Simulating Raman Spectra using molecular dynamics, and identification of high-pressure phases III and IV in hydrogen

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We present a technique for extracting Raman intensities from ab initio molecular dynamics (MD) simulations at high temperature. The method is applied to the highly anharmonic case of dense hydrogen up to 500 K for pressures ranging from 180 GPa to 300 GPa. On heating or pressurizing we find first-order phase transitions at the experimental conditions of the phase III - IV boundary.

There have been some notable recent successes of using total energy calculations based on density functional (DFT) to calculate expected signals from candidate structures, for comparison with inconclusive experimental data. Agreement provides validation of the DFT structure, and this combined approach can yield more information, with higher reliability, than either technique alone.

Raman spectroscopy provides one such experimental probe, applicable in extreme conditions but providing insufficient data to determine crystal structure or identification of the vibrational mode. Reliable calculation of Raman frequencies and intensities of mechanically stable structures can be obtained using density functional perturbation theory (DFPT) based on ab initio lattice dynamics (LD). However these methods do not include high temperature effects, and fail for dynamically-stabilized structures with imaginary phonon frequencies. One solution to this is to extract vibrational frequencies from molecular dynamics (MD) data.

For simple structures this is relatively straightforward; bcc titanium and zirconium being nice examples. In these materials the soft T_{1V} phonon eigenvector is well defined, and its frequency and width can be calculated from projection of the MD (or Monte Carlo) trajectories onto the relevant mode eigenvector, followed by Fourier Transform (FT).

In lower-symmetry molecular systems there may be many modes which are formally Raman active, and the coupling between lattice and molecular modes is typically highly temperature-dependent. Worst of all are plastic crystal phases where the molecules can reorient in MD and the eigenvectors calculated from perturbation theory become totally irrelevant.

In this Letter we present a method for calculating Raman frequencies from molecular dynamics, and apply it to the particularly awkward and topical case of the high-frequency vibron modes in high pressure hydrogen.

Although liquid and solid phases I, II of hydrogen have been well studied using MD, much interest recently has focussed on pressures around 200-300 GPa where several phases are reported. Generally accepted are a low temperature phase III and a high temperature phase IV. Theoretical predictions of many other phases have been made, and Raman data suggests phase IV may itself have a subtle structural change at 270 GPa.

At these pressures x-ray experiments are exceedingly difficult, while neutron diffraction is simply impossible; therefore most experimental data are extracted from Raman and infrared spectroscopy, alongside conductivity measurements. None of these techniques produce enough data to resolve crystal structures, so DFT studies have also been attempted. Although these calculations typically ignore quantum effects on the protons, they still provide a useful indication of the likely structures. Very recent papers applying path integral MD to high pressure hydrogen show no qualitative behavioural change to the phase diagram: the main effect is that tunnelling allows molecular rotations to occur at slightly lower temperatures than in classical MD, lowering the phase lines. Most importantly for the present work, the vibrational frequencies of the molecules are largely unchanged by the path integral dynamics.

Enthalpy is easily calculated in DFT, being the combination of total energy of binding of electrons to atoms, plus the zero point energy. Phase III should be the lowest enthalpy phase over a wide range of pressures. Ab initio structure search unveiled a number of candidate phases with low total energy, and evaluation of normal modes, phonon frequencies and zero point energy gave rise to prediction of a C2/c symmetry phase. From the phonon calculation it is further possible to calculate...
polarization and polarizability, from which Raman and infrared intensities may be deduced. These show reasonable agreement between $C2/c$ and experiment for phase III \cite{19, 23, 26}.

Phase IV exists at higher temperatures and is therefore stabilized by entropy. High temperature calculations are more challenging for DFT. Using the quasiharmonic approach based on zero-temperature calculations, Pickard et al. \cite{17} evaluated free energies at finite temperature to claim that phase IV should be a layered structure with alternating graphene-like hexagonal layers interspersed with ordered molecular layers and $Pc$ symmetry. We refer to these layers as $G$ and $B$-type respectively. The critical result here is that the two different layers give strongly Raman active vibron modes at two very different frequencies. Experimental work also finds two vibron modes, lending support to a two-layer model \cite{16}.

