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SENSING DYNAMICS OF THE ZONE TYPE MULTI-LEVEL SYSTEM IN A LASER FIELD: STOCHASTIZATION OF VIBRATIONAL MOTION FOR MOLECULES IN THE MULTI-PHOTON PHOTOEXCITATION REGIME

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Abstract

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We present new theoretical scheme to sensing dynamics of the zone type multi-level system in a laser field, based on the quantum stochastic kinetic approach. The multi-photon dissociation yield, selectivity and absorbed energy upon the laser pulse energy density for BCl_3 molecules in the oxygen O_2 buffer gas are calculated. It has been studied a stochastization of vibrational motion for molecules in the multi-photon photo-excitation regime on example of CF_3I, $SF_6$and BCl_3 molecules within the stochastic Focker-Plank model.

Key words: sensing, molecule in laser field, vibrational stochastization, kinetic modelling

Анотація

ДЕТЕКТУВАННЯ ДИНАМІКИ БАГАТОРІВНЕВИХ СИСТЕМ ЗОННОГО ТИПУ У ПОЛІ ЛАЗЕРНОГО ВИПРОМІНЮВАННЯ: СТОХАСТИЗАЦІЯ КОЛИВАЛЬНОГО РУХУ У МОЛЕКУЛАХ В УМОВАХ БАГАТОФОТОННОГО ЗБУДЖЕННЯ

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Запропоновано нову теоретичну схему детектування динаміки багаторівневих систем зонного типу у полі лазерного випромінювання, яка базується на квантовому, стохастичному, кінетичному підході. Виконано розрахунок залежності виходу та селективності багатофотонної дисоціації, поглиненої енергії від густини енергії лазерного імпульсу для молекул BCl_3 у буферному газі O_2. Вивчено стохастизацію коливального руху у молекулах в умовах багатофотонного збудження для молекул CF_3I, SF_6, BCl_3 з використанням стохастичної моделі Фоккера-Планка.

Ключові слова: детектування, молекула у лазерному полі, коливальна стохастизація, кінетичне моделювання.

Аннотация

ДЕТЕКТИРОВАНИЕ ДИНАМИКИ МНОГОУРОВНЕВЫХ СИСТЕМ ЗОННОГО ТИПА В ПОЛЕ ЛАЗЕРНОГО ИЗЛУЧЕНИЯ: СТОХАСТИЗАЦИЯ КОЛЕБАТЕЛЬНОГО ДВИЖЕНИЯ В МОЛЕКУЛАХ В УСЛОВИЯХ МНОГОФОТОННОГО ВОЗБУЖДЕНИЯ

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Предложен новый теоретический подход к детектированию динамики многоуровневых систем зонного типа в поле лазерного излучения, базирующийся на квантовом, стохастическом кинетическом подходе. Выполнен расчет зависимости выхода и селективности мульти-фотонной диссоциации, поглощенной энергии от плотности энергии лазерного импульса для молекул BCl_3 в буферном газе O_2. Изучена стохастизация колебательного движения в молекулах у условиях многофотонного возбуждения для молекул CF_3I, SF_6, BCl_3 с использованием стохастической модели Фоккера-Планка.

Ключевые слова: детектирование, молекула в поле лазерного излучения, колебательная стохастизация, кинетическое моделирование.

1. Introduction

A significant progress in development of laser technique stimulated a great interest to carrying out new non-linear optical, laser devices for solving a wide number of tasks in different applications (atomic, molecular chemical physics, quantum electronics, physics of elements, devices, sensor technologies etc.). Above cited problems it is of a great importance a studying of dynamics of the zone type multi-level systems in a laser field. Speech is about dynamics of the multi-atomic molecules in a strong laser field. A variety of multi-photon processes have been observed in molecules, including multi-photon excitation, ionization, dissociation (c. f. [1-9]). It is very important to note that using lasers allows highly selective introducing the energy quantities into definite freedom degrees of system. It can be used as physical basis for creation and construction of special devices for sensing physical, chemical properties of the molecular systems and can find application in solving problems of the nano-electronics, nano-atomic optics, quantum computing, molecular sensors technologies etc.

