

## Rotational Molecular Motion in Solid $H_2$ and $D_2$ Under Pressure\*

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*The rotational state of a  $H_2$  or  $D_2$  molecule in solid hydrogen or deuterium is calculated over the range of densities for which the molecular phases are expected to be stable. For para- $H_2$  and ortho- $D_2$  we predict sudden transitions as the pressure is increased from states where the molecules are rotating freely to states where they are librating about equilibrium orientations. These transitions are predicted to occur in the region of several hundred megabars of pressure. Although in principle observable, these first-order transitions are expected to lead to only small changes in the equation-of-state curves. These transitions from rotating to librating molecular motion are expected to be accompanied by changes in the crystal structures from hcp to fcc.*

### 1. INTRODUCTION

The equation of state of solid molecular hydrogen at high pressures has been the subject of several recent theoretical investigations.<sup>1-9</sup> No new experimental results have been available since the measurements of Stewart.<sup>10</sup> The recent interest in the high-pressure phases of solid hydrogen is partially motivated by current efforts to produce a high-pressure metallic phase of hydrogen and by the belief that the Jovian planets are composed mainly of solid hydrogen.<sup>7</sup>

At low pressures the lattice dynamics of solid  $H_2$  and  $D_2$  must be treated by the methods applicable to quantum crystals.<sup>1-3</sup> The ground-state properties of solid  $H_2$  have been calculated using both a truncated cluster expansion and Monte Carlo methods with a Jastrow wave function.<sup>1-3</sup> However, it has recently been shown that for densities corresponding

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to pressures higher than about  $10^3$  bar the harmonic approximation can be used with increasing accuracy.<sup>4,5</sup>

Most theoretical descriptions assume that the intermolecular potential and the two-body correlation function are spherically symmetric, that is, independent of the orientation of the diatomic  $H_2$  molecules. This is a reasonable assumption for relatively low pressures, where the hindrance to free rotation of the molecules is small. However, one calculation of the equation of state of molecular hydrogen at high pressures does assume that the rotational motion of the  $H_2$  molecules is more or less restricted so that they liberate about fixed equilibrium orientations.<sup>8</sup> This treatment, which then includes the zero-point librational motions of the molecules, is expected to apply at high pressures.

The contribution to the equation of state, made by the anisotropic part of the intermolecular potential, is expected to be small for either case. Even if the molecules in the crystal were not rotating or librating at all, the deviation of the molecular shape from sphericity is only about 8%. Kolos and Roothaan<sup>11</sup> have calculated the electronic charge distribution for the  $H_2$  molecule with the results  $\langle r^2 \rangle = 2.5430a_0^2$ , and  $\langle 3z^2 - r^2 \rangle = 0.5157a_0^2$ , so that  $\sqrt{\langle r^2 \rangle} \cong 0.84 \text{ \AA}$  and  $\sqrt{\langle 3z^2 \rangle} \cong 0.92 \text{ \AA}$ . Here,  $a_0$  is the Bohr radius. For a spherical molecule  $\langle r^2 \rangle = \langle 3z^2 \rangle$ .

The purpose of this paper is to determine the rotational state of an  $H_2$  molecule in solid hydrogen at zero temperature as a function of the density. Such a study would be useful in a calculation of the lattice dynamics and the equation of state of solid hydrogen at high pressures. The calculation would determine in which regions of density the molecules can be considered to be rotating freely, and in which regions they are librating about equilibrium orientations. This information is required for a realistic treatment of the lattice dynamics of solid  $H_2$ . In the rotating region the theories using spherically symmetric potentials can be applied. When the molecules are librating, the anisotropic intermolecular forces as well as the librational zero-point energy must be considered.<sup>8</sup> In the present paper we develop a description of the rotational state of an  $H_2$  molecule in a crystal of solid hydrogen at zero temperature within the framework of the mean field or molecular field approximation. We assume that the molecules will eventually align themselves along certain orientations in the crystal. These equilibrium orientations are taken to be the same as the directions of molecular alignment of ortho- $H_2$  and para- $D_2$  at atmospheric pressure.<sup>12-18</sup> That is, we expect the high-pressure phase of solid  $H_2$  to be face-centered cubic (fcc) with space group  $Pa3$  ( $T_h^6$ ). This assumption is reasonable since the  $Pa3$  space group does occur in other crystals of ordered diatomic molecules such as solid  $N_2$ .<sup>13</sup> There exists, of course, the possibility of a transformation into a different structure such as the  $\gamma$  phase of solid nitrogen,

