PRESSURE-INDUCED MICROWAVE ABSORPTION IN N$_2$ [*]

by

W. Ho
Science Center/Aerospace and Systems Group
North American Rockwell Corporation
Thousand Oaks, California
and
Columbia Radiation Laboratory
Columbia University
New York, New York

and

I. A. Kaufman[†]
Columbia Radiation Laboratory
Columbia University
New York, New York

and

P. Thaddeus
Goddard Institute for Space Studies
National Aeronautics and Space Administration
New York, New York

ABSTRACT

Pressure-induced absorption in nitrogen has been studied at a frequency of 9260 MHz over the temperature range 238°K - 495°K and to pressures as high as 135 atm. Expressing the dielectric loss, ϵ'', in the form, $\epsilon''/\bar{\nu} = A\rho^2$ where $\bar{\nu}$ is the frequency in cm^{-1}, and ρ is the density, we find $A = 1.7(1) \times 10^{-10} (T/273)^{-2.5(2)}$ cm-amagat^{-2}. The absorption coefficient α, in cm^{-1} is then $\alpha = 1.07(6) \times 10^{-9} (T/273)^{-2.5(2)} \bar{\nu}^2 \rho^2$. The molecular quadrupole moment for N_2, calculated via the Kramers-Kronig integral, using the result of the present investigation as the low frequency limit of $\alpha(\bar{\nu})/\bar{\nu}^2$ and the far-infrared result of Bosomworth and Gush for N_2 at 300°K, is then 1.5×10^{-26} esu.

I. INTRODUCTION

Induced absorption in N_2, previously observed by Birnbaum and Maryott,[1] has been studied over the temperature range 238°K - 493°K and to pressures up to about 135 atm. Since the dielectric loss ϵ'' is expected to be directly proportional to the frequency throughout the microwave region,[2,3] all measurements were made at a single frequency (9260 MHz). In our previous work at the same frequency, on microwave absorption in compressed CO_2,[2] we were able to determine the first two coefficients in the virial expansion of the loss in powers of the density. In the present investigation, we found the dielectric loss in compressed N_2 to be approximately 100 times smaller in magnitude than that in CO_2, and consequently the

sensitivity of the experimental apparatus enabled us only to measure the first term in the virial expansion of the dielectric loss proportional to the square of the density.

II. APPARATUS

The apparatus used to measure the dielectric loss is the same as that described previously[4],[5] except for some slight improvements in the stability of the electronic circuits which increased the sensitivity by about a factor of two from our previous work. A reflection-type resonant cavity operating in the TE_{012} mode and immersed in a temperature-regulated bath was filled with nitrogen and a tuning plunger allowed the cavity to be kept on resonance at 9260 MHz as the dielectric constant of the gas varied with pressure. The absorption was then determined by measuring the effect of the gas on the quality factor (Q) of the cavity. Argon was used as a lossless calibrating gas to determine the effect of tuning on wall losses. The pressure of the gas was measured by a Bourdon gauge to about 0.5% accuracy, while the bath temperature was regulated and measured to within ±0.5°C.

Gas samples of the purest commercially available grade (pre-purified grade for N_2 and ultra high purity grade for argon) were obtained from the Matheson Company, and were specified by the manufacturer to contain less than 10^{-5} polar impurities. Analysis by the supplier of these samples showed that they contained less than 5 ppm H_2O and no detectable amount of other polar impurities, such

as NH_3 or hydrocarbons, (less than 1 ppm). The purity of the samples was further checked during the course of the experiment by passing the samples through a cold trap at dry-ice temperature, and over silica gel. This produced no detectable change in the observed dielectric loss.

III. MEASUREMENT OF DENSITY

The density of the gas may be obtained from the pressure via the ordinary virial expansion of the compressibility, or alternatively by means of the virial expansion of the Clausius-Mosotti function,

$$\frac{\epsilon'-1}{\epsilon'+2} \frac{1}{\rho} = a + b\rho + c\rho^2 + \ldots \tag{1}$$

where the dielectric constant can be calculated from the displacement of the tuning plunger used to keep the cavity on resonance.

