

Trapped Hydronium Radical Produced by Ultraviolet Excitation of Substituted Aromatic Molecule

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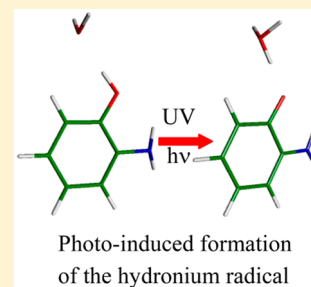
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Supporting Information

ABSTRACT: The gas phase structure and excited state dynamics of *o*-aminophenol-H₂O complex have been investigated using REMPI, IR-UV hole-burning spectroscopy, and pump-probe experiments with picoseconds laser pulses. The IR-UV spectroscopy indicates that the isomer responsible for the excitation spectrum corresponds to an orientation of the OH bond away from the NH₂ group. The water molecule acts as H-bond acceptor of the OH group of the chromophore. The complexation of *o*-aminophenol with one water molecule induced an enhancement in the excited state lifetime on the band origin. The variation of the excited state lifetime of the complex with the excess energy from 1.4 ± 0.1 ns for the 0–0 band to 0.24 ± 0.3 ns for the band at 0–0 + 120 cm⁻¹ is very similar to the variation observed in the phenol-NH₃ system. This experimental result suggests that the excited state hydrogen transfer reaction is the dominant channel for the non radiative pathway. Indeed, excited state ab initio calculations demonstrate that H transfer leading to the formation of the H₃O[•] radical within the complex is the main reactive pathway.



INTRODUCTION

It has long been observed that molecules like indole or phenol dissolved in water can be ionized with photon energy as low as 4.5 eV (the ionization potential (IP) of bare indole is 8.8 eV).^{1,2} Many hypotheses have been presented in the literature concerning the possible mechanism of ionization at such a low energy.^{3,4} One possibility, which has been the subject of strong controversy, is the role of the hydronium radical (H₃O[•]) in the first step of the process.⁵ Although some ab initio calculations suggest the formation of this radical,^{6–8} there was no direct evidence of this process. The existence of the free hydronium radical is also a subject of debate.^{9,10}

The observation of the formation of the ammonium radical cluster NH₄[•](NH₃)_{n-1} after excitation in the first excited state of the phenol(indol)-(NH₃)_n clusters was the first step demonstrating the possibility of radical reactions in both indole and phenol.^{11–13} The H₃O[•] hypothesis was waiting for a simple system for which high level ab initio calculations could be obtained and compared with experiment. In this work, we present experimental results coupled with ab initio calculations, which demonstrate the role of the H₃O[•] radical in the

deactivation process of the first excited state of a model system: the ortho-aminophenol-water complex (*o*-amPhOH-H₂O).

Excited state hydrogen detachment (ESHD) is a key mechanism in the photochemistry of so-called aromatic photoacid molecules (APA), that is, aromatic molecules containing OH, NH, or SH groups or heterocyclic NH groups and excited state hydrogen transfer (ESHT) is the equivalent mechanism in clusters containing these APA molecules with H acceptor molecules.^{14,15}

The ESHT mechanism was first evidenced from the generation of long-lived species occurring after the photoexcitation of PhOH-(NH₃)_n clusters, the long-lived species being neutral NH₄[•](NH₃)_{n-1} radicals, indicating that a photoinduced hydrogen transfer reaction takes place from the aromatic acid to the solvent moiety.^{11,12} The ESHT reaction has been computationally predicted and experimentally confirmed in many APA(NH₃)_n systems with APA = substituted PhOHs (XPhOH),^{16–18} pyrrole,¹⁹ and indole.¹³

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In 2002, the SDDJ model was introduced,¹⁴ which was able to explain, among many other observations, the variation of the phenol S_1 lifetime upon deuteration and complexation with H_2O and NH_3 in terms of the $\pi\pi^*/\pi\sigma^*$ and $\pi\pi/\pi\sigma^*$ conical intersections (CI). Briefly, the X–H ($X = O, N, S$) bond cleavage occurs on a potential energy surface of $\pi\sigma^*$ character, which is dissociative along the X–H coordinate. In most of the molecules, the S_2 ($\pi\sigma^*$) state is located significantly higher in energy than the S_1 ($\pi\pi^*$) state, which provides most of the transition strength. The $\pi\pi^*$ state is bound along the X–H bond stretching coordinate, which results in an avoided crossing with the $\pi\sigma^*$ state at a given X–H distance. In the absence of solvent molecule, the $\pi\sigma^*$ state also develops a second conical intersection (CI) with the ground S_0 ($\pi\pi$) state at longer X–H bond distances, which is removed upon complexation through a H-bond.

