10]. The corresponding 2-*cis* and 2-*trans* hexatriene isomers have been studied spectroscopically in the UV/vis spectral region to shed light on their excited electronic states and photophysical as well as photochemical behavior. While a systematic overview over the literature is far beyond the scope of the present study, we confine ourselves to recalling some of the work as far as relevant for our purposes. Since the notions "*cis*" and "*trans*" always refer to the central double bond in this work, the index "2" will be suppressed in the following.

As usual for polyenes, *cis*- and *trans*-hexatriene (HT) possess two low-lying singlet excited states, being of symmetry A_1 (A_g) and B_2 (B_u). Here the symmetry labels refer to the respective point group, C_{2v} for the *cis* isomer (C_{2h} for the *trans* isomer) and the spin multiplicities are suppressed hereafter. While the state of A symmetry contains a substantial doubly excited configuration and is mostly covalent in nature, that of B symmetry is mostly represented by a HOMO–LUMO excitation and of ionic character [11–13]. Only the latter transition is dipole allowed and the B_2 (B_u) state can be directly reached by a one-photon transition. The energetic ordering of the states has been intensely discussed experimentally [14–22] and theoretically [23–28]. The same holds for the behavior of their potential energy surfaces (PES) in and near the Franck–Condon (FC) zone [17,29,30], the ensuing near-degeneracy and vibronic interactions between these states [31,26,32] and the relation to lifetimes [19,33] and photophysical (such as fluorescence) properties [16,18]. Much of this work is, however, rather descriptive, and a proper understanding of the photodynamics, especially trends in a series of related molecules, is still missing. As an example we mention the intriguing observation that short polyenes like butadiene are non-fluorescent, while octatetraene and somewhat longer polyenes exhibit substantial emission, whereas for long chain lengths the latter disappears again [34,33]. For hexatriene it is necessary to distinguish between the two isomers. While *trans*-hexatriene shows no fluorescence [34], the $2A_1$ state of *cis*-hexatriene exhibits weak [14] but measurable fluorescence [18,35].

In the present line of work we intend to perform a rather systematic theoretical investigation of spectroscopic properties and photophysical behavior of short polyenes. It is based on a fully quantal approach relying on accurate underlying ab initio PES and coupling elements. In a recent paper we dealt with the shortest polyene, butadiene [36]. In the present publication we address *cis*- and *trans*-HT in a comparative manner. Whereas earlier both the spectroscopic and photophysical properties (internal conversion)

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have been covered, the larger number of relevant coordinates to be considered now leads us to limit ourselves here to the UV absorption spectrum and postpone the analysis of the internal conversion (population dynamics and lifetimes) to a later publication. Throughout this paper when *cis*- and *trans*-hexatriene are discussed in comparison, the *cis* isomer is mentioned first and *trans*-HT second in parentheses.

The paper is organized as follows: In the following Section 2 we present the underlying methods concerning the Hamiltonian applied, the time-dependent computations and the electronic structure details. In Section 3 we proceed with our results of the electronic structure calculations for *cis*- and *trans*-HT and the resulting spectra of both isomers in a comparative fashion. Finally, Section 4 concludes.

2. Theoretical methodology

2.1. Vibronic Hamiltonian

The vibronic Hamiltonian is constructed in a similar way as in our previous work on *s-trans*-butadiene, see Ref. [36]. *Cis*-HT belongs to the molecular point group C_{2v} and its 36 vibrational modes transform as follows:

$$\Gamma_{vib}^{cis} = 13a_1 + 5b_1 + 12b_2 + 6a_2 \quad (1)$$

Trans-HT has the point group C_{2h} and the vibrational modes have the following symmetry labels:

