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PARTITIONING OF EXCESS ENERGY IN THE PHOTOLYSIS OF CLCN AND BRC--ETC(U)
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TECHNICAL REPORT NO. 9

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ABSTRACT

The nascent quantum state distributions of $CN(X^2\Sigma^+)$ fragments produced in the dissociation of ClCN and BrCN by photolysis at 193nm, in an effusive beam have been measured. The rotational distribution of the fragments is highly excited. The results show that the excited electronic state which dissociates is bent. A simple parameterization is shown to fit the results. This parameterization is based on a classical model which has dynamical implications.

INTRODUCTION

Photolysis of cyanogen halides has been a favorite area of investigation for those seeking to learn about photodissociation. Yet results from these simple and much studied systems can still be surprising. The review of Ashfold, MacPherson and Simons provides a comprehensive summary of the many theoretical and experimental approaches that have been enthusiastically and profitably applied to this problem (1).

Fixed frequency lasers can be used as intense photolytic sources in the far ultraviolet, where ground state CN radicals are the dominant products. Investigations of the photodissociation of ICN in the A continuum have been made with quadrupled Nd-Yag lasers (2-5). Busch, et al, used a time-of-flight system with a mass filter as a detector to measure the halogen atom's translational distribution (2). Laser induced fluorescence (LIF) has proven to be a sensitive probe of nascent quantum state distributions of photolytic fragments (6). Baronavski and McDonald have used LIF detection to characterize the CN fragments created in the dissociation of ICN by 266 nm laser light (3). Recently they have extended their measurements, using four wave mixing in several atmospheres of hydrogen gas to shift the laser's wavelength (4,5).

The high sensitivity of LIF allows one to measure the quantum state distributions of fragments produced by relatively weak photolysis sources such as flashlamps. Sabety-Dzvonik and Cody measured the nascent CN distributions from flashlamp photolysis of ICN and ClCN (7,8). When ClCN was illuminated with a continuum lamp which overlapped the entire A and α systems, they observed a CN product distribution with two peaks, one at $N'' \sim 10$ and the other at $N'' \sim 65$. The lower peak declined in prominence as the pressure of the parent gas was decreased. However, the authors were unable to conclude whether the lower peak was entirely a result of collisional processes, or whether it was to some extent due to the primary dissociative process.

Recently, Heaven, Miller and Bondybey (9), have examined the production of CN from the ArF laser photolysis of BrCN at 193 nm as part of a larger work in which molecules were photolyzed close to the nozzle of a supersonic beam and the cooling of the photolytic fragments in the beam was measured. They observed the production of $v'' = 0$ and $v'' = 1$ CN radicals in the ratio of 4:1. The rotational distribution of these radicals could be approximated by a 4000K Boltzman distribution. This result is at odds with those reported here for the photolysis of BrCN in an effusive beam. The apparent contradiction will be addressed below and suggestions will be made that may explain it.

In this paper experiments will be described on the photodissociation of ClCN and BrCN by an ArF laser which emits at 193 nm. A simple, semi-classical model will be presented that can be used to understand the results. Combining this model with the one that we have proposed for the photolysis of C_2N_2 by predissociation from its $B^1\Delta_u$ state, shows that simple considerations of the conservation of energy and angular momentum place extremely strong constraints on the photolytic product distributions and, in fact, determine most of the details of the rotational distribution of the products.

In the far ultraviolet spectrum of BrCN one may distinguish two weak continuous absorption systems, called the A and the α systems. The A system is at longer wavelengths. BrCN is similar to ICN, where both systems are resolved. Both absorption systems of ICN are red shifted as compared to BrCN, and relatively better separated. In ClCN the two are completely overlapped and blue shifted even further than for BrCN. An early study of the absorption spectrum of the cyanogen halides was made by King and Richardson (11). They assigned these transitions to the promotion of a electron to the 7σ orbital, and thus concluded that the upper state was a linear $^1\Pi$ system. Rabelais, et al (12), in a study of the electronic structure of sixteen electron molecules assigned both continua to a $2\pi \rightarrow 3\pi$ electron promotion. They concluded that the A continuum is a $(^1A'') \leftarrow X(^1\Sigma^+)$ transition, while the α continuum corresponds to a $(^1A'$ or $^1A'') \leftarrow X^1\Sigma^+)$ transition.

If Rabelais, et al are correct in their conclusion that the excited state is bent, then the Franck-Condon principle requires that only a highly excited vibrational level of this state's bending mode can be populated. Conversely, if King and Richardson are correct, and the excited state is linear, then the Franck-Condon principle requires that only the first few levels of the bending mode will have any significant population. In such a case, our earlier work has shown that conservation of angular momentum requires that the rotational distribution of the thermally excited parent molecule maps directly into the rotational distribution of the fragments (10).

EXPERIMENTAL

The basic experimental apparatus has been previously described (10). The vacuum chamber was evacuated by a six inch diffusion pump, separated from the experimental cell by a large liquid nitrogen trap and a gate valve which was kept fully opened. A constant intensity effusive cyanogen halide beam was established and maintained by a Granville-Phillips automatic pressure controller that sensed the output of an ionization gauge and adjusted the flow of gas into the cell. The pressure in the chamber was held constant to within a few percent. The experiments that are reported here were done at total pressures in the chamber between 5×10^{-6} and 2×10^{-4} torr.

The molecular beam emerged from a 0.5 mm diameter hypodermic needle placed about 1 cm from the ArF laser beam and perpendicular to it. The dye laser beam, used to excite LIF, was propagated in the opposing direction and passed colinearly through the ArF laser beam. The ArF laser had a cross-sectional area of about 2 cm^2. The dye laser beam had a cross-sectional area of about 1 mm^2. Induced fluorescence was observed in a direction perpendicular to both the effusive beam and the lasers. A lens system imaged the fluorescence onto a filtered phototube.

A beam block inserted between the gas source and the laser beams decreased the LIF signal by half. No other difference was measured between the LIF spectra obtained with the beam block in place and those recorded in its absence. Nor were there any differences noted in the measured quantum state distributions of the fragments as the beam density was varied over almost two orders of magnitude. Therefore, the expansion did not cool the gas. Time-of-flight studies of other systems further indicate that the beam is effusive as long as the pressure in the beam chamber is kept below 2×10^{-4} torr (13).

Earlier it was shown that both ClCN and BrCN can be photolysed at 193 nm to yield $CN(B^2\Sigma^+)$ fragments via a two photon sequential absorption (14). In the present work the importance of such processes was estimated by comparing the B state emission from LIF with the direct emission following the ArF laser pulse. The direct signal was less than 1% of the LIF signal. Considering the relative physical cross-sections of the two laser beams, the two photon channel is of negligible importance in these experiments. This was confirmed by the fact that an order of magnitude variation in the ArF laser intensity resulted in a linear variation of the observed signal. Most experiments were run at a level of about 7.5 mj/cm^2. No change was seen in the quantum state distribution of the CN fragments when the ArF laser intensity was varied over an order of magnitude.

