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THE USE OF VIBRATIONAL SPECTRA IN THE STUDY OF THE STRUCTURE OF POLYATOMIC MOLECULES

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1. INTRODUCTION

One of the fundamental tasks in modern science is to study the structure and properties of polyatomic molecules. In the past two decades, in addition to traditional chemical methods, an ever-increasing and in many instances decisive part has begun to be played by various physical methods, particularly methods based on the study of the energy levels of polyatomic molecules. These methods include electronic, vibrational, and rotational spectroscopy and radiospectroscopic methods. The great importance of these methods lies primarily in the fact that they make possible the study of the structure and properties of molecules and molecular associates in any state of aggregation without breakdown of the molecules, as usually takes place when chemical methods are used. At present the methods most widely used are electronic and particularly vibrational spectroscopy. This is due both to the fact that historically they appeared before the radiospectroscopic methods and also to the high degree of development and ubiquity of electronic and vibrational spectroscopy and the wide range of varied problems which can be solved by these methods. The rapid development of experimental techniques and the appearance of automatic spectrophotometers have also been of considerable importance.

Unlike electronic absorption spectra and luminescence spectra, the overwhelming majority of vibrational spectra consist of a large number of discrete lines and bands, whose appearance is related to the presence and interaction of various atomic groups in the molecule, so that the very nature of the vibrational spectra gives considerable information on the detailed structure of a complex system.

Vibrational spectroscopy, however, is an indirect method. Experimental measurement of the parameters of the spectrum alone (the number of bands, their position on the frequency scale, intensities, etc.) is useless if a relationship has not been established between the observed quantities and the structure of the polyatomic molecule, that is, if the appropriate theory has not been developed. The need to develop a special theory of vibrational spectra arose in the nineteen-thirties and -forties as a result of the accumulation of experimental material on the infrared absorption spectra (IRS) and Raman spectra (RS) of complex molecules and the resulting desire to interpret these spectra. At that time a solution to the problem of the vibrational energy levels (normal vibrations) of polyatomic molecules had been roughly outlined; the problem involved primarily the development of a theory to explain the general features characteristic of the vibrational spectra of homologous series, to relate the vibrational spectra to the internal structure of molecules, and to carry out the necessary numerical calculations. This theory could be only semi-empirical, since direct quantum-mechanical methods were here quite inadequate.

A decisive step in this direction was taken by El'yashevich[1-6], who proposed a general method for formulating equations for the vibrations of polyatomic molecules in a special system of coordinates, which he called the natural system. An analogous method was developed independently by Wilson[7-10]. The introduction of natural coordinates made it possible to apply to the theory of vibra-

tional spectra the system of ideas developed in the structural chemistry of polyatomic molecules and this in turn made it possible to make the most important classification of all normal vibrations on the basis of the vibrations of the valency bonds (stretching vibrations), the vibrations of the valency angles (bending vibrations), and the vibrations of structural groups. This made it possible to explain the characteristic vibrations in the spectra of homologous theories. The theory of characteristic vibrations was later developed by Mayants [11] on the basis of a classification of the vibrations according to the characteristic nature of the frequency and mode, and also the frequency and mode themselves.

When natural coordinates were used, the coefficients in the expression for the potential energy (force constants) in a large number of molecules were found to be closely related to the properties of the corresponding structural elements, and specific calculations showed that the force-constant structural elements, within certain limits, retain their numerical value in a series of molecules containing the given structural elements. This property of the force constants, which is closely related to the comparatively unchanged nature of the individual "building bricks" of the molecule, predetermined the collection of a set of force constants necessary for numerical calculation of the vibration frequencies of a large number of molecules.

The creation of this set began after the development of effective methods for calculating the eigenvalues and eigenvectors of the equations for molecular vibrations, taking account of the specific features of these equations (the diagonalisation method of El'yashevich and Stepanov [12], the improved iteration method of Mayants [13]), and the determination of the force constants for a number of basic compounds by Stepanov and El'yashevich [14]. On the basis of the theory developed by these authors, Kovner's and Sverdlov's groups, together with Kovalev, Bogomolov, Peregudov, Popov, and a number of others, calculated the frequencies and modes of the vibrations and interpreted a large number of molecular spectra (chiefly organic molecules) and determined the force constants of the most important bonds and groups. This provided the necessary starting material for the extensive use of calculations and the solution of a variety of applied problems.

The development of the theory of molecular vibration frequencies was accompanied by the development of a theory of intensities in IRS and RS. By using an additive scheme for representing the dipole moment and polarizability tensor of a molecule in the form of the vector and tensor sums of the dipole moments and polarizability tensors of the individual bonds, Vol'kenshtein [15,16] formulated a semi-empirical theory of intensities in IRS and RS, later improved with El'yashevich [17,18]. Because of the lack of experimental material on the measurement of intensities in spectra at that time and the tedious nature of the calculation, however, the theory of intensities remained at this stage of development for a prolonged period.

Thus at the start of the nineteen-sixties considerable progress had been made in the theory of vibrational spectra (particularly in the theory of the frequencies and modes of the vibrations), as a result of which the extensive application of calculation methods to practical spectrochemical studies became possible. It was also shown for many examples that in the overwhelming majority of instances sufficiently well-founded and reliable conclusions regarding the structure and properties of a molecule could be obtained from spectroscopic data only by a theoretical study.

This possibility, however, could not be completely realised until all the calculation part had actually been reduced to programmes for electronic computers (EC). This important task in turn required the transformation of the entire mathematical technique of the theory into a form convenient for use with EC, and the development of a system of algorithms. EC were first used to calculate the eigenvalues and eigenvectors of the equations for the vibrations, and also for a number of other operations (normalisation, calculation of the displacements of atoms, etc.) [19]. This is related to the fact that the methods for solving the equations are already formulated in the form of algorithms and the problem involves merely encoding.

The choice of algorithm for formulating the equations, which is the specific task of the theory of molecular vibrations, was found to be much more complex. It is significant that programmes of this type have appeared only recently [20]. The solution of this problem required not only a change in the mathematical techniques but also the abandonment of most of the procedures used in manual calculation. For example, the use of standard formulae for calculating the kinematic coefficients was found to be unsuitable.

The reduction of the mathematical apparatus of the theory to a single form and its simplification inevitably concerned one of the most important sections of the theory — the consideration of the symmetry of the molecule and the calculation of the symmetry coefficients in the symmetry coordinates. All the other sections of the theory of molecular vibrations can be readily formulated in the language of vector and matrix algebra and require for their understanding a fairly limited knowledge of these branches of mathematics, but the calculation of the symmetry coefficients was based on the use of group theory, unfamiliar to the great majority of spectroscopist chemists. Despite the existence of tables of symmetry coefficients, this feature created serious difficulties in carrying out the calculations for specific molecules. The attempt by Mayants [21] to solve this problem without using group theory was thus understandable, but the method which he proposed was also tedious and was not widely accepted. A simple solution to this problem and clear selection rules depending on symmetry in the IRS were obtained only recently by introducing the concept of directed symmetry vectors and the study of their properties [22].

A most important problem, unfortunately still unsolved, is that of decreasing the arbitrary nature of the choice of force constants for polyatomic molecules. The existing modifications of the force functions have not led to a cardinal solution and cannot be regarded as satisfactory. Since direct application of the methods of quantum mechanics to the solution of this problem is still impossible, the development of the theory of molecular vibrations must apparently involve the construction of a theory which will also require the use of empirical parameters whose introduction, however, will be based on the results of quantum chemistry. The ordinary force constants should then be functions of these parameters.

In recent years the theory of intensities in the IRS has been further developed. As noted above, the work of Vol'kenshtein and El'yashevich, who laid the foundations of the theory, was followed by stagnation for several years. In this period the non-Soviet literature included a large number of papers (see the bibliography in the review by Gribov and Smirnov [23]) on the measurement of the absolute intensities of absorption bands in the IRS using methods

developed by Kemble and Bourgin[24,25], Wilson and Wells[26], and others[27]. On this basis attempts were made to calculate the dipole moments of the bonds in many molecules. The failure of these calculations (the lack of agreement between the dipole moments of the molecules determined by other methods and the values calculated from the IRS) produced a sceptical attitude towards the theory itself. Sverdlov's calculations[28-32] of the electro-optical parameters of a number of simple molecules, carried out from 1959 onwards according to the scheme of Vol'kenshtein and El'yashevich, did not greatly improve the situation, since the parameters which he found were obtained in the form of combinations which were so cumbersome that their physical significance was completely lost and their further use impossible.

Thus the theory of intensities was faced with the following tasks: the extension of the theory to any molecules (additive and non-additive), the creation of a convenient calculation scheme, the development of some of the most important general questions (the theory of characteristic intensities and the dependence of the intensities on the number of identical groups in the molecule) formulated in Vol'kenshtein's papers, determination of the numerical values of the electro-optical parameters for a number of the simplest groups, and proof that the values for these parameters are preserved in a series of molecules containing the given groups. This last problem determined the possibility of creating a set of electro-optical parameters for bonds and groups, similar to the set of force constants, and hence the possibility of using the theory to carry out numerical calculations of the absorption band intensities in the IRS. A number of papers by the authors of the present review were devoted to the solution of all these problems[33-43]. As a result it was possible for the first time to calculate the intensities of the absorption bands in the spectra of complex molecules[42,43]. In recent papers[44-46], the methods of the theory of intensities in the IRS are used to study the structure and properties of a number of compounds. It can thus now be stated that the theory which has been developed can serve as a basis for corresponding spectrochemical studies.

More work has also been carried out on the theoretical study of the electro-optical parameters for Raman spectra using a modernised form of Vol'kenshtein's calculation scheme[47-51], but the existing situation (the number of empirical parameters introduced is three times that for IRS) does not lead us to expect marked advances in this direction.

Methods for analysing molecules according to their vibrational spectra can be provisionally divided into two groups according to the nature of the problems to be solved. The first group includes methods which use only directly measurable quantities (the number of absorption bands or lines in the RS, their position on the frequency scale, and their intensities). These data make it possible to determine the symmetry of molecules and free radicals, to calculate thermodynamic functions, and to carry out qualitative and quantitative molecular analysis and the analysis of mixtures.

