COLLISION BROADENING OF THE MICROWAVE SPECTRUM OF METHYL CHLORIDE BY HYDROGEN AND ARGON AT PRESSURES UP TO 100 ATMOSPHERES

By R. W. Parsons,* C. H. Burton,*† and W. B. Lasich*

Summary

Measurements are reported of the absorption of microwaves with frequencies in the range 9·65–9·92 Gc/s by binary mixtures of methyl chloride with hydrogen and argon at pressures up to 100 atm. The results are interpreted in terms of the collision broadening of the inversion and rotational spectra of methyl chloride by the foreign gases. Reasonable agreement between experiment and the Van Vleck and Weisskopf theory of collision broadening is found in the case of hydrogen and the collision diameter for broadening of the rotational lines by hydrogen is found to be approximately 2·7 Å. For methyl chloride–argon mixtures the agreement is far less satisfactory and it appears that the theory requires modification.

I. Introduction

The absorption of microwaves of frequency 9·983 Gc/s by pure methyl chloride at pressures up to 2 atm has been discussed in a previous paper (Burton *et al.* 1964*a*); this will be referred to as paper I. The results were interpreted in terms of the theory of Van Vleck and Weisskopf (1945) for the collision broadening of spectral lines, and satisfactory agreement between theory and experiment was obtained by considering the effect of three-body as well as two-body collisions. This work has now been extended and measurements have been made of the absorption by small quantities of methyl chloride in both hydrogen and argon at pressures up to 100 atm; under these conditions, broadening of the spectral lines of methyl chloride should be due almost entirely to collisions between molecules of methyl chloride and those of the foreign gas. Such measurements are of interest since they provide a further test of the theory, and should also enable an estimate to be made of the collision diameter for broadening of the rotational spectral lines of methyl chloride by hydrogen and argon.

II. Experimental Procedure

The method used was similar to that described in paper I, but the extension to high pressures introduced some complications. A block diagram of the apparatus is shown in Figure 1, and a drawing of the resonant cavity in Figure 2. Although tunable cavities have been used for pressures up to 100 atm (Bussey and Birnbaum 1959), their construction is difficult, and for the present work a cavity of fixed dimensions was used. It was machined from a 5 in. diameter brass rod and, after being silver-plated, was coated with "Forminex" to prevent any chemical attack on the

* Department of Physics, University of Queensland, Brisbane.

† Present address: National Standards Laboratory, CSIRO, Chippendale, N.S.W.

silver. It was operated in the TE_{013} mode and when evacuated had a resonant frequency of $9 \cdot 921$ Gc/s. Two grooves, each $\frac{1}{8}$ in. wide and $\frac{1}{4}$ in. deep, were machined in the walls to remove the degeneracy of the TE and TM modes, and the gases were
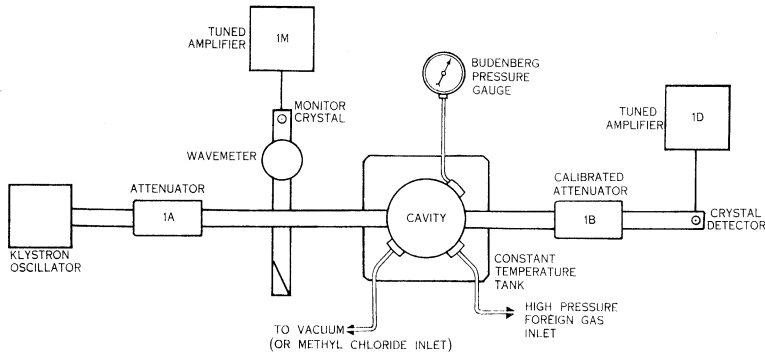

Fig. 1.—Block diagram of the apparatus.