We have extended these calculations of enthalpies and phonons using the CASTEP code \cite{28} across a wider range of frequencies and with a variety of pseudopotentials (both ultrasoft and norm-conserving with various tunings) and exchange-correlation functionals. We find that these previous results are robust \cite{29}. Despite qualitative agreement, the lower-frequency vibron is observed at much higher frequency than calculated, and with very large width (Fig. 2 and \cite{27}). We also used static calculations to investigate whether the $G$ layers have atomic or molecular character. Mulliken bond analysis shows very clearly that the $G$-layer hexagonal are rings of three $H_2$ molecules: the Mulliken charge in the molecular bond is at least double that between molecules (1.5e vs 0.3e at 180 GPa, closing to 1.3e to 0.65e at 350 GPa). This result is consistent with snapshots from MD. The reduction in molecular fidelity with pressure is accompanied by a steady reduction in the band gap.

In simulations starting in $Pc$, we find reversible transitions between two phases: a structure with $BGBG$ stacking similar to $Pc$, with threefold layer-symmetry but with the $B$-layer molecules rotating about their centres, and a high-temperature structure with hexagonal symmetry, stacked $BG'BG''$ with sixfold layer-symmetry where the $G'$ layer has hexagonal symmetry and the $G''$
layer exhibits fast rebonding which enables rotation of the hexagonal motifs of three hydrogen molecules. We refer to these phases as IVa and IVb (Fig. 1). This transition is observed in two ways [27]: a single MD run with a ramped temperature rise and subsequent decrease traverses a path IVa - IVb - IVa with little hysteresis; alternately, calculations at fixed T and P show the two phases. We use these latter calculations as the basis for our Raman calculations, to test the simulated structures against experiment. It should be noted that our simulations have only four layers, so more complex stackings may exist.

Our DFPT-LD calculations show that all modes in the \( P_c \) phase are Raman active. To compare with experiment we initially tried projecting the MD trajectories onto LD eigenmodes, multiplying by the calculated Raman intensity and taking the Fourier Transform [27]. This method relies on the normal mode vectors being invariant over time and with temperature. At the lowest temperature, 60 K, the structure remains in the initial configuration (metastable \( P_c \)) and the projection method gives a Raman signal in precise agreement with LD, as it should for harmonic vibrations [27]. At higher temperatures molecular rotations exchange atom positions, and this method fails.

Closer inspection shows that the strongly Raman active vibron modes in all phases involve in-phase stretches of the molecules in the \( G \) and \( B \) layers. Therefore we make the ansatz that, independent of molecular orientation, the Raman-active vibron modes will involve in-phase stretches. Extracting the Raman signal from the MD is now achieved by identifying molecular bondlengths at each step, which turns out to be always straightforward, and taking the time FT of the average projection of the velocity over the bondlengths [27]. We note that this procedure requires well-defined molecules, but does not require us to identify layers [30]. This method produces well-defined peaks, and an example of the fit between simulated and experimental data at 270 GPa is shown in Fig. 2.

In Figure 3 we show the pressure dependence of the MD-calculated Raman vibron frequencies compared with the experimental data. In phase III the MD has spectacular agreement with experiment [28]. DFPT gives similar

![FIG. 2. Comparison of Raman spectra at 270 GPa: Top DFPT lattice dynamics calculation (0 K); Middle MD calculation of Raman signal from IVb at 220 K; Bottom, experimental data at room temperature from Howie et al [16]. Note that the sensitivity of the detector is reduced at high frequency [20], so the peak amplitudes are not directly comparable.](image)

![FIG. 3. Pressure dependence of the vibron peaks. (a) experiment: phase IV, 300 K [16] (open grey circles), phase III, 90 K [23] (open grey squares) (b) MD: initialised in \( P_c \) at 220 K (solid red circles) and in \( C2/c \) at 220 K (solid red squares) (c) Lattice dynamics: in \( P_c \) (solid blue circles) and in \( C2/c \) (solid blue squares). The discontinuity in the \( P_c \)-MD at 270 GPa corresponds to the IVa-IVb transition. Inset: the bifurcation of the \( C2/c \)-MD at 250 GPa corresponds to the two Raman peaks which were calculated after \( C2/c \) was heated to 300 K and it transformed to a distorted structure similar to phase IV.](image)
frequencies, but with a much lower slope (Fig. 3). The simulation which started in C2/c at 250 GPa/ 220 K was also driven through the phase transition by heating to 300 K, where it formed a frustrated monoclinic, GBG-stacked structure [27], leading to the appearance of a second vibron: this structure has mixed-layer character like phase IV, but the frequencies are clearly not in agreement with experiment (Inset to Fig. 3).

