

COLLISION BROADENING IN THE INVERSION SPECTRUM OF METHYL CHLORIDE AT PRESSURES UP TO TWO ATMOSPHERES

By C. H. BURTON,* W. B. LASICH,* J. H. NOON,* and R. W. PARSONS*

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Summary

The power absorption coefficient α of microwaves of wave number $\bar{\nu} = 0.333$ cm^{-1} by methyl chloride at 33.7°C has been studied at pressures up to 2 atm, and the results are compared with theoretical predictions. Discrepancies which have previously been attributed to the effect of transitions between low-lying rotational states are shown to be due to three-body collisions. The collision diameter for pressure broadening of the inversion transition in methyl chloride is found to be $8.6 \text{ \AA}$; this is significantly larger than the figure of $7.2 \text{ \AA}$ reported by earlier workers who neglected the effect of three-body collisions.

INTRODUCTION

At frequencies in the microwave region, the widths of spectral lines from gases at room temperature are determined almost entirely by collision broadening for pressures above approximately 10^{-3} mmHg. Classically, if an electromagnetic wave is propagated through a gas, the atoms or molecules perform internal forced oscillations which are interrupted by collisions. Vibrational energy is then shared among all the available degrees of freedom and is consequently dissipated as heat. Absorption measurements can therefore be expected to give information about collision processes in gases.

The dissipation of electromagnetic energy in gases was discussed by Lorentz (1915), who assumed that, if a large number of particles is considered, the phases of the forced oscillations immediately following collision are randomly distributed. However, if the natural frequencies of the oscillators approach zero, the Lorentz theory should give the same result as that of Debye (1925) for non-resonant absorption; that it does not do so was interpreted by Van Vleck and Weisskopf (1945) as an indication that the Lorentz assumptions were incorrect. The latter authors assumed that, following collision, the phases do not have random values but have a distribution which is related to the instantaneous strength of the applied field by a Boltzmann factor. Their resulting expression for the contribution α_{ji} to the energy absorption coefficient α due to transitions from an initial state j to a final state i is

$$\alpha_{ji} = \frac{8\pi^3 N_j \bar{\nu}}{3hc} |\mu_{ij}|^2 F(\bar{\nu}_{ij}, \bar{\nu}, \Delta\bar{\nu}), \quad (1)$$

where

$$F(\bar{\nu}_{ij}, \bar{\nu}, \Delta\bar{\nu}) = \frac{1}{\pi} \frac{\bar{\nu}}{\bar{\nu}_{ij}} \left\{ \frac{\Delta\bar{\nu}}{(\bar{\nu}_{ij} - \bar{\nu})^2 + (\Delta\bar{\nu})^2} + \frac{\Delta\bar{\nu}}{(\bar{\nu}_{ij} + \bar{\nu})^2 + (\Delta\bar{\nu})^2} \right\}. \quad (2)$$

* Physics Department, University of Queensland.

In these expressions, N_j is the number of molecules per unit volume in the state j , $\bar{\nu}$ the wave number of the incident radiation, $\bar{\nu}_{ij}$ the natural wave number associated with the transition, μ_{ij} the dipole-moment matrix element for the transition, and $\Delta\bar{\nu}$ the line-width parameter. This latter quantity is related to the mean time-interval between collisions τ and the velocity of light c by the equation

$$\Delta\bar{\nu} = 1/2\pi c\tau, \quad (3)$$

so that a determination of the relation between α and the pressure should enable τ and hence the cross section for collision to be determined.

Many experiments have been performed in order to test the Van Vleck-Weisskopf theory; among the first were those of Walter and Hershberger (1946), Bleaney and Penrose (1947), and Bleaney and Loubser (1950). These authors measured the microwave absorption in a number of gases, including ammonia and several methyl halides, and reported that their results were in good agreement with the theory.

