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Richard Alan Lesar, *Harvard University*
D. R. Herschbach, *Harvard University*

states results from reaction with a metal contact, the prospects are not good for improving photovoltage for the CdTe/metal system by using a reducing pretreatment for CdTe. In this connection it is noteworthy that two earlier studies[3] of n-CdTe/liquid interfaces report the use of the Br_2/CH_3OH pretreatment and claim some results that parallel our findings for the reducing etch. However, photovoltages were not as high as those obtained here, and greater difficulty with reproducibility was apparently encountered. It may be that the most efficient devices would then be those based on liquid electrolyte contacts, but the lack of durability remains a major hurdle to the achievement of any useful photoelectrochemical device from exploitation of a reducing etch procedure for n-CdTe. The results, though, do establish that a reproducible surface pretreatment can yield reproducible photovoltage mea-

surements. Further, the finding that Fermi level pinning can be removed establishes that the extent of ionic vs. covalent bonding in the series CdS, CdSe, and CdTe does not control the value of E_B or its dependence on ϕ or E_{redox}.[4b] Rather, the presence of a layer of semimetallic Te on CdTe can rationalize the earlier observation[2] of a constant E_B vs. E_{redox} for n-CdTe. This work thus establishes one mechanism for Fermi level pinning. Preserving the integrity of the reduced CdTe surface is now the object of our future studies using n-CdTe photoanodes.

Likelihood of a High-Pressure Phase of Solid Hydrogen Involving Termolecular Complexes

R. LeSar and D. R. Herschbach*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138 (Received: July 22, 1981)

Electronic-structure calculations have shown that the six-center transition state for the concerted bond exchange among three hydrogen molecules lies ~2 eV or more below the dissociation energy of the diatomic molecule. This suggests that solid hydrogen might undergo a high-pressure transition to form a new phase involving termolecular complexes. This possibility is examined by means of lattice-energy calculations employing semitheoretical pair potentials. Although uncertainties in the pair potentials prevent a definite conclusion, the results obtained for a range of potentials indicate that a phase comprising a "largely dissociated" form of the six-center transition state may be stable at pressures above a few hundred kilobars. This complex would exist only because repulsive forces from the neighboring units in the crystal environment prevent its dissociation.

Introduction

Molecular crystals at very high pressures offer a unique environment for chemistry.[1] Since the molecular positions and orientations are fixed in restricted regions and neighboring molecules are crowded together, reactions that otherwise do not occur may be induced. Recent improvements in diamond anvil cells[2] make feasible studies of chemical reactions at static pressures up to several hundred kilobars. As yet this regime is almost unexplored, but prospects for novel chemistry are illustrated by some results for solid-phase systems at pressures up to 100 kbar. These include disproportionation reactions[3] such as

$$2CuCl \rightarrow CuCl_2 + Cu$$

$$2CO \rightarrow CO_2 + C$$

$$3NO \rightarrow NO_2 + N_2O$$
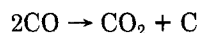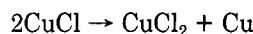
and observations of electronic spectra[4] from double-mol-

ecule transitions in solid oxygen. Another novel prospect for ultrahigh-pressure chemistry is the trapping and stabilization of species corresponding to transition states for known gas- or liquid-phase reactions. This paper reports a theoretical study of such a case, a hypothetical phase of solid hydrogen related to the transition state for termolecular bond exchange.

Our calculations were prompted by results of ab initio electronic-structure studies[5,6] of the H_{4n+2} polygons (with $n = 1$–15). Contrary to the usual orbital-symmetry criterion,[7] the results show that only the H_6 polygon ($n = 1$) can serve as a transition state for a concerted bond exchange (among $2n + 1$ hydrogen molecules). Only the H_6 polygon is stable with respect to the dissociation of one of the hydrogen molecules to atoms.[6] This result suggested that solid molecular hydrogen at high pressures might undergo a phase transition to form termolecular complexes before transition to the atomic or metallic phase at still higher pressures. Much work has been devoted to esti-

(1) H. G. Drickamer, *High Temp.-High Pressures*, 9, 535 (1977).
(2) See, for example: D. Schiferl, J. C. Jamieson, and J. E. Lenko, *Rev. Sci. Instrum.*, 49, 359 (1978); L. Merril and W. A. Basset, *ibid.*, 45, 290 (1975).
(3) (a) For the CuCl reaction, see G. J. Piermarini, F. A. Mauer, S. Blick, A. Jayaramin, T. H. Geballe, and G. W. Hull, Jr., *Solid State Commun.*, 32, 275 (1979); (b) For the CO and NO reactions, R. L. Mills, Los Alamos Scientific Laboratory, personal communication.

