



ON THE SHAPES OF BANDS OF LIGHT ABSORPTION AND EMISSION BY IMPURITIES

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The band shapes for the light absorption and emission by impurities and their variation with a change in temperature and the nature of a solvent are investigated. The question about the limits of validity of the “mirror symmetry” law is considered. The average radiation lifetime of an impurity in the excited state is calculated.

1. Light Absorption and Emission by Impurities Without Excitation of Their Local Vibration Levels. Shapes of Bands of Absorption and Emission

The previous work [2] presents the relations defining the intensities of lines of light absorption and emission by impurities for the transitions $l_1[n_s](0)\{0\} \rightarrow l_0[n'_s](0)\{1_\sigma\}$, $l_0[n_s](0)\{N_\sigma\} \rightarrow l_1[n'_s](0)\{N_\sigma - 1\}$. But these lines turned out infinitely narrow because the expression for the transition probability which was used by us in calculations of the intensity was deduced by solving the equations of perturbation theory for the time t small relative to the lifetime of the system in an excited state (only for those t , the transition probability is proportional to the time). The bandwidth for the absorption and emission by an impurity is obtained only due to the consideration of vibrations of the solvent lattice. In order to determine the shape of bands of absorption and emission by impurities with regard for the natural linewidth corresponding to the transition $l_1[n_s](0)\{N_\sigma\} \rightarrow l'_1[n'_s](0)\{N_\sigma\}$, it is necessary to find a solution of equations of perturbation theory which should be correct for arbitrary t . Here, we will use the Weisskopf–Wigner method [3] which was developed for the determination of the emission band shape for free atoms.

Let us expand the wave function of the “impurity + solvent + emission field” system as a series in the wave

functions of the stationary states of this system:

$$\Psi = \sum_{l\{n_s\}\{v_\tau\}\{N_\sigma\}} b_{l(n_s)(v_\tau)\{N_\sigma\}} \Psi_{l(n_s)(v_\tau)\{N_\sigma\}}. \quad (1.1)$$

Here, $\Psi_{l(n_s)(v_\tau)\{N_\sigma\}}$ is defined by Eq. (2.12) given in [2]. Let us substitute relation (1.1) in the wave equation¹ $ih \frac{\partial \Psi}{\partial t} = (H_0 + H_p + H')\Psi$, multiply the obtained expression by $\Psi_{l'(n'_s)(v'_\tau)\{N'_\sigma\}}^*$ from the left, and integrate it over all space, by taking $d\tau = dx dr d\xi dg$. Then we get

$$ih b_{l'(n'_s)(v'_\tau)\{N'_\sigma\}} = \sum_{l\{n_s\}\{v_\tau\}\{N_\sigma\}} (l'(n'_s)(v'_\tau)\{N'_\sigma\} \times$$

$$\times |\hat{H}'|l(n_s)(v_\tau)\{N_\sigma\} b_{l(n_s)(v_\tau)\{N_\sigma\}} \times$$

$$\times e^{\frac{it}{\hbar}[E_{l'(n'_s)(v'_\tau)\{N'_\sigma\}} - E_{l(n_s)(v_\tau)\{N_\sigma\}}]}.$$

Using this formula, we can calculate the transition probability of the system from one state to the others.

For the transition $l_1(n_s)(0)\{0\} \rightarrow l_0(n'_s)(0)\{1_\sigma\}$, the equation for the probability amplitudes takes the form

$$ih \dot{b}_{l_0(n'_s)(0)\{1_\sigma\}} = \prod_{\tau} G_{00}^{l_0 l_1} (0|\hat{H}'|1) \times \\ \times e^{i[\nu_\sigma - \Omega + \sum_s \omega_s^{l_0}(n'_s - n_s)]t} b_{l_1(n_s)(0)\{0\}}, \quad (1.2a)$$

$$ih \dot{b}_{l_1(n_s)(0)\{0\}} = \sum_{\{n'_s\}\sigma} \prod_{\tau} G_{00}^{l_1 l_0} (1|\hat{H}'|0) \times \\ \times e^{i[\Omega - \nu_\sigma + \sum_s \omega_s^{l_0}(n_s - n'_s)]t} b_{l_0(n'_s)(0)\{1_\sigma\}}, \quad (1.2b)$$

where Ω is determined² from Eq. (3.3b) [2], $(0|\hat{H}'|1) = (l_0(n'_s)\{1_\sigma\}|\hat{H}'|l_1(n_s)\{0\})$, and $(1|\hat{H}'|0)$ is conjugate to it.

¹Here and below, we retain the notations of work [2].

²For the sake of simplicity here and below, we drop the indices near Ω .

We seek for the solution of system (1.2) in the form

$$b_{l_1}(n_s)(0)\{0\} = b_{l_1} = e^{-\Gamma t}. \quad (1.3)$$

Substituting relation (1.3) into (1.2a), we have

$$b_{l_0}(n'_s)(0)\{1_\sigma\} = \dot{b}_{l_0} = \prod_{\tau} G_{00}^{l_0 l_1} \frac{0|\hat{H}'|1}{ih} \times \\ \times \exp\left\{it\left[\nu_\sigma - \Omega + \sum_s \omega_s^{l_0}(n'_s - n_s)\right] - \Gamma t\right\}.$$

At $\Gamma t \gg 1$, this yields

$$|b_{l_0}|^2 = G \frac{|\hat{H}'|^2}{h^2} \prod_s |M_{n'_s n_s}^{l_0 l_1}|^2 \times \\ \times \frac{1}{[\nu_\sigma + \sum_s \omega_s^{l_0}(n'_s - n_s) - \Omega]^2 + \Gamma^2}, \quad (1.4)$$

where $|H'| = |(l_0\{1_\sigma\}|\hat{H}'|l_1\{0\})|^2$, $G = \prod_{\tau} G_{00}^{l_0 l_1}$. To get the total transition probability, it is necessary to summarize relation (1.4) over all final states $\{n'_s\}$ and to average over all initial ones. Then we obtain

$$W^{jr} = G \frac{|\hat{H}'|^2}{h^2} \overline{\sum_{\{n'_s\}} \prod_s |M_{n'_s n_s}^{l_0 l_1}|^2} \times \\ \times \frac{1}{[\nu_\sigma - \Omega + \sum_s \omega_s^{l_0}(n'_s - n_s)]^2 + \Gamma^2}.$$

This expression coincides to within coefficients with that for $S(\omega)$, which was obtained earlier in [4]. We will calculate it, by using the δ -function.

