Chemisorption Theory: Dissociation of H_2 on Ti (0001)

P. Cremaschi[a] and J. L. Whitten
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

(Received 4 February 1981)

The chemisorption of H_2 on Ti(0001) is treated with use of an *ab initio* configuration-interaction theory for the surface region. Dissociation of H_2 occurs above the surface but more stable threefold coordination sites lie closer to the surface at ~ 1.3 Å. Adsorption in adjacent threefold sites is less stable than in separated sites sharing only one surface atom. Bonding is predominantly with the 4s electrons of the metal leading to hydridic hydrogens and a polarized lattice electronic distribution.

PACS numbers: 82.65.Nz, 73.20.-r

A localized orbital theory describing molecule-solid surface interactions using correlated wave functions for the surface region is applied to the chemisorption of H_2 on Ti(0001). Dissociative adsorption of H_2 is predicted with dissociation occurring above the surface layer, followed by migration of H atoms to energetically favored threefold coordination sites closer to the surface. The relative energetics of different adsorption sites is investigated and the role of s and d electrons in adsorbate-surface bonding is discussed.

The theory, described in detail by Whitten and Pakkanen,[1] is based on a self-consistent-field (SCF) cluster model for the lattice, treated approximately, from which an N-electron subspace for a local region is defined by a unitary localization transformation. This local subspace which includes the H_2 adsorbate is then treated accurately, with use of an improved orbital basis and ***ab initio*** configuration-interaction techniques, as embedded in the fixed field of the interior of the lattice.

The cluster model of the unreconstructed Ti(0001) surface and a seven-atom region defining the adsorption sites considered for dissociated H_2 is depicted in Fig. 1. In the initial SCF calculations the system is treated at the simplest possible level with use of only a Ti 4s and H 1s basis, with the 3d electrons localized in a spherically averaged $(3d)^3$ core configuration. Gaussian expansions of atomic orbitals are used throughout. A localization transformation of the SCF solution is carried out by exchange maximization with the seven Ti atoms in the adsorption region plus hydrogen. Thus, letting $\{\varphi_k\}$ denote the SCF orbitals and $\{\chi_k\}$ the set of valence atomic orbitals on the seven Ti atoms and H_2, the positive definite exchange integral sum

$$\gamma = \sum_k \langle \chi_k(1)\chi_k(2)|r_{12}^{-1}|\varphi'(1)\varphi'(2)\rangle \geq 0$$

is maximized, where $\varphi' = \Sigma_i c_i \varphi_i$. Occupied and virtual orbitals are transformed separately. The resulting eigenvalue spectrum, $\gamma_1 \geq \gamma_2 \geq \gamma_3 \cdots$, is used to identify orbitals localized in or near the adsorption region, i.e., those φ_k' with large γ_k. The basis was then improved locally by freeing d orbitals on the seven Ti atoms, and by adding Ti 4s' atomic orbitals and 1s' and $2p_\perp$ orbitals on each hydrogen. Ti 4p orbitals are not included since these orbitals show near linear dependency with the above basis and the localized lattice orbitals.[2] Final SCF calculations were carried out with use of these additional basis functions plus the nine occupied and seven virtual most localized orbitals from the transformed SCF solution. Remaining occupied orbitals define the fixed Coulomb and exchange field of the interior of the lattice in both the SCF and subsequent configuration-interaction (CI) treatment of the local region. CI expansions contain approximately 300 configurations, and based on molecular results this type of solution

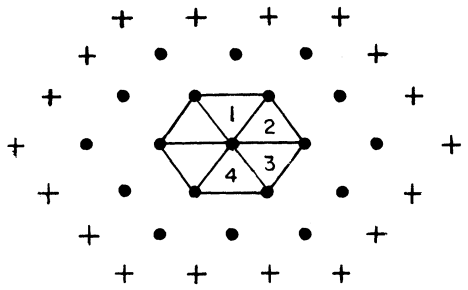

FIG. 1. Cluster model of Ti(0001) showing threefold hydrogen adsorption sites investigated. Only the surface layer is shown, the second and third layers of the hcp lattice contain 12 and 7 atoms, respectively, with a second layer atom under site 1. In addition, these atoms are surrounded by a total of 45 fixed atomic distributions, Ti 4s $(3d)^3$ spherically averaged, shown as pluses, which provide a slight stabilization of the boundary. The Ti-Ti nearest-neighbor distance is 5.5769 a.u. (2.9524 Å).

