

THE THEORY OF INTENSITIES IN THE INFRARED SPECTRA OF POLYATOMIC MOLECULES

L. A. GRIBOV

*V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry,
U.S.S.R. Academy of Sciences, Moscow*

Among various methods of studying the structure of polyatomic molecules, vibrational spectroscopy and infrared spectroscopy in particular are among the most fundamental methods. Until recently, information on molecular structure and on the influence of substitutions and intermolecular interactions was obtained mainly from observations of the number and positions of the absorption bands in spectra. Recently, however, interest has increased in the use of intensities and polarization of absorption bands in addition to the characteristics used previously. In most cases the intensities of the absorption bands are found to be more sensitive than the frequencies to various changes in molecular structure and the influence of the medium. The analytical value of measuring the absorption band intensities for studying the structure of polyatomic molecules must, however, be set against the considerable difficulties in interpreting the experimental data. The purely empirical approach successfully used before, is practically useless in this case.

It has been found that bands can exist whose frequencies are determined only by the properties of certain bonds or groups of atoms, while their intensities are determined by the properties of other bonds or groups. Thus the intensity of vibration of the double bond $C=C$ in the propylene molecule is determined mainly by the parameters of adjacent CH bonds¹, while its frequency depends almost completely on the value of the force constant of this bond. In many cases this fact can lead to mistakes in interpreting the experimental data.

For example, when a hydrogen atom is substituted for chlorine in the acetonitrile molecule a nearly eight-fold increase in the intensity of the absorption band is observed, while the frequency of this vibration remains unchanged; usually this band is interpreted as the vibration of the $C\equiv N$ bond. This experimental fact can be considered as an indication of the change in properties of the $C\equiv N$ bond with such a substitution. However a detailed analysis showed^{2, 3} that the observed increase in intensity is determined by the change in properties of the $C-C$ bond which affects the intensity of the band under observation because the form of the vibration considered is non-specific. The explanation of the phenomenon is thus found to be quite different from that given on the basis of empirical observations only.

In general, interpretation of the absorption band frequencies and intensities, where both are determined by consideration of the properties of a

certain group of atoms, can be made only for the few vibrations which are specific in intensity. Therefore for a successful study of the structure of polyatomic molecules by measuring the intensities of the absorption bands in the infrared, a clear connection between the observed spectra and the parameters characterizing the properties of the molecules must be established.

It is well known that the intensity of the absorption band is defined by the squared matrix element for dipole transition

$$\langle \vec{p} \rangle_{n,v'}^{n,v''} = \int \psi_n^*(\xi, Q) \chi_{v''}(Q) p \psi_n(\xi, Q) \chi_{v'}(Q) d\xi dQ \quad (1)$$

where $\psi_n(\xi, Q)$ is the electron eigenfunction of the molecule dependent on the vibrational coordinates Q_i as on the parameter in the Born–Oppenheimer approximation, $\chi_v(Q)$ is the vibrational eigenfunction of the molecule and p is a dipole moment operator of the molecule.

Without loss of generality, the function $\vec{p}(Q) = \int |\psi_n(\xi, Q)|^2 p d\xi$ can be represented by an expansion in a series with respect to the vibrational coordinates; then taking into account the matrix elements values for the coordinate in harmonic approximation, we obtain for a fundamental transition

$$\langle \vec{p} \rangle_{n,v'}^{n,v''} = \left(\frac{\partial \vec{p}}{\partial Q_i} \right)_0 \sqrt{\left(\frac{h}{8\pi^2\nu_i} \right)}$$

Therefore the problem is to analyse the value of $(\partial \vec{p} / \partial Q_i)_0$. If it were possible to calculate the precise value of either matrix element $\langle \vec{p} \rangle_{n,v'}^{n,v''}$ or the derivative $(\partial \vec{p} / \partial Q_i)_0$, the problem of establishing the physical connection between the observed band intensity and the molecular structure would have been solved. But this is not feasible. So we have to consider various models. At present there are two models recognized. The first one, older historically and more developed, is based on the parametric representation of the derivative $(\partial \vec{p} / \partial Q_i)_0$ in the form of a linear combination of empirical parameters, called electro-optic parameters, which characterize the electronic structure of either separate bonds or atomic groups for additive molecules. The vector function $\vec{p}(Q)$ is then represented by the sum

