COMMUNICATIONS

Dynamics of excited-state proton transfer systems via time-resolved photoelectron spectroscopy

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We investigate the applicability of time-resolved photoelectron spectroscopy to excited state intramolecular proton transfer (ESIPT) and internal conversion dynamics in the model system o-hydroxybenzaldehyde (OHBA) and related compounds. Photoelectron spectra of both the excited state enol and keto tautomers were obtained as a function of pump laser wavelength and pump-probe time delay. The ESIPT was found to occur in less than 50 fs over the whole absorption range of the $S_1(\pi\pi^*)$ state for both OHBA and its monodeuterated analog, suggestive of a small or nonexistent barrier. The subsequent keto internal conversion rate in OHBA varies from 0.63 to 0.17 ps^{-1} over the $S_1(\pi\pi^*)$ absorption band and the OD-deuterated analog shows no significant isotope effect. Based upon *ab initio* calculations and comparison with the two-ring analog, 1-hydroxy-2-acetonaphthone (HAN), we suggest that the internal conversion dynamics in OHBA is influenced by interactions with a close-lying $n\pi^*$ state. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1345876]

Time-resolved photoelectron spectroscopy (TRPES), being sensitive to both nuclear and electronic population dynamics, is well suited to the study of excited state nonadiabatic processes.[1–13] These processes, leading to both structural and charge density rearrangements, can be difficult to study because they usually involve large vibrational state densities and strongly varying transition moments. Here we consider the important nonadiabatic process of excited state intramolecular proton transfer (ESIPT).[14–16] Methyl salicylate (MS) has served as a model system in many studies since fluorescence detection allows for the study of the population dynamics in the excited state tautomers.[17,18] In many systems, however, fluorescence quantum yields can be very small and a more general detection method is needed. Due to the relaxed selection rules for ionization, photoelectron detection is especially suited to the detection of nonfluorescing zeroth-order ''dark'' states. In this communication, we investigate the applicability of TRPES to the study of ESIPT dynamics using the model systems o-hydroxybenzaldehyde (OHBA), its monodeuterated analog OD-o-hydroxybenzaldehyde (ODBA), and the two-ring analog 1-hydroxy-2-acetonaphthone (HAN).

OHBA is the smallest aromatic molecule displaying ESIPT[19] and was subject to numerous investigations. Fluorescence measurements in matrices[20] and in the liquid phase[21–23] helped to identify the nature of the excited states undergoing ESIPT. Theoretical studies predicted a small[24] or nonexistent barrier[25,26] for the proton transfer and suggested similar reaction dynamics for many ESIPT systems. Recent investigations of ESIPT dynamics in HAN used fluorescence spectroscopy[27] and time-resolved ion current measurements.[28]

The experimental scheme is depicted in Fig. 1 (left), showing energetics for the case of OHBA. Excitation with a tunable pump laser $h\nu_{pump}$ forms the enol tautomer in the $S_1(\pi\pi^*)$ state. ESIPT leads to ultrafast population transfer from the S_1 enol to the S_1 keto tautomer. On a longer time scale, the S_1 keto population decays via internal conversion to the ground state. Both the enol and keto excited state populations are probed by ionization with a probe laser $h\nu_{probe}$, producing the two photoelectron bands ε_1 and ε_2. The intensities of these two bands depend on the pump-probe time delay and the pump laser wavelength, yielding information about the excited state dynamics.

The femtosecond laser system and molecular beam magnetic bottle photoelectron spectrometer are discussed in detail elsewhere.[29] A 830 nm Ti:Sapphire pumped optical parametric amplifier with subsequent sum frequency mixing and harmonic generation stages was used to generate tuneable fs pump pulses between 280 and 370 nm. The fourth harmonic of the Ti:Sapphire laser (207.5 nm) was used as fixed probe pulse. The pulse duration of the UV pulses ranged from 90 to 150 fs. One- and two-color photoelectron spectra of NO were used to calibrate the photoelectron energies. The experiments were performed on cold molecular beams of sample molecule seeded in helium. OHBA (Aldrich 98%) and HAN (Aldrich 99%) were used without further purification. ODBA was prepared from OHBA by repeated refluxing with an excess of deuterated water and a 97% conversion to the monodeuterated compound was observed in ^{1}H-NMR (nuclear magnetic resonance) spectra.

