17 September 1999

Chemical Physics Letters 311 (1999) 1–7

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Rotational effects in the dissociation of H_2 on metal surfaces studied by ab initio quantum-dynamics calculations

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Received 29 March 1999; in final form 26 July 1999

Abstract

By performing six-dimensional quantum-dynamical calculations on potential energy surfaces derived from density functional theory total-energy calculations, we have determined the sticking probability of H_2 on Rh(100), Pd(100) and Ag(100). In particular, we have focused on the dependence of the sticking probability on the initial rotational state of the impinging hydrogen beam. The dynamical results are related to features of the relevant potential energy surface. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Detailed knowledge of the potential energy surface (PES) of molecules interacting with the solid surface is the prerequisite for a quantitative understanding of gas–surface interactions – chemisorption, catalysis, corrosion, etc. [1]. However, even the static information gained from the PES alone is not sufficient to assess the reactivity of a particular system [2]. To determine reaction probabilities, they have to be computed by actually performing dynamical calculations on the relevant PESs.

Due to recent progress in ab initio total-energy calculations and dynamical simulations, it is now possible to investigate the dynamics of reactions at surfaces for particular systems considering all relevant degrees of freedom entirely from first principles [3]. In this Letter, we present the results of detailed quantum-dynamic simulations of the dissociative adsorption of hydrogen molecules on the (100) surfaces of rhodium, palladium and silver. Our investigations are based on 6D-PESs constructed by density functional theory (DFT) calculations and the solution of the time-independent Schrödinger equation for the two H nuclei moving on the 6D-PES using a stable coupled-channel method. Rh, Pd and Ag have been chosen for our study because the PESs calculated for these metals cover the range from non-activated adsorption along most pathways (Rh) over activated as well as non-activated paths (Pd) to activated reactions only (Ag).

In a previous publication, we have shown that at low kinetic energies the sticking probability of H_2/Rh(100) and H_2/Pd(100) is rather similar [2] in spite of their different barrier distributions. In this

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PII: S0009-2614(99)00843-X

Letter, we extend this study by investigating, in particular, the dependence of the sticking probability on the initial rotational state. Experimentally it is possible to determine state-specific hydrogen sticking probabilities, either by performing the respective adsorption experiments [4–6] or by studying the desorption state-selectively [7–9] and relating the results to the adsorption probability via the principle of detailed balance. State-specific sticking probabilities then provide a very detailed data set to compare theoretical with experimental results. The quality of the PES or the dynamical calculations can thus be very carefully tested.

The theoretical simulations have one advantage, however, with respect to experiment, namely that the results of the simulations can be related to features of the underlying PES on which the reaction takes place. In this study, we will therefore carefully compare the potential along some typical reaction paths in the $H_2/Rh(100)$, $H_2/Pd(100)$ and $H_2/Ag(100)$ systems and assess the importance of particular features of the reaction path for the rotational dependence of the sticking probability in these systems. For $H_2/Pd(100)$, comparison with experiment has already revealed how reliable our calculations are [2,10]. Additionally we predict state-specific sticking probabilities that have not yet been measured and challenge the experimentalists to check the accuracy of our calculations.

2. Computational details

The quantum-dynamical calculations presented here are based on potential energy surfaces (PES) derived from ab-initio total-energy calculations [11] within the generalized gradient approximation [12] using the Vienna ab-initio simulation package VASP [13,14]. VASP works in a plane-wave basis and uses ultrasoft pseudopotentials [15] to achieve convergence at tolerable cut-off energies (for details, see Refs. [13,14] and references cited therein).

For each surface, 14 2-D cuts (consisting of about 200 data-points including forces) through the PES (‘elbow-plots’) have been calculated and used as an input for a parametrization similar to that in Ref. [16]. The potential is written as the sum of an adiabatic potential V^{a}, describing the energy of the molecule in its vibrational ground state, and a parabolic vibrational potential V^{v} using a frequency depending on the reaction path coordinate s [1].

$$V(s,r,x,y,\Theta,\varphi) = V^{a}(s,x,y,\Theta,\varphi) + V^{v}(s,r,x,y)\,. \qquad (1)$$

