NEAR THRESHOLD PHOTODISSOCIATION OF EXPANSION COOLED NCNO: NASCENT CN($X^{2}\Sigma^{+}$) WITHOUT INTERNAL EXCITATION $\stackrel{\diamond}{}$

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The dissociation of expansion cooled NCNO following $\tilde{A}^{-1}A'' - \tilde{X}^{-1}A'$ excitation transpires via vibrational predissociation, and the CN($X^{2}\Sigma^{+}$) fragments are *extremely* cold near reaction threshold. Only $\upsilon'' = 0$ is produced, and >90% of the CN is in N'' = 0 corresponding to ($E_{internal}$) <0.4 cm⁻¹. A revised value for the NCNO dissociation energy ($D_{0} = 17085 \pm 10 \text{ cm}^{-1}$) is reported.

1. Introduction

Photodissociation provides a convenient means whereby the dynamics of small molecular systems can be studied with high precision. Theory has progressed to the point where quantum mechanical calculations can provide reasonable estimates for product state distributions [1], and an interplay between experiment and theory will now be more useful than ever. Presently, it is routine to use supersonic free jet expansions to cool parent excitations to near 0 K. thereby characterizing systems accurately in collision free environments [2], and tunable lasers can excite specific rovibrational states of jet cooled parent molecules which then evolve into fragments. Nascent products can be detected in their occupied quantum states via state specific diagnostics such as laser induced fluorescence (LIF), whereas Doppler shift, polarization, and time-of-flight measurements provide velocity distributions and anisotropies in the lab and/or molecular frame [3]. Because this level of sophistication exacts a price in terms of energy and resources, it is important to choose candidate systems carefully so that the maximum information can be gleaned from the measurements. We believe that NCNO is particularly suitable, and will provide a test case for theories of unimolecular reactions of small molecules.

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In this communication, we report experimental results concerning the photodissociation of expansion cooled NCNO, via excitation of the $\widetilde{A}^{1}A'' \leftarrow \widetilde{X}^{1}A'$ system (hereafter referred to as $S_1 \leftarrow S_0$), using a tunable dye laser. Free jet expansion and one-photon excitation insure that monoenergetic NCNO ensembles with well characterized angular momenta are prepared above dissociation threshold. It is particularly noteworthy that both NO(X²II) and CN(X² Σ^+) photofragments can be detected in all of their available quantum states, and are also agreeable to velocity measurements. NCNO has a rich absorption spectrum throughout the UV, visible, and near IR [4-6], which allows for versatile and efficient excitation via one- and twophoton processes [5,7,8]. The vibrational and rotational constants of the S_0 and S_1 states have been determined [4,9], and the dissociation energy of NCNO was previously estimated mass spectrometrically at $28.8 \pm 5 \text{ kcal mol}^{-1}$ [10].

Our experiments show that subsequent to $S_1 \leftarrow S_0$ excitation of NCNO, photodissociation occurs via vibrational predissociation ^{**} on either S_1 or S_0 (fol-

^{**} We define vibrational predissociation as an excitation to a bound part of the potential surface above D₀ where the lifetime of the molecule before dissociation is longer than a few vibrational periods. The term electronic predissociation is used whenever dissociation follows crossing between the initially prepared bound state and a repulsive surface. Direct dissociation involves initial excitation to a repulsive state.

lowing internal conversion), and we observe nascent $CN(X^2\Sigma^+)$ via LIF. The threshold for photodissociation of expansion cooled NCNO following one-photon absorption is at 585.3 nm, which leads to a revised value for the dissociation energy, $D_0 = 17085 \pm 10$ cm⁻¹ (48.85 ± 0.03 kcal mol⁻¹). The *extremely* cold $CN(X^2\Sigma^+)$ product (v'' = 0, >90% in N'' = 0) observed at threshold must evolve via a vibrational predissociation mechanism, and above threshold the results are in excellent agreement with statistical theory. We also show that near threshold, effects due to quantum mechanical tunneling are manifest in long CN appearance times, and these effects should be included in calculations of unimolecular reaction rates [11,12].

