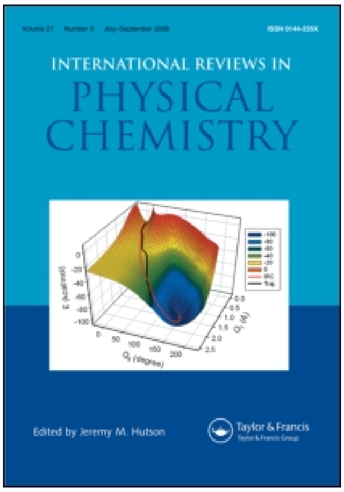

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Is there an Excited State Proton Transfer in phenol (or *1*-naphthol)–ammonia clusters? Hydrogen Detachment and Transfer to Solvent: a key for non-radiative processes in clusters

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This contribution highlights recent advances in the understanding of excited state dynamics in aromatic enols. This review will be mainly focused on the experimental and theoretical work performed on two model systems, *1*-naphthol–ammonia and phenol–ammonia, and most particularly on cluster studies. These systems have long been thought to be prototypes for the famous 'solvent-induced excited state proton transfer reaction', but recent results contradict this mechanism. The dynamics of these systems, excited in the S_1 ($\pi\pi^*$) state, is not governed by couplings with ion pair states, inducing intracluster proton transfer, but rather linked to a crossing with a higher excited singlet state of the $\pi\sigma^*$ Rydberg state character, dissociative along the OH coordinate, leading to a hydrogen transfer from the hydroxyl group to the ammonia cluster via a non-adiabatic process, a mechanism also referred to as 'concerted electron and proton transfer'. The crossing of the higher $^1\pi\sigma^*$ state with lower excited $^1\pi\pi^*$ and ground states seems to be a general property in aromatic enols and azines (indole derivatives) and can help to understand the non-radiative decays in amino acid molecules as well as in DNA bases.

Contents

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1. Introduction

Proton transfer is an important primary process involved in many chemical reactions and biological processes. It is a simple acid–base reaction $AH + B \rightarrow A^- + HB^+$. In the gas phase, numerous studies have been performed to characterize this process in neutral as well as in ionic clusters.

Proton transfer can be induced by electronic excitation of molecules that undergo a large change in acidity between their ground and excited states:

$$AH + B + h\nu \rightarrow AH^* + B \rightarrow A^{-*} + HB^+.$$

In solution, the excited state proton transfer (ESPT) process can be probed through fluorescence since the anion emission is different from the normal molecular fluorescence. In clusters, Cheshnovsky and Leutwyler (1985, 1988) initiated investigations of ESPT in 1985 in the *1*-naphthol–ammonia system. These first investigations were followed by many other studies on two model systems, i.e. *1*-naphthol–$(NH_3)_n$ and phenol–$(NH_3)_n$ clusters, where ESPT has been thought to have been observed (Bernstein 1996, Jouvet *et al.* 1996, Zhong and Castleman 2000), but as we will see this interpretation does not seem to be correct. In these systems, the ESPT reaction would result from the coupling of the first covalent excited state $ROH(S_1)$–$(NH_3)_n$ with the ion pair excited state of the anion-protonated ammonia cluster $\{RO^{-}*–(NH_4^+)(NH_3)_{n-1}\}$. In clusters, the critical sizes for proton transfer appearance are directly related to the pK_a value of the acids and to the proton affinity of the base cluster, which depends on the number of molecules (Cheshnovsky and

Leutwyler, 1985, 1988, Solgadi *et al.* 1988, Knockenmuss *et al.* 1988, Droz *et al.* 1990, Jouvet *et al.* 1990). We will focus our attention on the reactive process in phenol–$(NH_3)_n$ and *1*-naphthol–$(NH_3)_n$ clusters, and not on the related spectroscopic studies that have been very well described in recent reviews (Zwier 1996, Ebata *et al.* 1998, Zwier 1998). In the following, phenol, phenolate anion and phenoxy radical will also be referred to as PhOH, PhO^- and $PhO^\bullet$. For *1*-naphthol, naphtholate anion and naphthoxy radical the notations 1-NpOH, $1\text{-}NpO^-$ and $1\text{-}NpO^\bullet$ will also be used.

2. The Excited State Proton Transfer Reaction: a brief history

2.1. *ESPT in the condensed phase*

The concept of ESPT starts with Weber (1931) who found that the spectral shift of an acid–base equilibrium of some organic molecules occurred at a different pH when it was observed by absorption or fluorescence spectroscopy. Förster (1949, 1950) and Weller (1952, 1961) developed the field of ESPT and provided evidence that *1*-naphthol fluoresces very little while the fluorescence of the *1*-naphtholate anion is very strong in water. The *1*-naphtholate anion fluorescence is characterized by an emission around 450 nm, whereas the *1*-naphthol fluorescence is located around 340 nm. Later Nagakura and Gouterman (1957) studied the evolution of the *1*-naphtholate emission as a function of the proton affinity of the base and deduced a charge transfer mechanism, at least in the ground state. From the work of Harris and Sellinger (1980), it appears that the fluorescence of *1*-naphthol in water is around 200 times less intense than the naphtholate anion emission at pH 7. At high pH the *1*-naphthol emission is not seen at all, and even at very low pH the *1*-naphthol emission is still lower than that from the naphtholate anion.

Mataga and Kaifu (1965) followed the *1*-naphthol/naphtholate emission as the concentration of triethylamine (TEA) is increased in a cyclohexane or benzene solution. They observed a strong dependence of the naphtholate emission on the TEA concentration, implying the formation of a proton-transferred species. The simplest explanation for the absence of *1*-naphthol fluorescence and the very strong one of *1*-naphtholate is the ESPT mechanism. One of the arguments in favour of this process was the very strong enhancement of the hydrogen bond in the first excited state as compared with the ground state, leading to the idea of increased acidity in the excited states of *1*-naphthol and phenol .

Matrix isolation experiments have also resulted in observations which can substantiate the ESPT mechanism. In particular, Brucker and Kelley (1989a,b) have observed that excitation of *1*-naphthol–$(NH_3)_3$ clusters in an argon matrix leads to the appearance of the naphtholate fluorescence with a delay of 20 ps which implies that reaction of one leads to the other via the ESPT. The relationship between ESPT and triplet states has been outlined by Crépin and Tramer (1991).

It should be noticed that another process has also been evidenced in the liquid phase and forgotten afterwards in cluster studies: the excitation of phenol particularly into the S_2 state leads to the formation of H_2 (Köhler and Getoff 1976, Köhler *et al.* 1982), indicating that non-radiative decay routes different from ESPT also exist in this system.

2.2. *ESPT in clusters, the first experiments*

Following the idea that ESPT occurs in basic solutions, it was expected to happen also in the gas phase whenever the acid is complexed with a strong enough base. An interesting way to increase the basicity of the complexant—initiated in Leutwyler's group (Cheshnovsky and Leutwyler 1985, 1988, Droz *et al.* 1990)—is to use clusters of a base, such as ammonia clusters, since their proton affinities increase with cluster size ranging from 8.86 eV for ammonia (Hunter and Lias 1998) to 11 eV for the $(NH_3)_5$ cluster (Keesee and Castlemann 1986, Knochenmuss *et al.* 1988, Hunter 1998). Numerous studies have been performed along this line, to characterize the proton transfer reactions in neutral and ionic clusters. ESPT has been thought to be observed in two model systems: *1*-naphthol–ammonia (Cheshnovsky and Leutwyler 1985, 1988, Droz *et al.* 1990, Kim *et al.* 1991, Knochenmuss *et al.* 1993, Knochenmuss and Smith 1994, Yi and Scheiner 1996, Knochenmuss 1998, Kelley and Bernstein 1999, Knochenmuss 1999a,b, Knochenmuss *et al.* 1999, Dedonder-Lardeux *et al.* 2001, Knochenmuss *et al.* 2001), and phenol–ammonia (Solgadi *et al.* 1988, Jouvet *et al.* 1990, Steadman and Syage 1990, Syage and Steadman 1991, Steadman and Syage 1992, Hineman *et al.* 1993, Syage 1993a,b, Martrenchard-Barra *et al.* 1999, Pino *et al.* 1999, Kim *et al.* 2000, Pino *et al.* 2000).

