Charge redistribution and photoacidity: Neutral versus cationic photoacids

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A series of pyrene photoacids is used to investigate excited-state proton transfer with time-dependent pump-probe spectroscopy. The deprotonation dynamics of a cationic photoacid, 8-aminopyrene-1,3,6-trisulfonic acid trisodium salt (APTS), shows single exponential dynamics (~30 ps) in water. This is in contrast to what is observed for the neutral photoacids 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) and 8-hydroxy-*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylpyrene-1,3,6-trisulfonamide, which display biexponential dynamics. For the cationic photoacid, the vast majority of the intramolecular charge redistribution does not occur in the protonated state. Instead, the charge redistribution, which is responsible for the photoacidity and the observed spectroscopic changes, occurs primarily following the excited-state proton transfer. The lack of charge redistribution prior to proton transfer causes APTS to display single exponential kinetics. In contrast, the dynamics for the neutral photoacids are multiexponential because major charge redistribution precedes proton transfer followed by additional charge redistribution that accompanies proton transfer. Previous studies of HPTS in water are discussed in terms of the results presented here. © *2008 American Institute of Physics*.
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I. INTRODUCTION

For the past half century, photoacids have played a major role in both proton transfer and hydrogen bonding research.[1–4] Photoacids are aromatic molecules that have an excited-state pK_a much lower than in the ground electronic state. The change in pK_a can be quite dramatic for some photoacids, at times with a pK_a difference of much larger than seven units.

In recent years, with advances in ultrafast laser technology, photoacids (in particular, pyrene derivatives in the condensed phase) have been used to study the fundamental nature of proton transfer reactions on a very short time scale. Of particular interest in the last several years has been the research directed at understanding the mechanistic details of proton transfer in water.[5–9] However, as photoacids are studied on shorter and shorter time scales, understanding the basic photophysics of the photoacids themselves becomes essential if they are to be used as tools to investigate proton transfer in a more general sense.[10]

Despite the widespread use of photoacids, there still remain many questions about the fundamental properties that lead to photoacidity.[11] Following electronic excitation of a photoacid, it is clear that the charge distribution of the molecule is dramatically altered, which, in turn, reduces the pK_a of the molecule. When interpreting the ultrafast (picosecond and femtosecond) dynamics of photoacids, it is necessary to understand when the charge redistribution occurs that is responsible for photoacidity. It is frequently assumed that the charge redistribution occurs essentially instantaneously upon photoexcitation, and that the dynamics observed through spectral changes arise from excited-state proton transfer (ESPT). We have recently shown that the charge redistribution process in some situations can take as long as tens of picoseconds.[12] Also at issue is whether the charge redistribution responsible for proton transfer occurs primarily on the reactant side or product side of the reaction. That is, the charge redistribution process can stabilize the conjugate base's negative charge in addition to causing a reduction in binding of the hydroxyl proton.[13,14]

Photoacidity can be increased (greater reduction in the pK_a) by substituting electron withdrawing functional groups on the aromatic ring of the molecule.[15,16] The substituent in the photoacid that contains the acidic proton, such as a hydroxyl or amine functional group, serves as a π-electron donor. The electron donating and withdrawing functional groups work together in a push-pull fashion to transfer electron density to the aromatic ring. In this regard, strong photoacids are similar to many of the typical molecules used study to intramolecular charge transfer (ICT) processes. The ICT process is usually adiabatic and typically proceeds on the order of solvent reorganization time, although it can be much faster for molecules that do not require significant internal rearrangements to allow for the ICT.[17–20] In analogy to ICT, it is reasonable to expect stronger photoacids to display a distinct charge redistribution step that is solvent driven.

The recent studies of 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) in water.[5,7–9,21] illustrate why understanding the charge redistribution step in connection with the overall dynamics of photoacids is important. In the mid-1990s, HPTS was observed by fluorescence upconversion and pump-probe spectroscopy to show biexponential kinetics in water.[22] The dynamics consisted of a fast component (3 ps in H_2O and 5 ps in D_2O), which contributed to ~30% of the total decay, and a much slower component of 90 ps in H_2O

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and 210 ps in D_2O. (On a much longer time scale of nanoseconds, a power law is observed that is related to proton diffusion.) A significant amount of attention has been devoted to understand the multiexponential dynamics of HPTS because it might shed light on the mechanism for proton transfer in water, The slower 90 ps component can be observed by time correlated single photon counting and was assigned as ESPT. However, the faster component has produced several different interpretations in the past decade.[8,21,23,24]

The solvation times for dye molecules in water that are similar to HPTS are less than 1 ps.[25] The solvation time for the methoxy derivative of HPTS, which cannot undergo ESPT, is also less than 1 ps.[7] Furthermore, the slowest component of the solvation dynamics of HPTS in water has been measured to be just under 1 ps. Therefore, a general solvation process has been ruled out as responsible for the 3 ps component of the excited-state dynamics of HPTS in water. The first explanation suggested for the short time dynamics of HPTS in water was a two-step model for proton transfer reaction.[22] This view was later supported by an extended Eigen-Weller model by other authors.[8,9] In the Eigen-Weller model, the first 3 ps step (following fast solvation) is due to initial deprotonation that forms a contact ion pair with the accepting base molecule. The second step (90 ps) breaks contact between the ion pair and is followed by diffusion,

$$\mathrm{AH}\cdots\mathrm{B} \underset{\text{fast}}{\overset{\text{step 1}}{\rightleftharpoons}} [\mathrm{A}^-\cdots\mathrm{HB}^+] \underset{\text{slow}}{\overset{\text{step 2}}{\rightleftharpoons}} \mathrm{A}^- + \mathrm{HB}^+.$$

In the model, the first step is controlled by the solvent reorganization time for very strong acids and the second step requires a larger scale solvent restructuring to solvate the separated ion pair.[26]

The contending explanation of the short time dynamics of HPTS in water is an intramolecular charge redistribution model.[21,23] In this model, the fast 3 ps dynamics are due to an internal electron redistribution that is most likely caused by a hydrogen bonding rearrangement of the surrounding solvent. The electron redistribution then drives the subsequent proton transfer reaction, which is responsible for the longer time scale of ~90 ps decay.