While the dynamical aspects of ionization of molecules in a strong laser field are considered to be well understood at least within quantitative simplified models, the multi-photon dissociation and excitation is a topic of active interest [1-3,10-15]. Many experiments of studying the multi-photon processes were fulfilled in the conditions, when the collisional factor may be missed. A separation of the contributions of different relaxation processes in the experiment is complicated problem, though a hierarchy of relaxation times ($t_R \ll t_{V-V} \ll t_{V-T}$) exists. An influence of buffer gas on the processes of multi-photon excitation and dissociation results in more effective molecule involvement into quasicontinuum due to the rotational relaxation at lowest levels [2,3,10-12]. A question about stochastization of vibrational motion, when the vibrational energy is randomly distributed among the vibrational modes during interaction with laser pulse attracts especial attention.

In a number of papers (c. f. [13-19]) a stochastic, kinetic approach has been developed is used to calculate the integral parameters of the multi-photon excitation (dissociation) and relaxation of number of the molecules (CF_3Br, CF_3I, SF_6 etc). A process of excitation into continuum is described within the generalized kinetic equation model with account for stochastization of the vibrational motion. There have been calculated the dissociation yield and absorbed energy, dependence of the absorbed energy ε and dissociation yield β upon summarized pressure of the buffer gases. In this paper we present new theoretical scheme to sensing dynamics of the zone type multi-level system in a laser field, which is based on the quantum stochastic kinetic approach, developed in refs. [13,14]. Dependencies of the multi-photon dissociation yield, selectivity coefficient and absorbed energy upon the laser pulse energy density for BCl_3 molecules in the oxygen O_2 buffer gas are calculated. It has been studied a phenomenon of stochastization of the vibrational motion for molecules in the multi-photon photo-excitation regime on example of the CF_3I, SF_6 and BCl_3 molecules with using the non-linear inter-mode resonances interaction model and stochastic Focker-Plank equation. There are presented the theoretical estimates of the energy threshold, for which the vibrational energy can be randomly distributed among the vibrational modes during the interaction with the laser pulse.

2. Multi-photon excitation model for molecule in a laser field

We start our consideration from the kinetic equations, describing the temporal behaviour of occupancy of the vibrational levels for molecule in a laser field. Bur before, let us give some model representations regarding general Hamilton's description of stochastic features in the multi-photon excitation process for molecules. From theoretical point of view an effect of vibrational stochastization is related to very complex phenomena. Hitherto, there is absent an adequate theoretical explanation and corresponding comprehensive model (c. f. [2-6,11,13,20]. However, generally speaking, it is far obvious that this effect is provided by the non-linear inter-mode resonance interaction. In approximation of small vibrations a Hamiltonian of molecule can be written as [6]:

$$H = \sum_i H_i^{(l)} + E\sum_i c_i x_i + \sum_i H_i^{(nl)} + H^{(\mathrm{int})} + H^{(e-nl)} \quad (1)$$

where $H_i^{(l)} = (\dot{x}_i^2 + \omega_i^2 x_i^2)/2$ is an energy of separated modes in linear approximation; x are the normalized shifts of atoms from the non-perturbed position; second term is corresponding to the linear dipole interaction with a field; the term $H_i^{(nl)} = ax_i^3 = bx_i^4 + \ldots$ defines a non-linearity of modes and their interaction term $H^{(int)}$ is as follows:

$$H^{(\mathrm{int})} = \sum_i A^3_{i_1 i_2 i_3} x_{i_1} x_{i_2} x_{i_3} + \ldots$$

