CHEMICAL FORCES ASSOCIATED WITH DEUTERIUM CONFINEMENT IN PALLADIUM


Naval Research Laboratory, Washington, DC, USA

Received 13 April 1989; accepted for publication 13 May 1989
Communicated by J.I. Budnick

First-principles and empirical methods are used to study the effective interaction between two deuterons in a palladium lattice. No effects are found to suggest confinement of deuterons at distances much smaller than the gas-phase D₂ separation.

Fleischmann and Pons [1] have recently presented evidence for the nuclear fusion of deuterium induced by electrochemical means in palladium at ambient temperatures; additional work by Jones et al. [2] provides further support for this effect. At room temperature, where the kinetic energy of the nuclei is not a dominant factor, the fusion rate is strongly dependent on the equilibrium distance between the two nuclei [3]. The nuclear tunneling probability through the barrier introduced by internuclear Coulomb repulsion is such a sensitive function of this distance that fusion in liquid deuterium is negligible whereas muon catalyzed fusion occurs in $10^{-9}$ seconds because the nuclei are approximately 200 times closer together. Interpolating between these two rates, Jones et al. [2] suggest that the apparent fusion rate can be achieved by the “squeezing” of deuterons in the metal lattice to a separation on the order of ~0.3 Å. These authors speculate that such a confinement [2] might be achieved by quasi-electrons with large effective mass in the deuterated lattice. Screening of the bare deuterium–deuterium nuclei electrostatic repulsion requires variation of the electronic charge density on an even smaller scale. The uncertainty principle alone associates a high kinetic energy with this degree of localization. If “heavy” quasiparticles do not provide the mechanism for such deuteron confinement, then the question is raised of whether compressive forces exerted by the metal structure could lead to such a confinement of deuteron pairs at the necessary close proximity. Such confinement could conceivably be produced either by producing a minimum energy in the potential energy surface for a short D–D distance, or by screening effects from the metal charge distribution that substantially weaken the repulsive D–D internuclear potential.

To explore the possibility of such a mechanism, we have performed a set of model studies of the energetics of the deuterium–deuterium potential in a palladium crystal. One major objective has been to estimate, within the Born–Oppenheimer approximation, the effective interaction between two deuterons in a palladium lattice, at scales of 0.1–1.0 Å. We used embedded-atom empirical potential methods to study the effects of the periodic lattice on deuterium interstitials and used both local-density functional (LDF) and Hartree–Fock (HF) first-principles cluster calculations to study the energetics of deuterium nuclei in finite palladium clusters. Using these empirical and quantum chemical calculations we have sought, but not found, a position in the lattice where the deuterium pair has the unusually short internuclear separation that has been speculated as necessary for fusion [2]. These studies partially quantify the energetics of the deuterium–deuterium interaction in crystalline palladium. Because all of these results for electronic effects are based on the Born–Oppenheimer approximation and thus independent of nuclear mass, we will henceforth discuss all potentials with respect to hydrogen, with the
understanding that all such results are directly applicable to deuterium.

In our condensed-phase studies, energies and geometries are calculated using the embedded-atom method [4], an empirical potential approach. The potential functions for Pd and H are those reported by Daw and Baskes [4], with the potential functions for Pd determined by fitting to the lattice spacing, elastic constants, sublimation energy, vacancy formation energy and the binding energy difference between the bcc and fcc phases. The functions for hydrogen were determined by fitting to the embedding energies calculated by Puska et al. [5], and the heat of solution for H in Pd. Using these potentials, Daw and Baskes [4] have calculated a migration energy for H in Pd of 0.26 eV, and a lattice expansion of 4% upon formation of the PdH hydride. Both numbers are in agreement with the experimentally determined values of 0.26 eV and 3.5% (for PdH$_{0.6}$), respectively. These potentials have also been shown to predict subsurface occupation and phase changes for hydrogen adsorbed on Pd(111) [6].

The bulk crystal is modeled by 108 Pd atoms arranged in an fcc structure with periodic boundary conditions applied in all directions. Minimum energy structures were determined by relaxing the positions of all atoms using a direct minimization technique [7]. The cell boundaries were maintained at the 4% expansion of the hydride over pure Pd. In an attempt to locate a site within the Pd lattice where two hydrogen atoms might be held closely together, calculations were performed which differed in the number and initial positions of hydrogen atoms within the lattice. For hydrogen/palladium ratios less than one, the hydrogen atom prefers the octahedral interstitial site [8]. Therefore, we first considered two atoms in this site.

