Solid Molecular Hydrogen: The Broken Symmetry Phase

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By performing constant-pressure variable-cell *ab initio* molecular dynamics simulations we find a quadrupolar orthorhombic structure of $Pca2_1$ symmetry for the broken symmetry phase (phase II) of solid H_2 at $T = 0$ and $P = 110-150$ GPa. We present results for the equation of state, lattice parameters, and vibronic frequencies, in very good agreement with experimental observations. Anharmonic quantum corrections to the vibrational frequencies are estimated using available data on H_2 and D_2. We assign the observed modes to specific symmetry representations. [S0031-9007(97)02938-4]

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The quest for the structure of the high-pressure phases of hydrogen is a long standing one. Early predictions of an insulator-metal transition [1] led to a large body of experimental and theoretical work during the past 60 years. Metallization was not found as promptly as initially expected [2] but a rich phase diagram emerged. The current picture of the low and room-temperature phase diagram up to ∼230 GPa is essentially based on the optical studies performed in diamond anvil cell (DAC) devices during the past decade [3,4].

There is a consensus that hydrogen exhibits at least three different solid molecular phases. (1) At low pressures (<110 GPa for para-H_2) the centers of the H_2 molecules crystallize into an hcp lattice, but zero-point motion overcomes rotational energy barriers, leading to a free-rotator phase (phase I). (2) Between 110 and 150 GPa intermolecular interactions freeze the molecular rotations into an ordered broken-symmetry phase (BSP, or phase II). (3) Above ∼150 GPa, a third phase (H-A, or phase III) is attained, whose structure is unknown. Here we focus specifically on phase II. Optical measurements in phase II indicate the presence of two, possibly three, infrared (IR) active modes, in contrast to phase I, where only one mode is observed. Raman spectra show a single peak, at a frequency ∼10% lower than that of the IR modes. A consistent picture of the structural and dynamical properties of phase II is still lacking [5].

On the theoretical side, most of the existing work consists of static total energy calculations within the local density approximation (LDA). Zero-point energy (ZPE) of the protons has been in a few cases included *a posteriori* based on frozen phonon calculations [6,7]. Hexagonal close packed structures with two and four molecules per unit cell appear to be the strongest candidates for the ground structure of phase II, but the relative orientation of the molecules is uncertain [8–10]. Cubic structures were also suggested [9]. This uncertainty persists, due to the incomplete optimization of the lattice parameters and the *a priori* selection of a particular space group symmetry in static calculations. *Ab initio* molecular dynamics simulations, which do not rely on the choice of a specific space group, have also been reported [11,12]. However, these earlier attempts were hampered by a fixed simulation cell and a poor Brillouin zone (BZ) sampling.

We report extensive *ab initio* molecular dynamics simulations of solid H_2 in the 110−150 GPa range. Additional crucial ingredients are (i) a variable cell, constant-pressure approach that largely eliminates prejudice on the space group symmetry, molecular orientations, and lattice constants [13]; (ii) fully converged BZ sampling, achieved by a freshly implemented $k \cdot p$ technique [14]. Electronic correlations are treated within the LDA supplemented with Becke-Perdew gradient corrections [15], while the proton-electron interaction is described through a local pseudopotential [16] requiring an energy cutoff of 60 Ry [17]. We stress that electrostatic and band energies are fully included in this approach [10].

Preliminary runs using large simulation cells (up to 128 atoms) with Γ-point sampling only produced layered ground state structures with in-plane triangular ordering of molecules. However, we found a strong dependence of the results on cell shape and atom number, confirming that an accurate BZ sampling is crucial [10,18]. Convergence on BZ sums for insulating molecular H_2 turned out to require at least $8 \times 8 \times 8$ k points in the full BZ of a four-molecule cell [10]. This is particularly demanding in our approach because of the lack of symmetry constraints. Thus, at variance with the standard approach where the electronic orbitals for each k point in the BZ are expanded on a generic basis set (e.g., plane waves), we adopt a $k \cdot p$ expansion in terms of the (occupied plus empty) self-consistently generated Γ-point orbitals,

$$u_i^{\mathbf{k}}(\mathbf{r}) = \sum_{i=1}^{N} a_{ij}^{\mathbf{k}} u_j^{\mathbf{0}}(\mathbf{r}), \qquad (1)$$

where $u_i^{\mathbf{k}}(\mathbf{r})$ is the periodic part of the ith Bloch function at wave number $\mathbf{k}$, and $a_{ij}^{\mathbf{k}}$ are unitary matrices obtained by direct diagonalization the $k \cdot p$ Hamiltonian at $\mathbf{k}$

[19]. This expansion is strictly equivalent to the standard approach when the number of states N equals the size of the basis set [20]. In practice the sum can be truncated at a significantly smaller number of Γ-point orbitals with excellent accuracy [14]. With this improved functional we studied a system of 8 atoms with 512 k points in the full BZ [21], and with $N = 64$. We also performed simulations with 32 atoms, 128 k points, and $N = 96$, and with 64 atoms, 64 k points, and $N = 128$.

