# THE HEAT OF FORMATION OF CN RADICALS AND RADIATIVE LIFETIMES OF THE A$^1\Sigma^-$ STATE OF C$_2$N$_2$

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## ABSTRACT

Radiative lifetimes have been measured for the stable vibrational levels of the A$^1\Sigma^-$ electronic state of C$_2$N$_2$. They range from 1.3 $\mu$s for the $4_0^1$ level to 0.66 $\mu$s for the $1_0^1 4_0^1$ level and in general decrease with increasing vibrational excitation. Self-quenching rate constants range from gas kinetic to ten times that. Foreign gas quenching rates are slower. Observation of emission from the $1_0^1 4_0^1$ level sets a lower limit for the heat of formation of CN of 439.11 kJ mol$^{-1}$.

## INTRODUCTION

Simple nitriles play important roles in the photochemistry of nitrogen-methane planetary atmospheres. Cyanogen is a photochemically important molecule found in the atmosphere of Titan, and in other astronomical systems[1]. Cyanogen is also an extremely simple tetra-atomic system in which predissociation can be studied. Potential energy surfaces have been calculated for all of the excited states which means that models of dissociation dynamics can be tested in detail[2].

We have recently discovered that this molecule has a strong and distinctive emission spectrum. The lowest lying vibrational bands of A$^1\Sigma^-$ state of cyanogen (C$_2$N$_2$) fluoresce. The absorption, emission and photodissociation yield spectra of C$_2$N$_2$ have been measured between 220 and 210 nm, spanning the region between the $4_0^1$ and $1_0^1 4_0^1$ bands of the A$^1\Sigma^- \leftarrow X^1\Sigma^+$ system[3]. A recent paper deals with the emission and fluorescence spectra of the $4_0^1$ state and its radiative lifetime[4]. In this paper we report emission lifetimes of all the stable vibrational bands.

## EXPERIMENTAL

The apparatus was similar to that described in Reference 5. C$_2$N$_2$ from Matheson was purified by freeze-thaw cycling. The cyanogen gas flow from a 3 liter reservoir was controlled by a flowmeter. The pressure was monitored by a capacitance manometer.

The excitation source was a Spectra Physics PDL-2 dye laser pumped by a DCR-11 Nd-YAG system. Dye laser light was frequency doubled in a KDP crystal and Raman shifted in about 10 atmospheres of hydrogen. For this experiment the third anti-Stokes shifted beam was used.

Emission from C$_2$N$_2$ was detected directly through an unfiltered 11 stage EMR VUV photomultiplier. Emission decay lifetimes were measured by fixing the exciting laser on the absorption line and scanning the boxcar gate delay or by using a DSP 2100 100 MHz transient digitizer. The

experiments were controlled by an IBM PC\XT microcomputer based data acquisition system constructed in our laboratory. The firing of the lasers and the dye laser scanning was controlled by the microcomputer. Absorption spectra were measured directly on a Cary 2390 UV-VIS-NIR spectrophotometer.

## RESULTS

Figure 1 shows an absorption spectra measured on the Cary 2390 spectrophotometer between 200 and 230 nm. The lower half of the diagram shows the difference between spectra measured at 20 and 70 $^{\circ}$C when the cell was heated by water from a thermostated bath. This identifies lines that originate in excited vibrational states and makes the assignment of the vibrational bands quite easy. Extra bands at wavelengths below 210 nm belong to the $B^1_u \leftarrow X^1\Sigma^+$ transition. We are in the process of setting up a VUV monochromator with better (0.02 nm) resolution to be able to analyze this second electronic transition. Figure 2 shows the emission spectrum from the $1_0^1 4_0^1$ band and the yield of CN fragments as a function of wavelength. Figure 3 shows the yield of CN fragments as a function of wavelength in the region of the $1_0^1 4_0^1$ band.

Table I lists the measured radiative lifetimes and quenching rate constants.

