 Imaging HNCO Photodissociation at 201 nm: State-to-State Correlations between CO (X1Σ+) and NH (a1Δ)

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The NH(a1Δ)+CO(X1Σ+) product channel for the photodissociation of isocyanic acid (HNCO) on the first excited singlet state S1 has been investigated by means of time-sliced ion velocity map imaging technique at photolysis wavelengths around 201 nm. The CO product was detected through (2+1) resonance enhanced multiphoton ionization (REMPI). Images were obtained for CO products formed in the ground and vibrational excited state (v=0 and v=1). The energy distributions and product angular distributions were obtained from the CO velocity imaging. The correlated NH(a1Δ) rovibrational state distributions were determined. The vibrational branching ratio of 1NH (v=1/v=0) increases as the rotational state of CO(v=0) increases initially and decreases afterwards, which indicates a special state-to-state correlation between the 1NH and CO products. About half of the available energy was partitioned into the translational degree of freedom. The negative anisotropy parameter β indicates that it is a vertical direct dissociation process.

Key words: HNCO, Ion velocity map imaging, Energy distributions

I. INTRODUCTION

As a simple four atom molecule, isocyanic acid (HNCO) has received considerable attention due to its significance for life and major constituents of chemical species in biology and chemistry. HNCO and its aqueous anion isocyanate have been shown to be toxic and linked to human health such as rheumatoid arthritis, cataracts and atherosclerosis through carbamylation reactions [1]. Isocyanic acid is a product of various forms of combustion such as cigarette smoking, automobile exhaust, biomass burning, and cooking [1, 2]. Dixon et al. and Rabalais et al. have measured the ultraviolet absorption spectrum (180–280 nm) of HNCO [3–5], which has been assigned to an S1(1A′)→S0(1A′) transition. The spectrum is diffuse at wavelengths shorter than 265 nm and is unstructured below 244 nm. Photodissociation dynamics of HNCO has been the subject of wide investigations, both theoretically and experimentally, in the past few decades [6–33]. The photodissociation dynamics of HNCO is quite complex. There are three low-lying electronic states relevant to the dissociation process. The main photodissociation channels are summarized below:

\[ \text{HNCO} + h\nu \rightarrow \text{NH}(X^3Σ^-) + \text{CO}(X^1Σ^+) \]
\[ D_0 = (30060 \pm 30) \text{ cm}^{-1} \]  

\[ \text{HNCO} + h\nu \rightarrow \text{H}(2Σ) + \text{NCO}(X^2Π) \]
\[ D_0 = (38370 \pm 30) \text{ cm}^{-1} \]  

\[ \text{HNCO} + h\nu \rightarrow \text{NH}(a^1Δ) + \text{CO}(X^1Σ^+) \]
\[ D_0 = (42750 \pm 30) \text{ cm}^{-1} \]

For convenience, NH(a1Δ) and NH(X3Σ−) are denoted by 1NH and 3NH in the following sections.

The spin-forbidden channel (1) has been studied by Reisler and co-workers [18, 24]. The channel is observed at a wide range of excitation wavelengths (280–217 nm). By ion imaging technique, Reisler et al. probed CO product around 230 nm. Their results showed that the CO originating from channel (1) has isotropic angular distribution. The isotropic angular distributions of CO imply that the lifetime of the intermediate state exceeds 5 ps from S1 to T1. They proposed that the most likely dissociation pathway to channel (1) is S1→S0→T1. The quantum yield is relatively small at a wide range of excitation wavelengths, but the channel is still the main dissociation channel in the range just above the opening of channel (2).

