

Effect of intensity on fragment internal state distributions in the infrared multiphoton dissociation of vinyl cyanide

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The technique of laser induced fluorescence has been used to observe the C_2 and CN fragments produced in the infrared multiphoton dissociation of vinyl cyanide $CH_2=CHCN$ in a low pressure flowing gas. The rotational distributions of the lowest vibrational level of the C_2 fragment were found to be well characterized by temperatures. As was previously observed for the CN fragment of this parent molecule, a distinct decrease in the values of these temperatures is seen to occur during the photolysis laser pulse. This is interpreted as the result of an intensity effect in the later stages of the infrared pumping process. Additional information is also presented on the behavior of the CN radical. Modeling calculations within the framework of the energy-grained master equation support this interpretation.

I. INTRODUCTION

The phenomenon of infrared multiphoton dissociation of molecules has received a great deal of scientific attention in the decade since its discovery. Considerable effort, however, both experimental and theoretical, is still necessary to characterize this process by which a single, isolated molecule absorbs a sufficient number of infrared photons to cause decomposition. Increasingly sensitive and sophisticated techniques continue to be applied to this problem. This paper describes work on the infrared multiphoton dissociation of vinyl cyanide, $CH_2=CHCN$. In the present experiment, laser induced fluorescence (LIF) has been used to probe the internal energy content of the C_2 photolysis fragment. The complementary information provided by our earlier study¹ of the CN fragments formed in this process is compared with these results. Additional information on the behavior of the CN radical in this photolysis is also given. Theoretical studies are presented within the framework of the energy-grained master equation to elucidate the effect of intensity in this process.

Laser induced fluorescence provides a convenient and sensitive method by which to study diatomic and triatomic fragments of infrared photodissociations. It is especially applicable to small fragments for which characteristic spectral features are generally known. For two- and three-atom species, the vibrational and rotational energy levels provide a fine energy grain with which to probe the infrared multiphoton dissociation process, with spacings on the order of a few wave numbers. As such, the sensitivity of this technique to small changes in the pumping and dissociation process is improved, as compared to experiments in which the competition between thermodynamically nonequivalent reaction pathways is observed.² Information obtained from LIF is largely complementary to that obtained from molecular beam time-of-flight and mass spectrometric experiments,³ providing vibrational and rotational energy contents as opposed to translational energies of the detected fragments. Laser induced fluorescence has been used for optical time-of-flight measurements as well.⁴

A number of fragments created by infrared multiphoton dissociation have been studied by LIF. Recently, a relatively complete list of fragments studied by laser induced fluorescence has been compiled by Ashfold and Hancock.⁵ The C_2 radical has been observed previously in the dissociation of several molecules,⁶ including vinyl cyanide.^{7,8} Additionally, reactions of C_2 created by infrared multiphoton dissociation have been investigated in great detail.⁹ The CN molecule has also been studied, using vinyl cyanide^{8,10,11} as well as other molecules¹² as a precursor. Early work performed in this group on CN from vinyl cyanide infrared multiphoton dissociation has been previously reported.¹

Vinyl cyanide is an attractive candidate for infrared multiphoton dissociation in that it provides two simple fragments C_2 and CN for detection by laser induced fluorescence. Fundamental characteristics of the two products (e.g., appearance times and internal energy contents) may be readily compared. Previous work⁸ has considered similarities in the behaviors of C_2 and CN and suggested that these fragments result from the dissociation of C_2CN . Results presented here are supportive of this conclusion. Additionally, our initial studies on CN fragments¹ indicated the possibility of an intensity dependence of the internal energy distributions of that molecule. Subsequent work^{10,11} has confirmed the importance of laser intensity in the production of CN internal energy distributions. This work presents complementary data on the C_2 photolysis fragments.

Experiments described in this paper were performed using a flowing gas sample at sufficiently low pressures to provide essentially collision-free conditions for the dissociation and detection processes. Furthermore, comparison of these results with similar data for the CN fragment formed via photolysis in a molecular beam¹ allowed ready identification of the minor collisional effects occurring at relatively long delays after photolysis. The time delay between the photolysis pulse and the laser induced fluorescence detection was varied, allowing the determination of the internal energy distributions of the C_2 fragments as a function of time. As was found for CN fragments,¹ these distributions are well described by temperatures. A distinct cooling of the rotational temperature following dissociation under

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collisionless conditions was found, qualitatively similar to the behavior observed for CN. These results are consistent with an intensity effect in which the energy content of the precursor(s) to C_2 and CN mirrors the intensity profile of the photolysis laser.^{10,11}

The energy-grained master equation provides a convenient framework from which to model infrared multiphoton dissociation.^{13,14} This method is used to follow the fragmentation of the presumed precursor C_2CN , with respect to the internal energy contents of the observed products. Qualitative agreement between theory and results further supports the concept of intensity effects in the infrared pumping process near the thermodynamic threshold for dissociation.

