INTENSITIES IN THE INFRA-RED ABSORPTION SPECTRA OF POLYATOMIC MOLECULES

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IN the last few decades, the study of the vibrations of polyatomic molecules has become one of the most powerful and widespread methods of studying molecular structure. These vibrations are directly manifest in the infra-red absorption spectra and Raman spectra of gases, liquids, and solids.

By measuring the number and positions of the bands (frequencies or wavelengths), we can get important information on the geometric and mechanical properties of molecules, the types of chemical bonds, etc. It is now even difficult to enumerate the large list of specific problems that can be solved with the aid of measurements of vibrational frequencies. However, this does not exhaust the information which we can get from study of the vibration spectra.

The processes of emission, absorption, and scattering of light by molecules result from the interaction of the electrons and nuclei with the electromagnetic field of the light wave. When the nuclei oscillate, the electron cloud of the molecule is deformed. The nature of these deformations depends on both the structure of this cloud and on the characteristics of the vibrations themselves. Peculiarities in the structure of the electron cloud of the molecule are manifest most fully in the intensities and the polarizations of the spectral lines and bands.

By studying the intensities and polarizations of the vibrational spectra, we can get information on the parameters characterizing the electron cloud of the molecule. From among such parameters, the modern theory recognizes especially the dipole moment and the polarizability of the individual bonds in the molecule, and their derivatives with respect to the vibrational coordinates.

In recent years, the number of papers involving the measurement of the intensities of lines and bands in vibrational spectra has increased considerably. The experimental techniques are being perfected, and the list of problems making use of this parameter of the vibrational spectrum in their solution is expanding. We can distinguish a number of research trends in this field. Especially, these include the calculation of the dipole moments of the bonds and their derivatives from the measured intensities, the study of intra- and intermolecular interactions, and group-theoretical structure analysis.

To some degree, molecular spectroscopy is repeating the history of atomic spectroscopy, in gradually going over from studying the frequencies of the spectral bands to studying their intensities. However,

the method of studying the intensities is still not being applied widely enough, in spite of its high sensitivity, as attested by many researchers. This is due both to experimental difficulties and to difficulties in interpreting the data obtained. The researchers have often limited themselves to a mere recording of facts without any serious attempt to explain them. Sometimes, indeed, the conclusions drawn seem to be completely ungrounded.

In turn, certain theoretical problems have also not been given a proper treatment, e.g., the problem of taking into account intermolecular interactions.

This review is concerned with presenting the problems of the theory of the intensities of the infra-red absorption spectra of the fundamental vibrations of polyatomic molecules, and with the experimental methods of measuring the intensities.

The theory to be discussed is applicable to gases, and is a good approximation for liquids, but requires considerable modification for application to crystals.

1. THE THEORY OF THE INTENSITIES AND POLARIZATIONS OF INFRA-RED ABSORPTION SPECTRA OF POLYATOMIC MOLECULES

According to the general theory,[1,2] the intensity of an absorption band corresponding to a normal vibration of a molecule can be expressed in terms of the derivative of the electric dipole moment μ of the molecule with respect to the given normal coordinate Q. The polarization is determined by the direction of the vector $(\partial\mu/\partial Q_i)_0$.

Experimentally, what we can measure is the integrated intensity of the absorption band:

$$A_i = \frac{1}{nl} \int \ln \frac{I_0}{I}\, dv = \frac{1}{n} \int k(v)\, dv, \qquad (1.1)$$

where I_0 and I are the initial and final intensities of a parallel beam of light passing through an absorbing layer of thickness l. The integration is performed over the limits of the absorption band; n is the number of absorbing molecules.

The derivative of the dipole moment of the molecule with respect to the given normal coordinate is related to the integrated intensity by the simple relation[1-4]

$$A_i = \frac{\pi}{3c} \left(\frac{\partial\mu}{\partial Q_i} \right)_0^2. \qquad (1.2)$$

Let us take up now the problem of the relation of the derivative $(\partial\mu/\partial Q_i)_0$ to the structure of the mole-

cule and the form of the vibration, and the information which we may get from an experimental determination of the integrated intensity of the absorption band.

1. The Valence-Optical Theory

The complexity of structure of polyatomic molecules still prevents a direct application of the apparatus of quantum mechanics to the problem of the intensities of vibrational absorption spectra.

Even the use of the approximate molecular-orbital method[5] involves great difficulties, even in the simplest systems, and gives appreciable disagreement with experiment.

In this regard, at present the only actual basis for theoretical study of the intensities and polarizations of the vibrational spectra of polyatomic molecules is the so-called valence-optical theory.

The distinguishing feature of this theory is its relative simplicity and illustrative character. This is especially important in studying complex systems. The theory is also distinguished by its harmony with modern concepts of structural chemistry. We must recognize a basic defect of the theory in the necessity of introducing empirical quantities, namely, the dipole moments of the bonds and their derivatives with respect to the vibrational coordinates, the values of which must be found from the experimental data. However, it would seem that any other theory would require the introduction of some sort of parameters. Thus, this defect of the valence-optical method is not fundamental.

Most of the studies have been based on the valence-optical theory, both in this country and abroad. In its original form, the valence-optical theory was proposed by Vol'kenshteĭn[6,7] and later expanded by him in conjunction with El'yashevich.[7-9] It has subsequently been adopted by a number of authors, and brought to a state of greater precision and refinement.[10-11]

As was noted, the intensity of an absorption band corresponding to a certain normal vibration is determined by the derivative of the dipole moment of the molecule with respect to the given normal coordinate. Here, however, both quantities, μ and Q_i, are characteristics of the state of the molecule as a whole. If we are to be able to draw any conclusions on the internal structure and the intramolecular processes from the intensities of the vibrational spectrum, we must obviously go over to a description of the behavior of the individual parts of the molecule.

Modern structural chemistry treats as the fundamental structural units of a molecule the valence bonds between the atoms, which have quite definite directions. We may ascribe a dipole moment to each such bond.

Hence, we may quite naturally select a specific representation of the dipole moment as a vector sum of all the dipole moments of the bonds. The logical nature of such a representation is confirmed by the fact that in most compounds, definite chemical bonds and groups of atoms correspond to more or less constant values of the dipole moments and force constants, maintained in all compounds containing these bonds or groups.

In the zero-order approximation, all dipole moments of bonds and groups are assumed to be mutually independent. On this basis, many calculations have been performed of the dipole moments of bonds and their derivatives with respect to the stretching

Table I. Direct methods for determining the true values
of the integrated absorption coefficient

Method	Integration of the band in R(ν)	Integration of the band in D(ν)
Extrapolation methods (for bands of arbitrary shape)	The extrapolation method of Bourgin (first variant) $$K_\infty = (dR_\infty/dl^*)_{l^*=0}$$	The extrapolation method of Wilson and Wells (first variant) $$K_\infty = (1/l^*)[\lim_{l^* \to 0} D_\infty^\Omega]$$
	The extrapolation method of Bourgin (second variant) $$K_\infty = \lim_{l^* \to 0} [R_\infty/l^*]$$	The extrapolation method of Wilson and Wells (second variant) $$K_\infty = \lim_{l^* \to 0} [D_\infty^\Omega/l^*]$$
		The method of indirect extrapolation $$|K_\infty| = (1/l^*)[\lim_{\delta\nu \to 0} D_\infty^\Omega]|$$ $$= \lim_{\delta\nu \to 0} [D_\infty^\Omega/l^*]$$
Single-measurement methods (for bands of regular shape)	The calculation method $K_\infty = \varphi\,(R_\infty/l^*)$	The method of direct integration $K_\infty = \varkappa D_0^\circ\, \Delta\nu_D^\circ/l^*$
		The correction method $K_\infty = \psi\,(D_\infty^\Omega/l^*)$

of these bonds, using the experimental values of the intensities of infra-red absorption bands.

A resume of results obtained in this way is given in Table 1 of the Appendix. However, these calculations have shown that the values of the dipole moments of groups and their derivatives found from different vibrations of a single molecule very often differ (see Table I). The sum of the dipole moments of the bonds may turn out not to equal the total dipole moment of the molecule. As a result, certain authors[12-16] have drawn the conclusion that "vibrational" dipole moments exist, which are appreciably different from the static dipole moments, as determined by methods of radio spectroscopy or other methods. The observed discrepancies have been explained on the basis of the "theory of orbital sequences," electron redistribution, etc.

The reason for this failure is understandable if we take into account the fact that, according to Coulson[17] and Mulliken,[18,19] the dipole moment of a bond may be expressed as a vector sum of three moments: the primary dipole moment, due to the asymmetric distribution of the electrons directly participating in formation of the bond, the polarization (atomic) dipole moment, and the moment of the unshared electrons.

Each of these moments exerts an influence on the surrounding bonds, and may vary upon displacement of any of the atoms of the molecule. This is especially true of the component of the dipole moment of the bond due to the unshared electrons.

In certain cases[20-22] it has been possible to improve the results of calculations of dipole moments of bonds and their derivatives by introducing an additional vector for the unshared electrons. However, this problem can be solved most thoroughly by going over to the first-order approximation of the valence-optical theory. Here, we take into account the dependence of the dipole moments on their surroundings. Vol'kenshteĭn and El'yashevich have pointed out the necessity of doing this in the above-mentioned papers. In recent years, Sverdlov[23-28] has shown for a set of specific examples that application of the first-order approximation provides quite good agreement with experiment, free from discrepancies between the values of the dipole moments of molecules as calculated from the intensities in the infra-red spectrum and the static dipole moments.

This has demonstrated the competence of the valence-optical theory in the first-order approximation, and has shown clearly that the difficulties encountered by foreign authors are due only to the fact that they used the zero-order approximation. We shall write the dipole moment of the molecule in the form

$$\mu = \sum_k (\mu_0^{(k)} + \mu_a^{(k)} + \mu_{u.e.}^{(k)}),$$

where $\mu_0^{(k)}$ and $\mu_a^{(k)}$ are the primary and the atomic

moments, and $\mu_{u.e.}^{(k)}$ is the dipole moment of the unshared electrons of the k-th bond.

As for $\mu_0^{(k)}$, we can quite definitely consider it to be directed along the bond. By introducing unit direction vectors e_k for the bonds, we have

$$\mu = \sum_k (\mu_0^{(h)} e_h + \mu_a^{(h)} + \mu_{u.e.}^{(h)}).$$

We have no information on the directions of $\mu_a^{(k)}$ and $\mu_{u.e.}^{(k)}$ in most cases. It is even more difficult to determine the changes in these vectors as the atoms vibrate. The contribution of these vectors may be taken into account by introducing a perpendicular component of the dipole-moment vector of the bond (see reference 29). However, such a method is not very promising, since here we introduce into the treatment even further parameters (the direction and magnitude of the perpendicular vectors and their derivatives with respect to the vibrational coordinates). This makes any practical calculations impossible, even in the simplest systems.

We may most simply take into account the contribution of μ_a and $\mu_{u.e.}$ by finding their components in the directions of the bond vectors. As we may easily convince ourselves,[30] this is equivalent to making the corresponding corrections to the absolute values $\mu_0^{(k)}$.

In fact, we shall express $\mu_k' = \mu_a^{(k)} + \mu_{u.e.}^{(k)}$ in the form $\mu_k' = \sum_l \mu_{kl} e_l$. Then

$$\mu = \sum_k \mu_0^{(h)} e_h + \sum_k \sum_l \mu_{hl} e_l = \sum_k (\mu_0^{(k)} + \sum_l \mu_{lh}) e_h$$

$$= \sum_k (\mu_0^{(h)} + \mu_1^{(h)}) e_h = \sum_k \mu_h e_h. \tag{1.3}$$

Thus we obtain a formula completely analogous to the case of the zero-order approximation, but with additional terms $\mu_1^{(k)}$ including all the corrections introduced into the dipole moments of the bonds by the unshared electrons and the polarizing influence of the other bonds. $\mu_k = \mu_0^{(k)} + \mu_1^{(k)}$ can no longer be considered to be a quantity which is constant for a given bond and independent of the surroundings. It may vary from molecule to molecule, and to a considerable extent loses its significance as a direct characteristic of the bond. Rather, it is transformed into an empirical quantity corresponding to the concrete method of expression of the dipole moment of the molecule, and reflects both the properties of the given bond and the effect of the surroundings.

The components of the dipole moment of the molecule in the directions of the bonds are to be considered in this case to be unknowns to be determined from the solution of the electro-optic problem. In this approach, the expression of μ as a vector sum of $\mu_k e_k$'s is obviously always possible.

