PHYSICS

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1961

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Abstract

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QUANTUM-MECHANICAL THEORY OF THE ABSORPTION AND LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

Numerous attempts to explain the principal features of the absorption and luminescence spectra of complex molecules ([1]-[4]) have not yet led to definitive results. In the present communication we consider the question of the nature of continuous bands, of an analytical expression for their contour, and of the causes of Stokes losses. To solve this problem we use the ideas of predissociation theory in the form proposed in ([5], [6]). The solutions obtained there are exact, but pertain only to the special case of a one-dimensional problem and of the "interaction" of discrete levels with a set of continuous levels of identical density. For the case of complex molecules one can formulate, by analogy, only the general properties of the solution; nevertheless, these make it possible to explain the experimental facts correctly.

In accordance with the usual ideas about the properties of optically active electrons, we shall assume that electronic excitation is directly connected with a change in the vibrational state of only one or a few vibrational degrees of freedom (for brevity, let us call them group A), while all the remaining degrees of freedom play the role of a heat reservoir. This means that the potential functions of the upper and lower electronic states differ from one another only for the coordinates of group A and are identical for the coordinates of the heat reservoir.*

In the zeroth approximation the variables of the nuclear motion (q) of group A and of the entire remaining part of the molecule (Q) are separated. The eigenfunctions in the lower and upper electronic states, respectively, have the form**

$$\psi_1(x)\psi_w(q)\psi_\varepsilon(Q), \qquad \psi_2(x)\psi^*_{w^*}(q)\psi^*_\varepsilon(Q). \tag{1}$$

Here $\psi_1(x)$ and $\psi_2(x)$ are solutions of the electronic Schrödinger equation; $\psi_w(q)$ and $\psi^*_{w^*}(q)$ are solutions of the vibrational equation for group A; $\psi_\varepsilon(Q)$ is for the heat reservoir. Since the molecule is sufficiently complex, the energy values ε of the heat reservoir run through a continuous sequence; the eigenfunctions $\psi_\varepsilon(Q)$ of the upper and lower states are in no way connected with the state of the electron cloud and, for a given value of ε, are identical for the upper and lower states. The possible values of the vibrational energy w and w^* of group A in both electronic states are discrete and may be different. In view of the difference in the potential functions (there is, at least, a displacement of the minima), the eigenfunctions $\psi_w(q)$ and $\psi^*_{w^*}(q)$ are not orthonormal.

If the zeroth approximation were valid, i.e., if the interaction of group A with the remaining part of the molecule were absent, then the form of the spectrum would be determined only by group A. The intensities of individual discrete lines with frequencies $E_{\text{el}} + w^* - w$ would be proportional to the square of the transition matrix element:

$$|D_{ww^*}|^2 = \left| \int \psi_1(x) \hat{D} \psi_2^+(x)\, dx \right|^2 \left[\int \psi_w(q) \psi^*_{w^*}(q)\, dq \right]^2 =$$

$$= |D_{12}|^2 \left[\int \psi_w(q) \psi^*_{w^*}(q)\, dq \right]^2 . \tag{2}$$

The calculation has been carried out in the Franck-Condon approximation, i.e., assuming that the operator $\hat{D}$ is independent of the vibrational coordinates. We note that for transitions from a given initial state w

$$\sum_{w^*} \left[\int \psi_w(q) \psi^*_{w^*}(q)\, dq \right]^2 = \sum_{w^*} (M_{ww^*})^2 = 1. \tag{3}$$

To pass from the transition probability to the number of transitions, the values $|D_{ww^*}|^2$ must be multiplied by the population of the levels w.

Let us now consider the changes in the spectra that occur when the actually existing strong interaction of the vibrational degrees of freedom of group A with the entire remaining part of the molecule is taken into account. If the true vibrational eigenfunction is expanded in terms of the eigenfunctions of the zeroth approximation, then for the lower and upper electronic states we obtain, respectively:

$$\psi_E(q, Q) = \sum_{w,\varepsilon} \alpha_{w\varepsilon}(E) \psi_w(q) \psi_\varepsilon(Q), \tag{4}$$

[*] The advisability of introducing the concept of group A was first noted in (3). In (7) a number of detailed considerations were expressed concerning the properties of this group. Recently these ideas have been used by S. I. Kubarev (4).

