

Time-resolved Anisotropy Study on the Excited-State Intramolecular Proton Transfer of 1-Hydroxyanthraquinone

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The photodynamics of excited-state intramolecular proton transfer reaction of 1-hydroxyanthraquinone (1-HAQ) and 1-deuterioanthraquinone was investigated in toluene with time-resolved emission and femtosecond transient transmittance techniques at room temperature. The temporal profiles of transient transmittance of 1-HAQ could be well described with multi-decaying time constants. The ultrafast time constant within *ca.* 260 fs reflects the dynamics of proton transfer. The decay component of 2 ps is assigned to an additional proton translocation process induced by the intramolecular vibrational relaxation, whereas the decay component of 18 ps is assigned to the vibrational cooling process, while the long component (200 ps) can be explained in terms of the relaxation from excited-state *keto*-tautomer to its ground state. Time-resolved anisotropy decay dynamics and isotope effects on the photodynamics reveals that the ESIPT from *enol*-tautomer to *keto*-one of 1-HAQ is barrierless reaction and coupled to a vibrational relaxation process.

Key Words: 1-Hydroxyanthraquinone. Excited-state intramolecular proton transfer. Anisotropy. Time-resolved transient absorption spectroscopy

Introduction

Anthraquinone derivatives have been considered as the chemically important molecules due to their structural similarity to both quinone antitumor drug¹ and anthraquinoid vat dyes.² Extensive works have been carried out on their photodynamics in order to elucidate the intramolecular proton transfer, which results in a weak normal fluorescence together with a red-shifted emission.³ The red-shifted emission was attributed to the formation of a *keto*-tautomer from an *enol*-tautomer, through the excited-state intramolecular proton transfer (ESIPT).^{4,5} Such a peculiar property was also reported for 1,5-dihydroxyanthraquinone (1,5-DHAQ)^{3,5-8} and 1,8-dihydroxyanthraquinone (1,8-DHAQ).⁸⁻¹²

With the advent of the ultrafast laser spectroscopic technique, the ultrafast photodynamics of many ESIPT molecules in various solvents have been reported from a number of laboratories.¹³⁻¹⁸ In this study, *enol-keto* tautomerization reactions have been focused at femtosecond up to picosecond time scales. The ESIPT process is known to occur within a time scale of several hundreds of femtoseconds. In case of hydroxyanthraquinone derivatives, Arzhantsev *et al.* have reported the time shorter than 50 fs for the ESIPT process for 1,8-DHAQ.¹⁸ In addition to the proton transfer time of the order of a few hundred femtoseconds, some different time constants are frequently reported such as several picoseconds and a few ten picoseconds.¹⁶⁻¹⁹ These are attributed to an intramolecular vibrational redistribution and a vibrational cooling process, respectively. The vibrational redistribution process is

considered to take place in subpicosecond to a few picosecond time scales.²⁰ Meanwhile, the vibrational cooling process proceeds with a time constant of 10-20 ps.²¹ Since the electronic part of the molecular wave function varies significantly during the ESIPT reaction, it is conceivable that the proton transfer reactions give rise to the temporal components in the anisotropy.^{17,22,23} The temporal dependence of anisotropy could be involved in the changes in the electronic transition dipole moment associated with the vibrational relaxation process as well as the rotational diffusion.

In this work, the ESIPT reaction of 1-hydroxyanthraquinone (1-HAQ) and 1-deuterioanthraquinone (1-DAQ) was investigated in toluene by the time-resolved spontaneous emission and transient transmittance techniques. Their temporal profiles and anisotropy decays were described with a multi-exponential function. The observations such as the ultrafast spectral red shifts and absence of prominent isotope effects in the ultrafast decay component could be explained in terms of ESIPT reaction dynamics without any observable reaction barrier.

Experiment Section

1-HAQ was purchased from Aldrich Chemical Co. and further purified by several times of recrystallization. Toluene was received from Merck Co., and further dried carefully as described in a literature²⁴ just before doing experiment. 1-DAQ was obtained by a repeated isotope-exchange reaction in D₂O, which was purchased from Aldrich Chemical Co. (99.96% isotopic purity). 1-DAQ could be identified with an infrared spectroscopy by recording the increase of C-O-D bending mode intensity at 975 cm⁻¹, which is accompanied

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by the decrease in C-O-H bending mode intensity at 1226 cm^{-1} under moisture free condition. The emission lifetime of 690 ps for 1-DAQ in dried toluene further supports the above identifying procedure (see the following).

