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CONTRIBUTION TO THE THEORY OF ELEMENTARY ELECTRON TRANSFER REACTIONS IN POLAR LIQUIDS

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A general formula is derived for the probability $W_{I,II}$ of a nonradiative transition with charge transfer in a linear medium with an arbitrary dielectric constant $\epsilon(\mathbf{r}, \omega)$. The formula is applied to reactions of the type $Fe^{3} + Fe^{2+} \rightarrow Fe^{2+} + Fe^{3+}$ in water. If the real dispersion of water is taken into account, the energy activation of the process is found to differ by 25% from the values in other papers,[4,5] and the dependence of $W_{I,II}$ on the transition energy is found to be different. The effect of oscillations of the ion complexes on the transition probability is investigated.

CONSIDERABLE interest has been evinced recently in the mechanism of reactions with charge transfer in polar liquids (see the review[1-4]). Such transitions are characterized by very strong interaction of the ionic states with the medium. For solids, the theory of multiphonon transitions in the case of strong coupling with the medium was developed by Lax[5] and by Kubo and Toyozawa[6] and was applied to reactions in liquids by Levich and Dogonadze[7]. However, this theory employs essentially the model of vibrational oscillators of a solid. For a liquid, where the absorption of energy is connected mainly with reorientation relaxation of the molecules of the medium, it is therefore necessary to have a theory not based on model oscillator representations of medium. In this paper we obtain a general formula for the nonradiative transition probability, using only the assumption that the medium is linear, i.e., that Maxwell's equations hold in it.

The developed theory is applied to well-investigated reactions[1-4] of the type

$$Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}.$$

An essential feature of such reactions is that, besides the strong interaction of the ions with the nearest molecules of the medium, forming the so-called solvate complexes, an important fact (as first pointed out by Libby[8]) is also an interaction with large region of the medium, a region that can be regarded as a continuous dielectric. Although the existing calculations[4] of the complexes are not quantitative in character, they do show the need for taking the oscillations of the complexes in such reactions into account. To the contrary, the influence of the dielectric medium can be taken into account with sufficient accuracy. The most complete account of the dielectric medium was carried out by Marcus[9] and by Levich and Dogonadze[7][1]. Following Pekar, the polarization of the medium was subdivided into a fast part and a slow part that cannot follow the fluctuations of the field in the medium. In this case, the dependence of the reorganization energy on the dielectric properties of the medium is contained in the well known Pekar factor $E_r \sim (1/\epsilon(\infty) - 1/\epsilon(0))$. However, in the presence of a continuous dielectric-absorption spectrum the subdivision of the polarization into fast and slow parts is ambiguous. It follows already from the work of Dogonadze and Kuznetsov[13] that a criterion for the slowness should be a comparison of the frequencies with $kT/\hbar$. However, no quantitative expression was obtained for the characteristics of the process in terms of the experimentally observed frequency properties of the medium.

In this paper we express the transition probability (Sec. 1), in terms of $\epsilon(\omega)$—the dielectric constant of the medium—and apply the expression to reactions in water, with allowance taken for its real dispersion (Sec. 2). The energy dependence of the transition (or of the heat of the reaction) is investigated. Finally, in Sec. 3 we discuss the role of the high-frequency oscillations of the molecules of the complexes.

1. TRANSITION PROBABILITY IN A MEDIUM WITH ARBITRARY DIELECTRIC CONSTANT

For concreteness we derive the general formula with reactions of the type (1) as an example, although the results are directly applicable to any intramolecular transition with a redistribution of the charge in a polar medium.

We assume the following model of the medium. Inside certain spheres around the ions, we have a region of oriented molecules producing octahedral complexes of the type $Fe^{2+}(H_2O)_6$. These complexes are characterized by sets of vibrational coordinates. When the ion charges change, a change takes place in the equilibrium positions of these oscillators, and generally speaking in their frequencies. The region outside these spheres is described as a continuous dielectric with a dielectric constant $\epsilon(\mathbf{r}, \omega)$.

The Hamiltonian $\hat{H}^i$ of the system in each of the electronic states i = I and II is written in the form

$$\hat{H}^i = H_c{}^i + H_d{}^i + I^i. \qquad (1)$$

Here I^I and I^{II} are the electron energies in the electronic states I and II, without allowance for the interaction of the charges with the dielectric medium. The

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[1] This approach was used later for the analysis of electrode reactions [10,11], and also for reactions in which a proton takes part [12].

Hamiltonian

$$\hat{H}_{\mathrm{c}}^{i}=\sum_{j}\frac{1}{2}\hbar\Omega_{j}\left[\frac{\partial^{2}}{\partial Q_{j}^{2}}+(Q_{j}-\overline{Q}_{j}^{i})^{2}\right] \tag{2}$$

describes the vibrations of the molecules of the complexes. Finally, the second term is given by

$$\hat{H}_{\mathrm{d}}^{i}=\hat{H}_{0}+\hat{V}^{i}=\hat{H}_{0}+\int\int\rho_{i}(\mathbf{r})\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{3}}\hat{\mathbf{P}}(\mathbf{r}')\,dv\,dv', \tag{3}$$

where $\hat{H}_0$ is the Hamiltonian of the medium plus the electron field (without extraneous charges), $\hat{V}^i$ is the interaction with the extraneous charges, written in a Coulomb gauge, $\rho_i(\mathbf{r})$ is the density of these charges in the i-th electron state, and $\hat{\mathbf{P}}(\mathbf{r})$ is the polarization operator.

