

MICROWAVE ABSORPTION IN COMPRESSED CARBON MONOXIDE AND NITROUS OXIDE

By J. C. ANDREWS*

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Abstract

The absorption of microwaves by both CO and N₂O has been measured at a frequency of 9.75 GHz using a resonant cavity technique. The power absorption coefficients were measured at pressures up to 670 bars for CO at 20.5°C, 54 bars for N₂O at 25°C, and 121 bars for N₂O at 40°C. In all cases the power absorption coefficient was found to increase with density up to the highest pressures reached. The theory of Van Vleck and Weisskopf fails to account for the measured absorption except at low densities. At higher densities the measured absorption was in excess of that predicted by this theory and the discrepancy increased with increasing density. The theory of Ben-Reuven accounts for the absorption up to intermediate densities but at high densities it also predicts values which are smaller than the measured ones. However, it is possible to account for the measured absorption by considering it to be the sum of a resonant contribution, which is assumed to be given by the Van Vleck-Weisskopf theory, and a nonresonant collision-induced contribution which increases with density and is assumed to be the result of collisions so strong that rotation of the molecules is quenched.

I. INTRODUCTION

Measurements of the absorption of X-band microwave radiation by dilute binary mixtures of the polar gases NH₃, CH₃Cl, and COS in the nonpolar gases N₂, H₂, He, and Ar over pressure ranges of several hundred bars have been reported by Morris and Parsons (1970). A theoretical interpretation of these measurements has been given by Morris (1971). The contribution to the power absorption coefficient α from the rotational spectra of the polar molecules could not be explained in terms of the theory of Van Vleck and Weisskopf (1945) alone as the measured absorption for each of the gas mixtures was in excess of that predicted by this theory. Morris was able to explain the rotational loss in CH₃Cl and COS if he assumed that there was a nonresonant collision-induced contribution to the loss. This, he assumed, arose in molecules undergoing collisions so strong that their rotational freedom was destroyed for the duration of the collision with the result that the whole of the stationary dipole moment could take part in nonresonant, or orientation, absorption.

Morris (1971) was also able to account for his data by applying the theory of Ben-Reuven (1965, 1966) to the interpretation of the rotational loss in CH₃Cl and COS. This theory includes the effects of interference between the overlapping resonant lines and predicts that a resonant spectrum will degenerate to a nonresonant spectrum when the line width parameter is much larger than the transition frequencies.

Thus Morris (1971) used two models to describe the degeneration of the rotational spectrum with increasing pressure: one involving the application of the Ben-Reuven

* Department of Physics, University of Queensland; present address: Weapons Research Establishment, Department of Supply, P.O. Box 1424H, Adelaide, S.A. 5001.

theory alone and the other involving a combination of the Van Vleck–Weisskopf theory and the assumption of a collision-induced contribution to the absorption.

Morris (1971) also successfully applied existing theories of nonresonant absorption to the interpretation of the measured loss in NH_3 by assuming that the inversion spectrum degenerated and gave rise to nonresonant absorption at pressures exceeding 40 bars. At lower pressures, the whole of the absorption was assumed to be nonresonant in character because the lowest rotational frequency in NH_3 (600 GHz) was well above the frequency of measurement (9.58 GHz).

The object of the present work was to further the study of the behaviour of the rotational spectra of gases under compression. A linear molecule has no component of its dipole moment which is parallel to its angular momentum vector and does not rotate with the molecule. On the other hand, CH_3Cl and NH_3 do have such a component and hence exhibit nonresonant (orientation) absorption which complicates the interpretation of the resonant spectrum associated with the other component of the dipole moment which rotates with the molecule. This behaviour is a feature of all symmetric top and some asymmetric top molecules. Thus it was decided that gases with linear molecules would be studied in the pure state to remove the complications associated with gas mixtures and to ensure that the absorption could be assumed to result entirely from the rotational spectra of the molecules concerned. CO_2 is not suitable for study in the pure gaseous state as it has a large dipole moment and, at room temperature, is liquefied at relatively low pressures. A large dipole moment results in a large susceptibility and absorption coefficient, both of which would make measurement difficult with the existing equipment.