2. Experimental

The experimental arrangement has been described in detail before [5,7], and the only significant change is the cooling of NCNO using a pulsed free jet expansion, Briefly, the LIF chamber is connected directly to a vacuum system and is evacuable to 10^{-6} Torr. and experiments are done under completely collision free conditions. Pulsed expansions are achieved with a piezoelectrically driven valve (Laser Technics, 180 µs pulses) whoses insides are coated with teflon in order to minimize the destruction of NCNO which occurs on metal surfaces. When analyzing the rotational structure of expansion cooled NCNO using a He carrier, we obtain $T_{\rm R} \approx 2$ K [6]. With an Ar carrier, even lower temperatures are achieved, and this is useful when analyzing spectra and studying the dissociation threshold region [6]. The $S_1 \leftarrow S_0$ system of NCNO is excited using the output from a tunable dye laser (Quanta Ray, 6 ns fwhm, 0.6 cm⁻¹ resolution at 550 nm). CN is detected via LIF on the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ system, using a N2 laser pumped dye laser (Molectron, 6 ns fwhm, BBO dye, 0.3 cm⁻¹ resolution at 388 nm, with intracavity etalon - nominal 0.07 cm⁻¹). Because of the high sensitivity, only the oscillator portion of the dye laser system is needed ($\leq 10 \,\mu$ J/pulse). The delay between the lasers is adjusted digitally (10 ns resolution), and the unfocused laser beams, which are collinear and counterpropagating, intercept the free jet expansion 2 cm (40 nozzle diameters) downstream from the valve, and during the central portion of the time profile of the gas pulse. The fluorescence is viewed at

right angles with one or two photomultiplier tubes (PMTs) together with the appropriate filters. Signals from the PMTs are digitized and transferred to a lab computer which stores/averages the data, controls the frequencies of the dye lasers, normalizes signals as per the laser energies, and displays the results on a plotter.

NCNO is synthesized from AgCN and NOCl, following the procedure given in ref. [9]. Considerable care is required, since impure samples tend to detonate violently [13,14]. Samples are purified by fractional distillation, and are stored at 77 K. Fresh samples are distilled from pentane (142 K) or ethanol (157 K) slushes each day prior to use into a 5 ℓ sample container where He : NCNO or He : Ar : NCNO mixtures (900 : 4 Torr and 650 : 250 : 4 Torr respectively) are prepared. Since NCNO decomposes on metal surfaces, the preparation system is constructed from glass, teflon, and viton.

3. Results

One-photon and sequential two-photon photodissociation processes occur in NCNO following $S_1 \leftarrow S_0$ excitation [5.7,8]. In the two-photon process, absorption of a second photon promotes the excited molecules from the S_1 state to a dissociative surface that produces highly rotationally and vibrationally excited CN fragments ("hot" CN), whereas the CN produced via one-photon photodissociation is rotationally "cold" [5,7].

As the photolysis laser wavelength is varied from the band origin of the $S_1 \leftarrow S_0$ system (882 nm) to successively shorter wavelengths, an abrupt one-photon dissociation onset at 585.3 nm is found, as shown in fig. 1. The spectrum is obtained by monitoring $CN(X^2\Sigma^+, v''=0, N''=0)$ as the photolysis wavelength (λ_p) is scanned, and there is a one-to-one correspondence between the observed features and peaks in the NCNO absorption spectrum. However, [CN(v'')]= 0, N'' = 0)]/[CN(total)] varies with λ_p , and only by taking this into account could one convert the observed spectrum into an absorption spectrum, Although many vibrational bands have been analyzed up to $E'_{\rm vib} \approx 2500 \text{ cm}^{-1}$ [6], extrapolation of these assignments to the dissociation threshold region (E'_{vib}) $\approx 6000 \text{ cm}^{-1}$) is not feasible due to extreme spectral



