THE MULTIPHOTON SPECTRA OF ALL-TRANS 1,3,5 HEXATRIENE IN THE REGION OF 6.0 EV

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Abstract. The multiphoton spectra of all-trans 1,3,5 hexatriene, in the region of 6.0eV, is investigated using highly correlated wave-functions. On the basis of the computed transition energies and intensities, an attempt is made to explain the experimentally observed spectra.

The electronic spectra of linear polyenes has been the subject of intensive experimental and theoretical studies since they were first prepared in the early 1930's. Recently there has been a revival of interest in the subject[1]. By forming the basic chromophore of important photobiological systems, such as visual pigments[2] and bacteriorhodopsin[3], the longer polyenes (for which hexatriene serves as a model) have become the subject of numerous photochemical, spectroscopical and theoretical studies[1].

Several experimental techniques[4-6] have been applied to all-trans 1,3,5 hexatriene (hereafter hexatriene). Despite the numerous studies, there are still uncertainties concerning the character, location and assignement of the excited states. Most important is the characterization of the low-lying excited states which could be involved in the photochemistry of the visual process. There has been suggestions that the first excited state of all polyenes is a symmetry forbidden ^1A_g state[7]. For both butadiene and hexatriene, extensive ab-initio calculations[8] have placed the 2^1A_g state above the strong dipole allowed ^1B_u state. For butadiene the 2^1A_g state is calculated at 7.06eV (^1B_u at 5.92eV) and 5.87eV (^1B_u at 4.95eV) for hexatriene. Since the ^1A_g states are dipole forbidden, they would appear in the one-photon spectra as week vibronic transitions. These states should be more easily observed in the two-photon spectra of the polyene compounds. Johnson[9] has looked at the two-photon spectra of butadiene, and did not detect any ^1A_g state below 5.92eV as has been suggested[7]. Unfortunately, he was not able to record the spectra for energies above 6.79eV and, therefore, was unable to verify the state at 7.06eV. More recently, El-Sayed[10] investigated the two-photon spectra of hexatriene in the region of 6.0eV (6.0-6.7eV). In this region he observed a single transition at 6.23eV (and its vibronic structure). From polarization[11-12] studies he concluded that the excited state should have A_g symmetry. But following our ab-initio calculations, there should be three two-photon allowed states in this region, namely the $^1A_g(\pi\rightarrow 3p_x)$ and two $^1B_g(\pi\rightarrow 3p_y, 3p_z)$ Rydberg states.

Comparing the experimental and theoretical results, one sees that some questions remain to be answered. First of all, what is the nature of the observed ^1A_g state? Would it be the theoretical predicted $3p_x$ Rydberg state or the 2^1A_g valence state, placed at 5.87eV by the ab-initio calculations? If the theoretical predictions are correct, why the

^1B_g states were not observed?

To answer these questions we calculated the intensities for the transition from the X^1A_g state to all of the above mentioned states, for both linearly and circularly polarized light. We also computed Ω (the polarization ratio)[12], as an internal check to our calculations.

All the calculations we carried out using the Dunning[13] valence double-zeta contraction of Huzinaga[14] double zeta (9s/5p,4s) gaussian basis set, augmented with diffuse basis functions of $3p_\sigma$ and $3p_\pi$ character, in order to provide adequate description of the Rydberg excited states. With the molecule in the yz plane, we used the experimentally determined ground-state geometry[15] in all calculations. The states were solved self-consistently, the X^1A_g at the GVB level (the 2^1A_g valence state obtained as a second root in the CI calculation), and all the other states at the Hartree-Fock level. The CI calculations were performed allowing up to quadruple excitations in the π space, for the ^1A_g states. For the ^1B_g states one allowed up to triple excitations in the π space, simultaneously allowing the σ electrons to readjust (single excitations in the σ space). With these wave functions one computed the two-photon transition rates.

Table 1 shows the results of these calculations. From the results, we assign the transition at 6.23eV to the $\pi \rightarrow 3p_x(\pi^*)^1A_g$ state, because of the excellent agreement between the theoretical and experimental results for the transition energy and Ω. One also see from table 1 that the two-photon intensities of the transition to the $^1A_g(3p_{\pi_x})$ state relative to the ^1B_g states $(\pi \rightarrow \sigma^*)$ $[\omega_{A_g \rightarrow A_g}/\omega_{A_g \rightarrow B_g}]$ are 18.65 $(3p_y)$ and 12.05 $(3p_z)$ respectively, for circularly polarized light and 49.60 $(3p_y)$ and 31.35 $(3p_z)$, respectively, for linearly polarized light. Thus, the ^1B_g states should be much more difficult to detect in the El-Sayed experiment[10]. Finally, with respect to the 2^1A_g valence state, one sees that its transition rate is much larger than the ones for the Rydberg states, implying that it should be easily detected by El-Sayed, would it occur in the 6.0-6.7eV region of the spectra. Our calculations suggest that an experiment conducted at lower energies should reveal the presence of the 2^1A_g valence state.

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Table 1. Transition energies (ΔE), two-photon transition rates (τ) and polarization ratios (Ω) for some electronic transitions of the hexatriene molecule

State	$\Delta E(eV)^a$	τ_c^b	τ_ℓ^b	Ω^c
$2^1A_g(\pi \rightarrow \pi^*)$	5.87	3.40^d	4.90^d	0.69
$3^1A_g(3p_x)$	6.26	0.90^e	1.90^e	0.47^f
$1^1B_g(3p_y)$	6.00	4.82^g	3.83^g	1.26
$2^1B_g(3p_z)$	6.20	7.46^g	6.06^g	1.23

a. Transition energies relative to the ground state (X^1A_g) energy of -231.81913 hartrees

b. In units of F^2s^{-1}, where F is the photon flux in photons/cm².s

c. $\Omega = \tau_c/\tau_\ell$. $\Omega < 1$ for $A_g \leftrightarrow A_g$ transitions and equal 3/2 for $A_g \leftrightarrow B_g$ transitions. See ref. 12

d. (-50)

e. (-52)

f. $\Omega_{observed} \approx 0.25-0.40$. See ref. 10

g. (-54)

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