RELATIONS BETWEEN THE OPTICAL CHARACTERISTICS OF A SUBSTANCE AND THE EINSTEIN COEFFICIENTS OF THE MOLECULES CONSTITUTING IT FOR THE CASE OF CONDENSED MEDIA AND LEVELS OF FINITE WIDTH

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Abstract

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RELATIONS BETWEEN THE OPTICAL CHARACTERISTICS OF A SUBSTANCE AND THE EINSTEIN COEFFICIENTS OF THE MOLECULES CONSTITUTING IT FOR THE CASE OF CONDENSED MEDIA AND LEVELS OF FINITE WIDTH

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1. The task of any physical method for studying molecules consists in establishing a direct connection between the results of a physical experiment (a macroproperty of the object, which is measured experimentally) and a microproperty of the molecules constituting it (those molecular parameters for whose determination the experiment has been undertaken). In spectroscopy of the condensed state, the experimentally measured quantities are the absorption coefficient $K(\nu)$ and the emission intensity $I(\nu)$ of the samples under study (liquids, solutions, solids), while the molecular parameters to be determined are the spectral densities of the Einstein coefficients for stimulated emission $B_{\downarrow}(\nu)$, and absorption $B_{\uparrow}(\nu)$. Thus, as applied to spectroscopy, the problem consists in finding relations between the experimental quantities $K(\nu)$ and $I(\nu)$ and the molecular parameters $B_{\uparrow}(\nu)$ and $B_{\downarrow}(\nu)$.

In this connection it is first necessary to clarify the question of the relations between the Einstein coefficients in the case of condensed media and levels of finite width. The necessity of such a consideration is dictated, in particular, by the important circumstance that the experimental values of the spectral characteristics $K(\nu)$ and $I(\nu)$ are determined by the superposition of all possible transitions with frequency ν between different sublevels of the combining states, as a result of which the probabilities of the corresponding transitions inevitably depend on the distribution function of the particles over the indicated sublevels.

The question of the relations between the Einstein coefficients for isolated systems possessing levels of finite width was first considered in the works of B. S. Neporent (^{1}). In the present work, processes connected with the peculiarities of the interaction of a molecule with the light field in a condensed medium are also taken into account. For simplicity, we shall restrict ourselves here to the case of isotropic systems. It is obvious that the expressions obtained in the case of anisotropic media will characterize the relations between differential (with respect to particle orientations and radiation polarization) quantities ([2]).

2. The coefficients introduced by Einstein in 1917, A_{21}, B_{21}, and B_{12}, which characterize the total probabilities of spontaneous and stimulated emission and absorption of frequency $\nu_{12} = \nu_{21}$, refer to transitions between two infinitely narrow energy levels of an isolated system. It is important to note that the model for which these coefficients were introduced is idealized: in real systems, energy levels always have finite width, and the systems themselves in most cases are not isolated.

Let us consider an isotropic condensed medium containing, per unit volume, N particles (molecules) under study. Let each molecule in this medium be in one of the states under consideration, combining a set of sublevels.

within the framework of the Born-Oppenheimer approximation, is characterized by a definite set of stationary energy states, which in principle may be of any nature (for example, electronic states with vibrational-rotational sublevels, vibrational states with rotational sublevels, etc.).

Fig. 1

By analogy with the known expressions given in ([2,3]), the formulas for the spectral power density of absorption $W_{\uparrow}(\nu)$, spontaneous and stimulated emission $W_{\downarrow}^{c}(\nu)$ and $W_{\downarrow}^{b}(\nu)$ with frequency ν in transitions between any pair of combining states—for example, between the ground state g and the excited state e (Fig. 1)—may be written, using the distribution function of molecules over energy levels $\rho(Q^{j})$ $(j = e, g)$ and the Einstein coefficients for transitions from sublevels Q^{j}: $A^{eg}(Q^{e}, \nu)$, $B_{\downarrow}^{eg}(Q^{e}, \nu)$, and $B_{\uparrow}^{ge}(Q^{g}, \nu)$. On the other hand, it is useful to introduce coefficients $A^{eg}(\nu)$, $B_{\downarrow}^{eg}(\nu)$, and $B_{\uparrow}^{ge}(\nu)$, which are values of the Einstein coefficients averaged over the sublevels Q^{j}, with the aid of which the spectral power densities of emission and absorption are determined in the usual way ([2,3]). Accordingly,

