Theoretical Prediction of CHn Crystal Structures under High Pressures

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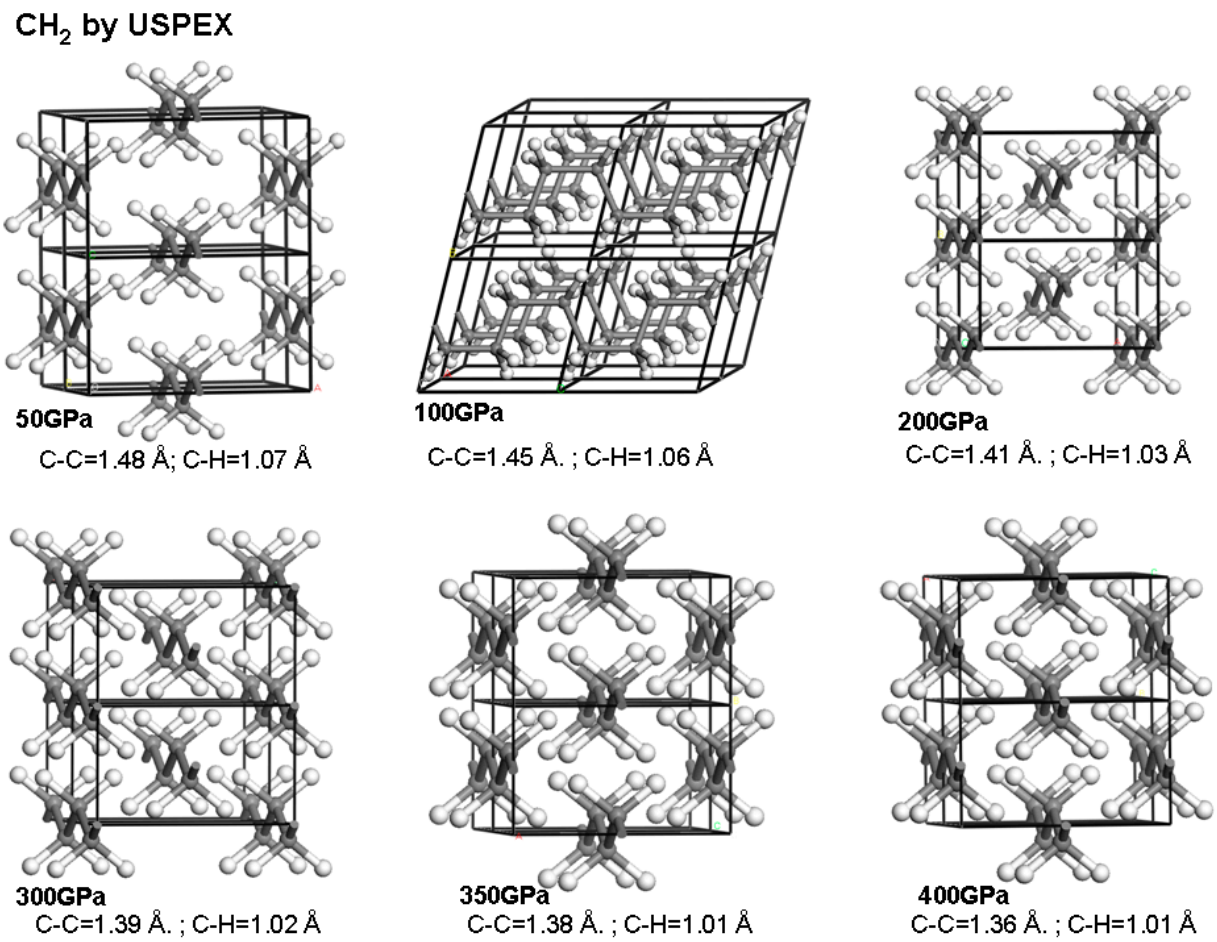


Figure S1. CH_2 structures under various pressure by USPEX.

Table S1. Calculated volume (Å), density (g/cm^3), r_s of CH_2 structures by USPEX. The Z and electron number in corresponding unit cell are show here.

CH_2	Z	$N_{elect.}$	V /A^3	ϱ g/cm^3	r_s
0 GPa	C_4H_8	16	118.40	0.79	2.29
50 GPa	C_4H_8	16	46.76	1.99	1.68
100 GPa	C_4H_8	16	39.01	2.39	1.58
200 GPa	C_4H_8	16	31.83	2.93	1.48
300 GPa	C_4H_8	16	27.95	3.33	1.41
350 GPa	C_4H_8	16	26.53	3.51	1.39
400GPa	C_4H_8	16	25.34	3.68	1.37

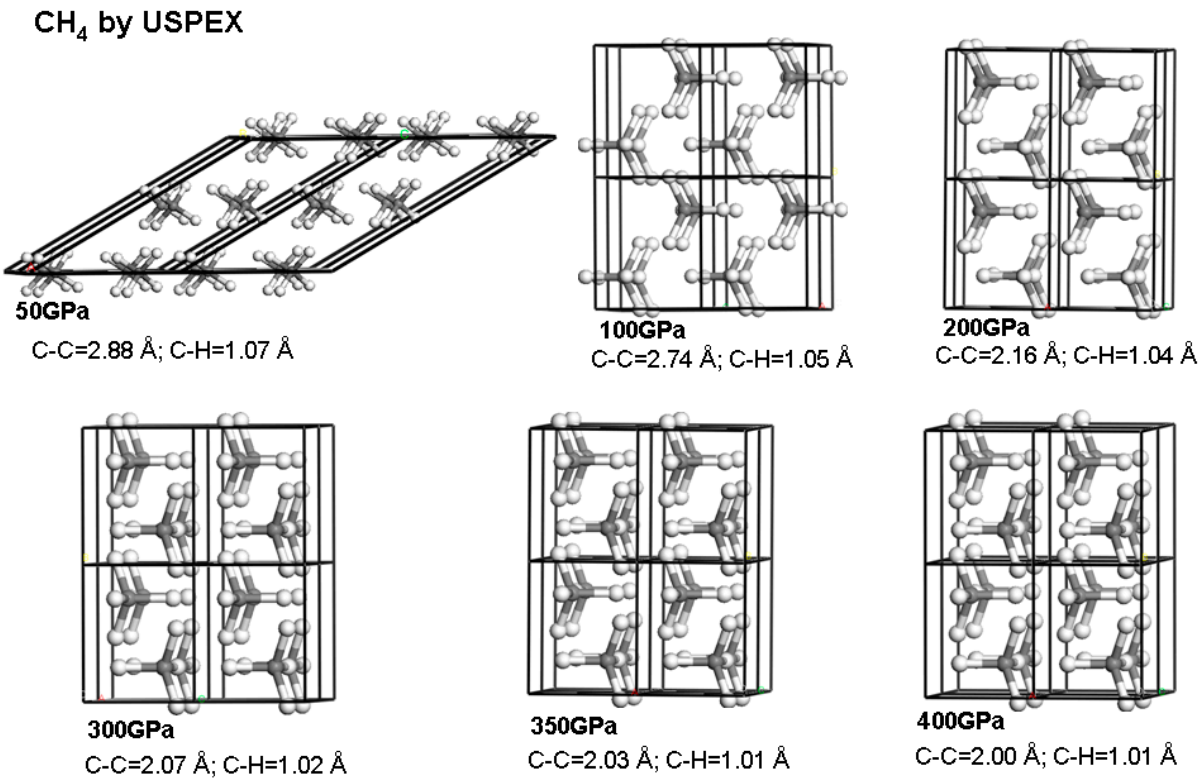


Figure S2. CH_4 structures under various pressure by USPEX

Table S2. Calculated volume (Å), density (g/cm^3), r_s of CH_4 structures by USPEX. The Z and electron number in corresponding unit cell are show here.