II. EXPERIMENTAL

Flowing gas infrared multiphoton dissociation experiments were performed within a large vacuum apparatus.¹⁵ Photolysis of vinyl cyanide and subsequent LIF detection of the C_2 fragments took place in the center of the chamber, with precautions to avoid wall effects and scattered laser light. Oil diffusion pumps and liquid nitrogen cryotrap allowed evacuation to a base pressure of 10^{-6} Torr. Vinyl cyanide was admitted directly to the photolysis chamber through a needle valve connected to an evaporating liquid source. A capacitance manometer (Datametrics Barocel model 1173) served to monitor the gas pressure. The vacuum system was throttled to maintain a flowing gas arrangement at pressures up to 20 mTorr of vinyl cyanide.

The infrared photolysis laser was a Lumonics 801A TEA CO_2 laser. A nondispersive cavity was employed, providing up to 1.3 J per shot at 15 Hz, with lasing occurring multimode primarily on the $P(20)$ and $P(18)$ lines of the (001)–(100) $10.6 \mu\text{m}$ vibrational transition. These frequencies lie slightly to the red of the $C=CH_2$ and $C=CHCN$ wag vibrations of vinyl cyanide.¹⁶ The laser was focused with a 2 in. diameter $f/4$ plano-convex BaF_2 lens. The resulting spot size was approximately 1 mm^2 , corresponding to a maximum focal fluence of over 130 J/cm^2 .

Laser induced fluorescence was performed using a nitrogen laser pumped dye laser. In most cases, a home-built system was used,¹⁵ based on a grazing incidence grating dye laser design.¹⁷ For low signal levels, a Moletron UV1000 pumped DL14P dye laser was used because of the higher intensity available. The C_2 radical was observed in the (0, 0) vibrational band of the $d^3\Pi_g - a^3\Pi_u$ Swan band system using the dye C500 with 0.010 nm resolution. Ideally one would like to probe the ground $X^1\Sigma_g^+$ state of C_2 , but the $a^3\Pi_u$ state which lies 716 cm^{-1} above the X state is easier to observe by laser induced fluorescence. For CN, the (0, 0) and (1, 1) vibrational bands of the $B^2\Sigma^+ - X^2\Sigma^+$ transition were excited using the dye BBQ with a resolution of 0.008 nm.

The CO_2 laser and dye laser were directed to be mutually perpendicular, crossing at the center of the photolysis chamber. The probe area was approximately 5 mm in diameter, surrounding the intersection. This region was imaged onto a photomultiplier (S-20 re-

sponse) external to the chamber through an aperture/lens/mirror system. Interference filters placed over the photocathode rejected unwanted light from the focal zone, especially the broadband visible luminescence which accompanies the collisionless infrared multiphoton dissociation of vinyl cyanide.¹⁸ For C_2 , the $d-a$ (0, 1) band was viewed after excitation of the (0, 0) band, with an interference filter centered at 560 nm; for CN, the $B-X$ (0, 0) and (1, 1) bands were viewed through a filter centered at 386 nm.

Signals originating in the photomultiplier were temporally discriminated using a boxcar integrator (PARC models 162/164). One channel of the integrator was used to trigger the nitrogen laser system; in this manner, the time delay between the photolysis and the probe lasers could be conveniently scanned. This was especially useful in following the time evolution of individual spectral features. In other instances, a synchronous motor scanned the wavelength of the dye laser, generating a laser excitation spectrum at a fixed delay. The output of the boxcar integrator was displayed on a strip-chart recorder; no additional signal averaging was required.

Vinyl cyanide was obtained from the Aldrich Chemical Company. The purity was determined to be greater than 99.95% by gas chromatography. Samples were degassed immediately prior to use. Because vinyl cyanide is known to be carcinogenic, appropriate precautions were taken to avoid contact with the liquid or vapor.

III. RESULTS

A. C_2 laser induced fluorescence

The internal state distribution of the C_2 radical was studied for the infrared multiphoton dissociation of vinyl cyanide in a flowing gas arrangement, although C_2 was clearly evident in molecular beam photodissociations as well. Spectra such as those shown in Fig. 1 were typically recorded. The C_2 $d-a$ laser induced fluorescence spectrum of the upper trace was taken at a relatively short delay between the photolysis and probe pulses, whereas the lower trace was obtained at a longer delay.

