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On the Reactivity of Hydrogen-Helium and Hydrogen-Nitrogen at High Pressures

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Through a series of Raman spectroscopy studies, we investigate the behaviour of hydrogen-helium and hydrogen-nitrogen mixtures at high pressure across a wide range of concentrations. We find that there is no evidence of chemical association or increased miscibility of hydrogen and helium in the solid state up to pressures of 250 GPa at 300 K. In contrast, we observe the formation of concentration-dependent N₂-H₂ van der Waals solids, which react to form N-H bonded compounds above 50 GPa. Through this combined study, we can demonstrate that the recently reported chemical association of H₂-He can be attributed to significant N₂ contamination and subsequent formation of N₂-H₂ compounds.

Understanding the behaviour of molecular mixtures under pressure is of a great importance to many scientific fields varying from chemistry to the studies of internal structures of astronomical bodies [1, 2]. A wide range of phenomena have been observed in high-pressure molecular-mixtures, such as: phase separation, co-crystallisation, host-guest structures and chemical reaction [3–6]. Since the discovery of solid van der Waals compounds in the high-pressure helium–nitrogen system, binary mixtures of elemental gases have attracted much attention both experimentally and theoretically [7–11]. Of particular importance, are binary mixtures of the four lightest elemental gasses: H₂, He, N₂ and O₂, which have been explored at high pressure [12–19]. Recently, there has been renewed interest in studies of both the hydrogen-helium and hydrogen-nitrogen systems at high pressure, with a focus on investigating the possible synthesis of compounds through the reaction of the constituent molecules [20–25].

H₂ and He are predicted to be chemically inert towards each other across wide pressure-temperature (P - T) and concentration regimes [26–32]. Theoretical simulations, motivated by potential miscibility within the Jovian planets, find evidence that even at these extreme conditions, hydrogen and helium remain phase separated or at most exhibit partial miscibility. Due to the theoretical predictions of no chemical reactivity between hydrogen and helium, there have been few experimental studies on mixtures. Early studies exploring the eutectic phase

diagram of hydrogen-helium mixtures found that the hydrogen intramolecular vibrational mode in the two-fluid state exhibited a marked redshift in He-rich concentrations which was explained semiquantitatively by a helium compressional effect [13]. However, in the solid state, the two species were shown to be completely immiscible up to 15 GPa. This observation of immiscibility was utilized to grow single crystals of H₂, and measure the equation of state up to 100 GPa without an observable chemical reaction between the two [33]. A recent high pressure study exploring H₂-He interactions as a function of mixture concentration, reported the unprecedented appearance of hydrogen-helium solids at pressures below 75 GPa [20]. Through the appearance of a vibrational Raman band at a frequency similar to that calculated for the H-He stretch in a linear H-He-F molecule [34], the authors claim the formation of H-He bonds [20]. These results are surprising given that the corresponding P - T regime has already been explored both experimentally and theoretically [13, 16].

In contrast to H₂-He mixtures, the H₂-N₂ system exhibits particularly rich physics under compression, which is strongly dependant on both pressure and N₂:H₂ composition. Two van der Waals compounds have been reported to form at pressures above ~ 7 GPa; (N₂)₆(H₂)₇ and N₂(H₂)₂ [22, 25]. At pressures between 35 - 50 GPa, these van der Waals compounds react to form N-H bonded solids, which cannot be characterized solely by known hydronitrogen compounds. On decompression,