Figure 3 also shows that the IVb structure with rotating trimers does correctly reproduce the experimental frequencies, while IVa and Pc structures do not. The phase IVb lower peak seems to be comprised of two overlapping peaks (Fig. 2). We can project the symmetric stretch modes layer by layer: for phase IVb with three different layers, this gives three different frequencies. The near-equal strength of the G′ and G″ peaks is due to having one layer of each in the simulation. This ratio is determined by finite size, and in reality the lower peak may be weaker. In fact, this feature is also probably present as a shoulder in the experiment, although its effect could be interpreted as an extended peak width (see Fig. 2). We therefore identify our phase IVb with the experimentally observed phase. IVa occurs in a region of PT space occupied by phase III, so we regard it as metastable.

The analysis of the detailed molecular motions gives a clear, intuitive picture of the high pressure phase behavior of hydrogen. At low temperature we observe a series of G layers to be the stable structure. Above 60 K molecular motion means that this layer has 3-fold symmetry, but at 0 K a symmetry-breaking distortion freezes in giving the C2/c structure. At a temperature of around 250-300 K (depending on pressure [27]) the transformation to phase IV (our IVb) occurs. The explanation for the entropy-driven transition is evident in the rapid rotational movement of the B layer atoms. The molecules rotate rapidly in the B layer such that their time-averaged positions have hexagonal symmetry. These rotations provide the entropy difference between phases III and IV. At higher temperature, the fast rebonding in the G′ layers enables the rotation of the hexagonal motifs and adds to the entropy, stabilising the IVb structure. Once this rotation begins, the non-rotating G layer adopts hexagonal symmetry. At lower temperatures, no rotation occurs and the hexagonal motifs are distorted and symmetry-broken, as in Pc.

Our 288-atom results are significantly different from previous MD work [31, 32] which has been equivocal about the structure of phase IV, due reorienting of molecules, transformation of one layer type to another, and “mixed” phases of apparently random B and G layer stacking. In our own calculations with 24 or 48 atoms per unit cell we find the same behavior as described in [31, 32].

A simple 1D model [27] of independent layers shows that the continual layer transformation (random layer stacking) is to be expected from finite size effects, rather than phase stability.

Proton “diffusion” in the G-layers requires two distinct steps:

- Rebonding within the rotating hexagonal motifs, a local process which can contribute to Raman broadening and may be enhanced by tunnelling. This is seen in all simulation sizes at sufficient temperature and illustrated in Figure 7.
- Rearrangement of the motifs themselves, a process which must occur system-wide, and is seen only in 48 atom simulations and smaller.

The rebonding and rotation of these motifs was also described by Liu et al [31], who also showed large diffusion of hydrogen which implies the rearrangement step.

The 48 atom cell has 2x2 trimer hexagons in a G layer, and we also observe correlated changes in the identity of pairs in these motifs, which combined with trimer rotation results in rapid diffusion of hydrogen through the system. This effect is not observed in our 288 atom simulations where the equivalent mechanism would require correlated changes in four trimers: we regard the apparent rapid diffusion in 48-atom simulations phase IV as a finite size effect [33, 34].

Our IVb structure is the best model for the observed phase IV. Our molecule-based technique shows vibron peaks appear which can be associated with each layer type. the B-layer gives the highest frequency, and analysis of the Raman active modes associated with G′ and G″ layers in IVb gives two distinct vibrons of slightly different frequency. In the overall pattern, these peaks overlap to give a single peak with a shoulder. The wide variety of environments in which the G-layer molecules find themselves leads to a very broad Raman width. The B layer molecules are well defined and the Raman peak associated with them is sharper. In Pc, IVa and IVb the B-layer vibron has similar frequency, however the G layer modes are quite different.

