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Abstract

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Intensities in Infrared Absorption Spectra and the Study of Polyatomic Molecules

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In recent years, interest has grown in the use of intensities in vibrational absorption spectra of polyatomic molecules for investigating the structure and properties of molecules and intermolecular interactions. This is connected above all with the great sensitivity of the method to various changes in molecular structure and in intermolecular interactions. Apparently, the intensities of absorption bands are a more delicate instrument of study than vibrational frequencies. However, the complex dependence of intensities on molecular structure means that their practical use requires special caution and a careful accounting of all factors that affect intensity.

In the present communication, certain conclusions following from a general theoretical consideration are systematized; failure to take them into account when using the method of measuring intensities and polarizations in IR spectra may lead to gross errors.

Let us compare the principal factors determining the position of a vibrational band in an IR spectrum (the vibrational frequency) and its intensity. The intensity of a given absorption band depends, as is known, on the amplitude and frequency of the change in the vector of the dipole moment of the molecule in space during vibration of the given form. In the existing theory of intensities and polarizations in IR spectra of complex molecules, the dipole moment of the molecule, being a function of the distribution of the electric field of the molecule, is customarily characterized by the vectors of the dipole moments of bonds (or groups). The change in the dipole moment during vibrations will be connected both with changes in the absolute values of the components of the dipole-moment vector and with changes in their directions. To characterize the former, derivatives of the dipole moments of bonds and groups with respect to the natural vibrational coordinates are introduced; the latter are characterized by rotations of bonds in space in the given vibration.

The set of dipole moments of bonds and their derivatives with respect to the natural vibrational coordinates forms a system of so-called electro-optical parameters. Rotations of bonds in space are functions of the internal vibrational coordinates in which the problem of the frequencies and forms of normal vibrations of a polyatomic molecule is usually solved, and also, very importantly, functions of the conditions for conservation of the angular momentum of the entire molecule during vibration of the given form. If the vibrational frequencies and their forms are determined entirely by the force field of the molecule, its geometry, and the distribution of the masses of the atoms, then the intensities of the same absorption bands, in addition to these factors, depend on the electro-optical parameters and on the conditions for conservation of the angular momentum of the entire molecule in the given normal vibration. Of fundamental significance is the fact that the intensity of an absorption band and its position in the spectrum are consequences of different parameters, and therefore their assignment (interpretation) may not coincide.

Let us explain this by the example of the simplest case of vibrations that are quite characteristic in frequency and form for a given group of coordinates.

(atoms). As is well known, in this case the frequency and form of the normal vibrations will be determined entirely by the properties of the force field, the masses of the atoms, and the geometry of only the selected group. The intensity of these vibrations, however, may depend substantially on the rest of the molecule. Indeed, for vibrations within the group under consideration, owing to the requirement that the angular momentum of the entire molecule be conserved, its change upon disturbances of the equilibrium configuration of the selected group must be compensated by vibrations of the same frequency of the entire molecule as a whole about some axis. As a result, rotations arise in the space of the bonds not belonging to the given group. For suitable values of the dipole moments of the bonds, this effect may make a noticeable, and sometimes even the principal, contribution to the intensity of the given band. For example, in antisymmetric vibrations of a symmetric nonlinear molecule XY_2, the angle between the bonds does not change, but, owing to vibrations of the molecule as a whole about an axis perpendicular to the plane XY_2, the dipole moment of the XY bond enters into the expression for the intensity of such a normal vibration (1). In molecules of the type X_3YU of symmetry C_{3v}, a pronounced valence vibration is usually distinguished by a fairly high characteristic nature with respect to form; however, in this case the YU bond will execute vibrations in space the more strongly, the smaller the mass of atom U in comparison with X, which will be reflected in the intensity of the corresponding band. In studying the hydroperoxide group $COOH$ (2), it was found that in the vibration associated mainly with a change in the length of the O—O bond and the COO angle, the OH bond, having a light atom at its end, executes large excursions in space not only because of the incomplete characteristic nature of these vibrations in form, but to a considerable degree owing to the requirement that the angular momentum of the whole group as a whole be conserved. Since the dipole moment of the OH bond is rather large, the result obtained is, at first glance, paradoxical: the intensity of the vibrations considered is determined mainly by the dipole moment of the OH bond!

In addition to this effect, the influence of the environment may prove decisive also in the case where the derivatives of the dipole moments of the bonds of the group with respect to their "own" coordinates are smaller than the derivatives, with respect to these same coordinates, of the dipole moments of neighboring bonds (³). For example, the intensities of vibrations of symmetric groups $C = C$, $C \equiv C$, $N = N$, etc., which are quite characteristic in frequency and form, must be completely characterized by the environment, whereas their frequencies depend mainly on the properties (force constants) of these bonds. Thus, the intensity of the valence vibration $C = C$ in propylene is determined by the dipole moments of the CH bonds (⁴).

Let us now suppose that we have replaced one of the atoms outside the characteristic group by another. Let the characteristic nature of the given vibration in frequency and in form not be disturbed thereby. Then only a change in the moment of inertia of the entire molecule and in the vibrations of the molecule as a whole associated with this may lead to a change in the band intensity, although the structure of the group, its electric and force field, and the vibration frequency do not change. For such substitutions as lead to disturbances of the form of the vibrations or of the electric field of the group, the changes in intensities will have an even more complex nature. In experiment, however, the total effect is observed. As a result, it becomes clear that, for fruitful use of the intensities of absorption bands in the vibrational spectrum and, in particular, for conclusions about processes inside the molecule under various kinds of substitutions, it is necessary to know the principal factors determining the intensity of the given band, i.e., to have an interpretation (assignment) of the intensities, just as is done for frequencies; moreover, it turns out that, in the general case, the assignments of frequencies and intensities may not coincide. Coincidence of the assignment of intensities and frequencies will occur only for those groups whose vibrations possess the property of characteristicity with respect to intensity and polarization (³). The identification of these vibrations is, in our opinion,

opinion, a task of primary importance. The general criteria derived by the author for characterizing vibrational absorption bands in terms of intensity and polarization can be of great help in this regard (³).

A quantitative analysis of the contribution of various factors to the intensity of a given band, and a separation of the causes producing a change in intensity upon substitution, can apparently be carried out using the computational method developed (⁴⁻⁷), especially if an entire class of compounds with repeating groups is studied consecutively, with extensive use of isotope-substituted molecules. The first results obtained are, in this sense, very encouraging.

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