Quantum and Classical Orientational Ordering in Solid Hydrogen

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We present a unified view of orientational ordering in phases I, II, and III of solid hydrogen. Phases II and III are orientationally ordered, but the ordering objects in phase II are angular momenta of rotating molecules, whereas in phase III the molecules order themselves. This concept provides a quantitative explanation for the vibron softening, libron and roton spectra, and the increase of the vibron effective charge in phase III, as well as a framework for understanding the topology of the phase diagram and ortho-para state at high pressure. The effective charge and the infrared and Raman vibron frequency shifts are all linear in the order parameter in phase III. [S0031-9007(97)02385-5]

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In the last decade, a wealth of information about the phase diagram of hydrogen at high pressures has been collected. However, even a qualitative understanding of the phase transformations in the solid is not yet in hand. Three phases are known in the experimentally accessible range of pressures, which extend to 300 GPa and span over an order of magnitude in compression (Fig. 1). The high-temperature phase consists of a closed packed lattice of freely rotating and, on average, spherically symmetric molecules [1]. The two low-temperature phases have lower symmetry, which implies at least partial ordering of the molecules [1–3]. The properties of the two phases are so distinct, however, that more general concepts than mere crystallographic dissimilarities must be invoked to understand the origin of various phenomena they exhibit. The most unusual features include a dramatic increase in the infrared (IR) activity of the main vibron, a strong vibron softening, an unconventional geometry of the phase boundaries, and drastic changes in rotational excitations [2–4]. Here we show that these disparate observations can be understood in terms of the concept of quantum versus classical orientational ordering in the dense solid.

Hydrogen at low temperature and pressure forms the only molecular quantum solid. As such, the excitations of the freely rotating molecules in phase I can be described by the rotational quantum number J. This contrasts with heavier molecular crystals, where molecular rotation is substantially hindered even at low pressures [5]. The properties of H_2 and D_2 crystals greatly depend on the ground state of the constituent molecules ($J = 0$ or 1), which in turn is determined by their total nuclear spin. Here we consider hydrogen solids having a substantial fraction of spherically symmetric ($J = 0$) molecules (e.g., para-H_2 or ortho-D_2). Solids containing a sufficiently high concentration of $J = 1$ molecules, including o-H_2/p-D_2, transform to a cubic phase (space group $Pa\bar{3}$) even at ambient pressures (e.g., 3.8 K) [5]. In this transition, the direction of angular momenta of individual molecules orientationally order. This transformation is driven by quadrupolar interactions, where the

ordered phase is the lowest-energy configuration for classical quadrupoles [5].

A different kind of orientational ordering occurs in phase II. In this case, solids consisting of spherically symmetric molecules (p-H_2 or o-D_2) transform to ordered (broken symmetry) phases at ~110 GPa in p-H_2 [3] or at ~28 GPa in o-D_2 [6] at $T \rightarrow 0$ K (Fig. 1). This transition was interpreted as arising from increasing intermolecular interaction that results in mixing of higher angular momenta (e.g., $J = 2, 4$ for p-H_2) into the ground state molecular wave function and imparting a finite angular moment for the molecules [6]. The nonzero angular momenta can then order, with molecular centers forming a lattice derived from hcp [1]. Even more exotic ordering schemes may exist for normal H_2 or D_2 [7]. We will refer to these low-pressure ordered phases collectively as phase II. Here ortho-para distinctions are valid in the sense that the wave function can be defined for individual molecules and is either even or odd.

One expects that at still higher pressure intermolecular interactions become so strong that all higher J states have
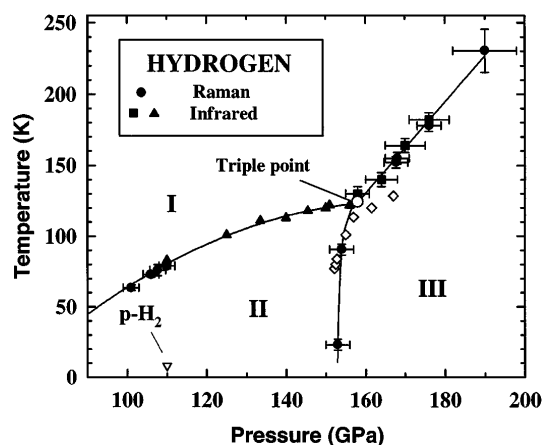

FIG. 1. Phase diagram of hydrogen at megabar pressures obtained from Raman and infrared measurements [1,2,12]. The open triangle and diamonds are from Ref. [3].

