Zero-Point Motion and the Insulator-Metal Transition in Solid Molecular Hydrogen

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Candidate structures for molecular hydrogen in the 150 GPa pressure range are examined using *ab initio* frozen-phonon calculations in the local density approximation. Vibronic zero-point motion yields important contributions to the relative energies of metallic versus insulating phases. A first-order insulator-metal transition is found, with features in qualitative accord with experiment. Our results imply that an observed transition in solid molecular hydrogen is an insulator-metal–molecular-orientation transition driven by the vibron zero-point motion itself.

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Raman spectroscopy measurements on solid hydrogen reveal a discontinuous softening of the intramolecular vibrational mode (vibron) at 77 K and approximately 150 GPa applied pressure [1, 2], implying a first-order transition to a new phase, called H-*A*. The magnitude of the vibron discontinuity decreases with rising temperature, until the phase line terminates in a critical point [3, 4]. A similar vibron softening, greater in magnitude, is observed for deuterium at 165 GPa and 77 K [5, 6]. The deuterium critical point lies at higher temperature and pressure [7].

Other measurements imply that the lattice of molecules remains approximately hexagonal close packed (hcp) [8] with an approximately continuous volume [9] through the transition. Thus, large first-order changes in the structure are limited to the orientation of the molecules. Experimental measurements [10, 11] as well as theoretical calculations [12] indicate that an orientational order-disorder transition occurs at pressures less than 150 GPa; therefore the H-*A* may be an orientational order-order transition.

The softening of the molecular vibration further suggests the H-*A* is an insulator-metal (IM) transition occurring by a band-overlap mechanism, which weakens the molecular bond. Observed changes in light absorption and reflection above 200 GPa have also been taken to support the IM conjecture [13, 14], although these observations are controversial [15–17].

To date, no *ab initio* theory has been able to identify the observed transition. No calculation has found a metallic phase that is energetically favorable compared to the optimal insulating structure at pressures near 150 GPa. Indeed, there is no theoretical evidence for any first-order phase transition in the vicinity of the experimental transition pressure to account for the discontinuous vibron softening.

Clearly, the effects of zero-point motion are significant and must be included in a theoretical treatment. The magnitude of the experimental vibron discontinuity is such that the associated zero-point energy difference at the transition can influence phase equilibria. This Letter demonstrates that the heretofore largely neglected zero-point contribution changes the relative energies of previously studied H_2 structures, and that the softer vibron of metallic structures dramatically lowers the calculated IM transition pressure. With this contribution, a plausible mechanism for the observed vibron discontinuity is revealed for the first time on the basis of *ab initio* calculations.

Most previous calculations for hcp molecular hydrogen in the 100–200 GPa pressure regime were performed in the local density approximation (LDA) which underestimates the metallization pressure [18] (see, however, Ref. [19]). Only one study included contributions to the total energy from the zero-point motion (ZPM) of the vibron modes [20]. There, one ordered molecular structure was examined on an hcp lattice (with full $P6_3/mmc$ symmetry). Subsequent calculations examined different orientational states in a two- [21] and four-molecule [22] hcp system without inclusion of ZPM (i.e., in the clamped-nuclei approximation).

At moderate density, the ground-state structure is dictated by the intermolecular electric-quadrupole-quadrupole (EQQ) interaction [12, 22]. Previous LDA calculations for an EQQ-optimized structure yield an IM transition at 135 GPa occurring by band overlap and without a change in structure [22]. However, the inclusion of a band gap correction to the LDA is expected to result in a calculated IM transition pressure that is substantially higher than experiment [18].

The discrepancies found with the corrected LDA band gap are due to the clamped-nuclei approximation, for two reasons. First, the present LDA calculations for hydrogen in the 100–200 GPa range reveal a group of ordered structures differing in energy by only 40 meV/dimer (see Fig. 1), comparable to the rotational energy of the molecules (e.g., $\Delta E_{J=0\to2}$ = 44 meV for para-H_2 [23]). Second, the fundamental band gaps vary greatly among these structures, so that frozen phonon calculations for the vibron indicate that the zero-point energy, $E_{\rm ZPM}$, can be substantially lower (up to 50 meV/dimer) in metallic structures than in insulating.

