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

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A plasma shutter has been used to remove the less intense tail of a CO_2 laser pulse without otherwise altering the pulse characteristics. It is found that variations in the pulse intensity distribution control the rotational distribution of CN fragments formed in the IR photolysis of vinyl cyanide $H_2C = CHCN$.

I. INTRODUCTION

In recent years a number of researchers have reported results of experiments which have studied the rovibrational energy distributions of fragments[1] formed in the infrared multiphoton dissociation (IRMPD) process.[2] One of the most remarkable features of these experiments is the fact that the internal energies of the fragment can be well characterized in terms of a Boltzmann distribution with a single temperature for each degree of freedom.

However, the actual temperatures observed for identical systems under similar experimental conditions differ significantly in both quantitative and qualitative ways from one laboratory to the next. A striking example of this is provided by studies of the C_2 and CN fragments formed in the infrared photolysis of vinyl cyanide ($H_2C = CHCN$) with a pulsed CO_2 laser.[3-7] In this case, differences in product rotational temperatures have been attributed primarily to the effects of laser intensity on the production of fragment energy distributions.

Laser induced fluorescence (LIF) has been used to determine the rotational energy content of the CN($X^2\Sigma^+$) and $C_2(a\,^3\Pi_u)$ radicals formed in these experiments. For the case of the CN products, Yu *et al.* have reported rotational temperatures of approximately 1000 K at short delays between the CO_2 and probe laser pulses.[3] No relaxation of the rotational distribution was observed at low pressures and/or short delays. Miller and Zare, on the other hand, observed an initial CN rotational temperature of 700 K followed by a rapid temperature decrease at short delays, even under molecular beam conditions.[5] This falloff occurred during the less intense "tail" of the CO_2 laser pulse and was interpreted as the convolution of two effects: (1) a dependence of the CN rotational temperatures on the laser intensity and (2) a statistical distribution in dissociation lifetimes which produces rotationally cooler fragments at later times. Complementary data recently reported by Miller *et al.*[6] for the C_2 products of vinyl cyanide show similar behavior. These authors argued that (1) was primarily responsible for the temperature falloff, but they were unable to rule out contributions from (2).

A dependence of fragment energy on the laser intensity is expected whenever a precursor to that fragment is pumped above its dissociation threshold in the final stages of the multiple photon excitation process. The ultimate energy content of this precursor is determined by the competition between further optical pumping and dissociation. Since the rate of optical pumping is proportional to the light intensity, the final energy of the parent molecule will be controlled by the laser. This internal energy is then partitioned into the fragments as the precursor dissociates. If all other parameters remain constant, a more intense laser pulse should produce more energetic fragments.

Ideally, experiments intended to probe this type of intensity effect would be performed with a single-mode laser producing both spatially and temporally well defined photolysis pulses. The intensity of these pulses would then be varied as the only experimental parameter.[8] Even with such a well characterized laser system, however, the Gaussian spatial intensity distribution in these pulses cannot be described by a single parameter such as a unique intensity. Quantitative measurements of the effect of laser intensity thus require at least the deconvolution of spatial intensity distributions to become meaningful. The variation of other laser parameters further complicates this convolution and makes quantitative comparison between results of different researchers difficult.

Qualitative information concerning the role of laser intensity in the production of fragment internal energy distributions, however, has already provided valuable insight into the final stages of the IRMPD process. Experimental evidence for this kind of effect has been obtained by Ashfold, Hancock, and Hardaker,[4] and by Renlund, Reisler, and Wittig[7] for the case of CN fragments formed in the IRMPD of vinyl cyanide. By removing N_2 from the CO_2 laser gas mixture Ashfold *et al.* produced output pulses free of the characteristic low intensity tail. At a fixed delay between the photolysis and probe lasers, hotter CN rotational temperatures were observed for the "tail-free" CO_2 laser pulses than for the usual "spike-plus-tail" pulses. This provided additional direct evidence that the less intense part of the photolysis pulse produces rotationally cooler fragments. In another experiment, Renlund *et al.* used a CO_2 laser operating either mode locked or single mode to vary the

