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Vibrationally mediated photodissociation of HCN

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Abstract

The dissociation mechanism of HCN by vibrationally mediated photodissociation has been examined. Exciting the C–H stretch with four quanta and photodissociating the molecule with 220 nm light generates CN in the first excited electronic $A^2\Pi$ state rather than the ground $X^2\Sigma^+$ state. The CN fragment is detected by probing the $B^2\Sigma^+ \leftarrow A^2\Pi(1-0)$ band and monitoring the laser-induced fluorescence (LIF) via the $B^2\Sigma^+ \rightarrow X^2\Sigma^+(1-1)$ transition. The CN product distributions are found to be rotationally cold indicating that HCN dissociates from a linear geometry. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Photodissociation is one of the most elementary chemical reactions. The distribution of the products among the possible quantum states gives vital information about the energetics and mechanism of the reaction. Vibrationally mediated photodissociation (VMP) provides a mechanism that allows excitation to regions of the upper potential surface that are Franck–Condon forbidden in traditional experiments. This, in turn, can reveal new aspects of the photodissociation, as well as allow one to produce products not previously accessible. In this Letter, we report our results on the VMP spectra of hydrogen cyanide (HCN).

HCN has long been an important test system for the study of molecular dynamics. It is known to dissociate to give $H + CN(X^2\Sigma^+)$ following electronic excitation in the deep ultraviolet [1]. The bond

dissociation energy for this process is 5.41 eV [2], which is less than the origin of the first excited singlet A^1A' state, 6.48 eV [3]. The second dissociation channel, to produce $H + CN(A^2\Pi)$, becomes energetically open at 6.55 eV [4,5]. At 8.60 eV [6], the third dissociation channel, to produce $H + CN(B^2\Sigma^+)$ opens up.

The earliest conjecture on the electronic identity of the CN product following photodissociation arose while studying the lowest energy electronic absorption of HCN in the energy region of 6.3–8.05 eV corresponding to the $A \leftarrow X$ transition [7]. It was surmised that CN would be produced in the A state following predissociation via the A^1A' surface. Since then, several authors have experimentally verified the production of CN(A) at various photolysis wavelengths. Using synchrotron radiation (8–11 eV) to photodissociate HCN at Rydberg states, Lee detects CN(A) produced in high vibrational levels [8]. Tereshchenko and Dodonova dissociate HCN in an analogous energy region and also observe vibrationally excited CN(A) fragments [9]. The majority

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of the molecules form in low vibrational states ($v' < 4$); however, emission from higher vibrational levels ($v' = 4$ –10) occurs but drops off monotonically as the vibrational quantum number increases. Investigating a similar energy region, Morley et al. apply photofragment translational spectroscopy to probe the photodissociation of HCN via a Rydberg state at 10 eV [2]. At this energy, CN is produced primarily in its first excited electronic $A^2\Pi$ state although a few percentage of the molecules form in the CN $B^2\Sigma^+$ state. The preponderance of CN(A) radicals form in their $v' = 0$ level with evidence for higher vibrational levels populated. West and Berry photodissociate HCN at 8 eV and lower energies and detect fluorescence from the $A^2\Pi$ ($v' = 0$) manifold [4]. They report a threshold energy for CN(A) production from the $1A''$ state is 6.8 eV and that the mechanism should be predissociative. At even lower energies Eng. et al. [1] explore the HCN photodissociation with 6.42 eV. The only detectable product is ground state CN($X^2\Sigma^+$, $v' = 0, 1, 2$) with no evidence for CN $A^2\Pi$ reported even though it is energetically feasible. This result is not surprising since CN(A) production is calculated to be 6.55 eV. Given that the $H + CN(X)$ in a singlet surface only correlates with the ground electronic state of HCN, it is likely that this dissociation is preceded by internal conversion to the ground surface or intersystem crossing to a repulsive triplet state.

All of the aforementioned photodissociation experiments involve single photon excitation. Unique to this study is the application of a double resonance photodissociation technique termed vibrationally mediated photodissociation (VMP). Originally pioneered by Crim and coworkers [10], VMP is a sequential two photon process in which photodissociation occurs from a vibrationally prepared state within the ground electronic state, and the ensuing fragments are detected by laser-induced fluorescence (LIF). The use of a double resonance photodissociation technique offers analogous advantages as double resonance spectroscopic studies, specifically, preparation of a homogeneous state rather than a collection of molecular eigenstates from which dissociation occurs and an enhanced understanding on the effect of nuclear motion on the dissociation dynamics.

