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Formation and Stability of Dense Methane-Hydrogen Compounds

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Through a series of x-ray diffraction, optical spectroscopy diamond anvil cell experiments, combined with density functional theory calculations, we explore the dense CH_4-H_2 system. We find that pressures as low as 4.8 GPa can stabilize $CH_4(H_2)_2$ and $(CH_4)_2H_2$, with the latter exhibiting extreme hardening of the intramolecular vibrational mode of H_2 units within the structure. On further compression, a unique structural composition, $(CH_4)_3(H_2)_{25}$, emerges. This novel structure holds a vast amount of molecular hydrogen and represents the first compound to surpass 50 wt % H_2. These compounds, stabilized by nuclear quantum effects, persist over a broad pressure regime, exceeding 160 GPa.

DOI:

Hydrogen and methane are, besides water, the most prevalent small molecules in the outer Solar System. Their interplay under extreme conditions is of key interest to understanding the evolution and interior dynamics of Neptune and Uranus, as well as of Earth and exoplanets [1–4]. The simplest molecule, H_2, has been shown to exhibit rich physical phenomena, including quantum rotational phases and pressure-induced steps toward an atomic metallic solid, while methane (CH_4), the simplest hydrocarbon, has been proposed to polymerize during compression to form long-chain hydrocarbons and at further extremes decompose into diamond plus H_2 [5–19].
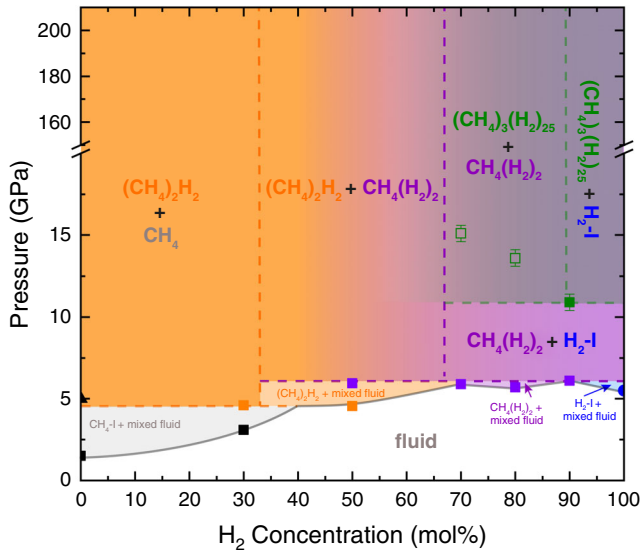
Hydrogen reacts with a number of materials at high pressures and temperatures but also has a propensity to form van der Waals compounds that can be stable far beyond 100 GPa [20–32]. Methane and hydrogen were first reported to crystallize into inclusion (host-guest) compounds over 25 years ago at pressures between 5 and 7 GPa. A range of compositions were claimed: $(CH_4)_2H_2$, CH_4H_2, $CH_4(H_2)_2$, and $CH_4(H_2)_4$ [21]. However, the experimental evidence for these compounds was limited, with only the shift of the hydrogen intramolecular vibrational mode ν_1-H_2 (vibron) relative to that of pure hydrogen being reported together with the lattice parameters of potential structures. Assuming that these structural compositions were correct, a later experimental study explored the recoverability of $CH_4(H_2)_4$ at low temperature to investigate its potential as a hydrogen storage media [33,34].

In contrast to experimental work, the CH_4-H_2 system has recently had a surge of theoretical investigations, predicting a variety of extremely hydrogen-rich compositions to emerge such as triclinic $(CH_4)_2(H_2)_3$, trigonal $(CH_4)_2(H_2)_7$, and hexagonal $CH_4(H_2)_9$, as well as several CH_4H_2 structures [18,35–37]. Furthermore, it was suggested that CH_4-H_2 structures could be the most stable form of carbon and hydrogen at pressures up to 200 GPa [18].

