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Effects of rotational states on the c/a ratio in solid hydrogens

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We propose an approach to the problem of lattice distortions at low temperatures and ambient pressure in the solid hydrogens in their rotational ground states that explicitly accounts for the molecular nature of the constituent particles. The model is based on the idea that the second-order rotation-related correction to the ground-state energy depends on the lattice parameters. The calculated ground-state rotation-related contributions, $\delta_{gs} = c/a - (8/3)^{1/2}$, are negative for all species, amounting to about -1.5×10^{-5} for H_2 and D_2, whereas for HD this contribution is about -0.6×10^{-3}, which is roughly 50 times larger. This substantial difference stems from the fact that the rotational dynamics in the homonuclear solids and in HD differ appreciably. The approach can be generalized to high pressures.

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I. INTRODUCTION

It is well known that spherical particles such as rare gas atoms [1] or hydrogen isotopomer molecules [2] crystallize at zero pressure into close-packed lattices (hcp or fcc) with the lattice parameter ratio c/a equal to $\sqrt{8/3}$ (fcc) or close to that (hcp). What drives the crystallization to one of those two close-packed lattices has been extensively discussed. The deviation

$$\delta \equiv c/a - \sqrt{8/3} \tag{1}$$

is one of the indicators of the interplay between the interactions that shape the crystal structure. An important consideration for predicting the value of δ is the magnitude of many-body forces [3,4], which becomes more important for high pressures. The magnitude and sign of δ are also controlled by rotational states, pressure, and temperature. In this regard, we note that many measurements as a function of density have been carried out at 300 K and the temperature substantially changes the distribution over rotational states. The changes in the rotational dynamics of the solid hydrogens at 300 K and high pressures have been treated within a phenomenological model by Freiman *et al.* [5]. The lattice structure of both H_2 and D_2 depends also essentially on the ortho-para content. Samples rich (60% or more) in $J = 1$ species crystallize into fcc structures. At high $J = 0$ fractions both homonuclear hydrogens form hcp lattices. Direct structure measurements in the homonuclear hydrogen solids [6,7] showed that the typical experimental values of δ are negative and of order 10^{-3}.

The solid heteronuclear hydrogens show a wealth of unusual properties as compared to the homonuclear species. Although structure data for HD crystals are scarce, THEED measurements [8] documented un unusual morphology of the HD deposits grown at liquid He temperatures: the structure was mainly cubic with two extra features, both of which could be explained as being due to diffraction on twin boundaries or/and stacking faults. It is only upon warming that the spectrum underwent a sharp transformation to hcp. The c/a ratio was found to be 1.634 ± 0.009. Subsequently, structure data obtained using x-ray diffraction [9] gave an unexpected result: $c/a = 1.618 \pm 0.003$. Moreover, whereas in both normal and para H_2 the c/a ratio slightly decreased [9] upon warming, the c/a ratio in HD grew with temperature, reaching the value 1.623 ± 0.005 at 17 K. The crude numerical evaluations of c/a based on non-renormalized values of the specific interactions between HD molecules gave values of the same order of magnitude as found in the above-mentioned experiment [9]. Now that the renormalized values and procedures are available [10], the respective theory can be developed more accurately.

The principal aim of the present paper is to understand how differences in the rotational dynamics affect the value of δ at low temperatures. Our approach is based on the following equation:

$$\frac{\partial}{\partial \delta}[\Delta E_{el}(\delta) + \Delta E_{rot}(\delta)] = 0, \tag{2}$$

where ΔE_{el} and ΔE_{rot} are the densities of the elastic and ground-state rotational energies, respectively, as functions of the deviation δ defined in Eq. (1). Even in the rotational ground state with all molecules occupying their $J = 0$ levels the rotational energy emerges due to a quantum self-polarization calculated in the second perturbation order in the anisotropic interactions which involve the relevant angular variables of the participating molecules. Since the elastic energy in Eq. (2) is proportional to δ^2, one needs to look for mechanisms that can produce a contribution linear in δ, in order that Eq. (2) could lead to a nonzero deviation δ.

We suggest that for the solid hydrogens the deviation δ should be evaluated by taking explicitly into account the molecular nature of the particles which constitute those crystals. Since the rotational dynamics differ essentially between homonuclear and heteronuclear hydrogen solids, one can expect that the deviations δ in such crystals will be different.

