Long-range ordering of methylidyne on Pt{110}(1×2)

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A $c(2\times4)$ LEED pattern is observed for methylidyne (CH) chemisorbed on Pt{110}(1×2) at a saturation coverage of 0.25 ML. Density functional calculations reveal that methylidyne is preferentially adsorbed in the fcc three-fold hollow site on the {111} microfacet of the reconstructed surface. A structure for the ordered overlayer is thus proposed, and both through-metal and through-space interactions are considered as possible causes for this unexpected long-range coherence. We argue that entropic effects may be implicated. © 2002 American Institute of Physics. [DOI: 10.1063/1.1483847]

I. INTRODUCTION

A key factor in controlling any heterogeneous catalytic process is a detailed understanding of the identity and bonding of the reactive intermediates. The intermediates of industrially important processes such as methane partial oxidation[1] and Fischer Tropsch Synthesis[2] have been investigated extensively in recent years, with the aim of understanding and controlling these processes at an atomic level.

It is widely accepted that the initial dissociation products of methane on most transition metals are methyl (CH_3) and atomic hydrogen. Adsorbed methyl groups have been prepared at low temperatures using a variety of techniques including thermal dissociation of methyl halides,[3–5] a hypothermal methane beam,[6] and methyl radical source.[7,8] The thermal chemistry of these metastable adlayers has been studied extensively using reflection absorption infrared spectroscopy (RAIRS).[6–8] On the Pt{111} surface, the general consensus is that adsorbed CH_3 is stable below a surface temperature of 240 K; above this temperature it decomposes at low coverage to adsorbed atomic carbon and atomic hydrogen, the latter recombining to form molecular hydrogen gas at 310 K.

Interestingly, however, density functional theory (DFT) slab calculations performed by Michaelides and Hu,[9] and DFT cluster calculations performed by Kua and Goddard[10] have predicted that adsorbed CH, and not CH_3, is the energetically most stable species on Pt{111}. Hitherto this species has only been observed on Ni{111} using high resolution electron energy loss spectroscopy (HREELS),[11,12] but its stability on Pt{110}(1×2) was recently confirmed by Watson *et al.*[13] They used temperature programmed reaction studies to identify the stable hydrocarbon fragments formed on Pt{110}(1×2) using a supersonic molecular beam, over a range of temperatures. They showed conclusively that adsorbed CH is the stable reaction intermediate on Pt{110}(1×2) at all coverages up to a temperature of 470 K, whereupon it decomposes to adsorbed carbon. The inability to observe CH on Pt{111} may therefore simply be due to

the lack of sensitivity of RAIRS to low coverages of CH_x, presumably due to screening of the C–H dipole by metal valence electrons.

In the present study, we observe an ordered CH overlayer on the Pt{110}(1×2) surface. The LEED analysis suggests a $c(2\times4)$ global periodicity. Density functional calculations are used to provide information on the local geometry of the methylidyne adsorbate at the surface. With this information, a static structure of the ordered methylidyne adlayer may be proposed. The results are rationalized on the basis of the interpretation of the nature of the intermolecular interactions.

II. METHODOLOGY

A. Experiment

The experimental apparatus has a base pressure of $<2\times10^{-10}$ mbar and is described in detail elsewhere.[14] The molecular beam used to dose the methane is sourced at a supersonic expansion from a 50 μm nozzle, skimmed, differentially pumped and collimated before entering the sample chamber.

The Pt sample, 11 mm diam by 1 mm thick, was cut to within 1° of the {110} plane. Initial cleaning of the crystal was achieved by repeated cycles of ion sputtering, annealing and oxygen treatment. Routine cleaning consisted of annealing at 1240 K, exposure to oxygen for 5 min while cooling from 1100 to 950 K, and annealing for 15 min at 950 K. This procedure yields a clean Pt{110}(1×2) surface which gives a sharp low energy electron diffraction (LEED) pattern and oxygen thermal desorption spectra that are in good agreement with the literature.[15] It should also be noted that Auger analysis performed during earlier studies found no evidence for impurities such as calcium, sulphur, and silicon, and the above cleaning procedure removed carbon which remained on the surface after experiments. The CH_4 used was >99.9995% pure, as quoted by the suppliers [Messer (UK) Ltd.]. The supersonic methane beam used in these experiments had a diameter of 5.6 mm. It had a composition of 9%CH_4–91%He and the nozzle was heated to 790 K, giving the methane molecular beam a translational energy of 580 meV, estimated on the basis of an ideal supersonic expan-

