

High temperature Raman analysis of hydrogen phase IV from molecular dynamics

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Abstract. We extend our previous studies on phase IV of solid hydrogen by employing larger cells and k -sampling. We show that uncorrelated hexagonal rotations in the weakly bounded G'' -layers are needed to account for the experimentally measured Raman spectrum. In large simulations we find no evidence of proton diffusion or layer fluctuations, which we believe are the result of finite size effects. In calculations at higher pressures (above 400 GPa) we identify a new possible candidate for phase IV. We, finally, proposed a revised phase diagram based on our previous and present results.

1. Introduction

The recent discovery of a high-pressure, high-temperature phase IV of solid hydrogen [1] has reignited the research interest in the field. Considerable work has been done to identify the true nature of this new thermodynamically stable phase. *Ab initio* Random Structural Searching (AIRSS) performed at 0 K [2, 3] had previously suggested a new class of mixed crystals, consisting of two types of layers: molecular (named “bromine-like”, B) and atomic (named “graphene-like”, G). These explained the observation of two Raman-active vibrons with very different frequency [1, 4]. Metadynamics simulations reported a structure similar to *Pc*, but with rotational disorder in the B-layer, and molecular dynamics [5] showed the possibility of a number of layered structure, stabilised at high temperature by the entropy of molecular rotations.

Further Molecular Dynamics calculations attempting to include temperature effects reported unusual behaviour like “pronounced proton diffusion” [6], “intralayer structural fluctuations” and “proton tunneling phenomena” [7]. In our recently published work [5] we showed that these predictions are an unwanted effect of the finite size simulations and we offer an alternative interpretation of phase IV.

The mixed cells explain the existence of two Raman vibrons [1, 4]. and the calculated hard vibron frequency, arising from the B-layer of free molecules in *Pc*-structure, is in good agreement with experiment. However, the soft vibron, from the interacting molecules in the G-layer does not agree well when calculated with Density Functional Perturbation Theory (DFPT) at 0 K. Additionally, more recent IR measurements at high pressures and room temperature have found disagreements with the theoretical predictions for phase IV [8–10].

We developed a method to extract Raman from Molecular Dynamics at finite temperature and found that rotation of the trimer rings in the G-layer could account for the hardening of the softer vibron mode [5]. Here, we extend our calculations to both larger *Pc*-cells and larger



k -point sampling to gauge the contribution of finite size effects to our previous simulations. We also examine the effects of initial conditions with MD simulations starting from two structures: Pc and Cc .

2. Calculation Details

We have performed systematic MD simulations across a large pressure-temperature range. Here, we report studies employing larger cells and denser k -point sampling than previously. All DFT calculations were performed using plane waves (PW) with 1200 eV cut-off, ultrasoft potentials and PBE functional. We start by relaxing our Pc and Cc cells and then carry out MD simulations as summarised in table 1. We have, additionally, performed MD simulations at 340, 410 and 480 GPa with Pc – 768 cells, but these exhibit interesting phase transitions, which will be detailed in the following. We extract Raman from trajectories using molecular projections [5]:

$$I(\omega) = FFT \sum_j \mathbf{v}_j(\mathbf{t}) \cdot [\mathbf{r}_{\mathbf{n}_j}(\mathbf{t}) - \mathbf{r}_j(\mathbf{t})] \quad (1)$$

where $\mathbf{r}_j(\mathbf{t})$ is the position of atom j , $\mathbf{r}_{\mathbf{n}_j}(\mathbf{t})$ is the position of the other atom in the molecule and $\mathbf{v}_j(\mathbf{t})$ is the velocity of atom j , all at time t measured starting after an equilibration period, and FFT stands for Fast Fourier Transform. We also evaluate the atomic square root displacements as:

$$D(t) = \frac{1}{N} \sum_j \sqrt{\mathbf{r}_j(\mathbf{t})^2 - \mathbf{r}_j(\mathbf{0})^2} \quad (2)$$

Table 1. Details of MD simulations.

