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New possible candidate structure for phase IV of solid hydrogen[†]

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1 Supporting Information

1.1 Vibrational analysis of Ama2 structure

Since the Ama2 structure has 24 atoms in primitive cell, there are 69 optical modes with the irreducible representation $\Gamma=20A1\oplus22B1\oplus16B2\oplus14A2$. All the optical modes are the Raman-active modes, whereas $A1$, $B1$, and $B2$ are the IR active modes. Here we focused on A1 modes with 3182/3939 cm^{-1} and $B1$ modes with 3765/4292 cm^{-1} corresponding to the experimental Raman and IR vibron frequencies, respectively. The rest of high frequencies modes with the Raman have a weak intensity and only influence peaks broadening or barely observable peaks in spectra. As illustrated in Figure S1, the lower and higher frequencies of Raman or IR vibrons correspond to hydrogen molecular vibrations of weakly bonded molecular layers and of strongly bonded molecular layers respectively.

1.2 Molecular projection method from first-principles molecular dynamics (FPMD) simulation

Here, we briefly introduce the calculated method about the Ama2 structure, while the detailed discussion about the molecular projection method can be found in papers.[1–3] All calculations were performed within the CASTEP code. Firstly, the Ama2 unit-cell was relaxed at 0 K and fixed pressure points. Then the Ama2 super-cell of 1×2×3 with 288 atoms was built as an initial structure for first-principles molecular dynamics (FPMD) simulations. The PBE functional and ultrasoft pseudopotential with 1200 eV cutoff, the k-point mesh of 2×1×1, and time step with 0.5 fs were used in the FPMD calculations. We adopted the isothermal-isobaric ensemble (NPT) to equilibrate the structure to the desired pressure and temperature condition in 500 steps. Then a longer 2000 steps microcanonical ensemble (NVE) simulation was applied to the equilibrated structure. The velocity of each atom during the NVE simulation was projected in the molecule onto the molecular stretching mode, and the Raman spectrum can be extracted by Fast Fourier Transform (FFT):

$$I(\omega) = FFT\{\sum_{j} v_j(t)\cdot[r_j(t)-r_{j_m}(t)]\} \tag{1}$$

where $r_j(t), r_{j_m}(t)$, and $v_j(t)$ are the position of atom j, the position of the other in molecule, and the velocity of atom j at time t, respectively.

1.3 Bond length

Vibronic frequencies of Raman and IR of solid hydrogen are strongly correlated with the H–H molecular bond length (BL). We used the vdW-DF2 and PBE functionals to calculate the BL of Ama2 and Pc, as illustrated in Figure S3. The relationship between bond length and pressure predicted by vdW-DF2 and PBE give a similar trend. The BL1 and BL2 of Pc and Ama2 phase predicted by the vdW-DF2 shorten with the pressure increasing, whereas BL3 and BL4 lengthen. But for the PBE functional, it tends to estimate a longer bond length than the vdw-DF2 functional at the same pressure. These results are consistent with the conclusion of exchange-correlation functionals benchmarked by QMC,[4] which shows that PBE overestimate significantly the BL of candidate structure, while vdW-DF2 underestimates the BL with a comparable magnitude. The detailed difference of structure between Ama2 and Pc can also be represented by the bond length in Figure S3. For example, Figure S3 (a) and (b) both show that BL3 and BL4 of the weakly bonded molecular layer of Pc are close to being equal gradually, whereas the difference between BL3 and BL4 of weakly bonded molecular layer of Ama2 keeps little change with the increasing of pressure. This shows that Ama2 remains the distorted hexagonal pattern formed by H_2 of the weakly bonded molecular layer whereas the graphene-like layer of Pc gradually evolves into the graphene sheet.

1.4 Raman and IR spectra of Ama2

Figure S4 shows Raman and IR spectra of Ama2 calculated by PBE functional. Previous researches have pointed out that the low-frequency IR section doesn't exhibit significant absorption in experiment[5], therefore, there is no plenty of IR data for frequency be-

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low 1800 cm^{-1}. The calculated Ama2 IR spectra show that intensities of low-frequency IR modes are very weak and the low-frequency IR modes are sparse. Here we just compared the calculated low-frequency Raman frequencies of Ama2 with experiment data. In Figure S5, the pressure dependence of frequencies of low-frequency Raman peaks of Ama2 and Pc can qualitatively coincide with the experimental L_1, L_2, L_3 modes. Particularly, the low-frequency Raman peak of Ama2 is in better agreement with experiment L_2 compared with that of Pc. In addition, the low-frequency Raman peaks of Ama2 also captured the phenomenon where experimental L_3 splits into two modes.

