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Raman study of phase transitions in compressed methane using moissanite anvil cells

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Thorough investigations using Raman spectra of solid methane (CH_4) were conducted using moissanite anvil cells in the range of 1−43 GPa at room temperature to identify high-pressure phases. Two novel phases that are distinguishable from previously reported phases were uncovered. One, with a narrow pressure range of 1 GPa centered at around 12.5 GPa and another, with a range of 3 GPa centered around 40.5 GPa. Our results do not support the existence of a phase transformation around 25 GPa. The high quality Raman spectra, obtained by using single crystal samples, narrow the boundaries of seven methane phases at pressures up to 43.2 GPa.

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I. INTRODUCTION

As the simplest hydrocarbon, methane is very important to planetary physics. It is known that methane exists on many planetary bodies and that it makes up around 40% of the mass of Uranus' atmosphere.[1] Knowledge of the properties of methane at high pressure is necessary to understand the formation of Jovian planets and the structure and constancy of hydrocarbons in Earth's mantle and crust.[2] Upon compression, this hydrogen-rich molecule is believed to metalize and become a superconductor with a high transition temperature.[3] This process can most likely be considered as a pathway to achieving metallic hydrogen within the current capabilities of diamond-anvil-cells. Depending on the pressure exerted on solid methane, different phases can be produced. This is because solid methane has a high degree of freedom of orientation. It has been established[4–10] that liquid methane crystallizes into phase I around 1.7 GPa, into phase A around 5.2 GPa, and further into phase B at 10-18 GPa. At higher pressure, phase B is thought to transform into a so-called high pressure phase 1 (HP1), around 25 GPa, which supposedly transforms into a high pressure phase 2 (HP2), around 37 GPa.[5] It is currently known that phase I has a fcc crystal structure and space group $Fm3m$ (O_h^5) with one freely rotating molecule in the unit cell.[11] Recently, the structure of phase A was assigned to have the $R3$ space group with 21 molecules in the unit cell.[12]

The high-pressure phases of solid methane and their stability above 5 GPa have long been the subject of a great deal of experimental and theoretical research, specifically with regards to the existence of a phase transformation around 25 GPa. Bini *et al.*[13] reported a slope change in the wavenumbers of the two modes for symmetric and antisymmetric stretching vibrations around 25 GPa, thus prompting them to declare that a phase transformation takes place from phase B to HP1 at this pressure. Structural measurements[6] show that there is a kink in the molecular volume versus pressure curve at 25 GPa, thereby supporting the existence of such a phase transformation. In a prior study where more data points were included, the pressure dependence of the frequency does not show a distinguishable change in slope at 25 GPa.[14] All prior spectroscopy studies observed only two to three peaks in the pressure range of 10 to 25 GPa.[6,13,14] Recently, Hirai *et al.*[5] demonstrated that well prepared samples should have five to six peaks within that range. Interestingly, they[5] reported a sudden change in the peak number at 25 GPa from Raman measurements, accompanying a volume change as determined by x-ray diffraction data. However, this structural change was not detected by an independent x-ray diffraction measurement.[15] The differing results from studying methane at 25 GPa makes the existence of a phase transformation at that pressure range debatable.

In recent years, there have been a few studies that deal with the high-pressure behaviors of solid methane above 30 GPa.[5,15–17] A high pressure phase was suggested in the range of 37−40 GPa from Raman measurements.[5,17] It is unknown what the path to this phase from the HP1 or the B phase would be if the phase transition at around 25 GPa did not exist. However, there were discrepancies concerning the existence (or nonexistence) of a phase at around 12 GPa.[4,13,18] A complete understanding of the phase shifts for solid methane under pressure could provide useful knowledge about the physics in hydrogen-bearing materials, which have been suggested to be high-temperature superconductors at high pressures.[3] In order to understand the rich phases of solid methane and their stability, a thorough study focused on the vibrational properties of methane at high pressures is required.

