## Rotational ordering in solid deuterium and hydrogen: A path integral Monte Carlo study

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The path-integral Monte Carlo method with a constant-pressure ensemble is used to study both translational and orientational transitions in the phase diagram of  $D_2$  and  $H_2$  up to megabar pressures. With an intermolecular interaction potential determined to agree with the experimental equation of state, a rotational order-disorder phase transition is observed. The phase line for this transition is in quantitative agreement with part of the phase diagram for both  $D_2$  and  $H_2$ . No structural phase transition, and no transitions to the D-A and H-A phases (phase III) are observed. We attribute this in part to the limitations of simulation cell size. [S0163-1829(97)05318-6]

### I. INTRODUCTION

The search for a possible metallic phase in molecular hydrogen and its isotopes has been pursued since the inception of the idea by Wigner and Huntington more than 60 years ago.<sup>1</sup> The most recent relevant experimental result is the observation of high electrical conductivity in shock compressed liquid H<sub>2</sub> and D<sub>2</sub>.<sup>2</sup> Further progress is expected from experiments in ultrahigh-pressure diamond anvil cells that are capable of subjecting solid H<sub>2</sub> and D<sub>2</sub> samples to pressures up to 200 GPa (2 Mbar or 2000 kbar).<sup>3-8</sup> In these experiments, the phase diagram for solid D<sub>2</sub> over a wide range of pressure P and temperature T has been agreed upon by several research groups. For H<sub>2</sub>, however, the phase diagram is still incomplete, and is furthermore in dispute in the ultrahigh-P $(P \ge 1 \text{ Mbar})$  region. Moreover, correct identification of each phase found in the diagram of either hydrogen isotope is still unclear.5-8

Although  $H_2$  and  $D_2$  are among the simplest molecular species, the highly quantum nature of their condensed phases poses a considerable challenge to theory. Frequently, the bosonic species para-H<sub>2</sub> and ortho-D<sub>2</sub> can be well approximated as spherical particles under ambient pressures.<sup>9</sup> However, the spherical approximation breaks down when the solid is subjected to high pressure, where the ordering of molecular rotational degrees of freedom becomes significant.<sup>3</sup> The identification of  $H_2$  and  $D_2$  phases under high pressure has been approached theoretically by direct calculation of electronic energies for various crystal structures with particular molecular orientational orderings imposed, within density functional theory in the local density approximation (LDA).<sup>10–17</sup> However, characterization of the lowest-energy states as well as the nature of the phase transitions remains unclear from ab initio calculations.<sup>18-20</sup> Attempts have also been made to study this system by quantum Monte Carlo (QMC) calculations of the electron-proton mixture.<sup>21-23</sup> This automatically takes account of electron correlations and zero-point motions, absent in LDA calculations, and avoids as well the need to employ model interaction potentials. The optimal approach to analysis of the phase diagram would be to perform constant pressure QMC electron-proton calculations, but it is currently not possible to carry these out without some approximation, at the low temperatures relevant to the experimental observations.

The third alternative is to average over electronic degrees of freedom and to employ intermolecular pair potentials in QMC calculations for the nuclear degrees of freedom only. We adopt this approach here, employing an anisotropic molecular interaction potential in the finite-temperature pathintegral Monte Carlo (PIMC) method. This does not allow the metallization transition to be studied, but should allow investigation of both lattice and orientational transitions in the molecular phase, with zero-point motions automatically incorporated. The particular potential employed here is a hybrid of empirical and scaled *ab initio* contributions, which gives very good agreement with the equation of state for both  $H_2$  and  $D_2$  over the experimentally investigated range of pressures. On the basis of the agreement with the experimental phase diagrams of both isotopes demonstrated in this paper, we can conclude that it is valid at pressures up to about 150 GPa.

Application of the PIMC technique to the translational (center-of-mass) motion in solid  $H_2$  was employed by Zoppi *et al.*<sup>24</sup> and by Wagner and Ceperley.<sup>25</sup> Both of these groups treated the  $H_2$  molecule with spherically averaged potentials. Runge and co-workers have applied PIMC to the rotational degrees of freedom, and studied orientational ordering with the molecular center of mass fixed at given lattice sites.<sup>17,26</sup> Although the translation (vibration) and molecular rotations are expected to be strongly coupled under pressure, no attempt has so far been made to perform finite-temperature calculations with both degrees of freedom simultaneously coexisting, with exception of a two-dimensional study of  $H_2$  on the surface of graphite<sup>27</sup> and a calculation for small

12 253

clusters.<sup>28</sup> The influence of rotational motion and orientation of  $H_2$  molecules on adsorption and desorption on Pd surfaces was also studied by a six-dimensional quantum dynamical calculation.<sup>29</sup>

The incorporation of both translational and rotational degrees of freedom in the PIMC method is straightforward if one starts from a high-temperature density matrix for both translational and rotational motions. The pair potential used here does not contain any dependence on the intramolecular bond length; i.e., each molecule is a movable, orientable rigid rotor. This neglects the density dependence of the bond length<sup>21</sup> which is expected to be important at ultrahigh pressures.<sup>12,15,17,30</sup> The famous "minus sign problem" in QMC studies associated with fermions is avoided by confining the study to solid systems and, furthermore to boson systems of para-H<sub>2</sub> and ortho-D<sub>2</sub>, i.e., for J=0, although such distinctions are expected to lose their meanings in very dense solids, where the angular momentum of each individual molecule, J, is no longer a good quantum number.<sup>3,9</sup> Most of the calculations are performed for D<sub>2</sub>, for which more experimental data is available. An important element of the calculations is that they are performed in a constantpressure ensemble, rather than the more usual and computationally simpler constant-volume ensemble. This enables us to monitor volume changes and therefore to directly observe possible first-order phase transitions.

The remainder of this paper is organized as follows: In Sec. II, the outline of the theoretical model is presented, including a brief summary of the PIMC formulation and its application to both translational and rotational degrees of freedom, a review of the intermolecular potential forms, a description of the potential used here, and a description of the constant-pressure ensemble. In Sec. III results for both  $D_2$  and  $H_2$  solids are shown, including their equations of state (EOS) and orientational order-disorder phase diagrams, with comparison to experimental data. Finally, Sec. IV summarizes and discusses the results.

### **II. THEORETICAL MODEL**

Within the approximation that (effective) pairwise interactions are valid, a quantum-molecular solid with translational and rotational degrees of freedom is described by the Hamiltonian

$$H = T + V,$$

$$T = -\frac{\hbar^2}{2m} \sum_{i}^{N} \nabla_{R_i}^2 + \frac{\hbar^2}{2I} \sum_{i}^{N} \mathbf{L}_i^2,$$
(1)

$$V = \frac{1}{2} \sum_{i \neq j}^{N} V(\mathbf{R}_{ij}, \mathbf{\Omega}_{i}, \mathbf{\Omega}_{j}),$$

where  $\mathbf{R}_i$  is the center-of-mass position vector of the *i*th molecule,  $\mathbf{\Omega}_i$  its orientation vector,  $\mathbf{L}_i$  its angular momentum operator, and  $\mathbf{R}_{ij} \equiv \mathbf{R}_i - \mathbf{R}_j$  is the intermolecular separation vector. The molecular mass and moment of inertia are denoted by *m* and *I*, respectively. With the intramolecular bond length fixed, for a linear molecule, *I* is a scalar constant. The values of m = 3676 and 7352 (atomic units) for  $\mathbf{H}_2$  and  $\mathbf{D}_2$ , respectively, and rotational constants  $B \equiv \hbar^2/2I = 84.98$  and

42.92 K for H<sub>2</sub> and D<sub>2</sub> respectively, are used.<sup>9,26</sup>  $V(\mathbf{R}_{ij}, \mathbf{\Omega}_i, \mathbf{\Omega}_j)$  is the intermolecular interaction potential. The form of this will be discussed below in Sec. II C.

