Photodissociation dynamics of indole in a molecular beam

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Photodissociation of indole at 193 and 248 nm under collision-free conditions has been studied in separate experiments using multimass ion imaging techniques. H atom elimination was found to be the only dissociation channel at both wavelengths. The photofragment translational energy distribution obtained at 193 nm contains a fast and a slow component. Fifty-four percent of indole following the 193 nm photoexcitation dissociate from electronically excited state, resulting in the fast component. The rest of 46% indole dissociate through the ground electronic state, giving rise to the slow component. A dissociation rate of $6 \times 10^5$ s$^{-1}$, corresponding to the dissociation from the ground electronic state, was determined. Similar two-component translational energy distribution was observed at 248 nm. However, more than 80% of indole dissociate from electronically excited state after the absorption of 248 nm photons. A comparison with the potential energy surfaces from the ab initio calculation has been made. © 2005 American Institute of Physics.

I. INTRODUCTION

Tryptophan fluorescence is widely used for characterizing the structure and dynamics of the surrounding protein environment. The importance of the research on the electronic structure and dynamics of indole stems from the fact that indole is a chromophore of the amino acid tryptophan. Indole has two absorption bands in the near UV, which can be assigned as $\pi^* \rightarrow \pi$ singlet–singlet transitions. The two excited states are labeled by $1L_a$ and $1L_b$ following the suggestion of Platt. The $1L_a$ state lies about 1400 cm$^{-1}$ below $1L_b$. The $1L_b$ state has a very strong $0_0^*$ transition at 35 232 cm$^{-1}$. The $S_0$–$S_1$ origin transition is ascribed to the $1L_a$ upper state. The $1L_a$ and $1L_b$ states have been used to explain most of the observed photophysics of indole.

However, in order to explain the anomalous increase in nonradiative decay of gas phase indole with excess energy above the $1L_a$ origin, Glasser and Lami suggested that $1L_a$ state undergoes efficient N–H bond fission under collision-free conditions. A model in which $1L_a$ and $1L_b$ couple to a dissociative state was proposed. In addition, the generation of NH$_2$(NH$_3$)$_3^+$ from UV-excited indole-(NH$_3$)$_3^+$ clusters was described as the photoproduits of intracluster hydrogen atom transfer reactions. The source of H atom was proposed to result from H atom elimination of indole in the excited state. Theoretical calculation from the complete active space self consistent field supported the existence of a third dissociative excited state, $\pi\sigma^*$, located about 0.5 eV above the $S_1$ state. This state is calculated to be dissociative along the NH coordinate. Recently, the study of infrared spectra in the electronically excited states of indole, indole-H$_2$O, 3-methyl indole, and 3-methyl-indole-H$_2$O indicates the existence of the $\pi\sigma^*$ state above $1L_a$. However, there is little direct evidence of this state yet.

In this work, we study the photodissociation of indole at 248 and 193 nm using multimass ion imaging techniques. Direct evidence of the H atom elimination from the excited electronic state was reported.

II. EXPERIMENT

The experiments have been described in detail elsewhere, and only a brief description is given here. Indole vapor was formed by flowing ultrapure Ne at pressure of 400 Torr through a reservoir filled with solid sample at 55 °C. The indole/Ne mixture was then expanded through a 800 µm high temperature (110 °C) pulsed nozzle to form the molecular beam. Molecules in the molecular beam were photodissociated by a UV photolysis laser pulse (Lambda Physik Compex 205; pulse duration: ~20 ns). Due to the recoil velocity and center-of-mass velocity, the fragments expanded to a larger sphere on their flight to the VUV laser beam path, and then were ionized by a VUV laser pulse. The distance and time delay between the VUV laser pulse and the photolysis laser pulse were set such that the VUV laser beam passed through the center-of-mass of the dissociation products, and generated the photofragment ions along the VUV beam path by photoionization. The length of the segment was proportional to the fragment recoil velocity in the center-of-mass frame multiplied by the delay time between the photolysis and the ionization laser pulses. To separate the different masses within the ion segment, a pulsed electric field was used to extract the ions into a mass spectrometer after ionization. While the mass analysis was being executed in the mass spectrometer, the length of each fragment ion segment continued to expand in the original direction according to its recoil velocity. At the exit port of the mass spectrometer, a two-dimensional ion detector was used to...
detect the ion positions and intensity distribution. In this
two-dimensional detector, one direction was the recoil velocity axis and the other was the mass axis. The schematic diagram of the experimental set up is shown in Fig. 1.

