observations on $LiAl(SiO_3)_2$ offers experimental evidence that q is not markedly different for a molecule containing Li^6 or Li^7. It is, therefore, concluded that the sign of the quadrupole moment of Li^6 is the same as that of Li^7. Previous data obtained by the method of molecular beams have been able to give only an upper limit for $|Q_6/Q_7|$. The present data indicate that Q_6 is other than zero and give at least a rough quantitiative verification of the result of Schuster and Pake of the value of $|Q_6/Q_7|$.

The aid of Mr. Thomas Eck in obtaining the data of the experiment is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 92, NUMBER 2 OCTOBER 15, 1953

Change in the Inversion Spectrum of ND_3 from Resonant to Nonresonant Absorption*

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(Received July 2, 1953)

The absorption due to the inversion spectrum of ND_3 centered near 1600 Mc/sec was measured at pressures from 0.3 to 80 cm Hg in the frequency interval 1100 to 2600 Mc/sec. The inversion frequency was found to decrease with increasing pressure and became substantially zero at about 9 cm Hg. This change occurs at pressures about 15-fold lower than for NH_3, a result in accord with Margenau's theory. At the higher pressures where the absorption is of the nonresonant or Debye type, the collision diameter is about 6.9A, a value roughly one-half that associated with resonant absorption at low pressures.

1. INTRODUCTION

COLLISION broadening in the microwave inversion spectrum of NH_3 near 24 000 Mc/sec has been studied extensively, both at pressures below 1 mm Hg where the considerable fine structure is completely resolved and at higher pressures where the lines become so broad that this structure is completely obliterated. Working in the pressure region from 10 cm Hg to several atmospheres, Weingarten[1] and Bleaney and Loubser[2] found that the unresolved spectrum could be represented by a single Van Vleck-Weisskopf line shape factor provided empirical values were chosen for the line width and resonance frequency. They showed that the resonance frequency decreased as the pressure was increased and became substantially zero for pressures above two atmospheres. The line width was found to rise much less rapidly than the pressure in the transition region, but, as shown by the more detailed experiments of Bleaney and Loubser, to become proportional to the pressure above four atmospheres. The effective collision diameter appeared to change from an initial value in the neighborhood of 13A to about 7.7A at the higher pressures, a change which was attributed to the effect of multiple collisions.

A similar behavior is to be expected for the completely deuterated ammonia ND_3 which in its ground vibrational state has an inversion resonance near 1600 Mc/sec.[3,4] However, on the basis of the theoretical treatment of Margenau,[5] the shift in the inversion frequency should occur at pressures about 15-fold lower than in the case of NH_3. In this event the effect of multiple collisions on the spectral broadening process should be relatively unimportant.

Measurements of the absorption in ND_3 were made at a number of pressures between 0.3 and 80 cm Hg in the frequency interval 1100 to 2600 Mc/sec. The results are in accord with the predictions from Margenau's theory. A definite shift in frequency is evident at a pressure as low as 1 cm Hg. Above 9 cm Hg the inversion frequency has become effectively zero and the transition from resonant to nonresonant or Debye absorption is virtually complete.

2. EXPERIMENTAL

A hybrid mode cylindrical cavity,[6] tunable by a movable center post from 1100 to 2600 Mc/sec, was used as the gas absorption cell. Over this frequency range the loaded Q of the empty cavity varied from 3000 to 5000. The absorption coefficient of the gas was determined as described previously[7,8] from the cavity response curve displayed on an oscilloscope. At the lower pressures the absorption was obtained from the initial Q and relative power transmitted by the cavity. At the higher pressures the absorption was also obtained from measurements of the Q's of the empty and gas-filled cavity.

Calibrated attenuators were used to obtain the law of the crystal detector several times throughout the course of the investigation. The power level at the

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* Presented at the St. Louis meeting of the American Physical Society, 1952 [Phys. Rev. **89**, 895 (1953)].

[1] I. R. Weingarten, Thesis, Columbia University, New York, 1948 (unpublished).

[2] B. Bleaney and J. H. N. Loubser, Proc. Phys. Soc. (London) A63, 483 (1950).

[3] Nuckolls, Rueger, and Lyons, Phys. Rev. **89**, 1101 (1953).

[4] Unpublished calculations of J. R. Madigan, A. Javan, and J. F. Lotspeich.