or even structures similar to those of solid chlorine, bromine, and iodine, as the pressure is increased. Such structural changes would, however, imply that a drastic change from the nearly spherical shape of the H<sub>2</sub> molecules had taken place. We do not consider the possibility of a change in the electron distribution of the H<sub>2</sub> molecule in the pressure range of interest. We thus assume the same intermolecular potential as determined at zero pressure. In addition, we assume that the rotational motion of the molecules is not significantly coupled to the translational motion so that a meaning can still be attached to a "rotational" state of the molecules. We thus consider a rigid lattice model, and concern ourselves only with the rotational part of the molecular motion. The rigid lattice model has been used to describe the properties of solid hydrogen as a function of temperature at zero pressure.<sup>12,14-17</sup> In the present paper we describe mainly solid hydrogen. The calculations can, of course, be readily applied to solid deuterium as well.

## 2. INTERMOLECULAR POTENTIAL

The isotropic part of the intermolecular potential for solid hydrogen is usually represented by Lennard-Jones or Buckingham potentials. At normal pressure the major contribution to the anisotropic part of the interaction of two H<sub>2</sub> molecules is the electrostatic quadrupole-quadrupole (EQQ) interaction.<sup>14-17</sup> As a first approximation, we assume that the anisotropic interactions of a particular molecule with its neighbors can be represented by an effective mean field. This approach, known also as the molecular field or internal field approximation, has been used to predict the ordering of H<sub>2</sub> molecules as a function of temperature.<sup>12,15</sup> For the *Pa3* structure the molecules are aligned along threefold axes of symmetry. It has been shown that, if a threefold axis is assumed, the effective EQQ interaction of two molecules can be written as<sup>15</sup>

$$V_{ij}^Q = -(95\pi/18)\Gamma_{ij}Y_{20}(\omega_i)Y_{20}(\omega_j) \quad (1)$$

Here,  $\Gamma_{ij} = \Gamma_0(R_0/R_{ij})^5$ , where  $\Gamma_0$  is the EQQ coupling constant,<sup>17</sup>  $R_0$  is the nearest neighbor distance, and  $R_{ij}$  is the separation between molecules  $i$  and  $j$ . The experimental values for  $\Gamma_0$ , deduced from Raman spectra, are  $0.539 \text{ cm}^{-1}$  for hydrogen and  $0.736 \text{ cm}^{-1}$  for deuterium.<sup>18</sup> In Eq. (1)  $\omega_i = (\theta_i, \phi_i)$  specifies the orientation of a molecule on site  $i$ , relative to its symmetry axis, and the  $Y_{JM}$  are spherical harmonics.

The anisotropic repulsive and dispersion interactions, although small compared with the EQQ interactions at normal densities, are expected to become more important as the pressure is increased. There exist currently no accurate potentials which describe the interaction energy of two H<sub>2</sub> molecules for arbitrary relative orientation. Estimates can be obtained from the work



of Margenau<sup>19</sup> and de Boer.<sup>20</sup> Alternatively, one may try to fit an empirical potential to the results of detailed valence-bond calculations of the interaction energy of two  $H_2$  molecules at a few fixed relative orientations, as described by Margenau and Kestner<sup>21</sup> and elsewhere.<sup>22</sup>

In the present paper we use the results obtained from the work of Margenau<sup>19</sup> and de Boer<sup>20</sup> as quoted by Nakamura.<sup>14</sup> The anisotropic repulsive interaction has the form

$$V_{ij}^{\text{VAL}} = \{\sqrt{20\pi}C_1[Y_{20}(\Omega_i) + Y_{20}(\Omega_j)] + 20\pi C_2 Y_{20}(\Omega_i)Y_{20}(\Omega_j)\} \exp[(R_0 - R_{ij})/\rho] \quad (2)$$

Here,  $\Omega_i$  specifies the orientation of molecule  $i$  relative to the  $i$ - $j$  intermolecular axis. The parameters  $\rho$ ,  $C_1$ , and  $C_2$  are defined below. When the interaction (2) is summed over the sites of a fcc or hcp lattice, the contributions of the first two terms will vanish, leaving only the third term.

