Semiclassical treatment of charge transfer in molecule-surface scattering

Christian Bach and Axel Groß
Physik-Department T30, Technische Universität München, D-85747 Garching, Germany

We have treated the ionization probability of iodine molecules scattered from diamond by a semiclassical surface hopping scheme, namely Tully's fewest-switches algorithm [J. Chem. Phys. **93**, 1061 (1990)]. The interaction is described by a model potential that has been adjusted to empirical data. We start with a one-dimensional two-state model in which just the molecular distance from the surface and the neutral and negatively charged state of I_2 are considered. We determine the ionization probability within the adiabatic and diabatic representation and compare it with exact quantum calculations. For this particular problem we find that the diabatic picture shows too little coherence, while the adiabatic representation yields satisfactory results. In the second part we have successively increased the complexity of the simulation by additionally taking a surface oscillator coordinate, the molecular rotation and vibration into account. Including more degrees of freedom damps out the Stückelberg oscillations present in the one-dimensional model. Our results qualitatively reproduce the observed dependence of the ionization probability on the incident energy of the molecules. This dependence is not given by the electronic coupling *per se*, but rather due to energy transfer to substrate and internal degrees of freedom during the scattering event. Finally, we are also able to reproduce the measured dissociation probability which can be explained in a centrifugal model. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1356457]

I. INTRODUCTION

In the last years we have witnessed a tremendous progress in the field of simulations modeling the interaction of molecules with surfaces. While 10 years ago mostly low-dimensional studies on model potentials were performed, now high-dimensional calculations on realistic potential energy surfaces derived from *ab initio* electronic structure calculations are possible.[1–3] Usually these studies still have one caveat: they do not include any electronic transitions, i.e., the gas-surface dynamics is assumed to proceed on a Born–Oppenheimer surface. There is no efficient scheme to determine electronically excited potential energy surfaces and the coupling between them. But even if they were known, any dynamical simulation including electronic transitions represents a significant challenge.

This situation is very unsatisfactory from a theoretical point of view because electronic transitions can play an important role in the interaction of molecules with surfaces. At metals, electron-hole pair excitation in the substrate might be an efficient dissipation channel. This has been demonstrated 20 years ago for the quenching of molecular vibrations of molecules adsorbed at surfaces.[4,5] Just recently it has also been observed in NO/Au(111) scattering.[6] However, the exact magnitude of the energy transfer from the molecule to the electron-hole pairs is largely unknown, and only a few studies have addressed this issue in a quantitative manner for atoms and molecules impinging on a surface.[7,8] There has been much more theoretical work on electronic excitations in molecules interacting with surfaces. In particular, desorption induced by electronic transitions (DIET) has been studied intensively (see Ref. 9 and references therein). Many of these studies have been performed quantum dynamically using the

jumping wave-packet method.[10–12] Furthermore, dissipation to a heat bath has been included in quantum dynamical calculations.[13–15]

In almost all of these simulations the dynamics of the molecule is treated in a low-dimensional framework. Usually only one or two molecular degrees of freedom are explicitly considered. For a quantitative and sometimes even for a qualitative understanding more realistic simulations are required.[1–3,16] Due to their light mass the dynamics of the electrons has to be treated quantum mechanically. The movement of the nuclei occurs on a much longer time scale because of the higher mass; consequently, often quantum effects in the dynamics can be neglected, even if hydrogen is concerned.[17–19] Furthermore, in studies involving electronic transitions mainly molecules like NO, CO or O_2 are considered. The dynamics of the nuclei of these molecules can often safely be treated by classical methods; however, the electronic degrees of freedom still have to be taken into account quantum mechanically.

The obvious choice in such a situation is to use semiclassical methods that treat the movement of the nuclei classically and the electron dynamics quantum mechanically, but allow for a self-consistent feedback between the classical and the quantum degrees of freedom. There is a long tradition in using semiclassical methods (see, e.g., Refs. 20–26), in particular for gas-phase problems. Compared to exact quantum calculations, the accuracy of these semiclassical schemes often depends on the particular problem. Relative errors of more than 50% are no exception.[27] Hence the reliability of these methods has to be tested very carefully.

