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:

$$RCN + h\nu \rightarrow R + CN.$$  

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.

$$CN(X^2\Sigma^+,v'',N'') + h\nu (laser) \rightarrow CN^*(B^2\Sigma^+,v',N')$$

$$CN^*(B,v',N') \rightarrow CN(X,v''N'') + h\nu \text{ (observed)}.$$  

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Figure 1. Diagram of Experimental Apparatus
Figure 2 shows two spectra taken for the photodissociation of cyanogen (C$_2$N$_2$). The spectral resolution is $\sim$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. Using photon-counting, the decay of rotational line intensities was measured after laser excitation. A radiative lifetime of $65.6 \pm 1.0$ nsec was determined for the unperturbed levels, and the quenching cross-section of the B state by C$_2$N$_2$ was $41 \pm 20 \AA^2$.

The energy partitioning between the CN radicals formed in the photodissociation of C$_2$N$_2$ 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 Herzberg

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

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$1500$^0$K and for the $v'' = 1$ level of $\sim$950$^0$K. The vibrational band intensity ratio, i.e. the vibration population
Figure 2. Spectra of CN Radicals Produced by Photodissociation of C$_2$N$_2$. 

$\tau_0 = 5$ \textmu sec

PURE C$_2$N$_2$

$P_1 = 0.012$ torr

$\tau_0 = 100$ \textmu sec

PURE C$_2$N$_2$

$P_1 = 0.120$ torr
ratio, of the v'"=0 to 1 levels is 2.3, which corresponds to an
"effective" Boltzmann temperature of 3600°K.

The photodissociation of C2N2 occurs in its first strong absorp-
tion 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 in-
dicate 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
(NC-C≡C-CN) were also found to have vibrational and rotational excita-
tion and probably translational as well. In comets if photodissociation
is one of the sources of radicals, then similar rotational and trans-
lational excitation of the fragments could heat the cometary atmosphere.

REFERENCES

Spectra of Diatomic Molecules", van Nostrand Reinhold Company