Quantum rotors in *Pca*2₁ lattice

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Analytical calculations of the potential barrier hindering rotation of the hydrogen molecules in the molecular field of neighboring molecules are performed for molecular solid hydrogen. The calculations are made for the four-sublattice *Pca*2₁ lattice which minimizes the electrostatic energy of classical quadrupoles on an hcp lattice.

1. Introduction

As a unique quantum molecular crystal, solid hydrogen has for a century of studies been a challenging subject of investigation and a source of new concepts in fundamental physics [1–4]. The large isotopic family of hydrogens (H₂, HD, D₂, HT, DT, T₂) presents a unique possibility for studying the diversity of quantum isotopic effects [1,3]. The behavior of the hydrogens at high pressures has been termed one of the "Key Problems of Physics and Astrophysics" [5]. Inspired by the search for the high-density metallic phase, there has been significant progress in recent years as a result of major advances in experimental high-pressure techniques. In particular, diamond-anvil cell experiments have revealed that the phase diagram of the solid H₂ is very rich and four phases have been clearly identified and studied [4,6–9]. Recently a new high-pressure high-temperature phase *V* was found [10]. These phases are related to rotational ordering of the molecules and are accompanied by structural changes. The metallization of hydrogen remains an open question.

Hydrogens at low temperature and pressure form the only molecular quantum solid in which both translational and rotational motions of molecules are quantum. By analogy with solid helium, which is an ultimate quantum solid at low pressures, it is generally believed that quantum effects become progressively less pronounced with increasing pressure. In the case of solid hydrogen, this is true only for the translational motion of molecules. As for rotational motion, strictly speaking, it is not so. At small pressures the molecules in *J*-even solid hydrogens (para-H₂ and ortho-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 [11,12].

Knowledge of the lowest-energy structure is fundamental for clarifying the properties of compressed solid hydrogen at low temperatures. At low density, the orientation-dependent energy comes mainly from the electric quadrupole-quadrupole (EQQ) interactions. On a rigid cubic lattice the molecules are arranged in a high-symmetry *Pa*3 structure, in which each molecule is directed along a threefold symmetry axis (space diagonals of the cube) [1–3,13]. As was shown first by Kitaigorodskii and Mirskaya, the lowest energy structure for the classical EQQ system belongs to the *Pca*2₁ space group [14]. This structure (Fig. 1) may be obtained from hcp lattice with all molecules aligned along *c* axis (space group *P*63/*mmc*) by doubling the unit cell and tilting the four molecules in the unit cell from *c* axis by an angle ϑ and rotated by the azimuthal angles $\pm\varphi, \pi\pm\varphi$. A more systematic studies of the arrangement of classical and quantum quadrupoles has been made by Felsteiner [15], Miyagi and Nakamura [16] and by James [17].
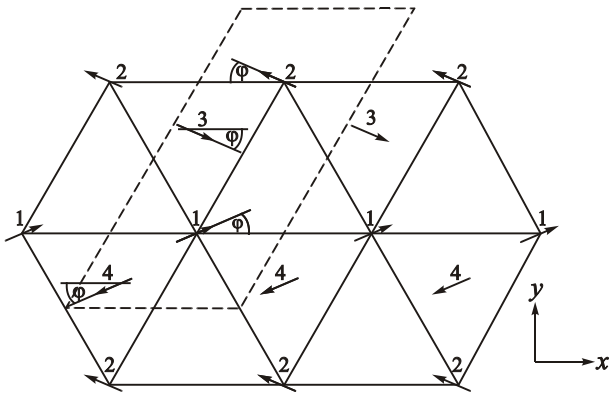
Fig. 1. Orientations of symmetry axes of molecular ground states. Arrows at vertices represent molecules in one of the hexagonal planes; arrows at the centers of triangles represent molecules in the hexagonal planes above or below. The unit cell is shown by dashed lines [17].