admitted through $\frac{1}{8}$ in. diameter holes leading into these grooves. High pressure taps were mounted directly on the outside of the cavity so that the volume of the tubing between the taps and the cavity was kept to a minimum; this was important since the gases were mixed in the cavity and unnecessarily long lengths of tubing
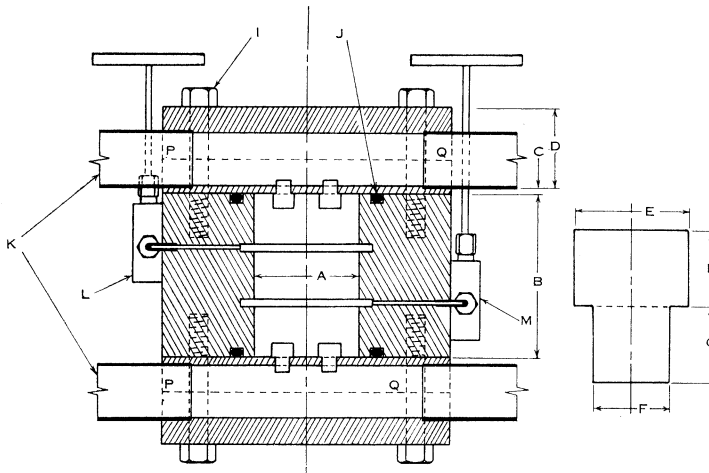

Fig. 2.—High pressure resonant cavity. Cavity diameter A = $1 \cdot 842$ in.; cavity length B = $2 \cdot 84$ in.; face thickness C = $\frac{1}{8}$ in.; end-plate thickness D = $1\frac{1}{2}$ in.; plug-head diameter E = $\frac{3}{8}$ in.; plug diameter F = $0 \cdot 254$ in.; plug length G = $\frac{1}{4}$ in.; plug-head length H = $\frac{1}{4}$ in.; I, $\frac{5}{16}$ in. diameter high tensile bolts (12 per end plate); J, VOR 160 O-ring; K, x-band waveguide soldered into end plate; L, M, "Autoclave" high pressure taps, type 10 V–2001 (the third tap is not shown). Each end plate was made in two sections, which were soldered together along the surfaces PQ.

would have introduced regions where mixing by diffusion would be very protracted. The cavity was mounted in an oil bath whose temperature was controlled to $\pm 0 \cdot 01$ degC, and the measurements were made at $33 \cdot 7°C$.

Microwave energy was coupled in at one end and out at the other using the two-hole coupling technique of Bleaney, Loubser, and Penrose (1947). The coupling holes had a diameter of $0\cdot250$ in. and were filled by "Teflon" plugs as shown (Fig. 2); the plug diameter was $0\cdot254$ in., and the plugs were shrunk in liquid air before being inserted. Identical plugs were tested under hydrostatic pressure to 3000 lb/in^2 for a continuous period of 10 days; in this time, the end face of the plug-head deformed slightly but there was no failure. At 1600 lb/in^2 there was no observable deformation.

The frequency-stabilized klystron was on-off cathode modulated at 1000 c/s, and its frequency could be adjusted to give maximum power transmission through the cavity as measured by the crystal and the tuned amplifier 1D (Fig. 1). This was first done with the cavity evacuated, and the readings of 1D and the monitor 1M were noted. Methyl chloride was admitted to a pressure that was read on a mercury manometer, and then either hydrogen or argon was admitted. After mixing had occurred, the tap to the 12 in. Budenberg pressure gauge was opened; this gave a full-scale deflection for 3000 lb/in^2 and was never used above 1600 lb/in^2. A calibration certificate to ±5 lb/in^2 was supplied by the manufacturers. The composition of the gas mixture was deduced from the pressure measurements and the virial coefficients of hydrogen and argon; the latter were taken from the data of Condon and Odishaw (1958).

With gas in the cavity, the klystron frequency was adjusted to give maximum power transmission through the cavity, and the attenuators 1A and 1B were adjusted to give the same readings on 1M and 1D as had been noted with the cavity evacuated. From the change of the reading of the calibrated attenuator 1B, the attenuation due to the gas was found. The pressure was then reduced to zero in steps of approximately 100 lb/in^2, and for each pressure the attenuation was measured.