Dissociation to spin-allowed channel (2) has attracted much attention. Spiglanin and co-workers [7] probed NCO product by laser-induced fluorescence (LIF) technique. Zhang et al. [14] researched this channel at 193 nm photolysis energy via the high-n Rydberg H
atom time-of-flight (TOF) spectroscopy. Their results showed that the translation energy release peaked near the maximum available energy and accounted for about 70% of the total energy. The NCO product was extensive bending excited and an anisotropic angular distribution of $\beta=0.85$ was observed. It suggested that the products of channel (2) accrued via direct dissociation on a repulsive potential energy surface. Crim et al. [11–13, 31, 32] studied this channel by LIF technique. Their study demonstrated that approximately 65% of the total available energy appeared in relative translation of the photoproducts near the channel (2) threshold, while about 30% went into vibration (dominated by the bending excitation of NCO) and 5% into rotation of NCO photoproducts. Furthermore, Crim’s group performed a series of experiments to investigate mode-selective dissociation dynamics to channel (2). Reisler and co-workers [15, 17, 24] studied this channel at excitation wavelengths in the range of 217–260 nm. They deduced that channel (2) dissociation proceeded not directly on $S_1$ but rather via IC (internal conversion) to $S_0$, followed by decomposition on $S_0$ without a barrier near its threshold. The barrier on $S_1$ state to channel (2) direct dissociation was found to be at least 8140 cm$^{-1}$. Using the hydrogen atom Rydberg tagging TOF technique, Yu and co-workers [28] reinvestigated this channel at excitation wavelengths in the region of 200–240 nm. They observed two competitive dissociation pathways. One was the indirect dissociation on the $S_0$ surface, following IC from $S_1$ to $S_0$, which is consistent with Reisler’s results. The other was the direct dissociation on the $S_1$ surface. As the photon energy increased, the direct dissociation pathway became much more important.

Photodissociation to spin-allowed channel (3) has been researched in the recent years. Fujimoto and co-workers [6] probed CO product with an average vibrational energy about 4.6 kcal/mol at 193 nm. Spiglanin and co-workers [7–10] examined the internal state distributions of $^1$NH and CO following photodissociation of HNCO at several wavelengths between 193 nm and 230 nm. Their results showed that the rotational state distribution of the CO was hot, but the $^1$NH rotational state distribution was cold. Reisler et al. [15, 17, 18, 23–25] performed a series of experiments to investigate channel (3) at excitation wavelengths in the range of 217–230 nm. Their results indicated that channel (3) dissociation proceeded via predissociation on $S_0$ surface following IC from $S_1$ to $S_0$, but after exceeding a small barrier of (470±60) cm$^{-1}$, direct dissociation on $S_1$ surface commenced and quickly dominated. Recently, we studied channel (3) by sliced velocity map imaging technique. The $^1$NH photoproduct was state-selectively probed via resonance enhanced multiphoton ionization (REMPI). We found that the rotational state distribution of CO($v$) was bimodal. By full-dimensional theoretical calculation, Bonnet and co-workers reproduced the bimodality of CO [33].

In this work, we further investigate channel (3) of HNCO photodissociation dynamics at 201 nm by the sliced velocity map ion imaging method probing the CO photoproduct. From the image of CO photoproduct, the $^1$NH internal state populations, photoproduct total kinetic energy distributions, and the angular distributions are obtained.

II. EXPERIMENTS

The sliced velocity map ion imaging arrangement has been described in detail elsewhere [34, 35], so a brief description of the experimental process will be given here. The repetition rate of the whole experiment is 10 Hz. A 2% mixture of HNCO and He with a stagnation pressure of 1 bar is expanded into vacuum through a pulsed valve (General valve series 9) with a 0.5 mm diameter nozzle orifice. About 22 mm downstream from the nozzle, the pulsed free jet expansion is collimated by a 1 mm diameter aperture skimmer and reaches the main chamber, where the HNCO/He beam is crossed at right angles by the focused photolysis and probe lasers pulses.

The focused photolysis laser (0.5 mJ per pulse) is produced by the tripled output of a tunable dye laser, which is pumped by the second harmonic of a Nd:YAG laser. The CO photofragment is detected about 20 ns later by a focused probe laser beam (0.3 mJ per pulse) generated by doubling the output of a tunable dye laser, which is pumped by the third harmonic of a second Nd:YAG laser. The CO products are interrogated via the $B^1\Sigma^+\leftarrow X^1\Sigma^+ (2+1)$ REMPI process around 230 nm. The linearly polarized direction of the photolysis light is parallel to the detector plane, while that of the probe light is set to be perpendicular to the detector plane.