$$W_{\downarrow}^{c}(\nu) = Nh\nu \int_{Q^{e}} \rho(Q^{e}) A^{eg}(Q^{e}, \nu)\, dQ^{e} = N^{e} h\nu A^{eg}(\nu),$$

$$W_{\downarrow}^{b}(\nu) = Nh\nu U_{\text{eff}}^{e}(\nu) \int_{Q^{e}} \rho(Q^{e}) B_{\downarrow}^{eg}(Q^{e}, \nu)\, dQ^{e} = N^{e} h\nu U_{\text{eff}}^{e}(\nu) B_{\downarrow}^{eg}(\nu), \qquad (1)$$

$$W_{\uparrow}(\nu) = Nh\nu U_{\text{eff}}^{g}(\nu) \int_{Q^{g}} \rho(Q^{g}) B_{\uparrow}^{ge}(Q^{g}, \nu)\, dQ^{g} = N^{g} h\nu U_{\text{eff}}^{g}(\nu) B_{\uparrow}^{ge}(\nu).$$

Here N^{e} and N^{g} are the total numbers of molecules in states e and g, and $U_{\text{eff}}^{j}(\nu)$ is the volume spectral density of the radiation of the effective field acting on a molecule in a condensed medium, averaged over the sublevels Q^j of the initial state. In this case

$$U^j_{\text{eff}}(\nu) = U(\nu)\delta^j(\nu), \tag{2}$$

where $U(\nu)$ is the volume spectral density of the radiation of the mean field in the medium, and $\delta^j(\nu)$ are effective-field factors depending on a number of characteristics of the molecule and the medium (4) and, in the general case, different for the ground and excited states. The integration in (1) is performed over all sublevels Q^j of the initial state from which transitions with frequency ν are possible. The limits of integration are not difficult to establish using the obvious equality (Fig. 1)

$$h\nu_i + Q^e = h\nu + Q^g. \tag{3}$$

From (1) we find

$$\begin{aligned}
A^{eg}(\nu) &= \int_{Q^e} \rho(Q^e) A^{eg}(Q^e,\nu)\, dQ^e \Big/ \int_{Q^e} \rho(Q^e)\, dQ^e, \\
B^{eg}_{\downarrow}(\nu) &= \int_{Q^e} \rho(Q^e) B^{eg}_{\downarrow}(Q^e,\nu)\, dQ^e \Big/ \int_{Q^e} \rho(Q^e)\, dQ^e, \\
B^{ge}_{\uparrow}(\nu) &= \int_{Q^g} \rho(Q^g) B^{ge}_{\uparrow}(Q^g,\nu)\, dQ^g \Big/ \int_{Q^g} \rho(Q^g)\, dQ^g.
\end{aligned} \tag{4}$$

In formulas (4), $A^{eg}(\nu)$ represents the spectral density of the probability of spontaneous emission, while $B^{eg}_{\downarrow}(\nu)$ and $B^{ge}_{\uparrow}(\nu)$, which may be na-

call the spectral densities of the integral (over frequency) Einstein coefficients, characterizing the total transition probability between states e and g, are the proportionality coefficients between the spectral densities of the probabilities of stimulated emission and absorption of frequency ν and the volume spectral density of the exciting radiation. Let us note that, in contrast to $A^{eg}(Q^e,\nu)$, $B^{eg}_{\downarrow}(Q^e,\nu)$, and $B^{ge}_{\uparrow}(Q^g,\nu)$, the coefficients (4) depend on the distribution function over the sublevels of the combining states, i.e., in the general case on the temperature.*

