

Photophysics and photochemistry of indole and indole derivatives: Electronic substitution effect and N-H photodissociation dynamics

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Indole, being the main chromophore of the amino acid tryptophan and several other biologically relevant molecules like serotonin and melatonin, has prompted considerable theoretical and experimental interest. Having three close-lying excited electronic states, the vibronic coupling effect becomes extremely important yet challenging in the photophysics and photochemistry of indole. This work focuses on the investigation of photophysical and photochemical properties of indole and indole derivatives using computational methodologies. The performance of time-dependent density functional theory (TDDFT) have been evaluated in comparison to available experimental and ab initio results. Following the benchmark, the electronic effects of ring substitution in indole have been investigated for tryptophan, serotonin and melatonin. A bathochromic shift has been observed in the absorption spectra of indole to melatonin due to the +R effect of the in-plane smaller adjacent groups in the indole derivatives. The out-of-plane longer substitutions have negligible effect. The calculated vibronic absorption spectra are in good agreement with experiments. The vibrational analysis is performed to identify important modes contributing to the photo-dissociation of indole N-H. One-dimensional excited state potential energy cuts of indole are calculated along the important vibrational modes using TDDFT methods. The vibronic model Hamiltonian is parametrized by the fitting of potential energy functions with the ab initio data. The time scale and mechanism of excited state N-H dissociation are explored using the multi-configuration time-dependent Hartree method. CCNH dihedral angle along with the N-H stretching mode is found to play a key role in the photodissociation of the indole N-H group.

References:

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