[5] H. Margenau, Phys. Rev. **76**, 1423 (1949).

[6] L. Essen, Wireless Engr. **23**, 126 (1946).

[7] G. Birnbaum and A. A. Maryott, J. Chem. Phys. (to be published).

[8] Birnbaum, Kryder, and Lyons, J. Appl. Phys. **22**, 95 (1951).

crystal was in the neighborhood of several microwatts, and the crystal was found to exhibit square law behavior in all instances.

The ND_3 gas[9] was condensed in a liquid nitrogen trap and used repeatedly. However, frequent checks of the absorption with fresh samples showed that no detectable contamination occurred in the sample. All measurements were made at a temperature of about 25°C.

The sensitivity of measurement corresponded to about 5×10^{-7} cm^{-1} in absorption. From the reproducibility of the data, test measurements on NH_3 whose absorption had been determined previously,[7] and a search for systematic errors, it is felt that the experimental accuracy is in the neighborhood of 5 percent except where limited by sensitivity at lower pressures.

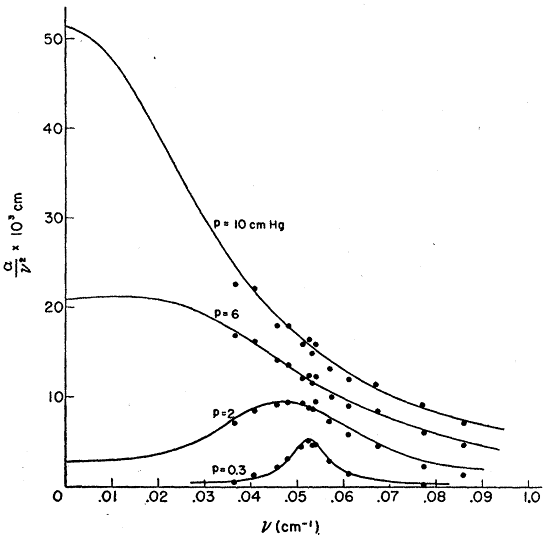

FIG. 1. Variation of $\alpha/\nu^2\times10^3$ with wave number ν at various pressures for ND_3.

3. RESULTS

Since the experimental results are interpreted with the aid of the Van Vleck-Weisskopf equation, it is convenient to describe first the manner in which this equation is used. When the widths of the individual lines become large compared with their separation, it becomes possible to represent approximately the absorption due to the unresolved band by the Van Vleck-Weisskopf formula[10] in the form,

$$\frac{\alpha}{\nu^2}=\frac{4\pi^2N}{3kT}\sum_{J,K}f_{J,K}|\mu_{JK}|^2\times\left(\frac{\Delta\nu}{\Delta\nu^2+(\nu_0-\nu)^2}+\frac{\Delta\nu}{\Delta\nu^2+(\nu_0+\nu)^2}\right),\quad(1)$$

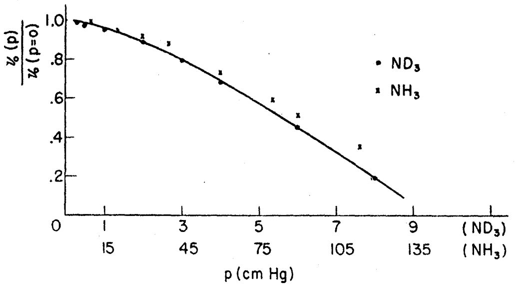

FIG. 2. Variation of the ratio of the inversion frequency at finite pressures $\nu_0(p)$ to that at zero pressure $\nu_0(p=0)$ as a function of pressure: ●ND_3—present data; ×NH_3—Bleaney and Loubser.

where the individual line shape factors have been replaced by a single term having an effective line breadth $\Delta\nu$ and a resonance frequency, ν_0. The quantities α, ν_0, ν, and $\Delta\nu$ are in cm^{-1}. The quantity $f_{J,K}$ is the fractional number of molecules occupying the J, K rotational energy levels, $|\mu_{J,K}|^2=\mu^2K^2/(J^2+J)$, and N is the number of molecules per cc. Calculations made at 25°C gave

$$\sum_{J,K}f_{J,K}|\mu_{J,K}|^2=0.40_0\mu^2,$$

a result virtually the same as that for NH_3. With the permanent dipole moment μ taken to have the value 1.47×10^{-18} esu,[11] Eq. (1) reduces to

$$\frac{\alpha}{\nu^2}=9.00\times10^{-5}p\left(\frac{\Delta\nu}{\Delta\nu^2+(\nu_0-\nu)^2}+\frac{\Delta\nu}{\Delta\nu^2+(\nu_0+\nu)^2}\right),\quad(2)$$

where p is the pressure in cm Hg.

