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OPTICAL ABSORPTION OF TRAPPED ELECTRONS IN POLAR MEDIA WHICH IS ACCOMPANIED BY CHARGE TRANSFER

R. R. Dogonadze and É. M. Itskovich

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Optical electron transitions between traps in polar media are analyzed. A relation for the shape of the spectrum is obtained with the aid of the dielectric-continuum model used to describe polar media and of an expression for the optical-transition probability. It is shown that the asymmetric spectrum of solvated electrons known from experiment can arise because of two reasons in this model: by simultaneous contributions from the 1s → 2p transition and from the transition that is attended by electron transfer, and by scatter in the distances between neighboring traps (in the latter case, line broadening is heterogeneous in character).

1. INTRODUCTION

Much attention is focused in recent years on the physical nature and optical properties of solvated and trapped electrons. It is known, in particular, that the electron's absorption band is a broad (a width of 0.5 to 1.5 eV at half height), structureless asymmetric line with a maximum in the region of 1 to 2 eV. The short-wave flank of the spectrum falls off much more slowly than the long-wave flank [1-3].

A large number of papers have dealt with the theoretical description of solvated and trapped electron spectra [4-11]. But in view of the fact that a number of questions of fundamental character relating to the physical nature of electron localization have not been answered definitely, these theories rest on different, often contradictory models. We list the chief questions.

(i) The relative importance in electron localization of the interaction with nearest molecules of the medium (short-range interaction) and of the interaction with dipoles in the bulk, which can be described as a continuous medium characterized by polarization $\vec{P}(\vec{r})$, where r is the coordinate of the medium (long-range interaction).

(ii) The nature of the final electronic state (or states) into which the transition occurs; is this a discrete state or does it belong to the continuum? This question is intimately linked to the previous one, since the answer to it depends on the shape of the potential well in which the electron resides.

(iii) Is the appreciable width of the spectrum (0.5 to 1.5 eV) caused by homogeneous broadening, i.e., broadening due to interactions of the electron with phonons (medium polari-

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zation fluctuations) and with local fluctuations (fluctuations of the nearest molecules, cavities), or is it caused by heterogeneous broadening (the presence of traps of different depth and, therefore, an entire set of electronic transitions rather than just one)?

It is assumed in a number of theoretical papers [4-6] that the electron is localized in a cavity formed by point dipoles of the medium, but interaction with the polar medium outside the cavity which is regarded as dielectric continuum is taken into account as well. On the assumption that the optical band is associated with the 1s → 2 p transition, and by suitable choice of the parameters, good agreement between the experimental and theoretical values for the positions of the maximum for water [5, 6] and ammonia [4] was obtained. The shape of the spectrum was also calculated in [4-6] while including homogeneous broadening arising because of interaction of the electron with the polar continuum and with the cavity fluctuations. The spectrum calculated was found to be practically symmetric, and much narrower than the experimental one.

Good agreement between experimental and theoretical spectra could be attained in [7] for ethanol by assuming that local vibrational degrees of freedom are involved in the transition and by appropriately matching the parameters (the frequency of vibrations and displacements of vibrational equilibrium coordinates). However, this broadening mechanism can only be confirmed by an independent computation or measurement of the corresponding parameters, and this has not been done up to now.

It was shown in [8] that quantitative agreement between experimental and theoretical spectra (for water, ammonia, ethylenediamine, and methanol) can also be obtained on the assumption that the electron is located in a spherically symmetric well of finite radius (short-range interaction) and performs the transition from the bound state into the continuum. Equally good agreement can be obtained for different types of such wells (one-step wells and two-step wells with different radii and depths).

In many experimental papers [12-15] the possibility of heterogeneous broadening was revealed (particularly for electrons trapped in glasses), but a theoretical discussion of this question does not exist so far. As far as we know, a sufficiently complete theoretical analysis of the shape of the absorption band corresponding to the transition to a continuous spectrum does not exist (a number of results have been obtained in [9, 10]).

