

IMPORTANCE OF THE ANISOTROPIC INTERACTION IN MOLECULAR SOLID H_2 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 calculations¹⁻⁴ 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 transition⁵ and apply the result to various astrophysical problems⁶ 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 measurements⁷ 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 potentials⁸ 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 formalism⁴ 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 $a \sim 3.7$ 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 molecules and angular momentum states¹² $l > 0$.

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

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

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 ($E-6$) potential¹³

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

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,

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

In our earlier work⁴ we calculate the single particle wave function $\phi_i(1, \omega_i)$ 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

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

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

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

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

where $B_l = 1/2I = 87$ K, I being the moment of inertia of the hydrogen molecule. The term Δ_{ij} contains some effects of three-body correlations; it is approximated⁴ by $P_{ij}(r_{12} - R_{ij})$ where P_{ij} is a constant such that the condition

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

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

In reference 4, where $V(\mathbf{r}; \omega_1, \omega_2)$ 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_l and V^{22}/B_l which is adequate for $V \gtrsim 10$ cm³; this volume is also the smallest reported by Stewart.⁷

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

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,

$$\begin{aligned} E = & \int \phi_i^*(1, \omega_1) (-\nabla_1^2/2m + u_i(1, \omega_1)/2) \phi_i(1, \omega_1) d^3 r_1 d\omega_1 \\ & + 6B_l \int \phi_{2i}^2(1) d^3 r_1 \end{aligned} \quad (11)$$