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Abstract

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ON THE CONTOUR OF THE ABSORPTION AND LUMINESCENCE BANDS OF COMPLEX MOLECULES

In the works of S. I. Vavilov (1) it was repeatedly emphasized that the shape of the absorption and luminescence bands of complex molecules, which possesses a certain universality, can be explained on the basis of purely statistical considerations. At present a number of attempts to solve this problem are known (2–8). In the present work a general relation is derived that connects the value of the absorption coefficient or of the radiation power for frequencies $\nu > \nu_{\text{el}}$ with the values of the same quantities for frequencies $\nu < \nu_{\text{el}}$. The results are applicable only to those molecules for which the mirror symmetry of the absorption and luminescence spectra discovered by Levshin (9) is observed.

In work (10) it was proved that the luminescence power of complex molecules in solution is connected with the absorption coefficient of the same frequency by the following universal relation:

$$W_\nu^{\text{lum}} = d(T)\nu^3 e^{-\frac{h\nu}{kT}} \varkappa_\nu. \tag{1}$$

On the other hand, for molecules with mirror symmetry of the absorption and luminescence spectra the relation (11,12) is valid:

$$\frac{W^{\text{lum}}_{\nu_{\text{el}}-\Delta\nu}}{(\nu_{\text{el}}-\Delta\nu)^4} = \alpha \frac{\varkappa_{\nu_{\text{el}}+\Delta\nu}}{\nu_{\text{el}}+\Delta\nu}, \tag{2}$$

where α is a proportionality factor independent of frequency. Rewriting (1) in the form

$$\frac{W^{\text{lum}}_{\nu_{\text{el}}-\Delta\nu}}{(\nu_{\text{el}}-\Delta\nu)^4} = d(T)e^{-\frac{h(\nu_{\text{el}}-\Delta\nu)}{kT}} \frac{\varkappa_{\nu_{\text{el}}-\Delta\nu}}{\nu_{\text{el}}-\Delta\nu}, \tag{3}$$

and comparing (2) and (3), we obtain

$$\alpha \frac{\varkappa_{\nu_{\text{el}}+\Delta\nu}}{\nu_{\text{el}}+\Delta\nu} = de^{-\frac{h\nu_{\text{el}}}{kT}} e^{\frac{h\Delta\nu}{kT}} \frac{\varkappa_{\nu_{\text{el}}-\Delta\nu}}{\nu_{\text{el}}-\Delta\nu}, \tag{4}$$

This formula is valid for any $\Delta\nu$ and, in particular, for $\Delta\nu = 0$. Substituting $\Delta\nu = 0$ into (4), we obtain

$$\alpha = de^{-\frac{h\nu_{\text{el}}}{kT}} \tag{5}$$

and, thus,

$$\frac{\varkappa_{\nu_{\text{el}}-\Delta\nu}}{\nu_{\text{el}}-\Delta\nu} = \frac{\varkappa_{\nu_{\text{el}}+\Delta\nu}}{\nu_{\text{el}}+\Delta\nu} e^{-\frac{h\Delta\nu}{kT}}. \tag{6}$$

Relation (6) can also be derived in another way, by writing explicit expressions for the absorption coefficient and the luminescence power.

For the contour of the luminescence band, from (2), (3), and (5) one obtains the analogous dependence:

$$\frac{W^{\text{lum}}_{\nu_{\text{el}}+\Delta\nu}}{(\nu_{\text{el}}+\Delta\nu)^4} = \frac{W^{\text{lum}}_{\nu_{\text{el}}-\Delta\nu}}{(\nu_{\text{el}}-\Delta\nu)^4} e^{-\frac{h\Delta\nu}{kT}}. \tag{7}$$

Expressions (6) and (7) possess a high degree of generality and may be invalid only for those molecules in which there is a deviation from mirror symmetry of the absorption and luminescence spectra (on the frequency scale). They are also inapplicable in those cases when, during the time the molecules remain in the excited electronic state, an equilibrium distribution over the vibrational energy levels does not have time to become established (see (10)).

Table 1

$\Delta\nu$, cm^{-1}	$\frac{\varkappa_{\nu_{\text{el}}+\Delta\nu}}{\nu_{\text{el}}+\Delta\nu} : \frac{\varkappa_{\nu_{\text{el}}-\Delta\nu}}{\nu_{\text{el}}-\Delta\nu}$	$h\Delta\nu/kT$
225	3.0	2.9
425	7.0	7.6
625	21.0	21.0
825	55.0	51.8
1025	127.5	134.8

$$\nu_{\text{el}} = 24475 \text{ cm}^{-1}$$

To verify the relations obtained, we used experimental data (13) on the spectra of phthalimides, supplied to us in tabular form. The results of the calculation for the absorption of a solution of 3-aminophthalimide are given in Table 1.

It follows from the table that formula (6) agrees well with experiment. Formula (6) can be represented in a form more convenient for comparison with experiment. Taking the logarithm of (6), we obtain

$$\ln \frac{\varkappa_{\nu_{\mathrm{el}}+\Delta\nu}}{\nu_{\mathrm{el}}+\Delta\nu} - \ln \frac{\varkappa_{\nu_{\mathrm{el}}-\Delta\nu}}{\nu_{\mathrm{el}}-\Delta\nu} = \frac{h\Delta\nu}{kT}. \tag{8}$$

In Fig. 1 are presented the values of $\ln \frac{\varkappa_\nu}{\nu}$ as a function of $\frac{\nu}{kT}$ for the absorption spectrum of a solution of 3-aminophthalimide in benzene. The solid lines mark the quantities corresponding to the left-hand side of equation (8) for different $\Delta\nu$, and the dashed lines mark the values of $\frac{\Delta\nu}{kT}$. As can be seen from the figure, the lengths of the solid and dashed lines are strictly identical, which confirms the validity of relation (6). The construction shown in Fig. 1 is expedient to use for determining ν_{el} from a single absorption band without measuring the luminescence spectrum (assuming that the law of mirror symmetry is approximately fulfilled).

Fig. 1. Absorption spectrum of a solution of 3-aminophthalimide in benzene.

Fig. 1

Analogous calculations and constructions for several phthalimides showed that relation (6) is always fulfilled, either exactly or approximately. The best results were obtained for absorption, somewhat worse ones for luminescence. It is characteristic that noticeable deviations from mirror symmetry

do not produce large deviations from (6). For vapor spectra formula (6) is less well justified. The latter is quite natural, since for vapors the original relation (1) is not valid.

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