

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Tmx - 71389

ON THE DETECTION OF NEWLY CREATED CN RADICALS AND COMETS

(NASA-TM-X-71389) ON THE DETECTION OF NEWLY
CREATED CN RADICALS AND COMETS (NASA) 15 p
HC A02/MF A01 CSCI 07D

N77-32264

Unclas

G3/25

48571

**BERTRAM DONN
REGINA J. CODY**

JULY 1977



**GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND**



ON THE DETECTION OF NEWLY CREATED
CN RADICALS AND COMETS

Bertram Donn and Regina J. Cody
NASA/Goddard Space Flight Center
Laboratory for Extraterrestrial Physics
Astrochemistry Branch
Greenbelt, Maryland 20771

ABSTRACT

Laboratory investigations of CN radical formation by photodissociation of parent molecules have suggested the possibility of observing emission lines in cometary spectra from newly formed CN radicals. These laboratory studies have shown that high initial internal excitation of CN is the rule with excitation of rotational levels N up to 70. In the collisionless environment of the cometary atmosphere this initial excitation would yield a corresponding distribution for the lowest vibrational level of the ground $X^2\Sigma^+$ state. Our calculations show that it is feasible with present observational techniques to detect photochemically excited lines with $N \sim 30$ in the 0-0 band of the violet system.

The mechanism(s) of formation of cometary radicals remains uncertain, although several sources, particularly, photodissociation of parent molecules, have been suggested (Whipple and Huebner, 1976). Recent laboratory investigations (Cody et al., 1977; Sabety-Dzvonik et al., 1976, 1977) on the formation of CN radicals by photodissociation indicate new spectroscopic cometary observations which could be used as a probe for the formation mechanism of radicals. This laboratory work measured the amount and the distribution of energy released into the newly formed radicals by the photodissociation process. A summary of the experimental method and results follows.

The experimental method consisted of flash-photolysis of the parent compound followed by laser induced fluorescence detection of the CN fragment (Cody et al., 1977). Two low energy (~1 joule) flashlamps with cut-off filters covered the photolysis region from 135 - 270 nm. A variable time delay of a few microseconds was introduced between the firing of the flashlamp and the triggering of an N₂-laser pumped dye laser. The flashlamp and the laser were pulsed at a rate of 50 Hz, while the dye laser was slowly scanned over the $\Delta v = 0$ band sequence of the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ system of the CN radical. The resulting fluorescence from the excited radicals in the B state was detected photoelectrically. The spectral resolution, (which was determined by the parameters of the dye laser output) was about 0.02 nm and allowed detection of individual rotational lines. By this method the relative populations of the vibrational-rotational levels of the X state were directly monitored.

CN formation in the A(²Π) electronically excited state was detected indirectly. In the $v' = 0$ vibrational level of the A state there are

some rotational levels which are nearly resonant with certain rotational levels in the $v = 4$ level of the X state. When a sufficient number of collisions occurs, there is a high probability of exciting the $CN(X, v = 4)$ state by collisional crossover from the A state. The number of collisions was controlled by the pressure and the time delay. The crossover was detectable as an intensity enhancement of the 4-4 band fluorescence over the band intensity under low collision conditions. Similarly, the higher vibrational levels of the A state can be detected by crossover into higher levels of the X state $v > 4$.

The photodissociative process was studied for a number of CN parent molecules: hydrogen cyanide (HCN), methylcyanide (CH_3CN), cyanoacetylene ($HC \equiv C-CN$), dicyanoacetylene ($NC-C \equiv C-CN$), cyanogen ($NC-CN$), and the halogen cyanides (XCN where X = Cl, Br, I). In order to observe the rotational and vibrational energy of the newly formed radicals in the X state, experiments were done under low collision conditions, pressures $P \sim 10-80 \mu$ and short time delays $\sim 2 \mu s$. Fig. 1 shows a spectrum of CN formed from cyanoacetylene under these conditions. For all parent molecules which produced $CN(X)$, the radicals were highly rotationally and vibrationally excited. Therefore, rotational and vibrational excitation of the product CN appears to be the rule. It would be expected that CN formed in the A state would also be rotationally excited, since there is ample energy left over from the photon after the dissociation and electronic excitation have occurred.

