RELAXATION IN NON-ADIABATIC RESONANCE TRANSITIONS

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We consider a system of two coupled parabolic terms which are arranged in a resonance position and which interact with a medium; this is used as a model for a fluorescence center in a liquid or a crystal. In the limit of weak friction we get a set of coupled kinetic equations which describes the electron-vibrational relaxation inside the center in the quasi-classical region. The transition rate found differs from the one evaluated by Landau and Zener.

WE have earlier[1] considered the problem of the relaxation in a system of two coupled parabolic terms interacting with a medium. Such a model reflects most of the important features of internally quenched radiationless processes such as intercombination conversion which occur in luminescence centers in crystals and liquids. The results obtained referred to the case where there was a sufficiently weak coupling between the terms when in a well-known sense the interaction of the system with the medium was stronger than the interaction of the states of the system with one another. This made it possible to restrict ourselves to assuming that the vibrational states of both states were in statistical equilibrium. This approximation which is physically justified in many cases (see, e.g.,[2]) may turn out to be inapplicable to describe fast conversion processes observed in activated laser crystals and in a number of organic molecules in solutions (see[3]). The best studied systems of this kind are ruby activated by chromium ions (cr^{3+}) and N-heterocyclics in liquids. The characteristic time for the intercombination conversion $^4T_2 \to {}^2E$ are of the order of 10^{-9}–10^{-12} sec (an upper estimate is provided by the moment the R-lines occur after excitation of the $^4T_1$ state and a lower estimate by the width of the phononless peak $^4A_2 \to {}^4T_2$). The transitions $S_{n\pi^*} \to T_{\pi\pi^*}$ and $S_{\pi\pi^*} \to T_{\pi\pi^*}$ occur in most N-heterocyclics within about 10^{-9}–10^{-10} sec. By virtue of multiplicity exclusion, the Landau-Zener parameter δ is usually estimated to be 10^{-6} for the processes considered, so that use of the simple Landau-Zener formula yields the value 10^{-7}–10^{-8} sec. The more exact relation for the transition probability found in[1] may also turn out to be inapplicable. (The widths of the vibrational states of the system are 10^{10}–10^{11} sec^{-1} and are comparable with the splitting of the levels appertaining to different states which are 10^{10}–10^{11} sec^{-1}.) This means at the same time that the interaction of the terms is no longer sufficiently large and the problem is a non-equilibrium one with respect to the vibrational sublevels of the system.

We start the study of a model with weak interaction between the system and the medium with the equation for the complete density matrix in the interaction representation

$$\frac{\partial \rho}{\partial t} = -i[V(t), \rho]. \tag{1}$$

Here ($\hbar$ = m = 1)

$$V(t) = e^{iHt} V e^{-iHt}, \tag{2}$$

$$H = \bar{H} + \Delta H \sigma_z + 2\beta\sigma_x; \quad \bar{H} = \frac{p^2}{2} + \frac{\omega^2}{2}x^2 + H_s,$$
$$\Delta H = Fx + \Delta E, \quad V = \alpha x q, \tag{3}$$

x and p are the coordinate and the momentum of the system, H_S the Hamiltonian of the medium about which we shall make some assumptions in the following, q the coordinate of the medium, F, ΔE, β, and α are constants determining the mutual position and the coupling of the terms with one another and the interaction of the system with the medium.

It is natural to use the Hamiltonian (3) for sufficiently small β; when the coupling of the states is strong one should change in (3) to an adiabatic base[4]

$$H = \bar{H} + \Delta H \sigma_z + 2iB\sigma_y, \quad \Delta H = [(Fx + \Delta E)^2 + 4\beta^2]^{1/2},$$
$$B = g'\frac{d}{dx} + \frac{1}{2}g'', \quad g = \frac{1}{2}\operatorname{arctg}\frac{2\beta}{Fx + \Delta E}. \tag{4}$$

In second-order perturbation theory in V we have

$$\rho(t+\tau) - \rho(t) = -\int_t^{\tau+t} dt' \int_t^{t'} dt'' [V(t'), [V(t''), \rho(t)]]. \tag{5}$$

Here and henceforth we assume that one of the following inequalities is satisfied:

$$\gamma\tau \gg 1, \quad \omega_D\tau \gg 1 \tag{6}$$

($1/\gamma$ is the correlation time in the medium, ω_D the Debye frequency) and this enables us to average the density matrix and the operators acting on it separately over the coordinate of the medium and finally it enables us to assume in (5) that

$$\rho(t) \to \frac{\operatorname{Sp}\rho(t)\exp(-H_s/kT)}{\operatorname{Sp}\exp(-H_s/kT)}. \tag{7}$$