Surprisingly, given these predictions and the advent of technological advances over the past 25 years, no further experimental exploration has been conducted despite undetermined CH_4-H_2 compound signatures emerging as a by-product in many prolific studies of hydrocarbons at planetary conditions [3,19,38–41]. Moreover, the doping of carbon (or methane) could even enhance the properties of materials at extreme pressures, with the unprecedented claim of room temperature superconductivity in the carbonaceous sulfur hydride system [42–44]. The lack of knowledge regarding CH_4-H_2 compound formation inhibits our understanding of these more complex ternary systems and how doping could induce novel properties. As such, it is of fundamental interest to know which methane-hydrogen compounds are actually formed and test their pressure stability limits.

In this Letter, we have conducted a series of high-pressure synchrotron powder x-ray diffraction and Raman spectroscopy experiments in diamond anvil cells combined with density functional theory (DFT) calculations and structural searching to explore the formation and properties of CH_4-H_2 compounds from mixtures of methane and hydrogen. In H_2-rich mixtures, we observe the formation of hexagonal $CH_4(H_2)_2$ above 5 GPa, before partially transforming into monoclinic $(CH_4)_3(H_2)_{25}$. $(CH_4)_3(H_2)_{25}$ represents a unique composition and contains an unprecedented 51.1 wt % H_2, which is the highest hydrogen content of any currently known

83 stoichiometric compound. In CH_4-rich mixtures, tetrago-
84 nal $(CH_4)_2H_2$ forms, which undergoes extreme hardening
85 of the H_2 intramolecular vibrational mode with pressure.
86 All three compounds exhibit remarkable stability, exceed-
87 ing pressures of 160 GPa.
88 At pressures below 1.5 GPa, all mixture concentrations
89 (30, 50, 70, 80, and 90 mol % H_2) are homogeneous well-
90 mixed fluids and display the Raman signatures of both
91 constituent species (see Fig. 1 for the pressure-composition
92 phase diagram, Supplemental Material [45] for experimental
93 methods, and Figs. S1–S9 [45] for Raman spectra of all
94 mixtures). On compression of hydrogen-rich CH_4-H_2 mix-
95 tures (50–90 mol % H_2) above 5 GPa, the fluid mixture
96 crystallizes into a solid which we identify as $CH_4(H_2)_2$.
97 X-ray diffraction measurements reveal that this compound
98 adopts a hexagonal MgZn$_2$ Laves phase structure (space
99 group $P6_3/mmc$), where the CH_4 molecules occupy the Mg
100 sites and the H_2 molecules occupy the Zn sites (see Fig. 2),
101 the lattice parameters of which are $a = 4.981$ Å and
102 $c = 8.125$ Å at 16.6 GPa. This structure and composition
103 was suggested previously but attributed to a compound
104 forming in a narrow pressure regime (between approxi-
105 mately 6 and 7 GPa) and between 35 and 65 mol % H_2
106 mixture concentrations [21]. Here, we find that $CH_4(H_2)_2$ is
107 the dominant phase across all H_2-rich mixtures and persis-
108 tent over a large pressure regime. Raman spectroscopy

