Semiclassical treatment of reactions at surfaces with electronic transitions

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Received 3rd April 2000
First published as an Advance Article on the web 29th September 2000

The semiclassical treatment of reactions at surfaces with electronic transitions based on the fewest-switches algorithm is compared with full quantum mechanical results. As a model system the ionization probability in I_2 scattering from a diamond surface is chosen. In the calculations we treat the molecular distance from the surface and one surface oscillator coordinate explicitly. Furthermore, we also consider molecular rotation in the semiclassical calculations. The semiclassical results agree with the quantum results although some discrepancies remain, as far as the phase coherence is concerned. We identify energy transfer to molecular and surface degrees of freedom as a possible mechanism that could explain the experimental dependence of the ionization probability on the incident kinetic energy of the molecule.

I. Introduction

There has been tremendous progress in the theoretical treatment of reactions at surfaces in recent years. In particular, for hydrogen dissociation on metal surfaces, high-dimensional dynamical calculations have been performed on potential energy surfaces which were derived from density-functional calculations.[1–4] These calculations allow quantitative comparison with experiment. However, they rely on one basic approximation, namely the Born–Oppenheimer approximation, *i.e.* in these simulations it is assumed that the electrons follow the motion of the nuclei adiabatically.

Dynamical calculations in the Born–Oppenheimer approximation exclude the treatment of processes such as surface photochemistry or charge transfer at surfaces. In these fields theory is far behind experiment since the theoretical treatment of reactions at surfaces with electronic transitions still represents a great challenge. Any reasonable theoretical description faces three major problems: (i) the potential energy surface of the ground *and* the excited states has to be determined; (ii) matrix elements between the different electronic states or the lifetimes of the excited states, respectively, have to be known; (iii) a simulation of the reaction dynamics including the electronic transitions has to be performed.

Quantum chemical algorithms still represent the main method to address the first two problems (see, *e.g.*, ref. 5), but methods based upon density-functional theory are also starting to be used to address this issue.[6,7] However, in this contribution we will focus on the third problem, reaction dynamics with electronic transitions at surfaces. On the one hand, these processes should be treated quantum mechanically because of the light mass of the electrons. On the other hand, to get a full and accurate understanding of dynamical processes on surfaces, a high-dimensional treatment including all relevant degrees of freedom is necessary. Low-dimensional studies might not

DOI: 10.1039/b002632h

only be quantitatively wrong, they can even prevent the detection of the correct qualitative mechanisms (see, *e.g.*, ref. 2). Unfortunately, despite all the progress in quantum dynamical methods in recent years a high-dimensional quantum treatment of reactions of interest with electronic transitions is not yet possible. These systems often involve oxygen or heavier atoms. Now the quantum effects in the motion of the nuclei are often negligible as long as hydrogen is not concerned, hence semiclassical schemes might be the method of choice to tackle these high-dimensional problems. In semiclassical methods the motion of the nuclei should be treated by classical methods, while the electronic transitions have to be described quantum mechanically. Still in such a scheme the feedback between classical and quantum mechanical degrees of freedom has to be treated self-consistently.

There have been quite a number of different methods proposed for the semiclassical treatment of reactions with electronic transitions which are not necessarily able to reproduce the correct quantum results (see, *e.g.*, ref. 8). Here we present a semiclassical study of charge transfer processes in the scattering of molecules at surfaces using the fewest-switches algorithm proposed by Tully.[9] This algorithm, which has already been tested for a number of model potentials,[10–12] impresses by its elegance and conceptual simplicity.