CH_4	Z	$N_{elect.}$	V /A^3	ϱ g/cm^3	r_s
0 GPa	C_2H_8	16	127.07	0.42	2.34
50 GPa	C_4H_{16}	32	73.71	1.45	1.55
100 GPa	C_2H_8	16	29.51	1.80	1.44
200 GPa	C_2H_8	16	23.40	2.28	1.33
300 GPa	C_2H_8	16	20.28	2.62	1.27
350 GPa	C_2H_8	16	19.15	2.78	1.25
400 GPa	C_2H_8	16	18.22	2.92	1.23

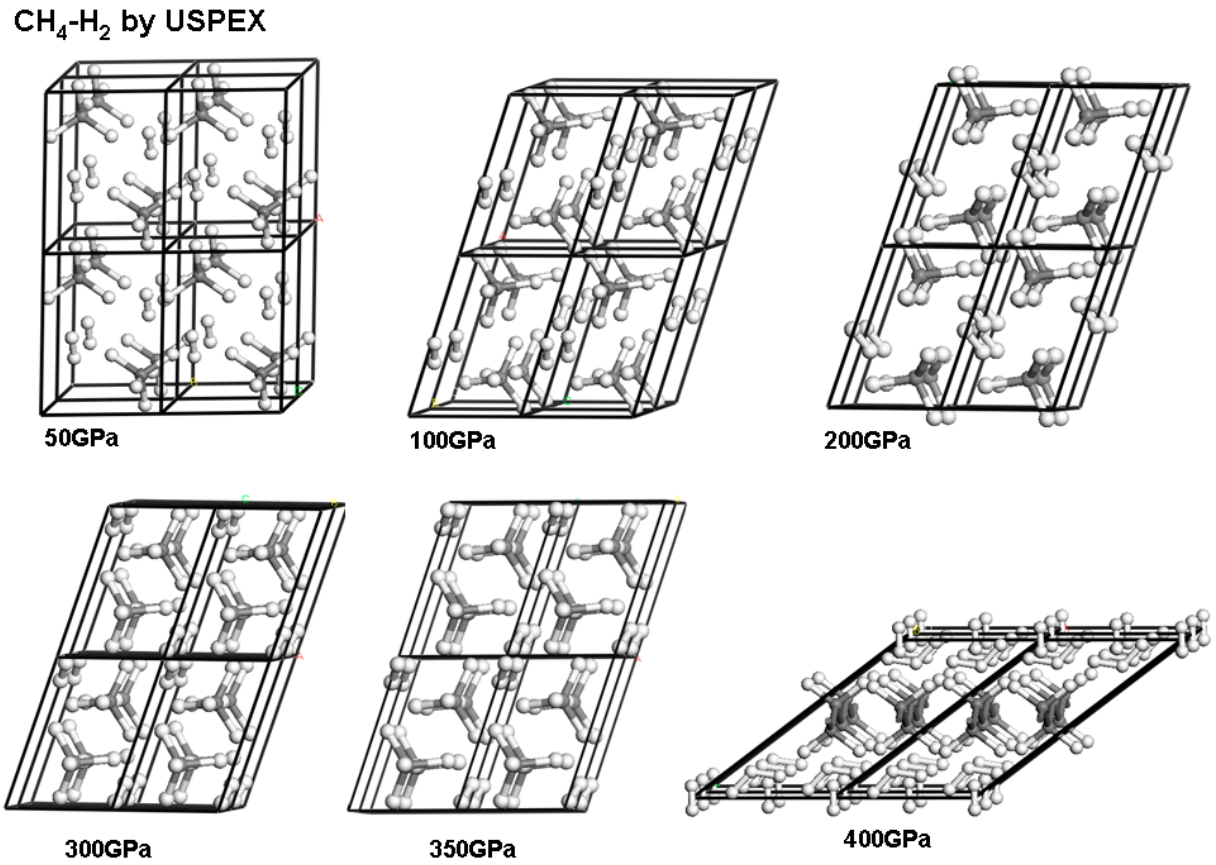


Figure S3. CH_4-H_2 structures under various pressure by USPEX

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 show here.

CH_4-H_2	Z	$N_{elect.}$	V /A^3	ϱ g/cm^3	r_s
0 GPa	C_2H_{12}	20	208.19	0.29	2.56
50 GPa	C_2H_{12}	20	48.31	1.24	1.57
100 GPa	C_2H_{12}	20	38.65	1.55	1.46
200 GPa	C_2H_{12}	20	30.45	1.97	1.35
300 GPa	C_2H_{12}	20	26.09	2.30	1.28
350 GPa	C_2H_{12}	20	24.58	2.44	1.26
400 GPa	C_4H_{24}	40	45.88	2.61	1.23

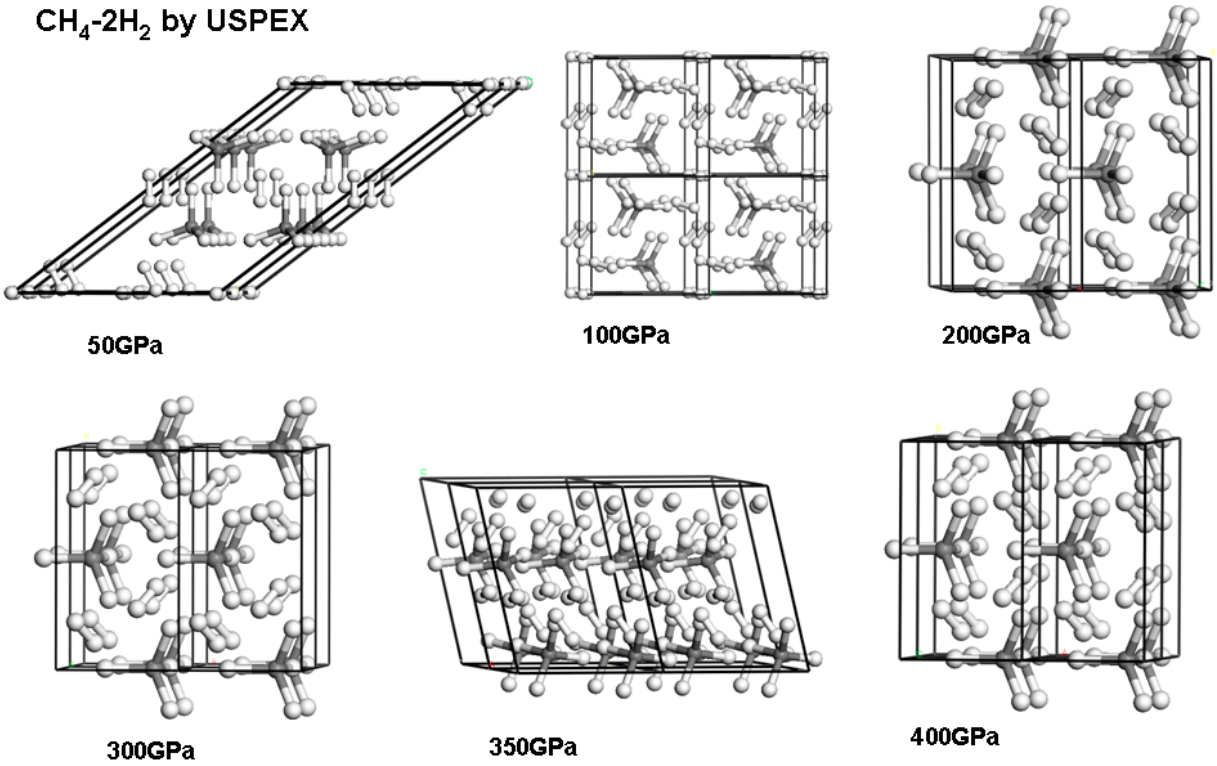


Figure S4. CH_4-$2H_2$ structures under various pressure by USPEX

Table S4. Calculated volume (Å), density (g/cm^3), r_s of CH_4-$2H_2$ structures by USPEX. The Z and electron number in corresponding unit cell are show here.

CH_4-$2H_2$	Z	$N_{elect.}$	V /A^3	ϱ g/cm^3	r_s
0 GPa	CH_8	12	132.66	0.25	2.61
50 GPa	C_4H_{32}	48	120.91	1.10	1.60
100 GPa	C_2H_{16}	24	48.11	1.39	1.48
200 GPa	C_2H_{16}	24	37.21	1.79	1.36
300 GPa	C_2H_{16}	24	31.87	2.09	1.29
350 GPa	C_4H_{32}	48	59.92	2.23	1.26
400 GPa	C_2H_{16}	24	28.43	2.35	1.24