The second group includes methods of structural group analysis, the isolation of atomic groups with closed structure in the molecule, the study of the influence of the environment of the group, substituents, intramolecular interaction, and intermolecular interaction, and the study of rotational isomers. In these studies, in addition to the measured parameters of the spectrum, it is necessary to have additional information on the relative amplitudes of the vibrations of the parts of the molecule in a given normal vibration (the mode of the vibration), and also on those factors (the geometry of the molecule, the characteristics of the interatomic forces and interactions between the groups, the dipole moments of the bonds, etc.) which determine the position of the bands or lines in the spectrum, and their intensity and polarisation (or depolarisation). The accumulation of information of this type is generally described as the interpretation of the band (or line). A sufficiently reliable and complete interpretation of a band can be obtained only on the basis of appropriate theoretical study and model calculations.

In studies of the first type, a close combination of theoretical and experimental methods is often necessary. For example, in the calculation of the thermodynamic functions of polyatomic molecules (free energy, entropy, heat capacity), calculation makes it possible to find all the vibration frequencies, which cannot always be done by purely experimental methods, and also to distinguish, among the observed bands or lines, those due to the fundamental frequencies.

At the present time, when it is constantly necessary in chemistry to use the results of spectroscopic studies, it is absolutely essential for chemists not only to be aware of the fundamental possibilities and characteristic features of the method, in general outline at the very least, but also to be familiar with the "pitfalls" characteristic of this method. Otherwise, it is impossible to adopt a critical attitude towards published material, and this may have very serious consequences. Unfortunately, it must be said that although the method of vibrational spectroscopy has for long been fruitfully used in chemical studies, a very large number of chemists, even sometimes those who make fairly extensive use of the infrared spectra and Raman spectra of polyatomic molecules, have insufficiently clear ideas regarding the most important aspects and concepts of the method. This situation has apparently arisen as a result of the fact that existing publications on the problems of vibrational spectroscopy can be fairly sharply divided into theoretical publications intended for specialists in this field and, if we can use the expression, experimental publications based chiefly on various types of empirical studies of individual classes of compound. The latter often contain very valuable material but their perusal gives an oversimplified and often incorrect picture of the methodology of vibrational spectroscopy.

It is of course impossible in a single paper to outline even briefly the essential features of the many important and interesting problems of vibrational spectroscopy. We shall therefore restrict ourselves to two of the most important: the influence of kinematics on the position of the frequencies in the spectrum, and its consequences, and also the problem of determining force constants. It is these two problems which arise most frequently in spectrochemical practice, and without a clear understanding of these problems any serious spectroscopic study of the structure and properties of polyatomic molecules is impossible. Most errors in spectrochemical work, moreover, are due to neglect of kinematic factors.

2. ELEMENTS OF THE THEORY OF VIBRATIONS OF POLYATOMIC MOLECULES

The appearance of the discrete vibrational spectrum of a polyatomic molecule results from the existence of definite

energy levels in the molecule. Of fundamental importance in the discussion of the problems of energy levels in polyatomic molecules is the possibility of examining separately, with a reasonable degree of approximation, the various forms of motion for the particles in the molecule: the motion of electrons, vibration of nuclei, rotational motion of the molecule as a whole, and finally the translational motion of the molecule.

We shall be interested in the purely vibrational motion, that is, the movement of the atoms in a force field which is determined by the given electronic state of the molecule. The equations of motion are usually formulated in the system of natural vibrational coordinates q_i (the changes in the equilibrium bond lengths, valency angles, etc.), the number of which is equal to the number of vibrational degrees of freedom for a system of N particles, that is, $3N$ - 6 (or $3N$ - 5 for linear molecules)†.

The coordinates q_i, which characterise the departure of the configuration of the molecule from the equilibrium configuration and become equal to zero for the equilibrium state, describe the state of the separate parts of the molecule. For small vibrations (of the order of hundredths of an ångström unit) they are linearly related to the Cartesian coordinates of the displacement of the atoms from their equilibrium positions, so that the kinetic energy of the vibrating atoms is described in the generalised momenta p_i corresponding to the coordinates q_i in the quadratic form

$$T_{\text{kin}} = \frac{1}{2}\sum_{i,j} \tau_{ij}\, p_i p_j,$$

with coefficients τ_{ij}, which can be calculated if the equilibrium geometry configuration of the system is known. The potential energy, which has the significance of the difference between the energies of the displaced and equilibrium configurations, depends only on the relative coordinates of the nuclei to a reasonable degree of approximation and is described by the function $V(q)$. By expanding $V(q)$ into a series with respect to powers of q_i close to the equilibrium position, it is possible to represent the potential energy of any displaced state by means of a set of derivatives of $V(q)$ with respect to q_i of different order and a set of values of q_i. These derivatives are constant for any small deformations of the molecule and are determined by the properties of the given electronic state. It is assumed (in the so-called harmonic approximation which is satisfactory for small vibrations) that the displacements of the atoms from the equilibrium positions during the vibrations are symmetrical and that the resulting restoring forces are linearly dependent on the magnitude of the displacement. We then have (with allowance for the conditions of stable equilibrium)

$$V = \frac{1}{2}\sum_{i,j} K_{ij} q_i q_j$$

The coefficients $K_{ij} = \left(\dfrac{\partial^2 V}{\partial q_i\, \partial q_j}\right)_0$ (the force constants) are at present found only from measurements of the vibrational frequencies of the molecule. This feature, which makes the theory of vibrations semi-empirical, is its chief weakness, since it restricts the possible applications of the theory in calculations chiefly to organic molecules. In order to solve the equation for the vibrations it is necessary to change to new coordinates, which have been called normal coordinates. When normal coordinates are used the expressions for the kinetic and potential energies acquire the form $T_{\text{kin}} = \frac{1}{2}\sum_i P_i^2$ and $V = \frac{1}{2}\sum_i \lambda_i Q_i^2$, that is, they do not contain the terms P_iP_j and Q_iQ_j $(i \neq j)$. This can be achieved by the following change of variables (coordinates)

$$\begin{aligned} q_1 &= l_{11}Q_1 + l_{12}Q_2 + \ldots + l_{1n}Q_n, \\ &\ldots\ldots\ldots\ldots\ldots \\ q_n &= l_{n1}Q_1 + l_{n2}Q_2 + \ldots + l_{nn}Q_n \quad (n = 3N - 6). \end{aligned}$$

The coefficients λ_i and elements l_{ij} are found from the solution for the system of $3N$ - 6 algebraic equations:

$$\begin{cases} (d_{11} - \lambda)q_1 + d_{12}q_2 + \ldots + d_{1n}q_n = 0 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ d_{n1}q_1 + d_{n2}q_2 + \ldots + (d_{nn} - \lambda)q_n = 0 \end{cases} \qquad (1)$$

where $d_{ij} = \sum_m \tau_{im}K_{mj}$.

This system of equations assumes a non-trivial solution for q_i only for certain values of the factor λ, which are calculated from the condition for solvability of the system; this makes it possible to formulate an equation of degree $3N$ - 6 in λ (the secular equation). For each root λ_i with subscript i for this equation we find from system (1) a set of unknowns $q_1 \ldots q_n$, whose value is given by the elements l_{ki} $(k = 1, \ldots, n)$ in the formulae for the transformation of the coordinates.

After the change to normal coordinates, the equation for the vibrations is broken down into $3N$ - 6 first-order equations, each of which describes a linear harmonic oscillator and can be readily solved. The frequencies of the vibrations of these oscillators (normal vibrations) will be equal to $\nu_i = \sqrt{\lambda_i}$. To characterise the vibrations of the individual parts of the molecule, it is necessary to change again from coordinates Q_i to natural coordinates. In each normal vibration, only one coordinate Q_i will be different from zero. We then have, for example, for the first coordinate according to the formulae for transformation of the coordinates,

$$q_1 = l_{11}Q_1,\ q_2 = l_{21}Q_1,\ \ldots,\ q_n = l_{n1}Q_1. \qquad (2)$$

Thus the relative amplitudes of the changes in all the natural coordinates in the vibrations will be given by the numbers l_{k_1}, and the relative phases will be determined by the signs of l_{k_1}. The set of elements l_{k_1} is therefore called the mode of the given normal vibration. It can also be seen that the changes in all q_i in a normal vibration will take place with frequency ν_i and that all q_i pass through zero simultaneously.

Despite its limitations (the harmonic approximation), the concept of normal vibrations is important in the theory of the vibrations of polyatomic molecules and provides a basis for solving the most varied problems.

3. CHARACTERISTIC VIBRATIONS OF POLYATOMIC MOLECULES

Study of the properties of normal vibrations makes it possible to reach general conclusions regarding the behaviour of the vibrational frequencies in the spectra on

† Strictly speaking, the coordinates used are the projections of these changes on the equilibrium unit vectors of the molecule (the directing vectors of the bonds, valency angles, etc.), which undergo translational movement and rotate with the molecule.

going from a given atomic group in one molecule to the same group in another molecule. This problem is important in applied spectroscopy, since the great majority of present-day spectrochemical investigations are aimed at studying the influence exerted on a given group of atoms by its immediate environment and in some instances by its more distant environment. Measurements are usually made of the displacements of the vibration frequencies for the given group with change in its environment. The magnitude of these displacements and the observed regular features in a series of compounds contain information on the structure and properties of the group itself and on the changes in the structure of the molecule. This obviously raises a most important question — does the displacement or change in the intensity of the absorption bands characteristic of a given group provide a sufficient indication of breakdown of its structure? It is known, for example, that this is in fact the case for the electronic absorption spectra of polyatomic molecules. This feature, and also the fact that some experimental workers are insufficiently familiar with the general theory of the vibrations of polyatomic molecules, leads to a situation where the authors of whole series of papers tend to interpret any change in the position or intensities of the vibrational absorption bands in the IRS or lines in the RS due to a given group as a sign of breakdown in the structure of the group; they forget long-familiar simple experimental facts which show directly that appreciable displacements of the frequencies may have no connection with breakdown of the electronic structure of the molecule. For example, the frequency of the vibrations of the C≡C bond is extremely stable in various compounds but changes from 1974 cm^{-1} in the acetylene molecule to 1851 cm^{-1} in monodeuterioacetylene and to 1765 cm^{-1} in dideuterioacetylene, that is, by a total of more than 200 cm^{-1}, although it may be assumed with a reasonable degree of approximation that no changes in the properties of the electronic ground state of the molecule take place when H is replaced by D.

It is quite obvious that without a clear understanding and detailed study of all the factors leading to change in the bands studied in the spectrum, no reliable conclusions can be reached regarding changes in the molecule.