Cell	No. Atoms	Layers	Pressure	Temperature	k -points	Length/Ensemble
Pc	48	4	250 GPa	325 K	5x3x3	3 ps NVE
Pc	288	4	250 GPa	325 K	1x1x2	1.5 ps NVE
Pc	288	4	270 GPa	300 K	2x2x4	1.5 ps NPT + 1.5 ps NVE
Cc	384	4	270 GPa	300 K	1x1x2	0.3 ps NPT + 2.0 ps NVE
Pc	768	8	270 GPa	300 K	1x1x1	0.2 ps NPT + 1.5 ps NVE

3. Results and discussion

All extended calculations are in good agreement with our previous results. As illustrated in figure 1, in the stability regime of phase IV, the B-layers are freely rotating, while the G-layers differentiate in two distinct types. The G' layers are stable and while snapshots show distinct molecules with electrons located in covalent bonds, on time-averaging the G' layers exhibit hexagonal symmetry. The strongly-bonded molecules seem to be part of two trimers at the same time, and molecular flips (out of the plane) are possible, but infrequent. By contrast, in the G'' layers, the trimers are uncorrelated and rotating giving strong inter-molecular interactions and quick rebonding. The bonds in this latter layer are characterised by an accentuated anharmonicity.

Our observations are in particular validated by the large 768 atoms simulation (Panel I in figure 1). We carefully prepare 8 extended layers, containing 16 trimers each, in the Pc structure. Initially, all 4 G-layers have the same symmetry, but during the course of the simulation, they differentiate in an alternating stacking of G' and G'' layers. We also find that simulations

started in the Cc cell (Panel II, figure 1) proposed by Liu *et al* [11] displays a very similar high temperature behaviour. The high temperature structure observed seems to be independent of the choice of initial conditions or unit cell (orthogonal/monoclinic), although finite size effects may play a role: in our smaller cell with a denser k -point mesh (Panel III, figure 1), the rotation of the hexagons took longer to initiate and was not consistent throughout the simulation.