Originating from a $^3\Pi - ^3\Pi$ transition, laser induced fluorescence spectra of the C_2 $d-a$ Swan system is relatively complicated. However, several general features may be readily identified, with exact assignments following from the data of Phillips and Davis.¹⁹ The unresolved triple head of the (0, 0) vibrational band is found at 516.5 nm; to show the detail of the rest of the spectrum it has been expanded off scale by approximately a factor of 8. The presence of Q branches can be seen near the band origin. These Q branches overlap low J'' members of the R branches of the spectrum, along with high J'' P branch members returning from the bandhead through the origin. In the R branches, to the blue of the origin, the triplet nature of the transition can be seen in the individually resolved rotational lines. It should be noted that the sets of triplets found grouped together in the spectrum do not arise from the same value of J'' in the three spin-orbit split levels, but rather from accidental near coincidences of the term energies. The

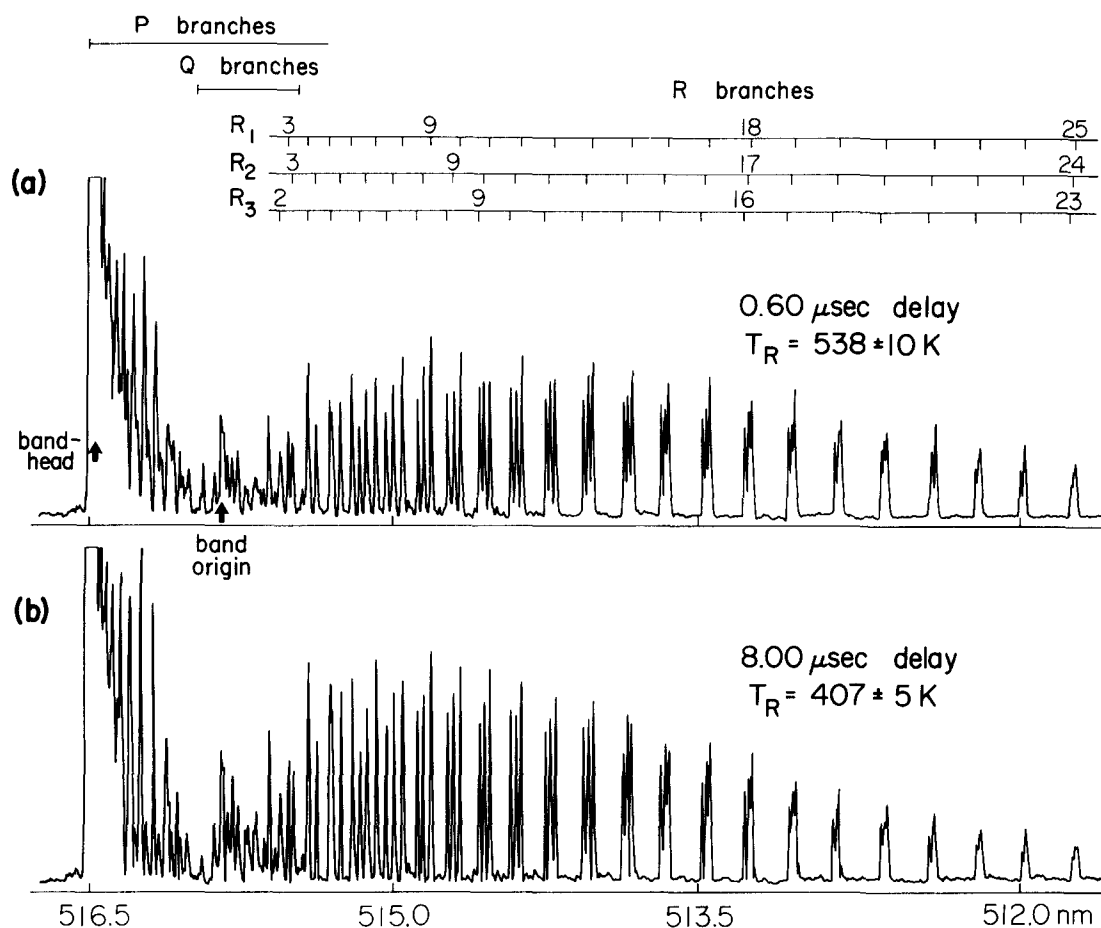


FIG. 1. Portion of the C_2 $d^3\Pi_g - a^3\Pi_u$ excitation spectrum showing the (0,0) band at a delay of (a) 0.60 μs and (b) 8.00 μs following the onset of the CO_2 laser pulse. The R branch members are labeled by J'' , the ground state total angular momentum quantum number.

three sets of R branch rotational lines are labeled in Fig. 1 to illustrate this fact.

The quality of the C_2 laser induced fluorescence spectra shown in Fig. 1 was typical of our data. Quantification of the internal energy contents of this radical could be readily performed, with a slight complication provided by the electronic energy difference of the three fine structure components. This splitting amounts to about 30 cm^{-1} for both the a and d states, and cannot be ignored. A three dimensional least squares fit was used to analyze the data: two axes (x, y) were set proportional to the electronic and rotational energies of the lines, with the third axis (z) taken as the logarithm of the line intensity divided by the line strength. A plane was fit to the data thus presented, with the slopes along the x and y axes being inversely proportional to the electronic and rotational temperatures, respectively.

