THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

2005, *109,* 9379−9383
Published on Web 10/05/2005

Quantum Effects in an Exoergic, Barrierless Reaction at High Collision Energies

Rocco Martinazzo*,† **and Gian Franco Tantardini**†,‡

Department of Physical Chemistry and Electrochemistry and CIMAINA, University of Milan, V. Golgi 19, 20133 Milan, Italy, and CNR Institute of Molecular Science and Technology, V. Golgi 19, 20133 Milan, Italy

Received: July 12, 2005; In Final Form: September 12, 2005

The exoergic Eley−Rideal hydrogen recombination on graphite surfaces is known to produce vibrationally hot product molecules. Realistic quantum scattering calculations at normal incidence over a wide range of collision energies show that the degree of vibrational excitation of the reaction product is a steep decreasing function of the collision energy. This results in selective population of the lower-lying vibrational levels and gives rise to an oscillating structure in the total reaction cross-sections at high energies, which cannot be reproduced by classical and quasi-classical trajectory calculations. An analogous quantum structure appears in the total collision-induced desorption cross-sections and is assigned to selective population of the metastable states of the transient molecular hydrogen.

I. Introduction

Quantum effects in chemical reactions are rarely observable and are usually limited to light atoms, at the reaction threshold or at relatively low collision energies. Among these, there are tunneling through the reaction barrier, quantization of the internal modes at the transition state, and (reactive) Feshbach resonances on purely repulsive potential energy surfaces. Although their presence in gas-phase reactions has been predicted by quantum scattering calculations for several collision systems, they are in general difficult to observe, because in simple terms, they tend to exist over a wide range of total angular momentum. Thus, for example, the time-delayed mechanism[1] in the $H + H_2$ isotopic family of reactions has been attributed[2] to the motion through a "quantized dynamical bottleneck", but only the observation of interference between different quantized transition-state pathways has been conclusive for quantum phenomena;[3,4] the observation of reactive resonances is limited to the atom−diatom systems $I + HI$[5] and $F + HD$,[6,7] and only recently has evidence been found for polyatomic reactions.[8−10]

The above-mentioned effects are related to the presence of a barrier separating products from reactants, which acts as a bottleneck in the reaction dynamics. As a consequence, they may strongly influence the reaction rate: carbon atom tunneling has been reported with a tremendous effect on the low-temperature isomerization rate of the 1-methylcyclobutylfluorocarbene;[11] the Feshbach resonance in the $F + HD$ reaction[6,7] completely determines the reaction outcome at energies below 1.0 kcal mol^{-1}, and this fact could be used to achieve a great deal of control on the products branching ratio.[12] Understanding such quantum effects is central to chemical reaction dynamics.

In principle, however, quantum effects may also arise from quantization of the *product* molecular states. This is a known source of ambiguities in classical trajectory (CT) calculations where, for example, the question arises of how to consider reactive trajectories ending up with products' internal energy less than the zero-point value. It is therefore important to know that these effects may manifest themselves in scattering observables. In this letter, we show how they may appear in *total* reaction cross-sections even when classical mechanics is expected to be adequate all the way in the route from reactants to products, considering an exoergic, barrierless gas−surface reaction. We further show that a "quantum" structure also appears in the total collision-induced desorption (CID) cross-sections, since this process partly proceeds through a two-step mechanism, metastable molecule formation and dissociation.

The reaction system is the Eley−Rideal (ER) hydrogen recombination on a graphite surface, i.e., the formation of H_2 from the collision of an incident hydrogen atom with a target hydrogen atom chemisorbed on graphite. This reaction has become a model system to study hydrogen formation on interstellar dust grains, for which a number of carbonaceous models exists;[13] it is also of importance for the hydrogen erosion of graphite-lined walls in fusion reactors and for H_2 storage in graphite nanostructures.[14] The reaction is known to produce, both experimentally[15,16] and theoretically,[17−19] vibrationally hot hydrogen molecules at low collision energies, in analogy with a number of exoergic, barrierless gas-phase reactions.[20] However, a particular feature of the present reaction system is the vibrational excitation decrease when increasing collision energy (see also ref 18).

II. Results and Discussion

We performed quantum scattering calculations for this collision system at normal incidence in the rigid, flat surface approximation,[21,22] neglecting the role of phonon and electron−hole excitations. In this approximation, one factors out the center of mass translational coordinates along the surface and the angle which describes overall rotations around the surface normal,

---

* Electronic address: rocco.martinazzo@unimi.it.
† University of Milan.
‡ CNR Institute of Molecular Science and Technology.

