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Pressure Broadening in the Infra-Red and Optical Collision Diameters*

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(Received October 29, 1946)

The pressure broadening effects of a number of foreign gases on the infra-red absorption of methane at 7.65μ have been determined. Also the pressure broadening effects of a number of foreign gases on the absorption of carbon dioxide at 4.3μ and 14.8μ have been investigated. The data have been analyzed to obtain optical collision diameters for the various gases and the absorbers. By optical collision is meant any collision which is effective in interrupting the processes of radiation absorption. The data are discussed in terms of the Lorentz theory of pressure broadening and are shown to confirm it. From the results obtained, it is clear that the pressure broadening effects of certain gases on one absorber cannot be reliably extrapolated to predict the effects on another absorber. Also the effects at one wave-length are not in general the same at another wave-length for the same absorber. The optical collision diameter effective for a foreign gas and an absorbing gas at a particular wave-length is a specific function of the two gases and the wave-length. Empirical results on the shape of the curves obtained are presented. The deviation from Beer's law of absorption evidenced by isobutylene at 11.23μ is shown to be not due to pressure broadening.

A NUMBER of gases are known to deviate from Beer's law of absorption when examined in the infra-red region. For example, the optical density of a given gas at a particular wave-length will depend upon the partial pressure but not be directly proportional to it. Also for these gases the optical density will, in general, depend upon the total gas pressure in the sample. For those gases whose molecules possess small moments of inertia and appreciable spacing between the rotational fine structure, these deviations from Beer's law are explained in terms of the Lorentz pressure broadening theory. This subject has been theoretically studied by a number of investigators,[1-3] and their results show that the shape of a rotational line is dependent upon the frequency of molecular collisions. Dennison[2] showed that this change of shape together with a consideration of the energy transmittance of a spectrometer would explain some of the characteristics of the infra-red spectrum of HCl.

A complete application of the theories of Dennison and others to the treatment of experimental data for any particular gas is very difficult unless the data have been obtained with a spectrometer of quite high resolution. However, with instruments of medium resolution, data may be obtained which can be interpreted to give information about the optical collision diameters of the gases studied. The optical collision diameters are the diameters which govern the frequency of effective collisions between molecules of absorbing gas or of absorbing and foreign gas. By effective collisions are meant collisions which are effective in interrupting the processes of radiation absorption.

The present work is an experimental study of the effects of various foreign gases on the infra-red absorption of methane, carbon dioxide, and isobutylene. Optical collision diameters between various pairs of molecules are obtained and discussed. The data show that results for one absorbing gas can only be applied in a general way in predicting the behavior of another.

EXPERIMENTAL DETAILS

The spectrometer used in this work was an NaCl prism type.[4] The method of obtaining optical densities for the gas mixtures was the same as described by us elsewhere.[5] In it, the

* Some of this material was presented at the Symposium on Molecular Spectroscopy and Molecular Structure, Ohio State University, June, 1946.
[1] H. A. Lorentz, *The Theory of Electrons* (Stechert & Company, New York, 1909), note 57.
[2] D. M. Dennison, Phys. Rev. **31**, 503 (1928).
[3] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

[4] Model 12-A manufactured by the Perkin-Elmer Corporation, Glenbrook, Connecticut.
[5] N. D. Coggeshall and E. L. Saier, J. App. Phys. **17**, 450 (1946).

radiation intensities are measured by a null method, which allows greater accuracy and convenience than the method of measuring galvanometer deflections. The optical densities were obtained by using a pair of cells. One of these cells was the gas cell and the other an evacuated comparison cell. The gas cell was evacuated, and the ratio of its transmission to that of the comparison cell was obtained for each wavelength being investigated. These ratios were then combined with the corresponding ones obtained for the sample in the gas cell to get the true optical densities.

