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Abstract

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PHYSICS

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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

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

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 ($\hbar = 1$):

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

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

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

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

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

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:

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

(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 $D_{00}(r_1 t_1, r_2 t_2) = -i \langle T \delta \varphi(r_1, t_1) \times \delta \varphi(r_2, t_2) \rangle_{H_1}$, $\delta \varphi = \varphi - \langle \varphi \rangle_{H_1}$, are equal to:

$$\langle \hat{\varphi} \rangle_{H_1} = \text{---}\bigcirc\text{---} + \text{---}\bigcirc\text{---}\bigcirc\text{---} + \dots, \quad D_{\bullet\bullet} = \text{---}\bigcirc\text{---} + \text{---}\bigcirc\text{---}\bigcirc\text{---} + \dots \quad (5)$$

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

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

where

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

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

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

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

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:

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

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

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

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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