Depending on the velocity of the molecular beam, it was necessary to change the distance between the photolysis laser beam and the VUV laser beam to match the delay time between these two laser pulses to ensure that the ionization laser would pass through the center-of-mass of the products. The change of the distance between the two laser beams changed the length of the fragment ion segment in the image. The relationship between the length of the ion image and the position of the photolysis laser is illustrated in Fig. 2. If the molecules did not dissociate after the absorption of UV photons, these high internal energy molecules would remain within the molecular beam. They flew with the same velocity (molecular beam velocity) to the ionization region and were ionized by the VUV laser. The wavelength of the VUV laser in this experiment was set at 118.2 nm such that the photon energy was only large enough to ionize parent molecules. The dissociation of parent molecule cations would not occur with the energy left after the VUV laser ionization. However, the dissociation occurred following the VUV laser ionization for those hot molecules, which absorbed UV photon and did not dissociate into fragments before the arrival of the VUV laser pulse. The ion image of the dissociative ionization was different from the image of the dissociation products of neutral parent molecules. Since ionization and dissociation occurred at the same position, the image of dissociative ionization was a 2D projection of the photofragment ion’s 3D-recoil velocity distribution. It was a disk-like image, rather than a line-shape image. From the shape of the image and its change with the delay time, the image from dissociation of neutral molecules can easily be distinguished from the dissociative ionization image.

The dissociation rate was measured from the product growth or disk-like image intensity decay as a function of delay time between pump and probe laser pulses.

III. RESULTS

A. 193 nm

Fragment ions, including \( m/e = 89, 90, 116, \) and \( 117 \), were observed. Figure 3(a) shows the images of \( m/e = 89 \) and 90. The shapes of the images of \( m/e = 89 \) and 90 are both disk-like. They overlapped and cannot be separated totally from each other. The widths of the images do not change with the delay time between pump and probe laser pulses, as illustrated in Fig. 3(b). Therefore, they must result from the dissociation of excited indole after ionization.

Figure 4 shows the images in the mass range from \( m/e = 114 \) to 122. The center parts of the images of \( m/e \)
The aromatic amino acids and the nucleic acid bases are some of the most important molecules in biochemistry. One important photochemical characteristic of these molecules is the low quantum yields of fluorescence. These have been explained by the existence of very fast nonradiative processes which efficiently quench the excited state.\textsuperscript{16,17} The

translational energy release of the slow component is small and the probability of fragment translational energy distribution decreases monotonically with the energy. It is the typical characteristic of dissociation from a molecule undergoes internal conversion to the ground electronic state with no exit barrier.

The dissociation rate of the neutral excited indole molecules due to the 193 nm photon excitation was measured from the disk-like image intensity change of $m/e=89$ and 90 at various delay times. A dissociation rate of $(6\pm1) \times 10^5$ s\(^{-1}\) was obtained, as shown in Figs. 6(a) and 6(b). The slow dissociation rate is ascribed to the dissociation from the ground electronic state. For $m/e=116$, a slow rise of the product growth sat on the top of a large signal was observed, as illustrated in Fig. 6(c). The slow rise shows the similar dissociation rate as that obtained from $m/e=89$ and 90. It must correspond to the dissociation from the ground electronic state. On the other hand, the large signal underneath the product growth must result from the disk-like image or a fast rise component that the rise is faster than our instrument time response, corresponding to the dissociation from the electronically excited state. A dissociation rate of $k=(6\pm1) \times 10^5$ s\(^{-1}\) was obtained by fitting the data to the equation: $A_1+A_2 \times \exp(-kt)+A_3 \times (1-\exp(-kt))$. The first term represents the fast rise component, the second term represents the decay of the disk-like image, and the third term represents the slow rise component.