In this paper, we present a vibrational study of solid methane using well-prepared single crystals at high pressures up to 43 GPa. By using Raman signals to probe for phase transitions, we discovered two new phase transitions at 12 and 39 GPa. We also examined all previously reported phase transitions. Our results do not show drastic differences between the spectral profiles around 25 GPa, which indicates the absence of a phase transition at that point. Based on the changes in the Raman spectra, we shall now present and discuss the mechanisms of phase transitions of methane.

II. EXPERIMENTAL

Gaseous CH_4 (99.99%) was loaded into moissanite anvil cells. Small pieces of ruby were placed in the sample chambers before gas loading. Such anvils have been used to reach pressures above half a megabar (>50 GPa).[19] Unlike diamonds, moissanite does not have any observable Raman peaks between 2000 and 4000 cm^{-1}, offering a relatively open and clean window to measure phase transformations of methane at high pressures. The culet sizes of the moissanite anvils that were used were about 400 μm. Tungsten gaskets with 100 μm diameter sample holes were used to hold the samples. Because a hydrostatic pressure environment can be maintained by methane itself, we did not load any other medium. Pressure was determined by using the ruby fluorescence method at room temperature.[20] Radiation at 514.5 nm from an argon ion laser was used to excite the sample. Pressure was applied gradually and typically resulted in the formation of single crystals of CH_4. Therefore, most of our solid samples are single crystals which have been confirmed by x-ray diffraction technique.

It has been established[5,7] that a relaxation period of at least 12 hours is required in order to form a stable phase after phase A. We used a relaxation period of 24 hours to form a stable phase at 12 GPa. However, we found that the profiles and peak positions of the observed spectra of the stable phases do not depend on the time duration once the stable phase around 12 GPa was formed. A time period of 30 minutes was used for the measurements at pressures beyond that phase.

III. RESULTS AND DISCUSSIONS

Raman scattering, which measures phonons in the Brillouin zone centre, possesses strong selection rules and is known to be a powerful technique for the investigation of even subtle structural distortions both within a space group (via band shifts) and due to phase transitions (via band splitting and/or soft modes etc.). The CH_4 molecule has four internal modes (A_1+E+$2F_2$), all of which are Raman active. Among these, $\nu_1(A_1)$ and $\nu_3(F_2)$ are symmetric and antisymmetric stretching vibrations. In the present study, we have measured the vibrational spectrum in the ν_1 and ν_3 regions, 2800−3600 cm^{-1}, as a function of pressure up to 43 GPa at room temperature.

Figure 1 shows the Raman spectra of methane at various pressures up to 43.2 GPa at room temperature. One can clearly see that the spectra of 1.0 GPa and 4.5 GPa are very similar; both include only the two most intense Raman modes (ν_1 and ν_3). When the pressure is increased to 9.2 GPa, a shoulder appears on the low frequency side of ν_1. It is noteworthy to mention that the Raman spectrum at 24.0 GPa behaves differently from other spectra at different pressures. It possesses six modes in the frequency regions investigated, whereas the spectra of other pressure ranges, shown in Fig. 1, do not. In addition, we were unable to detect the three phases that were reported recently based on mode number changes.[5] It is worth noting that the Raman spectra at 12.3 GPa has a different structure compared to that of other pressures. A new peak was observed at this pressure around 3075 cm^{-1}, situated between ν_1, ν_3, and their shoulders. The observed multiple characteristics of phonon modes above 12 GPa suggests that the obtained phases are stable, different from early observations of only two or three peaks at pressures above 12 GPa.

Figure 2 shows the pressure dependence of the peak positions of methane up to 43.2 GPa. Raman spectroscopy revealed that liquid methane crystallizes to solid phase *I* methane at 1.6 GPa. This was marked by a disparity in the wave number value. A transformation from phase *I* to phase *A* was observed as another disparity at 5.2 GPa. Recent structural studies on phase A reveal that a large number of Raman bands for the ν_1 and ν_3 are expected[12]. However, our observations clearly show only 3 major bands. This is probably because they are accidentally degenerate or other underlying mechanisms are at work. However, our results on phase A are in perfect agreement with all prior Raman measurements of the phase.

