

Crystal-field phenomena in hcp H₂ and D₂ at high pressuresYu. A. Freiman,^{1,*} S. M. Tretyak,¹ Alexei Grechnev,¹ Alexander F. Goncharov,^{2,3} and Russell J. Hemley²¹*B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Avenue, Kharkov, 61103, Ukraine*²*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, USA*³*Center for Energy Matter in Extreme Environments and Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, 350 Shushanghu Road, Hefei, Anhui 230031, China*

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Crystal-field effects in hexagonal closed-packed molecular H₂ and D₂ are examined over a broad range of pressures. The lattice distortion parameter (the deviation of the c/a ratio from the ideal value 1.633), orientational order parameter, and crystal-field parameter in hexagonal close-packed (hcp) structures of p -H₂, o -D₂, and n -H₂ are calculated using the semiempirical lattice-dynamic approach. It is shown that the lattice distortion in the J -even species is two order of magnitude smaller compared with that found in n -H₂ and n -D₂. The difference is due to splitting of the J -odd rotational levels in the J -even/ J -odd mixtures.

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I. INTRODUCTION

At zero pressure and temperature the molecules in J -even (p -H₂, o -D₂) and J -all (HD) solid hydrogens are in the ground state $J = 0$. Admixtures of higher rotational states into the ground-state wave function are very small and the molecules are virtually spherical. Rigid spheres crystallize into the face center cubic (fcc) or hexagonal close-packed (hcp) structures. As compared with fcc, the hcp structure has an additional degree of freedom associated with the axial c/a ratio. The lattice of close-packed hard spheres has $c/a = \sqrt{8/3} \approx 1.633$ (ideal hcp structure). The quantity $\delta = c/a - \sqrt{8/3}$, the lattice distortion parameter, describes the deviation of the axial ratio from the ideal value. In the case of $\delta < 0$, this distortion involves a relative expansion within the close-packed planes, or contraction along the c -axis direction; and vice versa, for $\delta > 0$ the lattice is expanded along the c axis and contracted within the close-packed planes.

Solid H₂ and D₂ crystallize in the hcp structure (phase I) over a broad range of pressures and temperatures [1]. Calculations with simple isotropic pair potentials have shown that the ideal hcp structure at zero pressure and temperature does not minimize the lattice energy [2–4], and the minimum energy hcp structure has a small but nonzero lattice distortion. Semiempirical and first-principles calculations performed for solid helium and other hcp rare-gas solids indicate that the pressure dependencies of the lattice distortion parameter δ for the many-body (two- plus three-body) and for the pair intermolecular potentials are qualitatively different [5,6]. Three-body forces flatten the structure ($\delta < 0$) while the pair forces at large compressions tend to elongate it ($\delta > 0$). Thus, the lattice distortion parameter is sensitive to many-body components of effective intermolecular potentials used to describe the properties of the system at high pressures [7]. Furthermore, the evolution of intermolecular interactions under pressure within phase I is important in view of both the high pressure phases and changes in electronic structure that are now evident at megabar pressures (e.g., phase III above

150 GPa at low temperature [8] and phase IV above 200 GPa at 300 K [9]).

For most hcp elemental solids except helium, hydrogen, and high-pressure Ar, Kr, and Xe the behavior of δ with pressure and temperature is well established from both theory and experiment. For closed shell nonmetallic systems typical values are of the order of 10^{-2} [10]. For solid helium δ is 1–2 orders of magnitude smaller [5,6]. The first measurements of the c/a ratio in solid hydrogens were performed by Keesom *et al.* [11], who found that at zero pressure the hcp lattice of p -H₂ is close to the ideal one. A x-ray zero-pressure study by Krupskii *et al.* [12] confirmed this result ($c/a = 1.633 \pm 0.001$) and extended it to the o -D₂. In fact, the only structural study of p -H₂ and o -D₂ at elevated pressures up to 2.5 GPa and low temperatures were made by Ishmaev *et al.* using the neutron diffraction method [13,14]. It was found that the ratio c/a is practically constant and is slightly lower than the ideal hcp value (1.631 ± 0.002).