The advantages of the Hamiltonian (3), (4) now become clear since the operator x is diagonal in the σ-representation and those terms in the equation which are connected with transitions of the system from one state to another can easily be split off. Writing

$$\rho = \begin{pmatrix} \rho_1 & \rho_{12} \\ \rho_{21} & \rho_2 \end{pmatrix}, \quad V = \begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}, \tag{8}$$

we get for ρ_1 the following equation:

$$\rho_1(t+\tau) - \rho_1(t) = D\rho_1(t) + \vec{T}\rho_1(t) + \overleftarrow{T}\rho_2(t) + I_1\rho_{12} + I_2\rho_{21}. \tag{9}$$

The first term on the right-hand side of (9) describes transitions between the vibrational levels of state 1 and has the form

$$D\rho_1 = -\int_t^{\tau+t} dt' \int_t^{t'} dt'' [V_1(t')V_1(t'')\rho_1 + \rho_1 V_1(t'')V_1(t') - V_1(t')\rho_1 V_1(t'') - V_1(t'')\rho_1 V_1(t')]. \quad (10)$$

Transitions between the states 1 and 2 are determined by the terms

$$\vec{T}\rho_1 = -\int_t^{t+\tau} dt' \int_t^{t'} dt'' [V_{12}(t')V_{21}(t'')\rho_1 + \rho_1 V_{12}(t'')V_{21}(t')], \quad (11)$$

$$\overleftarrow{T}\rho_2 = \int_t^{t+\tau} dt' \int_t^{t'} dt'' [V_{12}(t')\rho_2 V_{21}(t'') + V_{12}(t'')\rho_2 V_{21}(t')].$$

The interference terms in Eq. (9) have a more complex structure:

$$I_1\rho_{12} = -\int_t^{t+\tau} dt' \int_t^{t'} dt'' [-V_1(t')\rho_{12}V_{21}(t'') - V_1(t'')\rho_{12}V_{21}(t') + \rho_{12}(V_{21}(t'')V_1(t') + V_2(t'')V_{21}(t'))], \quad (12)$$

$$I_2\rho_{21} = -\int_t^{t+\tau} dt' \int_t^{t'} dt'' [-V_{12}(t')\rho_{21}V_1(t'') - V_{12}(t'')\rho_{21}V_1(t') + (V_1(t')V_{12}(t'') + V_{12}(t')V_2(t''))\rho_{21}].$$

We choose as the base for the transformations in (10)–(12) the eigenvectors of the equations

$$H_0'|n\rangle = E_n|n\rangle, \quad H_0^2|m\rangle = E_m|m\rangle, \quad (13)$$

where

$$H_0^{1,2} = \overline{H} \pm {}^1/_2\,\Delta H$$

and, depending on the magnitude of the coupling between the terms, ΔH is determined by Eqs. (3)–(4). Writing

$$\rho_1{}^{nn} = \rho_n, \quad \rho_2{}^{mm} = \rho_m, \quad \rho_{12}{}^{nm} = \rho_{nm}, \quad \rho_{21}{}^{mn} = \rho_{mn},$$
$$\langle n|V_1|n'\rangle = \langle n|V|n'\rangle, \quad \langle m|V_2|m'\rangle = \langle m|V|m'\rangle,$$
$$\langle n|V_{12}|m\rangle = \langle n|V|m\rangle, \quad \langle m|V_{21}|n\rangle = \langle m|V|n\rangle$$

and considering the matrix element of the left-hand side of (9), which is diagonal in n, we find the following expression for the "diffusion" term of the equation:

$$D\rho_1 = -\int_t^{t+\tau} dt' \int_t^{t'} dt'' \sum_{i=-1}^{i=1} [\langle n|V(t')|n+i\rangle\langle n+i|V(t'')|n\rangle + \langle n|V(t'')|n+i\rangle\langle n+i|V(t')|n\rangle](\rho_n - \rho_{n+i}). \quad (14)$$