The 8-atom simulation started from the $Pmc2_1$ structure proposed by Kaxiras and Broughton [8] (see Fig. 1) that is the most favorable among a class of structures containing also the $P2/m$. Pressure was set to 140 GPa. When constant-pressure dynamics was switched on, the system spontaneously transformed into Kitaigorodskii and Mirskaya's quadrupolar structure $Pca2_1$ [22], proposed for H_2 by Nagara and Nakamura [9] (see Fig. 1). We then performed additional runs starting with different initial structures, namely, the cubic $Pa3$ and the orthorhombic $Cmca$ (see Fig. 1), previously proposed for solid H_2 at lower and higher pressures, respectively [4,18]. Although these structures can be ruled out for phase II on the basis of the number of vibronic modes [5], they represent reasonable starting points for our dynamical structural search. In the range of existence of phase II, the $Cmca$ structure turned out to be unstable against $Pca2_1$, while $Pa3$ was found to be locally stable, but much higher in enthalpy than $Pca2_1$. The quadrupolar structure of
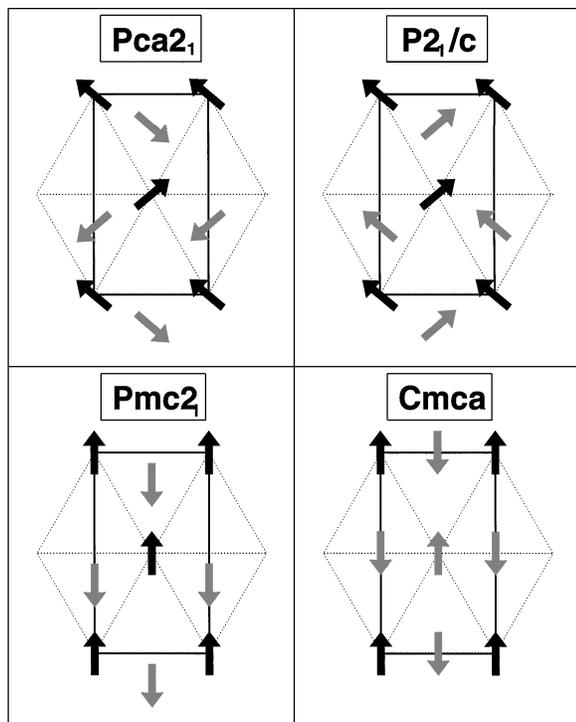

FIG. 1. Candidates for the ground state structure of solid H_2 in the broken symmetry phase (phase II), projected along the c axis. Black (gray) arrows represent molecules centered on the c ($c/2$) plane and pointing towards the positive-z hemisphere.

symmetry $P2_1/c$ [9] was also considered and found to be locally stable, with an enthalpy 0.015 eV/molecule higher than that of the $Pca2_1$ (at 140 GPa). The simulations were repeated with supercells of 32 atoms (double size along the two in-plane directions), and 64 atoms (double size in all directions). However, we failed to observe any signature of ground state structures with unit cells larger than 8 atoms, and $Pca2_1$ prevailed in all cases.

The above results have been obtained by treating the protons as classical particles, since quantum effects have been proven irrelevant to the relative hierarchy of molecular phases [23]. However, given the high level of accuracy of the present calculations, it seems wise to include the quantum effects. By rotating a single molecule on the $Pca2_1$ structure [24] we do not find multiple energy wells, suggesting that tunneling (of high order in $\hbar$) should not be important, at least near 150 GPa. Quantum corrections were therefore evaluated *a posteriori* within the harmonic approximation (i.e., to first order in $\hbar$). To this aim, we generated molecular dynamics trajectories at very low temperature ($T \approx 2$ K), from which we extracted [25] the frequencies of the 21 modes (4 vibrons, 9 phonons, and 8 librons) corresponding to the Γ point of the 4-molecule BZ. The ZPE, computed by summing over the above modes, was evaluated only for structures $Pca2_1$ and $P2_1/c$, the closest competitors for phase II. In fact, a $Pa3$ space group is incompatible with experimental data [5], while all remaining structures are unstable in the clamped-nuclei approximation. The instability implies the existence of a distortion with negative clamped-nuclei energy curvature, and excludes stabilization through quantum corrections, to first order in $\hbar$. The ZPE turned out to be lower in $P2_1/c$ by only 0.003 eV/molecule with respect to $Pca2_1$, yielding a quantum-corrected enthalpy difference of 0.012 eV/molecule, still in favor of the classically determined $Pca2_1$ structure.