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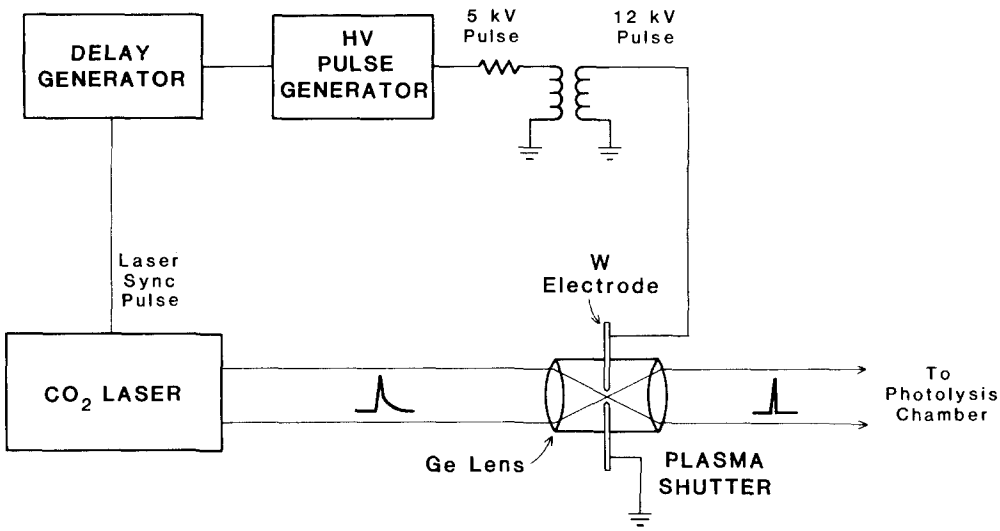

FIG. 1. Schematic diagram of the CO_2 laser/plasma shutter systems.

effective laser intensity.[7] The more intense mode-locked pulses were observed to produce appreciably hotter CN rotational temperatures.

Although both experiments measure changes in the fragment energies, which are undoubtedly the result of different effective laser intensities, they require the comparison of the effects of two completely different laser pulses. Variations in the spatial and temporal intensity distributions from one laser configuration to the next make it difficult to attribute these changes only to differences in the effective or average pulse intensity without additional experimental verification.

In this paper we present results of experiments in which the influence of variations in the effective laser intensity on the production of CN fragment rotational energy is observed *without* altering the basic nature of the CO_2 laser pulse. A plasma shutter has been used to remove the less intense "tail" of CO_2 laser pulses which dissociate a low pressure flowing gas of vinyl cyanide. The rotational energy distributions of the $CN(X^2\Sigma^+)$ fragments are then probed by LIF at different delays following this pulse and the resulting excitation spectra are characterized by temperatures. At short delays these temperatures are identical to those obtained with the full photolysis pulse. At longer delays in the short pulse experiments, collisional quenching causes these temperatures to decrease linearly with time. Comparison to experiments with the plasma shutter off confirms that the cooler CN rotational distributions observed at longer delays in the full pulse experiments are in fact due to dissociation by the less intense tail of the laser pulse. The different behaviors of the CN rotational energies observed in different laboratories can then be related to the characteristics of the CO_2 laser pulses used to photolyze vinyl cyanide.

