

ORIENTATION ORDER IN SOLID ORTHO-H₂†

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Past attempts^{1,2} to provide a theory of the ordering of the molecules in solid ortho-H₂ have for the most part been based on the assumption that the molecular lattice is rigid, of fcc or hcp form, and that the orientational coupling of the molecules arises from a quadrupole-quadrupole coupling. Recent x-ray³ and infrared experiments⁴ have indicated that the phase transition in solid ortho-H₂ is accompanied by a change in the form of the molecular lattice from fcc in the low-temperature phase to hcp in the high-temperature phase. If this is correct, a complete theoretical discussion of the transition will be complicated by changes in the free energy associated with the change in the molecular lattice. It is not the purpose of this Letter to give a full discussion of this transition, but to point out that previously existing treatments based on the fixed-molecular-lattice model are deficient in that the assumed equilibrium molecular orientations are not self-consistent, or are restricted to consideration of excessively simple types of orientational ordering. It will be shown that a variational treatment of the molecular ordering in solid ortho-H₂ that is self-consistent within the framework of the internal-field approximation leads to the calculation of free energies decidedly lower than those previously calculated for either fixed-lattice model.

The Hamiltonian for the model to be considered is

$$H = \sum_i H_i(\vec{\Omega}_i) + \frac{1}{2} \sum_i \sum_j V_{ij}(\vec{\Omega}_i, \vec{\Omega}_j), \quad (1)$$

where H_i is the rotational energy of a rigid rotator that represents a hydrogen molecule with fixed center of gravity, $\vec{\Omega}_i = (\theta_i, \varphi_i)$ describes the orientation of the molecule on site i , and V_{ij} is the potential energy of interaction of molecules i and j .

In the internal-field approximation, one treats each molecule i as subject to a fixed effective field $U^i(\vec{\Omega}_i)$ that represents its interactions with the other molecules. This effective field determines a set of orthonormal stationary-state functions ψ_μ^i that occur with probabilities P_μ^i independently of the states of the other mole-

cules in the crystal. Given the $U^i(\vec{\Omega}_i)$, one can, in principle, determine the ψ 's by solving

$$\{H_i + U^i\} \psi_\mu^i = \epsilon_\mu^i \psi_\mu^i, \quad (2)$$

and construct a corresponding set of crystal wave functions

$$\Psi_{\{\mu\}} = \prod_i \psi_{\mu_i}^i \quad (3)$$

that would occur, in a canonical ensemble, with probabilities

$$P_{\{\mu\}} = \prod_i P_{\mu_i}^i, \quad (4)$$

where $\{\mu\}$ denotes a set of μ_i and

$$P_\mu^i = \exp(-\beta \epsilon_\mu^i) / \sum_\nu \exp(-\beta \epsilon_\nu^i). \quad (5)$$

Self-consistency requires, not only that the ψ_μ^i and P_μ^i be derivable from the $U^i(\vec{\Omega}_i)$, but that

$$U^i(\vec{\Omega}_i) = \sum_{j\nu} \langle \psi_\nu^j | V_{ij} | \psi_\nu^j \rangle P_\nu^j, \quad (6)$$

where the sum is over all possible states of all other molecules of the crystal. It can be shown⁵ that

$$F_a = \sum_{\{\mu\}} [\langle H \rangle_{\{\mu\}} P_{\{\mu\}} + k T P_{\{\mu\}} \ln P_{\{\mu\}}] \quad (7)$$

is minimized, for given T or β , by ψ 's and P 's that are self-consistent, and that F_a is still an upper limit to the free energy F of a system with Hamiltonian H at the temperature T . In this sense, the ψ_μ^i and P_μ^i determined by the above equations are the most appropriate ones for the description of the model at temperature T .

