



Article **Theoretical Prediction of CH_n Crystal Structures under High Pressures**

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Abstract: CH_n is the precursor unit for graphene synthesis. We have theoretically predicated a series of CH_n structures with n = 1, 2, 4, 6, 8, 10, and 12 at elevated pressures (ambient pressure, 50, 100, 200, 300, 350, and 400 GPa) using evolutionary algorithms. The predicted CH and CH_2 structures are graphane-type and polyethylene over the whole considered pressure range, respectively. The molecular crystalline methane is predicted for the stoichiometry of CH_4 . The combination of methane and H_2 for CH_6 , CH_8 , CH_{10} , and CH_{12} up to 300 GPa are obtained. At 400 GPa, the mixture of polymer and H_2 for CH_6 , CH_{10} , and CH_{12} comes into play. From the computed enthalpy, higher pressure and more hydrogen concentration contributed to the decomposition (to carbon and H_2) of CH_n systems. The total density of states for these CH_n structures show that only the CH_{12} phase is metallic above 300 GPa. The rotational properties are traced in H_2 and the CH_n structures. The CH_4 rotation is more sensitive to the pressure. The H_2 units are nearly freely rotational. Other structures of CH_n , including fcc-type and experimentally known structures, are not competitive with the structures predicted by evolutionary algorithms under high pressure region. Our results suggest that the CH_n (n > 4) system is a potential candidate for hydrogen storage where H_2 could be released by controlling the pressure.

Keywords: CH_n crystal; evolutionary algorithms; high pressure

1. Introduction

A significant paper by N. W Ashcroft in 2004 [1] entitled "Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?" opened the door for the study of Group 14 hydrides. In the past few tens of years, a number of studies of Group 14 hydrides were performed; both experimental [2–4] and theoretical [5–8] studies have appeared. These studies were mainly focused on EH_x with $x \ge 4$ systems (E = Si, Ge, and Sn) which have a high atomic fraction of H (\ge 80%) and were predicted to metalize as hydrogen-dominant metallic alloys at lower pressures than pure hydrogen. These hydrogen-dominant alloys might become superconductors under high pressure with similar properties to those of pure metallic hydrogen. The strategy for the metallization of hydrogen-dominant metallic alloys is that due to the chemical precompression exerted by heavier atoms on hydrogen, the expected pressure needed for the required metallic transition as a preliminary step toward superconductivity might be within current experimental capabilities.

In Group 14, the member carbon is the basis of all known life on Earth, which is different to other members (Si, Ge, Sn, and Pb). We investigated their differences in the Group 14 elements at ambient pressure [9]. Carbon is the only element of Group 14 known to have metastable, kinetically persistent 0D (fullerenes), 1D (nanotubes), 2D (graphene, graphane), and 3D (diamond, graphite) allotropes. This kinetic persistence arises from



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). large barriers to oligo- and polymerization and bond reorganization. Moving down the Group 14 column reveals stark changes in chemical bonding that directly affect the types of structures each element favors. At high pressure, the stable phase of C is the diamond type (up to 500 GPa), which is insulating with a wide gap. Si, Ge, and Sn become metallic at 12, 11, and 1 GPa, respectively, owing to the phase transition from diamond type to β -Sn type (six-coordination) [10].

Based on the difference between carbon and other members, the carbon hydrides (CH_n) exhibit different chemical and physical properties to other Group 14 hydrides. For instance, from the thermodynamic point of view, the heat of formation is negative (exothermic) only for CH₄. Methane has been detected to exist in several locations of the solar system. According to the first-principle calculation by Martinez-Canales and Bergara [11], there is no evidence for the metallization of CH₄ up to 520 GPa which is quite high, well above the current experiment capabilities.

The high-pressure behavior of carbon hydrides, CH_n ($n \ge 4$), is just beginning to be studied. In 1996 [12], methane (CH_4) was discovered to form four stoichiometric compounds ($CH_4(H_2)_2$, ($CH_4)_2H_2$, $CH_4(H_2)_4$, and CH_4H_2), with hydrogen at pressures up to 30 GPa. These van der Waals compounds exhibit many interesting properties with relevance to many fields such as planetary science, hydrogen storage, energy, environment field, and so on. Experiments have demonstrated that the methane is unstable under high temperature and high pressures. At T = 2000 K and P = 20 GPa, the methane could dissociate to form diamond and hydrogen [7,13].

