NONRADIATIVE TRANSITION WITH CHARGE TRANSFER IN A POLAR MEDIUM

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Abstract

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NONRADIATIVE TRANSITION WITH CHARGE TRANSFER IN A POLAR MEDIUM

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Transitions with redistribution of charge in molecules or complexes placed in a polar liquid (water, alcohols, etc.) are characterized by strong interaction of the ionic states with the medium and by a large interaction region. Therefore the medium may be regarded as a continuous dielectric ([1]). We shall assume that the average values of the field operators are described by the linear Maxwell equations, and that the medium is characterized by the dielectric permittivity $\varepsilon(r, \omega)$. The aim of the present work is to find the transition probability $W_{1,2}$ between two electronic states in such a system. For a solid, the theory of multiphonon transitions under strong coupling has been developed in ([2,3]) and applied to a liquid in ([4]). However, the derivation of the formula for the transition probability in these works makes essential use of a model of phonon oscillators and is unsuitable for a liquid, where the absorption of energy is connected mainly ([5]) with reorientation of molecules (Debye absorption or resonance adsorption).

The Hamiltonian of the liquid-complex (or molecule) system in each electronic state ($i = 1, 2$) in the Coulomb gauge is equal to

$$H^i = H_0 + \int \rho^i(r)\hat{\varphi}(r)\, dV + E_i; \tag{1}$$

H_0 is the Hamiltonian of the medium without the complex; $\hat{\varphi}(r)$ is the scalar potential of the field; $\rho^i(r)$ is the charge density in each electronic state, and E_i are the electronic energy levels of the complex. Here the terms of the electron-vibrational interaction within the complexes are not written out, since their inclusion in the calculation of $W_{1,2}$ can be done trivially within the framework of the known theory ([2,3]) for oscillator Hamiltonians. For brevity the derivation is carried out for a homogeneous medium $\varepsilon(r, \omega) = \varepsilon(\omega)$, although the final result (9) is written for arbitrary $\varepsilon(r, \omega)$. The probability of the nonradiative transition $W_{1,2}$, in first order of perturbation theory with respect to the interaction $V_{1,2}$ between states 1, 2, is written ([2,3]) in the form ($\hbar = 1$):

$$W_{1,2} = |V_{1,2}|^2 \int_{-\infty}^{\infty} G(t)\, dt; \qquad G(t) = \langle e^{iH_1 t} e^{-iH_2 t} \rangle_{H_1}, \tag{2}$$

where the brackets denote averaging over the equilibrium state of the system with Hamiltonian H_1:

$$\langle A \rangle_{H_1} = \mathrm{Sp}\{e^{-\beta(H_1 - F_1)} A\}, \quad \beta = 1/kT.$$

In the Heisenberg representation with respect to H_1, the function $G(t)$ has the form:

$$G(t) = e^{-i\Delta E t} \left\langle T \exp\left\{ -i \int_0^t dt \int dV\, \Delta\rho(r) \hat{\varphi}(r,t) \right\} \right\rangle_{H_1}, \tag{3}$$

where T is the chronological-ordering operator; $\Delta\rho = \rho_2(r) - \rho_1(r)$, $\Delta E = E_2 - E_1$.

To calculate (3) we use the long-wavelength approximation developed in ([6]). In this case the interaction of the particles of the medium with the field is divided into a short-range part and an interaction with the long-wavelength-

by photons. After expanding the exponentials (3) in a series, finding the n-th term of the series reduces to calculating the average:

$$\int_0^t dt_1 \ldots \int_0^t dt_n \int \ldots \int dV_1 \ldots dV_n \Delta\rho(r_1) \ldots \Delta\rho(r_n)\, \frac{1}{n!} \langle T\varphi(r_1 t_1) \ldots \varphi(r_n, t_n) \rangle_{H_1} \tag{4}$$

