

Dynamics of light-induced quantum transitions in polyatomic molecules

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The applicability of classical concepts to light-induced nonadiabatic processes in polyatomic molecules has been studied. The time dependence of the molecular density matrix in the Wigner representation has been calculated, and an improved formula for the transition probability per unit time, the basic formula for quasiclassical modelling of quantum jumps, has been derived. The quantum nature of energy and momentum conservation during a quantum jump has been investigated. We have demonstrated that the quasiclassical approximation is efficient in modelling the dissociation of molecules under an intense laser beam. An investigation of the light-induced dissociation of an HCl^+ molecule is discussed. © 1996 American Institute of Physics. [S1063-7761(96)00806-2]

1. INTRODUCTION

Molecules are interesting from the theoretical standpoint because typical dynamic processes in them have both classical and quantum properties. Whereas the motion on a given electronic level may be considered as a purely classical process, the dynamics of electronic transitions is purely quantum. Most calculations of molecular dynamics taking into account all $3N$ vibrational and rotational degrees of freedom (N is the number of atoms in a molecule) can be performed using only the classical approach to a polyatomic system. Basic analytical results related to this problem were obtained long ago by Landau and Lifshits¹ and Zener.²

The quantum-mechanical approach to the dynamics of the electronic subsystem which is most simple and efficient in computer simulations was proposed by Tully and Preston.³ It describes the electronic dynamics of a molecule as a set of instantaneous quantum jumps between electronic levels. In the case of a system with two electronic levels, $|1\rangle$ and $|2\rangle$, the classical equations of motion for nuclei are integrated, then the electronic wave function along calculated classical trajectories is found, and the probabilities a_{jj}^2 of finding the system in each electronic state $|j\rangle$ ($j=1,2$) are determined. The system switches from one potential surface to another if the transition probability is larger than a number from the interval (0,1) produced by a random-number generator. After the transition, corrections to atomic momenta are added to satisfy the energy conservation condition for each trajectory.

This algorithm and its modifications have been applied to several physical problems.^{4–12} Its subject areas include the dynamics of collisions of simple molecules, the dynamics of clusters, light-induced dissociation of molecules in matrices, the dynamics of a molecule in a solvent, and light-induced conformation dynamics of multiple-atom molecules.

Blias *et al.*⁴ applied the algorithm of quantum jumps between surfaces of constant electronic energy to calculation of the cross section of the collision-induced reaction

$\text{H} + \text{H}_2(\nu, j) \rightarrow 3\text{H}$, where ν and j are specified vibrational and rotational quantum numbers. Using the Tully–Preston algorithm, they took into account the effects of interaction with the first excited state, which has a conical crossing with the ground state. They demonstrated that transitions between energy surfaces lead to an increase in the cross section and rate of dissociation from 2 to 44%. They compared calculations for two different directions along which the energy conservation relation is satisfied during the transition on each of the trajectories. Although the directions were almost orthogonal, the calculations did not depend on their choice.

A similar quantum-jump algorithm was proposed by Kuntz.⁵ He used this procedure to account for the large experimental cross section of the collision-induced dissociation reaction $\text{Ne} + \text{He}_2^+ \rightarrow \text{Ne}^+ + \text{He} + \text{He}$, whose dynamics is essentially nonadiabatic because of the vibration in the initial stage of the reaction.

This algorithm was also applied to the dissociation $\text{Ar}_3^+ \rightarrow \text{Ar}_2^+ + \text{Ar}$.⁶ Various dynamical processes were interpreted in terms of charge transfer and nonadiabatic dynamics, and the applicability of the algorithm to the dynamics of Ar_n^+ clusters was demonstrated.

Stine and Muckerman⁷ compared various modifications of the quantum-hop algorithm and proposed an algorithm of their own based on a special switch criterion in the context of the $\text{H}_2^+ + \text{H}_2$ collision. They demonstrated that the proposed modified algorithm is consistent with the original Tully–Preston algorithm and describes the process with an equal degree of accuracy.

The dynamics of light-induced dissociation of HCl and Cl_2 molecules in crystalline Xe matrices was investigated by Gersonde and Gabriel.⁸ They found out that nonadiabatic transitions between adiabatic states occur in less than one picosecond and lead to a fast recombination of fragments, which results in a lower degree of dissociation. In such systems, there exists a specific mechanism which destroys coherence between the adiabatic states.

Another subject area of quantum-jump algorithms is the

calculation of rates of nonadiabatic processes in condensed materials.^{9,10} The central idea of the method is computer simulation of molecular processes using the conventional quantum-mechanical formula for transition rates (the so-called "golden rule" of quantum mechanics) to calculate transition rates due to nonadiabatic processes. The formula can be expressed in terms of the quasiclassical approximation through a transformation which describes the system evolution using "frozen" quantum-mechanical Gaussian wave packets.¹¹ It turned out that the Tully–Preston technique directly applied to this case did not yield sufficiently accurate results.

In recent years we analyzed¹² the light-induced isomerization of an isolated stylobene molecule in the space of $3N$ coordinates (N is the number of atoms), including the dynamics of all 72 vibrational degrees of freedom, using computer simulation and conventional molecular dynamics technique. Since quantum-mechanical description of the electronic system of a polyatomic molecule is impracticable, we simulated the internal conversion using a modified Tully–Preston technique. We employed the approximate formula derived by Miller and George¹³ for the transition probabilities between electronic states along calculated classical trajectories of nuclei. The transition probability at each moment was a function of only the energy difference between the two states and their second derivatives at the respective point of the classical trajectory. The point of conventional phase space at which the molecule transfers from the excited electronic to ground state is very important for the subsequent evolution of the ground state and final distribution of reaction products.