Photoexcitation to the $\pi\pi^*$ state, below the energy barrier generated by the first CI is followed by a hydrogen tunneling mechanism from the $\pi\pi^*$ to the $\pi\sigma^*$ state,^{18,20,21} in which the σ^* orbital localized on the X–H substituent, promotes the neutral radical dissociation of the X–H bond or internal conversion (IC) to the ground state via the second CI.

PhOH and substituted XPhOHs are prototype molecules for studying the ESHT reaction, and we will continue the discussion on these molecules although this mechanism holds for most of the APA molecules. Complexation of PhOH with NH_3 or $(NH_3)_n$ enhances the ESHT reaction rate, because it is an energetically open channel in PhOH- $(NH_3)_n$ clusters, leading to the formation of the $NH_4^+(NH_3)_{n-1}$ radicals and the concomitant decreasing excited state lifetime from 2 ns in the PhOH molecule to 1.2 ns in the 0_0^0 transition for the PhOH- (NH_3) complex and up to a few picoseconds for larger clusters.²² At the opposite, the effect of complexation with water is to increase the excited state lifetime of the molecule up to 15 ns, because in this case the ESHT channel is energetically closed at the excitation energy near the 0_0^0 transition of the complex.¹⁴

The grounds for the opposite behaviors in NH_3 and H_2O clusters is the different H affinity (HA) of these molecules that makes the $NH_3 + H \rightarrow NH_4^\bullet$ reaction almost isoenergetic while the $H_2O + H \rightarrow H_3O^\bullet$ reaction is endothermic.¹⁴

Therefore, the ESHT reaction has never been observed or evidenced in clusters of aromatic photoacid molecules with water, and only a few studies have been devoted to $(H_2O)_n$ or mixed $(NH_3)_n(H_2O)_m$ clusters with aromatic molecules. Remarkable examples are the case of mixed 7-Hydroxyquinoline- $(NH_3)_n(H_2O)_m$ ²³ with $n + m = 3$ and p - CH_3 PhOH- $(NH_3)(H_2O)$ ²⁴ clusters, for which it was shown that the presence of the water molecule stops the ESHT reaction in the cluster.

Very recently, it was reported that ortho-substituted XPhOHs have remarkably short excited state lifetimes due to the coupling between the $\pi\pi^*$ and $\pi\sigma^*$ states.^{18,25–28} Particularly interesting is the *o*-aminophenol (*o*-amPhOH) molecule, for which the excited state lifetime for the trans isomer was reported to be 35 ± 5 ps.²⁵ This is because the gap between the $\pi\pi^*$ and the $\pi\sigma^*$ states for this molecule (0.1 eV) is a lot smaller than in PhOH (0.5 eV) leading to an easier access to the $\pi\sigma^*$ state. This is a necessary step to induce fast hydrogen loss in the free molecules and possibly the H transfer in the water complex.

We present here a study of the *o*-amPhOH- H_2O complex, combining spectroscopy with nanosecond lasers, excited state

lifetime determination by picosecond pump–probe experiments and theoretical calculations in the ground and electronically excited states, which show that the ESHT reaction from the aromatic to a water molecule in the gas phase is the most likely mechanism to explain the variation of the lifetime with internal energy.

METHODS

Experimental Section. Jet-cooled *o*-amPhOH- H_2O complexes were generated by expanding He or Ne seeded with water that passed over a reservoir containing *o*-amPhOH maintained at a temperature varying from 338 to 363 K. The *o*-amPhOH (from Sigma-Aldrich Chemie S.A.R.L.) was used without further purification. The backing pressure was 1 bar for Ne or 4 bar for He as buffer gas and the gaseous mixture was expanded to vacuum through a pulsed nozzle of either 300 or 800 μm diameter (solenoid general valve, series 9). The skimmed free jet was crossed at right angle by copropagated laser beams, 10 cm downstream from the nozzle. The ions produced were accelerated perpendicularly to the jet axis toward a microchannel plates detector located at the end of a 1.5 m field-free flight tube.

