GENERAL RELATIONS BETWEEN ABSORPTION AND EMISSION FOR MODULATION SPECTRA OF POLYATOMIC MOLECULES

`![Fig. 1](figure)`

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICS

B. S. NEPORENT

GENERAL RELATIONS BETWEEN ABSORPTION AND EMISSION FOR MODULATION SPECTRA OF POLYATOMIC MOLECULES

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The relations between absorption and emission spectra have been considered in a number of studies ([1−6]) from the point of view of elucidating the relation between the probabilities of transitions between vibrational levels of the lower and upper electronic states, taking into account the Franck–Condon principle. Blokhintsev ([7]), Förster ([8]), and Stepanov ([9]) considered these relations by summing the "elementary" transitions between individual vibrational levels of the normal and excited electronic states (Fig. 1).

Fig. 1

It seems to us that the problem of the relation between the absorption and emission spectra of polyatomic molecules of all types should be solved analogously to how this is done for a system with narrow levels: by considering the equilibrium of molecules with equilibrium radiation and, having thus obtained the characteristics of individual molecules, using them in the consideration of luminescence excited under stationary conditions.

Let us first consider molecules characterized by modulation spectra, i.e., those in which the electronic states may be regarded as independent of the vibrational ones ([5]). The equilibrium conditions for a system consisting of such luminescing molecules and equilibrium radiation are, obviously, the following:

A. The molecules must be distributed between the normal and excited electronic levels in accordance with the laws of statistical equilibrium.

B. With respect to their store of vibrational energy, the molecules must also be distributed in both electronic states in equilibrium.*

C. The emissive power of the system under consideration must be the product of its absorptive power and the spectral density of equilibrium radiation, i.e., the luminescence spectrum must coincide with the spectrum of the thermal radiation of the system. If the mean quantum yield γ of luminescence under the conditions considered is less than unity,

* In solutions this condition is considered fulfilled; in rarefied vapors, for complex molecules, according to ([14]), one may expect the establishment of equilibrium, although the corresponding "temperature" should depend on the excitation energy of the molecule.

then the emission deficit will be compensated by thermal emission, which in this case differs only in the mechanism of excitation.

Introducing the mean values of the spectral density of the Einstein coefficients $\overline{A}^*_\nu$ and $\overline{B}_\nu$ for individual molecules, the equilibrium condition C may be written as:

$$n^* \overline{A}^*_\nu = n \overline{B}_\nu U_\nu, \tag{1}$$

Here n, n^* are the numbers of molecules in the normal and excited electronic states; U_ν is the spectral density of equilibrium radiation. Denoting $\frac{8\pi h\nu^3}{c^3}\overline{B}_\nu = \overline{A}_\nu$ and using the expression for U_ν corresponding to the case $h\nu \gg kT$, we obtain

$$\frac{\overline{A}^*_\nu}{\overline{A}_\nu} = \frac{n}{n^*} e^{-h\nu/kT}. \tag{2}$$

Here $\overline{A}_\nu$ is the equivalent "emission probability" for the absorption spectrum; $\overline{A}^*_\nu$ is the probability for the emission spectrum. For a pair of narrow levels at equilibrium * $n/n^* = e^{h\nu/kT}$ and $\overline{A}^*_\nu/\overline{A}_\nu = 1$. In the case considered by us, as D. I. Blokhintsev pointed out (7), the relations are more complicated. In the frequency region $\nu < \nu_e$, emission can occur from all levels of the upper excited state, whereas absorption occurs only from levels $q \gg \nu_e - \nu$ (Fig. 1). Similarly, in the region $\nu > \nu_e$, emission can occur only from levels $q^* \gg \nu - \nu_e$. In what follows we shall treat these regions separately, using the minus subscript for the region $\nu < \nu_e$ and the plus subscript for $\nu > \nu_e$. If the equilibrium distribution functions of particles with respect to the values of vibrational energy are expressed in states 1 and 2, respectively, as $\rho(q)$ and $\rho^*(q^*)$, with $\int_0^\infty \rho(q)\,dq = 1$ and $\int_0^\infty \rho^*(q^*)\,dq^* = 1$, then it is evident (conditions A and B):

