

Spectroscopy and Dynamics of a Model Polyene Decatetraene: A Study of Non-Radiative Pathways in S_1 and S_2 States Under Isolated Conditions

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The spectroscopy and dynamics of decatetraene (DT), a model linear polyene, are studied in order to gain a greater understanding of photophysical properties of this class of molecule, which are pervasive in biological systems and which have interesting electro-optical properties. The photochemistry of a polyene is governed by its two low lying singlet excited electronic states. The optical excitation usually occurs to the S_2 state (1^1B_u), which is strongly allowed. However, due to rapid internal conversion (IC) from the S_2 to S_1 state (1^1A_g), the subsequent photochemistry occurs from the S_1 state. Because the $S_1 \leftarrow S_0$ transition is symmetry forbidden by single photon excitation, it is difficult to study the structure and dynamics of polyenes in their S_1 electronic states. The motivation for this work came from Bouwman *et al.*'s recent demonstration that when intermediate length polyenes (4 - 5 double bonds) are excited to the S_2 state in the gas phase, they emit from both S_2 and S_1 states [1]. This work presents unique spectroscopical and dynamical observations on the S_1 and S_2 states of DT and preliminary results on nonatetraene (NT) under isolated conditions in a molecular beam, where the non-radiative decay processes can be observed as a function of excitation energy without perturbation from a solvent.

The laser excitation spectra of S_1 state of DT are shown in Fig. 1. The S_1 state spectrum consists of a rich progression in low frequency skeletal bending modes,

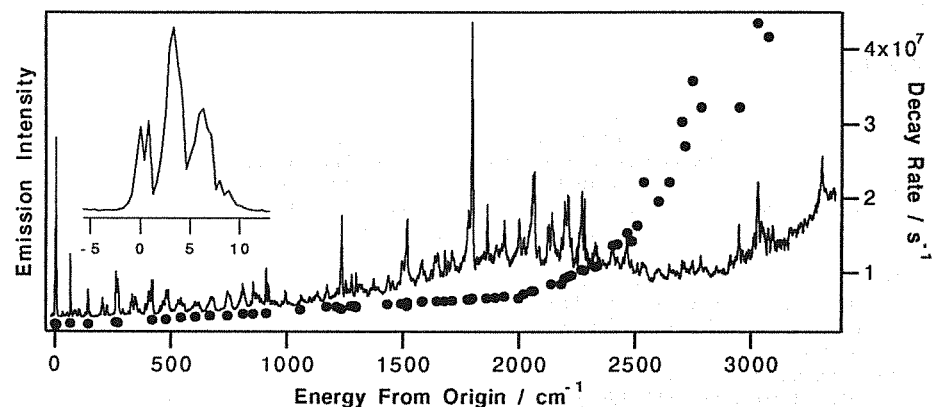


Figure 1. The $S_1 \leftarrow S_0$ fluorescence excitation spectrum of DT. The "false" origin at 344.61 nm in the insert shows triplet structure, which is ascribed to hindered methyl torsions. Decay rates for individual vibronic states are indicated by circles.

which are built on false origin at 344.61 nm, and other major features such as C - C and C = C stretching vibrations. This symmetry forbidden $1^1A_g \leftarrow 1^1A_g$ transition is made possible by Herzberg-Teller mixing of the b_u vibronic symmetry states in S_1 with the nearby S_2 state. The b_u character can be derived either from in-plane non-totally symmetric skeletal bending modes or from hindered methyl torsions. The triplet structure shown in the inset of Fig. 1 is a signature of modes which are allowed by coupling to the methyl torsion.

The measured decay rates for single vibronic states are also shown in Fig. 1. At the origin the lifetime is ~ 350 ns. There is a gradual decrease in the lifetime to higher energies due to increased mixing with the S_2 state. At $\sim 2,000$ cm^{-1} excess energy a sharp increase in the decay rate in both DT and NT is due to the availability of a non-radiative decay channel, possibly *trans-cis* isomerization. Kohler *et al.* found that *trans-cis* isomerization in the S_1 state of octatetraene (OT) is an activated process with a $1,400$ cm^{-1} barrier in solution [2], and they observed the formation of the *cis*-isomer [3]. The non-radiative decay due to *trans-cis* isomerization with a barrier of $1,400 - 2,000$ cm^{-1} appears to be common to *all-trans* tetraenes.

The $S_2 \leftarrow S_0$ fluorescence excitation spectrum shows broad vibrational lineshapes due to the rapid IC to the S_1 state. The peaks increase in width from 22 cm^{-1} at the origin to 40 cm^{-1} at 504 cm^{-1} above. Assuming that the widths are due to $S_2 - S_1$ coupling in the statistical limit, they correspond to an upper limit for the S_2 state lifetime of $0.50 - 0.27$ ps. This increase in linewidth may indicate that the low energy skeletal bending vibrations are promoting modes for IC. Similar widths are observed for NT, and Heimbrook *et al.* report a 12 cm^{-1} width for OT [4].

Based on these observations the following mechanism is proposed for the unimolecular decay of tetraenes in the gas phase. Following excitation to the S_2 state, tetraenes internally convert to the S_1 state on the <1 ps time scale. This horizontal radiationless transition leaves tetraenes with $>6,000$ cm^{-1} of excess energy in the S_1 state. Since this is much greater than the activation barrier to isomerization, tetraenes subsequently decay to the S_0 state in a statistical fashion. The low frequency hindered methyl torsions are an overwhelming factor in determining the density of states; therefore, given that the barriers for isomerization are nearly the same, at a given energy OT will decay the fastest, and DT the slowest.

References

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