109 reveals two distinct H_2 vibrons, ν_{1H} and ν_{2H}, the latter
110 of which is approximately 50 times lower in intensity.
111 The two most intense CH_4 stretching modes, ν_{1M} and ν_{2M},
112 are shifted to higher frequency compared to pure CH_4,
113 while the wagging mode is shifted to lower frequency
114 (see Figs. 3 and 4).
115 On further compression, we observe another compound
116 emerge evidenced by visual changes in the sample mor-
117 phology and the appearance of three distinct H_2 vibrational
118 modes (the lowest in frequency being the most intense by 2
119 orders of magnitude) and CH_4 stretching bands that can be
120 isolated from $CH_4(H_2)_2$ (see Figs. 3 and 4 and Supplemental
121 Material [45]). The most intense H_2 vibron is lower in
122 frequency than that of $CH_4(H_2)_2$, suggestive that the
123 compound has a higher H_2 content. X-ray diffraction
124 measurements indicate the compound is weakly scattering;
125 however, this could be in part due to only partial trans-
126 formation of the sample. The patterns could be indexed to a
127 hexagonal cell, with $a = 7.804$ Å and $c = 11.199$ Å at
128 17.3 GPa (see Fig. 2). Systematic absences, unit cell volume,
129 and c/a ratio suggest this compound has a close resem-
130 blance with the previously reported R-$3m$ structure of
131 $Xe(H_2)_8$ [23,26] and an initial composition estimate of
132 $CH_4(H_2)_8$. This seemed plausible given CH_4 and Xe have
133 similar van der Waals diameters (3.78 and 4.32 Å,
134 respectively).
135 We subsequently performed DFT calculations to help
136 identify this phase. We constructed a series of structures of
137 variable composition, starting by populating the hexago-
138 nal cell with randomly oriented CH_4 molecules on the Xe
139 sites of $Xe(H_2)_8$, before adding H_2 molecules on hex-
140 agonal close packed (hcp) arrangements commensurate
141 with the cell, using up to $3 \times 3 \times 4$ repeats of the hcp
142 lattice and a random offset against the CH_4 sublattice. H_2
143 molecules too close to CH_4 were removed before fully
144 optimizing the remaining atoms and all lattice parameters.
145 Several thousand of these structures were generated with
146 stoichiometries ranging from $CH_4(H_2)_7$ to $CH_4(H_2)_{11}$.
147 Of these, $CH_4(H_2)_{8.33}$ [or $(CH_4)_3(H_2)_{25}$] emerged as the
148 most energetically competitive and was found to be
149 dynamically stable at and above 20 GPa (see Figs. S19
150 and S20 [45]). It is also the only computationally obtained
151 structure which reproduces the positions and intensities of
152 the experimental diffraction peaks across the studied
153 pressure range (see Fig. S14 [45]), which is meaningful
154 given that no symmetry restrictions were applied in the
155 structures' construction and subsequent optimization. While
156 we find both $CH_4(H_2)_2$ and $(CH_4)_2H_2$ stable or close to
157 stability within the CH_4-H_2 phase diagram across a wide
158 pressure range, once zero point energies and vibrational
159 entropies are accounted for, $(CH_4)_3(H_2)_{25}$ remains meta-
160 stable throughout (see Supplemental Material [45]).
161 Considering methane and hydrogen molecules to be
