

A forgotten channel in the excited state dynamics of phenol-(ammonia)_n clusters: hydrogen transfer

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Small phenol-(NH₃)_n clusters have been studied through two-color two-photon and one-photon VUV ionization, in order to disentangle the contributions of various dissociation or reaction paths in the excited and ionic states. The most striking result of the two-color experiment is that (NH₄)⁺(NH₃)_{n-1, 5} fragments are observed with large delays (up to a few hundred nanoseconds) between the excitation and ionization lasers, whereas these same fragments are not observed in the VUV one-photon ionization experiment. In order to account for these findings, a new deactivation channel in the excited state of phenol-(NH₃)_n clusters has to be introduced: the hydrogen atom transfer PhOH(S₁)-(NH₃)_n → PhO[•] + (NH₄)(NH₃)_{n-1}. In this case, the delayed (NH₄)⁺(NH₃)_{n-1} signals correspond to direct ionization of the (NH₄)(NH₃)_{n-1} clusters produced in the excited state.

Introduction

Proton transfer is an important primary process involved in many chemical reactions and biological processes. In the gas phase, numerous studies have been performed to characterize this process in both neutral and ionic clusters. Excited state proton transfer (ESPT) has been observed and well characterized in two model systems: naphthol-ammonia¹⁻¹⁰ and phenol-ammonia.¹¹⁻¹⁸ In these systems, the ESPT results from the coupling of the first covalent excited state [phenol(S₁)-(NH₃)_n] with the ion pair excited state [PhO^{-*}-(NH₄⁺)(NH₃)_{n-1}] (phenolate anion excited state-protonated ammonia cluster).

The first observation of the ESPT appearance as the cluster size increases was carried out by monitoring the characteristic fluorescence of the naphtholate anion.^{1,2} Later, ionization potential measurements through a two-photon ionization scheme were achieved for both phenol^{11,12} and naphthol⁸ ammonia clusters, where the strong ionization potential decrease for *n* = 4 in the phenol-(ammonia)_n clusters (and *n* = 3 in naphthol-(NH₃)_n) was assigned to a signature of ESPT.

In benchmark time resolved experiments, the ESPT dynamics was studied using a picosecond pump-probe scheme with ion detection (in both naphthol⁵⁻¹⁰ and phenol clusters¹³⁻¹⁸). Picosecond decays were observed on [NaphOH-(NH₃)₃]⁺ as well as on [PhOH-(NH₃)_{n ≥ 5}]⁺ and were ascribed to the ESPT dynamics.

The most important features of the time resolved experiments on phenol-ammonia clusters are as follows. (i) The very clear picosecond decays observed at the mass of PhOH-(NH₃)_{n=5-7} (ref. 13-17) in the pump-probe experiments have been shown to depend on the probe laser wavelength. (ii) A corresponding a rise time is observed on the protonated ammonia clusters (NH₄⁺)(NH₃)_{n > 4}. (iii) This dynamics is not observed for clusters with less basic molecules (water, methanol, ...).

So far these data have been rationalized as follows.¹³⁻¹⁷ (i) The starting point is the non-proton-transferred cluster in the neutral ground state and, at time *t* = 0, the cluster is excited to the non-transferred part of the excited state potential energy surface (Fig. 1, arrow 1). (ii) The major dynamical

process which is evidenced is the proton transfer from PhOH* to (NH₃)_n on a time scale of 60 to 70 ps, while a longer time component is assigned to solvent reorganization. (iii) This process is detected by ionizing the excited phenol-ammonia cluster. If the excited cluster is ionized before proton transfer, then the ion observed is (PhOH-(NH₃)_n)⁺ (Fig. 1, arrow 2). In contrast, if ionization takes place after ESPT, the PhO⁻NH₄⁺(NH₃)_{n-1} part of the ionic surface is reached and because of the excess energy in the PhO⁻NH₄⁺(NH₃)_{n-1} ion, fragmentation into PhO[•] + NH₄⁺(NH₃)_{n-1} occurs: the PhO⁻NH₄⁺(NH₃)_{n-1} ion signal is no longer detected, and the NH₄⁺(NH₃)_{n-1} fragment becomes observable (Fig. 1, arrow 3). This accounts for the decay observed on the (PhOH-(NH₃)_n)⁺ masses as well as for the growth observed on the fragment NH₄⁺(NH₃)_{n-1} masses.

The above interpretation implies the existence of a significant barrier on the ionic surface between the non-proton-

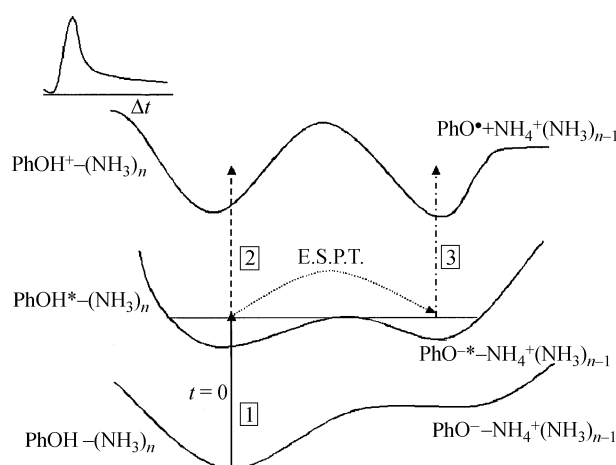


Fig. 1 Schematic potential energy diagram for a PhOH-(NH₃)_n cluster (e.g. *n* = 5). These curves represent the case where proton transfer can occur in the excited state. The ionic state presents a high barrier between non-proton-transferred and proton-transferred species as required for the observation of picosecond decays on the [PhOH-(NH₃)_n]⁺ mass peak and rise times on the NH₄⁺(NH₃)_{n-1} mass peaks (see text).

transferred and the proton-transferred species. This is necessary to ensure a selectivity in the ionic dissociation pathway, depending on the part of the ionic surface reached through ionization of the excited cluster. Before ESPT, the ionization photon brings the system into the $(\text{PhOH}-(\text{NH}_3)_n)^+$ well of the ionic potential energy surface and due to the barrier, the fragmentation in $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_{n-1}$ is impossible whereas after ESPT, the $\text{PhO}^--\text{NH}_4^+(\text{NH}_3)_{n-1}$ well is reached which leads to fragmentation.¹³⁻¹⁷

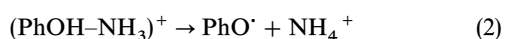
One should keep in mind that the observed signal reflects not only the dynamics in the excited state but also the way to probe it. In other words, if the dynamical process is induced by the pump photon, there must be a selectivity in the ionization process by the probe photon to observe a time dependent signal.

Since these very good studies on the picosecond dynamics in phenol and naphthol ammonia clusters,^{5-10,13-17} other investigations have been carried out on these systems, which have led to question this initial interpretation.

(i) A picosecond decay was recorded by Bernstein and co-workers¹⁸ upon detection of the $(\text{PhOH}-(\text{NH}_3)_2)^+$ mass, which is a cluster size where ESPT is *a priori* energetically forbidden. This has been interpreted as due to ESPT in larger clusters ($n \geq 5$), followed by evaporation of NH_3 units (three or more) in the ionic state. This result provides the hint that evaporation of ammonia units in the ion has to be seriously taken into account.

(ii) Another recent experiment performed by Jacoby *et al.*¹⁹ showed that the fingerprint of $\text{PhOH}^*(\text{NH}_3)_n$ ($n = 1-4$) complexes, *i.e.* the existence of resolved vibrational structures in the excitation spectra, can also be recorded on the $\text{NH}_4^+(\text{NH}_3)_{n-1}$ fragment masses when ionizing with 2 photons of the same color, which corresponds to a total energy of 8.9 eV. For the small sizes ($n = 1-3$), no ESPT is expected although the appearance of protonated fragments is necessarily linked to the proton transfer mechanism either in the excited or in the ionic state.

