Vector and scalar correlations in statistical dissociation: 
The photodissociation of NCCN at 193 nm

Simon W. North and Gregory E. Hall
Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973-5000

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Nascent Doppler profiles of CN ($X^2\Sigma^+$) fragments from the 193 nm photodissociation of NCCN have been measured using high-resolution transient frequency modulated (FM) absorption spectroscopy. This new method is highly suited for Doppler spectroscopy of nascent photoproducts. The experimental line shapes suggest an asymptotic available energy of 5300±100 cm$^{-1}$ and are well described by a model in which the available energy is partitioned between a statistical reservoir (4700 cm$^{-1}$) and a modest exit barrier (600 cm$^{-1}$). We have determined state dependent $v\cdot j$ correlations. A trend of $j$ becoming increasingly perpendicular to $v$ for the higher rotational states is in accord with phase space theory, although the observed correlations are more than twice as strong. The $v\cdot j$ correlations can be quantitatively modeled by further restricting the phase space model with an approximate conservation of the $K$-quantum number, the projection of total angular momentum about the linear axis of NCCN. Global rotational and vibrational product distributions have also been measured. The highest accessible rotational states are underpopulated, compared to a phase space calculation. The global vibrational distribution is substantially colder than the phase space theory predictions. Vibrational branching ratios for coincident fragments have been measured as a function of the detected CN state from a close analysis of high signal-to-noise Doppler profiles. The correlated vibrational distribution, $P(v_1,v_2)$, shows an excess of vibrationless coincident fragments, at the expense of dissociation to give one ground state and one vibrationally excited CN fragment. The correlated formation of two vibrationally excited CN fragments is as likely as the phase space prediction, yet the formation of $v=2$ is strongly suppressed. The fragment vector and scalar correlations provide a highly detailed view of the loose transition state typical for reactions well described by statistical reaction theories. © 1997 American Institute of Physics. [S0021-9606(97)01801-1]

I. INTRODUCTION

Dissociation and association reactions occurring on barrierless potential energy surfaces make up an important class of reactions for which statistical theories provide a simple first order description. Not only rates, but product distributions can be calculated as a function of total energy and angular momentum when the transition state is so loose as to be well approximated by weakly interacting fragments, and exit channel interactions are minimal.1,2 In the age of laser chemistry, ground state dissociation of small molecules following optical excitation has been extensively studied. Several particularly well-studied molecules can now be considered as prototypes for statistical dissociation: CH$_2$CO, NCNO, CF$_3$NO, NCCN, and H$_2$O$_2$, for example.3 Photoproduct state distributions, unimolecular decay rates, photofragment excitation spectra, and Doppler spectra have been measured for many of these and other systems, leading to a fairly thorough catalog of observations to compare to theory. Until recently, however, the question of angular momentum polarization had not come up for any of these statistical dissociations.

The measurement of angular correlations between parent transition moment, $\mu$, recoil velocity, $v$, and fragment rotation, $j$, in photodissociation4,5 has generally been undertaken to explore dynamical aspects of direct photodissociation, i.e., those photodissociations which show obvious signs of nonstatistical behavior. In such cases, the vector correlations provide a signature of the directed forces and torques that are responsible for product excitations, as well as an indication of the excited state symmetry. When there are no specific dynamical effects, and the product state distributions are well described by statistical partitioning, it is not necessarily the case that the vector correlations vanish, however. Recently, vector correlations were observed by Wu and Hall6 for selected states of the CN ($X^2\Sigma^+$) photofragments from the 193.3 nm dissociation of NCCN. The CN fragments were observed to possess modest $v\cdot j$ correlations, with an increasing preference for $j$ to be perpendicular to $v$ at higher rotational states. (We retain the conventional notation of “$v\cdot j$ correlation,” suppressing the small distinction between $N$, the integer rotational angular momentum of CN, and $J$, its half-integer total angular momentum, including spin.) Measurements by Wodtke and co-workers7 have also provided a similar example of state-dependent, perpendicular $v\cdot j$ correlations in the CO photofragments from the 308 nm dissociation of ketene.

Only in the last year have practical means for predicting the statistical expectation of such correlations been described. Klippenstein and Cline8 have performed Monte Carlo sampling of a classical phase space of fragment angular momenta and conjugate orientations at an assumed transition state to calculate center-of-mass frame $v\cdot j$ correlations.
within the approximations of phase space theory (PST)\(^9\) for NCCN, CF\(_2\)NO, and 2-chloro-2-nitrosopropane. We have shown\(^10,11\) that identical results can be obtained by a more conventional quantum state counting approach, i.e., when the PST is transformed to a helicity state representation.\(^12\) Applications to NCCN, CH\(_2\)CO, and NCNO have been described.\(^11\) Vector correlations which arise solely as a consequence of angular momentum conservation can be treated by this reformulated PST, which is intuitive and computationally efficient for small molecules.

In the modern study of molecular photodissociation, a dominant strategy has been to attempt to deduce the molecular dynamics of fragmentation from the experimentally determined partitioning of the available energy among the photofragment degrees of freedom.\(^1–3,13\) Chemical branching ratios and energy distributions of the fragments, as determined by various spectroscopic methods, provide valuable scalar information, that is, properties characterized by magnitudes, but not directions. Connections between qualitative features of the dissociative potential energy surfaces and the energy disposal in the fragments allow several broad classes and trends to be distinguished, each with a few classic molecular examples which have been worked out, often in great detail. An even more complete characterization of molecular fragmentation than a full state distribution for each fragment can in principle be obtained by measuring coincident state distributions. For a dissociation producing two fragments, this is a set of probabilities for producing pairs of fragments in simultaneously specified quantum states. The global state distribution of each fragment is a sum over all possible coincident fragment states, obliterating the information carried by the correlations, which may often provide a more telling account of the dissociative event. There are presently several ingenious methods of measuring such scalar correlations, and there are recent reviews on the subject.\(^11\)

Despite the increased insight that may be derived from the correlated state distributions, relatively few molecules have been investigated at the correlated state level, even fewer in which both fragments are more complex than single atoms. Eres, Gurnick, and McDonald,\(^15\) in a bold and farsighted experiment, used fluorescence sheet imaging to measure state resolved velocities in NCCN photodissociation, the same system we are now reinvestigating. Other examples include CH\(_3\)ONO,\(^16,17\) H\(_2\)O\(_2,18,19\) NCNO,\(^20\) 2-chloro-2-nitrosopropane,\(^21\) CH\(_2\)CO,\(^7\) and several van der Waals dimers.\(^22–24\)

The ultraviolet spectroscopy,\(^25–27\) photophysics, and photochemistry\(^6,15,28–32\) of cyanogen, NCCN, have been extensively studied. \textit{Ab initio} calculations of ground and excited states of NCCN have been reported,\(^33–35\) including the isomers CNCN and CNNC.\(^36–38\) The relevant excited states of NCCN and energetics are shown schematically in Fig. 1. Rotationally resolved absorption bands in the vibronically allowed \(^1\Sigma_u^+\rightarrow\Sigma_x^-\) transition occur below 226 nm. A threshold for the detection of CN fragments has been reported at 212.2 nm,\(^32\) which coincides with the beginning of a reduction in the \(^1\Sigma_u^-\) fluorescence lifetime and quantum yield, and an onset of a continuum in the absorption spectrum. Bands of the \(^1\Delta_g\rightarrow^3\Sigma_g^+\) transition begin below 210 nm. At 193.3 nm, the excitation is from the \(^1\Sigma_g^+\) ground state to the \(^1\Delta_g\) and \(^1\Sigma_u^-\) states, neither of which correlates directly to a pair of ground state CN fragments. The fragmentation must therefore be a predissociation, either via the ground state or the \(^1\Sigma_g^+\) state. The triplet state should have a substantial barrier,\(^34\) so it has been assumed that the dissociation proceeds by internal conversion to and dissociation on a barrierless \(^1\Sigma_g^+\) ground state.

\[
\text{NCCN}(^1\Sigma_g^+)+193.3\text{nm} \rightarrow \text{NCCN}(^1\Delta_g,^1\Sigma_u^-) \rightarrow \text{NCCN}(^1\Sigma_g^+) \rightarrow 2\text{CN}(X^2\Sigma^+).
\]

The state distributions of the CN fragments have been measured and compared to PST calculations at 193.3 nm\(^15,28,29\) and at wavelengths closer to the dissociation threshold.\(^30,31\) The agreement was considered satisfactory, although more recent Doppler measurements in this laboratory\(^6\) indicated that the statistically partitioned energy is less than the full asymptotic energy, and that the vector correlations were too strong to be statistical.\(^11\)

