

Picosecond Hydrogen Transfer in the Phenol-(NH₃)_{n=1–3} Excited State

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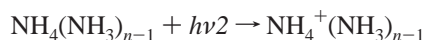
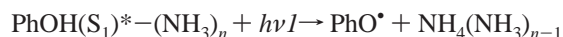
The phenol-(NH₃)_{n=1,2,3} (S₁) lifetimes have been measured near their band origins by a picosecond pump/probe scheme. The very short lifetimes observed reveal that the excited clusters undergo a reactive process, namely the following dissociative hydrogen transfer reaction: PhOH^{*}-(NH₃)_n → PhO^{*} + NH₄(NH₃)_{n-1}.

Introduction

Naphthol-ammonia^{1–10} and phenol-ammonia^{11–18} have long been considered as model systems to study proton-transfer reactions in molecular clusters. The excited-state proton transfer (ESPT) results from the coupling of the covalent excited-state PhOH(S₁)-(NH₃)_n with the ionic excited-state PhO^{*}-(phenolate)-(NH₄⁺)(NH₃)_{n-1} (protonated ammonia cluster). Both systems (phenol and naphthol) have been characterized through fluorescence^{1–3} and multiphoton ionization at the nanosecond or picosecond time scale.^{3–22} In the PhOH-(NH₃)_n system, the ground-state proton transfer has also been studied experimentally through VUV ionization²³ and theoretically.^{24,25}

Recent experiments performed in the group of Kleinermanns¹⁹ on PhOH-(NH₃)_n clusters have shown that the fingerprints of the 1–3 and 1–4 complexes (structured vibronic bands characteristic of each cluster size) are only detected when the observation is set on the (NH₃)_nH⁺ mass peaks, while the excitation spectra recorded on the [PhOH-(NH₃)_n]⁺ mass peaks are structureless. This result shows that, in the ion states, evaporation of ammonia molecules from large clusters is a major contributor to the [PhOH-(NH₃)_n]⁺ signal, whereas it does not occur in (NH₃)_nH⁺ fragments. The spectroscopic analysis realized in this experiment, makes it possible to excite selectively a specific cluster size up to *n* = 4.

In recent publications, we have evidenced that small excited phenol-(NH₃)_n clusters (with *n* = 2 to 4) react in the excited state to generate solvated ammonium radicals NH₄(NH₃)_{n=1–3} via dissociative hydrogen atom transfer.^{26–27} The NH₄⁺(NH₃)_n ions observed result from ionization of these neutral radicals.



This channel is energetically open, NH₄(NH₃)_n radicals are stable on the microsecond time scale and can be ionized in the same energy region as that used to probe phenol-ammonia clusters.^{28,29} This H-transfer mechanism is evidenced by using delayed ionization: NH₄⁺(NH₃)_{n=1,3} signals are observed for delays as long as 350 ns between excitation and ionization lasers.

Although larger phenol-(NH₃)_{n=5,6} clusters do not have structured spectra, NH₄⁺(NH₃)_{n=4} behaves like the smaller products, while NH₄⁺(NH₃)_{n=5} is the largest fragment observed but with much less intensity, which indicates that hydrogen transfer is effective in phenol-(NH₃)_n at least up to *n* = 5 and may be up to *n* = 6.

Solvated ammonium radicals are long-lived (μs), so they can be ionized with nanosecond lasers^{28,29} and easily detected, but this is not the case for the free NH₄ radical. Therefore, for the 1–1 complex, the question of H-atom transfer is still unsettled:

- The NH₄ radical lifetime is in the order of 15 ps²⁸ so that it will dissociate quickly before ionization and detection.

- Its ionization threshold (4.62 eV) is some 0.25 eV above the S₁ – S₀ transition of the phenol-ammonia clusters so that the probe laser also acts as a pump. Moreover the NH₄⁺ ion can be produced through evaporative processes in the (PhOH-(NH₃)_n)⁺ ions³⁰ or after the absorption of one photon in the ion.^{21,22}

We will present here lifetime measurements on the PhOH-(NH₃)_{1,2,3} complexes which will give evidence that H transfer in the excited state is a rather fast reaction and that it is also present in the 1–1 complex.

