

H₂-CH₄ van der Waals compounds under rapid compressionJinwei Yan¹, Israel Osmond¹, Ross T. Howie^{1,2}, Eugene Gregoryanz^{1,2,3} and Miriam Peña-Alvarez^{1,*}¹*Center for Science at Extreme Conditions and School of Physics and Astronomy, University of Edinburgh, Edinburgh EH9 3FD, United Kingdom*²*Center for High-Pressure Science and Technology Advanced Research, Shanghai 201203, China*³*Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China*

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Under high pressure, methane and hydrogen form (CH₄)₂H₂, CH₄(H₂)₂, and (CH₄)₃(H₂)₂₅ van der Waals compounds with stoichiometries determined by the H₂ concentration. This study investigates the effect of compression rates (up to 183 GPa/s) on the formation and morphology of these compounds at pressures up to 60 GPa utilizing dynamic diamond anvil cells combined with time-resolved Raman spectroscopy. Compression rates exceeding 100 GPa/s inhibit the formation of (CH₄)₃(H₂)₂₅, while CH₄(H₂)₂ and (CH₄)₂H₂ remain unaffected. Furthermore, lower compression rates yield distinct leaflike and globular sample morphologies depending on the H₂ concentration, while rates above 20 GPa/s consistently result in textureless mixtures, regardless of H₂ concentration. These combined results demonstrate the competition between transition time and kinetic barriers, together with the critical role of the compression rate during dynamic-pressure nonequilibrium processes.

DOI: [10.1103/PhysRevB.110.224109](https://doi.org/10.1103/PhysRevB.110.224109)**I. INTRODUCTION**

Hydrogen (H₂) and methane (CH₄) are of paramount importance in condensed matter physics and planetary sciences [1–9]. Their mixtures play a critical role in understanding the atmospheres and internal structures of ice giants such as Neptune and Uranus [1–3], and have been considered as potential hydrogen storage materials [10–12]. During static compression at room temperature, methane and hydrogen form three van der Waals compounds with stoichiometries dependent on the initial relative mixture concentration [10,13]. (CH₄)₂H₂ was identified above 4.6 GPa in mixtures of 30 and 50 mol% H₂, CH₄(H₂)₂ formed at 5.7 GPa, coexisting with (CH₄)₂H₂ or excess of H₂ in CH₄-H₂ mixtures with 50 mol% H₂ or higher, while further compression above 10.9 GPa of CH₄(H₂)₂ in excess H₂ led to the formation of (CH₄)₃(H₂)₂₅ [13]. The structure and stoichiometry of these various CH₄-H₂ van der Waals compounds were determined through x-ray diffraction combined with density functional theory calculations, with each compound exhibiting distinct vibrational Raman spectra.

Although (CH₄)₂H₂ and CH₄(H₂)₂ were found to be thermodynamically stable in density functional theory calculations, (CH₄)₃(H₂)₂₅ was found to be unstable [13–17]. Furthermore, a complete transformation to (CH₄)₃(H₂)₂₅ was never fully achieved, as it coexisted with an excess of H₂ and CH₄(H₂)₂ [13]. This coexistence suggests that although

the most hydrogen-rich compound might be the most thermodynamically stable product, large kinetic barriers prevent the system from reaching full equilibrium [18,19].

For nonequilibrium processes, in which kinetic barriers play an important role, varying the compression rate can be used to explore phase stability [20,21]. This is primarily due to the competition between the transition time τ and kinetic barriers ΔE [22–27]. The P - T phase diagram of methane has been demonstrated to have a strong dependence on compression rate, for example, the transformation from phase VII to phase VIII can be prevented depending on both the thermodynamic path and the rate of compression [28–31]. In recent studies of the hydrogen hydrates, the C₃ phase is not observed during fast compression, highlighting the crucial role of compression rate in the formation of H₂ bearing molecular compounds [32].

To study nonequilibrium processes bridging the gap between static compression diamond anvil cell experiments and shock compression studies, dynamic diamond anvil (dDAC) cells have been designed to facilitate rapid compression [27,33–36]. Building on the traditional DAC design, the dDAC is equipped with a piezoelectric actuator or a gas membrane to continuously apply pressures, where compression rates of up to 240 TPa/s can be reached [27,34–36]. Both H₂ [37] and H₂O have been studied [27,33] using the dDAC, studying the effect of compression rates on crystallization [37,38]. To date, most of these studies have focused on controlling crystal morphology and their use to study nonequilibrium processes remains limited [25,27,33,37,39–41].