It is our goal to establish a reliable semiclassical scheme to treat reactions at surfaces with electronic transition. In this work we apply the fewest-switches algorithm proposed by

Tully[24] to the charge transfer in molecule-surface scattering. The particular choice of the model potential we are using is motivated by experiments on the ionization probability in I_2/diamond scattering.[28] In a recent publication we have explicitly considered the molecular center of mass and one surface oscillator coordinate and compared the semiclassical results to full quantum calculations.[29] Here we first focus on one-dimensional two-state semiclassical results in the diabatic and adiabatic representation. In contrast to the first applications of the fewest-switches algorithm,[24] we do not use a localized coupling between the two electronic states. It turns out that in such a situation the fewest-switches algorithm in the diabatic representation does not reproduce the phase coherence correctly, while the results in the adiabatic representation agree reasonably well with the quantum results obtained in a coupled-channel scheme.[30] However, the mean transition probability ignoring the oscillations is well-reproduced in both semiclassical approaches. This opens the way to high-dimensional applications of the fewest-switching algorithm since often the phase coherence is suppressed in such situations.

We have furthermore included the molecular vibration and polar orientation in the semiclassical simulations and obtain qualitative agreement with the experiment with respect to the kinetic energy dependence of the ionization probability. We propose that it is not the electronic coupling *per se* that determines this dependence. It is rather the energy transfer to other degrees of freedom during the scattering event that reduces the number of molecules that have sufficient energy to become ionized. This suppresses the ionization probability, in particular at small kinetic energies. We have furthermore also determined the dissociation probability in I_2/diamond scattering which also compares well with experiment.

After briefly recalling the basics of the fewest-switches algorithm we will first introduce our model system to simulate the charge transfer in molecule-surface scattering. We will then present the comparison of quantum and semiclassical results in a one-dimensional two-state situation. Furthermore we will add some remarks concerning 2D calculations including one surface oscillator, and finally we will discuss our four-dimensional results of the ionization and dissociation probability in I_2/diamond scattering.

II. METHOD

In this section we briefly repeat the most important aspects of the fewest-switches algorithm, as proposed by Tully in Ref. 24. This algorithm, which has already been tested for a number of model potentials,[31–33] impresses by its elegance and conceptual simplicity.

The total Hamiltonian is written as

$$H = T_{\mathbf{R}} + H_0(\mathbf{r}, \mathbf{R}), \tag{1}$$

with $\mathbf{R}$ representing the atomic or classical coordinates and $\mathbf{r}$ the electronic or quantum ones. $H_0(\mathbf{r}, \mathbf{R})$ is the electronic Hamiltonian for fixed atomic coordinates and $T_{\mathbf{R}}$ the kinetic energy of the atomic or nuclei degrees of freedom.

The wave function of the electronic coordinates $\Psi(\mathbf{r}, \mathbf{R}, t)$ is expanded in a set of basis functions $\Theta_j(\mathbf{r}, \mathbf{R})$

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j c_j(t) \Theta_j(\mathbf{r}, \mathbf{R}) \tag{2}$$

with complex coefficients $c_j(t)$. The matrix elements of the electronic Hamiltonian are given by

$$V_{kl}(\mathbf{R}) = \langle \Theta_k(\mathbf{r}, \mathbf{R}) | H_0(\mathbf{r}, \mathbf{R}) | \Theta_l(\mathbf{r}, \mathbf{R}) \rangle. \tag{3}$$

In surface-hopping methods like the fewest-switches algorithm the diagonal elements $V_{kk}(\mathbf{R})$ represent the potential energy surfaces (PES) on which the nuclei are moving. This means the nuclear motion is given by a trajectory $\mathbf{R}(\mathbf{t})$, following classical equations of motion

$$\frac{d^2 \mathbf{R}(\mathbf{t})}{dt^2} = -\frac{1}{M} \nabla_{\mathbf{R}} V_{kk}(\mathbf{R}). \tag{4}$$

On which particular surface V_{kk} the motion takes place is dependent on the coefficients $c_k(\mathbf{R}(\mathbf{t}))$. The time evolution of the expansion coefficients is given by the time-dependent Schrödinger equation with the electronic Hamiltonian H_0 which leads to

$$i\hbar \dot{c}_k = \sum_j c_j [V_{kj} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}] \tag{5}$$

with the nonadiabatic coupling vector $\mathbf{d}_{kj}(\mathbf{R})$ defined through

$$\mathbf{d}_{kj}(\mathbf{R}) = \langle \Theta_k(\mathbf{r}, \mathbf{R}) | \nabla_{\mathbf{R}} | \Theta_j(\mathbf{r}, \mathbf{R}) \rangle. \tag{6}$$

Equation (5) holds for any set of basis functions $\Theta_j(\mathbf{r}, \mathbf{R})$. It demonstrates the self-consistent feedback between atomic and electronic degrees of freedom. The particular PES on which the atoms move in a classical fashion depends on the electronic expansion coefficients determined by integrating the time-dependent Schrödinger equation with a Hamiltonian that is time dependent via the atomic coordinates.