(4) M. Nicol, K. R. Hirsch, and W. B. Holzapfel, *Chem. Phys. Lett.*, 68, 49 (1979).
(5) D. H. Liskow, J. M. McKelvey, C. F. Bender, and H. F. Schaefer, III, *Phys. Rev. Lett.*, 32, 933 (1974).
(6) D. A. Dixon, R. M. Stevens, and D. R. Herschbach, *Faraday Discuss. Chem. Soc.*, 62, 110 (1977).
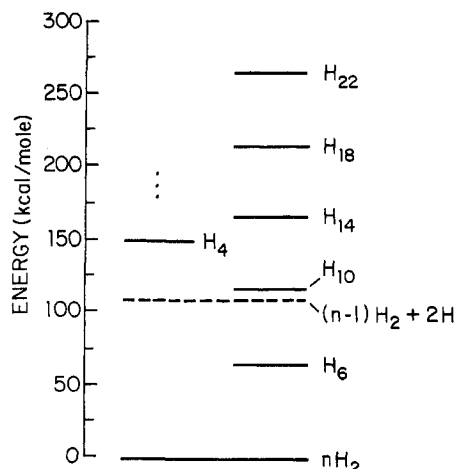(7) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, West Germany, 1970.

Figure 1. Energy of hydrogen polygons relative to energy of n H_2 molecules (from results collected in ref 6). Only H_6 lies below the $(n-1)H_2 + 2H$ asymptote.

mating the transition to the metallic state, expected to be above ~ 2 Mbar.[8] The chief mechanism previously treated involves direct dissociation of the H_2 bond,[8,9] but several variants have been considered, including linear chains,[10,11] planar sheets of atoms or molecules,[10,11] and a conducting molecular phase.[12] To examine the possibility that a distinct phase involving termolecular complexes might intervene, we employ customary approximate methods and semitheoretical pair potentials. The special feature is the transition-state character of the parent H_6 complex. According to the electronic-structure calculations,[6] at low pressures there is no barrier to the $H_6 \rightarrow 3H_2$ dissociation along the B_{2u} normal mode of the hexagon. If a high-pressure complex exists, it must correspond to a "partially dissociated", irregular $(H_2)_3$ species stabilized by virtue of compression by neighboring molecules.

Calculational Methods

We wish to examine the process

$$3H_2(\text{solid}) \rightarrow (H_2)_3(\text{solid})$$
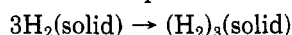
The free-energy change at 0 K is given by

$$\Delta G = G_l(H_6) - 3G_l(H_2) + \Delta E_r + \Delta E_v$$

with $G_l(H_6)$ and $G_l(H_2)$ the lattice free energies for the $(H_2)_3$ and H_2 phases, respectively, ΔE_r the energy change for the gas-phase reaction

$$3H_2(g) \rightarrow (H_2)_3(g)$$

and ΔE_v the corresponding change in intramolecular zero-point energy. The phase transition would occur at a pressure such that $\Delta G(P) = 0$. The lattice free energy $G_l = E_l + E_{zp} + PV$, where E_l is the static lattice energy, E_{zp} the lattice vibrational zero-point energy, P the pressure, and V the molar volume. The static term E_l can be calculated as a lattice sum of the intermolecular pair potentials

$$E_l = \frac{1}{2}\sum_i\sum_j\sum_l V_{ij}(\mathbf{r}_i - \mathbf{r}_j + \mathbf{r}_l) \qquad (1)$$

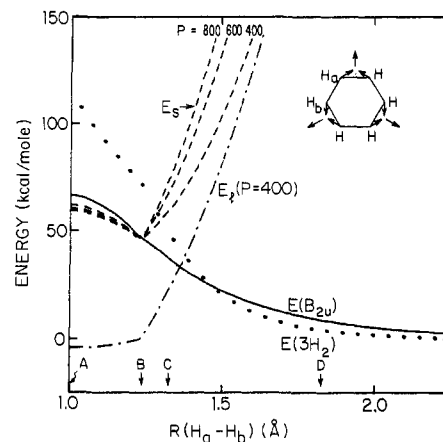where i and j are the molecules in the unit cell, $\mathbf{r}_l$ is a lattice

(8) For a recent review, see M. Ross and C. Shishkevitch, "Molecular and Metallic Hydrogen", Rand Corp., Santa Monica, CA, 1977.

(9) M. Ross, *J. Chem. Phys.*, **60**, 3634 (1974).

(10) E. G. Brovman, Yu. Kagan, and A. Kholas, *Zh. Eksp. Teor. Fiz.*, **61**, 2429 (1971) (*Sov. Phys.-JETP (Engl. Transl.)*, **34**, 1300 (1972)); **62**, 1492 (1972) (*Sov. Phys.-JETP (Engl. Transl.)*, **35**, 783 (1972)).