To transform from the total dipole moment of the molecule to an expression for it in terms of the dipole moments of the bonds obviously requires a corre-

sponding replacement of the normal coordinates by coordinates directly characterizing the positions of the atoms or the bonds in the molecule. The derivatives taken with respect to the normal coordinates are replaced by combinations of the derivatives with respect to these coordinates. The choice of a working system of coordinates is determined not only by convenience of calculation, but also by the physical meaning of the corresponding derivatives. In itself, this treatment of a polyatomic molecule as a set of bonds, each taken as a sort of "diatomic molecule" possessing its own dipole moment, has the natural consequence that we should use a system of coordinates in which the changes in the bond lengths play a role. Thus, we obtain the derivatives of the dipole moments of the bonds with respect to the stretching of these bonds. These derivatives are very similar in their physical meaning to the analogous derivatives for diatomic molecules, especially in those cases in which we are dealing with rather isolated bonds which retain their dipole moments in various compounds.

The very widely-used systems of valence-force-field and central-force-field coordinates in the theory of vibrations of polyatomic molecules are precisely this sort of coordinate system.

In the former system, the vibrational coordinates are taken to be the changes in the bond lengths and the valence angles, while in the latter system they are the changes in the bond lengths and in the inter-atomic distances between unbonded atoms. The set of dipole moments of the bonds, and the derivatives of these with respect to the vibrational coordinates are denoted as the electro-optic parameters of the molecule.

Before we go on to give an account of the methods of calculating these parameters, let us consider what information about the structure of the molecule we can get in this way. We have shown above that when we take into account various factors, the very concept of the dipole moment of a bond loses to a considerable degree the physical meaning of a direct characteristic of the bond. Rather, it is converted into an empirical quantity which we can calculate under various assumptions. The same is true, of course, of the derivatives of the dipole moments of the bonds.

However, even under these conditions, the investigation alone of the magnitudes of the derivatives of the dipole moments of the bonds with respect to the vibrational coordinates can give us highly valuable information on the mutual influences between certain atomic groups and others, on the behavior of the unshared electrons, the electron-cloud distribution, etc.

The values of the appropriate electro-optic parameters found from a study of certain molecules may be applied to predict the intensities of the spectra of similar molecules, and thus to improve the correctness of assignment of frequencies, which is an essential matter in every spectroscopic study. The strong dependence of the intensities on the form of the vibration (see below) makes it possible to test the correctness of the calculations. We shall not discuss here the fact that problems of this type aid in drawing a much fuller picture of the vibrations of a polyatomic molecule and in arriving at better-grounded conclusions concerning the intramolecular processes on the basis of observed spectral changes.

The most interesting results may be obtained by thorough study of an entire class of related compounds. Let us suppose that we find in this class that certain electro-optic parameters, e.g., the dipole moments of the bonds and their derivatives with respect to stretching of the bonds, are invariant. Then this demonstrates that these quantities actually reflect real properties of the bonds, and may be used to characterize them.

In particular, the dipole moment of a bond may serve as a rather unambiguous criterion of the bond type. Thus, for example, Smyth[15] gives the following values for the relation of typical dipole moments to the bond type:

Bond type	Dipole moment in Debye units (D)
Covalent	
Single	0–2.0
Double	0–2.5
Triple	0–3.5
Metallo-organic	2–4
Coordinate	3–4.5
Ionic	6–20

The values of the derivatives may also serve as valuable characteristics of the bond type.

Undoubtedly, the widespread permeation of theoretical methods into the practice of spectrochemical research will open up new possibilities for the use of the electro-optic parameters to study molecular structure and various kinds of intra- and intermolecular interactions.

2. The Direct and Inverse Electro-optic Problems

Above we considered in detail the general approach to the solution of the problems of the intensities in the absorption spectra of the normal vibrations, based on the concept of the dipole moment of the molecule as a vector sum of the dipole moments of the bonds.

Making use of the representation of the total dipole moment of the molecule in the form $\mu = \sum_k \mu_k e_k$, and transforming from the normal coordinates to the set of natural vibrational coordinates, we can write

$$\left(\frac{\partial \mu}{\partial Q_i}\right)_0 = \left[\sum_k \frac{\partial}{\partial q_k}\left(\sum_k \mu_k e_k\right)q_{ki} + \sum_n \frac{\partial}{\partial \gamma_n}\left(\sum_k \mu_k e_k\right)\gamma_{ni}\right]N_i.$$

Here, the coordinates for bond stretching are denoted by the symbols q, while any other coordinates (changes in valence angles, out-of-plane coordinates, changes in interatomic distances, etc.) are denoted by γ. N_i is a normalizing factor.

We can write the same equation in the simpler matrix form

$$\left(\frac{\partial \mu}{\partial Q_i}\right)_0 = \left[\{e\} \left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right| + \{\mu\} \left|\frac{\partial e}{\partial q} \frac{\partial e}{\partial \gamma}\right| \right] \left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i N_i. \quad (1.4)$$

Here we have used the following notation: $\{e\} = \{e_1, \ldots, e_m\}$ is a row matrix with elements e_k (where the e_k are the direction vectors of the bonds); $\{\mu\}$ is a row matrix with elements μ_k; $\left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right|$ is the rectangular matrix of the derivatives of the dipole moments of the bonds with respect to the vibrational coordinates, as follows:

$$\left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right| = \begin{vmatrix} \frac{\partial \mu_1}{\partial q_1} \cdots \frac{\partial \mu_1}{\partial q_m} \frac{\partial \mu_1}{\partial \gamma_1} \cdots \frac{\partial \mu_1}{\partial \gamma_n} \\ \cdots \cdots \cdots \cdots \\ \frac{\partial \mu_m}{\partial q_1} \cdots \frac{\partial \mu_m}{\partial q_m} \frac{\partial \mu_m}{\partial \gamma_1} \cdots \frac{\partial \mu_m}{\partial \gamma_n} \end{vmatrix}$$

and $\left|\frac{\partial e}{\partial q} \frac{\partial e}{\partial \gamma}\right|$ is the rectangular matrix of the derivatives of the direction vectors of the bonds with respect to the vibrational coordinates, having a form analogous to $\left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right|$; finally, $\left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i$ is a column matrix in which all of the relative amplitudes of the vibrational coordinates corresponding to a given normal coordinate are arranged in order. This set of amplitudes is ordinarily called the form of the vibration. Hence we shall always refer hereinafter to the column matrix simply as the form of the vibration. The normalizing factor in matrix notation has the form

$$N_i = \frac{\nu_i}{\sqrt{\{q,\gamma\}_i U \left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i}},$$

where U is the matrix of the force constants. The matrix $\left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right|$ characterizes the changes in the absolute values of the dipole moments of the bonds when the equilibrium configuration of the molecule is disturbed. The matrix $\left|\frac{\partial e}{\partial q} \frac{\partial e}{\partial \gamma}\right|$ characterizes their changes in direction due to rotations of the bonds during vibration. Since any changes in the dipole moment can be described in terms of the 3N—6 independent internal vibration coordinates, these matrices must consist solely of derivatives of the dipole moments of the bonds with respect to these independent coordinates.

As was stated in Sec. 1, the absolute values μ_k of the dipole moments of the bonds are assumed to be functions of all 3N—6 vibrational coordinates. This is also true of the positions of the bonds, which are given by the direction vectors e_k of the bonds.

Equation (1.4) may be separated into a valence (stretching) term $\{e\} \left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right| \left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i$ and a deformation term $\{\mu\} \left|\frac{\partial e}{\partial q} \frac{\partial e}{\partial \gamma}\right| \left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i$.

The basic difficulty consists in calculating the matrix $\left|\frac{\partial e}{\partial q} \frac{\partial e}{\partial \gamma}\right|$. The basic difference between the existing methods of calculating $(\partial \mu/\partial Q_i)_0$ lies precisely in the method of calculating this matrix.[1,6-11,31-33] The analysis and comparison of these methods is not part of our subject.

References 31 and 32 showed that $\left|\frac{\partial e}{\partial q} \frac{\partial e}{\partial \gamma}\right|$ $= S^{-1}(\Delta\epsilon\widetilde{B}T - E)$. Here, S^{-1} is the diagonal matrix of the reciprocals of the bond lengths; $\Delta\epsilon$ is the matrix obtained from the diagonal matrix of the reciprocals of the masses of the atoms by termwise subtraction from each other of the rows corresponding to the atoms of each bond; $\widetilde{B}$ is the transpose of the matrix for transformation from the Cartesian coordinates of the atomic displacements from the equilibrium positions to the vibrational coordinates (i.e., $\left\| \begin{matrix} q \\ \gamma \end{matrix} \right\| = B \| r \|$); T is the matrix of the kinetic energy of the vibrations in the given coordinate representation (this matrix is the inverse of the matrix of the kinematic coefficients ordinarily used in the theory of the vibrations of polyatomic molecules, and can be found either by inversion of the latter or directly[34]); E is the diagonal matrix of the direction vectors e_k.

Taking into account the form of the normalizing factor, we finally obtain

$$\left(\frac{\partial \mu}{\partial Q_i}\right)_0 = \left[\{e\} \left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right| + \{\mu\} S^{-1}(\Delta\epsilon\widetilde{B}T - E) \right] \left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i \frac{\nu_i}{\sqrt{\{q, \gamma\}_i U \left\| \begin{matrix} q \\ \gamma \end{matrix} \right\|_i}}. \quad (1.5)$$

The elements of the matrix $\left|\frac{\partial \mu}{\partial q} \frac{\partial \mu}{\partial \gamma}\right|$ and the dipole moments of the bonds are the electro-optic parameters of the molecule. Equation (1.5) is a general expression for $(\partial \mu/\partial Q_i)_0$, and hence for the intensity of the given normal vibration. We must recognize the advantage of this formula in representing $(\partial \mu/\partial Q_i)_0$ as the (matrix) product of two factors. One of these factors clearly combines all of the electro-optic and mechanical parameters of the molecule, and is invariant for all normal vibrations of the molecule. The second factor is simply the form of the given vibration. This characteristic of Eq. (1.5) makes it highly suitable for all sorts of general studies of the relation of the intensities to the characteristics of the molecule, as well as for deriving a number of consequences.

It is also important that Eq. (1.5) is very convenient for computer calculation. The symmetry of the molecule can also easily be taken into account.

In the zero-order approximation, the non-diagonal elements of the matrix $|\partial\mu/\partial q|$ are assumed to be zero. This corresponds to the assumption that the dipole moments of the bonds are independent of their surroundings. We can take into account the effect of the surroundings, the atomic polarization, and the unshared electrons by introducing into the treatment all or some of the derivatives of the dipole moments of the bonds with respect to the vibrational coordinates.

The formula given here permits us to calculate $(\partial\mu/\partial Q_i)_0$ unambiguously, and hence, to calculate the intensity and polarization of the absorption band, provided that we know the electro-optic and mechanical parameters of the molecule, and the frequency and form of the vibration. A problem of this type is ordinarily called a direct electro-optic problem.

Let us consider now the inverse problem of determining the electro-optic parameters, and clarify the theoretical side of this problem. In general, we may know from experiment two quantities: the derivative of the dipole moment of the molecule with respect to a normal coordinate (to be exact, without its sign, since the intensity of the absorption band is determined by the square of this derivative) and the direction of the vector $(\partial\mu/\partial Q_i)_0$, i.e., the polarization. In addition, we may assume that we know the form of the vibration from the solution of the mechanical problem.

We begin with the formula

$$\left(\frac{\partial\mu}{\partial Q_i}\right)_0 = \left[\{e\}\left|\frac{\partial\mu}{\partial q}\right| + \{\mu\}\left|\frac{\partial e}{\partial q}\right|\right]\|q\|_i,$$

where (as shown) $|\partial e/\partial q| = S^{-1}(\Delta\epsilon\widetilde{B}T - E)$ and q is the set of vibrational coordinates. For brevity, γ is included simply in the symbol q. We assume the coordinates to be normalized. We now transform the valence term into the form

$$\{e_1, \ldots, e_m\}\begin{vmatrix} \frac{\partial\mu_1}{\partial q_1} & \cdots & \frac{\partial\mu_1}{\partial q_n} \\ \cdot & \cdots & \cdot \\ \frac{\partial\mu_m}{\partial q_1} & \cdots & \frac{\partial\mu_m}{\partial q_n} \end{vmatrix}$$

$$= \left\{\frac{\partial\mu_1}{\partial q_1}, \ldots, \frac{\partial\mu_1}{\partial q_n}, \ldots, \frac{\partial\mu_m}{\partial q_1}, \ldots, \frac{\partial\mu_m}{\partial q_n}\right\}$$

$$\times \begin{vmatrix} e_1 \cdots 0 \\ \cdot \cdots \cdot \\ 0 \cdots e_1 \\ \cdot \cdots \cdot \\ \cdot \cdots \cdot \\ e_m \cdots 0 \\ \cdot \cdots \cdot \\ 0 \cdots e_m \end{vmatrix} \begin{matrix} \left.\right\}n \\ \\ \left.\right\}n \end{matrix} = \left\{\frac{\partial\mu}{\partial q}\right\}\epsilon.$$

Then we can write

$$\left(\frac{\partial\mu}{\partial Q_i}\right)_0 = \left[\left\{\frac{\partial\mu}{\partial q}\right\}\epsilon + \{\mu\}\left|\frac{\partial e}{\partial q}\right|\right]\|q\|_i$$

$$= \left\{\frac{\partial\mu}{\partial q}, \mu\right\}\begin{vmatrix} \epsilon \\ \frac{\partial e}{\partial q} \end{vmatrix}\|q\|_i = \{q_i\}\left|\widetilde{\epsilon}, \frac{\widetilde{\partial e}}{\partial q}\right|\begin{vmatrix} \frac{\partial\mu}{\partial q} \\ \mu \end{vmatrix}. \tag{1.6}$$

By finding the projections of all of the vectors of the matrices $|\partial e/\partial q|$ and ϵ on the polarization direction, and substituting in the corresponding forms of the vibrations, we can derive a system of scalar inhomogeneous linear equations in the electro-optic parameters.