Time-correlated single photon counting (TCSPC) technique is used for the picosecond time-resolved fluorescence experiment. The excitation source was a picosecond dye laser synchronously pumped by a mode-locked Nd:YAG laser as described in the previous paper.²⁵ The cavity dumped laser output has the pulse width of 2 ps, the average power of *ca.* 30 mW at 24 MHz cavity-dumping rate, and the tunability of 560-620 nm. The dye laser pulse was frequency-doubled by β -BBO crystal and used for an excitation source. Standard electronics from EG&G Ortec were used for TCSPC. The instrument response function was determined by measuring the scattered laser light from a quartz crystal, and typically found to be 40 ps in full-width at half maximum (FWHM). This method gives a time resolution of about 30 ps after deconvolution procedure.

Detailed description of a femtosecond transient absorption set-up employed in this work was given elsewhere.²⁶ Briefly, the excitation pulse at 405 nm was generated by second harmonic generation (SHG) of an amplified Ti:sapphire laser output (810 nm, 120 fs at 1 kHz). The transmittance changes of the sample solution in 1 mm path length cell upon photoexcitation at 405 nm was probed by a delayed femtosecond white light continuum pulses generated in water, and was recorded by a spectrograph equipped with a photodiode detector. The group delay dispersion in the white-light continuum was compensated by synchronously moving the optical delay for a photoexcitation beam to predetermined position at each probe wavelength. We have determined the time-resolution of the current transient transmittance set-up by measuring the instantaneous optical-Kerr signal from water in 1 mm path length cell. This method allows us to know that the traces of the signal exhibit the FWHM of 250 fs in the range of the probe wavelength from 430 to 750 nm. In an anisotropy measurement, ΔT_{\parallel} and ΔT_{\perp} have been recorded simultaneously to give the anisotropy,

$$r(t) = (\Delta T_{\parallel} - \Delta T_{\perp}) / (\Delta T_{\parallel} + 2\Delta T_{\perp}) \quad (1)$$

where ΔT_{\parallel} and ΔT_{\perp} represent the transmittance changes when the configuration of the pump and probe pulses polarization is mutually parallel or perpendicular, respectively. A population decay dynamics was measured at the magic angle of 54.7 degree between pump and probe.

Results

The absorption and fluorescence spectra of 1-HAQ and 1-DAQ dissolved in toluene are shown in Figure 1. The absorption and emission band maxima of 1-HAQ are found to be at 408 and 590 nm, respectively, which are consistent with the previously reported values.²⁷ The observed Stokes shift of $\sim 7600 \text{ cm}^{-1}$ suggests that the structural geometry of the emissive excited-state is significantly displaced from that of the ground state. An apparent additional emission band at

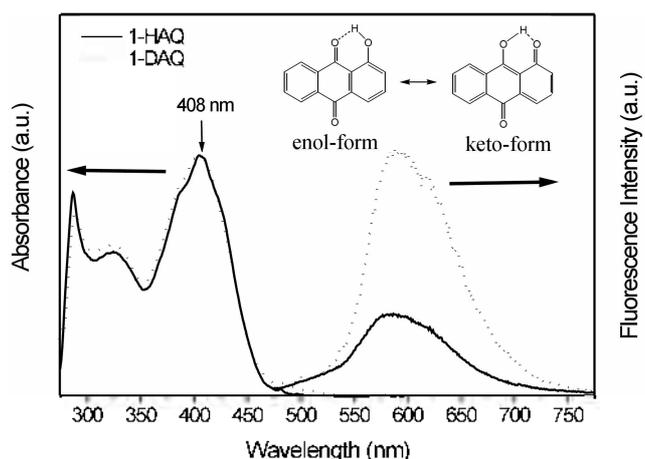


Figure 1. Absorption and emission spectra of 1-HAQ (solid lines) and 1-DAQ (dashed lines) in toluene at room temperature. The excitation wavelength for the emission spectra was set to be 408 nm, which is the absorption maximum of the two anthraquinone derivatives. The emission spectra were observed under the same experimental conditions such as optical densities, excitation wavelength and detection sensitivity for the two anthraquinone derivatives.

500 nm can be found by careful inspection of the emission spectrum. Based on the previous work on hydroxyanthraquinone derivatives,⁵ it is reasonable to assume that the emission bands at 500 and 590 nm could be attributed to *enol*- and *keto*-tautomer emission, respectively. The absorption and emission spectral features of 1-DAQ are almost the same as those of 1-HAQ in toluene. By controlling the photoexcitation condition, detection sensitivity, and optical density of the solution, the relative emission yield of 1-DAQ was found to be 3.4 times larger than that of 1-HAQ in toluene.

