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Correlated product state distributions in the unimolecular reaction of NCNO^{a)}

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Following excitation to S_1 , expansion-cooled NCNO undergoes nonradiative couplings to S_0 and predissociates to CN and NO. Doppler profiles of selected CN $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ rotational lines were recorded using LIF at several excess energies between 0 and 3000 cm⁻¹. This yields NO V,R distributions associated with specific CN($X^2\Sigma^+$) rotational states. The profiles can be fit using the statistical PST/SSE model, and the correlated distributions show no evidence of dynamical bias or exit channel barriers. Doppler profiles generated with polarized lasers show little or no spatial anisotropy of recoil velocities, and are fit by anisotropy parameters $\beta \sim 0$, even at excess energies where predicted unimolecular lifetimes are <1 ps. Possible causes for the lack of spatial anisotropy are discussed. Analyses of NO fragment LIF spectra obtained at excess energies of 2348 and 2875 cm⁻¹ show a slight preference for the $\Pi(A')$ Λ -doublet component for $J'' \geq 30.5$, suggesting planar dissociation. An in-plane orientation of the singly occupied $p\pi$ lobe in NO is to be expected for dissociation on the ground (A') electronic potential energy surface.

I. INTRODUCTION

The development of a predictive, quantitative understanding of unimolecular reactions has been a major experimental and theoretical goal for decades. Such reactions often show no memory of entrance channel properties and conditions, and the dissociation can often be successfully described by statistical theories. Recent progress in state-tostate photodissociation experiments has provided large and precise databases, ¹⁻³ with which it is now possible to test, modify, and reformulate the theories. In this regard, the predissociation of NCNO has become a benchmark against which such theories can be evaluated.^{1,4-6}

Previously, we established that the CN and NO state distributions obtained following monoenergetic NCNO predissociation could be fit using phase space theory (PST) in combination with the separate statistical ensembles (SSE) method.⁴⁻⁶ As with PST alone, PST/SSE assumes that energy and angular momentum are conserved during dissociation, but also includes a restriction on the coupling between parent vibration and rotation. It is assumed that energy is not transferred between vibrational and rotational degrees of freedom. This is a very good assumption for rotationally cold molecules. The SSE restriction on parent vibrationrotation exchange is not a part of PST and is not simply taken care of by conserving the total angular momentum. For example, the PST loose transition state model for $NCNO \rightarrow CN + NO$ allows $J_{total} = 0$ to be achieved with large NCNO overall rotation offset by CN and/or NO rotations within the loose transition state. To incorporate the SSE restriction into calculations, two ensembles are considered in turn. First, product vibrational distributions are estimated from an ensemble of parent degrees of freedom which excludes parent rotation. Second, product R,T excitations are estimated for each set of product vibrational states from an ensemble that includes those parent vibrations which transform to fragment rotations and translations (i.e., the "transitional" modes), as well as parent rotations. At this point, any of several statistical methods can be used, since the physical content of the SSE restriction is in place. For example, product R,T excitations could be estimated using PST, the statistical adiabatic channel model (SACM),⁷ etc. For expansion-cooled NCNO, product vibrations are "hotter" than product rotations since the parent molecule contains modest rotational energy. In a sense, product R,T excitations are *diluted* by the low parent rotational excitation, while product vibrational excitations are not. With PST/ SSE, this occurs without exit channel barriers, i.e., nonadiabatic evolution of the transitional modes to product R,T degrees of freedom may occur. Note that for excess energies, E^{\dagger} , below the lowest product vibrational levels, there is no SSE restriction, so that PST and PST/SSE are identical. In contrast to PST, the SACM requires that parent bendingtype motions evolve adiabatically into product angular momentum states, and consequently barriers associated with the zero point and potential energies of these modes arise along the reaction coordinate.⁷ In certain systems, this model may be required in order to reconcile the experimental observations, while in others, is may not. However, the SSE method should be incorporated when treating SACM-type systems as well, and these systems might be best described by SACM/SSE, analogous to PST/SSE.

In our previous work on the photodissociation of NCNO, we saw no evidence for exit channel barriers, and found excellent agreement between experiment and PST/SSE for E^+ in the range 0-5000 cm^{-1.4-6.8} The near-threshold product state distributions are fit precisely, and we concluded that NCNO dissociation proceeds via a loose transition state in the absence of barriers. CN appearance times

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were recently measured by Knundkar *et al.* for $E^{\dagger} = 0-700$ cm⁻¹, and their results also indicate a loose transition state, albeit with some deviations from statistical behavior.⁹ Although both CN and NO internal state distributions fit statistical predictions very well, such *global* product state distributions may obscure biases that depend on the shape of the PES along the reaction coordinate. These are better discerned by looking at *correlated* distributions. For example, the distribution of NO internal states associated with a specific CN internal state may be nonstatistical, even though global CN and NO distributions are quite statistical.

In this paper, we report measurements of Doppler profiles associated with specific $CN(X^2\Sigma^+)v'' = 0$ rotational states. These line shapes are governed by the NO internal energy distributions associated with the CN states being probed. The experimental Doppler profiles are simulated quite accurately using the same PST/SSE theory that was used to fit the global CN and NO distributions, thus maintaining the excellent accord between experiment and theory noted previously.¹⁰

The dissociation mechanism can be further probed by determining the relative populations of the NO($X^{2}\Pi$) Λ -doublet components. These populations can provide information about the motions and geometry of the dissociating molecule even for slowly dissociating systems, since they probe directional properties in the molecular rather than laboratory frame.¹¹ With NCNO, we find that some planarity is preserved during dissociation, and the results are best explained by assuming that reaction proceeds on S_{0} .

Measurements of Doppler profiles for specific v'' = 0rotational states also allow us to address issues concerned with the nature of the excitation process, namely, laser-initiated radiationless transitions.¹ For example, with NCNO, statistical calculations⁴⁻⁶ as well as extrapolation of experimentally obtained dissociation rates9 indicate that at $E^{\dagger} > 2000 \text{ cm}^{-1}$, S_0 unimolecular reaction rates should be faster than parent rotation, but slower than typical vibrations. Thus, spatial anisotropy in the products may ensue, with product state distributions still being statistical except perhaps for M_{I} . On the other hand, spatial anisotropies may be reduced if the radiationless transition becomes rate limiting and/or if parent rotation takes place prior to dissociation. The former is important, since it follows that product appearance times cannot be trivially associated with S_0 unimolecular reaction rates. Product state distributions need not be compromised, since IVR on the ground PES can still be complete prior to dissociation.

