INDUCED ABSORPTION OF INFRARED RADIATION BY MOLECULES

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1. INTRODUCTION

THIS review will discuss the infrared absorption associated with the so-called forced or induced vibrational transitions in molecules, which were first discovered and have been studied in detail during the last ten years.

As is known, the intensities of absorption bands in the infrared vibrational spectrum are determined by the values of the changes in the electric dipole moment for the given types of vibration of the molecule. Hence, the vibrational frequencies of nonpolar diatomic molecules and the frequencies of those vibrations of symmetrical polyatomic molecules which are not accompanied by changes in the dipole moments are forbidden under normal conditions in the infrared spectrum. They may be observed only in the Raman spectrum. However, it has recently been established that H_2, N_2, O_2, and other nonpolar gases, on compression to some tens of atmospheres, begin to absorb infrared radiation in the regions of their forbidden vibrational frequencies. The reason for the appearance of this absorption, which has been designated as pressure-induced absorption, is the mutual deformation of the electronic charge distributions in the molecules during collision. Since the electric dipole moment induced in the molecules at the moment of collision is a function of the polarizabilities of the molecules, it undergoes change for those vibrations of the molecules which involve changes in the polarizability. This leads to the appearance in the infrared spectrum of frequencies which under ordinary conditions are active in the Raman spectrum.

The intensity of the pressure-induced infrared absorption increases approximately proportionally to the square of the pressure of the gas. This peculiarity of induced absorption, which reflects the dependence of the concentration of colliding molecules on the density of the gas, permits us easily to distinguish it from absorption associated with magnetic dipole and electric quadrupole transitions. Another interesting peculiarity of induced absorption is the presence in the spectrum of bands with frequencies equal to the sum and the difference of vibrational frequencies of the

two different molecules. These appear as a result of the simultaneous excitation of the two interacting molecules by one light quantum. The appearance of these bands may be explained as follows: The electric field generated by one of the interacting molecules induces a dipole moment in the other molecule, varying with the frequency of vibration of the latter molecule. However, the electric field itself is also varying with the vibration frequency of the first molecule.

Infrared absorption associated with single and double induced vibrational transitions may be observed not only in gases, but also in liquids and solids. The existence of a close connection between the properties of induced absorption and the nature of the interacting molecules makes this a valuable method for study of intermolecular forces. Since in some cases it also reflects changes in the kinetic energies of the interacting molecules, induced absorption is, in addition, one of the most direct methods for study of translational motion of molecules in compressed gases, liquids, and solids.

In addition to the absorption induced by intermolecular forces, recent studies have also been made of infrared absorption resulting from the polarization of the molecules by an external electrostatic field. This type of induced infrared absorption is of especial interest in determining certain molecular constants.

2. ABSORPTION INDUCED BY A CONSTANT ELECTRIC FIELD

The Absorption Coefficient and the Selection Rules. The possibility of infrared absorption by molecules due to the appearance of a dipole moment induced in them was first indicated by Condon[1] in 1932. Condon showed that a substance placed in a constant electric field shows a new infrared vibration-rotation spectrum. The intensity of this spectrum, just like that of the Raman lines, is determined by the matrix elements of the polarizability of the molecule.

If we neglect magnetic dipole and electric quadrupole transitions, the probability of transition of the molecule from an energy level given

by a set of vibrational quantum numbers v and rotational quantum numbers r to a level with quantum numbers v' and r' is given by the expression

$$B = \frac{8\pi^3}{3h^2} |[M]_{v,r}^{v',r'}|^2,$$ (2.1)

where $[M]_{v,r}^{v',r'} = \int \psi_{v,r} M \psi_{v,r}'^* d\tau -$ is the matrix element of the electric dipole moment M, and $\psi_{v,r}$ and $\psi'_{v,r}$ are the wave functions of the lower and upper energy states of the molecule, respectively. The integral absorption coefficient of the band associated with the transition v, $r \to v'$, r' is

$$\int a(\nu) d\nu = \frac{Nh\nu}{c} B = \frac{8\pi^3 N\nu}{3hc} |[M]_{v,r}^{v',r'}|^2.$$ (2.2)

Here, the expression is integrated over all frequencies within the limits of the absorption band. $a(\nu)$ is the absorption coefficient at the frequency ν, as determined by the relation $I = I_0 e^{-al}$, where I_0 and I are the incident and transmitted intensities of light with frequency ν, and l is the thickness of the absorbing layer. N is the number of molecules per cm^3.

We shall denote the components of the polarizability tensor by a_{ij}, and the vector components of the electric dipole moment of the molecule by $M_i \cdot a_{ij}$ and M_i have definite values in a coordinate system referred to the molecule, being functions of the coordinates q which fix the configuration of the nuclei in the molecule. The ordinary infra-red vibrational spectrum is determined by the matrix elements of the components of the dipole moment M_σ, referred to coordinate axes fixed in space. M_σ and M_i are related by

$$M_\sigma = \sum_i a_{\sigma i} M_i.$$ (2.3)

where the $a_{\sigma i}$ are functions of the Eulerian angles ω defining the orientation of the molecular coordinate system with respect to the fixed coordinate system. The wave function, which depends on the motion of the nuclei of the molecule, may be written approximately as the product of vibrational and rotational wave functions

$$\psi_{v,r} = \psi_v(q) \psi_r(\omega).$$ (2.4)

It follows from Eqs. (2.2), (2.3), and (2.4) that the intensity of an absorption band associated with the transition v, $r \to v'$, r' will be determined in the ordinary infrared spectrum by the square of the quantity

$$[M_\sigma]_{v,r}^{v',r'} = \sum_i \int \psi_r a_{\sigma i} \psi_r'^* d\tau_r \int \psi_v M_i \psi_v'^* d\tau_v.$$ (2.5)

We shall now consider the absorption by a molecule placed in a constant electric field. Let E_σ be the components of the electric field intensity vector in the coordinate system fixed in space. Then the components of the induced dipole-moment vector, in this system will be:

$$\mu_c = \sum_k a_{ck} E_h,$$ (2.6)

where $a_{\sigma k}$ are the components of the polarizability tensor of the molecule in the fixed coordinate system. According to the laws of tensor transformation

$$a_{\sigma k} = \sum_{ij} a_{\sigma i} a_{kj} a_{ij}.$$ (2.7)

From Eqs. (2.6) and (2.7), we obtain the following expression for the matrix elements of the components of the induced dipole moment:

$$[\mu_c]_{v,r}^{v',r'} = \sum_{ijk} \int \psi_r a_{\sigma i} a_{kj} \psi_r'^* d\tau_r \int \psi_v a_{ij} \psi_v'^* d\tau_v E_k.$$ (2.8)

According to Eq. (2.2), the integral absorption coefficient of the induced band associated with the transition v, $r \to v'$, r' will be determined by the squares of the matrix elements given by Eq. (2.8). The intensity of the induced absorption will be proportional to the square of the external electric field intensity.

A comparison of Eqs. (2.5) and (2.8) shows that the transition probabilities, and hence the selection rules, for absorption associated with μ, will be different from those in the case of absorption resulting from a constant dipole moment. In distinction from the ordinary infrared spectrum, the induced vibrational spectrum will be determined by the matrix elements of the polarizability of the molecule. Crawford and Mac-Donald [2] have carried out a more detailed calculation of the matrix elements of the induced dipole moment for the case of the molecule H$_2$. However, even the general formula permits one to derive selection rules for the rotational quantum numbers in induced transitions in diatomic molecules. We shall express the rotational factors of the matrix elements $[\mu_\sigma]_{v,r}^{v',r'}$ in terms of the matrix elements which determine the selection rules in the ordinary infra-red spectrum. According to the laws of matrix multiplication

$$[a_{\sigma i} a_{kj}]_r^{r'} = \sum_{r''} [a_{\sigma i}]_r^{r''} [a_{kj}]_{r''}^{r'}.$$

Hence, the transitions $r \to r'$ permitted in the induced spectrum are transitions between levels, each of which combines with a certain third level

r'' under ordinary conditions. For diatomic molecules, this gives the selection rule ΔJ = 0, +2 (Q, S, and O branches), since for the ordinary spectrum ΔJ = +1 (R and P branches). Thus, in this case the selection rules for the induced infrared spectrum coincide with those for the Raman spectrum.

The infrared absorption of H_2. Crawford and Dagg[3] and Crawford and MacDonald[2] have experimentally studied the infra-red absorption of H_2 induced by an electric field. These authors observed the fundamental vibration-rotation band of H_2 in a chamber of path length 85 cm. The outer walls of the chamber were made in the form of two metal plates insulated from each other, and a high voltage was applied to them. The chamber was filled with hydrogen at pressures up to 130 atmos. Under these conditions, the field-induced absorption was superimposed on the pressure-induced absorption. However, these effects may easily be distinguished by the sharp difference in the half-widths of the bands.

In Fig. 1, the dotted curve shows the contour of part of the Q-branch of the absorption band of hydrogen induced by intermolecular interactions in the absence of a field. The gas density was 84 Amagat units.* The transmission maximum at
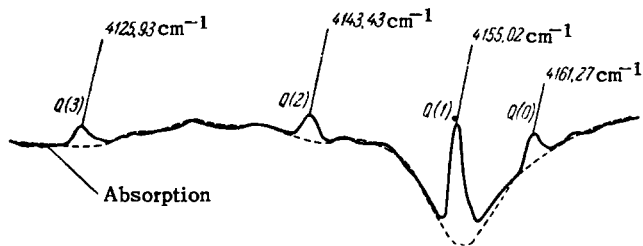

FIG. 1. Components of the Q branch of the fundamental vibrational absorption band of H_2, induced by a constant electric field.[2]

4155 cm^{-1} is a result of the splitting of the Q-branch (see Sec. 3). The solid line gives the contour of the band at an electric field intensity of 130,000 v/cm. As may be seen from the diagram, application of the field brings about the appearance of new, narrow absorption lines. These lines, as should be expected on the basis of the selection rules derived by Condon, are the components of the Q branch of the vibration-rotation band. A comparison of the frequencies of these lines with the frequencies of the com-

*The density in Amagat units is equal to the ratio of the gas density under the experimental conditions to that at 1 atmos and 0°C.

ponents of the Q branch of hydrogen obtained from the Raman spectrum is given in Table I.