(iii) A barrier to proton transfer in the ionic state of the 1-1 complex had been postulated by Mikami *et al.* to explain their results on the $\text{PhOH}-\text{NH}_3^+$ dissociation:²⁰ when the 1-1 complex is ionized through the S_1 state, the non-transferred part of the ionic surface is reached. Around 1 eV above the ionization threshold, two dissociation channels are open at the same energy:



Only the first dissociation channel has been observed even when ionizing with a total energy of 9 eV, *i.e.* 1.3 eV above the ionization threshold or 0.3 eV above the thermodynamical limit for these processes. The second channel (PhO^+ evaporation) is supposed to be observed only if proton transfer has occurred in the ionic state and may be regarded as the signature of this process. From the non-observation of NH_4^+ , the authors deduced that the height of the barrier in the 1-1 ionic state is at least 1.3 eV. However, the absorption spectrum of the $(\text{PhOH}-(\text{NH}_3)_{n=1,2})^+$ cations, later performed by the same group, has been assigned to the phenoxy radical, indicating that the proton transfer reaction has occurred in the ionic state and that the proton-transferred structure is the most stable one.^{21,22}

(iv) The ground state proton transfer in phenol- $(\text{NH}_3)_n$ clusters has also been investigated through the measurement of one VUV photon ionization thresholds, using synchrotron radiation.²³ As for the excited state proton transfer, an important decrease of the ionization threshold, which occurs for $n = 6$ ammonia molecules, may be regarded as the signature of the absorption from a proton-transferred structure in the ground state. This threshold cluster size is in qualitative agree-

ment with the $n = 5$ size suggested for ground state proton transfer in naphthol- $(\text{NH}_3)_n$ clusters,¹⁸ naphthol being a stronger acid than phenol. This experiment is also in good agreement with theoretical calculations.²⁴⁻²⁵ The major problem raised by this experiment is that if proton transfer occurs in the ground state for $n = 6$ or 7 ammonia molecules, then the picosecond dynamics observed in the excited state for $n = 6$ or 7 cannot be proton transfer.

(v) Calculations have been performed for the phenol- $(\text{NH}_3)_5$ in the ground^{24,25} and excited²⁶ states which confirm that the proton-transferred structure is metastable in the ground state, whereas it is the most stable structure in the excited state (by 0.17 eV) with a barrier from $\text{PhOH}^*(\text{NH}_3)_5$ to $\text{PhO}^*-\text{NH}_4^+(\text{NH}_3)_4$ of 0.14 eV. The authors agree to assign the fast decay component of the picosecond signal to proton tunneling through a barrier but calculate the solvent rearrangement rate to be much shorter than the long time component observed in the experiments. On the other hand calculations on the ionic $(\text{PhOH}-\text{NH}_3)^+$ cluster²⁷ predict no barrier between $\text{PhOH}^+-\text{NH}_3$ and $\text{PhO}^+-\text{NH}_4^+$, hence no barrier to dissociation in $\text{PhO}^+ + \text{NH}_4^+$.

To summarize, experimental results and theoretical calculations do not seem to give conclusive evidence for an important barrier to proton transfer in the ionic state, especially for medium cluster sizes. This led us to test the presence of a large barrier to proton transfer in the ionic state of phenol- $(\text{NH}_3)_n$ clusters, the barrier leading to a specific fragmentation, since it is one of the main implicit assumptions in the interpretation of picosecond dynamics.

Before starting with clusters, it may be useful to recall the photophysical processes occurring in the excited states of bare phenol, which can also be relevant to the dynamics of phenol embedded in an ammonia cluster. As many substituted benzenes, phenol has a weak fluorescence quantum yield (0.08 in a non-polar solvent²⁸) and consequently a short fluorescence lifetime (1.5-2 ns gas phase²⁹) as compared to the radiative lifetime of ≈ 30 ns, ref. 28), because of strong couplings with the triplet (ISC) and ground (IC) states.

Since the triplet state is around 1 eV below S_1 ($\Delta E(S_1-T_1) = 7744 \text{ cm}^{-1}$ in free phenol), intersystem crossing will lead to fragmentation of the clusters as shown in the case of the phenol-water complex.^{28,29} An ISC rate constant of $k_{\text{isc}} = 5 \times 10^7 \text{ s}^{-1}$ has been measured for free phenol and does not change significantly in the water complex: $k_{\text{isc}} = 2.3 \times 10^7 \text{ s}^{-1}$.²⁹ The sum of fluorescence and ISC yields varies between 0.16 and 0.46 depending on the authors.^{29,30} These values, far from 1, evidence an important yield for interconversion and eventually for photochemistry, since the dissociation channel $\text{PhOH} \rightarrow \text{PhO}^+ + \text{H}^+$ is lower in energy (by 0.66 eV) than S_1 ,³¹ so that S_1 excitation of phenol can also lead to the dissociation into phenoxy radical and a hydrogen atom.

The best way to disentangle the excited state proton transfer itself from the fragmentation processes in the ionic (or excited) state is to use a two-color ionization scheme. The small clusters ($n = 1-4$) can be selectively excited by the pump photon¹⁹ and the energy imparted to the ionic state can be partially controlled by varying the probe laser wavelength.

Fig. 2 shows the energetic diagram with the different energy levels in the ionic phenol-ammonia clusters. It has been built by scaling the two dissociation channels of the 1-1 complex ion: $\text{PhOH}^+ + \text{NH}_3$ and $\text{PhO}^+ + \text{NH}_4^+$ with known thermodynamical values: phenol gas phase acidity ($\Delta_{\text{acid}}H = 1460.9 \pm 8 \text{ kJ mol}^{-1}$),³¹⁻³³ phenol ionization potential (8.505 eV),³⁴ PhO^+ electron affinity ($\text{EA} = 217.4 \pm 0.6 \text{ kJ mol}^{-1}$),³⁵ ammonia proton affinity (8.85 eV),³² and $\text{PhOH}-\text{NH}_3$ ground state binding energy ($D_0 = 0.22 \text{ eV}$ experimental value²⁰ or $D_0 = 0.303 \text{ eV}$ calculated value³⁶). These values lead to:



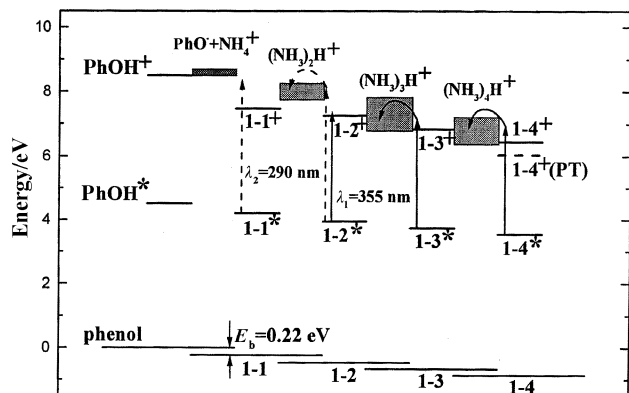


Fig. 2 Energy diagram for the phenol–ammonia ionic clusters. This energy diagram takes the phenol ground state as the zero of energy. (1- n) correspond to the energies of clusters in their ground states. (1- n^*) correspond to the clusters in the excited states ($v = 0$).¹⁹ (1- n^+) correspond to the vertical ionization thresholds.^{11,20,23} The boxes correspond to the thresholds for dissociation in $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_{n-1}$, the height of each box representing the uncertainty on the thermodynamical values.³⁷ The boxes are labeled $(\text{NH}_3)_n\text{H}^+$ instead of $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_{n-1}$ for visibility.

taking the energy scale origin on the bare phenol ground state. For larger clusters, $(\text{NH}_3)_n \text{NH}_4^+$ energy levels are deduced from the proton affinities³⁷ of ammonia clusters. The $\text{PhOH}-(\text{NH}_3)_n$ vertical ionization thresholds are experimental measurements.^{11,20,23}

This energy diagram helps us to design the required experiment, *i.e.* to choose the best probe wavelength for which the total energy brought into the ion is just above the $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_{n-1}$ dissociation channel for either the 1-2 or the 1-3 complex. No proton transfer in the excited state is expected for these cluster sizes, thus according to the previous model, the $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_{n-1}$ dissociation channel should not be observed because a high barrier to proton transfer is assumed in the ionic state. If we use a pump photon around 281.5 nm to excite the cluster (in the absorption range of 1-2 and 1-3 clusters)¹⁹ and a 355 nm photon to ionize, the total energy in the complex will be 7.90 eV. In the 1-3 cluster, this corresponds to an excess energy 0.25 eV larger than the dissociation energy of $(\text{PhOH}-(\text{NH}_3)_3)^+$ in $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_2$. On the other hand, the 1-2 complex can be ionized but the dissociation channel leading to $\text{NH}_4^+ + \text{NH}_3$ is energetically closed, which will be a good way to estimate the possible effects of multiphoton processes.

