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LETTERS

Dynamics of Hydrogen Atom Transfer in Indole$(NH_3)_n$ Clusters

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The hydrogen atom transfer reaction in indole $(NH_3)_n$ clusters excited at 263 nm to the $S_1(\pi\pi^*)$ state is studied in pump−probe experiments with femtosecond laser pulses. For small clusters the reaction is characterized by two successive processes on distinct time scales: the time constant of the primary process is in the sub-ps region, whereas the secondary decay time growing with the cluster size reflects a relaxation process within 25 to 150 ps. A preliminary model of the H-transfer reaction is discussed.

I. Introduction

The photochemistry of the indole molecule which represents the chromophore of the amino acid tryptophan is of particular interest because it enables some insight into processes of biological relevance. Extensive studies of indole in aqueous solution have shown[1,2] that photoexcitation leads to a fast charge separation process characterized by the formation of a solvated electron. To elucidate the microscopic mechanism of the solvation process, the study of gas phase indole-solvent clusters with polar solvent molecules such as water or ammonia is highly informative. Most of these studies have been focused on the spectroscopic properties of indole−water[3] and indole−ammonia clusters[4] in the UV spectral range.

Recent ab initio calculations of the photophysics of free indole[5] and indole−water clusters[6] have shown that the non-adiabatic coupling of the optically excited $\pi\pi^*$ state to a low-lying dark $\pi\sigma^*$ state plays the essential role in the photophysics of indole. In the $\pi\sigma^*$ Rydberg-type state of the free indole molecule, a significant amount of the electronic charge is displaced along the N−H coordinate from the N atom toward the H atom. In the indole−water clusters, the electron charge is completely separated from the indole molecule and solvated by the water molecules.[6] Analogous studies of the similar systems of phenol−water and phenol−ammonia clusters[7] suggest that the electron transfer in indole−water clusters is accompanied by a fast proton transfer.

First pump−probe experiments of indole$(NH_3)_n$ clusters on the ns time scale[8] have suggested that after photoexcitation of these complexes a H atom transfer reaction should proceed also here because $(NH_3)_{n-1}NH_4^+$ ions have been observed up to 800 ns after the pump pulse. Surprisingly, these signals have been detected only at larger delay times (> 10 ns) between the pump and probe pulses.

In the present paper we present first results on the ultrafast dynamics of the indole-ammonia clusters excited with femtosecond laser pulses at 263 nm to the $S_1(\pi\pi^*)$ state. For this excitation energy the different steps of the H-transfer reaction and their time evolution are analyzed and interpreted in the frame of a preliminary reaction model.

II. Experimental Section

The indole−ammonia clusters $(InNH(NH_3)_n)$ are formed by free adiabatic expansion of a gas mixture at 1 bar through a pulsed nozzle. The gas mixture contains indole vapor (pressure at room temperature: 0.3 mbar)[3] and about 5% ammonia in the He seed gas. Due to the low indole concentration, no indole

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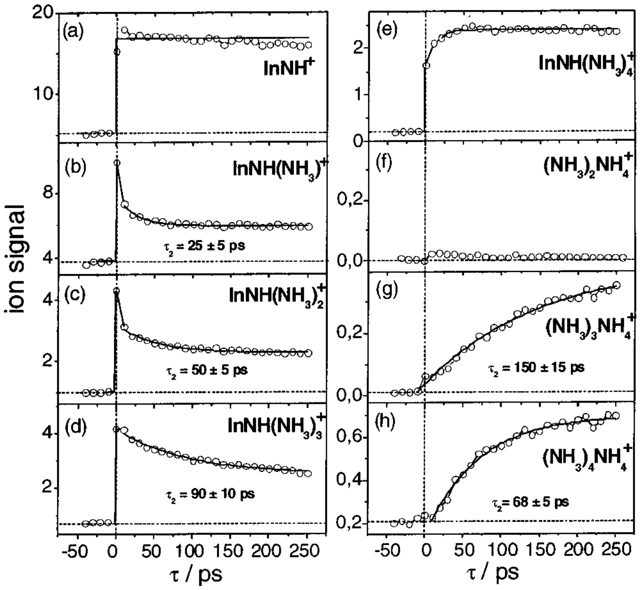

Figure 1. Ion signals of the $InNH(NH_3)_n$ clusters and their fragments $(NH_3)_{n-1}NH_4$ as a function of the delay time τ between the pump (263 nm) and probe (395 nm) pulses.