For the REMPI ($1 + 1'$) spectroscopy, UV beams were generated by SHG of Nd:YAG pumped dye lasers. The IR beam was generated by DFG in a KTA crystal between a Nd:YAG pumped dye laser and 532 nm from the Nd:YAG.

For the time-resolved picoseconds experiment, the third harmonic (355 nm) output of a mode-locked picosecond Nd:YAG laser (EKSPLA-SL300) was split into two parts in order to pump two optical parametric amplifiers (OPA) with second harmonic generation (SHG) systems (EKSPLA-PG411) to obtain tunable UV light. One of the systems was used as excitation laser λ_1 tuned on the different transitions of the molecule. The energy of laser1 was attenuated to preclude one-color two-photon ionization. The other OPA-SHG system was tuned to 310 nm and used as ionization laser λ_2 keeping the energy to approximately 120 $\mu\text{J}/\text{pulse}$. The temporal shapes of both pulses were determined in the fitting procedure to be Gaussian having a full width at half height (FWHM) of 10 ps, while the spectral line width was 15 cm^{-1} . As in the previous work,¹⁸ the measurement of a step function for the excited state lifetime of toluene within the 1.35 ns that can be recorded in the experiment was used as a criterion for a good alignment of the laser beams and gives the cross correlation of the laser temporal widths. Both laser pulses were optically delayed between -350 and 1350 ps by a motorized stage.

Computational. Ground-state calculations for different cis and trans isomers of the *o*-amPhOH- H_2O complex were performed with the Gaussian 09 program package²⁹ at the MP2 and DFT levels with the BHandHLYP and M062X functionals with the Dunning's correlation-consistent split-valence double- ζ basis set with polarization functions on all atoms.

Excited state calculations were performed making use of the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals³⁰ in the MP2 and CC2 theory levels with the TURBOMOLE program.³¹ Vertical excitation energies were calculated at the ground-state equilibrium geometry with the ADC(2) and CC2 methods.³² In addition to the ground-state geometry optimization and vertical excitation energy calculations, the geometry of the lowest excited state was also optimized at the RI-ADC(2) and CC2 levels. For the excited state calculations, two different basis set were used (aug-cc-pVDZ and cc-pVDZ).³³

RESULTS AND DISCUSSION

The REMPI ($1 + 1'$) spectra of the *o*-amPhOH-H₂O complex and free *o*-amPhOH molecule recorded with nanosecond lasers by monitoring the parent ions $m/z = 127$ and 109, respectively, in the spectral range 32900–34300 cm⁻¹ are shown in Figure 1a. Figure 1b shows an enlarged view of the same spectra in the

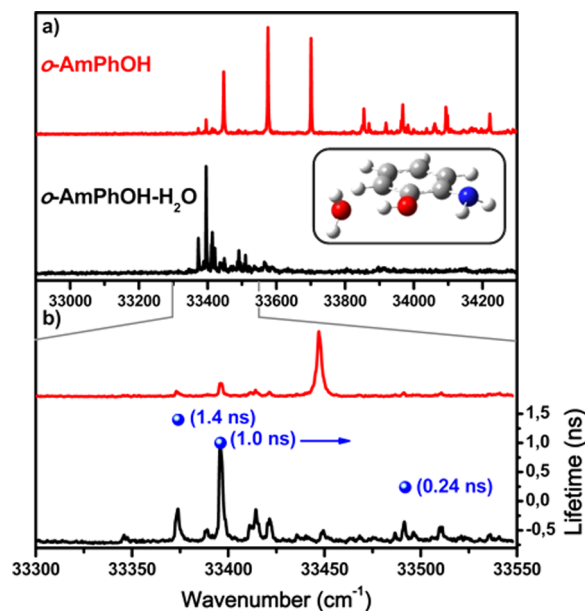


Figure 1. (a) REMPI ($1 + 1'$) spectra of *o*-amPhOH (red trace) and *o*-amPhOH-H₂O complex (black trace) in the (32900–34300) cm⁻¹ spectral region, recorded by integrating the intensity of the parent ions signal. The free molecule shows a long vibrational progression. Some bands in the reddest part of the spectrum of the free molecule are the same as those of the water complex showing that some evaporation of water occurs after ionization of the complex. (b) An enlarged view of the same spectra in the (33300–33550) cm⁻¹ spectral region, together with the excited state lifetime determined upon excitation of different vibrational levels (blue balls and right axis). In the inset, structure of the complex determined from the IR spectrum and ab initio calculations.

