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Proton Translocation and Electronic Relaxation along a Hydrogen-Bonded Molecular Wire in a 6-Hydroxyquinoline/Acetic Acid Complex

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A hydrogen-bonded network formed between 6-hydroxyquinoline (6-HQ) and acetic acid (AcOH) has been characterized using a time-resolved fluorescence technique. In the bridged hydrogen-bonded complex of *cis*-6-HQ and AcOH, an excited-state reaction proceeds via proton transfer along the hydrogen bond, resulting in a keto-tautomer (within ∼200 ps) that exhibits large Stokes-shifted fluorescence. The unbridged complex also undergoes excited-state proton transfer, but the Stokes shift is rather smaller.

Introduction

The proton-transfer/hydrogen-atom transfer reaction has an important role in a variety of chemical and biological processes,[1] e.g., key steps in induced mutation. Proton relay has been identified in proteins such as the photosynthetic reaction center and bacteriorhodopsin.[1,2] In fact, direct probing of proton-transfer dynamics at molecular levels is challenging because of the short time scale and complexity of processes involving the H-bond network rearrangement and other fluctuations. Of course, progress has been made with the advancement in ultrafast laser spectroscopy.[1,2]

It is known that the O−H and −N− functional groups of hydroxyquinolines are efficient in the release/uptake of proton to/from solvent, respectively, following absorption of light.[3] In addition, molecules like 7-hydroxyquinoline (7-HQ) also form hydrogen-bonded complexes with the guest molecules and the intermolecular proton-transfer reaction proceeds in the excited state.[4a] In special solvents, e.g., glycerol and ethylene glycol, and in polymers, e.g., poly(2-hydroxyethyl methacrylate) and poly(vinyl alcohol), the proton-transfer reaction takes place through the H-bonded network.[4b,c] It is also to be noted that in the 7-HQ:AcOH single-H-bonded complex, in which the hydroxyl proton of 7-HQ and carbonyl oxygen of AcOH are separated from each other by ∼0.386 nm,[5] a double proton transfer could be favored following rotational diffusion dynamics.

In another molecule of this family 3-hydroxyisoquinoline (3-HIQ), conjugated double-hydrogen-bonded complexes are formed with a single AcOH molecule, and subsequently, double proton transfer takes place in the excited state. However, this reaction requires a small displacement in the H atom and/or molecular skeleton.[5] This cooperative proton-transfer reaction may proceed either successively or simultaneously. The catalytic role of complexation in proton translocation has also been predicted theoretically in this case.[6a]

Cooperative hydrogen/proton-transfer reactions from both a theoretical and an experimental point of view have been the subject of intensive investigation in the past.[5,6] In AcOH and methanol H-bonded bridge, an exchange occurs via concerted transfer of two protons.[6a] The role of the cooperative proton-

transfer mechanism has also been proposed for similar molecules, e.g., carboxylic acid dimers [6a–d] and 7-azaindole.[6f,g]

Recently, Tanner et al.[7] suggested that hydrogen-bonded ammonia wires facilitate tautomer emission in *cis*-7-HQ. However, the distance between two functional groups of 7-HQ is ∼0.475 nm,[5] in contrast to 6-hydroxyquinoline (6-HQ) where the two functional groups are separated by ∼1.0 nm.[3c] Therefore, a longer and/or an efficient H-bonded chain should be a primary requisite for the proton relay in the case of 6-HQ. Tautomeric emission was not observed from 6-HQ when dissolved in methanol, but water was found to act as a catalyst in alcoholic solvent to form a H-bond network between two functional groups of 6-HQ for the proton relay.[3d,8a] We also investigated complexation of 6-HQ with the strong proton-acceptor trimethylamine, and it was found that H-bonded ion pairs are strongly favored following photoexcitation in nonpolar solvents which subsequently get dissociated.[8a] Stark spectroscopy revealed that 6-HQ can probe the local environment of the medium.[8c] In a recent article based on steady-state spectral measurements for 6-HQ in nonpolar solvents in the presence of AcOH guest molecules we tentatively suggested the role of a hydrogen-bridge wire on the excited-state intermolecular proton-transfer (ESIPT) mechanism.[8b] However, to demonstrate the role of the excited-state proton-transfer reaction effectively, probing the excited-state population by the time-resolved technique is necessary. Here, we report time-resolved measurements on the H-bonded complexes of 6-HQ and AcOH, which interestingly appear to support our earlier hypothesis. We show that the ground-state H-bonded complex of 6-HQ and AcOH undergoes excited-state proton translocations from the O−H group to the quinolinic −N− site along the H-bonded molecular wire and the proton relay gets completed in ∼200 ps.