It is exact for small β because of the linearity of V(x). At large β, matrix elements such as $\langle n|V|n+i\rangle$ $(i > 1)$, which have not been taken into account, decrease rapidly with i in the quasi-classical region[5], which is the region considered in the following:

$$E_n,\ E_m \gg \omega.$$

We have dropped in Eq. (14) also terms containing elements of the density matrix of the system which are off-diagonal in n; this is permissible when

$$\omega\tau \gg 1.$$

When the terms are in a resonance position,

$$E_n - E_m = k_0\omega, \quad k_0 = \Delta E/\omega \quad (15)$$

(k_0 = integer) the expression describing transitions from one state to another has the form

$$\vec{T}\rho_1 + \overleftarrow{T}\rho_2 = -\int_t^{t+\tau} dt' \int_t^{t'} dt'' (\langle n|V(t')|m\rangle\langle m|V(t'')|n\rangle + \langle n|V(t'')|m\rangle\langle m|V(t')|n\rangle)(\rho_n - \rho_m). \quad (16)$$

We have dropped here matrix elements such as $\langle n|V|m+\nu\rangle$ $(\nu > 0)$ which, as will become clear from the following, are small compared to the ones taken into account, if

$$k_0^2/n, \quad k_0^2/m \ll 1.$$

The resonance character of the level position (15), which can be postulated for small β, is recovered also for $\beta/\omega \gg 1$ in the quasi-classical region, and (16) is therefore valid also in the region of non-adiabatic coupling. The assumptions made are sufficient in order that we obtain for the interference term in Eq. (9) the expression

$$I_1\rho_{12} + I_2\rho_{21} = -\frac{1}{2}\int_t^{t+\tau} dt' \int_t^{t'} dt'' [\langle n|V(t')|m\rangle(\langle m|V(t'')|m\rangle - \langle n|V(t'')n\rangle) + \langle n|V(t'')|m\rangle(\langle m|V(t')|m\rangle - \langle n|V(t')|n\rangle)](\rho_{nm} - \rho_{mn}). \quad (17)$$

The mixing of the states $|n\rangle$ and $|m\rangle$ in the relations obtained occurs when we take into account the adiabatic $\beta/\omega \ll 1$ or non-adiabatic $\beta/\omega \gg 1$ coupling, but the operator x does not couple them. To show this explicitly we consider the S-matrix corresponding to non-adiabatic transitions

$$e^{iHt} = e^{iH_0 t}S(t), \quad H_0 = \overline{H} + \Delta H\sigma_z.$$

The following formulae are then valid:

$$\langle n|V(t)|m\rangle = a(\langle n|S(t)|n\rangle\langle n|xq(t)|n\rangle\langle n|S^{-1}(t)|m\rangle + \langle n|S(t)m\rangle\langle m|xq(t)|m\rangle\langle m|S^{-1}(t)|m\rangle),$$
$$\langle n|V(t)|n\rangle = a(\langle n|S(t)|n\rangle\langle n|xq(t)|n\rangle\langle n|S^{-1}(t)|n\rangle + \langle n|S(t)|m\rangle\langle m|xq(t)|m\rangle\langle m|S^{-1}(t)|n\rangle),$$
$$\langle n|V(t)|n \pm 1\rangle = ae^{\mp i\omega t}(\langle n|S(t)|n\rangle\langle n|xq(t)|n \pm 1\rangle\langle n \pm 1|S^{-1}(t)|n \pm 1\rangle + \langle n|S(t)|m\rangle\langle m|xq(t)|m \pm 1\rangle\langle m \pm 1|S^{-1}(t)|n \pm 1\rangle), \quad (18)$$

to obtain these we had to assume that the splitting of the levels of the first and the second states due to the coupling of the terms Δ_{nm} (see Fig. 1) satisfies the conditions

$$\Delta_{nm} \ll \omega, \quad \Delta_{nm}\tau \gg 1, \quad (19)$$

which allows us to disregard in (18) the off-diagonal

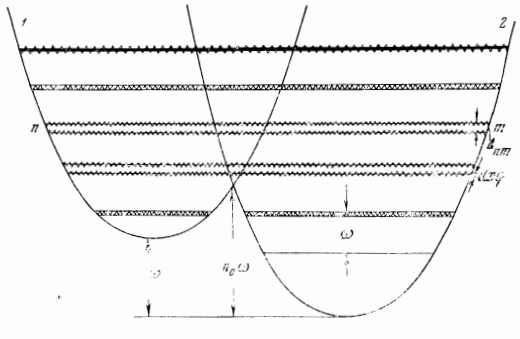

FIG. 1.

elements of the S-matrix such as $\langle n|S|n+\nu\rangle$, $\langle n|S|m\pm\nu\rangle$ $(\nu > 0)$.