This article is structured as follows. Sections II and III enumerate the anisotropic interactions that affect the c/a ratio as well as the perturbation energies used in subsequent calculations. Section IV describes the variations of the elastic energy due to lattice parameter deviations from the ideal values. The deviation of the lattice parameter ratio owing to the ground-state rotational energy, δ_{gs}, calculated for the three hydrogen species considered, H_2, D_2, and HD, is discussed in Sec. V. Section VI sums up the results and discusses possible consequences for the theory including effects at high pressures and high temperatures. Appendices contain further technical details about the calculations.

II. INTERACTIONS

The anisotropic interactions operating between the isotopes of hydrogen in the corresponding solids include the electrical quadrupole-quadrupole (EQQ) interaction as well as the rank-2 crystal field contribution [11], which can be represented as shown below.

From the complete Hamiltonian of the rank-2 crystal field we leave the part in which only the central (chosen) molecule with subscript 0 is supposed to be excited:

$$V_{\mathrm{cf2}} = \sum_i B_2(R_i)(\mathbf{C}_2(\mathbf{w}_0) \cdot \mathbf{C}_2(\mathbf{n}_i)). \tag{3}$$

Here i runs over the nearest neighbors; $\mathbf{R}_i \equiv R_i \mathbf{n}_i$; $\mathbf{C}_N(\mathbf{a})$ is the rank-N spherical harmonic of unit vector $\mathbf{a}$ in Racah's representation; $B_2(R)$ is the well-known [2,11] crystal field energy parameter; the big parenthesizes mean scalar product of spherical harmonics [12]. It should be also noted that there is another interaction, which is the rank-4 analog [11,13] of the rank-2 crystal field energy in Eq. (3). Unlike V_{cf2}, it does contribute to the rotational energy term that can influence the c/a ratio but, presumably, the corresponding effect is appreciable only at higher pressures [13].

The EQQ interaction, which inevitably produces excitation of *both* interacting molecules, can be represented in the form

$$V_{\mathrm{EQQ}} = \sum_i \theta(R_i)(\{\mathbf{C}_2(\mathbf{w}_0) \otimes \mathbf{C}_2(\mathbf{w}_i)\}_4 \cdot \mathbf{C}_4(\mathbf{n}_i)), \tag{4}$$

where we use the standard definitions for direct products of irreducible tensors:

$$\{\mathbf{C}_K(\mathbf{a}) \otimes \mathbf{C}_L(\mathbf{b})\}_{M\mu} \equiv \sum_{kl} C^{M\mu}_{Kk,\ Ll} C_{Kk}(\mathbf{a}) C_{Ll}(\mathbf{b});$$

$C^{Mm}_{Kk,Ll}$ are the Clebsch-Gordan coefficients; $\mathbf{a}$ and $\mathbf{b}$ are unit vectors. The EQQ energy function $\theta(R)$ can be represented in the form

$$\theta(R) = \tfrac{5}{6}\,\Gamma\,(R_0/R)^5, \tag{5}$$

where R_0 is the unperturbed nn distance and Γ is the EQQ interaction parameter. This general definition needs clarification. Most commonly, the parameter Γ is known as representing the electric quadrupole-quadrupole interaction between two $J = 1$ rotational states in the homonuclear solids, in which case the respective parameter is defined as [11]

$$\Gamma_{11} = \frac{6}{25\ R_0^5}\langle 1|Q_2|1\rangle^2, \tag{6}$$

where $\langle 1|Q_2|1\rangle$ is the matrix element of the electrical quadrupole moment Q_2 between $J = 1$ states of two neighbor molecules. In our calculations we will need the matrix element $\Gamma_{02} = \langle 0|Q_2|2\rangle$ between the $J = 0$ rotational ground state and the $J = 2$ excited state. As it can be seen from Table I, for all species to be considered all matrix elements differ between themselves insignificantly.

The effective parameters Γ, as renormalized to account for various quantum crystal corrections [16,17] and determined from experiment, amount to 0.9 ± 0.1 K for H_2 and 0.93 ± 0.5 K for D_2 [11]. Knowing the nn intermolecular distance in HD 3.701 Å [9], we calculate Γ_{11} in HD to be 0.916 K.

TABLE I. Matrix elements of the quadrupole moment of hydrogen molecules.