For cometary CN radicals, the parent molecules HCN and CH_3CN are particularly interesting, since both were observed in Comet Kohoutek (Huebner et al., 1974; Ulich and Conklin, 1974). Our preliminary

laboratory studies as well as the work of others (West and Berry, 1974) show that CN from these parents is formed predominately in the A state in the two lowest vibrational levels. In the collisionless environment of the cometary atmosphere the rotationally excited CN(A) radicals would impose through Red System (A-X) radiation a corresponding excitation upon the ground state rotational levels. In Fig. 1 rotational lines up to $N \sim 50$ in the B-X violet system appear. In spectra of CN formed from some of the other parent molecules, rotational levels with maximum $N \sim 60-80$ were measured.

In high dispersion cometary spectra the maximum CN rotational line has $N \sim 25$ as shown in the spectrum of Comet Bennett in Fig. 2. Detailed resonance fluorescence calculations of the CN(B-X) cycle in cometary spectra have been carried out by Arpigny (1965). Table I, abstracted from the calculations of Arpigny (1965) shows the relative populations of the higher rotational levels as a function of heliocentric distance r . The first row lists, in parenthesis, the level with the maximum population and the fraction in that level. The remaining rows show the population of the indicated level. We see from Table I that solar induced fluorescence significantly populates levels beyond $N = 25$ within about 0.5 AU. At 1 AU level $N = 25$ has $\ll 1\%$ of the peak population and near 1.5 AU level $N = 20$ has $< 1\%$ of the peak population. High levels not affected by solar induced fluorescence can be used to detect and study newly formed radicals.

We have calculated the expected relative intensities of the lines $N \sim 30$ from newly formed radicals as compared to the observed intensities of lines $N \sim 20$ from resonance fluorescence. The ratio, over the entire

coma, of the intensity of a high rotational line with $N = 30$ to that of a line $N = 20$ is given by

$$\frac{I_{N=30}}{I_{N=20}} = \frac{n_{30}}{n_{20}} = \frac{Q \tau_{30} \beta}{Q \tau_{CN} f_{20}} \quad (1)$$

where the n 's are the respective rotational populations in the X state, $v = 0$ level; Q is the CN production rate from the parent compound with lifetime τ_p ; τ_{30} is the radiative lifetime of the level $N = 30$ and is ~ 4 sec according to Arpigny (1965); τ_{CN} is the lifetime of the CN radical against dissociation or ionization; β is the fraction of newly created radicals which are formed in levels $N \geq 30$; f_{20} is the fraction of fluorescently excited CN in level $N = 20$. The quantity f_{20} was evaluated from the ratio $I_{20}/\sum_N I_N$ for the R-branch of the spectrum of Aikman et al. (1974) and has a value of ~ 0.01 . To obtain the fraction of CN in level $N = 30$ we assume that only a radiative cascade occurs for the newly formed CN fragments. This will be true throughout the region of the coma where the dissociating ultraviolet radiation penetrates. The dissociation process has a production rate q_N into a rotational level N and $\sum_{N=0}^{N_{max}} q_N = Q$. Under the assumption that the upper levels $N \geq 30$ are in a steady state and that a level with maximum $N(=M)$ exists, the following kinetic analysis can be performed:

$$\dot{n}_M = q_M - n_M \tau_M^{-1} = 0 \quad (2)$$

$$n_M \tau_M^{-1} = q_M \quad (3)$$

$$\dot{n}_{M-1} = q_{M-1} + n_M \tau_M^{-1} - n_{M-1} \tau_{M-1}^{-1} = 0 \quad (4)$$

$$n_{M-1} \tau_{M-1}^{-1} = q_{M-1} + q_M \quad (5)$$

$$\dot{n}_j = q_j + n_{j+1} \tau_{j+1}^{-1} - n_j \tau_j^{-1} = 0 \quad (6)$$

$$n_j = \tau_j \sum_{j=30}^M q_j \quad j \geq 30 \quad (7)$$

The fraction $\sum_j^M q_j = \beta Q$ is produced into levels $N > j$. The value of β was obtained by taking the ratio $\frac{\sum_{N=30}^M I_N}{\sum_{N=0}^M I_N}$ for the R-branch from an unpublished investigation of cyanoacetylene and has a value of about 0.3.