Experimental spectra were evaluated using only unblended lines of the R branches. Line strengths were calculated on the basis of the formulas of Kovács,²⁰ with care taken to correctly adapt them to an inverted electronic system.¹⁵ In all cases, a Boltzmann distribution could be used to describe the observed line intensities. The derived temperatures for the sample spectra are shown in Fig. 2, along with one standard deviation of the

fit. In general, it was possible to obtain spectra characterized by a rotational temperature to within $\pm 10 \text{ K}$, except for the shortest probe delays, when signal levels were particularly low. Spectra which had errors greater than $\pm 30 \text{ K}$ were retaken; through some effort a lower error limit could usually be obtained. Examination of the data analysis plots showed that the errors in the fits were the result of randomly scattered data, rather than systematic deviations from the Boltzmann distribution, even in the discarded (large error) spectra. Deviations from Boltzmann behavior would be observed in a poor planar fit.

Neither the (1,1) nor the (2,2) Swan bands could be observed, although they occur in the same wavelength region as the (0,0) band.

Figure 2 contains a compilation of the C_2 $v''=0$ rotational temperatures obtained in flowing gas experiments. Each data point, shown as a closed circle, represents the rotational temperature which best characterized the LIF spectrum taken at each particular delay. For comparison, the CN $v''=0$ rotational temperatures obtained under similar pressure conditions¹ are also included in Fig. 2.

Shown for reference in Fig. 2 is a low resolution

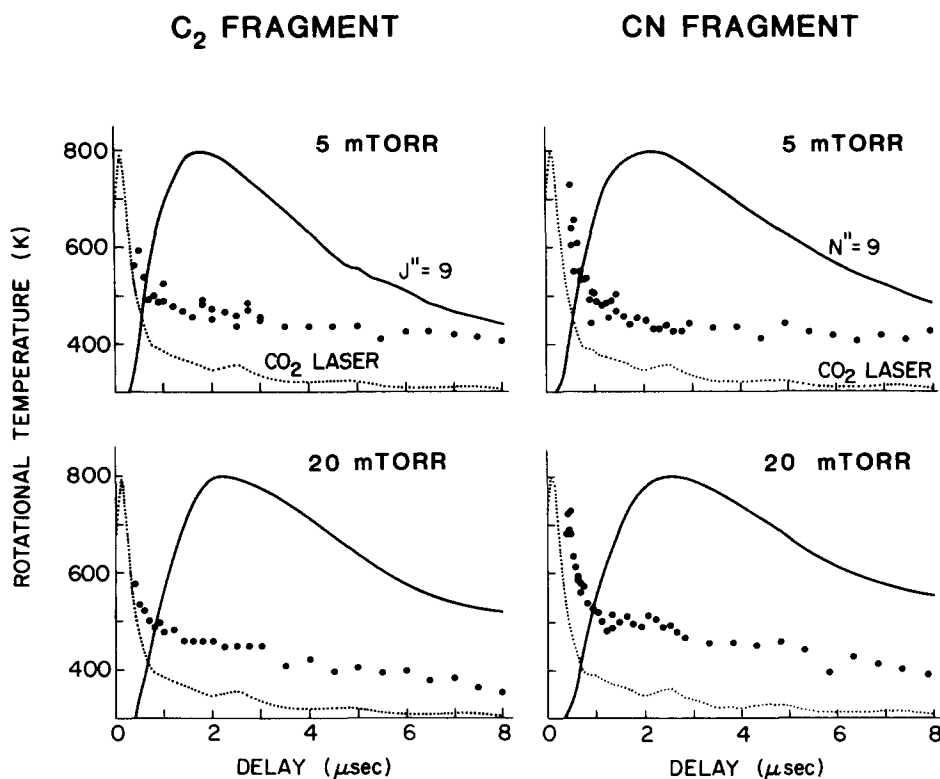


FIG. 2. Rotational temperature of the $C_2 v''=0$ state (closed circles) as a function of the delay from the onset of the photolysis pulse under various pressure conditions. The CO_2 laser pulse profile (dotted line) is included along with the intensity (solid line) of the $R_3(9)$ line. Rotational temperatures of the $CN v''=0$ state (from Ref. 1) for the same pressure conditions are included for comparison.

trace of the CO_2 laser output, as obtained from a fast pyroelectric detector. As can be seen, this pulse consists of a high intensity spike (350 ns FWHM) followed by a longer, low intensity tail. The energy of the pulse is divided approximately evenly between the two portions. The fast mode-beating of the laser cavity could be viewed with the detector, but has been smoothed by the signal averaging equipment producing the trace.