Notes and references

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Table S1 The convergence of vibrational energy (E_{ZP}) on the size of the supercell. The test was conducted at 200 GPa.

Primitive cell (No. Atoms)	Supercell (No. Atoms)	E_{ZP} (meV/proton)
C2c-24 (24)	2×2×1 (96)	308.63
C2c-24 (24)	3×2×1 (144)	308.64
Ama2 (24)	2×2×1 (96)	307.15
Ama2 (24)	3×2×1 (144)	307.09
Pc-48 (48)	2×1×1 (96)	309.77
Pc-48 (48)	2×1×2 (192)	309.79
Pbcn-48 (48)	2×1×1 (96)	309.17
Pbcn-48 (48)	2×1×2 (192)	309.26
Cmca-12 (12)	2×2×2 (96)	311.78
Cmca-12 (12)	3×2×2 (144)	312.00
Cmca-12 (12)	3×3×3 (324)	312.02
Cmca-4 (4)	3×3×2 (72)	303.16
Cmca-4 (4)	4×4×2 (128)	303.20
Cmca-4 (4)	4×4×3 (192)	303.28

**Table S2** Structural information of new founded Ama2 phase calculated by using the vdW-DF2.

| Space group atoms	Pressure (GPa)	Lattice parameters (Å, °)	Atomic coordinates (fractional)
Ama2 24	300	$a = 5.1670$ $b = 4.9990$ $c = 2.8788$ $\alpha = \beta = \gamma = 90.000$	H1 0.9987 0.2475 0.3427 H2 0.0223 0.3732 -0.0520 H3 1.0000 0.5000 -0.4320 H4 1.0000 0.0000 0.8318 H5 0.2500 0.2011 0.0717 