The integral absorption coefficient of the induced band of H_2 increases as the square of the electric field intensity. For the component Q(1) of the band, this coefficient is equal to 5.53 × 10^{-29} cm^{-1} per cm path length, per molecule per cm^3, per esu of potential per cm.[2, 3] The experimental determination of the intensity of induced absorption permits us to calculate very accurately the magnitude of the matrix element of the principal value of the polarizability of the molecule, and the matrix element of its anisotropy for the vibrational transition $0 \rightarrow 1$.[2]

TABLE I. Frequencies (in cm^{-1}) of the vibration-rotation spectrum of H_2.[2]. The transition $v \rightarrow v' = 0 \rightarrow 1$

$J \rightarrow J'$	Induced infra red spectrum		Raman spectrum at 1.5 Amagat
	83.9 Amagat	44.6 Amagat	
$0 \rightarrow 0$	4161.20	4161.21	4161.13
$1 \rightarrow 1$	4155.02	4155.13	4155.20
$2 \rightarrow 2$	4143.43	4143.44	4143.39
$3 \rightarrow 3$	4125.93	4125.90	4125.83
$1 \rightarrow 3$	4712.80		4712.86

Absorption induced by adsorption of molecules. Sheppard and Yates[4] have observed infrared absorption induced by the electric field of the surface of an adsorbent. They obtained infrared spectra of a number of molecules physically adsorbed on the surface of porous silica glass at -183 C. The effective path length of the light in the adsorbed compounds was 0.04--0.08 mm. Under these conditions the authors observed, besides the frequencies permitted in the infrared spectrum, the following: the breathing frequency of CH_4 ν_1 = 2899 cm^{-1}, the symmetric vibration frequency of C_2H_4 ν_1 = 3010 cm^{-1}, and the fundamental vibration frequency of H_2 at 4131 cm^{-1} (Fig. 2). The integral absorption coefficient for
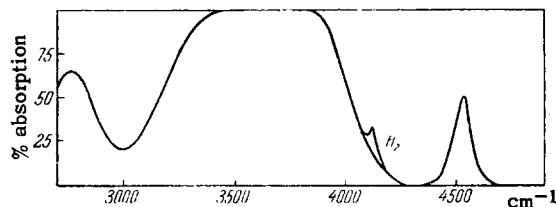

FIG. 2. Infrared absorption spectrum of porous silica glass with adsorbed hydrogen. The absorption band of H_2 indicated by the symbol H_2. The lower curve gives the spectrum of the porous silica glass without adsorbed molecules.[4]

hydrogen was equal to 4.5×10^{-20} cm^{-1} per cm path length per molecule per cm[3]. Making use of this value and the relation obtained in reference[3] between the absorption coefficient of H_2 and the external electric field intensity, Sheppard and Yates calculated the field intensity at the surface of the adsorbent. The value which they obtained for porous silica glass, 7×10^6 v/cm, is approximately an order of magnitude smaller than that given by theoretical calculations for ionic crystals.

3. ABSORPTION INDUCED BY INTERACTION OF MOLECULES

In the infrared vibrational spectrum induced by intermolecular interactions, in distinction to that induced by an electrostatic field, we may observe two types of absorption bands:

1) absorption bands corresponding to the fundamental and overtone vibrational frequencies of each of the interacting molecules;

2) absorption bands with frequencies equal to the sum and difference of the vibrational frequencies of two different molecules.

The occurrence in the infra-red spectrum of those two types of bands, as was first shown by van Kranendonk and Bird,[5] follows directly from consideration of the matrix elements of the electric dipole moment induced by the interaction of the molecules.

The induced dipole moment of the interacting pair of molecules is a function of the nuclear coordinates of the two molecules

$$\mu = \mu(\xi_1, \xi_2, \ldots, \eta_1, \eta_2, \ldots), \qquad (3.1)$$

where ξ_1, ξ_2, $\ldots$ and η_1, η_2, $\ldots$ are the normal coordinates of molecule 1 and molecule 2, respectively. Since we may consider as an approximation that the interaction of the molecules has no effect on the vibrational energy levels, the vibrational wave function of the system of two interacting molecules may be written in the form of the product of the vibrational wave functions of the separate molecules[5]

$$\psi = \psi_1(\xi_1, \xi_2, \ldots)\psi_2(\eta_1, \eta_2, \ldots). \qquad (3.2)$$

Expanding the induced dipole moment (3.1) in powers of the normal coordinates, we obtain:[6, 7]

$$\mu = \mu_0 + \sum_i \left(\frac{\partial \mu}{\partial \xi_i}\right)_0 \xi_i + \sum_j \left(\frac{\partial \mu}{\partial \eta_j}\right)_0 \eta_j + \frac{1}{2}\sum_i \left(\frac{\partial^2 \mu}{\partial \xi_i^2}\right)_0 \xi_i^2$$

$$+ \frac{1}{2}\sum_j \left(\frac{\partial^2 \mu}{\partial \eta_j^2}\right)_0 \eta_j^2 + \sum_{ij} \left(\frac{\partial^2 \mu}{\partial \xi_i \partial \eta_j}\right)_0 \xi_i \eta_j + \cdots, \quad (3.3)$$

where $(\partial \mu / \partial \xi_1)_0 = (\partial \mu / \partial \xi_1)_{\xi_1} = 0$, $\xi_2 = 0$, $\ldots$, $\eta_1 = 0$, $\eta_2 = 0, \ldots$ are functions of the distance between the molecules and of their relative orientations. It follows from Eqs. (3.2) and (3.3) that the matrix elements $\int \psi \mu \psi'^* d\tau$, , which determine the induced infrared spectrum, will contain terms of the type:

$$\left(\frac{\partial \mu}{\partial \xi_i}\right)_0 \int \psi_1 \psi_2 \xi_i \psi_1'^* \psi_2'^* d\tau = \left(\frac{\partial \mu}{\partial \xi_i}\right)_0 \int \psi_1 \xi_i \psi_1'^* d\tau \int \psi_2 \psi_2'^* d\tau$$

$$= \left(\frac{\partial \mu}{\partial \xi_i}\right)_0 \int \psi_1 \xi_i \psi_1'^* d\tau$$

and

$$\left(\frac{\partial^2 \mu}{\partial \xi_i^2}\right)_0 \int \psi_1 \psi_2 \xi_i^2 \psi_1'^* \psi_2'^* d\tau = \left(\frac{\partial^2 \mu}{\partial \xi_i^2}\right)_0 \int \psi_1 \xi_i^2 \psi_1'^* d\tau, \quad (3.4)$$

which contain the normal coordinates of only one of the interacting molecules, and terms of the type

$$\left(\frac{\partial^2 \mu}{\partial \xi_i \partial \eta_j}\right)_0 \int \psi_1 \psi_2 \xi_i \eta_j \psi_1'^* \psi_2'^* d\tau$$

$$= \left(\frac{\partial^2 \mu}{\partial \xi_i \partial \eta_j}\right)_0 \int \psi_1 \xi_i \psi_1'^* d\tau \int \psi_2 \eta_j \psi_2'^* d\tau, \quad (3.5)$$

which contain the normal coordinates of the two different molecules. Terms of the type (3.4) describe the induced vibrational transitions corresponding to the fundamental and overtone frequencies of each of the interacting molecules. Terms of the type (3.5) describe vibrational transitions in the system of two interacting molecules, in which both molecules take part. As a result of such a transition, one light quantum brings about simultaneous changes in the vibrational energies of both molecules. Transitions of this type, which have been designated as simultaneous vibrational transitions, lead to the appearance in the spectrum of frequencies equal to the sum and the difference of the frequencies of the two different molecules:

$$\nu = \nu_{1i} \pm \nu_{2j}.$$

In this section we discuss the absorption associated with induced vibrational transitions of the first type. Simultaneous vibrational transitions will be discussed in Sec. 4.

Infrared Absorption in Compressed Gases. Because of the small radius of action of intermolecular forces, the interaction of molecules in a gas phase is realized practically only at the moment of collision. At gas pressures which are not too high (up to some hundreds of atmospheres), only binary collisions of molecules play an essential role. The number of such collisions per cm^3 per second is proportional to the square of the density of the gas. Since at normal pressures the concentration of colliding molecules is relatively

small, the absorption induced by intermolecular interactions may be observed only in compressed gases.

In 1939-41, A. N. Terenin[8] first studied the vibration spectra in the near infra-red of a number of organic compounds in mixtures with H_2, N_2, and CO, compressed to 3000 atmos. It was shown that an increase in the pressure of the carrier gas causes an insignificant decrease in the valence-bond frequencies of the CH groups in the organic molecules, but sharply increases the width of the absorption bands.

In 1948, Crawford, Welsh, and Locke[9] attempted to establish the existence of the complex $(O_2)_2$ by means of infra-red spectra. They found that oxygen gas at a pressure of 60 atmos and an absorbing path length of 85 cm shows an appreciable absorption with a maximum at the fundamental vibrational frequency of O_2 at 1556 cm^{-1} (see Fig. 4). Under analogous conditions, nitrogen showed an absorption band at 2331 cm^{-1}, that is, at the vibrational frequency of the N_2 molecule. The authors showed that for pure oxygen the absorption coefficient increases approximately as the square of the oxygen pressure. When the partial pressure of the oxygen was held constant, but nitrogen was added to the chamber, the absorption by the oxygen increased linearly with the partial pressure of the nitrogen. Such a relation between the absorption and the density of the gas indicates that the former is not associated with magnetic dipole or electric quadrupole transitions in the isolated molecules, nor with the formation of stable molecular compounds. Rather, it is the result of induced transitions occurring at the moment of bimolecular collision.