NCNO was chosen as a prototypical molecule because it has many of the desirable features of other nitroso compounds,³ and furthermore, both fragments can be probed by LIF.³⁻⁵ Its $A^{1}A''(S_{1}) \leftarrow X^{1}A'(S_{0})$ absorption spectrum extends over a large part of the near-IR and visible,¹² and as a result, it was possible to study both CN and NO E,V,R,T excitations in detail for $E^{\dagger} = 0$ -5000 cm⁻¹.^{3-6,8} Following S_{1} excitation, the molecule undergoes nonradiative couplings to vibrationally excited S_{0} , either directly or with some participation of T_{1} .^{3,13} The T_{1} level density is small relative to that of S_{0} , so without large differences in coupling matrix elements, direct coupling to S_{0} will dominate.^{3,14} Recent *ab initio* calculations reveal substantial barriers to dissociation on the S_1 and T_1 surfaces (~7000 and 2100 cm⁻¹, respectively),¹⁴ and therefore it can be safely assumed that predissociation proceeds on S_0 when hv just exceeds D_0 .^{3,8} The terminal bending vibrations and out-of-plane torsion are efficient promoter modes for S_1 - S_0 couplings,^{12(b),13} and fluorescence lifetime measurements indicate that below D_0 , NCNO belong to the "small/intermediate molecule case" as defined by radiationless transitions theory.¹³

II. EXPERIMENTAL

The experimental arrangement is similar to the one described previously,⁴⁻⁶ and therefore only features pertinent to the present studies are outlined here. Premixed NCNO samples (4/1000 Torr in He) were expanded using a pulsed valve (Laser Technics, 0.5 mm diam orifice, \sim 150 μ s duration) into a fluorescence chamber maintained at a working pressure of $< 10^{-4}$ Torr. Two fluorescence chambers were used, a 20 cm cube and an octagonal chamber, the latter in experiments designed to determine spatial anisotropies in reaction products. Photolysis was achieved with the output from a YAG-pumped dye laser (Quanta Ray, DCR-1A/ PDL-1, \sim 5 ns duration, 0.5 cm⁻¹ FWHM) and the probe laser was an excimer-pumped dye laser (Lambda Physik EMG-101 MSC/FL2001, 15 ns duration ~ 0.3 cm⁻¹ FWHM), used in conjunction with an Inrad frequency doubler when detecting NO. The photolysis and probe beams were either collinear or perpendicular to each other, and the molecular beam was perpendicular to the plane containing both laser beams and the photomultiplier tube (**PMT**).

Timing was controlled by a homemade delay generator with 20 ns increments, and the delay between photolysis and probe was typically 40-80 ns. The photodissociation region was \sim 15, 20, and 40 nominal nozzle diameters downstream from the nozzle in the translational energy, Λ -doublet, and recoil anisotropy measurements, respectively. Since the effective opening of the valve used is smaller than the nozzle diameter, these distances ensure collision-free conditions on a 40–80 ns time scale, as well as efficient cooling ($T_{\rm NCNO} \simeq 5$ K). The observed LIF signals were normalized to both laser intensities, which were measured with photodiodes using sample-and-hold circuitry. The signals from 30-100 laser firings were averaged for each data point. The data acquisition system consisted of a digital oscilloscope (Nicolet Explorer III), a computer (LSI 11-23) and an A/D converter with the necessary interfaces.

NCNO was prepared by the reaction of dried AgCN with ClNO, as described previously.¹⁵ The sample was further purified by trap-to-trap distillations prior to mixing with He. *Caution: NCNO tends to explode violently when impure.*¹⁵

A. Measurements of $CN(X^2\Sigma^+)$ Doppler profiles

Nascent CN was detected in the usual way by one-photon LIF via the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition near 388 nm. Fluorescence was imaged onto a GaAs PMT (Hamamatsu



FIG. 1. Schematic of the arrangement used in the spatial anisotropy experiments. The photolysis beam, probe beam, and pulsed nozzle are mutually perpendicular, with the PMT in the plane of the laser beams at 45°. \mathbf{E}_{ph} could be set either parallel or perpendicular to \mathbf{k}_{pr} . $\mathbf{E}_{ph} \perp \mathbf{k}_{pr}$ is perpendicular to the plane of the paper. In some experiments the polarization was adjusted so that $\mathbf{E}_{ph} (\perp \mathbf{k}_{pr}) \cong \mathbf{E}_{ph} (\parallel \mathbf{k}_{pr})$ (see the text).

R943-02) through a narrow bandpass filter (Pomfret, $388.3 \pm 5 \text{ nm}$). To obtain Doppler profiles, the probe laser frequency was pressure tuned across each CN rotational line using an intracavity etalon (FSR = 1 cm⁻¹) with N₂ gas. In these experiments, the probe laser had to be set at the highest order (eighth grating order for $\lambda_{pr} \sim 388 \text{ nm}$) to obtain a linewidth $\leq 0.05 \text{ cm}^{-1}$.

