

Orientational structures in solid para-hydrogen in the broken symmetry phase

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Calculations of the rotational energies of different structures of solid hydrogen in the broken symmetry phase at $T=0$ K are performed. A method is used that has been applied recently to estimate the pressure transition. It determines the quantum-mechanical ground-state energy of a system of infinite rotors arranged according to a specified symmetry order and interacting through an intermolecular potential. The method is relatively simple and avoids all the approximations typical of simulation techniques. The calculations are performed for five different symmetry systems and the comparison shows that the $Pca2_1$ structure is the least energetic.

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I. INTRODUCTION

Solid hydrogen undergoes a transition to a broken symmetry phase (BSP) at about 110 GPa at low temperature.¹ The structure of the BSP is not yet understood completely. Actually, it seems now well established that the centers of mass of the molecules form a hexagonal-close-packed (hcp) structure.² On the contrary there is no uniform view with regard to the orientational order. According to the calculations of the energy of the system, the structure of $Pca2_1$ symmetry is preferred in Refs. 3–6, the $Cmc2_1$ in Ref. 7 and $P2_1/c$ in Ref. 8. On the other hand, numerical evaluations of orientational two-body correlation functions^{9,10} and of infrared and Raman vibrons¹¹ seem to indicate a Pa3-type local orientational order on a hcp translational lattice. This last structure seems to be preferred for deuterium from an analysis of experimental studies based on neutron and x-rays scattering.¹²

In this paper a method is used that is different from all those employed in the previously cited works. The method allows the calculation of the rotational energy of a system of rotors, with the inclusion of correlation effects. It was proposed years ago¹³ and has been reformulated recently.¹⁴ It can be viewed as an extension of the procedure employed in Ref. 15 to take account of correlation effects. The present method is relatively simple and allows to separate mean-field contributions and correlation effects to the energy of the system. It avoids approximations such as limited systems and finite lengths of runs typical of simulation techniques. Actually it treats an infinite system of rotors and the quantity of the orientational degrees of freedom is practically fully accounted for.¹⁴ In the present form, it is suitable to treat systems at 0 K.

The method employed here needs as input both the anisotropic intermolecular potential as a function of the molecular orientations and the structure of the system. The anisotropic intermolecular potential is taken from Ref. 16. It is a potential model derived from local-density approximation results for the total energy per molecule¹⁶ with the help of an *ab initio* pairwise potential.¹⁷ Finally, five structures are considered three of which have already been cited in this section. Also a system of symmetry $P6_3/m$ (Refs. 18 and 19) is considered with eight molecules per cell. Such a system is inter-

esting because it can be taken as an approximation of the Pa3-type orientational order on a hcp lattice.¹² All the structures considered here differ only as far as the orientational order is concerned, the centers of mass of the hydrogen molecules being arranged in a hcp lattice as requested by experimental results on the optical phonon.²

It turns out that the structure with lowest energy is $Pca2_1$, as already shown in some of the previously cited papers. Similar calculations have been performed also for the BSP of deuterium and lead to the same conclusion. The details of these calculations are not reported in this paper, though.

II. THEORY

The theory that is presented in this section is about the ground-state rotational energy of a system of rotors arranged in a regular lattice. It is the extension of a theory that was described in Ref. 14 to which one can refer to clarify some details.

The main idea is that a first approximate calculation of the ground-state rotational energy of an assembly of rotors is performed with single-molecule rotational states. These rotational states can be determined by means of a variational procedure as it will be explained shortly. The same states can be obtained also as eigenstates of a separable effective Hamiltonian that will be considered as an approximation of the real Hamiltonian. The difference between the real and the approximate Hamiltonian is then taken into account by means of perturbation theory. Note that, in case the single-molecule states are those obtained from the mean-field theory, the perturbative corrections to the energy account solely for correlation effects. Otherwise, perturbation theory takes account also of residual mean-field effects.

