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Limits of Chemical Effects on Cold Fusion

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Cold fusion enhanced by chemical confinement of deuterons has been suggested as an explanation of recent reports of the production of neutrons in electrochemically-generated palladium deuterides. To test this suggestion local-density-functional cluster calculations were used to study the coulomb barrier between two deuterons within the octahedral cage in crystalline palladium. The calculated repulsive forces were always greater than the corresponding forces between deuterons in molecular D_2. These results imply that the room temperature fusion rate at this site is negligible.

KEY WORDS: Palladium-deuterides; D_2; clusters; density-functional calculations.

1. INTRODUCTION

Two groups[1,2] have recently announced experimental evidence for fusion accompanying the room temperature electrochemical insertion of deuterons into palladium[1,2] and titanium[2] electrodes. Jones *et al.*[2] reported the detection of ~2.5 MeV neutrons, expected from the *d - d* fusion reaction

$$d + d \rightarrow {}^3He + n\ (2.45\ MeV) \qquad (1)$$

From their data they estimated that deuteron fusion processes were occurring at their metal cathodes roughly at rates of 10^{-23} fusions per deuteron pair per second (f/*dd*/sec)- more than 40 orders of magnitude larger than the corresponding fusion rate expected for deuterons in free D_2 molecules in their ground state.[2-4] Fleischmann, Pons, and Hawkins[1] (FPH) report the detection of 2.22 MeV gamma-rays expected from the neutron capture process

$$p + n \rightarrow d + \gamma(2.22\ MeV)$$

Assuming that the captured neutrons arose from Eq. (1), FPH estimated that deuteron fusion processes were occurring at their palladium cathodes at rates of about 10^{-19} f/*dd*/sec. FPH also report the observation of tritium expected from the deuteron fusion reactions,

$$d + d \rightarrow t + p$$

These remarkable experimental reports have attracted worldwide attention and caused considerable debate.[5] At this time, many experimental groups have found no evidence for electrochemically-induced fusion, while others have reported results which may support the existence of this effect.[6] Although the interpretation of the original experiments is still in dispute,[7,8] a number of ideas, which assume that observable levels of electrochemically-induced fusion do occur,[2,9-15] have been suggested to partially account for the results of Refs. 1 and 2.

In their original paper,[2] Jones *et al.* propose that the deuteron fusion they report results from what they term "cold fusion," where the dominant factor is not the relative kinetic energies of the two fusing deuterons but rather their equilibrium separation. These authors note that the cold fusion rate is strongly dependent on this equilibrium separation[16-18] and suggest that the fusion rate they report could be achieved by the "squeezing" of deuterons in the metal lattice to a separation of about half the molecular D_2 chemical bond distance, ~0.7 bohr.

If such a picture provides an explanation of the data, then the width of the coulomb barrier for deuteron-deuteron fusion in free D_2 molecules must be severely reduced in the metal lattice. To test this assumption, we have carried out an extensive set of model calculations using established embedded atom, local-density-functional (LDF), and Hartree–Fock (HF) methods. An account of some of the results of that study has already appeared.[19] The conclusions reported therein were subsequently supported by additional molecular dynam-

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ics,[20] LDF (both cluster[21] and band-structure)[22,23] and HF calculations.[24,25] Herein we focus on our LDF results. In Section 2, we outline our approach. Next, in Section 3 we describe and extend our earlier LDF cluster results for the effective interaction between two deuterons in the neighborhood of the octahedral site in crystalline palladium. The new results reported in Section 3 reinforce our earlier conclusion that cold fusion—enhanced by chemical confinement of deuterons in the palladium cathodes—is not important in interpreting the experiments of FPH and Jones *et al.*

2. COMPUTATIONAL METHODS

Our total-energy cluster calculations are based on first-principles spin-unrestricted (nonrelativistic) LDF theory. Relativistic corrections for palladium will have only minor effect on the results.[26] This LDF theory leads to the usual set of one-electron equations

$$\left[-\frac{1}{2}\nabla^2 + V_C + V_{xc\sigma} \right] \phi_{i\sigma} = \epsilon_{i\sigma}\, \phi_{i\sigma} \qquad (2)$$

for an electron of spin σ in spin orbital $\phi_{i\sigma}$ with eigenvalue $\epsilon_{i\sigma}$. The coulomb potential, V_C, includes both the electron-nuclear attraction and the classical interelectron coulomb repulsion; in what follows we assume the Slater Xα form for the local exchange-correlation potential,

$$V_{xc\sigma}(r) = -3\alpha\, [3\rho_\sigma(r)/4\pi]^{1/3}$$

with $\alpha = 0.7$. The quantity $\rho_\sigma(r)$ denotes the charge density of an electron with spin σ at the position r. The linear combination of Gaussian-type-orbitals (LCGTO) method of Dunlap, Connolly, and Sabin[27] is used to solve the differential Eq. (2) self-consistently. These solutions are then used to calculate the total energy of the cluster from the corresponding Xα energy functional.

The calculations were implemented by using a 17s/11p/8d basis[28] for Pd and a 6s basis[29] for D. Both basis sets were augumented with a polarization function of exponent of 1.0 bohr^{-2}. A more complete description of the basis sets used (including the orbital contraction scheme and the derived basis for fitting the potentials) is given elsewhere.[30] We have shown that this LCGTO-LDF method correctly predicts the ground state electronic configuration for atomic Pd and molecular PdH, and yields equilibrium bond lengths and vibrational frequencies in excellent agreement with experiment for molecular H_2 and ^{108}PdH. These results suggest that this approach should give reliable results for palladium-deuterium clusters.

