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The effect of hydrogen chemisorption on titanium surface bonding*

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The effect of hydrogen chemisorption on the strength of Ti–Ti bonds is studied by *ab initio* configuration interaction techniques using an embedding theory to describe the electronic structure. A Ti adatom on Ti(0001) is modelled by a $Ti_{20}H$ cluster with boundary potentials determined from the embedding treatment. Hydrogen atom chemisorption is highly exothermic for adsorption atop the adatom, a three-fold site formed by the adatom and in the interstitial site below the adatom. Compared to the planar Ti(0001) surface the adatom region binds hydrogen much more strongly. Removal of Ti from the surface is energetically much more favorable if H remains on the surface as opposed to the removal of TiH. The exchange reaction $Ti_{20} + H \rightarrow Ti_{19}H + Ti$ is endothermic by 0.3 eV. These results suggest high reactivity of the adatom region on Ti(0001) but not such that the surface is more easily fragmented by removal of Ti or TiH.

Key words: Chemisorption — TiH — Electronic structure of metal surfaces — Hydrogen adsorption — Titanium

1. Introduction

The reactivity of titanium with hydrogen has been studied previously using an embedding theory and a core density expansion method [1, 2] which made possible the calculation of the dissociation of H_2 at different adsorption sites on a Ti(0001) surface and the determination of the energetically preferred interstitial sites for a hydrogen atom inside the metal lattice [3-5]. These calculations were

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

performed on clusters of about 40 Ti atoms, and for low density coverage, the results supported the expectation based on strong coupling arguments involving metal-adsorbate bonds, that interactions are predominantly localized near the metal surface [6].

The effect of chemisorbed hydrogen on the strength of Ti–Ti bonds was considered in earlier work on small, four-atom, metal clusters consisting only of the dissociation fragment and its nearest neighbor atoms (7). In addition to identifying effects already present in small systems, the small clusters may model some of the features of rough surfaces containing metal adatoms. These studies showed surface and interstitial hydrogen to be effective in weakening the Ti–Ti bonds and thereby facilitating fragmentation of the metal cluster.

In order to model the low concentration limit more accurately, embedding calculations of the effect of chemisorbed hydrogen on Ti–Ti bonding were carried out and the results are reported in the present paper. Stronger bonding of hydrogen to the lattice is found to occur, and this leads to fragmentation energies that differ significantly from those obtained for small clusters.

2. General theory

In this section the theoretical formulation is briefly reviewed; details of the theory are given in [1, 2] and chemisorption applications to titanium, copper, silicon and alloy systems are reported in [3-5, 7-12].

The main premise of the theoretical approach is that a description of molecule-surface interactions and dissociative processes on metal surfaces may necessitate a reasonably sophisticated treatment of the surface region to account for changes in polarization and electron correlation accompanying reactions. In the embedding theory, one proceeds to define a local region as an N-electron subspace extracted from the remainder of the system by a localization transformation. The adsorbate and local region are then treated at high accuracy as embedded in the fixed Coulomb and exchange field of the remainder of the electronic system.

The use of electron exchange as the basis of a localization transformation is discussed in [1, 2]. After an initial, simplified SCF treatment of the metal s-band, a localization transformation of the SCF orbitals is carried out by exchange maximization with the atoms in the adsorption region. Letting $\{\phi_k\}$ denote the SCF orbitals and $\{S\}$ the valence atomic orbitals on atoms in the vicinity of the adsorption site, the positive definite exchange integral $\gamma = \langle \phi_i'(1)\phi_i'(2)|r_{12}^{-1}|S(1)S(2)\rangle$ is maximized with respect to coefficients c_i of $\phi_i' = \sum c_i\phi_i$, leading to an eigenvalue problem. The orbitals that result are localized about the adsorption site, and in the order of decreasing exchange eigenvalue, correspond to orbitals highly localized on the designed surface atoms, orbitals describing bonds linking the surface atoms with the remainder of the lattice, and finally the interior bonds of the lattice.

The basis set is then improved locally on the adsorbate and surface region by adding atomic orbitals to provide radial and polarization flexibility, and in the case of transition metal systems, by explicitly introducing d-type orbitals. The final basis set is fully orthogonal by construction. New SCF calculations are carried out using the additional basis functions and the most localized occupied and virtual orbitals from the transformed SCF solution. Remaining occupied orbitals define the fixed Coulomb and exchange field of the interior of the lattice in both SCF and subsequent configuration interaction treatments of the local region.

