

Raman spectroscopic findings of new molecular phase in hot dense hydrogen

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Raman spectroscopy, a versatile spectroscopic tool can be used to study the composition of solids, liquids and gases in chemical and biological systems. This spectroscopic technique has diverse applications such as detection of explosives and warfare agents, analysis of minerals and ores, detection of bacteria and viruses as well as analysis of coins, paintings and sculptures in archaeology. The technique is based upon the inelastic scattering of photons of monochromatic light in the visible, near-infrared or near-ultraviolet range of the electromagnetic spectrum by atoms and molecules. Raman scattering or Raman effect was discovered by the famous Indian physicist C. V. Raman in 1928 (ref. 1). The shift in wavelength or energy of the inelastically scattered photons provides the chemical and structural information of the molecule under study.

Hydrogen is considered as the most abundant element on earth and the major chemical constituent of stars in the galaxies. Therefore, it is important to study hydrogen at extreme pressures and temperatures for an overall understanding of the rich variety of unusual states and structures as well as unusual properties of dense hydrogen, which it can demonstrate inside stellar bodies and gas giants.

Behaviour of hydrogen at high densities has been widely studied in recent years, both experimentally and theoretically^{2,3}. Information, limited at temperature below 300 K and pressure ~300 GPa can be obtained from static compression experiments. However, various questions have not been answered clearly regarding the behaviour of hydrogen at high pressures and temperatures, results that have great significance from the point of view of both fundamental physics and planetary science.

It has been theoretically known that at high pressure, the increased energy of the zero-point oscillations in hydrogen will weaken the lattice and help in the formation of a ground fluid state at 0 K (ref. 4). Theoretical study has also suggested that this fluid state, which represents a new state of matter, might have

acquired unusual properties governed by quantum effects like superfluidity or superconductivity⁵. It has been widely accepted that the melting curve of hydrogen will exhibit a maximum, even though there is no credible experimental proof to establish the same. Datchi *et al.*⁶ carried out the first experiment on the melting of hydrogen at gigapascal pressures, where melting of hydrogen was observed between 5 and 15 GPa and later these data were extrapolated to much higher pressures (pressure above 300 GPa). It was found that the empirical Kechin law⁷ can provide the best fit to the data. There were further experimental studies, where melting was detected using Raman spectroscopy⁸. Subsequent laser heating experiments, combined with Raman spectroscopic study, extended the pressure range to 150 GPa (refs 9 and 10). However, no data above 150 GPa of pressure and 300 K temperature exist, and extrapolation of the existing data to higher pressures suggests that dense hydrogen might melt at room temperature above 250–300 GPa of pressure.

Theoretical first-principles calculations can be carried out, which will predict a structural phase transition in the solid prior to melting at pressures above 40–50 GPa and temperature in the range of 400–700 K (ref. 11). Other simulation studies indicate a transition to a dissociated liquid phase at temperatures above 1000 K at 150 GPa (ref. 12). However, the mechanism of phase transition to the fluid is highly questionable, and the data related to actual equation of state remain controversial until now. Vibrational spectroscopy is vital in such studies. In addition to information on bonding, these spectroscopic techniques are the only methods available for identifying phase transitions at high (e.g. 100 GPa) pressures¹³ as vibrational excitations are extremely sensitive to changes in crystal structure, including melting. The probing techniques to study hydrogen and its phase transitions at high pressures and temperatures are limited. Although X-ray diffraction technique can be used, it is not simple even in the solid state due to low atomic/mass number of hydrogen.

Recently, scientists under the leadership of Eugene Gregoryanz (University of Edinburgh, UK) have carried out the first phase transition experiment above 200 GPa pressure combining *in situ* high-temperature, high-pressure techniques with Raman spectroscopic study¹⁴. In their experiment, they demonstrated the occurrence of a new phase transition above 200 GPa pressure, with an increase in temperature. The phase transformation at temperature 480 K and 255 GPa pressure can be interpreted as melting and a new triple point between phases I and IV and the new phase was observed¹⁴. It was demonstrated that hydrogen will retain its molecular character around this point. They were able to confine hydrogen at high temperatures in the diamond anvil cell long enough to collect high-quality Raman spectra, tracking the evolution of the Raman modes in phases I, III, IV and a new phase, which can be speculated as a liquid state. The phase transformations at high pressures were monitored and studied elaborately using Raman spectroscopy, which was impossible to observe visually due to the large reduction in sample size. In their study, unusual Raman spectra were observed above 180 GPa at 300 K in phases III and IV(IV') with the presence of intense and temperature-dependent librational and vibrational bands. The existence of a third triple point was demonstrated from the measurements, providing limitations on the phase diagram, which suggests a melting minimum. Figure 1 demonstrates the proposed phase diagram (temperature versus pressure curve) of hydrogen up to 325 GPa pressure. The inset (Figure 1) shows the *P-T* paths (1 and 2) taken during temperature cycles. The *P-T* paths as shown in Figure 1 can provide further experimental limits on the phase diagram with the creation of a few interesting questions regarding the possible melting minimum and the proposed liquid ground state. The extrapolated melting curve as shown in the *P-T* paths (Figure 1) needs to alter slope after the I–IV–liquid triple point. The presence of proposed liquid state at temperatures below 300 K and pressures below 400 GPa was efficiently