Here we come up against the most important concept of characteristic vibrations. The existence of characteristic vibrations has to a large extent been responsible for the extensive application of vibrational spectroscopy in spectrochemical practice. At the same time no topic has been associated with so many errors as the interpretation of characteristic vibrations‡. To examine the essential features, let us take a simple example.

Let us imagine a given group of atoms. Let us assume that this group is present in a molecule. Since each vibration of the molecule is characterised by its frequency and mode, it is natural to classify vibrations according to their frequencies and modes [52]. When the frequencies of vibrations are measured, their mode is not recorded directly, but it is of decisive importance in the study of the intensities of vibrations. There may be vibrations which are stable with respect to frequency but not with respect to mode, so that the absorption bands in the IRS and lines in the RS retain their position in the spectrum, but with a change in intensity.

‡ It is paradoxical that in this an undesirable part has been played by various tables of characteristic vibrations, which in many cases are accepted too literally.

We shall describe a vibration as characteristic with respect to frequency for a given group if one of the normal vibrations of the molecule coincides in frequency with one of thenormal vibrations of the given group as a free molecule. If one of the normal vibrations of the molecule coincides with a normal vibration of the given group with respect to mode, that is, if the vibration is such that only the configuration of the isolated group changes, this vibration will be described as characteristic with respect to mode for the given group. If both conditions are satisfied, the vibration will be described as characteristic with respect to frequency and mode or completely characteristic. This distinction is meaningful (although strictly speaking there cannot be vibrations characteristic with respect to frequency but not characteristic with respect to mode, and vice versa), because the degree of non-characteristic nature of different types is different in a very large number of instances. This classification is to some extent arbitrary and approximate, but it has nevertheless been found to be extremely convenient in practice.

There may be instances where the above properties of normal vibrations are preserved in a series of molecules containing a given group. It is then usual to speak of the stable characteristic nature with respect to frequency, mode, and frequency and mode for a given group. The property of stability in characteristic nature with respect to frequency and with respect to frequency and mode is manifested by the appearance of absorption bands or lines in the same region of the IRS for a series of molecules containing the given group. This in turn makes it possible to carry out the qualitative analysis of unknown substances and mixtures from their IRS and RS and their structural group analysis.

Let us consider the basic hypotheses of the theory of characteristic vibrations. For this purpose let us examine a given group of atoms (radical) and let us introduce it in turn into different molecules of a given series, that is, let us examine a set of molecules consisting of two groups (first and second), where the first group remains unchanged. It is obvious that in these molecules we can expect the appearance of characteristically normal vibrations only if the contribution made by the group being studied is additive. It is also clear that the distortions of the normal vibrations of the selected group as a free group when it is attached to a molecule will be smallest when the group is attached to the molecule through a single atom. We shall therefore restrict ourselves to the case where the group has only one atom attached to the molecule.

Let us divide the natural coordinates characterising the vibrations of molecules into three sets: coordinates describing the movement of the first and second groups as free molecules (natural vibrations of the groups), and coordinates describing the movements of the first and second group relative to one another. If the first and second groups are assumed to be additive, with a reasonable degree of approximation, the expression for the potential energy need take account only of the coefficients K_{ij} (force constants), relating to the internal coordinates of the first and second groups and intermediate coordinates. Here the force constants of the groups will depend only on the properties of these groups taken separately. In the formulation and solution of the equations for the vibrations of the first and second groups as free molecules and the equation for the vibration of these groups relative to one another, we can change from natural coordinates to normal coordinates for each of the groups. This form of representation is convenient in the investigation of the nature of

the characteristic vibrations, since it makes it possible to describe the normal vibration of a molecule as the superposition of the normal vibrations of the individual groups. It should be remembered that the change to normal coordinates can be regarded as the construction of a molecular model in which the real system is replaced by a set of one-dimensional oscillators — bonds — selected in definite fashion. When two groups are combined to form a single molecule the various normal oscillators of the first and second groups will interact with one another and the resulting vibration will be complex. In order to analyse the qualitative picture we can restrict ourselves to the instance where only pairs of normal oscillators of the first and second groups interact, that is, to the interaction of pairs of hypothetical "bonds".

The equation for the vibrations of this pair of "bonds" will have the form

$$\begin{cases}(\lambda_1^{(0)}-\lambda)Q_1+\tau\lambda_2^{(0)}Q_2=0,\\ \tau\lambda_1^{(0)}Q_1+(\lambda_2^{(0)}-\lambda)Q_2=0,\end{cases} \qquad (3)$$

where $\lambda_1^{(0)}$ and $\lambda_2^{(0)}$ are the squares of the frequencies of the selected pair of normal vibrations of the first and second groups (these frequencies are usually called partial frequencies), and Q_1 and Q_2 the corresponding normal coordinates, which have the physical significance of the "elongation" of the hypothetical "bonds". The quantity τ (the coefficient of kinematic interaction of the pair of oscillators) is inversely proportional to the mass of the atom which is common to both groups and to the cosine of the angle α between the "directions" of the normal oscillators.

When the common atom has a high mobility and the angle α approaches 180°, the value of τ may become appreciable. It then follows from Eqn. (3) that the normal vibrations of the pair of "bonds" will not have frequencies equal to $\lambda_1^{(0)}$ and $\lambda_2^{(0)}$ and modes $Q_1 = 1$, $Q_2 = 0$ and $Q_1 = 0$, $Q_2 = 1$ respectively, that is, they will not be characteristic either with respect to frequency or with respect to mode for each of the "bonds". We thus reach an extremely important conclusion: the vibrations of a group of atoms may change both with respect to frequency and with respect to mode in a series of molecules containing the given group merely as a result of its kinematic associations with the rest of the molecule, even if the structure of the group itself remains quite unchanged. Thus the displacement of absorption bands assigned to a given group of atoms, or a change in their intensity (the latter depends very strongly on the mode of the vibrations) for different types of substitution outside the given group cannot provide a sufficient indication for breakdown of the structure of the group. On the other hand, absence of change in the frequency, and more particularly, the intensity of a band in the IRS or of a line in the RS indicates with a very high degree of probability that the group itself remains unchanged.

Despite its obvious nature, this feature has somehow been overlooked in many papers. It is sufficient to point out that errors of this type are not infrequent in Bellamy's well-known monograph[53], a handbook of the majority of spectrochemists. Displacements of frequencies as a result of kinematic associations are particularly large for groups situated inside a molecule but they may reach 100 cm^{-1} or more even for terminal groups. A classical example of this type is the marked displacement of the bands and changes in their intensities on deuteration, which often leads to a change in frequencies corresponding to the vibrations of groups in which no replacement of H by D has taken place.

The possibility of appreciable displacements of absorption bands or lines in the IRS as a result of kinematic interaction is responsible for fundamental difficulties in the study of molecules by the methods of vibrational spectroscopy. In order to make allowance for kinematic factors it is almost always necessary to calculate the frequencies and modes of vibrations for the selected molecular models. It is most convenient to begin with calculations for simplified models and then to proceed to more complicated structures as required.

Let us assumed that the atom by means of which the group is attached to the molecule is much heavier than the other atoms. It will then undergo almost no displacement when the group vibrates. It is obvious that then we shall be dealing with vibrations which are characteristic with respect to frequency and mode for the given group. In actual fact this corresponds to the case where $\tau = 0$. This property is shown, for example, by the vibrations of CH, OH, NH, CH_2, CH_3, NH_2, and other groups containing a light terminal atom.

For most groups $\tau \neq 0$. Of practical interest in this connection are the two extreme cases: $\lambda_1^{(0)} = \lambda_2^{(0)} = \lambda$ and $\lambda_1^{(0)} \gg \lambda_2^{(0)}$ $(\lambda_1^{(0)} \ll \lambda_2^{(0)})$.

Let us assume that $\lambda_1^{(0)} = \lambda_2^{(0)} = \lambda^{(0)}$; by solving Eqn. (3) we find that the kinematic interaction of the corresponding pair of normal vibrations of the first and second groups leads to the production of two vibrations, for which the squares of the vibrations are $\lambda_{1,2} = \lambda^{(0)} \pm \tau\lambda^{(0)}$ and the relative amplitudes (modes) are $Q_1^{(1)} = 1$, $Q_2^{(1)} = 1$, $Q_1^{(2)} = 1$, and $Q_2^{(2)} = -1$.

Thus the interaction of two normal vibrations of groups with identical frequencies leads to splitting of the frequencies and "mixing" of the amplitudes. This is one example of mechanical resonance. For its production, the natural vibrations of the first and second groups must contain vibrations with identical frequencies, and the displacement of the common atom in these vibrations of the first group should differ from zero and should not take place in a direction perpendicular to the displacements in the resonating vibration of the same atom of the second group. When resonance takes place the vibration of the first group extends throughout the entire molecule and will not be characteristic for this group either with respect to frequency or with respect to mode. The phenomenon of mechanical resonance is observed particularly frequently in the vibrations of molecular skeletons, so that they are almost never characteristic for individual bonds. This can readily be seen, for example, from Table 1, which gives the calculated modes of vibrations of the polyene chain in the $C_2H_5OOC[CH{=}CH]_4COOC_2H_5$ molecule.

If $\lambda_1^{(0)} \gg \lambda_2^{(0)}$, we obtain vibrations for which the squares of the frequencies are equal to

$$\lambda_1 \simeq \lambda_1^{(0)} + \frac{\tau^2\lambda_1^{(0)}\lambda_2^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}}; \quad \lambda_2 \simeq \lambda_2^{(0)} - \frac{\tau^2\lambda_1^{(0)}\lambda_2^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}}$$

and the relative amplitudes are

$$Q_1^{(1)} = 1; \quad Q_2^{(1)} = \frac{\tau\lambda_1^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}} \to \tau \neq 0,$$

$$Q_1^{(2)} = \frac{-\tau\lambda_2^{(0)}}{\lambda_1^{(0)}-\lambda_2^{(0)}} \to 0; \quad Q_2^{(2)} = 1.$$

TABLE 1*. Mode of the vibrations of the polyene chain in $C_2H_5OOC(CH=CH)_4COOC_2H_5$.

