PROBLEM OF IRREVERSIBILITY IN THE THEORY OF ELECTRONIC AND VIBRATIONAL TRANSITIONS IN POLAR MEDIA

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The paper analyzes the conditions for irreversibility of the electronic and vibrational transitions occurring between fixed centers in polar media. It is shown that a necessary condition for irreversibility is the presence of a continuous spectrum of the medium's intrinsic polarization vibrations. When the transition results in altered charge–medium interaction, then a second condition for irreversibility is the presence of medium polarization vibrations with infinitely low frequencies. But when this interaction is not altered, then irreversibility requires that the interaction of the intramolecular vibrations with the polarization vibrations be altered. In this case, irreversibility can be secured, either by vibrations with infinitely low frequencies, as before, or by resonance polarization vibrations having the same frequency as the intramolecular vibrations.

Most processes of light absorption and emission by complicated molecules [1], the electronic transitions at impurity centers in polar crystals [2, 3], and electron and proton transfer reactions in polar solvents [4, 5] essentially belong to the very general class of electronic and vibrational transitions where both the electronic and the vibrational state of the molecule and of the surrounding medium change.

Usually the relation for the transition probability in unit time [6],

$$W=\frac{2\pi}{\hbar}|V_{if}|^2\delta(E_i-E_f), \tag{1}$$

is used as a starting relation to calculate the probability of an intramolecular transition or of a transition between two fixed centers (impurity centers in polar crystals; atoms and molecules in liquids); in (1), E_i (E_f) is the energy of the initial (final) state, and V_{if} is an operator matrix element of the interaction giving rise to the transition.

This relation strictly applies when describing transitions in continuous spectra which are irreversible [6] and have a probability proportional to time. For such transitions the final expression contains an integration over the continuous spectrum which "removes" the δ-function.

However, relation (1) also is used to calculate transition probabilities in isolated molecules in the gas phase [7], which have a discrete electronic and vibrational spectrum, and the probability of electronic transitions in condensed media [8], which have various types of vibrational spectrum. The question arises what conditions determine applicability of this relation, and what is the physical mechanism securing irreversibility of the transition.

Collisions of the molecules with each other and with the container walls are believed to be the most natural mechanism securing irreversibility of a transition in molecules in the gas phase [8]. A more complicated situation exists with respect to transitions in the condensed phase, particularly in solids lacking translational motion.

Transitions in Condensed Phases. Electronic and vibrational transitions in polar media have been studied theoretically in a great number of papers (see, e.g., [2-5]). In particular, it was shown when studying charge transfer processes in polar solvents (for reviews see [4, 5]) that solvent properties have substantial influence on the kinetic parameters, in addition to the intramolecular characteristics of the reactants. It follows from a theoretical analysis of light absorption by an impurity particle in a polar liquid carried out in [9] that interaction with the solvent affects, both the shape and half width of the spectral line and the position of the maximum.

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The effect of the polar medium on the rate of electronic processes is explained by the change occurring in its vibrational state during the electronic transition. However, in addition to the quantitative changes listed above, the polar medium also has a substantial qualitative effect on electronic processes. First, owing to the presence of a continuous frequency spectrum of polarization vibrations, transitions associated with the stimulation or absorption of vibrational energy of the medium become possible in addition to the resonance transitions, i.e., in addition to those transitions for which $h\nu = E_f - E_i + \sum_k n_k^f \hbar\Omega_k^f - \sum_k n_k^i \hbar\Omega_k^i$ in the absorption of light of frequency ν, or $E_i - E_f = \sum_k n_k^f \hbar\Omega_k^f - \sum_k n_k^i \hbar\Omega_k^i$ for a radiationless transition, where E_i (E_f) is the electronic energy of the initial (final) state, and Ω_k^i (Ω_k^f) and n_k^i (n_k^f) are the frequencies and quantum numbers of the intramolecular vibrations of the initial (final) state.