In summary, the purpose of the localization transformation is two-fold: to introduce the delocalized character of the extended lattice into an electronic subspace involving the adsoprtion site, and to insulate the physically incorrect boundary of the cluster and the roughly described interior region from orbital refinements in the local region.

3. Boundary atom modelling

In some of the earlier studies [3-5], in order to improve the representation of boundary atoms of the cluster, both in the initial lattice, and in the refined calculations on the embedded subspace, atomic potentials were introduced at lattice sites around the cluster. These sites do not possess basis functions and thus do not contribute to the complexity of the calculations. However, neither are the calculations simplified compared to calculations on the cluster itself, other than through a reduction of the size of the configuration interaction subspace, i.e. through a reduction in the number of active electrons.

In the present work, we propose to model the boundary atoms of a small cluster to represent the s-band attributes of the larger cluster on which the initial s-band calculations are carried out. Calculations with the extended basis would then be simplified by the reduction of the number of active electrons, and by the reduction in the number of lattice basis orbitals.

There are two clusters relevant to the present argument, a large cluster of M atoms (in the present case $M=73$) that provides the initial model for the lattice valence s electrons, and a smaller cluster of M' atoms ($M'=19$ in the present case) derived from the larger lattice, see Fig. 1. The object is to modify the boundary atoms of the small cluster to take into account the fact that these atoms should be bonded to the now missing remainder of the lattice. In the present case, the Ti_{19} cluster has two layers of 12 and 7 atoms, respectively. The larger 73 atom cluster consists of Ti_{19} and all of its nearest neighbor atoms at their unperturbed *hcp* lattice sites, a total of three layers representing the Ti(0001) surface. The s-band of the larger cluster is described simply using a single $4s$ orbital per atom and a pseudopotential for all core and d-type electrons. Of the 19 atoms in the small cluster, 16 are on the nonphysical boundary of the cluster.

A SCF calculation on the large cluster, followed by a localization of the cluster (molecular) orbitals is used to define the number of electrons of the small cluster strongly involved in bonding with atoms outside the cluster; the latter atoms are referred to as the bulk. Orbitals are localized about the bulk atoms, the opposite of the procedure used in previous work, and for each localized orbital ϕ_i' the

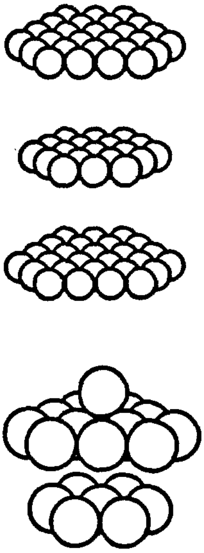

Fig. 1. Ti_{73} cluster used in the initial s-band calculations and the embedded Ti_{19} cluster plus Ti adatom derived from the Ti_{73} solution by modelling the Ti_{19} cluster boundary atoms (see text). Hydrogen atom adsorption is considered atop the adatom, at an interstitial site below the adatom and above a three-fold lateral site consisting of the adatom and two of its nearest neighbors in the surface layer (see text)

electron density is analyzed to determine the degree of localization. For a given localized orbital, ϕ_i', a truncated orbital is defined by deleting all of the basis functions that belong to the small cluster region, i.e. in the present case deleting the atomic orbitals of the Ti_{19} cluster. The resulting orbital ϕ_i'' is renormalized and the overlap $\langle \phi_i'' | \phi_i' \rangle$ with the original orbital is calculated. The value of the overlap is referred to as the degree of localization where a value of 1.0 corresponds to an orbital completely localized in the bulk. Table 1 gives the degree of localization of several orbitals that lie near the interface between the bulk and the embedded cluster. The localization is carried out with respect to the atoms of the bulk and the table shows that the first 26 orbitals (52 electrons) are highly localized in the bulk (note that there are 54 atoms in the bulk). The next four doubly occupied orbitals are shared equally between the bulk and the embedded cluster. The remaining occupied orbitals, including the singly occupied orbital which is extensively delocalized, are assigned to the embedded cluster. These assignments lead to a description of the system as a 19 atom cluster in which two of the s-type electrons are no longer available for valence interactions because of their involvement in binding with the bulk. In the next stage of the modelling these two electrons are distributed equally over the 16 boundary atoms of Ti_{19} and described subsequently by a spherically symmetric density $2/16\ 4s(1)4s(1)$. Thus the new 19 atom cluster has 17 electrons and is electrically neutral due to the modified potential on the boundary atoms.