As an additional equation we can use the equality $\mu = \sum_k \mu_k e_k$.

Since in the general case the number of electro-optic parameters is larger than the number of normal vibrations active in absorption, the system of equations cannot be solved unambiguously.

Hence, in practical calculations, we must search for a way to reduce the number of unknowns or to increase the number of equations. The number of unknowns may be reduced either by assuming that some of the derivatives in the matrix $\left|\dfrac{\partial\mu}{\partial q}\ \dfrac{\partial\mu}{\partial\gamma}\right|$ are equal to zero (since, as it seems, we can assume that the mutual influence of distant atoms and groups will be negligible), or by using the symmetry of the molecule, since the electro-optic parameters of equivalent bonds and groups are equal to each other. The number of equations may be increased by using isotopically-substituted molecules, for which the electro-optic parameters remain unchanged.

The second fundamental difficulty in calculating the electro-optic parameters consists in the indeterminacy of the signs of the derivatives $(\partial\mu/\partial Q_i)_0$. This is due to the impossibility of determining the relative phases of the different normal vibrations of the molecule.

Hence, we must perform the calculations of the electro-optic parameters with various independent combinations of signs of the $(\partial\mu/\partial Q_i)_0$. Thus, we obtain a corresponding set of values of the electro-optic parameters. Obviously, the combinations of $(\partial\mu/\partial Q_i)$'s obtained from each other by simultaneous change of the signs of all the derivatives will give the same values of the electro-optic parameters, but with the opposite signs. Hence it follows that the electro-optic parameters can be found only without the sign. This, of course, is not true of their relative signs.

The selection of the correct combination of the electro-optic parameters will be made below either from some indirect reasoning, or by applying the calculated values of the parameters to isotopically-substituted molecules, and comparing the calculated intensities with the experimental values. In order to do this, we may also use homologous series.

We must note that the accuracy of calculation of the electro-optic parameters (or if the latter are known, of the intensities) is highly dependent on the accuracy of determination of the form of the vibrations, i.e., fundamentally on the determination of the matrix U (of the force constants).

Thus, while the direct problem of calculating the intensities in the vibrational absorption spectra of polyatomic molecules, when we know the form of the vibrations and the mechanical and electro-optic parameters, may be solved unambiguously and rather simply for molecules of any complexity, the inverse problem of determining the electro-optic parameters encounters considerable difficulties even for the simplest systems.

Nevertheless, in a great number of cases, we can be assured of obtaining quite correct values of the electro-optic parameters, provided that we perform this determination not for a single molecule, but for an entire class of related compounds of gradually increasing structural complexity, with the use of isotopic molecules. The organic compounds are especially adapted to this purpose, for the presence of repeating groups permits us to assume that the corresponding electro-optic parameters will remain constant, thus leading to a decrease in the number of unknowns.

Here we can check the correctness of the calculations of the electro-optic parameters and improve their accuracy at each stage by making a preliminary calculation of the corresponding intensities in the next molecule and comparing them with experiment.

This type of calculation obviously requires an extensive use of computers to permit one to try different variants of the solution.

3. Specific Intensities in Infra-red Spectra

The study of vibrational absorption spectra of polyatomic molecules has shown that definite chemical groups correspond to definite so-called characteristic (specific) frequencies and forms of vibrations, which change relatively slightly upon transfer of these groups from one molecule to another.

This peculiarity of the vibrations of polyatomic molecules has been responsible to a considerable extent for the very widespread application of spectroscopic methods in science and industry. At the same time, it has been noted that often the specific vibrations are also distinguished by invariable (specific) intensities. This valuable property of certain of the specific vibrations may be widely applied in the solution of various problems. Recently this problem was subjected to a detailed theoretical study.[32,35-37] As a result, it turned out to be possible not only to find the conditions under which the intensity may be specific, but also to point out a number of methods of simplifying the calculation of the specific intensities.

The study of specific intensities (and polarizations) gives us, on the one hand, a supplementary criterion for the correctness of assignment of frequencies in the spectra of complex molecules, and on the other hand, it may act as an experimental proof that certain chemical groups have a closed electronic structure. This latter point is of extremely great value, not only in elucidating the structure of complex molecules, but also in constructing various sorts of simplified models of molecules.

The conditions under which the vibrations of some group of atoms in a molecule may exhibit specific intensity can be reduced to the following:

1) The vibration of the given group of atoms must be completely specific in frequency and form for the set of coordinates describing that group.

2) In the matrix $\left| \dfrac{\partial \mu}{\partial q}\ \dfrac{\partial \mu}{\partial \gamma} \right|$, the derivatives of the dipole moments of the bonds of the particular group of atoms with respect to the coordinates of this group must be large in comparison with the derivatives of the dipole moments of bonds outside the given group with respect to the coordinates of the group. If the specificity is to remain stable (over a series of compounds), it is also necessary that this requirement be fulfilled by the derivatives of the dipole moments of the bonds of this group with respect to the coordinates of the rest of the molecule. In essence, this implies the assumption that the electrical connection between the given group and the rest of the molecule is weak.

3) The given group must have as few as possible atoms in common with the rest of the molecule.

4) The bonds in the rest of the molecule must not rotate when the equilibrium bond lengths and angles in the given group are varied.

The latter two conditions result from the requirement of invariance of the position of the center of gravity and of the angular momentum of the entire molecule when the given group of atoms alone is vibrating. These same conditions are also valid criteria for specific polarization. However, in this case, the requirement that the frequency be specific is not obligatory. Besides, frequencies which are actually stably specific in the spectrum most often correspond to vibrations which are specific in both frequency and form. Thus, the special reservations regarding the specific nature of the polarization are not of essential interest.

Stability of the specificity of the frequencies and form (throughout a series of compounds) is ordinarily associated with specific chemical forces, as manifested in the smallness of the non-diagonal elements of the force-constant matrix. Since the potential and electric fields in the molecule must generally be interrelated, smallness of the derivatives of the dipole moments of the bonds with respect to the vibrational

coordinates will probably be associated with small-ness of the analogous elements in the force-constant matrix.

It follows from the general theory that vibrations which are specific in intensity will necessarily be specific in frequency and form, while vibrations which are specific in polarization must also be specific in form. If this conclusion is confirmed by experiment, we then may naturally classify the absorption bands in a vibrational spectrum as being specific in fre-quency and form, or specific in polarization, or spe-cific in frequency. Here, specificity of any type may be tested experimentally. The highest form of spe-cificity is that of intensity, since it requires an en-tire set of conditions for existence; thus it must be found relatively rarely.

Table 2 of the Appendix gives systematized data on the absolute intensities of certain functional groups exhibiting the property of specificity of intensity. All of the values are given for solutions in CCl_4 (or CS_2, when indicated with an asterisk). The comparison of the results of various authors permits us to estimate the error of the performed measurements.

4. The Relation of the Intensity to the Number of Equivalent Groups in Polyatomic Molecules

The problem of specific intensities is closely con-nected with that of the relation of the intensities of the fundamental vibrations of polyatomic molecules containing several identical groups to the number of such groups. This problem is essential in the development of methods of group-theoretical struc-ture analysis based on infra-red spectra.

A number of experimental studies have been de-voted to this problem.[38-45,48] However, the existing store of experimental material does not permit us to discern any general regularities of this sort in the spectra of polyatomic molecules. Indeed, most of the researchers have adhered to the opinion that the relation of the intensities to the number of groups is necessarily linear. Even if we do not mention the fact that this view is often contradicted by their own experimental data, we must note that it is based on the completely incorrect assumption of the independ-ence of the vibrations of the separate groups in the molecule. Besides other factors to be discussed be-low, the fact is completely ignored here that the vi-brations of all the groups in the molecule always exhibit definite phase relationships, while the groups themselves maintain mutual spatial relations.

The correct answer to this problem has been ob-tained[46,47] only on the basis of a thorough theoretical study.

Let us consider a molecule consisting of a certain invariable common portion (which we shall call the kernel), to which n identical groups of atoms are attached. The intensity of the absorption bands cor-responding to some normal vibration of the molecule will be determined both by the vibrations of the ker-nel and by those of the groups being considered. Be-sides, if the number of equivalent groups is increased, the electric and mechanical parameters, the forms of the vibrations, and the frequencies will undergo appre-ciable changes. Hence, in the general case, the rela-tion of the intensities of the corresponding absorption bands to the number of equivalent groups will be very complex and irregular. However, if we assume that the vibration of each equivalent group satisfies the conditions for specificity of intensity and polarization, and their forms of vibration differ only by a constant factor, we may infer a certain regularity in the behav-ior of the intensity of the absorption band correspond-ing to the vibrations of this group. This regularity will be expressed by the simple formula

$$A_i(n) = \text{const} \cdot \frac{v_i^2(n)}{\sum\limits_{k}^{n} a_k^2} \left(\sum\limits_{k}^{n} a_k h_k \right)^2, \qquad (1.7)$$

where h_k is the polarization vector of each equiva-lent group, i.e., a unit vector with a direction given by the derivative of the dipole moment of the equiva-lent group with respect to the normal coordinate de-scribing the vibration. a_k is a factor giving the rela-tive amplitudes and phases of the vibrations of the equivalent groups; n is the number of equivalent groups; and v_i is the vibration frequency in cm^{-1}.

The stated limitations are in complete agreement with experiment, since they are simply a more pre-cise expression for the conditions commonly applied by researchers for "independence" of equivalent groups.

In the special case in which all of the vectors h_k are parallel, and a_k is unity, the corresponding in-tensities are simply proportional to the number n of groups. In the general case, the intensities may either rise or fall, depending on the relative posi-tions of the groups. For example, this is observed in a study of the series $(CH_3)_nSiCl_{4-n}$, in which the vibration intensities agree well with Eq. (1.7) (see references 43 and 47).

In addition to its use for group-theoretical struc-ture analysis, the proposed relation may be applied as an experimental proof that certain groups exhibit specific intensities. Thus, it is a criterion of their closed character and the invariance of their structure.

We must also note that for group-theoretical structure analysis we must use those absorption bands having frequencies which vary relatively slightly when the number of groups is varied. A large shift in the frequency is almost always associated with disturb-ances in the structure of the molecule, leading also to changes in the electro-optic parameters.

2. THE EXPERIMENTAL DETERMINATION OF IN-TENSITIES IN INFRA-RED ABSORPTION SPEC-TRA

The measurement of the absolute intensities of infra-red absorption bands began more than thirty

years ago in the studies of Kemble and Bourgin.[49,50] As the technique of infra-red spectroscopy developed and methods of measurement were perfected, the number of such studies has gradually increased. However, the experimental and methodological difficulties have not yet been overcome in many respects; the complexity and laboriousness of the existing methods of obtaining and handling the experimental data seriously hinders this type of investigation.

The data on absolute intensities, obtained mainly from a set of the simplest compounds, are still inconveniently scattered at present in a large number of original papers in the literature. We cannot assume here that all existing values have the same degree of reliability; some of the measurements performed by different methods or different authors have led to appreciable discrepancies in the results.

5. The Fundamental Methods of Measuring the Integrated Intensities of Infra-red Absorption Bands

The quantity characterizing the intensity of an infra-red absorption band, directly associated in its physical meaning with the electro-optic parameters of the molecule, is the integrated absorption coefficient

$$K_\infty = \int_0^\infty K(v)\,dv, \qquad (2.1)$$

where the integration is performed over all frequencies of the band corresponding to the given vibrational or vibration-rotation transition. The absorption coefficient for a given frequency v is related to the optical density of the substance at the same frequency, $D(v) = \ln[I_0(v)/I(v)]$ by the relation

$$K(v) = \frac{D(v)}{l^*}.$$

If the band is measured in percent absorption, $R(v) = 1 - [I(v)/I_0(v)]$, then

$$K(v) = -\frac{\ln[1 - R(v)]}{l^*}, \qquad (2.2)$$

where l^* is the so-called effective path length of the light beam in the material, as defined by:

$$l^* = \begin{cases} l - & \text{for a homogeneous liquid,} \\ cl - & \text{for a solution, or} \\ pl - & \text{for a gas.} \end{cases}$$

Here I_0 is the intensity of the incident light, I is the intensity of the transmitted light, l is the path length of the cuvette containing the material, c is the concentration of the substance, and p is the partial pressure of the gas. Thus, the quantity $K(v)$ to be determined is related non-linearly to the quantities ordinarily measured experimentally, $I(v)$ and $I_0(v)$ (with single-beam instruments) or $R(v)$ (with double-beam instruments).