the same weight; that is, the molecules behave classically and can orientationally order as classical rotors. Such a pressure-driven transformation between two kinds of orientationally ordered states would be a transition between a quantum and a classical crystal. This would be unique in relation to known quantum crystalline transitions (e.g., solid He) in the sense that the quantum-classical distinction considered here is associated with rotational degrees of freedom. As discussed above, spectroscopic changes at the II-III transition near 150 GPa are significantly larger than those due to orientational ordering at the I-II boundary. Not surprisingly, the higher-pressure transition has been the focus of considerable theoretical study recently (e.g., [8–10]). We show that new and previously reported data, including the orientational order parameter, vibron effective charge, changes in roton and libron spectra, geometry of the phase diagram, and evolution of the ortho-para state, point to the transition to phase III as being such a transformation. This provides a simple and transparent model for orientational ordering in phases I, II, and III.

1. Order parameters and infrared intensity.—We first consider the increase in IR vibron absorption associated with passage into phases II and III (Fig. 2). At 167 GPa and 85 K, the effective charge of the vibron is $q^* \approx 0.032e$ [11]; it increases with pressure and reaches $0.037e$ at 230 GPa. In phase II, in contrast, q^* is $\lesssim 0.004e$ at 140 GPa and the same temperature, whereas phase I is characterized by a weak and broad disorder-induced band [4,12,13]. The origin of these differences can be understood from analysis of the temperature dependence of q^*. We find a striking correlation between the temperature dependence of $(q^*)^2$ (integrated intensity) and $\Delta\nu$, the frequency shift with respect to its value at the transition point (P_c, T_c) for phase III, i.e., $(q^*)^2 \propto \Delta\nu^2$ over the entire P-T range investigated [Fig. 3(a)]. The observation of $q^* \propto \Delta\nu$ can be interpreted to mean that both quantities

are linear functions of a scalar order parameter, $\Delta\nu \propto \eta$ and $q^* \propto \eta$ [14]. Recent measurements of the Raman vibron in phase III (for D_2) [15] showed that the temperature dependence of the frequency shift (proportional to η) can be described by a Maier-Saupe model, which characterizes the orientational ordering of classical rotors and initially was derived for liquid crystals. We show here that the same is true for the IR intensity and both IR and Raman shifts [1,3] [Fig. 3(b)]. In contrast, the normalized order parameter in phase II is qualitatively different, being much steeper as a function of T/T_c (cf. Ref. [13]).

2. Magnitude of the effective charge.—We now show that not only the temperature dependence of η but also the magnitude of q^* can be understood within the proposed framework. Previously, the origin of the vibron intensity in phase III was examined from various electronic standpoints [8–10]. We note here that a condition for vibron IR activity is that the two atoms in a molecule are crystallographically inequivalent [16]. If the molecules have nonzero quadrupole moments, a nonzero electric field is then induced at the lattice sites, which in turn polarizes the molecules and creates an effective dipole moment [17]. We have estimated the magnitude of the effect for H_2 by calculating the induced field in several well-studied quadrupolar lattices. The total field is proportional to the quadrupole moment, $E = \beta Q/a^4$, where a is the lattice parameter. The component of the field along the H-H bond, $E_\parallel$, is $\beta_\parallel Q/a^4$. The values for β depend on the structure and orientation, but for a large class of structures they are of order unity [18]. For a static molecule in the zero-pressure solid, $Q \approx 0.5$ a.u. [5] and near the II-III transition a is ~ 3.3 bohr. At the equilibrium bond length ($d = 1.5$ bohr) the polarizability $\alpha_\parallel$ of the H_2 molecule is 6.72 bohr^{-3} [19], which gives an effective static charge $q = \alpha E/d \approx 0.025e$. To find
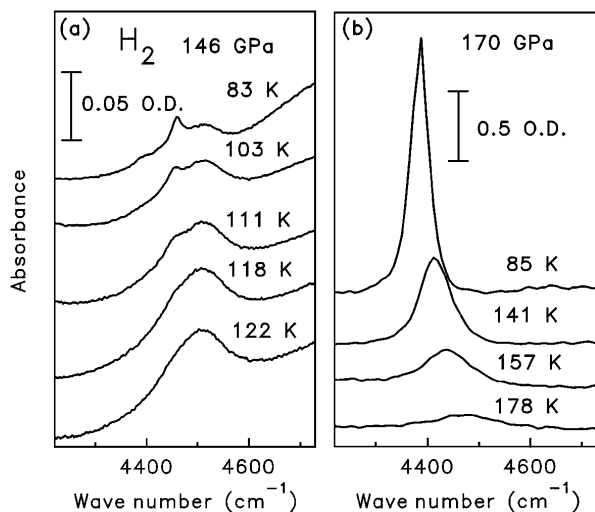