The goal of this investigation is twofold. On the one hand we want to check the performance and accuracy of this semiclassical treatment of reactions with electronic transitions. In particular, we are focusing on a situation with more than one nuclear degree of freedom that is treated classically and compare it with the exact quantum mechanical solution, *i.e.*, we are going beyond one-dimensional two-surface problems that is usually done.[9–15] On the other hand, we are also interested in gaining some qualitative insight into a particular reaction. Hence we have chosen the ionization probability in I_2 scattering from a diamond surface as our model system. This ionization probability has been measured as a function of the incoming kinetic energy of the scattered molecule by Danon and Amirav.[16]

For a low-dimensional treatment of the scattering process we compare semiclassical results with full quantum results. The comparison shows that the semiclassical method is capable of adequately reproducing the quantum results. Quantitative differences are identified, as far as quantum interference phenomena are concerned. In higher-dimensional applications, however, these differences will disappear. This becomes evident in the semiclassical calculations in which the rotational motion of the molecule is also taken into account.

In contrast to the quantum method, the semiclassical treatment can easily be extended to take into account surface degrees of freedom in the simulation. This makes a rather realistic description of the charge transfer in molecule–surface scattering possible. The method is, however, not limited to scattering processes. It represents a versatile tool for the description of reaction dynamics with electronic transitions. For example, we are currently planning to apply the semiclassical method to the description of electron-stimulated or photon-stimulated desorption from surfaces.

This paper is organized as follows. In the next section we briefly introduce the semiclassical and quantum methods that we have used. Then we describe the model system that we have chosen. In the main part of the paper the results of the semiclassical and quantum calculations are compared and discussed.

II. Method

In this section we briefly summarize the most important aspects of the theoretical methods that are essential for the following discussion.

The total Hamiltonian is written as

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

where $\boldsymbol{R}$ and $\boldsymbol{r}$ refer to the coordinates of the nuclei and the electrons, respectively. The wave function $\psi(\boldsymbol{r}, \boldsymbol{R}, t)$ is expanded in terms of some electronic basis functions

$$\psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_j c_j(t)\phi_j(\boldsymbol{r}, \boldsymbol{R}). \tag{2}$$

The matrix elements with respect to the electronic Hamiltonian H_0 are given by

$$V_{ij}(\boldsymbol{R}) = \langle \phi_i(\boldsymbol{r}, \boldsymbol{R}) | H_0(\boldsymbol{r}, \boldsymbol{R}) | \phi_j(\boldsymbol{r}, \boldsymbol{R}) \rangle. \tag{3}$$

$V_{ii}(\boldsymbol{R})$ describes the potential energy surface of the system in the electronic state ϕ_i. In surface hopping methods the system evolves for a particular period of time on one specific potential energy surface and the classical particles follow a trajectory $\boldsymbol{R}(t)$ that is determined by the integration of the classical equation of motion

$$M \frac{\mathrm{d}^2}{\mathrm{d}t^2} \boldsymbol{R} = -\nabla_{\boldsymbol{R}} \langle \phi_i | H_0(\boldsymbol{r}, \boldsymbol{R}) | \phi_i \rangle \tag{4}$$

Along the trajectory $\boldsymbol{R}(t)$ sudden hops between different potential energy surfaces occur according to some instruction that has to be specified. In the diabatic representation the non-diagonal matrix elements $V_{ij}(\boldsymbol{R})$ lead to these transitions to other potential energy surfaces. In the adiabatic picture it is the change of the eigenfunctions that cause these transitions. This change is described by the nonadiabatic coupling vector $\boldsymbol{d}_{ij}$:

$$\boldsymbol{d}_{ij} = \langle \phi_i(\boldsymbol{r}, \boldsymbol{R}) | \nabla_{\boldsymbol{R}} | \phi_j(\boldsymbol{r}, \boldsymbol{R}) \rangle \tag{5}$$

The electronic coefficients c_j are determined according to the time-dependent Schrödinger equation for the electronic Hamiltonian $H_0(\boldsymbol{r}, \boldsymbol{R})$ which is now time dependent through the trajectory $\boldsymbol{R}(t)$. This time-dependent Schrödinger equation can be written as[9]

$$\mathrm{i}\hbar \dot{c}_k = \sum_j c_j (V_{kj} - \mathrm{i}\hbar \dot{\boldsymbol{R}} \cdot \boldsymbol{d}_{kj}). \tag{6}$$

In this equation the basis functions ϕ_i can be any mixture of diabatic and adiabatic states. The probability of finding the system at time t in the electronic level k is then given by

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

In Tully's fewest-switches algorithm,[9] electronic transitions between different levels can occur at any point along the trajectories $\boldsymbol{R}(t)$. The transition probability is constructed in such a way that the number of state switches is minimized, under the constraint that in an ensemble of trajectories the average population of each level is given by the square modulus of the expansion coefficients c_k (eqn. (7)).

