

Acetylacetone photochemistry: Semi-classical study of UV absorption spectrum and nonadiabatic dynamics

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The simulation of the nonadiabatic dynamics of enolic acetylacetone (AcAc) was carried out, taking into account processes of molecular relaxation and internal conversion, by means of the trajectories surface hopping approach. Full absorption spectrum simulations are performed using the nuclear ensemble approach.

In the present study, the molecule is considered to have a C_s geometry in its ground state. To simulate the absorption spectrum, within the 200-500 nm window, the $S_0 \rightarrow S_1(n \rightarrow \pi^*)$ and $S_0 \rightarrow S_2(\pi \rightarrow \pi^*)$ transitions are taken into account. We generate 300 ground state geometries according to a harmonic-oscillator Wigner distribution. The calculations were carried out with a level of theory TDDFT/B3LYP using 6-311G as base functions. Geometry optimizations, oscillator strengths and energies were calculated using Gaussian and the absorption spectrum using the Newton-X program. The simulated spectrum is compared, in Figure 1, with the experimental absorption spectrum of the AcAc molecule in gas phase¹.

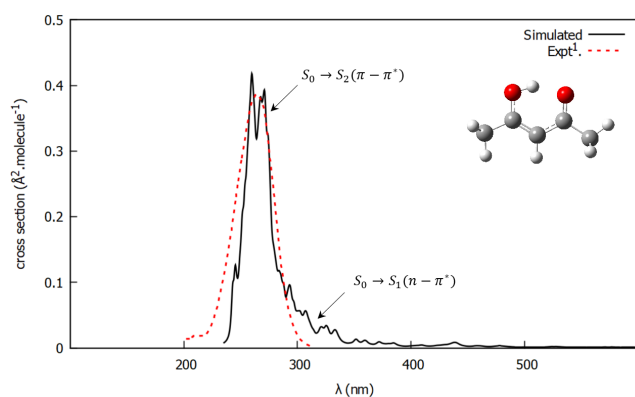


Figure 1: Simulated (TDDFT/B3LYP/6-311G) and experimental absorption cross section of AcAc in gas phase.

In the nonadiabatic dynamics of AcAc, the electronic states S_2 , S_1 and S_0 were included. All trajectories were propagated starting at state S_2 for 200 fs. The calculations of energy, energy gradients and nonadiabatic coupling vectors are performed at the same level of theory as that used for the simulation of the absorption spectrum. The transition probability among different Born-Oppenheimer surfaces is evaluated following the "fewest switches" criterion.

After the excitation of the molecule to the S_2 state, departs from the Franck-Condon region around 75 fs, where its first structural change is given by the transfer of the hydrogen atom from one oxygen to another (Figure 2). Then the AcAc molecule loses planarity as a result of the weakening of the π bond, and the hydrogen atom vibrates out of the initial molecular plane.

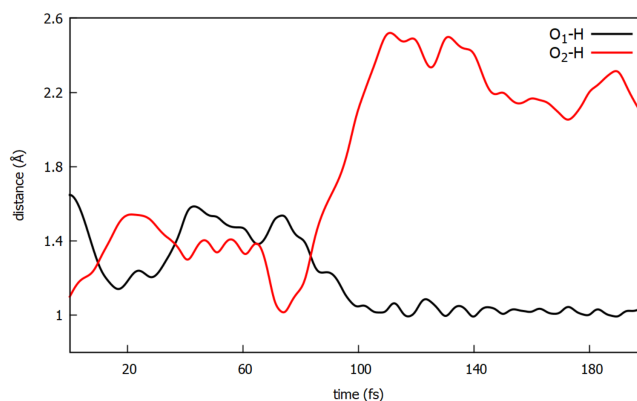


Figure 2: Behavior of O_x-H bond distance in time.

An efficient internal conversion mechanism between the $S_2 \rightarrow S_1$ states is observed around 94.9 fs, after the transition the molecule continues on the S_1 surface until the end of the trajectory, being consistent with the long lifetime of this excited state, approximately 247 ps, observed by Zewail et al².

Index Terms: trajectories surface hopping, nuclear ensemble approach, fewest switches

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