In this paper, we investigate how the compression rate affects phase transformations in CH₄ and H₂ and compound formation in the CH₄-H₂ system. Through the use of dynamic diamond anvil cells (dDACs) we achieve compression rates from 0.001 to 183 GPa/s and probe the samples *in situ* through time-resolved Raman spectroscopy (TRRS). We find

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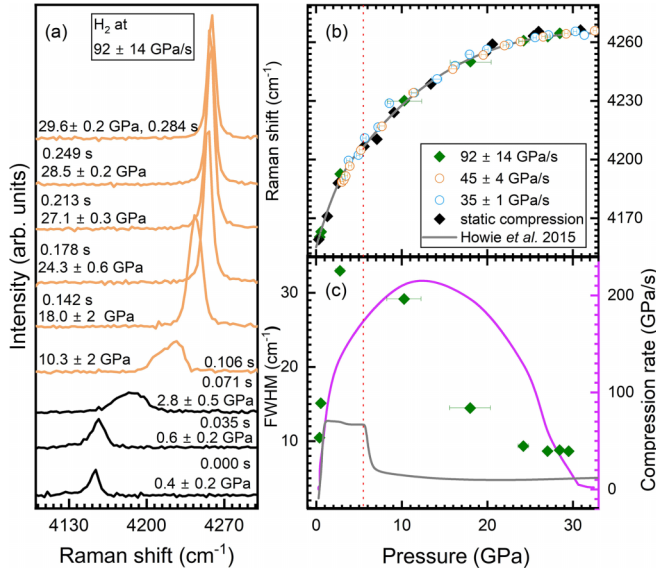


FIG. 1. Dynamic compression of H_2 at different compression rates. (a) Representative H_2 Raman spectra during compression at 92 ± 14 GPa/s. Black spectra correspond to fluid H_2 and orange to solid H_2 phase I. (b) Raman shift vs pressure from three independent experiments at 45 ± 4 GPa/s, 35 ± 1 GPa/s, 92 ± 14 GPa/s, and static compression. (c) Full width at half maximum (FWHM) (green diamonds, left axis) and compression rate at given pressures (purple curve, right axis) for the experiment at 92 ± 14 GPa/s. The dashed vertical line at 5.5 GPa in (b) and (c) are guides to mark for the solidification of H_2 , and the gray solid lines are static compression results from Howie *et al.* [42].

that the formation of $(\text{CH}_4)_3(\text{H}_2)_{25}$ is completely inhibited at compression rates above 100 GPa/s, while no obvious effects of the compression rate are observed for $(\text{CH}_4)_2\text{H}_2$ and $\text{CH}_4(\text{H}_2)_2$. Furthermore, the crystal morphologies in all concentrations of H_2 - CH_4 mixtures studied exhibit a strong dependence on the compression rate. For example, the “leaflike” texture is formed at compression rates of 7.5 GPa/s in 80–90 mol% H_2 mixtures while the sample is textureless at rates of 183 GPa/s.

II. METHODS

CH_4 , H_2 , and CH_4 - H_2 (British Oxygen Company (BOC), 99.9999% purity) with 30, 50, 80, and 90 mol% H_2 concentrations in $\pm 1\%$ tolerances were loaded at a pressure of 0.2 GPa into both DACs and dDACs. Type IIa diamonds were used with 200 μm anvil culet diameters, and rhenium gaskets were used to form the sample chambers. In all experiments, ruby was used as the pressure marker [44,45]. In static compression experiments, Raman spectra were collected after approximately 15 min at the target pressure. For dDAC compression experiments a gas membrane was actuated by high-pressure nitrogen-driving gas with the pressure and compression rate controlled by a DRUK PACE 5000, with 0.1–50 bars/s loading rates [36]. This can achieve average compression rates up to 60 GPa/s, however, the compression rate varied with time. A piezoelectric actuator (PSt 1000/35 VS45, Piezosystem Jena) driven dDAC was also used in these

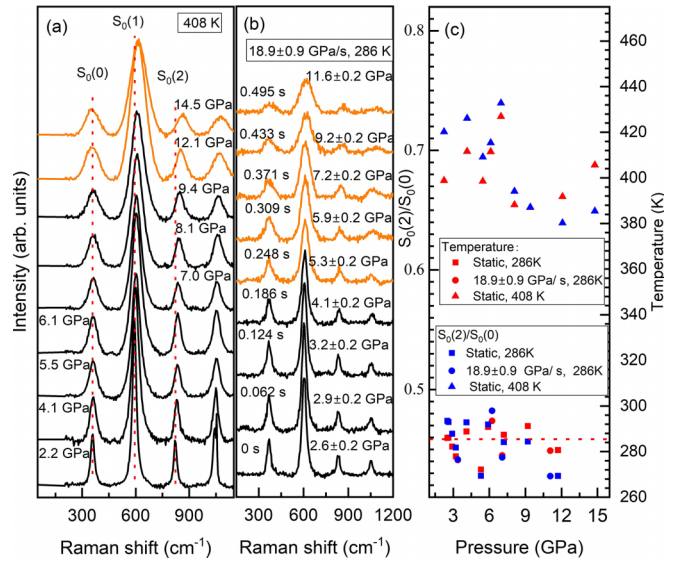


FIG. 2. Rotation Raman spectra of H_2 : (a) Isotherm static compression at 408 K, and (b) isotherm compression with 18.9 ± 0.9 GPa/s at 286 K. (c) Intensity ratio of other H_2 $S_0(2)/S_0(0)$ (the blue symbols) and the estimated temperature (the red symbols) with ± 10 K uncertainty, based on Eq. (2) in the Supplemental Material [43]. The red dashed line is a guide to the eye for the potential temperature fluctuation in dynamic compression.

experiments reaching compression rates up to 100 GPa/s. In this setup, voltage was linearly increased up to 650 V in a power amplifier (RCV 1000/7, Piezosystem Jena), giving a near constant compression rate with time.

