Hydrogenation of S to H 2 S on Pt(111): A first-principles study

A. Michaelides and P. Hu

Articles you may be interested in

A first-principles study of NO adsorption and oxidation on Au(111) surface
J. Chem. Phys. **129**, 134708 (2008); 10.1063/1.2985668

N 2 O and NO 2 formation on Pt(111): A density functional theory study
J. Chem. Phys. **117**, 2902 (2002); 10.1063/1.1490338

Density-functional theory studies of acetone and propanal hydrogenation on Pt(111)
J. Chem. Phys. **116**, 8973 (2002); 10.1063/1.1471247

The chemisorption and dissociation of ethylene on Pt{111} from first principles
J. Chem. Phys. **110**, 4699 (1999); 10.1063/1.478356

Reaction of S 2 and H 2 S with Sn/Pt(111) surface alloys: Effects of metal–metal bonding on reactivity towards sulfur
J. Chem. Phys. **109**, 4052 (1998); 10.1063/1.477005

Hydrogenation of S to H$_2$S on Pt(111): A first-principles study

A. Michaelides[a)] and P. Hu[b)]

School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, United Kingdom

Density-functional theory has been used to investigate the chemisorption of S, SH, and H$_2$S as well as the coadsorption of S and H and SH and H on Pt(111). In addition reaction pathways and energy profiles for the conversion of adsorbed S and H into gas-phase H$_2$S have been determined. It has been found that S, SH, and H$_2$S bind preferentially at face-centered-cubic (fcc), bridge, and top sites, respectively. Both the S+H and SH+H reactions have high barriers ($\sim$1 eV) and high exothermicities ($\sim$1 eV). This reveals that adsorbed H$_2$S and SH are highly unstable adsorbates on Pt(111) and that adsorbed S (and H) is the most stable SH$_X$ ($X=0,1,2$) intermediate on Pt(111) © *2001 American Institute of Physics.* [DOI: 10.1063/1.1410390]

I. INTRODUCTION

Sulfur containing molecules commonly impurify oil-derived feed-streams and fuels, and even small levels of S impurities can drastically reduce the catalytic efficiency of transition metal surfaces.[1–4] As a consequence S and S containing molecules have been intensively investigated in recent years.[3–19] From a surface science point of view this work has focused on the interaction of S and S containing molecules with the low-index planes of transition metal surfaces. Sulfur–platinum systems have received particular attention, mainly because of the importance of Pt in hydrogenation–dehydrogenation and oxidation processes.[1] Theoretical work in this area has focused on the interaction of adsorbed S with coadsorbates (for example, the effect of S on CO adsorption has been extensively investigated) and little is known about the reaction of S moieties themselves.[11–19] Understanding these elementary reaction steps is important, however, as a number of industrial processes (for example, those mentioned above) depend upon them. Here we examine for the first time with density-functional theory (DFT) the hydrogenation reactions to sulfur and sulfhydryl (SH) on Pt. We have chosen to examine these reactions on the (111) surface of Pt since this is the most stable Pt surface and the one that dominates in small particles used in catalysts. Our calculations are performed on idealized Pt(111) terraces, and at this stage we do not attempt to examine the adsorption or reaction of S moieties at steps or kinks on the substrate. Specifically, microscopic reaction pathways and energy profiles for the conversion of adsorbed S and H into gas-phase H$_2$S have been determined. In addition, the adsorption of S, SH, and H$_2$S as well as the coadsorption of S+H and SH+H has been examined.

Our recent investigation of catalytic reaction pathways provides further motivation for the study of S hydrogenation reactions. Recently on Pt(111) we performed a systematic study of nine different hydrogenation reaction pathways.[20] A relationship between the location of the transition state in each reaction and the valency of the reactants involved was identified. As the valency of a reactant decreases, so too does the coordination number of the site at which the transition state is located: Monovalent adsorbates (for example, CH$_3$, NH$_2$, and OH) tend to make transition states close to top sites; divalent adsorbates (CH$_2$, NH, and O) near bridge sites; and tri and tetra-valent adsorbates (CH, N, and C) near three-fold hollow sites. It is not clear, however, how far this framework may extend. Indeed, subsequent studies revealed that this relationship is by no means rigorously followed for all reactants.[21] Here we will investigate if this framework extends beyond reactions of first row adsorbates to the reaction of S and SH.

