

## LASER STUDIES OF THE DYNAMICS OF PHOTODISSOCIATION\*

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### Summary

One of the simplest dynamic processes that occurs in chemistry is the photodissociation of a molecule. Molecules are prepared on an excited potential energy surface by a Franck–Condon transition where they then evolve to products. In the process of evolving to products, predissociation can occur so that a new excited state is formed before the dissociation products appear. Other molecules will undergo direct dissociation so that the nascent energy distributions of the products reflect the characteristics of the original potential energy surface. By measuring the nascent energy distributions of the products and the branching ratios for the production of molecules in different excited states, we can unravel the processes that are occurring within a given system. From these measurements detailed mechanisms can be postulated that explain the photodissociation results. These mechanisms are discussed in terms of kinematic models which illustrate the various types of interactions that occur as excited states evolve toward complete dissociation on a potential energy surface.

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### 1. Introduction

Photochemical dynamics is one of the simplest dynamic processes that can be investigated. Ideally, it consists of selecting a molecule in a given excited quantum state and then measuring the translational energies and the quantum state distributions of the fragments. The ideal is seldom achieved in the laboratory because defining the vibrational, rotational and electronic state of a simple triatomic or polyatomic molecule requires a narrow-band light source in the region below 200 nm. For many molecules hot bands and spectral congestion make it difficult or impossible to analyze the spectra of even the first excited state [1]. For most molecules with heavy atoms there will only be a few cases in which we can define the vibrational level of the molecule, not to mention its rotational level. In the present work detailed photodynamic studies of several molecules are presented. In some cases the studies were performed as a function of the various vibrational levels of the excited state while in others the dynamics were determined at a single wavelength.

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Determination of the quantum state distributions of the fragments that radiate is much easier than selection of the quantum state of the reactant. The photochemical dynamic studies that are described in the present work are limited to those studies where the quantum state distribution of the fragment can be determined directly by using the laser-induced fluorescence technique. For dark fragments other techniques such as time-of-flight measurements [2] with a mass spectrometer must be used.

## 2. Experimental details

The photofragment spectrometer that employs a tunable vacuum UV flashlamp and a tunable dye laser for quantum state detection of the fragments has been described previously [3]. Several modifications were introduced which increased the signal-to-noise ratio in the original photofragment monochromator. These included better collimation of both the laser light and the viewing zone where the photochemical fragments were detected and the probing for fragments closer to the exit slit of the monochromator. With these modifications the photofragment monochromator permitted us to obtain laser-induced fluorescence spectra of the type shown in Fig. 1. This is a typical spectrum obtained when  $C_2N_2$  was photolyzed at 158.6 nm. Other spectra of this quality could be obtained at the other wavelengths.

The apparatus used for the photolysis of the various gases at 193 nm is shown schematically in Fig. 2. It consists of a crude molecular beam which is obtained by flowing the gas through a hypodermic needle with an inside diameter