Time-resolved Raman spectra (TRRS) were collected using a custom-built microfocused Raman system, with a 514.5 nm (± 0.03) excitation wavelength (Innova 70C argon ion laser). Raman spectra were continuously collected during compression with a Princeton Instruments PyLoN 100BRX CCD. We used exposure times within the range of 10–100 ms with a 2 MHz readout rate.

The ruby fluorescence spectra are used to monitor pressure during compression at the same time as the Raman acquisition [11]. As pressure varies during the acquisition time, the average pressure is given together with an error taking into account this variation [36]. The compression rate at a given time interval is calculated using the first derivative of the pressure as a function of time. The average compression rate is the mean rate across all pressure intervals for each experiment. The peak compression rate is the maximum compression rate achieved during the experimental run.

III. RESULTS AND DISCUSSION

A. Rapid compression studies of H_2 and CH_4

We initially conducted dDAC experiments on both pure H_2 and pure CH_4 species up to pressures of 40 GPa as a benchmark to study CH_4 - H_2 mixtures (see Figs. 1 and 3).

In the case of H_2 , all phase transitions have been previously determined by Raman spectroscopy, through changes in both the shift and the full width at half maximum (FWHM) of the H-H stretching mode as a function of pressure [42,46,47].

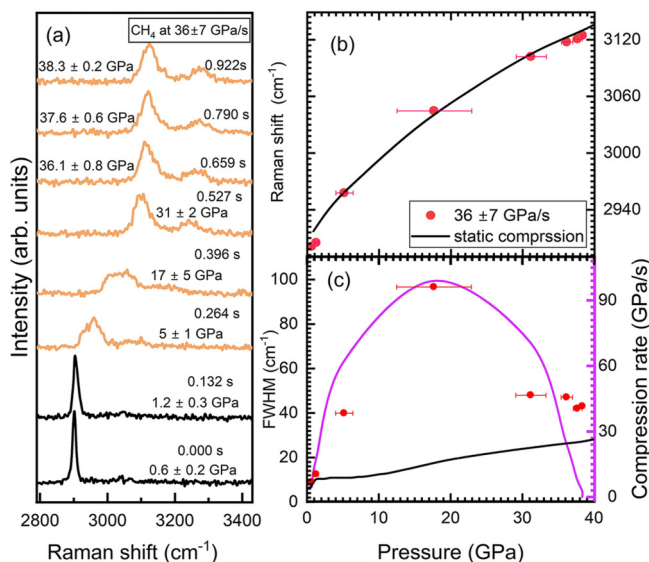


FIG. 3. Dynamic compression of CH₄ at an average rate of 36 ± 7 GPa/s. (a) Representative TRRS with 132 ms time resolution and 10 ms exposure time showing methane spectra. The black lines represent the spectra for fluid CH₄, while the orange lines represent solid CH₄. (b) Raman shifts as a function of pressure of the fitted ν_1 C-H stretching mode (red circles) and data from static compression experiments taken from Ref. [31] (black line). (c) Left axis: ν_1 FWHM results of dynamic compression at an average rate of 36 ± 7 GPa/s (red circles) and static compression results (solid black line) from Ref. [31]. Right y axis and purple line: Compression rate (see Fig. S1 [43] for the pressure vs time plot).

Notably, the transition from a fluid to solid phase, expected at 5.5 GPa at 300 K, is characterized by the narrowing of the H-H stretching mode and a continuous upshift in frequency [42,48].

Figure 1(a) displays the Raman spectra of H₂ at various pressures during compression at an average rate of 92 ± 14 GPa/s. While the Raman shift versus pressure exhibits a similar trend to static compression experiments [as shown in Fig. 1(b) [42,46,47]], there is a notable broadening of the H-H stretching mode between 2.8 and 10 GPa, as illustrated in Fig. 1(c). This broadening in the compression process is attributed to the rapid changes in the H₂ Raman shift within the 10 ms spectrum collection timeframe, rather than the persistence of H₂ in a fluid state up to 10 GPa. As such, the FWHM exhibits a similar trend to the compression rate, as depicted in Fig. 1(c) on the right axis. These results highlight the limits of the diagnostic technique used to pinpoint phase boundaries during rapid compression.