The basic difficulty in the experimental determination of the intensities of infra-red bands is the non-monochromaticity of the radiation involved to a greater or lesser extent in any actual spectroscopic instrument. This lack of monochromaticity is due to the finite width of the slit, diffraction, aberrations, etc. Hence, the quantities I_0 and I or R being measured no longer refer to a given frequency v, but are values averaged over a certain frequency range δv. The greater the value of δv is, the more strongly the observed spectrum is distorted. In distinction from the other distorting factors (see below), whose roles may be minimized by selection of definite optimum conditions for measurement, the effect of the non-monochromatic radiation cannot be diminished below a certain limit determined by the light-gathering power and general sensitivity of the instrument.

In most modern spectrometers, δv always amounts to several cm^{-1}, and is comparable in order of magnitude with the width of the absorption bands in the condensed states of matter, disregarding the fine rotational structure as occurs in the case of gases.

The existing methods of determining the true values of the integrated absorption coefficient are in essence various ways of taking into account the effect of the non-monochromatic character of the radiation. Let us discuss these methods.

1. Method of determining K_∞ based on integration of the band in terms of $R(v)$. As is known,[51,52] the integrated intensity of the absorption band $R(v)$, that is,

$$R_\infty = \int_0^\infty R(v)\,dv, \qquad (2.3)$$

is independent of the spectral slit width δv, which gives rise only to a redistribution of the energies over the band contour $R(v)$. This characteristic of the integrated absorption R_∞ is the basis of a number of methods for determining the true values of k_∞. The methods to be discussed below are divided into extrapolation methods, carried out on the basis of several measurements at different values of l^*, and methods based on a single measurement at a single value of l^*.

a) Bourgin's extrapolation method. This method is historically the very first method of precise quantitative measurement[49,50] in the infra-red spectral region. In order to derive the appropriate relation, we shall differentiate the following expression with respect to l^*:

$$R_\infty = \int_0^\infty [1 - e^{-K(v)l^*}]\,dv, \qquad (2.4)$$

where the integration is performed, as before, between the limits of the given absorption band $R(v)$. Then we have

$$\frac{dR_\infty}{dl^*} = \int_0^\infty K(v)\,e^{-K(v)\,l^*}dv$$

and hence,

$$K_\infty = \left(\frac{dR_\infty}{dl^*}\right)_{l^*=0}. \qquad (2.5)$$

Consequently, the value of the integrated absorption coefficient K_∞ may be determined from the measured integrated absorption R_∞ by performing an extrapolation to zero effective path length of the light beam in the material. In this case, K_∞ is defined as the slope of the curve of R_∞ plotted against l^* at the origin. Since R_∞ does not depend on the resolving power of the spectrometer, the form of the extrapolation curve is determined only by the shape of the band being measured. Ordinarily, as we approach the origin, the extrapolation curve increases greatly in curvature, thus leading to large errors in the measured slope.

There are two possible variants of this method.

If we expand $\ln[1 - R(\nu)]$ in Eq. (2.2) in series, we have

$$K_\infty^0 = \frac{1}{l^*} \int_0^\infty \left[R(\nu) + \frac{1}{2} R(\nu)^2 + \ldots \right] d\nu. \qquad (2.6)$$

References 50, 53, and 54 have shown that in the limit as $l^* \to 0$ the observed values of the integrated absorption coefficient K_∞^0 become equal to the true values, since the contributions of the quadratic and higher terms in the series in Eq. (2.6) become negligible, and the integral on the right-hand side reduces to R_∞. Thus,

$$K_\infty = \lim_{l^* \to 0} \left(\frac{R_\infty}{l^*}\right). \qquad (2.7)$$

This method permits us to a certain degree to avoid the difficulty of the previous method, which is due to a certain indeterminacy in the measurement of the slope at the origin. If we plot R_∞/l^* against l^*, then, according to Eq. (2.7), the problem of determining K_∞ is reduced to finding the intercept on the axis of ordinates, which can be done more accurately than the determination of the slope. However, as $l^* \to 0$ the extrapolation curve still has a curvature that depends only on the shape of the contour being studied, so that the measurements cannot be performed accurately enough. In order to improve the accuracy, we would have to follow the trend of the extrapolation curve to very small values of l^*, but this in turn is limited by the rapid increase in the errors in measuring small intensities.

b) The computation method. The two previous methods are universal, since they permit us to determine the true values of the integrated absorption coefficient for bands of any arbitrary shape, and in principle, for any values of the practical resolving power of the spectrometer. They have the defect of being experimentally cumbersome without having a high accuracy of measurement. For bands of regular form, not distorted by rotational structure (in the condensed states of matter), the problem becomes simpler, since it becomes possible to make a prior

theoretical calculation of the relation between the quantity K_∞ to be determined and the measured quantity R_∞:

$$K_\infty = \varphi \frac{R_\infty}{l^*}, \qquad (2.8)$$

where the coefficient φ is a function of the shape of the band contour and the magnitude of the absorption.

We shall expand the exponential in the expression for the integrated absorption R_∞ in a series,

$$R_\infty = \int_0^\infty [1 - e^{-K(\nu)l^*}] d\nu = l^* \int_0^\infty \left[K(\nu) - \frac{K(\nu)^2}{2} l^* + \ldots \right] d\nu \qquad (2.9)$$

and make the well-known assumptions on the form of the true contour of the band, such that we may substitute a dispersion function for $K(\nu)$. Then, after making the appropriate transformations, we derive an equation of the type of Eq. (2.8), containing an expression for φ of the form

$$\varphi = \frac{1}{1 - \frac{D_0}{4} + \left(\frac{D_0}{4}\right)^2 - \ldots}, \qquad (2.10)$$

where D_0 is the true value of the optical density at the band maximum, undistorted by the instrument. The relation of φ to D_0 has been tabulated in reference 55 in a similar way (see the third method given in the present paper).

The conversion factor φ can be calculated without recourse to series expansion by applying the concept of the form factor r, which enters into the expression for the integrated intensity:

$$R_\infty = r_R \Delta \nu_R R_0, \quad D_\infty = r_D \Delta \nu_D D_0. \qquad (2.11)$$

As was shown in reference 56, the form factors for bands in terms of $R(\nu)$ and $D(\nu)$ practically coincide in the optimum range of D_0 values. That is, $r_R = r_D$. Hence, the factor φ will be

$$\varphi = \frac{D_\infty}{R_\infty} = \frac{D_0}{1 - e^{-D_0}} \frac{\Delta \nu_D}{\Delta \nu_R}, \qquad (2.12)$$

where, in particular, we may show for bands having the form of a dispersion function (see reference 56):

$$\frac{\Delta \nu_D}{\Delta \nu_R} = e^{-\frac{D_0}{4}}. \qquad (2.13)$$

The quantity φ may also be expressed as a function of D_0. It is not difficult to transform the true values of D_0 into the observed D_0^0 values, for example, by using the tables in the cited papers.[55,56] One of the basic assumptions on which the computation method in the form discussed above rests is that the true contour of the band for liquids and solutions is a dispersion function. We must note that this assumption seems to be confirmed by most of the experimental tests which have been carried out.[55-58]

2. Methods of determining K_∞ based on integration of the band in $D(\nu)$. The methods already discussed, based on operations with $R(\nu)$, have the advantage

that they permit us to determine K_∞ directly from a recorded spectrogram without having to change the scale of the spectrum, i.e., without having to transform to the optical density $D(\nu)$, which is related non-linearly to $R(\nu)$:

$$D(v) = -\ln[1 - R(v)]. \tag{2.14}$$

Also, in view of the known relation (see references 54 and 59):

$$K_\infty > \frac{D_\infty^0}{l^*} > \frac{R_\infty}{l^*} \tag{2.15}$$

the transformation from the integrated absorption R_∞ to the integrated absorption coefficient K_∞ is a longer step, and hence, less precise, than the transformation from the integrated optical density D_∞ to K_∞. Further, since D_∞ is generally subject to distortion owing to the non-monochromatic radiation, the use of a spectrometer with better resolving power will obviously aid in the extrapolation $D_\infty^0/l^* \to K_\infty$, although it plays no role in the extrapolation $R_\infty/l^* \to K_\infty$.

The problem of how the optical density is recorded is not essential. Thus, for single-beam instruments, instead of performing a rather tedious and inefficient manual recalculation, it is rational to use a conversion scale, as described in reference 60. For double-beam instruments, the recording of the bands in terms of optical density may be carried out directly by means of a photometric wedge of the appropriate form, or if the wedge is linear, by using a special logarithmic integrator.[61] The problem has been discussed repeatedly in the literature of direct recording of optical density in the infra-red,[62-64] of automatic measurement of the integrated absorbancy,[65] etc. Thus, in spite of the fact that the transformation $R(\nu) \to D(\nu)$ of the bands sometimes requires supplementary experimental procedures, the transformation $D_\infty^0/l^* \to K_\infty$ is more convenient in a number of cases. The use of the integrated intensity D_∞^0 is the basis of a number of methods for determining the true values of the integrated absorption coefficient K_∞; as before, these methods may be divided into extrapolation and non-extrapolation methods.

a) The extrapolation method of Wilson and Wells. The basis of this method is the extrapolation relation

$$K_\infty = \frac{\lim\limits_{l^* \to 0} D_\infty^0}{l^*}, \tag{2.16}$$

which has been shown to hold true in reference 54. The problem of determining K_∞ consists in finding the observed values of the integrated optical density D_∞^0 for a wide range of values of the effective path length l^*. Then K_∞ is defined as the slope of the graph of D_∞^0 plotted against l^* at the origin. The form of the extrapolation curve now depends not only on the shape of the band, but also on the resolving power of the spectrometer: as $\delta\nu$ decreases, the curvature of the extrapolation curve at the origin decreases, and the accuracy of the measurements increases.

As in the case of the extrapolation methods of Bourgin, the accuracy of an extrapolation of this type, other conditions remaining the same, may be improved by replacing the determination of the slope by the finding of the intercept on the axis of ordinates. The corresponding extrapolation relation[54,59] may be written:

$$K_\infty = \lim_{l^* \to 0} \left(\frac{D_\infty^0}{l^*} \right), \tag{2.17}$$

and the experimental procedure is reduced to plotting the relation of D_∞^0/l^* to l^* and extrapolating to $l^* = 0$. The use of a better spectrometer improves the quality of the extrapolation by smoothing the extrapolation curve, and avoids recourse to the measurement of exceedingly small absorbancies, which always involve the greatest errors.

The extrapolation methods of determining the true values of the integrated absorption coefficient, in spite of their obvious experimental awkwardness, have a valuable characteristic: their applicability to absorption bands of any arbitrary shape. Thus they are indispensible in the study of the intensities in gas spectra. For the gaseous state of a substance, the problem of measuring the total intensity of a vibration-rotation band consisting of a large number of separate fine lines is rather complicated. The problem is that bands having fine structure, not nearly always resolvable with ordinary apparatus, will give extrapolation curves with very large curvature at $l^* \approx 0$, thus considerably reducing the accuracy of the measurements. In order to obtain satisfactory accuracy, we would have to perform the measurements at impractically small values of l^*. Hence, Wilson and Wells suggested, on the basis of the example given by reference 66, that the fine structure of the band should be smeared out by addition of a non-absorbing foreign gas at some definite pressure (often many atmospheres) which can be determined by an additional special experiment.

Thus, the problem of determining the true values by the extrapolation relations must be solved in two stages for gases. In the first stage, the pressure of the foreign gas (with a given concentration of the absorbing gas) is selected such that the measured integrated intensity becomes practically independent of further increase in the pressure. Only after this, in the second stage, is the extrapolation procedure itself carried out by varying the value of l^* (ordinarily by varying the partial pressure of the gas being studied). In working with spectrometers of high resolution, often the smearing out of the fine structure by the described method will alone be sufficient for the determination of K_∞ from one or two measurements without recourse to detailed extrapolation.

