CONVERSION OF SUBSTANCES BY THE APPLICATION OF LASER RADIATION

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Theoretical model of laser destruction process of chemical compounds by laser radiation is proposed in the work. Models for calculation of vibration spectrum of molecule in nonregular condensed medium and for kinetic parameters of electron transfer and photo-transfer process between the particles are presented within the framework of quantum-mechanical approach. In terms of obtained analytic results it is proposed to calculate frequency spectrum for valence vibrations of atoms in molecule and to split corresponding chemical bonds by the help of laser emission. Obtained radicals may be used for formation of other chemical compounds, particularly, with application of laser emission also.

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Introduction

Interaction of electromagnetic radiation with condensed medium can be used for purposeful destruction (with break of definite chemical bonds), synthesis or both processes simultaneously.

The processes can be realized by different mechanisms dependent on frequency (or frequencies) of the electromagnetic radiation. Radiation of IR-region can be used for destruction process of some particles in condensed medium or molecules of medium. Synthesis of substances can be realized by two mechanisms at least: 1) transfer of definite reactants in electron-excited state with following forming of a reacting complex and corresponding photochemical reaction; 2) with help of direct out-sphere a charge photo-transfer, leading to forming of purposeful product.

The most interesting processes from the point of view of perspective of their application might be two-photon (or many-photon) processes, when the radiation of one of the sources can be used for dissociation (destruction) of definite particles with the aim of ions obtaining, from which is possible construction (synthesis) of the photochemical products. Several sources of electromagnetic radiation can be used for obtaining of ions from the several different reagents. The subsequent synthesis of products can be conducted with the help of the other source, which will provide realization of one of two out-sphere mechanisms (or both simultaneously).

Schematic picture with brief analytic calculations for explanation of suggested approach is given below.

Model of system

We assume, that we have condensed medium with reacting particles. The Hamiltonian of the system has the form:

$$H^{\mathrm{f}} = H_{\mathrm{m}}^{\mathrm{f}} + H_{\mathrm{p}}^{\mathrm{f}} + H_{\mathrm{int}}^{\mathrm{f}} + H_{\mathrm{rad}} + H_{\mathrm{int}}^{\mathrm{rad}} \quad (1)$$

where $H^{\mathrm{f}}_{\mathrm{m}}$ is the Hamiltonian of condensed medium, $H^{\mathrm{f}}_{\mathrm{p}}$ is the Hamiltonian of particles, $H^{\mathrm{f}}_{\mathrm{int}}$ is the Hamiltonian of interaction of particles with medium, H_{rad} is the Hamiltonian of electromagnetic radiation (of two and more sources), $\mathrm{H}^{\mathrm{rad}}_{\mathrm{int}}$ is the Hamiltonian of interaction of radiation with particles in medium and with medium.

As it was shown by the number of workers, first three components in the first part of the formula (1) can be transformed in frames of the certain model approximations[1,2] and formula (1) for adiabatic "*v*" electronic states of particles will have the form:

$$H^{\mathrm{v}} = H_{\mathrm{m}} + H_{\mathrm{p}}^{\mathrm{v}} + H_{\mathrm{int}} + H_{\mathrm{rad}} + H_{\mathrm{int}}^{\mathrm{rad}} \quad (2)$$

where $H_{\mathrm{p}}^{\mathrm{v}}$ is the Hamiltonian of the particles with "*v*" electronic states.

Vibration spectrum of polarizable diatomic molecule in polar media

The first problem is calculation of the vibration spectra of particles, which should be dissociated. A diatomic particle in polar condensed media will be used as an example for calculation of vibration spectra.

The shift of the vibration levels of the molecules during their transition from gas phase to condensed one is explained in literature by action of Van der Waals forces. Models used in that case are based on Onzager-Betcher theory,[3,4] and doesn't take into account the shift, induced by fluctuation of medium polarization. As a rule, these models consider medium as structureless dielectric, and doesn't take into account the effects of space dispersion and frequency dispersion of dielectric polarization of medium.

