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ARTICLES

Has the Excited State Proton Transfer Ever Been Observed in Phenol−$(NH_3)_n$ Molecular Clusters?

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A deuterium atom transfer mechanism has been studied in the excited state of perdeuterated phenol−$(ND_3)_n$ clusters and compared to the hydrogen atom transfer process evidenced in phenol−$(NH_3)_{n=1,4}$ cluster excited state. A strong H/D effect is observed implying a tunneling reaction process. In view of these results, the question of the competition between proton transfer and H transfer is raised. An alternative to the excited-state proton-transfer dynamics paradigm is proposed to explain the present and previous observations. Good agreement with experimental observations can be obtained with the following three propositions: excited-state H atom transfer occurs for $n = 1$ to 6; ground-state proton transfer takes place for $n \geq 6$ and direct excitation of ground-state proton transferred structures leads to fast evaporation/relaxation events in the excited state; excited-state proton transfer, although energetically favored for cluster sizes $n \geq 4$, is not observed, probably because its rate is slow compared to the H transfer reaction rate.

Introduction

It has been shown recently that excited phenol−ammonia complexes were reacting through an H transfer mechanism: $PhOH^*{-}(NH_3)_n \rightarrow NH_4(NH_3)_{n-1} + PhO^\bullet$.[1−3] The recent paper of the group of M. Fujii, probing the $NH_4(NH_3)_{n-1}$ radical product coming from the reaction, has definitively assessed that, for small clusters, the $PhOH^*{-}(NH_3)_n$ excited-state dynamics are governed by the H transfer mechanism.[4]

In the 1−1 complex, the reaction is indirectly evidenced by measurement of the excited $PhOH^*{-}(NH_3)$ complex lifetime, which is abnormally short (1 ns or less as compared to lifetimes of the order of 10 ns for other phenol−solvent complexes[5−9]). This lifetime has been shown to be strongly dependent on the intermolecular vibration σ, the excitation of this mode leading to a strong decrease of the lifetime. For larger complexes, the excited-state lifetime decreases to 400 ps for $n = 2$ and down to 50 ps for $n = 3$.[3]

The object of this paper is to discuss the following issues, (i) What is the effect of deuteration on the H transfer mechanism i.e., the D transfer mechanism? (ii) What happens in larger clusters ($n \geq 6$): does the H transfer mechanism still exist when the proton transferred structure is the most stable species in the ground state?[10−13] (iii) What is the reaction mechanism? (iv) Since the H transfer mechanism exists in the excited state, how does it compete with excited-state proton transfer (ESPT)?[14−23] We will present new results on phenol-d_6−$(ND_3)_{n=1,2}$ and on larger phenol-h_6−$(NH_3)_{n>3}$ clusters and propose to reinterpret the data on phenol ammonia clusters. We assume that ESPT is not observed but that H transfer occurs in the excited state for small clusters ($n \leq 6$) and that the direct excitation of ground-state proton transferred species for $n \geq 6$ leads to strong evaporation.

In the following pages, although the products of the excited-state hydrogen transfer reaction are $NH_4(NH_3)_{n-1}$ radicals, which are detected as $NH_4^+(NH_3)_{n-1}$ ions, they will mainly be written as $H(NH_3)_n$ or $H^+(NH_3)_n$ for the ionized radicals, to keep in mind the parent phenol−$(NH_3)_n$ cluster size.

Experimental Section

We have studied the $PhOD^*{-}(ND_3)_n \rightarrow D(ND_3)_n + PhO^\bullet$ reaction using phenol-d_6 (C_6D_5OD) and ND_3 and the same pump−probe scheme as in ref 3. The clusters are produced by expanding a carrier gas seeded with ND_3 flowing over a reservoir containing phenol at room temperature through a 300 μm nozzle. A He/Ne mixture seeded with 0.5% ND_3 is used to study small deuterated clusters, whereas a mixture of 10% ammonia in argon is used for larger clusters. The backing pressure was typically 1.5−2 bar. The pump laser is an unfocused (≈4 mm^2 spot) frequency doubled excimer pumped dye laser, kept at low power (around 80 μJ). The probe ionizing laser is either the third harmonic of a YAG laser (355 nm) with a power between 1 and 5 mJ in a 25 mm^2 spot or a frequency doubled YAG pumped dye laser (200 μJ). The two lasers are synchronized electronically with a 1 ns resolution, but since the laser temporal width is 10 ns, the effective resolution cannot be better than a few ns (∼2 ns). The ions are detected in a 1 m reflectron time-of-flight mass spectrometer (Jordan Co.).