Since there is uncertainty in the assignment of the singly occupied orbital and in the approximation of the assigned boundary electron density by spherical atomic distributions, calculations of the ionization energy or work function of Ti_{19}, $Ti_{19}H$ and $Ti_{19}H_7$ were performed for differing numbers of electrons assigned to the boundary atoms. The ionization energies shown in Table 2 are calculated

Table 1. Localized orbitals from the 4*s*-band calculation of Ti_{73}. The cluster consists of 19 atoms in the local surface region and 54 bulk atoms; orbitals are localized with respect to atoms of the bulk. The degree of localization of orbitals that are spatially near the boundary of the 19-atom embedded cluster is given and the assignment of the orbitals as contributors to the bulk or boundary region is indicated

Orbital	Degree of localization[a]	Assignment
1-23	>0.94	Bulk
24	0.92	Bulk
25	0.94	
26	0.94	
27	0.56	Two to the bulk and two to the boundary region
28	0.56	
29	0.50	
30	0.57	
31[b]	0.23	Boundary region
32[b]	0.23	
33	0.04	
34[b]	−0.01	
35[b]	−0.01	
36	0.04	
37	0.80	Open shell

[a] $\langle \phi_i'' | \phi_i' \rangle$ where ϕ_i'' is a truncated orbital, renormalized, obtained from ϕ_i'

[b] Degenerate orbitals

Table 2. Work functions for Ti_{19}, $Ti_{19}H$ and $Ti_{19}H_7$ calculated as $\Delta E = E(M^+) - E(M)$. Calculations are for (a) all *s* electrons treated explicitly, (b) two electrons assigned to a boundary atom potential, and (c) three electrons assigned to a boundary atom potential where (b) and (c) are possible assignments based on the localized orbital analysis of Ti_{73}. The highest energy eigenvalue for each calculation is given and can be used to estimate the ionization energy by Koopman's theorem. The work function of titanium, determined experimentally, is 3.8 eV

Cluster	Calculation	e_{max} (a.u.)	ΔE (a.u.)	ΔE (eV)
Ti_{19}	a	−0.1479	0.1468	4.0
	b	−0.1353	0.1341	3.6
	c	−0.1661	0.1694	4.6
$Ti_{19}H$	a	−0.1415	0.1402	3.8
	b	−0.1641	0.1606	4.4
	c	−0.1697	0.1660	4.5
$Ti_{19}H_7$	a	−0.1612	0.1573	4.3
	b	−0.1485	0.1458	4.0
	c	−0.1403	0.1581	4.3

from independent calculations on the neutral and positive ion systems, $E(\mathrm{M}^+) - E(\mathrm{M})$; these energies are also in fairly good agreement with the Koopman values ($-e_{\max}$). Experimentally, the work function increases when an overlayer of hydrogen forms on titanium, and theoretical slab calculations by Feibelman et al. (13) show a change of 0.2 eV in good agreement with experiment.

For the present choice of boundary potentials, the change in work function in going from Ti_{19} to the H overlayer model $Ti_{19}H_7$ is +0.3 eV for the assignment of 0 or 2 electrons to the boundary potential, in agreement with experiment, but −0.3 eV for the assignment of 3 electrons to the boundary potential. A single H atom adsorbed on the surface does not show the same trend in ionization energy as the H overlayer. Clearly, a choice of spherical densities for the assigned boundary electrons is only qualitatively correct, and considerable refinement is needed before it can be argued that the Coulomb and exchange interactions of *s*-electrons excluded from the active valence space are accurately represented. In the present work, however, we proceed in all subsequent calculations to assign two electrons to the fixed, spherical boundary densities as described above.