In this paper, we will examine three different closely related photoacids to better understand the nature of intramolecular charge redistribution and its relation to ESPT. Despite the fact that hundreds of molecules display photoacidity, two of the most important classes of photoacids are hydroxypyrene and aminopyrene derivatives. By the existing terminology for photoacids,[3] hydroxypyrene derivatives are referred to as neutral photoacids because the acidic functional group (hydroxyl) is uncharged. Likewise, aminopyrene derivatives are known as cationic photoacids because the acidic group (ammonium ion) carries a positive charge. Therefore, even the aminopyrene derivative, 8-aminopyrene-1,3,6-trisulfonic acid trisodium salt (see Fig. 1), will be referred to as a cationic photoacid although the molecule has a total net charge of −2.

The charge redistribution properties of closely related cationic and neutral photoacids will be directly compared and shown to be fundamentally different. In doing so, we will also show that the short time 3 ps spectral changes of HPTS are caused by charge redistribution, which is possibly a general feature present in most strong neutral photoacids. Conversely, the results presented below for APTS suggest that, in general, cationic photoacids do not undergo an appreciable charge redistribution step before proton transfer because the electrons which ultimately participate in the charge redistribution process are contained in the sigma bond that is broken in the ESPT reaction.

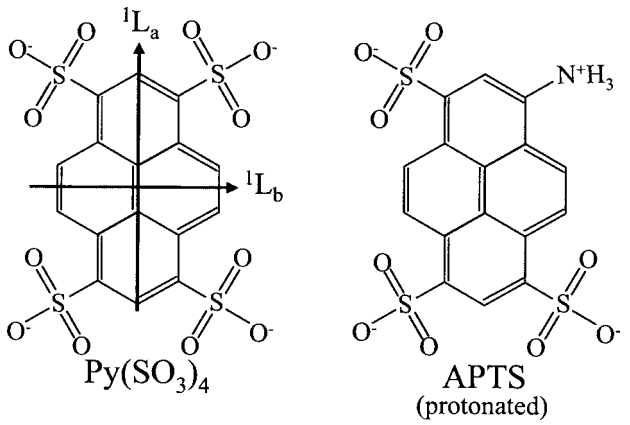

FIG. 1. The structures of APTS and $Py(SO_3)_4$.

II. EXPERIMENTAL PROCEDURES

Pyrene-1,3,6,8-tetrasulfonic acid tetrasodium salt $[Py(SO_3)_4]$ (>98%), HPTS (>98%), 8-hydroxy-*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylpyrene-1, 3, 6-trisulfonamide (HPTA) (>95%), and APTS (>96%) were purchased from Fluka. The water used was de-ionized. Anhydrous dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were purchased from Acros, Inc. Ultraviolet-visible absorption spectra were measured on a Cary-6000i spectrophotometer. Fluorescence spectra were taken on a Fluorolog-3 fluorescence spectrometer. The spectra were corrected for the Xe lamp intensity profile, monochromator, and photomultiplier response.

Pump-probe experiments in which a particular wavelength is used for the pump and a continuum is used as the probe were performed using a Ti:sapphire regenerative amplified source and a spectrometer–charge-coupled device (CCD) detection system. The pump beam was centered at 384 nm for APTS and 400 nm for HPTS and HPTA. The excitation used 7 μJ/pulse with 65 fs duration and a spot size diameter of 200 μm. A "white light continuum" used for the probe was generated by focusing 1–2 μJ of near-IR (~800 nm) light into a 1 mm cuvette of water. A half-wave plate/polarizer combination was used to attenuate the near-IR light to give the most stable white light. The continuum generated ranged from the near-IR to somewhat beyond 390 nm. The white light was separated into two beams with a beam splitter. One beam was used as the probe and crossed with the pump in the sample, and the other one was used as a reference to monitor the intensity and spectral characteristics of the white light. The timing between the pump and the probe was achieved by passing the pump beam down a high-resolution delay line with ~1 fs resolution. The probe and

reference beams were focused into two optical fibers. The outputs of the fibers were at the entrance slit of a 0.3 m monochromator. The dispersed outputs of the two input beams were detected by a 1340×100 pixel CCD detector. The probe and reference produce separately readout stripes on the CCD, which were used to obtain the difference absorption spectrum between pump on and pump off. The reference spectrum permits correction for variation over time of the white light characteristics.

III. RESULTS AND DISCUSSION

A. Cationic acidic group photoacids

In studying the photophyics of the cationic photoacid APTS, it is useful to compare it with the closely related molecule $Py(SO_3)_4$. The excited-state pK_a of the protonated form of APTS rivals that of strong mineral acids. Therefore, it is difficult to find a solvent that can be used to observe the protonated state without complications from the excited-state proton transfer process. The structures of both molecules are given in Fig. 1. $Py(SO_3)_4$ has an electronic structure analogous to APTS, but it cannot undergo ESPT. Both ammonium and sulfonate functional groups inductively pull electron density from the pyrene ring. The electron withdrawing strength is greater for the ammonium group than for the sulfonate functional groups,[27] which will slightly distort the D_{2h} symmetry for APTS, but since the difference is due to mild inductive interactions, the electronic structures of the two molecules correspond quite well to one another.

The similarity of the electronic states can be seen in the absorption and fluorescence spectra of $Py(SO_3)_4$ and APTS in Figs. 2(a) and 2(b), respectively. The electronic states of $Py(SO_3)_4$ were previously assigned by magnetic circular dichroism and polarized fluorescence spectroscopy.[28] In Platt notation,[29] the ^1L_a and ^1L_b states are nearly degenerate and the transition dipoles are orthogonal due to the D_{2h} symmetry. The ^1L_b transition is forbidden and is completely masked by the strongly allowed ^1L_a transition. The same properties can be expected for the lowest energy transitions of APTS, which is supported by the correspondence of the spectra for the two molecules.