162 spherical, the structure of $(CH_4)_3(H_2)_{25}$ is monoclinic with
163 space group $C2/m$ (coordinates are given in Supplemental
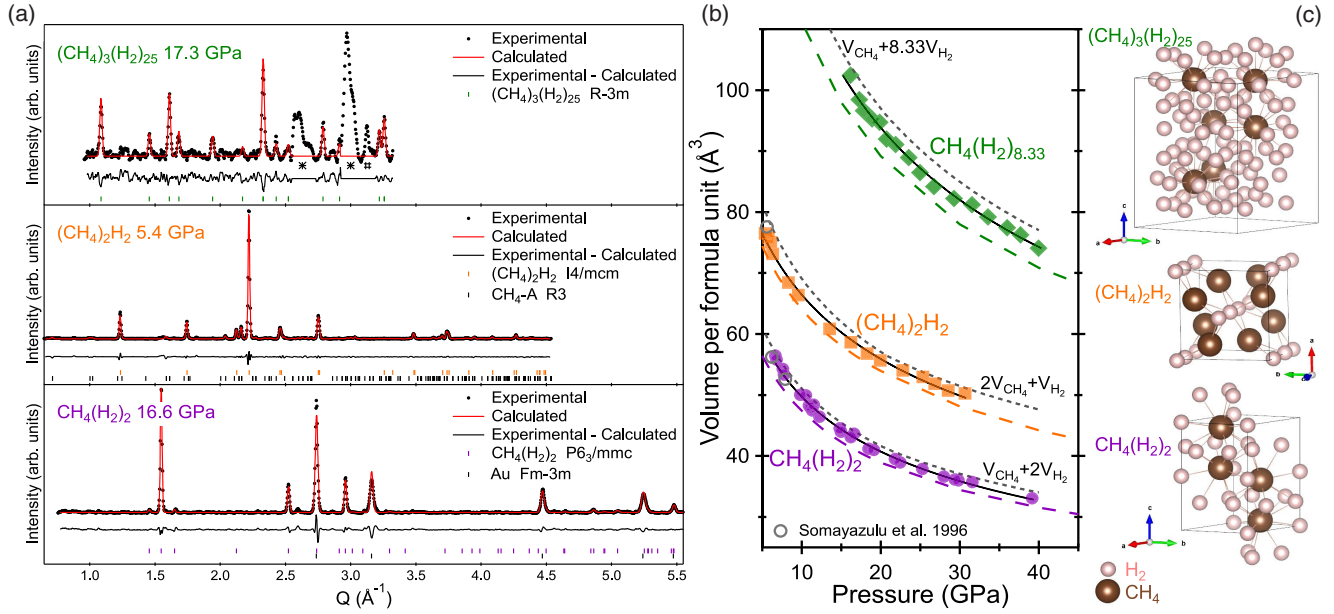
F2:1 FIG. 2. (a) Representative x-ray diffraction patterns of the three compounds plotted as a function of exchanged wave vector and their
F2:2 Le Bail refinements. Refinements include $(CH_4)_3(H_2)_{25}$-R-$3m$ ($a = 7.804$ Å and $c = 11.199$ Å), $(CH_4)_2H_2$-$I4/mcm$ ($a = 7.195$ Å
F2:3 and $c = 5.909$ Å), CH_4-A-$R3$ ($a = 12.306$ Å and $c = 15.520$ Å), $CH_4(H_2)_2$-$P6_3/mmc$ ($a = 4.981$ Å and $c = 8.125$ Å), and
F2:4 Au-Fm-$3m$ ($a = 3.976$ Å). Excluded regions in the pattern of $(CH_4)_3(H_2)_{25}$ correspond to rhenium (gasket material) and rhenium
F2:5 hydride (*) and excess H_2 (#). (b) Volumes per formula unit as a function of pressure. Symbols represent experimental data (the error
F2:6 bars are smaller than the symbol size), and black full lines represent their best second-order Birch-Murnaghan fits: $CH_4(H_2)_{8.33}$,
F2:7 $V_0 = 246 \pm 17$ Å^3 and $K = 3.0 \pm 0.6$ GPa; $(CH_4)_2H_2$, $V_0 = 101 \pm 2$ Å^3 and $K = 10.2 \pm 0.8$ GPa; $CH_4(H_2)_2$, $V_0 = 90 \pm 3$ Å^3 and
F2:8 $K = 5.0 \pm 0.4$ GPa. Dashed lines represent volumes derived from our DFT calculations, and gray dotted lines represent the volumes of
F2:9 ideal mixtures of CH_4-A/CH_4-B and H_2-I using the previously determined equations of state [14,17,69]. The experimental volumes
F2:10 given in Ref. [21] are represented by gray circles. (c) Structural models of the three compounds, where CH_4 and H_2 are represented by
F2:11 brown and white spheres, respectively, and lines indicate CH_4-H_2 nearest neighbors.
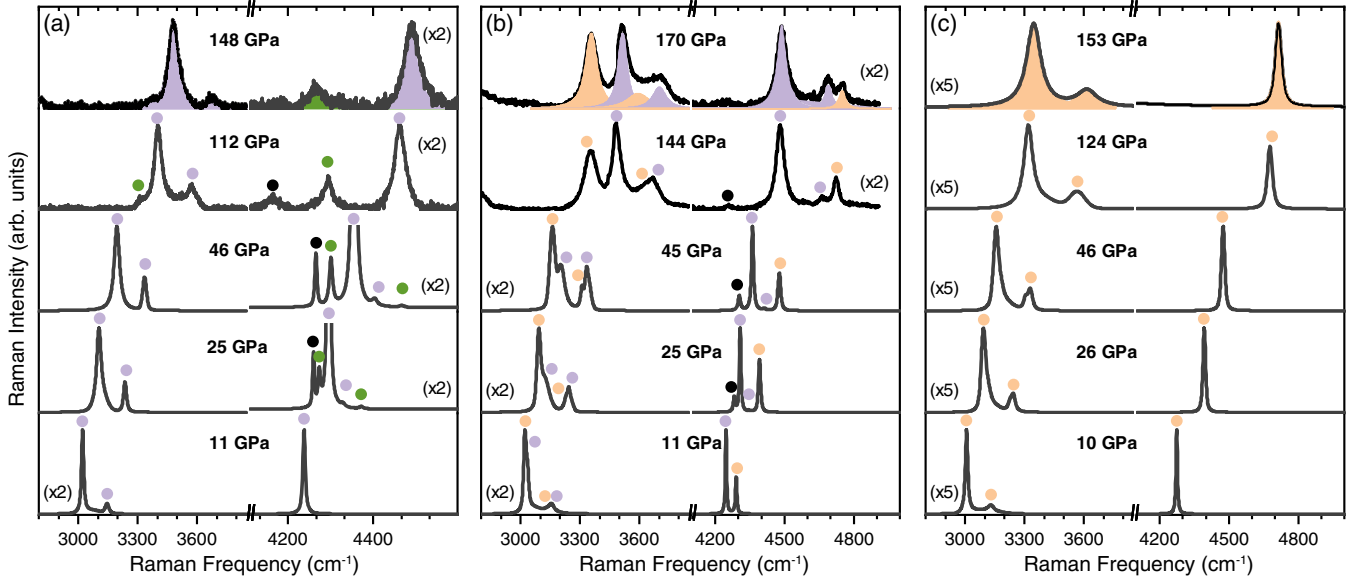
F3:1 FIG. 3. Representative vibrational Raman spectra of (a) 70% H_2, (b) 50% H_2, and (c) 30% H_2 mixtures. Colors indicate the modes
F3:2 assigned to $CH_4(H_2)_2$ (purple), $(CH_4)_3(H_2)_{25}$ (green), $(CH_4)_2H_2$ (orange), and excess H_2 (black).
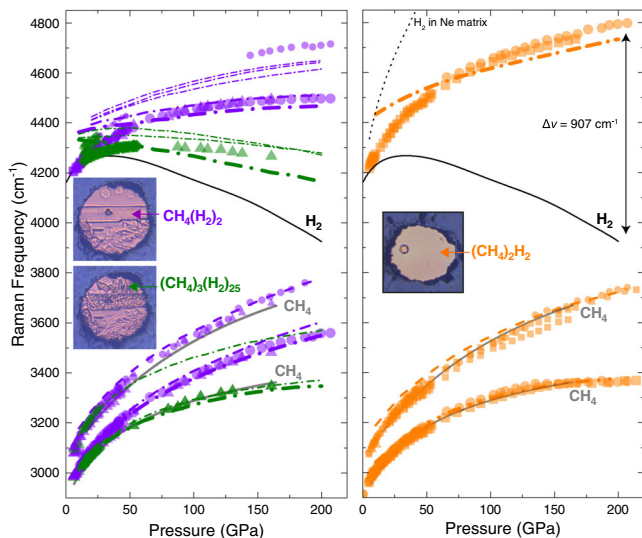
F4:1 FIG. 4. Raman shift as a function of pressure of the H_2
F4:2 vibrational modes and C-H stretching modes of $CH_4(H_2)_2$ and
F4:3 $(CH_4)_3(H_2)_{25}$ (left panel, purple and green symbols, respec-
F4:4 tively), and $(CH_4)_2H_2$ (right panel, orange symbols). Frequencies
F4:5 are collated from 30% (squares), 50% (circles), 70% (triangles),
F4:6 80% (diamonds), and 90% (hexagons) H_2 mixtures, with the
F4:7 most intense modes represented by larger symbols. Raman
F4:8 frequencies of individual mixtures are given in Supplemental
F4:9 Material [45]. The dot-dashed lines represent the calculated
F4:10 frequencies of the H_2 modes and C-H stretching bands of each
F4:11 compound, with the thickest line representing the most intense
F4:12 modes. Black and gray solid lines represent pure H_2 [6] and CH_4
F4:13 [15], respectively. The black dotted line represents the frequency
F4:14 of H_2 in a Ne matrix [70]. The error in pressure ranges from ±0.2
F4:15 below 50 GPa, ±1 below 150 GPa, and ±5 above. The error bars
F4:16 in frequency are smaller than the symbol size. Photomicrographs
F4:17 show examples of morphology of synthesised samples within the
F4:18 DAC sample chamber.