4. Geometries, basis set and embedding calculations

The titanium cluster used to study the effect of chemisorbed hydrogen on the strength of Ti-Ti bonds and the local energetics consists of two layers of 12 and 7 metal atoms each, as described previously, and by an additional Ti adatom above the surface, corresponding to the geometry of the unreconstructed *hcp* lattice, with metal-metal distances equal to that in the bulk (5.5769 bohr nearest neighbor distance). See Fig. 1. The local region is formed by the Ti adatom, its three nearest neighbors and hydrogen. All other Ti atoms are defined as boundary atoms and as such are modelled as described in the previous section. The model relates conceptually to the dissociation of a titanium adatom from a three-fold site on Ti(0001) surface.

A chemisorbed hydrogen atom is considered at three different sites: atop the Ti adatom at the optimized distance of 3.5 bohr [7], in the interstitial position at the center of the tetrahedron defined by the local region atoms, and finally, above the three fold site formed by the Ti adatom and two other Ti atoms in the surface layer. The dissociation fragments studied are Ti_{19}, $Ti_{19}H$, Ti_{20}, TiH and Ti.

The 1*s*, 1*s*′ functions of hydrogen and the 4*s*, 4*s*′, 3*d* and 4*p* basis orbitals of titanium are reported in Table 3, while the core functions are taken from [1]. The 4*s*′ orbital used to improve the flexibility of the valence region is more contracted spatially than the atomic 4*s* to better describe charge transfers to the hydrogen atom. The single-zeta *d* orbital is optimized for the $\mathrm{Ti}(d^3s)$ excited state which is the principal configuration of the bulk metal and the configuration obtained in previous studies on titanium [3-5].

The boundary atoms have only 4*s* and 4*s*′ orbitals with the *d* electrons treated by a core pseudopotential, and on the local region Ti atom there are 4*s*, 4*s*′ and 3*d* orbitals. In preliminary calculations, these atoms were also enriched by 4*p*

Table 3. Gaussian expansion of valence orbitals for titanium and hydrogen atoms. Titanium orbitals are orthogonal to the atomic core orbitals on the same nucleus

Orbital	Exponent	Coefficient	Orbital	Exponent	Coefficient
4*s*	129.0	−0.02793036	4*s*′	129.0	−0.04251376
	7.89	0.11573841		7.89	0.17700439
	0.716	−0.36757538		0.716	−0.59397975
	0.04	1.05140434		0.0774	0.133
3*d*	5.05771	0.26893976	4*p*	18.6	0.02839479
	1.1567	0.54125050		0.883	−0.13615484
	0.25896	0.51981596		0.0434	1.00656895
1*s*	32.39346	0.3154	1*s*′	0.10297	1.0
	4.95977	0.22826			
	1.1478	1.0			
	0.32585	2.47509			

functions, but these functions were deleted from the basis because of a near linear dependency with combinations of 4*s* and 4*s*′ functions on the surrounding nuclei.

A demonstration of the simulation of 4*p* orbitals by surrounding 4*s* orbitals can be seen in a calculation of the energy of a Ti atom with a 4*s*, 4*s*′ basis on the atom and 4*s* and 4*s*′ basis functions at origins corresponding to Ti_4. Without *p* functions the calculated CI energy is −3.3947 a.u. which is close to the value obtained for the free atom of −3.4007 a.u. calculated using 4*p* orbitals; the free atom energy is −3.3858 a.u. without 4*p* orbitals.

Calculations are carried out in three stages following the embedding theory described in Sect. 2. In the first stage only a basis set of 4*s*, 4*s*′, 1*s* and 1*s*′ functions is used to describe the Ti lattice and hydrogen; all *d* electrons are represented by a core potential. A localization transformation of the resulting molecular orbitals about the local region orbitals is carried out by exchange maximization, thus defining a local region electronic subspace. Localized occupied and virtual orbitals are then used together with the 3*d* functions in a second SCF calculation. CI calculations are then carried out after another localization transformation to enhance convergence, and all configurations arising from single and double excitations with an interaction energy greater than 1×10^{-5} a.u. with the SCF configuration are retained in the expansion; details of the procedure are given in [4].

Calculations are carried out for a variable number of singly occupied orbitals, but the lowest energy always corresponds to that of a system with three unpaired *d* electrons for each local region Ti and with the minimal number of singly occupied orbitals coming from the *s* electronic system. Calculations carried out without performing the first localization transformation and without any constraint in the exterior region did not always converge.

