

TIME DEPENDENCE OF CN INTERNAL ENERGY DISTRIBUTION FOLLOWING IR MULTIPHOTON DISSOCIATION OF VINYL CYANIDE

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Laser-induced fluorescence was used to study the CN radical produced by infrared multiphoton dissociation of vinyl cyanide. The time between the photolysis pulse and observation was varied. CN fragments produced at short times were hotter rotationally than those produced later, even under the collisionless conditions of a molecular beam

1. Introduction

The field of infrared multiphoton dissociation of molecules, although intensely studied in recent times, continues to generate a great deal of interest among the scientific community. Considerable research, both theoretical and experimental, remains to be done in order to understand the process by which a molecule absorbs many photons and undergoes decomposition. Some investigators have probed the excitation mechanism by seeking reaction products other than those coming from the lowest thermodynamic path [1]. Others have chosen molecules with two reaction routes that compete under conventional thermolysis [2]. While illustrative of the pumping process, the energy grain of these experiments may be on the order of tens of thousands of wavenumbers

A finer grain by which to study the infrared multiphoton dissociation process is provided by the internal energy levels of the fragments from a single reaction path. Laser-induced fluorescence offers a convenient technique to study the distribution of energy among these levels. Many small fragments have simple fluorescence excitation spectra, allowing examination of vibrational and rotational energy distributions. This approach has been used in the low-pressure studies of the fragments NH_2 [3], CF_2 [4], CH_2 [5], C_2 [6,7], OH [8], CH [8,9], and CN [9,10].

The present work utilizes the technique of laser-induced fluorescence to study the CN radical created by

the infrared multiphoton dissociation of vinyl cyanide (acrylonitrile), $\text{H}_2\text{C}=\text{CHCN}$. Vinyl cyanide has been observed to be an efficient source for both C_2 and CN [7]. Experiments were performed both in a flowing gas and under the collisionless condition of a supersonic molecular beam. The time was varied between the photolysis of the parent compound and the observation of the CN product. The CN rotational distribution under collisionless conditions is found to be cooler at longer times. This result appears to be indicative of the energy distributions created within the parent vinyl cyanide molecules by the infrared laser.

2. Experimental

These experiments were performed in a two-chamber molecular beam apparatus. A source chamber was attached to one side of the main observation chamber; on the opposite side a secondary port provided for a "beam dump" and additional pumping speed. Both the source and main chambers were cryopumped with liquid nitrogen. The base pressure of the apparatus was below 10^{-6} Torr.

The nozzle was a bearing jewel with a 0.13 mm diameter hole. The free expansion jet was skimmed through a 1 mm diameter opening. The skimmer-nozzle distance could be adjusted externally, thus spacing was typically 3.8 mm. The pressure of vinyl cyanide behind the nozzle was measured by a capacitance manom-

eter. For most beam experiments this was maintained at 75 Torr through evaporation from a liquid reservoir. These conditions correspond to a hard-sphere collision time of greater than 60 μs in the molecular beam. Vinyl cyanide could also be admitted to the main chamber through a valved opening in its side; a capacitance manometer measured the main chamber pressure in these cases.

The infrared laser was a Lumonics model 801A TEA CO_2 laser. The wavelength selective grating was replaced by a gold-coated flat. This caused the laser to operate multiline, primarily on the 10.6 μm P(20) line (944 cm^{-1}). This line lies slightly to the red of both the $\text{C}=\text{CH}_2$ and $\text{C}=\text{CHCN}$ wag vibrational modes of vinyl cyanide (963 and 1023 cm^{-1} , respectively) [11]. At a repetition rate of 15 Hz, we obtained 1.3 J per pulse in a roughly circular spot about 3 cm in diameter. The pulse power was divided almost equally between an initial spike (300 ns fwhm) and a long tail (several μs). Under finer temporal resolution, the entire pulse consisted of a series of short spikes, indicative of the multimode character of the laser. This resulted in a shot-to-shot variation in the peak of the pulse of up to 50 ns, although the trigger stability was better than 10 ns. The CO_2 laser beam was focused into the apparatus with a 50 mm diameter $f/4$ BaF_2 lens through an anti-reflection coated germanium flat. It crossed the axis of the molecular beam at right angles at a distance of 7 cm from the front surface of the skimmer.

A nitrogen pumped dye laser provided tunable light from 384 to 390 nm using the dye BBQ*. This region corresponds to the CN B-X violet system. The measured bandwidth was less than 0.03 nm. The dye laser beam crossed the reaction zone at approximately right angles to both the molecular beam and CO_2 laser axes.

