

Molecular rotation in p -H₂ and o -D₂ in phase I under pressure

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The orientational order parameter, rotational ground-state energy, and lattice distortion parameter (the deviation of the c/a ratio from the ideal hcp value 1.633) in hcp lattice of phase I of p -H₂ and o -D₂ are calculated using a semi-empirical approach. It is shown that the lattice distortion in these J -even species is small compared with that found in n -H₂, and n -D₂. The difference presumably is caused by the J -odd species.

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At zero pressure the molecules in J -even solid hydrogens (p -H₂ and o -D₂) are virtually spherical. Such spheres crystallize into a perfect hcp structure with the ideal axial ratio $c/a = \sqrt{8/3}$. A competition between the gain in the anisotropic energy and a loss in that of the isotropic component determines the deviation $\delta = c/a - \sqrt{8/3}$ from the ideal hcp value for given pressure and temperature. The orientational state of molecules in the distorted lattice is characterized by the orientational order parameter η . Thus, the state of the lattice can be described by two coupled order parameters, $\eta(P, T)$ and $\delta(P, T)$, which can be found by the minimization of free energy with respect to these parameters.

For all 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. Typical values are of the order of 10^{-2} . For solid helium δ is an order of magnitude smaller [1,2]. In the case of hydrogens the situation under discussion is rather controversial. There have been numerous experimental attempts to determine c/a in solid hydrogens starting from the first measurements by Keesom *et al.* [3] who found that at zero pressure p -H₂ has an ideal hcp lat-

tice. Precision x-ray zero-pressure measurements by Krupskii *et al.* [4] confirmed this result and extended it for o -D₂.

Systematic high-pressure neutron and x-ray structural studies of different isotopes and spin-nuclear species of solid hydrogen were started in the early of 1980's. The first structural studies 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 [5,6]. It was found that the ratio c/a is practically constant and is slightly less than the ideal hcp value (1.631 ± 0.002). A large number of x-ray [7,9,10] and neutron-diffraction [8,11,12] studies of the axial ratio of solid hydrogen and deuterium were performed in the late 1980's and early 1990's. These measurements on normal ortho-para samples established that the c/a ratio is very close to the ideal hcp value and weakly depends on pressure.

Synchrotron single-crystal x-ray diffraction measurements of n -H₂ and n -D₂ up to megabar pressures at room temperature [13] revealed an approximately linear decrease of the c/a ratio with increasing pressure. The observed lattice distortion has been interpreted as a gradual effect of orientation of the H₂ molecular axis within phase I. No isotope effect in the pressure dependence of the c/a ratio was found.

A somewhat weaker pressure dependence of c/a was displayed in the x-ray powder diffraction study of solid deuterium [14]. The lattice distortion parameter $\delta = -0.03$ was obtained for 94 GPa at 83 K, $\sim 25\%$ smaller than the room temperature single-crystal value by Loubeyre *et al.* [13]. When these results for the lattice distortion are compared with that for rare-gas solids ($\sim 10^{-3}$ at 100 GPa [1,2]) it is apparent that the difference in more than the order of magnitude is due to the rotational degrees of freedom.

There have been many attempts to calculate the pressure behavior of the axial ratio using different theoretical approaches: Hartree–Fock [15,16], local density approximation [17], Path Integral Monte Carlo [18], *ab initio* molecular dynamics [19]. In all proposed theoretical approaches the rotation-lattice coupling gives rise to positive δ which is in contradiction with experiment. In this paper we developed a self-consistent approach based on the many-body semi-empirical intermolecular potential proposed originally in Ref. 20. It is shown that the pressure behavior of the c/a -ratio in solid $p\text{-H}_2$ and $o\text{-D}_2$ in phase I is determined mainly by the translational degrees of freedom and is comparable in magnitude with that for rare-gas solids. The behavior of the axial ratio found in Ref. 13 is due to the presence of the J -odd component in normal ortho-para mixtures of solid hydrogens [21].

