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Abstract

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A NEW APPROACH TO THE CALCULATION OF INTENSITIES IN THE VIBRATIONAL SPECTRA OF MOLECULES

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The methods currently available for calculating intensities in the vibrational spectra of molecules (in the harmonic approximation) [1–15] are less general than the methods for calculating frequencies and modes of molecular vibrations, since they proceed from the additional assumption that the dipole moment and the polarizability of a molecule are additively composed of the dipole moments and, respectively, polarizabilities of the chemical bonds present in it.

The new approach to the calculation of intensities set forth below is free of the indicated shortcoming and is as general as in the case of calculating frequencies and modes of vibrations. This approach is based on taking into account the circumstance that, in contrast to the potential energy of a molecule, which depends only on internal coordinates, the dipole moment and polarizability of a molecule also depend on rotations of the molecule as a whole; if the number of atoms in the molecule is n, then the dipole moment and polarizability of the molecule depend on $3n-3$ coordinates.

As these coordinates it is convenient to choose the projections on the coordinate axes of $n-1$ vectors $\mathbf{R}_{ab}^{(i)} = \mathbf{R}_{b(i)} - \mathbf{R}_{a(i)}$ $(i = 1, 2, \dots, n-1)$, which completely determine the mutual arrangement of the atoms and the orientation of the molecule in space ($\mathbf{R}_{a(i)}$ and $\mathbf{R}_{b(i)}$ are the radius vectors of atoms $a(i)$ and $b(i)$ forming the bond $a(i) - b(i)$). With the aid of these coordinates we obtain

$$\vec{\mu} = \vec{\mu}\left(\mathbf{R}_{ab}^{(i)}\right), \qquad \hat{\alpha} = \hat{\alpha}\left(\mathbf{R}_{ab}^{(i)}\right), \tag{1}$$

where $\vec{\mu}$ is the dipole moment and $\hat{\alpha}$ is the polarizability tensor of the molecule.

It is easy to see that the usual representation of the dipole moment and polarizability in the form of a sum of the corresponding quantities over bonds is a special case of the general functional dependence (1).

In what follows we shall consider in detail only the case of infrared spectra. Spectra of combination scattering can be considered in an analogous way.

The absolute intensity of IR spectra is determined, as is known [16], by the quantity $A = \frac{1}{N}\int \chi(\nu)d\nu$, where N is the number of absorbing molecules per unit volume, $\chi(\nu) = (1/l)\ln(I_0/I)$ (I_0 and I are the initial and final intensities of a parallel beam of radiation that has passed through an absorbing layer of thickness l). This quantity for the k-th normal vibration has (in the harmonic approximation) the form [5,17]

$$A = \frac{\pi}{3c}\left|\left(\frac{\partial\vec{\mu}}{\partial Q_k}\right)_0\right|^2, \tag{2}$$

where c is the speed of light in vacuum, Q_k is the k-th normal coordinate, normalized so that $\bar{U}_k = \frac{1}{2}\omega_k^2 Q_k^2$ ($\bar{U}_k$ is the potential energy and ω_k the angular frequency of this vibration).

Using (1), we obtain

$$\left(\frac{\partial\vec{\mu}}{\partial Q_k}\right)_0 = \sum_j \left(\frac{\partial\vec{\mu}}{\partial \mathbf{R}_{ab}^{(j)}}\right)_0 \frac{\partial \mathbf{R}_{ab}^{(j)}}{\partial Q_k}. \tag{3}$$

Choosing some Cartesian coordinate system, let us introduce: the column matrix $\mu^{(k)} = ((\partial\mu_x/\partial Q_k)_0,\ (\partial\mu_y/\partial Q_k)_0,\ (\partial\mu_z/\partial Q_k)_0)$; the column matrix $X_\delta = (x_{b(1)} - x_{a(1)},\ y_{b(1)} - y_{a(1)},\ z_{b(1)} - z_{a(1)}, \dots, z_{b(n-1)} - z_{a(n-1)})$, whose elements are equal to the Cartesian coordinates of the displacement differences of atoms $b(i)$ and $a(i)$ forming the i-th bond (we shall assume that the bond is always directed from atom a to atom b; to each $a(i)$ and $b(i)$, for a definite numbering of the bonds and a definite choice of their directions, there corresponds one and only one atom of the molecule, but to each atom there may correspond several such designations); the rectangular matrix D of three rows and $3n-3$ columns, having in block notation the form $D = \|D_1 \ \vdots\ D_2 \ \vdots\ \dots\dots\ D_i\ \dots\ \vdots\ D_{n-1}\|$, where D_i is a square matrix of third order with elements $(\partial\mu_\alpha/\partial(\beta_{b(i)} - \beta_{b(i)}))_0$ $(\alpha, \beta = x, y, z)$, corresponding to the i-th bond $(i = 1, 2, \dots, n-1)$.