A comparison of the two methods were made and the results agreed well within 1% of each other. For convenience, the second method was used in reducing the experimental data. The virial coefficients for the real part of the dielectric constant, a and b, were obtained from the experimental work of De Wijn and Heineken.[6] By applying the recent theoretical work of McQuarrie and Levine,[7] we were able to demonstrate that the third dielectric virial coefficient term, $c\rho^2$, can be neglected for the maximum density under consideration, and that the correction to the computed value of ρ due to the temperature dependence of b over the temperature range $245°K - 500°K$ is only at most 0.2%.

IV. RESULTS

The measured dielectric loss as a function of density and temperature for three typical runs is shown in Fig. 1. Each run consisted of filling the cavity to maximum pressure and measuring the loss for various values of pressure as the gas was gradually released step by step. At each pressure, four separate measurements were made and the points in Fig. 1 represent the average value for the four measurements. Fig. 2 shows the typical scatter encountered for a run at elevated temperatures. At low temperatures, where the loss is greater, the scatter is reduced by about a factor of two. To within the experimental uncertainties, the loss was found to vary as the square of the density.

The data at each temperature was least-square fitted to the expression,

$$\epsilon''/\rho \; \bar{\nu} = A\rho \qquad (2)$$

where ρ is the density in amagat units, and $\bar{\nu}$ is the frequency in cm^{-1}.

Fig. 3 shows the observed temperature dependence of the coefficient A, where each point represents the average of two independent runs. A fit to this data, assuming a simple T^n dependence in temperature, yields,

$$A = 1.7(1) \times 10^{-10} (T/273)^{-2.5(2)} \; cm\text{-}amagat^{-2} \; , \qquad (3)$$

where the uncertainties in the last significant figure, given in parenthesis, are estimated.

The absorption coefficient α, in cm^{-1}, is then given by,

$$\alpha = 2\pi \bar{\nu} \epsilon'' = 1.07(6) \times 10^{-9} (T/273)^{-2.5(2)} \bar{\nu}^2 \rho^2 \qquad (4)$$

V. DISCUSSION

Birnbaum and Maryott[1] first measured the dielectric loss in N_2 at room temperature (298°K) and at a frequency of 24350 MHz ($0.812cm^{-1}$), and found that $A = 1.6 \times 10^{-10}$. When the present work, Eq. (3), is specialized to this temperature, the result is, $A(298°K) = 1.4(1) \times 10^{-10}$. The agreement therefore can be considered excellent in view of the low dielectric loss in N_2 and the uncertainties involved in the measurements.

Measurements by other workers of induced absorption in N_2 have been made in the far-infrared region. Heastie and Martin[8] measured the induced spectrum between 30 cm^{-1} and 100 cm^{-1} with a grating spectrometer, and Gebbie et al.[9] published similar results over a wider frequency range obtained by a Michelson interferometer. More recently, Bosomworth and Gush[10] succeeded in measuring the spectrum from about 40 cm^{-1} to over 300 cm^{-1} at 300°K and determined the integrated absorption $\int_{Band} \alpha(\bar{\nu}) d\bar{\nu}$, for the pressure-induced spectrum to an accuracy of about 5%. Their results, together with the results in the microwave region at 300°K, are shown in Fig. (4). It can be seen that the present result agrees well with the infrared data and,

as expected, the low-frequency wing of the absorption band is proportional to the square of the frequency. It would be very informative to see if such good agreement holds for other temperatures, but the necessary infrared data at temperatures other than 300°K are not presently available to the best of our knowledge.

Pressure-induced absorption in nonpolar gases with a permanent quadrupole moment such as N_2 are interpreted as being due to the presence of transient dipoles induced by intermolecular forces during encounters of two or more interacting molecules.[2,11-14] Previous works in the microwave[1,2] and far-infrared region[10,21] on N_2 have all indicated that the major source of induced dipoles is due to the permanent quadrupole moment of the molecules and that induction due to short-ranged overlap forces is probably negligible. The result presented here, as well as the data from the far-infrared region, show that in N_2, the absorption is proportional to the square of the density, and therefore only binary pair encounters are important over the density range considered. The absorption band consists of an induced rotational band corresponding to the transition $\Delta J = \pm 2$, and a pure translational band corresponding to the direct absorption of energy into the translational energy of the interacting molecular pair without changing their internal states, ($\Delta J = 0$). Fig. (4) indicates that, although the low frequency wing of the absorption spectrum is expected to be primarily due to translational absorption, the translational band is not resolved from the rotational band centered around 110 cm^{-1}.