Results

A. Deuterium Atom Transfer. The lifetime of phenol-d_6 and its complexes with ammonia-d_3, obtained with a nanosecond pump (280 nm)/probe (355 nm) scheme are presented in Figure 1. The phenol-d_6 excited S_1 lifetime, as already observed in the

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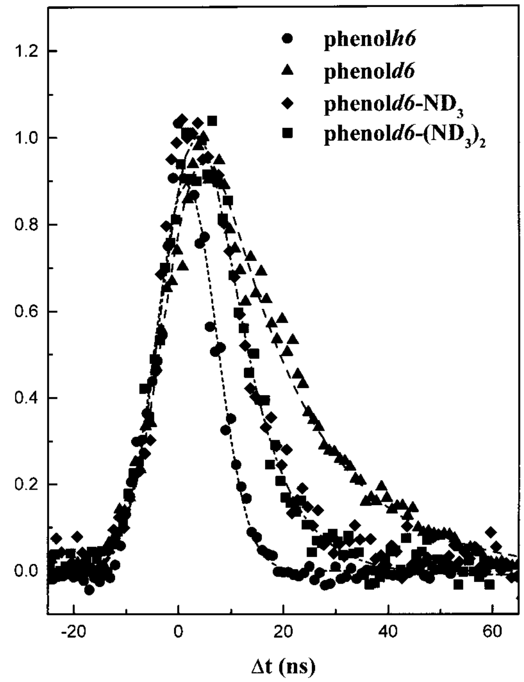

Figure 1. Lifetime measurements: the pump laser is set on the 0−0 transitions: 275.1, 273.8, 278.7, and 279.5 nm for phenol-h_6, phenol-d_6, phenol-d_6−ND_3, and phenol-d_6−$(ND_3)_2$, respectively. The probe laser is set at 298 nm in order to ionize all of these species. The experimental points are fit with a single-exponential decay. The lifetimes are $\tau = 2$ ns for phenol-h_6, $\tau = 16 \pm 1$ ns for phenol-d_6, and $\tau = 7 \pm 1$ ns for phenol-d_6−ND_3 and phenol-d_6−$(ND_3)_2$.

case of phenol-d_1 (C_6H_5OD) by Colson et al.,[7] is longer than that of hydrogenated phenol: 16 ± 2 ns, 16 ns,[7] and 2 ns [6] for phenol-d_6, phenol-d_1, and phenol-h_6, respectively. The lengthening of the lifetime upon deuteration and complexation with water is thought to correspond to a decrease of the internal conversion rate that has been assigned to the reduction in the effectiveness of the OH stretching mode as an acceptor for radiationless transitions.[7]

Phenol-d_6−$(ND_3)_{1,2}$ complexes present a lifetime shorter than that of the free molecule (7 ± 1 ns vs 16 ± 2ns), which may reflect the appearance of a new decay channel.

As seen in Figure 2, the decay time observed when exciting the origin of the 1−2 complex vibronic progression is linked to an increase of the signal recorded on the $D^+(ND_3)_2$ mass. More generally, the decay observed on the parent PhOD−$(ND_3)_{n=2,3}$ signal is seen as a rise time in the $D^+(ND_3)_{n=2,3}$ signal. Thus, it can reasonably be inferred that a deuterium atom transfer mechanism is responsible for the faster decay observed on the complexes. The deuterium transfer reaction is a slow process ($T_{\mathrm{reaction}} \approx 7$ ns) as compared to the hydrogen transfer ($T_{\mathrm{reaction}} = 400$ to 50 ps). Within the experimental uncertainty no dependence with cluster size is observed.

It was not possible to observe the ND_4 rise time in the present experiment: the ND_4 ionization potential (4.60 eV)[24] is such that the ionization laser also excites and ionizes the 1−1 complex (with an energy excess of 1700 cm^{-1} in the excited state and of 6600 cm^{-1} in the ionic state) and an eventual signal due to the D transfer is lost among strong signals due to multiphoton processes and evaporation in the ion.