Since

$$\int_{-\infty}^{\infty} f(\eta)\delta(\eta - a)d\eta = f(a),$$

we have

$$S(\nu) = \overline{\sum_{\{n_s\}} \prod_s |M_{n'_s n_s}^{l_0 l_1}|^2} \times \\ \times \frac{1}{[\nu_\sigma - \Omega + \sum_s \omega_s^{l_0}(n'_s - n_s)]^2 + \Gamma^2} =$$

$$= \int_{-\infty}^{\infty} \overline{\sum_{\{n'_s\}} \prod_s |M_{n'_s n_s}^{l_0 l_1}|^2} \frac{1}{(\nu_\sigma - \Omega + \eta)^2 + \Gamma^2} \times \\ \times \delta\left(\eta - \sum_s \omega_s^{l_0}(n'_s - n_s)\right) d\eta.$$

On the other hand,

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\mu x) d\mu.$$

Therefore,

$$S(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\eta \int_{-\infty}^{\infty} \frac{\exp\{i\mu\eta + g(\mu)\}}{(\nu - \Omega + \eta)^2 + \Gamma^2} d\mu, \quad (1.5)$$

where

$$g(\mu) = \frac{1}{2} \sum_s (\xi_{sl_0} - \xi_{sl_1})^2 [\bar{n}_s e^{i\mu\omega_s^{l_0}} + \\ + (\bar{n}_s + 1)e^{-i\mu\omega_s^{l_0}} - (2\bar{n}_s + 1)], \quad (1.6)$$

and $\bar{n}_s = \left\{ \exp\left(\frac{\hbar\omega_s^{l_1}}{kT}\right) - 1 \right\}^{-1}$ is the average number of phonons in the state s .

Using now the theory of residues, we integrate (1.5) over η . As a result, we get

$$S(\nu) = \frac{1}{\Gamma} \operatorname{Re} \int_0^{\infty} \exp\{i\mu(\Omega - \nu) - \mu\Gamma + g(\mu)\} d\mu. \quad (1.7)$$

Just the last expression defines the emission band shape of impurities.

In the general case, to integrate Eq.(1.7) is not possible. Therefore, we will consider only the limit cases. To this end, we write the expression for the function $g(\mu)$ in more details:

$$g(\mu) = g_0 + \sum_s (b_s + c_s) \cos \mu\omega_s^{l_0} + i \sum_s (b_s - c_s) \sin \mu\omega_s^{l_0}. \quad (1.8)$$

Here,

$$b_s = \frac{\bar{n}_s}{2} (\xi_{sl_0} - \xi_{sl_1})^2, \quad c_s = \frac{\bar{n}_s + 1}{2} (\xi_{sl_0} - \xi_{sl_1})^2,$$

$$g_0 = \sum_s (b_s + c_s).$$

Then relation (1.7) takes the form

$$S(\nu) = \frac{e^{-g_0}}{\Gamma} \operatorname{Re} \int_0^{\infty} \exp\{i\mu(\Omega - \nu) - \mu\Gamma +$$

$$+ \sum_s (b_s + c_s) \cos \mu\omega_s^{l_0} + i \sum_s (b_s - c_s) \sin \mu\omega_s^{l_0}\} d\mu. \quad (1.9)$$

In the limit case where, under excitation, impurities are in the equilibrium and the positions of solvent atoms are not changed ($\xi_{sl_0} - \xi_{sl_1} = 0$), the function $g(\mu) \equiv 0$. Then the emission curve shape is defined by the expression

$$W^{jr} = G \frac{|\hat{H}'|^2}{h^2} \frac{1}{(\Omega - \nu)^2 + \Gamma^2}.$$

This implies that the shape of the emission band of impurities coincides with that of the emission band of a free molecule; only a shift of the maximum of this band occurs on the frequency scale. The magnitude of this shift can be written down in the form

$$\Delta\Omega = \Omega + \sum_s \bar{n}_s (\omega_s^{l_1} - \omega_s^{l_0}) - \frac{E_{l_1} - E_{l_0}}{h}.$$

At $h\omega_s^{l_0} < kT$,

$$\Delta\Omega = \Omega + \frac{kT}{h} \sum_s \frac{\omega_s^{l_1} - \omega_s^{l_0}}{\omega_s^{l_1}} - \frac{E_{l_1} - E_{l_0}}{h},$$

so that the maximum of the emission band is shifted on the frequency scale with increase in the temperature. The shift direction depends on the sign of the difference $\sum_s (\omega_s^{l_1} - \omega_s^{l_0})/\omega_s^{l_1}$.

To calculate expression (1.9) in the case where $\xi_{sl_0} - \xi_{sl_1} \neq 0$, we expand the functions $\sin \mu\omega_s^{l_0}$ and $\cos \mu\omega_s^{l_0}$ in the series in powers of $\mu\omega_s^{l_0}$. Let $\omega_s^{l_0m}$ be the maximal value of the frequency $\omega_s^{l_0}$. We choose $\mu = \mu_0$ such that $\mu\omega_s^{l_0m} < 1$. Then, if the condition

$$\sum_s \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{sl_0} - \xi_{sl_1})^2 \left(\frac{\omega_s^{l_0}}{\omega_s^{l_0m}} \right)^2 > 1 \quad (1.10)$$

is fulfilled, integral (1.9) can be rewritten in the form

$$S(\nu) = \frac{1}{\Gamma} \operatorname{Re} \int_0^{\mu_0} \exp\{i\mu(\Omega - \nu) - \mu\Gamma +$$

$$+ \sum_s (b_s + c_s) \left[(-1)^s \frac{(\mu\omega_s^{l_0})^2}{2!} + \frac{(\mu\omega_s^{l_0})^4}{4!} + \dots \right] +$$

$$+ i \sum_s (b_s - c_s) \left[\frac{(\mu\omega_s^{l_0})}{1!} - \frac{(\mu\omega_s^{l_0})^3}{3!} + \dots \right] \} d\mu.$$

