

Pressure Effect in Bands of Several Dipole Molecules*

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Several photographic infrared bands, of H_2O , HCN, and NH_3 , have been investigated for line broadening due to increased pressure of the vapors themselves. The half-widths at one atmosphere have been found, and the excess broadening per atmosphere calculated in each case. Comparison with simple dipole interaction theory has been made. Conformity is found for one H_2O band, compared with HCN. Lack of conformity for another H_2O band,

and for two NH_3 bands, is discussed. For HCN a variation of half-width with J is found, in accord with theoretical considerations of a qualitative nature, leading to broader lines in the neighborhood of the thermal maximum of the rotational velocity distribution. Effect of change in slit width on the observed line width and rate of broadening, and the consequent precautions necessary, are discussed.

1. INTRODUCTION

AN investigation of the absorption spectrum of HCN in the far photographic infrared was carried out in 1934 by Herzberg and Spinks.¹ In particular, the intense (0,0,3,0) band at 1.038μ was photographed at various HCN vapor pressures, from 130 mm to 650 mm, and the authors concluded, from visual inspection of their spectrograms, that the pressure broadening present was exceptionally large, because of a strong interaction between HCN molecules at relatively large distances. A later investigation by Watson and the author,² using a somewhat larger slit width, indicated that no excessive increase in line width with pressure was present. This divergence of results led to the question of whether the apparent disagreement could have arisen entirely from the difference in slit widths used. Herzberg and Spinks¹ also concluded, from visual inspection, that the broadening decreases with increasing molecular rotation, the lines of high J (>20) in particular being less broadened than those of lower J value. Microphotometer measurements of the spectrograms of Herzberg and Spinks have been made by Watson,³ and a broadening of about 1 cm^{-1} per atmosphere found. Because of the plate grain and high background fog of the early Agfa plates used, no certain conclusions could be reached regarding

any variation of the broadening with the value of J . These two questions, of the rate of broadening with pressure, and of variation with J , for HCN, are taken up in the present investigation, along with some less extensive work on two other dipole molecules, H_2O and NH_3 .

2. EXPERIMENTAL PROCEDURE

The light source used throughout was a 100 C.P. Point-O-Lite lamp. Exposures ranged from 10 minutes to 24 hours, using in each case the type of Eastman spectroscopic plate appropriate for the wave-length region under observation. All spectrograms were taken in the first order of the 21-foot concave grating in a stigmatic mounting, the dispersion varying from 3.55 to $7.84\text{ cm}^{-1}/\text{mm}$. All the microphotometer plates were made with the 40 : 1 magnification of a Koch-Goos registering microphotometer.

In the case of H_2O two different experimental conditions were used. To obtain a sort of reference exposure, indicating the extent of the broadening influence of nonpolar foreign gas molecules alone, one spectrogram for each band was taken with no absorption tube in the light path, so that the absorption was due entirely to atmospheric water vapor present in the slit room and grating room. To obtain spectrograms of H_2O broadened by H_2O , an 80 cm Pyrex absorption cell was used, containing only water and water vapor, heated to about 100° by an electric furnace. The slit width was 0.04 mm. Only those lines in each band showing good intensity, with no apparent overlapping, were chosen for microphotometering. The 9400A band and the

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¹ G. Herzberg and J. W. T. Spinks, Proc. Roy. Soc. **A147**, 434 (1934).

² S. D. Cornell and W. W. Watson, Phys. Rev. **50**, 279 (1936).

³ W. W. Watson, J. Phys. Chem. **41**, 61 (1937).

11,350A band were photographed under the above two conditions.

For HCN a steel absorption tube 21 feet in length was employed, to provide more absorption than had previously been used, in an effort to get more accurately measurable microphotometer traces. HCN was generated by dropping a concentrated solution of sodium cyanide into concentrated sulfuric acid. After passing through a calcium chloride drying tube it was introduced into the previously evacuated absorption tube. The 10,380A band was photographed at HCN pressures of 120 mm, 340 mm, and 545 mm, using three different slit widths, 0.04 mm, 0.05 mm, and 0.06 mm, at each pressure. This band has a simple *P, R* branch structure on account of the linear nature of the molecule. The *P* branch, showing a line spacing sufficient to prevent overlapping, was in each case microphotometered to as high a *J* value as possible.