As an adiabatic basis we will understand a complete set of basis functions that diagonalizes the electronic Hamiltonian H_0. For a diabatic basis we choose a set independent of $\mathbf{R}$, i.e., $\mathbf{d}_{kj}(\mathbf{R}) = 0$ for all k, j (note that the diagonal elements of $\mathbf{d}_{kj}$ vanish identically).

The particular potential energy surface on which the atoms move in Eq. (4) depends on the probability

$$P_k(t) = |c_k(\mathbf{R}(\mathbf{t}))|^2 \tag{7}$$

of finding the system in state k at that time. In the fewest-switches algorithm the probabilities to jump to a particular state are constructed in such a way that for a swarm of trajectories the probability of finding a trajectory in state k is the same as $P_k(t)$. This is achieved in the following way. Equations (4) and (5) are integrated numerically over a certain time step Δt, and after each integration step it is decided whether to jump to a different PES or not. The probability to go from state k to state l is

$$p_{kl} = \frac{\Delta t \, 2[\hbar^{-1} \text{Im}(c_k^* c_l V_{lk}) - \text{Re}(c_k^* c_l \dot{\mathbf{R}} \cdot \mathbf{d}_{lk})]}{c_k^* c_k}. \tag{8}$$

In principle, the switches between the states can occur at any point along the trajectories. In order to ensure energy conservation, the kinetic energy has to be adjusted if the transition does *not* occur at a curve crossing point. This is done by

TABLE I. Parameters of the model potential for I_2/diamond scattering.

Potential	D_{ij}(eV)	α_{ij}(Å^{-1})	z_{ii}(Å)	S_{ii}(eV)
V_{11}	0.1	3.0	1.0	0.0
V_{22}	4.0	3.0	0.5	3.0
V_{12}	0.2	2.0		

changing the component of the velocity along the nonadiabatic coupling vector.[24] Switches that would lead to energetically forbidden states, are rejected.

The classical equations of motion Eq. (4) together with the Schrödinger equation (5) are numerically integrated with an Adams method using a variable time step.[34] The results thus obtained by the fewest-switches algorithm are compared to exact quantum simulations on the same potential for one- and two-dimensional situations. The quantum mechanical calculations of the ionization probability have been performed by solving the time-independent Schrödinger equation within a coupled-channel scheme.[30]

III. MODEL SYSTEM

In this section we present our choice of the potential used to simulate the ionization in I_2 scattering. We start with a one-dimensional potential, including only the molecular distance from the surface, and expand it step by step to a 4D model, including also a surface oscillator, the angle between the surface normal and the molecular axis and the intramolecular distance. For all dimensions we incorporate two electronic states, where state number one corresponds to the neutral molecule and the second state represents the ionized molecule I_2^-.

To the best of our knowledge, there are no calculations of the potential energy surface of I_2/diamond. Hence we assume a model potential for the interaction that is based on available experimental data. For all the parameters that could not be inferred from any empirical data we just picked physically reasonable values.

For the one-dimensional two-state problem, we begin with Morse potentials for the neutral and ionized state, $V_{11}(z)$ and $V_{22}(z)$, respectively. The coupling $V_{12}(z)$ is assumed to decrease exponentially with z. Here z is the I_2 center of mass distance from the surface. In the diabatic representation the potential can be written as a symmetric two by two matrix

$$V^{1D}(z) = \begin{pmatrix} V_{11}(z) & V_{12}(z) \\ V_{12}(z) & V_{22}(z) \end{pmatrix}, \qquad (9)$$

where the diagonal elements are given by

$$V_{ii}(z) = D_{ii}(e^{-2\alpha_{ii}(z-z_{ii})} - 2e^{-\alpha_{ii}(z-z_{ii})}) + S_{ii}, \qquad (10)$$

and the coupling is

$$V_{12}(z) = D_{12}e^{-\alpha_{12}z}. \qquad (11)$$

The corresponding parameters are given in Table I and the resulting potential is plotted in Fig. 1. Since in the experiment the diamond surface is assumed to be hydrogen covered,[28] we model the interaction of neutral I_2 with this passivated surface by a shallow physisorption well of 0.1 eV.
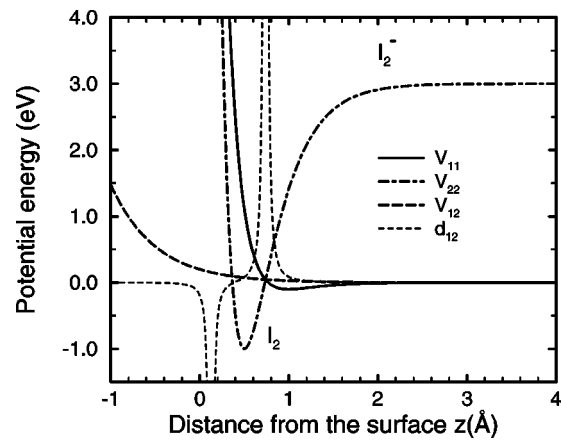