II. EXPERIMENTAL

Other than the addition of a plasma shutter between the CO_2 laser and photolysis chamber, the experimental apparatus was identical to that of previous work.[5,6,9] A CO_2 TEA laser (Lumonics model 801) operating multimode with a nondispersive cavity provided pulse energies of approximately 1.3 J/pulse at 10.6 μm with a repetition rate of 15 Hz. The laser output passed through the plasma shutter and was focused to an approximately 2 mm^2 spot by a 2 in. focal length BaF_2 lens inside the photolysis chamber. A schematic of the CO_2 laser/plasma shutter system is shown in Fig. 1. The plasma shutter design was based on that of Kwok and Yablonovitch.[10] In our design a pair of 2 in. focal length germanium lenses served to alternately focus and recollimate the beam. Clean, dry nitrogen was flowed continuously through the focal region between those lenses to prevent spontaneous breakdown. Plasma formation could then be reproducibly initiated by a spark across a pair of tungsten electrodes (5 mm gap) at the focal region. The short risetime high voltage pulses required to produce this discharge were obtained by transforming the output of a commercially available device (EG&G HV 100/N). By appropriate synchronization of the high voltage and laser pulses, plasma formation could be induced over a range of several hundred nanoseconds during the gain-switched spike of the CO_2 laser. This plasma efficiently blocked the transmission of the remainder of the laser pulse. Due to the rapid cutoff of the laser, the effects of wavelength shifts introduced by self-phase modulation of the infrared radiation[11] transmitted during these times should be minor.

After passing through the plasma shutter, the temporal characteristics of the CO_2 laser pulses were monitored by a fast pyroelectric detector (Plessey PPC511F) in conjunction with a microcomputer controlled programmable transient digitizer (Tektronix 7912AD). The full CO_2 laser pulses transmitted with the plasma shutter off were composed of a short gain-switched spike (500 ns FWHM) followed by a several microsecond tail [Fig. 2(a)]. With the plasma shutter on, output pulse widths of 80 to 300 ns (FWHM), corresponding to pulse energies of 0.2 to 0.5 J were easily obtained. Optimum signal and stability were produced for pulse widths of 210 ns (FWHM) yielding an energy of approximately 0.36 J per pulse [Fig. 2(b)]. The measured jitter in the width of these pulses was less than 10 ns; under these

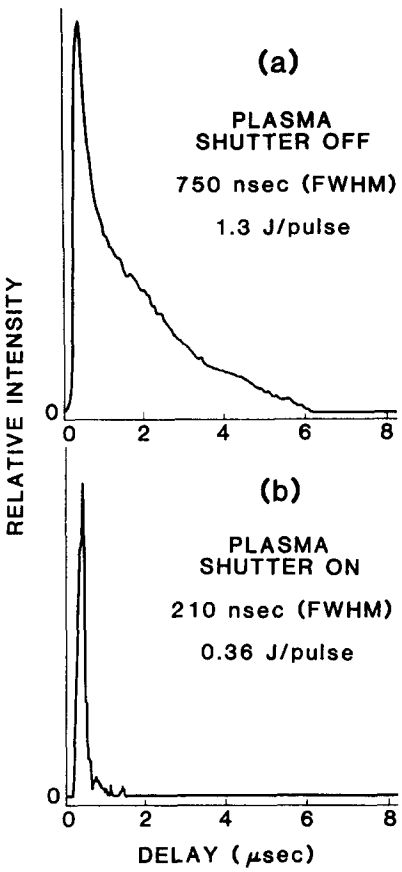

FIG. 2. CO_2 laser pulse temporal for (a) the full pulse transmitted with the plasma shutter off and (b) the shortened pulse produced with the plasma shutter on.

conditions the shot-to-shot fluctuation in the maximum intensity is $\leq 10\%$.

Laser excitation spectra of the CN fragments formed by both types of photolysis pulses were obtained using a home-built nitrogen-pumped dye laser. The beams of the dye laser and CO_2 laser crossed at right angles permitting an area of approximately 5 mm^2 surrounding the focal region to be probed. Individual rotational lines in the (0, 0) band of the CN $B^2\Sigma^+ - X^2\Sigma^+$ system were excited using BBQ dye with 0.02 nm resolution. The resulting fluorescence was isolated by an interference filter and imaged onto a photomultiplier tube (S-20 response). Fluorescence signals were temporally discriminated by a boxcar integrator (PARC model 162/164) and the boxcar output was displayed on a stripchart recorder without additional signal averaging.

