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Abstract

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PHYSICS

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OBSERVED AND TRUE ABSORPTION SPECTRA OF LIQUID $CHCl_3$ AND CCl_4 IN THE REGION 740-810 cm^{-1}

(Presented by Academician A. N. Terenin, 18 I 1963)

Usually the differences between the absorption spectra of molecules measured experimentally in a condensed medium, $K(\nu)$, and in the gas phase, $K_0(\nu)$, are explained by changes in the intrinsic spectroscopic characteristics of the molecules (shifts of energy levels, changes in transition probabilities, etc.) as a result of intermolecular interactions. It is assumed here that the spectral course of $K(\nu)$ for the condensed phase corresponds (as is the case for rarefied gases) to the course of the spectral density of Einstein' s absorption coefficient $B(\nu)$, determined by the internal properties of the molecule under study and therefore representing its true spectral characteristic in the given medium. However, between the observed spectrum of a molecule $K(\nu)$ and the true spectrum $B(\nu)$ in a condensed medium (in contrast to $K_0(\nu)$ and $B_0(\nu)$ in the gas phase) there may exist differences caused by universal effects that are usually not taken into account and that are associated with changes in the field strength of the light wave acting on a molecule in the medium ([1–4]). Obviously, without knowledge of the true spectra of a molecule it is impossible to obtain correct values of its spectroscopic parameters in different media and to compare them in a justified way.

It follows from the above that it is necessary to correct the observed spectra $K(\nu)$ in order to obtain the true spectra $B(\nu)$ by taking into account the change in the internal-field parameter within the limits of the spectrum under study ([5]). The general relation between the true spectrum $B(\nu)$ of a molecule in a condensed medium and the observed spectrum $K(\nu)$ or $\varepsilon(\nu)$* is expressed by the relation ([5])

$$B(\nu) = \frac{\varepsilon(\nu)c}{h\nu}\,\theta(\nu); \tag{1}$$

Fig. 1

Figure 1: Fig. 1

where c is the speed of light, $\theta(\nu)$ is the correction for the universal influence of the internal (effective) field. For one-component systems (in particular, liquids) and for the case of isotropically polarizable molecules, $\theta(\nu)$ has the form** when the internal field is taken into account according to the Lorentz model

$$\theta_{\text{I}}(\nu) = 9n\left|\frac{1}{\hat{n}^2+2}\right|^2 \tag{2}$$

and, according to the Onsager-Böttcher model,

$$\theta_{\text{II}}(\nu) = a^2 n\left|\frac{2\hat{n}^2+1}{3a\hat{n}^2+(\hat{n}^2-1)^2}\right|^2. \tag{3}$$

Here $\hat{n} = n - i\chi$ is the complex refractive index of the medium, $a = 2\pi N r^3$, where r is the radius of the Onsager cavity, and N is the number of particles per unit volume.

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* $K(\nu)$ is the Bouguer absorption coefficient, related to the molecular absorption coefficient $\varepsilon(\nu)$ by the relation $\varepsilon(\nu) = K(\nu)/N$, where N is the number of absorbing particles per unit volume of the medium.

** The derivation of the expression for $\theta(\nu)$, pertaining to the general case of anisotropic molecules and multicomponent systems, will be published in another article. Formulas (2) and (3) are particular cases of the general expression.

We shall find the true spectra of liquid $CHCl_3$ and CCl_4 in the region of the intense absorption band corresponding to the fundamental C—Cl vibration (740-810 cm^{-1}). The choice of the objects of study is due, first, to the characteristic behavior of the optical constants n and χ of the liquids in this spectral region, which makes it possible to expect substantial changes in the correction $\theta(\nu)$ within the band. In addition, the indicated molecules correspond well to the model of an isotropically polarizing particle used in deriving formulas (2) and (3). Finally, from general considerations one may assume the absence in these liquids of strong specific interactions ([6]), as a result of which the expected effect should appear in its purest form.

Fig. 1. Observed $K(\nu)$ and true $B(\nu)$ absorption spectra of gaseous and liquid $CHCl_3$ in the region 740-810 cm^{-1}. **a** —observed spectra: **1** —gas; **2** —liquid. **b** —true spectra: **1** —gas; **2** —liquid with allowance for the internal field according to Lorentz; **3** —liquid with allowance for the internal field according to Onsager —Böttcher.

Figure 2

Figure 2: Figure 2

The optical constants n and χ of liquid $CHCl_3$ and CCl_4 were found from measurements of reflection at the boundary with two crystalline media (KCl and CsI), characterized in this region by different values of the refractive index. For comparison with the spectra of the liquids, absorption spectra of the indicated molecules in the gas phase were obtained.

