Simulation of adsorbed hydrogen on tungsten surface

N N Degtyarenko* and A A Pisarev**

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe sh., 115409 Moscow, Russia

E-mail: *NNDegtyarenko@mephi.ru, **Pisarev@plasma.mephi.ru

Abstract. Calculations of the energy of the H-W system were performed using DFT method based on plane waves. Adsorption energies, equilibrium states, vibration spectra, saddle points, activation energies of jumps, and diffusion paths have been analyzed for H atom on W(100) and W(110). Diffusion coefficient for H on W(110) agrees very well with experimental data.

1. Introduction

Hydrogen adsorption on W was intensively studied both experimentally and theoretically [1-16]. Density functional theory (DFT) was previously used to calculate characteristic energies of H atom on the surface and analyze possible paths and activation energies for H diffusion on a reconstructed surface [10,11]. In this work, both energies and oscillation spectra were calculated for W(100) and W(110) surfaces. It was taken into account that the height of barriers for transitions along the surface are about the same as the energies of zero vibrations. Stability of hydrogen in some positions with minimal energies was also analyzed. Finally, paths of elementary jumps and the diffusion coefficients were obtained in the limit of non-reconstructed surface.

2. Features of calculations

Calculations were performed using DFT–RPBE–PW method. Usually, hydrogen atom is considered as a quantum oscillator vibrating in all directions in a deep potential well with infinite number of states. However, the well is high (1–2 eV) for vibrations perpendicular to the surface, but very shallow (fractions of eV) along the surface. In the latter case any state besides the zero one is over the well. Therefore, we take into account the whole range of oscillations perpendicular to the surface and only the zero oscillations along the surface. This feature was taken into account in calculations of the energy of the system both in equilibrium and saddle sites. Not only the energy, but also oscillation modes characterize these sites as well as possible paths of transitions of H-atom. The oscillation frequencies can be both real and imaginary. Imaginary frequency of oscillations in a direction indicates instability of the system in this direction. This allows selecting stable sites for H-atom and directions of possible jumps between equilibrium sites. Following this consideration, the diffusion coefficient was calculated as
where $\lambda_i$ is the jump length; $n_i$ is the number of nearest sites to jump; $\varepsilon_i$ is the barrier in the adiabatic approximation; $\nu_{g}$, $\nu_{s}$, $\nu_{g^*}$, $\nu_{s^*}$ – frequencies of normal vibrations of H in the equilibrium site and in the saddle point, respectively; $\nu_{g,e}$ and $\nu_{s,e}$ – frequencies of lateral oscillations of H in the equilibrium and saddle points; $\langle \nu_{g,e} \rangle$ – the frequency of lateral ground state oscillations of H corresponding to the direction of the jump over the barrier. Normally, this vibration has the smallest frequency in the ground state and disappears in the saddle site.

3. Adsorption sites and jumps

Two optimized configurations of H atoms on W(100) are shown in Figures 1a,b: site $s_1$ (twofold bridge) and site $s_2$ (fourfold position). Adsorption energies were calculated as the difference between the total energy of the optimized system “W atoms plus an adsorbed H atom” and that for the system “W atoms plus a free H atom far from the surface”. The heats of adsorption (the difference between the adsorption energy and the energy of one atom in H$_2$ molecule in gas phase (a half of the H$_2$ binding energy $1/2\varepsilon_{\text{bond}} \approx 2.3$ eV) for sites $s_1$ and $s_2$ on W(100) were equal to -2.21 and -1.91 eV, respectively.

![Figure 1. Hydrogen atom on W(100): a, b) – Optimized configuration in sites $s_1$ and $s_2$ (top view). Colors correspond to the electron density in electron/Å$^3$ in the plane of W surface atoms. c) – possible jumps of H atoms between sites $s_1$ from position 1 to positions 2, 3, and 4 through saddle points colored in red.](image)