NH₃, to a pressure slightly above atmospheric (about 78 cm), was introduced from a commercial tank into the evacuated 21-foot tube. The 7920A band and the 10,230A band were photographed at this pressure, and again only fairly sharp lines of good intensity were chosen for microphotometering.

The half-widths were measured with a millimeter scale from traces of the microphotometer plates. In tracing, the fluctuations due to plate grain were smoothed out as much as possible.

It is well to emphasize here the magnitude of the errors involved in half-width measurements, especially in the far photographic infrared. In plates sensitized for this region, the plate grain is generally large, and in the microphotometer may cause short period deflections of comparable magnitude to the line deflections themselves. Thus the line contours finally measured from the trace of the microphotometer plate become quite sensitive to the process of smoothing out the plate grain in tracing, especially in the case of lines of relatively low intensity, approaching the limit of sensitivity of the microphotometer. Likewise, in the case of lines which have a breadth comparable to their maximum height, since the half-width is measured along an abscissa drawn at one-half the maximum ordinate, the measured $\Delta\nu_{\frac{1}{2}}$ is very sensitive to the accuracy with which the maximum ordinate is determined

and bisected. As a consequence of these two facts in particular, the individual measurements have at best only a very low order of accuracy. In every case, therefore, a mean of as many lines as possible has been taken for any given band at a given pressure, and the mean deviation of the individual measurements from this mean has been found. This calculated error, then, gives an indication of the consistency of the measurements among themselves, but also, of course, is increased by any actual variation in half-widths within the band in question.

3. EXCESS BROADENING

The forces between dipole molecules leading to broadening of their spectral lines are in general made up of three principal components: (1) London's dispersion effect, (2) Debye's induction effect, and (3) the effect of dipole alignment.⁴ The complicated manner in which these three effects combine to make up the total line width is known theoretically, but has not been worked out on a practical basis. The dispersion effect, involving the mutual polarization of the electronic structures of the interacting molecules, is, of course, present in interactions between molecules which have no permanent dipole moment, as well as in the dipole case here considered. Consequently, if the dispersion broadening influence can be measured and subtracted from the total effect, we should, on the assumption of approximate additivity, obtain a fair idea of the broadening due to dipole interactions alone. From London's⁴ work on intermolecular forces, it appears that even for dipole molecules having dipole moments μ of ordinary magnitude, about 10^{-18} e.s.u., the dispersion effect is strongly predominant, but that for μ

TABLE I. Average values of half-width of band lines.

SUBSTANCE	BAND	PRESSURE	$\Delta\nu_{\frac{1}{2}}$ (cm ⁻¹)	AVERAGE OF
H ₂ O	9400	Atmos. Abs.	0.57 ± 0.06	37 lines
		0.8 Atmos.	0.67 ± 0.07	
HCN	10,380	Atmos. Abs.	0.40 ± 0.04	14
		0.8 Atmos.	0.63 ± 0.06	19
		120 mm	0.56 ± 0.08	19
		340 mm	0.88 ± 0.10	24
NH ₃	7920	545 mm	1.24 ± 0.16	23
		78 cm	1.45 ± 0.27	14
		10,230	78 cm	0.81 ± 0.19

⁴ F. London, Zeits. f. Physik 63, 245 (1930).

