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Letters to the Editor

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The Infra-Red Spectrum of Solid Hydrogen Cyanide*

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THE C−N stretching frequency, ν_1, of HCN has not been definitely observed in the gas. However, Choi and Barker[1] observed a band at a frequency, 2100 cm^{-1}, which is very close to the expected value for this fundamental. Because of the unusual structure of the band which they observed, they assigned the three peaks to $3\nu_2$, $4\nu_2(\Sigma^+)-\nu_2$, and $4\nu_2(\Delta)-\nu_2$. (ν_2 is the degenerate bending vibration at 712 cm^{-1}.) The difficulty with this assignment is that the Boltzmann factor for the last two transitions is only 0.06 while the three peaks are of approximately equal intensity. Another explanation for the complicated structure lies in a Coriolis interaction between $3\nu_2$ and ν_1 although this explanation is untenable unless the absorption region actually covers more than the 25 cm^{-1} observed by Choi and Barker.

One may expect the fundamental frequency, ν_2, to be considerably shifted in crystalline HCN so that any coincidence between $3\nu_2$ and ν_1 should be eliminated. We have, therefore, studied the infra-red spectrum of thin non-scattering films of HCN at −180°C. The frequencies and relative intensities in the crystal and the gas frequencies are compared in Table I.

All three fundamentals were observed, as well as the first overtone of the bending mode. The degeneracy in the bending vibration is split and the two components appear at 828 and 838 cm^{-1}. This behavior is illustrated in Fig. 1 where the component at 828 cm^{-1} is almost completely absent in the non-scattering film, indicating a highly oriented film, but both components appear in the more highly scattering film. The relative intensities of the two vary from film to film, apparently as a consequence of partial orientation. This frequency is more than 100 cm^{-1} higher than the corresponding frequency in the gas. There can therefore be no doubt that the very sharp line observed at 2097 cm^{-1} is the fundamental ν_1. This is confirmed by the appearance of the corresponding frequency of the isotopic molecule HC^{13}N with the proper frequency shift. This fundamental and the isotopic line are shown in

TABLE I. Frequencies and relative intensities of the bands observed in solid HCN.

Frequency		Relative intensity	Assignment
Gas*	Solid		
3312	3132	5.7	ν_3
2800	—	—	$\nu_2+\nu_1$
2089	2097	1.0	ν_1
—	2063	0.03	ν_1(HC^{13}N)
1412	1632	0.49	$2\nu_2$
712	838⎫ 828⎭	1.4	ν_2

* See G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 279.
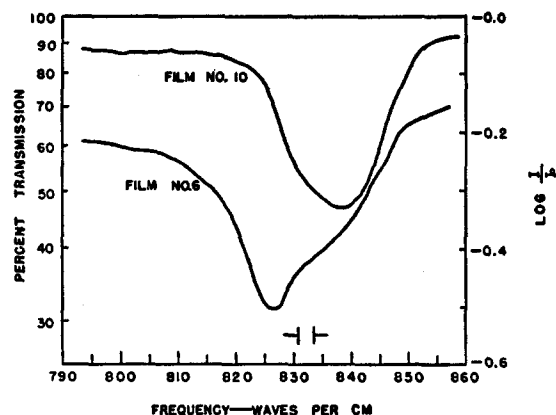

FIG. 1. The infra-red absorption due to the bending fundamental, ν_2, of HCN in the crystal at −180°C.

Fig. 2.[2] On the other hand, the second overtone of ν_2, $3\nu_2$, was not observed at all.

These observations suggest that the intensity in the vicinity of 2100 cm^{-1} in the gas originates primarily from ν_1 rather than $3\nu_2$. However, they do not necessarily negate the conclusions of Choi and Barker because of the remarkable intensity changes which take place upon crystallization. In the gas the bending vibration, ν_2, is approximately 250 times as intense as the C−H stretch and the C−N stretch is certainly extremely weak. In the crystal, on
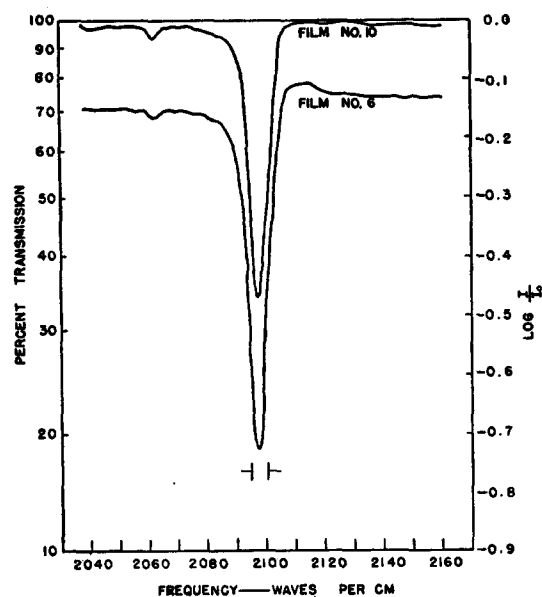

FIG. 2. The infra-red absorption due to the C−N stretching fundamental, ν_1, of HCN and HC^{13}N in the crystal at −180°C.

the other hand, the bending vibration is only $\frac{1}{4}$ as intense as the C−H stretch and only slightly more intense than the C−N stretch. These relative intensity changes of the order of 1000 times indicate very considerable structural changes accompanying the formation of the hydrogen bonds in the crystal.

1 K. N. Choi and E. F. Barker, Phys. Rev. 42, 777 (1932).
2 The distortion introduced by scattering, even when small, is quite evident in the thicker film in Fig. 2. It is usually characterized by a transmission maximum on one side of the peak and a tail on the other.