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ROTATIONAL DISTRIBUTION OF CN FRAGMENT PRODUCED BY THE 266 nm PHOTOLYSIS OF ICN IN A SUPERSONIC FREE JET

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Rotational distributions of CN($X^2\Sigma^+$, $\upsilon''=0$) generated by the 266.0 nm photolysis of ICN in a supersonic free jet have been determined by the measurements of the fluorescence excitation spectrum. The distributions are expressed as the sum of three Boltzmann distributions characterized by temperatures of 12, 230, and 2000 K.

Many experimental[1-8)] and theoretical[9-12)] investigations have been made in the elucidation of the dynamics of photodissociation of ICN. Resently, Baronavski[5)] has reported in detail the rotational distribution of the CN fragment generated by photolysis of ICN at 266 nm at room temperature. In the photodissociation process, the momentum, the angular momentum and the total energy must be conserved. Therefore, the internal states of the fragments produced by the photodissociation are greatly influenced by the initial state of the parent molecule. But, at room temperature, many levels are thermally populated in the parent molecule, and the initial state of the parent molecule is not well-defined. On the other hand, in a supersonic free jet, the parent molecule is cooled in a gas phase and the number of initially populated states is greatly limited. Therefore, more clear-cut information will be expected about the energy partitioning in the photodissociation. Very recently, Nadler et al.[8)] reported the photodissociation of ICN in a supersonic jet and discussed very qualitatively the energy partitioning. We also have completed a similar study in a supersonic free jet before we became aware of the work by Nadler et al. The experimental results obtained are essentially the same as those by Nadler et al. However, a quantitative analysis of the results allowed us to obtain more insight into the influence of the initial state distribution of ICN on the final rotational distribution of the CN fragment. Here, we report briefly the results from the analysis.

A Nd:YAG laser (Quanta Ray, DCR-1) was used both to provide the photolysis pulse and to pump a dye laser (Molectron, DL-14). The dye laser (Rhodamine B and Cresyl Violet in methanol) was pumped by the second harmonic of the YAG laser. To produce the photolysis pulse (266 nm), a part of the second harmonic was frequency-doubled by a KD*P crystal. The two laser beams were introduced coaxially, without any delay, into a gas cell or into a vacuum chamber to cross a supersonic free jet 10 mm downstream. In the gas cell experiment, ICN vapor was flowed slowly through the cell at a pressure of 8 Pa in order to refresh the sample. In the supersonic free jet experiment, solid ICN was heated up to 310 K in a nozzle chamber so as to obtain a sufficiently high vapor pressure, and the vapor was seeded in a carrier gas (He, 1.5 atm). The gaseous mixture was expanded into the vacuum chamber through an orifice with a 0.4-mm diameter. The rotational distribution of the $CN(X^2\Sigma^+)$ produced by the photodissociation was determined from the fluorescence excitation spectrum due to the $A^2\Pi_i \leftarrow X^2\Sigma^+$ (Red) transition of CN. The fluorescence was monitored perpendicularly to both the laser beams and the supersonic free jet through a filter (Corning 2-64) by a photomultiplier (HTV, R-562). The signal was averaged by a boxcar integrator (Brookdeal 9415/9425). ICN from Eastman Kodak was purified by vacuum sublimation.

Figure 1a shows the fluorescence excitation spectrum of CN obtained by the photolysis of ICN vapor at room temperature. The levels up to rotational quantum number N" = 43 were observed. The fluorescence intensities were normalized against a laser power of the probe laser to obtain the intensity of each line, $I_{N''}$. A quantity of $\ln[I_{N''}/S_{N''}\nu_{N''}]$ is plotted versus a rotational energy E_r in Fig. 2a, where $S_{N''}$ is the Hönl-London factor and $\nu_{N''}$ is the transition frequency. As Baronavski reported, the data can be analyzed as the sum of three components assuming a function

$$I_{N''}/S_{N''}\nu_{N''} = \alpha_1 e^{-E_r/RT_1} + \alpha_2 e^{-E_r/RT_2} + \alpha_3 e^{-E_r/RT_3}$$

In Fig. 2a, the best fitted curve is shown by a dotted line and the obtained parameters are given in Table 1a.

Figure 1b shows the fluorescence excitation spectrum of CN obtained by the photolysis of ICN in a supersonic free jet. In this case, we were able to observe the levels up to N" = 38. From Fig. 2b, it is apparent that higher rotational levels are less populated. However, similar to the result obtained at room temperature, the distribution can also be analyzed as the sum of the three components. The best-fitted parameters of the function are also given in Table 1b. The rotational temperature T_i of each component is lower than that of the corresponding component in the photolysis at room temperature. This can be understood as a result of cooling of the rotation and the bending vibration of ICN in a supersonic free jet. But the population ratios of individual T_i components are almost in agreement with those obtained at room tem-

