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Abstract

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ON THE ABSORPTION OF LIGHT AND LUMINESCENCE OF COMPLEX MOLECULES

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In the field of long-wavelength electronic spectroscopy of complex molecules there exist a number of theoretical problems that have not yet been fully solved. Such problems include, for example, explaining the origin of continuous bands, their universality (noted as early as 1922 by S. I. Vavilov ([1])), their dependence on temperature and on λ_{exc} ([2]), and the mirror-symmetry problem ([2], [3]).

In the present communication we shall show that these problems can be considered from a unified point of view if one assumes that the adiabatic approximation is applicable to them. This approximation can be justified if, first, the infrared spectrum of the molecules is discrete and, second, if the long-wavelength band is isolated from the rest of the spectral region ([4]). Following Lax ([5]), we obtain, in the adiabatic approximation, for the Fourier transforms of the spectral density of absorption and emission:

$$I_{\text{abs}}(t) = \frac{\text{Sp}\left[M^* \exp\left(\frac{it}{\hbar}\hat{H}_b\right) M \exp\left(-\frac{it}{\hbar}\hat{H}_a\right) \exp(-\beta\hat{H}_a)\right]}{\text{Sp}\left[\exp(-\beta\hat{H}_a)\right]},$$

$$I_{\text{em}}(t) = \frac{\text{Sp}\left[M \exp\left(-\frac{it}{\hbar}\hat{H}_a\right) M^* \exp\left(\frac{it}{\hbar}\hat{H}_b\right) \rho\right]}{\text{Sp}(\rho)}; \qquad (1)$$

ρ is the distribution function in the excited state.* The general form of formulas (1) makes it possible to obtain from them various approximations, for example for calculating band shapes, their temperature dependence, etc. For this it is sufficient approximately to disentangle the operator expressions entering into (1). At the same time, together with the criterion of applicability, the given approximation already has a quantum-mechanical justification in advance.

1. Until quite recently it was thought (see, for example, ([2]), p. 173) that the origin of continuous bands in electronic spectra is different for molecules of different classes (classification according to type of mirror symmetry);

> at present this point of view has been abandoned. The difference between modulation spectra and damping spectra (as they are now understood) is rather terminological than factual, since both are considered in the adiabatic approximation. Strictly speaking, the real meaning of damping spectra consists in taking nonadiabaticity into account, since relaxation of electronic levels is impossible in the adiabatic approximation. If the relaxation mentioned were large, one would expect the quantum yield of luminescence to be small, and this is far from always observed experimentally.

One of the possible explanations of the origin of continuous bands was put forward by us in qualitative form (^{11}). In the adiabatic approximation

the criterion for the applicability of the semiclassical approximation depends not only on the presence in the system of small quantities ω_k, but also on how the operators of the slow subsystem vary. For a quantitative estimate let us consider the simplest case: M = const; H_a, H_b are oscillator Hamiltonians, with $H_b - H_a = h\nu_0 + \sum A_{jx}j$. From Lax' s results $^{(5)}$ it follows that, in this case, those oscillators may be treated semiclassically for which either

$$C_j^2 = \frac{A_j^2}{2\hbar\mu_j\omega_j^3} \gg 1, \tag{2}$$

or

$$C_j^2 \sim 1, \qquad \bar{n} \gg 1. \tag{3}$$

Putting, for example, $\omega \simeq 10^{13}$ sec^{-1}, $\mu \simeq 10^{-22}$ g, and the displacement of the equilibrium distances of the ground and excited electronic states $\simeq 5 \cdot 10^{-9}$ cm, we obtain $C^2 \simeq 10$, i.e., for not very low temperatures the semiclassical procedure is approximately applicable.

