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# Violet Emission Bands of the CN Radical Produced by Photodissociation of BrCN

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The violet emission spectra of CN($B^2\Sigma-X^2\Sigma$), $\Delta v=0$, were observed by the photodissociation of BrCN by Lyman-$\alpha$ radiation (121.6 nm). The peak intensities for the vibrational levels $v'\geqq 1$ relative to $v'=0$ decreased with the BrCN pressure (up to 2 Torr), whereas at 0.1 Torr or lower the spectrum was essentially independent of the pressure. The relative vibrational populations ($v'=0$—10) and the effective rotational temperatures were estimated by a band-envelope analysis. The effective rotational temperature, estimated to be 2000±200 K for $v'=0$—4, was practically independent of the pressure. Within the low-pressure limit the distributions of the excess energy to vibration and rotation were estimated to be 0.50±0.08 and 0.17±0.02 eV, respectively.

The kinetic and internal energies contained in the fragments produced by dissociation of polyatomic molecules have been investigated by various methods. Wilson *et al.*[1,2] measured the translational energies of fragments by the time-of-flight technique applied to laser photodissociation of molecular beams. The internal excitation of fragments can be studied by emission spectroscopy. For instance, the rotational distribution of the OH($A^2\Sigma$) formed in the photodissociation of $H_2O$ was measured by Carrington.[3]

The emission spectra of the CN($B^2\Sigma$) produced in the vacuum-ultraviolet photodissociation of cyanides were measured by Mele and Okabe,[4] by whom the vibrational and rotational distributions were reported. Their estimations could be only qualitative,[5] since their spectral resolution was only about 0.5 nm and since their light sources, mostly rare-gas resonance lines, were not monochromatic. Despite these limitations, they showed that the distributions of internal energies contained in CN($B^2\Sigma$) had a characteristic dependence on the cyanides from which they were formed. Their estimates of the energy distributions were often referred to as a basis for theoretical considerations on the dynamics of dissociative excitation.[6—8] Furthermore, the distributions appeared to be remarkably different from those of the CN($B^2\Sigma$) radicals formed from the same cyanides by impact of electrons[9] or metastable argon atoms[10,11] instead of photons. In order to supply more quantitative information in this regard, we have undertaken systematic measurements of the CN violet bands produced from various cyanides by Lyman-$\alpha$ radiation using higher resolution. The present report is concerned with the BrCN case measured at different sample pressures.

## Experimental

The apparatus consists of a vacuum-ultraviolet source, a sample cell and a detection system (Fig. 1). The Lyman-$\alpha$ radiation was obtained by 2450 MHz microwave discharge in a 1:3 mixture of hydrogen and helium gases. This mixture, purified by a liquid-nitrogen trap filled with molecular sieve 13X, was introduced into a quartz discharge tubing (15 mm o.d.), and the light was admitted into the sample cell through a $MgF_2$ window of 1.0 mm thickness. The pyrex cell, o.d. about 40 mm and length 60 mm, was coated inside with graphite to reduce stray light. The sample gas was introduced through needle valves, the pressure being monitored during the observation with a Pirani gauge calibrated against a McLeod gauge.

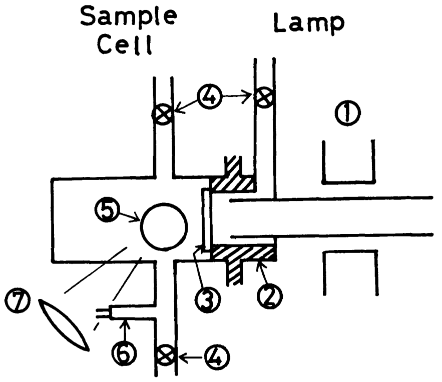

Fig. 1. A schematic design of the apparatus.
1) Microwave discharge, 2) water-jacket, 3) $MgF_2$ window, 4) needle valves, 5) quartz window, 6) Pirani gauge, 7) quartz lens.

