

The 1B_u Lifetime of Short All-Trans Polyenes: A Theoretical Study

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Introduction. The trend in the $S_2(^1B_u)$ lifetime of carotenoids as a function of conjugation length N cannot be rationalized by the energy gap law.¹ While the $S_2-S_1(^1B_u-2^1A_g)$ energy gap increases with conjugation length, fluorescence up-conversion experiments on a series of linear carotenoids with $N = 9$ to 11 revealed S_2 lifetimes decreasing with N .¹ An explanation for this reverse trend is still missing although it is apparent that the S_2-S_1 energy gap is not the only factor that determines the conversion rate. We intend to search for an explanation for the above-mentioned trend by theoretically studying the relaxation dynamics of the optically-allowed 1B_u state to the 2^1A_g state of a series of shorter linear all-trans C_{2h} polyenes by time-dependent wavepacket dynamics model simulation. We expect that the conclusions drawn from short polyenes can be extended to longer carotenoids.

Computational Details. The excitation energies of all-trans 1,3-butadiene (BTD, $N=2$), 1,3,5-hexatriene (HXT, $N=3$), and 1,3,5,7-octatetraene (OCT, $N=4$) are calculated by state-averaged CASSCF and MRCI techniques using the 6-31G(d) basis set. The geometry at the conical intersection that connect the two excited states is optimized by RASSCF techniques. The active space is carefully chosen to consist of $2N + 2$ electrons in $2N \pi$ orbitals and 2σ orbitals. In the RASSCF calculation, the ground state (1^1A_g), HOMO \rightarrow LUMO (1^1B_u), HOMO² \rightarrow LUMO² (2^1A_g), HOMO-1 \rightarrow LUMO (2^1A_g) configurations are selected. The tuning (\mathbf{g}) and coupling (\mathbf{h}) vectors that characterize the branching space of the conical intersection seam are analyzed in terms of the gradient difference and the derivative coupling matrix and are compared with normal vibrational modes that characterize the electronic ground state to identify the molecular motion that promote excited state relaxation. The Euclidian norm of the derivative coupling vector is used as an estimate of the relative strength of coupling between intersecting states. The coupling strength is then used to predict the trend in the lifetime of the 1^1B_u state.

Results and Discussion. Among the polyenes being studied, the following trend in the theoretical S_2-S_1 energy gap was observed: HXT < BTD < OCT (Figure 1). A similar trend was predicted by Nakayama *et al.*² using more sophisticated *ab initio* techniques. Thus, we believe that MRCI/6-31G(d) is adequate for our purpose.

As far as BTD and OCT are concerned, the calculated norm of the derivative coupling $|\mathbf{f}|$ is in keeping with the energy gap law, the BTD excited states being more strongly coupled at the conical intersection than OCT. However, it is interesting to note that HXT experimentally yields femtosecond 1^1B_u lifetime despite a negligible coupling between the S_1 and S_2 states as predicted by RASSCF calculations. The topology of the excited state PES, which are yet to be calculated, may play an

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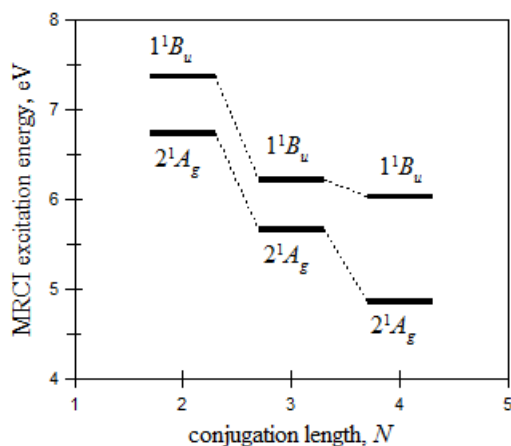


Figure 1: MRCI excitation energies.

important role in the relaxation dynamics.

Table 1. Relevant properties of small all-trans polyenes.

N	$ f ^a$	S_2-S_1 gap, eV ^b	1^1B_u lifetime, fs
2 (BTD)	3 817	0.63	54 ³
3 (HXT)	~0	0.57	<100 ⁴ ; <150 ⁵
4 (OCT)	441	1.18	~400 ⁶

^aRASSCF/6-31G(d) ^bMRCI/6-31G(d)

Analysis of the branching space reveals that the C-C stretching and carbon-backbone buckling modes are important tuning and coupling coordinates, respectively. Thus, the appropriate C-C bond distance and C-C-C-C bond torsion are chosen as coordinates in the construction of a multi-sheeted potential energy surface suitable for dynamics calculation.

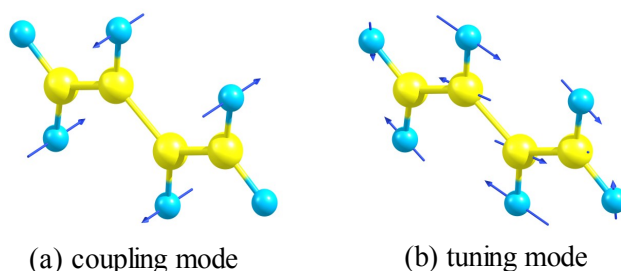


Fig. 2. Privileged directions at the optimized geometry at the BTD $1^1B_u-2^1A_g$ conical intersection.

Conclusion. The static properties calculated so far failed to explain the observed 1^1B_u lifetimes although the relative S_2-S_1 coupling strength indicates that the S_2-S_1 gap is not solely responsible for the 1^1B_u lifetime. We expect the PES and wavepacket dynamics calculation to reveal more intricate details otherwise not obtainable from static properties.

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5 Ohta K., Naitoh Y., Saitow K., Tominaga K., Hirota N, Yoshihara K. Chem. Phys. Lett., 256, 1996, Pages 629-634.

6 Ohta, K.; Naitoh, Y.; Tominaga, K.; Yoshihara, K. J. Phys. Chem. A.; 2001; 105(16); 3973-3980.