APTS is very acidic in the first excited electronic state.[3] The fluorescence spectrum in Fig. 2(b) was taken in a 9:1 sulfuric acid/water mixture. Even under these conditions, a significant amount of deprotonation occurs within the excited-state lifetime. There exists good mirror symmetry between absorption and fluorescence of the protonated state, but in the deprotonated state, electron density is donated into the aromatic ring, which broadens the fluorescence spectrum. The spectral changes can be described well by a simple Brownian oscillator model.[28]

The pump-probe spectra of $Py(SO_3)_4$ and the protonated state of APTS are given in Figs. 3(a) and 3(b). The spectra were taken in pure sulfuric acid to avoid excited-state proton transfer of APTS to the solvent. Much similar to the absorption and fluorescence spectra, the pump-probe spectra of $Py(SO_3)_4$ and APTS are quite similar. The entirely positive signal (increased absorption) at all wavelengths signifies that the most prominent transitions are due to excited-state absorption. Both molecules have the same excited-state absorption peaks, although the vibronic structure is somewhat different. The maximum excited-state absorption peak of APTS at 585 nm is blueshifted by approximately 25 nm relative to $Py(SO_3)_4$. Both molecules also demonstrate a negligible Stokes shift in the pump-probe spectrum, and the only dynamics observed for times of >100 fs is a slight broadening of the excited-state absorption peaks. The lack of Stokes shift is in agreement with previous steady-state studies in various solvents.[28]

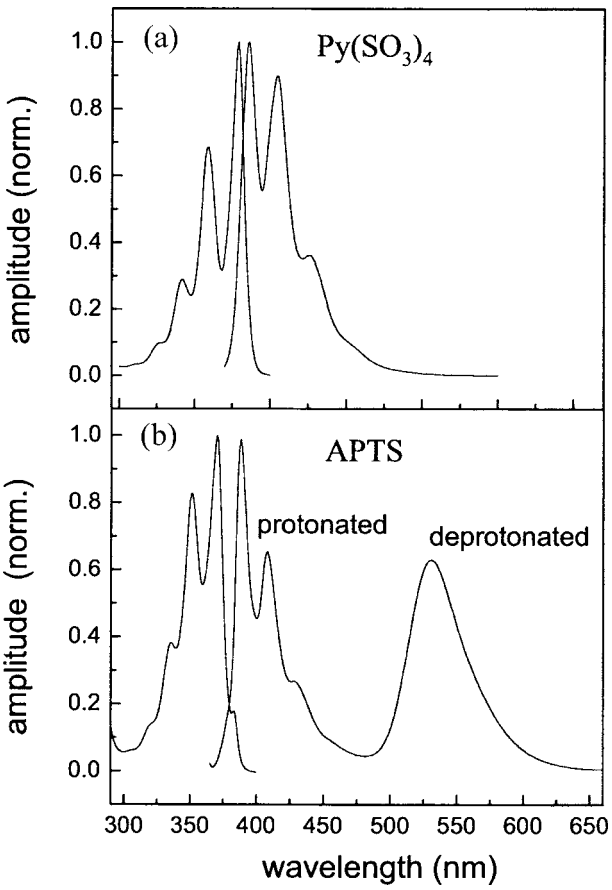

FIG. 2. (a) The absorption and fluorescence spectra of $Py(SO_3)_4$ taken in water. (b) The absorption and fluorescence spectra of APTS taken in a 9:1 sulfuric acid/water mixture.

To have an appreciable Stokes shift, it is necessary to have a substituent that is strongly electron donating following photoexcitation. This is illustrated by the excited-state dynamics of the deprotonated form of APTS. In the deprotonated form, the amine functional group is a strong π-electron donor. As can be seen in Fig. 4(a), a clear time-dependent Stokes shift is observed in polar aprotic solvents, such as DMF. As the first excited-state is solvated, the excited-state absorption peak blueshifts in time.

In protic solvents, the electron withdrawing strength of the sulfonate groups of APTS is increased by hydrogen bonding with the solvent. The sulfonate groups work in cooperation with the amine functional group to transfer charge density to the aromatic ring. Figures 4(b) and 4(c) show the charge redistribution process of deprotonated APTS in formamide and water. Both solvents are strong hydrogen bond donors. The initial transient absorption spectrum taken at

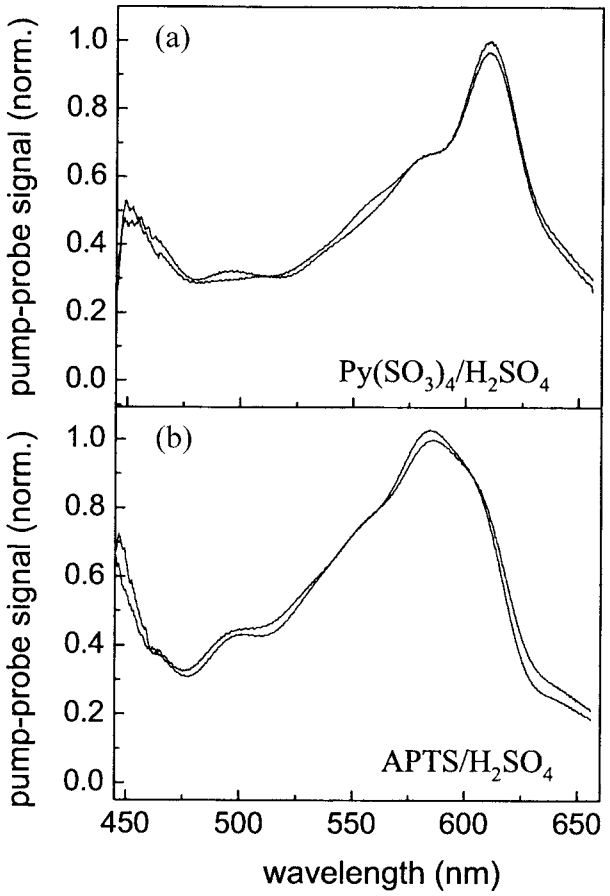

FIG. 3. (a) Pump-probe spectra of $Py(SO_3)_4$ in sulfuric acid at 200 fs and 50 ps. (b) Pump-probe spectra of APTS in sulfuric acid at 200 fs and 50 ps. Both molecules show no appreciable Stokes shift.

