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IMPORTANCE OF THE ANISOTROPIC INTERACTION IN MOLECULAR SOLID H₂ AT HIGH PRESSURE

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We find that by using a quantum crystal formalism the relatively small anisotropic molecular interactions in hydrogen can resolve the large discrepancy between the experimental equation of state and several recent theories in the solid phase at high pressure. This does not require the introduction of any new intermolecular potential.

THERE ARE several recent theoretical calculations[1-4] of the equation of state for solid H_2. These use quite different formalisms, reference 1 being a semi-classical harmonic calculation while reference 2 is a Monte Carlo variational calculation; reference 3 is a quantum crystal cluster expansion and reference 4, a self-consistent Green's function method. These theories agree in the high pressure ($P \gtrsim 10^3$ atm) regime which indicates that for some purposes (e.g. calculation of the ground state energy E) short-range correlations between molecules can be ignored at high pressure as in reference 1 without invalidating the calculation. In view of the consistent results of references 1–4, it would seem that one can calculate the equation of state of molecular hydrogen quite well and thus predict the molecular solid–metal phase transition[5] and apply the result to various astrophysical problems[6] in a range of pressure where experiments are difficult to perform. Unfortunately, even with $P \sim 10^4$ atm there is a large discrepancy between the theories listed above and measurements[7] of the PV curve near zero temperature. If we believe the experiments are reasonably accurate, then the most likely source of the disagreement is the inadequacy of the two-body potentials[8] which are obtained empirically from measurements on gaseous H_2. Needless to say, the introduction of a potential with new parameters cannot lead to any better understanding of the physics in the problem. The

purpose of this letter is to incorporate the anisotropic part of the intermolecular interaction V_{ani}[9,10] into our previous formalism[4] and to demonstrate that this can remove the discrepancy between theory and experiment for the ground state energy and pressure of molecular hydrogen within the framework of the present understanding of the interaction.

Even at relatively large molar volumes corresponding to a nearest neighbor distance a ~ 3.7 Å, V_{ani} is large enough to have a substantial effect on a given pair of molecules in certain relative orientations;[10] however, it has a small effect when averaged over many particles localized at lattice sites.[9] Several[3,5,11] attempts have been made to include V_{ani} in calculations of E; Neece, *et al.*[5] treat the molecules classically, giving them several particular orientations. In reference 3, on the other hand, they are treated quantum mechanically but are not allowed to be in angular momentum states $l \neq 0$. Such states are used in reference 11, but the molecules are otherwise treated as classical point particles placed on lattice sites. In the present work, we use a totally quantum mechanical approach, allowing both motion of the center of mass of the melecules and angular momentum states[12] $l > 0$.

The potential between two H_2 molecules depends on the displacement $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ between the

centers of mass of the molecules and on the directions of their axes. We shall write it as

$$V(\mathbf{r}, \omega_1, \omega_2) = \sum_{\substack{l=0,2 \\ l'=0,2}} V^{ll'}(r) Y_l(\omega_1) Y_l(\omega_2) \quad (1)$$

where ω_1 and ω_2 describe the orientations of the molecules relative to the crystal c-axis (h.c.p. structure is assumed) and Y_l is the spherical harmonic Y_{l0}; $V^{00}/4\pi$ is the isotropic potential $V(r)$ which we shall take as the empirical modified Buckingham ($E - 6$) potential[13]

$$V(r) = \begin{cases} \dfrac{\epsilon_0}{1-6/\alpha}\left[\dfrac{6}{\alpha}\cdot \exp[\alpha(1-r/r_m)] - (r_m/r)^6\right], & r > r_{max} \\ \infty, & r < r_{max} \end{cases}$$

where $\epsilon_0 = 38.02\,$K, $r_m = 3.339\,$Å, $\alpha = 14$, and $r_{max}/r_m = .20319$.

The anisotropic parts V^{20} and V^{02} are taken to be the first terms in Nakamura's expansion of de Boer's potential,

$$V^{20} = V^{02} = \frac{8\pi}{5}\left[\beta_1 e^{-(r-a_0)/\rho} - \beta_2\left(\frac{a_0}{r}\right)^6\right] P_2(\cos\theta_{12}) \quad (2)$$

with $\beta_1 = 2.6\,$K, $\beta_2 = 1.6\,$K, $\rho = .283\,$Å and $a_0 = 3.75\,$Å; θ_{12} is the angle between $\mathbf{r}$ and the c-axis while P_l is the Legendre polynomial of degree l. For V^{22} the dominant term is the electric quadrupole–quadrupole interaction,

$$V^{22} = 20\pi\,\Gamma_0\,P_4(\cos\theta_{12})\,(a_0/r)^5, \quad \Gamma = 1K \quad (3)$$