This study describes the VMP of HCN in which

the molecule is dissociated with ultraviolet light from a single rotational state in the third overtone of the C–H stretch. The initial vibrational excitation in the CH bond would be expected to favor direct dissociation of that bond which should lead to a CN(A) product, instead of internal conversion which should give CN(X) product. In the former case, one may expect that the dissociation is already well along upon Franck–Condon excitation, and thus the CN(A) product would be expected to be both vibrationally and rotationally cold. Our results confirm that the initial vibrational excitation does, in fact, change the electronic product produced and leads to the production of CN(A) radicals with very low vibrational and rotational excitation.

2. Experimental

A schematic of the experimental apparatus is illustrated in Fig. 1. An Nd:YAG (Continuum NY61) pumped titanium:sapphire (Ti:S) laser (Continuum TS 60) producing 35 mJ of ~ 790 nm light (1.57 eV) excites a single rotational line of the $4\nu_3$ (C–H stretch) band of HCN [11]. A photoacoustic cell containing 50 Torr of HCN and 200 Torr of argon monitors the signal from the overtone transition. Following 790 nm excitation, vibrationally excited molecules are photodissociated by 220 nm (5.64 eV) radiation. Ground vibrational state molecules do not absorb radiation at this wavelength. The 220 nm radiation was produced by frequency doubling the output of a XeCl excimer (Questek 2000) pumped dye laser (Lambda Physik FL 3002). The dye Coumarin 440 was used, producing ~ 200 μ J of 220 nm radiation. Light from a nitrogen pumped dye laser system (Molelectron UV 22 and DLII Model 12) probes the CN $B^2\Sigma^+$ ($v' = 1$) \leftarrow $A^2\Pi$ ($v'' = 0$) transition in the wavelength range of 533–525 nm. Fluorescence generated from the $B^2\Sigma^+ \rightarrow A^2\Pi(1-1)$ band (~ 386 nm) passes through a 390 nm bandpass filter and focuses onto a side-mounted photomultiplier tube (PMT). The output from the PMT enters a pulse amplifier and then is sent to a gated integrator, triggered by the N_2 laser output. Experimental data is accumulated by a personal computer.

Flashlamp fire signal from the Nd:YAG triggers a Stanford Research Systems delay box, which then

