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Abstract

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UNIVERSAL RELATION BETWEEN THE ABSORPTION AND LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

Several hundred works have been devoted to comparing absorption spectra and luminescence spectra. Of substantial importance for the theory of luminescence, in particular, was the discovery of mirror symmetry of the absorption and emission spectra ($^{1-6}$). In the present work it is shown that the absorption and luminescence spectra of many complex systems are connected by a universal relation that makes it possible to calculate the shape of the luminescence spectrum from the known shape of the long-wavelength absorption band, and conversely.

Let us consider, as an example, the luminescence of a solution of some dye. Numerous experiments have established that between the act of light absorption and the act of luminescence there occurs a process of redistribution of vibrational energy over the various vibrational degrees of freedom of the excited molecule, as well as an exchange of energy between the excited molecule and the solvent molecules. This process takes place extremely rapidly, and in a time of the order of 10^{-10}–10^{-12} sec., much shorter than the duration of the excited electronic state, an equilibrium distribution of vibrational energy over the degrees of freedom and over the vibrational levels of the excited molecule is established. The form of this distribution is completely determined by the temperature of the solvent. A criterion for the actual establishment of an equilibrium distribution in a given particular system may be, above all, the independence of the quantum yield and of the spectrum from the frequency of the exciting light (under Stokes excitation).

Fig. 1

The dependence of the luminescence power of a complex molecule on frequency is determined in general form by formula (^{7}):

$$W_{\nu}^{\text{lum}} = h\nu \cdot n^{*} \int \rho^{*}(E_{\text{vib}}^{*})\, A(E_{\text{vib}}^{*}, \nu)\, dE_{\text{vib}}^{*}. \tag{1}$$

Here n^{*} is the total number of molecules in the excited electronic state, $A(E_{\text{vib}}^{*}, \nu)$ is the probability of a spontaneous transition from the vibrational level E^*_{vib} to the vibrational level E_{vib} of the lower electronic state. The values E^*_{vib}, E_{vib}, and the emission frequency ν are connected by the relation (Fig. 1):

$$E^*_{\text{vib}} + h\nu_{\text{el}} = E_{\text{vib}} + h\nu. \tag{2}$$

The distribution function over vibrational energy levels is determined by the usual expression:

$$\rho^*(E^*_{\text{vib}}) = C^* g^*(E^*_{\text{vib}}) e^{-E^*_{\text{vib}}/kT}, \tag{3}$$

where $g^*(E^*_{\text{vib}})$ is the statistical weight of the level E^*_{vib}, and T is the temperature of the surrounding medium. Formulas (1) and (2) are always valid, while formula (3) is valid only when thermal equilibrium is established between the excited molecules and the surrounding medium.

The absorption power at frequency ν

$$W^{\text{abs}}_{\nu} = h\nu \cdot n \int \rho(E_{\text{vib}}) B(E_{\text{vib}}, \nu) u_{\nu}\, dE_{\text{vib}} + \tag{4}$$

$$+\, h\nu \cdot n \int \rho(E_{\text{vib}}) B'(E_{\text{vib}}, \nu) u_{\nu}\, dE_{\text{vib}}$$

is, in the general case, determined by two terms. The first of them determines the absorption associated with the transition of the molecule into an excited electronic state; the second is absorption associated with transitions between vibrational levels of the ground electronic state (nonexciting absorption). The second term, as a rule, is very small, and it began to be taken into account only in connection with the problem of anti-Stokes fluorescence ([7,8]). In formula (4), n is the total number of molecules, $\rho(E_{\text{vib}}) = Cg(E_{\text{vib}})e^{-E_{\text{vib}}/kT}$ is the distribution function over vibrational levels of the lower electronic state, $g(E_{\text{vib}})$ is the statistical weight of the level E_{vib}, u_{ν} is the density of the incident radiation, and $B(E_{\text{vib}}, \nu)u_{\nu}$ and $B'(E_{\text{vib}}, \nu)u_{\nu}$ are the probabilities of transitions with and without excitation of the upper electronic state.