For simplicity we shall consider uncharged diatomic dipole-active impurity particle in polar medium. The Hamiltonian of the system may be written down as:

$$H = H_{\mathrm{m}} + H_{\mathrm{p}} + H_{\mathrm{int}} \quad (3)$$

where H_{m} is the Hamiltonian of medium; H_{p} is the Hamiltonian of particle; H_{int} is the Hamiltonian of interaction between them.

Interaction H_{int} can be divided into two components[5,6]

$$H_{\mathrm{int}} = H_{\mathrm{int}}^{(1)} + H_{\mathrm{int}}^{(2)} \quad (4)$$

where $H_{\mathrm{int}}^{(1)}$ is interaction of impurity with average polarization of medium <P> (the task of determination of <P> we shall consider as quasi-static):

$$H_{\mathrm{int}}^{(1)} = -\int \langle P(r) \rangle E_0(r) dr \quad (5)$$

and $H_{\mathrm{int}}^{(2)}$ is interaction of impurity with fluctuations of medium polarization:

$$H_{\mathrm{int}}^{(2)} = -\int \delta P(r) E_0(r) dr \quad (6)$$

In formulae (5) and (6) $E_0(r)$ is electric field density, induced by impurity in point r.

In frames of the linear response theory the average value of the medium polarization in point r in quasi-static approximation can be expressed by Green function (*GF*) of medium polarization operators P, which characterizes polar medium, and by tensity of electric field of impurity $E(r)$, which induces given average polarization of medium:

$$\langle P_i(r) \rangle = -\int G_{p_i p_k}(r, r'; \omega \to 0) E_k(r) dr \quad (7)$$

where $G(r,r',\omega)$ is Fourier representation of the temporal retarded GF of medium's polarization operators. Fourier representation of that GF can be expressed by complex dielectric permeability when $\omega \to 0$, $\varepsilon(k; \omega \to 0)$. Particularly, for homogeneous systems:

$$G_{pp}(k,\omega) = -\frac{1}{4\pi}\left(1 - \frac{1}{\varepsilon(k,\omega)}\right) \quad (8)$$

In formula (5) it is assumed, that average polarization is equal to zero in absence of impurity. Expression analogous to E_0, where instead of gas phase dipole moment $\mu_0(r)$ will be written dipole moment in medium $\mu(r)$.

If impurity molecule is isotropic-polarized, then for dipole moment μ may be used the following expression:

$$\mu(r) = \mu_0(r) + \alpha(r) E(r) \quad (9)$$

where $\mu(r)$ is polarizability of the molecule; E is tensity of the electric field, which affects impurity molecule from medium.

The tensity of the electric field E can be expressed through GF of scalar potential operators $G_{\varphi\varphi}$:

$$E_i(r) = grad_{ri} \int dr' \, grad_{r'k} G_{\varphi\varphi}(r, r'; \omega = 0) P_k^{ex}(r') \quad (10)$$

where P^{ex} is polarization of impurity particle, for point dipole approximation $P^{ex}(r) = \mu\delta(r)$.

If intramolecular vibrations of impurity are described in harmonic approximation with frequency ω_{s} and equilibrium length $Q_0 = 0$, then consideration of interaction $H_{\mathrm{int}}^{(1)}$ will bring to change of the square frequency and equilibrium length of this vibration:

$$\Delta\omega^2 = \frac{1}{2}\frac{\partial E_0}{\partial Q} G_{PP} \frac{\partial E}{\partial Q} \quad (11a)$$

$$\Delta Q = \frac{1}{4\omega_S}\left(\frac{\partial E_0}{\partial Q} G_{PP} E + E_0 G_{PP} \frac{\partial E}{\partial Q}\right) \quad (11b)$$

where $\Delta\omega$ is the change of intramolecular frequency of the particle and ΔQ is the change of equilibrium length of vibration.

This change of $\Delta\omega^2$ may be sufficiently large quantity in some cases and endow real contribution in dissociation of the particle.