The first observation of ESPT was the appearance of a red-shifted fluorescence characteristic of the *1*-naphtholate anion as the cluster size increases (Cheshnovsky and Leutwyler *et al.* 1985, 1988). Later, ionization potential measurements through a two-photon ionization scheme were carried out for both phenol (Solgadi *et al.* 1988, Jouvet *et al.* 1990) and *1*-naphthol (Kim *et al.* 1991) ammonia clusters, where the strong decrease of ionization threshold for $n = 4$ in phenol–$(NH_3)_n$ clusters and $n = 3$ in *1*-naphthol–$(NH_3)_n$ has been considered as a signature of the ESPT reaction.

The ESPT dynamics was studied using a picosecond pump–probe scheme with ion detection in both *1*-naphthol and phenol clusters. Picosecond decays were observed for *1*-naphthol–$(NH_3)_3$ that have been ascribed to the ESPT dynamics (Breen *et al.* 1990, Hineman *et al.* 1992, Kim *et al.* 1994, 1995, Kelley and Bernstein *et al.* 1999, Knochenmuss *et al.* 1999). For phenol–$(NH_3)_n$ clusters, picosecond decays have been measured for $n = 5$–7 together with observation of similar rise times on fragment ions $NH_4^+(NH_3)_n$, these dynamics being also assigned to the ESPT reaction (Steadman and Syage 1990, Kim *et al.* 1991, Steadman and Syage 1991a,b, Syage and Steadman 1991, Steadman and Syage 1992, Syage 1993a,b).

2.2.1. 1-*Naphthol*–$(NH_3)_n$ *clusters*

The major features of the experiments on *1*-naphthol–$(NH_3)_n$ which have led to the suggestion that the ESPT mechanism is involved in these clusters are summarized below:

(1) A strong red-shifted emission is observed when clusters larger than $n = 4$ are present in the expansion. This emission has its maximum at 450 nm and is associated with the *1*-naphtholate emission, in contrast to the emission of the *1*-naphthol molecule peaking at 320 nm.

(2) There is a similarity between the fluorescence excitation spectrum when the naphtholate emission is monitored and the two-photon excitation/ionization spectrum of *1*-naphthol–$(NH_3)_4$.

(3) In the picosecond pump–probe experiment, a 60 ps decay is observed only for the cluster sizes $n = 3$ and 4, not for smaller clusters size or for larger ones: it was then concluded that ESPT occurs for *1*-naphthol–$(NH_3)_{3,4}$ clusters. This experiment has been repeated with lower probe photon energy (Knochenmuss *et al.* 1999), so as to limit ionic fragmentation, and the picosecond decay could only be observed on the *1*-naphthol–$(NH_3)_4$ mass. It was then concluded that the ESPT occurred at $n = 4$.

(4) When the excitation photon energy is decreased from 320 nm to 370 nm, only cluster sizes larger then $n = 5$ could be detected in multiphoton ionization: at this excitation energy, the fluorescence is characteristic of the naphtholate emission. It was then concluded that ground state proton transfer was occurring for $n \geq 5$.

(5) No sign of red-shifted emission was observed when weaker bases such as methanol were used as solvents in the cluster. In the case of water, a red emission has been observed for very large clusters.

2.2.2. *Phenol–$(NH_3)_n$ clusters*

Phenol–$(NH_3)_n$ clusters present a similar general behaviour with, however, slight differences.

The phenolate emission is less red shifted with respect to the phenol emission (320 nm for the phenolate as compared with 300 nm for the phenol–NH_3). The S_0–S_1 transition is higher in energy (4.507 eV (Mikami *et al.* 1988)) than in *1*-naphthol (3.9 eV): in the former case the transition energy is 0.66 eV higher than the ground state $O\cdots H$ bond dissociation energy (3.848 eV (Borges dos Santos and Martinho Simoes 1998)) while in *1*-naphthol the dissociation limit in $1\text{-NpO}^\bullet + H^\bullet$ is 3.56 eV (Borges dos Santos and Martinho Simoes 1998), only slightly below the excited state transition. This has an important implication for the possible reactive channels: in particular, a hydrogen atom transfer reaction of the form $PhOH^*(S_1)$–$NH_3 \rightarrow PhO^\bullet + NH_4^\bullet$ is energetically allowed; taking into account the binding energy in the ground state of the complex (0.223–0.303 eV (Mikami *et al.* 1988, Schiefke *et al.* 1995)) and the isoergeticity of the $H^\bullet + NH_3 \rightarrow NH_4$ reaction (Gellene *et al.* 1982, Cao *et al.* 1984, Kaspar *et al.* 1985, Kassab and Evleth 1987) leads to a thermodynamic threshold 0.28–0.36 eV below the 0–0 transition (4.428 eV).

Conversely, this H transfer reaction should be a closed channel in *1*-naphthol–$(NH_3)_n$ clusters: the dissociation limit in $1\text{-NpO}^\bullet + H^\bullet$ is 3.56 eV and taking into account the binding energy in the ground state of the complex (0.332 eV (Bürgi *et al.* 1995)), the thermodynamic threshold is 0.02 eV above the *1*-naphthol–NH_3 S_0–S_1 transition.

The most important features of the experiments on phenol–$(NH_3)_n$ clusters relevant to the ESPT mechanism are summarized below:

(1) A strong decrease of the ionization potential occurs for the $n = 4$ cluster as compared with the $n = 3$.

(2) A red-shifted emission is observed when large clusters are present in the expansion, as for *1*-naphthol–$(NH_3)_n$ clusters.

(3) Picosecond pump–probe experiments have shown that very clear decays observed at the mass of phenol–$(NH_3)_{n=5-7}$. The observation of these decays depends on the probe laser wavelength. Correspondingly, a rise time is observed on the protonated ammonia clusters $(NH_4^+)(NH_3)_n$.

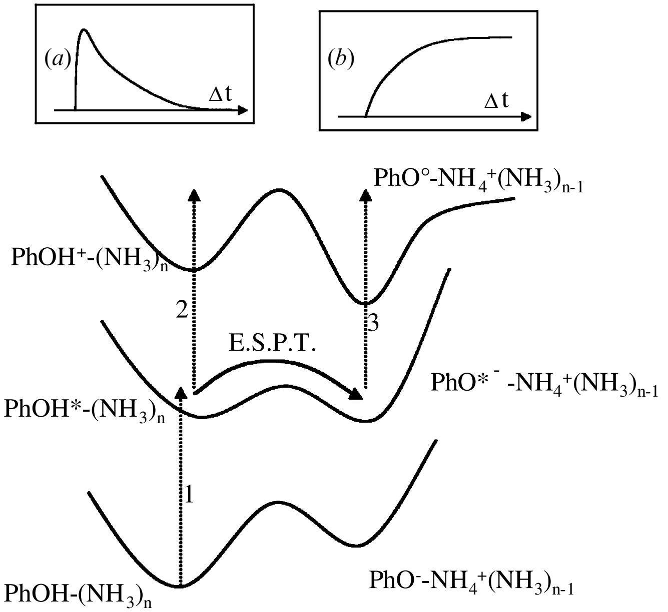

Figure 1. Schematic potential energy diagram for a PhOH–$(NH_3)_n$ cluster (e.g. $n = 5$). These curves represent the case where proton transfer can occur in the excited state. Arrow 1 represents the pump laser; excited clusters can be ionized before ESPT (arrow 2) to the non-proton-transferred part of the ionic potential, or after ESPT (arrow 3) to the proton-transferred part of the ionic potential. The ionic state presents a high barrier between non-proton-transferred and proton-transferred structures as required for the observation of picosecond decays on the $\{PhOH–(NH_3)_n\}^+$ mass peaks and rise times on the $NH_4^+(NH_3)_{n-1}$ mass peaks.

(4) These dynamics are not observed for clusters with less basic molecules (water, methanol, etc.).

According to Steadman and Syage (1990, 1991a,b), Syage and Steadman (1991), Steadman and Syage (1992), and Syage (1993a,b), the picosecond experiments can be understood with the following scheme. The starting point is the non-proton-transferred cluster in the neutral ground state PhOH–$(NH_3)_n$ and, at time $t = 0$, the cluster is excited to the non-transferred part of the excited state potential energy surface (see figure 1, arrow 1). The major dynamical process which is observed is the proton transfer from the excited PhOH*(S_1) to $(NH_3)_n$ on a timescale of 60–70 ps. This process is detected by ionizing the excited PhOH*–$(NH_3)_n$ cluster. If the excited cluster is ionized before proton transfer—figure 1, arrow 2—then the $\{PhOH–(NH_3)_n\}^+$ ion is observed. On the other hand, if ionization takes place after ESPT—figure 1, arrow 3—the $PhO^\bullet–NH_4^+(NH_3)_{n-1}$ part of the ionic surface is reached and, because there is an excess of energy in these ions, fragmentation in $PhO^\bullet + NH_4^+(NH_3)_{n-1}$ occurs and only the $NH_4^+(NH_3)_{n-1}$ fragment ions are detected. This explains the decays observed on the $\{PhOH–(NH_3)_n\}^+$ masses—figure 1(*a*)—as well as the rising signals observed on the $NH_4^+(NH_3)_{n-1}$ fragment masses—figure 1(*b*).