Following the trend of analyzing Group 14 hydrides, we studied a series of CH_n structures with n = 1, 2, 4, 6, 8, 10, and 12 at elevated pressures (up to 400 GPa) by evolutionary algorithm procedures. We examined whether pressure could lead to the formation of new compounds in this series or not. The structural and electronic properties were paid attention to in the current work to check the metallization of CH_n systems.

2. Materials and Methods

The calculations are based on the plane wave/pseudopotential approach using the computer program VASP (Vienna Ab-initio Simulation Package) [14,15], employing the PBE type and the projected-augmented wave (PAW) [16,17] method. The energy cutoff for plane-wave basis was set to 600 eV. The convergence criterion for electronic energy and force is 1.0×10^{-6} eV/atom and 0.01 eV/Å, respectively. The density of K-mesh was set to 0.04. In geometry optimization, we allow all structural parameters (atomic position, lattice constants, and symmetry) to relax. The evolutionary algorithm USPEX [18–20] was employed to find the lowest energy structures; the searching calculations were carried out at 1 atm, 50, 100, 200, 300, 350, and 400 GPa, which is consistent with our DFT calculations.

3. Results

3.1. The Tie Line of CH_n Systems

We performed evolutionary prediction methodology for searching ground state CH_n structures with x = 1, 2, 4, 6, 8, 10, and 12 at a series of pressures (ambient pressure, 50 GPa, 100 GPa, 200 GPa, 300 GPa, 350 GPa, and 400 GPa). The searched lowest energy CH_n structures at series pressure are shown in SI (Figures S1–S8). The predicted CH and CH_2 (Table S1) structures are graphane-type and polyethylene over the whole considered pressure range, respectively. The predicted structure of CH_3 depends very much on the pressure: at or below 50 GPa, it forms ethane molecules; at 100 GPa, it forms butane, which can be thought of as oligomerized ethane; at 200 GPa polymerization happens, forming polyethylene (200 GPa), polyethylene and methane (300 GPa), or graphene (350 GPa). The predicated CH_4 structures (Table S2) are the molecular crystalline methane. The combination of methane and H_2 for CH_6 (Table S3), CH_8 (Table S4), CH_{10} (Table S5), and CH_{12} (Table S6) up to 300 GPa are obtained. Interestingly, at 400 GPa, the mixture of polymer and H_2 for CH_6 , CH_{10} , and CH_{12} come into play.

Figure 1 (a tie line curve) shows the static-lattice enthalpies (eV/per C atom) for the most competitive CH_n structures at selected pressure. Note that the tie line energy curve has been used in our previous studies [21,22], which may be used to connect two phases, and if the enthalpy of a third falls below it, the first two will react to give the third. The enthalpy of formation of CH_n is defined as Δ H (CH_n) = H(CH_n) – H(C) – 1/2x·H(H₂). The carbon in graphite (0–10 GPa), diamond (10–400 GPa), and solid H₂ structures in the P63/m (0–100 GPa), C2/c (100–300 GPa), Cmca-12 (300–350 GPa), and Cmca (400 GPa) are taken as references.



Figure 1. Relative ground state enthalpies (with respect to carbon and H_2) of the most stable CH_n (n = 1, 2, 4, 6, 8, 10, and 12) solids. The abscissa x is the fraction of H in the structures: the mole fraction of H on top; the stoichiometry of CH_n on bottom.

It is important to recognize that in the light-element systems, ion dynamics can significantly change the total energies [23]. On the other hand, DFT static-lattice energies, in general, reproduce experimental phase stabilities well, even for light-element high-pressure phases [24], in part owing to the cancellation of the dynamical effects in the energy differences. In the discussions that follow, we use the static-lattice enthalpies. Note that kinetic effects and metastability are not considered at this level.

From the enthalpy curve in Figure 1, one can see that (I) all of the CH and CH₂ phases are stable relative to carbon and H₂ over the whole given pressure range; (II) the stabilization for CH₄, CH₆, and CH₈ are up to 300 GPa, while there is on stabilization for CH₁₀ and CH₁₂ above 300 GPa; (III) in the pressure region of 1 atm to 100 GPa, the "flat energy lines" for the CH_n ($n \ge 4$) are owing to the van der Waals forces in the combination of methane and H₂; (IV) higher pressure and more hydrogen concentration contribute to the decomposition of CH_n system; (V) when pressure lowers under 200 GPa, the CH₄, CH₆, and CH₈ are more stable than other compounds, but under high pressure (p > 200 GPa), the CH₄ becomes a metastable phase, which is consistent with previous studies [13]. We would like to propose that the CH_n (n > 4) system is a potential candidate for hydrogen storages since such a system can release H₂ under high pressure.

