

CN($B^2\Sigma^+$) PHOTOFRAGMENT FLUORESCENCE FOLLOWING TWO-PHOTON EXCITATION OF ICN WITH A KrF LASER

A. HOPKIRK and R. J. DONOVAN

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH 9 3JJ (Gt. Britain)

(Received September 19, 1981; in revised form October 8, 1981)

Summary

Two-photon excitation of ICN with a KrF laser (248 nm) is shown to give rise to CN($B^2\Sigma^+$) photofragment fluorescence. The vibrational distribution in the CN($B^2\Sigma^+$) state is characterized by a temperature T_v of 3200 ± 400 K. This is cooler than expected from previous work employing single-photon vacuum UV excitation. Possible reasons for this are discussed and it is suggested that two-photon excitation could populate different electronic states of ICN than those populated by a single-photon excitation. The role of the repulsive \tilde{A} state of ICN in the two-photon excitation process is also considered.

1. Introduction

The photochemistry of the cyanogen halides has attracted considerable experimental [1 - 13] and theoretical [12 - 18] interest. Experimental studies have been facilitated by the fact that strong fluorescence is observed from CN photofragments following excitation of the parent molecule in the far UV region. This fluorescence has been analysed in detail, particularly by Simons and coworkers [6 - 8, 12], to probe the dynamics of the photodissociation process. Laser-induced fluorescence studies of ground electronic state CN have also contributed significantly to our understanding of the photodissociation dynamics [10, 11].

It is clear from the work of Ashfold *et al.* [8] that the vibrational and rotational state distributions in the electronically excited CN photofragments are very sensitive to the identity of the photoexcited state, with parallel levels of excitation being observed in both the CN(A) and CN(B) states.

In the present communication we describe experiments in which ICN is simultaneously excited by two photons at 248 nm and show that this leads to photodissociation with the formation of CN($B^2\Sigma^+$). The vibrational state distribution and the approximate rotational distributions are determined and

the results are compared with those for single-photon excitation in the vacuum UV region.

2. Experimental details

The experimental arrangement for laser photolysis and the observation of photofragment fluorescence has been described previously [19, 20]. Briefly, the output from a high power excimer laser (Lambda Physik EMG 500) was passed through a cross-shaped fluorescence cell fitted with Spectrosil B windows.

For the present work the KrF line at 248.4 nm (0.6 nm bandwidth at 10% of maximum) was employed; the pulse duration was about 15 ns at this wavelength. The laser beam was focused to an area of about 0.03 cm² in the observation region giving a maximum photon flux of the order of 70 MW cm⁻².

ICN (Fluka, purum grade) was thoroughly degassed prior to use. The sample was then bled continuously through the photolysis cell using a conventional flow system. The flow rates used ensured that products were removed from the photolysis region between laser pulses (about 2 Hz). Some experiments were also carried out with a static gas fill.

A McKee-Pederson (MP1018B) 0.5 m monochromator (dispersion, 1.75 nm mm⁻¹) with an EMI 9661B(S5) photomultiplier at the exit slit was used to observe the photofragment fluorescence at right angles to the laser beam. The output of the photomultiplier was fed to a chart recorder via a preamplifier and a Brookdeal 2415 linear gate. We note that the use of this linear gate, in the absence of a delay generator, limits signal collection to the first microsecond after the laser pulse. Thus any long-lived fluorescence would be disregarded. In some experiments a delay generator was used to reduce the gate time below 1 μs but this was not found to have any significant effect on the recorded spectra.

3. Results

The only photofragment fluorescence observed when ICN ($P = 24 \text{ N m}^{-2}$) was excited at 248 nm with the KrF laser line was the $\Delta v = 0$ sequence of $\text{CN}(\text{B } ^2\Sigma^+ \rightarrow \text{X } ^2\Sigma^+)$ at about 380 nm (Fig. 1). A search was made for fluorescence from the $\text{A } ^2\Pi$, $\text{D } ^2\Pi$, $\text{E } ^2\Pi$ and $\text{F } ^2\Delta$ states of CN but we were unable to detect any such emission. Failure to detect $\text{CN}(\text{A } ^2\Pi)$ in fluorescence is not surprising as the spectrum of this species lies in a region where our photomultiplier tube becomes insensitive. We note, however, that a weak orange fluorescence could be observed by eye following the laser pulse, and this suggests that some $\text{CN}(\text{A } ^2\Pi)$ is formed by two-photon excitation of ICN.