III. RESULTS

In these experiments the full laser pulses transmitted with the plasma shutter off [Fig. 2(a)] or the shortened laser pulses produced with the plasma shutter on [Fig. 2(b)] were used to dissociate a low pressure flowing gas of vinyl cyanide. The rotational state distributions of CN fragments produced in both experiments were probed at various delays between the photolysis and dye laser pulses. Figure 3 shows examples of CN fragment excitation spectra observed at the same delay in experiments with each type of photolysis pulses. In order to decrease the time required for data acquisition only the R branch of the (0, 0) band in the CN $B^2\Sigma^+ - X^2\Sigma^+$ system was probed. The observed excitation spectra show features which are otherwise identical to those reported earlier,[5] although the slightly narrower dye laser bandwidth used in the present study better resolved individual R branch rotational lines.

As before, the intensities of these lines were fit to a Boltzmann distribution.[5] In all cases the observed rotational distributions could be characterized by a single temperature to within ± 20 K (one standard deviation). Once again no systematic deviation from a Boltzmann distribution was observed.

Comparison of the excitation spectra in Fig. 3 indicates that significantly hotter rotational distributions are observed at intermediate delays in the short pulse experiments. This is easily seen in the smaller populations observed at higher N in the full pulse experiments as well as by a quantitative comparison of the rotational temperature of each distribution. The reduced signal-to-noise ratio apparent in the spectra recorded with the plasma shutter on results from the

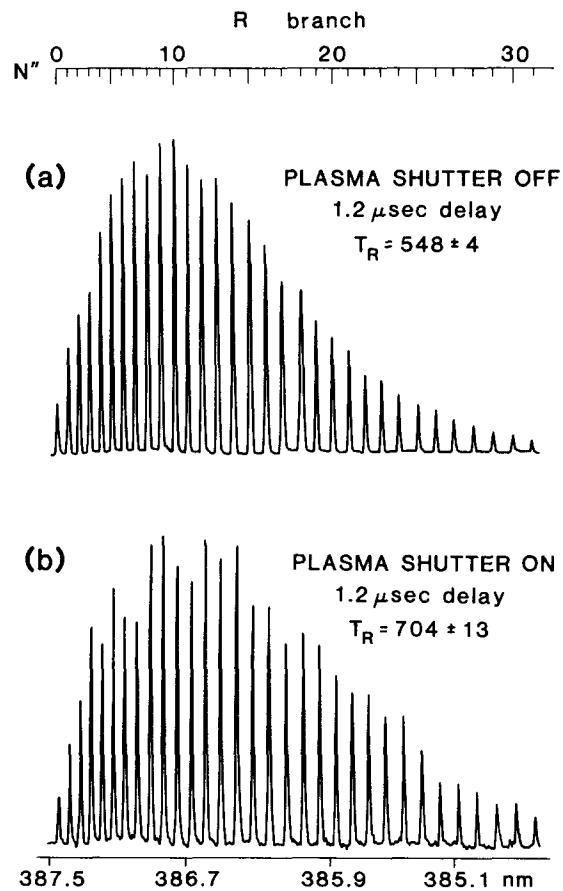

FIG. 3. CN excitation spectra obtained from the IR photolysis of vinyl cyanide (20 mTorr) at a delay of 1.2 μs following the CO_2 laser pulse with (a) the plasma shutter off and (b) the plasma shutter on. Only the R branch members of the CN B–X (0, 0) band are shown. The relative intensities in each spectrum are normalized to the most intense line; the absolute signal level in (b) is about ten times less than (a).

smaller numbers of fragments formed under these conditions.

In Fig. 4 we present a compilation of the $v=0$ CN rotational temperatures obtained in experiments at 20 mTorr pressure with the plasma shutter on. Each data point respesents the rotational temperature obtained from a LIF spectrum at the delay indicated. The CN rotational temperatures are observed to decrease linearly with delay in these short pulse experiments, from a maximum temperature of 740 K. Experiments in which the same "tail-free" photolysis pulse was used to dissociate a flowing gas of vinyl cyanide, at both 10 and 40 mTorr, exhibited similar behavior. The temperature decrease in these experiments could be characterized by a slope of 40, 50, and 80 K/μs at pressures of 10, 20, and 40 mTorr, respectively.

