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Dispersion of Microwaves in ND_3

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The dispersion of microwaves has been theoretically calculated in the case of gaseous deutero-ammonia on the basis of the Van Vleck-Weisskopf expressions for collision-broadened spectral lines, as applicable to the inversion of ND_3 molecule in its ground vibrational state. The inversion frequency lies at 1600 Mc/sec which shifts to zero frequency at 9-cm pressure. Dispersion curves are plotted at various pressures and frequencies.

THE phenomenon of the inversion of the symmetric top pyramidal ammonia molecule has been of great interest to the microwave spectroscopists for a long time. The molecule shows a copious absorption of centimeter wave radiations and the maximum absorption region lies at 0.88 cm^{-1}. In the case of deutero-ammonia, the reduced mass of the molecule is greater than that of ammonia by 2, and theoretically it is expected that the inversion of the ND_3 molecule in its ground state will occur at a frequency approximately eleven times, lower. The inversion line has been traced[1] at 1600 Mc/sec (0.052 cm^{-1}). The inversion frequency decreases with increasing pressure in the manner predicted by Margenau[2] for the ammonia molecule. The inversion spectrum of heavy ammonia transfers from resonant to nonresonant or Debye absorption at 9 cm pressure. The pressure-broadened spectral line of ND_3 can be represented by the following expressions for absorption and dispersion given by Van Vleck and Weisskopf,[3] which have excellently predicted[4] the line shape of the collision-broadened spectral line of NH_3 and the dispersion associated with it:

$$\frac{\alpha}{\bar{\nu}^2}=\pi.I.p\left[\frac{\Delta\bar{\nu}}{(\Delta\bar{\nu})^2+(\bar{\nu}+\bar{\nu}_0)^2}+\frac{\Delta\bar{\nu}}{(\Delta\bar{\nu})^2+(\bar{\nu}-\bar{\nu}_0)^2}\right], \tag{1}$$

$$\delta_{\mu\nu}=\frac{I.p}{2}\left[\frac{(\Delta\bar{\nu})^2+\bar{\nu}_0(\bar{\nu}+\bar{\nu}_0)}{(\Delta\bar{\nu})^2+(\bar{\nu}+\bar{\nu}_0)^2}+\frac{(\Delta\bar{\nu})^2-\bar{\nu}_0(\bar{\nu}-\bar{\nu}_0)}{(\Delta\bar{\nu})^2+(\bar{\nu}-\bar{\nu}_0)^2}\right], \tag{2}$$

TABLE I. Values of resonance frequency $\bar{\nu}_0$ and line-width parameter $\Delta\bar{\nu}$.

	Pressure cm Hg			
	1	5	10	1 atmos
$Ip\times10^5$	2.86	14.3	28.6	217
$\bar{\nu}_0(\text{cm}^{-1})$	0.05	0.026	0.0	0
$\Delta\bar{\nu}(\text{cm}^{-1})$	0.012	0.03	0.035	0.15

where α is the absorption coefficient (per cm), $\bar{\nu}_0$ the resonance frequency, $\Delta\bar{\nu}$ the line-width parameter (cm^{-1}), and $\delta_{\mu\nu}$ the dipolar contribution to the electric susceptibility of the gas at a frequency $\bar{\nu}(\text{cm}^{-1})$, p is the pressure in cm Hg, and I is a constant of proportionality for a given molecule at a given temperature. The calculated values of $I.p$ at various pressures and the values[1] of $\bar{\nu}_0$ and $\Delta\bar{\nu}$ have been tabulated in Table I. For pressures below 1 cm Hg, $(\Delta\bar{\nu})^2\ll\bar{\nu}^2$, the dispersion expression is approximated by

$$\delta_{\mu\nu}=Ip\left[\frac{\bar{\nu}_0{}^2}{\bar{\nu}_0{}^2-\bar{\nu}^2}\right], \tag{3}$$

and for pressures above 10 cm Hg, when the resonance frequency centers at zero wave number, the expression

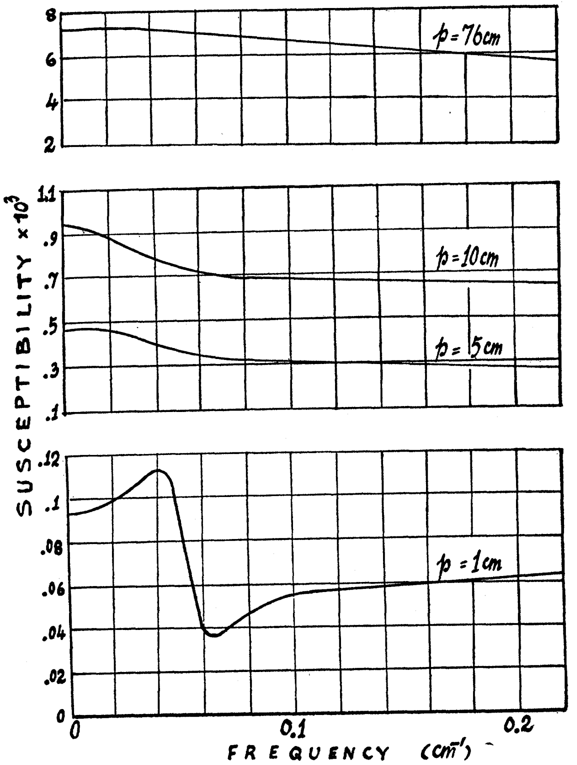

FIG. 1. Dispersion curves at various pressures in a wide frequency band.

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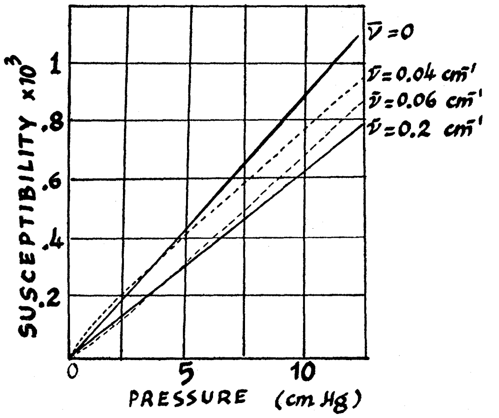

FIG. 2. Pressure variation of the electric susceptibility.

reduces to the Debye dispersion formula:

$$\delta_{\mu\nu}=Ip\left[\frac{(\Delta\bar{\nu})^2}{\bar{\nu}^2+(\Delta\bar{\nu})^2}\right]. \tag{4}$$

The net susceptibility δ_ν at the frequency $\bar{\nu}$ will also include contributions due to other polarizations, which remain constant in the region under consideration.

$$\delta_\nu=\delta'+\delta_{\mu\nu}.$$

δ' is due to polarizations other than dipolar. From the measurements of the susceptibility[5] at 1 Mc/sec, the value of δ' has been computed to be $0.0658\times 10^{-3}p$, where p is in cm Hg. The dispersion curves have been plotted in Fig. 1 at various pressures in a wide frequency band. It is observed that the dispersion is very significant at low pressures, but as the pressure increases and the resonance frequency becomes of the order of the line-width parameter the maximum and minimum points disappear, i.e., at 5 cm pressure. Figure 2 shows the pressure variation of the electric susceptibility. At all frequencies the susceptibility varies linearly with pressure, but the anomalous behavior near the inversion frequency is interesting. The graph shows concavity towards the pressure axis just before resonance and convexity after resonance. The dispersion in ND_3 can be checked by susceptibility measurements at 0.04 and 0.06 cm^{-1}.

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