Two absorption cells were used, one of 9.50 cm length and one of 3.15 cm length. Both had NaCl windows and were mounted in the manner described in reference 5. The spectrometer and gas blending equipment were located in an air conditioned room in which the temperature was kept within 1°C of a mean value. This was significant as the temperature is an important parameter in pressure broadening, and our method of analyzing the data required that it be constant. The blending and mixing of the gases was achieved in either of two ways, depending upon the relative concentrations of the components. One of these involved a special blending system in which mixing was achieved in a reservoir by moving an iron vane by means of exterior magnets. The other method was to introduce both gases into the absorption cell and mix them there by mechanical motion. This was possible as the cell contained a metal vane which lay out of the optical path when the cell was in an operating position, but which could otherwise be moved throughout the interior to mix the gases. A thorough mixing of the components is very important in obtaining data of this sort. The gases used were the purest obtainable commercially,[6] and in each case the impurities present were of such small concentration as not to affect the results.

DATA AND DISCUSSION

According to the Lorentz theory, the absorption for the individual line as a function of

frequency has the form,

$$K(\gamma) = \frac{a_i nl(1/\tau)}{4\pi^2(\gamma - \gamma_i)^2 + (1/\tau)^2}, \quad (1)$$

where a_i is a constant characteristic of the individual line; n is the number of absorbing gas molecules per unit volume; l is the length of the absorption cell; τ is the mean time between collisions; and γ_i is the frequency of maximum absorption for the line. In correlating the information included in (1) with actual experimental data the limitations on resolution of the spectrometer used must be considered. For this we use the energy transmittance function $f(\gamma, \gamma_0)$ which gives the energy as a function of frequency in the spectral band width transmitted by the instrument when set to pass radiation of frequency γ_0.[7] The transmission for a sample of gas is given by

$$T = A \int_{-\infty}^{\infty} \exp - \left\{ nl \sum_i \left(\frac{a_i(1/\tau)}{4\pi^2(\gamma - \gamma_i)^2 + (1/\tau)^2} \right) \right\} \times f(\gamma, \gamma_0) d\gamma, \quad (2)$$

where A is a constant which takes into account the integral of the transmittance function over the same spectral region. Although the limits of the integral in Eq. (2) are $-\infty$ and $+\infty$, this does not imply significant contributions from frequencies very far removed from γ_0. Actually the transmittance function $f(\gamma, \gamma_0)$ will be such that it goes to zero very rapidly for values of γ further removed from γ_0 than one-half the spectral slit width. Dennison[2] has found that for the transmittance function both a Gaussian and triangular form are about equally effective in calculating transmissions. The summation in the exponential under the integral in Eq. (2) must be taken over all frequencies which are included in the spectral slit widths. For this reason the analytical evaluation of (2) is very difficult unless a spectral slit width characteristic of an instrument of high resolution is used.

Despite the difficulties of directly using Eq. (2) to correlate theory and experiment or to obtain values of the characteristic constants, use may be made of it to obtain information

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[6] The companies from whom the gases were obtained were: The Linde Air Products Co., Buffalo, N. Y.; The Matheson Co., East Rutherford, N. J.; Phillips Petroleum Co., Special Products Division, Bartlesville, Oklahoma; The Ohio Chemical & Mfg. Co., Cleveland, Ohio.

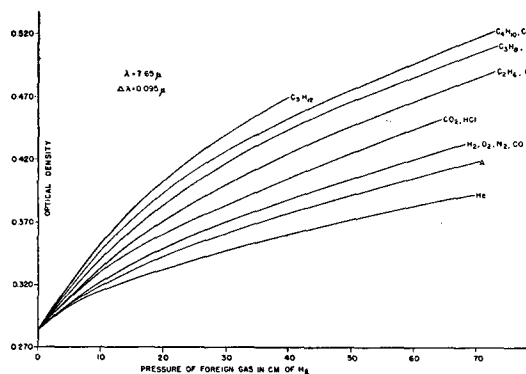[7] See for example: J. R. Nielson, V. Thornton, and E. B. Dale, Rev. Mod. Phys. **16**, 307 (1944).