Experimental Section

The clusters are produced by expanding a mixture of He/Ne seeded with ammonia (0.1 to 0.5%) and flowing over phenol contained in a reservoir at room temperature. The backing pressure used is typically 2 bar, and the nozzle diameter is 300 μm. Under these conditions, no large clusters are observed and nicely structured vibronic spectra can be obtained for small clusters. A homemade picosecond OPO laser has been used for the lifetime measurements. The picosecond pulses are produced with a Nd:YAG laser. Through a combination of saturable absorber and passive negative feedback, a macro-impulsion involving 50 pulses of 10 ps duration, separated by 10 ns is produced at a 20 Hz repetition rate. Thirty percent of the 1.064 μm pump power, e.g., 400 mW, is used to pump synchronously a LiNbO₃-based infrared OPO laser tunable from 2.5 to 4 μm. The remaining pump power (800 mW) is frequency tripled to 355 nm (220 mW) to pump synchronously a BBO-based visible OPO laser tunable from 410 to 2600 nm. The present experiment makes use of the latter visible OPO output around 560 nm which is frequency doubled and used to excite the S₀ → S₁ transition in the PhOH-(NH₃)_n clusters. A portion of the frequency tripled

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355 nm is optically delayed and used as the probe ionization laser. The spectral width of the visible OPO is less than 3 cm^{-1} which allows a good selection of the cluster size. The laser characteristics make it possible to monitor dynamical processes with a resolution of 10 ps, if the reactive system can relax within 10 ns corresponding to the laser pulse separation. The multipulse structure precludes, however, the rise time measurement of stable species (in this case $\text{NH}_4(\text{NH}_3)_n$).

The ions are detected in a 1 m reflectron time-of-flight mass spectrometer (Jordan Co).

Results

It has been already shown that an important fragmentation occurs in the ion even if the total energy of the system is quite low (8.15 eV).^{18,27} It is then difficult to assign a lifetime measured at a given ion mass to its neutral parent precursor except if the pump laser can excite specifically a given parent cluster. For the 1–1 complex, expansion conditions such that the larger clusters are not present in the molecular beam can easily be obtained. Moreover, the 0_0^0 band of the 1–1 complex is strong and can be easily excited, as well as higher vibronic bands located at +182, +486, and +788 cm^{-1} above the origin. These bands correspond to the σ intermolecular hydrogen-bond stretch, $6a_0^1$ and 12_0^1 intramolecular phenol modes, respectively.^{20,31} The lifetimes measured for the origin and these vibronic bands are 1230 ± 200 , 390 ± 90 , 470 ± 100 , and 270 ± 50 ps, respectively.

For the 1–2 complex, the experiment is a bit more complicated: even with mild expansion conditions, using a low NH_3 concentration (less than 0.5% in He or Ne), low pressures (1 bar) and the phenol maintained at room temperature to avoid the formation of large clusters, the 1–3 and 1–4 complexes are always present with the 1–2. Consequently, the signal resulting from the 1–2 complex vibrational band is superimposed on a background due to the excitation of larger clusters. To extract the 1–2 complex signal, we compare the decay curves obtained when the laser frequency is tuned to the center of a 1–2 complex vibrational band and then shifted 10 cm^{-1} off resonance (Figure 1). Because of the overlap of the larger clusters absorption bands, the corresponding signal is quasi frequency independent for such a small frequency shift which, however, entails a cancellation of the 1–2 cluster signal. As seen in Figure 1, the subtraction procedure allows the extraction of the 1–2 complex signal which shows a decay time very different from the one characteristic of the larger clusters.

For clusters larger than $n = 3$, sharp bands are not observed any more and background subtraction cannot be performed. The signal observed then corresponds to the superposition of different signals coming from different cluster sizes. It is similar to the background signal shown in Figure 1 and to what has been observed previously by Syage et al.¹⁴ using 266 nm /355 nm for the pump probe scheme: the signal is characterized by a small decay superimposed on a step function.