All these gases have symmetric-top molecules. Each rotational level is split into a closely spaced doublet, and transitions between the two components give rise to the inversion spectrum of the molecule. In ammonia, Bleaney and Penrose identified 29 lines at low pressure grouped around 0.78 cm^{-1} . At pressures above a few centimetres of mercury, the lines are broadened by collision and overlap; in addition, due to the displacement of levels caused by long-range interactions between the dipoles, the mean inversion frequency decreases to zero as the pressure is increased to approximately 2 atm, and this makes the interpretation more difficult. For methyl chloride and methyl bromide, however, the inversion frequency at all pressures is so low as to be essentially zero when compared with microwave frequencies. In this case, the Van Vleck-Weisskopf expression simplifies considerably and gives

$$\begin{aligned} \alpha_{\text{inv}} &= \sum_{ji} \alpha_{ji} \\ &= \frac{8\pi^2\bar{\nu}^2}{3kT} \left\{ \sum_{JK} N_{JK} |\mu_{JK}|^2 \right\} \frac{\Delta\bar{\nu}}{\bar{\nu}^2 + (\Delta\bar{\nu})^2}, \end{aligned} \quad (4)$$

if inversion transitions only are considered. In this expression, N_{JK} is the number of molecules per unit volume in the rotational state J, K ; for the pressures and power levels used in the work to be described, it was determined entirely by the temperature, as the departure from thermal equilibrium caused by the absorption of microwave energy was insignificant. The matrix element μ_{JK} is given in terms of the permanent dipole moment μ_0 by

$$|\mu_{J,K}|^2 = \mu_0^2 \frac{K^2}{J(J+1)}. \quad (5)$$

It is assumed in equation (4) that the line-width parameter $\Delta\bar{\nu}$, and hence the collision cross section, is independent of J and K . This is not strictly true; both Birnbaum (1957), who studied absorption, and Boggs and Deam (1960), who studied

dispersion, had to assume a distribution of line widths for methyl chloride corresponding to a Cole-Cole parameter of 0.05. The value of $\Delta\bar{\nu}$ appearing in equation (4) should, therefore, correspond to a mean value averaged over all the rotational states.

Bleaney and Loubser found that their experimental results for methyl chloride and methyl bromide at pressures up to 4 and 2 atm respectively could be explained satisfactorily by this equation if it was assumed that $\Delta\bar{\nu}$ is directly proportional to the pressure. They found $\Delta\bar{\nu}/P = 0.124 \text{ cm}^{-1} \text{ atm}^{-1}$ for methyl chloride, and from this result they deduced that the collision diameter is 7.7 Å. This is considerably larger than the value of 5 Å deduced from the kinetic theory of transport phenomena; this is not surprising, since transport phenomena require strong collisions such that the mean energy transferred may be of the order of kT , while the broadening of microwave lines may be effected by much weaker collisions for which the mean energy transfer is of the order of $h\nu \ll kT$.

In the above work the contribution to α arising from transitions between rotational states was neglected. This was pointed out by Birnbaum, who estimated that at $\bar{\nu} = 0.8 \text{ cm}^{-1}$, which corresponds to the highest frequency used by Bleaney and Loubser, rotational transitions would account for 25% of the absorption found in methyl chloride at a pressure of 4 atm.

For transitions between rotational states of a symmetric-top molecule which are subject to the selection rule $\Delta J = \pm 1$, $\Delta K = 0$, the Van Vleck-Weisskopf equation gives

$$\alpha_{\text{ROT}} = \frac{4\pi^3 N \bar{\nu} \mu_0^2}{3kT Q_R} \sum_{J=0}^{\infty} \sum_{K=-J}^J \left(J+1 - \frac{K^2}{J+1} \right) \bar{\nu}_{ij} F(\bar{\nu}_{ij}, \bar{\nu}, \Delta\bar{\nu}_R) \exp\left(-\frac{W_{J,K}}{kT}\right), \quad (6)$$

where

$$W_{JK} = \frac{h^2}{8\pi^2} \left\{ \frac{J(J+1)}{I_a} + K^2 \left(\frac{1}{I_c} - \frac{1}{I_a} \right) \right\}$$

is the energy of a symmetric top rotator whose principal moments of inertia are I_a and I_c , Q_R is the rotational partition function neglecting spin degeneracy given by

$$Q_R = \sum_{J=0}^{\infty} \sum_{K=-J}^J (2J+1) \exp\left(-\frac{W_{J,K}}{kT}\right),$$

and

$$\bar{\nu}_{ij} = \frac{h}{4\pi^2 c I_a} (J+1).$$

In evaluating this expression, Birnbaum assumed the result given by Bird (1954) that $\Delta\bar{\nu}_R/P = 0.53 \text{ cm}^{-1} \text{ atm}^{-1}$ for all rotational transitions, and also that $\bar{\nu}_{ij} \gg \bar{\nu}$ for all values of J .

