Theoretical Evidence for a Reentrant Phase Diagram in Ortho-Para Mixtures of Solid H$_2$ at High Pressure

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We develop a multiorder parameter mean-field formalism for systems of coupled quantum rotors. The scheme is developed to account for systems where ortho-para distinction is valid. We apply our formalism to solid H$_2$ and D$_2$. We find an anomalous *reentrant* orientational phase transition for both systems at thermal equilibrium. The correlation functions of the order parameter indicate short-range order at low temperatures. As the temperature is increased the correlation increases along the phase boundary. We also find that even extremely small *odd-J* concentrations (1%) can trigger short-range orientational ordering.

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Quantum effects dominate the low temperature ($T <$ 200 K) phase diagram of solid molecular hydrogen in a wide range of pressures from ambient up to ~100 GPa [1,2]. In this regime the coupling between molecules is smaller than the molecular rotational constant, so quantum effects are generally described by means of weakly coupled quantum-rotor models [3]. Homonuclear molecules (H$_2$ and D$_2$) can assume only even or odd values of the rotational quantum number J, depending on the parity of the nuclear spin. Important differences exist in the phase diagrams of even-J (para-H$_2$ and ortho-D$_2$), odd-J (ortho-H$_2$ and para-D$_2$) and all-J (HD) species. (For a summary of experimental results on the orientational ordering in H$_2$, D$_2$, and HD, see Fig. 1(b) of Ref. [4].) At low pressure or high temperature, even-J species are found in a rotationally disordered free-rotor state (phase I). Increasing pressure causes an increase of the intermolecular coupling and eventually leads to an orientationally ordered state (phase II). Odd-J systems, on the other hand, are orientationally ordered at low temperature and ambient pressure and remain ordered as pressure is increased. The stronger tendency of ortho-H$_2$ to order can be traced to the fact that its $J = 1$ lowest rotational state allows for a spherically asymmetric ground state, unlike the $J = 0$ ground state of even-J species. The pressure-temperature phase diagram of HD exhibits a peculiar *reentrant* shape [5]. Reentrance refers to phase diagrams where in some range of pressure the system reenters the disordered phase at ultralow temperatures (see HD in Fig. 1). The zero-temperature orientationally disordered phase is characterized by an energy gap against $J = 1$ excitations. When this gap is sufficiently small and the temperature is finite, the thermally generated $J = 1$ excitations suffice to induce ordering, which is then reentrant, as also shown by mean-field theory [6–8]. Reentrance is also found in models of two-dimensional rotors [9], such as the quantum anisotropic planar rotor model [10–12].

High pressure experiments have focused mainly on the behavior of pure species. While understanding the orientational transition on ortho-para mixtures of quantum rotors in two and three dimensions is a problem of long-standing theoretical and experimental interest [13–21], less attention has been given to establishing the effects of ortho-para distinction. Exceptions [13–16] are the investigation of vibrons in ortho-para mixtures by Feldman *et al.* [13] and a recent work by Goncharov *et al.* [14], where ortho-D$_2$ mixed with small amounts of para-D$_2$ indicated that the possibility of an orientationally frustrated phase between phases I and II (phase II$'$). Phase II$'$ persisted for a narrow pressure range (~2 GPa) for a thermally equilibrated ortho-para mixture.

At ambient pressure hydrogen is known to enter gradually a phase of short-range order (orientational glass) [19,21] when the concentration of ortho species is below ~53% [17–19]. Short-range order is believed to be a manifestation of the orientational frustration due to the
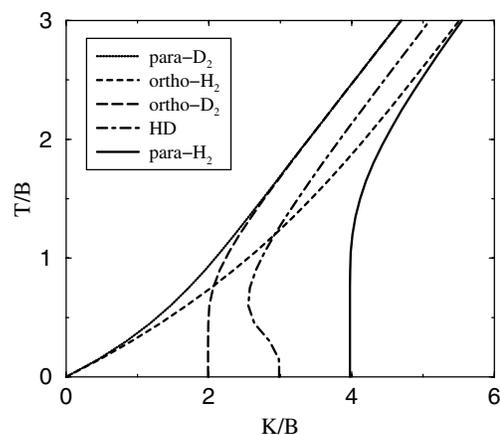
FIG. 1. Mean-field phase diagrams for coupled quadrupolar rotor models corresponding to solid molecular hydrogen and various isotopes.

