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THE PHOTOCHEMISTRY OF CYANO- AND DICYANOACETYLENE AT 193 NM

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ABSTRACT

This paper reports on a study of the photochemistry of cyano- and dicyanoacetylene at 193 nm. In particular, those photolysis channels have been characterized which lead to the production of excited state fragments and CN in the ground electronic state. In addition to direct production of CN and C_2H there is a second dissociation H there is a second dissociation channel leading to C_3N and H atoms. The results also show that at high laser intensity the HC_3N dissociates by two photon photolysis and that the C_3N undergoes secondary photolysis.

INTRODUCTION

In 1920 Moreau and Bongrand synthesized the first members of the cyanoacetylene family, cyano- [1] and dicyanoacetylene [2]. Since that time several additional cyano polyenes of the series $H-(C\ C)_n-CN$ and $NC-(C\ C)_n-CN$ have been found. Chemists, and particularly spectroscopists have studied the cyanoacetylenes because of their linear structure. Interest in these molecules increased in 1971, when Turner detected HC_2CN in the interstellar medium using the rotational spectrum [3] first measured in the laboratory by Westenberg and Wilson [4]. HC_2CN has also been observed in Titan's atmosphere by the Voyager missions to Saturn [5] and has been shown to play an important role in the odd nitrogen chemistry of that enormous moon [6].

Our laboratory has been studying the photochemistry of XCN species and C_2N_2 for some time [7]. The work reported on here was started because of the astrochemical relevance of cyanoacetylene photochemistry, and also to see if there were any dynamic effects in photolysis that could be related to the increase in the molecule's length as compared to C_2N_2.

This article reports on the photolysis of cyano- and dicyano-acetylene at 193 nm. Measurements were made of emission spectra from excited fragments and laser induced fluorescence spectra of ground state CN fragments. The photolysis was accomplished by an unfocussed ArF laser whose intensity was varied over more than two orders of magnitude.

Previous work on cyanoacetylene photochemistry has used VUV light. Okabe and Diebler have studied the photodissociative excitation and photoionization of HC_2CN below 150 nm [8]. Sabety-Dzvonik, et al. characterized the quantum state distribution of CN produced in the 160 nm photolysis of HC_2CN [9] and C_4N_2 [10]. Recently, the quantum state distribution from photolysis of C_4N_2 between 165 and 145 nm has been measured by us [11].

The UV spectrum of HC_2CN from 290 to 200 nm has been measured and assigned by Job and King [12,13]. Conners, et al. have measured the VUV spectrum below 170 nm, but not assigned it [14]. Miller and Hannon have measured the UV spectrum of C_4N_2 between 290 and 220 nm, and partially assigned the vibrational structure [15]. Conners, et al, also measured the VUV spectrum of C_4N_2 below 200 nm [14].

EXPERIMENTAL

The experimental apparatus has been described in detail elsewhere [16]. As shown in Figure 1, an ArF excimer laser (Lambda Physik EMG101) was used to photolyze the gas samples in a static gas reaction cell, and in effusive and pulsed molecular beams. The CN $(X^2\Sigma^+)$ fragments formed in the photolysis were detected by laser induced fluorescence (LIF) excited in the violet system of CN by a nitrogen pumped dye laser. The nitrogen laser could be pulsed at an arbitrary and adjustable delay after the excimer laser.

In some of the experiments a pulsed molecular beam source with a 0.5 mm nozzle (Laser Technics LPV) was set perpendicular to both of the counterpropagating laser beams. The cyanoacetylenes were diluted in helium or argon. The pressure behind the valve was of the order of an atmosphere. After expansion into the vacuum chamber, the rotational temperature of the polyatomic molecules is relaxed towards absolute zero. Although the vibrational degrees of freedom are also cooled, the vibrational energy transfer process is not especially efficient. Experiments were also done with an unexpanded beam giving a low pressure effusive flow of the cyanoacetylenes.

The fluorescence excited in the interaction region was detected by a photomultiplier tube (EMI 9789QB) placed at right angles to both the molecular beam and the lasers. The fluorescence was averaged by a boxcar analyzer (PAR 160) and displayed on a strip chart recorder. Direct fluorescence from

multiphoton excited fragments was measured through a 0.25 m
monochromator (Jobin-Yvon H20-UV) with a slit width of 1 mm and a
dispersion of 4 nm/mm. The LIF signal was measured with an
appropriate band pass filter between the photomultiplier and the
cell.

The excimer laser power was monitored by a Scientech power
meter. Corrections were made for variation in the dye and
excimer laser intensities.

The HC_2CN sample, synthesized by the method of Moreau and
Bongrand [1] as modified by Miller and Lemmon [17] was furnished
by Dr.Hideo Okabe. C_4N_2 was synthesized by the method of Moreau
and Bongrand [2]. GC/MS analysis of both samples showed no
impurities.

RESULTS

A.   Photolysis of Cyanoacetylene

Photodissociation of HC_2CN in a static gas cell at a pressure of 20 mtorr with 50 mJ/cm^2 of ArF laser light produced a fairly strong fluorescence. The temporal profile of the total fluorescence, measured with a boxcar analyzer with a resolution of 30 ns is shown in Figure 2. In Figure 2 there is a strong emission that is over within 200 ns, as well as a weak emission with a longer lifetime. The actual decay of the sharp peak may be faster but is broadened by a jitter of about 50 ns in the firing of the excimer laser, due to an old thyratron. In any case, the bimodal characteristic of the fluorescence decay is evident. The decay rate of the weak emission is about 3 s.

Figure 3 shows the dispersed fluorescence about 100ns after the excimer laser fired. This spectrum is dominated by the CN violet bands. Their intensity varies as the second power of the laser flux. There is also some emission from the C_2^* Swan bands and a diffuse emission below 350 nm. The fluorescence at times greater than a microsecond after the photolysis was much weaker. In addition to peaks in the CN violet bands, there is some diffuse emission between 300 and 400 nm.