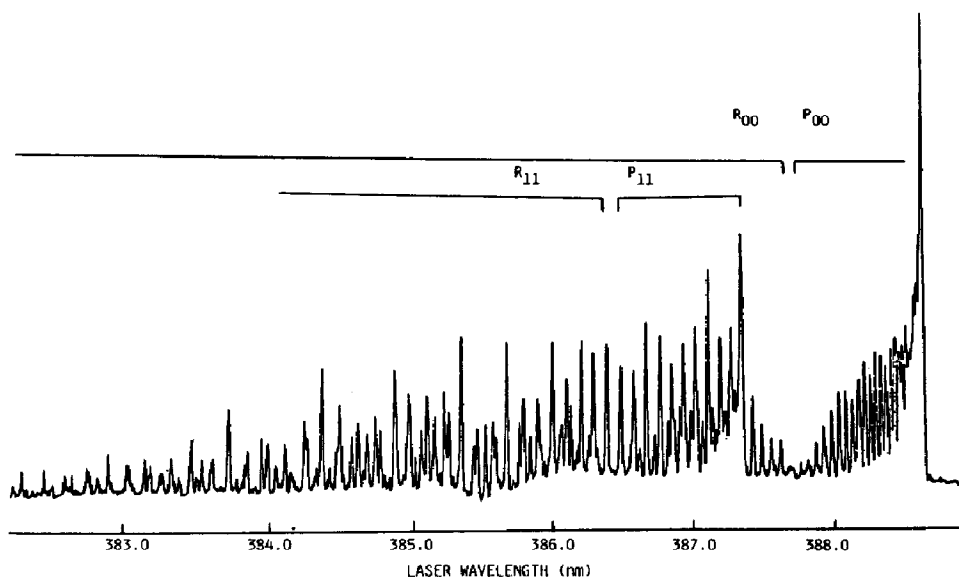


Fig. 1. A laser-induced fluorescence spectrum of the  $X^2\Sigma \rightarrow B^2\Sigma$  transition of CN produced in the photolysis of  $C_2N_2$  at 158.6 nm. The pressure was 0.15 Torr and the time delay between the flashlamp and the probe laser was 0.6  $\mu$ s.

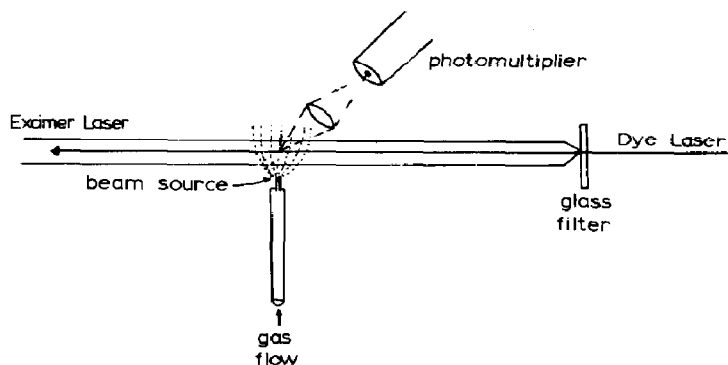


Fig. 2. A schematic representation of the molecular beam laser photolysis experiment.

