The Journal of Physical Chemistry A

VOLUME 102, NUMBER 41, OCTOBER 8, 1998

LETTERS

Selective Excitation of ICN Achieved via Brute Force Orientation

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Received: June 11, 1998; In Final Form: August 26, 1998

Brute force orientation of ICN was achieved using a strong uniform electric field and supersonic expansion. When the dissociation laser at 249 nm was polarized parallel to the orientation field, the $^3\Pi_{0+}$ surface was preferentially accessed. The yield of CN in low rotational states was enhanced by ~50% compared with that from dissociation under perpendicular polarization. Highly rotationally excited fragments were not affected by the polarization direction of the dissociation laser, providing evidence of the contribution of a perpendicular surface in the absorption process. This work demonstrates the selectivity achieved via brute force orientation and the advantages thus offered for studies of photodissociative processes.

1. Introduction

Brute force orientation makes use of supersonic expansion and electrostatic interaction between the permanent dipole moment of a polar molecule and a strong uniform electric field.[1−3] When this interaction overcomes the free rotation of the molecule, preferred orientation of the permanent dipole moment can be obtained. The feasibility and applications of this technique have been investigated over the past decade.[4−12] In particular, one of the most impending questions in brute force orientation—distribution of molecular axes—has been addressed both experimentally and theoretically.[13−15] Excellent agreement between theory and experiment has been reported. In this paper, we present results using brute force orientation to achieve selective excitation for photodissociation studies of ICN. Dynamical information obtained from photodissociation of oriented molecular species has been investigated using the hexapole field technique.[14,16,17] This work aims to demonstrate that orientation of parent molecules can reveal signatures of not only the upper state surfaces through selectivity in photoexcitation but also dynamics of the dissociation process on each surface.

The photodissociation dynamics of ICN has been investigated extensively.[18−31] To date, theoretical calculations[25−31] and experimental results[18−24] have achieved satisfactory agreement. Five potential surfaces resulting from the $(2\pi)^3(5\sigma)^1$ configuration are thought to be involved. Among these, the $^3\Pi_{0+}$ surface is the major component, while the $^1\Pi_1$ and $^3\Pi_1$ surfaces contribute to the minor perpendicular nature in the blue and red wings of the absorption band. The resulting CN fragments primarily populate the $v = 0$ level with multiple rotational temperatures. The parallel $^3\Pi_{0+}$ surface adiabatically correlates to the I $^2P_{1/2}$ product (denoted I* in the literature). It has a slight preference for bending along the dissociation coordinate at intermediate I−CN distances, resulting in a major component of rotationally cold products accompanied by a minor component of rotationally excited CN fragments. The perpendicular surfaces adiabatically correlate to I $^2P_{3/2}$ (denoted I in the literature). They have strong preferences for the bending geometry, yielding a rotational temperature as high as 2000 K when excited at 249 nm. Nonadiabatic coupling is believed to occur during dissociation, particularly in the bending geometry, but this effect is believed to be minor for trajectories leading to low rotational states of CN.

This experiment makes use of the adiabaticity in the production of low J states of CN to quantify the effectiveness of selective excitation achieved via brute force orientation. Without nonadiabatic coupling, the CN products with low rotational quantum numbers are solely results of dissociation on the

S1089-5639(98)02584-5 CCC: $15.00

parallel $^3\Pi_{0+}$ surface. According to J. F. Black,[32] at a dissociation wavelength of 249 nm, contributions of the perpendicular surfaces were negligible for CN with $J = 0$, while they amount to 50% at $J \sim 30$. If the parallel surface can be selectively excited through brute force orientation and polarized excitation, the yield of CN in low J states should be increased. This enhancement effect is expected to diminish as the rotational angular momentum quantum number reaches ∼30.

2. Experimental Section

The experimental apparatus is a standard differentially pumped supersonic molecular beam machine.[33] The orientation electrodes were two 6 × 3.5 cm rectangular plates made of stainless steel. The separation between the plates was 0.6 cm, and the resulting field strength was 50 kV/cm. Cyanogen iodide (Aldrich, purity: 93%) was used without further purification. The room-temperature vapor was carried into the reaction chamber using helium with a stagnation pressure of 1340 Torr. The rotational temperature of the skimmed molecular beam was 1.5−2 K measured from a rotationally resolved resonantly enhanced multiphoton ionization spectrum of pyridazine ($C_4H_4N_2$, 1,2-diazine).[33]

The dissociation and probe light sources were two Nd:YAG (Spectra Physics, GCR 230 and GCR 190) pumped dye laser (LAS, LDL 2051 and LDL 20505) systems. The line width of the probe laser was 0.1 cm^{-1}, insufficient to resolve the Doppler line shape of CN, while the line width of the dissociation laser was 0.2 cm^{-1}. To avoid partial saturation due to nonuniformity in the laser beams, pinhole systems were used to clean up the beam profile,[34] and the resulting beam diameters were 2 mm each. The power of the probe laser was 1 μJ, and the dissociation laser was 700 μJ. The delay between the two counterpropagating laser systems was set at 150 ns. The probe laser was tuned to the (1, 0) band of the B $^2\Sigma^+ - X\ ^2\Sigma^+$ transition of CN.[35] Fluorescence of the (0, 0) band was detected by a PMT (Thorn EMI 9125B) through two collection lenses and a stack of filters (a band-pass filter and two GG375 filters). The polarization direction of the dissociation laser was rotated by a double Fresnel-Rhomb (FR). Shift in the beam position was noticeable due to this rotation, so the dissociation beam was realigned after each rotation by overlapping with the fixed probe beam.

