

# Excited-state proton transfer in 1-naphthol · (NH<sub>3</sub>)<sub>n</sub> complexes: the threshold size is $n = 4$

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## Abstract

Resonant two-photon ionization, fluorescence and fluorescence-detected excitation spectra of 1-naphthol · (NH<sub>3</sub>)<sub>n</sub> clusters are reported and interpreted with emphasis on determining the smallest clusters for which excited-state proton transfer (ESPT) can occur. Consistent with the earliest studies but in contrast to more recent work, the ESPT threshold is found at  $n = 4$ , not  $n = 3$ . The confusion is shown to have arisen from weak, broad fluorescence of  $n = 1–3$  clusters extending to  $\sim 400$  nm. Excitation spectra of genuine ESPT emission at longer wavelengths gives no indication of contributions from  $n < 4$ . © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The excited-state proton transfer (ESPT) reaction of 1-naphthol has been one of the most important examples of its type for many years. Förster [1] and Weller [2] first recognized that the blue fluorescence from an aqueous solution of 1-naphthol is due to the naphtholate anion rather than neutral naphthol and that the hydroxyl proton is donated to the solvent in an excited-state reaction. Such excited-state acids have since become useful for photoinduced pH-jump experiments and many are now known.

As a result of the enormous general importance of proton transfer reactions in water, 1-naphthol has repeatedly served as a model compound in this solvent [1–6] and in water clusters [7–12]. In addition to the detailed spectroscopic information available in a cold molecular beam, cluster studies have the

unique advantage of observing solute properties as a function of the number of solvent molecules. In the case of water clusters, for example, ESPT is first observed at  $\sim 25$  water molecules [8,9]. Clusters are quite cold, therefore the internal dynamics can also be slowed to time scales that are relatively accessible [10,11] and these dynamics varied with cluster internal energy [11]. In water clusters, the ESPT dynamics were found to be largely controlled by solvent relaxation, which is a critical feature of the recently proposed ESPT mechanism [7]. This involves vibrationally-induced  $S_1/S_2$  coupling in naphthol, which induces solvent relaxation and is then itself amplified by the solvent response.

In pure common solvents, 1-naphthol ESPT is only observed in water. However, adding small amounts of nitrogen bases to other solvents can lead to ESPT as well [13,14]. A substantial acceptor proton affinity (PA) is required for the ESPT reaction to become favorable, since excited 1-naphthol is

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not a strong acid ( $\text{p}K_{\text{a}}^* \approx 0$  in water). On the other hand, if the acceptor PA is too large, the naphthol may react in the ground state. Studies of 1-naphthol ESPT to most nitrogen bases are therefore restricted to mixed solutions or to clusters.

Cheshnovsky and Leutwyler performed the first experiments on 1-naphthol  $\cdot (\text{NH}_3)_n$  clusters [15,16]. As in solution and water clusters, the appearance of a strong, broad emission with a large red shift ( $7000 \text{ cm}^{-1}$ ) was diagnostic for ESPT. The naphtholate band is centered at  $22000 \text{ cm}^{-1}$  (455 nm), and is  $\sim 3500 \text{ cm}^{-1}$  in width. Using resonant two-photon ionization and mass spectrometric detection, it was possible to measure the absorption spectra of the clusters individually. This knowledge enabled selective excitation of each cluster size, as well. For small clusters,  $n = 1-3$ , strong narrow line emission was observed, similar to that of free naphthol. For  $n = 4$ , only the red-shifted ESPT emission was found. This result is consistent with the  $n = 4$  ESPT threshold found for the closely related phenol  $\cdot (\text{NH}_3)_n$  system [17] and 2-naphthol  $\cdot (\text{NH}_3)_n$  [18].

For the stronger base piperidine, the ESPT threshold was observed at  $n = 2$  [8]. Analysis of these results led to the conclusion that a base or solvent cluster proton affinity of 243 kcal/mol is necessary to induce ESPT [8,9], if the cluster is small. The energetic cost of charge separation in the naphthol can be compensated by solvation of the proton, so the reaction occurs when the base cluster PA surpasses a well-defined threshold. The same picture does not hold for weaker bases with a substantially greater minimum reactive cluster size, since solvation of the naphtholate moiety then plays a larger role.