There have been numerous structural studies of n -H₂ and n -D₂ [15–21] (see also reviews [1,22]). Using then newly developed synchrotron x-ray diffraction techniques Mao *et al.* [17] and Hu *et al.* [18] reported a linear decline in c/a in n -H₂ up to 42 GPa with $d(c/a)/dP = -0.000441 \text{ GPa}^{-1}$. Subsequent synchrotron single-crystal x-ray diffraction measurements of n -H₂ [23–25] and n -D₂ [23] up to megabar pressures at room temperature revealed that the c/a ratio decreases with increasing pressure nearly linearly up to 180 GPa. However, solid hydrogens can support residual nonhydrostatic stresses as a function of compression at these temperatures, and the small uniaxial stresses can affect the measured c/a ratio. No isotope effect on the pressure (stress) dependence of the c/a ratio is evident from these studies.

There have been many calculations of the pressure behavior of crystal-field effects of dense hydrogen and deuterium using different theoretical approaches. Previously we reported detailed calculations of the pressure dependence of the intermolecular interactions for phase I for comparison with the low-temperature Raman spectrum [26]. Hartree-Fock [27,28], local density approximation [29], path-integral Monte Carlo [30], and *ab initio* molecular dynamics [31] have also been performed. In these theoretical approaches the rotation-lattice

*yuri.afreiman@gmail.com

coupling gives rise to positive δ which is in contradiction with experiment. Kitamura *et al.* [32] performed first-principles path-integral molecular dynamics (FP-PIMD) simulations at three P - T points corresponding to phases I, II, and III at the phase diagram and obtained the c/a ratio that decreases with pressure.

Here we develop a self-consistent approach based on a many-body semiempirical intermolecular potential proposed originally in Ref. [33]. We show that the pressure behavior of the c/a ratio in solid p -H₂ and o -D₂ in phase I is determined mainly by the translational degrees of freedom and is comparable in magnitude with that for rare-gas solids. In the case of n -H₂ and n -D₂ we show that the behavior of the axial ratio found in Refs. [23–25] is due to the presence of the J -odd component in normal ortho-para mixtures of solid hydrogens [34]. A detailed study of the lower pressure behavior, including the results for HD, will be presented elsewhere [35].

II. CRYSTAL FIELD AND LATTICE DISTORTION IN p -H₂ AND o -D₂

The Hamiltonian of the problem can be written in the form [22,26,33]

$$\mathcal{H} = \mathcal{H}_{\text{is}} + \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{int}}, \quad (1)$$

where \mathcal{H}_{is} is the contribution of the isotropic part of the intermolecular potential, \mathcal{H}_{rot} is the rotational part of the Hamiltonian, and \mathcal{H}_{int} describes the lattice-rotation coupling.

The isotropic part of the ground-state energy E_{is} can be written as a sum of contributions from the isotropic part of the static two- and many-body energies $E_{\text{is}}^{\text{pair}}$ and $E_{\text{is}}^{\text{m.b.}}$, and the zero-point vibrations E^{zpv} :

$$E_{\text{is}} = E_{\text{is}}^{\text{pair}} + E_{\text{is}}^{\text{m.b.}} + E^{\text{zpv}}. \quad (2)$$

In the mean-field approximation (MFA), the Hamiltonian of the system of quantum linear rotors has the form [22,33]

$$\mathcal{H}_{\text{rot}} = \sum_f \mathbf{L}_f^2 - U_0 \sqrt{4\pi/5} \eta \sum_f Y_{20}(\vartheta_f) + \frac{1}{2} N U_0 \eta^2, \quad (3)$$

where \mathbf{L}_f is the angular momentum operator, $Y_{LM}(\vartheta_f, \varphi_f)$ are spherical harmonics, and the angles ϑ_f and φ_f specify the orientational axis of the molecule at the lattice site f . All the energy quantities are expressed in units of the rotational constant B_{rot} .

In distinction to phases II and III, phase I has no orientational structure which would originate from the coupling term in the anisotropic interaction between the hydrogen molecules. A certain degree of orientational order in phase I, as will be shown below, originates from the crystal-field interaction. The orientational order parameter is defined as

$$\eta = \sqrt{4\pi/5} \langle Y_{20}(\vartheta_f, \varphi_f) \rangle, \quad (4)$$

where $\langle \dots \rangle$ means averaging with the Hamiltonian \mathcal{H}_{rot} [Eq. (3)], and N is the number of sites.