In the case of solid ortho-H₂, T is so low and the orientational coupling is so small that one can restrict attention to molecular orientational states for which $J=1$ is a good approximate quantum number⁶:

$$\psi_\mu^i = \sum_{M} c_{\mu M}^i Y_{1M}. \quad (8)$$

If one computes F_a by summing over any such

incomplete orthonormal set of functions, one obtains an upper limit to F . Minimization of F_α to variation of the sets of c 's and P 's yields ψ_μ^i that are correct zero-order solutions of Eq. (2) (U^i being considered as the perturbation), ϵ_μ^i that are corresponding first-order perturbed energies, and $P_{\mu i}^i$ that satisfy Eq. (5) when one sums over the finite set of states considered. For best results it is, however, essential that the U^i satisfy Eq. (6), and that the ψ_μ^i be correct zero-order functions for the perturbation function U^i . To assume that there is an "axis of quantization," the same for all molecules, and that the ψ_μ^i have the forms Y_{10} or $Y_{1,\pm 1}$, is highly restrictive; it may be incompatible with self-consistency.

On the other hand, without further loss of generality, one can restrict attention to real correct zero-order functions

$$\psi_\mu^i = \sum_\alpha \gamma_{\mu\alpha}^i \varphi_\alpha, \quad (9)$$

where⁷

$$\begin{aligned} \varphi_1 &= (1/\sqrt{2})(-Y_{11} + Y_{1-1}), \\ \varphi_2 &= (i/\sqrt{2})(Y_{11} + Y_{1-1}), \\ \varphi_3 &= Y_{10} \end{aligned} \quad (10)$$

are axially symmetric about the x , y , and z axes, respectively, and the $\gamma_{\mu\alpha}^i$ are direction cosines of the axis of symmetry of ψ_μ^i with respect to the (x, y, z) axes. By appropriately defining the reference axes x, y, z for each individual molecule, one can make

$$\psi_\mu^i = \varphi_\mu(\vec{\Omega}_\mu^i). \quad (11)$$

The orientational distributions for the three states of molecule i are then axially symmetric about these x, y, z axes, and all have the same form as $|Y_{10}|^2$ with respect to their various symmetry axes. This is an immediate consequence of restricting attention to real ψ 's with $J=1$, and is independent of T and the form of the orientational coupling. These latter factors do, however, determine the self-consistent choices of the reference axes and P 's.

The quadrupole-quadrupole interaction of molecules i and j can be expressed⁸ as

$$\begin{aligned} V_{ij} &= (20\pi/9)(70\pi)^{1/2} \Gamma_{ij} \sum_{MN} C(224; MN) \\ &\times Y_{2M}(\vec{\Omega}_i) Y_{2N}(\vec{\Omega}_j) Y_{4, M+N}(\vec{\Omega}_{ij})^*. \end{aligned} \quad (12)$$

Here $C(J_1 J_2 J; M_1 M_2)$ is a Clebsch-Gordan coefficient,⁹ and

$$\Gamma_{ij} = 6e^2 Q^2 / (25R_{ij}^5), \quad (13)$$

where Q is the effective molecular quadrupole moment and R_{ij} is the separation of the molecular centers. If this is the only orientational coupling, it follows from the assumptions of the preceding paragraph and from Eq. (12) that

$$U^i = \sum_M \kappa_M Y_{2M}(\vec{\Omega}_i), \quad (14)$$

with $\kappa_M = (-1)(M + |M|)/2\kappa_{-M}$, since U^i must be real.

In applying these results to the case of ortho- H_2 molecules on a rigid fcc lattice, one can be guided by the known structure of the low-temperature α phase of N_2 , in which there is also a fcc molecular lattice and the orientational couplings of the molecules have the character of quadrupole-quadrupole coupling.¹⁰ In α - N_2 the molecules are distributed over four simple cubic sublattices, with the molecules on each sublattice directed along a different threefold axis of the crystal; through the center of each molecule there passes a single threefold axis of the average charge distribution of the rest of the crystal.¹¹ The four sublattices are equivalent, except for orientation and translation in space. The space group is $Pa\bar{3}(T_h^6)$. It is natural to assume that in fcc ortho- H_2 , the orientational distributions are axially symmetric about equilibrium configurations that are similarly oriented, and that the sublattices are similarly equivalent. These assumptions, applied to molecules other than the i th, imply that the average charge distribution around molecule i will have a simple threefold axis of symmetry in the equilibrium direction assumed to be characteristic of molecules on that sublattice. This is consistent with Eq. (14) only if

