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NON-LINEAR CHAOTIC TREATING VIBRATIONAL MOTION FOR MOLECULES IN THE MULTI-PHOTON PHOTOEXCITATION REGIME

It has been studied a stochastization of vibrational motion for molecules in the multi-photon photo-excitation regime on example of the CF_3I, SF_5 molecules within quantum-stochastic kinetic approach and given more accurate data for stochastization threshold energies.

At present time the topics of laser –molecular interactions has a great interest as for molecular spectroscopy , laser physics, photochemistry as for different applied applications in construction of optical devices and optical [1-13]. It is known that 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 of molecules in real laser field is a topic of actuality and importance. Many experiments of studying the multi-photon processes were fulfilled in the conditions, when the collisional factor may be missed. A question about chaotic elements of the vibrational motion of molecules in a laser field, when the vibrational energy is randomly distributed among the vibrational modes during interaction with laser pulse is to be very actual and complicated task.

In Refs. [12,13] it has been presented 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. [11]. 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.

Here we study stochastization of vibrational motion for molecules in the multi-photon photo-excitation regime on example of a set of molecules within quantum- stochastic model [13] and obtain more accurate estimates for the stochastization energy. The obtained data are compared with earlier obtained theoretical and experimental results [2,10,13].

Taking into account the possible manifestations of a chaos phenomenon on molecular dynamics one should use molecular hamiltonian (in variables "action *I*-angle *q*")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 Dw_1 (look full details look in Refs. [12,15]):

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

Condition of periodicity on q results in the quantization of action and energy, i.e. $I_n=n\hbar$ and $E_n=H_0(n\hbar)$. Resonances are arisen for such values of the action that it is right:

$$kw(I_0)=lW\ ,\ w(I)=dH_0/dI$$

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

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

The first term in eq.(2) describes the inter mode relaxation; second term –the interaction with an external field. The whole process of the energy acceptance is in fact stochastic. Speech is about the diffusion with coefficient $D(E)$ (see below). Its calculation gives the following result:

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

$$J(\Omega)=|F(\Omega)|^2/\Delta_0 \quad (3)$$

Here a variable $J(W)$ has an essence of spectral intensity of the perturbation $H_1^{(int)}$ on the field frequency. In ref. [12-15] it has been formulated an effective Focker-Plank equation approach to process of the multi-photon molecular excitation. Till its application, the the vibrational spectrum is usually divided into two parts: a). the low-lying discrete states and b). high-excited levels of the quasicontinuum. 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]:

$$\partial Z_n / \partial t\ t=(W_{n-1,n}+k^{VT}_{n-1,n}p)Z_{n-1}+(W_{n+1,n}+$$
$$+k^{VT}_{n+1,n}p)Z_{n+1}-$$
$$(W_{n-1,n}+k^{VT}_{n,n-1}pW_{n+1,n}+k^{VT}_{n,n+1}p)Z_n-$$
$$-d_n Z_n+\partial/\partial n\ [\Theta(n-N_{min})D(R)n^3\ \partial Z/\partial n\ ] \quad (4)$$

where z_n are the populations of the laser-excited states with energy E_n ; $W_{n,n\pm1}$ is the rate of the radiative transitions; $W_{n,n\pm1}=s_{n',n\pm1}I(t)$, 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 model presented explicitly accounts 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. [2,15] the collisional redistribution of populations is determined by the probability function of transition due to the collision $k(E\to E')$. The physically significant variable is an energy, transmitted during collision:

$$\Delta E(E)=\int_0^\infty dE'(E-E')k(E\to E') \quad (5)$$

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

$$\Delta E_n=(k^{VT}_{n,n-1}-k^{VT}_{n,n+1})h\nu/Z \quad (6)$$

Here Z is a frequency of the gas-kinetic collisions. The condition $DE(E_n)=DE_n$ determines the relationship between phenomenological relaxation constants in eqs.(1) and microscopical variable $DE(E)$.

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. According to [14,15], the equations defining the molecule involvement into quasi-continuum during the laser pulse are as follows:

$$dN_0/dt=-W_0 z_0,$$

$$dz_0/dt=-W_0 z_0+k_{Vp}\,(fN_0-z_0),$$

$$dq/dt=-dN_0/dt, \qquad (7)$$

$$N_0(0)=l, \quad z_0(0)=f,$$

Here *f* is the part of molecules interacting resonantly with a laser field. In difference of the previous works [14,15] we have a real model for the shape of laser pulse [2,10]. This is related to more accurate data for dependence D*E(E)* in the quasicontinuum. The following estimate has been taken for. $D_n=k_{diss}r(E_n-D)r(E_n)$ [2], where r is the density of vibrational states.

From physical point if view, a chaotic c feature of vibrational motion is arisen during process of interaction with the IR laser field because of the non-linear inter-mode resonance interaction. In fact speech is about a strong non-linear interaction of resonances with possible

We carried out more accurate estimates of the stochastization threshold using more real input parameters of the quantum-stochastic modeling. Minimal density of energy of the CO_2 laser pulse was taken as 0,06J/cm^2 [2]. From known values of q and e_q (F) one can calculate an average absorbed energy. With accounting for initial average vibrational energy (T= 293 K) we obtained the following estimates for stochastization threshold energy E_b=4080 cm^{-1} that is in agreement with experiment [2,3,8,9]: E_b»(3900±500) cm^{-1} for SF_6. The theoretical value obtained in Ref. [13] is 3970 cm^{-1}. Data for other molecules are as: E_b= 3620 cm^{-1} for BCl_3, E_b=5760cm^{-1} for CF_3Br.

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Key words: molecule in laser field, vibrational stochastization

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НЕЛИНЕЙНОЕ ХАОТИЧЕСКОЕ РАССМОТРЕНИЕ КОЛЕБАТЕЛЬНОГО ДВИЖЕНИЯ В МОЛЕКУЛАХ В УСЛОВИЯХ МНОГОФОТОННОГО ВОЗБУЖДЕНИЯ

Резюме

Изучается стохастизация колебательного движения в молекулах у условиях многофотонного возбуждения для молекул CF_3I, SF_6 в рамках квантово-стохастического кинетического подхода и приведены уточненные данные энергий порога стохастизации.

Ключевые слова: молекула в поле лазерного излучения, колебательная стохастизация

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НЕЛІЙНИЙ ХАОТИЧНИЙ РОЗГЛЯД КОЛИВАЛЬНОГО РУХУ У МОЛЕКУЛАХ В УМОВАХ БАГАТОФОТОННОГО ЗБУДЖЕННЯ

Резюме

Вивчається стохастизація коливального руху у молекулах в умовах багатофотонного збудження для молекул CF_3I, SF_6 в межах вантово-стохастичного кінетичного підходу і наведені уточнені данні по енергіям порога стохастизації.

Ключові слова: молекула у лазерному полі, коливальна стохастизація