Maryott and Birnbaum[2,3] have derived an expression for the line shape of the translational band based on straight-line molecular trajectories and quadrupole-induced dipole absorption in binary pairs. Their expression for that part of A due to translational absorption, which we shall denote by A_t, is given by,

$$A_t = \frac{6\pi^{9/2} N_A{}^{3/2} c \bar{\alpha}^2 b_o M^{1/2} Y Q^2}{V_o{}^2 (kT)^{3/2}} \tag{5}$$

where N_A = Avogadro's number, c = velocity of light, M = molecular weight, V_o = molar volume under standard conditions, $\bar{\alpha}$ = average polarizability, b_o = kinetic collision diameter, Q = molecular quadrupole moment = $\sum_i e_i (3 z_i{}^2 - r_i{}^2)/2$ where z is along the molecular axis, and

$$Y = \int_0^\infty r^{-6} \exp[-E(r)/kT]\, dr \tag{6}$$

where $E(r)$ is the intermolecular potential.

Using Eq. (5) and the Lennard-Jones potential, $E(r) = 4\epsilon\left[(b_o/r)^{12} - (b_o/r)^6\right]$, we find that for $T = 300°K$, $b_o = 3.70\text{Å}$, $\bar{\alpha} = 1.75 \times 10^{-24} cm^{-3}$, and $\epsilon/k = 95.5°K$,

$$A_t = 1.6 Q^2 \times 10^{42} . \tag{7}$$

Assuming that the induced rotational band can be neglected in the low frequency wing of the spectrum, i.e. setting $A = A_t = 1.4 \times 10^{-10}$, we find $Q_{N_2} = 0.95 \times 10^{-26}$ esu, which is a somewhat lower value than that obtained by other methods.[15-17] The inclusion of any possible contribution to A in the low frequency wing due to the induced rotational

band will yield an even lower value for Q_{N_2}. Moreover, the temperature dependence of equation (5) is approximately $(T)^{-1.5}$ which is in disagreement with the measured temperature dependence of A. The agreement of the theory with the experimental data can probably be improved by considering more realistic orbits resulting from the attractive part of the intermolecular interaction.

More recently, Gersten and Foley[18] proposed a model based on the existence of dimers which was first predicted theoretically by Stogryn and Hirschfelder[19] and observed experimentally at moderate densities in N_2 by Lackenby and Robbins.[20] They found that the temperature dependence of A can be well understood if the major part of the effect at low frequency is attributed to electric dipole moments existing in dimers of N_2. On this basis, they predict theoretically that A_t is proportional to $(T)^{-2.65}$. Their calculations are, however, rather qualitative in nature and further detailed comparison of the experimental results with theory must await more theoretical studies of the dynamical aspects of bound and metastable dimer systems.

The theory for the integrated absorption of the pressure-induced spectrum in homonuclear diatomic gases and mixtures has been extensively investigated by many authors.[11-14] By assuming that the transient dipole moment in the gas is mainly due to induction by the electric quadrupole field of the individual molecules, their general results for the integrated absorption coefficient, $\int_{Band} \alpha(\bar{\nu})d\bar{\nu}$, have been used to evaluate the molecular quadrupole moment of N_2. Poll[21] and

Ketelaar and Rettschnick[22] used Gebbie et al's value for the integrated absorption for N_2 and deduced a value of $Q_{N_2} = 1.5 \times 10^{-26}$ esu. Using the slightly more accurate value of Bosomworth and Gush for the integrated absorption, the value for Q_{N_2} is then 1.6×10^{-26} esu.

Our present data in the microwave region, of course, do not change this result as the contribution of the low frequency wing of the spectrum to the total integrated absorption is negligible. However, the integral $\int_{Band}[\alpha(\bar{\nu})/\bar{\nu}^2]d\bar{\nu}$ may also be independently related to the molecular quadrupole moment if we assume, as in the above case, that the other molecular parameters are known. We shall now proceed to calculate the quadrupole moment of N_2 via this integral.