### A. Path-integral Monte Carlo method

The Hamiltonian in Eq. (1) poses a many-body problem which cannot be solved analytically. While variational Monte Carlo (VMC) and diffusional Monte Carlo (DMC) methods are capable of finding the ground state of the system, a numerical solution at finite temperature requires the application of the PIMC method. The quantum-statistical properties at any finite temperature are fully described by the density matrix. In position space this has the form

$$\rho(x,x';\beta) = \langle x | e^{-\beta H} | x' \rangle, \qquad (2)$$

where  $x = \{\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{\Omega}_1, \dots, \mathbf{\Omega}_N\}$  and  $\beta = 1/kT$ . The thermal expectation value of an operator *A* is then evaluated as Tr( $\rho A$ ), which is written as an integration over the configuration space:

$$\langle A \rangle = \frac{\int dx dx' \rho(x, x'; \beta) \langle x | A | x' \rangle}{\int dx \rho(x, x; \beta)}.$$
 (3)

In this work we are concerned only with thermodynamic or static properties determined by the diagonal elements of the density matrix,  $\rho(x,x;\beta)$ ; i.e., we are concerned only with local operators *A*. When the linear rotor degrees of freedom are added to the translational degrees of freedom, the integral in Eq. (3) then becomes 5N dimensional.

The exact many-body density matrix  $\rho(x,x';\beta)$  is unknown, but the path-integral description takes advantage of its product property to express  $\rho(x,x';\beta)$  as the convolution of *M* density matrices or "partitions" at a higher temperature *MT*:

$$\rho(x,x';\beta) = \int \cdots \int dx_1 \cdots dx_{M-1} \rho(x,x_1;\tau)$$
$$\times \rho(x_1,x_2;\tau) \cdots \rho(x_{M-1},x';\tau). \tag{4}$$

Here we have defined  $\tau \equiv \beta/M$ . In Eq. (4), as written,  $M \ge 3$ . The lowest-order convolution possible corresponds to M=2 partitions, while for M=1 there is only a single, trivial partition, and no convolution. For given M, the offdiagonal density matrix, Eq. (4), is thereby expressed as an (M-1) dimensional integral over paths defined by the set of M+1 points  $\{x=x_0,x_1,\ldots,x_{M-1},x'\}$ , and the diagonal density matrix  $\rho(x,x;\beta)$  as an (M-1)-dimensional integral over paths defined by the set of M points  $\{x=x_0,x_1,\ldots,x_{M-1},x_0\}$ . For ease of reference we shall refer to x and  $x_0$  interchangeably from now on.

In this discrete path integral representation,  $\text{Tr}(\rho)$  and expectation values of local operators  $\langle x|A|x'\rangle = A(x)$  then become explicit integrals over  $M \times 5N$  dimensions. Such multidimensional integration is performed with the Metropolis Monte Carlo sampling technique.<sup>31–33</sup> In the  $(M \times 5N)$ -dimensional space, each molecule i  $(0 < i \le N)$  is represented by a discrete, closed path of M "beads," with each bead j  $[0 < j \le (M-1)]$  denoting a "position" ( $\mathbf{R}_{ij}, \mathbf{\Omega}_{ij}$ ) in the 5N-dimensional configuration space. The extent of each path in this space represents the quantum fluc-

tuation in the molecular position, for both translational and rotational degrees of freedom. Therefore setting M=1 and removing the convolution in Eq. (4) ignores all such fluctuations. This limit displays a strong analogy with the classical system and provides a useful reference system, as will be explained in more detail below.

When *M* is large enough, the high-temperature density matrix  $\rho(x,x';\tau)$  can be well approximated by its classical or semiclassical value. Thus, the primitive approximation

$$e^{-\tau(T+V)} \approx e^{-\tau T} e^{-\tau V} \tag{5}$$

can be adopted. This neglects quantum corrections of order  $O(\tau^2[T,V])$ , and thereby avoids the problems associated with the lack of commutability of kinetic and potential energy terms in the Hamiltonian. For a spherical particle system, the use of an exact two-body density matrix is considerably more efficient than the primitive approximation.<sup>31</sup> However, the incorporation of the molecular orientational degrees of freedom for H<sub>2</sub> and D<sub>2</sub> renders this approach impractical here because of the excessive grid sizes required. Therefore we adopt the simpler primitive approximation for all degrees of freedom in this work, yielding

$$\rho(x,x';\tau) \approx \int dx'' \langle x | e^{-\tau T} | x'' \rangle \langle x'' | e^{-\tau V} | x' \rangle.$$
 (6)

In practice, because of the relatively strong localization in the solid phase, the primitive approximation is very efficient here, and small values of M are sufficient to ensure convergence. With the Hamiltonian in Eq. (1), each of the two contributing factors to the density matrix can then be written out explicitly:<sup>31</sup>

$$\langle x|e^{-\tau T}|x'\rangle = \left(\frac{2\pi\hbar^{2}\tau}{m}\right)^{-3N/2} \\ \times \exp\left[-\frac{m|\mathbf{R}-\mathbf{R}'|^{2}}{2\hbar^{2}\tau}\right] \sum_{\ell=0}^{\ell} \frac{2\ell+1}{4\pi} \\ \times \exp\left[-B\tau\ell(\ell+1)\right] P_{\ell}(\cos\theta), \quad (7)$$

$$\langle x|e^{-\tau V}|x'\rangle = e^{-\tau V(x)}\delta(x-x').$$
(8)

Here  $\theta$  is the polar angle between  $\Omega$  and  $\Omega'$ ,  $P_{\ell}(\cos\theta)$  is the Legendre polynomial of order  $\ell$ , and *B* is the rotational constant of the molecule. Since only the bosonic species *para*-H<sub>2</sub> and *ortho*-D<sub>2</sub> are being investigated, the angular momentum  $\ell'$  in Eq. (7) takes only even integer values.  $\ell'_{\text{max}}$  is an upper cutoff value, taken to be large enough so that the exponential  $e^{-B\tau\ell'_{\text{max}}(\ell'_{\text{max}}+1)}$  yields a negligible value.

In the primitive approximation, the reference system derived from M = 1 reduces the kinetic contribution to the diagonal density matrix to a normalization factor dependent only on *m* and *I*. For the quantities computed here, it therefore has a similar effect to taking a classical limit, i.e., with *m* and *I* large and finite. (This differs from the extreme limit of  $m \rightarrow \infty$  and  $I \rightarrow \infty$ . The latter would imply zero kinetic energy and delta function behavior of  $\langle x | \rho | x' \rangle$ , whereas for M = 1 the kinetic energy remains finite and the density matrix well behaved.) We shall therefore refer to this limit M = 1 as the "classical reference" system.



FIG. 1. Schematic showing the effect of intramolecular permutation moves. Vectors represent orientational directions  $\Omega_{ij}, j=0, \ldots, M-1$ , of path-integral "beads" of molecule *i*, with, e.g., partition number M=4. The permutation moves allow the path to more freely explore the angular space between 0° and 180°.

With the primitive approximation of Eq. (6), the Monte Carlo sampling of translations and rotations can now be performed separately. Each Monte Carlo step then consists of an attempted Metropolis move for every bead, with each single molecule move incurring one displacement in **R** and one rotation in  $\Omega$ . To enhance sampling efficiency, the whole path for each molecule also gets a random displacement at each MC step; i.e., every bead of the path is moved in the same way, with identical  $\Delta \mathbf{R}$  and  $\Delta \Omega$ . This corresponds to a simplified multilevel sampling.<sup>31</sup> In addition, intramolecule permutation moves are performed, which "flip" the molecular orientation by 180°. Exchange of two nuclei within a molecule returns to the same quantum state for J=0"bosonic" para- $H_2$  and ortho- $D_2$ , and for higher J=even states. This means that both values  $\mathbf{\Omega}_{iM-1}$  of the *M*th bead of the *i*th molecule "close" to  $\mathbf{\Omega}_{i0}$  of the first bead of the same molecule, and  $\Omega_{iM-1}$  "opposite" to  $\Omega_{i0}$  are permitted. We therefore make a Metropolis sampling of these two values in order to implement the intramolecule permutations. Such intramolecular permutation moves are designed as a supplement to the rotational processes discussed above, allowing the molecular orientational path more freedom. Figure 1 shows how this works, with the additional permutation moves allowing the motion corresponding to "opening of a fan'' between  $0^{\circ}$  and  $180^{\circ}$ . (The reverse process is allowed for as well, by detailed balance.) The additional boson symmetry deriving from the exchange of two molecules, which also yields the same quantum state, can be ignored here since intermolecular exchange symmetry has a negligible effect in a solid because of localization.<sup>31,33</sup> While this intermolecular exchange symmetry could also be established by making similar intermolecule permutation moves,<sup>31</sup> its neglect greatly simplies the algorithm.