Symmetry	ν, cm^{-1}	Mode of the vibration			
		Q	q	Q_1	q_1
A_g	1623	—0.28	0.05	0.27	—0.24
	1597	0.25	—0.31	0.26	—0.18
A_u	1626	0.15	—0.30	0.35	—
	1573	—0.36	0.10	0.19	—

* Q and q are the normalised modes of the vibrations in symmetry coordinates, characterising the changes in the lengths of the double and single bonds respectively (from the start of the chain to the centre).

Thus both frequencies will differ from the natural frequencies of the vibrations of the first and second groups, and if the natural frequency of the first group is greater than the natural frequency of the second group, its vibration will extend throughout the whole molecule with coefficient τ. If $\lambda_1^{(0)} \gg \lambda_2^{(0)}$, the relative displacement of the λ_1 relative to $\lambda_1^{(0)}$ will be small and we can speak of the production of vibrations characteristic for the first group with respect to frequency but not with respect to mode. This property is shown, in particular, by the stretching vibrations of non-conjugated C=C, C≡C, N=N, and certain other bonds. For example, in the ethylene molecule for the 1620 cm^{-1} vibration the extension of the C=C bond is accompanied by a marked change (of up to 50% in arbitrary units) in the HCC angles. In the stretching vibration with frequency 2270 cm^{-1} in the acetonitrile molecule, usually assigned to the vibration of the C≡N bond, a significant part is played by the neighbouring C–C bond (up to 50%). Neglect of this feature has led, in particular, to an incorrect explanation[54] for the almost eightfold change in the intensity of this absorption band when hydrogen atoms are replaced by chlorine[45].

The second normal vibration of the set of coupled oscillators when kinematic interaction takes place will have a frequency less than $\lambda_2^{(0)}$ (for $\tau > 0$), but it does not extend throughout the whole molecule. There appear vibrations which are not characteristic with respect to frequency for the first group but are characteristic with respect to mode.

Let us take one simple example (the HCN molecule) which effectively illustrates the case of the interaction of the vibrations of two groups described above. Since the C atom is much heavier than the H atom, the H–C vibration will be characteristic with respect to frequency and mode. Accurate calculation[39] gives $\nu_1 = 3312$ cm^{-1} and $q_1 = 1$ (stretching of the C–H bond) and $q_2 = -0.136$ (stretching of the C≡N bond). The frequency of the vibrations of the C≡N bond is lower than the frequency of the vibrations of the C–H bond, so that in the C≡N vibrations the change in the length of the C–H bond should be less than the change in the C≡N bond. We have $\nu_2 = 2089$ cm^{-1}, $q_1 = 0.37$, and $q_2 = 1$. When H is replaced by D for C≡N vibrations the decrease in the D–C frequency relative to the H–C frequency makes possible resonance of the D–C and C≡N vibrations. We have in fact: $\nu_1 = 1921$ cm^{-1}, $q_1 = 1.13$, and $q_2 = 1$. "Mixing" of the vibrations takes place. This case of resonance and in general change in the mode of the vibrations is found very frequently in deuteration, so that, as already noted, deuteration is often accompanied not only by displacement of many absorption bands in the spectrum but also by an extremely sharp change in their intensities. This may even introduce difficulties in the interpretation of the bands. A good example of this is provided by the acetonitrile molecule[44]. Its spectrum shows vibrations with frequencies of 919 cm^{-1} and 1059 cm^{-1}, which may be interpreted as the stretching vibration of the C–C bond and external bending vibrations of the HCC angles. It might seem that this interpretation can be readily verified by deuteration. When this is done we obtain two frequencies at 850 cm^{-1} and 833 cm^{-1}, that is, both of the controversial bands are displaced by a considerable amount. This is again due to resonance of the vibrations.

To summarise, we can reach a number of conclusions regarding the possibility of existence of vibrations characteristic of a given group. These conclusions are qualitative in character, but they may help, in a large number of instances, to achieve rapid orientation in a spectrum and evaluation of various phenomena, and also to select the analytical absorption bands necessary for solving appropriate specific problems. They can of course be used only to explain sufficiently marked effects.

1. If the atoms of the first group, shared with another part of the molecule, are much heavier than all the other atoms of this group, we should observe vibrations which are characteristic with respect to frequency and with respect to mode for the given group. The position of the band in the spectrum and its intensity (if the group is additive and if certain other conditions are satisfied)[33] will be determined only by the parameters of this group. When these conditions are satisfied in a series of molecules we shall observe absorption bands whose frequency and intensity are preserved. With substitution of any groups in the molecule, the displacements of the bands of the group being studied and the changes in their intensity will be associated with breakdown of its structure.

2. A vibration will also be characteristic with respect to frequency and with respect to mode when in a given normal vibration the set of atoms shared with the remainder of the molecule does not undergo displacement or when this displacement takes place perpendicular to the displacements of these atoms for all normal vibrations of the remainder of the molecule. The frequency and mode of this vibration is again determined chiefly by the properties of the given group, but they will now be more sensitive to the environment, since replacement of atoms outside the group may lead to breakdown of the above condition that the movements of the common atoms in the normal vibrations of the first and second groups be at right angles to one another.

3. If any of the normal frequencies of the selected group and one of the normal vibrations of the remainder of the molecule coincide and the common atoms in these vibrations do not move in mutually perpendicular directions, resonance between the vibrations of these two groups is possible. We then obtain two normal vibrations of the entire molecule, whose frequencies and modes will not coincide with the frequencies and modes of the component vibrations, that is, the vibration will not be characteristic with respect to frequency and mode, in particular for the first group. The position and intensity of the corresponding band in the spectrum will be determined by the properties of the entire molecule and will change with substitution outside the group being studied. As already noted, the various skeletal vibrations of organic molecules are extremely common examples of such vibrations.

4. If the frequencies of the normal vibrations of a given group are greater than the frequencies of the normal vibrations of the adjoining part of molecule and if the common atoms are mobile in the vibrations, we may observe vibrations which are characteristic with respect to frequency for the group being examined but which are not characteristic with respect to mode. The position of the corresponding bands in the IRS or of lines in the RS will be determined by the properties of this group, and their intensities will depend on the properties of the environment (they will sometimes even be determined entirely by the properties of the environment[33]). With substitution outside the group being examined, the frequencies of its vibrations may remain unchanged, but the intensities must alter. An example of such vibrations is provided by the previously mentioned stretching vibrations of the C≡N bond in the molecules of acetonitrile and trichloroacetonitrile. The frequencies of the C≡N vibrations in these molecules are extremely close (2267 cm^{-1} and 2256 cm^{-1} respectively), but the intensities of the absorption bands differ appreciably.

5. If the frequencies of the normal vibrations of the group being considered are lower than the frequencies of the normal vibrations of the surrounding groups, vibrations may be produced which are characteristic with respect to mode for the given group but which are not characteristic with respect to frequency. As an example we can take the bending vibrations of the C–C≡N group in the CH_3CN and CCl_3CN molecules. These vibrations show an appreciable difference in frequency (380 cm^{-1} and 160 cm^{-1} respectively) but have almost identical modes[44,45].

All our discussion has concerned the instance where the groups are additive, that is, where there is no mutual electronic influence. We have seen that, even with this condition, it is only as a result of purely mechanical factors that the absorption bands or lines observed in the IRS can undergo appreciable displacement and change in intensity. For real molecules this treatment is often too approximate, and the displacements of the absorption bands observed in practice for various types of substitution result from a large number of factors.

In recent years a large number of papers have given correlations, for many functional groups, between the vibration frequencies (and in a number of instances, the intensities) and the electronegativities of the substituents, the Hammett constant σ, the Taft constant, etc. The search for various types of correlation can only be welcomed, but it must be remembered that, as shown by the above discussion, the reduction of the large number of factors determining the value of the vibration frequencies, even of the characteristic vibrations for an individual group, to a single factor cannot in general be justified. In particular, such correlations are meaningful only when the influence of kinematics is taken into account or is known to be small. Unfortunately, this last feature is not always recognised, so that in a number of instances the relationships obtained have no physical significance.

The chief requirement for the correct utilisation of spectroscopic data is an estimate (as far as possible quantitative) of the influence of various parameters on the position and intensity of the frequencies. This is tedious but it is the only way. A basis for such studies may be provided by the existing theory of the vibrations of polyatomic molecules; despite a number of inadequacies, this theory is quite capable of solving a large number of very important general and specialised problems.

The simplest is the determination, on the basis of the assumed symmetry of the molecule, of the number of fundamental vibrations which will be shown in the infrared and Raman spectra. Comparison of the calculated total number of vibrational frequencies active in a given spectrum, or of only that fraction of the vibrations which should be observed in a narrow range of the spectrum, with the experimentally-observed number of frequencies often makes it possible to establish unambiguously the symmetry of the molecule being studied. This method has for long been widely applied in the study of the structure of molecules, particularly in the gaseous phase. For example, the absence from the infrared spectrum of frequencies observed in the Raman spectrum, and vice versa (mutual exclusion) indicates unambiguously the presence of a centre of symmetry. In particular, the use of the mutual exclusion rule often makes it possible to identify reliably the structure of *cis*- and *trans*-derivatives of ethylene and diene compounds with identical substituents.

By solving the equation for the vibrations for the example where a set of force constants is known even provisionally, it is possible to calculate all the vibration frequencies of the molecule. The importance of this even approximate calculation is that it makes it possible to find the frequencies of vibrations which are not revealed either in the absorption spectrum or in the Raman spectrum. Moreover, not all the frequencies of the vibrations can be determined experimentally because of the low intensity of the corresponding lines and bands or because of the absence of suitable instruments (for example, for measurement of frequencies in the infrared spectrum in the range below 400 cm^{-1}). A molecule often has a number of identical frequencies (degeneracy with respect to symmetry or accidental degeneracy). It is impossible to detect this effect experimentally. A knowledge of the complete vibrational spectrum is absolutely necessary, for example, for calculating the thermodynamic functions of a molecule.

We can also find the amplitudes of the displacements of atoms from their equilibrium positions during vibrations or the amplitudes of the changes in the equilibrium geometric parameters of the molecule, that is, the mode of the vibration. The fundamental importance of calculations of this type is obvious, since they provide a basis for the interpretation of spectra. Calculation methods make it possible to determine sufficiently accurately which groups are producing the vibrations responsible for the appearance of various frequencies in the spectra. It must be stated directly that all present-day interpretation of spectroscopic data is based to a certain extent on the appropriate calculations.