Once the structure of the system is given, the unperturbed rotational state for the molecule i is chosen in such a way that its angular momentum has null projection along the direction (Ω_i) assigned to that molecule by the structure that is being considered. Accordingly, such states are chosen as linear combinations of spherical harmonics of order zero when referred to the axis Ω_i . The molecular state ϕ thus reads

TABLE I. V_{cl} as a function of volume and structures (in wave numbers).

v (cm ³ /mol)	P (GPa)	Pca2 ₁	P6 ₃ /m	P2 ₁ /c	Cmc2 ₁	C2/m
2.70	112	-614.5	-567.1	-505.7	-396.7	-18.4
2.60	123	-665.6	-614.8	-543.8	-429.3	-12.6
2.50	134	-719.2	-668.8	-588.1	-461.8	-6.7
2.40	147	-779.9	-729.2	-638.1	-498.8	-0.6

$$\phi_i(\omega_i) = \frac{1}{\sqrt{1 + \sum_j |\lambda_j|^2}} (Y_{00} + \lambda_2 Y_{20}^{\Omega_i}(\omega_i) + \lambda_4 Y_{40}^{\Omega_i}(\omega_i) + \dots), \quad (1)$$

where $Y_{L0}^{\Omega_i}$ is the spherical harmonic referred to the axis Ω_i and ω_i is the orientation variable for the same molecule. L is taken as even because the system is assumed to be composed of para molecules. As already stated, the coefficients λ 's are determined as variational parameters. In the case in which spherical harmonics of non-null order can be excluded from the molecular state on the basis of symmetry considerations, the previous procedure leads to the mean-field molecular states.

In order to apply the variational procedure, the Hamiltonian of the system is now defined as

$$H = \sum_i T_i + \frac{1}{2} \sum_{i \neq j} V^{(2)}(\omega_i \omega_j), \quad (2)$$

where T_i is the rotational kinetic energy. The intermolecular potential has been taken as pairwise^{16,17} and $V^{(2)}(\omega_i \omega_j)$ represents the interaction potential between molecules i, j . Moreover, only rotonic contributions to the pair potential will be retained because crystal-field effects can be safely neglected in solid hydrogen.¹⁴

The average of the Hamiltonian H with orientational states as in Eq. (1) can be written as

$$\langle H \rangle = BF(\lambda_j) + V_{cl}G(\lambda_j)^2, \quad (3)$$

where F and G are functions of λ 's whose explicit expression can be found in Ref. 14. B is the rotational constant of the molecule and it is taken equal to 58 cm⁻¹ according to the result of Ref. 14. Moreover

$$V_{cl} = V(\Omega_1 \dots \Omega_N)/N, \quad (4)$$

where N is the number of molecules and $V(\Omega_1 \dots \Omega_N)$ is the orientational potential energy of the system when all the molecules are directed along the axes Ω_i . V_{cl} is thus the anisotropic part of the potential energy (per molecule) when all the molecules are aligned according to the structure that is considered.¹⁴

The parameters λ 's are obtained by minimizing the average of H in Eq. (3). At this level of approximation, the wave function (Ψ) of the system of molecules is the product of single-molecule eigenfunctions $\phi_i(\omega_i)$,

$$\Psi(\omega_1 \dots \omega_N) = \prod_i \phi_i(\omega_i) \quad (5)$$

with the λ 's determined by the minimization procedure.

It is easily seen that Ψ is also the ground-state wave function of the separable Hamiltonian H_0 defined as

$$H_0 = \sum_i T_i + 2GV_{cl} \sqrt{\frac{4\pi}{5}} \sum_i Y_{20}^{\Omega_i}(\omega_i) - NG^2V_{cl} \quad (6)$$

so that a detailed study of the eigenfunctions of the Hamiltonian H_0 allows the perturbative calculation of the energies and wave functions of the ground state of the full Hamiltonian H . The perturbation reads

$$\begin{aligned} \Delta H &= H - H_0 \\ &= \frac{1}{2} \sum_{i \neq j} V^{(2)}(\omega_i \omega_j) - 2GV_{cl} \sqrt{\frac{4\pi}{5}} \sum_i Y_{20}^{\Omega_i}(\omega_i) + NG^2V_{cl}. \end{aligned} \quad (7)$$

The first-order perturbative correction to the ground-state energy is null because the Hamiltonian H_0 has been built in such a way as to have an average equal to that of H in the ground state.