#### **B.** Constant-pressure ensemble

The extended solid is modeled by a simulation cell of finite size, which is periodically duplicated in all three spatial dimensions to minimize surface and finite size errors. The N molecules are initially placed according to a given crystal structure in the cell. The interactions are evaluated making use of the periodicity and the "minimum imaging" method.<sup>34</sup> A cutoff correction to the potential energy is included by assuming that beyond the cutoff length the solid is a continuous and uniform medium, with the same density as inside the cell. This allows integration over the exterior density. In this work, the cutoff length is chosen to be equal to half of the smallest cell dimension. The initial size and geometry of the cell are chosen to accomodate a particular density and structure. Most of the calculations are performed with N=96 and an initial simulation cell determined by two basis vectors ( $\mathbf{a}_{p}$  and  $\mathbf{b}_{p}$ ) forming a 60° angle and the third one  $(\mathbf{c}_p)$  perpendicular to both  $\mathbf{a}_p$  and  $\mathbf{b}_p$ . This choice, with the appropriate length ratio  $a_p:b_p:c_p=1:1:\sqrt{6}/2$ , has the advantage of accomodating both the fcc and hcp lattice structures. Thus there are six layers in the  $c_p$  direction and  $4 \times 4$  molecules in each layer. The packing pattern is either ABABAB in the hcp structure or ABCABC in the fcc structure. With the molecules placed initially at the lattice sites, this yields the ideal value of the crystallographic axial ratio,  $c/a = \sqrt{8/3}$  (c and a are the lattice parameters), for hcp. Extensive testing with different values of N and various initial cell geometries has also been made.

In order to avoid the bias of a restrictive cell geometry with a predetermined crystal structure, most of the calculations were performed in the constant-pressure (NPT) ensemble, instead of the simpler constant-volume ensemble (NVT) where the simulation cell remains fixed. The implementation of the NPT ensemble is achieved by an extra Metropolis move of the cell size and geometry, which generates a Markov chain of states having a limiting distribution proportional to

$$\exp[-\beta PV - \beta E(s) + N\ln V]. \tag{9}$$

Here *P* is the given pressure, *V* the cell volume, E(s) is the energy  $\langle H \rangle$  of the configuration *s*, and *s* represents a set of scaled coordinates.  $s \equiv (\mathbf{S}, \mathbf{\Omega})$  replaces  $x = (\mathbf{R}, \mathbf{\Omega})$ , where  $\mathbf{R} = \mathbf{h} \cdot \mathbf{S}$ , and  $\mathbf{h}$  is a 3×3 metric matrix for an arbitrarily shaped cell.<sup>35</sup> Each component of **S** takes only values between 0 and 1.<sup>34–36</sup> A new state is generated by independent random moves of the three basis vectors of the simulation cell, altering both the volume  $(V_0 \rightarrow V_n)$  and the shape of the cell. This leads to a new metric matrix,  $\mathbf{h}_0 \rightarrow \mathbf{h}_n$ , and therefore to a new expectation value of the Hamiltonian,  $E_0 \rightarrow E_n$ . The change in enthalpy is then calculated according to

$$\delta H = \delta v + P(V_n - V_0) - \frac{N}{\beta} \ln \left( \frac{V_n}{V_0} \right), \tag{10}$$

where  $\delta v$  is the change in the cutoff corrections to the potential energy, since the new state has a different density and cutoff length.<sup>34</sup> Apart from the direct evaluation of the potential energy, this is the only place where the cutoff affects the EOS calculated in the *NPT* ensemble. Fortunately, a relatively large cancellation occurs in  $\delta v$  when the change in volume is small, as is often the case. The changes in the cell size and geometry are monitored throughout the calculation, and are discussed below.



FIG. 2. Histogram of the angles between the three basis vectors making up the simulation cell, during a classical *NPT* Monte Carlo run for solid N<sub>2</sub> at the constant pressure of P=70 KBar. The sample temperature is lowered in five steps from 300 K to 50 K. A splitting of the cell angle degeneracy, associated with a transition from cubic to trigonal structure, is observed around T=150 K, in agreement with the results of a classical *NPT* molecular dynamics calculation (Ref. 37).

A Metropolis move of the simulation cell is typically performed every five Monte Carlo steps, where each step involves both single and collective translational and rotational moves as described above. About 2000 MC steps are required for equilibration. Statistical averages are collected from every second step after this, to a total of about 2000 data points. The constant-pressure PIMC code was tested by performing a classical calculation (with M=1) of the structural transformations in solid nitrogen under pressure. Interaction potentials and starting configurations were taken from previous molecular dynamics simulations.<sup>37</sup> The results for energies and correlation functions duplicate those in Ref. 37. In particular, the same cubic-to-trigonal structural transition is observed during a sequential lowering of the sample temperature at P = 70 kbar, signaled by a splitting of the degeneracy in the values of the three cell angles and summarized in Fig. 2.

## C. Interaction potentials

For this model for the hydrogen solid, the only remaining input required is the interaction potential between two molecules,  $V(\mathbf{R}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$ . This potential has been the subject of many studies.<sup>9</sup> Both *ab initio* basis-set quantum-chemistry calculations and empirical parameter-fitting schemes have been used. Most of these studies either originated from or are applicable to gas phase scattering and deal with the isolated  $H_2$ - $H_2$  interaction. Much less is known about the potential in a (dense) solid environment. Thus only semiempirical forms of the isotropic component of this potential have been established for solid hydrogen at this time.

Intermolecular interactions are inherently more complicated than interatomic ones, due to the larger number of degrees of freedom. A common and convenient way to express the multidimensional function  $V(\mathbf{R}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$  is through the spherical harmonic expansion<sup>9,38</sup>

 $C_8$  $C_9$ β  $R_m$  $C_6$  $C_{10}$ α γ 1.173 1.5671 0.00993 6.50 12.14 215.2 4813.9 143.1  $a_1$  $a_2$  $R_c$  $4.213 \times 10^{-4}$  $-8.045 \times 10^{-5}$ 5.2912

)

TABLE I. Parameter values (in atomic units) for the interaction potential between two  $H_2$  molecules (Refs. 40 and 43).

# $V(\mathbf{R}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$

$$= \sum_{\ell_{1},\ell_{2},\ell} A_{\ell_{1},\ell_{2},\ell}(R_{12})$$

$$\times \sum_{m_{1},m_{2},m} (\ell_{1}m_{1}\ell_{2}m_{2}|\ell_{1}\ell_{2}\ell_{m})Y_{\ell_{1}m_{1}}(\theta_{1},\phi_{1})$$

$$\times Y_{\ell_{2}m_{2}}(\theta_{2},\phi_{2})Y_{\ell_{m}}^{*}(\Theta,\Phi), \qquad (11)$$

where  $(\ell_1 m_1 \ell_2 m_2 | \ell_1 \ell_2 \ell m)$  are the Clebsch-Gordon coefficients,  $(\theta_1, \phi_1)$ ,  $(\theta_2, \phi_2)$ , and  $(\Theta, \Phi)$  are the spherical angles of  $\Omega_1$ ,  $\Omega_2$ , and the vector  $\mathbf{R}_{12}$ , respectively. The leading term in this expansion is the spherical averaged component:

$$V_0(R) \equiv A_{000}(R_{12}). \tag{12}$$

The other terms in this expansion make up the anisotropic part of the potential, which is responsible for the rotational orderings in the solid. The leading contributions are the long-range electronic quadrupole-quadrupole (EQQ) interaction  $A_{224}$  and the "atom-diatom scattering" term  $A_{022}=A_{202}$ .<sup>38</sup>

An alternative to the spherical harmonic expansion is to express the potential as a pairwise summation of interactions between the atomic constituents. Such atom-atom potentials have been used in some classical molecular simulations for other systems; see, e.g., Ref. 37 and 39. An atom-atom interaction has the advantage of simplicity and flexibility, and could be especially convenient for examining the effect of intramolecular bond changes and for analysis of Raman spectroscopy.<sup>39</sup> It may also avoid possible bias imposed by truncation of the spherical harmonic expansion.