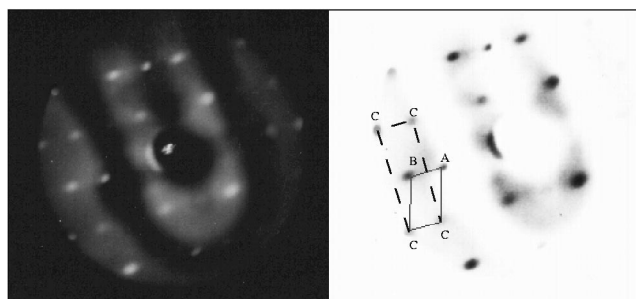[a]Author to whom correspondence should be addressed. Fax: +44 1223 336362; electronic mail: dak10@cam.ac.uk

FIG. 1. The $c(2\times4)$ LEED pattern from the saturated CH surface prepared as described in the text; electron energy 105 eV and sample temperature 300 K. The dark "U" shape with a circle in the middle seen in the left hand image is the sample mount obstructing the pattern as seen through the viewport. The reciprocal unit cell of $c(2\times4)$ symmetry is indicated in the right-hand negative LEED image by the solid parallelogram, and the corresponding (1×2) unit cell by the dashed rectangle. The (1×1) and (1×2) spots are indicated by A and B, respectively, while the spots which are unique to the $c(2\times4)$ symmetry are labeled C in the figure.

sion. All coverages are quoted in monolayers (ML) (1 ML $\equiv 9.22\times10^{14}$ molecules cm^{-2}).

B. Theory

Total energy pseudopotential calculations were performed within the framework of density functional theory (DFT) using the CASTEP code.[16] The electronic exchange-correlation energy was described with the Perdew–Wang form[17] of the generalized gradient approximation (GGA). Electronic wave functions were expanded in terms of a plane wave basis set up to a kinetic energy cutoff of 310 eV, and ultrasoft pseudopotentials[18] were used to account for the electron–ion interactions.

The Pt{110}(1×2) surface was modeled by a six-layer slab placed inside a (2×2) supercell. A vacuum region of eight Pt layers, ~11 Å, was included to prevent interaction between adjacent slabs. The absolute dimensions of the supercell were chosen to be consistent with the GGA-calculated bulk Pt lattice parameter $a=3.97$ Å [experimental $a=3.9236$ Å (Ref. 19)]. Methylidyne was adsorbed on only one side of the slab. At one molecule per cell, the adsorbate coverage is 0.25 ML (relative to the Pt atom density on the unreconstructed surface). In the calculations, the bottom two Pt layers were frozen in their bulk configurations, while the remaining four layers as well as the adsorbate layer were allowed to relax under the influence of the calculated forces. Reciprocal space integration was achieved by summation over a $4\times3\times1$ Monkhorst–Pack mesh[20] of special k-points. Convergence with respect to slab thickness, cutoff energy, and k-point sampling was tested and found to be satisfactory.

III. RESULTS AND DISCUSSION

A. Experiment: Formation of the $c(2\times4)$ overlayer

A sharp $c(2\times4)$ LEED pattern was obtained by dosing methane for 1 h at a surface temperature of 370 K, using the supersonic molecular beam described above with a flux of 0.4 ML s^{-1}. The corresponding saturation coverage of CH was found to be 0.25 ML,[21] which was determined using the
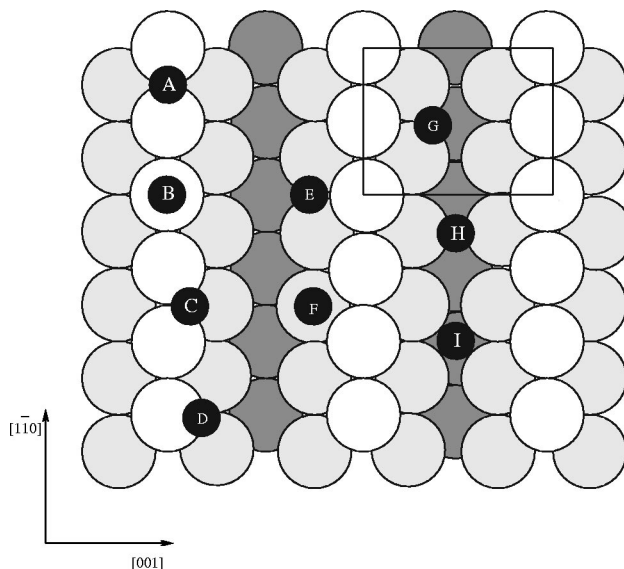