	$\langle 1\|Q_2\|1\rangle$	$\langle 0\|Q_2\|2\rangle$	Ratio	
H_2	0.48468	0.48516	0.99901	Ref. [14]
HD	0.48148	0.48185	0.99923	Ref. [15]
D_2	0.47702	0.47728	0.99946	Ref. [15]

In the heteronuclear solid hydrogens there are two other interactions; their origin [10,11] stems from the fact that the center of mass in these molecules is shifted respective to the charge distribution center by s, which in the HD molecules amounts to one-sixth of the internuclear distance $r_e = 0.74116$ Å. One of these specific interactions is the rank-1 crystal field energy, which referred to the central molecule can be represented as [11]

$$V_{\mathrm{cf1}} = \sum_i s\ dv(R)/dR(\mathbf{C}_1(\mathbf{w}_0) \cdot \mathbf{C}_1(\mathbf{n}_i)), \tag{7}$$

where $v(R)$ is the central (isotropic) part of the interaction potential.

The other specific interaction between HD molecules, also existing owing to nonzero s, can be written as

$$V_{11} = \sum_{N=0,\ 2} \gamma_N(R)(\{\mathbf{C}_1(\mathbf{w}_1) \otimes \mathbf{C}_1(\mathbf{w}_2)\}_N \cdot \mathbf{C}_N(\mathbf{n})). \tag{8}$$

Both $\gamma_0(R)$ and $\gamma_2(R)$ comprise two contributions [10,11]; the relevant renormalized values for the average equilibrium nn intermolecular distance can be found in Ref. [10].

III. ROTATIONAL ENERGIES

We first consider the contribution to the zero-point energies due to the rank-2 crystal field of Eq. (3). The second-order correction to the energy of the rotational ground state $|00\rangle$ per molecule owing to rank-2 crystal field interactions can be evaluated in the perturbative way [18], taking into account that only the central molecule gets virtually excited:

$$E^{(cf2)}_{\mathrm{rot}} = -\sum_\mu \frac{|\langle 00(0)|\ V_{cf2}\ |2\mu(0)\rangle|^2}{6B_0}. \tag{9}$$

Here and below $|N\mu(m)\rangle$ is the rotational state with $J = N$, $J_z = \mu$ of a molecule at site m, with $m = 0$ denoting the central molecule and m from 1 to 12 denoting the nearest neighbors; B_0 is the rotational constant of the respective molecular species, and $6B_0$ is the excitation energy of the $J = 2$ level.

Directing the reader for the technical details to Appendix A, the rotational energy under consideration is

$$E^{(cf2)}_{\mathrm{rot}} = -\frac{1}{30B_0}\left|\sum_{i,\mu} B_2(R_i) C_{2\mu}(\mathbf{n}_i)\right|^2. \tag{10}$$

It is a well-known fact (cf. Van Kranendonk [11]) that the sum appearing in Eq. (10) nullifies for an ideal hcp lattice with $c/a = (8/3)^{1/2}$. Therefore, its variation due to the crystal field interactions will be linear in the deviation δ; hence, $E_{\mathrm{rot}}^{(cf2)}$ will be proportional to δ^2. As argued in Sec. I, this conclusion renders this interaction inappropriate for our aims. The rank-1 crystal field in Eq. (7) helps as little and has to be discarded too.

Now we consider the interactions in which two molecules are simultaneously excited. The EQQ interaction has the same form as in Eq. (4) for all hydrogen crystals. The rotational energy caused by the EQQ interactions is

$$E_{\mathrm{rot}}^{(\mathrm{EQQ})} = -\sum_{j\mu\nu} \frac{|\langle 00(j)\ 00(0)|\ V_{\mathrm{EQQ}}\ |2\mu(0)2\nu(j)\rangle|^2}{24B_0},$$

where V_{EQQ} as in Eq. (4) accounts for transitions from the ground states 00 of both the central molecule, which is labeled (0), and (one by one) all its nearest neighbors, labeled with j running from 1 to 12, to, respectively, 2μ and 2ν states. The denominator is the total excitation energy of two molecules ($2 \times 6\omega_0$), while the extra factor 2 accounts for the fact that the sought-for rotational energy is per molecule rather than per pair. Details of the relevant calculations can be found in Appendix B, so that the final expression for the EQQ-related rotational energy is

$$E_{\mathrm{rot}}^{(\mathrm{EQQ})} = -\frac{1}{120B_0}\sum_j [\theta(R_j)]^2. \tag{11}$$

For $\theta(R_j)$ see Eq. (5) and the ensuing discussion.