Two laser configurations were used; a collinear geometry with counterpropagating photolysis and probe lasers was used routinely in the sub-Doppler measurements, while a perpendicular geometry (i.e., $k_{\rm ph} \! \perp \! k_{\rm pr}$) was used in the spatial anisotropy studies in order to achieve $\mathbf{E}_{ph} \| \mathbf{k}_{pr}$. In the latter, an octagonal chamber was used, with the PMT in the plane of the two laser beams (see Fig. 1). The photolysis laser was vertically polarized ($\mathbf{E}_{ph} \perp \mathbf{k}_{pr}$, $\mathbf{I}_{v} / \mathbf{I}_{h} > 20$) and the polarization was rotated with prism combinations to achieve $\mathbf{E}_{\rm ph} \| \mathbf{k}_{\rm pr}$. In experiments where it was important to not change alignment during the experiment, the polarization of the photolysis laser was rotated by a half-wave plate. This allowed rapid changes in polarization with little change in alignment. Unfortunately, only a 532 nm half-wave plate was available, whereas the anisotropy experiments were carried out at 514.6 nm. Consequently, complete polarization rotation could not be achieved. Instead, the polarization was rotated until \mathbf{E}_{ph} ($\perp \mathbf{k}_{pr}$) $\simeq \mathbf{E}_{ph}$ ($\parallel \mathbf{k}_{pr}$) was obtained. Doppler profiles were recorded with and without the half-wave plate in the photolysis beam, corresponding to $\mathbf{E}_{ph}(\mathbf{1}\mathbf{k}_{pr})$ $\cong \mathbf{E}_{ph}(\|\mathbf{k}_{pr}\|)$ and $\mathbf{E}_{ph}(\|\mathbf{k}_{pr}\|) = 0$, respectively.

B. NO Λ -doublet population measurements

In these experiments, the two lasers counterpropagated collinearly, and the NO fragment was detected via its $A^2\Sigma^+ \leftarrow X^2\Pi$ transition at ~225 nm. The UV fluorescence was collected through a bandpass filter (Corion 300 nm, 85 nm FWHM) onto a solar-blind photomultiplier (Hama-

matsu R166UH). Radiation near 225 nm was generated by frequency doubling using a β -BBO crystal; > 3% conversion efficiency was achieved with the beam collimated by a 1 m lens. The fundamental and 225 nm beams were separated by two Pellin–Broca prisms arranged to minimize physical walk during scanning. The probe laser intensity was maintained < 100 μ J to avoid saturation and NCNO photodissociation. Although the 300 K absorption coefficient of NCNO at 225 nm is much larger than at ~ 500 nm,¹⁶ dissociation and detection by the probe laser involves the sequential absorption of two photons, and this is largely eliminated by keeping $I_{pr} \ll I_{ph}$.

Small amounts of NO impurity proved impossible to eliminate. However, because of expansion cooling, NO contamination affects only low-J populations. Since in the Λ doublet experiments we are interested only in high-J states, impurities do not affect the observations.

III. RESULTS AND ANALYSES

A. Product state correlations

The correlation between the $CN(X^2\Sigma^+)$ and $NO(X^2\Pi)$ state distributions can be obtained from the Doppler profiles by using energy and momentum conservation. The excess energy available to the system when $CN(X^2\Sigma^+)$ is formed in the v'', N'' state is given by

$$E^{\dagger\dagger} = h\nu - D_0 - E_{\text{int}}(\text{CN}) = E^{\dagger} - E_{\text{int}}(\text{CN}).$$
 (1)

This is distributed between c.m. translation and NO($X^2\Pi$) E,V,R degrees of freedom:

$$E^{\dagger\dagger} = E_T(\text{c.m.}) + E_{\text{int}}(\text{NO}), \qquad (2)$$

where $E_T(c.m.)$ is related to $E_T(CN)$ by the mass scaling relation:

$$E_T(\text{CN}) = (m_{\text{NO}}/m_{\text{NCNO}})E_T(\text{c.m.}).$$
(3)

Thus, by recording Doppler profiles for selected values of E^{\dagger} , low-resolution NO($X^{2}\Pi$) internal energy distributions associated with specific CN states are obtained. In Fig. 2, we show Doppler profiles for selected E^{\dagger} values and CN transitions.

Although the CN $(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$ system near 388 nm is well characterized,¹⁷ some special features must be taken into account in the analysis of the Doppler profiles. First, for small J'' a Q satellite branch appears. The effect of the Qsatellite branch is important for N'' = 0 and 1, and in fact the R(0) and P(1) lines have Q components with transition probabilities that are half of those for the corresponding main branch lines.¹⁷ The satellite lines are very close in frequency to the main branch lines and are taken into account in the simulation of the Doppler profiles. Second, each rotational line is split into two spin-rotation components, F_1 and F_2 , whose separation increases with rotational energy. However, the tabulated spin-rotation constants γ_0 do not give simulated line shapes that are in good agreement with the observed ones.¹⁷ This stems in part from the fact that the published values do not have sufficient accuracy.¹⁷ Also, numerous perturbations by the $B^{2}\Sigma$ and $A^{2}\Pi$ states cause shifts and consequently deviations from the calculated splittings. Therefore, the low-N spin-rotation splittings were determined from the well-separated profiles at $E^{\dagger} = 411$ cm^{-1} , and experimental values were used in the simulations whenever possible.¹⁸ Lastly, the transition probabilities actually depend on J'', not N''.¹⁷ Consequently, the two spinrotation components are not of equal intensity, with the component of lower frequency being lower in intensity.

Another complication in the analysis is that, unlike most sub-Doppler resolution spectroscopy studies of direct photodissociation, the average E_T (CN) values involved in the unimolecular reaction of NCNO are very small, corresponding to Doppler widths not much larger than the laser linewidth [e.g., for $E^{\dagger} = 1670 \text{ cm}^{-1}$, we calculate an average kinetic energy, $\langle E_T(\text{CN},\text{N}'' = 10) \rangle = 443 \text{ cm}^{-1}$, corresponding to a FWHM linewidth of 0.09 cm⁻¹]. This makes the current experiments difficult. In order to enhance the energy resolution, we exploited the valley between the two spin-rotation branches of specific rotational lines (Fig. 2). We find that for R(7) and P(10), the spin-rotation splittings¹⁸ are comparable to the width of the Doppler profiles, and even small changes in $E_T (\sim 50 \text{ cm}^{-1})$ can be discerned as changes in the depth of the valley between the two spinrotation components. These lines were therefore used extensively in the present experiments, and we find that the fits are unique and reflect also changes in the distributions (*vide infra*).