Each of these terms favors a qualitatively different ground state. The clamped-nuclei total energy is lowest

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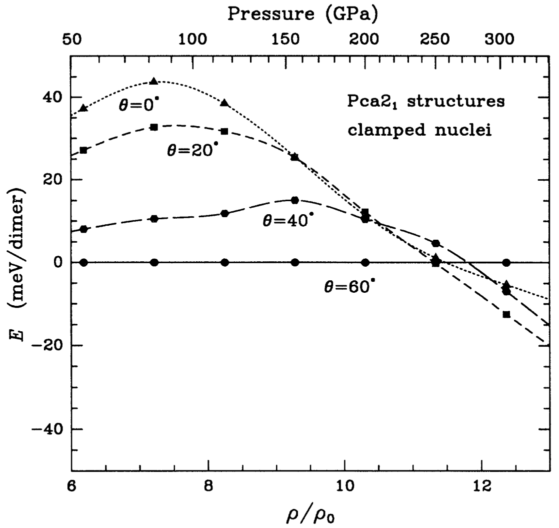

FIG. 1. Comparison between total energies per dimer of $Pca2_1$-type phases for clamped-nuclei LDA measured relative to the 60° phase. A first-order IM transition is predicted to occur at 210 GPa from an enthalpy-pressure construction. Compressions are given relative to the experimental density of H_2 at zero pressure, ρ_0, and the pressure scale is obtained from the experimental equation of state [26] for H_2. The dimer lengths are optimized for each structure, with polar angles of 0°, 20°, 40°, and 60°.

for the orientational states of insulating phases; the vibronic zero-point contribution is lowest for orientational states of metallic phases; and minimization of the rotational energy results in orientational disorder. Therefore, it can be hypothesized that the transition at the H-A phase line is derived from a competition among these three energies.

Extensive LDA calculations are presented here in support of this notion. Only the competition between the LDA energies and the vibronic ZPM can be fully considered; perfect orientational order is assumed in all calculations [24]. Variations of the four-molecule $Pca2_1$ phase of Ref. [22] are used in this model for the H-A transition. The polar angle θ of the dimers to the c axis is taken as a free parameter (between 0° and 60°), and molecular azimuthal coordinates are taken from Ref. [22]. The centers of mass of the molecules are frozen on an hcp lattice with the ideal c/a ratio. This minimizes the number of configurations that must be studied.

The $\theta = 0°$ and 60° phases are chosen because they represent the extrema for the total energy (see Fig. 1) as well as for band gaps of the structures studied. (The extremes of vibron ZPM are also found for these phases). The $\theta = 0°$ case corresponds to the $P6_3/mmc$ symmetry structure of Ref. [20]; while the 60° phase resembles the $Pca2_1$ phase of Ref. [22] (which had $\theta = 55°$). A partially disordered structure would have a band gap and carrier density intermediate to the extreme phases; it is assumed that the vibron zero-point energy is also intermediate, because it depends on the bond strength and so on the average carrier density. Thus, the effects of small orientational fluctuations from the 60° and 0° structures are modeled by examining ordered phases with intermediate polar angles of 40° and 20°.

LDA calculations are performed using a plane wave total-energy method with a 49 Ry cutoff and a Coulomb potential for the hydrogen-electron interaction. A set of 768 (= 8×8×12) **k** points is used in the full Brillouin zone. This ensures convergence for the clamped-nuclei total energy, E_{LDA}, versus polar angle.

The clamped-nuclei energies are shown in Fig. 1. The dimers are taken at their optimal lengths (i.e., minimizing the clamped nuclei LDA energy) rather than at values that include ZPM. At 150 GPa, the lowest-lying hcp configuration is found to be the 60° $Pca2_1$ phase, close to the structure which minimizes the EQQ interaction [22]. There is a first-order phase transition from the $Pca2_1$ structure with $\theta = 60°$ to $\theta = 20°$. The transition is an IM one, so a vibron discontinuity is expected along with a sudden increase in carrier density. However, the IM transition is predicted to occur at 210 GPa as determined from an enthalpy construction to the clamped-nuclei LDA energies [25].