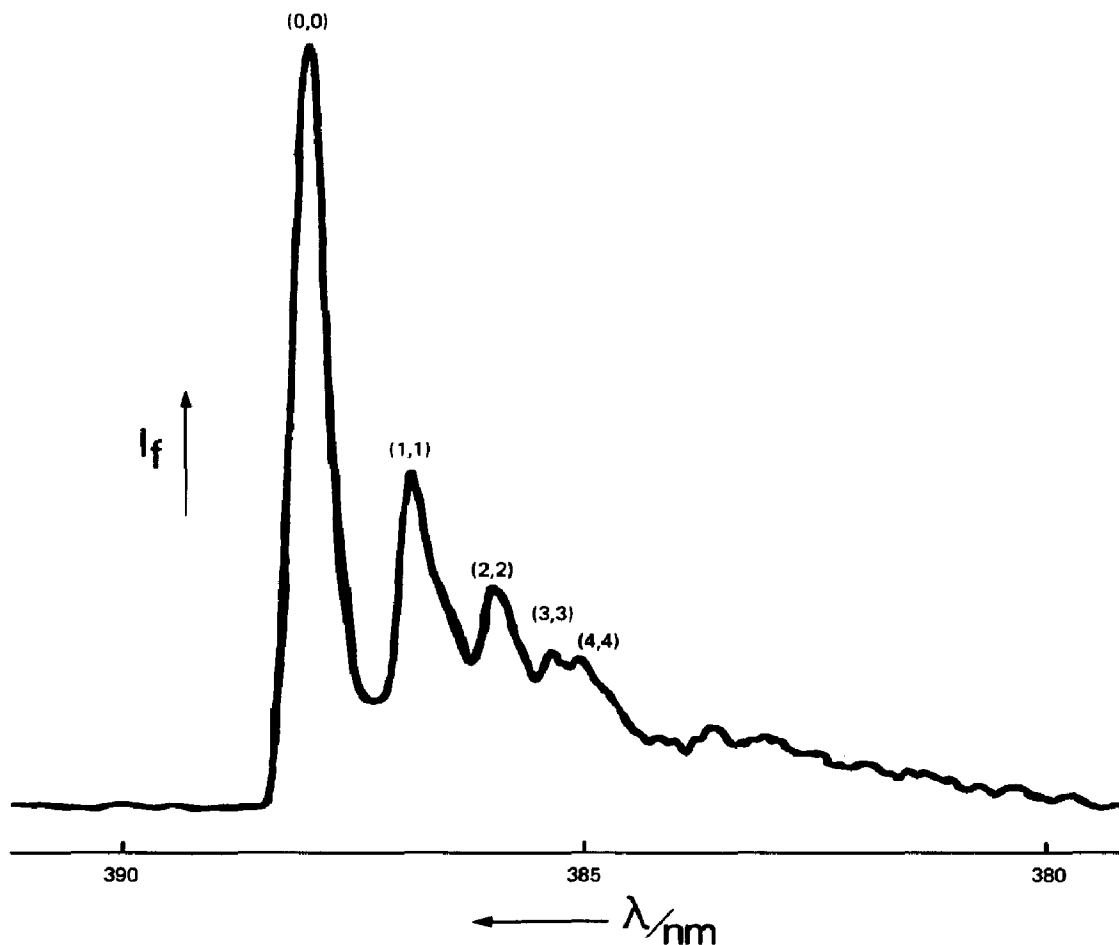


Fig. 1. Photofragment fluorescence from $\text{CN}(\text{B } ^2\Sigma^+ \rightarrow \text{X } ^2\Sigma^+)$ following the two-photon excitation of ICN with a KrF laser (248 nm): $P_{\text{ICN}} = 24 \text{ N m}^{-2}$.