We also include in Fig. 2 the time evolution of the intensity of the $C_2 R_3(9)$ line [and the $CN R(9)$ line]. This particular line was chosen because it lies near the maximum of the rotational distribution for all of the observed temperatures, and as an R branch line, it is not obstructed by other features. Thus the intensity of this line serves as a measure of the amount of the particular radical present in the observation zone. The intensity of this line does, like all others, depend upon the rotational temperature as well as the population of radicals, so that these curves do deviate slightly from the true amount of $C_2(CN)$ in the probe beam. This occurs to a lesser extent, however, than with a feature such as the bandhead, which displays a more prominent temperature dependence.

The temperature decrease of the C_2 rotational distribution, while obvious, is much less precipitous than that found previously for CN .¹ As before, this drop occurs simultaneously with the rapid increase in the amount of C_2 in the observation zone. As the photolysis ceases, the population curve peaks and the rapid initial rotational temperature drop ceases. A slower, pressure dependent decrease in both signal levels and temperatures occurs on a longer time scale. Thus a rough qualitative and quantitative equivalence of the rotational

temperature behaviors of the C_2 and CN fragments is observed.

The electronic temperatures of the C_2 fragments, as defined by the distribution of molecules among the fine structure components of the a state, were not as well behaved as the rotational temperatures. All values of the electronic temperature were on the order of 100 K, with standard deviations to ± 65 K. The scatter was considerably smaller than this error would indicate, and showed a rather constant value independent of the delay following photolysis.

B. Laser induced fluorescence of CN and other species

The $(0, 0)$ band of the $CN B-X$ system has been investigated previously¹ and further studies¹⁵ served only to confirm the original findings. Consequently, no new data on the CN temperature behavior from this band will be presented here.

The $(1, 1)$ and $(2, 2)$ vibrational bands of the $CN B-X$ system occur in the same spectral region as the $(0, 0)$, although Franck-Condon factors²¹ decrease our sensitivity to these bands. Careful examination of previous experimental data showed evidence of the $(1, 1)$ band in some spectra in the shoulders of the R branch lines. These intensities were consistent with assigning vibrational temperatures to the CN radicals equivalent to the derived rotational temperatures of the $(0, 0)$ band.¹ The error of these estimates is large, however, and is based only upon qualitative comparison of two vibrational levels. No estimate could be made from these spectra of the rotational temperature of the $v''=1$ level.

Recent modifications to the dye laser system, yielding

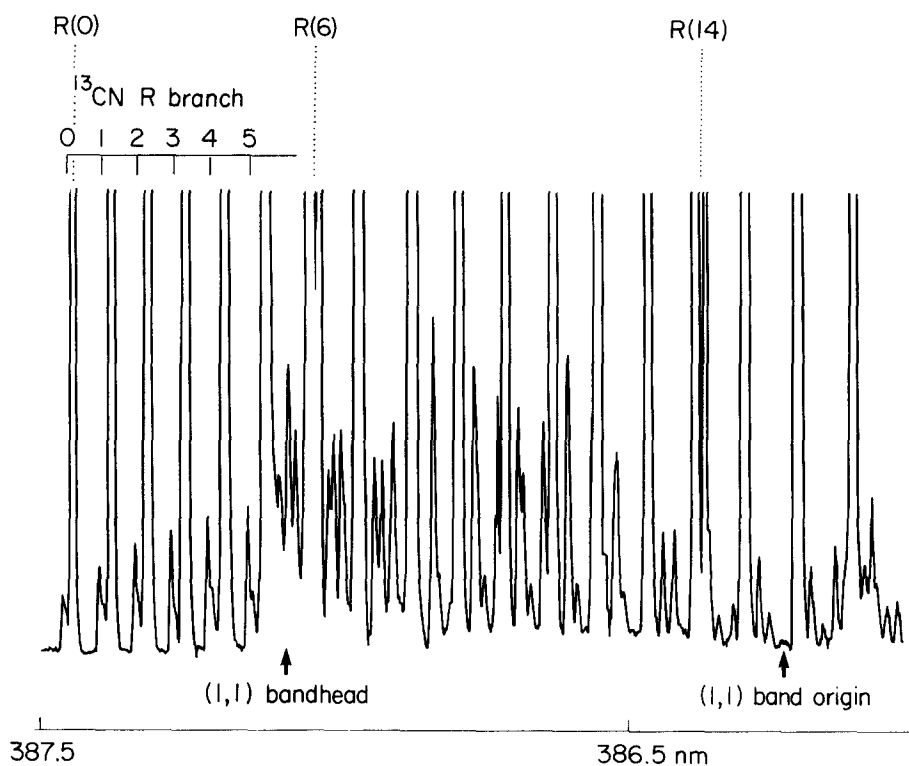


FIG. 3. The ^{12}CN $B-X$ (1,1) band as well as the unblended R branch members of the ^{13}CN $B-X$ (0,0) band shown with the R branch members of the ^{12}CN (0,0) band recorded off-scale at highest sensitivity. The off-scale $R(6)$ and $R(14)$ lines of the (0,0) band are clearly split by perturbations between the $A^2\Pi$ and $B^2\Sigma^*$ states. Note added in proof: Closer examination shows that lines identified as part of the ^{13}CN $B-X$ system have shoulders which are assigned to $^{12}\text{C}^{15}\text{N}$.

a narrower bandwidth through the use of beam expanding prisms as well as a grazing incidence grating, have clearly separated the (1,1) spectral features. In addition, the weak shifted spectrum of ^{13}CN is observed, originating from its natural isotopic abundance in the vinyl cyanide parent molecule. These features are shown in Fig. 3. This demonstrates the capabilities of LIF in experiments of this type.