With the aid of these matrices, and taking into account that $\partial X_\delta/\partial Q_k = X_\delta^{(k)}$, where $X_\delta^{(k)}$ is the normalized matrix X_δ corresponding to the k-th normal vibration (the form of the k-th normal vibration, written in Cartesian coordinates of the displacement differences of the atoms forming the bonds), we rewrite (2) in the form

$$A = \frac{\pi}{3c}\,|\mu^{(k)}|^2 \tag{4}$$

and (3) in the form

$$\mu^{(k)} = DX_\delta^{(k)}. \tag{5}$$

Using the known expression [18] for the column matrix $X^{(k)} = (x_1^{(k)}, y_1^{(k)}, z_1^{(k)}, \dots, z_n^{(k)})$ –the form of the k-th vibration, written in Cartesian coordinates of atomic displacements (numbered this time by the numbers $1, 2, \dots, n$), we obtain from (5)

$$\mu^{(k)} = \frac{1}{\omega_k^2} D\varepsilon_\delta \widetilde{B} p^{(k)}; \tag{6}$$

B is a rectangular matrix with $3n-6$ ($3n-5$ for linear molecules) rows and $3n$ columns, transforming the column matrix X into the column matrix q (the column of internal coordinates); $p^{(k)}$ is the normalized eigencolumn of the transposed vibration matrix, corresponding to the eigenvalue ω_k^2 of the latter; ε_δ is a rectangular matrix with $3n-3$ rows and $3n$ columns, having in block notation the form $\varepsilon_\delta = \|\varepsilon_{ij}\|$ ($i = 1, 2, \dots, n-1$ is the bond number; $j = 1, 2, \dots, n$ is the atom number), where ε_{ij} are scalar matrices of third order with the following properties: $\varepsilon_{ij} = \varepsilon_{b(i)} E_3$, if j corresponds to $b(i)$; $\varepsilon_{ij} = -\varepsilon_{a(i)} E_3$, if j corresponds to $a(i)$, and $\varepsilon_{ij} = 0$ in all other cases. Here $\varepsilon_{a(i)}$ and $\varepsilon_{b(i)}$ are the reciprocal masses of atoms $a(i)$ and $b(i)$, respectively; E_3 is the identity matrix of third order.

If the column $p^{(k)}$ is not normalized in the proper way, then

$$\mu^{(k)} = \frac{1}{\omega_k \left(\widetilde{p}^{(k)} q^{(k)}\right)^{1/2}} D\varepsilon_\delta \widetilde{B} p^{(k)}, \tag{7}$$

where $q^{(k)}$ is the corresponding eigencolumn of the vibration matrix (the form of the k-th vibration, written in internal coordinates), and formula (4) assumes the form

$$A = \frac{\pi}{3c\omega_k^2 \widetilde{p}^{(k)} q^{(k)}} \left| D\varepsilon_\delta \widetilde{B} p^{(k)} \right|^2. \tag{8}$$

We shall assume (as also in the case of the potential-energy matrix) that the matrix D does not depend on isotope substitution. The specific form of the matrices D_i constituting the matrix D depends, of course, on the choice of the coordinate system. It is therefore expedient to assign to each matrix D_i its "own" coordinate system, in which it has the simplest form. As such a system one may choose a system whose OZ axis is directed along the bond a—b in the equilibrium position, while the other two axes are oriented in some definite way relative to the other bonds. If there are symmetry elements in the fragment containing the given bond, it is expedient to use them for orienting the coordinate axes, with the symmetry imposing definite restrictions on the number of essentially different (nonzero) parameters that determine the matrix D_i^0 for this bond (D_i^0 denotes the matrix D_i in its "own" coordinate system).

On passing from one coordinate system to another, the matrix D'_i in the new coordinate system can be obtained from the matrix D_i in the old coordinate system by means of the corresponding similarity transformation. Thus, knowing the geometry of the molecule and the matrices D_i^0 in their "own" coordinate systems, one can find all D_i in a coordinate system common to the whole molecule and compose from them the matrix D.

In many cases it is apparently possible to assume (as also in the case of the potential-energy matrix) that the matrices D_i^0 corresponding to chemical bonds of the same type a—b are approximately equal. Then, having determined these matrices from simpler molecules, one may approximately transfer them to more complex molecules. If it turns out that this assumption is not sufficiently accurate, then, using experimental data, one can refine the values of the elements D_i in the new molecules.

In the presence of symmetry, calculations by formula (8) are simplified. It should also be borne in mind that all elements of the matrices D_i have the same dimension, namely the dimension of electric charge, and that their total number in a complex molecule is much smaller than the total number of parameters in an additive scheme. In accordance with the physical meaning of the matrices D_i, they could be called matrices of effective charges.

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Note: Figure translations are in progress. See original paper for figures.