(11) F. E. Harris and J. Delhalle, *Phys. Rev. Lett.*, **39**, 1340 (1977).

(12) See ref 8 and, for example, C. Friedli and N. W. Ashcroft, *Phys. Rev. B*, **16**, 662 (1977).

Figure 2. Potential-energy profiles: $E(B_{2u})$ is the energy of dissociation (solid curve) of the H_6 molecule to three H_2 molecules along the path shown in the insert and discussed in the text (cf. ref 6); $E(3H_2)$ is the energy of three H_2 molecules in the same configuration as calculated by summing over the pair potentials (dotted curve); E_i is the change (dot-dash curve) in energy of interaction of a central $(H_2)_3$ complex with its six in-plane nearest neighbors as it is allowed to vary from its equilibrium configuration (configuration B potential a' in text) with nearest-neighbor distance appropriate to a pressure of 400 kbar; E_s (dashed curve) is the sum of E_i and $E(B_{2u})$ for configuration B for molecules located at positions appropriate for pressures of 400, 600, and 800 kbar. Marked on this curve are positions corresponding to the configurations of Figure 3.

vector, and V_{ij} is the intermolecular potential. The lattice zero-point energy, E_{zp}, can be found by determining effective lattice force constants as lattice sums of the second derivatives of the potential. These terms were evaluated by summing over large spheres in the lattice about each molecule in the unit cell. The lattice energies and volumes were found by minimizing the lattice free energy with respect to volume for a given pressure. The reaction energy ΔE_r is found as the difference of the theoretical energy[6] of a gas-phase H_6 molecule and three H_2 molecules.

$(H_2)_3$ *Transition-State Complex.* Figure 1 shows the energies of a series of H_{4n+2} polygons relative to their dissociation asymptotes (to form $2nH_2 + 2H$). The results for regular hexagonal H_6 are from a detailed SCF–CI calculation[6] while the other results are from approximate ab initio calculations.[5] Only the hexagonal H_6 complex (with a bond length of 1.87 bohr radii) lies below the dissociation asymptote. H_6 can, however, dissociate to $3H_2$ along many pathways, all of which involve excitation of the B_{2u} vibrational mode. The energy along one such dissociation path is shown in Figure 2, designated $E(B_{2u})$. This path (from ref 6) was chosen for computational simplicity. The energy profile was calculated with an SCF wave function of modest accuracy and the result scaled to agree with the energy of the regular hexagonal configuration obtained in the most accurate available SCF–CI calculation.[6] On this path, the initial movements of the atoms conform to the B_{2u} vibrational coordinate; thus, they move perpendicular to the in-plane symmetry axes through the H atoms. When the emerging pairs of H atoms reach the gas-phase equilibrium H_2 bond length (1.401 bohr radii), the product molecules separate along radial paths. In Figure 2, the ordinate denotes the closest distance between H atoms in different H_2 molecules and is given in bohr radii by $r_{H_a-H_b} = 1.87 + 3^{1/2}(r_1 + r_2)$, where r_1 is the displacement along the B_{2u} mode (with a maximum value of ~ 0.266 bohr radii when the H_2 molecules are at their equilibrium bond lengths) and r_2 the radial displacement (which is zero until r_1 has its maximum value). Positions marked along the dissociation curve in Figure 2 correspond
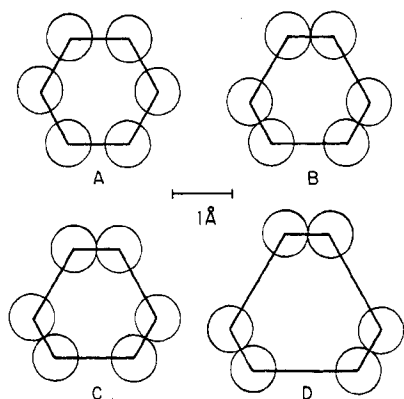
Figure 3. Configurations of termolecular complexes corresponding to the reaction profile of Figure 2. The circles drawn around each H atom have a radius of half the free H_2 bond length.

to the $(H_2)_3$ configurations in Figure 3.

$(H_2)_3$ Lattice Energy. Since pair interaction potentials between $(H_2)_3$ complexes are not available, and since theoretical methods would be inappropriately arduous, approximate pair potentials were generated by a procedure that has been often used in solid-state calculations.[13] The most important features of such pair potentials, especially when used to describe high-pressure crystals, are the size and shape ascribed to the molecules.