3. Results and Discussion

The P branch of the B $^2\Sigma$ (1) $\leftarrow$ X $^2\Sigma$ (0) transition of CN formed a band head, so only the well-resolved R branch was used in this measurement. Spin-rotation interaction causes splitting of the high J levels, while in an orientation field of 50 kV/cm, Stark effects result in a slight broadening (less than 0.1 cm^{-1} for $J = 1$) in the low J levels. The intensity of each transition was therefore determined by the integrated peak area. Figure 1 shows the ratios of the LIF signal of CN when the dissociation laser was polarized parallel or perpendicular to the orientation field. The data were obtained when the probe laser was polarized perpendicular to the orientation field, although within the present signal-to-noise level the values were independent of the polarization direction of the probe laser.

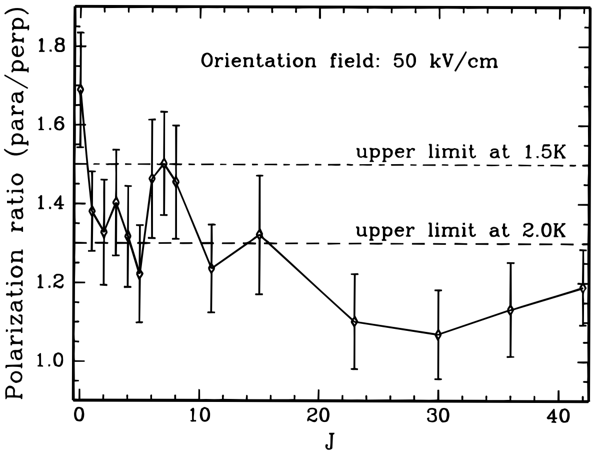

Figure 1. Polarization ratios of the CN product from photodissociation of ICN at 249 nm in an orientation field of 50 kV/cm. The dashed lines are estimated upper limits at rotational temperatures of 1.5 and 2.0 K (see text for details). The experimental values are obtained by taking ratios of the integrated LIF signal under two different polarization directions of the dissociation laser (parallel vs perpendicular to the orientation field). The probe laser was kept perpendicular to the orientation field.

The production of CN in the low J states is believed to originate from the parallel $^3\Pi_{0+}$ surface. The larger than unity ratios of Figure 1 demonstrate the efficiency of selective excitation. For the $J = 0$ fragment, more than 70% of CN fragments were produced when the dissociation laser was polarized parallel than when it was perpendicular to the orientation field. The ratio approaches unity as J approaches 30, but a slight increase in the polarization ratio is also observable as J further increases. These results are in agreement with those by J. F. Black.[32] The slight oscillation in the polarization ratio of Figure 1 is still under investigation. Interestingly, the rotational distribution of CN from perpendicular dissociation resembles that obtained under field-free conditions, i.e., from dissociation of a randomly oriented system. This observation is not difficult to understand given that the distribution from a randomly distributed system (I_r) should be the sum of the parallel excitation ($I_{\|}$, along the z direction) and twice the perpendicular excitation ($I_{\perp}$, the x and y directions):

$$I_r = I_{\|} + 2I_{\perp} \tag{1}$$

Quantitative interpretation of the experimental results relies on knowledge of the axis distribution. Using the approach by Loesch and Remscheid,[3] we reported excellent agreement between theory and experiment in a previous effort.[33] Figure 2 shows the calculated distribution function of molecular axes $P(\Theta)$ for ICN assuming a rotational temperature of 1.5 K, a permanent dipole moment of 3.8 D,[36] and a rotational constant of 0.1 cm^{-1}.[37] The function was normalized by setting the total population to unity:

$$\int_0^{\pi} P(\Theta) \cos\Theta \, d\Theta = 1 \tag{2}$$

At 50 kV/cm, 84% of the molecules have their iodine end preferentially pointing to the negative electrode, and 40% of the molecules are trapped within a cone of 45°. An upper limit of the polarization ratio can be calculated assuming a pure parallel transition; i.e., only the $^3\Pi_{0+}$ surface is directly accessed. The signal intensity should be proportional to $P(\Theta)\ (\cos\Theta)^2$ (or $^1/_2P(\Theta)\ (\sin\Theta)^2$) when the dissociation laser is polarized parallel (or perpendicular) to the orientation field. The polarization ratio should be