Since transitions can occur at any point along the trajectories, the potential energies of the electronic states can well be different at the moment of the state switch, *i.e.* $V_{kk}(\boldsymbol{R}(t)) \neq V_{ll}(\boldsymbol{R}(t))$. In order to conserve the total energy of the system, the velocities of the classical degrees of freedom have to be readjusted. It is not *a priori* clear how this adjustment has to be done. In the fewest switches algorithm as suggested by Tully the velocities are changed in the direction of the nonadiabatic coupling vector $\boldsymbol{d}_{ij}$. This choice has been proposed by Herman[17] and later been reconfirmed by Coker and Xiao.[18]

Per total energy, 1000 to 2000 trajectories are calculated to determine the transition probabilities. This means that all semiclassical probabilities have a statistical uncertainty of ± 0.02 to ± 0.03. The quantum mechanical calculations of the ionization probability have been performed by solving the time-independent Schrödinger equation within a coupled-channel scheme.[19] The convergence of the quantum dynamical results with respect to the basis set has been carefully tested. In the calculations including the surface oscillator (see below) up to 250 oscillator channels per electronic level had to be taken into account to reach convergence.

III. Model system

As already stated in the Introduction, the goal of this investigation is twofold: to test the semiclassical treatment in comparison to full quantum calculations and, rather than just study some theoretical model system, to try to learn something about a real system. We have chosen the ionization probability in I_2 scattering from surfaces as our model system. This ionization probability has been measured as a function of the incoming kinetic energy of the scattered molecule by Danon and Amirav.[16] The results are plotted in Fig. 1. They show a threshold at ~3.0 eV and an absolute I_2^- yield of ~1% at a kinetic energy of 10 eV.

To our knowledge, there are no theoretical data on the interaction potential of I_2 with a diamond surface. Hence we are left with inventing potential energy surfaces based on empirical

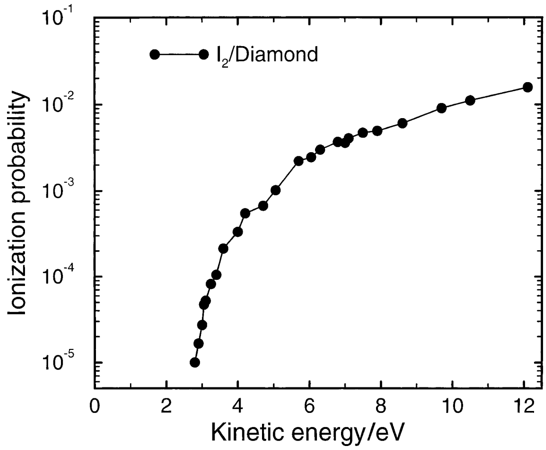

Fig. 1 Experimental results of the ionization probability in the scattering of I_2/diamond as a function of the incident kinetic energy of the molecule (after ref. 16).

data, experience and intuition. In our simulation we model the molecular center of mass distance from the surface z and one surface oscillator coordinate x. Without the surface oscillator the one-dimensional two-surface potential can be written as

$$V_{1D}(z) = \begin{pmatrix} V_{11}(z) & V_{12}(z) \\ V_{12}(z) & V_{22}(z) \end{pmatrix} \tag{8}$$