Limiting ourselves by only the first terms of the expansion of $\sin \mu\omega_s^{l_0}$ and $\cos \mu\omega_s^{l_0}$, we obtain

$$S(\nu) = \frac{1}{\Gamma} \operatorname{Re} \int_{-\infty}^{\infty} \exp\{i\mu(\Omega - \nu - A_0) - \mu\Gamma - \mu^2 B_0^2\} d\mu,$$

where

$$A_0 = \frac{1}{2} \sum_s \omega_s^{l_0} (\xi_{sl_0} - \xi_{sl_1})^2,$$

$$B_0^2 = \frac{1}{2} \sum_s (\omega_s^{l_0})^2 (\xi_{sl_0} - \xi_{sl_1})^2 \left(\bar{n}_s + \frac{1}{2} \right). \quad (1.11)$$

We introduce the following notation: $\mu\Gamma = y$, $x = \frac{(\Omega - \nu - A_0)}{\Gamma}$, $\zeta_0 = \frac{2B_0}{\Gamma}$. Then

$$W^{jr} = G \frac{|\hat{H}'|^2}{h^2 \Gamma^2} \psi(x\zeta_0), \quad (1.12)$$

where

$$\psi(x\zeta_0) = \frac{1}{\zeta_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \frac{\exp\left\{-\frac{(x-y)^2}{\zeta_0^2}\right\}}{1+y^2} dy. \quad (1.13)$$

Function (1.13) defines, as is known [5], the emission band shape in the gas, when the Doppler effect is taken into account. It has maximum at the point $x = 0$ (in our case, at $\nu = \Omega - A_0$) and, owing to relation (3.3b) [2], depends on the temperature. The behavior of the function $\psi(x\zeta_0)$ and, therefore, the band shape in this approximation were investigated in [4] in detail³.

Let us calculate now $S(\nu)$ with regard for the next terms of the expansions of $\sin \mu\omega_s^{l_0}$ and $\cos \mu\omega_s^{l_0}$. This calculation has practical meaning only for low temperatures, because, in this case, the term $\mu^2 B_0^2$ has the same order as the term $\mu^3 C_0 = \frac{\mu^3}{2 \cdot 3!} \sum_s (\omega_s^{l_0})^3 (\xi_{sl_0} -$

³In [4], only the absorption band shape was investigated. The problem of emission was not considered in that work at all. But, because the analytical expressions for the shapes of absorption and emission bands coincide, all the conclusions in [4] can be applied to the luminescence as well.

$\xi_{sl_1})^2$. So, for a more precise approximation of the integrand, it is necessary to consider orders in μ higher than the quadratic one.

Accounting the terms up to the fifth order in μ , we get

$$S(\nu) = \frac{1}{\Gamma} \operatorname{Re} \int_0^{\mu_0} \exp\{i\mu(\Omega - \nu - A_0) - \mu\Gamma - \mu^2 B_0^2 +$$

$$+ iC_0\mu^3 + \mu^4 D_0 - i\mu^5 E_0\} d\mu.$$

Here,

$$D_0 = \frac{1}{4!} \sum_s (\omega_s^{l_0})^4 \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{sl_0} - \xi_{sl_1})^2,$$

$$E_0 = \frac{1}{2 \cdot 5!} \sum_s (\omega_s^{l_0})^5 (\xi_{sl_0} - \xi_{sl_1})^2.$$

We now expand the integrand $\exp(i\mu^3 C_0 + \mu^4 D_0 - i\mu^5 E_0)$ in a series, by limiting ourselves only by the first terms of the expansion. Then the above-presented expression takes the form

$$S(\nu) = \frac{1}{\Gamma} \operatorname{Re} \left[\int_0^{\infty} e^{i\mu\alpha - \mu\Gamma - \mu^2 B_0^2} d\mu + \right. \\ \left. + iC_0 \int_0^{m_0} \mu^3 e^{i\mu\alpha - \mu\Gamma - \mu^2 B_0^2} d\mu + \right. \\ \left. + D_0 \int_0^{\mu_0} \mu^4 e^{i\mu\alpha - \mu\Gamma - \mu^2 B_0^2} d\mu - iE_0 \int_0^{\mu_0} \mu^5 e^{i\mu\alpha - \mu\Gamma - \mu^2 B_0^2} d\mu \right], \quad (1.14)$$

where

$$\alpha = \Omega - \nu - A_0.$$

The first integral in the square brackets can be calculated immediately. Supposing that $2B_0/\Gamma \gg 1$, we find

$$I_1 = \operatorname{Re} \int_0^{\infty} e^{i\mu\alpha - \mu\Gamma - \mu^2 B_0^2} d\mu = \frac{\sqrt{\pi}}{2B_0} e^{-\frac{\alpha^2}{4B_0^2}}.$$

For the approximate calculation of the rest integrals, we use the saddle-point technique [6].

The saddle-points are determined, as is known, from the condition of the extremum of a function in the exponent. In our case, we use the condition $f'(z) = \alpha + i\Gamma + 2B_0^2 z = 0$, where $z = i\mu$. This yields $z_0 \approx -\frac{\alpha}{2B_0^2}$.

Further, let us expand the function $f(z) = u + iv$ in a Taylor series in the vicinity of the extremal point

$$f(z) = f(z_0) + \frac{1}{2} f''(z_0)(z - z_0)^2 = f(z_0) + B_0^2 \rho^2 e^{2i\varphi},$$

where $z - z_0 = \rho e^{i\varphi}$, and choose the path of integration so that it passes through the saddle point in the direction, for which the expression $f''(z_0)(z_0 - z)^2$ is real and negative. That is, $\varphi = \pi/2$ in our case. It is easy to show that this direction coincides with that of one of the asymptotes for the set of hyperbolas $v = \text{const}$. Moreover, the function $u(xy)$ has the maximum for such a choice of the product sign. Then, from formula (1.14), we get

$$I_2 = \operatorname{Re} iC_0 \int_0^{\mu_0} \mu^3 \exp(i\mu\alpha - \mu\Gamma - \mu^2 B_0^2) d\mu =$$

$$= -C_0 \frac{\sqrt{\pi}}{2B_0} z_0^3 e^{f(z_0)} = \frac{\sqrt{\pi}}{2B_0} \frac{C_0 \alpha^3}{4B_0^6} e^{-\frac{\alpha^2}{4B_0^2}},$$

$$I_3 = \operatorname{Re} D_0 \int_0^{\mu_0} \mu^4 \exp(i\mu\alpha - \mu\Gamma - \mu^2 B_0^2) d\mu =$$

$$= \frac{\sqrt{\pi}}{2B_0} \frac{D_0 \alpha^4}{8B_0^8} e^{-\frac{\alpha^2}{4B_0^2}},$$

$$I_4 = -\operatorname{Re} iE_0 \int_0^{\mu_0} \mu^5 \exp(i\mu\alpha - \mu\Gamma - \mu^2 B_0^2) d\mu =$$

$$= \frac{\sqrt{\pi}}{2B_0} \frac{E_0 \alpha^5}{16B_0^{10}} e^{-\frac{\alpha^2}{4B_0^2}}.$$