$$\vec{p}(Q) = \sum_k p_k(Q) \vec{e}_k(Q)$$

where $p_k(Q)$ are parameters which depend on the atomic vibrational coordinates Q_i and can be considered as dipole moments of the bonds for additive molecules, and $\vec{e}_k(Q)$ are the unit direction vectors of the bonds which are also functions of the atomic coordinates^{4, 5}. Having differentiated the expression

$$\vec{p}(Q) = \sum_k p_k(Q) \vec{e}_k(Q)$$

we obtain⁶

$$\begin{aligned} \left(\frac{\partial \vec{p}}{\partial Q_i}\right)_0 &= \sum_k \vec{e}_k(0) \left(\frac{\partial p_k}{\partial Q_i}\right)_0 + \sum_k p_k(0) \left(\frac{\partial \vec{e}_k}{\partial Q_i}\right)_0 \\ &= \sum_k \vec{e}_k(0) \sum_j \left(\frac{\partial p_k}{\partial q_j}\right)_0 l_{ji} + \sum_k p_k(0) \sum_j \left(\frac{\partial \vec{e}_k}{\partial q_j}\right)_0 l_{ji} \end{aligned} \quad (2)$$

where l_{ji} are the elements j of the matrix column L_i for the transformation of the normal coordinates Q_i to internal vibrational coordinates. Usually this formula is written down in more compact matrix form⁷. The derivatives

$\left(\frac{\partial \vec{e}_k}{\partial q_j}\right)_0$ can be calculated if the geometric configuration of the molecule is known. The set of $p_k(0)$ and $\left(\frac{\partial p_k}{\partial q_j}\right)_0$ values forms a system of electro-optical parameters of the molecule introduced into the theory as empirical values which are derived from the inverse spectral problem for intensities. Of course, such a representation is not the only one possible. The function $\vec{p}(Q)$ can be put in the form

$$\vec{p}(Q) = \sum_n \eta_n(Q) \vec{\rho}_n(Q)$$

where $\eta_n(Q)$ represents effective atomic charges and $\vec{\rho}_n(Q)$ the corresponding radius vectors in the Cartesian system of coordinates associated with the molecule. Both these representations of the function $\vec{p}(Q)$ are actually equivalent and each can be easily transformed into the other. Some peculiarities can arise in describing the molecules containing cycles but they are not important. The choice of the $\vec{p}(Q)$ representation in the intensity theory is in any case purely conventional. For convenience we prefer the form

$$\vec{p}(Q) = \sum_k p_k(Q) \vec{e}_k(Q)$$

Using this representation, the expression for the derivatives $\left(\frac{\partial^2 \vec{p}}{\partial Q_i \partial Q_j}\right)_0$ and for derivatives of higher order can be easily obtained.

The other approach to the solution of the problem of the intensities of the vibrational absorption bands implies the choice of an approximate expression for the electron eigenfunction of polyatomic molecules, $\psi_n(\xi, Q)$, and the calculation of either matrix element, $\langle \vec{p} \rangle_{n,v}^{n,v'}$, directly, which is possible since the expression for dipole moment operator is available; or the value of $\left(\frac{\partial \vec{p}}{\partial Q_i}\right)_0$ can be obtained using a number of simplifying assumptions. For instance, if the state of an electron in a molecule is described by the function $\psi_n = \sum_m c_m \psi_m$, where ψ_m are atomic wave functions, then the contribution of this electron to the dipole moment of the molecule can be characterized by the value $\vec{p}_e = \sum_m c_m^2 \vec{\rho}_m$ where $\vec{\rho}_m$ are instantaneous radius-

vectors of the atomic nuclei of the molecule (the centres of the functions Ψ_m are assumed always to coincide with the nuclei positions). Then the derivative $(\vec{\partial p}_e/\partial Q_i)_0$ is equal to

$$2 \sum_m c_m \left(\frac{\partial c_m}{\partial Q_i} \right)_0 \vec{\rho}_m(0) + \sum_m c_m^2 \left(\frac{\partial \vec{\rho}_m}{\partial Q_i} \right)_0$$

and for its calculations it is sufficient to know the dependence of the coefficients c_m on the vibrational coordinates, i.e., actually the dependence of both the Coulomb and resonance integrals of the system on geometric parameters of the molecule.