The molecular-field rotational Hamiltonian has the form [20,22,23]

$$H_{\text{rot}} = B_{\text{rot}} L^2 - (U_0 \eta + \varepsilon_{2c}) \sqrt{4\pi/5} Y_{20} + U_0 \eta^2 / 2, \quad (1)$$

where the first term in the right side is the rotor kinetic energy (B_{rot} is the characteristic rotational constant, L is the angular momentum operator), U_0 is the molecular field constant, and Y_{LM} are spherical harmonics.

The orientational order parameter

$$\eta = \sqrt{4\pi/5} \langle Y_{20} \rangle, \quad (2)$$

where

$$\langle (\dots) \rangle = \frac{\text{Sp}(\dots) e^{-H_{\text{rot}}/T}}{\text{Sp} e^{-H_{\text{rot}}/T}}$$

denotes thermodynamic averaging with the Hamiltonian Eq. (1). The rotational Hamiltonian Eq. (1) includes the lattice-rotation coupling term

$$H_{\text{int}} = -\varepsilon_{2c} \sqrt{4\pi/5} Y_{20}, \quad (3)$$

where ε_{2c} is the crystal field parameter [23]

$$\varepsilon_{2c} = \tilde{B} \delta; \quad \tilde{B} = -\sqrt{6} \left(B + \frac{1}{2} R \frac{dB}{dR} \right); \quad (4)$$

and $B(R)$ is the radial function of the single-molecular term in the anisotropic intermolecular potential.

$$B(R) = \exp(\alpha_B R + \beta_B + \gamma_B R^{-1}) - f_c(R) \sum_{n=6,8,10} b_n R^{-n}, \quad (5)$$

The ground-state wave function can be written as a series in spherical harmonics Y_{LM} with L even and $M = 0$:

$$\Psi_0 = \sum_{L=0}^{\infty} c_L Y_{L0}, \quad (L = 2n). \quad (6)$$

The expansion coefficients c_L obey the normalization condition

$$\sum c_L^2 = 1. \quad (7)$$

It can be shown that in order to account for terms up to the fourth order in δ , only three first harmonics should be retained in the expansion Eq. (6). Then the rotational part of the ground-state energy and the rotational order parameter take the form

$$E_0^{\text{rot}} = 6c_2^2 + 20c_4^2 - (U_0 \eta^2 / 2 + \varepsilon_{2c} \eta); \quad (8)$$

$$\eta = \frac{2}{\sqrt{5}} c_0 c_2 + \frac{2}{7} c_2^2 + \frac{12}{7\sqrt{5}} c_2 c_4 + \frac{20}{77} c_4^2. \quad (9)$$

The order parameters η and δ can be found from minima conditions of the total zero-point energy with respect to these parameters. The isotropic part of the zero-point energy E_0^{is} does not depend from η and respective minimum conditions take the form:

$$\partial E_0^{\text{rot}} / \partial \eta = 0; \quad (10a)$$

$$\partial (E_0^{\text{is}} + E_0^{\text{rot}}) / \partial \delta = 0. \quad (10b)$$

Thus, the complete minimization can be carried out in two stages, first, with the help of Eq. (10a) 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. (10b)) we find δ and η as a function of U_0 (pressure).

The minimum condition (10a) can be replaced by the set of conditions

$$\partial E_0^{\text{rot}} / \partial c_L = 0, \quad (L = 2n, n = 0, 1, 2, \dots). \quad (11)$$

Equations (11) are necessary and sufficient conditions of the satisfiability of Eq. (10a). Together with the normalization condition Eq. (7) they are a complete set of equations defining the ground-state rotational wave function.