## 1. Isotropic interaction potentials

The most commonly used  $V_0(R)$  empirical forms are due to Buck *et al.*.<sup>38</sup> (BUCK) and to Silvera and Goldman (SG).<sup>40</sup> The BUCK potential was fit to gas phase data, while SG was fit to solid phase data. The two potentials have essentially the same analytic form, but SG found it necessary to incorporate an additional repulsive term to account for effective three-body interactions in the solid environment.<sup>40</sup> The most visible effects of this three-body contribution are a hardening of the potential in the short-range region and a slight raising of the well depth.<sup>41</sup> The SG potential takes the form

$$V_0(R) = V_{\rm SG}(R) = e^{\alpha - \beta R - \gamma R^2} - f(R) \left\{ \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} - \frac{C_9}{R^9} \right\},$$
(13)

$$f(R) = \begin{cases} e^{-(1.28R_m/R-1)^2}, & \text{if } R < 1.28R_m, \\ 1, & \text{otherwise.} \end{cases}$$
(14)

The parameter values are listed in Table I. The van der Waals (VDW) coefficients  $C_6$ ,  $C_8$ , and  $C_{10}$  are derived from *ab initio* calculations of the long-range interactions.<sup>42</sup> The other parameters, which determine the short-range repulsive core, are fit to reproduce thermodynamic data of the D<sub>2</sub> solid phase.<sup>40</sup>

More recently, Hemley *et al.* found that while the SG potential is adequate for solid  $H_2$  and  $D_2$  under ambient pressures, additional corrections are needed to fit high-pressure thermodynamic data.<sup>43</sup> In particular, they found the SG potential should be softened even more in the dense solid environment, due to enhanced many-body contributions in the short-range region. This effect can be incorporated by making an *ad hoc* short-range correction to the SG potential:

$$V_0(R) = V_{SG}(R) + V_{SR}(R),$$
 (15)

$$V_{\rm SR}(R) = \begin{cases} a_1 (R - R_c)^3 + a_2 (R - R_c)^6, & \text{if } R \le R_c, \\ 0, & \text{otherwise.} \end{cases}$$
(16)

The parameter values for this correction are also listed in Table I. Similar softening corrections were also constructed by fitting the EOS derived from liquid  $D_2$  shock wave data.<sup>43,44</sup> Both the SG- and Hemley-corrected SG potentials were tested here in the EOS calculation, and the Hemley-corrected SG potential, Eq. (15), was subsequently adopted as the isotropic part of the total potential.

#### 2. Anisotropic interaction potentials

Considerably less work has been done for the anisotropic part of the interaction potential. Since its contribution is negligible in low-pressure solids, it cannot be directly tested against available experimental data. Using ab initio quantum-chemical calculations, Schaefer and co-workers have evaluated the six leading terms in the harmonic expansion of the interaction, Eq. (11), between two H<sub>2</sub> molecules.<sup>45</sup> A pairwise sum of the anisotropic part, consisting of terms  $A_{022}$ ,  $A_{202}$ ,  $A_{220}$ ,  $A_{222}$ , and  $A_{224}$ , was later employed in a solid environment with a variety of lattice structures at various densities, to compare with results from electronic structure density functional calculations within the LDA.<sup>26</sup> The Schaefer potential was found to be too repulsive in the solid, by the comparison with the LDA. However, a simple scaling with the scaling factor linear in the nearestneighbor spacing  $R_{nn}$  can be applied to soften the Schaefer potential and thereby achieve excellent agreement with the LDA results:26

$$V_{\rm ani} = \alpha V_{\rm Schaefer}, \qquad (17)$$

$$\alpha = 0.61 + 0.31(R_{\rm NN}/R_{\rm NN}^0 - 0.5), \qquad (18)$$

where  $R_{\rm NN}^0 = 3.789$  Å is a constant, chosen to be the H<sub>2</sub> equilibrium nearest-neighbor spacing.

Both the bare  $V_{\text{Schaefer}}$  and the scaled  $V_{\text{ani}}$  for the anisotropic components have been tested here. It was found that  $V_{\text{ani}}$  yields results in significantly better agreement with experimental data for the orientational order-disorder transition (see below).

#### III. RESULTS

#### A. Equation of state

It has long been recognized that, as an easily compressible quantum solid, the EOS of H<sub>2</sub> and D<sub>2</sub> provide critical information for the study of equilibrium states. In particular, the EOS is a key test case for validation of both the theoretical model and the intermolecular potential.<sup>3,9</sup> Most previous theoretical studies have used the *NVT* ensemble, particularly the ground state (T=0).<sup>41,46-48</sup> The determination of pressure P in the NVT ensemble becomes numerically unreliable at low pressure, due to cancellation between the kinetic and potential terms.<sup>33</sup> The EOS can be obtained more reliably by evaluating the volume derivative of the total energy, E/N, which is obtained by numerical differencing and hence is not directly measured. However, the theoretical determination of E/N has corrections due to a finite-size cutoff.<sup>41</sup> The NPT ensemble, on the other hand, provides a direct means for testing the P-V-T relationship against experimental data. Here, both P and T are constant input parameters, with V (or  $\rho$ ) directly measured in the equilibrated simulation cell. The error incurred here by the cutoff of the interaction potential is relatively small, due to cancellations during the Metropolis moves of the cell itself.

The most recent measurements of the EOS for solid  $D_2$ and  $H_2$  were reported by Hemley *et al.*. in Ref. 43. Direct *P-V* measurements were made up to pressures of 26.5 GPa at T=300 K, by single-crystal x-ray diffraction. An approximate determination of the thermal contribution to the pressure, via thermal expansion, then leads to a low temperature (T=0) *P-V* EOS.<sup>43</sup> This thermal pressure correction is less than 0.6 GPa in magnitude, which is small compared to the pressures in the range considered. The T=0 EOS of  $H_2$  and  $D_2$  are then fit by an empirical formula which can be used to extrapolate the EOS into higher pressure regimes.

As a test of the intermolecular potential, the EOS for  $D_2$  was calculated with four different combinations for the total potential:

$$V_a = V_{\rm SG} + V_{\rm Schaefer}, \tag{19}$$

$$V_b = V_{\rm SG} + V_{\rm ani}, \qquad (20)$$

$$V_c = V_{\rm SG} + V_{\rm SR} + V_{\rm Schaefer}, \qquad (21)$$

$$V_d = V_{\rm SG} + V_{\rm SR} + V_{\rm ani} \,. \tag{22}$$

See Eqs. (13)-(17) for the forms of the individual components. A variety of different lattice structures and different values of *N* were chosen. However, the EOS proved to be



FIG. 3. The equation of state of D<sub>2</sub>. PIMC results calculated with the intermolecular potentials  $V_a$  (open squares),  $V_b$  (stars),  $V_c$  (open circles), and  $V_d$  (crosses), respectively, at T=20 K and N=32 on a fcc lattice. See Eqs. (19)–(22). Open triangles are experimental data corrected to T=0, from Ref. 43. Inset: solid circles are PIMC results at high pressure calculated with  $V_d$ , at T=300 K and N=96 on a hcp lattice. Solid triangles are experimental data at T=300 K from Ref. 43. The solid curves in both figures are from the experimental fitting formula of Ref. 43.

insensitive to these parameters, and negligible differences in P-V resulted. Figure 3 shows a segment of the D<sub>2</sub> EOS up to 50 GPa, calculated at T = 20 K with N = 32 on a fcc lattice. One observes that  $V_a$  and  $V_b$  yield the same result, while  $V_c$  and  $V_d$  show different behavior but are also very similar to one another. This is due to the fact that in each of these pairs, both components have the same isotropic part of the total potential, and this isotropic term dominates the EOS. In the low-pressure region ( $\leq 5$  GPa), all theoretical data overlap and are in good agreement with experimental measurements. For P > 5 GPa, however, the same deviations of the SG results from experimental data noted by Hemley et al.<sup>43</sup> are seen here  $(V_a \text{ and } V_b)$ . Inclusion of the Hemley correction, in Eq. (16) ( $V_c$  and  $V_d$ ), results in excellent agreement with the data. The inset of Fig. 3 shows our EOS result up to 200 GPa, calculated with  $V_d$  at T=300 K and N=96 on a hcp lattice. For P < 25 GPa, where direct experimental measurements are available, our result is in excellent agreement with the data. For larger P, our result also overlaps the extrapolation based on the T=0 fit formula. This is to be expected since the thermal correction is negligible in the highpressure regime.