Thus,

$$S(\nu) = \frac{\sqrt{\pi}}{2B_0\Gamma} e^{-\frac{\alpha^2}{4B_0^2}} \left[1 + \frac{C_0 \alpha^3}{4B_0^6} + \frac{D_0 \alpha^4}{8B_0^8} + \frac{E_0 \alpha^5}{16B_0^{10}} \right]. \quad (1.15)$$

It follows from this formula that the emission band is asymmetric relative to the line passing the maximum perpendicularly to the $O\nu$ axis. In this case, the curve falls more slowly on the left-hand side of the maximum than on the right-hand side.

In the case where condition (1.10) is not satisfied⁴, we can rewrite expression (1.7) in the form

$$S(\nu) = \frac{e^{-g_0}}{\Gamma} \text{Re} \int_0^\infty \sum_{\gamma\gamma_1} J_{\gamma\gamma_1}(\mu) \exp\{i\mu(\Omega - \nu + i\Gamma)\} d\mu, \quad (1.16)$$

where

$$J_{\gamma\gamma_1} = (\gamma!\gamma_1!)^{-1} \left(\sum_s b_s e^{i\mu\omega_s^{l_0}} \right)^\gamma \left(\sum_s c_s e^{-i\mu\omega_s^{l_0}} \right)^{\gamma_1}. \quad (1.17)$$

If the electron transition interacts only with vibrations of the s' type, and $\omega_s^{l_0} = \omega_0^{l_0}$, then

$$J_{\gamma\gamma_1} = \frac{b^\gamma c^{\gamma_1}}{\gamma!\gamma_1!} \exp\{i\mu(\gamma - \gamma_1)\omega_0^{l_0}\}, \quad (1.18)$$

where

$$b^\gamma = \left(\sum_{s'} b_{s'} \right)^\gamma, \quad c^{\gamma_1} = \left(\sum_{s'} c_{s'} \right)^{\gamma_1} \quad (1.19)$$

(the summation is fulfilled over the indices s' which correspond to one of the branches with $\omega_{s'}^{l_0} = \omega_0^{l_0}$).

Substituting relation (1.18) into (1.16), we obtain

$$S(\nu) = e^{-g_0} \sum_{\gamma\gamma_1} \frac{b^\gamma c^{\gamma_1}}{\gamma!\gamma_1!} \{[\Omega + (\gamma - \gamma_1)\omega_0^{l_0} - \nu]^2 + \Gamma^2\}^{-1}.$$

If the electron transition interacts with the several types of vibrations s_1, s_2, \dots , and $\omega_{s_1}^{l_0} = \omega_1^{l_0}$, $\omega_{s_2}^{l_0} = \omega_2^{l_0}, \dots$, then

$$S(\nu) = e^{-g_0} \sum_{\gamma_1\gamma_2 \dots \gamma_1'\gamma_2' \dots} \frac{b_1^{\gamma_1} b_2^{\gamma_2} \dots c_1^{\gamma_1'} c_2^{\gamma_2'} \dots}{\gamma_1!\gamma_2! \dots \gamma_1'!\gamma_2'! \dots} \times$$

$$\times \left\{ \left[\Omega + \sum_i \omega_i^{l_0} (\gamma_i - \gamma_i') - \nu \right]^2 + \Gamma^2 \right\}^{-1}.$$

⁴If condition (1.10) is satisfied, one says that there is the strong coupling of the electronic excitation with lattice vibrations; in the opposite case, the coupling is weak.

That is, the emission band consists of the sum of bands having the shape $1/(1+x^2)$ with the half-width equal to 2Γ for each of them. Under the interaction with acoustic vibrations, these bands are widened and, as a result, can form one continuous band, whose shape is defined by relations (1.12) and (1.15).

Having an analytical expression for the transition probability $l_1[n_s](0)\{0\} \rightarrow l_0\{n_s'\}(0)\{1_\sigma\}$, we can write the expression for the energy which is irradiated by the solvent atoms per unit time interval in the direction $d\Omega$ with a definite polarization

$$J_1^{jr} d\Omega = N d\Omega \sum_1^{N_{l_1}} \int J^{jr}(\nu) d\nu, \quad (1.20)$$

where N is the number of transitions of the type under consideration per unit time interval, $\sum_1^{N_{l_1}}$ includes the summation over all molecules being in the state l_1 . In the case of the arbitrary orientations of transition dipole moments, when the averaging over Θ will hold true, the sum gives simply the factor N_{l_1} .

But the same energy is given by the expression [2]

$$J_1^{jr} d\Omega = \sum_1^{N_{l_1}} \sum_p J_{1p}^{jr}(\nu_{p1}) d\Omega. \quad (1.21)$$

Therefore, by equating (1.20) with (1.21), we obtain

$$2\Gamma = N. \quad (1.22)$$

Thus, the energy which is irradiated by the solvent atoms per unit time interval in the frequency interval $\nu, \nu + d\nu$ of a given polarization in the direction $d\Omega$ can be expressed as

$$J_1^{jr}(\nu) d\nu d\Omega = \sum_1^{N_{l_1}} G \frac{2\nu |\hat{H}'|^2}{h} \rho_\kappa dk d\Omega \times \text{Re} \int_0^\infty \exp\{i\mu(\Omega - \nu) - \mu\Gamma + g(\mu)\} d\mu. \quad (1.23)$$

In particular, for the propagation direction which coincides with one of the $(Oxyz)$ axes of the Cauchy ellipsoid and for the Ox_i polarization, we get

$$J_1^{x_i r}(\nu) d\nu d\Omega = 2N_{l_1} n_{x_i}(\nu) \nu^4 L \cos^2 \alpha_i d\nu d\Omega \times \text{Re} \int_0^\infty \exp\{i\mu(\Omega - \nu) - \mu\Gamma + g(\mu)\} d\mu,$$

where $x_i = Ox, Oy, Oz$; $\alpha_i = \alpha_1, \alpha_2, \alpha_3$; $L = G \frac{e^2 \bar{x}^2}{(2\pi)^2 c^3} |(\mathbf{R})_{l_0 l_1}|^2$.