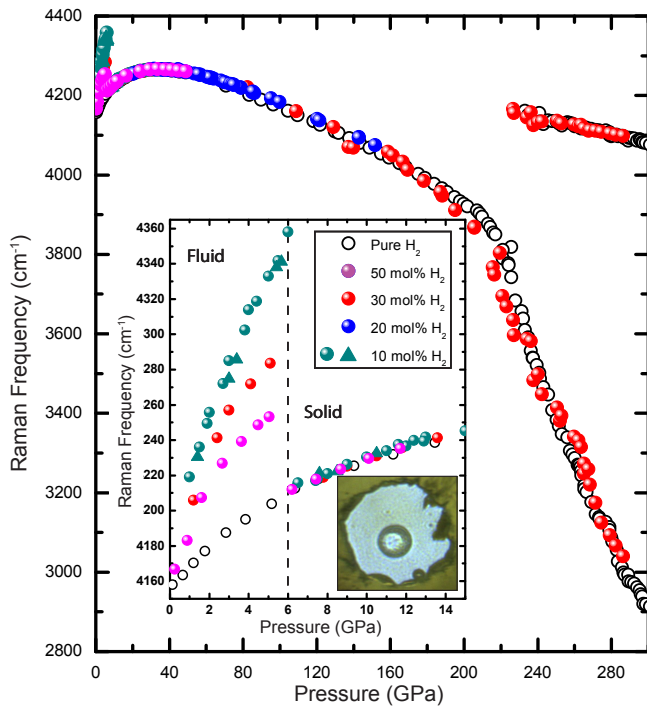


FIG. 1. Raman frequency *vs.* pressure for different H₂:He concentrations up to 285 GPa. Circles and triangles represent data collected on compression and decompression respectively. Inset: Raman frequency *vs.* pressure for different H₂:He concentrations up to 20 GPa. Photomicrograph of a 10 mol% H₂ in He sample. The single crystal of H₂, located in the centre of the sample chamber, is clearly phase separated from the surrounding He medium.

these solids transform to hydrazine (N₂H₄) on decompression below 10 GPa [22–25].

In this study, we have comprehensively investigated the pressure induced reactivity of H₂-He and H₂-N₂ mixtures as a function of mixture composition through Raman spectroscopy. Hydrogen and helium remain nearly immiscible across all concentrations up to pressures of 250 GPa, with no formation of van der Waals compounds nor any chemical reactivity across all mixture concentrations studied. Even at the extreme densities of hydrogen phase IV of hydrogen, which is thought to adopt a complex layered structure, no chemical association is observed. In contrast, modest pressures readily induce the formation H₂-N₂ van der Waals compounds, which, with the application of higher pressure, react to form N-H bonded compounds that remain stable on decompression. Through this combined study of both systems, we demonstrate that the recently reported chemical association between H₂ and He, can be described by the formation of N₂-H₂ compounds due to significant N₂ contamination of the H₂-He mixtures used in that study [20].

Research grade (99.9995%) hydrogen-helium mixtures with molar hydrogen concentrations of 10, 20, 30 and 50% were obtained commercially. Hydrogen–nitrogen

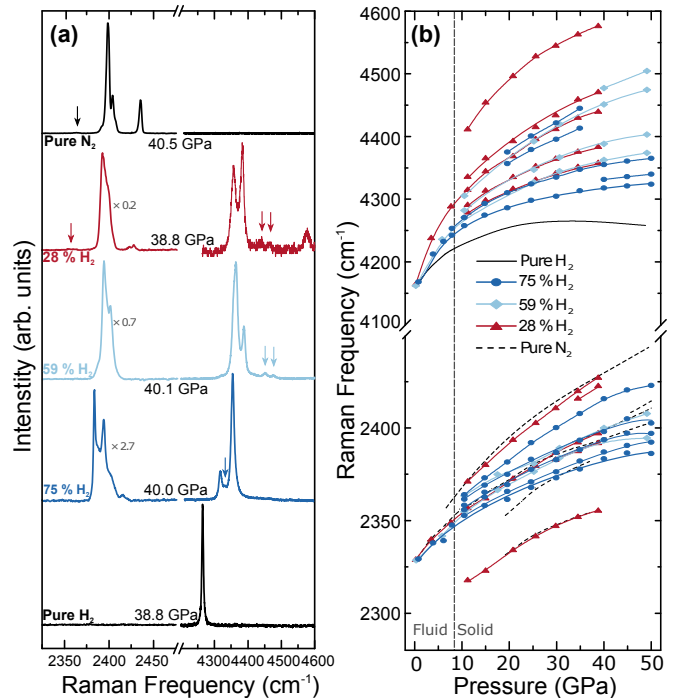


FIG. 2. (a) Evolution of the Raman spectra with composition in the solid state at around 40 GPa for the nitrogen-hydrogen compositions of: 28, 59 and 75 mol% H₂. The pure species are included for comparison in black. (b) Raman frequency *vs.* pressure plots corresponding to the data shown in (a). Solid and dashed black lines correspond to pure H₂ and pure N₂ respectively. Arrows indicate weak Raman bands.

compositions were prepared in-house from research grade (99.9995%) H₂ and N₂, with molar hydrogen concentrations of: 28, 50, 59 and 75 % as determined from the relative partial pressures. The mixtures were given several days to homogenise before being gas loaded into diamond anvil cells (DACs). All samples were gas loaded into the DACs at a pressure of 200 MPa. Raman spectroscopy was conducted using a custom-built microfocussed system, using the 514 and 647 nm excitation wavelengths (see SM for further details). Powder x-ray diffraction measurements of H₂-N₂ mixtures were collected at beamline P02.2, PETRA III, Germany using a monochromatic beam of $\lambda = 0.484693 \text{ \AA}$ and recorded on a Mar 345 image plate area detector. Pressure was determined using the ruby fluorescence scale below 100 GPa, and the stressed Raman edge of diamond above [35, 36].