The LIF measurements of the rotational and vibrational distribution of CN $(X^2\Sigma^+)$ fragment have been done at a variety of dissociating laser intensities. The delay time between the excimer and the dye laser was fixed at 500 ns, which maintained a

collision free condition while eliminating interference from the immediate fluorescence. At the highest laser intensity (50 mJ/cm^2), hot vibrational and rotational excitation spectra were observed. One can see in Figure 4b that CN radicals with vibrational levels as high as v" = 4 were excited at the highest ArF laser intensity. The population of levels other than v" = 0 disappeared when the excimer laser intensity was decreased to about 5 mJ/cm^2, and dramatic changes were seen in the rotational envelope of the excitation spectrum. The LIF signal of vibrationally and rotationally hot CN (X$^2\Sigma^+$) varies as the second power of the excimer laser intensity. Figure 4a shows a CN fragment excitation spectrum taken at lower excimer laser energy. Under these conditions both vibrational and rotational distributions were cold. The 1-1 band disappeared into the noise and lines originating from vibrational levels greater than two could not be found. The intensity of the low rotational lines increased linearly with the laser flux. The spectrum of Figure 4a can be converted into the quantum state distribution shown in Figure 5.

An attempt was made to dissociate HC$_2$CN in a seeded molecular beam to eliminate the contributions of hot bands to the dissociation. A mixture of 40 torr of HC$_2$CN with 720 torr He was used as the gas behind the pulsed beam valve. The ArF laser beam crossed the molecular beam 15 mm downstream from the exit of the pulsed nozzle. No quantitatively meaningful LIF spectrum of the CN (X$^2\Sigma^+$) radical could be obtained from the pulsed beam studies at low laser intensity. A CN radical excitation spectrum could

only be observed in the pulsed molecular beam studies when the
ArF laser power was very high. Though the spectra were noisy,
the envelope is similar to those of Figure 4b.

B. Photolysis of Dicyanoacetylene

The direct fluorescence from the photolysis of C_4N_2 at 193
nm was much weaker than that observed from HC_2CN photolysis under
similar conditions. On the other hand, the LIF signals from CN
$(X^2\Sigma^+)$ were much stronger than those seen in the HC_2CN
measurements described above. As a result of this the
fluorescence could be ignored when the ArF laser power was kept
below 20 mJ/cm^2 pulse. Better LIF spectra have been measured.
The excitation spectrum is shown in Figure 6, along with the
Boltzmann like fits to the observed quantum state distributions,
shown i- Figure 7. The latter are single exponential functions
described by thermodynamic temperatures of 1100 and 730 K for CN
fragments in the v" = 0 and 1 levels respectively.

We have also attempted to photolyze C_4N_2 in a pulsed
molecular beam. Unexpectedly, the direct emission relative to
the LIF spectra became much stronger than it was in the static
cell experiments. When C_4N_2 was seeded in Ar, the emission was
so strong, and had such a long decay time that one could not
measure the nascent fragment LIF distribution immediately after
photolysis. Figure 8 and 9 show the emission time profile and
the spectrum respectively from the molecular beam with 30 torr of
C_4N_2 diluted in 730 torr of Ar.

When He was used as a carrier gas instead of Ar the fluorescence became weaker. With 30 torr of C_4N_2 diluted in 250 torr of He, a usable LIF spectrum of CN $(X^2\Sigma^+)$ fragments was measured. Only the rotational distribution of the $v'' = 0$ level could be analyzed from this spectrum, but within experimental error, the rotational temperature was the same as in the static photolysis.

DISCUSSION

A. Spectroscopy

The absorption spectrum of cyanoacetylene between 260 and 200 nm has been studied by Job and King [12,13], and the VUV absorption between 165 and 105 nm has been examined by Conners, et al [14]. Job and King found a structured, but very weak absorption system at 260 nm, and a stronger system, described as a structured continuum, starting at 230 nm and extending to lower wavelengths. It was noted that the 260 nm bands became diffuse below 240 nm. The 230 nm system of cyanoacetylene consists of a number of diffuse sets of bands with a spacing of 2100 cm^{-1} between the sets. The 2100 cm^{-1} interval corresponds to the excited state stretching frequency ν_2. The bands have a halfwidth of 5 cm^{-1} at 230 nm, which increases to 25 cm^{-1} at 200 nm. The lack of a resolvable rotational absorption spectrum makes it impossible to assign the excited electronic state species. Argument by analogy is no help, as the equivalent state in C_2N_2 is $^1\Sigma_u^-$ [18], while in substituted acetylenes it is $^1\Delta_u$ [19].

Job and King's assignments can be extended to show that the state excited by the 1 nm bandwidth ArF laser at 193 nm is the $2_0^3 4_0^1 5_0^1$ level at 51,821 cm^1. The first state lies 2120 cm^{-1} above the assigned $2_0^2 4_0^1 5_0^1$ level at 49,701 cm^{-1}. The excitation of one quanta in the 4 mode makes the transitions $^1\Sigma^+ \longrightarrow {}^1\Delta_u$ or $^1\Sigma^+ \longrightarrow {}^1\Sigma_u^-$ allowed.

Because of the similarity of the low frequency bending modes in the ground and excited state, some hot bands would also be excited in the room temperature sample by the ArF laser. We have verified that there is a transition at 51,821 cm^{-1}, by measuring an absorption spectrum of cyanoacetylene in a spectrophotometer with 0.1 nm resolution. In addition to the vibronic structure there is a relatively strong continuum, rising smoothly from 230 nm. At 193 nm the absorption of cyanoacetylene is 4×10^{-19} cm^2 [11]. Most of this comes from the continuum.

Delon, et al., [20] have studied vibrational cooling in a nozzle beam of intermediate sized molecules, i.e. molecules having several vibrational degrees of freedom. For HC_2CN in a moderate expansion (a back pressure of 2 atmospheres, a nozzle diameter of 25μ and a mixing ration of 10:1 with Argon as a buffer gas) there was little or no vibrational cooling. Starting from a source temperature of 300 K vibrational temperatures of 100 and 235 K were seen in the ν_7 and ν_6 modes after the expansion. Efficient rotational cooling was observed with a measured temperature of 15 K. Since our expansion conditions are similar, we can assume that the thermally excited bending modes of ground state HC_2CN and C_4N_2 will at best be only partially relaxed by the expansion.