Using the above-obtained expressions, we can write now the expression for the energy which is absorbed by solvent atoms per unit time interval in the frequency interval $\nu, \nu + d\nu$ with the definite polarization

$$J_1^{j_a}(\nu) d\nu = \sum_1^{N_{l_0}} G \frac{2\nu |\hat{H}'|^2}{h} \rho_\kappa dk \times \\ \times \text{Re} \int_0^\infty \exp\{i\mu(\nu - \Omega) - \mu\Gamma + g'(\mu)\} d\mu,$$

where

$$g'(\mu) = \frac{1}{2} \sum_s (\xi_{sl_0} - \xi_{sl_1})^2 [\bar{n}_s e^{i\mu\omega_s^{l_1}} + \\ + (\bar{n}_s + 1) e^{-i\mu\omega_s^{l_1}} - (2\bar{n}_s + 1)]. \quad (1.24)$$

If the incident light propagates along one of the axes of the Cauchy ellipsoid, then the expression for the energy which absorbed per unit time interval in the frequency interval $\nu, \nu + d\nu$ takes the form

$$J_1^{x_i a}(\nu) d\nu = 2L \frac{(2\pi)^3 c^2 J_0(\nu) \nu}{h n_{x_i}(\nu)} \cos^2 \alpha_i \times \\ \times \text{Re} \int_0^\infty \exp\{i\mu(\nu - \Omega) - \mu\Gamma + g'(\mu)\} d\mu. \quad (1.25)$$

It is easy to show that both the ratio of the line intensities with the frequencies $\Omega - \omega_p^{l_0}$ and $\Omega + \omega_p^{l_1}$ and the total energy which absorbed per unit time interval, converge according to relations (3.22) and (3.21) in [1].

We will study the integral $S'(\nu) = \text{Re} \int_0^\infty d\mu e^{i\mu(\nu - \Omega) - \mu\Gamma + g'(\mu)}$, which enters relation (1.25) and defines the absorption band shape, in a similar manner as above. In this case, we have: (i) in the limiting case where the excitation of impurities is not accompanied by a change of the equilibrium positions of solvent atoms ($\xi_{sl_0} - \xi_{sl_1} = 0$),

$$S'(\nu) = \frac{\Gamma}{(\Omega - \nu)^2 + \Gamma^2};$$

(ii) in the case where $\xi_{sl_0} - \xi_{sl_1} \neq 0$, and condition (1.10) (with the change of $\omega_s^{l_0}$ by $\omega_s^{l_1}$) holds true,

$$S'(\nu) = \frac{1}{\Gamma} \psi(x\zeta_1), \quad (1.25a)$$

where $\psi(x\zeta_1)$ is defined by (1.13), $x = \frac{(\nu - \Omega - A_1)}{\Gamma}$, $\zeta_1 = \frac{2B_1}{\Gamma}$, $y = \mu\Gamma$, and

$$A_1 = \frac{1}{2} \sum_s \omega_s^{l_1} (\xi_{sl_0} - \xi_{sl_1})^2, \\ B_1^2 = \frac{1}{2} \sum_s (\omega_s^{l_1})^2 \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{sl_0} - \xi_{sl_1})^2. \quad (1.26a)$$

As was mentioned above, the function $\psi(x\zeta_1)$ has the maximum at the point $x = 0$, i.e. at the point $\nu = \Omega + A_1$ in the case of absorption. Because Ω depends on the temperature, the position of the absorption band maximum varies with change in the temperature. The direction of a shift is defined by the sign of the expression $\sum_s (\omega_s^{l_1} - \omega_s^{l_0})$. The distance between the maxima of the bands of absorption and emission is equal to $A_0 + A_1$. Moreover, because A_i ($i = 0; 1$) weakly depends on the temperature, this distance remains practically invariable in a quite broad temperature interval.

At $\zeta_1 \gg 1$ ($i = 0; 1$), the bands of absorption and emission have the Gauss shape, and their half-width can be presented as

$$\Delta\Omega_i = 2B_i \sqrt{\ln 2} = \\ \sqrt{2 \ln 2 \sum_s (\omega_s^{l_1})^2 \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{sl_0} - \xi_{sl_1})^2}. \quad (1.26)$$

At high temperatures where $h\omega_s^{l_i} < kT$ and $\bar{n}_s + 1/2 \simeq \frac{kT}{h\omega_s^{l_i}}$, we have

$$\Delta\Omega_i = \sqrt{A_i \frac{4 \ln 2}{h} kT}.$$

Accounting the terms up to the fifth order in μ in the expansion of $g'(\mu)$, we get

$$S'(\nu) = \frac{\sqrt{\pi}}{2B_1} \left[1 + \frac{C_1 \alpha^3}{4B_1^6} + \frac{D_1 \alpha^4}{8B_1^8} + \frac{E_1 \alpha^5}{16B_1^{10}} \right] e^{-\frac{\alpha^2}{4B_1^2}},$$

where

$$\alpha = \nu - \Omega - A_1, \quad C_1 = \frac{1}{2 \cdot 3!} \sum_s (\omega_s^{l_1})^3 (\xi_{sl_0} - \xi_{sl_1})^2,$$

$$D_1 = \frac{1}{4!} \sum_s (\omega_s^{l_1})^4 \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{sl_0} - \xi_{sl_1})^2,$$

$$E_1 = \frac{1}{2 \cdot 5!} \sum_s (\omega_s^{l_1})^5 (\xi_{sl_0} - \xi_{sl_1})^2.$$

This implies that the absorption band is asymmetric relative to the line passing through the maximum perpendicularly to the $O\nu$ axis. The decrease of the absorption coefficient to the long-wave side of the spectrum is stronger than that to the short-wave side. The asymmetric band shape for absorption was first obtained (to within ν^3) in work [7] for arbitrary impurities in an isotropic solvent.

(iii) If $\xi_{sl_0} - \xi_{sl_1} \neq 0$, but condition (1.10) does not hold, then the integral $S'(\nu)$ can be written in the form

$$S'(\nu) = \operatorname{Re} \int_0^\infty \sum_{\gamma, \gamma_1} J'_{\gamma\gamma_1}(\mu) \exp\{i\mu(\nu - \Omega) - \mu\Gamma\} d\mu,$$

where $J_{\gamma\gamma_1}$ is defined by (1.17), where $\omega_s^{l_0}$ should be changed by $\omega_s^{l_1}$.