All the papers listed above discuss the optical electron transition within the limits of one center. In the present work we present an analysis of the shape of the optical band that corresponds to electron transfer between different centers (traps), which basically could be responsible, too, for the absorption band. This is particularly true for transitions in frozen media (glasses) usually containing a large number of inhomogeneities which can serve as acceptors. The possibility of such processes has been pointed out in [11], but it remains obscure there how the characteristics of the spectrum depend on the distance over which this transition occurs. An analysis of this dependence requires a more detailed description of the interaction between the charge and the medium. Such an analysis is performed in the present work while allowing, both for short-range and for long-range forces. It is assumed that these interactions play different parts. Short-range interaction is the primary reason for localization of the electron, while long-range interaction deepens an already existing trap. Existing scatter in trap depths and distances between the traps must also be taken into account. It is seen from an averaging performed over the distances between traps that this peculiar kind of "heterogeneity" can be responsible, both for the considerable width of the spectrum and for its asymmetry.

2. DESCRIPTION OF THE MODEL

We assume that the polar medium has a certain random set of shallow traps constituting the primary reason for localization of the electron (short-range interaction). Such traps can be the defects in glasses, cavities formed by dipole molecules, clusters, etc. Once trapped there the electron, owing to its interaction with the polar medium (long-range interaction), significantly deepens it. Under the action of the field of a light wave, the electron transfers from the ground (steady) state of such a deepened trap into a neighboring, shallow trap (which then also is deepened owing to polarization of the medium close to it). We shall assume to be specific that both traps can be described with the aid of the coulombic potentials $U_i(\vec{r}) = \frac{z_i e^2}{|\vec{r}|}$, (for the trap where the electron exists prior to the transition) and

$U_2(\vec{r}) = -\frac{z_2 e^2}{|\vec{r}-\vec{r}_0|}$, (for the trap into which the electron transition occurs).* Here e is the electronic charge, z_i is the effective charge of the i-th trap (i = 1, 2), $r_0 = |\vec{r}_0|$ is the distance between traps, and r is the space coordinate.

The electron's wave function and its energy in the initial, steady state can be found by minimization of the functional $F_1[\Psi, \vec{P}]$, which depends on electron wave function $\psi(r)$ and medium polarization $\vec{P}(\vec{r})$ [16]:

$$F_i[\Psi, \vec{P}] = \frac{\hbar^2}{2\mu}\int |\vec{\nabla}\Psi(\vec{r})|^2 d\vec{r} - \int \vec{P}(\vec{r})\vec{D}(\vec{r}, \Psi(\vec{r}))\times$$
$$\times d\vec{r} + \frac{2\pi}{C}\int \vec{P}^2(\vec{r})d\vec{r} + \int \frac{U_i(\vec{r})}{\varepsilon_{st}}|\Psi(\vec{r})|^2 d\vec{r}, \quad i = 1, 2, \tag{1}$$

$$\vec{D}(\vec{r}, \Psi(\vec{r})) = -e\int \frac{|\Psi(\vec{r}_1)|^2(\vec{r}_1 - \vec{r})}{|\vec{r}_1 - \vec{r}|^2} d\vec{r}_1, \tag{2}$$

where the first term in (1) is the kinetic energy of an electron having the effective mass μ, the second term is the interaction energy between the electron and the polar medium, the third term is the potential energy of the medium ($C = 1/\varepsilon_{op} - 1/\varepsilon_{st}$ where ε_{op} and ε_{st} are the optic and static dielectric permittivities), the fourth term is the interaction energy between the electron and the trap, and $\vec{D}(\vec{r}, \Psi(\vec{r}))$ is the induction of the field set up by the electron.

Minimization of functional F_1 with respect to the polarization function $\vec{P}(\vec{r})$ leads to the following, well-known relation between $\vec{P}$ and $\vec{D}$ [16]:

$$\vec{P}_1(\vec{r}) = \frac{C}{4\pi}\vec{D}[\vec{r}, \Psi_1(\vec{r})], \tag{3}$$

where $\Psi_1(\vec{r})$ and $P_1(\vec{r})$ are the electron wave function of the initial steady state and the medium polarization corresponding to this state. Following [16] we approximate $\Psi_1(\vec{r})$ by the hydrogenlike function

$$\Psi_1(\vec{r}) = \sqrt{\frac{\alpha_1^3}{\pi}} e^{-\alpha_1|\vec{r}|}. \tag{4}$$