Non-linear corrections to interaction with a field are defined as:

$$H^{(e-nl)} = E(\sum_i a^2_{i_1 i_2} x_{i_1} x_{i_2} + \ldots)$$

The interaction between modes leads to their washing out, which is equivalent to broadening by external field. The estimated value of this effect is (for resonance $\omega_1=\omega_2+\omega_3$):

$$\Delta\omega_1 \sim (\omega_{1/}\hbar)^{1/3} (A^3_{123} x_1 x_2 x_3 \overline{n})^{2/3} \quad (2)$$

where $\overline{n}$ is an averaged number of quanta in the modes 2 and 3. It is clear that with growth of the molecule excitation degree (growth $\overline{n}$) it is increased a non-linear broadening. For definite value of $\overline{n}$ $\Delta\omega_1$ is comparable with frequency distance Δ_0 to another resonance of the same order, i. e. $\omega_1=\omega_2+\omega_4$. It is easily understand that $\Delta_0 \sim \omega_0/N_f^2$, where ω_0 is the characteristic value of frequaency and N_f is number of frequencies of the system. Under overlapping resonances ($\Delta\omega >> \Delta_0$) motion of each mode is defined at once by many resonant terms of the hamiltonian. In whole, a motion becomes by quasi random or stochastic. This is equivalent to the well-known Chirikov criterion [20] of the stochasticity:

$$\overline{n} \geq (\omega_0 / \hbar\omega')^{1/2} (\hbar\omega_0 / | A^{(3)} \overline{x}^{(3)} |)(1/N_f^3) \sim 10^2 / N_f^3 \quad (3)$$

Let us further to introduce a hamiltonian (in variables "action *I*-angle θ")of influence on the mode 1 from the side of other modes as a sum of resonant contributions, which are lying inside non-linear width $\Delta\omega_{1:}$

$$H_1^{\mathrm{int}} = I_1^{1/2} \sum_n F_n \cos(\theta_1 - \theta_n) \quad (4)$$

Condition of periodicity on θ results in the quantization of action and energy, i. e. $I_n = nh$ and $E_n = H_0(nh)$. It should be mentioned that resonances are arisen for such values of the action that it is right:

$$k\omega(I_0) = l\Omega, \ \omega(I) = dH_0/dI$$

for whole numbers *k,l*. The interaction (4) changes quasi-energy of the mode 1as follows:

$$dE_1 / dt = I_1^{1/2} [\Omega - \omega(I_1)] \times$$
$$\times \sum_n F_n \sin(\theta_1 - \theta_n) - (e\overline{x}_1 E / 2\hbar^{1/2}) \sum_n F_n \sin\theta_n \quad (5)$$

The first term in eq. (5) describes the inter mode relaxation; second term –the interaction with an external field. One could suppose that the phases θ_n are random. Then one has that $<\Delta E_l>=0$ and $<(\Delta E_l)^2>=\Delta(E)t$ (*t* is a time). It is obvious that a process of the energy acceptance is not regular. It has a character of the diffusion with coefficient *Δ(E)* (see below). Its calculation gives the following result:

$$D(E) = (\pi / 4\hbar)(e\overline{x}_1 E)^2 J(\Omega)$$
$$J(\Omega) = |F(\Omega)|^2/\Delta_0$$

Here a variable *J(Ω)* has an essence of spectral intensity of the perturbation $H_1^{(int)}$ on the field frequency. In ref. [6,20] it had been indicated on the possibility of describing a process of the multi-photon excitation of molecule by the Focker-Plank equation. At first the correct Focker-Plank approach has been proposed and realized in ref. [13-14].

As it is indicated, usually the vibrational spectrum is qualitatively divided into parts of the low-lying discrete states and high-excited levels of the quasicontinuum [2,3]. At the definite energy threshold the vibrational energy can be randomly distributed among the vibrational modes during the interaction with the laser pulse. The excitation process into continuum is described by system of the kinetic equations [13-15]:

$$\partial Z_n / \partial t\ t=(W_{n-1,n}+k^{VT}_{n-1,n}p)Z_{n-1}+$$
$$+(W_{n+1,n}+k^{VT}_{n+1,n}p)Z_{n+1} — (W_{n-1,n}+$$
$$+k^{VT}_{n,n-1}pW_{n+1,n}+k^{VT}_{n,n+1}p)Z_n-d_nZ_{n.}+$$
$$+\partial/\partial n\ [Q(n-N_{min})D(R)n^3\ \partial Z/\partial n\ ] \qquad (6)$$