OBSERVATIONS

ClCN

Figure 1 shows the $\Delta v = 0$ sequence of the CN($X^2\Sigma^+$) excitation spectrum measured 200 ns after a 5 mj/cm^2, 20 mm long ArF laser beam passed through an effusive beam of ClCN. There were no observable changes in the measured CN($X^2\Sigma^+$) distribution when the delay between the excimer laser and the dye laser was varied from zero to a few microseconds. The spectrum shown in Figure 1 is uncorrected for the dye laser intensity, which explains the relative sizes of the R and P branches. The quantum state analysis of the CN($^2\Sigma^+$) fragment was done using only the P branches in the LIF spectra, where the dye laser intensity is constant within a few percent.

Two perturbations of the $B^2\Sigma^+$ state can be seen in Figure 1, where levels of the CN($B^2\Sigma^+$) state are accidently degenerate with levels of the $A^2\Pi_i$ state. Gero, Schmidt and Zemplein (15), concluded that all of the perturbations between these two states involve the $A^2\Pi_{3/2}$ level. Moreover, they saw no perturbations of the $B^2\Sigma^+$ state by any other electronic state.

Figure 2 is an expansion of the P branch region of Figure 1 and clearly shows the perturbed $P_{00}(60)$ line. The relative amounts of CN($X^2\Sigma^+$) produced in the v"= 0 and v"= 1 levels can be measured by comparison of the P_{00} and P_{11} branches. Figure 3 shows the LIF excitation spectrum of the $\Delta v =$ -1 sequence. This can be used to determine the quantum state distributions of the CN($X^2\Sigma^+$) produced in the v"= 1 and v"= 2 levels. The complete absence of a band head in the P_{01} branch shows that CN($X^2\Sigma^+$, v''= 1) is only produced in high rotational states.

Using the data obtained from Figures 2 and 3 and similar spectra, we can generate a complete quantum state distribution of CN($X^2\Sigma^+$) produced from the photolysis of ClCN at 193 nm. This is displayed in Figure 4 as a function of total internal energy (the sum of the rotational and vibrational energy of the diatomic fragment). The total available energy following photolysis is 16,800 cm^{-1} (16). Table II lists the measured population of the three vibrational levels that are significantly populated. Although the population of the v''= 3 level is below the limits of quantitative measurment, indications of a minute population in rotational levels of v''= 3 can be seen on the left hand side of Figure 3.

Attempts were made to measure any population in low vibrational levels of the CN($A^2\Pi_i$) state by exciting the CN($A^2\Pi_i \rightarrow B^2\Sigma^+$) transition and then monitoring fluorescence from the B state (17). No signal could be detected.

BrCN

Similar experiments were done with BrCN. Figure 5 shows the LIF excitation spectra measured for this molecule. The observed distribution of the v''= 0 fragment is roughly similar to that seen for ClCN, but little vibrational excitation is observed. Figure 6 is a plot of the quantum state distribution of CN($X^2\Sigma^+$) fragments from the photodissociation of BrCN as a function of internal energy.

DISCUSSION

The conservation of total angular momentum and energy are stiff constraints on the motion of fragments formed through the photodissociation of triatomic molecules. Simple considerations lead to the identification of three interesting limiting cases in which either state is linear. In the first and simplest case both the ground and excited electronic states of the parent molecule are linear. In the second case the ground state is bent but the excited state is linear, while in the third case the ground state is linear but the excited state is bent. It is clear that the Franck-Condon principle must play a controlling role in determining the molecular configuration immediately after a photon is absorbed.

The ground state of both ClCN and BrCN is linear but as pointed out earlier there have been spectroscopic conclusions that the upper state excited at 193 nm will be either linear (11) or bent (12). Some time ago Morse, Freed and Band (17) pointed out that if the photodissociation of a triatomic molecule belonged to the first case, the probability of finding the diatomic fragment in the rotational quantum state J must be the same as the probability of the parent molecule having been in the state J. Thus, if the quantum states of the parent molecule were thermally populated the diatomic fragment would have a nascent Boltzmann distribution characterized by a temperature, T_{fragment},

$$T_{\text{fragment}} = T_{\text{parent}} \frac{B_{\text{fragment}}}{B_{\text{parent}}} \tag{1}$$

where B is the rotational constant and T the temperature of the species. We have recently observed a case I transition in C_2N_2 (11). The equivalent relation for a four atom molecule has been experimentally verified. Moreover, it was shown that for case I, the fragments produced in different vibrational states of the diatomic molecule will always have identical rotational distributions. In this case the rotational and vibration degrees of freedom are decoupled since there is no possibility of removing excess energy via orbital angular momentum.

This is certainly not what is seen following the photolysis of ClCN and BrCN at 193 nm. The rotational distribution of the CN fragments is not Boltzmann. In ClCN, where several vibrational states of the CN fragment are detected following photodissociation, the rotational distributions of the different states are not identical. In both molecules the level of rotational excitation is inverted and a considerable amount of rotational energy appears in the CN fragment. Thus it can be stated that the upper electronic state from which the two cyanogen halides dissociate is bent, in agreement with the assignment of Rabelias, et al. (12) and in contradiction to the conclusions of King and Richardson (11).

In such a case III photodissociation the Franck-Condon principle suggests that only highly excited levels of the bending mode can be reached by photoexcitation. The reason for this can be seen from the potential energy diagram in Figure 7 where the equilibrium configuration of the linear ground state at 180° is shown to be at the local maximum of the upper state's bending motion. Because the potential of the bending vibration must be symmetric about the linear geometry there will be at least a local maximum of the potential at 180° and repulsive walls at zero and 360°.

The difference in energy between $h\nu$ and the height of the local maximum will determine the probability of absorption. If this energy difference is small the probability of absorption will be large since the vibrational overlap between the excited state wave function and the ground state wave function will be large. On the other hand if this energy difference is large then the overlap will be small so that the transition will be almost Franck-Condon forbidden. Since the absorption coefficient for BrCN and ClCN are of the order of 10^{-19} cm^2 (11) this is certainly not a Franck-Condon forbidden transition and we conclude that the energy difference must be small.

Conservation of angular momentum requires that the vector sum of the orbital angular momentum of the fragments $\underline{L}$ and the rotational angular momentum of the diatomic fragment $\underline{J}$ be equal to the total angular momentum of the parent molecule $\underline{j}$. Thus the possible values of $\underline{j}$ are:

$$(2) \qquad |\underline{J} - \underline{L}| \leq \underline{j} \leq |\underline{J} + \underline{L}|$$

Consider the dissociation process in the non-rotating frame of the parent cyanogen halide. The bending motion of the three atoms define a plane. The orbital angular momentum of the dissociating fragments must be perpendicular to this plane, and since the molecule is not rotating in the chosen frame, the orbital angular momentum $\underline{L}$ must be equal and opposite to the rotational angular momentum of the CN fragment $J = -L$. In a direct dissociation the orbital angular momentum is a result of the snapping of the halide-carbon bond as the excited molecule moves from the linear configuration towards and perhaps through the equilibrium angle. From the above argument it is clear that the rotation of the CN fragment will compensate and be retrograde to the orbital rotation. Examination of the nascent quantum state distribution of CN produced in the photolysis of ClCN and BrCN leads to a parameterization that we believe to be dynamically meaningful. We assume that the orbital angular momentum is almost constant and justify this assumption with data in Figure 4 which shows a sharp cut-off in the amount of energy that can appear as internal energy in the CN fragment. If it is further assumed that the orbital angular momentum quantum number, L, is equal to the maximum observed value of the rotational quantum number for each of the vibrational states of CN then the measured rotational distributions shown in Figures 4 and 6 can be transformed into distributions over $j' = L - J$.