The molecular-field constant is defined by

$$U_0 = \sum_{ff'} \sum_{\alpha\beta\gamma\delta} V_{ff'}^{\alpha\beta\gamma\delta} Q_f^{\alpha\beta} Q_{f'}^{\gamma\delta}, \quad (5)$$

where $V_{ff'}^{\alpha\beta\gamma\delta}$ is the interaction matrix defined by the parameters of the intermolecular potential, $Q_f^{\alpha\beta} = \Omega_f^\alpha \Omega_f^\beta - \frac{1}{3} \delta_{\alpha\beta}$, and Ω is the unit vector specifying the equilibrium orientation of the molecule at site f . There is a near linear correspondence between dimensionless pressure in units of U_0/B_{rot} and pressure in GPa. For the $Pca2_1$ structure we have the following approximate relations for rescaling the pressure: P in U_0/B_{rot} units corresponds to $0.5P$ for H₂, $0.75P$ for HD, and $1.25P$ for D₂ [33].

We used a simple many-body potential based on the sum of the pair of the well-tested SG potential [36] (discarding the R^{-9} term) and two three-body terms: the long-range Axilrod-Teller dispersive interaction and the short-range three-body exchange interaction in the Slater-Kirkwood form [37,38]. It has been successfully used for the description of the equation of state, the pressure dependence of the Raman-active E_{2g} mode [39], and the sound velocities in solid hydrogen under pressure [40]. The explicit form and parameters of the potential used in this work are given in Ref. [41]. The contribution of the zero-point vibrations E^{zpv} was taken into account in the Einstein approximation.

In the nonrigid lattice there is a strong lattice-rotation coupling associated with the crystal field. The origin of this coupling can be explained in the following way. With increasing pressure the anisotropic interaction increases and admixtures of $J \neq 0$ rotational states into the ground-state wave function become more and more appreciable. With the nonzero admixture the molecules acquire anisotropy. The anisotropic molecules tend to be packed into a distorted lattice. The lattice distortion δ is given by a competition of the anisotropic interactions (which favor strong distortion) and the isotropic interactions (which favor a near-ideal hcp lattice).

The lattice-rotation coupling is described by the the Hamiltonian

$$\mathcal{H}_{\text{int}} = -\varepsilon_{2c} \sqrt{4\pi/5} Y_{20}, \quad (6)$$

where ε_{2c} is the crystal-field parameter [42] which is linear with respect to δ :

$$\varepsilon_{2c} = \tilde{B} \delta, \quad \tilde{B} = -\sqrt{6} \left(B + \frac{1}{2} R \frac{dB}{dR} \right), \quad (7)$$

where $B(R)$ is the radial function of the single-molecular term in the anisotropic intermolecular potential [42]. Thus, the state of the lattice can be described by two coupled order parameters, $\eta(V, T)$ and $\delta(V, T)$, which can be determined by the minimization of the free energy with respect to these parameters. In the calculations we restrict ourselves to $T = 0$ K, so we will minimize the total ground-state energy, in terms of the translational and rotational subsystems, i.e., $E_0^{\text{tot}} = E_0^{\text{tr}} + E_0^{\text{rot}}$.

The translational part of the ground-state energy E_0^{tr} does not depend on η and the respective minimum conditions take the form

$$\partial E_0^{\text{rot}} / \partial \eta = 0, \quad (8)$$

$$\partial (E_0^{\text{tr}} + E_0^{\text{rot}}) / \partial \delta = 0. \quad (9)$$

Thus, the complete minimization can be carried out in two stages, first, with the help of Eq. (8) we find η as a function of

U_0 and δ and then by minimizing the total ground-state energy with respect to δ [Eq. (9)] we find δ and η as a function of U_0 (volume V).