In sum, we have shown how Raman frequencies can be extracted from molecular dynamics data allowing direct comparison to experiment. We have applied the method to hydrogen at high pressure, showing that the anharmonicity is so extreme as to invalidate use of DFPT normal modes, but that in-phase vibrons are the appropriate coordinates for projection. Our simulations show several different phases, some of which are doubtless metastable, but by comparison to experiment we identify phase III with a structure similar to C2/c, and phase IV with a high-entropy hexagonal structure of rotating molecules and trimer motifs. Our simulations give no support to the notions that phase IV exhibits either proton transfer, proton tunneling or mixed molecular and atomic character.

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[29] We note that convergence of the Raman signal requires a much higher $k$-point sampling than either structure or phonon calculations.
[30] It is possible to identify the layers, and to project only onto molecules in one layer. Each different layer produces a single peak: the higher frequency peak is associated with the B layers. However, there is interference between similar layers, so the sum of the layer projections does not give the correct Raman signal.

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Finite Temperature Phonons by projection onto normal modes

In order to study a particular vibrational mode in a crystal, we first define the calculation supercell, and relax the structure at 0 K. The atoms are now located at positions given by 3N cartesian coordinates $X_j$. We regard the supercell as a non-primitive unit cell, in which case $X_j$ are the basis positions.

We now do a lattice dynamics calculation at 0 K using either finite displacements (Ref. [6] from the paper) or DFPT (Ref. [5] from the paper). This gives us a set of normal mode coordinates $\xi_i$. With each of these normal modes we can calculate harmonic phonon frequency ($\omega_i$), Raman activity and oscillator strength ($R_i$), IR activity and oscillator strength. $i$ runs from 1 to 3N, the number of normal modes. all of this is already standard in CASTEP.

From an MD simulation with T timesteps we generate trajectories of the atoms, $x_j(t)$, at finite temperature. We can expand each cartesian component of the trajectory in terms of the normal modes (ignoring translations):

$$x_j(t) = X_j + \sum_{i=4}^{3N} \alpha_i(t) e_{ij}$$

So far all this is exact, we just made a linear transformation of the coordinate system. $\alpha_i(t)$ is fully determined by the MD. Similarly for velocities:

$$\dot{x}_j(t) = \sum_{i=4}^{3N} \dot{\alpha}_i(t) e_{ij}$$

Now we assume that we are in the harmonic regime.

$$\alpha_i(t) = Re \left[ a_i \exp^{i(\omega_i t + \phi_i)} \right]$$

$$\dot{\alpha}_i(t) = Im \left[ a_i \omega_i \exp^{i(\omega_i t + \phi_i)} \right]$$

This assumption means that $a_i$, $\omega_i$ and $\phi_i$ are independent of time.

It is now straightforward to use the MD data to obtain $\omega_i$ from the FT. The FT of $\alpha_i$ is problematic since at high temperature $<\alpha> \neq 0$, but the same information is present in $\dot{\alpha}$ which is more convenient since $<\dot{\alpha}> = 0$. In the harmonic limit $FT[\dot{\alpha}_i(t)]$ is simply a delta function at $\omega = \omega_i$.

Note we have NOT used the frequencies from the lattice dynamics, we have calculated them from the MD. In the harmonic approximation, the same modes will be Raman/IR Active in the MD as in the lattice dynamics. As usual, we can calculate the occupied phonon density of states from the velocity autocorrelation function:

$$FT \left[ \sum_j \dot{x}_j(t) \dot{x}_j(0) \right] = FT \left[ \sum_i \sum_j \dot{\alpha}_i(t) \dot{\alpha}_i(0) e_{ij}^2 \right]$$

By analogy, the total Raman signal becomes:

$$FT \left[ \sum_{ij} R_i \dot{\alpha}_i(t) \dot{\alpha}_i(0) e_{ij} \right]$$

and we can obtain the mode frequency for each mode $i$ from the peak in: $FT[\dot{\alpha}_i(t) \dot{\alpha}_i(0)]$.

