PHYSICAL CHEMISTRY

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1963

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ON THE QUESTION OF THE PHYSICAL MEANING OF FORCE CONSTANTS AND THE CONSTRUCTION OF THE POTENTIAL FUNCTION OF POLYATOMIC MOLECULES

(Presented by Academician A. N. Terenin on 8 IV 1963)

One of the most important tasks of vibrational spectroscopy is to obtain information about the properties of the interatomic forces acting in a polyatomic molecule. A complete solution of this problem, as well as the further development of computational theory that makes it possible to interpret the observed spectra of molecules, requires clarification of the physical meaning of the force constants (the second derivatives of the potential function with respect to vibrational coordinates, taken for the equilibrium state), which are usually used to characterize the elastic properties of a molecule. A significant shortcoming of force constants (and of compliance coefficients, i.e., the elements of the matrix inverse to the matrix of force constants) is the impossibility of establishing an exact correspondence between one (even a diagonal) element of the force-constant matrix and the true elasticity of a structural element. The latter, evidently, must have the meaning of a proportionality coefficient between the vibrational coordinate describing the given structural element and the force conjugate to this coordinate, with both the coordinate and the force being in principle measurable by some hypothetical instrument. Usually the problem of the vibrations of a polyatomic molecule is solved in a system of natural vibrational coordinates. In this case the system of conjugate forces is not invariant with respect to the coordinates and changes entirely under a partial replacement of coordinates; that is, unlike the coordinates, it cannot be measured by an instrument. Just as natural vibrational coordinates and the forces conjugate to them are generalized coordinates and forces, so force constants have the meaning of generalized parameters of interatomic forces. Therefore, in particular, in the language of force constants it is difficult to formulate an additive approximation that takes into account only the elastic interactions of atoms forming a bond.

The indicated difficulties are removed by passing to the characterization of interatomic forces by means of symmetric second-rank tensors of elastic interactions of atoms, specified in a system of Cartesian coordinates associated with the molecule. For additive molecules the elastic properties will then be characterized by the aggregate of the elasticity tensors of the bonds. In a sufficiently good approximation it may be assumed that one of the principal directions of the bond-elasticity tensor coincides with the direction of the bond, while the other two are perpendicular to it. For a bond with cylindrical symmetry, the perpendicular components are identical. The introduction of perpendicular components for describing the elastic properties of a bond is dictated by the fact that in polyatomic molecules the atoms are "fixed" by the action of neighboring bonds. As a result, the vibrational motion of atoms perpendicular to a bond, leading to a rotation in space of the directing vector of the bond, will be associated with its "bending" and will require a certain expenditure of energy. The presence of a perpendicular component of the bond-elasticity tensor, or of the elasticity of bending, naturally explains the appearance of forces that hinder a change in the valence angle, even if there is no direct interaction at all between nonbonded atoms. In a certain approximation

one may apparently consider that the tensors of bond elasticities, at least for additive molecules, are entirely determined by the properties of the bond. On the other hand, specification of this tensor completely characterizes the bond (apart from the torsional energy of the bond).

The introduction of the concept of tensors of bond elasticities makes it possible to obtain a number of conclusions about the physical meaning of the force constants of molecules. Here we shall confine ourselves to presenting some results.

It turned out that the magnitude of the force constants depends on the vibrational angular momentum, which is conserved in the general case and in the coordinate system associated with the molecule. This leads, first, to the appearance of off-diagonal elements in the force-constant matrix corresponding to the interaction of remote coordinates, even if there are no "electronic" influences; and, second, to a dependence of the force constants on isotopic substitution. Although both of these effects are small, in principle they exist and must be taken into account in accurate calculations. The influence of the vibrational angular momentum is associated with allowance for the inertial properties of the system when using coordinates in which the entire consideration is conducted from the point of view of an observer located inside the molecule.

Neglecting the vibrational angular momentum, in additive molecules the force constant is equal to the longitudinal component of the tensor of bond elasticity. The off-diagonal elements of interaction between two bonds and between a bond and an adjacent angle are equal to zero. The force constant of an angle is equal to the sum of the perpendicular components of the tensors of elasticity of the bonds forming the given valence angle, multiplied by the scalar squares of the coefficients of proportionality between the rotation of the given bond in the plane of the valence angle and the angular coordinate. The magnitude of this constant thus depends not only on the flexural elasticities of the bonds, but also on their relative angular mobility. The force constants for changes in dihedral angles have an analogous meaning. The off-diagonal element of interaction between two angular coordinates having a common side and vertex is equal to the product of the perpendicular component of the tensor of elasticity of the common bond (for bonds of cylindrical symmetry) and the scalar product of the coefficients of angular mobility of the bond in the planes of the valence angles. It is obvious that this element can have a considerable magnitude even in completely additive molecules. The elements of interaction of angles with a common bond but not a common vertex are likewise not equal to zero. The off-diagonal element of interaction between two angles having only a common vertex is equal to zero. Consequently, even when the vibrational angular momentum is neglected, in the approximation of additive bonds the force-constant matrix is not diagonal even in the valence-force coordinate system, which is best suited for describing molecules within the valence scheme. The influence of the vibrational angular momentum may become substantial in molecules with atoms close in mass and with close bond elasticities. In this case none of the elements of the force-constant matrix can be equal to zero; moreover, for example, the force constant of a bond will also depend on the perpendicular components of the tensors of bond elasticities.