The gases CO and N_2O were chosen as they have small dipole moments and although their lowest rotational spectral lines lie above the frequency of measurement (9.75 GHz) they are sufficiently close to it to give measurable absorption.

II. EXPERIMENTAL SYSTEM AND METHOD

The microwave absorption coefficient α was measured at various pressures using the equipment and method established by Morris and Parsons (1970). The dimensions of their resonant cavity were altered in order to accommodate the TE_{011} mode, as the susceptibility χ to which the cavity would tune in this mode was approximately 0.45. Previously the cavity operated in the TE_{013} mode and could only be used if χ lay in the range 0–0.16. In addition, the coupling plugs were improved by using a dielectric of 75% powdered glass in a 25% base of Araldite.

The number of CO molecules per unit volume was determined from the pressure by means of the compressibility data of Bartlett *et al.* (1930). The number density of N_2O , however, could not be found in a similar manner as this gas was investigated near its critical point. Here the compressibility changes rapidly with small changes in pressure as the critical density is approached, so that any uncertainty in the pressure would give rise to a large uncertainty in the number density.

For gases with no permanent dipole moment, the relationship between the number N of molecules per unit volume and the susceptibility χ is given by the Clausius–Mossotti equation

$$(\epsilon' - 1)/(\epsilon' + 2) = \chi/(\chi + 3) = Np/3\epsilon_0. \quad (1)$$

Here ϵ' is the real part of the relative dielectric constant, ϵ_0 the permittivity of free space, and p the polarizability of the gas concerned. As equation (1) is valid for argon in the microwave region, this gas was used to calibrate the resonant length of the cavity as a function of pressure for pressures up to 820 bars. The compressibility data of Michels, Wijker, and Wijker (1949) and Michels, Lunbeck, and Wolkers (1951) were then used to calculate the values of N corresponding to the recorded values of pressure and the corresponding values of χ were calculated from equation (1). Hence a series of values of the cavity length and the corresponding susceptibility at which the cavity would resonate were found. The susceptibility of any dielectric in the cavity could then be determined from a knowledge of the resonant length of the cavity.

An extension of equation (1) which would apply to systems of molecules with permanent electric dipoles of moment μ is

$$\chi = \frac{(1 + \frac{1}{3}\chi)N}{\epsilon_0} \left(p + \frac{\mu^2}{3kT} (1 + \frac{1}{3}\chi)^2 \right), \quad (2)$$

where k is Boltzmann's constant and T is the absolute temperature. Equation (2) holds provided that the frequency at which χ is measured is sufficiently below the natural rotational frequencies of the molecules to avoid anomalous dispersion. The local field factor of Fröhlich (1948) has been included by assuming that the effective dipole moment is $\mu(1 + \frac{1}{3}\chi)$. The polarizability p in equation (2) is the result of processes which contribute to the polarization in the optical and infrared regions of the spectrum. The term $\mu^2/3kT$ is associated with the tendency of the permanent dipoles to align themselves in the direction of an impressed field and, for this reason, is often referred to as orientation polarization. The ratio of this orientation polarization to the total polarization, which was estimated to be approximately 0.04 for N_2O and CO , was obtained by considering the dielectric constants at optical frequencies and the static dielectric constants of the gases concerned. Thus it may be concluded that the dipole polarization of the linear molecules used here is not more than a small fraction of the total polarization so that any modification of equation (2) to account for resonant or liquid dispersion is of little consequence to the total polarization. This is largely due to the fact that CO and N_2O have small dipole moments.

It was from equation (2) that the molecular number density of N_2O was calculated. At each point at which the absorption coefficient was measured, the cavity length was recorded and this value was used to calculate the susceptibility and hence the value of N .

In order to check the experimental method, the cavity was filled with CO gas and the pressure and tuning length were recorded at a series of pressures up to 670 bars. The number density N was calculated from the compressibility data and χ was calculated from the cavity length. A plot of $\chi/(\chi + 3)$ against N was found to satisfy equation (2) to within 0.8%.