FIG. 1. One-dimensional two-state model potential for the ionization of I_2 in the scattering from diamond surfaces. V_{11} corresponds to the potential energy surface for the neutral molecule (solid line) and V_{22} to the potential for the charged molecule (dashed–dotted line). V_{12} is the coupling between the two potentials (dashed line). The one-dimensional nonadiabatic coupling vector $\mathbf{d}_{12}$ (thin dashed line) is given in arbitrary units.

Since diamond has a large band gap of 5.4 eV, image charge effects in the interaction of the I_2^- anion with the diamond surface should be small. However, we assume that the electron transfer from the surface to the I_2 molecule leads to a localized hole on the time scale of the collision which causes an attractive interaction with a well depth of 1.0 eV. This *ansatz* has also been made in the simulation of charge transfer in atom scattering from insulator surfaces.[35,36] On the other hand, it is known that hydrogenated diamond surfaces exhibit a substantial surface conductivity.[37,38] However, due to the lack of reliable microscopic information on the electronic structure and properties of the diamond surface in the scattering experiment we have to rely on speculation. Consequently, the strength of the coupling V_{12} is also guessed.

The ionization threshold of 3 eV was chosen to reproduce the experimental results by Danon and Amirav.[28] In Fig. 1 we have also plotted the nonadiabatic coupling vector $d_{12}(z)$ which is a scalar in the one-dimensional problem. It is obvious that $d_{12}(z)$ is strongly localized around the curve-crossing point of the two diabatic potential energy surfaces. In the repulsive region of the potential there is actually a second curve crossing point at an energy of 16.3 eV.

In order to achieve a more realistic simulation of the molecule-surface scattering we first added a surface oscillator with coordinate x and potential

$$V_{osc}(x) = \frac{m_{osc}}{2}\omega^2 x^2 \qquad (12)$$

and coupled it by replacing z with $z-x$. Thus the 2D potential is given by

$$V^{2D}(z,x) = \begin{pmatrix} V_{11}(z-x)+V_{osc}(x) & V_{12}(z-x) \\ V_{12}(z-x) & V_{22}(z-x)+V_{osc}(x) \end{pmatrix}. \qquad (13)$$

The frequency of the oscillator was chosen to be $\hbar\omega = 50$ meV with a mass m_{osc} of 180 amu. The frequency of the oscillator corresponds to the lower edge of the measured surface phonon band for clean and hydrogen covered dia-

mond surfaces.[39] The mass of the oscillator, however, is unrealistically large, it equals the mass of 15 surface atoms. Usually the mass of the surface oscillator is taken to be one to three times the mass of a surface atom.[40–43] However, because of the relatively high frequency that we have chosen a surface oscillator with a mass of three surface atoms follows the perturbation due to the impinging heavy iodine molecule almost adiabatically. This means that there is almost no energy transfer (less than 0.1 eV) from the molecule to the surface. In order to model at least some energy transfer to the surface we have chosen the rather large mass of 15 surface atoms. For a detailed discussion of the surface oscillator effects in the calculations see Ref. 29.

We then included molecular rotation and vibration in the potential via

$$V_{ii}^{4D}(z,x,r,\theta) = \frac{1}{2}\left[V_{ii}^{2D}\left(z-x-\frac{r}{2}\cos\theta\right)\right.$$
$$\left. + V_{ii}^{2D}\left(z-x+\frac{r}{2}\cos\theta\right)\right] + V^{mol}(r), \quad (14)$$

where the molecular potential V^{mol} is chosen as a Morse potential

$$V^{mol}(r) = D_3(1-e^{-\alpha_3(r-r_0)})^2 \quad (15)$$

with parameters $D_3 = 1.555$ eV, $\alpha_3 = 2.89$ Å^{-1} and equilibrium distance $r_0 = 2.666$ Å, taken from Ref. 44. Note that for simplicity we have chosen the vibrational potential V^{mol} not to depend on the charge state of the molecule. The coupling between the two charge states is the same as in the 2D model, depending only on the distance of the center of mass of the molecule from the surface $(z-x)$. In total, our model potential corresponds to the interaction of the I_2 molecule with a flat, structureless vibrating surface.

IV. RESULTS AND DISCUSSION

In this section we first focus on the one-dimensional two-state calculations. We will compare exact quantum mechanical results with semiclassical results obtained in the diabatic as well as in the adiabatic representation. We will then further include the surface oscillator and the molecular rotational and vibrational degrees of freedom and compare semiclassical calculations with the experiment.