Without proceeding further with detailed calculations for the specific interaction, Eq. (8), which can be found in Appendix C, we sum up that the two contributions due to V_{11} with $N = 0$ and $N = 2$ "split" (that is, the cross-term vanishes) in the final expression. Thus, the specific interactions produce another two contributions to the rotational energy:

$$E_{\mathrm{rot}}^{(\mathrm{sp0})} = -\frac{1}{24B_0}\sum_j \gamma_0^2, \tag{12}$$

$$E_{\mathrm{rot}}^{(\mathrm{sp2})} = -\frac{1}{24B_0}\sum_j \gamma_2^2. \tag{13}$$

IV. ELASTIC ENERGY

The density of elastic energy per unit volume is

$$W_{\mathrm{el}} = (1/2)\sigma_{ij}\varepsilon_{ij}, \tag{14}$$

where summation runs over Cartesian indices i and j, ε_{ij} is the deformation tensor, and σ_{ij} is the tensor of elastic stresses. Within the elastic theory, σ_{ij} is a linear function of ε_{ij}; the proportionality elements constitute the tensor of elastic moduli, c_{ij}. The deformation tensor is defined as

$$\varepsilon_{ij} = \frac{1}{2}\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_m \frac{\partial u_m}{\partial x_i}\frac{\partial u_m}{\partial x_j}\right]. \tag{15}$$

Any of the hexagonal crystals considered here is deformed uniformly but isotropically only within the basal plane. For this type of deformation the following derivatives will be nonzero: $\partial u_x/\partial x = \partial u_y/\partial y = \Delta a/a_0$ and $\partial u_z/\partial z = \Delta c/c_0$, where a_0 and c_0 are the "ideal" hexagonal lattice parameters (with their ratio being equal to $\sqrt{8/3}$) while Δa and Δc are their variations due to the virtual rotational excitation. Unlike in the case with sound, when displacements in the sonic wave are oriented arbitrarily, the deformation in our case is uniform. As a result, the cross-terms in the deformation tensor (like ε_{xz}) are zero and only the following elements are involved [19]: c_{11}, c_{12}, c_{13}, c_{33}. Thus, we obtain that

$$\sigma_{xx} = \sigma_{yy} = (c_{11} + c_{12}) \times \Delta a/a_0 + c_{13}\Delta c/c_0, \tag{16}$$

$$\sigma_{xx} = 2c_{13}\Delta a/a_0 + c_{33}\Delta c/c_0. \tag{17}$$

Finally, the corresponding density of elastic energy ΔE_{el} takes the form

$$\Delta E_{\mathrm{el}} = (c_{11} + c_{12})\left(\frac{\Delta a}{a_0}\right)^2 + 2c_{13}\frac{\Delta a}{a_0}\frac{\Delta c}{c_0} + \frac{c_{33}}{2}\left(\frac{\Delta c}{c_0}\right)^2. \tag{18}$$

The elastic moduli in the homonuclear hydrogen crystals at low pressures have been determined using various techniques and at different temperatures from 4 to 13 K for solid hydrogen [20–22] and deuterium [20]. The scatter of values is quite broad, especially for c_{13}. A complete model for the elastic moduli in H_2 and D_2 was developed by Goldman first for zero pressure [23] and subsequently [24] as functions of pressure (or molar volume). Zha *et al.* [25] directly measured the elastic moduli in H_2 at pressures up to 23.6 GPa at room temperature and at normal ortho-para (3:1) content. Notwithstanding the fact that many molecular and crystal parameters for solid HD are known [26], in our numerical evaluations for HD we rely on the average of c_{ij} for hydrogen and deuterium. The high-pressure behavior will be discussed in more detail in a subsequent paper.

