

COMPUTER SIMULATION OF FEMTOSECOND MOLECULAR DYNAMICS:  
HOW TO COMBINE CLASSICAL AND QUANTUM APPROACHES?

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ABSTRACT

Quasiclassical methods for simulation of electronically excited polyatomic molecule's dynamics in pulsed laser field, which are the combinations of classical molecular dynamics method and quantum calculations of the electronic excitation, are discussed. It is argued that just three major approaches are sufficient to calculate both classical dynamics of nuclei and dynamics of the electronic transition, namely, (i) surface-hopping procedure, which describes dynamics of the transitions to the ground electronic state caused by external laser field, (ii) quantum calculations of electronic transitions within a frame of potential energy surfaces harmonic approximation, and (iii) calculations based on the random Quantum Jumps model. First two approaches are suitable in the weak-field limit. The latter one works well in strong-field limit. Applications of the discussed approaches to stilbene photoisomerization dynamics and  $\text{HCl}^+$  molecule photodissociation dynamics are presented.

1. INTRODUCTION

The majority of molecules that are of biological and chemical interest are polyatomic ones. Their dynamics on a relatively short time-scales (up to some  $\sim 10^{12}$  s) plays an important role in photoinduced chemistry and photobiology (for instance, in photoisomerization processes, laser-induced chemical reactions, molecule-solvent dynamics, etc). Exact quantum treatment of such processes in polyatomic molecules is practically impossible, and computer simulation methods that use an appropriate model (models) should come into the play.

Here we discuss an approach that combines classical and quantum calculations of photoexcited polyatomic molecule's dynamics. Basically, molecule's dynamics within an (ground or excited) electronic state can be described classically in terms of Classical Molecular Dynamics (MD) on a multidimensional potential energy surface determined, for example, by Molecular Mechanics (MM) method [1, 2]. In addition to this classical dynamics that describes just nuclei dynamics there is a number of intramolecular processes, which have to take into consideration an electronic dynamics of the molecule as well and therefore demand an appropriate quantum treatment. These basic processes are listed below.

First, (electronic) relaxation process to the ground electronic state from an excited or transition one. Such a process can be modeled by potential energy surface hopping and stochastic switching algorithm [3] giving within a number of trajectories a flux to trans-, cis- or transient state of the molecule. This algorithm is based on a model random non-adiabatic electronic transitions between the coupled electronic states, which involve a localized region of electronic coupling [4]. However, even for extended regions of coupling, for a swarm of trajectories entering the broad region of coupling, some trajectories will switch early, others later, and the net result will be a gradual flow of flux from one state to another. The described algorithm leads to an essential hopping probabilities just in case of relatively small energy differences between electronic levels.

Then, process of an initial electronic excitation of a molecule by pulsed resonant laser field. We elaborated a special approach based on exact quantum calculations within a harmonic approximation of the potential surfaces of the ground and the excited states [5] and obtained an effective method to justify the parameters of the MM surfaces. For both these processes the computer simulation results on photoisomerization of an isolated stilbene molecule are discussed [5].

Finally, molecule's dynamics in intense pulsed IR laser field when coupling of electronic levels plays an important role during the laser field action. Here we discuss the random Quantum Jumps (QJ) model we offer to describe molecule's dynamics in superintense laser field. QJ model is based on classical nuclei trajectories and random quantum jumps between the electronic levels dressed by laser field [6]. These jumps occur regardless to the energy

difference between the dressed electronic states and is due only to the dependence of the wave functions of the dressed states on time and dephasing influence of nuclei movement within a single level. Computer simulation results based on QJM on HCl<sup>+</sup> dissociation dynamics in intense IR pulsed laser field are presented.

## 2. SURFACE HOPPING AND SWITCHING ALGORITHM AS A TOOL FOR MODELING LASER INDUCED ISOMERIZATION PROCESS

Physics of laser induced isomerization process in polyene-like molecules can be illustrated by cis-trans (trans-cis) transformation in stilbene molecule. The dependence of its potential on the C<sub>e</sub>-C<sub>e</sub> torsional angle  $\theta$  is approximated by truncated Fourier series of the form:

$$U_{\text{tor}} = 0.5 \sum_{\theta} \{V_2[1 - \cos(2\theta)] + V_4[1 - \cos(4\theta)]\} = \sum_{\theta} [V_2 \sin^2(\theta) + V_4 \sin^2(2\theta)]. \quad (1)$$

Here the force constants  $V_2$  and  $V_4$  are the parameters that are known for the ground state and are to be adjusted for the excited state. This dependence for  $V_2 = -22.4$  kcal/mol and  $V_4 = 9.3$  kcal/mol representing electronically excited state is displayed on Fig. 1. Degree values  $\theta \approx 0^\circ$  and  $\theta \approx 180^\circ$  correspond there to trans- and cis-states, respectively.

In the process of electronic excitation by short laser pulse molecule undergoes a transition from the initial ground state to the excited one with conservation of the torsional angle. After that it moves within the excited electronic state and Intramolecular Vibrational Redistribution (IVR) between its degrees of freedom takes place. Due to nonadiabatic coupling between the states it has a finite probability to undergo a transition to the ground state (surface hopping) and reach a stable cis- or trans-state after the subsequent IVR process and some additional slow relaxation processes are completed.