A. One-dimensional two-state results

In Fig. 2 we have plotted the ionization probability as a function of the incident kinetic energy. The thick solid line corresponds to the quantum mechanical results which were obtained using a coupled-channel method.[30] For the semiclassical simulations within the adiabatic (dashed line) and diabatic representation (thin solid line) 1000 trajectories were used. This leads to a statistical uncertainty of approximately 3%. In addition, we have included results according to the Landau–Zener approximation[29,45] (dashed–dotted line).

The quantum and semiclassical methods give a oscillatory behavior of the ionization probability around nearly the same mean value which is approximately given by the Landau–Zener results. The scattered molecule can become
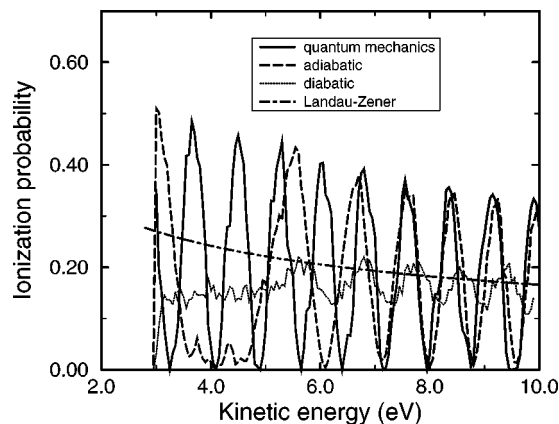

FIG. 2. Theoretical results of the ionization probability of I_2/diamond as a function of the incident kinetic energy of the molecule using the one-dimensional two-surface potential of Eq. (9). Thick solid line, quantum mechanical result; dashed line, semiclassical result within the adiabatic representation; thin solid line, semiclassical result within the dabatic representation; dashed–dotted line, Landau–Zener approximation.

ionized on the way to or from the surface. The oscillations, so-called Stückelberg oscillations, result from coherent interference between these two possible pathways. For the adiabatic and the quantum results also the amplitudes are the same, but the phases are different for energies below 7 eV. The fact that the phases do not agree might be understood from the fact that the semiclassical approximation breaks down at the classical turning points where the de Broglie wavelength of the molecule becomes infinite. Furthermore, in the adiabatic calculation one peak of the Stückelberg oscillations is missing at approximately 4 eV. We have tried to analyze the reasons for this missing peak. This peak reappears if we change the potential parameters somewhat, but we have not found any obvious explanation why the constructive interference is destroyed at this energy for this particular potential.

The diabatic calculations, on the other hand, show much smaller amplitudes. This is somewhat surprising, since the fewest-switches algorithm is actually known to show too much coherence for certain potentials (see Refs. 24 and 29). In principle the adiabatic and diabatic pictures should lead to the same results when performing quantum mechanical simulations. But in mixed quantum classical approaches there are some differences between the two. As Tully already showed,[46] the adiabatic picture is more accurate in a curve-crossing situation because it results in a more correct barrier on the lower potential due to the avoided crossing. However, this situation does not apply to our stimulations where we only consider energies that are much larger than the potential energy at the curve crossing.

Hence the semiclassical calculations within the adiabatic and diabatic representation should give the same results. As far as the accuracy of our numerical integration scheme is concerned, the results are well converged for the adiabatic as well as for the diabatic representation, as we have carefully checked. Therefore, we trace back the discrepancy between the semiclassical results in the adiabatic and diabatic representation to our particular choice for the coupling V_{12}. Due to its extended nature it allows switches over a larger region.

In the adiabatic representation the probability for a state switch depends on the magnitude of the nonadiabatic coupling vector [see Eq. (8)]. Although the diabatic coupling V_{12} is extended, the nonadiabatic coupling vector is still strongly localized in the region of the curve crossing (see Fig. 1). In the Landau–Zener approximation the transition probability is determined only at the curve-crossing points. Thus, the fact that the Landau–Zener expression agrees so nicely with the mean quantum and semiclassical results indicates that the transition probabilities are indeed dominated by the curve-crossing points.

On the other hand, in the diabatic representation the jumps between the different states occur over an extended region along the trajectories. This is demonstrated in Fig. 3, where we have plotted the average number of switches between the two states per trajectory as a function of the kinetic energy. In the diabatic regime four to seven switches occur on the average in the calculated energy range while in the adiabatic representation only a little bit less than two switches happen. Note that a jump in the diabatic picture close to the curve-crossing point corresponds to no jump in the adiabatic one, and vice versa.