where z_n are the populations of the laser-excited states with energy E_n; $W_{n,n}\pm_1$ is the rate of the radiative transitions; $W_{n,n}\pm_1=\sigma_{n',n\pm1}I(t)$, where $s_{n',n\pm1}$ are the cross-sections of the radiative transitions up and down, $I(t)$ is the laser radiation intensity (photon×cm^{-2}×s^{-1}); $k^{VT}_{n,n\pm1}$ are the constants of rate of the V-T relaxation; d_n is the mono-molecular decay rate; $Q(n-N_{min})$ is the Heaviside function as an additional multiplier in the diffusion coefficient $D(R)n^3$, which "freezes" the stochastic processes in the area of the low-lying states according to the well known Chirikov's criterion [10]. The key difference between our model and other theoretical models is in an explicit accounting for effect of stochastic diffusion into quasi-continuum. The constants of relaxation rate $k^{VT}_{n,n-\pm1}$ are defined by the physical parameters of molecule. According to ref. [2,13] the collisional redistribution of populations is determined by the probability function of transition due to the collision $k\ (E\rightarrow E')$. The physically significant variable is an energy, transmitted during collision:

$$\Delta E(E)=\int_0^\infty dE'(E-E')k(E\rightarrow E') \qquad (7)$$

The similar parameter in eqs. (6) is defined as follows:

$$\Delta E_n=(k^{VT}_{n,n-1-}k^{VT}_{n,n+1})hv/Z \qquad (8)$$

Here Z is a frequency of the gas-kinetic collisions. The condition $\Delta E(E_n)=\Delta E_n$ determines the relationship between phenomenological relaxation constants in eqs. (1) and microscopical variable $\Delta E(E)$. To describe an influence of the collisions on excitation of the molecule at the lowest discrete levels, we suppose that q-factor in the uncollisional case is created due to the heterogeneity of interaction of the different initially populated states with a field. System of the low levels is characterized by two rates: the radiative rate of excitation of the states W_0 and rate of the rotational relaxation k_{Rp}, which is proportional to the pressure. The equations defining the molecule involvement into quasicontinuum during the laser pulse are as follows:

$$dN_0/dt=-W_0z_0,$$
$$dz_0/dt=-W_0z_0+k_{Vp}\ (fN_0-z_0, \qquad (9)$$
$$dq/dt=-dN_0/dt,\ N_0(0)=l,\ z_0(0)=f,$$

Here f is the part of molecules interacting resonantly with a laser field. The shape of laser pulse is modelled in accordance to the experiment [10,12]. Regarding a dependence $W_o(t)$ in eqs. (4) on the laser field intensity $I(t)$, it can be noted that the assumption $W(t)\sim I(t)$ is quite acceptable for the quasicontinuum. For low levels it is more acceptable the assumption on more strong dependence of $W(t)$. To calculate the dissociation yield we use the assumption that the molecule decay has to be instantaneous from the level, at which the mono-molecular fragmentation rate exceeds the radiative transition rate on the order. Estimate within the RRK-theory allows to write [2]): $D_n=k_{diss}\rho(E_n-D)\rho(E_n)$,where ρ is the density of vibrational states. Regarding a dependence $DE(E)$ in the quasicontinuum it can be noted that a precise data for molecule CF_3Br are absent. The estimate can be received by comparison of the data on deactivation of the molecules by the nitrogen (see ref. [2]).

