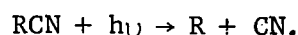


LASER INDUCED PHOTOLUMINESCENCE SPECTROSCOPY OF COMETARY RADICALS

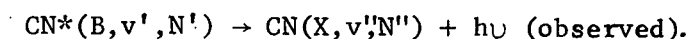
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A relatively new technique called Laser Induced Photoluminescence Spectroscopy has been applied to laboratory studies of cometary radicals. This technique can be used to measure properties of radicals, to determine photodissociation processes in parent molecules, and to investigate reactions of radicals in specific vibration-rotation levels. Thus far, the LIPS method has been applied to the CN radical to determine: (1) the radiative lifetime and quenching constants for the $B^2\Sigma^+$ state and (2) the photodissociative formation of CN from several parent molecules.

This experimental technique combines flash photolysis together with laser excitation of the product fragments. Figure 1 is a schematic diagram of the apparatus, and the experimental sequence of events is summarized below. The parent molecule is photodissociated:



After a variable time delay, the tunable dye laser is fired and excites those radicals in a specific vibration-rotation level of the ground electronic state to the B state via the $\Delta V = 0$ sequence of the Violet Band system. The reradiated light is then detected.



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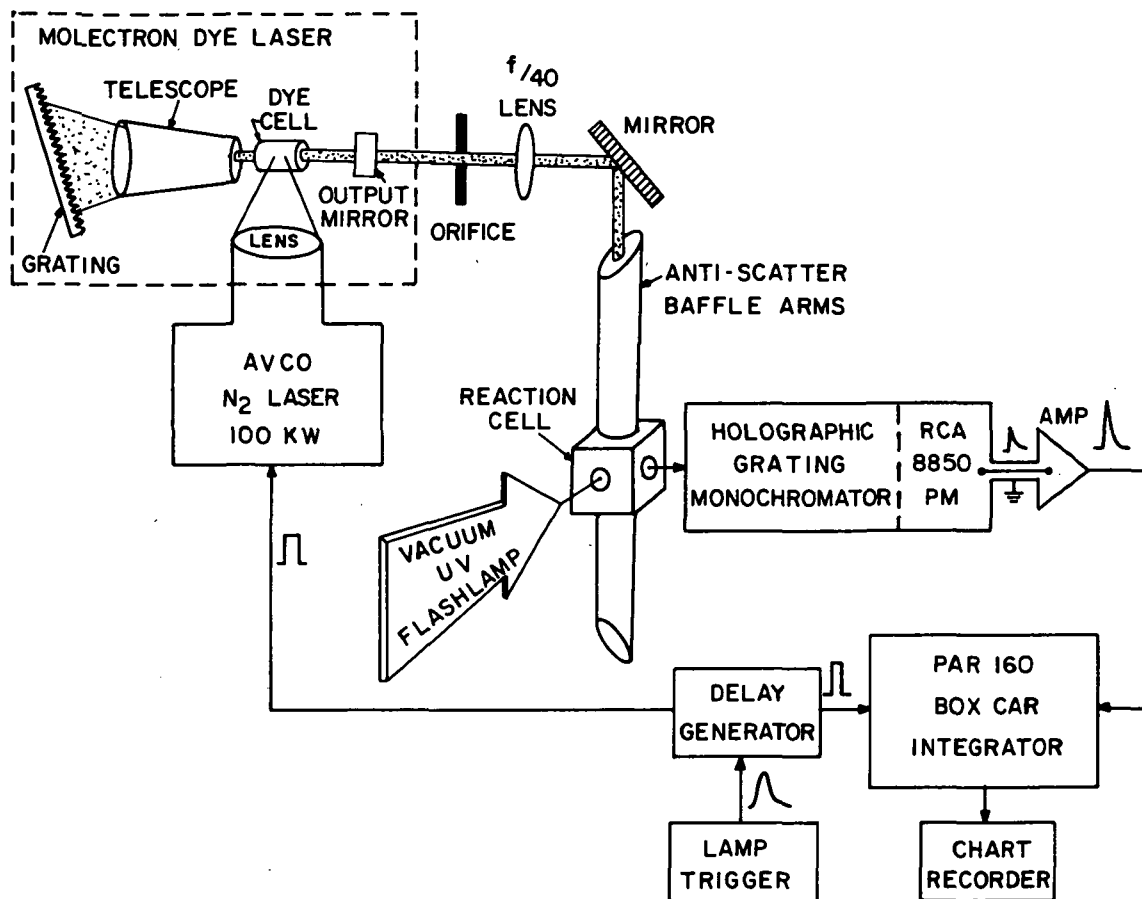


