

## FUSION RATES FOR DEUTERIUM IN TITANIUM CLUSTERS

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Ab initio Hartree-Fock self-consistent field calculations for hydrogen atoms in a titanium atom matrix have been performed. Computed potential energy surfaces for the deuterium motion are used to calculate fusion rates. These calculations suggest that no stable state of titanium deuteride exists with the small inter-deuteron distances required for measurable fusion rates.

### 1. Introduction

Recently two groups [1,2] reported observations of various phenomena during electrolysis of  $D_2O$  on palladium and titanium electrodes. These phenomena were assumed to result from d-d fusion in the metallic lattice. Subsequently, a large number of attempts to reproduce these findings ended with negative results (see, e.g., refs. [3-5]). Various aspects of the Fleischmann, Pons, and Hawkins experiment [1] have been criticized [3,4,6]. Still, partial confirmations of the experiments [1,2] have been announced by a few groups [7-10]. In addition to electrolytical experiments, bursts of neutrons have been reported when metals infused with deuterium have been subjected to cooling [11,12]. Negative results for these experiments have been obtained by some other groups (see, e.g., refs. [4,13]). Most of the theoretical investigations came to the conclusion that large amounts of heat such as those reported by Fleischmann, Pons, and Hawkins [1] cannot be accounted for by any known physical process [14-19]. Even the much smaller fusion rates reported by Jones et al. [2] seem to be impossible to explain if fusions were to take place in a regular lattice. These rates might, however, be explained by a crack mechanism leading to local "hot fusion" pockets [20,21]. It is

interesting that while the majority of electrolytical experiments have been performed with palladium, the experiments which infuse metal with deuterium by other means deal mainly with titanium. In the case of palladium lattice one of the major arguments against the possibility of fusion stems from the fact that the distances between deuterons in palladium are significantly larger than in the isolated  $D_2$  molecule. This conclusion can be reached either by applying standard solid state methods [18,19] or by performing calculations for palladium-hydrogen clusters [18,22]. In view of the interest in titanium hydrides, similar calculations for this system are needed. Kang and Wilkins [23] carried out density-functional calculations for a pair of hydrogen atoms occupying octahedral and tetrahedral interstitial sites. In the present paper we describe our calculations for hydrogen atoms placed inside small Ti clusters. The calculations have been performed using the ab initio Hartree-Fock (HF) self-consistent field (SCF) method. We explore the possibility that there might be a stable configuration for hydrogen atoms in a titanium lattice with the inter-proton separation significantly less than that in hydrogen gas. If such a stable state existed, the tunneling probability would increase and so would the fusion rate compared to an isolated deuterium molecule.

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## 2. Calculations

Our HF SCF calculations for  $Ti_nH_m$  clusters have been performed with an STO-3G minimal basis set [24,25]. We assumed the clusters to be in the spin states with the lowest possible multiplicity. For the  $Ti_4H$  cluster we have used spin restricted open-shell Hartree-Fock theory (ROHF) [26] and imposed spin 1/2. For the remaining clusters -  $Ti_5H_2$  and  $Ti_6H_2$  - we have used closed-shell Hartree-Fock theory. Calculations were also attempted using unrestricted Hartree-Fock (UHF) theory but these were plagued with problems. The single point energies did not fall on a smooth curve but exhibited scatter, due in part to the great difficulty encountered in achieving SCF convergence. Several of the points failed to reach convergence entirely. In addition, the energy barrier between tetrahedral sites was calculated to be  $\sim 7$  kcal/mole which is inconsistent with experimental data (see discussion below).