Using successive approximation methods we can find solutions of Eqs. (8) and (9) in any necessary approximation [33,41]. Up to third order in the crystal-field parameter, the orientational order parameter and orientational ground-state energy have the following form:

$$\eta = \kappa \frac{\epsilon_{2c}}{B_{\text{rot}}} + \frac{15^2}{14} \kappa^3 \left(\frac{\epsilon_{2c}}{B_{\text{rot}}} \right)^2, \quad (10)$$

$$\frac{E_0^{\text{rot}}}{B_{\text{rot}}} = -\frac{1}{2} \kappa \left(\frac{\epsilon_{2c}}{B_{\text{rot}}} \right)^2 - \frac{75}{14} \kappa^3 \left(\frac{\epsilon_{2c}}{B_{\text{rot}}} \right)^3, \quad (11)$$

where

$$\kappa = \frac{1}{15 - U_0/B_{\text{rot}}}. \quad (12)$$

The expansion parameter ϵ_{2c} [Eq. (7)] is negative for all pressures, so the expansions Eqs. (10) and (11) are oscillating and converge if the terms of the expansions are decreasing. Due to the presence of a singular factor κ [Eq. (12)] in the expansions Eqs. (10) and (11), the validity of this analytical solution is limited by the condition $U_0/B_{\text{rot}} < 15$, which corresponds to pressure of ~ 30 GPa for p -H₂, and 20 and 12 GPa for HD and o -D₂, respectively. To extend the solution into the higher pressure region a numerical approach should be used.

As can be seen from Eqs. (10) and (11), at low pressures the rotational part of the ground-state energy contains no linear term in δ . The same is also true at high pressures. The admixture of higher rotational states to the rotational wave function is proportional to the lattice distortion:

$$\Psi_0 = Y_{00} + c_2 \delta Y_{20} + \dots \quad (13)$$

The ground-state energy

$$E_0^{\text{rot}} = \langle \Psi_0 | \mathcal{H}_{\text{rot}} | \Psi_0 \rangle = 6c_2^2 \delta^2 - (U_0 \eta^2 / 2 + \epsilon_{2c} \eta). \quad (14)$$

Since $\eta \sim \delta$ and $\epsilon_{2c} \sim \delta$, $E_0^{\text{rot}} \sim \delta^2$ at all pressures.

Let us consider the contribution of the translational degrees of freedom. Up to terms of the second order in δ the translational part of the ground-state energy is

$$E_0^{\text{tr}} = E_0(0) + b_1^{\text{tr}} \delta + b_2^{\text{tr}} \delta^2, \quad (15)$$

where E_0 is the ground-state energy of the ideal lattice and b_i^{tr} ($i = 1, 2$) are the coefficients which depend on the parameters of the intermolecular potential and molar volume. The total ground-state energy is

$$E_0^{\text{tot}} = E_0(0) + b_1^{\text{tr}} \delta + b_2^{\text{tot}} \delta^2, \quad (16)$$

where $b_2^{\text{tot}} = b_2^{\text{tr}} + b_2^{\text{rot}}$. Minimizing $E_0(\delta)$ over δ , we obtain

$$\delta = -b_1^{\text{tr}} / (2b_2^{\text{tot}}). \quad (17)$$

At lower pressures the contribution of the rotational degrees of freedom to b_2 as follows from Eq. (11) is $b_2^{\text{rot}} = -\kappa(\epsilon_{2c}^2 / 2B_{\text{rot}})$. It is negative and increases in the absolute value with pressure. The total b_2^{tot} is a sum of the respective contributions

$$b_2^{\text{tot}} = b_2^{\text{tr}} + b_2^{\text{rot}}. \quad (18)$$

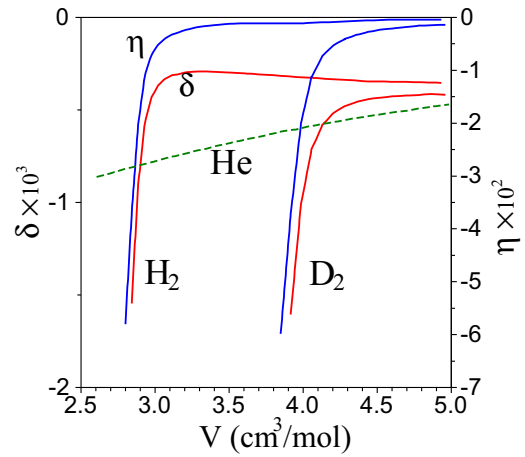


FIG. 1. (Color online) Lattice distortion parameter δ and orientational order parameter η in p -H₂ and o -D₂ as functions of molar volume. Lattice distortion parameter of solid He [5] is shown for comparison (dashed line)

Figure 1 presents the lattice distortion parameter δ and orientational order parameter η for p -H₂, and o -D₂ as functions of molar volume. The calculations were performed for the molar volumes $V < 18$ cm³/mol ($P > 0.5$ GPa) outside of the region where quantum crystal effects are decisive and extended up to the point of the I–II transition.