Thus the critical problem is to describe in detail the dynamics of internal conversion as a random quantum-mechanical process in terms of the density matrix. Most theoretical studies in this field performed until now have described the molecular dynamics in terms of wave functions,^{13–18} which is insufficient in the case of polyatomic molecules when, generally speaking, additional noise is introduced to simplify the description of a quantum transition between two electronic states.

The paper presents an investigation based on the molecular dynamics described in terms of the density matrix using the Wigner representation (Sec. 2). A formula for the density matrix has been derived. Its analysis, on one hand, justifies the concept of quantum jumps between classical trajectories on different surfaces of equal potential, on the other hand, demonstrates that significant corrections to the Tully–Preston algorithm are needed. In particular, we have interpreted the energy conservation condition in quantum transitions differently. The resulting formula for the state transformation due to a jump may be also reduced in specific cases to the analytical formulas for the transition probability proposed by Miller and George.¹³

2. QUASICLASSICAL STOCHASTIC REPRESENTATION OF QUANTUM DYNAMICS

In this section we discuss the problem of two electronic levels in a molecule. It can be generalized to the case of a

molecule in an intense IR field,¹⁹ which will be demonstrated in Sec. 3. In the full Hamiltonian $\hat{\mathcal{H}} = \hat{T} + \hat{V}$ the kinetic energy can be expressed as

$$\hat{T} = \hat{T}_{11} + \hat{T}_{22} + \hat{T}_{12} + \hat{T}_{21}, \quad \hat{T}_{kl} = \hat{P}_k \hat{T} \hat{P}_l, \quad (1)$$

where $\hat{P}_k = P_k(\hat{q})$ are orthogonal projectors on the k th electronic eigenstates ψ_k of the adiabatic potential operator $\hat{V} = V_1 \hat{P}_1 + V_2 \hat{P}_2$, which are functions of the vibrational coordinates \hat{q} and time t . The diagonal elements

$$\hat{\mathcal{H}}_{kk} = \hat{P}_k \hat{\mathcal{H}} \hat{P}_k \quad (2)$$

describe motion on fixed adiabatic levels, whereas nondiagonal elements $\hat{\mathcal{H}}_{kl} = \hat{T}_{kl}$ correspond to electronic transitions $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |1\rangle$ due to nonadiabatic processes. These elements are nonzero because the operators \hat{T} and \hat{q} are not commutative, hence the respective perturbation is proportional to the Planck constant \hbar and small if the dynamics on a single level is quasiclassical.

Thus, the nonadiabatic interaction is, generally speaking, weak, although the dimensionless parameter which characterizes the applicability of the perturbation theory must be estimated in each specific case. As concerns the dynamics on a single electronic level described by the operator in Eq. (2), it is, apparently, controlled in the lowest-order approximation by classical equations with the Hamiltonian $\hat{\mathcal{H}}_k = \hat{T} + \hat{V}_k$, which does not include the nonadiabatic interaction. Heller²⁰ and Stenholm²¹ described several approaches to the problem of nonadiabatic dynamics, including quantum effects on the dynamics of vibrations. In this paper, we only discuss the real problems of computer simulation of polyatomic molecules.

In our approach, we use perturbation theory to first and second order in the nonadiabatic interaction. In the case of two electronic levels with the initial state $|1\rangle$, we obtain the following expression for the diagonal element of the density operator in the state $|2\rangle$:

$$\hat{\rho}_{22}(t) = \frac{1}{\hbar^2} \int_0^t \int_0^t d\tau_1 d\tau_2 \mathcal{U}_2^{-1}(\tau_1) \hat{T}_{21} \mathcal{U}_1(\tau_1) \times \hat{\rho}_{11}^0 \mathcal{U}_1^{-1}(\tau_2) \hat{T}_{12} \mathcal{U}_2(\tau_2). \quad (3)$$

Here $\hat{\rho}_{kk}$ are kk th diagonal elements of the molecule density matrix $\hat{\rho}$, $\mathcal{U}_k(\tau)$ are operators for temporal evolution on the k th electronic level due to the Hamiltonian $\hat{\mathcal{H}}_k$.

In order to obtain quasiclassical equations of motion, we must use an adequate mathematical description of the quantum dynamics on a single electronic level. One of widely used techniques of this kind is the Wigner representation²² based on a special representation $\hat{f} \rightarrow f(X)$ of quantum operators \hat{f} in terms of classical functions f of coordinates and momenta, $X = (q, p)$. Assume that a molecule is in the state $|1\rangle$ at the time moment $t=0$. Then we derive the following equation using second-order perturbation theory and the Wigner representation (see Appendix):

$$\Delta w_{22}(X, t) = \int_0^t ds \mathcal{S}_-^2(t-s) \mathcal{P}(s) \mathcal{S}_-^1(s) w_{11}(X, 0). \quad (4)$$