Also included in Fig. 4 are the $v''=0$ CN rotational temperatures observed in experiments with the full CO_2 laser pulse (plasma shutter off). Due to the higher signal levels of these experiments error limits of ± 10 K could be assigned to these temperatures. As was the case for the CN fragments produced by the tail-free laser pulse, a maximum rotational temperature of approximately 740 K was observed at shortest delays. However, a more precipitous initial drop in rotational temperatures was observed in these experiments, followed by a slower decrease at longer delays. These temperatures agree quantitatively with those obtained previously, in experiments performed without the plasma shutter under otherwise identical conditions.[5] This indicates that any additional spatial inhomogeneities introduced into the CO_2 laser pulse by the plasma shutter optics do not alter the observed features of the dissociation process. No simple model could account for the temperature behavior observed in these experiments.

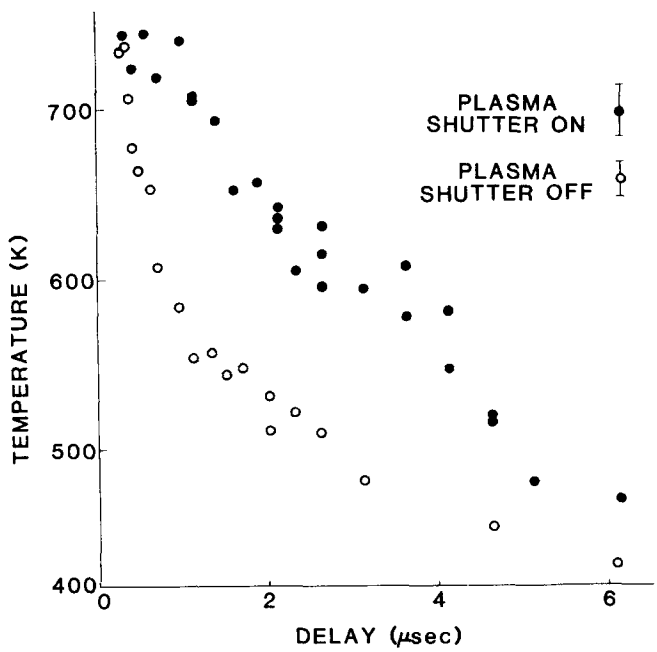

FIG. 4. Plot of the CN $v''=0$ rotational temperature as a function of delay for experiments performed with the plasma shutter on and off at a vinyl cyanide pressure of 20 mTorr.