<div align="center">

TABLE I
LIFETIMES AND QUENCHING RATES OF CYANOGEN $A^1\Sigma^-$
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| BAND | WAVELENGTH nm | VIBRATIONAL ENERGY cm$^{-1}$ | LIFETIME $\mu$s | QUENCHING GAS | QUENCHING RATE cm$^3$-s/molecule |
|------|-----------|----------------------|----------|----------------|-----------------|
| $4_0^1$ | 218.9 | 276 | 1.34 | $C_2N_2$ | 4.3 |
| $4_0^1$ | | | | He | 1.7 |
| $4_0^1$ | | | | Ar | 1.9 |
| $4_0^1$ | | | | $N_2$ | 2.5 |
| $4_0^1$ | | | | $CH_4$ | 3.4 |
| $4_1^2$ | 220.1 | 519 | 0.72 | $C_2N_2$ | 8.4 |
| $4_0^3$ | 216.6 | 770 | 0.67 | $C_2N_2$ | 10.4 |
| $4_0^3$ | | | | Ar | 6.7 |
| $2_1^1 4_1^0$ | 218.3 | 632 | 1.25 | $C_2N_2$ | 9.9 |
| $2_1^1 4_0^1$ | 218.6 | 908 | 0.94 | $C_2N_2$ | 12.5 |
| $2_0^1 4_0^1$ | 214.7 | | 0.68 | Ar | 3.1 |
| $1_0^1 4_0^1$ | 208.3 | 2606 | 0.66 | $C_2N_2$ | 13.0 |
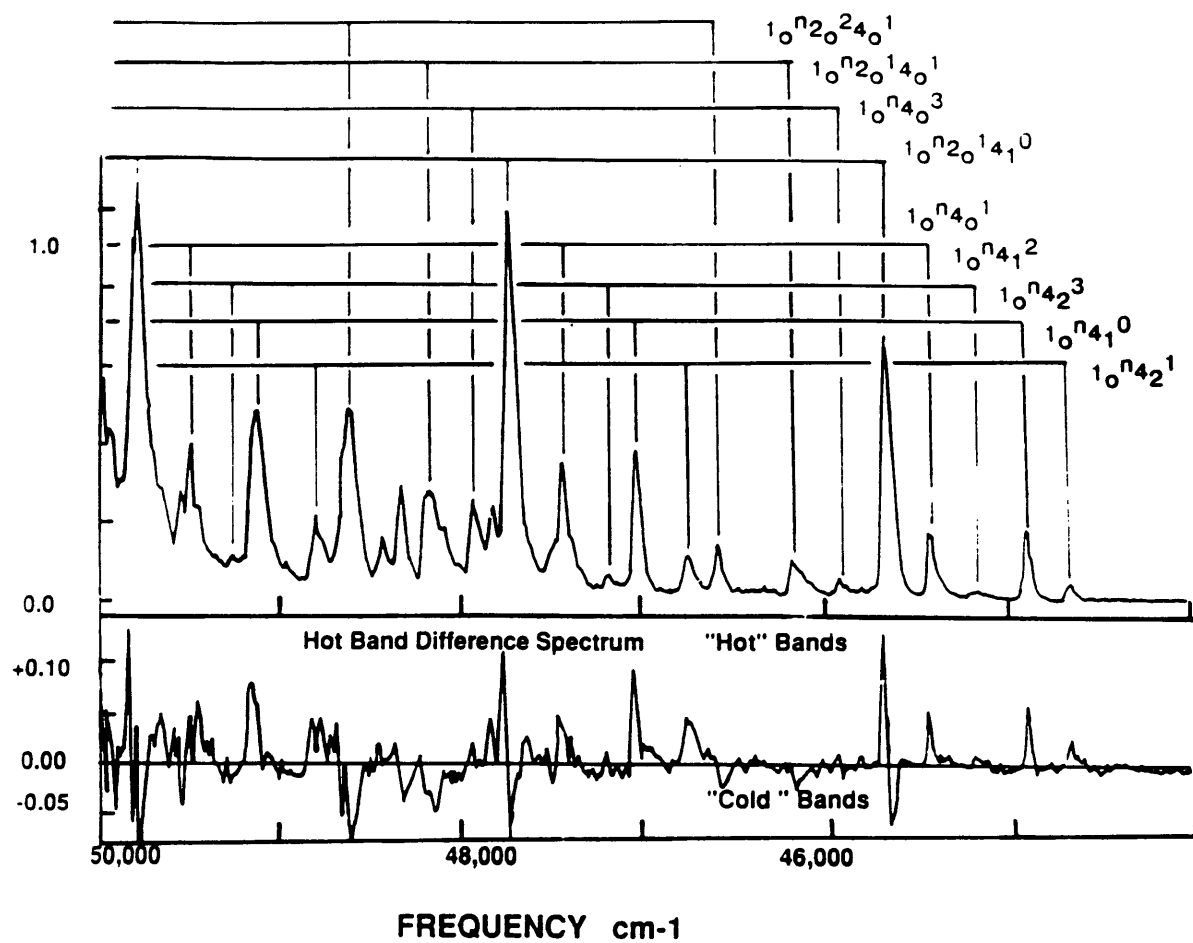
FIGURE 1. Absorption spectrum of $C_2N_2$
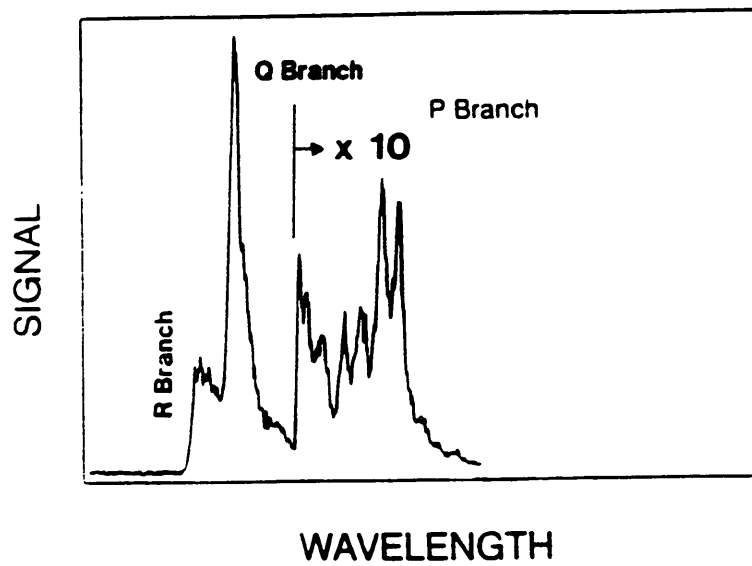
**Figure 2. CYANOGEN EMISSION SPECTRUM**