164 Material [45]). Le Bail refinements of the experimental
165 diffraction patterns were performed using the trigonal space
166 group $R\text{-}3m$, which is obtained considering the carbon atoms
167 only, and the hexagonal setting, which resulted in good fits
168 to the data. The obtained volume per methane molecule is
169 close to $V_{CH_4} + 8.33V_{H_2}$ (see Fig. 2), the volume of an ideal
170 mixture of CH_4 and H_2 with the same composition. A
171 comparison between the experimental and computational
172 vibrational Raman modes of $CH_4(H_2)_2$-$P6_3/mmc$ and
173 $(CH_4)_3(H_2)_{25}$-$C2/m$ is given in Fig. 4, where we see
174 qualitatively good agreement between the number of modes,
175 relative intensity, and frequency for both compounds.
176   In methane-rich concentrations of 30 mol % H_2, we
177 observe a body-centered tetragonal Al_2Cu-type structure
178 (space group $I4/mcm$) to form above 4.6 GPa (with $a =$
179 7.195 Å and $c = 5.909$ Å at 5.4 GPa), which is consistent
180 with the previously reported composition of $(CH_4)_2H_2$ [21]
181 (see Fig. 1). Raman spectroscopy measurements show that
182 the CH_4 stretching bands of $(CH_4)_2H_2$ are close to the
183 frequencies of pure solid CH_4, while two wagging modes are

