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Excited-State Intramolecular Hydrogen Transfer (ESIHT) of 1,8-Dihydroxy-9,10-anthraquinone (DHAQ) Characterized by Ultrafast Electronic and Vibrational Spectroscopy and Computational Modeling

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Supporting Information

ABSTRACT: We combine ultrafast electronic and vibrational spectroscopy and computational modeling to investigate the photoinduced excited-state intramolecular hydrogen-transfer dynamics in 1,8-dihydroxy-9,10-anthraquinone (DHAQ) in tetrachloroethene, acetonitrile, dimethyl sulfoxide, and methanol. We analyze the electronic excited states of DHAQ with various possible hydrogen-bonding schemes and provide a general description of the electronic excited-state dynamics based on a systematic analysis of femtosecond UV/vis and UV/IR pump–probe spectroscopic data. Upon photoabsorption at 400 nm, the S₂ electronic excited state is initially populated, followed by a rapid equilibration within 150 fs through population transfer to the S₁ state where DHAQ



exhibits ESIHT dynamics. In this equilibration process, the excited-state population is distributed between the 9,10-quinone (S_2) and 1,10-quinone (S_1) states while undergoing vibrational energy redistribution, vibrational cooling, and solvation dynamics on the 0.1–50 ps time scale. Transient UV/vis pump–probe data in methanol also suggest additional relaxation dynamics on the subnanosecond time scale, which we tentatively ascribe to hydrogen bond dynamics of DHAQ with the protic solvent, affecting the equilibrium population dynamics within the S_2 and S_1 electronic excited states. Ultimately, the two excited singlet states decay with a solvent-dependent time constant ranging from 139 to 210 ps. The concomitant electronic ground-state recovery is, however, only partial because a large fraction of the population relaxes to the first triplet state. From the similarity of the time scales involved, we conjecture that the solvent plays a crucial role in breaking the intramolecular hydrogen bond of DHAQ during the S_2/S_1 relaxation to either the ground or triplet state.

INTRODUCTION

Photoinduced excited-state intramolecular hydrogen transfer (ESIHT) is one of the archetypical elementary chemical reactions, lending itself as a versatile vehicle for ultrafast spectroscopic studies. In these ESIHT reactions, a proton is transferred from a donating to an accepting group being part of the same molecular system upon a change in electronic charge distribution in response to an electronic excitation, making ESIHT a special type of proton-coupled electron-transfer reaction.¹ In the pioneering work by Weller on derivatives of salicylic acid, strongly red-shifted fluorescence spectra had been ascribed to originate from a profound rearrangement of the molecular structure resulting from a proton transfer along a pre-existing hydrogen bond after electronic excitation.^{2,3}

Numerous cases have since then been studied with steadystate UV/vis absorption and emission spectroscopy, ranging from hydroxyflavones, salicylaldehydes, to 2-(2'hydroxyphenyl)benzothiazole, including derivatives and related molecules.^{4–7} By emission of a fluorescent photon from the ESIHT product state that is energetically much more stable than the reactant state reached after initial photoexcitation, these molecular systems typically show strongly red-shifted fluorescence emission spectra. This is indicative of an ultrafast ESIHT reaction along a hydrogen-transfer coordinate occurring

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on time scales much shorter than the electronic excited-state relaxation. Hydroxy- and aminoanthraquinones form another class of molecular systems exhibiting ESIHT.⁶ For these compounds, it has been argued, based on fluorescence spectra measured in the gas phase, in supersonic expansions, or in low-temperature Shpol'skii matrixes, that a dual emission occurs from both reactant and product molecules in the electronic excited singlet state.^{8–18} This implies that equilibration dynamics are completed between reactants and products of electronic excited-state hydroxy- and aminoanthraquinones within the respective fluorescence lifetimes.