Let's rewrite Hamiltonian of the system in such form:

$$H = H_{\mathrm{ms}} + H_{\mathrm{ps}} + H^{(2)}_{\mathrm{int}} + F_{\mathrm{s}} \quad (12)$$

where H_{ps} is Hamiltoninan of the particle in polar medium (with parameters ω^2 - $\Delta\omega^2$, Q-ΔQ) and F_{s} has the following form:

$$F_s = -\frac{1}{2} E^0 G_{pp} E \quad (13)$$

Expanding the tensity of electric field $E(r,Q)$ from the expression for $H_{\mathrm{int}}^{(2)}$ into series up to linear term we obtain:

$$H_{\mathrm{int}} = -\int \delta P E_0(r, Q=0) dr - \int \delta P(r) U(r) Q dr \quad (14)$$

$$U(r) = \left.\frac{\partial E}{\partial Q}\right|_{Q=0}$$

The first component in the right side of the expression results in change of equilibrium polarization of medium, and second one results in change of frequency spectrum of impurity and medium and oscillation damping of impurity.

Calculation method of frequency spectrum of the system, when the interaction of intra-molecular vibrations of impurity particle with fluctuations of medium polarization is taken into account was presented in work.[2] The expression for temperature GF of operators of normal coordinates of intra-molecular vibrations of diatomic dipole-active impurities was obtained in work:[2]

$$G_{QQ}(\omega_n) = \frac{1}{\omega_s^2 + \omega_n^2 - U(\omega_n)} \tag{15}$$

$$\omega_n = 2\pi nKT,$$
$$n = 0; \pm 1; \pm 2, ...,$$

where K is Boltzmann constant; T is Kelvin temperature, and renormalized interaction $U(\omega_n)$ characterized effects of interaction of impurity with medium:

$$U(\omega_n) = \int \frac{\partial E_i(r)}{\partial Q} G_{\delta P\delta P}(r,r';\omega_n) \frac{\partial E(r')}{\partial Q} drdr' \tag{16}$$

For Green's function $G_{\delta P\delta P}$ we shall use factorization approximation according to space and time dispersion of dependence:

$$G_{\delta P\delta P}(r,r';\omega_n) = G(r,r')f(\omega_n) \tag{17}$$

where $f(\omega_n)$ is normalization function of frequency dispersion of medium.

Here we'll choose the model, where frequency dispersion of GF of medium's polarization operators has resonance character:

$$f(\omega_n) = -\frac{C}{8\pi}\frac{\Omega_r^2 + \gamma_2}{\omega_n} \times \left(\frac{1}{i\omega_n - \Omega_r + i\gamma} - \frac{1}{i\omega_n + \Omega_r + i\gamma} \right) \tag{18}$$

where C, Ω_r, and γ are experimental parameters.

Equation for vibration spectrum of particle has form:

$$\omega_{1,2} = \omega_s \left[1 + k\frac{\Omega_r^2 + \gamma^2}{2} \frac{\omega_s^2 - \gamma^2 - \Omega_r^2}{(\omega_s^2 - \gamma^2 - \Omega_r^2)^2 + 4\gamma^2\omega_s^2} \right] - \frac{ik\gamma\omega_s^2(\Omega_r^2 + \gamma^2)}{(\omega_s^2 - \gamma^2 - \Omega_r^2)^2 + 4\gamma^2\omega_s^2} \tag{19a}$$

$$\omega_{3,4} = \Omega_r \left[1 + k\omega_s^2 \frac{2(\Omega_r^2 + \gamma^2)(\Omega_r^2 - \gamma^2 - \omega_s^2)}{2\Omega_r^2 \left[(\Omega_r^2 - \gamma^2 - \omega_s^2)^2 + 4\gamma^2\Omega_r^2 \right]} \right] - i\gamma \left[1 - \frac{k\omega_s^2(\Omega_r^2 + \gamma^2)}{(\Omega_r^2 - \gamma^2 - \omega_s^2)^2 + 4\gamma^2\Omega_r^2} \right] \tag{19b}$$

where, k is parameter of coupling with medium.

