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Location of the 2^1A_g state in hexatriene

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Perhaps the most striking feature of electronic structure in the linear polyenes with four or more double bonds in conjugation is the fact that the ordering of excited singlet states predicted by molecular orbital theory at the Hartree-Fock level is different from that observed experimentally.¹⁻³ While this is well established for the longer polyenes by a number of high resolution spectroscopic experiments^{4,5} and theoretically understood to follow from the unusual importance of electron correlation in these 1-dimensional systems,^{4,6,7} the ordering of excited states in hexatriene and butadiene has remained a matter of controversy.

Further, while the excitation energies of the 2^1A_g and 1^1B_u states in isolated molecules can be reasonably predicted from the dependence of excitation energy on solvent polarizability, no one has yet directly observed the 2^1A_g state in an unsubstituted linear polyene in the gas phase. This communication reports the direct observation of the 2^1A_g state in unsubstituted hexatriene. By measuring the dependence of mass selectively detected multiphoton ionization of *cis*- and *trans*-hexatriene seeded into a supersonic helium expansion we have obtained the fully resolved 1^1A_g to 2^1A_g absorption spectrum. (Although the symmetry labels for C_{2v} *cis* hexatriene are A_1 and B_2 instead of A_g and B_u , respectively, we use the C_{2h} labels A_g and B_u for corresponding states of both isomers.)

In our experiments, room temperature *cis*- or *trans*-hexa-

triene (extracted from material purchased from Aldrich Chemical Co. by gas chromatography using a column packed with 10% β,β' -oxidipropionitrile on 60/80 mesh Chromosorb P/AW) at its room temperature equilibrium vapor pressure was mixed with 3 atm He and expanded into a differentially pumped vacuum chamber to form a skimmed collision free beam between the collection electrodes of a time-of-flight mass spectrometer (R.M. Jordan Co.). There it was intersected by the beam of a tunable pulsed dye laser (Quanta Ray DCR-3 pumped dye laser with WEX-1). Standard boxcar techniques were used to monitor the signal at a given e/m ratio. This apparatus can measure excitation spectra (ion counts versus laser wavelength at fixed power) as well as dynamics (ion counts versus laser power at fixed wavelength).

Figure 1 shows the spectrum (ion counts at $e/m = 80$ versus laser wavelength) measured for the *cis* isomer. That the multiphoton ionization was due the $1 + 1$ process (one photon excitation to a resonant level followed by one photon excitation to the continuum) was established by measuring the intensity dependence of the resonance enhanced signal (Figure 2). The 2^1A_g origin appears as two lines at 2908.0 Å and 2907.6 Å ($34\,388\text{ cm}^{-1}$ and $34\,393\text{ cm}^{-1}$). The 5 cm^{-1} splitting is plausibly associated with two nearly equivalent ways of realizing a very slight distortion from planarity. These features are approximately 5270 cm^{-1} below the ori-