The coordinates are a coordinate r normal to the reaction path, two lateral coordinates x and y fixing the position of the center of mass of the molecule, i.e. the unit cell and two rotational degrees of freedom for azimuthal φ and polar orientation Θ. The adiabatic potential is parametrized as a sum of terms of the following structure

$$C_{l,m,i,j}(s)\,Y_{lm}(\Theta,\varphi)\cos\left(\frac{2\pi}{a}\,\mathrm{i}\,x\right)\cos\left(\frac{2\pi}{a}jy\right), \qquad (2)$$

where a denotes the nearest-neighbour distance a and $C(s)$ is a parameter. In total, we use a set of 15 s-dependent parameters fitted at 200 discrete s values.

The quantum-dynamical calculations have been performed by solving the time-independent Schrödinger equation in the six hydrogen degrees of freedom (6D) in a numerically very stable coupled-channel scheme [17]. Within this setup, convergence could be reached with a basis set consisting of rotational eigenfunctions with quantum numbers up to $j_{\max} = 12$ for Rh and Pd ($j_{\max} = 14$ for Ag) and parallel momentum states with maximum parallel momentum $p_{\max} = 9\hbar G$ for Rh and Pd ($p_{\max} = 10\hbar G$ for Ag) with $G = 2\pi/a$. The hydrogen vibrations follow the reaction dynamics almost adiabatically [18]; therefore we have analysed the state-specific sticking probabilities in detail by performing vibrationally adiabatic 5D calculations. However, it has been carefully checked that the results of these 5D calculations only differ by less than 5% from the full 6D calculations.

3. Results and discussion

In Fig. 1 we show the potential for molecules approaching the surface over the on-top position for

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[1] s is a linear reaction coordinate, connecting the initial configuration (free molecule + clean surface) $s \to +\infty$ with the final one (adsorbed atoms) $s \to -\infty$.

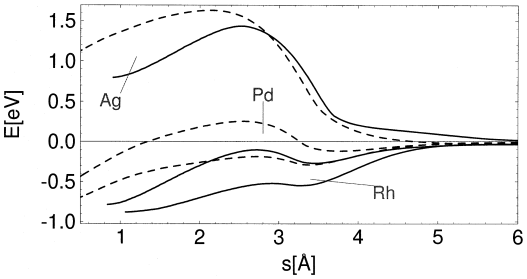

Fig. 1. Potential energy for the dissociative adsorption of H_2 on Rh(100), Pd(100) and Ag(100) surface as a function of the reaction coordinate s for the hydrogen center of mass over the top position with the molecular axis parallel to the surface for two different azimuthal orientations. Solid lines correspond to molecules dissociating into the bridge positions while the dashed lines denote molecules orientated towards the fourfold hollows. For the definition of the reaction coordinate, cf. text.

two azimuthal orientations as a function of the reaction path coordinate s (see footnote 1). For Rh(100) and Pd(100), there are H_2 dissociation paths without any barrier, i.e., non-activated dissociative adsorption is possible. However, while for H_2 in the other azimuthal orientation on Rh(100) barrierless dissociation is still possible, on Pd(100) this pathway becomes activated. On Ag(100), on the other hand, all dissociation pathways are hindered by high energy barriers larger than 1.1 eV. In addition, dissociation of H_2 on Ag(100) is endothermic. Interestingly enough, the energy difference between the two pathways for the two different azimuthal orientation is rather small compared to Rh and Pd.

Another pathway for the molecule approaching the surface in a parallel orientation is shown in Fig. 2, namely for dissociation over the fourfold hollow position. There is a small barrier for Rh and Pd, but then dissociation is exothermic. At this site, the dissociation pathways on both transition metals are relatively similar.

But more importantly, Fig. 2 shows the potential energy along pathways for molecules approaching the surface in an upright orientation. In this orientation, the interaction between H_2 and *all* metal surfaces is strongly repulsive. Fig. 2 demonstrates that hydrogen can only dissociate on metal surfaces if the molecular axis is parallel to the surface.

The sticking probabilities for H_2 molecules under normal incidence on Rh(100), Pd(100) and Ag(100) are shown in Fig. 3. The sticking probabilities have been determined for various initial rotational states j of the molecules where j is the rotational quantum number. The initial states in Fig. 3 correspond to the so-called cartwheel rotation, for which the azimuthal quantum number is $m = 0$. These molecules have their rotational axis preferentially oriented parallel to the surface.