In the case where the electron transition interacts only with vibrations of a single type (e.g., with the s -type vibrations) and $\omega_s^{l_1} = \omega_0^{l_1}$, the absorption band shape is determined by

$$S'(\nu) = e^{-g_0} \sum_{\gamma, \gamma_1} \frac{b^\gamma c^{\gamma_1}}{\gamma! \gamma_1!} \frac{1}{[\nu + (\gamma - \gamma_1)\omega_0^{l_1} - \Omega]^2 + \Gamma^2}.$$

The last expression can be easily generalized to the case where the electron transition interacts with vibrations of several types.

The results obtained above gives opportunity to make the following qualitative conclusions about the spectra of absorption and emission for solvents with small concentrations:

I. F o r a g i v e n d i s s o l v e d s u b s t a n c e :

(i) The band shape for absorption and emission depends on both the nature of a solvent and the temperature. In the case where the electron transition in the impurity is accompanied by a considerable displacement of the solvent atoms from equilibrium positions [condition (1.10) is satisfied starting with the $T = 0$, and $B_i \gg C_i (i = 0; 1)$], the bands of absorption and emission have the shape of absorption curves for free molecules, when the Doppler effect is taken into account (analytically, they are defined by the function $\psi(x\zeta_1)$); at $\zeta \gg 1$, they have the Gauss shape.

If the condition $B_i \gg C_i$ is not satisfied, then the bands of absorption and emission are asymmetric relative to the line passing through the maximum perpendicularly to the $O\nu$ axis. With increase in the temperature, the quantities B_i grow, and, above a certain value of T , the condition $B_i \gg C_i$ is

satisfied. Then the asymmetry of the curves disappears, and the band shape is defined by the function $\psi(x\zeta)$.

If the electron transition in the impurity is accompanied with minor displacements of solvent atoms from an equilibrium position [condition (1.10) is not satisfied], then the bands of absorption and emission are the collections of lines like those of atom spectra. The half-width of each line is equal to 2Γ , and the line shape is defined by the expression $1/(1+x^2)$. The interaction with acoustic phonons results in the broadening of these lines. As the temperature grows, each of the separate lines forming the band is widened. Starting with the temperature at which condition (1.20) is satisfied, the separate lines of the band overlap one another. Moreover, in the spectrum appears the continuous band which is asymmetric relative to the line perpendicular to the frequency axis. The further increase in the temperature lead to the disappearance of the asymmetry, and then the band shape is defined by the function $\psi(x\zeta)$.

(ii) The positions of the maxima of absorption and emission curves depend on the type of a solvent. The greater the displacements of the solvent atoms from equilibrium positions on the electron transitions in impurities, the greater the distance between the maxima of the curves.

(iii) The bandwidth is varied with changing the solvent type. The greater the displacements of the solvent atoms from equilibrium positions on the electron transition, the greater the width.

II. F o r a g i v e n s o l v e n t :

(i) With change in the temperature, the distance between the maxima of the curves of emission and absorption remains practically invariable in a quite broad temperature interval; the variation occurs only due to the slight dependence of the quantities ξ_{sl_0} and ξ_{sl_1} on T .

(ii) Because the areas limited by the curves corresponding to the emission and absorption do not depend practically on the temperature⁵, the heights of the maxima of these curves decrease and the half-widths of the bands increase, as the temperature grows. If the band shape is that of the Gauss curve of errors, then its

⁵The independence of the luminescence yield on the temperature is obtained under the assumption that the nonradiative transitions do not occur, or one can neglect them. Taking the nonradiative transitions into account shows that the yield depends on the temperature, because their probability varies with the temperature [8].

half-width is defined by the formula

$$\Delta\Omega_i = C_i \sqrt{\sum_s \left[\frac{1}{\exp\left(\frac{h\omega_s^{l_i}}{kT}\right) - 1} + \frac{1}{2} \right]}, \quad (1.27)$$

which has the same form as the expressions obtained earlier in works [9] and [4]. Their difference consists in that the frequencies ω_s depend on the electronic state of an impurity l_i . Therefore, the half-widths of the bands and their temperature dependence are generally different for absorption and emission.

Thus, taking the dependence of the frequencies of vibrations of a lattice on the electron state of an impurity into account shows that the mirror-symmetry law [1] holds only approximately or is not fulfilled at all.

In the case where the electronic transition interacts only with optical vibrations of the lattice, whose frequencies are of the order of 10^{14} , the band half-width remains practically constant up to room temperature. Let us now consider the interaction with acoustic phonons, whose frequencies vary in a rather broad interval. In this case, with increase in the temperature, the half-width grows at first slowly. But, starting from the temperature, for which $h\omega_s^{l_i} < kT$, it will grow as the square root of the temperature.

(iii) The positions of the maxima of the curves for absorption and emission on the frequency scale change, as the temperature varies. For Gauss curves, the direction of a shift is determined by the sign of the expression $\sum_s (\omega_s^{l_1} - \omega_s^{l_0})$.

2. Calculation of the Average Radiation Lifetime of an Impurity in the Excited State

The above-developed mathematical apparatus allows us to calculate the value of Γ which is, according to (1.3), reciprocal to the lifetime (with respect to the emission) of an impurity in the excited state. For this purpose, we substitute (1.3) and b_{l_0} into (1.2b), which gives

$$ih\Gamma = \sum_{\sigma\{n'_s\}} G \frac{|\hat{H}'|^2}{h} \prod_s |M_{n'_s n_s}^{l_0 l_1}|^2 \times \frac{\exp\left\{it\left[\Omega + \sum_s \omega_s^{l_0}(n_s - n'_s) - \nu_\sigma\right] + \Gamma t\right\} - 1}{\left[\Omega + \sum_s \omega_s^{l_0}(n_s - n'_s) - \nu_\sigma\right] - i\Gamma}.$$

In view of the properties of the δ -function, the last relation can be represented as

$$i\Gamma = G \sum_\sigma \frac{|\hat{H}'|^2}{2\pi h^2} \int_{-\infty}^{\infty} d\eta \times \frac{\exp\{it(\Omega - \nu_\sigma + \eta) + \Gamma t\} - 1}{(\Omega - \nu_\sigma + \eta) - i\Gamma} \int_{-\infty}^{\infty} e^{i\mu\eta + g''(\mu)} d\mu,$$

where

$$g''(\mu) = \frac{1}{2} \sum_s [(\bar{n}_s + 1)e^{i\mu\omega_s^{l_0}} + \bar{n}_s e^{-i\mu\omega_s^{l_0}} - (2\bar{n}_s + 1)](\xi_{sl_0} - \xi_{sl_1})^2.$$