All the following results use in an essential way the detailed form of the S-matrix which as we have shown in[6] can be found in the region above the intersection point

$$E_n, E_m \gg \frac{(k_0\omega)^2}{2F^2}\omega^2$$

after N periods as

$$S = s^N, \tag{20}$$

where

$$s = \begin{pmatrix} e^{-2\delta} + (1-e^{-2\delta})e^{2i\tau}, & -2ie^{-\delta}\sqrt{1-e^{-2\delta}}\sin\tau \\ -2ie^{-\delta}\sqrt{1-e^{-2\delta}}\sin\tau, & e^{-2\delta} + (1-e^{-2\delta})e^{-2i\tau}, \end{pmatrix} \tag{21}$$

$\delta = \pi\beta^2/F\sqrt{(\omega n')}$ is the Landau-Zener parameter, $n' = n - n_0$, τ is the difference in phase of the waves corresponding to the states 1 and 2 between the point of intersection of the terms and the turning points. When (19) and (20) are satisfied we can also introduce a continuous time putting

$$N = \omega t / 2\pi.$$

Then

$$S_{nm}(t) = \begin{pmatrix} L\sin\zeta_{nm}t + \cos\zeta_{nm}t, & K\sin\zeta_{nm}t \\ K\sin\zeta_{nm}t, & -L\sin\zeta_{nm}t + \cos\zeta_{nm}t \end{pmatrix} \tag{22}$$

Here

$$\zeta_{nm} = \frac{1}{2\pi}\varphi\omega, \qquad \cos\varphi = e^{-2\delta} + (1-e^{-2\delta})\cos 2\tau, \tag{23}$$

$$L = i\frac{(1-e^{-2\delta})\sin 2\tau}{\sin\varphi}, \quad K = -2i\frac{e^{-\delta}\sqrt{1-e^{-2\delta}}\sin\tau}{\sin\varphi}.$$

Then

$$S^+S = 1 \quad (\mathrm{Det}\, S = 1),$$

which reflects the condition of conservation of current. Using the equation found in[6] for the eigenvalues of the problem with coupled parabolic terms

$$e^{-2\delta}\cos\gamma_1\cos\gamma_2 + (1-e^{-2\delta})\cos(\gamma_1+\tau)\cos(\gamma_2-\tau) = 0, \tag{24}$$

where γ_1 and γ_2 are the actions in the states 1 and 2, one can show that under the resonance conditions (15)

$$\zeta_{nm} = {}^1/_2\Delta_{nm},$$

$$\Delta_{nm} = \begin{cases} \frac{2\omega}{\pi}\sqrt{2\delta}\,|\sin\tau|, & \delta \ll 1 \\ \frac{2\omega}{\pi}e^{-\delta}\,|\sin\tau|, & \delta \gg 1. \end{cases} \tag{25}$$

If we now assume that the spectral density of the correlation function of the medium

$$R(\tilde{\omega}) = \int_{-\infty}^{\infty} e^{-i\tilde{\omega}t}\,\mathrm{Sp}_s(q(0)q(t))\,dt \tag{26}$$

changes little near ω, and using the relation (see, e.g.,[7])

$$R(-\omega) = \theta R(\omega) \qquad (\theta = e^{\omega,\hbar T}), \tag{27}$$

we find

$$D\rho_1 = \tau[-(W_{n,\,n+1}\theta + W_{n,\,n-1})\rho_n + (W_{n,\,n+1}\theta\rho_{n+1} + W_{n,\,n-1}\rho_{n-1})]. \tag{28}$$

Here

$$W_{n,\,n\pm1} = {}^1/_2\alpha^2R(\omega)\theta^{-1}[(v_n^{\pm})^2\bar{M}_{11}^2 + v_n^{\pm}u_m^{\pm}M_{11}M_{22}K^2 + (u_m^{\pm})^2\bar{M}_{22}^2K^4]; \tag{29}$$

$$v_n^{\pm} = \langle n|x|n\pm1\rangle, \quad u_m^{\pm} = \langle m|x|m\pm1\rangle, \quad \bar{M}_{11}^2 = (L^4 - L^2 + 2), \quad \bar{M}_{22}^2 = {}^3/_2, \quad M_{11}M_{22} = -(1-3L^2). \tag{30}$$

It is clear that the diffusion along the vibrational levels of the first term is appreciably altered due to such processes which lead to transitions to a second state with a subsequent change in the energy of the system due to the interaction with the medium. One can assign diagrams to Eq. (29) (Fig. 2) which are convenient to use for an analysis of more complicated cases.