Here w_{kl} are density-matrix elements in the Wigner representation, $\mathcal{S}_{\pm}^k(t) = \exp(\mathcal{L}_{\pm}^k t)$ are the evolution operators for the k th levels defined by Eqs. (A2) and (A3), and

$$\mathcal{P} = \frac{1}{\hbar^2} \int_{-s}^s d\tau \mathcal{S}_+^2(-\tau) (\hat{T}_{21} \odot \hat{T}_{12}) \mathcal{S}_+^1(\tau) \quad (5)$$

is the operator of the electronic transition, where the quantum transformation ($\hat{T}_{21} \odot \hat{T}_{12}$) must be written in the Wigner form, and integration may be performed in reality over infinite limits. Equations (4) and (5) describe not only the quasiclassical asymptotic form,¹³ but also all second-order quantum effects. Equation (5) describes the operator of the electronic transition rate calculated on a classical trajectory. Nonetheless, it is demonstrated in the Appendix that the resulting approximate expression for Eq. (5) is the same as in Ref. 13 if the quasiclassical approximation is valid, i.e.,

$$\mathcal{P}(s) = \langle \dot{2} | 1 \rangle_s^2 \mathcal{P}(X_s), \quad (6)$$

where $\langle \dot{2} |$ is the time derivative of the vector $\langle 2 |_s$, which is a function of the coordinates $q(s)$, and $\mathcal{P}(s)$ is simply the time-dependent density of the quantum-jump probability, which can be expressed as the product of the squared element of the nonadiabatic transition rate operator times the effective duration $\mathcal{P}(X_s)$ of the nonadiabatic interaction between electronic levels at the point X_s . It can be expressed as (the derivation is given in Appendix)

$$\mathcal{P}(X) = \frac{2\hbar}{\sqrt{3\pi} V_{12}} K_{1/3}(\chi) \approx \frac{2\sqrt{2\pi} \hbar^{1/3} e^{-\chi}}{3^{1/6} \ddot{V}_{12}^{1/3} \chi^{1/2}},$$

$$\chi(X) = \frac{4\sqrt{2} V_{12}^{3/2}}{3\hbar \ddot{V}_{12}^{1/2}}. \quad (7)$$

This approximation uses the exponential asymptotic form of the Bessel function $K_{1/3}(\chi)$ at large χ . Miller and George¹³ used a similar expression with the exponential function $e^{-\chi}$ to calculate the transition probability.

We calculate nondiagonal elements by means of first-order perturbation theory. After similar calculations in the quasi-classical approximation, we obtain the following equation for the dynamics on one electronic level:

$$w_{21}(t) = \int_0^t \langle \dot{2} | 1 \rangle_s \mathcal{S}^{21}(t-s) w_{11}(X_s) ds, \quad (8)$$

where the operator

$$\mathcal{S}^{21}(\tau) = \exp \left[-\frac{i}{\hbar} (V_{21}\tau - \{\mathcal{H}_2, \mathcal{H}_1\} \tau^2 / 2) \right] \bar{\chi}^{21}(\tau) \quad (9)$$

describes the transformation due to the combined potential of two electronic levels, the exponential describes the phase difference due to the energy gap between the two levels, V_{21} , and the operator

$$\bar{\chi}^{21}(\tau) = \exp[\{(\mathcal{H}_1 + \mathcal{H}_2)/2, \odot\} \tau]$$

describes classical motion due to the average potential generated by the two electronic levels $|1\rangle$ and $|2\rangle$. If the nondiagonal elements can be neglected, Eq. (4) describes molecular quantum jumps (Fig. 1) in the quasiclassical

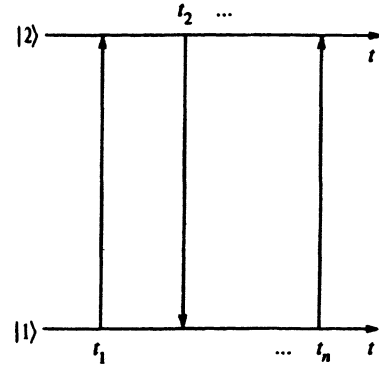


FIG. 1. Energy levels of a quantum system described by the quantum-jumps model. The system switches between the levels at random moments of time $t_1, t_2, \dots, t_n, \dots$. The motion between sequential quantum jumps at the moments t_n and t_{n+1} is described in classical terms.

approximation for $\mathcal{S}^k(\tau)$. In this case the process is modelled by integrating the classical equations of motion for nuclei, calculating the probability of the transition [Eq. (6)], and switching to another potential surface if the transition probability is higher than the number produced by a random-number generator. Arguments in favor of the noncoherent approximation for some objects are given in Refs. 3 and 23, and some specific cases, in which coherence effects are essential, are discussed in Refs. 24 and 25.