The logarithm of the probability of finding a fragment in a state labeled by j' divided by $2j' + 1$ is plotted against $j'(j' + 1)$ in Figures 8 and 9. The fit to a Boltzmann like form is good, especially considering the ad hoc nature of the model. Each of these distributions can be described by a simple parameter that is a measure of the slope of the curve. For a thermal distribution this slope is $-B/kT$, where B is the rotational constant of the molecule under consideration and T is its temperature.

In the present case it is not clear what B and T refer to. If T is the temperature of the XCN molecule when it is photolyzed then B must be some "effective" rotational constant. Table II lists the value of L and B for the three vibrational states of CN produced in the photodissociation of ClCN and for the ground state of CN produced in the photodissociation of BrCN assuming that T is 300K. For comparison the measured rotational constants of the ground states of the triatomic molecules and the correlation coefficients of the fits are also shown.

While the distributions, $P(j',v'')$, are Boltzmann in character they are different from the XCN ground state thermal distributions, $P(j)$. One might have expected them to be the same and if they had been the model would have been fully satisfactory. A possible interpretation is that $\underline{j}'$ is the projection of $\underline{j}$ onto the plane of the bending motion. The remainder of the total angular momentum of the parent then occurs in a plane perpendicular to the orbital angular momentum of the fragments. Another interpretation would be that the rotational constant measures the average position in the bending motion at the instant when dissociation occurs.

Conservation of energy requires that:

$$(3)\quad h^2L^2/2\mu b^2 + B_{CN}J(J+1) + h\nu_o(v''+1/2) + E_{tr} = h\nu_{193} - Do + B_{XCN}j(j+1)$$

where E_{tr} represents the translational energy, b is the impact parameter, the reduced mass, and D_o, is the dissociation energy.

The difference between the photon energy and the dissociation energy is about 17,000 cm^{-1} for ClCN and either 18,000 cm^{-1} or 22,700 cm^{-1} for BrCN depending on whether the $Br_{1/2}$ or $Br_{3/2}$ state is produced.

These experiments were done with the cyanogen halides at room temperature. Considering the magnitude of the available excess energy, the last term in Equation 3 which is the rotational energy of XCN, can be neglected.

Equation 2 would seem to suggest that j' + L could also equal J which would result in higher values of J being observed. Yet, this would require that the rotational energy of the CN fragment increase substantially. An increase of 3 quantum numbers in J at the observed limit would result in an increase of over 1000 cm^{-1} in the rotational energy of the CN. This additional amount could only come from translational energy. The experimental evidence shows that this does not happen. This means that either there is no translational energy (above that available from orbital angular momentum) or there is no flow of energy between E_{tr} and the rotational motion of the CN fragment.

Simons and Trasker derived a formula for calculating the impact parameter in the photodissociation of a non-rotating parent molecule (18). In the model presented here the maximum observed value of J is associated with the non-rotating parent. Using their result the impact parameters have been calculated and are listed in Table I.

The model implies that a particular vibrational level and rotational level in the excited state is populated in the absorption process. If one knew the particular rotational quantum state of the parent molecule, one could use this model to assign the rotational state of the CN fragment that will be produced. This implies that the dissociation process is direct and that there is little or no randomization of energy on the excited state potential energy surface.

In summation, we have presented a parameterization which needs only two parameters to describe the observed rotational distributions of the CN fragments from the photolysis of ClCN and BrCN at 193nm. This parameterization has a dynamical interpretation which leads to a simple picture of the dissociation process in which both energy and angular momentum are conserved. There are several interesting experiments that can be done to extend and test this model. Using a supersonic expansion to cool the parent molecule's rotational and vibrational distributions would be a key experiment. The cooling should simplify the interpretation of the rotational distribution of the CN fragments since all of the XCN molecules will be in the (0,0,0) vibrational level and the lowest j levels. By changing the laser frequency one will be able to access different places on the excited state potential surface, and thus be able to map out the product distribution as a function of this position. Further refinements such as polarization of the ArF laser will pick the orientation of the XCN and thus help to determine how the original angular momentum maps onto the plane determined by the bending motion.

In the case of BrCN, laser time of flight experiments should enable us to determine the branching ratio between the $Br_{1/2}$ and $Br_{3/2}$ states. The latter lies, 3668 cm^{-1} above the former.

The results of Heaven, Miller and Bondybey are clearly in disagreement with the results presented here. They indicate that their measurements may be nascent distributions. They were obtained in a supersonic molecular beam under conditions where the formation of dimers may be significant and where the number of molecules in a given cross-sectional area can be much greater than in the experiments described here. In the former case the observed distributions may result from photodissociation of the dimer. In the experiments reported here there will be no dimers formed. In the latter case CN radicals recoiling isotropically will have a higher probability for collisions than they would under effusive beam conditions. The vibrational excitation they observe would then be a result of collisional process, where rotationally hot CN in the v" = 0 level loses rotational energy and is promoted into a lower rotational level in the v" = 1 level. The change in the rotational distribution would also be a result of these collisions.

In addition to the basic information obtained from these experiments there are two practical benefits. The photolysis of BrCN at 193 nm has been shown to be a copious source of rotationally excited CN molecules. Cooling of the beam might produce CN rotational distributions which are narrower than those measured from thermal distributions. This source can be used to compare the efficiency of rotational energy in various CN reactions, as opposed to translational or vibrational energy. The relatively large yield of CN in rotational states which can be pumped into perturbed levels of the B state can be useful to those interested in level crossing experiments on the perturbed states.

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TABLE I

FITTING PARAMETERS

parent	CN	L	B cm^{-1}		b Å		B_{parent} cm^{-1}
ClCN	v"=0	73	1.02	0.990	0.94		0.199
	v"=1	66	2.91	0.995	0.85		
	v"=2	60	2.53	0.980	0.80		
BrCN	v"=0	77	0.79	0.994	0.86	Br($P_{3/2}$)	0.137
					0.75	Br($P_{1/2}$)	

FIGURE CAPTIONS

Figure 1. LIF excitation spectrum of CN($X^2\Sigma^+$) produced in the photodissociation of ClCN in an effusive beam at 193 nm. The figure shows the $\Delta v=0$ sequence.

Figure 2. Enlargement of the P branch region of Figure 1.