We will seek the minimum condition Eq. (11) with the constraint Eq. (7) using the Lagrange method, that is, we will seek the minimum of the function

$$\tilde{E}_0 = E_0^{\text{rot}} + \lambda (1 - \sum_L c_L^2), \quad (12)$$

where λ is the Lagrange factor to be found. The resulting set of equations for the coefficients c_L ($L = 2n$, $n = 0, 1, 2, \dots$) has the form

$$L(L+1)c_L - (U_0\eta + \varepsilon_{2c}L) \frac{\partial \eta}{\partial c_L} - 2\lambda c_L = 0. \quad (13)$$

For small U_0 we will seek solutions of the set Eq. (13) in the form of series in powers of the crystal field parameter ε_{2c} or in fact in powers of the lattice distortion parameter δ

$$c_L = \sum_{k=0}^{\infty} q_{Lk} \varepsilon_{2c}^k = \sum_{k=0}^{\infty} q_{Lk} \tilde{B}^k \delta^k. \quad (14)$$

Let us expand the combinations $c_L c_{L'}$ in power series in ε_{2c} :

$$c_L c_{L'} = \sum_{n=0}^{\infty} c_{LL'}^n \varepsilon_{2c}^n. \quad (15)$$

Then the orientational order parameter Eq. (9) can be also presented in the form of the expansion in ε_{2c} :

$$\eta = \sum_{n=0}^{\infty} p_n \varepsilon_{2c}^n, \quad (16)$$

where p_n can be expressed in terms of the coefficients of the expansion Eq. (15):

$$p_n = \frac{2}{\sqrt{5}} c_{02}^{(n)} + \frac{2}{7} c_{22}^{(n)} + \frac{12}{7\sqrt{5}} c_{24}^{(n)} + \frac{20}{77} c_{44}^{(n)} + \dots \quad (17)$$

Expressing the Lagrange factor λ from Eq. (13) for c_0 and substituting it to the remaining equations we arrive at the following set of algebraic equations

$$\sum_{i=1}^{\infty} \left(y_n^{(i)} - \sum_{k=0}^{\infty} r_i g_n^{(k)} \varepsilon_{2c}^k \right) \varepsilon_{2c}^i = 0, \quad n = 1, 2, 3, \dots \quad (18)$$

Here functions $g_n^{(k)}$; r_i , and $y_n^{(i)}$ were introduced:

$$\begin{aligned} g_1^{(k)} &= \frac{2}{\sqrt{5}} c_{00}^{(k)} + \frac{4}{7} c_{02}^{(k)} - \frac{2}{\sqrt{5}} c_{22}^{(k)} + \frac{12}{7\sqrt{5}} c_{04}^{(k)} + \dots, \\ g_2^{(k)} &= \frac{12}{7\sqrt{5}} c_{02}^{(k)} + \frac{40}{77} c_{04}^{(k)} - \frac{2}{\sqrt{5}} c_{24}^{(k)} + \frac{30}{11\sqrt{13}} c_{04}^{(k)} + \dots, \\ g_3^{(k)} &= \frac{30}{11\sqrt{13}} c_{04}^{(k)} + \frac{28}{55} c_{06}^{(k)} - \frac{2}{\sqrt{5}} c_{26}^{(k)} + \dots, \end{aligned} \quad (19a)$$

for $k = 1, 2, 3, \dots$ and

$$g_1^0 = \frac{2}{\sqrt{5}}; \quad g_2^0 = 0; \quad g_3^0 = 0; \dots \quad (19b)$$

$$r_i = U_0 p_i + \delta_{li}, \quad (20)$$

(δ_{ik} is the Kroneker symbol).

$$y_n^{(i)} = 2L(L+1)c_{0L}^{(i)}; \quad (L = 2n, \quad n = 1, 2, 3, \dots). \quad (21)$$

Equations (18) are supplemented by the normalization condition (7), which can be written as a set of equalities

$$c_{00}^{(i)} + c_{22}^{(i)} + c_{44}^{(i)} + c_{66}^{(i)} + \dots, \quad i = 1, 2, 3, \dots \quad (22)$$

Using the successive approximation method we can find solutions of Eq. (18) in any necessary approximation. Up to the third order in the crystal-field parameter the orientational order parameter and orientational ground-state energy have the following form:

$$\eta = \kappa \varepsilon_{2c} + \frac{15^2}{14} \kappa^3 \varepsilon_{2c}^2 + \frac{15\kappa^4}{2 \cdot 49} (15^3 \kappa - 316) \varepsilon_{2c}^3; \quad (23)$$

$$E_0^{\text{rot}} = -\frac{1}{2} \kappa \varepsilon_{2c}^2 - \frac{75}{14} \kappa^3 \varepsilon_{2c}^3. \quad (24)$$

where

$$\kappa = \frac{1}{15 - U_0}. \quad (25)$$

In Eqs. (23)–(25) ε_{2c} , E_0^{rot} , U_0 are given in units of B_{rot} .