B. Large Hydrogenated Clusters. Typical mass spectra recorded when large PhOH−$(NH_3)_n$ clusters are excited are presented in Figure 3. A reflectron time-of-flight mass spectrometer is used to ensure a good resolution of the observed mass peaks. The excitation laser is set at 298 nm (33613 cm^{-1}) below the energy necessary to excite small clusters (1−1 to 1−4). The 355 nm third harmonic of a YAG laser is used to ionize the clusters, and the two spectra have been recorded with different delays between the pump and probe lasers ($\Delta t = 0$ and $\Delta t = 400$ ns).

These spectra deserve a few comments. (1) Only PhOH−$(NH_3)_n$ clusters with $n > 4$ can be excited at the wavelength used, but smaller PhOH−$(NH_3)_{n=0-4}$ clusters are readily detected even without delay between the pump/probe lasers. The initial distribution of excited clusters must be drastically affected by evaporation processes in the excited and/or ionic states. The initial cluster size distribution is then certainly shifted to larger masses. (2) When the pump/probe delay is 400 ns, the $[PhOH-(NH_3)_n]^+$ mass peaks are observed with a distribution peaking at low masses ($n = 0-3$), whereas these clusters are not excited. Clearly parent clusters of unknown size are stabilized in a long-lived state and evaporate to produce these small $n = 0-3$ complexes. (3) For clusters with $n \geq 4$, mixed phenol−$(NH_3)_n(H_2O)_m{}^+$ ions appear, despite the overwhelming concentration of NH_3 in the expansion (10% NH_3 in Ar). Traces of water are sufficient to produce mixed clusters. Here, the mass resolution is very good so that there is no problem to discriminate masses differing by one unit, but the presence of mixed ammonia/water clusters may lead to artifacts in experiments where the mass resolution is weaker. (4) $H^+(NH_3)_n$ ions issued from the H transfer reaction are clearly observed up to $n = 5$, $n = 6$ is only weakly observed, and $n = 7$ not at all, whereas the PhOH−$(NH_3)_n$ precursors are definitely observed up to $n = 12$. The $H^+(NH_3)_n(H_2O)$ ion products are also observed up to $n = 6$ at both delay 0 and 400 ns.

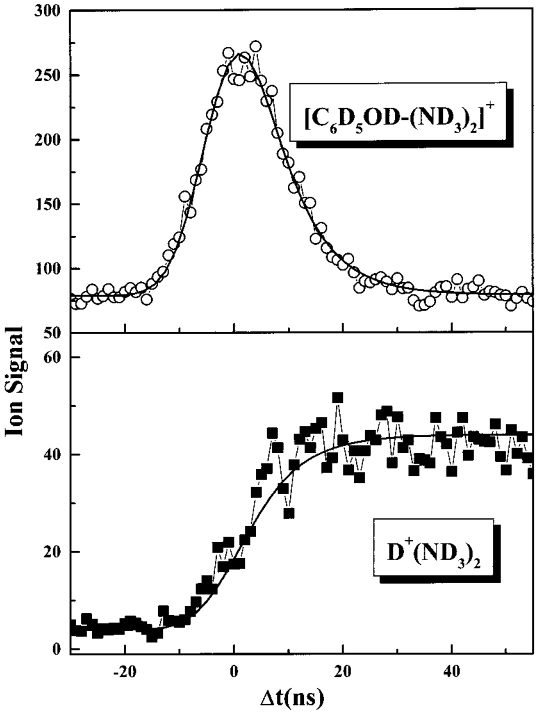

Figure 2. Time evolution of the parent phenol-d_6−$(ND_3)_2$ and product $D^+(ND_3)_2$ signals as a function of the pump/probe delay. The pump laser is set on the phenol-d_6−$(ND_3)_2$ 0−0 transition (279.5 nm) and the probe laser at 298 nm. The solid lines are calculated fits using a decreasing exponential function for the parent and an increasing one for the product with the same time constant $\tau = 7 \pm 1$ ns.