Light from the intersection of the three axes was imaged by a lens through a bandpass interference filter onto the cathode of an EMI 9558 QA photomultiplier tube (S-20 response). The interference filter had a 50% pass band of 10.1 nm centered at 387.8 nm. This served to eliminate much of the luminescence which accompanies the multiphoton dissociation of vinyl cyanide

* Initial difficulty with this dye was overcome by using a concentration of 2.6×10^{-3} M in 1:1 by volume toluene:ethanol. The solvent was dried over anhydrous magnesium sulfate and filtered immediately before use.

[12]. The output of the photomultiplier was viewed on an oscilloscope and fed to a PAR model 162/164 boxcar integrator for temporal discrimination. The output of the integrator was plotted with a stripchart recorder.

The synchronization output of the CO_2 laser provided the time reference for these experiments. The boxcar integrator and oscilloscope were both triggered by this signal. One channel of the integrator was used to initiate the firing of the dye laser system, while the other supplied the detection gating. In this manner the time at which the CN radicals were probed could be set at a particular value or scanned.

The vinyl cyanide was obtained from the Aldrich Chemical Company and was degassed under vacuum prior to use. The purity was checked by gas chromatography and a single peak was recorded. Detection limits placed impurity levels at less than 0.05%.

3. Results and discussion

Fig. 1 shows two laser-induced fluorescence spectra of the CN radical. Both were obtained after IR multiphoton dissociation of vinyl cyanide in a molecular beam. The upper spectrum (fig. 1a) was taken with a relatively short delay between the start of the CO_2 laser photolysis pulse and the dye laser probe pulse. The lower trace (fig. 1b) was taken with the probe near

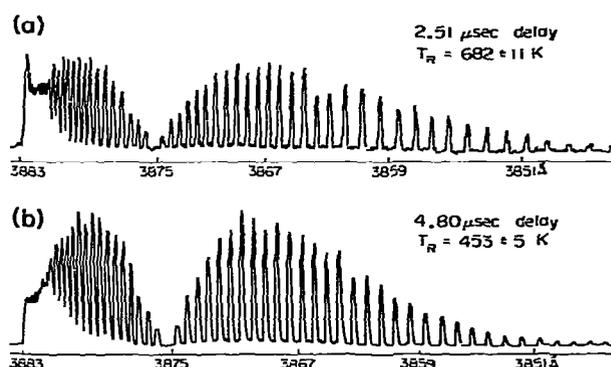


Fig. 1. Excitation spectra of CN radicals produced by the IR photolysis of vinyl cyanide in a molecular beam, taken at two different time delays. The spectra correspond to the rotational structure of the (0, 0) band of the $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$ violet system.

the end of the CO₂ laser pulse. The times listed refer to the beginning of the triggering process, the CO₂ laser pulse begins at 1.95 μ s.

The observed spectra correspond to the (0, 0) vibrational band of the CN violet system. The band origin occurs at 387.5 nm; the R branch proceeds to shorter wavelengths. The P branch moves to longer wavelengths before folding back onto itself to form the bandhead at 388.3 nm. The bandhead is the most commonly observed feature in high temperature CN spectra [13, 14, p. 31]. Increasing amounts of rotational energy result both in a more pronounced bandhead and a more distributed R branch. Qualitatively fig. 1a represents CN radicals with greater rotational energy than those of fig. 1b.

The rotational energy distribution of the CN fragments may be further quantified. Let N'' denote the ground-state rotational quantum number. A plot of the logarithm of the intensity of the N'' th line divided by $(2N'' + 1)$ against the quantity $N''(N'' + 1)$ yields a straight line for a Boltzmann rotational distribution [14, p. 124]. The slope of this line is inversely proportional to the rotational temperature. Our spectral data were interpreted in this manner, using the distinct rotational lines of the R branch; all rotational distributions appeared to be Boltzmann in nature. Errors listed in fig. 1 are one standard deviation.

The (1, 1) and (2, 2) vibrational bands also occur in this region of the spectrum. The absence of features of these bands in our spectra leads us to conclude that only small amounts of vibrationally excited CN are present. If the vibrational distribution is also Boltzmann in nature, then we can set an upper limit of 1000 K on the vibrational temperature.

Experiments were performed with both a molecular beam and with flowing gas in the chamber. Pressures ranged from 5–100 mTorr in the latter case. With each set of conditions a series of spectra were taken at various delays between the photolysis and probe lasers. Individual spectra were reduced to the rotational temperature which best described them. Two typical data sets are shown in fig. 2.