FIG. 2. High symmetry adsorption sites on the Pt{110}(1×2) surface.

titration method described by Walker and King.[22] Moving the electron beam to a region outside the molecular beam spot, resulted in a sharp (1×2) LEED pattern. Heating the above adlayer to temperatures above 470 K, resulted in a (1×1) pattern with faint (1×2) spots.

It is important to distinguish between two possible surface geometries which might give rise to the observed LEED pattern, since certain adsorbates (e.g., C) are known to lift the substrate reconstruction. A $c(2\times4)$ arrangement of molecules should give rise to a $c(2\times4)$ LEED pattern, regardless of whether the underlying substrate shows (1×2) or (1×1) symmetry, so the symmetry of the pattern alone cannot distinguish between the two cases. To eliminate one or the other, it is necessary to examine the variation of spot intensities with beam energy. As the beam energy is increased, one expects that the substrate contribution to the scattering ought to increase relative to that of the adsorbate. We find that the spots that are exclusive to the $c(2\times4)$ pattern [i.e., do not occur in (1×2) or (1×1) patterns] do indeed become relatively less intense as the beam energy is increased. Conversely, however, the spots which occur in both $c(2\times4)$ *and* (1×2) LEED patterns do not change their intensity relative to the (1×1) spots. This indicates that a clear (1×2) symmetry remains, even when we are primarily probing the substrate atom scattering (Fig. 1).

We can also offer a further plausibility argument against the lifting of the reconstruction. If the 0.25 ML CH structure were due to an ordered $c(2\times4)$ overlayer on the (1×1) substrate, alternate top layer Pt rows should be unoccupied by CH. It is difficult to envisage why methane dissociation would not occur when CH$_4$ impinges on these vacant ridge atoms; and also difficult to understand why the CH–CH interactions should lead to such a structure.

B. Theory: Local adsorption geometry

The calculated C–H bond energy of the free methylidyne radical is 3.70 eV, which is in good agreement with the reported experimental value of 3.51 eV.[19] The corresponding

TABLE I. The calculated structures and binding energy E_b for CH on the Pt{110}(1×2) surface at 0.25 ML coverage. The number in brackets for d_{C-Pt} represents the number of C–Pt bonds with that length. The CH tilt angle is relative to the macroscopic surface normal, away from the Pt ridge.

Site	E_b (eV)	d_{C-Pt} (Å)	d_{C-H} (Å)	Tilt angle (°)
A	6.25	1.90 (2)	1.09	0
B	4.44	1.77 (1)	1.09	0
C	6.72	2.00 (3)	1.09	30.9
D	6.61	1.99 (1), 2.00 (2)	1.09	30.6
G	6.39	1.97 (2), 2.02 (1)	1.09	35.9
H	5.97	2.06 (2), 2.05 (1), 2.04 (1)	1.10	0.7
I	5.36	2.29 (4), 2.04 (1)	1.09	0

optimal C–H bond length is 1.12 Å, in excellent agreement with the reported experimental value of 1.1199 Å (Ref. 19) for gas phase CH.

The reconstructed Pt{110}(1×2) surface exhibits a missing-row structure,[23,24] and a consequently large number of high symmetry adsorption sites which must be considered for methylidyne chemisorption (Fig. 2). Not all of these sites necessarily correspond to a local minimum on the potential energy hypersurface, but we have chosen to impose maximal symmetry in our initial calculations, so that symmetry-breaking site-switching is disallowed. The calculated optimal geometry and the corresponding adsorption energy for each of the sites in Fig. 2 is shown in Table I. The binding energy E_b of the adsorbed molecule on the surface is calculated with reference to the energies of the clean (1×2) surface and the free CH radical.

