Department of Chemistry, Bowdoin College, Brunswick, Maine 04011-8466, and Department of Chemistry,
University of Connecticut, Storrs, Connecticut 06269-3060

Room temperature absorption and emission spectra of the all-trans isomers of decatetraene, dodecapentaene, tetradecahexaene, and hexadecaheptaene have been obtained in a series of nonpolar solvents. The resolved vibronic features in the optical spectra of these model systems allow the accurate determination of S_0 ($1^1A_g^-$) f S_2 ($1^1B_u^+$) and S_1 ($2^1A_g^-$) f S_0 ($1^1A_g^-$) electronic origins as a function of solvent polarizability. These data can be extrapolated to predict the transition energies in the absence of solvent perturbations. The effects of the terminal methyl substituents on the transition energies also can be estimated. Franck−Condon maxima

absorption and fluorescence of these systems in low-temperature mixed crystals,[27] in the gas phase,[28] and in supersonic jets[29] provide a substantial background of information, which facilitates the analysis and understanding of the less-resolved room solution temperature spectra presented here.

2,4,6,8-Decatetraene, 2,4,6,8,10-dodecapentaene, 2,4,6,8,10,12-tetradecahexaene, and 2,4,6,8,10,12,14-hexadecaheptaene were synthesized from all-trans polyene aldehydes via Wittig reactions as previously described.[30,31] These reactions tend to favn5 toh

orbital (LUMO).[2,19,20,35] The transition energies (ΔE) exhibit an asymptotic approach to a long polyene limit following the approximation $\Delta E \approx A + B/N$, where N is the number of π-electron conjugated double bonds and A represents the S_0 f S_2 transition energy of the infinite polyene. For dimethyl polyenes, A is ~14 000 cm^{-1}, corresponding to a $1^1A_g^-$ f $1^1B_u^+$ (0−0) wavelength of ~700 nm in the long polyene limit.[3,36−39] Similar empirical, $1/N$ doublgy   3,36

vibronic band, whereas for $N = 4$, the emission maximum corresponds to the "(0−3)" vibronic band. The $S_1 \rightarrow S_0$ emission spectrum of decatetraene points to a larger displacement of the excited state S_1 ($2^1A_g^-$) potential energy surface relative to that of the ground state ($1^1A_g^-$), consistent with electronic excitation having the largest impact on π-bonding in the smallest polyene in the series. The vibronic spacings observed in the $N = 4−7$ absorption and emission spectra also should be noted. The 1470, 1410, 1355, and 1325 cm^{-1} vibrational progressions seen in emission systematically decrease with increasing conjugation. This is in agreement with trends seen in the ground state vibrational spectra of modes assigned to totally symmetric C−C and C=C stretches in other polyene systems.[3]

It is important to emphasize that the distinctive vibronic progressions observed in the room temperature spectra are due to complicated superpositions of vibrations, including combination bands involving the C−C and C=C totally symmetric (a_g) modes. For example, the low-temperature, high-resolution emission spectrum of 4-*cis*-hexadecaheptaene in 10 K *n*-pentadecane[30] has a maximum at 2700 cm^{-1} (cf. 2650 cm^{-1} calculated from the low-resolution emission spectra presented in Figure 3), which can be assigned to the combination of a C−C vibration (1148 cm^{-1}) and the dominant C=C vibration (1555 cm^{-1}). The frequencies (3)Tju/F5 1 TfTj/F-241 TfTj/(u/F5 1 TfT.4(frequey)-241.6(syequeric)-263.70.661 2976579 TD[(prog-)Tj/J6.733 0
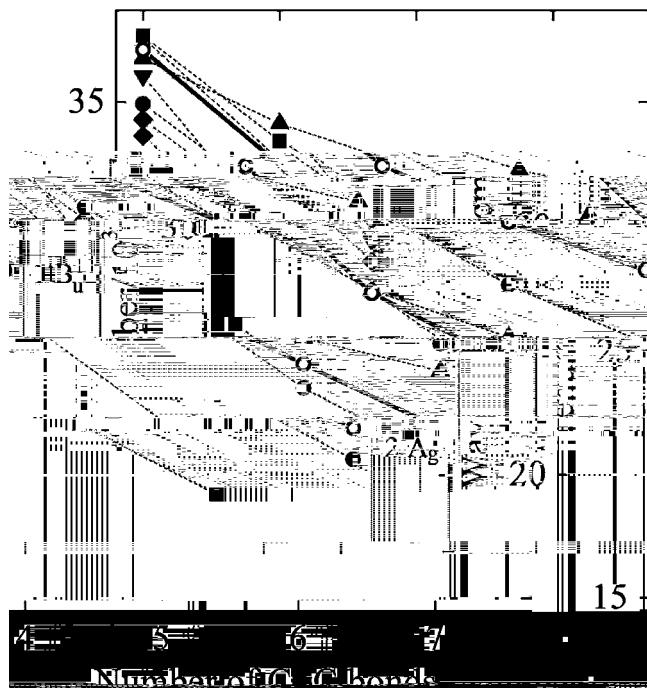
Figure 6. Energies of the S_1 ($2^1A_g^-$) and S_2 ($1^1B_u^+$) states of unsubstituted polyenes as a function of the number of conjugated double bonds. Theoretical values (dashed lines) for vertical transitions are from Tavan and Schulten (2),[20] Nakayama et al. (1),[22] Head-Gordon et al. ([ ),[23] Dreuw et al. (O),[25] and Marian and Gilka (b).[26] Experimental data (O, solid lines) are from Table 3 and include corrections for solvent perturbations, the effect of methyl substitution, and the differences between (0−0) and vertical transition energies. Estimated errors for the experimental points are given in Table 3.

