Hydrogen atom transfer in indole(NH₃)ₙ clusters: formation dynamics of (NH₃)ₙ₋₁NH₄, n = 1–6, fragments

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Abstract. The H atom transfer reaction in electronically excited indole(NH₃)ₙ clusters is studied in pump-probe experiments with femtosecond laser pulses. By applying different probe photon energies we are able to detect the dissociation products $(NH_3)_{n-1}NH_4$ for $n = 1$–6. Furthermore we show that the analysis of the corresponding ion signals is not distorted by contributions from larger cluster ions due to evaporation of NH_3 molecules. The formation times of the products are *ca.* 140 ps for $n = 2$–4 and about 80 ps for $n = 5, 6$.

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1 Introduction

Among small biologically relevant molecules, indole – the chromophore of the amino acid tryptophan – is of special interest, in particular when embedded into clusters of polar molecules such as water or ammonia. It allows *e.g.* a microscopic study of the mechanisms involved in the solvation process of optically excited indole molecules in aqueous solution, a process which has been identified as an essential step in the photochemistry of this system (see *e.g.* [1]): the photo-excitation of indole in aqueous solution leads to a fast charge separation process characterized by the formation of a solvated electron.

Recent *ab initio* calculations of the potential energy surfaces of the free indole molecule [2] and indole-water clusters [3] have shown that a low-lying $\pi\sigma^*$ Rydberg-type state of the indole molecule plays the crucial role in the photophysics, because in this state a large amount of the electronic charge is displaced along the N–H coordinate towards the H atom. In indole-water clusters the electron charge is completely separated from the indole molecule and is solvated by the water molecules [3]. The $\pi\sigma^*$ state of indole is a dark state but can be populated by nonadiabatic coupling through the optically accessible $\pi\pi^*$ states of the molecule.

Analogous studies of the similar phenol-water and phenol-ammonia cluster systems have shown [4] the photoinitiated electron transfer to be accompanied by a fast proton transfer. Together this results in a fast hydrogen atom transfer, a process which has also been ob-

served in pure ammonia clusters (see *e.g.* [5,6] and references cited there). According to recent studies [7] a H-transfer is expected to characterize also the photochemistry in indole-water and indole-ammonia clusters. Their electronic properties are very similar to those of the corresponding clusters with the phenol chromophore. In particular, the σ^* orbitals of the calculated $\pi\sigma^*$ states – which determine the reaction in phenol(H₂O)ₙ as well as in indole(H₂O)ₙ – have been found to be strongly comparable (*cf.* [3,7]). Indeed, first pump-probe experiments with indole-ammonia clusters have confirmed the expectation. By applying nanosecond laser pulses at 272 nm (pump pulse) and at 355 nm (probe pulse) $(NH_3)_{n-1}NH_4^+$ ions have been observed for pump-probe delay times up to 800 ns indicating the formation of the long-living neutral species by a dissociative H-transfer reaction [8] of the indole-ammonia clusters (in the following denoted by $IndNH(NH_3)_n$) according to the following scheme:

$$\xrightarrow{272 \text{ nm}} IndNH(NH_3)_n^* \rightarrow IndN(NH_3)_{n-1}NH_4 \rightarrow$$
$$IndN + (NH_3)_{n-1}NH_4. \quad (1)$$
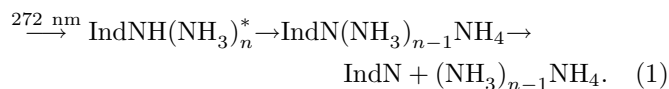
Very recently, in a pump-probe experiment with femtosecond laser pulses we have found the formation time for the $(NH_3)_{n-1}NH_4$ radicals to be on the order of about 100 ps for $n = 4, 5$ [9]. The indole-ammonia clusters were excited by pump pulses at a wavelength of 263 nm (4.71 eV) to the $S_1(\pi\pi^*)$ state (as in [8]). After the ultrafast internal conversion to the $\pi\sigma^*$ state (probably on the fs time scale) the H-transfer reaction proceeds according to equation (1). Finally, on a ps time scale, the clusters in the H-transfer state may dissociate after internal rearrangement of the cluster geometry. The corresponding time

