

$N' = 2\pi n R_0 a^2$  with  $n$  the density. Thus the line form is given by

$$I(\omega) = A / [(n\pi a^2 \bar{v})^2 + \omega^2] \quad (37)$$

which is the Lorentz formula, with frequencies measured from the line center.

Under the two extreme physical conditions

the wave mechanical and classical treatments lead to the same expressions for the line form.

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### Self-Broadening in the $14\mu$ Band of HCN

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The intensity distribution in the positive branch of the  $14\mu$  HCN band has been measured at pressures of 2.5 cm, 16 cm, 40 cm, and 58 cm. Because of the large permanent dipole moment of this molecule, there is considerable line broadening at these pressures. The overlapping of lines, slit width effects, and finite thickness of the absorbing layer of gas are taken into account in relating the theoretical line widths to the intensity distribution. The two constants giving the effective slit width and the absolute vibration intensity are determined from the low pressure lines, and these constants with the theoretical line widths determine the intensity distribution throughout the band. Reasonably good agreement is found at all pressures, and no systematic disparity of theory and experiment is indicated. The predicted shifts in the lines, which are just within the limits of detection, are in qualitative agreement with the observed values. The absolute value of the dipole strength of this vibration transition is determined.

**I**N a preceding paper,<sup>1</sup> formulas were developed for the width and shifts of the lines of the infra-red vibration bands of polar molecules. Table IV of reference 1 gives the widths and half-widths per atmosphere of the rotational lines for bands of HCl and HCN.

Inasmuch as the polar molecules are among the few cases in which the interactions important in line broadening may be calculated accurately, it has appeared worth while to determine experimentally the intensity distribution at various pressures in a band of such a molecule. Hydrogen cyanide gas was chosen for several reasons. Since it is a linear molecule, the spectrum is especially simple. It has a very large dipole moment ( $2.65 \times 10^{-18}$  c.g.s. e.s.u.), which indicates that considerable broadening will occur at moderate pressures. The spectrum is not complicated by the lines due to an isotope, as is the case with HCl. The positive branch of the  $14\mu$  band was

chosen for measurement, as there are no interfering bands of atmospheric  $H_2O$  or  $CO_2$  in this region. The line positions in the band have been measured previously by Barker and Choi.<sup>2</sup>

The infra-red spectrometer employed was that described by Hardy.<sup>3</sup> The writer was very kindly permitted the use of the instrument by Professor E. F. Barker. The grating used was of the echelette type, ruled with 700 lines to the inch. This spectrometer is equipped with a KBr fore prism to remove the higher order spectra of short wave-lengths.

Measurements of the absorption of the gas were made at pressures of 2.5 cm, 16 cm, 40 cm, and 58 cm of mercury, with absorption cell lengths of 12 cm, 2.5 cm, 1 cm, and 1 cm, respectively. The total amount of gas through which the radiation passed was thus roughly constant. 58 cm was the highest pressure that could be maintained at

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<sup>1</sup> H. M. Foley, *Phys. Rev.* **69**, 616 (1946).

<sup>2</sup> E. F. Barker and K. N. Choi, *Phys. Rev.* **42**, 777 (1932).

<sup>3</sup> J. D. Hardy, *Phys. Rev.* **38**, 2162 (1931).