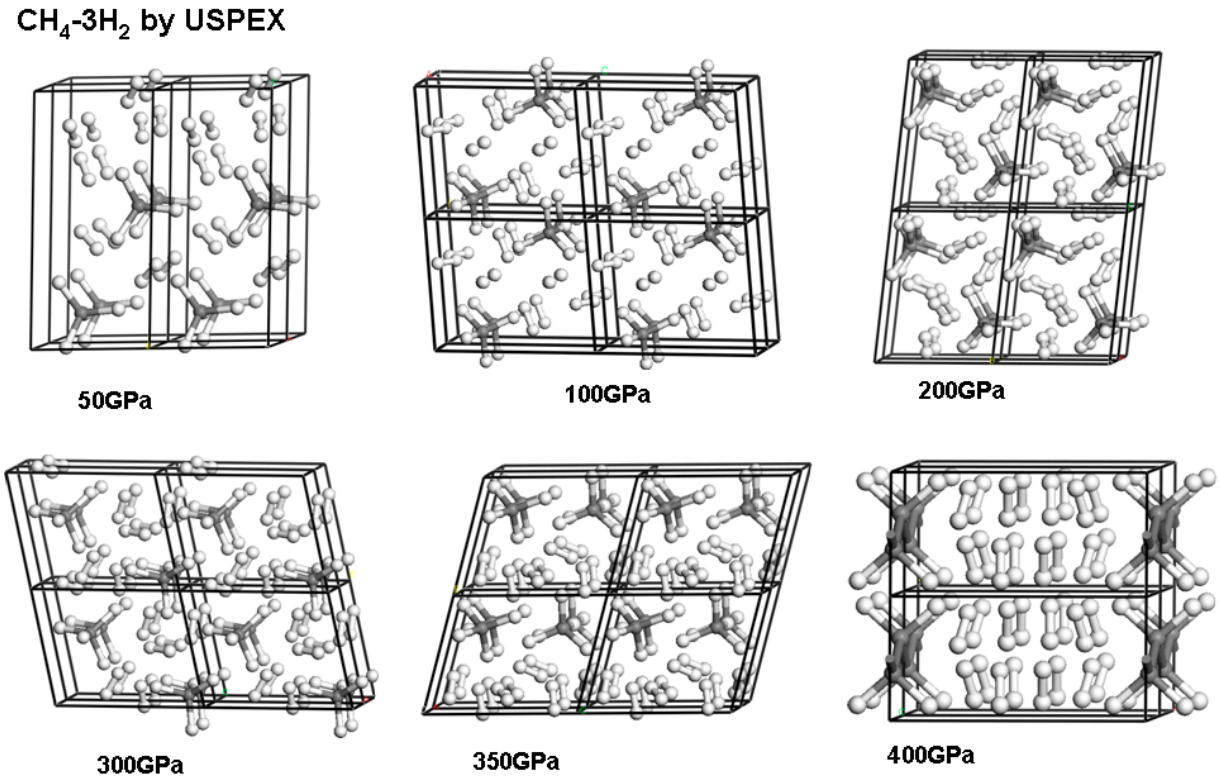


Figure S5. CH_4-$3H_2$ structures under various pressure by USPEX

Table S5. Calculated volume (Å), density (g/cm^3), r_s of CH_4-$3H_2$ structures by USPEX. The Z and electron number in corresponding unit cell are show here.

CH_4-$3H_2$	Z	$N_{elect.}$	V /A^3	ϱ g/cm^3	r_s
0 GPa	CH_{10}	14	165.89	0.22	2.67
50 GPa	C_2H_{20}	28	72.30	1.02	1.61
100 GPa	C_2H_{20}	28	57.29	1.28	1.49
200 GPa	C_2H_{20}	28	44.43	1.65	1.37
300 GPa	C_2H_{20}	28	37.84	1.94	1.30
350 GPa	C_2H_{20}	28	35.58	2.06	1.27
400 GPa	C_2H_{20}	28	33.22	2.21	1.24

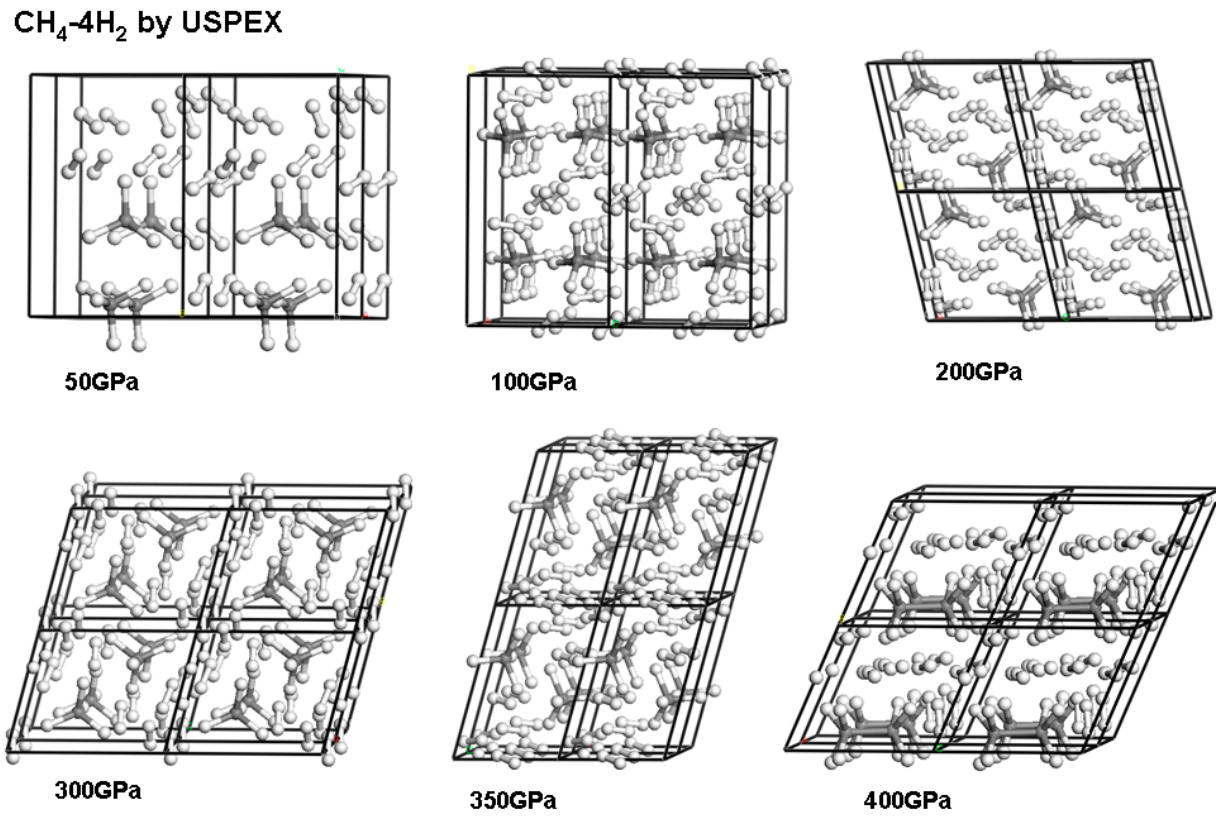
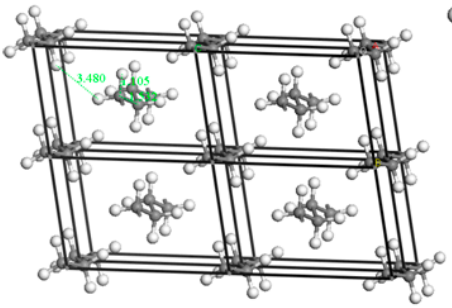


Figure S6. CH_4-$4H_2$ structures under various pressure by USPEX

Table S6. Calculated volume (Å), density (g/cm^3), r_s of CH_4-$4H_2$ structures by USPEX. The Z and electron number in corresponding unit cell are show here.

CH_4-$4H_2$	Z	$N_{elect.}$	V /A^3	ϱ g/cm^3	r_s
0 GPa	CH_{12}	16	196.56	0.20	2.71
50 GPa	C_2H_{24}	32	84.80	0.94	1.62
100 GPa	C_4H_{48}	64	132.59	1.21	1.50
200 GPa	C_2H_{24}	32	51.35	1.56	1.37
300 GPa	C_2H_{24}	32	43.58	1.84	1.30
350 GPa	C_2H_{24}	32	40.98	1.95	1.27
400 GPa	C_2H_{24}	32	38.17	2.09	1.24