Both approaches have their own advantages and defects. The parametric theory which was developed predominantly, until recently, led to a whole number of valuable general conclusions, as well as enabling calculations to be made of the spectra of a great number of polyatomic molecules. It is characterized by the representation of the dipole moment of the molecule as completely universal if, of course, the parameters $p_k(0)$ are not considered as the dipole moments of the bonds. As a result the conclusions drawn prove true for any class of molecules, either organic or inorganic. Various models of molecules (additive or non-additive) differ from each other in only the concrete form of the matrix of derivatives $(\partial p_k/\partial q_j)_0$. For the model of the molecule with additive bonds, all elements of this matrix except those elements which are related to the coordinates of bond-stretching have to be put equal to zero. The parameters $p_k(0)$ in this case will be dipole moments of the bonds. For the more complex model some other derivatives are also non-zero, and for non-additive molecules in general all elements $(\partial p_k/\partial q_j)_0$ should be non-zero. This possibility of varying the form of the final formulae $(\vec{\partial p}/\partial Q_i)_0$ for the concrete molecules is extremely important especially when studying complicated molecules with the use of various simplified models.

On the other hand, the necessity to calculate the parameters $p_k(0)$ and $(\partial p_k/\partial q_j)_0$ on the basis of experimental intensities leads to a number of difficulties and limits considerably the application of the parametric theory to the numerical estimation of the intensities of absorption bands of polyatomic molecules. To illustrate this point let us write down the formula for $(\vec{\partial p}/\partial Q_i)_0$ in the form

$$\begin{aligned} \left(\frac{\vec{\partial p}}{\partial Q_i} \right)_0 = & \sum_k \vec{e}_k(0) \sum_j \left(\frac{\partial p_k}{\partial q_j} \right)_0 l_{ji} + \sum_k p_k(0) \sum_j \left(\frac{\partial \vec{e}_k}{\partial q_j} \right)_0 l_{ji} - \\ & - \left[\vec{p}(0) \times \sum_j \left(\frac{\partial \vec{\omega}}{\partial q_j} \right)_0 l_{ji} \right] \quad (3) \end{aligned}$$

where $(\partial \vec{e}_k/\partial q_j)_0$ are the derivatives with respect to the internal vibration coordinates without taking into account the angular momentum. These

derivatives, unlike the derivatives $(\partial \vec{e}_k / \partial q_j)_0$ in formula (2), neither depend on the atomic mass nor change with isotope substitution and differ from real ones by terms depending on the rotation of the whole molecule and the dipole moment of the molecule.

Let us denote by $(\partial \vec{p} / \partial q_j)_0$ the combination

$$\sum_k \vec{e}_k(0) \left(\frac{\partial \vec{p}_k}{\partial q_j} \right)_0 + \sum_k \vec{p}_k(0) \left(\frac{\partial \vec{e}_k}{\partial q_j} \right)_0$$

It is easily seen that if the dipole moment of the molecule is of known magnitude and direction relative to the molecule, then only the magnitudes of $(\partial \vec{p} / \partial q_j)_0$, i.e., certain combinations of the parameters $\vec{p}_k(0)$ and $(\partial \vec{p}_k / \partial q_j)_0$ can be found from the solution of the inverse spectral problem even with the isotopic molecules involved. If the molecule does not possess additive properties, such combinations can contribute little to the understanding of the molecular structure. To use them even for intensity calculations in the related molecules is also impossible. However if the molecules of a certain series exhibit additive properties (not necessarily those of the bonds, but at least of a whole group of atoms), then the values of $(\partial \vec{p}_k / \partial q_j)_0$ can preserve their magnitudes for the series of such additive molecules; this enables us to use them for the prediction of the intensities in a certain molecule from the intensities of the absorption bands in the related molecules. Moreover a considerable portion of the derivatives $(\partial \vec{p}_k / \partial q_j)_0$ can become zero. This leads to a simplified form of the combinations of the parameters and allows them to be found separately. A number of highly valuable conclusions concerning the structure and interactions of separate atomic groups in the molecule can be drawn. Therefore the calculation aspect of the parametric theory is restricted only to the sets of molecules exhibiting the additive properties distinctly.