This interpretation implies that there is a significant barrier in the ionic surface between the non-proton-transferred and the proton-transferred forms. This is necessary to ensure selectivity in the ionic dissociation pathway, depending on which part of the ionic surface is reached through ionization of the excited cluster. Before ESPT, the ionization photon brings the system into the inner well $\{PhOH–(NH_3)_n\}^+$ of the ionic potential energy surface and, because of the barrier, the fragmentation in $PhO^\bullet + NH_4^+(NH_3)_{n-1}$ is impossible whereas, after ESPT, the outer well $PhO^\bullet–NH_4^+(NH_3)_{n-1}$ is reached and fragmentation is complete. The barrier was thought to result from a crossing between the ground state of the cation correlating with $PhOH^+ + NH_4^\bullet(NH_3)_n$ and an excited state correlating with $PhO^\bullet + NH_4^+(NH_3)_n$ and has been evaluated in the range 1.5–1.0 eV for $n = 1–4$ (Steadman and Syage 1991a).

All these converging experiments led to the conclusion that the ESPT reaction was occurring in 1-NpOH*–$(NH_3)_n$ clusters for $n = 4$ ammonia molecules and in PhOH*–$(NH_3)_n$ from $n = 4$ or 5–7.

3. Phenol and its clusters

3.1. *Some difficulties with the ESPT model*

Since these pioneering studies on the picosecond dynamics in phenol and *1*-naphthol ammonia clusters, many other investigations have been carried out on these systems, which have raised some questions with respect to the initial interpretation, mostly in the case of phenol clusters.

(1) A picosecond decay has been recorded by Bernstein and coworkers (Hineman *et al.* 1993) on detection of the $\{PhOH–(NH_3)_2\}^+$ 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 molecules (three or more) in the ionic state. This result already shows that evaporation of ammonia units in the ion has to be seriously taken into account.

(2) In the case of phenol–$(NH_3)_n$ clusters, a great part of the interpretation of the picosecond dynamics rests on the existence of a high barrier between the proton-transferred and the non-proton-transferred species in the ionic state. Such a barrier to proton transfer in the ionic state of the 1–1 complex had been postulated by Mikami *et al.* (1988) to explain their results on the $PhOH–NH_3^+$ dissociation: when this 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:

$$(PhOH–NH_3)^+ \rightarrow PhOH^+ + NH_3 \tag{1}$$

$$(PhOH–NH_3)^+ \rightarrow PhO^\bullet + NH_4^+. \tag{2}$$

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 thermodynamic limit for these processes. The second channel ($PhO^\bullet$ 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 $(PhOH–NH_3)^+$ ionic state is at least 1.3 eV. However, the absorption spectrum of the $(PhOH–(NH_3)_{n=1,2})^+$ cations, later obtained 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 (Mikami *et al.* 1993, Sato *et al.* 1994). Recent experiments have revised the relative position of the two dissociation channels, indicating that channel (2) opens at 4.5 kcal mol^{-1} higher in energy than channel (1) which explains why Mikami *et al.* only observed the NH_3^+ fragment in the $(PhOH–NH_3)^+$ dissociation (Kim *et al.* 2000).

(3) Theoretical calculations on ionic $(phenol–NH_3)^+$ clusters all seem to agree that there is no barrier to the proton transfer reaction in the ion (Yi and Scheiner 1996, Siebrand *et al.* 1997, Vener 1998, Vener and Iwata 1998, Sobolewski *et al.* 2001), as indicated by the observation of phenoxy radical absorption.

(4) Another recent experiment performed by Jacoby *et al.* (1998) shows that the fingerprint of $PhOH^*–(NH_3)_n$ with $n = 1–4$ complexes, i.e. resolved vibrational structures in the excitation spectra, can be recorded on the $NH_4^+(NH_3)_{n-1}$ fragment masses when ionizing with two photons of the same colour, which corresponds to a total energy of 8.9 eV. The appearance of protonated fragments is necessarily linked to the proton transfer mechanism either in the excited or in the ionic state. However, for the small cluster sizes ($n = 1–3$), no ESPT is expected. This experiment also suggests that the barrier separating the proton-transferred from the non-proton-transferred species in the ionic state is lower than previously assumed.

(5) The ground state proton transfer in $phenol–(NH_3)_n$ clusters has also been investigated through the measurement of vacuum ultraviolet (VUV) single-photon ionization thresholds, using synchrotron radiation (Martrenchard-Barra *et al.* 1999). As for the excited state proton transfer, a significant decrease of the ionization threshold, which occurs for $n = 6$ or 7 ammonia molecules, may be regarded as the signature of the absorption from a proton-transferred structure in the ground state. This cluster size is in agreement with the $n = 5$ threshold size suggested for ground state proton transfer in *1*-naphthol–$(NH_3)_n$ clusters, *1*-naphthol being a stronger acid than phenol. This experiment is also in good agreement with theoretical calculations (Yi and Scheiner 1996, Siebrand *et al.* 1997, Vener 1998, Vener and Iwata 1998, Siebrand and Zgierski 2001). The major problem raised here is that, if proton transfer has occurred in the ground state for $n = 6$ or 7 ammonia molecules, then the picosecond dynamics observed for $n = 6$ or 7 cannot be due to the excited state proton transfer reaction.

3.2. *The key experiments*

3.2.1. *Nanosecond pump–probe experiments*

As already mentioned, one of the key points in the ESPT picosecond mechanism in the $phenol–(NH_3)_n$ experiments is the presence of a barrier in the ionic state, this barrier being necessary to explain the rise times observed for the protonated ammonia clusters and the decays on the $phenol–(NH_3)_n$ ions.

The experimental work of Jacoby *et al.* (1998) shows that it is possible to excite the $phenol–(NH_3)_n$ complexes with $n = 1–4$ selectively. For cluster sizes $n = 1–3$, no ESPT is expected; thus, according to the ESPT model, the $PhO^{\bullet} + NH_4^+(NH_3)_{n-1}$ dissociation channel should not be observed because a high barrier to proton transfer is assumed in the ionic state. By pumping on a vibronic band of the $n = 3$

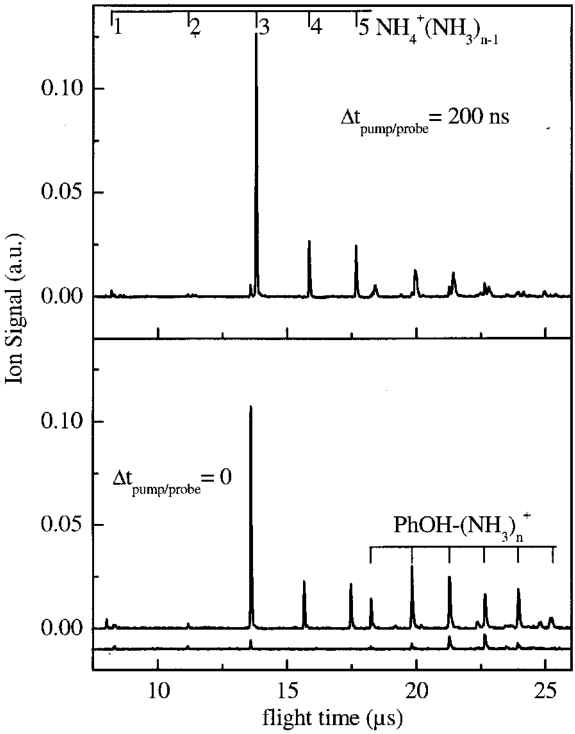

Figure 2. Mass spectra recorded in exciting the phenol–$(NH_3)_3$ cluster vibronic band at 281.65 nm. Lower trace: two-photon one-colour signal ($\lambda_1 = 281.65$ nm). Middle trace: two-photon two-colour signal (pump $\lambda_1 = 281.65$ nm, probe $\lambda_2 = 355$ nm) without delay between pump and probe lasers. Upper trace: two-photon two-colour signal with a 200 ns delay between the pump and probe lasers. It may seem that the upper trace is misaligned by one mass unit as compared with the lower trace. However, in this mass spectrum, the origin of time of flights is defined by the pump laser ($\lambda_1 = 281.65$ nm). Thus, for example, the small peak to the left of the main $NH_4^+(NH_3)_2$ peak corresponds to the two-photon one-colour signal and is exactly the same as in the lower trace. The probe laser being delayed by 200 ns, the flight time of the $NH_4^+(NH_3)_{n-1}$ ions coming from pump–probe with two colours is also lengthened by 200 ns, leading to an apparent misalignment of the peaks. The small increase in intensity as compared with the middle trace reflects a small change in the laser beams' overlap as the clusters move down the jet.

cluster and probing with 355 nm light, the two-photon energy was kept at an energy of 7.9 eV, i.e. only 0.45 eV above the ionization threshold, much less than that used by Syage and Steadman in their picosecond experiments (9.3 eV). Following the ESPT model, no protonated ammonia clusters should be detected. In fact they are (see figure 2), implying that there is no high barrier in the ionic potential (Pino *et al.* 1999, 2000).