Ultrafast spectroscopy provides key insight into the time scales and mechanisms of ESIHT reaction dynamics. Following pioneering work by Paul F. Barbara and co-workers,¹⁹ ultrafast UV/vis electronic spectroscopy has shown that ESIHT reactions typically occur on a subpicosecond time scale,^{7,20,21} with a key role for low-frequency Raman-active modes with a key role for low-inequency relation and modulating the hydrogen bond distance, 22-26 which typically shows a large displacement upon electronic excitation.² Insight into detailed structural aspects of ESIHT can, however, only to a limited extent be obtained from electronic absorption and emission spectra, which are usually substantially broadened in condensed-phase solution. Instead, ultrafast vibrational spectroscopy of structure-specific marker modes has the potential to reveal the nature of reactant and product states,^{33–37} in particular, when a combined experimental and theoretical approach is followed, as evidenced in studies on 2-(2'-hydroxyphenyl)benzothiazole³⁸ and 3-hydroxyflavone.³⁹

Ultrafast studies on hydroxyl- or aminoanthraquinones have remained sparse,⁴⁰⁻⁴⁷ which is to some extent surprising given potential applications of these compounds as artificial DNA building blocks⁴⁸ and docking sites for interfacial electrondonor-acceptor systems.⁴⁹ Building on previous femtosecond spectroscopy work by the Tahara and Vöhringer groups,^{42,43} we present here results on 1,8-dihydroxy-9,10-anthraguinone (1,8dihydroxyanthracene-9,10-dione; DHAQ) (see Scheme 1) in a series of nonpolar, polar aprotic, and polar protic solvents. Using a combined approach of ultrafast UV/vis electronic and UV/IR vibrational spectroscopy measurements and quantum chemical calculations, we aim to elucidate the ESIHT reaction time in the electronic excited states and the possible relaxation routes through internal conversion, intersystem crossing, or fluorescence emission processes. The possible role of hydrogenbonding interactions with the solvent is explored as well.

DETAILS ON EXPERIMENTS AND CALCULATIONS

Chemicals. The perdeuterated solvents dimethyl sulfoxide d_6 (DMSO- d_6), methanol- d_4 (MeOD), and acetonitrile- d_3 (ACN- d_3) were obtained from Deutero GmbH (99.8% deuteration grade), while the solvents acetonitrile (ACN), tetrachloroethene (TCE), carbon tetrachloride (CCl₄), methanol (MeOH), and 1,8-dihydroxy-9,10-anthraquinone (DHAQ) were purchased from Sigma-Aldrich. For the steady-state IR spectra, DHAQ was dried over P₂O₅ under vacuum conditions. With this procedure, no significant amounts of water were present in the DHAQ samples, as evidenced by the recorded steady-state IR spectra. All experiments were performed at room temperature (24 ± 2 °C).

Steady-State Spectroscopy. All steady-state spectra were recorded on a double-beam UV/vis spectrometer (PerkinElmer), a spectrofluorometer (Spex), and a FT-IR spectrometer (Bio-Rad).

Scheme 1. Reaction Scheme of DHAQ, Showing the Basic Photophyscial Processes a



^{*a*}Amended from ref 42. Ultrafast ESIHT leads to population distributed among the 9,10-quinone S_2 and 1,10-quinone S_1 states and is followed by intramolecular vibrational redistribution, cooling, and hydrogen bond dynamics, resulting in an altered population distribution function among the two excited singlet states.

Broad-Band Transient UV/Vis Absorption Spectroscopy. A small fraction of the fundamental output from a Ti:sapphire femtosecond regenerative amplifier (Libra, Coherent, 800 nm, 100 fs fwhm, 1 kHz), amounting to a few μ J pulse energies, was used to generate pump and probe beams. Generating the second harmonic from the fundamental beam in a 100 μ m thick BBO crystal resulted in the 400 nm pump pulses, whereas white light continuum probe pulses were obtained by focusing the fundamental beam onto a 2 mm thick sapphire plate (contained in an Ultrafast System LLC spectrometer). The pump and probe pulses were spatially overlapping with a small angle $(<5^{\circ})$ in a 2 mm thick cuvette cell containing the DHAQ solution. It is worth pointing out that the solution was constantly stirred to have a fresh sample volume for each laser shot to avoid photodegradation. The optical density of the sample at the excitation wavelength was less than 0.80 in a 2 mm quartz cell. The transmitted probe light from the samples was collected and focused on the broadband UV/vis detector for recording the time-resolved excitation-induced difference spectra (ΔA). The time resolution of this setup was 150 fs. The nano- and microsecond dynamics were measured using a broad-band pump-probe subnanosecond transient absorption spectrometer with an extended time window (EOS, Ultrafast Systems, U.S.A.).

