

Pressure Effect in the HCN Bands in the Near Infrared

S. D. CORNELL AND WILLIAM W. WATSON, *Sloane Physics Laboratory, Yale University*

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Contrary to the observations of Herzberg and Spinks it is found that all the lines of the HCN absorption band at 1.04μ are broadened equally by increase in HCN gas pressure. The half-widths increase linearly with pressure at the rate of 0.56 cm^{-1} per atmosphere. This value is slightly

less than that found by H. Becker for the first harmonic band of HCl, as is to be expected from the relative polarizabilities of the two molecules. The results indicate dispersion forces to be the predominant broadening influence.

INVESTIGATIONS of the absorption spectrum of HCN in the photographic infrared have been made by Badger and Binder¹ and by Herzberg and Spinks.² Both of these comment on the considerable breadth of the rotational lines when saturated vapor pressures of HCN are used in the absorption tube. Herzberg and Spinks photographed the intense (0, 0, 3, 0) band³ at 1.04μ , which has a simple *P*, *R* branch structure due to the linear nature of the HCN molecule, at several vapor pressures from 130 mm to 650 mm. They observed that whereas at the lower pressure the absorption lines were as sharp as could be expected from the slit width used, at the highest pressure all the lines became very broad. The broadening effect of a partial pressure of air was noted to be very much smaller than the influence of the HCN molecules on each other. Additional observations were that these lines are considerably more broadened by increase in the HCN pressure than are the lines of the second overtone HCl band at corresponding pressures of HCl, and that the broadening decreases with increasing molecular rotation.

It was concluded by Herzberg and Spinks that this pressure broadening could not be pure Lorentz collision broadening, and that an apparently necessary condition for the effect is that the molecule be rather easily deformable as shown by one small vibration frequency. Their observations of this pressure broadening seem to have been only qualitative, however. And since a reconciliation of these facts with other pressure

broadening effects appeared to be very difficult, quantitative measurements on the variation of the half-widths of these lines with density of absorbing vapor and with rotational quantum number *J* were to be desired. Such measurements do not reveal any unusual pressure broadening effect and are susceptible to simple theoretical interpretation.

EXPERIMENTAL PROCEDURE

The HCN was generated by dropping a concentrated solution of sodium cyanide into sulphuric acid, dried with calcium chloride and introduced into the previously evacuated absorption cell. This cell was made from a Pyrex tube 200 cm long and 4 cm diameter with flat Pyrex windows fused on to each end. A heating coil was provided to raise the temperature of the cell somewhat above the boiling point (26°C) of HCN when necessary. The light source was either a 150 c.p. Point-o-lite lamp or a 32 c.p. double filament automobile headlight lamp run on 16 volts with the two filaments in series. After passing through the absorption cell twice the light was focused on the slit of the 21-foot concave grating in a stigmatic mounting.

All spectrograms of the 1.04μ absorption band were taken in the first order of this grating, the dispersion being $4.72\text{A}/\text{mm}$. Using a slit 0.04 mm in width the exposure times with Eastman *I-Z* plates ranged from 8 to 24 hours. Fe lines in the second order served as a comparison spectrum. HCN vapor pressures used were 131, 230, 265 and 525 mm at the room temperature of 21°C and 820 mm at 40°C . This highest pressure reduced to 21°C for pressure effect comparison with the others is 770 mm. A number of lines of both low and high *J* values in the *P* branch of the band as

¹ R. M. Badger and J. L. Binder, *Phys. Rev.* **37**, 800 (1931).

² G. Herzberg and J. W. T. Spinks, *Proc. Roy. Soc.* **A147**, 434 (1934).

³ The vibrational energy level assignments for the infrared HCN bands have been made by A. Adel and E. F. Barker, *Phys. Rev.* **45**, 277 (1934).

TABLE I. Half-value widths $\nu_{1/2}$ in cm^{-1} for P branch lines of the 1.04μ HCN absorption band.

J	$P=131$ mm	$P=230$ mm	$P=265$ mm	$P=525$ mm	$P=770$ mm
1				1.08	
2				1.19	
3				1.19	1.26
4	0.87	0.92	0.98	1.10	1.20
5				1.14	1.34
6				1.21	
7					1.18
8					1.40
9					1.51
10					1.26
11	0.91		1.05		1.62
12	0.84	0.92	1.03		1.73
13	0.94	0.89	0.89	1.27	1.18
14	0.82	0.99	1.08	1.23	1.38
15	0.97	0.98	0.94	1.36	1.08
16	0.80	1.04	0.86	1.26	1.20
17	0.89	0.93	0.98	1.26	1.52
18				1.19	
19				1.06	1.40
20				0.86	
Ave.	0.88	0.95	0.98	1.17	1.35

produced at each of these pressures were photometered with the 40 : 1 magnification of a Koch-Goos registering microphotometer. The dispersion for these photometer traces is $0.108 \text{ cm}^{-1}/\text{mm}$.