Depending on correlation of parameters ω_n, ω_s, Ω_r and k solutions of equation (19) describe vibrations with attenuation or pure attenuations. We'll cite solutions of equation (19) for most realistic model – when constraint force with medium is weak, when k<<1. In that case:

$$F(\omega) = -\omega^4 - 2i\gamma\omega^3 - (\Omega_r^2 + \omega_s^2 + \gamma^2)\omega^2 - 2i\omega_s\omega + \omega_s^2(\Omega_r^2 + \gamma^2)(1-k) = 0 \tag{20}$$

It is obvious, from obtained expressions, that consideration of interaction $U(\omega_n)$ brings to frequency shift and appearance of attenuation of these vibrations. It's easy to see that when $\omega_n < \omega_s$ one of the proper frequencies of the system shifts aside high energies.

The calculations of the vibration spectrum can be carried out in an analytical form for polyatomic particle also.

Electron transfer and photo-transfer processes

The second problem for photo-induced processes is a problem of an absorption spectrum of system in electronic region of the frequencies. It is possible to receive a correlation between kinetic parameters of chemical reactions and curve shape of light absorption in this region of frequencies.

The correlation function of GF formalism is one of the most general techniques for research of electron non-adiabatic charge-transfer processes in condensed media. It permits the development of a general theory capable of describing, from common point of view, charge-transfer processes in condensed homogeneous and heterogeneous systems; that is optical processes including charge-transfer processes in condensed media. This technique sets up different correlations between kinetic characteristics of dark processes and corresponding optical processes and makes it possible to analyze the kinetics of charge-transfer processes by means of the absorption curves.[2]

The rate constant for n particles of an electronic, non-adiabatic transition is:[5]

$$K_{\mathrm{n}} = \frac{\beta V^{\mathrm{n-1}}}{i\hbar}\exp(\beta F_{\mathrm{i}})\int d\theta Sp\left[e^{-\beta(1-\theta)\mathrm{H_i}}Le^{-\beta\theta\mathrm{H_f}}L^{+}\right]$$

$$\beta \equiv \frac{1}{k_{\mathrm{B}}T} \qquad (21)$$

where H_{i} and H_{f} are the Hamiltonians for the ingoing and outgoing channels, F_{i} is the initial-state Gibbs energy, V is volume of the system, L is the electronic resonance integral; the integration contour, C_{A}, for the variable θ is parallel to the imaginary axis in the planar strip when $0 \le \mathrm{Re}\,\theta \le 1$; k_{B} is Boltzmann constant and T is the absolute temperature.

The rate constant, K_{n} within the Condon approximation can be represented in the form:

$$K_n = \int\prod_{i=2}^{n}\frac{d\rho_i\prod_{\alpha} d\varphi_{i\alpha}}{\Omega_0}\Phi_i(\rho,\varphi)\left|L_{fi}(\rho,\varphi)\right|^2 \times$$

$$\frac{\beta}{i\hbar}\int_{C_\theta} d\theta\exp\left[-\beta\theta\Delta F_m(\rho,\varphi)-\Psi_m(\theta)\right]\left\langle e^{\beta\theta H_i^v}e^{-\beta\theta H_f^v}\right\rangle \qquad (22)$$

where the angular brackets denote quantum-statistical averaging, ρ_{i} is the radius-vector of the center of gravity of the i-th particle with respect to the first particle, φ_α are three angles determining the orientation of the particle with respect to the first particle (as $\varphi_{\omega\alpha}$ can be used, for example, Euler's angles); Ω_0 is normalization factor, which is $8\pi^2$, or $4\pi^2$, or 1 (depending upon the particle symmetry); $\Phi_{\mathrm{i}}(\rho,\varphi)$is the reactants distribution function which has the form:

$$\Phi_{\mathrm{i}}(\rho,\varphi) = \frac{\exp\left[-\beta F_{\mathrm{i}}(\rho,\varphi)\right]}{\left[\prod_{i=2}^{n} d\rho_{\mathrm{i}}\frac{1}{V\Omega_0}\int\prod_{\alpha} d\varphi_{\mathrm{i\alpha}}e^{-\beta F_{\mathrm{i}}(\rho,\varphi)}\right]} \qquad (23)$$

Here $F_{\mathrm{i}}(\rho, \varphi)$ is the Gibbs energy of the system in the initial state with fixed value of reactants' coordinates ρ and φ.