CH_x structures at 1 atom



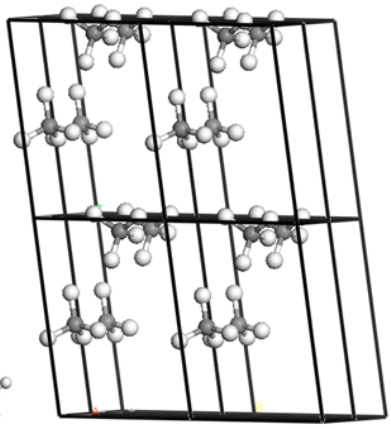
CH_2 by USPEX at 1 atm

ΔH_f=–0.52 eV per C

C-H = 1.11 Å

C-C = 1.53 Å

Inter-(H----H) = 2.84 Å



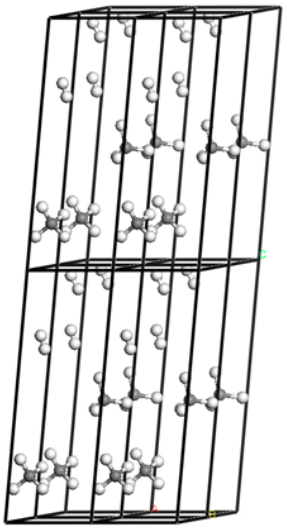
CH_4 by USPEX at 1 atm

ΔH_f=–1.27 eV per C

C-H = 1.10 Å

C-C = 4.20 Å

Inter-(H-----H)= 2.68 Å



CH_4-H_2 by USPEX at 1 atm

ΔH_f=–1.27 eV per C

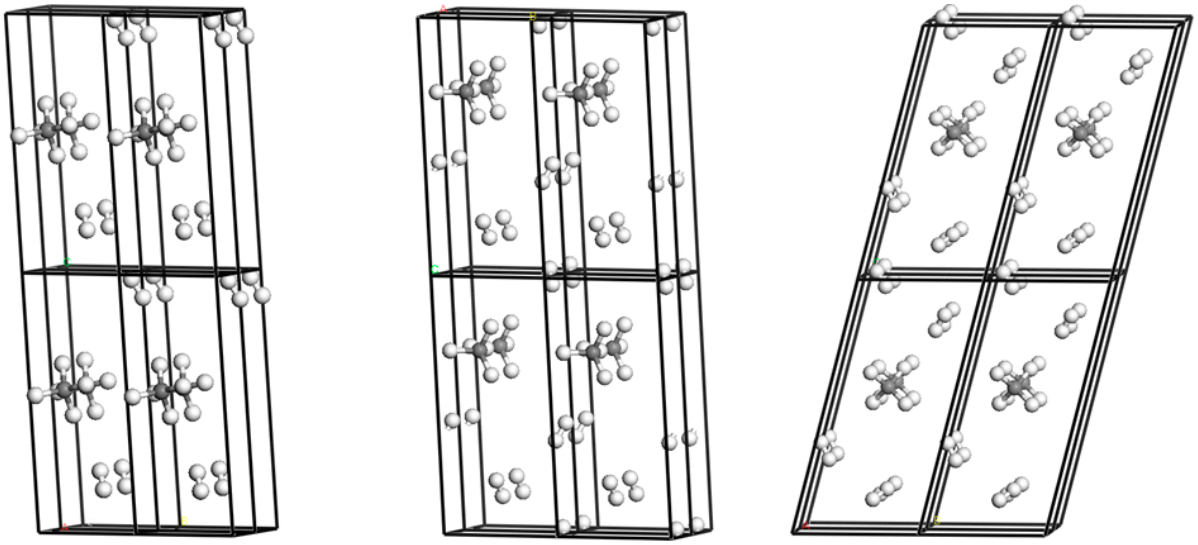
C-H = 1.10 Å

C-C = 4.19 Å

Inter-(H----H)= 2.78 Å

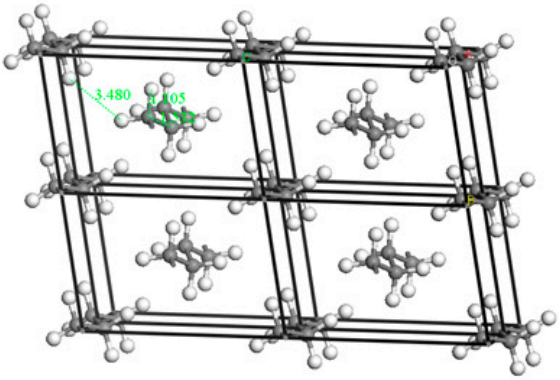
Inter-(H_2—H_2)= 3.13 Å

Inter-(H_2-CH_4) = 2.78 Å



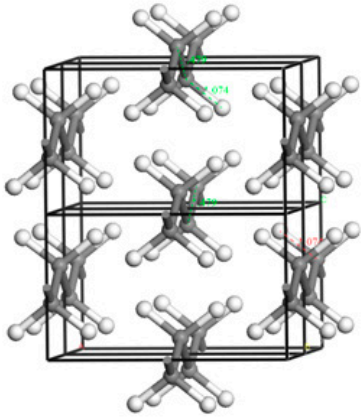
CH_4-$2H_2$ by USPEX at 1 atm	CH_4-$3H_2$ by USPEX at 1 atm	CH_4-$4H_2$ by USPEX at 1 atm
ΔH_f=–1.26 eV per C	ΔH_f=–1.27 eV per C	ΔH_f=–1.27 eV per C
C-H = 1.10 Å	C-H = 1.10 Å	C-H = 1.10 Å
C-C = 3.96 Å	C-C = 4.07 Å	C-C = 4.09 Å
Inter-(H----H)= 2.83 Å	Inter-(H----H)= 2.95 Å	Inter-(H----H)= 2.92 Å
Inter-(H_2—H_2)= 3.65 Å	Inter-(H_2—H_2)= 2.95 Å	Inter-(H_2—H_2)= 3.07 Å
Inter-(H_2-CH_4) = 2.87 Å	Inter-(H_2-CH_4) = 3.02 Å	Inter-(H_2-CH_4) = 2.92 Å

Figure S7. CH_x structures at 1 atm by USPEX



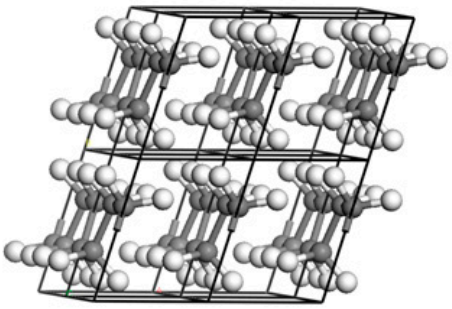
CH_2 by USPEX at 1 atm

ΔH_f=–0.52 eV per C



CH_2 by USPEX at 50GPa

ΔH_f=–0.54 eV per C



CH_2 structure at 50GPa
(taken from 100GPa by USPEX)

ΔH_f=–0.52 eV per C

Figure S8. CH_2 structures by USPEX

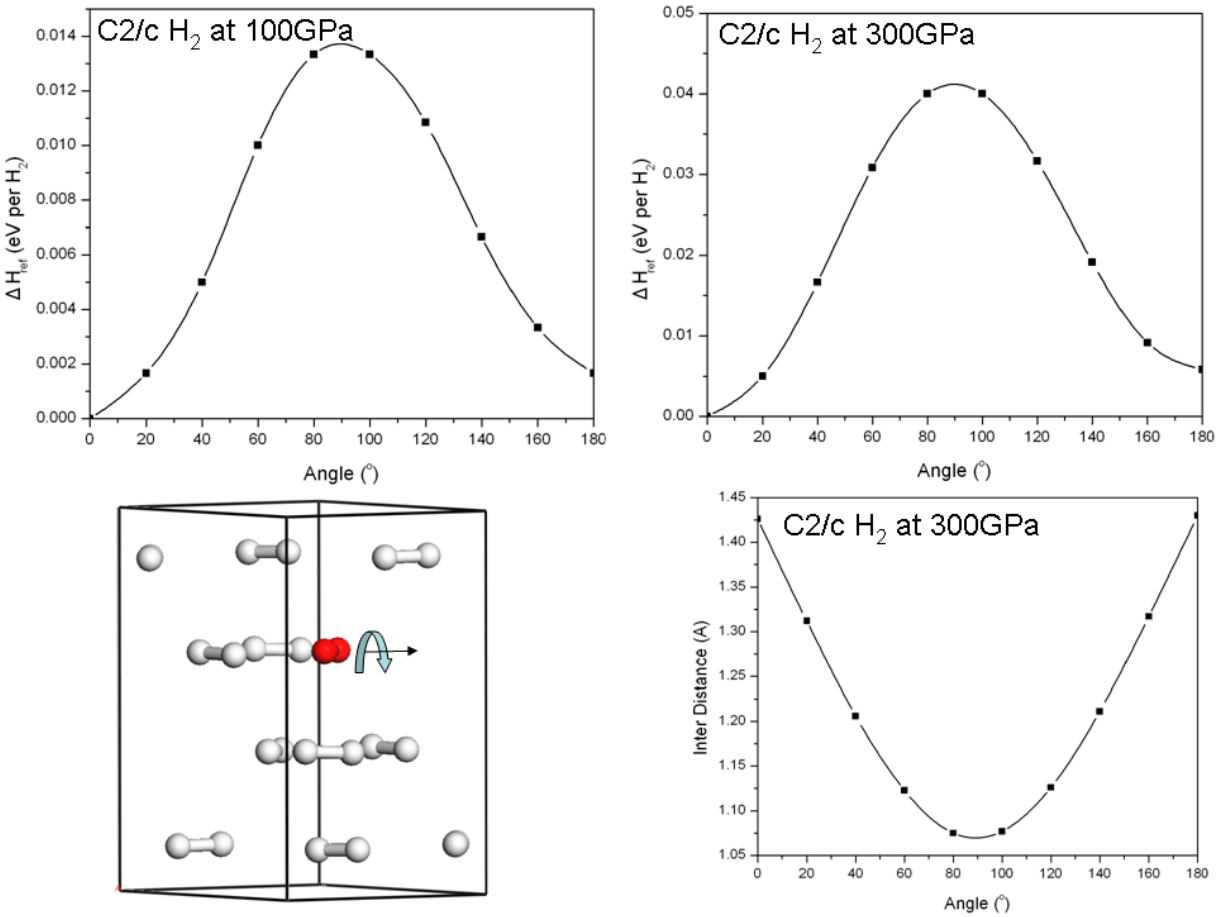


Figure S9. Scanned potential energy surfaces of rotation in two solid H_2 structures (at 100 GPa and 300 GPa, respectively).

Figure S9 shows the calculated potential energy surface of H_2 rotation in two solid H_2 structures (100 GPa and 300 GPa, respectively). The H_2 (red color) rotational direction is inserted in the shown structure. Note that only one H_2 molecule is rotated. The rotational barrier at 100 GPa is around 0.014 eV per H_2, which is 3 times lower than that of at 300 GPa (0.04 eV per H_2). As expected, the barrier is increased with pressure. To put it another way, the pressure can play a role on stopping a rotation.