A semiclassical treatment of the degrees of freedom satisfying conditions (2), (3), when light is absorbed or emitted by the fast subsystem, will lead to the result that each line in the band is broadened by an amount determined by the total second moment of the semiclassical oscillators:

$$\Lambda^2 = \sum_{j(\text{semicl})} C_j^2(2\bar{n}_j + 1)(\hbar\omega_j)^2. \tag{4}$$

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* When considering luminescence we assume that ρ exists. For solutions and the dense gas phase $\rho = \exp(-\beta\hat{H}_b)$. This also explains the independence of the luminescence band from λ_{exc}. Sometimes it is assumed that $\rho = \rho(T^*)$ (^{6}), where T^* differs from the temperature of the medium. One may think that the dependence on λ_{exc} is contained entirely in ρ.

The broadening may reach several hundred reciprocal centimeters. For complex molecules, where the frequency distribution is sufficiently compact, this will lead to a continuous spectrum. Taking into account that $M \neq \text{const}$, and that $\hat{H}_a, \hat{H}_b$ are operators of anharmonic oscillators, complicates the picture, additionally introducing the configurational influence of the semiclassical degrees of freedom.

The proposed explanation of continuous bands is, of course, not the only possible one. Let us point out one more possibility. It is usually assumed (see, for example, $^{(2)}$, Ch. 2) that strong coupling between vibrations occurs as a result of large anharmonicity. However, if one recalls that optically active electrons are localized on a finite number of bonds, then the influence of the "peripheral" parts of the molecule can already be taken into account in a linear approximation with respect to the coordinates of these parts. This observation seems to us essential for justifying the oscillator approximation for complex molecules. Since the number of "peripheral" groups for a complex molecule may be very large, in a good approximation they may be regarded as a heat bath, interaction with which leads to a smearing of the structure. Let us emphasize that a quantitative treatment of the indicated possibility can also be obtained from the general relations (1).

2. An explanation of the approximate universality of the bands, together with the question of their shape, can be given on the basis of the central limit theorem $^{(12)}$. In the present case its content will be that the distribution of the normalized quantity $q = (\nu - \bar{\nu})/\sigma$ tends to the normal function as $n \to \infty$. Here $\bar{\nu}$ is the position of the maximum, and σ^2 is the second moment. By n we understand approximately the following: if N is the number of degrees of freedom of the molecule and $N = \sum n_i$, where n_i is the number of oscillators of frequency i, then $n = \sum n_i \bar{n}_i$; $\bar{n}_i$ is the Planck mean. For a sufficiently complex molecule n is large and the distribution can be represented by an asymptotic expansion. One of such expansions (proposed already in 1955 by Edgeworth $^{(12)}$) has the form (see also $^{(5)}$)

$$I(q) \simeq [\varphi(q)] - \left[\frac{1}{3!}\frac{\mu_3}{\sigma^3}\varphi^{(3)}(q)\right] + \left[\frac{1}{4!}\left(\frac{\mu_4}{\sigma^4} - 3\right)\varphi^{(4)}(q) + \frac{10}{6!}\left(\frac{\mu_3}{\sigma^3}\right)^2 \varphi^{(6)}(q)\right]$$

$$- \left[\frac{1}{5!}\left(\frac{\mu_5}{\sigma^5} - 10\frac{\mu_3}{\sigma^3}\right)\varphi^{(5)}(q) - \frac{35}{7!}\frac{\mu_3}{\sigma^3}\lambda\left(\frac{\mu_4}{\sigma^4} - 3\right)\varphi^{(7)}(q) - \frac{280}{9!}\left(\frac{\mu_3}{\sigma^3}\right)^3 \varphi^{(9)}(q)\right] + \cdots \tag{5}$$

Here $\varphi(q) = (2\pi)^{-1/2}\exp(-q^2/2)$; $\varphi^{(i)}(q)$ is the derivative of $\varphi(q)$ of order i; μ_i are the central moments; $\mu_2 \equiv \sigma^2$. This series gives the expansion of $I(q)$ in powers of $1/\sqrt{n}$, with a remainder term of the order of the first omitted term (12) (the terms of one order are enclosed in brackets). For finite n, especially if μ_3, μ_4 are large, the deviations from the Gaussian form may be appreciable; however, for large n, to a good approximation one may restrict oneself to terms of order n^{-1} (i.e., to the first three terms in (5)). As a result, we obtain that, for a large class of complex molecules, the spectral density both of absorption and of emission can be represented in the form of one and the same expression. The individual characteristics of the molecules are contained in the moments μ_i, which can be calculated from (1).

