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Relative Optical Collision Diameters from the Pressure Broadening of Individual Infrared Absorption Lines*

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A matching method for the study of the widths of individual infrared absorption lines is used to obtain relative values of optical collision diameters, and to determine qualitative features of molecular interactions in pressure broadening phenomena. Isolated vibration-rotation lines of HCl and CH_4 are successively broadened by the same fourteen gases, and collision diameters derived are compared with each other and with previously published values of optical collision diameters. Striking correlations are found between the HCl relative diameters and absolute values of optical collision diameters obtained by other investigators using microwave techniques on the inversion spectrum of NH_3. The experimental data here presented are consistent with the presence of a pressure broadening interaction between the induced dipole of a broadener molecule and some undefined property of the absorber, for any broadener used. An additional interaction between the quadrupole moment of the broadener and the dipole of the absorber appears to exist when unsymmetrical molecules are employed to broaden the spectral lines of polar absorbers.

INTRODUCTION

THE study of pressure broadening has often received its impetus from the necessity of understanding the effect of this phenomenon on other problems of a spectroscopic nature. In the microwave region, the pressure ranges usable for experimental spectroscopy are effectively dictated by the pressure-controlled line widths. In the infrared region, the increased absorption often associated with pressure broadening constitutes a major factor in both atmospheric transmission and quantitative gas analysis problems. The frequency shift resulting from pressure broadening warrants attention in the accurate determination of wavelengths in the visible region. As a consequence, much of the interest in this field has centered on corrections for or circumvention of the pressure effect.

Recently, some investigators[1–4] have adopted the viewpoint which welcomes pressure broadening as an observable manifestation of interactions between molecules, and as a consequent key to the nature of these interactions. The present work is concerned with this latter trend of investigation, with a further interest in the possibility of applying the process in reverse, that is, predicting the pressure broadening properties of various gases from their structure or from semi-empirically determined interaction parameters. Principally because of this emphasis upon molecules and their properties, the extensive pressure broadening experiments in the visible region with the atomic spectra of metals are not considered here.

Most infrared pressure broadening experiments have been carried out using total band absorption, largely as a result of the experimental difficulty of resolving individual vibration-rotation lines. In order to avoid certain limitations in the interpretation of the data obtained from low resolution studies, the present investigation has been directed to the measurement of individually resolved vibration-rotation lines, namely, the $J=2\rightarrow 3$ line of the HCl band at 3.46μ and the $J=4\rightarrow 5$ line of the CH_4 band at 3.25μ. By thus confining attention to isolated rotational lines, one obtains pressure broadening data comparable to that of the microwave region, where the line widths of individual pure rotation lines have been studied as functions of pressure.

The direct measurement of line width being beyond the reach of available infrared instrumentation, the present work has employed a matching method to establish a comparison between line widths. An absorption line has here been broadened an arbitrary convenient amount, the same for each broadening gas. The quantities of broadening gas necessary to produce this predetermined line breadth (for a fixed number of absorbers) are an inverse measure of the relative efficacies for broadening by these gases. In the case of absorption by HCl, the line as broadened by each of thirteen foreign gases was compared with the self-broadened line, the numbers of absorbing molecules in either path remaining equal. For the CH_4 absorption line, the nitrogen-broadened line was used as standard, and the line broadened by each of the other thirteen foreign gases was compared with this.

PROCEDURE

The equipment consisted of a carbon arc light source, a prism-grating infrared spectrometer, a lead telluride detector, and appropriate auxiliary electronic, record-

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[1] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **60**, 540 (1948).

[2] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[3] W. V. Smith and R. Howard, Phys. Rev. **79**, 132 (1950).

[4] R. M. Hill and W. V. Smith, Phys. Rev. **82**, 451 (1951).

ing, and optical apparatus. In conjunction with this array, two identical absorption cells of two-meter path length were arranged for easy and rapid insertion in the beam and it was the gas in these cells that originated the absorption lines which were compared.

It was determined in preliminary exploratory tests that a highly sensitive measure of line width can be obtained (by proper adjustment of spectrograph slit widths) from the line height as observed on the recorder. This is not true in general, but it does apply to conditions commonly obtaining in infrared absorption spectroscopy. If the spectral slit width of the instrument is larger than the line width, and if in addition the line is essentially black at its center, then the line as observed on the recorder increases rapidly in height as the spectral line is broadened. The spectral slit widths used here ranged from about 0.5 to 1.5 cm^{-1} while the half-widths of the lines remained below 0.01 cm^{-1}. The total pressures for this work varied between 5 and 75 mm Hg, including from 1 to 4 mm Hg of the absorbing gas. For the path lengths and pressures used here, both absorbing lines were sensibly black over a spectral interval of several half-widths breadth.

