

**Symmetry Control of Radiative Decay in Linear Polyenes:  
Low Barriers for Isomerization in the S<sub>1</sub> State of  
Hexadecaheptaene**

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carotenoids, which they postulated facilitates internal conversion between the  $S_2$  ( $1^1B_u^+$ ) and  $S_1$  ( $2^1A_g^-$ ) states. Van Grondelle and co-workers<sup>11</sup> observed a wavelength dependence of the dynamics of spirilloxanthin that was interpreted in terms of another singlet electronic state,  $S^*$ , thought to be an intermediate in the depopulation of  $S_2$  ( $1^1B_u^+$ ). Fast pump–probe optical techniques were applied to  $\hat{a}$ -carotene by Larsen et al.,<sup>12</sup> and the results suggested yet another carotenoid excited state ( $S^\ddagger$ ) formed directly from  $S_2$  ( $1^1B_u^+$ ). The nature of these states remains uncertain, and recent work has called into question the

to the methyl groups showed distinct chemical shifts, indicating an asymmetric structure. Exploiting the 2D correlation peaks starting from the methyl protons, signals due to the ethylenic protons were assigned based on splittings, coupling constants, and COSY cross-peaks between neighboring protons. These assignments are summarized in Figure S1



$S_1 (2^1A_g) \rightarrow S_0 (1^1A_g)$

which include the melting of the *n*-pentadecane crystal at 10 °C. In addition to the least-squares analysis, we also have employed simulations to explore the parameter space and to better understand the data and the model (eq 1). The determination of relative fluorescence yields as a function of temperature on samples undergoing photoisomerization is particularly challenging, especially for weakly emitting species. In spite of the limitations of both the model and the data, the parameters extracted from eq 1 are consistent with thermally activated, 4-*cis* f

with that associated with the symmetry forbidden transition of the *all-trans* isomer. The excitation spectra for both the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  absorptions show the classic pattern of vibronic intensities built on combinations of carbon–carbon single and double bond symmetric stretching modes. The vibronic spectrum shown in Figure 7 previously was analyzed by Simpson et al. and assigned to the *all-trans* isomer.<sup>18</sup> However, our current work shows that the vibronic states observed are due to 4-*cis* hexadecaheptaene.

## Conclusions

The results presented here require a reinterpretation of fluorescence experiments previously carried out on *all-trans* isomers of longer polyenes and of related carotenoids. Several previous studies of longer linear polyenes ( $N > 4$ ) have assigned  $S_1 \rightarrow S_0$  fluorescence signals to *all-trans* isomers. Examples include the high-resolution work of Simpson et al. on hexadecaheptaene<sup>18</sup> and of Kohler et al. on octadecaheptaene.<sup>40</sup> The excitation and fluorescence spectra were assigned to *all-trans* species, but our work indicates that the  $S_1 \rightarrow S_0$  emission spectra of these longer polyenes most likely are due to *cis* isomers, present as impurities or formed as photochemical products in the  $S_1$  state. This is a significant finding, given that existing theoretical work (almost all on simple *all-trans* polyenes)<sup>4,5,55,56</sup> has been compared with experimental work on what now must be assigned to *cis* species. Rapid isomerization in  $S_1$  ( $2^1A_g^-$ ) explains the typically small differences between the  $S_1$  ( $2^1A_g^-$ )  $\rightarrow$   $S_0$  ( $1^1A_g^-$ ) emission spectra and quantum yields of *cis* and *trans* systems in room temperature solutions. The almost negligible  $S_1$  ( $2^1A_g^-$ )  $\rightarrow$   $S_0$  ( $1^1A_g^-$ ) fluorescence yields from  $C_{2h}$ , *trans* species and the relatively low resolution of solution and glass spectra prohibit a ready distinction between emissions due to *trans* isomers from those due to *cis* impurities or from *trans* molecules with conformational distortions that relax the rigorous selection rules. We thus conclude that, except for the very detailed studies of *all-trans* octatetraene, *previous reports of  $S_1$  emissions from all-trans,  $C_{2h}$  polyenes and carotenoids most likely are due to less symmetric species.* These species may be present as ground state impurities, including photochemical products, or formed in the  $S_1$  ( $2^1A_g^-$ ) state following the excitation of *all-trans* polyenes.

Our results suggest that steady-state fluorescence experiments and time-resolved measurements, e.g.,  $S_1 \rightarrow S_N$  transient absorption experiments, detect different distributions of  $S_1$  ( $2^1A_g^-$ ) conformers and geometric isomers, even for samples with a single, *all-trans*, ground state structure. For example, the elegant  $S_1$  ( $2^1A_g^-$ )  $\rightarrow$   $S_2$  ( $1^1B_u^+$ ) absorption experiments of Polívka et al.<sup>57</sup> on several *all-trans* carotenoids, including spheroidene, zeaxanthin and violaxanthin, were compared with the transition energies for the strongly allowed  $S_0$  ( $1^1A_g^-$ )  $\rightarrow$   $S_2$  ( $1^1B_u^+$ ) absorptions. The energy difference in the electronic origins ((0–0) bands) of these two symmetry-allowed transitions yields the  $S_1$  ( $2^1A_g^-$ ) energy. However,  $S_1$  electronic energies