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constants for the different cluster sizes were determined in a pump-probe experiment with time-delayed probe pulses of 395 nm (3.14 eV) [9]. At this wavelength we were able to detect besides parent $IndNH(NH_3)_n^+$ cluster ions only $(NH_3)_{n-1}NH_4^+$ fragment ions with $n \geq 4$. Since the ionization potentials for $(NH_3)_{n-1}NH_4^+$, $n \leq 3$, exceed the probe photon energy of 3.14 eV [10] this is an indication that we have indeed observed neutral ammoniated NH_4 radicals resulting from a dissociative H-transfer.

In the present paper we will confirm the suggested H-transfer reaction

1. by applying a strong probe pulse at 790 nm (1.57 eV) which allows for detection of all neutral $(NH_3)_{n-1}NH_4$, $n = 1$–6, radicals through multiphoton ionization
2. and by repeating the experiments with a weak probe pulse at a wavelength of 395 nm.

By comparing the results for the larger radicals with $n \geq 4$ we provide evidence that the formation times observed are *not* obscured by evaporation of NH_3 molecules from $(NH_3)_{n-1}NH_4^+$ cluster ions with higher excess energies. Furthermore the observation of smaller products with $n \leq 3$ which is only possible by applying the strong laser pulses at 790 nm reveals the formation times also for these clusters. Thus, we provide the complete information about the size dependence of the formation dynamics for all observable $(NH_3)_{n-1}NH_4$ fragments. We will restrict the present discussion to the latter. In contrast, the detection of the parent indole$(NH_3)_n$ clusters is strongly affected by NH_3 evaporation from the cluster ions when the high intensity probe pulses at 790 nm is applied. This will be discussed in a forthcoming paper.

2 Experimental

The indole-ammonia clusters are formed by a free adiabatic expansion of a gas mixture through a pulsed nozzle. The gas mixture (stagnation pressure: 1 bar) contains indole vapor (vapor pressure at room temperature) and ammonia (about 5%) in the He seed gas. Due to the low indole concentration no indole clusters are formed in the molecular beam. The width of the $IndNH(NH_3)_n$ cluster distribution interacting with the laser field has been reduced by irradiating the molecular beam pulse in its front region where the cluster formation is just starting. The molecular beam is crossed by two weakly focused co-propagating laser beams in the interaction region of a time-of-flight (TOF) mass spectrometer.

The laser system used is a commercial Ti:sapphire laser and amplifier system (Clark MXR) tuned to 790 nm for the experiments presented here. The third harmonic of the fundamental wave at $\lambda_1 = 263$ nm (4.71 eV) is used to pump the clusters whereas the second harmonic at $\lambda_2^{(1)} = 395$ nm (3.14 eV) or the fundamental wave at $\lambda_2^{(2)} = 790$ nm (1.57 eV) is applied to probe the excited clusters as well as the reaction products by ionization. While the laser fluences for the wavelengths λ_1 and $\lambda_2^{(1)}$

are kept relatively small (0.5 and 6 mJ/cm^2, respectively) the fluence of the probe pulse at $\lambda_2^{(2)}$ has to be chosen high enough (about 25 mJ/cm^2) in order to enable the absorption of 2 or 3 probe photons necessary for the ionization of all fragments. The width of the laser pulses is about 140 fs. A standard delay line is used to scan the delay time between the pump and the probe pulses.

The ion signals are detected by a microchannel plate detector in the TOF mass spectrometer, digitized by a fast digital oscilloscope (Tektronix TDS 520A) and stored and processed by a PC. At a repetition frequency of 50 Hz the mass spectra are accumulated typically for 100 laser pulses at each delay time τ and averaged over 80 up- and down-scans of the delay line.