Probability of this electronic transition is non-zero because the corresponding wave functions  $\psi_{g,e}$  of the ground and excited states are not exactly orthogonal within a non-adiabatic approach [7]. For the time  $\tau$  it is presented by the formula:

$$P(\tau) = \left[ \int_0^\tau \langle \psi_g | \frac{\partial \psi_e}{\partial t} \rangle a_1(t) \exp \left( -\frac{i}{\hbar} \int_0^t \Delta E_{ge} dt' \right) dt \right]^2. \quad (2)$$

Here  $\psi_{g,e}$  depends on vibrational coordinates which are functions of time  $t$ ,  $\Delta E_{ge} = E_e - E_g$  is the time-dependent potential energy difference between the excited and ground states. The term  $\langle \psi_g | \partial \psi_e / \partial t \rangle$  represents the coupling as a result of non-orthogonality of the electronic wave functions caused by their dependence on vibrational coordinates. It is possible to calculate the integrals in Eq. (2) and obtain the correspondent simplified expression [4]:

$$P(\tau) = \exp \left( -\frac{4\Delta E_{ge}(\tau)}{3\hbar} \left[ \frac{2\Delta E_{ge}(\tau)}{\partial^2 \Delta E_{ge} / \partial t^2 |_{t=\tau}} \right]^{1/2} \right). \quad (3)$$

This simple expression shows that hopping is essential within a vicinity of the points of minimal energy difference  $\Delta E_{ge}$  between the levels.

With the use of Eqs. (2), (3) one can apply the switching algorithm suggested by Tully [3, 7] to calculate the quantum yield and the time of isomerization. This method was applied to MD investigation of laser induced isomerization of stilbene molecule in Ref. [8] and is an essential part of the complete calculation scheme [9].

## 3. CALCULATIONS OF ABSORPTION/EMISSION SPECTRA WITHIN A HARMONIC APPROXIMATION OF THE POTENTIAL ENERGY SURFACES

We assume an adiabatic excited state potential energy surface (PES) and express it in terms of internal coordinates using molecular mechanics (MM) empirical potential functions [1, 10]:

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = U_b + U_{va} + U_{\text{tor}} + U_{\text{vw}}, \quad (4)$$

where  $U_b$ ,  $U_{va}$ ,  $U_{\text{tor}}$ ,  $U_{\text{vw}}$  are the contributions due to deviations from the equilibrium chemical bond lengths, the valence bond angles, the torsional (dihedral) angles, and the interatomic van der Waals interactions, respectively.

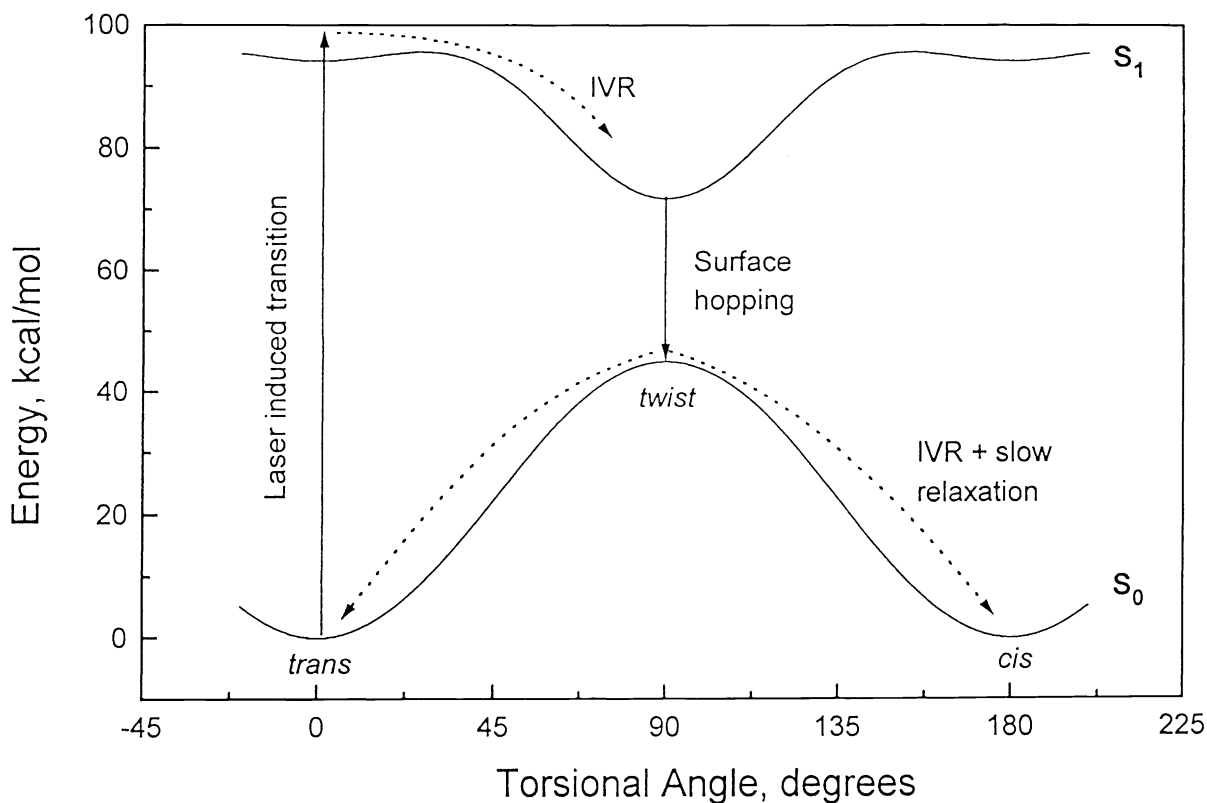


Fig. 1. The potential energy surface for the first excited singlet electronic state of stilbene as a function of torsional coordinate  $\theta$ , the local barrier  $E_1$  and its position  $\theta_1$  are determined by the parameters  $V_2$  and  $V_4$  in Eq. 1.