There are many papers devoted to the calculation of the frequencies and modes and to determination of the force constants. Work by Soviet authors has some advantages over other work. In the first place, all the work has been carried out in a single system of coordinates by a single procedure for complete classes of compounds, and this has made it possible to obtain data which are comparable for different molecules and also to create a single set of force constants, and in the second place the authors have tried to select a potential function in general form with allowance for all possible interactions. A list of molecules for which theoretical studies have been carried out in the USSR is given in the Appendix (p. 227).

The proportion of the total number of spectroscopic studies devoted to calculation is quite insufficient. This is particularly true of the spectra of inorganic compounds, where it is difficult to make extensive use of existing

methods of calculation, for purely objective reasons (the impossibility of using for the calculations the spectra of isotopically-substituted molecules and the absence of homologous series).

Another noteworthy feature is that the methods of calculating the frequencies and modes of vibrations are as yet used only very rarely to solve various problems of molecular structure. The great majority of calculations which have been carried out, aimed at interpreting the observed spectra, are based on a molecular structure which is already known. This approach was unavoidable until a basic set of force constants for polyatomic molecules had been developed. It is now desirable, however, that these methods should be widely introduced into spectroscopic laboratory practice, particularly since the use of fast computers makes it possible to test many models without great effort.

In particular, computer methods are indispensible in spectroscopic studies aimed at investigating the influence of various types of substitution, breakdown in the geometric structure, etc. As shown above, here the observed changes in the frequencies in the spectra may be related to a change in the force field of the molecule or to a change in the masses or geometric parameters.

A characteristic example in this connection is that of the stretching vibrations of the C≡N bond in the HCN, CH_3CN, CCl_3CN, and $(CN)_2$ molecules. The frequencies and intensities of the absorption bands due to the C≡N vibrations in these molecules differ appreciably (for example, the frequencies have the values 2089, 2267, 2256, and 2329 and 2149 cm^{-1} respectively). At first sight the experimental data indicate a significant difference in the properties of the C≡N bonds in these compounds. This explanation has in fact been put forward [54], but theoretical analysis [39,44,45] has shown that the force and electro-optical parameters of the C≡N bond remain almost unchanged in the above series of molecules and that the appreciable changes in the corresponding frequencies and intensities of the absorption bands are due chiefly to the influence of kinematic factors. Another example is provided by the molecules of *gem*-dinitroethane and trinitromethane, whose spectra show a marked displacement of the frequencies of the so-called symmetrical stretching vibrations of NO_2 [1402 cm^{-1} and 1343 cm^{-1} for $C_2H_4(NO_2)_2$ and 1371 cm^{-1} and 1305 cm^{-1} for $HC(NO_2)_3$]. Appropriate calculation [55] showed that this displacement can also be attributed entirely to kinematic factors. Allowance can readily be made for these effects using calculation methods. This, of course, is not the only value of calculation methods. Often it is possible to obtain extremely valuable information on molecular structure. For example, theoretical analysis of the frequencies of the normal vibrations and the intensities of the absorption bands in the IRS of the molecules of butadiene, hexatriene, and other linear polyenes with longer chains [56] has made it possible to study the important problem of double-bond conjugation. In particular, it was shown that in the ground electronic state of the molecules with alternating double and single bonds there is appreciable bond interaction due to partial displacement of the π-electron density from the double bonds to the single bonds. No tendency towards further levelling of the bond orders takes place with increase in the length of the polyene chain. It was also shown that in conjugated molecules in the stationary state the intramolecular mutual influence of substituents is rapidly extinguished with increase in the length of the conjugated chain, despite the π-electron delocalisation.

In the study of characteristic vibrations, calculation methods help to establish the maximal group of atoms whose vibrations will exhibit the property of characteristic nature of a given type. In particular, theoretical study of the characteristic nature of the vibrations has shown that the reproducebility of various frequencies in a spectrum does not always indicate that the vibration is localised. This must be taken into account in experimental practice. A rigorous solution to the problem of the characteristic nature of vibrations of given functional groups can be obtained only on the basis of appropriate theoretical analysis. In this, in order to determine the smallest group of atoms responsible for a given characteristic frequency, it is sufficient to know merely the orders of magnitude of the force constants. By then calculating the sensitivity of this frequency to changes in various quantities characterising the molecule as a mechanical system, it is possible to investigate the influence of the quantities used in the calculation and sometimes the nature of the changes in this frequency on going to other molecules.

The calculation of the sensitivity of the characteristic frequencies to change in various quantities for three-dimensional molecular configurations can be used successfully to identify rotational isomers of certain molecules from the vibrational spectra.

Calculation methods should undoubtedly play an important part in the study of intermolecular interactions and molecular association, where the interpretation of the observed changes in the spectra often presents an extremely complex problem.

The importance of theoretical methods in vibrational spectroscopy will undoubtedly increase greatly in the near future.

4. FORCE CONSTANTS OF POLYATOMIC MOLECULES AND THEIR DETERMINATION

The most important problem in vibrational spectroscopy is to determine the coefficients K_{ij} in the expression for the potential energy. A knowledge of these quantities is necessary for carrying out numerical calculations on the vibrational spectra of polyatomic molecules. For the determination of the coefficients τ_{ij} in the expression for the kinetic energy it is sufficient to have information on the geometric structure of the molecule and the distribution of the masses, obtained independtly using other methods for studying molecules, but in the present state of the theory the force constants can in practice be determined only on the basis of experimentally measured frequencies of vibrations. This type of problem is described as the inverse spectroscopic problem and is specific for the theory of molecular vibrations.

In the study of polyatomic molecules a characteristic closed logical circle has developed: numerical calculations on molecular spectra require the introduction of quantities which are themselves found from these spectra. A way out of this situation is possible only because it has been found that some force constants can be put equal to zero and, moreover, that the force constants corresponding to individual additive groups remain unchanged within certain limits in a series of molecules containing these groups. This makes it possible to use the numerical values of the force constants, found from some molecules, for calculations on the spectra of related compounds. A consequence of this is the restriction of the possible

application of the theory chiefly to calculations on organic compounds.

When force constants are used for numerical calculations of spectra and for reaching conclusions regarding the structure of a molecule and the nature of chemical bonds it is necessary to understand clearly the physical significance of the quantities and their complex nature. Force constants depend not only on the properties of interatomic forced but also on the method adopted for describing the vibrations (the system of coordinates).[52] The same model of interatomic forces will be expressed in different ways in different systems of coordinates. In the general case when interactions take place between all the atoms, the force constants will not be characterised merely by the individual structural elements but will depend on the properties of the whole molecule.

It may be said that the force constants are representations of the elastic properties of the interatomic forces in the system of coordinates selected. Thus the choice of a working system of coordinates should correspond to the model of interatomic forces adopted. A criterion of the correspondence between the model and the system of coordinates is the smallness of the elements K_{ij} $(i \neq j)$ compared with K_{ii} $(K_{ii} \gg K_{ij})$. This requirement in turn arises because here the vibrations of the molecules can be described by the minimum number of empirical parameters (force constants); this is fundamental, since, as already noted, they are determined on the basis of experimental data on the frequencies of vibrations.

Let us examine briefly various models of interatomic forces.

Central-forces model. The central-forces model involves the assumption that the forces of interaction between all pairs of atoms depend only on the distance between the atoms and act along the straight line joining them. This model has not justified itself and is now almost never used. The inadequate nature of the model is particularly clearly seen for the bending vibrations of linear molecules. The frequencies of these vibrations should then be equal to zero, but this contradicts experimental results.

Valency-forces model. The valency-forces model is free from the above difficulties associated with the central-forces approximation for linear molecules and is closer to chemical ideas regarding interatomic forces. It is thus not accidental that the valency-forces model gives much better results in the great majority of cases. This model has formed the basis for all fundamental calculations on the spectra of polyatomic molecules in the Soviet Union and for the creation of a set of force constants suitable for the theoretical analysis of a very large number of compounds. In this model we consider the forces related to the change in the bond lengths, valency angles, and other elements forming the natural vibrational coordinates. In the expression for the potential energy it is usual to introduce, in addition to the elements K_{ii}, a series of small elements K_{ij}, that is, to use the valency-forces model not in the pure form but with slight corrections. The chief advantage of this approximation is the possibility of examining the individual structural elements of the molecule, which may be expected to be sufficiently closed units, and thus to reduce the problem of the force field of the molecule to the problem of studying the properties of its individual elements. The following rules have been empirically established for selecting the force constants in this model in the system of coordinates formed by the changes in the bond lengths, valency angles, etc.

1. The largest force constants are encountered for the bond stretching coordinates; the force constants for the other coordinates are smaller by approximately one order of magnitude.

2. The constants K_{ij} $(i \neq j)$ usually must be taken into account only for coordinates having common atoms (for angular coordinates, a common bond). This rule applies usually, but there may be exceptions. It is difficult to verify it accurately, since the attempt to find the values of force constants from experimental data is usually made (see below) on the assumption that this rule applies.

Unfortunately, these rules do not eliminate the arbitrariness in the choice of force constants, although they limit it to some extent. This intermediate character is still appreciable, and this is the weakest aspect of the present-day theory of the vibrational spectra of polyatomic molecules. Thus the actual calculations on the spectra in many instances are model calculations and this must be taken into account when theoretical methods are used to solve a given spectrochemical problem.

Analysis of the experimentally-obtained expressions for the potential energy shows that the appearance of the elements K_{ij} $(i \neq j)$ often leads to a change in the corresponding elements K_{ii}, that is, a definite functional relationship exists between K_{ij} and K_{ii}. This relationship is not examined in the valency-forces approximation. An attempt to take account of this functional relationship is made in the approximation of Urey and Bradley, which is based on an approximation of the valency-forces type but which includes several additional terms corresponding to central forces between atoms which are not joined by valency bonds. With the inclusion of the extra coordinates thus produced in the force-constants matrix, there appear coefficients for the interaction of the bonds with one another and the angle, with a simultaneous change in their force constants. Thus the introduction of the force constant for the interaction of the pair of terminal atoms in addition to the angular elasticity in the same valency angle to some extent makes it possible to take account of the above relationship between the different force constants by means of a single parameter. In the method of Urey and Bradley, however, linear terms appear in the expression for the potential energy of the vibrations. In addition to a number of contradictions which then arise, this feature leads to complication of the mathematical formalism. The Urey–Bradley approximation has not found extensive application in the Soviet Union. In practice it has no advantages over the valency forces approximation (with the addition of certain non-diagonal elements) and for many molecules it is not satisfactory and requires refinement.