The probability of transition between two electronic states, in first order of perturbation theory in the interaction between them, is equal to[6]:

$$W_{\mathrm{I,\,II}}=|V_{\mathrm{I,\,II}}|^{2}\int_{-\infty}^{\infty}G(t)\,dt, \tag{4}$$

$$G(t)=\{\mathrm{Sp}\,(\exp\,[-\beta\hat{H}^{\mathrm{I}}])\}^{-1}\,\mathrm{Sp}\,\{\exp\,[(it-\beta)\hat{H}^{\mathrm{I}}]\exp\,[-i\hat{H}^{\mathrm{II}}t]\}, \tag{4a}$$

$V_{\mathrm{I,II}}$ are the matrix elements of the perturbation causing the transition, and are assumed for simplicity to be independent of the coordinates of the medium. Assuming the operators $\hat{H}_c$ and $\hat{H}_d$ to commute, we rewrite the function G(t) in the form

$$G(t)=G_{\mathrm{K}}(t)G_{\mathrm{d}}(t)\exp\,(-i\Delta\tilde{I}t),\qquad \Delta\tilde{I}=I^{\mathrm{II}}-I^{\mathrm{I}}, \tag{5}$$

and the functions $G_c(t)$ and $G_d(t)$ are determined by formula (4a) in which the Hamiltonians $\hat{H}^i$ are replaced by $\hat{H}_c^i$ and $\hat{H}_d^i$, respectively.

The functions $Q_c(t)$ were calculated for oscillator Hamiltonians several times[6,7]. We present the corresponding formulas for the case when the frequencies Ω_j of the oscillators remain unchanged

$$G_{\mathrm{c}}(t)=\exp\left\{\sum_{j}\frac{(\Delta Q_{j})^{2}}{2}\frac{\mathrm{ch}(\Omega_{j}/2kT-i\Omega_{j}t)-\mathrm{ch}(\Omega_{j}/2kT)}{\mathrm{sh}(\Omega_{j}/2kT)}\right\}, \tag{6}$$
$$\Delta Q_{j}=Q_{j}^{\mathrm{II}}-Q_{j}^{\mathrm{I}}.$$

We proceed not to derive the formulas for the function $G_d(t)$, which describes a nonradiative transition with charge transfer in a dielectric medium:

$$G_{\mathrm{d}}(t)=\langle\exp\,(-i\hat{H}_{\mathrm{d}}^{\mathrm{II}}t)\exp\,(i\hat{H}_{\mathrm{d}}^{\mathrm{I}}t)\rangle_{\hat{H}_{\mathrm{d}}^{\mathrm{I}}},$$

where the angle brackets denote averaging over the equilibrium state:

$$\langle\hat{A}\rangle_{\hat{H}}=[\mathrm{Sp}\exp\,(-\beta\hat{H})]^{-1}\,\mathrm{Sp}\,[\hat{A}\exp\,(-\beta\hat{H})].$$

In the Heisenberg representation in terms of $\hat{H}_d^I$, the function $G_d(t)$ is rewritten in the form

$$G_{\mathrm{d}}(t)=\langle T\exp\,\{-i\int_{0}^{t}\Delta\hat{H}_{\mathrm{d}}(t)\,dt\}\rangle_{\hat{H}_{\mathrm{d}}^{\mathrm{I}}}, \tag{7}$$

where T is the chronological ordering parameter and

$$\Delta\hat{H}_{\mathrm{d}}=\hat{H}_{\mathrm{d}}^{\mathrm{II}}-\hat{H}_{\mathrm{d}}^{\mathrm{I}}=-\int\Delta\mathbf{D}(\mathbf{r})\hat{\mathbf{P}}(\mathbf{r})\,dv. \tag{8}$$

Here $\Delta\mathbf{D}=\mathbf{D}^{\mathrm{II}}(\mathbf{r})-\mathbf{D}^{\mathrm{I}}(\mathbf{r})$ is the difference of the vectors of the electric inductions produced by the charges $\rho^{\mathrm{II}}(\mathbf{r})$ and $\rho^{\mathrm{I}}(\mathbf{r})$. Since the averaging is carried out over the equilibrium state for the first arrangement of the charges, we represent the polarization vector $\mathbf{P}(\mathbf{r})$ in the form

$$\hat{\mathbf{P}}(\mathbf{r})=\mathbf{P}_{\mathrm{I}}(\mathbf{r})+\delta\hat{\mathbf{P}}(\mathbf{r}), \tag{9}$$

$\mathbf{P}_{\mathrm{I}}(\mathbf{r})=\langle\hat{\mathbf{P}}(\mathbf{r})\rangle_{\hat{H}^{\mathrm{I}}}$ is the equilibrium polarization in the first state, which is obtained from the solution of Maxwell's equations with $\rho(\mathbf{r})=\rho^{\mathrm{I}}(\mathbf{r})$, and equals

$$\mathbf{P}_{\mathrm{I}}(\mathbf{r})=\frac{\varepsilon(\mathbf{r},0)-1}{4\pi\varepsilon(\mathbf{r},0)}\mathbf{D}^{\mathrm{I}}(\mathbf{r}). \tag{10}$$