$$U^i = \kappa_0 Y_{20}(\vec{\Omega}_i), \quad (15)$$

with the z_i axis along the threefold axis. From this it follows that one of the ψ_μ^i will have the same axis of symmetry, while the other two ψ_μ^i correspond to a twofold degenerate level and together make a contribution to the average charge distribution that is axially symmetric about the same axis. The derived charge distribution of molecule i thus has the symmetry assumed for other molecules on the same

sublattice; assumed symmetries of the molecular distributions are self-consistent. The equivalence of the sublattices leaves only a single potential constant κ_0 to be determined. It also implies that for every molecule

$$P_1^i + P_2^i + P_3^i = 2P_1 + P_3 = 1, \quad (16)$$

in view of the degeneracies of the orientational states ψ_1^i and ψ_2^i . One can make a straightforward calculation of κ_0 and F_a in terms of

$$\rho = 1 - P_3. \quad (17)$$

Neglecting all interactions except those between nearest neighbors, one finds

$$F_a/N = -(19/3)\Gamma[1 - 3\rho + (9/4)\rho^2] \\ + kT[\rho \ln \rho + (1 - \rho) \ln(1 - \rho) - \rho \ln 2].$$

The problem has then been reduced to the form considered by Strässler and Kittel.¹² Their arguments lead to the conclusion that at $T = 0$ there is an ordered phase with $P_3 = 1$. As T increases, P_3 falls, reaching the value $\frac{2}{3}$ at a temperature T_C defined by $kT_C = -19\Gamma/(4 \ln 2)$. If $\Gamma/k = 0.654^\circ\text{K}$,¹³ $T_C = 4.48^\circ\text{K}$. At this point the rigid-lattice model undergoes a first-order orientational transition as P_1 , P_2 , and P_3 abruptly assume the common value $\frac{1}{3}$ characteristic of the orientationally disordered phase, which is stable at all higher T . The numerical value of $-(19/3)\Gamma$ obtained here for $F_a(T=0)/N$ is to be compared with the corresponding value of $-\frac{7}{2}\Gamma$ of Ref. 1, for the case of a fcc lattice and for a simpler orientational ordering that is self-consistent, but merely makes $F_a(T=0)$ a local minimum that lies far above its absolute minimum.

In the case of the hcp molecular lattice, there is no similar guide in the treatment of ortho- H_2 , since the molecular orientations in hcp $\beta\text{-N}_2$ have not been uniquely determined. However, a classical discussion of the ordering of quadrupoles at zero temperature has been given for a limited number of low-symmetry lattices.¹⁴ Quantum-mechanical treatments of ortho- H_2 with the same equilibrium orientations of the molecules yield, for $T=0$, free energies F_a

that differ only by the factor $4/25$. Of the structures considered in Ref. 14, that which yields the lowest free energy has lattice symmetry $Pca2_1$. Generalizing the self-consistent quantum-mechanical treatment of this structure to higher T , one finds that molecular equilibrium orientations change with T , instead of being constant, as in the case of the fcc lattice. The $Pca2_1$ structure, treated with nearest-neighbor interactions only, yields $F_a(T=0)/N = -5.72\Gamma$, and undergoes a second-order transition to the orientationally disordered phase at 4.50°K . These values are to be compared with the corresponding values -1.125Γ and 1.47°K , respectively, of Ref. 2.

Though neither of the present treatments of fixed-lattice models can be confidently compared with experiment, they make clear the importance of self-consistency in the treatment of orientational ordering.

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