V. LATTICE PARAMETER RATIO

Prior to substituting ΔE_{rot} into Eq. (2) we must account for the fact that, by definition, the elastic energy is normalized to unit volume whereas the rotational energy was calculated per molecule. Therefore, to obtain the correct dimension of ΔE_{rot} we divide it by the volume per molecule $v_0 = V_M/N_{\mathrm{Av}}$ where V_M is the molar volume and N_{Av} is the Avogadro number. Thus, the rotational energy with account of Eqs. (11)–(13) will be

$$E_{\mathrm{rot}} = -\frac{1}{120B_0v_0}\sum_j \left[\theta^2 + 5\gamma_0^2 + 5\gamma_2^2\right], \tag{19}$$

where all terms are known functions of the twelve nearest neighbor distances. Likewise, the corresponding variation of the rotational energy with account of the deformation to be found is

$$\Delta E_{\mathrm{rot}} = -\frac{1}{60B_0v_0}\sum_j [\theta\Delta\theta + 5\gamma_0\Delta\gamma_0 + 5\gamma_2\Delta\gamma_2]. \tag{20}$$

The fact of importance with regard to this formula is that all the functions involved are such that the signs of their derivatives are opposite to those of the functions themselves, which means that the total sign of ΔE_{rot} is definitely positive.

We calculate how the relative deformations $\Delta a/a_0$ and $\Delta c/c_0$ change the total rotational energy. Since the summation in Eq. (20) runs over nn neighbors of the central molecule, we need to define the shifts of their *distances* to the central molecule. Obviously, the shift within the same plane is purely radial and equal to Δa. It can be easily shown that the molecules in the next plane, for instance, above the reference plane, shift by $\Delta c/2$ along the z axis and by $\Delta a/\sqrt{3}$ in the radial direction. Now it is easy to calculate, for example, the sum $\sum_i \theta(R_i)\Delta\theta(R_i)$. Within our perturbation procedure all R_i in the expression $\theta(R_i)$ are the same and equal to a_0. Any of the six in-plane variations is $\Delta\theta_{\text{in}}(R_i) = \partial\theta(R)/\partial R \times \partial R/\partial x \times \Delta a = (\partial\theta/\partial R) \times \Delta a$. Similarly, the corresponding expressions for any of the six out-of-plane neighbors can be calculated as

$$\Delta\theta_{\text{out}}(R_i) = \frac{\partial\theta(R)}{\partial R}\left[\frac{\Delta c}{\sqrt{6}} + \frac{\Delta a}{3}\right]. \tag{21}$$

Finally, Eq. (20) takes the form

$$\Delta E_{\text{rot}} = -\frac{1}{10B_0 v_0}\left[\frac{4\Delta a}{3} + \frac{\Delta c}{\sqrt{6}}\right] \times S(R), \tag{22}$$

where

$$S(R) \equiv \theta\frac{d\theta}{dR} + 5\gamma_0\frac{d\gamma_0}{dR} + 5\gamma_2\frac{d\gamma_2}{dR}. \tag{23}$$

We note here that only the first term applies for H_2 and D_2 whereas all the three terms “work” for HD.

Now we will return to Eq. (2) with the remark that actually we have two independent variables Δa and Δc which are to be found by equating to zero the two respective derivatives of the sum of Eqs. (18) and (22), which leads to two equations

$$2(c_{11} + c_{12})\frac{\Delta a}{a^2} + 2c_{13}\frac{\Delta c}{ac} = \frac{4S(R)}{30B_0 v_0}, \tag{24}$$

$$2c_{13}\frac{\Delta a}{ac} + c_{33}\frac{\Delta c}{c^2} = \frac{4S(R)}{10B_0 v_0\sqrt{6}}. \tag{25}$$

The solution to this set of equations can be cast as

$$\Delta a = \frac{A_2 ac(c_{33}/2 - c_{13})}{c_{33}(c_{11} + c_{12}) - 2c_{13}^2}, \tag{26}$$

$$\Delta c = \frac{8A_2 a^2}{3c_{13}} \times \frac{(c_{11} + c_{12})(c_{13} + c_{33}/2) - 2c_{13}^2}{c_{33}(c_{11} + c_{12}) - 2c_{13}^2} \tag{27}$$

with

$$A_2 = \frac{4S(R)}{10B_0 v_0\sqrt{6}}. \tag{28}$$

Here we note that Δa and Δc have the same sign. The lattice constant ratio deviation, as defined in Eq. (1) and expressed through Δa and Δc, has the form $\delta = \sqrt{8/3}(\Delta c/c_0 - \Delta a/a_0)$, which yields

$$\delta_{\text{gs}} = \frac{cS(R_0)}{15B_0 v_0 c_{13}} \times D \tag{29}$$

with

$$D = \frac{(c_{11} + c_{12})(c_{13} + c_{33}/2) - c_{13}(c_{33}/2 - c_{13})}{c_{33}(c_{11} + c_{12}) - 2c_{13}^2}. \tag{30}$$

Note that the denominator in Eq. (29) contains c_{13}, the smallest of the elastic moduli. In addition, the expression D is convenient for the reason that if c_{ij} are scaled to the same exponential function of the molar volume V, then D will be independent of V. As our subsequent evaluation showed, D varies with molar volume by far less as compared with any of c_{ij} and the nn distance R_0.

