

THE REFRACTIVE INDEX OF METHYL CHLORIDE AT 10 Gc/s*

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The dielectric behaviour of gases in an electromagnetic field has been studied theoretically by Van Vleck and Weisskopf (1945). They found expressions for the contributions to the absorption coefficient α and the refractive index n at a frequency ν arising from transitions between quantum states j and i . If ν is much less than the natural frequency ν_{ij} associated with the transition, and if the line width is also small compared with ν_{ij} , their results give:

$$\alpha_{ji} = 0, \quad (1)$$

$$4\pi\chi_{ji} = (n^2 - 1)_{ji} = \frac{8\pi}{3\hbar} \frac{N_j |\mu_{ij}|^2}{\nu_{ij}}, \quad (2)$$

where N_j is the number of particles per unit volume in the state j , μ_{ij} is the dipole matrix-element corresponding to the transition, and χ_{ji} the resulting contribution to the susceptibility. Since, at constant temperature, N_j is directly proportional to N , it follows that the contribution to the susceptibility should also increase linearly with N .

Methyl chloride, however, is a symmetric-top molecule and each rotational state J, K will be split into a very closely-spaced doublet for which ν_{ij} is effectively zero in comparison with microwave frequencies. Writing $\nu_{ij} = 0$, the Van Vleck-Weisskopf expressions then give, for the contributions arising from inversion transitions,

$$\frac{\alpha_{\text{inv}}}{\bar{\nu}^2} = \frac{8\pi^2}{3kT} \left\{ \sum_{J,K} N_{JK} |\mu_{JK}|^2 \right\} \frac{\Delta\bar{\nu}}{\bar{\nu}^2 + (\Delta\bar{\nu})^2}, \quad (3)$$

$$4\pi\chi_{\text{inv}} = (n^2 - 1)_{\text{inv}} = \frac{4\pi}{3kT} \left\{ \sum_{J,K} N_{JK} |\mu_{JK}|^2 \right\} \frac{(\Delta\bar{\nu})^2}{\bar{\nu}^2 + (\Delta\bar{\nu})^2}, \quad (4)$$

where $\bar{\nu} = \nu/c$ and $\Delta\bar{\nu}$ is the line width, which is assumed to be independent of J, K . At the pressures used in the present work, $\Delta\bar{\nu}$ arises almost entirely from collision-broadening and, according to the Van Vleck-Weisskopf theory, should be directly proportional to N . It therefore follows from (4) that χ_{inv} should rise more rapidly than N .

Microwave absorption by methyl chloride has been studied by various authors. Bleaney and Loubser (1950) found that for pressures up to 4 atmospheres and frequencies up to 24 Gc/s, the absorption is described by equation (3) if the line width is related to the pressure P in atmospheres by the equation

$$\Delta\bar{\nu} = 0.124P \text{ cm}^{-1}.$$

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Recent work by Birnbaum (1957) shows that a more accurate result is $\Delta\bar{\nu} = 0.115P$ cm^{-1} ; this result applies for a temperature of 26°C . At a frequency of 10 Gc/s ($\bar{\nu} = 0.33$ cm^{-1}) therefore, $\Delta\bar{\nu}$ should be comparable with $\bar{\nu}$ for pressures of the order of 2 atmospheres and so the non-linear behaviour predicted by equation (4), although small, should become apparent. However, most previous work has been concerned with absorption, and accurate measurements of the susceptibility do not appear to have been reported. Krishnaji and Swarup (1954) studied methyl bromide, which also can undergo inversion transitions, in the 3-cm microwave region and found that, within their experimental error, the susceptibility varied linearly with pressure up to one atmosphere. Walter and Hershberger (1946), using a waveguide cell technique, studied methyl chloride, but found that at a pressure of one atmosphere their observations were only in approximate agreement with the Van Vleck-Weisskopf predictions. No results are given for the variation of refractive index with pressure.