It will be seen in the present study that although ESPT is not energetically allowed for clusters with two or three ammonia molecules, the $\text{NH}_4^+(\text{NH}_3)_{1,2}$ fragments are observed in REMPI experiments, even when a delay as large as 350 ns is applied between excitation and ionization lasers. These fragments may come from dissociation in the ionic state: in that case, excited $\text{PhOH}-(\text{NH}_3)_n$ clusters must live much longer than the initially excited S_1 state and triplet states must be involved. The $\text{NH}_4^+(\text{NH}_3)_n$ fragments may alternatively come from ionization of stable $\text{NH}_4(\text{NH}_3)_n$ produced through intracuster hydrogen transfer in the excited S_1 state: $\text{PhOH}^*(S_1)-(\text{NH}_3)_n \rightarrow \text{PhO}^+ + (\text{NH}_4)(\text{NH}_3)_{n-1}$. This mechanism is analogous to the reaction occurring in excited ammonia clusters: $(\text{NH}_3)_n^* \rightarrow \text{NH}_2 + (\text{NH}_4)(\text{NH}_3)_{n-2}$.^{38,39}

These two possibilities will be analyzed and discussed in comparison with other experimental data from different groups.

Experimental

The clusters are produced by expanding a mixture of Ne seeded with NH_3 (0.5%) and passing over a reservoir contain-

ing phenol at room temperature. The backing pressure used is typically 1.5–2 bar and the nozzle diameter is 300 μm . Under these conditions no large clusters are observed and a clean spectrum of the smaller clusters (1 to 4) can be obtained as in ref 12. The pump laser is an unfocused ($\approx 4 \text{ mm}^2$ spot) frequency doubled excimer pumped dye laser, whose power is kept low (around 80 μJ). The probe ionizing laser is either the third harmonic of a YAG laser (355 nm) kept at very low power (from 1 to 5 mJ) in a 25 mm^2 spot or a frequency doubled YAG pumped dye laser (200 μJ). The two lasers are electronically synchronized with 1 ns precision but due to the lasers' temporal width (10 ns), the effective resolution cannot be better than a few ns (≈ 2 ns). The ions are detected in a 1 m time of flight mass spectrometer.

Results

(1) Mass resolved excitation/ionization spectra

Two experiments have been performed: one-color two-photon excitation spectra where a tunable photon in the 282.5–275 nm region excites the complexes and a second photon of the same laser ionizes them. This is similar to the work of Jacoby *et al.*¹⁹ and similar results—well resolved structures of $\text{NH}_4^+(\text{NH}_3)_{0-3}$ masses—have been obtained as long as the mean cluster size is small. Two-color two-photon excitation spectra in which the excited clusters are ionized by a 355 nm photon have also been recorded and the band structures are also observed at the $\text{NH}_4^+(\text{NH}_3)_{n=2,3}$ mass peaks. The ionizing photon energy (355 nm, *ca.* 3.5 eV) is too low to reach the dissociation limits leading to the observation of NH_4^+ or $\text{NH}_4^+ + \text{NH}_3$. In agreement also with ref. 19, the intermolecular vibrational band structures are not observed on $(\text{PhOH}(\text{NH}_3)_{n>2})^+$ ion signals.

(2) Mass spectra

Since small $\text{PhOH}-(\text{NH}_3)_n$ complexes have structured absorption spectra, it is easy to precisely select one cluster size. Fig. 3 presents mass spectra obtained when the 1-3 complex is excited at 281.75 nm (first intense absorption band of this cluster, located 40 cm^{-1} above the origin).

The one-color two-photon signal is the lower trace. When the 355 nm laser is added without delay (upper trace), the most abundant fragment observed is the $\text{NH}_4^+(\text{NH}_3)_2$ fragment. All the $\text{NH}_4^+(\text{NH}_3)_{n-1,2}$ are strongly enhanced with the 355 nm laser whereas the $\text{NH}_4^+ + \text{NH}_3$ signal is not affected. These results imply first that $\text{NH}_4^+(\text{NH}_3)_2$, which is the most intense peak, is derived from the $\text{PhOH}-(\text{NH}_3)_3$ complex, which is preferentially excited at 281.75 nm and second that

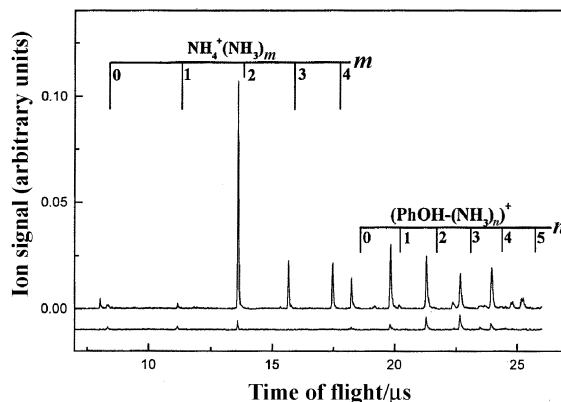


Fig. 3 Mass spectra recorded in exciting the $\text{PhOH}-(\text{NH}_3)_3$ cluster band at 281.75 nm. Lower trace: one-color (281.75 nm) two-photon mass spectrum; upper trace: two-color (281.75 nm + 355 nm) two-photon mass spectrum. The two spectra are on the same y scale.

multiphoton ionization of $\text{NH}_4(\text{NH}_3)_{n-1}$ is not very important under these conditions, since the NH_4^+NH_3 ion signal is not enhanced by the 355 nm probe laser.

Besides, although the phenol, 1–1 and 1–2 complexes are not resonantly excited when the excitation wavelength is set at 281.75 nm (this band of the 1–3 cluster is located at lower energy than the band origins of these complexes: 275.1, 280.0 and 281.34 nm respectively), $(\text{PhOH}-(\text{NH}_3)_{0-2})^+$ mass peaks are clearly seen in the mass spectrum. This indicates the presence of an efficient NH_3 evaporation in ionic clusters, after absorption of two 355 nm photons.

The most unexpected result is presented in Fig. 4, when a large delay between the pump and probe pulses is applied. When the excitation wavelength is set on the 1–3 complex band, the 355 nm pulse arriving 200 ns after the pump pulse can still ionize the complexes, quite as efficiently as when the two lasers are simultaneous. The delayed ionization signal has been observed with delays as high as 350 ns and was not investigated further, due to the limitation of the synchronization electronics.

It should be noticed that the excitation spectra recorded at the $\text{NH}_4^+(\text{NH}_3)_2$ mass with delayed ionization is identical to that recorded either with one-color two-photon ionization or with two-color two-photon ionization without delay between pump and probe pulses. The $(\text{PhOH}-(\text{NH}_3)_n)^+$ mass peaks are also enhanced but less significantly than in the experiment without delay.

When the 1–2 complex is resonantly excited (281.34 nm), the 355 nm ionizing laser does not affect the NH_4^+NH_3 ion signal, in agreement with the energy diagram of Fig. 2. Using a 290 nm probe laser, similar results as for the 1–3 clusters are obtained, *i.e.* observation of an enhanced signal on the NH_4^+NH_3 mass, even with a 200 ns delay between pump and probe pulses.