If the second term in (4) is neglected, formula (2) and the relation between the Einstein coefficients are taken into account,

$$\frac{A(E^*_{\text{vib}}, \nu)}{B(E_{\text{vib}}, \nu)} = \frac{g(E_{\text{vib}})}{g^*(E^*_{\text{vib}})} \frac{8\pi h\nu^3}{c^3}, \tag{5}$$

then we obtain

$$\frac{W_\nu^{\text{lum}}}{W_\nu^{\text{abs}}/u_\nu} = \frac{n^*\displaystyle\int_{h\nu-h\nu_{\text{el}}}^{\infty} C^* g^*(E^*_{\text{vib}})e^{-E^*_{\text{vib}}/kT}A(E^*_{\text{vib}},\nu)\,dE^*_{\text{vib}}}{n\displaystyle\int_0^\infty Cg(E_{\text{vib}})e^{-E_{\text{vib}}/kT}B(E_{\text{vib}},\nu)\,dE} =$$

$$= \frac{n^*C^*e^{h\nu_{\text{el}}/kT}}{nC}\frac{8\pi h\nu^3}{c^3}e^{-h\nu/kT} = D\frac{8\pi h\nu^3}{c^3}e^{-h\nu/kT}. \tag{6}$$

The limits of integration in (6) correspond to the values $\nu > \nu_{\text{el}}$. If $\nu < \nu_{\text{el}}$, then the integral in the numerator must be taken from $E^*_{\text{vib}} = 0$ to $E^*_{\text{vib}} = \infty$, and the integral in the denominator from $E_{\text{vib}} = h\nu_{\text{el}} - h\nu$ to $E_{\text{vib}} = \infty$.

Since W_ν^{abs}/u_ν is proportional to the absorption coefficient $\varkappa_\nu$, we have

$$\frac{W_\nu^{\text{lum}}}{\varkappa_\nu} = D(T)\frac{8\pi h\nu^3}{c^2}e^{-h\nu/kT} = d(T)\nu^3e^{-h\nu/kT}. \tag{7}$$

It is appropriate to compare relation (6) with Kirchhoff’ s law, which determines the thermal emission of the same system. Without taking induced emission into account, i.e., for $h\nu \gg kT$, Kirchhoff’ s law has the form

$$\frac{W_\nu^{\text{therm. em}}}{W_\nu^{\text{abs}}/u_\nu} = \frac{8\pi h\nu^3}{c^3}e^{-h\nu/kT}. \tag{8}$$

In the denominator of the left-hand sides of (6) and (8) there stands one and the same quantity, $\dfrac{W_\nu^{\text{abs}}}{u_\nu}$—the absorptive capacity of the system under study at temperature T. Thus,

$$W_\nu^{\text{lum}} = D(T)W_\nu^{\text{therm. em}} \tag{9}$$

and, consequently, the luminescence power (at frequency ν) is proportional to the power of the thermal emission of the system. The proportionality factor $D(T)$ depends, for a given molecule, only on the temperature and on the conditions of excitation of luminescence (on n^*), but does not depend on ν. At a given temperature the contour of the luminescence band coincides with the contour of the thermal-emission band. Thus, according to (6)–(9), knowing the contour of the absorption band from experiment, it is not difficult to find the contour of the luminescence band. This may make it possible to investigate the fulfillment of the laws of mirror symmetry, to determine the frequency of the purely electronic transition without measuring the luminescence spectrum, and to clarify better the factors affecting the formation of absorption and emission bands. In a number of cases it is difficult to measure the contour of the absorption band. Under these conditions it can be found by carrying out careful measurements of the contour of the emission band.

Relations (6), (7), and (9) possess a very high degree of generality. They may fail to be satisfied only in two cases: if, during the time the molecules remain in the excited electronic state, a thermal distribution over the vibrational sublevels of the excited state has no time to become established, or if non-exciting absorption is large and it is necessary to take into account the second term in formula (4). The study of both these factors is of considerable interest, and it can be carried out by systematically investigating violations of relations (6), (7), and (9). Here attention should be drawn only to the change in the contour of the luminescence band on passing from Stokes to anti-Stokes excitation. Such a change is observed not only in vapors ([9]), but even in solutions ([10]). If, under Stokes excitation, the contour of the luminescence band corresponds to relation (6), then on passing to anti-Stokes excitation (6) will cease to be fulfilled. This result proves unambiguously that, under anti-Stokes excitation of complex molecules, an equilibrium distribution of excited molecules does not have time to become established (see ([7])).

Verification of relations (6), (7), and (9) on the existing experimental material is impossible, since measurements are usually confined to W_ν^{lum} and W_ν^{abs} near the center of the band and careful measurements are not carried out at the edge of the band, where W_ν^{lum} and W_ν^{abs} are sufficiently small. In addition, before comparison with theory it is necessary to take into account the influence of reabsorption and secondary luminescence.

Relations (6), (7), and (9) are strictly applicable only to the condensed phase. In vapors of complex molecules they can be fulfilled only approximately, since exchange of vibrational energy with the medium is absent and an equilibrium distribution of excited molecules over vibrational energy levels is not established.

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