Since, for the calculation of intensities in a series of related molecules, it is sufficient to find the magnitudes of $(\partial \vec{p} / \partial q_j)_0$, it may seem that there is no necessity to use any concrete form of $\vec{p}(Q)$ representation (for instance, $\vec{p}(Q) = \sum_k \vec{p}_k(Q) \vec{e}_k(Q)$) since it only complicates recording⁸. However, this is not the case. It is clear that when evaluating a theory one should consider not only its ability to answer a particular question which for this case is the prediction of the intensities in a homologous series, but also its usefulness when drawing conclusions of a general nature. Thus, for example, the solution of such fundamental problems as those of specificity of intensities, dependence of the absorption band intensities on the number of identical groups in the molecule, distribution of intensities over the spectra of periodic molecules and polymers, etc., is impossible without attempts to introduce such a representation of $\vec{p}(Q)$ which would be connected with the properties of separate parts of the molecule. The possibility of reflecting the simplified models of the system under consideration in the formula to

be used is of great importance in studying the structure of complicated molecules and we try to apply it in some way whatever method of investigation we are using.

Such a possibility actually occurs in using formulae (2) and (3) and vanishes if the derivative $(\vec{\partial p} / \partial Q_i)_0$ is expressed in the form

$$\left(\frac{\vec{\partial p}}{\partial Q_i}\right)_0 = \sum_j \left(\frac{\vec{\partial p}}{\partial q_j}\right)'_0 l_{ji} - \left[\vec{p}(0) \times \sum_j \left(\frac{\partial \omega}{\partial q_j}\right)_0 l_{ji}\right]$$

Thus we see that the form of record we have chosen for the derivative of the molecular dipole moment with respect to the normal coordinate is quite convenient. However the parametric theory under consideration suffers also from some shortcomings. These include: the large number of parameters to be introduced for the description of a rather complex molecule lacking distinctly pronounced additive properties; the necessity of using a separate system of parameters not connected directly to the parameters used for the calculation of the vibration frequencies (force constants); the electro-optical parameters of the molecule being less transferable within the homologous series compared to the force constants within the same series and, as a result, the accuracy of the calculation of the absorption band intensities being in some cases unsatisfactory; the necessity of using sometimes quite complicated combinations of the parameters which considerably reduces the value of the information obtained; and finally the uncertainty in physical meaning of some parameters, for instance of the derivatives $(\partial p_k / \partial q_j)_0$ with respect to both the angle and out-of-plane coordinates.

The shortcomings of the parametric theory make one search for a new approach, for example, the attempt to use various representations for the electron function of polyatomic molecules. Of this we have as yet little experience, but it is possible to draw some conclusions of a general nature. The most attractive aspect of this theory is that it is based on a function which can be used for the description of various properties of polyatomic molecules. Thus one can hope to calculate the electronic and vibrational spectra of molecules by means of a single system of parameters. For the study of vibrational spectra, the system of concepts and methods already developed in the quantum chemistry of complex molecules can be used. Generally speaking, the further development of the theory of vibrational spectra of polyatomic molecules seems to require the construction and application of various models of electron functions.

The possibilities inherent in the application of the electron function models to the calculation of the vibrational spectra of polyatomic molecules cannot however be realized completely due mainly to the arbitrariness in the selection of the simplified electron functions for the polyatomic molecules. The only practicable basis for the construction of such functions at present are various modifications of molecular orbitals in the form of linear combinations of atomic orbitals. It is known that functions of this kind can be applied to the numerical description of properties of molecules only in the case where these molecules possess a fairly-developed system of conjugations and where the properties we are concerned with are mainly determined by

the π -electrons. The situation is somewhat more difficult where the σ -electron skeleton of the molecule and, especially, where molecules with a great number of heteroatoms are concerned. Thus it is quite clear that the influence of the σ -bonds of the molecule may by no means be ignored when studying the vibrational molecular spectra (except probably for a few highly-symmetric aromatic molecules⁹).