It is worth stressing that in $Pca2_1$ the centers of the H_2 molecules occupy the sites of a slightly distorted hcp lattice. The temperature-induced transformation of phase II into phase I should then be accompanied by orientational disordering and by full recovery of the hcp symmetry. Thus, the equation of state (EOS) of phases I and II are expected not to be significantly different. In Fig. 2 we report our EOS and the c/a ratio calculated for the $Pca2_1$ structure in the range from 100 to 150 GPa. The b/a ratio turns out to be essentially pressure independent, although slightly smaller ($b/a \approx 1.715$) than the hcp value of $\sqrt{3}$. Comparison with the experimental results for the EOS and the c/a ratio in phase I [26] (full line) is also rather satisfactory.

A structure with $Pca2_1$ symmetry is compatible with optical measurements on phase II, where a strong Raman peak, and two IR modes are observed [3,5]. A symmetry analysis of the four vibronic modes of the $Pca2_1$ structure, usually labeled as A_1, A_2, B_1, and B_2 [5,27], shows that all of them should be Raman active, and three of
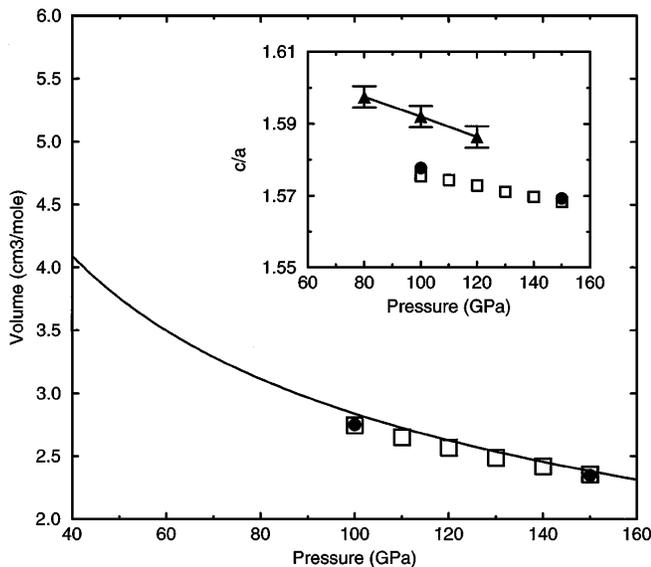
FIG. 2. Calculated equation of state of H_2 in phase II: 8-atom simulation cell (solid circles), and 64-atom simulation cell (open squares). The experimental EOS of H_2 in phase I [26] is also reported (solid line). The inset shows the pressure dependence of the c/a ratio (triangles are data from [26], other symbols as above).

them (A_1, B_1, and B_2) IR active. The frequencies of these four modes were evaluated by decomposing molecular dynamics trajectories at 100 and 150 GPa into the symmetry representations of space group $Pca2_1$ [28]. The resulting frequencies turned out to be substantially higher than experiment. Moreover, they *increased* as a function of pressure, in agreement with the calculated reduction of the molecular bond length (see Table I), but in flagrant disagreement with the observed trends, particularly for the Raman mode.

A closer glance at the experimental data, however, indicates that quantum effects are far from negligible (see Fig. 7 of Ref. [3]). In fact, the D_2 Raman frequency (scaled by $\sqrt{2}$) is roughly 200 cm^{-1} higher than that of H_2. To first order in $\hbar$, quantum corrections to the frequency are known to scale as the inverse of the particle's mass, no matter what the potential is [29]. Thus, using the experimental H_2 and D_2 frequencies, we obtain empirical but accurate quantum corrections to the classical values following Ref. [30]. In the case of the H_2 Raman mode the correction is as large as 500 cm^{-1}, while

for the IR modes the effect is more modest, amounting to about 150 cm^{-1}. The resulting quantum-corrected vibron frequencies are reported in Fig. 3, and compared with experimental data on H_2 [3]. The agreement with experiment is now very good, and shows that the Raman vibron turnover is a purely quantum effect. Moreover, the agreement allows us to interpret the experimental Raman mode as our A_1 mode: a totally symmetric, in-phase vibration of the four molecules in the unit cell. According to its symmetry classification, this mode should also be IR active. It does not appear in the experimental IR spectra, possibly due to a small oscillator strength. This is reasonable for a mode where all molecules oscillate in phase, since IR activity can only come from a small intramolecular asymmetry.