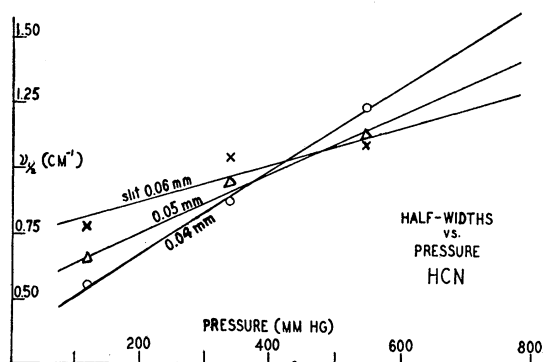


FIG. 1. Half-widths of the lines of the 1.038μ HCN band as a function of pressure for three different slit widths.

larger, about 2×10^{-18} e.s.u., the alignment effect becomes of comparable magnitude with the dispersion effect, and may become predominant for exceptionally large values of μ . This dipole interaction broadening may be thought of as an "excess broadening," present only in dipole molecules, and appreciable only in dipole gases of relatively large dipole moments. London's⁴ Eq. (26) gives the interaction energy for the case of two linear dipoles, of dipole moment μ and moment of inertia A (perpendicular to μ), a distance R apart:

$$\epsilon_{lk}^{(2)} = \frac{8\pi^2 \mu^4 A}{R^6 h^2} \times \text{a function of } l \text{ and } k,$$

where l and k are the angular momenta of the perturbed and perturbing molecules, respectively. The condition of large intermolecular distances, necessary for the validity of this expression, is best fulfilled at low pressures, such as are here used (< 1 atmosphere). Resonance interactions, between molecules for which l and k differ by one unit, are, of course, present, but nevertheless the excess broadening might be expected to be roughly proportional to μ^4 .

Table I gives the average values of $\Delta\nu_{1/2}$, the half-width in cm^{-1} , found at the various pressures for H_2O , HCN, and NH_3 , together with the mean deviations from the mean for each, and the number of lines represented in each average. It is to be noted that for comparison purposes, the relative vapor densities are important, or the relative pressures at constant temperature. Consequently, the H_2O vapor pressures of 1 atmosphere, at 100° , have been reduced to room

temperature (20°) for comparison with the other pressures, all of which were obtained at room temperature, leading to a corrected pressure of 0.8 atmosphere. In the case of absorption by atmospheric H_2O alone, the H_2O pressure is only a few millimeters (about 1.5 cm or less for relative humidity 60 percent), and N_2 and O_2 molecules, at a total pressure of 1 atmosphere, are the perturbers. The half-widths found under these conditions, then, may be considered to represent the breadth due to all such effects as apparatus width, dispersion forces, and the small contributions of Doppler broadening and natural line width. The two values found, for the 9400A and 11,350A bands, do not agree within the approximate errors. Part of the discrepancy may be explainable on slit width considerations, which will be taken up later. On the whole, however, the difference has found no satisfactory explanation. However, if we take a mean of the two, we may assume that the half-width for these forces alone lies between 0.45 cm^{-1} and 0.50 cm^{-1} . Such a value is supported by other measurements, such as those on CH_4 and C_2H_2 mentioned by Watson,³ which indicate that the half-width for dispersion and collision forces alone is in general in this region.

Now, the half-width *vs.* pressure relation for HCN (Fig. 1) is linear (the curve for slit 0.04 mm is the one under consideration) and gives a value for the half-width, at 1 atmosphere, of 1.55 cm^{-1} , assuming linearity up to one atmosphere, an assumption apparently justified.² The excess broadening, then, would appear to be in the neighborhood of 1.05 to 1.10 cm^{-1} per atmosphere. For HCN, μ is 2.5 to 2.6×10^{-18} e.s.u.; μ for H_2O is 1.87×10^{-18} e.s.u. The ratio $\mu^4_{\text{HCN}} : \mu^4_{\text{H}_2\text{O}}$ is about 3.45. This ratio indicates an expected broadening for H_2O of roughly 0.3 cm^{-1} per atmosphere. From the data of Table I the excess broadening for the 11,350A band of H_2O is found to be 0.29 cm^{-1} per atmosphere, in good agreement with the expected value. For the 9400A band, however, a value of 0.13 cm^{-1} per atmosphere is calculated, for which no explanation has been found, unless it be in a variation in μ for the upper states in vibrational transitions, or possibly in the effect of slit width on observed line width at different wave-lengths, a question which will be taken up below.