spectral range (33300–33550) cm⁻¹. The lowest energy band in the spectrum of the complex at 33374 cm⁻¹ (4.14 eV) was assigned to the band origin, which is red shifted by -73 cm⁻¹ from the band origin of the bare molecule (33447 cm⁻¹).²⁵

The second band is stronger than the origin and this Franck–Condon pattern resembles that of the monomer.²⁵ Almost no bands can be observed at higher energy than $\sim 0_0^0 + 200$ cm⁻¹, showing that a nonradiative process that leads to a product with low ionization efficiency occurs when a small amount of energy is imparted to the excited state. This is very reminiscent of the hydroxyquinoline-(NH₃)₃ cluster in which the migration of the H or H⁺ along the NH₃ wire is observed at small excess energy.³⁴ The intensity of a weak band at 33346 cm⁻¹ depends on the cooling conditions and it becomes weaker under optimal conditions for the main features, suggesting that it is a hot band as observed in the monomer.²⁵

Figure 1b also shows the excited state lifetime recorded with picosecond lasers by exciting different transitions: 0_0^0 (1.4 ± 0.1 ns), $0_0^0 + 22$ cm⁻¹ (1.0 ± 0.1 ns), and $0_0^0 + 120$ cm⁻¹ (0.24 ± 0.03 ns) bands, the last band being assigned to the intermolecular stretching mode σ_0^1 . The excited state lifetime of the complex is larger than the corresponding excited state

lifetime of the bare molecule (35 ± 5) ps,²⁵ as expected for complexation of XPhOHs with water.¹⁴ Remarkably, the excited state lifetime strongly decreases by a factor of 6 upon vibrational excitation in the S₁ state within 120 cm⁻¹. This behavior was already observed in PhOH-NH₃²² and substituted XPhOH-NH₃ complexes¹⁸ for which the shortening of the S₁ state lifetime upon excitation of the σ mode is due to an enhancement of the tunneling rate for the ESHT reaction, which is an open channel in complexes with ammonia. However, this ESHT reaction leading to the free H₃O⁺ release is expected to be energetically closed for complexes with water. Therefore, the excited state dynamics in the *o*-amPhOH-H₂O complex responsible of the shortening of the S₁ state lifetime has to be investigated.

To disentangle the excited state dynamics of the *o*-amPhOH-H₂O complex, it is first necessary to assign its ground-state structure. The bare molecule has two almost isoenergetic isomers, cis and trans, although only the trans isomer can be observed by electronic spectroscopy because the cis isomer has very small Franck–Condon factors to be detected.²⁵ In addition, the water molecule may interact either with the hydroxyl or the amino groups and, on both groups could act as H-donor or H-acceptor. This leads to at least eight possible isomers for the complex. Calculations at different levels of theory (see Supporting Information) indicate that all these isomers are found within 4 kcal/mol and then cannot be ruled out as responsible for the experimental spectrum. Therefore, further information was obtained from double resonance IR–UV spectra of the monomer and cluster, shown in Figure 2.

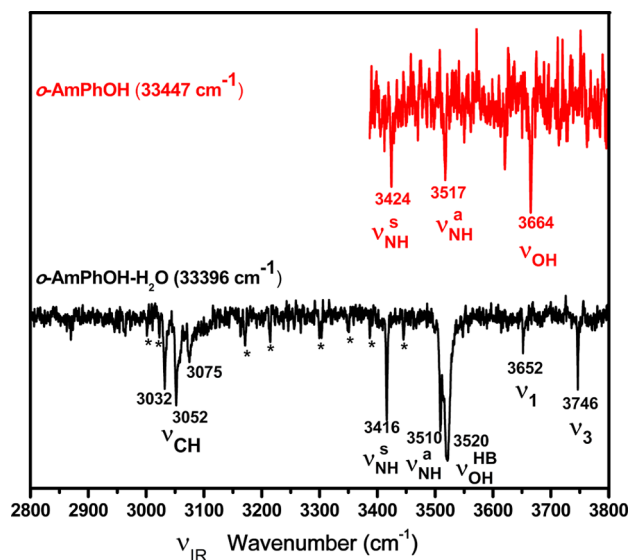


Figure 2. IR–UV double resonance spectra of (upper) *o*-amPhOH monitoring the monomer mass channel by probing at 33447 cm⁻¹ and (lower) *o*-amPhOH-H₂O complex monitoring the complex mass channel by probing at 33396 cm⁻¹. Depletions marked by asterisks (*) are artifacts due to misfires of the pump laser.