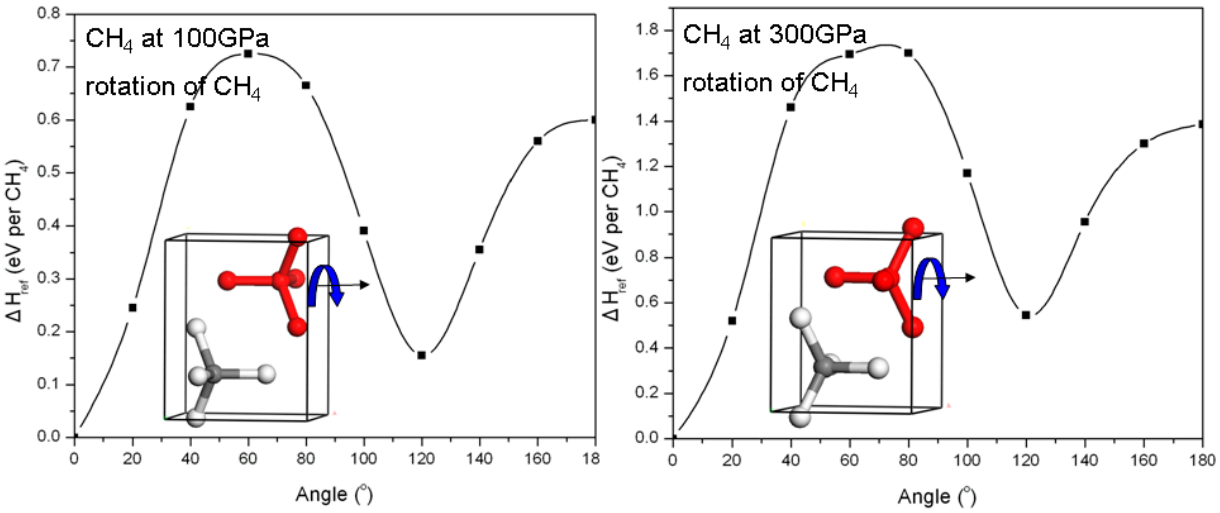


Figure S10. Scanned potential energy surfaces of rotation in two solid CH_4 structures (at 100GPa and 300GPa, respectively).

The potential energy surfaces of CH_4 rotation in two solid CH_4 structure is shown in **Figure S10**. At 100 GPa, the biggest barrier of CH_4 rotation is 0.75 eV per CH_4; it is increased to 1.70 eV per CH_4 at 300 GPa. Such barriers are quite higher than in the solid H_2 structures at corresponding pressure.

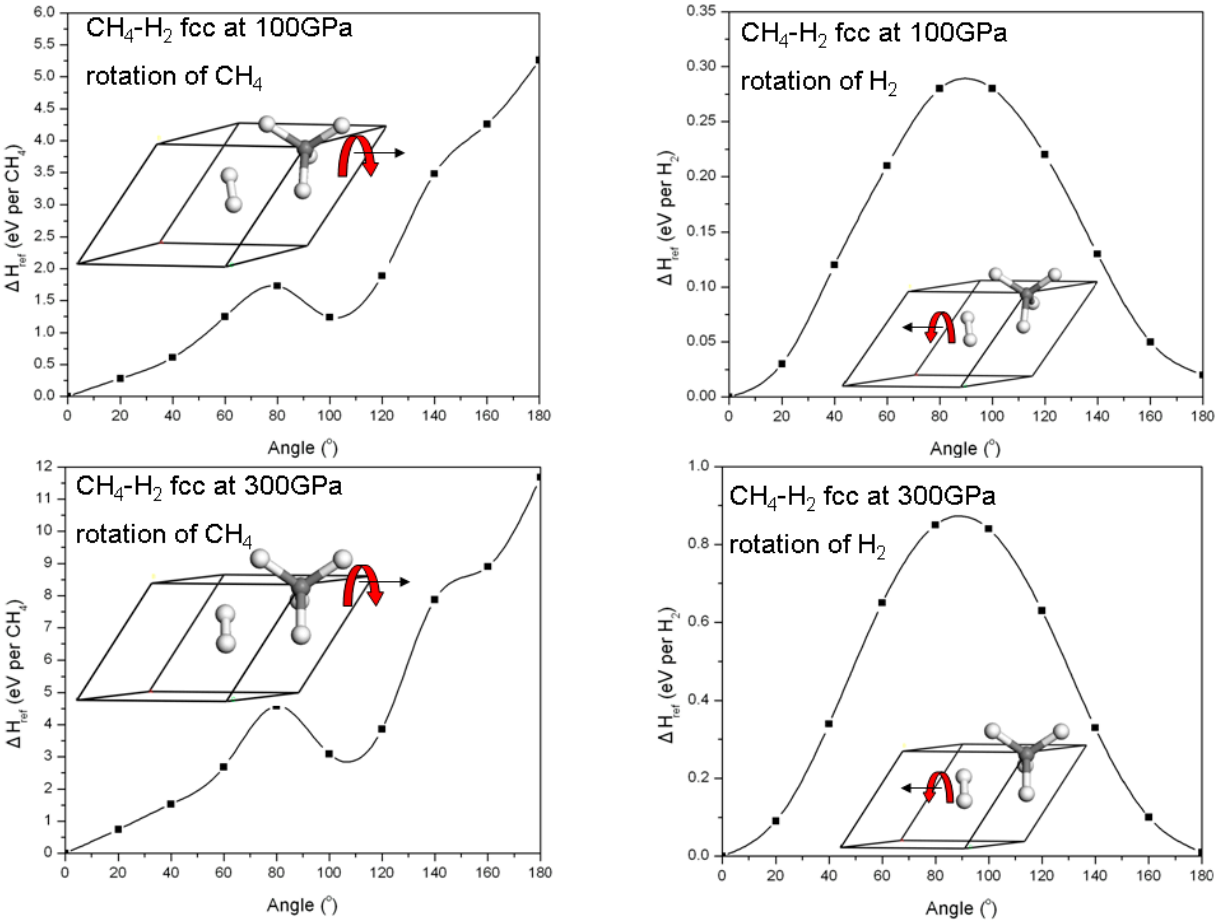


Figure S11. Scanned potential energy surfaces of rotation in two solid CH_4-H_2 fcc (at 100GPa and 300GPa, respectively) structure.

We also repeat the calculations at CH_4-H_2 fcc structures. In the CH_4-H_2 structure, there are two kinds of rotations considered – CH_4 and H_2 rotation. At each pressure (100 GPa and 300 GPa), the barrier of CH_4 rotation is higher than that of H_2 rotation. One can see there are uphill in the potential energy surfaces of CH_4 rotations, indicating the CH_4 rotation is blocked by pressure. For the rotation of H_2 in CH_4-H_2, they, 0.30 eV per H_2 at 100 GPa and 0.85 eV per H_2 at 300 GPa, are higher than in pure H_2 structures (0.014 vs. 0.04 eV per H_2).