The expansion parameter ε_{2c} (Eqs. (4), (5)) is negative for all pressures, so the expansions Eqs. (23), (24) are oscillating and converge if the terms of the expansions are decreasing.

To find the total ground state energy we must include into consideration the contribution of the translational degrees of freedom. As known, pure pair potentials are too stiff to describe properly EOS at high pressures and many-body corrections should be taken into account. In the calculations we used a many-body potential having pair and triple forces (Appendix, Eqs. (A.1), (A.2)).

Using the smallness of δ and expanding the total ground state energy in powers of δ we may restrict ourselves to terms of the second order in δ

$$E_0(\delta) = E_0(0) + b_1 \delta + b_2 \delta^2, \quad (26)$$

where E_0 is the ground-state energy of the ideal lattice, b_i ($i = 1, 2$) are the coefficients depending on the parameters of the intermolecular potential and molar volume. Minimizing $E_0(\delta)$ over δ , we obtain

$$\delta = -b_1 / (2b_2). \quad (27)$$

As was shown in Ref. 1, the contributions of the first two shells of neighbors to b_1 are exactly equal to zero. The first non-vanishing contribution comes from the two molecules of the third shell. The contribution from the pair intermolecular potential $U(R)$ is

$$b_1^{\text{tr}} = \frac{2}{3} a \left(\frac{dU}{dR} \right)_{R=c}, \quad (28)$$

where a and c are the lattice parameters of hcp lattice. The contribution of the rotational degrees of freedom to b_1

as can be seen from Eq. (24) is also exactly zero. The contribution of the first shell from the pair potential is

$$b_2^{\text{tr}} = \frac{3a}{8} \left(\frac{dU}{dR} \right)_{R=a} + \frac{a^2}{8} \left(\frac{d^2U}{dR^2} \right)_{R=a}. \quad (29)$$

The contribution of the rotational degrees of freedom to b_2 as follows from Eq. (24) is

$$b_2^{\text{rot}} = -\kappa(\tilde{B}^2 / B_{\text{rot}}). \quad (30)$$

The total b_2^{tot} is a sum of the respective contributions

$$b_2^{\text{tot}} = b_2^{\text{tr}} + b_2^{\text{rot}}. \quad (31)$$

Due to the presence in the terms of the expansions Eqs. (23), (24) of a singular factor κ (Eq. (25)), a validity of the developed analytical solution is limited by the condition $U_0 < 15$, which corresponds to pressure of ~ 30 GPa for the case of solid p -H₂. To extend the solution into the higher pressure region a numerical analysis should be used.

Let us estimate obtained crystal field ε_{2c} . For $P \approx 30$ GPa ($V \approx 4.6$ cm³/mol) using parameters given in Appendix we obtained

$$B(R) = 1.44 \cdot 10^{-3} \text{ a.u.}; \quad \tilde{B} = 5.80 \cdot 10^{-3} \text{ a.u.};$$

$$b_1^{\text{tr}} = 9.658 \cdot 10^{-5}; \quad b_2^{\text{tr}} = 21.386 \cdot 10^{-3}; \quad b_2^{\text{rot}} = -6.55 \cdot 10^{-3}.$$

Finally we have

$$\delta = -3.26 \cdot 10^{-3}; \quad (32)$$

$$\varepsilon_{2c} = -18.9 \cdot 10^{-6} \text{ a.u.} = -4.1 \text{ cm}^{-1}. \quad (33)$$

The two third of the total lattice distortion is due to the translational degrees of freedom. Without regard for the rotational degrees of freedom we would have $\delta^{\text{tr}} = -b_1^{\text{tr}} / (2b_2^{\text{tr}}) = -2.26 \cdot 10^{-3}$.