For the second-order perturbative correction, excited states of the Hamiltonian H_0 are to be derived. That can be done according to the methods shown in Refs. 14 and 15. The formulas for the resulting equations are obtained by means of standard methods of perturbation theory and will not be given here. It is may be important to notice that second-order perturbative corrections can involve both single-molecule and two-molecules rotational excitations. The former, named $\epsilon_1^{(2)}$, are due to virtual transitions to excited rotational states of one molecule whereas the latter, $\epsilon_2^{(2)}$, involve simultaneous rotational transitions of two molecules. The appearance of single-molecule excitations is due to the fact that the tentative molecular wave function in Eq. (1) is not the most general expression for a single-molecule state.

III. RESULTS

One of the first structures that was proposed for the BSP of hydrogen is the Pa3 one,¹⁵ that is the same structure of the ordered phase of orthohydrogen at low temperature. In that structure the centers of mass of the molecules sit on a face-centered-cubic (fcc) lattice and the molecular orientations are aligned along the diagonals of the cube. The details for such a structure can be found in Ref. 20.

However, the detection of the optical-phonon mode² indicates that the centers of mass of the molecules in the BSP form a hcp structure. On the other hand, the Pa3 orientational order in a hcp lattice implies topological frustration and con-

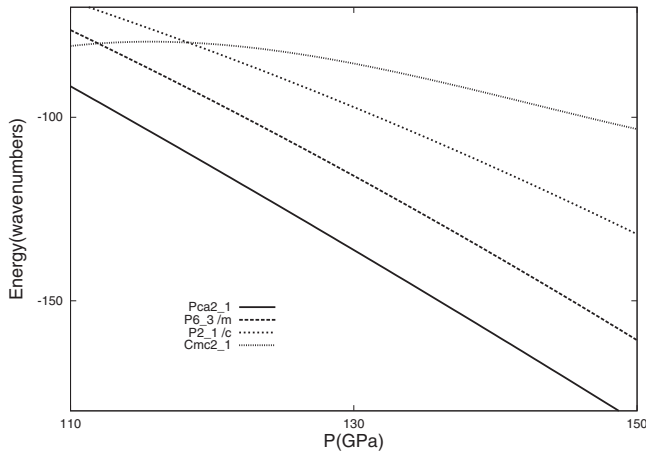


FIG. 1. Comparison of the ground-state orientational energies for different structures of solid hydrogen in the broken symmetry phase ($T=0$ K).

sequently the possibility either of a short-range-ordered structure or of incommensurate long-range order.¹² The frustration can be avoided, as suggested in Ref. 12, by using the eight molecules per cell structure $P6_3/m$ introduced by James for orthohydrogen.^{18,19} In order to study the Pa3-type orientational order on a hcp lattice, it is thus useful to start from a Hamiltonian H_0 with molecules oriented according to the $P6_3/m$ structure. Regarding this, it is important to remember that in the $P6_3/m$ structure, the molecules oriented orthogonally with respect to the c axis do not have a fixed azimuth (ϕ in Ref. 18). However, ϕ must be set equal to $\pi/2$ to reproduce the Pa3 orientational order most closely and that is the value used throughout this paper.

The other structures considered are $Pca2_1$, $Cmc2_1$, $P2_1/c$, and $C2/m$. They are described in Refs. 3, 5, and 8. They are orthorhombic structures with four molecules per cell. The azimuth and polar angles are (in degrees) 43.5 and 55.0 for $Pca2_1$, 46.0 and 90.0 for $Cmc2_1$, 37.6 and 59.3 for $P2_1/c$, 49.0 and 90.0 for $C2/m$.