There is an apparent difference between our results and calculations by Tully and Preston.³ Our scheme does not explicitly contain the condition of energy conservation in each quantum transition postulated by Tully and Preston.³ In our opinion, their interpretation of the energy conservation law is not correct because of the energy uncertainty in the process of a nonadiabatic quantum jump. This uncertainty takes place because the transition occurs between the initial state, which is an eigenstate of the adiabatic Hamiltonian in Eq. (2), and a superposition of eigenstates owing to nondiagonal elements in Eq. (1), which are nonzero during the time when the nonadiabatic interaction is important. The energy uncertainty determined by the finiteness of this time is, according to Eq. (7), comparable to or greater than V_{12} . This uncertainty is inevitable because the nonadiabatic Hamiltonian does not commute with the adiabatic Hamiltonians and causes energy nonconservation during the jump. Nonetheless, the average change in the vibrational kinetic energy can be calculated using Eq. (A8), where the term with $\partial/\partial p$ corresponds to the momentum shift, but the physical sense of this term is different from that of the energy conservation condition proposed by Tully. It accounts for the momentum shift due to the force generated by the difference between electronic potentials during the transition. This specific quantum shift is not directly related to the energy conservation; rather, it is an analogue of such relatively small effects as the Lamb shift. It neither forbids the energy jump nor significantly affects the dynamics of the process. The transition operator in Eq. (6) is modified to describe the momentum shift because of the additional term $(1/4)V_{12}'' \dot{q} \tau \partial/\partial p$ in Eq. (A9), derived from Eq. (A7) after the

above mentioned transformation of $\partial/\partial p$ described by Eq. (A8):

$$\mathcal{A}(s) = \langle 2|1 \rangle_s^2 \int_{-\infty}^{+\infty} d\tau \exp \left\{ -\frac{i}{\hbar} \left[V_{12}(q)\tau + \frac{1}{24} V''_{12}(q) \dot{q}^2 \tau^3 \right] \right\} \mathcal{S}_p(V''_{12} \dot{q} \tau^2 / 8), \quad (10)$$

where $\dot{q} = p/m$ and $\mathcal{S}_p(\eta)$ denotes the operator of momentum shift $p \rightarrow p + \eta$.

Equation (10) describes the interference properties of the molecular state after the quantum transition. The larger the momentum shift, the faster the phase oscillations of the corresponding component of the new electronic state. In reality, large shifts do not occur because fast oscillations are washed out, although at each moment of time τ all shifts have equal amplitudes, irrespective of their values. The typical momentum shift can be estimated as

$$\Delta p \approx \frac{1}{8} V''_{12} \dot{q} \mathcal{T}^2, \quad (11)$$

and, using Eq. (7), we can estimate the corresponding kinetic energy:

$$\Delta E_{\text{kin}} \sim V''_{12} a^2 / 8,$$

where a is the dimension of the jump area. This energy is of the same order of magnitude as V_{12} , and the energy is not conserved in the motion along a given trajectory. To conclude our discussion of the momentum shift, we assert on the basis of Eqs. (A2) and (A3) that, at least from the formal viewpoint, the vibrational dynamics during a quantum transition is controlled by the potential difference between levels, rather than by their sequence in time, as was postulated in Ref. 13. Really, we have two different time variables, namely $s = (t_1 + t_2)/2$ and $\tau = t_2 - t_1$, where s corresponds to the motion on a fixed level and τ to the transition between levels. The dynamics of a jump with respect to the variable s can be treated in terms of classical theory only in the Markovian approximation, when jumps are considered to be instantaneous, since the dynamics with respect to the variable τ is essentially quantum and is an analogue of the dynamics of wave functions, rather than classical variables.

In order to verify our results, we considered a one-dimensional model of a molecule with two electronic states and a potential energy operator presented as a 2×2 array of the form

$$\hat{U} = \begin{pmatrix} U_2(\hat{x}) & \Delta V \\ \Delta V & U_1(\hat{x}) \end{pmatrix}, \quad (12)$$

where $U_{1,2}(\hat{x})$ and ΔV are the operators of unperturbed adiabatic vibrational levels and the matrix element of interaction between the levels, respectively. The elements $U_{1,2}$ are functions of the vibrational-coordinate operator \hat{x} . The array in Eq. (12) corresponds to the previously introduced adiabatic potentials $V_{1,2}$, which can be described in terms of its eigenvalues.

We have used the approximation

$$U_2(x) = D_2(x - \pi/2)^2 - E_2,$$

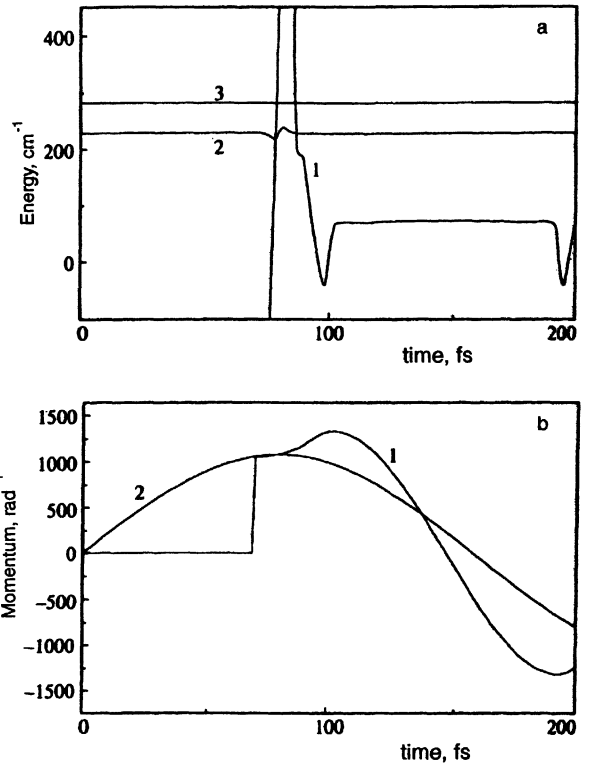


FIG. 2. (a) Quasiclassical energy of wave packets of (1) lower and (2) upper levels, and (3) average quantum-mechanical energy of the system versus time; (b) generalized average momentum on (1) lower and (2) upper levels versus time.