In subsequent papers, Welsh and his associates [10, 11, 12, 13, 14, 15, 16, 17] have studied in detail the absorption of H_2 in pure hydrogen and in mixtures with other gases at pressures up to 5000 atmos. These studies have shown that infrared absorption in compressed nonpolar gases is a general molecular phenomenon associated with the polarization of the molecules at the moment of close collision. Here, it has been established that absorption may be induced not only by molecules having dipole or quadrupole moments, but also by atoms of the inert gases, which have neither dipole nor quadrupole fields.

Later, the induced vibrational absorption spectra of an entire series of molecules have been studied in detail. Vodar, Coulon, and their associates have studied absorption induced in CO, HCl, [18, 19, 20, 21, 22] HBr,[23] and HF[24] by nonpolar gases. Welsh, Crawford, and Locke,[10]

and Fahrenfort and his associates [25, 26, 6] have studied the induced absorption of CO_2. In addition, studies have been made of the induced vibrational spectra of CH, [27, 28, 29] C_2H_2,[30, 31, 32, 33, 34] and NH.[35] For H_2, O_2, and N_2, induced absorption bands belonging to the vibrational overtones of these molecules have been observed, [12, 17] in addition to the fundamental vibrational bands. We must mention that, even before the work of Crawford, Welsh, and Locke,[9] Herzberg[36] studied the absorption of hydrogen in the near infrared at a pressure of 10 atmos and an absorbing path length of 5500 meters (by multiple reflection), and observed absorption bands corresponding to the first and second overtones of the vibration of the H_2 molecule. However, this absorption was associated with quadrupole rather than with induced transitions. This is shown, in particular, by the small value of the half-widths of the bands observed by Herzberg.

In addition to the vibrational induced absorption spectra, pressure-induced electronic and rotational spectra have been widely studied recently. [37, 38, 39, 40] A discussion of these spectra, however, is outside the limits of this review.

The Intensity of the Absorption Bands. The integral absorption coefficient $A = \int a(\nu)d\nu$ for pressure-induced transitions obeys the experimental relation: [17, 32]

$$A = a_1 \varrho_a \varrho_p + a_2 \varrho_a \varrho_p^2, \qquad (3.6)$$

where ρ_a and ρ_p are the densities of the absorbing and perturbing gases, respectively, and $\rho_a \ll \rho_p$ for gas mixtures. In Fig. 3 is shown the
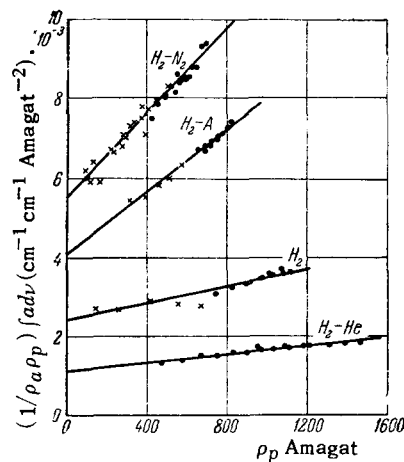

FIG. 3. The change in the value of $\rho_a d\nu / \rho_a \rho_p$ for H_2 as a function of the perturbing gas ρ_p.[17]

TABLE II. Absorption coefficients
for the fundamental vibrational
absorption band of H_2 at 298° K.[17]

Perturb-ing gas	Absorbtion coefficients	
	$[a_1(cm^{-1} cm^{-1} Amagat^{-2})]$	$[a_2(cm^{-1} cm^{-1} Amagat^{-3})]$
H_2	$2.4 \cdot 10^{-3}$	$1.1 \cdot 10^{-6}$
He	$1.1 \cdot 10^{-3}$	$0.55 \cdot 10^{-6}$
Ar	$4.1 \cdot 10^{-3}$	$3.9 \cdot 10^{-6}$
N_2	$5.4 \cdot 10^{-3}$	$5.5 \cdot 10^{-6}$

relation of $A/\rho_a\rho_p$ to ρ_p for pure H_2 and H_2 mixed with other perturbing gases. As may be seen from the diagram, the experimental points lie on a straight line over a broad range of densities, in agreement with Eq. (3.6). The numerical values of the coefficients a_1 and a_2 for H_2 are given in Table II. Since $a_1 \gg a_2$, the second term in expression (3.6) may be neglected at gas densities which are not too high. In this case, the increase in absorption due to the foreign gases is proportional to ρ_p, but for one gas alone $(\rho_a \equiv \rho_p)$), A varies as the square of the density. Thus, at not-very-high pressures, the absorption intensity is proportional to the number of bimolecular collisions. At high densities, the second term in expression (3.6) begins to play an appreciable role, leading to a more rapid increase in absorption. This term is apparently the result of the superposition of two effects: the influence of the finite volume of the molecules, and ternary collisions.[17] The first of these leads to a more rapid increase in the absorption, since at high pressures the volume of the molecules becomes an appreciable fraction of the total space which they may occupy, and thus the number of collisions increases. On the contrary, ternary collisions and those of higher order lead to a slower increase in the absorption. This is because they reduce the number of binary collisions, whereas the dipole moment which appears during the collision of several molecules is smaller in magnitude, due to the partial mutual compensation of the induced dipole moments of the separate molecules.[41] A calculation carried out without taking ternary collisions into account leads to a value of a_2 four or five times greater than the experimental value.

In the case of oxygen, A increases more slowly than the square of the density; this may possibly be due to the formation of O_4 molecules.[42]

The integral absorption coefficient decreases with decreasing temperature.[14, 34] This may be explained qualitatively by the fact that at lower temperatures, the closest approach attained in the

collisions of molecules is less close, on the average. Hence, the interaction inducing the dipole moment is weaker. A general theory of the dependence of the integral absorption coefficient on the density and temperature, and an application to the fundamental vibration-rotation bands of symmetric diatomic molecules, in particular for pure H_2 and mixtures of H_2 with other gases, are given in the papers of van Kranendonk.[41, 43]

The value of the integral absorption coefficient for pressure-induced transitions depends on the nature of the absorbing and perturbing gases. As a rule, it increases with increase in the dipole moment and polarizability of the perturbing molecules.[20, 44, 33] For non-polar molecules at not-too-high gas densities, such that the second term in expression (3.6) may be neglected, the integral absorption coefficient ordinarily amounts to $10^{-3} - 10^{-2}$ cm^{-1} per cm path length per Amagat[2]. However, this value may not be directly compared with the absorption coefficient for transitions allowed in the infrared spectrum, since the number of molecules which can undergo the induced vibrational transition is considerably less than the total number of molecules.

If we assume that the number of colliding molecules is equal to the total number of molecules of the gas at 1 atmos, then for the induced bands of CO_2 at frequencies 1286 and 1389 cm^{-1} $(v_1$ and $2 v_2)$, we obtain values of the integral absorption coefficients of 6.60×10^{-2} and 1.14×10^{-1} $cm^{-1} cm^{-1}$, respectively (for 2.69×10^{19} absorbing units per cm^3).[6] The integral absorption coefficients for the active bands of CO_2, 667 cm^{-1} (v_2) and 2349 cm^{-1} (v_3), under the same conditions, amount to 1.87×10^2 and 2.87×10^3 $cm^{-1} cm^{-1}$, respectively. Thus, for equal numbers of absorbing units per cm^3, the integral absorption coefficient for pressure-induced transitions is three or four orders of magnitude lower than that of bands allowed in the infra-red spectrum.

The Structure of the Absorption Bands. Since the dipole moment which appears as a result of intermolecular interactions is a function of the polarizabilities of the molecules, pressure-induced infra-red absorption, just like that induced by an external electric field, obeys the vibration-rotation selection rules for the Raman spectrum. In the case in which the vibration of a diatomic molecule is normally allowed in the infra-red spectrum, induced absorption leads to a distortion of the vibration-rotation band, which consists of P and R branches, due to the appearance of a Q branch.[18, 19, 20 24, 45, 38] The absorption bands of symmetrical diatomic mole-

cules consist of Q, S, and O branches. The corresponding selection rules ($\Delta J = 0$, ± 2) for the H_2 molecule were derived theoretically by van Kranendonk and Bird.[5, 46]

The individual rotational lines of the induced bands are highly broadened because of the short lifetime of the intermolecular interaction inducing the dipole moment. The time of interaction estimated from the half-width of the induced purely-rotational band of H_2 is approximately 10^{-13} sec.[39]. Since the lifetime of the interaction is inversely proportional to the velocity of the molecules, the half-width of the induced lines is proportional to the square root of the absolute temperature.[11, 34, 41]

In Fig. 4 is shown the fundamental vibration-rotation absorption band of O_2 gas, consisting of Q, S, and O branches. In the case of the light molecule H_2, the rotational structure is better resolved. This permits the establishment of the supplementary details in the structure of the induced band. In Figs. 5, 6, and 7, taken from the paper of Chisholm and Welsh,[14] the absorption in pure hydrogen and the increase in the absorption by hydrogen caused by helium and argon at various gas densities are shown. The greatest densities correspond to pressures of about 1500 atmos. Along the ordinate axis is plotted the logarithm of the ratio of the light intensity which passes through the chamber when filled with the gas being studied to that passing through the empty chamber (Fig. 5) or the chamber with H_2 alone (Figs. 6 and 7). For comparison, the dotted curves give the contours of the absorption band expected for the highest of the density values studied, as obtained by recalculation by Eq. (3.6) from the low-density
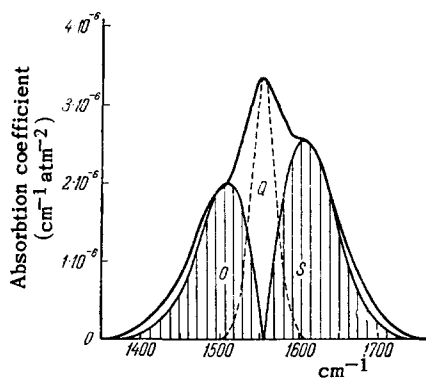