Similar behavior of the EOS is observed for solid H<sub>2</sub>, as shown in Fig. 4. Note that the EOS for H<sub>2</sub> and D<sub>2</sub> are virtually identical for P > 2 GPa, where the molar volume of the solid is about 10 cm<sup>3</sup>/mol or density  $\rho \sim 0.06$  Å<sup>-3</sup>. At lower pressures, H<sub>2</sub> possesses a slightly larger molar volume (smaller density), due to its smaller molecular mass. This leads to larger quantum zero-point contributions for the lighter isotope. The overlap of the EOS for the two isotopes at high pressure indicates a trend toward semiclassical behavior in dense quantum solids. Because of this overlap, either *P* or  $\rho$  can be used interchangeably as the independent variable when comparing D<sub>2</sub> and H<sub>2</sub> properties at high pressures.



FIG. 4. The equation of state of H<sub>2</sub>. Circles are PIMC results calculated with the intermolecular potentials  $V_d$ , see Eq. (22), at T=300 K and N=96 on a hcp lattice. Triangles and solid curves are experimental data and fit formula from Ref. 43.

Within the primitive approximation of the PIMC calculation, the kinetic energy of the solid, K/N, can be evaluated with the estimator<sup>31</sup>

$$K = K_t + K_r, \qquad (23)$$

$$K_{t} = -\frac{m}{\beta Z} \frac{\partial Z}{\partial m} = \left\langle \frac{3N}{2\tau} - \frac{m |\mathbf{R}_{ij} - \mathbf{R}_{i(j-1)}|^{2}}{2\hbar^{2}\tau} \right\rangle, \quad (24)$$

$$K_{r} = -\frac{B}{\beta Z} \frac{\partial Z}{\partial B} = \left\{ \frac{\sum_{\ell=0}^{\ell} B \ell(\ell+1) [(2\ell+1)/4\pi] P_{\ell}(\cos\theta) e^{-\tau B \ell(\ell+1)}}{\sum_{\ell=0}^{\ell} [(2\ell+1)/4\pi] P_{\ell}(\cos\theta) e^{-\tau B \ell(\ell+1)}} \right\}.$$
(25)

Here *K* has been separated into a translational (vibrational) and a rotational part,  $K_t$  and  $K_r$ , respectively. *Z* is the partition function. As before, the subscript *j* denotes the bead index on the *i*th path, and  $\theta$  the polar angle between orientation vectors  $\Omega_{ij}$  and  $\Omega_{i(j-1)}$ . The potential energy *V*/*N* is given directly by

$$V = \langle V(x) \rangle. \tag{26}$$

Figure 5 shows the total energy and the individual kinetic contributions. One observes that the kinetic energy values are significantly larger than the thermal kinetic energy of a classical system  $(3kT/2 \text{ for } K_t \text{ and } kT \text{ for } K_r)$ , testifying to the quantum nature of the solid which gives additional zeropoint energy. A more detailed analysis of these zero-point contributions will be made below. On the other hand, the total energy is nevertheless dominated by the (highly repulsive) potential energy in the dense solid environment, to the extent that the contribution of the kinetic energy is negligible (*K*/*E* ≤ 5%). This explains the fact that the EOS of H<sub>2</sub> and D<sub>2</sub> are virtually identical at high pressures, despite their 1:2 ratio in molecular mass.



FIG. 5. Total energy and quantum corrections to the kinetic energies for D<sub>2</sub> and H<sub>2</sub> solids, as a function of density. (a) Quantum correction to the rotational kinetic energy,  $K_r/N-kT$ . (b) Quantum correction to the translational kinetic energy,  $(K_t/N-3/2kT)\sqrt{n}$ , with n=2 for D<sub>2</sub> and n=1 for H<sub>2</sub>, respectively. (c) Total energy E/N. Data points: D<sub>2</sub> at T=100 K (circles) and 200 K (squares); H<sub>2</sub> at T=100 K (diamonds) and 180 K (triangles). The *x* axis shows number density: corresponding pressures are indicated above (a). All data are calculated with N=96 in a hcp lattice with the intermolecular potential  $V_d$ .

#### **B.** Orientational ordering

The structure of a solid is usually monitored by the pair distribution function  $g(\mathbf{R})$ . It is generally difficult to gather enough statistics to sample the vectorial nature of  $\mathbf{R}$  in a numerical simulation, and thus it is conventional to use only its spherical average  $g(\mathbf{R})$ :

$$g(R) = \frac{1}{4\pi R^2 \rho} \left\langle \sum_{i < j} \delta(R_{ij} - R) \right\rangle.$$
(27)

Thus g(R) only shows the (statistical) number of molecules that are at a distance R from a given molecule. More definitive information of the relative distribution in the threedimensional space is lost, due to the spherical averaging. As is seen in the following figures, g(R) has well-defined peaks that denote the neighbor shells. The width of the peak is a measure of the quantum and thermal fluctuations in the distances. For hcp and fcc lattices, the first two peaks (the nearest neighbor and the next-nearest neighbor, respectively) are identical.



FIG. 6. An illustration of the orientational ordering parameter O(R), defined in Eq. (28), for several "ideally" ordered phases (no fluctuations allowed). Structural details for Pa3 are given in Refs. 9 and 13; for *c*-hcp, flat and tilted herringbone in Ref. 12; for  $Pca2_1$  and  $P2_1/c$  in Ref. 13. The bottom panel shows the corresponding g(r) up to second-nearest-neighbor distances.

In order to monitor the correlations in molecular orientations, an analogous two-body correlation function O(R) is defined as

$$O(R) = \left\langle \frac{\sum_{i < j} P_2(\cos\theta) \,\delta(R_{ij} - R)}{\sum_{i < j} \delta(R_{ij} - R)} \right\rangle.$$
(28)

This function measures the two-body orientation correlation at the intermolecular distance R, normalized by the number of molecules at that distance.  $\theta$  is the polar angle between the orientation vectors of the molecules located at  $\mathbf{R}_i$  and  $\mathbf{R}_i$ , i.e., the relative angular orientation. If the molecular orientations are completely disordered in a solid,  $\theta$  has a uniform distribution between  $0^{\circ}$  and  $180^{\circ}$  [note that due to the molecular symmetry  $P_2(\cos\theta)$  averages to zero]. This is true for all intermolecular distances and thus yields O(R) = 0 everywhere. On the other hand, parallel orientations mean  $\theta = 0$  and  $P_2(\cos \theta) = 1$ , so that, for example, in the *c*-hcp ordered phase proposed earlier,  ${}^{12}O(R) = 1$  everywhere. More complicated ordered phases yield distinctly different features in O(R). O(R) signatures for some of the structures suggested by recent ab initio calculations are shown in Fig. 6. For some ordered phases, pairs of molecules at the same distance, for example, within the nearestneighbor shell, can have different relative angular orientations  $\theta$ . In this case, a weighted average is taken according to the number of pairs of molecules for each value of  $\theta$ . Fluctuations in the orientation are ignored in Fig. 6 for purposes of demonstration. Realistic O(R) are notably rounded and have maxima well below their peak values, due to such fluctuations. Nonetheless, comparing the calculated O(R) with these "ideal" ones can provide crucial hints in deciphering the orientational order. Except for the *Pa3* phase, which is based on fcc, all the ordered phases in Fig. 6 are based on hcp lattices.<sup>12,13</sup> Because of the above-mentioned similarity of the fcc and hcp lattices at short range, the signature for *Pa3* is identical up to second-nearest neighbor on both lattices, and can therefore be compared to the hcp-based orientational signatures at short range.