$$\begin{aligned} n^*_- &= n_0 e^{-E_2/kT}; \qquad n^*_+ = n_0 e^{-E_2/kT}\int_\Delta^\infty \rho^*(q^*)\,dq^*; \\ n_- &= n_0 e^{-E_1/kT}\int_\Delta^\infty \rho(q)\,dq; \qquad n_+ = n_0 e^{-E_1/kT}, \end{aligned} \tag{3}$$

where $E_2 - E_1 = h\nu_e$; n_0 is the number of molecules in 1 cm^3; $\Delta = |\nu_e - \nu|$.

From (2) and (3), denoting $\int_\Delta^\infty \rho(q)\,dq = \rho_\Delta(\nu)$ and $\int_0^\infty \rho^*(q^*)\,dq^* = \rho^*_\Delta(\nu)$, we obtain

$$\frac{\overline{A}^*_{-\nu}}{\overline{A}_{-\nu}} = e^{h\Delta/kT}\rho_\Delta(\nu); \qquad \frac{\overline{A}^*_{+\nu}}{\overline{A}_{+\nu}} = \frac{1}{e^{h\Delta/kT}\rho^*_\Delta(\nu)}. \tag{4}$$

Let us now introduce into consideration experimentally determined quantities: the molecular absorption coefficient ε_ν, the spectral density of the quantum yield of fluorescence γ_ν, and the measured lifetime of the excited state τ'. In experiment these quantities are referred to the total number of molecules at the corresponding levels; therefore, on the basis of well-known relations and (3):

$$\frac{\gamma_{-\nu}}{\tau'} = \overline{A}^*_{-\nu}, \qquad \frac{\gamma_{+\nu}}{\tau'} = \overline{A}^*_{+\nu}\rho^*_\Delta(\nu), \qquad \nu^2\varepsilon_{-\nu} = \frac{c^2}{8\pi}\overline{A}_{-\nu}\rho_\Delta(\nu), \qquad \nu^2\varepsilon_{+\nu} = \frac{c^2}{8\pi}\overline{A}_{+\nu}, \tag{5}$$

* We do not take into account here possible differences in the values of the statistical weights of the electronic states. The corresponding corrections can easily be introduced.

and from (4) and (6), for the entire spectral region:

$$\frac{\gamma_\nu/\tau'}{\frac{8\pi}{c^2}\nu^2\varepsilon_\nu} = e^{h\Delta\nu/kT}, \tag{6}$$

where $\Delta\nu = \nu_e - \nu$.

An expression analogous to (6) was obtained by B. I. Stepanov ([9]), who, proceeding from less general considerations, could not determine in it the values of the constant coefficients.

It follows from expression (6) that the spectral curves of absorption and emission, with a proper choice of scales, intersect at $\nu = \nu_e$, i.e., at this point the probabilities of direct and reverse transitions are always equal. Let us note that, although the values γ_ν and τ' are often determined experimentally in many modern works, there is no necessity for this, since the emission spectrum can be measured in relative units I_ν of the spectral quantum intensity of luminescence, normalizing the area under the spectral curve I_ν so that it is equal to the area under the curve $\nu^2\varepsilon_\nu$. Such a choice of scales follows from the equilibrium condition A, according to which the integral probabilities of transitions between levels 1 and 2 (Fig. 1) must be equal, i.e.,

$$A_{21} = \int_0^{\nu_e} \overline{A^*_{-\nu}}\,d\nu + \int_{\nu_e}^\infty \overline{A^*_{+\nu}}\rho^*_\Delta(\nu)\,d\nu = \int_0^{\nu_e} \overline{A_{-\nu}}\rho_\Delta(\nu)\,d\nu + \int_{\nu_e}^\infty \overline{A_{+\nu}}\,d\nu = A_{12}, \tag{7}$$

whence, taking into account the known relations (7),

$$\frac{1}{\tau_{21}} = \frac{1}{\tau'} \int_0^\infty \gamma_\nu \, d\nu = \int_0^\infty I_\nu \, d\nu = \frac{8\pi}{c^2} \int_0^\infty \nu^2 \varepsilon_\nu \, d\nu. \tag{8}$$

Relations (4) and (7) can, obviously, also be written for the coefficient B (and the equivalent B^*), and relations (6) and (8)—for I_ν/ν^3 and ε_ν/ν, etc.