Fluorescence from the emission region was detected in a direction perpendicular to the incoming photons. The emission was focussed through a Suprasil window (20 mm diameter) and a collimating lens into the entrance slit of Nikon P-250 grating monochromator (1200 Gr/mm). The slit width was adjusted in the range between 10—60 μm. The slit width of 50 μm corresponds to an energy resolution of 0.2 nm. The signal from a photomultiplier (HTV R585) was measured by a photon counting system. The relative intensity response of the spectrometer and the detection system was calibrated by a halogen standard lamp (JC 12V-50W of Ushio Electric Co.), the color temperature of which was determined at the Electrotechnical Laboratory.

A commercial sample of BrCN (Nakarai Chemical, Co.) was purified by vacuum distillation. The IR spectrum showed no evidence of impurities. The emission spectra were observed at BrCN pressures ranging from about 0.01 to 2 Torr.

The reproducibility of the observed spectra depends mainly on the stability of the light source and the sample pressure, which was kept constant by needle valves during the observation. Though the intensity of the lamp was not monitored during the spectral measurement, its stability was tested by recording the emission intensity at a fixed wavelength over the time interval needed for scanning the whole spectral region. Moreover, a check of reproducibility of the intensity signal was made immediately before and after each measurement. From these tests, the total error in the observed spectrum, including the random errors caused by the instability of the light source, the sample pressure and the detection system, was estimated to be less than 10% of the highest peak.

## Results and Analysis

*Observed Spectra.* The $\Delta v=0$ series of the CN violet band ($B^2\Sigma-X^2\Sigma$) observed around 388 nm (Fig. 2) was assigned according to the table prepared by Pearce and Gaydon.[12] Though the sequences of $\Delta v=0$ and $\Delta v=-1$ of the violet system were observed, the former was used in the analysis, because the intensity of the latter was not strong enough. The $v'=0$ peak is the strongest and the intensities of the $1\leqq v'\leqq 4$ peaks decrease with $v'$. Bands of the $5\leqq v'\leqq 10$ levels are overlapped by those of the lower levels, and the $v'\geqq 11$ bands, which should appear above 391 nm, are not detectable.

The observed dependence of the spectrum on the BrCN pressure is shown in Fig. 3. Below about 0.1 Torr the spectrum is nearly independent of the sample pressure, but at a higher pressure the peak intensities for $v'\geqq 1$ relative to $v'=0$ decrease with the pressure, until at about 2 Torr they are almost completely obscured by the R-branch tail of the (0,0) band. On the other hand, there is no observable effect of pressure on the band shapes, particularly as regards the peak (the P-branch head) of the (0,0) band.

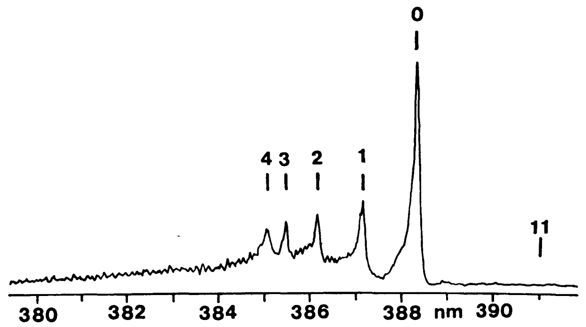

Fig. 2. Emission spectra of the CN($B^2\Sigma-X^2\Sigma$), $\Delta v=0$ band from BrCN taken with a slit width of 10 μm. The numbers indicate positions of the P-branch heads for the $v'=0$—4 and 11 bands.

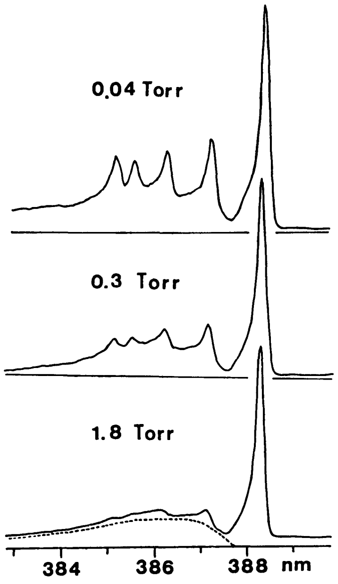

Fig. 3. Emission spectra of the CN($B^2\Sigma-X^2\Sigma$), $\Delta v=0$ band produced by the photodissociation of BrCN taken at different sample pressures with a slit width of 40 μm.
The broken line represents the background contribution from the R-branch contour of the (0, 0) band calculated at $T_r=2000$ K.

