Dynamic Properties of the Sulfur Contaminated Fe(110) Surface

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Introduction

Surface reactions can be beneficial as in the case of catalysis and film growth, but also detrimental, causing corrosion or embrittlement of a substrate. Recent advances in *ab initio* molecular dynamics (MD) enable such reactions to be examined in a "real time" regime. Such theoretical treatment allows one to systematically control the substrate and reagent composition, temperature and pressure thus providing a fundamental understanding of the effects of the reaction conditions on the resultant surface structure and properties.

Sulfur is one of the most common impurities found in Fe and has been shown to produce undesirable attributes in the metal, affecting its adhesion, friction, and wear behaviour. We have previously examined the properties of sulfur contaminated Fe surfaces [1,2] at different coverages and in different adsorption sites, using density functional theory at 0K. At ¼ monolayer coverage, S adsorbs in a p(2x2) arrangement in 4-fold hollow sites ([2] and references therein). The bridge site is less stable than the 4-fold hollow site with the atop site being least stable. To the best of our knowledge, the reaction of S on the Fe(110) surface at temperatures above 0K has not been examined computationally. In addition, it has not been determined whether the different adsorption sites are true minima on the potential energy surface. Calculation of the vibrational frequencies can be used to ascertain such information and in the case of transition states or saddle points, the displacements associated with the imaginary frequencies can indicate the direction the adsorbate will move on the surface towards a minimum. Also, the frequencies can be compared directly to experimental values, such as obtained from Vibrational Electron Energy Loss Spectroscopy (also known as High Resolution Electron Energy Loss Spectroscopy), although we are unaware of such experiments on this system.

This study determines the vibrational frequencies of the S contaminated Fe(110) surface with sulfur adsorbed in atop, bridge and 4-fold hollow sites in a p(2x2) arrangement (corresponding to ¼ monolayer coverage). Ab initio molecular dynamics simulations are performed at 4 different temperatures, starting with the S adsorbed in the atop site in order to monitor its mobility on the surface and the effect of heating, up to the melting point of Fe.

Method

Our calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [3-5], using ultrasoft pseudopotentials of Vanderbilt [6]. The generalized gradient spin approximation (GGSA), using the functional of Perdew and Wang (PW91) [7] was employed, with a plane wave basis set with energy cut-off of 308.76 eV. A Monkhorst and Pack [8] k-point mesh of 6x6x1 was used.

The Fe surface models have been described previously [2]. Surfaces were cleaved from a crystal structure of (bcc) Fe (with a calculated lattice constant of 2.855 Å [2]), corresponding to the (110) Miller plane and comprised five Fe layers and a [2x2] cell with one S atom on one side of the slab, corresponding to a p(2x2) arrangement. The surface is produced by replication of the central supercell in the x-, y-directions, and a vacuum spacer of 12Å was inserted in the z-direction to prevent interactions occurring between mirror images. Three adsorption sites were modelled, including atop, bridge and 4-fold hollow sites (see Figure 1).
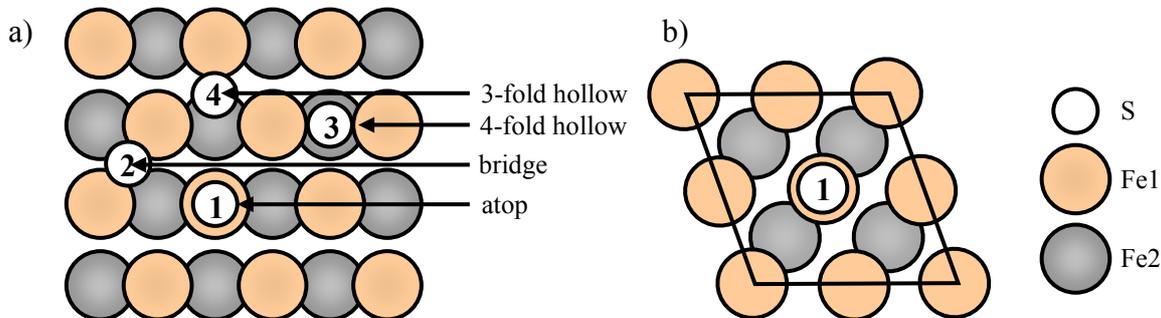

Figure 1: a) Fe(110) surface showing high symmetry adsorption sites; b) top view of supercell used to model S adsorbed on Fe(110) in a p(2x2) arrangement.