(3) Fluorescence spectra and fluorescence excitation spectra

Low resolution fluorescence spectra (resolution: 10 nm FWHH) have been recorded for cluster sizes from $n = 1$ to $n \geq 5$. For cluster sizes $n = 1-4$, the procedure described below has been followed, to ensure that the observed fluorescence is really due to the excitation of a particular vibronic

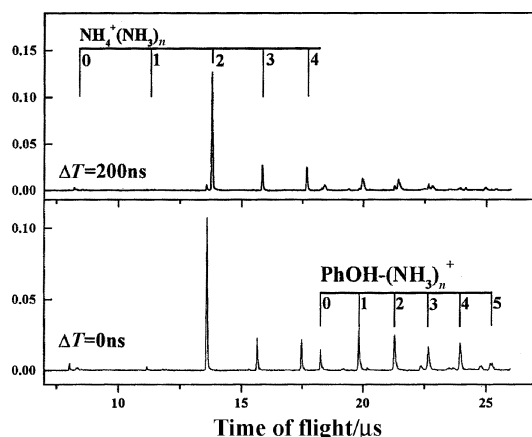


Fig. 4 Mass spectra recorded in exciting the $\text{PhOH}-(\text{NH}_3)_3$ band at 281.75 nm and ionizing with 355 nm. Lower trace: pump-probe delay = 0 ns; upper trace: pump-probe delay = 200 ns. It may seem that the upper trace is misaligned by one mass unit as compared to the lower trace. But in this mass spectrum, the origin of time of flights is defined by the pump laser ($\lambda_1 = 281.75$ nm), thus, for example, the small peak to the left of the main $(\text{NH}_3)_3\text{H}^+$ peak corresponds to the two-photon one-color signal and is exactly the same as in the lower trace; the probe laser being delayed by 200 ns, the flight time of $(\text{NH}_3)_3\text{H}^+$ ions coming from pump-probe with two colors is also lengthened by 200 ns leading to an apparent misalignment of the peaks.

band characteristic of the selected cluster size: the excitation laser is set on a particular band of the 1– n cluster, which is monitored by looking at the $\text{NH}_4^+(\text{NH}_3)_{n-1}$ peak in the mass spectrometer and the fluorescence spectrum is recorded; the excitation laser wavelength is then moved by a few wavenumbers to be out of resonance with the vibrational band and a second fluorescence spectrum is recorded. This procedure enables one to estimate the role of larger clusters in the fluorescence spectra (their absorption spectrum is structureless, and their contribution is the same on the vibrational band and just aside). The “true” fluorescence spectra are obtained by subtracting the ‘off resonance’ spectrum from the ‘on resonance’ one. This procedure can be followed up to $n = 4$ where the vibrational levels are clearly identified. For larger clusters, the excitation laser is set to the red of the small clusters absorption at 282.5 nm. The spectra are presented in Fig. 5 for $n = 1, 2$ and larger than 5, for $n = 3$ and 4 almost no signal is left when the background has been subtracted, indicating that 1–3 and 1–4 clusters have very low fluorescence quantum yield, smaller than 1–1, 1–2 or larger clusters.

Fluorescence excitation spectra have also been recorded by monitoring the fluorescence at two wavelengths: 295 and 340 nm. Only the bands assigned to the 1–1 and 1–2 complexes can be clearly identified on the background.

(4) Pump-probe nanosecond dynamics of small complexes

The pump laser is set on a vibrational band characteristic of a particular complex and the delay between the pump and the probe laser is varied in time while the ion signal is recorded. As done for fluorescence spectra, the pump laser is then set on the background that lies between vibronic bands and this background is subtracted in order to get only the dynamics of the particular cluster size of interest.

For the 1–3 complex, the ionizing laser is set at 355 nm. This ionization energy was chosen in order to reach the ionic dissociation channel $\text{PhO}^+ + \text{NH}_4^+(\text{NH}_3)_2$ in a one-photon step. In Fig. 6, it can be seen that when the background is not subtracted, a fast decay is observed on the 1–3 mass peak followed by a plateau, whereas a fast rise and a plateau is observed on the $\text{NH}_4^+(\text{NH}_3)_2$ fragment mass peak. With the temporal resolution of the experiment and the signal-to-noise ratio, no dynamic shorter than 2 ns can be observed. The process leading to a protonated ammonia final product occurs within less than 2 ns for the 1–3 complex.

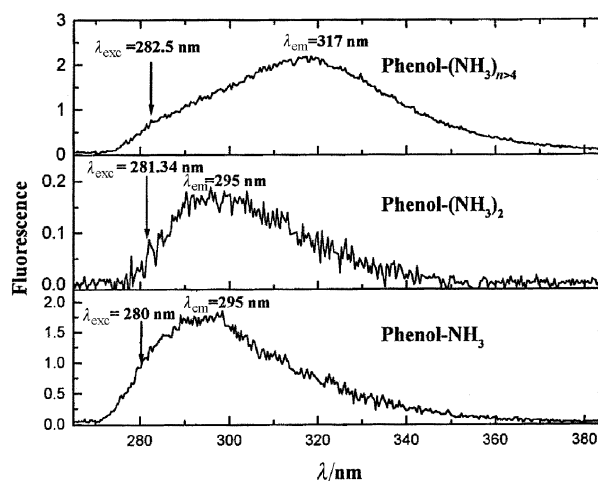


Fig. 5 Fluorescence spectra of the $\text{PhOH}^*(\text{NH}_3)_n$ clusters. Lower trace: 1–1 complex, $\lambda_{\text{exc}} = 280$ nm; middle trace: 1–2 complex, $\lambda_{\text{exc}} = 281.34$ nm; upper trace: 1– $n > 4$, $\lambda_{\text{exc}} = 282.5$ nm. For 1–1 and 1–2 complexes, the spectra result from the subtraction of the signal obtained by excitation of a vibrational band and the signal obtained on the background. The fluorescence signals recorded on the 1–3 and 1–4 clusters vanish when the background is subtracted.

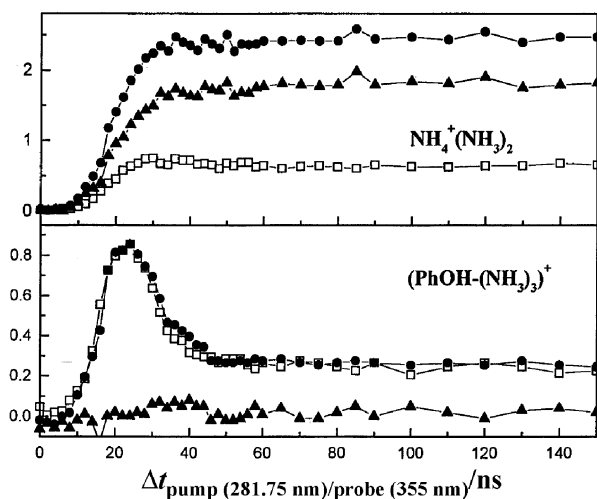


Fig. 6 PhOH*(NH₃)₃ nanosecond dynamics: pump 281.75 nm and probe 355 nm. (●) Excitation of the 1–3 band at 281.75 nm; (□) non-resonant excitation (281.85 nm); (▲) resonant signal (●) minus background (□). Upper panel: H⁺(NH₃)₃ detection; lower panel: PhOH-(NH₃)₃⁺ detection. No signal on the 1–3 ion mass comes from the 1–3 complex. The signal observed at long times reflects the excitation of larger clusters.

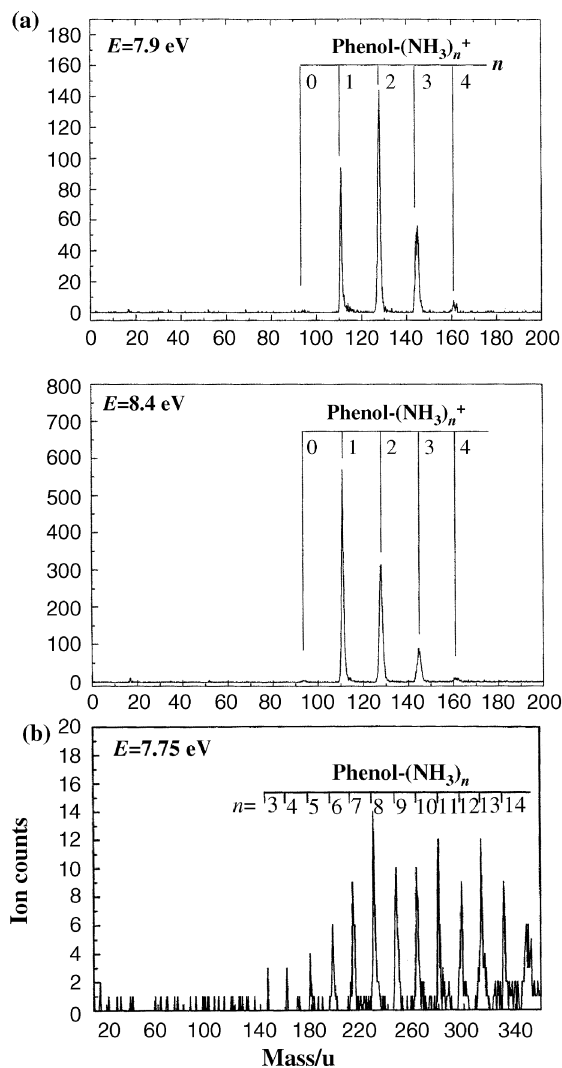


Fig. 7 Mass spectra obtained using single photon ionization. (a) Small cluster condition; upper trace: ionization energy 7.9 eV, lower trace: ionization energy 8.4 eV. Protonated ammonia clusters are not observed. (b) Large clusters conditions at 7.75 eV.