In phase I both η and δ are small and negative. The negative δ means that the lattice is slightly flattened compared with the ideal one; the negative η means that the molecules precess around the c axis with the molecular axis inclined to the c axis by the angle slightly over $\langle \vartheta_0 \rangle = \cos^{-1}(1/\sqrt{3}) \approx 54^\circ 44'$. With increasing pressure, η decreases monotonically (the limiting value $\eta = -1/2$ means that the molecules classically precess around the c axis with the precession angle $\vartheta = \pi/2$). At large molar volumes (~ 18 cm³/mol) the deviation of the molecular ground state from the pure spherical one is very small. This deviation is characterized by the orientational order parameter $\eta = -3.3 \times 10^{-4}$ for p -H₂ and $\eta = -1 \times 10^{-5}$ for o -D₂. The lattice is very close to ideal. While η decreases monotonically on compression, δ changes with pressure nonmonotonically (Fig. 1). This nonmonotonic behavior is connected with the mutual changes of the coefficients b_1^{tr} , b_2^{tr} , and b_2^{rot} in Eq. (17) with pressure.

Significant changes are seen between $V = 3.1$ cm³/mol (80 GPa) and 2.93 cm³/mol (92.2 GPa) for H₂ and between $V = 4.05$ cm³/mol (37.45 GPa) and 4.2 cm³/mol (33.8 GPa) for D₂. This corresponds to the region of the transition to phase II (experimentally, 110 GPa in p -H₂ [43], 28 GPa in o -D₂ [44,45]).

Before comparing the theoretical and experimental pressure dependencies of the lattice distortion parameter for the hydrogens isotopes, we compare the theoretical results for solid helium [5] obtained for the semiempirical many-body potential, similar to that used for the hydrogens. Such a comparison is useful because these systems belong to the same class of solids, simple molecular crystals characterized by van der Waals interactions (at low densities). The most significant difference is the fact that for solid hydrogen in addition to

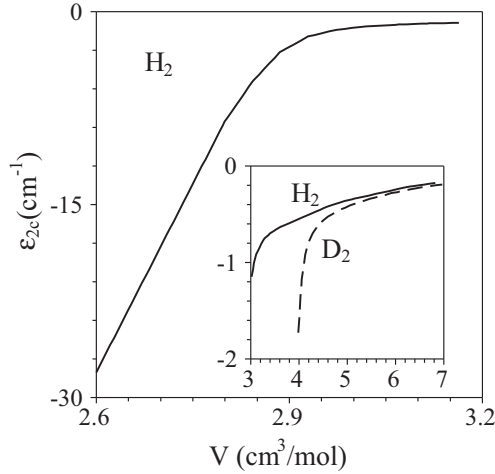


FIG. 2. Crystal-field parameter ϵ_{2c} p -H₂ and o -D₂ (inset) as functions of molar volume.

the isotropic forces there is a small contribution from the anisotropic interactions. It is this part of the intermolecular potential that is responsible for the increasing difference between the curves for hydrogen and helium as the I-II transition region is approached.

Given the estimates of the pressure dependence of δ , we can constrain the pressure dependence of the second-harmonic crystal-field parameter ϵ_{2c} (Fig. 2). This parameter together with the fourth-harmonic crystal-field parameter ϵ_{4c} determines the splitting of the purely rotational band $S_0(0)$ in p -H₂ and o -D₂ and splitting of the rotational levels of impurity $J = 1$ molecules in $J = 0$ solids [42]. In the absence of direct experimental data, some quantitative conclusions on the pressure behavior of the c/a ratio in the $J = 0$ solid hydrogens were obtained using effects related to the deviation of the axial ratio from the ideal value $\sqrt{8/3}$.