The lifetime of the CN radical τ_{CN} is taken as 10^5 sec. (Delsemme, 1976). Substituting the above numbers into equation 1 yields an intensity ratio for the entire coma of $I_{30}/I_{20} = 10^{-3}$. However, the photolytic fragments are produced within a time $\sim \tau_p = 10^4$ sec and are contained within a volume of $\sim 10^4$ km radius with the usual expansion velocity of 1 km/s. For a characteristic projected slit length of $\sim 10^4$ km only the CN radicals within this distance of the nucleus contribute to the spectrum. A more accurate estimate of the CN molecules in a fluorescent steady state which contribute to the spectra is obtained using $\tau_{CN} = 10^4$ sec. Therefore, for a spectrum the ratio I_{30}/I_{20} becomes ~ 0.01 . When spectra are obtained at a heliocentric distance ≥ 1 AU, lines with $N = 25$ may be used for the newly created radicals according to Table I. This will increase the relative intensity ratio. We conclude that the relative intensity ratio of lines from newly formed CN to fluorescently excited lines will be in the range 0.1 - 0.01. It is possible that existing plates may reveal these high rotational lines, and a search is planned using computer image processing techniques.

It appears likely that observations of these lines could be made in a future bright comet by concentrating on the high rotational lines rather than the entire CN violet system. Because of the greatly different lifetimes of photochemically and fluorescently excited CN radicals, the spatial distribution of the two species will differ considerably. It is also likely that other mechanisms suggested for CN production, such as ion-molecule reactions (Oppenheimer, 1975; Shimizu, 1975) or electron currents (Ip and Mendis, 1977) will produce rotationally excited CN. The spatial distribution of newly formed, rotationally excited CN can be expected to vary with the production mechanism. Hence the detection and intensity variation along the slit of high rotational lines of CN may make an important contribution to the study of radical production. This problem will be discussed in a later paper. A similar analysis is expected to be applicable to other radicals e.g. OH, NH and C₂. A laboratory and theoretical study is planned for them.

TABLE I

RELATIVE POPULATIONS OF ROTATIONAL LEVELS AS
FUNCTIONS OF HELIOCENTRIC DISTANCE

N/r (AU)	0.4	0.6	0.8	1.0	1.4
N_{\max}	(15) .055	(13) .066	(11) .076	(10) .084	(8) .099
15	.055	.061	.056	.044	.021
20	.046	.031	.015	.006	.0007
25	.023	.006	.001	.0002	0
29	.006	.0006	0	0	0

REFERENCES

- Aikman, G.C.L., Balfour, W.J., and Tatum, J.B. (1974). The cyanogen bands of Comet Bennett 1970 II. *Icarus* 21, 303-316.
- Arpigny, C. (1965). A study of molecular and physical processes in comets. *Acad. R. Belg. Mem. Cl. Sci. Collect.* 8^o 35, 1-157.
- Cody, R.J., Sabety-Dzvonik, M.J., and Jackson, W.M. (1977). Laser-induced fluorescence of $CN(X^2\Sigma^+)$ produced by photolysis of C_2N_2 at 160 nm. *J. Chem. Phys.* 66, 2145-2152.
- Delsemme, A.H. (1976). The neutral coma of comets: a review. In "The Study of Comets" (B. Donn, M. Mumma, W. Jackson, M. A'Hearn, R. Harrington, eds.), pp. 711-732. NASA SP-393, U.S. Govt. Printing Office, Washington, D.C.
- Huebner, W.F., Snyder, L.E. and Buhl, D. (1974). HCN radio emission from Comet Kohoutek (1973f). *Icarus* 23, 580-584.
- Ip, W.-H., and Mendis, D.A. (1977). Proc. of IAU Colloquium No. 52, "Interrelations among comets, asteroids, and meteorites" (A.H. Delsemme, ed.), Univ. of Toledo Press, in preparation.
- Oppenheimer, M. (1975). Gas phase chemistry in comets. *Astrophys. J.* 196, 251-259.
- Sabety-Dzvonik, M.J., Cody, R.J., and Jackson, W.M. (1976). Product state distributions of $CN(X)$ produced in the photodissociation of C_4N_2 at 160 nm. *Chem. Phys. Lett.* 44, 131-134.
- Sabety-Dzvonik, M.J. and Cody, R.J. (1977). The internal state distribution of CN free radicals produced in the photodissociation of ICN. *J. Chem. Phys.* 66, 125-135.

Shimizu, M. (1975). Ion Chemistry in the Cometary Atmosphere.

Astrophys. Space Sci. 36, 353-361.

Ulich, B.L., and Conklin, E.K. (1974). Detection of methyl cyanide in Comet Kohoutek. Nature, 248, 121-122.