FIG. 2. Temperature dependence of IR vibron spectra. (a) I-II transition. (b) I-III transition.
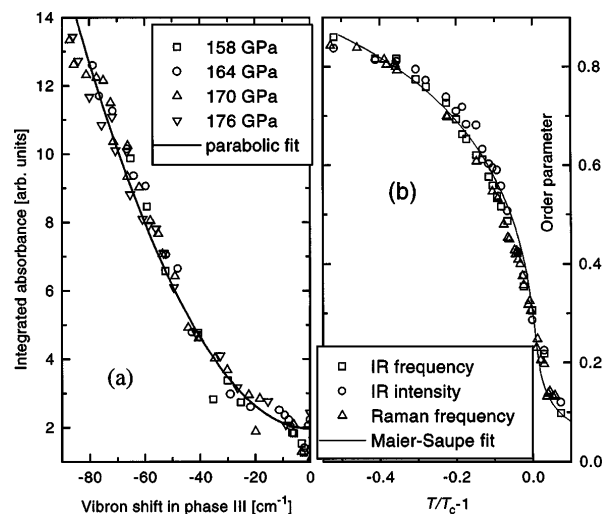

FIG. 3. (a) Experimental integrated IR intensity versus frequency shift $\Delta\nu$ for phase III. (b) Order parameter from IR intensity and IR and Raman frequency shifts at 176 GPa.

the dynamic charge, we substitute α by $d(\partial\alpha/\partial d)$. From Ref. [19], we have $q_d \approx 1.5q$, which gives $q^* \approx 0.06e$ for the total effective charge, close to the experimental value of $0.03-0.04e$ [20].

This result should be contrasted with the behavior of the vibron in "quantum" phase II. In this phase, the narrow absorption peak appears on the shoulder of the broad disorder-induced band (Fig. 2) [1,4]. This sharp peak is a symmetry-allowed IR-active vibron and signals the onset of orientational ordering of angular momenta. The maximum intensity of this vibron ($q^* \approx 0.004e$) is an order of magnitude smaller than that for phase III (e.g., at 165 GPa) at the same temperature [4,11]. Several factors reduce the effective charge in phase II compared to that in III: (a) In a pure quantum state in which $\{J,M_J\} = \{l,l\}$, the expectation value of Q is reduced by a factor of $(2l+3)/l$ [21] with respect to that of a static molecule, and (b) the polarizability perpendicular to the molecular bonds is smaller than that parallel. The smaller polarizability not only diminishes the static charge by 40%, but also reduces the dynamic charge by a factor of 3. As a result, the effective charge is reduced by $2-3.5$ from the change in $\langle Q \rangle$ and $2-2.5$ from the polarizability change, giving a total reduction by a factor of $5-10$, in agreement with experiment.

3. Rotons and librons.—The proposed picture further implies that elementary excitations corresponding to the angular degrees of freedom in the system (rotons and librons) must be very different in phases II and III. Indeed, IR and Raman data reveal a striking change in these low-frequency excitations upon crossing the II-III phase boundary. Figure 4 shows rotational and librational mode frequencies from new and earlier spectroscopic data up to 230 GPa. No discontinuity is observed in the broad roton bands at the I-II transition for normal H_2 (110 GPa and 85 K). In contrast, the rotons disappear at the II-III transition and are replaced by new excitations in the same energy range. This change can be understood by considering the difference in libron spectra for quantum and classically ordered phases. For the former, J remains a good quantum number and the roton excitations characteristic of the disordered phase are supplemented by $M_J \rightarrow M_{J'}$ "libron" excitations of the ordered phase, as in the $Pa\overline{3}$ structure of ortho-rich H_2 [5]. Likewise, phase II consists of *rotating* molecules with a similar set of excitations. In contrast, the molecules in phase III behave as classical objects (as in solid N_2), and J is no longer a good quantum number. The elementary excitations associated with rotational degrees of freedom are neither $J \rightarrow J'$ rotons nor $M_J \rightarrow M_{J'}$ transitions but are anharmonic classical librons, quantized angular oscillations about the equilibrium orientation in which full rotation is strongly hindered. Moreover, the phase III librons harden dramatically with pressure and extrapolate to zero about 70 GPa below the transition (Fig. 4). This strong pressure dependence is expected for librons and can be contrasted with
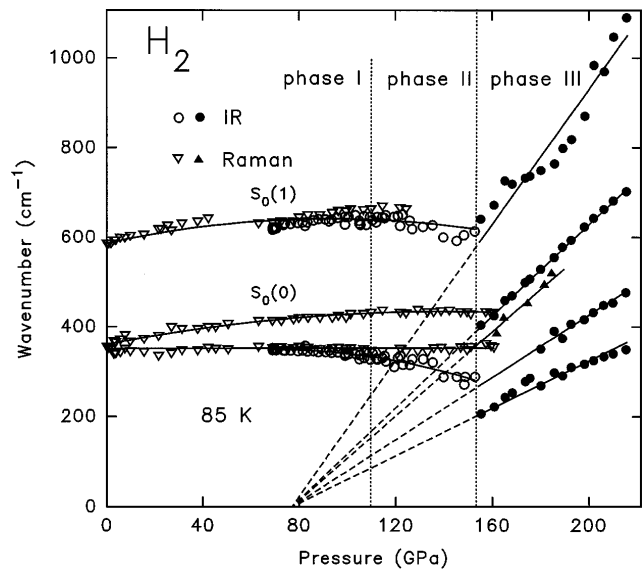