The configurations of $(H_2)_3$ considered here are taken from the dissociative path of Figure 2. We modeled the pair potential for molecules of three configurations: (A) $r_1 = 0$, $r_2 = 0$ (regular, hexagonal H_6); (B) $r_1 = 0.266$, $r_2 = 0$ (emerging H_2 molecules just at equilibrium separation); (C) $r_1 = 0.266$, $r_2 = 0.1$ (radial expansion). These configurations (A–C) are shown in Figure 3. Because H_2 molecules emerge from the H_6 complex, the interactions between $(H_2)_3$ complexes were found as a sum of H_2 molecule–molecule potentials, where only interactions between complexes with parallel planes were considered. The H_2 pair potential used here was taken from the work of Raich et al.[14] (their potential d), who fit potentials calculated with the Hartree–Fock SCF method to an analytical form in the region $2 < R < 8$ bohr radii (the RAE potential). By angular averaging around the normal to the planes containing the molecules, the potentials were smoothed out and could then be described simply as a function of two variables, r, the distance between the centers of the complexes, and θ, the angle between the normals and the vector connecting the centers. The potentials were fitted to a Kihara hard-core potential,[15] where they were parametrized by the minimum distance ρ between disks of radius r_c in the plane of the complexes. The well depth for each configuration was found to be fitted closely by the form

$$U(\theta) = U_0(1 + a \cos^2 \theta) \qquad (2)$$

where U_0 and a are constants. Two forms of the pair potential were considered, a Leonard-Jones $m - 6$ potential

$$V(r,\theta) = U(\theta)\left[\frac{6}{m - 6}(\rho_0/\rho)^m - \frac{m}{m - 6}(\rho_0/\rho)^6\right] \qquad (3)$$

and an exp 6 potential

$$V(r,\theta) = U(\theta)[A_1 e^{-\alpha\rho} - A_2 f(\rho)/\rho^6] \qquad (4)$$

TABLE I: Parameters for $(H_2)_3$ Pair Potentials[a]

config-uration	U_0	a	ρ_0	r_c	m	α
A, a'	45.5	2.45	5.0	1.50		1.85
b'	45.5	2.45	5.1	1.53		2.00
c'	45.6	2.42	5.1	1.55	7.5	
d'	45.6	2.42	5.1	1.55	10.7	
B, a'	44.5	2.52	5.0	1.55		1.85
b'	44.5	2.52	5.1	1.58		2.00
c'	44.5	2.52	5.0	1.50	7.50	
d'	44.5	2.52	5.1	1.58	7.62	
C, a'	42.0	2.69	5.0	1.70		1.85
b'	42.0	2.69	5.1	1.75		2.00
c'	40.0	2.69	5.0	1.70	7.5	
d'	42.0	2.69	5.1	1.75	10.7	

[a] All values are in atomic units. The parameters A_1 and A_2 in the exp 6 potential are given by $A_1 = 6[\exp(\alpha\rho_0)]/(\alpha\rho_0 - 6) \times 10^{-5}$ and $A_2 = \alpha\rho_0{}^7/(\alpha\rho_0 - 6) \times 10^{-5}$. All parameters are defined in the text in eq 2–4.
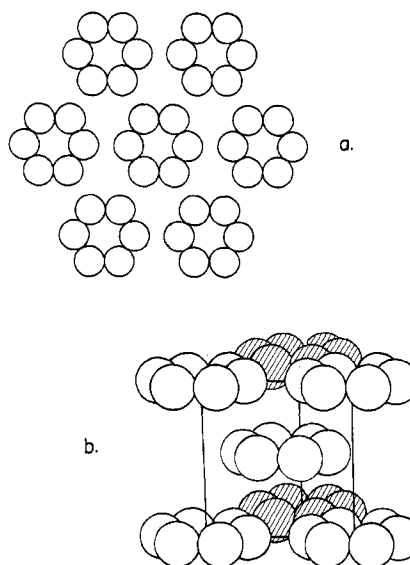

Figure 4. Crystal structure considered here for H_6 system: (a) the in-plane collection of seven molecules considered in the calculation of E_l in Figure 2 and (b) the stacking of those planes.

In the exp 6 potential the second term is multiplied by a cutoff function, $f(\rho) = \exp(-400/\rho^6)$, suggested by Trubitsyn[16] to prevent unrealistic behavior at small separations. The parameters (m, ρ_0, and A_1, A_2, α) were fitted to the well-depth, position of the minima, and the slope of the repulsive wall and were found to scale with the size of the complex (the radius of the circle which circumscribes the hexagon). The potential between complexes of configuration A (regular hexagon), which has no distinguishable H_2 units, was determined by extrapolating the results of the other complexes. These parameters and the relations determining A_1 and A_2 are given in Table I.

Since we are treating the $(H_2)_3$ complexes as oblate spheroids, the only crystal structure considered for these high-pressure calculations was a close-packed structure, namely, the hexagonal closest-packed structure shown in Figure 4. The static lattice energies were determined as in eq 1.

