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Collision induced absorption in CO₂ at 0.091 cm⁻¹ (*)

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Résumé. — On étudie l'absorption induite par collisions à 0,091 cm⁻¹ et 293 K, jusqu'à la densité de 60 amagat. En exprimant les pertes diélectriques ε'' sous la forme $\varepsilon'' = A\nu\rho^2(1 - B\rho)$, ν étant la fréquence en cm⁻¹ et ρ la densité, nous trouvons $A = 0,22 \times 10^{-7}$ (cm.amagat⁻²) et $B = 0,0082$ (amagat⁻¹). A la suite de cette étude, le moment quadrupolaire de la molécule CO₂ est calculé et trouvé égal à $5,6 \times 10^{-26}$ (esu).

Abstract. — Collision induced microwave absorption has been studied at 0.091 cm⁻¹ and 293 K up to 60 amagat density. Expressing the dielectric loss ε'' in the form $\varepsilon'' = A\nu\rho^2(1 - B\rho)$, where ν is the frequency in cm⁻¹ and ρ is the density, we find $A = 0.22 \times 10^{-7}$ (cm.amagat⁻²) and $B = 0.0082$ (amagat⁻¹). As a result the molecular quadrupole moment of CO₂ is calculated to be 5.6×10^{-26} (esu).

1. Introduction. — Weak absorption in the non-dipolar gas CO₂ has been previously reported in the microwave region [1-6]. For gases with substantial molecular electric quadrupole moments, such as CO₂, this absorption would be expected to be due to dipoles induced by the quadrupole field. The comparatively long-range and angular dependence of the quadrupole field make its moment an important parameter in the molecular description of various physical properties and processes. It was therefore suggested that the study of the microwave losses in CO₂ might provide a sensitive method of obtaining information on the quadrupole moments and their effects.

Previous results on CO₂ in the microwave region lie between 0.3 cm⁻¹ and 4.6 cm⁻¹. In the present work, absorption measurements are presented at a lower frequency, that is 0.091 cm⁻¹ or 2.7 GHz. The extension of the measurements to such a low frequency point is interesting for two reasons : first, in the interpretation of collision-induced absorption in non-dipolar gases it is important to have available and absorption spectrum as complete as possible [5]. Furthermore, as has been shown for various gases, it is important to maintain accuracy at very low frequencies, since the zeroth moment of the spectrum approaches a maximum value in the region below 5 cm⁻¹ [6-8]. On the other hand, measurements at

lower microwave frequencies become progressively difficult, because the loss tangent decreases almost linearly with the frequency.

2. Experimental method. — Extremely small absorptions of electromagnetic energy in gases can be detected and measured by the use of a high Q resonant cavity [9]. Changes in the quality factor Q , due to the presence of a gas in the cavity, can be related to the loss factor, $\tan \delta$, where the gas is treated as a dielectric of complex dielectric constant $\varepsilon = \varepsilon' - j\varepsilon''$, giving $\tan \delta = \varepsilon''/\varepsilon'$. Such a very sensitive cavity method has been used in the present absorption measurements. First, the resonant cavity is filled with the low-loss gas under study and its quality factor Q is measured. Then, a reference loss-less gas is substituted at a pressure which gives the same resonant frequency and Q_r is also measured. The loss tangent of the low-loss gas is : $\tan \delta = (1/Q) - (1/Q_r)$. Note that it is not necessary to measure the unloaded Q of the cavity [10, 11].

The schematic diagram of the measuring system is shown in figure 1. The microwave source is Systron-Donner's sweep generator. The resonant curve was obtained by manually sweeping the generator. The Q 's were measured on a precision digital voltmeter. Since in CO₂ ε'' depends linearly on frequency at 0.091 cm⁻¹, it is very difficult to measure any losses. To overcome this, first some modifications were made

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Fig. 1. — Simplified block diagram of the measuring system. MSG : microwave sweep generator, M : CRT monitor, C : cavity, B : pressure bomb, D : detector, A : attenuator, DV : digital voltmeter, DFM : digital frequency meter, G : gas inlet.

to improve the fine frequency tuning of the generator. Second, an indirect method for measuring frequencies was used : the voltage V_f , which is proportional to the signal frequency, was measured with the same voltmeter. Then, the system was calibrated (switches of figure 1 in position 2) using a precision digital frequency meter.

A cylindrical copper cavity was used (with $Q \approx 1\,200$) totally enclosed in a pressure vessel to eliminate the pressure dependence of the Q measurements. The sensitivity of the system, given by the minimum $\tan \delta$ which is effectively measurable, is 10^{-7} . As a reference gas we used Ar. Both Ar and CO_2 commercially available are with a purity of 99.998 %. Pressure measurements were taken with a Bourdon gauge. All measurements were taken at room temperature (20 °C).