The decay profiles of the two different emissions at 460 and 630 nm were obtained for both 1-HAQ and 1-DAQ in toluene (Figure 2). The probe wavelengths were selected to minimize any possible overlap between the two emission bands. One measured at 460 nm is mainly responsible for the emission decay profile of *enol*-tautomer and other measured at 630 nm is for that of *keto*-tautomer. The temporal profiles of *enol*-tautomer for both 1-HAQ and 1-DAQ were very similar to each other. The decay profiles of *enol*-tautomer in the early delay time look like the instrumental response function of the current TCSPC system. These results led us to conclude that the fluorescence lifetimes of *enol*-tautomer are shorter than 30 ps, which is consistent with the low fluorescence quantum yield of *enol*-tautomer. It should be noted that within the current time resolution the decay kinetics of the *enol*-tautomer does not exhibit any apparent isotope effects. Meanwhile, the emission decay profiles measured at 630 nm, which was mainly attributed to *keto*-tautomer emission, exhibit a prominent isotope effects as shown in Figure 2. This decay profiles could be well fitted with a single exponential function, of which lifetimes were determined to be 200 and 690 ps for 1-HAQ and 1-DAQ, respectively. The lifetime of 200 ps for 1-HAQ is in good agreement with the previously

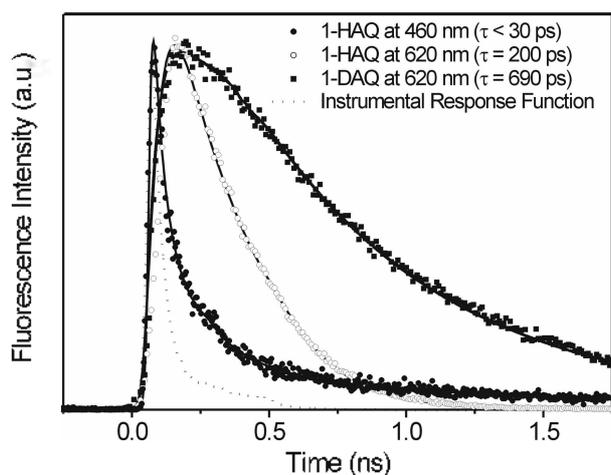


Figure 2. Temporal profiles of spontaneous emission at the probe wavelengths of 460 (solid circles) and 620 nm (open circles) with the concentration of 1×10^{-5} M of 1-HAQ in toluene solution. Solid rectangular represents the observation from 1-DAQ at 620 nm. The best-fitted results with an instrumental response function (dotted lines) are shown with the solid lines in each profile. It should be noted that the temporal profile observed from 1-DAQ at 460 nm is identical to that from 1-HAQ at the same emission wavelength. The instrumental response function is only responsible for the temporal profiles of *enol*-forms

reported values of 190 ps.²⁷ The lifetime of 1-DAQ was found to be 3.4 times longer than that of 1-HAQ. Flom *et al.* has reported that the emission lifetime of 1,5-DHAQ increased by a factor of ~ 3 when the hydroxyl protons are exchanged by deuterium.⁶ If this is the case for the current system of 1-HAQ, the observed isotope effects lead us to

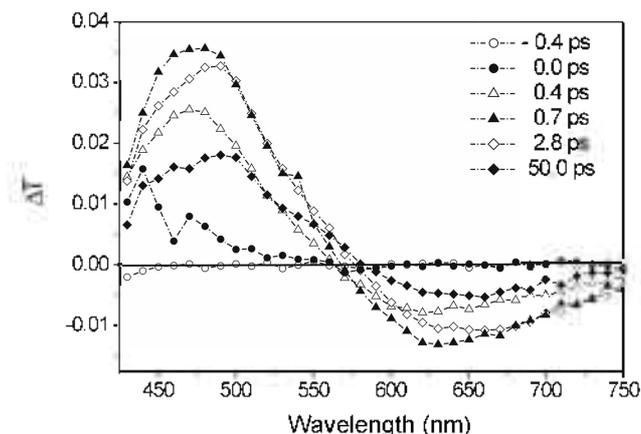


Figure 3. Time-resolved transient transmittance spectra of 1-HAQ in toluene with varying the delay times from -0.4 to 50.0 ps. The excitation wavelength was set to be 405 nm. The polarization between pump and probe beam was set to be a magic angle configuration.

propose that O-H vibration in hydroxyl group of 1-HAQ plays an important role in the relaxation process of the excited-state *keto*-tautomer.