3.2. Compression of CH_n

Figure 2b shows the calculated Wigner–Seitz radius (r_s) as a function of pressure (r_s -P curve) for the lowest energy structure of carbon, H_2 , and CH_n systems. The Wigner–Seitz radius (r_s) is defined by $4\pi r_s 3/3 = 1/\rho$, where ρ is the average valence-electron density. In the work, we set up $\rho = N/V$, where N is the number of valence electrons in the unit

cell; V is the volume of the unit cell. Let r_s be the standard measure of the average valence electron density for a system. The volume reductions for all these structures are rapid from 0 GPa to 50 GPa due to squeezing out van der Waals space in H_2 and CH_n structures, and the phase transition in carbon (graphite to diamond). The computed r_s for CH_n structures are located between the value of H_2 and carbon. The corresponding slopes reflect the compressible properties.



Figure 2. (a) Wigner–Seitz radius (r_s) of carbon, H_2 , and CH_n structures (n = 1, 2, 4, 6, 8, 10, and 12) as a function of pressure. (b) Computed relative compression as a function of pressure. The relative compression is defined by $\left(\frac{r_s(0)}{r_s(p)}\right)^3$, where $r_s(0)$ and $r_s(p)$ is the Wigner–Seitz radius at ambient pressure and certain high pressure, respectively.

Figure 3a shows the closest distance between C and C and the closest inter-distance of H and H (Figure 3b) in CH_n structures. We can see that there are C–C chemical bonds in carbon, CH, and CH_2 phase, while the carbon atoms in CH_n ($n \ge 4$) are separated by forming methane molecules. After 350 GPa, the complexes of polymer and H_2 are formed in CH_6 , CH_{10} , and CH_{12} phase, as shown in the jump of C–C distances. With increasing pressure (0 to 50 GPa), the distance of the closest inter H–H in CH_n structures is decreased rapidly due to squeezing the van der Waals space, as shown in Figure 3b.



Figure 3. (a) the closest distance of C and C in CH_n structures and carbon as a function of pressure. (b) the closest inter distance of H and H in CH_n structures and H_2 as a function of pressure.

3.3. Electronic Properties of CH_n Phase

The Goldhammer–Herzfeld criterion states that a material becomes metallic when the quantity $(1 - f\alpha V_m)^{-1}$ diverges, where α is the molecular polarizability. Vm is the volume per molecule in the solid, and f is a dimensionless factor determined only by the packing of the molecules in the crystal. The divergence occurs when $f\alpha/Vm = 1$. For cubic systems, f is $4\pi/3$, and this gives $V_m = 4\pi\alpha/3$. Using the definition of r_s , $4\pi r_s^3/3 \equiv V_m/N_{ve}$ (where Nve is number of electrons), we then have the following equation for cubic systems, $r_s = (\alpha/N_{ve})^{1/3}$, where the polarizability of a material, α for C, CH₄, and H₂ is 7.437, 17.53, and 5.42 bohr, respectively. One readily obtains $r_s = 1.23$, 1.30, and 1.40 bohr for the metallization of CH₄ and H₂, respectively.

Figure 4 shows the computed total density of states for carbon (diamond), H_2 (C2/c), and CH_n structures at 300 GPa. One can see that only the CH₁₂ phase is almost metallic above 300 GPa. The band gap for the CH_n phase is decreased with the increasing concentration of H. Note that the free-electron-like shapes are also shown in Figure 4.



Figure 4. Computed total density of states of diamond, H_2 , and CH_n (n = 1, 2, 4, 6, 8, 10, and 12) phases at 300 GPa. The free electron models are shown.

3.4. The Rotational Solid for CH_n

The term—the rotational solid—is mainly used to describe the properties of a molecular crystal, such as solid H_2 [25], solid CH_4 [26], and C60 crystal structure [27]. For molecular crystals, the rotational dynamic might be an important factor for the complicated phase transition at low temperature and pressure.

The rotational barriers in H₂ and CH_n ($n \ge 4$) structures are examined via scanning potential energy surface (shown in Figures S9–S15). Table 1 and Table S7 show the rotational barriers of H₂ unit and CH₄ unit in corresponding structure at 100 GPa and 300 GPa. As expected, the rotational barriers for H₂ and CH₄ units are elevated with increasing pressure. At ambient pressure, these rotations are free (no energy barriers were found), owing to the dispersion forces. The energy barrier of CH₄ rotation is higher than that of H_2 rotation under same pressure, indicating that the CH₄ rotation is more sensitive to the pressure. From the small rotational barriers for H_2 units, even at 300 GPa, one can know that the these H_2 units are nearly in free rotation. The rotational solid is a good term to describe the CH_n phases.