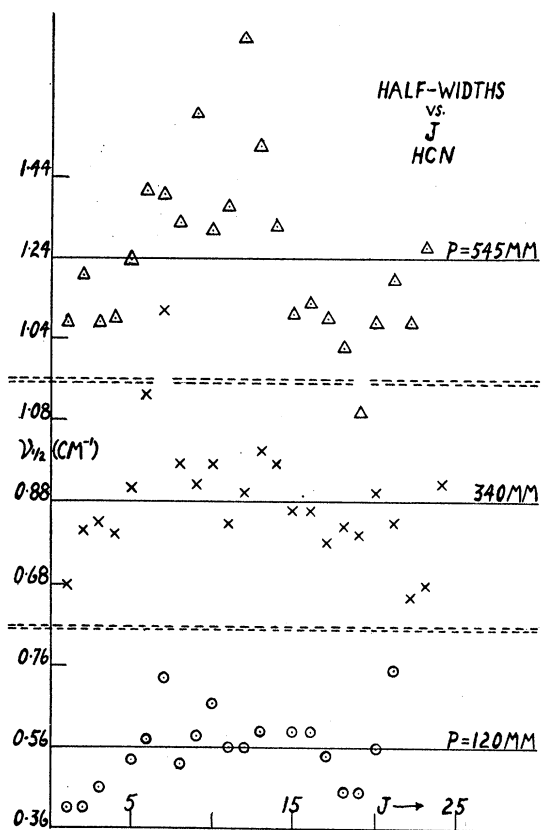


FIG. 2. Variation of the half-widths in the 1.038μ HCN band with the rotational quantum number, J , for three different pressures.

For NH_3 , $\mu = 1.44 \times 10^{-18}$ e.s.u., smaller than for H_2O . And yet, for the 10,230A band Table I indicates an excess broadening slightly larger than that for the H_2O 11,350A band. The 7920A band shows a very much larger excess broadening, but comparison may be risky because of wavelength and slit width considerations. Although the actual measurements on NH_3 are very unreliable, as indicated by the small number of lines found suitable for microphotomentering, and the large mean deviations, half-widths of this order are indicated also in other work on NH_3 .⁵ There are, however, some promising explanations for this unexpectedly large excess broadening. The symmetrical top structure, of which NH_3 is an example, shows, as is well known, a first-order Stark effect, and hence first-order van der Waals forces.⁶ London⁴ did not consider this type of van

⁵ S. H. Chao, Phys. Rev. 50, 27 (1936).

der Waals interaction. Margenau and Warren⁶ have made some absolute calculations on the interactions between symmetrical top dipoles, indicating that $\Delta\nu_{1/2}$ for NH_3 at one atmosphere might be expected to be of the order of 1.5 cm^{-1} . Comparison with experiment is of no quantitative reliability because of the uncertainty of the effect of slit width on the observed value, but at least it can be said that a considerably larger value is to be expected than that calculated from the H_2O or HCN line widths by the simple μ^4 ratio. These top interactions increase with J , and consequently a comparable effect would not be expected in H_2O , which is a top structure (asymmetrical), because for most of the observable band lines in H_2O , J is not greater than 4, as has been pointed out by Dennison.⁷

4. HALF-WIDTH VARIATION WITH J

In earlier quantitative work on HCN ,⁸ no reliable evidence could be found for any variation of the half-width with rotational quantum number J , although Herzberg and Spinks¹ had reported, as has been mentioned, an apparent lessening of the broadening for the highest observable values of J . The simple P , R branch structure renders HCN particularly suitable for comparison of lines of different J , and the experimental conditions in the present investiga-