If there is interaction between atoms of different bonds, this will lead not only to the appearance of off-diagonal elements in the force-constant matrix, but also to corresponding changes in the diagonal ones.

Thus, the notion of the tensor of bond elasticity proves to be very fruitful and makes it possible to clarify the sometimes rather complicated physical meaning of force constants. It is natural, therefore, to try to construct on this basis a computational theory, in particular a potential function of the molecule.

The construction of the potential function is based on the following propositions.

1) In the initial approximation, only the elastic interactions of pairs of atoms forming bonds are taken into account. The potential energy is represented as the sum of the bond energies.
2) Each bond is characterized by stretching and bending energy. The former depends only on the stretching of the bond. The bending energy is a function of the difference of the perpendicular displacements of the atoms from their equilibrium positions during vibrations and, consequently, can be characterized by the product of the bond length and the rotation vector of the unit vector of the bond direction during vibrations. The latter can easily be expressed in terms of the chosen vibrational coordinates ([1,2]).
3) The stretching energy is described by a Morse-type function. For the bending energy one should choose a function symmetric with respect to the equilibrium position and having a minimum in the equilibrium state. We have chosen a function of the form

$$f(x) = [1 - \exp(-\beta x^2)].$$

The choice of such functions is, of course, not unique, and can be justified only on the basis of extensive experimental material on the study of anharmonic terms in the expression for the potential energy of vibrations. In the present case the aim was only to indicate a method for constructing the potential function, and also to obtain a number of general conclusions. At the same time, for solving the problem in the harmonic approximation as well, considerable arbitrariness may be allowed in the choice of the bond potential functions.

4) It is assumed that the dissociation energy of a bond D_i does not depend on the character of the deformation.

The introduced conditions lead to a potential function in the additive approximation of the form:

$$V = \sum_i D_i \{ (1 - \exp[-\alpha_i q_i])^2 + \tag{1}$$

$$+ [1 - \exp[-\beta_i^{(1)} (s_i \Delta e_i^{(1)})^2 - \beta_i^{(2)} (s_i \Delta e_i^{(2)})^2]] \}.$$

The summation is carried out over all bonds. Here α_i are the Morse constants for stretching of the bonds; $\beta_i^{(1)}$ and $\beta_i^{(2)}$ are the bending constants of the bond, respectively in two mutually perpendicular directions. For bonds with cylindrical symmetry only one term remains, characterizing the bending of the bond. s_i is the length of the i-th bond, and $\Delta e_i^{(1)}$, $\Delta e_i^{(2)}$ are the projections of the rotation vector of the unit direction vector of the bond onto the principal directions of perpendicular elasticity. For a bond with cylindrical symmetry, the corresponding term will contain simply the scalar square of the vector Δe_i.

Function (1) is invariant with respect to the chosen coordinate system, since it depends only on the elastic characteristics of the bonds, their stretchings and rotations in space during vibrations. It is easy to see that the second and higher derivatives with respect to the vibrational coordinates do not possess such invariance. Function (1) can also be written in symmetry coordinates.

This function makes it possible to obtain all the conclusions given above concerning the physical meaning of the force constants. Indeed, Δe_i are functions of all coordinates of the molecule; therefore, for example, the force constant of a bond will depend not only on the stretching potential, but also on the bond-bending potentials, if one does not neglect the dependence of Δe_i on q_i, i.e., on the vibrational moment of momentum. Hence also follows the dependence of the force constants, and to an even greater extent of the terms of mechanical anharmonicity, on isotope substitution, which is associated with the change of Δe_i in a series of isotopic compounds. The remaining conclusions are also easily obtained.

On the basis of the proposed function, it may apparently be possible to construct an empirical theory for calculating the frequencies and modes of molecular vibrations, requiring the introduction of a smaller number of constants than is done at present. Indeed, there is every reason to expect that, for many molecules, an approximation will be satisfactory in which only the elastic interactions of pairs of atoms forming bonds are taken into account. In any case, such a possibility cannot be rejected a priori, especially since the matrix of force constants is not diagonal even in the additive approximation, and the interaction elements of the angular coordinates may be large. Consequently, the dynamics of harmonic vibrations can apparently be described if only the bond stiffness constants are specified (the products $2D_i\alpha_i^2$ and $2D_i\beta_i$). If one takes into account that some of the bonds in a molecule possess cylindrical symmetry, the number of parameters introduced may become even smaller than the number of diagonal elements in the matrix of force constants. Moreover, it may be expected that methods of quantum chemistry can be applied to determine the magnitudes of such parameters.

Allowing for the interaction of atoms belonging to different bonds is complicated by the fact that the form of the tensor of such an interaction is unknown. In the general case one can formally introduce "bonds" between atoms of different bonds with their own "stretching" and "bending" functions. The corresponding stretching coordinates of the fictitious bonds and their rotations are expressed through the set of independent coordinates chosen to describe the molecule. Obviously, in this case the values of all force constants of a polyatomic molecule change.

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Received
8 IV 1963

CITED LITERATURE

1. L. A. Gribov, DAN, **127**, 788 (1959).

2. L. A. Gribov, *Optics and Spectroscopy*, **8**, 769 (1960).

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