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The dynamics of excited state indole-(NH₃)_n clusters has been investigated with two-color two-photon ionization. Mass spectra recorded with delayed ionization indicate that a hydrogen transfer reaction indole(S₁)-(NH₃)_n → C₈H₆N⁺ + NH₄(NH₃)_{n-1} occurs for *n* = 3, 4, 5.

Introduction

Indole and its substituted derivatives have often been used as a model compound for the tryptophan amino acid, which exhibits absorption and fluorescence spectra that are very sensitive to environmental effects. A way to address these effects is to selectively add molecules on the indole chromophore and monitor the photochemical and photophysical properties of indole clusters under supersonic jet conditions. This was the subject of many investigations in the last twenty years.¹⁻¹⁰ The questions that have been addressed concern the dynamics of the excited states in the free molecules and in their complexes, the site of complexation, the effect of the complexation on the ¹L_a-¹L_b inversion, but the possible reactivity of indole-solvent clusters has not been investigated.

In 2,3-dimethylindole, the lifetime shortening of the excited state above the origin (6 ns at the origin and below 1 ns 300 cm⁻¹ above) has demonstrated the appearance of a non-radiative process probably associated with L_a mixing: this non-radiative process has been postulated as the N-H bond dissociation but no direct experimental proof could confirm this hypothesis.⁴

In recent theoretical papers Sobolewski and Domcke^{11,12} showed that the lowest πσ* singlet state was repulsive along the N-H coordinate crossing the ¹L_a, ¹L_b of ππ* character as well as the ground state, providing a mechanism for the experimentally observed non-radiative process.

During the past three years it was shown¹³⁻¹⁷ that the excited state dynamics of small phenol-(NH₃)_n clusters is not governed by an excited state proton transfer (as previously assumed) but by a hydrogen transfer as follows: PhOH(S₁)-(NH₃)_n → PhO⁺ + NH₄(NH₃)_{n-1}. The mechanism of this reaction is not yet fully understood but it seems to proceed directly by a tunneling mechanism through a barrier.¹⁷ In these experiments, the ammonia clusters have shown their ability to trap hydrogen atoms and therefore to be used as indicators for a X-H bond rupture.

Since the N-H bond is expected to be predissociated through mixing with higher excited states, one might conjecture a H transfer reaction in the indole-(NH₃)_n system and we present here preliminary results that demonstrate that the H transfer mechanism occurs.

Experimental

Hydrogen transfer in indole-(NH₃)_n was investigated by using the same strategy as for phenol-(NH₃)_n clusters.^{13,14} The clusters are produced in a supersonic expansion using a heated pulsed valve maintained at 100 °C to vaporize indole. The expanding gas is a mixture of He and NH₃ (1%) at 2 atm

(1 atm = 101325 Pa). The indole concentration is estimated to be between 0.1 and 0.5% in the gas mixture. After passing through a skimmer the clusters are ionized and detected in a reflectron time of flight mass spectrometer.

A first laser (doubled dye laser) excites the indole-(NH₃)_n cluster to the S₁ state. The reaction proceeds leading to indolyl radical in its ground state and to free NH₄(NH₃)_m (*m* = *n* - 1) clusters. A second laser (the third harmonic of a YAG laser at 355 nm) is used to ionize the NH₄(NH₃)_m clusters that are metastable (μs lifetime^{18,19}).

This second laser is delayed in time (800 ns) and spatially moved downstream to minimize the possible absorption of the indole⁺-(NH₃)_n ions and the subsequent ionic reactions. Since the extraction field (250 V cm⁻¹) stays on between the two laser pulses, most of the ions are extracted from the beam when the second laser is fired. The lifetime of the S₁ state being around 17.5 ns,⁴ nearly all the excited molecules and clusters have relaxed to their ground state when the second laser is fired and cannot be ionized anymore.

Results

The mass spectra obtained with one color (272 nm) and two color processes are presented in Fig. 1. With one color at 272 nm only the indole-(NH₃)_n clusters are observed (Fig. 1a). Due to the velocity of the beam and the detection perpendicular to the beam axis, large clusters are not detected efficiently in these experimental conditions. However larger clusters can be detected by applying a deflection voltage.

When the second laser (355 nm) is fired 800 ns after the first one, three new peaks appear in the mass spectrum corresponding to NH₄⁺(NH₃)₂, NH₄⁺(NH₃)₃, NH₄⁺(NH₃)₄ (Fig. 1b). For both spectra the time *t* = 0 is given by the delayed 355 nm laser. Therefore the indole-(NH₃)_n clusters that are produced by two 272 nm photons, 800 ns before the start of the acquisition have a flight time shifted by -800 ns.

Fig. 1c presents the true two-color ion signal obtained by subtracting the one color spectrum 1a from spectrum 1b. Clearly, under the conditions used, indole-(NH₃)_n ion peaks come only from excitation and ionization with the 272 nm laser, while NH₄⁺(NH₃)_m peaks correspond to a two color process.