Comparing with the results obtained by Loubeyre *et al.* [13] we see that the lattice distortion parameter for J -even species (p -H₂, o -D₂) is more than the order of magnitude smaller than that for normal ortho-para mixtures. These results are in accord with conclusions made by Goncharov *et al.* in Ref. 24. The authors have measured low-frequency Raman spectra at low temperature for the pressure range up to the I–II phase transition. These spectra were employed to estimate the crystal-field parameters. The authors estimated ε_{2c} parameter assuming that only the second-order crystal field is responsible for the splitting of the roton triplet band $S_0(0)$ and get that $|\varepsilon_{2c}| \sim 1 \text{ cm}^{-1}$ and thus $|\delta| \sim 10^{-3}$, more than the order of magnitude smaller than experimental data by Loubeyre *et al.* [13].

In conclusion, the rotational order parameter, rotational ground-state energy, and the lattice distortion parameter for hcp lattice of phase I of p -H₂, o -D₂ are calculated using

the semi-empirical many-body intermolecular potential. It is shown that the lattice distortion in these J -even species is small compared with that found in n -H₂, and n -D₂ where the main contribution to the lattice distortion is introduced by the J -odd species.

Appendix

The pair potential:

$$U_p(R) = \exp(\alpha - \beta R - \gamma R^2) - f_c(R) \sum_{n=6,8,10} C_n R^{-n} \quad (A.1)$$

(R is the interparticle distance). The damping function

$$f_c(R) = \begin{cases} \exp[-(R^*/R - 1)^2], & R < R^* \\ 1, & R > R^* \end{cases} \quad (A.2)$$

where $R^* = DR_m$, R_m is the position of the potential minimum.

The three-body potential:

$$U_{\text{tr}} = \left\{ -A \exp[-a(r_1 + r_2 + r_3)] + C_{\text{tr}} r_1^3 r_2^3 r_3^3 \right\} \times \\ \times (1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3), \quad (A.3)$$

Potential parameters (in atomic units)

Parameters of the pair potential:

$$\alpha = 1.713, \quad \beta = 1.5671, \quad \gamma = 0.00993.$$

Dispersion coefficients:

$$C_6 = 12.14, \quad C_8 = 215.2, \quad C_{10} = 4813.9.$$

Parameters of the damping function:

$$D = 1.28, \quad R_m = 6.44.$$

Parameters of the three-body potential:

$$A_{\text{tr}} = 6.085, \quad a_{\text{tr}} = 0.737858;$$

$$C_{\text{tr}}^{\text{H}_2} = 49.49815, \quad C_{\text{tr}}^{\text{D}_2} = 48.84650.$$

Parameters of the function $B(R)$ (Eq. 5):

$$\alpha_B = -1.3252, \quad \beta_B = -1.9292, \quad \gamma_B = 3.8103.$$

$$b_6 = 1.368, \quad b_8 = 50.53, \quad b_{10} = 1185.$$

1. Yu.A. Freiman, S.M. Tretyak, A. Grechnev, A.F. Goncharov, J.S. Tse, D. Errandonea, H.-k. Mao, and R.J. Hemley, *Phys. Rev.* **B80**, 094112 (2009).
2. A. Grechnev, S.M. Tretyak, and Yu.A. Freiman, *Fiz. Nizk. Temp.* **36**, 423 (2010) [*Low Temp. Phys.* **36**, 333 (2010)].
3. W.H. Keesom, J. de Smedt, and H.H. Moon, *Leiden Commun.* **19**, Suppl. No. 69, No. 209d (1929/1930).
4. I.N. Krupskii, A.I. Prokhvatilov, and G.N. Shcherbakov, *Fiz. Nizk. Temp.* **10**, 5 (1984) [*Sov. J. Low Temp. Phys.* **10**, 1 (1984)]; I.N. Krupskii, A.I. Prokhvatilov, and G.N. Shcherbakov, *Fiz. Nizk. Temp.* **9**, 83 (1983) [*Sov. J. Low Temp. Phys.* **9**, 42 (1983)].
5. S.N. Ishmaev, I.P. Sadikov, A.A. Chernyshov, B.A. Vindryaevskii, V.A. Sukhoparov, A. Telepnev, and G.V. Kobelev, *Zh. Eksp. Teor. Fiz.* **84**, 394 (1983) [*Sov. Phys. JETP* **57**, 228 (1983)].