When the background corresponding to the excitation of larger clusters is subtracted, the signal observed on the 1–3 complex mass becomes very small (if present at all) indicating that this long time scale signal arises actually from the excitation-ionization of larger clusters. In contrast, the 1–3 complex excitation leads efficiently to the NH₄⁺(NH₃)₂ ion product on a long time scale. Similar observations have been obtained for the 1–2 complex using a 290 nm probe laser.

(5) VUV one-photon ionization using synchrotron radiation

The complexes are directly ionized by one VUV photon issued from synchrotron radiation, using the SAPHIRS experiment.⁴⁰ As can be seen in Fig. 7a and 7b, the protonated ammonia clusters are not observed in this case (or represent less than 1% of the intensity of total ion current) for energies up to 8.5 eV (at higher energy the protonated ammonia complexes are observed but they come from the ionization of neat ammonia clusters).

Discussion

We will first discuss the case of the 1–2 and 1–3 complexes and in particular the observation of the protonated ammonia products when the delay between pump and probe is large (up to 350 ns). This result is surprising since so far, PhOH*(S₁)-(NH₃)_{2,3} have been thought to be non-reactive species. Thus ionization by the second laser should occur during the lifetime of PhOH*(S₁)-(NH₃)_{2,3}. The phenol (S₁) lifetime is short (2 ns, ref. 29 and 30) and we do not expect the PhOH*(S₁)-(NH₃)_{2,3} lifetime to be much greater (it is 15 ns for PhOH*(S₁)-H₂O, ref. 29). Thus, to explain the results, we have to find either a long-lived state or an alternative way to produce NH₄⁺(NH₃)_n other than fragmentation in the ionic state.

For the sake of clarity, Fig. 8 presents the different states that can be involved in the case of PhOH(NH₃)₃. Two main hypotheses can be postulated: intersystem crossing and hydrogen transfer.

(1) Intersystem crossing

The excitation of [PhOH*(S₁)-(NH₃)₃] leads to a fast intersystem crossing: the (NH₃)₂NH₄⁺ fragment then comes from dissociation of the [PhOH-(NH₃)₃]⁺ ion resulting from the probe photon absorption by a triplet state.

(i) The triplet state corresponding to [PhOH*(T₁)-(NH₃)₃] is lower than the S₁ state by roughly 1 eV as in the free molecule. With this excess energy, a fast evaporation of ammonia

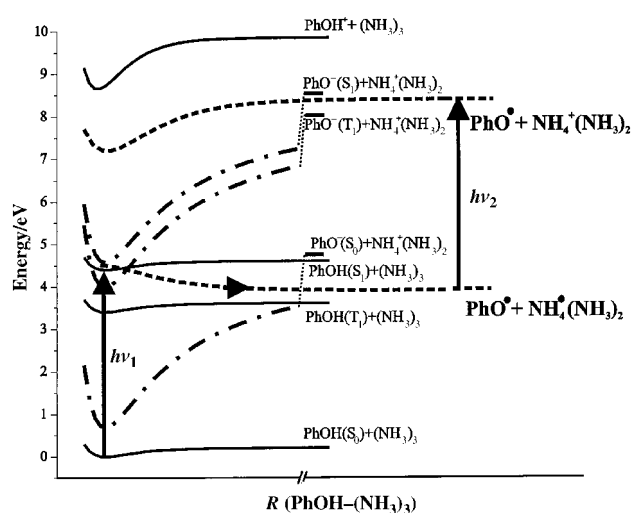


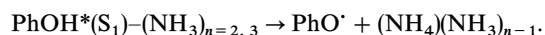
Fig. 8 Crude representation of the potential curves involved in the PhOH-(NH₃)₃ two-photon two-color ionization. The reaction coordinate being PhOH··(NH₃)₃ or PhO··(NH₄)(NH₃)₂.

units is expected, as observed for phenol–water.^{29,30} Therefore, excitation of the 1–3 complex should be detected on the $(\text{NH}_3)_{n=0,1}\text{NH}_4^+$ mass peaks, which is not the case. Moreover, high vibrational levels of the triplet state should be populated by $S_1 \rightarrow T_1$ transfer, thus high levels of the ionic state have to be reached by the probe photon (Franck–Condon principle), and ionization of the triplet state should require a much more energetic photon than the 355 nm photon to reach the $[\text{PhO}^-\text{NH}_4^+(\text{NH}_3)_2]$ threshold.⁴¹

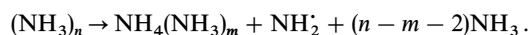
(ii) The triplet state corresponding to the ion pair $[\text{PhO}^-(T_1)\text{NH}_4^+(\text{NH}_3)_2]$ is expected to lie around 0.5 eV^{42,43} below the excited singlet ion pair state $[\text{PhO}^-(S_1)\text{NH}_4^+(\text{NH}_3)_2]$. The $[\text{PhO}^-(S_1)\text{NH}_4^+(\text{NH}_3)_2]$ ion pair singlet state lies higher in energy than the covalent $[\text{PhOH}^*(S_1)\text{NH}_3]$ state by roughly 0.5 eV (indeed the excited state proton transfer is expected to occur for clusters containing 4 (ref. 11) or 5 (ref. 13) ammonia molecules and the solvation energy per NH_3 molecule is in the order of 0.5 eV). Thus the $[\text{PhO}^-(T_1)\text{NH}_4^+(\text{NH}_3)_2]$ state is expected to be in the vicinity of the $[\text{PhOH}^*(S_1)\text{NH}_3]$ state. Since the signal is observed with no rise time (on the nanosecond time scale), this process which corresponds to intersystem crossing together with proton transfer, must occur quite quickly. However, the $[\text{PhOH}^*(T_1)\text{NH}_3]$ state remains lower in energy and we do not see why the reverse proton transfer $[\text{PhO}^-(T_1)\text{NH}_4^+(\text{NH}_3)_2] \rightarrow [\text{PhOH}^*(T_1)\text{NH}_3]$ would not occur, leading to evaporation of NH_3 units. Besides, if this process seems energetically allowed for the 1–3 complex, it is obviously not possible for the 1–2 complex where the ion pair triplet state will be 0.5 eV higher in energy.

(2) Hydrogen transfer

Another possible explanation has been discarded so far: the 1–3 and 1–2 complex can undergo a dissociative hydrogen atom transfer according to:



This process is energetically allowed. In phenol, the dissociation threshold in $\text{PhO}^\cdot + \text{H}^\cdot$ is at 3.848 eV,³¹ 0.66 eV below the $S_1 \leftarrow S_0$ transition (4.507 eV);²⁰ the $\text{H} + \text{NH}_3 \rightarrow \text{NH}_4$ reaction is quasi-isoenergetic^{44,45} and the PhOHNH_3 ground state binding energy is between 0.223 and 0.303 eV.^{20,36} Therefore in the 1–1 complex, the $\text{PhOH}\text{NH}_3 \rightarrow \text{PhO}^\cdot + \text{NH}_4$ thermodynamical reaction threshold is 0.28–0.36 eV below the PhOH^*NH_3 $S_1 \leftarrow S_0$ transition (4.428 eV). Assuming that the solvation energy corresponding to the addition of two NH_3 molecules is comparable in PhOH^*NH_3 and in NH_4 , the $\text{PhOH}^*(S_1)\text{NH}_3 \rightarrow \text{PhO}^\cdot + \text{NH}_4(\text{NH}_3)_2$ channel is likely to be open and exoergic by about 0.3 eV.⁴⁶ This process is similar to the reaction occurring in excited ammonia clusters^{38,39} where the photodissociation channel of NH_3 in $\text{NH}_2^\cdot + \text{H}^\cdot$ evolves in



Actually, this excited state reaction has been used by Fuke and co-workers to generate the $\text{NH}_4(\text{NH}_3)_m$ radicals which were further studied through ionization.^{47,48} Two conditions must be fulfilled in order to observe the hydrogen transfer process: the $\text{NH}_4(\text{NH}_3)_n$ radicals must have a lifetime longer than hundreds of nanoseconds, and their ionization potentials must be lower than the probe laser wavelength.

