CONTRIBUTIONS TO THE THEORY OF ABSORPTION AND EMISSION SPECTRA OF FLUORESCENT MOLECULES

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Considering qualitatively the correlation between the electrons and atomic vibrations of fluorescent molecules, it is supposed that in the case of the light absorption one part of the absorbed energy $\hbar(\omega - \omega_0)$ and in the case of a radiative transition between the excited and the ground state of the molecules the resting energy $\hbar(\omega - \omega_0)$ may be converted into heat, $\hbar\omega_0$ being the energy difference between the pure electronic states and $\hbar\omega$ the energy of the photon playing part in the processes mentioned. In this way the temperature of the molecules rises against the temperature of the thermal equilibrium at the beginning of the absorption and emission processes. Owing to this natural supposition, BLOKHINTSEV's theory of absorption and emission spectra can be improved by taking into account the correlation-fluctuations during the transitions and obtained an analytical expression for the absorption and emission spectra previously experimentally found by DOMBI et al [1]. Based on the spectra derived, the LEVSHIN's relation of mirror symmetry and the generalized STEPANOV's radiation law can be obtained. Finally, the vibrational specific heat as well as the relaxation time of the thermal interaction process between the fluorescent and the solvent molecules are calculated in good agreement with previous estimations.

§ 1. Introduction

The relation between the absorption spectrum $\alpha(\omega)$ and the emission spectrum $\varepsilon(\omega)$ of fluorescent molecules have recently been investigated by several authors from experimental as well as from theoretical point of view. The present investigation was inspired by a more recent investigation of J. DOMBI, I. KETSKEMÉTY and L. KOZMA [1], who observed that considering LEVSHIN's relation of the mirror symmetry of the absorption and emission spectra as well as the generalized STEPANOV's law [2, 3]

$$\varepsilon(\omega)/\alpha_{\text{act}}(\omega) = d(\theta) n^2(\omega) \omega^2 \exp\left\{-\hbar\omega/\theta^*\right\} \tag{1,1}$$

with

$$\alpha_{\text{act}}(\omega) = \alpha(\omega)\eta^*(\omega), \quad \theta^* = kT^* \quad \text{and} \quad \theta = kT, \tag{1,2}$$

the active absorption spectrum $\alpha_{\text{act}}(\omega)$ and the emission spectrum can analytically be written in the following from:

$$\alpha_{\text{act}}(\omega) = \alpha_0 n(\omega) \omega e^{B\omega} \operatorname{ch}^{-1}\left\{A(\omega - \omega_0)\right\} \tag{1,3}$$

and

$$\varepsilon(\omega) = \varepsilon_0 n^3(\omega) \omega^3 e^{-B\omega} \operatorname{ch}^{-1}\left\{A(\omega - \omega_0)\right\}. \tag{1,4}$$

Here $d(\theta)$ is a constant independent of the frequency $\omega = 2\pi\nu$, but it depends on

the temperature θ (in energy units!); $\eta^*(\omega)$ and $n(\omega)$ are the relative quantum yield and refractive index of the solution, respectively; $2\pi\hbar = h$ and k are PLANCK's and BOLTZMANN's constants, finally α_0, ε_0, A and B are constants depending on the temperature which should be experimentally determined. The formulae reproduce excellently the contour of the spectra mentioned if θ^* is a sligthly higher temperature than θ being the temperature of the solution. Due to Eq. (1,1) one can see that $B = \hbar/2\theta^*$ and based on an elementary dimensional reasoning one obtains immediately that $A = \hbar/\theta'$. However, it was, indeed, a fascinating problem to explain the meaning of θ^*, θ' and to derive the formulae (1,3) and (1,4).

It will be presented in the following that based on obvious suppositions, considering some time-correlation and fluctuation effects in the course of the radiative processes, the formulae (1,3) and (1,4) can easily be obtained by a straightforward generalization of BLOKHINTSEV's method [4] used for the derivation of LEVSHIN's relation of mirror symmetry of absorption and emission spectra, furthermore it will be proved that $\theta' = 2\theta$ and θ^* may be interpreted as the vibrational temperature of the molecules at the moment of absorption and emission, respectively. Finally, if θ^* is experimentally determined (based, *e. g.* on the experiments of DOMBI *et al.* [1]) the vibrational specific heat of the molecules and (based on the knowledge of the mean life time of the excited state) the relaxation time of the interaction process between the fluorescent molecules and the solvent can be calculated in very good agreement with earlier results.

