

Short Communication

Laser intensity effects in the rotational distributions of CN radicals formed by IR multiple photon dissociation of C_2H_3CN

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Measurements of the distributions of internal and translational energies in the fragments of IR multiple photon dissociation (MPD) processes can provide important details about the dynamical behaviour of molecules excited above their energy barrier to dissociation. During the dissociating IR laser pulse two competing processes can take place for these molecules under collision-free conditions: unimolecular decomposition (via one or more dissociation channels) and further up-pumping by IR photon absorption. The rate of the former process increases markedly with internal energy content of the molecule above the dissociation barrier; that of the latter depends upon the laser intensity. Hence the relative rates of these processes will determine the average energy that molecules reach above the dissociation barrier and thus the energy available for partitioning into fragments. We report the very marked change in rotational temperature of $CN(X^2\Sigma^+)$ fragments which takes place during the CO_2 laser pulse in the IR MPD of C_2H_3CN , which we believe is caused by the IR laser intensity.

C_2H_3CN contained in a cell at low pressures was dissociated by the loosely focused output of a TEA CO_2 laser operating on the P(20) line at $10.6\ \mu m$ [1]. $CN(X^2\Sigma^+)$ fragments in their ground vibrational state $v'' = 0$ were detected at specific times during the CO_2 laser pulse by laser-induced fluorescence (LIF) of the $CN\ B^2\Sigma^+(v' = 0) - X^2\Sigma^+(v'' = 0)$ transition; excitation spectra of the radicals were recorded by stepping the wavelength of the tunable dye laser and monitoring the resonant fluorescence output through a narrow-band interference filter. Figure 1 shows such excitation spectra observed at two times during the laser pulse: at 160 ns from the peak of the gain-switched laser spike and at $3\ \mu s$ from the peak during the low intensity tail. Although both spectra originate from the ground vibrational level, clearly the rotational distributions are very different in the two cases; the measurements at $3\ \mu s$ show the absence of a pronounced P branch head at 388.34 nm and the maximum in the R branch envelope appears at longer wavelengths, indicating less rotational excitation than in the fragments formed near the peak of the CO_2 laser pulse.

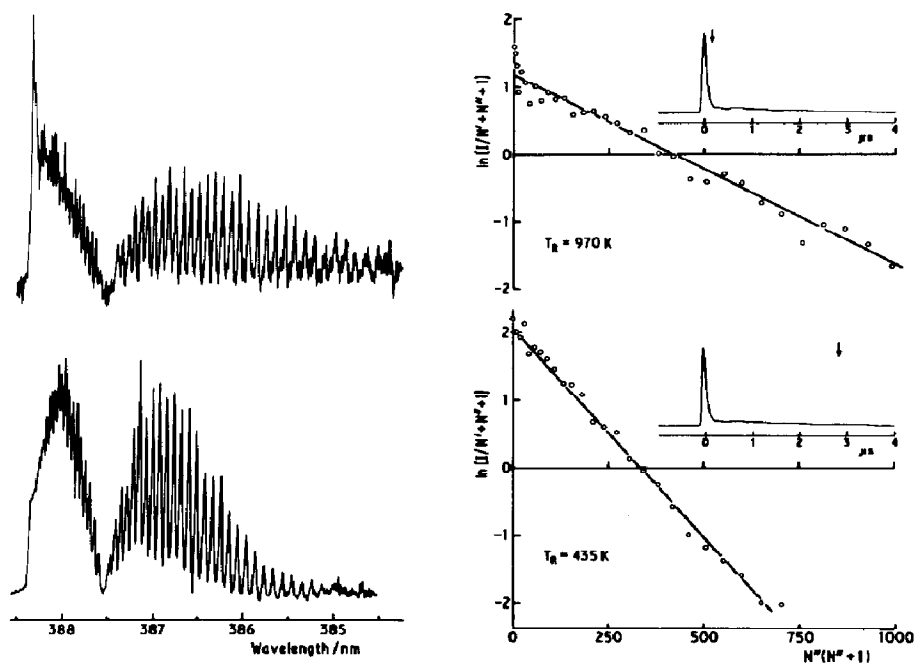


Fig. 1. Rotational distributions of $\text{CN}(X^2\Sigma^+, v'' = 0)$ produced in the IR MPD of 10 mTorr $\text{C}_2\text{H}_3\text{CN}$. On the left are fluorescence excitation spectra taken at times of 160 ns (upper trace) and 3 μs (lower trace) from the peak of the CO_2 laser pulse. The pulse shape, with these times indicated, is illustrated to the upper right of the figure (the time resolution of the detection system does not show the mode beating which is present in this multimode laser pulse). The plots of $\ln \{I/(N' + N'' + 1)\}$ against $N''(N'' + 1)$ to the right of each excitation spectrum show that the rotational distributions of CN fragments appear to be Boltzmann, with very different rotational temperatures T_R of 970 K and 435 K for the 160 ns and 3 μs observations respectively. The fluence was 18 J cm^{-2} at 160 ns and 55 J cm^{-2} at 3 μs .