In our earlier work[4] we calculate the single particle wave function $\phi_i(1,\omega_1)$ localized around lattice position R_i using a self-consistent potential field $u_i(1)$. A straightforward extension of this theory leads us to expand ϕ_i as

$$\phi_i(1,\omega_1) = Y_0(\omega_1)\phi_{0i}(1) + Y_2(\omega_1)\phi_{2i}(1) \quad (4)$$

while

$$u_i(1,\omega_1) = Y_0(\omega_1)Y_0(\omega_1)u_{0i}(1) + Y_0(\omega_1)Y_2(\omega_1)u_{2i}(1) \quad (5)$$

is the self-consistent field; u_0 and u_2 are written in the harmonic approximation by expanding

$$u_i(1,\omega_1) = \sum_{j\neq i} \int V(\mathbf{r},\omega_1,\omega_2)\,\chi_{ij}(1,2,\omega_1,\omega_2) \\ |\phi_j(2,\omega_2)|^2\,d^3r_2\,d\omega_2 \quad (6)$$

to second order in the displacement $|\mathbf{r}_1 - \mathbf{R}_i|$. Here χ_{ij} is the correlation function for particles 1 and 2; it is expanded as

$$\chi_{ij} = 4\pi \sum_{l,l'=0,2}' \chi_{ij}^{ll'}(12) Y_l(\omega_1) Y_{l'}(\omega_2) \quad (7)$$

and is found from the equation

$$(H_{ij} - \lambda_0)\chi_{ij}\phi_i\phi_j = 0, \quad (8)$$

$$H_{ij} = -(\nabla_1^2 + \nabla_2^2)/2m + l_1(l_1+1)B_I + l_2(l_2+1)B_I$$
$$+ V(\mathbf{r},\omega_1,\omega_2) + u_i(1,\omega_1) + u_j(2,\omega_2) + \Delta_{ij}(1,2)$$
$$-[\int \chi_{ij}(\bar{1},2,\bar\omega_1,\omega_2)V(\overline{\mathbf{r}_1-\mathbf{r}_2},\bar\omega_1,\omega_2)|\phi_i^2(\bar 1,\bar\omega)|^2 d^3\bar r_1 d\bar\omega_1$$
$$+\int \chi_{ij}(1,\bar 2,\omega_1,\bar\omega_2)V(\overline{\mathbf{r}_1-\mathbf{r}_2},\omega_1,\bar\omega_2)|\phi_j^2(\bar 2,\bar\omega_2)|^2 d^3\bar r_2 d\bar\omega_2] \quad (9)$$

where $B_I = 1/2I = 87\,$K, I being the moment of inertia of the hydrogen molecule. The term Δ_{ij} contains some effects of three-body correlations; it is approximated[4] by $P_{ij}(r_{12} - R_{ij})$ where P_{ij} is a constant such that the condition

$$\int \chi_{ij}(1,2,\omega_1,\omega_2)R_{ij}\cdot(\mathbf{r} - \mathbf{R}_{ij})|\phi_i(1,\omega_1)|^2$$
$$|\phi_j(2,\omega_2)|^2\,d^3r_1\,d^3r_2\,d\omega_1 d\omega_2 = 0$$

is satisfied. Also, λ_0 is chosen to give physically reasonable behavior of χ_{ij} for $r_{12} \to \infty$.

In reference 4, where $V(r;\omega_1,\omega_2)$ consists only of V^{00}, equations (6) and (8) plus the Schrodinger equation for ϕ_i are solved simultaneously. In the present work, equation (8) is decomposed into four equations; it is very difficult to solve the resulting set of equations self-consistently. We have determined χ_{ij} to first order in V^{20}/B_I and V^{22}/B_I which is adequate for $V \gtrsim 10\,$cm^3; this volume is also the smallest reported by Stewart.[7]

$$\chi_{ij}^{02} = -\chi_{ij}^{00}(\phi_{2j}/\phi_{0j} + V^{02}/24\pi B_I)$$
$$\chi_{ij}^{20} = -\chi_{ij}^{00}(\phi_{2i}/\phi_{0i} + V^{20}/24\pi B_I)$$
$$\chi_{ij}^{22} = -\chi_{ij}^{00} V^{22}/48\pi B_I \quad (10)$$

where χ_{ij}^{00} is the correlation function of reference 4. Using equation (10), we solve equation (6) and the single-particle Schrödinger equation self-consistently. It is then easy to find the crystal energy per particle,