In titanium metal the titanium atoms are hexagonally close packed with the minimum separation between the atoms of 2.94 Å [27]. This arrangement leaves each titanium atom cubically coordinated by tetrahedral sites. In titanium hydride the hydrogen atoms fill these sites. With all such sites occupied, the stoichiometry is  $TiH_2$ . Each titanium is cubically coordinated by H atoms and each hydrogen is tetra-

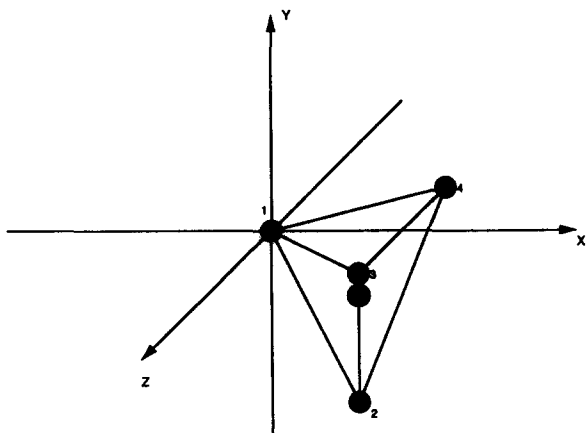


Fig. 1. Geometry used in calculating the potential well constraining a hydrogen atom to a tetrahedral site. The solid dots are titanium atoms. Atoms 1, 3, and 4 are in the  $xz$  plane. The shaded dot is a hydrogen atom in the tetrahedral site.

hedrally coordinated by titaniums. This is the well known fluorite structure [27].

Geometrically it is clear that the shortest path for moving a hydrogen from one tetrahedral site to an adjacent one is directly through the center of one of the faces of the tetrahedron described by the four closest titanium atoms. In order to find the approximate size and shape of the well constraining a hydrogen atom in one such site, fifteen points on this

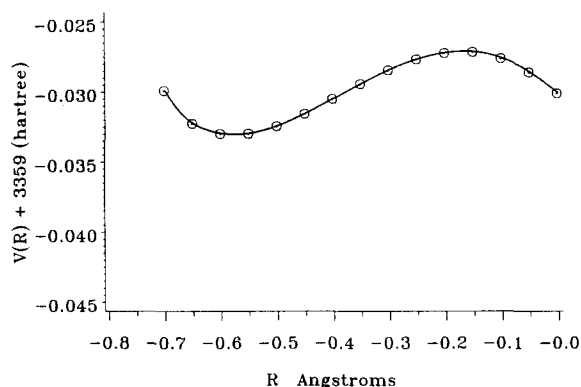


Fig. 2. Potential energy curve for extracting a hydrogen atom from a tetrahedron of titanium atoms.  $R$  is the  $y$  coordinate of the hydrogen atom as shown in fig. 1.

Table 1

Data points on the potential energy curve for extracting a hydrogen atom from  $Ti_4H$  through a face of the tetrahedron (see also fig. 1). Distances given (in Å) are measured from the plane of the face of the tetrahedron. Energies are in hartrees.

Distance	Energy
0.00	-3359.03002
-0.05	-3359.02853
-0.10	-3359.02753
-0.15	-3359.02708
-0.20	-3359.02715
-0.25	-3359.02760
-0.30	-3359.02837
-0.35	-3359.02935
-0.40	-3359.03043
-0.45	-3359.03149
-0.50	-3359.03238
-0.55	-3359.03292
-0.60	-3359.03293
-0.65	-3359.03221
-0.70	-3359.02985
-0.75	-3359.02398