With the aid of minimization of F_1 with respect to α_1 (and after substituting (3) and (4) into (1)) one then can find the value of this parameter. The last term in F_1 can be neglected when determining α_1, since we assume that the "priming" traps are sufficiently shallow (the condition of $z_{1,2} \ll \varepsilon_{st}C$ must be fulfilled to this end). In this case we have for α_1,

$$\alpha_1 = \frac{5}{16}\frac{C}{\rho}, \tag{5}$$

$$\rho = \frac{\hbar^3}{\mu e^2}, \tag{6}$$

which coincides with the result obtained for polarons [16]. There is no time for medium polarization to change during the electron transition; hence the electron wave function of the final state, $\Psi_2(\vec{r})$, ought to be determined by minimizing the functional $F_2[\Psi, \vec{P}_1]$ with respect to Ψ. The second and third term in F_2 can be neglected when the distance between traps, r_0, is sufficiently large (since the medium near the second trap in this case will practically not be polarized). This means that $\Psi_2(r)$ can be written as

$$\Psi_2(\vec{r}) = \sqrt{\frac{\alpha_2^3}{\pi}} e^{-\alpha_2|\vec{r}-\vec{r}_0|}, \tag{7}$$

*This approximation undoubtedly is very rough. We use it in order to bring the computation to an end, and to estimate qualitative rather than quantitative laws.

$$\alpha_2 = \frac{z}{\varepsilon_{st}\rho}. \tag{8}$$

Equality (7) holds under the condition that

$$r_0\alpha_2 \gg 1. \tag{9}$$

Moreover, since the original traps are sufficiently shallow, a further condition is fulfilled:

$$n = \frac{\alpha_1}{\alpha_2} \gg 1. \tag{10}$$

3. DETERMINATION OF ABSORPTION BAND SHAPE

On the assumption of tight binding of the electron with the medium, the function I(ν) can be used to describe the shape of the absorption band corresponding to the transition between two fixed traps [17]:

$$I(\nu) = \text{const}\,|\vec{d}_{1\to 2}|^2 \exp\{-(h\nu - h\nu_{max})^2/W^2\}, \tag{11}$$

$$|\vec{d}_{1\to 2}|^2 = |\int d\vec{r}\,\Psi_1(r)\,e\,r\,\Psi_2(r)|^2, \tag{12}$$

$$h\nu_{max} = F_2[\Psi_2, \vec{P}_1] - F_1[\Psi_1, \vec{P}_1]; \tag{13}$$

$$W^2 = \sum_{\vec{k}} \left(\frac{\partial F_2(\Psi_2, \{\vec{P}_{\vec{k}}\})}{\partial \vec{P}_{\vec{k}}}\right)^2_{\vec{P}_{\vec{k}} = \vec{P}^1_{\vec{k}}} \times 2KT \Big/ \frac{\partial^2 F_1[\Psi_1, \{\vec{P}_{\vec{k}}\}]}{\partial \vec{P}^2_{\vec{k}}}, \tag{14}$$

where $\vec{P}_{\vec{k}}$ and $\vec{P}^1_{\vec{k}}$ are the components of Fourier-series expansion of functions $\vec{P}(\vec{r})$ and $\vec{P}^1(\vec{r})$, T is the temperature, and K is the Boltzmann constant. In writing down (14) we have made use of the general relation obtained in [17] for line half-width in the case of potential-energy surfaces of arbitrary form. In the present case, the final term in the region of $\vec{P}_{\vec{k}}$-values corresponding to the electron transition deviates significantly from the harmonic, since the electron function corresponding to equilibrium polarization in the final state differs from Ψ_2 (the functional $F_2[\Psi, \vec{P}]$ where $\vec{P} = \frac{C}{4\pi}\vec{D}[\vec{r}, \Psi]$ must be minimized with respect to Ψ if one wants to find this wave function). To be specific we have assumed, moreover, that the characteristic frequencies of the medium polarization fluctuations are much smaller than KT (the high-temperature approximation [17]). In the opposite case, quantity W is independent of temperature, and the full frequency dependence of dielectric permittivity must be used in order to determine it, and not merely its limiting values ε_{op} and ε_{st} [17].