*Band-Envelope Analysis.* The relative vibrational populations were estimated by a band-envelope simulation using a MELCOM 7000 computer in the Educational Computer Center of the University of Tokyo.

The relative intensity (the number of photons) of a transition from the ($v',N'$) level to the ($v'',N''$) level can be expressed[13] by

$$I(v', N'-v'', N'') \propto \frac{P_{v'}}{Q_{r,v'}}\cdot\nu^3\cdot q_{v',v''}\cdot S_{N',N''}\cdot R_{v'}(N') \quad (1)$$

where $v$ and $N$ are the vibrational and rotational quantum numbers, respectively, $\nu$ is the transition frequency, $P_{v'}$ is the population, $q_{v',v''}$ is the Franck-Condon factor, $S_{N',N''}$ is the rotational line strength, and $R_{v'}(N')$ is the rotational distribution function. The rotational state sum, $Q_{r,v'}$, is given by

$$Q_{r,v'} = \sum_{N'} g_{N'}R_{v'}(N') \quad (2)$$

where $g_{N'}$ represents degeneracy. If the rotational distribution is described by a Boltzmann function, then $R_{v'}(N')$ is given by

$$R_{v'}(N') = \exp\{-hcB_{v'}N'(N'+1)/kT_r(v')\} \quad (3)$$

where $T_r(v')$ is an effective rotational temperature for the vibrational state $v'$.

The band envelope was obtained from $I(v',N'-v'',N'')$ by use of the experimental parameters of the band origin $\nu_0$,[14,15] $B_{v'}$,[14,15] and $q_{v',v''}$.[16] A Gaussian slit function, which was estimated from the observed shape of the Hg 404.7 nm line measured under similar experimental conditions, was taken into account. The

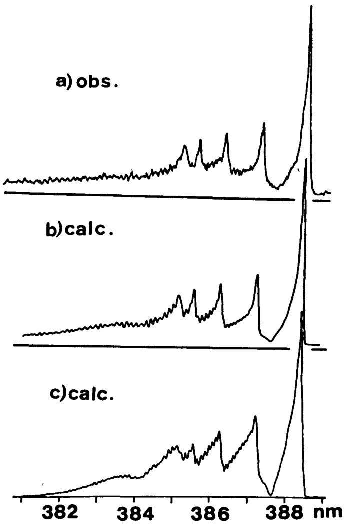

Fig. 4. Comparison of the calculated band envelopes of the CN violet $\Delta v=0$ bands with the observed spectrum produced by the photodissocation of BrCN. a) Observed at 0.03 Torr, b) calculated with $T_r(v'=0$—$10)=2000$ K; best-fit, c) calculated with $T_r(v'=0$—$10)=1000$ K.

parameters, $N_{v'}$ and $T_r(v')$, were adjusted in such a way that the calculated band envelope fits the observed spectrum. A typical comparison of the observed and calculated band envelopes is shown in Fig. 4.

It was possible to estimate the effective rotational temperatures for $v'=0$—4 independently from their individual band shapes. The values turned out to be essentially equal, 2000±200 K. On the other hand, the band shapes were insensitive to the assumed values of $T_r(v')$ for $v'=5$—10. The effective temperatures were therefore assumed to be all equal, 2000 K.

The relative vibrational populations of CN($B^2\Sigma$) thus estimated are plotted in Fig. 5 for the different sample pressures. The population for $v'=11$ level, which has a negligible intensity, is assumed to be zero, and those for the levels $v'=5-10$ are estimated by a smooth interpolation. Since the vibrational populations estimated for pressures lower than 0.1 Torr are essentially unchanged, they are assumed to be the initial populations unaffected by collisional relaxation (see Discussion), as listed in Table 1.

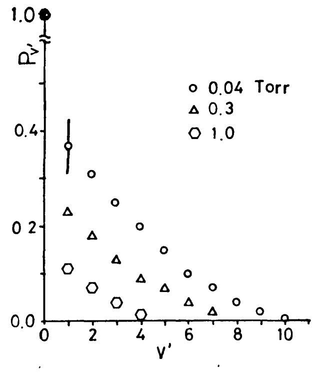

Fig. 5. Pressure dependence of the relative vibrational populations, $P_{v'}/P_0$, of CN($B^2\Sigma$) produced by the photodissociation of BrCN. Estimated from the analysis of the spectra at different sample pressures. A bar indicates estimated limit of uncertainties.