Doppler profiles were also recorded for NCNO near dissociation threshold, and the zero kinetic energy Doppler profile was determined from the R(0) line (N'' = 0 is the only level populated significantly at threshold).⁸ The Doppler profile could be adequately fit by a Gaussian line shape with FWHM = 0.07 ± 0.01 cm⁻¹. The effect of the Qsatellite branch was included in the fit. The two main sources for the 0.07 cm⁻¹ linewidth are the laser bandwidth and the transverse velocity components of the parent molecules in the jet. The laser linewidth (0.05 cm⁻¹) was determined from the Doppler profiles of 300 K CN and was usually 0.05 cm⁻¹, although for experiments that required better resolution a laser linewidth of 0.04 cm⁻¹ was achieved.

The simulated Doppler profiles were generated as follows. First, for each excess energy and CN(N''), we obtained the c.m. kinetic energy distribution from the same algorithm that successfully predicted the global V,R state distributions in CN and NO.⁴⁻⁶ This computer program is based on PST/SSE, and is described in detail elsewhere.^{1,4-6} E_T (c.m.) was converted to E_T (CN) by Eq. (3). Second, for each recoil speed a Doppler profile was generated. The width of the line shape reflects the speed while the area is normalized to the probability of producing the specific CN(N'')





FIG. 2. $B^{2}\Sigma^{+} \leftarrow X^{2}\Sigma^{+}$ Doppler profiles of nascent CN at several excess energies. Data are indicated by points, while simulations are given by solid or broken lines as indicated in the figure. The two peaks in the R(7) and P(10)lines are F_{1} and F_{2} spin-rotation components. In these experiments the combined laser linewidth (0.05 cm⁻¹) and the width due to the transverse velocity components in the jet was 0.07 cm⁻¹.

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state. Next, we sum over the profiles for all the possible speeds in the distribution. The spin-rotation splitting is then introduced by separating the simulated profiles by their spin-rotation splitting with the appropriate weighting factors. Lastly, the simulated profiles are convoluted with the zero kinetic energy profiles. These simulations were done with $\beta_{\text{eff}} = 0$. This is reasonable for a predissociation process involving simple bond fission and was also verified experimentally as described in Sec. III B. It is noteworthy also that there are no adjustable parameters in the simulation procedure. The zero kinetic energy profile was obtained from the threshold study, and the spin-rotation splittings were determined experimentally as described above.

As can be seen from Fig. 2, when E^{\dagger} is less than that required to populate NO(v'' = 1) ($E^{\dagger} < 1860 \text{ cm}^{-1}$), the agreement with PST is very good. The calculated NO rotational distribution which is correlated with a specific CN(N'') state reflects the angular momentum constraints in the system. For example, when $J_{CN} = 0$ and the initial parent angular momentum is J_0 , a "pseudotriatomic" case arises where $|J_{NO} - L| \leq J_0 \leq |J_{NO} + L|$. When $J_{CN} > 0$, the number of open channels is computed numerically, as described before.⁴⁻⁶ The relative populations of the NO(J'') states rise initially with increasing J'', in accord with the angular momentum conservation requirements, and then



FIG. 3. Higher resolution Doppler profiles for the P(10) line obtained at (A) $E^{\dagger} = 1670 \text{ cm}^{-1}$ and (B) $E^{\dagger} = 2348 \text{ cm}^{-1}$. In these experiments the combined laser linewidth (0.04 cm^{-1}) and the width due to the transverse velocity components in the jet was 0.05 cm^{-1} (see the text). On the righthand side, Doppler profiles calculated using the PST and PST/SSE models at infinitely narrow laser linewidth are shown. These are convoluted with the experimental linewidths (shown on the left-hand side of part A) to yield the simulated spectra which are compared with the experimental data (dots). Notice that PST/SSE gives a better fit to the data at $E^{\dagger} = 2348 \text{ cm}^{-1}$ than does PST. Also, the profiles of the two spin–rotation components at $E^{\dagger} = 2348 \text{ cm}^{-1}$ appear narrower than those at 1670 cm^{-1} despite the fact that the average translational energy associated with the former is higher (see Table I and the text).

reach a constant value. The populations drop abruptly at J''_{max} determined by energy conservation. At low E^{\dagger} (<400 cm⁻¹), the plateau is never reached, while at high E^{\dagger} (>2000 cm⁻¹) most of the J_{NO} levels have equal populations.

When E^{\dagger} is larger than that required to populate the NO vibrations (e.g., $E^{\dagger} = 2348 \text{ cm}^{-1}$), PST/SSE provides a better simulation to the experimental data than does PST alone. This is consistent with the results obtained before for the global CN and NO state distributions.⁴⁻⁶ The observed Doppler profiles show a deeper valley between the spin-rotation peaks than predicted by PST. This is readily explained by the fact that at $E^{\dagger} = 2348 \text{ cm}^{-1}$, NO(v'' = 1) can be populated in addition to v'' = 0. As was shown before, PST underestimates the amount of excess energy deposited in vibrational excitation.⁴⁻⁶ A higher fraction of NO(v'' = 1) results in a correspondingly higher fraction of CN(N'') fragments with low kinetic energy and a smaller Doppler shift, thus accounting for the sharper peaks in the Doppler profiles.

The SSE restriction was put into the simulations as follows. For $E^{\dagger} > 1860 \text{ cm}^{-1}$, the NO vibrational distributions work,4,6 were taken from previous and $[\Sigma_{J''} P_{NO}(v'' = 1, J'')]_{PST/SSE} / [\Sigma_{J''} P_{NO}(v'' = 1, J'')]_{PST}$ was obtained, where $P_{NO}(v'' = 1, J'')$ is the probability of forming NO in v'' = 1 and rotational level J'', regardless of kinetic energy. We then multiplied the calculated rotational probabilities for NO(v'' = 1) by this factor, and obtained a satisfactory fit with the experimental profiles. It is assumed implicitly that the above factor is independent of J''; we doubt that a more precise scheme would change the results of the simulations at their present level of sensitivity.