3. Results and discussion. — The results for collision-induced absorption in pure CO_2 at 293 K are shown in figure 2, in which ϵ'' is plotted against the density ρ in amagats. Each point corresponds to the average of three measurements. An accurate method for calculating the density of a non-dipolar gas is the use of the virial expansion of the Clausius-Mossotti function [5, 2]. This method is widely applicable in microwave measurements since $\tan \delta$ and ϵ' can be measured simultaneously. The dielectric virial coefficients for the Clausius-Mossotti function we used were obtained from the experimental work of Bose and Cole [12]. The solid line shown in figure 2 is the best fit to the present data and may be expressed as :

Fig. 2. — A plot of ϵ'' versus the density ρ for pure CO_2 . Present results at 2.7 GHz are indicated by 'x' s. Numbers in parentheses indicate plots of the corresponding relations in the text.

$$\epsilon''_{293} = 0.22 \times 10^{-7} \nu \rho^2 (1 - 0.0082 \rho) \quad (1)$$

where ν is the frequency in cm^{-1} and ρ the density in amagats. From the work of Ho *et al.* [2] at 0.3 cm^{-1} (9.26 GHz) and at various temperatures one obtains :

$$\epsilon''_{293} = 0.20 \times 10^{-7} \nu \rho^2 (1 - 0.0089 \rho) \quad (2)$$

Also the work of Dagg *et al.* [6] at 2.3 cm^{-1} (70 GHz) gives :

$$\epsilon''_{293} = 0.14 \times 10^{-7} \nu \rho^2 (1 - 0.0027 \rho) \quad (3)$$

(2) and (3) are plotted in figure 2 with dotted and dashed lines respectively.

There is a more quantitative agreement between relation (2) and our results, even though the latter are 12-18 % greater in the region of the pressures that the measurements have been done. Relation (3) gives closest values to the measurements of this work at about 55 amagat, but increases substantially at higher densities. There is a number of systematic errors which can affect measurements of the present kind, but we believe that they can't account for this discrepancy.

Since CO_2 is a symmetric linear molecule, it has no dipole moment. In spite of this it has the capability to absorb the microwave energy at medium and at high pressures. This is due to the fact that CO_2 has a considerable permanent quadrupole moment. The intermolecular forces of two closest molecules during a binary collision can induce a transient dipole moment. Such transient dipoles are responsible for the observed absorption [13]. The selection rule

for the rotational transitions is $\Delta J = \pm 2$. The frequencies for the rotational lines are then given, to a good approximation, by : $\nu_{J,J+2} = 4B(J + 3/2)$. For CO₂, $B = 11.79$ GHz, so the rotational transition frequencies are 70.74 GHz, 117.9 GHz, 165.06 GHz and so on. In addition to the rotational lines, transitions may exist for $\Delta J = 0$. These give rise to a translational absorption, which is non-resonant or Debye type [14]. Computations for CO₂ indicate that the non-resonant component of the absorption is the most significant compared to the rotational contribution at low frequencies [15].

Maryott and Birnbaum [1] have examined in an approximate way the absorptivity of a gas consisting of quadrupolar molecules by constructing a simple model. They assumed that the molecules move along straight-line trajectories. As one molecule passes another the quadrupolar fields induce a net dipole in the pair. By Fourier analysing the pulse and averaging over all impact parameters, they obtain a line-shape for the absorption. Also one can find a quantum theory encompassing both translational and rotational bands which gives relatively simple results in closed form in [16].

Using their expression for the translational line-shape and Lennard-Jones 6-12 potential, Birnbaum and Maryott obtained a simple formula for the calculation of the molecular electric quadrupole moment from microwave collision-induced absorption measurements [17]. (This method is referred as B-M method in this paper.) A more accurate method of using the spectral moments is now available [18], but this requires the knowledge of the entire spectrum. Although B-M method is based upon an approximate line-shape, it has the advantage to give the quadrupole moment from measurements in one frequency only. B-M method and the results of the present work give,

with the same molecular parameters as in [17], a value of 5.6×10^{-26} esu (for CO₂ at 293 K). Finally, table I gives previous derived values for the molecular quadrupole moment of CO₂ by different methods.

Table I. — *Derived values for the molecular quadrupole moment of CO₂ by different methods.*

$\frac{Q}{10^{26}} \text{ esu}$	5.9 ^(a)	4.6 ^(b)	4.85 ^(c)	6.7 ^(d)	4.1 ^(e)	4.3 ^(f)	4.5 ^(g)	5.4 ^(h)	5.6 ⁽ⁱ⁾
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^(a) from microwave collision induced absorption and B-M method [17]

^(b) from viscosity and second virial coefficients [19]

^(c) from nuclear spin relaxation [20]

^(d) method as in ^(a) [2]

^(e) method as in ^(b) [21]

^(f) from birefringence measurements [22]

^(g) from far-infrared collision induced absorption [15]

^(h) theoretical calculation [23]

⁽ⁱ⁾ this work.

All the values obtained from microwave collision-induced absorption measurements and B-M method are greater than those derived by other methods. Also our result is the closest to a recent theoretical calculation [23].

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