In eq. (22) $\Delta G_{\mathrm{m}}(\rho,\varphi)$ is the Gibbs energy change of the medium during the process at fixed values of reactant coordinates ρ and φ. Similarly, L_{fi} is the matrix element of the electronic resonance integral, $H_{\mathrm{i}}^{\mathrm{v}}$ and $H_{\mathrm{f}}^{\mathrm{v}}$ are vibrational Hamiltonians of the reactants and products, and the function $\Psi_{\mathrm{m}}(\theta)$has the form:

$$\Psi_m(\theta) = (\pi\hbar)^{-1}\int\int drdr'\Delta E_{\alpha}(r)\Delta E_{\beta}(r')\times$$

$$\int_{-\infty}^{\infty} d\omega\,\mathrm{Im}\,G^{\mathrm{R}}(r,r';\omega)sh\frac{\beta\hbar\omega\theta}{2}sh\frac{\beta\hbar\omega(1-\theta)}{2}\left[sh\left(\frac{\beta\hbar\omega}{2}\right)\omega^2\right]^{-1} \qquad (24)$$

In eq. (24) $\Delta E(r)$ is the electronic field strength change of the reactants during the process and $G^{\mathrm{R}}(r,r',\omega)$ is retarted Green function of the medium polarization operators. By using, for the factorization approximation,

$$\mathrm{Im}\,G^{\mathrm{R}}(r,r';\omega) = \pi f(\omega)G^{\mathrm{R}}(r,r';\omega=0) \qquad (25)$$

we obtain the following expression for $\Psi_{\mathrm{m}}(\theta)$:

$$\Psi_{\mathrm{m}}(\theta) = \frac{2E_{\mathrm{r}}^{\mathrm{m}}}{\hbar}\times$$

$$\times\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}f(\omega)\frac{sh(\frac{\beta\hbar\omega\theta}{2})sh\left[\frac{\beta\hbar\omega(1-\theta)}{2}\right]}{sh(\frac{\beta\hbar\omega}{2})} \qquad (26)$$

where $E_{\mathrm{r}}^{\mathrm{m}}$ is reorganization energy of the medium

$$E_{\mathrm{r}}^{\mathrm{m}} = \frac{1}{2}\iint drdr'\Delta E_{\alpha}(r)\Delta E_{\beta}(r')G_{\alpha\beta}^{\mathrm{R}}(r'r';\omega=0) \qquad (27)$$

The function $f(\omega)$ can be determined from the experimental data of the frequency dependence of the dielectric constant of the system, considering different correlations between the Green functions and dielectric properties of the medium.[7]

The integration with respect of φ in eq. (22) is carried out in various ways. The simplest results are obtained for the case of strong coupling with the medium, when the integral can be calculated by the saddle-point method.

It must be noted that the expression in the angular brackets can also make allowance for such effects as ionic atmosphere fluctuation around the reactants (i.e. whatever can be described by vibrational degrees of freedom) in addition to the reactant vibrations.

For adiabatic processes it is essential to allow the interaction between the reactant electronic state and the vibrational degrees of freedom, which have been ignored so far. In particular, for limiting adiabatic processes, the allowance for additional low frequency relaxation degrees of freedom of the medium leads to the dependence of the pre-exponential factor in the rate constant expression on the characteristic relaxation time τ.[5]

$$K \approx (A/\tau)\exp(-\beta E_{\mathrm{a}}) \qquad (28)$$

The Green function technique makes possible to analyze the kinetics of the elementary act of charge photo-transfer processes in detail.