184 observed. The number of modes and frequencies are in good
185 agreement with our calculated values (see Fig. 4). The ν_{1H}
186 mode, corresponding to H_2 units within the structure,
187 exhibits the most extreme hardening of any stoichiometric
188 molecular compound [25,28]. At a pressure of 207 GPa,
189 $(CH_4)_2H_2$-ν_{1H} has a frequency of 4798 cm^{-1}, over
190 900 cm^{-1} higher than H_2-ν_1 (see Fig. 4). Remarkably, the
191 frequencies we observe reach similar values to an impurity
192 H_2 molecule isolated in a noble gas matrix, albeit at higher
193 pressure [70]. Up to pressures of 207 GPa, we do not observe
194 a turnover of ν_{1H} (and 500 GPa in our calculations), unlike in
195 pure H_2, which exhibits a maximum frequency at approx-
196 imately 38 GPa [5].
197   These results highlight the enormous impact that the
198 local environment around a H_2 molecule can have on its
199 vibron frequency. In Supplemental Material [45], we
200 present a simple molecular model demonstrating that
201 the vibron frequency of a H_2 surrounded by two CH_4
202 (respectively, H_2) will continuously increase (respectively,
203 decrease) if the surrounding molecules are pushed closer.
204 A molecular orbital analysis reveals that, in H_2-dominated
205 environments, intermolecular interactions lead to occu-
206 pancy of antibonding H-H σ^* states, which does not
207 happen in CH_4-dominated environments. In $(CH_4)_2H_2$,
208 every H_2 has two nearest H_2 neighbors and eight nearest
209 CH_4 neighbors; as a result, the vibron exhibits extreme
210 hardening [see Fig. 2(c) and Supplemental Material [45]
211 for graphical representations of the unit cells and inter-
212 molecular distances]. This local environment is reversed
213 in $(CH_4)_3(H_2)_{25}$ with an average of 9.8 H_2 neighbors but
214 only 2.24 CH_4 neighbors per H_2 molecule; still, it remains
215 very different from H_2-I, having a coordination number of
216 12 and considerably shorter H_2-H_2 distances [28]. For
217 $(CH_4)_3(H_2)_{25}$, the ν_{1H} mode has a maximum at about
218 70 GPa, and the vibron frequencies tend toward the values
219 found for pure H_2. In $CH_4(H_2)_2$, where each H_2 has six
220 nearest H_2 neighbors and six nearest CH_4 neighbors, the
221 vibron frequencies are interpolated between $(CH_4)_3(H_2)_{25}$
222 and $(CH_4)_2H_2$.
223   We find that the pressure-composition phase diagram is
224 simpler than previously reported [21], with only three
225 stable CH_4-H_2 compositions. In 50 mol % H_2 mixtures,
226 we observe the coexistence of both $(CH_4)_2H_2$ and
227 $CH_4(H_2)_2$, together with some excess H_2, indicative that
228 equilibrium has not been reached. Furthermore, we observe
229 trace amounts of $(CH_4)_3(H_2)_{25}$, which can be attributed to
230 macroscopic inhomogeneity within the sample chamber. In
231 70 mol % mixtures and 80 mol % H_2 mixtures, we first
232 observe the Raman signatures of $(CH_4)_3(H_2)_{25}$ at 14.5 GPa
233 and in 13.6 GPa (shown as open symbols in Fig. 1),
234 respectively, while in 90 mol % mixtures, we observe
235 $(CH_4)_3(H_2)_{25}$ at 10.9 GPa. It is possible that, in 70 mol
236 % ~~mixtures~~ and 80 mol % H_2 mixtures, formation occurs at
237 lower pressure but is below the detection limit in the Raman
238 spectra. We find that even in 90 mol % mixtures the