potential energy curve were calculated. Four titanium atoms were arranged in a tetrahedron 2.94 Å on each edge as shown in fig. 1. The SCF energy for this system was calculated with a hydrogen atom at various positions along the line connecting Ti atom 2 with the geometric center of the equilateral triangle described by Ti atoms 1, 3, and 4. Fig. 2 and table 1 show the energy as a function of the  $y$  position of the hydrogen atom. In this approximation one can see that the hydrogen atom is bound to a site by only 3.67 kcal/mole. Although the potential barrier would certainly increase if the neighboring sites were occupied, it appears that the hydrogen atoms are reasonably free to move through the lattice. Weaver and Van Dyke [28] have been measured the activation energy ( $E_{\text{act}}$ ) for diffusion of hydrogen in titanium metal and found it to have a linear dependence on stoichiometry, i.e. on  $n$  in  $\text{TiH}_n$ . They found, for example,  $E_{\text{act}}=9.4$  kcal/mole for  $n=1.607$ , and  $E_{\text{act}}=10.4$  kcal/mole for  $n=1.933$ . Upon extrapolation to the exact stoichiometry  $\text{TiH}_2$ , they obtained  $E_{\text{act}}=10.5$  kcal/mole. Our calculation represents the empty lattice limit and agrees reasonably well with the extrapolated value of 4.47 kcal/mole for  $\text{TiH}_0$ .

In the next calculation, five titanium atoms were arranged in a trigonal bipyramid as shown in fig. 3 (two tetrahedra sharing a face) and one hydrogen atom was inserted into each site. The geometry was optimized keeping the titanium atoms fixed and allowing the hydrogens to move along the symmetry

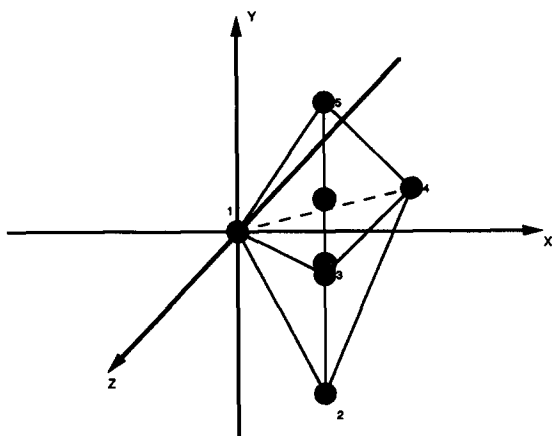


Fig. 3. Geometry used in calculating the hydrogen-hydrogen interaction potential in a titanium matrix. The hydrogens (shaded dots) were constrained to lie on the threefold symmetry axis.

axis. Two such tetrahedral sites are 1.21 Å separated, but the optimized separation is 1.41 Å. This slight shift could quite possibly be a consequence of approximating the lattice with only five titanium atoms. Our result is in good agreement with the value of 1.4 Å obtained in ref. [23]. A potential energy curve for this interaction was then calculated by fixing one hydrogen atom in the center of the upper tetrahedral site and calculating the SCF energy for various positions of the other hydrogen along the line of axial symmetry. The resulting potential curve is presented in fig. 4 and table 2. Evidence exists that hy-

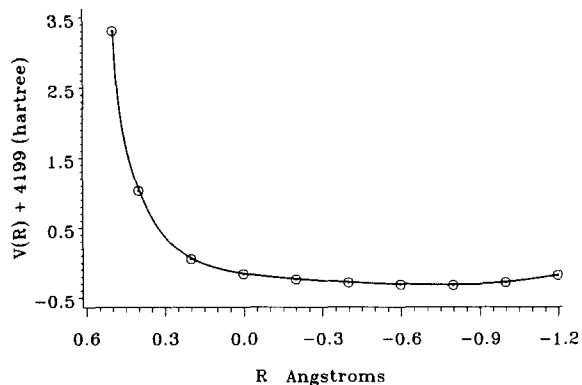


Fig. 4. Interaction potential for two hydrogen atoms in a titanium cluster. One hydrogen atom was fixed in the upper tetrahedral site. The energy is given as a function of the  $y$  coordinate of the other hydrogen atom.

Table 2

SCF energy of  $\text{Ti}_5\text{H}_2$  with one hydrogen fixed in the center of the upper tetrahedral site and the other allowed to move along the threefold axis of symmetry (see also fig. 3). Distances given (in Å) are those of the lower hydrogen atom from the  $xz$  plane. Energies are in hartrees.