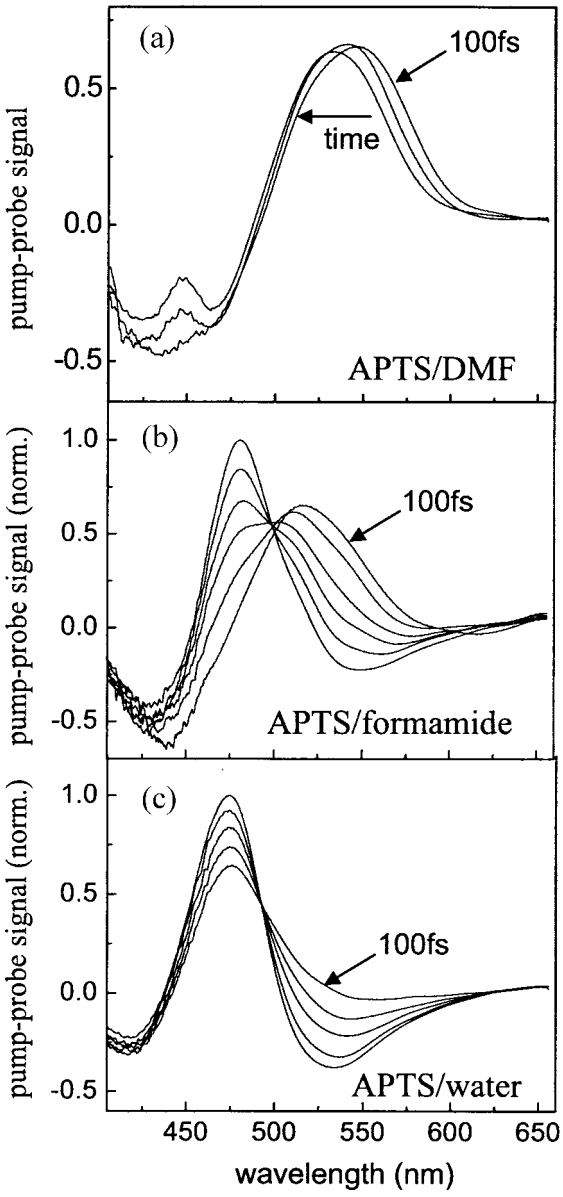

FIG. 4. (a) Pump-probe spectra of APTS in DMF displaying a time-dependent Stokes shift at 100 fs, 4 ps, and 400 ps. (b) Pump-probe spectra of APTS in formamide at 100 fs, 600 fs, 2 ps, 4 ps, 9 ps, and 400 ps showing the intramolecular charge redistribution process. (c) Pump-probe spectra of APTS in water at 100 fs, 400 fs, 1 ps, 3 ps, and 400 ps. Much of the ICT process happens faster than our resolution (~150 fs).

100 fs of APTS in formamide [Fig. 4(b)] is very similar to the transient absorption spectrum at the same time in DMF [Fig. 4(a)]. However, at later times, spectra in Figs. 4(a) and 4(b) differ considerably. In contrast to the simple Stokes shift of the excited-state absorption peak displayed by APTS in DMF, APTS in formamide results in the positive excited-state absorption peak at ~525 nm turning negative into stimulated emission. Likewise, an excited-state absorption peak grows at 475 nm in the place of stimulated emission in Fig. 4(b). The spectral evolution has an isosbestic point at ~500 nm, which signifies the conversion of one chemical species to another. This process for APTS has previously been explained by an intramolecular charge redistribution mechanism.[12] APTS is initially excited into a locally excited state, which gives rise to the pump-probe spectrum at 100 fs in Fig. 4(b). APTS then undergoes a solvent-induced transition into a CT state, where charge density is redistributed from the amine group to the pyrene moiety. The dynamics in Fig. 4(b) can be fitted to a single exponential giving a 5.4 ps time constant, which agrees with the reported longest time scale component of the solvation of aromatic dyes in formamide.[7,30]

The same type of dynamics observed for deprotonated APTS in formamide is also present for deprotonated APTS in water [Fig. 4(c)]. In water, much of the charge redistribution process occurs faster than our time resolution (~150 fs), which is indicated by the absence of excited-state absorption peak at wavelengths of greater than 500 nm. The observed charge redistribution time of APTS in water in Fig. 4(c) is 1.0 ps, which nearly perfectly matches the measured Stokes shift time of the methoxy derivative of HPTS (MPTS) in water.[7] It has previously been demonstrated that the majority of the solvation dynamics of a similar aromatic dye, C343, in water are induced by the inertial motions of the water and occur faster than 50 fs,[25] which could explain why a large portion of the charge redistribution dynamics of APTS is not visible with our time resolution.

As shown through Figs. 2(b) and 3(b), the protonated form of APTS has a negligible excited-state charge redistribution or Stokes shift, while a significant charge redistribution process occurs in the deprotonated form (Fig. 4) and is controlled by solvation dynamics. This same behavior is

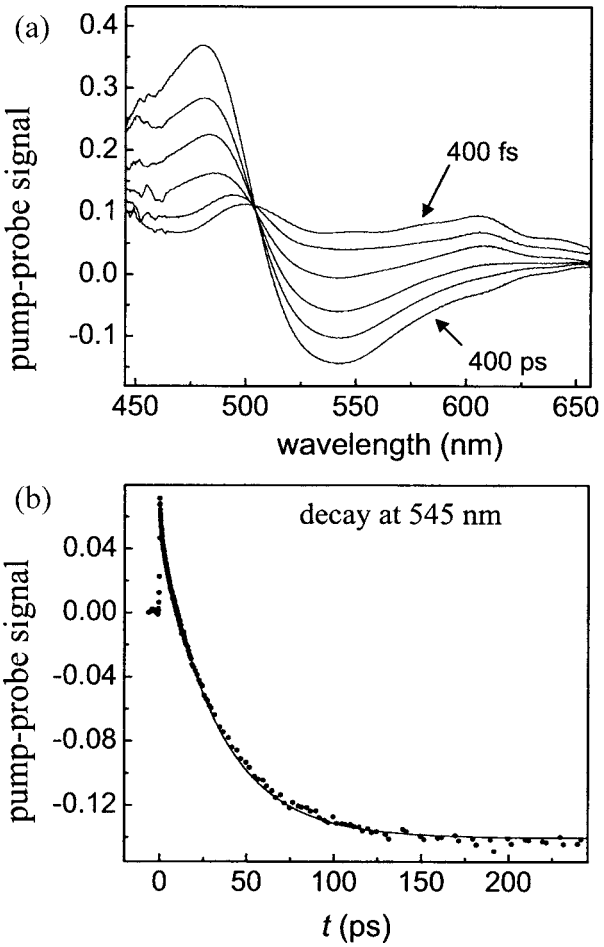

FIG. 5. (a) Pump-probe spectra of APTS in 0.5*M* HCl. Times shown: 400 fs, 3 ps, 11 ps, 30 ps, 55 ps, and 400 ps. (b) The pump-probe decay at 545 nm. The pump-probe signal (dotted line) is fit to a single exponential (solid line).