In Fig. 3, we compare in greater detail the experimental and simulated CN(N'' = 10) profiles for $E^{\dagger} = 1670$ and 2348 cm⁻¹. At these energies, both the differences between the profiles and the better fit obtained using PST/SSE for $E^{\dagger} = 2348 \text{ cm}^{-1}$ are highlighted, since the experiments were carried out at the highest resolution. The laser bandwidth was narrowed to 0.04 cm^{-1} , and the contributions of the transverse velocity components in the jet were minimized by increasing the distance between the nozzle orifice and the laser intersection region, and imaging the fluorescence only from the central section of the jet where the transverse velocity components are the smallest. We thus achieved a combined laser and transverse velocity component linewidth of 0.05 cm⁻¹. In Table I we list the average kinetic energies calculated for CN(N'' = 10) at different E^{\dagger} , and note that although the Doppler profile at $E^{\dagger} = 1670$

TABLE I. Average kinetic energies (cm^{-1}) for CN(v'' = 0, N'' = 10) predicted by PST and PST/SSE.

| E^{\dagger} | $\langle E_T(CN) \rangle$ | $\langle E_{\tau}(\mathrm{c.m.})\rangle$ |
|----------------|---------------------------|--|
| 411 | 45.6 | 85.1 |
| 939 | 209.4 | 390.9 |
| 1670 | 443.3 | 827.5 |
| 2348 (PST/SSE) | 479.5 | 895.1 |
| 2348 (PST) | 615.5 | 1148.9 |

cm⁻¹, appears broader than at 2348 cm⁻¹, the average kinetic energy associated with it is slightly smaller. Thus, the *shapes* of the computed profiles are sensitive to differences in the translational energy *distributions*. We also note that although the difference between the PST and PST/SSE calculated $\langle E_T(CN) \rangle$ is only 136 cm⁻¹, the derived Doppler profiles are quite different (Fig. 3).

B. Spatial anisotropy

Recent studies of near-threshold NCNO dissociation indicate lifetimes < 10 ps for $E^{\dagger} > 600$ cm⁻¹.⁹ Since theory predicts a rapid increase of dissocation rate with energy,¹⁹ we expect unimolecular lifetimes at higher E^{\dagger} to be shorter than typical rotational periods, but longer than vibrational periods. For example, when the dissociation time is < 1 ps, the recoil anisotropy should be observable experimentally (see Sec. IV B). It is important therefore to check whether the spatial anisotropy generated by excitation with polarized light is preserved in dissociation at high excess energies. The Doppler profile for a single recoil speed can be written as $A[1 + \beta_{\text{eff}} P_2(\chi_D)]$, where $\chi_D = (\nu - \nu_0) (\Delta \nu_D)^{-1}$, ν_0 is the frequency at line center, v is the probe frequency, $\Delta v_D = (v/c)v_0$ is the maximum Doppler shift, and $\beta_{\rm eff} = \beta P_2(\cos \alpha)$ where β is the anisotropy parameter and α is the angle between \mathbf{E}_{ph} and \mathbf{k}_{pr} . The simulated profile is derived by summing over the profiles for all possible speeds in the distribution as described in Sec. III A.²⁰ For the case of a linear molecule with a perpendicular transition moment, $\beta_{\rm eff} = \beta = -1$ when $\mathbf{E}_{\rm ph} \| \mathbf{k}_{\rm pr}$. When the photolysis polarization is arranged such that the parallel and perpendicular polarization components are equal [i.e., $\mathbf{E}_{ph}(\perp \mathbf{k}_{pr})$ $\cong \mathbf{E}_{ph}(\parallel \mathbf{k}_{pr})$], $\beta_{eff} = -1/4$.²⁰ As discussed in Sec. II, these two polarization schemes were chosen, since they allowed rapid changes in polarization with minimum changes in alignment during the experiment.

In Fig. 4, experimental results are compared to simulations for the two polarization schemes described above. Both profiles are best represented by simulations with $\beta_{\rm eff} \sim 0$ showing no evidence of spatial anisotropy. For comparison, we also show simulations with $\beta_{\rm eff} = -1/4$ and -1. It is evident that despite the inherently low sensitivity of the simulations to small changes in $\beta_{\rm eff}$, the experimental results are best represented by $\beta_{\rm eff} = 0 \pm 1/4$.

FIG. 5. NO Λ -doublet population ratios in the ${}^{2}\Pi_{1/2}$ (O) and ${}^{2}\Pi_{3/2}$ (\bullet) states obtained at $E^{\dagger} = 2348 \text{ cm}^{-1}$. $\Pi(A'')$ and $\Pi(A')$ refer to the singly occupied $p\pi$ orbital perpendicular to and in the plane of rotation of NO, respectively. J_{max} is the highest rotational level allowed by energy conservation.

C. NO Λ -doublet populations

Since the NO ground state is $^{2}\Pi$, one can obtain information about dissociation dynamics relative to the molecular frame from the Λ -doublet populations.¹¹ For sufficiently high rotational states [Hund's case (b) limit] one Λ -doublet component corresponds to the singly occupied $p\pi$ orbital aligned with the nuclear rotational angular momentum, while the other component corresponds to the $p\pi$ orbital lying in the plane of rotation (POR). We adopt here the notation of Alexander et al.,²¹ in which the $p\pi$ orbitals lying in the POR and perpendicular to it are designated $\Pi(A')$ and $\Pi(A'')$, respectively. The advantage of using A-doublet populations is that they probe properties of the dissociating molecule that evolve within the molecular rather than laboratory frame, and distinct preferences for populating one A-doublet component have been reported for many molecules.¹¹ However, this geometrical interpretation is valid only for high-J NO states, 11(b) and mechanistic implications apply to only the high-J subset of product molecules. Also, when extensive electron rearrangements accompany the fragmentation process, correlation between the initial excitation and the fragment electronic configuration is not straightforward.

FIG. 4. Sub-Doppler resolution spectra of the CN $B^2\Sigma^+ \leftarrow X^2\Sigma^+ P(10)$ line at $E^{\dagger} = 2348$ cm⁻¹ obtained using linearly polarized lasers. In (A) the photolysis laser horizontal and vertical polarization components are equal, while in (B) the photolysis laser is polarized horizontally (parallel to \mathbf{k}_{pr}). Simulations obtained by using different values of β_{eff} are also displayed.