To determine the temperature dependence of the bands, one must either calculate the traces (1), or calculate several of the first moments. Traces of type (1) have been calculated in a number of special cases by several authors.

The case in which $M = \text{const}$, $\hat{H}_a, \hat{H}_b$ are oscillator operators, and the difference $\hat{H}_b - \hat{H}_a$ is a linear function of the coordinates, was considered by Lax (5) (see also (7)). In this approximation

$$I_{\text{abs}}(t) = \exp\left\{ i2\pi\nu_0 t + \sum_j |w_j|^2 \left[(\exp(-i\omega_j t) - 1) + \frac{\exp(i\omega_j t) + \exp(-i\omega_j t) - 2}{\exp(\beta\hbar\omega_j) - 1} \right] \right\}. \tag{6}$$

A more general case, in which both the equilibrium distances and the oscillator frequencies change, was considered by Kubo and Toyozawa ((13); (5), p. 45). For $M = \text{const}$, assuming that the frequencies change only slightly, we have

$$I_{\text{abs}}(t) = \exp\left\{ i2\pi\nu_0 t + \sum_j |w_j|^2 \left[i\sin\omega_j t - \operatorname{cth}\frac{\beta\hbar\omega_j}{2}(1 - \cos\omega_j t) \right] - \operatorname{cth}\frac{\beta\hbar\omega_j}{2}\frac{it}{2}\Gamma_j \right\}; \quad \Gamma_j = \omega_j(a) - \omega_j(b). \tag{7}$$

It is not difficult to see that the first moment for (6) does not depend on the temperature, i.e., in this approximation the position of the band maximum does not change with temperature. The first moment for (7) already depends on the temperature.

3. Consideration of the mirror symmetry of bands on the frequency scale with the aid of (1) presents no particular difficulty.* The condition of mirror symmetry with respect to ν_s is written, up to factors, in the form:

$$I_{\text{abs}}(t)\exp(-i2\pi\nu_s t) \simeq I_{\text{em}}(-t)\exp(i2\pi\nu_s t). \tag{8}$$

One of the solutions is the following: $\nu_s = \nu_0$, $\operatorname{Sp} e^{-\beta H} = \operatorname{Sp} e^{-\beta T H}$, $T^2 = 1$. Here ν_0 is the frequency of the purely electronic transition, $H_b = h\nu_0 + TH$, $H_a = H$. Moreover, M satisfies the condition $TM = \text{const} \cdot M$. This solution may be regarded as a derivation of Levin' s well-known conditions (14).

In order to obtain, in principle, the possibility of a quantitative estimate of the mirror symmetry on the λ scale, let us find the analytic expression for the Fourier transforms in this case. Using the known property of the delta function

$$\delta\left(E_{bn} - E_{am} - \frac{hc}{\lambda}\right) = \frac{\delta(\lambda - \lambda_1)}{|hc/\lambda_1^2|}, \qquad \lambda_1 = \frac{hc}{E_{bn} - E_{am}}, \tag{9}$$

and then introducing its integral representation, we obtain

$$I_{\text{abs}}(\tau) = Av_m \sum_n \langle am|M|bn\rangle\langle bn|M|am\rangle \frac{hc}{(E_{bn} - E_{am})^2} \exp\left(-\frac{i\tau hc}{E_{bn} - E_{am}}\right). \tag{10}$$

It is more convenient to carry out the summation with the kernel:

$$\frac{1}{y^2} \exp\left[i\tau\left(\lambda_s - \frac{hc}{y}\right)\right];$$

here λ_s is the line of symmetry. It can be shown that

$$\frac{1}{y^2} \exp i\tau\left(\lambda_s - \frac{hc}{y}\right) = -\int ikA(k)e^{iky} \frac{I_1\left(2\sqrt{k\tau(\lambda_s y - hc)}\right)}{\sqrt{k\tau(\lambda_s y - hc)}}\, dk; \tag{11}$$

$$A(k) = -i/4\pi \quad \text{for } k > 0; \qquad A(k) = 0 \quad \text{for } k = 0; \qquad A(k) = i/4\pi \quad \text{for } k < 0.$$

Here I_1 is the Bessel function of imaginary argument, $y = E_{bn} - E_{am}$.