Our chosen model potential is plotted in Fig. 2. It corresponds to a typical one-dimensional curve-crossing problem. The diabatic potential energy surfaces V_{ii} are parametrized as Morse potentials

$$V_{ii}(z) = D_{ii}(e^{-2\alpha_{ii}(z-z_{ii})} - 2e^{-\alpha_{ii}(z-z_{ii})}) + S_{ii} \tag{9}$$

while the diabatic coupling between the surfaces V_{12} has an exponential form

$$V_{12}(z) = D_{12}e^{-\alpha_{12}z}. \tag{10}$$

The parameters we have chosen are listed in Table 1. We assume that in the experiment the diamond surface has been hydrogen-covered.[16] Due to this passivation we have chosen only a

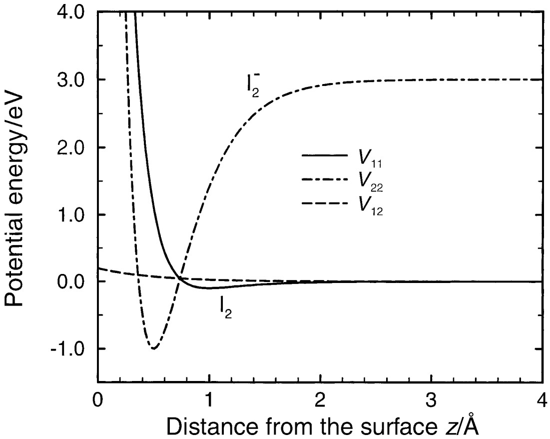

Fig. 2 One-dimensional model potential for the ionization of I_2 in the scattering from diamond surfaces. V_{11} corresponds to the potential energy surface for the neutral molecule (——) and V_{22} to the potential for the charged molecule (— · —). V_{12} is the coupling between the two potentials (— —).

Table 1 Parameters of the model potential for I_2/diamond scattering according to eqn. (9)

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	—	—

small physisorption well of 0.1 eV for neutral I_2. As for the I_2^-/diamond well-depth, we have to rely on speculation. Since diamond has a large band gap of 5.4 eV, image charge effects should be small. However, during the charge transfer process there will be a locally charged complex at the surface which could cause an attractive potential of the order of 1 eV. The strength of the coupling V_{12} had to be guessed. The shift of $S_{22} = 3.0$ eV between the two Morse potentials for $z \to \infty$ was chosen to reproduce the threshold of the I_2 ionization at a kinetic energy of ~ 3.0 eV.

The surface oscillator is coupled to the molecular motion *via* $V_{1D}(z) \to V_{1D}(z - x)$. The whole 2D potential is given by

$$V_{2D}(z, x) = \begin{pmatrix} V_{11}(z - x) + V_{osc}(x) & V_{12}(z - x) \\ V_{12}(z - x) & V_{22}(z - x) + V_{osc}(x) \end{pmatrix} \tag{11}$$

with

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

For the surface oscillator we have chosen $\hbar\omega = 50$ meV and $m_{osc} = 180$ u. These parameters are not very realistic for a diamond surface. For example, m_{osc} corresponds to 15 times the mass of a carbon atom. Usually one selects one to two times the mass of a surface atom for the surface oscillator model.[20–23] We had tried more realistic parameters like for example used in ref. 22. However, with these parameters the surface oscillator did not really participate dynamically in the scattering process. It mainly recoiled adiabatically upon impingement of the iodine molecules with very little energy transfer. This is caused by the stiffness of the diamond surface. We have selected parameters for the surface oscillator that result in a larger energy transfer from the impinging molecule to the surface; this oscillator should, rather, be regarded as a general mode for energy transfer during the scattering process.

We have, furthermore, coupled the molecular rotation to the scattering process *via*

$$V_{1D}(z) \to \tfrac{1}{2}\left[V_{1D}\left(z - \frac{r}{2}\cos\theta\right) + V_{1D}\left(z + \frac{r}{2}\cos\theta\right)\right], \tag{13}$$

where $r = 2.66$ Å is the bondlength of I_2 and θ is the angle of the molecular axis with the surface normal. Note that in this model I_2 is treated as a rigid rotor, *i.e.* no molecular vibrations are included. We would like to emphasize at this point that we are trying to reproduce qualitative trends of the experiment. We are looking for a qualitative explanation that is *consistent with the experiment*. This does not necessarily exclude that the true explanation might be quite different. However, by such an approach the number of possible mechanisms underlying an experimental finding can be narrowed down.

