THEORETICAL ASPECTS OF TWO-PHOTON CHARGE TRANSFER PROCESSES IN HOMOGENEOUS CONDENSED SYSTEMS

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Abstract

The paper presents theoretical models for two-photon processes occurring in homogeneous condensed systems with polyatomic impurity particles. Theoretical calculations were carried out mainly for resonance processes, which make the main contribution to the two-photon processes of absorption and emission of photons. The calculation of the double differential cross section of the processes was carried out using the apparatus of Green's functions of polarization operators of a condensed medium.

Analytical expressions for the kinetic parameters of two-photon processes in condensed systems are obtained. Numerical calculations can be carried out for various model systems.

1. System model

When studying complex condensed systems, systematic research is of great importance - a variety of methods for studying complex processes that can occur in the system under study. Optical research methods are widely used because they are well-tested and relatively easily accessible methods. At the same time, a detailed study of complex condensed systems requires an increasingly wide range of methods, in particular from the point of view of the use of optical methods too.

Of great interest is the use of two-photon methods for research [1 – 24], in which the system can be irradiated with photons at a certain frequency, and the analysis of the irradiation results takes place in a wide range of optical frequencies.

We write the probability of an elementary act of the phototransfer process of a condensed system with impurity particles on which a photon is absorbed during the transfer process in the form:

$$dW^{(2)} = 2\pi \sum_{n\{N_{\mathbf{k}\sigma}\}} \sum_{l\{N'_{\mathbf{k}\sigma}\}} exp[\beta(F_i^0 - E_{in}^o)]\Phi_i(\{N_{\mathbf{k}\sigma}\}) \times \left| \sum_{d,m\{N''_{\mathbf{k}\sigma}\}} \frac{\langle l,f,\{N_{\mathbf{k}\sigma}\}|V|m,d,\{N''_{\mathbf{k}\sigma}\}\rangle\langle m,d,\{N''_{\mathbf{k}\sigma}\}|V|n.i,\{N_{\mathbf{k}\sigma}\}\rangle}{E_{in}-E_{dm}} \right|^2 \delta(E_{in} - E_{fl}) \quad (1)$$

Where $E_{in}, E_{dm}$and E_{fl} are the energy spectra of the initial, intermediate and final states, respectively; *n*, *m*, and *l* are sets of quantum numbers that determine the state of the system (except electronic) in the initial, intermediate and final states, respectively; $N_{\mathbf{k}\sigma}$ and $N'_{\mathbf{k}\sigma}$ are sets of occupation numbers of photons in the initial and final states, $\Phi_i(\{N_{\mathbf{k}\sigma}\})$ is the distribution function of photons in the initial state, E_{in}^o is free energy of the reactants and the medium in the initial state.

It is easier to carry out further calculations under the assumption that during the process the system absorbs one photon with frequency ω_k and emits one photon with frequency $\omega_{k'}$. In this case

$$E_{in} = E_{in}^0 + \omega_k; E_{fl} = E_{fl}^0 + \omega_{k'} \quad (2)$$

Where E_{in}^0, E_{fl}^0 are the energy spectra of the initial and final terms without photon energies, in units $\hbar = 1$. and the energy of the intermediate state of the system can take one of two values

$$E_{dm} = E_{dm}^0 \quad (3)$$

$$E_{dm} = E_{dm}^0 + \omega_k - \omega_{k'} \quad (4)$$

Where E_{dm}^0 is the energy spectrum of the intermediate state of the system without photon.

The interaction of particles with the electromagnetic field, leading to the process of charge phototransfer, can be represented in the form

$$V = -\int d\mathbf{r}\, \mathbf{P}(\mathbf{r})\mathbf{E}(\mathbf{r}) \quad (5)$$

Where $\mathbf{P}(\mathbf{r})$ is polarization operator of reagent particles, $\mathbf{E}(\mathbf{r})$ is the operator of the electric field strength of photons.

$$\mathbf{E(r)} = i\sum_{\mathbf{k}\sigma}(2\pi\omega_k/V)^{0.5}\, e_{\mathbf{k}\sigma}(a_{\mathbf{k}\sigma} exp(i\mathbf{kr}) - a^+_{\mathbf{k}\sigma} exp(-i\mathbf{kr})) \quad (6)$$

Here V is the periodicity of the system, $e_{\mathbf{k}\sigma}$ - the unit polarization vector of photons with wave number k and polarization σ (σ = 1, 2), $a^+_{\mathbf{k}\sigma}$ and $a_{\mathbf{k}\sigma}$ are the operators of photon creation and annihilation, ω_k is the photon frequency.