The $\text{NH}_4(\text{NH}_3)_n$ products are stable enough.

$\text{NH}_4(\text{NH}_3)_n$ radicals are known to be much more stable than free NH_4 ⁴⁹ and their lifetimes have been measured by Fuke *et al.* to be 3 μs and 7 μs for $n = 1$ and 2, respectively, whereas NH_4 is a very short-lived species (15 ps).^{47,48}

The $\text{NH}_4(\text{NH}_3)_n$ products can be ionized.

The 355 nm (3.5 eV) probe photon used here is energetic enough to ionize the $\text{NH}_4(\text{NH}_3)_2$ dissociation product

(ionization potential of 3.31 eV from the work of Fuke *et al.*⁴⁷). At this wavelength $\text{NH}_4(\text{NH}_3)^+$ is not detected in agreement with its higher ionization threshold (3.88 eV). But when the probe wavelength is changed to 290 nm (4.3 eV), $\text{NH}_4(\text{NH}_3)^+$ is observed.

If we assume that the hydrogen atom transfer is the reactive process observed here through the delayed ionization signals, the first consequences are as follows.

(i) The appearance of the vibronic fingerprints of phenol–ammonia clusters on the mass of $\text{NH}_4^+(\text{NH}_3)_{n>1}$ fragments is due to the ionization of ground state $\text{NH}_4(\text{NH}_3)_{n>1}$ clusters resulting from the H transfer reaction. Although we cannot measure the appearance times of the $\text{NH}_4^+(\text{NH}_3)_{n>1}$ ion with nanosecond lasers, the fluorescence of the 1–2 complex can be easily detected whereas that of the 1–3 complex is not (or only barely) observed, indicating that the reaction in the 1–3 complex is faster than in the 1–2 complex.⁵¹

(ii) For large clusters (larger than 1–4), a red shifted fluorescence is observed again, which seems at first in contradiction with the above assertion of a fast H transfer reaction in the 1–3 complex leading to the absence of fluorescence in this case. But, a new channel opens for $n \geq 4$: the excited state proton transfer. This process, which is not energetically allowed for small complexes becomes possible for larger ones since the stabilization energy of the ion pair $[\text{PhO}^-(S_1)\text{NH}_4^+(\text{NH}_3)_{n-1}]$ by NH_3 is larger than that of the covalent $[\text{PhOH}^*(S_1)\text{NH}_3]_n$ species. For a large enough cluster size, ESPT should be energetically more favorable than H transfer. In the light of previous measurements, proton transfer should occur at $n = 4$ or 5.^{11,13} In this case, after proton transfer the $[\text{PhO}^-(S_1)\text{NH}_4^+(\text{NH}_3)_{n-1}]$ clusters can fluoresce, the fluorescence being that of solvated phenolate anion and no longer that of solvated phenol.^{12,42}

We can now review and explain our results as well as previous studies in the light of this new H transfer process.

(a) *Picosecond decay observed at the 1–2 complex mass.*

Hineman *et al.*¹⁸ have observed a picosecond decay on the mass of the 1–2 complex, in complete disagreement with the proton transfer hypothesis. This decay, which depends on the cluster distribution, has been ascribed to an extensive fragmentation in larger clusters which have undergone a proton transfer reaction (which in this interpretation should be the 1–5 complex). In the new interpretation, the observed decay would correspond to the decay through hydrogen transfer of either the 1–2 complex or most probably the 1–3 complex which would evaporate only one ammonia molecule and not three as previously assumed. It should be mentioned that in Fig. 1 of ref. 13 and Fig. 5 of ref. 14 a fast picosecond decay is also observed on the 1–3 complex mass in agreement with the above assumption.

(b) *Clean vibrational fingerprint observed on the $\text{NH}_4^+(\text{NH}_3)_{n-1}$ ions and not on $\text{PhO}^-\text{NH}_4^+(\text{NH}_3)_{n-1}$.*

In the spectroscopic investigation of Jacoby *et al.*,¹⁹ the band structure of the 1–3 complex is clearly seen on the $\text{NH}_4(\text{NH}_3)_2^+$ mass, weakly on the NH_4^+NH_3 mass but is not observed at its own mass. This can be readily explained: some $(\text{PhOH}\text{NH}_3)_n$ complexes are excited and ionized before reacting through the H transfer mechanism. They are detected on the $(\text{PhOH}\text{NH}_3)_n^+$ or rather on the $(\text{PhOH}\text{NH}_3)_{n-1}^+$ mass channel after an evaporation process in the ionic state. The evaporation process is quite important as seen for the 1–2 complex which is mainly observed on the 1–1 ion mass. Hydrogen atom transfer is faster in 1–3 complex than in 1–2, thus ionization by the nanosecond laser is less efficient and evaporation of larger clusters causes an intense background from which structured bands cannot be extracted. The selectivity observed in the spectroscopy of $\text{NH}_4^+(\text{NH}_3)_{n-1}$ implies that there is no evaporation in this fragment ion, which can be understood since the excess energy can be released as kinetic energy of the neutral fragments before ionization, leading to a

less extensive fragmentation in the $\text{NH}_4^+(\text{NH}_3)_{n-1}$ ion and thus to a better detection of the parent cluster vibrational pattern.

(c) *Evaporation in the ion.*

The single-photon ionization experiment carried out with synchrotron radiation shows that no protonated ammonia products are formed even with a large energy excess. This could be interpreted as in ref. 13–15 and 20 as the effect of a barrier between $\text{PhOH}^+(\text{NH}_3)_n$ and $\text{PhO}^-\text{NH}_4^+(\text{NH}_3)_{n-1}$, since for these small clusters a ground state proton transfer structure is not expected. However even when ionizing large clusters (n up to 15), which have most probably a ground state proton-transferred structure, no protonated ammonia clusters are detected. Therefore it seems that, independently from the most stable initial structure (proton-transferred or not), dissociation leading to protonated ammonia clusters is not favored in the ion. Evaporation of NH_3 molecules seems to be the most competitive channel in the relaxation of the excess energy in the ionic state. A simple explanation can be proposed: NH_3 molecules are much lighter (17 u) than the PhO^{\cdot} radical (93 u) and will evaporate more easily, the two dissociation limits (loss of NH_3 or loss of PhO^{\cdot}) being of the same order of magnitude (it is unfortunately difficult to settle exactly by thermodynamical calculations the energy ordering of these two dissociation channels due to the uncertainties of proton affinities and of adiabatic ionization thresholds of the large ammonia clusters).

(d) *Picosecond experiment on large clusters and the barrier to proton transfer in the ionic state.*

The present work was originally undertaken to evidence or dismiss the presence of a large barrier to proton transfer in the ionic state, but does not provide any new evidence for or against the existence of such a barrier.

However the presence of the H transfer in the excited state shows that the observation of the $\text{NH}_4^+(\text{NH}_3)_{n-1}$ fragment is not necessarily connected to the ESPT followed by a specific evaporation in the ion. In fact the question of a barrier may be totally disconnected to the observed processes. At this stage of the discussion, we can only suggest that the picosecond decays observed for the $n = 5-7$ clusters are certainly linked to proton transfer either in the excited state or in the ground state but that evaporation of NH_3 molecules either in the singlet or in the triplet state must also be taken into account.