Some details of our first-principle total energy calculations are presented below. Following this we discuss the adsorption of H, S, SH, and H$_2$S on Pt(111). We then present reaction pathways for the hydrogenation of S and SH on Pt(111). In Sec. IV we discuss our findings and place them in the wider context. Our conclusions are drawn in the final section.

II. CALCULATION DETAILS

First-principle total energy calculations within the DFT framework were performed.[22] Ultrasoft pseudopotentials[23] were expanded within a plane wave basis set up to a cut-off energy of 300 eV. Electron exchange and correlation effects were described by the generalized gradient approximation of Perdew and Wang.[24] A Fermi smearing of 0.1 eV was utilized and the corrected energy extrapolated to zero Kelvin. The Pt(111) surface was modeled by a periodic array of slabs. Each slab consisted of three layers of metal atoms fixed at bulk-truncated positions in a $p(2\times2)$ unit cell. A $p(2\times2)$ unit cell was selected because S forms an ordered and well characterized (2×2) overlayer on Pt(111).[5,10] The vacuum region between adjacent slabs was in excess of 12 Å. A calculated Pt lattice constant of 3.9711 Å (expt. 3.9239 Å) and a Monkhorst–Pack mesh[25] with $4\times4\times1$ **k**-point sampling within the surface Brillouin zone were used through-

[a)]Current Address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

[b)]Author to whom correspondence should be addressed. Electronic mail: p.hu@qub.ac.uk

out. Previous studies[26,27] and extensive testing calculations[21] have shown that this model provides a satisfactory description of the adsorbate–substrate interface. In particular testing calculations were conducted for the S+H reaction on a Pt(111) surface in which the top layer of Pt atoms was allowed to relax. The barrier between this and the chosen model differed by <0.1 eV and the surface degrees of freedom were found to play only a minor role.

Reaction pathways and transition states were searched with a constrained minimization technique.[28–31] Our approach was to fix the distance between the two reactants and minimize the total energy with respect to all remaining degrees of freedom. Through a series of such constrained structure optimizations, with a different reactant separation in each case we determine an energy profile for the reaction. Since the only constraint is the distance between the reactants, the reactants are free to rotate and translate subject to the above constraint. The transition state is identified when (i) the forces on the atoms vanish and (ii) the energy is a maximum along the reaction coordinate but a minimum with respect to all remaining degrees of freedom.

III. RESULTS

A. Chemisorption

Let us consider the chemisorption on Pt(111) of the pertinent atomic and molecular fragments involved before looking at each hydrogenation reaction in turn. Chemisorption energies (E_{ads}) are calculated from

$$E_{ads} = E_A + E_{Pt} - E_{A/Pt},$$

where E_A, E_{Pt}, and $E_{A/Pt}$ are the total energies of the isolated adsorbate, the clean Pt surface and the chemisorption system, respectively. The energy of the isolated adsorbate is calculated by performing a spin-polarized calculation in a 12 Å^3 cell. The reference state for the S atom is the triplet state.

1. Hydrogen adsorption on Pt(111)

We have examined hydrogen absorption on Pt(111) in a previous study,[32] and therefore, only some of the key findings will be recalled here. It was found, in agreement with experiment[33] and a recent DFT study of Hoffmann and co-workers[34] that H has a very smooth potential energy surface (PES) for adsorption on Pt(111). H binds at each adsorption site on Pt(111) [top, bridge, fcc, and hexagonal-close-packed (hcp)] with a similar energy, exhibiting only a slight (~0.1 eV) preference for adsorption at threefold fcc sites. Chemisorption energies at each site were calculated to be ~2.9 eV and a H–Pt bond length at the fcc site of 1.85 Å was obtained.

2. Sulfur adsorption on Pt(111)

At 1/4 monolayer S forms a well-ordered $p(2\times2)$ overlayer. Low-energy electron diffraction (LEED) studies have revealed that in this overlayer S adsorbs at fcc threefold hollow sites with an equilibrium S–Pt bond length of 2.24–2.28 Å.[5,10] Here, we present an examination of S adsorption at the four adsorption sites of Pt(111). Table I lists the calculated chemisorption energies and structural parameters for S at

TABLE I. Chemisorption energies (E_{ads}) and optimized structural parameters for sulfur adsorption at the four high-symmetry sites of Pt(111).