Experimental Section

6-HQ was purified by recrystallization from ethanol. All solvents were of spectroscopic grade and used without further purification. AcOH, sulfuric acid (Merck Inc.), and KOH (Aldrich) were used without further purification. Decay time measurements were done by the time-correlated single-photon counting technique combined with a diode-pumped Ti−sapphire laser (Spectra Physics, Tsunami, pulse width of 80 fs and repetition rate of 80 MHz). The third harmonics (THG) of the laser light, whose pulse width was ∼200 fs, was used to excite

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the sample. The repetition rate was reduced to 3 MHz with a pulse picker. The concentration of 6-HQ was around 10^{-4} M, and the sample was kept in a quartz cell of 1 cm path length. Emission was detected by a microchannel-plate photomultiplier (Hamamatsu, R3809U-52). Emission decay profiles were obtained with a multichannel pulse height analyzer. The time resolution of the setup was found to be around 10 ps. Measurements were carried out for varying concentrations of AcOH. Data were stored and analyzed with a deconvolution method.

Results and Discussion

The absorption spectrum of 6-HQ in benzene shows a band maximum at around 331 nm.[8b] Formation of complexes with AcOH was observed in the ground state with a broad absorption band and long extended tail. In addition to the normal fluorescence emission (340−400 nm), two new emission bands with 6400 and 13 200 cm^{-1} Stokes shifts were observed for 6-HQ:AcOH. Fluorescence−excitation spectra for these emission bands correlate with the absorption bands, confirming complexation between 6-HQ and AcOH in the ground state. Association constants were also examined for complexation of 6-HQ with one or more AcOH molecules, and the results indicate the presence of 1:1 and 1:2 complexes.[8b]

Time-resolved emission spectra of 10^{-4} M 6-HQ in benzene at a concentration of 0.078 M AcOH are recorded in the 330−650 nm wavelength region with 310 nm excitation (Figure 1). In the initial 0.0−61 ps time scale, a broad emission spectrum in the region of 340−500 nm appears (Figure 1a). As time increases from 61 to 183 ps (Figure 1b) a second emission band at around 416 nm appears with a long tail extending up to 650 nm, which is well resolved and becomes stronger together with the appearance of a third emission band at 576 nm in the next time scale (Figure 1c). In the 335−640 ps time duration, the intensity of the normal band decreases significantly and the 416 nm band became predominant (Figure 1d). In the 0.64−1.25 ns time scale, the intensities of the 416 and 576 nm bands are nearly equal (Figure 1e). Further, in the 1.25−2.78 ns time scale, the intensity of the 416 nm band diminishes substantially and the 576 nm band become predominant (Figure 1f). Finally, during the 2.78−4.30 ns time frame, although the intensity of all three bands decreases, it is interesting to see that the 416 nm band is virtually diminished (Figure 1g). As discussed earlier,[8b] the large Stokes-shifted band arises due to proton relay through the hydrogen-bonded network and the 416 nm band arises from single proton transfer. It is clear that at short times only normal fluorescence is present because of its short decay time, whereas at long times the tautomer is dominant probably because it is formed from the normal emission and has a longer decay time. The intermediate emission around 416 nm is dominant in the middle range. As at long times (Figure 1g) only normal and tautomer emission are present, it indicates that the tautomer at 576 nm and the species emitting at 416 nm are produced from two different routes from the normal molecule and the reaction may not be proceeding in a stepwise manner.