Several simple experiments were performed with other vibrational bands of the $\text{CN } B-X$ transition. The (0,1) and (1,2) bands were probed, observing fluorescence in the (0,0) and (1,1) bands. Both the $v''=1$ and $v''=2$ levels of the $\text{CN } X$ state could readily be seen under flowing gas conditions. No attempt was made to quantify these observations.

The radical CH was probed by LIF through both the $A-X$ and $B-X$ band systems.^{22,23} In the former spectral region, CH could be observed at high pressures (0.3 Torr vinyl cyanide) and long delays ($>10 \mu\text{s}$). The signal level dropped rapidly with decreasing pressure and shorter delay times, leading us to conclude that a collisional mechanism rather than direct photolysis was responsible for the creation of CH . No CH could be seen using the $B-X$ transition, placing it a factor of 3000 lower in intensity than the nearby $\text{CN } B-X$ bandhead.

Singlet methylene²⁴ was not observed even at high pressures and long delay times.

C. Temporal evolution of the CN and C_2 populations

A close comparison of the temporal behavior of the C_2 and CN fragments was undertaken, motivated by the

similar values and behaviors of the rotational temperatures, as well as the similarities discussed by Yu *et al.*⁸ Fixed wavelength laser induced fluorescence was employed with the $\text{C}_2 R_3(9)$ and $\text{CN } R(9)$ rotational lines. By choosing the same value of N'' for CN as J'' for C_2 , we also examine fragments with the same amount of angular momentum for both C_2 and CN . Efforts were made to ensure that experimental conditions were as identical as possible for each fragment. This included considerations such as laser mode and intensity, gas pressure in the photolysis chamber, timing, and the region probed by the dye laser system. The rising portions of the population curves were found to be identical for both fragments within the 50 ns resolution of our experiments. A slight pressure dependence of the rise times of the fragments indicated that our data were not instrumentally limited. In the later stages of observation (after $\sim 3 \mu\text{s}$ delay), differing population behavior was observed for each molecule, probably indicative of the different reactivities of the diatomic fragments.

D. Intensity/fluence studies

The role of the CO_2 photolysis laser fluence in determining CN rotational temperatures was explored. Short time delays were used, in order to view the earliest set of fragments and minimize the averaging process following photolysis. The laser intensity/fluence was attenuated with NaCl flats, in order to leave the laser mode structure and timing unaltered. A 25% decrease in the laser fluence was found to decrease fragment yield by a factor of 5 with no discernible effect upon the product rotational temperature. Reference 8 contains a more detailed study of the effect of fluence on the photo-

dissociation yields for vinyl cyanide. Our loss of signal with decreasing power levels prevented a study at lower fluences.²⁵ Experiments are currently in progress with a plasma shutter system to allow the fluence and intensity of the CO₂ laser to be independently modified, without altering the mode structure of the laser.

IV. DISCUSSION

A. Rotational temperature behavior

The rapid rotational temperature decrease of the C₂ and CN radicals immediately following the start of photolysis is a most distinctive feature. This is observed to occur at the same time that the total amount of each radical is rapidly increasing. We propose the following explanation for this behavior, consistent with our earlier results¹ and the work of others.^{10,11} We have found that the initial fragments which are formed in the dissociation of vinyl cyanide are characterized by a high rotational temperature. It is postulated that those which are created at longer delays have lower rotational temperatures.¹⁰ When these fragments are added to those initially formed, the overall distribution among the rotational levels will take on an intermediate character which is then probed spectroscopically. As the photodissociation proceeds, this addition process continues: more and more of the cooler C₂ and CN fragments are added to the observation zone. This causes both a rise in the total amount of radicals seen, as indicated by the $J'' = 9$ and $N'' = 9$ curves, and a fall in the overall rotational energy, as shown by the rotational temperatures. This temperature decrease ceases when the initial hot fragments are completely masked by the larger numbers of cooler fragments. This occurs shortly before the last radicals are created during the low intensity tail of the CO₂ laser, as indicated by the peaks of the population curves.