In the course of a subsequent study on water and ammonia clusters of 1-naphthol, Kim et al. (KLB) measured two-color R2PI spectra of  $n = 3$  ammonia clusters, with the result that one peak became more prominent at low ionization energy [19]. Since multiple conformations of hydrogen bonded clusters are common, it was suggested that this peak corresponded to a conformer of  $n = 3$  with unusual properties. KLB also measured fluorescence-detected excitation spectra of 1-naphthol–ammonia clusters, using cutoff filters for wavelength selectivity. Even for filters passing only wavelengths longer than  $26000 \text{ cm}^{-1}$  (380 nm), absorption bands could be observed

that corresponded to the special  $n = 3$  conformer. In view of the possibility that  $n = 3$  clusters undergo ESPT in an argon matrix [20], they took this as evidence for ESPT in this conformer, even though the filter cutoff was substantially higher in energy than the ESPT emission found in Refs. [8,15,16]. The claim of ESPT at this cluster size contradicted the threshold thermodynamic model of Refs. [8] and [9], and was discussed in terms of semi-empirically calculated cluster geometries.

Following the KLB work, pump–probe two-photon ionization transients of 1-naphthol–ammonia clusters were reported [21–24]. For  $n = 0, 1$  and 2, weak fast transients were observed on top of the radiative decay. Remarkably, for  $n = 3$  the fast component was dominant, but became small again for  $n = 4$  and 5. The fast transients were slower for  $\text{ND}_3$  than  $\text{NH}_3$  clusters. It was suggested that ESPT was the reason for the large fast  $n = 3$  component, in agreement with the spectroscopic conclusions of KLB.

Pump–probe results for the related phenol–ammonia clusters were reported by Syage and Steadman, who found fast transients only for  $n \geq 5$  clusters [25,26] rather than  $n \geq 4$  [17]. In this case, however, the clusters fragment to a much greater extent than with 1-naphthol, and it was suggested that this makes assignment of a threshold uncertain [27]. This and other aspects of pump–probe measurements on proton transfer clusters have been recently reviewed [28].

The KLB proposal of an ESPT active 1-naphthol  $\cdot (\text{NH}_3)_3$  conformer would add disconcerting complexity to the otherwise straightforward thermodynamic explanation for 1-naphthol ESPT to strong bases. The threshold for ESPT in this test system must be correctly identified if we are to develop a clear understanding of the ESPT phenomenon. The present work was undertaken because of the importance of the question and the need to reconcile differing interpretations of the data. For example, no  $n = 3$  ESPT emission was found in Refs. [8,15,16], in spite of a search for it. Also, as noted in Refs. [22] and [23] there are some puzzling aspects of the time-resolved results. The fast transient for  $n = 4$ , where ESPT is agreed to be quantitative, is small; yet the transient for  $n = 3$ , where only a minority ESPT component was postulated, is large. Reexamining

nation of the spectroscopy of small 1-naphthol·(NH<sub>3</sub>)<sub>n</sub> clusters shows that the KLB interpretation was a result of insufficient selectivity for ESPT emission and that no ESPT activity can be ascribed to any  $n = 3$  conformer on spectroscopic grounds.

## 2. Experimental

The experimental method was similar to that reported in earlier studies on this molecule [7–12], we present only a brief summary. 1-naphthol was entrained in a stream of neon carrier gas at a partial pressure of < 3 mbar, the total stagnation pressure was 1–1.5 bar. This mixture was passed through a pulsed valve into a vacuum, the expansion cooled molecules were then interrogated with nanosecond pulses from a frequency-doubled pulsed dye laser (Lambda Physik FL-2002), using DCM dye. The ammonia complexes were generated by adding 1% anhydrous NH<sub>3</sub> vapor to the gas stream.

The one-color resonant two-photon ionization (R2PI) spectra were obtained by crossing the skimmed molecular beam with the unfocused, doubled dye-laser pulses, inside the acceleration region of a 1 m linear time-of-flight mass spectrometer. The acceleration voltage used was 5 kV and the ions were detected with a micro-sphere plate (El-Mul Technologies, Israel). The laser was scanned while observing the relevant mass peak with a transient digitizer.

The fluorescence was dispersed with a SPEX 0.5 m grating monochromator (500M) and detected with either a photomultiplier (Hamamatsu R3896) or CCD array (Princeton Instruments, 2500 × 600 pixels).