Experimental values of α/ν^2 plotted against ν for several pressures are shown in Fig. 1 together with the curves computed from Eq. (2) by using empirical values of ν_0 and $\Delta\nu$ to give the best fit at each pressure. The calculated curves show satisfactory agreement with the experimental data. At a pressure of 0.3 cm Hg, the absorption maximum appears at a wave number of 0.0526 cm^{-1}. However, a plot of ν_0 *versus* pressure suggests that even at this low pressure a slight shift in resonance frequency has occurred. Extrapolation to zero pressure gives an effective value of 0.0532 cm^{-1}. This value is in very close agreement with that calculated by Madigan *et al.*[4] for the inversion splitting of the ground vibrational level, namely 0.0534 cm^{-1}. As the pressure increases, there is a progressive shift in the frequency of maximum absorption to lower frequencies. When the pressure reaches about 10 cm Hg, the resonance frequency appears to be indistinguishable from zero.

In Fig. 2 the ratio of the inversion frequency of ND_3 at some pressure p to the value extrapolated to zero pressure is plotted for each pressure examined in the region 0.3 to 8 cm Hg. Values at the two highest pres-

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[9] Synthesized from 99.8 percent D_2O by the Texas Research Foundation, Renner, Texas.

[10] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).

[11] Within the experimental accuracy, $\mu(NH_3)=\mu(ND_3)$. See A. A. Maryott and F. Buckley, "Table of dielectric constants and electric dipole moments of substances in the gaseous state," National Bureau of Standards Circular 537.

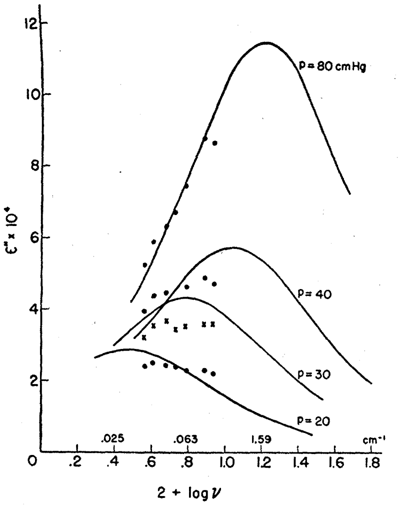

FIG. 3. Variation of the dielectric loss factor $\epsilon''\times10^4$ of ND_3 with logν at various pressures above 10 cm Hg.

sures where the calculated absorption is relatively insensitive to the choice of ν_0 are rather approximate. For comparison, the data of Bleaney and Loubser[12] on NH_3 are included but on a pressure scale reduced by a factor of 15. The significance of the close parallelism of the two sets of data when compared on this basis will be discussed subsequently.

At the higher pressures where the resonance frequency is zero, Eq. (2) reduces to

$$\frac{\alpha}{2\pi\nu} = \epsilon'' = 2.86\times10^{-5}p\left(\frac{\nu\Delta\nu}{\Delta\nu^2+\nu^2}\right), \qquad (3)$$

where ϵ'' is the dielectric loss factor. In this case it is convenient to represent the data by plots of ϵ'' against logν, as shown in Fig. 3. Such plots are customarily used for the nonresonant absorption found in polar liquids and solids, and as may be easily verified, ϵ'' has a maximum value when $\nu = \Delta\nu$.

In view of the considerable breadth of the nonresonant absorption band, the present data cover a rather limited portion of the pertinent frequency region. However, at pressures of 60 (not shown) and 80 cm Hg, the data are in good agreement with the curves calculated by empirical adjustment of $\Delta\nu$. At 20, 30, and 40 cm Hg the absorption band appears to be somewhat broader than that required by Eq. (3). Such behavior is observed in liquids and solids when there is a distribution of relaxation times, or in the present terminology a distribution of $\Delta\nu$'s. On the other hand, data at 10 cm Hg where ν_0 was also zero show no such anomaly. However, data over a more extended range of frequencies are needed before any particular significance can be attached to the deviations noted.