As a result, for the probability of an elementary act of the charge phototransfer process we obtain:

$$dW^{(2)} = 2\pi \sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} \sum_{nl} exp[\beta(F_i^0 - E_{in}^o)] \cdot \Phi_i(\{N_{\mathbf{k}\sigma}\}) \left| \int \boldsymbol{d\mathbf{r}d\mathbf{r}} e^{i(\mathbf{kr}-\mathbf{k'r'})} \sum_{dm} \left[\frac{(\mathbf{P}(\mathbf{r'})_{di}\mathbf{e}_{\mathbf{k}\sigma'})(\mathbf{P}(\mathbf{r'})_{fd}\mathbf{e}_{\mathbf{k}\sigma})}{E_{in}^0 - E_{dm}^0 - \omega_{k'\sigma'} + i\gamma} + \frac{(\mathbf{P}(\mathbf{r'})_{di}\mathbf{e}_{\mathbf{k}\sigma'})(\mathbf{P}(\mathbf{r})_{fd}\mathbf{e}_{\mathbf{k}\sigma})}{E_{in}^0 - E_{dm}^0 + \omega_{k\sigma} + i\gamma} \right] \cdot \frac{2\pi}{V_0} \sqrt{\omega_{k\sigma}\omega_{k'\sigma'}} \sqrt{\langle N_{\mathbf{k}\sigma}\rangle(\langle N_{\mathbf{k}\sigma}\rangle + 1)} \right|^2 \delta(E_{in} - E_{fl} + \omega_{k\sigma} - \omega_{k'\sigma'}) \quad (7)$$

Here $(\mathbf{P}(\mathbf{r}')_{di}\mathbf{e}_{\mathbf{k}\sigma'})$ and $(\mathbf{P}(\mathbf{r}')_{fd}\mathbf{e}_{\mathbf{k}\sigma})$ are the matrix elements of the polarization of transitions between the intermediate and initial and between the final and intermediate states. $\{N_{\mathbf{k}\sigma}\}$ are sets of photon occupation numbers in the initial state.

We assume that in the process under consideration $\gamma \to 0$.

If we assume that the wave vectors of the photons of the incident beam are distributed in the interval from **k** to **k** + Δ**k**, and for the emitted photons are distributed in the interval from **k**' to **k**' + Δ**k**′, then we obtain for the probability of an elemental act of the process.

2. Double differential process cross section.

Let us introduce the double differential cross section of the process (DDC) in the form

$$\frac{\Delta^2 W^{(2)}}{\Delta\omega_{k'}\Delta\Omega_{k'}} = \sum_{\sigma\sigma'}\sum_{nl} e^{\beta\left(F_i^0 - E_{in}^0\right)}\,\omega_{k'}^3\omega_k I_{\mathbf{k}\sigma}\delta\left(E_{in}^0 - E_{fl}^0 + \omega_k - \omega_{k'}\right)\left\{\left|\sum_{dm}\frac{P^{*\sigma}(\mathbf{k})_{fd}P^{\sigma'}(\mathbf{k})_{di}}{E_{in}^0 - E_{dm}^0 - \omega_{k'} + i\gamma}\right|^2 + \right.$$