Recently we have developed a time-resolved spectrometer based on a frequency modulation (FM) scheme that permits the measurement of real-time kinetics of chemical processes with submicrosecond time resolution and high sensitivity.\(^39–43\) Historically, FM spectroscopy has been applied primarily to the measurement and identification of weak spectral features.\(^42,43\) FM methods provide sensitivity near the shot-noise limit, which in our experience corresponds to signal-to-noise enhancements of 10 to 50 over our previous dual-beam absorption methods.\(^6,44\) Application to the measurement of Doppler-broadened photofragment line shapes has not previously been attempted, despite several apparent advantages, even compared to laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization spectroscopy (REMPI). By acquiring transient waveforms as a function of probe laser tuning, a full time-dependent spectrum can be acquired in a single scan of probe laser tuning.
laser frequency, instead of the single time-delayed spectrum, as would be acquired with two pulsed lasers in a pump-probe scheme. Further advantages can often be realized by the low background in the FM absorption method, compared to LIF or REMPI. While all three methods are in principle zero background techniques, the intrinsically more sensitive LIF and REMPI techniques are sometimes limited in practice by background ions, parent fluorescence induced by the photolysis laser, scattered light, or power-broadening effects, which can prevent attainment of their theoretical quantum limits. The absorption methods can take advantage of large illuminated volumes in a long cell, and furthermore, the use of a single mode laser with a linewidth \(<1\) MHz eliminates the necessity for deconvolution of laser linewidth from the present experimental measurements.

Despite these advantages of FM spectroscopy, the application of FM methods to the measurement of Doppler-broadened line shapes has not previously been pursued. Two obstacles have restricted the use of FM spectroscopy in the analysis of nascent line shapes. The first has been the requirement for accurate determination of the absolute phase of the detected FM signal. The FM line shapes contain absorption and dispersion components in quadrature. The underlying velocity distributions, however, are most directly deduced from spectra that depend only on the frequency-dependent absorption, and not the associated dispersion. We have described a two-channel detection scheme, using an I & Q demodulator, which gives both an absolute phase calibration, and a procedure to combine the two channel data to give a phase-corrected spectrum uncontaminated by the dispersion component. The second obstacle has been a method to recover the Doppler-broadened absorption spectrum from the phase corrected finite difference FM signal. Our previous work described a recursion relation for this transformation, and discussed some of its stability and noise properties. We have recently found an alternate approach with less noise sensitivity, described in the Appendix to this paper. The results and analysis of this paper are the first application of the FM line shape analysis to the investigation of molecular photofragmentation.

Equipped with a superior set of Doppler profiles from FM measurements, and the new theory of statistical vector correlations as a guide, we are now in a position to extend our earlier study of the vector and scalar correlations in NCCN dissociation at 193.3 nm.

II. EXPERIMENT

The general features of the Brookhaven FM spectrometer have been described in some detail previously, and the modifications required to extract accurate Doppler line shapes were the subject of a recent publication. Briefly, a cw Ti:sapphire ring laser pumped by an Ar-ion laser and operating near 800 nm was frequency modulated at \(\omega_m=200\) MHz. The beam was attenuated to \(\approx40\) mW in a 3–4 mm diameter beam in the sample to avoid saturation of the CN molecular transitions, and steered through a 1.5 m single-pass glass cell. The beam from an excimer photolysis laser running at 193.3 nm overlapped the counterpropagating probe beam. The unfocused excimer laser provided fluences of 2–5 mJ/cm\(^2\) to the sample. The ground state \((X^2\Sigma)\) CN radicals, produced from the excimer photolysis, were probed in the \(\Delta v=+2\) bands of the \(A^2\Pi\rightarrow X^2\Sigma\) system. A slow flow (2 sccm) of cyanogen (Matheson) was maintained with a partial pressure of 50 mTorr. Nascent signals were selected from the first 100 ns following photolysis. No appreciable relaxation of the line shape occurs in this time scale. Thermalized lines were obtained by adding Ar to a total pressure of 1.0 Torr, and selecting spectra 3–4 \(\mu\)s after photolysis.

The two-channel detection scheme for phase calibration and correction of transient FM line shapes has been described previously. The differential absorption or retardation of the two sidebands by the photochemically generated CN radicals was detected as a 200 MHz beat note on a fast photodiode with phase sensitive detection in an I & Q demodulator. The demodulator, which consists of 0° and 90° power splitters and a pair of double-balanced mixers, resolves the input signal into in-phase (I) and quadrature (Q) components. The output signals were filtered using 70 MHz low-pass Bessel–Thompson filters to eliminate the 2\(\omega_m\) component at 400 MHz. The transient I and Q signals were each averaged in the digital oscilloscope over multiple excimer laser shots. The averaged I and Q transient waveforms were archived in a lab computer, the ring laser was moved one scan increment, 50 MHz in these experiments, and new averages were acquired until the laser had been scanned across the selected CN rotational line. All data shown were acquired with 50 shot averaging at each step of the carrier frequency. The resultant data set is a pair of I and Q of two dimensional arrays of signal voltage versus time and laser frequency, from which the time-dependent line shapes and intensities can be selected for subsequent analysis. A proper linear combination of the I and Q components eliminates the contribution of the dispersion to the line shape.

Figure 2 shows representative FM line shapes (I channel) at three selected time delays following photolysis. The top panel is nascent data from 50 to 100 ns, the middle panel is selected from 1.2 to 1.3 \(\mu\)s delay, corresponding to partially relaxed line shape, and the lower panel shows a thermalized line shape. The upper left corner of each panel shows the corresponding Doppler profile, obtained using the phase correction procedure as described in Ref. 45 followed by reconstruction from the finite difference spectrum as described in the Appendix. The sequence of phase corrections and transformations of FM spectra to obtain nascent Doppler profiles and rotationally thermalized spectra for relative intensity measurements is summarized here to establish the nomenclature. Two channels, (I&Q) of time-dependent FM signals are acquired. Relaxed spectra are fit to Gaussian absorption and dispersion line shapes to give an accurate phase angle calibration. This phase angle is used to rotate the nascent I and Q spectra into pure absorption and dispersion components. The absorption component is both integrated and differentiated numerically with respect to frequency. The transformation to Doppler profile consists of the integral with a small correction proportional to the derivative. This is
what we mean by ‘phase-corrected and transformed Doppler profile.’

Line positions for the CN $A \ ^{3} \Pi - X \ ^{3} \Sigma ^{+}$ rotational transitions of the (2-0), (3-1), and (4-2) vibrational bands were calculated from the spectroscopic constants of Cerný et al.,\textsuperscript{46} which were sufficiently accurate to permit unambiguous spectral assignments.

III. RESULTS

A. Global rotational distribution

There have been several previously published measurements of CN state distributions based on $B$-$X$ LIF following ArF laser photodissociation.\textsuperscript{15,28,29} These measurements differ substantially, however, and apparently include some measurements distorted by partial saturation and/or relaxation. We have measured the relative populations of selected rotational states in CN ($v = 0$) from the areas of phase corrected and transformed Doppler profiles, plotted in Fig. 3A as open circles. The rotational quantum number $N$ denotes the total angular momentum of CN excluding spin. The distribution is generally similar to the one reported in the molecular beam fluorescence imaging study of Eres, Gurnick, and McDonald\textsuperscript{15} (hereafter referred to as EGM), shown as solid symbols in Fig. 3(A), but substantially hotter than those reported by other workers. In other previous studies,\textsuperscript{28,29} the CN rotational distributions were characterized by rotational temperatures of 900 K and 540–800 K for a variety of sample conditions. For comparison, the linear region of a Boltzmann plot describing the present measurements and those of EGM gives an effective rotational temperature of about 2200 K. We have measured the relative populations of the highest rotational levels with particular care, since it is the falloff in the populations of these levels which is the most characteristic feature of these broad distributions. A Boltzmann plot of the highest rotational levels is shown in Fig. 3(B), compared again to the jet-cooled data of EGM.\textsuperscript{15} The two data sets have been normalized at $N = 30$ to highlight the small difference in the falloff, which appears to reflect only the increase in NCCN rotational energy at room temperature compared to the supersonic expansion, and no significant hot band contribution to the absorption at 193 nm in the room temperature sample.

B. Global vibrational distribution

To determine the global distribution of vibrational states, we measured relative intensities of rotational lines in the (2-0), (3-1), and (4-2) bands of the $A$-$X$ system under partial relaxation conditions, where translation and rotational degrees of freedom have been thermalized, but the nascent vibrational distribution is not significantly altered. Transient
verify that in the 3–5 the recombination, wall reactions and relaxation except to is slower still. We have not attempted to fully characterize signal is hundreds of times slower, and vibrational relaxation is slower still. The asterisks denote unassigned lines.