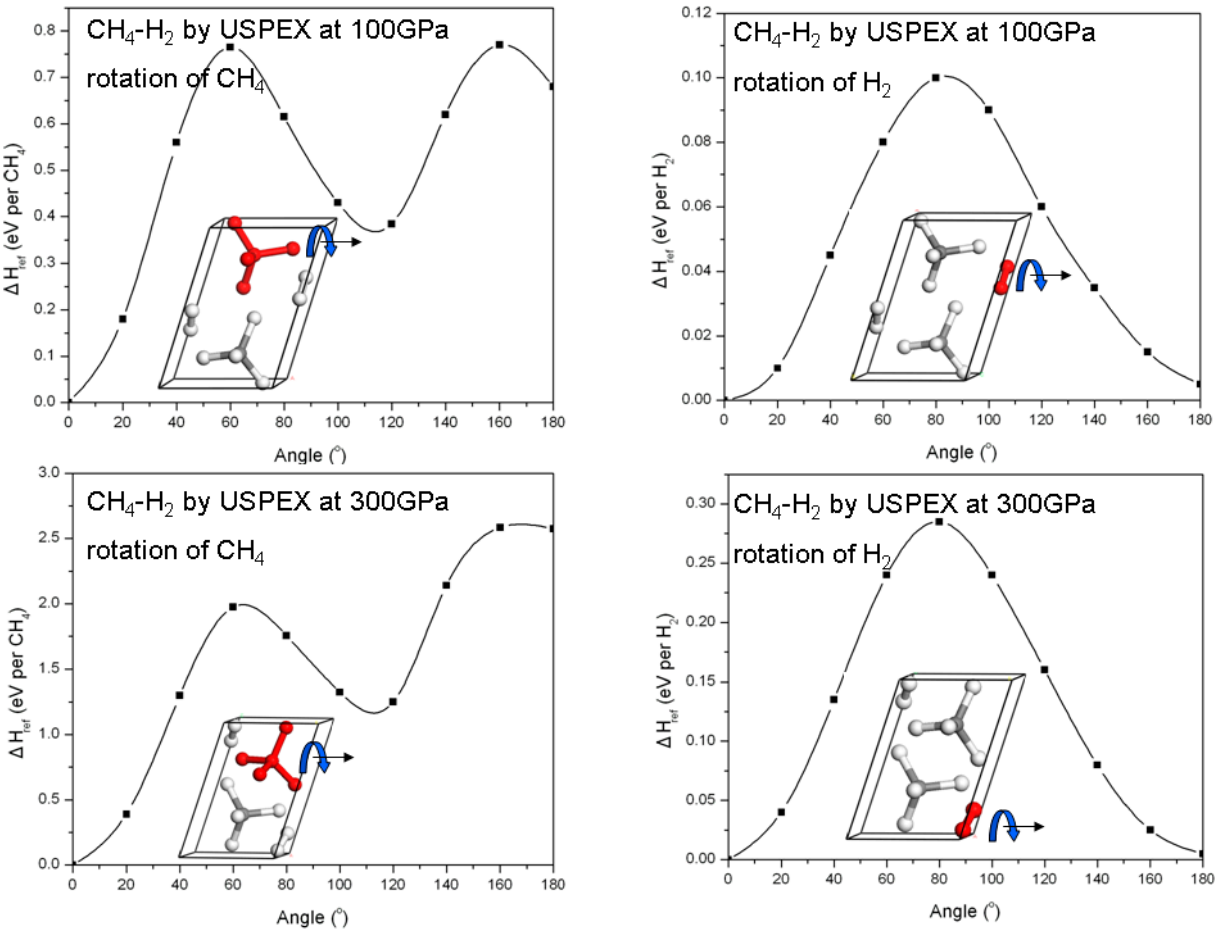


Figure S12. Scanned potential energy surfaces of rotation in two solid CH_4-H_2 structures (at 100 GPa and 300 GPa, respectively) by USPEX.

The potential energy surfaces of rotation in the CH_4-H_2 structures by USPEX are scanned, as shown in **Figure S12**. The barriers of CH_4 and H_2 rotation are quite lower than corresponding rotations in the CH_4-H_2 fcc structures.

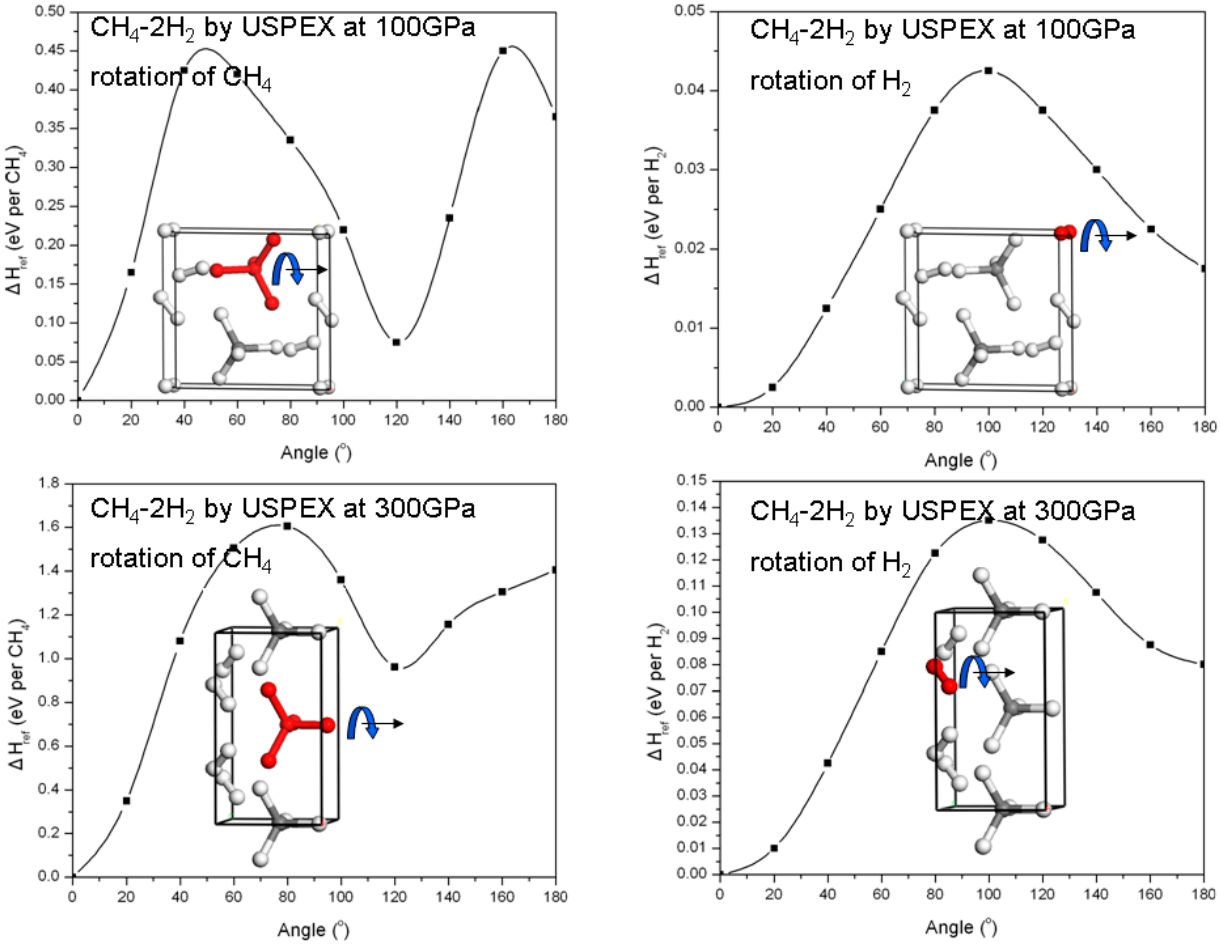


Figure S13. Scanned potential energy surfaces of rotation in two solid CH_4-$2H_2$ structures (at 100 GPa and 300 GPa, respectively) by USPEX.

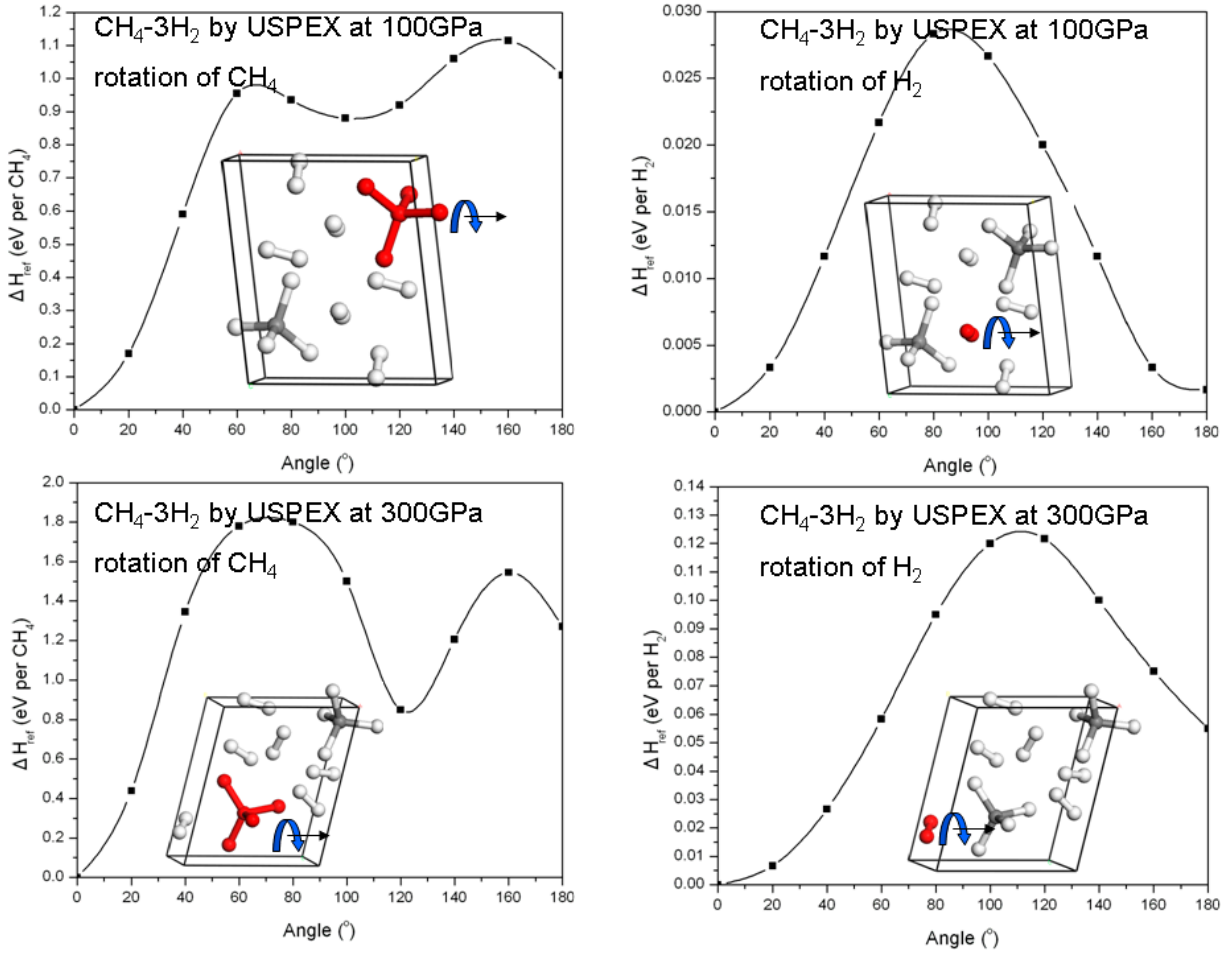


Figure S14. Scanned potential energy surfaces of rotation in two solid CH_4-$3H_2$ structures (at 100 GPa and 300 GPa, respectively) by USPEX.