§ 2. General remarks to the theory of absorption and emmission spectra and fundamental assumptions on the structure of fluorescent molecules

As it is well known, the emission and absorption of light by an atom or molecule can easily be understood by referring to the theory of perturbation. A molecule and the radiation field from two quantum mechanical systems with an interaction energy

$$\mathbf{H}_{\text{int}} = - \frac{e}{mc} (\mathfrak{v} \cdot \mathfrak{A}). \tag{2,1}$$

This interaction, regarded as a perturbation, will cause transitions of the unperturbed system (molecule + radiation field) in general consisting of a transition of the molecule from one quantum state to another and of an absorption or emission of photon. Here e and m are the charge and mass of the electrons of the molecule, $\mathfrak{v}$ means the velocity of the electron responsible for the radiative transition, finally $\mathfrak{A}$ represents the vector potential of the radiation field.

Based on the very common method [5], if the transition proceeds between two non-degenerate quantum states $(E_a < E_b)$ of the molecule and the induced emission of radiation can be neglected, in the case of dipole radiation one obtains for the absorption and emission spectra [4]:

$$\alpha(\omega) = Nn(\omega) \frac{4\pi^2}{c} \omega |\langle a|\mathfrak{D}|b\rangle|^2 \delta(E_b - E_a - \hbar\omega) \tag{2,2}$$

and
$$\varepsilon(\omega) = \frac{4}{3} n^3(\omega) \frac{\omega^3}{\hbar c^3} |\langle a|\mathfrak{D}|b\rangle|^2 \delta(E_b - E_a + \hbar\omega), \tag{2,3}$$

where $\langle a|\mathfrak{D}|b\rangle = e\langle a|\mathfrak{r}|b\rangle$ represents the matrix element of the transition dipole moment for the transition $b \to a$ and N is the number of absorbing molecules per unit volume.

Considering the absorption and emission spectra of fluorescent molecules one meets rather complicated situation than in the special case mentioned above. The mean point of the difficulties emerged are not reduced to the facts that

(i) the quantum states of such molecules are strongly degenerated, owing to which the principle of correspondence cannot be rigorously applied (or at least the results of the argumentations based on the classical quantum theory of radiation may be very questionable),

(ii) considerable interactions exist between the fluorescent and solvent molecules, but it is due to the complexity of the structure of the fluorescent molecules as well.

An exact or at least an approximately acceptable theory of fluorescent molecules based on the common methods of quantum chemistry seems to be even nowdays hopeless in this case. Nevertheless, owing to the very abundant experimental material in this field [6, 7], just the complexity of the fluorescent molecules makes possible to formulate some natural assumptions about the structure and the enrgy spectrum of these molecules, based thereon the general features of the absorption and emission spectra as well as the validity of this reasoning can be obtained.

Of course, the Hamiltonian of the molecules can be formally written in the form:

$$\mathbf{H}^{(m)} = \mathbf{H}_{el}^{(m)} + \mathbf{H}_{v}^{(m)} + \mathbf{H}_{int}^{(m)}, \qquad (2,4)$$

where $\mathbf{H}_{el}^{(m)}$ and $\mathbf{H}_{v}^{(m)}$ represent the parts of the Hamiltonian corresponding to the electrons and atomic vibrations of the molecules, respectively, and $\mathbf{H}_{int}^{(m)}$ is the interaction between them. This is just the usual decomposition of the Hamiltonian.

Considering the general feature of the absorption and emission spectra it seems — as it has been suggested by several authors — that the fluorescent molecules differ from the simple two- and simple many-atomic molecules especially in the structure of $\mathbf{H}_{v}^{(m)}$. In the latter case the harmonic approximation is an adequate description for the atomic vibrations. This means that the vibrational field can be regarded as a system of non-interacting normal vibrations. However, in the case of fluorescent molecules the harmonic approximation breaks down and it has to be assumed that strong interaction among the normal vibrations takes place, so far that the energy absorbed by one of the normal vibrations, dissipates very quickly among the vibrational degrees of freedom. Owing to this reasoning it may be assumed that the energy distribution on the vibrational levels is approximately independent of the electronic states, at least in the case of the two lowest electronic quantum states, important in the processes of fluorescence. Bearing in mind the chemical structure of the fluorescent molecules, the quasi-continuity of the vibrational energy spectrum, due to the very closely placed vibrational levels, as a further natural assumption can be regarded.

The interaction part of the Hamiltonian between the electrons and molecular vibrations depends on the strength of the coupling between these two essentially different degrees of freedom.

Even should we not try to suggest an explicit expression for $\mathbf{H}_{int}^{(m)}$, it can be supposed that one part — say $\hbar\omega_0$ (being the energy difference between the two

electronic states treated) — of the energy $\hbar\omega$ absorbed excites the system of electrons and the remaining part of the absorbed energy $\hbar(\omega - \omega_0)$ dissipates on the vibrational degrees of freedom. Namely, the magnitude of the energy dissipated depends on the coupling constant contained by $\mathbf{H}_{int}^{(m)}$ being a characteristic quantity of the fluorescent molecules. Due to the inertia of the atomic vibrations in comparison with the excitations of the electrons, it can be assumed that (at least in the Stokesian domain of the spectrum) $\hbar(\omega - \omega_0) \ll \hbar\omega_0$. However, we have to emphasize that the expectation value of the energy dissipated on the vibrational levels depends last of all on the energy state of the molecules and actually it makes a slight fluctuation, if the time-evolution of the system is taken into account. Indeed, in the following we shall observe that the consideration of this fluctuation will be very important if one treats the derivation of the absorption spectrum (1,3) found experimentally by DOMBI and co-workers.