For the study of phase transitions, it is convenient to use an averaged order parameter

$$O = 4 \pi \rho \int_{0}^{R_{\text{max}}} dR R^{2} [O(R)]^{2}, \qquad (29)$$

where  $R_{\text{max}}$  is a distance cutoff imposed by the finite size of the simulation cell. For convenience,  $R_{\text{max}}$  is chosen to be equal to the second nearest-neighbor spacing. Another averaged order parameter can be defined as

$$\overline{O} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{3}{2} \lambda_i^{\max} - \frac{1}{2} \right),$$
(30)

where  $\lambda_i^{\text{max}}$  is maximium eigenvalue of the matrix equation

$$\begin{pmatrix} \langle x_i^2 \rangle & \langle x_i y_i \rangle & \langle x_i z_i \rangle \\ \langle y_i x_i \rangle & \langle y_i^2 \rangle & \langle y_i z_i \rangle \\ \langle z_i x_i \rangle & \langle z_i y_i \rangle & \langle z_i^2 \rangle \end{pmatrix} \begin{pmatrix} \langle d_{ix} \rangle \\ \langle d_{iy} \rangle \\ \langle d_{iz} \rangle \end{pmatrix} = \lambda_i \begin{pmatrix} \langle d_{ix} \rangle \\ \langle d_{iy} \rangle \\ \langle d_{iz} \rangle \end{pmatrix},$$

and where  $x_i$ ,  $y_i$ , and  $z_i$  are the Cartesian coordinate components of orientation vector  $\Omega_i$  of the *i*th molecule. Still another alternative way to monitor the lattice ordering is through the lattice biased order parameter

$$\widetilde{O} = \left[\frac{1}{N_{i=1}^{N}} P_2(\mathbf{\Omega}_i \cdot \hat{\mathbf{z}})\right]^2, \qquad (31)$$

where  $\hat{\mathbf{z}}$  is the unit vector along a chosen direction in space. For hcp the *c* axis of the starting lattice configuration is taken as  $\hat{\mathbf{z}}$ . For fcc the initial (111) direction is taken as  $\hat{\mathbf{z}}$ . In both cases, the  $\hat{\mathbf{z}}$  axis coincides with the initial  $\mathbf{c}_p$  basis vector of the simulation cell. Although *O* has the advantage of being completely independent of a given spatial orientation bias,  $\tilde{O}$  sometimes provides a clearer signal of the orientational ordering.  $\tilde{O}$  is useful even in an *NPT* ensemble, since the overall orientation of the lattice does not change much during a simulation run. Previously, Runge *et al.* have used a still different averaged order parameter<sup>26</sup>

$$\hat{O} = \left[\frac{1}{N}\sum_{i=1}^{N} P_2(\mathbf{\Omega}_i \cdot \mathbf{u}_i)\right]^2.$$
(32)

Here  $\{\mathbf{u}_i\}$  are the unit vectors pointing along a particular set of ordered directions on the lattice sites *i*. By definition, this order parameter can only measure the extent of ordering relative to a given orientational structure defined by the set  $\mathbf{u}_i$ .



FIG. 7. Orientational ordering phase transition in D<sub>2</sub> solid at the temperature T = 100 K. Top row shows the orientational correlation function O(R), defined in Eq. (28), at pressures P = 60 (a), 85 (b), 90 (c), and 160 (d) GPa. The bottom row shows the pair distribution function g(R) at the same pressures. These are calculated with M = 8 and N = 96 in a hcp lattice.

In the calculations made here, all of these different order parameters in Eqs. (28)–(32) give essentially the same indication in the onset of a disorder-order transition, i.e., a sharp change from zero (or near zero) to a finite value, with only small differences in the location (P or  $\rho$ ) of the transition.

Figure 7 shows the O(R) characteristics of a typical molecular orientational ordering phase transition for  $D_2$ . For a given temperature T, the molecular orientation is disordered in the solid at low pressure (below the values shown here), as evidenced by the fact that O(R) averages to approximately zero. As P is increased and approaches a transition pressure  $P_{\rm tr}$ , deviations from O(R) = 0 become visible and then become more pronouced as P continues to increase. A welldefined structure in O(R) is then clearly evident and stable throughout the simulation for  $P > P_{tr}$ . The onset of this transition is more clearly seen in Fig. 8, in which the averaged order parameter O, Eq. (29), is shown as a function of P. A steplike increase is seen in the function O(P) at  $P = P_{tr}$ , indicating a phase transition which is rounded by the finite size and fluctuation effects. The transition pressure  $P_{tr}$  is identified as the point where the averaged order parameter O first shows the most abrupt upward turn. Thus for  $D_2$  at T = 100 K,  $P_{tr} \sim 85$  GPa.

## C. D<sub>2</sub> phase diagram

Figure 9 shows the resulting phase diagram in the *T-P* plane for  $D_2$ . The effects of variable number of particles *N* (*N*=32, 48, 64, 96) have been tested, as well as different choices of the cell geometry, in both the hcp and fcc phases. Although a lattice structural phase transition, e.g., between these two phases, is allowed in our *NPT* ensemble, no sign of this is observed. The lattice stays in the start-up structure (either hcp or fcc) throughout a simulation run, including when passing through the orientational order-disorder phase transition. The positions of such transitions do, however, shift noticably with the two different initial choices of lattice,



FIG. 8. The orientational order parameter *O*, defined in Eq. (29), as a function of pressure *P*, for a D<sub>2</sub> solid at T = 100 K. The arrow indicates our identification for the transition pressure,  $P_{tr} \sim 85$  GPa (see text).

hcp and fcc, as is evident in Fig. 9. Figure 10 shows the ratio of the crystallographic axes, c/a, for a simulation with the initial hcp lattice. Details of the computation of the c/a ratio are summarized in the Appendix. The ratio is a little smaller than the ideal value of 1.633, and is aproximately constant over the pressure range studied. The value is somewhat less than the approximately constant value reported for D<sub>2</sub> at lower pressures (up to 14.2 GPa in Ref. 43 and up to 30 GPa in Ref. 49). Precise comparison with experiment is difficult since the measurements were made for  $n-D_2$  rather for  $o-D_2$ , and may furthermore be influenced by experimental artifacts such as hydrostatic strains.<sup>43</sup>



FIG. 9. The phase diagram of  $D_2$  solid. The curves are the experimental boundaries between three phases I, II, and III, taken from Refs. 3 (solid line) and 7,8 (dashed line), respectively. Solid circles are PIMC data for the orientational order-disorder phase transition in the hcp phase; open circles are for fcc. Both of these are calculated with  $V_d$ , and the scaled anisotropic potential, Eq. (17). Open squares are hcp results with the *unscaled* anisotropic potential [ $\alpha = 1$  in Eq. (17]. All calculations are done with N=96. The PIMC partition number M is given in Table II.

TABLE II. Partition number M used in the PIMC calculations.

T (K)	20	60	80	100< <i>T</i> <200	300
М	20	16	12	8	4

The orientational correlation function O(R) is found to be rather similar for fcc and hcp lattices in the ordered phases. This is not too surprising, since these two lattices are very similar. With the energetics of the dense solids dominated by the short-range repulsions, the small difference in the energies of the two lattices for distances beyond second-nearestneighbor separations is unresolvable within the accuracy of the simulation. The signature of O(R) in the ordered phase for both lattices resembles that for the *Pa3* structure (compare Fig. 6 and Fig. 7) and has, in contrast, very little resemblance with the ordering signatures of the other structures shown in Fig. 6.