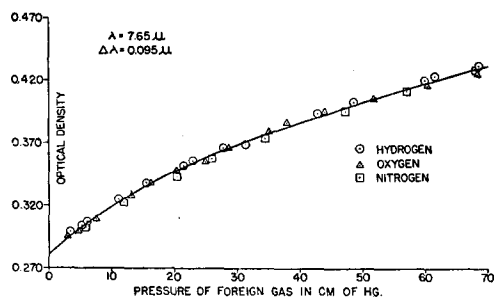FIG. 1. Effects of various foreign gases on the infra-red absorption of methane at 7.65μ.

FIG. 2. Detail of similar effects of H$_2$, O$_2$, and N$_2$ on methane absorption at 7.65μ.

FIG. 3. Detail effects of isobutane and cis-butene-2 on methane absorption at 7.65μ.
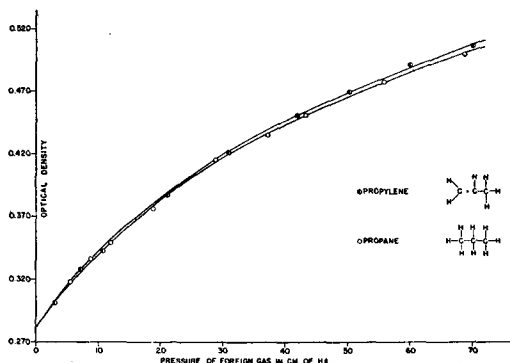
FIG. 4. Detail of effects of propylene and propane on methane absorption at 7.65μ.

concerning the optical collision diameters of various molecules. A consideration of the terms in (2) shows that if the concentration of the absorbing gas, the wave-length, and the slit settings are kept constant, while various foreign, non-absorbing gases are used, the only varying parameter between separate evaluations of (2) will be τ, the mean time between collisions. Figure 1 shows some experimental data taken under the conditions set forth above. Here is plotted the optical density D, $D = \log(1/T)$ for 13.5 cm of Hg pressure of CH$_4$ in the presence of the different foreign gases indicated. This data was taken with the 9.50 cm cell.

Figure 1 indicates that the effect of foreign gases varies widely and depends upon the individual gases showing a general trend of increasing effect with molecules of increasing multiplicity of atoms. It is to be noticed that for a number of cases more than one foreign gas is represented by one curve. For these cases the effects were so similar that only a single curve was drawn. In Fig. 2 may be seen a more detailed curve for one
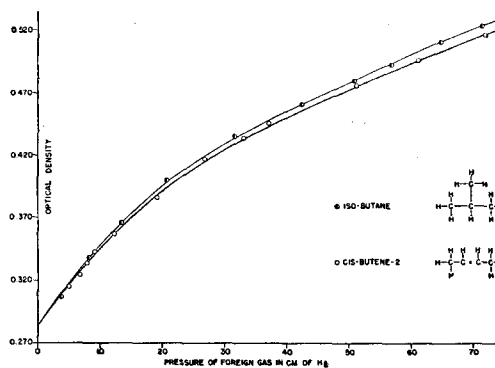
of these cases. Here it is seen that the foreign gases H$_2$, O$_2$, and N$_2$ have the same effects to within the scattering of the data. It might be inferred that the similar effects were caused by some common characteristic of these gases, but, as will be discussed later, we believe it to be merely fortuitous. In a similar study of the effects of foreign gases on the infra-red absorption of N$_2$O, Cross and Daniels[8] found the order of gases with increasing effects on the optical density to be as follows: A, O$_2$, N$_2$, C$_2$H$_6$, CO$_2$, and H$_2$. From our data when compared with this it is obvious that the order of increasing effect cannot be extrapolated from one absorbing gas to another, and this will be further confirmed by additional data below.