We also recorded decay data for the 6-HQ and AcOH system for 310 nm excitation and probed at different emission wavelengths as well as for various concentrations of AcOH. The fluorescence decay profiles of 6-HQ fit with biexponential function, i.e., $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the lifetimes and A_1 and A_2 are the pre-exponential factors. At the normal fluorescence (360 nm, in the absence of AcOH) the observed decay times are 110 ps (0.936) and 0.59 ns (0.064), where pre-exponential factors are given in parentheses. The
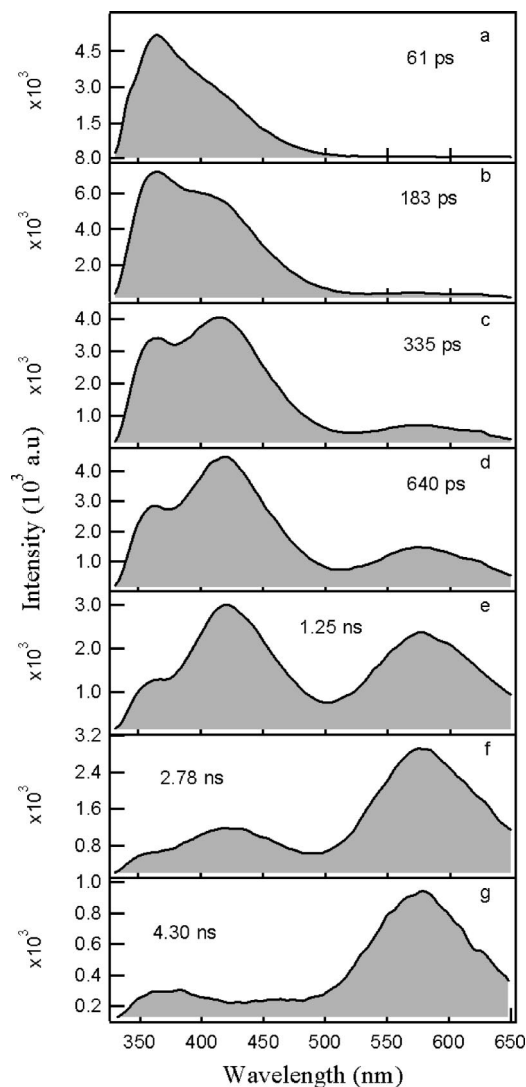

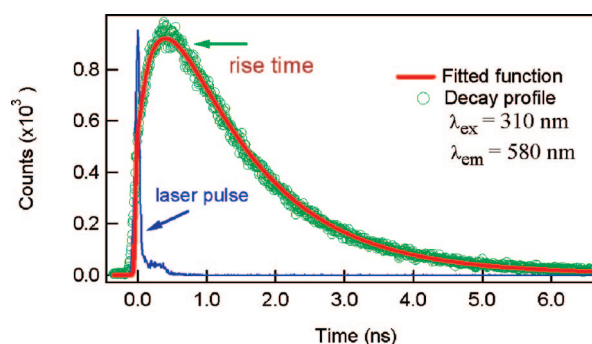**Figure 1.** Time-resolved emission spectra of 6-HQ at 0.078 M AcOH; $\lambda_{ex} = 310$ nm.

Figure 2. Fitted decay profile of 6-HQ in the presence of 0.078 M AcOH; $\lambda_{ex} = 310$ nm and $\lambda_{em} = 580$ nm.

biexponential decay may be due to the presence of two different configurations, namely, the cis and trans forms of 6-HQ. In the presence of 0.012 M AcOH, again the decay at 360 nm exhibits two components, however with shortened decay times. Both decay times are further shortened with increasing concentration of AcOH. In the presence of 0.078 M AcOH, the decay times are 75 ps (0.918) and 0.36 ns (0.082). One can also expect a biexponential decay when there is a back reaction. However, backward proton transfer from the tautomer to the normal configuration may not be energetically feasible because of the
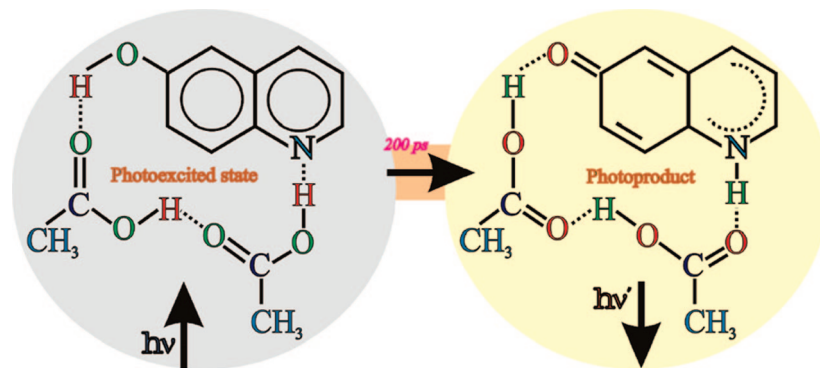
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Figure 3. Photoinduced excited-state proton relay along the O—H···AcOH···AcOH···N wire.

