Modeling 2DUV spectra of nucleobases: damped dynamics through conical intersections

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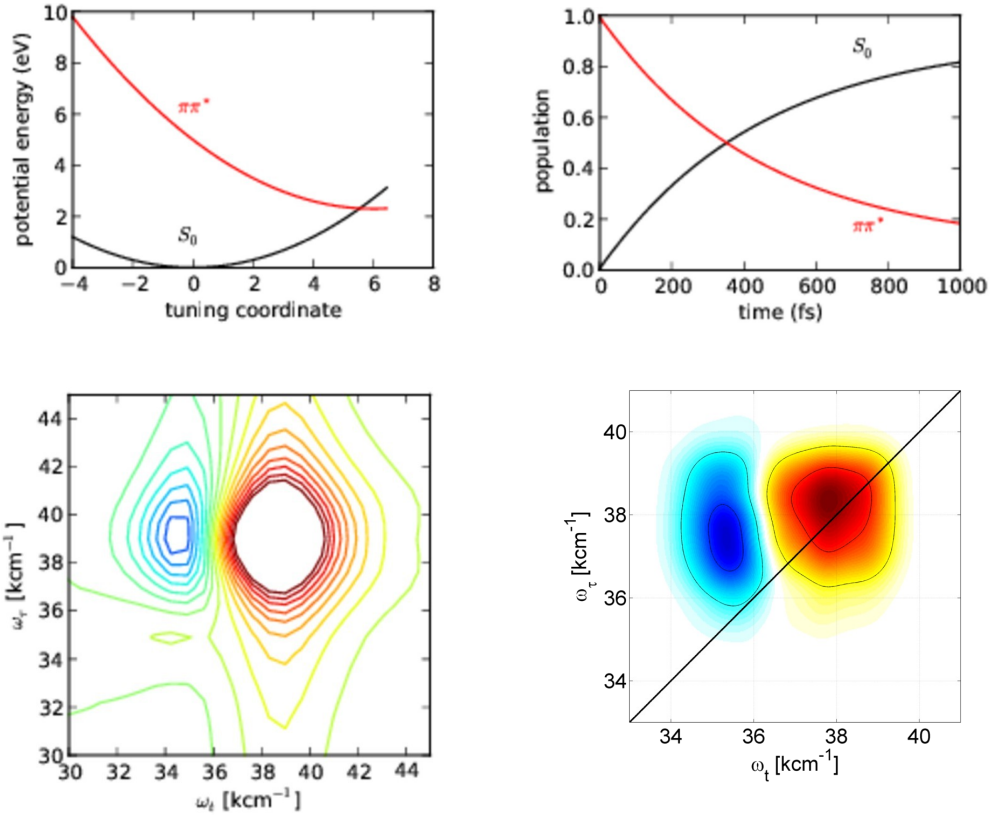
We propose a model of damped dynamics on potential energy surfaces that exhibit conical intersections. The resulting ultrafast populations are compared with experimental 2DUV spectra.

Two-dimensional optical spectroscopy can be used to characterize dynamics on femtosecond time scales, which makes it an ideal tool to study systems with conical intersections, where ultrafast decay can be observed. Such intersections are known to be ubiquitous in molecular systems, and, in particular, are thought to enable nucleobases to return to their ground state quickly, thereby avoiding photodamage.

We present quantum simulations of damped dynamics on systems with conical intersections using the hierarchy of equations of motion approach. We use quantum chemistry simulations and a spectroscopic model based on measured data as input for our simulations and compare the results of our calculations with experiment. Our combined experimental and simulation approach is especially valuable when applied to important biological molecules.



Figures: (top left) potential energy surfaces for the model; (top right) calculated dynamics; (bottom left) calculated 2DUV spectrum; (bottom right) real part of the experimental 2DUV spectrum of adenine in water (waiting time T=500 fs).