3. Results and discussion

Figure 1 shows the calculated dependence of the dissociation yield $^{10}\beta$ and selectivity α on density of energy for the first Φ_1 (the solid line) and second Φ_2 (the dashes line) laser pulse for BCl_3 molecules. The experimental data (triangles and cycles in figure 1) are taken from ref. [12]. All parameters are corresponding to experiment [12]: acceptor — O_2, pressure p_{O2}=4,5 Torr, p_{BCl3}=0,1 Torr; first laser pulse: Φ_1=3,7 J/cm^2, frequency Ω_1=985,49 cm^{-1} (line 10R36); second laser pulse: Φ_2=3,0 J/cm^2, frequency Ω_1=931,00 cm^{-1} (line 10P34). Theoretical stochastic, kinetic model gives physically reasonable agreement with experiment. As it was waited for, the dissociation yield dependence upon the laser pulse energy density has the degree character. Analysis has shown that for $^{10}BCl_2$ molecules this is quadratic dependence and for $^{11}BCl_2$ molecules — linear one. Such a difference provides unusual behaviour of the multi-photon dissociation selectivity, which has a linear growth with increase of Φ_1 and Φ going from 3 J/cm^2 to 4 J/cm^2.

This important fact has been at first noticed in ref. [12]. Further let us present on figure 2 the calculated [17,18] dependence of the excited molecule part q (above) and their averaged energy ε_q (down)

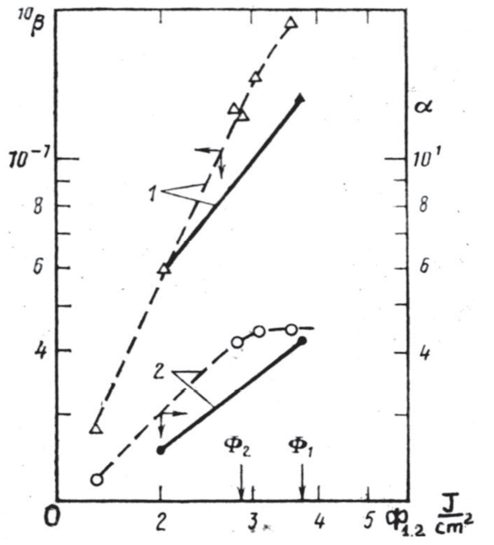

Fig 1. Calculated dependence of the dissociation yield ${}^{10}b$ and selectivity α on density of energy for the first F_1 (the solid line) and second F_2 (the dashes line) laser pulse and experimental data (triangles and cycles) [12] for BCl_3 molecules (see text).

upon density of energy of the CO2 laser pulse for molecules CF_3I and SF_6: the solid lines — calculation data [17,18]; experiment -• — and o- data [2,3,10]. An analysis of the obtained data shows that an agreement between the theory and experiment is physically reasonable. An account of the stochastization effect leads to more correct description of the excitation dynamics in the quasicontinuum and allows to obtain the better quantitative agreement with experiment in comparison with other theoretical models (c. f. [2,3]. The value of the factor q allows defining a true level of excitation of the molecules. The characteristic feature of the ε_q (Φ) dependence (c. f. fig. 2) is a slow initial growth of level of the excitation of molecules. Presented data allow to understand how it is realized he process of the multi-photon excitation. Usually observed growth for dependence ε_q (Φ) is determined by increasing number of excited molecules. Under large values of Φ (Φ>0,3-0,5 J/cm²) a growth of the absorption is connected with growth of level of the excitation, as the value of q changes here very slowly. During the process of multi-photon excitation two ensembles of excited and non-excited molecules are forming. As under collisions an averaged energy of excited molecules can decrease so, that it will become an essential the quantum character of thermo-capacity of the vibrational degrees of freedom. In whole, during multi-photon excitation there are formed states, which are corresponding to statistically equal distribution of the absorbed energy by all, or more correctly, by majority of vibrations of the molecules. Stochastic feature of vibrational motion is arisen during process of interaction with the IR laser radiation field because of the non-linear inter-mode resonance interaction. In figure 3 there are presented the schemes of disposition of the inter-mode resonances for CF_3I, $SF_6$and BCl_3 molecules. Let us give the theoretical estimates of the stochastization threshold. Minimal density of energy of the CO_2 laser pulse was 0,06J/cm² [2]. From known values of q and ε_q (Φ) one can find an average absorbed energy. With account for the initial average vibrational energy (temperature 293 K) we got the following estimates for stochastization threshold energy E_b=3970cm^{-1} that is in agreement with experiment [2,3,10,12]: E_b≈(3900±500) cm^{-1} for SF_6.