$$\left.\left|\sum_{dm}\frac{P^{\sigma'}(\mathbf{k'})_{di}P^{*\sigma}(\mathbf{k})_{fd}}{E_{in}^0 - E_{dm}^0 + \omega_k + i\gamma}\right|^2 + \sum_{d,d',m,m'}\frac{P^{*\sigma}(\mathbf{k})_{fd}P^{\sigma'}(\mathbf{k})_{di}P^{*\sigma'}(\mathbf{k'})_{di}P^{\sigma}(\mathbf{k})_{fd}}{\left(E_{in}^0 - E_{dm}^0 - \omega_k + i\gamma\right)\left(E_{in}^0 - E_{dm}^0 + \omega_k - i\gamma\right)} + \frac{P^{\sigma}(\mathbf{k})_{fd}P^{*\sigma}(\mathbf{k})_{di}P^{\sigma'}(\mathbf{k'})_{di}P^{\sigma}(\mathbf{k})_{fd}}{\left(E_{in}^0 - E_{dm}^0 - \omega_{k'} - i\gamma\right)\left(E_{in}^0 - E_{dm}^0 + \omega_k + i\gamma\right)}\right\} \quad (8)$$

Later on, we will consider only one (resonant) term of this relation (the rest can be studied by analogy):

$$\frac{\Delta^2 W^{(2)}}{\Delta\omega_{k'}\Delta\Omega_{k'}} = -\sum_{\sigma\sigma'}\sum_{nl} e^{\beta\left(F_i^0 - E_{in}^o\right)}\frac{\beta^3\omega_{k'}^3\omega_k}{2\pi}I_{\mathbf{k}\sigma}\sum_{d,d',m,m'}P^{*\sigma'}(\mathbf{k}')_{id}P^{\sigma}(\mathbf{k})_{df}\cdot P^{\sigma}(\mathbf{k})_{fd'}P^{*\sigma'}(\mathbf{k}')_{d'i}\cdot$$

$$\int_0^{i\infty} d\tau_1 exp\left[\beta(E_{in}^0 - E_{dm}^0 - \omega_{k'} + i\gamma)\tau_1\right]\int_{-i\infty}^{0} d\tau_2 exp\left[\beta\left(E_{in}^0 - E_{d'm'}^0 - \omega_{k'} - i\gamma\right)\right]\int_{-i\infty}^{\infty} d\theta exp\left[\beta\left(E_{in}^0 - E_{fl}^0 + \omega_k - \omega_{k'} + \frac{i\gamma}{|\theta|}\right)\theta\right] \quad (9)$$

Since E_{in}^0, E_{dm}^0, $E_{d'm'}^0$, E_{fl}^0 are the eigenvalues of the Hamiltonians of the initial H_i^0, intermediate (H_d^0 and $H_{d'}^0$) and final H_f^0 states, the DDS can be represented as:

$$\frac{\Delta^2 W_R^2}{\Delta\omega_{k'}\Delta\Omega_{k'}} = \frac{\beta^3\omega_{k'}^3\omega_k}{2\pi}I_{k\sigma}\int_0^{i\infty} d\tau_1\int_{-i\infty}^{0} d\tau_2\int_{-i\infty}^{i\infty} d\theta\, e^{\beta F_i^0}\cdot$$

$$Sp\left[e^{-\beta(1-\theta-\tau_1-\tau_2)H_i^0}P^{*\sigma'}(\mathbf{k}')_{di}e^{\tau_1 H_d^0}P^{\sigma}\left(\vec{k}\right)_{fd}e^{-\beta\theta H_f^0}P^{\sigma}(\mathbf{k})_{fd'}e^{-\beta\tau_2 H_{d'}^0}P^{*\sigma'}(\mathbf{k}')_{d'i}\right]\cdot e^{\beta[(\omega_k-\omega_{k'})\theta-\omega_{k'}(\tau_1+\tau_2)]} \quad (10)$$

In the last formula, taking a spur is assumed along all coordinates of the system, except electronic ones.

For two-photon processes, it is possible to obtain correlation relations between thermal and corresponding photoprocesses of charge transfer. In this case, it will be the correlation relationship between the DDS and the parameters of the bridge reaction.

We write the probability of electron transfer in a bridging reaction as:

$$W_R^2 = -\beta^3\int_0^{i\infty} d\tau_1\int_{-i\infty}^{0} d\tau_2\int_{-i\infty}^{i\infty} d\theta\, e^{\beta F_i^0}\cdot$$

$$Sp\left[e^{-\beta(1-\theta-\tau_1-\tau_2)H_i^0}V_{id}^* e^{-\beta\tau_1 H_d^0}V_{df}e^{-\beta\theta H_f^0}V_{df'}e^{-\beta\tau_2 H_{d'}^0}V_{id'}^*\right] \quad (11)$$

Where V_{di} are the matrix elements from the interaction between the intermediate and the initial state, similarly the remaining matrix elements in this formula.