In the case of emission of the light (of an energy $\hbar\omega$) by fluorescent molecules, one part of the emitted energy (say $\hbar\omega_0$) originates again from the transition between two quantum states of the system of electrons and the remaining second part $\hbar(\omega - \omega_0)$ is added to the first one by changing the vibrational state. The fluctuational effect in this case has to be considered, too.

At this point it seems worthwhile to mention a well known analogy with the absorption and emission processes of the atoms. If the motion of atoms interacting with the radiation field is taken into account, a part of the absorbed and emitted energy is, respectively, consumed and increased by the kinetic energy of the atoms. Such a dissipation or gaining of the radiation energy on or from the translational "mechanical degrees of freedom", respectively, appears in the case of considerable $\hbar\omega$ in the broadening of the line width as well as in the separation of the maxima of the absorption and emission spectra and causes a mirror symmetry between them. Such effect in the case of the heavy fluorescent molecules can completely be neglected, but the mirror symmetry of the absorption and emission spectra observed, if the dissipated or the gained energy is attributed to the vibrational mechanical degrees of freedom, can be understood in a very similar way.

For the sake of simplicity we consider radiative transitions of the fluorescent molecules only between the two lowest electronic states (being in a distance $\hbar\omega_0$) and we suppose that these electronic levels are not degenerated. It is well known that such a reasoning has previously been very common in the theory of fluorescence, too. This means, however, that the degeneration of the corresponding quantum states of the molecules is only due to the energy of vibrations. Let us denote the lowest electronic energy state by E_0, the corresponding energy of the molecule by E_a, and the energy of the upper quantum state of the molecule by E_b, then we have

$$E_a = E_0 + W_a \quad \text{and} \quad E_b = E_0 + \hbar\omega_0 + W_b, \tag{2,5}$$

where W_a and W_b mean the energy of the vibrational levels, respectively. Owing to the energy conservation, a transition $a \to b$ can be induced by the absorption of a photon of energy $\hbar\omega$ fulfilling the relation:

$$E_b - E_a = \hbar\omega \tag{2,6}$$

and it is immediately seen, that

$$W_b - W_a \equiv \hbar\omega_{ba} = \hbar(\omega - \omega_0). \tag{2,7}$$

The corresponding ket vectors fulfilling the time-independent SCHRÖDINGER equations

$$\mathbf{H}^{(m)}|a\rangle = E_a|a\rangle \text{ and } \mathbf{H}^{(m)}|b\rangle = E_b|b\rangle, \tag{2,8}$$

respectively, depend on the co-ordinates of the electrons $(\mathbf{r}_i)$ and on the normal co-ordinates (q_r) of the atomic vibrations. We have to emphasize that — due to the considerable interaction between the electrons and vibrations — the two kinds of co-ordinates cannot be separated, *i. e.*, the kets cannot be decomposed into the product of two kets depending only on the electronic and vibrational co-ordinates, respectively. In this respect we cannot agree with B. J. STEPANOV, who in his excellent monography [7], *e. g.*, on the occasion of a simplified deduction of the mirror symmetry introduced such a separation.

As a matter of fact, under real experimental circumtances we have to investigate a system of fluorescent molecules embedded into a system of another sort of molecules alike in the vapour, fluid and solid state of the system. Let us suppose for simplicity that only thermal intractions between the fluorescent and the extraneous molecules must be taken into account. At the first instant is perhaps surprising, but it seems that just the dilute solutions of the fluorescent molecules would represent the simplest systems from theoretical point of view. Its reason can be given by the argumentation that in dilute solutions — at least in the case when the radiationless energy transfer among the fluorescent molecules is sufficient to be considered — the direct (even thermal) interaction among them can be neglected. Namely, as the number of fluorescent molecules is negligible against the number of the solvent molecules, collisions among the fluorescent molecules practically do not take place. This means, however, that the system of the fluorescent molecules — as a component-system of the solution — from statistical point of view can be regarded as a perfect gas in the heat-bath of the solvent molecules, because the very lack of direct interactions is the mean point of the definition of a perfect gas. As a matter of fact, the system of the fluorescent molecules may satisfactorily be repredensed by a Gibbsian ensemble and the number of molecules having the quantum state E_n is proportional to $\exp\{(\Psi_n - E_n)/\theta\}$, where Ψ_n represents the free energy of the electrons at the temperature θ, furthermore the interaction between the system of fluorescent molecules and the solvent molecules may be described with the phenomenological method of heat conduction. In the case of vapours as a consequence of the more considerable diffusion and in solid state due to the phonon excitation rather complicated effects may occur, too.