Here $\epsilon(\mathbf{r}, 0)$ is the static dielectric static at the point $\mathbf{r}$. Taking (9) and (10) into account, we rewrite ΔH_d in the form

$$\Delta\hat{H}_{\mathrm{d}}=E-\int\Delta D_{j}(\mathbf{r})\delta\hat{P}_{j}(\mathbf{r})\,dv, \tag{11}$$

$$E=\frac{1}{8\pi}\int\Delta\mathbf{D}^{2}(\mathbf{r})\left[1-\frac{1}{\varepsilon(\mathbf{r},0)}\right]dv$$
$$-\frac{1}{8\pi}\int\left[1-\frac{1}{\varepsilon(\mathbf{r},0)}\right][(\mathbf{D}^{\mathrm{II}}(\mathbf{r}))^{2}-(\mathbf{D}^{\mathrm{I}}(\mathbf{r}))^{2}]\,dv. \tag{12}$$

For the function $G_d(t)$ we then have

$$G_{\mathrm{d}}(t)=\exp\,(-iEt)\,\langle T\exp\,\{-i\int\frac{\Delta D_{j}(\mathbf{r})}{4\pi}\int_{0}^{t}dt\,\delta\hat{P}_{j}(\mathbf{r},t)\,dv\}\rangle_{\hat{H}^{\mathrm{I}}}. \tag{13}$$

It is shown in[14] that in the long-wave approximation[15,16] the latter mean value is equal to

$$\langle T\exp\,\{-i\int\frac{\Delta D_{j}(\mathbf{r})}{4\pi}\int_{0}^{t}dt\,\delta\hat{P}_{j}(\mathbf{r},t)\,dv\}\rangle_{\hat{H}^{\mathrm{I}}}=e^{\Phi(t)}, \tag{14}$$

$$\Phi(t)=\frac{-i}{2}\int\int dv_{1}\,dv_{2}\Delta D_{i}(\mathbf{r}_{1})\Delta D_{j}(\mathbf{r}_{2})\int_{0}^{t}dt_{1}\int_{0}^{t}dt_{2}M_{ij}(\mathbf{r}_{1},\mathbf{r}_{2},t_{1}-t_{2}), \tag{15}$$

where

$$M_{ij}(\mathbf{r}_{1},\mathbf{r}_{2},t_{1}-t_{2})=-i\,\langle T\delta P_{i}(\mathbf{r}_{1},t_{1})\,\delta P_{j}(\mathbf{r}_{2},t_{2})\rangle_{\hat{H}^{\mathrm{I}}}. \tag{16}$$

Taking the Fourier transform with respect to time

$$M_{ij}(\mathbf{r}_{1},\mathbf{r}_{2},\tau)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega\tau}M_{ij}(\mathbf{r}_{1},\mathbf{r}_{2},\omega)\,d\omega,$$

we get

$$\Phi(t)=\frac{-i}{2\pi}\int_{-\infty}^{\infty}d\omega\,\frac{1-\cos\omega t}{\omega^{2}}\int\int\Delta D_{j}(\mathbf{r}')\Delta D_{i}(\mathbf{r})M_{ij}(\mathbf{r},\mathbf{r}',\omega)\,dv\,dv'. \tag{17}$$

However, the correlation function $M_{ij}(\mathbf{r}, \mathbf{r}', \omega)$ can be readily expressed in terms of the dielectric constant of the medium $\epsilon(\mathbf{r}, \omega)$. To this end we use the relation[15]

$$\begin{aligned}M_{ij}(\mathbf{r},\mathbf{r}',\omega)&=\mathrm{Re}\,M_{ij}^{R}(\mathbf{r},\mathbf{r}',\omega)\\&+i\,\mathrm{cth}\frac{\omega}{2kT}\,\mathrm{Im}\,M_{ij}^{R}(\mathbf{r},\mathbf{r}',\omega),\end{aligned} \tag{18}$$

where $M_{ij}^{R}(\mathbf{r}, \mathbf{r}', \omega)$ is the Fourier transform of the retarded correlation function

$$M_{ij}^{R}(\mathbf{r},\mathbf{r}',t)=\begin{cases}-i\,\langle\delta\hat{P}_{i}(\mathbf{r},t)\,\delta\hat{P}_{j}(\mathbf{r}',t)-\delta\hat{P}_{j}(\mathbf{r}',0)\,\delta\hat{P}_{i}(\mathbf{r},t)\rangle_{\hat{H}^{\mathrm{I}}}, & t>0.\\ 0, & t<0\end{cases}$$

We relate the latter with $\epsilon(\mathbf{r}, \omega)$ by using the traditional reasoning[15]. Assume that we produce, besides $\mathbf{D}^{\mathrm{I}}(\mathbf{r})$, an additional induction $\mathbf{D}^{\mathrm{ext}}(\mathbf{r}, t) = \mathbf{D}^{0}(\mathbf{r})e^{i\omega t}$ with the aid of additional $\rho^{\mathrm{ext}}(\mathbf{r}, t)$ and $j^{\mathrm{ext}}(\mathbf{r}, t)$ (such, however, as to yield $\int\mathbf{A}(\mathbf{r})j^{\mathrm{ext}}(\mathbf{r})dv = 0$ under the condition $\mathrm{div}\,\mathbf{A}(\mathbf{r}) = 0$).