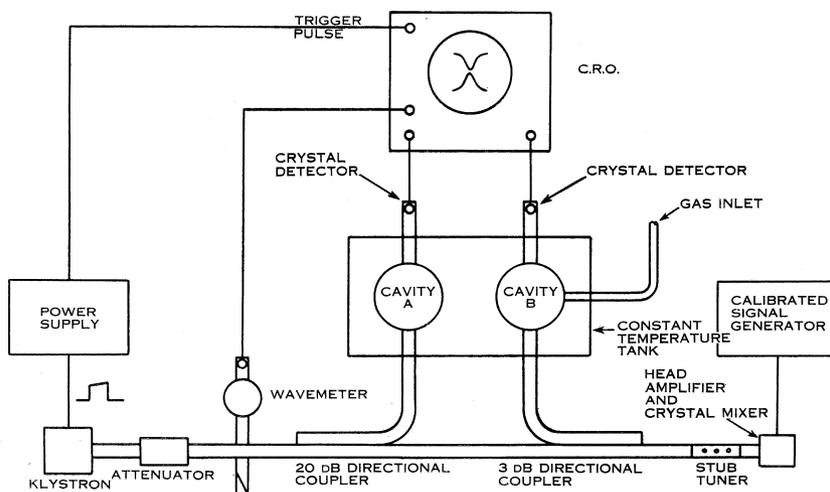


Fig. 1.—Block diagram of apparatus.

The object of the present work was to determine whether the susceptibility of methyl chloride at 10 Gc/s rises more rapidly than N , as would be predicted by equations (3) and (4) using existing absorption data.

Experimental Procedure

A block diagram of the apparatus is shown in Figure 1. The output of the klystron oscillator was swept from 10.00 to 10.01 Gc/s with a repetition rate of 1000 c/s. Some of the microwave energy was coupled into the evacuated cavity A whose resonant frequency was 10.006 Gc/s. This was operated as a transmission cavity and so an approximate resonance curve was traced on the oscilloscope screen.

The cavity B had when evacuated a resonant frequency approximately 12 Mc/s lower than that of A. It was supplied with microwave energy reflected from the crystal mixer. By suitable adjustment of the stub-tuner, appreciable amounts of

energy were reflected in the first upper and lower sidebands whose frequencies differed from the instantaneous klystron frequency by $\pm f$, where f is the frequency delivered by the signal generator. The latter was adjusted so that, as the klystron swept through the resonant frequency of A the first lower sideband swept through the resonance of B. A double-beam Tektronix oscilloscope Model 502 was used to indicate when this condition was fulfilled as indicated by the coincidence in time of the peaks of the two resonance curves.

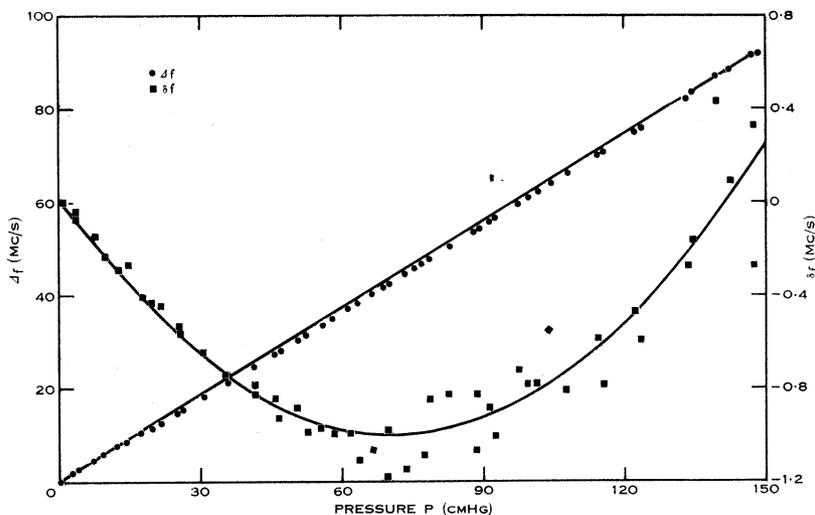


Fig. 2.—Change of frequency (Δf) with pressure P . The deviations δf of the experimental points from the straight line $\Delta f = 0.62P$ are also plotted against P .

Both cavities were machined from a 5-in. diameter brass rod, and were designed so that a pressure change of 2 atmospheres would produce a negligible change of dimensions. They were operated in the TE_{013} mode and the low- Q degenerate TM modes were displaced by machining grooves in the cavity end-faces. Energy was coupled in at the bottom and out at the top using the input coupling arrangement described by Bleaney, Loubser, and Penrose (1947). The unloaded Q of each cavity exceeded 23 000.