Raman observations revealed a previously unobserved phase transformation from phase *A* to phase α at 12.3 GPa where three new peaks appeared. Phase α transforms to phase *B* at 13 GPa when the mode at around 3075 cm^{-1} can no longer be observed. An additional Raman mode appears in pressure ranges near both 8 and 15 GPa. No phase transformations occur near either of these two ranges because the modes were present before both 8 and 15 GPa. These modes were simply much weaker before those pressures and could not be clearly distinguished from other modes. Above 13 GPa, the wave number of the peaks monotonously increases with pressure. No obvious slope change in frequency or in peak number is observed. The obtained phase transformations around 1.6 and 5.2 GPa (from fluid to solid phase *I* and solid phase *I* to solid phase *A*) are consistent with early measurements.[4] The newly appearing modes between ν_1 and ν_3 were used to identify the boundaries of phase *A* and other high-pressure phases. Phase *A* enters phase α around 12 GPa, while phase *B* begins around 13 GPa and remains in this phase up to 39 GPa, where phase B then enters a high-pressure phase (HP1). At 42 GPa, methane once again enters another high-pressure phase and transforms from phase HP1 to phase HP2.

Our evidence suggests that the spectrum at 12.3 GPa corresponds to a novel phase. The transformation from phase A to phase α is quite significant due to the fact that this phase transformation has never been observed prior to this work. Phase α has a narrow range of only 1 GPa from 12 GPa to 13 GPa (see Fig. 3). A Raman mode appears around 12.3 GPa, increases in intensity until 12.8 GPa, and then decreases in intensity significantly and can no longer be observed. Phase α is distinguishable from phase A and phase B since it has a mode between ν_1 and ν_3 that is not present in either phase A or phase B. The phase transformation to phase α was also observed with decreasing pressure near 9.5 GPa. This hysteresis behavior indicates that phase transformations from phase A to α and from phase α to B are first order. Phase α is a different phase than the *preB* phase described by Hirai *et al.*[5] because phase α has 6 modes while the *preB* phase has only 2 modes. Another difference is that while the *preB* phase will not transform into phase B through the application of pressure, phase α transforms into phase B around 13 GPa with increasing pressure. Although this confirms earlier claims of a phase transformation around 12 GPa,[14,18] our results indicate that the phase α at ∼12.5 GPa is a novel one.

The Raman spectra of phases α and B are very similar; any differences between the two structures are small. However, there is a major difference between the two phases that makes phase α quite different from phase B. Specifically, the new mode at around 3075 cm^{-1} in phase α is not observed in phase B. The rather drastic changes observed in the Raman spectrum from phase α to phase B as the pressure increased suggest that an ordering process was taking place, probably a decrease in the rotational amplitudes of the molecules. It is also possible that in phase B, molecules on certain sites continue to rotate freely, whereas others switch to librational motion.

Recent Raman measurements[5] suggest that a phase transformation from phase B to HP1 at around 25 GPa and a phase transformation from HP1 to HP2 at around 37 GPa exist. These claims were based on changes in the number of Raman modes. In Fig. 4, we present detailed Raman spectra of methane covering these pressure regions. Our results reveal a gradual evolution of wave number with pressure. Around 25 GPa, no clear changes in the number of modes occur and no change in the slope of the pressure to wave number plot is observed (Fig. 2). These observations do not support any previously declared phase transformations at 25 GPa. The results are consistent with recent x-ray diffraction measurements.[15]

Our results are also supported by methane hydrate studies,[17] in which no visible discontinuities in frequency to pressure or changes in the peak number occur between 15−37 GPa. Molecular methane in methane hydrate behaves identically to pure methane when exposed to pressures above 14 GPa. In our results, no phase transformations appear from 13 to 39 GPa. The similarities between the two experiments provide further support for the idea that no phase transformations occur around 25 GPa.

It is important to note that our data confirms the existence of a phase change at around 39 GPa. Beyond this, two new peaks appear on the high-frequency side of ν_1 and the low-frequency of ν_3. A change in peak number provides evidence for a phase transformation at about 39 GPa from phase B to phase HP1. Although this transformation pressure is very close to that of another recently reported transition at 37 GPa,[5] the profiles of the Raman modes are different.