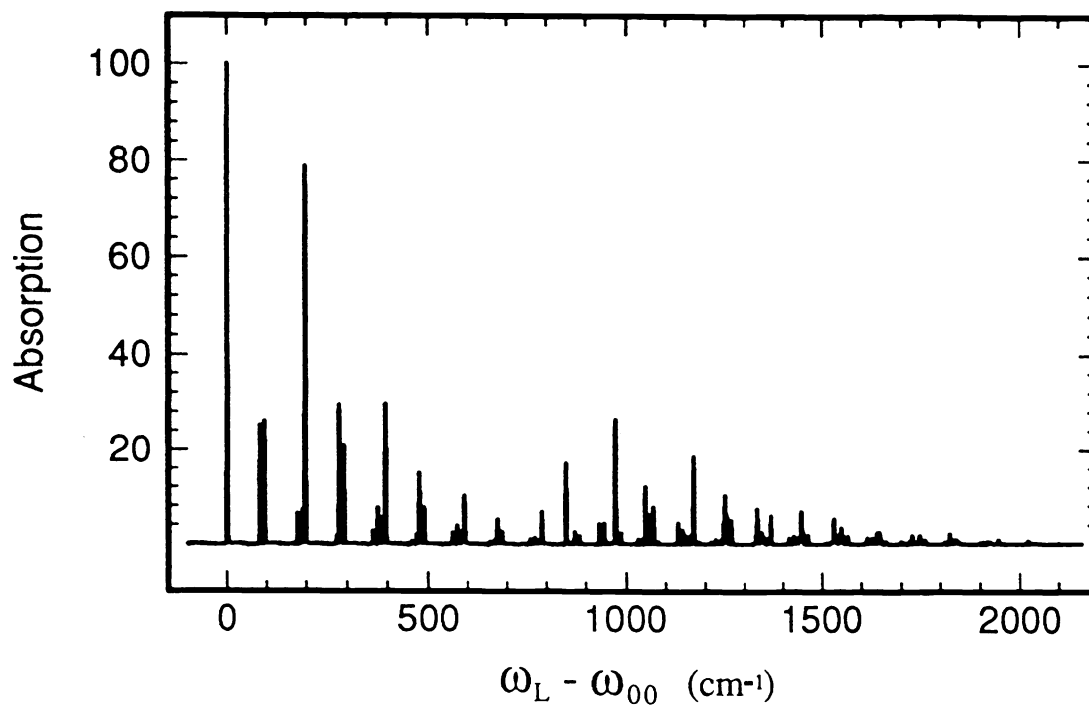


Fig. 2. The calculated absorption spectrum of jet-cooled *trans*-stilbene. The calculation is made using Eqs. in Ref. [5] and potential energy surfaces determined by Molecular Mechanics method using Eqs. (4-5);  $\omega_{00}$  is the vibrationless electronic transition frequency.

For the deformations of the chemical bonds and valence angles we assume quadratic potential functions:

$$U_b = 0.5 \sum_b k_b (b - b_0)^2, \quad U_{va} = 0.5 \sum_\varphi k_\varphi (\varphi - \varphi_0)^2.$$

The potentials for the torsional angles  $\theta$  are given by Eq. (1), where one must set the values of the force constants  $V_2$  and  $V_4$  for each different type of torsional angle.

Van der Waals (nonbonded) interactions are calculated for all pairs of atoms ( $i, j$ ) which do not belong to the same chemical bond or the same valence angle:

$$U_{vw} = \sum f[-2.25/r_n^6 + 8.28 \times 10^5 \exp(-r_n/0.0736)], \quad (5)$$

where  $f$  is the force constant;  $r_n = r_{ij}/s$ ,  $s$  is sum of the van der Waals radii determined by the types of atoms  $i$ ,  $j$ , and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ .

For our simple model we will assume the same potential functions in Eqs. 4 for the ground and excited states and will be interested in determining the parameters in accordance with the absorption spectrum and the kinetics of the molecule.

To calculate an absorption/emission spectra we used a formalism described in Ref. [5]. The potential parameters which reproduce reasonably well the ground state structure of *trans*-stilbene are known [2, 13, 14] and we only slightly adjust the force constants to fit the frequencies of the optically active vibrations more precisely. We, are then interested in determining the changes in the parameters for the excited state, accounting for the absorption spectrum of the isolated molecule [15]. First, we have the equilibrium structure, the frequency matrix, and the form of the normal mode vibrations in the ground state. Although, the normal modes are mixed in terms of internal coordinates, some of them may be distinguished as having more stretching, or angle deformation, or torsional character. Consequently, by changing the corresponding force constants and equilibrium parameters when determining the excited state PES, we can adjust the relative frequency and intensity of the corresponding line in the absorption spectrum. This procedure includes calculation of the frequency matrices for the ground and excited states and the vector of displacements  $\mathbf{D}$  between the points of minima for the energy surfaces, and the calculation of the absorption spectrum.

A more practical procedure for a rough evaluation of the parameters is the following. Having the experimental spectrum [15], we know the frequencies of the prominent modes in the spectrum and the relative intensities. Then, we can easily determine the vector of displacements  $\mathbf{D}$ . This simulation is straightforward as the modes are independent and a few calculations are enough to obtain excellent correspondence with the experimental spectrum limited only by the validity of the imposed constraints in the model, i. e. neglecting anharmonicities and Dushinsky rotation [16, 17]. Now, we begin changing the parameters of the excited state potential functions, calculate the vector of displacements and compare it with the already fixed one. This simulation, however, is not straightforward as the modes are mixed and changing the parameters connected with an internal coordinate will lead to changes in a number of modes. Therefore, a large number of iterative steps is necessary, and avoiding the calculation of the spectrum may save significant time. In this nontrivial simulation useful guidelines are available for the changes in the excited state: the ethylenic bond becomes weaker and longer, the  $C_e-C_{ph}$  bonds become stronger and shorter; other bonds usually become larger in the excited state; some estimates about the changes in the angles are also available [18, 19, 20, 21].