## 3. Results

### 3.1. Resonant two-photon ionization spectra

The upper three traces of Fig. 1 show the one-color resonant two-photon ionization (R2PI) spectra of the  $n = 1$ –3 clusters of 1-naphthol·(NH<sub>3</sub>)<sub>n</sub> in the  $S_1 \leftarrow S_0$  electronic origin region. These correspond well with those measured earlier [15,16,19]. In our molecular beam, one conformer is dominant for  $n = 1$ ,

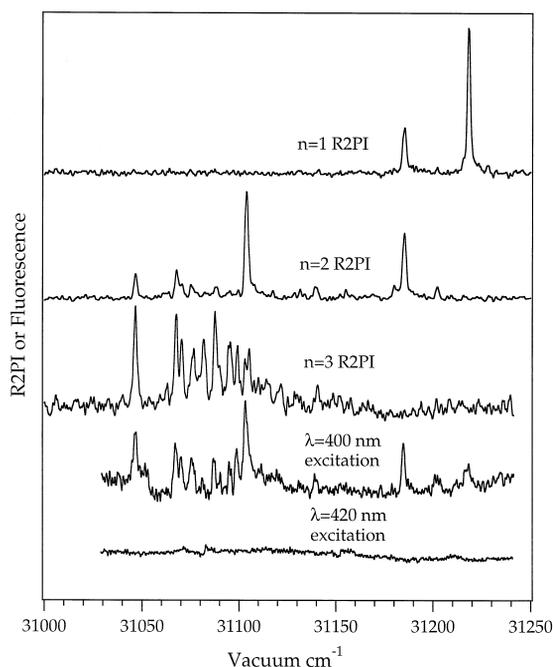


Fig. 1. One-color resonant two-photon ionization (R2PI) and fluorescence-detected excitation spectra of 1-naphthol·(NH<sub>3</sub>)<sub>n</sub> clusters. The R2PI spectra have been scaled relative to one another for clarity. The center wavelengths of the excitation spectra are indicated, the bandpass was 2.4 nm. At 400 nm observation wavelength absorption features from all cluster sizes  $n = 1, 2$  and 3 are visible. At 420 nm observation wavelength, no such structure remains and the excitation spectrum reflects only the featureless  $n \geq 4$  absorption.

absorbing at 31218 cm<sup>-1</sup>. For  $n = 2$ , there are at least two conformers, with electronic origins at 31184 and 31103 cm<sup>-1</sup>. The loss of 1 ammonia molecule is not uncommon in one-color R2PI and no  $n = 1$  signal appears at 31103 cm<sup>-1</sup>, therefore the possibility exists that this band is due to  $n = 3$ , which fragments into the  $n = 2$  channel. It was found that the dominant contribution is in fact from  $n = 2$ , as shown by: changing expansion conditions to discriminate strongly against  $n = 3$  clusters (all other  $n = 3$  bands could be reduced to < 10% of the  $n = 2$  signals) and by performing 2-color R2PI at 2500 cm<sup>-1</sup> lower ionization energy, which did not lead to significant change in the  $n = 3$  vs.  $n = 2$  relative intensities.

The  $n = 3$  electronic origin region is congested and several conformers are likely, but different origin bands cannot be distinguished from the low-en-

ergy vibrational or sequence band structure in the absence of more information. Some  $n = 3$  clusters fragment into the  $n = 2$  channel, but the lower abundance of the larger cluster means that the resulting structure in the  $n = 2$  spectrum is weak. The  $n = 4$  cluster has a broad absorption [15,16], so its spectrum shows no structure on the scale presented here.

### 3.2. Fluorescence spectra

Shown in Fig. 2 are the fluorescence spectra of 1-naphthol  $\cdot$   $(\text{NH}_3)_n$  clusters when exciting at  $31184 \text{ cm}^{-1}$ , or on one of the  $n = 2$  conformers. The lower trace was taken with the array detector at moderately