Birnbaum measured α for several methyl halides at pressures up to 2 atm and at frequencies in the range corresponding to $\bar{\nu} = 0.04$ to 0.78 cm^{-1} . He subtracted the calculated rotational contribution, and found that at pressures above

approximately $\frac{1}{2}$ atm his results for the absorption in methyl chloride due to inversion transitions, α_{inv} , varied with pressure in the manner predicted by equation (4). In making the comparison between experiment and theory, Birnbaum assumed that N is directly proportional to pressure; this is equivalent to assuming that methyl chloride vapour behaves as a perfect gas. From his results at 26°C for pressures between $\frac{1}{2}$ and 2 atm, he deduced that $\Delta\bar{\nu}/P = 0.115 \text{ cm}^{-1} \text{ atm}^{-1}$; this corresponds to a collision diameter of $7.2 \text{ \AA}$. Below $\frac{1}{2}$ atm, the absorption was larger than that predicted by equation (4). The discrepancy was greatest at the highest frequency used and Birnbaum attributed this to the failure of the approximation $\bar{\nu}_{ij} \gg \bar{\nu}$ used

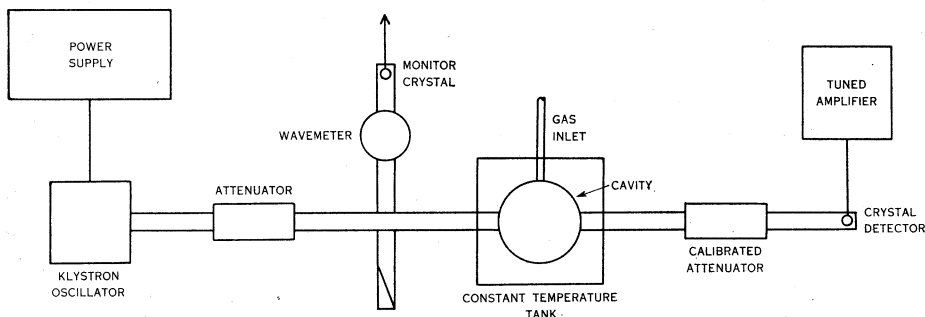


Fig. 1.—Block diagram of apparatus.

in evaluating the rotational contribution, since for methyl chloride the first line in the rotational spectrum has $\bar{\nu}_{ij} = 0.88 \text{ cm}^{-1}$ (Gordy, Simmons, and Smith 1948).

The object of the present work was to investigate further this anomalous absorption reported by Birnbaum, and to determine whether it can be attributed to the effect of rotational transitions.

EXPERIMENTAL PROCEDURE

A block diagram of the apparatus is shown in Figure 1. The klystron oscillator, whose cathode was subjected to square-wave modulation at 1000 c/s, supplied microwave energy which was transmitted through the resonant cavity using the same coupling arrangement as that of Burton *et al.* (1963). The resonant frequency of the cavity when evacuated was 9.984 Gc/s. After admission of gas, the pressure was measured with a mercury manometer and the oscillator frequency adjusted to give maximum power transmission through the cavity. The attenuator adjacent to the oscillator was adjusted to give a constant value of the power supplied to the cavity as measured by the monitor crystal, and the calibrated attenuator was then adjusted to give a fixed value of transmitted power as measured by the crystal detector and tuned amplifier. The reading of the calibrated attenuator was then plotted as a function of gas pressure and the absorption coefficient at any pressure found from the relation

$$\alpha = \frac{2\pi\bar{\nu}}{Q_0} \left\{ \text{antilog}_{10} \frac{\Delta \text{db}}{20} - 1 \right\},$$

where $Q_0 = 23300$ is the Q -value of the evacuated cavity and Δdb the difference

in decibels between the settings of the calibrated attenuator with and without gas in the cavity. This method of measuring α does not involve any assumptions about crystal characteristics, since power levels are adjusted to give the same crystal current for each pressure.

