SIMULATIONS OF THE FEMTOSECOND PHOTOELECTRON SPECTROSCOPY OF PYRAZINE BASED ON ACCURATE QUANTUM DYNAMICS CALCULATIONS

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Pyrazine is a well established example of a molecular system undergoing ultrafast electronic relaxation after UV excitation due to the existence of a conical intersection between its two lowest excited electronic states, the $B_{3u}(n\pi^*)$ state and the $B_{2u}(\pi\pi^*)$ state. The femtosecond photodynamics of pyrazine has been the subject of numerous experimental and computational investigations, and it is now used as a reference system in the study of ultrafast non-adiabatic molecular processes.

Electronic structure calculations show that a dark electronic state, the $A_{u}(n\pi^*)$ state, lies close to the bright $B_{2u}(\pi\pi^*)$ state in energy. In previous contributions\(^1\), we have proposed that this dark state is involved in the photodynamics of pyrazine. This proposition has been challenged in recent VUV time-resolved photoelectron spectroscopy measurements reported by the group of T. Suzuki\(^2\).

We present simulations of the experiments of the Suzuki group based on accurate quantum dynamics calculations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method. The spectra obtained from two models, one including and one excluding the dark $A_{u}(n\pi^*)$ state, are very similar. Thus our results suggest that the experiment is essentially blind to the $A_{u}(n\pi^*)$ state.