FIG. 5. The fundamental absorption band of H_2 at gas densities of 340, 406, 556, and 663 Amagat. Thickness of absorbing layer 1.3 cm, $T = 298°K$.[14]

absorption contours. On the frequency axis are marked the positions of the frequencies of the purely vibrational transition, ν_0, and the lines $S(0)$ ($J = 0 \rightarrow J = 2$) and $S(1)$ ($J = 1 \rightarrow J = 3$), as calculated from the constants of the free molecule. At low gas densities, these frequencies agree well with the absorption maxima of the induced bands. At greater densities, a minimum is formed at ν_0, due to the splitting of the Q branch into two components, designated as Q_P and Q_R. The distance $\Delta\nu_{PR}$ between the maxima of Q_P and Q_R, at not-too-high densities, increases linearly with the density of the perturbing gas from a certain initial value which may be obtained by extrapolation to $\rho_P = 0$. At great densities, $\Delta\nu_{PR}$ increases more rapidly, reaching about 400 cm^{-1} at 5000 atmos.[17] Here, in a number of cases a new absorption maximum Q_Q appears at the frequency ν_0.

FIG. 4. The induced vibration-rotation absorption band of O_2. The heavy curve gives the experimental contour of the absorption band; the light curves give the O and S branches calculated theoretically; the Q branch obtained by subtracting intensities is shown by the dotted curve.[9]
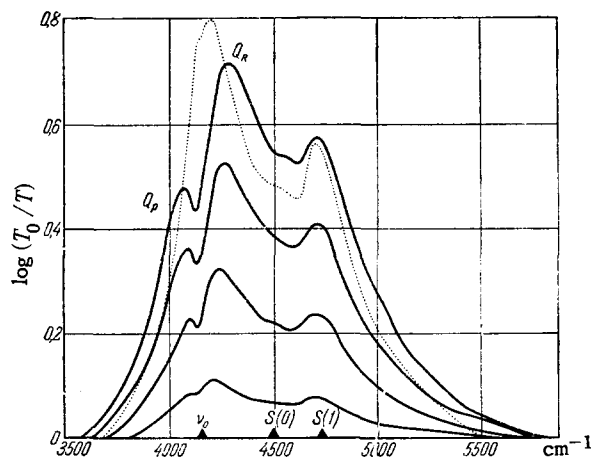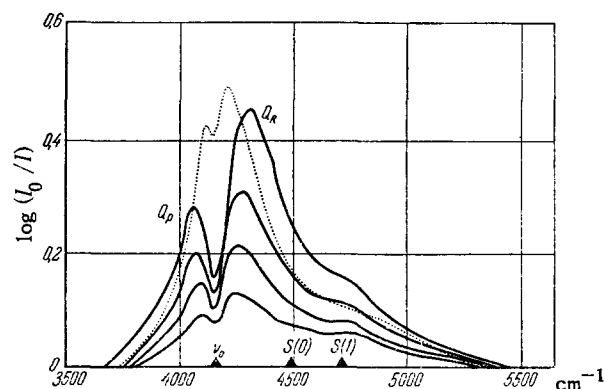

FIG. 6. Intensification of the fundamental absorption band of hydrogen by helium. H_2 density: 168 Amagat; He densities: 188, 348, 517, and 796 Amagat. Thickness of absorbing layer 2.1 cm, $T = 298°$ K.[14]
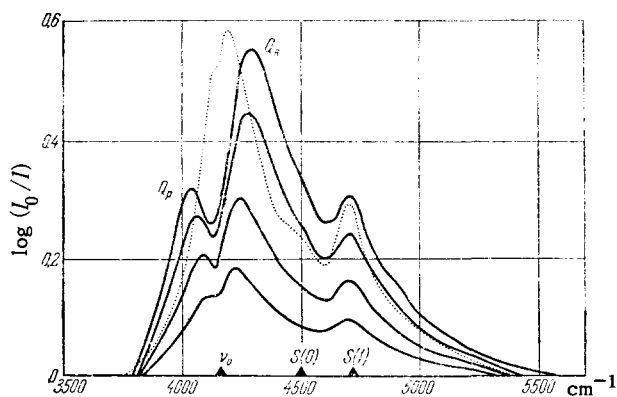
FIG. 7. Intensification of the fundamental absorption band of hydrogen by argon. H_2 density: 144 Amagat; Ar densities: 228, 341, 503, and 571 Amagat. Thickness of absorbing layer 2.1 cm, $T = 298°$ K.[14]

Welsh and his associates [14, 16, 17] have explained the occurrence of the Q_P and Q_R components as due to the change in the relative kinetic energy of the colliding molecules at the moment of light absorption. Since the molecules are moving with respect to one another during collision, the induced dipole moment rotates, being directed along the line joining the two molecules. Thus the colliding pair has a certain angular momentum depending on the parameters of the collision. The splitting of the Q branch is a result of the change in this angular momentum at the time of the light-absorption process. The appearance of the low-frequency maximum Q_P is associated with the fact that a certain amount of the rotational energy of the colliding pair may be used in transferring the molecule into its first excited vibrational state. The high-frequency maximum Q_R appears as a result of a process in which a fraction of the energy of the absorbed photon is spent in increasing the rotational energy of the pair of molecules. Thus, the Q_P and Q_R components are analogous in a certain degree to the P and R branches of the absorption bands of diatomic molecules in the ordinary infra-red spectrum. They may be considered as difference and sum components with frequencies $\nu_0 \mp \nu_k$, where ν_0 is the frequency of the vibrational transition and ν_k is the kinetic energy (in cm^{-1}) which is removed from or transferred to the surrounding molecules. This interpretation is confirmed by a determination of the intensities within the Q_P and Q_R maxima, which obey the characteristic relation for difference and sum components: [13, 14]

$$\ln \frac{I_R(\nu_k)}{I_P(\nu_k)} \sim \frac{\nu_k}{kT}$$

where $I_R(\nu_k)$ and $I_P(\nu_k)$ are the intensities at points within the Q_R - and Q_P -peaks at equal distances ν_k from the center of the band (ν_0). T is the absolute temperature. The increase in $\Delta\nu_{PR}$ with increase in the density of the perturbing gas is caused by an increase in the number of ternary collisions. In these, the amount of kinetic energy which is available to participate in the light-absorption process is greater than in binary collisions.

Recently Kiss and Welsh[47] have reported a new type of infra-red absorption which is directly associated with the translational motion of the molecules. In binary mixtures of the inert gases, these authors observed absorption rapidly falling from 350 cm^{-1} (the limit of measurement) toward higher frequencies, and increasing in proportion to the product of the densities of the components of the mixture. This absorption was explained by the appearance of an induced dipole moment in the system of two colliding atoms. This dipole moment varies rapidly in time as a result of the translational motion of the atoms with respect to one another and the rotation of the colliding pair.

In addition to the splitting of the Q branch into three fundamental components, Q_P, Q_Q, , and Q_R, the Q_P component itself shows an additional structure at increased temperatures and relatively low densities. This structure disappears when the density of the perturbing gas is increased. Coulon, Galatry, Robin, and Vodar [44, 45] consider that this structure is produced by the superposition on the Q_P maximum of the lines Q_3 ($J = 3 \rightarrow J = 3$) and Q_4 ($J = 4 \rightarrow J = 4$); these lines belong to the absorption bands of molecules not participating directly in collisions, but situated in the electric fields of the induced dipole moments of colliding pairs. However, in the opinion of Welsh and his associates,[16] this additional structure is caused by an increase in the intensity of the Q_3 line of the absorption band of the colliding molecules themselves. This line is split into two components, just as is the line Q_1 ($J = 1 \rightarrow J = 1$), which ordinarily plays a dominant role in the formation of the Q_P and Q_R maxima.

In distinction from the Q_P and Q_R components, the lines of the S branch show no noticeable shift on increasing the gas density; their frequencies at all studied pressures coincide with the corresponding frequencies of the free H_2 molecule. A slight splitting of the $S(1)$ maximum which is observed at higher temperatures and relatively low densities[44] disappears when the pressure is increased. The intensity of the

S branch depends strongly on the nature of the perturbing gas.

The Q_Q maximum, just as the S branch, does not shift nor split on increasing the density of the gas. Its intensity is closely related to the intensity of the S -branch. As was shown in reference 17, the $S(1)$ and Q_Q components are both strong and relatively sharp in mixtures of $H_2 +$ Ar, weak and broad in mixtures of $H_2 + N_2$, and both are practically absent in mixtures of $H_2 +$ He.

The difference in the behavior of the Q_P and Q_R components, on the one hand, and the Q_Q and S components, on the other hand, may be explained by the fact that the occurrence of these components of the band is associated with changes in the dipole moments induced by different intermolecular forces.

The Induced Dipole Moment. The induced absorption of molecules in a gas phase arises as a result of the polarization of the molecules by their electrostatic and exchange interaction at the moment of collision. Various intermolecular forces may dominate in the production of the induced dipole moment of the colliding pair, depending on the nature of the molecules.

