Melting of Hydrogen Above 200 GPa

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Supplementary Materials

Experimental Details

In the present study we have chosen to use the resistive heating instead of the laser heating technique because of the relatively low temperatures at which transformation take place, higher precision of the temperature measurements and higher signal-to-noise ratio of the Raman signals. This technique provides some some major technical problems if one wants to reach pressures above ∼150 GPa. One of the key inhibitors to reaching high temperatures in multi-megabar regime conditions is the irreproducibility and lack of stability in the alignment of the diamond anvils. High temperature diamond anvil cells are normally machined with a slack fit to prevent jamming after the thermal expansion of the cell material. The slack fit of the cell can cause the diamonds (typically 15-25 µm culets) to shift (as much as 15 µm) during loading and through compression, leading to non uniform anvil stresses, sample loss and anvil failure. Furthermore, large pressure losses are usually common in high temperature experiments due to heat deformation of the diamond anvil cell and the force supplying equipment. In collaboration with the technical staff at the University of Edinburgh School of Physics mechanical workshop, we have designed and produced high pressure and high-temperature diamond anvil cells and the force supplying equipment with markedly improved mechanical stability. The cells are tight-fitting, improving the ease and consistency of the anvils alignment with minimal anvil movement upon compressions (less than 3 µm). The minimal pressure fluctuations were observed on heating with the newly built equipment.

This improvement in experimental apparatus, which significantly decreased the time needed for cell preparation, combined with the efficient procedure of hydrogen/deuterium loading, allowed a huge number of experiments to be conducted. As an indication, the data presented in this paper represents roughly 35% of all hydrogen loadings with all other loadings deemed unsuitable for reaching multi-megabar pressures before they even exceed 30 GPa.
Figure S1: Previous melting data of hydrogen from both resistive heating ([1, 2]) and laser heating ([3, 4]). Although melting data has been obtained through laser heating techniques to 146 GPa, the inherent experimental complications with such experiments result in a spread of melting points and large errors in melting temperatures. The Kechin fit (dashed line), signifying a turnover in melting temperatures, could be fitted to the data, other melting laws (solid line) could equally be plausible with similar goodness of fit. As such, previous experiments have yet to conclusively show either a maximum or turnover in the melting curve.
Pressure Measurements

Figure S2: (A) The top spectra is the first order Raman signal from diamond, the dashed line shows the determined edge from the minimum in the differentiated spectra below. Representations of estimated pressure fluctuations during two heating runs. (B) The pressure increase of a heating run starting at 198 GPa up to 423 K. Pressure was measured on heating (solid triangles) and cooling (empty upside-down triangles), pressure was found to increase by \( \sim 30 \) GPa over the complete cycle. (C) Pressure fluctuations in an “isobaric” run on heating to 555 K, isobar was maintained to within \( \sim \pm 5 \) GPa of 225 GPa.
Detecting Phase Transitions A

**Figure S3:** (A) Representative Raman spectra taken in the fluid state at 0.2 GPa up to 3.2 GPa, showing the amalgamation of several rotational-vibrational excitations of low density fluid into a single vibron at higher densities. The frequency of the vibrational mode (B) and full width at half maximum (FWHM) (C) as function of pressure along an isotherm at 300 K. The solidification at 5.5 GPa is marked by the black dashed line.

Several pressure dependent factors determine the changes of the vibron frequency and its width through the liquid-solid phase transition. The frequency of the vibron has a particularly complex function with pressure defined by the interplay between the following parameters (S3A):

1. In the solid state the vibrational in-phase mode (Raman) is on the bottom of the vibrational band while out-of-phase mode (infra red) is on the top. During the solidification that would require the Raman frequency to soften and IR mode to harden compared to their positions in the liquid state. The difference between IR and Raman frequencies in solid is increasing with pressure.

2. The Raman vibron frequency increases with pressure (volume/density), \( \frac{d\nu}{dp} \), is positive, up to \( \sim 35 \) GPa, where it reaches the maximum after which frequency starts to decrease. \( \frac{d\nu}{dp} \) ranges from \( \sim -0.5 \text{ cm}^{-1}\text{ GPa}^{-1} \) between 40 GPa and 180 GPa to \(-12 \text{ cm}^{-1}\text{ GPa}^{-1} \) at 250 GPa. Therefore softening (hardening) of the vibron through the phase transition will depend on the relative densities of the phases. Since the melting curve goes through maximum at 130 GPa the liquid state is less dense than phase I below melting maximum and more dense above.