We finally determine the parameters and obtained the calculated spectrum. It presented in Fig. 2. The temperature is fixed at  $T = 5$  K, Eqs. (1–13) and the determined parameters were used in the calculation, performed with a spectral resolution of  $\Delta\omega = 4 \text{ cm}^{-1}$ . It compares favorably well with the experimental spectrum from Ref. [15], showing the same trends for the dominant peaks and a similar background. Recently, a similar calculation has been reported, using the QCFF/PI semiempirical force field for determining the PES [22]. By using here a simple functional form for the PES, however, we are able to perform explicit calculations of the excited state dynamics with a reasonable computational effort.

To model *cis*-stilbene, we rotate one of the phenyl rings by  $180^\circ$  about the double bond, minimize the potential energy and obtain its equilibrium structure. The resulting energy difference between the two isomers is  $\Delta E_s = 2.4 \text{ kcal/mol}$ , and in the ground state the  $C_e-C_e$  torsional angle is  $\theta = 4.2^\circ$ ,  $C_e-C_{ph}$  torsional angle is  $\phi = 13.1^\circ$ , and the  $C_e-C_e-C_{ph}$  bond angle is  $\alpha = 133^\circ$ . A comparison with the experimental values  $\phi = 45^\circ \pm 10^\circ$  and  $\alpha = 129.5^\circ$ , and the theoretically predicted value  $\theta = 13^\circ$  [23] shows a difference in the resulting geometry, which

is evident due to the simplicity of the potential functions used here. It is possible to obtain better values for angles by changing some bond lengths, but it is preferable to use the present bond lengths as they are more precisely determined experimentally and theoretically than the angles.

The results presented above makes possible to simulate excitation by ultrashort laser pulse [9], assuming the molecule is harmonic on the time-scale of 100 fs and obtain the corresponding results. Using classical simulation of *cis*-stilbene excited state dynamics after excitation with an ultrashort 100 fs gaussian laser pulse with excess vibrational energy  $4000\text{ cm}^{-1}$  we have obtained the following results [5]. For barrierless potential surface the time for transition to the twisted state is approximately 30 fs and is fairly independent of changes in the vibrational energy, or in the initial coordinates and momenta, when the vibrational energy is fixed. This time depends on the depth of the potential well (the parameter  $V_2$  in Eq. 1), which we have assumed to be  $-7850\text{ cm}^{-1}$  in accordance with the evaluation of the slope of the surface from Raman intensities [24]. However, even with a value half as large ( $V_2 = -3925\text{ cm}^{-1}$ ) the time is approximately 40 fs, still much smaller than the value of approximately 300 fs from the kinetic spectroscopic experiment [24]. We, therefore, conclude that a barrier exists along the double bond torsional coordinate. We have estimated the unimolecular barrier (the quantity representing the barrier to twisting around the double bond when all other internal coordinates are fixed) to be between  $510$  and  $640\text{ cm}^{-1}$ .

A comparison of the dynamical behavior of the *cis* and *trans*-isomers has shown that the much faster *cis*-stilbene dynamics may be determined much more by the steric interactions than by differences in the microscopic potential energy functions.

#### 4. QUANTUM JUMPS MODEL AS A TOOL FOR SIMULATION OF MOLECULE'S DISSOCIATION DYNAMICS IN SUPERINTENSE LASER FIELD

Using of superintense laser pulses with intensities comparable with the threshold intensity for tunnel ionization of atoms  $I_T \sim 10^{15}\text{ W/cm}^2$  provides new possibilities for controlling photoinduced reactions in molecules. For example, at moderate intensities  $I \ll I_T$  a non-resonant laser field electronic excitation of a molecule is insignificant, while at  $I \sim I_T$  strong excitation of electronic degrees of freedom takes place, despite of non-resonant character of interaction. In this case, dynamics of nuclei is governed simultaneously by the potential energy surfaces of a number of the excited states, and is expected to be essentially different from that one typical for resonant excitation by laser field with moderate intensities (see, for example, Ref. [25]).

Molecule's dynamics in strong laser field ( $10^{12}$ – $10^{14}\text{ W/cm}^2$ ) could lead to at least two competitive processes, namely photodissociation and photoionization [26, 27, 28]. Better understanding of the dynamics of these processes is necessary to achieve control over them, and this is a goal of experimental and theoretical studies [29].

This section is focused on molecule's photodissociation dynamics. Here we offer an adequate theoretical model for computer simulation of the dynamics of such processes.

There is a simple molecule,  $\text{HCl}^+$ , that could be a probe tested both theoretically and experimentally. The experimental results on  $\text{HCl}^+$  photodissociation in strong laser field with  $I \leq 10^{14}\text{ W/cm}^2$  are presented by P. Dietrich and P. Corcum in Ref. [30]. They suggested an electronic structure of  $\text{HCl}^+$  molecule leads to the dissociation process, which was obtained as an intermediate product of ionization of neutral HCl molecule. In particular, it was predicted there that in sufficiently strong laser field the lower term can become a barrierless one. The structure of the two electronic levels considered is presented in Fig. 3 for the intensities  $I = 0$  and  $I = 10^{15}\text{ W/cm}^2$ . The analysis of  $\text{HCl}^+$  molecule dynamics presented in Ref. [30] was restricted to classical description of a dynamics within the single dressed electronic state and there were no attempts to elaborate a quantum dynamical calculations.