	H ₂ Rotation (eV per H ₂)		CH ₄ Rotation (eV per CH ₄)	
	100 GPa	300 GPa	100 GPa	300 GPa
H ₂	0.014	0.04	-	-
CH_4	-	_	0.70	1.70
CH_4-H_2 by USPEX	0.10	0.27	0.75	2.00
CH_4-2H_2 by USPEX	0.04	0.14	0.45	1.60
CH_4-3H_2 by USPEX	0.027	0.13	1.10	1.80
CH_4-4H_2 by USPEX	0.012	0.09	0.60	2.10

Table 1. The computed barriers of rotation in H_2 and CH_n ($n \ge 4$) structures.

3.5. Other Possible Structures for CH_n Systems

In 2009, Strobel et. al. [4] reported novel molecular compound formation from silane– hydrogen mixtures (SiH₄–2H₂) and proposed that the molecular compound adopts an fcc lattice. The study on SiH₄–2H₂ offers possible structural information for the methane– hydrogen mixtures, even though the C is different to Si, as mentioned.

The fcc primitive cell with CH₄ unit (one CH₄ in the cell) is shown in Figure 5. There are two tetrahedral holes (at site 2 and 3) and one octahedral hole (at site 1) along the diagonal—red dot line in the primitive cell. When only the one site is H₂-occupied, the stoichiometry of the phase is CH₄H₂. The CH₄–2H₂ can be obtained via occupying one more. The sites will be all occupied in CH₄–3H₂. In the work, we pick up the CH₄–H₂ containing one occupied octahedral hole, CH₄–2H₂, with occupied octahedral hole and tetrahedral hole. Note that there are similar energies for other possible (H₂-occupied) fcc isomers. Though these structures begin with fcc type, they will not adopt perfect fcc-type at high pressure any more (see Figure S16). This might be attributed to the properties of rational solid.



Figure 5. Schematic fcc primitive cell with CH_4 unit. 1, 2, and 3 denotes the location of atoms in fcc structures.

The calculated enthalpy (with respect to carbon and H_2) of these fcc-type CH_n structures as a function of pressure is shown in Figure 6. For comparison, the corresponding CH_n structures by USPEX are also inserted as dot lines. Due to van der Waals interaction, it is not surprising that the relative enthalpies of these structures are close together in

the low-pressure zone, while they are separated with elevating pressure. As one can see, the structures searched for by evolutionary algorithm are more stable than their corresponding fcc type structures, indicating that the fcc-type CH_n structures are not competitive (Table S8). These fcc-type CH_n structures at 300 GPa are still semiconductors or insulators.



Figure 6. Computed enthalpy (with respect to carbon and H₂) as a function of pressure.

Experimentally, the observed CH_4-H_2 in the range of 7.9–30 GPa is consistent with the wurtzite structure. The CH_4-2H_2 (which is stable between 5.8 and 7 GPa) is that of a MgZn₂ (Laves phase; H_2 occupy the Zn sites and the CH_4 is in the Mg sites) structure.

Based on the observation in experiment, the CH_4-H_2 wurtzite phase and CH_4-2H_2 MgZn₂ phase are also examined, as shown in Figure 7. The enthalpy curve shows that the CH_4-H_2 wurtzite phase is more stable than the corresponding fcc type below 180 GPa, while the CH_4-2H_2 MgZn₂ phase is more favorable than fcc-type CH_4-2H_2 phase over the whole range of pressure. Note the blue line (CH_4-H_2 wurtzite) undergoes a big jump, indicating that there might be a phase transition (see Figures S17 and S18).



Figure 7. Computed enthalpy of wurtzite-type structures (with respect to carbon and H₂) as a function of pressure.

In a word, the considered fcc-type CH_n structures and the experimental known structures are not competitive with the corresponding CH_n structures obtained by evolutionary algorithms above 50 GPa. However, the relative enthalpies of these considered CH_n structures are close together in the low-pressure zone. These phenomena are possibly owing to the rotational solid or liquid-like.