Thus, in addition to the necessity indicated in ([7–9]) of expressing the intensities of emission and absorption spectra in comparable units (the authors of ([7–9]) proposed using the values B, I_ν/ν^3, and ε_ν/ν), the spectral curves should also be normalized to equality of the areas under them. The commonly accepted normalization by $I_{\max} = \varepsilon_{\max} = 1$ is strictly suitable only for mirror-symmetric spectra, and for others only for studying shapes, but not intensities and not relations between spectra.

The necessity of normalizing spectra by area also follows from the experimental results of B. S. Neporent and N. G. Bakhshiev ([10]), where, for complex molecules of various types, compliance with the well-known relation connecting the Kravts integral and the lifetime of the excited state is shown.

It follows from the results obtained, in particular, that with a correct method of normalization and representation, the spectral curves described by the expressions obtained intersect at the value $\nu = \nu_e$ for any ratios of the distributions $\rho(q)$ and $\rho^+(q^+)$.

The general expressions obtained describe all relations between the absorption and emission spectra of polyatomic molecules that are characterized by modulated spectra. These expressions can equally well be applied both to simple polyatomic molecules, in which the structure of the spectrum is preserved, and to complex ones, in which, as shown in ([5], [13]), strong interactions between normal vibrations lead to an equalization of the properties of the vibrational systems in the normal and excited electronic states, and the symmetry of the spectra is a certain limiting regularity.

Formulas (4) and (8), taking into account the obvious relations

$$\overline{A^*_{-\nu}} = \int_0^\infty \rho^*(q^*, T)\, A^*(q^*, \nu)\, dq^*; \qquad \overline{A^*_{+\nu}} = \frac{1}{\rho^*_\Delta(\nu)} \int_\Delta^\infty \rho^*(q^*, T)\, A^*(q^*, \nu)\, dq^*;$$

$$\overline{A_{-\nu}} = \frac{1}{\rho_\Delta(\nu)} \int_\Delta^\infty \rho(q, T)\, A(q, \nu)\, dq; \qquad \overline{A_{+\nu}} = \int_0^\infty \rho(q, T)\, A(q, \nu)\, dq, \tag{9}$$

lead, as special cases, to the expressions obtained in ([7–9]). For simple molecules, the integration over q, ν (or, taking into account $\nu_e + q^* = \nu + q$, over q and q^*) should obviously be replaced by summation over i, j (see Fig. 1).

Let us note especially that the results obtained by us testify to the impossibility of describing fading spectra within the framework of the scheme under consideration, since H. A. Borishevich and B. S. Neporent ([11]) established experimentally that the frequency corresponding to the electronic transition is not located at the point of intersection of the spectra under any method of representing them, but, in the cases investigated, is situated near the maximum of the absorption spectrum. A. P. Kazachenko and B. I. Stepanov ([12]), having obtained, under additional conditions and assumptions, certain particular relations, attempted, on the basis of their results, to explain the formation of fading spectra only as a consequence of differences in equilibrium distributions and transition probabilities while preserving the scheme of the phenomenon corresponding to the formation of modulation spectra. These attempts, as has been shown here, cannot be regarded as valid. The condition for the formation of fading spectra is, as was shown in ([5,14]), the dependence of the position of the electronic levels on the vibrational and electronic states of the molecule, i.e., in other words, the impossibility of considering separately the electronic and vibrational states of the molecule. We are carrying out an analysis, analogous to that proposed here, of the corresponding systems.

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