The low-pressure phase I is considered as rotationally disordered hcp solid. Phase II, the so-called broken symmetry phase or BSP, is orientationally ordered. The crystal structure of high-pressure phases II and III has not been determined unambiguously. It is generally believed that centers of mass of the molecules form an hcp lattice. Optical (Raman and infrared) vibron modes which are observed in phase II in hydrogen and deuterium indicate an orientational ordering of four molecules per cell. The structure considered the most relevant for the high-pressure phases of hydrogen is the $Pca2_1$ (Fig. 1). This structure may be obtained from hcp lattice with all molecules are aligned parallel to c axis (space group $P6_3/mmc$) by doubling the unit cell and tilting the four molecules in the unit cell from c axis by an angle ϑ and rotated by the azimuthal angles $\pm\varphi, \pi\pm\varphi$. This structure is known to minimize the electrostatic energy of classical quadrupoles on an hcp lattice, at $\vartheta \approx 55°$ and $\varphi \approx 43°$ [14]. The energy profile for the single-particle movement of the hydrogen molecules was calculated in Ref. 18 in LDA approximation. Azimuthal and polar librations movements in this profile are quite different: while polar librations in the relatively deep well are near harmonic, the azimuthal movement in the shallow well is strongly anharmonic [18] (Fig. 2). The influence of the orientational motion on the electronic band structure of molecular hydrogen was studied using different *ab initio* approaches in Refs. 19–22.

In this paper we developed an analytical approach to calculate the potential well profile for the orientational movement of the hydrogen molecules in the four-sublattice $Pca2_1$ structure. This approach generalizes the approach developed by Felsteiner and Friedman for $Pa3$ lattice [13].

2. Energy of anisotropic interaction

Let us consider a system of symmetrical quantum rotors represented hydrogen molecules on a rigid lattice interact-
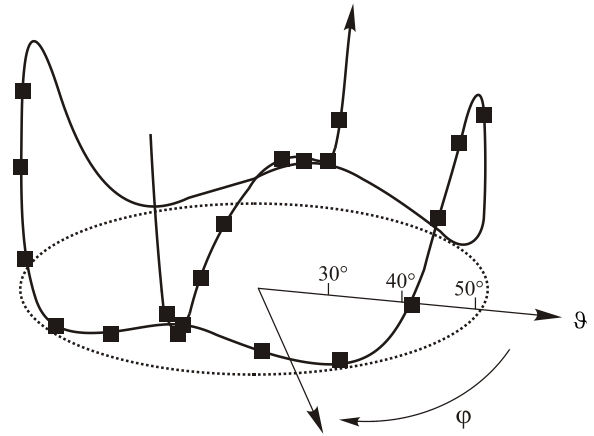

Fig. 2. Orientational dependence of the total energy of of $Pca2_1$ hydrogen [18].

ing *via* anisotropic orientational forces. Molecular orientations relative the crystal frame are defined by unit vectors $\mathbf{\Omega}_i$. The Hamiltonian of the rotor system can be written in the form

$$\mathcal{H} = \mathcal{H}_{kin} + \frac{1}{2}\sum_{ij}V_{ij}(\mathbf{R}_{ij},\mathbf{\Omega}_i,\mathbf{\Omega}_j), \qquad (1)$$

where $\mathcal{H}_{kin}$ is the rotor kinetic energy operator and V_{ij} is the intermolecular interaction energy. Retaining in the equation for the two-particle interaction only terms with $l_1 = l_2 = 2$, we get the anisotropic interaction energy in the form [1–3]

$$V_{ij}(\mathbf{R}_{ij},\mathbf{\Omega}_i,\mathbf{\Omega}_j) = 4\pi^{3/2}\sum_l \alpha_l \varepsilon_l(R) \sum_{m_1 m_2 \mu} \frac{(-1)^\mu}{\sqrt{2l+1}} C^{2\ 2\ l}_{m_1 m_2 \bar{\mu}} \times$$
$$\times Y_{2m_1}(\mathbf{\Omega}_i)Y_{2m_2}(\mathbf{\Omega}_j)Y_{l\mu}(\mathbf{\Omega}_{ij}), \qquad (2)$$

where $C^{2\ 2\ l}_{2\ \bar{2}\ 0}$ are Clebsch–Gordan coefficients, the coefficients $\alpha_l = (C^{22l}_{2\ \bar{2}\ 0})^{-1}$ and functions $\varepsilon_i(R)$ characterize the interaction of l-type and are defined by the type of the intermolecular interaction. The unit vector $\mathbf{\Omega}_{ij}$ defines the orientation of the intermolecular axis and thus is a lattice vector.