(4) is represented by the sum of the contributions of all diagrams with n free photon ends. Following [6], we shall take into account only those diagrams in which there is no integration over the momenta of long-wavelength photons. In the language of diagrams, the quantities $\langle\varphi(r)\rangle_{H_1}$ and $D_{00}(r_1 t_1, r_2 t_2) = -i\langle T\delta\varphi(r_1, t_1) \times \delta\varphi(r_1, t_2)\rangle_{H_1}$, $\delta\varphi = \varphi - \langle\varphi\rangle_{H_1}$, are equal to:

$$\langle\hat{\varphi}\rangle_{H_1} = ---\bigcirc + ---\bigcirc---\bigcirc + \cdots, \qquad D_{\bullet\bullet} = ---\bigcirc--- + ---\bigcirc---\bigcirc--- + \cdots \tag{5}$$

Summing all diagrams of the indicated type, we obtain for (4) an expression of the form

$$\frac{1}{n!} \sum_{m=0}^{[n/2]} f^{\,n-2m} g^m C_n^{2m} (2m-1)!!, \tag{6}$$

where

$$g(t) = -i \int_0^t dt_1 \int_0^t dt_2 \iint dV_1 dV_2\, \Delta\rho(r_1)\Delta\rho(r_2) D_{00}(r_1, r_2, t_1 - t_2). \quad (7)$$

$$f(t) = -it \int \langle \varphi(r) \rangle_{H_1} \Delta\rho(r) dV = -\frac{it}{4\pi} \int \frac{\left| D^{\mathrm{II}}(r) - D^{\mathrm{I}}(r) \right| D^{\mathrm{I}}(r)}{\varepsilon(0)}\, dV.$$

Here $D^i(r)$ is the induction vector in the i-th state. Summing all terms (6), we obtain

$$G(t) = e^{f(t)} e^{g(t)} e^{-i\Delta E t}. \quad (8)$$

The function $D_{00}(r_1, r_2, \omega)$ is related by a known relation to the retarded Green' s function $D_{00}^R(r_1, r_2, \omega)$, which in turn is expressed through the dielectric permittivity $\varepsilon(r, \omega)$ of the medium [6].

Taking all this into account and carrying out simple transformations, we obtain:

$$G(t) = \exp\left\{ -i\widetilde{\Delta E} t + \int \frac{|\Delta D(r)|^2}{8\pi^2} \left[\int_{-\infty}^{\infty} \frac{d\omega}{\omega^3} \frac{\varepsilon''(r,\omega)}{|\varepsilon(r,\omega)|^2} \times \frac{\mathrm{ch}(\hbar\omega/2kT - i\omega t) - \mathrm{ch}\,\hbar\omega/2kT}{\mathrm{sh}\,\hbar\omega/2kT} \right] dV \right\}, \quad (9)$$

where $\Delta D(r) = D^{\mathrm{II}}(r) - D^{\mathrm{I}}(r)$ and

$$\widetilde{\Delta E} = \Delta E + \int \left\{ \frac{|D^{\mathrm{I}}(r)|^2}{8\pi} - \frac{|D^{\mathrm{II}}(r)|^2}{8\pi} \right\} \left(1 - \frac{1}{\varepsilon(r, 0)} \right) dV -$$

is the transition energy with allowance for the change in the electromagnetic energy of the dielectric during the transition. Formulas (2), (9) solve the problem posed.

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1. R. Marcus, *J. Chem. Phys.*, **24**, 979 (1956); **38**, 1858 (1963).

2. R. Kubo, Y. Toyozawa, *Progr. Theor. Phys.*, **13**, No. 2, 160 (1955).

3. M. Lax, *J. Chem. Phys.*, **20**, 1752 (1952).

4. V. G. Levich, R. R. Dogonadze, *DAN*, **124**, 123 (1959); **133**, 158 (1959).

5. R. Saxton, *Proc. Roy. Soc. A*, **213**, 473 (1952).

6. A. A. Abrikosov et al., *Methods of Quantum Field Theory in Statistical Physics*, Ch. VI, Moscow, 1962.

Note: Figure translations are in progress. See original paper for figures.