In practical calculations of the frequencies and modes of molecular vibrations, use is made of the values of the force constants of bonds and groups of atoms, on which a large volume of material has accumulated. In the USSR all calculations are carried out according to a single scheme, and this has made it possible to obtain a single set of force constants. The actual force constants are found from experimental data on frequencies of vibrations. Their number, even if we neglect many non-diagonal elements, is generally found to be greater than the number of experimentally observed frequencies for a single mole-

cule. Thus the determination of the force constants of a molecule entirely from its spectrum, that is, a rigorous solution of the inverse spectroscopic problem, its impossible. It becomes possible, however, if we impose a number of additional conditions, and also make use of the spectra of isotopically substituted molecules (for which it may be assumed with sufficient accuracy that K_{ij} do not change) and the spectra of molecules of a homologous series. Considerable work has been done in this direction and an extensive set of force constants has been developed, making it possible to carry out model calculations of the frequencies and modes of vibrations, and to solve a variety of problems associated with the estimation of the characteristic nature of vibrations, the influence of substitution, etc., for almost any class of organic compound.

The material at present available on force constants is scattered in a large number of original papers. The appendix to the present review (p. 227) gives the values of the force constants characterising the elastic properties of the bonds and valency angles in some of the most important groups of organic molecules. Table 3 gives the most reliable data obtained by sufficiently correct solution of the vibrational problem. Nevertheless it should be noted that the numerical values of some of the force constants given in Table 3 must be regarded as provisional, particularly in the study of the vibrations of other molecules§.

In view of its unique importance, let us consider the problem of the determination of the force constants on the basis of experimentally-measured frequencies. Let us make use of the property of the quasidiagonality of the force-constants matrix, that is, the property $K_{ii} \gg K_{ij}$, which can be taken as proved, since there are no exceptions in all the molecules which have been studied up to the present. We shall restrict ourselves initially to the simplest case in which the values of the squares of the frequencies are close to the values of the diagonal elements. This is often encountered in practice. We shall moreover assume that the assignment of the frequencies is already known. Let us assume that the force-constants matrix is diagonal, that is that all $K_{ij} = 0$ $(i \neq j)$. The approximate values of the diagonal force constants are then found from the formulae

$$K_{ii}^{(0)} = \frac{\lambda_{i\,\mathrm{exp}}}{\tau_{ii}},$$

where $\lambda_{i\,\mathrm{exp}}$ represents the experimental values of the squares of the frequencies of the vibrations. The set of values of $K_{ii}^{(0)}$ for all ith vibrational coordinates forms the zeroth approximation of the force-constants matrix¶. The values of $\lambda_i^{(1)}$ for variation of the force constants by the quantity ΔK_{ij} can obviously be written in the form

$$\lambda_i^{(1)} = \lambda_i^{(0)} + \sum_{i,j}\left(\frac{\partial \lambda_i}{K_{ij}}\right)_0 \Delta K_{ij}, \qquad (4)$$

where $\lambda_i^{(0)}$ represents the eigenvalues of the secular equation with the force matrix in the zeroth approximation. Here it is necessary to impose certain restrictions on the values of ΔK_{ij}; the values of $\lambda_i^{(1)}$ calculated from the approximate formulae of type (4) should agree within the limits of permissible error with the values calculated by exact solution of the secular equation. The derivatives $\left(\frac{\partial \lambda_i}{\partial K_{ij}}\right)_0$ of λ_i with respect to the force constants for a given force-constants matrix are readily calculated[52]. The summation is carried out with respect to all varying force constants, which are regarded as independent. In order to simplify the subsequent notation we shall replace the double subscript for the force constants by a single subscript, arranging all the force constants in a definite order.

By varying ΔK_j within the above range, we can obtain different values of $\lambda_i^{(1)}$. We shall write $\lambda_i^{(1)} = \lambda_{i\mathrm{exp}} + \alpha_i$, where α_i represents certain fractions. We then have

$$\alpha_i = \lambda_i^{(0)} - \lambda_{i\,\mathrm{exp}} + \sum_j \left(\frac{\partial \lambda_i}{\partial K_j}\right)_0 \Delta K_j.$$

The problem of constructing a force-constants matrix from the given set of squares of the normal vibration frequencies will be solved (where solution is possible with the restrictions noted above) if we can select values of ΔK_j such that all $\alpha_i = 0$. This is equivalent to finding a solution for a system, of nth order, of non-homogeneous linear equations with respect to the unknowns ΔK_j:

$$\lambda_i^{(0)} - \lambda_{i\,\mathrm{exp}} + \sum_j \left(\frac{\partial \lambda_i}{\partial K_j}\right)_0 \Delta K_j = 0. \qquad (5)$$

This system will have a single solution if the number of variable force constants is equal to the number of experimentally observed frequencies, and an infinite number of solutions if the number of variable force constants is greater than the number of observed frequencies. The maximal number of unknown force constants for a non-symmetrical molecule is equal to $\frac{(3N-6)(3N-5)}{2}$, where N is the number of atoms in the molecule, and is hence much greater than the number of normal vibrations of the molecule $(3N-6)$, that is, the number of $\lambda_{i\mathrm{exp}}$ measurable in principle for a single molecule. Thus the inverse spectroscopic problem in the general case has no single solution. It becomes soluble only when some of the force constants are assumed to be equal to zero (an approximate model for the force field of the molecule is selected) or are obtained by analogy with related compounds. In order to increase the number of observable frequencies it is possible to use isotopically-substituted molecules in addition to the main molecule. The system of equations including various isotopically-substituted molecules will be consistent since it may be assumed with a reasonable degree of approximation that the coefficients K_j remain unchanged in a series of isotopically-substituted molecules. It should be noted, however, that not all the equations related to various isotopically-substituted molecules will be linearly independent. This is due to the existence of definite correlations between λ_i for different isotopically-substituted compounds.

Despite the fact that this problem has already been discussed[145], the problem of the a priori choice of independent equations for isotopically-substituted molecules in specific instances cannot be regarded as solved. It is not clear, moreover, which force constants can be determined with greatest reliability from the available system of equations. However, the use of a set of vibration frequencies for isotopic molecules is always necessary for averaging the calculated force constants. Essentially different equations are obtained with a marked change in the masses of the atoms. Thus in practice use is made chiefly of the replacement of H atoms by D atoms and of vibrations in which these atoms play the main part.

§ The data are taken only from Soviet literature.

¶ In many instances it is convenient to use as the zeroth approximation of the force-constants matrix the product of the matrix which is the reciprocal of the kinematic-coefficients matrix from the right and the diagonal matrix of the squares of the experimental vibration frequencies.

If, however, the number of observed frequencies of the main molecule plus its isotopically-substituted derivatives is still less than the number of variable elements in the force-constants matrix, it is obviously always possible to select a set of elements ΔK_j, which will completely satisfy experiment but which will not be the only set. It is, of course, possible to impose on the variation of ΔK_j the condition that they lie within a given section, but then the set of values of ΔK_j and hence the final force-constants matrix will not be single ones, and at present there is no criterion for selecting the most reliable from the various sets, unless certain assumptions are made regarding the magnitudes of some of the force constants.

Let us next assume that the number of $\lambda_{i\,\mathrm{exp}}$ with the use of isotopic molecules becomes greater than the number of unknown elements K_j. The number of equations of type (5) for $\alpha_i = 0$ will then be greater than the number of unknowns and from these it is possible to separate various groups of equations which, generally speaking, will give various sets of ΔK_j, that is, the problem again to some extent loses its definite character. In such instances use is made of the method of least squares proposed by Gauss, and the problem is formulated as follows: we have to select values of ΔK_j which will satisfy the extra system of equations (5) with the highest degree of probability. It is possible to satisfy all the equations only with a certain error $\Delta\alpha_i$, that is, for the values of ΔK_j being sought we have:

$$\Delta\alpha_i = \lambda_i^{(0)} - \lambda_{i\ \mathrm{exp}} + \sum_j \left(\frac{\partial\lambda_i}{\partial K_j}\right)_0 \Delta K_j \text{ (for all values of } i).$$

These values will be the most probable values if $\sum_i (\Delta\alpha_i)^2$ has its smallest value, which is possible for values of ΔK_j satisfying the conditions $\frac{\partial}{\partial K_j}\left[\sum_i (\Delta\alpha_i)^2\right] = 0$, which lead to a system of non-homogeneous linear equations whose order is equal to the number of unknowns ΔK_j. By solving this system of equations we find a single set of ΔK_j and hence the force-constants matrix.

The method of least squares can also be extended to where the initial approximation for the force-constants matrix is not sufficiently close to the true one for linear extrapolation to be satisfactory [146].

In the solution of the problem by the method of least squares according to the scheme described it is necessary to make allowance for the following important features. Firstly, considerable arbitrariness may be introduced in the formulation of the differences $\lambda_i^{(0)} - \lambda_{i\,\mathrm{exp}}$ (particularly if $\lambda_i^{(0)}$ differ greatly from $\lambda_{i\,\mathrm{exp}}$). As a result, different solutions of the inverse problem will be obtained for different combinations of $\lambda_i^{(0)}$ and $\lambda_{i\,\mathrm{exp}}$. It can be shown, for example, that the number of solutions of the inverse problem for a single molecule with $3N - 6$ force constants to be determined, for a given set of $3N - 6$ squares of experimental frequencies, is equal to $(3N - 6)!$ [147]. It can also be shown that not all of these solutions satisfy isotopically substituted molecules; when the frequencies of the vibrations of certain isotopically substituted derivatives are used in addition to the frequencies of the single molecule, this makes it possible to decrease the arbitrariness in the choice of the single solution. At present, however, we do not have at our disposal methods which in the solution of the problem according to the scheme described would make it possible, for all isotopically substituted molecules, to select in advance combinations of $\lambda_i^{(0)}$ and $\lambda_{i\,\mathrm{exp}}$ in the differences between the calculated and experimental squares of the frequencies such that the above arbitrariness would be decreased to the maximal extent or eliminated. This becomes possible only when the selection of the zeroth approximation of the force-constants matrix is so successful that the frequencies of the vibrations calculated on this basis are close to the experimental values for all isotopic molecules and the interpretation of the frequencies is known.