Fig. 1. Spectra showing the competition between non-dissociative one-photon excitation and one-photon photodissociation. The upper trace is obtained by monitoring $CN(X^2\Sigma^+, v''=0, N''=0)$ via LIF and shows an abrupt onset for product formation. The rather weak features at 590-595 nm result from excitation of v_5^{ν} hot bands of NCNO [6]. In the lower trace, we monitor only high N'' (near the bandhead) which derive from two-photon photodissociation. These N'' are inaccessible energetically via one-photon photodissociation, and therefore cannot be produced if NCNO dissociates rapidly following $S_1 - S_0$ excitation [5].

congestion (vibrational density of states ≈ 2.5 states/ cm⁻¹) and unknown Franck–Condon factors and anharmonicity corrections. The *lack* of one-photon dissociation at longer λ_p can be monitored via the sequential two-photon excitation of NCNO [5,7]. By monitoring nascent "hot" CN states which derive solely from the two-photon process, we can probe NCNO molecules in the S₁ state which have not dissociated. In doing this, we find that NCNO dissociates *completely* following one-photon absorption at λ_p < 585 nm, and does not dissociate at $\lambda_p > 585$ nm, as shown in fig. 1.

The competition between dissociation following one-photon absoption and the absorption of a second photon (leading to two-photon dissociation) is manifest in the threshold region where the product appearance times are long (see below). In this region, both processes occur simultaneously as is seen in fig. 1. By increasing the photolysis laser intensity (focusing the beam with a 1 m focal length lens), the optical pumping rate increases, and the two-photon process is weakly observed even at $\lambda_p = 571.6 \text{ nm} (411 \text{ cm}^{-1} \text{ above dissociation threshold}).$

At $\lambda_p > 585.2$ nm, where CN(X ${}^2\Sigma^+$, $\upsilon'' = 0$, N'' = 0) is quite dominant, a finite risetime is observed for its production. By varying the delay between the photolysis and the probe lasers, we find an exponential growth, with $\tau_{ap} \approx 34 \pm 5$ ns at $\lambda_p = 585.5$ nm. This risetime is shortened to 18 ± 5 ns for $\lambda_p = 585.3$ nm. and is no longer measurable at $\lambda_p \leq 585.2$ nm (τ_{ap} \leq 10 ns, the experimental resolution). Fig. 2 presents three traces taken with 70 ns delay between the photolysis and probe laser pulses, and scanning the photolysis laser at 0.6 cm⁻¹ steps. In both the upper and the middle traces, $CN(X^2\Sigma^+, v''=0, N''=0)$ is monitored as λ_p is scanned. In the latter case, the beam temperature is very low (<2 K, J_{max} (NCNO) <7, stagnation pressure: He : Ar : NCNO = 650 : 250 : 4 Torr respectively), and an abrupt onset for producing N'' = 0is observed. In the upper trace (warmer expansion, stagnation pressure: He : NCNO = 350 : 4 Torr) the production of N'' = 0 is extended to longer λ_p due



Fig. 2. Data showing the near threshold behavior of NCNO photodissociation as a function of parent rotational excitation. In traces (a) and (b) $CN(X^{2}\Sigma^{+}, v'' = 0, N'' = 0)$ is monitored as the photolysis laser wavelength is scanned. In trace (a) the expansion conditions produce inefficient rotational cooling. The peaks are broad, and the threshold region extends to longer wavelengths (see text). In trace (b), the beam temperature is ≈ 2 K, and an abrupt onset for CN(N'' = 0) production is observed. Trace (c) is obtained under similar expansion conditions, but CN(N'' = 1) is monitored. Notice the higher threshold wavelength in this case. In all three traces, the delay between the onsets of the photolysis and probe lasers is maintained at 70 ± 10 ns. The insets show the appearance times (τ_{ap}) of N'' = 0 at wavelengths 585.5, 585.3 and 585.2 nm. For N'' = 1, τ_{ap} at threshold is <10 ns.