Measurements were made with methyl chloride at 33.7°C and at pressures up to 2 atm. The number of molecules per unit volume, N , was determined from Avogadro's number N_0 and the pressure P by using the relation

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

where the virial coefficient B was taken from the paper of Fogg, Hanks, and Lambert (1953) to be $-415 \text{ cm}^3/\text{mole}$.

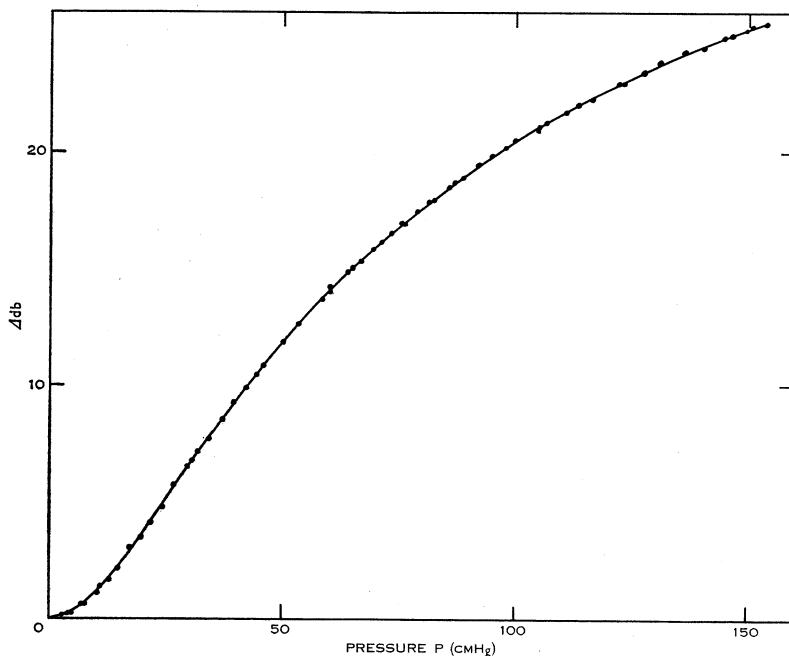


Fig. 2.—Attenuation Δdb versus pressure P .

RESULTS AND DISCUSSION

Experimental values of Δdb versus pressure P are plotted in Figure 2, and the corresponding graph of α versus N^2 is shown in Figure 3. The measured value of α will be the sum of the contributions due to inversion transitions α_{inv} and that due to rotational transitions α_{ROT} . The latter was found by evaluating equation (6) with a GE 225 computer, assuming that $\Delta \bar{\nu}_R/P = 0.53 \text{ cm}^{-1} \text{ atm}^{-1}$ and $\bar{\nu}_{ij} = 0.88(J+1) \text{ cm}^{-1}$. The results of these calculations are shown in Figure 4, and it is seen that α_{ROT} rises almost linearly with N^2 .

In order to compare the experimental results with the Van Vleck-Weisskopf theory for absorption due to inversion transitions, it is convenient to write equation (4) in the form

$$\frac{N^2}{a_{\text{inv}}} = \frac{\bar{\nu}^2}{AB} + \frac{B}{A} N^2, \quad (7)$$