Using this method of observation a reference line was established by one cell and an adjustable line by the other. Pressure in the reference line cell was held constant, while the pressure in the adjustable line cell was increased by stepwise addition of a foreign gas to produce a match. A condition of "balance" was said to have occurred at that pressure where the two lines as observed on the recorder were of equal height. The corresponding spectral lines at balance must necessarily have had also the same width (if the line shape remains unchanged) since they originated from the same number of absorbing molecules at the same temperature.

PRESENTATION OF DATA

The ratio of the pressures of the broadening gases at balance gives an immediate measure of their comparative broadening abilities, for these pressures indicate the amount of each foreign gas which is required to produce the same degree of broadening. Preliminary experiments demonstrated that the broadening abilities so defined are independent of the amount or percentage of absorber in the cells, within the limits of pressure used. As a continuous check on the consistency of the data, several balance points were obtained for each of the broadening gases, using different amounts or percentages of absorber. Broadening abilities for the various gases used, expressed in terms of that for helium, are given in column 2 of Table I for the HCl absorption line, and in column 3 of the same table for the CH_4 absorption line.

In order to consider a quantity which is characteristic of the interaction between molecules in single encounters, it is desirable to apply the experimentally determined information on broadening ability to the computation of relative optical collision diameters. Invoking the expression, $\Delta\nu=f/2\pi$, which relates line width $\Delta\nu$ to collision frequency f, it will be seen that at balance the collision frequencies of the absorbing molecules in the two cells are equal. In order to compute relative collision diameters, it is necessary to equate the expressions for the collision frequencies at balance, derive therefrom values of the collision cross sections, and extract the square root of each cross section to obtain the corresponding collision diameter.

It is customary to calculate optical collision diameters by analogy with the kinetic theory concept of elastic spheres with fixed radii. This allows the formulation of the following simple relationship between collision frequency, collision diameter, and mean relative velocities of the molecules involved in broadening collisions:

$$f_{ab}=n_bS_{ab}(\bar{v}_a^2+\bar{v}_b^2)^{\frac{1}{2}}. \tag{1}$$

Here f_{ab} is the collision frequency per molecule of type a (absorber), n_b is the density of molecules of type b (broadener), S_{ab} is the cross section for the broadening encounter, and $\bar{v}_a$ and $\bar{v}_b$ are the rms velocities of the respective molecules. If we consider the situation of balance, with broadeners of type b and b', it can easily be shown that

$$\left(\frac{D_{ab}}{D_{ab'}}\right)^2=\frac{S_{ab}}{S_{ab'}}=\frac{n_{b'}}{n_b}\left[\frac{1+(m_a/m_{b'})}{1+(m_a/m_b)}\right]^{\frac{1}{2}}, \tag{2}$$

where D_{ab} and $D_{ab'}$ are the relative optical collision diameters and the m's are the molecular masses.

Because the pressure broadening interactions do not all occur at one fixed distance, the optical collision diameters derived from the above expression do not measure a simple geometrical quantity, but instead they constitute a quantitative indication of the average strength and range of the interactions between the various broadening and absorbing molecules. Furthermore, the emphasis on definite size, which is often adopted in kinetic theoretical applications, is unacceptable here because of the more exclusive dependence of pressure broadening phenomena on long-range forces. The continuum of separations of interacting molecules made possible by these forces overshadows the role of the inner portion of the potential curve where the influence of a large-exponent law constitutes a sharp boundary.

It can be seen from Eq. (2) that the optical collision diameters are proportional to the product of the pressure ratio at balance, representing the broadening ability, and a velocity normalization term. The relative diameters thus computed are given in Table I, those for the HCl absorption line in column 4 and those for the CH_4 line in column 5. In the table several cases appear where the values of broadening ability do not vary even qualitatively with the collision diameters. This emphasizes the distinction between the intrinsic propensity for interaction (collision diameter) which is