Discussion

A. Excited-State Hydrogen Transfer Mechanism. Although the H transfer reaction in the 1−1 complex has not been

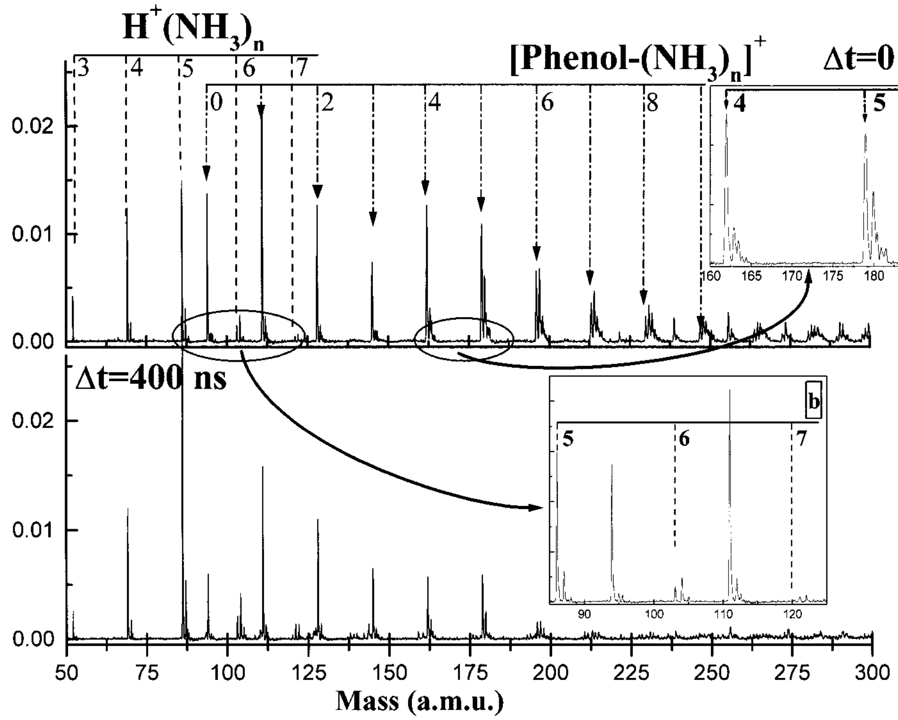

Figure 3. Pump−probe mass spectra of phenol−$(NH_3)_n$ clusters. The pump laser is set at 298 nm to excite clusters with $n > 4$; the probe laser is set at 355 nm. The upper spectrum is recorded without delay between pump and probe lasers. In inset a, an enlarged view of the mass spectrum shows the phenol−$(NH_3)_{4,5}$ ion peaks and the mixed phenol−$(NH_3)_n(H_2O)_m$. The second inset b shows that $H^+(NH_3)_n$ products are detected up to $n = 6$, whereas parent phenol−$(NH_3)_n$ clusters are detected up to $n = 12$. The lower spectrum is recorded with a delay of 400 ns between pump and probe lasers.

definitively observed and characterized, due the very short lifetime of the NH_4 radical (13 ps),[25] the shortening of the excited-state lifetime observed in ref 3 strongly suggests that this process does take place. Let us assume at the moment that the H transfer reaction does happen also in the 1−1 complex.

From an energetic point of view, the H transfer mechanism is one of the most unfavored open channels for small complexes (1−1, 1−2, 1−3). For the 1−1complex, the possible reactive channels are as follows. (a) Internal conversion leading to ground-state phenol + NH_3. The excess energy is then in the order of the S_0−S_1 transition, i.e., 4.43 eV.[26−28] (b) Proton transfer to the ground PhO^- ...NH_4^+ state. Previous studies indicate that the excess energy will be about 1.8 eV for the 1−1 complex.[17,29] (c) Intersystem crossing leading to the PhOH-(T_1)−NH_3 triplet state. Assuming that the S_1−T_1 energy gap is not drastically changed upon complexation, the excess energy can be estimated to be 1 eV,[5,30] enough to lead to evaporation.[5,6] (d) The two channels leading to the excited proton transferred states, either in S_1 or T_1 states, are endoenergetic. For the 1−1 complex, the S_1 (PhO^{-*} NH_4^+) excited state is about 1 eV above the initially excited state S_1(PhOH*−NH_3),[11,17] and the triplet T_1(PhO^{-*} NH_4^+) should be around 0.5 eV below S_1(PhO^{-*} NH_4^+).[30,31] (e) The dissociative H transfer reaction PhOH*(S_1)−NH_3 → $PhO^\bullet$+NH_4 is expected to be exoenergetic by 0.21−0.3 eV (using 4.507 eV for the 0−0 transition[27,32] and 3.9 eV for the dissociation energy in free phenol[33,34]) depending on the ground-state binding energy.[26−28]