Site	E_{ads} (eV)	S–Pt (Å)	S–surf. (Å)[a]
hcp	4.97	2.27 2.27[b]	1.59
fcc	5.14	2.27 2.26[b] 2.24[c] 2.28±0.03[d]	1.59
Bridge	4.47	2.23 2.23[b]	1.73
Top	3.04	2.16 2.18[b]	2.16

[a]S–surf is the Sulfur–Surface perpendicular distance.
[b]Reference 9.
[c]Reference 5.
[d]Reference 10.

each site as well as results from previous experimental and theoretical studies. The calculations reveal that all sites are minima on the potential energy landscape and, in agreement with previous studies, the fcc threefold hollow site is the most stable. The chemisorption energy of S at the fcc site of Pt(111) is 5.14 eV. In agreement with previous determinations our calculated S–Pt bond length is 2.27 Å.

3. Sulfhydryl (SH) adsorption on Pt(111)

Sulfhydryl is a short-lived catalytic intermediate and as such is difficult to observe and characterize experimentally. A theoretical approach is, therefore, particularly amenable to the study of reaction intermediates, providing important information on the structure and energetics of adsorption. Table II lists chemisorption energies and optimized structural parameters for SH adsorption on Pt(111). Figure 1 displays the most stable structure for SH at the top, bridge, and fcc sites. SH at the hcp site is not shown because the structure is essentially the same as that obtained at the fcc site. At all sites SH molecules are inclined to the surface normal with the S end down. This appears to be consistent with high-resolution electron energy loss spectroscopy (HREELS) data, which indicates that SH molecules may be tilted on Pt(111).[7] In fact SH lies more or less flat on the surface. An inclined SH is favored over an upright SH because in the inclined structure the p orbitals of S mix more effectively with the Pt bands. Our calculations reveal that SH binds most strongly at the bridge site with a chemisorption energy of 3.00 eV. The S–Pt and S–H distances at this site are 2.39 and 1.40 Å,

TABLE II. Chemisorption energies (E_{ads}) and optimized structural parameters for sulfhydryl (SH) adsorption at the four high-symmetry sites of Pt(111).

Site	E_{ads} (eV)	S–H (Å)	S–Pt (Å)	S–surf (Å)[a]	α (°)[b]
hcp	2.62	1.39	2.40	1.77	115.4
fcc	2.70	1.39	2.39	1.76	114.7
Bridge	3.00	1.40	2.31	1.83	99.4
Top	2.39	1.36	2.27	2.27	99.4

[a]S–surf is the Sulfur–Surface perpendicular distance.
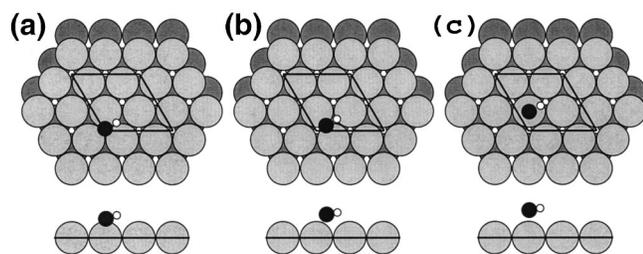[b]α is the Surface–Sulfur–Hydrogen angle.

FIG. 1. Most stable adsorption structures of SH at the fcc, bridge, and top sites of Pt(111). Only two layers of Pt atoms are shown for clarity. The solid lines designate the surface unit cell. The gray, black, and white circles correspond to Pt, S, and H atoms, respectively. This coloring protocol is used throughout. The optimized geometrical parameters for SH at each of these sites (and the hcp site) are listed in Table II.

respectively. It is interesting to note that the SH bond length has increased upon adsorption. At the bridge site, for example, the SH bond length has increased from 1.35 to 1.40 Å. Similar behavior has been observed for CH_2 and CH_3 adsorption on transition metal surfaces and in these cases it was attributed to a C–H–metal three-center bond.[35–37] It is possible that the increased S–H bond lengths observed here are a result of a analogous S–H-metal three-center bond.