The lattice zero-point energy E_{zp} makes a relatively small contribution to the total lattice energy and the lattice free energy at high pressures. Because of the relative unimportance of this term, and to simplify the calculations, only the radial derivatives of the potential were used in its

(13) A. I. Kitaigorodsky, "Molecular Crystals and Molecules", Academic Press, New York, 1973.

(14) J. C. Raich, A. B. Anderson, and W. England, *J. Chem. Phys.*, **64**, 5088 (1976).

(15) T. Kihara, *Rev. Mod. Phys.*, **25**, 831 (1953).

(16) V. P. Trubitsyn, *Fiz. Tverd. Tela.*, **8**, 862 (1966) (*Sov. Phys.–Solid State (Engl. Transl.)*, **8**, 688 (1966)).
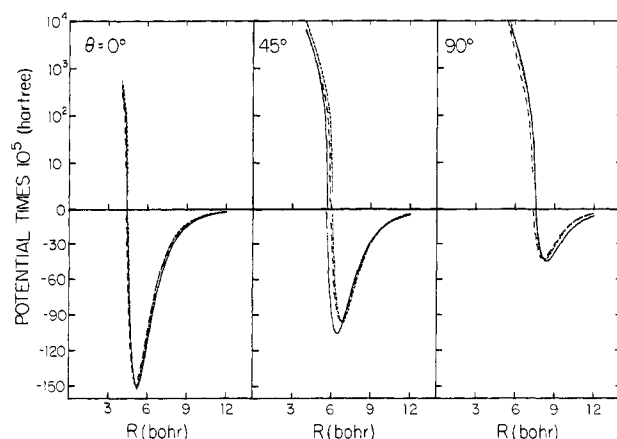
Figure 5. (H$_2$)$_3$ pair potentials for configuration B (defined in text) showing averaged sum of H$_2$ potentials (solid curve) and fits by a′ (long dashed curve) and b′ (short dashed curve) parameter sets. All energies and distances are in atomic units. The angle θ is defined in the text.

determination by use of the Domb–Salter approximation.[17] With this approximation, we find that at 1 Mbar the lattice zero-point energy is ~5% of the total lattice energy and 1% of the lattice free energy.

H$_2$ Lattice Energies. There have been many calculations of the structure and the energy of solid molecular H$_2$ crystals, using a great variety of forms of the pair potential.[8] These potentials employ empirical fits of experimental data and a variety of theoretical determinations.[9,18] Because of the uncertainty in the H$_2$–H$_2$ potential, and especially its variation at high pressure,[19,20] we consider here results derived from a set of potentials which may at least bracket the correct values.

For comparison with the other results on the H$_2$ phase, we performed calculations with the potential used to generate the (H$_2$)$_3$ pair potentials, the RAE potential.[14] Since the anisotropy of the H$_2$ potential is not large, and the zero-point energy makes a small contribution to the total energy, the Domb–Salter approximation was used in the form for spherically symmetric potentials.[17] From the methods of Neece et al.,[21] we estimate that neglecting the anisotropy causes an error of ~7% at 200 kbar and 2% at 1 Mbar, with the zero-point energy ca. 30% and 10% of the lattice energy, respectively. Only the face-centered cubic structure (space group *Pa*3) was considered, and all many-body contributions were neglected.

Results

Table I gives the parameters that fit the angularly averaged (H$_2$)$_3$ potentials. Since there is no information available about the (H$_2$)$_3$ potentials, and the methods adopted here are crude at best, we have considered for each configuration four representations of the pair potentials (potentials a′–d′ for each configuration). Each of these representations was found by making small variations in the parameters obtained by fitting the molecule–molecule potentials. These parameters are included in Table I. Potentials a′ and b′ for each configuration are exp 6 potentials (eq 4), and c′ and d′ are $m - 6$ potentials (eq 3).

(17) C. Domb and L. Salter, *Philos. Mag.*, **43**, 1083 (1952).
(18) See ref 2 and, for example: (a) R. D. Etters, R. Danilowicz, and W. England, *Phys. Rev. A*, **12**, 2199 (1975); (b) A. B. Anderson, J. C. Raich, and R. D. Etters, *Phys. Rev. B*, **14**, 814 (1976); (c) W. England, R. Etters, J. Raich, and R. Danilowicz, *Phys. Rev. Lett.*, **32**, 758 (1974).
(19) F. H. Ree and C. F. Bender, *J. Chem. Phys.*, **71**, 5362 (1979).
(20) R. LeSar and D. R. Herschbach, *J. Phys. Chem.*, **85**, 2798 (1981).
(21) G. A. Neece, F. J. Rogers, and W. G. Hoover, *J. Comput. Phys.*, **7**, 621 (1971).