LINE WIDTHS

The measurements of the half-value widths $\nu_{1/2}$ of all the lines we have photometered are collected in Table I. In Fig. 1 is displayed the distribution of these line widths about their mean values for two of the pressures. Inspection of the table and the graph shows a random variation of the widths with rotational quantum number J about the mean values at each pressure. There is certainly no decrease in line width with increasing molecular rotation. It is true that at a first glance at a spectrogram such as the one reproduced in Fig. 2 for a fairly high vapor pressure the lines near the band origin do look definitely broader. But the maximum of the rotational energy distribution comes at a rather low quantum number ($J=7$) the greater resulting intensity for these lines thus giving the false impression that they are broader than the weaker high J lines. Such an error of judgment is one commonly made. It should be emphasized that

the relative breadths of absorption lines of unequal intensity may only be learned from measurements of their half-value widths from photometer traces with any necessary correction for plate characteristic.

Fig. 3 is a plot of the mean values of the half-widths as a function of the pressure of the absorbing HCN vapor. The vertical dashed double-headed arrows indicate by their length the average numerical deviation of the individual widths from their mean. These deviations would naturally be expected to increase with increasing line breadth. The mean values show the usual strictly linear increase with pressure, the change being 0.56 cm^{-1} per atmosphere. This is only slightly larger than the pressure broadening produced by foreign gases both for atomic and molecular spectral lines.^{4, 5}

DISCUSSION

The magnitude of this pressure broadening, its linear increase with pressure and its independence of the rotational energy of the absorbing molecule all indicate that dispersion forces are the predominant broadening influence. This is in agreement with London's⁶ work on the attractive force between rotating dipoles in which it is shown that even for a strong dipole gas such as HCl the dispersion effect is considerably larger than the Debye induction effect and the direction effect. Furthermore, the expression for the

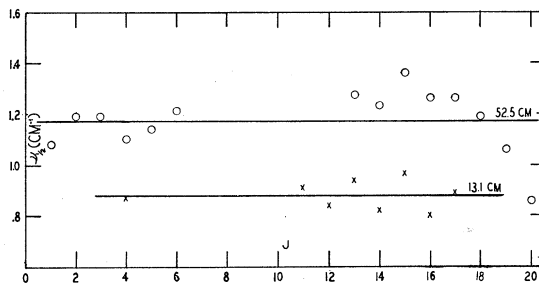


FIG. 1. Half-value widths of $P(J)$ lines of the 1.04μ absorption band of HCN at pressures of 131 mm and 525 mm. Note the random distribution about the mean values (horizontal lines).

⁴ H. Margenau and W. W. Watson, *Rev. Mod. Phys.* **8**, 22 (1936).

⁵ W. W. Watson and G. F. Hull, Jr., *Phys. Rev.* **49**, 592 (1936).

⁶ F. London, *Zeits. f. Physik* **63**, 245 (1930).

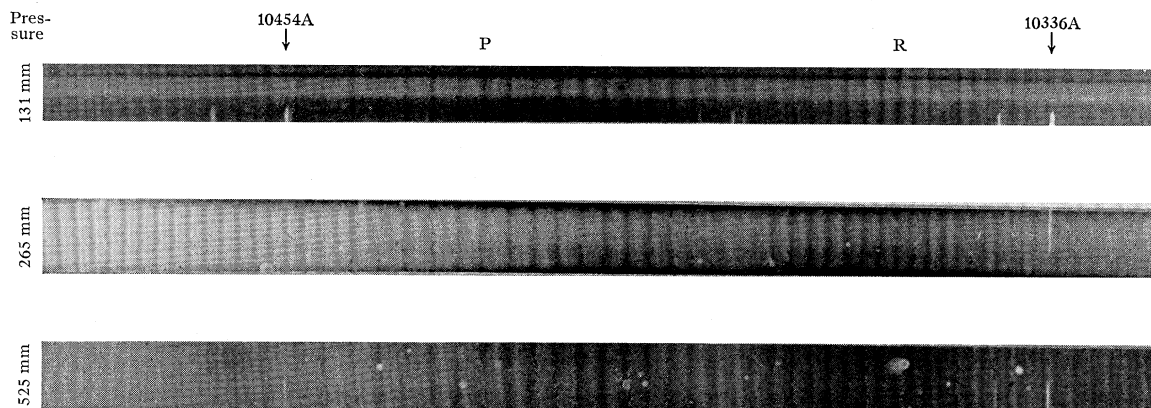


FIG. 2. 1.04μ HCN band with HCN pressures of 131,265 and 525 mm.

interaction energy between a molecule of polarizability α and a rigid rotator of dipole moment μ developed recently by Margenau⁷ indicates an insignificant dependence on the rotational quantum number J .