We substitute (4) and (7) into (12) in order to compute the square of the matrix element of the electron's dipole moment, $|\vec{d}_{1\to 2}|^2$. Using spherical coordinates to evaluate the integral and allowing for (9) and (10) we than have,

$$|\vec{d}_{1\to 2}|^2 \simeq 32\frac{e^2}{\alpha_1^2}\frac{1}{n^5}e^{-2\alpha_1 r_0}. \tag{15}$$

Thus, $|d_{1\to 2}|^2$ decreases exponentially at sufficiently large distances. The expression for the position of the absorption band maximum, $h\nu_{max}$, can be split into two parts when the term that does not depend on r_0 is isolated as the first part:

$$h\nu_{max} = h\nu^{(1)}_{max} + h\nu^{(2)}_{max}, \tag{16}$$

$$h\nu^{(1)}_{max} = \frac{\hbar^2}{2\mu}\int |\vec{\nabla}\Psi_2(\vec{r})|^2 d\vec{r} - \frac{\hbar^2}{2\mu}\int |\vec{\nabla}\Psi_1(\vec{r})|^2 d\vec{r} + \int \vec{P}_1(\vec{r})\,\vec{D}(\vec{r}, \Psi_1)\,d\vec{r} + \int \frac{U_2(\vec{r})}{\varepsilon_{st}}|\Psi_2(\vec{r})|^2 d\vec{r} - \int \frac{U_1(\vec{r})}{\varepsilon_{st}}|\Psi_1(\vec{r})|^2 d\vec{r}, \tag{17}$$

$$h\nu^{(2)}_{max} = -\int \vec{P}_1(\vec{r})\,\vec{D}(\vec{r}, \Psi_2(\vec{r}))\,d\vec{r}. \tag{18}$$

After using (2) and performing Fourier transformation we can write the integrals contained in (17) and (18) as,

$$\int \vec{P}_1(\vec{r})\,\vec{D}(\vec{r},\Psi_2)\,d\vec{r}=\frac{Ce^2}{2\pi^2}\int d\vec{k}\,\frac{1}{|\vec{k}|^2}\int d\vec{r}_1\,|\Psi_1(\vec{r})|^2 e^{C\vec{k}\vec{r}_1}\int d\vec{r}_2\,|\Psi_2(\vec{r}_2)|^2 e^{i\vec{k}\vec{r}_2}, \tag{19}$$

$$\int \vec{P}_1(\vec{r})\,\vec{D}(\vec{r},\Psi_1)\,d\vec{r}=\frac{Ce^2}{2\pi^2}\int d\vec{k}\,\frac{1}{|\vec{k}|^2}\left[\int d\vec{r}_1\,|\Psi_1(\vec{r}_1)|^2 e^{i\vec{k}\vec{r}_1}\right]^2. \tag{20}$$

Using the explicit form of wave functions (4) and (7), substituting (19) and (20) into (17) and (18), and evaluating the integrals contained in them we have,

$$h\nu_{\max}^{(1)}=\frac{\hbar^2\alpha_2^2}{2\mu}-\frac{\hbar^2\alpha_1^2}{2\mu}+\frac{5}{8}\alpha_1 Ce^2+\frac{z_2e^2\alpha_2}{\varepsilon_{st}}-\frac{z_1e^2\alpha_1}{\varepsilon_{st}}\simeq$$

$$\simeq\frac{5}{8}\alpha_1 Ce^2\simeq 0{,}15\frac{e^2C^2}{\rho}, \tag{21}$$

$$h\nu_{\max}^{(2)}=-\frac{Ce^2}{r_0}\left[1-\left(1-\frac{3}{n^2}\right)e^{-2\alpha_2 r_0}-\frac{\alpha_2 r_0}{\left(1-\frac{1}{n^2}\right)^2}e^{-2\alpha_2 r_0}-\right.$$

$$\left.-\frac{3\left(1-\frac{1}{3n^2}\right)}{\left(1-\frac{1}{n^2}\right)^3}\frac{1}{n^4}e^{-2\alpha_1 r_0}-\frac{1}{n^4}\frac{r_0\alpha_1 e^{-2\alpha_1 r_0}}{\left(1-\frac{1}{n^2}\right)^2}\right]\simeq-\frac{Ce^2}{r_0}. \tag{22}*$$

