H Atom Recombination on W(001): a Semiclassical Molecular Dynamics Study

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Abstract. The Eley-Rideal recombination reaction of H chemisorbed on the four-fold site of W(001) at a surface temperature T_S=500K was studied using the fully-dimensioned semiclassical collisional model and an accurate potential energy surface for the H-W(001) system. The recombination probabilities calculated at impact energies in the range (0.05-5)eV, the energy distributions in the final states as well as other relevant collisional data are presented and discussed.

INTRODUCTION

In this contribution we report a preliminary Molecular Dynamics (MD) study on the H_2 formation and desorption after H atoms recombination on W(001) *via* the Eley-Rideal (E-R) mechanism at T_S=500K. According to this mechanism the recombination involves an H atom chemisorbed on a specific surface site, in thermal equilibrium with the tungsten surface, and a gas-phase H atom colliding with the surface at a given impact energy and approaching angles.

$$H_{ad}*W + H_{gas} --> H_2(v,j) + W + \Delta E_{exo} \qquad (1)$$

In this study we assume that H_{ad} is initially chemisorbed on the four-fold (4F) site of W(001).

These recombination collisions can be both an important channel for surface atom abstraction and an effective source of vibrationally and rotationally excited H_2 molecules. In fact, heterogeneous atom recombination plays a key role in the reactivity of various gaseous and plasma systems used in basic research and in the technology of plasma reactors for fusion [1].

The potential energy surface assumed here is that proposed by Forni and al. [2] and used by the same authors in Monte Carlo quasi-classical trajectory calculations to study the dissociative chemisorption of v-selected H_2 molecules on tungsten (001).

The reaction dynamics is modeled using the fully three-dimensional semiclassical collisional model [3,4] that is able to handle the most relevant features of the atom/molecule-surface interaction, including the inelastic molecule-surface energy exchange processes.

THE SEMICLASSICAL COLLISIONAL METHOD

The semiclassical collisonal method has been used in our previous studies on various atom/surface reactive systems, among which are H+H/Cu [5], H+H/graphite(0001) [6], O+O/SiO$_2$[7].

According to this approach [3,4] the translational and internal states of the gas-phase particles are modeled classically, whereas the phonons (and the electron-hole pair, eventually) are considered quantum mechanically. The dynamics of the two sub-systems are coupled *via* the definition of an 'effective' potential, V_{eff}, defined as the expectation value of the interaction potential over the total wave function of the phonon state.

$$V_{eff}(r,R,t,T_S) = \langle \Psi_{ph}(t,T_S)|V_{int}(r,R)|\Psi_{ph}(t,T_S)| \rangle \tag{2}$$

where $\Psi_{ph}(t,T_S)$ is the phonon wave function taken as a statistical distribution of pure phonon states at a given surface temperature and $V_{int}(r,R)$ is the interaction potential between the gas-phase particle and the surface.

The energy exchanged between the gas-phase particles and the surface phonons is given by:

$$\Delta E_{ph} = \sum_k \Delta E_k^{(+)} + \Delta E_k^{(-)} \tag{3}$$

$\Delta E_k^{\pm}$ is the energy transferred to (+) or from (-) the k-th phonon mode due to the excitation/de-excitation processes induced in the substrate.

The molecular dynamics simulation proceeds *via* three main steps: I. A 3D model surface is built up for the unit cell of W(001); II.The potential energy surface (PES) relevant to the H-W system is constructed and inserted in the semiclassical scattering code; III. The collision dynamics is performed and a sufficiently large batch of trajectories is propagated.

I. Lattice Crystal and Phonon Dynamics

We assumed that unreconstructed surface model of W(001) consisted of 255 atoms disposed on six layers according to the symmetry of the W(001) unit cell. This crystal represents the minimum size surface sample that assures a stable, convergent phonon frequency spectrum. The phonon dynamics is determined, as usually, by diagonalizing the dynamical matrix of the force constants between nearest and next-nearest lattice atoms.

The interaction potential is that reported in [8] and it is given as sum of two contributions V_S and V_B, the surface and bulk potential, respectively. The obtained density of the phonon states shows a local peak at nearly 106 cm^{-1} and a maximum around 212 cm^{-1}, close to the tungsten Debye frequency of 214 cm^{-1}.

II. Potential Energy Surface

For this catalytic system various interaction potentials have been proposed in the literature. Thus, a LEPS potential was firstly calculated by McCreery et al. in their pioneering work [9]. Here, the LEPS parameters were taken from EHMO (extended Hückel molecular orbital) calculations for H chemisorbed in the on top (T), bridge (B) and four fold (4F) W(001) surface sites. According to these data the hydrogen atom is preferentially adsorbed on the top lattice site. Later, an improved LEPS potential was proposed by Jackson and Persson for H interacting perpendicularly in the bridge W(001) site [10], while a highly accurate *ab initio* six-dimensional PES was obtained by White et al. [11] within the DFT approximation, according to which H is preferentially bonded in the bridge site.