NCCN with 1.0 Torr added Ar. The disappearance of the CN distribution by EGM. Additional comparisons were made 0.15 obtained from a summation of the nascent rotational lines, the relative vibrational populations can be determined from the intensities of a rotationally thermalized absorption lines, where the 1

$P_{1}(28.5)$ $P_{1}$

$R_{2}$ $Q_{2}$

FIG. 4. FM spectrum of the CN ($A$ $^2\Pi$-$X$ $^2\Sigma^+$) transition in the region of the (4–2) $R_2$ bandhead. Assignments are derived from the spectroscopic constants given in Ref. 46. The asterisks denote unassigned lines.

signals confirm that translational and rotational relaxation is achieved within 2 $\mu$s for samples containing 50 mTorr of NCCN with 1.0 Torr added Ar. The disappearance of the CN signal is hundreds of times slower, and vibrational relaxation is slower still. We have not attempted to fully characterize the recombination, wall reactions and relaxation except to verify that in the 3–5 $\mu$s wait before measuring the vibrational ratios, there is no significant vibrational relaxation.

Under conditions of thermalized rotation and translation, the relative vibrational populations can be determined from the intensities of a rotationally thermalized absorption lines, given by

$$I(N,v) \approx q_{v'v} \cdot S_{J'J} \cdot \exp \left( -\frac{E_{rot}}{kT} \right) P(v),$$

where $q_{v'v}$ is the ($A$ $^2\Pi$–$X$ $^2\Sigma^+$) Franck–Condon factor, $S_{J'J}$ is the line strength factor, and $P(v)$ is the probability of forming fragments in a particular vibrational state. The FM measurements were phase corrected, transformed to absorption, and integrated to give raw $I(N,v)$ values. The ratio of intensities of two lines in different vibrational bands, after correcting for both the photolysis and probe power, then yields the ratio of product vibrational states through Eq. (2). In order to determine the $v=1;v=0$ branching ratio, thermalized $R_1$ 15.5 lines were measured in the (3–1) and (2–0) vibrational bands, yielding 0.151$\pm$0.006, where the 1 $\sigma$ error is obtained from the comparison of numerous scans. The result agrees precisely with the value of 0.15 obtained from a summation of the nascent rotational distribution by EGM. Additional comparisons were made between several other rotational lines in the (2–0) and (3–1) bands for independent confirmation and all were found to be quantitatively consistent with this ratio. In order to verify our assumption of rotational thermalization, we also compared the intensities of various $R_1$ lines from the (2–0) band, and found their ratios to be accurately described by a 300 K Boltzmann distribution.

The available energy at 193.3 nm is sufficient to form CN ($X$ $^2\Sigma^+$) fragments with two quanta of vibrational energy. Previous studies, however, were unable to detect CN ($v=2$) products from cyanogen photodissociation at 193.3 nm using $B$-$X$ LIF. Figure 4 shows a partially thermalized CN ($A$-$X$) FM spectrum scanning a region near the (4–2) $R_2$ bandhead. The series of $R_2$ and $Q_2$ satellite lines corresponding to CN ($v=2$) fragments from $N=1$ to $N=9$ are indicated by the comb calculated from the spectroscopic constants given by Cerny et al. The two most intense lines to the red of the bandhead are the $P_{2}(28.5)$ and $P_{2}(28.5)$ lines of the (3–1) band. Quantitative comparisons between selected thermalized $v=1$ and the $R_2$ $v=2$ lines using Eq. (2) yield a $v=2;v=1$ branching ratio of 0.02$\pm$0.01. The $v=1;v=0$ and $v=2;v=1$ vibrational branching ratios can be used to obtain the global vibrational distribution, $P(v)$. The final results are given in the experimental row of Table I.

### Table I. Global vibrational populations for CN ($X$ $^2\Sigma^+$) from NCCN dissociation at 193.3 nm.

<table>
<thead>
<tr>
<th>$v$</th>
<th>Experiment</th>
<th>PST</th>
<th>PST ($\Lambda=1$)</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.87$\pm$0.02</td>
<td>0.759</td>
<td>0.225</td>
<td>0.016</td>
</tr>
<tr>
<td>1</td>
<td>0.13$\pm$0.02</td>
<td>0.241</td>
<td>0.028</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.003$\pm$0.001</td>
<td>0.670</td>
<td>0.275</td>
<td>0.050</td>
</tr>
</tbody>
</table>

$^aE_{\text{av}}=4700$ cm$^{-1}$.

The absence of laboratory-frame alignment of CN product velocity was first determined by EGM who observed symmetric rings of fluorescence following photodissociation of jet-cooled NCCN at 193.3 nm. Wu and Hall later reported no measurable differences in photofragment Doppler line shapes in two geometries, also consistent with an isotropic velocity distribution. We have also compared a few CN rotational lines in a transverse multipass cell with the transient FM Doppler method. The observed similarity of the Doppler profiles measured in two geometries leads to a would not be possible if the velocity anisotropy parameter, $\beta$, deviated from 0 by as much as $\pm$0.04.

Although a small rotational alignment of CN fragments was reported by Lin et al. at 206.1 nm, more extensive subsequent work by Wannenmacher et al. concluded that the alignment was negligible at multiple excitation energies closer to the dissociation threshold than at 193.3 nm. We have looked for rotational alignment at 193.3 nm, where faster dissociation might be expected to preserve some laboratory-frame anisotropy, by measuring the intensity ratio of the nascent (2–0) $Q_1$ 13.5 line and its $R_{12}$ satellite for two different photolysis polarization directions. A nonvanishing rotational polarization would cause one line to increase and the other to decrease in intensity as the photolysis polarization is changed. We observe no systematic difference, and conclude that there is only very small, if any, laboratory anisotropy to the fragment rotational polarization.
No differences in populations of the $F_1$ and $F_2$ spin components ($J=\frac{N}{2} \pm \frac{1}{2}$) of the ground state CN photoproducts are expected, or observed. A few Doppler lines of $F_2$ levels were measured for comparison to the corresponding $F_1$ levels, and no differences have been found in their nascent line shapes. In this study we have arbitrarily selected $F_1$ components of CN to measure Doppler profiles. In the $^2\Pi - ^2\Sigma$ transition, the $R_1$ and $P_2$ branches have no satellites, so when choosing a set of $Q$ and $P$ or $R$ lines to measure, the $F_1$ levels are best probed with $Q_1$ and $R_1$ lines, while the $F_2$ levels would be best probed with $Q_2$ and $P_2$ lines. The satellite lines of $Q$ branches are incompletely resolved for nascent rotational levels below about $N=15$. The most accurate line shapes are thus obtained for the higher rotational levels, although the partially blended lines can still be analyzed, taking advantage of the line symmetry, and the simultaneous acquisition of thermalized Doppler lines to determine the satellite splitting and the line centers of the two components. We measured a selection of lines to probe a range of accessible rotational levels in vibrational states $v=0, 1,$ and 2, primarily choosing those for which the corresponding $R_1$ and $Q_1$ lines were free of accidental blended lines, including the $^{13}\text{C}^{14}\text{N}$ lines, which we can observe in natural abundance.

D. Experimental speed distributions and the v·j correlation

Earlier work in this laboratory by direct transient absorption disclosed systematic differences in the $Q$- and $R$-branch Doppler profiles of CN photofragments from the 193.3 nm dissociation of NCCN that were attributed to a $v\cdot j$ correlation. We have now remeasured this system with transient FM Doppler spectroscopy to verify the technique in comparison with previous work, and to provide an improved and extended set of data for comparison to PST.