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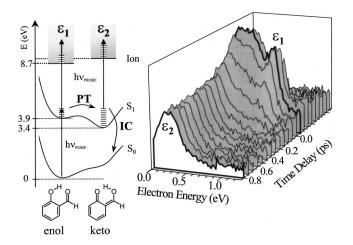
FIG. 1. Experimental scheme (left) for the investigation of excited state dynamics in OHBA. Excitation of OHBA from the enol ground state (S_0) to its first excited state (S_1) triggers an excited state proton transfer reaction (PT), forming the S_1 keto tautomer. The populations in the S_1 enol and S_1 keto tautomers were monitored by photoionization with detection of the corresponding photoelectron signals ε_1 and ε_2. Variation of the time delay between the excitation laser ($h\nu_{pump}$) and the ionization laser ($h\nu_{probe}$) yielded information about the proton transfer dynamics and the subsequent decay of the S_1 keto tautomer due to internal conversion (IC). Experimental photoelectron kinetic energy spectra (right) are plotted as a function of pump-probe delay, shown here for a pump wavelength of 326 nm. Such spectra were recorded as a function of pump laser wavelength. The photoelectron signals ε_1 and ε_2 are separated by about 0.5 eV and easily distinguished.

FIG. 2. Integrated signals ε_1 and ε_2 for OHBA (top), ODBA (middle), and HAN (bottom) plotted as a function of the time delay at the indicated excitation wavelength. Note the change in ordinate time scales. Signal ε_1 always followed the laser cross-correlation (small circles) at positive time delays, indicating a rapid proton transfer reaction. The decay of signal ε_2 was fitted with a mono-exponential decay (solid line), yielding the time constant for internal conversion in the S_1 keto state in each molecule.

In Fig. 1 (right), we present TRPES spectra of OHBA at an excitation wavelength of 326 nm. Two photoelectron bands ε_1 and ε_2 with distinct dynamics were observed. Band ε_1 at 0.5–1 eV electron energy was observed only when the pump and probe laser beams overlapped in time. Band ε_2 at <0.5 eV electron energy displayed a wavelength-dependent lifetime in the picosecond range. Within the time overlap, we expected photoelectrons from ionization of the initially excited Franck–Condon region of the S_1 enol state and, indeed, the vertical ionization potential of 8.9 eV and the band shape of band ε_1 correspond well to the previously reported He(I) photoelectron spectrum.[22] Band ε_1 was thus assigned to the photoionization of the initially populated S_1 enol tautomer of OHBA. At longer delay times, we expected photoionization of the proton transfer product and, as discussed in more detail below, band ε_2 was assigned to the photoionization of the S_1 keto tautomer. Both bands were observed across the whole absorption range of the S_1 state (286–346 nm). At higher excitation energies, the low-energy shoulder of band ε_1 was stronger, reflecting the broader Franck–Condon distribution accessible at these energies.

Ab initio calculations predicted a keto-enol splitting of 0.52 eV (CASPT2) or 0.29 eV (TDDFT) in the S_1 state.[26] For the cation, we calculated degeneracy for the keto and enol states within the accuracy of the methods used (HF and DFT). According to our Franck–Condon calculations, 0–0 transitions dominate the spectrum and the observed keto-enol splitting of the photoelectron bands should therefore be equal to the sum of the keto-enol splittings in the S_1 state and the cation. The calculated splitting agrees well with the mea-
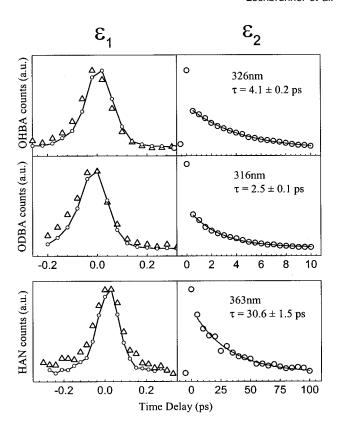
sured splitting of ~0.5 eV between the threshold of band ε_1 and ε_2 and confirms our assignment above.