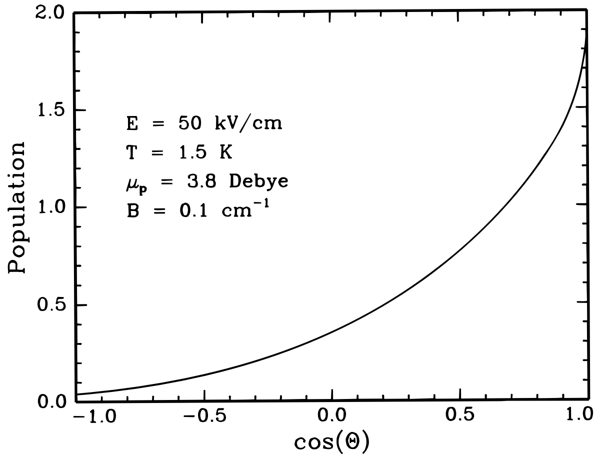

Figure 2. Distributions of the molecular axis of ICN under an orientation field of 50 kV/cm. The angle Θ was defined by the orientation field and the molecular axis of ICN. The population was normalized by setting the integration of the distribution function to unity.

$$R = \frac{\int_0^{\pi} P(\Theta)\,(\cos\Theta)^3\,\mathrm{d}\Theta}{\frac{1}{2}\int_0^{\pi} P(\Theta)\,(\sin\Theta)^2\cos\Theta\,\mathrm{d}\Theta} \qquad (3)$$

The estimated upper limit is 1.5 at 1.5 K and 1.3 at 2 K. These ratios are slightly smaller than that observed for the $J = 0$ fragment but in good agreement with the $J \geq 1$ states.

The fact that the ratio for the $J = 0$ fragment (1.69 ± 0.15) is higher than the estimated upper limit requires closer examination. Future theoretical modeling of the dissociation dynamics and the effect of the orientation field on the parent molecules will be carried out. However, a qualitative interpretation can be achieved based on angular momentum constraints of the dissociation process. If the $J = 0$ fragment originated mainly from the parallel surface, it should come from low rotational states. Molecules in these states are most effectively oriented in the electric field. The estimation of eq 3 is an average effect for a system at 1.5 K, while orientation of only a few of the low J levels of ICN should be more effective. For fragments with $J \geq 1$, on the other hand, the angular momentum of the fragment could originate from either the parent rotation or the slight bending motion during dissociation. Less strict angular momentum constraints should result in a smaller enhancement effect due to less effective orientation.

An important issue in this type of experiment is the effect of the orientation field on the photofragments. In an electric field of 50 kV/cm, the $J = 0$ level of CN is also oriented by the field. However, since the polarization direction of the probe laser was fixed relative to the orientation field, the detection efficiency of the $J = 0$ level should not be affected by the polarization direction of the dissociation laser. Stark effects on the energy levels of the $J \geq 1$ states are negligible given the line width (0.1 cm^{-1}) of the probe laser. At 249 nm, the CN fragments are known to demonstrate alignment under field-free conditions.[38,39] The LIF signal was reported to be stronger by ~20% when the polarization directions of the dissociation and the probe lasers were the same. Alignment of CN should have a detrimental effect on the polarization ratios in the present experimental setup. The strong enhancement in the CN product under cross-polarization conditions between the dissociation and probe lasers demonstrates the overwhelming effect of preferred excitation to the parallel $^3\Pi_{0+}$ surface.

Compared with the kinetic or potential energy of the electronic Hamiltonian of the molecular system, the orientation field at 50 kV/cm is still a perturbation. The brute force orientation technique therefore does not affect the electronic wave function or the dissociation dynamics. The nonadiabaticity during dissociation should be unperturbed, and the projection of the electronic angular momentum along the molecular axis is still a good quantum number. However, for loosely bound systems, such as van der Waals clusters, the electrostatic interaction between the permanent dipole moment and the orientation field could be nonnegligible compared with the vibrational energy of the van der Waals bond. As demonstrated by R. E. Miller's group in the case of $(HF)_2$,[40] interesting new dynamics could be induced.

This work demonstrated the possibility of selective excitation through brute force orientation and polarized excitation. For ICN with a permanent dipole moment of 3.8 D and a rotational temperature of 1.5 K, enhancement of ~ 50% in the CN fragments of low rotational energies was observed when the excitation laser was polarized parallel to the orientation field. Preferential excitation to one set of potential surfaces is particularly advantageous for simplification of complex dissociation processes from large molecular systems. Moreover, brute force orientation and alignment offers a new approach for the determination of the transition dipole moment direction relative to the permanent dipole moment. The near unity polarization ratio of the rotationally excited CN fragments offers direct evidence of the participation of a perpendicular potential surface. This approach is independent of the lifetime of the upper state. It is therefore advantageous for studies of slow predissociative systems.

Acknowledgment. This work was supported by the National Science Foundation, Division of Chemistry, through the Faculty Early Career Development Program. The authors are grateful to valuable discussions with G. E. Hall and P. L. Houston on the photodissociation dynamics of ICN.

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