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to the fact that excitation of rotationally unrelaxed NCNO molecules to levels above the dissociation limit requires less energy (i.e. longer λ_p). The appearance rates are consistent with the existence of a small centrifugal barrier to the dissociation, as discussed in section 4. In the lowest trace, N'' = 1 is monitored as λ_p is varied, and the slightly higher photolysis energy $(\approx 4 \text{ cm}^{-1})$ which is required to produce this state corresponds to the difference in energy between CN N'' = 0 and 1 levels.

The observed CN(N'' = 0) appearance times depend within experimental error, solely on λ_p (indicated by the vertical broken lines in fig. 2), and do not vary when the expansion conditions are changed to yield



Fig. 3. Data showing the dissociation of expansion cooled NCNO (He carrier, $T \approx 5$ K), following excitation of the $\tilde{A}^{1}A'' - \tilde{X}^{1}X'$ system. The upper spectrum is obtained by monitoring $CN(X^{2}\Sigma^{+}, v'' = 0, N'' = 0)$ as λ_{p} is varied. The lower traces are LIF spectra of $CN(B^{2}\Sigma^{+} - X^{2}\Sigma^{+}$ system) showing nascent $X^{2}\Sigma^{+}$, v'' = 0 rotational states. Notice the dominance of N'' = 0 at $\lambda_{p} = 585.3$ nm. The full circles on the traces at $\lambda_{p} = 582.04$ nm and 580.4 nm are the relative peak heights calculated using PST (see text).

different NCNO rotational temperatures. However, the dissociation yield at $\lambda_p > 585.3$ nm decreases significantly with better cooling, and for the coldest expansion an abrupt onset is detected at $\lambda_p = 585.3$ nm. We interpret this as corresponding to the dissociation threshold (see below).

At each λ_p , a LIF spectrum of CN reveals the nascent rovibrational excitations, and these are shown for four wavelengths λ_p at the bottom of fig. 3 (in all cases, CN(X $^2\Sigma^+$, v'' = 0)). A significant result is the *extremely* cold rotational distribution obtained at λ_p = 585.3 nm. Analysis of this CN LIF spectrum [5.6] indicates that >90% of the CN are in N'' = 0 and the remainder are in N'' = 1. Product distributions such as this, where the average internal energy of CN is <0.4 cm⁻¹, have not been encountered previously in photodissociation studies.

The translational energy of CN was estimated from measurements of the shapes of the $N'' \approx 0-3$ rotational lines with the probe laser bandwidth narrowed by an intracavity etalon. The probed lines have a width smaller than expected for 300 K CN (≈ 0.07 cm⁻¹).

From these results, we derive a revised value for the dissociation energy of NCNO. It corresponds to the wavelength of the abrupt onset of dissociation under conditions of the coldest expansion (fig. 2, middle trace), where the ratio [CN(N'' = 0)]/[CN(N'' = 1)]is maximum. The error estimate reflects uncertainties in the absolute calibration of λ_p , and in the exact onset for dissociation of rotationless NCNO. Thus, the value of $D_0 \approx (585.3 \text{ nm})^{-1} = 17085 \text{ cm}^{-1}$ is rather accurate, and an uncertainty of $\pm 10 \text{ cm}^{-1}$ is safe.

4. Discussion

Our results show that NCNO dissociates completely via one-photon absorption with $\lambda_p < 585$ nm, and does not dissociate with $\lambda_p > 585$ nm (fig. 1). As discussed before [5], by monitoring CN fragments produced via two-photon photodissociation, we monitor NCNO molecules which do not dissociate rapidly following the absorption of a single photon. Therefore, the disappearance of the two-photon process is due to competition between dissociation following onephoton excitation, and the absorption of a second photon. Since the duration of the photolysis pulse is \approx 6 ns fwhm, the complete disappearance of the twophoton process indicates that the one-photon photodissociation rate at wavelengths <585 nm greatly exceeds the rate of optically pumping out of the initially excited state, and must be >10⁹ s⁻¹. However, with focused radiation, the optical pump rate can be made competitive with the dissociation rate, and we can monitor CN which derives from two-photon excitation with λ_p as short as 571.6 nm. Deriving the dissociation rate from these measurements is not straightforward, and further work is required for quantitative interpretation of these results.