Both sets of data show similar trends. At the earliest times studied, the rotational temperature had a value of about 700 K. This dropped rapidly to approximately 450 K as the delay was increased. This initial sharp rotational temperature drop is independent of pressure under the pressure range studied. With the flowing gas

arrangement, a slower drop in temperature continued as time progressed. Other flowing gas data sets are similar—a sharp initial drop followed by a slower decrease in rotational temperature. The rate of the latter temperature decrease increases with increasing pressure, indicating collisional rotational cooling is occurring on this longer time scale. The temperature at long times under beam conditions remains constant, within experimental error.

The population of CN radicals in the observation zone changes with time, while the individual fragments do not. This can be seen in the curves marked "band-head CN" in fig. 2. These were obtained by tuning the dye laser wavelength to the CN bandhead, then scanning the time delay of the dye laser. After an induction period, this signal rose rapidly and reached a peak during the tail of the CO₂ laser pulse. This represents a rapidly growing number of CN radicals within the observation region. This signal deviates from the true population of CN radicals to the extent that the intensity of the bandhead changes with rotational temperature. Thus the initial rapid drop in temperature is not collisional cooling of a single group of CN radicals, but the decrease in the average value of the tempera-

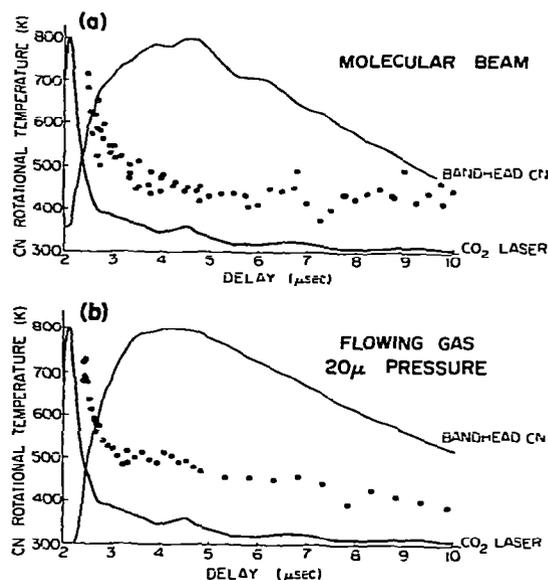


Fig. 2. CN rotational temperature (●) versus delay time between IR photolysis and laser-induced fluorescence observation. Also shown are the CO₂ laser pulse and the (scaled) excited fluorescence signal from the CN B-X (0, 0) bandhead.

ture through the creation and addition of progressively cooler fragments to the total CN population †. The pressure independence of this feature is consistent with this interpretation.

At a time shortly after 4 μ s, the CN bandhead signal begins to decrease. Under molecular beam conditions this can be accounted for in terms of mass movement of the reaction fragments out of the observation zone along the axis of the molecular beam. Diffusion and reactive collisions remove CN radicals in the case of the flowing gas experiments.

The mechanism by which vinyl cyanide yields CN is not presently established, although the collisionless nature is clear. It is not known in what order the bonds break and to what extent additional infrared pumping occurs during the dissociation ‡. The evolution of the group of CN molecules at short times may be explained in terms of the energy content of its immediate precursor prior to dissociation. It is reasonable to assume that the precursor has a distribution of energies above its dissociation threshold. Those precursor molecules with the largest amounts of excitation decompose most rapidly. We postulate that this higher energy content is reflected in a higher rotational temperature of the resulting CN fragment. Those precursor molecules with a lesser degree of excitation decompose more slowly, and also yield a fragment with lower rotational energy. The temperature and yield curves of fig. 2 suggest that the majority of the CN fragments originate from precursors having this lesser degree of excitation.

4. Conclusion

We have observed the time evolution of the rotational temperature of the CN radical under collisional and collisionless conditions in the infrared multiphoton dissociation of vinyl cyanide. A sharp temperature fall-off occurs at times soon after the beginning of the dissociation process. We believe that this behavior reflects

† Strictly speaking, the sum of two Boltzmann distributions with temperatures T_1 and T_2 is not a Boltzmann distribution itself. It may be approximated by a Boltzmann distribution at a temperature $T = 2T_1T_2/(T_1 + T_2)$

‡ Future experiments are planned in which the temporal and spatial character of the CO₂ laser will be varied. Other fragments and precursors will also be examined.

the distribution of energy in the immediate precursor to the CN fragment.

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