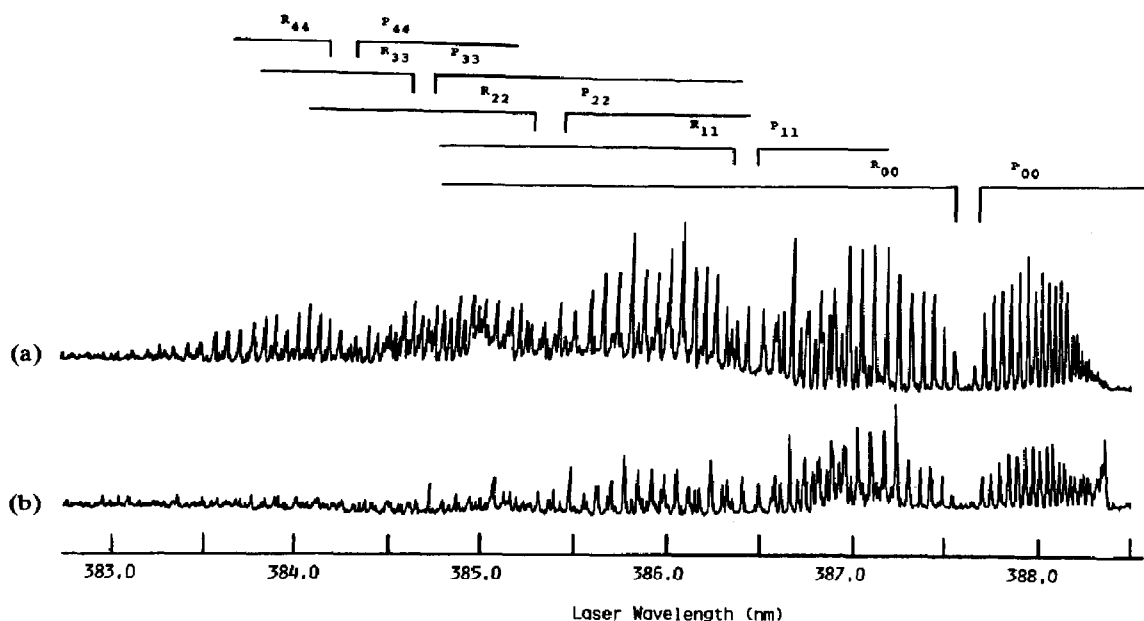


Fig. 3. Laser-induced fluorescence spectra at 154 nm of the CN( $X^2\Sigma$ ) state ( $X^2\Sigma \rightarrow B^2\Sigma$ ,  $\Delta v = 0$  transition) produced in the photolysis of an Ar-C<sub>2</sub>N<sub>2</sub> (62:1) mixture at a pressure of 10 Torr. Two time delays between the flashlamp and the laser are shown: (a) 20  $\mu$ s; (b) 600 ns.

of 1 mm. This crude beam is crossed with an excimer laser a few centimeters behind the needle. The light from the tunable dye laser passes collinearly along the excimer laser axis but in the opposite direction. The dye laser has a diameter of 1 mm, which is completely overlapped by the 1 cm  $\times$  2 cm beam of the excimer laser. The scattered radiation from the excited fragments is collected by a lens and passed through an interference filter onto a photomultiplier which is perpendicular to the plane defined by the laser and the molecular beam. The type of photomultiplier used to collect the light was an EMI 9386 QB which has

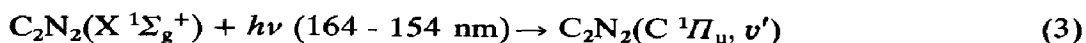
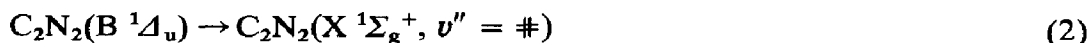
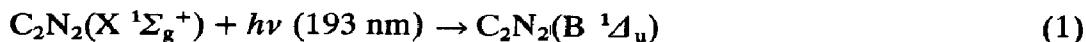
a very small photocathode. This serves as an optical stop, permits better definition of the interaction zone that is being observed and thus reduces the scattered light arriving at the detector. A typical spectrum that can be obtained with this system is shown in Fig. 3, which demonstrates the very good signal-to-noise ratio obtained.

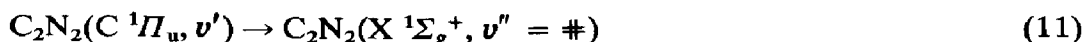
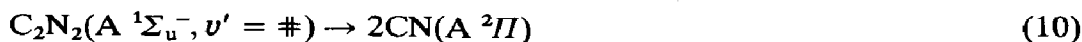
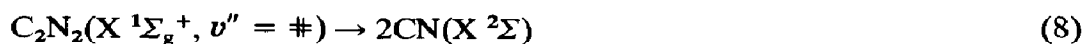
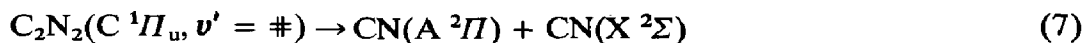
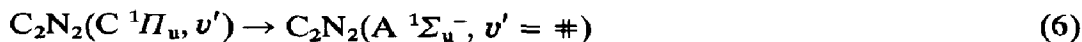
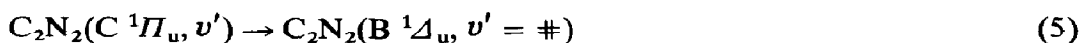
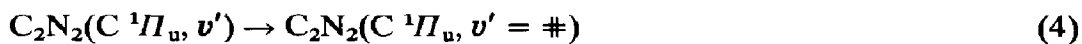
### 3. Results