Having in mind the theoretical foundation of the experimental spectra, in the form as they can actually be observed, one has — *e. g.*, in the case of the absorption spectrum — to average formula (2,1) over all vibrational levels of the initial and of the excited electronic states as well; finally, one has to multiply with the number of fluorescent molecules in the different vibrational states having the energies $E_a = E_0 + W_a$. If we suppose that the molecules in the initial state are in thermal equilibrium with their surroundings (*i. e.*, with the solvent molecules) at a temperature θ, this means — as it was otherwise discussed, *e. g.*, by BLOKHINTSEV [6] in details — that we have to average over the statistical ensemble, too, and one has to calculate the expression

$$\sum_a \sum_b \exp\{(\Psi_1 - E_a)/\theta_1\} g(E_a) g(E_b) |\langle a|\mathfrak{D}|b\rangle|^2 =$$
$$= \int dW_a \int dW_b \exp\{(\Psi_1 - E_a)/\theta\} g(E_a) g(E_b) F(E_a, E_b), \tag{2,8}$$

where Ψ_1 denotes the free energy of the molecules in the initial state; $g(E_a)dW_a$ and $g(E_b)dW_b$ are the number of vibrational levels in the energy intervals $(E_0 + W_a,\ E_0 + W_a + dW_a)$ and $(E_0 + \hbar\omega_0 + W_b,\ E_0 + \hbar\omega_0 + W_b + dW_b)$, respectively; finaly, $F(E_a, E_b) \equiv F(E_a, E_a + \hbar\omega)$ is an abbreviation of the square of the transition matrix element for the transition $a \to b$. Owing to the densiteness, i. e., quasi-continuity of the vibrational levels, the summations over the vibrational states are approximated by integrals.

It is well known that this method, being very common in spectroscopy, gives excellent results for the absorption and emission spectra in the case of atoms and simple manyatomic molecules as well. Furthermore, BLOKHINTSEV showed that also the mirror symmetry of the absorption and emission spectra can be obtained in this way. Nevertheless, it seems that in the case of fluorescent molecules one would have slightly to modify the way of thinking. Namely, due to the lack of the explicit knowledge of the operators $\mathbf{H}_{\mathrm{int}}^{(m)}$ and $\mathbf{H}_v^{(m)}$ containing the interaction rules of the electronic motions with the molecular vibrations and among the vibrational modes as well, it is so far undetermined that in the case of the absorption of a photon with energy $\hbar\omega$ how large is the energy $\hbar(\omega - \omega_0)$ exciting the molecular vibrations and in which way is it distributed between the vibrational degrees of freedom? Therefore, as matters stand, we have to formulate a reasonable supposition to overcome this difficulty. Since the energy exciting the molecular vibrations can reach the vibrational modes in different phases, consequently the vibrations can be both increased and damped, it may be concluded that one has every reason to suppose that from a definite initial state E_a every excited states E_b can be reached with equal probability. Of course, the number of the excited molecules cannot depend on this indefiniteness, therefore one has to average also in the states b over the statistical ensemble; this means, however, that before the summation over b we have to multiply by a factor $\exp\{(\Psi_2 - E_b)/\theta_2\}$, where Ψ_2 denotes the free energy of the molecules in the excited states. Instead of the temperature θ_1 we have written here any temperature θ_2, because the molecules due to the excitation of their vibrational degrees of freedom "warm up" and they will be in thermal equilibrium at any temperature $\theta_2 > \theta_1$. If this reasoning can be accepted, BLOKHINTSEV's formula (2,8) has to be replaced by

$$\sum_a \sum_b \exp\{(\Psi_1 - E_a)/\theta_1\} \exp\{(\Psi_2 - E_b)/\theta_2\} g(E_a) g(E_b) |\langle a|\mathfrak{D}|b\rangle|^2 =$$

$$= \int dW_a \int dW_b \exp\{(\Psi_1 - E_a)/\theta_1\} \exp\{(\Psi_2 - E_b)/\theta_2\} g(E_a) g(E_b) F(E_a, E_b). \quad (2,9)$$