A summary of the experimental ranges in p and N is given in Table 1. All measurements were made at a frequency of 9.75 GHz. The molecular number density N_{liq} in the liquid phase was estimated from the specific gravity for liquid CO

and the dielectric constant for liquid N_2O , both of which are given in the "Handbook of Chemistry and Physics" (Weast 1969-1970).

Following Morris and Parsons (1970), an estimate of the error in the absorption coefficient was found by adding the estimated errors from all possible sources. In practice the actual error would be expected to be less than this. Thus α was found to be accurate to within $\pm 8\%$ and the calculated number density was estimated to be accurate to within $\pm 1.2\%$ for CO and $\pm 4\%$ for N_2O . The conclusion that the actual errors may be substantially smaller than these values was supported by an experiment in which the absorption in compressed CO_2 was measured and the results were compared with those obtained by other workers.

TABLE 1
EXPERIMENTAL RANGES IN PRESSURE AND DENSITY

Gas	T ($^{\circ}C$)	p_{max} (bars)	N_{max} ($10^{26} m^{-3}$)	N_{max}/N_{liq} (%)
N_2O	25	54	23.4	18
N_2O	40	121	97.7	78
CO	20.5	670	105	61.5

III. RESULTS AND DISCUSSION

(a) Application of the Van Vleck-Weisskopf and Ben-Reuven Theories

In this section the experimental results are presented as graphs of α versus N and, following the method of Morris (1971), they are compared with the absorption coefficients predicted by the Van Vleck-Weisskopf theory (α_{VVW}) and the Ben-Reuven theory (α_{BR}). Ben-Reuven derived his theory on the basis that all collisions are binary so that in the calculation of α_{BR} a linear relation between the relaxation parameter, the coupling rate, and the density was used. In the calculation of α_{VVW} , both the binary and multiple collision formulae were employed (see equations (6) and (22) of Morris 1971). These formulae were found to be equally applicable in the low density region but neither gave satisfactory results in the high density region. The curves for α_{VVW} presented in Figure 1 were computed using the binary collision relation.

The experimental results are plotted for N_2O at $25^{\circ}C$ in Figure 1(a), for N_2O at $40^{\circ}C$ in Figure 1(b), and for CO at $20.5^{\circ}C$ in Figure 1(c). The curves labelled VVW and BR represent the absorption calculated from the Van Vleck-Weisskopf and Ben-Reuven theories respectively. The parameters used for these calculations were chosen to give agreement between theory and experiment at low pressures. The Ben-Reuven coupling parameter x was 0.5, 0.6, and 0.1 respectively for the three cases considered in Figures 1(a), 1(b), and 1(c). The values of the collision diameters used to determine the theoretical curves are listed below.

Curve	N_2O at $25^{\circ}C$	N_2O at $40^{\circ}C$	CO at $20.5^{\circ}C$
VVW	7.7	11.5	4.6
BR	4.8	5.9	4.2