$$\Gamma_{vib}^{trans} = 13a_g + 5b_g + 12b_u + 6a_u \quad (2)$$

In order to describe the nuclear degrees of freedom symmetry-adapted internal coordinates are used. Previous works [26,27,37] indicate that the most important vibrations to describe the absorption spectrum involve the movement of the carbon atoms. The 9 in-plane symmetry adapted internal coordinates of the carbon skeleton are listed in Table 1. The atom numbering is defined in Figs. 1 (*cis*-HT) and 2 (*trans*-HT). From extensive investigations of the 1D-cuts of the potential energy surfaces (PES) along the vibrational modes we determined up to six modes to be the most relevant for the molecular dynamics and simulation of the HT absorption spectra. Four of these modes transform as the totally symmetric representation (a_1 for *cis*, a_g for *trans*), while the two other modes, with the representations b_2 for *cis* and b_u for *trans*, lead to a coupling of the $2A_1$ and $1B_2$ ($2A_g$ and $1B_u$) excited electronic states. The totally symmetric coordinate S_1 (see Table 1) is the symmetric stretching of the two terminal double bonds. S_2 represents the symmetric stretching of the single-bonds. The third important coordinate is the stretching of the central double bond (in this work referred to as S_3). The last relevant totally symmetric mode is the symmetric angle deformation of the angles $\varphi_{1,2,3}$ and $\varphi_{6,5,4}$, denoted as S_6. For the coupling b_2 (b_u) modes the antisymmetric stretching of the terminal double bonds S_4 and the antisymmetric angle deformation of $\varphi_{2,3,4}$ and $\varphi_{5,4,3}$ (denoted as S_9) were used. To set up the vibronic Hamiltonian we need to define expressions for the kinetic energy of the nuclear motion. To this end we employ the familiar **G**-matrix technique of Wilson [38,39] and use the **G**-matrix elements for the localized internal coordinates of hexatriene as tabulated by Frederick and Woywod [40]. With these terms it is possible to write the well-established vibronic coupling Hamiltonian as follows [41]:

$$\mathbf{H} = T_N\mathbf{1} + \mathbf{W}(\mathbf{Q}) \quad (3)$$

with the kinetic energy

$$2T_N = \mathbf{p}^T\mathbf{G}\mathbf{p}. \quad (4)$$

Here **p** refers to the vector of momenta conjugate to the applied symmetry coordinates and **1** denotes the 2×2 unit matrix. Note that the matrices **1** and **W** refer to electronic function space, while within T_N boldface notation refers to nuclear coordinate space. In Eq. (3) a (quasi-) diabatic electronic basis is used and the potential energy matrix is constructed as follows:

$$\mathbf{W}(\mathbf{Q}) = \begin{pmatrix} W_a(Q) & W_{ab}(Q) \\ W_{ab}(Q) & W_b(Q) \end{pmatrix} \quad (5)$$

The potentials along the aforementioned coordinates enter the potential energy matrix of the vibronic Hamiltonian. The diagonal elements W_a and W_b representing the diabatic $2A_1$ and $1B_2$ ($2A_g$ and $1B_u$) electronic states are taken as sums of the 1D potential energies along the coordinates S_i.

$$W_{a,b} = \sum_{i=1-4,6,9} V_{a,b}(S_i) \quad (6)$$

To fit the ab initio data we used polynomials up to the 4th order following the general expression:

$$V_\alpha = \sum_{\substack{k=0 \\ i=1,2,3,6}}^{4} V_{\alpha,i}^{(k)} S_i^k \quad (\alpha = a, b) \quad (7)$$

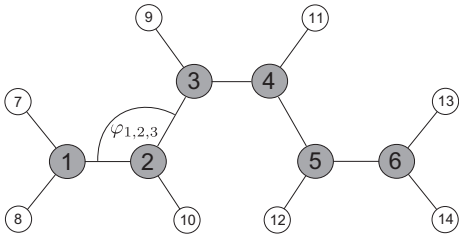

Fig. 1. Atom numbering scheme for *cis*-hexatriene.

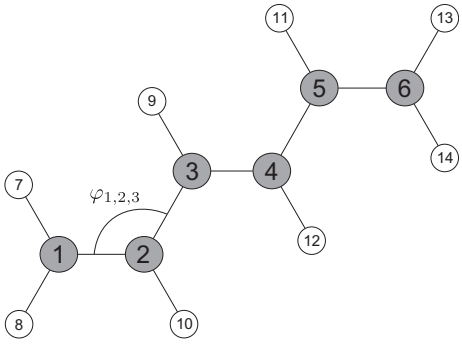

Fig. 2. Atom numbering scheme for *trans*-hexatriene.

Table 1
In plane symmetry-adapted internal displacement coordinates for the carbon skeleton of *cis*- and *trans*-hexatriene. The atom numbering refers to Figs. 1 and 2. Positive linear combinations represent totally symmetric coordinates, while negative linear combinations denote coordinates of b_2 (b_u) symmetry.

Bond length change		Angle deformation	
S_1	$\Delta r_{1,2} + \Delta r_{5,6}$	S_6	$\Delta\phi_{1,2,3} + \Delta\phi_{4,5,6}$
S_2	$\Delta r_{2,3} + \Delta r_{4,5}$	S_7	$\Delta\phi_{2,3,4} + \Delta\phi_{3,4,5}$
S_3	$\Delta r_{3,4}$	S_8	$\Delta\phi_{1,2,3} - \Delta\phi_{4,5,6}$
S_4	$\Delta r_{1,2} - \Delta r_{5,6}$	S_9	$\Delta\phi_{2,3,4} - \Delta\phi_{3,4,5}$
S_5	$\Delta r_{2,3} - \Delta r_{4,5}$		