Distance	Energy
-1.2	-4199.16677
-1.0	-4199.27326
-0.8	-4199.30893
-0.6	-4199.30401
-0.4	-4199.27523
-0.2	-4199.22892
0.0	-4199.15053
0.2	-4198.93750
0.4	-4197.96040
0.5	-4195.68700

drogen atom diffusion is more likely to occur between second-nearest neighbor sites [29], i.e. between two tetrahedral sites with a common edge. Since, however, two such sites are 2.055 Å separated, the fusion rate for second-nearest neighbor interactions will certainly be considerably lower than for the nearest neighbor interaction calculated here.

In view of the above it is rather obvious that the fusion rates will be substantially lower than in the isolated D<sub>2</sub> molecule where the equilibrium separation is 0.7 Å. In order to find the magnitude of this difference, we have computed the fusion rate using the WKB approximation in exactly the same manner as described in ref. [15]. To find the lowest vibrational level we have assumed that the deuterium atoms occupying the two neighbouring tetrahedral sites move in a three-dimensional harmonic oscillator potential with the same harmonic constants in all dimensions. This constant was obtained by a fit to the curve of fig. 4. This is certainly an approximation since one slope of the curve represents approach in the direction of a Ti atom while the other slope represents approach in the direction of another D atom. Nevertheless, in all other directions the hypersurface will be very strongly repulsive, therefore for low vibrational levels this approximation is justified. We have calculated the lowest vibrational level to be at 0.0133 hartree above the minimum of the potential.

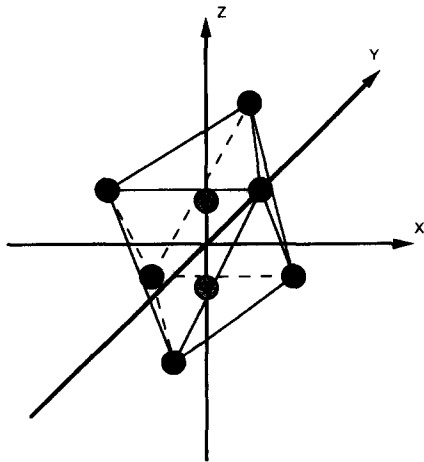


Fig. 5. Geometry used to calculate the interaction potential for two hydrogen atoms in an octahedral site. The hydrogen atoms (shaded dots) were placed symmetrically about the origin along the z axis.

For this state the fusion rate is  $3 \times 10^{-84} \text{ s}^{-1}$ . This rate is 20 orders of magnitude smaller than the rate for D<sub>2</sub> which is equal to  $2 \times 10^{-64} \text{ s}^{-1}$  [15]. As pointed out in ref. [15] the fusion rate is larger for higher vibrational states. For the first excited state it is equal in our case to  $3 \times 10^{-82} \text{ s}^{-1}$ , an insignificant change.

Several attempts were made to find a stable con-

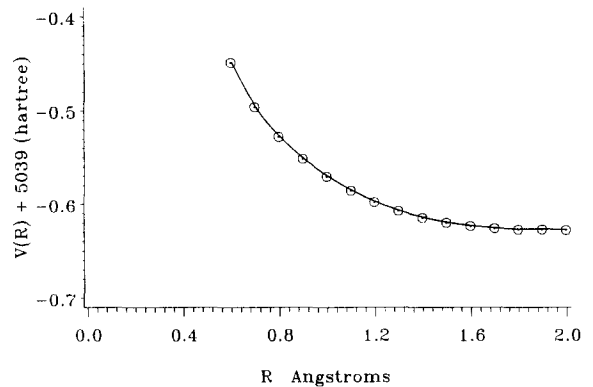


Fig. 6. Potential energy curve for the interaction of two hydrogen atoms in a single octahedral cluster of titanium atoms. The hydrogens were constrained to move symmetrically along the three-fold symmetry axis.