Theoretical studies of such processes are to be based on approximate methods of molecular dynamics within the framework of quantum theory. Simplicity of the approximation used determines its practical efficiency, because the exact solution of the quantum mechanical problem for multiatomic molecules is considered to be impossible. The earlier approaches similar to the Gaussian wave packet approach [30] and others that could be applied to atoms [32] seems to be not appropriate for the case of dissociation dynamics of multiatomic molecules. There have been developed also several very promising approaches [33, 34, 35] utilizing semiclassical properties of dynamics within a single electronic level. Some limitations on their validity closely concerned with our specific problem were discussed in Ref. [35]. There are direct indications, especially in case of very strong field, that these powerful approaches are also inappropriate due to the specific chaotic-like behavior of trajectories strongly disturbed by a coupling effect. Calculations of autoionization rate of atoms in IR laser field demonstrate a very strong dependence

on the parameters of atomic states [36] due to the well known exponential factor that is typical for tunnel effects [37]. So, we can suggest that the dynamical model we are discussing is an example of a quantum stochastic system. This model differs from a well known Jaynes and Cummings model due to its Hamiltonian, but their quantum space structures are identical. In the dynamical behavior of the latter model one can also reveal a kind of stochasticity [38].

The goal of the section is twofold. First, to reveal specific quantum dynamical features of the model offered below to describe the dissociation process in  $\text{HCl}^+$  molecule. Second, to discuss dynamical properties which are expected to be typical for different molecules in strong non-resonant fields and obtain appropriate methods of computer simulation, which could be used in case of multiatomic molecules.

Here, we present a new approach, which combines a quantum description of the dynamics of electronic states of a molecule and classical dynamics within a single electronic state. The quantum transitions between electronic states are described by Quantum Jumps (QJ) model. They are similar to the jumps used to simulate quantum stochastic processes induced by an external noise [39]. Our previous pure quantum calculations of wave packets dynamics for a short time distances show that such approach can be effective [40]. Actually, one can expect that electronic dynamics of a molecule in a strong laser field turns to be irregular as a result of strong modulation of electronic wave function with the nuclear vibrations.

To apply this approach to multiatomic molecules one should provide an appropriate information about the molecule's electronic structure and the corresponding parameters determining an interaction with an external field. Of course, this information is more reliable if we take into consideration just a few electronic states, which are supposed to be of any importance in the dissociation process. So, the simplest model we are discussing here is a tool to understand a new mechanism of quantum stochastic dynamics of a molecule in intense laser field.

#### 4.1. Quantum Jumps Model

To clarify the QJ model, we consider here a one-dimensional model of a diatomic molecule with two electronic levels. In this model Hamiltonian takes the form

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \hbar\hat{O}(t), \quad (16)$$

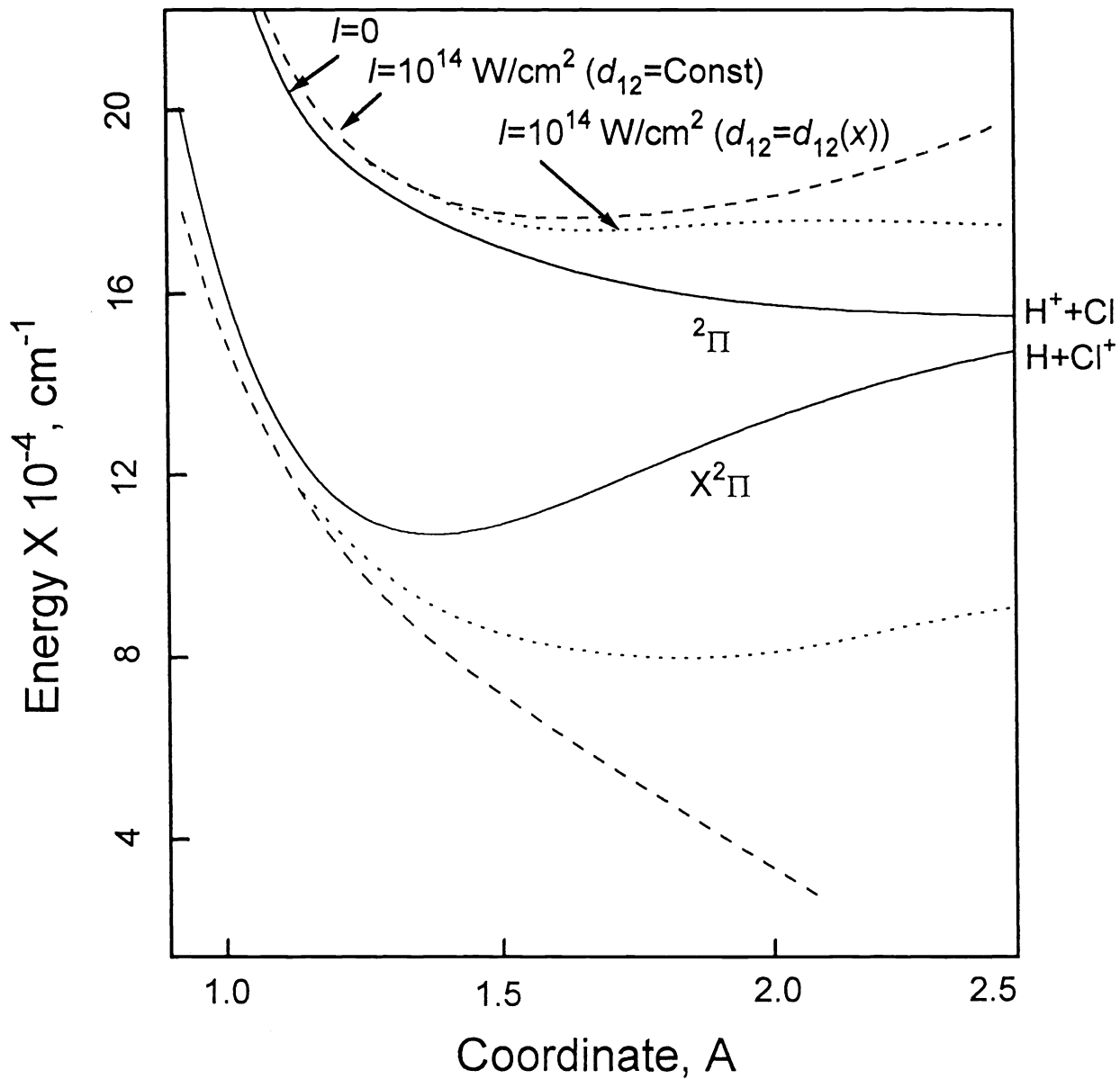
where  $\hbar\hat{O}(t)$  is the potential energy operator of the molecule in IR field:

$$\hat{O}(t) = \begin{pmatrix} \omega_1(\hat{x}, t) & \Omega(\hat{x}, t) \\ \Omega(\hat{x}, t) & \omega_2(\hat{x}, t) \end{pmatrix}. \quad (17)$$

Here  $\omega_{1,2}(\hat{x}, t) = [V_{1,2}(\hat{x}) + d_{1,2}(\hat{x})E_L(t)]/\hbar$ ,  $\Omega(\hat{x}, t) = E_L(t)d_{12}(\hat{x})/\hbar$ ;  $V_{1,2}(\hat{x})$  and  $d_{1,2}(\hat{x})$  are the potentials and the dipole moments of the electronic terms, correspondingly;  $\hat{p}$  is the momentum operator,  $m$  is the reduced mass, and  $E_L(t)$  is the electric field strength. Elements of the matrixes  $\hat{\mathcal{H}}$ , and  $\hat{O}(t)$  are functions of the operator  $\hat{x}$  of the vibrational coordinate  $x$ . The off-diagonal terms in Eq. 2 feature a nonresonant interaction of IR laser field with the electric dipole moment described by the transition matrix element  $d_{12}(\hat{x})$ .

As far as molecule's dynamics in an external IR laser field is concerned, there are two field limits, weak-field and strong-field limits. In case of weak-field limit needless to take into account the molecule's electronic dynamics, and one can calculate the molecule's dynamics by means of classical Molecular Dynamics (MD) simulation [5, 9]. By contrast, in case of strong-field limit the off-resonant terms in Eq. (17) come into the play and it is necessary to take into account the molecule's electronic dynamics as well. It follows that classical MD simulation cannot be applied directly in this case, and we have to, generally speaking, integrate numerically the Schrödinger equation or to imply QJ model we are offering here.

The key idea of QJ model is to simulate a quantum electronic dynamics of the molecule in strong IR laser field as a sequence of random quantum jumps between the electronic states due to the presence of intense IR field. The molecule's dynamics between the jumps is treated as a classical one and is calculated by means of classical MD simulation [15]. The probabilities of the jumps are calculated as transition probability between the two successive electronic states corresponding to two different instants  $t, t + \Delta$ . Such an approach is fairly different from Tully's switching algorithm [3, 7] as far as it completely ignores quantum coherence of nuclear movement. It treats the molecule's electronic state as an incoherent superposition of two dressed time-dependent eigen electronic states which are produced from the initial ones by strong electronic coupling under the strong laser field. Therefore the



**Fig. 3.** Potential structure of  $\text{HCl}^+$  molecule (ground and first excited states) in the presence of external laser field:  $I = 0$  (solid line);  $I = 10^{14} \text{ W/cm}^2$  with (dotted line) and with no (dashed line) spatial dependence of the transition dipole moment  $d_{12}$  of the molecule.

probabilities of the both electronic states in general case are non-zero despite of the large value of their energy difference.

## 4.2. Computer simulation results

We applied the described above QJ model to a computer simulation of  $\text{HCl}^+$  dissociation dynamics in strong IR pulsed laser field, which is governed by Eqs. (16)–(17). To do so we adopt the electronic structure of  $\text{HCl}^+$  molecule similar to that one in Ref. [30]. Functions and parameters used in our model are listed below:

$$V_1(x) = D_1(1 - e^{-a_1 x})^2, \quad V_2(x) = D_2 e^{-a_1(x+r_0)} + D_1,$$

$$D_1 = 1.0625 \times 10^4 \text{ cm}^{-1}, \quad D_2 = 5.0 \times 10^6 \text{ cm}^{-1}, \quad (18)$$

$$a_1 = 1.84 \text{ \AA}^{-1}, \quad a_2 = 4.10 \text{ \AA}^{-1}, \quad m = 1.59 \times 10^{-24} \text{ CGS}; \quad (19)$$

$$d_{1,2}(x) = e_{1,2}^{\text{eff}} x, \quad e_1^{\text{eff}} = e_2^{\text{eff}} = 1.486 \times 10^{-10} \text{ CGS}. \quad (20)$$

In contrast to Ref. [6] we define the spatial dependence of the transition dipole moment of the molecule in the following form:

$$d_{12}(x) = d_{12}^0 \times \begin{cases} 1, & x < 0 \\ \exp(-x/r_{12}^{\text{eff}}), & x \geq 0 \end{cases}, \quad x = r - r_0, \quad (21)$$

$$d_{12}^0 = 1 \text{ Db}, \quad r_0 = 1.5142 \text{ \AA}, \quad r_{12}^{\text{eff}} = 5.0 \text{ \AA}.$$

Hence,  $d_{12}(x)$  goes to zero for large internuclear distances  $r$ .