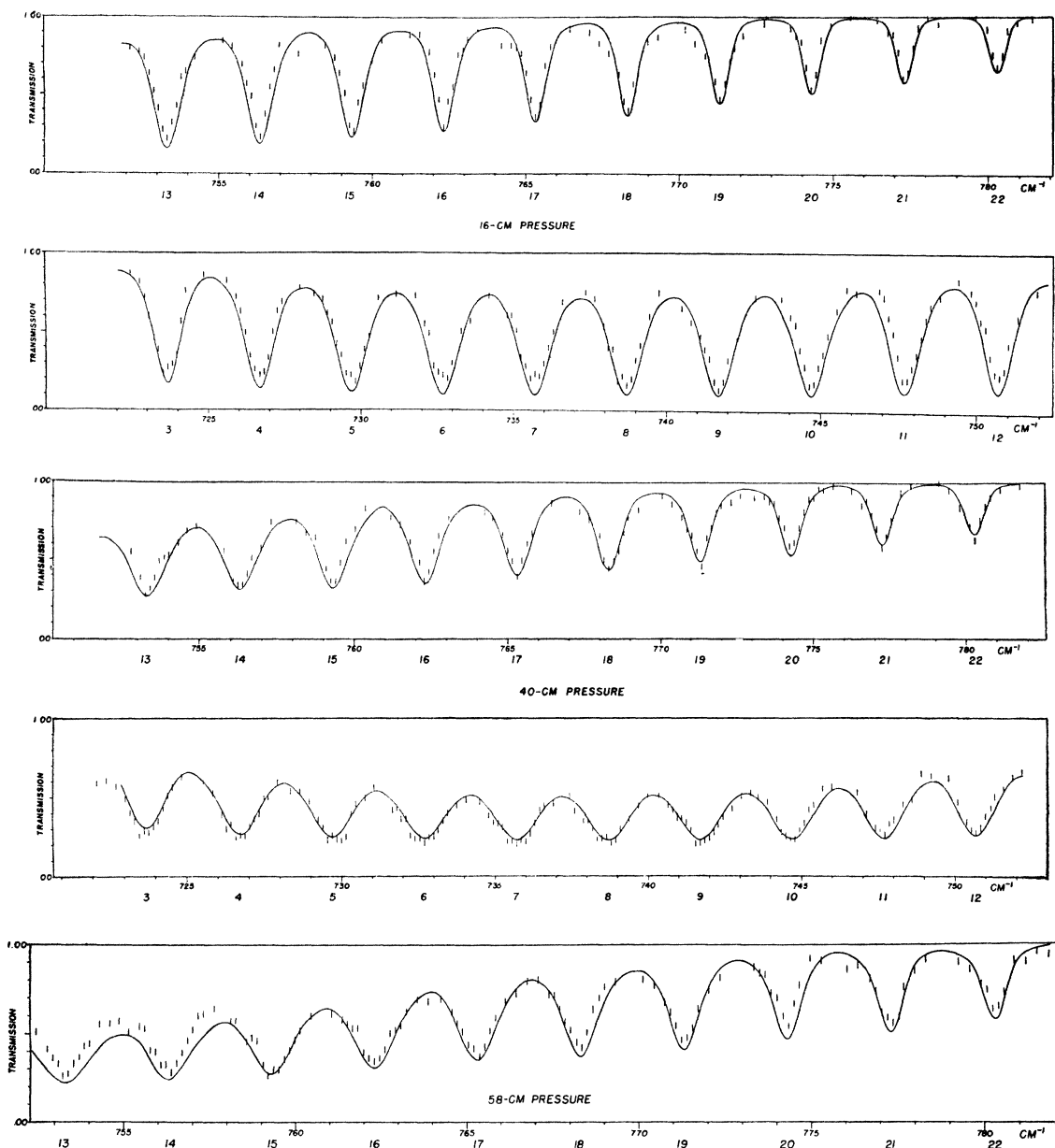


FIG. 1. Distribution of intensity of absorption in HCN. Experimental points and curve calculated from pressure broadening theory are shown. Absorption lines are numbered according to rotational quantum numbers of initial states.

room temperature, as this is very nearly the vapor pressure of the gas. Values of the percent transmission were measured at intervals of fifteen or thirty seconds of angle of the grating in the region covered by the lines with  $l=3$  to  $l=22$  inclusive, where  $l$  is the rotational quantum number of the initial state of the transition. The strong absorption of the  $Q$  branch of the band

overlaid the first three lines of this branch. At the 58-cm pressure, the absorption for the lines with  $l=13$  was so heavy that significant data could not be obtained in this region. An apparent polymerization of the HCN gas in the cell made it difficult to maintain the higher pressures and may have affected the results slightly.

After a number of trials, a slit width of 0.2

mm was chosen as the smallest practical width. The intensity falling on the thermopile was then so low that an abnormally high amplification had to be employed, with a consequent increase in the unsteadiness of the galvanometer deflections. Several readings were taken at each point. The observed transmissions for the pressures of 16 cm, 40 cm, and 58 cm are plotted in Fig. 1. Each value is represented by a line segment, the length of which indicates the uncertainty in the observed transmission, as judged from the deviations in the readings.