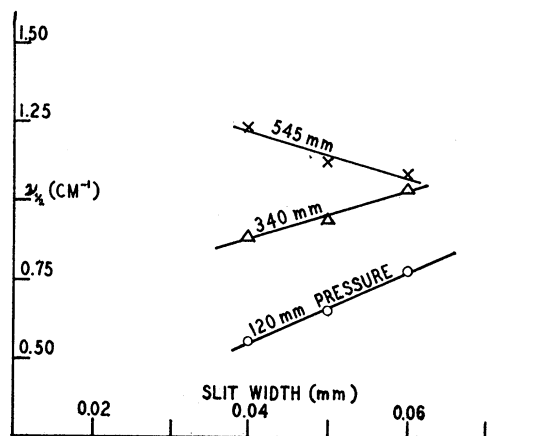


FIG. 3. Half-width as a function of slit width for three different pressures of HCN.

⁶ H. Margenau and D. T. Warren, Phys. Rev. 51, 748 (1937).

⁷ D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

⁸ G. Herzberg, J. W. T. Spinks and W. W. Watson, Phys. Rev. 50, 1186 (1936).

tion are more favorable than before for detecting any true J dependence, because of the considerably increased absorption path used.

It has been pointed out by Watson and Margenau⁹ on the basis of qualitative theoretical considerations, that, ignoring the London dispersion effect and the Debye static induction effect, and assuming the dipole alignment effect alone to be present, a slight variation with J is to be expected, the selectivity of dipole interactions for rotational states of nearly equal quantum number giving rise to a noticeable maximum broadening for values of J in the neighborhood of the maximum of the Maxwell distribution of rotational velocities. In the case of HCN the alignment effect is strong, certainly comparable to the other effects present, because of the rather large value of μ for HCN. A variation in half-width with J , then, from the above considerations, is to be expected, leading to somewhat broader lines in the neighborhood of $J=7$ or 8, where the maximum of the rotational velocity distribution occurs. The HCN measurements bear out this theory in a convincing manner. For one thing, Table I shows that the mean deviations from the mean half-widths for HCN are somewhat larger, amounting to from 11 percent to 14 percent, than for H_2O , where 10 percent seems to be a fairly consistent value, and this despite the fact that any difference in quality of the lines, for measuring purposes, was quite negligible. Thus a definite trend of some sort is indicated. Fig. 2 shows the half-widths, $\Delta\nu_{1/2}$, plotted against J for the three pressures of HCN used. Obviously, the individual measurements for a given pressure show a very large spread, which in large part is to be expected from the error considerations discussed above. Greater average consistency than about 10 percent can scarcely be hoped for under the photographic conditions obtaining in this region of the infrared. Striking, however, is the fact that superposed on this random variation from line to line there is a marked tendency, unmistakable at all three pressures, toward maximum half-widths in the expected region.

In connection with a narrowing for high J values such as Herzberg and Spinks¹ thought to be present, it should be emphasized that the

intensity at $J=20$ and above is falling off very rapidly, making it impossible to measure lines much farther out. Up to $J=24$, however, as is clear from Fig. 2, no narrowing is evident, the tendency, if any, being to slightly wider lines at the high values of J .

5. EFFECT OF SLIT WIDTH

In most absorption work at high dispersion in the photographic infrared, slit widths of about 0.05 mm are found to give the best results, as regards intensity, resolving power, etc. The disagreement in the measured rate of broadening from two earlier investigations,^{1,2} as has been mentioned, gave rise to the question of whether this disagreement could be attributed entirely to the difference in slit widths used. The evidence found is certainly in the affirmative, and both previous results are confirmed for the conditions prevailing. Fig. 1 and Fig. 3 show clearly how the measured, or apparent, rate of broadening decreases as the slit is widened from 0.04 mm to 0.06 mm, the curves of Fig. 1 intersecting each other in a very indefinite region, between 30 and 50 cm pressure. This is confirmed by other data, such as that obtained by Watson⁸ from the plates of Herzberg and Spinks, and by Watson and the author.² An interesting consequence, then, is that for pressures above this region, the measured half-width decreases as the slit width is increased from 0.04 mm to 0.06 mm. Nothing can be said concerning the quantitative relation between the slopes for the three slit widths in Fig. 1, but qualitatively their relative order is definitely established.