4. Hydrogen sulphide (H₂S) adsorption on Pt(111)

Table III lists optimized structural parameters and chemisorption energies for H₂S adsorption on Pt(111). Figure 2 illustrates the most stable H₂S structure at each site. It can be seen from Fig. 2 that when H₂S adsorbs at the fcc (and hcp) and top sites it is tilted but upright at the bridge site. Our calculations reveal that H₂S binds most strongly to the surface at the top site with chemisorption energy of 0.70 eV. The S–Pt and S–H distances at this site are 2.30 and 1.36 Å, respectively. The H–S–H internal angle (θ) remains unchanged from its gas phase value at 92°.

B. Hydrogenation reactions

For the first time, DFT has been utilized to determine microscopic reaction pathways for the hydrogenation of S and SH on Pt(111)
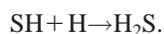
$$S + H \rightarrow SH,$$

$$SH + H \rightarrow H_2S.$$

TABLE III. Chemisorption energies (E_{ads}) and optimized structural parameters for hydrogen sulfide (H₂S) adsorption at the four high-symmetry sites of Pt(111).

Site	E_{ads} (eV)	S–H (Å)	S–Pt (Å)	S–surf (Å)[a]	α (°)[b]	θ (°)[c]
hcp	0.36	1.37	2.58	2.01	118.2	90.1
fcc	0.36	1.37	2.56	1.99	117.4	90.3
bridge	0.31	1.36	2.33	1.86	131.8	96.4
top	0.90	1.36	2.30	2.30	100.8	92.0

[a]S–surf is the Sulfur–Surface perpendicular distance.
[b]α is the Surface–Sulfur–Hydrogen angle.
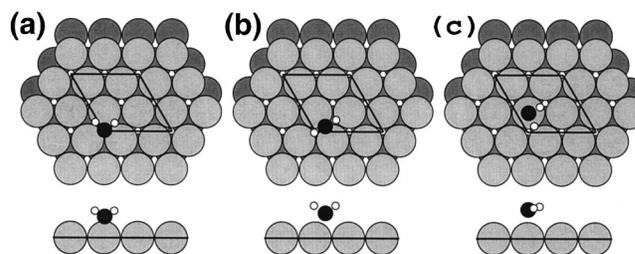[c]θ is the Hydrogen–Sulfur–Hydrogen internal angle.

FIG. 2. Most stable adsorption structures of H₂S at the fcc, bridge, and top sites of Pt(111). The optimized geometrical parameters for SH at each of these sites (and the hcp site) are listed in Table III.

1. Sulfur hydrogenation

When H adsorbs upon the $p(2\times2)$ S covered surface an atop site becomes the preferred chemisorption site. The structure of this coadsorption system is shown in Fig. 3(a). S atoms are at fcc sites and H atoms at the top sites of the fourth atom of each surface cell. This is the initial state for the reaction, which is 0.15 eV less stable than that when S and H are chemisorbed in separate $p(2\times2)$ unit cells, indicating a slight repulsive interaction between coadsorbed S and H. At the transition state [Fig. 3(b)] of the reaction, the S–H distance is 1.64 Å. Sulfur is close to a bridge site and H is in a plane perpendicular to the Pt–Pt bond of the bridge site. The energy required for this process is 1.08 eV. Taking together the chemisorption energies of the separate H and separate S phases we find that the overall reaction barrier is 1.23 eV. After the transition state, S and H combine to produce SH chemisorbed at the bridge site [Fig. 3(c)], which as we have seen is the most stable site for SH adsorption. Given that the S–H distance at the transition state (1.64 Å) is just 17% greater than the equilibrium S–H bond length (1.40 Å) in adsorbed SH in the final state it is clear that this is a late barrier reaction. This is also reflected in the energy of the final state, which is just 0.04 eV less than the transition state. This elementary step is 1.19 eV endothermic.