These differences are shown quantitatively in Fig. 1 as plots of $\ln \{I/(N' + N'' + 1)\}$ against $N''(N'' + 1)$, where I is the total fluorescence intensity observed following pumping of a specific $N' \leftarrow N''$ transition in the R branch of the (0,0) band of the $\text{CN}(\text{B}-\text{X})$ system (the spin doublets of these transitions are not resolved with the laser bandwidth of approximately 0.02 nm). $I/(N' + N'' + 1)$ is proportional to the population of the N'' rotational level of $\text{CN}(X, v'' = 0)$ of energy $B''N''(N'' + 1)$ [2]; hence this plot should give a straight line for a Boltzmann rotational distribution of CN radicals from the slope of which a rotational temperature T_R can be found. The figure shows that the distributions appear to be Boltzmann within experimental error with $T_R = 970$ K and 435 K for the early and late times respectively. Measurements at times between 160 ns and 3 μs showed decreasing values of T_R between these limits.

At 10 mTorr and an observation time of 3 μs it was calculated that an upper limit of 20% of the observed radicals undergo a single gas kinetic collision before observation. The "rotational cooling" apparent with time during the laser pulse was, however, shown not to be due to collisional

relaxation of radicals formed early in the pulse. At a constant delay time, changing the C_2H_3CN pressure such that the fraction of molecules undergoing a single gas kinetic collision was varied between 1 and 50% produced no change in the rotational temperature and the fluorescence intensity showed a linear increase with precursor pressure.

The majority of radicals observed at $3 \mu s$ delay are produced following absorption of radiation in the low intensity CO_2 laser tail and not by dissociation of relatively long-lived species formed with little energy above the dissociation barrier in the early high intensity part of the pulse. This was demonstrated in experiments in which two different pulse shapes were used. When a nitrogen-free pulse consisting of a high intensity spike lasting approximately 90 ns and with no low intensity tail was used, the dissociation yield at $3 \mu s$ was a factor of eight lower than that measured at the same delay for a conventional pulse comprising an initial spike of the same intensity followed by a tail containing approximately the same energy. Furthermore, the temperature observed at $3 \mu s$ in the "no-tail" pulse was considerably higher than that measured for the "spike-plus-tail" pulse. In the former case molecules dissociated in the high intensity spike were still present in their original distribution at the longer delay times, the geometry of the experiment ensuring that very few fragments were lost on this time scale by flight out of the probing dye laser beam. The distribution at $3 \mu s$ shown in Fig. 1 thus contains contributions from the high temperature fragments produced early in the laser pulse, although this contribution is minor in comparison with the total dissociation yield taking place during the low intensity tail.

It appears that laser intensity is controlling the average energy reached above the dissociation limit and thus the energy distributed into rotation in the $CN(X^2\Sigma^+)$ fragment. This internal energy observation demonstrates a second effect of laser intensity upon MPD: the overall dissociation yields of NH_2 from CH_3NH_2 [3] and CF_2 from CF_2HCl [4] have previously been shown to be intensity as well as fluence dependent, and indeed we observe this also to be the case in the overall yield of CN from C_2H_3CN . The present results have several important consequences in IR MPD studies.

(1) Measurements of dissociation yields as a function of laser fluence are normally carried out under conditions in which intensity and fluence are simultaneously varied. LIF measurements at a single excitation wavelength under these conditions can result in distorted estimates of total relative dissociation yields (as illustrated in Fig. 1, where LIF measurements at the P branch band head at 388.34 nm would not reflect accurately the total dissociation yields).

(2) The laser intensity needs to be specified for measurements of energy distributions: this effect almost certainly accounts for the discrepancies in internal [5] and translational [3, 6] energy distributions for the same MPD process measured in different laboratories.

(3) To quantify these effects CO_2 laser pulses of well-defined intensity and fluence are required. Single-mode pulses of this kind shaped by electro-optic crystals are to be used in this laboratory to investigate intensity effects quantitatively.

On completion of this initial study we learnt of very similar observations of this effect in the CN radical carried out under both "bulk" and "beam" conditions by Miller and Zare [7].

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