The interaction potential assumed in our study was that calculated by Forni et al. [2] in the tight binding approximation. This potential was validated by the same authors by comparing the dissociation sticking probabilities of (v,j) state-selected H_2 molecules obtained from classical trajectory calculations with those measured in molecular beam experiments.

According to the potential assumed in our calculations, fitted to the Forni et al. potential, the H atom was chemisorbed on 4F, T and B site with chemisorption energy of 3.03eV, 1.75eV and 1.84eV, respectively, while the bond length were 0.52 Å, 2.0Å and 1.65Å respectively. These values are in good agreement with those given by the reference potential.

Our PES reproduces well the bond energy and length in 4F site [2,12] while when we compare the chemisorption energy for the other sites we find a discrepancy of 5% and 20% respectively on bond energy when compared with values of 1.75eV and 2.43eV, reported in [2] for T e B site, respectively.

II. Trajectory Propagation

The rate determining step of the E-R recombination mechanism (Eq. (1)) was simulated.

The adsorbed H atom is placed on 4F site in thermal equilibrium with the surface at a distance of 0.52Å. The gas-phase H atom is initially placed at a distance of 7.0Å from the surface, far into the asymptotic region. The planar coordinates of gas-phase atom are chosen randomly in an aiming area of 10.02 Å^2 which corresponds to the W unit cell area. The incident angles (θ, φ) of H_{gas} are fixed to $(0,0)$, while the kinetic energy is varied in the interval 0.05eV-5eV. For each kinematics condition we propagate 500 trajectories that assure a numerical convergence of the calculated data of about 10%.

In our analysis, a collision is considered reactive, thus leading to H_2 formation, if the H-H interatomic distance is less than 2.5Å and the centre of mass distance sufficiently large to consider H_2 as a free molecule.

Moreover two different criterions have been assumed for the adsorption processes. A collisional event is considered as having led to adsorption if: i) the z-component of the momentum of the H atoms is negative and the H z-distance from the surface is close to the chemisorption length; ii) the available energy to the H atom to escape from the chemisorption potential well, ΔE_{esc}, is less than the effective potential, ΔV_{eff}, experienced by the hydrogen at the specific interaction time. ΔE_{esc} is defined as: $E_{tot}-\Delta E_{ph}-V_0$, where V_0 is the zero point energy of the chemisorbed H atom.

RESULTS AND DISCUSSION

The recombination probability for hydrogen atom recombination as a function of the kinetic energy of H_{gas} is reported in Figure 1. From the Figure 1 we notice that the semiclassical recombination probability exhibits an energy threshold to recombination close to 0.05eV and a broad maximum around 1.5 eV. At the higher impact energies, $E_{kin}>2.5$eV, the probability smoothly declines with the impact energy increasing. At $E_{kin} =5$eV, the recombination probability is close to 0.045.

The trajectory analysis shows that the interaction dynamics very much depends on the impact energy. In fact, the decrease of the recombination probability at higher kinetic energies is an indication of the opening of other surface processes. The results are shown in Table (1) where the probability for each surface process energetically open to the dynamics is reported as a function of the kinetic energy of H_{gas}.

The reported results show that two collisional regimes can be identified: a) $E_{kin}<2.5$eV and b) $E_{kin}>2.5$eV. For impact energies below 2.5eV the recombination process dominates, although at the two lowest energies close to the energy threshold the most effective process is $H_{ad} +H_{gas} \longrightarrow H_{ad} + H_{ad}$.

In the higher collisional regime, $E_{kin}>2.5$eV, the inelastic scattering, $H_{ad} +H_{gas} \longrightarrow H_{ad} + H_{gas}$, controls the full hydrogen-surface interaction dynamics.
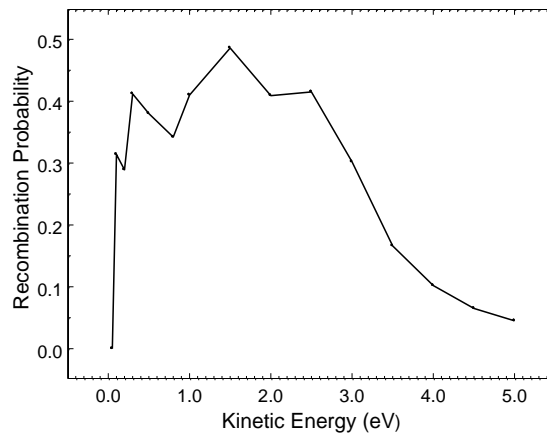

FIGURE 1. E-R semiclassical recombination probability (see Equ. (1)) as a function of collisional energy. $T_S=500K$

TABLE (1). Probability for the different surface processes in the reaction: $H_{ad} + H_{gas} \longrightarrow$ "products" at different kinetic energies E_{kin} of the gas-phase H atom.