The UV absorption spectrum of C_4N_2 has been studied by Miller and Hannon [15] and the VUV spectrum has been studied by Conners, Roebber and Weiss [14]. As in HC_2CN, Miller and Hannon found that there are two UV absorption systems in C_4N_2. A weak,

red degraded system has its origin at 280 nm, and there is a stronger system with an origin at 264 nm. They list four bands of this system at 264, 250, 237 and 226 nm. No other bands are listed, but there is a notation that the spectrophotometer that was used could not maintain its narrowest resolution (0.1 nm) for the last band. There is some possibility that their lamp was running out of intensity below 225 nm, and there may be one or more other bands. The second band, at 250 nm, is by far the strongest.
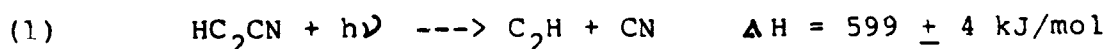
They were able to resolve sharp vibrational structures in the 280 nm system using a 2 m spectrograph with a 5.2 A/mm dispersion, but in no case did they have enough resolution to measure rotational structure. Judging from the low resolution spectrum and assignments given by Miller and Hannon, the bands at 264 and 250 nm are equally sharp, while the 237 nm band is only a bit more diffuse, and the 226 nm band is obviously broadened. None of this is conclusive as to the dissociation limit, but it is consistent with the thermochemical limit given below.

Conners, et al., see an irregular absorption growing from 50,100 to 55,000 cm^{-1} (198 to 180 nm) where a far stronger system begins. They offer no assignment, but using a CNDO/2 method SCF-MO calculation, they find that there are five possible states in the region which may be responsible for this absorption. Briefly they are $^1\Delta^-_g$, $^1\Delta_g$, $^1\Sigma^-_u$, $^1\Delta_u$ (different from the pair of the same symmetries responsible for the 264 absorption) and $^1\Delta_g$. The 198 nm absorption is not broadened by a pressure of many

atmospheres of helium, which means that it is due to a valence transition. The absorption cross-section at 193 nm is about 1×10^{-19} cm^2. From the shape of the spectrum this absorption is not a continuation of the 264 nm system, and indeed the peaks do not fall where one would expect the observed progression in the ν_1 mode of the 264 system to be. The electronic origin of this third electronic state must be near 198 nm. Thus, absorption of 193 nm (51,813 cm^{-1}) light would not excite any high frequency stretching modes ($\nu_1 - \nu_5$) of the C_4N_2, but might involve excitation of a few low frequency stretches, and, of course, thermally excited hot bands of such modes. For most of the possible electronic species, at least one quanta of the π_g ν_6 or ν_7 modes would have to be excited.

B.   Thermochemistry

The thermochemistry of cyano and dicyanoacetylene is summarized in Table I. The one photon allowed processes for cyanoacetylene photolysis at 193 nm are

(1) $HC_2CN + h\nu \longrightarrow C_2H + CN$ $\Delta H = 599 \pm 4$ kJ/mol

(2) $HC_2CN + h\nu \longrightarrow H + C_2CN$ $\Delta H = 490 \pm 21$ kJ/mol

where the heat of reaction 2 is based on our measurement of the heat of formation of C_3N from the photodissociative excitation of C_4N_2 [11].

Although the absorption of C_4N_2 at 193 nm is four times smaller than that of HC_2CN, the CN LIF signal is much weaker. We have measured the branching ratio between processes (1) and (2).

It is at least 1:20 at 193 nm. We note that the absorption of a second photon by C_3N would lead to

(3) $\qquad C_2CN + h\nu \quad \text{---}> C_2 + CN \qquad \Delta H = 621 \pm 25 \text{ kJ/mol}$
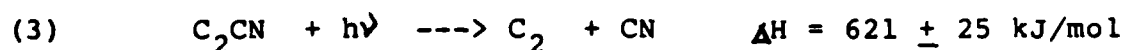
The thresholds for processes 1, 2, and 3 would be 200, 244 and 193 nm respectively.

For 193 nm photolysis processes 1 and 3 can only produce CN in the ground state. With respect to 193 nm photolysis, process 1 is 1,730 cm^{-1} exothermic and process 3 is about thermoneutral, but with an uncertainty of about 2,000 cm^{-1} associated with the heat of formation of C_3N. Thus no vibrational excitation of the CN stretch can be produced directly from processes 1 and 3.

Process 2, is about 10,800 cm^{-1} exothermic with respect to 193 nm photolysis, but, again, there is a large associated uncertainty. There is evidence from this work and that of Sato that the C_3N is created with a significant amount of internal energy [21]. This point will be discussed further below. Some of this energy can remain in the CN fragment following photolysis of C_3N leading to the excitation spectrum observed at high laser intensities by a two step sequential process. The maximum energy available to the CN fragment would be 10,656 $\pm$ 1050 cm^{-1}. It is energetically possible that some of the CN could be in the excited $(A^2\pi_i)$ state.

For reasons which have been dealt with in detail in Xie, et al [21], it is extremely unlikely that a ground state CN radical

can absorb a second photon at 193 nm. Only a few levels of the CN ($A^2\Pi_i$) state can do so, and the resulting fluorescence is well characterized, leading to emission from the F and E states of CN. Even at the highest intensities, no such emissions were seen in the photolysis of either HC_2CN or C_4N_2.

Production of $CN(B^2\Sigma^+)$ can only proceed via the two photon process

(4) $\quad HC_2CN + 2h\nu \longrightarrow C_2H + CN(B^2\Sigma^+) \quad \Delta H = -669$ kJ/mol
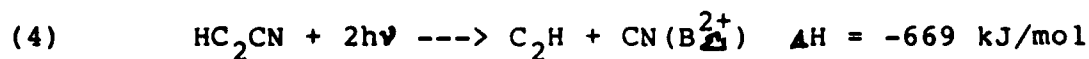
or the overall three photon process of reaction 2 followed by

(5) $\quad C_2CN + 2h\nu \longrightarrow C_2 + CN(B^2\Sigma^+) \quad \Delta H = -659$ kJ/mol
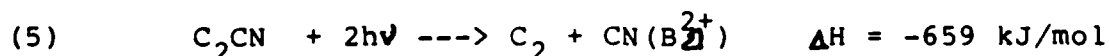
The amount of energy available to the $CN(B^2\Sigma^+)$ fragment after two photon absorption at 193 nm is 332 kJ/mole or 27,750 cm^{-1} in process (4), , while that available after process (2) followed by (5) is 322 kJ/mol or 26,915 cm^{-1}.