Femtosecond Broad-Band Fluorescence Upconversion Measurements. To detect the entire time-resolved fluorescence spectrum simultaneously, we decided to use a Halcyone MC multichannel fluorescence upconversion spectrometer with 150 fs temporal resolution (Ultrafast Systems, U.S.A.). In these experiments, a 1 mm thick cuvette containing a solution of DHAQ was excited with 0.5 mW of 400 nm light generated from the second harmonic of a 100 fs Ti:sapphire regenerative amplifier operating at 1 kHz (Libra, Coherent). The residual fundamental pulse after the second harmonic generation was used as a gate pulse for the upconversion process. Finally, the sample fluorescence was mixed with the gate pulse in a nonlinear crystal (BBO), and the sum-frequency signal was detected by a photon-counting method.

Transient UV Pump/IR Probe Spectroscopy. The UV pump pulses at 400 nm were straightforwardly obtained by the second harmonic of a home-built 1 kHz Ti:sapphire regenerative and multipass amplifier operating at 800 nm. About 50 μ J of the laser output was focused in a 100 μ m BBO crystal with a pulse energy of about 5–7 μ J. Tunable mid-IR probe pulses were generated by difference frequency mixing of signal and idler pulses from a near-infrared optical parametric amplifier. Probe and reference pulses, split off by a ZnSe wedge, were spectrally dispersed in a grating spectrometer and recorded simultaneously in a single-shot detection using a liquid-nitrogen-cooled double array $(2 \times 31 \text{ pixels})$ of MCT (HgCdTe) detectors. Spectrally resolved absorbance changes in the mid-IR have been recorded with a 2-7 cm⁻¹ spectral resolution. Synchronous chopping of the UV pump pulses is also applied to eliminate long-term drift effects, allowing a comparison of the probe intensity with and without the pump pulse within two subsequent laser shots. The change of absorbance of the probe is then calculated by normalization with respect to the transmission of the reference pulses and by comparison between excited and unexcited cases on two subsequent laser shots. The time resolution in these UV pump/ IR probe experiments was ~150 fs.

Computational Methods. Ab initio calculations were performed by using Gaussian 09.⁵⁰ The ground and excited electronic state geometries of DHAQ and DHAQ/ACN (1:1) complexes were optimized at the B3LYP/6-31G* level for different hydrogen-bonding states, in either the gas phase or embedded in a dielectric continuum (see the Supporting Information). The same level of ab initio methods was applied for calculations of molecular orbitals, dipole moments, solvation energies, and simulations of absorption, emission, and vibrational spectroscopy. Solvation energies involved in geometry relaxation and calculations of vibrational frequencies, transition energies, and oscillator strengths were performed according to the PCM model as implemented in Gaussian 09.

LINEAR SPECTROSCOPY EXPERIMENTS AND QUANTUM CHEMICAL CALCULATIONS

Figure 1 shows the linear electronic absorption and emission spectra of DHAQ recorded in TCE, ACN, DMSO, and MeOH. The electronic absorption band is located in the 360-450 nm wavelength range. A small hypsochromic shift of 6 nm, accompanied by a modest additional spectral broadening, can be noted when going from nonpolar TCE to polar MeOH. This absorption band, with a maximum at 432 nm in TCE, shows a substructure due to Franck-Condon progressions. Comparing the reported 0-0 transition of DHAQ in a Shpol'skii matrix of octane at 10 K at 473.46 nm $(21121 \text{ cm}^{-1})^{11,13-15}$ with the room-temperature spectra recorded in TCE (our measurements) and in polyethylene¹⁶ suggests a hypsochromic shift of about 20 nm between these two cases, making the location of the 0-0 transition of DHAQ in TCE at room temperature closer to that of gas-phase DHAQ measured in a free jet expansion.11

Upon excitation at 400 nm, fluorescence emission between 450-750 nm is observed for DHAQ solution at room temperature, peaking at 586 nm in TCE and at 582 in MeOH, suggesting similar hypsochromic shifts in the