random location of ortho molecules in the lattice and eventually transforms into long-range order at ortho concentrations approaching unity. The pressure-induced increase of the intermolecular anisotropic coupling causes a decrease of the minimum concentration of ortho species required to trigger the orientational transition [1]. At extremely high pressures ($\sim$110 GPa) orientational freezing is observed also in pure para-H_2, as stated above. Ambient pressure experiments on pure species as well as on samples with fixed concentration are possible because the rate of interconversion between para and ortho H_2 species is extremely slow at low pressure. Samples with fixed ortho-para concentration are prepared by letting the system thermalize at the corresponding temperature for very long times and experiments are then performed at any other temperature by rapid heating or quench (*rapid* on the time scale of interconversion). At high pressures, however, the interconversion rate rises steeply [22]. At 58 GPa, the highest pressures where the conversion rate has been measured, interconversion takes place in the time scale of seconds. While interconversion is still orders of magnitude slower than molecular rotation, the ortho-para distribution in this range of pressure is likely to be determined by thermal equilibrium. On the other hand, ortho-para distinction is still valid.

Previous theoretical studies addressing quantum effects in compressed hydrogen (mean-field [6–8] or quantum Monte Carlo [23–26] studies) have in most cases neglected the distinction between even-J and odd-J species [23], and in those cases where the distinction was explicitly considered, the analysis was restricted to pure even-J or odd-J species [24–26]. On the other hand, theoretical modeling of mixed ortho-para systems [13,17,20] at low pressure is generally limited to $J = 0/J = 1$ states [17,20]. This is not an accurate model for compressed H_2, as pressure and temperature cause a non-negligible admixture of rotational states with higher J's in the ground state of both ortho and para species. A binary alloy model [13] was also used to analyze the low-pressure vibrons in ortho-para mixtures.

In order to calculate the phase diagram of ortho-para mixtures of hydrogen in the solid phase we develop a multiorder parameter (MOP) mean-field theory which accounts explicitly for ortho-para distinction in systems of coupled rotors. Our formalism enables us to treat a system of $\sim$3000 molecules, which would be extremely computationally intensive with quantum Monte Carlo calculations. Our formalism also includes correlations due to ortho-para distinction, a feature that is absent in standard mean-field theory. We apply the formalism to a system of coupled quadrupolar rotors whose centers of mass form a face-centered cubic lattice. We find that the phase line separating the orientationally disordered state (phase I) from the orientationally ordered state is *reentrant* in the case of thermally equilibrated ortho-para mixtures for both H_2 and D_2. We also find that orientational order is short ranged

at low temperatures. The validity of our conclusion is supported by the fact that for the two-dimensional model mean-field theory [9,10] is in agreement with quantum Monte Carlo [11,12] simulations on the overall shape of the phase diagram.

The Hamiltonian of a system of N coupled quadrupolar quantum rotors interacting through a quadrupole-quadrupole potential can be written in the form

$$H = B \sum_{i=1}^{N} \hat{L}_i^2 + \frac{K}{2} \sum_{i<j}^{N} \left(\frac{R_0}{R_{ij}}\right)^5$$
$$\times \sum_{m,n} C(224; mn) Y_{2m}(\Omega_i) Y_{2n}(\Omega_j) Y_{4m+n}^*(\Omega_{ij}), \quad (1)$$

where B is the molecular rotational constant, K is the coupling strength, $C(224; mn)$ are Clebsch-Gordan coefficients, Ω_i denote the coordinates of rotor i, and Ω_{ij} denote the direction of the vector connecting rotors i and j. We define R_0 to be the nearest neighbor distance; R_{ij} is the distance between molecules i and j. Our MOP mean-field theory is based on the trial Hamiltonian

$$H_0 = B \sum_{i=1}^{N} \hat{L}_i^2$$
$$+ K \sum_{i<j}^{N} \left(\frac{R_0}{R_{ij}}\right)^5 C(224; 00) Y_{20}(\Omega_i) \gamma_j Y_{40}^*(\Omega_{ij}), \quad (2)$$

where γ_i are parameters. Variation of the free energy leads to the self-consistent expression

$$\gamma_i = \langle Y_{20}(\Omega_i) \rangle_0. \quad (3)$$

Since the trial Hamiltonian in Eq. (3) is a sum of single-rotor Hamiltonians, it follows that for each γ_i in Eq. (3) the average needs to be performed over the corresponding coordinate Ω_i only. Ortho-para distinction can be implemented by restricting a particular average to be over odd-J or even-J states.

