CHEMISTRY SEMINAR 291

Modeling Accurate Spectral Shapes of Molecules in Solution: Combining Ensemble and Vibronic Broadening Effects

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ABSTRACT

The correct treatment of vibronic effects is vital for the modeling of absorption spectra of solvated dyes, as many prominent spectral features can often be ascribed to vibronic transitions. Vibronic spectra can be computed within the Franck-Condon approximation for small dyes in solution using an implicit solvent model. However, implicit solvent models neglect specific solute-solvent interactions and temperature-dependent solvent broadening effects can only be accounted for using a phenomenological broadening parameter chosen to match experimental spectra. An alternative way of computing optical spectra is the ensemble approach, where vertical transitions are calculated for an ensemble of representative solute-solvent conformations and averaged over. This approach accounts for temperature-dependent solvent broadening effects through the ensemble averaging, but generally treats the nuclei as classical particles and lacks any vibronic effects. We address these shortcomings by introducing a combined approach, where vertical excitations computed for a room-temperature ensemble of solute-solvent configurations are broadened by a zero-temperature Franck-Condon shape function accounting for the vibronic fine structure of the transition. In this combined approach, all temperature-dependent broadening is therefore treated classically through the sampling of configurations, with vibronic contributions included as a zero-temperature correction to each vertical transition. We test the proposed method on Nile Red and the green fluorescent protein chromophore in polar and non-polar solvents. For systems with strong solute-solvent interaction, the approach yields a significant improvement over the ensemble approach, whereas for systems with weaker interactions, both the shape and the width of the spectra are in excellent agreement with experiment. We also compare the approach to an alternative formulation of the absorption line shape function in terms of the autocorrelation function of the excitation energy, and discuss a number of different strategies to further improve on our combined ensemble plus Franck-Condon approach.

BIO:

Tim Zuehlsdorff obtained his PhD in 2015, working under the supervision of Professor Peter D. Haynes at the Centre for Doctoral Training in Theory and Simulation of Materials at Imperial College London. He then spent two years as a Postdoctoral Research Associate at the Theory of Condensed Matter group at the Cavendish Laboratory of the University of Cambridge, working under the supervision of Professor Mike Payne. In 2016, he joined the Isborn group at UC Merced as a Postdoctoral Scholar. His research focuses on modeling excited states in complex environments, with a special interest in absorption spectra of solvated systems. He also works on linear-scaling approaches to density-functional theory (DFT).