large difference in the excited singlet states of the two forms (emission energies have quite a big difference). Conversion of the molecule from the S_1 state of the keto-tautomer to the ground state of the normal form is expected to be less feasible as it requires both energetic as well as conformational changes simultaneously. At the longer emission wavelength (580 nm, in the presence of 0.078 M AcOH) the decay profile shows a rise time of about 200 ps (−0.386) and decay time of about 1.4 ns (0.614). A typically fitted decay profile probed at an emission wavelength of 580 nm is shown in Figure 2. The observed rise component for the longer emission wavelength is clear evidence for a subnanosecond excited-state proton-transfer reaction in the 6-HQ:AcOH system. On the other hand, at the intermediate emission band (416 nm) the decay profiles fit with the biexponential decay in the range of ~100−150 and ~500−550 ps. The absence of rise time for the 416 nm emission can be attributed to a faster rise (a faster proton-transfer process) as compared to our time resolution.

Nevertheless, these results demonstrate that 6-HQ may form two types of hydrogen-bonded complexes with AcOH in a bridged and an unbridged manner in the ground state. Unbridged complex can be formed with a single H-bond of 6-HQ(−N−): AcOH(−OH) and/or 6-HQ(−OH):AcOH(C=O), which produces the 416 nm fluorescence emission as a result of single proton transfer following photoexcitation. Here, we would like to point out that the emission from the cationic (observed at pH ≈ 1) and anionic (observed at pH ≈ 14) forms of 6-HQ also appears around 442 and 484 nm, but the decay time for the cationic form of 6-HQ is 23.4 ns and for the anionic form is 5.3 ns. In the present case, the decay components are shorter as compared to the decay times of the cationic and ionic forms of 6-HQ, which rules out the presence of ionic species formed due to trace amount of impurity (if any).

In another (1:2) complex, $(AcOH)_2$ molecules may get involved in formation of a bridged hydrogen-bonded molecular wire with the functional groups of *cis*-6-HQ only. When this complex is excited, charge redistribution initiates the acid−base reaction in the electronic excited state via coupled electron−proton transfer and produces a photoproduct, i.e., keto-tautomer, within 200 ps (Figure 3). The proton-transfer reaction takes place in a unidirectional fashion from the O—H to quinolinic −N− site of *cis*-6-HQ along the O—H···AcOH···AcOH···N wire, and the resulting tautomer has a decay time of ~1.4 ns (Figures 3 and 4).

In short, time-resolved fluorescence spectroscopy was employed to probe the excited-state properties of the proton relay in 6-HQ:AcOH complexes. Intermolecular H-bonding interactions and formation of a bridged H-bonded complex result in proton translocations, which is in agreement with our earlier
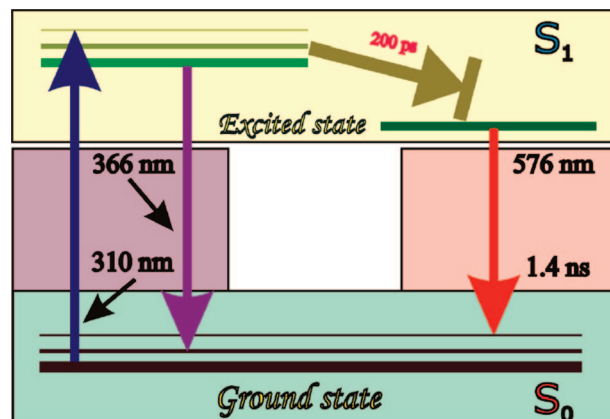

Figure 4. Transition energy route between the S_0 and S_1 states of the 6-HQ:AcOH system.

proposed hypothesis.[8b] Another important aspect of the present study is observation of a proton relay in the 6-HQ:AcOH wire which is completed in ~200 ps. We feel that the observed trends and proposed reaction mechanism related to proton transfer along the H-bonded molecular wire may have far fetched implications in biological systems as well as in molecular electronics.

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