Using the Lorentz-Lorenz relation with the known index of refraction for HCN, one computes the polarizability α to be 2.58×10^{-24} . Since

for HCl $\alpha = 2.71 \times 10^{-24}$ it is to be expected that the HCl band lines should actually show a somewhat greater pressure broadening than do these HCN lines. Becker⁸ has measured the half-width of a line of the first harmonic band of HCl at 1.74μ at pressures of 3, 5, 7, 9 and 11 atmospheres as 8.65, 14.0, 17.1, 21.75 and 25.1A respectively. The rate of increase of this width with pressure is about 0.7 cm^{-1} per atmosphere, a value in good agreement with our expectations. The same broadening influence, dispersion forces, is undoubtedly in large part responsible for the pressure broadening in both cases, and there is no evidence for molecular association.

It has been reported by Mecke that the H_2O band lines are relatively quite sharp. Now H_2O does have a polarizability but little more than half that of HCN. If vapor pressures comparable to those used in the present work were employed, however, one would certainly expect to observe the H_2O lines to be broadened to almost the same extent as these HCN lines.

We wish to thank Professor H. Margenau for helpful discussion.

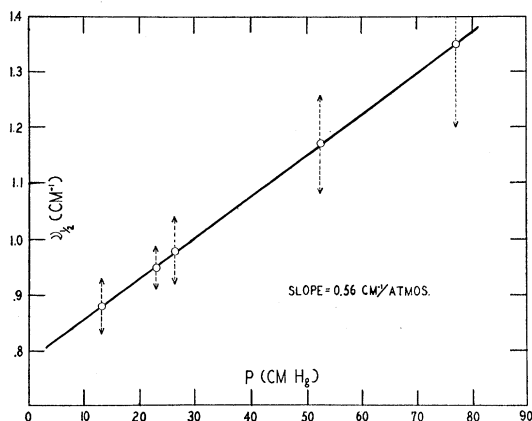


FIG. 3. Mean value of line half-widths vs. HCN vapor pressure.

⁷ H. Margenau, Phys. Rev. 49, 596 (1936).

⁸ H. Becker, Zeits. f. Physik 59, 583 (1930).

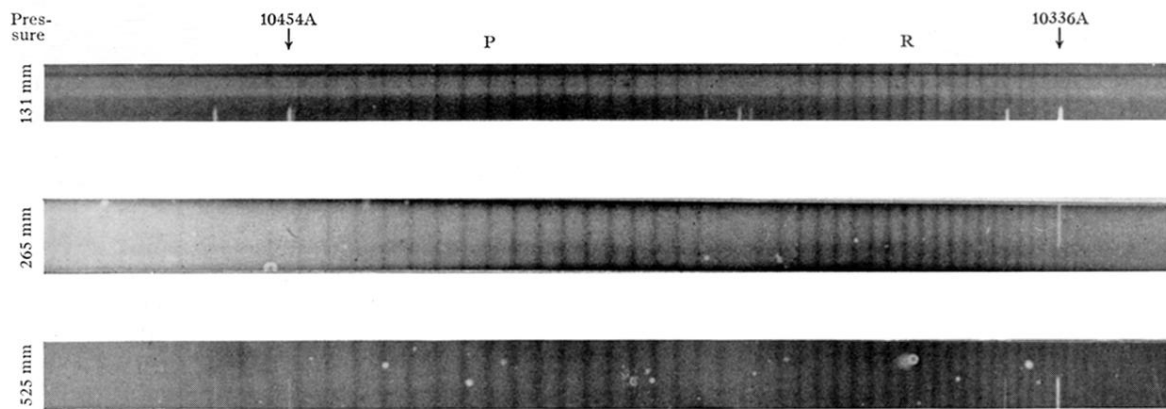


FIG. 2. 1.04μ HCN band with HCN pressures of 131,265 and 525 mm.