Table 3

Data points on the potential curve representing the interaction of two hydrogen atoms in an octahedral cluster of titanium atoms (see also fig. 6). Distances given (in Å) are the separations of the hydrogen atoms. Energies are in hartrees.

Distance	Energy
0.600	-5039.44793
0.700	-5039.49526
0.800	-5039.52696
0.900	-5039.55062
1.000	-5039.56938
1.100	-5039.58456
1.200	-5039.59676
1.300	-5039.60636
1.400	-5039.61367
1.500	-5039.61899
1.600	-5039.62265
1.700	-5039.62497
1.800	-5039.62629
1.900	-5039.62630
2.000	-5039.62711
2.100	-5039.62711
2.200	-5039.62711

figuration with two hydrogens in a single tetrahedral site. Two hydrogens were initially located in the upper site and their positions were energetically optimized. In all cases one of the hydrogens moved after the optimization to the lower site. Within the SCF model, therefore, a doubly occupied site is unstable with respect to dissociation to two singly occupied sites.

Finally, a potential curve was calculated for the interaction of two hydrogen atoms in a single octahedral site. An octahedral cluster of titanium atoms was formed by placing six titanium atoms symmetrically about the origin in such a fashion that the  $z$  axis was an axis of threefold symmetry, as shown in fig. 5. Two hydrogen atoms were then placed on the  $z$  axis equidistant from the origin. The SCF energy of this system was calculated for different separations of the hydrogen atoms. The results are shown in fig. 6 and in table 3. Clearly, a doubly occupied octahedral site is dissociative. This tendency of the H atoms to migrate toward opposite faces of the octahedron is consistent with similar findings by Mintire et al. for H atoms in palladium octahedra [18]. Our conclusion disagrees with that of Kang and Wilkins [23] who found – using a density-functional theory – an equilibrium distance of 1.6 Å for two hydrogens in a Ti octahedral site. This disagreement is, however, irrelevant for the cold fusion in deuterium-loaded metals since the equilibrium separation of this size would lead to extremely small fusion rates. Let us mention that we have also tried other arrangements of the hydrogen atoms in the octahedral site, all of them resulting in higher energies than the configuration described above. Some of these arrangements exhibited saddle points on the potential energy surface. These saddle points could be misinterpreted as equilibrium points.

### 3. Conclusions

We have performed ab initio SCF calculations for various configurations of  $Ti_nH_m$  clusters. A potential energy curve for the removal of a hydrogen atom from a titanium tetrahedron has been computed. This calculation shows that hydrogens are reasonably free to move about in a titanium metal lattice. Attempts to find a stable configuration with two hydrogen at-

oms in a single tetrahedral lattice site failed. Doubly occupied sites are dissociative to two singly occupied sites. Also a doubly occupied octahedral site is dissociative. We found that the closest separation of deuterons in a titanium lattice can be achieved when they occupy adjacent tetrahedral sites. Even for this configuration, however, the equilibrium distance is larger than in an isolated  $D_2$  molecule, and therefore the fusion rate is only about  $10^{-84} s^{-1}$ , i.e. about 60 orders of magnitude smaller than one would need for explaining the results of recent experiments [1,2]. Although the validity of our conclusions is limited by the relatively low level of theory employed and by the restrictive assumptions about the total spin of the clusters, it is hard to imagine that more sophisticated calculations could change the potential energy surfaces to an extent allowing the fusion rates to increase by 60 orders of magnitude.

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### References

- [1] M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanal. Chem.* 261 (1989) 301; 263 (1989) 187 (E).
- [2] S.E. Jones, E.P. Palmer, J.B. Czirr, D.L. Decker, G.L. Jensen, J.M. Thorne, S.F. Taylor and J. Rafelski, *Nature* 338 (1989) 737.
- [3] N.S. Lewis, *Nature* 340 (1989) 525.
- [4] M. Gai, S.L. Rugari, B.J. Lund, Z. Zhao, A.J. Davenport, H.S. Isaacs and K.G. Lynn, *Nature* 340 (1989) 29.
- [5] J.F. Ziegler et al., *Phys. Rev. Lett.* 62 (1989) 2929.
- [6] R.D. Petrasso et al., *Nature* 339 (1989) 183, 264, 667.
- [7] R.A. Huggins et al., reported at Santa Fe Workshop on Cold fusion, May 1989.
- [8] S. Srinivasan et al., reported at Santa Fe Workshop on Cold fusion, May 1989.