#### 3.1. $C_2N_2$

$C_2N_2$  was photolyzed in several regions of the spectrum. The original studies were done with the vacuum UV flashlamp. With this flashlamp we were able to isolate the  $C_2N_2$  vibrational bands of the  $C\ ^1\Pi_u$  state of  $C_2N_2$ . These occur at 164, 158.6 and 154 nm. High resolution studies [4] of this spectral region indicate that the small splittings that are observed are due to Renner–Teller interactions. The splittings defined by the previously quoted bands correspond to excitation of the  $\nu_3$  antisymmetric stretch frequencies in  $C_2N_2$ . The  $C\ ^1\Pi_u$  state is thought to correlate with two CN radicals, one of which is the  $A\ ^2\Pi$  state and the other is the  $X\ ^2\Sigma^+$  state. However, it can also predissociate via a curve crossing into the continuum of the ground state, which would result in two CN radicals being produced in the  $X\ ^2\Sigma^+$  state. Furthermore, at the shortest wavelength there is also enough energy [5] to predissociate into the continuum that corresponds to dissociation into two  $A\ ^2\Pi$  state fragments. Photodissociation dynamics should help us to discriminate between these possibilities.

The ArF laser was also used to photolyze  $C_2N_2$  at 193 nm. The laser radiation excites the  $B\ ^1\Delta_u$  state. Although the absorption to this state is weak, it does show structure, some of which has been analyzed by Woo and Badger [6]. Their analysis suggests that several vibrational progressions can be identified in this region. The vibrational progression that is excited by the ArF laser has been designated by these researchers as the D vibrational band. This D band corresponds to an excitation of a vibrational band with a frequency of approximately  $2000\text{ cm}^{-1}$  which is probably the  $\nu_3$  antisymmetric CN stretching frequency. It is also the fourth band in the progression, which means that this vibration has at least four quanta of energy. Both the states that were excited in the present study are states that predissociate. We can now ask the question whether the dynamics determined from the fragments change when two different electronic states which are vibrationally excited and have different symmetries predissociate. In the photolysis of  $C_2N_2$  at 193 nm predissociation can only occur into the vibrational continuum since this is the only energetically allowed channel, whereas at shorter wavelengths several different dissociation channels are available to the  $C\ ^1\Pi_u$  state. The overall photodissociation mechanism can be summarized by the following reaction scheme:





This scheme shows that excitation of the  $\text{C } ^1\Pi_u$  state ultimately leads to the production of two CN radicals that may or may not be in different electronic states. A method was devised to determine the  $\text{A } ^2\Pi:\text{X } ^2\Sigma$  ratio directly by using time-delayed studies of the laser-induced fluorescence spectra of the X state of CN to distinguish between A and X state fragments.

The gas mixture (10 Torr) introduced into the system comprised 9.84 Torr of argon and 0.16 Torr of  $\text{C}_2\text{N}_2$ . Two laser-induced fluorescence spectra of CN in the X state were taken, one spectrum with a  $0.6 \mu\text{s}$  delay, the other with a  $20 \mu\text{s}$  delay between the laser and the flashlamp. An example of the spectra that were obtained is shown in Fig. 3. Since the lifetime of the  $\text{A } ^2\Pi$  state [7] is approximately  $7 \mu\text{s}$ , only 10% of the  $\text{A } ^2\Pi$  state radicals will have decayed to the ground state during the short time delay. At the longer delay 95% of the A state radicals will have decayed to the ground state. By analyzing the spectra and counting the total number of radicals in each vibrational band it is possible to determine the ratio of the A to X state populations. This ratio as a function of the energy of photolysis is given in Table 1, which clearly shows that the A state population increases as the vibrational excitation of the  $\text{C } ^1\Pi_u$  state increases. The results suggest that at 164 nm predissociation occurs both via reaction (11) followed by reaction (8) and via reaction (4) followed by reaction (7). At 158 nm the relative importance of these two channels changes, while at 154 nm predissociation into the continuum of both the  $\text{B } ^1\Delta_u$  and the  $\text{A } ^1\Sigma_u^-$  states becomes energetically possible and apparently occurs. Although the ratio of the branching between the electronic states of the product reflects the available dissociation channels, the question remains whether the rotational and vibrational distributions of the CN product exhibit similar behaviors.