The dielectric loss may be related to the static dielectric constant ϵ' via the Kramers-Kronig relationship,

$$(\epsilon' - 1) = \frac{1}{\pi^2} \int_0^\infty \frac{\alpha(\bar{\nu})}{\bar{\nu}^2} \, d\bar{\nu} \qquad (8)$$

where $\bar{\nu}$ is the frequency in cm^{-1}.

Explicit expressions for the dielectric virial coefficients of non-polar axial molecules possessing permanent quadrupole moments and anisotropic polarizabilities have been derived by many authors.[7,23-26] Expanding the dielectric constant in terms of the virial coefficients and retaining only terms appropriate for the far-infrared and microwave region and proportional to ρ^2, we find,

$$\frac{1}{\pi^2} \int_{Band} \frac{\alpha(\bar{\nu})}{\bar{\nu}^2} \, d\bar{\nu} = \frac{16\pi^2\bar{\alpha}^2\theta^2\rho^2}{kT}\left(1 + \frac{4}{5}\varkappa\right)Y \qquad (9)$$

where $\varkappa$ is the anisotropy, and all other symbols are as previously
defined in expressions (5) and (6). We neglect here terms of order
$\bar{\alpha}^3\theta^2$ and higher.

If we use the usual Lennard-Jones 6-12 potential for the
intermolecular potential, then

$$Y = (1/b_o^5)\ I_3(kT/\epsilon) \tag{10}$$

where the integral $I_3(kT/\epsilon)$ has been tabulated for different values
of (kT/ϵ) by Levine and McQuarrie.[24]

Using the data of Bosomworth and Gush,[10] and the result of
the present investigation as the low-frequency limit for $\alpha(\bar{\nu})/\bar{\nu}^2$,
(Fig. 5), we find for $T = 300°K$,

$$\int_{Band}\left[\alpha(\bar{\nu})/\bar{\nu}^2\right]d\bar{\nu} = 8.5\times10^{-8}\ \text{amagat}^{-2} \tag{11}$$

Taking, as before, $b_o = 3.70\text{Å}$, $\bar{\alpha} = 1.75\times10^{-24}\text{cm}^{-3}$, $\epsilon/K = 95.5°K$,
and $\varkappa = 0.18$, we find,

$$Q_{N_2} = 1.5\times10^{-26}\ \text{esu}, \tag{12}$$

a value which is in excellent agreement with that obtained by other
methods, which are extensively discussed in recent review papers by
Stogryn and Stogryn,[15] Krishnaji and Prakash,[16] and Birnbaum.[17]

We note that the anisotropy correction is only about 1% in
the evaluation of the quadrupole moment, and hence can be neglected.
We further note that the integral $I_3(kT/\epsilon)$ is almost independent of
(kT/ϵ) for rather large variation of ϵ at $T = 300°K$. As $\bar{\alpha}$ is well-
known for N_2, the uncertainty in Q then is mainly due to the uncertainty

in the dynamic collision range b_o, and the integral $\int_{Band} [\alpha(\bar{\nu})/\bar{\nu}^2]d\bar{\nu}$. We estimate that the calculated value of Q_{N_2} is probably accurate to about ±5%.

The agreement between our result for the quadrupole moment of N_2 as computed from the Kramers-Kronig integral, and that obtained via the integrated absorption $\int_{Band} \alpha(\bar{\nu})d\bar{\nu}$, is better than can be reasonably expected on the basis of the accuracy of the experimental measurement and the accuracy with which the other molecular parameters are known. We therefore conclude that there is good self-consistency between the two methods and our result demonstrates the validity of the use of the integrated intensity and the Kramers-Kronig relationship to deduce molecular moments from pressure-induced absorption data. As it is unlikely that the contribution to the absorption due to overlap induction in N_2 is the same for both integrals, we further confirm the conclusions of previous investigators that overlap induction is negligible compared to quadrupolar induction in the pure translational and rotational spectrum of N_2.