In addition to the phase change at 39 GPa, we find that the spectrum at 42.2 GPa corresponds to a new phase of methane, phase HP2. The phase that we observed at 42.2 GPa is clearly distinguishable from that of phase HP1. As one can see, in Fig. 4, the two modes on the low-frequency side of ν_3 merge into one single peak. However, a new mode appears on its high frequency side. This signals a phase transformation from phase HP1 to phase HP2. Our data also shows that phase HP1 is only valid in a narrow pressure range of 3 GPa centered around 40.5 GPa.

The frequency versus pressure plots of all ν_1 and ν_3 components have a monotonous behavior and have no change in slope from 13 to 39 GPa. This suggests that a fully ordered, single site structure has been reached. It is clear that further research on CH_4 is needed before a full understanding of its various crystalline phases can be obtained. In particular, the completion of methane's phase diagram at various temperatures and pressures using neutron techniques and NMR studies of the molecular motions in all of its phases would be useful.

Guillot's model of the interior structure of Jovian planets[21] shows that Jovian planets have a helium and ice layer, a water-methane-ammonia ice mantle, and a rocky/metallic core. It is particularly interesting to note that the estimated amount of pressure at the boundary between the helium layer and the ice mantle shown in Guillot's model is about 10 GPa. This pressure is in close proximity to the pressure range of the novel phase (approximately 12 GPa). Neglecting the temperature effect, our results seemingly support the existence of a narrow layer between the ice mantle and the helium layer consisting mainly of solid phase α methane. In addition, if the ice mantle does indeed contain methane, the methane near the surface of the ice layer would most likely be in the form of solid phase B methane. Similarly, if the helium and ice layer contains methane, the methane near the ice mantle is most likely in the form of solid phase A methane.

IV. CONCLUSIONS

In summary, we performed Raman measurements on solid methane using moissanite anvil cells up to 43 GPa at room temperature. The measurements do not support the existence of any phase transformations around 25 GPa. Two novel phases can be found in narrow pressure ranges centered at about 12.5 GPa and 40.5 GPa. Further research is required to understand the implications of these phase transformations. Our obtained results have important implications in understanding the physical properties and in modeling the interior structure of Jovian planets.