Secondly, irreversibility of the processes under discussion is secured precisely by interaction with the medium, provided this satisfies certain conditions. These conditions have been analyzed in [10, 11] in terms of a model where the dynamic behavior of medium polarization is described by two oscillators with frequencies ω_0 and $\omega_0 + \Omega$. It was shown that irreversibility of the process requires that the dispersion of vibrational frequencies, Ω, satisfy the following condition: $(\omega_0/\sqrt{z}) \ll \Omega \ll (1/\tau_g)$, where τ_g is the length of time for which the reactants are close to each other, and z is a quantity depending on temperature and on the vibration characteristics. This condition means that the transition probability should be proportional to time during a time on the order of the characteristic "residence" time of the reactants in the reaction zone ($\sim 10^{-9}$ sec). When a transition occurs during this time, the reverse transition will not occur, since the reactants move a large distance apart.

Recently a model was developed for dielectric media which takes into account the continuous spectrum of the polarization fluctuations [4, 5]. It is the aim of the present work to analyze in terms of this model the conditions under which transitions between centers located at a fixed relative distance are irreversible. This problem arises when studying intramolecular transitions in liquids and solids and intermolecular transitions in solids lacking translational motion.

According to [4], after averaging over the initial, and summation over all possible final vibrational states, relation (1) for the transition probability can be transformed to

$$W_{i\to f} = \frac{\beta}{\hbar} |V_{if}|^2 \int_{-\infty}^{\infty} dt \langle\!\langle T \exp \varphi(t) \rangle\!\rangle = \frac{\beta}{\hbar} |V_{if}|^2 \int_{-\infty}^{\infty} dt \exp\{f(t)\}, \tag{2}$$

$$\varphi(t) = -i\beta \int_0^t \exp(i\beta \hat{H}_i s)(\hat{H}_f - \hat{H}_i) \exp(-i\beta \hat{H}_i s)\, ds, \tag{3}$$

where $\langle\!\langle\ \rangle\!\rangle$ designates the quantum-statistical average over the initial state, and T is the chronological operator. It is assumed that the initial state is an equilibrium state. The second part of equality (2) is the definition of function f(t); the properties of this function will be discussed below.

The adiabatic Hamiltonians of the initial and final channel, $\hat{H}_i$ and $\hat{H}_f$, are of the form of [12]:

$$\hat{H}_i = \sum_\varkappa \frac{1}{2}\hbar\omega_\varkappa \left[q_\varkappa^2 - \frac{\partial^2}{\partial q_\varkappa^2} \right] + \frac{1}{2}\hbar\Omega \left[Q^2 - \frac{\partial^2}{\partial Q^2} \right] - \sum_\varkappa u_\varkappa^i q_\varkappa - \frac{1}{2}\sum_\varkappa \gamma_\varkappa^i q_\varkappa Q, \tag{4}$$

$$\hat{H}_f = \Delta J + \sum_\varkappa \frac{1}{2}\hbar\omega_\varkappa \left[q_\varkappa^2 - \frac{\partial^2}{\partial q_\varkappa^2} \right] + \frac{1}{2}\hbar\Omega \left[(Q-Q_0)^2 - \frac{\partial^2}{\partial Q^2} \right] - \sum_\varkappa u_\varkappa^f q_\varkappa - \frac{1}{2}\sum_\varkappa \gamma_\varkappa^f q_\varkappa (Q-Q_0), \tag{5}$$

where $\{\omega_\varkappa\}$, $\{q_\varkappa\}$ are the sets of eigenfrequencies and coordinates describing the medium's polarization vibrations; $\varkappa \equiv \bar{k}$ or ν; $\bar{k}$ is the wave vector; ν determines the character of the polarization and passes through a continuous set of values; Ω and Q are the frequency and coordinate of the intramolecular vibration; Q_0 is the change in the equilibrium value of the intramolecular coordinate occurring as a result of the electronic transition (for the sake of definition we consider only one intramolecular vibration; the possibility that a larger number of intramolecular vibrations are involved in the electronic transition does not introduce any fundamentally new aspects into the discussion); and ΔJ is the difference between the minimum energies in the final and initial state (in processes accompanied by the emission or absorption of light, the energy of the light quantum must be added to or subtracted from this difference). The last two terms in (4) and (5) arise when the expression for the energy of molecule–medium interaction, which in terms of the linear approximation is given by $-\int \bar{p}(\bar{r})\bar{\mathcal{E}}(\bar{r}, Q)\, d\bar{r}$ [$\bar{p}(\bar{r})$ is the polarization vector of the medium in point $\bar{r}$, and $\bar{\mathcal{E}}(\bar{r}, Q)$ is the electric field which