The analysis of Doppler-broadened line shapes is particularly simple for the case of single photon detection as first demonstrated experimentally by Hall and Wu, using the bipolar moment theory of Dixon. The Doppler profile for an ensemble with a single laboratory speed, $v$, can be written as

$$D_v(w) = \frac{1}{2v} \left[ g_0 + g_2 P_2 \left( \frac{w}{v} \right) + g_4 P_4 \left( \frac{w}{v} \right) \right],$$

where $w$ is the component of the laboratory velocity along the probe direction, $P_2$ and $P_4$ are Legendre polynomials, and the coefficients $g_i$ depend on five low-order bipolar moments of the correlated velocity and angular momentum distribution, as defined by Dixon. If the velocity distribution is isotropic and the rotational alignment is negligible, $g_0$ is unity, $g_2$ simplifies to a single term sampling only the $v\cdot j$ correlation, and $g_4$ vanishes. The Doppler profile for an isotropic distribution of velocities, $v^2 f'(v)$ can then be written as

$$D'(w) = \int_{-\infty}^{\infty} \frac{1}{2v} \left[ 1 - h^{(2)}(2) \right] g_0 P_2(w/v) v^2 f'(v) dv,$$

where the primes denote laboratory-frame distributions, and the depolarization factor has the value $h^{(2)} = 1$ for absorption on a $Q$-branch line, and $h^{(2)} = -J(2I+3)$ for absorption on an $R$-branch line. The laboratory velocity-dependent bipolar moment $\beta^{(2)}(22)_v$ is the ensemble average of $P_2(\vec{v} \cdot \vec{j})$ for each laboratory speed $v$. A particular advantage of making these measurements with a frequency modulated single frequency laser (linewidth < 1 MHz) is that the convolution over the laser line shape is negligible; only the accurately known Gaussian broadening due to the thermal velocity distribution of the parent molecules relates the center-of-mass distributions to the experimentally measured Doppler profiles.

The laboratory frame speed distribution, $v^2 f'(v)$, can be determined from a composite of two measured lines. The observed Doppler profiles are normalized to unit area and added with a $Q:R$ weighting of 1:(2+3$J$) to remove the effect of the $v\cdot j$ correlation, giving the isotropic composite Doppler profile, $D_v(w)$, for which the apparent $\beta^{(2)}(22)_v$ vanishes. This composite Doppler profile represents the angle-averaged projection of the laboratory speed distribution $v^2 f'(v)$ onto a line. The laboratory speed distribution can be recovered by differentiation.

$$v^2 f'(v) = -2v \left( \frac{dD_v(w)}{dw} \right)_{w=v}.$$ (5)

Nascent Doppler profiles have been measured for selected $Q$ and $R$ branch lines of numerous rotational states for CN in vibrational levels 0 and 1. The weighted combinations to give $D_v(w)$ are analyzed in Sec. IV B to probe the total energy balance, and in Sec. IV E-G to probe the coincident state distribution.

The difference between normalized $Q$-branch and $R$-branch lines probing the same initial state is a measure of $\beta^{(2)}(22)_v$. Methods have been described to extract center-of-mass speed distributions and vector correlations from a set of

<p>| Table II. Laboratory-frame velocity averaged $v\cdot j$ correlations ($\beta^{(2)}(22)_v$) for CN fragments from NCCN. Detected CN fragments in selected rotational state $N$, vibrational state $v$ = 0. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>$v$ = 0;</th>
<th>$N$ = 13</th>
<th>$N$ = 17</th>
<th>$N$ = 24</th>
<th>$N$ = 30</th>
<th>$N$ = 35</th>
<th>$N$ = 40</th>
</tr>
</thead>
<tbody>
<tr>
<td>PST*</td>
<td>-0.01</td>
<td>-0.02</td>
<td>-0.05</td>
<td>-0.07</td>
<td>-0.10</td>
<td>-0.13</td>
</tr>
<tr>
<td>$\Lambda$ = 1*</td>
<td>-0.05</td>
<td>-0.06</td>
<td>-0.10</td>
<td>-0.14</td>
<td>-0.21</td>
<td>-0.29</td>
</tr>
<tr>
<td>Expt.</td>
<td>-0.04±0.03</td>
<td>-0.08±0.02</td>
<td>-0.09±0.02</td>
<td>-0.15±0.02</td>
<td>-0.19±0.02</td>
<td>-0.21±0.02</td>
</tr>
<tr>
<td>-----------------</td>
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<td>-----------------</td>
<td>-----------------</td>
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<td>-----------------</td>
<td>-----------------</td>
</tr>
</tbody>
</table>

*State distributions calculated using $E_{rot}$ = 4700 cm$^{-1}$, center-of-mass velocities calculated assuming additional 600 cm$^{-1}$ relative translational energy.
TABLE III. Laboratory-frame velocity averaged v-j correlations \(\langle \beta^2(2) \rangle_v \) for CN fragments from NCCN. Detected CN fragments in selected rotational state \(N\), vibrational state \(v\) = 1.

<table>
<thead>
<tr>
<th>(v = 1)</th>
<th>(N = 16)</th>
<th>(N = 21)</th>
<th>(N = 24)</th>
<th>(N = 28)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PST (^a)</td>
<td>-0.02</td>
<td>-0.04</td>
<td>-0.05</td>
<td>-0.07</td>
</tr>
<tr>
<td>(\Lambda = 1)</td>
<td>-0.10</td>
<td>-0.11</td>
<td>-0.15</td>
<td>-0.23</td>
</tr>
<tr>
<td>Expt.</td>
<td>-0.08±0.02</td>
<td>-0.13±0.02</td>
<td>-0.17±0.02</td>
<td>-0.19±0.02</td>
</tr>
</tbody>
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\(^a\)State distributions calculated using \(E_{\text{vib}} = 4700\) cm\(^{-1}\); center-of-mass velocities calculated assuming additional 600 cm\(^{-1}\) relative translational energy.

Doppler profiles, using orthogonal polynomial fitting and analytic deconvolution and inversion using the fit coefficients.\(^{16,51,52}\) To compare to earlier work, however, we can characterize the v-j correlations quite accurately with a simpler, approximate, separable form, in which the velocity-dependent \(\beta^2(2)\) is replaced by its average value, \(\langle \beta^2(2) \rangle_v \). Using the experimentally determined speed distribution from Eq. (5) and a single adjustable parameter, \(\langle \beta^2(2) \rangle_v \), all of the measured Doppler profiles can be well fit by Eq. (6):

\[
D'(w) \approx \frac{1}{2v} \left[1 - h(w)\right] \times \langle \beta^2(2) \rangle_v \cdot P_2(w/v) |w^2f'(v)dv.
\]

Figure 5 shows a selection of \(Q\)- and \(R\)-branch Doppler profiles and the best fits using Eqs. (5) and (6) for CN rotational states in \(v = 0\). Figure 6 similarly shows selected data and fits for CN rotational states in \(v = 1\). The weak \(v = 2\) lines do not extend to high enough \(N\) to measure \(Q\) lines sufficiently resolved from their satellites to allow an accurate measurement of the vector correlations. The velocity-averaged v-j correlations are summarized in Tables II and III. These measurements and analysis can be compared directly with the previously reported transient absorption Doppler spectroscopy.\(^6\) The present vector correlations are within the cited error bounds of the previous work, although a trend for the \(N, v = 1\) CN states to be more strongly polarized than the corresponding \(N, v = 0\) states is now clear.

IV. ANALYSIS AND DISCUSSION

A. Phase space theory and global distributions

The specialization of phase space theory to the case of a pair of diatomic fragments has been previously described.\(^{8,11,53,54}\) According to PST, the probability of forming a coincident \(j_2, v_2\), state of CN, given a detected state \(j_1, v_1\), is given by

\[
P(j_2, v_2; j_1, v_1, E, J) = \frac{N(j_2, v_2; j_1, v_1, E, J)}{N(E, J)},
\]

where \(N(j_2, v_2; j_1, v_1, E, J)\) is the number of states with these quantum numbers and \(N(E, J)\) is the total number of states consistent with a fixed total energy and angular momentum. The total state count can be computed by\(^3\)
where the integer counting indices include the space-fixed
the PST predictions. A previously published PST fit to the
are well described by this model, although the measured dis-
compare with the jet-cooled data. The low rotational states
find that these parameters also overestimate the population of
barrier,
the high rotational states in the jet-cooled data, although the
larger deviations at the higher rotational states are observed. The discrepancies could be ascribed to deviations from PST, the rotational distributions. The PST prediction for vibrationally excited CN exceeds our measurement in a room temperature sample by about a factor of 2 (see Table I). The population of $v=2$ is lower than the PST prediction by an even larger margin.

The failure of PST to accurately predict product vibrational distributions, while often providing excellent agreement with experimental rotational distributions, is well documented. One modification of the theory that has been shown to give better agreement with vibrational distributions in some cases is the separate statistical ensembles (SSE) method of Wittig and co-workers. The SSE method assumes that product vibrations become adiabatic sooner than rotation, and uses two separate ensembles to calculate the vibrational and rotational energy distributions. The SSE vibrational distribution is equivalent to the vibrational prior:

$$P(v) = \frac{E_{\text{avail}} - E_{\text{vib}}}{\sum_{E_{\text{vib}}=0}^{E_{\text{vib}}=0} [E_{\text{avail}} - E_{\text{vib}}]}. \tag{9}$$

The rotational distributions within each vibrational channel are calculated using PST. SSE is, therefore, equivalent to PST in the absence of product vibrations but yields hotter vibrational distributions than PST above vibrational threshold. Table I includes a row of vibrational populations predicted by the SSE method, to compare with the restricted helicity PST and experimental populations. Since the measured populations are colder than PST, the SSE modifications to PST actually increase the discrepancy with experiment in the case of NCCN.