In the photolysis of C_4N_2 the first step will be

(6) $\quad C_4N_2 + h\nu \longrightarrow CN + C_3N \quad \Delta H = 515 \pm 6$ kJ/mol
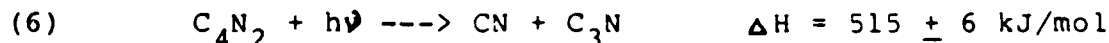
followed, possibly by reaction (3). At 193 nm, process 6 would leave 8723 cm^{-1} of excess energy in the modes of motion of the fragments. Reaction 6 has a threshold of 232 $\pm$ 1 nm.

Excited CN could be formed by the two photon excitation of C_4N_2 or reaction 5.

C. Photochemistry

In the following discussion we will restrict ourselves to the photochemistry of the various species at 193 nm, except where specifically noted. Starting with cyanoacetylene, we first consider the LIF spectrum of CN fragments obtained at the lowest laser intensity. As can be seen in Figure 4a there is a vanishingly small population in $v" = 1$, if any at all. Only the relatively poor signal to noise of the spectrum prevents us form asserting that there is no vibrational excitation of the product. This is in agreement with the proposition that all of the observed $CN(X^2 {}^+)$ population originates from process 1, where there is only about 1700 cm^{-1} of excess energy available to be distributed among the remaining modes of motion of the fragments.

The quantum state distribution of the $CN(X^2\Sigma^+, v'=0)$ fragments is seen in Figure 5. The last observable rotational state, $N=24$, corresponds to an energy of 1134 cm^{-1}. The line drawn through the points is the result of a least squares fit to the data of

$$(7) \quad I/(N'+N"+1) = A_1 \exp[-B_0 \, N(N+1)/k_B T_1] + A_2 \exp[B_0 \, N(N+1)]$$

where

$$A_1/A_2 = 5.2$$
$$T_1 = 332 + 65 \text{ K}$$
$$T_2 = 2170 + 500 \text{ K}$$

I is the LIF signal, $B_{v''}$ is the rotational constant of the v" level and k_B is Boltzmann's constant.

Measurements have been made of the signal intensity of the R_{00} (4) line as a function of photolysis laser intensity. The signal varies linearly with the laser intensity, indicative of a single photon process. All of the above points to process (1) being the source of CN radicals in the low intensity photolysis.

Figure 4b shows the LIF spectrum obtained at high laser intensity. Contributions are measured from vibrational levels up to at least v" = 3, with some indication of population in v" = 4. The rotational distributions are hot, as can be seen from the absence of a true band gap between the P_{00} and R_{00} bands.

The process leading to the observed $CN(X^2\Sigma^+)$ distribution at high laser intensities is most likely reaction 2 followed by 3. The total excess energy available to the $CN(X^2\Sigma^+)$ after these two steps is about 10656 ± 1050 cm^{-1}. This is consistent with the cutoff in the vibrational distribution at v" = 3 or 4 (ν_e for CN is 2064 cm^{-1}). The absence of a clear band gap between the P_{00} and R_{00} bands also shows that at least some rotational states are populated with energies up to about 8000 cm^{-1}. The second order dependence of the LIF signal for higher vibrational and rotational levels is consistent with this mechanism.

The only other channel which could lead to these vibrationally and rotationally excited CN radicals would be process 4 followed by radiative decay to the $CN(X^2\Sigma^+)$ state.

This would be more than 3.5 eV exothermic, and should be able to form CN in much higher vibrational states.

We are then left to ask about the relative importance of the direct process 1 and the sequential process 2 and 3 for the production of CN. We know that process 2 dominates over process 1 at low intensities by a factor of about twenty. This comes from both a direct measurement of the branching ratio at 193 nm [11] and the observation that the CN LIF signal is much greater following the photolysis of C_4N_2 than following the photolysis of HC_3N, even though the absorption cross-section of C_4N_2 is four times lower. Thus the question reduces to what is the cross-section of process 3 at 193 nm. At all intensities, CN is produced in a single step in process 1, and it requires at least two additional photons to remove a CN radical from the states that are energetically accessible. Given an absorption cross-section of 4×10^{-19} cm^2, even at the highest ArF laser intensities less than 1% of the HC_2CN molecules are photolyzed via reactions 1 and 2.

Simple kinetics shows that the ratio of CN produced by the one photon process to that produced by the two photon process will be

$$(8) \qquad R = q_1 / \qquad E_{laser})$$

where q_i is the relative quantum yield of a reaction and σ_i the cross-section.

In Figure 4b, the envelope of the P_{00} band is similar to, but not exactly the same as that in Figure 4a, and the population found in $v" = 1$ is smaller, but of the same order of magnitude as that found in $v" = 0$. At a laser flux of 5×10^{15} photons/cm^2-pulse R is less than or equal to $1/20$. Increasing the flux by an order of magnitude increased the relative yield of radicals from the two photon mechanism by about the same factor. If we estimate the relative yields of the two pathways to produce CN to be of the order of unity at 5×10^{16} photons/cm^{2}pulse, and use our measure of the relative yields of processes 1 and 2, then we arrive at a crude estimate for the absorption of C_2CN at 193 nm of 2×10^{-18} cm^2. The branching between reactions 1 and 2 accounts for the much smaller LIF signal when HC_2CN is photolyzed as against when C_4N_2 is irradiated.

Excited fragments are also created in the photolysis. Consideration of the thermochemistry shows that absorption of at least two photons is needed to form excited radicals. From Figures 1 and 2, we can see that the emission in the first microsecond after the photolysis is dominated by the CN violet system. There is also some emission observed from the Swan bands of C_2. The intensity of the CN ($B^2\Sigma^+ \longrightarrow X^2\Sigma^+$) fluorescence varies as the second power of the laser intensity. This favors the direct two photon absorption mechanism as the source of excited CN. Dissociation of C_3N to excited CN would require three photons overall. Moreover, one would expect to see the about the same pattern and strength of emission following the

photolysis of C_4N_2 in the bulb experiments if this were the mechanism.