It should be noted that the gas phase, $S_2 - S_1$ (0−0) energy differences presented here (6780, 7160, 7650, and 8000 cm^{-1}) are consistent with previously reported values (6380, 7060, 7420, and 8690 cm^{-1}) for the transition energies of unsubstituted polyenes with $N = 4-7$.[42,43] The energy values reported here are considerably more reliable due to the care taken to identify and isolate all-trans isomers by using HPLC techniques and the more careful analysis/deconvolution of the room temperature absorption and emission solvent shift data.

Appropriate estimates of the differences between (0−0) and vertical transition energies are critical for comparing the experimental results with theoretical predictions (Figure 6). The small geometry change between $1^1A_g^-$ and $1^1B_u^+$ leads to relatively good agreement on the difference between the vertical and (0−0) transition energies for octatetraene: cf. theory (2600 cm^{-1}; 1850 cm^{-1})[22,26] and experiment (1540 cm^{-1}). However, there are large discrepancies for the $1^1A_g^- \to 2^1A_g^-$ transition. Analysis of the Franck−Condon envelopes (Figure 2) indicates a 4440 cm^{-1} difference for $N = 4$, considerably lower than the values (7900 cm^{-1} and 6200 cm^{-1}) suggested by Nakayama et al.[22] and by Marian and Gilka.[26] Marian and Gilka calculate 5000−5800 cm^{-1} differences for $N = 5-7$, which are significantly higher than the 2700 ± 100 cm^{-1} differences we estimate from the Franck−Condon envelopes. Accounting for these discrepancies offers a fertile opportunity for reconciling the vibronic intensities in polyene/cartotenoid absorption and emission spectra with more accurate descriptions of excited state geometries, especially for the $2^1A_g^-$ state. This also will lead to a better understanding of the theoretical and experimental data presented in Figure 6.

It is important to relate the current studies to our recent work on the symmetry control of S_1 ($2^1A_g^-$) $\to$ S_0 ($1^1A_g^-$) radiative decay in polyenes.[32] This indicated that the $S_1 \to S_0$ emissions from highly purified samples of long, symmetric all-trans polyenes most likely are due to cis isomers and/or comformationally distorted trans molecules. Less symmetric, more highly fluorescent cis species can be produced photochemically from pure all-trans samples. The fluorescence also may be due to thermal distributions of all-trans isomers that are conformationally distorted in their ground states or produced during relaxation from S_2 to S_1. Low barriers to isomerization and conformational distortion in S_1 ($2^1A_g^-$) are consistent with the significant rearrangement of the ground state C−C and C=C bonds in $2^1A_g^-$,[3,4,22,24] and explain the unique ability of polyene

S$_1$ states to undergo isomerization. The emission spectra and

(43) D′Amico, K. L.; Manos, C.; Christensen, R. L. *J. Am. Chem. Soc.* **1 0**, *102*, 1777.

(44) Heimbrook, L. A.; Kenny, J. E.; Kohler, B. E.; Scott, G. W. *J. Chem. Phys.* **1 1**, *75*, 4338.