The aggregate of experimental facts shows that, in the overwhelming majority of cases, absorption and emission processes for molecules in condensed media (i.e., capable of rapid exchange of energy with the medium) occur with an equilibrium distribution of molecules over the sublevels of the initial state. It is therefore useful to consider the question of the relation between the coefficients $A^{eg}(\nu)$, $B^{eg}_{\downarrow}(\nu)$, and $B^{ge}_{\uparrow}(\nu)$ for the most important case of thermodynamic equilibrium, bearing in mind the applicability of the relations obtained to any stationary regime in which the equilibrium distribution of molecules over the sublevels Q^j is preserved. At thermodynamic equilibrium the condition is satisfied

$$W_{\downarrow}^{c}(\nu) + W_{\downarrow}^{b}(\nu) = W_{\uparrow}(\nu). \tag{5}$$

Substituting expressions (1) into (5), solving the resulting equation with respect to $U(\nu)$, and comparing it with Planck' s formula for a condensed medium [5], we find, using the formula for the equilibrium distribution of molecules over levels [2, 3] and taking into account, according to (3), the possible limits of integration,

$$A^{eg}(\nu) = \frac{8\pi h\nu^3}{c^3}\, n^3(\nu)\, \delta^e(\nu) B_{\downarrow}^{eg}(\nu), \quad B_{\downarrow}^{eg}(\nu) = \frac{C^e(T)}{C^g(T)} e^{(h\nu_i - h\nu)/kT} B_{\uparrow}^{ge}(\nu) \frac{\delta^g(\nu)}{\delta^e(\nu)}, \tag{6}$$

where $n(\nu)$ is the refractive index of the medium,

$$C^j(T) = \left[\int_{Q^j} g(Q^j) e^{-Q^j/kT}\, dQ^j \right]^{-1};$$

$j = e, g,\ g(Q^j)$ is the statistical weight of the corresponding sublevel. Let us note that formulas (6) for the gas phase ($n(\nu) = 1,\ \delta^j(\nu) = 1$) go over into the expressions obtained by B. S. Neporent.

3. We now turn to establishing the relation between the spectral densities of the Einstein coefficients and the experimentally determined quantities $\widetilde{K}(\nu)$ and $I(\nu)$. Let us first consider absorption. By analogy with (4), comparing the expression for the spectral density of the absorbed power, written using the absorption coefficient $K(\nu)$,

$$W_{\uparrow}(\nu) = K(\nu) \frac{C}{h(\nu)} U(\nu),$$

with the expression for this quantity through $B_{\downarrow}^{eg}(\nu)$ and $B_{\uparrow}^{ge}(\nu)$

$$W_{\uparrow}(\nu) = U(\nu) h\nu \left[N^g(U) B_{\uparrow}^{ge}(\nu) \delta^g(\nu) - N^e(U) B_{\downarrow}^{eg}(\nu) \delta^e(\nu) \right],$$

and also using relation (6), we obtain

$$B_{\uparrow}^{ge}(\nu) = \frac{\varepsilon(\nu) C}{n(\nu) h\nu \delta^g(\nu)} \frac{1}{\left[\frac{N^g(U)}{N} - \frac{N^e(U)}{N} \frac{C^e(T)}{C^g(T)} e^{(h\nu_i - h\nu)/kT} \right]}. \tag{7}$$

Here $\varepsilon(\nu) = K(\nu)/N$, N is the total number of molecules under study per unit volume, and $N^e(U)$ and $N^g(U)$ are the numbers of molecules in states e and g, depending on in the general case, on the volume density of radiation U. Under ordinary experimental conditions $N^g \approx N,\ N^e \approx 0$, and formula (7) becomes the expression

$$B_{\uparrow}^{ge}(\nu) = \frac{\varepsilon(\nu)C}{h\nu}\frac{1}{n(\nu)\delta^g(\nu)} = \frac{\varepsilon(\nu)C}{h\nu}\theta_{\uparrow}(\nu), \tag{8}$$

obtained earlier in papers (4) without taking induced emission into account.