In Figure 2, the strong peak between 380 and 390 nm comes from the $\Delta v = 0$ progression of the CN violet system. Weaker, associated $\Delta v = +1$ and -1 progressions of this system can be seen at 360 and 415 nm. The peaks between 400 to 410 nm and 465 to 475 nm are from excited C_2. Some other bands from C_2 would be hidden below the CN violet bands.

The lifetime of the C_2 Swan transitions is 170 ns [23], which would fall into the 200 ns region of the fast emission in Figure 1. Black carbon deposits on the window are also consistent with C_2 production. We have not looked for ground state C_2, or C_2 in the $a^3\pi$ state.

Sato studied the emission from cyanoacetylene [21]. In one experiment he varied the excitation frequency from 265 to 215 nm and recorded the dispersed emission. In the region from 265 to 250 nm, relatively strong direct fluorescence was seen centered at the irradiation wavelength. At 240 nm, where there is no absorption, there was no response. Below 230 nm, there was a sharp emission at the excitation frequency, which may have been scattered light and a broad emission between 300 and 400 nm. Quite a large range of vibronic states must be excited judging from the broad region of emission.

The photolysis of thermal C_4N_2 at 193 yielded a fairly strong LIF signal from the $CN(X^2\Sigma^+)$. This can be seen in Figure

6. The signal intensity in the bandhead region was measured as a function of laser intensity and found to be linear. Thus, the primary process in the photolysis of C_4N_2 is Reaction 6. The quantum state distribution shown in Figure 7. Thermochemically the CN fragment can have up to 8700 cm^{-1} of excess energy. The LIF spectrum shows that CN ($X^2\Sigma^+$) is formed only in v" = 0 and v" = 1 levels. There is no evidence of v" = 2 or higher vibrational levels. Vibrational populations are probably controlled by Franck-Condon factors in the parent molecule. The highest amount of internal energy in any populated state is between 3000 and 3500 cm^{-1}. About 17% of the CN is created in the v" = 1 level. This indicates that there is a dynamic restriction in the motion of the fragments as they separate.

The direct emission following the photolysis of C_4N_2 at room temperature is much weaker than that from HC_2CN. This grows much stronger when C_4N_2 is diluted in argon and expanded through a pulsed nozzle. Dilution in helium decreases the fluorescence. Most likely this emission is related to the formation of van der Waals complexes between the C_4N_2 and the argon. There are two peaks in the spectrum. The one at 386 nm is from CN (B^{2+}). The band at 325 nm is very broad and very much like that from the photolysis of HC_2CN seen by Seki. We conclude that this emission is from excited C_3N formed in the multiphoton photolysis of Ar-C_4N_2 complexes.

CONCLUSIONS

The single photon photolysis mechanism of cyano and dicyanoacetylene has been studied. Quantum state distributions of CN fragments have been measure. Multiphoton photolysis schemes of these two molecules have also been determined, and some characteristics of the fragments measured.

A broad emission from the photolysis of C_4N_2-Ar complexes has been tentatively identified as coming from excited C_3N.

It has been shown that secondary photolysis of the C_3N radical leads to the formation of CN radicals, from which we infer that the photolysis is also a source of C_2 radicals. Some excited C_2 has been seen from higher order processes. An estimate of the cross-section of the C_3N radical at 193 nm has been made.

Cyano-acetylene is commonly found in the interstellar medium, nitrogen-methane atmospheres, and probably in comets. On a simple calculation, it should be the second most common odd nitrogen species in these environments. It has been shown here that the primary photochemical process is a two step mechanism leading to the formation of C_2 and CN radicals.

ACKNOWLEDGEMENT

TABLE I

Heats of Formation and Heats of Reaction for Ground State
Molecules and Radicals

ΔH_f	kJ/mole		
HC_2CN	356	$\pm$ 4	
C_4N_2	533	$\pm$ 4	[23]
H	216.03	$\pm$ 0.004	
CN	422	$\pm$ 4	
C_2H	531	$\pm$ 1	
C_2	829.3	$\pm$ 3	
C_3	833	$\pm$ 1.5	
C_3N	629	$\pm$ 17	[10]
N	471	$\pm$ 4	

Reaction			ΔH_R	Threshold
HC_2CN + $h\nu$	--->	H + C_3N	490 kJ/mol	244 nm
	--->	CN(X) + C_2H	599 kJ/mol	200 nm
C_4N_2 + $h\nu$	--->	CN(X) + C_3N	515 kJ/mol	232 nm
C_3N + $h\nu$	--->	C_2 + CN(X)	621 kJ/mol	193 nm
	--->	C_3 + N	656 kJ/mol	182 nm

All heats of formation are from Reference 24 unless otherwise
noted.

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FIGURE CAPTIONS

Figure 1 - A schematic diagram of the experimental apparatus. The apparatus consisted of a vacuum chamber with windows through which laser beams could enter and fluorescence emission of the fragments could be observed. For LIF experiments the ArF and dye laser beams entered the cell along the same axis but were counterpropagating. Fluorescence was observed through a filter by a photomultiplier. Emission was measured by replacing the filter with a small (0.25 m) monochromator which could be tuned over the region 200-800 nm. The photomultiplier signal was captured by a boxcar analyzer, and displayed on a strip chart recorder.

Figure 2 - Temporal profile of the total emission signal following the photolysis of HC_2CN by an unfocussed ArF laser if 50 mJ/cm^2 fluence.

Figure 3 - Dispersed fluorescence from the high intensity photolysis of HC_2CN, from the initial part of the temporal profile shown in Figure 2.

Figure 4 - LIF spectra of the ground state CN fragments produced in the photolysis of HC_2CN at 193 nm. (a) shows the LIF spectrum when the laser fluence as 50 mJ/cm^2 and (b) shows the spectrum at low laser energy.

Figure 5 -   Quantum state distribution of CN from the photolysis of HC_2CN at low laser energy. The solid line is the result of a fit to a sum of exponentials.

Figure 6 -   LIF spectra of CN fragments from the photolysis of C_4N_2 at 193 nm under conditions of low laser intensity.