IV. Results and discussion

The quantum and semiclassical results using the one-dimensional two-surface potential of eqn. (8) are plotted in Fig. 3. The semiclassical results have been obtained in the adiabatic representation. First, the oscillatory structure of the quantum and semiclassical results is evident. These are typical Stückelberg oscillations due to the fact that the molecule can be ionized on the way either to or from the surface, and these two paths interfere. It is evident that the quantum and semiclassical results show the same amplitude of the Stückelberg oscillations, the phase, however, does not

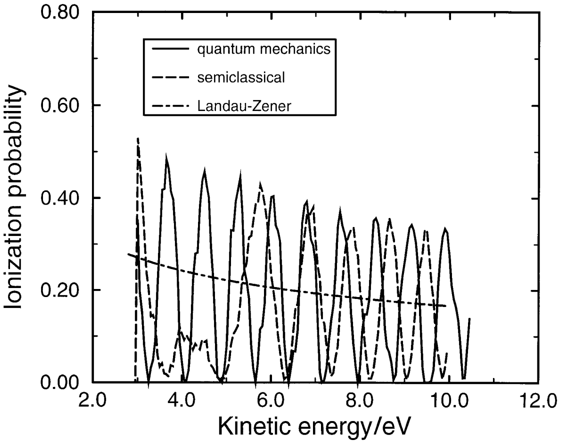

Fig. 3 Theoretical results of the ionization probability of I_2/diamond as a function of the incident kinetic energy of the molecule using the one-dimensional two-surface potential of eqn. (8). (——) Quantum mechanical result; (— —) semiclassical result; (— · —): Landau–Zener approximation.

agree. In addition, in the semiclassical calculation one peak of the Stückelberg oscillations at approximately 4 eV is missing. The fact that the phases do not agree is not too surprising considering that the semiclassical approximation breaks down at the classical turning points where the de Broglie wavelength of the molecule becomes infinite.

In addition, we have included results according to the Landau–Zener approximation.[24] In this approximation the transition between two *adiabatic* states which we denote by a and b is given by

$$w_{\mathrm{ab}} = \exp\left(-\frac{2\pi V_{12}^2}{\hbar v \left|\frac{\mathrm{d}V_{11}}{\mathrm{d}z} - \frac{\mathrm{d}V_{22}}{\mathrm{d}z}\right|}\right), \tag{14}$$

where the values of the coupling V_{12}, of the derivatives of the potentials and of the velocity v are all taken at the curve-crossing between the *diabatic* states. Now the molecule passes the location of the curve-crossing twice before it is scattered back into the gas phase, hence the total probability of the ionization in the Landau–Zener approximation is given by

$$P_{12} = 2w_{\mathrm{ab}}(1 - w_{\mathrm{ab}}). \tag{15}$$

Note that in the gas phase the diabatic states which we have denoted by 1 and 2 and the corresponding adiabatic states are the same. In the Landau–Zener approximation the Stückelberg oscillations are absent since no phase information is included. But the Landau–Zener results correspond rather accurately to the averaged quantum and semiclassical results. This tells us that indeed surface hopping occurs in both methods rather close to the surface crossing point. This is also confirmed by an analysis of the semiclassical trajectories. The Landau–Zener probability w_{ab} alone rises with increasing kinetic energies. However, P_{12} has its maximum for $w_{\mathrm{ab}} = 0.5$ (see eqn. (15)). Hence the decreasing ionization probability is due to the fact that w_{ab} is larger than 0.5.