Despite its unfavorable energetics, the H transfer channel seems to be a very efficient reactive pathway. What are the possible mechanisms?

(1) Through internal conversion.

$$\mathrm{PhOH^*(S_1)-NH_3 \rightarrow PhOH(S_0,}v,J\mathrm{)-NH_3}$$

$$\mathrm{PhOH(S_0,}v,J\mathrm{)-NH_3 \rightarrow PhO^\bullet ...H...NH_3 \rightarrow PhO^\bullet + NH_4}$$

The first step would be internal conversion leading to very hot vibronic levels of the phenol ground state, the hot complexes would dissociate into $PhO^\bullet$ and H while the H atom would be captured by the nearby NH_3 molecule. This process is quite improbable for the following reasons: (a) The dissociation of the complex in phenol + ammonia (equivalent to an evaporation process in larger clusters) is much more exoenergetic and should be the dominant channel. (b) The binding energy of the H atom to NH_3 is weak. The H + NH_3 → NH_4 reaction being quasi isoenergetic,[25,35−37] there is no driving force to lead the H atom to attach to NH_3 instead of leaving freely the complex.

(2) Through an internal conversion to the ground ion pair state PhO^-−NH_4^+.

$$\mathrm{PhOH\ ^*(S_1)-(NH_3) \rightarrow PhO^-(S_0)-NH_4^+}$$

$$\mathrm{PhO^-(S_0)\text{-}NH_4^+ \rightarrow PhO^\bullet + NH_4}$$

where the former is an internal conversion and the latter is a back electron transfer and dissociation. This process might be more reasonable. The internal conversion would lead to a decrease of the complex lifetime. However in naphthol−NH_3, the first step of internal conversion to the ground state proton transferred state is open, but the lifetime of the complex is essentially the same (38 ns) as that of the free molecule (60 ns).[38] The increase of the nonradiative processes in this complex is weak as compared to the phenol case. In naphthol, conversely to phenol, the second step of the process, leading to the $NpO^\bullet$ radical is not open (the OH bond dissociation energy is 3.6 ± 0.07 eV,[33] the $S_1 \leftarrow S_0$ transition in naphthol−ammonia is 3.87 eV, the ground-state binding energy is 0.332 eV,[39] and the NpOH*(S_1)−NH_3 → $NpO^\bullet$ + NH_4 reaction is slightly endoergic by 0.06 ± 0.07 eV). Indeed, $NH_4^+(NH_3)_n$ ions are not observed in R2PI experiments on naphthol−$(NH_3)_n$ clusters.

(3) Direct mechanism through a barrier. The most probable pathway might be a direct mechanism through a barrier, the reaction proceeding by a tunneling motion along the O...H...N coordinate. In a theoretical paper on indole, Sobolewski and Domcke showed that the third excited state of $\pi\sigma^*$ character was repulsive along the N−H coordinate crossing the excited ^1L_a, ^1L_b states of $\pi\pi^*$ character as well as the ground state.[40] This produces a barrier on the potential energy surface of the lowest excited state with respect to hydrogen detachment. As in the case of phenol clusters, we have evidenced a hydrogen transfer reaction in excited indole−$(NH_3)_n$ clusters for $n = 3$, 4, 5.[41]

Such a predissociation mechanism could be active in phenol and would explain many of the present results.