Further, as has already been mentioned, the dependence of the Coulomb and resonance integrals on the geometric parameters of a molecule must be known for carrying out definite calculations. Such dependences are often semi-empirical, especially those for the valence angles, and they are of restricted use. Of course, one can try to find those dependences by solving the inverse spectral problems of frequencies and intensities in the vibrational spectra of polyatomic molecules, but the number of unknown quantities to be introduced will not be less, and may even exceed, that of the parameters used in the semi-empirical theory considered above. Attempts to apply the simplified electron functions to the calculation of vibrational spectra and, in particular, to the absorption band intensities are as yet quite rare and the experience so far obtained does not help to settle which form of electron function is more advantageous for this type of problem or even to make an approximate estimation of the number of parameters which will be satisfactory for the calculations of the intensities with sufficient accuracy. In this respect, more work including numerous calculations of definite molecular spectra is required, provided that all calculations are performed under comparable conditions and on the basis of a single requirement in the selection of molecular electron function.

Now let us consider the parametric theory of intensities in the infrared spectra of polyatomic molecules once more and review its achievements and practical possibilities. The appearance of a term dependent on dipole moment of the whole molecule in the expression for the derivative $(\partial p / \partial Q_i)_0$ (see formula (3)) is specific for a polyatomic molecule.

In some cases the influence of this term may be dominating¹⁰. Hence it follows that in asymmetric polyatomic molecules, even if there is a complete additivity of their bonds, the parameters $(\partial p / \partial q_j)_0$ will always depend on the properties of the whole molecule and therefore they will change with the transfer of any bond from one molecule to another. Of course, the influence of this effect depends strongly on the mass ratio in the molecule. Thus it should be taken into account for the vibrations ν_{as} NO_2 if the intensities of the CH_3NO_2 molecule are analysed^{11, 12}, while its contribution is negligible in the CH_3NH_2 molecule¹³.

The most important factor among those having influence on the vibrational intensities is the form of vibrations. There are vibrations specific by frequency which are at the same time non-specific in form. As a result there are absorption bands for which the maximum position and intensity depend on the properties of different atomic groups.

The effect of the change in the form of vibrations is especially distinct on deuteration. For example, the intensity of the band $\text{C}\equiv\text{N}$ changes almost 20 times with the substitution of H for D in the molecule HCN ¹⁴. Therefore to ascertain the conditions for the appearance of the absorption bands

exhibiting the properties of specific intensity is rather an urgent problem.

Theoretical analysis of absorption band intensities on the basis of the parametric theory permits the factors necessary for the appearance of the absorption bands with specific intensities in spectra to be ascertained. It has been found⁷ that for fundamental vibrations the specific intensities of the bands may be observed for additive end groups with vibrations specific in frequency and form; the bonds of the rest of the molecule do not change when the given group of atoms vibrates. The overtones of the fundamentals specific in intensities are also specific in intensities. For binary frequencies there is a sort of selection rule, namely, the binary frequency being a combination of two normal vibrations such that the corresponding fundamental absorption bands are specific in intensities for two different groups in the molecule.

The question of the dependence of the absorption band intensities on the number of identical groups in polyatomic molecules is closely connected with that of the specific intensities in infrared spectra. This problem can also be solved by the parametric theory⁷.

It was found that a definite simple regularity can be obtained when the vibration of each equivalent group satisfies the conditions for the specificity in intensity while the forms of vibrations of the groups differ by factors a_{ki} . This means that the mutual dependence of equivalent groups is shown by their vibrations exhibiting definite phase and amplitude relationships while the groups themselves occupy a definite position relative to one another.