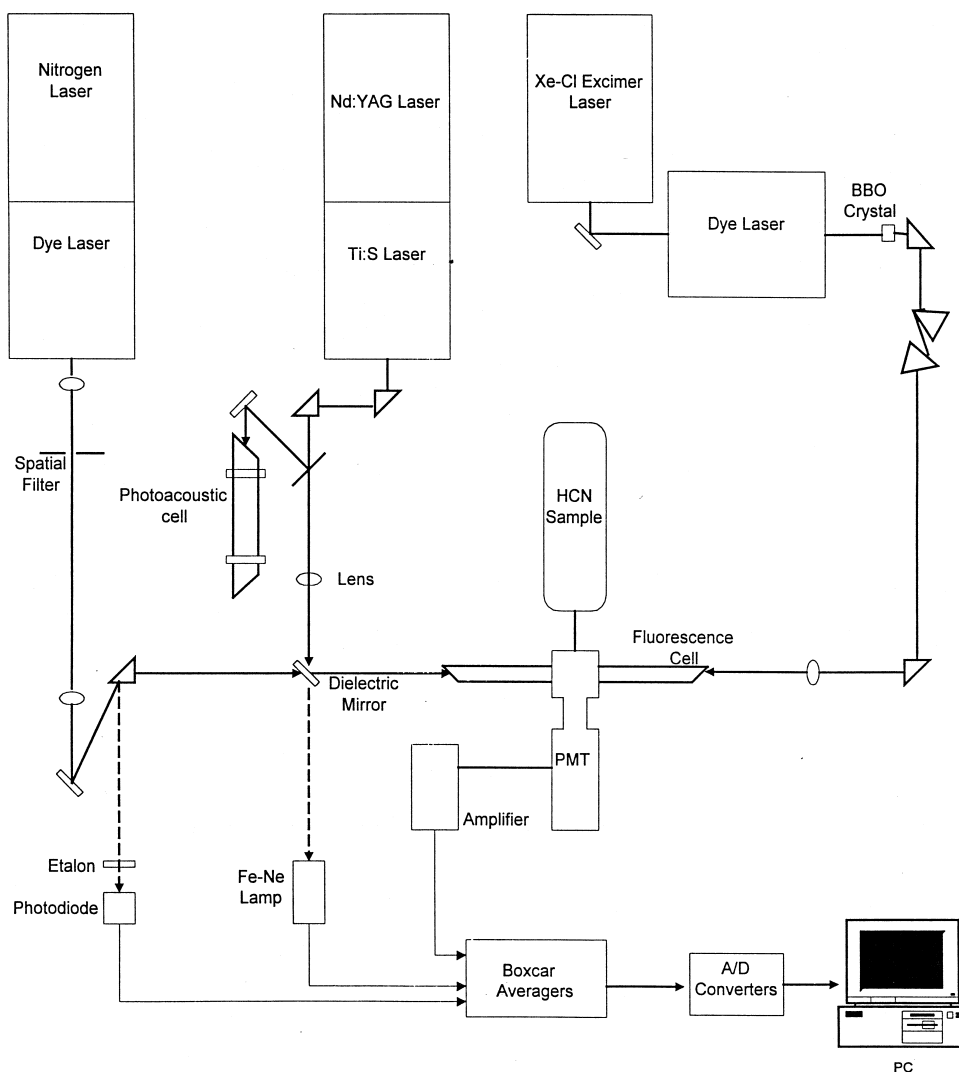


Fig. 1. Schematic of the experimental apparatus.

triggers the timing delay of the remaining two laser systems. The dissociation pulse from the excimer pumped dye laser system is delayed 200 ns from the Ti:S pulse. A delay of 600 ns between the excimer and nitrogen pumped dye laser was used. Timing jitter from the excimer limits the delay to a minimum of 200 ns. The smallest possible time delay between dissociation and probe laser is desired for an accurate representation of the nascent product rotational distribution of the CN fragment after photodissociation. However, it was found that some CN B →

X emission was created by the 220 nm laser due to multiphoton excitation (this channel is closed in one photon excitation). We used the time delay between the UV and LIF probe lasers to reduce the influence of this direct emission, which decayed with the 60 ns lifetime of the CN(B) state.

Interaction of the lasers with HCN occurs in a fluorescence cell consisting of a central viewing section and two baffled side arms with Brewster angle windows. Because of the weakness of the overtone transition, the 790 and 220 nm beams were

focused to a spot size of $\sim 100\ \mu\text{m}$, while the LIF laser was focused to $\sim 1\ \text{mm}$. Spatial overlap of the three lasers was accomplished by use of a retractable iris, covered with aluminum foil. The Ti:sapphire radiation burned a hole in the foil in a few shots. The radiation from the other lasers was aligned through this hole. Measurement of the diffraction rings produced by the hole provided a convenient way to estimate the spot size of the Ti:sapphire laser in the interaction region.

The pressure of HCN in the cell is 1 Torr. The HCN sample is synthesized from stearic acid and potassium cyanide. The simple vacuum line procedure combines stearic acid and KCN in a 2:1 ratio in a 2-l round-bottom flask. The solids are heated and begin to slowly react once the stearic acid melts. The HCN vapor passes through a moisture filter and collects in a 100-l gas cylinder. The reaction proceeds for several hours until bubbling ceases in the mixture. An FTIR spectrum of the sample confirms production of HCN.

3. Results

The VMP of HCN from three distinct rotational states in the third overtone ($\nu = 4$) of the C–H stretch has been performed. Selection of a single ro-vibrational state in HCN is possible since the Ti:sapphire laser linewidth ($< 0.1\ \text{cm}^{-1}$) is sufficiently narrow to resolve the rotational structure. The R(3), R(8) and R(15) lines were used as intermediate states.