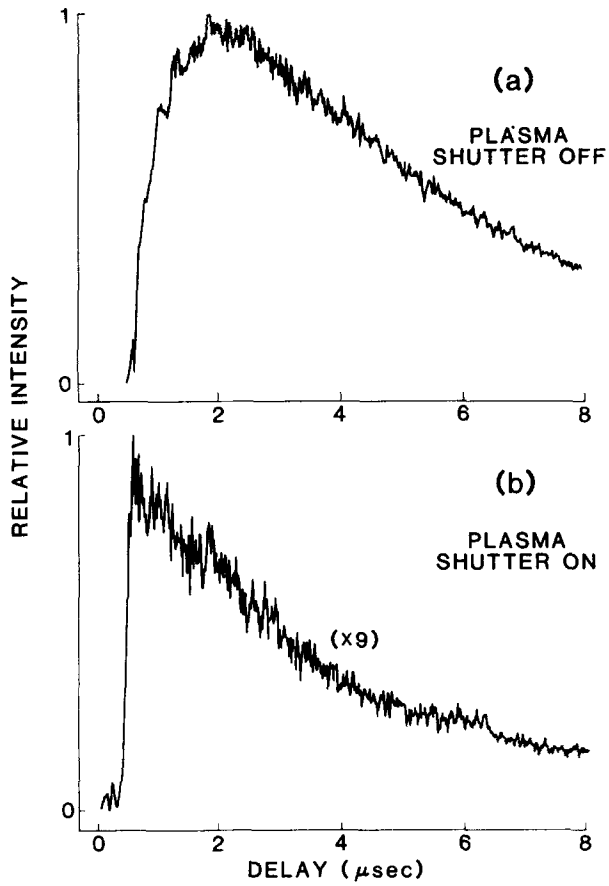

FIG. 5. The fluorescence intensity of the $R(9)$ line of the CN $B-X$ (0,0) band as a function of delay for (a) the plasma shutter off and (b) the plasma shutter on at a vinyl cyanide pressure of 20 mTorr.

As in previous work,[5,6] no significant amounts of vibrationally excited CN were observed in experiments performed with either type of photolysis pulse.

Figure 5 presents the time evolution of the $N''=9$ R branch line laser induced fluorescence signal observed for CN fragments produced in experiments with both types of photolysis pulses. These experiments were performed at a constant vinyl cyanide pressure of 20 mTorr. The $R(9)$ line was found to be the most intense resolved feature in the CN $B-X$ spectrum since the rotational populations observed in these experiments peak at or near the $N''=9$ level. The intensity of this line relative to other resolved features in the excitation spectrum is also independent of the dye laser bandwidth, unlike the P branch bandhead.[9] Due to the effect of changes in rotational temperature on the relative intensity of this line, some deviations of the fluorescence intensity from the true concentration of CN are expected. The $R(9)$ fluorescence intensity does, however, serve as a good measure of the population of CN fragments in the observation zone.

From the $R(9)$ fluorescence observed with the full CO_2 laser pulses [Fig. 5(a)] it is obvious that CN fragments are still being formed several microseconds after the

onset of the laser pulse. This contrasts sharply with the behavior observed for dissociation with the plasma shutter on [Fig. 5(b)]. In this case approximately a factor of 10 fewer fragments are formed, and only at very short delays following the onset of the laser pulse. This corresponds to times when the laser pulse is actually present. The sharp rising edge and immediate falloff of this curve indicates that the total time scale for production of CN in this process is not significantly longer than the laser pulse and is consistent with CN precursor lifetimes on the order of a few nanoseconds.[7,9] Since the maximum effective intensity of both photolysis pulses is approximately the same, the higher CN fragment yield observed with the full CO_2 laser pulse reflects the reduced intensity and fluence requirements for the production of CN molecules from highly excited precursors via dissociation during the pulse tail.[6]

The observed decrease in CN fluorescence at longer delays is characteristic of the diffusion of fragments out of the cylindrical observation region defined by the dye laser. Similar experiments performed at 40 mTorr yielded essentially the same results indicating that the role of reactive collisions in this loss is quite small. Detailed calculations to estimate a translational temperature were not attempted, however, since they are complicated by the unknown initial distribution of fragments in the probe beam and the unknown role of velocity-changing collisions.

IV. DISCUSSION

The CN fragment rotational energy distributions observed in these experiments are necessarily the result of averages over several independent effects in the IRMPD process. During the initial stages of multiple photon absorption, optical pumping of precursors undoubtedly produces a distribution of energies both above and below the dissociation threshold. At first, the initial precursor populations are mapped onto a wide range of excited vibrational states. Once these molecules are pumped above the dissociation threshold further competition between optical pumping and dissociation produces the final distribution of precursor energies which is available for fragment excitation. The apparent Boltzmann nature of the observed distribution most likely results from the statistical partitioning of this available excess energy into CN rotation through some unknown dissociation mechanism which is itself averaged over the distribution of precursor energies.[12]

In addition to these intrinsic averaging processes, the detection scheme employed in these experiments forces us to view averages over variations in the laser pulse as well. Since the dye laser effectively probes the entire focal region of the CO_2 laser, all observed fragment distributions are *the result of averaging over both spatial and temporal variations in the laser pulse.* If the temporal variations in the laser intensity occur on time scales which are shorter than the experimental resolution (here approximately 100 ns), the observed fragment distributions can be thought of as the product of a single "effective" laser intensity distribution. In general, this distribution will be characterized spatially by its moments and temporally by a complicated pulse "shape". Variations in these parameters from one laser to the next can yield substantially different effective intensity distributions, e.g., the temporal intensity variations of mode-locked vs single-mode lasers. In this case the large changes in average intensity between the different laser pulses would produce measurably different fragment energies, although each pulse may be characterized by a single effective intensity distribution (subject to the above experimental constraints).

