Absorption-emission symmetry breaking and the different origins of vibrational structures of the ^{1}Qy and ^{1}Qx electronic transitions of pheophytin *a*

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The vibrational structure of the optical absorption and fluorescence spectra of the two lowest-energy singlet electronic states (Qy and Qx) of pheophytin a were carefully studied by combining low-resolution and high-resolution spectroscopy with quantum chemical analysis and spectral modeling. Large asymmetry was revealed between the vibrational structures of the Qy absorption and fluorescence spectra, integrally characterized by the total Huang-Rhys factor and reorganization energy in absorption of SA vib = 0.43 ± 0.06, λA = 395 cm−1 and in emission of SE vib = 0.35 ± 0.06, λE = 317 cm−1. Time-dependent density-functional theory using the CAM-B3LYP, ωB97XD, and MN15 functionals could predict and interpret this asymmetry, with the exception of one vibrational mode per model, which was badly misrepresented in predicted absorption spectra; for CAM-B3LYP and ωB97XD, this mode was a Kekulé-type mode depicting aromaticity. Other computational methods were also considered but performed very poorly. The Qx absorption spectrum is broad and could not be interpreted in terms of a single set of Huang-Rhys factors depicting Franck-Condon allowed absorption, with Herzberg-Teller contributions to the intensity being critical. For it, CAM-B3LYP calculations predict that SA vib (for modes >100 cm−1) = 0.87 and λA = 780 cm−1, with effective x and y polarized Herzberg-Teller reorganization energies of 460 cm−1 and 210 cm−1, respectively, delivering 15% y-polarized intensity. However, no method was found to quantitatively determine the observed y-polarized contribution, with contributions of up to 50% being feasible.

Słowa kluczowe

Time dependent density functional theory, Computational methods, Optical absorption, Absorption spectroscopy, Emission spectroscopy, Fluorescence spectroscopy, High resolution spectroscopy, Chlorophyll, Chemical analysis

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