H6 0.2500 0.4803 0.0368 H7 0.2500 0.3333 0.4021 H8 0.2500 0.0735 0.1627 H9 0.7500 0.1788 0.1408 H10 0.7500 0.4063 0.1789
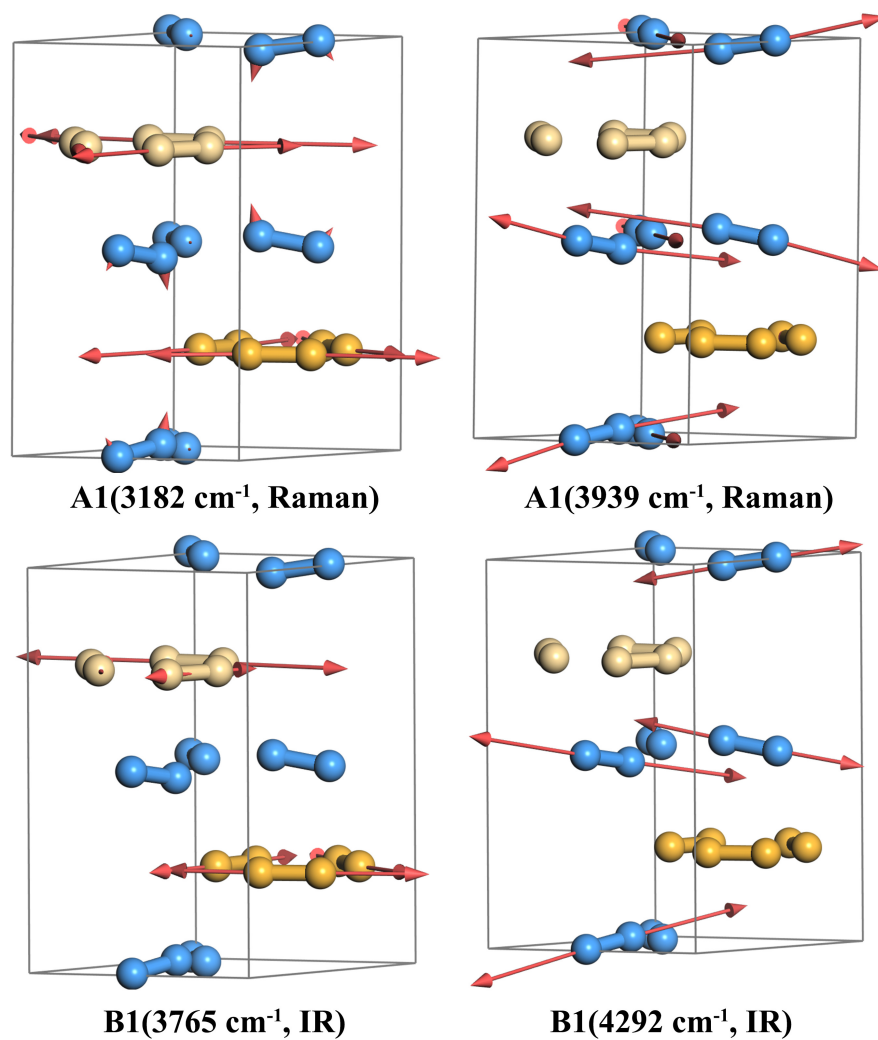
Figure S1. The four eigenvectors of Ama2 structure at 300GPa. The red arrows represent the vibrational direction of hydrogen molecule and the lengths of arrows represent the vibrational intensities.
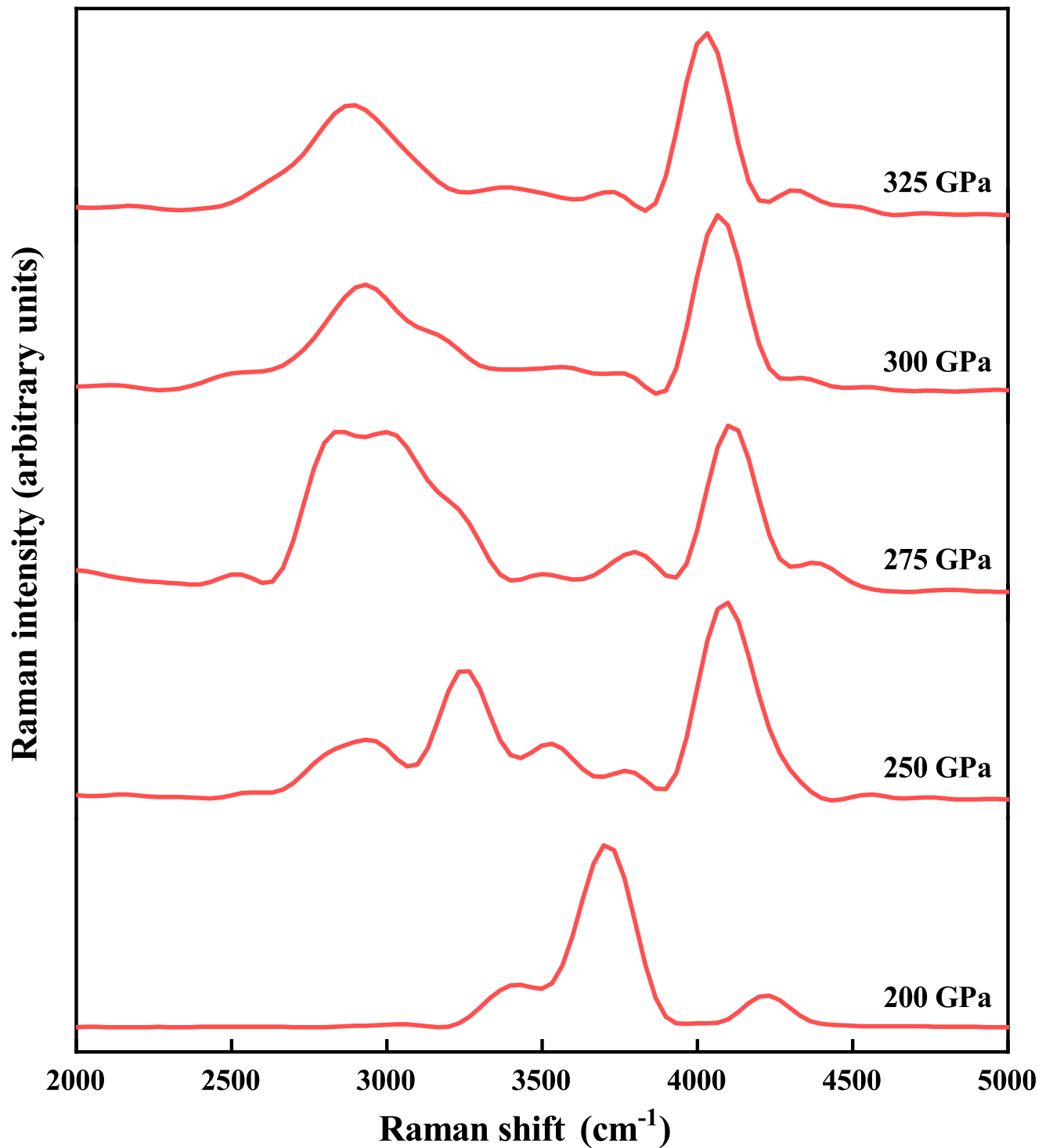
Figure S2. Calculated Raman peaks of Ama2 from FPMD at 220 K for a series of pressure points between 200 GPa and 325 GPa.
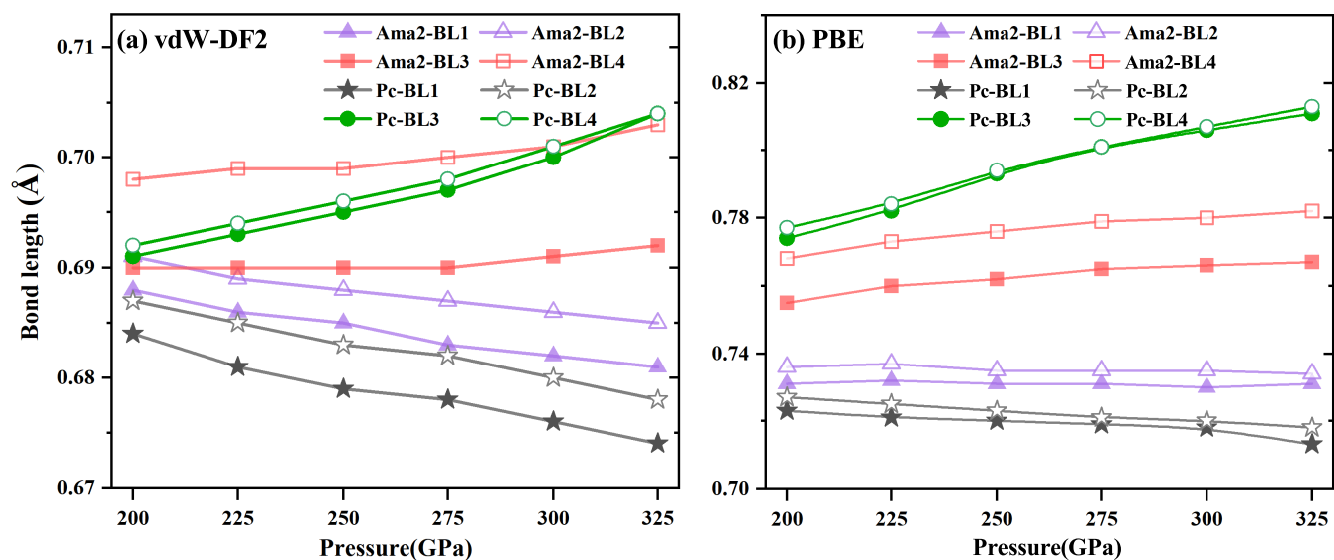