Within the framework of the molecular field approximation, where one assumes a threefold axis of symmetry, one again finds that the only term of Eq. (2) which contributes to the molecular field is

$$V_{ij}^{\text{VAL}} = -5\pi C_2 e^{-(R_{ij}-R_0)/\rho} Y_{20}(\omega_i)Y_{20}(\omega_j) \quad (3)$$

where we have transformed to the symmetry axis of molecules  $i$  and  $j$ ,<sup>16</sup> so that  $\omega_i$  and  $\omega_j$  are defined as in Eq. (1). Nakamura's values are  $\rho = 0.283 \text{ \AA}$  and  $C_2 = 0.0783 \text{ cm}^{-1}$ . An expression for the anisotropic dispersion interaction can also be obtained from Ref. 14. We shall neglect that contribution in the present paper. At normal densities the dispersion interaction for hydrogen contributes less than 10% of the total anisotropic interaction, and the volume dependence of the dispersion interaction is roughly  $1/R^6$  which is not appreciably faster than the  $1/R^5$  of the EQQ interactions.

We thus approximate the total anisotropic intermolecular potential by

$$V_{ij} = C_{ij} Y_{20}(\omega_i)Y_{20}(\omega_j) \quad (4)$$

where

$$C_{ij} = (-95\pi/18)\Gamma_0(R_0/R_{ij})^5 - 5\pi C_2 e^{-(R_{ij}-R_0)/\rho} \quad (5)$$

and all parameters have been defined previously.

### 3. MEAN FIELD APPROXIMATION

At zero temperature the effective mean field seen by a molecule on site  $i$  can now be constructed from Eqs. (4) and (5) in the usual way<sup>12</sup>:

$$V_i = \sum_j C_{ij} \langle \psi_0(\omega_j) | Y_{20}(\omega_j) | \psi_0(\omega_j) \rangle Y_{20}(\omega_i) \quad (6)$$

where the brackets  $\langle \rangle$  indicate a quantum mechanical average over the single-particle rotational ground-state wave functions of all neighboring molecules  $j$ . The summation runs over all neighbors of the molecule  $i$ . The wave function  $\psi_0(\omega_i)$  is determined from the solution of the wave equation:

$$(T_i + V_i)\psi_0(\omega_i) = E_0\psi_0(\omega_i) \quad (7)$$

where  $T_i$  is the rotational kinetic energy,  $T_i = BJ_i^2$ , and  $B = h^2/2I$ . Here,  $I$  is the moment of inertia of the molecule and  $J_i$  is the orbital angular momentum operator which satisfies

$$J_i^2 Y_{JM}(\omega_i) = J(J+1)Y_{JM}(\omega_i) \quad (8)$$

For H<sub>2</sub>  $B = 59.34 \text{ cm}^{-1}$  while for D<sub>2</sub>  $B = 29.91 \text{ cm}^{-1}$ . Using the mean field approximation,  $\psi_0(\omega_i)$  is then determined by the self-consistent solution of Eqs. (6) and (7). The potential (6) can be written in the form

$$V_i = -V_0 Y_{20}(\omega_i) \quad (9)$$

where, for the present work,  $V_0$  is a volume-dependent quantity defined by

$$V_0 = -\sum_j C_{ij} \langle \psi_0(\omega_j) | Y_{20}(\omega_j) | \psi_0(\omega_j) \rangle \quad (10)$$

The Schrödinger equation (7) for the rotational states of a H<sub>2</sub> molecule in crystalline hydrogen can also be written as

$$\{ -(B/\sin \theta) [(\partial/\partial \theta) \sin \theta (\partial/\partial \theta) + (1/\sin \theta) (\partial^2/\partial \phi^2)] + V \} \psi = E\psi \quad (11)$$

where, for convenience, we have left off the molecular labels. The eigenvalues  $E$  of Eq. (11) are the energy levels of the hindered rotor. For a potential of the form (9), Eq. (11) is separable into  $\theta$ - and  $\phi$ -dependent equations. The  $\theta$ -dependent equation reduces to the oblate spheroidal wave equation<sup>23-25</sup>:

$$\begin{aligned} (d/d\eta)[(1-\eta^2)(d/d\eta)S_{ml}(-ic, \eta)] \\ + \{\lambda_{ml} + c^2\eta^2 - [m^2/(1-\eta^2)]\} S_{ml}(-ic, \eta) = 0 \end{aligned} \quad (12)$$

where  $\eta = \cos \theta$ ,  $\lambda_{ml} = E_{ml}/B - \frac{1}{3}c^2$ , and

$$c^2 = \frac{3}{4}\sqrt{(5/\pi)}(V_0/B) \quad (13)$$

The oblate spheroidal functions  $S_{ml}$  and eigenvalues  $\lambda_{ml}$  are characterized by two quantum numbers  $m$  and  $l$ , where  $l \geq 0$  and  $|m| \leq l$ . The functions  $S_{ml}$  are either even or odd with respect to inversion of the rotator.<sup>23,24</sup>