Another limit to consider is the Franck–Condon mapping of vibrational states of the parent molecule and the dissociated fragments. The CN stretching frequencies and bond lengths in ground state NCCN are very similar to those of free CN, suggesting that the fragment vibrational distributions should mirror those of the parent. If the Franck–Condon mapping is strictly obeyed, the colder-than-statistical fragment vibrational distributions could only come from colder-than-statistical CN stretching in the parent molecule. Interestingly, the strongest vibronic band near 193.3 nm in NCCN has been assigned by Huang as the $1^3\Sigma_u^+$ transition to the $A^3\Sigma_u^+$ state containing three quanta of CN symmetric stretching ($v_J$). One would not be surprised to lose most memory of the mode-selective excitation in the course of internal conversion and dissociation, but the ini-
tially excited CN stretching modes apparently cool even beyond the statistical limit.

B. Dissociation energetics

Rather than attempting to fit the state distributions by adjusting the available energy, assuming PST is precisely realized, we use the state-resolved velocity distributions to test the total energy balance. The maximum center-of-mass velocity of a state-selected fragment immediately gives a value for the available energy if the internal energy of the coincident fragment extends down to zero. The approximate fit of previously measured global state distributions to PST encourages us to use the PST coincident state distribution as first approximation to model the lab frame kinetic energy distributions, testing the total energy balance. Phase space theory was used to calculate the coincident ro-vibrational state distributions $P(j_2,v_2;j_1,v_1)$ for each detected state, $j_1,v_1$ with trial values of the available energy.

The state distributions were converted to center-of-mass speed distributions, $P(v,j_1,v_1,E,J)$, using energy and linear momentum conservation relations. These center-of-mass speed distributions were averaged over the room temperature Boltzmann distribution of parent rotational states, which affects both the available energy and angular momentum constraints, and then convolved with the parent velocity distribution to obtain laboratory speed distributions for each detected state. The calculated laboratory distributions, $v^2f(v)$, were then finally converted to the corresponding isotropic Doppler profiles using

$$D_0(v) = \frac{1}{2} \int_{|v|}^{\infty} v^2 f(v) dv,$$

and compared to the experimental composite Doppler profiles. Figures 7(A) and 7(B) show such forward convolution fits to the detected $v=0, N=40$, and $v=1, N=24$ line shapes, where the absence of coincident $v=1$ fragments simplifies the analysis. In each case, energy conservation furthermore limits the range of coincident rotational states to those that are globally well described by PST. The open circles represent the experimental data, and the dot-open and dash curves are PST calculations using an available energy of 4600 cm$^{-1}$ and 5300 cm$^{-1}$, respectively. Previous work in this laboratory had suggested an asymptotic available energy closer to 5300 cm$^{-1}$, based on the Doppler profiles, although the state distributions are significantly colder than a PST distribution with 5300 cm$^{-1}$ of available energy. Figure 7 shows the calculated PST Doppler profiles to be far narrower than the experimental measurements for either trial available energy. Qualitatively similar discrepancies are observed for all detected rotational states. The flat-topped Doppler profiles imply a lack of high $N$ coincident fragments. Very satisfactory fits, shown as the solid lines, can, however, be obtained by calculating the state distributions with PST using an available energy of 4700 cm$^{-1}$, but then computing center-of-mass velocities with a larger total available energy of 5300 cm$^{-1}$, as previously suggested by Wu and Hall.

Very recent ab initio calculations at the QCISD (T)/6$-311G(3df)$ level of theory have been specifically optimized to determine the NCCN dissociation energy. The reported C–C bond dissociation energy of 132.8 ± 2 kcal/mol corresponds to 5253 cm$^{-1}$ available energy at 193.3 nm. This would be consistent with Huang, Barts, and Halpem’s threshold measurements if the threshold is identified not with the asymptotic energy, but rather the top of a small barrier to recombination. Changes in the size of this 600 cm$^{-1}$ exit barrier as small as ±100 cm$^{-1}$, with a compensating change in the statistical component, produce noticeably poorer fits to the Doppler profiles, if we assume that the exit barrier potential energy is completely converted to translation. This partitioning of the asymptotic energy into a statistical reservoir and a small repulsive energy release is consistent with the vast majority of the experimental data, both the $v,j$ correlations to be described in the next section, and the state-resolved speed distributions.

C. Calculation of statistical $v,j$ correlations

A prescription for calculating the statistical expectation of the $v,j$ correlation has been recently presented using both classical and quantum phase space theory. For the sake of completeness the quantum state counting method we use will be briefly summarized.
Instead of working in the traditional basis of the original PST we count states in the helicity basis where \( j l \) quantum numbers are replaced by \( \lambda_1 \) and \( \lambda_2 \), the projections of \( j_1 \) and \( j_2 \) on the relative velocity axis. The state count in the helicity basis can be expressed as

\[
N'(E, J) = \sum_{v_1, j_1, \lambda_1, v_2, j_2, \lambda_2} \Theta[E - E_1(v_1, j_1)] - E_2(v_2, j_2)] \times \Theta(J - |\lambda_1 - \lambda_2|).
\]

(11)

The angular momentum conservation constraints involving \( j \) and \( l \) in the traditional state count [Eq. (8)] have been replaced by upper and lower bounds on the total helicity, represented as the Heaviside function of \( J - |\lambda_1 - \lambda_2| \). It is to be understood that the summations over projection numbers \( \lambda_i \) are bounded by \( \pm j_i \). The normalized probability of forming the detected fragment in ro-vibrational state \( v_1, j_1 \) with a particular helicity \( \lambda_1 \) in coincidence with ro-vibrational state \( v_2, j_2 \) is given by

\[
p'(\lambda_1; E, J, v_1, j_1, v_2, j_2) = \frac{(2J+1) \times \Theta[E - E_1(v_1, j_1) - E_2(v_2, j_2)]}{N'(v_1, j_1, v_2, j_2; E, J)} \times \sum_{\lambda_2} \Theta(J - |\lambda_1 - \lambda_2|),
\]

(12)

where the primes in Eqs. (11) and (12) indicate a temporary neglect of the centrifugal barrier. Small corrections to include the exact effect of the centrifugal barrier are performed, as described in our previous work.\(^{11}\) The desired theoretical \( v \cdot j \) correlation at each center-of-mass velocity, corresponding to a specific \( v_2, j_2 \) coincident state, is simply the second Legendre moment of the corrected and normalized distribution of helicity states, \( p(\lambda_1; E, J, v_1, j_1, v_2, j_2) \):

\[
\langle P_2(\hat{\mathbf{v}} \cdot \hat{\mathbf{j}}) \rangle = \sum_{\lambda_1 - j_2} \rho(\lambda_1) P_2(\frac{\lambda_1}{\sqrt{j_1(j_1+1)}})
\]

(13)

A comparison of the theoretical results to the present experiments requires a transformation from center-of-mass to laboratory frame, degrading the \( v \cdot j \) correlations due to the thermal distribution of parent velocities.\(^{11}\) The azimuthally averaged addition (AAA) theorem\(^{60}\) permits evaluation of the laboratory \( v \cdot j \) correlation in terms of the center-of-mass \( (u \cdot j) \) correlation, and a center-of-mass to laboratory factor, provided \( j \) is azimuthally symmetric about the center-of-mass velocity, \( u \). The Boltzmann average over parent velocities can be performed analytically,\(^{61}\) giving

\[
\beta^0_{(22)}(u) = \frac{\beta^0_{(22)}(22, j_2, L_{22}) I_{1/2}[v/u, \sigma^2]}{I_{1/2}[v/u, \sigma^2]},
\]

(14)

which is the \( v \cdot j \) correlation as a function of laboratory velocity \( v \) for each \( j_2 \) state with its center-of-mass velocity \( u \). \( I_{1/2} \) and \( I_{5/2} \) are modified spherical Bessel functions, \( \sigma^2 = (k_B T/m) \), and \( \beta^0_{(22)}(22) \) is the center-of-mass \( u \cdot j \) vector correlation for a specific \( j_2 \) coincident state. The desired velocity-dependent \( v \cdot j \) correlation in the laboratory frame, \( \beta^0_{(22)}(22) \), is obtained by a weighted sum over coincident states.\(^{11}\) An average of the laboratory velocity-dependent \( v \cdot j \) correlation for each parent \( J \), over both the laboratory speed distribution and a Boltzmann distribution of parent \( J \), yields the final \( \langle \beta^0_{(22)}(22) \rangle \) for each coincident vibrational channel. The contributions from coincident \( v = 0 \) and \( v = 1 \) fragments were combined using the \( v = 1: v = 0 \) vibrational branching ratios determined in Sec. IV E below, which, however, makes only a small difference compared to the PST vibrational branching ratios. The final results are listed in Tables II and III in the rows labeled PST and compared to the experimental values in Fig. 8(A). The calculated average \( v \cdot j \) correlations are at least a factor of 2 less than the experimentally determined values, as previously noted.\(^{8,11}\) We show in the next section that this difference is entirely consistent with a restriction on the total helicity, which makes the state counts resemble those obtained for an ensemble of very low total angular momentum.