TABLE I. Adsorption sites for H_2 on Ti(0001) and binding energies. Adsorption energies from configuration-interaction calculations on the surface region plus adsorbate are given for molecular and dissociated H_2 cases. The H-H axis is always parallel to the surface plane.

Distance above surface (a.u.)[a]	Description[b]	Adsorption energy (eV)[c] SCF	CI
∞	clean surface + molecular H_2	0.0	0.0
4.0	adsorption,[d] molecular H_2	−0.1	−0.1
3.25	adsorption,[d] molecular H_2	−0.7	−0.5
3.25	adsorption,[d] dissociated H_2, threefold site 1-4	−0.2	1.5
2.5	adsorption,[d] dissociated H_2, threefold site 1-4	0.4	1.5
2.5	adsorption,[e] dissociated H_2, threefold site 1-3	0.5	1.7 (40 kcal/mole)
2.5	adsorption, dissociated H_2, threefold site 1-2	−0.4	0.4

[a] Vertical distance from H to the surface plane of Ti nuclei, 1 a.u. = 0.5294 Å.

[b] Surface sites labeled in Fig. 1. Molecular H_2 refers to the free-molecule equilibrium distance of 1.42 a.u.

[c] $E(\text{cluster}) + E(H_2) - E(\text{cluster}\cdot H_2)$. The clean-surface treatment includes H $2p_\perp$ functions at 4 a.u. to decrease the basis-set superposition error (Ref. 3). A positive sign indicates an exothermic reaction.

[d] H atoms are equidistant from the central Ti in a plane perpendicular to the surface containing sites 1 and 4 of Fig. 1.

[e] H atoms are above second-layer atoms in the hcp extension.

should give a binding energy accuracy of ~0.3 eV.

Preliminary calculations on H-Ti_4 (tetrahedral) and H_2-Ti_7 (planar) showed atop-atom and bridge adsorption sites to be energetically less stable than the threefold coordination site for which a shallow energy minimum was found for H at a vertical distance of 2.5 a.u. (1.32 Å) above the plane. Based on this information, seven different molecular and dissociated H_2 adsorption cases were selected for the present study. In all cases, the H-H axis is parallel to the surface with hydrogens in different threefold sites on the surface and at different distances from the surface.

Table I shows calculated binding (adsorption) energies for each adsorption site. In assessing the reliability of these energies, there is some uncertainty in assuming that the clean surface plus molecular H_2 limit is treated at the same accuracy as the adsorption cases. However, the error appears minimal since the system is calculated to be within 0.1 eV of the desorbed H_2 limit at 4 a.u. from the surface. The differences between the SCF and CI results show the importance of electron correlation in the description of the H_2-Ti (surface) bonding.[4]

Several definitive conclusions can be drawn from the results of Table I. First, if H_2 approaches the surface with the H-H bond parallel to the surface atop a Ti atom the potential becomes repulsive if the H-H distance is not lengthened. Second, the energy decrease on H-H stretch suggests dissociation of H_2 at a distance significantly above the surface (>1.72 Å), but energetically more stable hydrogen positions lie closer to the surface at ~1.32 Å, in threefold coordination sites. Adsorption in adjacent threefold sites (H's at 1 and 2 in Fig. 1) is unfavorable compared to separated (1-3) or across-atom (1-4) sites. Of the latter two sites the (1-3) site is favored but the small difference in binding energy may not be significant. The calculated binding energy of 1.74 eV (40 kcal/mole) is in good agreement with the experimental value of 35 kcal/mole for H_2 adsorption on Ti films.[5] No experimental evidence is available for the structure of H on Ti, but low-energy electron diffraction (LEED) studies[6] on the close-packed surface of Ni, which is similarly reactive to hydrogen, shows adsorption in threefold sites with avoidance of the adjacent sites as described above. In addition, local density of states calculations by Feibelman and Hamann[7] show good agreement with ultraviolet photoelectron spectroscopy data for H adsorbed in threefold sites above the surface.

