Molecular photodynamics and its manifestation in UV-Vis and X-ray time-resolved spectra. Insights from quantum chemistry and quantum dynamic

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Time-resolved spectroscopies performed on functional molecules - with UV-Vis pump and probes from all kinds of spectral domains - can bear signatures of multimode nuclear dynamics, nonadiabatic effects and quantum mechanical coherences. Relating these observations to the underlying molecular dynamics is instrumental to the ability of designing and controlling photoactive molecules. This talk illustrates computational strategies which combine quantum chemistry and quantum dynamics to investigate which aspects of the photochemical mechanisms can be unambiguously inferred from time-resolved spectra. Two examples will be shown.

The first one is the prototypical excited state intramolecular proton transfer of 10-hydroxybenzo[h]quinoline. Transient absorption and fluorescence spectroscopies revealed a number of long lived multimode quantum beats due to the ultrafast reaction mechanism [1,2]. The most recent investigations regard these coherences as a signature of a nonadiabatic reaction involving two coupled states [3]. The quantum dynamical simulations of this contribution, based on ab initio potential energy surfaces, show that the dynamics initiated by the S1 ← S0 excitation actually proceed mostly on a single Born-Oppenheimer surface. The observed coherences are generated by mode mixing along the reaction path. The reaction mechanism following the S2 ← S0 excitation is instead nonadiabatic and involves a $n\pi^*$ state which becomes stable at the geometries of the photoproduct.

The second example is the gas-phase photoprotection mechanism of the nucleobase analogue 2-thiouracil (2-TU), which is studied using time-resolved X-ray photoelectron spectroscopy (XPS) at the sulphur 2*p* edge [4]. The relaxation following the S2 ($\pi\pi^*$) ← S0 excitation involves the three lowest singlet and triplet states. The mechanism is disentangled by comparing the time-dependent shift of the XPS signal with the core ionization potential calculated at the coupled-cluster level for the different electronic states. The excited molecules relax from S2 to S1 and T1 on a time scale faster than 100 fs and, a 200 fs relaxation channel to S0 is found, and a coherent electronic population exchange is observed. The quantum chemical data allow us to formulate a potential model [5] to invert the observed changes in the core ionization potential to the partial charge at the probed atom.

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