We now compare the PIMC phase lines with the experimental phase diagram for D<sub>2</sub>. Two sets of experiments have found three distinct phases for  $D_2$  at pressures below 200 GPa (Fig. 9).<sup>3,7,8</sup> The phases are alternatively referred to as phases I, II, and III,<sup>3</sup> or (orientationally disordered) hcp, broken-symmetry phase (BSP), and A phase,<sup>7,8</sup> respectively. A triple point is identified at  $P_t \sim 150-165$  GPa and  $T_t \sim 125$  K. For  $T < T_t$ , solid D<sub>2</sub> is observed to go through two phase transitions (I to II, and II to III) as pressure is increased, while only one transition (I to III) occurs for  $T > T_t$ . The positive identification of these phases is still uncertain. Single-crystal x-ray diffraction data have shown that phase I, which extends to the low-temperature and -pressure region, has a hcp lattice structure.<sup>3,43</sup> The molecular orientations are disordered here, as for the solid under ambient pressures.<sup>3,9</sup> On the other hand, both phases II and III are believed to be orientationally ordered phases. The available experimental evidence suggests that they also have hcp-based lattice structures,<sup>3,4,8</sup> although the exact nature of these phases is still unknown. Based on the assumed hcp or fcc lattice structures, electronic structure calculations have identified a few energetically preferred, orientationally ordered structures, including those illustrated in Fig. 6.37,8,10-13 A comprehensive summary of these structures is given in Ref. 8. Some of these orientationally ordered phases have already been observed in classical molecular solids such as N<sub>2</sub>, which exhibits a similar phase diagram.<sup>39</sup> Recently, a group-theoretical analysis of experimental Raman and IR spectra has been made in the attempt to distinguish between these alternative structures. This analysis eliminated several of the more popular structures for phase III, including the hcp  $Pca2_1$  and fcc  $Pa3.^8$ 

In contrast to the experiments, only one phase transition, a pure orientational ordering, is observed here. It is evident from Fig. 9 that the Monte Carlo results for the orientational disorder-order phase transition with a hcp lattice in the relatively low-pressure region, P < 130 GPa, show excellent agreement with the experimental I-II phase boundary for D<sub>2</sub>. In contrast, the phase line derived for ordering on the fcc lattice lies far too high, i.e., occurs at too low pressure for a given temperature. This discounts the possibility of a sequence of transitions, hcp-fcc-hcp, proposed by Runge and co-workers<sup>17,26</sup> At the higher pressures, the PIMC data show



FIG. 10. Dependence of the crystallographic axis ratio c/a in the hcp structure on pressure for D<sub>2</sub> (circles) and H<sub>2</sub> (stars) at T=300 K. We use the method of calculating c/a described in the Appendix, subsection 1. The dashed line is the ideal value 1.633.

an upward turn in the T-P plane, approximately parallel to the experimental I-III phase boundary but displaced to lower pressures by about 15 GPa. Since only one transition is observed below the experimental triple-point temperature, no further distinction between phase II and a structure corresponding to the experimental phase III can be made. However, the fact that our orientational transition is parallel to the experimental I-III phase boundary suggests that phases II and III might be structurally quite similar.

The effect of the different choices of the interaction potential listed in Sec. III A have also been tested, just as in the EOS study. In contrast to the situation for the EOS, the isotropic part of the potential plays little role here in determining the orientational phase transition, apart from holding the lattice at the proper density. The I-II transition is, however, sensitive to the choice of the anisotropic part of the potential, as might be expected. It is found that the best agreement of the I-II transition location with the experimental transition line for pressures P up to 130 GPa can be achieved by using  $V_d$ , i.e., with the scaled anisotropic potential of Eq. (17), for the solid in the hcp phase. Figure 9 clearly demonstrates that the unscaled potential forms are too strong and predict the transition to occur at too low a pressure. This difference, and thus the necessity of the scaling, was also observed in the prior, fixed lattice, PIMC study.<sup>2</sup>

## D. H<sub>2</sub> phase diagram

The phase diagram of solid  $H_2$  has not yet been investigated experimentally in the same detail as that for solid  $D_2$ . Indeed it is still unclear to what extent the  $H_2$  phase diagram is analogous to that for  $D_2$ . In particular, the existence of a triple point or, alternatively, of a critical point that terminates the II-III phase boundary is a matter of some debate.<sup>5,7,8</sup> Unfortunately, considerably fewer experimental measurements of phase transition points have been made for  $H_2$ . Figure 11 depicts the experimental II-III phase boundary and the projected I-II boundary which is obtained by interpolation between the single measurement of the lowtemperature experimental orientational transition<sup>50</sup> and the



FIG. 11. Phase diagram of  $H_2$  solid. The solid curve is the experimental phase boundary between phases II and III. The dashed curve is the expected boundary between phases I and II, from the two measured data points marked by stars (Refs. 7 and 8). Solid squares are PIMC results in the hcp phase for the orientational order-disorder phase transition, calculated with  $V_d$  and the scaled anisotropic potential of Eq. (17).

controversal higher-temperature transition point to the H-A structure at T=77 K and 150 GPa, when the latter is interpreted as a triple point. Superimposed are our PIMC phase transition results for solid H<sub>2</sub> in the hcp phase (solid squares). The calculations show that this is also a purely orientational transition between the SP and an ordered phase with *Pa3*-type local orientational order, with no associated lattice structural transition. Just as for D<sub>2</sub>, the crystallographic c/a ratio also stays approximately constant, at a value somewhat below the ideal value (Fig. 10). This is consistent with the available experimental measurements for H<sub>2</sub><sup>51</sup>.

We can identify the observed transition in  $H_2$  with the same I-II transition as in D<sub>2</sub>. The theoretical phase line clearly agrees rather well with the I-II boundary obtained by interpolation between the experimental points. It also clearly continues beyond the disputed transition point at T=77 K and 150 GPa. Whether or not the location of this continuation is quantitatively accurate or not (as for  $D_2$ , it may lie too high), the fact that we do actually see it is consistent with the experimental identification of the transition point at T = 77 K and 150 GPa as a triple point rather than a critical point.<sup>7,8</sup> Furthermore, the agreement of the H<sub>2</sub> I-II phase boundary with the experimental phase line is consistent with the good agreement reached for the corresponding boundary in  $D_2$ . This isotopic consistency, both for the EOS and the orientational phase diagrams, provides a strong validification of the potential used. Thus the hybrid potential  $V_d$  with the scaled anisotropic interaction of Eq. (17) is therefore expected to be an excellent candidate for further theoretical investigations of the dense phases of the hydrogen isotopes.

#### E. Zero-point energies

The quantum contributions to the molecular rotational degrees of freedom are reflected in the rotational kinetic energy



FIG. 12. Comparison of the molecular orientational orderdisorder phase boundary for the "classical reference" solid (M=1) with the phase boundaries derived from the D<sub>2</sub> and H<sub>2</sub> PIMC data when scaled to the effective rotational temperature defined by Eq. (33). Diamonds and solid line; classical reference. Plusses: D<sub>2</sub> phase boundary. Stars: H<sub>2</sub> phase boundary. The *x* axis shows number density: corresponding pressures are indicated at the top. All calculations were made for a hcp lattice, with N=96.

defined in Eq. (25). The equipartition theorem in classical statistical physics predicts a rotational kinetic energy of  $K_r/N \sim kT$  for the two degrees of freedom in the molecular orientation. However, the measured  $K_r/N$  noticably exceeds this value, as is evident from Fig. 5(a). One can define the difference  $K_r/N - kT$  as the quantum correction to the temperature for the rotational degrees of freedom. It is clear from Fig. 5(a) that this quantum correction decreases with increasing temperature, and increases with pressure. Both of these trends are understandable in terms of standard pictures of hindered rotators. The motion becomes less hindered, approaching pure rotation, at high temperatures as higher rotational states are populated, while it becomes more hindered at high pressures when the rotors interfere with one another, resulting in greater vibrational (librational) character and consequently higher kinetic energy.