Figure 1. Diagram of Experimental Apparatus

Figure 2 shows two spectra taken for the photodissociation of cyanogen (C_2N_2). The spectral resolution is ~ 0.01 nm and is determined by the characteristics of the dye laser.

The LIPS method has been used to measure the radiative lifetimes of the individual rotational levels in the zeroth vibrational level of the B state of CN.¹ Using photon-counting, the decay of rotational line intensities was measured after laser excitation. A radiative lifetime of 65.6 ± 1.0 nsec was determined for the unperturbed levels, and the quenching cross-section of the B state by C_2N_2 was $41 \pm 20 \text{ \AA}^2$.

The energy partitioning between the CN radicals formed in the photodissociation of C_2N_2 was also studied. The spectrum at the top of Figure 2 is that of CN radicals which are newly formed in the X state and have suffered no more than a few collisions. The band-heads of both the 0-0 and the 1-1 bands are clearly visible which indicates rotational excitation. The lower spectrum was taken after the radicals had undergone several hundred collisions which are sufficient to thermalize the rotational levels. Analysis of the spectral line intensities by the following equation from Herzberg²

$$\ln \left[\frac{I_R}{U(N'+N''+1)} \right] \propto -E_R(N'') * \frac{hc}{kT_R}$$

yielded "effective" rotational temperatures (T_R) for the two lowest vibrational levels. The newly formed CN had rotational temperatures for the $v''=0$ level of $\sim 1500^\circ\text{K}$ and for the $v''=1$ level of $\sim 950^\circ\text{K}$. The vibrational band intensity ratio, i.e. the vibration population

