

Initial Process of Proton Transfer in Salicylideneaniline Studied by Time-resolved Photoelectron Spectroscopy

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Proton transfer is a fundamental and important process in biological systems. To understand this process in complicated biological activities, one fruitful approach is the investigation of simpler molecular systems to gain insight into the proton transfer dynamics. Salicylideneaniline (SA), shown in Fig. 1, is one of the most attractive molecules and was investigated extensively so far [1]. The basic understanding of excited state proton transfer in SA is as follows: In the ground state, the enol form is more stable than the keto form, while in excited states, the proton-transferred keto form is preferred. Thus, the proton of the hydroxy group migrates on a fs-timescale upon photoexcitation. From there, *cis-trans* isomerization takes place by passing a conical intersection with the ground state and produces a photochromic product: the *trans*-keto form.

However, advances of experimental and theoretical investigations have revealed that the relaxation process is more complicated; SA has many vibrational and pseudo-rotational modes which govern additional relaxation pathways. To gain insight into the intrinsic nature of proton transfer dynamics, it is useful to investigate non-interacting molecules. Time-resolved photoelectron spectroscopy (TRPES) of isolated molecules from a supersonic gas jet provides a unique opportunity for such an investigation.

Experimental setup for TRPES was as follows: Ti:sapphire laser pulses were used to pump optical parametric amplifier to generate ~1400-nm pulses, which was doubled twice by nonlinear crystals to generate ~350-nm pulses used for a pump beam. The pump wavelengths were set to 370 and 330 nm. 400-nm pulses by second harmonic generation were used for probe pulses. The excited SA molecules were ionized via two-photon absorption of 400-nm photons. The temporal resolution of the system was 152 fs. Sample molecules were heated at ~333 K in a pulsed gas jet and were expanded into a vacuum chamber as the supersonic molecular beam with helium gas. The ejected photoelectrons were recorded by a magnetic bottle photoelectron spectrometer.

In this work, we found drastic changes in decay dynamics of photo-induced photoelectron signals depending on the excitation energy. Figure 2 shows the time dependent electron count for photoelectrons with kinetic energies between 1.0 and 1.2 eV. When SA was excited by 370-nm photons, a fast decay within ~50 fs was observed prominently. This decay is attributable to the proton transfer process. However, when the pump wavelength was shifted to 330 nm, the decay time was lengthened to 1.1 ps. Similar features were observed in all energy regions between 0.1 and 2 eV.

To elucidate the drastic change in the decay time, the energy levels of SA were calculated at B3LYP/aug-cc-pVDZ level of theory. These calculations predict the following points: i) The ground state of SA is twisted about the anil group by ~35 degrees. However, the molecule can basically rotate freely about this group. ii) On the other hand, in S_1 state, the planar structure is more stable. Here, the energy strongly correlate with the twist angle. iii) Proton transfer predominantly takes place in the planar structure in excited states because of an increasing barrier upon twisting the anil-group. From these predictions, the different decay dynamics can be understood as follows: 370-nm photons exclusively excite the near-planar SA, in which the proton transfer can happen just after excitation. The lifetime of proton transfer is predicted to be less than 50 fs. At 330-nm, all molecules are excited. The increased barrier reduces the rate constant and forces the molecule to planarize before the proton transfer can happen. The observed 1.1-ps relaxation should correspond to the twisting motion. Hence, planarity of is an important parameter for proton transfer SA [2].

[1] T. Sekikawa et al., J. Phys. Chem. A **101**, 644, (1997)

[2] M. Barbatti, et al., Phys.Chem.Chem.Phys **11**, 1406-1415 (2009)

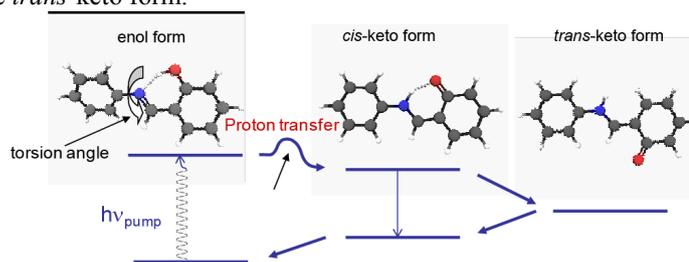


Fig. 1: Schematics of the relaxation processes of photo-excited salicylideneaniline.

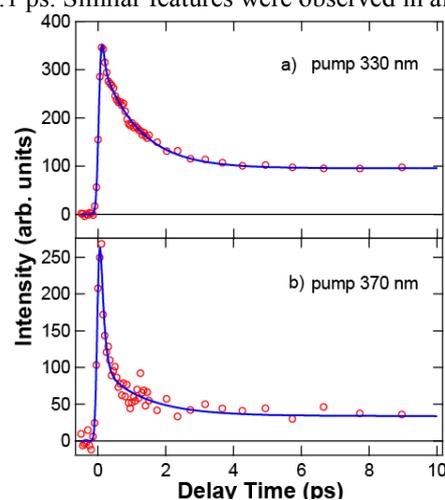


Fig. 2: Decay dynamics of photoelectron signals pumped at a) 330 and b) 370 nm.