Figure S3. Pressure dependence of the bond lengths of Ama2 and Pc calculated by using the vdW-DF2 and PBE, respectively. Since Ama2 and Pc both have the two types of layer, we focused on the shorter and longer bond length in the strongly bonded and weakly bonded molecular layers, which are denoted as BL1, BL2 (for the strongly bonded molecular layer) and BL3, BL4 (for the weakly bonded molecular layer) respectively.
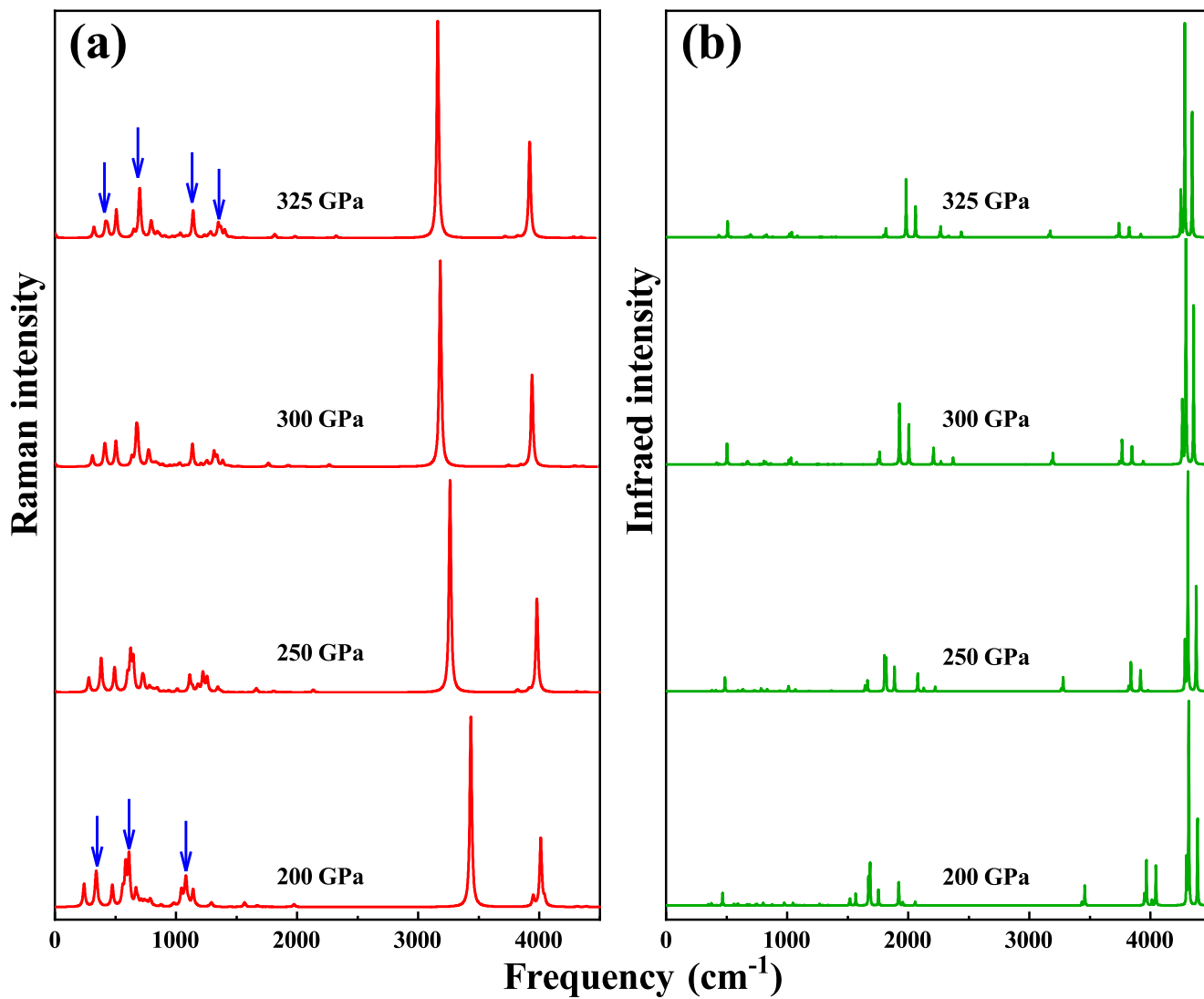