However, excitation at the same energy (and up to 8.4 eV) with a single VUV photon did not show any fragmentation leading to the formation of PhO$^\bullet$ and protonated ammonia clusters $(NH_4^+)(NH_3)_{n-1}$ (Pino *et al.* 2000).

There is an inconsistency between these results, unless it is assumed that protonated ammonia clusters come from an excited state reaction. However, the ESPT channel is energetically closed for the $n = 3$ cluster.

A totally unexpected result came out from the two-photon two-colour experiment on phenol–$(NH_3)_3$ (Pino *et al.* 1999, 2000), which leads to a total re-examination of the ESPT mechanism in clusters and to the experimental discovery of the hydrogen transfer mechanism and is presented in figure 2. In this figure two mass spectra are compared: the lower one is obtained when the pump (set on a vibronic band of the phenol–$(NH_3)_3$ cluster) and the probe laser (355 nm) are delayed by a few nanosecond and the upper mass spectrum has been recorded with a long delay (200 ns) between pump and probe laser.

The remarkable fact is that the signal observed on the $NH_4^+(NH_3)_{n-1=2-4}$ does not decay whereas the signal observed on the phenol–$(NH_3)_n$ decreases in time. At very long delays only the signal on the protonated ammonia cluster remains. This result was interpreted as a hydrogen atom transfer mechanism, as shown below:

$$PhOH^*(S_1)\text{-}(NH_3)_n \rightarrow PhO^\bullet + NH_4^\bullet(NH_3)_{n-1}.$$

The interpretation was made possible from the knowledge obtained by Fuke and coworkers of solvated ammonium clusters. Indeed, the 355 nm (3.5 eV) probe photon used here is energetic enough to ionize the $NH_4(NH_3)_{n\geq 2}$ dissociation products (which have an ionization potential of 3.31 eV for $n = 2$ (Fuke *et al.* 1994)). At this wavelength $NH_4(NH_3)^+$ is not detected, in agreement with its higher ionization threshold (3.88 eV). However, when the probe wavelength is changed to 290 nm (4.3 eV), $NH_4(NH_3)^+$ is observed. Moreover, the work of Fuke and coworkers shows that $NH_4(NH_3)_n$ have long lifetimes (3 μs and 7 μs for $n = 1$ and 2 respectively), which is necessary to observe a delayed ionization, whereas NH4 is very short lived (16 ps) (Fuke *et al.* 1994, Fuke and Takasu 1995).

This process is similar to the reaction occurring in excited ammonia clusters (Misaisu *et al.* 1989, 1993, Purnell *et al.* 1993, Wei *et al.* 1993) where the photodissociation channel of NH_3 in $NH_2^\bullet + H^\bullet$ evolves in $(NH_3)_n \rightarrow NH_4^\bullet(NH_3)_m + NH_2^\bullet + (n\text{-}m\text{-}2)NH_3$. This excited state reaction has been used by Fuke and co-workers to generate the $NH_4^\bullet(NH_3)_m$ radicals which were further studied through ionization (Fuke *et al.* 1994, Fuke and Takasu 1995).

Since this first observation, the hydrogen atom transfer reaction has been strongly substantiated by other experiments.

3.2.2. *Spectroscopic evidence for the H transfer: IR spectrum of the ammonium radicals*

An IR depopulation spectrum has been obtained by Ishiuchi *et al.* (2000): in this experiment the $NH_4(NH_3)_2$ cluster is produced by excitation of phenol–$(NH_3)_3$, a second IR laser induces the vibrational dissociation of the complex, while a third laser ionizes the surviving cluster. Scanning the IR laser gives the equivalent of the IR absorption spectrum. This experiment led to the observation of a broad vibrational band at 2900 cm^{-1}, associated with the excitation of the NH stretching vibration of the ammonium radical, the width of the band corresponding to a very fast predissociation of $NH_4(NH_3)_2$. The same group has performed a similar depopulation experiment in the visible and near-IR region and the spectrum obtained is very similar to that obtained previously for $NH_4(NH_3)_n$ clusters by photolysis of ammonia clusters (Nonose *et al.* 1999).

3.2.3. Phenol–$(NH_3)_n$ decay

The PhOH*(S_1)–$(NH_3)_n$ lifetimes have been recorded for $n = 1$–3 to obtain the variation of the hydrogen transfer rate with excess energy. For the $n = 1$ complex, the lifetime is strongly dependent on the vibrational coordinate. Exciting the stretching intermolecular vibration that is closely related to the reaction coordinate decreases the lifetime much more than exciting an intramolecular phenol vibration. As an example, excitation of the $+486\,\mathrm{cm}^{-1}$ intramolecular vibration leads to a lifetime of 470 ps whereas excitation of the intermolecular stretching mode $+182\,\mathrm{cm}^{-1}$ results in a 390 ps lifetime. Similarly, for the $n = 2$ complex the 0–0 transition has a lifetime of 400 ps and one quantum in the intermolecular vibration shortens the lifetime to 60 ps. The lifetime decreases to 50 ps for the 0–0 band of the $n = 3$ complex. (Grégoire *et al.* 2000a)

In deuterated clusters, the lifetimes come back to the nanosecond scale (Grégoire *et al.* 2001). It is thus concluded that the H transfer mechanism occurs via tunnelling through a barrier.

4. The H transfer mechanism or concerted electron proton transfer

A new insight have been brought to the experimental evidence by the theoretical work done by Sobolewski and Domcke (2001) on the excited states of phenol and its complexes with water and ammonia. The potential energy profiles calculated along the reaction coordinate OH (OH···N or OH···O for the complexes) are presented in figure 3. The first excited state of $^1\pi\pi^*$ character is crossed by a $^1\pi\sigma^*$ state, repulsive along the OH coordinate. In the C_s symmetry, these states transform according to A$'$ and A$''$ representations respectively, so the crossing is allowed by symmetry, but, as the planar symmetry is broken, the $^1\pi\pi^*$ and $^1\pi\sigma^*$ couple to each other and a conical intersection of their potential energy surfaces is formed.

In free phenol the $^1\pi\pi^*$–$^1\pi\sigma^*$ crossing occurs about 1 eV above the equilibrium geometry of the $^1\pi\pi^*$ state, and the $^1\pi\sigma^*$ state further crosses the ground state for a OH distance of about 1.5 Å (figure 3(*a*)). This second (symmetry-allowed) crossing, which transforms into a conical intersection when the out-of-plane deformations are included, is responsible for the efficient non-radiative decay. The $^1\pi\sigma^*$–S_0 crossing is expected since the $^1\pi\sigma^*$ state of A$''$ symmetry correlates asymptotically with the $^2\pi$ ground state of the radical and the hydrogen atom in its *1s* state, which is the lowest dissociation limit. The ground state, being of ^{1}A$'$ symmetry, cannot correlate with this lowest dissociation limit of A$''$ symmetry. The ^{1}A$'$ ground state thus must correlate with a higher dissociation limit (of ion-pair type). The existence of a conical intersection of the lowest $^1\pi\sigma^*$ state with the ground state is thus a generic property of planar aromatic systems with hydroxyl (OH) and/or azine (NH) bonds.

In the phenol–H_2O complex, the $^1\pi\sigma^*$ state is pushed upwards owing to the strong repulsion between the hydrogen atom and the oxygen atom of the nearby water molecule (figure 3(*b*)). As a result, a new shallow minimum develops in the $^1\pi\sigma^*$ state, where the hydrogen atom of phenol is transferred to the water molecule, and the intersection with the ground state is removed.