Figure 3 shows a detail graph of the effects of isobutane and cis-butene-2. This was of interest in view of the much greater chemical reactivity of the olefin and the possible relation of this

8 P. C. Cross and F. Daniels, J. Chem. Phys. 2, 6 (1934).

difference of chemical reactivity to the pressure broadening effects. A similar graph for propane and propylene may be seen in Fig. 4. From Figs. 3 and 4 it is seen that apparently the chemical reactivity has no direct connection with the pressure broadening, as in one case the more reactive compound of two of about the same molecular weight has a slightly greater effect and in the other case the situation is reversed. It should be mentioned at this point that at the wave-length investigated some of the hydrocarbons used had absorption coefficients which were quite small but not zero. To correct the results for their absorption, Beer's law was assumed to be obeyed by them at this wave-length, and the observed optical density was accordingly corrected. From the general consistency of results discussed below, it is believed that this procedure is correct.

The manner of obtaining data used here wherein only the partial pressure of the foreign gas is varied is equivalent to varying the parameter τ in Eq. (2). Cross and Daniels[8] showed that this procedure may be used to obtain information about the optical collision diameters of the absorbing and foreign gas molecules. Their postulate that the mean free path of the absorbing molecules is the same in all gas mixtures which exhibit the same relative absorption coefficient is equivalent in this case to assuming that Eq. (2) is correct. They showed that if the partial pressures of different foreign gases which produced the same increase of optical density under the conditions above could be experimentally determined, the ratios of their optical collision diameters could be deduced. This is done by straightforward application of the kinetic

TABLE I. Values of p_Y/p_X for different values of D.

D	p_{He}/p_{CO_2}	p_A/p_{CO_2}	p_{H_2}/p_{CO_2}
0.330	1.86	——	1.33
0.340	1.95	1.43	1.33
0.350	1.99	1.44	1.31
0.360	2.00	1.46	1.29
0.370	1.99	1.44	1.28
0.380	2.00	1.45	1.28
0.390	2.02	1.46	1.28
0.400	——	1.47	1.29
0.410	——	1.47	1.29
0.420	——	1.49	1.31

theory of gases and the result is:

$$D_{AX}/D_{AY} = (p_Y/p_X)^{\frac{1}{2}}$$
$$\times [M_X(M_A + M_Y)/M_Y(M_A + M_X)]^{\frac{1}{4}}, \quad (3)$$

where D_{AX} is the distance between the centers of absorbing molecule A and the foreign gas molecule X, at which the process of absorption of radiation by A is interrupted. It is then the sum of the optical collision radii of each of the two molecules. D_{AY} is the corresponding quantity for the case of foreign gas Y in the presence of A. P_Y and P_X are partial pressures of gases Y and X which produce the same optical density. M_A, M_X, and M_Y are the molecular weights. For the derivation of (3) from the principle that equal values of τ used in (2) will produce equal optical densities, it is necessary that the temperature of the gas be the same for the different observations. This was achieved in our experiments by allowing equilibrium to be reached between the gas and the room temperature which was controlled.

In the determination of molecular diameters from viscosity or other gas kinetic data, values are obtained which are representative of the distance between molecular centers such that momentum may be transferred. Or, in other words, only those collisions wherein there is a transfer of momentum affect the experimental results. Certainly each such collision would be expected to interrupt the process of radiation absorption by an absorbing molecule. In addition the perturbation of vibrational and rotational states by Van der Waals interactions would be expected to alter the absorption processes in many encounters not close enough to affect momentum transfer. For this reason, a determination of molecular diameters by an application of Lorentz pressure broadening theory gives values called optical collision diameters which are larger than the molecular diameters obtained from kinetic data. The present work gives only ratios between diameters for reasons which will be discussed below. Recently Bleaney and Penrose,[9] in a study of the ammonia bands in the 1-cm region using the microwave technique, have found that the optical diameter effective in

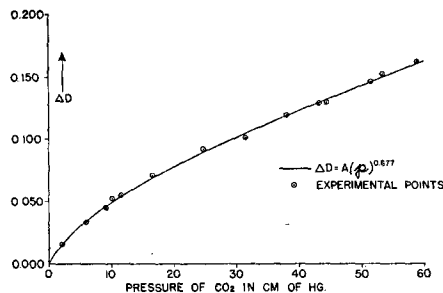[9] B. Bleaney and R. P. Penrose, Nature **157**, 339 (1946).