We attribute the two IR vibrons to the B_1 and B_2 modes. The predicted splitting of the two IR vibrons turns out to be in fairly good agreement with the data. Finally, we predict a Raman vibron, of symmetry A_2, with a "classical" frequency similar to that of the IR modes, being similarly an out-of-phase oscillation of the four molecules. Applying the same type of quantum correction as for the IR modes, the A_2 should in principle be observed in the region around 4500 cm^{-1}. Failure to observe modes A_2, B_1, and B_2 in Raman spectroscopy could be attributed to their small Raman strength, contributions from out of phase vibrations canceling out. The observed Raman mode could alternatively be attributed to mode A_2, but this would imply a quantum-corrected frequency of 4370 cm^{-1} (at 150 GPa), in clear disagreement with experiment. Symmetry lowering arguments and larger unit cells have been very recently invoked to explain a larger

TABLE I. Bond length, volume, and band gap in the two quadrupolar structures $Pca2_1$ and $P2_1/c$, as a function of pressure.

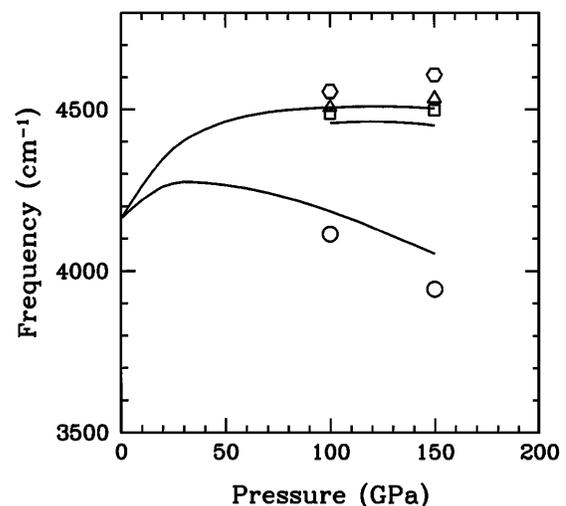|	P (GPa)	d_{HH} (a.u.)	V (cm^3/mole)	E_g (eV)
$Pca2_1$	100	1.377	2.75	4.12
$Pca2_1$	150	1.373	2.35	2.53
$P2_1/c$	150	1.374	2.35	2.61

FIG. 3. IR and Raman vibron frequencies of H_2 as a function of pressure. The lower and the couple of upper solid lines are the experimental Raman and IR data [3,5], respectively. Circles are calculated Raman vibrons (mode A_1). Squares and hexagons are calculated IR active vibrons (modes B_1 and B_2, respectively). Open triangles are estimates for the new A_2, Raman-only vibron.
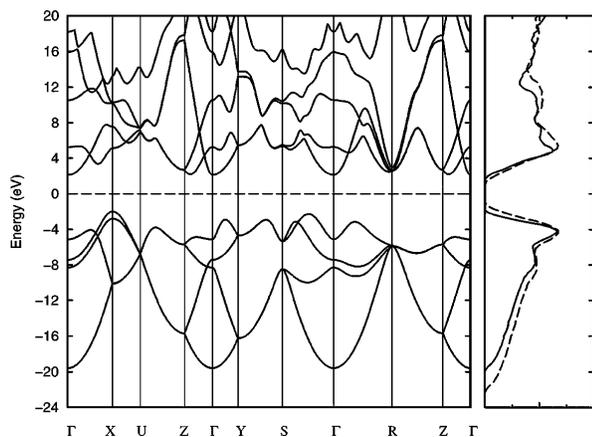
FIG. 4. Electronic band structure (left panel) and density of states (right panel) of solid H_2 in the $Pca2_1$ structure, at $P = 100$ GPa. The energy gap is 4.12 eV. The density of states at 150 GPa is also reported (dashed line, right panel).

number of optical modes by band folding in ortho-para D_2 mixtures [31]. The ortho-para distinction is, however, not included in our calculation.

Finally, our calculation provides the full electronic structure and pressure coefficients, and in principle the optical properties. In Fig. 4 we report the band structure and the electronic density of states of the $Pca2_1$ structure, at $P = 100$ GPa (the density of states at 150 GPa is also reported, for comparison). A gap of about 4 eV opens up the otherwise fairly free-electron-like bands. As shown (see also Table I), the gap decreases monotonically with pressure but is always finite and large in the range of stability of phase II.

In summary, by means of extensive and accurate constant-pressure *ab initio* molecular-dynamics simulations we have obtained what appears to be a definitive description of the broken symmetry phase of H_2. The $Pca2_1$ structure, first described by Kitaigorodskii and Mirskaya [22] for the ground state of a classical quadrupolar system, and later proposed for H_2 [9], is favored. Equation of state and vibronic frequencies turn out to be in very good agreement with available experimental data.

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