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J″ **(**Ω) $E^{\dagger} = 2348 \text{ cm}^{-1}$ $E^{\dagger} = 2875 \, \mathrm{cm}^{-1 \, \mathrm{b}}$ 300 K NO 17.5 (1/2) 0.95 ± 0.13 22.5 (1/2)0.98 22.5 (3/2)1.01 0.99 0.93 ± 0.15 0.95 ± 0.08 27.5 (1/2)(3/2) 0.99 1.09 0.87 29.5 30.5 1.00 1.00 (1/2)1.21 31.5 1.08 1.01 (1/2)1.32 1.08 32.5 (1/2)1.33 1.13 33.5 (3/2)1.39 1.41 1.02 34.5 1.29 1.42 1.07 (1/2)35.5 (1/2)0.96 1.24 0.98 37.5 (1/2)1.20 0.95

TABLE II. $\Pi(A')/\Pi(A'')$ population ratios for NO A doublets.^{*}

^a $\Pi(A')$ and $\Pi(A'')$ denote π lobes perpendicular and parallel to **J**, respectively.

^bSignals are ~0.2 as large as at $E^{\dagger} = 2348$ cm⁻¹; S/N is thus lower.

NO was probed using $A^{2}\Sigma^{+} \leftarrow X^{2}\Pi$ one-photon LIF. The transition dipole moment μ_{NO} is perpendicular to the internuclear axis, so for Q-branch lines μ_{NO} is parallel to J while for P- and R-branch lines it is perpendicular to J.²² Thus, Q-branch lines probe $\Pi(A'')$, while P- or R-branch lines probe $\Pi(A')$. The R_{11} and Q_{11} branches were used to probe $\Pi(A')$ and $\Pi(A'')$, respectively, for the ${}^{2}\Pi_{1/2}$ state, while R_{22} and Q_{22} were used for ${}^{2}\Pi_{3/2}$. (P_{11} and P_{22} are overlapped by other branches.) Figure 5 shows the ratio $\Pi(A')/\Pi(A'')$ for $E^{\dagger} = 2348 \text{ cm}^{-1}$. For low J'', the ratio is ~1, while for high J'', a noticeable deviation from the statistical limit is observed, with $\Pi(A')$ more populated than $\Pi(A'')$.

Several experimental errors can affect $\Pi(A')/\Pi(A'')$ ratios: (i) since Q-branch transitions are stronger than Rbranch transitions,¹⁷ saturation can increase apparent $\Pi(A')/\Pi(A'')$ ratios, (ii) errors can be introduced when converting line intensities to populations, and (iii) with LIF detection, bandpass filters can cause collection efficiencies to be different for R- and Q-branch lines originating from the same lower state. Therefore, A-doublet populations were determined from LIF spectra of 300 K NO samples, and $\Pi(A')/\Pi(A'') = 1$ was observed for all J's, indicating that systematic errors do not affect the NCNO A-doublet measurements.

The Λ -doublet population ratios were measured at two excess energies, 2348 and 2875 cm⁻¹. The results are summarized in Table II, and we find that for J'' > 30.5, $\Pi(A')/$ $\Pi(A'') > 1$. In earlier experiments, we failed to detect this small effect, since two-photon LIF detection was employed and the S/N ratio was not good enough at the high J's, whose relative populations are small.^{12(b)}

IV. DISCUSSION

A. Correlated product state distributions

One of the goals of experimental studies of state-to-state unimolecular reactions is the provision of databases with which theory can be tested. $PST/SSE^{1,4-6,23}$ has been used successfully to model the dissociation of $NCNO^{4-6}$ and ketene²⁴ on ground potential energy surfaces, while SACM⁷ has been used to fit OH distributions obtained following overtone excitation of H₂O₂.²⁵ Although these theories are all statistical in nature, they treat differently those vibrational degrees of freedom in the parent that evolve into product R,T excitations. According to the SACM, parent bendingtype motions evolve adiabatically into product angular momentum states, and consequently barriers arise along the reaction coordinate.⁷ In PST, the available phase space is determined only by energy and angular momentum conservation.²³ During bond rupture, several vibrations, rotations, and hindered rotations of the parent may evolve nonadiabatically into translations, rotations, and orbital motions of the fragments. Thus, barriers do not appear in the exit channel of a loose transition state reaction. Experimentally, the differences between SACM and PST are best manifest near D_0 and at the high-J tails of the fragment rotational distributions. SACM predicts higher thresholds for high rotational states of the fragments,^{24(b)} and colder rotational distributions.^{25(b)}

The CN Doppler profiles reported here are sensitive to the associated NO internal energy distributions, and even subtle differences between PST and PST/SSE can be discerned. The same model that was used to simulate the global CN and NO state distributions is successful in modeling the Doppler profiles. It has no adjustable parameters, and the results confirm that the PST/SSE model works also for the correlated distributions. We find less R,T excitation and more vibrational excitation than predicted by PST at excess energies where product vibrations can be excited. At lower E^{\dagger} , there is excellent agreement with PST, which assumes that only E and J are conserved with no further constraints. Doppler profiles for high rotational states of CN are correlated with low NO(J'') states, indicating that the orbital angular momentum of the separating fragments is directed oppositely to the CN rotational angular momentum, since the NO angular momentum is low.