The perturbation acting in this case is equal to

$$\hat{V}_{\mathrm{ext}}(t)=-\int\mathbf{D}_{i}^{\mathrm{ext}}(\mathbf{r},t)[(\mathbf{P}_{\mathrm{I}}(\mathbf{r}))_{i}+\delta\hat{P}_{i}(\mathbf{r})]\,dv.$$

According to the theory of the linear response, we obtain for the additional polarization the value

$$\langle \delta \hat{P}_i(\mathbf{r}, t)\rangle = -e^{i\omega t}\int M_{ij}^R(\mathbf{r}, \mathbf{r}', \omega)\,(D_j^0(\mathbf{r}'))\,dv'. \tag{19}$$

From the condition that Maxwell's equations hold for the mean values in the linear medium, we require

$$\langle \delta \hat{P_i}(\mathbf{r}, t)\rangle = \frac{1}{4\pi}\frac{\varepsilon(\mathbf{r}, \omega) - 1}{\varepsilon(\mathbf{r}, \omega)} D_i^{\text{ext}}(\mathbf{r}, t) \tag{20}$$

Hence, comparing (18) and (19), in view of the arbitrariness of $D^0(\mathbf{r})$, we obtain

$$M_{ij}^R(\mathbf{r}, \mathbf{r}', \omega) = -\frac{\delta_{ij}}{4\pi}\left[1 - \frac{1}{\varepsilon(\mathbf{r}, \omega)}\right]\delta(\mathbf{r} - \mathbf{r}'). \tag{21}$$

Substituting (18) and (21) in (17) we get

$$\Phi(t) = i\int dv \frac{[\Delta \mathbf{D}(\mathbf{r})]^2}{8\pi^2}$$

$$\times \int_{-\infty}^{\infty} d\omega \frac{1 - \cos \omega t}{\omega^2}\left\{\operatorname{Re}\left(1 - \frac{1}{\varepsilon(\mathbf{r}, \omega)}\right) - i \operatorname{cth}\frac{\omega}{2kT}\operatorname{Im}\frac{1}{\varepsilon(\mathbf{r}, \omega)}\right\}. \tag{22}$$

Taking (5), (13), (12), and (14) into account, we obtain

$$G(t) = G_c(t)\exp\left\{-i\Delta I t - it\int \frac{[\Delta \mathbf{D}(\mathbf{r})]^2}{8\pi}\left(1 - \frac{1}{\varepsilon(\mathbf{r}, 0)}\right)dv + \Phi(t)\right\}, \tag{23}$$

where

$$\Delta I = \Delta \tilde{I} + \frac{1}{8\pi}\int\left[1 - \frac{1}{\varepsilon(\mathbf{r}, 0)}\right][(\mathbf{D}^{\text{II}}(\mathbf{r}))^2 - (\mathbf{D}^{\text{I}}(\mathbf{r}))^2]\,dv \tag{24}$$

is the transition energy with allowance for the change of the electromagnetic energy of the dielectric during the transition.

Using the identity

$$|t| = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}(1 - \cos \omega t)$$

and the dispersion relation for the quantity

$$\frac{1 - e^{i\omega t}}{\omega^2}\left[\frac{1}{\varepsilon(\mathbf{r}, \omega)} - \frac{1}{\varepsilon(\mathbf{r}, 0)}\right]$$

we can easily transform (23) and (22) into

$$G(t) = G_c(t)\exp\left\{-i\Delta I t + \frac{1}{8\pi^2}\int [\Delta \mathbf{D}(\mathbf{r})]^2 \cdot\right.$$

$$\left.\times\left[\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}\frac{\varepsilon''(\mathbf{r}, \omega)}{|\varepsilon(\mathbf{r}, \omega)|^2}\frac{\operatorname{ch}(\omega/2kT - i\omega t) - \operatorname{ch}(\omega/2kT)}{\operatorname{sh}(\omega/2kT)}\right]dv\right\}, \tag{25}$$

where $\epsilon''(\mathbf{r}, \omega) = \operatorname{Im}\epsilon(\mathbf{r}, \omega)$. Formula (25) solves the problem of nonradiative transition with charge transfer in a linear medium with arbitrary $\epsilon(\mathbf{r}, \omega)$.

It is shown in the Appendix that for a medium consisting of oscillators with frequency ω_0, formula (25) coincides with the Kubo formula which is applicable to this case[5,6]. Indeed, for such a medium

$$\varepsilon(\omega) = \frac{a}{\omega_0^2 - \omega^2} + \varepsilon_\infty,$$

$$\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2} = \frac{\pi a}{2\tilde{\omega}_0}[\delta(\omega - \tilde{\omega}_0) - \delta(\omega + \tilde{\omega}_0)],$$

where $\tilde{\omega}_0 = (\omega_0 + a)^{1/2}$ is precisely the frequency of the longitudinal oscillations that take part in the transition, as distinguished from the frequency ω_0 of the transverse oscillations. Here $a = 4\pi\alpha^2\omega_0/v_0$ is expressed in terms of the volume of one oscillator v_0 and the coefficient α of the proportionality of the dipole moment d of the oscillator to its vibrational coordinate q.