The pressure dependent factors of the vibron’s width (S3B):

1. At low densities in the liquid state (<3 GPa) vibrational-rotational modes are resolved in the spectra, with a prominent sharp vibrational mode with a width of 2.3 cm\(^{-1}\) at 0.2 GPa. At higher densities we see the amalgamation of these rotational vibrational modes forming an asymmetric up to 2 GPa and finally a symmetric vibron above 3 GPa with a width of \( \sim 12 \text{ cm}^{-1} \) in the fluid phase. The comparatively large scatter seen between 0.75 and 3 GPa is attributed to the difficulty of fitting a Voigt with the presence of the asymmetry.

2. Molecular collisions are present within the high density liquid state. These molecular collisions broaden the vibrational mode by inhibiting the lifetime of the photon emission within the Raman Effect in turn affecting the uncertainty of the energy of the emitted photon. Within the solid state these molecular collisions are forbidden and as a result collision-induced broadening will not have an effect. This is shown by a discontinuity in the width of this excitation around the solidification pressure 5.5 GPa at 300 K. The vibron’s width reduces by a factor of 2 from \( \sim 12 \text{ cm}^{-1} \) to \( \sim 6 \text{ cm}^{-1} \).
3. Upon solidification the FWHM then slowly decreases with pressure reaching shallow minimum at $\sim 19$ GPa. After which it linearly increases due to the pressure induced broadening, Fig. 3 in Ref. (18), at a rate of $0.5 \text{ cm}^{-1}/\text{GPa}$ until $210$ GPa where changes in the width become much more pressure dependent, $6.5 \text{ cm}^{-1}/\text{GPa}$, associated the change from phase I into phase III.

Due to its less complex pressure dependence and more significant changes upon melting, the FWHM could be used as an additional and more reliable parameter to detect transformations at high temperatures. The phase transformations were previously detected through the position of the vibrational mode, which downshifts upon solidification at lower pressures, typically by a few cm$^{-1}$ Ref. (9). However, due to the vibrational band frequency complex dependency on pressure and its high sensitivity to any change of compression (S4), its position during the experiment can change dramatically due to factors other than melting and mask out the moment of transformation.

We also note that when the vicinity of the expected melting at higher pressures was reached (with melting temperatures above $\sim 600$ K) the sample loss becomes very common and is extremely rapid, due the increased mobility and diffusion of hot liquid hydrogen.

Figure S4: (A) Representative raman spectra at 14 GPa, melting is indicated by the change of colour in the spectra at 593 K. Panels (B) and (C) show the position and frequency of the vibrational mode at 8 GPa (orange), 14 GPa (blue) and 20 GPa (black) up to $\sim 660$ K. Melting at each pressure is indicated by a respectively coloured dashed line
Detecting Phase Transitions B

At higher pressure >200 GPa we enter into a comparatively complex regions of phase space, illustrated by 3 consecutive heating cycles in which pressure changes were unimpeded (S5):

1\textsuperscript{st} Heating: (S4A and S4B) Pressure was found to increase roughly by 30 GPa within the first heating cycle. On cooling hydrogen was found to enter into phase III with the vibron characteristically broadening and softening, this phase transition was found to agree with previous results in literature.

2\textsuperscript{nd} Heating: (S4C and S4D) Pressure again increased throughout the cycle with a net increase of 10 GPa. On heating the phase III to phase I transition is again observed and is agreement with previous studies on the III-I phase line. However, on cooling we observe hydrogen entering into phase IV at around 332 K and 243 GPa characterised by the appearance of an additional vibrational mode. This demonstrates that Phase IV is not stable at elevated temperatures at this pressure and transforms into the Phase I configuration.

3\textsuperscript{rd} Heating: (S4E and S4F) In this heating cycle the previously undetermined IV-I phase line is further experimentally constrained with the transformation observed at 349 K at 245 GPa and 373 K at 253 GPa.

\textbf{Figure S5:} Representation several consecutive heating runs conducted on hydrogen: 1st heating (A and B), 2nd heating (C and D) and 3rd heating (E and F). Each pair of graphs has the vibrational modes positions and FWHMs plotted. The solid and empty circles represent points taken on heating and cooling respectively. Colours of the circles signify different phases in which the measurement was taken: I (orange), III (green) and IV (purple). During the first heating the sample was at a nominal pressure of 198 GPa, which increased to 229 GPa. In the second heating cycle the starting pressure was 223 GPa, which increased to 242 GPa. In the final heating the pressure increased from 249 GPa to 258 GPa.

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