The intensity of the $\text{CN}(\text{B-X})$ emission was found to vary quadratically with laser intensity at low intensities (below 10 mJ) but saturation was evident at higher intensities as the intensity exponent tended towards a value of 1.5.

The relative peak heights of the P branch band heads (allowance was made for overlap between the P and R branches which occurs for all but the P branch of the (0,0) band) of the $\text{CN}(\text{B-X})$ emission were used together with the known Franck-Condon factors [21] to derive a set of vibrational level populations for $0 \leq v' \leq 4$. These are presented in Table 1. The population of levels with $4 < v' < 11$ could not be determined as the bands are headless and are overlapped by the levels $v' = 0 - 4$; however, the rapid decline in population towards $v' = 3$ suggests that the population of higher levels is negligible. Levels higher than $v' = 11$ would have been readily observed had they been populated. We conclude that levels $v' = 0 - 3$ contain at least 95% of the vibrational population of $\text{CN}(\text{B } ^2\Sigma^+)$. A plot of $\ln N_v$ against

TABLE 1

The vibrational distribution N_v/N_0 of $\text{CN}(\text{B } ^2\Sigma^+)$ following two-photon and single-photon excitation of ICN.

v'	N_v/N_0	
	<i>Two-photon excitation</i> ($\frac{1}{2} \times 248 \text{ nm}$)	<i>Single-photon excitation</i> (123.6 nm) [22]
0	1.0	1.0
1	0.4	0.77
2	0.2	0.75
3	≈ 0.1	0.52
4	< 0.1	0.54

E_v gave a reasonable straight line corresponding to a vibrational temperature T_v of $3200 \pm 400 \text{ K}$.

As we are unable to resolve the rotational structure with our present equipment (maximum resolution about 0.18 nm) we can only obtain an approximate value for the overall rotational temperature by comparing the observed spectrum with spectra produced by computer simulation. The rotational contour for the $\Delta v = 0$ sequence is quite sensitive to changes in the range $300 - 2000 \text{ K}$ and contour analysis is a well-established method for determining the rotational temperature of CN. From our results we estimate the overall rotational temperature T_R of the $\text{CN}(\text{B } ^2\Sigma, v' = 0 - 3)$ levels to be $1700 \pm 400 \text{ K}$. The addition of argon ($P_{\text{Ar}} = 13.3 \text{ kN m}^{-2}$) to the ICN in the fluorescence cell led to a marked shift in the position and the shape of the band heads. This is due to rotational relaxation within the $\text{CN}(\text{B } ^2\Sigma^+)$ vibrational manifold and can be readily reproduced with our computer simulation. In the presence of 13.3 kN m^{-2} of argon the rotational distribution is close to that for 300 K .

Although most experiments were carried out with ICN pressures of 24 N m^{-2} some were also done at both higher and lower pressures. The signal-to-noise ratio declines rapidly below 24 N m^{-2} but reasonable traces could be recorded down to 9 N m^{-2} . Pressures as high as 133 N m^{-2} of ICN were also used; however, this led to a rapid build-up of products when a static fluorescence cell was used, and the sample was also optically thick to the incident laser radiation. The vibrational distribution in $\text{CN}(\text{B } ^2\Sigma^+)$ was found to remain essentially constant over the entire range studied; and this strongly suggests that little $\text{CN}(\text{A } ^2\Pi, v' = 10)$ is present under our conditions as this vibrational level is known to be rapidly quenched into the $\text{CN}(\text{B } ^2\Sigma^+, v' = 0)$ level and can therefore enhance the signal observed from this particular level [23].

4. Discussion

Single-photon absorption by ICN at 248 nm in the $\tilde{\text{A}}-\tilde{\text{X}}$ continuum leads to the formation of iodine atoms (predominantly in the ground spin-

orbit state $^2P_{3/2}$) and ground electronic state CN radicals [13]. The formation of CN($A \ ^2\Pi$) is energetically possible below 292.4 nm but the yield has been shown [11] to be negligible (less than 0.1%). There is insufficient energy for the formation of CN($B \ ^2\Sigma^+$) at 248 nm other than by a two-photon process. Secondary excitation of CN by the laser pulse appears to be unlikely and would definitely not lead to fluorescence from the levels observed here. We therefore conclude that the process leading to CN($B \ ^2\Sigma^+$) formation is a two-photon excitation process in which the ICN molecule is pumped to states which lie about $80\,500\text{ cm}^{-1}$ above the ground electronic state. It is well known from earlier work [12] that states of ICN in this region dissociate to yield both CN($B \ ^2\Sigma^+$) and CN($A \ ^2\Pi$), although the yield of the latter is expected to be low at this energy [5].