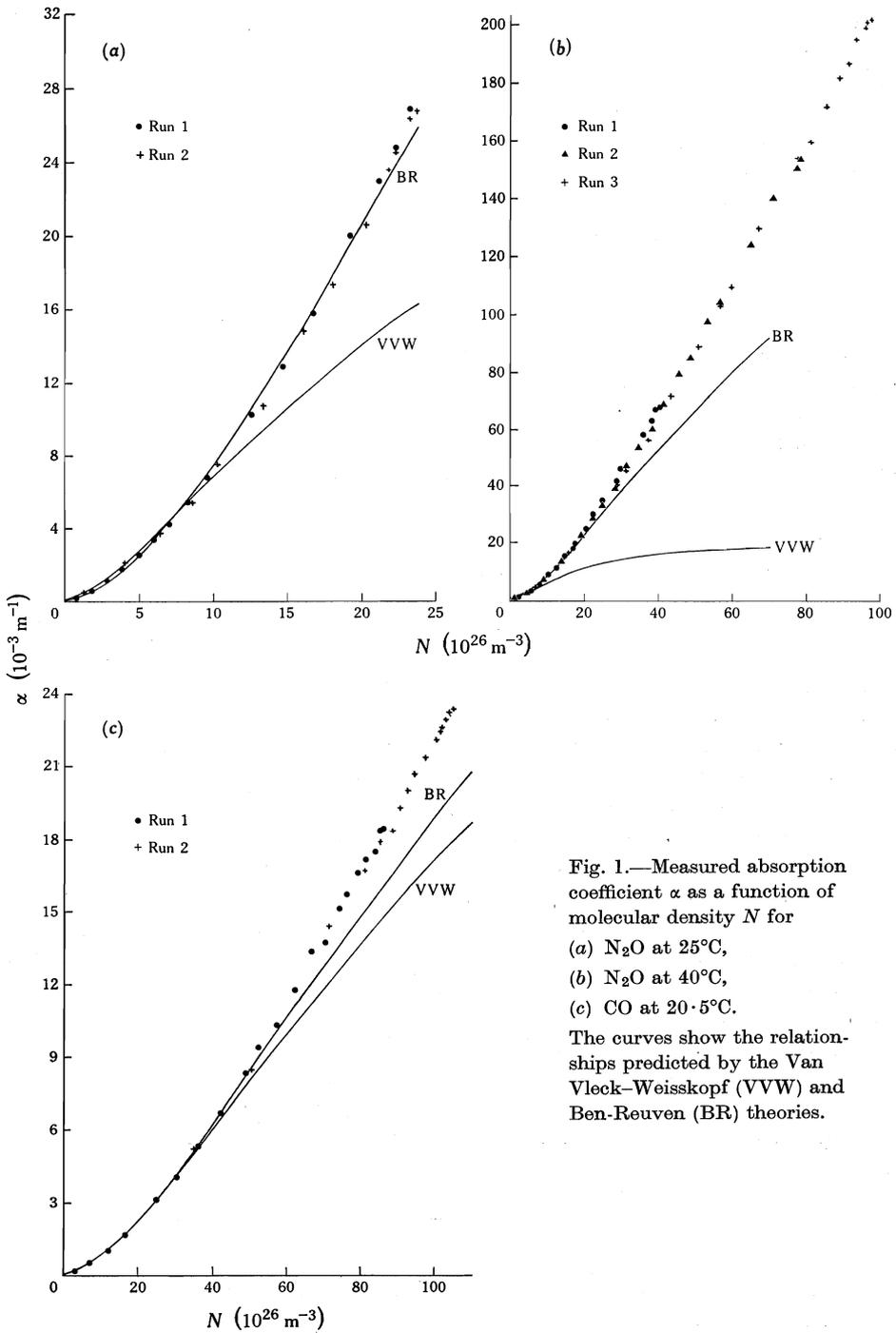


Fig. 1.—Measured absorption coefficient α as a function of molecular density N for (a) N_2O at $25^\circ C$, (b) N_2O at $40^\circ C$, (c) CO at $20.5^\circ C$. The curves show the relationships predicted by the Van Vleck-Weisskopf (VVW) and Ben-Reuven (BR) theories.

It is evident from Figure 1 that the Van Vleck–Weisskopf theory is inadequate except at low densities. The theory applies at densities up to 5% of the liquid density of N_2O (corresponding to a pressure of 27 bars) and at densities up to 23% of the liquid density of CO (135 bars). On the other hand, the Ben-Reuven theory can be seen to predict the absorption well to higher densities, being applicable at densities up to 16% of the liquid density of N_2O (50 bars) and to 29% of the liquid density of CO (180 bars). For greater pressures, the measured absorption exceeds that predicted by either theory.