3 Results and discussion

Figure 1 shows time-dependent ion signals from $(NH_3)_{n-1}NH_4$ radicals formed after excitation of $IndNH(NH_3)_n$ clusters at 263 nm (4.71 eV) and ionized at 395 nm (3.14 eV). The results shown in Figures 1a–1c agree within the experimental errors with the corresponding curves already shown in [9]. Additionally the much weaker ion signal of $(NH_3)_5NH_4^+$ (see Fig. 1d) is represented. The ionization potentials of indole (7.76 eV [11]) and indole-ammonia clusters (≤ 7.25 eV [11]) allow ionization of the parent clusters by a single probe photon. The product radicals $(NH_3)_{n-1}NH_4$ are ionized by one probe photon as long as their ionization potential is below the probe photon energy of 3.14 eV. As shown in Figure 1 this holds for $(NH_3)_3NH_4$, $(NH_3)_4NH_4$ and $(NH_3)_5NH_4$ ($IP = 2.97$ eV, 2.73 eV and 2.62 eV, respectively [10]), whereas for $(NH_3)_2NH_4$ the ionization potential of 3.31 eV [10] is larger than the probe photon energy so that the $(NH_3)_2NH_4^+$ signal nearly vanishes (see Fig. 1a). This demonstrates, that the rising signals in Figure 1 reflect indeed the formation of neutral radicals which are ionized by the probe photon. Possible contributions by fragmentation of the parent cluster ions are negligibly small.

Figure 2 shows the $(NH_3)_{n-1}NH_4^+$ ion signals as measured at an identical pump wavelength of 263 nm but ionized now by probe pulses of 790 nm (1.57 eV). Here the absorption of *two* probe photons leads to the same pump plus probe photon energy as before at the probe photon energy of 3.14 eV and, thus, to the detection of the $(NH_3)_{n-1}NH_4$ products with $n \geq 4$ (*cf.* Figs. 2d–2f). In addition, also the smaller radicals with $n \leq 3$ are ionized by absorption of *three* probe photons (see Figs. 2a–c) albeit with about one order of magnitude lower intensity due to the smaller cross section for the three photon process.

The solid lines in Figures 1 and 2 represent single-exponential fit curves. The time constants τ_2 for the rising ion signals in Figures 1b–1d, *i.e.* the observed fragment formation times, decrease substantially from 140 ps for $(NH_3)_3NH_4$ down to 60 ps for $(NH_3)_5NH_4$. These values agree within the experimental errors with those obtained for $(NH_3)_{n-1}NH_4$, $n = 4$–6, probed at 790 nm