The experimental results, on the other hand, showed an increase with increasing energy. From eqn. (14) and (15) we see directly that the coupling V_{12} between the *diabatic* curves actually has to become larger so that w_{ab} becomes smaller than 0.5 in order to reproduce the rising behavior of the experimental ionization probability. This means that we would get closer to the adiabatic limit. In fact, with $D_{12} = 1.5$ eV we can almost exactly reproduce the experimental curve. But first, this coupling seems to be unrealistically large, however, as there are no reliable calculations for the coupling such a value cannot be excluded. Even more importantly, very simple low-dimensional model calculations should not try to reproduce experimental data exactly in order to leave enough room for the influence of all the other neglected degrees of freedom. In fact, we believe that the electronic coupling is not responsible for this rising behavior but energy transfer to other degrees of freedom, as we will discuss below.

There are no Stückelberg oscillations apparent in the experimental results. Usually one argues that quantum mechanical interference effects wash out in realistic high-dimensional situation (although this is not always true[3]). And indeed, if the surface oscillator is included in the quantum mechanical calculations these oscillations disappear almost entirely as is shown in Fig. 4. These results correspond to the surface oscillator initially in its ground state. It is remarkable how close the quantum mechanical results follow the simple Landau–Zener expression at higher kinetic energies (note that in the Landau–Zener results the surface oscillator is not considered).

Now the quantum mechanical results actually show an initial increase at low kinetic energies. This is simple due to energy transfer to the oscillator. Due to this energy transfer the number of molecules that have enough energy to become ionized is reduced. In fact we believe that this is the qualitative explanation for the rising behavior of the ionization probability in the experiment. Regarding the facts that I_2 has very soft vibrational modes with $\hbar\omega = 20$ meV, that the dissociation energy of I_2 is only 1.5 eV which results in a large I_2 dissociation probability[25] and also that rotations can be excited very efficiently in the scattering (see ref. 26 and below), we see that a lot of energy is transfered to other degrees of freedom during the scattering event. This limits the number of molecules that have enough energy to be ionized, in particular close to the threshold energy.

Turning to the semiclassical results, we see that the Stückelberg oscillations are not washed out at all, their amplitude is almost the same as in the rigid surface case. It seems to be a paradox that in the semiclassical calculations more phase coherence is retained than in the quantum calculations, however, this has already also been observed in one-dimensional two-surface calculations.[9] Now in these calculations the surface oscillator has been treated fully classically, *i.e.*, the surface oscillator was initially at rest. In the quantum calculations, on the other hand, the surface oscillator has zero-point motion according to a zero-point energy of 25 meV. This actually corresponds to a temperature of 300 K in a classical picture. It is possible that this uncertainty in the position and momentum of the oscillator contributes to the suppression of the Stückelberg oscillations. Hence we have performed semiclassical calculations in which the surface initially had a vibrational energy of 25 meV and in which the initial phase of the oscillator was sampled randomly. Indeed, the Stückelberg oscillations are reduced significantly if the zero-point energy is taken into account in the semiclassical calculations, as is demonstrated in Fig. 5. But still these oscillations are much stronger than in the full quantum calculations. However, the mean value of the semiclassical results closely follows the quantum results.

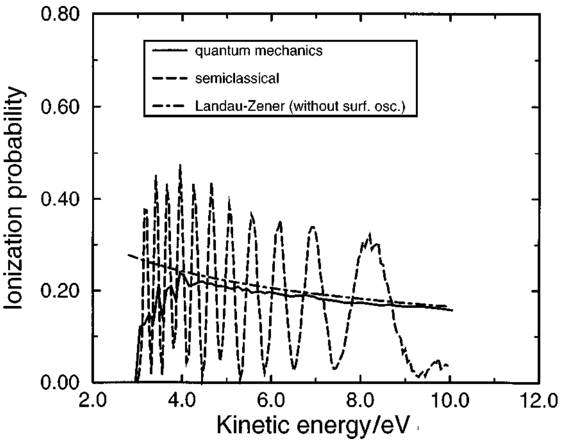

Fig. 4 Theoretical results of the ionization probability of I_2/diamond as a function of the incident kinetic energy of the molecule including the surface oscillator according to eqn. (11). The notation is the same as in Fig. 3. No zero-point energy corrections for the surface oscillator have been taken into account. The results in the Landau–Zener approximation in which no surface oscillator is considered are also plotted as a guide to the eye.