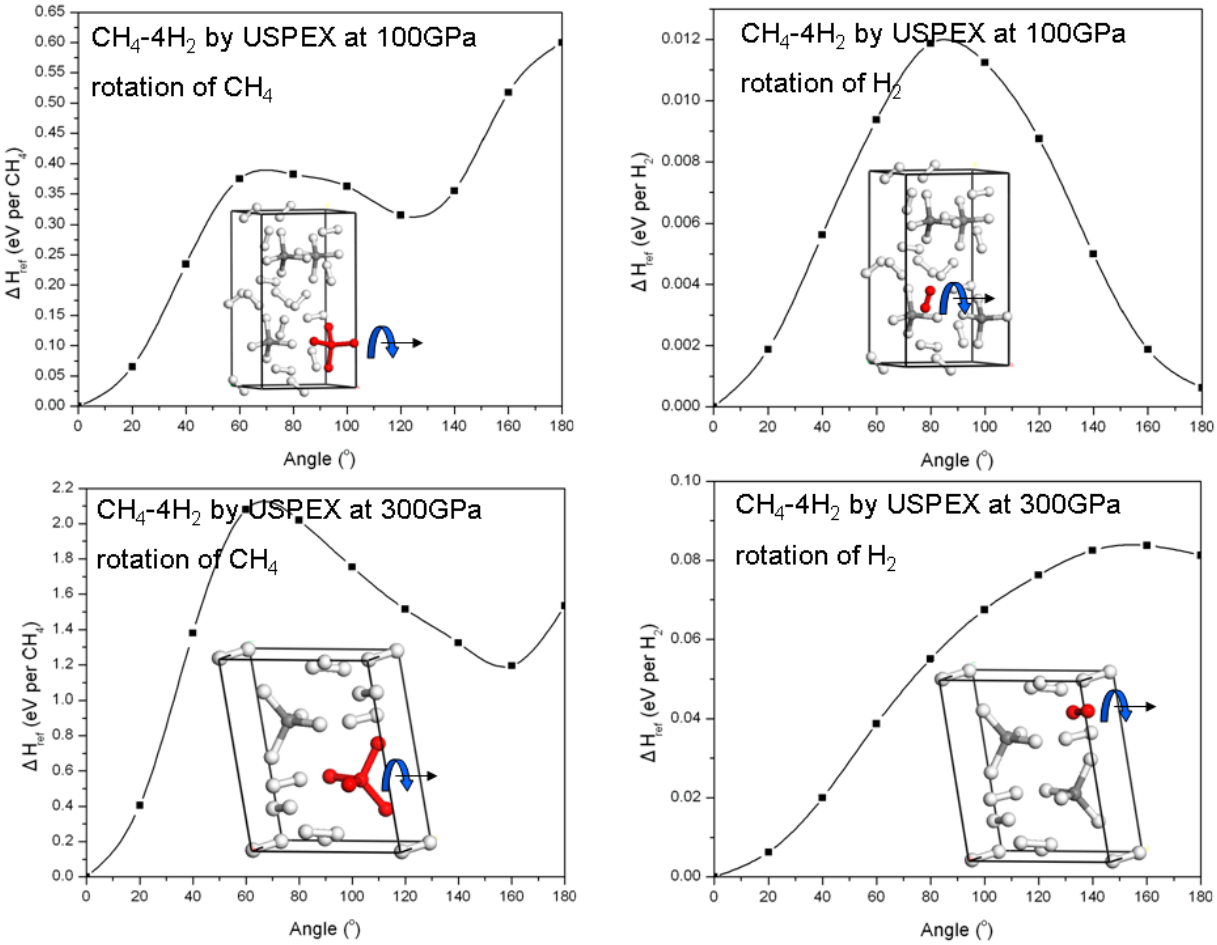


Figure S15. Scanned potential energy surfaces of rotation in two solid CH_4-$4H_2$ structures (at 100 GPa and 300 GPa, respectively) by USPEX.

Table S7. The biggest barriers of rotation in H_2 and CH_x structures.

	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 fcc	0.30	0.90	5.50	11.50
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

Though these structures are begun with fcc type, they will not adopt "fcc" type at high pressure any more. Here, only the case of "fcc" CH_4 is shown in **Figure S16**. The simulated XRD of a perfect fcc CH_4 structure is quite different to the one of the optimized "fcc" CH_4 structure at 300 GPa. This also happens on other fcc type CH_x structures. It might show the properties of rational solid.

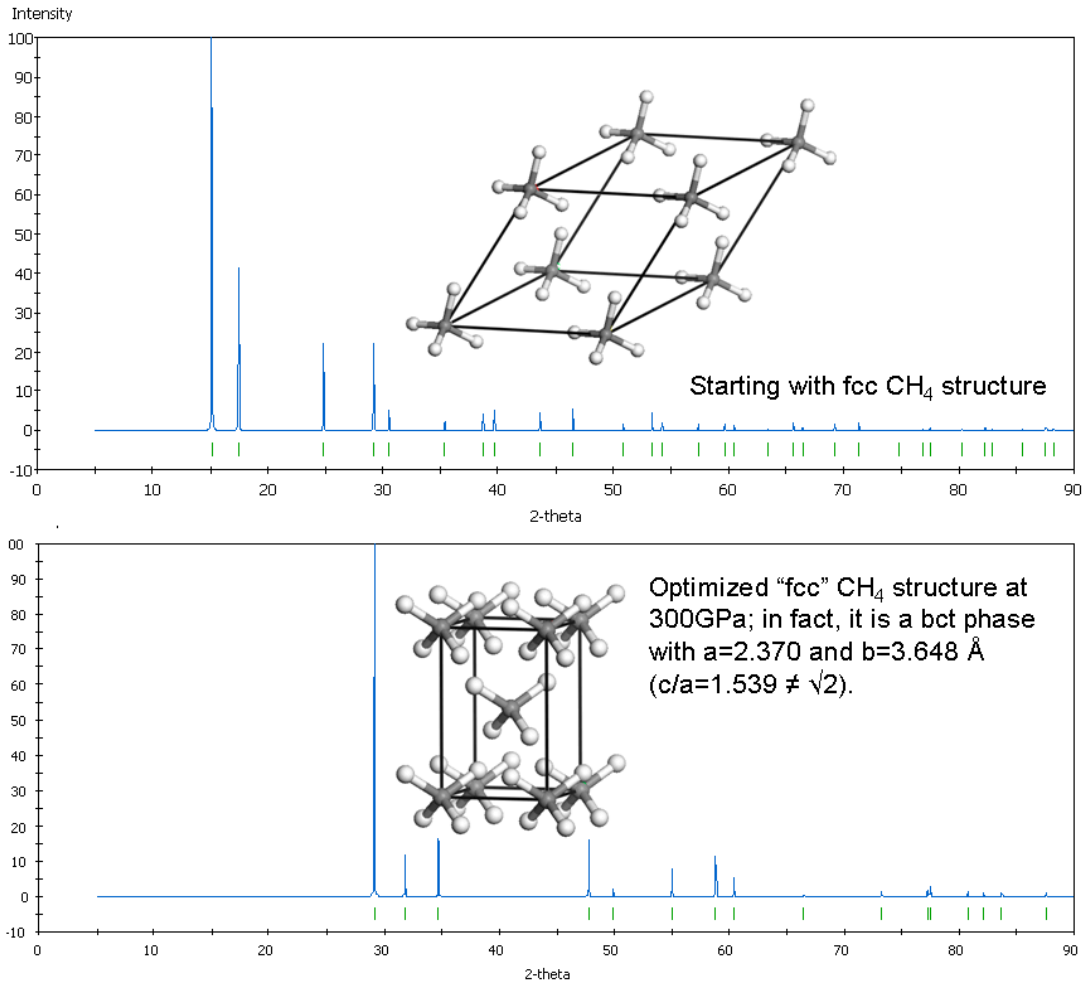


Figure S16. Simulated XRD pattern of a perfect fcc CH_4 structure and optimized "fcc" CH_4 structure at 300 GPa. The Synchrotron with a wave length by 1.000 Å is used.

In **Figure S17**, the blue line (CH_4-H_2 "wurtzite") has a big jump, indicating that there might be a phase transition. For the complicated system, it is difficulty to check the phase change via bond distance or space group. However, checking XRD pattern is an easy way to see what happened. **Figure S17** shows the difference of XRD between the two CH_4-H_2 wurtizte structures at 300GPa and 350GPa, respectively; it indicates the possible phase transition.