Methylidyne chemisorption preferentially occurs in the fcc threefold hollow site (site C) situated on the {111} microfacets which make up the trough walls on the reconstructed surface. The optimal Pt–C bond length is 2.00 Å, while the C–H bond length is contracted to 1.09 Å, which compares well with the experimental C–H bond length in methane of 1.0870 Å.[19] The C–H axis is tilted away from the Pt ridge by 1.4° relative to the normal of the {111} microfacet, i.e., 30.9° relative to the macroscopic surface normal (Fig. 3). The calculated adsorption energy of 6.72 eV corresponds to an average C–Pt bond energy of 2.24 eV/bond. For ethylidyne on Pt{110}(1×2), the experimental average C–Pt bond energy
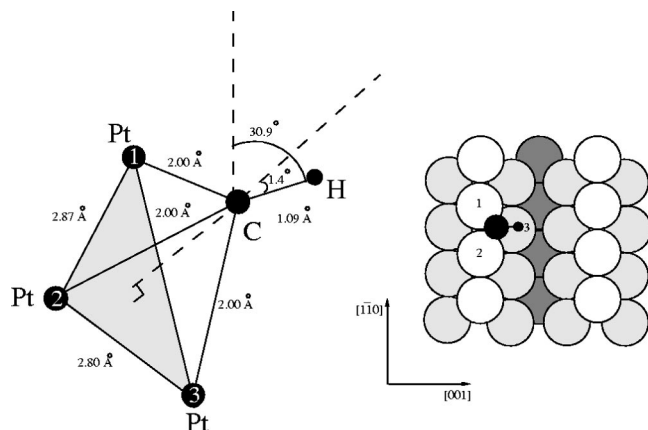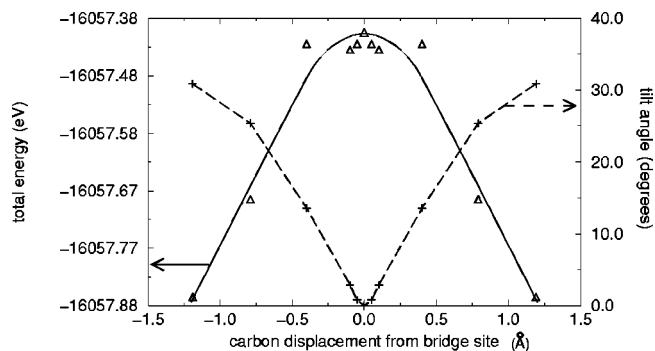

FIG. 4. Total energy and CH tilt angle as a function of carbon displacement in the [001] direction from the twofold bridge site.

for chemisorption in a threefold site is 2.30 eV/bond, as measured by microcalorimetry.[25] There is thus a striking agreement between the calculated and measured values for the C–Pt bond energy of a hydrocarbon chemisorbed through a carbon atom in a threefold site on this surface.

The stretching frequency for both CH and CD adsorbed in the threefold site on the Pt{110}(1×2) surface was calculated within the harmonic approximation, assuming static substrate atoms. For CH adsorption, a frequency of 3088 cm^{-1} was obtained, while for CD, the corresponding frequency was 2252 cm^{-1}. Analogous measured values for the CH and CD stretch in CH$_4$ and CD$_4$ are 3019 and 2259 cm^{-1}, respectively.[19] The similarity of these values reflects the essentially tetrahedral coordination of the carbon atom in a threefold site.

Only a 0.11 eV energy difference separates the hcp site (D) from the fcc site (C), while the only other threefold hollow site on the surface, denoted G in Fig. 2, is 0.32 eV less stable than the fcc site on the ridge. The ridge bridge site (A), 0.47 eV higher in energy than site C, is stable within the symmetry constrained calculations, but upon further investigation is found to correspond to a saddle-point on the potential energy surface, and not a local minimum (Fig. 4). Neither site E nor site F were found to correspond to a stationary point on the potential energy hypersurface.

C. Rationalization: Resonance, repulsion, and entropy

The theoretical methodology described above corresponds to a $p(2×2)$ ordered adlayer of methylidyne on the Pt{110}(1×2) surface at a coverage of 0.25 ML. The LEED analysis, however, reveals a $c(2×4)$ ordered structure at this coverage. The calculated energy difference between the fcc and the hcp hollow sites in both the $p(2×2)$ and the $c(2×4)$ geometry was tested,[26] and was found to differ by only ~0.01 eV, indicating that the relative stability of the adsorption sites is essentially independent of the ordering of the overlayer structure at 0.25 ML. Furthermore, the difference in the total energy of the $c(2×4)$ and $p(2×2)$ systems, and of the local geometry of CH placed in the energetically most favorable threefold fcc sites at a coverage of 0.25 ML, was tested[26] and found to be negligible to within the accuracy of the DFT calculations.