10.1021/jp053820c CCC: $30.25

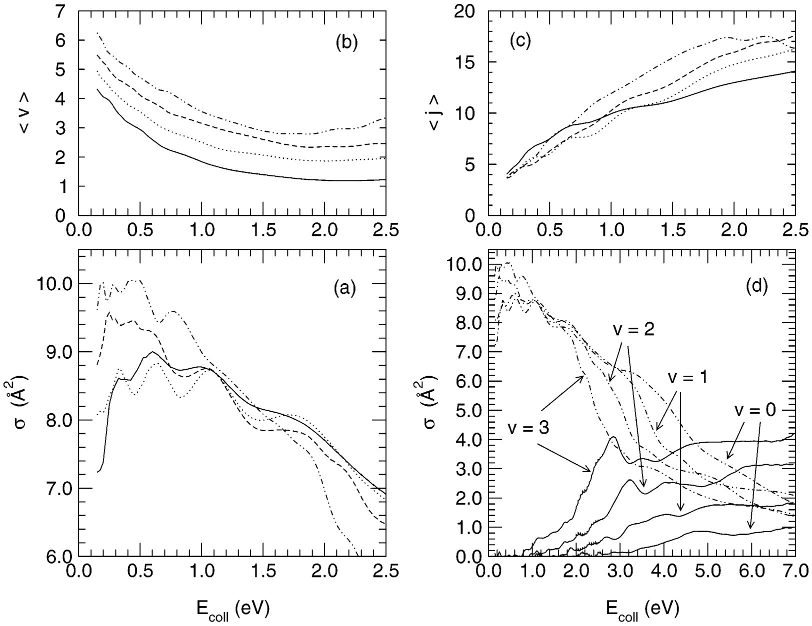

Figure 1. Panel (a): Total ER cross-sections for some values of the target vibrational quantum number (full, dotted, dashed, and dot−dashed lines for $v = 0$, 1, 2, and 3, respectively). Panels (b) and (c): Average vibrational (b) and rotational (c) quantum numbers for the product molecules (lines as in (a)). Panel (d): Total CID (solid lines) and ER (dot−dashed lines) cross-sections for the indicated initial states of the adsorbate.

thereby reducing the problem to a tractable three-dimensional one. This approximation is expected to work particularly well in the present system, since the H−H interaction dominates over the H−surface one; dynamics is fast, and in absence of substrate relaxation, the projectile H atom experiences a weakly corrugated, essentially repulsive, physisorption potential. Phonon excitations are expected to play a minor role in the dynamics, thanks to the mass mismatch between projectiles and substrate atoms and to the stiffness of the graphite surface.

For what concerns the potential, several models were developed in the past, differing mainly in the H−graphite chemisorption potential. The first periodic density functional theory (DFT) calculation was that of Farebrother et al.,[23] which seemed to contradict previous results of Jeloaica and Sidis[24] based on cluster calculations on coronene. Indeed, the H−graphite results of ref 23 showed no puckering of the C atom and no barrier to chemisorption. The corresponding 2H−graphite potential was later extended and used in the first quantum calculation of the above Eley−Rideal reaction within the rigid, flat surface approximation.[17] Later, Sha and Jackson[25] found that with more converged DFT periodic calculations the puckering of the C atom and the barrier to chemisorption agreed well with the results of Jeloaica and Sidis.[24] Their ab initio data were subsequently used to build two modified London−Eyring−Polanyi−Sato potentials for the case in which the target atom is initially chemisorbed on the surface.[18] Here, the case A potential of ref 18 (that in which the substrate relaxation—the puckering of the C atom—is expected to be slow with respect to the reaction dynamics) was adopted. With this potential, the hydrogen recombination reaction is exoergic by about 3.2 eV.