is created by the particle and depends on the positions of its nuclei], is expanded into a series in terms of deviations Q from the initial equilibrium value (Q = 0) or final value (Q = Q_0).

One can show that

$$u_\varkappa^i \sim \bar{\mathscr{E}}_k(0), \qquad u_\varkappa^f \sim \mathscr{E}_k(Q_0),$$
$$\gamma_\varkappa^i \sim \frac{\partial \bar{\mathscr{E}}_k}{\partial Q}\Big|_{Q=0}, \qquad \gamma_\varkappa^f \sim \frac{\partial \bar{\mathscr{E}}_k}{\partial Q}\Big|_{Q=Q_0}, \tag{6}$$

where $\bar{\mathscr{E}}_k(Q)$ are the Fourier components of $\bar{\mathscr{E}}(r, Q)$.

Terms proportional to $q_\varkappa$ in (4) and (5) describe the direct interaction between the molecule's charge and the medium. The last terms in (4) and (5) describe interaction of the intramolecular vibrations with the vibrations of the medium molecules.

Divergence of the integral over t in relation (2) is the mathematical manifestation of the lack of irreversibility in (2). Thus, studying the conditions securing irreversibility of the transition implies, mathematically, studying the conditions under which the integral over t in (2) converges, i.e., studying the behavior of f(t) at $|t| \to \infty$.

Direct Charge–Medium Interaction. We commence the discussion with the case where the transition results in charge redistribution in the molecule (impurity center) and, hence, in a change in charge–medium interaction. Initially we shall disregard the interaction of intramolecular vibrations with the vibrations of the medium. This means that we discuss the case where

$$u_\varkappa^i \neq u_\varkappa^f \neq 0,$$
$$\gamma_\varkappa^i = \gamma_\varkappa^f = 0. \tag{7}$$

Conditions (7) imply that the particle's interaction with the dielectric continuum gives rise to nonzero average polarization of the medium (corresponding to a displacement of the equilibrium coordinate by the amount $q_{\varkappa 0}^{i(f)} = u_\varkappa^{i(f)}/\hbar\omega_\varkappa$). This average polarization is not the same in the initial and final state [$q_{\varkappa 0}^f - q_{\varkappa 0}^i = (u_\varkappa^f - u_\varkappa^i)/(\hbar\omega_\varkappa) \neq 0$].

One must examine the behavior of Re f(t) at $|t| \to \infty$ in order to analyze convergence of the integral of (2). In [9] $\bar{W}_{i\to j}$ was calculated on the assumption that conditions (7) are satisfied, and an expression for function f(t) was obtained in which the real part is of the form of

$$\mathrm{Re}\, f(t) = -\frac{1}{2\pi^2\hbar}\sum_k |\Delta\bar{\mathscr{E}}_k|^2 \cdot \int_0^\infty \frac{\mathrm{Im}\,\varepsilon(\omega)}{\omega^2|\varepsilon(\omega)|^2}\,\mathrm{cth}\frac{\beta\hbar\omega}{2}\sin^2\frac{\beta\hbar\omega}{2}t\,d\omega - Q_0^2\,\mathrm{cth}\frac{\beta\hbar\Omega}{2}\sin^2\frac{\beta\hbar\Omega}{2}t \equiv g_1(t) + g_2(t), \tag{8}$$

where $\varepsilon(\omega)$ is the medium's dielectric permittivity, and $\Delta\bar{\mathscr{E}}_k \equiv \bar{\mathscr{E}}_k(Q_0) - \bar{\mathscr{E}}_k(0)$.