Figure 1. Electronic absorption and emission spectra of DHAQ in TCE, ACN, DMSO, and MeOH. The experimental spectra shown in panel (a) show only minor solvent-dependent frequency shifts of the $S_0 \rightarrow S_2$ absorption manifold, whereas the fluorescence spectra have solvent-dependent relative contributions of the $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ emission manifolds. The calculated spectra (b) show that the intramolecular hydrogen bonds strongly affect the location of the $S_0 \rightarrow S_2$ absorption transition and that the electronic spectra are dominated by the DHAQ-2HB species.

fluorescence emission bands due to solute-solvent interactions (Figure 1a). The lower wavelength shoulder at around 525 nm, however, increases in magnitude when going from TCE to MeOH. This part of the emission is, however, much smaller for DHAQ in DMSO, which may explain the apparent red shift of the main emission band to 600 nm. Together with the absence of a clear mirror symmetry between electronic absorption and emission bands, this solvent dependence of the relative contributions in the emission bands supports the notion that structural rearrangements occur after electronic excitation of DHAQ ascribed to ESIHT where initially excited 9,10-quinone tautomer converts into the 1,10-quinone form.⁸⁻¹⁸ Dual emission ascribed to be due to both DHAQ 9,10-quinone and 1,10-quinone tautomers in the S_2 and S_1 states, respectively, appears to have a moderate solvent dependence for room-temperature solutions.

The linear FT-IR spectra of DHAQ in TCE, ACN- d_3 , DMSO- d_{6i} and MeOD are shown in Figure 2. Fingerprint bands due to C=O stretching and C=C ring modes are pronounced in all solvents. The O-H/C-H stretching region has its maximum absorption at 3060 cm⁻¹. We assign in line with a previous publication⁵¹ the narrow band located between 3000 and 3100 cm⁻¹ to C-H stretching transitions, suggesting that the broader weaker absorbance extending from 2900 to 3400 cm^{-1} (with a possible tail to lower frequencies) is due to O-H stretching absorption. Empirical relationships between hydrogen bond distances and hydrogen stretching oscillators⁵²⁻⁵⁵ would suggest then a weak to medium-strong hydrogen bond for the intramolecular hydrogen bonds between the OH and C=O moieties in DHAQ, with an $O \cdots O$ distance of 2.65–2.75 Å. These findings are, however, not in accordance with previously reported values for the O…O distance of 2.49⁵⁶ and 2.535 $Å^{57}$ from X-ray diffraction data obtained on DHAQ crystals but are more in line with quantum chemical calculations that rather indicate an O…O distance of 2.569-2.608 Å. 18,58 In fact, our DFT optimized structures have $O{\cdots}O$



Figure 2. Experimental (a) and calculated (b) FT-IR spectra of DHAQ in TCE, ACN- d_3 , and DMSO- d_6 .

distances of 2.58 Å in DHAQ-2HB, 2.60 Å in DHAQ-0HB, and 2.56 and 2.61 Å in DHAQ-1HB.

To discern the contributions of the DHAQ tautomers with different hydrogen bond geometries in the linear FT-IR and UV/vis, we determined the relative energetics of DHAQ 9,10quinone tautomers with 0, 1, and 2 intramolecular hydrogen bonds (abbreviated as DHAQ-0HB, DHAQ-1HB, and DHAQ-2HB, respectively; see Figure 3). 1,10-Quinone tautomers turned out to have no local minima in these calculations, making them unstable species relaxing back to the 9,10-quinone tautomer when DHAQ was in the electronic ground state. Having each intramolecular hydrogen bond contribute with an energy stabilization of 12 kcal/mol results in having DHAQ- 2HB as the only relevant tautomer in the gas phase under room-temperature conditions. This can also be stated when embedding DHAQ in nonpolar TCE. In polar solvents like ACN or DMSO, one could envisage the situation where an intramolecular hydrogen bond is broken to be replaced with a hydrogen bond with a solvent molecule. However, the hydrogen bonds with these solvent molecules are much weaker, and DHAQ-2HB remains the preferred geometry in ACN or DMSO. These findings fully support the notion that the experimentally measured FT-IR spectra of DHAQ in TCE, ACN- d_{31} and DMSO- d_{6} are in agreement with the theoretical IR-active transitions of fingerprint modes calculated for the DHAQ-2HB configuration (see Figure 2). With respect to a comparison between experimental and calculated O-H stretching transitions, we note that anharmonic couplings to hydrogen bond low-frequency modes⁵⁹ and Fermi resonances with fingerprint modes such as the O-H bending degree of freedom have not been implemented in the calculated O-H stretching transitions. As a result, the calculated O-H stretching frequency is only a first approximation indicative of the hydrogen bond strength.