An estimation of the vibron contribution to the total energy is difficult to obtain accurately. The vibron zero-point energy E_{ZPM} requires an average over the Brillouin zone of anharmonic phonon modes. Since the eigenmodes are unknown, the Brillouin-zone average is calculated from frozen-phonon calculations for a single vibrating dimer in the four-dimer unit cell. The expectation value of the dimer length $\langle d_0 \rangle$ depends on the fluctuating lengths of its neighbors. This dependence is treated in mean field in which the lengths of the surrounding dimers d_i are held constant such that $\langle d_0 \rangle = d_i$. In practice, the anharmonic oscillator problem for $\langle d_0 \rangle$ in terms of d_i is solved self-consistently to within 0.5%.

The dimer lengths and E_{ZPM} also depend on the Born-Oppenheimer adiabatic approximation and the plane wave basis cutoff. The 49 Ry cutoff gives vibron energies converged to only some 10 meV per dimer, however, higher numerical precision is impractical.

The relative energies of the four structures including the zero-point correction E_{ZPM} appropriate for H_2 are indicated in Fig. 2. It is important to examine the intermediate structures $\theta = 20°$ and $\theta = 40°$ to ensure that the transition is not a continuous one in which the θ parameter decreases smoothly to zero as the pressure is increased. A direct transition from $\theta = 60°$ to $\theta = 0°$ is predicted to occur at 78 GPa with a 3% volume decrease. The zero-point contribution changes both the transition pressure and the nature of the metallic state (i.e., a polar angle of 0° instead of 20°). The vibron discontinuity is 120 meV, 10 times the experimental value of 12 meV observed at 152 GPa and 77 K [6]. (The experimental discontinuity will be larger at 0 K but by less than a factor of two as estimated from Fig. 4 of Ref. [4].) If the

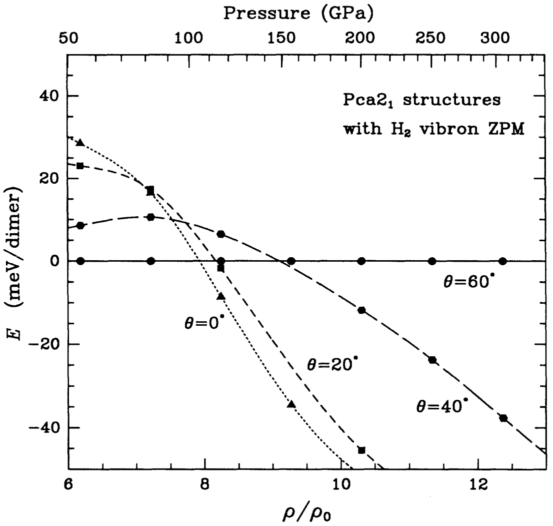

FIG. 2. Comparison between total energies per dimer of $Pca2_1$-type phases including vibron E_{ZPM} for hydrogen. The 60° to 0° transition is a first-order IM transition occurring at 78 GPa from an enthalpy-pressure construction. (The effects of rotational and molecular center-of-mass ZPM are not included.) The 40° to 20° transition occurs at 73 GPa.

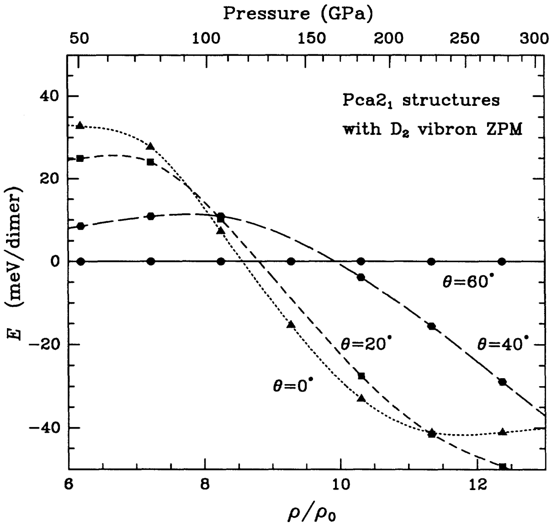

FIG. 3. Comparison between total energies per dimer of $Pca2_1$-type phases including vibron E_{ZPM} for deuterium. The pressure scale here is obtained from the experimental equation of state [26] for D_2; however, to facilitate comparison with the H_2 results, the compression is again expressed relative to the density of H_2 at zero pressure. The 60° to 0° transition occurs at 98 GPa, and the 40° to 20° at 90 GPa, from enthalpy-pressure construction.

transition were assumed to occur between the $\theta = 40°$ and $\theta = 20°$ phases, the transition pressure would be 73 GPa, and the vibron discontinuity 80 meV. The calculated first-order transition does lie at lower pressure than the observed one, as expected from the LDA band gap underestimate [21].