As we have already pointed out [2], for $j = 0$, i.e. for initially non-rotating molecules, the sticking probabilities of H_2/Rh(100) and H_2/Pd(100) are rather similar in spite of the different barrier distributions. The large sticking probability for H_2 on Pd(100) is caused by the steering effect [19,20]: at low kinetic energies, molecules impinging in an unfavorable configuration are redirected and reoriented by the corrugation and anisotropy of the PES to non-activated pathways leading to the high sticking probability.

At higher kinetic energies, the molecules cannot be reoriented that efficiently any more, leading to the decrease in the sticking probability for H_2/Pd(100) which is in very good agreement with the experiment [21]. In fact, an analogous mechanism is also responsible for the decrease in the sticking probability for H_2/Pd(100) for larger rotational quantum numbers j. Higher rotational quantum numbers mean more rapidly rotating molecules. Even if these rapidly rotating molecules are in a favorable orientation towards dissociation, they will rotate out of this orientation before the dissociation is completed. As

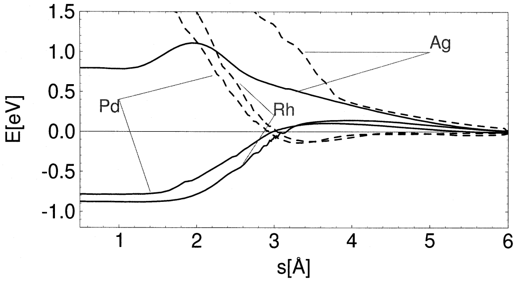

Fig. 2. Potential energy for the dissociative adsorption of H_2 on Rh(100), Pd(100) and Ag(100) surface as a function of the reaction coordinate s. Solid lines correspond to molecules dissociating into the bridge sites with the center of mass over a hollow position, while the dashed lines denote molecules approaching the surface upright over the bridge position. For the definition of the reaction coordinate, cf. text.

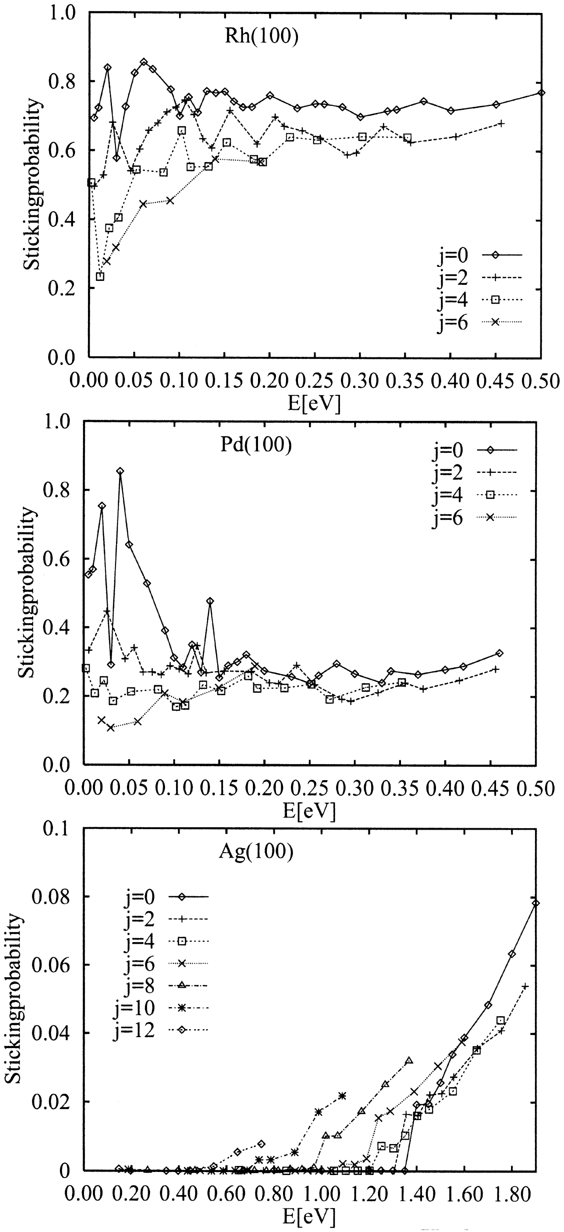

Fig. 3. Sticking probability versus kinetic energy for a H_2 beam under normal incidence on Rh(100), Pd(100) and Ag(100) at various j with $m = 0$ (cartwheel rotation).