Spectra of HAN at excitation wavelengths between 355 and 370 nm were qualitatively similar to those observed for OHBA. The corresponding bands ε_1 and ε_2 were assigned to the photoionization of S_1 enol and S_1 keto, respectively. The low-energy shoulder of ε_1 showed distinct and structured peaks, pointing to a deeper minimum in the potential energy surface at the enol geometry and a resulting structured Franck–Condon progression. The measured splitting between the thresholds of band ε_1 and ε_2 was ~0.25 eV. This smaller observed splitting correlates with a smaller calculated keto-enol splitting of 0.03 eV in S_1 (CIS, lower energy for the keto) and of 0.08 eV in the ion (DFT, lower energy for the enol). The similar observations for OHBA and HAN, both of which are known to undergo ESIPT, give us additional confidence in our assignments.

The decay of band ε_1 corresponds to the decay of the S_1 enol population and contains information about the proton transfer dynamics. The left side of Fig. 2 shows the integrated signal ε_1 for all molecules, plotted as a function of the pump-probe delay. Across the whole absorption band of OHBA the time dependence of signal ε_1 towards positive time delays was identical to the laser cross correlation,[30] indicating that ESIPT in OHBA is faster than our time resolu-

tion. Accordingly, we estimated an upper limit of 50 fs for the lifetime of the S_1 enol tautomer.

Proton transfer reactions often proceed via tunnelling of the proton through a barrier.[15,31] Deuteration of the transferred proton should then significantly prolong the lifetime of the S_1 enol tautomer. In experiments with ODBA, we did not observe an isotope effect—i.e., the ESIPT reaction was again complete within the laser cross correlation. We conclude that the barrier in the OH stretch coordinate must be very small or nonexistent. This interpretation is matched by TDDFT *ab initio* calculations,[25,26] which predict no barrier for the proton transfer. Our HF-CIS calculations, which reproduced the reported structures in the absorption and emission spectra,[20] predicted a barrier of 3.5 kcal/mol along the proton transfer coordinate. We estimated the corresponding reaction rate with an instanton calculation, which takes the multi-mode character of the proton transfer into account.[32] The resulting S_1 enol lifetimes were 30 fs for the transfer of a proton and 300 fs for the transfer of a deuteron. It is clear that this large isotope effect is not confirmed by our experiment. Lowering the barrier to 2.4 kcal/mol, however, resulted in an ODBA S_1 enol lifetime of less than 50 fs and this value may be considered as an upper limit for the proton transfer barrier.

In HAN at excitation wavelengths between 355 and 370 nm, the proton transfer was also complete within 50 fs. It must be noted that the origin of the $S_1(\pi\pi^*)$ state is at 410 nm and we probed only an area with considerable excess energy of >2500 cm^{-1}. Vibronic states closer to the S_1 origin are known to have a longer lifetime.[15,28]

The proton transfer time of less than 50 fs presented for OHBA and for higher vibronic levels in HAN is very similar to the proton transfer rates of many related systems, e.g., methyl salicylate,[18] 2-(2′-hydroxyphenyl)benzoxazole[33] and TINUVIN P[34] and may be a common time scale for direct ESIPT processes. The observation of signal oscillations by transient absorption experiments on 2-(2′-hydroxyphenyl)benzothiazole show that the ESIPT is mediated by deformations of the whole chelate ring,[35] in agreement with theoretical work.[25,26,36] This indicates that the common time scale of ESIPT processes may be given by the inertia of the involved ring modes and not by a transition rate over a barrier along the OH coordinate.