Thus, quantity $h\nu_{max}$ increases monotonically with increasing r_0, and tends asymptotically to $h\nu$. Using (14), (1), (2), (19), and (20) one can obtain the following expression for the square of line half-width:

$$W^2=\frac{Ce^2}{\pi^2}\int d\vec{k}\,\frac{1}{k^2}\left[\int d\vec{r}\,|\Psi_2(\vec{r})|^2 e^{i\vec{k}\vec{r}}-\int d\vec{r}\,|\Psi_1(\vec{r})|^2 e^{i\vec{k}\vec{r}}\right]^2=$$

$$=\left[\frac{5}{4}e^2C\alpha_2+\frac{5}{4}e^2C\alpha_1+4h\nu_{\max}^{(2)}\right]kT\simeq\frac{5}{4}e^2C\alpha_1 KT. \tag{23}$$

It is of interest to compare the oscillator strength of the transition described above with that of a transition of the 1s → 2p type between two electron states of the same trap. Writing $|\vec{d}_{1s\to 1p}|^2$ for the square of the operator matrix element of the dipole moment of the 1s → 2p transition, which is $5{\cdot}6\frac{\rho^2e^2}{C^2}$, we find

$$\frac{|\vec{d}_{1\to 2}|^2}{|\vec{d}_{1s\to 2p}|^2}\approx\frac{1880}{n^5}e^{-2\alpha_2 r_0} \tag{24}$$

for the corresponding ratio of oscillator strengths. One can see from (24) that the contribution made to the total absorption band by the electron transition with charge transfer can be comparable to the contribution made by the transition of the 1s → 2p type when n and r_0 have values which are realistic but not too high (e.g., for n = 2 we have $\alpha r_0=2-\frac{|\vec{d}_{1\to 2}|^2}{|\vec{d}_{1s\to 2p}|^2}\simeq 1.1$, while for n = 2.5 we have $\alpha_2 r_0=2-\frac{|\vec{d}_{1\to 2}|^2}{|\vec{d}_{1s\to 2p}|^2}\simeq 0.35$). The maximum of the absorption band corresponding to the 1s → 2p transition $\left(h\nu_{\max}^{1s\to 2p}\simeq 0.07\frac{e^2C^2}{\rho^2}\,[16]\right)$, is displaced in the direction of lower energies relative to the maximum of the charge-transfer band (see Eq. (21)). The observed asymmetry of the total band can, therefore, arise from the combined contribution of both bands, with a slight predominance of the 1s → 2p transition.

It must be pointed out, however, that ratio (24) certainly is merely an estimate, primarily because of the crude description of trap fields in terms of hydrogenlike potential.

*The term $h\nu_{max}^{(2)}$ is a small addition to $h\nu_{max}^{(1)}$, but the origin for spectrum asymmetry upon averaging with respect to r_0 resides in precisely this term. A similar term in W can be cropped.

4. AVERAGING OVER DIFFERENT TRAP TYPES

Function $I(\nu)$ describes the band shape of light absorption accompanied by charge transfer between two fixed traps. Such bands have symmetric Gaussian shape. In reality, however, one is dealing with a set of traps of different depths which are at different distances from each other. It is necessary, therefore, to perform averaging, both over trap depths (the only depth that is of significance in our case is that of the trap into which the transition occurs; it is characterized by parameter Z_2) and over distances between neighboring traps (parameter r_0). Function $I(\nu)$ depends on Z_2 only via the factor $|\vec{d}_{1\to 2}|^2$, so that the averaging over Z_2 only produces a change in band intensity but no change in band shape.