$$E = \int \phi_i^*(1,\omega_1)(-\nabla_1^2/2m + u_i(1,\omega_1)/2)\phi_i(1,\omega_1)d^3r_1 d\omega_1$$
$$+ 6B_I \int \phi_{2i}^2(1)\,d^3r_1 \quad (11)$$
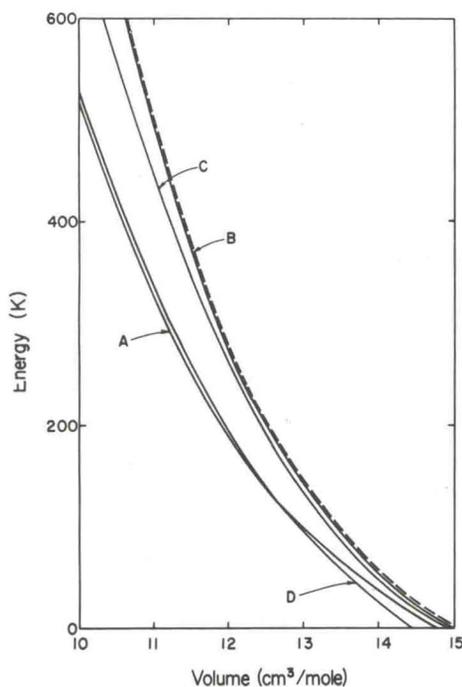
FIG. 1. The ground state energy (K) of solid H_2 vs. molar volume (cm^3).

V_{ani}) about three or four times larger than those found here.[15] As a result, the calculated energy will be too low. However, the situation is rectified if we also decrease β_1 in equation (2) by about a factor of 2 to $\sim 1.3\,K$; there is considerable independent evidence that this is more nearly correct than $\beta_1 = 2.6\,K$. For example, the calculated volume dependence[4] of the λ-transition temperature agrees better with measurements when β_1 is decreased by about a factor of two. Harris[16] gives a thorough discussion of further evidence supporting a smaller β_1.

An interesting feature of our calculation is that V^{20} and V^{02} make by far the most important contributions ($\gtrsim 90\%$) to ΔE_a at all molar volumes investigated, even though V^{22} is larger at large V. The reason is that zero-point motion and correlations are important in modulating the strength of the interactions; V^{02} and V^{20} are strongly enhanced[4] by these quantum crystal effects at large volume. At smaller volume, they are larger than V^{22}.

Using the anisotropic interaction of equations (2) and (3) we find curve C of Fig. 1; A is experimental[7] and B is from reference 4, corresponding to $V_{ani} \equiv 0$. The dashed curve is the calculation of Krumhansl and Wu[3] also employing the E-6 potential. From the plot we see that the introduction of V_{ani} improves the agreement of theory and experiment but that there is still a significant discrepancy. We believe that an important point in this connection is the value of ρ in equation (2). The value $0.283\,\text{Å}$ is theoretical; according to the empirical E-6 potential, however, ρ should be $r_m/\alpha = 3.339/14 = 0.239\,\text{Å}$. Since the exponential parts of V^{00} and V_{ani} should in principle have the same r dependence, we believe that the smaller ρ is preferred. Its use in V_{ani} leads to curve D of Fig. 1 which agrees quite well with Stewart's measurements, especially at high pressures where our general formalism is most reliable.

The good agreement is, of course, conditional depending on the validity of the approximations. We believe the only questionable point is that some terms proportional to Y_{2m}, $m \neq 0$, are ignored in V_{ani}. It is straightforward but very tedious to include them; we expect that they will lead to values of ΔE_a (the correction to E produced by

These results are in conflict with the work of Raich and Etters[11] who find a vanishing contribution from V^{20} and V^{02}. This occurs because they treat the H_2 molecules as quantum mechanical rigid rotators pinned to the lattice sites with no zero-point motion and, naturally, no correlated motions. Consequently, V^{20} and V^{02} give zero net contribution to u_i when summed over nearest neighbors of a given molecule in an h.c.p. or cubic crystal. Because we have zero-point motion and find the field u_i according to equation (6), we find a non-vanishing and in fact large contribution from these potentials. It vanishes only in the classical limit of $\phi_i^2 \to \delta\,(\mathbf{r}_1 - \mathbf{R}_i)$ as implicity assumed in reference 11. We conclude that a quantum crystal formalism is essential in calculating ΔE_a and leads to a much larger correction than would otherwise be found.

Another interesting result of our calculation is the amplitude ϕ_{2i} for each molecule to be in the $l = 2$ state. For $V \gtrsim 11\,cm^2$ it varies slowly, being 2–4% of the total amplitude. The amplitude rises to about 15% at $V = 10\,cm^3$ in the case of curve D, indicating that our approach is not valid for much smaller V. Similarly, we note that $\Delta E_a \sim 200\,K$ is large for curve D at $V \sim 10\,cm^3$; however,

the energy shift for a given pair of molecules is ~ 30 K, still considerably smaller than the energy ~ 200 K required to produce a rotational or translational excited state.

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On étudie l'équation d'état d'Hydrogène solide à haute pression. Il existe une contradiction importante entre théorie et expérience. On attribue cette contradiction à une anisotropic faible de l'interaction moléculaire. On montre que la théorie de 'quantum crystal' utilisée avec le potentiel intermoléculair conventionnel peut résoudre complètement cette dilemme.