A cavity of fixed dimensions, while simpler to construct than a tunable one, suffers from the disadvantage that its resonant frequency, which depends on the dielectric constant of the gas within it, cannot be kept constant when the gas pressure is changed. In the present work, the resonant frequency changed from $9\cdot921$ to $9\cdot65$ Gc/s, and over this range there was a significant change in the monitor and detector characteristics. Since matched crystals were not available, the apparatus was calibrated with argon and checked with hydrogen; for both of these gases Birnbaum and Maryott (1962) found that the imaginary part of the dielectric constant at pressures up to 100 atm is less than 2×10^{-7}, and hence they can be considered as non-absorbing for the present work.

The power absorption coefficient α was found from the expression

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

where $\bar{\nu}$ is the wave number at the frequency of the measurement, Δdb the corrected change in the reading of the calibrated attenuator 1B, and Q_0 the Q-value of the cavity when filled with a non-absorbing gas so that it resonates at a frequency $c\bar{\nu}$. The Q also changed significantly over the frequency range used, primarily because the coupling from waveguide to cavity and vice versa is frequency dependent, and at lower frequencies less power is able to leave the cavity and be dissipated externally.

It was measured at six frequencies in the range $9 \cdot 921$–$9 \cdot 696$ Gc/s using the technique described by Burton *et al.* (1964*b*); the measurements were made by filling the cavity with argon to enable it to resonate at the desired frequency. The Q changed approximately linearly with frequency from $19\,400$ at $9 \cdot 921$ Gc/s to $20\,400$ at $9 \cdot 696$ Gc/s.

Nine mixtures of methyl chloride with hydrogen and ten with argon were measured. The mix ratio M, defined as the relative number of foreign gas molecules per unit volume to those of methyl chloride, varied from $57 \cdot 1$ to 233 in the case of hydrogen and from $53 \cdot 4$ to 393 for argon. In addition, measurements were made with pure methyl chloride at pressures up to 2 atm and these were in good agreement with the measurements reported in paper I.

III. Results and Discussion

According to the theory of Van Vleck and Weisskopf (1945), the absorption coefficient should be given by

$$\alpha = \Sigma \, \alpha_{ij}, \tag{2}$$

where the contribution α_{ij} arising from transitions of the methyl chloride molecule from an initial state i to a final state j is given by

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

where

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

In this expression, N_i is the number of methyl chloride molecules per unit volume in the state i, $\bar{\nu}$ the wave number of the radiation being absorbed, $\bar{\nu}_{ij}$ the natural wave number associated with the transition, μ_{ij} the dipole-moment matrix element for the transition, and $\Delta\bar{\nu}_{ij}$ the line-width parameter. This latter quantity is related to the mean time interval τ_{ij} between collisions resulting in the transition ij by the equation

$$\Delta\bar{\nu}_{ij} = 1/2\pi c \tau_{ij}. \tag{4}$$

For sufficiently low pressures, $\Delta\bar{\nu}_{ij}$ should vary linearly with the number of methyl chloride molecules per unit volume N, but this will not be the case if other than two-body collisions occur. Under these conditions the form of the relation between $\Delta\bar{\nu}_{ij}$ and N may be found from the following simple argument. Suppose that only interactions involving the transition ij are considered and that the methyl chloride molecule has a region of influence of volume v_{ij}; the molecule will be in a state of collision if it has one or more neighbours within this region. If, because of the large value of M, broadening is entirely due to collisions between methyl chloride and molecules of the foreign gas, it follows that the probability that at a given instant a particular methyl chloride molecule will be in a state of collision is

$$P_{ij} = 1 - (1 - v_{ij})^n,$$

where n is the number of foreign gas molecules per unit volume. Hence, if the mean duration of a collision is T_{ij}, the mean number per second will be

$$1/\tau_{ij} = P_{ij}/T_{ij}.$$

It follows from (4) that

$$\Delta\bar{\nu}_{ij} \simeq B_{ij}\,n\left(1 - \frac{1}{2!}\,n v_{ij} + \frac{1}{3!}\,n^2 v_{ij}^2 - \ldots\right), \tag{5}$$

where

$$B_{ij} = v_{ij}/2\pi c T_{ij}.$$

This is similar in form to equation (8) of paper I, although for the pressures used in that work only two terms in the expansion for $\Delta\bar{\nu}_{ij}$ were considered.