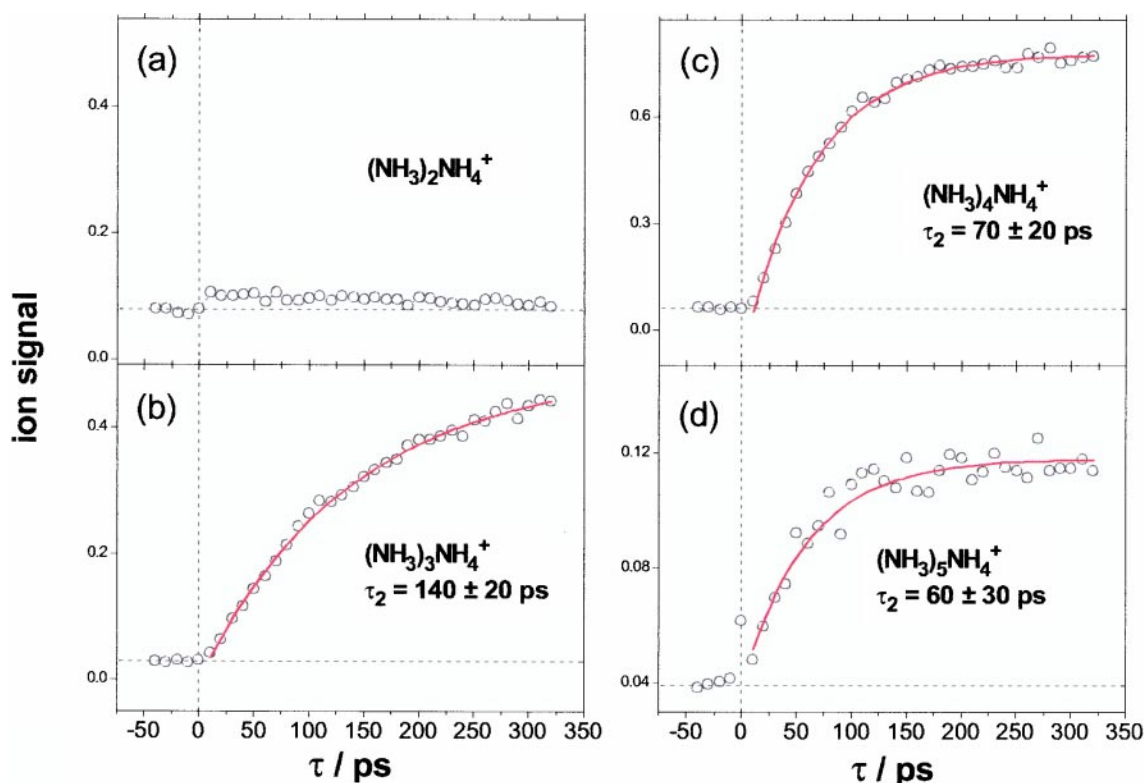**Fig. 1.** Dissociation products $(NH_3)_{n-1}NH_4$ of IndNH(NH$_3$)$_n$, $n = 3...6$, clusters excited at $\lambda_1 = 263$ nm. The products are ionized by probe pulses at $\lambda_2^{(1)} = 395$ nm, delayed by a time τ. Note the different intensity scales for different cluster sizes.
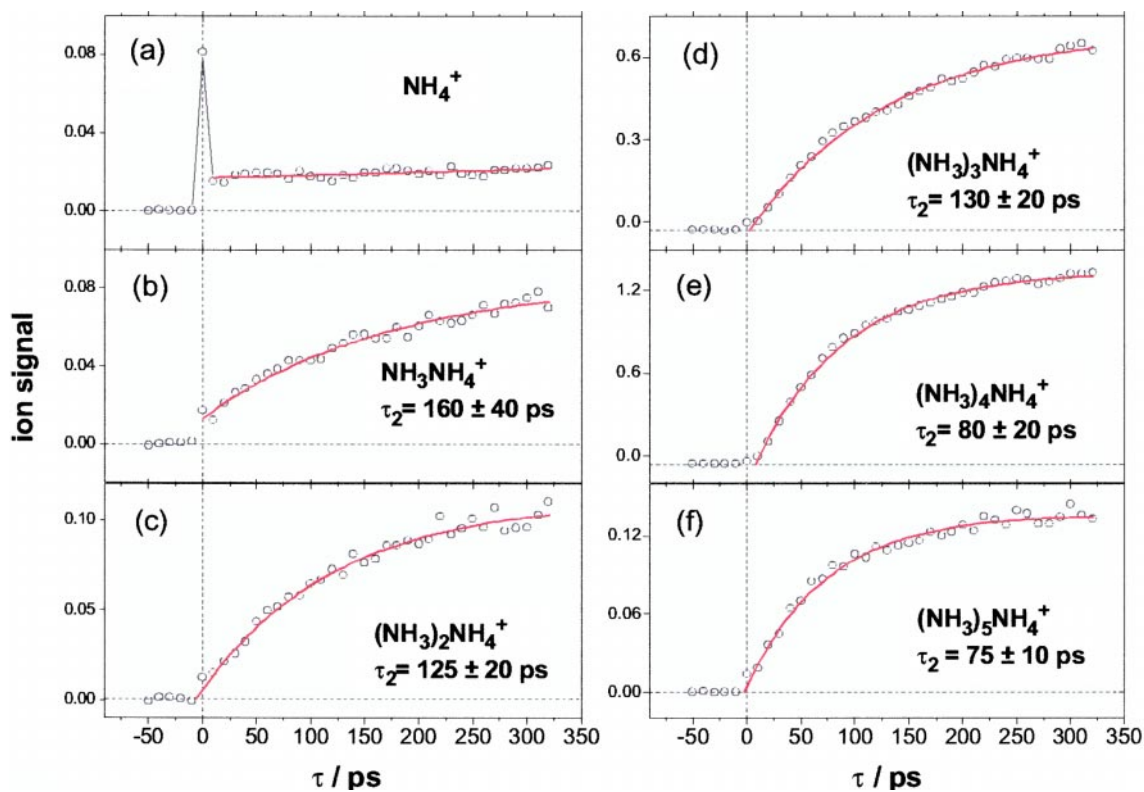

Fig. 2. Dissociation products $(NH_3)_{n-1}NH_4$ of IndNH(NH$_3$)$_n$, $n = 1...6$, clusters excited at $\lambda_1 = 263$ nm. The products are ionized in a multi-photon process induced by the strong probe pulse at $\lambda_2^{(2)} = 790$ nm delayed by a time τ. Note the different intensity scales for different cluster sizes.