Let us now examine the effects obtained when we include averaging over the distances r_0 between traps. Writing $F(r_0)$ for the probability that the distance between an arbitrarily selected trap and its next neighbor is r_0 we find that absorption band shape must be written as

$$\overline{I(\nu)} = \text{const} \int_0^\infty |\vec{d}_{1\to 2}|^2 \exp\left\{-\frac{(h\nu - h\nu_{\max})^2}{W^2}\right\} F(r_0)\, dr_0. \tag{25}$$

The form of function $F(r_0)$ must be known if one wants to find band shape. The trap distribution in space usually is unknown, generally speaking. However, certain properties of trap distribution can be obtained from models. When we make the usual assumption that the trap represents a cavity formed by dipole molecules (Fig. 1), we find that the traps cannot be at distances closer than $R_1 + R_2 + r_1 + r_2$, in order of magnitude (where r_i is the radius of the i-th cavity, and R_i is the length of the dipole involved in formation of the i-th cavity), owing to their mutual repulsion. Thus, $F(r_0)$ rapidly tends toward zero for $r_0 < R_1 + R_2\, r_1 + r_2$. At large values of the argument, function $F(r_0)$ begins to decrease because of the fact that the trap concentration is finite. It follows from what has been said that function $F(r_0)$ can be visualized as follows. It has a maximum at $r_0 = \bar{r}_0$, and decreases drastically with increasing $\bar{r}_0 - r_0$; it practically becomes zero at $r_0 \leqslant R_1 + R_2 + r_1 + r_2$ (we write $\delta_1,\ \delta_1 \ll \bar{r}_0$ for the characteristic scale of the decrease). The function also decreases with increasing $r_0 - r_0$, but much more slowly so than in the previous case (we write $\delta_2,\ \delta_2 \gg \delta_1$ for the characteristic scale of this decrease). Condition (9) is sufficiently well met for $r_0 \in [\bar{r}_0 - \delta_1,\ \bar{r}_0 + \delta_2]$, when the length of the dipoles is two or three times larger than the radius of the cavity. The function described is shown as a solid line in Fig. 2.

The experimental absorption band becomes markedly asymmetric already at a distance on the order of its half-width from the transition maximum; its high-energy flank falls off more slowly than its low-energy flank. Let us see under what conditions the function $\bar{I}(\nu)$ specified by equality (25) has the same quality.

To be specific we shall assume that $\delta_2 \ll \bar{r}_0$ (the case of $\delta_2 \gg \bar{r}_0$ can be examined in an analogous fashion). Then quantity $h\nu_{\max}$ underneath the integral sign in (25) can be written as

$$h\nu_{\max} \simeq h\nu_{\max}^{(2)} - \frac{Ce^2}{r_0} \simeq h\nu_{\max}^{(2)} - \frac{Ce^2}{\bar{r}_0} + \frac{Ce^2(r_0 - \bar{r}_0)}{\bar{r}_0^2}. \tag{26}$$

It follows from expressions (25) and (26) that the contribution of the total band, $\bar{I}(\nu)$, to the short-wave flank yields a whole set of individual transitions of the form of (11) when the change which occurs in $h\nu_{\max}$ when r_0 increases from $\bar{r}_0$ to $\bar{r}_0 + \min(\alpha_2^{-1},\ \delta_2)$ is larger than W:

$$\frac{Ce^2}{\bar{r}_0^2} \min(\alpha_2^{-1},\ \delta_2) \gg W, \tag{27}$$

and the law of change of the short-wave flank can be written as

$$I(\nu) \sim |\vec{d}_{1\to 2}(x)|^2 F(x), \quad x > r_0, \tag{28}$$

$$x = \frac{r_0}{Ce^2}\left(h\nu - h\nu_{\max}^{(2)} + \frac{2Ce^2}{\bar{r}_0}\right).$$