To understand the consequences of the rotational quantum correction for the phase diagram, one can alternatively define an effective rotational temperature,  $T_{eff}^r$ , by

$$kT_{\rm eff}^r = K_r / N. \tag{33}$$

This allows one to analyze the extent to which the orientational transition can be described classically for each isotope. Figure 12 shows the order-disorder phase boundaries for  $D_2$  and  $H_2$  which result when the temperatures are scaled to the effective rotational temperature. One observes that the phase boundary for  $D_2$  almost overlaps with that of the effective "classical reference" system. For  $H_2$  there is less agreement with the classical reference, although it also approaches this in the high-temperature and high-density limit, as would be expected. This tells us that for  $H_2$ , the molecular orientational transition is strongly dependent upon the quantum nature of the molecule, up to pressures of 140 GPa.

It is of interest to compare the scaling behavior of the rotational kinetic energy with that of the translational kinetic



FIG. 13. Comparison of c/a ratio for hcp-based D<sub>2</sub> obtained with the two procedures described in the Appendix, subsections 1 and 2. Circles represent the same data shown in Fig. 10 and are calculated with the g(R),  $\rho_{hcp}$  method (Appendix, subsection 1). Squares are calculated from the simulation cell dimensions (Appendix, subsection 2) The error bar is statistical error bar only (see discussion in text). The dashed line is the ideal c/a value for hcp, 1.633.

energy. The latter effectively becomes vibrational energy in the solid phase. Quantum corrections to this kinetic energy term can therefore be viewed as deriving primarily from zero-point vibrations, which scale as  $\sqrt{n}$  in a harmonic model, where *n* is the mass index (for  $H_2$ , n=1, and for  $D_2$ , n=2). Then the quantum correction to the translational kinetic energy,  $(K_t/N - 3/2kT)\sqrt{n}$ , should be independent of isotope and temperature. This is indeed the case for the two hydrogen isotopes over the range of pressure studied here, as is evident from Fig. 5(b). Note also that the translational quantum corrections deriving from vibrations induced by restricted translation are significantly larger than the rotational corrections deriving from librations induced by hindered rotation. One can then similarly define an effective translational (vibrational) temperature,  $3kT_{eff}^{t}/2 = \sqrt{n}K_{t}/N$ , which has the mass dependence of the zero-point motion eliminated.  $T_{eff}^{t}$  is of course not necessarily equal to the effective rotational temperature  $T_{eff}^{r}$ . The behavior of the different isotopes when scaled to such effective temperatures is useful for developing simple understanding of features of the phase diagram in quantum materials. The example shown above, scaling the molecular orientational transition with  $T_{eff}^{r}$  could be valuable for predicting the phase diagram of the related quantum solid HD (Refs. 7 and 8) if a reliable estimation of its quantum rotational kinetic energy can be made.

#### **IV. SUMMARY AND DISCUSSION**

In this study of the phase diagrams of  $D_2$  and  $H_2$  up to megabar pressures, we showed that the PIMC method may be applied in a constant-pressure ensemble with simultaneous translation and rotational molecular motion incorporated. Utilizing an intermolecular interaction potential determined to agree with the experimental equation of state over a large range of pressures, a rotational order-disorder phase transition is observed for both isotopes which agrees quantitatively with the experimental phase lines up to about 150 GPa. This represents a significant improvement over the previous best theoretical estimates of the I-II transition for the two isotopes.<sup>17,26</sup> Use of the constant-pressure ensemble allows different lattices to be accessed during the simulation and thereby vastly increases the configurational space which can be explored. The agreement with experiment implies that the interaction potential used here is reliable up to pressures of about 150 GPa.

The nature of the orientational transition observed to agree with experiment is for both isotopes a transition from rotationally disordered hcp to an ordered hcp structure, with an ordering signature similar to that of Pa3 (out to secondnearest neighbors). This transition agrees with the experimentally observed I-II transition up to  $\sim 150$  GPa. No lattice structural transition is observed for either isotope up to 200 GPa, and the crystallographic c/a ratio remains approximately constant. We believe that no structural transitions are observed because during the finite period of a typical Monte Carlo run with the sample sizes used here, it is only realistically feasible to observe displacement type transitions, such as that reproduced for the classical  $N_2$  system.<sup>37</sup> Since no such signal was observed for D<sub>2</sub> or H<sub>2</sub>, this suggests that neither the I-II transition nor the II-III transition (which is not seen here) is of displacement type.

One limitation of the current study is that the specific choice of N and the geometry of the periodic simulation cell was designed to accomodate primarily the fcc and hcp lattice structures, and several orientationally ordered phases related to these lattices. Orientational ordering with longer wavelength than the cell dimensions could not be studied. More importantly, there are many other crystal structures with periodic boundary conditions that require unit cells very differ-ent from the fcc/hcp cell.<sup>12,13,39</sup> The recently studied orthorhombic structure is an interesting case for future study in this regard.<sup>16</sup> One other such example is the  $\epsilon$  phase in N<sub>2</sub>, which requires a tetragonal simulation cell and a unit cell with 32 molecules.<sup>39</sup> Such a structure would be impossible to realize through natural fluctuations in a constant pressure ensemble starting with a hcp simulation cell of 96 particles. Therefore, the observation of more complex orientationally ordered crystal structures is precluded within the current computational constraints. The possibility of phase III being similar to the  $\epsilon$  phase of N<sub>2</sub> could alternatively be investigated via investigation of the free energy differences between specific structures for phases II and III, to establish which is thermodynamically stable at high pressure.

Speculations have been made that phase III may involve some kind of elongation of the intramolecular bond which could alter the total energy and consequently the structure of the solid.<sup>3,15,19</sup> Having shown here the usefulness of the PIMC method with intermolecular interactions for covering relatively large areas of the configuration space, it would be interesting to now apply the PIMC method with an atomatom interaction potential which would allow the intramolecular vibron motion to be incorporated.

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## APPENDIX: ESTIMATION OF HCP ASPECT RATIO

There are several ways to calculate the c/a ratio in constant pressure PIMC calculations. One can either extract it from knowledge of the pair distribution function g(R) and the number density in the hcp structure,  $\rho_{hcp}$ , or directly from sampling of the simulation cell dimensions  $a_p$ ,  $b_p$ , and  $c_p$ .

## **1.** From g(R) and $\rho_{hcp}$

The molecular number n(R) located at point R from some origin can be easily obtained from g(R). One can then define the lattice constant a by means of the weighted average

$$a = \frac{\sum n(R)R}{\sum n(R)},\tag{A1}$$

where  $\Sigma n(R) = 12$  is the number of first-nearest-neighbor molecules in the hcp structure. From the number density of the hcp lattice,  $\rho_{\rm hcp} = 4\sqrt{3}/3a^2c$ , the ratio c/a is then obtained from

$$c/a = \frac{4\sqrt{3}}{3a^3\rho_{\rm hcp}},\tag{A2}$$

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with *a* given by Eq. (A1). Estimation of the statistical error of c/a with this method is difficult, because it derives partially from the error in g(R).

### 2. From simulation cell dimensions

In the case of the initially perfect hcp lattice with N=96 described in Sec. II B, the three simulation cell dimensions are related to c and a as follows:

$$a_p = 4a,$$
  

$$b_p = 4a,$$
  

$$c_p = 3c.$$
 (A3)

If one can assume that the system does not deviate much from the ideal hcp structure (as is indeed true in our simulations), then one can derive an estimate for c/a from

$$c/a = \frac{8c_p}{3(a_p + b_p)}.$$
 (A4)

In this case the statistical error bar of c/a can easily be derived from the statistical error of the three dimensions  $a_p$ ,  $b_p$ , and  $c_p$ .

Methods 1 and 2 give almost identical results, but the system fluctuations influence the data from the second method noticeably more than in the first method using g(R) (see Fig. 13). We therefore take the first method, employing g(R) and  $\rho_{hcp}$ , to be more reliable. The data in Fig. 10 are produced with method 1.

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