Since in this study we are interested only in the phase diagram we expand to first order in the potential [9]. Such an expansion is expected to be valid here, since the transition between the long-range ordered state and the disordered state is only weakly first order [4]. Furthermore, the transition between the short-range ordered state and the disordered state is known to be continuous at ambient pressure [17]. The resulting expression can be written

$$\gamma_i = K3\sqrt{\frac{2}{35}} \Phi_i \sum_j \gamma_j \left(\frac{R_0}{R_{ij}}\right)^5 Y_{40}(\Omega_{ij}), \quad (4)$$

where Φ_i is the phase correlator defined as $\Phi_i = \int_0^\beta d\tau \langle Y_{20}[\Omega(0)] Y_{20}[\Omega(\tau)] \rangle_{\text{free},i}$. The averaging is to be performed over a free rotor at inverse temperature β, and ortho-para distinction can be invoked by restricting the average as described above. Thus, for a given temperature and rotational constant, Φ_i can take on two values depend-

ing on whether rotor i is odd-J or even-J. Order will be signaled by nonzero solutions for γ_i, disorder by solutions in which all γ_i are identically zero. The standard mean-field theory [6,7] is automatically recovered for pure systems.

We calculated the phase diagrams for systems of a fixed odd-J fraction, as well as at the thermal equilibrium distribution, taking account of nuclear spin degeneracy. D_2 and H_2 differ by the values of the rotational constants ($2B_{D_2} = B_{H_2}$) and in the degeneracies of states. Ortho (para) H_2 is restricted to be odd-J (even-J) angular momentum and in D_2 the reverse. In our calculations for mixed systems, configurations of 2916 molecules on a face-centered cubic lattice were used. For a given odd-J fraction 20 configurations are generated. A cutoff distance of 2.65 times the lattice constant is used; thus 134 nearest neighbors are included in the interaction calculation. The phase transition point is obtained by diagonalizing Eq. (4) (which is a matrix equation) and finding the lowest coupling constant for which a nonzero solution exists.

In Fig. 1 we present the results of standard mean-field theory phase diagrams of pure odd $- J$/even $- J$ of H_2 and D_2, and HD, all in excellent qualitative agreement with the experimental results [see Fig. 1(b) of Ref. [4]]. The energy scale is defined to be the rotational constant of the H_2 molecule. The main difference between the phase diagrams of odd-J and even-J systems is accurately captured, namely, that at low pressures odd-J systems are always ordered, whereas even-J systems order at finite pressures. As expected from experiment odd-J D_2 orders at a lower coupling strength that odd-J H_2, and the reentrant phase transition in HD is also well reproduced by mean-field theory [6–8].

In Fig. 2 the results of the formalism presented above are shown for solid H_2. As the ortho concentration is decreased the system tends towards disorder entering the ordered state at higher coupling constants for a given temperature.
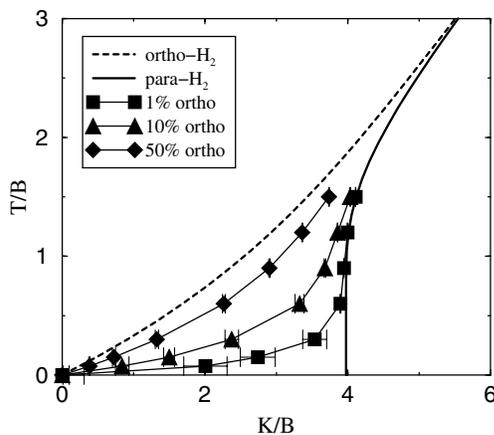
A noteworthy result of our calculations is that even at an ortho concentration of 1% the system enters an ordered state at coupling constants quite different from that of pure para hydrogen, and that for any ortho concentration the ground state is always ordered. The 50% ortho system is very close to the pure ortho one. Our results are consistent with the phase diagram shown in Fig. 1 of Ref. [15] in which the pure para-H_2 phase transition occurs at $\sim$110 GPa, and ortho containing samples show ordering at lower pressures.

In order to assess the nature of the ordering we calculated correlation functions of the local order parameters $\{\gamma_i\}$. This is an advantage of our multiorder parameter formalism over the standard mean-field theory, since in single-site mean-field theory only phases of complete order or disorder are possible. In particular, we have calculated

$$G(r) = \langle [\gamma(0)\gamma(r)]^2 \rangle. \tag{5}$$

The results along the phase line of the 10% ortho system of hydrogen are shown in Fig. 3. The correlation increases along the phase boundary with increasing temperature indicating the onset of long-range order. The onset of long-range order is due to the fact that ortho-para distinction ceases as temperature and coupling constant (pressure) are increased.