The number of switches does not necessarily have to be the same in both representations, but apparently the increased number of switches in the diabatic representation leads to a faster decoherence and hence to less amplitude in the oscillations. We are not aware of any tests of the fewest switches algorithm[24,31–33] that have used delocalized, exponentially increasing diabatic coupling. Hence, the question of coherence as a function of the number of switches has not been addressed yet. However, a similar artificial decoherence phenomenon has been observed in the fewest-switches algorithm if nonadiabatic transitions can occur for arbitrarily long times.[32] As far as the calculations presented here are concerned, it is at least comforting that the diabatic simulations approximately reproduce the mean ionization probability although they do not preserve the coherence.

B. 2D model

In order to perform more realistic simulations, we have also taken into account one surface oscillator coordinate and the molecular vibration and rotation. For such a 2D problem quantum calculations are still possible. We have just recently compared quantum calculations for this 2D scenario with semiclassical results within the adiabatic representation.[29] There we found that in fact the semiclassical calculations showed too *much* coherence compared to the exact quantum results, a fact that has already been observed for other potentials.[24] If the zero-point vibrations of the surface oscillator are not considered in the initial conditions, then the amplitude of the oscillations is almost as strong as in the 1D calculations, while in the 2D quantum calculations the Stückelberg oscillations are almost entirely suppressed. Taking into account the zero-point vibrations reduces the oscillations, but not completely. However, since in high-dimensional calculations usually the coherence is strongly suppressed, this issue might not be relevant as long as the average transition probability is correctly reproduced.
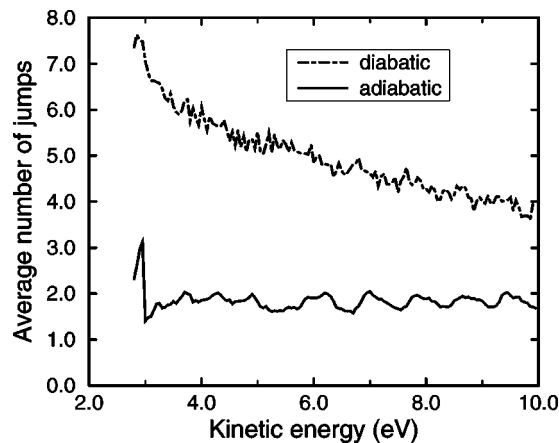

FIG. 3. The average number of switches between the two potential energy surfaces per trajectory as a function of the kinetic energy for the diabatic representation (dashed–dotted line) and the adiabatic representation (solid line).

In Ref. 29 we had also speculated that the stochastic nature of the energy change in the different degrees of freedom upon a switch is not correctly reproduced in the semiclassical scheme. In this scheme the component of the velocity along the nonadiabatic coupling vector is adjusted *if* the potential energy of the two states is different at the location of the jump. This is in general the case employing the adiabatic representation because curve crossings are in general avoided in the approach. In our case including the surface oscillator, the nonadiabatic coupling vector has equal components both in the molecular center of mass as well as in the surface oscillator coordinate due to our specific choice of the coupling [Eq. (13)].

In order to test whether this adjustment exhibits the correct limiting behavior, we have increased the mass of the surface oscillator significantly. In the limit of infinite surface oscillator mass, the 2D results should merge with the 1D results because in this limit the oscillator acts as a hard wall. However, for large surface oscillator masses we obtained ionization probabilities that were much smaller than the 1D results. For our choice of the coupling between the two charge states, both the velocity of the molecule as well as the velocity of the surface oscillator have to be adjusted by the same amount in the case of a switch, but in the limit of infinite mass the surface oscillator is basically at rest. Consequently, there is no energy available to perform the adjustment if the jump is to the upper potential energy surface, and the switch has to be rejected. This results in an incorrectly low transition probability. The 1D results could in fact be reproduced by adjusting the center of mass velocity of the molecule-surface oscillator system instead of both velocity components individually.

Hence there is some inconsistency in the definition of the energy adjustment upon a state switch. This point certainly deserves further attention.