Figure 3. LIF excitation spectrum of CN($X^2\Sigma^+$) produced in the photodissociation of ClCN in an effusive beam at 193 nm. The figure shows the P branches of the $\Delta v=-1$ sequence.

Figure 4. Nascent quantum state distributions of CN($X^2\Sigma^+$) produced in the photodissociation of ClCN in an effusive beam at 193 nm.

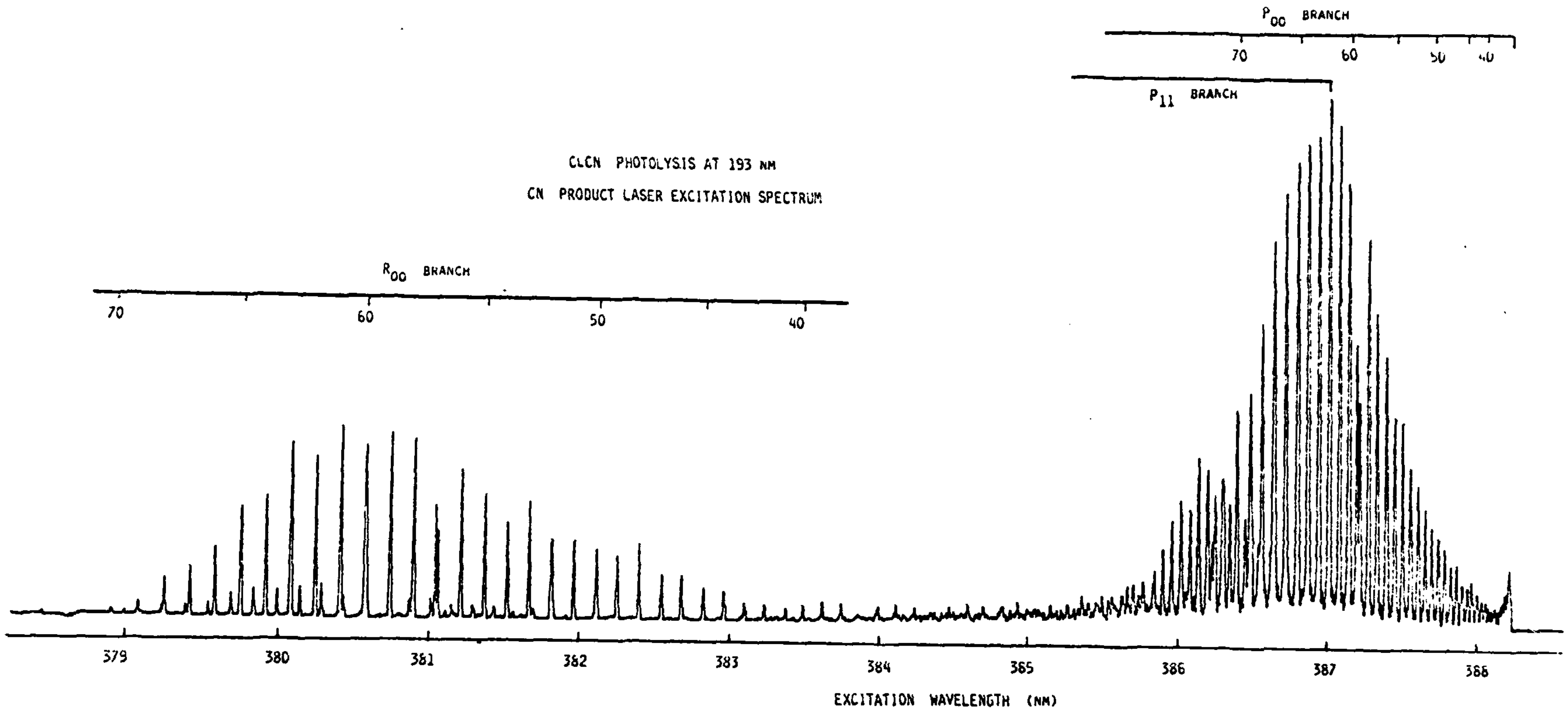
Figure 5. LIF excitation spectrum of CN($X^2\Sigma^+$) produced in the photodissciation of BrCN in an effusive beam at 193 nm. The figure shows the P branches of the $\Delta v=0$ sequence.

Figure 6. Nascent quantum state distribution of CN($X^2\Sigma^+$) produced in the photodissociation of BrCN at 193 nm.

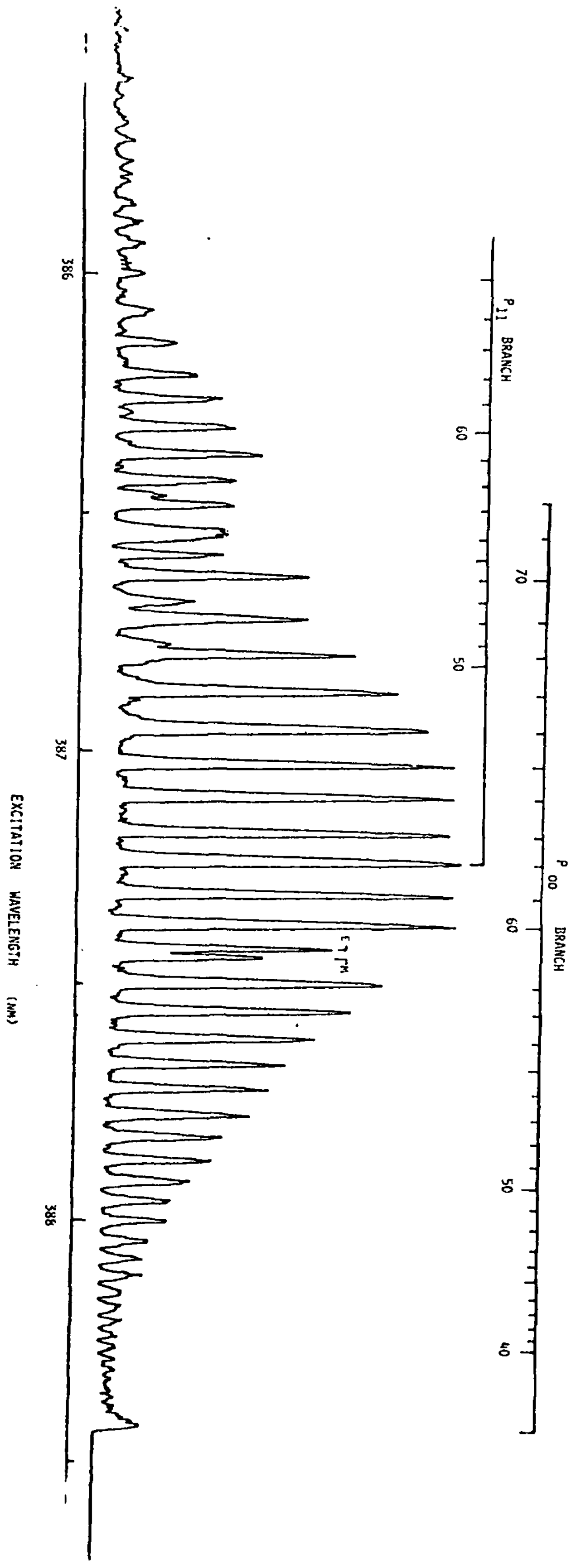
Figure 7. Schematic representation of a linear to bent transition. Here, θ is the bending angle, while the ordinate is an arbitrary energy axis. The bent state must be symmetic about 180°. The potential maximum in the excited state at this angle results in a quasi-stationary point in the nuclear motion. This, in turn, implies that the Franck-Condon overlap for absorption must be high at 180°.