Upon loading the samples of hydrogen-helium, all concentrations exhibited only the Raman modes that can be attributed to rotational modes (rotons) and vibrational modes (vibron) of H₂ (see Fig. 1 and S1-S7 [37]). In the fluid state (below 6 GPa), the two species are mixed well and the intensity and frequency of the hydrogen mode is constant when measured at different points across the sample chamber. The hydrogen vibron in the fluid sample does however exhibit a red-shift in frequency, when

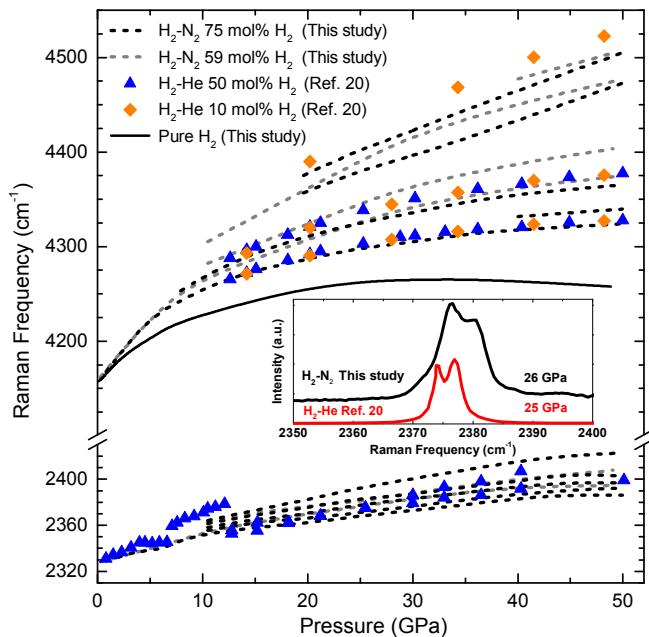


FIG. 3. A comparison of the Raman frequencies as a function of pressure between our data on $\text{H}_2\text{-N}_2$ mixtures (dashed lines), pure H_2 (black line), and the $\text{H}_2\text{-He}$ compound (known as ‘ S_2 ’) reported in Ref. [20] (symbols). Inset: Comparison between ‘ H-He ’ vibrons from Ref. [20] and the N_2 vibrons from a 3:2 $\text{H}_2\text{-N}_2$ mixture.

compared with the pure species, which increases with greater helium concentrations (see inset of Fig.1). This is in good agreement with previous studies on the binary phase diagram [13]. In addition, we observe significant broadening of the H_2 vibron with pressure in the fluid-fluid phase compared with the pure species (see Fig. S8). At 4 GPa, there is a 5-fold increase in the full width at half maximum (FWHM) of the H_2 vibron compared to pure H_2 (a comparable vibron width to phase III of H_2 at 200 GPa and 300 K), and the rate of broadening is independent of concentration.

At pressures greater than 5.2 GPa, the immiscibility of H_2 and He becomes evident by the visible phase separation as hydrogen enters the solid state. Across all concentrations, the Raman frequency of the hydrogen vibron reverts to the same frequency as that exhibited by the pure species under the same P - T conditions, and the frequency shift is completely reversible on decompression back into the fluid state. Slow sample compression between the H_2 and He solidifications pressures causes nucleation of hydrogen crystals, at the edge of the sample chamber, which coalesce over time (see insert of Fig. 1 and S9). On rapid compression from the fluid-fluid to the solid-solid state, small H_2 crystallites form across the whole sample chamber. In the majority of our rapid compression experimental runs, we still observed a weak H_2 vibron in the He medium, which we attribute to H_2 molecules trapped in the He lattice. There is no

detectable H_2 vibron in the He medium of low H_2 concentration samples which are held below the He solidification pressure for a period of weeks. Across all concentrations there is negligible frequency difference between the H_2 vibron in the He medium compared with the bulk H_2 . To rule out any kinetic effects, samples at each concentration were held in the fluid/solid states for a period of one week and no changes were observed with time. One sample at a concentration 20 mol% H_2 was held for a period of eight years at a pressure of 120 GPa with no evidence of a chemical reaction.