According to the Lambert-Beer law, the optical density for absorption of the electromagnetic radiation is

$$D = \chi d \qquad (29)$$

where d is the thickness of the adsorbing layer and χ is related to the extinction coefficient ε, by the equation (29).[6-11]

$$\chi = \varepsilon_a c_a + \varepsilon_{ab} c_a c_b + ... \quad (30)$$

where c_a is the concentration of particle a and ε are the extinction coefficients. The first term in eq. (30) describes light absorption by isolated particles, both with transition into an excited state and with charge transfer from one part of a particle to another. The second term characterizes light absorption by reactants, which leads to charge photo-transfer between reactants.

The result of microscopic calculation of the extinction coefficient in the more complicated second term is given below. As for the first term, the expression for ε_a can be easily obtained from the expression for ε_{ab}.

If the absorption at the frequency ω_k, leading to a photo-transfer between n particles, occurs in the system with the volume V, then the extinction coefficient has the form

$$\varepsilon_n = (\frac{2\pi\hbar\omega_k}{c})V^{n-1} \times \times \int_{C_\theta} d\theta e^{\beta\theta\hbar\omega_k} \left\langle e^{\beta\theta H_i} d_{fi}^{k\Lambda} e^{-\beta\theta H_f} d_{fi}^{k\Lambda} \right\rangle \quad (31)$$

where L is the absorbed photon polarization, H_i and H_f are initial- and final-state nuclear Hamiltonians of the system with no photons and $d_{fi}^{K\Lambda}$ is the dipole matrix element projection on the photon polarization vector.

Comparing the latter expression with that of the rate constant of the dark n-particle reaction, one can see, that the extinction coefficient can be derived from the rate constant of the dark reaction by the formal substitution in eq. (21)

$$L_n \rightarrow \sqrt{\frac{2\pi\hbar\omega_k}{cd_{fi}^{k\Lambda}}} \quad (32a)$$

$$\Delta F \rightarrow \Delta F - \hbar\omega_k \quad (32b)$$

If an exchange of heavy fragments does not occur during the charge transfer process, the medium can be represented by the linear approximation and a translational and rotational reactant motion can be represented by the classical approximation, then it is not difficult to obtain, for the extinction coefficient in the Condon's approximation,

$$\varepsilon_n = (2\pi\omega_k / 3c)\int\prod_{i=2}^{n} d\rho \frac{\prod d\varphi_{i\alpha}}{\Omega_0}\Phi_i(\rho,\varphi)\frac{\beta}{i}\times \times \int_{C_\theta} d\theta \left\langle e^{\beta\theta[H_i(\rho,\varphi)+\hbar\omega_k]} d_{fi} e^{-\beta\theta H_f(\rho,\varphi)} d_{fi} \right\rangle_i \quad (33)$$

where $\theta_i(\rho,\varphi)$ is the reactant distribution function, ρ and φ are the coordinates of the i-th particle, determining the position ρ and the orientation φ with respect to the first particle. The expression in the angular brackets includes contributions to the extinction coefficient, both of the intra-molecular vibration degrees of freedom of the reactants and the vibration degrees of freedom, describing ionic atmosphere fluctuations around the reactants.

While the expression in the angular brackets in formula (33) is computed, the harmonic approximation allows this function to be calculated precisely. In so doing we obtain the following expression for the extinction coefficient

$$\varepsilon_n = (2\pi\beta\,\omega_k / 3ic\int\prod_{i=2}^{n} d\rho_i \frac{\prod_x d\varphi_{i\alpha}}{\Omega_0}\Phi_i(\rho,\varphi)\left|d_{fi}(\rho,\varphi)\right|^2 \times \int_{C_\theta} d\theta \exp\left\{\beta\theta\left[\hbar\omega_k - \Delta J(\rho,\varphi)\right] - \Psi(\theta)\right\} \quad (34)$$

where $\Delta J=\Delta F_m+\Delta J_v$; $\Psi(\theta)=\Psi_m(\theta)+\Psi_v(\theta)$; ΔJ_v is the difference between the minimal vibration energies and the function $\Psi_v(\theta)$ resembles the function $\Psi_m(\theta)$ in structure. To make it simple we take its form for the case when there is no mixture of normal coordinates in the beginning and at the end of the reaction. In this case