3.Condon approximation for the double differential cross section of a process

In the Condon approximation, formula (11) can be represented as:

$$W_R^2 = -\beta^3 V_{id}^* V_{df}V_{df'}V_{id}^* V_{id'}^*\int_0^{i\infty} d\tau_1\int_{-i\infty}^{0} d\tau_2\int_{-i\infty}^{i\infty} d\theta\, e^{\beta F_i^0}\cdot$$

$$Sp\left[e^{-\beta(1-\theta-\tau_1-\tau_2)H_i^0}e^{-\beta\tau_1 H_d^0}e^{-\beta\theta H_f^0}e^{-\beta\tau_2 H_{d'}^0}\right] \quad (12)$$

Similarly, for the Condon approximation, we represent the double differential cross section in the form

$$\frac{\Delta^2 W^{(2)}}{\Delta\omega_{k'}\Delta\Omega_{k'}} = \frac{\beta^3\omega_{k'}^3\omega_k}{2\pi}I_{k\sigma}P^{*\sigma'}(\mathbf{k}')_{id}P^{\sigma}(\mathbf{k})_{df}P^{\sigma}(\mathbf{k})_{fd'}P^{*\sigma'}(\mathbf{k}')_{d'i}\cdot\int_0^{i\infty} d\tau_1\int_{-i\infty}^{0} d\tau_2\int_{-i\infty}^{i\infty} d\theta\, e^{\beta F_i^0}\times$$

$$Sp\left[e^{-\beta(1-\theta-\tau_1-\tau_2)H_i^0}e^{-\beta\tau_1 H_d^0}e^{-\beta\theta H_f^0}e^{-\beta\tau_2 H_{d'}^0}\right] \quad (13)$$

A comparison of the last two expressions allows us to establish a correlation between the DDS and the probability of a bridging reaction in the form:

$$\frac{\Delta^2 W_R^{(2)}}{\Delta\omega_{k'}\Delta\Omega_{k'}} = \frac{\omega_{k'}^3\omega_k}{2\pi}I_{k\sigma}\frac{P^{*\sigma'}(\mathbf{k'})_{id}P^{\sigma}(\mathbf{k})_{df}P^{\sigma}(\mathbf{k})_{fd'}P^{*\sigma'}(\mathbf{k'})_{d'i}}{V_{id}^* V_{df}V_{d'f}V_{d'i}^*}W_R^{(2)}\left(\Delta F_{fi} - \omega_k + \omega_{k'}, \Delta F_{di} - \omega_k\right) \quad (14)$$

Also of interest is the expression of the correlation relationship between the DDS and the two-particle temperature Green's function $G_{\sigma\sigma'}^{(2)}$ of the polarization operators of the system:

$$\frac{\Delta^2 W^{(2)}}{\Delta\omega_{k'}\Delta\Omega_{k'}} = \frac{\beta^3\omega_{k'}^3\omega_k I_{k\sigma}}{2\pi}\int_0^{i\infty} d\tau_1\int_{-i\infty}^{0} d\tau_2\cdot\int_{-i\infty}^{i\infty} d\theta\, e^{\beta\omega_k\theta-\beta\omega_{k'}(\theta+\tau_1+\tau_2)}\cdot G_{\sigma\sigma'}^{(2)}(\mathbf{k}',\mathbf{k},\mathbf{k}\,\mathbf{k}',;\ \tau_1+\tau_2+\theta,\tau_2+\theta,\tau_2,0) \quad (15)$$

where

$$G_{\sigma\sigma'}^{(2)}(\mathbf{k}'\mathbf{k},\mathbf{k}\,\mathbf{k}';\ \tau_1+\tau_2+\theta,\tau_2+\theta,\tau_2,\theta) = -\langle T_\tau P^{*\sigma'}(\mathbf{k}'\tau_1+\tau_2+\theta)_{id}P^{\sigma}(\mathbf{k}'\tau_2+\theta)_{df}\cdot$$
$$P^{\sigma}(\mathbf{k}'\tau_2)_{d'f}P^{*\sigma'}(\mathbf{k};0)_{id'}\rangle_i \quad (16)$$

The above formulas are of interest for estimating the parameters of bridging reactions and two-photon processes. However, transfer processes in which one-photon charge transfer from the initial state to the intermediate state, and from the intermediate state to the final state, can be sequentially studied are of no less interest. We assume that during the transfer process only a reorganization of the medium, in which the reactant particles are located, occurs.