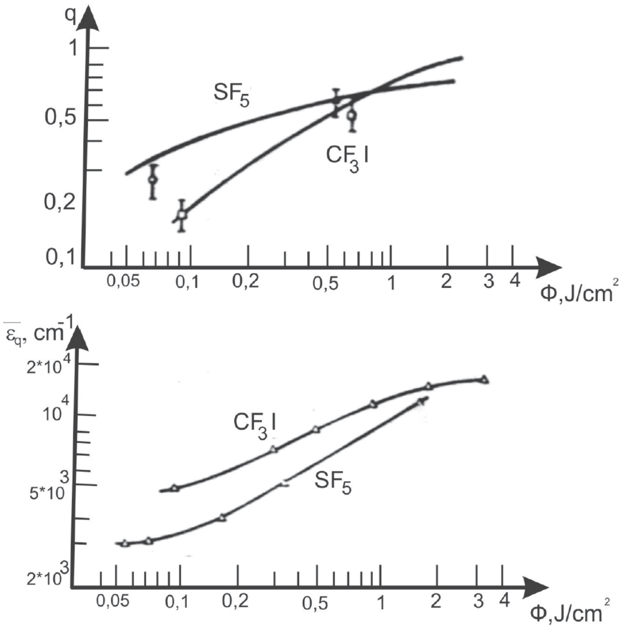

Fig. 2. The dependence of the excited molecule part *q* (above) and their averaged energy e_q (down) on density of energy of the CO_2 laser pulse: continuous lines — our calculation data [17,18]; experiment -•, o- data [2,3,10];

Other our estimates are as follows: E_b=3500cm^{-1} for BCl_3 and E_b=5650cm^{-1} for CF_3Br.

So, we presented new theoretical scheme to sensing dynamics of the molecules in a laser field and studied a stochastization of molecules vibrational motion in the multi-photon photo-excitation regime on example of CF_3I, SF_6, BCl_3 molecules within the Focker-Plank model. Surely, these phenomena taking into account for possibility of the highly selective laser introducing the energy quantities into definite freedom degrees, can be used as physical basis for creation and construction of sensors for physically-chemical properties of the molecular systems and devices.

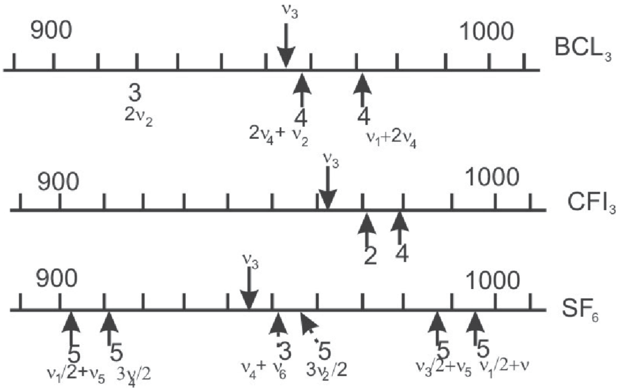

Fig. 3. Schemes of disposition of inter-mode resonances for CF_3I,SF_6,BCl_3 molecules [6,13]