(e) *Ion signal observed on the $\text{PhO}^-\text{NH}_4^+(\text{NH}_3)_{n-1}$ mass at long pump-probe delay (nanosecond time scale).*

When the 1–3 complex is excited, a signal is observed on the 1–3 mass peak at long delays (>200 ns) between pump and probe lasers (see Fig. 6). This signal does not come from the 1–3 complex itself but from larger clusters since it remains identical when the pump laser is set on a vibronic band of the 1–3 complex or on the background. This signal is probably due to the ionization of a triplet state issued from larger clusters. The presence of a strong evaporation implies that a lot of energy is released in the formation of the triplet state. The process we propose is the following. As mentioned in ref. 43 the singlet and triplet states have the same electronic configuration in the PhO^- anion whereas they differ in the PhOH molecule. Therefore the energy gap is smaller in the case of the phenolate anion (0.5 eV as compared to phenol (1 eV)).^{42,43} Intersystem crossing is expected to be easier for the proton transferred species than for the non-proton-transferred ones (remember that for bare phenol, the triplet yield is already important and remains of the same order of magnitude in the phenol– H_2O complex²⁹). The observation of an important intersystem crossing leading probably to the $[\text{PhO}^*(\text{T}_1)]\text{NH}_4^+(\text{NH}_3)_{n-1}$ state might be considered as a consequence of the excitation of the large $[\text{PhO}^-\text{NH}_4^+(\text{NH}_3)_{n-1}]$ clusters. An energy of 0.5 eV is released in this process leading to an important fragmentation in

the triplet state, and ionization occurs through a two-photon triplet–triplet absorption, leading also to an important evaporation in the ionic state. This process should be fast (less than 10 ns) and will contribute to the blurring of the vibrational bands in the $\text{PhOH}(\text{NH}_3)_n^+$ detection.

(f) *Proton transfer vs. hydrogen transfer.*

When the cluster size increases, H transfer becomes less competitive against proton transfer. For large clusters ($n > 6$), H transfer disappears: in the two-photon mass spectra recorded with large clusters, the $\text{NH}_4^+(\text{NH}_3)_{n-1}$ fragments disappear for $n > 6$ (see for example Fig. 3 and 5 of ref. 15). This is consistent with the ground state proton transferred structure at $n > 6$ or with a very fast proton transfer in the excited state.

(g) *Naphthol–ammonia clusters.*

In the case of naphthol–ammonia clusters, we do not know if the hydrogen atom transfer is an open channel for the small clusters: indeed, the $\text{S}_1 \leftarrow \text{S}_0$ transition energy in naphthol is at 3.9 eV, and the dissociation energy $\text{NaphOH} \rightarrow \text{NaphO}^{\cdot} + \text{H}^{\cdot}$ is at 3.56 eV,³¹ only 0.34 eV below S_1 . The ground state binding energy for the 1–1 complex is 0.332 eV⁵² while the $\text{S}_1 \leftarrow \text{S}_0$ transition energy is slightly lower than in free naphthol (-0.029 eV). Thus, on an energy scale where the ground state of naphthol (NaphOH) is the origin, the $\text{NaphOH}^*(\text{NH}_3)$ S_1 is at 3.54 eV and the $\text{NaphO}^{\cdot} + \text{H}^{\cdot}$ limit at 3.56 eV: the exact energy difference and barrier height between $\text{NH}_3 + \text{H}$ and NH_4 are not known well enough to settle whether the $\text{NaphOH}^*(\text{NH}_3)_n \rightarrow \text{NaphO}^{\cdot} + \text{NH}_4(\text{NH}_3)_{n-1}$ is an open channel or not. New experiments on naphthol–ammonia clusters are planned to address this issue.

Conclusion

The dynamics of excited phenol–ammonia clusters seems to be more complicated than previously expected: a new channel, the hydrogen atom transfer is introduced in the present study to rationalize the nanosecond pump–probe observations. The evolution of the excited state dynamics as the cluster's size increases can be summarized including this new channel (although the exact cluster size might still be subject to further investigation) as follows. (i) For the 1–2 and 1–3 clusters, the most important reactive channel is H transfer. This process is slow enough in the 1–2 complex to observe fluorescence and probably faster in the 1–3 complex. (ii) For the 1–4, 1–5, 1–6 clusters, in addition to the H transfer channel, the proton transfer channel becomes energetically allowed, enhancing the intersystem crossing (towards triplet states). (iii) For larger clusters ($n \geq 7$) the proton transfer already occurs in the ground state, and the H transfer reaction is closed.

The case of the 1–1 complex is still under investigation: its strong fluorescence indicates that if hydrogen transfer occurs, it is a slow process. NH_4 has a very short lifetime (15 ps) and therefore its concentration will remain very small in the jet. Its ionization threshold (4.66 eV) is some 0.25 eV above the $\text{S}_1 \leftarrow \text{S}_0$ transition of the phenol–ammonia clusters so that the probe laser also acts as a pump leading to a low signal-to-noise ratio. For these reasons, no conclusions can be drawn at present.

The previous analysis of time resolved experiments was perfectly reasonable in view of the experiments available at the time. It is only because new experiments^{18,19,21–23} were in contradiction with the previous interpretation^{13–17} that we have reached the conclusion that the dynamics in this system has to be revisited, including new channels.

With the new hypothesis of hydrogen transfer, much more work has to be done to understand this “simple” phenol–ammonia system in which many photophysical and photochemical processes are observed to compete and evolve with the cluster size.