For simplicity of calculations, we will neglect the interaction of intramolecular vibrations with fluctuations in the polarization of the condensed medium. Similar model of the system corresponds to processes of electron scattering on large molecules or binuclear centers, in which 3 or 4 electron terms take part in the process. For simplicity, we will consider a process with three electron terms.

In this case, the DDS can be represented in the form

$$\frac{\Delta^2 W^{(2)}}{\Delta\omega_{k\prime}\Delta\Omega_{k\prime}} = \sum_{d\sigma\sigma\prime} \frac{\beta\omega_k I_{k\sigma}\omega_{k\prime}^3}{2\pi} \left|P(\mathbf{k})_{fd}\right|^2 |P(\mathbf{k})_{di}|^2 w(\omega_k, \omega_{k\prime}) \tag{17}$$

where function $w(\omega_k, \omega_{k\prime})$ has the form:

$$w(\omega_k, \omega_{k\prime}) = -i\int_0^{i\infty} d\tau_1 \int_{-i\infty}^{0} d\tau_2 \int_{-i\infty}^{i\infty} d\theta\, e^{\beta\omega_k\theta - \beta(\tau_1-\tau_2+\theta)\theta\omega_{k\prime} + i\beta(\tau_1+\tau_2)\Gamma_{id}} e^{-i\beta\frac{\theta\Gamma_{if}}{|\theta|}} e^{\beta F_i^0} \cdot Sp\left\{e^{-\beta H_i^0} e^{\beta\theta H_i^0} e^{-\beta\theta H_f^0} e^{-\beta(\tau_1-\tau_2)H_d^0} e^{\beta(\tau_1-\tau_2)H_i^0}\right\} \tag{18}$$

In the last formula, $\Gamma_{id} = \gamma_i + \gamma_d$, $\Gamma_{if} = \gamma_i + \gamma_f$ - represent the widths of the peaks of transitions from the initial to the intermediate and from the intermediate to the final state, respectively. We accept these quantities as some parameters characterizing the process of electron transfer.

After simple transformations

$$w(\omega_k, \omega_{k\prime}) = w + c.c \tag{19}$$

where function w has the form:

$$w = \int_{-\infty}^{\infty} d\acute{\eta}\, e^{\beta F_i} e^{i\beta\acute{\eta}(\omega_{k\prime}-\omega_k)} e^{-\beta\frac{\acute{\eta}}{|\acute{\eta}|}\Gamma_{if}} \int_0^{\infty} dp e^{-2\beta\Gamma_{id}p} \int_0^p ds e^{i\beta\omega_{k\prime}s} \cdot Sp\left[e^{-\beta H_i^0} e^{i\beta\acute{\eta}H_i^0} e^{-\beta H_f^0} e^{-i\beta s H_d^0} e^{-i\beta s H_i^0}\right] \tag{20}$$

If the Hamiltonians of the initial, intermediate and final states are represented as sums of the Hamiltonian of the medium and the interactions of the system in the initial, intermediate and final states:

$$\begin{aligned} H_i^0 &= H_m + H_{int}^i;\ H_{int}^i = -\int \mathbf{P}(\mathbf{r})\,\mathbf{E}^i(\mathbf{r})d\mathbf{r} \\ H_f^0 &= H_m + H_{int}^f;\ H_{int}^f = -\int \mathbf{P}(\mathbf{r})\,\mathbf{E}^f(\mathbf{r})d\mathbf{r} \\ H_d^0 &= H_m + H_{int}^d;\ H_{int}^d = -\int \mathbf{P}(\mathbf{r})\,\mathbf{E}^d(\mathbf{r})d\mathbf{r} \end{aligned} \tag{21}$$