The IR–UV spectrum of the bare molecule, recorded on the mass of the monomer by probing the 0_0^0 band at 33447 cm⁻¹ corresponding to the trans isomer, agrees with previous reports^{25,35} and is shown here for comparison with the spectrum of the complex.

The spectrum of the complex, recorded on its own mass by probing the band at 33396 cm⁻¹ presents five absorption bands

in the (3400–3800) cm^{-1} spectral region. In the higher frequency region, two weak bands at 3746 and 3652 cm^{-1} , very close to those of free water molecule, are readily assigned to free OH stretching vibrations of the water molecule indicating that it acts as H-bond acceptor. The strongest feature is a broadened (and saturated) absorption band at 3520 cm^{-1} . In addition, there are two strong sharp bands at 3510 and 3416 cm^{-1} whose positions are red shifted only -7 and -8 cm^{-1} from the NH stretching vibrations of the monomer. This observation suggests that the NH_2 group is kept free from the hydration and that the direction of this group is still trans to the OH group. Therefore, the broad and strong band at 3520 cm^{-1} is assigned to H-bonded OH group that acts as H-donor to the water molecule, which produces a red shift of -144 cm^{-1} as compared to the band of the free OH group that appears at 3664 cm^{-1} in the monomer. The bands in the (3000–3100) cm^{-1} spectral region correspond to the CH stretching vibrations of the complex. Thus, the ground-state structure can be assigned to the trans1 isomer depicted in the inset Figure 1.

To allow the description of the Rydberg type states involved in the $\text{H}_3\text{O}^\bullet$ radical, diffuse functions must be used in the basis set, thus the (aug-cc-pVDZ) basis set was used for the calculations. In addition to the valence $\pi\pi^*$ state, two others states built on Rydberg orbitals lie in the vicinity (within ± 0.2 eV) of this valence state at the S_0 geometry (see Table 1). The

Table 1. Calculated Excited State at the S_0 Geometry at the RI-CC2 Level with the aug-cc-pVDZ Basis Set

	vertical transition energy	transition moment	orbital	%	
S_1	4.44 eV	0.025	36	37%	mainly $\pi\sigma^*$ on NH_2
			35	19%	
			44	12%	
S_2	4.56 eV	0.046	44	40%	mainly $\pi\pi^*$
			35	16%	
			36	5%	
S_3	4.79 eV	0.002	35	62%	mainly $\pi\sigma^*$ on H_2O
			36	33%	
			44	2%	

$\pi\sigma^*$ (NH Rydberg) state is the first excited state (vertical) and the $\pi\pi^*$ and $\pi\sigma^*$ (H_2O Rydberg) states are calculated 0.12 and 0.35 eV higher in energy, respectively (Table 1 and upper panel of Figure 3). It is worth mentioning that the cluster is not planar, thus the distinction between $\pi\pi^*$ and $\pi\sigma^*$ is an approximation, the states being mixed. Both S_1 and S_2 states have similar oscillator strengths. Upon optimization of the S_1 state, the complex acquires a planar symmetry, the hydrogen is transferred to the H_2O partner and the electronic character becomes a pure $\pi\sigma^*$ on OH (see the σ^* orbital of the product in the lower part of Figure 3). The most stable structure in the first excited state is then a radical pair of the type $o\text{-amPhO}^\bullet \cdots \text{H}_3\text{O}^\bullet$, in which the H atom from the OH group of the $o\text{-amPhOH}$ molecule has been transferred to the H_2O molecule. This diradical structure is calculated at 3.81 eV, lower in energy by 0.3 eV than the $\pi\pi^*$ transition (experimental value 4.14 eV). This is in contrast to the $\text{PhOH-H}_2\text{O}$ case for which this excited state reaction is endothermic by 0.8 eV.¹⁴

The H-transferred structure is clearly more stable than the non-H transferred structure, indicating that it is the global minimum in the excited state potential energy surface. It means

that upon electronic excitation of the trans1 isomer to the Franck–Condon region of the S_1 state (non-H transferred structure), ESHT takes place without energy barrier (from calculation) or with a very low energy barrier (from experiment) to produce the radical pair.