Figure 7 -   Quantum state distribution of CN as measured from the spectrum shown in Figure 7.
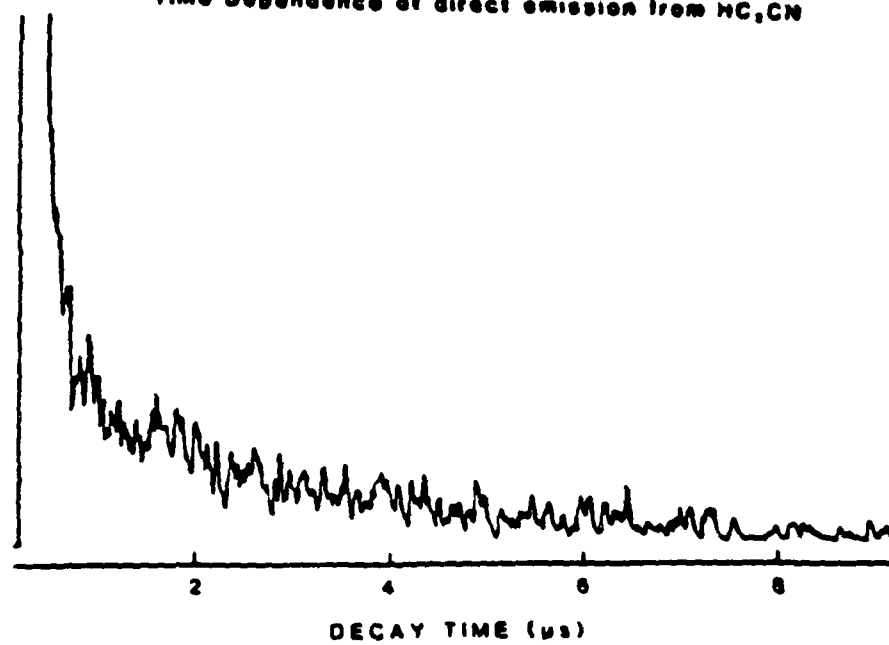
Figure 8 -   Emission time profile of CN from the 193 nm photolysis of expansion cooled C_4N_2.

Figure 9 -   Dispersed emission from fragments following the photolysis of expansion cooled C_4N_2 at 193 nm.
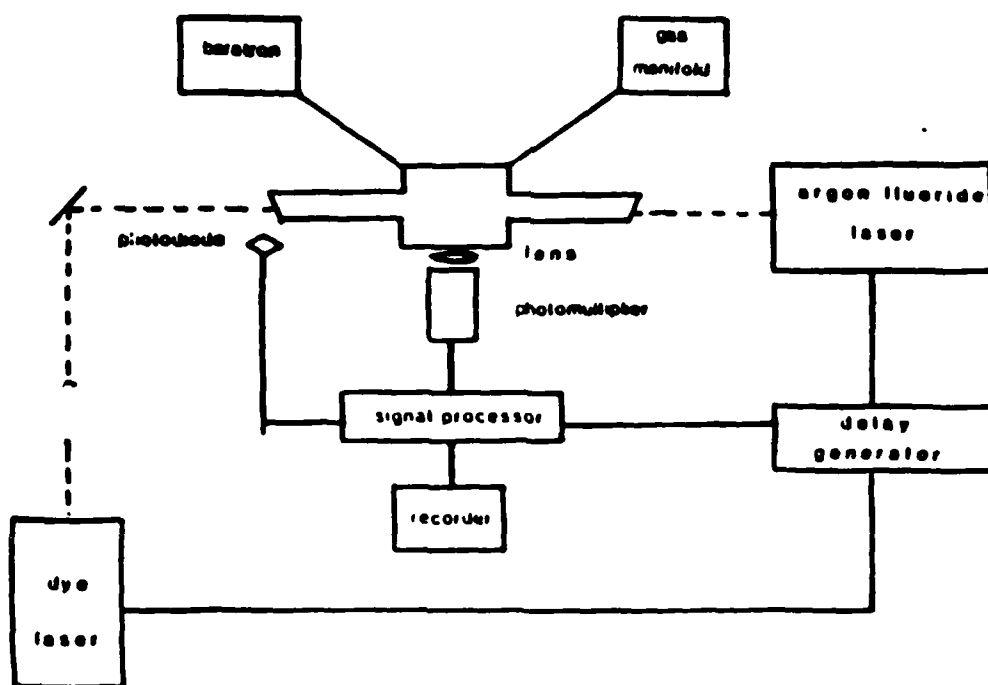
SCHEMATIC OF LIF APPARATUS

Time Dependence of direct emission from HC₃CN

DECAY TIME (μs)