In the harmonic limit, the Raman signal is simply the sum of individual modes.

All of this has been applied in classical MD by numerous authors, e.g. Ref. [8] from the paper. We now, consider applying exactly the same process to an anharmonic MD. Modes with strong Raman/IR signals will still have strong Raman signals, since the polarisability ultimately depends on the motion of the atoms.

There are some issues about the magnitude of the oscillations. In the harmonic case it will never equilibrate. To get close to equilibrium it seems sensible to set initial displacements and velocities based on temperature from the normal modes (with random phase $\phi$).

$$\alpha_i(t = 0) = \sqrt{kT/m\omega_i^2} \sin(\phi)$$
\[ \dot{\alpha}_i(t = 0) = \sqrt{kT/m \cos(\phi)} \]

This is done, e.g. in SCAILD (Ref. 11 from the paper), but not automatically in CASTEP. This could be important in evaluating Raman intensities and line widths, since the anharmonic effects will depend on the phonon amplitude. However, for high pressure studies the experimental Raman intensities depend strongly on the apparatus and are not used quantitatively.

For H\(_2\) vibrons the Raman activity comes from the symmetric molecular stretch. It is therefore necessary to associate \(\alpha\) not with fixed normal modes, but with the molecule stretches:

\[ \alpha(t) = \sum_j r_j(t) - r_{jm}(t) \]

where \(r_{jm}(t)\) is the vector position of the molecular partner atom to \(j\), at time \(t\).

This requires us to identify molecules at each time step \(t\) (i.e. molecule labelling might change during the simulation, which could cause discontinuities in the velocity functions). Since the stretching modes can change at each time step, \(\dot{\alpha}(t)\) is not the simple time derivative of \(\alpha(t)\), but can be calculated by projecting the velocity \(v_j(t)\) of each atom onto the stretching mode. Finally, the spectrum for the vibron modes is:

\[ FT \left[ \sum_j v_j(t) \cdot [r_j(t) - r_{jm}(t)] \right] \]

Here we investigate vibrons, but the method is completely general provided that the Raman-active molecular mode can be identified. To validate our code, we performed an MD simulation at 60 K starting in the \(P_c\) structure. Figure 5 shows very good agreement in this simple regime where only harmonic effects are present. The MD projection onto normal modes or symmetric stretches give indistinguishable results.

**Finite size effects and a simplified layer model for dense H\(_2\)**

We have seen that the primary feature of the structural hierarchy is the layer, the secondary feature is the interaction between layers, and that interactions beyond this are weak. From the MD we note that adjacent B layers are not observed, presumably high in energy, while numerous relative translations of the G layers are observed, depending on kinetics: this implies little energy preference.

It is possible to understand the transition using a simple 1D model. We assign differences in energies (\(U_{GB} = U_G - U_B < 0\) and entropies \(S_{GB} = S_G - S_B < 0\) to each layer, and a layer interaction \(J_{ij}\) where \(i\) and \(j\) represent G or B layers. In this model the free energies of various \(N\) atom supercells with \(L\) layers are given in table I.

| Phase | Stacking | Free energy |
|-------|----------|-------------|
| III   | all-G    | \(N(U_G - TS_G + J_{GG})\) |
|       | all-B    | \(N(U_B - TS_B + J_{BB})\) |
| IV    | GBGB     | \(N(U_B - TS_B + U_G - TS_G + J_{GB})/2\) |
|       | random   | \(N(2U_B - 2TS_B + 2U_G - 2TS_G + J_{BB} + J_{GG} + 2J_{GB})/4 - LT \ln 2\) |

**TABLE I.** Energies of four possible “phases” which could be realised in an \(L=4\) layer supercell, where in the general case \(L\) is the number of layers.

Assuming \(J_{GG} < J_{GB} < J_{BB}\) this model gives a phase diagram as shown in figure 4 including a III-IV transition and a phase of all freely rotating molecules (rather similar to phase I). As discussed above in the context of 48 atom simulations, random stacking is favoured by the \(LT \ln 2\) term, which is significant only for small system sizes where the number of layers is comparable to the number of atoms.