We have also evaluated thermal effects during rapid compression by monitoring the H₂ rotational modes (rotons), which have a temperature-dependent intensity distribution [49–51]. From the relative intensity of the $S_0(0)$ and $S_0(2)$ rotors, we can calculate the temperature of the sample *in situ* [see the Supplemental Material (SM) [43] for further details]. As shown in Fig. 2(a), during static compression at 408 K the $S_0(2)$ is almost as intense as $S_0(0)$. However, during compression of H₂ at 286 K at 18.9 GPa/s there is no significant intensity redistribution in the rotors, with $S_0(2)$ intensity considerably lower to that of $S_0(0)$, indicating that

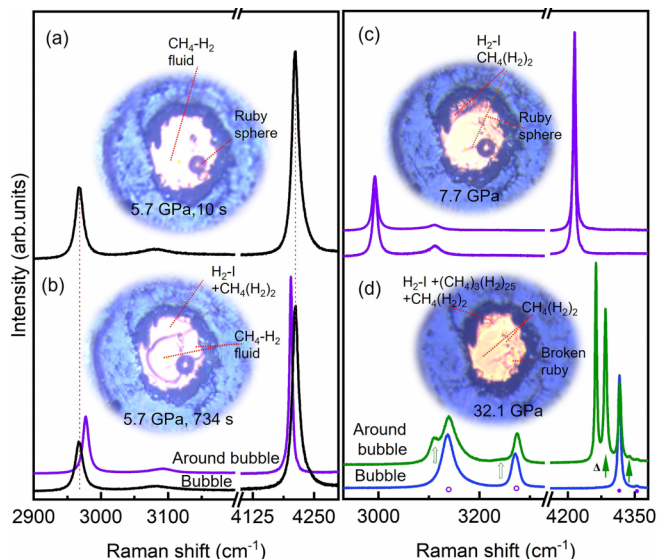


FIG. 4. Raman spectra and microphotographs of an 80 mol% H₂ mixture in static compression at selected pressures. (a) Compression to 5.7 GPa resulted in a well-homogenized fluid CH₄-H₂ mixture. (b) After 735 s, a “bubble” containing CH₄-H₂ at 5.7 GPa appeared, surrounded by a sample characterized by Raman spectra of a solid CH₄-H₂ mixture. (c) At 7.7 GPa, the “bubble area” solidified, and Raman prints matched those of the central area. (d) Compression beyond 12 GPa (e.g., 32.1 GPa) revealed the presence of CH₄(H₂)₂ at the central area corresponding to the bubble at 5.7 GPa, while the surrounding sample exhibited excess H₂ (black triangle), (CH₄)₃(H₂)₂₅ (green arrows, solid symbols for the H-H stretching mode and open ones for the C-H stretching modes), and CH₄(H₂)₂ (purple solid circles for the H-H stretching modes and open circles for C-H stretching modes). A single ruby sphere positioned in the bottom-right corner serves as a pressure marker [11].

any thermal effects induced during compression are below the uncertainty (10 K).

Unlike H₂, CH₄ has been previously determined to have a time dependence on phase transformations at high pressure [29]. For example, the phase VII(A) to phase VIII(B) transition at pressures between 8 and 14 GPa requires a timescale of up to 17 h to fully transform [29]. We have rapidly compressed methane at an average rate of 36 ± 7 GPa/s up to pressures of 38.3 GPa. Similar to H₂, we observe a significant broadening of ν_1 (see Fig. 3), compared with the static compression [31]. We again attribute this to a continuum of vibrational modes corresponding to different pressures and phases [fluid–phase I–phase VII(A)] observed during the collection time limited by the detector [Fig. 3(c)]. As mentioned above, the transition from phases VII(A) to VIII(B) necessitates hours to complete at room temperature between 8 and 14 GPa, rendering it undetectable under rapid compression.

B. Rapid compression studies of CH₄-H₂ mixtures

We have studied CH₄-H₂ mixtures with H₂ molar concentrations of 30, 50, 80, and 90 mol % with various average compression rates. It has previously been observed that (CH₄)₂H₂ forms in 30 and 50 mol% H₂, and CH₄(H₂)₂ and