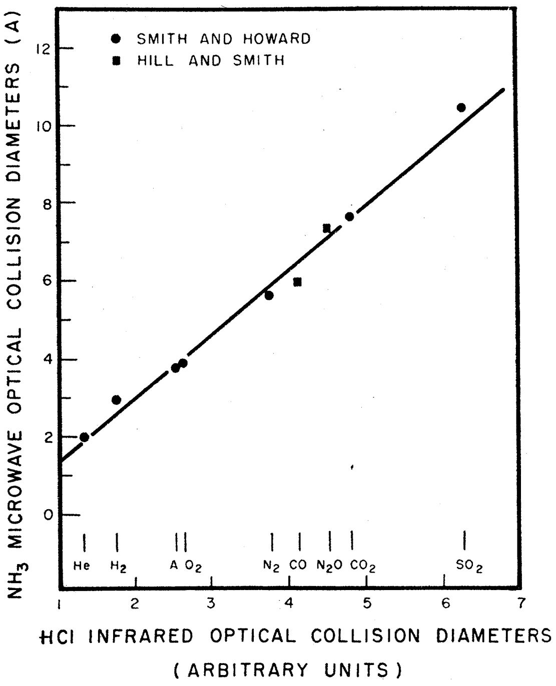

FIG. 1. Optical collision diameters obtained from broadening of a microwave absorption line of NH_3 compared with relative optical collision diameters obtained from broadening of an infrared line of HCl.

a molecular property not directly measured, and the observed manifestation (broadening ability) of this interaction weighted according to an activity factor which depends upon the better known property, molecular mass. The principal value of Eq. (2) is that it relates these two important quantities simply.

RESULTS

In order to compare different groups of values of collision diameters, whether absolute or relative, it is convenient to plot one group against the other as in Fig. 1. In a representation of this type the degree of correlation between two sets of data is indicated by the proximity of the set of points thus obtained to a smooth curve. If the two sets of data increase proportionately, this curve is a straight line through the origin. In Fig. 1 the abscissa of each point represents the value of relative optical collision diameter obtained from the present work on the HCl absorption line, while the corresponding ordinates are a group of values of absolute collision diameters obtained by Smith and Howard[3] and Hill and Smith[4] from the pressure broadening of the microwave inversion spectrum of NH_3, using the same broadening gases. The experimental errors estimated from statistical fluctuations in the data of the two coordinates of points of Fig. 1 and Fig. 2 are comparable, generally amounting to about 2 percent for both the infrared and microwave optical collision diameters.

The correlation indicated by the arrangement of points in Fig. 1, in addition to providing a gratifying confirmation of the quality of these two sets of data, emphasizes the fundamental similarity of pressure broadening results in the microwave and infrared regions. The pressure broadening theory of Anderson[2] is sufficiently generally based to be applicable, in principle, to both infrared and microwave spectra, and in his original paper, foreign gas broadening in the microwave region was considered as an example. The example chosen, however, demonstrated that the results obtained in specific applications of the general theory depend upon the particular interactions postulated to occur. For this reason the application of the same broad theory to pressure broadening experiments in the infrared and microwave regions with dissimilar absorbing molecules might not be expected to result in detailed agreement comparable to that of Fig. 1. In fact, a graphical comparison of this type between NH_3 microwave optical collision diameters and low resolution infrared diameters obtained with the spectra of nonpolar absorbers shows no such correlation.

The two spectral regions, microwave and infrared, are often considered as distinct if only as a consequence of the overwhelming disparity in frequency (which in the present comparison amounts to a ratio of some 3000 to 1) leading to a corresponding disparity between the duration of the collision and the period of the absorbed radiation. There are other differences. The HCl line originates in molecular vibration-rotation,

TABLE I. Relative broadening abilities and optical collision diameters of the present work. Also included are molecular polarizabilities and collision diameters calculated by kinetic theory from viscosity experiments.

Colliding molecule B	Pressure ratio (broadening ability) $\Delta P_{He}/\Delta P_B$ (HCl)	$\Delta P_{He}/\Delta P_B$ (CH_4)	Optical collision diam[a] $D_{B\text{-}HCl}$ (HCl)	$D_{B\text{-}CH_4}$ (CH_4)	Kin. theory diam[b] $D_{viscosity}$ cm	Polarizability cm^3
He	1.00	1.00	2.00	2.00	2.174×10^{-8}	$0.205^c\times10^{-24}$
Ne	0.896	1.00	2.59	2.59	2.594	0.39^c
A	1.87	1.39	3.75	3.24	3.664	1.63^c
Kr	1.88	1.58	4.16	3.59	4.172	2.46^c
Xe	2.06	1.65	4.76	4.20	4.916	4.0^c
SF_6	2.64	2.27	5.42	4.40	—	5.89^d
O_2	1.79	1.47	3.92	3.62	3.620	1.57^c
H_2	2.35	1.73	4.61	2.28	2.730	0.81^c
N_2	3.76	1.60	5.58	3.82	3.756	1.74^c
CO	4.56	1.73	6.13	3.51	3.766	1.95^d
CO_2	5.48	1.79	7.12	3.70	4.630	2.86^c
N_2O	4.87	1.88	6.70	3.79	4.662	3.00^d
SO_2	8.67	2.31	9.27	4.30	5.494	3.72^d
HCl	10.6	2.23	9.70	4.09	4.498	2.63^c

[a] Arbitrarily normalized to make $D_{He}=2$. The values of Figs. 1 and 2 were differently normalized for ease in plotting.