FIG. 5. Increase in optical density of constant pressure of methane as a function of foreign gas pressure.

broadening these bands to be about four times the normal diameter.

Since the optical collision diameters should be independent of gas pressure, Eq. (3) may be used to confirm the physical basis and reasoning used in deriving it. For if these are correct, Eq. (3) may be applied to any pair of partial pressures giving the same optical densities. Therefore the ratio p_Y/p_X should be constant for all values of optical density for which it is determined. Table I gives the values of this ratio for several different pairs of foreign gases at different values of optical density D using the data of Fig. 1.

In this table we may see that the ratios of the pairs of pressure determinations do not vary more than a few percent over the range of optical density used. The greatest variation occurred for the smaller values of optical density, and this could have been caused by experimental difficulties in obtaining the lower end of the curves in Fig. 1. Certainly the values of p_Y/p_X are constant enough to give confirmation to the correctness of Eq. (3).

Returning for the moment to Eq. (2), we note that n, the number of absorbing centers per unit volume, and l, the cell length, enter the integral as a product. Thus, if the product nl is kept constant and the mean time between collisions is kept constant it is possible to achieve the same value of the integral under various experimental conditions. For example, if one has the absorbing gas at a high pressure p_1, in a short cell of length l_1, with no foreign gas present, a certain optical density is obtained. If a second pressure p_2 is used in a cell of greater length l_2, yet adjusted so that $p_1 l_1 = p_2 l_2$, foreign gas must be added to the longer cell to get the same optical density as obtained with the shorter one.

This is because the τ due to the absorbing gas alone will change with change of pressure. Using these two different arrangements allows a determination of D_{AA}/D_{AX}. This is given by Eq. (4) which is derived by the same arguments as Eq. (3).

$$D_{AA}/D_{AX} = [p_X/(p_1 - p_2)]^{\frac{1}{2}}$$
$$\times [(M_A + M_X)/2M_X]^{\frac{1}{4}}. \quad (4)$$

Here p_X is the pressure of foreign gas X that must be added to get an optical density using the longer cell equal to that obtained with the shorter one. In our work, the short cell was 3.15 cm in length, and the pressure of methane used in it was 39.70 cm of Hg. The values of p_X used to evaluate Eq. (4) were obtained by reading off from the curves in Fig. 1. The results of using Eq. (4) on the data obtained with the short cell and the data of Fig. 1 are given in Table II.

We note here that, in general, the ratio D_{AA}/D_{AX} decreases with increasing complexity of the X molecules, or in other words the optical diameters of the X molecules increase with increasing size. HCl is somewhat out of place in this respect, but its large optical diameter is believed to be owing to its large dipole moment.

An interesting empirical result is illustrated in Fig. 5. Here ΔD which is the difference between the observed optical density when a foreign gas is used and the optical density obtained for the methane in the cell alone is plotted *versus* the partial pressure of foreign gas, in this case CO_2. Here it is seen that ΔD is given by the equation:

$$\Delta D = A p^s, \quad (5)$$

where A and s are empirically determined constants. As may be seen the agreement between the points and the curve fitted to two of them is

TABLE II. Values of D_{AA}/D_{AX} for various foreign gases. (A = methane; X = foreign gas used; $\lambda = 7.65\mu$.)