Fig. 2 shows, the PES for molecules with their axis perpendicular to the surface is strongly repulsive for all studied systems. Thus the initial rotation of the molecules leads to a suppression of the sticking probability. This rotational hindering in the dissociation of H_2/Pd has also been confirmed experimentally [4]. At larger kinetic energies above 0.2 eV direct dissociative adsorption becomes dominant. In this regime there is only a small j-dependence of the sticking probability.

For H_2/Rh(100) experimentally the sticking probability has been found to be 'near unity' [22]. This is reproduced by our calculations for molecules initially in the rotational ground state $j = 0$ for which the sticking curve is rather flat. This does not mean that no interesting dynamics is underlying the sticking probabilities. Steering is still operative at low kinetic energies which is indicated by the fact that, ignoring the oscillations, there is still a slight decrease in S_0 up to kinetic energies of 0.3 eV. The influence of steering is, however, much more evident in the analysis of the dependence of the sticking probability on the initial rotational state of the molecules. There is a strong suppression of the sticking probability for higher initial j-states. This prominent effect of rotational hindering demonstrates the influence of steering at low kinetic energies also for H_2/Rh(100).

To our knowledge, there are no experiments for the hydrogen dissociation on Ag(100), only for Ag(110) and Ag(111) [23,24]. However, the similarity of the PES with that for the extensively studied system H_2/Cu [25,26] allows to compare our results qualitatively to the wealth of available data for H_2/Cu. The sticking probability of H_2/Ag(100) in Fig. 3 shows the typical behavior of activated systems for which dissociation is hindered by a substantial barrier. For initially non-rotating molecules, the kinetic energy has to be larger than the minimum barrier height in order to rise significantly. However, there is now an interesting difference to the former systems in the dependence of the sticking probability on the rotational quantum number. In contrast to the reactive systems H_2/Pd(100) and H_2/Rh(100), rotational excitation enhances the sticking probabilities even for cartwheeling molecules, however in a non-monotonous way. For $j \leqslant 4$ rotational motion still hinders the dissociation for $E_i \geqslant 1.3$ eV, but for $j > 4$ additional rotational motion helps to overcome the dissociation barrier. This non-monotonous behavior has indeed been found for the dissociation of H_2/Cu(111) [27]. Qualitatively this behavior has been understood [28]. It can only occur in so-called late barrier systems where the minimum barrier to dissociation is at a position where the molecular bond is already elongated. The hindering effect of the rotational motion is counterbalanced by the transfer of rotational energy to translational energy along the reaction path which is caused by the stretching of the molecular bond due to the late barrier. This mechanism becomes the more effective, the larger *j* is, because then a larger amount of rotational energy can be transferred to the translational motion.

So far we have only considered molecules rotating in the so-called cartwheel fashion. If the azimuthal quantum *m* equals the rotational quantum number *j*, i.e. $m = j$, then the rotational axis is oriented preferentially perpendicular to the surface, or put differently, the molecular axis is oriented preferentially parallel to the surface. As noted above, only in this orientation the molecules can dissociate on the surface. Furthermore, as the comparison of Fig. 1 and Fig. 2 demonstrates, the energetic cost to rotate a molecule with the rotational axis perpendicular to the surface is much less than for a molecule with the rotational axis parallel to the surface. In other words, the azimuthal anisotropy of the PES is much smaller than the polar anisotropy.

As a consequence, a steric effect should result [19]: molecules rotating in the helicopter fashion with $m = j$ should dissociate more easily than molecules rotating in the cartwheel fashion with $m = 0$. This is confirmed in Fig. 4, in which the sticking probability in the three systems for molecules initially rotating in the helicopter fashion with $m = j$ is plotted. Except at low kinetic energies, for H_2/Rh and H_2/Pd the orientational effect is even so strong that it over-compensates the rotational hindering since the helicoptering molecules show a larger sticking probability than the non-rotating molecules.