The electronic absorption spectra are also governed by the electronic absorption spectra of the DHAQ-2HB configuration. Here, we observe that the existence of intramolecular hydrogen bonds strongly affects the location of the calculated electronic absorption band (see Figure 1b). Interestingly, for the DHAQ-2HB configuration, the oscillator strength to the first electronic excited state S_1 is calculated to be small. Instead, electronic excitation occurs to the second electronic excited state S_2 (see Table 1). In contrast, after structural relaxation, fluorescence emission is calculated to have the largest cross section for the $S_1 \rightarrow S_0$ transition, indicative of large changes in electronic charge



Figure 3. Calculated minimum-energy structures of DHAQ-0HB, DHAQ-1HB, and DHAQ-2HB.

Table 1. Vertical Transition Energies (eV), Wavelengths (nm), and Oscillator Strengths (f) for DHAQ Optimized in the S₀-State without Internal H-Bonds (0HB), with two Internal H-Bonds (2HB), and in the S₁ State with Two Internal H-Bonds

S ₀	eV	nm	f
(0HB)			
1	2.6402	469.59	0.0000
2	3.1866	389.08	0.0000
3	3.2684	379.34	0.1543
4	3.4224	362.27	0.0001
5	3.9451	314.28	0.0174
6	4.2360	292.69	0.0000
7	4.6227	268.21	0.1406
8	4.8285	256.77	0.0372
9	4.8313	256.62	0.0148
10	4.9033	252.86	0.0004
S ₀	eV	nm	f
	((2HB)	
1	2.8834	430.00	0.0000
2	2.9209	424.47	0.2173
3	3.1761	390.36	0.0066
4	3.5770	346.62	0.0001
5	3.6271	341.83	0.0000
6	4.4697	277.39	0.1295
7	4.5250	274.00	0.0069
8	4.6652	265.77	0.0024
9	4.6933	264.17	0.0000
10	5.0572	245.17	0.0000
S ₁	eV	nm	f
	((2HB)	
1	2.1521	469.59	0.1745
2	2.4030	389.08	0.0000
3	2.9171	379.34	0.0000
4	3.1696	362.27	0.0365
5	3.3533	314.28	0.0307
6	3.6693	292.69	0.0361
7	4.3056	268.21	0.0235
8	4.3654	256.77	0.0000
9	4.4235	256.62	0.0741
10	4.8621	252.86	0.0000

distribution and nuclear equilibrium positions, in line with the absence of mirror symmetry between the measured electronic absorption and emission spectra. This comparison shows that internal conversion between the S_2 and S_1 states occurs at times well within the fluorescence lifetime of the S_1 state. The experimental fluorescence emission spectra, however, indicate the existence of two emission bands. This suggests that the energy separation between the S_2 and S_1 states after structural and solvent relaxation is on the order of kT.

In line with previous reports on DHAQ, our geometry optimizations show that the most stable configuration of DHAQ in the S_2 state is of the 9,10-quinone form with two intramolecular hydrogen bonds, whereas DHAQ in the S_1 state has a 1,10-quinone form with only one intramolecular hydrogen bond (see the Supporting Information for more details on the geometry optimizations).

RESULTS AND DISCUSSION OF TIME-RESOLVED EXPERIMENTS

Having established a detailed picture of the role of the different electronic excited states, as well as the relative stabilities of intramolecular hydrogen bonds compared to hydrogen bonds between DHAQ and (polar) solvents molecules, we have the right frame to present and discuss the experimental results of the ultrafast UV/IR pump-probe, UV/vis pump-probe, and time-resolved fluorescence experiments.

Figure 4 shows an overview of the response of DHAQ in the mid-IR spectral region upon electronic excitation at 400 nm.



Figure 4. Transient IR spectra of DHAQ in TCE, ACN- d_3 , DMSO- d_6 , and MeOD.