All of the octahedral interstitial sites within the crystal were first filled with H atoms. An additional H atom was then randomly placed in the vicinity of a filled octahedral site, and the system was allowed to relax. Ten positions were tried, and in each case the hydrogen atoms repelled each other and migrated towards opposite faces of the surrounding octahedral cell. The relaxed H–H bond distances varied from 1.68 to 1.35 Å, with no minima found at shorter distances. Next, the same PdH structure was used, but with one octahedral site occupied with three hydogens this time instead of two. Again the hydrogen atoms repelled one another and no potential energy minima were found for H–H bond distances shorter than 1.4 Å. The shortest H–H bond distances that we found occurred for the local configuration drawn in fig. 1a in the octahedral cage. The two relevant hydrogen atoms are darkened in the figure and the others (unshaded) occupy the remaining octahedral sites. As can be seen in the figure, the two hydrogen atoms repel each other along the diagonal of the cubic unit cell.

These results using empirical potential methods led us to carry out linear-combination-of-Gaussian-type-orbitals local-density functional (LCGTO-LDF) calculations [9] (X$\alpha$ with $\alpha=0.7$) on a D$_{4h}$-symmetric Pd$_6$H$_2$ cluster. This cluster contains the six equivalent palladium atoms that are at the faces of a cube surrounding the octahedral interstitial region. The hydrogen atoms were constrained to lie symmetrically along the diagonal of the cube. The Pd positions were fixed at the pure palladium fcc lattice geometry. The Pd orbital basis set was a 17s/11p/8d basis [10] and the H orbital basis set was a 6s basis [11]. Both basis sets were augmented with a polarization function of exponent 1.0 bohr$^{-2}$. All exponents greater than 10.0 bohr$^{-2}$ were contracted according to an atomic calculation. Basis sets for fitting the potential were derived from these orbital bases [9]. Several variations on this approach to selecting basis sets for fitting the potential all give nearly identical isomerization energies for 13-atom first-transition-series clusters [12]. The calculations are nonrelativistic. Relativity is marginally important in describing the electronic structure of totally symmetric octahedral and tetrahedral clusters containing a hydrogen atom [13].

Within this eight-atom cluster model the H–H in-
teraction energy in an octahedral site is tabulated in table 1. For our cluster calculations we define the H–H binding energy to be the total energy of a pair of hydrogen atoms in the cluster minus twice the energy of a single hydrogen at the symmetric position plus the total energy of the empty cluster. As table 1 directly indicates, two hydrogen atoms repel each other quite strongly in the octahedral site. Furthermore, for short internuclear separations the H–H repulsive interaction is significantly stronger than in the gas phase.

We also considered the case where two hydrogen atoms are in a single tetrahedral interstice. As before, the embedded-atom method calculations started with hydrogen atoms centered in all octahedral sites in the Pd lattice, producing a lattice with stoichiometry PdH. Two additional H atoms were then placed in one tetrahedral cell and ten sets of calculations were run using different starting positions for the pair of hydrogens. The relaxed H–H distances ranged from 1.32 to 1.60 Å. Then five trials were run where three atoms were introduced into one tetrahedral site. In every case the H atoms again repelled each other to opposite sides of the interstice, just as occurred for the octahedral interstice, but now, the closer of the three H–H distances varied from 1.27 to 1.63 Å. A representative case of the short bond distances in the tetrahedral cage is drawn in fig. 1b. In this figure, the two relevant hydrogen atoms are shaded. The other hydrogen atoms in the figure lie at the centers of the octahedral intersices as before.

Both hydrogen atoms end up being very close to the plane of three palladium nuclei, as can be noticed most readily for the lower-left hydrogen in fig. 1b. From the other darkened hydrogen atom in the figure it is apparent that both hydrogen atoms lie off the center of the triangular face towards the center of a nearest-neighbor palladium bond. Therefore, we chose to do LCGTO-LDF calculations for two geometries. If the hydrogen atoms went through the center of two faces the relevant Pd4H2 cluster has C2v symmetry. If the hydrogen atoms went to the center of opposite bonds the cluster would have D2d symmetry. The results are given in table 2 and again we find strong repulsive forces. However, we do find a minimum in the forces and a bound H2 complex in the D2d symmetry, in large part because of the additional steric hindrance introduced by forcing the hydrogen nucleus directly through the Pd–Pd bond.