TABLE 1. RELATIVE VIBRATIONAL POPULATIONS ($P_{v'}/P_0$) AND THE EFFECTIVE ROTATIONAL TEMPERATURES OF CN($B^2\Sigma$) PRODUCED BY THE PHOTODISSOCIATION OF BrCN

| $v'$ | $P_{v'}/P_0$ | $E_{v'}$/eV[a)] | $T_r(v')$/K |
|---|---|---|---|
| 0 | 1.00 | 0.0000 | 2000±200 |
| 1 | 0.37(6)[b)] | 0.2633 | 2000±200 |
| 2 | 0.31(6) | 0.5216 | 2000±200 |
| 3 | 0.25(6) | 0.7746 | 2000±200 |
| 4 | 0.20(6) | 1.0221 | 2000±200 |
| 5 | 0.15[c)] | 1.2636 | 2000[c,d)] |
| 6 | 0.10 | 1.4989 | |
| 7 | 0.07 | 1.7276 | |
| 8 | 0.04 | 1.9492 | |
| 9 | 0.02 | 2.1634 | |
| 10 | ≦0.01 | 2.3699 | |

a) Vibrational energies taken from Ref. 17 (above zero-point energy). b) Uncertainties represent estimated limits of error in the last significant digits. c) The $P_{v'}/P_0$ and $T_r(v')$ values for $v'=5$—10 are only rough estimates. d) The effective rotational temperatures for $v'=5$—10 are assumed to be equal.

The uncertainties in $P_{v'}$ and $T_r(v')$ estimated in Table 1 originate mainly from the limitation in recording the spectrum, the overlapping of bands, and the approximations made in the analysis. Since the $5\leqq v'\leqq 10$ bands are buried within those of the lower vibrational levels, the estimated values of $P_{v'}$ and $T_r(v')$ for $v'=5$—10 are less reliable than those for $v'=0$—4. In addition, a strong correlation is found between the vibrational population and the rotational temperature for each of the $v'\geqq 5$ bands. For these reasons, the above estimates of $P_{v'}$ and $T_r(v')$ for the $v'\geqq 5$ simply represent one of the most probable sets of the parameters for which calculated envelope agrees well with the observed spectrum. However, the values of $P_{v'}$ and $T_r(v')$ for the $v'=0$—4 bands can be estimated independently, since each of the $v'=0$—4 bands forms a distinct head peak.

## Discussion

*Internal Energy Distribution.* The average energy distributed to the vibration of CN($B^2\Sigma$) is estimated as a sum of the vibrational energies[17)] multiplied by the estimated populations to be 0.50±0.08 eV above the zero-point energy. Since the effective rotational temperature is estimated to be 2000±200 K, the average rotational energy is 0.17±0.02 eV. Therefore, the rotational excitation, about one third of the vibrational excitation, is much lower than that of OH($A^2\Sigma$) formed by the photodissociation of $H_2O$.[3)]

Energetically possible processes producing CN($B^2\Sigma$) from BrCN by Lyman-α radiation (10.20 eV) are the following:

$$\mathrm{BrCN} + h\nu \rightarrow \mathrm{Br}(^2\mathrm{P}_{3/2}) + \mathrm{CN}(\mathrm{B}^2\Sigma) \qquad (v'\leqq 14) \qquad (1)$$

$$\rightarrow \mathrm{Br}(^2\mathrm{P}_{1/2}) + \mathrm{CN}(\mathrm{B}^2\Sigma) \qquad (v'\leqq 12) \qquad (2)$$

The threshold of process (1) was estimated by Davis and Okabe[18)] to be 6.97 eV. They reported that process (2) was insignificant, because they observed no apparent inflection in the excitation curve of CN($B^2\Sigma$) near the threshold of process (2), 7.43 eV. If the Br($^2P_{3/2}$) atom is produced, then the available excess energy distributed to the fragments is 3.23 eV. Thus the average kinetic energy is estimeted to be *ca.* 2.56 eV. From the conservation of momenta, the CN radical has an average kinetic energy of *ca.* 1.9 eV.