2. Sulfhydryl hydrogenation

For the sake of consistency the SH+H reaction was also investigated in a $p(2\times2)$ unit cell. The initial state for this reaction, i.e., the most stable coadsorption of SH and H within the $p(2\times2)$ unit cell, is illustrated in Fig. 4(a). Sulfhydryls are at bridge sites and H atoms are at top sites. As with the coadsorption of S and H, there is a repulsive interaction between SH and H with the coadsorbed state being 0.24 eV less stable than that when SH and H are adsorbed in
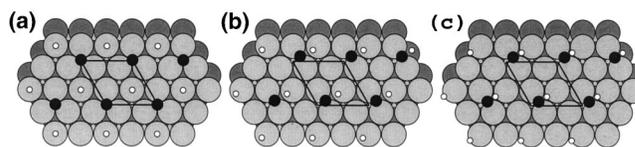

FIG. 3. Selected points along the S+H reaction pathway on Pt(111) in a $p(2\times2)$ unit cell. (a) The initial state is the most stable coadsorption of a single S and a single H in a $p(2\times2)$ unit cell. (b) is the transition state of the reaction. (c) Is the final state, in which SH is chemisorbed on a bridge site. The optimized geometrical parameters at the initial, transition, and final states are listed in Table IV.

TABLE IV. Optimized structural parameters for the initial, transition, and final states of the S+H and SH+H reactions on Pt(111).

Reaction		S–H$_{ads}$ (Å)[a]	S–H (Å)	S–Pt (Å)	S–surf. (Å)[b]	H$_{ads}$–Pt (Å)	H–surf. (Å)[c]	αH$_{ads}$ (°)[d]	θ[e] (°)
S+H	Initial(a)	3.25	⋯	2.27	1.59	1.56	1.56	89.5	⋯
	TS(b)	1.64	⋯	2.28	1.80	1.76	1.60	83.0	⋯
	Final(c)	1.40	⋯	2.31	1.83	2.33	2.06	99.4	⋯
SH+H	Initial(a)	2.73	1.38	2.33	1.86	1.56	1.55	83.5	177.5
	TS(b)	1.70	1.36	2.32	2.25	1.72	1.58	66.6	89.2
	Final(c)	1.36	1.36	2.30	2.30	2.88	2.54	100.5	92.0

[a]S—H$_{ads}$ is the Sulfur–adsorbed Hydrogen (hydrogenating hydrogen) distance.
[b]S–surf is the Sulfur–Surface perpendicular distance.
[c]H–surf is the Hydrogen–Surface perpendicular distance.
[d]αH$_{ads}$ is the Surface–Sulfur–adsorbed Hydrogen angle.
[e]θ is the Hydrogen–Sulfur–Hydrogen internal angle.

separate $p(2\times2)$ unit cells. The reaction is initiated by the diffusion of adsorbed H (H$_{(ads)}$) towards SH. As the H$_{(ads)}$–SH distance decreases, SH diffuses towards a top site. At an H$_{(ads)}$–SH separation of 1.70 Å, the transition state is accessed [Fig. 4(b)]. The energy required for this process is 0.68 eV. Taking together the chemisorption energies of the separate H and separate SH phases we find that the overall reaction barrier is 0.92 eV. After the transition stage the H$_{(ads)}$–SH distance decreases, yielding H$_2$S chemisorbed at a top site [Fig. 4(c)]. Although the transition state occurs at a greater S–H separation than in the S+H reaction this is still a late barrier reaction. Moreover, as with the S+H reaction the energy of the final state in this reaction is similar to the transition state. This reaction is 0.90 eV endothermic.

IV. DISCUSSION

Recently on Pt(111) we performed a systematic study of nine different hydrogenation reaction pathways.[20] All the elementary steps in the hydrogenation of carbon to methane, nitrogen to ammonia, and oxygen to water were investigated. We found that the pathways followed in each reaction depended upon the valency of the reactants involved. This relationship is best observed by a consideration of the transition states of each reaction. As the valency of a reactant decreases, so too does the coordination number of the site at which the transition state is located: Monovalent adsorbates (for example, CH$_3$, NH$_2$, and OH) tend to make transition states close to sites; divalent adsorbates (CH$_2$, NH, and O) near bridge sites; and tri and tetra-valent adsorbates (CH, N, and C) near threefold hollow sites. Having determined reaction pathways for S and SH hydrogenation on Pt(111) we see that these fragments indeed behave in a similar manner to the other adsorbates. Divalent S accesses a transition state at a bridge site and monovalent SH makes transition state at a top site. These reactions are the first indication that the transition state-valency relationship may extend beyond reactions involving first row adsorbates.