V_{cl} for the different structures are reported in Table I at different specific volumes (in cm^3/mol) and for different orientational structures. Also the pressures are reported (in GPa) as obtained from the equation of state determined in Ref. 21 minus the contribution of thermal pressure.²² The pressures considered cover all the range of the BSP of hydrogen at $T=0$ K. It is seen that V_{cl} for $C2/m$ is much larger than for the other structures. Moreover, no mean-field ordered state is possible for such a structure and thus it will not be considered in the following.

In Fig. 1, the rotational ground-state energies per molecule are reported for four different structures in the pressure range of the BSP at $T=0$ K. It is seen that the $Pca2_1$ structure is the least energetic.

In Table II the three contributions to the rotational ground-state energy (per molecule) are reported for the different structures. The contributions are the ground-state energy of H_0 ($\epsilon^{(0)}$) and the two contributions to the second-order perturbative corrections ($\epsilon_1^{(2)}$ and $\epsilon_2^{(2)}$). Only the results for the specific volume of $2.7 \text{ cm}^3/\text{mol}$ are reported. No qualitative differences appear at the other densities.

TABLE II. Rotational energies for different structures at $v=2.7 \text{ cm}^3/\text{mol}$ (in cm^{-1}).

Structure	$\epsilon^{(0)}$	$\epsilon_1^{(2)}$	$\epsilon_2^{(2)}$	ϵ_{tot}
$Pca2_1$	-76.0	-0.1	-20.4	-96.5
$P6_3/m$	-55.8	-4.0	-20.8	-80.6
$P2_1/c$	-32.3	-7.2	-31.9	-71.4
$Cmc2_1$	-1.6	-11.1	-67.1	-79.8

It is seen that the $Pca2_1$ structure has a negligible $\epsilon_1^{(2)}$ which means that the eigenfunctions of H_0 are practically the molecular mean-field solutions.

The same is not true for the $P2_1/c$ and $Cmc2_1$ structures. They have non-null $\epsilon_1^{(2)}$. Also, the $\epsilon_2^{(2)}$ corrections for these two structures are larger than the one for $Pca2_1$. Particularly $Cmc2_1$ has a large second-order correction that amounts to almost 70 cm^{-1} for the double excitations. Questions can arise on the accuracy of the results due to this relatively large correction. It is to remember, however, that double excitations energies in hydrogen are larger than ten times that correction. Moreover, at the end of this section, the accuracy of the calculations will be established on a more quantitative basis.

Few more words are necessary for the $P6_3/m$ structure. As already stated, $P6_3/m$ can be considered a good system to approximate the Pa3-type ordering with hcp translational lattice. In the $P6_3/m$ structure, the $\epsilon_2^{(2)}$ correction is very close to the one for the $Pca2_1$ structure and the correction due to single-molecule rotational excitations is relatively small. That seems to indicate that the effect of the perturbation does not change much the orientation of molecular axes with respect to the $P6_3/m$ orientational order.

Contrary to this, Pa3-type ordering implies that the polar angle of the axis of the molecules that lie in the planes orthogonal to the c axis (ab planes) in the $P6_3/m$ structure, should change by the relatively large angle of 19.471° .

With regard to this consideration, it is interesting to analyze the case of the real Pa3 structure and compare it with a structure similar to $P6_3/m$, that is $R\bar{3}$. The Pa3 structure is not applicable to the BSP of hydrogen but the comparison is useful to estimate the energy correction due to a deviation of molecular axes of 19.471° . Moreover, the same comparison can be used to test the accuracy of the perturbative method, as it will be shown in the following.

Indeed, the energy of the Pa3 structure can be evaluated to a relatively high degree of accuracy. That is done by taking as V_{cl} in H_0 the potential energy of a classical system of rotors aligned along the cubic diagonals of a fcc lattice and then applying perturbation theory as it is shown in the previous section. In Table III the results are reported for the rotational energy. It is seen that the correction to the single-molecule excitation is null, thus indicating that the Pa3 structure is a mean-field solution. The correction due to double excitations to the unperturbed ground state amounts to -11.3 cm^{-1} which is small with respect to rotational excitations and thus indicates a fast convergence of the perturbative method.

