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The Influence of Foreign Gases on the Intensity of Infrared Absorption

PAUL C. CROSS AND FARRINGTON DANIELS, *Laboratory of Physical Chemistry, University of Wisconsin*

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Measurements have been made on the effect of helium, argon, oxygen, nitrogen, ethane, carbon dioxide and hydrogen on the maximum absorption by nitrous oxide in the region of 4.5μ , by using a spectrometer of low resolving power. Some measurements have also been made with carbon monoxide and ethyl bromide as the absorbing gases. Relative "optical" collision diameters, calculated on the

postulate that the mean free paths are equal in gas mixtures having the same relative absorption coefficients, show a linear relationship with the gas-kinetic diameters as determined by viscosity measurements. The applicability of Beer's law is discussed in connection with the use of infrared absorption measurements as a means of analysis.

THE effect of foreign gases in increasing the infrared absorption of a given amount of absorbing gas was first investigated by Ångström.¹ von Bahr² extended the study with measurements which indicated that the intensity was the same function of the total pressure for all foreign gases. Hertz³ found that there was a difference in the effects of hydrogen and air on the intensity of the absorption by carbon dioxide. The present investigation was undertaken in order to obtain a quantitative measure of the effect of various non-absorbing gases on the intensity of the maximum absorption of certain unresolved bands in the infrared.

Nitrous oxide was selected as one of the absorbing gases because the effect of foreign gases on its thermal decomposition had been investigated by Volmer and his co-workers.⁴ Their results showed that there is a wide variation in the effective cross sections of the foreign gas molecules for an activation collision, and that these cross sections are not related to the gas kinetic cross sections. It seemed important to determine whether the effective cross sections of foreign gases for increasing infrared absorption are related to the effective diameters for chemical

activation, or to the gas kinetic diameters, or to neither. The results show that they are related to the gas kinetic diameters.

Measurements were also made with carbon monoxide and ethyl bromide as the absorbing gases. The foreign gases were helium, argon, oxygen, nitrogen, ethane, carbon dioxide and hydrogen.

APPARATUS

A rocksalt prism spectrometer having a Wadsworth mounting of prism and plane mirror was used. The intensities were measured with a thermopile-galvanometer circuit, taking the average of several galvanometer deflections at each setting of the spectrometer table. As the galvanometer was of the Paschen type, it had the disadvantage that the deflection was not a linear function of the current from the thermopile. The amount of the deviation from linearity depended upon the sensitivity, and since the sensitivity varied from day to day, it was necessary to devise a method of calibration which was simple enough to enable its application with each set of data.

Two light sources were arranged so that they could shine either separately or simultaneously on the thermopile slit. Measurements of the deflections produced by the separate and combined sources indicated that the corrections to be added to the observed deflections to obtain values which were proportional to the intensity could be represented quite accurately by a parabolic function of the deflection. The unit of intensity was selected as one-two hundredth of a 200 mm

¹ L. Ångström, *Ark. f. Math., Astron. och Fys.* 30 (1908).

² E. v. Bahr, *Ann. d. Physik* 29, 780 (1909); 33, 585 (1910); *Verh. d. D. Phys. Ges.* 15, 673 and 710 (1913).

³ G. Hertz, *Verh. d. D. Phys. Ges.* 13, 617 (1911).

⁴ M. Volmer and H. Froehlich, *Zeits. f. physik. Chemie* 19, 89 (1932). M. Volmer and H. Kummerow, *Zeits. f. physik. Chemie* 9, 141 (1930).

deflection on a scale 3 meters from the galvanometer. The deflection, d , produced by the simultaneous illumination of the thermopile slit by the two lights which separately gave deflections of 200 mm was measured. Then

$$y = (400 - d)(x^2 - 200x)/(d^2 - 200d),$$

where x is the observed deflection and y is the correction to be added. Plots of y as a function of x were made for a series of values of d . A determination of d was made with each set of data and the corrections taken from the appropriate curve. Readings taken with various combinations of intensity of the two light sources showed that the deviations of the corrected values from linearity were of the same order of magnitude as the deviations due to the experimental error in the reading of the galvanometer deflections. The corresponding error in the transmission is less than one percent under the experimental conditions employed.