It is interesting to note that in both the S+H and SH+H reactions it is necessary to "activate" S or SH from their preferred chemisorption site in order to achieve a transition state. S must be activated from an fcc to a bridge site and SH from a bridge to a top site. In other words, S and SH are unreactive (inert) at their preferred chemisorption sites and in order to become reactive they must first diffuse to sites of lower coordination. This is analogous behavior to that exhibited by NH$_X$ and OH$_X$ fragments on certain transition metal surfaces. In particular in the CO oxidation and oxygen-hydrogenation reactions on Pt(111) the activation of O atoms from threefold hollow sites to bridge sites is an essential aspect of each reaction pathway. The inertness of chemisorbed O atoms at threefold hollow sites on the (111) facets of transition metal surfaces has recently been explained by Zhang and Hu.[38]

Figure 5 reveals the complete energy profile for the conversion of adsorbed S and H into gas-phase H$_2$S. Both the S+H and SH+H reactions have moderately high barriers and endothermicities. As a result the formation of H$_2$S from adsorbed S and H is quite a difficult process with an overall endothermicity of >2 eV. The reverse process, however, H$_2$S dissociation, is very facile. Both the H$_2$S and SH dissociation barriers are <0.1 eV and the S+H state is more stable than both the H$_2$S and SH states. This is consistent with experiments that find that H$_2$S is very unstable on clean Pt(111). Indeed in the low coverage regime H$_2$S decomposes into adsorbed S and H on Pt(111) at temperatures as low as 110 K.[6,7]

V. CONCLUSIONS

Density-functional theory has been applied to the adsorption and reaction of S moieties on Pt(111). Stable adsorption structures and chemisorption energies for S, SH, and H$_2$S on Pt(111) have been identified. In addition, reaction pathways and energy profiles for the conversion of adsorbed

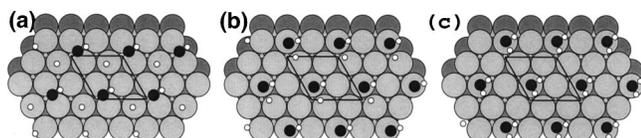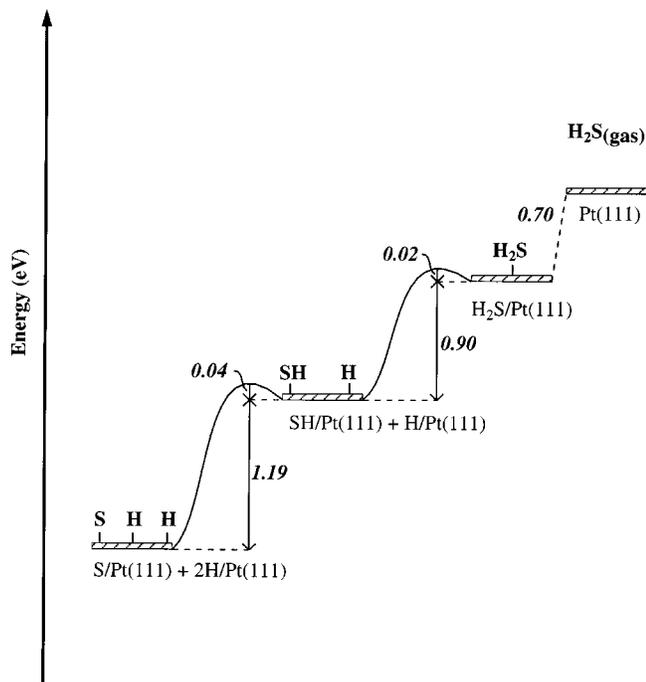FIG. 4. Top view of initial (a), transition (b), and final (c) state for the reaction of SH and H on Pt(111) in a $p(2\times2)$ unit cell. The optimized geometrical parameters at the initial, transition, and final states are listed in Table IV.

FIG. 5. Relative energy diagram for gas phase H_2S $(H_{2S(g)})$ formation from adsorbed S and H on Pt(111) in a $p(2 \times 2)$ unit cell.

S and H into gas-phase H_2S have been determined. Our calculations indicate that S and SH react in an analogous manner to first row adsorbates. Divalent S accesses a transition state at a bridge site and monovalent SH at a top site. In each case this requires the activation of the S species from their preferred chemisorption site. Both the S+H and SH+H reactions have moderately high barriers (~1 eV) and high exothermicities (~1 eV). This reveals that adsorbed H_2S and SH are highly unstable on Pt(111) and that adsorbed S (and H) is the most stable SH_X $(X = 0, 1, 2)$ intermediate on Pt(111).

