

Molecular dynamics and electronic properties of pyridinium-iodide charge-transfer complexes in acetonitrile solution

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Abstract: The formation of charge-transfer complexes (CTC) is characterized by the appearance of a new absorption band on the electronic spectra, in organic polar solvents like acetonitrile [1,2]. These type of systems have recently received much interest in a broad variety of fields, for example, organic electronics, nonlinear spectroscopy, medical biochemistry, pharmaceutical industry, etc [3,6].

In this work, we have studied theoretically CTC formed by a pyridinium derivative, the $C_3\text{bis}(4\text{CP})^{2+}$, with anions iodide [7]. We have used density functional theory (DFT) and time dependent density functional theory (TDDFT) to calculate electronic properties and the excitation energies. We have found that functional with long-range corrections (CAM-B3LYP and wB97X-D) are essential for an accurate description of the charge-transfer excitations.

A better description of the complex in acetonitrile solution was obtained using classical molecular dynamics, with a fine-tuned OPLS-AA force field. Using this approach, the classical molecular dynamics was able to reproduce results of a first principle Born-Oppenheimer molecular dynamics. No dissociation were observed, i.e., the complexes were formed by the association of two I^- to the $C_3\text{bis}(4\text{CP})^{2+}$. We also have found that only one iodide, however, participates in the charge transfer process, what explain why a stoichiometry of 1:1 was observed in the experiment. The calculated charge-transfer band are in excellent agreement with experiment.

Key-words: CTC, TDDFT, Molecular Dynamics

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