The failure of α_{BR} to account for the measured absorption may be due to the fact that no allowance was made in the calculations for a distribution over the rotational states of the relaxation parameters or coupling parameters. Also it may be possible to improve the agreement between the measured absorption and α_{BR} by assuming a different density dependence for the relaxation parameter, although it should be borne in mind that Ben-Reuven derived his theory for the case in which all collisions are binary. Perhaps it would be relevant to point out that α_{VW} is a limiting case of α_{BR} , the two being equal when x is zero and line shifts are unimportant. Also, for N_2O above a density of approximately $8 \times 10^{26} \text{ m}^{-3}$ there is no value of the relaxation parameter which will cause α_{VW} to increase to the measured value. These two facts would indicate that there may be a limiting density for the application of α_{BR} regardless of the form of the dependence of the relaxation parameter on density.

(b) Collision-induced Absorption

In an attempt to interpret the excess absorption at high pressures, a very simplified model was developed. Suppose that a molecule has a "hard core" of volume v , which is assumed to be a region inaccessible to the "centre" of any other molecule. Surrounding this, let there be a region of volume V such that if the centre of a second molecule penetrates V the rotational freedom of the colliding molecules is temporarily quenched. Also surrounding v let there be a region of volume $V' (> V)$ such that if the centre of a second molecule penetrates V' the collision results in broadening of the rotational spectrum. Two types of collision are thus postulated: if a molecule B enters the volume V' of a molecule A but does not penetrate to V then the molecules have undergone a line-broadening collision, whereas if B does penetrate V there is line broadening and also a temporary quenching of the rotational freedom of the molecules. Then at any instant a fraction f_{ci} of the molecules present will have their rotation quenched by very strong collisions. These molecules will be responsible for nonresonant collision-induced absorption. The remaining fraction f_{res} will continue to contribute to resonant absorption.

If the collision-induced absorption is assumed to be given by the expression of Debye (1945) for nonresonant absorption in liquids then, for N molecules per unit volume,

$$\alpha_{ci} = \frac{2\pi f_{ci} N F^2 \mu^2 \nu^2}{3\epsilon_0 ckT(\epsilon')^{\frac{1}{2}}} \frac{2\pi t_c}{1 + (2\pi \nu t_c)^2}. \quad (3)$$

In this equation F is the local field factor of Fröhlich (1948), ν the frequency of measurement, and t_c the mean duration of a rotation-inhibiting collision. Following Morris (1971), it has been assumed that the relaxation rate is the inverse of the mean