$$U_1(x) = -D_1 \sin^2[a(x - \pi/2)], \quad |x - \pi/2| < \pi/2$$

with a smooth extrapolation of the function $U_1(x)$ outside the quantum-jump region so that the motion on the lower level should be finite. Exact solutions have been obtained for this model using the Schrödinger equation and appropriate techniques.³⁰ The parameters selected for this model were chosen so that, on one hand, they corresponded to the quasiclassical nature of motion on the upper level $|2\rangle$, on the other hand, they approximately described a one-dimensional model of the torsion dynamics of the stybene molecule: $D_2 = 10^5 \text{ cm}^{-1}$, $D_1 = 1.7 \times 10^4 \text{ cm}^{-1}$, $\Delta V = 50 \text{ cm}^{-1}$, and $E_2 \leq 100 \text{ cm}^{-1}$.

Figure 2a shows quasi-classical energies corresponding to mean coordinates of wave packets of both levels corresponding to the initial condition in the form of a Gaussian packet localized around $x=1$ at $t=0$. For comparison, the average exact quantum-mechanical energy taking into account interaction between levels is also given. The difference between it and the quasi-classical calculation on the upper level is due to the fluctuation component of the kinetic energy, which equals $\hbar\omega_2/4$, where ω_2 is the frequency of harmonic oscillation on the upper level. Our result demonstrates nonconservation of vibrational energy in the transition from the upper to lower level, the energy defect being close to the energy gap between the adiabatic levels. Figure 2b demonstrates that in the region where the packet of the lower level is formed, approximate conservation of momentum but not energy takes place.

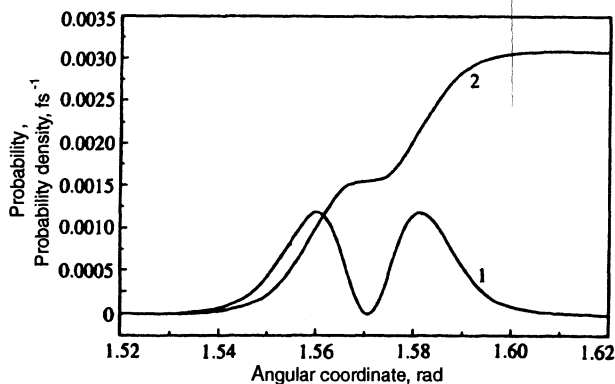


FIG. 3. (1) Probability per unit time of the quasiclassical transition and (2) its distribution function versus coordinate.

The transition probability per unit time calculated using Eq. (6) and the corresponding distribution of probability are shown in Fig. 3. For the values of $D_{1,2}$ and ΔV given above and an effective mass $M_{\text{eff}} = 10^{-37} \text{ g} \cdot \text{cm}^2$, the conditions when the quasiclassical approximation can be applied to the quantum jump are satisfied for $E_2 - E_1 \geq 500 \text{ cm}^{-1}$, which corresponds to the transition probability $\mathcal{P} \leq 10^{-3}$.

In Sec. 3, the analytical calculations are applied to computer simulation of molecular dynamics in an intense non-resonant optical field generated by a laser that leads to a strong nonadiabatic interaction between electronic levels due to the interaction between the optical field and electronic dipole moment.

3. QUANTUM TRANSITIONS INDUCED BY A STRONG LASER FIELD

Our approximation can be easily applied to simulations of molecular dynamics induced by a strong laser field, when the quantum nature of the vibrations is not important and the quantum features of the process are only due to the nonzero nondiagonal elements of the interaction Hamiltonian, which are responsible for interaction among quantum levels.

We consider as an example the one-dimensional model with two electronic levels. The potential energy of the system can be described by the array in Eq. (12), where

$$U_{1,2}(\hat{x}, t) = [V_{1,2}(\hat{x}) - d_{1,2}(\hat{x})E_L(t)],$$

$$\Delta V(\hat{x}, t) = -E_L(t)d_{12}(\hat{x}),$$

$V_{1,2}(\hat{x})$ and $d_{1,2}(\hat{x})$ are the potential energies and dipole moments of the electronic levels, respectively, and $E_L(t)$ is the laser-field intensity. The elements of the array are functions of the vibrational coordinate operator \hat{x} . In the general case, the nondiagonal elements in Eq. (12) describe the nonresonant interaction between the laser field and dipole-moment element $d_{12}(\hat{x})$ responsible for the electronic transition. In this case, the potentials $V_{1,2}(q)$ determined in Sec. 2 correspond to the eigenvalues $V_{g,e}(x, t)$ of the array in Eq. (12), which is a function of time through the laser-field intensity. At time $t_k = 2\pi k / \omega_L$, the field intensity is zero and the parameter $V_{g,e}(x, t_k) = V_{g,e}(x, 0)$, which is independent of the field intensity, determines the coupling between the levels in Eq. (12). At the same time, the second derivative