Quantum calculations were performed within the time-dependent approach of Jackson and Lemoine,[22] which uses the split-operator scheme and a pseudospectral strategy to evaluate the time-evolution operator. We used two different sets of coordinates (a "product" and a "reagent" coordinate set) in order to directly compute state-resolved reaction cross-sections and the remaining "two-body" probabilities; then, total collision-induced desorption cross-sections follow from flux conservation. Details of the present implementation and of the calculations will be reported in a future publication. Results of these quantum calculations for the first four vibrational levels of the target atom in the adsorption well are displayed in Figure 1. In panel (a), we report the total Eley−Rideal cross-sections in the range 0−2.5 eV. They are large, much larger than ER cross-sections for the same reaction on metal surfaces,[26,27] decrease as the collision energy increases (with the exception of the low collision energy regime, $E_{\mathrm{coll}} < 0.2-0.5$ eV, depending on v), and show an evident oscillating structure. In panels (b) and (c), we report the average vibrational and rotational quantum numbers of the reaction products, respectively. As already noted by Sha et al.[18] in a more restricted energy range, the degree of vibrational (rotational) excitation is a decreasing (increasing) function of the collision energy. This behavior, which is of relevance for the present work, is partially responsible for the dynamic thresholds appearing in the total CID cross-sections. These cross-sections are shown in panel (d) along with the ER results over an extended energy region. They are rather small, particularly when the target is initially in low-lying vibrational states, and show a peak structure which is clearly evident in the cases $v = 2$ and 3.

The overall dynamical behavior can be understood in terms of a classical picture (Figure 2). The reaction is driven by the strong H−H interaction, and molecule formation occurs in the entrance channel. At low energy, the projectile impinges directly on the target, leading to vibrationally hot and rotationally cold product molecules; a slight increase of the collision energy in this regime results in an increase of the cross-section, since more trajectories with high impact parameters (b, the initial asymptotic H−H distance projected on the surface plane) can be "captured" by the target atom before being reflected by the physisorption potential. Further increase of the collision energy results in a loss of reactivity of the small b trajectories (say, $b \lesssim r_{\mathrm{eq}}$, where r_{eq} is the H_2 equilibrium distance) either because the projectile undergoes two subsequent collisions with the target and regains much of its energy or because it is scattered away from the target. Reaction occurs only at high impact parameters ($r_{\mathrm{eq}} \lesssim b \lesssim 2r_{\mathrm{eq}}$) through a "glancing" collision, and this leads to enhanced rotational excitation and reduced vibrational excitation (see below). The resulting reactive opacity functions ($P(b)$, the reaction probability for a given value b of the impact parameter)

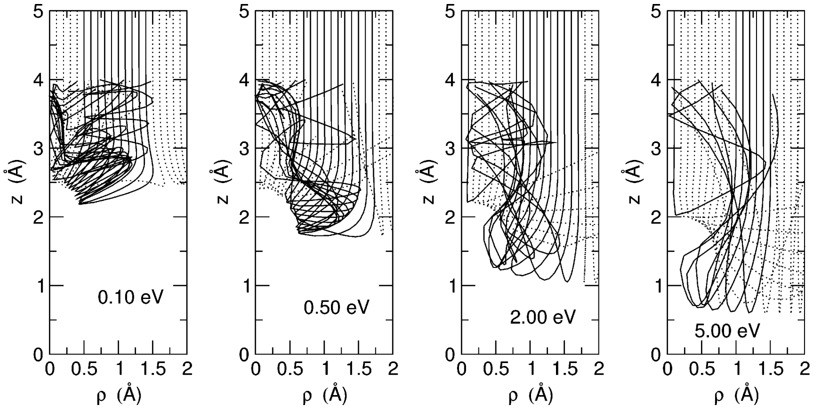

Figure 2. A representative set of trajectories in the $\rho-z$ plane, where ρ is the HH distance projected on the surface plane and z is the height of the incident atom. The target is initially placed at rest at the equilibrium position (which occurs 1.52 Å, above the surface). Full and dotted lines for reactive and nonreactive trajectories, respectively.

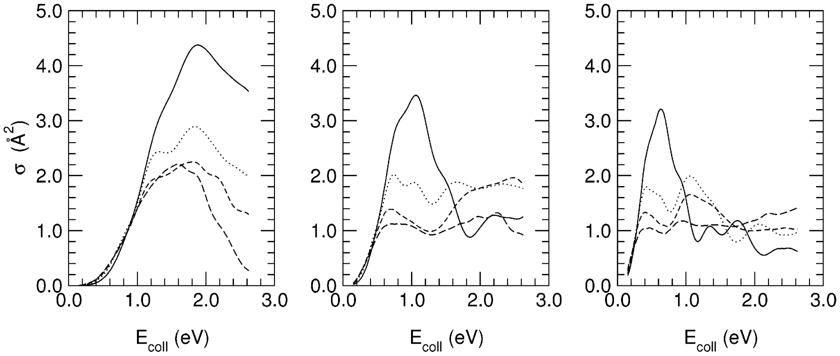

Figure 3. Rotationally summed, vibrationally resolved cross-sections for the $v' = 0$ (left), 1 (middle), and 2 (right) level of the H_2 molecule. Lines as in Figure 1a.

