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VERIFICATION OF THE KRAMERS–KRONIG RELATIONS IN THE VIBRATIONAL PART OF THE SPECTRUM

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The well-known Kramers–Kronig dispersion relations ([1]) have been tested experimentally in a small number of cases, mainly in the region of electronic transitions of solids ([2,3]), etc. In particular, for molecular crystals a substantial deviation from these relations was established, increasing with decreasing temperature. It was therefore of interest to investigate the case of molecular liquids, especially in the region of vibrational transitions, where the Kramers–Kronig relations are widely used, for example in calculating oscillator strengths of intense transitions on the basis of dispersion data in transparency regions ([4–6]) (naturally, a violation of the aforementioned relations would make calculations of this kind unjustified). This constituted the aim of the present work.

The investigation was carried out in the region of: 1) the most intense vibrational band ν_5 of chloroform and 2) the doublet ν_3 and $\nu_1+\nu_4$ of carbon tetrachloride. These bands are completely isolated and determine the principal contribution to the infrared dispersion of $CHCl_3$ and CCl_4, which is undoubtedly an important condition for the uniqueness of the verification undertaken.

In the calculations we followed the method developed by Rasp and described in ([2]). According to this method, one should construct the curve $n(\nu)\chi(\nu)$ as a function of ν (n and χ are the refractive index and the absorption coefficient) and approximate it by a set of Gaussian curves of the form $A_i \exp[-(\nu-\nu_i)/\delta_i]$ with specially chosen parameters A_i, ν_i, and δ_i. After this it is sufficient to verify the validity of the relation

$$n^2(\nu) = 1 + \chi^2(\nu) - \frac{4}{\sqrt{\pi}} \sum_i A_i W\left(\frac{\nu-\nu_i}{\delta_i}\right), \quad (1)$$

where $W(t)$ is a known tabulated function ([7]). Taking into account that the specific approximation procedure is also well developed ([2]), the application of this method for verifying the Kramers–Kronig relations proves to be simpler than numerical integration of the experimental curves.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

The experimental data for $n(\nu)$ and $\chi(\nu)$ were taken from previous works (8–10). The error in measuring $n(\nu)$ and $\chi(\nu)$ near the maxima of the absorption bands was $\sim$ 15–20%; in the middle part of the bands and on the wings the error in $\chi(\nu)$ was $\sim$ 5–7%. The curves $n(\nu)\chi(\nu)$ were approximated by 7–10 Gaussian curves with an accuracy of up to several percent in area.

The experimental and calculated values of n^2 are shown in Figs. 1 and 2. The measure of fulfillment of the Kramers–Kronig relations should first of all be taken as the agreement of the magnitudes of the spreads $\Delta n^2 = n^2_{\mathrm{max}} - n^2_{\mathrm{min}}$ of both dispersion curves, since Δn^2 almost does not depend on the influence of other transitions and is practically completely determined by the vibrational transition under consideration.*

* Distant transitions make, in the region of the given band, a contribution almost independent of ν and therefore cancel out when forming the difference for Δn^2. However, the curve n^2 itself may experience a displacement as a whole.

It is seen from Fig. 1 that for the vibration ν_3 of $CHCl_3$, $\Delta n^2_{\mathrm{exp}}/\Delta n^2_{\mathrm{theor}} = 1.3$. Since the error in determining Δn^2 for both curves may in the worst case reach 35%, within the limits of the errors of calculation and experiment one may state the validity of the Kramers-Kronig relations. True, there is still a certain shift of the extreme values of n^2 along the frequency scale, which was a reflection of the experimentally observed nontrivial relative arrangement of the $n(\nu)$ and $\chi(\nu)$ curves: the maxima of χ were appreciably shifted toward the long-wavelength side in comparison with the center of the $n(\nu)$ curve.

Fig. 1. Dispersion curves of chloroform: 1—experimental; 2—calculated with the aid of the Kramers-Kronig relations

Fig. 2. Dispersion curves of carbon tetrachloride: 1—experimental; 2—calculated with the aid of the Kramers-Kronig relations

An attempt to repeat the calculation, shifting the experimental $\chi(\nu)$ curve without deformation until its maximum coincided with the center of $n(\nu)$, eliminated the frequency shift, but the ratio of the amplitudes Δn^2 increased to 2. The reason for the mentioned shift is not entirely clear; however, the effect itself is not very large and apparently does not greatly weaken the conclusion concerning the validity of the dispersion relations in the present case. An analogous result was recorded in (3) in the region of the first electronic transition for dilute solutions of anthracene. A different picture is found for the Fermi-resonance doublet ν_3 and $\nu_1+\nu_4$ of carbon tetrachloride. In this case there is not only no quantitative, but not even qualitative, agreement between the calculated and experimental curves (Fig. 2). On the calculated curve the higher maximum corresponds to the higher frequency, whereas on the experimental curve it corresponds to the lower one. The ratios of the amplitudes are 0.3 and 0.9 for the long-wavelength and short-wavelength components of the doublet, respectively. The first of these, as we see, differs substantially from unity, indicating a violation of the Kramers-Kronig relation. The general character of the proof of these relations (1) does not permit the discrepancy to be attributed to the Fermi resonance. Possibly, we are dealing here with a manifestation of spatial dispersion, as in (2).

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