X	D_{AA}/D_{AX}	X	D_{AA}/D_{AX}
He	1.72	C_2H_4	0.82
A	1.07	C_2H_6	0.82
H_2	1.59	C_3H_6	0.72
N_2	1.03	C_3H_8	0.73
O_2	1.01	C_4H_8	0.68
CO	1.03	C_4H_{10}	0.66
CO_2	0.87	C_5H_{12}	0.63
HCl	0.88	——	——

FIG. 6. Effects of various foreign gases on the infra-red
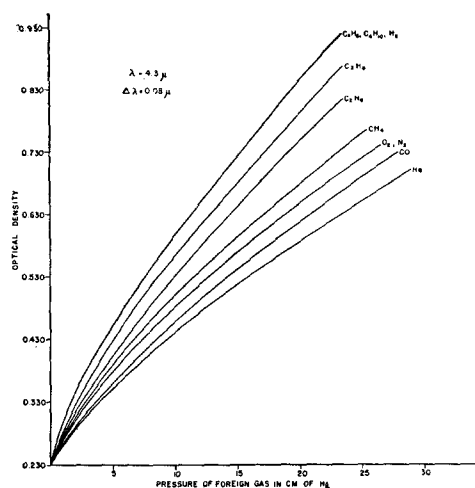absorption of carbon dioxide at 4.3μ.

FIG. 7. Effects of various foreign gases on the infra-red
absorption of carbon dioxide at 14.8μ.

quite good. From the agreement of the data with Eq. (5) for the case of CO_2 and from constancy of the ratios in Table I we may conclude that agreement may be had for the other foreign gases and that the value of the exponent will be 0.677 for each. A curve of optical density *vs.* pressure for various pressures of methane alone in the 9.50 cm cell gave good agreement with the empirical equation $D = Ap^s$ which is very similar to Eq. (5). The value of the exponent in this case was 0.743.

In addition to the work done on methane the effect of various foreign gases on the absorption of CO_2 was investigated at two different wavelengths 4.3μ and 14.8μ at which absorption takes place due to stretching and bending vibrations respectively. The results for the 4.3μ investigation are seen in Fig. 6, and the results for the 14.8μ work are seen in Fig. 7. Here again the 9.50-cm cell was used, and the partial pressure of CO_2 used at 4.3μ was 3.50 cm of Hg, and at 14.8μ a partial pressure of 9.86 cm of Hg was used. Since with the instrument used the optical path at one place passed through an open space this created some experimental difficulty. This was owing to the fact that if the carbon dioxide content in the room was not constant then the transmittance function $f(\gamma, \gamma_0)$ used in Eq. (2) would not be the same in each case. For this reason data for CO_2 studies were only taken after a CO_2 equilibrium was reached in the room.

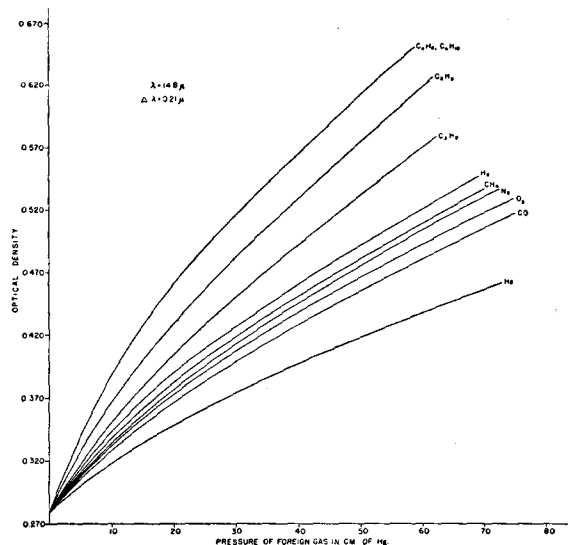Reproducibility tests indicated the equilibrium concentration to be nearly the same each day.

An inspection of Figs. 6 and 7 shows that in general the order of increasing effect of the foreign gases is the same for the two different spectral regions. Two exceptions to this are that O_2 and N_2 have the same effect at 4.3μ but distinctly different effects for 14.8μ. Another and more striking exception is that of H_2 which has an effect similar to that of methane for 14.8μ absorption but has a relatively much greater effect at 4.8μ, being of the same magnitude as for isobutane and butadiene. In connection with the latter point, it is interesting to note that the two compounds, isobutane and butadiene, which differ radically in chemical reactivity, have the same pressure broadening effect for CO_2 for both the 4.3μ and 14.8μ bands. From this and the observations on methane it seems safe to conclude that chemical reactivity is not to be directly correlated with optical collision diameters.