5. Results

Calculated energies of all Ti_n and Ti_nH fragments are given in Table 4 along with charges on H, the Ti adatom and the neighboring three Ti atoms. Energies are from configuration interaction calculations. For Ti and TiH, energies are also reported for the treatment including 4*p* orbitals since near linear dependence does not occur in these systems and these values are used to compute dissociation energies when Ti or TiH occur as products. Figure 2 gives an overview of the relative energetics of the various fragments and the fragmentation reactions that could occur on hydrogen atom adsorption; included in the figure is a similar analysis of the results from the previous small cluster studies of Ti_4 and Ti_3H. Table 5 gives additional details for each reaction.

The basis superposition errors for Ti_{19} and $Ti_{19}H$ are evaluated with respect to Ti_{20} and $Ti_{20}H$, with H in each of the three adsoprtion sites, while for Ti and TiH they are computed with respect to Ti_4 and Ti_4H. These corrections are also reported in Table 5. Such superposition error calculations are only approximate since in the combined system the basis is already partially occupied. The results of Table 5 show that the 4*p* and the superposition corrections do not modify the energetic trend of the dissociation reactions.

There are several points of qualitative agreement between the small cluster results and the present embedding calculations. As seen in Fig. 2, the reaction of H with the metal is exothermic in both cases, but much stronger bonding occurs with the adatom surface. In both cases, the energy required to remove a Ti atom from the surface after adsorption of H is comparable to the exothermicity of the initial reaction of H with the surface. Thus, for the adatom surface, the exchange reaction

$$Ti_{20} + H \rightarrow Ti_{19}H + Ti$$

Table 4. Energies of Ti_n and Ti_nH fragments from CI calculations. Boundary atoms are modelled to simulate the embedding of the clusters in a metal lattice (see text). Charges from a Mulliken population analysis are reported for H, the Ti adatom in Ti_{20} systems and the sum of populations on nearest neighbor Ti_3 atoms in the surface layer

System	Energy (a.u.)	q(H)	q(Ti)	$q(Ti_3)$
H	−0.499809			
H_2	−1.146122			
Ti	−3.385857[a]			
	−3.400716[b]			
TiH	−3.939170[a]			
	−3.943664			
Ti_{19}	−12.968916			0.156
Ti_{20}	−16.520684		0.413	0.039
$Ti_{19}H$ (above surface)	−13.608426	−0.698		0.946
$Ti_{20}H$ (apical)	−17.159598	−0.662	0.482	0.191
$Ti_{20}H$ (lateral)	−17.173433	−0.701	0.522	0.095
$Ti_{20}H$ (interstitial)	−17.199054	−0.616	0.213	0.628