(a) Lifetimes. In ref 3, we have observed that the lifetime of the PhOH−NH_3 complex was 1.2 ns when exciting the 0−0 band, 390 ps when exciting the intermolecular stretching mode (σ at +182 cm^{-1}), and 470 ps when the phenol intramolecular vibration is excited (+486 cm^{-1}). The decrease of the lifetime observed when the intermolecular stretching vibration is excited can be related to a decrease of the barrier width with the O...H...N motion that would lead to a more efficient tunneling of the H atom.[22,42−44]

(b) Isotopic effect. The reaction rate decreases drastically in the deuterated complex, being typically 10 ns for deuterium transfer to hundreds of ps for the H transfer (1.2 ns for the 0−0 band of the 1−1 complex, 400 ps for the 1−2 and 50 ps for the 1−3). Such a large isotopic effect has been observed in the cases of phenol−$(NH_3)_{n>4}$[20−23] and naphthol−$(NH_3)_{n>3}$[42−44] and have been tentatively assigned to the excited state proton transfer reaction. The measured reaction time assigned to excited state proton transfer is in the order of 50 ps, and the deuteron transfer lies in the ns range. The effect observed here for the H transfer reaction in small clusters is of the same order of magnitude, and consequently a barrier equivalent to that calculated under the ESPT assumption can be expected, i.e., a barrier of 6000 cm^{-1} with a 0.2 Å width.[20−22,42−44]

Note that the isotope effect is even more drastic in ammonium radicals where the NH_4 and ND_4 lifetimes are 13 ps and 10 μs, respectively, for a barrier evaluated to be 0.52−0.65 eV with a half width 0.34−0.4 Å,[36,37] not very different from that calculated for phenol−$(NH_3)_n$.

(c) Formation of $NH_4(NH_3)_{n-1}$ radicals. A repulsive force along the O−H−N coordinate is necessary in order for the $PhO^\bullet$ and $NH_4(NH_3)_{n-1}$ products to escape the van der Waals attraction. When the H atom has crossed the barrier, a strong repulsive force applies between the two reaction fragments.

B. Ground-State Proton Transfer. Another striking result is that large $H^+(NH_3)_{n>6}$ are not observed in the experiment, whereas parent clusters with n up to 12 are observed in the expansion. However, if we refer to the studies of other groups, large $NH_4^+(NH_3)_{n>5}$ are readily observed under various conditions,[45] and $NH_4(NH_3)_{n>5}$ clusters are as stable as the smaller ones.[24]

Ground-state proton transfer can explain the absence of H^+-$(NH_3)_{n>6}$ radical products. The ground-state proton-transfer reaction was postulated to take place for six or seven ammonia molecules from ionization threshold measurements performed with a single VUV photon.[11] If phenol−$(NH_3)_{n\geq6}$ clusters are in a charge transferred ground state, excitation will bring them to the PhO^{-*}−$NH_4^+(NH_3)_{n-1}$ S_1 state (excited ion pair state) with an excess energy, which gives rise to the red-shifted fluorescence observed in solution and in large clusters.[2]

C. Mixed Phenol/Water/Ammonia Clusters. As can be seen in the mass spectra, the expansion also contains mixed phenol/water/ammonia clusters. Despite the fact that no water has been added in the tubing and that the buffer gas was a 10% Ar−NH_3 mixture, the quantity of water is not negligible, due to strong hygroscopic properties of phenol.

Product ions corresponding to mass formulas $H^+(NH_3)_m(H_2O)_p$ are observed when the ionizing laser is set at either $\Delta t = 0$ or at $\Delta t = 400$ ns. As in the case of $H^+(NH_3)_n$, these ions come from an excited-state reaction, indicating that (i) the product structure must be $NH_4(NH_3)_{m-1}(H_2O)_p$: the $H + H_2O \rightarrow H_3O$ reaction is endothermic,[46−49] and oxonium radicals, unlike ammonium radicals, are not stable (nor metastable) with respect to dissociation.[50,51] Calculations place the H_3O radical 1 eV above the $H+H_2O$ limit.[46−49] Thus, $H_3O(NH_3)_m(H_2O)_{p-1}$ radicals, even if they are metastable species, are not accessible with the excitation energy used here. (ii) The H transfer reaction is not strongly affected by the presence of water and the mixed $NH_4(NH_3)_{m-1}(H_2O)_p$ radicals are as stable as the $NH_4(NH_3)_n$ clusters.