6. S.N. Ishmaev, I.P. Sadikov, A.A. Chernyshov, B.A. Vindryaevskii, V.A. Sukhoparov, A. Telepnev, G.V. Kobelev, and R.A. Sadikov, *Zh. Eksp. Teor. Fiz.* **89**, 1249 (1985) [*Sov. Phys. JETP* **62**, 721 (1985)].
7. R.M. Hazen, H.K. Mao, L.W. Finger, and R.J. Hemley, *Phys. Rev.* **B36**, 3944 (1987).
8. V.P. Glazkov, S.P. Besedin, I.N. Goncharenko, A.V. Irodova, I.N. Makarenko, V.A. Somenkov, S.M. Stishov, and S.Sh. Shil'shtein, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 661 (1988) [*JETP Lett.* **47**, 763 (1988)].
9. H.K. Mao, A.P. Jephcoat, R.J. Hemley, L.W. Finger, C.S. Zha, R.M. Hazen, and D.E. Cox, *Science* **239**, 1131 (1988).
10. R.J. Hemley, H.K. Mao, L.W. Finger, A.P. Jephcoat, R.M. Hazen, and C.S. Zha, *Phys. Rev.* **B42**, 6458 (1990).
11. S.P. Besedin, I.N. Makarenko, S.M. Stishov, V.P. Glazkov, I.N. Goncharenko, A.V. Irodova, V.A. Somenkov, and S.Sh. Shil'shtein, *High-Pressure Res.* **4**, 447 (1990).
12. S.P. Besedin, I.N. Makarenko, S.M. Stishov, V.P. Glazkov, I.N. Goncharenko, A.V. Irodova, V.A. Somenkov, and S.Sh. Shil'shtein, in: *Molecular Systems Under High Pressure*, R. Pucci and G. Piccitto (eds.), Elsevier, North-Holland (1991) p. 89.
13. P. Loubeyre, R. LeToullec, D. Hausermann, M. Hanfland, R.J. Hemley, H.K. Mao, and L.W. Finger, *Nature* **383**, 702 (1996).
14. H. Kawamura, Y. Akahama, S. Umemoto, K. Takemura, Y. Ohishi, and O. Shimomura, *J. Phys.: Condens. Matter* **14**, 10407 (2002).
15. S.I. Anisimov and Yu.V. Petrov, *Pis'ma Zh. Eksp. Teor. Fiz.* **26**, 595 (1977) [*JETP Lett.* **26**, 446 (1977)].
16. S. Raynor, *J. Chem. Phys.* **87**, 2795 (1987).
17. T.W. Barbee, A. Garcia, and M.L. Cohen, *Phys. Rev. Lett.* **62**, 1150 (1989).
18. T. Cui, E. Cheng, B.J. Alder, and K.B. Whaley, *Phys. Rev.* **B55**, 12253 (1997).
19. J. Kohanoff, S. Scandolo, G.L. Chiarotti, and E. Tosatti, *Phys. Rev. Lett.* **78**, 2783 (1997).
20. Yu.A. Freiman, S. Tretyak, A. Jeżowski, and R.J. Hemley, *J. Low Temp. Phys.* **122**, 537 (2001).
21. J. Igarashi, *J. Phys. Soc. Jpn.* **59**, 2811 (1990).
22. *Physics of Cryocrystals*, V.G. Manzhelii and Yu.A. Freiman (eds.), AIP Press, New York (1997).
23. J. Van Kranendonk: *Solid Hydrogen*, Plenum, New York (1983).
24. A.F. Goncharov, M.A. Strzhemechny, H.K. Mao, and R.J. Hemley, *Phys. Rev.* **B63**, 064304 (2001).