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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ANOMALOUS DISTRIBUTION OF INTENSITIES IN BANDS OF VIBRATIONS RESONATING BY FERMI

(Presented by Academician I. V. Obreimov, 13 IV 1962)

For polyatomic molecules, cases of proximity or even coincidence of different vibrational terms are not uncommon. When the corresponding wave functions have the same symmetry, the accidental degeneracy is lifted and, in the absorption spectrum, a doublet is observed instead of a single band. This widespread and still insufficiently studied phenomenon, called Fermi resonance, is associated with the presence of anharmonic terms in the potential energy of nuclear motion.

Previously it was assumed ([1]) that the ratio of the intensities of the bands (denoted by $I_{\nu'}/I_{\nu}$), corresponding to tones of higher and lower order*, in the case most favorable for resonance cannot exceed unity. However, it was later shown that the additional perturbation arising upon condensation of a vapor is accompanied by an enhancement of the effect of equalization of intensities ([2]). The ratio $I_{\nu'}/I_{\nu}$ turned out to be close to unity even when the magnitude of the natural "splitting" was not zero. Moreover, study of a series of Fermi doublets on crystalline samples made it possible to identify three cases with anomalous distribution of intensities, where $I_{\nu'}/I_{\nu}$ not only reaches unity but considerably exceeds it.

Fig. 1. Absorption in the bands of the vibrations ν_3 and $\nu_1+\nu_4$ of CCl_4. Liquid $+20^\circ$ (1); crystal -30° (2), -80° (3), -120° (4), -160° (5), -160° in polarized radiation (6)

These results are presented in Figs. 1-3 in the form of families of curves obtained for various temperatures of the solid phase. At room temperature (liquid) the ratio $I_{\nu'}/I_{\nu}$ is close to unity only in the case of CCl_4 (in the other two it does not exceed 0.1),

* Here and below, each component is associated by us purely conventionally with a tone of a definite order, since the resonant interaction of the levels leads to mixing of the wave functions corresponding to them.

and for crystals at a temperature close to the melting point this ratio already exceeds unity, reaching 10 for iodobenzene. Before turning to the interpretation of the observed anomaly, it is appropriate to note two more interesting facts.

The first of them concerns the temperature dependence of the integrated absorption in the components of the doublet. For CCl_4 and iodobenzene, lowering the temperature leads to an increase in $I_{v'}/I_v$, whereas the chlorobenzene doublet shows the qualitatively opposite result: on decreasing, the ratio under consideration becomes equal to unity, and then less than unity.

It is characteristic that the short-wavelength component of the doublet corresponding to the fundamental tone is practically not affected by temperature. The intensities of the remaining five bands of the doublets studied vary with temperature; however, for iodobenzene and chlorobenzene the increase in the latter is accompanied by an increase in absorption—a fact most often encountered for molecular crystals—whereas the intensity of both bands of carbon tetrachloride decreases, which is characteristic of infrared absorption spectra of molecular liquids ([3]).

Let us consider the second interesting fact. The cryostat used in the work made it possible to obtain polycrystalline layers whose individual single-crystal blocks were arranged in a definite predominant direction, thus allowing measurements to be made in polarized radiation. These were carried out for CCl_4. It turned out (Fig. 1) that both components of the doublet correspond to transitions of one and the same polarization. Since Fermi resonance in the condensed phase is a special case of intermolecular resonance, first established by I. V. Obreimov ([4]) and theoretically substantiated in the work of A. S. Davydov ([5]), this fact may at first sight seem unusual, since the components of "Davydov" splitting are polarized in mutually perpendicular directions. It turns out that the point is that the latter is caused by the interaction of vibrations of different molecules in the crystal cell that are oriented differently (with respect to frequency), whereas in our case the interaction of vibrations of one and the same molecule comes to the fore; the directions of their transitions coincide completely, although the frequencies may differ somewhat.

Fig. 2. Absorption in the bands of the planar deformation vibration of symmetry B_1, ν 1061 cm^{-1}, and of the combination tone of the same symmetry, ν 1069 cm^{-1}, of iodobenzene. Liquid −20° (1); crystal −35° (2), −70° (3), −100° (4), −130° (5), −167° (6).

In conclusion, let us dwell on the interpretation of the anomalous ratio $I_{v'}/I_v$. The criterion for when this is possible is not difficult to establish using the results of work ([6]). Let the terms v and v' resonate, with the order of the first

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Figure 2: Fig. 2. Absorption in the bands of the planar deformation vibration of symmetry B_1, ν 1061 cm^{-1}, and of the combination tone of the same symmetry, ν 1069 cm^{-1}, of iodobenzene. Liquid −20° (1); crystal −35° (2), −70° (3), −100° (4), −130° (5), −167° (6).

of them lower by one. Then the inequality $I_{v'}/I_v > 1$ is satisfied

when the condition

$$\frac{2L_{vv'}}{\delta} < -\frac{k^2-1}{k}\frac{\delta}{|\delta|}, \tag{1}$$

is satisfied, where $L_{vv'}$ is the matrix element of transfer of vibrational-excitation energy from molecule to molecule under the condition of alternate realization of one and the other intramolecular vibration; δ is the magnitude of the "natural" splitting, dependent on the matrix elements L_{vv} and $L_{v'v'}$, $k = p^0_{0v}/p^0_{0v'}$ $(k \geq 1)$, p^0_{0v} and $p^0_{0v'}$ are the matrix elements of the dipole moment for the corresponding transitions, calculated on the wave functions of the isolated molecule.

Fig. 3. Absorption in the region of the planar deformation vibration of symmetry B_1 (ν 1088 cm^{-1}) of chlorobenzene and of the combination tone of the same symmetry (ν 1075 cm^{-1}). Liquid −−45° (1); crystal 50° (2), −80° (3), −110° (4), −140° (5), −160° (6).

Let, for example, $\delta > 0$, and $L_{vv'} < 0$; then (1) can be written as

$$\left|\frac{2L_{vv'}}{\delta}\right| > \frac{k^2-1}{k} \quad \text{or} \quad \sqrt{\left(\frac{\chi}{\delta}\right)^2 - 1} > \frac{k^2-1}{k}, \tag{2}$$

where χ is the total splitting, i.e., the distance between the maxima observed experimentally. Relations (1) and (2) indicate that the cause of the anomalous intensity ratio lies in the presence of migration of vibrational-excitation energy through the crystal, ensuring the appearance of intermolecular resonance. The absence of long-range order adversely affects the migration mechanism, and therefore the effect found for the solid phase is not observed in the liquid phase.

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