The resulting CO ions are accelerated by the focusing electric fields of ion optics and pass through a 500 mm long time-of-flight tube before hitting a dual 40 mm diameter Chevron-type microchannel plates (MCP) coupled to a phosphor screen (P-47). A fast high-voltage switch is used to gate the central slice of the ion products at a specific mass. The typical pulse width is about 50 ns. The resulting electron avalanche strikes a P-47 phosphor screen, thereby creating the ion image, which is captured by a charge-coupled device (CCD) camera (ImagerPro2 M 640×480 pixels, LaVision) and transferred to a computer on an every shot basis for event counting [36] and data analysis. The final images are accumulated over $2 \times 10^4$ laser shots or more, depending on the signal-to-noise ratio. The timing of the pulsed valve, the photolysis and probe lasers, and the gate pulse applied to the MCP detector are controlled by using two multichannel digital delay generators (DG645, SRS).

III. RESULTS AND DISCUSSION

The CO product ion images of HNCO photodissociation were measured at 201 nm. The images were
FIG. 1 Raw sliced images of CO($v=0$) products after photodissociation of HNCO at 201 nm. The double arrow indicates the polarization direction of the photodissociation light.

obtained by accumulating the CO$^+$ signals with probe laser tuned to the Q branch of $B^1\Sigma^+\leftarrow X^1\Sigma^+$ transition of the CO product around 230 nm. All measured signals appearing in the images are pump-probe dependent. The background was taken with the photolysis light and molecular beam on. FIG. 1 displays typical CO($v=0$) sliced images after photodissociation of HNCO at 201 nm. The vertical red arrow indicates the polarization direction of the photolysis light. The polarization direction of the probe light is perpendicular to the image plane and the polarization direction of the photolysis light. No significant effects are observed in the ion images when the polarization direction of the probe light is changed. As seen in FIG. 1, two anisotropic rings are clearly displayed in the CO($v=0$) sliced images. The outer ring corresponds to vibrational ground state $^1\text{NH}(v=0)$ partner product, while the inner ring corresponds to the vibrationally excited $^1\text{NH}(v=1)$ partner product.

From the raw sliced images, the CO speed distributions were extracted and converted to the total translational energy distributions of $^1\text{NH}+\text{CO}$. The energy information of the whole system is shown as the following:

$$E_{hv} - D_0 = E_T + E_{\text{int}}(^1\text{NH}) + E_{\text{int}}(\text{CO})$$  \hspace{1cm} (4)

where $E_{hv}$ denotes the energy of photolysis light, $D_0$ represents the dissociation threshold energy of channel (3), $E_T$ is the photoproduct total kinetic energy, $E_{\text{int}}(^1\text{NH})$ and $E_{\text{int}}(\text{CO})$ are the internal energy of $^1\text{NH}$ and CO products.

The corresponding center-of-mass total kinetic energy distributions for the individual rovibrational states of CO($v=0$) are shown in FIG. 2. It is obvious that FIG. 2 reflects the rovibrational state distributions of the correlated $^1\text{NH}$ product. Two vibrational peaks ($v=0$ and 1) of $^1\text{NH}$ are clearly resolved. It is interesting that the proportion of vibrationally excited $^1\text{NH}(v=1)$ does not decrease monotonously with the increase of CO rotational energy. We have done a more in-depth analysis for this.

To extract the vibrational branching ratio ($v=1/v=0$) of $^1\text{NH}$ products, a qualitative fitting of the total kinetic energy distributions was carried out. FIG. 3 displays the correlation between vibrational branching ratio ($v=1/v=0$) of $^1\text{NH}$ products and rotational states of CO($v=0$). As can be seen in the graph, the vibrational branching ratio ($v=1/v=0$) of $^1\text{NH}$ products increases first and then decreases as the rotational excitation of CO($v=0$) increases. At $j=23$ of CO($v=0$), it reaches the maximum value. The vibrational excitation of the $^1\text{NH}$ products is not simply anti-correlated to the rotational excitation of CO($v=0$), which indicates a special state-to-state correlation between the $^1\text{NH}$ and CO products.

FIG. 4 shows vibrationally excited CO($v=1$) sliced images of HNCO photodissociation at 201 nm. From the images, the ring sizes of vibrationally excited
FIG. 3 Vibrational branching ratio ($v=1/v=0$) of $^1\text{NH}$ products for different rotational states of CO($v=0$).

FIG. 4 Raw sliced images of CO($v=1$,$j$) products after photodissociation of HNCO at 201 nm. The double arrow indicates the polarization direction of the photodissociation light.