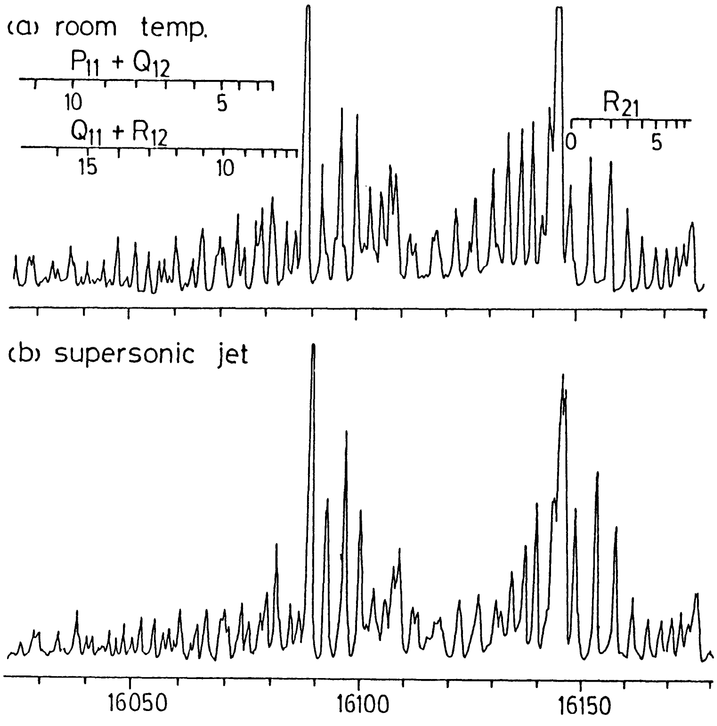

Fig. 1. The fluorescence excitation spectra of CN for the 266.0 nm photolysis of ICN. The spectra are not normalized by probe-laser power.

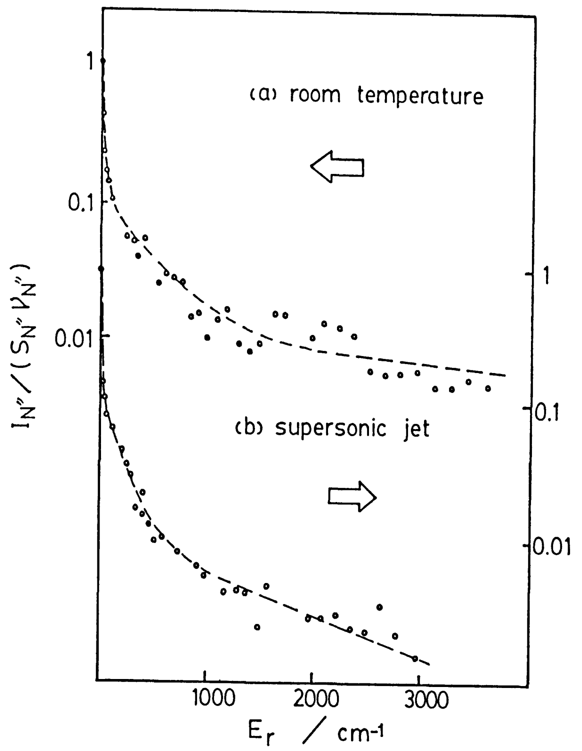

Fig. 2. A plot of $\ln[I_{N''}/S_{N''}\nu_{N''}]$ versus rotational energy. The best-fitted curve is shown by a dotted line in each case. See the text.

perature.

The above results suggest that CN is produced via three channels in the photodissociation of ICN at 266 nm. As indicated in Table 1b, component 3 exhibits extremely high rotational temperature, 2000 K, even though the parent molecule is cooled in a supersonic free jet. This high rotational excitation indicates that component 3 is produced from the excited ICN molecule having a bent equilibrium structure. It is also concluded from the conservation of the energy that component 3 corresponds to a channel leading to formation of a ground state I atom($^2P_{3/2}$).5) On the other hand, the lower temperature components 1 and 2 are considered to correspond to formation of an excited state, I atom($^2P_{1/2}$) based on a good agreement of the sum of the population ratios of component 1 and 2 with the reported yield of I($^2P_{1/2}$) (60 %).4,5)

The fairly high temperature of component 2 suggests that it is produced also from ICN in a bent equilibrium configuration. However, in the channel corresponding to component 2, the formation of the I($^2P_{1/2}$) requires additional 7600 cm^{-1} for the excitation. This is probably the reason for the much lower temperature for component 2 than component 3. Component 1 exhibits very low temperature. Therefore, it is possibly produced from the excited ICN having a linear equilibrium structure.

Ling and Wilson reported from their molecular beam study that I($^2P_{1/2}$) and I($^2P_{3/2}$) are formed through the molecule excited by a parallel transition from the ground state molecule. Morse et al.9) pointed out that the findings of Ling and Wilson are explained only if the excited state molecule has a bent equilibrium

Table 1. Rotational distribution of CN($X^2\Sigma^+$, υ"=0) for the photolysis of ICN at 266.0 nm

(a) room temperature measurements

Component	α_i	T_iK	population ratio (%)
1	0.90	35	21.8-26.9
2	0.085	540	30.9-38.0
3	0.010	7800	35.1-47.3

(b) supersonic-jet measurements

Component	α_i	T_iK	population ratio (%)
1	0.88	12	18.6-19.5
2	0.11	230	42.5-44.6
3	0.012	2000	35.9-38.9

structure. In a linear configuration, a parallel transition leads only to $I(^2P_{1/2})$ as a product, while in a bent configuration it leads both $I(^2P_{1/2})$ and $I(^2P_{3/2})$. The bent structure suggested for component 3 is also supported from this argument.

We have determined nascent rotational energy distribution of the CN fragment for the dissociation of ultra-cold ICN at 266 nm. The results suggested that both the linear and bent structure molecules in the excited states are involved in the dissociation process. However, there remains a possibility that the final-state interaction,[6,12] which we neglected here, may cause an important effect on the dissociation process. In order to elucidate the dynamics of the dissociation process, further theoretical studies including the final-state interaction are indispensable. Experimentally, by changing the frequency of the light for the photolysis and measuring the ratios of the three components, it is possible to study the nature of the three channels and also the final-state interaction. A measurement of the translational energy of the CN fragment for each rotational level would also give useful information about the dissociation process.

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