In solid hcp hydrogens, five of ten $J = 0 \rightarrow 2$ roton modes are Raman active. The fivefold degeneracy of these roton modes is partially lifted by crystal-field interactions [46]

$$V_c(\mathbf{\Omega}) = \epsilon_{2c} \sqrt{\frac{4\pi}{5}} Y_{20}(\mathbf{\Omega}) + \epsilon_{4c} \sqrt{\frac{4\pi}{9}} Y_{40}(\mathbf{\Omega}), \quad (19)$$

where $\mathbf{\Omega}$ is the orientation of a central molecule relative to a frame with the z axis along the c axis of the crystal. As a result, the rotors are observed in the Raman spectrum as three spectral lines with the lowest energy line of E_{1g} symmetry and corresponding to $m_J = \pm 1$, the middle one of E_{2g} symmetry corresponding to $m_J = \pm 2$, and the upper line of A_{1g} symmetry corresponding to $m_J = 0$ with energies $E(2,0)$, $E(2,\pm 2)$, and $E(2,\pm 1)$, respectively. Taking into account the quadrupolar contribution with the characteristic constant ϵ_4^{02} [26,46,47] for the two Raman splittings $\Delta_1 = E(2,0) - E(2,\pm 2)$ and $\Delta_2 = E(2,\pm 2) - E(2,\pm 1)$ we have

$$\begin{aligned} \Delta_1 &= \frac{4}{7}\epsilon_{2c} + \frac{5}{21}\epsilon_{4c} + \frac{35}{6}\epsilon_4^{02}, \\ \Delta_2 &= -\frac{3}{7}\epsilon_{2c} + \frac{5}{21}\epsilon_{4c} + \frac{35}{6}\epsilon_4^{02}, \end{aligned} \quad (20)$$

$$\Delta_1 - \Delta_2 = \epsilon_{2c}. \quad (21)$$

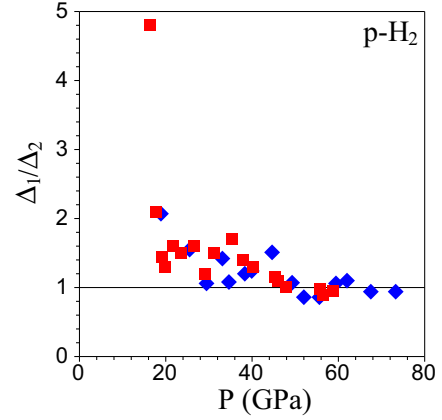


FIG. 3. (Color online) Ratio Δ_1/Δ_2 of the roton Raman splittings as a function of pressure. Experiment: red squares [47] and blue diamonds [26]. Solid straight line: Corresponds to equidistant splitting ($\Delta_1/\Delta_2 = 1$).

As follows from Eqs. (20) both fourth-harmonic components would produce the equidistant splittings $\Delta_1 = \Delta_2$, whereas the second-harmonic crystal field would result in a highly nonequidistant splittings $|\Delta_1|/|\Delta_2| = 4/3$.

We now compare these theoretical results with experiment. Wijngaard and Silvera [48], Wijngaard [47], and Goncharov *et al.* [26] reported Raman studies of roton spectra p -H₂ at low temperatures at pressures up to the I-II phase transition from which we estimated the crystal-field parameter ϵ_{2c} and lattice distortion parameter δ . From these experiments it is seen that at 20 GPa $\Delta_1/\Delta_2 \simeq 2$. There are two effects which lead to such strong deviation from the equidistance: First, the phonon-roton coupling of the E_{2g} phonon and the roton line $E(2,\pm 2)$ [45], and second, the anharmonic shifts of the roton lines $E(2,0)$, $E(2,\pm 2)$, and $E(2,\pm 1)$. The lowest frequency line $E(2,\pm 1)$ has the strongest anharmonic shift. Both effects markedly decrease with pressure. As a result, with increasing pressure the ratio Δ_1/Δ_2 decreases and approaches unity (Fig. 3). The equidistance may be considered as a signature of a smallness of both phonon-roton coupling and anharmonic effects if Eqs. (20) and (21) hold. Applying Eq. (21) to the experimental splitting of the roton triplet band $S_0(0)$ [26,47] it was estimated [26,41] that $|\epsilon_{2c}| \approx 1 \text{ cm}^{-1}$ [Fig. 4(a)]; thus $|\delta| \approx 10^{-3} - 10^{-4}$ [Fig. 4(b)] is in accord with our theoretical results (Figs. 1 and 2).