In the limiting case where the equilibrium positions of the solvent atoms are not changed during the excitation of impurities [$\xi_{sl_0} - \xi_{sl_1} = 0$ and $g''(\mu) = 0$], we obtain

$$i\Gamma = G \sum_\sigma \frac{|\hat{H}'|^2}{h^2} \frac{\exp\{it(\Omega - \nu_\sigma) + \Gamma t\} - 1}{(\Omega - \nu_\sigma) - i\Gamma}.$$

In this relation, we replace the summation over σ by the integration over $d\nu_\sigma$, which yields

$$\Gamma = G \frac{\pi}{h^2} \rho_{\text{vac}}(\Omega) \int \bar{n}_{\lambda_j}^3 |\hat{H}'|^2 d\Omega, \quad (2.1)$$

where $\int d\Omega$ means the integration over all the light propagation directions, and the summation over both the polarization directions should be performed. It follows from this formula that, in the case of rigidly fixed atoms of a solvent, the value of Γ for an impurity molecule differs from that for a free molecule by the emission frequency (which is involved in the matrix element $|\hat{H}'|$), the emission intensity, and the refraction index. If the solvent is isotropic, then $n_{\lambda_j} = \frac{1}{\alpha_{\lambda_j}}$ and $\alpha_{\lambda_j} = 1/\sqrt{\varepsilon}$. Therefore,

$$\Gamma = G \frac{\pi}{h^2} \rho_{\text{vac}}(\Omega) \int \varepsilon^{3/2} |\hat{H}'|^2 d\Omega.$$

For $\varepsilon = 1$, we have $\Omega = \nu_{l_1 l_0}$, and the above-obtained formula is identical to that for a free molecule.

If $\xi_{sl_0} - \xi_{sl_1} \neq 0$, and condition (1.10) is satisfied, the expression for Γ with regard for only the terms quadratic in μ in the expansion of $g''(\mu)$ can be rewritten as

$$\Gamma = -iG \sum_\sigma \frac{|\hat{H}'|^2}{2\pi h^2} \int_{-\infty}^{\infty} d\eta \times$$

$$\times \int_{-\infty}^{\infty} \frac{\exp\{it(\Omega - \nu_{\sigma} + \eta) + \Gamma t\} - 1}{(\Omega - \nu_{\sigma} + \eta) - i\Gamma} e^{i\mu\eta + i\mu A_0 - \mu^2 B_0^2} d\mu.$$

Integrating over μ , we get

$$\Gamma = -iG \sum_{\sigma} \frac{|\hat{H}'|^2}{2\sqrt{\pi}h^2 B_0} \times \int_{-\infty}^{\infty} \frac{\exp\{it(\Omega - \nu_{\sigma} + \eta) + \Gamma t\} - 1}{(\Omega - \nu_{\sigma} + \eta) - i\Gamma} e^{-\frac{(\eta + A_0)^2}{4B_0^2}} d\eta.$$

We now introduce the notation: $\frac{\eta + A_0}{2B_0} = x$. Then

$$\Gamma = -iG \sum_{\sigma} \frac{|\hat{H}'|^2}{\sqrt{\pi}h^2} \times \int_{-\infty}^{\infty} \frac{\exp\{it(\Omega - \nu + 2B_0x - A_0) + \Gamma t\} - 1}{(\Omega - \nu + 2B_0x - A_0) - i\Gamma} e^{-x^2} dx.$$

In the last relation, let us pass from the summation over σ to the integration over $d\nu_{\sigma}$. We get

$$\Gamma = \frac{\sqrt{\pi}}{h^2} G \times \sum_{j=1}^2 \int_{4\pi} \int_{-\infty}^{\infty} \bar{n}_{\lambda_j}^3 |\hat{H}'|^2 d\Omega \frac{[(\Omega - A_0) + 2B_0x]^2}{(2\pi c)^3} e^{-x^2} dx.$$

While calculating this expression, it is necessary to take into account that the matrix element $|\hat{H}'|^2$ is proportional to the $\Omega - A_0 + 2B_0x$. Therefore, by performing the integration over dx , we finally obtain

$$\Gamma = \frac{\pi}{h^2} G \left[\rho_{\text{vac}}(\Omega - A_0) + \frac{6B_0^2}{(2\pi c)^3} \right] \times \sum_{j=1}^2 \int \bar{n}_{j\lambda}^3 |H'(\Omega - A_0)|^2 d\Omega, \quad (2.2)$$

where $\bar{n}_{\lambda_j}^3$ is the average refraction coefficient $n_j^3(\Omega - A_0 + 2B_0x)$.

It follows from formula (2.2) that, in the case of the transitions accompanied by considerable displacements of the solving atoms from equilibrium positions, the lifetime of an impurity molecule in the excited state depends significantly on the nature of a solvent. Moreover, this dependence reveals itself not only

through the refraction index, but also through the quantities A_0 and B_0^2 which are defined by (1.11).

The quantity A_0 , as was already indicated, does not depends practically on the temperature. Therefore, using Eq.(2.2) and neglecting the difference $\omega_s^{l_0} - \omega_s^{l_1}$, we find

$$\Gamma = C_1 + C_2 \sum_s (\omega_s^{l_0})^2 \left[\frac{1}{\exp\left(\frac{h\omega_s^{l_0}}{kT}\right) - 1} + \frac{1}{2} \right], \quad (2.3)$$

where C_1 and C_2 are practically independent of the temperature.

Let the electron transition interact only with optical vibrations of the solvent lattice, whose frequencies are of the order of 10^{14} . Then relation (2.3) implies that the radiation lifetime of an impurity molecule in the excited state remains practically invariable to room temperature. At high temperatures (when $h\omega_s^{l_0} < kT$), $\bar{n}_s + 1/2 \sim \frac{kT}{h\omega_s^{l_0}}$, and then

$$\Gamma = C_1 + C_2' T. \quad (2.4)$$

The last formula coincides with a semiempirical expression for $1/\tau$ which was obtained in work [10] for exciton bands.

Let now the electron transition interacts with acoustic vibrations, whose frequencies vary in a broad interval. In this case, the value of Γ firstly grows slowly with increase in the temperature. Further, starting from the temperature, for which $h\omega_s^{l_0} < kT$, Γ will increase in accordance with the linear law (2.4).