thus show a "hole" at small impact parameters due to "hard" collisions between the projectile and the target atom. This behavior is common to other Eley−Rideal processes, including H_2 formation on metals[27] and HCl formation on Au.[28,29] At higher energy, high b projectiles deflected by the HH potential at the first round trip bounce on the surface and become able to collide from *below* with the target atom, thereby causing the onset of a sizable CID process.

Of relevance here is the rovibrational excitation; vibrational (rotational) distributions of the product molecules (here not shown) are rather narrow and steadily shift toward lower (higher) quantum numbers as the collision energy increases in the range 0.5−2.5 eV. Analysis of classical and quasi-classical trajectory (QCT) calculations[30,31] show that this behavior is due to high impact parameter trajectories ($b \gtrsim 1.2$ Å). For these trajectories, the incident atom is only slightly deflected in its incoming motion, collides with the surface while the target gets nearer, and picks it at a distance close to the equilibrium value (for the resulting high j value). Increase of the collision energy in this range causes the vibrational excitation of the product molecule to steeply decrease up to a minimum where products may even be formed with energy less than the zero-point value (this occurs in CT and QCT ($v = 0$) dynamics at about 2.0 eV). In classical mechanics, product rovibrational states can be continuously populated, but in quantum mechanics, selection of the appropriate final state must occur even if the collisional dynamics is "classic" in the reactant and interaction region; this is particularly true for the widely spaced vibrational levels of the product molecular hydrogen as we show below.

When considering the rotationally summed, vibrationally resolved reaction cross-sections for low values of the vibrational quantum number v' of the product molecule, a well-defined and distinct threshold behavior appears as a consequence of the above scattering mechanism (see Figure 3). It is clear that the threshold behavior does *not* depend on v and that the vibrationally resolved cross-sections peak at different values of the collision energy.

The situation is particularly simple when the target atom is initially in its ground state, since in this case, the overall vibrational excitation can be quite small (Figure 1, panel (b)). In this case, the oscillations in total reaction cross-sections may be neatly assigned to selective population of the product vibrational levels. This is shown in Figure 4, panel (a), where the total reaction cross-section is reported along with the vibrationally resolved cross-sections for the lower-lying product states $v' = 0-4$. In panel (b) of Figure 4, the same cross-section is compared with the results of CT and QCT ($v = 0$) calculations. It is clear from this figure that classical mechanics correctly reproduces the *average* behavior of the cross-section but it is unable to reproduce the oscillations in the quantum results. In panel (c), we report the CID cross-section for the target initially in the $v = 3$ state along with the vibrational populations of the Eley−Rideal *reaction* products for some selected values of v'. In this case, a correlation between the collision-induced desorption and the recombination process is found, thereby suggesting that part of the CID process proceeds through a two-step mechanism, formation of metastable H_2 molecules and subsequent dissociation. This can be easily checked with classical calculations, since rotationally excited H_2 molecules trapped by the centrifugal potential appear as stable products (with an internal energy higher than the dissociation limit). The results of these calculations are reported in panel (d) of Figure 4 where a bump in the classical results

