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A VALENCE-OPTICAL SCHEME AND THEORETICAL STUDIES OF INTENSITIES AND POLARIZATIONS IN THE ABSORPTION SPECTRA OF FUNDAMENTAL VIBRATIONS OF POLYATOMIC MOLECULES

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The material accumulated to date on the intensities and polarizations of absorption bands in the infrared spectra (IR spectra) of complex molecules indicates a much more complicated dependence of intensities and polarizations on the parameters of the molecule than is the case for frequencies. This circumstance substantially hampers the interpretation of experimental facts and makes a purely empirical approach of little use. In this connection, the problem of a theoretical analysis of intensities and polarizations in the IR spectra of complex molecules acquires fundamental importance for the further development of spectral methods of investigation.

The theory most satisfactory for the needs of practice at present is the valence-optical theory developed by M. V. Vol'kenshtein and M. A. El'yashevich (^1) and improved by one of the authors of the present communication (^2). A feature of this theory is the necessity of introducing empirical parameters: the dipole moments of bonds and their derivatives with respect to vibrational coordinates.

Two main problems arise: whether these parameters can in general be found separately or in sufficiently simple combinations from experimental data and, second, whether the electro-optical characteristics of individual bonds and groups of atoms will have similar values in similar molecules. Obviously, only in this case is there hope of developing a limited set of electro-optical quantities (similar to a set of potential-energy coefficients), with the aid of which it will be possible to carry out a theoretical analysis of intensities and polarizations in the IR spectra of an enormous number of molecules. These questions have not been solved either in the numerous works of foreign authors or in the later works of Sverdlov (^3).

In the present communication the principal conclusions from the investigations we have carried out are set forth.

We shall proceed from the formula for the derivative of the dipole moment of a molecule with respect to a normal coordinate, proposed in (^2, ^3), retaining the notation adopted there:

$$\left(\frac{\partial\vec{\mu}}{\partial Q_i}\right)_0 = \left[\{e\}\left|\frac{\partial\mu}{\partial q}\right| + \{\mu\}\left|\frac{\partial e}{\partial q}\right|\right]\|q\|_i; \qquad \left|\frac{\partial e}{\partial q}\right| = S^{-1}\left(\Delta E\tilde{B}\tilde{T} - E\right). \quad (1)$$

From experiment we may know the magnitude of the derivative $(\partial\vec{\mu}/\partial Q_i)_0$ up to its sign, and its direction. We shall also regard the forms of the vibrations as known. The elements of the matrices $|\partial\mu/\partial q|$ and $\{\mu\}$ form the required set of electro-optical parameters. For branched asymmetric molecules the total number of unknowns is $(3N-5)(N-1)$. Substituting into equality (1) the corresponding experimental values $(\partial\mu/\partial Q_i)_0$ and the forms $\|q\|_i$, we obtain a system of $(3N-6)$ independent vector equations with respect to the electro-optical parameters, which is equivalent to a system of $3(3N-6)$ independent scalar equations. As additional

of the equation one may use the equality $\vec{\mu} = \sum \mu_k \vec{e}_k$, which is likewise equivalent to three scalar equations. As we see, the total number of equations for determining electro-optical parameters in the case of asymmetric molecules will be equal to $3(3N-5)$. Already for $N \geq 5$ the number of unknowns exceeds the number of possible equations. If the molecule possesses symmetry elements, then the number of electro-optical parameters to be determined decreases. However, at the same time the number of equations that can be used for their calculation also decreases, since some of the scalar equations become identities. The same also applies to vibrations inactive in the IR spectra. Thus, the number of different electro-optical parameters and independent equations that can be used to determine them is connected with the configuration of the molecule. It is desirable to reduce the number of unknowns, which can be done by choosing a simplified form of the matrix $|\partial\mu/\partial q|$, and to increase the number of equations with the aid of isotopically substituted molecules, in which both $(\partial\vec{\mu}/\partial Q_i)$ and $\|q\|_i$, as well as $|\partial e/\partial q|$, change. It is especially advantageous to use isotopically substituted molecules of lower symmetry. The impossibility of determining the absolute signs of the quantities $(\partial\vec{\mu}/\partial Q_i)_0$ leads to the fact that, from the solution of the inverse electro-optical problem, the parameters are found only to within an absolute sign.

On the basis of the general theory developed, electro-optical parameters were determined for a number of molecules: HCN(DCN); H_2C_2(D_2C_2, HDC_2); C_2H_4(C_2D_4, cis- and trans-$C_2H_2D_2$); CH_4(CD_4, CH_3D, CD_3H, CH_2D_2); C_2H_6(C_2D_6).