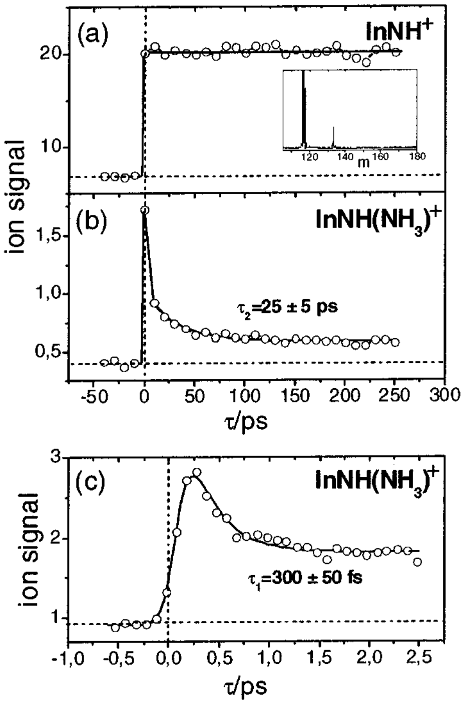

Figure 2. Ion signals of the indole molecule and the indole(NH_3) heterodimer versus delay time τ at identical laser parameters as in Figure 1, but for an extremely narrow cluster distribution. The mass (m) spectrum is shown in the inset in Figure 2a.

clusters are formed in the molecular beam. The width of the $InNH(NH_3)_n$ cluster distribution interacting with the laser field has been restricted to small values of n by irradiating the molecular beam pulse in its front part, where cluster formation just starts. The molecular beam is crossed by two weakly focused co-propagating laser beams in the interaction region of a time-of-flight mass spectrometer.

The laser used is a commercial Ti:sapphire laser and amplifier system tuned to 790 nm. The third harmonic of the fundamental wave at 263 nm (4.71 eV) is used to pump the clusters, whereas the second harmonic at 395 nm (3.14 eV) is applied to probe the excited clusters as well as the reaction products by ionization. The width of the laser pulses is about 140 fs. The laser fluences are reduced to such levels that single photon absorption dominates for the pump as well as for the probe pulse. A standard delay line is used to scan the delay time between the pump and the probe pulses. At a repetition frequency of 50 Hz, the mass spectra are accumulated typically for 80 laser pulses at each delay time τ and averaged over 40 up-scans and down-scans of the delay line.

III. Results and Discussion

In Figure 1 the time-dependent ion signals of $InNH(NH_3)_n^+$ and $(NH_3)_{n-1}NH_4^+$ are displayed for a cluster distribution up to about $n = 6$. The pump photon energy of 4.71 eV is significantly above the energy of the $S_1(\pi\pi^*,{}^1L_b)$ state of indole (4.37 eV)[3] and $InNH(NH_3)$ (4.34 eV).[4] For indole the next higher electronic state, $S_2(\pi\pi^*,{}^1L_a)$, has a calculated energy of 4.73 eV,[9] which is slightly above the pump photon energy. For $InNH(NH_3)$ the position of this state is unknown but probably below 4.71 eV. The resulting total energy (7.85 eV) of one pump and one probe photon exceeds only slightly the ionization potential of the indole molecule (7.76 eV)[3] but strongly the ionization potentials of the heterodimer $InNH(NH_3)$ (7.25 eV)[4] and the larger clusters. Hence, we expect a relatively large fragmentation probability of the clusters in the ionic state.

As shown in Figure 1a, no time dependence is obtained for the ion signal of the bare indole molecule. For the $InNH(NH_3)_n$ clusters, however, at longer delay times a single-exponential decay with the time constant τ_2 is observed for $n = 1, 2, 3$ (cf. Figures 1b−d), which is preceded by a fast transient for $n = 1$, 2 at short delay times. The decay time τ_2 increases for larger cluster sizes n. The nearly constant signal of $InNH(NH_3)_4^+$ (Figure 1e) probably reflects the compensation of the decaying cluster signal by a rising term with an identical time constant (see below). Larger clusters with $n = 5, 6$ (significantly weaker, not displayed here) show a similar time dependence as the complex for $n = 4$.