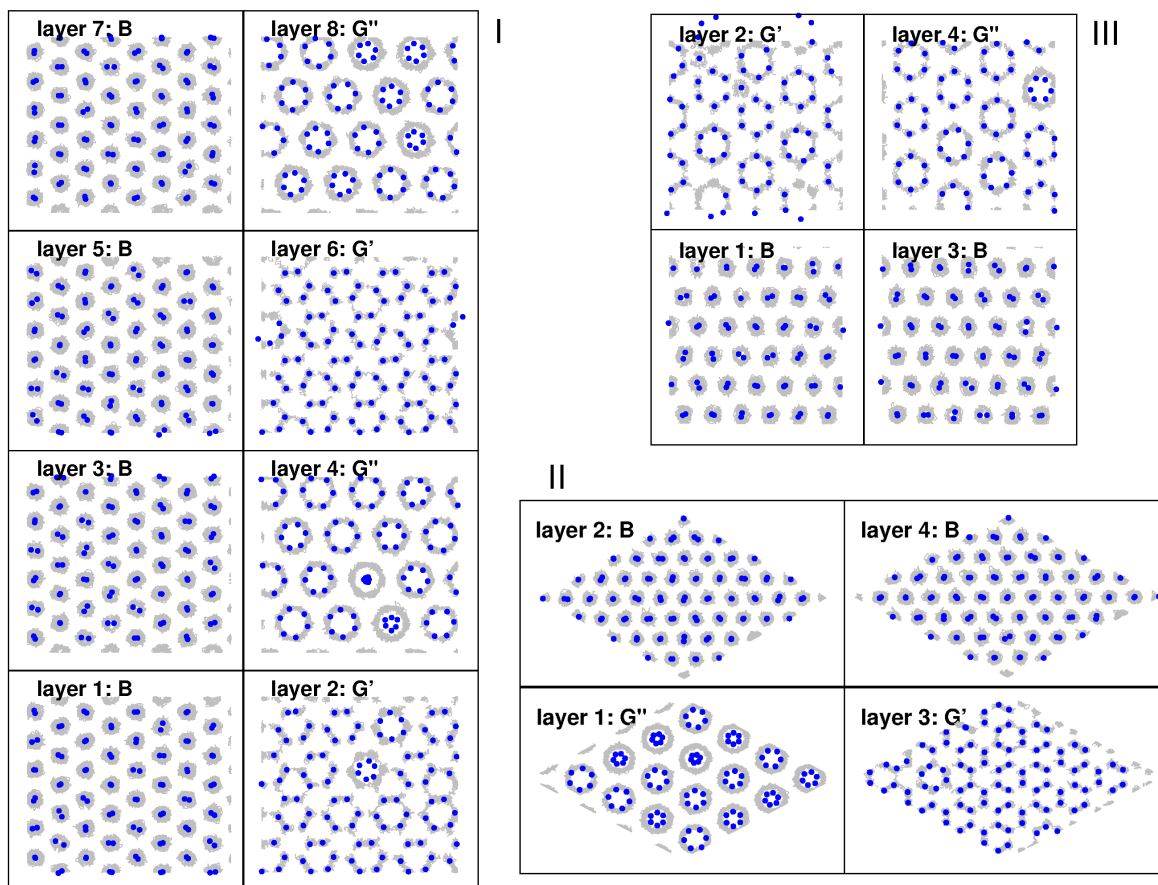


Figure 1. The figures shows trajectories (grey) and average atomic positions (blue dots) extracted from MD simulations at 270 GPa and 300 K. Panel I: Pc , 768 atoms, $1 \times 1 \times 1$ k -points; Panel II: Cc , 384 atoms, $1 \times 1 \times 2$ k -points; Panel III: Pc , 288 atoms, $2 \times 2 \times 4$ k -points. When averaged over a long enough period to allow full rotations, the two blue dots in the B-layer molecule / six blue dots in the G'' trimer become coincident at the centre of molecule / thorium.

Also, our calculation is based on a classical description. Across a range of systems, the effect of including zero-point energy or using nuclear wavefunctions is similar to increasing temperature. Including the quantum effects of the protons (especially the in-molecule indistinguishability implied by para-hydrogen) would facilitate the hexagon rotations in the G'' layers, increasing the vibron frequency and reducing the small disagreements with experiment still further.

We further compare the Raman spectrum of Pc –768 and Cc –384 cells at 270 GPa and room temperature as shown in figure 2. In both cases, we obtain two well defined peaks at around 4150 cm^{-1} and 3000 cm^{-1} . The results are consistent and in good agreement with our previous study on smaller systems [5] and also in accordance with the experimental measurements [1] at the same conditions of pressure and temperature. We find no dependence on whether the simulation was initiated in Pc or Cc .

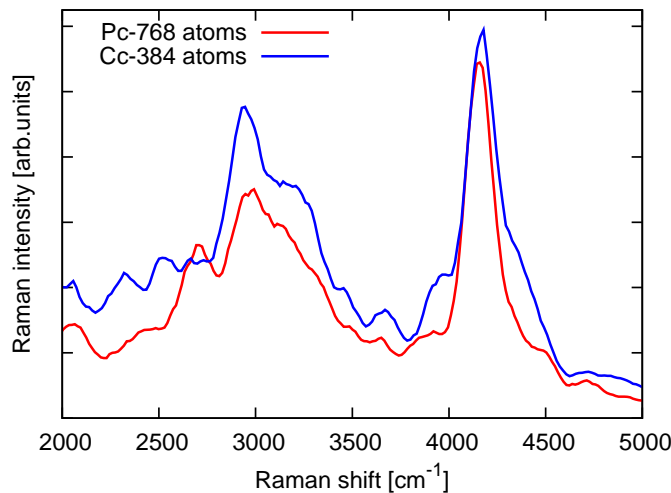


Figure 2. We show Raman computed with the molecular projection method for: Pc (768 atoms) (red) and Cc (384 atoms) (blue). The results are consistent.

sible for the hardening of the softer IR peak which is currently the topic of much debate in the literature. We intend to calculate IR with similar methods in future studies and confirm that mixed structures are the best candidates for phase IV of solid hydrogen.

Apart from the Raman spectra, we also use the MD trajectories to investigate previously-claimed proton diffusion [6]. We extract the mean square root displacements (MSD) from the MD trajectories and plot it against time as shown in figure 3.

It is clear that increasing the size of the cells drastically reduces the MSD and apparent diffusion.

In the 48-atom cell, various finite size effects, like layer fluctuations and simultaneous hexagon rotations, combined with unclear trimer identity, can facilitate effects like proton diffusion. This is illustrated by the sudden jumps in the red curve (see figure 3). However, when larger cells are involved, there is a rapid increase in MSD which can be explained by the free rotation of the molecules in the B-layers and uncorrelated rotations of the hexagons in the G''-layers. The MSD then stabilises at a constant value representing the radius of the trimer/molecule (grey torus in Fig 2). This effect is already present in cells of 288 atoms, which we note is larger than any simulation for which data is presented in previous work [6, 7].