In phenol–NH_3, the $^1\pi\sigma^*$ energy is more strongly stabilized by hydrogen transfer. As a result, the crossing with the $^1\pi\pi^*$ state occurs at lower energy, and the minimum of the $^1\pi\sigma^*$ surface lies below the minimum of the $^1\pi\pi^*$ surface (figures 3(*c*)). The excited state hydrogen transfer process is predicted to be exothermic by 0.04 eV ($0.9\,\mathrm{kcal\,mol}^{-1}$). As for the phenol–$H_2O$ complex discussed above, the conical

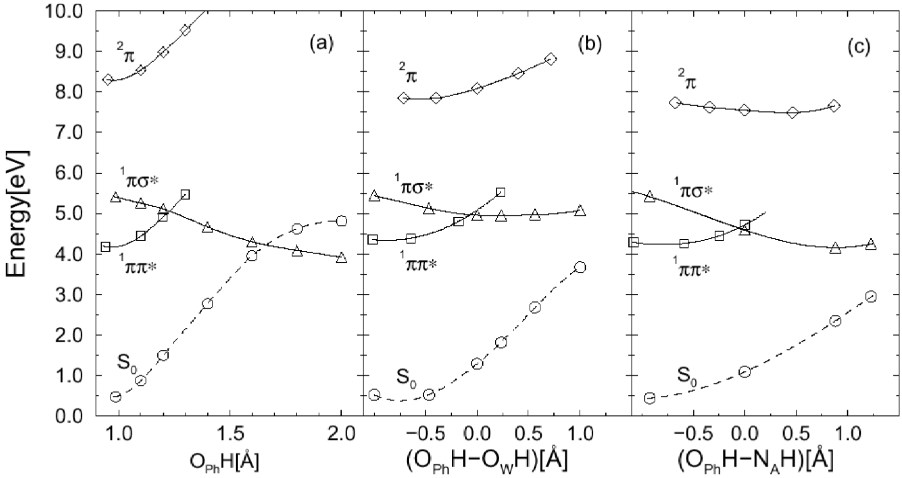

Figure 3. CASPT2 potential energy profiles of the (*a*) phenol, (*b*) phenol–water and (*c*) phenol–ammonia complexes as a function of the hydrogen transfer reaction coordinate: □, 1 $\pi\pi^*$ state; △, 1 $\pi\sigma^*$ state; ○, S_0 state; ◇, ionic state. (Figure from A. L. Sobolewski, private communication.)

intersection of the $^1\pi\sigma^*$ state with the ground state occurring in bare phenol is removed in the phenol–NH_3 complex. Thus, the hydrogen transfer reaction is exothermic already for phenol–NH_3 but is hindered by a barrier associated with the $^1\pi\pi^*$–$^1\pi\sigma^*$ curve crossing. This is consistent with the observation that hydrogen transfer is a slow process in phenol–NH_3. It is expected that the $^1\pi\sigma^*$ minimum be stabilized relative to the $^1\pi\pi^*$ minimum in larger phenol–$(NH_3)_n$ clusters, leading eventually to the disappearance of the barrier for the hydrogen transfer reaction.

These computational results are helpful for the interpretation of the large amount of spectroscopic and kinetic data that have been collected in recent years for phenol–water and phenol–ammonia clusters.

(1) The fluorescence lifetime of the deuterated phenol is nearly 10 times longer than the lifetime of the hydrogenated phenol (Lipert and Colson 1989). This is in good agreement with the control of the non-radiative process by tunnelling through a barrier due to the $^1\pi\pi^*$ and $^1\pi\sigma^*$ crossing.

(2) The fluorescence lifetime measured on the phenol–H_2O 0–0 transition is of the order of 15 ns, longer than in free phenol (Lipert *et al.* 1988). This can be easily understood on the basis of the potential energy profiles: since the $^1\pi\pi^*$–$^1\pi\sigma^*$ crossing is removed, the non-radiative transition rate is much lower in the complex and, the hydrogen transfer reaction being endothermic in this complex, the lifetime lengthens. Indeed, no signature of H transfer has been observed in phenol–H_2O. In the phenol–NH_3 complex, on the other hand, the fluorescence lifetime of the 0–0 transition is 1.2 ns, shorter than in free phenol, and the H transfer reaction leading to the phenoxy radical is energetically allowed. This is strong evidence that the $^1\pi\pi^*$ lifetime in phenol–$(NH_3)_n$ clusters is determined by the excited state hydrogen transfer reaction.

(3) The reaction rate for H transfer depends strongly on the excess enery in the $S_2(^1\pi\pi^*)$ state in a mode-specific manner (Grégoire *et al.* 2000a). The excitation of the intermolecular stretching vibration enhances the reaction

rate as expected for a tunnelling mechanism (Syage 1995). The observed deuteration effect is also perfectly in agreement with the calculated mechanism (Grégoire *et al.* 2001).

(4) The $^1\pi\pi^*$ lifetime of phenol–$(NH_3)_n$ clusters decreases when the cluster size increases (Grégoire *et al.* 2000a). This result can be understood in terms of lowering of the barrier associated with the $^1\pi\pi^*$–$^1\pi\sigma^*$ curve crossing on solvation. The $^1\pi\sigma^*$ state will be more stabilized than the $^1\pi\pi^*$ state, because of its large dipole moment, and this should lead to a decrease and eventually a disappearance of the barrier.

We will come back to the conclusions that can be drawn from this model in later sections, but we will first finish the discussion of the proton transfer.

5. Hydrogen transfer vs. proton transfer in phenol–$(NH_3)_n$ clusters

5.1. *Ground state proton transfer*

5.1.1. *Evidence for ground state proton transfer*

Even though the ESPT mechanism is not really operative in these clusters (as we will see later), the ground state proton-transferred structure of the large cluster sizes is well characterized by experiemental as well as theoretical work in both *1*-naphthol– and phenol–ammonia clusters.

(1) Many calculations predict that, in the ground state, proton-transferred structures will be more stable for phenol–$(NH_3)_n$ clusters with $n > 5$ (Yi and Scheiner 1996, Siebrand *et al.* 1997, Vener 1998, Vener and Iwata 1998, Siebrand and Zgierski 2001).

(2) In phenol–$(NH_3)_n$ the ground state proton transfer (GSPT) reaction was postulated to take place for six or seven ammonia molecules from ionization threshold measurements performed with a single VUV photon (Martrenchard-Barra *et al.* 1999).

(3) The GSPT inhibits the H transfer mechanism. If PhOH–$(NH_3)_{n>6}$ 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). Because of the Coulomb attraction the phenolate anion and the $NH_4^+(NH_3)_{n-1}$ entities cannot separate from each other and cannot lead to the formation of free $NH_4(NH_3)_n$ entities. Experimentally, large $NH_4^+(NH_3)_{n-1}$ are not observed, whereas parent clusters with n up to 12 have been observed in the explansion (Grégoire *et al.* 2001).

(4) The absorption spectrum of *1*-naphthol–$(HN_3)_{n\geq 5}$ is strongly red shifted (down to 70 nm) as compared with the absorption of smaller clusters (around 320 nm). The fluorescence of these large clusters is shifted to 450 nm, characteristic of the *1*-naphtholate emission (Cheshnovsky and Leutwyler 1985, 1988, Dedonder-Lardeux *et al.* 2001b).

The exact cluster size for which the GSPT occurs is still not totally certain but 6 seems to be correct for both *1*-naphthol and phenol (see later) clustered with ammonia.

5.1.2. *GSPT and the triplet state*

One aspect which has not been well investigated in phenol or *1*-naphthol ammonia clusters is intersystem crossing. It can be seen in figure 1 that it is still possible to ionize phenol–$(NH_3)_n$ clusters 200 ns after their excitation. The intensity of this signal decays in time, in contrast to the signal observed for protonated ammonia clusters. This long lifetime strongly suggests that some triplet states are produced after the excitation of the clusters. In free phenol as well as in small phenol–water clusters, the triplet state cannot be ionized and detected with a 355 nm photon. However, since the proton-transferred species have a very low ionization potential (Martrenchard-Barra *et al.* 1999) (6.5 eV), it seems reasonable to assign the triplet state observed to proton-transferred triplet species, but the mechanism still has to be studied in detail.

5.2. *Excited state: revisting the previous experiments in the light of the Hydrogen transfer mechanism*

In the light of the experiments that have evidenced the H transfer reaction in phenol–$(NH_3)_n$ clusters with $n = 1–6$, the question comes up as to whether ESPT has been observed or not. The previous experimental results which suggested ESPT include the following:

- the appearance of a red-shifted fluorescence when large clusters are excited;
- the appearance of the $NH_4^+(NH_3)_n$ fragments when large clusters are present in the expansion;
- the ionization threshold decrease for phenol–$(NH_3)_4$;
- the fast picosecond decays observed for phenol–$(NH_3)_{n=5,6,7}$ together with the absence of decays for smaller clusters when proton transfer is not expected and the slower decays observed on deuterium substitution, indicating a tunnelling mechanism.