West, G.A., and Berry, M.J. (1974). CN photodissociation and predissociation chemical lasers: molecular electronic and vibrational laser emissions. J. Chem. Phys. 61, 4700-4715.

Whipple, F.L., and Huebner, W.F. (1976). Physical processes in comets. In "Annual Review of Astronomy and Astrophysics" (G.R. Burbidge, D. Layzer, and J.G. Phillips, eds.), pp. 143-172. Annual Reviews Inc., Palo Alto, Ca.

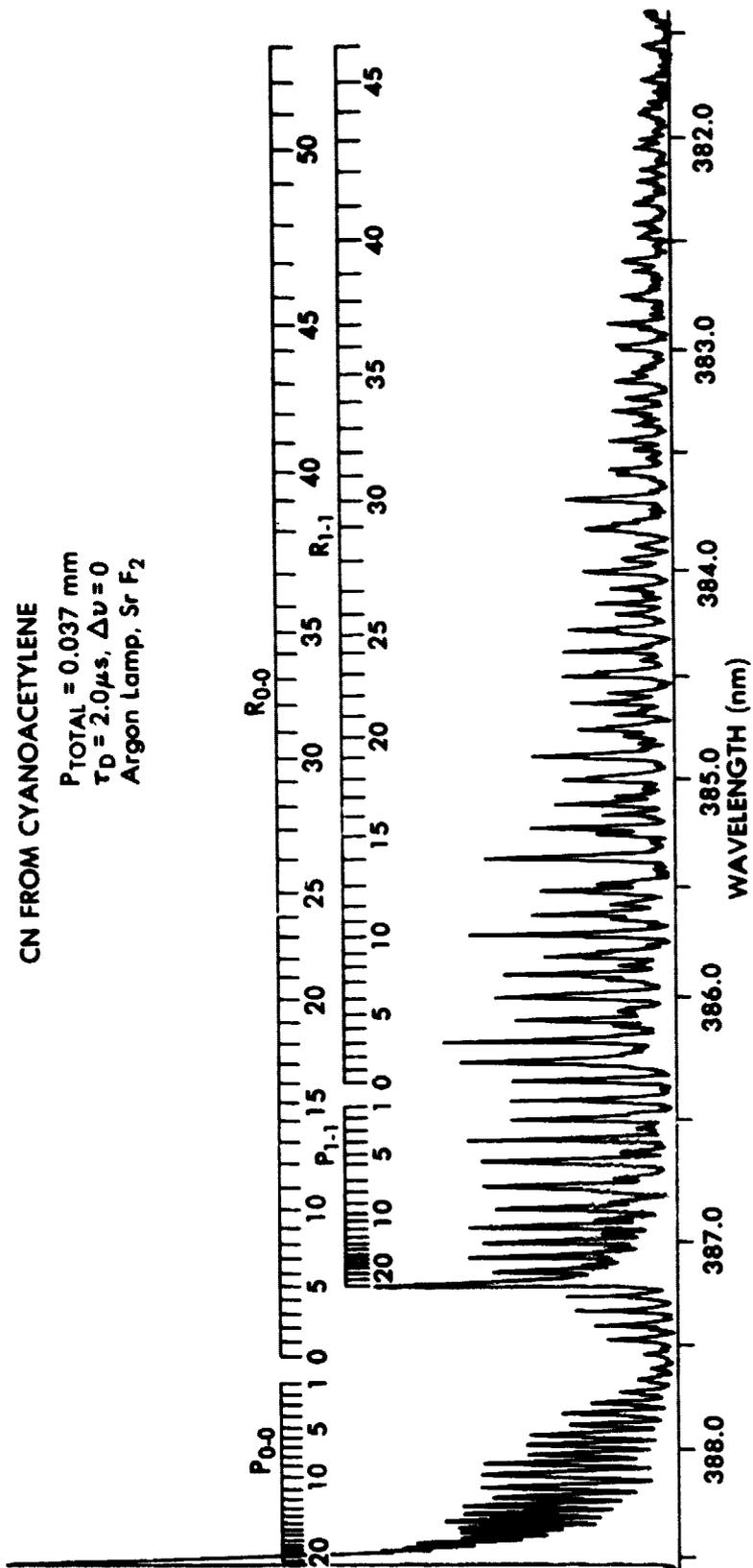
FIGURE CAPTIONS

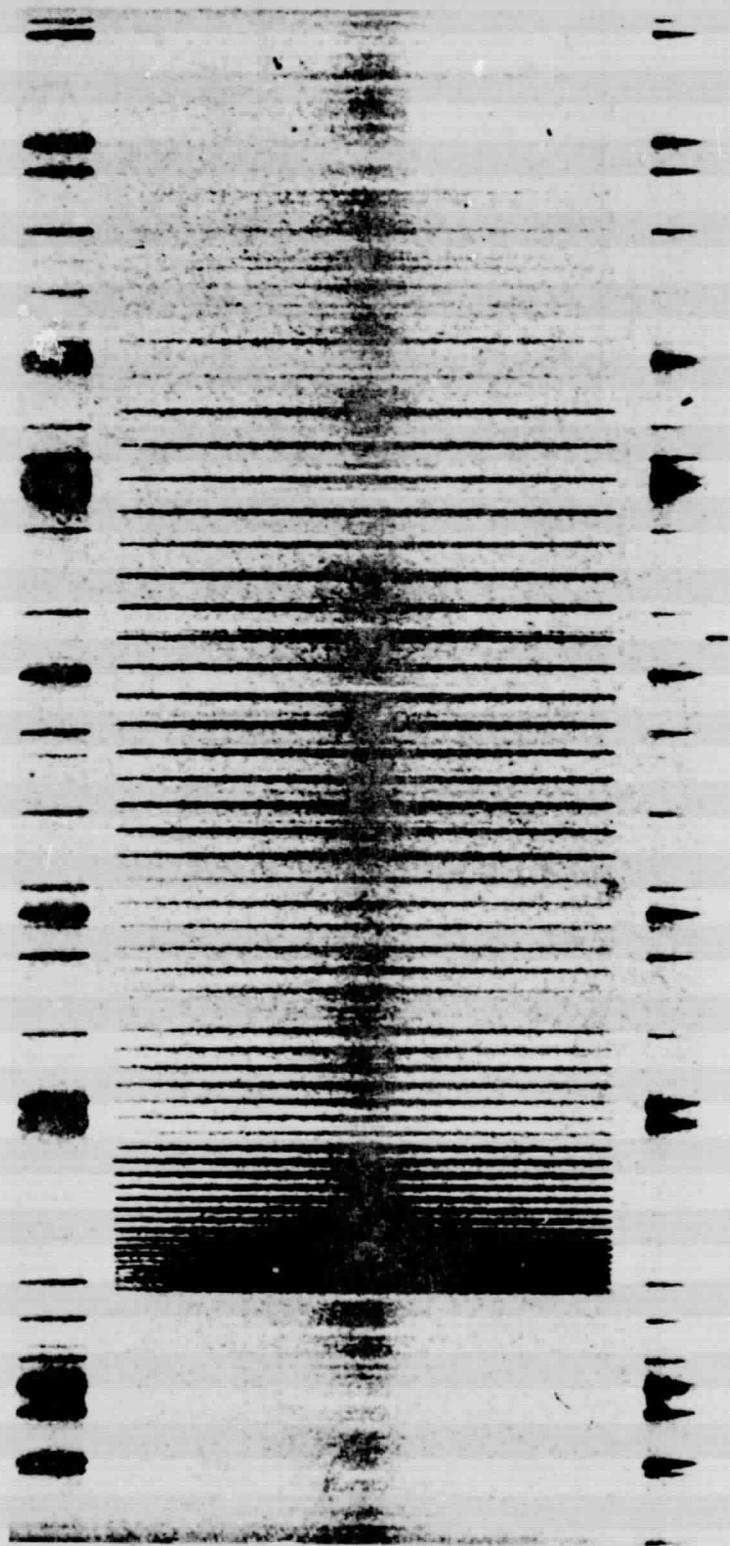
Figure 1. Laser induced fluorescence spectrum (Violet System) of $CN(X^2\Sigma^+)$ formed by photodissociation of cyanoacetylene under low collision conditions.

Figure 2. The CN Violet (0,0) band in Comet Bennett (1970 II) (Mount Wilson Observatory; original dispersion: $4.5 \text{ \AA}/\text{mm}$).

CN FROM CYANOACETYLENE

$P_{TOTAL} = 0.037 \text{ mm}$
 $\tau_D = 2.0 \mu s, \Delta\nu = 0$
Argon Lamp, Sr F₂





The CN Violet (0,0) band in Comet Bennett (1970II) (Mount
Wilson Observatory; original dispersion : 4.5 Å/mm).