For  $c = 0$  the quantum numbers  $l$  and  $m$  reduce to the quantum numbers  $J$  and  $M$ , respectively. The energy eigenvalues are then given by  $E = BJ(J+1)$ , the energy levels of a free rotator, and the eigenfunctions are the spherical

harmonics  $Y_{JM}(\omega_i)$ . For small  $c$  it is convenient to expand  $S_{ml}$  in terms of associated Legendre polynomials<sup>23-25</sup>:

$$S_{ml}(-ic, \eta) = \sum_r' d_r^{ml}(-ic) P_{m+r}^m(\eta) \quad (14)$$

where the prime over the summation sign indicates that the summation is over only even values of  $r$  when  $l - m$  is even, and over only odd values of  $r$  when  $n - m$  is odd. Thus, the ground-state wave function for para- $H_2$  and ortho- $D_2$  has the form

$$\psi_{00} = a_0^{00} Y_{00} + a_2^{00} Y_{20} + a_4^{00} Y_{40} + \dots \quad (15)$$

while for ortho- $H_2$  and para- $D_2$  the ground-state wave function is

$$\psi_{01} = a_0^{01} Y_{10} + a_2^{01} Y_{30} + a_4^{01} Y_{50} + \dots \quad (16)$$

The coefficients  $d_r^{ml}$  and the related coefficients  $a_r^{ml}$  are determined in the manner shown in Refs. 23 and 24.

For large  $c$  the motion of the molecules becomes oscillatory. An expansion of  $S_{ml}$  in terms of Laguerre polynomials is more convenient.<sup>23,24</sup> Alternatively, for large  $c$  the amplitude of oscillation about equilibrium is expected to be small so that the potential (9) can be expanded in powers of the angle  $\theta_i$ . Keeping terms to  $O(\theta_i^2)$

$$V_i = -(5/4\pi)^{1/2} V_0 (1 - \frac{3}{4} \theta_i^2) \quad (17)$$

The wave equation (11) with the potential (17) can be simplified to that of a two-dimensional oscillator.<sup>26,27</sup> The energy levels are

$$\begin{aligned} E = & -(5/4\pi)^{1/2} V_0 \\ & + (n + 1) [\hbar\omega + (2qB^2/\hbar\omega) - (2q^2B^4/\hbar^3\omega^3) + (4q^3B^6/\hbar^5\omega^5) + \dots] \\ & + (B/3)(m^2 - 1) \end{aligned} \quad (18)$$

where  $\hbar\omega/B = \sqrt{2}V_0$ ,  $q = (m^2/15) - \frac{1}{60}$  and the quantum numbers  $n$  and  $m$  are restricted to

$$n = 0, 1, 2, \dots \quad |m| = n, n - 2, n - 4, \dots \quad (19)$$

It is thus seen that when the hindering potential is small (small  $c$ ) a description in terms of rotating molecules is convenient. For a large hindering potential (large  $c$ ), a description of the molecule as a librator is more realistic. A plot of a selected set of energy levels of a hindered rotor in a mean field of the form (9) is shown in Fig. 1 vs. the parameter  $c$ , which measures the strength of that field. A more extensive table of  $E_{ml}$  vs.  $c^2$  is found in Ref. 25.