transformation from $CH_4(H_2)_2$ and H_2 to $(CH_4)_3(H_2)_{25}$ is never complete, suggestive that the transformation is kinetically sluggish and due to hindered diffusion of H_2 in the solid state. Although our liquidus curve is in good agreement with that reported previously, we do not observe either CH_4H_2 and $CH_4(H_2)_4$ and attribute this to a misinterpretation of $CH_4(H_2)_2$ [21]. The experimental volume given for hexagonal wurtzite CH_4H_2 is identical to our experimental volume for $CH_4(H_2)_2$ at the same given pressure. Furthermore, after extensive structure searches, with randomly oriented molecules in the reported wurtzite center-of-mass positions, we do not find any version of the hexagonal wurtzite structure to be dynamically stable. The evidence for $CH_4(H_2)_4$ was predominantly based on Raman spectroscopy, and we find to be a misinterpretation of the coexistence between the CH_4-H_2 mixed fluid and solid $CH_4(H_2)_2$ (see Fig. S8 [45]).

$(CH_4)_3(H_2)_{25}$ possesses 51.1 wt % molecular hydrogen (63.4 wt % if the hydrogen of methane is included), which is the highest hydrogen content of any currently known stoichiometric compound. Notwithstanding the good agreement between the experimental and calculated data, $(CH_4)_3(H_2)_{25}$ represents an unusual and unique composition. All three compounds exhibit remarkable stability, with the Raman signatures of $(CH_4)_2H_2$ and $CH_4(H_2)_2$ detectable to at least 215 GPa and $(CH_4)_3(H_2)_{25}$ up to 165 GPa. We estimate the melting temperatures T_m of $(CH_4)_2H_2$ and $CH_4(H_2)_2$ using Lindemann's equation based on calculated Debye temperatures and found T_m significantly higher than molecular hydrogen at all pressures (see Supplemental Material [45]). This would imply that hydrogen mixed with methane would potentially not possess the melting line turnover that is observed in pure hydrogen [7]. Taken together in a planetary context, this could influence critical properties of planetary matter such as thermal conductivities and viscosities. In a materials science context, high Debye temperatures coupled with extremely large vibron frequencies ν_H are promising ingredients for high-T_c superconductivity—provided a reasonable density of states $N(E_F)$ at the Fermi energy. The molecular compounds described here are insulators (all remain transparent in the visible up to the highest pressures reached), but the presence of an electron or hole dopant would metallize the system, with partially charged entities $H_2^{\pm\delta}$ present. This motif, at least in calculations, can lead to T_c close to 200 K [71].

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