The above-presented formulae are in qualitative agreement with the experimental data [11–14].

The magnitude of Γ for an impurity molecule differs from Γ for a free molecule not only by factor \bar{n}_j^3 , but by the values of A_0 and B_0^2 as well, i.e. by the greater or lesser displacements of solvent atoms from equilibrium positions on a transition of the impurity molecule from one state to another one. For the majority of solvents, we may suppose apparently that $\Omega > A_0$ and $\Omega > B_0$ at room temperature, so that the difference will be insignificant. But the distinction can be considerable (one order or more) for those molecules and solvents, for which $\Omega < B_0$.

The relation for Γ can be related to the luminescence band half-width defined by (1.26). Indeed, $B_0 = \frac{\Delta\Omega_0}{2\ln 2}$; therefore, by substituting the last expression into (2.2), we get

$$\Gamma = \frac{\pi}{h^2} G \left[\rho_{\text{vac}}(\Omega - A_0) + \frac{6(\Delta\Omega_0)^2}{(2\pi c)^3 (2\ln 2)^2} \right] \times$$

$$\times \sum_{j=1}^2 \int \bar{n}_j^3 |\hat{H}'|^2 d\Omega. \quad (2.5)$$

This implies that the radiation lifetime of impurity molecules in the excited state decreases with increase of the band half-width.

It is worth to emphasize once more that all these conclusions remain true only provided that Γ is determined solely by emission, i.e., the radiationless transitions do not occur, or one can neglect them. As the temperature grows, one can expect the growth of radiationless transitions [8], then the results stated here stop be true.

In the case where $\xi_{sl_0} - \xi_{sl_1} \neq 0$ but condition (1.10) does not hold, the expression for Γ can be written as

$$\begin{aligned} \Gamma &= -iGe^{-g_0} \sum_{\sigma} \frac{|\hat{H}'|^2}{2\pi h^2} \int_{-\infty}^{\infty} d\eta \times \\ &\times \int_{-\infty}^{\infty} \frac{\exp\{it(\Omega - \nu_{\sigma} + \eta)\} - 1}{(\Omega - \nu_{\sigma} + \eta) - i\Gamma} e^{i\mu\eta} \sum_{\gamma, \gamma_1} J_{\gamma, \gamma_1}(\mu) d\mu, \end{aligned}$$

where

$$J_{\gamma, \gamma_1}(\mu) = (\gamma! \gamma_1!)^{-1} \left(\sum_s c_s e^{i\mu \omega_s^{l_0}} \right)^{\gamma} \left(\sum_s b_s e^{-i\mu \omega_s^{l_0}} \right)^{\gamma_1}.$$

If the electron transition interacts only with the s_1 -type vibrations, and $\omega_s^{l_0} = \omega_0^{l_0}$, then

$$J_{\gamma, \gamma_1}(\mu) = (\gamma! \gamma_1!)^{-1} c^{\gamma} b^{\gamma_1} \exp\{i\mu(\gamma - \gamma_1)\omega_0^{l_0}\},$$

where $b^{\gamma_1} = \left(\sum_{s_1} b_{s_1} \right)^{\gamma_1}$ and $c^{\gamma} = \left(\sum_{s_1} c_{s_1} \right)^{\gamma}$. Then the formula for Γ takes the form

$$\begin{aligned} i\Gamma &= Ge^{-g_0} \sum_{\gamma_1} \frac{b^{\gamma_1} c^{\gamma}}{\gamma! \gamma_1!} \times \\ &\times \sum_{\sigma} \frac{|\hat{H}'|^2}{h^2} \frac{\exp\{it[\Omega - \nu_{\sigma} + \omega_0^{l_0}(\gamma_1 - \gamma)] + \Gamma t\} - 1}{[\Omega + \omega_0^{l_0}(\gamma_1 - \gamma) - \nu_{\sigma}] - i\Gamma}. \end{aligned}$$

Passing from the summation over σ to the integration over $d\nu_{\sigma}$, we get

$$\begin{aligned} \Gamma &= G \frac{\pi e^{-g_0}}{h^2} \sum_{\gamma_1} \frac{b^{\gamma_1} c^{\gamma}}{\gamma! \gamma_1!} \times \\ &\times \rho_{\text{vac}}[\Omega + \omega_0^{l_0}(\gamma_1 - \gamma)] \sum_j \int \bar{n}_j^3 |\hat{H}'|^2 d\Omega. \end{aligned} \quad (2.6)$$

But if the electron transition interacts with several types of vibrations s', s'', \dots , and $\omega_s^{l_0} = \omega_1^{l_0}$, $\omega_{s''}^{l_0} = \omega_2^{l_0}$, then

$$\begin{aligned} \Gamma &= G \frac{\pi e^{-g_0}}{h^2} \sum_{\gamma_1 \gamma_2 \dots \gamma'_1 \gamma'_2} \frac{c_1^{\gamma_1} c_2^{\gamma_2} \dots b_1^{\gamma'_1} b_2^{\gamma'_2} \dots}{\gamma_1! \gamma_2! \dots \gamma'_1! \gamma'_2!} \times \\ &\times \rho_{\text{vac}} \left[\Omega + \sum_i \omega_i^{l_0} (\gamma_i - \gamma'_i) \right] \sum_i \int \bar{n}_j^3 |\hat{H}'|^2 d\Omega. \end{aligned} \quad (2.7)$$

It follows from (2.6) and (2.7) that, with decrease in the temperature, the average radiation lifetime of impurity molecules in the excited state decreases. At that, the temperature behavior of the quantity $1/\tau$ is defined by the relation

$$\frac{1}{\tau} = C_3 e^{-g(\tau)}, \quad (2.8)$$

where

$$g(T) = \sum_s \left[\frac{1}{\exp\left(\frac{h\omega_s^{l_0}}{kT}\right) - 1} + \frac{1}{2} \right] (\xi_{sl_0} - \xi_{sl_1})^2.$$

At high temperatures, when $\frac{h\omega_s^{l_0}}{kT} < 1$, $g(T) = C_4 T + C_5$, and, therefore,

$$\tau = C_3' e^{C_4 \tau}.$$

The quantities C_3' and C_4 are practically independent of the temperature.

The increase of τ with the temperature was really observed for anthracene dissolved in naphthalene [15].

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