Sites $s_1$ and $s_2$ differ principally with respect to vibration spectra. H atom in site $s_1$ on the bridge has two real lateral oscillation modes ($h\nu_{2,3} = 50, 130$ meV) and one mode perpendicular to the surface ($h\nu_1 = 160$ meV). Site $s_1$ is dynamically stable, and H atom after small deviation from this site returns back to the original position. Contrary, site $s_2$ is unstable. H atom there has a real frequency only perpendicular to the surface ($h\nu_1 = 80$ meV), while frequencies in lateral directions are imaginary ($h\nu_{2,3} = i40$ meV). Besides, site $s_2$ is surrounded by four sites $s_1$, which are energetically preferential. There are three kinds of jumps between sites $s_1$ on W(100) (Figure 1c): 1) curvilinear transition 1→2 to a perpendicular bridge through the threefold site, 2) jump 1→3 along the bridge over W atom, and 3) transition 1→4 to the opposite bridge through the fourfold site. The adiabatic barriers for these transitions are 0.22, 0.87, and 0.65 eV, respectively. The saddle points of transition 1→2 are of a
simple type (one imaginary frequency – 175 meV, and two real frequencies 40 and 190 meV, while those for transitions 1→3 and 1→4 have two imaginary frequencies).

Four positions for H atom on W(110) are shown in Figure 2a: two normal bridge sites (long bridge s1 and short bridge s4), as well as one diagonal bridge s2 and a threefold site s3. The adsorption heats of sites s1, s2, s3, and s4 on W(110) are -1.40, -1.55, -1.59 eV, and -1.45 eV, respectively. Phonon spectra for s1 (i94, 137, 143 meV) and s4 (i98, 139, 150 meV) are similar and have one imaginary frequency. Contrary, all frequencies of sites s2 (30, 145, 170 meV) and s3 (90, 105, 162 meV) are real. That is, sites s2 and s3 are more stable from the point of view of both energy and vibration spectra. Possible transitions through sites s2 and s3 are shown in Figure 2b. Parameters of transitions between various positions are given in Table. Most barriers are of a simple saddle type (one imaginary frequency), and only saddle point for jump 2→3 over a W atom is of the second order (two imaginary frequencies).

![Figure 2](image)

**Figure 2.** a) Four sites for adsorption of hydrogen on W (110). Different colors correspond to different electron densities in electron/Å$^3$ calculated in the plane of W surface atoms; b) – possible jumps of H atoms between sites s2 (positions 1,2,3) and s3 (positions 4,5,6).

| Types of sites | Path | Adiabatic barrier, $\varepsilon_{ad}$, eV | Jump length, $\lambda$, Å | Number of neighbour sites | Oscillation frequencies at saddle points $h\nu^*$, meV |
|----------------|------|---------------------------------|-----------------|-----------------|-----------------|
| s2→s2         | 1→2  | 0.20                            | 1.56            | 2               | i 70, 137, 140  |
| s2→s2         | 1→3  | 0.58                            | 2.23            | 2               | i 90, 139, 142  |
| s2→s2         | 2→3  | 0.72                            | 3.13            | 2               | i 90, i 90, 145 |
| s2→s3         | 3→4  | 0.02-0.05                       | 1.0             | 2               | i 80, 138, 140  |
| s3→s3         | 4→5  | 0.16                            | 1.42            | 2               | i 80, 138, 140  |
| s3→s3         | 5→6  | 0.20                            | 1.48            | 1               | i 82, 139, 142  |

4. Surface diffusion

Of the three jumps considered for W(100), the diagonal jumps 1→2 between bridge sites s1 are responsible for H diffusion from the point of view both of energy and vibration spectra. Adiabatic activation energy for W diffusion from W(100) is $\varepsilon_{ad}=0.22$ eV. Diffusion on W(110) is possible through various paths between sites s2 and s3. Jumps between two s2 sites (path 1→2) have the activation energy of 0.20 eV. Jumps between s3 sites are sequence of two jumps (path 4→5→6); with activation energies of 0.16 eV for 4→5 and 0.2 eV for 5→6. The latter value can be considered as a diffusion barrier through s3 sites. Interesting that the activation energies for diffusion through s2 and s3 sites on W(110) are the same.