The transient transmittance spectra of 1-HAQ were measured in toluene upon photoexcitation at 405 nm under the magic-angle configuration of the pump and probe with varying the delay times, as shown in Figure 3. Considering the ground state absorption spectrum of 1-HAQ, the observed spectra consist of ground state bleach of the *enol*-tautomer, stimulated emission of *enol*-tautomer, and photoinduced absorption due to the *enol*- and *keto*-tautomers

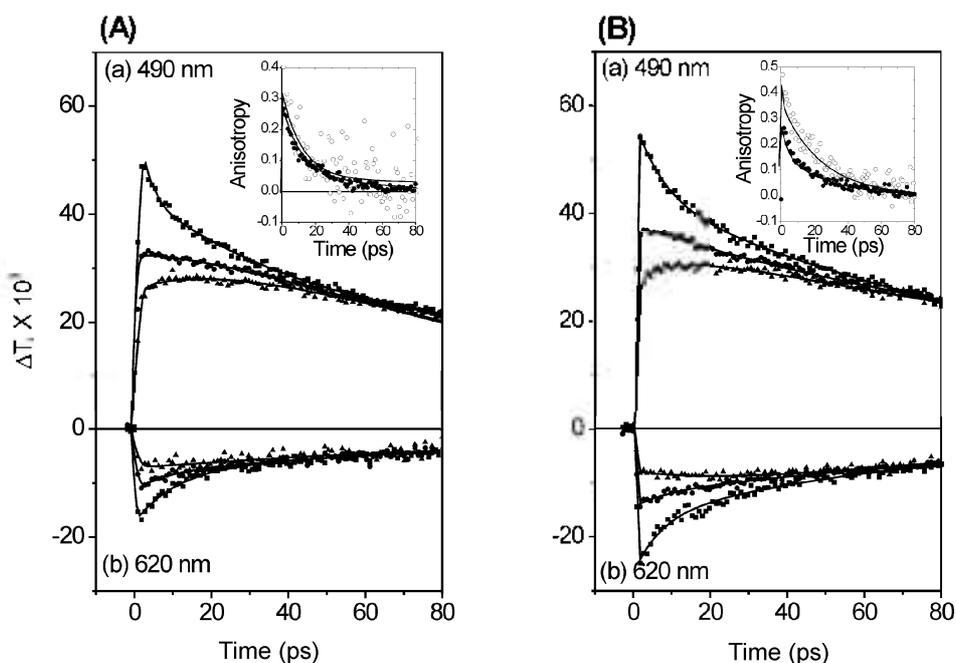


Figure 4. Temporal profiles of transient transmittance signal observed from 1-HAQ (A) and 1-DAQ (B) in toluene at the probe wavelengths of 490 (a) and 620 nm (b). In each figure, the polarization of pump and probe beam were set to be parallel (■), perpendicular (▲), and magic-angle (●). The solid lines represent the best-fitted results with a multi-exponential function (see text). The anisotropy decay profiles calculated from the results measured at 490 (○) and 620 nm (●) are shown in inset.

in the excited state. At the very early delay time, the maximum of stimulated emission band shifts from 440 to 470 nm within 0.72 ps. Even though it requires a detailed data points, the time constant of this process should be shorter than 260 fs. Subsequently, the stimulated emission band is further red-shifted to the wavelength longer than 490 nm. The transient absorption signal at around 620 nm is a sum of the photoinduced absorption and the stimulated emission of the *keto*-tautomer, although the former has large amplitude. The photoinduced absorption at around 620 nm also shifts to the longer wavelength with increasing the delay time.

The temporal profiles of 1-HAQ were also measured at two different probe wavelengths of 490 and 620 nm and are shown in Figure 4(A). The transient transmittance signals at 490 and 620 nm could be attributed to the stimulated emission and photoinduced absorption, respectively. We have examined the transient transmittance signal with three different configurations of parallel, and perpendicular and magic angle between pump and probe beam polarization. Multiexponential function with time constants of *ca.* 2, 18 and 200 ps well describes all the temporal profiles of 1-HAQ in toluene with changes in its amplitude.²⁸ The rise time in the perpendicular configuration of the polarization has the same value as in the decay time of the parallel polarization. Nevertheless, it is interesting to note that the temporal profiles obtained at the magic angle configuration give the decay time constants of 18 and 200 ps. We have calculated the anisotropy with eq. (1) as a function of delay time, and the results are shown in the inset of Figure 4(A). The fast anisotropy decay profiles are well described by a multiexponential function with time constants of 2 and 18 ps at the two probe wavelengths.

Finally, we have examined the isotope effects in the transient transmittance changes (see Figure 4(B)). The 690 ps decay time of 1-DAQ exhibits a prominent isotope effect like as the emission decay profiles as shown in Figure 2. However, in the fast decay time region within 18 ps, the temporal profiles of any polarization configuration does not exhibit any observable isotope effects as shown in Figure 4(B).