The presence of the ICN($\tilde{A}-\tilde{X}$) continuum is expected to enhance the coherent (simultaneous) two-photon excitation cross section but sequential two-photon excitation could also be important. The latter process should be less selective than the former and should lead to the population of a broader range of excited ICN states (the up-pumping process will sample a wide range of I-CN internuclear separations in the \tilde{A} state and thus a range of intermediate state energies). The present results do not allow us to distinguish between these two mechanisms but this may be possible by using a narrow-band tunable laser to scan the $\tilde{A}-\tilde{X}$ continuum. Alternatively a two-laser two-colour experiment might allow these mechanisms to be distinguished.

In principle the states of ICN populated by two-photon excitation can differ from those excited by single-photon excitation as the two-photon selection rules allow Λ to change by up to two units (compared with $\Delta\Lambda = 0, \pm 1$ for single-photon transitions) if the molecule remains linear in the upper state. If the molecule is significantly bent in the upper state the electronic selection rules are less restrictive but differences between single-photon and two-photon excitation still persist in the rotational and some of the vibrational states populated owing to the selection rule for angular momentum changes (± 2 or zero for two photons and ± 1 for a single photon).

The only information that currently exists on the states of ICN which lie in the region around $80\,000\text{ cm}^{-1}$ is based on single-photon absorption studies. Some of the discrete features observed in this region have been assigned to Rydberg series converging on the first ionization potential of ICN. There is also clear evidence of an underlying continuum or a very congested set of transitions. The work of Ashfold *et al.* [8] shows that the photodissociation dynamics of the discrete and continuum states of the cyanogen halides differ markedly, with the discrete features generally producing high energy vibrational and rotational distributions in both A and B state CN photofragments. By contrast, excitation into the continuum states of ICN produces relatively cold vibrational and rotational distributions in both the A and the B states of CN.

In Table 1 we compare our results for two-photon excitation with those of Simons and Ashfold [22] for single-photon excitation at 123.6 nm (krypton resonance line). The only other results with which we could make a

comparison were those of Mele and Okabe [1], but unfortunately their resonance lamp emitted at two wavelengths (123.6 and 116.5 nm). The distribution reported by these workers [1] differs very significantly from that of Simons and Ashfold [22], presumably because of the presence of the 116.5 nm line, and therefore we have not included these earlier data in Table 1. It is clear that we observe a much cooler vibrational distribution than that of Simons and Ashfold. This could result from a difference in the electronic states of ICN excited by two-photon absorption but there are other possible causes. The bandwidth of the KrF laser (0.6 nm at 10% of maximum intensity) is considerably broader than that of a typical krypton resonance line and we might therefore expect a broader distribution of excited ICN states to be populated. The only available absorption spectrum of ICN in the region of 124 nm is of low resolution (reproduced in ref. 12) and does not allow a detailed assessment of the relative contributions from discrete and continuum features. However, the dominant feature within the two-photon bandwidth is a discrete transition which has been assigned as terminating in the $8s\sigma(^3\Pi)$ Rydberg level [12]. This feature is essentially coincident with the centre of the laser line but would not overlap with the krypton resonance line. We therefore expect a difference in the photofragment energy distributions in view of the small difference in excitation energy for the two processes. However, the conclusion reached by Simons and Ashfold, that discrete spectral features generally give vibrationally and rotationally hot distributions in $\text{CN}(B^2\Sigma^+)$, leads us to expect a much hotter distribution than that observed. We can offer two explanations for this apparent deviation from the expected hot distribution. First, two-photon excitation of ICN could lead to the population of different upper electronic states of ICN compared with single-photon excitation. If this is the case the vibrational distributions produced by the two processes could be entirely different. The second possible explanation is based on a sequential pumping mechanism involving the repulsive \tilde{A} state of ICN. This would be expected to produce a broader and cooler distribution of $\text{CN}(B)$ vibrational states because of the wide range of I-CN internuclear separations which occur during dissociation on the repulsive intermediate surface. Of these two explanations we favour the former as the probability of a molecule absorbing a second photon during the dissociation process is small owing to the short lifetime of the molecule on a repulsive intermediate surface (less than 10^{-12} s).