The increase in the intensity of bands observed upon increasing the pressure is commonly attributed to the broadening of the individual lines of the fine structure. Now, the true integrated absorption coefficient of any component of the fine structure is larger than the observed value [cf. Eq. (2.15)]. Hence, as the pressure is increased, the individual lines of the vibration-rotation band will broaden and the effect of the instrument will diminish. Thus, the observed intensity must increase and approach the true value, up to the pressures at which the fine structure completely vanishes. Thus explanation of the role of the pressure is generally accepted at present, and in practice, it is the basis of the extrapolation methods discussed above for measurement of the intensity of infra-red absorption bands in gases.

Nevertheless, we cannot be satisfied with the assumption that the pressure only brings about a broadening of the bands without affecting the integrated intensity in any way. Thus, it was shown in references 67 and 68, in which very high pressures of various foreign gases were used, that the observed integrated intensity of the absorption bands continues to rise even when the fine structure has completely vanished. Further, in a number of cases,[69-71] the pressure increase brings about the appearance of pressure-induced absorption at the sites of the bands which are normally forbidden by the selection rules.

In other words, the method of measurement being discussed does not take into account the effect of the molecular collisions on the probabilities of energy transitions. We must keep this fact in mind in applying the extrapolation methods in practice.

b) The method of direct extrapolation. If we carry out the extrapolation procedure, as is often done in practice, not by varying the length l of the cuvette, but by changing the pressure p of a gas or the concentration c of a solution, the value of K_∞ determined may be distorted, in the general case, as a result of certain physical deviations from the Lambert-Bouguer Law. These deviations, namely the gas-pressure effect or the concentration-dependence of the absorption, have been little studied in themselves. Hence, we should give especial consideration to a method of eliminating the effect of the lack of monochromaticity in the determination of K_∞ by directly varying the quantity $\delta\nu$ itself, that is,

$$K_\infty = \frac{\lim\limits_{\delta\nu \to 0} D_\infty^0}{l^*} = \lim_{\delta\nu \to 0} \left(\frac{D_\infty^0}{l^*} \right). \qquad (2.18)$$

Ordinarily, this method is used to carry out an experimental verification[72] of some particular theoretical calculations. It is obvious that, in the case of gases having a marked rotational fine structure, this method may be applied only with instruments of high resolving power.

c) The method of direct integration. Up until now, we have discussed the determination of the true val-

ues of the integrated absorption coefficient K_∞ from the observed integrated optical density for bands of any arbitrary shape. For bands of regular shape, as a rule, such as are found in the condensed state of a substance, the problem can be simplified. On the basis of a theoretical analysis of the effect of finite slit-width, we can replace the rather cumbersome extrapolation technique by a simpler method of measurement. One of these methods is based on direct integration of the band expressed in terms of $D(\nu)$, the shape of the band being assumed to be known. For well-known reasons, the shape of $D(\nu)$ may be expressed by a dispersion function. Then [cf. Eq. (2.11)],

$$D_\infty = \int_0^\infty D(\nu)\, d\nu = \frac{\pi}{2} D_0 \Delta\nu_D = \varkappa D_0^0 \Delta\nu_D^0, \qquad (2.19)$$

where

$$\varkappa = \frac{\pi}{2} \frac{D_0}{D_0^0} \frac{\Delta\nu_D}{\Delta\nu_D^0}. \qquad (2.20)$$

Hence

$$K_\infty = \frac{\varkappa D_0^0 \Delta\nu_D^0}{l^*} \qquad (2.21)$$

and the problem of determining K_∞ is thus reduced to finding the observed values D_0^0 and $\Delta\nu_D^0$. Thus, we may limit ourselves to measuring the band contour from three points, without having to measure areas. This is sometimes very convenient for rapid but not very accurate intensity estimates. Values of the coefficient $\varkappa$ are tabulated in reference 55 for various values of the experimentally determined quantities D_0^0 and $\delta\nu/\Delta\nu_D^0$ (see the first method in reference 55), and may be determined from the results in reference 56 by the relation $\varkappa = r_0 D_\infty / D_\infty^0$ (see Table 2c in reference 56).

d) The correction method. The method of measuring three points, which leads to large errors in the results, is not very applicable to precise quantitative measurements of the intensities of infra-red absorption bands. Hence, for bands of regular shape, the most widespread method has been that of corrections. In this method, we may simply write

$$K_\infty = \psi \frac{D_\infty^0}{l^*}, \qquad (2.22)$$

where the correction factor ψ is calculated from theory based on certain assumptions on the shape of the absorption band and the instrumental parameters A number of papers[55,56,73-75] have been devoted to the solution of this problem.

Thus, in reference 55, the correction concerned here was calculated on the basis of the extrapolation relation of Wilson and Wells and the assumption that the true contour of the band in $D(\nu)$ has the form of the dispersion function. The theoretically-calculated form of the extrapolation curve permitted the derivation of the following expression for the correction factor ψ:

$$\psi = \frac{1}{1 - \Theta D_0^0},$$ (2.23)

where the values of the slope coefficient Θ are tabulated for various values of the ratio $\delta\nu/\Delta\nu_D$ (see the second method in reference 55). Here $\Delta\nu_D$ is the true width of the band in $D(\nu)$.

In reference 56, another method was used, based on the use of Voigt functions to fit the observed contours of the infra-red absorption bands. Here the values of the correction factor ψ, which is equal to the ratio D_∞/D_∞^0, are directly tabulated as functions of the experimentally-measured quantities D_0^0 and $\delta\nu/\Delta\nu_D^0$ (see Table 2 in reference 56). The latter paper discusses the problem of the quantitative agreement between the methods of making the corrections proposed by the various authors. In order to avoid the necessity of recalculating the contours by the transformation $R(\nu) \rightarrow D(\nu)$ in applying the correction method in practice, we may calculate the quantities D_∞^0 and $\Delta\nu_D^0$ directly from the corresponding values of R_∞ and $\Delta\nu_R^0$ obtained under the given conditions of measurement,[113] just as we may do in the previous methods.

Experimental verifications of the method have been carried out repeatedly. Thus, in references 55—58, as was noted, the basic assumption on which this method is based, the assumption that the true form of the band is a dispersion function, was confirmed for most of the investigated bands by direct measurement of their contours for liquids and solutions. A direct experimental check on the magnitude of the corrections calculated in reference 55 has been performed by Russell and Thompson,[72] using the above-mentioned extrapolation method, by narrowing the slit width (to 0.4 cm^{-1}) on prism and diffraction spectrometers. It was shown in another paper[76] that the results obtained by the computation method (Ramsay's third method) and the correction method (Ramsay's second method) agree within a precision of 2%, and differ from the results obtained by the method of direct integration (Ramsay's first method) by 5—10%. Undoubtedly, the data obtained from the results of measurements at three points of the contour are less reliable than those based on measurements along the entire band contour.

The discussed methods of determining the integrated intensities of infra-red absorption bands, comprising the fundamental methods commonly applied in practice in infra-red spectroscopy, are systematized in Table I. We must emphasize again that the extrapolation methods, as a rule, are used in studying the gaseous state of a substance, while the simpler computation and correction methods based on single measurements for bands of regular form are used in studying substances in condensed phases.

3. Other methods of determining K_∞. The other methods proposed by various authors for direct measurement of intensities in infra-red spectra are either approximate[77] or seldom-used[78-80] modifications of the methods discussed above, or they are complex, inconvenient, and not always applicable in practice (the method of curves of growth,[81] the method of correction of the observed contour,[82-83] etc.).

The integrated intensities of infra-red absorption bands may also be determined indirectly from the dispersion, the emissive power, or the reflectivity. We cannot consider these indirect methods as competing with the direct methods of measurement, but as supplementing them. Indeed, in studying the intense absorption bands of liquids or solids, we must work with very thin layers of the substance (as thin as several microns). The precise measurement of the thickness of these layers is always difficult, even when we use the interference method, since very small irregularities in the inside surfaces of the cuvette begin to play an appreciable role, as well as slight wedge-shaped forms of the layers, etc. Besides, when the cuvette is of thickness comparable with the wavelength of the infra-red radiation, multiple reflection and interference phenomena within the absorbing layer lead to considerable deviations from the Lambert-Bouguer Law.[84-85] Hence, the accuracy of these measurements is low, although the development of methods[87] permitting one to avoid these difficulties to some extent has recently begun.

However, it is just at the sites of the most intense absorption bands that the use of the direct methods involves great experimental difficulties. At these points, as is known, it is easiest to perform measurements of the dispersion, the reflectivity, or the emissivity, which are related in a definite manner to the absorbence of the substance. Thus, in reference 90 for the case of a liquid, the following relation was established between the dispersion of the refractive index in the infra-red and the integrated absorption coefficient:

$$n^2(\nu) - n_{vis}^2 = C \sum_i \frac{\bar{n}_i K_\infty^{(i)}}{\nu_i^2 - \nu^2},$$ (2.24)

where the summation is carried out over all the bands active in absorption. Here the ν_i are the characteristic frequencies of the vibrations, C is a normalizing factor, n_{vis} is the refractive index extrapolated from the visible region of the spectrum, and $\bar{n}_i$ is the "mean" refractive index, defined by:

$$\bar{n}_i = \frac{\int_i n(\nu) K_i(\nu) d\nu}{\int_i K_i(\nu) d\nu}.$$ (2.25)

For the case of a gas, $\bar{n}_i = 1$, and the equation is reduced to the well-known[88,89] Kramers dispersion relation. The technique of measuring the refractive index in the infra-red has become quite well developed at present.[91-93]

The numerical values of the absorption coefficients

can also be determined from the thermal radiation spectrum.[94-96] This problem has also been studied recently in more detail in reference 97. The problems of reflection spectroscopy have been quite fully discussed in references 86, 98, and 99.

6. The Accuracy of Measurement of the Intensities of Infra-red Absorption Bands

The intensity of an infra-red absorption band is a parameter affected by a large number of highly varied distorting factors. The ways of taking into account the basic factor, the lack of monochromaticity of the radiation, have been discussed above. In the general case, the systematic distortions occurring in the measurement of the intensities of infra-red bands may be divided into: 1) instrumental distortions due to the non-monochromatic radiation and the lag in the recording apparatus; 2) systematic errors in measuring the areas of the bands, due to the finiteness of the interval of integration; and 3) systematic distortions which arise in certain special studies (e.g., in temperature measurements: the effect of the thermal-radiation background;[97] in studies with very thin layers of material: multiple reflections,[84] etc.). Distortions of the latter type and systematic errors which are not general in nature will not be discussed here.

The problems of accuracy of measurement also involve the problems of selecting the optimum conditions of measurement so as to minimize the accidental errors.[113]

In precise quantitative intensity measurements, we must above all eliminate or take into account the instrumental distortions. A rather large number of studies has been devoted to the analysis of these distortions. We shall refer to the specialized literature [55-57,73-75,100-105,112] for the details, and mention only the basic results.

In its general form, the distorting effect of the instrument on the form of a spectral line may be described by an equation of the form

$$R_0(\nu) = \int_0^\infty f(\nu - \nu') R(\nu') d\nu', \qquad (2.26)$$

relating the distribution function of the observed absorption band $R_0(\nu)$ with that of the true contour $R(\nu')$ by means of the so-called apparatus function (also termed the "slit" or "transmission" function) $f(\nu - \nu')$. By definition, this function is the output function generated when the input signal is a δ-function.[104,105] With appropriate forms of the apparatus function, Eq. (2.26) is equally applicable to the description of the effects on the form of a spectral line of both the optical system of the monochromator and the recording system of the spectrometer.

According to the theoretical analysis of the subject,[51,52,55-57,73-75,101-105] the effective influence of the apparatus function of the monochromator on the in-

tensities of infra-red absorption bands is determined by the width of the apparatus function (effective slit-width) $\delta\nu$ and the width of the absorption band $\Delta\nu$, and depends as well on the magnitude of the absorption D_0 at the band maximum.

When the ratio $\delta\nu/\Delta\nu$ is large, we must take into account the lack of monochromaticity of the radiation by introducing corrections or performing an extrapolation (see Sec. 5). According to current recommended practice,[101] $\delta\nu$ must be determined experimentally in the wavelength range below 2μ by measurement of the mercury emission lines (a very narrow helium line was used for this purpose in reference 75). In the range $> 2\mu$, $\delta\nu$ may be determined by approximation formulas[55,57,106,107] taking into account the dispersion of the apparatus, the aberrations, and diffraction phenomena.

As the analysis of the subject has shown,[108-111] the effect of the apparatus function of the detecting and recording apparatus on the intensity of an infra-red absorption band is determined by the relation between the time constant δt defining the lag in the recording of the spectrum and the bandwidth in terms of time Δt, that is, the time taken to traverse the half-width of the band. The ratio $\delta t/\Delta t$ plays the same role here as the quantity $\delta\nu/\Delta\nu$ does in the distortion of the spectrum due to non-monochromatic radiation.