In this case we obtain

$$\left(\frac{\partial \vec{p}}{\partial Q_i}\right)_0 = \text{const.} \frac{v_i(n)}{\sqrt{\sum_k^n a_{ki}^2}} \left(\sum_k^n a_{ki} \vec{h}_{ki}\right) \quad (4)$$

$$\left(\frac{\partial^2 p}{\partial Q_i \partial Q_j}\right)_0 = \text{const.} \frac{v_i(n) v_j(n)}{\sqrt{\left[\sum_k^n a_{ki}^2\right] \left[\sum_k^n a_{kj}^2\right]}} \left(\sum_k^n a_{ki} a_{kj} \vec{h}_{kij}\right) \quad (5)$$

The unit vectors \vec{h}_{ki} and \vec{h}_{kij} characterize respectively the polarizations of vibrations of the equivalent groups for the fundamental transitions and overtones and the binary frequencies. These vectors depend on both the form of vibrations of groups and their relative positions. It is seen from (4) and (5) that the intensities of the absorption bands may decrease when the number of additive groups increases. The dependences of the intensities of the fundamental absorption bands and the overtones and binary frequencies on the number of equivalent groups may be different.

It should be noted that different normal vibrations often have similar frequencies. As a result, the band observed in the spectrum will be complex. Certainly it is not often that these effects cause a considerable distortion of the band contour and therefore it cannot always be detected experimentally. In that case the dependence of the intensity of such a compound absorption band on the number of groups will of course be different. When we observe a linear dependence of the intensities of the fundamental bands on the

THE THEORY OF INTENSITIES IN THE INFRARED SPECTRA

number of groups it is due, as a rule, to the superposition of the different vibrations superimposed. It should be realized that the dependence of the absorption band intensities on the number of groups may be non-linear even when the groups are additive (see *Tables 1-3*).

Table 1. The relation of the intensities of valence vibrations of Si-C bonds to the number of bonds in methyl chlorosilane molecules

<i>Compound</i>	<i>Frequency</i> cm ⁻¹	<i>Calculated</i> <i>intensity</i>	<i>Experimental data</i> <i>(in conventional units)</i>
CH ₃ SiCl ₃	764	1	1
(CH ₃) ₂ SiCl ₂	691	0.54	0.45
(CH ₃) ₃ SiCl	631	0.225	0.214

In *Tables 1, 2 and 3* the intensities have been calculated according to formula (4); the linear increase in ν_{as} NO₂ intensities with the increase in the number of NO₂ groups is accounted for by the superposition of the normal vibrations of different symmetry types.

Table 2. The relation of the intensities of the valence vibrations of Ge-Cl bonds to the number of Ge-Cl bonds in methyl chlorogermane molecules

<i>Compound</i>	<i>Frequency</i> cm ⁻¹	<i>Calculated</i> <i>intensity</i>	<i>Experimental data</i> <i>(in conventional units)</i>
(CH ₃) ₃ GeCl	378	1	1
CH ₃ GeCl ₃	399	0.37	0.39

Table 3. The dependence of the intensities of antisymmetric valence vibrations of NO₂ groups on the number of groups in molecules

<i>Compound</i>	<i>Frequency</i> cm ⁻¹	<i>Calculated</i> <i>intensity</i>	<i>Experimental data</i> <i>(in conventional units)</i>
C ₂ H ₅ NO ₂	1562	1	1
CH ₃ CH(NO ₂) ₂	1583	2	2.1
HC(NO ₂) ₃	1605	3	3.1

A very important result of the parametric theory is the analysis of the typical contour of the absorption bands for the finite periodic molecules and polymers for various chain conformations and under different conditions of observation¹⁵ (see *Figure 1*). So the parametric theory being quite simple and clear permits a number of very interesting general conclusions to be drawn.

Now the possibilities of numerical intensity calculations in the vibrational spectra of polyatomic molecules will be considered briefly.

As has already been pointed out, at least approximate additivity in a series of molecules is required for the performance of numerical calculations. The situation here is quite analogous to that in the calculation of the vibrational frequencies. Two problems arise: (a) the determination of the electro-optical parameters from experimental data on the intensities and polarization of the absorption bands in infrared spectra (inverse spectral problem); and (b) utilization of the electro-optical parameters of separate bonds and

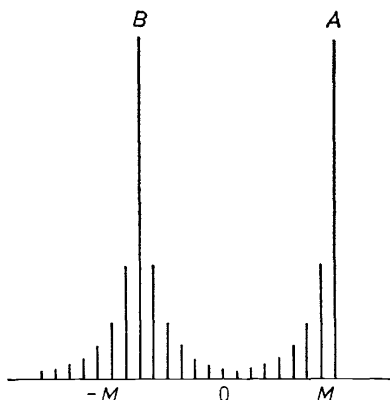




Figure 1. Intensity distribution in the band of a helical polymer for components polarized (A) parallel and (B) perpendicular to the axes of the molecule

atomic groups for the calculation of the absorption band intensities in the spectra of molecules similar in structure (direct spectral problem).