The DFT calculations are thus insensitive to the periodicity of the overlayer, but reveal the local geometry of the
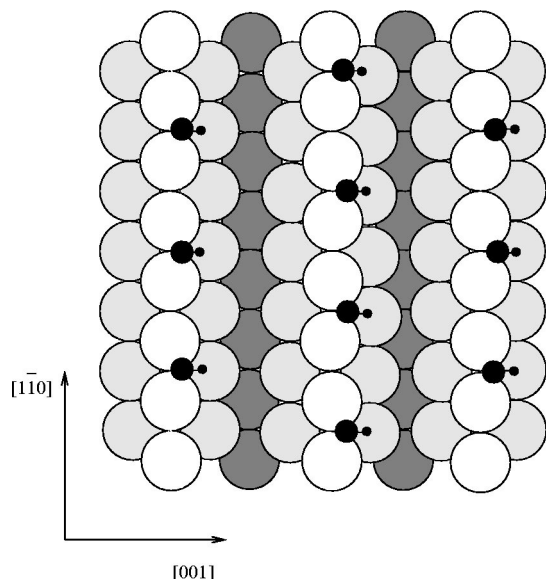

FIG. 3. Geometry of CH adsorbed in the fcc threefold hollow site on the Pt ridge.

FIG. 5. Proposed $c(2\times4)$ geometry of methylidyne adsorbed on Pt{110}(1×2) at a saturation coverage of 0.25 ML.
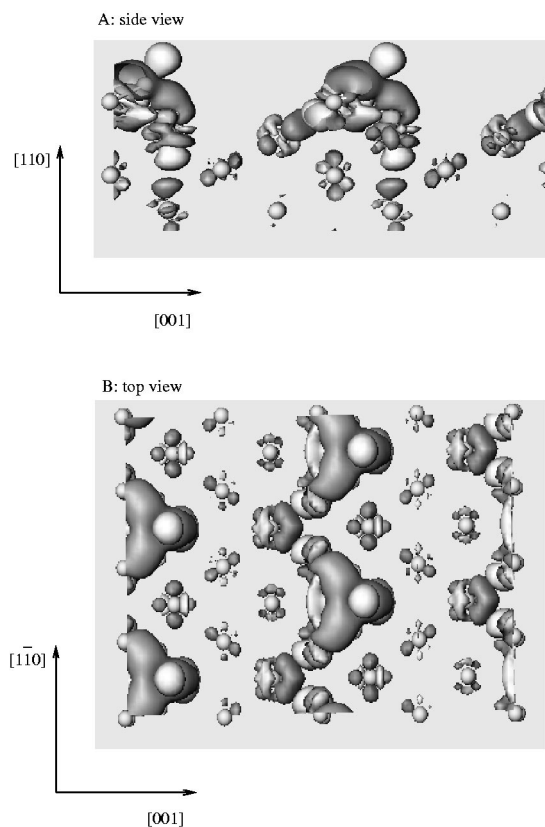

FIG. 6. Isosurfaces of the difference electron density (dark gray, regions of electron density increase; light gray, regions of electron density decrease) (A) side view; (B) top view.

adsorbate on the Pt surface. Conversely, the LEED analysis yields the global periodicity of the adsorbate system, but due to the limitations of the experimental setup, a full structural determination is not possible. However, by combining the results of our DFT calculations and LEED analysis, a static structure of the ordered methylidyne adlayer may be proposed (Fig. 5). There is an asymmetry in the proposed structure, with the methylidyne placed in the threefold fcc site on only one side of the Pt ridge. This asymmetry extends to the Pt substrate as well. The first layer Pt ridge atoms each undergo a 0.03 Å displacement away from the CH adsorbate along the [1$\bar{1}$0] direction, while the second layer Pt atom bonded to the methylidyne adsorbate is displaced 0.09 Å in the [001] direction away from the ridge atoms. The remaining second layer atoms are essentially unaffected by the presence of the adsorbate. Thus, in terms of a static structure, the adsorbate molecules must be positioned on equivalent sides of the ridge on adjacent ridges in order for a $c(2\times4)$ LEED pattern to be observed. However, taking dynamic effects into consideration, since the calculated minimum diffusion barrier for CH moving across the ridge is "just" 0.47 eV, the CH adsorbate is expected to flip back and forth across the ridge at a frequency of ~1 MHz at 370 K. The time-averaged structure is therefore symmetric, with thermal disorder across each ridge merely giving rise to a slight increase in the LEED background scattering.