Discussion

From the Stokes-Einstein relation, the molecular rotational correlation time, τ_{rot} , is given by $\tau_{rot} = 8\pi\eta R_{eq}^3/6k_B T$, where R_{eq} and η are the hydrodynamic radius of 1-HAQ and the viscosity of toluene, respectively. By using the literature value of $\eta_{toluene} = 0.6 \times 10^{-3} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ for toluene, τ_{rot} is estimated to be 133 ps under stick boundary condition with $R_{eq} = 0.6 \text{ nm}$ at room temperature. Therefore, the anisotropy decay time constants (about 2 and 18 ps) are too fast to be interpreted with any molecular rotational correlation. The origin of the fast decay components cannot be clearly discussed because any detailed theoretical work on the transition dipole moment changes lacks in the current

system. However, these experimental observations may include fast anisotropy decay components resulting from an electronic transition to other state coupled to either vibronic interaction or vibrational motion. In fact, the observation of the red-shifts in the stimulated emission and photoinduced absorption as shown in Figure 3 with a similar time constant reveals the presence of an appreciable either vibration redistribution or vibrational cooling process accompanied by ESIPT process of 1-HAQ. A similar interpretation on the ultrafast photodynamics of 1,8-DHAQ was reported that the vibrational redistribution in its excited-state induces the additional proton translocation from *enol*-tautomer to *keto*-tautomer.²⁷ If this is the case, we could suggest that the ultrafast component within 260 fs is the typical collapse of the Franck-Condon state implying the dynamics of ESIPT and the dynamics of the 2 ps time scale is the additional proton translocation reflecting intramolecular vibrational redistribution. The dynamics within 18 ps could be assigned to the vibrational cooling process. Therefore, the two decay time constant of 2 and 18 ps on the anisotropy could be also described in terms of intramolecular vibrational redistribution and intermolecular vibrational relaxation (vibrational cooling), respectively.

It is interesting to note that there are no apparent isotope effects in the fast photodynamics for both the population and polarization changes accompanied by the ESIPT as well as the vibrational relaxation, of which time constants are around 2 and 18 ps. Meanwhile, the relaxation of excited *keto*-tautomer has a prominent isotope effects. The latter observation is consistent with the previous interpretation that the stretching mode (or bending mode) of O-H bond plays an important role in the relaxation process of excited *keto*-tautomer.²⁹ Nevertheless, no significant deuterium isotope effects is measured in anisotropy decay, indicating that high frequency O-H(D) stretching vibrations do not act as significant accepting modes in the ESIPT process. Chudoba *et al.* suggest that the highly anharmonic in-plane-deformation mode modulates the separation between proton donor and acceptor atom and plays a key role in the proton transfer reaction.³⁰ This proposition is in part supported by the experimental observation as follow. If the proton transfer as well as vibrational relaxation of excited *enol*-tautomer have any observable isotope effect, the production yield of excited *keto*-one between 1-HAQ and 1-DAQ depends on the nature of the isotope, hydrogen or deuterium. Furthermore, it is well known that the emission quantum yield of an excited chromophore is proportional to the product of its initial concentration and decay time constant. However, the relative emission quantum yield of 3.4 folds between 1-HAQ and 1-DAQ is essentially the same to the ratio of emission decay rate constant between the two different excited *keto*-tautomers: $5.00 \times 10^9 \text{ S}^{-1}$ and $1.45 \times 10^9 \text{ S}^{-1}$ for 1-HAQ and 1-DAQ, respectively. These results lead us to suggest that the change from hydrogen to deuterium in the hydroxyl group hardly affect the rate of ESIPT as well as the vibrational relaxation processes due to its negligible activation barrier.

Conclusion

Time-resolved emission as well as transient transmittance experiments on 1-HAQ and 1-DAQ in toluene were carried out to have a detail understanding on their ESIPT process. The temporal profiles of spontaneous emission, stimulated emission and the photoinduced absorption of 1-HAQ could be well described by multiple time constants. The ultrafast component within *ca.* 260 fs reflects the dynamics on ESIPT. The 2 ps decay component is assigned to an additional proton translocation induced by the intramolecular vibrational redistribution, whereas the 18 ps component is assigned to the vibrational cooling. The long component (200 ps) can be explained in terms of the population relaxation from excited-state *keto*-tautomer to its ground state. Finally, the comparative studies on photodynamics between 1-HAQ and 1-DAQ are consistent with the proposition that the ESIPT process is very fast due to its negligible activation barrier, and the vibrational relaxations could not involve high energy O-H(D) vibrations. In contrast to this, the relaxation of excited *keto*-tautomer has a prominent isotope effects.

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