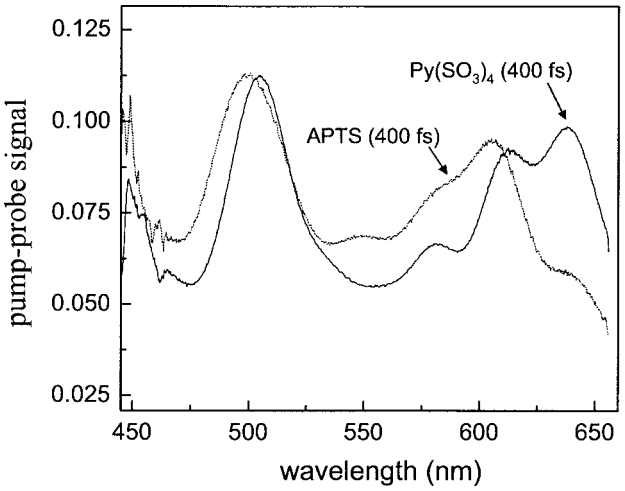

FIG. 6. Comparing the initial pump-probe spectrum of APTS in 0.5*M* HCl to $Py(SO_3)_4$ at initial time (400 fs). The two spectra agree well to show APTS in the initially totally protonated state.

manifested in the excited-state proton transfer process for the protonated form of APTS in water. Figure 5(a) shows the pump-probe spectra of APTS in water with 0.5*M* hydrochloric acid. Previous studies of aqueous salt solutions have shown that the ultrafast dynamics of water at ionic strengths similar to the 0.5*M* HCl are essentially the same as pure water.[31] The spectrum at relatively short time (400 fs) displays only excited-state absorption (positive signal). The spectrum at 400 fs in Fig. 5(a) is analogous to the spectrum of the protonated state of APTS in concentrated H_2SO_4, shown in Fig. 3(b), which both only display excited-state absorption. The spectra are not identical because of the extreme conditions of APTS in concentrated H_2SO_4, which will protonate the sulfonate groups and produce other perturbations of the chromophore. The long time spectrum (400 ps) shown in Fig. 5(a) matches the spectrum of the deprotonated form for APTS in water [Fig. 4(c)] at long times after the charge redistribution process is complete. [In Fig. 4(c), the last curve is taken at 400 ps to show that there is no long time dynamics. This limiting spectrum is obtained after ~10 ps.] In Fig. 5(a), there is an isosbestic point at ~500 nm that signifies the conversion between two distinct chemical species. The sharpness of the isosbestic point is due to the lack of an appreciable Stokes shift for the protonated state. The deprotonated state of APTS likely has charge redistribution dynamics, as demonstrated in Fig. 4(c), but since the charge redistribution occurs only after deprotonation and happens on a fast time scale relative to proton transfer (~30 ps), the charge redistribution is not observable as a distinct step in the ESPT process. The pump-probe dynamics at 545 nm are displayed in Fig. 5(b). At relatively short times (several hundred picoseconds and less), the effect of geminate recombination can be ignored and the dynamics can be described as a single molecular dissociation process. For single step dissociation, the dynamics should be a single exponential decay. The solid curve through the data in Fig. 5(b) is a single exponential fit with a 30 ps time constant. As can be seen in the figure, a single exponential function fits the data very well.

To ensure that all of the proton transfer dynamics were captured by the time resolution of our measurements (~150 fs), the pump-probe spectrum of APTS at short time (400 fs) is compared to that of $Py(SO_3)_4$ in Fig. 6. As demonstrated by Figs. 2 and 3, the spectra for the protonated form of APTS and $Py(SO_3)_4$ are quite similar. The pump-probe spectra of the two molecules at 400 fs are again very similar. The excited-state absorption vibronic bands at around 625 nm differ somewhat for the two molecules. The maximum peak of APTS is blueshifted by ~25 nm relative to $Py(SO_3)_4$, but this difference is precisely what is observed in the pump-probe spectra in Figs. 3(a) and 3(b). Therefore, at 400 fs, APTS is in the protonated state and all of the deprotonation dynamics are included in the decay curve shown in Fig. 5(b), which displays simple single exponential dynamics.

B. Neutral acidic group photoacids

The short time dynamics of neutral (hydroxyl) pyrene photoacids have been studied in much more detail than their cationic (ammonium) counterparts.[3,4] The two neutral photoacids to be discussed here are HPTS and HPTA, the structures of which are shown in Fig. 7. Their structures are very similar, and the electronic spectra have been characterized

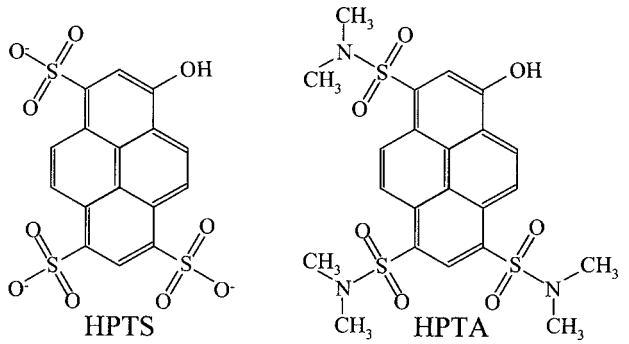

FIG. 7. Structure of the neutral acidic group photoacids HPTA and HPTS.

previously.[12,28] HPTS has been used extensively for investigating various aspects of proton transfer dynamics in water.[5,6,8,32] The electron withdrawing groups of HPTA are stronger than of HPTS, which lowers the excited-state pK_a of HPTA (−0.7) compared to that of HPTS (1.3).[4] The lower excited-state pK_a makes HPTA capable of ESPT in nonaqueous solvents, which is not possible for HPTS.