However, the new results on hydrogen transfer in small phenol–$(NH_3)_n$ clusters cause some contradictions to appear.

The H transfer rate for the 1–2 and 1–3 clusters is in the 100–50 ps regime. Since the energetics of this reaction should be more favourable in larger clusters, the reaction should be even faster for larger clusters ($n = 4–6$). The $NH_4^+(NH_3)_{3,4}$ signals observed with delayed ionization are strong, indicating that H transfer is strongly allowed for $n = 4$ and 5. So a lifetime shorter than 50 ps is expected for phenol–$(NH_3)_{n=4,6}$. The previous kinetic measurements performed by Steadman and Syage (Steadman and Syage 1990, 1991a,b, Syage and Steadman 1991, Steadman and Syage 1992, Syage 1993a,b) did not show clearly marked decays for the $n = 4$ and smaller clusters: it can be concluded that the results are obscured by another process, probably the evaporation of larger clusters.

The problem of evaporation in phenol–$(NH_3)_n$ clusters has already been outlined by Hineman *et al.* (1993), who observed picosecond decays for cluster sizes $n = 1$, 2 and 3, depending on the ammonia concentration and on the excitation/ionization energy. These evaporation problems also seem important in the picosecond decays observed for *1*-naphthol–$(NH_3)_{n=3,4}$ clusters.

Another set of assumptions can be put forward to account for the ensemble of picosecond and nanosecond experiments.

(1) For small cluster sizes ($n = 1–5$), the dynamics is mainly governed by the H transfer mechanism.
(2) 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. The excess energy can lead to fast internal vibrational redistribution (IVR), intersystem crossing and evaporation processes.

(3) When clusters are ionized, they undergo a proton transfer reaction releasing a lot of energy, which is lost through evaporation processes. The initial parent cluster size is totally lost.

The results used to ascertain ESPT can all be re-interpreted under these assumptions.

(1) The red-shifted fluorescence can be assigned to the fluorescence of the directly excited proton-transferred species.
(2) The $NH_4^+(NH_3)_n$ fragments in the mass spectra are due to the hydrogen transfer reaction in the excited state and are not connected to proton transfer, neither in the excited nor in the ground state.
(3) The lowering of the ionization threshold observed for the $n = 4$ complex in a two-colour two-photon experiment but not in single VUV ionization experiment can be assigned to evaporation from larger clusters in the excited and/or ionic states.
(4) The pump–probe picosecond dynamics observed for phenol–$(NH_3)_{n=5,6,7}$ 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–$(CH_3OH)_n$ and phenol–$(H_2O)_n$, 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.

5.3. *ESPT in the phenol case?*

Phenol–$(NH_3)_n$ clusters with $n = 4$ and 5 can energetically undergo both hydrogen and proton transfer in the excited state, and the question of competition between these mechanisms is open.

The H transfer occurs for very small cluster sizes ($n = 1$), indicating that it is not controlled by the solvent, i.e. the solvent reorganization. The process is certainly affected by solvent effects since the reaction rate increases with the cluster size, but the effect is rather weak.

On the contrary, the proton transfer reaction should be strongly driven by the solvent. This has been thoroughly discussed by Syage (1993b, 1994) using the Hynes–Borgis (Borgis and Hynes 1991) or Cukier–Morillo scheme (Cukier and Morillo 1990, Morillo and Cukier 1990), 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 (figure 4(*a*)). In this scheme, the reaction rate is controlled by the free energy of activation $\Delta G^{\#}$ through an $\exp(-\Delta G^{\#}/kT)$ term (T is the cluster temperature) (figure 4(*b*)). This $\Delta G^{\#}$ value is strongly dependent on the solvent reorganization energy: the reorganization energy has been estimated by Vener (1998) to be around 2 to 3 kcal mol^{-1}. According to these models, the ESPT reaction requires the solvent reorganization and a tunnelling process and should be slower than the H transfer mechanism in which only the tunnelling process is required. In such a model the ESPT reaction should be forbidden in cold clusters produced in a supersonic jet, where the temperature is very low, and should not be seen unless some energy is brought into the system by optical excitation. Even so, the key point to

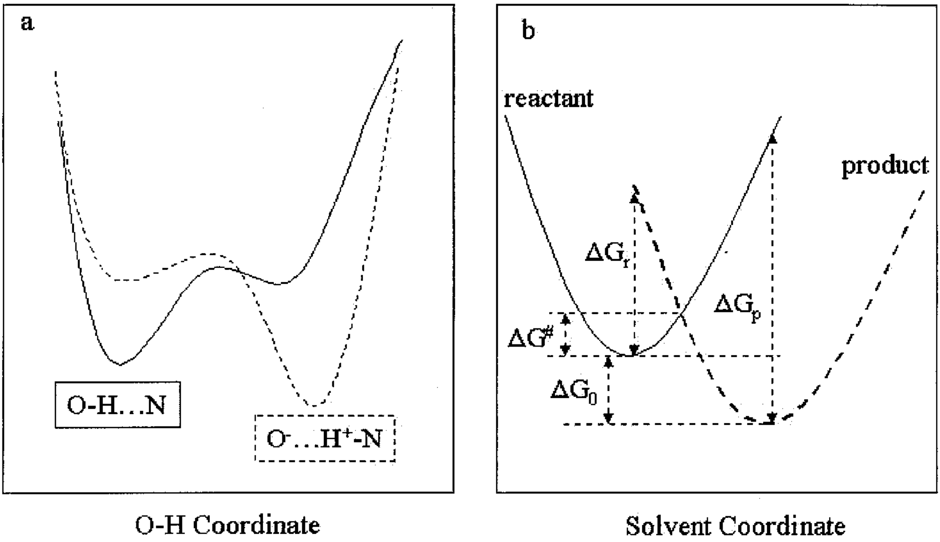

Figure 4. Schematic representation of the solvent-induced proton transfer. (*a*) Potential energy curve along the proton transfer coordinate for fixed solvent configurations: ———, the solvent is arranged around the neutral phenol–ammonia cluster (reactant) and the proton transfer reaction is then endothermic; – – – –, the reaction is exothermic when the solvent is equilibrated with the ion pair structure (product). (*b*) Potential energy curve along the 'solvent cordinate': ———, neutral reactant; – – – –, ion pair product. ΔG_0 is the free energy of reaction for an equilibrating solvent, ΔG_r and ΔG_p are the free energies of reaction for fixed solvent configurations. On thermal fluctuation the system can reach the crossing point between the full and broken curves, and the proton transfer then occurs. It requires an energy $\Delta G^{\#}$, the free energy of activation.

ESPT will be the comparison between the solvent free energy of activation $\Delta G^{\#}$ and the energy necessary to evaporate one solvent molecule from the cluster $E_{n,n-1}$. If $E_{n,n-1}$ is smaller than $\Delta G^{\#}$, it will be impossible to observe ESPT: each time energy is added to overcome the $\Delta G^{\#}$ barrier, the cluster will cool down by evaporation before ESPT can proceed. Thus ESPT is not expected to be competitive with H transfer.

6. Does ESPT occur in *1*-naphthol–$(NH_3)_n$ clusters?

Since there seems to be no good evidence for ESPT in phenol–$(NH_3)_n$ clusters, the question arises as to whether this mechanism is present or not in *1*-naphthol–$(NH_3)_n$ clusters. What are the experimental observations that support the ESPT mechanism?

(1) A red-shifted emission (maximum at 450 nm) is observed, similar to the naphtholate anion emission in solution, which correlates with the appearance of the $n = 4$ cluster. In the energy-resolved (420 nm) fluorescence excitation spectrum, the well-structured bands assigned to small clusters are not observed. The structured spectra were previously assigned to clusters with $n = 1$–3, which thus do not lead to the ESPT reaction.

(2) A fast picosecond decay (50 ps) is observed on the $n = 4$ cluster when the probe laser is set near the ionization threshold.

Furthermore, a significantly red-shifted absorption is observed for cluster sizes $n \geq 5$ that has been interpreted as evidence of the ground state proton transfer. What are the concerns with this interpretation?

(1) As in the phenol case, the ionic reaction has been neglected too much. The proton transfer reaction in the ion leads to a strong release of energy and therefore to evaporation processes, even at the vertical ionization threshold. These evaporation processes have been evidenced experimentally (Dedonder-Lardeux *et al.* 2001b) using delayed ion extraction methods. All the *1*-naphthol–$(NH_3)_{n>2}$ clusters evaporate at least one molecule upon ionization (for $n = 3$ and 4 evaporation of two ammonia units is clearly observed). These experiments lead to a reevaluation for the threshold cluster size for GSPT at $n = 6$.

