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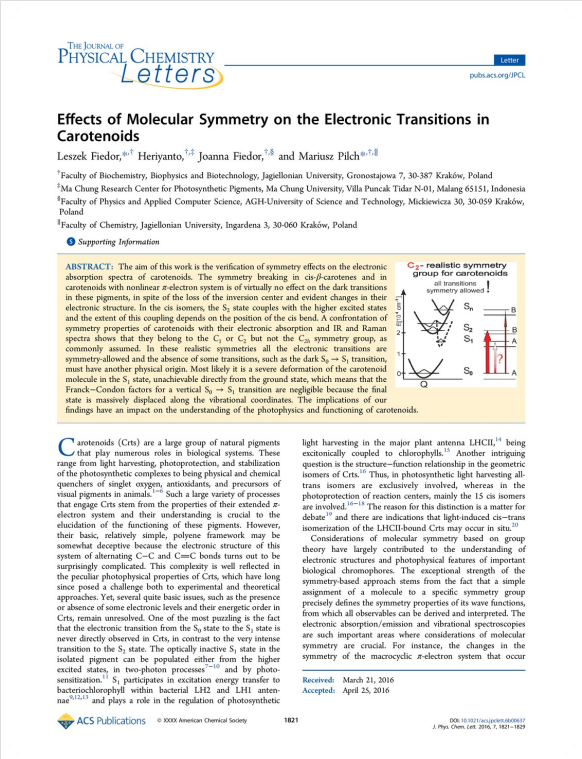

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Effects of Molecular Symmetry on the Electronic Transitions in Carotenoids

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Supporting Information

ABSTRACT: The aim of this work is the verification of symmetry effects on the electronic absorption spectra of carotenoids. The symmetry breaking in cis-β-carotenes and in carotenoids with nonlinear π-electron system is of virtually no effect on the dark transitions in these pigments, in spite of the loss of the inversion center and evident changes in their electronic structure. In the cis isomers, the S_2 state couples with the higher excited states and the extent of this coupling depends on the position of the cis bend. A confrontation of symmetry properties of carotenoids with their electronic absorption and IR and Raman spectra shows that they belong to the C_1 or C_2 but not the C_{2h} symmetry group, as commonly assumed. In these realistic symmetries all the electronic transitions are symmetry-allowed and the absence of some transitions, such as the dark $S_0 \rightarrow S_1$ transition, must have another physical origin. Most likely it is a severe deformation of the carotenoid molecule in the S_1 state, unachievable directly from the ground state, which means that the Franck−Condon factors for a vertical $S_0 \rightarrow S_1$ transition are negligible because the final state is massively displaced along the vibrational coordinates. The implications of our findings have an impact on the understanding of the photophysics and functioning of carotenoids.

Carotenoids (Crts) are a large group of natural pigments that play numerous roles in biological systems. These range from light harvesting, photoprotection, and stabilization of the photosynthetic complexes to being physical and chemical quenchers of singlet oxygen, antioxidants, and precursors of visual pigments in animals.[1−6] Such a large variety of processes that engage Crts stem from the properties of their extended π-electron system and their understanding is crucial to the elucidation of the functioning of these pigments. However, their basic, relatively simple, polyene framework may be somewhat deceptive because the electronic structure of this system of alternating C−C and C=C bonds turns out to be surprisingly complicated. This complexity is well reflected in the peculiar photophysical properties of Crts, which have long since posed a challenge both to experimental and theoretical approaches. Yet, several quite basic issues, such as the presence or absence of some electronic levels and their energetic order in Crts, remain unresolved. One of the most puzzling is the fact that the electronic transition from the S_0 state to the S_1 state is never directly observed in Crts, in contrast to the very intense transition to the S_2 state. The optically inactive S_1 state in the isolated pigment can be populated either from the higher excited states, in two-photon processes[7−10] and by photosensitization.[11] S_1 participates in excitation energy transfer to bacteriochlorophyll within bacterial LH2 and LH1 antennae[9,12,13] and plays a role in the regulation of photosynthetic light harvesting in the major plant antenna LHCII,[14] being excitonically coupled to chlorophylls.[15] Another intriguing question is the structure−function relationship in the geometric isomers of Crts.[16] Thus, in photosynthetic light harvesting all-trans isomers are exclusively involved, whereas in the photoprotection of reaction centers, mainly the 15 cis isomers are involved.[16−18] The reason for this distinction is a matter for debate[18] and there are indications that light-induced cis−trans isomerization of the LHCII-bound Crts may occur in situ.[20]

Considerations of molecular symmetry based on group theory have largely contributed to the understanding of electronic structures and photophysical features of important biological chromophores. The exceptional strength of the symmetry-based approach stems from the fact that a simple assignment of a molecule to a specific symmetry group precisely defines the symmetry properties of its wave functions, from which all observables can be derived and interpreted. The electronic absorption/emission and vibrational spectroscopies are such important areas where considerations of molecular symmetry are crucial. For instance, the changes in the symmetry of the macrocyclic π-electron system that occur

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