The radical pair has a planar symmetry, the NH_2 being in the aromatic ring plane. The OH distances in the hydronium radical are 1.044 Å for the transferred atom and 1.020 Å for the other two out of plane H atoms. The distance between the oxygen atom of the $o\text{-amPhO}^\bullet$ radical and the transferred H atom is 1.556 Å.

Unlike the case of the PhOH-NH_3 complex in which after ESHT the radical pair dissociates to PhO^\bullet and NH_4^\bullet radicals, the threshold for the dissociation of the $o\text{-amPhO}^\bullet \cdots \text{H}_3\text{O}^\bullet$ radical pair is calculated at 5.58 eV at the uMP2/aug-cc-pVDZ level of theory, which is about 1.44 eV above the excitation energy of the complex. This allows trapping the radical pair in a potential well.

The ionization of the radical pair cannot be achieved with the 4 eV photons used in this experiment because the ionization energy of the $\text{H}_3\text{O}^\bullet$ (5.25 eV)³⁶ or the $o\text{-amPhO}^\bullet$ (7.0 eV calculated at the B3LYP/cc-pVDZ level) radicals are much higher. Therefore, once the radical pair is formed, ionization cannot occur and the excited state lifetime measured is directly associated with the ESHT process itself.

Excitation to the 0_0^0 or $0_0^0 + 22$ cm^{-1} bands shows that the ESHT process lifetime is in the order of 1.4–1.0 ns, while excitation to the σ_0^1 band reduces the lifetime of the process to 240 ps. This is the same behavior as observed in the PhOH-NH_3 complex,²² suggesting that at low excess energy the reaction takes place by tunneling through a barrier and that excitation of the intermolecular stretching mode, which is directly connected to the reaction coordinate, reduces the width of the energy barrier or places the system above it. The excited state dynamics discussed can be qualitatively summarized in Figure 4.

The variation of the excited state lifetime points to a nonradiative process occurring in this system, which varies quite rapidly with the excess energy as was observed in PhOH-NH_3 ²² due to the ESHT process. This interpretation of the experimental results relies on calculations, so it is important to know how accurate the calculations are. For once, we have a very good test of the methods through the comparison between theory and experiment on a very similar system (PhOH and PhOH-NH_3). The theory has predicted¹⁴ that PhOH should lose a H atom by tunneling through the $\pi\pi^*-\pi\sigma^*$ barrier, leading to H atom with a small kinetic energy distribution, which has been experimentally verified.^{20,21}

For substituted XPhOH-NH_3 systems, the agreement between experiments and theory is also impressively good, explaining the variation of the excited state lifetime in a complete series of substituted XPhOHs in the framework of the $\pi\pi^*-\pi\sigma^*$ coupling model.¹⁸ It has also been shown that the CC2 method gives equivalent results that those obtained by using multiconfigurational methods.¹⁴

The present system is very similar for both theory and experiment except that NH_3 is replaced by H_2O and thus we demonstrate here the formation of the hydronium radical in the complex through the excitation of the $o\text{-aminophenol}$ molecule.

CONCLUSIONS

This is the first time that the ESHT from an aromatic alcohol to a water molecule has been experimentally evidenced and this