$$\Psi_v(\theta) = \prod_l \frac{2\exp\left[\theta\left(x_l^f - x_l^i\right)\right] shx_l^i}{\left\{4sh^2\left[x_l^i\lambda + x_l^{f\theta}\right] - (1 - \frac{x_l^i}{x_l^f})sh\left[2x_l^i\lambda\, sh(2x_l^f\theta)\right]\right\}^{1/2}} \times \exp\left\{-\frac{x_l^f(Q_{l0}^f - Q_{l0}^i)^2}{x_l^f cthx_l^i(1-\theta) + x_l^i cthx_l^f\theta}\right\} \quad (35a)$$

$$x_l^{i(f)} = \frac{\beta\hbar\omega_l^{i(d)}}{2} \quad (35b)$$

$$\lambda = 1 - \theta \quad (35c)$$

where ω_l^i and ω_l^f are the frequencies of vibrations in the initial and final states, and Q_{l0}^i and Q_{l0}^f are the equilibrium meanings of normal coordinates in the initial and final states.

In the case of strong coupling with the medium, when the integral over θ can be calculated by the saddle-point method,

$$\varepsilon_n = \frac{(2\pi)^{3/2}\beta\omega_k}{3c\left|\Psi''_{\theta\theta}\right|^{1/2}}\int\prod_{i=2}^{n} d\rho_i \frac{\prod_\alpha d\varphi_{i\alpha}}{\Omega_0}\Phi_i(\rho,\varphi)\left|d_{fi}(\rho,\varphi)\right|^2 \times\exp\left\{\beta\theta^*\left[\hbar\omega_k - \Delta J(\rho,\varphi)\right] - \Psi(\overset{*}{\theta})\right\} \quad (36)$$

where the saddle-point θ* can be determined from the equation

$$\beta(\hbar\omega_k - \Delta J) - \Psi'_\theta(\theta) = 0 \quad (37)$$

The expression for the extinction coefficient related to the absorption by isolated particles can be easily obtained from eq. (36), if we omit the factor $\Phi_i(\rho,\varphi)$, and integrals ρ, φ and the normalization factor Ω_0.

Discussion

In case when the initial substance is toxic, toxicity of some complex particles may be connected with presence of some functional groups. The reconstruction of exactly these functional groups is necessary for change of toxic properties. Thereto at the first stage it is necessary to break certain chemical bonds.

As obtained results have shown, selection of polar solvent is enough sometimes for dissociation of the particles see form. (11) and (19). If in this case the dissociation of the particles will not take place at least the change of vibration frequency will occur, in the direction of frequency decrease as a rule. Concentration of vibration energy on exact chemical bonds, e.g. of toxic molecules (nonequilibrium processes) is more effective method of particles destruction. Radiation exposure of given frequency on the systems (formula (19)) is necessary for this. Transfer of the particles in electron-excited state where dissociation of particle takes place is effective method as well. Extinction coefficient for these processes has the form (36).

Products obtained during destruction may recombine or take part in chemical processes thermally with other particles. To ensure passing of purposeful chemical processes probably is necessary to provide destruction of other molecules. Fragments of dissociated toxic molecule will interact with fragments of these molecules. Meanwhile it is necessary to influence the system by two sources of radiation at least.

The most interesting case is when photo-synthesis of new particles is realized from fragments of disrupted toxic molecules and fragments of other particles. Meanwhile it is necessary to use additional radiation source, which will ensure photosynthesis. The processes of direct out-sphere photosynthesis of new complex particles are described by formula (35), synthesis processes via electron-excited particles appropriately by expression of ε_a (formula (30)).

Conclusion

It is evident from the results of the investigations, that selection of polar solvent is enough sometimes for dissociation of the particles. Analytic expressions describing the processes of direct out-sphere photosynthesis of new complex particles, synthesis processes via electron-excited particles, extinction coefficient for transfer of the particles in electron-excited state have been obtained. Use of laser emission for splitting of specified chemical bonds and for formation of other chemical compounds is proposed as well.

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