A NOTE ON SATURATION IN THE MICROWAVE SPECTRUM OF METHYL CHLORIDE[1]

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The saturation of the microwave transition $J = 0 \longrightarrow 1$ of CH_3Cl^{35} has been measured by the method of Baird and Bird.[3] The results constitute the first

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[3] D. H. Baird and G. R. Bird, Rev. Sci. Inst. 25, 319 (1954).

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measurement on saturation of a rotational absorption line, all other microwave saturation measurements having been made on the $J = 3$, $K = 3$ line of the ammonia inversion spectrum.[4,5] As in the case of the ammonia line, the exper-

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[4] B. Bleaney and R. P. Penrose, Proc. Roy. Soc. 60, 83 (1948).

[5] R. L. Carter and W. V. Smith, Phys. Rev. 73, 1053 (1948).

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imental results are described by the formula derived by Karplus and Schwinger.[6]

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[6] R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).

Their derivation contains the assumption that collisions which broaden the absorption line are identical with collisions which transfer rotational energy and reduce the displacement from thermal equilibrium caused by the absorption of radiation. This corresponds to the case of diabatic (non-adiabatic or inelastic) collisions, which is expected to apply in the microwave region, but is known not to apply in the visible and ultraviolet regions.[7]

[7] W. V. Smith and R. R. Howard, Phys. Rev. 79, 132 (1950).

The experimental uncertainty in the actual measurement of the rate of saturation with increasing power is about 30% and is largely due to uncontrollable variations in the standing wave properties of the Stark-effect absorption cell. Reduction of the uncertainty requires the design of a more satisfactory waveguide, and work on this is now in progress. A detailed discussion of the measurements and calculations has been given elsewhere,[8]

[8] G. R. Bird, Properties of Spectral Absorption Lines, Doctoral Thesis, Harvard University, 1952.

and will not be repeated.

The line breadth constant $\frac{\Delta\nu}{p}$ has been measured for each of the three quadrupole fine structure lines of this transition and found to be 21 $\pm$ 1 mc./mm. Hg at 300°K, a result largely independent of the errors which enter into the saturation measurements. The intensity of the strongest line ($J = 0 \longrightarrow 1$, $F = 3/2 \longrightarrow 5/2$) is revised to $7.9 \cdot 10^{-6}$ cm^{-1} from the figure of $6.6 \cdot 10^{-6}$ cm^{-1} calculated by Kisliuk and Townes[9] for an assumed line breadth of 25 mc./mm. Hg.

[9] P. Kisliuk and C. H. Townes, Molecular Microwave Spectra Table, National Bureau of Standards Circular 518, June 23, 1952, p. 26.

If the line-broadening interactions are idealized as hard-sphere collisions, a collision diameter of $16._{1}$ Å may be calculated. This is much greater than the value of 5.6 Å obtained from viscosity measurements and the kinetic theory of gases.[10] The large size of the microwave collision diameter indicates that

[10] J. H. Jeans, The Dynamical Theory of Gases, Cambridge, England (1916), p. 295.

dipole-dipole interactions are the principal mechanism for line-broadening and rotational energy transfer.

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