TABLE II. Chosen parameters for the solid hydrogens at low temperatures and low pressures.

	p-H_2	HD	o-D_2
nn distance R_0, cm^{-1}	3.783	3.701	3.618
Molar volume $v_0 \times 10^{23}$, cm^3	3.829	3.584	3.350
EQQ constant $\Gamma(R_0)$, cm^{-1}	0.626	0.637	0.646
Rank-0 energy $\gamma_0(R_0)$, cm^{-1}	N/A	0.161	N/A
Rank-2 energy $\gamma_2(R_0)$, cm^{-1}	N/A	− 0.472	N/A
Rotational constant B_0, cm^{-1}	59.339	44.667	29.913
c_{11}, kbar	4.14	5.51	6.88
c_{12}, kbar	0.95	1.42	1.88
c_{33}, kbar	4.51	6.00	7.50
c_{13}, kbar	0.57	0.91	1.25

Prior to numeric evaluations we make a few notes. First, we recall that when dealing with the homonuclear species one needs to take into account only the first (EQQ) term in Eq. (23) whereas in calculations for HD all terms “work.” Second, as stated above, in our evaluations we use the zero-temperature elastic moduli as calculated by Goldman [23] and shown in Table II. For lack of anything better, the c_{ij} values for HD were taken to be an average of the respective data for the homonuclear solids. To get insight, we evaluate the dimensionless quantity D in Eq. (30) to be 0.602 for H_2, 0.650 for D_2, and 0.631 for HD. The first term of $S(R)$ in Eq. (23), with account of Eq. (5), can be written as $\partial\theta/\partial R = -5\theta(R_0)/R_0$.

Final calculations yield $\delta_{\text{gs}} = -1.39 \times 10^{-5}$ for hydrogen and $\delta_{\text{gs}} = -1.65 \times 10^{-5}$ for deuterium. The EQQ-related contribution to δ_{gs} in solid HD is of the same order of magnitude (-1.34×10^{-5}) but there are two extra terms to be taken into account. Let us consider one of them, for instance, the rank-0 one. This contribution is proportional to the second term on the right-hand side of Eq. (23), which involves both $\gamma_0(R_0)$ and $d\gamma_0(R)/dR$. The values [10] of $\gamma_0(R_0)$ and $\gamma_2(R_0)$ are shown in Table II. The values of both $d\gamma_0(R)/dR$ and $d\gamma_2(R)/dR$ without quantum-mechanical renormalization can be easily obtained numerically by using the known expressions [10]. A more difficult task is to evaluate renormalization factors for the quantities under discussion $d\gamma_0(R)/dR$ and $d\gamma_2(R)/dR$. Both of these quantities comprise two contributions [10], one of which comes from the direct isotropic interaction and the other, from the rank-2 crystal field energy in Eq. (3). Luckily, the respective renormalization parameters are known [10] for all four constituent contributions of both above-mentioned energies, which allows us to implement a simplified, albeit less accurate but resulting only in slight underestimates, procedure explained below.

Let us take, for example, the rank-0 specific interaction energy

$$\gamma_0(R) = \gamma_0^{(\text{V})}(R) + \gamma_0^{(\text{B})}(R). \tag{31}$$

Knowing the renormalization factors for each of the two terms, we ascribe them to the corresponding derivatives in the sum for $d\gamma_0(R)/dR$. This procedure is based on the following reasoning. All four γ contributions involved are rather steep functions of R, which increase fast with decreasing R, such as the EQQ energy $\propto R^{-5}$. Renormalization is carried out by integrating this function with a bell-shaped wave function, which symbolizes quantum mechanical spread. It can be easily shown that the renormalization factor that emerges for the *derivative* is even slightly (by a few percent) smaller than for the *function* itself. Concluding our reasoning, the known renormalization factors for the respective functions we ascribe to be the renormalization factors of the respective derivatives of the four γ's involved. Finally, we obtain the following renormalized values: $\gamma_0 = 0.161\ \text{cm}^{-1}$ and $\gamma_2 = -0.472\ \text{cm}^{-1}$ (as in Ref. [10]) and $\gamma_0' = -0.960\ \text{cm}^{-1}/\text{Å}$ and $\gamma_2' = 6.809\ \text{cm}^{-1}/\text{Å}$.