**B. 248 nm**

Ion images obtained at this wavelength are similar to that at 193 nm. As shown in Fig. 7(a), a line shape image of $m/e=116$ was obtained at 248 nm, indicating the H atom elimination channel. Since the photon energy is much smaller at 248 nm, the length of the image at 248 nm is shorter than that at 193 nm. Although the experimental delay time between pump and probe laser pulses is as long as 248 ms, the length of the image at 248 nm is still very short due to the small available energy. It is difficult to totally separate the slow component from the interference from parent ion image even at such a long delay time. Therefore, we cannot determine the ratio between fast and slow components accurately. The probability of the slow component shown in Fig. 7(b) includes the interference from parent molecules. The slow component was estimated to be less than 25% of the fast component. The peak of the fast component is located at 15 kcal/mol, and the translational energy as much as 30 kcal/mol can be released. It reaches the maximum available energy of the reaction $C_8NH_7+\text{hv}(248\text{ nm}) \rightarrow C_8NH_6^+$. The distribution of the fast component indicates that it results from the electronically excited state.

**IV. DISCUSSION**

The aromatic amino acids and the nucleic acid bases are some of the most important molecules in biochemistry. One important photochemical characteristic of these molecules is the low quantum yields of fluorescence. These have been explained by the existence of very fast nonradiative processes which efficiently quench the excited state.\textsuperscript{16,17} The

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nonradiative processes presumably are ultrafast internal conversion (IC) back to the electronic ground state. Following the internal conversion, they quickly dissipate the photon energy to solvent molecules by various energy transfer processes before more profound chemical rearrangements can take place. This so-called photostability is obviously particularly essential to protect these molecules from UV radiation.

Phenol and indole are the chromophores of the aromatic amino acid tyrosine and tryptophan, respectively. Recently *ab initio* calculations and experimental results have suggested a different nonradiative process for these two molecules. Instead of internal conversion to the ground state, they quickly dissipate the photon energy to solvent molecules by various energy transfer processes before more profound chemical rearrangements can take place. This so-called photostability is obviously particularly essential to protect these molecules from UV radiation.

Although indole has been studied extensively, most of the studies focused on the spectroscopy and nonradiative decay rate, photodissociation of indole has received little attention. Our experimental measurement demonstrated that H atom elimination is the only dissociation channel of indole at 248 and 193 nm. The ratio between the fast and the slow components in the translational energy distribution changes from larger than 4.0 at 248 nm to 1.2 at 193 nm. The increase of the slow component with the increase of photon energy indicates that the internal conversion rate from the corresponding photoexcited state to the ground electronic state increases with the photon energy. The increase is likely due to the increase of the density of state at higher energy levels. Since there is no significant exit barrier of C₈NH₆⁺H in the ground electronic state, the fast component in the translational energy distribution must result from the dissociation in the excited electronic state. This excited state can be a state with a repulsive potential. It can also be the other excited state with a large exit barrier. For example, the dissociation in the excited electronic state. This excited state can be a state with a repulsive potential. It can also be the other excited state with a large exit barrier. For example, the dissociation in the excited electronic state. This excited state can be a state with a repulsive potential. It can also be the other excited state with a large exit barrier. For example, the dissociation in the excited electronic state. This excited state can be a state with a repulsive potential. It can also be the other excited state with a large exit barrier. For example, the dissociation in the excited electronic state. This excited state can be a state with a repulsive potential. It can also be the other excited state with a large exit barrier.
the triplet state might have an exit barrier.\textsuperscript{24,25} Although the πσ\textsuperscript{2} state with a repulsive potential suggested by the calculation is most likely the state that results in the fast component of translational energy, we cannot completely exclude possibility of the other excited states at this moment due to the lack of the information of the other states.

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