[a] Calculation without 4*p* orbitals

[b] Calculations with 4*p* orbitals

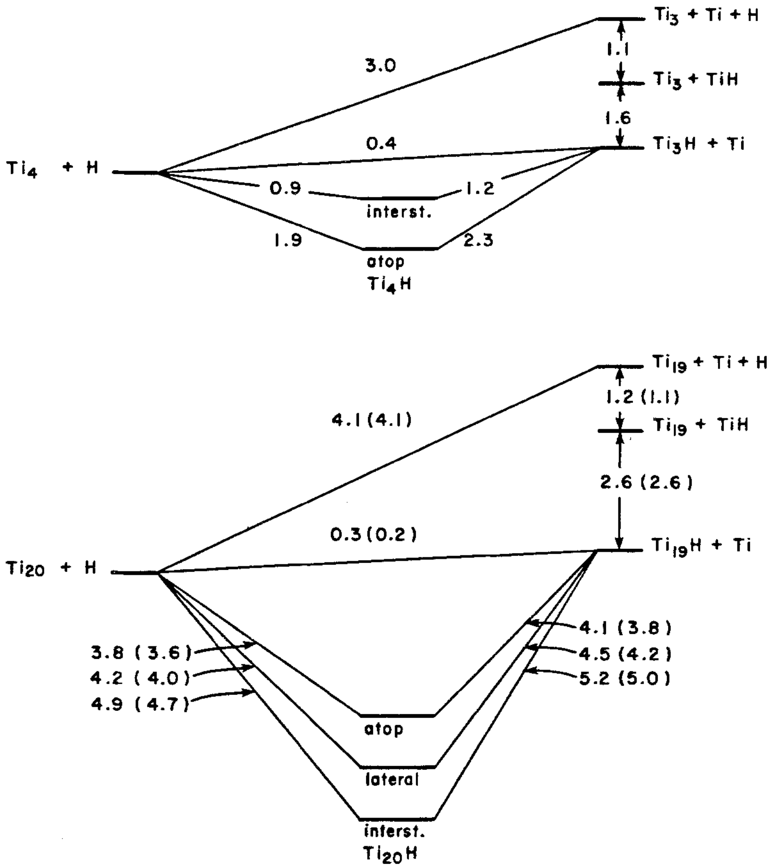

Fig. 2. Relative energetics (in eV) of H adsorption on Ti_4 and Ti_{20} and of fragmentation reactions involving removal of the Ti adatom. Hydrogen atom adsorption on the Ti_{20} adatom surface is highly exothermic for all three adsorption sites. Energetically favored products leave H on the Ti(0001) surface in a 3-fold adsorption site. The exchange reaction of H with the Ti adatom is only slightly endothermic, 0.3 (0.2) eV. Energy changes calculated employing basis superposition corrections (in parentheses) are only slightly smaller than the uncorrected values

is endothermic by only 0.3 eV. If the source of the hydrogen were H_2, however, the reaction

$$Ti_{20} + 1/2H_2 \rightarrow Ti_{19}H + Ti$$

would be endothermic by 4.72/2 eV + 0.3 eV = 2.7 eV, where 4.72 eV is the dissociation energy of H_2.

Another point of agreement of the two studies is the relative energies of the products. As shown in Fig. 2, the energetically most stable product always leaves H on the surface (in the present work in a three-fold adsorption site 1.3 Å above the surface). The bonding in TiH is not strong enough, compared to bonding of H with the surface, to favor formation of the TiH product.

Table 5. Energetics of the fragmentation reactions of Ti_{20} and $Ti_{20}H$. The H adsorption sites in Ti_{20} are: atop atom, at a lateral 3-fold site involving the adatom and two Ti atoms in the surface layer, and in an interstitial tetrahedral site below the adatom. Basis superposition energy corrections must be subtracted from ΔE to obtain the corrected dissociation energies. All values are in eV

		Basis[c] superposition corrections		
$A+B \rightarrow C+D$	ΔE^a	I	II	ΔE^b (corrected)
$Ti_{20} \rightarrow Ti_{19}+Ti$	4.11	0	0.06	4.05
$Ti_{20}+H \rightarrow Ti_{19}H+Ti$	0.31	0.01	0.06	0.24
$\rightarrow Ti_{19}+TiH$	2.94	0	0.03	2.91
$Ti_{20}H$ (apical) $\rightarrow Ti_{19}H+Ti$	4.09	0.01	0.24	3.84
$\rightarrow Ti_{19}+TiH$	6.72	0	0.03	6.69
$Ti_{20}H$ (lateral) $\rightarrow Ti_{19}H+Ti$	4.47	0.01	0.23	4.23
$\rightarrow Ti_{19}+TiH$	7.10	0.32	0.03	6.75
$Ti_{20}H$ (interst.) $\rightarrow Ti_{19}H+Ti$	5.17	0.01	0.21	4.95
$\rightarrow Ti_{19}+TiH$	7.79	0.90	0.03	6.86

[a] All reactions are endothermic as written

[b] Dissociation energies are calculated including 4*p* orbitals on Ti and TiH. Without 4*p* orbitals the energies of Ti and TiH would increase by 0.4 and 0.1 eV, respectively

[c] Column I refers to energy correction to Ti_{19} or $Ti_{19}H$. Column II refers to energy correction to Ti or TiH

Figure 2 shows the reaction of H with Ti_{19} to be exothermic by 3.8 eV in fair agreement with previous studies of H on the Ti(0001) surface which gave 3.5 eV. Differences in the two studies can be ascribed partly to differences in treating the correlation energy of H_2. The present values are those directly calculated for H atom adsorption, while the 3.5 eV value was deduced from calculation on the dissociative adsorption of H_2.

