

Short Communication

Vibrational inversion of CN produced by flash photolysis of BrCN in excess Xe*

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The flash photolysis of BrCN vapor in excess N₂ is known to produce vibrationally excited CN in the ground electronic state¹. This source has been used to do a high-resolution analysis of the absorption spectrum of the CN violet system². For this purpose, 0.05 to 0.5 Torr of BrCN diluted with 20 times as much He was flash photolyzed. The experimental details were very similar to those used in a study of the NO spectrum from the flash photolysis of ClNO³. Absorption spectra of CN in the X²Σ ground state with $v'' \leq 7$ were observed in the $\Delta v = 0$ and $+1$ sequences of the violet system around 388 and 359 nm, respectively. All spectra mentioned here were obtained immediately following the peak of the photolysis flash, since vibrationally excited CN decays within a few tens of microseconds. A typical absorption spectrum of the $\Delta v = 0$ sequence is shown in Fig. 1(a).

Spectra at higher pressures were taken so that collision widths of the CN rotational lines could be obtained, similar to a study made on OH⁴. Mixtures containing 600 Torr of He, N₂, CO₂, Xe, Ar, CO, SF₆, H₂, or CH₄ and between 0.05 and 0.5 Torr of BrCN were flash photolyzed as already described^{3,4}. The last four mixtures yielded no CN absorption, perhaps due to rapid reactions with any CN produced. The first three gas mixtures gave strong CN (0,0) band absorption spectra and very weak or absent (1,1) and higher sequence bands, this being a consequence of very rapid vibrational relaxation. The rotational lines of the (0,0) band were diffuse due to collision broadening by the inert gas. The rotational temperature, as judged from the maximum intensity rotational lines, is only slightly above room temperature.

Figure 1(b) shows the $\Delta v = 0$ sequence bands from BrCN in the presence of 600 Torr of Xe. The broadened (0,0) band is present as described for the other gases. In addition, the broadened (3,3) band occurs and is only slightly weaker than the (0,0). The (3,3) band also seems to appear weakly with the Ar and N₂ mixtures.

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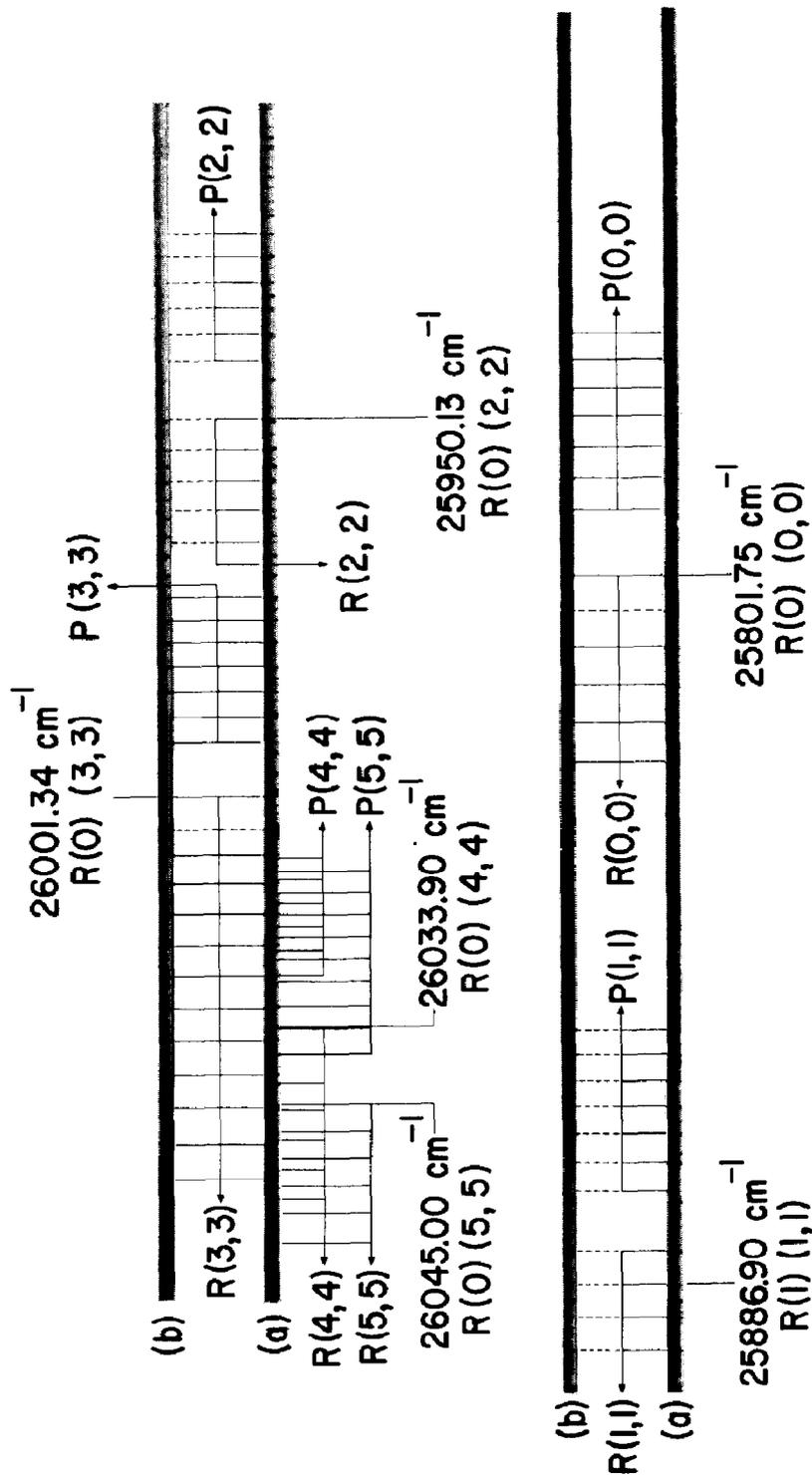
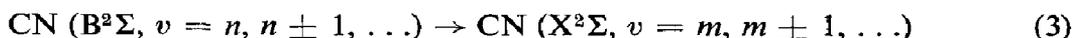
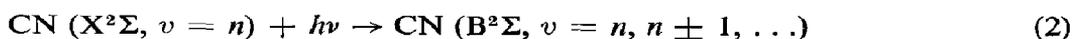