On writing $N = n/M$ and substituting (5) and (3) into (2), the latter equation becomes, on rearranging,

$$M\alpha = \frac{8\pi^2 n^2 \bar{\nu}^2}{3hc} \sum B_{ij} f_i \, \Phi_{ij}(n)/\bar{\nu}_{ij}, \tag{6}$$

where f_i is the fraction of methyl chloride molecules in the state i, and $\Phi_{ij}(n)$ is a function of n that does not involve M. It follows that for sufficiently large values of M the relation between $M\alpha$ and n should be independent of the mix ratio M. This is in general agreement with the experimental results, which are plotted in Figures 3 and 4 for mixtures of methyl chloride with hydrogen and argon respectively. In each of these figures, however, the scatter of the points is considerably greater than would be expected from an analysis of the errors involved in the microwave measurements and may be due to errors in the estimation of M for the various mixtures used.

At 10 Gc/s the only transitions that make a significant contribution to the sum of equation (6) are those corresponding to inversion or to changes in the rotational states of the molecules; the vibrational spectral lines of methyl chloride have natural frequencies very much above the microwave region and so their contributions may be neglected. For the inversion transition, $\bar{\nu}_{ij} \approx 0$, and so from (2) and (3) the contribution to the absorption is

$$\alpha_{\mathrm{inv}} = \frac{8\pi^2 \bar{\nu}^2}{3kT} \sum_{JK} N_{JK} |\mu_{JK}|^2 \frac{\Delta\bar{\nu}_{JK}}{\bar{\nu}^2 + (\Delta\bar{\nu}_{JK})^2}, \tag{7}$$

where μ_{JK} is related to the permanent dipole moment μ_0 by

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

The sum in equation (7) extends over all the rotational states J, K, since molecules in any of these states can undergo inversion. Experiments at pressures up to several atmospheres by Birnbaum and Maryott (1964) and also unpublished work in this laboratory suggest that $\Delta\bar{\nu}_{JK}$ depends on the values of J, K; this implies that the collision diameter for broadening of the inversion spectrum depends on the rotational state of the molecules. Thus Birnbaum and Maryott found that their results for

mixtures of methyl chloride with several non-polar gases could be interpreted in terms of the semi-empirical equation of Cole and Cole (1941), which may be put in the form

$$\alpha_{inv} = \frac{\frac{1}{2}A \cos \frac{1}{2}c\pi}{\cosh\{(1-c)\ln(\bar{\nu}/\Delta\bar{\nu})\} + \sin \frac{1}{2}c\pi}, \qquad (8)$$

where

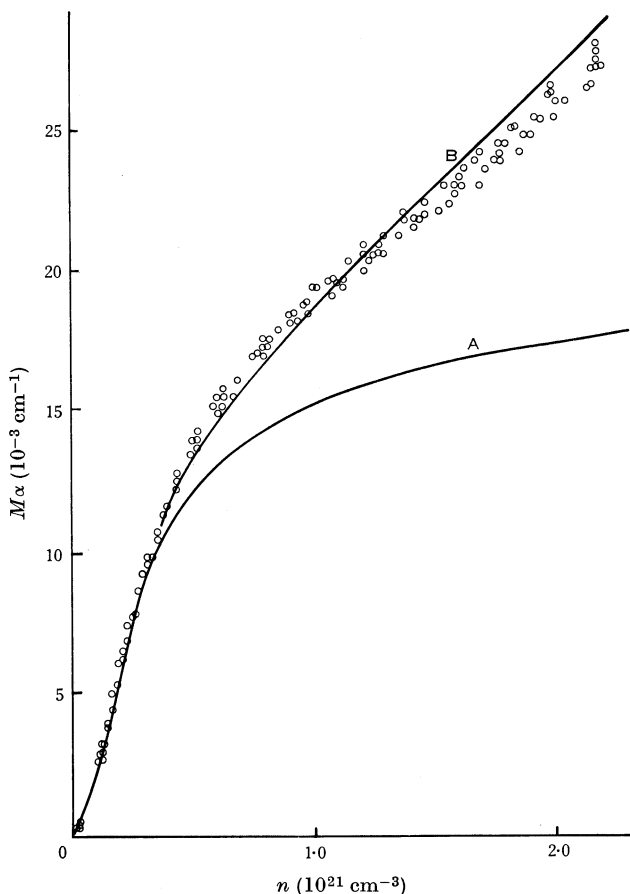$$A = \frac{8\pi^2 \bar{\nu}}{3kT} \sum_{JK} N_{JK} |\mu_{JK}|^2,$$