The above empirical and quantum chemical calculations show that two hydrogen atoms in either the octahedral site or the tetrahedral site repel each other towards the boundaries of the interstitial cells. We therefore considered two hydrogen atoms approaching each other symmetrically about the three-palladium-atom boundary between these two sites. Calculations of the total energy of a Pd4H2 cluster were performed using the LCGTO-LDF method using the above basis and with an ab initio Hartree–Fock approach using an STO-3G basis set [14]. The complex was placed in a trigonal bipyramidal arrangement with the hydrogen atoms occupying the apexes of the pyramids. The distance of the hydrogen atoms from the plane of the palladium atoms was varied.
and the Pd–Pd bond length was held fixed at 2.75 Å. The results of these calculations of the relative LDF energy (defined above) and of the total HF energy are given in table 3. They demonstrate that the total energy of the system increases as the separation between the hydrogen atoms decreases in both local-density functional and HF. This position is close to the maximum barrier for diffusion of H in Pd, 0.26 eV. Therefore 0.5 eV should perhaps be added to the repulsive energy for close approaches.

On a still smaller scale, we performed HF PdH₂ calculations to see whether confinement or collisions within the Pd 4d electronic shell might yield a relatively low-energy conformation of two deuterium nuclei near a palladium nucleus. Again all repulsions were greater than without the palladium atom.

Our calculations suggest that at short distances the H–H forces in the palladium crystal are more strongly repulsive than in free molecular hydrogen, and that the mutual repulsion of the two hydrogen atoms within an interstitial will cause them to maximize the distance separating them. Both effects should decrease rather than increase the probability for fusion in the lattice over that in free D₂. The concentration of H atoms in PdH is nearly the same as that for solid hydrogen at 4 K. The separation between octahedral sites in the PdH lattice, however, is 2.86 Å, while because of its molecular nature solid hydrogen has a shorter separation of 0.74 Å between hydrogens in each pair. This again suggests that based on chemical forces the probability for fusion should be less in the metal than in solid hydrogen. Finally, we note that experimental evidence [15] suggests that the stoichiometry of the palladium hydrides for which appreciable fusion is detected may be PdH₂. Calculations using the embedded-atom method described above, in which the dimensions of the cell were allowed to change, showed an additional average expansion of the lattice parameter of 9.5% for PdH₂ over PdH. Hence, the separation between an octahedral site and an adjacent tetrahedral site is 1.9 Å, a distance which is still too large for appreciable fusion to occur. These calculations suggest that confinement of deuterium within the Pd lattice resulting from chemical forces is not responsible for the enhanced fusion of deuterium observed in palladium.

We wish to thank the Research Advisory Committee of the Naval Research Laboratory for a grant of computer time which was used in performing a portion of these calculations.

Table 3
Pd₅H₅ cluster H–H potentials in LDF and HF.

<table>
<thead>
<tr>
<th>R_{H-H} (Å)</th>
<th>Relative LDF energy (hartrees)</th>
<th>Total HF energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.693</td>
<td>0.02280</td>
<td>-14668.68762</td>
</tr>
<tr>
<td>1.482</td>
<td>0.02110</td>
<td>-14668.66878</td>
</tr>
<tr>
<td>1.270</td>
<td>0.01248</td>
<td>-14668.65495</td>
</tr>
<tr>
<td>1.058</td>
<td>0.00308</td>
<td>-14668.57368</td>
</tr>
<tr>
<td>0.953</td>
<td>0.01415</td>
<td></td>
</tr>
<tr>
<td>0.847</td>
<td>0.02907</td>
<td></td>
</tr>
<tr>
<td>0.741</td>
<td>0.05248</td>
<td></td>
</tr>
<tr>
<td>0.529</td>
<td>0.15606</td>
<td></td>
</tr>
<tr>
<td>0.243</td>
<td>0.28568</td>
<td></td>
</tr>
</tbody>
</table>

References