REFERENCES

1. Birnbaum, G., and Maryott, A. A., J. Chem. Phys. $\underline{36}$, 2032 (1962).

2. Maryott, A. A., and Birnbaum, G., J. Chem. Phys. $\underline{36}$, 2026 (1962).

3. Birnbaum, G., Levine, H. B., and McQuarrie, D. A., J. Chem. Phys. $\underline{46}$, 1557 (1967).

4. Ho, W., Kaufman, I. A., and Thaddeus, P., J. Chem. Phys. $\underline{45}$, 877 (1966).

5. Ho, W., Kaufman, I. A., and Thaddeus, P., J. Geophys. R., $\underline{71}$, 5091 (1966).

6. De Wijn, H. W., and Heineken, F. W., Physica $\underline{25}$, 615 (1959).

7. McQuarrie, D. A., and Levine, H. B., Physica $\underline{31}$, 749 (1965).

8. Heastie, R., and Martin, D. H., Can. J. Phys. $\underline{40}$, 122 (1962).

9. Gebbie, H. A., Stone, N. W. B., and Williams, D., Mol. Phys. $\underline{6}$, 215 (1963).

10. Bosomworth, D. R., and Gush, H. P., Can. J. Phys. $\underline{43}$, 751 (1965).

11. Van Kranendonk, J., Physica $\underline{23}$, 825 (1957).

12. Van Kranendonk, J., and Kiss, Z. T., Can. J. Phys. $\underline{37}$, 1187 (1959).

13. Poll, J. D., and Van Kranendonk, J., Can. J. Phys. $\underline{39}$, 189 (1958).

14. Colpa, J. P. and Ketelaar, J., Mol. Phys. $\underline{1}$, 343 (1958).

15. Stogryn, D. E., and Stogryn, A. P., Mol. Phys. $\underline{11}$, 371 (1966).

16. Krishnaji, and Prakash, V., Rev. Mod. Phys. $\underline{38}$, 690 (1966).

17. Birnbaum, G., Intermolecular Forces, Edited by J. O. Hirschfelder, (Interscience Publishers, New York, 1967), Chap. 9, pp. 487-548.

18. Gersten, J., and Foley, H., J. Chem. Phys. $\underline{45}$, 3885 (1966).

19. Stogryn, D. E., and Hirschfelder, J. O., J. Chem. Phys. 33, 942 (1960).

20. Leckenby, R. E., and Robbins, E. J., Proc. Roy. Soc., A291, 389 (1965).

21. Poll, J. D., Phys. Letters 7, 32 (1963).

22. Ketelaar, J. A. A., and Rettschnick, R. P. H., Mol. Phys. 7, 191 (1963).

23. Kielich, S., Acta Physica Polonica 28, 95 (1965).

24. Levine, H. B., and McQuarrie, D. A., J. Chem. Phys. 44, 3500 (1966).

25. Buckingham, A. D., and Pople, J. A., J. Chem. Phys. 27, 820 (1956).

26. Jansen, L., Phys. Rev. 112, 434 (1958).

FIGURE CAPTIONS

Fig. 1   Dielectric loss of N_2 as a function of temperature and density.

Fig. 2   Dielectric loss of N_2 at 90°C showing typical scatter before averaging.

Fig. 3   The first virial coefficient, A, of the dielectric loss of N_2, where $A = \epsilon''/\rho^2\bar{\nu}$, as a function of temperature.

Fig. 4   Observations of induced absorption in N_2 at 300°K. HKT is the result of the present investigation, MB is the result of the work of Maryott and Birnbaum, and BG is the result in the far-infrared of Bosomworth and Gush where only some selected values are shown.

Fig. 5 $\alpha/\bar{\nu}^2$ at 1 amagat density as a function of frequency for N_2. The far-infrared data are typical values selected from the work of Bosomworth and Gush and the uncertainties are estimated.

AMAGAT DENSITY

FIGURE 1

$\epsilon''/\rho\bar{\tau} \times 10^7$

0.4

0.3

0.2

0.1

20 40 60 80 100 120 140

-45°

0°C

60°C

FIGURE 2

$$A = 1.7(1) \times 10^{-10} (T/273)^{-2.5(2)}$$

FIGURE 3

FIGURE 4

Frequency (cm^{-1})

$\alpha/\nu^{-2} \times 10^{10}$ (cm-Amagat^{-2})

FIGURE 5