

A Semiclassical Glimpse into the Azulene Photophysics and Spectroscopy

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Azulene molecule is a prototype system violating Kasha's rule, *i.e.*, its fluorescence occurs from the second, instead of the first excited singlet state [1]. To study the role of nonadiabatic couplings that cause the unusual fluorescence behavior in azulene, we compute the semiclassical fidelity (*i.e.* adiabaticity) *via* multiple surface dephasing representation method [2] combined with on-the-fly *ab initio* evaluation of the potential. Adiabaticity measures explain the different dynamical behavior of the lowest excited states in azulene. The analysis was compared to the standard measures from nonadiabatic dynamics, such as state population decay. Azulene absorption and emission vibronic spectra cannot be properly described within the standard Condon approximation [3]. To account for important Herzberg-Teller and anharmonicity effects, we employ a single-Hessian [4] version of the on-the-fly *ab initio* extended thawed Gaussian approximation [5], which compares fairly well with the experimental reference.

Overall, two semiclassical approaches provide efficient tools to tackle the photophysics and spectroscopy of challenging molecular systems.

References

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