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A “Hot” Perspective on Symmetry Breaking and Vibronic Coupling in *cis*-1,3,5-Hexatriene

R. Arjan Rijkenberg, Dick Bebelaar, and Wybren Jan Buma*

University of Amsterdam, Faculty of Science, Institute of Molecular Chemistry, Nieuwe Achtergracht 127-129
1018 WS Amsterdam, The Netherlands

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The highly versatile role of polyenes[1,2] has raised considerable interest in their photophysical and photochemical properties.[3] By now, it has been firmly established that the HOMO → LUMO excitation, leading for *all-trans* polyenes of C_{2h} symmetry to the strongly dipole-allowed ionic 1^1B_u state, is not the first excited singlet state S_1 but S_2. Instead, the pioneering experimental work of Kohler and Hudson[4] and the theoretical work of Schulten and Karplus[5] has shown that S_1 (for *all-trans* polyenes of A_g symmetry) is in a zeroth-order picture described by a linear combination of the HOMO → LUMO + 1, HOMO − 1 → LUMO, and $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$ excitations. This implies that for *all-trans* polyenes the one-photon $S_1 \leftrightarrow S_0$ transitions are not only forbidden on symmetry grounds ($g \leftrightarrow g$), but also on account of the double excitation character of S_1.

all-trans-1,3,5,7-Octatetraene can be considered as the prima donna among unsubstituted polyenes with inversion symmetry. For this molecule the above concepts have convincingly been demonstrated by both experimental[6] as well as theoretical research[7]—one-photon transition intensity is induced via vibronic coupling between the dipole-forbidden 2^1A_g (S_1) and the dipole-allowed 1^1B_u (S_2) states. An intriguing question, whose answer has so far remained elusive, is how the lack of inversion symmetry, for example by the presence of *cis*-linkages, influences the spectroscopy of polyenes. Theoretical[8] and solid-state experimental studies[9] on *cis,trans*-1,3,5,7-octatetraene indicate that for this isomer vibronic coupling between S_1 and S_2 dominates the one-photon spectroscopy of S_1, but gas-phase spectroscopic studies that would be able to validate their results quantitatively are unfortunately still lacking.

Another possibility to compare the role of symmetry breaking with that of vibronic coupling—and the one that is pursued here—is to study the one-photon spectroscopy of *cis*-1,3,5-hexatriene. This molecule was the first unsubstituted polyene for which the S_1 (2^1A_1) ← S_0 (1^1A_1) transition could actually be observed under isolated conditions.[10] It can in principle take place as a *direct perpendicular* transition, or as a *vibronically induced parallel* transition. In the latter case transition intensity is borrowed from the S_2 (1^1B_1) ← S_0 (1^1A_1) transition via b_1 modes. The one-photon excitation spectrum of S_1 is dominated by a double band around 34 380 cm^{-1}. The key question is now whether this band corresponds to the 0_0^0 transition, or to a vibronically induced transition. In the original REMPI work[10] a direct transition was assumed, while a vibronically induced character was concluded from subsequent gas-phase fluorescence excitation[11] and resonance Raman[12] studies. Time-resolved measurements of the rotational anisotropy,[13] however, seemed to give evidence for a perpendicular polarized $2^1A_1 \leftarrow 1^1A_1$ transition, that is, not vibronically induced.

In the present work high-resolution fluorescence excitation spectroscopy of jet-cooled *cis*-hexatriene and ab initio calculations have been employed to resolve these issues. In the first instance we will concentrate on the nature of the 34 380 cm^{-1} transition by analyzing its rotational structure. To this purpose excitation spectra have been recorded using relatively “hot” expansions.[14] Under such conditions partially rotationally resolved spectra can be obtained as is shown in Figure 1 for the doubled band at 34 380 cm^{-1}. A rotational contour analysis of this band within the symmetric rotor approach and employing a two-temperature model ($T^1_{\text{rot}} = 60$ K; $T^2_{\text{rot}} = 100$ K)[15] strongly suggests that the rotational features derive from a *parallel* transition and, consequently, that this band corresponds to a vibronically induced transition along normal coordinates of b_1 symmetry. In general, fully resolved spectra are required to determine unambiguously the orientation of an electronic transition moment in the molecular frame.[16] In the present case, however, we can be reasonably sure of our assignment because the values of the rotational constants of the zero-point vibrational level of S_0 and the b_1 vibrational level of S_1 excited in the 34 380 cm^{-1} transition derived from the fit shown in Figure 1 are in excellent agreement with the results of CASSCF/6-31G* geometry optimizations of the 1^1A_1 and 2^1A_1 states (vide infra) as can be seen in Table 1. The rotational constants show that upon excitation a significant increase occurs in the A rotational constant associated with rotation around the long axis, and a decrease in the (B + C) rotational constant. This result is consistent with the idea of a significant bond order reversal upon excitation.