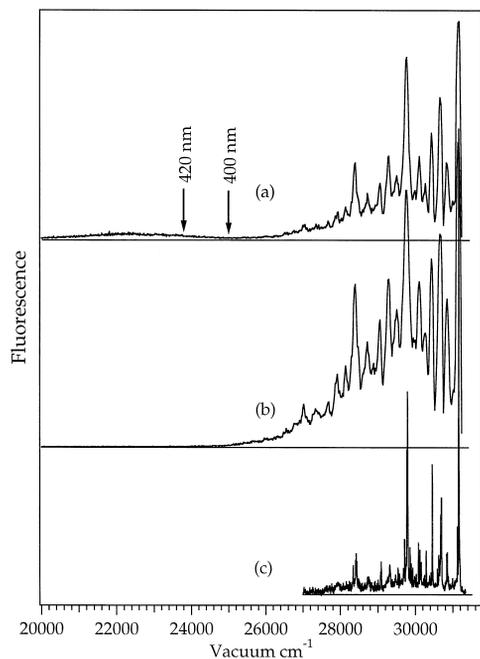


Fig. 2. Fluorescence spectra of the 1-naphthol  $\cdot$   $(\text{NH}_3)_2$  cluster, excited at  $31184 \text{ cm}^{-1}$ , or the rightmost strong absorption of the  $n = 2$  spectrum in Fig. 1. The upper spectra were taken with wide slits and high sensitivity, the lower one shows the correct intensities of the strong narrow bands. In all spectra the broad underlying emission is clear, extending to  $\sim 25000 \text{ cm}^{-1}$  or  $\sim 400 \text{ nm}$ . Under the conditions used to measure spectrum (a) small amounts of the  $n = 4$  were present and excited (3% of the  $n = 2$  signal in the mass spectrum), leading to the ESPT emission at  $22000 \text{ cm}^{-1}$ . The conditions used for spectrum (b) were changed to strongly reduce the  $n = 4$  population, only the ESPT emission is eliminated. The arrows are at the observation wavelengths of the excitation spectra in Fig. 1.

high resolution. The rightmost peak is at the excitation wavelength and it includes some scattered laser light. Otherwise the spectral intensities are correct. The vibrational structure is similar to that of free 1-naphthol, as was previously observed [15,16]. It should be noted that between the sharp lines, the signal does not return to the baseline, there is a weak, broad underlying emission. This is consistent with the results of Refs. [15,16], although it was not explicitly noted there. Also as in those works, similar results were obtained for both the  $n = 1$  and 3 clusters.

The upper two spectra of Fig. 2 were taken at high sensitivity but with low resolution. The measurement system was partially saturated at the intense sharp bands, their intensities are no longer entirely representative. However, the extent of the broad underlying emission is now apparent, reaching to  $25000 \text{ cm}^{-1}$  ( $400 \text{ nm}$ ). The two spectra were taken under slightly different conditions, corresponding to the temporal position of the laser pulse with respect to the gas pulse. At longer delays after the start of the gas pulse, small amounts of  $n = 4$  (3% of the  $n = 2$  signal) are seen in the mass spectrum. These lead to the emission band at low energy in the upper trace, as a result of weak  $n = 4$  absorption at the excitation frequency. Moving the laser forward in the gas pulse by  $50 \mu\text{s}$  results in nearly undetectable amounts of  $n \geq 4$  in the mass spectrum. The ESPT emission at  $22000 \text{ cm}^{-1}$  correspondingly vanishes, as seen in the middle trace of Fig. 2. The broad background extending to  $25000 \text{ cm}^{-1}$ , on the other hand, does not decrease, and even increases since more of the smaller clusters are present.

### 3.3. Excitation spectra

Opening the monochromator slits to their maximum value (3 mm) and setting the center wavelength to  $25000 \text{ cm}^{-1}$  ( $400 \text{ nm}$ ), the laser was again scanned over the region of Fig. 1. This was intended to correspond to the most red-shifted observation conditions of fig. 5 of KLB. The result labelled as the 400 nm excitation spectrum in Fig. 1. All the narrow absorption bands of the  $n = 1, 2$  and 3 clusters are visible in this trace. The relative intensities do change vs. the R2PI scans, so there are apparently some

slight differences in the intensities or widths of broad emissions from the different conformers. Most prominent in this spectrum, as in fig. 5 of KLB, is a band at  $31103\text{ cm}^{-1}$  (measured at  $31105\text{ cm}^{-1}$  by KLB). While this corresponds to a band of the  $n = 3$  R2PI spectrum, it is also accidentally degenerate with the strongest  $n = 2$  signal.

