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$_3$I, SF$_6$, 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$_3$I, SF$_6$, 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]):

$$H_1^{\text{int}} = I_1^{1/2} \sum_n F_n \cos(\theta_1 - \theta_n)$$ (1)
Condition of periodicity on q results in the quantization of action and energy, i.e. $I_q=nh$ and $E_q=H_q(nh)$. Resonances are arisen for such values of the action that it is right:

$$kw(l_j)=|W|, \quad w(l)=dH/dl$$

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

$$dE_1/dt=I_1^{1/2}[\Omega-\omega(l_1)]\times$$

$$\times \sum_{n} F_n \sin(\theta_n-\theta_0)-(e\tilde{\omega}_1 E/2h^{1/2}) \sum_{n} F_n \sin \theta_n \quad (2)$$

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:

$$D(E)=(\pi/4h)(e\tilde{\omega}_1 E)^2 J(\Omega)$$

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

Here a variable $J(W)$ has an essence of spectral intensity of the perturbation $H^{(\text{mod})}$ 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 vibrational spectrum is usually divided into two parts: a). the low-lying discrete states and b). high-excited states with energy $\Delta E_1$. The excitation process into continuum is described by system of the kinetic equations [13-15]:

$$\partial Z_n/\partial t=(W_{n-1,n}+k_{VT,n-1,n}p)Z_{n-1}+(W_{n+1,n}+k_{VT,n+1,n}p)Z_{n+1}-$$

$$(W_{n-1,n}+k_{VT,n-1,n}pW_{n,n}+k_{VT,n,n}p)Z_n^-$$

$$-d_nZ_n+\partial / \partial n [\Theta(n-N_{\text{min}})D(R)n^2 \partial Z / \partial n]$$

$$\quad (4)$$

where $z_n$ are the populations of the laser-excited states with energy $E_n$: $W_{n,n+1}$ is the rate of the radiative transitions; $W_{n,n+1}=s_{n,n+1}I(t)$, where $s_{n,n+1}$ are the cross-sections of the radiative transitions up and down, $I(t)$ is the laser radiation intensity (photon/cm$^2$/s$^{-1}$); $k_{VT,n,n+1}$ are the constants of rate of the V-T relaxation; $d_n$ is the mono-molecular decay rate; $Q(n-N_{\text{min}})$ is the Heaviside function as an additional multiplier in the diffusion coefficient $D(R)n^2$, 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 $k_{VT,n,n+1}$ 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 $k(E\Rightarrow E')$. The physically significant variable is an energy, transmitted during collision:

$$\Delta E_n=(k_{VT,n,n+1}k_{VT,n,n+1})h\nu/Z \quad (5)$$

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 $DE(E_j)=DE_n$ 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 $W_n$ and rate of the rotational relaxation $k_\delta$, 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:
\[
\frac{dN_j}{dt} = -W_0 z_j, \\
\frac{dz_j}{dt} = -W_0 z_j + k v_p (fN_0 - z_j), \\
\frac{dq}{dt} = -\frac{dN_j}{dt},
\]
(7)

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 \( DE(E) \) in the quasicontinuum. The following estimate has been taken for:

\[
D_n = k_d r(E_n - D_j) r(E_j)
\]  
[2], where \( r \) is the density of vibrational states.

From physical point of view, a chaotic 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 0.06 J/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 \( (T = 293 \text{ K}) \) we obtained the following estimates for stochastization threshold energy \( E_b = 4080 \text{ cm}^{-1} \) that is in agreement with experiment \[2,3,8,9\]: \( E_b = (3900 \pm 500) \text{ cm}^{-1} \) for \( SF_6 \). The theoretical value obtained in Ref. \[13\] is 3970 cm\(^{-1}\). Data for other molecules are as: \( E_b = 3620 \text{ cm}^{-1} \) for \( BCI_3\), \( E_b = 5760 \text{ cm}^{-1} \) for \( CF_3Br\).

References


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Abstract
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Key words: molecule in laser field, vibrational stochasticization