Let us turn to the consideration of emission. If by the intensity of emission $I(\nu)$ one understands the number of quanta of frequency ν emitted by a molecule per unit time, then

$$I(\nu) = \frac{W_{\downarrow}(\nu)}{h\nu N^e\langle U\rangle} = A^{eg}(\nu) = \frac{8\pi h\nu^3}{C^3}n^3(\nu)\delta^e(\nu)B^e,$$

whence

$$B_{\downarrow}^{eg}(\nu) = I(\nu)\frac{C^3}{8\pi h\nu^3 n^3(\nu)\delta^e(\nu)} = A_{\downarrow}^{eg}(\nu)\frac{C^3}{8\pi h\nu^3}\theta_{\downarrow}(\nu). \tag{9}$$

It follows from these expressions that the spectral density of the Einstein coefficient $A^{eg}(\nu)$ is a quantity directly determined from experiment, in contrast to the coefficients $B_{\downarrow}^{eg}(\nu)$ and $B_{\uparrow}^{ge}(\nu)$, for whose determination it is necessary to take into account the difference between the macroscopic field E_{av} and the microfield E_{eff}^{j} acting on the molecule.

It is not difficult to show that relations (8) and (9) satisfy the basic laws of thermal radiation and luminescence, which connect the experimentally observed spectral characteristics of the processes of absorption and emission.

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[*] The coefficients B_{21} and B_{12} were introduced by Einstein precisely as proportionality coefficients between the probabilities of the corresponding transitions and the spectral density of the radiation. From this point of view the coefficients $B_{\downarrow}^{eg}(\nu)$ and $B_{\uparrow}^{ge}(\nu)$ may be regarded, in physical meaning, as quantities analogous to the Einstein coefficients. However, from the discussion given above it is clear that, in the case of systems with levels of finite width, the values $B_{\downarrow}^{eg}(\nu)$ and $B_{\uparrow}^{ge}(\nu)$ depend not only on the internal properties of the molecules but also on the function of their distribution over energy states; moreover, this fact is a fundamental feature of systems with levels of finite width.

4. With the aid of relations (8) and (9) one can obtain refined expressions for a number of quantities used by spectroscopists. Let us consider, in particular, the question of the lifetime τ of the excited state for molecules in a condensed medium. By definition (6)

$$\frac{1}{\tau} = A^{eg} = \int_{\nu} A^{eg}(\nu)\, d\nu. \tag{10}$$

Using (6) and (8), we obtain, for the case of an equilibrium distribution of molecules without allowance for induced emission,

$$\frac{1}{\tau} = \frac{8\pi}{C^2}\frac{C^e(T)}{C^g(T)} e^{h\nu_i/kT} \int_{\nu} \nu^2 n^2(\nu) e^{-h\nu/kT} \varepsilon(\nu)\, d\nu. \tag{11}$$

The essential difference between expression (11) and the relations given in the literature that connect the lifetime τ of the excited state with the absorption spectrum $\varepsilon(\nu)$ consists in the presence of the factor $e^{(h\nu_i - h)/kT}$. Its appearance is connected with allowance for the finite width of the combining levels and the distribution of molecules over the sublevels of the initial states, and makes it possible in a natural way to eliminate the difficulties caused by the difference in the spectral positions of the absorption and fluorescence bands. For the gas phase and infinitely narrow levels, expression (11) becomes the well-known Füchtbauer–Ladenburg formula (7).

Thus, it follows from the results of the present work that, in the relations establishing the connection between the Einstein coefficients of molecules, and in the expressions connecting the Einstein coefficients with the optical characteristics of condensed media, one must take into account the correction factors $\theta(\nu)$, due to the difference between the effective field of the light wave acting on the molecule and the average field in this medium. In this connection, the spectral dependence of $\theta(\nu)$ within the corresponding absorption or emission bands assumes special significance.

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