2. INVESTIGATION OF $W_{I,II}$ WITH ALLOWANCE FOR THE DIELECTRIC MEDIUM ONLY. APPLICATION TO WATER

In this section we investigate the dependence of the transition mobility on the temperature T and on the transition energy ΔI with allowance for the interaction of the charges only with the dielectric medium. For simplicity we assume further that the medium is homogeneous. Then the transition probability is described by the formula

$$W_{\text{I, II}} = |V_{\text{I, II}}|^2\int_{-\infty}^{\infty} dt\,\exp\{-i\Delta I t - F(t)\}, \tag{26a}$$

$$F(t) = \frac{B}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2}\frac{\operatorname{ch}(\omega/2kT) - \operatorname{ch}(\omega/2kT - i\omega t)}{\operatorname{sh}(\omega/2kT)}.$$

$$B = \int \frac{(\Delta \mathbf{D}(\mathbf{r}))^2}{8\pi}\,dv. \tag{26b}$$

An important factor in the calculation of the integral in (26a) is the presence of the large parameter $B/kT \sim 80 \gg 1$ (from estimates given in[9]). To calculate (26) we can certainly use the saddle-point method, if the saddle point $t_0 = -i\,|\,t_0\,|$ does not go outside the analyticity band $-1/kT < 0$ of the argument of the exponential in (26a).

Let us consider first the case of resonant reactions, when $\Delta I = 0$. Then the saddle point, independently of the form of $\epsilon(\omega)$, is equal to $-i/2kT$. Indeed, $F'(-i/2kT) = 0$. In this case the transition probability is

$$W_{\text{I, II}} = |V_{\text{I, II}}|^2\sqrt{2\pi}\left[F''\left(\frac{-i}{2kT}\right)\right]^{-1/2}\exp\left\{-\frac{B}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2}\operatorname{th}\frac{\omega}{4kT}\right\}. \tag{27}$$

For a concrete application of (26) and (27) to reactions in water, we turn to the dielectric properties of water, which have been thoroughly investigated for all frequencies, and are discussed in detail, for example, in the survey of Saxton[17]. It has been shown that there are two broad regions of absorption at $\omega^{-1} \sim 10^{-11}$ sec and $\omega^{-1} \sim 0.4 \times 10^{-14}$ sec, called the Debye dispersion and the resonance absorption regions. In the first region $\epsilon'(\omega)$ decreases from its static value $\epsilon_s = \epsilon(0) = 78$[2] to an intermediate value $\epsilon_{\text{int}} = 4.9$, and finally in the second absorption region $\epsilon'(\omega)$ decreases from $\omega_{\text{int}} = 4.9$ to $\omega_{\text{opt}} = 1.8$. Analytic expressions for $\epsilon'(\omega)$ and $\epsilon'(\omega)$, which describe the experiment well, are given in[14]. Combining them in one formula, we get for water

$$\varepsilon(\omega) = \varepsilon_{\text{opt}} + \frac{\varepsilon_s - \varepsilon_{\text{int}}}{1 + i\omega\tau_D} + \frac{\varepsilon_{\text{int}} - \varepsilon_{\text{opt}}}{2}\left[\frac{1 - i\omega_r\tau_r}{1 - i(\omega + \omega_r)\tau_r} + \frac{1 + i\omega_r\tau_r}{1 - i(\omega - \omega_r)\tau_r}\right], \tag{28}$$

where the parameters are[14]: $\tau_D = 0.85 \times 10^{-11}$ sec ($T = 300°$), $\omega_r = 6.67 \times 10^{12}\ \text{sec}^{-1}$, and $\tau_r = 3.84 \times 10^{-14}$ sec. Since $\tau_D \gg \tau_r$, we can easily obtain an analytic expression for $\epsilon''(\omega)/|\epsilon(\omega)|^2 = \operatorname{Im}(1/\epsilon(\omega))$:

$$\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2} = A_0\frac{\omega\tau_0}{1 + \omega^2\tau_0^2} + A_1\frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + A_2\frac{\omega\tau_2}{1 + \omega^2\tau_2^2}, \tag{29}$$

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[2] Further in the calculations we use $\epsilon_s = 60$, as in [7,9], in order to take into account the influence of the electric field.

where

$$\tau_0 = \frac{\varepsilon_{\text{int}}}{\varepsilon_s}\tau_D, \quad \tau_{1,2} = \frac{\tau_2}{a_{1,2}},$$

$$a_{1,2} = \frac{\varepsilon_{\text{int}} - \varepsilon_{\text{opt}}}{2\varepsilon_{\text{opt}}} \pm \left[\left(\frac{\varepsilon_{\text{int}} - \varepsilon_{\text{opt}}}{2\varepsilon_{\text{opt}}}\right)^2 - \frac{\varepsilon_{\text{int}}}{\varepsilon_{\text{opt}}}\omega_r^2\tau_r^2\right]^{1/2},$$

$$A_0 = \frac{1}{\varepsilon_{\text{int}}} - \frac{1}{\varepsilon_s}, \quad A_1 = \frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_{\text{int}}} + \delta, \quad A_2 = -\delta.$$

Since the expression for δ is complicated, we present only the numerical value, $\delta = 0.026$. Substitution of (29) and (26) and a change to the dimensionless variable $\omega\tau_j \to \omega'$ yields

$$F(t) = \frac{B}{4kT}\sum_{j=0}^{2}\frac{A_j}{x_j}\frac{2}{\pi}\int_{-\infty}\frac{d\omega'}{\omega'(1+\omega'^2)}\frac{\operatorname{ch}(x_j - it/\tau_j)\omega' - \operatorname{ch} x_j\omega'}{\operatorname{sh} x_j\omega'}. \quad (30)$$

We have introduced here the dimensionless quantities $x_j = \frac{1}{2}kT\tau_j$.