Introducing the Sonin–Schläfli integral representation [15]

$$\frac{2I_1(z)}{z} = \frac{1}{2\pi i} \int_C \exp\left(\zeta + \frac{z^2}{4\zeta}\right) \zeta^{-2}\, d\zeta, \tag{12}$$

we obtain

$$\tilde{I}_{\text{abs}}(\tau) = -Av_m \int ikA(k)\, dk \cdot \frac{1}{2\pi i} \int_C \exp(\zeta)\zeta^{-2}\, d\zeta \cdot \exp\left(-\frac{k\tau hc}{\zeta}\right) \times$$

$$\times \left\langle am \middle| M \exp\left[\left(ik + \frac{k\tau\lambda_s}{\zeta}\right) H_b\right] M \exp\left[-\left(ik + \frac{k\tau\lambda_s}{\zeta}\right) H_a\right] \middle| am \right\rangle. \tag{13}$$

An analogous expression is obtained for emission.

The condition of mirror symmetry with respect to λ_s:

$$\tilde{I}_{\text{em}}(\tau) = \tilde{I}_{\text{abs}}(-\tau).$$

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* Here and below we assume that $\rho = \exp(-\beta \hat{H}_b)$.

Analysis of the sufficient condition for mirror symmetry by means of relation (7) leads to the following formula for λ_s:

$$\lambda_s = \frac{hc}{h\nu_0 - \frac{\hbar}{2}\sum_j \Gamma_j \operatorname{cth}\frac{\beta\hbar\omega_j}{2}}. \tag{14}$$

Since usually $\Gamma_j > 0$, it follows from (14) that $\nu_0 > \nu_s$, i.e., the frequency of the purely electronic transition in this case is shifted toward the absorption maximum, which agrees with experiment [16].

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CITED LITERATURE

1. S. I. Vavilov, *Works*, **1**, p. 8, 1952.
2. B. I. Stepanov, *Luminescence of Complex Molecules*, Publishing House of the Academy of Sciences of the BSSR, Minsk, 1955.
3. B. S. Neporent, ZhETF, **21**, 172 (1951).
4. M. Born, Huang Kun, *Dynamical Theory of Crystal Lattices*, IL, 1958, Appendix 8.
5. M. Lax, J. Chem. Phys., **20**, 1752 (1952) (Russian translation in the collection *Problems of Semiconductor Physics*, IL, 1957, p. 42).
6. B. I. Stepanov, Bulletin of the Academy of Sciences of the USSR, ser. phys., **22**, 1034 (1958).
7. O. R. Mcayzen, Proc. Roy. Soc., **A241**, 480 (1957).
8. B. S. Neporent, Proceedings of the State Optical Institute, **25**, issue 50 (1957).
9. B. S. Neporent, DAN, **92**, 927 (1953).
10. B. S. Neporent, N. A. Borisevich, *Optics and Spectroscopy*, **1**, issue 2 (1956).

11. S. I. Kubarev, DAN, **126**, 971 (1959).
12. H. Cramér, *Mathematical Methods of Statistics*, IL, 1948.
13. R. Kubo, Y. Toyozawa, Progr. Theor. Phys., **13**, 160 (1955).
14. V. L. Levshin, *Photoluminescence of Liquids and Solids*, 1951, p. 96.
15. M. A. Lavrent' ev, B. V. Shabat, *Methods of the Theory of Functions of a Complex Variable*, 1958, p. 592.
16. N. A. Borisevich, DAN, **99**, 695 (1954).

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

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