where

$$A = \frac{8\pi^2 \bar{\nu}^2}{3kT} \sum_{J,K} |\mu_{JK}|^2 \frac{N_{JK}}{N},$$

$$B = \Delta \bar{\nu} / N.$$

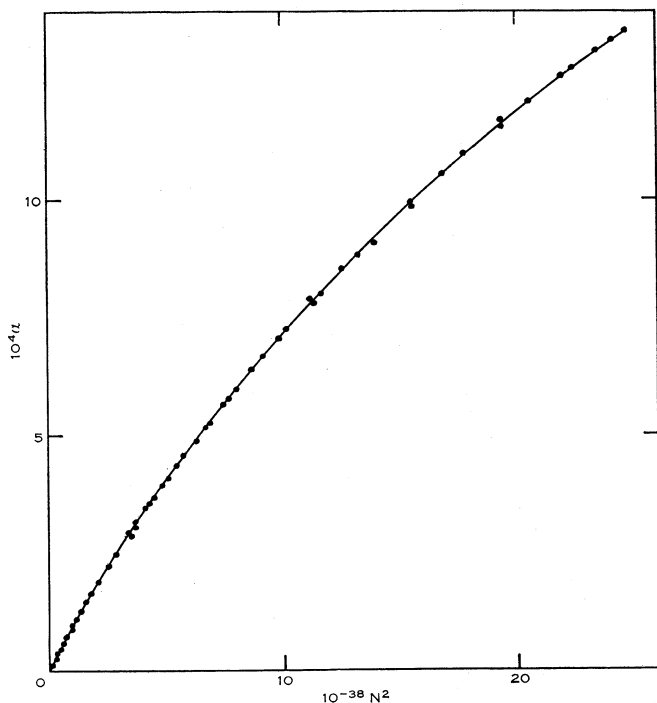


Fig. 3.—Power absorption coefficient a versus N^2 .

From this it follows that if $\Delta \bar{\nu} \propto N$, so that B as well as A is constant, the graph of N^2/a_{inv} versus N^2 should be linear. Results are shown in Figure 5. There is general agreement with the results obtained at 9.280 Gc/s by Birnbaum in that N^2/a_{inv} increases approximately linearly with N^2 for pressures between roughly $\frac{1}{2}$ and 2 atm, and that deviations from the straight line occur for lower pressures.

In order to determine whether the experimental technique was giving rise to spurious absorption at low pressures or leading to an over-estimate of the absorption at high pressures, measurements were made first with carbon dioxide and later with helium at pressures up to 4 atm; in the former case, the resulting change in the resonant frequency of the cavity was of the same order as that produced by $\frac{1}{2}$ atm

of methyl chloride. No significant absorption was observed in either case, and so it is concluded that the deviation from linearity in Figure 5 cannot be due to experimental error.

It was pointed out by Birnbaum that the departure from linearity in the low pressure region could be explained if α_{ROT} rises less rapidly than N^2 ; in his calculations of α_{ROT} he assumed that $\bar{\nu}_{ij} \gg \bar{\nu}$ for all rotational transitions, and suggested that the contribution from the few transitions for which this is not valid might be responsible for the observed effect. In the evaluation of α_{ROT} reported in the present paper no such approximation was made, and it is apparent that the deviation from linearity in Figure 5 is not due to an error in the evaluation of the rotational contribution. This was tested further by evaluating equation (6) on the assumption that Bird's value for $\Delta\bar{\nu}_R/P$ is incorrect; values of 1.06 and 1.59 $\text{cm}^{-1} \text{ atm}^{-1}$ were

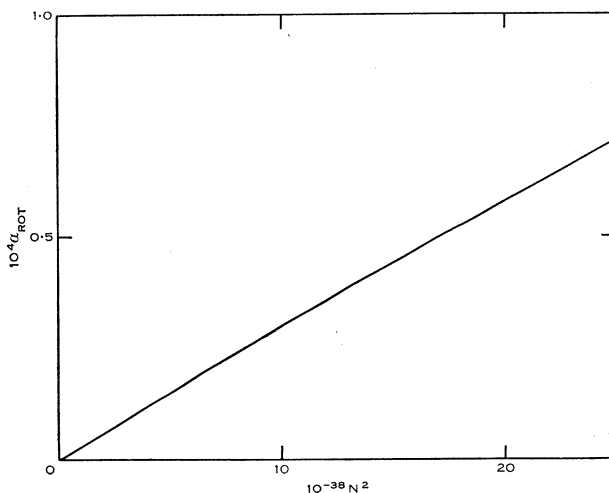


Fig. 4.—Absorption due to rotational transitions α_{ROT} , calculated from (6), versus N^2 .

also tried. However, the resulting graphs of $N^2/(\alpha_{\text{exp}} - \alpha_{\text{ROT}})$ versus N^2 , α_{exp} being the measured value of α , were very similar in shape to that of Figure 5 and were definitely non-linear.