Fig. 1. Absorption spectra of the CN $\Delta v'' = 0$ sequence around 388 nm taken during the flash photolysis of BrCN vapor. A 2100 J photolysis flash and a 20 μsec delay before firing the absorption lamp were used with an absorption path length of 2 m. Only a few K values, starting with the lowest allowed lines of the P and R branches, are marked. In addition, fragments of bands with $v'' > 5$ are also present, but unmarked. Doubling of lines above $K \sim 15$ is quite noticeable in (a), as are the well known perturbation lines in the (0,0) band. The wide line near the center of each exposure is an artifact of the spectrograph. A vacuum wavenumber measurement for a line in each band is also given. (a) 0.5 Torr BrCN in 10 Torr He. (b) 0.05 Torr BrCN in 600 Torr Xe.

The (1,1) and (2,2) bands were very weak and the (4,4) and higher bands were absent for these mixtures. Since the calculated Franck–Condon factors for the CN ($B^2\Sigma \rightarrow X^2\Sigma$, $\Delta v = 0$) bands vary only slowly as a function of v''^5 , the unexpected strength of the (3,3) band would not seem to be due to differences in the absorption coefficients of the bands in the $\Delta v = 0$ sequence.

Thus there seems to be a strong vibrational population inversion between the $v'' = 3$ and $v'' = 2$ levels of $X^2\Sigma$ when excess Xe is present. This would suggest the possibility of infra-red laser action in the (3,2) band. A preliminary attempt to operate such a laser was not successful⁶. The only CN laser that has been reported uses the flash photolysis of low-pressure $(CN)_2$, but the lasing transition in this case was (4,3)⁷.

Earlier workers¹ have argued that an optical pumping mechanism is responsible for the formation of vibrationally excited CN during the flash photolysis of BrCN in N_2 :



The initial CN production comes from BrCN photolysis, but, due to the large absorption coefficient of CN, many repetitions of reactions (2) and (3) can occur during the photolysis flash, leading to an abnormally hot vibrational distribution. The last step could involve either fluorescence or collisional deactivation. This mechanism neglects vibrational deactivation, which will generally lower the concentration of the higher levels of CN. The effect of vibrational deactivation was very apparent in the experiments with 600 Torr of added gas; almost no $v'' > 0$ CN was observed except for $v'' = 3$ with Xe mixtures. The observation of the (3,3) CN band in the presence of Xe does not appear to fit into this mechanism.

It has been suggested that collisional transfer from $B^2\Sigma$ to $A^2\Pi$ could result in this type of distribution⁸. However, the absence of $X^2\Sigma v'' = 4$, which coincides with $A^2\Pi v' = 0$, and the strength of $v'' = 3$ in the Xe mixtures leaves this explanation open to question. More experimental work would be necessary to determine what other mechanisms, such as deactivation of $(\text{BrCN})^*$ or involvement of CN ($A^2\Pi$), might be reasonable. It is unfortunate that this Xe effect was noted after the apparatus for producing it was no longer available. Further investigations, particularly of the pressure and time dependence and the use of other CN sources (ICN, ClCN) would seem warranted, since this appears to be a unique vibrational distribution, unlike those observed in ClNO flash photolysis and similar systems.

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