Equation (2) may be rewritten in the form

$$V_{ij}(R_{ij},\mathbf{\Omega}_i,\mathbf{\Omega}_j) = \frac{4\pi}{5}\sum_{m_1 m_2} F_{m_1 m_2}Y_{2m_1}(\mathbf{\Omega}_i)Y_{2m_2}(\mathbf{\Omega}_j), \quad (3)$$

where

$$F_{m_1 m_2} = 5\sqrt{4\pi}\sum_l \alpha_l \varepsilon_l(R)\sum_\mu \frac{(-1)^\mu}{\sqrt{2l+1}} C^{2\ 2\ l}_{m_1 m_2 \bar{\mu}} \mathbf{Y}_{l\mu}(\mathbf{\Omega}_{ij}).$$
$$(4)$$

The anisotropic interaction energy can be expressed in terms of components of the molecular quadrupole moment q_μ:

$$V_{ij}(\mathbf{R}_{ij},\mathbf{\Omega}_i,\mathbf{\Omega}_j) = \sum_{\mu\nu}v^{ij}_{\mu\nu}q^i_\mu q^j_\nu. \qquad (5)$$

Here q^i_μ is the μ-component of the quadrupole moment of the molecule in the site i. The quantities q^i are defined by

the equilibrium orientations of the molecules described by the angles $\mathbf{\Omega}(\vartheta_i, \varphi_i)$:

$$q_1 = \frac{1}{\sqrt{2}}\left(4\pi/5\right)^{1/2}\left[Y_{22}(\mathbf{\Omega}) + Y_{2,-2}(\mathbf{\Omega})\right];$$

$$q_2 = \left(4\pi/5\right)^{1/2} Y_{20}(\mathbf{\Omega});$$

$$q_3 = \frac{1}{\sqrt{2}}\left(4\pi/5\right)^{1/2}\left[Y_{21}(\mathbf{\Omega}) + Y_{2,-1}(\mathbf{\Omega})\right]; \qquad (6)$$

$$q_4 = \frac{1}{\sqrt{2}}\left(4\pi/5\right)^{1/2}\left[-Y_{21}(\mathbf{\Omega}) + Y_{2,-1}(\mathbf{\Omega})\right];$$

$$q_5 = \frac{1}{\sqrt{2}}\left(4\pi/5\right)^{1/2}\left[-Y_{22}(\mathbf{\Omega}) + Y_{2,-2}(\mathbf{\Omega})\right].$$

The components of the quadrupole moment satisfy the normalization condition:

$$\sum_{i=1}^{5} q_i^2 = 1. \qquad (7)$$

Comparing Eqs. (2) and (5) we get the relations between elements of the interaction matrices $v_{\mu\nu}$ and $F_{m_1 m_2}$. Performing summations in Eq. (4), we obtain elements of the interaction matrix $v_{\mu\nu}$ expressed in terms of parameters of the intermolecular potential $\varepsilon_0, \varepsilon_2$, and ε_4 and Cartesian coordinates of the molecules in the lattice:

$$v_{11} = 5\varepsilon_0 + \frac{5}{2}(3n_z^2 - 1)\varepsilon_2 + \frac{5}{8}[(35n_z^4 - 30n_z^2 + 3) + 35(n_x^4 - 6n_x^2 n_y^2 + n_y^4)]\varepsilon_4;$$

$$v_{12} = \frac{5\sqrt{3}}{2}[(n_x^2 - n_y^2)\varepsilon_2 + \frac{5}{2}(n_x^2 - n_y^2)(7n_z^2 - 1)\varepsilon_4];$$

$$v_{13} = \frac{5}{2}\{3n_y n_z \varepsilon_2 + \frac{5}{2}[n_y n_z(7n_z^2 - 3) + 7n_y n_z(3n_x^2 - n_y^2)]\varepsilon_4\};$$

$$v_{14} = -\frac{5}{2}\{3n_x n_z \varepsilon_2 + \frac{5}{2}[n_x n_z(7n_z^2 - 3) + 7n_x n_z(3n_y^2 - n_x^2)]\varepsilon_4\};$$

$$v_{15} = \frac{175}{2} n_x n_y (n_x^2 - n_y^2)\varepsilon_4;$$

$$v_{22} = 5\varepsilon_0 - \frac{5}{2}(3n_z^2 - 1)\varepsilon_2 + \frac{15}{4}(35n_z^4 - 30n_z^2 + 3)\varepsilon_4;$$

$$v_{33} = 5\varepsilon_0 - \frac{5}{4}[(3n_z^2 - 1) - 3(n_x^2 - n_y^2)]\varepsilon_2 + \frac{5}{2}[(35n_z^4 - 30n_z^2 + 3) + 5(n_x^2 - n_y^2)(7n_z^2 - 3)]\varepsilon_4;$$