**D. The low helicity restriction**

The axial recoil limit for dissociation is approached when the kinetic energy of recoiling fragments significantly...
Exceeds the rotational energy of the precursor molecule.\(^{62,63}\)
In this limit, the recoil axis can be identified with the molecular axis, and the total fragment helicity can be identified with the body-fixed projection of total angular momentum along the axis of a linear molecule. Ground state cyanogen is linear and, even for a rotationally warm sample, has no component of angular momentum along its linear axis. Upon excitation to the \(^{1}\Sigma_u^+\) or \(^{1}\Delta_u^+\) states, a single quantum of vibrational angular momentum is transferred, populating states of \(\pi\) vibronic symmetry, with a unit projection of total angular momentum on the linear axis: \(K=1\). The matrix elements mediating internal conversion do not couple states with \(\Delta K>1\), and the rate of \(K\) scrambling in the ground state prior to dissociation is an open question. Relatively efficient \(K\) scrambling, due to Coriolis mixing in energetic symmetric and asymmetric top molecules, is invoked to describe the high-resolution stimulated emission pumping spectra of small molecules such as acetylene\(^{64}\) and formaldehyde.\(^{65}\)

The relevant time scales for this \(K\) mixing in the bound molecules is many nanoseconds in the case of the fluorescence-dip experiments,\(^{64,65}\) whereas the ground state cyanogen lifetime prior to dissociation is unlikely to be more than a few rotational periods. If the dissociation is faster than \(K\) mixing, the total helicity of coincident CN pairs will be limited to small integers, even if the total angular momentum is high. The hypothesis of \(K\) conservation is, in any case, worth testing.

The restriction of \(K\), or total helicity, \(\Lambda\), to low values is easily incorporated into the helicity state counting algorithm, simply replacing \(K\) for \(J\) as the upper bound on the total helicity:

\[
N'_{\text{linear}}(E,J) = \sum_{v_1,j_1,\Lambda_1,v_2,j_2,\Lambda_2} \Theta[E-E_1(v_1,j_1) - E_2(v_2,j_2)] \times \Theta(K - |\Lambda_1 - \Lambda_2|).
\]

Assuming the optically selected \(K=1\) is fully conserved gives the low helicity limit of PST. The thermal average over \(J\) in this limit has a much smaller effect than in the full PST. The available energy is broadened by the distribution of parent rotational energy, and the centrifugal barrier has a somewhat larger effect for high \(J\), but the coincident state distribution and a \(v,j\) correlation closely resemble unrestricted PST at \(J=0\). Tables II and III have \(v,j\) correlation entries in the rows labeled “\(\Lambda=1\)" which have been obtained in this way. The differences between \(v,j\) correlations in PST with full 300 K averaging, and PST restricted to \(\Lambda=1\) at 300 K can be seen in Fig. 8B, which also shows the present measurements. It can be seen that the deviations between PST and our observed \(v,j\) correlations are described very well by the low helicity restriction. Test calculations, relaxing this restriction to \(\Lambda=5\), for example, show little change, and fit the measured \(v,j\) correlations as well as a strict restriction to \(\Lambda=1\).

A similar plot was shown in our recent work,\(^{31}\) anticipating the present result, but with two differences. First, the previous calculations assumed 4700 cm\(^{-1}\) of available energy, but no exit barrier. The additional 600 cm\(^{-1}\) of translational energy included in the present calculation reduces the thermal degradation and results in higher calculated \(v,j\) correlations, especially for those detected states with significant internal energy. Second, the state-dependent vibrational branching ratios, assumed to follow PST in our initial study, have been found to deviate substantially from the PST prediction. The calculated \(v,j\) correlations now use the measured rotational state-dependent vibrational branching ratios, instead of the PST vibrational branching ratios.

One might worry that the change in state counts and product state distributions implied by a restricted helicity constraint could alter the arguments accompanying Fig. 7 concerning the dissociation energetics. While the global state distributions are rotationally colder as a result of the helicity restriction, the coincident state distributions for high internal energy fragments are not strongly affected. The calculated solid curves shown in Fig. 7 with or without a \(\Lambda=1\) restriction are indistinguishable. Thus, the conclusions regarding the dissociation energy and the size of the exit barrier are unchanged. The effects of the helicity restriction on the global vibrational distribution are similarly minor, as can be seen by comparing the restricted and unrestricted helicity PST rows in Table I.

### E. State-dependent vibrational branching ratios

The strength of Doppler resolution for characterizing scalar properties of a fragmentation is not in determining the global state distributions, but the correlated distributions, as revealed by the state-resolved speed distributions. In particular, the composite Doppler profiles can give estimates for \(P(v_2|v_1,N_1)\), the vibrational distribution of the coincident CN for each measured rovibrational state \(v_1,N_1\). We adopt the labeling notation for the photodissociation

\[
\text{NCCN} + 193.3 \text{ nm} \rightarrow \text{CN}(N_1,v_1) + \text{CN}(N_2,v_2),
\]

where fragment 1 is the spectroscopically detected fragment in rotational state \(N_1\) and vibrational state \(v_1\). The coincident fragment 2 will have a distribution of internal energies revealed by the velocity distribution of fragment 1. While there is a potential ambiguity arising from isoeNERGETIC pairs of states with lower \(N_2\), \(v_2=1\) and higher \(N_2\), \(v_2=0\), prior knowledge that the global rotational state distributions are close to statistical and that the global vibrational distributions are not, encourages forward convolution fitting of the composite Doppler profiles, using PST to describe the coincident rotational state distributions, adjusting only the vibrational branching ratios. A comparison with direct inversion to center-of-mass speed distributions using techniques described by Taages, Cline, and Leone\(^{51}\) yields similar conclusions.

To help visualize the correlated state distributions and the nature of the Doppler measurements, consider Fig. 9, which depicts as contour plots the PST joint distribution \(P(N_1,N_2)\) in each square representing the coincident vibrational states, \(v_1,v_2\). The total volume under the surface in each square is the total probability of the corresponding vibrational channel, plotted using experimental values to be...
derived in Sec. IV F below. The shape of the contour lines in each square depicts the negative $N_1, N_2$ correlation imposed by energy conservation. The total measured rotational distribution for each $v_1$ is a projection onto the $N_1$ axis of the joint distribution, summing over all coincident $v_2$ and $N_2$ states. The solid lines represent this total projection, the global rotational distributions for $v_1 = 0, 1, 2$. The dotted lines show the partial contributions for each coincident $v_2$ state. The indistinguishability of the two CN fragments requires that the plots have reflection symmetry about the diagonal from the upper left to the lower right, although the off-diagonal coincident vibrational channels need not in general have identical rotational distributions for the vibrationally distinct fragments.