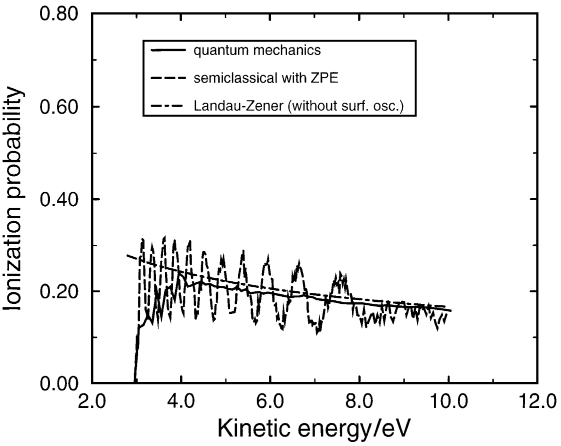

Fig. 5 Theoretical results of the ionization probability of I_2/diamond as a function of the incident kinetic energy of the molecule including the surface oscillator according to eqn. (11). The notation is the same as in Fig. 1. In the semiclassical calculations a zero-point energy of 25 meV of the surface oscillator was taken into account.

There may be several reasons why the Stückelberg oscillations in the semiclassical calculations are not suppressed in the same way as in the quantum calculations. First, in the scattering at the surface oscillator a superposition of oscillator states is excited in the quantum dynamics which causes a distribution in the kinetic energy of the scattered molecule. In the semiclassical calculations, for a fixed kinetic energy a fixed amount of kinetic energy is transferred to the surface oscillator, if the surface oscillator is initially at rest, so that no distribution of kinetic energies results which could suppress the Stückelberg oscillations. If the surface oscillator is initially already vibrating with the zero-point energy, a certain distribution in the energy transfer is the consequence, but apparently this distribution is not wide enough to fully suppress the Stückelberg oscillations, as Fig. 5 demonstrates.

Secondly, the coupling $V_{12}(z - x)$ also leads to transitions between different surface oscillator states in the quantum dynamics. One can show[27] that

$$\begin{aligned}\langle m | V_{12}(z - x) | n \rangle &= \langle m | D_{12} \mathrm{e}^{-\alpha_{12}(z-x)} | n \rangle \\ &= D_{12}^{*}(z) \tilde{\alpha}^{|m-n|} \sum_{k=0}^{\infty} \frac{\tilde{\alpha}^{2k}}{k!(k + |m - n|)!|} \frac{(\max(m, n) + k)!}{(m!n!)^{1/2}}, \end{aligned} \tag{16}$$

with

$$D_{12}^{*}(z) = D_{12} \mathrm{e}^{-\alpha_{12} z} \mathrm{e}^{\tilde{\alpha}^2/2} \tag{17}$$

and

$$\tilde{\alpha} = \alpha_{12} \left(\frac{\hbar}{2 m_{\mathrm{osc}} \omega} \right)^{1/2}, \tag{18}$$

where $| m \rangle$ and $| n \rangle$ are harmonic oscillator states.

Eqn. (16) demonstrates that there is a non-vanishing probability that the transition between the two electronic states is accompanied by a change in the surface oscillator states at *any* point along the trajectories. This leads to a change in the kinetic energy of the molecule in the quantum dynamics even if $V_{11}(\boldsymbol{R}(t)) = V_{22}(\boldsymbol{R}(t))$ at the point of the transition between the two electronic states in the quantum dynamics. On the other hand, in the semiclassical calculations the kinetic energy of the molecule will not be altered in such a situation. These oscillator transitions will contribute to the loss of phase coherence in the quantum dynamics, while it is absent in the semiclassical calculations.