If a non-polar diatomic molecule 1 interacts with a polar molecule 2, the exchange interaction of the molecules may be neglected. In this case, the induced dipole moment of the colliding pair will be: [6, 7]

$$\mu = a_1 \mathbf{E}_2 + a_2 \mathbf{E}_1, \qquad (3.7)$$

where a_1 and a_2 are the polarizabilities of molecules 1 and 2. $\mathbf{E}_1$ and $\mathbf{E}_2$ are the intensities of the electric fields of molecules 1 and 2 at the centers of gravity of molecules 2 and 1, respectively. $\mathbf{E}_2$ will be produced by the dipole moment M_2 of the polar molecule, while $\mathbf{E}_1$ will be produced by the quadrupole moment Q_1 of the non-polar molecule and by the dipole moment produced in it by the polar molecule (inverse induction). In agreement with (3.3) and (3.7), the part of the induced dipole moment which brings about absorption at the vibration frequency of the non-polar molecule 1 may be written in the form [6]

$$\frac{M_2}{r^3}\left(\frac{\partial a_1}{\partial \xi}\right)_0 \xi + \frac{M_2}{r^3}\left(\frac{\partial a_1}{\partial \xi}\right)_0 \frac{a_2}{r^3}\xi + \frac{a_2}{r^4}\left(\frac{\partial Q_1}{\partial \xi}\right)_0 \xi, \quad (3.8)$$

where r is the intermolecular distance, and ξ is the normal coordinate of the non-polar molecule. We must stress that, although the second and third terms refer to the dipole moment induced in molecule 2, they bring about absorption at the vibration frequency of molecule 1, just as the first term does. This is because they depend on Q_1 and a_1, which in turn depend on ξ. The relative magnitudes of the separate terms in expression (3.8) may differ, depending on the nature of the molecules and the distance between them. For the pair HCl-H_2, taking $r = 4A$ (approximately corresponding to the maximum in the radial distribution function of the molecules), Fahrenfort [6] obtained the following values for the coefficients of ξ:

$$\frac{M_2}{r^3}\left(\frac{\partial a_1}{\partial \xi}\right)_0 = 2{,}9 \cdot 10^{-12} \text{ esu}$$

$$\frac{M_2}{r^3}\left(\frac{\partial a_1}{\partial \xi}\right)_0 \frac{a_2}{r^3} = 1{,}0 \cdot 10^{-13} \text{ esu}$$

$$\frac{a_2}{r^4}\left(\frac{\partial Q_1}{\partial \xi}\right)_0 = 1{,}3 \cdot 10^{-12} \text{ esu}.$$

Thus, for the pair HCl-H_2, inverse induction is even more negligible, in that the corresponding dipole moment decreases rapidly with increase in the intermolecular distance. The two other effects play approximately equal roles in the generation of the absorption band.

By averaging the value obtained for the induced dipole moment over all possible orientations of the molecules and all intermolecular distances within the radius of action of the polarizing forces, we may obtain theoretically the integral absorption coefficient for induced transitions from the expression

$$\int a(\nu)\,d\nu = \frac{8\pi^3 N_{12}\nu}{3hc}\left|\int \psi_1\psi_2\mu\psi_1'^*\psi_2'^*\,d\tau\right|^2, \quad (3.9)$$

where N_{12} is the number of pairs of colliding molecules per cm^3 per Amagat[2]. In order to determine N_{12} we may use the formula [6]

$$N_{12} = N_1 N_2 \int_{r_0}^{r_a} e^{-\frac{V_{12}(r)}{kT}} \cdot 4\pi r^2\,dr, \quad (3.10)$$

derived from the statistical theory of a nonideal gas. Here N_2 and N_2 are the numbers of molecules of types 1 and 2, respectively, in 1 cm^3 at a density of one Amagat, $V_{12}(r)$ is the potential energy of intermolecular interaction, and r_0 and r_a are the minimum and maximum radii of interaction. In the case of induced absorption in a pure gas, the number N_1 obtained from Eq. (3.10) must be multiplied by 1/2, since otherwise each colliding pair would be counted twice.

For the absorption band of H_2 induced by HCl, the calculated value of the integral absorption coefficient is 2.1×10^{-2} cm^{-1} per cm path length per Amagat[2], which is close to the experimental value (2.7×10^{-2} cm^{-2} Amagat[2]).[48]

Induced absorption in a nonpolar gas was first studied theoretically by Mizushima.[49, 50] However, this author proceeded on the basis of a false assumption that the absorption of light by a nonpolar diatomic molecule takes place solely because of its polarization by the quadrupole moment of another nonpolar molecule. The theory of Mizushima could not explain all of the peculiarities of induced absorption, and in particular, the absorption induced by atoms of the inert gases, which have neither dipole nor quadrupole moments.

Van Kranendonk and Bird[51, 5] have carried out a detailed calculation of induced absorption in H and D , and have shown that the absorption at the vibration frequency of the nonpolar molecule 1, when it collides with a nonpolar molecule 2, is caused by a dipole moment resulting from the superposition of the three following effects:

1) perturbation of the electronic wave functions of the molecules by overlap of their electron clouds; this perturbation decreases exponentially with increasing intermolecular distance;

2) polarization of the absorbing molecule 1 by the quadrupole field of molecule 2, which is proportional to r^{-4};

3) polarization of molecule 2 by the quadrupole field of molecule 1, also proportional to r^{-4}.

The second of these effects brings about an absorption which is proportional to the square of the derivative of the polarizability of molecule 1 with respect to the internuclear distance. The third effect produces an absorption proportional to the square of the derivative of the quadrupole moment of this molecule. All three effects, at least in the case of H_2 and D_2, give terms of the same order of magnitude in the expression for the coefficient of induced absorption. Since the forces which appear upon overlap of the electron clouds do not depend much on the relative orientations of the molecules, they are not effective in inducing rotational transitions, and they bring about absorption chiefly in the Q branch. On the other hand, the quadrupole forces, which have a greater angular dependence, lead basically to absorption in the O and S branches. The absorption band corresponding to the first vibrational overtone of a non-polar molecule arises primarily from the quadrupole interaction of the molecules, as shown 17 for the H_2 molecule.

The dipole moment which brings about light absorption by a nonpolar diatomic molecule during collision with an atom of an inert gas was explained by van Kranendonk and Bird.[46] This dipole moment is the result of the overlap of the electronic orbitals of the interacting partners and of the polarization of the inert-gas atom by the quadrupole field of the diatomic molecule.

The theory developed by van Kranendonk and Bird permits the calculation of values of the integral absorption coefficients in H_2 and H_2-He mixtures which are close to the experimental values. It also gives the correct value of the ratio of intensities of the separate branches. Thus, for example, the theory gives for pure H_2 a ratio of intensities of the branches $Q : S : O = 1 : 0.87 : 0.05$, while the experimental ratio is $1 : 0.8 : 0.04$. In particular, the calculation shows that the intensity of the Q branch must be approximately the same in pure H_2 and in H_2-He mixtures, while the S branch must be appreciably weaker in the mixtures. As may be seen from Figs. 5 and 6, this relation of intensities is actually observed experimentally.

A detailed calculation of the integral absorption coefficient for induced transitions in H_2 and D_2 has also been carried out by Britton and Crawford.[52]

Since the Q branch is basically the result of the overlap of the electron clouds of the molecules, while the S-branch results from the polarization of the molecules by their quadrupole fields, absorption in the Q branch takes place at the moment of close approach of the molecules, while absorption in the S branch may appear at relatively great distances between the colliding molecules. Thus it becomes clear why the lines of the S branch in the absorption band of hydrogen, in distinction from the Q branch, do not split at high pressures. Actually, the splitting of the components of the S branch must be considerably less than that of the components of the Q branch, since the amount of splitting, being associated with the rotation of the colliding pair, is inversely proportional to the distance between the molecules.

Welsh and his associates[17] have used the value of the splitting of the Q branch $\Delta \nu_{PR}$ for $\rho_p = 0$ in estimating the mean distance r of closest approach of the molecules during collision by means of the formula

$$\Delta \nu_{PR} = \sqrt{\frac{8BkT}{hcv}}, \qquad (3.11)$$

where $B = h/8\pi c m r^2$, m is the reduced mass of the molecules, T is the absolute temperature, and ν is the frequency in cm^{-1}. For H_2-He mixtures, a value $r = 3.6$ A was obtained. This result may be considered as an experimental confirmation of the idea that the absorption in the Q branch takes

place at intermolecular distances close to the sum
of the molecular radii (2.8 A for the H_2-He pair).

The fact that the Q_Q maximum is not resolved
in the absorption band of H_2 and the connection
noted in the previous section between its intensity
and that of the S branch permit us to assume that
the Q_Q component is the part of the Q branch
which is caused by quadrupole interaction of the
molecules.[14, 17]

Induced absorption in condensed phases.
Intermolecular interaction in liquids and solids
also leads to the polarization of the molecules and
the appearance of their induced vibrational ab-
sorption spectra. The absorption bands of such
non-polar compounds as H_2, [53, 54, 55] N_2 and
O_2 [56, 57, 58] in condensed phases are analogous
in their structure to the induced vibration-rotation
bands of the corresponding gases. The absorp-
tion bands of liquid and solid hydrogen (Fig. 8)
consist of Q branches and lines $S(0)$ and $S(1)$.
The branch has two maxima: Q_Q, with a fre-
quency close to that of the purely-vibrational
transition in the free molecule, and Q_R. The Q_P
maximum is absent because of the low intensity of
difference components $(\nu_0 - \nu_k)$ at low tempera-
tures. Each of the S lines also consists of two
fundamental maxima. One of these, which is
sharper and more intense, has a frequency close
to that of the corresponding S line of the free
molecule. The other, S', is shifted toward
higher frequencies, and has about the same con-
tour as the Q_R maximum. As was shown in
references 53 and 54, the absorption at the Q_Q
maximum and the maxima of the S branch, which
occur at the characteristic frequencies of the free
molecule, is caused by quadrupole interaction of
the molecules; absorption at the Q_R and S' max-
ima is due to exchange interaction. In the cry-
stal, an asymmetric perturbation of the absorb-
ing molecules may be produced by the chaotic
orientation of freely-rotating molecules and by
crystal-lattice vibrations. Experiment shows [53]
that the first type of perturbation takes place in
quadrupole interactions, while both types take
place in exchange interaction. The shift of the
Q_R and S' maxima toward greater frequencies
with respect to the frequencies of the Q branch
and the S lines of the free molecule is asso-
ciated with changes in the translational kinetic
energy of the absorbing molecules. In the case
of solid H_2, this translational motion acquires the
character of lattice vibrations.[53, 54]