TABLE II: Calculated Properties of (H$_2$)$_3$ Configuration B[a]

potential	P	V	E_1	$G_1(H_6)$
a′	400	11.86	0.0335	0.2142
b′	400	13.09	0.0369	0.2364
a′	600	10.87	0.0518	0.3002
b′	600	12.13	0.0552	0.3323
a′	800	10.28	0.0673	0.3805
b′	800	11.46	0.0728	0.4218

[a] The intermolecular potentials a′ and b′ for (H$_2$)$_3$ are discussed in the text. Table I gives the parameters. P is the pressure (kbar), V the volume (cm^3/mol), E_1 the lattice energy of eq 1 (hartree), and $G_1(H_6)$ the lattice free energy (hartree).
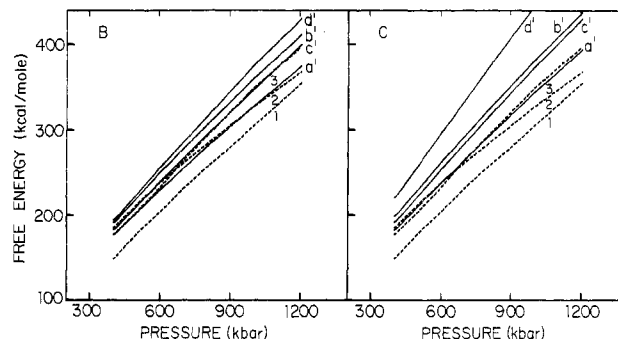

Figure 6. Free energy vs. pressure for configurations B and C (defined in the text). Shown (solid curves) are calculations with all four parameter sets given in Table I, where $G' = G_1(H_6) + \Delta E_r$, and ΔE_r is the energy of reaction from Figure 2. Also shown (dashed curves) are results for $3G_1(H_2)$ from calculations on solid molecular H$_2$. The curve marked 1 is from ref 18a, 2 is from ref 9, and 3 was calculated here with the pair potential of ref 14.

In all cases, potentials a′ and c′ represent smaller molecules (r_c, the radius of the hard-core disk in the plane of the molecule, is smaller) and have a softer hard-core wall than do b′ and d′. To illustrate the fit of these potentials, Figure 5 shows the potential for configuration B at three angles (with the molecular planes parallel). The angular average of the molecule–molecule potential is shown as well as the exp 6 potentials a′ and b′. The actual differences in the two parameter sets are relatively small, although for crystals at high pressure the behavior is rather different. This is apparent in Table II, where we give calculated crystal parameters for configuration B as a function of pressure and parameter set. Small changes in the size and shape of the repulsive potential, which may not be noticeable at low pressures, cause fairly large differences in calculations at high pressure.

Figure 6 plots the calculated lattice free energy as $3G_1(H_2)$ for solid hydrogen taken from the sources cited above.[9,18a] We also include the results obtained by using the RAE[14] potential that was used to generate the (H$_2$)$_3$ intermolecular potentials. There is a fairly large discrepancy among the results calculated with these potentials, especially at high pressures, where the RAE potential used here consistently had a much softer repulsive wall. The range of energies from the different calculations is ca. 10 kcal/mol or 10% at 500 kbar and 12 kcal/mol or 2.5% at 1.5 Mbar. At high pressures, the lattice free energies from the different calculations are bounded roughly from above by those of Etters et al.[18a] (denoted 1) and from below by the calculations with the RAE potential (denoted 3). The results of Ross[9] (his anisotropic potential 9, here denoted 2) fall in the middle of the range.

Figure 6 also shows the free energy of configurations B and C of (H$_2$)$_3$ as calculated with each of the four potential

sets. The quantity plotted is $G' = G_1(H_6) + \Delta E_r$. Intersection of the H_2 and $(H_2)_3$ curves gives the transition pressure. The energies calculated with the $m - 6$ potentials are consistently higher than those with the exp 6 potentials, because of the steeper slope in the repulsive wall region in $m - 6$ potentials. For both configurations, the potentials representing smaller molecules (a' and c') give lower free energies than their counterparts (b' and d'). The free-energy curves for configuration A, the undissociated H_6 molecule, are all higher in energy than the H_2 curves. Only if the potentials for the $(H_2)_3$ interactions are best described by the (a') parameter sets is there a possibility of an $(H_2)_3$ phase, with the most stable phase not being the free, gas-phase regular hexagonal structure, but rather a distorted $(H_2)_3$ complex, configuration B being most likely. For configuration B potential a', the calculated free energies are lower in energy than two of the H_2 curves but higher than the curve calculated with the RAE potential. The transitions shown in Figure 6 for this configuration actually represent transitions from an H_2 phase to an $(H_2)_3$ phase. Because of the large uncertainties in the free-energy curves, for H_2 as well as $(H_2)_3$, it is only possible to estimate a transition pressure to be in the range of several hundred kilobars.