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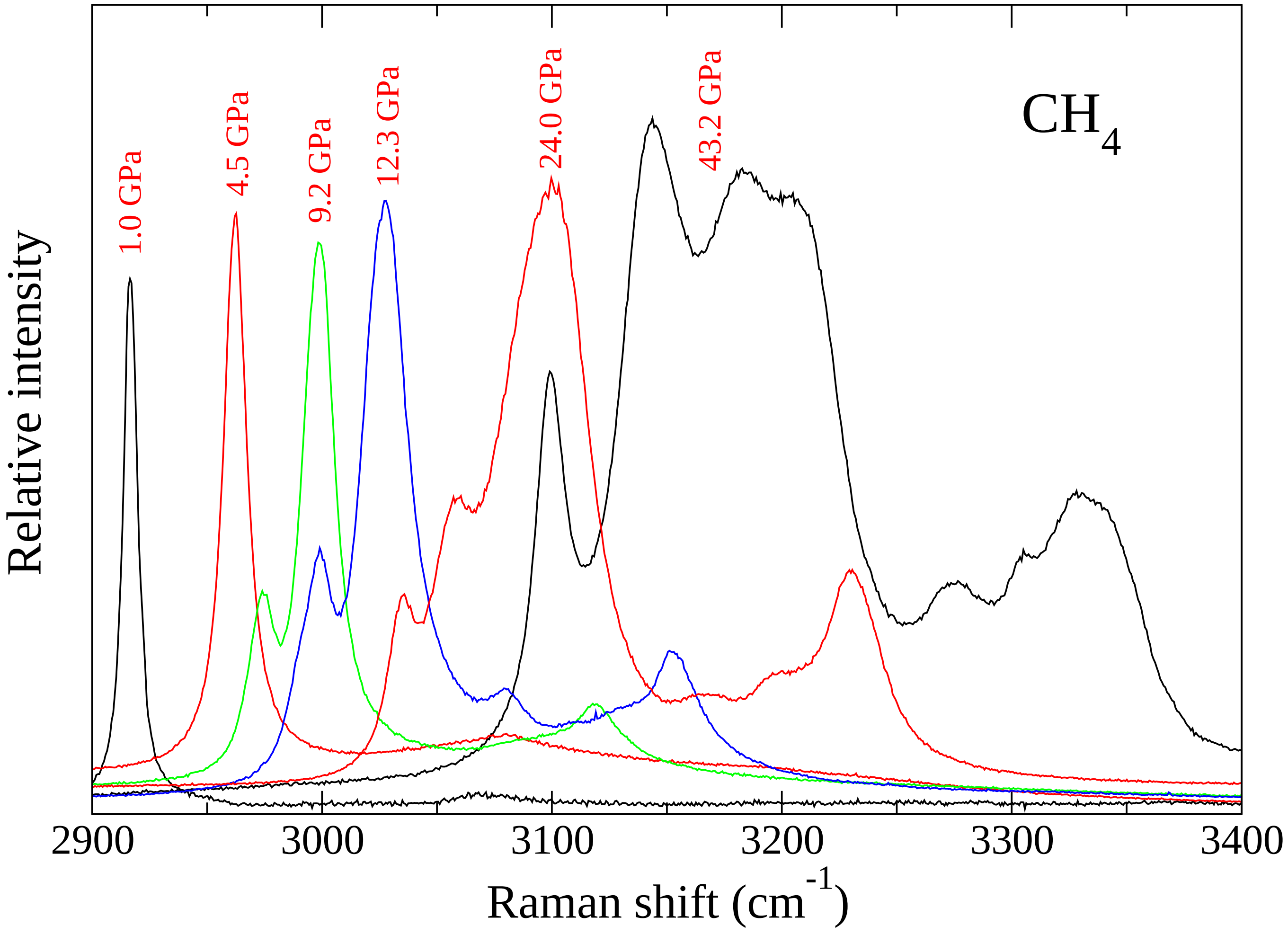

FIG. 1: (color online) Raman spectra of methane at key pressures from 1.0 to 43.2 GPa in different phases.