It should also be noted that when the method of least squares is used to solve the inverse spectroscopic problem it is strictly speaking necessary to take account of the statistical weights of the squares of the experimental frequencies and this introduces difficulties associated with the fact that it is not always clear which physical principles should form the basis of the selection of the values of these weights.

It is also important to understand that the use of the simple method of least squares is in general justified only when the quantities obey the Gaussian distribution and the number of equations used is much greater than the number of force constants to be determined. These two conditions are comparatively rarely satisfied in practice, however.

An undoubted advantage of the method is the simplicity of the mathematical formalism, and this is the main reason why this method has recently found extensive application.

There is another possible method for solving the inverse problem of determining the values of the force constants of a molecule from the given frequencies of its vibrations; this method is convenient chiefly in that it does not require the formulation of differences between experimental and calculated squares of the frequencies, where, as already noted, a certain arbitrariness may be introduced. Here it is most natural to use as experimental points not the numbers $\lambda_{i\,\mathrm{exp}}$, but their combinations. In particular, we can obtain a non-linear system of equations for the values of K_j being sought; these are used since the equation for determining λ_i, with the usual form:

$$\mathrm{Det}\begin{pmatrix} (d_{11} - \lambda); d_{12}; \ldots; d_{1n} \\ \cdots\cdots\cdots\cdots \\ d_{n1}; d_{n2}; \ldots; (d_{nn} - \lambda) \end{pmatrix} = 0,$$

is equivalent to the equation

$$\lambda^n + p_1\lambda^{n-1} + p_2\lambda^{n-2} + \ldots + p_n = 0,$$

where p_1 is a function of the first powers of K_{ij}, p_2 a function of the squares and paired products of K_{ij}, etc. The coefficients p_i are in turn related to λ_i by the relationships:

$$p_i = (-1)^i \sum_{1 \leqslant n_1 < n_2 \ldots < n_i < n} \lambda_{n1}\lambda_{n2}\lambda_{n3} \ldots \lambda_{ni}.$$

Thus the problem of determining K_{ij} can be reduced to the solution of the non-linear system of equations:

$$p_i = (-1)^i \Sigma\lambda_{n_1} \ldots \lambda_{ni}.$$

In practice it is more convenient to use not this system of equations but the system converted into the form $p_i' = \sum_n \frac{1}{i}\lambda_n^i$. This can be done by taking account of the fact that the quantities $\sum_n \lambda_n^i$ and p_i are related to one another by simple relationships. This last system of equations can be solved if even only the orders of magnitude of the force constants are known and it is possible to construct

in approximate force-constants matrix; it is significant that it may differ from the true one to a much greater extent than is possible when the method of least squares is used. Approximate matrices of this type can almost always be constructed if account is taken of the fact that usually the interpretation of the spectra of polyatomic molecules begins with the simplest molecules of the selected homologous series, which generally exhibit fairly high symmetry, so that when symmetry coordinates are used and the stretching and bending vibrations are separated approximately, we obtain secular equations and equations of extremely low degrees for determining force constants. As a result of work by a number of authors there has now been created such an extensive set of force constants for individual atomic groups and molecules that a rough approximation of the force-constants matrix can be constructed for almost any organic molecule. We can thus start from a certain approximation for the force-constants matrix. It is then possible, for the solution of the system of equations

$$p_i' = \sum_n \frac{1}{i} \lambda_{n\,\mathrm{exp}}^i \text{ (for all values of } i\text{)}, \qquad (6)$$

to use the so-called method of steepest descents[148]. The method of solution can be demonstrated by the following illustrative geometric method. Let us assume that we have a certain surface Φ (1), inside which we have a point corresponding to the solution of the system. The initial approximation is given by a certain point on the surface. We draw a perpendicular to the surface and move along it. The function Φ, which has the significance of the "distance" of the moving point from the solution of the system (the point *O*), will then decrease until it reaches point 2, the closest point on the perpendicular to point *O*, after which it will begin to increase. We then take point 2 for the start of a new process and construct a new perpendicular to the surface, passing through this new point [Φ (2)]. By moving along this perpendicular, we find a point 3 which will now lie much closer to the solution being sought, etc.

A disadvantage of the method described is that the system of equations being considered, in the range of force constants in which we are interested, may have more than one solution. In order then to find all the solutions or to satisfy ourselves that the solution obtained is the single solution, we must select different initial points on the surface $\Phi(k)$, separated as far as possible from one another. A choice of solution corresponding to the true set of force constants (the set having physical significance) can then be made only be studying isotopically substituted molecules and homologous series.

The methods described are extremely tedious and their use requires the extensive application of electronic computers. In practice, in the great majority of investigations, the force constants are found by selecting (varying) them within a definite range until satisfactory agreement is obtained between λ_i and the experimental values $\lambda_{i\,\mathrm{exp}}$ (method of trial and error). To facilitate the variations, a set of partial derivatives of λ_i with respect to the force constants is usually also calculated. Unfortunately, this type of approach involves a considerable contribution from factors which are difficult to take into account, such as the experience and intuition of the author.

Thus the solution of the inverse spectroscopic problem involves appreciable difficulties. In the great majority of instances it is, in general, impossible to determine the force-constants matrix without making assumptions regarding the magnitude of some of its elements. Such approximations, as already noted, include the assumptions that the non-diagonal elements are small compared with the diagonal elements, that the force constants of the interaction of coordinates at a distance from one another are equal to zero, and that the force constants of the individual atomic groups in a series of similar compounds remain unchanged. These assumptions are based on a definite view of the nature of chemical forces in a molecule and the existence of characteristic vibrations.

With certain assumptions, these methods can also be extended to the study of homologous series. In doing so, some of the force constants are always put equal to zero, and some are assumed to be unchanged at least within a range of two to three adjacent molecules in a series. It is on this basis that an appreciable set of force constants has been created for molecules and functional groups, shown to be completely satisfactory for many calculations on specific compounds. It should be remembered, however, that because of the limitations noted above, the force constants are obtained with a certain error, which may be particularly large in the non-diagonal elements. A major shortcoming is the impossibility at present of making an objective estimate of this error. At the present stage, however, this feature presents almost no restriction to the study of the frequencies and modes of vibrations of polyatomic molecules, but it must be taken into account in all attempts to compare the values of force constants and other molecular parameters. It is for this reason that in a number of instances little trust can be put in the comparison of force constants and interatomic distances, bond energies, etc., frequently encountered in the literature.

The most reliable set of force constants is that which describes sufficiently accurately the frequencies of vibrations of a given molecule and its available isotopically substituted derivatives, and is preserved in the closest members of a homologous series.

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The development of studies of polyatomic molecules by the methods of vibrational spectroscopy are characterised primarily by the ever-increasing use of theoretical analysis to solve applied problems. The reason for this is to be found in the constant increase in the complexity of the materials and problems being studied and also in the gradual recognition by experimental workers of the fact that in principle it is only on the basis of theoretical analysis that it is possible to distinguish more or less confidently the various factors leading to the phenomena observed in spectra and to reach sufficiently well-founded conclusions regarding intramolecular interactions. The choice of appropriate spectroscopic characteristics for the solution of applied problems should also be based on theoretical analysis. Thus modern spectrochemical study must consist of a close combination of experiment and calculation of the spectrum for a model of the molecule being studied.

The need arises, however, for extensive calculations, so that theoretical methods cannot be introduced into practical spectrochemical studies until the entire calculation side has passed completely to electronic computers and is in fact reduced to the form of the input to be supplied

to the computer. Considerable progress has been made in this direction in recent years. Programmes have appeared which not only solve the equations for the vibrations but also formulate them[20] and also carry out a number of other operations. The situation is much less satisfactory in the development of programmes for solving the inverse spectroscopic problem and for the automatic interpretation of the spectra for homologous series. The existing programmes are far from perfect and their possibilities are extremely limited.

The extensive use of electronic computers in spectrochemical practice makes it possible, with very little expenditure of effort (for example, the preparation of material for the calculation for a molecule containing 9–10 atoms according to a programme developed by one of the present authors[20] occupies a total of 2–2½ h) and in a short time to carry out a large number of calculations for the selected molecules in order to establish the characteristic nature of the vibrations, the reasons for the displacements of the frequencies as a result of given substitutions, etc. It has also become possible to use theoretical methods for the analysis of a variety of regular features and to assign frequencies in those compounds for which the system of force constants is as yet insufficiently developed.

At the same time another extremely important problem is being solved; it is becoming possible for proper numerical calculations for the spectra of molecules to be carried out by persons who are not completely equipped with the mathematical apparatus of the theory. The latter is not necessary using the system of programmes developed, paradoxical as it may seem at first glance. Thus it is possible to confound the great principle: "No one can comprehend the infinite!" and to bring modern theoretical methods to a wide range of spectroscopists without imposing upon them the great additional task of studying a number of new disciplines.

The calculation methods of the theory, based on electronic computers, give to research workers a powerful tool for the study of spectra, but it is necessary to understand the use of this tool. The chief difficulty in the practical application of modern theoretical methods, after the transfer of all the calculation side to electronic computers, lies in the choice of problem in which these methods can be applied with the greatest efficiency.

The study of vibrational spectra has become one of the fundamental means of investigating the structure and properties of polyatomic molecules. It is difficult even to list approximately the vast range of problems which are solved by the methods of vibrational spectroscopy. These methods are far from having exhausted their possibilities. There is no doubt that in the near future we shall witness considerable progress in this branch of science. This requires primarily the extensive introduction of theoretical methods which have already been developed and which until recently were the acquisition of a narrow group of specialists, into everyday practice in spectroscopic laboratories. This will undoubtedly result in a sharp raising of the level of spectrochemical studies. This process is already taking place, as indicated, in particular, by the continuously increasing proportion of papers dealing with calculations.

At the same time the next urgent problem concerns the further improvement of the theory itself and the development of new aspects of the theory. Unfortunately, it must be stated that this work is not proceeding rapidly enough at present.

5. APPENDIX

Table 2 lists the compounds whose vibrational spectra have been calculated as a result of work published in Soviet literature up to the middle of 1964. The formulae for isotopically substituted molecules whose spectra have been used to determine the set of force constants are given in parentheses after the name of the compound.

TABLE 2.