Finally, we have to find the relations between the fictive temperatures θ_1 and θ_2 as well as the temperature θ of the solution (measured experimentally) and the temperature θ^* of excited molecules (predicted by the supposition that one part of the energy absorbed by the mechanical degrees of freedom is converted into the heat of the ensemble of the excited molecules). One can qualitatively argue as follows: We considered in the Hamiltonian (2,3) — as it is usual — only the energies due to the electronic motions and molecular vibrations, but neglected the translational energy of the molecules. This means, however, that the energy E_a (in the exponent of the Gibbsian weight factor) is smaller than the real energy of the molecules in the initial state; therefore in the quotient E_a/θ_1 the temperature θ_1 yes to be also smaller than the real temperature of the solution in order that the

value of the ratio may not undergo a change. Conversely, in the case of excited. states we have „distributed" (in our approximation) the energy reached the mecha-- nical degrees of freedom only between the vibrational degrees of freedom (due to· the neglection of the translational motion again); this means, however, that in this way "more energy has reached" the vibrational degrees of freedom than it happens in reality, therefore W_b and E_b, respectively, are higher than the real energy of the excited states. In order that the value of the ratio E_b/θ_2 may not change, θ_2 has to be higher than the real temperature θ^* of the excited molecules. Conse-- quently, it can be concluded that $\theta_1 < \theta < \theta^* < \theta_2$. This is, of course, only a quali-- tative relation, but — based on a reasonable semi-empirical way — it can be con-- verted into a quantitative one as it is obtained in the next paragraph [Eq. (3,12)].

It seems that the heuristic argumentation detailed above can be replaced by· a more rigorous method based on the BORN's approximation, if one adopts the perturbational procedure being well known in the theory of rearrangement col-- lisions. This method will be exposed in a next paper.

Finally, due to the fluctuations in the interaction between the system of elec-- trons and the atomic vibrations of the fluorescent molecules, on calculating (2,9), it has to be considered the time-correlation effect in course of the time-evolution. of the system, too, as it will be discussed in the next paragraph.

§ 3. Mean square of the fluctuating dipole moment

In order to calculate the mean square of the fluctuating dipole moment, let· us consider its matrix elements in HEINSENBERG-picture:

$$\langle a|\mathfrak{D}(t)|b\rangle = \langle a|\exp\{i\mathbf{H}^{(m)}t/\hbar\}\,\mathfrak{D}\exp\{-i\mathbf{H}^{(m)}t/\hbar\}|b\rangle$$

$$= \langle a|\mathfrak{D}|b\rangle\exp\{i(E_a-E_b)t/\hbar\} = \langle a|\mathfrak{D}|b\rangle\exp\{i(\omega_{ab}-\omega_0)t\} \qquad (3,1)$$

and their FOURIER-amplitudes

$$\langle a|\mathfrak{D}(\omega)|b\rangle = \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty}\langle a|\mathfrak{D}(t)|b\rangle e^{i\omega t}\,dt =$$

$$= \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty}\langle a|\mathfrak{D}|b\rangle e^{i(\omega-\omega_0+\omega_{ab})t}\,dt = \langle a|\mathfrak{D}|b\rangle\delta(\omega-\omega_0+\omega_{ab}), \qquad (3,2)$$

respectively. The operators $\mathfrak{D}(t)$ and $\mathfrak{D}(t')$ for different instants of time do not,. in general, commute, therefore the corresponding time-correlation function must. be defined [8] as

$$\Phi(t'-t) \equiv \frac{1}{2}\overline{\{\mathfrak{D}(t)\mathfrak{D}(t')+\mathfrak{D}(t')\mathfrak{D}(t)\}}, \qquad (3,3)$$

where the bar denotes averaging by means of the quantummechanical probabili-- ties. Owing to the inversion theorem of the FOURIER transformation

$$\mathfrak{D}(t) = \int\limits_{-\infty}^{+\infty} d\omega\,\mathfrak{D}(\omega)e^{-i\omega t}, \qquad (3,4)$$

one obtains

$$\Phi(t'-t) = \frac{1}{2} \int\limits_{-\infty}^{+\infty} d\omega \int\limits_{-\infty}^{+\infty} d\omega' \overline{\{\mathfrak{D}(\omega)\mathfrak{D}(\omega') + \mathfrak{D}(\omega')\mathfrak{D}(\omega)\}} e^{-i(\omega t + \omega' t')}. \qquad (3,5)$$

The integral on the right-hand side will be a function of the difference $(t'-t)$ only if the integrand contains a δ-function of $\omega + \omega'$. This requires that the spectral density of the mean square fluctuation of the dipole moment has to be defined as

$$\frac{1}{2} \overline{\{\mathfrak{D}(\omega)\mathfrak{D}(\omega') + \mathfrak{D}(\omega')\mathfrak{D}(\omega)\}} \equiv \mathfrak{D}_\omega^2 \delta(\omega + \omega'). \qquad (3,6)$$