In all cases the smallest set of electro-optical parameters was found that correctly described the observed intensities in the spectra of the given molecule and its isotopically substituted forms. Along with other electro-optical parameters, the characteristics of C–H bonds of the most important groups were determined:

Figure 1. Experimental spectrum of propylene

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≡CH $\mu = 1.10$ D, $\partial\mu/\partial q = 1.00$ D/Å; =CH$_2$ $\mu = 0.70$ D, $\partial\mu/\partial q = 0.53$ D/Å, $\partial\mu/\partial q' = 0.10$ D/Å; –CH$_3$ $\mu = 0.28$ D, $\partial\mu/\partial q = 0.74$ D/Å, $\partial\mu/\partial q' = 0.31$ D/Å. Primes denote derivatives with respect to the coordinates of changes in the lengths of neighboring CH bonds. It was noted that there is a definite relationship between the coefficients of the potential energy and the electro-optical parameters, manifested, in particular, in the fact that equality to zero of the potential-energy coefficients is accompanied by the smallness of the corresponding electro-optical parameters. This property can be used to choose the initial form of the matrix $|\partial\mu/\partial q|$.

Knowledge of the electro-optical parameters of CH-, CH$_2$-, and CH$_3$-groups allowed us to attempt to calculate intensities in the spectra of complex molecules. Dimethylacetylene and propylene molecules were chosen as the objects. In the calculations, in order to reduce the number of electro-optical parameters introduced, a number of unavoidable assumptions were made. As a result we hoped to obtain only qualitative agreement with experiment. Quantitative agreement was expected only for valence CH vibrations, for which the high characteristic nature of the form sharply reduced the errors associated with possible inaccuracy in specifying some electro-optical parameters. The results of the calculations are given in Table 1 and in Fig. 1. In the propylene molecule the experimental ratio of the integral intensities of the bands in the region 3100; 2950; 1650 cm^{-1} is equal to $1 : 5 : 0.45$, and the calculated ratio is respectively $1 : 4.9 : 0.38$.

Analysis of the data obtained shows that the intensities and polarizations in the IR spectra of complex molecules can be calculated on the basis of the electro-optical parameters of related molecules. The presence of repeating groups, especially in organic molecules, makes it possible to assert that it is possible to create a set of electro-optical parameters suitable for the analysis of a large number of compounds. At the same time it must be noted,

that, as was also shown by the calculation of the halomethane molecules, the electro-optical parameters are more sensitive to the environment than are the elements of the potential-energy matrix. In this connection, the accuracy of calculating intensities

Fig. 1. Experimental spectrum of propylene (gas, pressure 50 mm Hg, cell length 100 mm). The bars show the calculated values $(\partial\vec{\mu}/\partial Q_i)^2_0$. The triangles denote bands for which $(\partial\vec{\mu}/\partial Q_i)^2_0 < 1 \cdot 10^{-2}\,(\mathrm{D/Å})^2$. In the region 2900–3000 cm^{-1} there is an overlap of four absorption bands corresponding to stretching vibrations of CH bonds. The figure shows $\sum_i^4 (\partial\vec{\mu}/\partial Q_i)^2_0$.

and polarizations, especially at first, will be considerably lower than the accuracy of calculating vibrational frequencies. It is interesting to note that the intensity of the vibration of the C=C bond in propylene is determined entirely by the electro-optical parameters of the CH bonds. In other words, if the frequency of a vibration depends mainly on the properties of the given bond or group of atoms, then the intensity of this same vibration may be connected primarily with the environment. This circumstance must be taken into account in any attempts to judge intra- and intermolecular influences from changes in the intensities of absorption bands. In most organic molecules we deal with various vibrations of CH bonds, which almost always are characteristic in form. As our calculations have shown, knowing the corresponding electro-optical parameters, one can comparatively simply and with fairly high accuracy calculate the absolute intensities of any bands (or their sums) belonging to these vibrations. Then the absolute intensities of all other bands can be found from the relative intensities in the spectrum, using the calculated intensities of the CH-vibration bands as an internal standard.

Table 1

Experimental and calculated values for dimethylacetylene (D/Å)

ν, cm^{-1}	$(\partial\vec{\mu}/\partial Q_i)_0$, exp.$^{(4)}$	$(\partial\vec{\mu}/\partial Q_i)_0$, calc.
Type A_{2u}		
2915	1.14	1.15
1382	0.25	0.36
1152	0.08	0.08
Type E_u		
2973	0.72	0.80
1456	0.60	0.40
1054	0.12	0.23

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