Raman Spectroscopy of Hydrogen Confined under Extreme Conditions

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Abstract. The challenge of confining hydrogen and its isotopes at high pressures and temperatures has hindered exploration of the predicted novel phases and their properties in static high P-T experiments. We have developed new methods to achieve good local confinement of hot, dense hydrogen that additionally protects the diamond anvils during the experiments. Raman spectra of such locally confined hydrogen and deuterium samples at high P-T conditions reveal interesting and rich features which include some that may be related to melting and some related to possible formation of species like metal hydrides and clathrates. These are discussed in the context of difficulties associated with establishing unambiguous diagnostics of melting of hydrogen, and thereby determination of the melting curve in laser and resistive heating diamond cell experiments at high pressures.

1. Introduction

Experimental efforts have been underway to confirm the prediction of novel forms of hydrogen under pressure for the past few decades [1]. Most past experiments have concentrated on the pressure induced behavior of hydrogen at 300 K or lower temperatures. In the recent years, experiments on hydrogen that employ either laser-heating or resistive heating techniques in conjunction with \textit{in situ} spectroscopic experiments have been reported [2,3]. Apart from enabling determination of the melting curve of hydrogen as a function of pressure, such experiments have sought to explore the phase diagram of hydrogen and deuterium at high P-T conditions including molecular and monatomic phases. A key problem that faces experimenters is to confine the hot and reactive hydrogen in the sample chamber at high pressures long enough to make meaningful measurements of physical properties. Even cold hydrogen is difficult to contain at ultrahigh pressures (e.g. several megabars) with common gasket materials, and that makes confinement of hot hydrogen all the more challenging. Here we describe new methodologies to achieve good local confinement of the hydrogen and discuss some results from \textit{in situ} laser heated diamond anvil cell (LHDAC)--Raman spectroscopy measurements made on samples up to \~{}130 GPa and temperatures more than 2500 K. We discuss appropriate diagnostic criteria for melting in LHDAC experiments in light of the discrepancies between the recent experiments seeking to verify the predicted maximum in the melting curve of hydrogen [2, 4-7].
2. Experimental Details

Confinement is accomplished by locking-up the hydrogen in a hole (5-8 µm diameter and ~ 6 µm depth) made in an IR absorbing iridium coupler, which in turn is sandwiched in an inert buffer layer between the tips of the two diamond anvils (Fig.1 inset) in a composite gasket assembly. With this configuration, we have measured in situ Raman spectra on hydrogen and deuterium while performing double sided laser-heating to ~ 130 GPa and temperatures above ~ 2500 K. An advantage in having this complex assembly is the ability to have hydrogen predominantly within the coupler hole (Fig.1), thereby reducing the effects of pressure and temperature gradients across the probed sample. Thus high resolution Raman spectra with minimal contributions from the cold sample areas can be obtained from a 5µm diameter sample region locked in the coupler hole. With this sample loading, we can perform experiments on multiple heating cycles per loading, each lasting for several minutes, without significant loss of sample or damage to the diamond anvils. Many different substances have been tested as a material for the buffer (e.g. various salts, alumina, CaF$_2$ or mixtures of these). We find that all of them can be used to confine hydrogen at high temperatures. However, some of these materials develop a very large fluorescence under pressure (e.g. KBr), which complicates their use in Raman experiments.

![Figure 1](image.png)

**Figure 1.** Spatially resolved vibron spectra of molecular hydrogen from various regions in and around the IR absorbing metal coupler. The results shows that the hydrogen is confined predominantly to the small (8 µm diameter x 6 µm depth) coupler hole region.

Double sided laser heating experiments were carried out using the combined Raman-LHDAC system described in detail by Goncharov *et al* [8]. In this set-up, heating is done with an Yb-based fiber laser that can be operated in either continuous wave (CW) or pulsed mode. For the work presented here, we have employed CW heating. At each laser power step, thermal radiation spectra were recorded using both a liquid nitrogen cooled InGaAS detector (for temperatures below 1000 K) in the 1400-1600 nm range as well as with a CCD spectrometer in the 500-950 nm range to determine sample temperature.
by spectroradiometry [8]. In some experiments, temperatures below ~750 K were below detection limit of the IR spectrometer and were estimated from the known variation of vibron position with temperature and pressure [2,3]. Pressures were determined either using ruby fluorescence method or the vibron frequency at 300 K [1]. Raman spectra were recorded at each laser power step using either the 488 nm, 457 nm or 514.5 nm lines from an argon ion laser or the 457 nm line from a solid state laser. Speckle patterns generated from the sample region using another laser at 532 nm were monitored carefully throughout the experiments.