In summary, although the interpretation of the data may not be unique, the correlated distributions show excellent agreement with PST/SSE, with no hint of barriers. They confirm our previous conclusions which were based on the global CN and NO distributions.^{3–6,8} Recent results by Moore and co-workers on the jet-cooled laser predissociation of ketene on S_0 lead to the same conclusion.^{24(b)} A formulation which takes account of the nonadiabatic evolution of the transitional modes has been published recently by Marcus,²⁶ and comparisons with NCNO data show good agreement.²⁷

The Λ -doublet population ratios can shed light on the motions and geometry of the dissociating molecule. Since dissociation occurs from S_0 which is of A' electronic symmetry, and $CN(X^2\Sigma^+)$ is also of A' symmetry, we expect NO($X^{2}\Pi$) to be of A' symmetry if dissociation is planar. In this case, the singly occupied NO $p\pi$ orbital will be preferentially oriented in the POR.¹¹ The NCNO ground state is planar, and the small preference for the $\Pi(A')$ A-doublet component suggests that this is preserved to some extent during dissociation. One should be aware however that the Λ -doublet measurements can only be thus interpreted for high rotational levels of NO [Hund's case (b)].¹¹ In fact, in our measurements, $\Pi(A')/\Pi(A'') > 1$ is observed only for NOJ" levels that are close to the maximum allowed by energy conservation. The relative population of these levels is $\leq 10\%$ for E^{\dagger} 's of 2348 and 2785 cm⁻¹. These high NO(J") states are associated with CN fragments with very small rotational angular momentum. The small subset of NO fragments with J'' near the thermochemical limit is thus correlated with CN fragments which are hardly rotating. The NCNO transition state associated with this subset may be viewed as pseudotriatomic, with almost no torque exerted on

the CN. Thus, the propensity for planar dissociation for these molecules is not surprising.

B. Spatial anisotropy in fast unimolecular reactions

Although both calculations and measurements indicate that the unimolecular lifetimes of NCNO at $E^{\dagger} > 600 \text{ cm}^{-1}$ are < 10 ps,⁹ we do not observe significant spatial anisotropy in the product recoil distributions even at $E^{\dagger} \sim 3000 \text{ cm}^{-1}$. All Doppler profiles are best modeled assuming $\beta_{\text{eff}} \sim 0$. Several reasons may account for this lack of spatial anisotropy: (i) the unimolecular reaction rate is slower than the rate of parent rotation, (ii) the radiationless transition rate is slower than the rate of parent rotation, and (iii) nonplanar motions during dissociation cause loss of directionality of v with respect to μ . Some evidence that the overall dissociation rate is not much faster than a rotational period derives from the fact that we observed relatively sharp features in the absorption spectrum even at $E^{\dagger} \sim 5000 \text{ cm}^{-1.4}$ These sharp features are associated with CN and NO stretching modes, and do not show substantial broadening.⁴ In order to distinguish between the contributions of the different possible factors, one needs to examine the relevant time scales involved in the dissociation.

1. Parent rotation during dissociation

The effect of parent rotation during dissociation has been examined by several authors, ^{20,28} who showed that ro-

FIG. 6. Schematic description of nonradiative processes and decay widths relevant to S_1-S_0 couplings above and below D_0 . The laser pulse duration is 5 ns, corresponding to a coherent width of $\sim 10^{-3}$ cm⁻¹. The bottom inset describes the situation for $E^{\dagger} < D_0$. The Ψ_n are molecular eigenstates whose decay widths γ_n are $< 5 \times 10^{-5}$ cm⁻¹. We assume $\rho_l = 100$ per cm⁻¹. The upper inset describes the situation for $E \gg D_0$, where γ_l is given by the decay width of the S_0 levels ($\gamma_l = 5$ cm⁻¹ for $\tau_{diss} = 1$ ps). Because of the broad decay width, many levels in S_0 overlap and are excited coherently. We assume $\rho_l = 300$ per cm⁻¹.

tation can decrease β substantially, and the limiting value for long lifetimes is -1/4. NCNO is a near planar, prolate top, and has two relevant rotational constants, $A \simeq 5 \text{ cm}^{-1}$ and $B \simeq C \simeq 0.2 \text{ cm}^{-1.12(b)}$ Of these, rotation around the C axis (perpendicular to the molecular plane) does not affect the orientation of μ relative to \mathbf{E}_{ph} , and thus has no effect on the recoil anisotropy even for slow dissociation. B-axis rotation is slow, and a calculation following Jonah^{28(a)} indicates that it would hardly affect β . For A-axis rotation, the loss of anisotropy depends on the geometry of the molecule. For a near prolate top with a large A/(B,C) ratio, rotation about the A axis would cause the velocity vector to precess about the A axis with a relatively small angle, causing only a modest reduction in anisotropy. Thus for $\tau_{diss} = 1$ ps, the loss of anisotropy should be modest. One should bear in mind however that with expansion cooled samples, $J_{\rm NCNO} = 0-6$ and the extent of the initial alignment of μ is smaller for these low J levels.

2. Unimolecular reaction rates

NCNO lifetimes were measured by Khundkar et al.9 for $E^{\dagger} = 0-600 \text{ cm}^{-1}$. Although the shortest lifetime measured was ~ 10 ps, both extrapolation of the data and theoretical estimates yield lifetimes ≤ 1 ps at $E^{\dagger} > 2000$ cm⁻¹. Thus, at the highest excess energies employed in this study, some anisotropy should have been preserved if the rate limiting step had been the unimolecular rate. However, Khundkar et al. observe rates which become progressively slower than those predicted by PST as the excess energy increases, and in addition exhibit some structure which cannot be explained by simple statistical theories.⁹ Although no unique explanation for these observations has been offered, one of the mechanisms that has been advanced is a progressive tightening of the transition state as the excess energy increases, leading to slower dissociation rates than those expected in cases involving a very loose transition state.⁹

3. Radiationless transition rates

Since the excitation method used in this study involves initial excitation to S_1 followed by dissociation on S_0 , a careful look at the nonradiative couplings between S_1 and S_0 is in order. A schematic diagram of the relevant states and linewidths is given in Fig. 6. If the barrier to dissociation on T_1 is ~2100 cm⁻¹,¹⁴ dissociation at $E^{\dagger} < 2100$ cm⁻¹ must proceed on S_0 . Indeed, our spectroscopic studies show numerous perturbations between S_1 and S_0 even near the S_1 band origin, with bending and out-of-plane motions being the promoter modes.^{12(b)} We have shown that below D_0 , NCNO's behavior is characteristic of the "small/intermediate molecule case" (i.e., $\tau_{\rm fl} > \tau_{\rm rad}$), and we find $\tau_{\rm fl} > 100$ $\mu {\rm s}$.¹³ We note however, that a short dephasing component cannot be ruled out.