We have recently shown that HPTA undergoes a two-step ESPT process in nonaqueous solvents.[12] Figure 8(a) shows the pump-probe spectra of the protonated and deprotonated forms of HPTA. These spectra were taken in acetonitrile at 500 ps. HPTA cannot undergo ESPT in acetonitrile, and by 500 ps, all solvation processes are complete. The two-step deprotonation dynamics are illustrated by the time

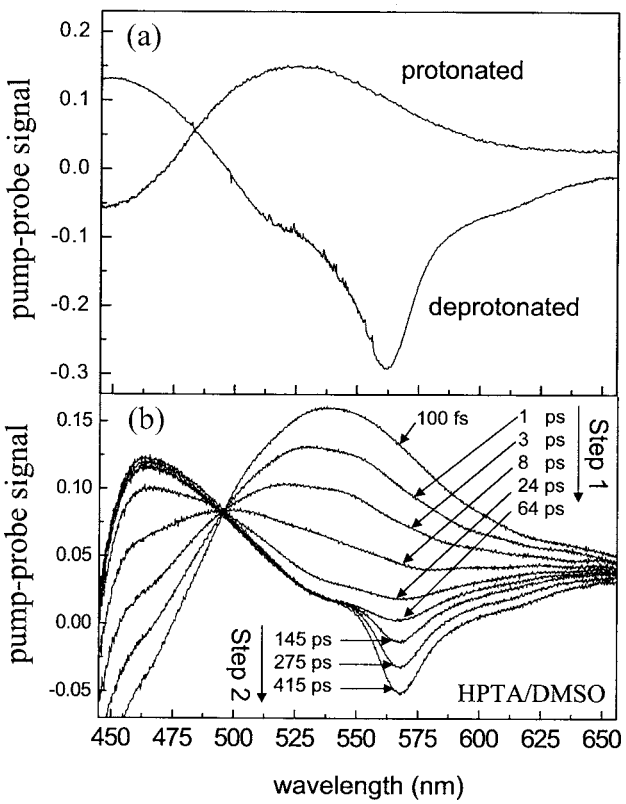

FIG. 8. (a) Pump-probe spectra of protonated and deprotonated forms of HPTA in acetonitrile at 500 ps. (b) The pump-probe spectra of HPTA in DMSO at 100 fs, 1 ps, 3 ps, 8 ps, 24 ps, 64 ps, 145 ps, 275 ps, and 415 ps. The spectral changes below 64 ps are due to the formation of a charge transfer state. Dynamics occurring on longer time scales are due to ESPT and are marked by the appearance of a stimulated emission peak at 570 nm.

dependence of the pump-probe spectra of HPTA in DMSO displayed in Fig. 8(b). Comparing the pump-probe spectrum at 100 fs with the protonated HPTA spectrum in Fig. 8(a) demonstrates that HPTA is initially in the protonated state. The first step leading to deprotonation is intramolecular electron redistribution in which electron density is transferred from the hydroxyl functional group to the aromatic ring. This charge redistribution is the same process discussed above for the deprotonated form of APTS in protic solvents [Figs. 4(b) and 4(c)] and has been discussed in more detail elsewhere.[12] The charge redistribution step in DMSO displays biexponential kinetics with time constants (and relative weighting) of 2.3 ps (0.46) and 13.4 ps (0.54). The reported long time component of the solvation of coumarin in DMSO is 2 ps.[33] Roughly, half of the HPTA charge redistribution dynamics occurs within the normal solvation time and the other half occurs on a significantly longer time scale. There is evidence that suggests that the longer time scale component of the charge redistribution is controlled by specific rearrangements of the hydrogen bond between the hydroxyl functional group of HPTA and the accepting base molecule.[12]

The second step in Fig. 8(b), with an onset of after tens of picoseconds, corresponds to proton transfer and happens on a time scale of ~700 ps. It is marked by the growth of a sharp stimulated emission peak at 570 nm. This stimulated emission peak matches precisely with the steady-state fluorescence spectrum of the HPTA anion in DMSO.[12] The long time pump-probe spectrum is essentially the same as the deprotonated HPTA spectrum shown in Fig. 8(a).

The spectral dynamics in Fig. 8(b) involve three distinct chemical species. HPTA is initially protonated, which is confirmed by comparison to the protonated spectrum in Fig. 8(a). On a time scale from picoseconds to tens of picoseconds, the initial protonated state forms an intermediate state in which charge redistribution has occurred but deprotonation has yet to take place. The charge transfer state then undergoes ESPT to form the anion on a much longer time scale (~700 ps), which again is confirmed by the anion spectrum in Fig. 8(a).

As discussed in the Introduction, HPTS also follows a two-step process for ESPT. Time-dependent pump-probe spectra of HPTS are shown in Fig. 9(a). These spectra agree with those that have been reported previously.[7,8,23] The solvation dynamics of the methoxy derivative, MPTS, were studied in water. The Stokes shift of MPTS occurs with a time constant of 990 fs.[7] The pump-probe dynamics at 440 and 530 nm are displayed in Fig. 9(b). At these wavelengths, the contribution to the decay from a Stokes shift is relatively small [the Stokes shift response of HPTS is shown in Fig. 10(b)]. There are a relatively fast ~3 ps component and a slower ~90 ps decay. An immediate difference that can be seen when comparing HPTS to its cationic counterpart, APTS, in Fig. 5(a), is the lack of a sharp isosbestic point near 500 nm at early times. This indicates that solvation is significant for HPTS, while it is not visible for APTS in Fig. 5(a). However, the most important difference between the neutral and cationic acids is that HPTS follows biexponential kinetics (following the very fast Stokes shift), while the kinetics

