N. G. BAKHSHIEV, O. P. GIRIN, and V. S. LIBOV

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Abstract

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N. G. BAKHSHIEV, O. P. GIRIN, and V. S. LIBOV

ON THE RELATION BETWEEN THE OBSERVED AND TRUE ABSORPTION SPECTRA IN A CONDENSED MEDIUM

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The absorption spectrum of a substance is customarily taken to mean the curve of dependence of the experimentally observed absorption coefficient $K(\nu)$ on the radiation frequency ν. In this case, as a measure of the total probability of a transition with absorption of light between the energy levels of a quantum system (the integral intensity), one takes the value of the absorption integral, defined by the area bounded by the spectral absorption curve and the frequency axis,

$$A = \int \varepsilon(\nu)\, d\nu = \frac{1}{N} \int K(\nu)\, d\nu, \tag{1}$$

where $\varepsilon(\nu)$ is the molecular absorption coefficient, $K(\nu)$ is the coefficient appearing in Bouguer' s law, and N is the number of absorbing particles per unit volume of the medium.

It is not difficult to show that, in the case of isolated systems, the experimentally measured absorption coefficient $K_0(\nu)$ is uniquely related to the spectral density of the Einstein coefficient for absorption $B_0(\nu)$, which is determined by the internal properties of the particle and is therefore the true spectral characteristic of the absorbing center.

Indeed, the amount of energy absorbed per unit time in a unit spectral interval in a volume $dV = q\, dx$ is written in the form [1]

$$\frac{dw(\nu)}{dt} = B_0(\nu)\, u_0(\nu)\, h\nu\, N_0 q\, dx, \tag{2}$$

where $u_0(\nu) = E_0^2(\nu)/8\pi$ is the volume spectral energy density of a light wave in vacuum.

On the other hand, according to Bouguer' s law:

$$\frac{dw(\nu)}{dt} = K_0(\nu)\, F_0(\nu)\, dx = \varepsilon_0(\nu)\, S_0(\nu)\, N_0 q\, dx, \tag{3}$$

where $S_0(\nu) = cE_0^2(\nu)/8\pi$ is the Umov-Poynting vector (^{1,2}).

From (1) and (2) it follows that

$$B_0(\nu) = \frac{\varepsilon_0(\nu)c}{h\nu}, \tag{4}$$

$$A_0 = \frac{h}{c}\int B_0(\nu)\, d\nu = \frac{h\nu_{\text{cp}}}{c}\int B_0(\nu)\, d\nu = B_0\,\frac{h\nu_{\text{cp}}}{c}. \tag{5}$$

In the case of a condensed medium (liquids, solutions, solids, gases at high pressures), it must be borne in mind that the experimentally measured values $\varepsilon(\nu)$ and $K(\nu)$ are no longer related to the Einstein coefficient $B(\nu)$ of the particle under study by a simple relation of the type (4), in which the influence of intermolecular interactions on absorption is not taken into account. In addition, we emphasize that, owing to a change in the internal properties of the particle when it is placed in a condensed medium, the Einstein coefficient $B(\nu)$ may differ from $B_0(\nu)$.

Let us find the relation between the quantities $B(\nu)$ and $\varepsilon(\nu)$ (or $K(\nu)$) for a condensed medium. Analogously to (2) and (3),

$$\frac{dw(\nu)}{dt} = B(\nu)u(\nu)h\nu N q\, dx, \tag{6}$$

$$\frac{dw}{dt} = K(\nu)F(\nu)\, dx = \varepsilon(\nu)S(\nu)Nq\, dx, \tag{7}$$

where $u(\nu) = E_{\text{eff}}^2(\nu)/8\pi$, $S(\nu) = cn(\nu)E_{\text{av}}^2(\nu)/8\pi$ (^{2}). Here $E_{\text{eff}}(\nu)$ is the effective (internal) microfield of the light wave acting on the absorbing center; $E_{\text{av}}(\nu)$ is the macroscopic mean field of the light wave in the dielectric; $n(\nu)$ is the refractive index of the medium.

Comparing (6) and (7), we obtain

$$B(\nu) = \varepsilon(\nu)\frac{n(\nu)c}{h\nu}\frac{E_{\text{av}}^2(\nu)}{E_{\text{eff}}^2(\nu)} = \varphi(\nu)\frac{\varepsilon(\nu)c}{h\nu}. \tag{8}$$

Thus, from (4) and (8) it follows that, in the case of a condensed medium, the spectral behavior of the experimentally determined quantity $\varepsilon(\nu)$ does not coincide with the behavior of the true spectral characteristic of the absorbing center $B(\nu)$, and depends substantially on the properties of the medium.

In accordance with the above, it is natural to take as the measure of the integral absorption intensity of a particle located in a condensed medium not the quantity A (see formula (1)), but the value

$$A^* = \frac{h\nu_{\text{av}}}{c} \int B(\nu)\, d\nu = \bar{B}\frac{h\nu_{\text{av}}}{c} \tag{9}$$

(cf. (5)). Using (8), we have

$$A^* = \int \varphi(\nu)\varepsilon(\nu)\, d\nu, \tag{10}$$

i.e., the integral intensity usually determined with the aid of (1) (as well as the spectrum) in the case of a condensed medium is not a true characteristic of the absorbing particles.

Therefore, in order to obtain the true spectra of the particle under study, $B(\nu)$, in different media and to compare them with one another and with the gas-phase spectrum $B_0(\nu)$ in a justified manner, an additional quantitative treatment of the experimental spectra $\varepsilon(\nu)$ is necessary, in order to take into account the universal influence of the effective (internal) field. Generally speaking, the question of the need to take into account the field E_{eff} and of methods for doing so has been considered in recent years in a number of works (see, for example, ([3,4])). However, in all cases the correction for the influence of the internal field is taken to be constant within the absorption band, i.e., it is assumed that $\varphi \neq \varphi(\nu)$. In this case one uses the formula

$$A = \varphi \int \varepsilon(\nu)\, d\nu. \tag{11}$$

From comparison of expressions (8), (10), and (11) it follows that if the quantity $\varphi(\nu)$ depends sufficiently strongly on ν, then, not to mention the spectrum, even for the integral intensity different results may be obtained.

To determine the form of the function $\varphi(\nu)$, it is necessary to use some model of the system absorbing particle—medium. This question will be considered in more detail in other works. Here we shall only indicate that, for this purpose, one may use, for example, the general expression for the polarization $\hat{P}$ of a unit volume of absorbing medium containing particles of different types:

$$\hat{P} = \frac{\hat{n}^2 - 1}{4\pi}\hat{E}_{\text{av}} = \sum_i N_i \hat{\alpha}_i \hat{E}_{\text{eff}\,i},$$

where $\hat{\alpha}_i$ is the complex polarizability of particles of species i. Let us also note that significant changes in the quantity $\varphi(\nu)$ within the absorption band may occur even in the case of dilute solutions, since the magnitude of the field E_{eff} is determined, in particular, by a number of microcharacteristics of the molecule under study (for example, by the polarizability, as follows directly from the Onsager model ([5,6])), which may vary strongly in the region of the band.

Thus, it follows from the foregoing that, in the general case, the observed and true absorption spectra of particles placed in a condensed medium need not coincide with one another either in position, or in intensity, or in shape.

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