The absorption cell was in two compartments, 2 cm and 18 cm in length. The transmission was first measured with a certain pressure of gas in the 2 cm compartment, then with one-tenth the original pressure in the entire cell. Following this determination, transmissions were measured after the addition of various amounts of foreign gas. Thus in all cases the number of absorbing molecules (or the path length, x = length of cell in centimeters \times pressure of gas in atmospheres, at a specified temperature) was constant and the observed variations in the absorption were functions of the environment of the absorbing molecules. It was found best to work with pressures such that the transmission was between 20 percent and 60 percent. The path lengths employed were 0.526 cm atm. for the N_2O band at 4.5μ and 2.63 cm atm. for the CO band at 4.66μ ,

($T = 298^\circ K$). Under these conditions the enhancement produced in the absorption by the addition of a foreign gas was sufficient to enable its quantitative determination. Measurement of the transmissions of the compressed gas in the 2 cm compartment was omitted in the carbon monoxide experiments since the cell was not constructed to withstand pressures greater than one atmosphere.

EXPERIMENTAL RESULTS

The results are given in Table I. The "relative absorption coefficient" is the ratio of the observed absorption coefficient as calculated by Eq. (2) to that of the pure absorbing gas before the addition of the foreign gas. Most of the added gases were transparent but corrections were applied for the slight absorptions of carbon dioxide and ethane in the regions being investigated. The value 2.8 for N_2O is the ratio of the observed absorption coefficient for N_2O at 200 mm pressure in the 2 cm cell to the coefficient for N_2O at 20 mm pressure in the 20 cm cell.

The effect of the various gases on the absorption of nitrous oxide is shown graphically in Fig. 1.

Additional experiments were carried out on gaseous ethyl bromide. In no case did the addition of a transparent foreign gas affect the infrared absorption by ethyl bromide. The measurements were carried down to 10 mm of ethyl bromide, and one atmosphere of the foreign gas.

DISCUSSION

If α_ν is the absorption coefficient for light of frequency ν , the intensity I_ν of the light of this frequency which is transmitted through l cm of the absorbing gas at a pressure of p mm of mercury is given by the relation

$$I_\nu = I_\nu^0 e^{-\alpha_\nu l p},$$

where I_ν^0 is the incident intensity of the light of frequency ν . It is assumed throughout this discussion that the temperature is not varied.

In actual practice, measurements of transmission are always made on a range of frequencies from ν to $\nu + \Delta\nu$, and T , the fraction of the energy transmitted, becomes

$$T = \int_{\nu}^{\nu+\Delta\nu} I_\nu^0 e^{-\alpha_\nu l p} d\nu / \int_{\nu}^{\nu+\Delta\nu} I_\nu^0 d\nu. \quad (1)$$

TABLE I. Relative absorption coefficients.

Foreign gas	Total pressure (mm of mercury)							
	N_2O (partial pressure = 20 mm)					CO (partial pressure = 100 mm)		
	50	100	200	400	700	200	400	700
He	1.39	1.87	2.44	3.06	3.56	1.32	1.74	2.21
A	1.41	1.86	2.44					
O_2	1.42	1.87	2.47	3.13	3.58	1.32	1.77	2.23
N_2	1.44	1.93	2.56			1.36	1.85	2.39
C_2H_6	1.48	2.03	2.69			1.41	1.91	2.52
(N_2O)			2.8					
CO_2	1.53	2.07	2.87					
H_2	1.57	2.19	2.91	3.53	3.85	1.45	2.01	2.59

It can readily be seen from this formula that the apparent absorption coefficient α' as determined from the experimental measurements of T ,

$$\alpha' = (1/lp) \cdot \ln (1/T) \quad (2)$$

will not be a constant unless α_ν is independent of lp and has the same value for all frequencies from ν to $\nu + \Delta\nu$. Many infrared bands possess a fine structure of such separation that α_ν varies over a wide range between the frequencies ν and $\nu + \Delta\nu$, and thus one would expect deviations from Beer's law as the product lp is varied. Furthermore, the values of α' will vary with p even though the product lp is held constant because the nature of the function $\alpha_\nu = f(\nu)$ depends upon the pressure. The absence of a pressure effect on the ethyl bromide bands may be attributed to the fact that their fine structure components overlap so much that α_ν is nearly constant over small frequency ranges.

Dennison⁵ has been quite successful in explaining experimentally observed absorption intensities on the assumption that the nature of $\alpha_\nu = f(\nu)$ is determined essentially by the limitation of the length of the wave trains which may be absorbed by the molecules. This limitation is caused by the approach of another molecule to a distance sufficiently close to alter the phase of the absorbing molecule. The effective diameter of a molecule for this type of collision was found to be larger than the gas kinetic diameter, but is of the same order of magnitude.⁶

Let D_{AX} , D_{AY} and D_{AN_2} represent the distance between the centers of the molecule of absorbing gas, A , and the foreign gas molecules X , Y and N_2 , respectively, at which a change in phase of the absorbing molecule is effected. Making the postulate that the mean free path of the absorbing molecule is the same in all gas mixtures which have the same relative absorption coefficient, one may readily calculate the ratio D_{AX}/D_{AY} from the experimental data. The equation for the mean free path, Λ , of the absorbing gas molecule is

$$1/\Lambda = (2)^{1/2} \pi n_A D_{AA}^2 + \pi n_X D_{AX}^2 [(m_A + m_X)/m_X]^{1/2} \quad (3)$$

⁵ D. M. Dennison, Phys. Rev. **31**, 503 (1928).