We now turn to discuss the resonant reaction. For the argument of the exponential in (27) we then have the expression

$$F\left(\frac{-i}{2kT}\right) = \frac{B}{\pi kT}\sum_{j=0}^{2}\frac{A_j}{x_j}\left[\psi\left(\frac{1}{2} + \frac{x_j}{2\pi}\right) - \psi\left(\frac{1}{2}\right)\right\}; \quad (31)$$

where $\psi(z)$ is the psi-function[18].

The result of Marcus[9] and of Levich and Dogonadze[7] for the argument of the exponential when $\Delta I = 0$ with allowance for the relation

$$\sum_{j=0}^{2} A_j = \frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_s}$$

is written in our notation in the form

$$F(t_0) = \frac{E_{\text{p}}}{4kT}; \quad E_{\text{r}} = B\sum_{j=0}^{2} A_j. \quad (32)$$

Recognizing that $\psi'(\frac{1}{2}) = \pi^2/2$, we can readily see that (32) is the first term of the expansion (31) in terms of $x_j/2\pi = \hbar/4\pi kT\tau_j$, i.e., of the high-temperature expansion. (The parameters x_0, x_1, and x_2 at $T = 300°$ are equal respectively to 1.83×10^{-2}, 0.867, and 0.368.) Since, however, $E_r/4kT$ is large, we cannot confine ourselves to the first term of the expansion (31). Substituting in (31) the numerical parameters for $T = 300°$, we obtain

$$F(t_0) = 0.81 E_{\text{r}}/4kT. \quad (33)$$

Let us consider now the dependence of $W_{\text{I,II}}$ on the heat of the reaction ΔI for nonresonant reactions. The equation has on the saddle point t_0 the form

$$i\Delta I = F'(t_0 = -iz/2kT),$$

$$F'\left(\frac{-iz}{2kT}\right) = -\frac{iB}{\pi}\sum_{j=0}^{2} A_j \int_{-\infty}^{\infty}\frac{d\omega'}{1+\omega'^2}\frac{\operatorname{sh} x_j(1-z)\omega'}{\operatorname{sh} x_j\omega'} \quad (34)$$

and the argument of the exponential L in the formula $W_{\text{I,II}} \sim \exp(-L)$ no longer has the simple form $L = (\Delta I + E_r)^2/4E_r kT$, which is quadratic in ΔI, as in[7,9]. We present its form for the case of small resonance defects $\Delta I \ll E_r$:

$$L = \frac{\alpha_1 E_{\text{r}}}{4kT} + \frac{\Delta I}{2kT} - \frac{\Delta I}{4kT\alpha_2 E_{\text{r}}}\left[1 + O\left(\frac{\Delta I}{E_{\text{r}}}\right)\right]. \quad (35)$$

At $T = 300°\text{K}$ we have for water $\alpha_1 = 0.81$ and $\alpha_2 = 0.85$. It is interesting to note that (35) is close to the simple quadratic form[7,9] when E_r is replaced in it by $0.8E_r$.

Finally, in the case of large negative resonance defects $\Delta I < -E_r$[3)] the activation dependence of $W_{\text{I,II}}$ on T no longer holds. Indeed, when $\Delta I = -iF'(0) = -E_r$, the saddle point t_0 coincides with $t = 0$, which is the branch point of the function $F(t)$, namely $F(t)_{t\to 0} \sim t^2 \ln t$. Therefore at $\Delta I < -F(0)$, when $\operatorname{Im} t_0 > 0$, the integral (26) is estimated as a sum of two contributions: from the contour around the cut from $t = 0$, and from the saddle point t_0. The latter contribution is smaller, so that calculation of the integral along the cut yields

$$W_{\text{I, II}} = \frac{2E_{\text{r}}|V_{\text{I, II}}|^2\sum_{j=0}^{2}(A_j/\tau_j)}{(\Delta I - E_{\text{r}})^3(\sum_j A_j)}. \quad (36)$$

It is easy to explain physically this difference between our result and the result of[7], where the spectrum consisted of only one frequency ω_0. It is due to the fact, well known in the theory of nonradiative transitions, that it is easier to dissipate a large transition energy with high-frequency quanta than with low-frequency quanta. Thus, in our system, in which the dielectric-loss spectrum is continuous, the center of gravity of the frequencies at which the reaction energy ΔI is mainly absorbed changes with changing ΔI. It is seen from (36) that when $\Delta I < -E_r$ the absorption occurs mainly in the region of resonant absorption.

3. ALLOWANCE FOR THE INFLUENCE OF THE OSCILLATIONS OF THE ION COMPLEXES

The calculated activation energies can be compared with experiment only when account is taken of the internal oscillations of the ion complexes. In fact it is known that reactions with charge transfer, of the type (1), have for different ions (for example Fe^{2+} and V^{2+}) different activation energies[4)], whereas the dielectric part of the activation energy is the same for such relations.

According to the present notions, multiply charged ions of metals form in water octahedral complexes (of the type $Fe(H_2O)_6^{3+}$[19]). The oscillations of the water molecules forming the hydrate shell of the ion are hindered to a considerable degree compared with the oscillations of the molecules of the normal water.

Attempts to calculate the ion complexes on the basis of the electrostatic model are contained in a number of papers (see, for example[19]). A prominent position is occupied in the calculation by the radius of the complex, which is calculated as the sum of the radii of the nonhydrated ion of the metal and the crystalline radius of the water in ice.