Since $\Delta t = \Delta\nu/v$, the problem of taking into account the instrumental distortions of the recording system is often reduced to selecting a recording speed v of the spectrum such that the effect of lag may be eliminated in effect, without the necessity of introducing corrections and other like procedures. We may estimate whether lag distortions have been eliminated from the shape of the contour of a recorded spectral line by the rule: there must be no fewer than ten noise maxima within the width of the band.[101] Thus, the scanning speed v and the instrumental time constant δt must be chosen such that their product $v\delta t$ is at least an order of magnitude less than the band width $\Delta\nu$, in order to eliminate instrumental distortions.

In measuring the integrated intensity of infra-red absorption bands, we often have to make use of all sorts of truncations of the observed band contour. This fact may have a considerable effect on the results of the measurements. The simplest case of the truncation of a band contour is neglect of the "skirts" in measuring its area. The correction for the "skirts" for a band having the form of a dispersion function has been calculated in reference 55, and for a Gaussian band in reference 110. The correction considered in reference 113 was calculated for an observed band form described by Voigt functions, and having a form intermediate between the Gaussian and dispersion distributions. The latter correction is presented in a convenient form for practical use.

In infra-red spectroscopy, and especially in the study of complex polyatomic molecules, cases often occur in which a given band overlaps the skirts of neighboring closely-spaced bands which cannot be separated from it graphically, or the band may be superimposed on some background of continuous absorption due essentially to scattered radiation. Besides, it is sometimes technically difficult for a number of reasons to select a comparison cuvette so that its transmission in the spectral range being studied may give the desired 100%-transmission level (for double-beam instruments), or the source level I_0 (for single-beam instruments). For some reason or another, it is often difficult in performing the measurements to determine the exact position of the base line of the band, as is necessary to determine its area.

Bearing in mind these difficulties, such as actually occur in the measurement of the integrated intensity of bands, a truncation method has been developed in reference 113 (in accordance with reference 114) as a means of establishing the correct parameters of bands in the spectra of polyatomic molecules.

In reference 113, the corrections were calculated for a type of truncation such that the background line is drawn between the farthest observable points of the band, truncating its base. The calculations were performed for various band forms expressible by Voigt functions for various relative truncation limits down to twice the half-width. The values of the corrections are tabulated directly as functions of experimentally-determined quantities.

7. The Absolute Intensities in the Infra-red Spectra of Molecules

According to the general ideas presented in Sec. 1, the intensity of any absorption band is proportional to the number n of absorbing molecules per unit volume of the substance. The integrated absorption coefficient calculated per molecules of substance is generally called the absolute intensity of the given band:

$$A = \frac{K_\infty}{n}. \tag{2.27}$$

For a long time, one of the factors hindering the performance of these intensity measurements was the lack of a single generally-accepted scale of absolute intensities. This fact hindered and sometimes rendered impossible the comparison of experimental results obtained by different authors. In consideration of this, the International Commission on Molecular Spectroscopy, created at the initiative of the IUPAC (International Union of Pure and Applied Chemistry), recommended definite units for the absolute intensities of infra-red absorption bands in a special resolution.[115] The absolute unit was taken to be the quantity $A = (1/nl)\int \ln (I_0/I)\,d\nu$, which has the dimensions of $cm^2 \cdot molecule^{-1} \cdot sec^{-1}$.

Table II gives the units most often used by various authors for measurements of absolute intensity, and the appropriate conversion factors are given.*

We must make the following remarks concerning the units of measurement given in the table. The unit $[cm^{-2} \cdot mole^{-1} \cdot liter]$ is denoted in the terminology of reference 115 as the practical unit, is most often used in research on solutions, and is symbolized here by B. This unit is identical with the so-called unit "darks", which has the dimensions $[cm \cdot millimole^{-1}]$, and is used primarily in the foreign literature. The units having the dimensions $[cm^{-2} \cdot atm^{-1}]$, $[cm^{-1} \cdot atm^{-1}]$, and $[cm^{-1} \cdot sec^{-1} \cdot atm^{-1}]$ are used in gas studies as a rule. The unit $[cm^2 \cdot molecule^{-1}]$ is denoted as the Q unit in the terminology of reference 115, or as the Crawford unit in the foreign literature, with the symbol Γ; it is very convenient in a number of theoretical studies. The Crawford intensity[116-118]

$$\Gamma = \frac{1}{nl^*} \int D(\nu)\,d\ln\nu$$

is related to A by the simple relation

$$\Gamma = \frac{A}{\nu}. \tag{2.28}$$

Strictly speaking, Eq. (2.28) is an approximation, but in practice it is obeyed to a sufficient degree of accuracy. One must take this point into account in using Table II.

The absolute intensities of infra-red absorption bands having dimensions given in Table II are simply related by Eq. (2.27) to the experimentally-determined integrated absorption coefficient K_∞, which is ordinarily expressed in units of $[cm^{-2}]$ or $[cm^{-1}sec^{-1}]$. Indeed, for a liquid, $n = N\rho/M$, and hence

$$A \left[\frac{cm^2}{molecule \cdot sec} \right] = K [\ cm^{-2}] \frac{cM}{N\rho},$$

where c is the velocity of light, M is the molecular weight, ρ is the density of the liquid, and N is Avogadro's number. For solutions, $n = C_M N = C_V(N\rho/M)$, and hence,†

$$A \left[\frac{cm^2}{molecule \cdot sec} \right] = K_\infty [cm^{-2}] \frac{cM}{C_v N\rho},$$

where C_M is the molar concentration, or number of moles of the substance being studied per unit volume of solution, and C_V is the volume concentration.

*Translator's note: The authors have neglected to state that the frequency ν has the dimensions of sec^{-1} in the definitions of the units A, A', and β, and cm^{-1} in the other defined intensity units. Further, the Q unit, which in the original literature has the units $[cm^2 \cdot molecule^{-1}]$, is treated inconsistently by the authors as having these units at times, and as having units $[cm^2 \cdot mole^{-1}]$ at other times. The procedure followed here in translation is to express the Q unit always in $[cm^2 \cdot molecule^{-1}]$ in the body of the text, making corrections where necessary, but in $[cm^2 \cdot mole^{-1}]$ in Table II in accordance with the tabulated values.

†In the approximation in which the volumes of the initial components are additive.

Table II. Conversion factors between the units of measurement of the absolute intensities of infra-red absorption bands

Dimensions of the units of measurement		Absolute unit, cm²·molecule⁻¹·sec⁻¹	The unit cm²·mole⁻¹·sec⁻¹	The unit "darks", cm·millimole⁻¹	The practical unit, cm⁻²·mole⁻¹·liter	The Q-(or Γ-) unit, cm²·mole⁻¹	The unit cm⁻¹·atm⁻¹	The unit cm⁻²·atm⁻¹	The unit cm⁻¹·sec⁻¹·atm⁻¹
		A	A'	D	B	Γ	g	α	β
Absolute unit, cm²·molecule⁻¹·sec⁻¹	A	1	$1.66 \cdot 10^{-24}$	$4.98 \cdot 10^{-11}$	$4.98 \cdot 10^{-11}$	$4.98 \cdot 10^{-14} \cdot \nu$ cm⁻¹	$1.12 \cdot 10^{-9} \cdot \nu$ cm⁻¹	$1.12 \cdot 10^{-9}$	$3.73 \cdot 10^{-20}$
The unit cm²·mole⁻¹·sec⁻¹	A'	$6.02 \cdot 10^{23}$	1	$2.99 \cdot 10^{13}$	$2.99 \cdot 10^{13}$	$2.99 \cdot 10^{10} \cdot \nu$ cm⁻¹	$6.75 \cdot 10^{14} \cdot \nu$ cm⁻¹	$6.75 \cdot 10^{14}$	$2.24 \cdot 10^{4}$
The unit "darks", cm·millimole⁻¹	D	$2.01 \cdot 10^{10}$	$3.34 \cdot 10^{-14}$	1	1	$1.00 \cdot 10^{-3} \cdot \nu$ cm⁻¹	$22.4 \cdot \nu$ cm⁻¹	22.4	$7.50 \cdot 10^{-10}$
The practical unit, cm⁻² mole⁻¹·liter	B	$2.01 \cdot 10^{10}$	$3.34 \cdot 10^{-14}$	1	1	$1.00 \cdot 10^{-3} \cdot \nu$ cm⁻¹	$22.4 \cdot \nu$ cm⁻¹	22.4	$7.50 \cdot 10^{-10}$
The Q-(or Γ-) unit, cm²·mole⁻¹	Γ	$2.01 \cdot 10^{13} \cdot \nu^{-1}$ cm⁻¹	$3.34 \cdot 10^{-11} \cdot \nu^{-1}$ cm⁻¹	$1.00 \cdot 10^{3} \cdot \nu^{-1}$ cm⁻¹	$1.00 \cdot 10^{3} \nu^{-1}$ cm⁻¹	1	$2.24 \cdot 10^{4}$	$2.24 \cdot 10^{4} \cdot \nu^{-1}$ cm⁻¹	$7.50 \cdot 10^{-7} \cdot \nu^{-1}$ cm⁻¹
The unit cm⁻¹·atm⁻¹	g	$8.95 \cdot 10^{9} \cdot \nu^{-1}$ cm⁻¹	$1.48 \cdot 10^{-15} \cdot \nu^{-1}$ cm⁻¹	$4.46 \cdot 10^{-2} \cdot \nu^{-1}$ cm⁻¹	$4.46 \cdot 10^{-2} \nu^{-1}$ cm⁻¹	$4.46 \cdot 10^{-5}$	1	ν^{-1} cm⁻¹	$3.34 \cdot 10^{-11} \cdot \nu^{-1}$ cm⁻¹
The unit cm⁻²·atm⁻¹	α	$8.95 \cdot 10^{8}$	$1.48 \cdot 10^{-15}$	$4.46 \cdot 10^{-2}$	$4.46 \cdot 10^{-2}$	$4.46 \cdot 10^{-5} \cdot \nu$ cm⁻¹	ν cm⁻¹	1	$3.34 \cdot 10^{-11}$
The unit cm⁻¹·sec⁻¹·atm⁻¹	β	$2.68 \cdot 10^{19}$	$4.46 \cdot 10^{-5}$	$1.33 \cdot 10^{9}$	$1.33 \cdot 10^{9}$	$1.33 \cdot 10^{6} \cdot \nu$ cm⁻¹	$2.99 \cdot 10^{10} \nu$ cm⁻¹	$2.99 \cdot 10^{10}$	1

For gases, n = Np/RT, and hence,

$$A\left[\frac{cm^2}{molecule \cdot sec}\right] = K_\infty\,[cm^2]\,\frac{cRT}{Np}\ ,$$

where R is the gas constant, T is the absolute temperature, and p is the gas pressure.

In spite of the complexity of the experimental technique, the absolute intensities in the infra-red spectra of a large number of molecules have already been measured. Basically, the simplest molecules in the gas phase have been studied in order to calculate the values of the electro-optic parameters of the molecules on the basis of the absolute-intensity data.

Owing to the lack of standards in this region of measurements, it is rather difficult at present to judge the true accuracy of the results of different authors. The estimates which they have made of the accuracy of the absolute-intensity measurements (about 10—20% on the average) are somewhat conditional, since the error in A is determined by a large number of highly varied factors. We can get an objective estimate of the accuracy of the measurements in this case only by comparing the results of different authors for the same substances.

The experimental absolute-intensity data of a number of simple molecules in the gas phase, which have been scattered through a large number of separate papers, have been systematized in Table 3 of the Appendix. The quantitative results, which have been expressed by different authors in different systems of units (shown in column 6) have been reduced to a single absolute scale with the dimensions [cm²/molecule-sec]. The method of measurement is given in column 5 to characterize the results more fully. Finally, in view of possible deviations from the Lambert-Bouguer Law due to the effect of pressure, we have deemed it useful to give in the table information on the pressures at which the measurements were performed (asterisks denote pressures expressed in psig units). Since the discrepancies between the results of different authors often exceed their estimated errors of measurement, Table 3 of the Appendix gives as full as possible a presentation of the results obtained by different authors for the same bands, so as to give an objective characterization of the accuracy of the measurements (the most doubtful data are indicated with question marks). We must make the reservation that the amount of absorption for a condensed phase is larger than in the gas phase, even when the probability of the corresponding transition does not change. This is due to the change in the field intensity of the light wave upon going to a denser medium. Since we cannot go into the details of this important problem, we refer the reader to the study of Neporent and Bakhshiev,[118] where a rather complete bibliography is also given.

We must note in conclusion that the problems of calculation and experimental determination of the intensities of infra-red absorption bands are in a state of development. The importance of their further progress is dictated by the vast possibilities which infra-red spectroscopy possesses in the study of the structure and properties of molecules and for analytical purposes. Undoubtedly, these pressing problems of molecular spectroscopy will receive much attention in the coming years.