Vibrational frequencies of the adsorbed S were calculated on the geometry optimised S/Fe(110) surfaces [2]. The molecular dynamics calculations were performed starting from the atop S/Fe(110) model at 298, 500, 800 and 1808 K, using a timestep of 2fs. The highest temperature corresponds to the melting point of Fe. A Verlet algorithm is used to integrate the equations of motion, with the temperature being controlled by the algorithm of Nose. The bottom two Fe layers were fixed while the rest of the layers, as well as the S atom, were allowed to relax. We found that a 4ps MD simulation was sufficient to see the transition of the S from the atop site (previously determined as the least stable [2]) towards the lowest energy hollow state [2].

Results and Discussion

Vibrational Frequencies
The calculated vibrational frequencies for sulfur adsorbed on Fe(110) in atop, bridge and 4-fold hollow adsorption sites are presented in Table 1.

Table 1: Calculated vibrational frequencies for S/Fe(110) in the sites indicated. (* indicates an imaginary frequency). The calculated S-Fe perpendicular distances (Å) [2] are also shown.

	atop	**bridge**	**4-fold hollow**
ν_z **(cm^{-1})**	381.27	343.70	303.49
ν_y **(cm^{-1})**	111.22*	237.25	254.90
ν_x **(cm^{-1})**	122.36*	102.04*	119.55
d$\perp$(S-Fe) (Å)	1.78	1.60	1.49

They indicate that the 4-fold hollow adsorption site is the only true minimum as no imaginary frequencies are present. The bridge adsorption site contains one imaginary frequency, indicating it is a transition state. The atop site has two imaginary frequencies, hence it is a second order saddle point. The displacements indicated by the imaginary frequencies of the S

atom in the atop site suggest that the S will displace towards the transition state or bridge site. The bridge site was previously determined to be 0.5eV higher in energy than the 4-fold hollow site and 0.8eV lower than the atop site [2].

The calculated stretching frequency, ν_z, for each site is found to increase from the 4-fold hollow site to the bridge and then atop sites, in line with the height of the adsorbed S atom above the surface. Previously [2], we showed that the S atom is 1-fold bonded to the Fe atom directly below it in the atop site, whereas it is 2-fold bonded to the two closest top layer Fe atoms in the 4-fold hollow and bridge sites. In the 4-fold hollow site, these atoms are located further apart than in the bridge site, hence the S sits closer to the surface. Therefore, as expected, the stretching vibrational frequency increases as the S sits further from the surface and the coordination number decreases.

Molecular Dynamics
The trajectories of the S atom during the MD calculations at different temperatures are presented in Figure 2.