For the protonated ammonia cluster ions in Figure 1 we find signals only if the probe photon energy is larger than the ionization potential (IP) of the neutral species $(NH_3)_{n-1}NH_4$.[10] This holds for $(NH_3)_3NH_4$ with IP = 2.97 eV (Figure 1g) and for $(NH_3)_4NH_4$ with IP = 2.73 eV (Figure 1h) but not for $(NH_3)_2NH_4$ with IP = 3.31 eV (Figure 1f). This result is a clear indication of a dissociative H atom transfer reaction in the electronically excited indole−ammonia clusters. The rise times of the fragment signals are clearly correlated to the decay times of parent clusters. However, in contrast to the parent cluster ion signals to which also the larger parent fragments may contribute, the protonated ammonia signals should arise from the reaction of only one precursor cluster.

To reduce the contributions of fragments from larger clusters to the $InNH(NH_3)_n^+$ ion signals, we have narrowed the cluster distribution such (see section II) so that besides the bare molecule only the heterodimer ion can be observed (see Figure 2). On the long time scale the $InNH(NH_3)$ signal decays with the time constant $\tau_2 = (25 \pm 5)$ ps (cf. Figure 1b). The finite signal at long delay times (see Figure 2b) is somewhat decreased in comparison to the tail of the corresponding signal for the broader distribution (Figure 1b) because larger clusters contribute to the latter signal due to NH_3 evaporation in the ionic state. On the short time scale the fit procedure with our theoretical model[11] (solid curve in Figure 2c) reveals a decay time of $\tau_1 = (300 \pm 50)$ fs. This decay time τ_1 grows up for $InNH(NH_3)_2$ ($\tau_1 \approx 450$ fs) but is not observable for $InNH(NH_3)_3$.

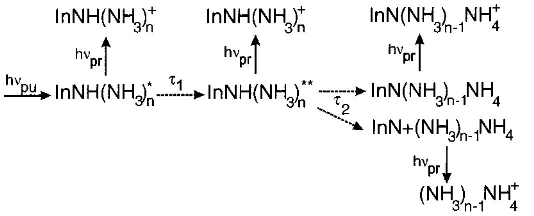

Figure 3. Possible reaction scheme for the H atom transfer reaction in $InNH(NH_3)_n$ clusters excited by the pump photon $h\nu_{pu}$ and ionized by the probe photon $h\nu_{pr}$.

As a result of our experimental observations, we propose the preliminary reaction model given in Figure 3. After the initial excitation of the $InNH(NH_3)_n$ clusters to the $S_1(\pi\pi^*)$ state (denoted by *), a fast process with the time constant τ_1 in the sub-ps range is observed. Tentatively, this process is attributed to the internal conversion from the $\pi\pi^*$ to the $\pi\sigma^*$ state, possibly followed by the ultrafast H-transfer. The secondarily populated, intermediate state $InNH(NH_3)_n^{**}$ decays with the time constant τ_2, probably due to the reorientation and vibrational relaxation of the cluster geometry after the H-transfer. For larger clusters with a larger number of degrees of freedom, this reorientation process needs longer times, causing the increase of the time constant τ_2 with the cluster size n. If during this relaxation process the vibrational energy is concentrated in the $InN-(NH_3)_{n-1}NH_4$ bond, the cluster in the H-transfer state dissociates instantaneously. Thus, the reorientation process with the time constant τ_2 will lead to stable clusters in the H-transfer state and as well (at a certain fraction) to the formation of the $(NH_3)_{n-1}NH_4$ radicals. After ionization the former contribution causes a rise of the parent ion signal with the time constant τ_2 which may compensate the decaying ion signals resulting from the ionization of the intermediate cluster state. Thus the stable long time ion signals, in particular for the larger cluster sizes, are understandable. A detailed discussion of these facts will be given in a forthcoming paper.

The time dependence of the $(NH_3)_{n-1}NH_4^+$ signals reflects the formation of the neutral species from the intermediate cluster state on the ps time scale. Generally, we have detected no $(NH_3)_{n-1}NH_4^+$ signals for $n > 6$, which is due to the fact that for larger clusters the H-transfer reaction occurs in the electronic ground state[8] which cannot be observed by our method.

In conclusion, first results were obtained to understand the H-transfer reaction in indole$(NH_3)_n$ clusters. The characterization of the primary reaction step leading to the intermediate cluster state is still an open question. Here, the study of the dynamics as a function of the pump wavelength will reveal further elucidation. Furthermore, we expect more detailed information by applying the femtosecond time-resolved photoelectron spectroscopy as developed in our group.[12]

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