The experimental observations can only be reconciled with a vibrational predissociation mechanism and the absence of any appreciable barier. The extremely cold CN rotational distribution obtained at $\lambda_p = 585.3$ nm indicates that >90% of the CN molecules are in N'' = 0, and their average internal energy is <0.4 cm⁻¹. As explained below, it would be impossible to have such a cold rotational distribution accompany direct dissociation or electronic predissociation.

Classically, in the event that there is significant recoil, the CN bond axis would have to be aligned along the exit channel minimum in order to prevent CN from acquiring rotational excitation during the dissociation process. At sufficiently large separations ($\gtrsim 6$ Å), the dominant interaction between the fragments is dipoledipole, and the minimum energy dissociation pathway corresponds to all four nuclei being collinear. Thus, it is likely that forces would be directed mainly along the CN axis. However, one cannot localize the nuclei with such precision. Even for a linear configuration, the three "bending-type" vibrations for NCNO (ν_4 , ν_5 , and ν_6) [4] which evolve, in concert with motion along the reaction coordinate, into product R,T excitations still have their zero point energies, as dictated by the uncertainty principle. This leads to a distribution of geometries and velocities among these three parent degrees of freedom which convolutes with the reaction coordinate recoil during the dissociation process to produce the final state distributions. Where a direct dissociation process of any kind involved, the combined zero-point kinetic energies of v_4 , v_5 , and v_6 (270) cm^{-1} on S₀, 290 cm⁻¹ on S₁ [4,9]) would have to be accounted for, especially since these motions are strongly correlated to product rotation [15]. Since direct dissociation and electronic predissociation often place the departing fragments on a repulsive potential

with considerable energy above D_0 (e.g. thousands of cm⁻¹), the convolution of this energy with the zero point motions will result in $\langle E_{rot} \rangle_{CN} \ge 0.4 \text{ cm}^{-1}$. Thus, it is required that parent vibrations evolve into product motions via the loose transition state expected for a unimolecular reaction which produces radical fragments [12]. From the absence of CN internal excitation, it is obvious that coupling is facile during reaction, and there is no hint of suddenness in the product excitations (e.g. parent motions carried over adiabatically to products).

Other experimental observations are also in accord with this interpretation. At each λ_p studied to date, CN rotational states are observed up to the limit imposed by energy conservation, but not above it, and the same D_0 is also derived from the observed threshold for production of CN v'' = 1 and 2 [6]. The average rotational energy in CN, and the shape of the energy distribution depend only on the excess energy, and in comparing distributions obtained by photolyzing the molecules via different rovibronic bands, no mode specific effects are observed. Finally, the low CN translational energy is incompatible with the existence of a large barrier to dissociation, as required by $D_0 = 28.8$ kcal mol⁻¹ [10].

Thus, we conclude that $D_0 = 17085 \pm 10 \text{ cm}^{-1}$ (48.85 ± 0.03 kcal mol⁻¹), and that NCNO dissociates via vibrational predissociation. The previous experimental value for D_0 was obtained from measuring appearance potentials, and is quite low. This value has been criticized by Bjorkman and Bagus [16], whose ab initio calculations give $D_0 = 48 \text{ kcal mol}^{-1}$. and Benson who suggested $48-50 \text{ kcal mol}^{-1}$ [17]. The present measurement is in excellent agreement with these estimates, and falls in between the dissociation energies for NOF and NOCI [18], as expected for CN which is a pseudo halogen. Thus, we believe that the dissociation energy of NCNO is now well established.