Figure S4. Raman (a) and infrared (b) spectra of Ama2 structure calculated LD at 200, 250, 300 and 325 GPa. Noting that only the relative intensities at the same pressure are meaning. Blue arrows represent intense Raman peaks which the low-frequency Raman frequencies are taken from.
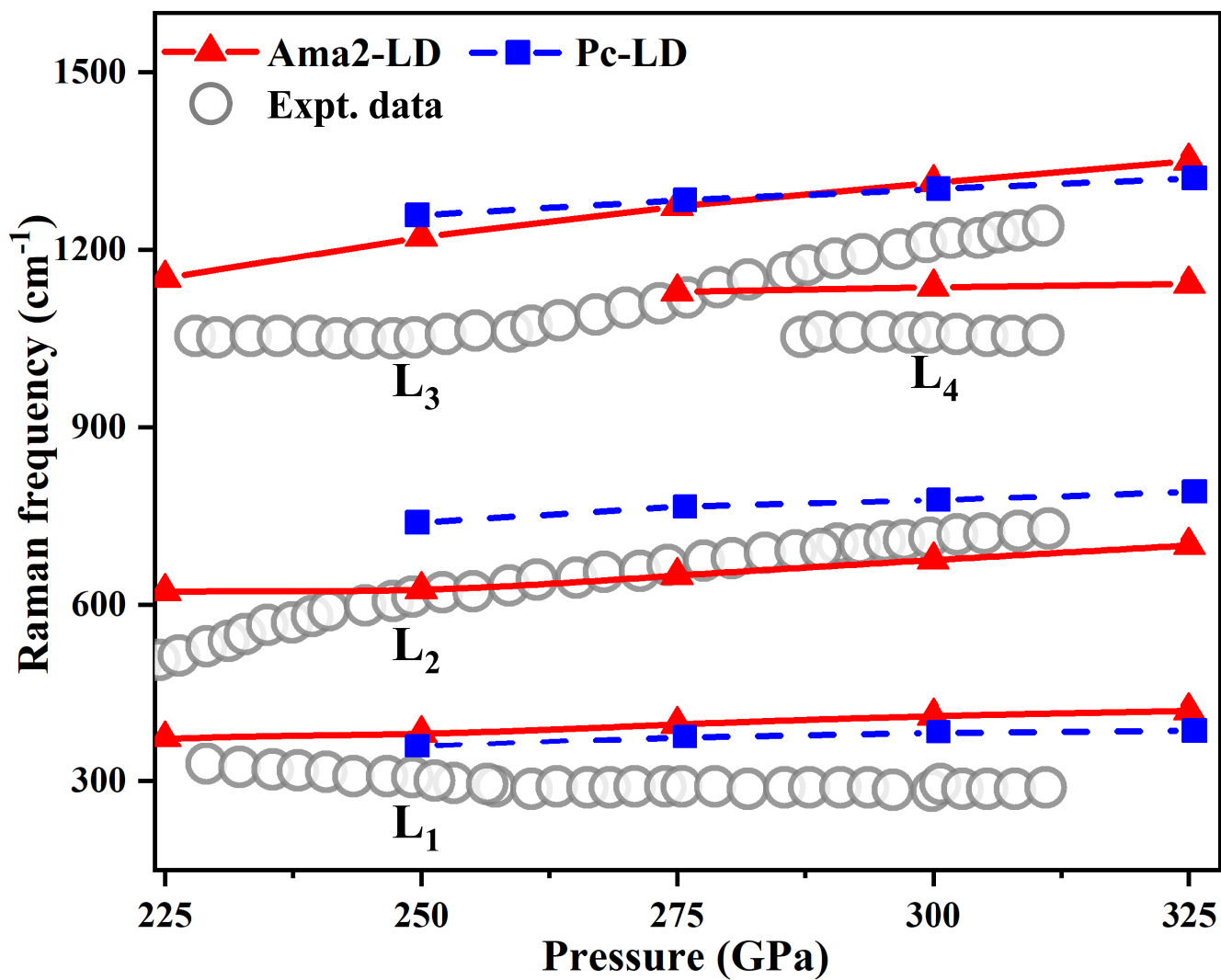
Figure S5. Pressure dependence of low-frequency Raman frequency of solid hydrogen. LD calculations were performed at 0 K for Ama2 (red triangle) and Pc LD data (blue square) are taken from [6] Monserrat *et al.*. Experimental data are taken from Howie *et al.* (blue open circle). [7]