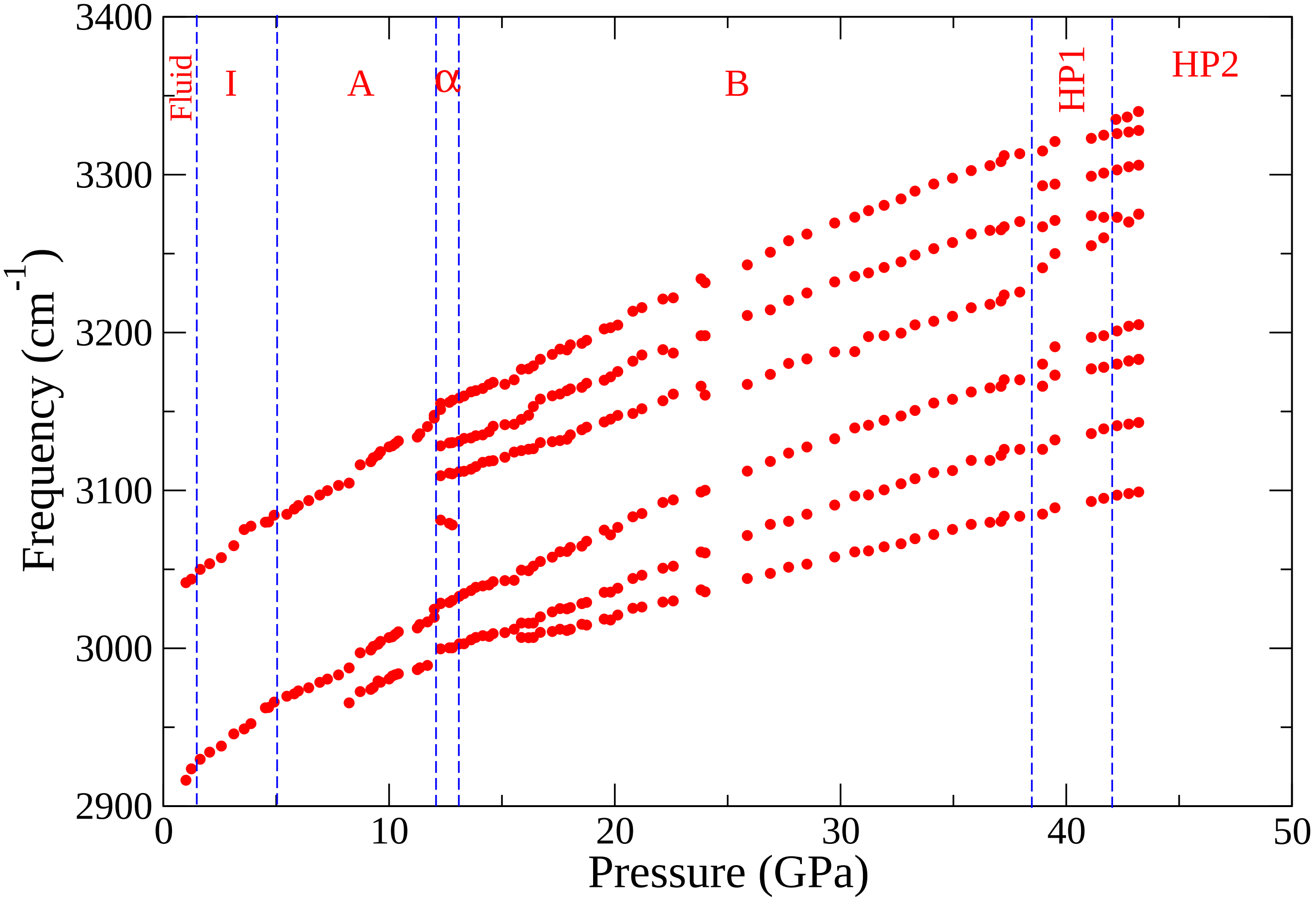

FIG. 2: (color online) Pressure dependence of Raman peaks (cm^{-1}) of methane at room temperature. The vertical dashed lines indicate the phase transformations.