Fig. 2 shows the LIF spectrum of the CN radical following photodissociation from the R(8) rotational line. The probing excitation is the $B^2\Sigma^+ \leftarrow A^2\Pi(1-0)$ band since it has a favorable Franck–Condon factor [12], and fluorescence is monitored via the $B^2\Sigma^+ \rightarrow X^2\Sigma^+(1-1)$ transition, which can be spectrally separated from all scattered light signals by using an interference filter. This spectrum verifies production of CN in the first excited electronic state. We failed to observe LIF signals exciting on the (2–1) transition, which demonstrates that the product is almost exclusively in the ground vibrational state. In addition, we failed to observe LIF using the $B \rightarrow X(1,0)$ excitation transition, demonstrating negligible direct production of CN(X). We used pho-

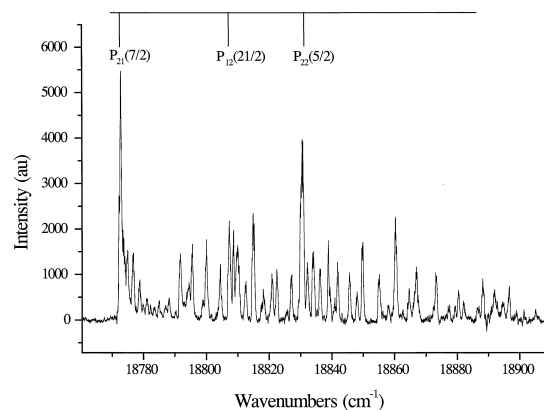


Fig. 2. LIF spectrum of $\text{CN } B^2\Sigma^+ \rightarrow A^2\Pi(1-0)$. The spectrum can be divided into two sections corresponding to transitions stemming from the upper $^2\Pi_{1/2}$ spin-orbit sub-band at energies below $18800\ \text{cm}^{-1}$ and transitions arising from the lower $^2\Pi_{3/2}$ spin-orbit sub-band above $18800\ \text{cm}^{-1}$.

todissociation of ICN at 220 nm to verify our sensitivity to detection of CN(X) molecules. Similar LIF spectra were recorded for photodissociation following excitation of the $J = 3$ and 15 levels of the $4\nu_3$ state.

The LIF spectra are quite congested at our LIF resolution ($0.3\ \text{cm}^{-1}$), and Fig. 2 shows the position of three P branch bandheads for reference. However, both states involved in this transition have been observed in combination with the ground state, so the rotational structure could be predicted, with rotational populations as the only adjustable parameters. The dominant splitting in the spectrum is the spin-orbit interaction in the A state. Transitions arising from the upper $^2\Pi_{1/2}$ spin-orbit sub-band occur at wavenumbers below $18800\ \text{cm}^{-1}$ and those from the lower $^2\Pi_{3/2}$ spin-orbit sub-band above $18800\ \text{cm}^{-1}$. Our probe laser resolution was not enough to resolve the spin-rotation splitting in the spectrum, leading to many overlapping transitions. Despite the number of transitions, there is very little energy dispersed into the rotational states after photodissociation indicating that the CN product is produced rotationally cold. We note that the observed rotational distribution is colder than that for a room temperature gas of CN molecules, thus the effect of collisions between dissociation and probing could only increase the observed rotational energy in the products.

The photodissociation wavelength was changed by a modest amount (10 nm). The qualitative results

did not change. In particular, no sharp structure in the photodissociation cross-section was observed.

4. Discussion

In the linear configuration, HCN has three low lying singlet excited states that arise from $\pi-\pi^*$ excitation. These are $^1\Sigma^-$, $^1\Delta$, and $^1\Pi$ in order of increasing energy. Only the last is dipole allowed from the ground $^1\Sigma^+$ state. However, the lowest two surfaces are known to have minima at bent geometries, where they are of $^1A'$ and $^1A''$ symmetries, respectively, allowing dipole allowed transition from the ground state. For these transitions the transition moments are always small and go to zero at the linear geometry of the ground state, and thus these transitions are quite weak in absorption.