Let us denote the spur in formula (20) as S

$$S = Sp\left[e^{-\beta H_i^0} e^{i\beta\acute{\eta}H_i^0} e^{-\beta H_f^0} e^{-i\beta s H_d^0} e^{-i\beta s H_i^0}\right]$$

In this case we get the expression:

$$S = e^{\beta F_i} Sp[\dots] = \exp[i\beta\acute{\eta}\int d\mathbf{r}\, \boldsymbol{P_{0i}}(\mathbf{r})\Delta\mathbf{E}^{\boldsymbol{fi}}(\mathbf{r}) - i\beta s\int d\mathbf{r}\, \boldsymbol{P_{0i}}(\mathbf{r})\Delta\mathbf{E}^{\boldsymbol{di}}(\mathbf{r})]\,\langle T_\rho exp\left(-i\int_0^{\beta\acute{\eta}} H_{int}^{fi}(\rho)d\rho\right) T_u exp\left(i\int_0^{\beta\acute{\eta}} H_{int}^{di}(u)d\,u\right)\rangle \tag{22}$$

Where $\boldsymbol{P_{0i}}$ is the equilibrium polarization of the medium in the initial state, quantum statistical averaging is carried out over the states of the Hamiltonian H_i^0, and the time dependence in the HamiltoniansH_{int}^{fi} and H_{int}^{di} has the form:

$$H_{int}^{fi}(\rho) = e^{i\rho H_i} H_{int}^{fi}(0) e^{-i\rho H_i} \tag{23}$$

Expanding the exponentials in a series under angle brackets and using the approximation of decoupling quantum statistical averages from the operators of medium polarization fluctuations into paired averages according to the rules of Wick's theorem, we obtain the function S:

$$S = \frac{1}{1+A} exp\left[i\acute{\eta}\beta\left(\Delta F^{fi} - E_r^{fi}\right) + is\beta(\Delta F^{di} - E_r^{di}) - \psi^{fi}(\acute{\eta}) - \psi^{di}(s) - \beta\acute{\eta}E_r^{fi} - \beta s E_r^{di}\right] \tag{24}$$

where

$$\mathrm{A} = \int_0^{\beta\eta} d\rho \int_0^{\beta s} du \int d\mathbf{r}\, d\mathbf{r}'\boldsymbol{\Delta}E_\alpha^{fi}(\mathbf{r})\,\boldsymbol{\Delta}E_\beta^{di}(\mathbf{r}')g_{\alpha\beta}^t(\mathbf{r},\mathbf{r}',\rho-u) \tag{25}$$

Function $g_{\alpha\beta}^t(\mathbf{r},\mathbf{r}',\rho-u)$ is time retarded Green's function of polarization operators at finite temperature, periodic with period β.

In the formulas (8.37) E_r^{fi} is the energy of reorganization of the medium during the transition of the system from the initial state to the final state:

$$E_r^{fi} = -\int d\boldsymbol{r}d\boldsymbol{r}'\Delta E_{\boldsymbol{\alpha}}^{\boldsymbol{fi}}(\mathbf{r})\Delta E_\beta^{fi}(\mathbf{r})g_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega=0)\cdot\frac{1}{2} \tag{26}$$

Analogously E_r^{di} :

$$E_r^{di} = -\int d\boldsymbol{r}d\boldsymbol{r}'\Delta E_{\boldsymbol{\alpha}}^{\boldsymbol{di}}(\mathbf{r})\Delta E_\beta^{di}(\mathbf{r})g_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega=0)\cdot\frac{1}{2}$$