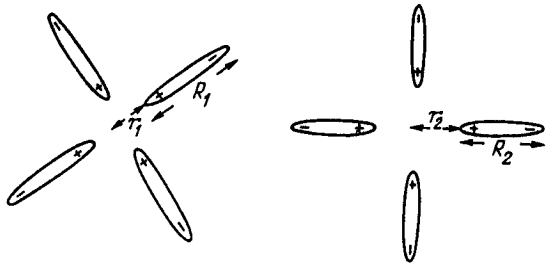

Fig. 1

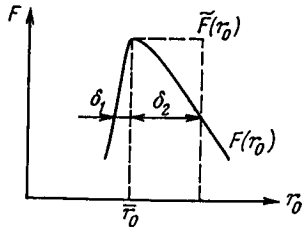

Fig. 2

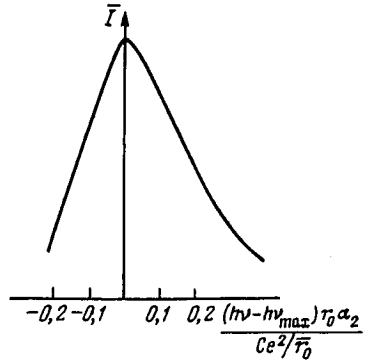

Fig. 3

When in addition a condition of the type of (27) where δ_2 is replaced by δ_1 is fulfilled, then the entire spectrum is described by expression (28). Otherwise the long-wave flank has the form of

$$\bar{I}(\nu) \sim \exp\left\{-\frac{\left(h\nu - h\nu^{(2)}_{max} + \frac{Ce^2}{\bar{r}_0}\right)^2}{W^2}\right\} \frac{1}{\left|h\nu - h\nu^{(2)}_{max} + \frac{Ce^2}{\bar{r}_0}\right|},$$

$$h\nu < h\nu^{(2)}_{max} - \frac{Ce^2}{\bar{r}_0}.$$

Thus, when condition (27) is met, the total absorption band is described by an asymmetric curve the short-wave flank of which falls off more slowly than the long-wave flank; the position of the curve's maximum $\left(h\nu_{max} = h\nu^{(2)}_{max} + \frac{Ce^2}{\bar{r}_0}\right)$ depends on the average distance between traps. Band broadening in this case is governed by the scatter in distances between traps.

We substitute expressions (23), (5), and (6) and the numerical values of physical parameters $\hbar$, e, and m (m is the electron mass) into (27) and rewrite it as

$$\sqrt{\frac{4}{5}\frac{Ce^2\alpha_1}{KT}}\frac{1}{\alpha_1\bar{r}_0}\frac{\min(\alpha_2^{-1},\delta_2)}{\bar{r}_0} \simeq \sqrt{\frac{7\,\text{eV}}{KT}\,C^2\frac{\mu}{m}}\frac{1}{\alpha_1\bar{r}_0}\frac{\min(\alpha_2^{-1},\delta_2)}{\bar{r}_0} \geqslant 1. \qquad (27a)$$

Condition (27a) can be fulfilled with certain realistic values of the parameters C and μ/m even when inequalities (9) and (10) are taken into account (lower temperatures offer the better possibility). Therefore, under certain conditions the existence of traps which are unequally spaced can give rise to asymmetry of the observed optical band.

Figure 3 shows a plot of function $\bar{I}(\nu)$ obtained in a calculation via relation (25) when the simplified function $\bar{F}(r_0)$ was used instead of $F(r_0)$ ($\bar{F}(r_0)$=const, $\bar{r}_0 \leqslant r_0 \leqslant \bar{r}_0 + \delta$, $\bar{F}(r_0) \equiv 0$ for other r_0-values) together with the following values of the parameters: $\delta = \frac{1}{\alpha_2}$, $\frac{Ce^2}{\bar{r}_0\alpha_2 W} = 2$.

5. CONCLUSIONS

In the present work we have discussed a new optical transition mechanism for solvated or trapped electrons. It consists in electron transfer between two neighboring traps under the action of the light wave's field. Indications for the existence of such "priming" traps (clusters can fill this function, for instance) are found in the correlation existing between cluster formation and the position of the optical band maximum over a wide range of concentrations in mixtures of monohydric alcohols and ammonia [18]. It was shown that under certain conditions, band shape and maximum position substantially depend on the properties of the spatial trap distribution function (particularly on parameters $\bar{r}_0$ and δ). Should media actually exist where the new mechanism is responsible for the optical absorption band (which definitely demands additional theoretical and experimental proof), then the observation becomes understandable that often, different optical properties are found in media which are similar in their dielectric properties, and vice versa [19, 20].