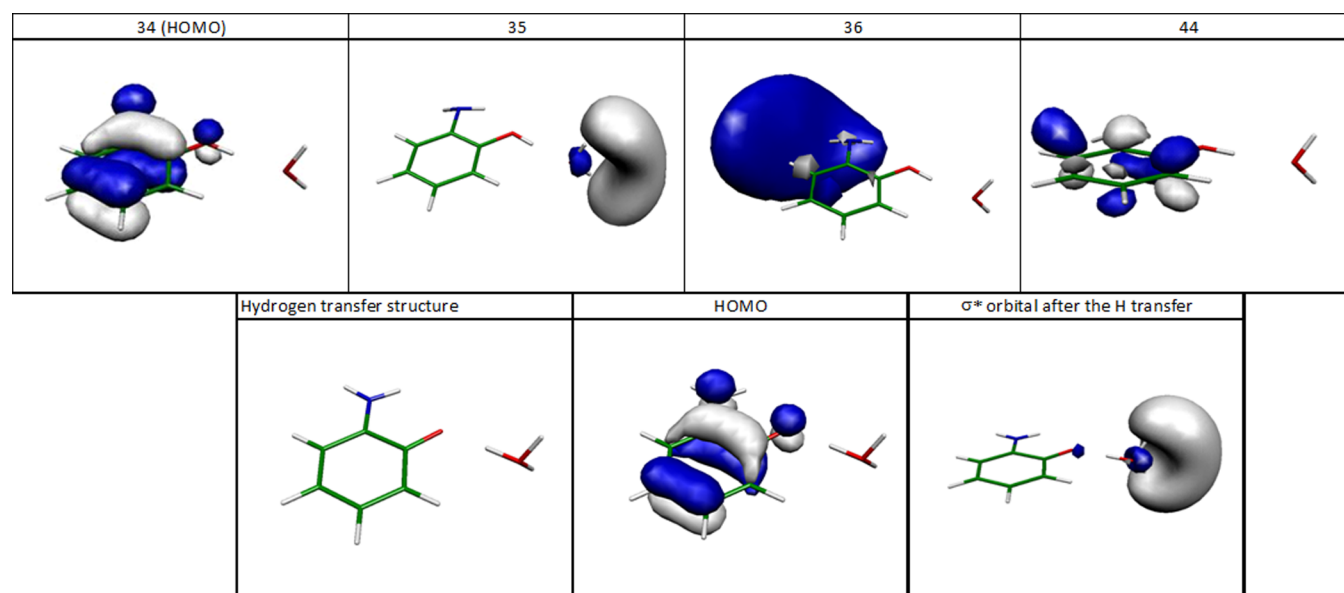


Figure 3. Upper panels: Orbitals involved in the excited states of the *o*-amPhOH-H₂O complex at the ground state geometry. Lower panels: Structure of the diradical and the two orbitals involved in the optimized excited state.

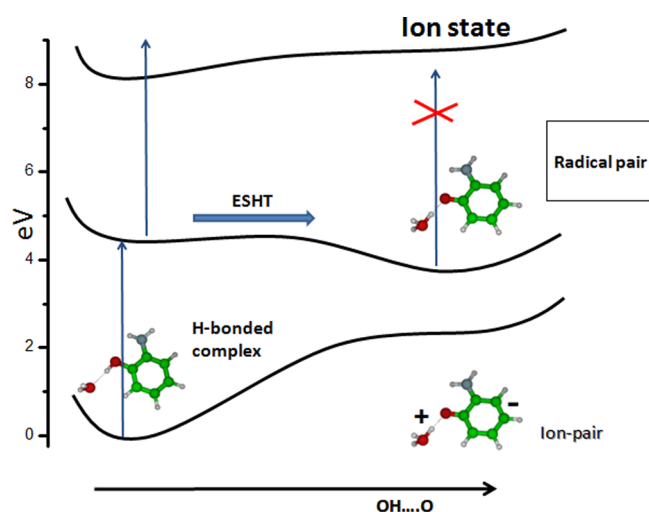


Figure 4. Qualitative scheme of the relevant potential energy curves involved in the excited state dynamics of the *o*-amPhOH-H₂O complex.

opens the possibility of studying this process in an environment more biologically relevant than ammonia clusters. The experimental confirmation of this prediction is not as easy as in the ammonium case due to the instability of the hydronium radical³ and will be a challenge for further experiments. Since H₃O[•] spectroscopy is unknown, we will have to trust ab initio calculations to assign it.

Experiments with deuterated *o*-aminophenol are in progress as well as pump/probe experiment trying to probe the H₃O[•] radical trapped in the radical pair through its optical excitation. This gives the opportunity to obtain spectroscopic signatures of the hydronium radical.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b10142.

Excited state optimized structure (*xyz* coordinates) and structure of the *o*-amPhO[•] ...H₃O[•] complex. Ground-state structures calculated at different theory levels. (PDF)

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Notes

The authors declare no competing financial interest.

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