The rapid proton diffusion which we observe in smaller simulations can be traced to reconstructions of *entire layers*. The stochastic probability of such reconstructions drops exponentially with the number of molecules in each layer, so the proton-diffusion “mechanism” is absent in larger simulations, and will be absent in still-larger experimental samples. The

In the smaller *Pc* cell with denser k -meshing, the softer vibron is too soft, similar to LD calculation. In other words, when hexagons are not rotating, the MD simulation is the same as a simple oscillation around the equilibrium position, consistent with LD. Similarly, we previously reported that at lower temperatures the rotation stops and the Raman frequencies soften [5]. This is further evidence that the rotating-trimer G'' layers describe the true nature of phase IV.

We thus conclude that uncorrelated trimer rotations in the G'' layers are necessary to explain the measured Raman spectrum. We expect that quantum effects on the protons will only enhance the rotation.

The same effect could be respon-

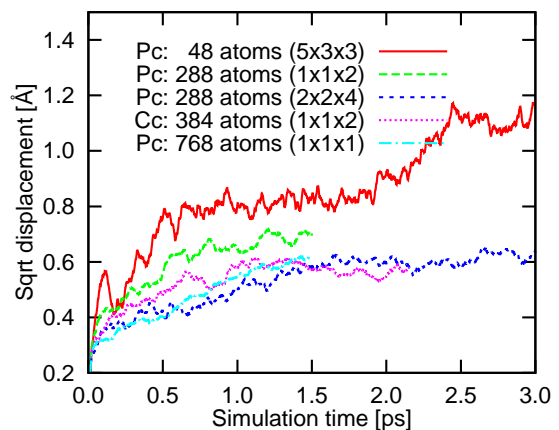


Figure 3. Figure shows the square root displacement extracted from MD calculations at various conditions as summarised in table 1. Numbers in brackets are the k -point set.

absence of proton diffusion can also be observed in the trajectories plotted in figure 1, in which all protons stay in their initial B-molecules or G-trimers.

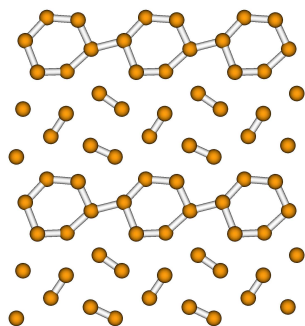


Figure 4. A layer of the new ABAB stacked structure discovered at 480 GPa. The novel cell could possibly be a candidate for phase IV or another higher-pressure phase.

We have already shown that the proton-diffusion mechanism is not needed to explain the measured Raman spectra as was previously claimed: the rotation of the trimers is sufficient.

In simulations at higher pressures we find a series of phase transitions. The slowly-converging relaxation of the Pc – 768 atoms cell at 480 GPa finally transformed to a new, unreported structure as shown in figure 4. Although unstable at these conditions, the new layered cell is interesting because it contains two different molecular environments within the same layer. As seen in other mixed-structures, this is the kind of setup that could give two Raman vibrational peaks of different natures. Further shaking and relaxations of the new cell at 0 K resulted in a transformation to the previously predicted $Cmca$ – 12 [2].

We started MD simulations with the large cells (768 atoms) using the NPT ensemble at room temperatures (see figure 7). After less than 0.2 ps all structures above 340 GPa went through a phase transition as shown in figures 5 and 6. The average atomic positions in this new phase are very similar to Pickard's $Cmca$ –4 structure [3]. The transition involves an abrupt change in the lattice parameters, especially cell length a and cell angle β as shown in figure 6. Since this phase has only one type of molecular layer, transitions from Pc could easily be identified in experiments by disappearance of one of the Raman vibrons.

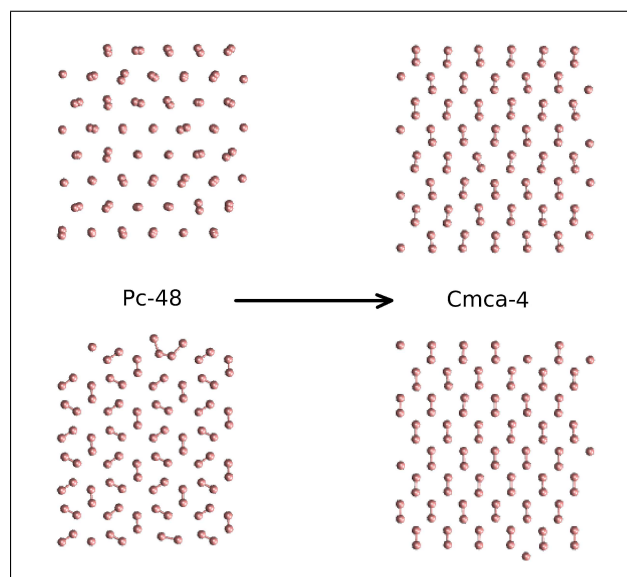


Figure 5. Figure shows average atomic positions extracted from the MD runs at 340 GPa. The Pc structure (left) transforms to $Cmca$ -4 (right) in less than 0.2 ps of NPT simulation.