At 300 K, pure hydrogen has been shown to go through a phase transition sequence of I-III at 180 GPa, and III-IV above 225 GPa [42]. Phase IV is believed to adopt a two-layer molecular structure, giving rise to two distinct vibrational modes. One would expect that hydrogen in this phase would be more reactive, due to the much shorter molecular lifetime. It is also known that above 200 GPa, H_2 and D_2 tend to form a molecular alloy with each other which does not happen at lower pressures [43]. Fig. 1 (and Fig. S10) shows the hydrogen vibron frequency as a function of pressure for a 30% hydrogen in helium mixture up to the conditions of phase IV. We see only slight deviation in the vibron frequency when compared to pure H_2 and the deviation is well within experimental error of pressure determination.

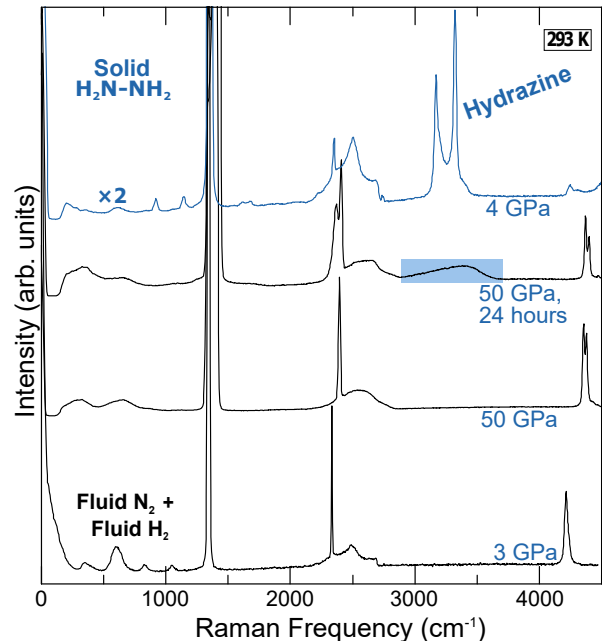


FIG. 4. Raman spectra on compression of a 50 mol% H_2 composition demonstrating the time dependent chemical reaction of N_2 and H_2 above 50 GPa. Shaded blue region indicates the formation of N-H bonds. The blue spectrum shows the recovery of hydrazine on decompression to 4 GPa. For a comparison between this data and Ref. [20], see Figs. S14-15.

Our data clearly show that over a broad pressure

regime, and over wide-ranging concentrations, there is no evidence of any chemical interactions between H₂-He and they remain nearly immiscible up to pressures of 250 GPa. This is in disagreement with the recent results reported in Ref. [20] that reported chemical association between H₂ and He. The evidence for chemical association was primarily through the appearance of a Raman band at $\sim 2330\text{ cm}^{-1}$ upon loading of the sample, which the authors attribute to an H-He bonded molecule. We do not observe this mode across all concentrations studied (see Fig. 1 and S1-S7). However, the N₂ molecule exhibits the same characteristic vibrational frequency (2330 cm^{-1} at 0.5 GPa) as that of the claimed H-He vibrational mode. Although the authors of Ref. [20] make efforts to rule out N₂ contamination by comparing their data to N₂ (and N₂ in He) Raman vibrational frequencies in the solid state, however, crucially they do not consider the possibility of N₂-H₂ interactions. As such, we present our own data, investigating the chemical interactions in H₂ and N₂ mixtures, in the pressure regime at which H₂-He chemical association was reported.

In the fluid state, hydrogen-nitrogen mixtures are characterized only by the vibrational modes exhibited in the pure H₂ and N₂ species (see Fig. S11). Across all concentrations studied, the H₂ vibron exhibits a red shifted which increases with greater N₂ concentration. In contrast, the N₂ vibron shows little effect by concentration in the fluid, and the pressure dependence follows closely with the pure species (see Fig. 2b). The solidification pressure of pure N₂ is 2 GPa, while it is 5.5 GPa for hydrogen. Interestingly, in mixtures of N₂ and H₂, all concentrations are homogeneous fluids below 8 GPa, before solidifying into N₂-H₂ van der Waals compounds which exhibit no N-H bond vibrational modes.