C. 4D model

Finally we present our results obtained for the three- and four-dimensional model system in the adiabatic picture.
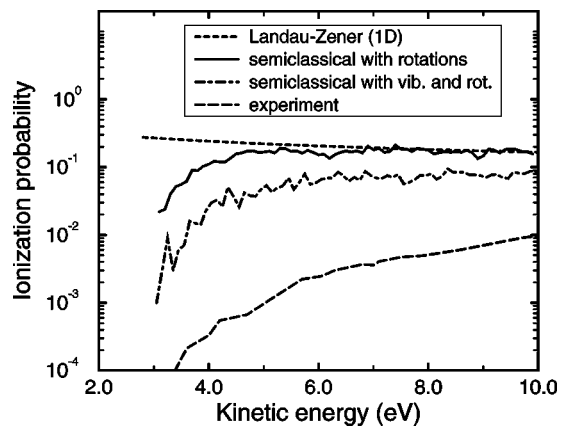
FIG. 4. Theoretical results of the ionization probability of I_2/diamond as a function of the incident kinetic energy of the molecule. Solid line, 3D calculations including surface oscillator and the molecular rotation; dashed–dotted line, 4D calculations taking additionally the molecular vibrations into account. The experimental results from Ref. 28 (long-dashed line) and the 1D Landau–Zener results (short-dashed line) are plotted as a guide to the eye.

FIG. 5. Dissociation probability as a function of the kinetic energy of the I_2 molecules impinging on a diamond surface. The dashed line correspond to 4D calculations just considering neutral dissociated molecules while for the solid lines also ionized molecules are taken into account. The diamonds show the experimental results (Ref. 47). The experimental data are published with the kind permission of Kolodney and Amirav.

Again for each energy 1000 trajectories were calculated. In addition to the semiclassical results we have plotted in Fig. 4 the experimental results of the ionization probability in I_2/diamond scattering measured by Danon and Amirav[28] as a function of the incident kinetic energy. They found an increase in the ionization probability with the energy and a maximum yield of around 1% at 10 eV. No positively charged ions were measured and the relative intensity of I^- was under 3%.

Our averaged 1D results that are close to the Landau–Zener calculations so far have not shown any increase. Rather there was even a slight decrease. Already the inclusion of the surface oscillator leads to a light suppression of the calculated ionization probability at low kinetic energies.[29] As Fig. 4 shows, by taking into account more degrees of freedom, namely the molecular rotation and vibration, a further much more dramatic suppression is obtained, in particular at low kinetic energies. The rotational and vibrational degrees of freedom are not explicitly considered in the coupling V_{12} between the two charge states. Consequently, it cannot be the electronic coupling directly but only an indirect effect that causes this reduction.

The reason for the suppression can be explained by a simple energy argument. The inclusion of more degrees of freedom in the scattering simulation causes an efficient energy transfer to these modes during the impulsive encounter. In our simulations up to several eV are transferred to the surface oscillator and the molecular rotations and vibrations. This energy is then missing for the transition over the ionization threshold of 3 eV. Thus we propose that it is not the electronic coupling *per se* that leads to the observed trend in the kinetic energy dependence of the ionization probability. It is rather the energy transfer to other degrees of freedom which causes the suppression of the ionization probability in particular for energies close to the ionization threshold. This explanation actually demonstrates the importance of high-dimensional simulations because it could not have been found in a one-dimensional model.
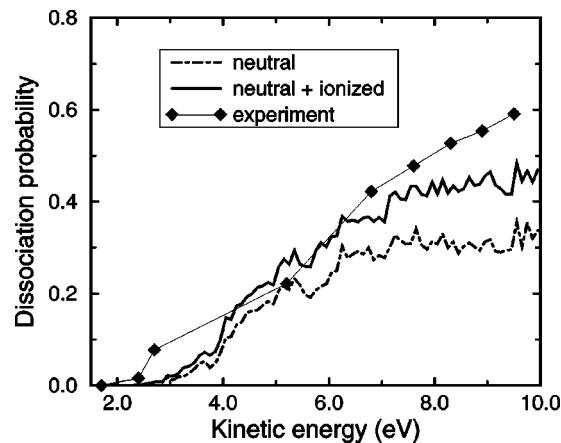
Of course we have to admit that this proposition is based on a model interaction potential. Hence we cannot rule out other possible mechanisms. We have not tried to achieve quantitative agreement with the experiment, either. Since our simulations are still performed within a limited geometry, there must still be room for the influence of other degrees of freedom in a more realistic simulation. However, our calculations reproduce the observed qualitative dependence of the ionization probability in I_2/diamond scattering rather well and provide a physically reasonable explanation for this dependence. In fact, the inclusion of the surface corrugation and azimuthal anisotropy would further improve the agreement with experiment since they lead to a further reduction of the ionization probability due to additional energy transfer processes.

It is also obvious from Fig. 4 that the Stückelberg oscillations are almost completely washed out in the higher-dimensional simulations. The multidimensionality of the charge transfer process leads to the loss of coherence. The still remaining oscillations are due to the statistical uncertainty of ± 0.03 in the summation over the trajectories.