$$v_{44} = 5\varepsilon_0 - \frac{5}{4}[(3n_z^2 - 1) + 3(n_x^2 - n_y^2)]\varepsilon_2 - \frac{5}{2}[(35n_z^4 - 30n_z^2 + 3) - 5(n_x^2 - n_y^2)(7n_z^2 - 3)]\varepsilon_4;$$

$$v_{55} = 5\varepsilon_0 + \frac{5}{2}(3n_z^2 - 1)\varepsilon_2 + \frac{5}{8}[(35n_z^4 - 30n_z^2 + 3) - 35(n_x^4 - 6n_x^2 n_y^2 + n_y^4)]\varepsilon_4;$$

$$v_{23} = \frac{5\sqrt{3}}{2}[n_y n_z \varepsilon_2 - 5n_y n_z(7n_z^2 - 3)\varepsilon_4];$$

$$v_{24} = \frac{5\sqrt{3}}{2}[-n_x n_z \varepsilon_2 + 5n_x n_z(7n_z^2 - 3)\varepsilon_4];$$

$$v_{25} = 5\sqrt{3}[n_x n_y \varepsilon_2 + \frac{5}{2}n_x n_y(7n_z^2 - 1)\varepsilon_4];$$

$$v_{34} = -\frac{15}{2}n_x n_y \varepsilon_2 + 25 n_x n_y(7n_z^2 - 1)\varepsilon_4;$$

$$v_{35} = -\frac{15}{2}n_x n_z \varepsilon_2 - \frac{25}{4}[n_x n_z(7n_z^2 - 3) + 7n_x n_z(n_x^2 - 3n_y^2)]\varepsilon_4;$$

$$v_{45} = -\frac{15}{2}n_y n_z \varepsilon_2 - \frac{25}{4}[n_x n_z(7n_z^2 - 3) - 7n_y n_z(3n_x^2 - n_y^2)]\varepsilon_4.$$

$$(8)$$

In the molecular-field approximation the single-particle anisotropic energy can be written in the form

$$U_0 = \sum_j \sum_{\mu\nu} v_{\mu\nu}^{ij} \langle q_\mu^i \rangle q_\nu^j, \qquad (9)$$

where $\langle q_\mu^j \rangle$ are the thermal average of q_μ^j calculated self-consistently with the Hamiltonian Eq. (1) taken in the molecular-field approximation (orientational order parameters). Assuming that the molecular field is uniform and the sublattices are equivalent we have

$$U_0 = \eta \sum_j \sum_{\mu\nu} v_{\mu\nu}^{ij} q_\mu^i. \qquad (10)$$

This quantity plays the role of the molecular-field constant for the single-particle Shrödinger equation describing orientational behavior of the hydrogen molecule. Specific form of the function $U(q_1^i, q_2^i, q_3^i, q_4^i, q_5^i)$ is defined by the crystal structure. Studying properties of the BSP phase of solid hydrogens one needs to consider only fcc-based (*Pa*3) and hcp-based models.

3. Calculation of the molecular field constant U_0 for *Pa*3 lattice

In this lattice, which consists of four sublattices the molecule centers of gravity lie on fcc cites that are centers of inversion, and the molecular axes are directed along a body diagonal of the cube The sublattice structure (the interrelation between the coordinates of the molecules and their orientations) for *Pa*3 lattice is shown in Table 1.

Table 1. Molecular positions, $\mathbf{R}_j = a\mathbf{n}_j + \mathbf{t}$, and orientations, Ω_j for the *Pa*3 lattice. ($\mathbf{n}_j$ is the radius vector of the center of mass of a molecule on the jth sublattice, $\mathbf{t}$ is the translation vector, $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors of the cubic lattice; Ω_j is the equilibrium orientation of a molecule on the jth sublattice)

Sublattice number	Molecular orientation Ω_j	j
1	(1,1,1)	0
2	(1,1,−1)	$\frac{1}{\sqrt{2}}(\mathbf{j}+\mathbf{k})$
3	(1,−1,1)	$\frac{1}{\sqrt{2}}(\mathbf{i}+\mathbf{j})$
4	(−1,1,1)	$\frac{1}{\sqrt{2}}(\mathbf{i}+\mathbf{k})$