The second term, which depends on the intramolecular vibration, is restricted in absolute value when $t \to \pm\infty$. Integral (2) converges when the medium's average polarization does not change as a result of the transition [$\mathscr{E}_k(Q_0) = \mathscr{E}_k(0)$]. This means that irreversibility of the process is not secured when the transition only involves intramolecular vibrations. This is due to the discrete character of the spectrum exhibited by the whole system.

The behavior of $g_1(t)$ at $t \to \pm\infty$ depends on the properties of function $\mathrm{Im}\,\varepsilon(\omega)/|\varepsilon(\omega)|^2 \cdot \omega$ at $\omega \to 0$. In cases where the medium characterized by this quantity has a spectrum with band structure, i.e., where $\mathrm{Im}\,\varepsilon(\omega)/\omega|\varepsilon(\omega)|^2 = 0$ for $\omega \leq \omega_0$ (which is typical, e.g., for crystals), $|g_1(t)|$ will be finite for $t \to \pm\infty$, and the integral of (2) will be divergent. But under the condition where

$$\lim_{\omega\to 0}\frac{\mathrm{Im}\,\varepsilon(\omega)}{|\varepsilon(\omega)|^2}\frac{1}{\omega} = \mathrm{const}, \tag{9}$$

which is typical for polar liquids [5] (since their spectra contain absorption bands corresponding to hindered rotation of the solvent molecules), we have

$$\lim_{|t|\to\infty} g_1(t) = -\frac{1}{4\pi\hbar}\sum_k |\Delta\bar{\mathscr{E}}_k|^2 \left[\frac{\mathrm{Im}\,\varepsilon(\omega)}{|\varepsilon(\omega)|^2}\frac{1}{\omega}\right]_{\omega=0} |t|. \tag{10}$$

This behavior of function $g_1(t)$ at $|t| \to \infty$ secures convergence of the integral over t in (2), and hence irreversibility of the process. It follows from the above analysis that even in systems containing an infinite

number of vibrational degrees of freedom, irreversibility need not always take place. For the case discussed, the requirement essentially is that of a really continuous spectrum, i.e., of a spectrum containing limitingly low frequencies ($\omega \to 0$) (see condition (9)).

The final expressions resulting in this case for $\bar{W}_{i \to f}$ for tight and weak binding have been reported in [9]. Thus, in the case of tight binding with the medium, the light absorption spectrum (its shape is governed by $\bar{W}_{i \to f}$ as function of the frequency, ν, of the absorbed light) represents a Gaussian line or a set of Gaussian lines of different intensities. In the case of weak binding with the medium, the spectrum is Lorentzian in shape or consists of Lorentzian lines of different intensities. A similar result is obtained for the dependence of the electron transfer rate constant on ΔJ.

Interaction of the Intramolecular Vibrations with the Vibrations of the Medium. The approximation where the electronic transition is tightly bound to the intramolecular vibration but interaction with the surrounding medium is weak is discussed as a reasonable physical model for a number of processes. The question arises as to the physical mechanism that can secure irreversibility of the transition in this case.

It had been shown above that in cases where condition (9) is fulfilled, irreversibility is found when $u_\varkappa^i \neq u_\varkappa^f$. Thus, when there is a change in interaction with the medium due to the charge redistribution occurring in the molecule as a result of the electronic transition, it will suffice to secure irreversibility of the transition no matter how small it is.

But when there is no change in the interaction of charge with the medium as a result of the transition ($u_\varkappa^i = u_\varkappa^f$), then one must examine whether irreversibility can come about on account of interaction of the intramolecular vibrations with the vibrations of the medium.