For all solvents used, the response of fingerprint modes can be summarized as follows. Within the time resolution (150 fs), bleach signals due to ground-state vibrational modes and absorption signals due to excited-state vibrational transitions appear throughout the fingerprint region. The excited-state fingerprint patterns rearrange on a time scale ranging from tens to hundreds of picoseconds, by spectral shifting, partial decay, as well as appearance of new absorption bands. These vibrational dynamics are accompanied by a partial refilling of ground-state bleach contributions. The relative magnitudes of these different features appear to be solvent-dependent. To illustrate the different contributions in more detail, we present in Figure 5 transient UV pump/IR probe spectra of DHAQ in TCE at particular pulse delay ranges. In Figure 5a, the early response shows the appearance of, in particular, an excited-state band at 1419 cm⁻¹ within the time resolution, followed by frequency upshifting to a value of 1429 cm⁻¹, accompanied by spectral narrowing with a characteristic time constant of 8.7 ps. We ascribe the frequency upshifting/spectral narrowing to intramolecular vibrational redistribution and vibrational cooling, based on previous similar observations in numerous



Figure 5. (a) Transient IR spectra of DHAQ in TCE recorded on a time scale of vibrational cooling dynamics; (b) transient IR spectra of DHAQ in TCE on longer time scales indicative of electronic excited-state decay, ground-state recovery, and triplet-state formation.

cases.^{60–65} Figure 5b shows that on a time scale of several hundreds of picoseconds, the excited-state band at 1429 cm⁻¹ decays, accompanied by appearance of new fingerprint bands, for example, at 1365 and 1389 cm⁻¹. We have also observed that the appearance of these new fingerprint bands occurs on a similar time scale as the (partial) bleach recovery. This strongly suggests that DHAQ in TCE reaches a quasi-equilibrium within the S₂ and S₁ states within the time resolution, with additional energy dissipation to the solvent within 40 ps, but that subsequent electronic excited-state decay from the S₂/S₁ states follows a pathway branching into either the electronic ground state or another state with a lifetime clearly longer than 1 ns. Similar conclusions can be drawn for DHAQ in the other solvents, although spectral line broadening in the more polar solvents may obscure some of the details.

To substantiate these findings, we have performed timeresolved fluorescence emission measurements. An example measured on DHAQ in ACN is shown in Figure 6. Emission of the electronic excited state of product DHAQ between 490 and 700 nm appears within our time resolution, with a minor change in shape within the first few hundreds of femtoseconds. The decay of the emission band can be fitted with a singleexponential function with a 210 \pm 20 ps time constant. The location and shape of the emission bands at early pulse delay are already close to those of the steady-state emission spectrum. This result again shows that structural rearrangements upon electronic excited-state equilibration with the S_2/S_1 product states is ultrafast, that is, within the time resolution of 150 fs (Scheme 1), in accordance with previous findings of the Tahara and Vöhringer groups.^{42,43} The longer 210 ps decay is then consistent with electronic excited-state decay.

Transient UV/vis pump–probe spectra of DHAQ provide similar information on the electronic excited-state dynamics of DHAQ. Figure 7 depicts transient UV/vis pump–probe spectra of DHAQ in MeOH. Clearly observable is the $S_1 \rightarrow S_0$ stimulated emission contribution between 560 and 720 nm. In addition to that $S_2/S_1 \rightarrow S_n$ excited-state absorption can be seen to occur between 460 and 560 nm. It follows that both the stimulated emission and the excited-state absorption for DHAQ



Figure 6. Transient fluorescence emission spectra of DHAQ in ACN, showing the early (a) and late (b) response. Whereas the emission at 618 nm appears within the time resolution (d), its exponential decay can be fitted with a 210 \pm 20 ps time constant (c).

in ACN decay with a similar 210 ± 30 ps time constant as the time-resolved fluorescence data, whereas in MeOH, the kinetics can be fitted with an averaged 190 \pm 30 ps time constant. A comparison between transient UV/IR pump-probe, UV/vis probe, and time-resolved fluorescence measurements shows that in all solvents investigated, this long time component ranging from 139 (DMSO) to 210 ps (ACN) can be ascribed to population decay out of the S₂/S₁ manifolds.