The observed LIF spectrum demonstrates that $\text{CN}(A^2\Pi, v=0)$ is the dominant photoproduct produced by 220 nm excitation from the $4\nu_3$ state. In the linear configuration, the $\text{H}(\text{C}^2\text{S}) + \text{CN}(A^2\Pi)$ products correlate with the upper $^{1,3}\Pi$ states. In a bent configuration, these products correlate with lower states of $^{1,3}A'$ and $^{1,3}A''$ symmetries. Previously, discrepancies appeared in the literature over the symmetry and the number of excited electronic states of HCN in the energy region of 6.6 eV [2,4,5,13,14]. It had been predicted that two states of $^1A''$ symmetry existed in the vicinity of each other based on an anomaly in anharmonic constants. The second assigned $^1A''$ state or 'B' state was later reassigned to a bending progression in the A state built on a quantum of C–H vibrational excitation [15]. As a result, there is only one $^1A''$ state in this energy region, and it adiabatically correlates to the $\text{H} + \text{CN}(A)$ products in nonlinear geometries.

Although the $^1A'$ correlates to the $\text{CN}(A)$ state, it has two predissociative channels which yield either $\text{CN}(X)$ or $\text{CN}(A)$ products [5,16]. These two dissociation pathways are rationalized in terms of a potential energy barrier. Theoretical calculations by Peric et al. [17] predict that there is a potential barrier of 0.4 eV (measured from the $^1A''$ minimum) to dissociation of the CH bond in the A state. This barrier originates from a conical intersection between the A^1A' state of HCN (which is $^1\Sigma^-$ in linear geometries) and the potential curve leading to $\text{CN}^2\Pi$,

which has $^1\Pi$ linear symmetry. The electronic configurations responsible for the states mixing are $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a' 7a'$ for HCN [13] and $1\sigma'^2 2\sigma'^2 3\sigma'^2 4\sigma'^2 1\pi'^3 5\sigma'^2$ for CN [18]. Dissociation energies below the barrier will predissociate to $\text{CN}(X)$ via coupling with either the $1^3A''$ or the $X^1\Sigma^+$ state, while a second predissociative channel opens up leading to $\text{CN}(A)$ for energies above the barrier. For example, Eng et al. photodissociate HCN from the (000) and (010) vibrational levels of $\text{HCN}(A)$ at an energy of 6.42 eV and only detect ground state CN fragments, whereas West and Berry photolyze HCN at energies of 8 eV, which is above the potential barrier, and observe fluorescence from $\text{CN}(A)$. West and Berry determine that the threshold energy for $\text{CN}(A)$ production is 6.88 eV. Therefore, it could be argued based on the West and Berry findings that the energy minimum for the $\text{CN}(A)$ channel to open up is 0.32 eV instead of 0.4 eV as previously calculated by Ref. [17]. The West and Berry chemical laser experiments demonstrate that there is a population inversion produced between the CN A and X states, but they could not directly determine the fraction of population produced directly in the two states.

This investigation deposits 7.2 eV of energy into HCN and finds that $\text{CN}(A, v=0)$ is the dominate product. Based on the above reasoning, $\text{CN}(A)$ would be expected since the total energy is above the energy barrier for $\text{CN}(A)$ production. In comparison to the isoenergetic studies of West and Berry, the results are similar. Both studies produce $\text{CN}(A)$ in low vibrational levels unlike other studies where photolysis occurs at higher energies and produces vibrationally excited $\text{CN}(A)$ [2,8,9]. Using a less state selective technique of flash photolysis, West and Berry account for the production of $\text{CN}(A)$ as being due to a predissociative mechanism since bound to free transitions should have negligible Franck–Condon density in this spectral region from the ground vibrational state of HCN. Since the results of this study are consistent with single photon isoenergetic studies, it seems reasonable to assume that the mechanism to produce $\text{CN}(A)$ in this study is also predissociative. However, we varied the photolysis wavelength and did not observe structure in the photodissociation cross-section, which suggests direct dissociation. It is believed that the four quanta of vibrational excitation extends the C–H bond length

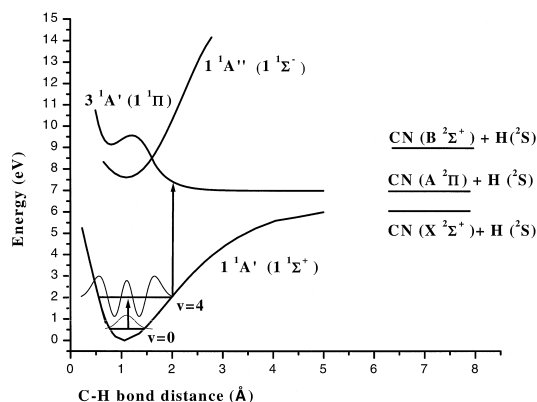


Fig. 3. Ground and excited state potential energy curves for linear HCN (adapted from Ref. [17]).