Fig. 3.—$M\alpha$ versus n for hydrogen.   Curve A shows the inversion contribution calculated from equation (8), and curve B the calculated values of $M(\alpha_{inv} + \alpha_{rot})$, using $b_{inv} = 2\cdot 2$ Å and $b_{rot} = 2\cdot 7$ Å.

c is the Cole–Cole line-width dispersion parameter, and $\Delta\bar{\nu}$ the mean value of $\Delta\bar{\nu}_{JK}$. If $c = 0$, indicating no dispersion, equation (8) reduces to (7) when $\Delta\bar{\nu}_{JK}$ in the latter is replaced by $\Delta\bar{\nu}$; however, Birnbaum and Maryott found that their results required c to have the value $0\cdot 05$.

Values of $M\alpha_{inv}$ calculated from equation (8) are plotted against n in Figures 3 and 4. Following equation (5), values of $\Delta\bar{\nu}$ used in these calculations were found from the equation

$$\Delta\bar{\nu} = Bn\left\{1 - \frac{1}{2!}\,nv + \frac{1}{3!}\,n^2v^2 - \ldots\right\}$$
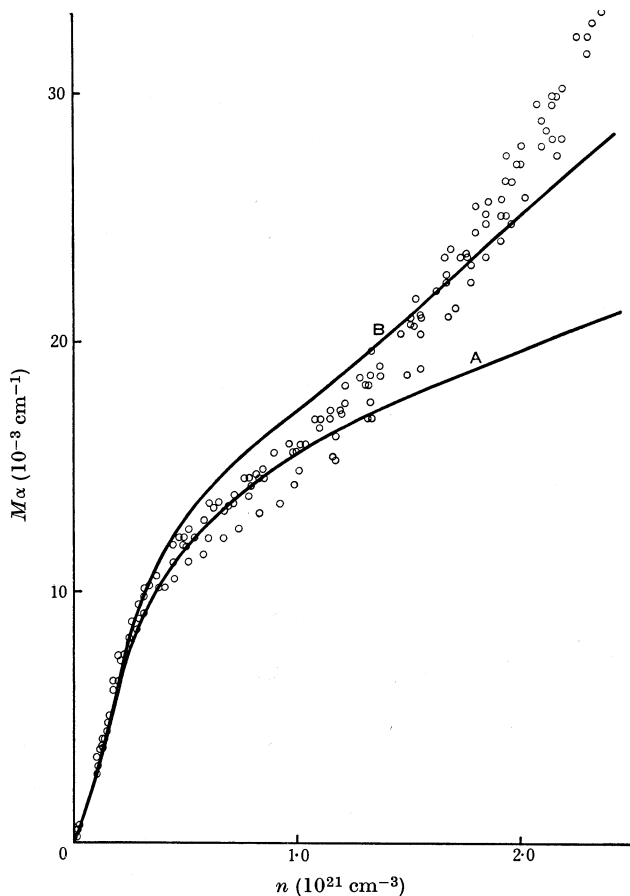
$$= \frac{B}{v}\{1 - \exp(-nv)\}. \tag{9}$$

Fig. 4.—$M\alpha$ versus n for argon. Curve A shows the inversion contribution calculated from equation (8), and curve B the calculated values of $M(\alpha_{inv} + \alpha_{rot})$, using $b_{inv} = 4\cdot3$ Å and $b_{rot} = 5$ Å.

In evaluating this expression the values of B used were $1\cdot45 \times 10^{-21}$ and $1\cdot67 \times 10^{-21}$ cm^2 for the mixtures with hydrogen and argon respectively; these correspond to collision diameters b_{inv} for broadening of the inversion spectrum of $2\cdot2$ and $4\cdot3$ Å respectively. The volume v was assumed to be $4\pi b_{inv}^3/3$; this can only be a

rough approximation since the interactions involved are presumably of the dipole induced-dipole type, and the dipole field is not spherically symmetrical. It is seen, however, that this equation is in good agreement with the experimental data up to 15 atm; at higher pressures the measured absorption rises more rapidly and this is presumably due to the contribution from rotational transitions.