Depending on the method used, early time components in the transient signals can be observed. The magnitudes of these components relative to the long population decay component are also dependent on the solvent used. We compare the transient absorbance of the 1190 cm⁻¹ band of DHAQ measured in TCE, ACN- d_3 , and DMSO- d_6 in Figure 8a. Whereas the transient response in TCE can be described with a single-exponential decay function (fitting time constant of 147 \pm 25 ps), double-exponential fits for ACN- d_3 (20 \pm 3 and 180 \pm 30 ps) and DMSO- d_6 (35 \pm 3 and 139 \pm 32 ps) appear to be more appropriate. A comparison of data measured on DHAQ in ACN/ACN-d₃ using transient UV/IR pump-probe, transient UV/vis pump-probe, and time-resolved fluorescence show that the long time component is similar, but the relative contributions at early pulse delay are dependent on the method used (Figure 8b). To discern these early time dynamics, a modeling of ultrafast intramolecular vibrational redistribution, excess vibrational energy dissipation and cooling, as well as solvent shell reorganization dynamics would be required. As the different mechanisms translate with a different degree for the methods used, such a modeling would be rather involved. This is beyond the purpose of the current study.

To illustrate the intricacies of the electronic excited-state dynamics between 9,10-quinone and 1,10-quinone first singlet states, we have rescaled the transient UV/vis pump-probe spectra of DHAQ at the long wavelength stimulated emission



Figure 7. Transient UV/vis pump-probe of DHAQ in MeOH at early pulse delay times (a) and at later delay times (b), showing the excited-state absorption contribution between 460 and 560 nm and the stimulated emission between 560 and 720 nm. Kinetics can be exponentially fitted to an exponential decay function (c) with a time constant of 190 ± 25 ps for the transient absorption at 486 nm and of 180 ± 20 ps for the transient stimulated emission contribution at 632 nm.

part to correct for electronic excited-state decay effects (see Figure 9). With this, one can distinguish between the relative contributions of excited-state absorption and stimulated emission contributions and identify possible effects of frequency shifts caused by intramolecular vibrational relaxation, cooling, and solvation dynamics (including hydrogen bond dynamics). It appears that on a time scale of tens to hundreds of picoseconds, the stimulated emission between 560 and 720 nm does not change in shape in TCE, only slightly in ACN, but more so in MeOH as the solvent. Reshaping of the stimulated emission may suggest a long time component in the solvation dynamics, for example, hydrogen bond interactions, albeit a general understanding now has indicated that room-temperature hydrogen bond dynamics has its major contributions on subpicosecond time scales.^{66–72} Longer time components well extending into the picosecond time regime have been reported on numerous occasions with transient electronic vibrational spectroscopic studies, which may have its roots in more collective motions of hydrogen bond networks or in interfacial aspects of hydrogen bond donor and acceptor interactions.^{73,74} Interestingly, in the same time range, the excited-state absorption increases in relative magnitude in TCE and in MeOH but less so in ACN. From this seemingly puzzling result, one can conclude that the relative contribution of stimulated emission of the 9,10-quinone S₂ state decreases significantly compared to that of the 1,10-quinone S_1 state. This



Figure 8. (a) Population kinetics of DHAQ in TCE (black), ACN- d_3 (red), and DMSO- d_6 (blue) extracted from the 1190 cm⁻¹ band in transient IR spectra with single-exponential fit for TCE (time constant 147 ± 25 ps) and double-exponential fits for ACN- d_3 (20 ± 3 and 180 ± 30 ps) and DMSO- d_6 (35 ± 3 and 139 ± 32 ps). (b) Comparison of the kinetics for DHAQ in ACN/ACN- d_3 taken from transient UV/IR data at 1190 cm⁻¹, transient fluorescence at 618 nm, and transient UV/vis spectroscopic data at 510 nm, scaled to the same initial value.

rather slow exchange dynamics between 9,10-quinone and 1,10quinone states may contradict the observation of ultrafast ESIHT transfer dynamics faster than 150 fs.^{42,43} We suggest that the initial equilibration dynamics between the 9,10quinone S₂ state and the 1,10-quinone S₁ state occurs at elevated vibrational excitations but that the equilibrium populations readjust upon vibrational cooling when DHAQ reaches the energy minima in the excited singlet states. It may be an interesting topic for further research to investigate the role of the intramolecular hydrogen bonds of the OH groups in DHAQ in reaching this transient equilibrium, before the electronic excited states decay electronically. Here, one could envisage a possible interplay of intramolecular vibrational energy redistribution, vibrational energy dissipation to the first solvent shell, and hydrogen bond breaking of the intramolecular hydrogen bond by the solvent molecules in contact with the OH groups in DHAQ.

