

CTTS states provide a sensitive spectroscopic probe of local structure around solute

Ronit Sarangi and Anna I. Krylov
Department of Chemistry
University of Southern California

Charge transfer to solvent (CTTS) excitations are precursors to solvated electrons and their theoretical modeling is important to understand the solvation of small anions. We explore the CTTS excitations of aqueous SCN^- ion and their sensitivity to the local structure via classical force-field based and hybrid QM/MM dynamics followed by EOM-EE-CCSD calculations to obtain the electronic spectra. We demonstrate that in the excited state calculations we need more than the first solvation shell solvents in the QM region in order to obtain a converged CTTS spectrum and capture essential chemistry. Radial distribution functions (RDFs) show that the solvation shell of SCN^- in QM/MM dynamics is larger than the one obtained using classical dynamics. This change is reflected in the CTTS spectra as follows: The CTTS type excitations redshift in the QM/MM case and the intramolecular excitations blueshift as compared to spectrum obtained from the classical MD trajectory. Additionally, the spectrum obtained from QM/MM dynamics' snapshots show better agreement with the experimental data compared to the one from classical dynamics data. The observed results stress the importance of CTTS spectrum of aqueous SCN^- as a probe of local structure and vice versa.