Several trial experiments with this sample assembly led us to evolve an important criterion for satisfactory hydrogen loading for LHDAC experiments. An acceptable loading was one in which the Raman measurement from the middle of the coupler yielded a high intensity hydrogen Raman vibron signal (at ~4200 cm\(^{-1}\)) well above a background (e.g. diamond fluorescence), so it could be collected with a signal-to-noise ratio better than ~100 for a 5-10 second accumulation time; the latter are needed for our laser heating experiments. As a rule of thumb, the hydrogen vibron peak must be comparable or higher than the intensity of the first-order Raman peak of the diamond anvil (~1332 cm\(^{-1}\)) in our confocal Raman system. A reasonably good signal-to-noise ratio of the vibron is needed at very high temperatures, as the heating cycle progresses the vibron intensity starts dropping rapidly; this effect is described further in the next section. A good hydrogen signal during the first heating cycle also ensures that we could perform multiple LHDAC experiments with the same sample. Other criteria include verifying the absence of any moisture in the sample chamber, use of low fluorescence materials in the composite gasket, and ensuring minimal presence of hydrogen in regions away from the coupler hole (Fig.1). All these criteria are crucial for confining, heating and making reliable measurements on dense hydrogen over many cycles.

3. Raman Spectroscopy of Hydrogen at High Pressures and Temperatures

High resolution Raman spectra of hydrogen at ~109 GPa at representative temperatures during a typical heating cycle are shown in Fig. 2a. Up to ~820 K, the vibron peak softens and broadens systematically and there is a clear separation of a low frequency “hot” vibron peak (at ~4099 cm\(^{-1}\)) and a higher frequency “cold” vibron peak (~4129 cm\(^{-1}\)), which appears as a shoulder. A weak, broad peak can be seen at the left foot of the hot peak, rendering an asymmetry and contributing to an increase in the overall peak width. With increasing temperature, this feature can be seen to increase in intensity. It is also noted that as temperature increases the hot peak shifts increasingly further away from the cold peak, which remains relatively unshifted but with a reduced intensity. The ratio of hot to cold hydrogen content in the 820 K measurement is estimated as ~11 at this temperature assuming the same cross-section for the hot and cold material. This estimation can suffer from a reduction of intensity away from a focal plane, which suppresses the peak from cold hydrogen due to the use of the confocal geometry.

The high temperature spectra could be deconvoluted into three peaks, one of which is the cold peak that varies very slowly with temperature (Fig. 2b). The hottest peak shows a dv/dT that is about 5 times larger in magnitude than the cold peak (dv/dT ~ -0.039) and also broadens with an increasing rate with temperature compared to the other two peaks (Fig. 2c). The relative contributions of high P-T band broadening and possible melting in the 800-1000 K range is under study. The 1070 K spectrum shows a new high frequency peak on the right of the cold hydrogen peak. This peak persists with weakened intensity down to room temperature during the cooling cycle, indicating that in the 1000 K range, a definite irreversible process, such as new compound formation that may or may not be related to melting, has taken place (e.g. ref.[3]).

These observations indicate good confinement of high P-T hydrogen leading to highly localized heating and spectra measurements from this region, wherein the effects of pressure and thermal gradients are small. The cold peak that is seen has its origin in the hydrogen present in the buffer region isolating the anvil from coupler hole region. This is further exemplified in Fig. 3, which shows spectra during the cooling cycle. The hot peaks shift towards the cold peak as the sample is cooled; as a consequence, the vibron signal narrows down with pick-up in intensity and hardening towards its
starting position. Finally, when the sample is brought to room temperature, the vibron peak reverts back to its original position and linewidth. There is some drop in intensity though owing to a small loss of the hot hydrogen, probably upon melting and/or involvement in a chemical reaction. The fact that there is good recovery and we could do repeated heating experiments shows that the confinement procedure we have followed works well.

Experiments up to ~130 GPa reveal similar trends during laser heating. Figure 4 contains photographs of the sample at 130 GPa before and after laser heating. Formation of light absorbing species is evident. Upon gradual release of pressure, the sample region was seen to regain some transparency.

4. Diagnostics of Hydrogen Melting in Laser Heating Experiments
Melting behavior of hydrogen has been examined using first principles molecular dynamics by Scandalo [4] and Bonev et al [5]. Using a single-phase approach, Scandalo [4] has predicted a reentrant behavior of the melting curve, with an abrupt reversal of slope, at ~140 GPa and ~ 1100 K and attributes it to the intersection of the molecular fluid to non-molecular fluid transition line with the melting line. Bonev et al [5], using a two-phase approach to melting, instead has predicted a smooth turnover in the melting curve with the maximum at ~90 GPa and ~850 K. This has been ascribed to a differential softening of the intermolecular potential in the fluid relative to the solid above ~90 GPa. Irrespective of the mechanisms and the theoretical approaches employed, both computations converge
Relative Intensity