The NH₄⁺(NH₃)_n distribution is peaking at *m* = 3. It is well known that delaying the excitation laser pulse relative to the opening time of the pulsed valve enhances the excitation of larger clusters. At short delay, the intensity of the NH₄⁺(NH₃)_m ion peaks decreases, indicating that the cluster distribution is shifted to smaller sizes but it has not been possible to significantly change the observed intensity ratios of

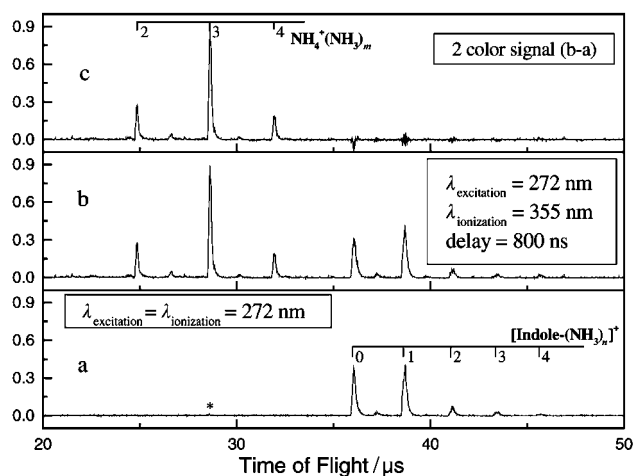


Fig. 1 Indole-(NH₃)_n one and two color mass spectra. (a) One color two-photon mass spectrum $\lambda_{\text{excitation}} = 272$ nm. (b) Mass spectrum obtained with $\lambda_{\text{excitation}} = 272$ nm, $\lambda_{\text{ionization}} = 355$ nm; the delay between excitation and ionization is 800 ns. (c) The top mass spectrum is obtained by subtracting the one color signal a from spectrum b: indole-(NH₃)_n clusters disappear because their excited state has decayed before the ionization laser is triggered. The NH₄(NH₃)_m clusters ($m = n - 1$) issued from the H transfer reaction are ionized by the 355 nm laser delayed by 800 ns and displaced a few mm downstream. The 355 nm laser is 100 times more intense (1 mJ/10 μ J) than the 272 nm laser, so that NH₄(NH₃)_n clusters are ionized much more efficiently in the two color process (with the 272 nm laser, the main NH₄⁺(NH₃)₃ ion peak appears very weakly although not observable on the scale of the figure). No signal is observed with the 355 nm laser alone. The small ill defined peaks located between the NH₄⁺(NH₃)_m are probably due to ionization by the 355 nm laser of dissociation products issued from ionic reaction in indole-ammonia clusters.

the three NH₄⁺(NH₃)_n clusters observed. At such long ionization delay we have not observed larger NH₄⁺(NH₃)_{n>4} clusters. With the probe laser wavelength used (355 nm), the NH₄⁺NH₃ complex cannot be ionized and therefore its absence is not significant.

The NH₄⁺(NH₃)_m distribution is peaking at $m = 3$. It is well known that delaying the excitation laser pulse relative to the opening time of the pulsed valve enhances the excitation of larger clusters. At short delays, the intensity of the NH₄⁺(NH₃)_m ion peaks decreases, indicating that the cluster distribution is shifted to smaller sizes but it has not been possible to significantly change the observed intensity ratios of the three NH₄⁺(NH₃)_m clusters observed. At long ionization delays we have not observed NH₄⁺(NH₃)_m clusters with $m > 4$. With the probe laser wavelength used (355 nm), the NH₄⁺NH₃ complex cannot be ionized and therefore its absence is not significant.

Discussion

Similarly to what has been shown for phenol-(NH₃)_n, the NH₄⁺(NH₃)_m signal is observed a long time after the indole-(NH₃)_n cluster excitation, indicating that these clusters, excited to S₁, undergo a dissociative hydrogen transfer reaction.

As in the case of phenol-(NH₃)_n clusters, large NH₄⁺(NH₃)_{m>4} ion products are not observed. The deprotonation reaction enthalpies for phenol and indole are similar (1461 ± 10 kJ mol⁻¹ (ref. 20) and 1471 ± 10 kJ mol⁻¹ (ref. 21), respectively). It has been assumed that a proton transfer reaction occurs in the ground state of phenol-(NH₃)_n clusters for $n > 5$ and the same mechanism could be possible in indole clusters. The excitation of the proton transferred species is not expected to lead to the formation of the NH₄(NH₃)_m radicals by an electron transfer mechanism. According to the work on phenol-ammonia clusters,^{13,15} it seems that excitation of the

ion pair states rather leads to a significant evaporation and to a strong intersystem crossing.

Assuming that the ionization efficiency of the indole-(NH₃)_n S₁ state is similar to that of the NH₄(NH₃)_m clusters, the absence of the NH₄⁺(NH₃)_m ions in the one-color two-photon process indicates that only a few NH₄(NH₃)_m radicals are produced during the laser pulse (≈ 10 ns): it can be so if the reaction is not fast as compared to the lifetime of the excited state.⁴ It should be noticed that the NH₄⁺(NH₃)_m peak intensities in the two-color spectrum as compared to the indole-(NH₃)_n peaks do not reflect the reaction efficiency: the experiment is set to enhance the reactive product.

The NH₄⁺(NH₃)_m mass distribution presents a maximum at $m = 3$, when large indole-(NH₃)_n ions are present in the distribution. When the expansion conditions are changed so that the parent clusters are expected to be produced in similar quantity, the NH₄⁺(NH₃)₂ is always smaller than the H transfer in phenol-(NH₃)_n where the NH₄⁺(NH₃)₂ ionised product can be larger than the NH₄⁺(NH₃)₃ when small clusters are produced in the expansion. However, in the phenol case the H transfer reaction is a fast process occurring in the 50 ps range, much shorter than the radiative lifetime.

This is also an indication that the H transfer reaction time for the indole-(NH₃)₃ cluster is 4 times slower than for the indole-(NH₃)₄ cluster (ratio of the two peak intensities).

Conclusions

The present experiment shows that the hydrogen transfer mechanism, which has been often forgotten, can be seen in many systems. Obviously more work has to be done on these systems: time and energy dependence of this hydrogen transfer reaction is underway in our laboratory. The case of 2,3-dimethylindole has to be investigated since a fast reaction is expected in view of the very short lifetime of the free molecule.

A general question emerges: are the NH₃ clusters very important to trigger this reaction or are they the most simple systems which reveal a general trend to H transfer to solvent in substituted aromatic molecules?

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