It is well known that, in particular, $\Phi(0)$ is just the mean square of the fluctuating quantity itself, therefore we have to calculate $\mathfrak{D}_\omega^2$. Since

$$\frac{1}{2} \overline{\{\mathfrak{D}(\omega)\mathfrak{D}(\omega') + \mathfrak{D}(\omega')\mathfrak{D}(\omega)\}} =$$

$$\frac{1}{2} \sum_n \sum_m \{\langle n|\mathfrak{D}(\omega)|m\rangle\langle m|\mathfrak{D}(\omega')|n\rangle + \langle n|\mathfrak{D}(\omega')|m\rangle\langle m|\mathfrak{D}(\omega)|n\rangle\} =$$

$$= \frac{1}{2} \sum_n \sum_m |\langle n|\mathfrak{D}|m\rangle|^2 \times$$

$$\times \{\delta(\omega - \omega_0 + \omega_{nm})\delta(\omega' + \omega_0 + \omega_{mn}) + \delta(\omega' - \omega_0 + \omega_{nm})\delta(\omega + \omega_0 + \omega_{mn})\} =$$

$$= \frac{1}{2} \sum_n \sum_m |\langle n|\mathfrak{D}|m\rangle|^2 \{\delta(\omega - \omega_0 + \omega_{nm}) + \delta(\omega - \omega_0 + \omega_{mn})\}\delta(\omega + \omega'),$$

we have, in general,

$$\mathfrak{D}_\omega^2 = \frac{1}{2} \sum_n \sum_m |\langle n|\mathfrak{D}|m\rangle|^2 \{\delta(\omega - \omega_0 + \omega_{nm}) + \delta(\omega - \omega_0 + \omega_{mn})\}. \qquad (3,7)$$

Now, beside the quantum-mechanical average, we have to calculate the ensemble-average, too. As a matter of fact, one obtains

$$\frac{1}{2} \sum_a \sum_b \exp\left\{\frac{\Psi_1 - E_a}{\theta_1}\right\} \exp\left\{\frac{\Psi_2 - E_b}{\theta_2}\right\} |\langle a|\mathfrak{D}|b\rangle|^2 \times$$

$$\times \{\delta(\omega - \omega_0 + \omega_{ab}) + \delta(\omega - \omega_0 + \omega_{ba})\} =$$

$$= \frac{1}{2} \sum_a \sum_b \exp\left\{\frac{\Psi_1 - E_a}{\theta_1}\right\} \exp\left\{\frac{\Psi_1 - E_b}{\theta_2}\right\} \left[1 + \exp\left\{-(W_b - W_a)\left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right)\right\}\right] \times$$

$$\times |\langle a|\mathfrak{D}|b\rangle|^2 \delta(\omega - \omega_0 + \omega_{ab}) =$$

$$= \exp\left\{-\frac{\varkappa\hbar(\omega - \omega_0)}{2\theta_1}\right\} \mathrm{ch}\left\{\frac{\varkappa\hbar(\omega - \omega_0)}{2\theta_1}\right\} \sum_a \sum_b \exp\left\{\frac{\Psi_1 - E_a}{\theta_1}\right\} \exp\left\{\frac{\Psi_2 - E_b}{\theta_2}\right\} \times$$

$$\times |\langle a|\mathfrak{D}|b\rangle|^2, \qquad (3,8)$$

with

$$\varkappa = \frac{\theta_2 - \theta_1}{\theta_2}. \qquad (3,9)$$

This means, however, that Eq. (2,10) has to be replaced by

$$\sum_a \sum_b \exp\left\{\frac{\Psi_1 - E_a}{\theta_1}\right\} \exp\left\{\frac{\Psi_2 - E_b}{\theta_2}\right\} g(E_a)g(E_b)|\langle a|\mathfrak{D}|b\rangle|^2 =$$

$$= \exp\left\{\frac{\Psi_1}{\theta_1} + \frac{\Psi_2}{\theta_2} + \frac{\varkappa\hbar(\omega - \omega_0)}{2\theta_1}\right\} \mathrm{ch}^{-1}\left\{\frac{\varkappa\hbar(\omega - \omega_0)}{2\theta_1}\right\} \times$$

$$\times \int dW_a \int dW_b\, e^{-E_a/\theta_1} e^{-E_b/\theta_2} g(E_a)g(E_b)F(E_a, E_b). \qquad (3,10)$$

Inserting the last relation in Eq. (2,2) instead of $|\langle a|\mathfrak{D}|b\rangle|^2$ for the absorption spectrum

$$\alpha_{\mathrm{act}}(\omega) = \alpha_0' n(\omega)\omega \exp\left\{\frac{\hbar(\omega - \omega_0)}{2\theta^*}\right\} \mathrm{ch}^{-1}\left\{\frac{\hbar(\omega - \omega_0)}{2\theta}\right\} I_\alpha(\omega - \omega_0) \qquad (3,11)$$

can be obtained with the abbreviations (1,2) and

$$\theta^* \equiv \theta_1/(3\varkappa - 2), \quad \theta \equiv \theta_1/\varkappa = (3\varkappa - 2)\theta^*/\varkappa \qquad (3,12)$$

$$I_\alpha(\omega - \omega_0) \equiv \int dW_a \exp\left\{\frac{(\varkappa - 2)W_a}{\theta_1}\right\} g(E_0 + W_a) \times$$

$$\times g(E_0 + \hbar\omega_0 + W_a + \hbar(\omega - \omega_0)F(E_0 + W_a, E_0 + \hbar\omega_0 + \hbar(\omega - \omega_0)). \qquad (3,13)$$

The constant α_0' introduced in (3,11) is independent of ω and contains all the further factors originatig from Eqs. (2,2) and (3,10).