Values of the line breadth parameter $\Delta\nu/p$ obtained by fitting Eqs. (2) or (3) to the data at each pressure are plotted in Fig. 4. For comparison the corresponding values obtained for NH_3 by Bleaney and Loubser[12] are included but on a pressure scale reduced by a factor of 15. Except for the ND_3 points at 20 and 30 cm Hg where the significance of a single $\Delta\nu$ appears to be uncertain, the line breadth parameters show comparable variations for both gases.

4. DISCUSSION

A qualitative interpretation of the observed frequency shift in NH_3 has been given by Anderson[13] and a quantitative treatment has been attempted by Margenau.[5] They pointed out that the dipole interaction between two isolated ammonia molecules can become large enough to cause a change in the molecular wave functions and hence in the selection rules for the inversion transition. In this case Margenau found that two possible transitions with different frequencies are produced, one smaller and the other larger than the normal frequency. With increasing interaction the strength of the lower frequency transition increases greatly at the expense of the other. By considering only the dominant or low-frequency component, the resonance frequency for a pressure p is given by

$$\nu_0' = \nu_0[(1+\lambda^2)^{\frac{1}{2}} - \lambda],$$

where $\lambda \approx 2\mu^2N/\Delta E$ and $\Delta E = h\nu_0 c$ is the transition energy associated with the unperturbed inversion. As $\Delta E(NH_3)/\Delta E(ND_3) = 14.8$, a given fractional shift in resonance frequency for each gas should occur at pressures in the inverse ratio.[14] This relationship is substantiated by the data of Fig. 2 which show that a given fractional change in the resonance frequency of ND_3 takes place at a pressure approximately 15 times lower

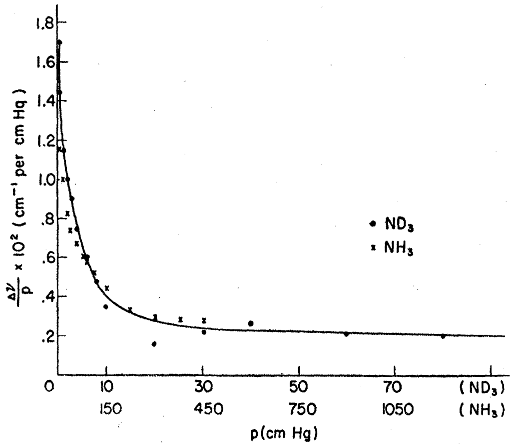

FIG. 4. Variation of the bandwidth parameter $\Delta\nu/p$ with pressure: ●ND_3—present data; ×NH_3—Bleaney and Loubser.

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[12] Reference 2 and a private communication.

[13] P. W. Anderson, Phys. Rev. **75**, 1450 (1949).

[14] The absorption spectrum of ND_3 in its first excited vibrational state was measured between 24 000 and 145 000 Mc/sec at 20, 50, and 76 cm Hg by J. H. N. Loubser and J. A. Klein [Phys. Rev. **78**, 348 (1950) and Columbia Radiation Laboratory Quarterly Report, Sept. 1949 (unpublished)]. At these pressures the absorption curves show that the resonance frequency is at 1.2×10^5 Mc/sec. It would be interesting to see if this frequency shifts downward at higher pressures.

than in NH_3. At a pressure of 6 cm Hg where $\lambda=0.81$ for ND_3, $\nu_0'/\nu_0=0.48$ which is virtually the same as the experimental value of 0.45. At higher pressures the resonance frequency drops to zero more rapidly than predicted from a consideration of two interacting molecules. As indicated by Margenau, such behavior would be expected if interactions between three or more molecules become effective at these higher pressures.