Previously we have successfully employed quantum-chemical modeling to simulate the intensity pattern of vibronically induced false origins in the one-photon excitation spectrum of *all-trans* octatetraene.[7] Here the same approach is used to calculate vibronically induced transition intensities in the $2^1A_1 \leftarrow 1^1A_1$ one-photon excitation spectrum of *cis*-hexatriene.[17] The results in Table 2 clearly show (i) that vibronic coupling along b_1 normal modes is by far the dominant source of transition intensity in the $2^1A_1 \leftarrow 1^1A_1$ one-photon excitation spectrum, and (ii) that ν_{31}

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(14) The experimental setup has been described in Zwier, J. M.; Wiering, P. G.; Brouwer, A. M.; Bebelaar, D.; Buma, W. J. *J. Am. Chem. Soc.* **1997**, *119*, 11523 with the change that in the present experiments pulsed supersonic expansions, created by a 0.5 mm pulsed valve (General Valve Iota One System), were employed instead of continuous expansions. To probe molecules that are not as efficiently cooled as one would normally wish, 500 mbar He mixed with room-temperature hexatriene was expanded into a vacuum of 0.05 mbar, and excitation occurred within one nozzle diameter.

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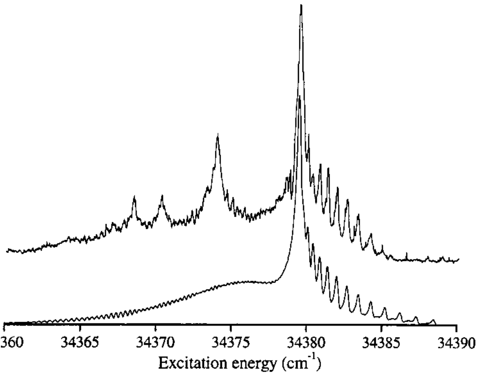

Figure 1. One-photon fluorescence excitation spectrum of the apparent origin region of the $S_1 \leftarrow S_0$ transition in *cis*-1,3,5-hexatriene. The top and bottom spectra display, respectively, the experimental spectrum and the fitted spectrum leading to the rotational constants given in Table 1.

Table 1. Rotational Constants (cm^{-1}) of the Vibrationless Level of the Ground State of *cis*-1,3,5-Hexatriene and the Vibronic Level of S_1 Accessed in the 34380 cm^{-1} Transition

1^1A_1 (S_0)	expt	ab initio	2^1A_1 (S_1)	expt	ab initio
A	0.496	0.496	A	0.534	0.529
B + C	0.096	0.098	B + C	0.093	0.093

Table 2. Calculated Intensities for Direct (0_0^0) and Vibronically Induced ($(b_1)_0^1$) $2^1A_1 \leftarrow 1^1A_1$ Transitions in *cis*-1,3,5-Hexatriene

transition	freq[a]	freq[b]	inten.[c]	transition	freq[a]	freq[b]	inten.[c]
0_0^0			0.02	27_0^1	1405	1280	12.1
31_0^1	365	355	100.0	26_0^1	1492		17.7
30_0^1	722		43.8	25_0^1	1617	1451	3.9
29_0^1	1024		7.3	24_0^1	1769	1623	2.4
28_0^1	1294	1187	8.1				

[a] Calculated unscaled S_0 vibrational frequency (cm^{-1}). [b] Experimental frequency (cm^{-1}).[20] [c] Intensities are given with respect to the calculated intensity of the 31_0^1 band taken as 100.0.

is most effective in inducing transition intensity. In terms of pseudoparity quantum numbers, the 2^1A_1 and 1^1B_1 states are of opposite parity. Pseudoparity considerations predict in such a case that vibronic interaction will be most effective for coupling via bending vibrations.[18] This is nicely borne out from the calculations: ν_{31} and ν_{30}, the two most active modes, are CCC deformations.