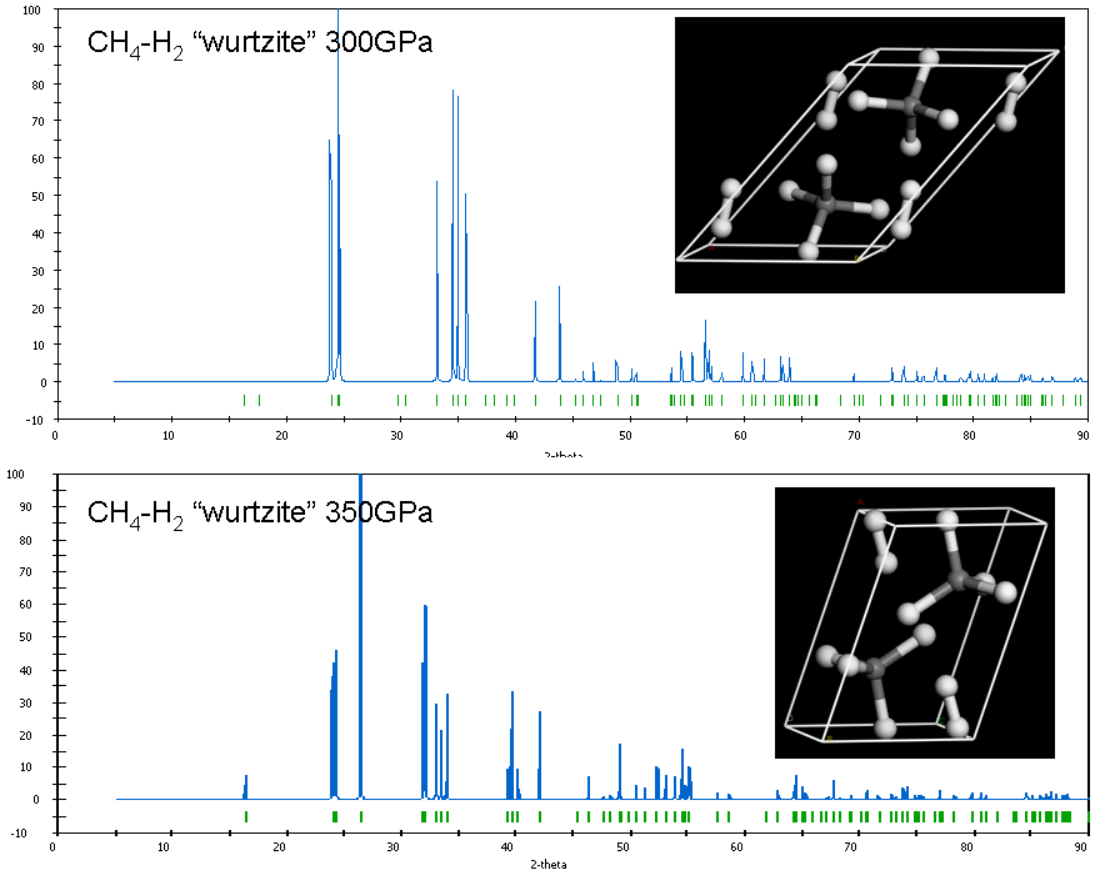


Figure S17. Simulated XRD pattern of CH_4-H_2 wurtizte structure at 300 GPa and 350 GPa. Here, the radiation source is from Synchrotron with a wave length by 1.000 Å.

It is interesting to know or check whether USPEX is good at searching the most stable CH_x structures. Here, I just take the CH_4-H_2 wurtzite structure as an example. **Figure S18** shows the simulated XRD of three structures- the starting CH_4-H_2 wurtzite structure, the optimized CH_4-H_2 "wurtzite at 5 GPa and CH_4-H_2 by USPEX at 5 GPa. Compared the XRD patterns of the starting CH_4-H_2 wurtzite structure and the optimized "wurtzite" at 5 GPa, it is hard to say that the CH_4-H_2 wurtzite structures can be survived at high pressure, as mentioned before. However, the relative positions of carbon atoms in both optimized "wurtzite" structure at 5 GPa and the one by USPEX at 5 GPa are located at the "hcp".

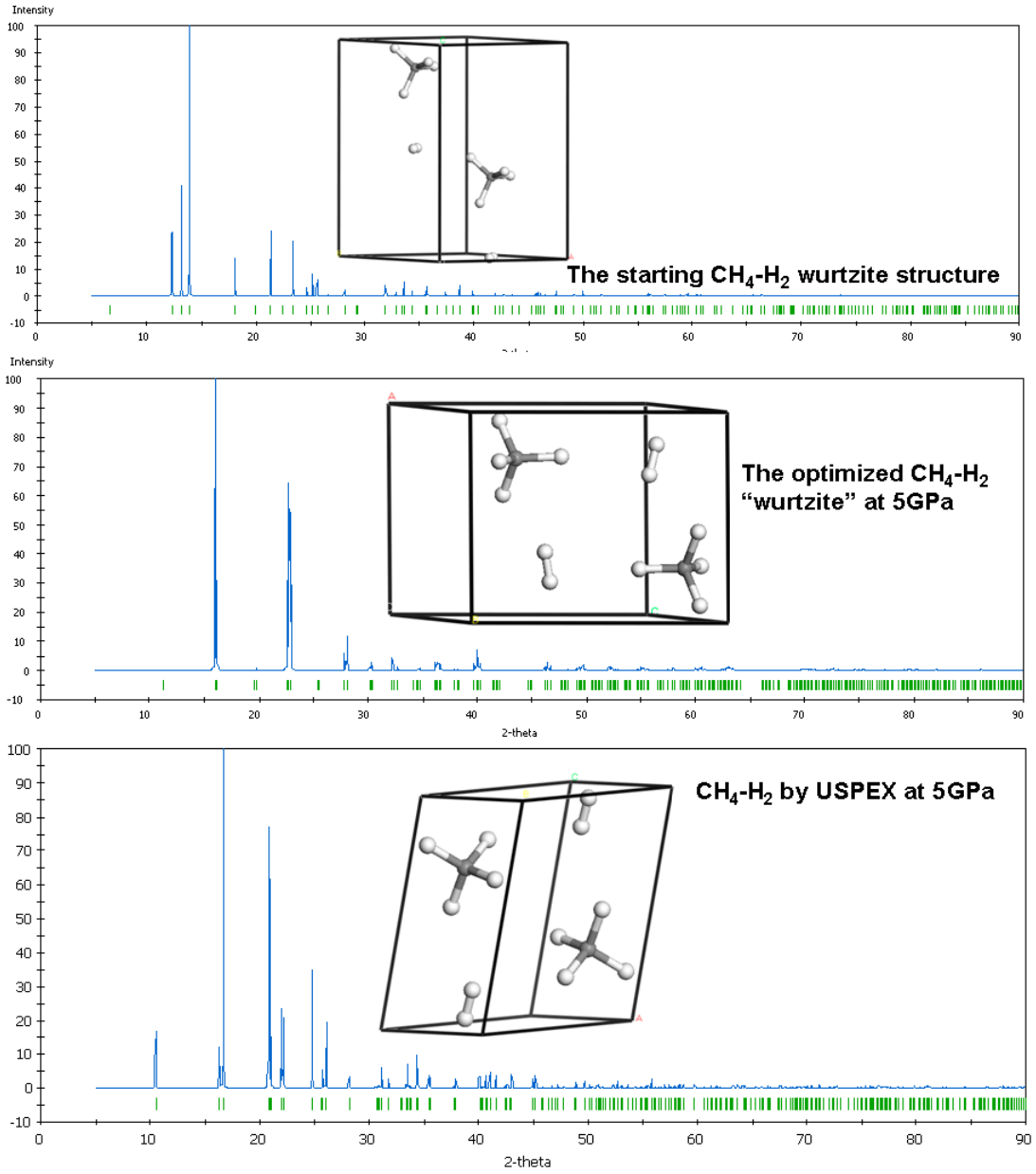


Figure S18. Simulated XRD pattern of CH_4-H_2 "wurtizte" structure (the strarting structure and optimized at 5 GPa) and CH_4-H_2 by USPEX at 5 GPa.

The energy will make sense to check the different. **Table S8** listed the relative enthalpy of three different CH_4-H_2 structures at 5 GPa. The "fcc" type CH_4-H_2 is not

competitive among three structures. Well, the energy of another two structures is quite close (if we do not believe the difference by 0.02 eV). How well is the USPEX?

Table S8. Computed the relative enthalpy of three CH_4-H_2 structures at 5 GPa.

	$H\text{-}H_{diamond+H2}$ (eV per C atom)
CH_4-H_2 "fcc" type at 5 GPa	-1.29
CH_4-H_2 "wurtzite" type at 5 GPa	-1.34
CH_4-H_2 by USPEX at 5 GPa	-1.36