1. First we consider the case where this interaction is the same in the initial and final state:

$$u_\varkappa^i = u_\varkappa^f; \quad \gamma_\varkappa^i = \gamma_\varkappa^f = \gamma_\varkappa \neq 0. \tag{11}$$

Conditions (11) imply that in each of the electronic states, interaction of the particle with the medium gives rise to a change, both in the system of normal coordinates and frequencies of the medium and in the frequency of the intramolecular vibration. But this change is the same in the initial and final state. Accurately to terms on the order of $\gamma_\varkappa$, the difference in the medium's normal equilibrium coordinates is given by $\gamma_\varkappa Q_0/2(\hbar\Omega - \hbar\omega_\varkappa)$ (we assume that $\omega_\varkappa < \Omega$ for all $\varkappa$). Thus, interaction of the intramolecular vibrations and polarization vibrations of the medium also gives rise to a change in average medium polarization.

Assuming that $\gamma_\varkappa$ is a small parameter, one can show tha Ref(t) is given by

$$\mathrm{Re}\, f(t) \simeq -\frac{Q_0^2}{8\pi^2\hbar}\sum_k \left|\frac{\partial \bar{\mathscr{E}}_k}{\partial Q}\right|^2 \cdot \int \frac{\mathrm{Im}\,\varepsilon(\omega)}{|\varepsilon(\omega)|^2}\,\mathrm{cth}\frac{\beta\hbar\omega}{2}\sin^2\frac{\beta\hbar\omega t}{2}\frac{1}{(\Omega-\omega)^2}\,d\omega - Q_0'^2\,\mathrm{cth}\frac{\beta\hbar\Omega'}{2}\sin^2\frac{\beta\hbar\Omega'}{2}t \equiv g_3(t) + g_4(t), \tag{12a}$$

$$Q_0' \simeq Q_0 - \frac{1}{8}\sum_\varkappa \frac{\gamma_\varkappa^2(2\hbar\omega_\varkappa - \hbar\Omega)}{(\hbar\Omega - \hbar\omega_\varkappa)^2\hbar\Omega}$$

$$\hbar\Omega' \simeq \hbar\Omega + \sum_\varkappa \frac{\gamma_\varkappa^2}{4(\hbar\Omega - \hbar\omega_\varkappa)}, \tag{12b}$$

which is accurate to terms on the order of $\gamma_\varkappa^2$.

In deriving (12), as in (8), we have made use of the sum rule of [4], where the sum over ν can be expressed as an integral over ω. The condition $(\mathrm{Im}\,\varepsilon)/(|\varepsilon|^2)\,(1/\omega) \sim (1/\omega^2)$ must be satisfied for $\omega \to 0$ when it is required that $g_3(t)$ increase in absolute value for $t \to \pm\infty$ (one can show that this condition is not tied to the use of perturbation theory with respect to $\gamma_\varkappa$ but arises with $\gamma_\varkappa$ of any order of magnitude). But equality (9) holds for most physically reasonable approximations of $\mathrm{Im}\,\varepsilon/|\varepsilon|^2$ in polar liquids and disordered solids, and implies that the integral of (2) is divergent when (11) is fulfilled.

Thus, interaction of the intramolecular vibrations with the vibrations of the medium has the effect that the medium is somehow (randomly) acting upon the molecule, but this action does not secure irreversibility when it is the same in the initial and final state.

It will be seen from what follows that a stronger inverse action of the molecule on the medium is needed to secure irreversibility, viz., a change in the interaction of vibrations during the transition.

2. Consider the case where direct interaction of the charge with the medium does not change but interaction of the vibrations in the initial and final state is different:

$$u_\varkappa^i = u_\varkappa^f,$$
$$\gamma_\varkappa^i \neq \gamma_\varkappa^f \neq 0. \tag{13}$$