⁶ For a general discussion of the breadth of spectral lines see V. Weisskopf, Phys. Zeits. **34**, 1 (1933).

where D_{AA} is the "optical" diameter of the N_2O molecule, the n 's are the number of the molecules per cc, and the m 's are their masses. Equating the mean free paths in two systems having equal relative absorption coefficients, one obtains the ratio

$$\begin{aligned} D_{AX}/D_{AY} &= (n_Y/n_X)^{1/2} [m_X(m_A + m_Y)/m_Y(m_A + m_X)]^{1/2} \\ &= (p_Y/p_X)^{1/2} [M_X(M_A + M_Y)/M_Y(M_A + M_X)]^{1/2}, \quad (4) \end{aligned}$$

where p_X and p_Y are the equivalent partial pressures of the foreign gases as obtained from the intercepts of horizontal lines with the respective curves of plots such as shown in Fig. 1, and M_X and M_Y are the molecular weights. Ratios obtained with the use of Eq. (4) are given in the second and third columns of Table II. The effective distances of approach of the foreign gases are referred to that of nitrogen. The values given

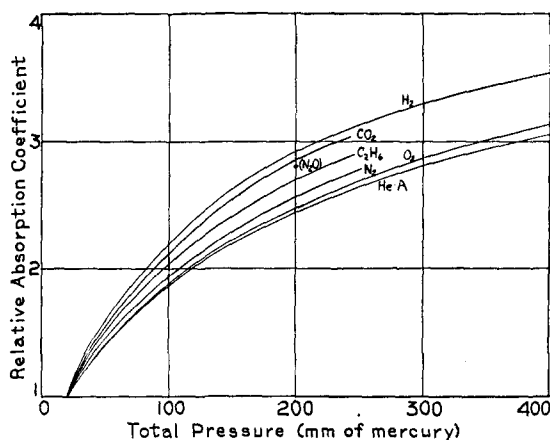


FIG. 1. Influence of pressure on relative absorption coefficients at 4.50μ of nitrous oxide (partial pressure = 20 mm).

TABLE II. Collision diameter ratios.

X	D_{AX}/D_{AN_2}		$D_{XX}/D_{N_2N_2}$	
	A = N_2O	A = CO	Optical	Viscosity
He	0.63	0.64	0.07	0.62
H ₂	0.70	0.68	0.24	0.70
O ₂	0.97	0.95	0.93	0.97
A	0.98		0.95	0.96
N ₂	1.00	1.00	1.00	1.00
C ₂ H ₆	1.09	1.07	1.23	
N ₂ O	1.21		1.53	1.22
CO ₂	1.23		1.58	1.20

are averages of the values obtained from the equivalent pressures at the relative absorption coefficients 2.8 and 2.32 on the N_2O curves and 2.3 and 1.9 on the CO curves. All the separate values are within 0.01 of the average.

Let D_{N_2O} , D_{N_2} , etc., represent the optical collision radii. Then the data on the effect of nitrogen and nitrous oxide itself on the absorption coefficient of nitrous oxide show that $2D_{N_2O} = 1.21D_{N_2O} + 1.21D_{N_2}$ or $0.79D_{N_2O} = 1.21D_{N_2}$ whence, $D_{N_2O, N_2O}/D_{N_2, N_2} = 1.53$. The ratios of the optical diameters of the various gases to that of nitrogen are given in column 4 of Table II. The corresponding ratios of the molecular diameters obtained from viscosity measurements are given in the last column for comparison.⁷

The ratios in the last two columns are plotted against each other in Fig. 2. There appears to be a

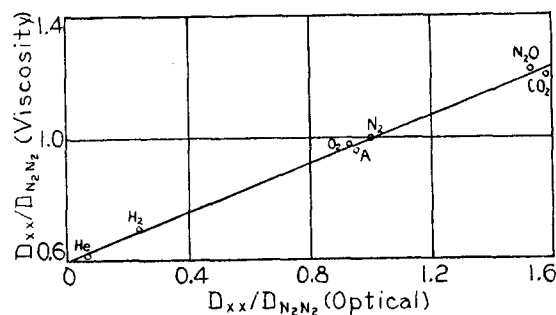


FIG. 2. Relation between "optical" diameters and gas-kinetic diameters.

linear relationship between the two types of effective diameters even though the optical diameters vary over a much wider range than do the viscosity diameters. The points are all as close to the line as can be expected from the accuracy in the determination of either type of ratio. Similar data on larger molecules and on molecules possessing electric moments are necessary to fully establish this relationship but it is unlikely that agreement with a linear relationship involving so many gases can be fortuitous. The same fundamental molecular property may determine both of the effective diameters.⁸

⁷ L. B. Loeb, *The Kinetic Theory of Gases*, p. 529, McGraw-Hill Book Co., New York (1927).