ACKNOWLEDGMENT

[1] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).
[2] R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces* (Wiley, New York, 1996).
[3] M. Kiskinova, Surf. Sci. Rep. **8**, 359 (1998).
[4] D. W. Goodman, J. Phys. Chem. **100**, 13090 (1996).
[5] H. A. Yoon, N. Materer, M. Salmeron, M. A. van Hove, and G. A. Somorjai, Surf. Sci. **376**, 254 (1997).
[6] R. J. Koestner, M. Salmeron, E. B. Kolin, and J. L. Gland, Chem. Phys. Lett. **125**, 134 (1986).
[7] R. J. Koestner, M. Salmeron, E. B. Kolin, and J. L. Gland, Surf. Sci. **172**, 668 (1986).
[8] J. A. Rodriguez, S. Chaturvedi, T. Jirsak, and J. Hrbek, J. Chem. Phys. **109**, 4052 (1999).
[9] J. A. Rodriguez, J. Hrbek, M. Juhn, T. Jirsak, S. Chaturvedi, and A. Maiti, J. Chem. Phys. **113**, 11284 (2000).
[10] K. Hayek, H. Glassl, A. Gutmann, H. Leonhard, M. Prutton, S. P. Tear, and M. R. Welton-Cook, Surf. Sci. **152/153**, 419 (1985).
[11] P. J. Feibleman and D. R. Hamann, Phys. Rev. Lett. **52**, 61 (1984).
[12] P. J. Feibleman and D. R. Hamann, Surf. Sci. **149**, 48 (1985).
[13] J. M. Maclaren and J. B. Pendry, Surf. Sci. **178**, 856 (1986).
[14] N. D. Lang, S. Holloway, and J. K. Nørskov, Surf. Sci. **150**, 24 (1985).
[15] J. K. Nørskov, S. Holloway, and N. D. Lang, Surf. Sci. **137**, 65 (1984).
[16] S. Wilke and M. Scheffler, Surf. Sci. **329**, L605 (1995).
[17] S. Wilke and M. Scheffler, Phys. Rev. Lett. **76**, 3380 (1996).
[18] C. J. Zhang, P. Hu, and M. H. Lee, Surf. Sci. **432**, 305 (1999).
[19] E. Wimmer, C. L. Fu, and A. J. Freeman, Phys. Rev. Lett. **55**, 2618 (1985).
[20] A. Michaelides and P. Hu, J. Am. Chem. Soc. **122**, 9866 (2000).
[21] A. Michaelides and P. Hu, in *Theoretical Aspects of Heterogeneous Catalysis* (Kluwer) (to be published).
[22] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
[23] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).
[24] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[25] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[26] A. Michaelides and P. Hu, J. Chem. Phys. **114**, 513 (2001).
[27] A. Michaelides and P. Hu, J. Chem. Phys. **114**, 5792 (2001).
[28] A. Michaelides, P. Hu, and A. Alavi, J. Chem. Phys. **111**, 1343 (1999).
[29] A. Alavi, P. Hu, T. Deutsch, P. L. Silvestrelli, and J. Hutter, Phys. Rev. Lett. **80**, 3650 (1998).
[30] C. J. Zhang, P. Hu, and A. Alavi, J. Am. Chem. Soc. **121**, 7931 (1999).
[31] A. Michaelides and P. Hu, J. Chem. Phys. **112**, 6006 (2000).
[32] A. Michaelides and P. Hu, J. Am. Chem. Soc. **128**, 4235 (2001).
[33] L. J. Richter and W. Ho, Phys. Rev. B **36**, 9797 (1987).
[34] G. Papoian, J. K. Nørskov, and R. Hoffmann, J. Am. Chem. Soc. **17**, 4129 (2000).
[35] A. Michaelides and P. Hu, Surf. Sci. **437**, 362 (1999).
[36] A. Michaelides and P. Hu, J. Chem. Phys. **112**, 8120 (2000).
[37] A. Michaelides and P. Hu, J. Chem. Phys. **114**, 2523 (2001).
[38] C. J. Zhang and P. Hu, J. Am. Chem. Soc. **122**, 2134 (2000).