The analysis of the data is rather complicated, as the finite thickness of the absorbing layer, the diffusing effects of the spectrometer, and the overlapping of the rotational lines must be taken into account. The observed transmission is a function of the form

$$T(\nu_0) = \int_{-\infty}^{\infty} d\nu \rho(\nu - \nu_0) e^{-\alpha(\nu)d}, \quad (1)$$

in which  $\alpha(\nu)$  is the absorption coefficient of the gas per unit length and is compounded from the overlapping line absorption intensities.  $d$  is the absorption cell path length.  $\rho(\nu - \nu_0)$  is the function describing the distribution in intensity due to the spectrometer slit width and aberrations. If the slits are the sole source of this diffusion of energy and are of equal width, the function  $\rho(\nu - \nu_0)$  is triangular in form with a base-width equal to twice the slit width in frequency units. Equation (1) may be considered as an integral equation for  $\alpha(\nu)$  and solved stepwise over the band. For strong absorptions this is not a feasible procedure, however, as  $\alpha(\nu)$  can then be determined only with poor accuracy.

For the comparison of the theoretical intensity distributions with the data, we shall integrate Eq. (1) throughout the region of observation. The agreement with the observed absorption will serve as the test of the line broadening theory. This is a more complete comparison of the theory with the observed distribution in intensity than is obtained by determining only the observed half-widths, as the overlapping absorption from "tails" of the lines is of considerable importance at the higher pressures.

In addition to the theoretical half-widths of Table IV of reference 1, two other constants are

TABLE I. Data obtained from pressure broadening of HCN lines.

$l$	$T_m$	(Abs. $\times$ Min.)	(Abs. $\times$ Min.) $\log_{10} T_m$	(Abs. $\times$ cm $^{-1}$ ) $^2$ $4\pi\delta\nu d(l+1)e^{-\nu_l/kT}$	Shift per atmos- phere
2.5-cm pressure					
3	0.355	0.760	1.67	$2.10 \times 10^{-5}$	+0.34 cm $^{-1}$
4	0.370	0.800	1.85	2.11	+0.06
5	0.340	1.085	2.32*	2.91*	0.00
6	0.355	0.980	2.18	2.14	+0.16
7	0.331	0.950	1.98	1.91	+0.07
8	0.31	0.993	1.95	2.08	+0.26
9	0.32	1.12	2.26	2.83*	+0.16
10	0.305	1.29	2.50*	4.29*	+0.29
11	0.38	0.820	1.95	1.91	+0.36
12	0.43	0.651	1.78	1.44	+0.09
13	0.45	0.560	1.61	1.24*	0.00
14	0.455	0.675	1.97	2.51	-0.06
15	0.55	0.460	1.77	1.54	-0.16
16	0.59	0.384	1.67	1.50	-0.13
17	0.62	0.420	2.02	2.54	0.00
18	0.66	0.346	1.92	2.60	-0.03
19	0.63	0.340	1.69	3.78*	-0.03
20	0.76	0.232	1.95	2.65	-0.24
21	0.75	0.197	1.58	2.14	+0.06
22					0.00
4-cm pressure					
20	0.56	0.36	1.43	1.89	
21	0.61	0.34	1.58	2.56	
22	0.71	0.22	1.48	1.75	
			1.86 min.	$2.07 \times 10^{-5}$	
			Averages	$\nu$ in cm Hg	

necessary for the integration of Eq. (1). These are the width of the function  $\rho(\nu - \nu_0)$  and the absolute intensity constant of this vibration transition.

Because of the presence of the finite absorption and the slit effects, in general no very simple relation between the observed intensity distribution and the theoretical line strengths and line widths can be given. Dennison,<sup>4</sup> however, has given several useful relationships of the parameters determining the line shape for the case of narrow, intense, non-overlapping lines. The absorption coefficient is taken to be of the form

$$\alpha(\nu) = c\delta/\pi(\delta^2 + \Delta^2\nu), \quad (2)$$

with  $c$  the total intensity of the line, and  $\Delta\nu$  the frequency measured from the line center.  $\delta$  is equal to half the width listed in Table IV of reference 1. Dennison shows that the total absorption obtained by integrating Eq. (1) over the line is

$$\text{Abs.} = 2(c\delta d)^{\frac{1}{2}} \quad (3)$$

for lines which satisfy the condition

$$cd/\pi\delta \gg 1.$$

For these lines he also obtains the result

$$\text{Abs.}/\log_{10} T_m = 2.42a, \quad (4)$$

in which  $T_m$  is the transmission at the line center.