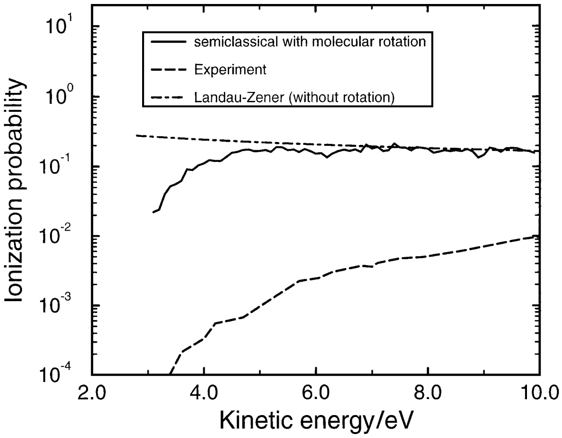

Fig. 6 Theoretical results of the ionization probability of I_2/diamond as a function of the incident kinetic energy of the molecule taking the molecular rotation into account according to eqn. (13) (——). In addition, the experimental results from ref. 16 (— —) and the Landau–Zener results without rotations (—·—) are plotted as a guide to the eye.

However, instead of trying to change the semiclassical algorithm in order to suppress the artificial oscillations we are led by the notion that, in a high-dimensional application which we have in mind, such oscillations will be washed out. Indeed, if we consider the molecular rotation in the semiclassical calculations according to eqn. (13) instead of the surface oscillator, there are no longer any Stückelberg oscillations evident, as Fig. 6 demonstrates. First, in the semiclassical calculation the initial orientation of the molecule is sampled randomly, which increases the stochastic nature of the scattering event; and secondly, while the energy transfer to the surface oscillator is less than 1 eV at all kinetic energies for the chosen parameters, up to more than 3 eV is transferred to the molecular rotation in the scattering. Both effects cause a suppression of the Stückelberg oscillations. Note that we have not performed quantum dynamical calculations taking into account the molecular rotation. Due to the small rotational energy quantum of I_2 more than 1000 channels have to be considered in the quantum calculations per electronic levels which makes these calculations computationally much too expensive. This is actually precisely the reason why we are applying the semiclassical treatment to the electron transfer problem.

In Fig. 6 we have also included the experimental results. Due to the low dimensionality of the calculations we have not tried to reach quantitative agreement with experiment. However, it is evident that due to the energy transfer to the molecular rotation the ionization probability is suppresssed by more than one order of magnitude close to the ionization threshold compared to the Landau–Zener probability without rotations. The qualitative trend in the calculated ionization probability is rather similar to experiment. The inclusion of the molecular vibrations and also the molecular dissociation channel will further suppress the ionization probability. This confirms our qualitative explanation of the experiment that it is not the electronic coupling *per se* that causes the strong increase in the ionization probability with rising kinetic energy. Instead, the large energy transfer to other degrees of freedom during the scattering event leads to a large suppresion of the ionization probability, in particular for energies close to the ionization threshold.

V. Conclusions

We have calculated the ionization probability in the scattering of molecules from surfaces by a quantum mechanical and a semiclassical treatment. In our low-dimensional description the molecular center of mass distance from the surface and either a surface oscillator coordinate or the molecular orientation have been considered. The parameters of the model potential have been chosen to resemble the system I_2/diamond.

The semiclassical results agree with the quantum results although some discrepancies remain as far as the phase coherence is concerned. These discrepancies, however, will most probably be absent in high-dimensional applications, as our semiclassical calculations in which the molecular rotation is taken into account demonstrate. Thus the semiclassical method opens the way to the description of electronically non-adiabatic processes in realistic high-dimensional simulations.

The results of these particular low-dimensional simulations suggest that the strong increase in the ionization probability in the scattering of I_2/diamond with increasing kinetic energy observed in the experiment is not caused by the electronic coupling *per se*. Due to the efficient energy transfer to other degrees of freedom in the scattering process the number of molecules that have enough kinetic energy to become ionized is strongly reduced, in particular for energies close to the ionization threshold. At higher kinetic energies the fraction of molecules retaining sufficient kinetic energy in the scattering process becomes larger, leading to the increase in the ionization probability.

Acknowledgements

We thank E. Kolodney for providing us with the unpublished data of the I_2 dissociation probability in the I_2/diamond scattering.

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