During the course of the reaction, only the radius of the complex changes. The frequency of the fully-symmetrical oscillations corresponding to a change of this

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[3)] Although such a situation is not realized in reactions of the type (1), nonetheless this is the most typical case for nonradiative electronic transitions inside one molecule situated in a polar solvent.

[4)] The difference usually amounts to several kcal [3].

radius is ~400 cm^{-1}. Recognizing that the difference of the ionic radii of the non-hydrated iron ions Fe^{2+} and Fe^{3+} amounts to 0.16 Å, the reorganization energy of the complex on going from Fe^{2+} to Fe^{3+} was calculated in the book[15] and turned out to be ~ 30 kcal. The additional activation energy in the reaction constant amounts in this case to 7—8 kcal, which cannot be reconciled in any way with the experimental value. Thus, the use of the electrostatic model and ionic radii is not satisfactory. Moreover, from quantum-chemical calculations of such complexes[20] follows the need for taking into account the exchange forces, and this brings other types of oscillations into play in the transition, particularly librations. Another indication of the part played by libration oscillations is the increase of the activation energy of the process in heavy water[3].

Starting from these considerations, we present a model calculation of the activation energy of the transition, assuming that the coordinates of the libration oscillators with frequency $\Omega_j = \Omega_0 = 1000\ cm^{-1}$ change during the course of the reaction. Such a frequency is reasonable if it is recognized that the frequency of the libration oscillations in water is 670 cm^{-1} and should increase strongly as the ion molecules become fixed in the field of the ion.

Let us consider again the case $\Delta I = 0$. Then the saddle point in the integration (4) remains equal to $t_0 = -1/2kT$ also in the case when $G_c(t)$ is chosen in the form (6). In this case the transition probability $W_{I,II}$ has the following form (disregarding the factor preceding the exponential)

$$W_{\mathrm{I,II}} \sim \exp\left[-F(t_0) - F_c(t_0)\right], \tag{37}$$

where $F(t_0)$ is given by (31) and $\exp[-F_c(t_0)] = G_c(t_0)$. The activation energy E_a of the transition, which differs from the total activation energy of the reaction-rate constant by the ion-repulsion energy[5], is defined as the derivative of the argument of the exponential in (37) with respect to $1/kT$. Calculating this derivative, we obtain at T = 300°

$$E_a = 0.75\frac{E_r}{4} + \frac{E_c}{4}\,\mathrm{ch}^{-2}\frac{\Omega_0}{4kT}. \tag{38}$$

The reorganization energy of the medium E_r is in this case, according to[4], equal to 6.8 kcal for a distance 6.9 Å between ions, and $E_c = (1/2)\Omega_0\sum_j[\Delta Q_j]^2$ is a parameter characterizing the difference between the elastic energy of the complexes of the ions Fe^{2+} and Fe^{3+}, and will be estimated by comparing the reactions in water and in heavy water. At T = 300° we get for H_2O

$$E_a(H_2O) = 0{,}75\frac{E_r}{4} + 0.28\frac{E_c}{4}.$$

At the same time, for D_2O in the same model ($\Omega_0 = 710\ cm^{-1}$), we have (the dielectric constants of H_2O and D_2O differ little[3]):

$$E_a(D_2O) = 0.75\frac{E_r}{4} + 0.50\frac{E_c}{4}.$$

Since experimentally $E_a(D_2O) - E_a(H_2O) = 0.9$ kcal, we get from this $E_c/4 \sim 4.1$ kcal. Thus, the contribution of the oscillations of the complexes to the activation energy of the transition amounts to 20% of the entire activation energy for H_2O.

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APPENDIX

We shall show that formula (23) coincides with the Kubo formula for a medium consisting of three-dimensional oscillators with frequency ω_0. The Hamiltonian of such a medium and of the electromagnetic field, including the interaction with the extraneous charges $\rho(\mathbf{r})$, currents $\mathbf{j}(\mathbf{r})$, with a gauge div $\mathbf{A}(\mathbf{r}) = 0$, is given by

$$\begin{aligned}\hat{H} = {} & \sum_n \hbar\omega_0 \sum_i \left(\frac{\partial^2}{\partial q_n^{i2}} + q_n^{i2}\right) + \frac{1}{2}\iint \frac{\operatorname{div}\mathbf{P}(\mathbf{r})\operatorname{div}\mathbf{P}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,dv\,dv' \\ & - \iint \frac{\rho(\mathbf{r})\operatorname{div}\mathbf{P}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^2}\,dv\,dv' + \frac{1}{8\pi}\int\left\{\left(\frac{\partial\mathbf{A}}{\partial t}\right)^2 + (\operatorname{rot}\mathbf{A})^2\right\}dv \\ & - \int \mathbf{P}(\mathbf{r})\mathbf{A}(\mathbf{r})\,dv - \int \mathbf{j}(\mathbf{r})\mathbf{A}(\mathbf{r})\,dv.\end{aligned} \tag{A.1}$$

The dipole moment of the oscillator at the point $\mathbf{r}_n$ is proportional to its vibrational coordinate: $\mathbf{d}_n = \alpha \mathbf{q}_n$, so that $\mathbf{P}(\mathbf{r}) = \alpha\Sigma \mathbf{q}_n\delta(\mathbf{r} - \mathbf{r}_n)$. The dielectric constant of such a medium can be readily obtained, for example, from the linear response to the perturbation $V = -\int \mathbf{P}(\mathbf{r})\mathbf{A}(\mathbf{r})dv$, and is equal to

$$\varepsilon(\omega) = 1 + \frac{a}{\omega_0^2 - (\omega + i\delta)^2}, \quad \delta \to 0, \quad a = \frac{4\pi\alpha^2\omega_0}{v_0},$$

v_0 is the volume of one oscillator. From this we get directly

$$\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)|^2} = -\operatorname{Im}\frac{1}{\varepsilon(\omega)} = \frac{a}{2\tilde{\omega}_0}\pi[\delta(\omega - \tilde{\omega}_0) - \delta(\omega + \tilde{\omega}_0)], \qquad \tilde{\omega}_0^2 = \omega_0^2 + a. \tag{A.2}$$

Formula (A.2) in conjunction with (23) gives the calculated value of G(t).