The cavities were mounted in an oil bath whose temperature was regulated to $\pm 0.01^\circ\text{C}$. Cavity A was continuously evacuated and the gas to be studied was admitted to B. The pressure was read to ± 0.05 cmHg and the frequency f could be read to ± 20 kc/s; at the highest pressures, however, the absorption due to methyl chloride causes the resonance curve to become very broad, and the error involved in setting f was of the order of ± 200 kc/s.

Results and Discussion

The results of a series of measurements are shown in Figure 2, in which $\Delta f = f - f_0$ is plotted against the pressure P ; f_0 is the value of f for zero pressure, and is equal to the difference between the resonant frequencies of A and B when both cavities

are evacuated. The straight line has the equation $\Delta f = 0.621P$ and the deviations δf of the experimental points from this straight line are also plotted against P in Figure 2. These deviations lie close to a parabola, and a least-squares calculation gives

$$\begin{aligned}\Delta f &= 0.621P + \delta f \\ &= 0.593P + 1.99P^2 \times 10^{-4} \pm 0.13 \text{ Mc/s,}\end{aligned}$$

where P is in centimetres of mercury.

The refractive index n was found from the relation

$$n^2 - 1 = 2\frac{\Delta f}{F} + 3\left(\frac{\Delta f}{F}\right)^2,$$

where $F = 9994$ Mc/s is the resonant frequency of cavity B when empty. The number of particles per unit volume was calculated from the pressure P and Avogadro's number N_0 by using the relation

$$N = N_0 \{RT/P + B\},$$

where the second virial coefficient B was taken from the paper by Fogg, Hanks, and Lambert (1953) to be -415 cm³ per mole. This yielded the relation

$$n^2 - 1 = 3.778N \times 10^{-22} + 2.38N^2 \times 10^{-43} \pm 0.000025.$$

A convenient measure of the curvature over the range of measurement is found by subtracting the value of $n^2 - 1$ at $N = 2.45 \times 10^{19}$ ($P \approx 1$ atm) from half its value at $N = 4.90 \times 10^{19}$. The result is 0.00014, which can be compared with the value deduced from existing absorption data. Thus it follows from equations (1), (3), and (4) that

$$(n^2 - 1)_{\text{inv}} = \alpha \Delta \bar{\nu} / 2\pi \bar{\nu}^2.$$

This can be evaluated from the data of Bleaney and Loubser (loc. cit.) assuming $\Delta \bar{\nu}/P = 0.124$ cm⁻¹ atm⁻¹ and taking $\alpha/\bar{\nu}^2 = 0.029$ cm⁻¹ for $\bar{\nu} = 0.33$ cm⁻¹ at a pressure of 4 atm from their Figure 4. In accordance with equation (2), higher transitions should make no contribution to the non-linearity, and so it follows from these calculations that the curvature as measured above should be 0.00017. A similar calculation using the numerical values for absorption and line width calculated from Table 4 of the paper by Birnbaum (loc. cit.) gives 0.00015. This is in satisfactory agreement with the value 0.00014 found experimentally in the present work.

As a check of the apparatus, measurements were made with carbon dioxide up to a pressure of 2 atm. In this case, there was no observable absorption and no broadening of the resonance curve at high pressures, so that the frequency could be measured to better than ± 20 kc/s over the whole range. The measurements were analysed in exactly the same way as for methyl chloride, and it was found that $n^2 - 1$ increased linearly with N over the whole range; any deviation from linearity was less than 0.000002.

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References

- BIRNBAUM, G. (1957).—*J. Chem. Phys.* **27**: 360.
BLEANEY, B., and LOUBSER, J. H. N. (1950).—*Proc. Phys. Soc. Lond.* A **63**: 483.
BLEANEY, B., LOUBSER, J. H. N., and PENROSE, R. P. (1947).—*Proc. Phys. Soc. Lond.* **59**: 185.
FOGG, P. G. T., HANKS, P. A., and LAMBERT, J. D. (1953).—*Proc. Roy. Soc. A* **219**: 490.
KRISHNAJI and SWARUP, P. (1954).—*J. Chem. Phys.* **22**: 568.
VAN VLECK, J. H., and WEISSKOPF, V. F. (1945).—*Rev. Mod. Phys.* **17**: 227.
WALTER, J. E., and HERSHBERGER, W. D. (1946).—*J. Appl. Phys.* **17**: 814.