The intensity of induced absorption in liquids
and solids, as in gases, is small in comparison
with the intensity of the ordinary dipole absorp-
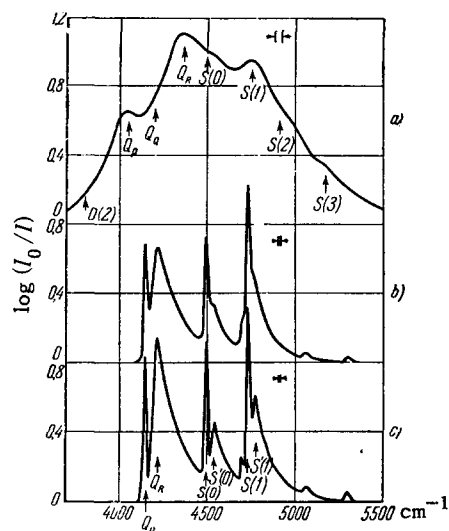tion. While the optimum thickness of the ab-

FIG. 8. The fundamental vibration-rotation
absorption band of hydrogen: a--gas, 3400 atmos,
298°K. (density: 1014 Amagat); b--liquid, 18°K.
(density: 817 Amagat); c--solid H_2, 11°K. (den-
sity: 972 Amagat). [53]

sorbing layer for polar liquids ordinarily amounts
to 0.005--0.05 mm, a layer of liquid H_2 8 mm
thick is required in order to obtain a sufficiently
strong absorption band of the fundamental vibra-
tion of H_2. Nevertheless, in liquids and crystals,
the induced absorption is more intense than the
quadrupole absorption. In gases, the relative
intensities of the induced and quadrupole absorp-
tions naturally depend on the density of the gas.

4. SIMULTANEOUS VIBRATIONAL TRANSITIONS

Infrared absorption associated with simul-
taneous vibrational transitions in molecules was
first observed by Welsh, Crawford, MacDonald,
and Chisholm[12] in 1951. In studying induced ab-
sorption in gases at high pressures, these authors
found that the absorption band of H_2 in the fre-
quency range of the first vibrational overtone of
this molecule has a complex structure. This
structure could be explained by the superposition
on the overtone vibration-rotation band of hy-
drogen of a second absorption band with the same
rotational structure, but somewhat shifted toward
higher frequencies. The authors advanced the
hypothesis that this second absorption band
results from binary transitions, in which both
colliding molecules undergo a fundamental vi-
brational transition.

Later, the possibility of such transitions was
proved by a large number of experimental studies
on induced absorption in binary mixtures. Here,
the simultaneous vibrational transitions are mani-
fested by new absorption bands observable only in

the given mixture, but absent in the spectra of either of the components alone. Fahrenfort and Ketelaar [59, 60, 61, 6] have observed the following new absorption bands in the gas mixtures of CO_2 with H_2, O_2, and N_2:

$$CO_2 + H_2 \quad 6505 \pm 7 \text{ cm}^{-1},$$
$$CO_2 + O_2 \quad 3895 \pm 5 \text{ cm}^{-1},$$
$$CO_2 + N_2 \quad 4670 \pm 5 \text{ and } 2995 \pm 3 \text{ cm}^{-1}.$$

These absorption bands were ascribed by the authors to simultaneous vibrational transitions in which the frequencies ν_3 and ν_2 of the CO_2 molecule combine with the fundamental vibrational frequencies of the diatomic molecules. Calculations give values for the frequencies of these transitions which are close to the experimental values:

$$\nu_3(CO_2) + \nu(H_2) = 2349 + 4160 = 6509 \text{ cm}^{-1},$$
$$\nu_3(CO_2) + \nu(O_2) = 2349 + 1555 = 3904 \text{ cm}^{-1},$$
$$\nu_3(CO_2) + \nu(N_2) = 2349 + 2331 = 4680 \text{ cm}^{-1},$$
$$\nu_2(CO_2) + \nu(N_2) = 667 + 2331 = 2998 \text{ cm}^{-1}.$$

As an example, in Fig. 9 is shown the appearance of a new absorption band at 4670 cm $^{-1}$ on adding N_2 to CO_2 (the thickness of the absorbing layer was 100 cm, and the maximum pressure of the gas mixture was 75 atm). The weak absorption band at 4640 cm $^{-1}$ in the spectrum of pure CO_2 corresponds to the first overtone of the ν_3 vibration of the CO_2 molecule; its intensity increases only little as the gas density is raised.

Coulon, Robin, and Vodar [62] have observed simultaneous vibrational transitions of the molecules HCl and H_2. In Fig. 10 are given the infrared spectra of H_2, HCl, and mixtures of these gases, at different gas densities. The extinction coefficient $\epsilon = (1/l) \log (I_0/I)$ is plotted as the
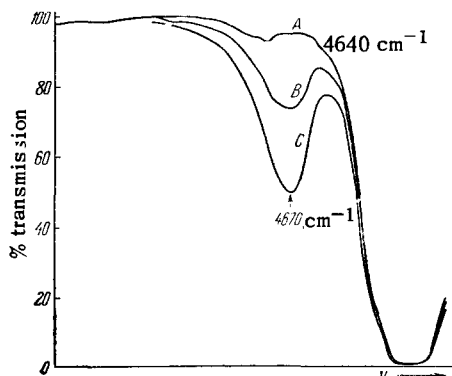
FIG. 9. The occurrence of absorption bands associated with simultaneous vibrational transitions in CO_2–N_2 mixtures: A--CO_2 at 41.8 Amagat; B--CO_2 at 41.8 Amagat + N_2 at 36.2 Amagat; C--CO_2 at 41.8 Amagat + N_2 at 94.3 Amagat.[60]
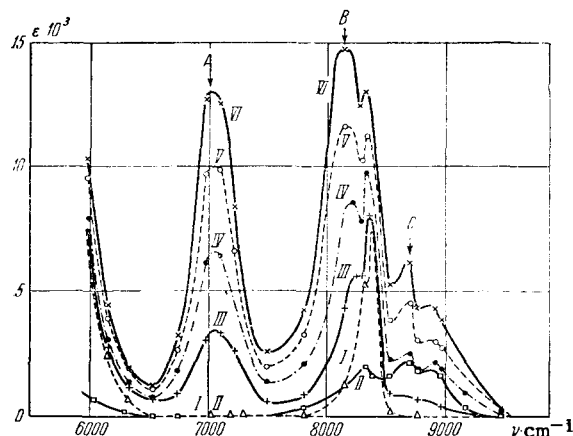
FIG. 10. Infrared absorption spectra of mixtures of HCl with H_2 : I--HCl, 106 Amagat; II--H_2, 500 atmos; III--HCl + H_2, 220 atmos; IV--HCl + H_2, 430 atmos; V-- HCl + H_2, 620 atmos; VI--HCl + H_2, 845 atmos; Thickness of absorbing layer 42 cm, temperature 105°C.[62]

ordinate. As one may see from the diagram, an absorption band (A) is observed in spectra of the gas mixtures, but is absent in the spectra of pure HCl and H_2. Its frequency is equal, within the limits of accuracy of measurement, to the sum of the vibrational frequencies of the molecules HCl and H_2:

$$\nu(HCl) + \nu(H_2) = 2886 + 4160 = 7046 \text{ cm}^{-1}$$

The appearance in the infrared spectrum of frequencies equal to the sum of the vibrational frequencies of two different molecules has also been found in the gas mixtures HBr + H_2, [23] $N_2 + H_2$, and $N_2O + H_2$.[38]

Infrared absorption due to simultaneous vibrational transitions is observed not only in gases, but also in binary liquid mixtures, when a sufficient thickness of absorbing layer is used. Ketelaar and Hooge [63, 64, 65, 66, 39] have studied in detail the simultaneous vibrational transitions in mixtures of CS_2 with a large number of different compounds, and also in mixtures of chloroform and bromoform with SO_2Cl_2. Here, the authors found difference combinations of the frequencies of two molecules, as well as sum combinations. In Fig. 11 are reproduced the infrared absorption spectra of pure CS_2 and Br_2 and of mixtures of equal parts by volume of these compounds, at a thickness of absorbing layer of 5 mm. In the spectrum of the CS_2-Br_2 mixture, two new absorption bands are visible at 1807 and 1204 cm $^{-1}$, distributed on both sides of the very intense absorption band at 1510 cm $^{-1}$, which belongs to the antisymmetric valence-bond vibration ν_3 of the CS_2 molecule. The frequencies of the
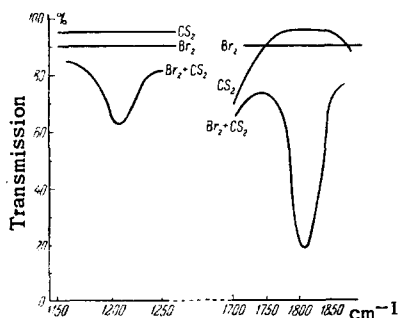
FIG. 11. Infrared absorption spectra of CS_2, Br_2, and a CS_2-Br_2 mixture.[63]

FIG. 12. Infrared absorption due to simultaneous vibrational transitions in the molecules CS_2 and $SOCl_2$.[65]

new bands agree well with the calculated frequencies for simultaneous transitions in the CS_2 and Br_2 molecules:

$$v_3(CS_2) + v(Br_2) = 1510 + 306 = 1817 \text{ cm}^{-1},$$
$$v_3(CS_2) - v(Br_2) = 1510 - 306 = 1204 \text{ cm}^{-1}.$$

Analogous absorption spectra were obtained by Ketelaar and Hooge for mixtures of CS_2 with I_2, IBr, SnI_4, $SnBr_4$, S_2Br_2, and an entire series of other compounds. For complex molecules, simultaneous vibrational transitions lead to the appearance in the infra-red spectrum of an entire system of bands reproducing the low-frequency vibrational spectrum of the given compound, but shifted to higher frequencies by addition of the frequency v_3 of CS_2. In Fig. 12 is shown the infra-red vibrational spectrum due to simultaneous transitions in the molecules CS_2 and $SOCl_2$. The absorption maxima are situated at frequencies 1716, 1807, 1863, 1950, and 2003 cm^{-1}, which are combinations of the v_3 frequency of CS_2 with frequencies of the $SOCl_2$ molecule at 201, 292, 348, 435, and 488 cm^{-1}, respectively. These values are in good agreement with the vibrational frequencies of $SOCl_2$ obtained from Raman spectra: 192, 283, 343, 443, and 488 cm^{-1}.