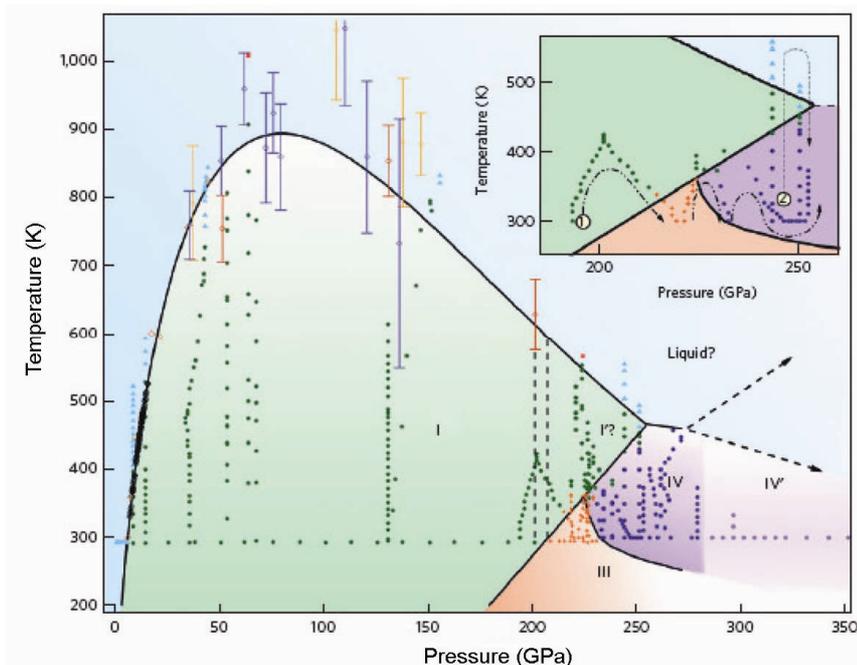


Figure 1. The proposed phase diagram by Howie *et al.*¹⁴ (temperature versus pressure curve) of hydrogen up to 325 GPa pressure. (Reprinted with permission from Howie *et al.*¹⁴; Copyright (2015) Nature Publishing Group.)

ruled out by the extension of melting curve. In reality, a recent theoretical study established that the melting curve remains flat at temperature around 300 K with pressure up to 500 GPa (ref. 15), where it gets back a positive slope. Hypothetically, the liquid ground state could still exist at much higher pressures such as above 500 GPa and the existence of such phase would be determined by different factors like the P - T conditions at which the molecular dissociation of hydrogen occurs, by the zero-point energy terms of the atomic liquid and/or solid versus other energy terms making contribution to the Gibbs free energy.

It was speculated that the extreme changes observed in the Raman spectra on increasing temperature could be explained by solid–solid phase transformation. The combined data could probably rule out this speculation due to the simplicity of the observed Raman spectra at the highest temperatures, which can be characterized by a moderately narrow

single vibrational mode and absence of rotational modes. In the present study, it was assumed that Raman spectra were identical in nature in the liquid state over a broad pressure range, which would also imply that there is a new solid molecular phase of hydrogen between 130 and 270 GPa with very high melting temperatures. The presence of a new high-temperature solid phase would be an interesting observation and generate several questions that will totally change the overall theoretical understanding of hydrogen under these conditions. Therefore, new models are clearly needed proposing such a new high-temperature solid phase structure and predicting melting temperatures that do not decrease above 120–140 GPa. The presented results as illustrated in various theoretical papers based on melting are in reasonable qualitative agreement with the recent measurements^{15,16}.

However, there are limitations of Raman spectroscopic method to detect

melting. This can be further overcome using more advanced techniques such as Brillouin spectroscopy, X-ray diffraction, neutron reflectivity studies as well as consideration of other phenomena which could have led to changes in the Raman spectra during the melting studies. The presented data further expand the overall understanding of a system that was previously found to be highly intangible experimentally at these conditions.

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