Functions and parameters defining the electromagnetic field are as follows:

$$E(t) = E_L \exp[-(t - t_c)^2 / \tau_d^2],$$

$$t_c = 4\tau_d, \quad \tau_d = 1.0 \text{ ps}, \quad \omega_L = 1591.5 \text{ cm}^{-1}, \quad (22)$$

where  $t_c$  is the time delay of the intensity peak with respect to the starting point.

Using the above listed functions and parameters we simulated the  $\text{HCl}^+$  dissociation dynamics basing on the QJ model, i. e. on classical dynamics within the effective electronic states, accompanied by the random quantum jumps between these states. The main computer simulation results on  $\text{HCl}^+$  dissociation dynamics in intense pulsed IR laser field are as follows.

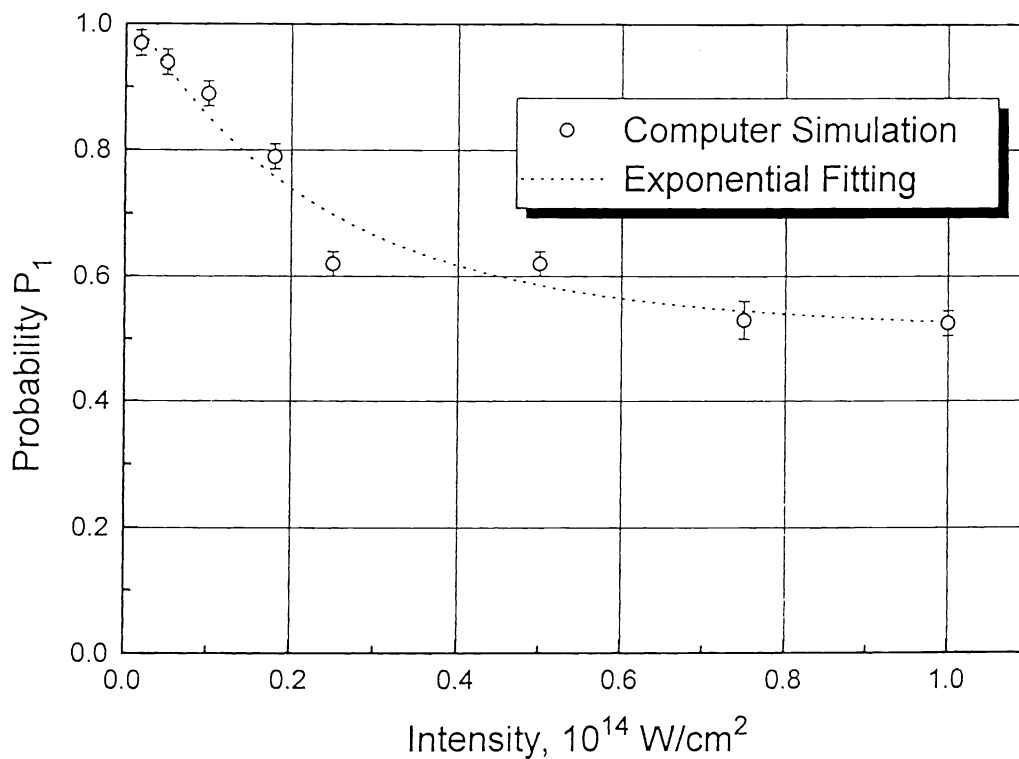
We discovered that effects of dressing of the electronic states by the IR field are essential that is in accordance with the predictions in Ref. [30]. It is necessary to stress that if the spatial dependence of the transition dipole moment is not taken into account the lower effective potential curve  $\omega_{1\text{eff}}$  corresponds to the repulsion for all distances  $x$  and molecule dissociates within this single electronic state with the corresponding products  $\text{H} + \text{Cl}^+$ .

The calculated dissociation threshold intensity is about  $1.0 \times 10^{14} \text{ W/cm}^2$ . This result is not sensitive to the details of the spatial dependence of the transition dipole moment. Nevertheless, this dependence is of a great importance for the dissociation dynamics. Using an appropriate approximation of this dependence and the expected parameters we reveal new dynamical features that are in contrast with the calculations presented in Ref. [30] where the spatial dependence of the transition dipole moment was ignored. Namely, the potential curve for the lower dressed state does not correspond to the repulsive one (Fig. 3) and the dissociation dynamics is also essentially different. The analysis of molecule's dynamics in our computer simulation runs shows that a number of jumps occur before the molecule undergoes complete dissociation.