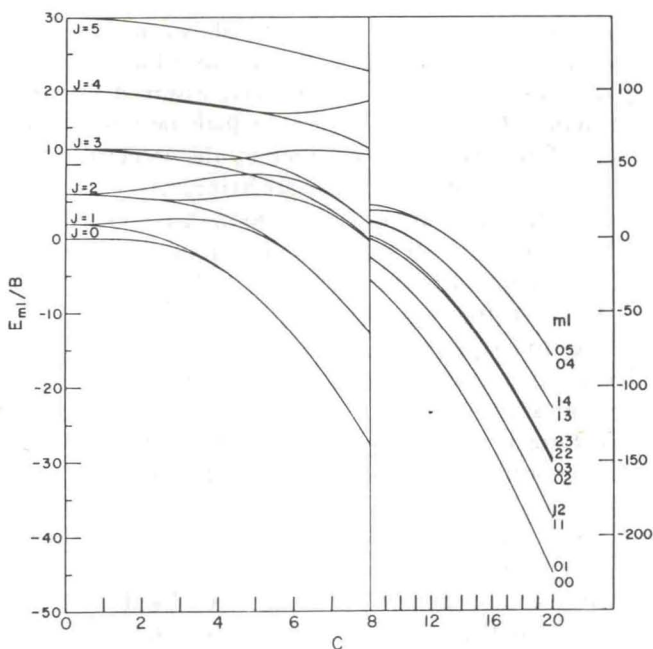


Fig. 1. Energy levels of a hindered rotator. The hindering potential has the form  $c^2 Y_{20}(\theta, \phi)$ .

#### 4. CALCULATIONS

We have iterated Eqs. (6) and (7) numerically until self-consistency for the average  $\langle Y_{20} \rangle \equiv \langle \psi_0 | Y_{20} | \psi_0 \rangle$  (1 part in  $10^5$ ) was obtained. Because of the limited accuracy of the volume dependence of the potential (9), as well as the known shortcomings of the molecular field approximation, we have limited our calculations to nearest neighbor interactions. We have considered para-H<sub>2</sub> and ortho-D<sub>2</sub> as well as ortho-H<sub>2</sub> and para-D<sub>2</sub>. The appropriate ground wave functions are then  $\psi_{00}$  for para-H<sub>2</sub> and ortho-D<sub>2</sub>, or  $\psi_{01}$  for ortho-H<sub>2</sub> and para-D<sub>2</sub>. We have used the method outlined by Curl *et al.*<sup>25</sup> The Hamiltonian matrix corresponding to the Schrödinger equation (7) can be calculated using the orthonormal set  $Y_{JM}$ . Diagonalization of this infinite matrix yields the energy levels and eigenfunctions directly. The Hamiltonian matrix for each  $M = 0, 1$  was truncated at  $20 \times 20$  and diagonalized. This procedure has previously proven sufficient for values of  $c^2$  up to 500.<sup>25</sup> The resulting eigenfunctions are then used to calculate the factor  $V_0$  for the potential (9). This potential is then inserted into Eq. (7) to calculate new eigenfunctions and so on until self-consistency is obtained.



The results for ortho- and para- $H_2$  are shown in Fig. 2, which gives the self-consistent ground-state average  $\langle Y_{20} \rangle$  as a function of the reduced nearest neighbor distance  $R/R_0$ . Here we have assumed that  $R_0 = 3.756 \text{ \AA}$  for the fcc structure. For para- $H_2$  it is seen that there is no change in the rotational wave function from  $Y_{00}$ , that is, the molecules rotate freely, until a density corresponding to  $R/R_0 = 0.670$  is reached. There a first-order transition to a state where the molecular motion is much more restricted takes place. For  $R/R_0 < 0.670$  the molecular motion is hindered and more librational than rotational in character. From the work of Pollock *et al.*<sup>4</sup> a value of  $R/R_0 = 0.670$  would correspond to a pressure of about 290 kbar when a Lennard-Jones potential is used, or 200 kbar using a Buckingham potential. Thus, a quenching of the rotational motion does not occur until an appreciable pressure is reached. This pressure is less than most predictions of the pressure at which the metallic phase is stabilized. Such a sudden transition to a more or less ordered state does not occur for ortho- $H_2$ . At normal pressure the ortho- $H_2$  molecules are for all practical purposes in the state  $J = 1$ .<sup>12</sup> The molecules in solid ortho- $H_2$  are already oriented along the  $Pa3$  symmetry directions.<sup>12-16</sup> A decrease of the intermolecular separations will increase the contributions made by the higher rotational states with  $J \geq 3$  to the ground-state wave function (16). At very high pressures the librational motion of the  $H_2$  molecule, for either the ortho or para modifications, can be described by classical lattice dynamics, since the deviation of  $\langle Y_{20} \rangle$  from  $(5/4\pi)^{1/2}$  is small.