NCNO, which evolves into two coupled rotors, is an ideal candidate for studies of energy disposal in a unimolecular reaction. Since product vibrations are not accessible for $E^{\pm} - D_0 < 1876 \text{ cm}^{-1}$, only product R, T excitations need be considered, and in this case the phase space theory of unimolecular reactions (PST) [19-26] can be used to estimate product exciexcitations † . PST calculations were performed for all but the smallest $E^{\pm} - D_0$ (<20 cm⁻¹), where attention must be paid to proper angular momentum addition [27], and typical results are shown in fig. 3 for $E^+ - D_0 = 96$ and 144 cm⁻¹. The fit is excellent, and we find similar agreement for $E^+ - D_0$ up to ≈ 2000 cm⁻¹. The validity of a PST perspective at these energies derives from combining parent motions (overall rotation + 4 "disappearing oscillators") to form product states which cannot be represented diagonally in terms of the parent states [6]. The accord between experiment and theory at modest $E^+ - D_0$ is very encouraging, and we believe that the NCNO system will provide an excellent oportunity to examine statistical unimolecular processes in detail.

Finally, we would like to comment on the >10 ns risetime which is observed in the production of $CN(X^2\Sigma^+, v''=0, N''=0)$ near dissociation threshold. It is possible that rotational effects in the excited state of the parent molecule play a significant role in the predissociation mechanism either due to symmetry consideration or to centrifugal barrier associated with higher rotational levels. For example, sample RRKM calculations show that the fast increase in the dissociation rate with a very small increase in excess energy near threshold cannot be reconciled with a statistical theory unless quantum tunneling effects are taken into account [11,12]. In order to estimate the tunneling through a centrifugal barrier, we used the barrier transmission coefficient for an asymmetric Eckart potential [28-30]:

$$T(E) = [\cosh(a + b) - \cosh(a - b)]$$

$$\times [\cosh(a + b) + \cosh(d)]^{-1}, \qquad (1)$$

$$a = (2\mu E^{+})^{1/2} L/h,$$

$$b = [\hat{2}\mu (E^{+} - D_{0})]^{1/2} L/h,$$

$$d = \{2\mu [(D_{0} + V_{b})^{1/2} + V_{b}^{1/2}]^{\frac{2}{2}} - (\pi h/L)^{2}\}^{1/2} L/h.$$

where μ is the reduced mass. V_b is the barrier height. and L is related to the width of the barrier. In our case, $D_0 = 17085$ cm⁻¹, $\mu = 14$ amu, and we consider $V_b = 1-5$ cm⁻¹ and L = 1-3 Å. These values allow the following simplification of eq. (1),

$$T(E) = [1 - \exp(-2b)] / [1 + \exp(d - a - b)] .$$
 (2)

⁷ When product vibrations *are* accessible, PST cannot be used, since it does not take explicit account of the parent being vibrationally excited but rotationally cold, and this will be discussed in detail elsewhere [6].

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Under these conditions, we find, using eq. (2), that T(E) varies by a factor of ≈ 5 for incident energies $2-10 \text{ cm}^{-1}$ above and below $D_0 + V_b$. The experimental results show that the observed lifetime in the threshold region varies by a factor of at least 4 over a range of <4 cm⁻¹. These results are easily fit with $V_{\rm b}$ $\geq 1-2$ cm⁻¹, which is quite reasonable for a centrirugal barrier. The barrier was estimated [11,12] using an attractive potential of the form $-Cr^{-6}$ (where C is estimated from the dissociation energy), and the repulsive rotational energy term. The latter was calculated as a function of r by estimating the variation of the rotational constant along the c-axis of NCNO with the elongation of the central CN bond. We find that barriers of 0.5-4 cm⁻¹ are expected for NCNO in rotational levels 5-15 respectively. Since in the jet expansion of NCNO only rotational levels ≤7 are populated [6], barriers of the order 0.5-1 cm⁻¹ should be typical and the rapid change in τ_{ap} with λ_p in the region near D_0 is consistent with tunneling through a barrier of that magnitude. The amount of rotational excitation in parent NCNO can be varied by varying the expansion conditions, and, as expected, the long lifetime component becomes more prominent in "warmer" expansions (fig. 2).

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