In Fig. 4 we have only plotted the *molecular* ionization probability, i.e., the fraction of ionized molecules after the scattering event. In our calculations we also obtained a significant fraction of ionized dissociated molecules. However, in most of the combined ionization *and* dissociation events one of the atoms remains trapped at the surface. Furthermore, in our simplified model potential we cannot determine which of the two atoms is ionized. Due to this uncertainty in the interpretation of this scattering channel we have not included it in the results of Fig. 4.

We have furthermore determined the dissociation probability in I_2/diamond scattering. In Fig. 5 we have first plotted the dissociation probability of molecules that remain neutral. In this context it makes sense to include the ionized dissociated molecules because these molecules are also missing from the fraction of nondissociatively scattered molecules. Hence we have additionally plotted the *total* disso-

ciation probability. Experimentally the dissociation probability in I_2/diamond was measured by Kolodney.[47] We see a good agreement between theory and experiment. We have to emphasize that we did not adjust our potential at all in order to reproduce the experimental dissociation probability.

Our calculations actually confirm the centrifugal mechanism for molecular dissociation proposed by Gerber and Elber.[48,49] Molecules that hit the surface in an upright configuration which at first glance should be most favorable for an efficient vibrational excitation hardly dissociate. Instead dissociation occurs after efficient rotational excitation of the molecule in the scattering. If the rotational torque is large enough, the centrifugal force then causes the molecule to break apart.

Some time ago the existence of temporary negative ions in molecule-surface scattering has been proposed to be an efficient channel for the excitation of molecular vibration.[50,51] In the temporary negative ion state the molecular bond is weakened, i.e., elongated, and the transition between two molecular charge states with different interatomic potentials leads to the excitation of molecular vibrations and also molecular dissociation. However, our scattering scenario corresponds to the diabatic limit, i.e., most scattered molecules stay on the diabatic potential energy surface during the scattering event. Hence the transient negative ion mechanism cannot account for the large dissociation probability, and it is also not necessary in our model, since the impulsive centrifugal mechanism is already sufficient. But again we have to emphasize that we cannot rule out any other mechanism like the charge transfer mechanism as long as there are no reliable calculated interaction parameters for the I_2/diamond system.

V. CONCLUSION

We have determined the ionization probability in I_2/diamond scattering by a semiclassical surface hopping method. The interaction of I_2 with the diamond surface has been modeled by a potential energy surface that has been adjusted to the few experimental data known for this system. In this paper we have compared the semiclassical results obtained in the adiabatic and diabatic representation with quantum calculations for a one-dimensional two-state treatment of the I_2/diamond scattering. While the adiabatic treatment gave satisfactory results, the diabatic calculations showed too little quantum coherence. We attribute this difference to the higher number of switches per trajectory in the diabatic case which causes a suppression of the quantum coherence.

Both methods agree well with the quantum calculations as far as the averaged results are concerned, i.e., if the Stückelberg oscillations due to the quantum coherence are ignored. These oscillations are also suppressed if the simulations are performed within a higher dimensionality. In addition to the molecular center of mass we have included one surface oscillator coordinate, the molecular rotation and vibration. Taking these degrees of freedom into account, we were able to reproduce the observed trend of the ionization probability as a function of the incident kinetic energy of the molecules as well as the measured dissociation probability. According to

our model calculations the dependence of the ionization probability on the kinetic energy is not determined by the electronic coupling *per se*, but by the energy transfer to other degrees of freedom during the scattering process. This suppresses the ionization probability because less molecules have sufficient energy to overcome the ionization threshold, in particular at energies close to this threshold.

The description of the I_2/diamond scattering within our model parameters corresponds to the diabatic limit, i.e., most molecules do not change their charge state during the scattering process. Thus the large dissociation probability is not due to the existence of transient negative ions. It can rather be explained by the centrifugal model. There is a very efficient rotational excitation in the I_2/diamond scattering, and the strong centrifugal forces lead to the dissociation of a significant fraction of the scattered molecules.

In our comparison between the exact quantum results and the semiclassical calculations using the fewest switches algorithm we have identified some problems that are concerned with the quantum coherence and the energy adjustment upon a state switch. These problems deserve further attention. However, especially for higher-dimensional systems the quantum coherence is often washed out anyway. If furthermore the total energy is much larger than the potential energy at the curve crossings, as it is the case in our simulations, then the energy adjustment upon a state switch does not represent a severe problem. Our calculations demonstrate that under these circumstances semiclassical calculations can be a powerful tool for the simulation of charge-transfer processes in molecule-surface scattering. Unfortunately a reliable and efficient scheme for the determination of interaction potentials and coupling matrix elements for electronically excited states at surfaces is still missing. Once they become available, a realistic description of reactions with electronic transitions at surfaces should be possible.

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