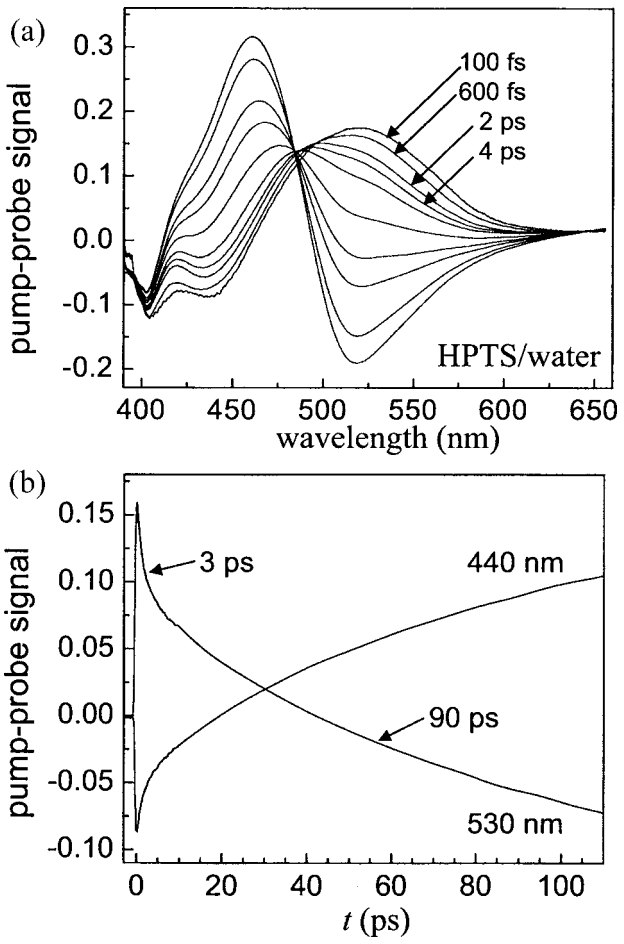

FIG. 9. (a) Pump-probe spectra of HPTS in water at 100 fs, 600 fs, 2 ps, 4 ps, 9 ps, 28 ps, 59 ps, 90 ps, 180 ps, and 300 ps. (b) The pump-probe dynamics showing biexponential behavior at 440 and 530 nm.

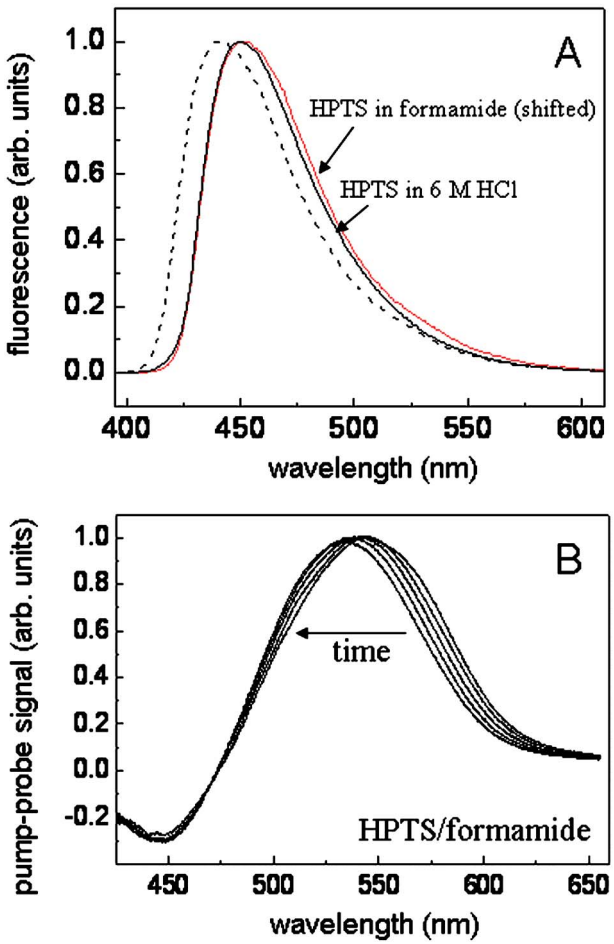

FIG. 10. (Color online) (a) Fluorescence spectrum of HPTS in formamide (dotted) and 6*M* HCl. The spectrum of formamide data has also been shifted to overlap with the spectrum in 6*M* HCl for comparison. (b) The time-dependent Stokes shift of HPTS in formamide at 100 fs, 600 fs, 2 ps, 4 ps, and 300 ps.

observed for APTS are strictly single exponential. The dynamics at 530 nm 440 nm in Fig. 9(b) clearly show the biexponential behavior.

The fast component (~3 ps) of HPTS in water can be isolated by increasing the acid concentration. Figure 10(a) compares the fluorescence spectra of HPTS in formamide (dashed curve) and HPTS in a 6*M* HCl solution (solid black curve). HPTS cannot undergo ESPT in formamide and fluoresces entirely from the protonated state. The fluorescence spectrum of HPTS in formamide is also shifted and overlaid with the spectrum of HPTS in 6*M* acid for comparison (red curve). The two fluorescence curves are nearly identical, which demonstrates that only the protonated state of HPTS exists, and ESPT is not possible to any appreciable extent in the acid solution. The pump-probe spectral dynamics of HPTS in formamide are displayed in Fig. 10(b). At short times relative to the excited-state lifetime (~5 ns), the only spectral change in the pump-probe spectrum is a Stokes shift of the excited-state absorption peak. The oscillator strengths (areas) of both the stimulated emission and excited-state absorption transitions are conserved at all times. This is again an indication that no ESPT occurs for HPTS in formamide. This same solvation response has been reported for HPTS in other solvents where ESPT is not possible, as well as for MPTS in water.[7]

Figure 11(a) shows pump-probe spectra responsible for the fast time response (first several Picoseconds) of HPTS in water taken from Fig. 9(a). The pump-probe spectra of HPTS in 6*M* HCl are in Fig. 11(b) for comparison. As previously demonstrated by the fluorescence spectrum, HPTS cannot undergo ESPT at this high acid concentration. At the short times displayed, the spectral responses in Figs. 11(a) and 11(b) are virtually the same. HPTS spectra in both systems decay in amplitude in both the excited-state absorption and stimulated emission regions to a similar extent. Therefore, the response shown in Fig. 11(b) cannot be due to a proton transfer process.