If $R(\tilde{\omega})$ changes little also for small values of its argument, it follows from (16) that

$$\vec{T}\rho_1 + \vec{T}\rho_2 = -\tau\bar{W}_{nm}K^2(\rho_n - \rho_m), \tag{31}$$

where

$$\bar{W}_{nm} = -{}^1/_4\alpha^2R(0)z_{nm}^2M_{11}M_{22}, \quad z_{nm} = \langle n|x|n\rangle - \langle m|x|m\rangle, \tag{32}$$

to which the diagrams of Fig. 3 correspond, the second of which is repeated twice.

There remains only for us to estimate the interference term (17). To do this it is sufficient merely to calculate the elements of the S-matrix which are off-diagonal in n and m assuming that $S_{nn} = S_{mm} = 1$. When (19) is valid,

$$I_1\rho_{12} + I_2\rho_{21} = J\frac{\sin\Delta_{nm}t}{\Delta_{nm}}(\rho_{nm} - \rho_{mn}),$$
$$J \sim \alpha^2z_{nm}^2R(0)K(1 + {}^1/_2K^2).$$

Assuming that

$$J/\Delta_{nm} \ll \bar{W}_{nm}K^2\tau, \quad W_{n,\,n\pm1}\tau, \tag{33}$$

we get finally, when

$$\tilde{W}_{nm}K^2\tau, \quad W_{n,\,n\pm1}\tau \ll 1 \tag{34}$$

the following set of kinetic equations for the populations which are already written in differential form ($W_{nm} = \tilde{W}_{nm}K^2$):

$$\frac{\partial\rho_n}{\partial t} = -(\overline{W}_{n,n+1}\theta + \overline{W}_{n,n-1})\rho_n + (\overline{W}_{n,n+1}\theta\rho_{n+1} + \overline{W}_{n,n-1}\rho_{n-1}) - \overline{W}_{nm}(\rho_n - \rho_m),$$
$$\frac{\partial\rho_m}{\partial t} = -(\overline{W}_{m,m+1}\theta + \overline{W}_{m,m-1})\rho_m + (\overline{W}_{m,m+1}\theta\rho_{m+1} + \overline{W}_{m,m-1}\rho_{m-1}) - \overline{W}_{mn}(\rho_m - \rho_n). \tag{35}$$

In (35) $W_{m,m\pm1}$ is obtained by replacing n by m in (29) and $W_{nm} = W_{mn}$. Moreover, in (35) we have averaged over the large phase difference τ:

$$\overline{W} = \frac{1}{\pi}\int_0^{\pi} W(\tau)\,d\tau. \tag{36}$$

It is clear from (23) that

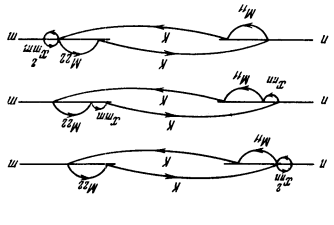

FIG. 2.

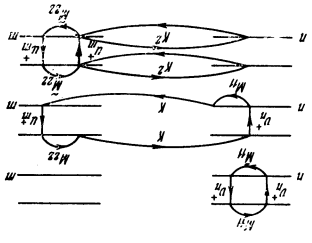

FIG. 3.

$$L = \begin{cases} 0, & \delta \ll 1, \\ i, & \delta \gg 1 \end{cases}$$
$$\overline{K}^2 = -e^{-\delta}, \quad \overline{K}^4 = {}^1/_2(1 + e^{-2\delta})e^{-\delta}, \tag{37}$$

and $\overline{K}$ and $\overline{K}^3$, which are needed only for estimates, are given by:

$$\overline{K} = \begin{cases} 1 \\ \delta e^{-\delta}, \end{cases} \qquad \overline{K}^3 = \begin{cases} 1, & \delta \ll 1 \\ Ce^{-\delta}, & \delta \gg 1 \end{cases}. \tag{38}$$

These equations, and also the inequalities (6), (19), (33), and (34), enable us to write down the final criteria for the applicability of the basic set (35) in the quasi-classical region:

$$W_{n,\,n\pm1}, \quad W_{m,\,m\pm1}, \quad \overline{W}_{nm} \ll \omega\sqrt{\delta}, \quad \gamma(\omega_D),$$
$$\overline{W}_{nm}\frac{\overline{W}_{nm}}{W_{\substack{n,n\pm1\\ m,m\pm1}}} \ll \omega\sqrt{\delta}, \quad \delta \ll 1, \tag{39}$$

$$\overline{W}_{nm} \ll \frac{\omega}{\delta}, \ \gamma(\omega_D); \quad W_{n,\,n\pm1}, \ W_{m,\,m\pm1} \ll \omega\frac{e^{-\delta}}{\delta}, \ \gamma(\omega_D),$$
$$\overline{W}_{nm}\frac{\overline{W}_{nm}}{W_{\substack{n,n\pm1\\ m'm\pm1}}} \ll \omega\frac{e^{\delta}}{\delta}, \quad \delta \gg 1. \tag{40}$$