The vibrational and rotational distributions of the X state fragment are given in Table 2. This table shows that the X state internal energy distribution appears to be insensitive to the particular channel that is available for dissociation. The rotational and vibrational distributions of the X state fragment do not change as the vibrational energy of the  $\text{C } ^1\Pi_u$  state of  $\text{C}_2\text{N}_2$  is increased. Certainly randomization does not occur in the excited state even though the spectra and the electronic branching ratios of the fragment indicate that predissociation does occur from this state. This statement is true despite the fact that the excited

TABLE 1

The ratio of A state to X state populations of CN

$\lambda$ (nm)	$\frac{[A]+[X]}{[X]}$	$\frac{[A]}{[X]}$
153.6	2.63	1.63
158.6	1.84	0.84
164.0	2.09	1.09

TABLE 2

Summary of the results for the  $\Delta v = 0$  series

$\lambda$ (nm)	Vibrational band	Rotational temperature (K)	Intercept		Normalized intercept		$\frac{N_{v''=1}}{N_{v''=0}}$
			$R_{0-0}$	$R_{1-1}$	$R_{0-0}$	$R_{1-1}$	
153.6	0-0	1800 $\pm$ 70	0.30	0.18	0.33	0.24	0.72
153.6	1-1	1400 $\pm$ 100					
158.6	0-0	1700 $\pm$ 60	0.69	0.45	0.76	0.59	0.78
158.6	1-1	1100 $\pm$ 70					
164.0	0-0	1600 $\pm$ 80	0.55	0.28	0.60	0.37	0.62
164.0	1-1	1100 $\pm$ 10					

molecule lives for some time before dissociation and should have time for internal equilibration.

The results in Table 2 also show that the vibrational and rotational distributions of the CN( $X^2\Sigma^+$ ) state fragments that result from predissociation of the B  $^1\Delta_u$  state into the vibrational continuum of the ground state are similar to the results obtained when the C  $^1\Pi_u$  state predissociates. These observations suggest that there is a common tie between the observed results. Could it be that the rotational and vibrational distributions reflect mechanical constraints? For example, most of the observed rotational distribution may be due to the fact that in the X  $^1\Sigma_g^+$  state of C<sub>2</sub>N<sub>2</sub> a large number of the molecules populate the excited levels of the bending vibration. This is a consequence of both the degeneracy of this level and its frequency, which is only 220 cm<sup>-1</sup>.

If these suppositions are correct, then the rotational and vibrational distributions of the A  $^2\Pi$  state should be similar to the distributions observed for the X  $^2\Sigma^+$  state. Although the data for this state are still being analyzed, present indications suggest that this is the case.

### 3.2. C<sub>1</sub>CN and BrCN

In the C<sub>2</sub>N<sub>2</sub> molecule, photodissociation occurs after the molecule in a linear ground state has been excited to a linear excited state. Both C<sub>1</sub>CN and BrCN are linear in the ground state but have non-linear excited states. An exami-

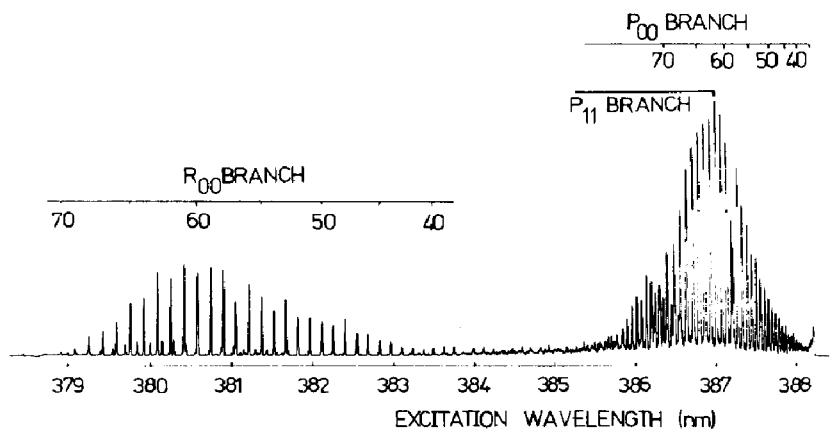


Fig. 4. A laser-induced fluorescence spectrum of the CN( $X^2\Sigma$ ) state produced in the 193 nm photolysis of a C1CN molecular beam. The absence of the band origin indicating the high rotational excitation in CN should be noted.