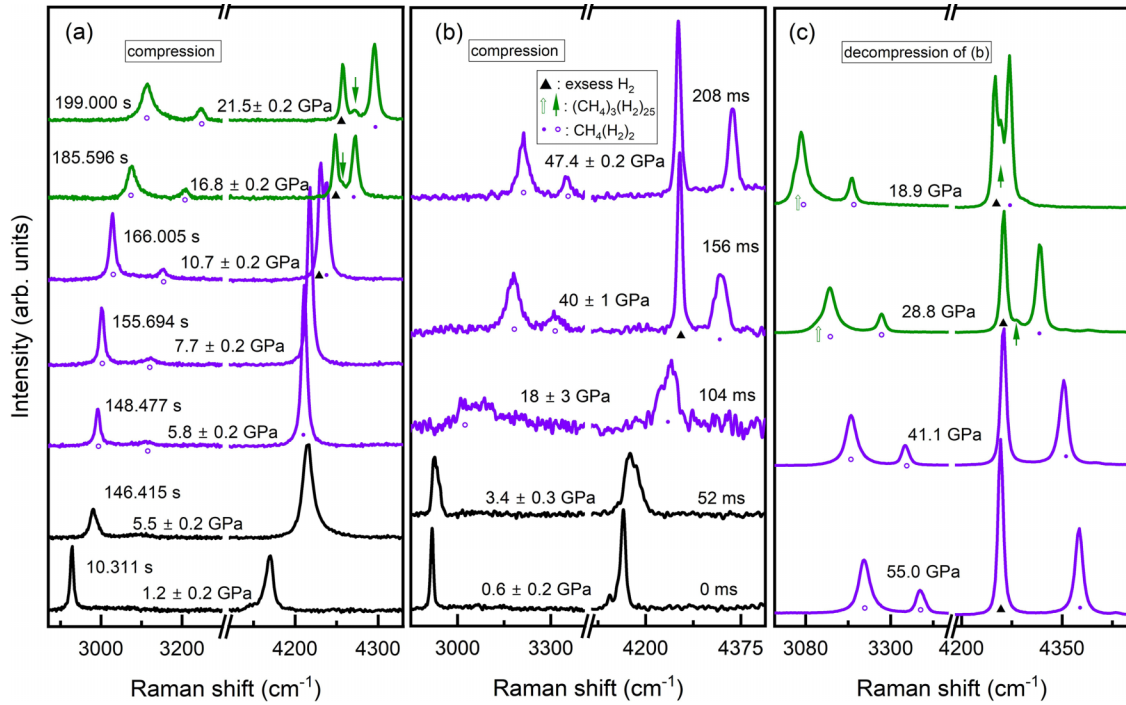


FIG. 5. Representative time-resolved Raman spectra of the 80 mol% H_2 mixture. (a) Average compression rate of 0.2 ± 0.2 GPa/s. (b) Compression at an average rate of 183 ± 17 GPa/s. (c) Static decompression with 30 s exposure time from the sample in (b). Black spectra correspond to the mixed fluid, purple spectra indicate the $\text{CH}_4(\text{H}_2)_2$ compound, and green spectra represent the $(\text{CH}_4)_3(\text{H}_2)_{25}$ system. Solid purple circles are used to mark the H-H stretching mode from $\text{CH}_4(\text{H}_2)_2$, while solid green arrows are used for the H-H stretching modes from $(\text{CH}_4)_3(\text{H}_2)_{25}$, triangles for the H-H stretching mode from the excess H_2 , open purple circles are for the C-H stretching modes from $\text{CH}_4(\text{H}_2)_2$, and green open arrows for CH stretching modes from $(\text{CH}_4)_3(\text{H}_2)_{25}$.

$(\text{CH}_4)_3(\text{H}_2)_{25}$ in 80 and 90 mol% H_2 upon static compression [13].

For $\text{CH}_4\text{-H}_2$ mixtures containing 80 and 90 mol% H_2 , conventional static compression experiments show the formation of $\text{CH}_4(\text{H}_2)_2$ at pressures of 5.7 GPa, coexisting with a fluid mixture of CH_4 and H_2 [Fig. 4(b)]. These distinct regions can be differentiated due to each phase having characteristic H_2 vibrons at distinct frequencies. This is due to the sensitivity of the H_2 stretching mode to the local environment of hydrogen molecules [13]. When this mixture is compressed above 15 GPa, three distinct H-H vibrons at approximately 4240, 4265, and 4300 cm^{-1} are distinguished, indicating a coexistence of H_2 , $(\text{CH}_4)_3(\text{H}_2)_{25}$, and $\text{CH}_4(\text{H}_2)_2$. This is in good agreement with previous studies correlating Raman spectroscopy with structural characterizations [13].

At relatively slow average compression rates of 0.2 GPa/s, the solidification pressure and the phase formation sequence are comparable to that observed upon static compression up to 21.5 GPa [see Fig. 5(a)]. Under the faster average compression rate of 183 ± 17 GPa/s, we observe the formation of $\text{CH}_4(\text{H}_2)_2$ with an excess of H_2 , however, there is no spectral evidence indicating the formation of $(\text{CH}_4)_3(\text{H}_2)_{25}$ up to 47 GPa [see Fig. 5(b)]. Furthermore, holding the sample at a pressure of 55 GPa for 72 h did not facilitate the formation of $(\text{CH}_4)_3(\text{H}_2)_{25}$. It was only upon static decompression of the sample below approximately 30 GPa that we observe the formation of $(\text{CH}_4)_3(\text{H}_2)_{25}$ by the characteristic H-H and C-H vibrational modes [Fig. 5(c)]. Analogous

results were observed for 90 mol% mixtures upon similar average compression rates (0.151 ± 0.003 and 70 ± 6 GPa/s) and upon static decompression (Fig. S3 [43]). These results are indicative that the pressure stability field of $(\text{CH}_4)_3(\text{H}_2)_{25}$ is in a narrow regime (17 and 30 GPa). Even within this pressure interval, the transformation of this phase is kinetically sluggish and is in coexistence with $\text{CH}_4(\text{H}_2)_2$. These observations suggest that for high hydrogen concentrations, $\text{CH}_4(\text{H}_2)_2$ is energetically metastable but kinetically favored, whereas $(\text{CH}_4)_3(\text{H}_2)_{25}$ is thermodynamically stable but kinetically hindered. Our findings underscore the application of Ostwald's rule in our study, with 80 and 90 mol% H_2 concentrations transitioning under rapid compression to the energetically nearest $\text{CH}_4(\text{H}_2)_2$ metastable state, rather than to the thermodynamically stable $(\text{CH}_4)_3(\text{H}_2)_{25}$.