On the other hand, to use the Kubo formula[8] it is necessary to diagonalize the Hamiltonian (A.1). To this end, it is convenient to change over to the second-quantization operators

$$q_{\mathbf{n}}^i = \frac{\overset{+}{a}{}_{\mathbf{n}}^i + a_{\mathbf{n}}^i}{\sqrt{2}}; \quad \overset{+}{a}{}_{\mathbf{k}}^\lambda = \sum_{n,j}\frac{1}{\sqrt{N}}e^{i\mathbf{k}\mathbf{n}}e_j^\lambda \overset{+}{a}{}_{\mathbf{n}}^j, \quad a_{\mathbf{k}} = (\overset{+}{a}_{\mathbf{k}})^{+}.$$

The vectors $\mathbf{e}^\lambda$ correspond to different polarizations, of which one is longitudinal ($\mathbf{e}^1 = \mathbf{k}/k$) and two are transverse ($\mathbf{e}^2, \mathbf{e}^3 \perp \mathbf{k}$). In these variables, the Hamiltonian (A.1) breaks up into two independent parts $\hat{H}_{long}$ and $\hat{H}_\perp$, corresponding to longitudinal (with frequency $\tilde{\omega}_0$) and transverse (with frequency ω_0) oscillations. Only the term $\hat{H}_{long}$ includes the interaction with $\rho(\mathbf{r})$, and therefore this is the only term determining G(t) for a transition with change of $\rho(\mathbf{r})$. The expression for $\hat{H}_{long}$ is:

$$\begin{aligned}\hat{H}_{\mathrm{long}} = {} & \sum_{\mathbf{k}}\hbar\omega_0\overset{+}{a}_{\mathbf{k}}a_{\mathbf{k}} + \frac{\pi\alpha^2}{v_0}\sum_{\mathbf{k}}(\overset{+}{a}_{\mathbf{k}}a_{\mathbf{k}} + a_{-\mathbf{k}}a_{-\mathbf{k}} + a_{\mathbf{k}}a_{-\mathbf{k}} + \overset{+}{a}_{\mathbf{k}}\overset{+}{a}_{-\mathbf{k}}) \\ & + \frac{4\pi}{\sqrt{N}}\frac{(-i\alpha)}{v_0}\sum_{\mathbf{k}}\rho_{\mathbf{k}}\frac{\mathbf{k}}{k^2}\frac{\overset{+}{a}_{-\mathbf{k}} + a_{\mathbf{k}}}{\sqrt{2}}; \\ & \rho_{\mathbf{k}} = \int \rho(\mathbf{r})e^{-i\mathbf{k}\mathbf{r}}\,dv.\end{aligned} \tag{A.3}$$

The three terms in (A.3) correspond to the first three terms of the Hamiltonian (A.1). The operator (A.3) is diagonalized by a u-v transformation to the form

$$\hat{H}_{\text{long}} = \hbar\tilde{\omega}_0 \sum \overset{+}{b}_{\mathbf{k}} b_{\mathbf{k}} + \frac{4\pi}{\sqrt{N}} \frac{-i\alpha}{\sqrt{2v_0}} \sqrt{\frac{\omega_0}{\tilde{\omega}_0}} \sum_{\mathbf{k}} \frac{1}{k} (\rho_{-\mathbf{k}} \overset{+}{b}_{\mathbf{k}} - \rho_{\mathbf{k}} b_{\mathbf{k}}).$$

Here $\rho_k = (\rho^{I})_k$, or $\rho_k = (\rho^{II})_k$ in the first or in the second electronic states, and $\overset{+}{b}_k = u\overset{+}{a}_k + v\overset{+}{a}_{-k}$ and $b_k = ua_{-k} + v\overset{+}{a}_k$.

For transitions with such a Hamiltonian, the theory of nonradiative transitions developed in[6,7] yields for the function G(t) in formula (4)

$$G(t) = \exp\left\{\frac{E}{\hbar\tilde{\omega}_0}\left[i \sin \omega_0 t - \operatorname{cth}\left(\frac{\tilde{\omega}_0}{2kT}\right)(1 - \cos \tilde{\omega}_0 t)\right]\right\},$$

where

$$\frac{E}{\hbar\tilde{\omega}_0} = \frac{2\pi\alpha^2\omega_0}{v_0(\tilde{\omega}_0)^3} \frac{1}{4\pi} \int [\Delta \mathbf{D}(\mathbf{r})]^2 dv,$$

which coincides with our formula (23) in which we substitute $\operatorname{Im}(1/\epsilon(\omega))$ of the given medium in accordance with formula (A.2). It is assumed here that the dimension of the oscillator is much smaller than the characteristic wavelengths, $(v_0)^{1/3} \ll 1/k$.

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