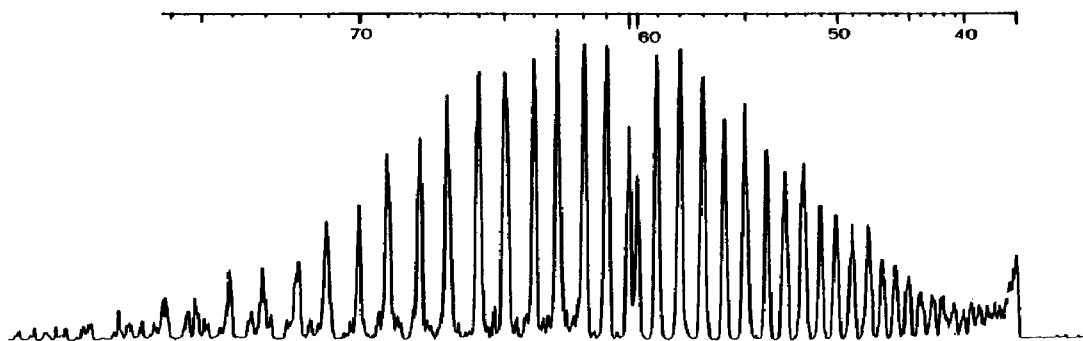


Fig. 5. A laser-induced fluorescence spectrum of the CN( $X^2\Sigma$ ) state produced in the 193 nm photolysis of a BrCN molecular beam. Only the P branch is shown.

nation of the spectra of C1CN and BrCN suggests that in these molecules direct dissociation can occur, since very little structure is observed. This may, however, be due to the size of the atoms that are involved rather than an inherent property of the excited state. Nevertheless in view of the previous results it is important to determine how these changes will be reflected in the observed dynamics. Both BrCN and C1CN absorb light at 193 nm so that both can be studied by laser photolysis at this wavelength. Typical spectra that were obtained from C1CN and BrCN are shown in Figs. 4 and 5. These spectra are remarkably similar and, contrary to the quantum state distributions that were observed in  $C_2N_2$ , the CN radicals that are produced from the 193 nm photolysis of C1CN and BrCN are highly rotationally excited. Fragments are observed with rotational energies up to  $10\,000\text{ cm}^{-1}$ . More vibrational excitation is observed in the CN fragment produced when C1CN is photolyzed than when BrCN is photolyzed, but since more energy is available in the latter molecule we must conclude that energy random-

ization cannot explain this result. Rather, this vibrational excitation must be the result of interfragment interactions as the molecule dissociates. Evidently, since bromine is so much heavier than chlorine, the interfragment interaction must be considerably reduced.

#### 4. Conclusions

The results described in this paper indicate that randomization is not a good mechanism for describing the distribution of the excess energy that goes into photochemical fragments. Most of the rotational excitation can be explained by the geometrical changes that occur in the molecule when excitation of the precursor occurs. When these changes are large a great deal of energy appears in rotational motion of the fragments. Even when the molecule undergoes a transition from a linear ground state to a linear excited state, if the bending modes of the ground state are excited it can lead to the appearance of increased amounts of energy as internal rotational excitation. It is not clear what causes the observed vibrational excitation of the fragments since increasing the vibrational excitation of the excited state does not dramatically increase the vibrational excitation of the fragment. Increasing the available energy also does not increase the vibrational excitation of the fragments. There appears to be a heavy atom effect which suggests that motion of the fragment may somehow affect how much vibrational excitation appears in the fragments. The heavier and hence the slower the recoiling fragment is, the less probable it is that vibrational excitation of the fragment occurs.

#### Acknowledgments

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