<sup>4</sup> D. M. Dennison, Phys. Rev. **31**, 503 (1928).

$a$  is the half-width of the function  $\rho(\nu - \nu_0)$ , when taken to be of Gaussian form

$$\rho(\nu - \nu_0) = \exp[-\Delta\nu^2/2.77a^2]/2(2.77\pi)^{1/2}a.$$

It is also shown that the result (3) is quite insensitive to the choice of  $\rho(\nu - \nu_0)$  as a Gaussian or triangular function. The theoretical line strengths are given by

$$c_l = n\nu_l(l+1)\alpha \exp[-l(l+1)h^2/2IkT], \quad (5)$$

in which  $\alpha$  is a constant independent of  $l$  and contains the transition matrix element. Thus the constants  $a$  and  $\alpha$ , together with the  $\delta_l$  from Table IV of reference 1 determine the intensity distribution at all pressures.  $a$  and  $\alpha$  may be determined from a study of a set of narrow lines showing considerable absorption. In Table I is given the data obtained from the nineteen lines at 2.5-cm pressure and three of the narrowest lines, at 4-cm pressure. In the second and third columns are given the line center transmission and the total absorption. From column four the effective slit width given by Eq. (4) is determined. The numbers appearing in this column are by no means constant in value, but no systematic trend is observable. From the fifth column, the value of  $\alpha$  may be determined, using Eqs. (3) and (5). The quantities marked with an asterisk were omitted from the averages because the corresponding values either of Abs. or  $T_m$  differed from those of neighboring lines in a very irregular manner. The value  $18.70 \times 10^{-40}$  g cm<sup>2</sup> for the moment of inertia was employed, and is taken from Barker and Choi.

It was now possible to calculate the transmissions at all points in the spectrum with the use of Eq. (1). A triangular form was taken for  $\rho(\nu - \nu_0)$  with a base width of 1.0 cm<sup>-1</sup>, as determined from Eq. (4). The integrations were carried out by summations, using five intervals over the 1 cm<sup>-1</sup> integration region. Thus the predicted values of transmission were calculated at 0.2 cm<sup>-1</sup> intervals throughout the region from  $l=3$  to  $l=22$  for the pressures of 16, 40, and 58 cm Hg. The calculated curves are shown in Fig. 1.

The agreement at 40-cm pressure is considered to be good. In the cases of the lines at 16-cm and 58-cm pressure, the form of the theoretical curves

agree well with the distribution of experimental points, but in general the observed transmission is somewhat greater than the theoretical values. This may be due to the difficulty in maintaining pressure described above. The general agreement of theory and experiment, considering the variation across the band as well as the dependence on pressure, is sufficiently good that it may be stated that, in this case, the effect of pressure on the intensity distribution has been completely accounted for.

In the theoretical treatment no correction to the intensities due to vibration-rotation was made. Inasmuch as the lines in this band show almost no convergence, it appears that this effect is small.

The accuracy with which the position of the centers of the lines is determined is approximately 0.1 cm<sup>-1</sup>. From Table IV in reference 1 it is clear that, with respect to line shifts, no very exact quantitative agreement of theory and experiment can be expected. From a plot of the line positions at the observed pressures, an approximate determination of the shift per atmosphere was made. These numbers appear in Table I. The values of Table I, while not agreeing line for line with the theoretical values of Table IV, suffice to show the existence of the effect predicted by the theory, namely the shift of all rotational lines towards the intense part of the band. The lines in the most intense region,  $l=8$  to  $l=11$ , show an abnormal position shift. These lines suffer the greatest broadening and hence the positions are determined with the least accuracy.

From the quantity  $\alpha$ , the absolute value of the "dipole moment" of the vibration can be calculated. Adjusting the expression given by Dennison<sup>3</sup> for diatomic band intensities to this case, we have

$$\alpha = (8\pi^3/3hc)D^2/\sum_l (2l+1) \exp[-W_l/kT].$$

From the observed value of  $6.45 \times 10^{-23}$  cm<sup>2</sup> for  $\alpha$ , we obtain for the effective dipole moment

$$D = 1.47 \times 10^{-19} \text{ e.s.u.}$$

It is believed that this is the first case of the evaluation of the dipole moment of a "bending vibration" of a molecule.