The electro-optical parameters of a molecule are found from a system of linear equations obtained by the substitution of the experimental values of the derivatives $(\partial p / \partial Q_i)_0$ in (2) or (3). To reduce the number of unknowns, simplified models of molecules are generally used, the correctness being tested later by studying the isotopically-substituted molecules and those of the homologous series. It must be taken into account that the system of equations may prove to be incompatible if the models are unduly simplified. The overlooking of this fact caused the introduction by some authors of the concept of the 'dynamic' dipole moment of bond devoid of physical sense.

Table 4. The electro-optical parameters CH, CH₂, and CH₃ in alkanes, alkenes and alkynes

$\equiv\text{C}-\text{H}$	$p = 1.10;$	$\frac{\partial p}{\partial q} = 1.00;$	$\frac{\partial p}{\partial q'} = 0$
	$p = 0.70;$	$\frac{\partial p}{\partial q} = 0.53;$	$\frac{\partial p}{\partial q'} = 0.10$
		$\frac{\partial p}{\partial \beta} - \frac{\partial p}{\partial \alpha} = 0.12;$	$\frac{\partial p}{\partial \beta'} - \frac{\partial p}{\partial \alpha'} = 0.60$
	$p = 0.28;$	$\frac{\partial p}{\partial q} = 74;$	$\frac{\partial p}{\partial q'} = 0.31$
	$\frac{\partial p}{\partial \beta} - \frac{\partial p}{\partial \beta'} = -0.04;$	$\frac{\partial p}{\partial \alpha} - \frac{\partial p}{\partial \alpha'} = 0.04$	

In this table the dipole moments CH are in D and the rest of the parameters are in D/Å. The hatched coordinates refer to either adjacent bonds or alternate angles.

Electro-optical parameters for some of the bonds or atomic groups have been determined (see *Table 4*). It has been observed that there is a definite correlation between the force constants and the electro-optical parameters of separate molecules and the fact that non-diagonal force constants are zero is often associated with smallness of the corresponding electro-optical parameters and v.v. Electro-optical parameters of both separate bonds and atomic groups prove to have transferability properties to a certain extent. This permits the calculation of the distribution of intensities in the absorption spectra of rather complex molecules using electro-optical parameters of separate atomic groups in these molecules^{2, 3, 7, 11-13, 16-23}. The qualitative agreement of these calculations with experiment is quite satisfactory for the solution of problems concerned with interpreting the intensities, discovering general regularities in spectra etc. In many cases a fairly good quantitative agreement between the calculated and experimental spectra (*Table 5*) has been obtained. Some of the examples of the calculated spectra are given in *Figures 2-5*.

Table 5. Calculations of intensities for the dimethyl acetylene molecule performed on the basis of electro-optical parameters of separate groups

Frequency cm ⁻¹	The derivatives of the dipole moment with respect to the normal coordinates in D/Å	
	Experimental	Calculated
	<i>Type A</i>	
2915	1.14	1.15
1382	0.25	0.36
1152	0.08	0.08
	<i>Type E</i>	
2973	0.72	0.30
1456	0.60	0.40
1054	0.12	0.23

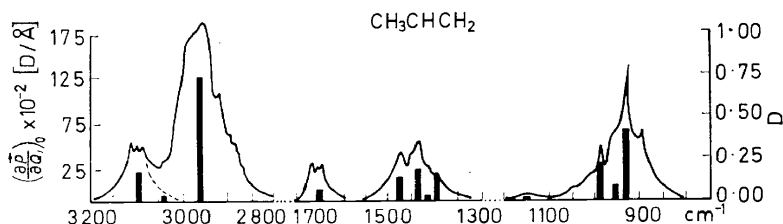


Figure 2. Experimental and calculated (shown by dark columns) spectra of propylene

A list of molecules which have been studied theoretically in the U.S.S.R. is given in *Table 6*.