In the formula (24) the functions ψ^{fi} and ψ^{di} have the form:

$$\psi^{fi}(\acute{\eta}) = \frac{1}{\pi}\int d\boldsymbol{r}d\boldsymbol{r}'\Delta E_{\boldsymbol{\alpha}}^{\boldsymbol{fi}}(\mathbf{r})\Delta E_\beta^{fi}(\mathbf{r})\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2} Img_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)\frac{sin[\beta\omega(1-\acute{\eta})/2]sin[\beta\omega\acute{\eta}/2]}{sin[\beta\omega/2]} \tag{27}$$

$$\psi^{di}(s) = \frac{1}{\pi}\int d\mathbf{r}d\mathbf{r}'\Delta E_{\alpha}^{\boldsymbol{di}}(\mathbf{r})\Delta E_{\beta}^{di}(\mathbf{r})\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}Img_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)\frac{sin[\beta\omega(1-s)/2]sin[\beta\omega s/2]}{sin[\beta\omega/2]}$$

where $\Delta E_{\beta}^{fi}(\mathbf{r})$ is the change in the electric field strength of the system during the transition from the initial state to the final state, $g_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)$ - is the time retarded Green's function of the polarization operators of the medium.

4. Classical approximation for describing condensed matter.

In the classical approximation, it is not difficult to obtain expressions for the functions in formulas (27) and (25)

$$A = \beta s\eta\int d\mathbf{r}\,d\mathbf{r}'\Delta E_{\boldsymbol{\alpha}}^{\boldsymbol{fi}}(\mathbf{r})\Delta E_{\beta}^{di}(\mathbf{r})g_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega=0) \quad (28)$$

The functions $\psi^{fi}(ή)$ and $\psi^{di}(s)$ are expressed through the reorganization energies of transitions from the initial state to the intermediate state E_r^{di} , and from the initial state to the final E_r^{fi}

$$\psi^{fi}(ή) = -ή(1-ή)\beta E_r^{fi}$$
$$\psi^{di}(s) = -s(1-s)\beta E_r^{di} \quad (29)$$

Further theoretical calculations can be carried out by integrating over θ in the formula using the saddle point method, as a result

$$w + c.c = \left(\beta E_r^{fi}\right)exp\left[-\beta(\omega_{k'} - \omega_k + \Delta F^{fi} - E_r^{fi})/4E_r^{fi}\right]\left[\frac{exp\left[-\beta\left(\omega_{k'}+\Delta F^{\alpha i}-E_r^{di}\right)\right]}{2\beta\Gamma_{id}\sqrt{\beta E_r^{di}(1-ibs^*)}} + \Phi\right];$$

$$b = \frac{E^{idf}}{E_r^{fi}}\beta(\omega_{k'} - \omega_k + \Delta F^{fi} - E_r^{fi}) \quad (30)$$

where

$$\Phi = -2Re\int_0^{\infty} dp e^{-2\beta\Gamma_{idP}}\int_p^{\infty} ds\, exp[-s^2\beta E_r^{di} + i\beta(\omega_{k'} + \Delta F^{di} - E_r^{di})s/(1-ibs)] \quad (31)$$

As a result of the calculations carried out, we obtain analytical results for the probability of a two-photon process, in which further calculations with integration over two parameters p and s are possible numerically. It is also possible to carry out calculations of integrals over two parameters approximately if sufficiently stringent conditions are met

$$\frac{1}{\sqrt{\beta E_r^{di}}} \ll \frac{1}{\beta(\omega_{k'}+\Delta F^{di}-E_r^{di})} \quad (32)$$

$$\frac{1}{\sqrt{\beta E_r^{di}}} \gg \frac{1}{\beta(\omega_{k'}+\Delta F^{di}-E_r^{di})} \quad (33)$$

But the analytical expressions obtained in this case will be very cumbersome and numerical calculations will still be required to estimate the parameters.

3. Conclusion.

The paper presents some theoretical aspects of two-photon charge transfer processes in homogeneous condensed systems. One of the most popular research methods are optical methods. Such methods are widely used because they are well-tested and relatively easily accessible methods for experimental measurements.

Based on the use of optical methods for studying complex condensed systems with impurity particles, calculation methods are proposed for the kinetic parameters of charge transfer and phototransfer processes in such systems. The work proposes the use of two-photon methods for research, in which the system can be irradiated with photons at a certain frequency, and the analysis of the irradiation results takes place in a wide range of optical frequencies.

Analytical expressions for the kinetic parameters of transfer and phototransfer processes in complex condensed systems are obtained, and methods for numerical calculation of the characteristic parameters of the processes under study are presented.

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