[**] We assume here that the adiabatic approximation is valid and that the variables of electronic motion x and nuclear motion q, Q are separated.

$$\psi^*_{E^*}(q,Q) = \sum_{w^*,\varepsilon^*} \alpha^*_{w^*\varepsilon^*}(E^*)\psi^*_{w^*}(q)\psi_{\varepsilon^*}(Q). \tag{5}$$

The values E and E^* take on a continuous series of values. Strictly speaking, in (4) and (5) the summation over ε should be replaced by integration. However, as shown in (^{5,6}), in a concrete calculation the continuous system of levels may be replaced by a discrete system with very small spacings between the levels. Since the initial systems of functions $\psi_w(q)$, $\psi^*_{w^*}(q)$, $\psi_\varepsilon(Q)$, as well as the final systems of functions ψ_E and $\psi^*_{E^*}$, are orthonormal, a number of relations exist among the expansion coefficients (4) and (5):

$$\sum_{w,\varepsilon}[\alpha_{w\varepsilon}(E)]^2 = 1; \qquad \sum_{w^*,\varepsilon^*}[\alpha^*_{w^*\varepsilon^*}(E^*)]^2 = 1. \tag{6}$$

for any E and E^*;

$$\sum_{E}[\alpha_{w\varepsilon}(E)]^2 = 1; \qquad \sum_{E^*}[\alpha^*_{w^*\varepsilon^*}(E^*)]^2 = 1 \tag{7}$$

for any w, w^*, and ε.

The functions $\psi_E(q,Q)$ and $\psi^*_{E^*}(q,Q)$ are not orthogonal to one another. In the most general case

$$\sum_{E^*}\left[\int \psi_E(q,Q)\psi^*_{E^*}(q,Q)\,dq\,dQ\right]^2 = \sum_{E^*}(M_{EE^*})^2 = 1; \tag{8}$$

$$\sum_{E}\left[\int \psi_E(q,Q)\psi^*_{E^*}(q,Q)\,dq\,dQ\right]^2 = \sum_{E}(M_{EE^*})^2 = 1. \tag{9}$$

The value $[\alpha_{w\varepsilon}(E)]^2$ in (4) determines the probability that, in the true state of a molecule with vibrational energy E, the properties of the discrete level w of group A and simultaneously of the level ε of the heat reservoir will be found. The probability $[\alpha^*_{w^*\varepsilon^*}(E^*)]^2$ has an analogous meaning, but

for the upper electronic state. Thus, the characteristic properties of group A—namely, its ability to participate in the process of an electronic transition and to determine the probability of absorption and emission of individual frequencies—are manifested in all real vibrational states of the molecule with all possible energy values. The energy of group A in a given state of the molecule is indefinite. The specific form of the dependences $[\alpha_{\omega\varepsilon}(E)]^2$ on E, ω, ε and $[\alpha^*_{\omega^*\varepsilon^*}(E^*)]^2$ on $E^*, \omega^*, \varepsilon^*$ is determined by the properties of group A and of the thermal reservoir, as well as by the form of the operator of interaction between them. However, some basic features of the functions $[\alpha_{\omega\varepsilon}(E)]^2$ and $[\alpha^*_{\omega^*\varepsilon^*}(E^*)]^2$ can be established even without calculations, on the basis of the law of conservation of energy and the data of works (^{5,6}) on predissociation theory. Thus, for example, the maximum value of the probability $[\alpha_{\omega\varepsilon}(E)]^2$ will occur at those values of E for which $\omega + \varepsilon$ is equal to E or close to it. The half-width of the curves $[\alpha_{\omega\varepsilon}(E)]^2$ and $[\alpha^*_{\omega^*\varepsilon^*}(E^*)]^2$, as functions of E and E^*, will be the greater, the stronger the interaction of group A with the rest of the molecule and the greater the density of levels of the thermal reservoir.

Let us now consider optical transitions between the vibrational sublevels of the lower and upper electronic states. The probabilities of transitions with frequency $h\nu = E_{\text{el}} + E^* - E$ are, in the general case, proportional to the square of the matrix element

$$|D_{EE^*}|^2 = \left| \int \psi_1(x)\, \psi_E(q, \hat{Q})\, \hat{D}\, \psi_2^+(x)\, \psi_{E^*}(q, Q)\, dx\, dq\, dQ \right|^2 =$$

$$= |D_{12}|^2 \left[\iint \left\{ \sum_{\omega,\varepsilon} \alpha_{\omega\varepsilon}(E)\, \psi_\omega(q)\, \psi_\varepsilon(Q) \right\} \left\{ \sum_{\omega^*,\varepsilon^*} \alpha^*_{\omega^*\varepsilon^*}(E^*)\, \psi^*_{\omega^*}(q)\, \psi_{\varepsilon^*}(Q) \right\} dq\, dQ \right]^2 =$$

$$= |D_{12}|^2 \left[\sum_{\omega,\omega^*,\varepsilon} \alpha_{\omega\varepsilon}(E)\, \alpha^*_{\omega^*\varepsilon}(E^*)\, M^2_{\omega\omega^*} \right]^2 .$$

In calculating (10) we have used the orthonormality of the functions of the zeroth approximation.