The orientational ordering of the system with ortho-para concentrations at thermal equilibrium is shown in Fig. 4 along with the phase diagrams of the pure systems (also shown in Fig. 1) for comparison. For H_2 and D_2 we calculated the phase diagrams via the MOP mean-field theory presented here, and via the standard mean-field theory. The resulting phase diagrams indicate reentrance in both D_2 and H_2. Reentrance is also seen [27] in the corresponding 2D model [10]. Reentrance is stronger in the case of H_2, due to higher relative weight of the odd-J contribution (nuclear spin degeneracy), and higher rotational constant (stronger quantum effects). The correlation functions for different temperatures along the reentrant

FIG. 2. Multiorder parameter (MOP) mean-field phase diagrams for coupled quadrupolar rotor models corresponding to solid molecular hydrogen at various ortho concentrations.
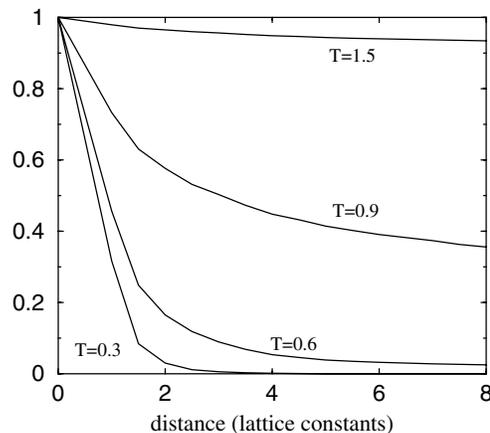
FIG. 3. Correlation functions along the phase boundary of the 10% ortho system of solid H_2.
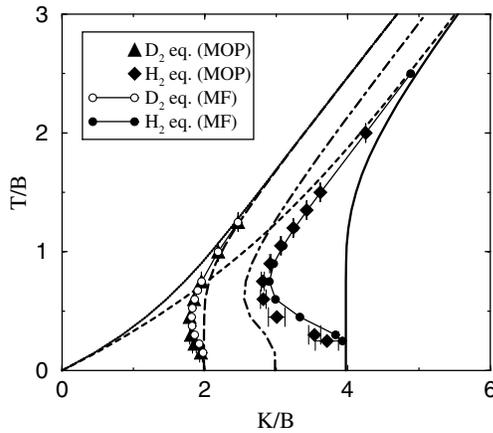
FIG. 4.   Phase diagrams of Fig. 1 and those of the pure systems H_2 and D_2 at thermal equilibrium distribution calculated using our multiorder parameter (MOP) mean-field theory and the standard mean-field theory (MF). For the mean-field phase diagrams, see the legend of Fig. 1.

phase diagram are shown for H_2 in Fig. 5. As the temperature increases correlation increases along the phase boundary. At high temperatures ($T > 1$) the order is definitely long range. We conclude that short-range order may be present up to $T = 0.75$. In the case of D_2 reentrance is less severe.

In summary, we calculated the phase diagrams of solid hydrogen and its isotopes. We found that the I-II phase line is interspersed by another phase, likely to be orientationally frustrated, as suggested by the experiments of Goncharov et al. [14]. For a thermal distribution of ortho-para rotors we find a reentrant phase diagram for both H_2 and D_2. At low temperatures the order is short ranged. Most experimental signatures of the long-range
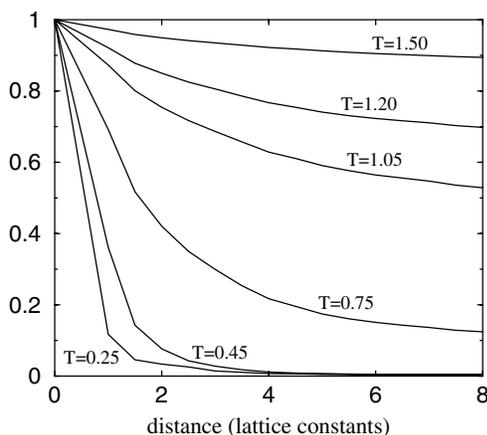
FIG. 5.   Correlation functions along the phase boundary of the solid H_2 at thermal equilibrium.

ordered phase are well-known [1,2]; the short-range ordered phase may be seen by probing the distribution of the local order parameter. While nuclear magnetic resonance [17] is a useful probe, it may be difficult to apply at high pressure. The II′ phase was found [14] by investigating the Raman vibronic shift and it is known to be sensitive in ortho-para mixtures [13]. Rotational Raman lines are also sensitive to local order. Experimental studies to resolve the issues raised here would be helpful.

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