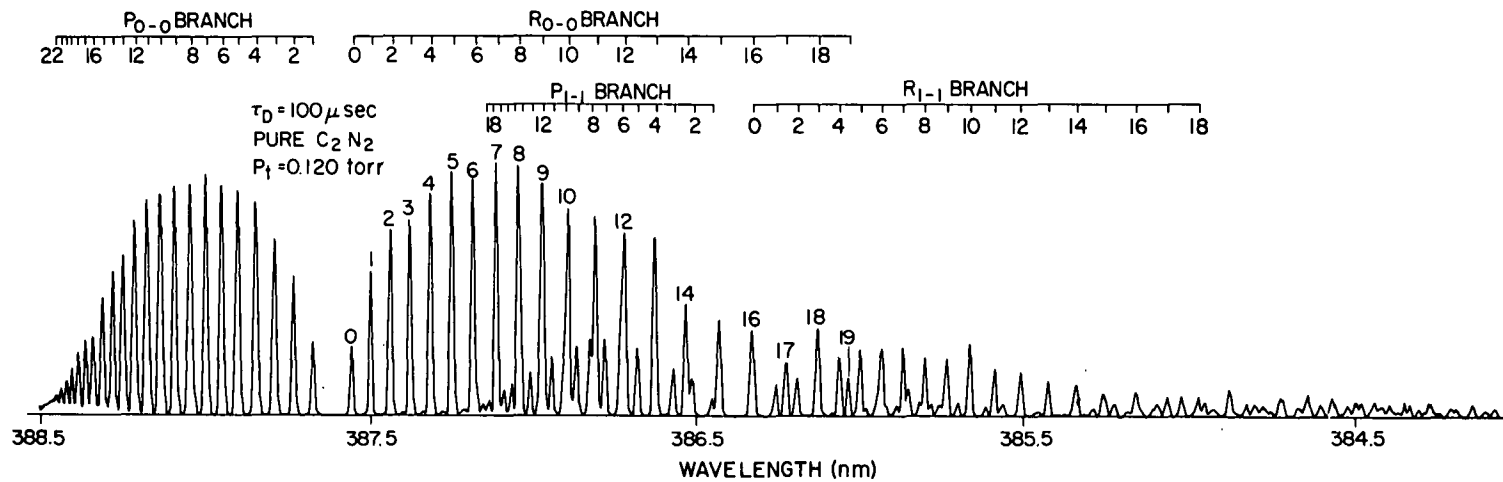
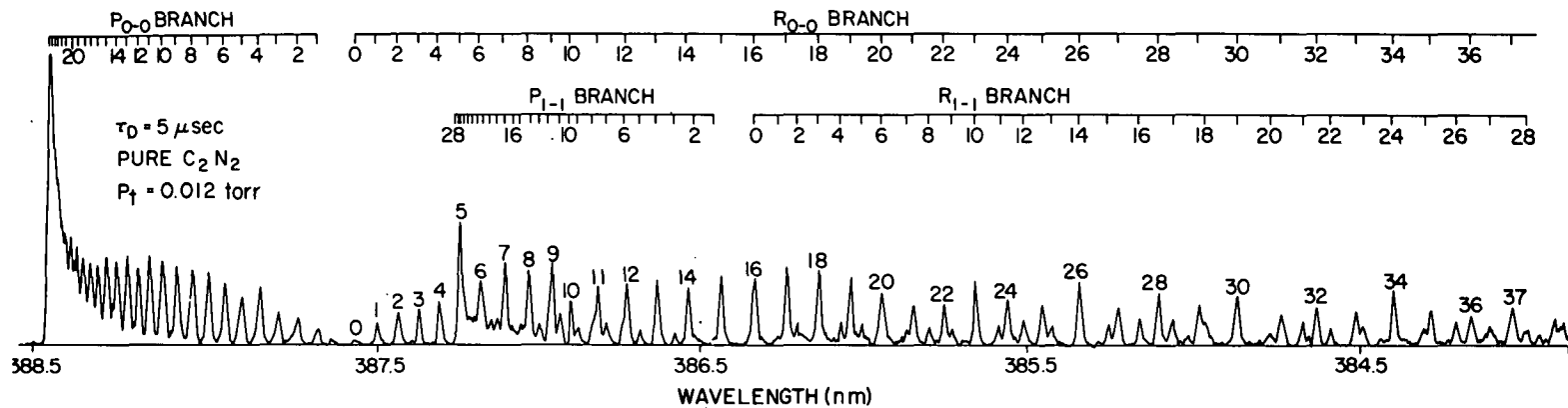


Figure 2. Spectra of CN Radicals Produced by Photodissociation of C_2N_2 .

ratio, of the $v''=0$ to 1 levels is 2.3, which corresponds to an "effective" Boltzmann temperature of 3600°K .

The photodissociation of C_2N_2 occurs in its first strong absorption band between 150.0 and 170.0 nm above the cutoff of the sapphire window. At these photon energies there are two possible mechanisms: formation of the CN radicals (1) both in the X state or (2) one in the X and one in the A state. Results of indirect experiments indicate that the primary photochemical ratio of A to X is ~ 1 , pointing to process (2) as predominant. When electronic, vibrational, and rotational excitation is accounted for, there remains ~ 0.67 eV of energy for translational excitation, i.e. a translational temperature of 2600°K for equal energy partitioning.

CN radicals formed in the photodissociation of dicyanoacetylene ($\text{NC-C}\equiv\text{C-CN}$) were also found to have vibrational and rotational excitation and probably translational as well. In comets if photodissociation is one of the sources of radicals, then similar rotational and translational excitation of the fragments could heat the cometary atmosphere.

REFERENCES

1. W. M. Jackson, J. Chem. Phys. 61, 4177 (1974).
2. G. Herzberg, "Molecular Spectra and Molecular Structure: Vol. I. Spectra of Diatomic Molecules", van Nostrand Reinhold Company (New York, 1950), p. 126.