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References

1. J. D. Lambert,Vibrational and Rotational Relaxation in Gases (Oxford,1977).
2. Letokhov V. S., Nonlinear selective photoprocesses in atoms and molecules (Moscow, 2003).
3. V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov, E. A. Ryabov, Multi-photon processes in molecules in IR laser field (Moscow, 1991).
4. Gutzwiller M.,Chaos in Classical and Quantum Mechanics (N. — Y.,Springer-Verlag, 2003).
5. Kleppner D., Chun-Ho I., Welch G. R., Irregular Atomic Systems and Quantum Chaos, Ed. J. C. Gay (N-Y., Kluwer, 2001).
6. Shuryak E. V. Non-linear resonance in quantum systems// JETP. — 1986. — Vol. 71. — P. 2039-2050.
7. Glushkov A. V., Malinovskaya S. V., Co-operative laser nuclear processes: border lines effects// In: New projects and new lines of research in nuclear physics. Eds. G. Fazio and F. Hanappe, (Singapore, World Sci., 2003). — P. 242-250.
8. Glushkov A. V., Ambrosov S. V., Ignatenko A. V., Korchevsky D. A., DC Strong Field Stark Effect for Non-hydrogenic Atoms: Consistent Quantum Mechanical Approach // Int. Journ. Quant. Chem. — 2004. — Vol. 99,N5. — P. 936-939.
9. Glushkov A. V., Prepelitsa G. P., Svinarenko A. A. Sensing the stochastic laser pulse structure and chaotic and photon-correlation effects in the nonlinear multi-photon atomic dynamics in laser and DC electric field// Sensor Electr. & Microsyst. Techn. — 2004. — N2. — P. 89-95
10. Bagratashvili V. N., Vayner Y. G., Dolzhikov V. S. etal, Inter and intra-molecular distribution of vibration energy for multi-photon excitation by IR laser field//JETP. — 1980. — Vol. 80-P. 1008-1018.
11. Makarov A. A., Platonenko V. T., Tyakht V. V., Interaction of quantum system "level-zone" with quasi-resonant monochromatic field// JETP. — 1978. — Vol. 85. — P. 2075-2086.
12. Laptev V. B., Ryabov E. A., Isotopically-selective dissociation BCl_3 in a two-colour IR laser field// Soviet Chem. Phys. — 1988. — Vol. 7,N2. — P. 165-170.
13. Glushkov A. V., Malinovskaya S. V., Shpinareva I. M., Kozlovskaya V. P., Gura V. I. Quantum stochastic modelling multi-photon excitation and dissociation for CF_3Br molecules: An effect of rotational and V-T relaxation // Int. Journ. Quant. Chem. — 2005. — Vol. 104,N3. — P. 541-546.
14. Glushkov A. V., Zelentsova T. N., Shpinareva I. M., Svinarenko A. A., Kinetics of energy transfer in molecules of CF_3Br in the buffer gas medium in an intense laser radiation field// Phys. Aerodisp. Systems. — 2002. — Vol. 39. — P. 129-136.
15. Shpinareva I. M., Gura V. I., Kozlovskaya V. P., Kinetics of energy transfer in molecules of SF_6 in an intense laser field; Stochastic effects// Phys. Aerodisp. Systems. — 2004. — Vol. 41. — P. 133-138.
16. Shpinareva I. M., Selective photo-ionization and dissociation of molecules method for cleaning of semiconductor materials from admixtures// Func. Materials. — 2003. — Vol. 10. — P. 211-214.
17. Shpinareva I. M., New scheme of method for selective photo dissociation of the molecules in problem laser cleaning the semiconductor materials in gas phase: quantum-kinetical modelling for molecules CF_3I // Photoelectronics. — 2003. — Vol. 12. — P. 96-100.
18. Shpinareva I. M., Gura V. I., Koltzova N. Yu., Stochastic effect mechanism in the multi-photon processes for molecules in an intense laser field// Photoelectronics. — 2005. — Vol. 14. — P. 113-118.
19. Glushkov A. V., Ambrosov S. V., Shpinareva I. M., etal, Spectroscopy of diatomic van-der-waals molecules: atom of inert gas- atom of galogen// Opt. Spectr. — 1998. — Vol. 84. — P. 567-572.
20. Zaslavsky G. M., Chirikov B. V. Studied on theory of non-linear resonance and stochasticity// Usp. Phys. Nauk. — 1971. — Vol. 105. — P. 3.