Similar results are obtained for ortho- and para- $D_2$ , where we have assumed  $R_0 = 3.593 \text{ \AA}$  for the fcc structure. The volume dependence of the

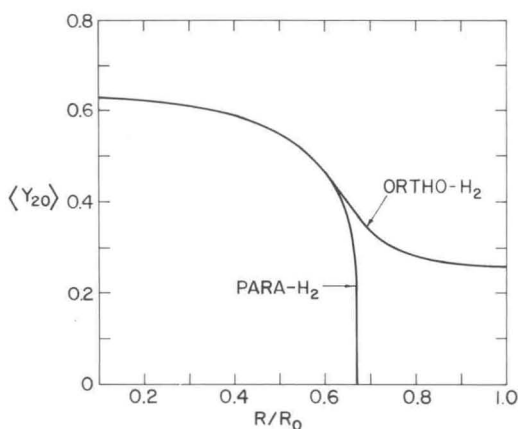


Fig. 2. The ground-state average  $\langle Y_{20} \rangle$  vs. the reduced nearest neighbor distance  $R/R_0$  for ortho- and para- $H_2$ .



average  $\langle Y_{20} \rangle$  is shown in Fig. 3. The onset of librational motion for ortho- $\text{D}_2$  occurs at  $R/R_0 = 0.737$ . The corresponding values of the square of the internal field parameter  $c$ , as calculated from Eqs. (10) and (13), are shown in Fig. 4. The "rotational" energy levels of  $\text{H}_2$  and  $\text{D}_2$  can then be determined from Fig. 1 or Table I of Ref. 25 for any value of  $c$ . For example, at a density of  $0.2023 \text{ mole/cm}^3$ , or  $R/R_0 = 0.603$ , Pollock *et al.*<sup>4</sup> predict a ground-state energy of  $2.080 \times 10^4 \text{ K}$  and a pressure of 1.459 Mbar for molecular  $\text{H}_2$ , using a spherically symmetric Lennard-Jones potential. With a

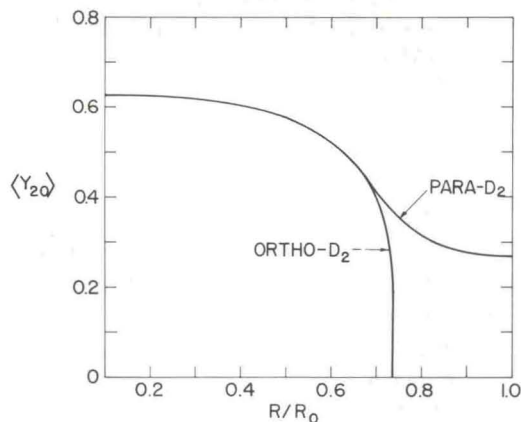


Fig. 3. The ground-state average  $\langle Y_{20} \rangle$  vs. the reduced nearest neighbor distance  $R/R_0$  for ortho- and para- $\text{D}_2$ .

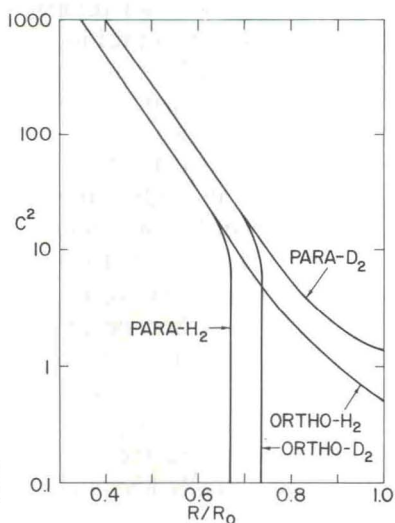


Fig. 4. The internal field parameter  $c^2$  vs. the reduced nearest neighbor distance  $R/R_0$  for hydrogen and deuterium.

Buckingham potential they predict somewhat lower energies and pressures. From Figs. 1 and 4 it is found that the reduction of the total ground-state energy due to the quenching of the molecular rotation is about  $9.6 \times 10^2$  K, or roughly 5% of the total energy. For deuterium the effect is slightly larger. At  $R/R_0 = 0.603$  one finds a corresponding "rotational" energy contribution of  $1.3 \times 10^3$  K.