Summing up the three terms in Eq. (23) we calculate that the lattice parameter ratio deviation δ for HD actually at zero temperature is -0.609×10^{-3}. We estimate the uncertainty in δ_{gs}, as defined in Eqs. (29) and (30), making use of the available experimental errors. We found that the largest contribution to the net uncertainty comes from errors in the elastic moduli in the expression for D/c_{13} in Eq. (30). Therefore, the final estimate for δ_{gs} in solid HD is

$$\delta_{\text{gs}}(\text{HD}) = -(0.61 \pm 0.08) \times 10^{-3}. \qquad (32)$$

Note that δ_{gs} is also negative and approximately 50 times larger in magnitude than in H_2 or D_2. Nonetheless, the above value is by a factor of approximately 20 smaller compared with what was determined experimentally [9] but the trend is more than meaningful.

VI. DISCUSSION

We suggest a theoretical approach to the problem of the deviation δ in the solid hydrogens at low temperatures and low pressures due to a specific reason, which explicitly accounts for the fact that the constituent particles are molecules with different rotation dynamics. The deviations δ_{gs} appear as a reaction of the lattice to virtual excitation to higher rotational states. These mechanisms differ substantially between homonuclear (H_2 and D_2) and heteronuclear (HD) species. It is also evident that other contributions to δ, for example, due to three-body interactions, are to be simply added to obtain the total value.

Evaluations at zero pressure yield negative δ_{gs} values, the absolute values of δ_{gs} in HD being substantially greater (by a factor of 50) compared to the homonuclear hydrogen solids. This difference is owing to the fact that additional specific interactions exist between HD molecules compared to their homonuclear counterparts. However, the calculated δ_{gs} in HD is still approximately 20 times smaller than reported for solid HD at low temperatures [9].

This paper focuses on how differences in the rotational dynamics of molecules in the various hydrogen solids affect their structure at low temperatures and low pressures. The corresponding contribution should be summed up with the other ones. Our approach allows its application to the solid at reasonably high pressures (e.g., to 100 GPa) where the molecules remain intact; in other words, the intramolecular energy significantly exceeds the intermolecular interactions. But unlike low pressures, at high pressures (which frequently go together with room temperature) there are a greater number of contributions at play. In addition to high pressures (densities) and high temperatures, specific details of the rotational spectra as well as the ortho-para content play a role. The results are important for developing a more complete understanding of condensed phases of hydrogen, including its isotopic mixtures, for energy applications. For T close to zero and ambient pressure there are actually only two mechanisms that determine the c/a ratio, namely, the ground-state rotational energy discussed in this article and the three-body interactions considered by Tretyak *et al.* [27] for solid p-H_2. Unfortunately, the three-body contribution for solid HD has not yet been calculated.

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APPENDIX A: CALCULATIONS FOR RANK-2 CRYSTAL FIELD

The second-order rotational energy, $E_{\text{rot}}^{(cf2)}$ in Eq. (9), in complete form is

$$-\sum_{\mu} \frac{\left| \sum_{i,m} B_2(R_i) C_{2m}^*(\mathbf{n}_i) \langle 00|C_{2m}(\mathbf{w}_0)|2\mu\rangle \right|^2}{6B_0}.$$

Here i runs over all nearest neighbors of the central molecule. Substituting into this formula the matrix element in explicit form

$$\langle 00|C_{2m}(\mathbf{w}_0)|2\mu\rangle = \delta(m+\mu)(-1)^{\mu}/\sqrt{5}, \qquad \text{(A1)}$$

we obtain Eq. (10).