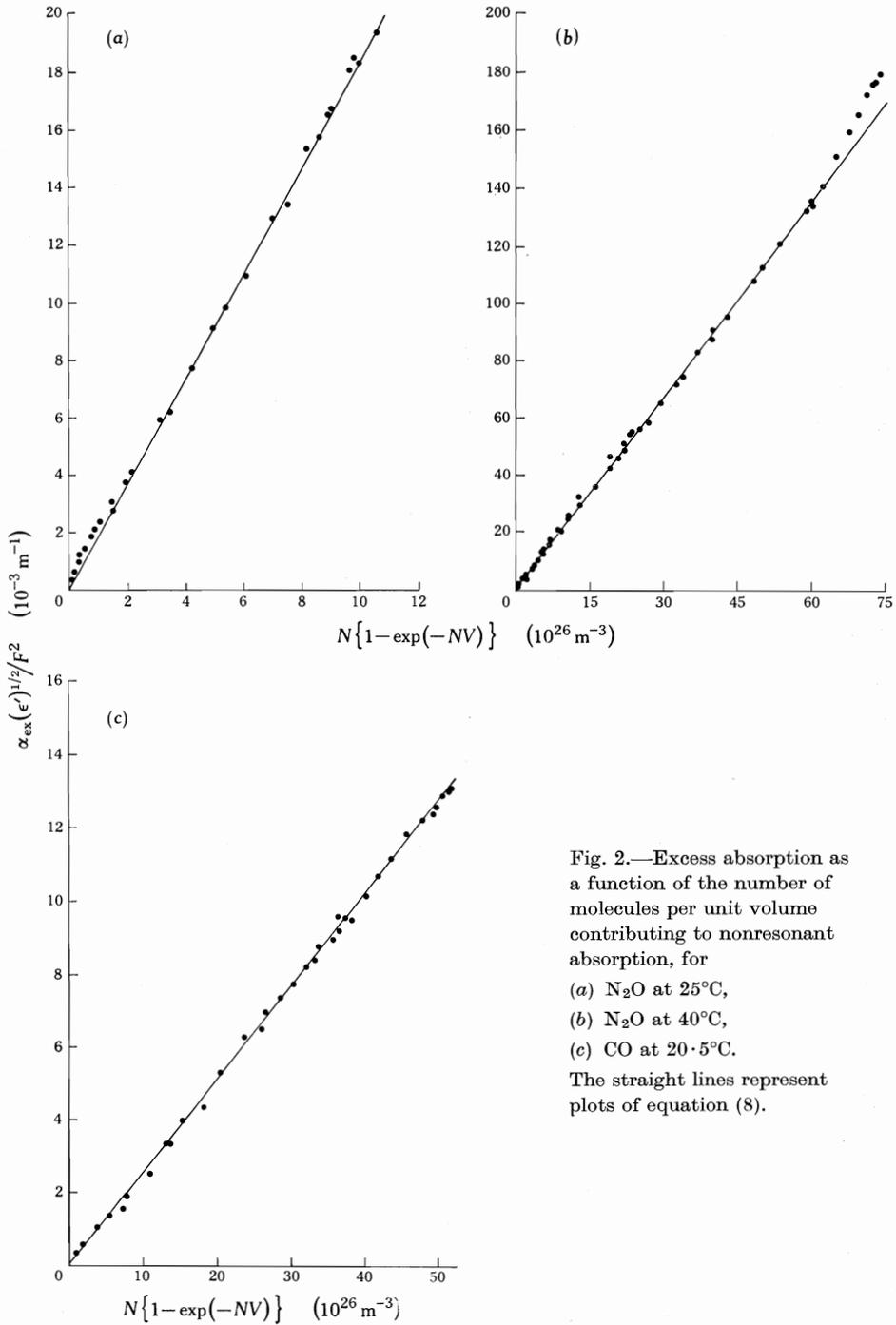


Fig. 2.—Excess absorption as a function of the number of molecules per unit volume contributing to nonresonant absorption, for
 (a) N₂O at 25°C,
 (b) N₂O at 40°C,
 (c) CO at 20.5°C.
 The straight lines represent plots of equation (8).

collision duration. For the cases under consideration, $2\pi\nu t_c$ was found to be very small compared with unity so that equation (3) can be restated as

$$\alpha_{ci} = Kf_{ci}F^2N(\epsilon')^{-\frac{1}{2}}, \quad \text{where} \quad K = 4\pi^2\mu^2\nu^2t_c/3\epsilon_0ckT. \quad (4a, b)$$

It will be assumed that the resonant contribution to the absorption is given by the Van Vleck-Weisskopf theory. A necessary modification is the replacement of N , which is the total number of molecules per unit volume, by $f_{res}N$ the number of molecules per unit volume contributing to resonant absorption. Hence the resonant contribution to the absorption is

$$\alpha_{res} = f_{res} \alpha_{vVW}(V', N). \quad (5)$$

The quantity V' is an adjustable parameter in the calculation of the resonant contribution to the absorption and may be related to a collision cross section or collision diameter by assuming spherical symmetry. It enters into the formula for α_{vVW} in the calculation of the relaxation parameter.

It can be shown by simple probability arguments similar to those used by Parsons, Burton, and Lasich (1966) that if multiple collisions are important then

$$f_{ci} = 1 - \exp(-NV) \quad \text{and} \quad f_{res} = \exp(-NV). \quad (6a, b)$$

Two assumptions are used in the derivation of equations (6), namely (i) $v \ll N^{-1}$ and (ii) the screening effect of molecules is unimportant. The first assumption must fail for sufficiently large N , while the second assumption is only completely valid when the hard core volume is zero.

If multiple collisions are important within the volume V they must also be important within the larger volume V' and the multiple collision expression for the relaxation parameter must be used in the calculation of α_{vVW} in equation (5).