APPENDIX

Table 1. The moments and effective charges of certain bonds, as determined from the absolute intensities of infra-red absorption bands in the zero-order approximation of the valence optical theory

Molecule	Dipole moment μ (in D)		Reference	Effective charge $\partial\mu/\partial r$ (in D/A)		Reference
1. The C–H bond						
Methane CH_4		0.3	77		0.6	77
		0.4	108			
Ethane C_2H_6		0.3	107	For class A_{2u}	1.24	70
		0.3	70	For class E_u	0.75	70
Ethylene C_2H_4	For vibrations ⊥ C = C	0.77	107			
	For vibrations ‖ C = C	0.52	107			
	For out-of-plane vibrations	0.37	107			
Acetylene C_2H_2	From deformation vibrations	1.0	46	From valence-bond vibrations	0.52	46
	Ditto	1.05	22	Ditto	0.87	22
	,,	1.0	102	,,	1.6	18
HCN	,,	1.13	37	,,	1.05	37
CH_3F	From valence-bond vibrations	0.4	4	,,	1.4 or 2.2	4
	From deformation vibrations	0.3	4	From deformation vibrations	0.4–0.8	4
CH_3Cl	For class A_1	0.15	19	For class A_1	1.0	19
	For class E	0.41–0.37	19	For class E	0.24	19
CH_2Cl_2		0.45	93		0.2 or 0.3	93
CHF_3		0.15	67		0.3	67
$CHCl_3$		0.6	67		0.03	67
Benzene C_6H_6	In plane of the ring	0.31	90	In plane of the ring	0.45	90
	For out-of-plane vibrations	0.61	90			
	Mean value	0.42	7			
CH_3I	For class A_1	0.43–0.52	4	For class A_1	0.92–0.99	4
	For class A_1	0.38	19	For class A_1	0.73	19
	For class E	0.32	4	For class E	0.02–0.23	4
	For class E	0.39–0.42	19	For class E	0.13	19
CH_3D, CD_3H, CH_2D_2		0.33	32		0.61	32
CH_3Br	For class A_1	0.25	19	For class A_1	0.98	19
	For class E	0.34–0.44	19	For class E	0.19	19
CH_2I_2	For class B_1	0.5	88		0.2	88
	For class B_2	0.86	88			
H_2CO		0.5	34		1.3	34
2. The C–F bond						
CH_3F	From deformation vibrations	1.5	4	From valence-bond vibrations	4.0	4
CH_2F_2	For class A_1	0.7 or 1.8	63		5.7 or 6.2	63
	For class B_2	1.0 or 1.8	63			
CHF_3		2.8	67		4.5	67
CF_4		2.4	60			
		1.1 or 2.4	85		3.4 or 4.9	85
C_2F_6	For class A_{2u}	2.2	63	For class A_{2u}	3.4	63
	For class E_u	0.7 or 1.6	63	For class E_u	3.8	63
3. The C–Cl bond						
CH_3Cl	From deformation vibrations	1.5	4	For class A_1	2.3	4
				For class A_1	2.24	19
CH_2Cl_2		0.95	93		3.7	93
Chloroform $CHCl_3$		0.4	67		4.2	67
Phosgene Cl_2CO		2.9	53		8.1	53
Thiophosgene Cl_2CS		0.39	53		4.21	53

Table 1 (continued)

Molecule	Dipole moment μ (in D)		Reference	Effective charge $\partial\mu/\partial r$ (in D/Å)		Reference
				4. The C—Br bond		
CH₃Br	From deformation vibrations	1.4	4	From valence-bond vibrations	1.6—2.0	4
				Ditto (class A₁)	1.5	19
CH₂Br₂		0.7	88		3.3	88
				5. The C—I bond		
CH₃I	From deformation vibrations	1.2	4	From valence-bond vibrations	0.44 or 1.05	4
				Ditto (class A₁)	0.64	19
CH₂I₂		0	88		2.1	88
				6. The C—D bond		
C₂D₂		0.89	22		0.785	22
		0.94	102			
				7. The C=O bond		
CO		0.1	74		3.14	74
CO₂		1.1	21		6.0	107
					5.8	120
					5.85	21
OCS	From deformation vibrations	0.63	101	From valence-bond vibrations	8.55	18
				Ditto	6.7	76
Phosgene Cl₂CO		3.91	53		4.08	53
Formaldehyde H₂CO	For class B₁	1.9	34		1.9	34
				8. The C=S bond		
OCS	From deformation vibrations	0.09	101	From valence-bond vibrations	5.9	18
				Ditto	4.3	76
CS₂		1.24	24		5.9	61
		1.16	82		5.6	78
					5.7	47
Thiophosgene Cl₂CS		0.70	53		3.54	53
				9. The C ≡ N bond		
HCN		1.8	37		0.66	37
C₂N₂		1.2	65		0.72	69
				10. The N=O bond		
NO		0.1	75		1.7	75
N₂O		0.7	108		6.5	18
				11. The S=O bond		
SO₂		0.27 or 1.53	22		2.03 or 3.30	22
				12. The B—F bond		
BF₃	For class A₂″	1.7	60	For class E′	4.0 or 6.1	60
	For class E′	2.6 or 0.9	60			

Table 2. The characteristic intensities of infra-red absorption bands of certain functional atomic groups (determinations in CS_2 solution marked*)

1. Functional group $C \equiv N$

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
Acetonitrile	2267	2,10	[89]	4-Cyanopyridine	2240	2.39	[26]
	2267	2,11	[6]	Ethylcyanide	2247	2.40	[89]
	2267	3,04	[26]	n-Propylcyanide	2250	2,50	[89]
	2267	2,49*	[6]				
Trichloro-acetonitrile	2249	3,15	[106]	n-Pentylcyanide	2251	3.20	[89]
	2249	3,20	[38]		2251	3,26	[106]
Phenylaceto-nitrile	2251	2,50	[89]	Benzonitrile	2232	4,20	
					2232	8,60	[57]
Acrylonitrile	2232	3,24	[26]		2232	9,64	[6]
Propionitrile	2262	3,18	[6]		2232	9,96	[13]
	2262	2.94*	[6]		2232	10.7	[26]
Phthalonitrile	2244	4.82	[6]		2232	8.03*	[6]
	2244	4,36	[6]	Acetylcyanide	2221	14,2	[26]

2. Functional group $C = O$

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
Acetone	1717	77.3	[2]	Benzophenone	1668	104	[1]
	1717	79,7	[5]		1668	110	[2]
	1717	82,0	[104]		1668	104*	[1]
	1717	83.0	[28]	Propiophenone	1694	108	[66]
	1717	86.0	[103]	Methyl acetate	1750	110	[2]
	1717	75.0*	[104]		1750	128	[28]
Diethyl ketone	1727	77,3	[2]		1750	125*	[78]
Butanone	1720	84,0	[28]	Ethyl acetate	1750	129	[2]
Benzaldehyde	1710	105	[2]		1750	149	[28]
	1710	106	[105]		1750	165*	[78]
	1710	132	[50]	Methyl propionate	1700	129	[28]
Acetophenone	1692	105	[2]	Methyl formate	1700	148	[78]
	1692	108	[66]	Methyl carbonate	1763	189	[2]
	1692	110	[39]				

3. Functional group $S - H$

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
Ethyl mercaptan	2570	1,15	[91]	Butanethiol	2570	1.74	[91]
Thiophenol	2570	1,89	[91]	2-Methylpropane-2-thiol	2570	1.79	[91]
Propane-1-thiol	2570	1,64	[91]				

4. Functional group $O - H$

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
Methanol	3644	16,6	[109]	Propargyl alcohol	3600	34.3	[14]
	3644	26.4	[3]				
	3644	26,9	[14]	Trans-dihydrocryptol	3621	23,2	[17]
Ethanol	3634	30,9	[3]				
Cyclopentanol	3600	24,9	[14]	Tricyclopropyl carbinol	3620	18.5	[15]
Cyclohexanol	3600	21,9	[14]				
n-Propyl alcohol	3640	22.8	[29]	Diphenylamine	3434	22.5	[80]
	3640	25,9	[14]	Phenol	3609	49.3	[12]
Allyl alcohol	3600	28,9	[14]		3609	59.8	[3]
Benzyl alcohol	3600	32,8	[14]		3609	63,3	[109]

5. Functional group NH_2

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
Aniline (symmetric vibrations)	3395	3,5	[58]	Para-chloro-aniline (symmetric vibrations)	3390	19,1	[16]
	3395	14,1	[49]				
	3395	16,1	[16]				
	3395	14.8*	[49]				
Aniline (antisymmetric vibrations)	3478	3.6	[58]	Para-chloro-aniline (antisymmetric vibrations)	3470	18.6	[16]
	3478	14.5	[49]				
	3478	18.7	[16]				
	3478	14.3*	[49]				

6. Functional group CH_3

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
Aliphatic hydrocarbons	2900	44,1	[27, 28]	Ketones	2900	7,40	[27, 28]
	1460	5,44	[27, 28]		1460	13,1	[27, 29]
	1460	6,38	[54]		1370	19,4	[27, 28]
	1370	3,94	[27, 28]	Ethers	2900	25,4	[27, 28]
	1370	2.49	[54]		1460	20,0	[27, 28]

Table 2 (continued)

Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference	Substance	Vibration frequency (in cm⁻¹)	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Reference
7. Functional group CH₂							
Aliphatic hydrocarbons	2900	38.1	[27, 28]	Ketones	2900	4.80	[27, 28]
	1460	2.17	[54]		1460	11.7	[27, 28]
	1460	2.32	[27, 28]		1370	8.30	[27, 28]
	720	0.604*	[54]				
	720	0.593*	[56]				
8. Functional group C—H							
Aliphatic hydrocarbons	2900	13.9	[27, 28]				

Table 3. Absolute intensities of the infra-red absorption bands of certain simple molecules in the gas state

Molecule	Band position (in cm⁻¹) and form of vibration	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Total pressure (in atm)	Method of measurement	Units of absolute-intensity measurement used by the authors	Reference
1. Diatomic molecules (symmetry C∞v)						
CO	2144	26.6	700*	extrapolation	α	[74]
	2144	26.8			α	[94]
NO	1883	7.06	700*	extrapolation	α	[75]
	1883	8.40			α	[94]
HCl	2887	15.0			α	[8]
	2887	17.5		extrapolation	α	[10]
	2887	17.9	1500*	,,	α	[74]
HBr	2500	6.16	700*	extrapolation ,,	α	[74]
BrCl	440	0.52	1,6—8	,,	D	[11]
ICl	382	3.24	1	,,	D	[11]
2. Triatomic molecules						
OCS (symm., C∞v)	521v₂	1.34	30*	extrapolation	β	[101]
	859v₁A₁	4.11	1	,,	β	[76]
	859	13.0	2	,,	β	[18]
	2070v₃E	295	1	,,	β	[76]
	2070	481	2	,,	β	[18]
HCN (symm., C∞v)	712v₂	22.9		,,	α	[37]
	2089v₁(CN)	0.075		,,	α	[37]
	3312v₃(CH)	27.0		,,	α	[37]
DCN (symm., C∞v)	569v₂	6.83		,,	α	[37]
	1921v₁(CN)	1.33		,,	α	[37]
	2629v₃(CD)	15.2		,,	α	[37]
ClCN (symm., C∞v)	714v₂	0.635		,,	β	[69]
	2214v₁(CN)	8.20		,,	β	[69]
CO₂ (symm., D∞h)	670	18.0	2	,,	β	[21]
	670	19.0		,,	α	[95]
	670	20.9		,,	α	[107]
	670	24.6		,,	α	[44]
	670	27.0	68	,,	α	[72]
	670	20.1		from dispersion	α	[25]
	670	26.9	1.25	from the	α	[45]
	2350	301	2	curve of growth	α	[21]
	2350	320		growth	β	[107]
	2350	286		extrapolation ,, ,,	α	[25]
CSe₂ (symm., D∞h)	1523v₃(CS)	282	1	from dispersion	β	[76]
	1523	278		extrapolation	β	[47]
	1523	287	1		β	[61]
CSi₂ (symm., D∞h)	1303v₃	141	1	,,		[99]

Table 3 (continued)

Molecule	Band position (in cm^{-1}) and form of vibration	Absolute intensity $A \times 10^6$ (in cm^2/molecule-sec)	Total pressure (in atm)	Method of measurement	Units of absolute-intensity measurement used by the authors	Reference
N_2O (symm., $D_{\infty h}$)	589	2.33 (?)	1	extrapolation	β	21
	589	4.47		,,	β	108
	589	4.03		from dispersion	β	25
	1285	27.4	1	extrapolation	β	21
	1285	42.9 (?)		,,	β	108
	1285	29.9		from dispersion		25
	2225	181	3	extrapolation	β	21
	2225	184	1	,,	β	18
	2225	209		,,	β	108
	2225	171		from dispersion		25
SO_2 (symm., C_{2v})	519v_2	9.58 (?)	100*	extrapolation	β	22
	519	13.4		,,	β	68
	519	14.0	1—3	,,	β	59
	519	13.0	200*		β	23
	1151v_1	8.43 (?)	100*	,,	β	22
	1151	13.0		,,	β	68
	1151	11.8	1—3	,,	β	59
	1151	10.4	200*	,,	β	23
	1361v_3	59.9 (?)	100*	,,	β	22
	1361	98.5		,,	β	68
	1361	95.4	1—3	,,	β	59
	1361	94.0	200*		β	23