The significant contribution of the vibron ZPM to the ground-state energy provides an explanation for the experimentally observed isotope dependence of the H-*A* transition. Figure 3 shows the relative energies of the four candidate structures including vibron ZPM for the case of D_2. The mean-field dimer lengths and the zero-point energy have been adjusted to self-consistently account for the isotope effect. The 60° to 0° D_2 transition occurs at 98 GPa, higher than for the same structures of H_2. The calculated vibron discontinuity is 86 meV. The 40° to 20° transition occurs at 90 GPa with a vibron discontinuity of 55 meV. These results are to be compared to experimental data of 165 GPa and 16 meV at 77 K [5, 6].

Note that the heavier D_2 will have greater orientational order than H_2 and so will experience a larger discontinuous increase in carrier density at the H-*A* transition. The effect of disorder is approximated by taking the $\theta = 20°$ (40°) phase to represent the ground state of H_2 at pressures above (below) the H-*A* transition. At the same time, the $\theta = 0°$ and 60° phases represent an extreme model for D_2 (with no fluctuations). Comparing the results of our calculations for these cases, it is seen that the D_2 transition is expected to occur at higher pressures *and* exhibit a larger vibron discontinuity than H_2, in agreement with experiment.

Thus, the major result of our analysis is that competition among the EQQ, vibrational, and rotational energies drives an orientational and IM transition, leading to a qualitative explanation of the observed H-*A* transition. Of course, the numerical details are governed by the specifics of this competition, so that current *ab initio* approximations fail to obtain quantitative agreement with experiment. Nevertheless, the proposed competition is expected to yield an orientational transition in solid hydrogen near the onset of metallization for some structures (provided that molecular dissociation does not occur first). Highly accurate many-body calculations predict band overlap metallization in the 100–200 GPa range [18]. Experimentally, solid hydrogen is known to be in a molecular phase from 110 GPa to some 250 GPa [13], while the H-*A* is the only transition clearly observed within this range. Thus, we identify the H-*A* transition with our orientational transition plus band-overlap mechanism.

While the proposed H-*A* phase transition exhibits many of the features seen experimentally, the predicted magnitude of the vibron discontinuity is too large. A neglect of orientational disorder certainly results in some overestimate of the calculated vibron shift. Furthermore, it is possible that the H-*A* transition actually proceeds to an ordered structure different from the $P6_3/mmc$, one that partially optimizes both the EQQ and vibronic energy terms; this would also reduce the magnitude of the vibron discontinuity. Unfortunately, the LDA band gap problem will preclude any quantitative analysis of this EQQ-vibron competition from first-principles analysis.

To summarize, it is suggested that the observed H-A transition is an IM plus orientational transition, based on *ab initio* calculations of candidate structures for molecular hydrogen. The model can be categorized as a transition from an insulating structure dictated mainly by EQQ interactions (more generally, by the clamped-nuclei energy E_{LDA}) to a metallic structure with a smaller vibron zero-point energy E_{ZPM}. However, it is too crude a model to identify the precise nature of the ground states near the transition.

Regardless of the details, it is shown for the first time that the reduction in ZPM for metallic phases can be sufficient in molecular hydrogen to drive the IM transition at densities for which it would be unfavorable if the nuclei were classical objects. Hence, it is clear that the hydrogen phase diagram cannot be studied theoretically without fully accounting for the effects of molecular zero-point motion.

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[24] Electronic bandwidths will rise exponentially with compression of the linear dimensions while the EQQ interaction rises at most as $1/r^5$ (neglecting increases in screening). Thus, growing differences in the carrier density among various orientational configurations will yield differences in the vibron zero-point energies. This angle-dependent zero-point contribution eventually overcomes the EQQ interaction, and the IM transition is determined by competition between these two terms.

[25] Note that the results of this clamped-nuclei calculation differ from those of Ref. [22]. In part, this is because a 55° $Pca2_1$ phase was studied there rather than a 60° one. Also, the 55° phase was calculated with less convergence than the others. However, calculations with a 60 Ry cutoff do not change the situation depicted in Fig. 1, so that the inclusion of zero-point motion is of greater importance than improved convergence at this point.

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