CO($v=1|j$) become smaller compared with that of CO($v=0|j$). For $j=21$ of CO($v=1$), the intensity of the inner ring is very weak. FIG. 5 displays the corresponding total kinetic energy distributions for the individual rovibrational states of CO($v=1|j$). It can be seen that the correlated $^1\text{NH}$ products are mainly distributed in the vibrational ground state. The rotational excitation of $^1\text{NH}$ decreases as the CO rotational excitation increases. This result shows that the rotational excitation of the $^1\text{NH}$ products is anti-correlated to the rotational excitation of CO.

Our previous studies [29, 30] found that the rotational state distributions of CO are bimodal, which is further confirmed by Bonnet and co-workers [33] via theoretical calculation. In this study, however, we did not find the bimodal rotational distribution of $^1\text{NH}$ from the image of CO product. It may be that the rotational energy of $^1\text{NH}$ is relatively low and it is not easy to observe the bimodal phenomenon. As seen in FIG. 2 and FIG. 5, the $^1\text{NH}$ products are mainly distributed in the low rotational states ($j\approx2$–12), which is in consistence with the results of Spiglanin et al. [9] and Reisler et al. [15].

Based on total kinetic energy distributions, excitation energy and bond dissociation energy, we obtained the ratio of the average total kinetic energy to the available energy, $[E_T/E_{av}]$, as shown in FIG. 6 (a) and (b). For the CO($v=0|j$) product, about 50% of the available energy is partitioned into the translational degree of freedom. For the CO($v=1|j$) product, about 40% of the available energy is partitioned into the translational degree of freedom.

The angular distributions were obtained by integrating the imaging signals over the relevant radius region. FIG. 6 (c) and (d) display the corresponding anisotropy parameters. As seen in FIG. 6(c), the anisotropy parameters are near $-0.8$ and $-0.6$ for $^1\text{NH}(v=0$ and $v=1)+\text{CO}(v=0)$. The $^1\text{NH}+\text{CO}(v=1)$ products display a similar anisotropic angular distribution as shown.
FIG. 6 Ratio of the average total kinetic energy to the available energy for (a) the CO($v=0,j$) product and (b) the CO($v=1,j$) product. Anisotropy parameter for individual $^1$NH vibrational state correlated to (c) CO($v=0,j$) and (d) CO($v=1,j$).

in FIG. 6(d). However, the $^1$NH($v=1$)+CO($v=1$) anisotropy parameters are as low as $-0.4$, the low anisotropy should be due to the weak signal-to-noise ratio. The negative anisotropic angular distribution usually indicates that the dissociation process is fast.

Previous studies have shown that there are two different dissociation pathways leading to $^1$NH+CO channel [24]. Near the threshold of channel (3), excited HNCO dissociates on $S_0$ surface by IC from $S_1$ to $S_0$. At higher excitation energy, the barrier on $S_1$ surface to channel (3) will be exceeded and direct dissociation on $S_1$ prevails. It is obvious that the barrier on $S_1$ surface to channel (3) is exceeded at 201 nm. Under this condition, $S_1$ surface has a strong repulsive gradient along the C–N bond. So the photodissociation of HNCO should be a fast direct dissociation process at 201 nm. The negative anisotropic angular distribution further confirms this conclusion.

IV. CONCLUSION

The photodissociation dynamics of isocynic acid for $^1$NH+CO channel has been investigated by means of time-sliced velocity map imaging technique at photolysis wavelengths around 201 nm. The CO product has been detected by (2+1) REMPI. From analysis of the product total kinetic energy distributions, the correlated $^1$NH rovibrational state distributions for CO($v=0$ and $v=1$) products are obtained. The vibrational branching ratio of $^1$NH ($v=1/v=0$) increases first and then goes down as the rotational state of CO($v=0$) increases, which indicates a special state-to-state correlation between the binary $^1$NH and CO products. Because of the low rotational energy of $^1$NH, we do not observe the bimodal rotational distribution of $^1$NH from the image of CO product. The negative anisotropy parameter $\beta$ indicates that it is a vertical direct dissociation process at 201 nm. These results shown here provide a sensitive testing basis for the study of HNCO photodissociation dynamics.

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