The formation of either $\text{CH}_4(\text{H}_2)_2$ (in 90, 80, and 50 mol%) or $(\text{CH}_4)_2\text{H}_2$ (in 50 and 30 mol%) depended solely on the concentration of H_2 , regardless of the average compression rates. Figure 6 shows the Raman spectra before compressing a mixture of 50 mol% H_2 at an average rate of 61 ± 8 GPa/s up to 50.4 GPa. The result is in agreement with previous static compression results [13]. For 30 mol% H_2 mixtures compressed at an average rate of 59 ± 8 GPa/s to a pressure of 44.2 GPa, Raman spectroscopy shows that only $(\text{CH}_4)_2\text{H}_2$ is produced.

Interestingly, the H-H, for H_2 , and C-H, for CH_4 stretching frequencies of $\text{CH}_4(\text{H}_2)_2$, $(\text{CH}_4)_2\text{H}_2$, and $(\text{CH}_4)_3(\text{H}_2)_{25}$ (at

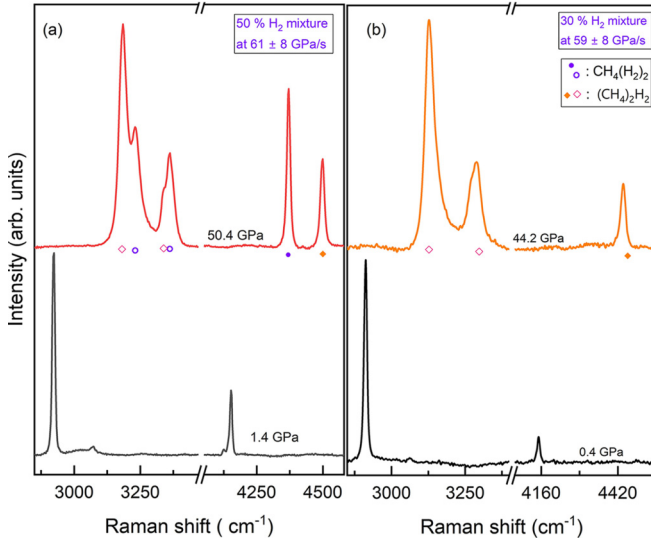


FIG. 6. Methane-rich fluids under dynamic compression. (a) Raman spectra of 50 mol% H₂ at 1.4 GPa before dynamic compression, and at 50.4 GPa, after being compressed at 61 ± 8 GPa/s. The fluid mixture (black line) at 1.4 GPa transforms into (CH₄)₂H₂ (yellow diamonds) and CH₄(H₂)₂ (violet dots). (b) Raman spectra of 30 mol% H₂ at 0.4 GPa before dynamic compression, and at 44.2 GPa, after being compressed at 59 ± 8 GPa/s. The fluid mixture at 0.4 GPa transforms into (CH₄)₂H₂ (yellow diamond). Open symbols are used to mark the C-H stretching modes, and solid symbols for the H-H stretching modes. These are color coded, using purple for CH₄(H₂)₂ and orange for (CH₄)₂H₂.

slow compression rates) do not exhibit any deviation from static compression experiments. This supports the compound assignment and is indicative that no new compounds form as a result of high compression rates (see Fig. 7).

C. Compression rate effects on crystal morphology

Under thermodynamic equilibrium conditions for phase transitions, small single crystals typically originate from a stable nucleation site, and then grow either through gradual expansion or the merging of multiple nuclei [52–55]. This phenomenon is evident in the static compression of 80, 50, and 30 mol% H₂ mixtures (see Figs. 4 and 8). For example, in the static compression of an 80 mol% H₂ mixture, a CH₄(H₂)₂ crystal slowly grows (on a timescale of approximately 750 s) from the periphery of the sample chamber towards the center, as illustrated in Fig. 4(b). If multiple compounds are formed, such as in 50 mol% H₂ mixtures, many small crystals grow as pressure approaches the solidification point. If the pressure is held, then the number of crystals decrease as nucleation progresses (Fig. 8). This results in the spatial separation of phases within the sample chamber, allowing Raman spectroscopy to assign the characteristic spectra of each crystal.

We find that the morphology of samples changes significantly depending on both the compounds formed and the rate of compression. When compressing 80 or 90 mol% H₂ mixtures at average rates ranging from approximately 0.1 to 20 GPa/s, the sample shows a leaflike morphology [Fig. 9(a)], formed by CH₄(H₂)₂, (CH₄)₃(H₂)₂₅, and