3. Tetratomic molecules (of C_{3v} symmetry)

Molecule	Band position	Absolute intensity	Total pressure	Method	Units	Ref.
NH_3	950v_2A_1	67.2	34	extrapolation	α	62
	1627v_4E	12.3	34	,,	α	62
	3337v_1A_1	2.24	34	,,	α	62
	3448v_3E	1.46	34	,,	α	62
PH_3	992v_2A_1	9.19		,,	α	62
	1122v_4E	11.4		,,	α	62
	2323v_1A_1	29.1		,,	α	62
	2328v_3E	29.1		,,	α	62
NF_3	492	0.677	1	,,	g	86
	642	0.769	1	,,	g	86
	906	199	1		g	86
	1032	14.8	1	,,	g	86
BF_3 (D_{3h})	718v_2A	29.8	500*	,,	α	60
	1504v_3E	296	1	,,	α	60
	482v_4	8.68	1	,,	α	60

4. Methane and its derivatives

Molecule	Band position	Absolute intensity	Total pressure	Method	Units	Ref.
CH_4 (symm., T_d)	1305v_4	16.6		from dispersion	β	77
	1305	16.8		extrapolation	β	107
	1305	17.6	300	,,	β	98
	3020v_3(CH)	36.2		from dispersion	β	77
	3020	33.6		,,	β	107
	3020	40.1	600	extrapolation	β	97
CD_3H (symm., C_{3v})	1300v_5	3.33		,,	β	32
	3000v_1(CH)	7.83		,,	β	32
CH_3D (symm., C_{3v})	2200v_1(CD)	3.13		,,	β	32
CF_4 (symm., T_d)	633v_4F_2	4.67	1	,,	α	85
	1267v_3F_2	509	1	,,	α	85
SiF_4 (symm., T_d)	391v_4F_2	56.8	1	,,	α	85
	1031v_3F_2	295	1	,,	α	85
CH_3F (symm., C_{3v})	1050v_3A_1	54.1		,,	β	4
	1200v_6E	0.86		,,	β	4
	1468v_2A_1	1.68		,,	β	4
	1470v_5E	2.98		,,	β	4
	2863v_1A_1	18.6		,,	β	4
	2967v_4E	18.6		,,	β	4

Table 3 (continued)

Molecule	Band position (in cm⁻¹) and form of vibration	Absolute intensity $A \times 10^5$ (in cm²/molecule-sec)	Total pressure (in atm)	Method of measurement	Units of absolute-intensity measurement used by the authors	Reference
CH₃Cl (symm., C_{3v})	732v_3A_1	10.4		extrapolation	β	4
	732	11.5	80	,,	Γ	19
	1015v_6E	2.00	80	,,	Γ	19
	1015	2.09		,,	β	4
	1355v_2A_1	4.48		,,	β	4
	1355	3.39	80	,,	Γ	19
	1455v_5E	6.13	80	,,	Γ	19
	1455	4.85		,,	β	4
	2966v_1A_1	10.1		,,	β	4
	2966	8.74	80	,,	Γ	19
	3042v_4E	4.83	80	,,	Γ	19
	3042	4.85		,,	β	4
CH₃J (symm., C_{3v})	533v_3A_1	0.97		,,	β	4
	533	0.96	80	,,	Γ	19
	880v_6E	4.43	80	,,	Γ	19
	880	4.00		,,	β	4
	1252v_2A_1	12.0		,,	β	4
	1252	10.3	80	,,	Γ	19
	1440v_5E	5.28	80	,,	Γ	19
	1440	4.11		,,	β	4
	2970v_1A_1	5.97		,,	β	4
	2970	5.49	80	,,	Γ	19
	3060v_4E	1.07	80	,,	Γ	19
	3060	1.01		,,	β	4
CH₃Br (symm., C_{3v})	611v_3A_1	5.41		,,	β	4
	611	4.31	80	,,	Γ	19
	952v_6E	3.57	80	,,	Γ	19
	952	2.98		,,	β	4
	1305v_2A_1	8.21		,,	β	4
	1305	6.96	80	,,	Γ	19
	1445v_5E	5.97	80	,,	Γ	19
	1445	4.85		,,	β	4
	2972v_1A_1	8.40		,,	β	4
	2972	8.00	80	,,	Γ	19
	3056v_4E	2.28	80	,,	Γ	19
	3056	2.05		,,	β	4
CD₃Cl (symm., C_{3v})	695v_3A_1	7.65	80	,,	Γ	19
	775v_6E	0.55	80	,,	Γ	19
	1029v_2A_1	5.36	80	,,	Γ	19
	1058v_5E	3.45	80	,,	Γ	19
	2161v_1A_1	5.67	80	,,	Γ	19
	2286v_4E	2.55	80	,,	Γ	19
CD₃I (symm., C_{3v})	501v_3A_1	0.49	80	,,	Γ	19
	660v_6E	1.59	80	,,	Γ	19
	2155v_1A_1	3.03	80	,,	Γ	19
	2300v_4E	0.344	80	,,	Γ	19
CD₃Br (symm., C_{3v})	578v_3A_1	3.36	80	,,	Γ	19
	712v_6E	1.00	80	,,	Γ	19
	933v_2A_1	5.62	80	,,	Γ	19
	1056v_5E	3.52	80	,,	Γ	19
	2157v_1A_1	4.34	80	,,	Γ	19
	2293v_4E	1.07	80	,,	Γ	19
CH₂Cl₂ (symm., C_{2v})	742v_8	53.0	100*	,,	β	93
	898v_7	0.485	100*	,,	β	93
	1262v_9	14.0	100*	,,	β	93
	3048v_6(CH)	1.78	100*	,,	β	93
CH₂I₂ (symm., C_{2v})	573v_8	17.6	1	,,	β	88
	717v_7	2.91	1	,,	β	88
	1106v_9	41.3	1	,,	β	88
	3049v_6(CH)	1.39	1	,,	β	88
CH₂Br₂ (symm., C_{2v})	636v_8	37.4	1	,,	β	88
	814v_7	1.80	1	,,	β	88
	1189v_9	23.0	1	,,	β	88
	3040v_6	0.544	1	,,	β	88
CHF₃ (symm., C_{3v})	508v_6E	2.57	1	,,	β	67
	700v_3A_1	7.46	1	,,	β	67
	1150v_2A_1,v_5E	429	1	,,	β	67
	1377v_4E	48.5	1	,,	β	67
	3035v_1A_1	17.6	1	,,	β	67
CHCl₃ (symm., C_{3v})	681v_2A_1	2.98	1	,,	β	67
	769v_5E	134	1	,,	β	67
	1221v_4E	20 9	1	,,	β	67
	3034v_1A_1	0.22	1	,,	β	67

Table 3 (continued)

Molecule	Band position (in cm⁻¹) and form of vibration	Absolute intensity A × 10⁶ (in cm²/molecule-sec)	Total pressure (in atm)	Method of measurement	Units of absolute-intensity measurement used by the authors	Reference
5. Ethane and its derivatives (symmetry D_{3d})						
C_2H_6	$822\nu_9 E_u$	2.72	50	extrapolation	Γ	107
	822	3,04	50	,,		70
	$1379\nu_6 A_{2u}$	1.99	50	,,	Γ	70
	$1472\nu_8 E_u$	6.67	50	,,	Γ	70
	$2915\nu_5 A_{2u}$	23.8	50	,,	Γ	70
	$2996\nu_7 E_u$	61.3	50	,,	Γ	70
C_2D_6	$594\nu_9 E_u$	1.65	50	,,	Γ	70
	$1077\nu_6 A_{2u}$	1.45	50	,,	Γ	70
	$1082\nu_8 E_u$	4.54	50	,,	Γ	70
	$2095\nu_5 A_{2u}$	12.1	50	,,	Γ	70
	$2236\nu_7 E_u$	32,0	50	,,	Γ	70
C_2F_6	$219\nu_9 E_u$	2.14	1	,,	D	63
	$522\nu_8 E_u$	3,93	1	,,	D	63
	$714\nu_6 A_{2u}$	16.3	1	,,	D	63
	$1116\nu_5 A_{2u}$	118	1	,,	D	63
	$1250\nu_7 E_u$	408	1	,,	D	63
6. Ethylene and its derivatives (symmetry V_h)						
C_2H_4	$949\nu_7 B_{1u}$	51.7		extrapolation		108
	949	39,7	700*	,,	D	30
	$1444\nu_{12} B_{3u}$	4.86	700*	,,	D	30
	1444	7.82		,,	D	108
	$2990\nu_{11} B_{3u}$	10.1		,,	D	108
	2990	6,73	700*	,,	D	30
	$3106\nu_9 B_{2u}$	12.4	700*	,,	D	30
	3106	21.2		,,	D	108
C_2D_4	$720\nu_7 B_{1u}$	20.8	700*	,,	D	30
	$1078\nu_{12} B_{3u}$	2,58	700	,,	D	30
	$2200\nu_{11} B_{3u}$	3.79	700	,,	D	30
	$2345\nu_9 B_{2u}$	6,07	700*	,,	D	30
7. Acetylene and its derivatives						
C_2H_2 (symm., $D_{\infty h}$)	$730\nu_5$	80,9	200*	extrapolation	β	102
	730	89,5	300*	,,	β	22
	730	90.0		from dispersion	β	46
	$3290\nu_3$(CH), E	31.1	3	extrapolation	β	18
	3290	34.5	300*	,,	β	22
	3290	36.4		from dispersion	β	46
C_2D_2 (symm., $D_{\infty h}$)	$539\nu_5$	38.8	200*	from dispersion	β	102
	539	35.2	300*	extrapolation	β	22
	$2200\nu_3$	15.2	300*	,,	β	22
C_2HD (symm., $C_{\infty v}$)	$3335\nu_1$	12.2	300*	,,	β	22
	$2585\nu_2$	0,313	300*	,,	β	22
	$1851\nu_3$	9,32	300*	,,	β	22
	$679\nu_4$	9,73	300*	,,	β	22
	$520\nu_5$	41.6	300*	,,	β	23
$C_2(CH_3)_2$ (symm., D_{3h})	$1054\nu_{11} E'$	0,59	1	,,	β	64
	$1382\nu_7 A_2''$	1.27	1	,,	β	64
	$1456\nu_{10} E'$	14.5	1	,,	β	64
	$2915\nu_6 A_2''$	25.5	1	,,	β	64
	$2973\nu_9 E'$	20,6	1	,,	β	64
8. Benzene and its derivatives (symmetry D_{6h})						
C_6H_6	$673 A_{2u}$	43.9	1	extrapolation	β	90
	$1038 E_{1u}$	4.4	1	,,	β	90
	$1486 E_{1u}$	6.5	1	,,	β	90
	3036—72—92 (triplet) ν(CH)	37.8	1	,,	β	90
C_6F_6	$315 E_{1u}$	70,0	1	,,	β	92
	$1002\text{-}1020 E_{1u}$ (doublet)	203	1	,,	β	92
	$1531 E_{1u}$	272	1	,,	β	92

Table 3 (continued)

Molecule	Band position (in cm^{-1}) and form of vibration	Absolute intensity $A \times 10^8$ (in cm^2/mol-ecule-sec)	Total pressure (in atm)	Method of meas-urement	Units of absolute-intensity measure-ment used by the authors	Ref-er-ence
9. Other molecules						
H_2CO (symm., C_{2v})	1490v_3	4.63	400*	extrapolation	β	34
	1760v_2	29.1	400*	,,	β	34
	2860v_1v_4 (unresolved)	63.8	400*	,,	β	34
Cl_2CO (symm., C_{2v})	575v_1	5.04	20*	,,	α	53
	849v_4	117.5	20*	,,	α	53
	1827v_2	87.5	20*	,,	α	53
Cl_2CS (symm., C_{2v})	502v_1	2.75	20*	,,	α	53
	802v_4	65.6	20*	,,	α	53
	1138v_2	61.7	20*	,,	α	53
C_2N_2 (symm., $D_{\infty h}$)	235v_5	8.39	0,5	,,	β	65
	2150v(CN)	3.36	1	,,	β	69
SF_6 (symm., O_h)	615v_6F_{1u}	31.4		,,	α	85
	947v_5F_{1u}	537		,,	α	85

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