Assuming that large phenol−$(NH_3)_m(H_2O)_p$ ($m + p > 5$) and phenol−$(NH_3)_n$ ($n > 5$) clusters have equivalent absorption/ionization efficiencies, the intensity ratio of the peaks indicates that the water is in a 10% proportion. The presence of the H transfer reaction also implies that the mixed clusters favor structures where the phenol makes an hydrogen bond with ammonia and not with water, at least for the isomers we have observed. This would be coherent with a PhOH−NH_3 bond stronger than the PhOH−H_2O bond,[26,28−29,52−53] as in the case of naphthol.[39]

D. Hydrogen Transfer versus Proton Transfer. Since recent experiments[1−4] have evidenced the H transfer reaction in PhOH−$(NH_3)_n$ clusters with $n = 1$ to 6, the question comes up whether excited-state proton transfer (ESPT) has been observed or not. The previous experimental results, which suggested ESPT observed include: the appearance of a red shifted fluorescence when large clusters are excited;[15,30,54−58] the appearance of the $NH_4^+(NH_3)_n$ fragments when large ($n > 2$) clusters are present in the expansion;[16−23] the ionization threshold decrease for phenol−$(NH_3)_4$[14,15] and naphthol−$(NH_3)_4$;[59−6] the fast picosecond decays observed on PhOH−$(NH_3)_{n=5,6,7}$ together with the absence of decays for smaller clusters when proton transfer is not expected;[16−22] and the slower decays observed upon deuterium substitution, indicating a tunneling mechanism.[20−23,42−44]

However, the new results on hydrogen transfer in small PhOH−$(NH_3)_n$ clusters cause some contradictions to appear. The H transfer mechanism for the 1−2 and 1−3 clusters is in the 100/50ps regime. Since the energetics of this reaction should be more favorable in larger clusters,[24,37] the reaction should be even faster for larger clusters ($n = 4$ to 6). The $H^+(NH_3)_{4,5}$ signals observed with delayed ionization are strong, indicating that H transfer is strongly allowed for $n = 4$ and 5 (Figure 3). So a lifetime shorter than 50 ps is expected for PhOH−$(NH_3)_{n=4,6}$. The previous kinetic measurements performed by J. Steadman and J. A. Syage did not show clearly marked decays for the $n = 4$ and smaller clusters: if the reactive processes were the only processes occurring, a picosecond decay due to the H transfer reaction should have been observed on the mass peaks corresponding to 1−2, 1−3, and 1−4 clusters, but nice decays are only reported for the 1−5, 1−6, 1−7 clusters.[16−22] Other processes are then obscuring the signals observed on small PhOH−$(NH_3)_n$ clusters, the most likely being evaporation (in these experiments, the excess energy is 0.23−0.28 eV in the excited state and more than 2 eV in the ionic state). The problem of evaporation in phenol-ammonia clusters has already been outlined by Hineman et al., who observed picosecond decays for the 1−1, 1−2, and 1−3 clusters, depending on the ammonia concentration and on the excitation/ionization energy.[23] These evaporation problems seem also important in the picosecond decays observed for naphthol$-(NH_3)_{n=3,4}$ clusters.[61]

Another set of assumptions can be put forward to account for the ensemble of picosecond and nanosecond experiments. (i) For small cluster sizes ($n = 1-5$), the dynamics is mainly governed by the H transfer mechanism. (ii) For larger sizes ($n > 6$), proton transfer has occurred in the ground state and direct excitation of the $PhO^{-}-H^{+}(NH_3)_n$ proton transferred species in the vicinity of 280 nm (4.43 eV) leads well above the $PhO^{-*}-H^{+}(NH_3)_n$ 0−0 transition.[15,30] The excess energy can lead to fast IVR, intersystem crossing, and evaporation processes.

The $PhOH-(NH_3)_6$ cluster seems to be an intermediate case: $H^{+}(NH_3)_6$ ions are observed only weakly, indicating that the H transfer is less efficient, and one photon ionization thresholds indicate that ground-state proton transfer has occurred. It could be that, for the 1−6 cluster, the two ground-state structures, neutral and ion pair, are isoenergetic.