*Comparison with Other Experiments.* The CN($B^2\Sigma$) states formed from cyanides exited by photons (10.2 eV), electrons (≈300 eV) and metastable argon atoms (11.5 and 11.7 eV) have distinctly different vibrational populations, as illustrated in Fig. 6. The intensity enhancements in higher vibrational levels ($v'\geqq 11$) observed in the case of metastable-atom impact[9)] are interpreted as a result of the rotational perturbation between the A and B states. In the electron-impact case,[10,11)] lower vibrational levels have larger relative populations than in the metastable-atom impact case. In contrast with either case, photodissociation gives a monotonically decreasing curve. Photodissociation by Lyman-α radiation can excite the CN($B^2\Sigma$) radical up to $v'=14$. However, only a small fraction of the available energy goes into vibrational excitation so that

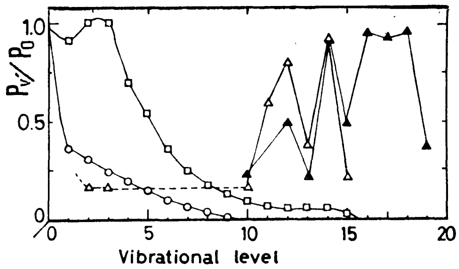

Fig. 6. Relative vibrational populations, $P_{v'}/P_0$, of the CN($B^2\Sigma$) radicals produced from BrCN by photodissociation (○), electron impact (□ for Ref. 9) and impact of metastable argon ($^3P_{0,2}$) atoms (▲ for Ref. 10 and △ for Ref. 11).

no detectable populations in the $v' \geqq 11$ levels are observed, and overall vibrational excitation is very much weaker than in the electron-impact case.

*Effect of Collisions.* From the following argument, the present estimates can be regarded as "initial" energy distributions since the values relate to a pressure region where any energy transfer processes induced by collision may be disregarded.

The spontaneous radiative lifetime of CN($B^2\Sigma$) is reported to be 60—85 ns by measurements of a decay curve[19,20] or phase shifts.[21,22] The cross section for electronic quenching was estimated by Luk and Bersohn[20] to be 19.4 Å$^2$ as a lower limit calculated from a measurement of the electronic quenching rate of BrCN. If one assumes that excited CN radicals have average translational energy of 1.9 eV, the mean time between collisions of CN($B^2\Sigma$) with BrCN is estimated to be about 60 ns when the sample pressure is about 0.7 Torr, which is comparable with the radiative lifetime of CN($B^2\Sigma$). This pressure is much higher than that used in the present study from which the energy distribution was determined. In other words, in the pressure region of the present measurements electronic quenching is probably negligible. Furthermore, the vibrational and rotational distributions have been estimated at a low-pressure limit, where no pressure-dependence was observed. Therefore, the distribution seems to be free from the effect of collisions.

*Pressure Dependence.* The relative vibrational populations depend strongly on the BrCN pressure when it is higher than 0.1 Torr. In particular, the emission spectrum is essentially that of the (0,0) band (Fig. 3) when the BrCN pressure is higher than about 0.8 Torr. Possible processes causing the vibrational relaxation are the following: 1) The vibrational energy of CN($B^2\Sigma$) is transmitted to the translational and/or vibrational energy (possibly the $\nu_3$ mode) of BrCN. In the latter case, the deficiency of the energy ranging from 75 cm$^{-1}$ (from $v'=1$ to $v'=0$) to 250 cm$^{-1}$ (from $v'=5$ to $v'=4$) has to be supplied by the translational energy of the CN radical. 2) The rates of collision-induced transitions (B-X) for higher vibrational levels may be much larger than those for lower levels. However, no further experimental evidence for any of these processes has yet been provided.

On the other hand, the effective rotational temperature of the (0,0) band, *ca.* 2000 K, seems to be essentially independent of the sample pressure up to 2 Torr. Therefore, the pressure effect seems to appear only in the vibration and not in the rotation in the pressure region of the present study (from 0.01 to 2 Torr). However, such a trend has not been observed for any other cyanides studied so far,[23] namely, HCN, DCN, ICN and $(CN)_2$.

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