For $H_2/Ag(100)$, the steric effect is particularly strong. This is a consequence of the fact that the azimuthal anisotropy in this system is relatively weak, as Fig. 1 shows, so that the hindering of the helicopter rotations is rather weak. One interesting point should be mentioned. In Fig. 4 the width of the sticking curves, i.e. the range over which the sticking probability increases, is almost the same for all rotational states, i.e. it is independent of *j*. Again, exactly such a behavior has been observed for $H_2/Cu(111)$ [27], but low-dimensional studies within a restricted geometry were not able to reproduce this behavior [28]. Actually this disagreement has been quoted as being ‘‘one of the remaining challenges associated with understanding the dynamics of the $H_2/Cu(111)$ system’’ [27]. Of course one has to be

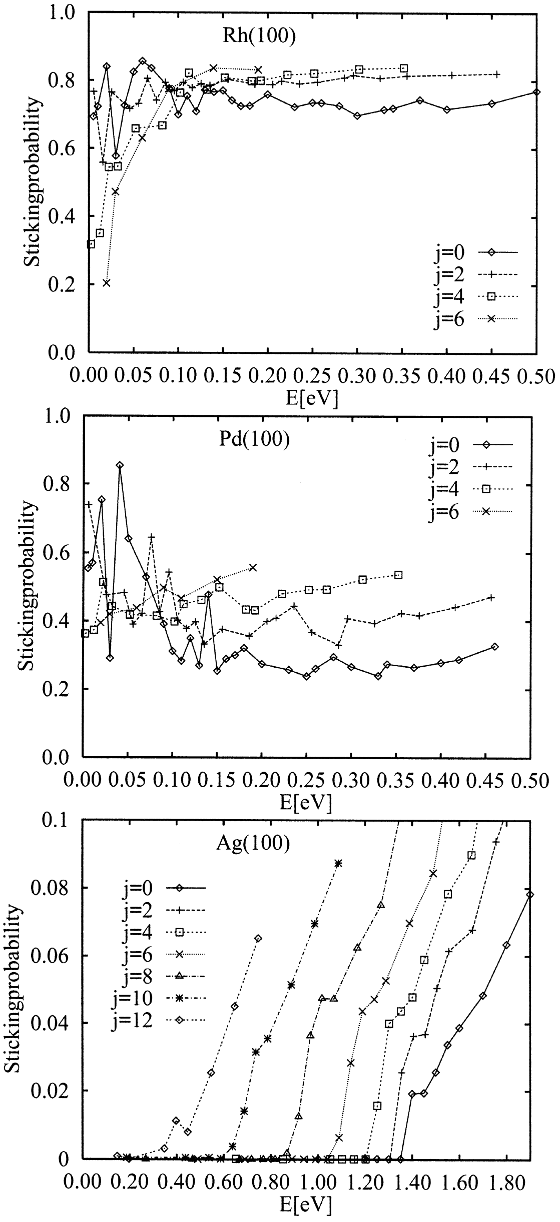

Fig. 4. Calculated sticking probability versus kinetic energy for a H_2 beam under normal incidence on (100) surfaces at various *j* with $m = j$ (helicopter rotation).

cautious to compare results for $H_2/Cu(111)$ and $H_2/Ag(100)$. However, we still believe that this comparison is meaningful due to the similarities of the PES. This result demonstrates that it is often not sufficient to perform low-dimensional studies on model potentials, instead it is necessary to perform high-dimensional dynamical calculations on reliable potential energy surfaces in order to be able to faithfully reproduce experiments.

In order to verify these steric effects in the dissociate adsorption experimentally, one has to align the incoming molecular beam. Since hydrogen has no permanent electric dipole moment, this is hard to achieve. However, one can study the time-reverse process, the associative desorption. By laser-induced fluorescence (LIF) it is possible to measure the rotational alignment parameter $A_0^{(2)}(j)$, which is given by

$$A_0^{(2)}(j) = \left\langle \frac{3J_z^2 - \boldsymbol{J}^2}{\boldsymbol{J}^2} \right\rangle_j . \tag{3}$$

$A_0^{(2)}(j)$ corresponds to the quadrupole moment of the orientational distribution and assumes values of $-1 \leqslant A_0^{(2)}(j) \leqslant 2$. Molecules rotating preferentially in the cartwheel fashion have an alignment parameter $A_0^{(2)}(j) < 0$, for molecules rotating preferentially in the helicopter fashion $A_0^{(2)}(j) > 0$.