$H_{ad} + H_{gas} \rightarrow$ / $E_{kin}(eV)$	$H_{ad}+H_g$	H_g+H_{ad}	$H_{ad}+H_{ad}$	$(H_2)_{ad}$	H_g+H_g	$H_2(v,j)$
0.05	1	0	0	0	0	0
0.1	0.150	0.004	0.484	0.035	0.011	0.314
0.2	0.236	0.012	0.441	0.016	0.005	0.289
0.3	0.223	0.007	0.341	0.011	0.004	0.412
0.5	0.325	0.025	0.26	0.007	0.002	0.380
0.8	0.346	0.020	0.265	0.020	0.007	0.342
1.0	0.342	0.018	0.218	0.007	0.005	0.410
1.5	0.360	0.025	0.122	0.002	0.005	0.486
2.0	0.411	0.057	0.113	0	0.009	0.409
2.5	0.410	0.051	0.091	0	0.031	0.415
3.0	0.506	0.054	0.124	0	0.013	0.302
3.5	0.651	0.055	0.098	0	0.023	0.166
4.0	0.663	0.063	0.121	0	0.050	0.102
4.5	0.725	0.055	0.120	0	0.035	0.065
5.0	0.763	0.050	0.071	0	0.071	0.045

The trajectory analysis reveals that, in the energy range explored in the simulation, the recombination occurs mainly *via* a "direct" mechanism and that, very often, H_2 is formed very close to the tungsten surface at a distance of about 1.5 Å.

The reaction energy partitioning between the degrees of freedom of the formed H_2 molecules is shown in Figure 2. One can note that the energy delivered in the recombination reaction is transferred mainly into the translational motion of the desorbing H_2 molecules which are, therefore, accelerated. The coupling between the translational and rotational motion appears to be dominant at the low/medium energies, whereas a stronger translation-to-vibration coupling seems the most effective one in the higher energy range. We also observe a small, almost negligible energy flux toward the W surface, due to the large frequency mismatch between the typical Debye frequency of the substrate and the interatomic H-W frequency.
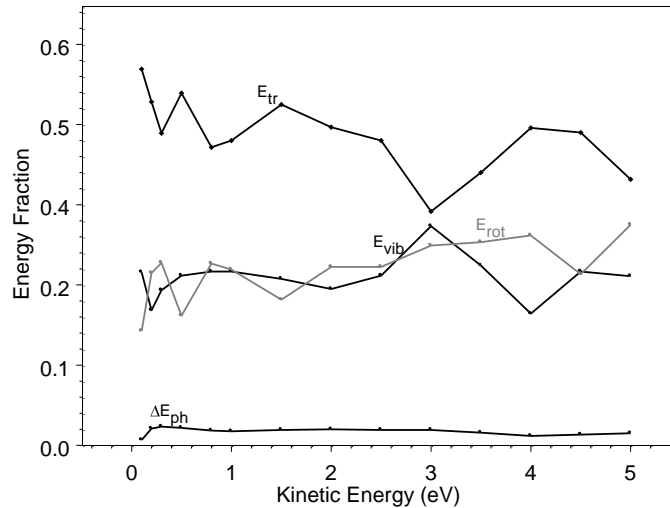

FIGURE 2. Average energy fraction transferred to the vibrational (E_{vib}), rotational (E_{rot}), translational (E_{tr}) mode of the H_2 molecules formed in the E-R recombination reaction as a function of the impact kinetic energy. The average energy transferred to the surface phonons (ΔE_{ph}) is also reported.

The vibrational distributions of the desorbing H_2 molecules show that, at low impact energies, the first two excited vibrational levels are energetically accessible to the recombination dynamics, the largest part of the exothermic energy being stored into the v=0 state. At higher E_{kin} the population of the three low-lying vibrational levels is depressed while the vibrationally excited levels up to v=7 are slightly populated. Consequently, the maximum of the distributions is shifted from v=0 to v=1 with the kinetic energy increasing.

In Figure 3 the roto-vibrational distribution for E_{kin}=0.5eV is reported. From Figure 3 we can infer that at lower vibrational levels the rotational distributions are more extended toward higher rotational quantum numbers.
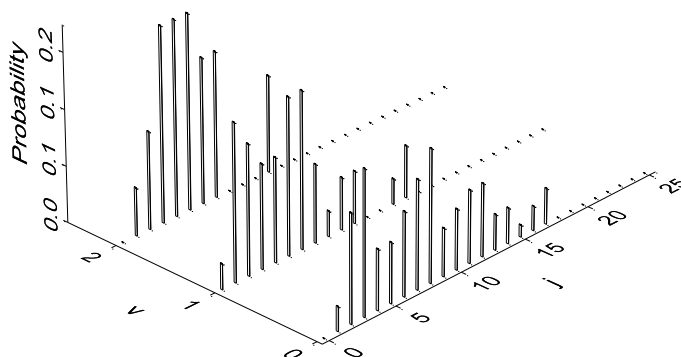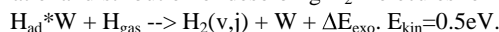

FIGURE 3. Roto-vibrational distribution of desorbing H_2 molecules formed in the E-R process: $H_{ad}*W + H_{gas} \rightarrow H_2(v,j) + W + \Delta E_{exo}$. E_{kin}=0.5eV.

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