On the question of 3*d* vs 4*s* bonding to the hydrogens, the bonding predominantly involves 4*s* electrons.[8] Although many $d \rightarrow s$ excitations occur in the CI expansion the Ti 3*d* population remains within 0.02*e* of being d^3 on the seven atoms surrounding the adsorption sites. The hydrogens are strongly hydridic with electron density transferred mainly from neighboring Ti atoms of the lattice but with significant changes occurring on the next nearest neighbors as well.[4]

This work was supported by the U. S. Department of Energy under Contract No. DE-AC02-77ER04387 and by the Petroleum Research Fund administered by the American Chemical Society. One of us (J.L.W.) wishes to acknowledge support by the Alexander von Humboldt Foundation. Work began at the Lehrstuhl für Theoretische Chemie der Universität Bonn.

---

[a] Permanent address: Centro del Consiglio Nazionale delle Ricerche per lo Studio delle Relazioni tra Struttura e Reattività Chimica, Milano, Italy.

[1] J. L. Whitten and T. A. Pakkanen, Phys. Rev. B 21, 4357 (1980).

[2] The diffuse H 1s' orbital when orthogonalized to lattice 4s orbitals creates a lobe representation of the Ti 4$p_\perp$ orbital. Similarly, in-plane 4p orbitals are approximated by combinations of 4s orbitals on other nuclei.

[3] W. Kolos, Theor. Chim. Acta 51, 219 (1979).

[4] A more detailed analysis of bonding including comparisons with small-cluster results on H_2-Ti_7 will be published.

[5] G. F. Wedler and H. Strothenk, Z. Phys. Chem. (Frankfurt am Main) 48, 86 (1966).

[6] M. A. von Hove, G. Ertl, K. Cristmann, R. J. Behm, and W. H. Weinberg, Solid State Commun. 28, 373 (1978).

[7] P. J. Feibelman and D. R. Hamann, Phys. Rev. B 21, 1385 (1980).

[8] The same result has been found in *ab initio* calculations of H-atom adsorption on Ni clusters, T. H. Upton, W. A. Goddard, III, and C. F. Melius, J. Vac. Sci. Technol. 16, 531 (1979).

Dynamics of the Iron-Containing Core in Crystals of the Iron-Storage Protein, Ferritin, through Mössbauer Spectroscopy

S. G. Cohen,[a] E. R. Bauminger, I. Nowik, and S. Ofer
Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

and

J. Yariv
Department of Biophysics, Weizmann Institute, Rehovot, Israel

(Received 19 January 1981)

^{57}Fe γ-ray resonance-absorption spectra in crystals of the iron-storage protein, ferritin, display above 265 °K, in addition to a normal quadrupole doublet, wide Lorentzian wings extending to velocities of ± 2 cm/sec. The results are interpreted in terms of the dynamics of the iron-containing core of the protein, undergoing bounded diffusive motion within a "cage," characterized by a jump probability per unit time of about 0.5×10^8 sec^{-1} and a mean-square displacement of about 4.8×10^{-2} Å^2 at 298 °K.

PACS numbers: 87.15.By, 33.45.+x, 63.90.+t

We report here on measurements of ^{57}Fe γ-ray resonance absorption in crystals of the iron-storage protein, ferritin.[1] The spectra obtained above 265 °K are of a striking and unusual shape. In addition to a relatively narrow part, characteristic of the Mössbauer effect as usually observed in solids, the spectra display very broad wings extending to velocities up to ± 2 cm/sec. Upon freezing, the broad wings disappear. The results are interpreted in terms of the dynamics of the iron-containing core of the protein undergoing bounded diffusive motion within a "cage."

Ferritin is the well-known soluble iron-storage protein widely found in man, animals, plants, and fungi and is composed of a protein and an iron-containing inorganic material. The protein part is composed of 24 identical subunits and has the shape of a spherical shell of 120-Å outer diameter and 70-Å inner diameter. The iron inorganic compound of approximate formula $(FeOOH)_8$-$(FeO\cdot OPO_3H_2)$ is contained in the inner cavity.[2,3] The occupancy of the inner cavity by iron is variable from zero to full corresponding to a maximum of about 4000 iron atoms per molecule.

The protein can be crystallized as cubic crystals, which contain about 50% water by weight. Absorbers I and II consisted of a suspension of single crystals of horse-spleen ferritin in an agar gel (2% agar in an aqueous solution of pH 7.0 with 0.05*M* *tris*-acetate buffer and containing