When analyzing the properties of an optical absorption band one often tries to obtain quantitative fit of theoretical and experimental parameters. As indicated before, however, this often can be done by selecting the parameters in terms of very diverse models. It will be more productive, in our opinion, to explain the qualitative features. From this viewpoint, absorption band asymmetry is one of the most important band properties. It has been shown in [17, 21] that in transitions between two discrete states, the absorption band always is symmetric when the electron is tightly bound to the vibrational subsystem (for polar media, the tight-binding criterion [17] is very nicely fulfilled). Asymmetry can be caused by weak binding with local high-frequency fluctuations. This can be verified, since in this case the absorption band ought to be the sum of several Gaussian components spaced distances Ω apart (Ω is the local fluctuation frequency, with $\hbar\Omega \gg KT$). Unfortunately, such an analysis of the experimental spectra has not been performed so far.

Basically, asymmetry can also be caused by transitions to higher, localized electronic states. According to estimates performed in [22], these transitions provide an insignificant contribution to the total band within its half-width. A special examination is required to answer the question whether this result is general or due to the model used by the authors (long-range Coulomb interaction plus influence of the cavity). Another possible reason for asymmetry that cannot be rejected is transitions into the continuous spectrum.

The mechanism discussed in the present work can be responsible for spectrum asymmetry for two reasons. The total band will have the observed symmetry when the intensity due to this mechanism is not much lower than that of the usual 1s → 2p transition without charge transfer, since the corresponding spectrum is displaced in the direction of high energies.

But the resulting band also can be asymmetric when the transition with charge transfer is much more intense than the 1s → 2p transition, provided condition (27) is fulfilled. In this case band width and asymmetry are determined by "heterogeneous" broadening, which in the present case we understand as a contribution of different transitions between traps which are at different distances from each other, rather than that of transitions into traps of different depth (which is the usual connotation).

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TWO-DIMENSIONAL CONDENSATION AND REORIENTATION OF ORGANIC MOLECULES IN ADSORBED LAYERS. INCLUSION OF ATTRACTIVE INTERACTIONS IN THE TWO ORIENTATIONS

Yu. I. Kharkats

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The behavior of an adsorbed system of interacting organic molecules present on the surface in two different orientations is analyzed. The relation between the degree of coverage and bulk adsorbate concentration is examined as a function of the relative size of the attraction constants holding for different orientations. It is shown that depending on the relative values of the isotherm parameters, one or two reorientation transitions can be realized in the system.

The possibility of reorientation of adsorbed organic molecules has been examined in a large number of experimental and theoretical papers [1-20]. The general conclusion that can be drawn from this work is this: For sufficiently strong attractive interactions between the molecules, reorientation of the adsorbed molecules as well as two-dimensional condensation are discontinuous and have the character of phase transitions of the first kind.

The adsorption of organic molecules present on the surface in two different orientations (parallel and perpendicular to the surface) usually is described by the isotherms suggested in [2]:

$$B_1c=\frac{\theta_1}{(1-\theta_1-\theta_2)^n}\exp\{-2a_1n\theta_1-2a_{12}n\theta_2\}, \quad (1)$$

$$B_2c=\frac{\theta_2}{(1-\theta_1-\theta_2)^m}\exp\{-2a_2m\theta_2-2a_{12}m\theta_1\}. \quad (2)$$

Here θ_1 and θ_2 are the degrees of coverage for orientations 1 and 2, c is the bulk adsorbate concentration, B_1 and B_2 are the adsorption coefficients, n and m are the numbers of adsorption sites taken up on the surface by molecules in orientations 1 and 2, a_1 and a_2 are the interaction constants of the molecules in orientations 1 and 2, and a_{12} is the cross-interaction constant.

Equations (1) and (2) are a generalization of the well-known isotherms of Frumkin and Flory–Huggins, and determine functions $\theta_1(c)$ and $\theta_2(c)$.

In certain ranges of values of the parameters and of concentration c, functions $\theta_1(c)$ and $\theta_2(c)$ can be nonsingle-valued. That state of the adsorption system will then be realized which corresponds to the minimum value of free energy:

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