The shift of the low-frequency spectrum of molecules toward higher frequencies permits us to use the simultaneous transitions for analysis of vibrational spectra of compounds which are not suited for study by Raman spectroscopy.[66, 77] This method, however, may be applied only to a limited number of compounds, which retain sufficient transparency in the region of simultaneous-transition frequencies with a thickness of absorbing layer of 2--10 mm. If the vibrational frequencies of the compound being studied lie within the limits 160--500 cm^{-1}, then CS_2 may be conveniently used as the second component, since it has no absorption bands in the region 1500--2100 cm^{-1}.
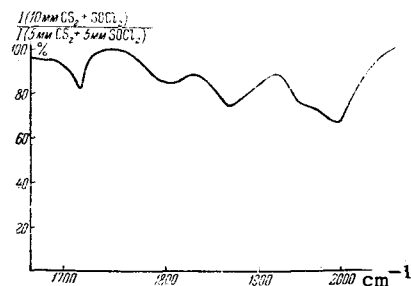
Besides the purely-vibrational simultaneous transitions described above, electronic-vibrational and vibration-rotation simultaneous transitions in molecules have also recently been discovered and studied (see reference 39). The latter play an especially important role in the induced infrared absorption of liquids and solids, since the effectiveness of simultaneous transitions, in distinction from single induced transitions, is not decreased in the case in which the induced dipole moment arises through the interaction of several molecules.[41, 55]

Absorption Intensity and the Mechanism of Interaction of Molecules. The infrared absorption intensity due to simultaneous vibrational transitions, for gas mixtures, increases approximately proportionally to the product of the densities of the components of the mixture. This indicates that, in a gas phase, the simultaneous transitions take place at the moment of bimolecular collision, when the molecules form an unstable complex with a lifetime of the order of 10^{-13} sec. This behavior is analogous to the case of the single induced transitions.

The numerical values of certain integral absorption coefficients per cm path length per Amagat[2], extrapolated to zero gas density, are given in Table III. For convenient comparison with the absorption coefficients of ordinary

TABLE III. Integral absorption coefficients for simultaneous vibrational transitions.

	Frequency (cm^{-1})	Absorption coefficient (cm^{-1}cm^{-1} Amagat^{-2})	Absorption coefficient (cm^{-1}cm^{-1}) for 2.7×10^{19} absorbing units per cm^{-3}
		Ref.	Ref.
CO_2+H_2	6510	$8.8 \cdot 10^{-4}$ 39	$2.8 \cdot 10^{-2}$ 6
CO_2+O_2	3903	$0.29 \cdot 10^{-4}$ 39	$0.63 \cdot 10^{-3}$ 6
CO_2+N_2	4670	$0.83 \cdot 10^{-4}$ 39	$1.8 \cdot 10^{-3}$ 6
CO_2+N_2	2996	$0.91 \cdot 10^{-4}$ 39	$1.9 \cdot 10^{-3}$ 6
$HCl+H_2$	7050	$3.3 \cdot 10^{-4}$ 48	
$HBr+H_2$	6720	$2.0 \cdot 10^{-4}$ 48	

infrared bands, values are given in the last column of the table for the integral absorption coefficients of the same simultaneous transitions, as calculated under the assumption that the number of colliding molecules is equal to the total number of molecules of the gas at a pressure of 1 atmos.

Considering the existence of two large partial dipole moments in the CO_2 molecule, we may assume that the induced dipole moment which arises when the CO_2 molecule approaches a non-polar diatomic molecule is almost completely due to electrostatic interaction of the molecules. In this case, as has been shown by Fahrenfort,[6] the integral absorption coefficient for the simultaneous transitions may be calculated theoretically.

The dipole moment of a colliding pair of molecules induced by their electric fields is equal to:

$$\mu = a_1 E_2 + a_2 E_1, \qquad (4.1)$$

where a_1 and a_2 are the polarizabilities of molecules 1 and 2, and E_1 and E_2 are the intensities of the electric fields of molecules 1 and 2 at the centers of gravity of molecules 2 and 1, respectively. According to Eq. (3.5), the part of the induced dipole moment (3.3) which results in absorption at the frequency $\nu_{1i} + \nu_{2j}$ will be:

$$\left(\frac{\partial^2 \mu}{\partial \xi_i \partial \eta_j}\right)_0^2 \xi_i \eta_j = \left(\frac{\partial^2 (a_2 E_1 + E_2 a_1)}{\partial \xi_i \partial \eta_j}\right)_0 \xi_i \eta_j. \qquad (4.2)$$

For a simultaneous transition in which the vibration frequency of a diatomic molecule combines with the frequency of the antisymmetric valence-bond frequency ν_3 of CO_2, the integral absorption coefficient per colliding pair is equal to

$$\frac{8\pi^3 (\nu_{13} + \nu_2)}{3hc} \left[\left(\frac{\partial E_1}{\partial \xi_3}\right)_0 \left(\frac{\partial a_2}{\partial \eta}\right)_0\right]^2 \cdot \left|\int \psi_1 \xi_3 \psi_1'^* d\tau \int \psi_2 \eta \psi_2'^* d\tau\right|^2, \qquad (4.3)$$

since E_1 is not a function of η, and E_2 is not a function of ξ_3, and $(\partial a/\partial \xi_3)_0 = 0$. Expression (4.3), which contains $a_2(\omega)$ and $E_1(\omega, r)$, depends on the relative orientation ω and the intermolecular distance r of the colliding molecules. By averaging these quantities over all possible values of ω and all values of r within the limits of action of the polarizing forces, and applying Eq. (3.10) to determine the concentration of colliding molecules, we may obtain the integral absorption coefficient for the band of frequency $\nu_{13} + \nu_2$. By using the value of $\partial a_2/\partial \eta$ for the H_2 molecule (which is known from measurements of the absolute intensities of Raman lines), and making certain assumptions concerning the electric-

charge distribution in the CO_2 molecule, Fahrenfort[6] obtained a value of the integral absorption coefficient for the 6510 cm^{-1} band in the spectrum of CO_2-H_2 mixtures of 9.6 x 10^{-4} cm^{-1} per cm path length per Amagat^2. The good agreement between the calculated and experimental values (see Table III) may be considered as confirmation of the idea that induced absorption in this case is chiefly associated with the electrostatic interaction of the molecules.

A calculation carried out by Galatry[48] for simultaneous vibrational transitions in the mixtures HCl-H_2 and HBr-H_2 gave values of the absorption coefficient of 1.9 x 10^{-4} and 0.6 x 10^{-4} cm^{-1} per cm per Amagat^2, respectively.

In the case in which one of the frequencies ν_1 taking part in a simultaneous vibrational transition is permitted in the Raman spectrum, while the other frequency ν_2 is permitted in the infra-red spectrum, the intensity of the induced absorption may be expressed in terms of the intensities of the corresponding lines in the Raman and infra-red spectra, as has been shown by Colpa and Ketelaar[68] and by Mukhtarov[69]. If A_2 is the integral absorption coefficient for the infra-red band at frequency v_2, the intensity of the simultaneous-transition band is given by the expression[68]

$$\int a(\nu)\, d\nu = A_2 \frac{N_1 h (\nu_1 + \nu_2)}{\pi m c \nu_1 \nu_2} \left(a_1'^2 + \frac{2}{9}\Delta_1'^2\right) \int e^{\frac{-V(r)}{kT}} r^{-4}\, dr, \qquad (4.4)$$

where N_1 is the number of molecules per cm^3 undergoing the transition active in the Raman spectrum; a_1' and Δ_1' are the derivatives of the mean polarizability and the anisotropy of the polarizability for these same molecules; m is the reduced mass; and $e^{(-V(r)/kt)}$ is an approximate expression for the radial distribution function for the molecules in the region of interaction. Here, the distribution of $V(r)$ is such that $V(r) \to 0$ as $r \to \infty$. A calculation carried out by Eq. (4.4) gives values for the integral absorption coefficient of the 6510 cm^{-1} band in CO_2-H_2 mixtures of 6.3 x 10^{-4} or 12 x 10^{-4} cm^{-1} per cm path length per Amagat^2. The choice of value calculated depends on which of the two values given in the literature for the derivative of the polarizability of the H_2 molecule is used in the calculation.