Taking into account ony the interaction with the nearest neighbors from Eq. (5) we have:

$$U_0 = \frac{1}{3}\left\{\sum_{j\in\mathrm{II}}[(-v_{33}^{ij}-v_{44}^{ij}+v_{55}^{ij})-2v_{34}^{ij}]+\right.$$

$$+\sum_{j\in\mathrm{III}}[(-v_{33}^{ij}+v_{44}^{ij}-v_{55}^{ij})-2v_{35}^{ij}]+$$

$$\left.+\sum_{j\in\mathrm{IV}}[(v_{33}^{ij}-v_{44}^{ij}-v_{55}^{ij})-2v_{45}^{ij}]\right\}. \tag{11}$$

Substituting $v_{\mu\nu}$ from Eq. (8) into Eq. (11) and summing over the sublattices we obtain for the molecular field constant the following expression:

$$U_0 = 5\left(4\varepsilon_0^{(1)}-2\varepsilon_2^{(1)}+19\varepsilon_4^{(1)}\right). \tag{12}$$

The upper index at the quantities ε_l shows that the respective contribution is calculated for the distance to the nearest neighbors $R = a/\sqrt{2}$.

4. Calculation of the molecular field constant U_0 for *Pca*2_1 lattice

In this section we will perform calculations of the molecular field constant for the quadrupolar orthorhombic structure *Pca*2_1, which was considered as a possible candidate for the BSP phase in Refs. 18–22. In this structure

which consists of four sublattices, the molecular centers of gravity lie on of hcp lattice. The *Pca*2_1 structure consists of four sublattices with the molecules aligned along four directions close to the respective combinations of angles $\cos\vartheta = \pm 1/\sqrt{3}$, $\cos\varphi = \pm 1/\sqrt{2}$, where the polar angle ϑ is taken off *c*-axis and the azimuthal angle φ is counted off the line to the nearest neighbor in the *ab*-plane.

The interrelation between the coordinates of the molecules and their orientations are shown in Table 2.

Table 2. Sublattice structure of *Pca*2_1 lattice (**a**, **b**, **c** are translation vectors which generate the lattice, n_1, n_2, n_3 are arbitrary integers)

Sublattice number	**a**	**b**	**c**	Molecular orientation
I	n_1	n_2	n_3	$\Omega_\mathrm{I} = (\vartheta_0, \varphi_0)$
II	$n_1+\frac{1}{2}$	$n_2+\frac{1}{2}$	n_3	$\Omega_\mathrm{II} = (\vartheta_0, \pi-\varphi_0)$
III	$n_1+\frac{1}{2}$	$n_2+\frac{1}{6}$	$n_3+\frac{1}{2}$	$\Omega_\mathrm{III} = (\vartheta_0, \pi+\varphi_0)$
IV	n_1	$n_2-\frac{1}{3}$	$n_3+\frac{1}{2}$	$\Omega_\mathrm{IV} = (\vartheta_0, 2\pi-\varphi_0)$

Taking into account equilibrium orientations of the molecules in the sublattices we obtain the following relations between components of the quadrupole moment of the molecules belonging to the different sublattices:

$$q_1^\mathrm{I} = \frac{\sqrt{3}}{2}\sin^2\vartheta_0(\cos^2\varphi_0-\sin^2\varphi_0); \qquad q_1^\mathrm{II} = q_1^\mathrm{III} = q_1^\mathrm{IV} = q_1^\mathrm{I};$$

$$q_2^\mathrm{I} = \left(\frac{3}{2}\cos^2\vartheta_0-\frac{1}{2}\right); \qquad q_2^\mathrm{II} = q_2^\mathrm{III} = q_2^\mathrm{IV} = q_2^\mathrm{I};$$

$$q_3^\mathrm{I} = \sqrt{3}\cos\vartheta_0\sin\vartheta_0\sin\varphi_0; \qquad q_3^\mathrm{II} = q_3^\mathrm{I};\ q_3^\mathrm{III} = -q_3^\mathrm{I};\ q_3^\mathrm{IV} = -q_3^\mathrm{I};$$

$$q_4^\mathrm{I} = \sqrt{3}\cos\vartheta_0\sin\vartheta_0\cos\varphi_0; \qquad q_4^\mathrm{II} = -q_4^\mathrm{I};\ q_4^\mathrm{III} = -q_4^\mathrm{I};\ q_4^\mathrm{IV} = -q_4^\mathrm{I};$$

$$q_5^\mathrm{I} = \sqrt{3}\sin^2\vartheta_0\sin\varphi_0\cos\varphi_0; \qquad q_5^\mathrm{II} = -q_5^\mathrm{I};\ q_5^\mathrm{III} = q_5^\mathrm{I};\ q_5^\mathrm{IV} = -q_5^\mathrm{I}. \tag{13}$$