This proposed mechanism necessitates the addition of species characterized by different rotational temperatures. In general, the addition of two Boltzmann distributions will not yield a third Boltzmann distribution. However, several conditions of the present experiment do make this a reasonable approximation. First, the characteristics of the molecular system in question restrict the temperature range observed to about 300 K; thus the approximation need not account for widely disparate distributions. Secondly, in our experiments, LIF is capable of observing only the first 20 to 30 members of the *R* branch. The lines associated with more energetic rotational levels, whose relative intensity changes most dramatically with temperature, are obscured by the baseline noise. Numerical trials, in which various Boltzmann distributions were created, summed, and analyzed, subject to these constraints, showed that composite distributions could be described by a rotational temperature to within ± 20 K. At this level of error, any slight systematic deviation may not be detected because of the noise in the spectra.

Collisional cooling can be eliminated as the source of the short-time temperature drop for two reasons. The first is the independence of this short-time behavior

from the pressure or density of the background vinyl cyanide gas. In our previous study¹ of CN there was over an order of magnitude difference in gas density, and thus collision rate, between the molecular beam and higher pressure flowing gas experiments. Yet the short-time segments were superimposable within the scatter of the data. The same behavior is also observed for C₂. Secondly, the time scale of the temperature drop is much too short for a collisional origin: even at 20 mTorr pressure, radical-parent collisions occur at times on the order of several microseconds.²⁶ However, collisional cooling becomes increasingly apparent in the long-time behavior of the temperature curves at 20 mTorr pressure.

It might also be expected that rotationally hot fragments would have a correspondingly high translational energy. This could cause them to leave the observation zone more rapidly than cooler radicals, lowering the temperature through a loss rather than a dilution mechanism. For realistic velocities, the time scale of such a process is too long to account for our observations. Moreover, such an effect contradicts the form of the population curves.

Another alternative mechanism suggests that the initially observed rotationally hot fragments are the result of rapid decompositions, while the cooler fragments are seen later because of the longer decay time for less excited precursors. According to RRKM theory, more highly energized precursors would dissociate more rapidly and their extra energy content would be reflected in the internal energy of their fragments. As has been previously noted,¹¹ the time scale for the decomposition of small molecules is only a few nanoseconds, which is much more rapid than the observed effect. Such short precursor lifetimes have been confirmed by experiments on vinyl chloride infrared multiphoton dissociation²⁷ and by calculations outlined below for the postulated decomposition of C₂CN. However, the role of sequential decompositions, which most likely occur before the eventual production of C₂ and CN is difficult to assess. Thus, although one might expect this to play a minor role in the observed temperature falloff, it cannot be ruled out on the basis of our data.

We are led instead to an intensity dependent mechanism for the explanation of how rotationally hot fragments are observed initially while cooler fragments appear later. This mechanism assumes that the degree of excitation of a precursor molecule above the dissociation threshold depends upon the laser intensity; excitation continues until dissociation effectively competes with further absorption.^{3,28} One would thus expect that molecules pumped above the dissociation threshold during the sharp initial spike of the CO₂ laser would be excited to higher levels than those crossing during the relatively lower intensity tail. Such a higher degree of excitation would be reflected in the fragment energies and thus the rotational temperatures. Each point of the temperature curves of the C₂ and CN radicals would thus reflect the effect of the CO₂ laser intensity on the resulting ensemble of dissociated molecules. The long residence time of the fragments in the observation zone

forces us to view the integrated history of the photolysis up to the time of the probe.

Such a dependence of the internal energy of the fragments on the photolysis laser intensity has been proposed by Ashfold, Hancock, and Hardaker¹⁰ as well as by Renlund, Reisler, and Wittig.¹¹ In the work of Ashfold *et al.*¹⁰ the rotational temperature of the CN radical was observed at a short and a long delay following photolysis. With the CO₂ laser operating in a fashion similar to ours, with both a gain-switched spike and low intensity tail, lower rotational temperatures were observed at increasing delays. With the low intensity tail removed from the laser pulse through adjustment of the laser gas mixture, however, the later temperatures were seen to remain closer to the initial temperatures. In the context of the mechanism discussed here, this is equivalent to removing the later, cooler fragments which dilute and mask the early set. In addition, these results contradict to some degree the mechanism of delayed decomposition of lesser excited precursors discussed above. In the work of Renlund *et al.*,¹¹ intensity variation was produced by the use of an intracavity gas cell, allowing the photolysis laser to be operated with either a series of mode-locked spikes or a smooth single mode. Comparable fluences were used in both cases. The CN radicals produced by the higher intensity mode-locked laser were found to be rotationally hotter, as would be expected.