(Figs. 2d–2f). This implies that the measured formation time for a given fragment size is not distorted by NH_3 evaporation from larger fragment ions when the intense laser pulses at longer wavelength are applied. The ions may be formed with higher excess energy due to multiphoton absorption at the high intensity. For example, the time-dependent parent cluster ion signals at 790 nm (not shown here) are strongly affected by contributions from larger clusters due to evaporation of NH_3 molecules. Obviously, such an effect is not observed for the $(NH_3)_{n-1}NH_4^+$ fragment ions.

As first preliminary results of time-resolved photoelectron spectroscopy [12] suggest the cluster dynamics on the picosecond time scale is correlated to a structural rearrangement of the clusters leading to changes of the internal energy and, hence, of the fragmentation rate. Thus, the significant drop of the product formation time between $n = 4$ (140 ps resp. 130 ps, Fig. 1b and Fig. 2d) and $n = 5$ (70 ps resp. 80 ps, Fig. 1c and Fig. 2e) may reflect a considerable difference of the parent cluster geometries. We also note that the intensity of the observed $(NH_3)_{n-1}NH_4^+$ ion signals decreases by approximately one order of magnitude from $n = 5$ to $n = 6$ as it is indicated by the different intensity scales in Figure 1c (Fig. 2e) compared to Figure 1d (Fig. 2f). This may reflect the fact [8] that for $IndNH(NH_3)_n$ clusters with $n > 5$ the H-transfer reaction mainly occurs in the electronic ground state which cannot be observed by our method.

As can be seen in Figure 1b and Figures 2b–2d the formation times τ_2 for NH_3NH_4, $(NH_3)_2NH_4$ or $(NH_3)_3NH_4$ radicals are comparable. This indicates that the time needed for a geometrical rearrangement of the smaller excited clusters $IndNH(NH_3)_n$, $n \leq 4$, is nearly size-independent but significantly longer than for the larger clusters with $n > 4$. The NH_4^+ signal in Figure 2 shows only a small and very slow rise of the signal. Obviously, in this case after H-transfer in the excited state of the parent cluster $IndNNH_4$ no rearrangement of NH_3 molecules around the NH_4 group is possible and no vibrational energy can be gained. This may possibly explain the low formation rate of NH_4. As a cross check, we have further reduced the cluster size distribution as described above ($n \leq 3$): no significant changes in the time constants τ_2 of $(NH_3)_{n-1}NH_4$ were observed for $n = 2, 3$ at a probe wavelength of 790 nm. Hence, we may safely assume, that the protonated ammonia cluster signals arise only from direct fragmentation of a parent cluster and are not superimposed by contributions of larger clusters having lost NH_3 molecules by evaporation.

4 Conclusions

By selective detection of $(NH_3)_{n-1}NH_4$ radicals the dissociative H-transfer reaction in electronically excited $indole(NH_3)_n$ clusters has been confirmed. As determined in pump-probe experiments the formation times for the products significantly change from roughly 140 ps for $n = 2$–4 to about 80 ps for $n = 5, 6$. The detection of all fragmentation products ($n = 1$–6) is possible by applying different probe photon energies. We have demonstrated that contributions of larger cluster ions due to evaporation of NH_3 molecules to any of the observed specific product ion signal is negligibly small. Further insight into the reaction dynamics and the correlation between $(NH_3)_{n-1}NH_4$ product formation and rearrangement processes within the $indole(NH_3)_n$ clusters after the H atom transfer, will be gleaned from the analysis of photoelectron spectra [12].

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