a) 298K   b) 500K
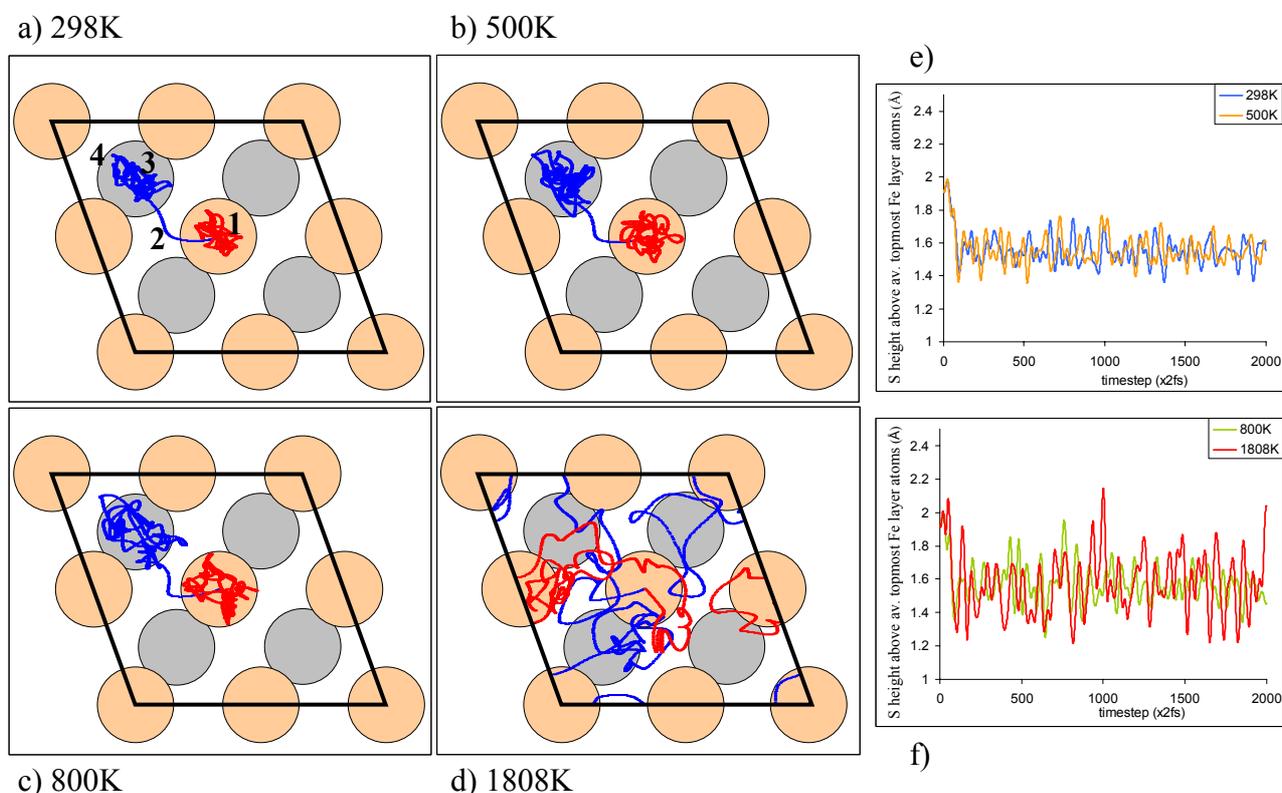
c) 800K   d) 1808K

Figure 2: Trajectories of the sulfur atom (blue) and central surface Fe layer atom (red) during the MD calculations at the temperatures indicated. Different surface states are labelled in a) only; e), f) height of S above the average position of the top Fe layer as a function of time.

At 298K, as suggested by the vibrational frequency analysis, the S atom moves from the atop site (point 1- as labelled in Figure 2), towards the bridge site (point 2), before moving to the 4-fold hollow site (point 3). The 500K and 800K trajectories show the same trend but the S atom is noticeably more mobile at the higher temperatures. In particular, it can be seen that the S moves into the 3-fold hollow site (point 4) at 500K and 800K during the simulation, before moving back to the 4-fold hollow site again. The height of the S atom above the surface (Figure 2 e, f) at these temperatures varies as expected during the simulation, starting at ~1.9 Å in the atop site and decreasing as it moves towards the bridge site, where it sits

closer to the surface (compare with values in Table 1). In the 4-fold hollow site the height of S above the surface is again smaller and is found to oscillate in amplitude as it moves across the surface during the simulation. As the temperature increases to 800K, the height of S above the surface oscillates more than at the lower temperatures. It does not move above the surface, however, by more than ~2Å, suggesting it is still bonded to the surface. Such surface mobility indicates that the barriers between the different sites on the surface are low enough for S surface diffusion to occur at these temperatures. However, additional energy needs to be supplied for S to desorb from the surface. It is also clear that at all temperatures examined the 4-fold hollow site is populated more than the other sites.

The trajectories of the surface Fe atoms were also plotted (Figure 2- red). At 298K, the Fe atoms vibrate around their crystal lattice positions, showing slightly larger displacements as the temperature is increased. However, the position of the Fe atom is still relatively unchanged at 800K, as this temperature is still well below the melting point of 1808K for Fe.

At 1808K, the S and Fe atom trajectories are significantly different, as expected. The mobility of both the S and Fe atoms have increased drastically compared to the lower temperatures and the melting of the surface is obvious. Also the oscillation of the S atom with respect to the surface is greater than at the lower temperatures, with the S moving both further away from as well as closer to the surface during the simulation. The S-Fe distances are again, however, not large enough to indicate that the S desorbs from the surface. In addition, even though the S atom approaches the surface very closely (1.2 Å) during the simulation, it does not appear to diffuse into the bulk within our simulation timeframe.

Conclusion

The vibrational frequencies of S adsorbed on Fe(110) in atop, bridge and 4-fold hollow sites at ¼ monolayer coverage and p(2x2) arrangement, have been calculated and show that only the 4-fold hollow site is a true minimum, with the bridge site being a transition state and the atop site a 2nd order saddle point.

Ab initio molecular dynamics calculations performed at 298, 500 and 800 K show that the adsorbed S moves from the high energy atop site to the true minimum via the transition state, as suggested by the frequency analysis. At 1808K, the MD confirms the surface melting but shows that the S does not desorb, nor diffuse into the bulk within the simulation timeframe.

Further work will examine the mobility of the adsorbed S at different coverages on single crystal Fe surfaces. The adsorption of H_2S will also be investigated in order to examine the dissociative adsorption mechanism at different temperatures. Longer MD simulations will be performed to enable further insights into the surface melting and S-Fe dissolution processes.

References

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