The intensity effect postulated here is separate from those occurring in the early stages of the pumping process, where the sparse vibrational manifold must be traversed. The effect of laser intensity on dissociation yields has previously been demonstrated.^{5,29} However, the observation of intensity effects near the dissociation threshold, such as seen in our rotational temperatures, is dependent upon the production of sufficient radicals to be probed. Both intensity and fluence effects contribute to this yield. Our experiments with attenuated laser intensity/fluence would appear to be dominated by lower level bottleneck effects, with the yield dropping rapidly with decreasing photolysis laser power. In the range studied in the present work, the intensity effect at a fixed delay following photolysis appears to be minor. In the experiments with tighter focusing,²⁵ yield limitations are less important because of the higher fluences available, and intensity effects in the latter stages of pumping appear visible at fixed delays. Although the yield of the reaction does approach saturation at high laser fluences,⁸ one would expect a continued increase in the fragment energies as the intensity is raised.

The intensity difference between the sharp spike and tail sections of the CO₂ laser is approximately a factor of 5. One might expect this to produce an effect in the fragment energies. The yield of radicals in the tail region is enhanced, compared to the attenuated pulse experiments, most probably because of the initial exposure of the molecules to the gain-switched spike, which drives the precursor molecules to some intermediate energy levels where intensity plays less of a role in the pumping process. Thus, while some molecules are rapidly excited and dissociate during the spike, a larger

number are left below the dissociation threshold to be slowly pumped over the threshold by the tail. As the fragment energies are determined by the final stages of pumping, in our mechanism, the rotational temperatures of the fragments created at a given instant would reflect the laser intensity at dissociation. Those molecules dissociating first, during the high intensity gain-switched spike, would be expected to be hotter, while those dissociating in the tail region later in time would be predicted to be cooler.

B. Dissociation modeling

Modeling of the infrared multiphoton dissociation process for vinyl cyanide is a difficult task because the exact mechanism of the photolysis is not known. However, exploratory work has been performed for this case, and surprisingly close agreement between modeling and experimental data has been found. In addition, there are indications that intensity effects in product energies are a general phenomena.

The work presented here as well as previously by Yu *et al.*⁸ is supportive of the C₂CN molecule as the immediate precursor to the observed products C₂ and CN. Accordingly, we have chosen to model the infrared photolysis of C₂CN within the framework of the energy-grained master equation. The application of this formalism to infrared multiphoton processes has been discussed by Barker¹⁴ and will not be repeated here. Following the procedures outlined in Ref. 14, a set of coupled differential equations was generated, with the appropriate parameters (transition cross sections and dissociation rates) estimated from data available for cyanoacetylene,³⁰ C₂CN,³¹ and the diatomic fragments.³² Laser parameters were chosen to be compatible with experimental conditions. Solutions to the equations were obtained using the stochastic or random walk method of Bunker *et al.*³³ Details of the modeling process may be found in Ref. 15.

The results of the random walk data showed a consistent increase in the energy available for the dissociation products with increasing intensity in a constant fluence pulse. The magnitude of the excess energy ranged from 1000 to 2000 cm⁻¹, or one to two infrared photons above threshold. Assuming equipartition and accounting for free rotation in the excited complex,¹⁵ these energies translate into temperatures corresponding closely, possibly fortuitously, to our experimental results. In contrast to the excess energy results, dissociation yield was found to be fluence dependent.

Our modeling also shows a consistent correlation between the product energy and the ratio of the absorption and dissociation rates at threshold. As the absorption rate is dependent upon laser intensity rather than fluence, this is equivalent to a general intensity dependence of dissociation product energies, regardless of the absolute values of the parameters involved, reflecting only the competition between dissociation and continued absorption in the last steps of the photolysis process. Although additional inquiry into this correlation is necessary and the magnitude depends upon the specific system in question, it would appear that intensity effects

in product energies are to be expected in general.

V. CONCLUSION

The technique of laser induced fluorescence has been applied to the infrared multiphoton dissociation of vinyl cyanide, producing a rotational energy analysis of the C₂ fragments. Experiments were performed in low pressure flowing gas which allowed the observation of nascent product energy distributions with high sensitivity. Each rotational spectrum was found to be well characterized by a temperature. These were seen to decrease rapidly in a short period following the onset of photolysis. This decrease is qualitatively similar to that observed for the rotational temperatures of CN fragments produced under the same conditions.¹ A collisional origin of this effect is ruled out because of the time scale and pressure/density independence of the change. Collisional effects causing a gradual falloff of the rotational temperatures could be observed at relatively longer times.

The observed temperature changes can be explained in terms of a process by which an initial small set of rotationally hot fragments is diluted by the addition of larger numbers of cooler radicals. This is consistent with a laser intensity effect in the final stages of the infrared pumping process, reflecting the competition between dissociation to the observed fragments and continued up-pumping of the precursor. In this manner, the rotationally hot initial populations of C₂ and CN originate from dissociation during the high intensity gain-switched spike of the photolysis laser, while the cooler radicals are created by the low intensity tail of the pulse which follows. Simple model calculations, based on the presumed C₂CN precursor, agree in the scope and magnitude of this laser intensity effect. We conclude that these intensity effects on the internal energy content of the fragments are a general characteristic of infrared multiphoton dissociation of polyatomic molecules.

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