- [9] K.L. Wolf et al., reported at Sante Fe Workshop on Cold fusion, May 1989.
- [10] A. Bertin et al., *Nuovo Cimento A* 101 (1989) 997.
- [11] A. de Ninno et al., *Nuovo Cimento A* 101 (1989) 841.
- [12] H.O. Menlove et al., reported at Santa Fe Workshop on Cold fusion, May 1989; preprint Los Alamos National Laboratory, LA-UR 89-1974.
- [13] Y. Dufour et al. (the Bugey collaboration), reported at Sante Fe Workshop on Cold fusion, May 1989.
- [14] J. Rafelski, M. Gajda, D. Harley and S.E. Jones, Univ. of Arizona preprint AZPH-TH/89-19 (1989).
- [15] K. Szalewicz, J.D. Morgan III and H.J. Monkhorst, *Phys. Rev. A* 40 (1989) 2824.
- [16] S.E. Koonin and M. Nauenberg, *Nature* 339 (1989) 690.
- [17] A.J. Leggett and G. Baym, *Phys. Rev. Lett.* 63 (1989) 191.
- [18] J.W. Mintmire, B.I. Dunlap, D.W. Brenner, R.C. Mowrey, H.D. Ladouceur, P.P. Schmidt, C.T. White and W.E. O'Grady, *Phys. Lett. A* 138 (1989) 51.
- [19] Z. Sun and D. Tomanek, *Phys. Rev. Lett.* 63 (1989) 59.
- [20] V.A. Klyuev et al., *Sov. Tech. Phys. Lett.* 12 (1986) 551.
- [21] J.S. Cohen and J.D. Davies, *Nature* 338 (1989) 705.
- [22] F.F. Muguet and P.M.P. Bassez-Muguet, reported at Sante Fe Workshop on Cold fusion, May 1989.
- [23] M.H. Kang and J.W. Wilkins, reported at Santa Fe Workshop on Cold fusion, May 1989.
- [24] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* 51 (1969) 2657.
- [25] J.B. Collins, P. v. R. Schleyer, J.S. Binkley and J.A. Pople, *J. Chem. Phys.* 64 (1976) 5142.
- [26] R. McWeeny and G. Diercks, *J. Chem. Phys.* 49 (1968) 4852.
- [27] N.N. Greenwood and A. Earnshaw, *Chemistry of the elements* (Pergamon, Oxford, 1984).
- [28] H.T. Weaver and J.P. Van Dyke, *Phys. Rev. B* 6 (1972) 694.
- [29] B. Stalinski, C.K. Coogan and H.S. Gutowsky, *J. Chem. Phys.* 34 (1961) 1191.
- [30] M.J. Frisch, J.S. Binkley, H.B. Schlegel, K. Raghavachari, C.F. Melius, R.L. Martin, J.J.P. Stewart, F.W. Bobrowicz, C.M. Rohlfing, L.R. Kahn, D.J. Defrees, R. Seeger, R.A. Whiteside, D.J. Fox, E.M. Fleuder and J.A. Pople, *Gaussian 86* (Carnegie-Mellon Quantum Chem. Publ. Unit, Pittsburgh, 1984).
- [31] M.W. Schmidt, J.A. Boatz, K.K. Baldrige, S. Koseki, M.S. Gordon, S.T. Elbert and B. Lam, *QCPE Bull.* 7 (1989) 115 [original program assembled by M. Dupuis, D. Spangler and J.J. Wendoloski].