Labels on figure: Q Branch, P Branch, R Branch, x 10, SIGNAL, WAVELENGTH



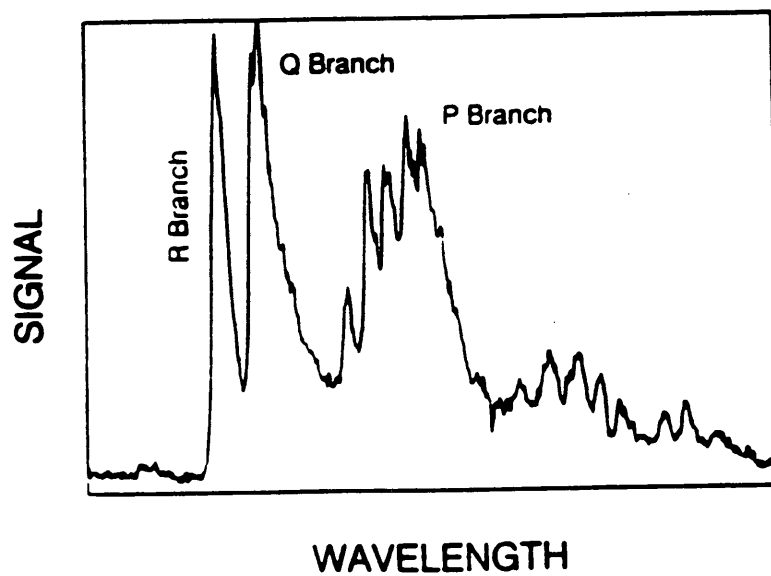**Figure 3. CN FRAGMENT QUANTUM YIELD**

Labels on figure: Q Branch, P Branch, R Branch, SIGNAL, WAVELENGTH

## DISCUSSION

Using photodissociative excitation Davis and Okabe measured a dissociation energy of 5.58 $\pm$ 0.05 eV and a threshold wavelength of 222.2 nm[6]. Eres, Gurnick and McDonald observed the rotational distribution of CN ($X^2\Sigma^+$) fragments in the 193 nm photolysis of $C_2N_2$[7]. Based on the highest observed fragment rotational state they calculate a bond strength of 5.83 $\pm$ 0.04 eV and a photodissociation limit of 212.7 $\pm$ 1.5 nm. Most of the uncertainty is related to the 1 nm bandwidth of the excimer laser. Recently Lin, Johnston and Jackson have used a narrower bandwidth doubled dye laser to photodissociate cyanogen at 206 nm[8]. Their fragment LIF spectra implies an upper limit to the bond energy of 5.70 eV and a dissociation limit of 217.5 nm, assuming that there were no hot band contributions to the photolysis. The observation of rotational structure in bands above 218 nm[9] show that the actual dissociation limit must lie below this point.

The observation of strong fluorescence from the $1_0^1 4_0^1$ band at 209.5 nm is strong evidence that at least some rotational states of this level are bound. As can be seen in Figures 2 and 3 the Q branch of the emission spectrum is narrower than the Q branch in the fragment yield spectrum. The P and R branches in the emission spectrum are much weaker than those in the fragment yield spectrum. This also shows that low rotational states of the $1_0^1 4_0^1$ band are bound and high rotational states are dissociative. Thus, we assign a lower limit of the NC-CN bond strength of 5.92 eV. Using the standard value of the heat of formation for $C_2N_2$ of 307.223 $\pm$ 1.80 kJ mol$^{-1}$,[10] this yield a lower limit of 439.11 $\pm$ 2.00 kJ mol$^{-1}$ for the heat of formation of CN radicals, as compared to Davis and Okabe's value of 423 $\pm$ 4 kJ mol$^{-1}$.[6]

The radiative lifetimes range from 1.4 $\mu$s in the $4_0^1$ band to 0.6 $\mu$s for the $1_0^1 4_0^1$ band. Self quenching rates range from gas kinetic (4.3 x $10^{-10}$ cm$^3$/molecule-s) for the $4_0^1$ band to 13.0 x $10^{-10}$ cm$^3$/molecule-s for the $1_0^1 4_0^1$ band. Foreign gas quenching rates for the $4_0^1$ band have been measured against He, Ar, $N_2$ and $CH_4$. As expected the quenching rate constants increase as the molecular weight and the complexity of the quenching gas, with the rate for quenching against He being the slowest and that against $CH_4$ being the fastest.


## CONCLUSIONS

Earlier work done in our laboratory has demonstrated that dicyanoacetylene ($C_4N_2$) will also have several bound vibrational states in the $A^1\Sigma^+$ electronic state. We are currently synthesizing a sample of this compound in order to look for the fluorescence. Cyanoacetylene is known to have no bound levels in its first excited singlet state, and cannot be monitored by fluorescence. The UV emission of simple nitriles offers a method of remote detection, and will also be useful in the laboratory for study of such reactions as CN + HCN --> $C_2N_2$ + H.

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