Unlike the previous case, the entire system of normal vibrations and frequencies changes as a result of the electronic transition. Accurately to terms in $(\gamma_\varkappa^{i,f})^2$ the real part of function f(t) is of the form of

$$\operatorname{Re} f(t) \simeq g_5(t) + g_6(t) + g_4(t); \tag{14}$$

$$g_5 = -\frac{Q^2}{8\pi^2\hbar}\sum_{\bar{k}}\left|\frac{\partial\bar{\mathscr{E}}_{\bar{k}}(0)}{\partial Q}\right|^2 \int \frac{\operatorname{Im}\varepsilon}{|\varepsilon|^2}\operatorname{cth}\frac{\beta\hbar\omega}{2}\sin^2\frac{\beta\hbar\omega}{2}t\frac{1}{(\Omega-\omega)^2}d\omega -$$

$$-\frac{Q^2}{8\pi^2\hbar}\sum_{\bar{k}}\left|\frac{\partial\Delta\bar{\mathscr{E}}_{\bar{k}}}{\partial Q}\right|^2 \int \frac{\operatorname{Im}\varepsilon}{|\varepsilon|^2}\operatorname{cth}\frac{\beta\hbar\omega}{2}\sin^2\frac{\beta\hbar\omega}{2}t\frac{d\omega}{\omega^2} -$$

$$-\frac{Q^2}{4\pi^2\hbar}\sum_{\bar{k}}\left|\frac{\partial\bar{\mathscr{E}}_{\bar{k}}(0)}{\partial Q}\frac{\partial\Delta\bar{\mathscr{E}}_{\bar{k}}}{\partial Q}\right|^2 \int \frac{\operatorname{Im}\varepsilon}{|\varepsilon|^2}\operatorname{cth}\frac{\beta\hbar\omega}{2}\sin^2\frac{\beta\hbar\omega}{2}t\frac{d\omega}{\omega(\Omega-\omega)}; \tag{14a}$$

$$g_6 = -\frac{1}{4\pi^2\hbar}\sum_{\bar{k}}\left|\frac{\partial\Delta\bar{\mathscr{E}}_{\bar{k}}}{\partial Q}\right|^2 \int \frac{\operatorname{Im}\varepsilon}{|\varepsilon|^2}\left\{\frac{\sin^2\frac{\beta\hbar(\omega+\Omega)t}{2}}{(\omega+\Omega)^2}\left[\frac{\exp(\beta\hbar\Omega)}{\exp(\beta\hbar\Omega)-1}+\frac{\operatorname{cth}\frac{\beta\hbar\Omega}{2}}{\exp(\beta\hbar\omega)-1}\right]+\right.$$
$$\left.+\frac{\sin^2\frac{\beta\hbar(\Omega-\omega)t}{2}}{(\Omega-\omega)^2}\left[\frac{1}{\exp(\beta\hbar\Omega)-1}+\frac{\operatorname{cth}\frac{\beta\hbar\Omega}{2}}{\exp(\beta\hbar\omega)-1}\right]\right\}d\omega, \tag{14b}$$

where $\frac{\partial\Delta\bar{\mathscr{E}}_{\bar{k}}}{\partial Q} \equiv \frac{\partial\bar{\mathscr{E}}_{\bar{k}}}{\partial Q}\Big|_{Q=Q_0} - \frac{\partial\bar{\mathscr{E}}_{\bar{k}}}{\partial Q}\Big|_{Q=0}$. At least one of two conditions must be satisfied for perturbation theory to apply with respect to the $\gamma_\varkappa^{i,f}$, and hence for (14) to be correct: a) the medium is transparent in the region of $\omega=\Omega$, i.e., $\operatorname{Im}\varepsilon(\Omega)=0$; and b) in the initial state there is no binding between the vibrations, i.e., $\frac{\partial\bar{\mathscr{E}}_{\bar{k}}(0)}{\partial Q}=0$.

Using condition (9) one can readily show that

$$\lim_{t\to\pm\infty}\left\{\frac{g_5(t)}{|t|}\right\} \simeq \frac{Q_0^2}{16\pi\hbar}\sum_{\bar{k}}\left|\frac{\partial\Delta\bar{\mathscr{E}}_{\bar{k}}}{\partial Q}\right|^2\left[\frac{\operatorname{Im}\varepsilon}{|\varepsilon|^2\omega}\right]_{\omega=0}.$$

Thus, irreversibility of the transition is secured by interaction of the intramolecular vibration with the vibrational modes of the solvent corresponding to infinitely low frequencies when the interaction is different in the initial and final state.