The characteristics of the rotational motion of molecules in p -H₂ and o -D₂ can be compared with those obtained with the results of density functional theory (DFT) with a path-integral molecular dynamics (PIMD) [49]. For the latter, the authors used the orientational order parameter $\eta = [N^{-1} \sum_i^N \sqrt{4\pi/5} Y_{20}(\mathbf{\Omega}_i \cdot \mathbf{u}_i)]^2$, where $\mathbf{\Omega}_i$ is a unit vector specifying the equilibrium orientation of the molecule at site i , and \mathbf{u}_i is a site-specific unit vector which defines the orientational structure), which excludes negative values of the order parameter. Nonetheless, the pressure evolutions of the order parameters in the both approaches are similar.

III. LATTICE DISTORTION IN n -H₂

We now turn to n -H₂. For a single $J = 1$ molecule in the lattice of $J = 0$ molecules there is an additional contribution

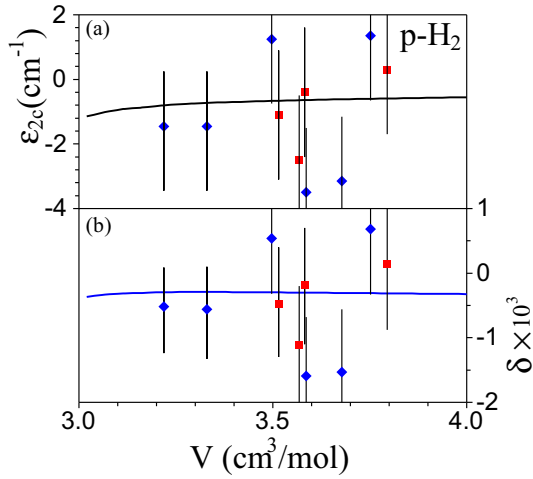


FIG. 4. (Color online) (a) Crystal-field parameter ϵ_{2c} and (b) lattice distortion parameter δ for p -H₂ as functions of molar volume. In (a) and (b) the solid lines are the theoretical results from this work. The experimental data are from Refs. [47] (red squares) and [26] (blue diamonds.) Error bars correspond to an uncertainty in the $S_0(0)$ roton lines of $\pm 1 \text{ cm}^{-1}$.

to the ground-state energy arising from the polarization of the surrounding $J = 0$ molecules by the electric quadrupole field of the $J = 1$ molecule. The polarization energy due to the interaction of quadrupole moments of the $J = 1$ molecule with the induced dipole moments of the surrounding nearest neighboring $J = 0$ molecules is equal to

$$\epsilon_1 = -18\alpha Q^2 V^{-8/3}, \quad (22)$$

where α is the polarizability of the $J = 0$ molecules and Q is the quadrupole moment of the $J = 1$ molecule [42].

If the crystal shows a homogeneous deviation from the ideal hcp structure specified by the lattice distortion parameter δ , the polarization energy contains a crystal-field term [42]

$$V_c = \epsilon_{2c} \sqrt{\frac{4\pi}{5}} Y_{20}(\mathbf{\Omega}), \quad (23)$$

where $\mathbf{\Omega}$ specifies the orientation of the $J = 1$ molecule with

$$\epsilon_{2c} = -\frac{24}{7}\epsilon_1\delta. \quad (24)$$

The triplet $J = 1$ level is split in the crystal-field V_c , and this splitting is given by

$$\Delta_c = E(\pm 1) - E(0) = \frac{3}{5}|\epsilon_{2c}|, \quad (25)$$

where $E(M)$ is the energy of the state $J = 1$, $J_z = M$ with z direction parallel to the c axis of the crystal. The positive sign of Δ_c implies that $J_z = 0$ is the ground state of the triplet. Due to this splitting the ground-state energy is brought down by $2|\epsilon_{2c}|/5$. The gain in the anisotropic energy due to polarization in the $J = 0/J = 1$ mixture is linear in δ , in contrast to the contribution quadratic in δ in J -even solids. At the same time, this distortion introduces an additional positive contribution to the ground-state energy from the isotropic part of the intermolecular interaction. This contribution is quadratic in the lattice distortion parameter δ [41]. The loss and gain in the isotropic and anisotropic parts of the ground-state

energy, respectively, determine the lattice distortion at a given molar volume. One cannot obtain a reliable value of δ from Eqs. (22)–(25) because of other contributions to the splitting Δ_c not included in Eq. (25) [42]. Moreover, the structure of n -H₂ in phase I is that of a disordered mixture of ortho and para molecules.