Based on pulsed laser heating, Deemyad and Silvera report [6] a maximum in the melting curve at ~65 GPa and ~1055 K. Their maximum appears as a sharp cusp that departs from the empirically and theoretically predicted curves [4,5]. Their diagnostics of melting relied upon

![Figure 3](image)

**Figure 3.** Evolution of the Raman spectrum of the hydrogen vibron during a cooling cycle at ~109 GPa.

![Figure 4](image)

**Figure 4.** *(Left)* Hydrogen sample at ~130 GPa present in the metal coupler hole before laser heating; *(Right)* After laser heating to about 750 K, the coupler hole region can be seen absorbing visible light; The coupler and gasket hole region are shown enlarged in the insets of both photographs

on the prediction of a change in sign of the slope of the melting curve at high pressure and temperatures.

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observation of changes in speckle pattern at 1.065 µm, induced by the heating laser, recorded with a CCD and the attainment of a plateau in the laser-power versus temperature curve. We point out that the speckle motion seen at infrared wavelengths can easily arise from constantly varying coupling between the laser and metal absorber which in the presence of reactive samples like hydrogen may in turn be a result of the metal-hydrogen chemical reaction [10,11]. The observation of a plateau in a laser-power versus temperature curve does not necessarily imply melting and may be interpreted as due to the attainment of optimal heating conditions for that particular sample configuration [9]. Unfortunately, Deemyad and Silvera [6] did not report physical property measurements on the hydrogen samples either during or after the heating experiments to confirm the presence of hydrogen that was melting. This is important in the context of the extreme mobility and reactivity of hydrogen.

As pointed out above, our in situ Raman-LHDAC experiments done on localized hydrogen samples at various pressures does show chemical effects at high temperatures. For example, analysis of the Raman spectra in conjunction with the observation of dark patches appearing suddenly in the transparent 8 µm diameter sample hole in the metal coupler at the 109 GPa and 1070 K hint that these new features in the high frequency region as well as in the low frequency region (400-1000 cm⁻¹) are related to formation of iridium-hydrogen reactions. The possibility that this could have happened subsequent to melting around this temperature cannot be ruled out, and certainly motivates us to evolve stringent diagnostic criteria for melting.

Eremets and Trojan [7] used CW laser heating and electrical resistance measurements and Raman spectroscopy and reported observation of a maximum in the melting curve at 106 GPa and 1050 K, that is in general accordance with the theoretically predicted curves [5]. As stated by the authors, while they were able to successfully confine the hydrogen sample to make repeated physical property measurements, they could not delineate the hot hydrogen region from the cold hydrogen region in their Raman measurements possibly due to the sample assembly and heating method employed. Their diagnostics for melting were based on sudden changes in electrical resistance, which they attribute to shunting of the leads by conductive hydrogen, and an increase in the vibron linewidth. The high resolution Raman spectra we measure from locally confined, well insulated samples at temperatures quite below the predicted melting temperatures show onsets and growth of new lower frequency bands (Figs. 3, 4), that can show up as a lower-frequency shoulder due to large temperature and pressure gradients, if present. Additional evidence for melting is presented from the observation of speckle motion and visible changes in the sample.

We do observe discrete changes in the speckle patterns with a 532 nm laser whenever hot bands or these new left side hot peaks start appearing, and a discontinuous change in refractive index upon melting is possible. However a solid-solid phase transition including chemical reactions that involves sudden refractive index change can produce similar effects in the speckle. In the megabar regime the uncertainty with this method enhances manifold as usually the density or refractive difference between the solid and liquid can be below the sensitivity limits of the speckle method and pose difficulties in interpreting the subtle effects expected from speckle variations. Measurements in the vicinity of the predicted melting curve maximum have been sparse. Both Eremets and Trojan [7] and Deemyad and Silvera [6] report three to four experimental points in the region of the reentrant melting and these are mutually contradictory. Experiments aimed at achieving conclusive diagnostics of hydrogen melting in this P-T region are thus in order.

5. Concluding Remarks
We have developed new approaches to confine dense hydrogen in laser-heating Raman experiments that minimize the effects of thermal and pressure gradients. With this, we are now able to perform in situ Raman measurements on hydrogen for many heating cycles, each lasting for several minutes, without significant sample loss. A limiting factor on the number of heating cycles and maximum sample temperature stems from the eventual closure of the coupler hole to visible light. Analysis of the collapsed hole hints at possible chemical reactions involving hydrogen and the IR absorber at elevated
temperatures and pressures. Any development of diagnostics for hydrogen melting such as speckle motion or resistance studies should take this factor into account.

Acknowledgements
The authors thank H. K. Mao and V. V. Struzhkin for valuable discussions. This work was supported by DOE-NNSA (CDAC) and NSF-DMR. One of us (N.S) thanks the management of IGCAR, India for grant of leave to visit the Geophysical Laboratory.

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