The Energy Gap Law Revisited: Implications to the Excited-State Lifetime of Short All-Trans Polyenes

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The trend in the $S_2(1^1B_u)$ lifetime of carotenoids as a function of conjugation length N cannot be rationalized by the energy gap law [1]. While the S_2–$S_1(1^1B_u$–$2^1A_g)$ 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 1^1B_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.

The excitation energies of all-trans 1,3-butadiene (N=2), 1,3,5-hexatriene (N=3), and 1,3,5,7-octatetraene (N=4) are calculated by state-averaged RASSCF 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 tuning (g) and coupling (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. Quasi-diabatic potential energy surfaces of the 1^1A_g, 2^1A_g and 1^1B_u states of the three polyenes are constructed using MRCI techniques. The magnitude of coupling between states is estimated through the off-diagonal elements of the diabatic electronic Hamiltonian.

The topology of the singlet excited states of polyenes as well as the relative magnitude of coupling between states offer interesting insights that warrant a rethinking of the role the energy gap law plays in predicting the trend of the 1^1B_u lifetime of polyenes and possibly, carotenoids.

[1]. T. Polivka and V. Sundstrom, Chem. Rev. **104**, 2021-2072 (2004).