4. Conclusions

We have systematically investigated the CH_n crystalline structures with n = 1, 2, 4, 6, 8, 10, and 12 under various pressures (ambient pressure, 50, 100, 200, 300, 350, and 400 GPa) by evolutionary algorithms procedures (USPEX). CH and CH₂ are the graphane-type and polyethylene, respectively, over the whole considered pressure range. The predicted stoichiometry of CH₄ is molecular crystalline methane. The combination of methane and H₂ for CH₆, CH₈, CH₁₀, and CH₁₂ up to 300 GPa are obtained. The mixture of polymer and H_2 for CH_6 , CH_{10} , and CH_{12} come into play at 400 GPa. From the computed static-lattice enthalpy, the CH_n (n \geq 4) phase decomposes to carbon and H_2 under high pressure (above 300 GPa). In addition, the concentration of hydrogen also contributes to the decomposition (of carbon and H_2). Based on the calculations, we propose that the CH_n (n > 4) system is a potential candidate for hydrogen storages since such a system can release H_2 under high pressure. The calculated total density of states for the CH_n structures shows that only the CH_{12} phase is almost metallic above 300 GPa. The rotational properties are traced in H_2 and the CH_n structures. The energy barrier of CH_4 rotation is higher than that of H_2 rotation under the same pressure, indicating that the CH₄ rotation is more sensitive to the pressure. From the small rotational barriers for H₂ units, even at 300 GPa, one can know that the H_2 units are nearly freely rotational. Other structures of CH_n , including fcc-type and experimentally known structures, are not competitive with the structures predicted by evolutionary algorithms under high pressure.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/cryst11121499/s1, Figure S1: CH₂ structures under various pressure by USPEX, Table S1: Calculated volume (Å), density (g/cm^3) , r_s of CH₂ structures by USPEX. The Z and electron number in corresponding unit cell are shown here, Figure S2: CH₄ structures under various pressure by USPEX, Table S2: Calculated volume (Å), density (g/cm^3) , r_s of CH₄ structures by USPEX. The Z and electron number in corresponding unit cell are shown here, Figure S3: CH_4-H_2 structures under various pressure by USPEX, Table S3: Calculated volume (Å), density (g/cm^3) , r_s of CH_4-H_2 structures by USPEX. The Z and electron number in corresponding unit cell are shown here, Figure S4: CH_4 -2 H_2 structures under various pressure by USPEX, Table S4: Calculated volume (Å), density (g/cm^3) , r_s of CH_4 -2 H_2 structures by USPEX. The Z and electron number in corresponding unit cell are shown here, Figure S5: CH₄–3H₂ structures under various pressure by USPEX, Table S5: Calculated volume (Å), density (g/cm³), r_s of CH₄-H₂ structures by USPEX. The Z and electron number in corresponding unit cell are shown here, Figure S6: CH₄-4H₂ structures under various pressure by USPEX, Table S6: Calculated volume (Å), density (g/cm^3) , r_s of CH₄–4H₂ structures by USPEX. The Z and electron number in corresponding unit cell are shown here, Figure S7: CH_x structures at 1 atm by USPEX, Figure S8: CH₂ structures by USPEX, Figure S9: Scanned potential energy surfaces of rotation in two solid H₂ structures (at 100 GPa and 300 GPa, respectively), Figure S10: Scanned potential energy surfaces of rotation in two solid CH₄ structures (at 100GPa and 300GPa, respectively), Figure S11: Scanned potential energy surfaces of rotation in two solid CH₄–H₂ fcc (at 100GPa and 300GPa, respectively) structures, Figure S12: Scanned potential energy surfaces of rotation in two solid CH₄-H₂ structures (at 100 GPa and 300 GPa, respectively) by USPEX, Figure S13: Scanned potential energy surfaces of rotation in two solid CH₄-2H₂ structures (at 100 GPa and 300 GPa, respectively) by USPEX, Figure S14: Scanned potential energy surfaces of rotation in two solid CH₄-3H₂ structures (at 100 GPa and 300 GPa, respectively) by USPEX, Figure S15: Scanned potential energy surfaces of rotation in two solid CH₄–4H₂ structures (at 100 GPa and 300 GPa, respectively) by USPEX, Table S7: The biggest barriers of rotation in H₂ and CH_x structures, Figure S16: Simulated XRD pattern of a perfect fcc CH₄ structure and optimized "fcc" CH₄ structure at 300 GPa. The Synchrotron with a wave length by 1.000 Å is used, Figure S17: Simulated XRD pattern of CH₄–H₂ wurtzite structure at 300 GPa and 350 GPa. Here, the radiation source is from Synchrotron with a wave length by

1.000 Å, Figure S18: Simulated XRD pattern of CH_4 – H_2 wurtzite structure (the starting structure and optimized at 5 GPa) and CH_4 – H_2 by USPEX at 5 GPa, Table S8: Computed the relative enthalpy of three CH_4 – H_2 structures at 5 GPa.

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