Under these assumptions, the results used to ascertain ESPT can all be reinterpreted. (i) The red-shifted fluorescence can be assigned to the fluorescence of the charge transferred species directly excited. (ii) The $H^{+}(NH_3)_n$ fragments in the mass spectra are due to the H transfer in the excited state and are not connected to proton transfer, in the excited or ground state.[11] (iii) The lowering of the ionization threshold observed for the 1−4 complex in a two-color two-photon experiment[14,15] but not in single VUV ionization experiment[11] can be assigned to evaporation from large clusters in the excited and ionic states. A 1−6 cluster (proton transferred structure in the ground state) excited at 280 nm can undergo an evaporation in the excited state, the resulting 1−5 cluster can absorb one or two photons and evaporate another ammonia unit in the ion. (iv) The pump/probe picosecond dynamics observed for phenol$-(NH_3)_n$ $n =$ 5, 6, 7[16−22] can be due to direct excitation of the ground-state proton transferred species followed by fast IVR and evaporation of ammonia units (50 ps). Indeed, in systems where GSPT is not expected such as phenol$-CH_3OH$, phenol$-(H_2O)_n$,[17,21−22] naphthol$-H_2O$,[41] the excess energy in the first excited state is a lot smaller so that IVR and evaporation are slower and no picosecond decays are observed.

E. Competition between Hydrogen and Proton Transfer? As already stated above, 1−4 and 1−5 clusters can energetically undergo both hydrogen and proton transfer in the excited state, and the question of competition between these mechanisms is open.

Let us first discuss the reaction mechanisms. The H transfer occurs for very small cluster sizes, indicating that it is not controlled by the solvent. The process is certainly affected by solvent effects since the reaction rate increases with the cluster size, but the effect is rather weak. The solvent reorganization around the $PhO^{\bullet}-NH_4$ product before the dissociation is expected to be small since the charge distribution is not greatly affected by the hydrogen motion.

On the contrary, the proton transfer reaction should be strongly driven by the solvent. This has been thoroughly discussed in refs 20−22 by Syage using the Hynes/Borgis[62] or Cukier/Morillo scheme,[63] where it is shown that the reaction does not proceed if there is no solvent rearrangement: the proton transfer channel is energetically closed if the solvent stays in the configuration it has around the neutral phenol$-(NH_3)_n$ species. In this scheme, the reaction is strongly controlled by the $\Delta G^{\#}$ value through an $\exp(-\beta\Delta G^{\#})$ term where $\Delta G^{\#}$ is the free energy of activation and $\beta = 1/kT$. This $\Delta G^{\#}$ value is strongly dependent on the solvent reorganization energy: this reorganization energy is not known but it should be possible to get an estimation using molecular dynamic simulations. According to these models, the ESPT reaction requires first the reorganization then a tunneling process and should be slower than the H transfer mechanism in which only the tunneling process is required. Thus ESPT is not expected to be competitive with H transfer.

As a matter of fact, the key point to ESPT is the solvent free energy of activation $\Delta G^{\#}$, and most particularly the comparison between $\Delta G^{\#}$ and the energy necessary to evaporate one NH_3 molecule, E_{evap}. If E_{evap} is smaller than $\Delta G^{\#}$, it will be impossible to observe ESPT: each time energy will be added to overcome the $\Delta G^{\#}$ barrier, the cluster will cool by evaporation before ESPT can proceed.

Conclusion

The excited state hydrogen transfer reaction in small phenol ammonia clusters seems now a well established mechanism. The comparison with deuterated clusters indicates that the reaction likely proceeds by tunneling through a barrier. The reaction is not greatly affected by adding small amounts of water in the solvent: the mechanism is robust. The presence of this hydrogen transfer channel makes it necessary to reanalyze previous experiments, especially experiments on the picosecond dynamics. A good agreement with experimental observations can be obtained using three hypotheses: (1) excited-state H atom transfer occurs for $n \leq 6$, (2) ground-state proton transfer takes place for $n \geq 6$ and direct excitation of ground-state proton-transferred structures leads to fast evaporation events in the excited state, and (3) excited-state proton transfer, although energetically favored for cluster sizes $n \geq 4$, is not observed, probably because its rate is too low as compared to the H transfer reaction rate: the important solvent rearrangement required for ESPT makes it an unlikely mechanism in cold clusters.

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