The lifetimes measured for the 1–1, 1–2, and 1–3 complexes are reported in Figure 2.

Three points emerge from these measurements:

(1) Short lifetimes are measured, and they decrease with increasing excess energy and with cluster size.

(2) For the 1–2 complex, the lifetime measured in this experiment is quite similar to the lifetime measured by Bernstein and co-workers:¹⁸ since we have subtracted the background due to the evaporation of large clusters, one can definitely assess that the lifetime of the 1–2 complex is short (400 ps at the

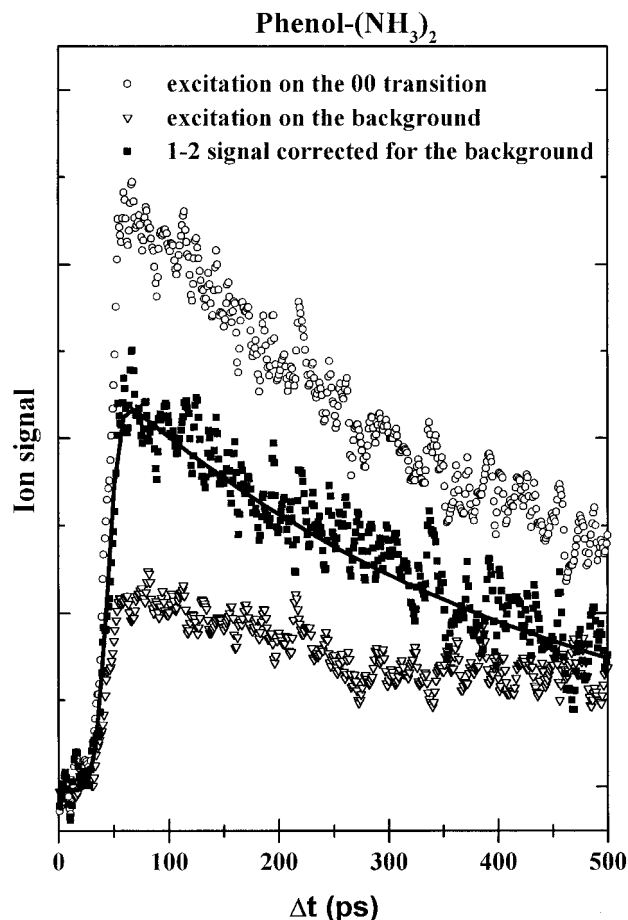


Figure 1. Lifetime of the 1–2 complex. \circ , excitation on the origin of the 1–2 complex vibrational progression; ∇ , excitation on the background (larger clusters), 10 cm^{-1} lower in energy; \blacksquare , corrected signal due to the 1–2 complex. The fit obtained with a 410 ps lifetime is represented by the full line.

origin) and decreases to 60 ps when a small excess energy (180 cm^{-1}) is added.

(3) In the 1–1 complex, excitation of the intermolecular vibrational mode seems to affect specifically the lifetime as can be seen in Figure 2: the lifetime measured when exciting the +182 cm^{-1} vibrational band assigned to the $\text{PhOH}\cdots\text{NH}_3$ σ stretching mode is 390 ps, whereas it is 470 ps upon excitation of the $6a_0^1$ intramolecular mode at 486 cm^{-1} .

Discussion

The 1–2 and 1–3 Complexes. Very short lifetimes are observed for the 1–2 (400 ± 50 ps on the 0–0 band to 60 ± 10 ps at higher energy) and 1–3 (50 ± 10 ps at the origin) complexes. For these clusters the H-transfer mechanism has been clearly evidenced in nanosecond delayed ionization experiments.²⁷ In such experiments with nanosecond lasers, the appearance time of the solvated ammonium cluster was not measurable, and could be estimated to be shorter than 2 ns. It is therefore quite natural to assign the very short lifetime of the S_1 state to the hydrogen atom transfer reaction.