The calculations indicate that, apart from ν_{31}, also several other vibronic transitions involving b_1 modes should have a significant intensity, which might seem to be at odds with the experimental excitation spectrum.[10,11] This comparison between experiment and theory is, however, only valid if the lifetimes of the accessed vibrational levels in the excited state are about the same. For the 2^1A_1 state of *cis*-hexatriene this is definitely not the case.[10,11,13] Previous fluorescence studies[11] showed that the S_1 state of *cis*-hexatriene is subject to at least two nonradiative decay processes, which were subsequently associated with *c*/*t* and *Z*/*E* interconversion.[19] The present conclusion that the 34 380 cm^{-1} band should be associated with a vibronically induced b_1 band, and not with the 0_0^0 transition implies that the barriers for these processes in S_1 are about 1 kcal/mol higher than what was previously suggested.

The calculations predict that under the appropriate experimental conditions a number of important, but hitherto unobserved, transitions might become visible. First, careful inspection of the excitation spectrum might reveal the 0_0^0 transition as a very weak feature. Second, if the 31_1 level would have enough population, the 31_1^0 vibronically induced hot band should become detectable. Figure 2 displays the fluorescence excitation spectrum obtained under the same "hot" expansion conditions as those in Figure 1, albeit over a larger range of excitation energies. As expected, the spectrum contains a significant number of hot bands close to the 34 380 cm^{-1} band. However, two bands that are significantly more red-shifted deserve further attention. The first band is a feature observed at ~33 735 cm^{-1}, 645 cm^{-1} displaced from the dominant 34 380 cm^{-1} band. It disappears under better cooling conditions, and can thus be assigned as a hot band. The second band is a doubled band near ~34 100 cm^{-1}. As the signal-to-noise ratio already indicates, this band is even weaker than the previous one. As a result, a definite assignment in terms of it being an hot band or not is not warranted. The intensities of the hot bands near the 34 380 cm^{-1} band make it hard to believe that the 33 735 cm^{-1} band would involve a vibrational level at 645 cm^{-1} in the ground state, an idea that is reinforced by the conclusion that a vibrational energy of 645 cm^{-1} in the ground state cannot be associated with totally symmetric vibrational levels.[20] An alternative assignment is that this band is the vibronically induced 31_1^0 hot band, in line with the conclusion that the one-photon excitation spectrum of the 2^1A_1 state is dominated by vibronic coupling. In that case the doubled band near ~34100 cm^{-1} can be assigned to the 0_0^0 transition − the fundamental frequency of ν_{31} in the ground state has been reported as 355 cm^{-1},[20] in good agreement with our calculations (see Table 2). These assignments would at the same time imply, however, that the frequency of ν_{31} decreases considerably upon excitation or that the doubled band around 34 380 cm^{-1} does not correspond to the 31_0^1 transition.

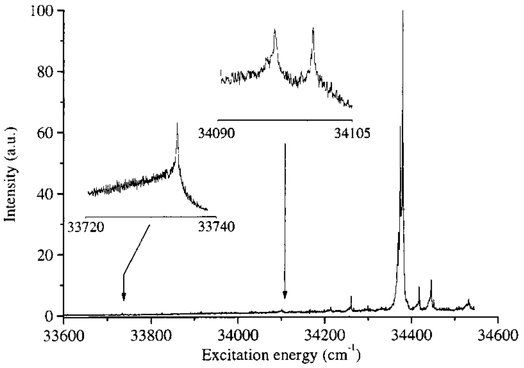

Figure 2. One-photon fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ transition in *cis*-1,3,5-hexatriene. The insets show two weak but reproducible features that under the experimental conditions employed are 3 orders of magnitude weaker than the 34 380 cm^{-1} band.

In conclusion, we have investigated by rotational analyses of the dominant bands in the $2^1A_1 \leftarrow 1^1A_1$ excitation spectrum of *cis*-hexatriene and by the ab initio calculation of direct and vibronically induced transition intensities, the role of symmetry breaking and vibronic coupling. From these experimental and theoretical efforts, it can be concluded that even for a polyene without inversion symmetry vibronic coupling is still of dominant importance for describing the photophysics of the lowest excited singlet state.

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