We attempt to determine the state-dependent vibrational ratios from the composite Doppler profiles by forward convolution. Partial contributions to the composite Doppler profiles due to coincident $v_2 = 0$ and $v_2 = 1$ channels are calculated separately. The $v_2 = 1$ coincident channel is slower, and makes a narrower contribution to the total Doppler profile than the $v_2 = 0$ contribution. The detailed shape of the Doppler contribution of each vibrational channel is calculated from the helicity-restricted PST and energetics deduced from the Doppler profiles of those states for which only one coincident vibrational channel is open. The asymptotic energy has been taken to be $5300 \text{ cm}^{-1}$ with $4700 \text{ cm}^{-1}$ available to partitioning according PST and $600 \text{ cm}^{-1}$ added to the center-of-mass translational energy. The simulated laboratory-frame Doppler profiles for separate $v_2 = 0$ and $v_2 = 1$ channels were then combined using a single adjustable parameter representing the $N_1$-dependent $v_1 = 1: v_2 = 0$ ratio and compared to the experimental composite line shape. Figure 10(A) shows the optimum decomposition of the experimental $v_1 = 0, N_1 = 24$, composite Doppler profile into partial contributions from coincident $v_2 = 0$ and $v_2 = 1$ channels. Phase space theory with restricted helicity predicts a $v_2 = 1: v_2 = 0$ ratio of 0.56 for this state; the best fit has a ratio of 0.25, about half the PST value. The vibrational branching ratio for detected state $v_1 = 1, N_1 = 16$ is illustrated in Fig. 10(B). In this case, the restricted helicity PST predicts a $v_2 = 1: v_2 = 0$ ratio of 0.25; the corresponding forward convolution Doppler profile is shown as a solid line, which provides a satisfactory fit to the data. If there were no $v_2 = 1$ channel, as had been argued,28 the Doppler profile would be noticeably broader. Similar decompositions of the composite Doppler profiles into partial contributions of coincident vibrational states have been performed for a range of detected states. The minor $v_2 = 2$ coincident channel, which is energetically inaccessible for all but the lowest energy $v_1 = 0$ rotational states detected, was not included.

The summary of state-dependent $v_2 = 1: v_2 = 0$ ratios determined in this way is presented in Fig. 11 for the detected $v_1 = 0$ (upper panel) and $v_1 = 1$ (lower panel) rotational states.
The solid lines are the $\Lambda=1$ PST predictions. We find for $v_1=0$, that the probability of forming a coincident $v_2=1$ state drops off at lower $N_1$ than the PST limit. In contrast, the $v_1=1$, $v_2=1$ channel behaves exactly as predicted by PST. These experimental $N_1$-dependent $v_2$ ratios were used in Secs. IV C and D to weight the PST $v_2$-dependent vector correlations to compare to experiment. The agreement was slightly improved with these vibrational weightings, compared to the purely theoretical PST vibrational weightings.

**F. Correlated vibrational distribution**

The state-resolved vibrational branching ratios shown in Fig. 11 can be combined with the global vibrational distributions to yield a correlated vibrational distribution, $P(v_1,v_2)$. The global vibrational distributions are projections of the correlated distribution:

$$P(v_1) = \sum_{v_2} P(v_1,v_2).$$

From the satisfactory agreement between the rotationally selected $v_2$ branching ratio and restricted helicity PST shown in Fig. 11 for $v_1=1$, we take the rotationally summed ratio $P(v_1=1,v_2=1):P(v_1=1,v_2=0)$ to have the statistical value of 0.136. This and the measured global vibrational ratios uniquely determines an experimental correlated vibrational state distribution, $P(v_1,v_2)$, illustrated in Fig. 12, and contrasted with the unrestricted helicity PST $P(v_1,v_2)$. We see the observed $v=2$ channels strongly suppressed compared to the $v_1=v_2=1$ channel, channels that should be equally populated in a statistical theory. The $v_1=0$, $v_2=0$ channel is observed to exceed the PST calculation by 35%, primarily at the expense of the $v_1=0$, $v_2=1$ and $v_1=1$, $v_2=0$ channels. These correlated vibrational distributions represent the most dramatic deviations from the statistical predictions, and should be the most challenging aspect of the dissociation for theoretical description.

**G. Correlated rotational distributions**

The Doppler measurements allow us to test the symmetry of the $P(N_1,N_2)$ distribution in the vibrationally unsymmetric channels forming CN $v=0$ in coincidence with CN $v=1$. Referring to Fig. 9, the $v_2=1$: $v_2=0$ measurements for $v_1=0$ test the high $N_1$ falloff of the $v_2=1$, $v_1=0$ channel. The deviations from PST show that the $v=0$ member of this pair is rotationally colder than the PST calculation. We can compare this to the global rotational distribution of $v_1=1$ states, which at high rotational levels is exclusively sampling the $v_2=0$, $v_1=1$ channel. This global $v=1$ rotational distribution is also observed to fall off faster than PST calcu-
tions, based on the data from EGM. The rotational distributions of both the \( v = 0 \) and \( v = 1 \) components of this vibrationally coincident channel fall off in a similar way, suggesting that there is no significant asymmetry in the \( N_1, N_2 \) distributions for these asymmetric coincident vibrational channels, although both \( N_1 \) and \( N_2 \) distributions fall off faster than PST predictions.

There is a small inconsistency in the analysis described in Sec. IV E, as the rotational state distributions used to generate the partial Doppler profiles for each coincident vibrational channel are calculated from PST, yet both the global and the correlated rotational distributions are found to be deficient in the highest accessible rotational states. The problem is evidently not serious for the highest rotational states detected, since energy conservation limits the coincident states to those which are globally well described by PST. For lower energy states, the partial Doppler contribution for the \( v_2 = 0 \) states should have a reduced contribution for the highest rotational states, flattening the top of the \( v_2 = 0 \) contribution, and increasing the true \( v_2 = 1 : v_2 = 0 \) ratios above those plotted in Fig. 11. One could contemplate an iterative back-projection analysis, making adjustments to the correlated state distribution to simultaneously fit the global state distributions and the full set of Doppler spectra. The required adjustments would be minor ones, but the uncertainties arising from multiple vibrational channels, along with ambiguity in the way to adjust the correlated state distribution, have dissuaded us from pursuing this analysis any harder. Future experiments with slightly reduced dissociation energy to close the \( v = 2 \) and the \( v_1 = 1 : v_2 = 1 \) channels should reduce the number of unknown parameters enough to make such a construction of the full \( P(v_1, N_1, v_2, N_2) \) distribution quantitatively self-consistent. For example, a comparison of the \( v = 1 \) global rotational distribution and the Doppler profiles of selected \( v = 1 \) rotational lines will allow a more rigorous test of the symmetry of the correlated rotational distributions for the coincident \( v_1 = 1, v_2 = 0 \) channel.

**H. The exit barrier**

The qualitative observation of flat-topped Doppler profiles for the CN fragments provides clear evidence that the highest accessible states of CN are not populated as efficiently as PST predicts for any sensible choice of available energy or centrifugal barrier. We have found that the observed line shapes are quantitatively indistinguishable from the predictions of a model with restricted helicity PST partitioning of 4700 cm\(^{-1}\) followed by an additional 600 cm\(^{-1}\) of translational energy release, as if from an exit barrier. A barrier to radical radical recombination of CN had not been anticipated, and we are led to inquire what it could be.

The \( \tilde{\alpha} \Sigma^+ \) state must be considered as a possible predissociation pathway. Correlation arguments\(^{35}\) indicate that the NCCN \( \tilde{\alpha} \) state correlates diabatically to two excited \( \tilde{A} \) state CN fragments. The triplet-coupled pair of \( X \) state CN fragments is asymptotically repulsive, so that the lowest adiabatic triplet surface correlates to ground state CN fragments through a barrier caused by an avoided crossing. The dissociation mechanism could thus be intersystem crossing, followed by dissociation over the triplet barrier. This possibility is supported by the quantum beat spectroscopy\(^{66}\) of the nondissociating \( 4 \) vibronic level of the NCCN \( \tilde{A} \Sigma^+_u \) state, pumped near 219 nm. Magnetic field effects on the quantum beats identified the strongly coupled perturbers of the zero-order singlet states as rovibrionic levels of a triplet state, most likely the \( 3 \Sigma^+ \) state. Several arguments, however, can be made against the triplet state as the predissociation pathway. First, it would be hard to explain why internal conversion through the barrierless singlet ground state does not compete, particularly at energies near or below the barrier. Second, although we are not aware of any \( ab \) initio calculations of the size of the triplet barrier, a barrier as small as 600 cm\(^{-1}\) seems unlikely. Our experiments alone cannot rule out a larger barrier, if the barrier energy were to be expressed partly in the rotational excitation of CN fragments. The threshold detection of CN by Huang et al.\(^{32}\) when combined with our estimate of the total asymptotic energy puts an upper bound on the barrier close to 600 cm\(^{-1}\). While further study could show the triplet state to be the dominant predissociation pathway, we consider another more speculative possibility.