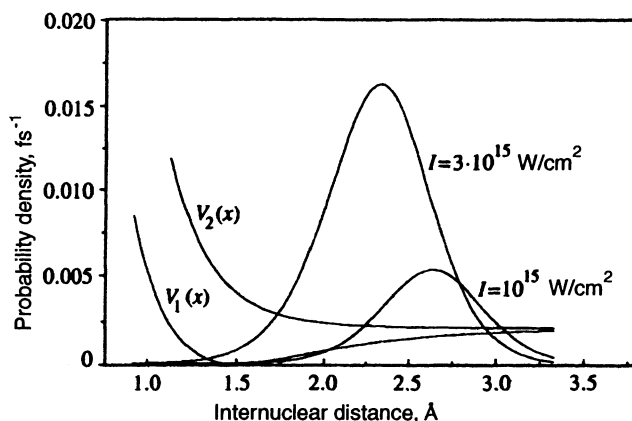


FIG. 4. Expected transition probabilities per unit time. The energies of levels modified by electric field are expressed in arbitrary units.

$$\ddot{V}_{eg} \sim V''_{eg}\dot{x}^2 + V'_{e,g}\ddot{x},$$

which determines the probability in Eqs. (4) and (6), depends sensitively on the field through the acceleration \ddot{x} , i.e., the nonadiabatic interaction is proportional to the field intensity $E_L(t)$. Moreover, when the dipole moments $d_{1,2}(\hat{x})$ are non-zero, the energy gap $V_{g,e}(x, t)$ at some time t may be significantly smaller than its unperturbed value if the difference $\Delta d = d_2 - d_1$ is larger than the dipole-moment nondiagonal element. Therefore, the intense laser field is the natural driving force for quantum jumps when the field intensity is close to zero.

In order to estimate the efficiency of this mechanism, we have calculated the probability of the $|g\rangle \rightarrow |e\rangle$ transition using Eq. (6) at different points x , assuming that at each point the molecule moves at a velocity corresponding to the kinetic energy gained in the absence of the intramolecular potential. The time t is chosen to maximize the probability. The resulting calculations are shown in Fig. 4. This diagram indicates that the transition probability in a time of 1 fs at an optical-power density of $I \sim 10^{15} \text{ W/cm}^2$ is $\sim 10^{-2}$, which justifies our perturbation approach to the problem. Nonetheless, these estimates are insufficient for an exact description of the dynamics of the process because they do not take into account the specific shapes of trajectories, so direct calculations of molecular dynamic parameters are necessary. Our results indicate that the molecular motion can be described as classical motion on fixed electronic levels and instantaneous quantum jumps between them with probabilities determined by Eq. (6). This conclusion is based on Eq. (8), which demonstrates that the nondiagonal elements of the density operator include fast phase factors randomly changing during a quantum transition. Since there is no specific mechanism establishing coherence, these elements may be omitted when perturbation formulas are generalized for the case of large time intervals. These considerations justify the quantum-jumps approximation.

The approximation was applied¹⁹ to the one-dimensional, two-level model of light-induced dissociation of HCl^+ molecule in an intense IR field. As in the case of isolated quantum jumps between potential surfaces discussed

in Sec. 2, our calculations indicate that for a strong nonresonant field, the semiclassical approximation of quantum jumps also yields a good description of molecular dynamics if it really involves few active electronic levels. In this case, the dynamics is essentially stochastic as a result of a lot of quantum jumps and presents a specific example of stochastic dynamics due to nonzero probability of random quantum jumps at each instant of time. A similar example of stochastic dynamics due to quantum jumps was discussed by Boiron *et al.*²⁴ and Heller.²⁶

4. CONCLUSION

In Sec. 2 we demonstrated that the dynamics of a free molecule subjected to a nonadiabatic perturbation due to an isolated pseudocrossing of levels is really a random process that can be described as a combination of random jumps between quantum levels and quasiclassical motion on each electronic level, which is the common quasiclassical approach to molecular dynamics. But in this case, the postulate of vibrational energy conservation during a jump, which leads to a change in the electronic potential, is not necessarily valid. The nature of the switching is consistent with the conservation of mean energy in an incoherent ensemble of trajectories, so they are similar to quantum jumps in models of Markovian processes in quantum systems expressed in terms of wave functions.²⁷

The quasiclassical approximation of random quantum jumps also applies to the nonadiabatic dynamics of light-induced dissociation of a molecule in an intense nonresonant laser IR field if only a few electronic levels participate. Hence, the approximation can be efficiently applied to computer simulation of light-induced dissociation of polyatomic molecules.

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APPENDIX

The Wigner representation is based on a special representation $\hat{f} \rightarrow f(X)$ of quantum operators \hat{f} through classical functions f of coordinate and momenta, $X=(q,p)$. The product of two operators is expressed as²⁸

$$\hat{f}\hat{g} \rightarrow \mathcal{N}_{X,\partial X} f \left(X + \frac{1}{2} C \frac{\partial}{\partial X^T} \right) g(X), \quad (\text{A1})$$

where the ordering operator \mathcal{N} indicates that the operator $\partial/\partial X$ is applied before multiplication by X , the symbol T means transposition of the vector X , and C is the commutation matrix of the \hat{X} operator corresponding to the canonical variable X . This representation permits a simple description of the quasiclassical limit used in our computer simulations of molecular dynamics. Possibilities offered by different quantum-mechanical representations were discussed, in particular, by Torres-Vega and Frederick.²⁹