It should be recalled that the temporal profile of our laser (a macro impulsion composed of 50 pulses of 10 ps separated by 10 ns) does not allow the measurement of the appearance time of the solvated ammonium $\text{NH}_4(\text{NH}_3)_n$. However, the appearance times of the $\text{NH}_4^+(\text{NH}_3)_{n=2-5}$ ion signals have been already measured by Syage and co-workers¹³⁻¹⁵ and by Bernstein et al.¹⁸ to be around 60 ps. These rise times are perfectly

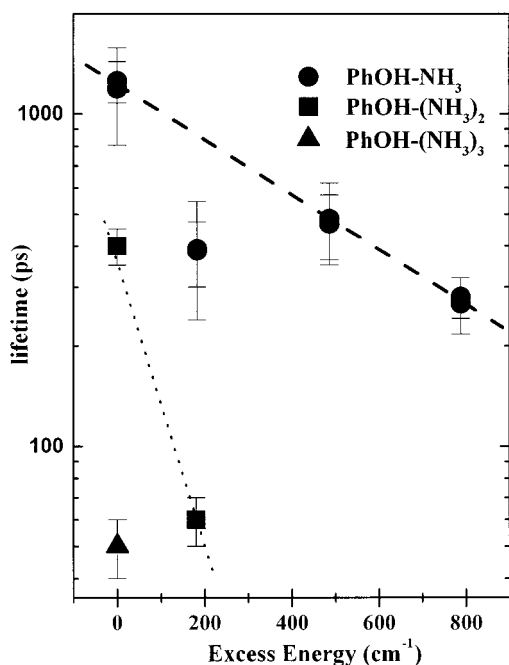


Figure 2. Measured lifetimes for the $\text{PhOH}-(\text{NH}_3)_{1-3}$ clusters as a function of vibrational excess energy in the S_1 state (the left axis is in a logarithmic scale). ● 1-1 complex, the dashed line indicates that the lifetime decreases monotonically when intramolecular phenol modes are excited. ■ 1-2 complex, the dotted line is just for guidance. ▲ 1-3 complex.

compatible with the present experiment, but have to be assigned to the H transfer and not as the evidence of proton transfer followed by evaporation as previously accepted.

The 1-1 Complex. The lifetimes of the phenol-ammonia complexes have to be compared with those of the free phenol and other phenol complexes.

Phenol has a short lifetime (2 ns) compared to its radiative lifetime,³²⁻³⁴ with a low fluorescence quantum yield (8%).³² Inter-system crossing (ISC) and internal conversion (IC) are responsible for this short lifetime.^{33,34}

It has been shown that the $\text{PhOH}-(\text{H}_2\text{O})_n$ ³⁴⁻³⁶ lifetimes are longer (15, 6, 18 ns for $n = 1, 2, 3$ respectively) since for the water complexes, the rate of internal conversion decreases considerably, although the density of isoenergetic S_0 states increases in the complex through the low-frequency intermolecular modes. This decrease of IC is thought to be due to the perturbation of the OH stretching frequency by the hydrogen bonding with water, this mode being the most important accepting mode for radiationless transitions. This assumption is corroborated by the long lifetime of PhOD (16 ns) where the IC rate is reduced by 2 orders of magnitude.³⁵ Similar observations have been done with methanol as solvent, the lifetime of phenol in liquid methanol being in the order of 6 ns³² and the phenol-methanol complexes (with $n \leq 11$) are also long-lived (≥ 10 ns).^{14,15}

Complexation of benzene with phenol also shows a lengthening of the complex lifetime with respect to the free phenol,³⁷ monitored on the $(\text{PhOH}-\text{Bz})^+$ ion signal as a function of the pump/probe delay. Moreover, no decrease of the complex lifetime is observed until the threshold for predissociation of the complex is reached (around 1400 cm^{-1} of excess energy), indicating that non radiative processes such as ISC, IC, and eventually vibrational relaxation are not sensitive to the vibrational energy.