Here we have, of course, stipulated that hydrogen and deuterium are still in their molecular phases at the densities mentioned above. The metallic phase of hydrogen<sup>6-9,30</sup> is believed to become stable at very high pressures. Past estimates of the pressure necessary to stabilize the metallic phase have ranged from 0.25 to 20 Mbar.<sup>8,9</sup> Most estimates are in the neighborhood of 1-2 Mbar.

## 5. CONCLUSIONS

The volume dependence of the rotational state of a  $H_2$  or  $D_2$  molecule in solid hydrogen or deuterium has been calculated. It has been shown that for para- $H_2$  and ortho- $D_2$  the onset of librational motion is sudden in the manner of a first-order transition. Above the transition volume all molecules in the solid are predicted to rotate freely. Thus, previous theories which assume spherically symmetric potentials and correlation functions<sup>1-6,9</sup> are correct in that assumption over the freely rotating region. In the librating region the asymmetry of the potential should be considered in the manner of Neece *et al.*<sup>8</sup> The transitions are expected to occur at a pressure of several hundred kilobars. The contributions of the anisotropic interactions are shown to be less than roughly 5% of the isotropic interaction energies. Thus, although the transition from the rotational to the librational state is sudden, only small changes in the  $p$ - $V$  relationship are expected to occur. For ortho- $H_2$  and para- $D_2$ , where the rotation is already hindered at normal densities, the change to the librating state is more gradual.

Using arguments stated in this paper, we have assumed that the ordered structures for all modifications of hydrogen and deuterium are fcc. We have thus described the quenching of the rotational motion for molecules on a fcc lattice. The correct structures of para- $H_2$  and ortho- $D_2$  at atmospheric pressure are hcp.<sup>31</sup> However, the difference in the lattice energies for para- $H_2$  for the fcc and hcp phases are extremely small; current estimates are  $\Delta E_{\text{fcc-hcp}} \sim 10^{-3}$  K.<sup>32</sup> Therefore, the assumption of a fcc structure at zero pressure for para- $H_2$  should not introduce any appreciable numerical error. However, we are predicting the para- $H_2$  molecules to become orientationally ordered in the fcc structure. Since the structure at atmospheric pressure is actually hcp, a change in the crystal structure must take place. This change in the crystal structure is most likely to occur very close to

the ordering transition, as is the case of the fcc-hcp transition for ortho-H<sub>2</sub> at atmospheric pressure.<sup>33</sup> On the basis of the present theory, we would, therefore, predict a change in the crystal structure of para-H<sub>2</sub> and ortho-D<sub>2</sub> from hcp to fcc as the pressure is increased. For para-H<sub>2</sub> this transition is expected to occur at densities corresponding to  $R/R_0 = 0.670$  while for ortho-D<sub>2</sub> the value is  $R/R_0 = 0.737$ .

In addition, several assumptions have been made which could lead to large errors in the predicted results.

(1) The anisotropic part of the intermolecular potential for H<sub>2</sub> is not well known. The orientation-dependent valence interaction terms (2) are the first few of an expansion which includes the higher spherical harmonics  $Y_{JM}$  with  $J \geq 4$ . At zero pressure, these terms do not contribute since  $J = 0$  (para-H<sub>2</sub>) and  $J = 1$  (ortho-H<sub>2</sub>) are essentially good quantum numbers. At higher pressures, where we have shown that a significant admixture of the higher rotational states occurs, these terms may become important. In addition, the interactions of higher multipole moments, which are neglected at zero pressure, should be considered at the higher densities. These difficulties could perhaps be solved by further theoretical calculation of the interaction potential for two H<sub>2</sub> molecules at various relative orientations. If possible, the relative orientations which occur for the *Pa3* structure should be included.

(2) The mean field approximation based on a rigid lattice model is known to be inaccurate in predicting the ordering transition for solid H<sub>2</sub> and D<sub>2</sub> at normal pressure. Corrections to the molecular field terms are known to be large.<sup>28,29</sup>

(3) The present paper has assumed that no change in the electronic configuration of the H<sub>2</sub> molecule takes place when the molecule is placed in the solid at high densities. A change of the interatomic spacing is likely to occur as the metallic state is approached. For example, for iodine which becomes metallic at a much lower pressure than hydrogen, the internuclear separation for the I<sub>2</sub> molecule, which is 2.66 Å in the gas, increases to 2.70 Å in the solid at normal pressure.

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