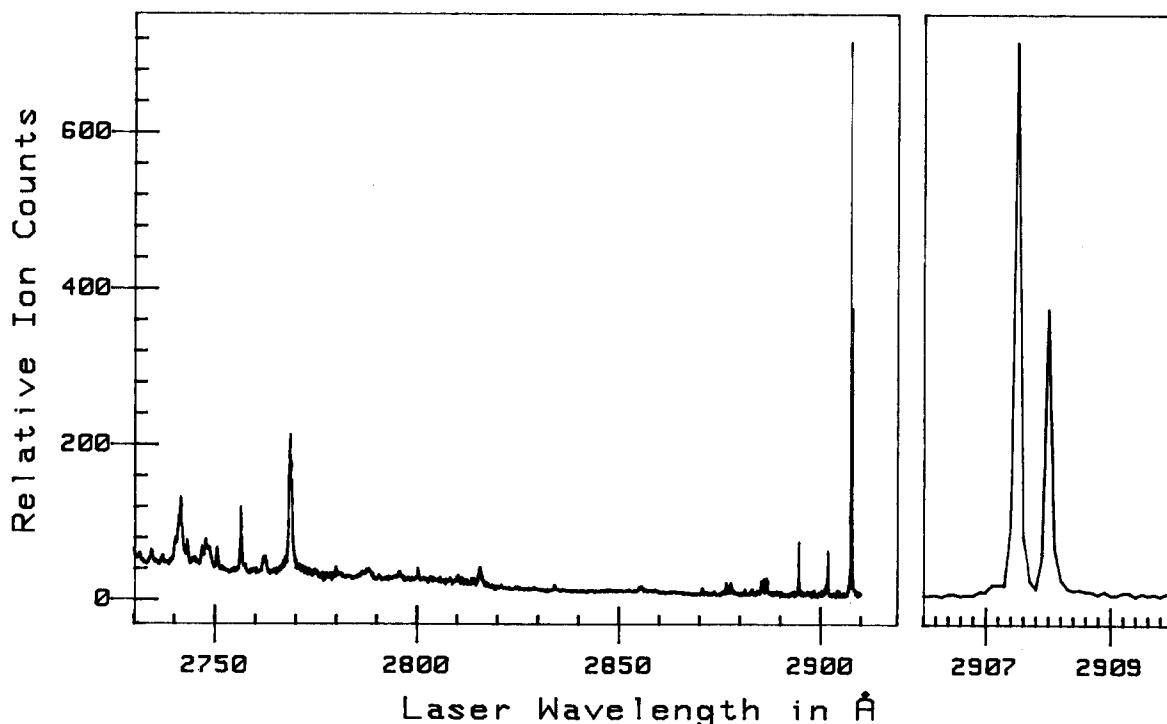


FIG. 1. The low energy portion of the excitation profile for resonantly enhanced $1 + 1$ multiphoton ionization of *cis*-hexatriene. The left panel shows the region from the origin to 1900 cm^{-1} vibronic energy. The right panel shows the doubled origin at $16\times$ horizontal scale expansion.

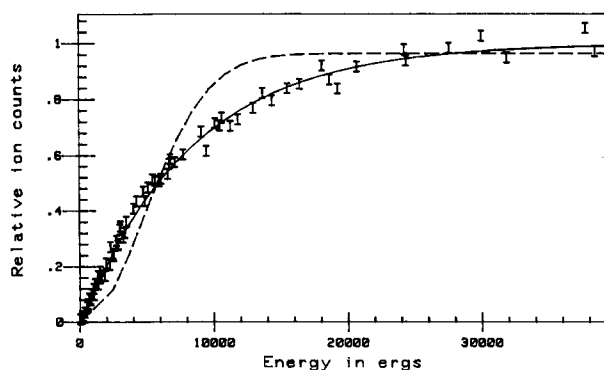


FIG. 2. The dependence of ion counts at $e/m = 80$ on laser power for the lowest energy peak shown in Fig. 1. The solid line is the best fit to these data by the $1 + 1$ kinetic model (1 photon to a resonant state followed by 1 photon to ionize). The best fit by the model involving two-photon ionization (broken line) is significantly poorer, showing large systematic deviations.

gin for the transition to the 1^1B_u state.⁸ Because the intensity at the origin is high relative to the rest of the spectrum, the vertical excitation energy for both conformers must be close to the observed origin. Thus, 5270 cm^{-1} is a lower bound for the difference between the 1^1B_u and 2^1A_g vertical excitation energies. As is the general situation for the linear polyenes, the vibronic development consists primarily of combinations and overtones of the C–C and C=C stretches (1125 cm^{-1} and 1730 cm^{-1} , respectively). The origin of the frequency increase in both C–C and C=C modes follows from the electronic properties of the 2^1A_g state as discussed recently.⁹

At the origin the bands are narrow compared to the $\approx 1\text{ cm}^{-1}$ bandwidth of the excitation laser. Higher in the vibrational manifold the bands appeared broader but, at higher resolution, exhibited a complex but sharp multiplet structure. This may reflect large amplitude motion on a hindered rotor potential for rotation about bonds that have single bond character in the excited state. Even at these higher vibronic levels, the envelopes of the multiplet structures never exceeds 13 cm^{-1} .

We have also observed vibronic features in the 1^1A_g to 2^1A_g transition for the *trans* isomer, although the resonance enhanced intensities are at least an order of magnitude smaller than those seen for the *cis* isomer. In the *trans* isomer the 1^1A_g to 2^1A_g transition may be strictly symmetry forbidden, so it is reasonable that the one-photon cross sections for the 1^1A_g to 2^1A_g transition should be much smaller than they are for the *cis* isomer. Limitations on our present signal-to-noise ratio have prevented us from making an unambiguous assignment of the origin, but we know that it must have an energy $\leq 34\,038\text{ cm}^{-1}$, the lowest energy band so far seen. Thus, in the *trans* isomer the origin of the 2^1A_g state lies at least 5748 cm^{-1} below that of the 1^1B_u .⁸ The quality of the measured spectra can be improved by either significantly increasing signal-to-noise ratio or measuring two color two-photon resonance enhanced multiphoton ionization excitation spectra. We are currently working on both of these strategies.

Preliminary studies indicate that these techniques will allow similar spectra to be measured for butadiene and octatetraene. This work is also in progress.

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Effect of optical resonances on the second harmonic response from Ag(111) and Ag(110) in solution

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Although many experimental and theoretical studies have recently appeared which use optical second harmonic generation (SHG) to probe metallic surfaces, few have addressed the effect of optical resonances occurring between

the incident or outgoing radiation and surface electronic or bulk electronic transitions of the native metal.¹⁻³ In this Communication, we demonstrate for the first time the significant effect that these resonances can have on both the rota-