Similarly, the results for the emission spectrum is

$$\varepsilon(\omega) = \varepsilon_0' n^3(\omega)\omega^3 \exp\left\{-\frac{\hbar(\omega - \omega_0)}{2\theta^*}\right\} \mathrm{ch}^{-1}\left\{\frac{\hbar(\omega - \omega_0)}{2\theta}\right\} I_\varepsilon(\omega - \omega_0) \qquad (3,14)$$

with

$$I_\varepsilon(\omega - \omega_0) \equiv \int dW_b \exp\left\{\frac{(\varkappa - 2)W_b}{\theta_1}\right\} g(E_0 + W_b + \hbar(\omega - \omega_0) \times$$

$$\times g(E_0 + \hbar\omega_0 + W_b)F(E_0 + \hbar\omega_0 + W_b, E_0 + W_b + \hbar(\omega - \omega_0)). \qquad (3,15)$$

In order to compare the formulae (1,3) and (3,11) as well as (1,4) and (3,14), we have to study the properties of the integrals $I_\alpha(\omega - \omega_0)$ and $I_\varepsilon(\omega - \omega_0)$, respectively.

§ 4. General relations between the absorption and emission spectra

Bearing in mind the absorption and emission spectra determined in the last paragraph, one obtains the important relation

$$\frac{\varepsilon(\omega)}{\alpha_{\mathrm{act}}(\omega)} = \frac{\varepsilon_0'}{\alpha_0'} n^2(\omega)\omega^2 \exp\left\{-\frac{\hbar(\omega - \omega_0)}{\theta^*}\right\} \frac{I_\varepsilon(\omega - \omega_0)}{I_\alpha(\omega - \omega_0)} \qquad (4,1)$$

being a new generalization of STEPANOV's radiation law (1,1). Unfortunately this relation is only an implicit one, because the solution of the SCHRÖDINGER-equations (2,8) and simultaneously $F(E_a, E_b)$ as well as the functions $g(E_a)$ and $g(E_b)$ are unknown, so the integrals cannot be explicitly evaluated.

One observes, however, on the one hand that

$$\varepsilon(\omega_0)/\alpha_{\text{act}}(\omega_0) = \frac{\varepsilon_0'}{\alpha_0'} n^2(\omega_0)\omega_0^2 \qquad (4,2)$$

and on the other that with the abbreviations

$$\varepsilon_0 \equiv \varepsilon_0' \exp\{-\hbar\omega_0/2\theta^*\} I_\varepsilon(\omega - \omega_0) \approx \varepsilon_0' \exp\{-\hbar\omega_0/2\theta^*\} I_\varepsilon(0), \qquad (4,3)$$

$$\alpha_0 \equiv \alpha_0' \exp\{+\hbar\omega_0/2\theta^*\} I_\alpha(\omega - \omega_0) \approx \alpha_0' \exp\{+\hbar\omega_0/2\theta^*\} I_\alpha(0),$$

Eq. (4,1) is the same as the generalized STEPANOV's radiation law (1,1) which has been experimentally proved by KETSKEMÉTY et al. [3] for a small, but practically considerable frequency interval $(\omega_0 - \omega, \omega_0 + \omega)$. So BLOKHINTSEV's assumption [4], can be accepted whereby — whenever $\hbar(\omega - \omega_0)$ is negligible against E_0 — both integrands are slowly varying functions of ω, so far that more precisely

$$I_\varepsilon(\omega \mp \omega_0) \approx I_\alpha(\omega \pm \omega_0), \quad \text{if} \quad \hbar|\omega - \omega_0| \ll \overline{E(2\theta)} \qquad (4,4)$$

being $\overline{E(2\theta)}$ the mean value of the energy of the molecules at the temperature 2θ. This frequency interval approximately agrees with the domain, where the absorption and emission spectra are overlapped.

Owing to the relation (4,4), we have

$$[\alpha_{\text{act}}(\omega)/n(\omega)\omega]_{\omega \pm \omega_0} = \text{const} [\varepsilon(\omega)/n^3(\omega)\omega^3]_{\omega \pm \omega_0}. \qquad (4,5)$$

As to the experimental evidence in the frequency interval considered $n(\omega) \approx \text{const.}$, the relation (4,5) is essentially just the analytical from of LEVSHIN's law of mirror symmetry.