in the ground state potential of HCN and moves the Franck–Condon region past the barrier (maximum of barrier occurs at a C–H bond length of 1.56 Å [17]) to a purely repulsive region (see Fig. 3). In this region, the transition should become allowed at linear geometries, and thus much stronger from the lower vibrational state which is on average linear. In similar infrared + UV dissociation experiments with isoelectronic acetylene (C_2H_2), the observance of C_2H $A^2\Pi$ is attributed to either the excess energy overcoming a barrier on the A^1A_u state or overtone preparation relocates the Franck–Condon region and may affect nonadiabatic processes [19,20]. One other possible explanation for CN $A^2\Pi$ is tunneling through the barrier.

The product distribution gives information on the forces that occur as the HCN dissociates. As previously mentioned, LIF with excitation on the $B^2\Sigma^+ \rightarrow A^2\Pi(2-1)$ vibrational transition was not observed. This is consistent with a direct dissociation in which the CN bond length either having a small change from the initial state to the final state or adiabatically changing along the dissociation coordinate. The 0.08 Å increase in CN bond length upon going from HCN to CN(A) would suggest vibrational excitation of the CN product. A plot of the vibrational wavefunctions for the $4\nu_3$ state calculated using the potential of Mills et al. [21] shows that at the outer turning point of the CH stretch (what we believe to be the Franck–Condon region), the CN is compressed by 0.05 Å compared to the equilibrium value of 1.153 Å. For our excess energy over the

CN(A) threshold (0.73 eV), dissociation channels with up to 3 quanta of vibration in the CN(A) state are open. Thus we would have expected to have observed some vibrational excitation in the CN(A) product. One possible explanation is that vibrational excitation of the CN(A) will raise the thermodynamic threshold and as a result push out the region of Franck–Condon overlap with the dissociating molecule. Since we are likely in the low energy tail of the absorption from the $4\nu_3$ state, we expect the cross-section to decrease exponentially with increasing outer turning point in the final state.

The effect of initial rotational preparation in HCN is demonstrated in the R_{22} rotational progression, as indicated in Fig. 2. Given the large collisional rotational relaxation rates of HCN, our results are certainly effected by partial rotational relaxation between excitation and photodissociation lasers, and thus we expect the observed distributions to be more ‘thermal’ than the true nascent distribution. The R_{22} progression is selected since it contains well-isolated transitions from other overlapping branches, which facilitates peak assignments, and no spurious intensity measurements can be made due to stronger overlapping branches. Fig. 4a represents the distribution of the relative population of the CN fragment among the R_{22} branch following photodissociation from one of the three rotational states initially selected. As the rotational quantum number increases in HCN $\nu_3 = 4$ from which photodissociation occurs, the mean of the distribution also increases so that higher rotational states are populated in the CN radical. In addition, as photodissociation increases from $R(3)$ to $R(15)$, the tail of the spread extends to higher rotational levels and the maximum of the peak shifts to higher rotational quantum states. Therefore, the relative rotational population among the quantum states in CN is governed by the rotational line first prepared in HCN. These results are in agreement with other fully state resolved photodissociation experiments of water [22,23] in which the distribution of the products among their rotational state relies strongly on the initial state selected in the vibrational overtone step.

None of these plots, however, suggests a thermal distribution obeying Boltzmann statistics. Fig. 4b reveals the Boltzmann distribution of the population among the rotational states at a temperature $T = 298$