In liquids, simultaneous transitions may take place either as a result of the interaction of two molecules which approach each other especially closely for a short period of time, or as the result of the interaction of one of the absorbing molecules with all of its neighbors at the usual intermolecular distances. In order to settle this question, Ketelaar and Hooge[70, 66] studied the

temperature-dependence of the absorption band at 1807 cm^{-1} in CS_2-Br_2 mixtures. In distinction from the observations on induced bands in compressed gases, they showed that the half-width of a simultaneous-transition band in a liquid mixture does not change on lowering the temperature. The intensity of the band increases on lowering the temperature, the intensity ratio for -78.5° and +28°C being 1.44 for a CS_2-Br_2 mixture with 3:1 volume ratio. If we assume that the simultaneous transitions take place during the collisions of two molecules, then a decrease in temperature should increase the intensity of the band only because of the increase in the number of molecules in the optical path due to the contraction of the liquid. If, however, one of the absorbing molecules interacts with all of its neighbors, the increase in absorption will be produced by another effect, in addition. This is the increase in the electric field intensity of the surrounding molecules due to the shortened intermolecular distances. In the second case, the following relation must hold true:

$$\frac{I_{T_1}}{I_{T_2}} = \left(\frac{V_{T_1}}{V_{T_2}}\right)^{-3} \qquad (4.5)$$

where V_{T_1} and V_{T_2} are the molar volumes of the mixture at temperature T_1 and T_2, respectively. From Eq. (4.5) we obtain for a mixture of CS_2 and Br_2 in 3:1 volume ratio:

$$\frac{I_{-78.5}}{I_{+28}} = 1.52.$$

The good agreement between the calculated and experimental values for the intensity ratio, as well as the absence of a change in the half-width of the band, indicates that in liquids the simultaneous transitions apparently take place by way of the general interaction between all neighboring molecules. We must note that, even when one of the absorbing molecules is symmetrically surrounded by other molecules, the effectiveness of the simultaneous vibrational transitions is not decreased by the mutual compensation of the electric fields of the surrounding molecules. This is because the absorption intensity is proportional to the mean square of the electric field intensity. This value differs from zero at any given moment because of the difference in phase angles of the vibrations of the surrounding molecules.[66, 65]

The Intensity Ratio of the Sum and Difference Bands. The occurrence of simultaneous vibrational transitions with frequencies equal to the sum and difference of frequencies of two different molecules is illustrated in Fig. 13. Here the system of vibrational energy levels of the two
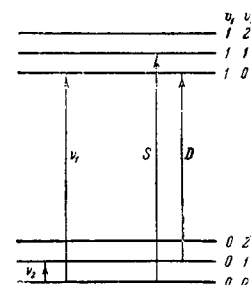

FIG. 13. Energy levels of two interacting oscillators.[70]

interacting molecules is shown. Transitions in which only one of the interacting molecules participates are indicated by the arrows marked ν_1 and ν_2. The simultaneous transitions with frequencies $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$ are indicated by the arrows S and D, respectively.

The intensity ratio of the sum and difference bands is given by the expression:[66, 70]

$$\frac{I_-}{I_+} = \frac{\nu_{1i} - \nu_{2j}}{\nu_{1i} + \nu_{2j}} e^{-\frac{hc\nu_{2j}}{kT}}, \qquad (4.6)$$

which may be obtained directly by comparing the integral absorption coefficients for simultaneous transitions with frequencies $\nu_{1i} + \nu_{2j}$ and $\nu_{1i} - \nu_{2j}$, taking into account the relative populations of the energy levels. The Boltzmann coefficient $e^{-(hc\nu_{2j}/kT)}$ gives the fraction of molecules 2 occurring in the first excited state, from which it is possible for them to undergo a simultaneous transition with the frequency $\nu_{1i} - \nu_{2j}$.

It follows from consideration of Eq. (4.6) that difference absorption bands may appear at room temperature only in case that the frequency ν_{2j} is not greater than several hundred cm^{-1}. Thus it becomes clear why only sum absorption bands were found in the gas mixtures studied, for which $hc\nu_{2j} \gg kT$. In solutions, where difference absorption bands are found together with the sum bands, their intensity ratios agree with the value calculated by Eq. (4.6).[65]

Selection Rules. The selection rules for simultaneous vibrational transitions have been studied by Hooge and Ketelaar,[70] Colpa and Ketelaar,[68] and Mukhtarov.[69]

From the expression (3.5) for the matrix elements of the induced dipole moment, it follows that simultaneous vibrational transitions with frequencies $\nu_{1i} \pm \nu_{2j}$ may appear in the infra-red spectrum if the coefficient of $\xi_i \eta_j$ in the series expansion of the induced dipole moment (3.3) has a finite value. We consider three cases.

1. We assume that molecule 1 has a dipole moment M_1, whose value depends on ξ_i as follows:

$$M_1 = (M_1)_0 + \left(\frac{\partial M_1}{\partial \xi_i}\right)_0 \xi_i + \ldots \qquad (4.7)$$

while the polarizability α_2 of molecule 2 depends on η_j such that

$$\alpha_2 = (\alpha_2)_0 + \left(\frac{\partial \alpha_2}{\partial \eta_j}\right)_0 \eta_j + \cdots \qquad (4.8)$$

As the molecules approach, the electric field of molecule 1 induces a dipole moment in molecule 2, with a value proportional to $M_1 \alpha_2$. Calculating this product from (4.7) and (4.8), we obtain a series analogous to (3.3), in which the coefficient of $\xi_i \eta_j$ is equal to

$$\left(\frac{\partial M_1}{\partial \xi_i}\right)_0 \left(\frac{\partial \alpha_2}{\partial \eta_j}\right)_0 . \qquad (4.9)$$

In order that this expression may be different from zero, it is necessary that the frequency ν_{1i} be active in the infra-red spectrum $((\partial M_1/\partial \xi_i)_0 \neq 0)$ and the frequency ν_{2j} must be active in the Raman spectrum ($(\partial \alpha_2/\partial \eta_j)_0 \neq 0$). Interchanging the designations for molecules 1 and 2, we obtain an expression analogous to (4.9) for the case in which ν_{2j} is active in the infra-red spectrum, while the frequency ν_{1i} is active in the Raman spectrum. Thus, if the induced dipole moment is completely due to the dipole interaction of the molecules, simultaneous transitions with frequencies $\nu_{1i} \pm \nu_{2j}$ will appear in the infrared spectrum only in case that: one of the combining frequencies is permitted, at least in the infra-red, while the other is permitted, at least in the Raman spectrum. We must emphasize that for dipole induction, which explains most of the simultaneous vibrational transitions observed up to now, to take place, it is not necessary that the value of the permanent dipole moment $(M_1)_0$ or $(M_2)_0$ differ from zero. It is only necessary that $(\partial M_1/\partial \xi_i)_0$ or $(\partial M_2/\partial \eta_j)_0$ should have a finite value.

2. We assume that the value of the quadrupole moment of molecule 1 depends on ξ_i as follows:

$$Q_1 = (Q_1)_0 + \left(\frac{\partial Q_1}{\partial \xi_i}\right)_0 \xi_i + \cdots, \qquad (4.10)$$

while the dependence of the polarizability α_2 of molecule 2 on η_j is given by Eq. (4.8). In this case, the expression for the induced dipole moment will contain a term proportional to

$$\left(\frac{\partial Q_1}{\partial \xi_i}\right)_0 \left(\frac{\partial \alpha_2}{\partial \eta_j}\right)_0 \xi_i \eta_j. \qquad (4.11)$$

The quadrupole moment behaves in the same way under symmetry operations as the polarizability of the molecule. Hence, if $(\partial \alpha_1/\partial \xi_i)_0 = 0$ for symmetry reasons, and hence, the frequency ν_{1i} is forbidden in Raman scattering, $(\partial Q_1/\partial \xi_l)_0$

is also zero. Hence it follows that (4.11) will differ from zero only if the frequencies ν_{1i} and ν_{2j} are both active in the Raman spectrum. In this case, the simultaneous vibrational transition will be due to the polarization of one of the absorbing molecules by the field of the oscillating quadrupole of the other molecule. Induction of this type may be used to explain simultaneous vibrational transitions of two H_2 molecules [12] and in the H_2-N_2 pair.[38] For the simultaneous transitions observed in mixtures of CO_2 with H_2, O_2, and N_2, the dipole moment induced by quadrupole interaction of the molecules is rigorously equal to zero, since the frequencies ν_2 and ν_3 of CO_2 are forbidden in the Raman spectrum.

3. As was shown in Sec. 3, an essential role is played by exchange interactions of molecules, as well as by electrostatic forces, in the production of an induced dipole moment. The intensities of simultaneous transitions associated with exchange interactions of molecules will apparently be less than those of transitions induced by dipole and quadrupole interactions. However, in the case in which both frequencies ν_{1i} and ν_{2j} are forbidden in the Raman spectrum or one of these frequencies is forbidden in both the infra-red and Raman spectra, that is, when a simultaneous vibrational transition cannot be induced by the electrostatic fields of the molecules, the appearance in the infra-red spectrum of bands with frequencies $\nu_{1i} \pm \nu_{2j}$ due to exchange interaction of the molecules is possible. Transitions of this type have not yet been observed.

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Translated by M. V. King

Translator's Comments—This review may best be characterized by comparison with another review article on the same subject which has appeared recently.[1] Both reviews cover essentially the same subject and the same set of original papers, emanating largely from the University of Amsterdam, the University of Toronto, and the Laboratoire des Hautes Pressions, Bellevue, France. However, the subject of transitions induced by an external electric field is included in the review by Filimonov, while it is not covered in Ketelaar's review. Very few of the cited papers are of Soviet origin, but these few were missed in Ketelaar's review.

The chief difference between these two reviews is in the relatively more expanded treatment given by Filimonov, who gives the details of far more of the spectroscopic studies than does Ketelaar, and reproduces more of the original figures from the cited papers. Further, Filimonov provides a much fuller discussion of the selection rules obeyed in induced transitions. While there is some difference in the detail of the mathematical treatment in the two reviews, essentially the same theories are presented.

Both reviews are well-recommended for a clear-cut treatment of the subject, the review by Filimonov being favored for thoroughness of treatment, and that by Ketelaar for conciseness.

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