§ 5. Concluding remarks

One observes that in the suggested theory the assumption was very important that in the case of absorption one part of the energy absorbed and in the case of emission the remaining energy, respectively, rises the vibrational energy of the molecule. However, our reasoning — owing to Eq. (3,12) — can only be accepted, if $\varkappa > \frac{2}{3}$, namely, the sign of the temperature cannot be changed. Using the experimental values given by DOMBI et al [1], the temperatures calculated by Eqs. (3,12) and (3,9) are summarized in Table I. It has to be mentioned that DOMBI et al. looking for the parameters A and B have used a fixed value for B and determined the best value for A. In fact, we have, however, understood above, that the parameter A contains the temperature θ being the temperature of the solution which means that the parameter A must be fixed. Therefore, we recalculated their curves varying the parameter B in good agrement with their results. Table I contains the temperatures of our calculations.

It is, however, a real problem whether the temperature θ^* introduced would have an experimental evidence? Of course, θ^* cannot be directly checked experi-

mentally. However, if the preceding arguments may be accepted, the energy $\hbar(\omega - \omega_0)$ is converted into heat, and the relation

$$T^* - T = \frac{\gamma \hbar (\omega - \omega_0) N}{MC} \qquad (5,1)$$

could be obtained (where $N = 6{,}02486 \cdot 10^{23}$ (g·mol)$^{-1}$, $\gamma = 4{,}184 \cdot 10^{-8}$ cal/erg; M and C denote the molar weight and vibrational specific heat of the solute „gas", respectively) and the unknown specific heat can be determined. Indeed, having used the parameters determined by DOMBI et al. [1], we calculated T^* — characteristic of the coupling between the electrons and atomic vibrations of the molecules treated — and the specific heat. The results are summarized in Table I being in good agreement with the data given by N. A. BORISSEVICH [9] and with the estimations of L. KOZMA, L. SZALAY and J. HEVESI [10].

Table I

	T	T*	C	τ	T_f^*	τ^*
	°K	°K	$\dfrac{\text{cal}}{\text{degree·g}}$	10^{-9} s	°K	10^{-9} s
Fluorescein	298,1	377,7	0,323	5,05	331	8,55
Rhodamine B	298,1	407,2	0,033	5,6	332,6	6,89
Trypaflavine	298,1	396,2	0,186	4,0	325,6	4,70

As a further checking the following consideration may be useful. Since the system of excited molecules as a component-system of temperature θ^* is in thermal interaction with the component-system of the solvent molecules of temperature $\theta < \theta^*$, applying DE GROOT's considerations [11] we have

$$\frac{d}{dt} \Delta T = -\frac{1}{\tau^*} \Delta T \qquad (\Delta T \equiv T^* - T) \qquad (5,2)$$

τ^* being the relaxation time of the interaction process. This means that

$$(5,3) \qquad \Delta T(\tau) = \Delta T(0) \exp \{ -\tau/\tau^* \},$$

where $\Delta T(0)$ and $\Delta T(\tau)$ denote the temperature difference of the component-system $t = \tau$ (i. e. at the moment of emission), respectively. We have calculated T^* at the moment of absorption, so $\Delta T(0)$ is a known difference of temperature, therefore using the fluorimetrically measured [12] values of τ and $\Delta T(\tau) = T_f^* - T$, the relaxation time can be calculated. The results summarized in Table I. are in good agreement both with the dielectric relaxation time and the estimations of KOZMA et al [10]. The similar order of magnitude of the dielectric relaxation time and that of introduced in Eq. (5,3) seems to be very probable, since both processes are governed by weak thermal interaction.

* * *

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ПРИМЕЧАНИЯ К ТЕОРИИ СПЕКТРОВ АБСОРБЦИИ И ЭМИССИИ ФЛУОРЕСЦЕНТНЫХ МОЛЕКУЛ

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Качественно имея в виду корреляцию электронов и атомных колебаний флуоресцентных молекул предполагается, что в случае абсорбции света часть абсорбированной энергии, $\hbar(\omega - \omega_0)$, и в случае лучевого перехода между основным и возбужденным положением, остаточная энергия, $\hbar(\omega - \omega_0)$, превращается в тепло, так как $\hbar\omega_0$ является разницей энергии между чистыми электронными положениями и $\hbar\omega$ является энергией фотона, играющего роль в процессе абсорбции или эмиссии. Таким образом температура молекулы увеличивается относительно той температуры, которая сформировалась в термическом равновесии в начале процесса абсорбции и эмиссии. На основе этого естественного предположения можно обобщить теорию *Блохинцева*, относящуюся к спектрам абсорбции и эмиссии, из расчета корреляционной флуктуации во время перехода, и вывести для спектра абсорбции и эмиссии аналитическое выражение [1], экспериментально определенное *Домби* и его сотрудниками. На основе выведенных спектров получается закон зеркальной симметрии по *Левшину* и обобщенный лучевой закон по *Степанову*. Наконец, вычисляется удельная теплота колебаний, а также и релаксационное время термического взаимодействия, происходящего между флуоресцентными молекулами и молекулами растворителя, причем получается хорошее соответствие с прежними оценками.