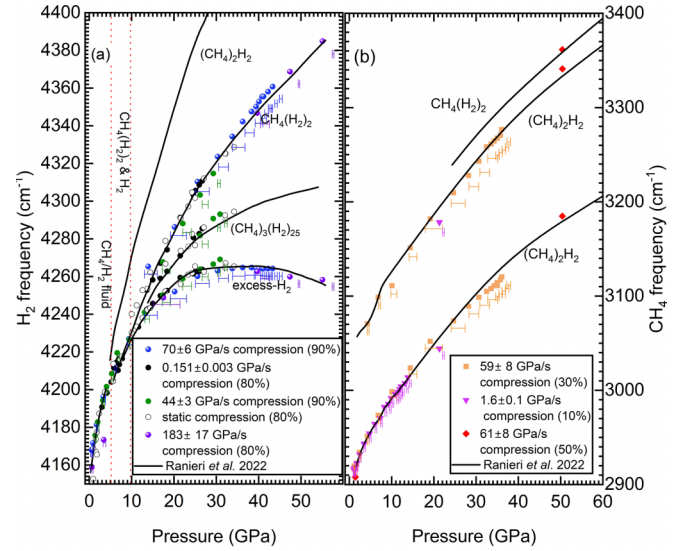


FIG. 7. Molecular vibrational frequencies of H₂-CH₄ van der Waals compounds as a function of pressure under various average compression rates, compared to Ranieri's previous work on static compression (black lines) [13]. (a) In the static and dynamic compression experiments with 80 and 90 mol% H₂, the vibrational modes of H₂ were utilized to detect the formation of van der Waals compounds. However, the signals of CH₄ in these experiments were too weak to characterize CH₄(H₂)₂ and (CH₄)₃(H₂)₂₅. (b) Conversely, the stretching modes of CH₄ were employed to identify the formation of H₂-CH₄ compounds in the dynamic compression of hydrogen-poor fluid (<50 mol%), given the weak signal of H₂-CH₄.

excess H₂. This distinctive morphology arises from the multiphase sample and the rapid growth of randomly oriented crystalline dendrites [52–55]. In this scenario, the compression rates are sufficiently rapid to impede a clear phase separation between the two van der Waals compounds and hinder equilibrium crystal growth. Similar morphologies described as two-dimensional (2D) carpet-type fractals have been observed in the dynamic compression of water [52,53].

Interestingly, higher compression rates (approximately 100 GPa/s and above) not only prevent the formation of (CH₄)₃(H₂)₂₅ but also impede any nucleation process leading to identifiable crystallites. As depicted in Fig. 9(b), the 80 mol% H₂ mixture, when compressed at an average rate of 183 ± 17 GPa/s to 55 GPa, presents as a textureless morphology comprising H₂ and CH₄(H₂)₂. Although the appearance seems textureless, most likely the compression rates are such that the crystallites are smaller and the boundaries are indistinguishable to the resolution of our imaging setup. Upon decompression of this mixture below 34 GPa, the sample morphology changes with the appearance of dendritic crystals [Fig. 9(c)] coinciding with the formation of (CH₄)₃(H₂)₂₅.

In lower H₂ concentration mixtures, such as 50 mol% mixtures where both (CH₄)₂H₂ and CH₄(H₂)₂ form, the sample forms a globular morphology at rates below 2 GPa/s [refer to Fig. 10(a)]. However, faster average compression rates, >40 GPa/s, also yield a textureless morphology [Fig. 10(b)]. These findings align with previous research on the freezing behavior of water under varying compression rates [33,56,57], providing insight into how the compression rate influences

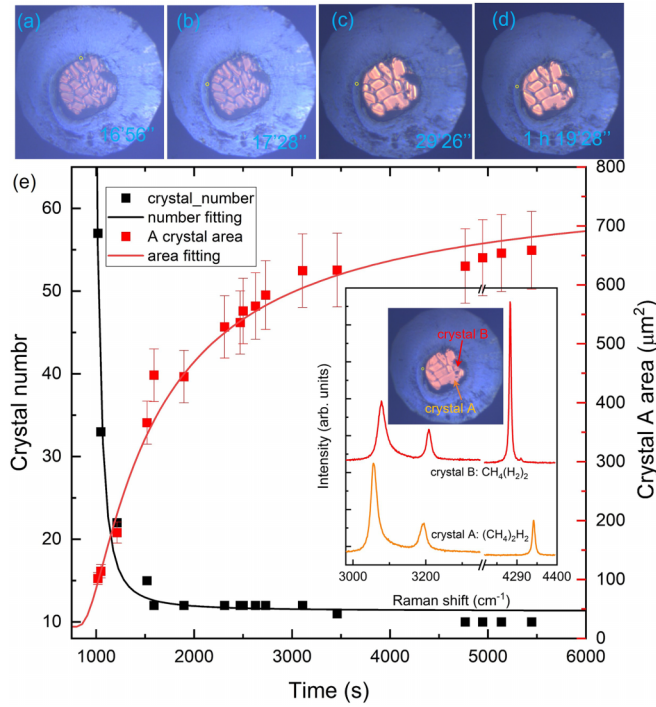


FIG. 8. Crystal growth of $(\text{CH}_4)_2\text{H}_2$ in a 50 mol% H_2 mixture at 4.9 GPa. (a)–(d) Microscopic images of the sample at 4.9 GPa captured under both reflected and transmitted light at various time intervals. (e) Evolution of crystal count (left axis) and the variation in the area of crystal A over time (right axis). The rapid decline in crystal count coincides with the emergence of multiple $(\text{CH}_4)_2\text{H}_2$ crystals. Inset: Raman spectra and photomicrography sample at 18 GPa. Most areas of the sample are identified as a large $(\text{CH}_4)_2\text{H}_2$ crystal, whereas a small crystal exhibits characteristics of a $\text{CH}_4(\text{H}_2)_2$ single crystal (red arrow).