The HPTS decay in high acid concentrations is slower and of slightly lower in amplitude than in it is in pure water, which has been noted previously.[9] In 6*M* HCl, the pump-probe signal of HPTS decays with a 5.5 ps time constant. However, the slowing of the spectral dynamics can be expected from any solvent driven process at high ionic strengths. It has been demonstrated that the dynamics of water slow significantly at high salt concentrations.[31] For example, the orientational anisotropy decay of pure water is 2.6 ps.[34] In 6*M* NaBr solutions, the water anisotropy decay slows to 6.7 ps.[31] At a concentration of 6*M* HCl, there is

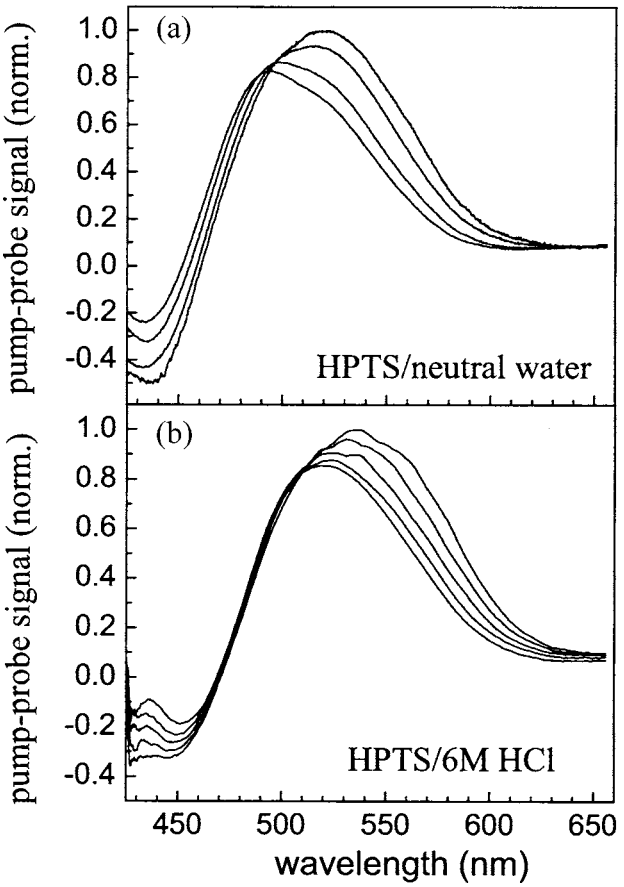

FIG. 11. (a) The pump-probe spectra responsible for the initial decay for HPTS in water (times at 100 fs, 600 fs, 2 ps, and 4 ps). (b) Pump-probe spectra of HPTS in 6*M* HCl at 100 fs, 1 ps, 3 ps, 9 ps, and 425 ps.

very little free water unassociated with either a hydronium or chloride ion. This hinders the solvating ability of water. At HCl concentrations much higher than 6*M* the solubility of HPTS is dramatically reduced.

Separating the charge redistribution step from ESPT using pump-probe spectroscopy can be difficult in some situations. The acts of charge redistribution and deprotonation both transfer charge density from the acidic substituent to the aromatic ring and, therefore, may produce similarities in the pump-probe spectra. The spectra of the deprotonated state of HPTA [Fig. 8(a)] and that of the charge redistribution state [Fig. 8(b), 64 ps] only differ because the deprotonated spectrum displays stimulated emission (~565 nm). Recently, the dynamics of HPTS were analyzed by fitting the entire pump-probe spectrum at all times to a linear combination of the pump-probe spectra of the initial protonated state (taken at 100 fs), the deprotonated state (long time limit of the pump-probe spectrum), and a function to account for very short time of Stokes shift.[7] The fits were excellent at all times. It was incorrectly concluded that all of the observed dynamics following the Stokes shift were due to ESPT.[7] The data presented in this study demonstrate that the initial dynamics of HPTS in water are due to a charge redistribution process and the spectrum of the intermediate state is represented well by a linear combination of the protonated and deprotonated states. It is also difficult to decouple the processes of charge redistribution and ESPT because the charge redistribution step typically happens only in situations where ESPT is possible. However, as shown in Fig. 11(b), in 6*M* HCl, HPTS displays the charge redistribution but does not undergo proton transfer because of the low *p*H of the water. In most solvents that do not facilitate ESPT, such as formamide, methanol, and DMSO, HPTS only displays a Stokes shift and there is no evidence of charge redistribution. The same properties have also been reported for HPTA.[12] Furthermore, while HPTS clearly shows a charge redistribution step in water, the methoxy derivative MPTS does not.[7] This suggests that the charge redistribution step is controlled by a specific interaction in the donation of a hydrogen bond from the hydroxyl of the photoacid to an accepting solvent/base molecule. Therefore, the reaction coordinate of the charge redistribution step could overlap significantly with the reaction coordinate of the proton transfer step, which can further complicate the separation of the two steps spectroscopically.

IV. CONCLUDING REMARKS

The excited-state dynamics of strong photoacids with cationic and neutral acidic groups are quite different. Cationic photoacids in the protonated state do not have the available electron density to permit an intramolecular charge redistribution process upon photoexcitation. The sigma bond that contains the acidic hydrogen must first be broken, which frees up the necessary electrons to induce the charge redistribution step. The absence of charge redistribution in the electronically excited protonated state of cationic photoacids results in APTS showing single exponential kinetics for excited-state proton transfer. The lack of a π donor in the protonated state also results in APTS showing no noticeable time-dependent Stokes shift.

Conversely, the neutral counterpart to APTS, HPTS, shows biexponential excited-state proton transfer kinetics because it is able to undergo charge redistribution to some extent before the proton transfer step. The two-step process is even more noticeable for the closely related molecule HPTA because the electron withdrawing functional groups are significantly stronger and are able to pull electron density more effectively into the aromatic ring.

It is likely that the lack of a significant charge redistribution preceding ESPT is a general feature for all cationic photoacids. In this respect, it is possible that cationic photoacids could be more useful for understanding ground-state proton transfer reactions because there should be fewer complications arising from the photoacid being in a nonequilibrium solvation configuration upon excitation. The observation of a definite charge redistribution step may only occur for stronger neutral photoacids. Weaker photoacids that do not have strong electron withdrawing substituents, such as pyrenol, may not be able to pull a significant amount of charge density from the oxygen of the hydroxyl group in the protonated state.

As illustrated by the example of cationic photoacid APTS, the presence of a charge transfer state in the protonated state is not a strict requirement for photoacidity. By a simple thermodynamic (Förster) cycle,[4] as long as the energy separation between the ground and first excited states is

smaller for the deprotonated state relative to the protonated state, the molecule will be a photoacid. There is evidence from computational studies that suggest that even for photoacids with neutral acidic groups, the largest amount of excited-state charge redistribution also happens in the anionic state following deprotonation.[13,14] However, as verified by this study, when interpreting the fast ESPT dynamics of strong photoacids with neutral acidic groups, it is important to recognize that the first step can be a relatively slow (picoseconds) observable charge redistribution in the protonated state that is followed by deprotonation.

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