Further detailed studies of both the vacuum UV spectrum of ICN in the 124 nm region and the two-photon excitation using a frequency-narrowed tunable laser will be required to resolve the questions raised by this work.

Acknowledgments

We thank the Science Research Council for an equipment grant and for support for A.H. We also thank J. P. Simons and M. N. R. Ashfold for making their unpublished results available to us.

References

- 1 A. Mele and H. Okabe, *J. Chem. Phys.*, 51 (1969) 4798.
- 2 K. E. Holdy, L. C. Klotz and K. R. Wilson, *J. Chem. Phys.*, 52 (1970) 4588.
- 3 J. H. Ling and K. R. Wilson, *J. Chem. Phys.*, 63 (1975) 101.
- 4 G. A. West and M. J. Berry, *J. Chem. Phys.*, 61 (1974) 4700.
- 5 G. A. West and M. J. Berry, *Chem. Phys. Lett.*, 56 (1978) 423.
- 6 M. N. R. Ashfold and J. P. Simons, *J. Chem. Soc., Faraday Trans. II*, 73 (1977) 858; 74 (1978) 280.
- 7 M. T. MacPherson and J. P. Simons, *J. Chem. Soc., Faraday Trans. II*, 75 (1979) 1572.
- 8 M. N. R. Ashfold, A. S. Georgiou, A. M. Quinton and J. P. Simons, *J. Chem. Soc., Faraday Trans. II*, 77 (1981) 259; *Nuovo Cimento*, 63 (1981) 21.
- 9 S. Tatematsu, T. Kondow, T. Nakagawa and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 50 (1977) 1056.
- 10 M. J. Sabety-Dzvonik and R. J. Cody, *J. Chem. Phys.*, 66 (1977) 125.
- 11 A. P. Baronavski and J. R. McDonald, *Chem. Phys. Lett.*, 45 (1977) 172.
W. M. Pitts and A. P. Baronavski, *Chem. Phys. Lett.*, 71 (1980) 395.
- 12 M. N. R. Ashfold, M. T. MacPherson and J. P. Simons, *Top. Curr. Chem.*, 86 (1979) 3.
- 13 S. R. Leone, *Adv. Chem. Phys.*, to be published.
- 14 R. C. Mitchell and J. P. Simons, *Faraday Discuss. Chem. Soc.*, 44 (1967) 208.
- 15 M. Shapiro and R. D. Levine, *Chem. Phys. Lett.*, 5 (1970) 499.
- 16 J. P. Simons and P. W. Tasker, *Mol. Phys.*, 26 (1973) 1267; 27 (1974) 1691.
- 17 M. D. Morse, K. F. Freed and Y. B. Band, *J. Chem. Phys.*, 70 (1979) 3620.
- 18 K. F. Freed, M. D. Morse and Y. B. Band, *Faraday Discuss. Chem. Soc.*, 67 (1979) 297.
- 19 C. Fotakis, M. Martin, K. P. Lawley and R. J. Donovan, *Chem. Phys. Lett.*, 67 (1979) 1.
- 20 C. Fotakis, C. B. McKendrick and R. J. Donovan, *Chem. Phys. Lett.*, 80 (1981) 598.
- 21 R. J. Spindler, *J. Quant. Spectrosc. Radiat. Transfer*, 5 (1965) 165.
- 22 J. P. Simons and M. N. R. Ashfold, personal communication, 1981.
- 23 M. N. R. Ashfold and J. P. Simons, *Chem. Phys. Lett.*, 47 (1977) 65.