In Fig. 5 we have collected our results for the rotational alignment parameter $A_0^{(2)}(j)$ of H_2 desorbing from Pd(100), Rh(100) and Ag(100). Since we have determined the dissociation probability only for molecules with an even azimuthal quantum number m, there is some uncertainty associated with our results for the rotational alignment parameter, however, as Fig. 5 shows, the estimated uncertainty is rather small. The results for $H_2/Pd(100)$ are also compared to recent experimental results [29]. This comparison shows that within the error bars our results agree with experiment, as was already the case for our previous calculations [30].

All three systems show a positive alignment in desorption confirming the steric effects in the dissociation probability. The fact that the alignment for $H_2/Rh(100)$ is rather small is due to the fact that the dissociation probability for molecules rotating in the cartwheel fashion is already rather large due to the high reactivity of this surface so that there is little room for larger steric effects. The system $H_2/Ag(100)$, on the other hand, shows a large rotational alignment in desorption. This is due to the fact that $H_2/Ag(100)$ is a late barrier system where the molecular bond is rather elongated at the minimum barrier position. This fact enhances the rotational and steric effects in dissociative adsorption and associative desorption.

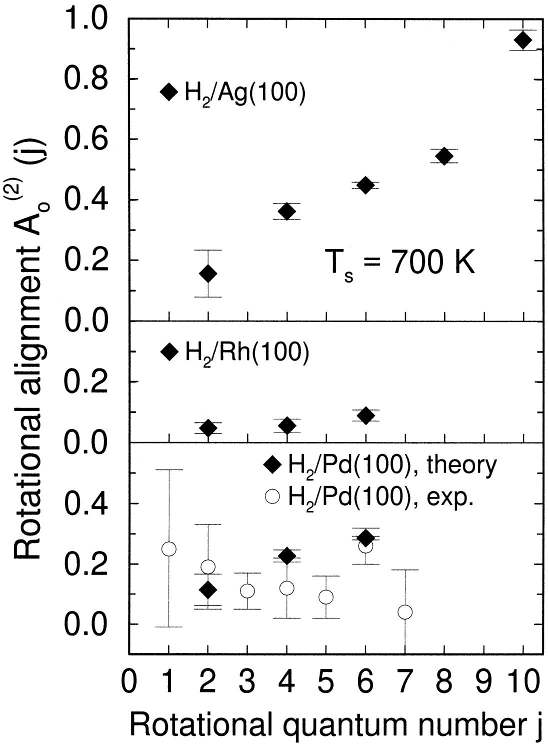

Fig. 5. Rotational alignment parameter $A_0^{(2)}(j)$ for desorbing H_2 molecules at a surface temperature of $T_s = 700$ K. The experimental results for $H_2/Pd(100)$ are taken from Ref. [29]

4. Conclusions

In conclusion, in this Letter we have presented results of the rotational effects in the dissociative adsorption of H_2 on Rh(100), Pd(100) and Ag(100) obtained by ab initio quantum-dynamics calculations. The anisotropy of the potential energy surface leads to a suppression of the sticking probability for rotating molecules. This rotational hindering can be overcompensated by steric effects for H_2 molecules whose rotational axis is perpendicular to the surface. The strong suppression of the sticking probability by rotational hindering at low kinetic energies for the reactive systems H_2/Rh(100) and H_2/Ag(100) is a consequence of the importance of steering. For the activated late-barrier system H_2/Ag(100) the rotational hindering is in addition counterbalanced by the energy transfer from the rotational to the translational motion due to the stretching of the molecular bond. The width of the sticking curves for H_2/Ag(100) is almost independent of the rotational state.

Acknowledgements

This work has been supported by the Austrian Science Funds under Project No. P11353. The Berlin–Wien cooperation has been supported by the Human Capital and Mobility Network ‘Electronic Structure’.

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