It is quite possible that for sufficiently narrow slits, the measured half-widths and rate of broadening would approach definite limiting values, in which case the curves of Fig. 1 would approach a definite slope, somewhat greater than the one shown for 0.04 mm, and those of Fig. 3 would become horizontal at some point below 0.04 mm. Because of this uncertainty the lines of Fig. 3 have not been extrapolated beyond the observed points.

From the work of Stockbarger and Burns¹⁰ it appears that the effect of slit width on observed

⁹ W. W. Watson and H. Margenau, *Phys. Rev.* **51**, 48 (1937).

¹⁰ D. C. Stockbarger and L. Burns, *J. Opt. Soc. Am.* **23**, 379 (1933).

line width may depend to some extent on the particular wave-length used. (The wave-length enters linearly in the expression for optimum slit width.) It must, of course, be remembered that this work was done only for narrow emission lines, and, so far as the author is aware, no comparable investigation has been made for the case of broad lines in absorption, which are in question here. Moreover, in infrared absorption work, slits much wider than the narrow optimum slits calculated by Stockbarger and Burns for emission work are generally used. However, some effect of wave-length is to be expected, although its nature and exact extent are unknown. It may be stated, then, that comparison of half-widths at the same slit widths for bands of widely different wave-length is probably risky. Just what conditions must obtain for reliable comparison is a matter of question. These considerations may enter in when the 7920A NH_3 band is compared with the 1.038μ HCN band, and when the two H_2O bands are compared with each other. But for comparison of the H_2O bands and the longer wave-length NH_3 band with HCN, all are

certainly nearly enough in the same spectral region so that any error from this source is overshadowed by the large inherent errors in measurement.

The value of the broadening per atmosphere for HCN measured from the plates of Herzberg and Spinks, using a slit of 0.05 mm, is 1.17 cm^{-1} . The value found for the case of 0.04 mm slit in the present work is 1.22 cm^{-1} . These two, within the approximate errors in each, are sensibly the same, indicating that what might be called the "apparatus width" was about the same in both cases. The conclusion is, then, that for comparison of pressure broadening effects in one band, or in several bands in the same region of the spectrum, at the slit-widths generally used in this work, care must be taken that all comparisons involve the same apparatus width, or, preferably, the same apparatus and slit width.

I wish to express my appreciation to Professor W. W. Watson for much helpful advice and for his many suggestions in connection with this work, and to Professor H. Margenau for valuable discussions on several points.

Drift of Ions and Electrons in a Magnetic Field

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Townsend's equations for the drift motion of ions under the combined action of magnetic field, concentration gradient and electric field are shown to be inconsistent with the Boltzmann equation. Other relations according to which a gradient contributes a perpendicular component to the drift are shown to be satisfactory in this respect. It is proved that such contributions exist and the fallacy in the demonstration that they do not exist is exposed. These equations lead to the simple result that the drift speed is the same as would occur if the components of concentration gradient and electric field perpendicular to it, as well as the magnetic field itself, did not exist. All of the equations are only semiquantitatively correct and are subject to refinement by a more adequate statistical treatment.

THE most complete analysis of the motion of ions through a gas in the presence of a magnetic field has been given by Townsend.^{1, 2} Basing his definition of diffusion coefficient upon

the time rate of increase of the mean square of the distance of particles from a line, he derived the fact that the coefficient of diffusion K_H at right angles to a magnetic field is given by

$$K_H = K(1 + \omega^2 \tau^2)^{-1}, \quad (1)$$

where K is the normal coefficient, $\omega = eH/mc$ and

¹ Townsend, Proc. Roy. Soc. **86**, 571 (1912).

² Townsend, *Electricity in Gases*, §§ 89-92.