⁸ Attention may also be called to the apparent agreement between the ratios $D_{AX}D_{AN_2}$ from spectroscopic data and D_X/D_{N_2} from viscosity data. If such agreement should

From measurements of the absorption of mixtures of carbon monoxide and air at a total pressure of one atmosphere and very low partial pressures of carbon monoxide, Matheson⁹ found $D_{CO \text{ Air}}$ to be 5.5Å. If this value is assumed for the diameter of the N_2 molecule, the provisional values shown in Table III are obtained for the optical diameters.¹⁰

TABLE III. Optical collision diameters (Angstroms).

Hc	0.4	N_2	5.5
H_2	1.4	C_2H_6	6.8
O_2	5.1	N_2O	8.4
A	5.2	CO_2	8.7

Sufficient data on other absorbing gases are not available to determine whether or not these diameters are the same for all systems. It also remains to be seen whether or not the same values are obtained from the variation of absorption intensity with temperature.

Approximate effective collision diameters for the thermal activation or deactivation of nitrous oxide by foreign gases may be deduced from their effect upon the decomposition rate of nitrous oxide. These diameters also vary over a wide

be substantiated by further data on systems such as those just mentioned, it would seem to imply that the contribution of the absorbing molecule A to the effective distance of approach in the spectroscopic process may be small in comparison with the contribution of the perturbing molecule, which latter is proportional to the viscosity diameter. This would be quite inconsistent with the present theories of the nature of the process. Additional confirmation of this unusual circumstance would appear to be present in the fact that D_{COH_2}/D_{CON_2} and D_{COH_2}/D_{CON_2} are much greater than the values calculated from the absolute values for the diameters as given in Table III (assuming $D_{CO} = 5.5$ Angstroms.) More detailed experiments on carbon monoxide would be desirable to establish these values since the measurements on carbon monoxide reported here were not made under the most favorable conditions. If these values are substantiated it may mean that the optical diameters are different in different systems.

⁹ L. A. Matheson, *Phys. Rev.* **40**, 813 (1932).

¹⁰ Since D_{O_2}/D_{N_2} is nearly 1, Matheson's data may be used for D_{CON_2} . This may then be taken as the diameter of the nitrogen molecule because of the isosterism of nitrogen and carbon monoxide. Absolute values of the optical diameters could have been calculated by a more accurate method based on the fine structure data, but the experimental data are not sufficiently accurate to justify such an elaborate method.

range, but there does not appear to be any relation between them and the optical or viscosity diameters. The chemical activation process is much more violent than the optical effect or the viscosity effect. It is quite possible then that the latter effects should be dependent on the size of the foreign gas molecules whereas the chemical activation might be quite specific.

The influence of transparent, foreign gases on the absorption spectra is of practical importance as well as theoretical interest, in the application of Beer's law to the analysis of mixtures. Colorimetric methods for analysis, which have been successful in the visible, have been used only to a slight extent in the infrared.¹¹ The experimental technique is more difficult and more specialized but measurements of the intensity of infrared absorption should find application in analyzing

mixtures, and in determining equilibrium constants and reaction rates, provided that Beer's logarithmic relation between intensity of light and concentration can be relied on. When the absorbing gas shows fine structure the addition of the same or another gas broadens the fine-structure lines and increases the absorption of a beam of light in such a way as to invalidate the applicability of Beer's law. If the fine structure has been completely blurred out by many collisions or if the molecule is so complex as to have no fine structure the addition of further gas has no effect, and Beer's law can be applied. The data of the present investigation and those of von Bahr² show that Beer's law is applicable to the infrared absorption spectra of complex substances of high molecular weight but that it is applicable to simple diatomic and triatomic gases only when the total pressure is sufficiently great.

The authors are glad to acknowledge the generous support of the Wisconsin Alumni Research Foundation during this investigation.

¹¹ Warburg and Leithauser, *Ann. d. Physik* **28**, 315 (1909), used infrared absorption measurements successfully in the analysis of mixtures of the nitrogen oxides.