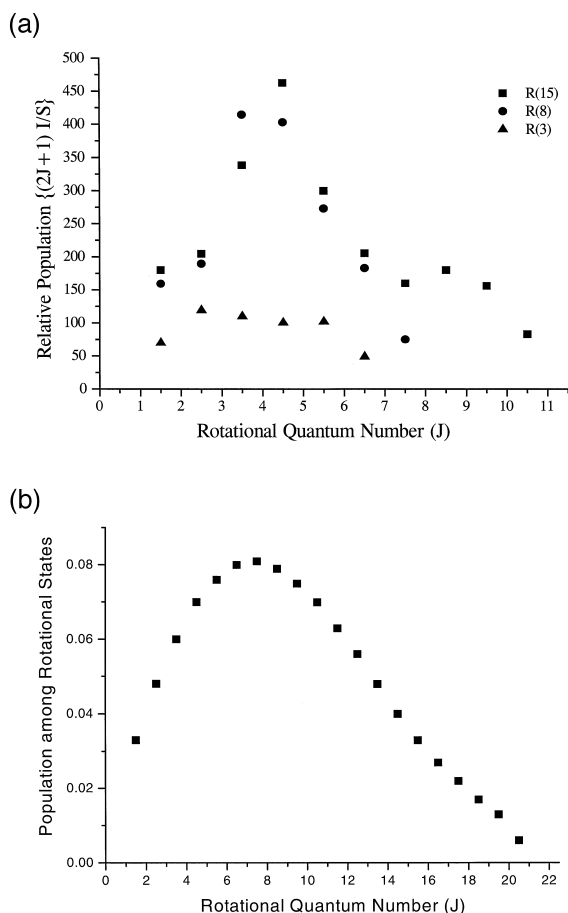


Fig. 4. (a) Relative population of R₂₂ branch rotational energy levels following photodissociation of HCN from the R(15), R(8) and R(3) rotational line in the $v = 4$ vibrational level. (b) Boltzmann distribution for CN rotational population at $T = 298$ K and $B = 1.7$ cm⁻¹.

K and a rotational constant $B = 1.7$ cm⁻¹. Clearly, the range of the distribution covers more rotational levels and the peak appears at a higher rotational quantum number. This comparison suggests that the CN radical is produced rotationally cold with very little of the excess 0.73 eV of energy going into rotational energy when the C–H bond breaks. Classically, if the force that breaks the bond is along the internuclear axis, then CN is produced with its rotational distribution peaked according to the following equation:

$$J_{\text{CN}} = \left(\frac{I(\text{CN})}{I(\text{HCN})} \right) J_{\text{HCN}} \quad (1)$$

where I is the moment of inertia and J is the rotational quantum number. The initially prepared rotational state of HCN is $J = 8$, and the ratio of moments of inertia is ~ 0.75 . Thus, $J_{\text{CN}} = 6$ which is in agreement with the previously presented rotational distribution plot. This implies that the departing H atom imparts negligible torque on the CN, which suggests a near linear dissociation path. If the C–H bond were to leave in a bent configuration ($\theta > 0$), then there would be an additional torque based on the bending angle:

$$\Delta J = |r| |\Delta p| \sin \theta / h / 2\pi \quad (2)$$

where $r = 0.63$ Å is the distance between the C atom and the center of mass of the CN fragment and Δp is the impulse defined by the following equation:

$$\Delta p = (2 m_{\text{H}} E_{\text{trans}})^{0.5} \quad (3)$$

E_{trans} is the excess energy (0.73 eV) going off with the hydrogen atom. Eq. (2) then reduces to

$$\Delta J = 11.9 \sin \theta \quad (4)$$

This will add to the rotation already present, producing a broader distribution, shifted to higher peak J . If we interpret the experimental results as implying that $\Delta J = 3$, then $\theta = 15^\circ$. This further suggests that the excitation Franck–Condon region is after the barrier, which occurs at a conical intersection. A wave packet passing through the region of the conical intersection would be strongly defocused by the forces that favor a nonlinear geometry, which would be expected to produce a large θ .

5. Conclusion

The vibrationally mediated photodissociation of HCN from three rotational states in the third overtone of the C–H stretch has been measured. Dissociation proceeds via the A^1A' state of HCN to yield vibrationally cold CN $A^2\Pi$ photofragments. The rotational distributions of the CN products depend on the rotational state selected in the vibrationally excited HCN molecule; however, photodissociation from all three ro-vibronic levels results in rotationally cold product distributions in comparison to thermal distributions. This lack of rotational population suggests that the bond breaks when HCN is in a

linear arrangement rather than a bent geometry. If HCN were dissociating from a bent configuration, the angular rotation would be affected resulting in an increased product distribution.

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