For these reasons, the initial CN fragment energy observed in experiments with the shortened photolysis pulses may be attributed to dissociation by a single effective laser intensity distribution. The initial CN rotational temperature observed in these experiments primarily reflects the average of all fragment energies produced by dissociation over a range of laser intensities. In addition, the short photolysis pulses used here result in the production of CN fragments on a time scale which is comparable to the temporal resolution of the experiment. The observed CN distributions are therefore insensitive to any temporal variations in the laser intensity. Because of this, the initial CN fragment distributions observed in these experiments with the plasma shutter on may be described as the averaged result of all intensity variations in the laser pulse, i.e., the effective laser intensity distribution.

At increasing delays in the short pulse experiments the initial CN distribution evolves in time (see Fig. 4). The observed decrease in rotational temperature can be completely accounted for, however, by considering the relaxation of the initial CN distribution due to energy transfer collisions with the background gas. Evidence for this is provided by calculations that consider the case in which excited fragments are completely relaxed to the room temperature thermal distribution by a single collision. With this assumption it is possible to derive an effective collision frequency for this process at each pressure. All three of the observed temperature falloffs are well described by this model (correlation coefficients of ~96%). However, at longer delays, small contributions to the decrease of rotational temperatures with time may also be provided by the diffusion of hotter fragments out of the observation region, if translational and rotational excitation are correlated.

The similar behavior of CN and C_2 fragments observed in previous experiments suggests that both fragments are formed with an equivalent amount of translational energy.[3,6] Time-of-flight measurements of the C_2 fragments of vinyl cyanide[13] indicated that their translational energy distribution could be described by a temperature of 500 ± 100 K. If CN fragments are formed with the same translational temperature, an effective cross section of 34 ± 5 Å^2 can be estimated for this process. This reflects the effective cross section for relaxation of an ensemble of rotationally hot CN fragments to a room temperature distribution as a result of single collisions with the background gas of vinyl cyanide and other fragments. For comparison, a hard sphere cross section of 15 Å^2 was found for CN by Evenson, Dunn, and Bro-

ida[14] in microwave line broadening experiments.

Additional contributions to the observed temperature decrease might also be expected as a result of distributions in dissociation lifetimes of the precursor(s) to CN. The distribution of excess energy in these precursors results in a range of dissociation lifetimes with more energetic precursors dissociating at earlier times. Since the precursor energy is partitioned into the fragments during dissociation, such a process would result in the observation of hotter CN radicals at shorter delays. Previous work, however, indicates that the most likely precursors to CN have dissociation lifetimes on the order of a few nanoseconds, much shorter than the temporal resolution of this experiment. Therefore, any intrinsic relaxation of CN rotational temperatures due to a distribution of dissociation lifetimes on this time scale would not be observed in these experiments. Averaging over this distribution would, however, affect the initial rotational temperature observed.

If larger precursors contribute to the formation of CN, then dissociation lifetimes on the order of several microseconds might be expected. These molecules would have to absorb sufficient energy during the laser pulse either to fragment directly to yield CN or form highly energetic fragments which in turn dissociate to CN without absorbing additional photons. Both of these processes seem highly unlikely,[13] however, and are directly contradicted by the rapid rise of CN population during the short laser pulse, followed by the immediate falloff of population with time. The observed decrease of CN rotational temperatures in these experiments, then, is completely consistent with the collisional relaxation of an initial hot distribution formed by the short photolysis pulse.