It is clear that the equations found here which correspond to a different character of the transition compared with the one found by Landau and Zener, are inapplicable for very small and very large δ, i.e., in the regions where the multiplicity of the passage is unimportant and where one can use the results of[1]. Of course, (35) can likewise not be used in the region close to the maximum of the probability near the point of intersection of the terms (see in this connection[8]).

The set of coupled equations (35) splits up at high temperatures ($kT \gg k_0\omega$) and for a symmetric position of the terms ($k_0 = 0$). In those cases it is convenient to introduce the quantities

$$\Sigma_n = \rho_n + \rho_m, \quad \Delta_n = \rho_n - \rho_m.$$

Then

$$\frac{\partial\Sigma_n}{\partial t} = -(\overline{W}_{n,\,n+1}\theta + \overline{W}_{n,\,n-1})\Sigma_n + (\overline{W}_{n,\,n+1}\theta\Sigma_{n+1} + \overline{W}_{n,\,n-1}\Sigma_{n-1}),$$
$$\frac{\partial\Delta_n}{\partial t} = -(\overline{W}_{n,\,n+1}\theta + \overline{W}_{n,\,n-1})\Delta_n + (\overline{W}_{n,\,n+1}\theta\,\Delta_{n+1} + \overline{W}_{n,\,n-1}\Delta_{n-1}) - 2W_{nn}\Delta_n; \tag{41}$$

here

$$v_n^{\pm} = u_m^{\pm}, \quad z_{nn} = 2\langle n|x|n\rangle \quad (k = 0).$$

The first of Eqs. (41) has for small values of δ which are the ones most often encountered experimentally a well-known solution in the form of Gottlieb polynomials[9] which makes it possible to study the second equation by the method of degenerate perturbations.[10] However, the situation studied is by virtue of the first of Eqs. (37) essentially different from[10] because we must include perturbations of sufficiently high rank. If the rank of the perturbation Δn (the number of levels which basically take part in the transition from one state to another) is not too large

$$(\Delta n)^2 / n_0 \ll 1$$

(n_0 is the lowest of the levels important for the transition) the smallest of the roots of the characteristic system corresponding to (41) has the form

$$\lambda_0 = \frac{W_{nn}(1 - e^{-\Delta n\omega/kT})}{1 + \Delta n(1 - \theta^{-1})W_{nn}/W_{n_0,\,n_0+1}}e^{-n_0\omega/kT}. \tag{42}$$

Since (39) does not impose a limit on the ratio $W_{nn}/W_{n,n+1}$ the process can proceed with an appreciable breakdown of equilibrium in the region which is important for the transition and its speed can exceed the speed of predissociation evaluated by means of the usual Landau-Zener formula: $\lambda_0 \sim \omega\delta$. In particular, for the combination $\omega \sim 10^{14}$ sec^{-1}, $\delta \sim 10^{-6}$, $\widetilde{W}_{nn} \sim 10^{10}$ sec^{-1} mentioned at the beginning of this paper inequalities (39) are satisfied and the multiplying factor in front of the exponential in (42) turns out to be of the order of 10^{10} sec^{-1} under equilibrium conditions.

The transition rate is obtained as estimated earlier by the simple Landau-Zener formula also in the range of parameters

$$\omega\sqrt{\delta} \ll \overline{W}_{nn} \ll \omega, \quad \delta \ll 1,$$
$$\omega/\delta \ll \overline{W}_{nn} \ll \omega, \quad \delta \gg 1.$$

This was already discussed in[11]. When $\omega \sim 10^{13}$ sec^{-1}, $\delta \sim 10^{-6}$, $\widetilde{W}_{nn} \sim 10^{11}$ sec^{-1} the first of these inequalities are satisfied and the transition takes place after a time 10^{-9} sec.

In conclusion we note that the method given here to derive kinetic equations for electron-vibrational relaxation processes can be generalized to include in the discussion a non-resonance position of terms, a level splitting which is large compared with ω, and tunneling effects. The latter requires, however, knowledge of the S-matrix in the region below the quasi-intersection point.

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