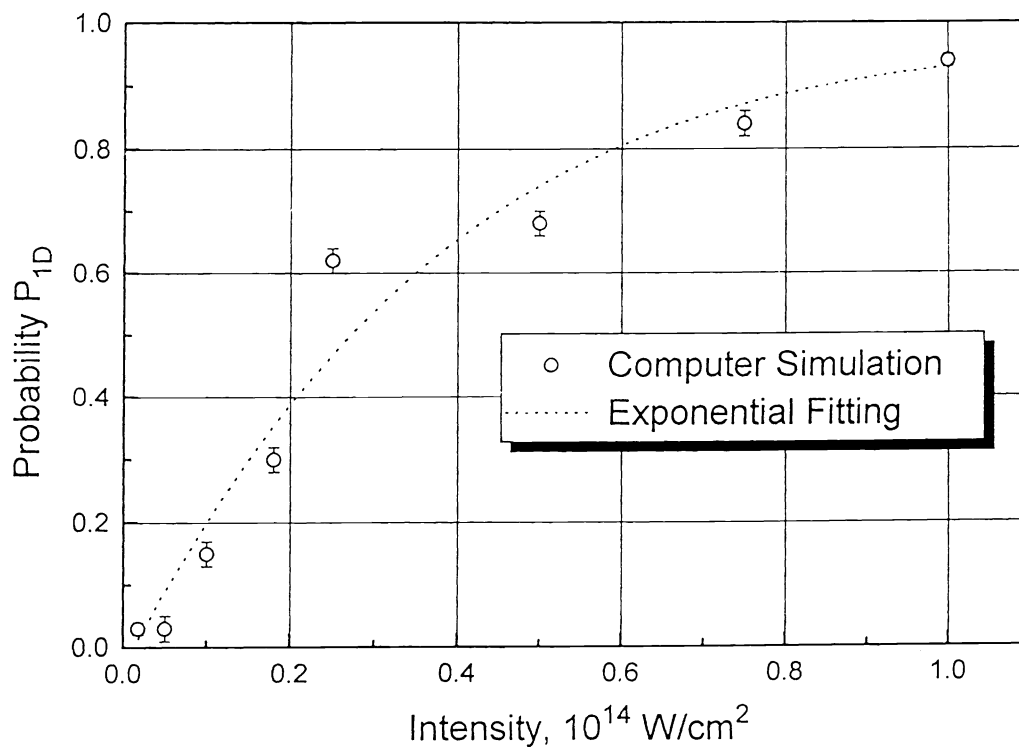
Actually, in the case of such a simple molecule like  $\text{HCl}^+$  these jumps are not exactly the real ones and are used in our QJ model to simulate the exact quantum dynamics when we are not interested in investigation of quantum correlation effects. Nevertheless, the existence of an essential number of the jumps demonstrates an important role of the both electronic states in the dissociation process. Jumps feature the specific jump-like origin of stochasticity deals with a high value of the laser field strength. Intense laser field leads to the electronic excitation of the molecule, plus to stochastization of the molecule's dynamics due to the coupling between the electronic levels.

The only quantities that could be measured experimentally at the modern state of experimental techniques are the probabilities to find the different dissociation reaction products by the end of laser field action, namely, the probabilities  $P_1$  and  $P_2 = 1 - P_1$  to find the dissociation products at the lower/upper electronic state regardless to that whether the dissociation occurred or not, and the probabilities  $P(\text{H} + \text{Cl}^+)$  and  $P(\text{H}^+ + \text{Cl})$  to find the





**Fig. 4.** Probability  $P_1$ , the probability to find the photodissociation reaction products by the end of laser pulse action at the lower electronic state regardless to that whether the dissociation occurred or not, vs laser field intensity.



**Fig. 5.** Conditional probability  $P_{1D}$ , the probability to find the dissociation products  $\text{H}+\text{Cl}^+$  divided to the probability  $P_1$ , vs laser field intensity.

dissociation products corresponding to the lower/upper electronic states. To calculate the probability  $P_1$  for the different intensities we performed a great variety of dynamical calculations and analyzed the final states. The results presented in Fig. 4 show that  $P_1, P_2 \rightarrow 0.5$  if one increases the field intensity up to the value of  $I \gg 1 \times 10^{14}$  W/cm<sup>2</sup>. The conditional probability of the dissociation  $P_{1D}$ , the probability to find the dissociation reaction products H+Cl<sup>+</sup> divided to the probability  $P_1$ , is presented in Fig. 5 (probability  $P_{2D}$  for the upper level is equal to 1 for all the intensities due to the repulsive structure of this state with no laser field).

#### 4.3. Quantum Jumps Model: Concluding remarks

The dissociation dynamics of HCl<sup>+</sup> molecule described in the frame of QJ model has several specific features stressed below.

First, it is not simply a dissociation dynamics within a single electronic level. The dissociation process is strongly modified because of the coupling of the electronic levels in intense IR field resulting to much more complicated dynamics. Its quantum nature can be described as a sequence of random quantum jumps between the electronic levels even for the simplest two-level model with a single vibrational coordinate.

Then, the spatial dependence of the transition dipole moment is of great importance. Its introducing in the model changes the molecule's dynamics so that the dissociation process cannot be described as a dissociation within the single lower electronic level dressed by the IR field and the role of the upper dressed level is also significant and leads finally to acceleration of the molecule nuclei by the repulsive potential of the upper level.

It is also possible to apply our calculations to the rigorous quantitative analysis of the experimental data [6]. Actually, the results already obtained may be considered as qualitatively correspondent to the available experimental data. To evaluate the validity of the QJ approach the exact quantum calculations (that are in progress) for the same molecule and the following comparing are needed.

Finally, our computer simulation results demonstrate that the proposed QJ model yields a proper physical description of a molecule's dissociation dynamics in the presence of a strong IR laser field. The nature of the multilevel dynamics of strongly excited molecules is a stochastic one, and this type of quantum stochasticity is rather different from the ones discussed earlier (see, for example, Ref. [41]). In our view, QJ model seems to be even more effective in the case of multiatomic molecules because the Markov's approach is expected to be more appropriate one to complex systems, plus at the moment there are no other effective methods to simulate molecule's dynamics in a strong laser field. In addition, QJ model could be easily run on PC-like computers for diatomic and multiatomic molecules as well.

## 5. CONCLUSION

Basing on the results presented above we conclude that there several methods, which combine classical and quantum approaches in order to describe dynamics of a molecule excited by short laser pulse. These methods are the Tully's stochastic switching algorithm, exact quantum calculations within a PES harmonic approximation, and Quantum Jumps model.

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