Figure 3 shows the diffusion coefficient $D(T)$ calculated according to (1) using barriers and frequencies obtained. Paths with higher barriers give small contribution. Also, two experimental points for W(110) from [3] are also shown. One can see a good agreement between the calculations and the
experiment for W(110). Note that the slope of the curve for W(100) (1b) is smaller than that for W(110) (1a), while the adiabatic barriers $\varepsilon_{ad}$ on these surfaces are equal to 0.22 and 0.20 eV, respectively. This is due to the temperature dependence of the frequency factor (1) for these surfaces. Indeed, the difference between half the sum of energies of zero-point oscillations with real frequencies for the ground states and saddle points (energies ZPE) is $\Delta \varepsilon_{ZPE} = 1/2[(h\nu_{x,z} + h\nu_{y,z} + h\nu_{t}) - (h\nu_{x,z}^* + h\nu_{y,z}^* + h\nu_{t}^*)]$ and gives $\Delta \varepsilon_{ZPE} = 0.064$ and 0.034 eV for the diffusion jumps on surfaces (100) and (110), respectively. Thus the values of effective barriers become 0.156 and 0.166 eV for W(100) and W(110), respectively.

One must mention that our activation energies 0.22(0.156) eV for W(100) agree well with the energies obtained in other DFT calculations 0.17(0.11) eV [10], 0.21 eV [9] but differ from the experimental values 0.47 eV [13]. Two numbers mean adiabatic barrier and barriers with ZPE taken into account. For W(110) our activation energies 0.20 (0.166) eV agree well with the experimental values 0.22 [14], while calculated values 0.31 eV [8] differ from both. One must mention that calculations [8-10] were performed for the reconstructed surface, while our calculations were performed for non-reconstructed surface and low concentration of hydrogen. Also there was a difference in the number of states taken into account in the potential well.

5. Conclusions
Hydrogen adsorbed on W(100) and W(110) planes was analyzed by DFT methods for the case of non-reconstructed surface at the low H concentration. Calculations of the energy of the H-W system and oscillation spectra demonstrate that stable configuration of H atom on the W(100) plane is the short bridge, while the plane W(110) has two stable configurations: the diagonal bridge and threefold site with approximately similar energies and oscillation frequencies. Only these sites have only real frequencies of oscillations, while other sites have either one or two imaginary lateral frequencies, though they are associated with potential deeps. The heats of adsorption are $-1.9$ eV for W(100) and $-(1.5\pm1.6)$ eV for W(110). The number of H sites per W atom is 1:1 for W(100) and >2:1 for W(110). The minimal adiabatic barrier between neighbor equilibrium sites are $=0.22$ eV for W(100) surface and $=0.20$ eV for W(110). Vibrations of hydrogen atoms reduce the effective barrier to the value $=0.156$ and 0.166 eV, respectively. Diffusion coefficients were estimated using activation energies and frequencies obtained, and the values calculated for W(110) are in a good agreement with experimental data. For W(100) a good agreement with other DFT calculations was obtained though the later were performed for the reconstructed surface.

6. Acknowledgements
The work was supported by Grant № 14.Y26.31.0008 from the Ministry of Education and Science of the Russian Federation and by National Research Nuclear University MEPhI in the framework of the Russian Academic Excellence Project (contract No. 02.a03.21.0005, 27.08.2013).
References

[1] Grimleyt T B, Torrini M 1973 *J. Phys. C Solid State Phys.* **6** 868
[2] Zhdanov V I, Zamaraev K I 1986 *Physics-Uspekhi* (rus) **149** (4) 635
[3] Auerbach A, Freed K F and Gomer R 1987 *J. Chem. Phys.* **6** 2356
[4] Balden M, Lehwald S, Ibach H 1994 *Physical Review Letters* **73** (6) 854
[5] Meyerherm H L et al. 2001 *Surface Science* **475** 103
[6] Ammi D et al. 2004 *Surface Science* **554** 60
[7] Henriksson K O E et al. 2006 *Surface Science* **600** 3167
[8] Nojima A, Yamashita K 2007 *Surface Science* **601** 3003
[9] Heinola K, Ahlgren T 2010 *J. Appl. Phys.* **107** 113531
[10] Johnson D F, Carter E A 2010 *J. Mater. Res.* **25** (2) 315
[11] Lu G-H, Zhou H-B, Becquart C S 2014 *Nucl. Fusion* **54** 086001
[12] Kolasinski R D et al. 2015 *Journal of Nuclear Materials* **463** 1053
[13] Cai L et al. 2002 *Phys. Rev. Lett.* **88** 226105
[14] DiFoggio R and Gomer R 1982 *Phys. Rev. B* **25** 3490
[15] Degtyarenko N, Pisarev A 2015 *Physics Procedia* **71** 30
[16] Degtyarenko N, Pisarev A 2016 *Journal of Physics: Conference Series* **748** 012010