To second order in the perturbation [see Eq. (3)], two transformations which are very important in the description of processes in a quantum system with the classical Hamiltonian $\mathcal{H}(X)$ are derived. They correspond to two evolution

processes described by two time variables, $s=(t_1+t_2)/2$ and $\tau=t_2-t_1$, where t_1 and t_2 are the time variables of the second order of perturbation theory described by the operators $\hat{T}_{12}(t)$ and $\hat{T}_{21}(t)$ in combinations like $\hat{T}_{21}(t_1) \odot \hat{T}_{12}(t_2)$. The symbol \odot denotes the location of the density operator $\hat{\rho}$ to be transformed. In terms of Wigner's representation, these two basic dynamic transformations are presented by the evolution operators

$$\mathcal{L}_- = -\frac{i}{\hbar} \mathcal{N}_{X,\partial X} \left[\mathcal{H} \left(X + \frac{1}{2} C \frac{\partial}{\partial X^T} \right) - \mathcal{H} \left(X - \frac{1}{2} C \frac{\partial}{\partial X^T} \right) \right], \quad (\text{A2})$$

$$\mathcal{L}_+ = -\frac{i}{2\hbar} \mathcal{N}_{X,\partial X} \left[\mathcal{H} \left(X + \frac{1}{2} C \frac{\partial}{\partial X^T} \right) + \mathcal{H} \left(X - \frac{1}{2} C \frac{\partial}{\partial X^T} \right) \right], \quad (\text{A3})$$

where \mathcal{L}_- is the quantum Liouvillian, i.e., the transformation ("superoperator") $(-i/\hbar)[\hat{H} \odot - \odot \hat{H}]$ of the density matrix $\hat{\rho}$. The operator conjugate to \mathcal{L}_- determines the equation of motion in the Heisenberg representation. Its eigenvectors correspond to projection operators $\hat{P}_{kl} = |k\rangle\langle l|$ of transitions between eigenstates, their eigenvalues being $-i\omega_{kl} = i(E_l - E_k)/\hbar$. To lowest order in the Planck constant, this is the classical Poisson bracket $\mathcal{L}_1 = \{\mathcal{H}, \odot\}$, which is derived from Eq. (A2) to first order in $C \sim \hbar$. \mathcal{L}_+ corresponds to the superoperator $(-i/2\hbar)[\hat{H} \odot + \odot \hat{H}]$ with eigenvalues $-i\omega_{kl} = i(E_l + E_k)/2\hbar$. The terms of its perturbation series are $\mathcal{L}_0 = -i\mathcal{H}(X)/\hbar$ in zeroth order and $\mathcal{L}_2 = (-i/\hbar)[\hbar^2 \mathcal{D}_2/8 + \mathcal{H}(X)]$ in second order, where

$$\mathcal{D}_n = -\left(\frac{i}{\hbar}\right)^n \frac{\partial^n \mathcal{H}}{\partial X_1 \dots \partial X_n} C_1 \dots C_n \frac{\partial}{\partial X_1^T} \dots \frac{\partial}{\partial X_n^T}, \quad (\text{A4})$$

C_k and X_k denote copies of C and X . The transformation \mathcal{L}_+ describes the Schrödinger equation in terms of functions of the variables $X=(q;p)$ instead of the standard representation in terms of Hilbert space whose elements $\psi(q)$ are functions only of the coordinates q .

The exact equation (5) for the transition operator is excessively for general the quasiclassical approximation. The easiest way to simplify this equation is to ignore the operator nature of the product $\hat{T}_{21} \odot \hat{T}_{12}$ and reduce the product of operators $\mathcal{S}_+^{A2}(\tau) = \mathcal{S}_+^2(-\tau) \mathcal{S}_+^1(\tau)$ to a factor which is not an operator and after integration with respect to τ yields the factor \mathcal{F} in Eq. (6). The function $\mathcal{S}_+^{A2}(\tau)$ can be derived from the equation for its time derivative:

$$\frac{d}{dt} \mathcal{S}_+^{A2}(\tau) = e^{-\mathcal{L}_2^{(2)}\tau} [\mathcal{L}_2^{(1)} - \mathcal{L}_2^{(2)}] e^{\mathcal{L}_2^{(1)}\tau}, \quad (\text{A5})$$

where, according to Sec. 2,

$$\mathcal{L}_2^{(k)} = -\frac{i}{\hbar} \left[V_k(q) + \frac{p^2}{2m} - \frac{\hbar^2}{8} \left(V_k'' \frac{\partial^2}{\partial p^2} + \frac{1}{m} \frac{\partial^2}{\partial q^2} \right) \right]. \quad (\text{A6})$$

The difference between the superoperators can be expressed, using Eq. (A1), as

$$\mathcal{L}_2^{(1)} - \mathcal{L}_2^{(2)} = -\frac{i}{\hbar} \left[V_{12}(q) - \frac{\hbar^2}{8} V''_{12}(q) \frac{\partial^2}{\partial p^2} \right], \quad (\text{A7})$$

where only the first term on the right-hand side is an operator. The approximate equation (6) is derived by omitting in Eq. (A6) all the operators with the factor \hbar^2 and using the approximation $\mathcal{L}_2^{(2)} = -(i/\hbar)[V_2(q) + p^2/2m]$. Since the operators p and $\partial^2/\partial p^2$ do not commute in Eq. (A7), by calculating the commutator of the first exponent in Eq. (A5) and the respective term we obtain the following substitution:

$$\partial/\partial p \rightarrow \partial/\partial p - ip\tau/\hbar m. \quad (\text{A8})$$

