ELECTRONIC STRUCTURE OF THE FLEXIBLE BICHROMOPHORE DIPHENYLMETHANE

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Fundamental studies of electronic coupling between flexible bichromophores are needed to validate and refine models used for solar energy conversion in conjugated organic semiconductors and models found in many other areas which involve energy transfer or exciton propagation. Diphenylmethane (DPM) is a prototypical flexible bichromophore for which highly accurate spectroscopic data is available.[a] We investigated the splitting between the S_1 and S_2 exciton states of DPM along the C_2 axis with respect to the ring torsional coordinate. We showed that the state crossing occurs at $\tau_1 = \tau_2 = 70^\circ$ torsional angles and explained it qualitatively with orbital analysis. We constructed the relaxed ground state potential energy surface and the S_1 and S_2 excited energy potential energy surfaces of DPM with regards to ring torsional angles using EOM-CCSD/cc-pVDZ and TD-DFT(ωB97X-D)/cc-pVTZ levels of theory. We found that TD-DFT and EOM-CCSD surfaces are qualitatively similar, however, both methods overestimate the experimentally observed $S_1 - S_2$ splitting of $123\,\mathrm{cm}^{-1}$ by four to five times.[b] We also obtained the transition dipole moment surface and investigated the accuracy of the dipole-dipole model in the prediction of the coupling of the exciton states in DPM.

[a] J. A. Stearns, N. R. Pillsbury, K. O. Douglass, C. W. Müller, T. S. Zwier, and D. F. Plusquellic, *J. Chem. Phys.* **129**, 224305, (2008).
[b] N. R. Pillsbury, J. A. Stearns, C. W. Müller, D. F. Plusquellic, and T. S. Zwier, *J. Chem. Phys.* **129**, 114301, (2008).