The predicted pressure would be increased somewhat by inclusion of the change in intramolecular zero-point energy in going from three H_2 molecules to an $(H_2)_3$ complex. For the undissociated, regular hexagonal form (configuration A), the vibrational zero-point energy of the H_6 complex is estimated[6] as 25.8 kcal/mol, ca. 7.1 kcal/mol greater than that for three free H_2 molecules. As the $(H_2)_3$ complex dissociates and the H_2 components form, this difference would decrease.

The stabilization of the $(H_2)_3$ complex by the compressed lattice can be demonstrated by a simple heuristic calculation. Using the correlation between size of the molecule and potential parameters, and the nearest in-plane neighbors (Figure 4a) with lattice parameter appropriate to a given pressure (for configuration Ba'), one can calculate the change in interaction energy as a function of molecule size. The results for molecules at positions found for 400 kbar are shown as the E_1 curve in Figure 2. As the molecules expand, the interaction energy goes up, but the molecular self-energy $E(B_{2u})$ goes down. The sum of these energies E_s has a minimum. As the pressure increases, the minimum shifts inward and is sharper.

Also plotted in Figure 2 is the interaction energy of three independent H_2 molecules found with the RAE potential. It is clear that the $(H_2)_3$ complex is better described as a molecular complex rather than merely a trio of independent H_2 molecules.

Discussion

The small differences in energies of solid phases (a few kcal/mol for most cases) make it difficult to theoretically predict transition pressures of solid–solid transitions. Especially at high pressures, small differences in the pair potential can lead to relatively large differences in the calculated energies. Figure 7 summarizes the situation for solid hydrogen. Energy–volume curves are plotted for the metallic phase,[22,23] the molecular H_2 phase (from ref 9, 18a, and 22 and the present results), and the molecular $(H_2)_3$ phase calculated here. The upper curves for the metallic phase (curves 4–6) are results from different theoretical methods (without correlational energy) and show a spread
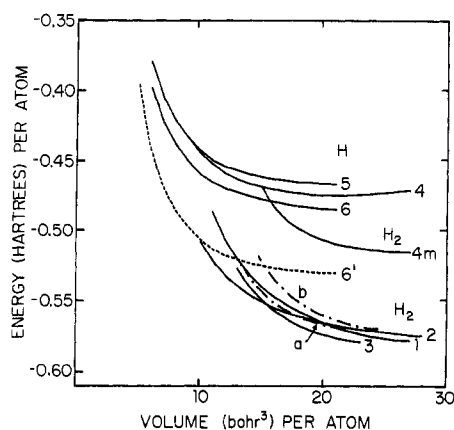

Figure 7. Energy per atom (hartree) for metallic hydrogen (H) and solid molecular hydrogen (H_2, solid curves). The curves for metallic hydrogen were taken from ref 23 (curves 5, 6, and 6') and ref 22 (curve 4), where only curve 6' (dashed line) includes correlation and zero-point energy. The molecular curves were taken from ref 22 (4m), ref 9 (2), and ref 18a (1). The present results with the RAE potential of ref 14 are given in curve 3. Curve 4m is from an ab initio calculation and does not include correlation or zero-point energies, while curves 1–3 are calculated with a pair potential formulism. The dot–dash curves are for the molecular $(H_2)_3$ phase (configuration B and potentials a' and b') discussed here. All energies are relative to infinite separation of all protons and electrons.

TABLE III: Estimated Transition Pressures in Solid Hydrogen[a]

transition	version[b]	P	ΔV
molecular H_2-metallic H	(1–6')	1.93	0.464
	(2–6')	3.16	0.223
	(3–6')	2.45	0.500
	(4m–4)	1.94	0.553
molecular $(H_2)_3$-metallic H	(a–6')	2.20	0.491
molecular H_2-molecular $(H_2)_3$	(1–a)	4.345	0.143
	(2–a)	0.963	0.143

[a] Transition pressures between phases of solid hydrogen estimated from Figure 7. P is the transition pressure (Mbar) and ΔV is the volume change between the two phases (cm^3/mol of H atoms). [b] The quantities in parentheses refer to the curves in Figure 7 and thereby indicate different approximate versions of the transition parameters.

in energy of ~ 0.015 hartree (9.4 kcal/mol) at a volume of 0.5 cm^3/mol. The correlation energy for the metallic phase can be estimated by using the expression for an electron gas with the metallic electronic density and is included on the lowest metallic curve (6') along with the estimated vibrational zero-point energy.[23] This expression overestimates the correlation energy somewhat.[24] The highest-energy molecular H_2 curve (4m) is from a Hartree–Fock study of the compressed crystal and does not include correlation energy or zero-point energy.[22] The other curves for molecular H_2 are from calculations using empirical pair potentials and include the van der Waal's and zero-point energy.[9,18a] The $(H_2)_3$ curves were generated here. All energies and volumes are given per H atom. The uncertainty in the molecular curves roughly parallels that of the metallic curves. Although it is not possible to make an accurate prediction of any phase transition in solid hy-

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drogen, from Figures 6 and 7 it is apparent that there may be a transition from a molecular H_2 phase to a molecular $(H_2)_3$ phase.