The nature of the nonradiative processes changes markedly with excitation below and above D_0 . Below D_0 , only a very small number of molecular eigenstates, Ψ_n , are excited coherently²⁹

$$\Psi_n = a_s^n \phi_s + \sum b_l^n \phi_l , \qquad (4)$$

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where ϕ_s is the optically accessible state (S₁), and ϕ_i are levels of the lower electronic states coupled to ϕ_s . The coherence width of a temporally smooth 5 ns pulse is $\sim 10^{-3}$ cm^{-1} , and it is unlikely that pulsations under the envelope of our laser pulse will result in a coherence width exceeding 10^{-2} cm⁻¹. The density of vibrational states in S₀, ρ_1 , is 50– 280 per cm⁻¹ between the S_1 origin and D_0 .¹³ The number of effectively coupled states may be lower due to symmetry restrictions, and we have not taken into account the rotational density of states. Nevertheless, $\rho_{\text{eff}} = 100 \text{ per cm}^{-1}$ appears to be a reasonable estimate. The width of the level γ_n is governed by the fluorescence lifetime of the mixed states, leading to $\gamma_n \sim 5 \times 10^{-5}$ cm⁻¹ (~3 MHz). Thus, below D_0 , $\Delta E_l \ge \Delta E_{\rm coh} > \gamma_n$, where ΔE_l is the average energy spacing between the bath states (assuming $\Delta E_l \approx \Delta E_n$), and $\Delta E_{\rm coh}$ is the coherence width.²⁹ Under these conditions, coherent excitation of a single molecular eigenstate can be achieved (the "small molecule" case).²⁹ This situation is shown schematically in the lower inset in Fig. 6.

The situation changes strikingly when $E^{\dagger} \ge D_0$. Because of fast dissociation, γ_l is now determined by the unimolecular decay rate, and for $\tau_{diss} = 1$ ps, $\gamma_l = 5$ cm⁻¹ (see top inset in Fig. 6). Thus, assuming $\rho_{eff} \sim 300$ per cm⁻¹, we calculate that ≈ 180 levels can be coherently excited. This situation has been termed "weak mixing by efficient damping" in radiationless transition theory,³⁰ and has been shown to apply when $\gamma_l \ge \Delta E_l$ and $V_{sl} \le \gamma_l/2$, where V_{sl} is the coupling matrix element between S_1 and S_0 .³⁰ Hence, due to the large decay width, the statistical limit of irreversible decay is effectively achieved, and for this "large molecule limit", the internal conversion time τ_{IC} can be estimated using Fermi's Golden rule:

$$\Gamma_{\rm IC} = 2\pi |V_{sl}|^2 \rho_{\rm eff} , \qquad (5)$$

where $\Gamma_{\rm IC}$ is the decay rate of the optically accessible state. Assuming $\rho_{\rm eff} = 300$ per cm⁻¹, we get $\tau_{\rm IC} \ge 5$ ps for $V_{sl} \leq 0.02 \text{ cm}^{-1}$. This value of the coupling matrix element can be favorably compared with the value of $\sim 0.1 \text{ cm}^{-1}$ estimated for S_1 - S_0 coupling near the S_1 origin.^{12(b)} Therefore, for $\tau_{\rm diss} \sim 1$ ps the conditions for weak mixing by efficient damping are fulfilled, and the radiationless transition rates may indeed become rate limiting at high E^{\dagger} . Consequently, the overall dissociation rate will be slower than predicted by the statistical theories, and a loss of anisotropy may ensue. Measurements of the rates of unimolecular reactions initiated by radiationless transitions are therefore limited only to those excess energies where the dissociation rate is the limiting step (i.e., low E^{\dagger}). The product state distributions, however, are not affected by changes in the nonradiative rates, and should remain statistical.

4. Nonplanar motions during dissociation

Another factor that may be responsible for the loss of spatial anisotropy is nonplanar motions during the dissociation. NCNO is planar both in the S_0 and in the S_1 states, and the $S_1(A^{-1}A^{-n}) \leftarrow S_0(X^{-1}A^{-1})$ transition dipole moment μ is perpendicular to the molecular plane.^{3,12(b)} Thus, interactions of A^{-n} symmetry promote the couplings with S_0 . However, any motion with A^{-n} symmetry will also tend to change the direction of μ relative to the laboratory frame, thereby reducing the observed spatial anisotropy.

The direction of μ with respect to E_{ph} may also be altered as a result of Coriolis couplings and mixings which change the direction of the K rotational vector with concomitant loss of fluorescence polarization.^{31,32} The time frame for such fluorescence depolarization, however, is longer than a rotational period, and this effect is unimportant on the time scales of interest in these experiments.³³

V. CONCLUSIONS

(1) The Doppler profiles for specific $CN(X^2\Sigma^+)$ rotational states yield NO state distributions which are correlated with specific CN rotational states. The Doppler profiles can be nicely fit by PST/SSE, and the correlated distributions do not show evidence of dynamical biases or exit channel barriers. The results confirm previous conclusions, based on the *global* CN and NO state distributions that the SSE method is required to describe the state distributions when product vibrations are accessible. They also support a mechanism where the parent rotations, hindered rotations and bending motions can evolve nonadiabatically into product rotations and translations. We conclude, therefore, that in some cases (e.g., NCNO, ketene) dissociation can proceed from a loose transition state in the absence of channel barriers.

(2) The Λ -doublet population ratios in NO reveal some preservation of planarity during the dissociation, at least for the subset of fragments where the NO is rotationally excited to near the thermochemical limit and the CN fragment is cold. A preferential orientation of the $\Pi(A')$ Λ -doublet component is to be expected for predissociation on S_0 .

(3) All the Dopper profiles can be fit with $\beta = 0 \pm 1/4$, even at high E^{\dagger} where unimolecular reaction is faster than parent rotation. The lack of anisotropy can be attributed to one or more of the following processes: (i) unimolecular reaction rates slower than those predicted by statistical theories or extrapolated from experimental results at low E^{\dagger} , (ii) radiationless transition rates that are slower than parent rotation rates, (iii) nonplanar motions during the dissociation, and (iv) reduced initial alignment. More experiments (e.g., time resolved measurements at high E^{\dagger}) are needed to sort out the contributions of the different mechanisms to the loss of recoil anisotropy.

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