A modified form of the Van Vleck-Weisskopf equation has been derived by Anderson (1949); it includes the possibility of a change in the natural frequency of a transition as the pressure is increased. The resulting expression for the absorption is similar to that given by equation (1), but equation (2) is replaced by

$$F(\bar{\nu}_{ij}, \bar{\nu}, \Delta\bar{\nu}) = \frac{1}{\pi} \frac{\bar{\nu}}{\bar{\nu}_{ij}} \left\{ \frac{\Delta\bar{\nu}}{(\bar{\nu} - \bar{\nu}_{ij} - a\Delta\bar{\nu})^2 + (\Delta\bar{\nu})^2} + \frac{\Delta\bar{\nu}}{(\bar{\nu} + \bar{\nu}_{ij} + a\Delta\bar{\nu})^2 + (\Delta\bar{\nu})^2} \right\},$$

where the wave-number change $a\Delta\bar{\nu}$ is expected to be small for microwave absorption. If it is assumed that both $a\Delta\bar{\nu}/\bar{\nu}$ and $(\Delta\bar{\nu})^2/\bar{\nu}^2$ are small compared with unity, which should certainly be true in the present work at pressures up to 1 atm, equation (7)

must be replaced by

$$\frac{N^2}{a} \simeq \frac{\bar{\nu}^2}{AB} + \frac{B}{A}(1-3a^2)N^2 + \frac{4a^2(a^2+1)B^3}{A\bar{\nu}^2}N^4,$$

where A and B have the same significance as before. Since the coefficient of N^4 is positive, any deviation from linearity in the N^2/a versus N^2 graph should therefore be in the direction of increasing N^2/a ; this is in the opposite direction to the behaviour observed, which is shown in Figure 5, so that the non-linearity cannot be attributed to a change in the already low natural frequency of the inversion transition.

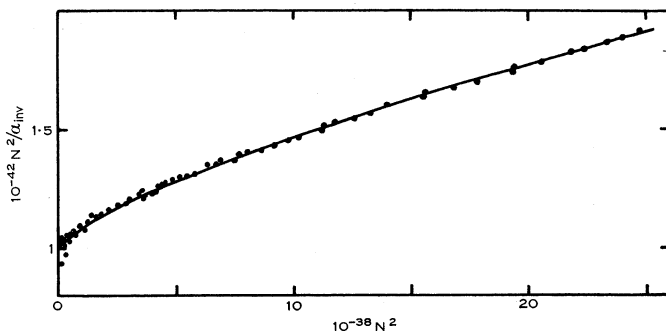


Fig. 5.— N^2/a_{inv} versus N^2 . The experimental points were found by subtracting the calculated values of a_{ROT} from the measured absorption a to give a_{inv} . The full curve is a graph of equation (10) using the parameters given in the text.

It was pointed out by Bleaney and Loubser in their work on ammonia that as the pressure is increased $\Delta\bar{\nu}$ should not rise quite linearly with N if three-body collisions occur. If, while a radiating or absorbing molecule is interacting with one of its neighbours it is struck by a third molecule, the latter does not contribute to the line width since the radiation has already been interrupted. Bleaney and Loubser derived the relation

$$\Delta\bar{\nu} = B(1-\beta N)N, \quad (8)$$

where

$$\beta = \frac{4}{3}\pi b^3, \quad (9)$$

b being the collision diameter. If (8) is substituted into equation (7) and if $\beta N \ll 1$, the latter becomes

$$\frac{N^2}{a} = \frac{\bar{\nu}^2}{AB}(1+\beta N) + \frac{B}{A}(1-\beta N)N^2, \quad (10)$$

where A and B are constants as before. As can be seen from Figure 5, an equation of this form is in good agreement with the experimental results. The following values of the parameters were found to give the best fit: $\bar{\nu}^2/AB = 10^{42}$, $B/A = 356$,

and $\beta = 5.6 \times 10^{-21}$. This gives $B = 6.28 \times 10^{-21}$ and it follows from the equation used by Bleaney and Loubser,

$$b^2 = \frac{1}{2} Bc \left(\frac{\pi M}{RT} \right)^{\frac{1}{2}},$$

that the collision diameter b is $8.6 \text{ \AA}$. This is significantly larger than the figure of $7.2 \text{ \AA}$ deduced by Birnbaum, who neglected the effect of three-body collisions. Using $\beta = 5.6 \times 10^{-21}$ the probability of a molecule actually being in collision with one of its neighbours when it is struck by a third is found to be twice as large as that calculated from equation (9) using $b = 8.6 \text{ \AA}$. In view of the rather naive assumptions involved in the derivation of (9), this measure of agreement is regarded as satisfactory.

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