Moving the monochromator center wavelength 20 nm further to the red, to enter the known ESPT band, the lowest trace of Fig. 1 is obtained. The offset from the base of the figure represents the true intensity. Obviously there is in this case no structure corresponding to any of the R2PI spectra. This spectrum corresponds to a segment of the  $n = 4$  absorption.

#### 4. Discussion

From the lower traces in Fig. 1, it is clear that the structure observed in fig. 5 of KLB at wavelengths longer than 380 nm was due to the tail of the broad non-ESPT emission shown in Fig. 2. This cutoff wavelength is not sufficient to eliminate non-ESPT emission. That only the  $31103\text{ cm}^{-1}$  absorption was identified in long-wavelength emission is an artifact of the weakness of the other emissions. Close inspection of KLB's fig. 5 indeed reveals other structure besides the  $31103\text{ cm}^{-1}$  band. The strength of the  $31103\text{ cm}^{-1}$  emission is not a reflection of the emission spectrum of the special  $n = 3$  conformer, but is rather due to the abundance of the  $n = 2$  conformer which emits at the same wavelength. The  $31103\text{ cm}^{-1}$  conformer of  $n = 3$  remains unusual in that its ionization potential is somewhat lower than that of other conformers, but this now appears to have no bearing on its ESPT properties.

A possible reason for the broad emission of the  $n = 1$ –3 clusters is mixing of the first two electronic excited states. This leads to some  $S_2$ -like emission superimposed on the 'typical'  $S_1$  spectrum. Vibrationally induced  $S_1/S_2$  mixing has been observed in free 1-naphthol (7) and the 1-naphthol · water complex [29]. A broad long-wavelength emission from the 7-azaindole · water complex has also been observed and attributed to  $S_1/S_2$  mixing, although ESPT does not occur [30]. Solvent or cluster induced inversion of these states is the mechanism by which

1-naphthol ESPT becomes possible, so as the number of ammonia molecules approaches the ESPT threshold the  $S_2$  could approach the  $S_1$  and become more strongly mixed with it. This picture is supported by the 400 nm excitation spectrum in Fig. 1. The  $n = 3$  features are disproportionately strong vs.  $n = 1$  or 2, despite the greater abundance of the smaller clusters in the molecular beam. The same is true for  $n = 2$  vs.  $n = 1$ .

The results presented here are also important for interpretation of the pump–probe transients measured for 1-naphthol ·  $(\text{NH}_3)_n$  clusters [21–24]. While the results remain fascinating, the large amplitude transient for  $n = 3$  can no longer be assigned to ESPT on the basis of spectroscopic results. As noted in the introduction, this is somewhat reassuring, since other aspects of the those studies were hard to reconcile with the spectroscopy. Instead of  $n = 3$  ESPT, these data may reflect dynamics of higher clusters (possibly but not necessarily ESPT) and fragmentation after ionization. The  $n = 4$  ion state excess energy in Refs. [21–24] was  $3500$ – $4500\text{ cm}^{-1}$  under the conditions where  $n = 3$  transients were seen. This is in the same excess energy range where  $n = 1$  and 2 fragmentation is observed for 1-color R2PI. This conclusion has been recently supported by preliminary pump–probe results using a variety of wavelengths [31]. Under conditions where  $n = 3$  transients were observed, they appeared to be assignable to decay from larger clusters.

#### 5. Conclusions

Resonant two-photon ionization, fluorescence and excitation spectra of 1-naphthol ·  $(\text{NH}_3)_n$  clusters are reported for  $n = 1, 2, 3$  and 4. A previously unnoticed broad, weak emission from  $n = 1, 2$  and 3 clusters was found to extend to  $\sim 25000\text{ cm}^{-1}$  (400 nm). Comparison of R2PI spectra and the excitation spectra observed at 400 nm show that  $n = 1, 2$  and 3 definitely emit at 400 nm. Excitation spectra taken at a wavelength of 420 nm show no such contribution. Since ESPT emission begins only beyond 400 nm, we conclude that no  $n = 3$  conformers undergo ESPT. The threshold cluster size for 1-naphthol ·  $(\text{NH}_3)_n$  ESPT is therefore  $n = 4$ , in agreement with the earliest studies on this system and the thermody-

namic model for ESPT in these clusters. The broad emission from the smaller clusters is tentatively assigned to  $S_2$ -like fluorescence as a result of electronic state mixing, which increases with cluster size.

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