In the terms of the component of the quadrupole moments Eq. (4) molecular field constant for the *Pca*2_1 lattice takes the form:

$$U_0 = -U^i = q_1\left[\sum_{j\in\mathrm{I+II+III+IV}}\left(v_{11}^{ij}+v_{12}^{ij}\right)+\sum_{j\in\mathrm{I+II}}v_{13}^{ij}+\sum_{j\in\mathrm{I+IV}}v_{14}^{ij}+\sum_{j\in\mathrm{I+III}}v_{15}^{ij}\right]+$$

$$+q_2\left[\sum_{j\in\mathrm{I+II+III+IV}}\left(v_{12}^{ij}+v_{22}^{ij}\right)+\sum_{j\in\mathrm{I+II}}v_{23}^{ij}+\sum_{j\in\mathrm{I+IV}}v_{24}^{ij}+\sum_{j\in\mathrm{I+III}}v_{25}^{ij}\right]+$$

$$+q_3\left[\sum_{j\in\mathrm{I+II}}\left(v_{13}^{ij}+v_{23}^{ij}\right)+\left(\sum_{j\in\mathrm{I+II}}v_{33}^{ij}-\sum_{j\in\mathrm{III+IV}}v_{33}^{ij}\right)+\left(\sum_{j\in\mathrm{I}}v_{34}^{ij}-\sum_{j\in\mathrm{III}}v_{34}^{ij}\right)+\left(\sum_{j\in\mathrm{I}}v_{35}^{ij}-\sum_{j\in\mathrm{IV}}v_{35}^{ij}\right)\right]+$$

$$+q_4\left[\sum_{j\in\mathrm{I+IV}}\left(v_{14}^{ij}+v_{24}^{ij}\right)+\left(\sum_{j\in\mathrm{I+IV}}v_{44}^{ij}-\sum_{j\in\mathrm{II+III}}v_{44}^{ij}\right)+\left(\sum_{j\in\mathrm{I}}v_{34}^{ij}-\sum_{j\in\mathrm{III}}v_{34}^{ij}\right)+\left(\sum_{j\in\mathrm{I}}v_{45}^{ij}-\sum_{j\in\mathrm{II}}v_{45}^{ij}\right)\right]+$$

$$+q_5\left[\sum_{j\in\mathrm{I+III}}\left(v_{15}^{ij}+v_{25}^{ij}\right)+\left(\sum_{j\in\mathrm{I+III}}v_{55}^{ij}-\sum_{j\in\mathrm{II+IV}}v_{55}^{ij}\right)+\left(\sum_{j\in\mathrm{I}}v_{35}^{ij}-\sum_{j\in\mathrm{IV}}v_{35}^{ij}\right)+\left(\sum_{j\in\mathrm{I}}v_{45}^{ij}-\sum_{j\in\mathrm{II}}v_{45}^{ij}\right)\right]. \tag{14}$$

Finally, we have

$$U_0 = \eta\left[60(q_1+q_2)\varepsilon_0 + 5(3q_3 - 2q_4 + 2q_5)\varepsilon_2 + \right.$$
$$\left. + \frac{5}{18}(21q_1 + 126q_2 + 240q_3 - 616q_4 - 300q_5)\varepsilon_4 \right]. \quad (15)$$

There is the following correspondence between the energetic parameters $\varepsilon_0, \varepsilon_2, \varepsilon_4$ and parameters of the Kohin potential used in literature devoted to systems with quasiquadrupole intermolecular orientational forces [3]:

$$V_1 = \frac{525}{4}\varepsilon_4; \; V_2 = -\frac{15}{2}; \; V_3 = \frac{15}{2}(\varepsilon_0 + \varepsilon_2 + \varepsilon_4).$$

The parameters of the potential V_1, V_2, V_3 depend on the molecular and lattice constants.

5. Concluding remarks

In phase I both η and δ are small and negative. The negative δ means that the lattice is slightly flattened compared to 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 $\langle\vartheta_0\rangle = \cos^{-1}(1/\sqrt{3}) \approx 54°44'$. 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 $\eta = -3.3\cdot10^{-4}$ for p-H₂ and $\eta = -1\cdot10^{-5}$ for o-D₂.

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) [23]. 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 the 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.

In memory of Kirill Borisovich Tolpygo, a remarkable physicist, and more — a great person, nonconformist.

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