Each layer contains only 12 atoms. For a free energy difference of \(F_{BG}\) per atom between the distinct layer types, Boltzmann statistics shows that the probability of finding the B layer is \(1/(1 + \exp(-12F_{BG}/KT))\). Static calculation implies a \(F_{BG} \approx 2\text{meV/atom}\), so at 300 K the unfavoured layer is present 28% of the time.
FIG. 4. Schematic drawing of the effect of finite size and temperature for the simple layer model. Random represents the phase observed in simulations with 24 or 48 atoms, BB, BGBG, and GGG are similar to phases III, IV and I respectively. For small enough systems (low N/L) randomly oriented layers will always be stable, however in the thermodynamic limit N/L → ∞ the phase sequence increasingly favours free-rotor B-layers, the mixed layer appearing whenever BB interactions are strongly disfavoured. The actual values of T and N/L at the phase boundary depend on the parameters, which in turn depend on pressure and temperature.

Calculation details

Data was collected from DFT calculations using the CASTEP package. The MD calculations involved 288 atoms initiated in prerelaxed monoclinic supercells of either Pc (β ≈ 91°) or C2/c (β ≈ 144°) structures, and used a constant-stress Parrinello-Rahman barostat. Observed phase transitions involved small changes of cell shape, but nothing close to the 53° change required to go from Pc to C2/c.

We used the PBE exchange correlation functional which has become the standard for work in hydrogen. Two different pseudopotentials were developed, an ultrasoft (300eV cut off) generated “on the fly” for the molecular dynamics and a harder norm-conserving pseudopotential (1200eV cut off) for which Raman calculations are more easily carried out. The structural results obtained were similar for the two methods. For the DFPT lattice dynamics a single unit cell k-point set of 9x5x5 was used, giving 69 independent k-points.
TABLE II. Structural details from static relaxations of $Pc$ and $C2/c$ structures. These structures were used for DFPT-LD calculation, and to initialise the MD calculations.

Two vibron modes from MD at 60K

FIG. 5. Fourier transform of projected velocity autocorrelation function of Raman active normal mode. The two Raman-active vibron modes were chosen, and can be seen to be in excellent agreement with lattice dynamics values 2845 cm$^{-1}$ and 4187 cm$^{-1}$. From MD calculation on $Pc$ at 250 GPa, 60 K. Data in Fig.2 were obtained from peaks in graphs such as this.
| No. | Initial Structure | Atoms | Ensemble | Number of Iterations | Time Step | Pressure | Temperature |
|-----|------------------|-------|----------|----------------------|-----------|----------|-------------|
| 1   | Pc               | 48    | NVE      | 9000                 | 0.5 fs    | 250 GPa  | 60 K        |
| 2   | Pc               | 48    | NVE      | 6000                 | 0.5 fs    | 250 GPa  | 145 K       |
| 3   | Pc               | 48    | NVE      | 6000                 | 0.5 fs    | 250 GPa  | 215 K       |
| 4   | Pc               | 48    | NVE      | 6000                 | 0.5 fs    | 250 GPa  | 285 K       |
| 5   | Pc               | 48    | NVE      | 6000                 | 0.5 fs    | 250 GPa  | 360 K       |
| 6   | Pc               | 48    | NVE      | 6000                 | 0.5 fs    | 250 GPa  | 430 K       |
| 7   | Pc               | 48    | NVE      | 6000                 | 0.5 fs    | 250 GPa  | 500 K       |
| 8   | Pc               | 288   | NVE      | 3000                 | 0.5 fs    | 250 GPa  | 215 K       |
| 9   | Pc               | 288   | NVE      | 3000                 | 0.5 fs    | 250 GPa  | 285 K       |
| 10  | Pc               | 288   | NVE      | 3000                 | 0.5 fs    | 250 GPa  | 360 K       |
| 11  | Pc               | 288   | NVE      | 3000                 | 0.5 fs    | 250 GPa  | 430 K       |
| 12  | Pc               | 288   | NVE      | 3000                 | 0.5 fs    | 250 GPa  | 500 K       |
| 13  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 180 GPa  | 220 K       |
| 14  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 200 GPa  | 220 K       |
| 15  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 220 GPa  | 220 K       |
| 16  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 220 GPa  | 220 K       |
| 17  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 220 GPa  | 220 K       |
| 18  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 220 GPa  | 220 K       |
| 19  | Pc               | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 300 GPa  | 220 K       |
| 20  | C2/c             | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 200 GPa  | 220 K       |
| 21  | C2/c             | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 200 GPa  | 220 K       |
| 22  | C2/c             | 288   | NPT + NVE| 500 + 1500           | 0.5 fs    | 200 GPa  | 220 K       |
| 23  | GGGG stacking    | 288   | NPT      | 7 x 200 + 6 x 200    | 0.5 fs    | 250 GPa  | 100 K → 400 K (+50 K) |
| 24  | C2/c             | 288   | NPT      | 400 + 600 + 200      | 0.5 fs    | 250 GPa  | 200 K → 300 K → 400 K |
| 25  | C2/c             | 288   | NPT + NVE| 800 + 2000           | 0.5 fs    | 250 GPa  | 300 K       |