(2) The fluorescence spectrum of large clusters (GSPT species) shows no resonant fluorescence: the energy difference from the excitation at 371 nm to the maximum of the fluorescence at 450 nm represents more than 4000 cm^{-1}. This energy shift is the sum of two contributions: the difference between the region reached by Franck–Condon excitation and the excited state energy minimum and the difference between the energy levels reached by emission to the ground state and the energy minimum of the ground state. If one assumes that these two contributions are of the same order of magnitude, the 371 nm excitation corresponds to 2000 cm^{-1} excess energy in the excited state. In the picosecond experiments, the clusters have been excited at 320 nm and the 1-NpO^{-*}–$(NH_4^+)(NH_3)_{n>4}$ then have 6000 cm^{-1} of excess energy. With such an excess energy the cluster must relax first by IVR and then by evaporating a molecule. However, in the picosecond experiments on *1*-naphthol–$(NH_3)_{n>5}$ clusters no dynamics is observed (Kim *et al.* 1994, 1995).

Why is this dynamics not observed? Such a phenomenon has been well evidenced and characterized for the evaporation processes observed in hot Na–$(NH_3)_n$ clusters (Grégoire *et al.* 1999, 2000b) with similar internal energy (0.5 eV). The signal observed at a given mass does not reflect the evaporation dynamics because it results from two contributions that cancel each other. Briefly, the time evolution of the signal observed on cluster size n is coming from cluster size $n + 1$:

- One possibility is through ionization of the $n + 1$ cluster before evaporation in the excited state: the vibrational energy of the excited state will be transferred to the ion and the ionic cluster will fragment and be observed at mass n. The time evolution of this process is an exponential decay.
- The alternative is through ionization after evaporation in the excited state. The population at mass n produced by evaporation in the excited state is an exponentially growing signal. After this evaporation the clusters are cold (evaporative cooling) and the ionic clusters do not fragment as efficiently.

Because the observed signal is the sum of these two contributions, it appears as a step function.

In the case of *1*-naphthol–$(NH_3)_n$ clusters, the dynamics observed in the picosecond experiments can be modelled with evaporation processes, including the single and double evaporation (three molecules can be lost if the ionization photon is energetic enough), coming from the excitation of ground state proton-transferred species, without taking into account any other reactive channel (Dedonder-Lardeux *et al.* 2001b).

The similarity between the fluorescence excitation spectrum when the *1*-naphtholate emission is recorded and the multiphoton ionization excitation/ionization spectrum of the *1*-naphthol–$(NH_3)_4$ has been assigned as the signature of ESPT. However, because of the strong evaporation process occurring in this system, signals observed on the $n = 4$ mass are certainly due to larger masses and may come from the excitation/ionization of the $n = 6$ parent cluster which is a ground state proton-transferred species. Accordingly what has been ascribed to ESPT may in fact be due to the presence of ground state proton-transferred species, and there is no good evidence for ESPT in *1*-naphthol–$(NH_3)_n$ clusters.

In the naphthol case, the $^1\pi\pi^*$ state is lower in energy than in phenol and thus the $^1\pi\pi^*$–$^1\pi\sigma^*$ crossing occurs at higher energy. The H transfer is not expected in this system, and experimentally no $NH_4^+(NH_3)_n$ product clusters have been detected.

7. Some remaining questions about ESPT

Many questions are still open about the ESPT mechanism, either in the liquid phase or in clusters.

One of the arguments used in the liquid phase to infer the ESPT is the increase of the hydrogen bond strength in the excited state. From experiments in the jet, it appears that this assumption is not correct. The binding energy of 1-naphthol–NH_3 in the ground state has been measured in supersonic expansion to be 2680 cm^{-1} (2035 cm^{-1} for water). The binding energy of the complex in its excited state can be deduced from the spectral shift of the 0–0 transition. It increases by only 9% (Bürgi *et al.* 1995) from 2680 cm^{-1} to 2916 cm^{-1}. Moreover, in the phenol case, it is clear that the excited state H bonding, with water for example (Lipert and Colson 1990), does not decrease the fluorescence quantum yield (the phenol–water lifetime is 10 ns, compared with 2 ns for the free molecule (Lipert and Colson 1990)). The enhanced H bonding is then not the major factor which can induce ESPT.

Another argument often used is the higher acidity of the excited state. However, for phenol, the dipole moment is almost unchanged on electronic excitation to S_1 (Krauss *et al.* 1995, Lorentzon *et al.* 1995, Granucci *et al.* 2000). Hence, one expects charge transfer from the oxygen to the ring to have a negligible contribution in S_1, in contrast with the standard explanation for the enhanced excited state acidity.

The strong spectral shift between the absorption spectrum and the emission spectrum is associated with the ESPT mechanism. However, this effect is also observed in large *1*-naphthol–$(NH_3)_n$ clusters where a ground state proton-transferred structure is assumed (Knochenmuss 1999a, 1999b, Dedonder-Lardeux *et al.* 2001b). On excitation of GSPT species, a strong solvatochromism is induced. This is certainly due to the nature of the 1-naphtholate anion excited state. If the excited states of the 1-naphtholate anion are not well characterized, some information can be obtained from theoretical work on the phenolate anion (Granucci *et al.* 2000). From Granucci *et al.*, the dipole moments and charge distributions are similar in the S_0 and $^1B_1$ states but strongly differ in the $^1A_1$ state. In particular, a non-negligible contribution of charge-transfer character from the oxygen to the ring is present in the $^1A_1$ state: considering the variation of the dipole moment between $^1A_1$ and S_0 (2.3 au, both at the CASSCF and at the CIPSI level), one can roughly estimate that a negative charge of $0.45e$ is transferred from the oxygen to the ring centre on the

$S_0 \rightarrow {}^1A_1$ transition. Such a charge transfer within the anionic chromophore might lead to a strong solvatochromism as observed.

Finally, the role of triplet states has not been investigated. In all the preceding discussion, the triplet states have not been taken into account. In the free phenol molecule, intersystem crossing is quite important (Lipert and Colson *et al.* 1989). What about intersystem crossing in the excited state proton-transferred species?

In the H transfer process, at long OH distance the biradical pair is formed, and thus the triplet and singlet states may be nearly degenerate. In the case of phenol–$(NH_3)_n$ clusters, for example, it might be possible that the H transfer yield is not 100% and that some recombination between NH_4 and $PhO^\bullet$ occurs. In this case this might lead to the formation of either ground state or triplet state. Indeed long-lived species, probably triplet states, are produced in the excitation of phenol–$(NH_3)_n$ clusters (see figure 1 top), but the mechanism has not been seriously investigated.

8. Generalization of the H detachment mechanism: aromatic enol and azine compounds and DNA bases

8.1. *Substituted phenols*

It seems now well established both experimentally and theoretically that the excited state dynamics of small phenol–$(NH_3)_n$ clusters is governed by a hydrogen transfer reaction:

$$PhOH(S_1)-(NH_3)_n \rightarrow PhO^\bullet + NH_4^\bullet(NH_3)_{n-1}.$$

This reaction proceeds via tunnelling through a barrier due to the crossing of the initially excited ${}^1\pi\pi^*$ state with a higher dissociative ${}^1\pi\sigma^*$ state. The ammonia clusters have shown their ability to trap hydrogen atoms and therefore to be used as indicators for an X—H bond rupture.

Since the H transfer channel is a property of the electronic states, it should also exist in related compounds such as substituted phenols. Experiments carried out on *o*-fluorophenol–ammonia clusters and on catechol–ammonia clusters substantiate this mechanism: in both cases delayed ionization experiments indicate the formation of ammonium radicals (Dedonder-Lardeux *et al.* to be published). As for phenol–$(NH_3)_n$ clusters, only $NH_4^\bullet(NH_3)_{n-1}$ radicals with $n \leq 5$ are clearly observed, suggesting that ground state proton transfer takes place for six ammonia molecules in all these compounds, although the deprotonation enthalpies vary from $\Delta H = 1461\,\mathrm{kJ\,mol^{-1}}$ for phenol to $\Delta H = 1445\,\mathrm{kJ\,mol^{-1}}$ for *o*-fluorophenol and $\Delta H = 1421\,\mathrm{kJ\,mol^{-1}}$ for catechol.