Considering the obervations of a subnanosecond averaged lifetime of the equilibrated electronic excited S_2/S_1 states of DHAQ and the only partial refill of the electronic ground state, a further investigation is propelled on the long time scale of photophysics of DHAQ. Figure 10 shows transient UV/vis pump-probe spectra of DHAQ in ACN, measured on longer nanosecond time scales. It follows that transient absorption bands persist into the nanosecond time scale. In fact, the excited-state absorption between 460 and 560 nm narrows to 460 and 520 nm, and a new transient absorption band between 570 and 720 nm appears, with the same time constant as that of the stimulated emission in this spectral region, and diminishes



Figure 9. Transient UV/vis pump-probe spectra of DHAQ at a few selected pulse delay times in (a) TCE, (b) ACN, and (c) MeOH, rescaled to the long-wavelength flank of the stimulated emission between 650 and 720 nm, showing the relative increase of excited-state absorption in the 460–560 nm range compared to the stimulated emission contribution at longer wavelengths. The inverted steady-state fluorescence emission spectrum is shown as a dashed gray curve for comparison.

to zero. Only with a 200 ns time constant do these transient absorption bands decay to zero. We suggest that these spectral features on nanosecond time scales are indicative of the first excited triplet state of DHAQ. Considering the fact that the average decay time of the S_2/S_1 electronic excited states and the electronic ground-state recovery and the triplet formation times are similar suggests that a common underlying mechanism is at play here in the photophysics of DHAQ. We propose here that the breaking of the intramolecular hydrogen bond of DHAQ by the solvent has a decisive role in the relaxation dynamics of the S_2 and S_1 electronic excited states of DHAQ into either the triplet state or the internal conversion back into the electronic ground state.

CONCLUSIONS AND PROSPECTS

We have investigated the photoinduced dynamics of DHAQ in TCE, ACN, DMSO, and MeOH. Using previous literature and quantum chemical calculations, we have analyzed the electronic excited-state level schemes to provide the right framework to interpret our observations with time-resolved spectroscopy. On the basis of the results of femtosecond UV/IR pump-probe, femtosecond UV/vis pump-probe, and femtosecond fluorescence measurements presented here, we can draw the following general description of the electronic excited-state dynamics. Upon absorption of a UV photon at 400 nm, the S₂ electronic excited state is reached. Ultrafast equilibration between the S₂ and S₁ excited states occurs faster than 150 fs. As a result, DHAQ exhibits ESIHT dynamics in a similar fashion as that



Figure 10. Transient UV/vis pump-probe DHAQ in ACN at long pulse delay times, showing the appearance of the triplet state at early subnanosecond time scales (a), followed by a decay (b). The population kinetics of the triplet state can be estimated from the transient absorption at 670 nm to decay exponentially with a 200 ns time constant (c) after an increase with a 200 ps time constant (d).

concluded for other ESIHT systems,⁷ with one specific difference, namely, that the population remains distributed between 9,10-quinone (S_2) and 1,10-quinone (S_1) states. After vibrational energy redistribution, vibrational cooling, and solvation dynamics in the 0.1-50 ps time scale, these two electronic excited states decay with an averaged time constant ranging from 139 to 210 ps, depending on the solvent used. Transient UV/vis pump-probe data in MeOH also suggest additional relaxation dynamics on the subnanosecond time scale, which we tentatively ascribe to hydrogen bond dynamics of DHAQ with the protic solvent, affecting the equilibrium population dynamics within the S_2 and S_1 electronic excited states. Subsequent electronic ground-state recovery is only partial as a major fraction of the DHAQ molecules relax into the first triplet excited state. As these time scales are similar, we suggest a key role of solvent-induced breaking of the intramolecular hydrogen bond of DHAQ in the relaxation of the S_2/S_1 electronic excited states to either the electronic ground state or to the first triplet state of DHAQ.

ASSOCIATED CONTENT

S Supporting Information

Full listing of ref 50. Results of geometry optimizations of DHAQ in the electronic ground and first two excited states. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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