Since the same CO_2 laser is used in both full and short pulse experiments, much of the complicated behavior observed for CN fragments in the full pulse experiment can be attributed to the low intensity tail of that laser pulse. At short delays, both experiments view the same initial distribution of CN fragments created by the rising edge of the gain-switched laser spike. The full CO_2 laser pulse, however, is characterized by temporal variations in the laser intensity which occur over several microseconds. In these experiments, then, it is more appropriate to consider the production of the observed fragment energies as the result of various effective intensity distributions.

As was predicted in earlier experiments on both the CN and C_2 fragments of vinyl cyanide,[6] the rapid initial decrease in rotational temperatures observed in the full photolysis pulse experiments is thus the result of the decreasing effective intensity in the tail of the CO_2 laser pulse. The lower effective intensity of the pulse tail results in less excited precursors, which in turn is reflected in lower fragment rotational temperatures. As seen from a comparison of the rotational temperature plot (Fig. 4) and the population curve [Fig. 5(a)] for this experiment, the rapid initial decrease of CN rotational temperatures is caused by the dilution of the initial hot distribution by the larger numbers of cooler fragments produced during the less intense tail of the CO_2 laser pulse.

From the short photolysis pulse experiments it is apparent that collisions can also produce temperature changes on time scales similar to that of the rapid initial decrease in the full pulse experiments. Previous results of similar full pulse experiments exhibited the same behavior for a wide range of pressure conditions, indicating that collisions do not play a significant role in the rapid initial decrease.[5] Such an effect is most likely masked by the large numbers of fragments which are continuously formed during these times. At longer delays, following the end of CN production, collisional relaxation of the distribution is evident in the more linear temperature decrease observed with delay.

In light of these results it is also possible to reconcile the different behavior of CN rotational temperatures reported by Miller and Zare[5] and by Yu, Levy, and Wittig[3] for the IRMPD of vinyl cyanide. From the previous discussion it is clear that the time dependent CN rotational temperatures reported by Miller and Zare were due to the observable effects of variations in the effective intensity distribution during the laser pulse. The ~100 ns resolution of these experiments could easily resolve contributions to the observed distribution of fragments resulting from CN molecules formed at various times during the several microsecond laser pulse. In the work of Yu *et al.*, however, the duration of the photolysis pulse was only 50 ns (FWHM), significantly shorter than even the plasma shutter produced pulses of this work. The time dependence of CN rotational energy produced by variations in laser intensity could not be observed in these experiments. The hotter CN rotational temperature of ~1000 K reported by these workers reflects the much higher effective intensity of the laser used in these experiments, 1 J per 50 ns pulse, as opposed to the 0.36 J per 210 ns pulses produced by the plasma shutter. The observed differences in the results of these experiments, then, can also be attributed to the effects of different effective intensity distributions in the IRMPD of vinyl cyanide.

V. CONCLUSION

The different behavior of CN rotational temperatures observed in these experiments can be attributed to the effect of different effective laser intensity distributions in the IRMPD of vinyl cyanide. In the short pulse experiments with the plasma shutter on, a single effective intensity distribution creates a population of CN fragments characterized by a single rotational temperature. This population is then relaxed by collisions with the bath of background gas molecules.

A similar hot distribution of CN fragments is also created during the initial stages of photodissociation with the full CO_2 laser pulse. The lower effective intensity of the tail of this pulse also produces larger numbers of cooler CN fragments at longer delays. The observed rapid decrease in rotational temperatures in these experiments may thus be identified as the result

of dilution of the initial hot distribution by the majority of cooler CN fragments formed at longer delays. Collisional energy transfer also results in some decrease of these temperatures at longer delays.

Finally, the different behavior of CN rotational temperatures reported by different groups for the IRMPD of vinyl cyanide can be attributed to the effects of different effective laser intensity distributions. As in these experiments, the much shorter photolysis pulses of Yu *et al.*[3] can be thought of in terms of a single effective laser intensity distribution. The higher effective laser intensity used in these experiments results in a single distribution of CN fragments characterized by a hotter rotational temperature than observed in experiments performed by Miller *et al.*[5,6]

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