8.2. *Indole and derivatives*

In recent theoretical papers, Sobolewski and Domcke have shown that the electronic states of indole behave as those of phenol: the lowest $\pi\sigma^*$ singlet state is repulsive along the N–H coordinate crossing the ${}^1L_a$ and ${}^1L_b$ states of $\pi\pi^*$ character as well as the ground state, providing a mechanism for the experimentally observed non-radiative processes (Sobolewski and Domcke 1999, 2000). Since the N—H bond is expected to be predissociated, one might conjecture an H transfer reaction in the indole system and in its derivatives. Experimentally, the H transfer reaction has been shown to occur in indole (Dedonder-Lardeux *et al.* 2001a), 3-methylindole, tryptamine and hydroxypyridine clustered with ammonia (Dedonder-Lardeux *et al.* to be published).

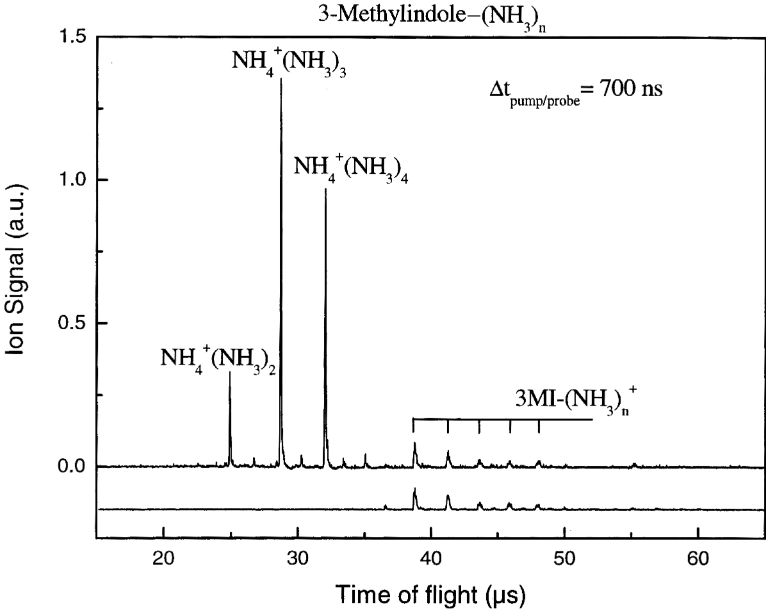

Figure 5. One- and two-colour mass spectra of 3-methylindole–$(NH_3)_n$ clusters. Lower trace: one-colour two-photon mass spectrum with $\lambda_{pump} = 270$ nm. Upper trace: two-colour two-photon mass spectrum with $\lambda_{pump} = 270$ nm, $\lambda_{probe} = 355$ nm; the delay between pump and probe laser is 700 ns. The $NH_4(NH_3)_m$ clusters ($m = n - 1$) that issue from the H transfer reaction are ionized by the 355 nm laser delayed by 700 ns and displaced a few mm downstream. The 355 nm laser is 100 times more intense (1 mJ 10 μJ) than the 270 nm laser, so that $NH_4(NH_3)_n$ clusters are ionized much more efficiently in the two-colour process (with the 270 nm laser, the main $NH_4^+(NH_3)_3$ ion peak appears very weakly although it is not observable on the scale of the figure). No signal is observed with the 355 nm laser alone. The 3-methylindole–$(NH_3)_n^+$ clusters only come from the one-colour excitation/ionization: after 700 ns the excited state has decayed and the clusters cannot be ionized with the probe laser.

As an example, figure 5 shows the pump–probe signal obtained with a delay between pump and probe of 700 ns for clusters of 3-methylindole with ammonia. As in the case of phenol, the $NH_4^+(NH_3)_n$ signal at long pump–probe delays is a signature of the excited state reaction:

$$\begin{aligned}\text{3-methylindole}-(NH_3)_n + h\nu_1 &\rightarrow \text{3-methylindole}^* - (NH_3)_n\\ &\rightarrow \text{3-methylindolyl}^\bullet\\ &\quad + NH_4^\bullet(NH_3)_{n-1}NH_4^\bullet(NH_3)_{n-1} + h\nu_2\\ &\rightarrow NH_4^+(NH_3)_{n-1}.\end{aligned}$$

8.3. *DNA bases*

As for phenol and indole, DNA bases present several heteroatoms with lone pairs. In all DNA bases a low-lying non-radiative threshold is observed, at which an abrupt quenching of the fluorescence occurs. It has been suggested that $^1\pi\pi^*$–$^1n\pi^*$ coupling is responsible for the fluorescence quenching of the $^1\pi\pi^*$ state of the DNA bases but this argument does not provide an explanation of the postulated ultrashort lifetime of the $^1n\pi^*$ state. The presence of several heteroatoms with lone pairs results in the existence of a number of low-lying $^1n\pi^*$ and $^1\pi\pi^*$ states and in addition $^1\pi\sigma^*$ states which are dissociative along the NH coordinate as recently shown by Sobolewski and Domcke (2002) for adenine.

9. Possible consequences of the H transfer mechanism

The H detachment mechanism has been introduced very recently, and all the implications of this mechanism have not yet been investigated. However, it seems to be a very general mechanism that will allow the understanding of many non-radiative processes in aromatic enols or azines (Sobolewski, *et al.* 2002b).

Some points already seem to emerge from the H transfer mechanisms and will need to be more carefully investigated.

9.1. *Hydrogen affinity*

It might be necessary to generalize the concept of hydrogen affinity, used in the case of radical cations (Aue *et al.* 1976), to characterize the ability of a neutral molecule (or cluster) to be linked to an H atom. Ammonia clusters are good H acceptors and can be used as a simple H atom detector. At the opposite extreme, cold water clusters do not favour H atom capture, but what about other molecules?

9.2. *Solvent-induced non-radiative process*

The $^1\pi\sigma^*$ states are highly polar in the ground state geometry, which implies that their energetic location relative to the less polar $^1\pi\pi^*$ and $^1n\pi^*$ states is strongly dependent on the environment. Since the coupling between these states is probably responsible for the non-radiative processes in the excited state, one might expect a strong variation of the excited lifetime depending on the environment of molecules in which the H transfer process can occur. This can be the key to understanding the lifetime variations of the tryptophan residue in a protein.

9.3. *H transfer and solvated electron*

The most fascinating aspect of this H transfer mechanism is certainly the role that it can play in the formation of the so-called ‘solvated electron’.

Experiment and theory clearly demonstrate that, for molecules clustered with ammonia, the H transfer mechanism leads to the formation of the solvated ammonium radicals. A striking result obtained both experimentally and theoretically is that the $NH_4(NH_3)_n$ electronic spectra rapidly converge to a spectrum very similar to that of the solvated electron in liquid ammonia (Nonose *et al.* 1999, Tuttle and Golden 1991, Hashimoto 2001).

Recent calculations suggest that a similar phenomenon can exist in water: the calculated spectra of solvated hydronium radicals are also very similar to the absorption spectrum of the solvated electron in water (Muguet *et al.* 1996, Sobolewski *et al.* 2002a, 2002b). The formation of hydronium radicals by excitation of indole or phenol in water could readily explain some experimental results which seem contradictory in the commonly accepted picture of the solvated electron, such as the very low energy threshold for the formation of the solvated electron (Bernas *et al.* 1980) and the absence of geminate recombination of the solvated electron with the cation on a scale as long as a few hundred picoseconds when indole or phenol is excited in aqueous solutions (Mialocq *et al.* 1982, Peon *et al.* 1999).

This hypothesis has not yet been seriously tested experimentally and will require more experimental and theoretical work, but it opens a new explanation for the photo-initiated electron transfer in proteins containing tyrosine and tryptophan that have the phenol and indole chromophore.

10. Conclusions

The excited state hydrogen transfer reaction in small phenol–ammonia clusters now seems a well-established mechanism. The comparison with deuterated clusters indicates that the reaction probably proceeds by tunnelling through a barrier. This H transfer mechanism is in excellent agreement with the calculated $^1\pi\sigma^* - ^1\pi\pi^*$ coupling leading to predissociation along the OH coordinate.

The presence of this hydrogen transfer channel makes it necessary to re-analyse 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 $n < 6$, in the phenol–$(NH_3)_n$ case.
(2) Ground state proton transfer takes place for $n \geq 6$ (phenol and 1-naphthol) and direct excitation of ground state proton-transferred structures leads to fast (50 ps) evaporation events in the excited state.
(3) The ESPT mechanism is not necessary to explain the experimental results, and probably does not exist.

The H transfer mechanism, which has just begun to emerge, seems to be a very promising model to explain many non-radiative processes in the gas phase, in liquids and also in biological environments.

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