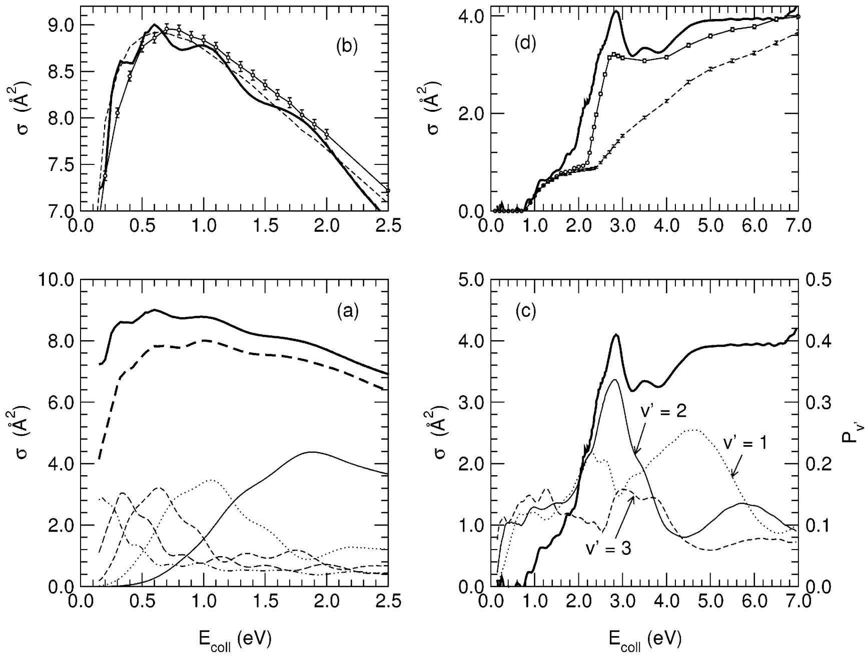

Figure 4. Panel (a): Thick solid line is the total reaction cross-section for $v = 0$; thin solid, dotted, dashed, long-dashed, and dot−dashed lines are rotationally summed, vibrationally resolved cross-sections for product molecules in the $v' = 0$, 1, 2, 3, and 4 vibrational levels, respectively; thick dashed line is the vibrationally resolved cross-section summed over the $v' = 0{-}4$ levels. Panel (b): The quantum cross-section of (a) (thick solid line) and the QCT ($v = 0$) (points connected by solid lines) and CT (dashed lines) results. Bars represent estimated standard deviations. Panel (c): The CID cross-section for $v = 3$ (thick solid line, left scale) and the vibrational populations of the ER products for the indicated values of v' (right scale). Panel (d): The quantum cross-section of panel (c) (solid line) and QCT results, with (points connected by solid lines) and without (dashed lines) the contribution of metastable hydrogen molecules.

due to formation of metastable H_2 appears but is much less pronounced than in the quantum case.[32]

III. Conclusions

In this work, we have studied a simple exoergic, barrierless reaction for which classical mechanics is expected to be adequate, showing that some quantum effects appear in global observables such as total reaction cross-sections. These effects may be simply ascribed to quantization of *product* molecular states and may be found, in general, at relatively high collision energies if the scattering mechanism and the reaction product allow a selective population of widely spaced internal states. The reaction considered here is the Eley−Rideal hydrogen recombination reaction on graphite, for which quantum scattering calculations are feasible in the rigid, flat surface approximation. Although the flat surface approximation is quite reliable for the present system, the accuracy of the rigid surface approximation cannot be clearly ascertained, and further work is needed in order to understand the role of phonon excitations. However, our main finding that a rapid decrease of vibrational excitation of the reaction products may allow the quantum nature of the product states to manifest itself in a *scattering* observable is of general validity. The reactions F + CHD_3[9] and F + H_2/HD/D_2[33] show a vibrational behavior of FD(FH) products similar to that found here, and for the F + H_2/HD/D_2 cases, QCT results at high energies are somewhat at variance with quantum mechanical and experimental ones (e.g., see ref 33).

It is clear from our results that in studying light atoms dynamics one should be cautious in applying classical methods even when the reaction system, the reaction conditions, or the observable to be computed suggest them to be adequate.

Acknowledgment. The authors thank Bret Jackson for critically reading the manuscript and the C.I. L.E.A. Supercomputing Center for having allowed the use of its computational facilities.

References and Notes

(1) Althorpe, S. C.; Fernandez-Alonso, F.; Bean, B. D.; Ayers, J. D.; Pomerantz, A. E.; Zare, R. N.; Wrede, E. *Nature (London)* **2002**, *416*, 67−70.

(2) Harich, S. A.; Dai, D.; Wang, C. C.; Yang, X.; S. Chao, D.; Skodje, R. T. *Nature (London)* **2002**, *419*, 281−284.

(3) Dai, D.; Wang, C. C.; Harich, S. A.; Wang, X.; Yang, X.; Chao, S. D.; Skodje, R. T. *Science* **2003**, *300*, 1730−1734.

(4) Skodje, R. T.; Yang, X. *Int. Rev. Phys. Chem.* **2004**, *23*, 253−287.

(5) Waller, I. M.; Kitsopoulos, T. N.; Neumark, D. N. *J. Phys. Chem.* **1990**, *94*, 2240−2242.