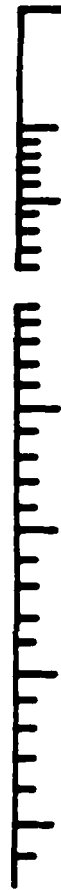**Direct Fluorescence Observed from CN from Photolysis of Cyanoacetylene**
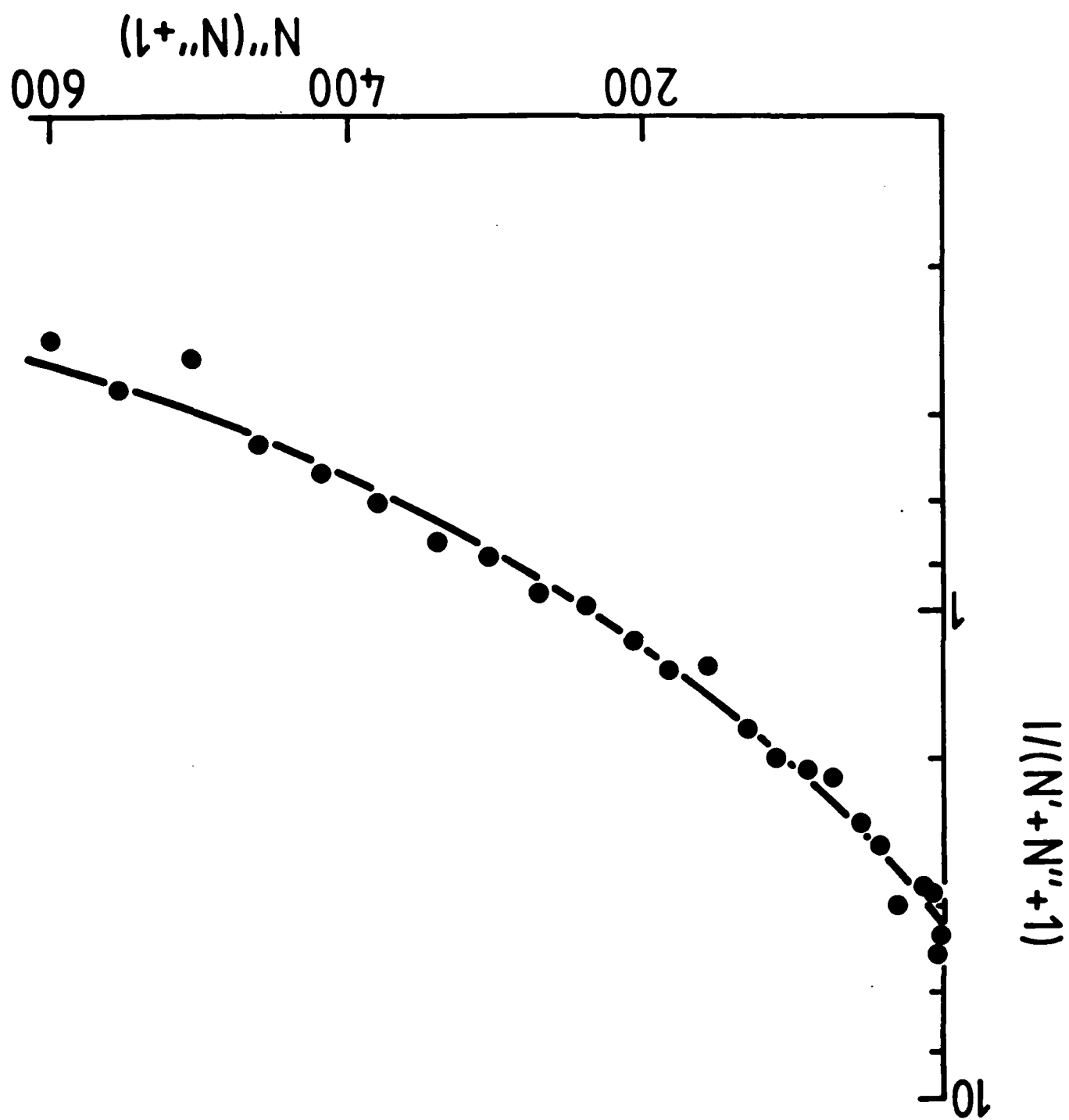
v''

0   1   2   3   4

(b)

(a)

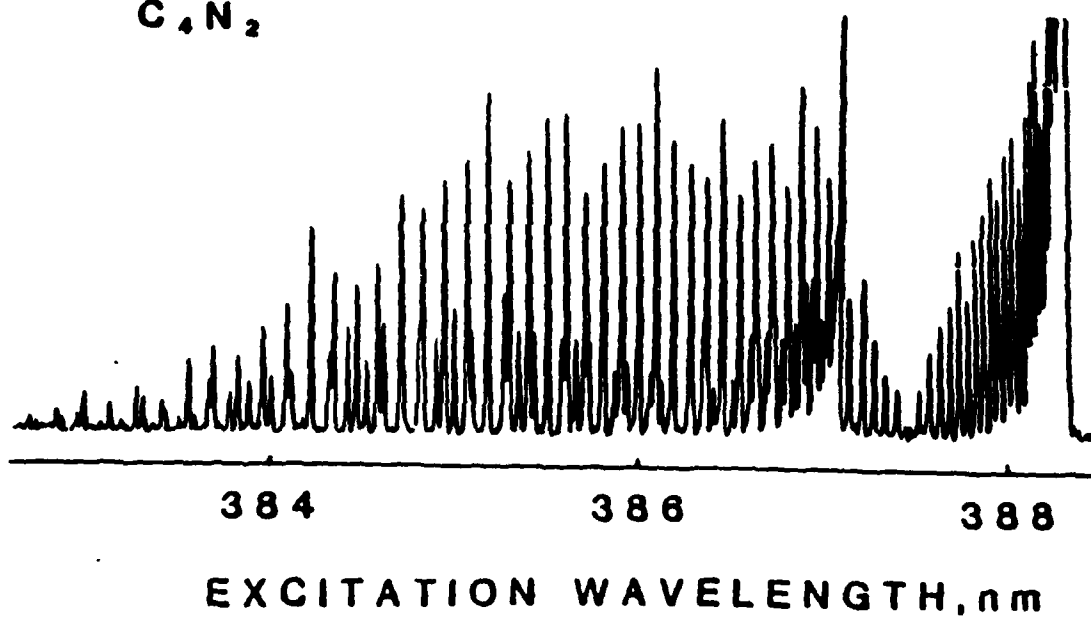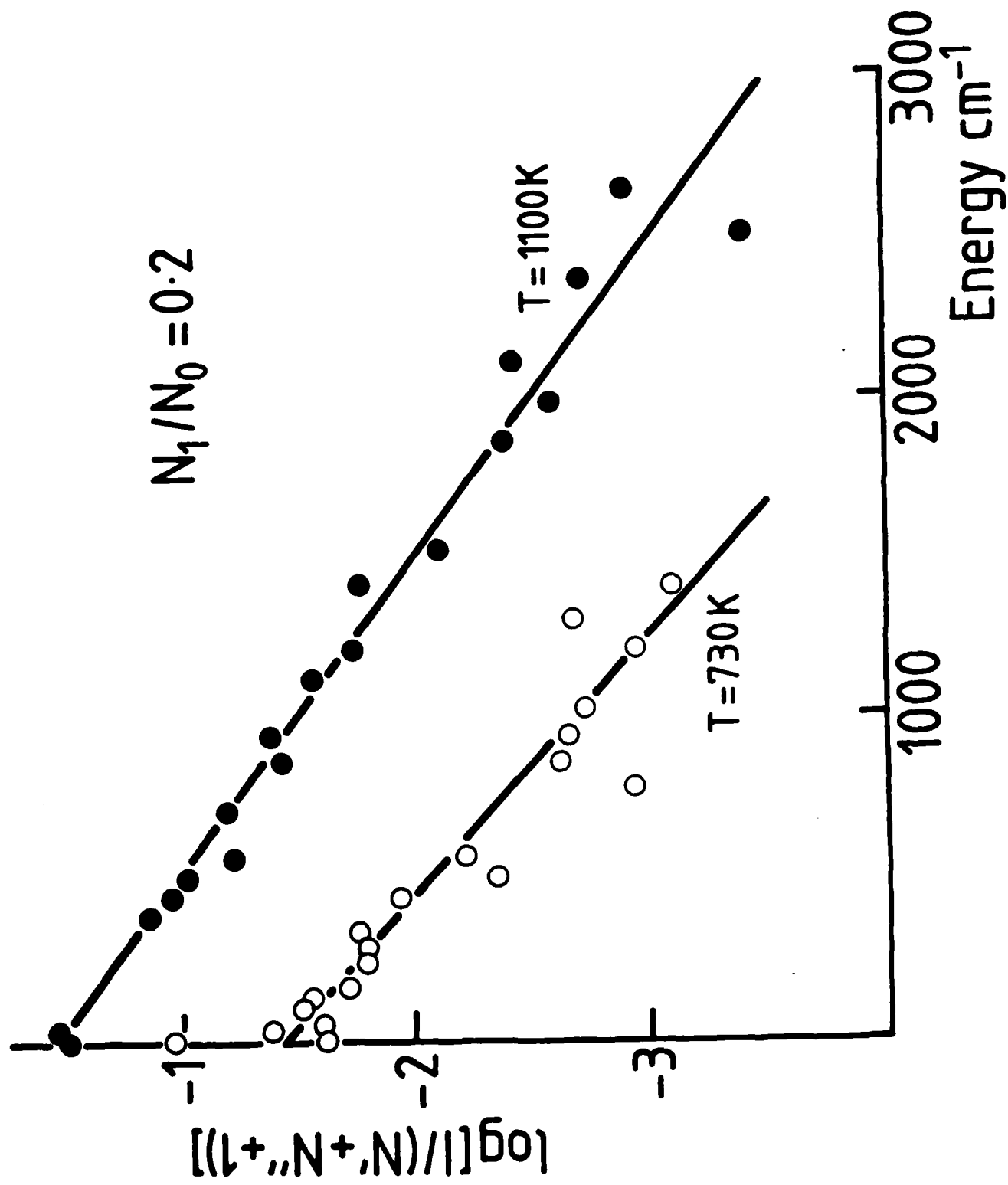384   386   388