It seems reasonable to assert that a fairly limited set of electro-optical parameters for organic compounds exist suitable for numerical analysis of the intensities and polarization of a great number of molecules. It should be noted, however, that such a problem is for a number of reasons much more complicated than the construction of an analogous set of force constants. The accuracy of the determination of electro-optical parameters and their

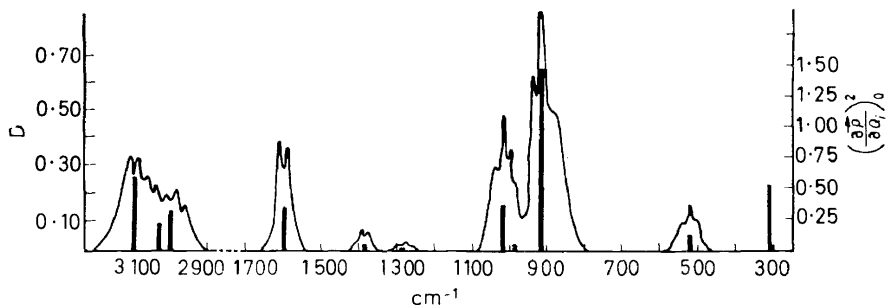


Figure 3. Experimental and calculated (shown by dark columns) spectra of butadiene, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$

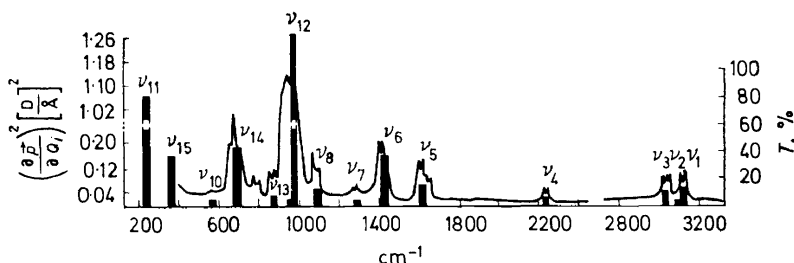


Figure 4. Experimental and calculated (shown by dark columns) spectra of acrylonitrile, $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$

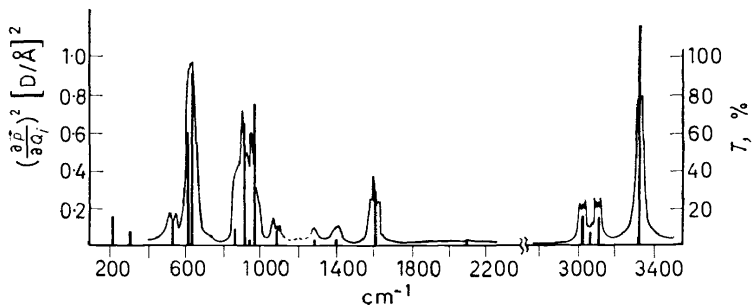


Figure 5. Experimental and calculated (shown by dark columns) spectra of vinyl-acetylene

Table 6. A list of the molecules, for which the absorption band intensities have been analysed within the parametric scheme

1. Cyanhydride	9. Nitromethane
2. Acetylene	10. Acetonitrile
3. Ethylene	11. Trichloroacetonitrile
4. Ethane	12. Butadiene
5. Methane	13. Diacetylene
6. Ammonia	14. Vinyl-acetylene
7. Silane	15. Acrylonitrile
8. Chloro-, bromo- and iodomethanes	16. Benzene

transferability within the series of molecules is much lower than for those of the force constants. Thus the parametric theory should be applied mainly to problems where high accuracy is not required. These include problems of interpreting absorption band intensities, and those of introducing more clarity into assignments of the closely-spaced absorption bands with highly different intensities etc. The methods described can also be effectively applied to the solution of the problems concerning the peculiarities in structure of complex molecules (see references 2, 3 and 20).

In conclusion it can be said that the parametric theory of intensities may become quite a powerful means of the analysis of absorption band intensities in the infrared spectra of polyatomic molecules. It may be used to solve a number of problems. It has helped to reveal a number of highly important properties of the absorption band intensities. However, the further development of the theory of intensities necessitates various modifications of electron functions.

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