TABLE III. Summary of MD calculations.

FIG. 6. Phase III transformation observed in NPT MD initialized in C2/c structure and heated at 250 GPa (see simulation 24 from Table III and Fig. 11). Left side shows MD supercell, while right side shows the corresponding layers. Top structure is Pickard’s C2/c (Ref. 19 from the paper) relaxed at 250 GPa, while bottom structure is a snapshot from MD, after the transformation has occurred: the G-layer stacking of the C2/c at the top is clear. The alternating BGBG stacking in the high temperature phase (lower) is similar to phase IV, but there is some frustration, which leads to a lower Raman-mode frequency (around 2980 cm\(^{-1}\)). The frustration illustrates the hierarchical nature of the bonding: a primary tendency to form layers, secondary to order as B or G within the layers, and a tertiary effect of interlayer interactions.
FIG. 7. As per figure 1 in the main paper, average positions of atoms over 1.5ps at 250 GPa and temperatures (from top left) 145 K, 215 K, 285 K, 360 K, 430 K, 500 K. Stacking is $BGBG$ and $BG'BG''$, respectively.
FIG. 8. As per figure 1 in the main paper, average positions of atoms over 1ps at 220 K and pressures (from top left) 180 GPa, 200 GPa, 220 GPa, 250 GPa, 270 GPa, 300 GPa. Stacking is $BGBG$ and $BG'BG''$, respectively.
FIG. 9. Calculated Raman peaks from MD at 220 K for a range of pressures traversing the VIa-VIb transition between 250 GPa and 270 GPa.
FIG. 10. Calculated Raman peaks from MD started in Pc at 220 K, 270 GPa, individually for each layer with two different methods: identifying molecules at $t = 0$ and keeping the same labels throughout the simulation (red), identifying molecules at each time step (blue). For B and G' layers the same results are found, while G'' gives very different results depending on the method, suggesting continuous rebonding. Note that the sum of the four spectra will be slightly different from the spectrum of the whole structure, for which the complex FT phases have to be taken into account.
FIG. 11. Figure showing lattice parameters and angles for a long MD run with a ramped temperature rise, started in the $C2/c$ structure (see simulation 24 from Table III and Fig. 6). The phase transition from III-IV appears evident, however close comparison of Raman data with experiment reveals that the high-T phase is not consistent with experiment. Parrinello-Rahman dynamics is not able to achieve the massive cell-shape change required to reach phase IVb.

| Phase | symmetry | conditions | description |
|-------|----------|------------|-------------|
| gas   | hcp      | ambient    | molecular $H_2$ |
| I     | distorted hcp | low-T + pressure | quantum rotation of $H_2$ molecules. |
| II    | C2/c     | Low temperature, <150 GPa | symmetry-breaking distortion of I |
| III   | C2/c     | 150+ GPa, 300- K | layer molecules arranged in hexagonal trimers. |
| IV    |          | 200+ GPa, ambient temperature | hexagonal and free-rotating molecular layers |

TABLE IV. Summary of known properties of phases on hydrogen; phase boundaries in hydrogen are not yet definitively established.