Even though the singlet-coupled pair of \( X \) state CN radicals has only attractive bonding interactions, the collinear asymptotic electrostatic interaction is dipole–dipole repulsion. The electrostatic interaction energy of two opposed 1.45 D permanent dipoles 3.5 Å apart is about 585 cm\(^{-1}\), suggestively close to the apparent exit barrier. With orientational averaging, the dipole–dipole interaction vanishes. This interaction cannot produce a true barrier, in the sense of a saddle point connecting reactants and products, since paths to products exist with lower energy at nonlinear configurations. The situation is illustrated schematically in Fig. 13. The \( ab \) initio energies\(^{37}\) of \( C_2N_2 \) isomers and transition states are connected along a generalized isomerization coordinate. Above that is shown the dipole–dipole energy for the corresponding configurations at a separation of 4 Å, illustrating the attractive electrostatic interaction of the unsymmetrical CNCN isomer, and the repulsive electrostatic interactions of the symmetric isomers NCCN and CNNC. These curves are cuts at two values of the dissociation coordinate from the schematic potential energy surface shown in Fig. 14. If dissociation occurs prior to large amplitude bending motions connecting different isomeric regions of the configuration space, the dissociative trajectories will be forced to surmount the electrostatic barrier characteristic of the near-linear NCCN configuration, as depicted by the curved arrows. One might argue that the corregation of the potential energy surface along the orientational coordinates would convert some of the barrier energy into rotation, but we estimate the radial recoil velocity beyond the barrier to be fast enough compared to CN rotation that the exit channel anisotropy does not couple strongly to rotation. We are anxious to repeat these experiments at a lower photolysis energy, which should provide new tests of our interpretation of exit channel effects. The classical plausibility of these orientational effects in the late exit channel are currently being investigated by
trajectory methods. The approximate conservation of the K projection number deduced from the fragment vector correlations is fully consistent with this view of the dissociation. We find it interesting that this type of dynamical barrier would not be evident in the recombination of CN radicals or in the pyrolysis of NCCN, as the K selectivity of optical preparation would be absent.

V. CONCLUDING REMARKS

High-resolution transient FM spectroscopy has been applied to measure Doppler-broadened nascent line shapes of a photodissociation for the first time, providing accurate, low noise Doppler profiles, suitable for detailed analysis. The 193.3 nm photodissociation of NCCN to produce a pair of ground state CN radical fragments, a classic statistical fragmentation, has been reinvestigated. Laboratory frame speed distributions and velocity-averaged v·j correlations have been determined for state-selected CN photofragments. We have found that the available energy for fragments is 5300 ±100 cm⁻¹, an amount in excess of recent threshold measurements by what appears to be an exit barrier of about 600 cm⁻¹. The photodissociation has low anisotropy in its velocity and angular momentum distributions, but shows quite strong v·j correlations, increasing at higher rotational levels. A PST calculation of the v·j correlations with an approximate conservation of K produces an excellent, no-parameter fit to the measured vector correlations.

A state-dependent coincident vibrational branching ratio is the only free parameter then required to give good fits to almost all the measured Doppler profiles. The state-dependent vibrational branching ratios are combined with the global vibrational distribution to give a joint vibrational distribution for the CN pairs, which is significantly colder than statistical, and a surprising excess of v = 1 pairs compared to v = 2 formation. Quantitative discrepancies in this simple model are confined to the highest rotational states in each vibrational level, which fall off faster than the PST model. The apparent small barrier to CN recombination leading to the excess kinetic energy was unexpected, and we have considered the participation of a triplet state, and an orientation-
ally constrained dipole–dipole repulsion in the singlet exit channel as possible explanations.

We are planning further experiments at lower photolysis energies, which should probe the nature of the apparent exit barrier, as well as reduce the error bounds on the asymptotic dissociation energy by pumping vibronic bands of well-established assignment with a narrow-band dissociation source. We are optimistic that the partially resolved rotational structure in the NCCN absorption spectrum will also allow some measure of $J$ selection in the photolysis step.

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APPENDIX

In a recent work, we have described an exact recursive approach to the inversion of a frequency modulated line shape to obtain the underlying absorption spectrum in the case where the sideband spacing is comparable to the absorption linewidth. The noise propagation of the inversion produces periodic variations related to the sampling interval, reflecting random walk accumulation of errors in uncorrelated subsets of the FM data. We have found an alternative, approximate form of the inversion, which is independent of the sampling interval and displays better stability to noise.

Let the Doppler-broadened absorption spectrum in the vicinity of an isolated line be described by its amplitude attenuation coefficient, $\delta(\omega)$, a function of the optical frequency. The FM absorption signal after phase correction to remove the dispersion component is given by the difference of the absorption at the two sideband frequencies:

$$A(\omega) = \delta(\omega - \omega_m) - \delta(\omega + \omega_m).$$  \hfill (A1)

Expanding the absorption spectrum as a Taylor series:

$$\delta(\omega + \Delta \omega) = \delta(\omega) + \Delta \omega \frac{d \delta}{d \omega} + \frac{\Delta \omega^2}{2} \frac{d^2 \delta}{d \omega^2} + \frac{\Delta \omega^3}{6} \frac{d^3 \delta}{d \omega^3} + \cdots$$  \hfill (A2)

allows us to express the FM signal as

$$A = 2 \omega_m \frac{d \delta}{d \omega} + \frac{2 \omega_m^3}{3!} \frac{d^3 \delta}{d \omega^3} + \frac{2 \omega_m^5}{5!} \frac{d^5 \delta}{d \omega^5} + \cdots.$$  \hfill (A3)

Integrating (A3) gives a solution for $\delta(\omega)$:

$$\delta(\omega) = \frac{1}{2 \omega_m} \int_{-\infty}^{\infty} A \, d\omega - \frac{\omega_m^2}{3!} \frac{d^2 \delta}{d \omega^2} \bigg|_{\omega_0} + \frac{\omega_m^4}{5!} \frac{d^4 \delta}{d \omega^4} \bigg|_{\omega_0} + \cdots.$$  \hfill (A4)

Differentiating (A3) with respect to $\omega$ and rearranging terms gives

$$\frac{d^2 \delta}{d \omega^2} = \frac{1}{2 \omega_m} \frac{dA}{d\omega} - \frac{\omega_m^2}{3!} \frac{d^4 \delta}{d \omega^4} \bigg|_{\omega_0} + \cdots.$$  \hfill (A5)

Combining (A4) and (A5), we arrive at the desired absorption line shape:

$$\delta(\omega) = \frac{1}{2 \omega_m} \int_{-\infty}^{\infty} A \, d\omega - \frac{\omega_m dA}{12} \bigg|_{\omega_0} - \frac{7 \omega_m^3}{360} \frac{d^4 \delta}{d \omega^4} \bigg|_{\omega_0} + \cdots.$$  \hfill (A6)

This shows the underlying absorption spectrum to be approximated by a specific weighted combination of the integral of the FM spectrum and its numerical first derivative, with a leading error in fourth order terms. A partial correction to higher order can be made by adjusting the coefficient of the derivative term to optimize the self-consistency of the reconstruction. The working equation is

$$\delta(\omega) \approx \frac{1}{2 \omega_m} \int_{-\infty}^{\infty} A \, d\omega - c \frac{dA}{d\omega} \bigg|_{\omega_0}.$$  \hfill (A7)

The coefficient $c$ is adjusted for a least-squares optimum match between the measured FM signal, $A(\omega)$, and the finite difference spectrum computed with (A1) from $\delta(\omega)$ derived iteratively from (A7). This gives a somewhat better recon-

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**FIG. 15.** The open circles show a nascent CN ($X^\Sigma^+$) Q1 30.5 absorption spectrum reconstructed using the recursive method outlined in Ref. 45. The solid line is the reconstructed absorption spectrum obtained using Eq. (A7). The lower panel shows the expanded residual.
construction of $\delta(\omega)$ than a simple truncation of (A6), because the fourth derivative of $\delta(\omega)$ is not orthogonal to the first derivative of the FM spectrum.

Test calculations were performed for a synthetic 300 K CN($\Sigma^+ \rightarrow \Pi^-$) Doppler profile measured with 200 MHz frequency modulation. The residual between the integrated FM term alone and the true absorption spectrum was at most 3% of the absorption peak height. Including the fixed FM derivative term of (A6) further reduces the residual by an order of magnitude. Optimizing the coefficient $c$ to a value about 10% larger than $\omega_0/12$ further reduces the error by a factor of 2.

The broader nascent features are even more accurately reconstructed with the two-term approximation of (A7). Figure 15 shows, for example, the recursive reconstruction of the phase corrected nascent (2-0) $Q_{305}$ data with open circles. The two-term inversion using (A7) is shown as a solid line, which has no systematic deviations from the recursive reconstruction, but shows better stability and avoids the periodic “noise” of the recursive reconstruction described in Ref. 45. We use (A7) followed by left–right symmetrization for all Doppler reconstructions in this work. The center frequency for symmetrization can be located accurately by the zero crossing of the raw FM spectra.