To calculate the polarization energy for such a structure we used a mean-field model of an ortho-para mixture assuming each site of the lattice is occupied by a superposition of even- J and odd- J molecules and every ortho-molecule component induces a crystal-field splitting. Assuming a volume dependence of the polarization energy of the same form in Eq. (22), we included into the ground-state energy a term

$$E_{\text{pol}} = A(V_0/V)^{8/3}\delta, \quad (26)$$

where A is an adjustable parameter in the theory. In the x-ray data, the effects of residual uniaxial stresses on oriented single crystals of n -H₂ cannot be completely separated from the effects of pure hydrostatic compression. We show the dependence of δ on the parameter A . As can be seen, the resulting $\delta(P)$ dependencies are nonlinear with an inflection point where the curvature changes its sign. Despite the scatter in experimental points this trend is clearly seen in experiment. Assuming no uniaxial effects, we obtain a good fit for $A = 5.1 \text{ K}$. The resulting pressure dependence of the lattice distortion parameter is presented in Fig. 5. The comparison to p -H₂ shows that the introduction of the $J = 1$ molecules increases the hcp lattice distortion by two orders of magnitude (see Fig. 1).

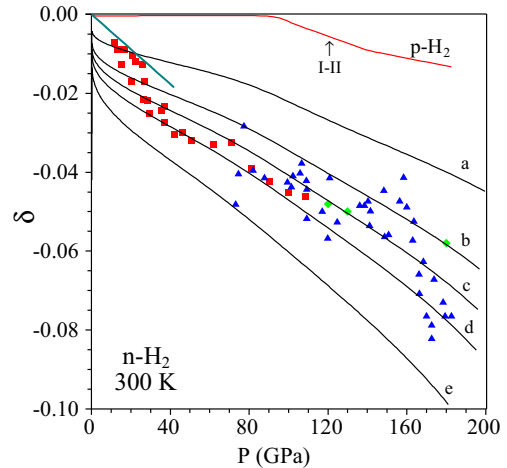


FIG. 5. (Color online) Lattice distortion parameter for n -H₂. Curves a–e correspond to present theory with $A = 2.55, 4.25, 5.1, 6.0,$ and 7.85 K , respectively. The red line data for p -H₂ correspond to that shown in Fig. 1. The arrow shows the experimental I–II transition pressure for p -H₂ [26,43]. Experiment: Data are from Refs. [23] (red squares) and [25] (blue triangles). The solid straight line $\delta = -4.41 \times 10^{-3} P$ [17,18]. The green diamonds are the results of first-principles PIMD simulations [32].

IV. CONCLUDING REMARKS

We have developed the lattice-dynamics theory of the lattice distortion in p -H₂, o -D₂, and n -H in the hexagonal closed-packed structure under pressure. It is shown that the lattice distortion in p -H₂ and o -D₂ is negative and very small (of the order of 10^{-3}) and their structures have axial ratios very close to ideal. In this respect, the even- J modifications of hydrogens behave very similarly to solid He. The main contributions to the lattice distortion come from translational degrees of freedom, although there is a nonzero contribution from rotation as well that give rise to slightly flattening of the structure (negative distortion parameter). The calculated orientational order parameter was shown to be small and negative. In a classical sense, the results indicate that the molecules rotate around the c axis with an inclination angle $\vartheta \approx 55^\circ$.

Finally, we note that the extent to which the decline in c/a above 160 GPa reported experimentally in Ref. [25] is related to a possible weak transition in phase I (transition to I'), such as that found in vibron data [50], remains to be investigated experimentally.

The mean-field model developed for ortho-para mixtures provides a determination of the polarization energy connected with the impurity ortho molecules. It is shown that there is a considerable gain in the ground-state energy of the mixture due to polarization, which in turn enhances the lattice distortion. The corresponding loss in the energy of the isotropic interaction determines the resulting value of the lattice distortion parameter. The calculated c/a ratio as a function of hydrostatic pressure is compatible with available x-ray diffraction data, though the effects of uniaxial stresses on the reported axial ratio as well as possible distortions from hcp remains to be determined experimentally.

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