Methane (CH_4, CH_3D, CH_2D_2, CHD_3, CD_4)[14]; ethane (C_2H_6, C_2D_6)[14]; propane[14,87,88]; butane[87-89]; isobutane ($HC(CH_3)_3$, $DC(CH_3)_3$)[14,61]; 2,3-dimethylbutane[62]; pentane[60]; isopentane[14]; neopentane[14]; cyclopropane (C_3H_6, C_3D_6)[63]; methylcyclopropane[64]; 1,1-dimethylcyclopropane[64]; cyclobutane[65]; cyclopentane (C_5H_{10}, C_5D_{10})[66-69]; cyclohexane (C_6H_{12}, $C_6H_{11}D$, C_6D_{12})[70,71]; methylcyclohexane[72]; ethylcyclohexane[72]; *trans*--1,4-dimethylcyclohexane[71]; *cis*-1,3,5-trimethylcyclohexane[71]; halogeno-derivatives of methane[14,41]; chloro-derivatives of ethane[14]; methanol (CH_3OH, CH_3OD, CD_3OH, CD_3OD)[14]; methanethiol[14]; ethylene (C_2H_4, C_2H_3D, C_2HD_3, *asym*-$C_2H_2D_2$, *trans*-$C_2H_2D_2$, *cis*-$C_2H_2D_2$)[14,73,74]; propene (C_3H_6, C_3D_6)[75]; but-1-ene[76]; *cis*-but-2-ene[76]; *trans*-but--2-ene[76]; isobutene[77]; *cis*- and *trans*-isomers of ethylene[79,80]; 2,3-dimethylbut-2--ene[76]; penta-1,4-diene[78]; halogeno-derivatives of ethylene[81,82]; allene (C_3H_4, HDC_3H_2, $D_2C_3H_2$, C_3D_4)[83,85]; methylallene[85]; 3-methylbuta-1,2-diene[78]; cyclobutene (C_4H_6, C_4D_6)[84]; butadiene (C_4H_6, C_4D_6)[86,86]; acetylene (H_2C_2, HDC_2, D_2C_2)[39]; methyl vinyl ether[87]; methyl vinyl sulphide[88]; hydrogen cyanide (HCN, DCN)[89]; acetonitrile (CH_3CN, CD_3CN)[44]; mono-, di-, and tri-chloroacetonitriles[45]; cyanamide (H_2NCN, D_2NCN)[89]; nitromethane (CH_3NO_2, CD_3NO_2, $CH_3N^{18}O_2$)[90]; nitroethane[90]; *gem*-dinitroethane[88]; trinitromethane ($HC(NO_2)_3$, $DC(NO_2)_3$)[88]; silane (SiH_4, SiH_2D_2, $SiHD_3$, SiD_4)[91]; methylsilane (CH_3SiH_3, CH_3SiD_3)[92,93]; dimethylsilane[93]; trimethylsilane[93]; tetramethylsilane ($Si(CH_3)_4$, $Si(CD_3)_4$)[94]; halogenomethylsilanes[96-99]; disilane (Si_2H_6, Si_2D_6)[100]; chloromethylgermanes[101]; germanium tetraiodide[102]; benzene (C_6H_6, C_6H_5D, $C_6H_4D_2$, $C_6H_3D_3$, $C_6H_2D_4$, C_6D_6)[103-108]; toluene ($C_6H_5CH_3$, $C_6H_5CD_3$)[106-108]; ethylbenzene[109]; isopropylbenzene[110]; *o*-xylene[111,112]; *m*-xylene[113]; *p*-xylene[114]; 1,3-diethylbenzene[115]; mesitylene[116,117]; durene[116,117]; 1,2,3-trimethylbenzene[118]; biphenyl ($C_{12}H_{10}$, $C_{12}H_9D_1$, $C_{12}H_8D_2$, $C_{12}D_{10}$)[119-121]; naphthalene ($C_{10}H_8$, α-$C_{10}H_7D_1$, β-$C_{10}H_7D_1$, $C_{10}D_8$)[122-124]; pyridine (C_5H_5N, 4-C_5H_4DN, 2-C_5H_4DN, 3-C_5H_4DN, 2,6-$C_5H_3D_2N$, 3,5-$C_5H_3D_2N$, C_5D_5N)[125,126]; pyrazine[127]; *sym*-triazine ($C_3H_3N_3$, $C_3D_3N_3$)[127]; *sym*-tetrazine ($C_2H_2N_4$, C_2HDN_4, $C_2D_2N_4$)[127]; the cyclopentadienyl ring of ferrocene (C_5H_5, C_5D_5)[128]; the hydroperoxide group (C—O—OH)[129]; trimethyl phosphate[130]; trimethyl thiophosphate[130]; phosphorus oxide trichloride[131]; phosphorus oxide tribromide[131]; phosphorus sulphide trichloride[131]; phosphorus sulphide tribromide[132]; ammonia (NH_3, ND_3)[14]; methylamine (CH_3NH_2, CD_3NH_2, CH_3ND_2, CD_3ND_2)[132]; boron trifluoride–ammonia ($F_3B.NH_3$, $F_3B.NH_2D$, $F_3B.NHD_2$, $F_3B.ND_3$)[133]; the tetrahalides of C, Si, Ge, Ti, Sn, and Pb[134]; boric oxide ($^{10}B_2O_3$, $^{11}B_2O_3$, $^{10}B^{11}BO_3$)[135]; boron sulphide ($^{10}B_2S_3$, $^{11}B_2S_3$)[135]; SF_4[136]; SF_3Cl[137]; titanium tetrachloride[138]; silicates[139-141]; the UO_2^{2+} ion[142]; water (H_2O, D_2O, HTO, DTO, T_2O)[143]; hydrogen sulphide (H_2S, D_2S, HDS, DTS, HTS, T_2S)[143,144]; hydrogen selenide (H_2Se, HDSe, D_2Se, HTSe, DTSe, T_2Se)[143].

TABLE 3. Force constants $\times 10^5$ (cm^{-2}).

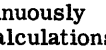
Compound	Coordinates *i* and *j*	K_i	K_j	K_{ij}	References
Ethane H_3C-CH_3		8.34	8.34	0.05	14
		8.34	7.02	0.05	
		7.02	0.92	0.43	
		8.34	0.71	0.35	
		0.92	0.71	—0.035	
Propane $H_3C-CH_2-CH_3$		7.02	7.02	0	14, 57, 58
		7.02	0.80	0.43	
Fluoromethane H_3CF		8.53	9.80	0.30	14
		9.80	1.56	1.25	
		0.76	1.56	0.12	

TABLE 3 (contd.)

Compound	Coordinates i and j	K_i	K_j	K_{ij}	References
Chloromethane H_3CCl		8.53	5.80	0.15	14, 41
		5.80	1.10	0.80	
		0.75	1.10	0.12	
Bromomethane H_3CBr		8.53	4.60	0.10	14, 41
		4.60	0.95	0.65	
		0.73	0.95	0.11	
Iodomethane H_3CI		8.53	3.90	0.08	14, 44
		3.90	0.85	0.55	
		0.72	0.85	0.10	
Methanol H_3C-OH		8.0	12.65	0	14
		12.65	1.15	0.40	
Methanethiol H_3C-SH		5.0	6.5	0	14
		6.5	1.05	0.50	
Methylamine H_3C-NH_2		10.77	10.77	0.05	132
		10.77	8.60	0.05	
		10.77	0.80	0.40	
Ethylene $H_2C=CH_2$		14.2	8.63	0.10	14, 73, 74
		8.63	8.63	0.03	
		14.2	0.80	0.45	
		8.63	0.58	0.37	
		0.80	0.58	−0.035	
Propene $H_2C=CH-CH_3$		14.2	7.02	0.10	75
2-Methylpropene $H_2C=C(CH_3)_2$		7.02	7.02	0	78
Fluoroethylene $H_2C=CFH$		15.00	10.20	0.50	81
		15.00	1.07	1.00	
		10.20	8.82	0.30	
		10.20	0.73	1.00	
Chloroethylene $H_2C=CClH$		14.20	6.00	0.28	81
		14.20	1.11	0.80	
		6.00	8.80	0.15	
		6.00	0.69	0.66	
Allene $H_2C=C=CH_2$		15.05	15.05	0.15	83, 85
		15.05	8.55	0.25	
1,2-Butadiene $H_3CHC=C=CH$		15.05	15.05	0.15	86
		15.05	7.02	0.10	
1,3-Butadiene $H_2C=CH-CH=CH_2$		12.00	10.40	0.40	58
		12.00	12.00	−1.50	
		12.00	8.63	0.10	
Acetylene $HC\equiv CH$		24.48	9.85	0.20	39
Hydrogen cyanide HCN		27.70	9.70	0.20	39
Acetonitrile H_3C-CN		27.70	8.10	0.20	44

TABLE 3 (contd.)

Compound	Coordinates i and j	K_i	K_j	K_{ij}	References
Trichloroacetonitrile Cl_3C-CN		27.70	7.80	0.20	45
		7.80	5.40	0.10	
		7.80	1.55	0.85	
		5.40	1.50	0.60	
Nitromethane H_3C-NO_2		14.00	14.00	1.60	90
		7.67	14.00	0.35	
		14.00	1.95	0.55	
		7.67	1.26	0.60	
		1.95	1.26	−0.06	
Disilane $H_3Si-SiH_3$		4.51	4.51	0.03	100
		4.51	2.75	−0.008	
		2.75	0.602	0.30	
		4.51	0.72	0.23	
		0.602	0.72	0.084	
Methylsilane H_3C-SiH_3		5.11	4.31	−0.008	92, 93
		5.11	0.932	0.346	
Chlorotrimethylsilane $Cl-Si(CH_3)_3$		5.077	4.00	0.080	96
		5.077	1.247	0.35	
		5.077	0.845	0.35	
Chlorotrimethyl-germane $Cl-Ge(CH_3)_3$		4.48	2.75	0.08	101
		4.48	1.245	0.35	
		4.48	0.68	0.40	
		1.245	1.245	0.315	
Benzene C_6H_6		11.36	11.36	1.04	103–105
		11.36	11.36	−0.87	
Ammonia H_3N		10.72	10.72	0.05	14
		10.72	0.79	0.40	
		0.79	0.79	−0.07	

Table 3 summarises the force constants of bonds and valency angles and also the constants for their interaction for some of the most important atomic groups in organic molecules.

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NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME ELECTRON-DEFICIENT COMPOUNDS: BORON HYDRIDES, DIMERS OF ALKYLALUMINIUMS, AND ORGANOLITHIUM COMPLEXES

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