Figure 8. Parameterized fit of the CN radical quantum state distribution from the photolysis of ClCN at 193 nm. See Table I for the fitting parameters, and the text for details of the calculation.

Figure 9. Parameterized fit of the CN radical quantum state distribution from the photodissociation of BrCN at 193 nm. See Table I for the fitting parameters, and the text for details of the calculation.


CLCN PHOTOLYSIS AT 193 NM

CN PRODUCT LASER EXCITATION SPECTRUM


P11 BRANCH
60
70
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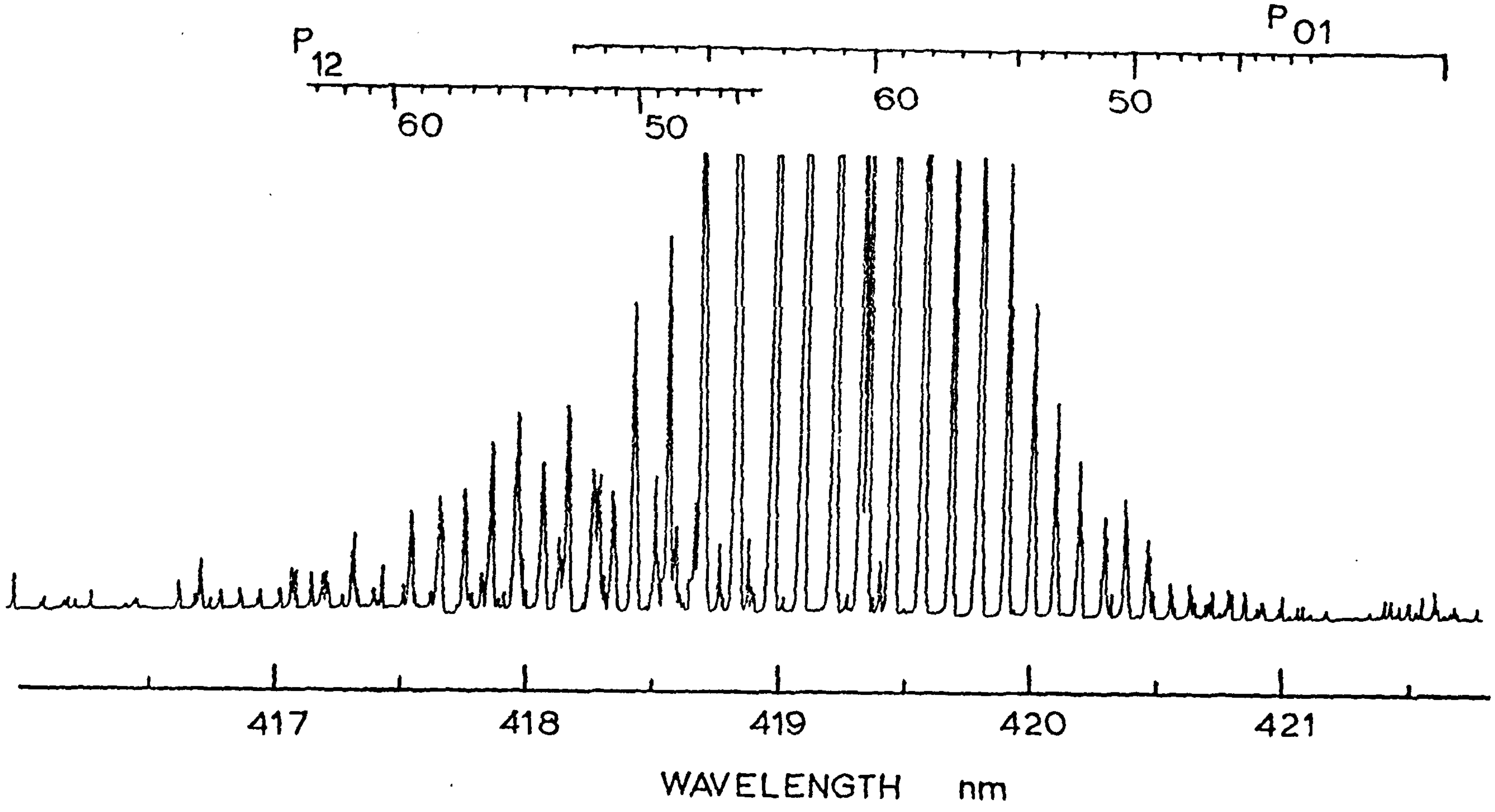
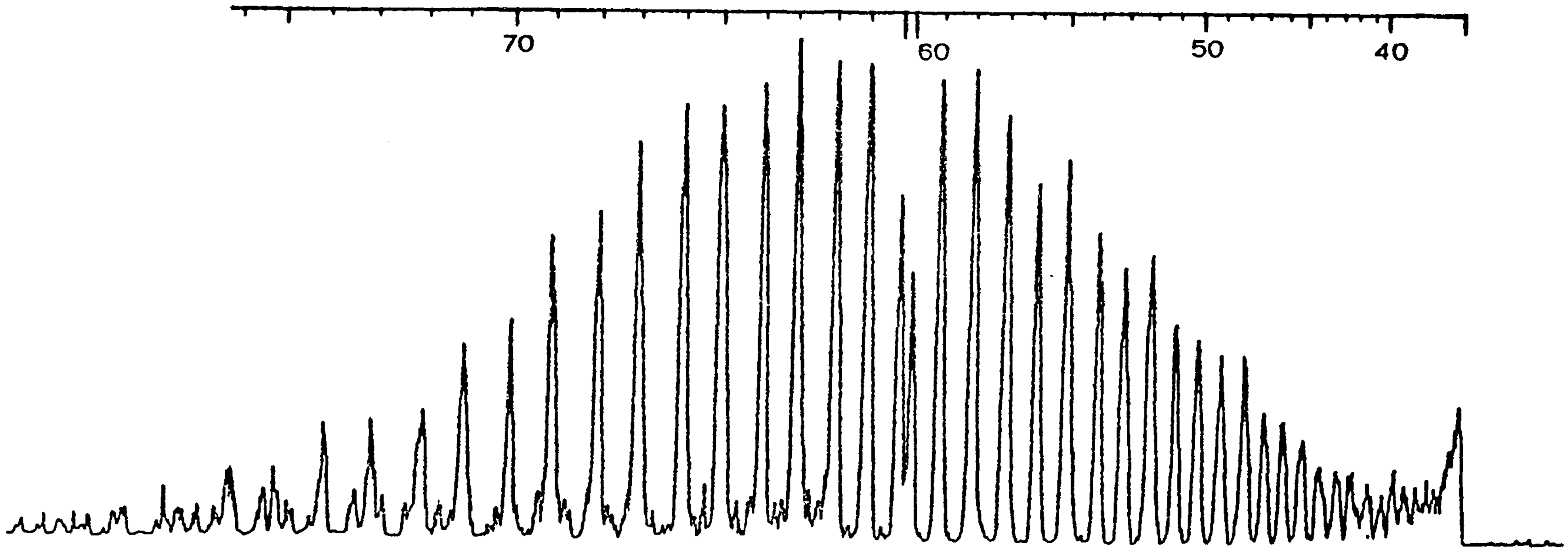
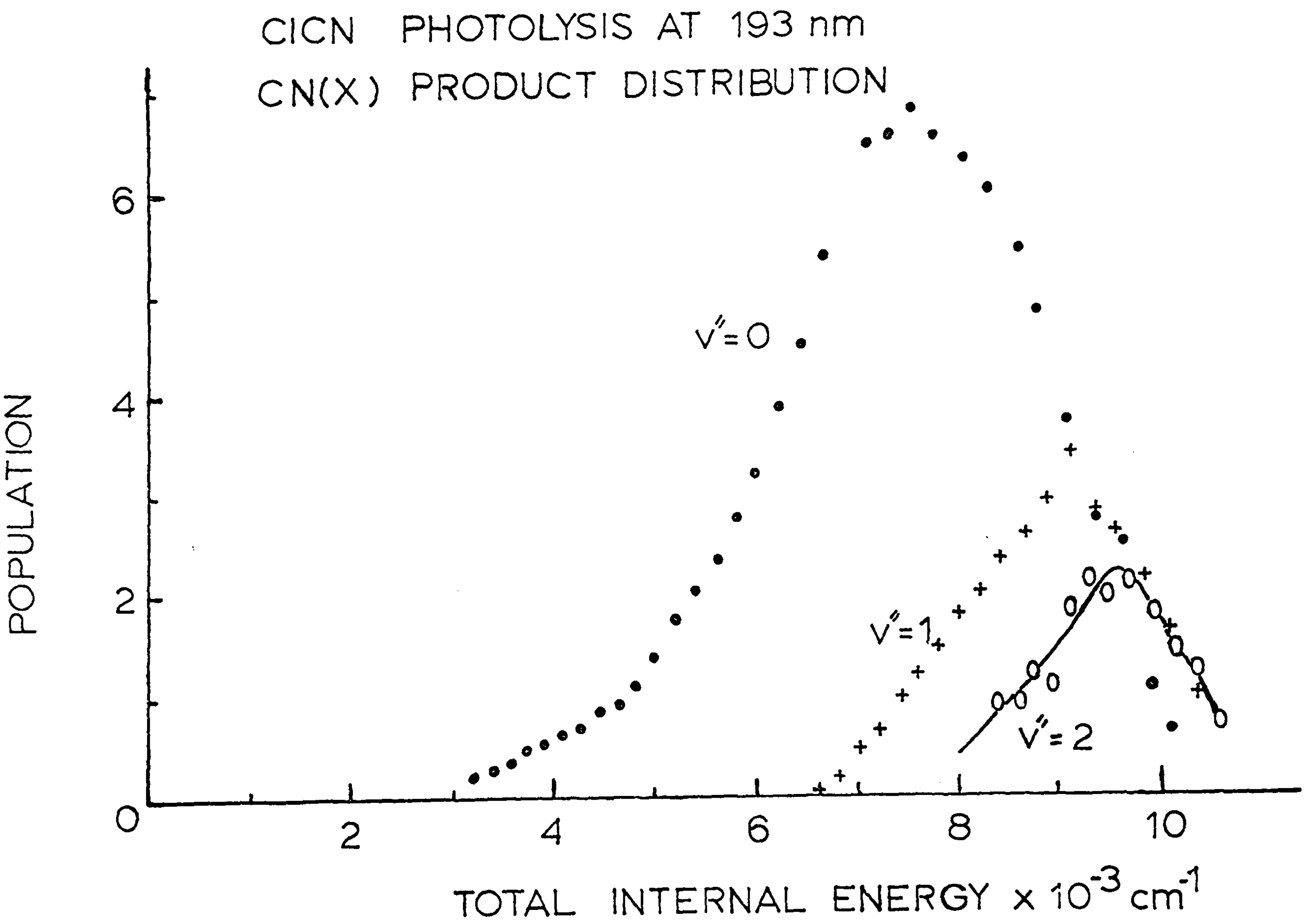
EXCITATION WAVELENGTH (NM)