Expression (10) determines the shape of the contour of the absorption band that would occur if all molecules were in one and the same initial state with energy E. The true absorption contour of vapors of complex molecules is obtained if (10) is multiplied by the distribution function $\varrho(E)$ and integrated over all E.

According to (10), optical transitions are possible between any vibrational sublevels of the combining pair of electronic levels. Although group A, which directly participates in the process of the electronic transition, possesses a discrete set of vibrational levels, the true absorption and emission spectra of the molecule as a whole will have continuous bands. This character of the spectra arises as a result of the interaction of the vibrational degrees of freedom of group A with the rest of the molecule and of the predissociation broadening of the discrete levels as a result of nonoptical transitions of the part of the vibrational energy obtained as a result of excitation and initially concentrated in group A into the energy of the thermal reservoir.

The continuous character of the absorption and emission bands is realized only when there is strong interaction between group A and the rest of the molecule, and also for sufficiently complex molecules with continuous values of the energy of the thermal reservoir. If the interaction of group A and the reservoir is absent, then the coefficients $\alpha_{\omega\varepsilon}(E)$ and $\alpha^*_{\omega^*\varepsilon^*}(E^*)$ in (10) are different from zero only for $E = \omega + \varepsilon$ and, correspondingly, for $E^* = \omega^* + \varepsilon^*$, and expression (10) goes over into (2), which characterizes a discrete set of frequencies. For small interactions, predissociation is small, the distributions $\alpha_{\omega\varepsilon}(E)$ and $\alpha^*_{\omega^*\varepsilon^*}(E^*)$ have a sharp maximum, and expression (10) determines a discrete spectrum with broadened, sometimes overlapping, lines.

Expression (10), together with (4) and (5), makes it possible to explain other experimentally observed features of the spectra as well. If the potential functions in the upper and lower electronic states are identical, then $\alpha^*_{w^*\varepsilon^*}(E^*) = \alpha_{w\varepsilon}(E)$ for $E^* = E$, $w = w^*$, $\varepsilon^* = \varepsilon$, and $(M_{ww^*})^2 = (M_{w^*w})^2$ for transitions with absorption and emission between the same initial and final levels of group A. In this particular case, according to (10), the squares of the matrix elements of the transition for the frequencies $\nu_{\text{abs}} = \nu_{\text{el}} + \Delta\nu$ and $\nu_{\text{em}} = \nu_{\text{el}} - \Delta\nu$ are equal to one another and, consequently, when the distribution functions $\rho(E)$ and $\rho(E^*)$ are equal—as occurs for solutions—the contours of the absorption and emission bands are symmetric to one another (Levshin' s mirror-symmetry rule). The frequency of symmetry of the spectra coincides with ν_{el}. If one of these conditions is not fulfilled, the symmetry of the spectrum is violated. It is violated, in particular, for vapors, since in this case $\rho(E) \neq \rho(E^*)$.

It follows from (8), (9), and (10) that the integrals of $|D_{EE^*}|^2$ over E and of $|D_{E^*E}|^2$ over E^* are equal to $|D_{12}|^2$; consequently, the areas of the absorption and emission bands (Kravts integrals) do not depend on the structural features of the vibrational levels of the molecule and are determined only by the probability of the electronic transition. They do not depend on the form of the distribution functions and, in particular, on temperature or on the method of excitation.

Since the transition probabilities $|D_{EE^*}|^2$ and $|D_{E^*E}|^2$ depend on the initial level, the contours of the absorption and emission bands are connected with the form of the distribution function and, consequently, with temperature. The contour of the luminescence band in the general case depends on the frequency of the exciting light. In solutions the distribution function $\rho^*(E^*)$, and hence the contours of the luminescence bands, do not depend on the frequency of the exciting radiation.

From the analysis of (10) it follows that the contour of the absorption band is determined mainly by the dependence of $(M_{ww^*})^2$ on w and w^*, i.e., by the mutual arrangement of the potential functions of the upper and lower states for the variables of group A. If $(M_{ww^*})^2$ did not depend on w and w^*, then the value (10) would be only a monotonic function of the frequency of the absorbed light. In reality the band contour is a somewhat distorted envelope of the discrete spectrum that would exist in the absence of interaction between group A and the thermal reservoir. Since the maximum of $(M_{ww^*})^2$ occurs at $w^* < w$, the maximum of the absorption band falls at a frequency exceeding the frequency of the purely electronic transition. It follows from this that the absorption process is accompanied (on the average) by an increase in the store of vibrational energy inside the molecule. All the excess vibrational energy initially released in group A is transferred to the thermal reservoir, and the state of group A before the act of emission is close to the initial one that existed before the act of absorption. The act of emission is again accompanied by an increase in the vibrational energy of group A, which is also the cause of the red shift of the maximum of the emission band relative to the maximum of the absorption band.

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Received
9 XII 1960

CITED LITERATURE

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

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