The ratios of D_{AA}/D_{AX} were obtained in the same manner as for methane, using the 3.50 cm cell, and the results are given in Tables III and IV.

An examination of the values of D_{AA}/D_{AX} in Tables III and IV shows that for each different gas X considered the values for the two wavelengths are equal to within about 8 percent

except for the gases H_2, C_3H_8, C_4H_{10}, and C_4H_6. These differences, however, plus the variations in order of increasing effect shown for the different absorbing gases confirm our belief that the optical collision diameter ratio is a specific function of the pair of gases under consideration and of definite absorption frequencies. That is, the pressure broadening effect of a gas on one absorber cannot reliably be extrapolated to predict the effect on another. Nor can the results for one particular wave-length be reliably extrapolated to another for the same pair of gases. Thus, optical collision radii have definite quantitative meaning only for specific cases. These conclusions are in line with the recently published work of Foley[10] which indicates the complicated nature of the dependence of the pressure broadening on the molecular interactions. As would be expected, the optical collision diameters depend upon the nature of the Van der Waals interactions and upon the excited states of the gas molecules.

Although data of the type discussed above can give only relative results, i.e., ratios between various optical collision diameters, recent work

TABLE III. Values of D_{AX}/D_{AA} for various foreign gases. (A =carbon dioxide; X =foreign gas used; $\tau =4.3\mu$.)

X	D_{AA}/D_{AX}	X	D_{AA}/D_{AX}
He	2.18	CH_4	1.26
O_2	1.20	C_2H_6	1.00
N_2	1.19	C_3H_8	0.85
H_2	1.90	C_4H_{10}	0.72
CO	1.29	C_4H_6	0.72

TABLE IV. Values of D_{AA}/D_{AX} for various foreign gases. (A =carbon dioxide; X =foreign gas used; $\lambda =14.8\mu$.)

X	D_{AA}/D_{AX}	X	D_{AA}/D_{AX}
He	1.98	CH_4	1.25
O_2	1.17	C_2H_6	1.07
N_2	1.19	C_3H_8	0.97
H_2	1.64	C_4H_{10}	0.86
CO	1.27	C_4H_6	0.87

[10] H. M. Foley, Phys. Rev. **69**, 616 (1946).

in microwave technique has demonstrated its possibilities for obtaining absolute values for those wave-length regions.[9, 11, 12]

Another gas given some investigation was isobutylene. If the optical density is plotted *vs.* pressure of isobutylene at the wave-length of 11.23μ (the center of the Q branch) there results a curved line similar in appearance to Fig. 5. This deviation from Beer's law would not seem likely to be caused by pressure broadening due to the large moments of inertia and consequent small spacing between rotational levels for the isobutylene molecule. However, the pressure broadening possibility was checked by comparing the optical density of a particular pressure of isobutylene with the optical density obtained when various pressures of foreign gases were added. In this work a constant pressure of 2.35 cm of isobutylene was used in the 9.50-cm cell. To this were added various pressures of H_2, N_2, and CO_2 ranging from 20 to 75 cm. For each observation regardless of type or pressure of foreign gas the optical density was equal, within experimental error, of the optical density obtained for the isobutylene by itself. This we believe is conclusive evidence that this particular deviation from Beer's law is not due to pressure broadening. It seems likely that it may be owing only to the combined effect of line shape and finite slit widths.

The above data are of interest for applications of infra-red absorption spectroscopy for analytical uses. Gases subject to pressure broadening may be quantitatively measured in mixtures, but allowance must be made for the pressure broadening effects.[5]

[11] R. Beringer, Phys. Rev. **70**, 53 (1946).
[12] W. E. Good, Phys. Rev. **70**, 213 (1946).