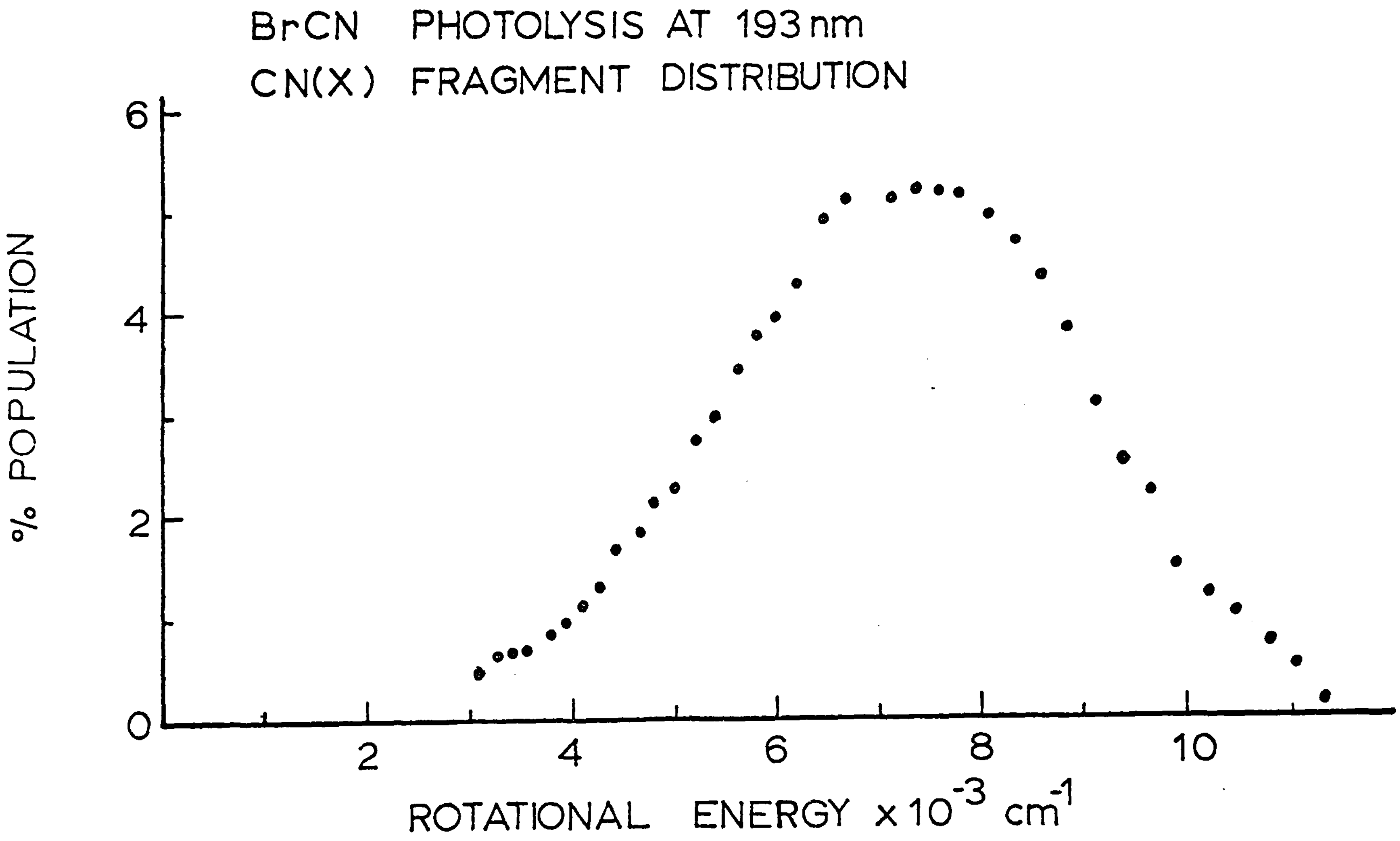
PHOTOLYSIS OF ClCN AT 193 nm
CN(X) FRAGMENT EXCITATION SPECTRUM $\Delta v = -1$