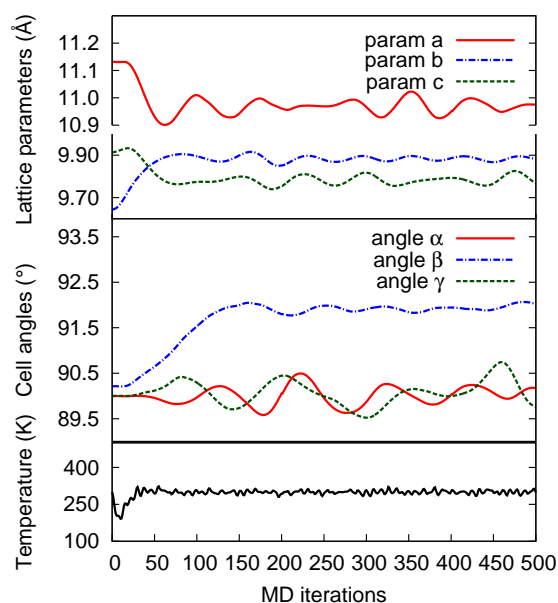


Figure 6. The Pc to $Cmca$ -4 transition leads to an abrupt change in the lattice parameters a and β as shown in the middle and top panels.

Recent experiments reported by Howie at this meeting, suggest such Raman transformations

induced by heating. This could be accounted for by either a liquid phase, or possibly the $Cmca-4$ structure which we have also found in MD simulations in agreement with previous metadynamics studies [11].

Summing up the results from our previous studies and our current work we speculate a revised phase diagram. We expect that future experiments at both low and room temperatures will find new phases upon increasing the pressure. We, further, found no evidence of melting in our MD simulations in agreement with other recent studies which predict a minimum in the melting curve [12]. The possibility of a ground liquid state [13] at these pressure is questionable.

4. Conclusions

In conclusion, we have validated our previous studies [5] by extending the simulations to larger cells and denser k -meshes. We have also checked our simulations against the work of other groups [6, 7].

Specifically, we have shown that the layer reconstruction, which can lead to linearly-increasing MSD and “proton diffusion”, is a finite size effect. We found no evidence of such a phenomenon in larger cells on the simulated time scale. Uncorrelated rotations of trimers explain the Raman spectra as observed in experiments and are most probably the cause of similar changes in IR vibrons. Possible candidates for phase V of hydrogen ($Cmca-4$) and VI ($Cmca-12$) might become stable at certain conditions. Finally, we speculate a new, revised phase diagram based on our old and present calculations.

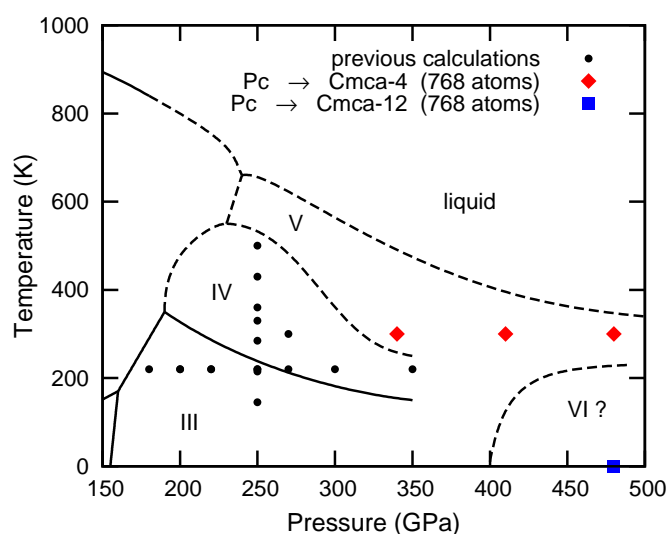


Figure 7. Revised Phase Diagram.

Acknowledgments

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