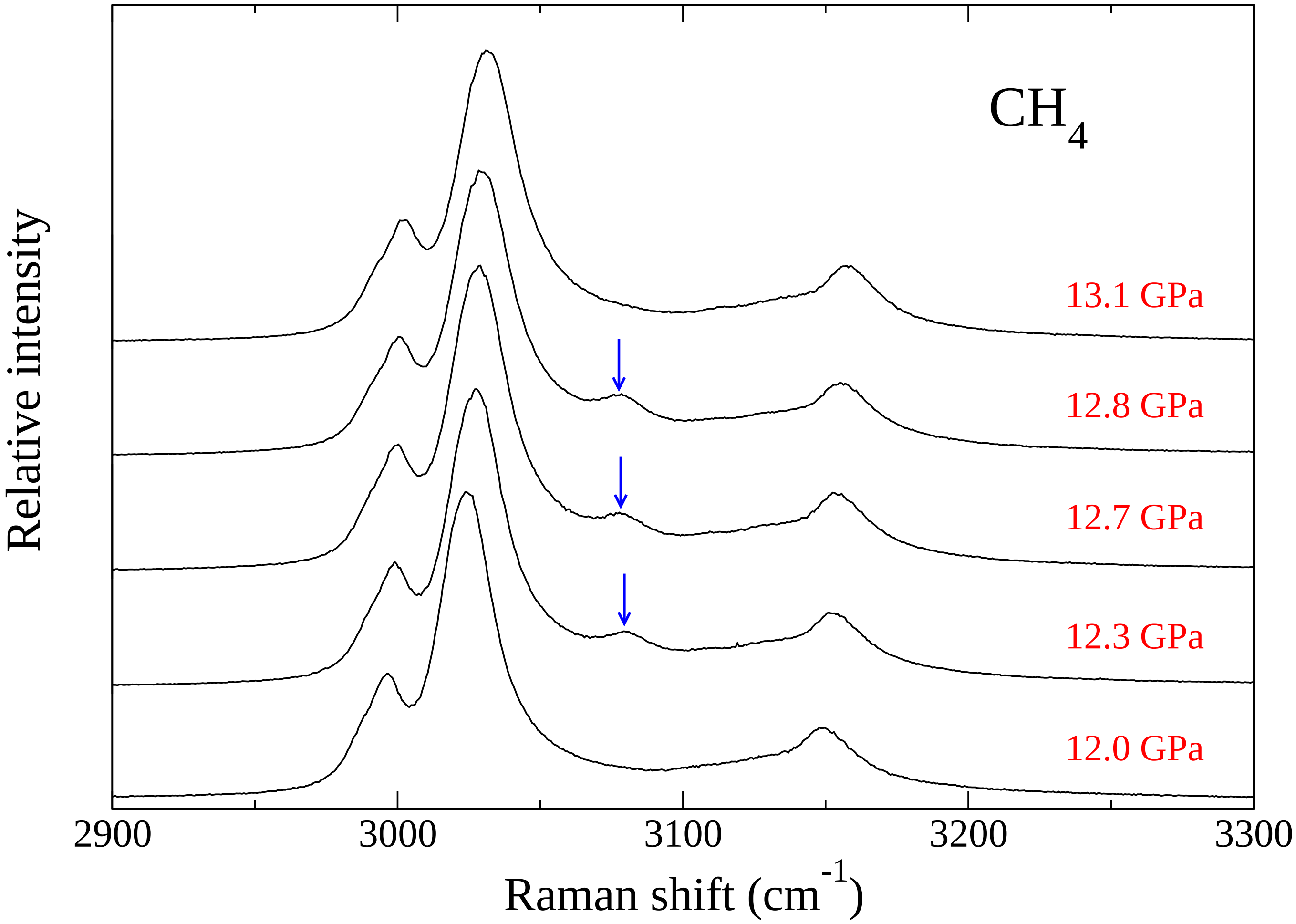

FIG. 3: (color online) Raman spectra of solid CH$_4$ in the pressure range of 12.0−13.1 GPa. The arrows indicate new vibrational mode.

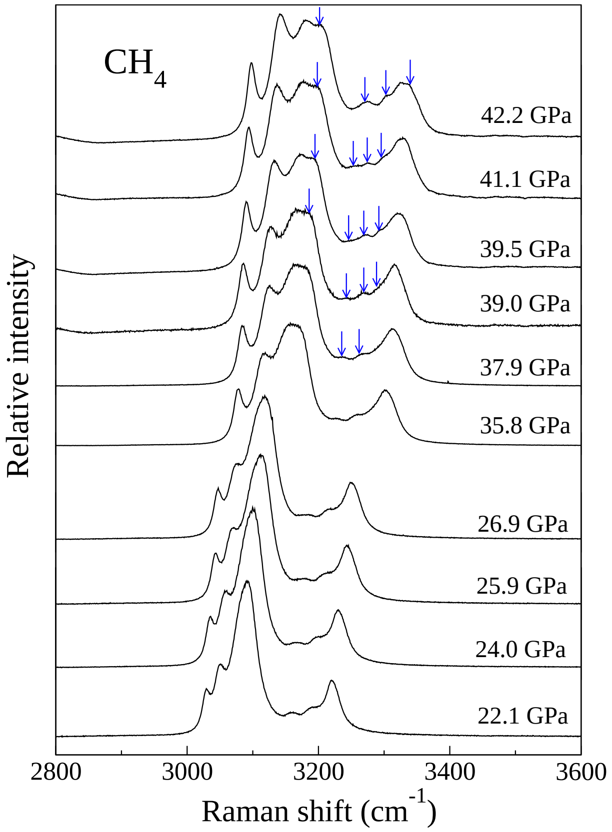

FIG. 4: (color online) Raman spectra of solid CH$_4$ in the pressure range of 22.1−42.2 GPa. The arrows indicate mode evolutions.