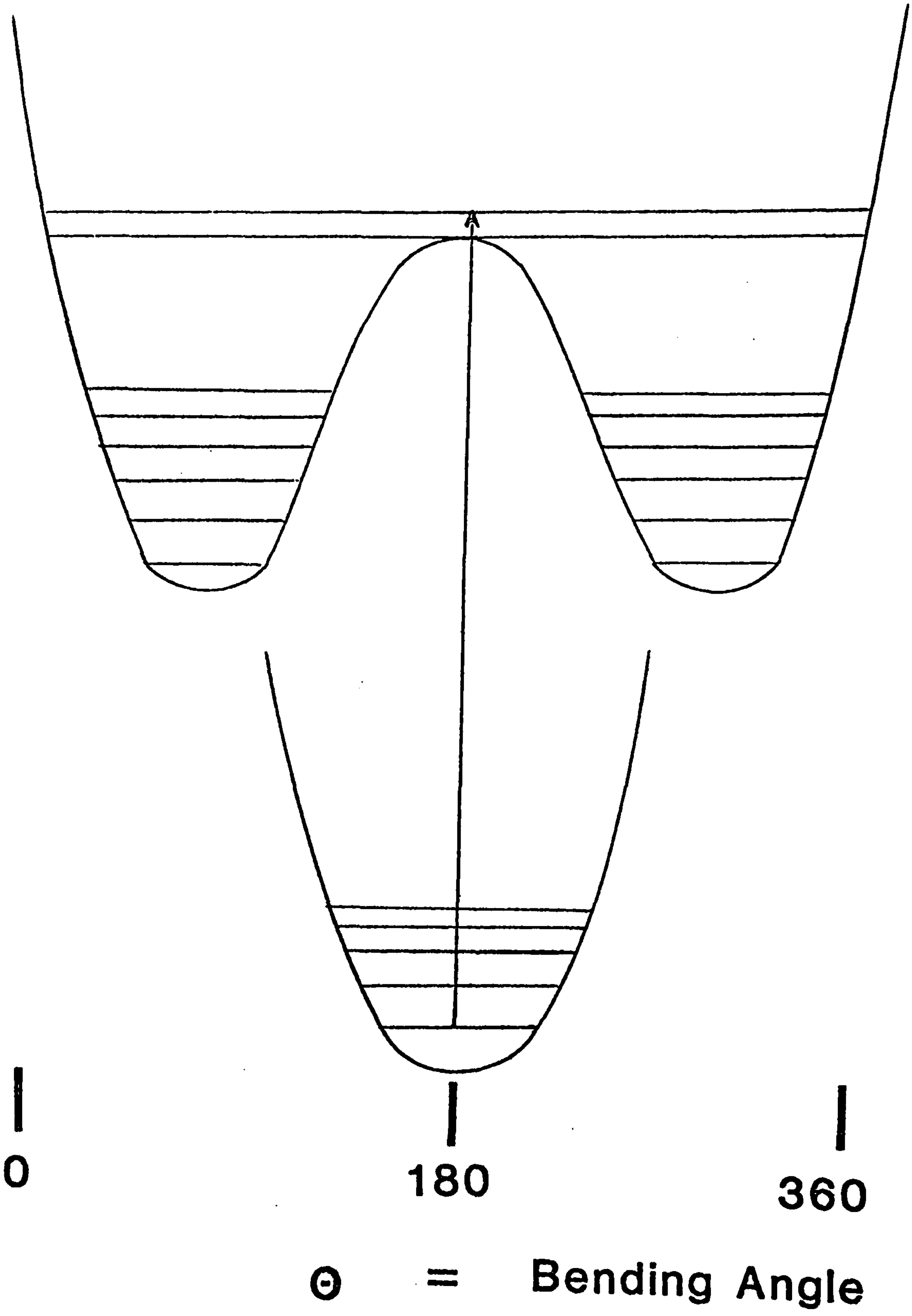
PHOTOLYSIS OF BrCN AT 193 nm
CN FRAGMENT EXCITATION SPECTRUM