The absorption in excess of the resonant contribution involves the adjustable parameters V and V' , and is defined by

$$\alpha_{ex}(V, V') = \alpha_{meas} - \exp(-NV) \alpha_{vVW}(V'). \quad (7)$$

If this excess absorption is equal to α_{ci} , it follows from equation (4a) that

$$\alpha_{ex}(V, V')(\epsilon')^{\frac{1}{2}}/F^2 = KNf_{ci} = KN\{1 - \exp(-NV)\}. \quad (8)$$

Hence a graph of $\alpha_{ex}(\epsilon')^{\frac{1}{2}}/F^2$ versus $N\{1 - \exp(-NV)\}$ should be a straight line with a gradient of K . This enables t_c to be deduced from equation (4b).

Values of $\alpha_{ex}(\epsilon')^{\frac{1}{2}}/F^2$ are plotted against $N\{1 - \exp(-NV)\}$ for N_2O at $25^\circ C$ in Figure 2(a), for N_2O at $40^\circ C$ in Figure 2(b), and for CO at $20.5^\circ C$ in Figure 2(c). The values of the parameters V and V' were determined by trial and error in an effort to obtain straight line graphs. These values, together with the slopes of the resulting lines and the values of t_c derived from them, are listed in Table 2.

In Figure 2(b) the experimental points in the high density region fall increasingly above the straight line as the density increases. This may be due to a failure of

equations (6) or may be due to the beginning of a transition in the relaxation rate γ as the liquid density is approached. Morris (1971) has shown that the relaxation rate in a liquid decreases with increasing pressure. Since γ is the inverse of t_c , equation (4b) predicts that an increase in K , such as that observed in the high density region of Figure 2(b), would be the result of a fall in γ .

TABLE 2
PARAMETERS EVALUATED FROM COLLISION-INDUCED ABSORPTION ANALYSIS

Gas	T (°C)	V (10^{-24} cm ³)	V' (10^{-24} cm ³)	K (10^{-30} m ²)	t_c (10^{-13} s)
N ₂ O	25	230	452	18.3	5.2
N ₂ O	40	225	448	22.4	6.7
CO	20.5	65	234	2.55	1.4

Some further parameters may be deduced from this analysis if spherical symmetry is assumed. The nonresonant collision volume V , the kinetic collision diameter b_K , and the nonresonant collision diameter R_0 , are related by

$$V = (4\pi/3)(R_0^3 - b_K^3). \quad (9a)$$

The resonant collision volume V' , the kinetic collision diameter b_K , and the microwave collision diameter b are similarly related by

$$V' = (4\pi/3)(b^3 - b_K^3). \quad (9b)$$

The kinetic collision diameter may be estimated as the diameter at which the energy of interaction of two colliding molecules is equal to their mean translational energy. From this postulate, the values of b_K for N₂O and CO were calculated using the Lennard-Jones potential (Hirschfelder, Curtiss, and Bird 1954). From these values and the values of V and V' in Table 2, b and R_0 could then be calculated from equations (9). The collision diameters obtained in this way are given in Table 3.

TABLE 3
COMPARISON OF KINETIC, NONRESONANT, AND MICROWAVE COLLISION DIAMETERS

Gas	T (°C)	b_K (Å)	R_0 (Å)	b (Å)
N ₂ O	25	3.65	4.69	5.40
N ₂ O	40	3.65	4.68	5.39
CO	20.5	3.35	3.76	4.44

Thus it can be seen that, even though a simple model for the degeneration of the resonant spectrum has been used, not unreasonable values of the collision diameters have been deduced from the analysis.

IV. CONCLUSIONS

For each of the gases studied it has been possible to account for the measured absorption as the sum of a resonant component and a nonresonant collision-induced component. The fraction of molecules contributing to resonant absorption decreases with increasing density while the fraction contributing to collision-induced absorption increases with increasing density. However, it must be pointed out that even the simplified model presented here involves the introduction of two arbitrary parameters V and V' and, although the values obtained for these are not unreasonable, their arbitrariness makes the theory less convincing.

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