However, one can see from the expression for g_6 that irreversibility can also be secured by interaction of an intramolecular vibration of frequency Ω with the continuous set of medium vibrations having frequencies in the neighborhood of $\omega=\Omega$. Indeed, one can readily show that

$$\lim_{t\to\pm\infty}\left\{\frac{g_6(t)}{|t|}\right\} = -\frac{1}{\pi\hbar}\sum_{\bar{k}}\left|\frac{\partial\Delta\mathscr{E}_{\bar{k}}}{\partial Q}\right|^2\left[\frac{\operatorname{Im}\varepsilon}{|\varepsilon|^2\omega}\right]_{\omega=\Omega}\frac{1}{4\left(\operatorname{sh}\frac{\beta\hbar\Omega}{2}\right)^2}.$$

Analyzing the behavior of function Re f(t) in the different regions of values of parameter t one can obtain information as to the dependence of the transition rate, $\bar{W}_{i\to f}$, on ΔJ or about the shape of the absorption spectrum, $\bar{W}_{i\to f}(\nu)$. The latter, for instance, can be Gaussian or Lorentzian (with or without structure), depending on the degree of binding between the vibrations.

In the case of weak binding, the basic contribution to W is produced, as in the preceding case, precisely by the asymptotic function which is linear in t and secures convergence of the integral of (2). The corresponding transitions are called phononless. Their probability changes with ΔJ according to a Lorentzian law. More detailed relations and criteria will be reported in a separate paper.

It follows from the above analysis that degrees of freedom with a continuous set of frequencies must take part if the electronic transition (intramolecular or between fixed centers) is to occur irreversibly (in the case of polar media, the polarization vibrations of the medium, i.e., phonons, can function as such degrees of free-

dom). This participation can become manifest as a change in charge–medium interaction resulting from the transition or, when such interaction is lacking, as a change in interaction between the intramolecular vibrations and the polarization vibrations of the medium. However, these requirements alone are insufficient. At least one of the following conditions must also be fulfilled:

a) Among the characteristic vibrations of the medium, vibrations with arbitrarily low frequencies are found, i.e., the medium's absorption spectrum is "not trimmed" at zero ($[\mathrm{Im}\,\varepsilon/|\varepsilon|^2\omega]_{\omega=0}\neq 0$). This condition is fulfilled for polar liquids having an absorption band corresponding to hindered rotations of the solvent molecules. The requirement that this condition be met derives from the fact that in the harmonic approximation, transitions with respect to each degree of freedom occur independently within the entire continuous set, and continuity of the spectrum can only be secured by the presence of infinitely low frequencies. Absence of such frequencies mathematically would have the effect that relation (2) contained an infinite number of summations, but each of these summations would be made over a discrete set of values.

b) Among the vibrations of the medium, vibrations with a resonance frequency relative to the intramolecular vibration are found, i.e.,

$$\left[\frac{\mathrm{Im}\,\varepsilon}{|\varepsilon|^2\omega}\right]_{\omega=0}\neq 0.$$

Phononless transitions in impurity centers in polar crystals which occur with weak binding have been analyzed in [13]. The expression used there for $\Delta\hat{H}=H^f-\hat{H}^i$ contains a term $\sum_{\varkappa\varkappa'}\gamma_{\varkappa\varkappa'}q_\varkappa q_{\varkappa'}$. This term describes mutual interaction of the phonon vibrations. The condition of convergence of the integral over t obtained in this work (analyticity of the zeroth Green's function $D_0(\omega)$ on the real axis, and $D_0(\omega)\to 0$ for $\omega\to\infty$) actually is equivalent to the condition of analyticity of $\mathrm{Im}\,\varepsilon(\omega)/|\varepsilon(\omega)|^2$ with respect to the real axis and to the condition of

$$\left[\frac{\mathrm{Im}\,\varepsilon}{|\varepsilon|^2\omega}\right]_{\omega=0}\neq 0.$$

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