Complexation with ammonia introduces the same kind of perturbation on the OH stretching vibration as water or methanol

(the shifts of the IR band are -133 and -363 cm^{-1} for water and ammonia, respectively).³⁸ Therefore, on the aforementioned basis, a lengthening of the lifetime was also expected, but the reverse is observed. It seems that a different deactivation channel is acting in phenol-ammonia complexes.

The lifetime of the 1-1 complex decreases monotonically with increasing excess energy in the S_1 state when intramolecular phenol modes are excited. This is what is expected for a statistical process and has been observed for the vibrational predissociation of phenol-benzene for energy excess larger than 1400 cm^{-1} . We have however small energy excesses, well under predissociation threshold and therefore this mechanism is not responsible for the short decay time. Moreover, the lifetime is shorter when the $+182$ cm^{-1} vibronic band is excited than for the $+486$ cm^{-1} band which is unexpected on the basis of increasing density of states. The $+182$ cm^{-1} vibronic level corresponds to the excitation of the intermolecular stretching and thus involves directly the coordinate corresponding to H-atom transfer. The specific increase of the non radiative rate constant for this vibration, as well as the short lifetimes of intramolecular vibrations, may then be linked to the photoreaction $\text{PhOH}^*-\text{NH}_3 \rightarrow \text{PhO}^* + \text{NH}_3^*$ which has been clearly evidenced for $\text{PhOH}-(\text{NH}_3)_{n=2,3}$ clusters.

Larger Clusters. For larger clusters $\text{PhOH}-(\text{NH}_3)_{n>3}$ mass peaks, no decay of the signal as a function of the pump/probe delay is observed. But, it does not mean that the reaction leading to the H transfer does not exist any more. From previous experiments^{13,15,18} a 60 ps rise time has been observed for the appearance of $\text{NH}_4(\text{NH}_3)_n^+$, up to $n = 5$, thus the large clusters (up to $\text{PhOH}-(\text{NH}_3)_{n=6}$) undergo H transfer at a rate comparable to what has been observed for $n = 2$ or 3. The flat picosecond transient observed for $[\text{PhOH}-(\text{NH}_3)_{n>3}]^+$ is certainly not due to the excitation of the neutral cluster of the same mass, since these clusters are decaying via the H-transfer process. As already mentioned in previous studies, the evaporation mechanisms have to be taken into account:^{18,27} since it is no longer possible to select only one cluster size by the wavelength of the pump photon, the larger clusters are also excited and ionized and contribute to the $[\text{PhOH}-(\text{NH}_3)_{n>3}]^+$ mass peak: the decay due to H transfer is thus hidden.

In light of the present experiment, previous picosecond experiments¹³⁻¹⁸ have to be discussed. Let us first mention that the present experiment is in agreement with the experimental results of Bernstein et al. on the 1-2 complex.¹⁸ It then appears that the H-transfer mechanism is a fast process, 50 ps for the 1-3 complex as well as for the vibrationally excited 1-2 cluster (60 ps) and that the 60 ps rise time observed for the $\text{NH}_4(\text{NH}_3)_2$ fragment is **not** connected to the proton-transfer mechanism.¹⁸ Certainly, the dynamics of large clusters is more complicated than was previously thought and now needs to be reconsidered.

Conclusion

In the case of the 1-2 and 1-3 complex, where H-atom transfer occurs in the excited state as demonstrated in previous experiments, the lifetime is shortened as compared to free phenol and to phenol-water or phenol-methanol complexes. The lifetimes measured are in good agreement with the previous measurements for the appearance time of the solvated ammonium radical, showing the direct link between the fast decay and the reaction. For the 1-1 complex, there is no direct evidence for the excited-state dissociation into phenoxy + ammonium radicals, but the short lifetimes as compared to phenol-water complexes are indicative of a supplementary nonradiative process in phenol-ammonia. The mode specific

behavior of the intermolecular stretching mode points to the hydrogen atom transfer as a likely candidate.

The ammonium radical will be difficult to probe because of its short lifetime, but the detection of hydrogen atoms issued from the NH_4 dissociation could be used to assess the mechanism.

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