[b] From S. Chapman and T. C. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1939).

[c] From H. Margenau, Revs. Modern Phys. 11, 1 (1939).

[d] FromL andolt-Börnstein, *Phys. Chem. Tables* (Springer-Julius Verlag, Berlin, 1950).

whereas the NH_3 line results from the inversion of the ammonia molecule. Furthermore, the dipole (and quadrupole) moments are different, and the NH_3 molecule has the uncommon feature of a symmetric top that its dipole moment does not average to zero in time.

The important, and perhaps surprising, implication of Fig. 1 is that in spite of these differences, the same interactions predominate in both NH_3 microwave and HCl infrared pressure broadening. Until the present work, there was no such quantitative confirmation of similarity between foreign gas broadening results in the infrared and microwave regions.

It was in order to determine the effect of the mere existence of a dipole moment in the absorbing molecule that nonpolar CH_4 was chosen as the companion absorber for HCl in this investigation. The relative collision diameters obtained with CH_4 as absorber disagreed sharply with the HCl diameters, and also, consequently, with the NH_3 diameters. Furthermore, there was much closer correlation between the methane diameters and the diameters obtained in previous low resolution work[5,6] on CO_2, N_2O, and CH_4 than between the present CH_4 and HCl diameters, although this was not an agreement comparable to that of Fig. 1. It is noteworthy that HCl and NH_3 have large permanent dipole moments, whereas N_2O has only a very small one, and CH_4 and CO_2 are nonpolar. A qualitative, but not close, agreement between the present HCl results and collision diameters obtained from previous low resolution infrared results on HCl[7] helped to substantiate a coarse grouping according to the presence or absence of a strong dipole in the absorber molecule.

Figure 2 is constructed in the same manner as Fig. 1, in this case by plotting the relative optical collision diameters for HCl absorption (Table I, column 4) against those for CH_4 absorption (Table I, column 5). Although the points clearly fail to show even approximate agreement when considered as a single group, the two straight lines drawn through the points demonstrate that a correlation approaching to that of Fig. 1 is possible on the basis of two distinct groupings of broadener types. Here we see one of the principal advantages of the present work over much of the previous work. Points representing fourteen broadening gases here are available to map the details of the disagreement.

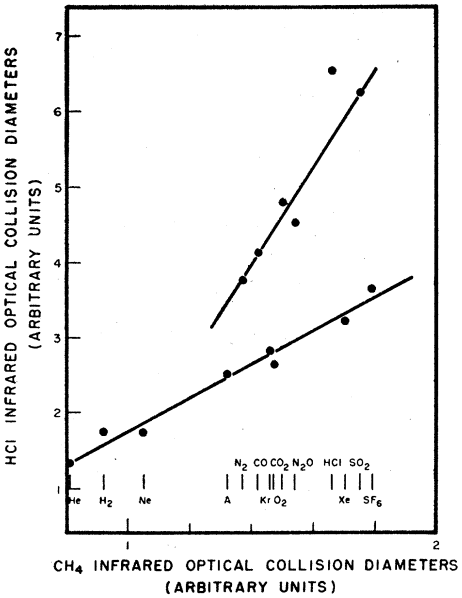

FIG. 2. Relative optical collision diameters obtained by pressure broadening of an HCl infrared absorption line compared with those obtained by pressure broadening of a CH_4 infrared absorption line with the same gases.

The points falling along the lower line in Fig. 2 belong to molecules whose optical collision diameters increase proportionately from point to point regardless of the difference in absorbers. It will be seen that these molecules as a group are characterized by a high degree of symmetry, including, as they do, the five rare gases and SF_6. In addition, there exists independent evidence[8] for a certain degree of symmetry for the O_2 molecular wave function as compared with that of N_2.