Figure 2 also shows the reaction of H with the adatom surface in the lateral 3-fold site is 0.35 eV more exothermic than reaction with the planar Ti(0001) surface at a 3-fold binding site. For the other sites as well, the adatom surface binds H more strongly than the planar surface based on previous studies on Ti(0001). In agreement with previous results on titanium-hydrogen interactions [3–5, 7] and experimental inferences [6–14] there is always a net transfer of electrons from titanium to hydrogen with a clear indication of hydridic hydrogen for both interstitial and surface H, see Table 4.

A hydrogen adsorbed in an interstitial site is energetically favored over H above the surface even without considering lattice reconstruction. This result does not agree with the previous calculation of H in a tetrahedral interstitial site below the Ti(0001) surface nor with the small cluster result for Ti_4H. As noted above, the binding energy of H to the surface is larger than in the previous work on Ti(0001) apparently due to greater reactivity of the adatom region. In the small cluster model apparently insufficient charge transfer can occur to the H to produce a stable interstitial H. Similarly, the binding energy of H to the Ti lattice is now found to be much larger than in the small Ti cluster as shown in Fig. 2. This result does not support the energetic trend found in Ti_4H calculations [7], where the cluster with interstitial hydrogen was less stable than that with H in an atop position. Moreover, the energy required to remove a Ti atom starting with H in the interstitial site is now greater than required starting with H adsorbed at the atop site, the latter is comparable to the energy (4.1 eV) required to remove the adatom in the absence of hydrogen. Consequently, one should infer that H chemisorption has not weakened the bonding of the adatom to the surface. However, the high exothermicity of the initial reaction of H with titanium could lead to extensive lattice reconstruction.

The physical basis of the embedding argument applied in the present work is discussed in [2] where convergence studies of surface localized orbitals are presented for titanium clusters ranging from 1 to 84 atoms. The purpose of embedding is to create a local subspace that is accurately described, but which by virtue of its improved description (extended basis and CI) does not produce electron polarization of the cluster as an artifact. The work function calculations suggest that the present modelling is consist with experiment both for the W_f of Ti and ΔW_f on formation of a hydrogen overlayer.

In the present work, large differences are found between the bonding capabilities of Ti_4 and Ti_{20} (embedded) systems. There are, however, many examples in the literature involving adsorbate energetics and vibrations where small cluster models provide accurate descriptions, and the question arises in what instances should a small cluster description such as Ti_4 fail. In clusters such as Ti_3 and Ti_4, the absence of neighboring atoms of the lattice means that the $4s$-$4p$ bonding is largely determined by symmetry leading to open shell occupancies, whereas in much larger clusters, the near degeneracy of the s-band orbitals near the Fermi level allows singlet states to develop, and more importantly, decreases the physical significance of different orbital occupancies on the boundary of the clusters [2]. In addition, small metal clusters differ from large clusters in their ability to transfer charge to adsorbates. For electronegative adsorbates such as O, and even H in the case of bonding to a metal (see Table 4), considerable charge transfer occurs from the metal to the adsorbate. In the case of a small cluster, these electrons must come from a small number of metal atoms, and to preserve the metal-metal bonding this necessarily limits charge transfer. For large, multilayer clusters, smaller charge transfer can take place from individual atoms while still achieving large charge transfer to the adsorbate.

In summary, the conclusions of the present study of a Ti adatom on the close packed (0001) surface of titanium and its interactions with a H atom are as follows:

1. The Ti adatom is strongly bound to the surface (4.1 eV dissociation energy).
2. Reaction of a H atom with a clean Ti(0001) surface or with a Ti adatom on the surface is highly exothermic (3.6 eV–4.7 eV depending on the site) with higher coordination adsorption sites preferred for hydrogen.
3. Hydrogen atom adsorption at the adatom site, once the energy of the H atom reaction is dissipated, does not weaken the bonding of the adatom to the lattice;

more energy is required to remove the Ti adatom after H adsorption than for a Ti adatom on the clean surface.

4. The energetically preferred product for removal of the adatom is a Ti atom and not TiH; H remains on the surface in a three-fold site.

5. Reaction of H already adsorbed on Ti(0001) with a Ti adatom on the surface is exothermic leading to the possibility of structural rearrangements in the H-Ti-surface region.

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