We next wish to consider the observed variation of the band width parameter ($\Delta\nu/p$) with pressure. However, before doing so, it will be instructive to consider the variation of the individual line widths with pressure from pressures where the lines are completely resolved up to pressures where the fine structure is completely obliterated but the frequency shift is not appreciable.[15] Bleaney and Penrose[16] have shown that $\Delta\nu_{JK}$ is proportional to p for NH_3 in the region in question by demonstrating close agreement between the experimental peak absorption and that obtained by summing the Van Vleck-Weisskopf equation over the rotational states. We proceeded similarly for ND_3 by using the empirical formula of Nuckolls *et al.*[3] for the resonance frequencies and the formula of Bleaney and Penrose[16] for the line widths. The latter formula is based on measurements of the individual NH_3 lines, but according to Anderson's theory[17] it should apply without large error to the ND_3 lines, whose widths have not been measured as yet. The theoretical value of α/ν^2 (at 0.3 cm Hg and at 0.0526 cm^{-1}) was thus found to be 4.7×10^{-3} cm, about 10 percent lower than the experimental value. However, this difference might easily arise from the error in the measured value and from inaccuracies in the line width and frequency formulas.

With reference to Fig. 4, it is seen that $\Delta\nu/p$ for both NH_3 and ND_3 first decreases very rapidly in the transition region, and finally becomes substantially constant as the pressure is increased to the highest values. At the lowest pressures the separation of the individual unresolved lines is not yet negligible compared with their widths. Thus the values of $\Delta\nu/p$ which represent the width of the band of lines are significantly larger than the average width of the individual lines. Therefore the initial rapid change of the apparent $\Delta\nu/p$ with pressure does not necessarily imply a nonlinear variation of widths or a change in collision diameters of the individual lines.

At intermediate pressures $\Delta\nu/p$ falls well below the value calculated from the low-pressure collision diameters. Bleaney and Loubser[2] attributed this behavior in the case of NH_3 to the effect of multiple collisions. On this basis they derived the expression:

$$\Delta\nu/p \propto 1-(4\pi b^3 N)/3,$$

which fitted surprisingly well their measured variation of $\Delta\nu/p$ in the transition region. In the above expression b is the collision diameter for which they used an average value of 13A. This expression, however, cannot account for the corresponding $\Delta\nu/p$ variation in ND_3 for this occurs at pressures 15-fold lower, yet the value of b is almost the same as that for NH_3. Thus $(4\pi b^3 N)/3$, the term arising from multiple collisions, should be small and $\Delta\nu/p(ND_3)$ in contrast with experiment should be rather insensitive to pressure in the region under consideration.

At the highest pressures where $\Delta\nu/p$ is substantially constant, the collision diameter for ND_3 calculated from the usual kinetic formula,

$$\Delta\nu=\frac{2N}{c}\left(\frac{RT}{\pi M}\right)^{\frac{1}{2}} b^2,$$

reaches the limiting value of 6.9A, which is somewhat lower than the value 7.7A reported for NH_3. It is interesting to observe that these collision diameters are considerably less than those associated with the resonance absorption but still definitely larger than the kinetic diameters. There appears to be no theoretical treatment of collision diameters for non-resonant absorption in dilute gases.[18]

In the preceding discussion it may have been noticed that use was made of both statistical and impact theories. Thus on the one hand, the molecules were considered always under the influence of intermolecular interactions which are sufficiently strong to destroy the inversion resonance at a pressure of only 9 cm Hg (ND_3) where the average intermolecular distance is 70A. On the other hand, the line-shape equation used is based on impact theory. Furthermore, collision cross sections were obtained on this basis which requires that most of the time a molecule is sufficiently far from other molecules so that it may be considered as free. As yet there appears to be no unified treatment of the ammonia problem.

ACKNOWLEDGMENT

The authors take pleasure in thanking Mr. S. J. Kryder for assisting with the measurements, Dr. C. R. Greenhow for several valuable discussions, and Dr. H. Lyons for his interest in this work.

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[15] About 0.3 cm Hg for ND_3 and 10 cm Hg for NH_3.

[16] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **69**, 418 (1947).

[17] Provided that broadening arising from rotational resonance is neglected, Anderson's theory shows that $\Delta\nu$ is proportional to $\bar{\mu}_2$, the dipole moment along the axis of total angular momentum averaged over the states of the colliding molecule. [See W. F. Smith and R. Howard, Phys. Rev. **79**, 132 (1950)]. The quantity $\bar{\mu}_2$ for ND_3 equals 0.797×10^{-18} esu, about 3 percent higher than that for NH_3. Consequently, corresponding line widths for ND_3 should differ by the same amount.

[18] A suggestion in this direction has been made by P. W. Anderson in reference 13.