FIG. 4. Rotational and librational frequencies for phases I, II, and III of hydrogen (85 K)[1,4,11]. The IR data were obtained by subtracting the vibron frequency from IR combination bands measured. A new Raman band in phase III having a strong pressure dependence identical to one of the IR modes is shown. The dashed line suggests "latent soft mode" behavior of the librons.

the behavior of the higher frequency lattice mode, which shows at most a small discontinuity across the II-III transition [1]. These observations, together with the continuous and discontinuous changes in the vibrons [15], are indicative of a first-order, but nonreconstructive, mechanism for the transition.

4. Geometry of the phase diagram.—The geometry of the phase boundaries near the I-II-III triple point (Fig. 1) also fits the picture of a "quantum-classical" orientational transition. Near the triple point, now established for H_2 and D_2 [1,12,13,15], the I-II boundary is nearly horizontal, $dT_c/dP_c \lesssim 0.4$ K/GPa, while the II-III boundary is nearly vertical up to ~ 80 K, $dT_c/dP_c \gtrsim 30$ K/GPa in H_2; this effect is even more pronounced in D_2 [15]. Such a configuration is highly unusual for a crystallographic transition. One can use the Clapeyron equation, $\Delta V/\Delta S = dT_c/dP_c$, to estimate the volume change across each phase transition. Assuming an entropy change $\Delta S \approx 0.2R$/mole (Ref. [5], p. 238), we estimate ΔV at the I-II transition to be 0.0007cm^3/mol. An analogous calculation for the I, II-III transition gives about 0.05 cm^3/mol. Indeed, one should expect large changes in intermolecular forces for the latter because of modifications in quadrupole-quadrupole interactions [1]. This effect can be estimated for static molecules from the electrostatic energy of quadrupolar close-packed lattices, $U = 1.5\kappa Q^2/a^5$, $\kappa \approx 7$ [5]. Differentiating this with respect to volume, we calculate an "electrostatic" pressure of about 8 GPa, which gives 0.05 cm^3/mol at 150 GPa [23]. Note that the quadrupolar energy is reduced by a

factor of 4/25 [5] for rotating $J = 1$ molecules; this is consistent with the much smaller volume change at the I-II transition.

5. Ortho-para state. — The "quantum-classical" transition associated with phase III has important implications for the evolution of ortho-para states as a function of pressure. There is evidence for ortho-para distinguishability under moderate pressures, but its persistence to the megabar range has been a subject of debate [1]. The above analysis naturally leads to the conclusion that the wave function of the crystal in phase III can no longer be factored into individual molecular wave functions, so single-molecule ortho-para distinguishability is lost. In contrast, despite the mixing of J states in phase II, the notion of parity of the wave function of nuclei in an individual molecule is valid. This is supported by recent measurements for D_2: in phases I and II significant differences in IR and Raman bands are observed for samples starting out as pure ortho versus normal [7]; in phase III, however, the number and frequencies are identical and independent of sample history [12,13].

In conclusion, we suggest that orientational ordering in the high-pressure molecular phase of hydrogen (phase III) is qualitatively different from that observed at lower pressures (phases I and II). The molecules in phase III are orientationally ordered in the sense that the time average of the molecular bond direction is nonzero, whereas in phase II the ordering objects are axes of quantization of angular momentum. This concept provides a natural explanation for the striking IR vibron activity and other properties of phase III. Further quantitative treatment should take into account detailed structural changes at these transitions and such effects as zero-point motion (e.g., Ref. [9]).

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