Excitation wavelength, nm
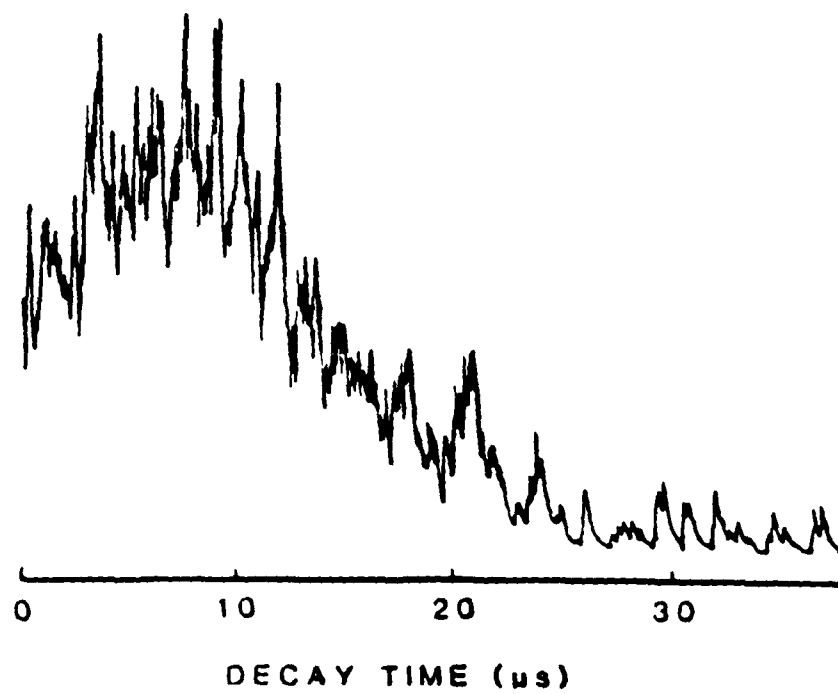
C_4N_2

384　　　　386　　　　388

EXCITATION WAVELENGTH, nm

Time Dependece of direct fluorescence fom C_4N_2

DECAY TIME (us)

Fluorescence Spectrum from C_4N_2

WAVELENGTH (nm)
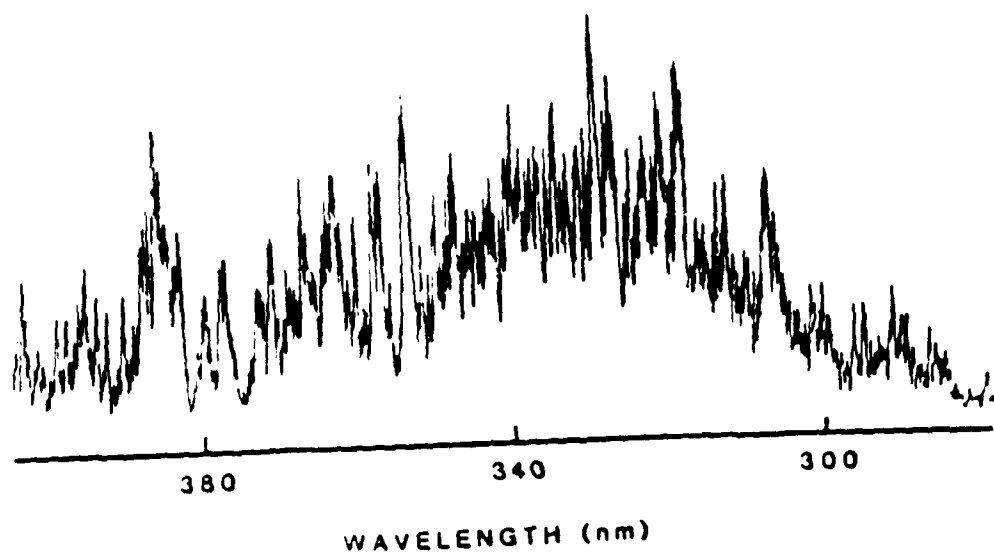
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