For the power levels used in the present work the departure from thermal equilibrium is negligible and so the numbers of molecules N_{JK} in the various rotational states may be found from Boltzmann statistics. Rotational transitions must satisfy the selection rules $\Delta K = 0$, $\Delta J = \pm 1$ and under these conditions equations (2) and (3) give, for the rotational contribution to $M\alpha$,

$$M\alpha_{\text{rot}} = \frac{8\pi^2\mu_0^2 n\bar{\nu}^2}{3kTQ_{\text{r}}} \sum_{J=0}^{\infty} \sum_{K=-J}^{J} \left(J+1-\frac{K^2}{J+1}\right) F(\bar{\nu},\bar{\nu}_{ij},\Delta\bar{\nu}_{ij})\exp\left(-\frac{W_{JK}}{kT}\right), \quad (10)$$

where

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

$$\bar{\nu}_{ij} = \frac{h}{4\pi^2 cI_{\text{a}}}(J+1),$$

and W_{JK} is given in terms of the principal moments of inertia I_{a} and I_{c} of the methyl chloride molecule by

$$W_{JK} = \frac{h^2}{8\pi^2}\left\{\frac{J(J+1)}{I_{\text{a}}} + K^2\left(\frac{1}{I_{\text{c}}}-\frac{1}{I_{\text{a}}}\right)\right\}.$$

In equation (10), $\Delta\bar{\nu}_{ij}$ is the line width for the transition $J+1 \to J$. In the absence of any experimental data on the foreign gas broadening of the rotational spectrum of methyl chloride, it was assumed that there is no dispersion of rotational line-width parameters, i.e. that the relation between $\Delta\bar{\nu}_{ij}$ and n is independent of the rotational states involved. $M\alpha_{\text{rot}}$ was then evaluated as a function of n with a GE225 computer, using values of B and v in equation (9) corresponding to various collision diameters b_{rot}. These calculated values of $M\alpha_{\text{rot}}$ were then added to the values of $M\alpha_{\text{inv}}$ calculated from equation (8) and the resulting values of $M(\alpha_{\text{inv}}+\alpha_{\text{rot}})$ were compared with the experimental values of $M\alpha$. It is seen from Figure 3 that reasonable agreement between the calculated and experimental values for hydrogen is obtained if $b_{\text{rot}} = 2\cdot7$ Å. This can be compared with the kinetic value of $3\cdot5$ Å; it is not surprising that it is much smaller than the value of $16\cdot1$ Å found by Bird (1954) for self-broadening of the rotational spectrum since the dipole–dipole forces involved in self-broadening will have a much longer range than the induced dipole interactions responsible for broadening by hydrogen.

It was not possible to find a value of b_{rot} that would bring the calculated values of $M(\alpha_{\text{inv}}+\alpha_{\text{rot}})$ into agreement with the experimental values for argon. In view of the fairly satisfactory agreement for hydrogen it seems unlikely that the argon discrepancy is due to a dispersion of the rotational line-width parameters. This is also supported by the work of Plyler and Thibault (1962), who studied foreign gas broadening of the infrared spectrum of hydrogen chloride and found that the line-

width parameter decreased with increasing J. If this is also true for methyl chloride, transitions between states of high J would give a smaller contribution than that calculated. These transitions, however, make their maximum contribution when the pressure is sufficiently high to broaden their lines significantly into the microwave region, and hence the net effect would be to make the agreement between experiment and theory even worse. It seems more likely that the Van Vleck–Weisskopf expression is not valid at the higher pressures used. One of the assumptions of this theory is that the duration of the collisions is small compared with the mean interval between collisions. The duration will depend on the collision diameter, and hence if this is smaller for hydrogen than for argon it would be expected that the theory would fail at lower pressures for argon than for hydrogen. This appears to be substantiated by the present work.

IV. ACKNOWLEDGMENTS

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