The points in the upper group of Fig. 2 again fall nearly along a straight line, with the exception of the point for HCl. The much greater slope of this line is an indication that the ratio of the interaction strength between these molecules and HCl to that between the same molecules and CH_4 is much greater for this group than for the more symmetric group below. The particularly high value for the HCl–HCl collision cross section indicates the presence of a resonance interaction preferential to self-broadening.

DISCUSSION

The emergence of two distinct groups of molecules with respect to their ability to broaden HCl and CH_4 lines removes some of the difficulty which has hitherto been encountered in trying to formulate an adequate theory of microwave foreign gas pressure broadening. Bleaney and Penrose,[1] in making one of the earlier attempts to find a plausible correlation between molecular parameters and microwave collision diameters, investigated the relation between collision diameter and polarizability of the broadener. They were unable to find satisfactory agreement. Anderson, in a thorough quantum-mechanical formulation of the problem, investigated first a dipole:induced-dipole type of interaction[2] and later a quadrupole:induced-dipole model.[9]

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[5] P. C. Cross and F. Daniels, J. Chem. Phys. **2**, 6 (1934).

[6] N. D. Coggeshall and E. L. Saier, J. Chem. Phys. **15**, 65 (1947).

[7] W. Grasse, Z. Physik **89**, 261 (1934).

[8] C. Greenhow and W. V. Smith, J. Chem. Phys. **19**, 1298 (1951).

[9] P. W. Anderson, Phys. Rev. **80**, 511 (1950).

In the latter case, the dipole absorber polarizes the broadener, and the induced dipole in turn interacts with the quadrupole moment of the absorber. Here again the agreement with experiment was unsatisfactory except for the cases of a few simple symmetric molecules. Smith and Howard[3] postulated a dipole: quadrupole interaction for correlation with their values of collision diameter, but this could not have been expected to account for the variations in diameter of, say, the rare gas sequence.

These investigations represent a rather exhaustive search among the single-mechanism hypotheses defined by the nine possible types of long-range interactions between the dipole moment, induced dipole moment, and quadrupole moment of the absorber and the broadener. The present work serves to indicate the source of difficulty inherent in these previous interpretations. It shows that while a single type of interaction may be capable of explaining the broadening abilities of one particular group of molecules, at least two different types of interactions are involved in the pressure broadening of a dipole absorber when a variety of broadeners is used.

Conjecture into the probable nature of the interactions involved here is based on interpretation of Fig. 2. Apparently there is a basic, assured mechanism available to all molecules, however inactive, which entitles them to a position on the lower line of this figure. The consistent grouping along this line (which, like the line of Fig. 1, nearly passes through the origin) is evidence of the dependence of the interaction on a parameter which is associated with the broadening molecule and which determines the ratios of the interaction strengths regardless of the presence or absence of a dipole moment in the absorbing molecule. This is not to say, of course, that such a dipole may not serve to enhance all of the interaction strengths by a constant factor.

The parameter which governs this basic interaction would seem to be associated with the polarizability of the broadening molecules because of the absence of dipole and quadrupole moments in these molecules. The correlation between the polarizabilities and the optical collision diameters of the molecules falling along this lower line resembles that between these polarizabilities and collision diameters obtained through viscosity experiments (columns 4, 5, 6, and 7 of Table I). However, there is sufficient discrepancy, particularly for the case of oxygen, to indicate that the broadener polarizability, although the principal factor in determining relative interaction strength here, probably cannot be held completely accountable for the magnitude of the optical collision diameter.

Of the points which fall along the upper line in Fig. 2, it may be said that their associated molecules have been additionally influenced by the dipole moment of the HCl molecule. There is, apparently, some parameter inherent in these molecules which, in conjunction with the dipole moment of the absorber, produces an increment of interaction strength above the basic common value dictated by the polarizability-linked attributes of these molecules. The source of this exceptional interaction may best be sought in the anisotropy of the fields which may be expected to surround the upper line molecules. As a group, these molecules, where lacking dipole moments, are those which should be most highly suspected of having quadrupole moments, and in this light it would appear that the minimum requirement for the appearance of the exceptional interaction is the presence of a quadrupole moment in the broadening molecule. The assignment of this role to the quadrupole moment, of course, must remain for the present hypothetical, for no values of molecular quadrupole moments are now available.

In conclusion, we should like to express our appreciation to W. S. Benedict for the opportunity of holding many enlightening discussions with him. We are grateful to G. M. Skinner of Linde Air Products Company for making available to us the rare gases at easily manageable pressures. Finally, it is a pleasure to acknowledge the guidance and help we have received from John Strong, in whose laboratory these experiments were conducted.