(6) Skodje, R. T.; Skouteris, D.; Manolopoulos, D. E.; Lee, S. H.; Dong, F.; Liu, K. *Phys. Rev. Lett.* **2000**, *85*, 1206−1209.

(7) Skodje, R. T.; Skouteris, D.; Manolopoulos, D. E.; Lee, S. H.; Dong, F.; Liu, K. *J. Chem. Phys.* **2000**, *112*, 4536−4552.

(8) Shiu, W.; Lin, J. J.; Liu, K. *Phys. Rev. Lett.* **2004**, *92*, 103201 (4 pp).

(9) Zhou, J.; Lin, J. J.; Liu, K. *J. Chem. Phys.* **2004**, *121*, 813−818.

(10) Zhang, B.; Liu, K. *J. Chem. Phys.* **2005**, *122*, 101102 (4 pp).

(11) Zuev, P. S.; Sharidan, R. S.; Albu, T. V.; Truhlar, D. G.; Hrovat, D. A.; Borden, W. T. *Science* **2003**, *299*, 867−870.

(12) Zeman, V.; Shapiro, M.; Brumer, P. *Phys. Rev. Lett.* **2004**, *92*, 133204 (4 pp).

(13) Papoular, R.; Conrad, J.; Guillois, O.; Nenner, I.; Reynaud, C.; Rouzand, J.-N. *Astron. Astrophys.* **1996**, *315*, 222−236.

(14) Meregalli, V.; Parrinello, M. *Appl. Phys. A* **2001**, *72*, 143−146.

(15) Gough, S.; Schermann, S. C.; Pichou, F.; Landau, M.; Cadez, I.; Hall, R. I. *Astron. Astrophys.* **1996**, *305*, 687−693.

(16) Perry, J. S. A.; Price, S. D. *Astrophys. Space Sci.* **2003**, *285*, 769−776.

(17) Meijer, A. J. H. M.; Farebrother, A. J.; Clary, D. C.; Fisher, A. J. *J. Phys. Chem. A* **2001**, *105*, 2173-2182.

(18) Sha, X. Jackson, B.; Lemoine, D. *J. Chem. Phys.* **2002,** *116*, 7158−7169.

(19) Morisset, S.; Anguillon, F.; Sizun, M.; Sidis, V. *Phys. Chem. Chem. Phys.* **2003**, *5*, 506.

(20) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, U. K., 2005.

(21) Persson, M.; Jackson, B. *J. Chem. Phys.* **1995**, *102*, 1078−1093.

(22) Lemoine, D.; Jackson, B. *Comput. Phys. Commun.* **2001**, *137*, 415−426.

(23) Farebrother, A.; Meijer, A. J. H. M.; Clary, D. C.; Fisher, A. J. *Chem. Phys. Lett.* **2000**, *319*, 303−308.

(24) Jeloiaca, L.; Sidis, V. *Chem. Phys. Lett.* **1999**, *300*, 157.

(25) Sha, X.; Jackson, B. *Surf. Sci.* **2002**, *496*, 318−330.

(26) Jackson, B.; Lemoine, D. *J. Chem. Phys.* **2001**, *114*, 474−482.

(27) Jackson, B. In *The Chemical Physics of Solid Surfaces*; Woodruff, P., Ed.; Elsevier Science B. V.: Amsterdam. 2003; Vol. 11, pp 51−77.

(28) Lemoine, D.; Quartucci, J. G.; Jackson, B. *Phys. Rev. Lett.* **2002**, *89*, 268302 (4 pp).

(29) Quattrucci, J. G.; Jackson, B.; Lemoine, D. *J. Chem. Phys.* **2003**, *118*, 2357−2366.

(30) Martinazzo, R.; Assoni, S.; Marinoni, G.; Tantardini, G. F. *J. Chem. Phys.* **2004**, *120*, 8761−8771.

(31) Here and in the following, CT is used for classical trajectory calculations with the target initially at rest at the bottom of the adsorption well. QCT(v) stands for standard quasi-classical trajectory calculations with the target initially in the v vibrational state.

(32) Analysis of the QCT results reveals that the change of behavior at about 2.0 eV is due to the onset of the indirect scattering mechanism (that in which the projectile impinges on the surface and then collides with the target from below). This occurs for high values of b and gives rise to much larger cross-sections and formation of intermediate metastable hydrogen molecules.

(33) Dong, F.; Lee, S.-H.; Liu, K. *J. Chem. Phys.* **2000**, *113*, 3633−3640.