APPENDIX B: CALCULATIONS FOR EQQ INTERACTION

The second-order rotational energy due to electric quadrupole-quadrupole interaction, Eq. (9), is

$$E_{\text{rot}}^{(\text{EQQ})} = -\frac{\sum_{j\mu\nu} \left| \sum_{i,m,n} \theta(R_i) C_{4n}^*(\mathbf{n}_i) C_{2m\ 2(n-m)}^{4n} \langle 00(j)|C_{2m}(\mathbf{w}_i)|2\nu(j)\rangle \langle 00(0)|C_{2(n-m)}(\mathbf{w}_0)|2\mu(0)\rangle \right|^2}{24B_0}. \qquad \text{(B1)}$$

Applying Eq. (A1), after some simple algebra we find

$$E_{\mathrm{rot}}^{(\mathrm{EQQ})} = -\frac{\sum_{j\nu\kappa}\left|\theta(R_j)C_{4\kappa}^{*}(\mathbf{n}_j)C_{2\nu\,2(\kappa-\nu)}^{4\kappa}\right|^2}{120B_0}.$$

Making use of the normalization rule for Clebsch-Gordan coefficients

$$\sum_{\nu}\left[C_{2\nu\;2(\kappa-\nu)}^{4\kappa}\right]^2 = 1$$

as well as the unitarity rule for spherical harmonics

$$\sum_{\kappa} C_{4\kappa}^{*}(\mathbf{n}_i)C_{4\kappa}(\mathbf{n}_i) = 1,$$

we come to

$$E_{\mathrm{rot}}^{(\mathrm{EQQ})} = -\frac{1}{120B_0}\sum_j[\theta(R_j)]^2. \tag{B2}$$

APPENDIX C: CALCULATIONS FOR SPECIFIC INTERACTIONS

We start with the complete form of the rotational energy due to the specific interactions of Eq. (8),

$$E_{\mathrm{rot}}^{(\mathrm{sp})} = -\frac{1}{8B_0}\sum_{j\,\mu\,\nu}\left|\sum_{Ni}\gamma_N(R_i)M_{Ni}^{(j\mu\nu)}\right|^2, \tag{C1}$$

where $N = 0,\ 2$ and the matrix element in the internal summation can be cast as

$$M_{Ni}^{(j\mu\nu)} = \sum_{mn} C_{1m\;1(n-m)}^{Nn}\,\langle 00(0)|C_{1m}(\mathbf{w}_0)|1\mu(0)\rangle$$
$$\times\,\langle 00(j)|C_{1(n-m)}(\mathbf{w}_i)|1\nu(j)\rangle C_{Nm}^{*}(\mathbf{n}_i). \tag{C2}$$

The expressions appearing in this equation are

$$\langle 00(0)|C_{1m}(\mathbf{w}_0)|1\mu(0)\rangle = (-1)^{\mu}\delta(m+\mu)/\sqrt{3}$$

and

$$\langle 00(j)|C_{1(n-m)}(\mathbf{w}_i)|1\nu(j)\rangle = \delta_{ij}(-1)^{\nu}\delta(\nu+n-m)/\sqrt{3},$$

which yields

$$M_{Ni}^{(j\mu\nu)} = \tfrac{1}{3}\,\delta_{ij}\,C_{1\mu\;1\nu}^{N(\nu+\mu)}C_{N\,(\nu+\mu)}(\mathbf{n}_i), \tag{C3}$$

in the derivation of which we made use of the symmetry and normalization properties [12] of Clebsch-Gordan coefficients and spherical harmonics. Substitution of Eq. (C3) into Eq. (C2) after simple operations yields for $E_{\mathrm{rot}}^{(\mathrm{sp})}$

$$(24B_0)^{1/2}\sum_{j\mu\nu,N}\left|\gamma_N(R_j)\,C_{N(\nu+\mu)}(\mathbf{n}_j)\,C_{1\mu\;1\nu}^{N(\nu+\mu)}\right|^2. \tag{C4}$$

Now we analyze the cross-term in Eq. (C4), i.e., the term in which the sums with $N = 0$ and $N = 2$ appear together. It can be easily shown that this term V_{02} can be brought to the following form:

$$V_{02} = \frac{1}{24\sqrt{3}}\sum_j \gamma_0(R_j)\gamma_2(R_j)C_{2\,0}(\mathbf{n}_j)\sum_{\mu}(-1)^{\mu}C_{1\mu\;1\overline{\mu}}^{2\,0}. \tag{C5}$$

By virtue of the known general relation [12] the sum over μ is zero and, thus, the cross-term vanishes. Therefore, Eq. (C4) becomes a sum of two terms, respectively with $N = 0$ and $N = 2$. The calculations with both are straightforward and similar to those in Appendix B. The results are two contributions, Eqs. (12) and (13).

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