Examination of the difference electron density provides insight into the nature of the bonding of CH to the Pt{110}(1×2) surface. Isosurfaces of the difference electron density are illustrated in Fig. 6, in which regions of electron density increase (dark gray) and electron density decrease (light gray) are shown. The CH molecule adopts a threefold coordination to the metal surface, in which electrons are donated from the orbital framework of the CH molecule to the metal, with concurrent backdonation from the metal d-states into the sp^3 hybrid orbitals located on the carbon atom. The CH fragment gains a net negative charge on the surface of

$-0.2e$, as calculated from the total electron density using the Bader topological model.[27]

One particularly interesting feature of the electron redistribution upon adsorption, is the strong interaction of the methylidyne adsorbate with the second layer Pt atom located on the opposite side of the ridge. A comparison of the difference electron density for the $p(2\times2)$ overlayer structure with that of the $c(2\times4)$ geometry indicates that the effect is independent of the relative positions of CH molecules on the opposite side of the trough. Thus, the interaction between the CH molecule and the second layer Pt atom occurs predominantly across the ridge, rather than across the trough. This resonant effect may be related to the ordering of adsorbates in the [1$\bar{1}$0] direction along the ridges, but the similarity between the difference electron density distributions of the $c(2\times4)$ and the $p(2\times2)$ overlayer structures suggests that the origin of the ordering between neighboring ridges is not due to through-metal interactions between the CH fragments. Instead, the ordering may be due to through-space interactions between the adsorbates on adjacent [1$\bar{1}$0] ridges.

Considering the separation between adjacent CH molecules adsorbed on equivalent sides of neighboring ridges, the H–H distance is 7.95 Å for the $p(2\times2)$ structure, and is even greater for the $c(2\times4)$ geometry, suggesting that for these cases the van der Waals interactions (not fully included within DFT) are negligible. Electrostatic repulsion between molecules in these geometries (due to their net negative charges) are already included in the energies reported above.

However, for two CH fragments adsorbed on adjacent ridges and orientated *towards* each other in the [001] direction, the H–H separation is just 4.32 Å in the $p(2\times2)$ geometry, increasing to 5.13 Å for the $c(2\times4)$ structure. In the latter case, the time-averaged *dynamic* through-space repulsive interactions are likely to be minimized relative to the $p(2\times2)$ case. Consequently, at any given temperature, thermal disorder of CH molecules across each ridge will presumably be greater in the $c(2\times4)$, leading to an increased entropic contribution to the free energy. This limited thermal disorder ought not to adversely affect the formation of the LEED pattern, but may explain the observed preference for a $c(2\times4)$ overlayer, compared to the $p(2\times2)$.

IV. CONCLUSIONS

The adsorption of CH on Pt{110}(1×2) at a saturation coverage of 0.25 ML results in a $c(2\times4)$ LEED pattern. From DFT calculations, the fcc threefold hollow site on the side of the Pt ridge is found to be the most stable site for CH chemisorption. The calculated adsorption geometry leads to a tetrahedral hybridization of the methylidyne carbon atom bonded to the Pt surface. The DFT analysis provides no evidence of through-metal interactions between methylidyne fragments on neighboring ridges, and we conclude that entropic contributions, arising due to through-space interactions, may conceivably account for the experimentally observed $c(2\times4)$ ordering of the methylidyne adlayer.

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[26] The calculation of the adsorption energy difference between the fcc and the hcp hollow sites in the $c(2\times4)$ geometry was achieved using a non-orthogonal surface unit cell. As before, a six-layer Pt slab was used, and adsorption was confined to one side of the slab. A 4×3×1 Monkhorst–Pack mesh was used in the calculations. For the calculation of the total energy difference between the $c(2\times4)$ and $p(2\times2)$ systems, a (2×4) orthogonal surface unit cell was used in each case to minimize numerical errors. Reciprocal space integration was achieved by summation over a 4×1×1 Monkhorst–Pack mesh.
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