the morphology of $\text{CH}_4\text{-H}_2$ crystals. Earlier studies on ice have also documented the compression rate dependency of 2D carpet fractal morphologies [33,56,57], similar to the dendritic, low-symmetry microstructures observed at faster

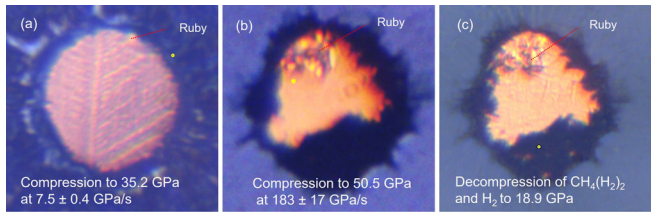


FIG. 9. Crystal morphology of $\text{CH}_4\text{-H}_2$ after (de)compression 80 mol% H_2 mixture. (a) Dynamic compression of an 80 mol% H_2 mixture at an average rate of 7.5 ± 0.4 GPa/s to 32 GPa, resulting in a 2D leaflike texture with homogeneously distributed $\text{CH}_4(\text{H}_2)_2$, $(\text{CH}_4)_3(\text{H}_2)_{25}$, and H_2 . (b) Dynamic compression of an 80 mol% H_2 mixture at an average compression rate of 183 ± 17 GPa/s to 55.1 GPa, producing a textureless morphology with a homogeneous mixture of $\text{CH}_4(\text{H}_2)_2$ and H_2 . (c) A dendriticlike texture is observed when the $\text{CH}_4(\text{H}_2)_2$ and H_2 mixture was decompressed below 30 GPa, indicating the formation of $(\text{CH}_4)_3(\text{H}_2)_{25}$, as shown in Fig. 5(c). A broken ruby sphere is visible at the top of the image.

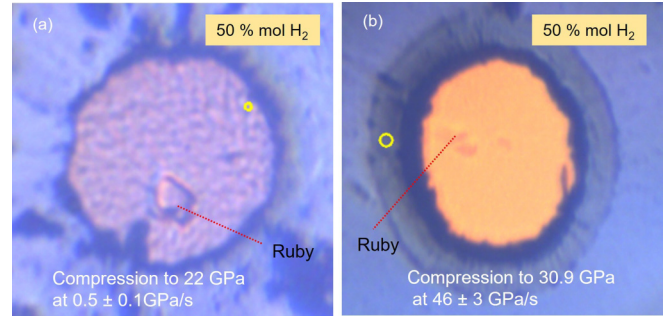


FIG. 10. Crystal morphology of $\text{CH}_4\text{-H}_2$ dynamic compression of a 50 mol% H_2 mixture. (a) Compression to 22 GPa at an average rate of 0.5 ± 0.1 GPa/s, producing multiple small crystals of $(\text{CH}_4)_2\text{H}_2$ and $\text{CH}_4(\text{H}_2)_2$ giving this globular morphology. (b) Compression at an average rate of 46 ± 3 GPa/s to 30.9 GPa, resulting in a homogeneous mixture of both $(\text{CH}_4)_2\text{H}_2$ and $\text{CH}_4(\text{H}_2)_2$ with no visible crystalline boundaries.

compression rates in this study. Recently, Pépin *et al.* [21] further demonstrated that the compression rate can influence the freezing process of water [21], which is in agreement with the mechanism of crystallization in $\text{CH}_4\text{-H}_2$ fluids. This connection underscores the significance of comprehending the impact of compression dynamics on the evolution of crystal morphology. Furthermore, our findings support previous reports [37] suggesting that average compression rates exceeding 100 GPa/s facilitate an apparent textureless morphology.

IV. CONCLUSIONS

The influence of compression rate on CH_4 , H_2 , and the formation of a $\text{CH}_4\text{-H}_2$ van der Waals compound have been investigated up to 40 GPa. Benchmark compression rate studies of both CH_4 and H_2 show no obvious changes in the pressure response of their molecular vibrational modes compared to static studies. Through an analysis of the rotational modes of H_2 no thermal effects are observed up to average rates of 18.9 GPa/s, with a peak compression rate of 43 GPa/s. We find that average compression rates exceeding 100 GPa/s to 50 GPa hinder the formation of $(\text{CH}_4)_3(\text{H}_2)_{25}$, and this compound can only form below pressures of 30 GPa. This suggests that this compound is only energetically competitive with $(\text{CH}_4)(\text{H}_2)_2$ in the 17–30 GPa pressure regime. We also find that the sample morphology depends not only on compounds formed, but also on the compression rate.

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Correction: A footnote indicating the contact author was missing and has been added.