Transition pressures can be derived from Figure 7 by finding the slope of the line that is a common tangent for the curves describing the phases of interest. Table III lists the rough ranges for transition pressures thus estimated. Note that the pressure required for transition to an atomic metallic state would not be substantially changed by the existence of an $(H_2)_3$ phase.

The existence of an $(H_2)_3$ phase is more consistent with a more gradual transition[8,22] rather than a direct first-order change to the metallic state.[8,9] Ramaker et al.,[22] in an ab initio study of solid hydrogen at high pressures (see curves 4 and 4m in Figure 7), found that indeed there is a gradual weakening of the H_2 bonds as an extended cluster of H_2 molecules is formed. Other workers have suggested various clusters of the metal that include planes or strings of H atoms. Brovman et al.[10] suggest that a filamentary structure may be a stable form of the metal and may be metastable at zero pressure. Harris and Delhalle[11] point out that at zero pressures there would be an explosion to form H_2 molecules and that such a chain would need a minimum of ~700 kbar to maintain hydrostatic stability. Brovman et al.[10] also suggest that the metal contains planes of H atoms. The work of Dixon et al.,[6] however, indicates that, of the possible clusters of hydrogen molecules, H_6 is the most stable. This suggests that, in the process of extended cluster formation, a phase involving termolecular clusters would be a first step. The forces driving such a process are displayed in Figure 2. As the H_6 complex dissociates, the molecular self-energy drops, but, as the volume expands, the repulsive forces with neighboring molecules increase. Of course, this is a greatly oversimplified view, since all bonding between the center molecule and its neighbors is neglected. At some pressure, the neighboring molecules will be driven together with such force that bonding may occur.

The view that there is a gradual transition to a metallic phase is qualitatively consistent with a recent experimental study which looked at the Raman scattering from solid H_2 at room temperature to 630 kbar.[18] The H_2 stretching frequency increased as the pressure was increased to 350 kbar, leveled off near 400 kbar, and then decreased slightly. The initial increase is expected from compression of the H_2 bond.[20] Since the formation of clusters of H_2 molecules at higher pressures is expected to lead to a decrease in frequency (with longer bonds in the clusters), the theoretical pictures is at least qualitatively compatible with this experiment.

Perhaps the most useful aspect of the present calculation is the suggestion that species related to transition states may be trapped in compressed solids. The most stable form of the termolecular complex expected in the solid is not the most stable transition state, but rather a distorted, partially dissociated form. Configuration B, in which the molecule is really a bonded cluster of H_2 molecules, is a compromise between the loss of energy through dissociation of the molecule and the gain of energy through expansion of the lattice. Since we have not examined other configurations, including all nonplanar ones, we cannot say that this configuration is the most stable; however, it should be more stable than the undissociated molecule. This implies not only a pressure-induced reaction (such as the disproportionation reactions given above) but a pressure-stabilized reaction for which the products could not exist in the gas phase. By performing the reaction in the solid state, the molecules are fixed close together and do not have the entropic handicap suffered by termolecular processes in the gas phase.

Use of Core Electron Binding Energies for the Comparison of Valence-Shell Ionization Potentials and the Quantification of the Bonding and Antibonding Character of Molecular Orbitals

William L. Jolly

Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720 (Received: July 27, 1981)

A localized-orbital ionization potential (LOIP) is defined as the ionization potential that an atomic orbital would have if it were in a hypothetical nonbonding state and were localized on a particular atom in a molecule. The LOIP includes the entire molecular potential at the atom and the electronic relaxation energy associated with the creation of a positive charge on the atom. It is shown that differences in core electron binding energy between compounds of the same element are proportional to the corresponding difference in LOIP. Thus, it is possible to measure quantitatively the relative bonding or antibonding character of actual molecular orbitals, relative to hypothetical nonbonding atomic orbitals, by using experimental valence and core ionization potentials.

The traditional interpretation of a valence-shell photoelectron spectrum consists of the assignment of the various peaks to molecular orbitals (MOs), a procedure which is usually aided by comparison of the measured ionization potentials with values estimated by quantum-mechanical methods. Knowledge of the ionization potential corresponding to a particular MO is of limited value to a chemist because the absolute magnitude of an ionization