Let us see now how $R\bar{3}$ can be considered an approximation of Pa3 system in a way similar to how $P6_3/m$ is an

TABLE III. Rotational energies for fcc-based structures at $v = 2.7 \text{ cm}^3/\text{mol}$ (in cm^{-1}).

Structure	$\epsilon^{(0)}$	$\epsilon_1^{(2)}$	$\epsilon_2^{(2)}$	ϵ_{tot}
Pa3	-133.2	0.0	-11.3	-144.5
$R\bar{3}$	-67.0	-51.3	-18.8	-137.1

approximation of the hcp-based Pa3 system. In the Pa3 structure the translational lattice is fcc. The fcc lattice is close packed and similar to the hcp one, the difference consisting in the stacking sequence of the ab planes. Thus, in the structure approximating Pa3, the molecules are directed as in the $P6_3/m$ structure but the stacking sequence of the ab planes is as in the fcc system. The resulting structure is actually a rhombohedral one with space group $R\bar{3}$ in the international notation.²³ Similarly to what happens in comparing the Pa3-type order on hcp with the $P6_3/m$ system, also in this case some of the molecules of one structure must rotate by an angle of 19.471° to get the other structure. The results for the energy of such a rhombohedral system are reported in Table III. It is seen that now the perturbative term is large, particularly for the single-molecule excitation, indicating a large mixing of spherical harmonics and presumably a large reorientation of the molecular symmetry axes initially lying in the ab planes.

The comparison of the total rotational energies obtained by the two calculations shows that the perturbative method is effective in reproducing the energy of the Pa3 system starting from a structure similar to the $P6_3/m$. The accuracy with which that result is obtained is about 5%. The same value can be taken as an estimate of the typical error that affects the rotational energies of hydrogen calculated in this paper.

IV. CONCLUSIONS

The energies of the orientational ground state of five structures of different symmetry for solid hydrogen in the

BSP have been calculated. The method starts from mean-fieldlike molecular states and then introduces correlation effects perturbatively. It accounts properly for the quantity of the system and avoids the approximations typical of simulation techniques. The anisotropic intermolecular potential is taken from Ref. 16 where it was derived from local-density-approximation calculations together with the assumption of a pairwise intermolecular potential. Moreover, the intermolecular potential is assumed to be formed by the same symmetry components¹⁶ as those of the gas-phase model.¹⁷

The results show that the $Pca2_1$ structure has the lowest energy, apparently also when including Pa3-type structures on a hcp lattice.

On the other hand, experimental results¹² seem to indicate that, at least for deuterium, a Pa3-type orientational order on hcp lattice structure is to be preferred.

With regard to this result, it is may be worth to note that the most important component in the anisotropic potential in the gas phase is due to the quadrupole-quadrupole interaction.¹⁷ Such a result is true also for the potential model that has been used in this work. Actually this model was obtained¹⁶ by multiplying the gas-phase potential¹⁷ by a simple density-dependent renormalization factor. In such a procedure the symmetry properties of the potential are not altered, particularly the interacting quadrupoles are supposed to remain symmetric around the molecular symmetry axis as in the gas phase.

In the $Pca2_1$ structure that is reasonable because each molecule is fully symmetric along its molecular axis. In the $P6_3/m$ system, however, the two quadrupole components orthogonal to the symmetry axis are not necessarily equal, thus changing drastically the symmetry of the interaction.¹⁹ Moreover, in Ref. 19 it is shown that an anisotropy of the orthogonal components of the molecular quadrupole moment can be responsible for a decrease in the orientational energy. It would thus be of interest to know how the molecular quadrupole moments are changed in the crystal structure, particularly the components orthogonal to the molecular axis.

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