The experimental data and the results of their processing are presented in Figs. 1 and 2 and in Tables 1 and 2. In Figs. 1a and 2a are shown, respectively, the observed spe-

Table 1

Values of the spectroscopic characteristics of gaseous and liquid $CHCl_3$ and CCl_4*

Substance	State	Observed values: ν_{max}	Observed values: $\Delta\nu_{1/2}$	Observed values: $\frac{\int K(\nu)\,d\nu}{\int K_0(\nu)\,d\nu}$	True values**: ν_{max}	True values**: ν_{max}	True values**: $\Delta\nu_{1/2}$	True values**: $\Delta\nu_{1/2}$	True values**: $\frac{\int B(\nu)\,d\nu}{\int B_0(\nu)\,d\nu}$	True values**: $\frac{\int B(\nu)\,d\nu}{\int B_0(\nu)\,d\nu}$
					I	II	I	II	I	II
$CHCl_3$	vapor	772	14	1.6	772	772	14	14	1.2	1.3
$CHCl_3$	liquid	760	27	1.6	769	773	22	13	1.2	1.3
CCl_4	vapor	794	8	1.4	794	794	8	8	1.0	1.2
CCl_4	liquid	787	19	1.4	790	794	15	5	1.0	1.2

* The values of the frequencies of the maxima and the half-widths of the bands were measured with an accuracy of about 1 cm^{-1}; the accuracy of measurement of the integral intensity is of the order of 15%.

** I —calculation by formula (2) (Lorentz model); II —calculation by formula (3) (Onsager—Böttcher model).

absorption spectra of $CHCl_3$ and CCl_4 in the gaseous (1) and liquid (2) phases, reduced to the band maximum. In Figs. 1b and 2b are given the true spectra of the same molecules in the gas (1) and in the liquid, obtained from the observed spectra by recalculation according to formulas (2) and (3) (curves 2 and 3, respectively). The values of the frequencies of the band maxima (ν_{max}), their half-widths ($\Delta\nu_{1/2}$), and the ratios of the integrated intensities of the observed ($\int K(\nu)d\nu/\int K_0(\nu)d\nu$) and true ($\int B(\nu)d\nu/\int B_0(\nu)d\nu$) spectra for different aggregate states are given in Table 1.

Fig. 2. Observed $K(\nu)$ and true $B(\nu)$ absorption spectra of gaseous and liquid CCl_4 in the region 750-810 cm^{-1}. The designations are the same as in Fig. 1.

It follows above all from the data presented that the true spectra $B(\nu)$ of $CHCl_3$ and CCl_4 molecules in the condensed phase differ strongly from the observed $K(\nu)$ spectra in all characteristics—the position, shape, and intensity of the bands. As a result of introducing the corrections $\theta(\nu)$, the true spectra of the liquids approach the spectra of the gas phase, and when $\theta_{II}(\nu)$ is used the indicated spectra practically coincide. This confirms the assumption made above regarding the absence in liquid $CHCl_3$ and CCl_4 of strong specific interactions. Moreover, the coincidence, within the limits of experimental error, of the true spectra of the liquid $B(\nu)$ and of the gas $B_0(\nu)$ indicates that intermolecular interactions in these liquids in general exert only a weak influence on the spectral characteristics of the molecules studied, whereas on the basis of an analysis of the observed spectra $K(\nu)$ and $K_0(\nu)$ a completely opposite conclusion might be drawn. Also noteworthy is the fact of the strong change in the relative intensity of the components of the Fermi-resonance doublet in the spectra of CCl_4 upon introducing the corrections $\theta(\nu)$, as illustrated by the data of Table 2. It follows from these data that the widespread opinion according to which the Fermi resonance is enhanced in liquid CCl_4 in comparison with the gas (see Table 2) requires clarification.

Table 2

Ratio of intensities at the maxima of the bands $\nu_1+\nu_4$ and ν_3 of gaseous and liquid CCl_4

State	Observed values	True values*
Vapor	0.17	0.17
Liquid	0.63	0.43(I); 0.13(II)

* See note ** to Table 1.

Thus, the results of the present investigation confirm the conclusions of work (^5) that the observed and true absorption spectra of molecules placed in a condensed medium may differ significantly from one another in all characteristics. It follows from this that it is important and necessary to take quantitative account of the influence of the internal field (i.e., to determine the true spectrum of molecules in a given medium from the observed one), in order to avoid errors and misunderstandings that may be made in interpreting experimental results.

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