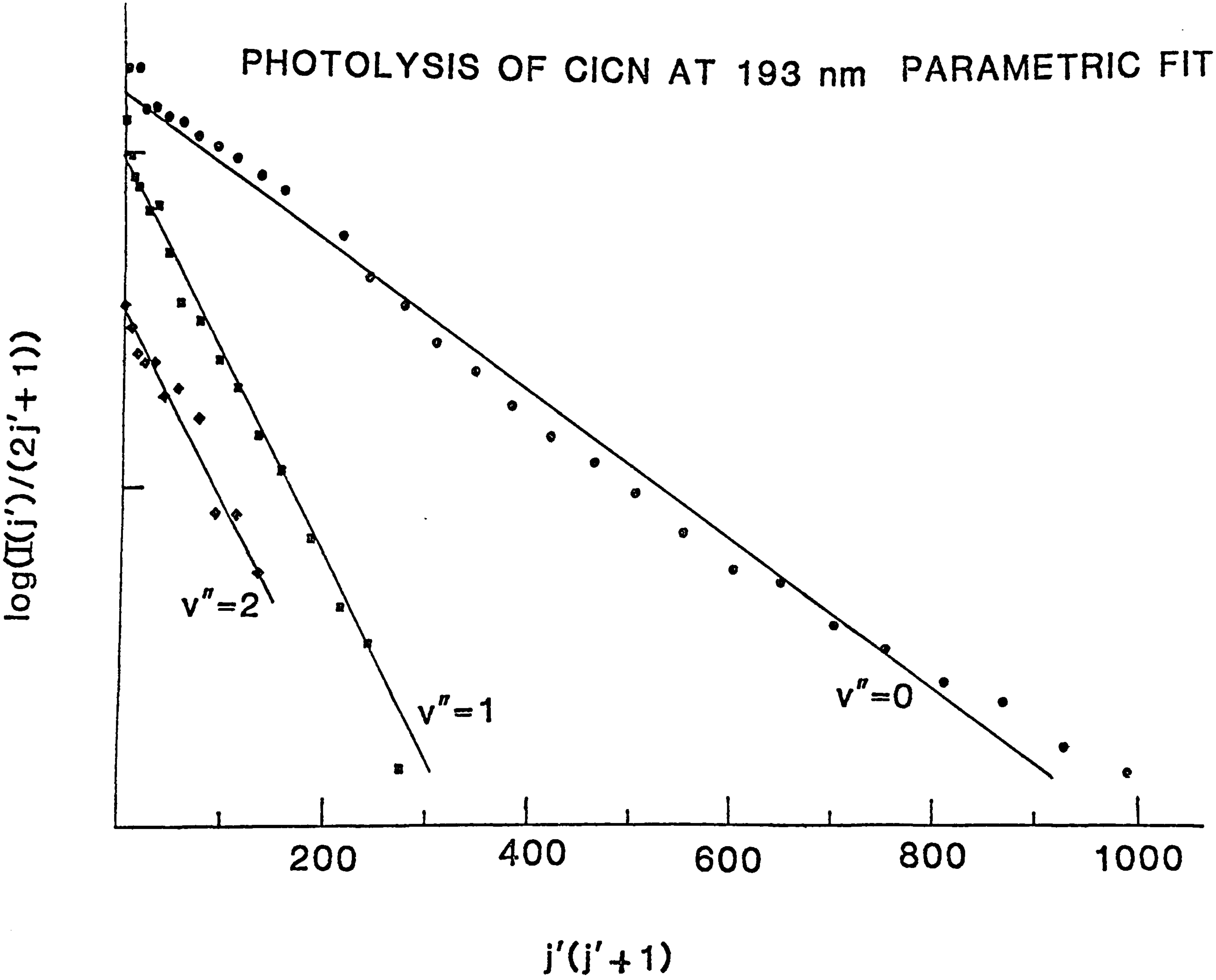


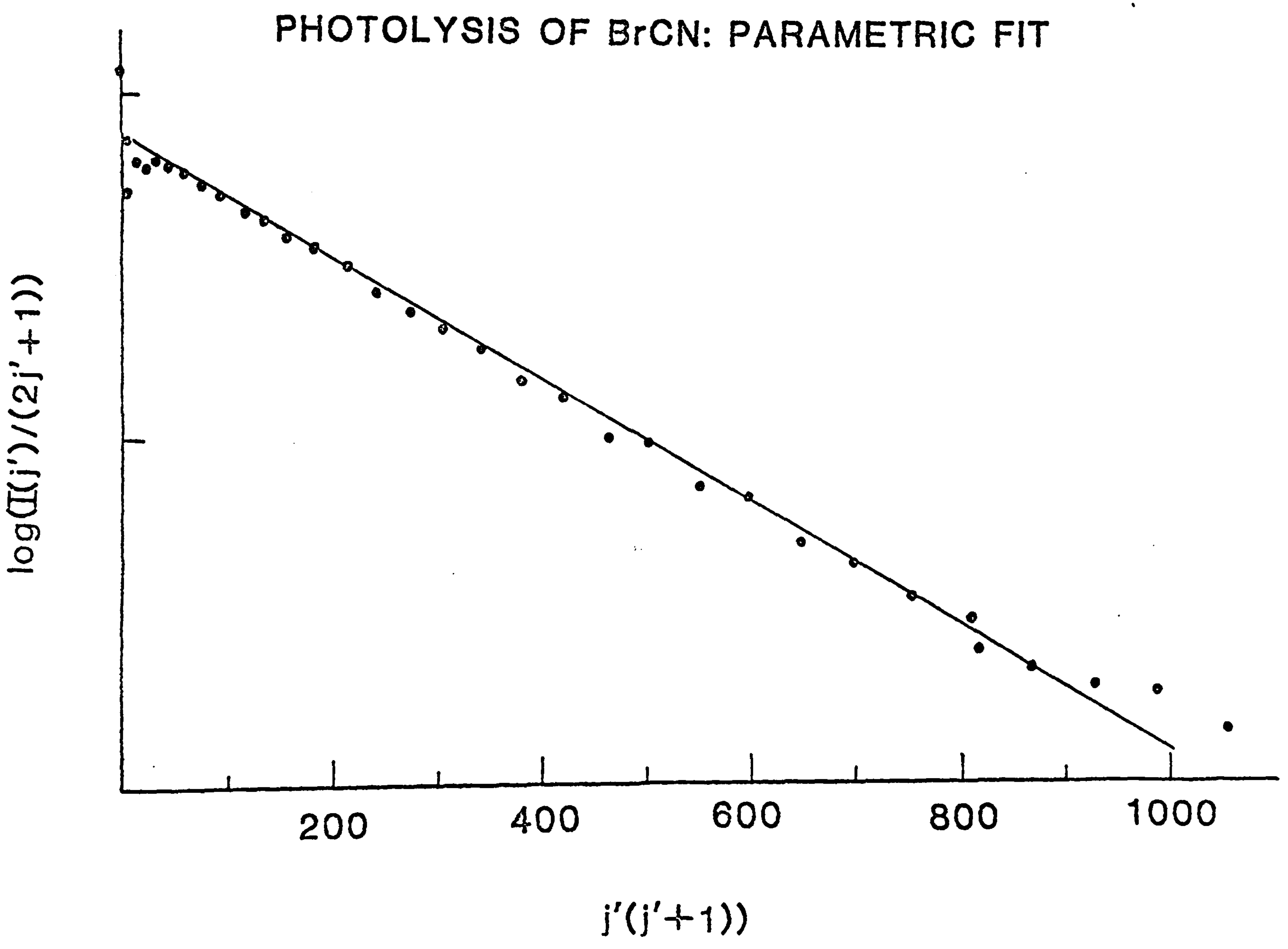


CICN PHOTOLYSIS AT 193 nm
CN(X) PRODUCT DISTRIBUTION


BrCN PHOTOLYSIS AT 193 nm
CN(X) FRAGMENT DISTRIBUTION
% POPULATION
0
2
4
6
2
4
6
8
10
ROTATIONAL ENERGY x 10^{-3} cm^{-1}


A
0
180
360
Θ = Bending Angle


PHOTOLYSIS OF ClCN AT 193 nm PARAMETRIC FIT



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