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References

- 1 O. Cheshnovsky and S. Leutwyler, *Chem. Phys. Lett.*, 1985, **121**, 1.
- 2 O. Cheshnovsky and S. Leutwyler, *J. Chem. Phys.*, 1988, **88**, 4127.
- 3 T. Droz, R. Knochenmuss and S. Leutwyler, *J. Chem. Phys.*, 1990, **93**, 4520.
- 4 R. Knochenmuss, *Chem. Phys. Lett.*, 1998, **293**, 191.
- 5 J. J. Breen, L. W. Peng, D. M. Willberg, A. Heikal, P. Cong and A. H. Zewail, *J. Chem. Phys.*, 1990, **92**, 805.
- 6 S. K. Kim, J. K. Wang and A. H. Zewail, *Chem. Phys. Lett.*, 1994, **228**, 369.
- 7 S. K. Kim, J. J. Breen, D. M. Willberg, L. W. Peng, A. Heikal, J. A. Syage and A. H. Zewail, *J. Phys. Chem.*, 1995, **99**, 7421.
- 8 S. K. Kim, S. Li and E. R. Bernstein, *J. Chem. Phys.*, 1991, **95**, 3119.
- 9 M. F. Hineman, G. A. Brucker, D. F. Kelley and E. R. Bernstein, *J. Chem. Phys.*, 1992, **97**, 3341.
- 10 D. F. Kelley and E. R. Bernstein, *Chem. Phys. Lett.*, 1999, **305**, 230.
- 11 D. Solgadi, C. Jouvet and A. Tramer, *J. Phys. Chem.*, 1988, **92**, 3313.
- 12 C. Jouvet, C. Dedonder-Lardeux, M. Richard-Viard, D. Solgadi and A. Tramer, *J. Phys. Chem.*, 1990, **94**, 5041.
- 13 J. Steadman and J. A. Syage, *J. Phys. Chem.*, 1990, **92**, 4630.
- 14 J. A. Syage and J. Steadman, *J. Chem. Phys.*, 1991, **95**, 2497.
- 15 J. Steadman and J. A. Syage, *J. Am. Chem. Soc.*, 1991, **113**, 6786.
- 16 J. A. Syage, *Chem. Phys. Lett.*, 1993, **202**, 227.
- 17 J. A. Syage, *Faraday Discuss.*, 1994, **97**, 401.
- 18 M. F. Hineman, D. F. Kelley and E. R. Bernstein, *J. Chem. Phys.*, 1993, **99**, 4533.
- 19 C. Jacoby, P. Hering, M. Schmitt, W. Roth and K. Kleinermanns, *Chem. Phys.*, 1998, **23**, 239.
- 20 N. Mikami, A. Okabe and I. Suzuki, *J. Phys. Chem.*, 1988, **92**, 1858.
- 21 N. Mikami, S. Sato and M. Ishigaki, *Chem. Phys. Lett.*, 1993, **202**, 431.
- 22 S. Sato, T. Ebata and N. Mikami, *Spectrochim. Acta A*, 1994, **50**, 1413.
- 23 S. Martrenchard, C. Dedonder, C. Jouvet, D. Solgadi, M. Vervloet, G. Grégoire and I. Dimicoli, *Chem. Phys. Lett.*, 1999, **310**, 173.
- 24 W. Siebrand, M. Z. Zgierski, Z. K. Smedarchina, M. Vener and J. Kaneti, *Chem. Phys. Lett.*, 1997, **266**, 47.
- 25 M. V. Vener and S. Iwata, *Chem. Phys. Lett.*, 1998, **292**, 87.
- 26 W. Siebrand, M. Z. Zgierski and Z. K. Smedarchina, *Chem. Phys. Lett.*, 1997, **279**, 377.
- 27 M. Yi and S. Scheiner, *Chem. Phys. Lett.*, 1996, **262**, 567.
- 28 S. L. Murov, I. Carmichael and G. L. Hug, in *Handbook of Photochemistry*, Marcel Dekker, Inc., New York, Basel, Hong Kong, 2nd edn., 1993, and references therein.
- 29 R. J. Lipert, G. Bermudez and S. D. Colson, *J. Phys. Chem.*, 1988, **92**, 3801.
- 30 A. Sur and P. M. Johnson, *J. Chem. Phys.*, 1986, **84**, 1206.
- 31 R. R. Borges Dos Santos and J. A. Martinho Simoes, *J. Phys. Chem. Ref. Data*, 1998, **27**, 707.
- 32 E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 410.
- 33 M. Fujio, R. T. McIver and R. W. Taft, *J. Am. Chem. Soc.*, 1981, **103**, 4017.
- 34 N. Gonohe, H. Abe and N. Mikami, *J. Phys. Chem.*, 1985, **89**, 3642.
- 35 R. F. Gunion, M. K. Gilles, M. L. Polak and W. C. Lineberger, *Int. J. Mass Spectrom. Ion Processes*, 1992, **117**, 601.
- 36 A. Schiefke, C. Deusen, C. Jacoby, M. Gerhards, M. Schmitt, K. Kleinermanns and P. Hering, *J. Chem. Phys.*, 1995, **102**, 9197.
- 37 (a) J. D. Payzant, A. J. Cunningham and P. Kebarle, *Can. J. Chem.*, 1973, **51**, 3242; (b) M. R. Arshadi and J. H. Futrell, *J. Phys. Chem.*, 1974, **78**, 1482; (c) R. G. Keese and A. W. Castelman, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1012.
- 38 (a) F. Misaisu, P. L. Houston, N. Nishi, H. Shinohara, T. Kondow and M. Kinoshita, *J. Phys. Chem.*, 1989, **93**, 7041; (b) F. Misaisu, P. L. Houston, N. Nishi, H. Shinohara, T. Kondow and M. Kinoshita, *J. Chem. Phys.*, 1993, **98**, 336.
- 39 (a) S. Wei, J. Purnell, S. A. Buzza and A. W. Castelman, Jr, *J. Chem. Phys.*, 1993, **99**, 755; (b) J. Purnell, S. Wei, S. A. Buzza and A. W. Castelman, Jr, *J. Phys. Chem.*, 1993, **97**, 12530.
- 40 C. Dedonder-Lardeux, I. Dimicoli, C. Jouvet, S. Martrenchard-Barra, M. Richard-Viard, D. Solgadi and M. Vervloet, *Chem. Phys. Lett.*, 1995, **240**, 97.
- 41 M. A. Duncan, T. G. Dietz, M. G. Liverman and R. E. Smalley, *J. Phys. Chem.*, 1981, **85**, 7.
- 42 C. Crepin and A. Tramer, *Chem. Phys.*, 1991, **156**, 281.
- 43 M. Krauss, J. O. Jensen and H. F. Hameka, *J. Phys. Chem.*, 1994, **98**, 9955.
- 44 G. I. Gellene, D. A. Cleary and R. F. Porter, *J. Chem. Phys.*, 1982, **77**, 3471.
- 45 (a) H. Cao, E. M. Evleth and E. Kassab, *J. Chem. Phys.*, 1984, **81**, 1512; (b) E. Kassab and E. M. Evleth, *J. Am. Chem. Soc.*, 1987, **109**, 1653; (c) J. Kaspar, H. Smith, Jr and B. N. McMaster, *Chem. Phys.*, 1985, **96**, 81.
- 46 Note added as proof of this. The successive binding energies for $\text{NH}_4(\text{NH}_3)_n$ clusters have been evaluated by Fuke *et al.*^{47,48} using the thermodynamical proton affinities of $(\text{NH}_3)_n$ clusters³⁷ and their ionization threshold measurements: 0.34, 0.12, 0.26 eV for $n = 1, 2, 3$ respectively. For $\text{PhOH}(\text{S}_1)-(\text{NH}_3)_n$, the successive transition energies for $n = 1-3$ are only weakly dependent on the cluster size (4.428 eV for $n = 1$, 4.407 and 4.395 for $n = 2$ and 3, respectively¹⁹); the ground state binding energy is known for $n = 1$ with a large uncertainty (0.22–0.30 eV) and the binding energy in the excited state is then between 0.30 and 0.38 eV. For $n = 2$ the ground state binding energy (E_b) can only be estimated: it cannot be less than the binding energy of the ammonia dimer ($D_0 = 0.079$ eV,^{50a} $D_0 < 0.13$ eV,^{50b} $D_0 < 0.124$ eV,^{50c} $D_0 = 0.071$,^{50d} nor more than the binding of the first ammonia molecule to phenol (0.22–0.30 eV); thus 0.07 eV $< E_b$ (2–1) < 0.30 eV. For $n = 3$ the same estimation can be proposed, between the binding energy of the ammonia trimer (0.247 eV,^{50d} 0.124 eV $< D_0 < 0.248$ eV^{50e}) and the binding energy of $\text{PhOH}-\text{NH}_3$. These values allow us to estimate the binding energies in the S_0 state for $n = 2$ and 3 to be of the order of 0.17 ± 0.09 and 0.21 ± 0.09 eV, respectively, and leads to S_1 binding energies of the same order of magnitude as in the ground state, 0.19 ± 0.09 and 0.22 ± 0.09 eV. To resume, in going from NH_4 to $\text{NH}_4(\text{NH}_3)_2$, the binding energy is 0.48 eV and in going from $\text{PhOH}-\text{NH}_3$ to $\text{PhOH}-(\text{NH}_3)_3$ E_0 is between 0.41 ± 0.18 , so that the difference between solvation energies of NH_4 and $\text{PhOH}-\text{NH}_3$ by two more ammonia molecules is 0.07 ± 0.18 eV. The H transfer reaction channel should be open for $n = 2$ and 3, in agreement with the aforementioned assumption.
- 47 K. Fuke, R. Takasu and F. Misaisu, *Chem. Phys. Lett.*, 1994, **229**, 597.
- 48 K. Fuke and R. Takasu, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 3309.
- 49 G. I. Gellene and R. F. Porter, *J. Phys. Chem.*, 1984, **88**, 6680.
- 50 (a) E. H. T. Olthoff, A. van der Avoird and P. E. S. Wormer, *J. Chem. Phys.*, 1994, **101**, 8430; (b) D. D. Nelson, Jr, W. Klemperer, G. T. Fraser, F. J. Lovas and R. D. Suenram, *J. Chem. Phys.*, 1987, **87**, 6364; (c) B. Heijmen, A. Bizarri, S. Stolte and J. Reuss, *Chem. Phys.*, 1988, **126**, 201; (d) C. E. Dykstra and L. Andrews, *J. Chem. Phys.*, 1990, **92**, 6043.
- 51 Picosecond pump-probe experiments with resonant excitation are now in progress in our group to measure the kinetics of the hydrogen transfer reactions.
- 52 T. Bürgi, T. Droz and S. Leutwyler, *Chem. Phys. Lett.*, 1995, **246**, 291.

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