Then we omit the terms with $\partial/\partial p$, which are responsible for a slight transformation of a wave packet, and obtain an equation which does not contain operators:

$$\frac{d}{dt} \mathcal{S}_+^{12}(\tau) = -\frac{i}{\hbar} \mathcal{S}_+^{12}(\tau) \left[V_{12}(q) + \frac{1}{8} V''_{12}(q) \frac{p^2}{m^2} \tau^2 \right]. \quad (\text{A9})$$

After integration with respect to τ and using the expression

$$\begin{aligned} \hat{T}_{21} \odot \hat{T}_{12} &= |2\rangle \langle 2| \hat{T}|1\rangle \langle 1| \odot |1\rangle \langle 1| \hat{T}|2\rangle \langle 2| = \langle 2| \hat{T}|1\rangle^2 |2\rangle \\ &\times \langle 1| \odot |1\rangle \langle 2| = [(\hbar p/m) \langle 2| d/dq |1\rangle]^2 |2\rangle \\ &\times \langle 1| \odot |1\rangle \langle 2|, \end{aligned}$$

where the last term includes a quantum transition operator, which is a numerical nonoperator factor with respect to the vibrational coordinates, we obtain the following expression for \mathcal{S} (see Sec. 2):

$$\mathcal{S}(X) = \frac{2\hbar}{\sqrt{3}\pi V_{12}} K_{1/3}(\chi).$$

¹L. D. Landau and E. M. Lifshits, *Quantum Mechanics. Nonrelativistic Theory*, McGraw Hill (1976).

²C. Zener, Proc. Roy. Soc. London. A **137**, 696 (1932).

³J. C. Tully and R. K. Preston, J. Chem. Phys. **55**, 562 (1971); J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

⁴N. C. Blais and D. G. Truhlar, J. Chem. Phys. **79**, 1334 (1983); N. C. Blais, D. Truhlar, and C. A. Mead, J. Chem. Phys. **89**, 6204 (1988); D. G. Truhlar, J. W. Duff, N. C. Blais *et al.*, J. Chem. Phys. **77**, 764 (1982).

⁵P. J. Kuntz, J. Chem. Phys. **95**, 141 (1991).

⁶P. J. Kuntz and J. H. Hogreve, J. Chem. Phys. **95**, 156 (1991).

⁷J. R. Stine and J. T. Muckerman, J. Phys. Chem. **91**, 459 (1991).

⁸J. H. Gersonde and H. Gabriel, J. Chem. Phys. **98**, 2094 (1993).

⁹E. N. Neria and A. Nitzan, J. Chem. Phys. **99**, 1109 (1993).

¹⁰E. N. Neria, A. Nitzan, R. Barnett, and U. Landman, Phys. Rev. Lett. **67**, 1011 (1981).

¹¹E. J. Heller, J. Chem. Phys. **75**, 2923 (1981).

¹²V. D. Vachev, J. H. Frederick, B. A. Grishanin *et al.*, Chem. Phys. Lett. **215**, 306 (1993); V. D. Vachev, J. H. Frederick, B. A. Grishanin *et al.*, J. Phys. Chem. **99**, 5247 (1995).

¹³W. H. Miller and T. F. George, J. Chem. Phys. **56**, 5673 (1972).

¹⁴B. Space and D. F. Coker, J. Chem. Phys. **94**, 1976 (1991).

¹⁵D. F. Coker and L. Xiao, J. Chem. Phys. **102**, 496 (1995).

¹⁶S. Sawada and H. Metiu, J. Chem. Phys. **84**, 227 (1986).

¹⁷F. Webster, E. T. Tang, P. J. Rossky, and R. A. Friesner, J. Chem. Phys. **100**, 4835 (1994).

¹⁸M. F. Herman, J. Chem. Phys. **81**, 754 (1984).

¹⁹B. A. Grishanin and V. N. Zadkov, in *Quantum Measurement and Communications*, ed. by V. P. Belavkin, O. Hirota, and R. L. Hudson, Plenum Press, New York, London (1995), p. 281.

²⁰E. J. Heller, J. Chem. Phys. **65**, 1289 (1976).

²¹S. Stenholm, Phys. Rev. A **47**, 2523 (1993).

²²E. P. Wigner, Phys. Rev. **40**, 749 (1932).

²³J. M. Onuchic and P. G. Wolynes, J. Chem. Phys. **92**, 6495 (1988).

²⁴M. Boiron, M. Lombardi, and L. Wiseseinfeld, Phys. Rev. A **50**, 1409 (1994).

²⁵H. Rosenthal, Phys. Rev. A **4**, 1030 (1971).

²⁶E. J. Heller, J. Chem. Phys. **92**, 1718 (1990).

²⁷K. Mølmer, Y. Castin, and J. Dalibard, J. Opt. Soc. Amer. B **10**, 524 (1993).

²⁸B. A. Grishanin, *Quantum Electrodynamics for Radiophysicists* [in Russian], Izd. Mosc. Univ., Moscow (1981).

²⁹G. Torres-Vega and J. H. Frederick, J. Chem. Phys. **98**, 3103 (1993).

³⁰R. B. Gerber, R. Kosloff, and M. Berman, Comput. Phys. Rep. **5**, 59 (1986); R. Kosloff, J. Phys. Chem. **92**, 2087 (1988).

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