3. RESULTS AND DISCUSSION

For PdD_x with $x \leq 1$, deuterium atoms prefer the octahedral interstitial site.[31] Therefore, we chose to concentrate on calculating the effective interaction between two deuterium atoms within the octahedral cage surrounding this site. In these calculations, we modeled the octahedral site by a cluster containing the six surrounding Pd atoms. The positions of these six atoms were fixed at their locations in the empty fcc lattice. Two deuterium atoms were introduced into the interior of this cluster, and the interaction between them was studied along several specified directions. The center of the octahedral site is the lowest energy position of a single D atom, hence, only centrosymmetric positions of these two deuterium atoms within the cluster were considered. An example of the sort of Pd_6D_2 clusters we have treated is shown as an insert in Fig. 1. In that example, the D-D axis is oriented along the {100} direction of the fcc lattice.

The binding energy for two deuterium atoms along a given axis separated by a distance r within the same octahedral cage, $U_{DD}(r)$, was defined with respect to the energy of the system when each of these two atoms is at a different octahedral site. Therefore, if U_{DD} is negative, the system energy is lowered by pairing deuterium

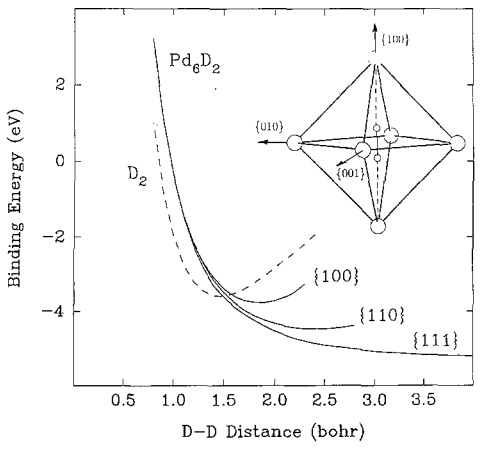

Fig. 1. The solid curves depict calculated total energies of the Pd_6D_2 cluster within LCGTO-LDF approach for centrosymmetric arrangements of deuterium pairs along {100}, {110}, and {111} directions of the fcc lattice. The dashed line depicts the D_2 gas-phase potential, also calculated using LCGTO-LDF method. The insert illustrates a sample Pd_6D_2 cluster with the D-D axis along the {100} direction.

atoms in the immediate vicinity of octahedral sites, but if U_{DD} is positive, single occupation of these sites is favored. Within our cluster approach U_{DD} is given by

$$U_{DD}(r) = E(Pd_6D_2;r) - 2 \cdot E(Pd_6D) + E(Pd_6)$$

where $E(Pd_6D_2;r)$, $E(Pd_6D)$, and E (Pd_6) are the total energies of the Pd_6 cluster containing two, one, and zero deuterium atoms, respectively. These energies were calculated using the LCGTO-LDF method sketched previously. Spin-unrestricted calculations were required to treat the odd-electron cluster Pd_6D but spin polarization effects were nil in the even-electron clusters, Pd_6D_2 and Pd_6.

We have calculated $U_{DD}(r)$ for the D-D axis oriented along the {100}, {110}, and the {111} directions of the fcc metal lattice. In all three cases and for all values of r studied, $U_{DD}(r)$ was always greater than zero. Therefore, provided empty octahedral sites are available in the metal lattice, these results predict that the system energy is never lowered by pairing deuterium atoms within a single octahedral cage. This conclusion is in agreement with the known behavior of low concentrations of H in Pd.

Our results for $U_{DD}(r)$ are summarized in Fig. 1. In plotting these results, U_{DD} was shifted downward by twice the energy required to remove a deuterium atom from the center of the octahedral cluster, 5.87 eV. Therefore, the solid curves in Fig. 1 represent the energy gained by bringing together within the octahedral cluster two deuterium atoms from the vacuum. This rigid shift in U_{DD} allows easy comparison of our results to the gas phase D_2 binding energy curve—D_2, in contrast to two deuterium atoms in the octahedral cage, is bound.

For the D-D axis constrained to lie along the {100} direction there is a minimum in $U_{DD}(r)$ at $r \approx 1.9$ bohr. This minimum was also found by Sun and Tománek[22] in their recent LDF band structure studies. Figure 1 shows, however, that this D-D orientation is unstable with respect to orientations with the D-D axis along either the {110} or {111} directions. Because orienting the D-D axis along the {111} direction yields the lowest relative energy, these results confirm our earlier conclusions based on embedded atom calculations[19] that two deuterium atoms placed in the octahedral cage of crystalline palladium would tend to maximize their separation along the {111} direction. These embedded atom results led us to consider only this direction in our initial LDF studies.[19] Although in Fig. 1 there is no local minimum along the {111} direction, the repulsive interaction with the octahedral site's next-nearest neighbors-which lie along the {111} direction outside the Pd_6 cluster studied-must eventually lead to a minimum as r increases. Wei and Zunger[23] have also very recently found that the {111} orientation is the most stable.

As Fig. 1 shows, we find no unusually short stable D-D separations within the octahedral cluster. Also comparing, for the same r, these results to the calculated D_2 binding energy curve (depicted in Fig. 1 as a dashed line) shows that the repulsive force between deuterons along all three directions is always greater than in molecular D_2. These results imply that the rate of cold fusion in the immediate neighborhood of the octahedral site in crystalline palladium is less than the corresponding fusion rate in free D_2 molecules[2-4]-10^{-64} to 10^{-74} f/dd/sec.

We have also studied the effective interaction between deuterons in the neighborhood of the tetrahedral site in crystalline palladium and titianium. Again we find no unusually short D-D equilibrium separations and at internuclear d - d distances less than 0.74 bohr the calculated d - d repulsion was always greater than the repulsive force between deuterons in D_2. These results, taken all together, imply that confinement of deuterium within metal-deuterides resulting from chemical forces cannot be used to explain the results of FPH and Jones *et al.*

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