Fig. 2a shows the Raman spectra for each N₂:H₂ concentration at ~ 40 GPa compared with the pure species. At 75 mol% H₂, we can identify the formation of both (N₂)₆(H₂)₇ and N₂(H₂)₂ through our powder x-ray diffraction measurements (Fig. S12), which are consistent with structures previously identified through single crystal x-ray diffraction analysis [22, 25]. The coexistence of these compounds is different with respect to the previously reported binary phase diagram, which reported an overlap region between 54 mol% and 66 mol% [22]. At lower H₂ concentrations of 59% and 28%, we see only (N₂)₆(H₂)₇ and δ -N₂ in the diffraction patterns.

Fig. 3 compares the Raman frequencies of our 75 mol% and 59 mol% H₂-N₂ mixtures with that of 50 mol% and 10 mol% H₂-He mixtures in Ref. [20]. Below 7 GPa, there is a close match, in both the frequency and pressure dependency, between the claimed ‘H-He’ vibrational mode and that of N₂ in the H₂-N₂ mixture. It is unlikely that an ‘H-He’ vibrational mode would have the same frequency dependence over a 7 GPa interval as a triple-bonded nitrogen molecule. At higher pressures, we find that the vibrational Raman modes of the ‘S₂-phase’ of

Ref. [20] in a 5:5 H₂-He mixture closely match that of a 3:2 H₂-N₂ mixture across the whole pressure regime studied. At the mixture ratio of 3:2, N₂(H₂)₂ is the dominant compound but it co-exists with (N₂)₆(H₂)₇. At 12 GPa, the Raman mode at $\sim 4265\text{ cm}^{-1}$ corresponds to the H₂ vibron in N₂(H₂)₂, whilst the higher frequency vibron at $\sim 4288\text{ cm}^{-1}$ corresponds to the most intense H₂ vibrons in (N₂)₆(H₂)₇. In the high He content mixtures, there is a third H₂ vibrational mode at frequencies $\sim 4390\text{ cm}^{-1}$ which corresponds to the second most intense Raman band of (N₂)₆(H₂)₇. The behaviour of N₂ vibrons is also very different in H₂-N₂ compounds than in either pure N₂ or N₂:He compounds. We find excellent agreement, shown in Fig. 3 (and Fig. S13) between the N₂ stretches in N₂(H₂)₂ and the claimed ‘H-He’ vibrational mode of Ref. [20].

Above the critical pressure of 50 GPa at room temperature all samples exhibited loss of intensity of the hydrogen and nitrogen Raman vibrational bands over hour-long time-scales (see Fig. 4). The loss of vibron intensity occurred simultaneously with the emergence of a broad asymmetric peak centred around 3400 cm^{-1} (highlighted in blue in Fig. 4). The broad asymmetric peak around 3400 cm^{-1} can be attributed to the vibrational modes of N-H bonded compounds, however the overall appearance does not match the known hydronitrogen compounds. [41, 44] This difference could be attributed to the formation of a combination of azanes, and/or the presence of excess reactants. This solid phase remained on decompression until 10 GPa, after which the broad peak around 3400 cm^{-1} evolved into two sharp peaks accompanied by four lower frequency modes (see Fig. 4) unambiguously identifying hydrazine [44, 45]. Solid hydrazine was observed on decompression below 10 GPa in all isothermal compression-decompression experiments and across all concentrations studied.

The spectral changes shown in Fig.4 were also observed in Ref. [20], but interpreted as the formation another ‘H-He’ solid (‘S₁’). We find good agreement between the spectra of this solid and the N-H compounds we observe to form (see Fig. S14-15). This, together with the above analysis, shows that the previously reported chemical association between H₂ and He could be attributed to significant nitrogen contamination of the samples. The authors of Ref. [20] produce the gas mixtures themselves, and it is possible that the N₂ contaminant is introduced at the initial gas mixing stage or during sample loading. Our own experience in producing gas mixtures demonstrates that great care needs to be taken to ensure that the ballast volume between gas bottles in the mixture setup is adequately purged with the constituent gases [4, 43]. We have sometimes observed trace nitrogen contamination from air due to this and in these cases we would disregard the contaminated gas bottle. In this study, we obtain our H₂-He mixtures commercially with guaranteed levels of purity and do not reproduce

any of the observations of Ref. [20].

Our results show that, even at extreme compressions, H₂ and He remain immiscible and chemically inert towards each other, both properties which will prove advantageous for future structural studies of phase IV hydrogen. In agreement with previous theoretical results, it is likely that extreme P - T conditions in excess of that in the interiors of Jovian planets would be required for H₂ and He to become miscible, let alone form chemical bonds.

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