The decay of band ε_2 (Fig. 2, right) corresponds to the depletion of the S_1 keto population due to internal conversion to the ground state. We note that photochemical decay channels are not energetically accessible at our pump photon energies. Furthermore, intersystem crossing to triplet states has never been observed in the gas phase or in nonpolar solvents.[31] We observed mono-exponential decay for the ε_2 band in all spectra. The wavelength-dependent internal conversion rates in OHBA and ODBA are shown in Fig. 3, revealing no significant isotope effect. The wavelength dependence of the measured rates for OHBA correlated well with that estimated by comparing fluorescence quantum yields[22,23] to the integrated absorption coefficients for the S_1 keto state. The measured internal conversion rates are very fast, considering the large energy gap of 3.2 eV between ground and excited state. Sobolewski *et al.* suggested the
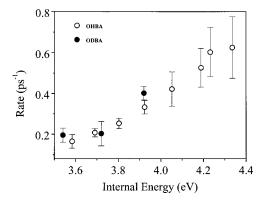

FIG. 3. Internal conversion rates of the S_1 keto state of OHBA (open circles) and ODBA (full circles) determined with single exponential fits to the ε_2 band decay, as shown in Fig. 2 (right). Both show a monotonic increase in rate as a function of the excitation energy. No significant isotope effect was observed.

existence of a rate-determining barrier followed by an efficient conical intersection involving an OH bending mode.[26,36] The observed absence of an isotope effect in ODBA does not support this mechanism, but a conical intersection might be present along other modes, which do not involve vibrational motion of the active hydrogen atom. The energy dependence of the internal conversion rate could also be explained by Franck–Condon factors for the nonadiabatic coupling between the adiabatic keto S_0 and S_1 states.[37] The absence of an isotope effect in ODBA then implies that the OH mode does not act as accepting mode and it can be assumed that the internal conversion is mediated by skeletal modes. However, as discussed below, interactions with a nearby $n\pi^*$ state may also play a role in the keto internal conversion.

For HAN, we found an internal conversion rate of ~0.03 ps^{-1}, which is an order of magnitude slower than that for OHBA. The calculated energy gap between the ground state and the S_1 keto tautomer in HAN (2.9 eV) is smaller than that in OHBA (3.2 eV), whereas the density of states is considerably larger. According to the golden rule expression, both factors should lead to an increased internal conversion rate. The observation of a slower rate for HAN indicates that some other effect must be present. A major difference between the two molecules is the position of a $n\pi^*$ state, which is almost isoenergetic with the investigated $S_1(\pi\pi^*)$ state in OHBA[25,38] but more than 0.5 eV higher in HAN.[38] A possible influence of this $n\pi^*$ state on the excited state dynamics was discussed in previous theoretical[25] and experimental papers.[23] The coupling of the $\pi\pi^*$ and $n\pi^*$ states, mediated by out-of-plane vibrations, might increase the rate of internal conversion in OHBA. Similar effects were shown to mediate the rates of nonradiative processes in several aromatic ring systems.[39] The local mode character of the OH out-of-plane bending vibration makes this mode inefficient for the coupling of the $n\pi^*$ and $\pi\pi^*$ states. As a result, the bending modes of the aromatic ring dominate this interaction, which explains the absence of an isotope effect.

In conclusion, we have investigated ESIPT in simple model systems using femtosecond TRPES. The method reveals dynamics in both the excited state enol and keto tau-

tomers via their photoelectron spectra. The ultrafast character of the OHBA proton transfer reaction and the lack of a significant isotope effect points to an almost barrierless reaction coordinate in the gas phase. The dynamics of the keto state formed by ESIPT is dominated by internal conversion to the keto ground state. We found markedly different internal conversion dynamics for OHBA and HAN, which we interpret as evidence for the involvement of a close-lying $n\pi^*$ state in OHBA.

The ability to observe and assign all involved species, including nonfluorescing ''dark'' states such as the excited state enol tautomers, shows the strength of our experimental approach. In the near future, we plan to investigate other chemically relevant processes such as excited state intra- and intermolecular electron transfer reactions.

ACKNOWLEDGMENTS

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