Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Topological study of chemical bonds under pressure: solid hydrogen as a model case

Vanessa Riffet [a]†*, Vanessa Labet [b]*, Julia Contreras-García [a]

[a] *Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire de Chimie Théorique (LCT), 4 place Jussieu F-75005 Paris, France*

[b] *Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire de la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies (MONARIS), 4 place Jussieu F-75005 Paris, France*

Corresponding author:

vanessa.riffet@laposte.net **; vanessa.labet@upmc.fr**

Present Addresses

†Institut Photovoltaïque d'Ile de France (IPVF), 8 rue de la Renaissance 92160 Antony, France and Institute for Research and Development of Photovoltaic Energy (IRDEP), UMR 7174 CNRS / EDF R&D / Chimie ParisTech-PSL, 6 quai Watier, 78401 Chatou, France

General

Table S1. Correlation between the radius d (pm) and the dimensionless Wigner-Seitz radius r_s, along with the evolution of NCI peaks

Figure S1. a) Molecular orbital diagram of $3H_2$ molecular model for the point-group *D_{3h}*. b) Energy of MOs labeled a_1', 1e', 2e', a_2'' (in Hartree) for the $3H_2$ molecular model. c) Evolution of the electron population in the frontier molecular orbital in function of r_s. Data were calculated using the CASSCF/cc-pVQZ level.

Table S2. NCI results for our molecular model at different values of d. Plot of $s(\mathrm{sign}(\lambda_2)\rho)$ and NCI isosurfaces using s = 0.5 a.u and the color scale $-0.05 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u.

Figure S2. Superposition of plots $s(\rho)$, those of $3H_2$ molecule model in red and those of isolated H_2 extracted from $3H_2$ in green. For the sake of clarity, the y-axis is shift of +0.1 a.u for the plot of isolated H_2.

Figure S3. a) Energy evolution of $3H_2$ molecular model without and with the dispersion correction under compression. b) Dispersion energy as a function of r_s.

Figure S4. a) Total exchange-correlation (covalent-like) interaction energy for H_1. b) Total classical ionic-like interaction energy for H_1.

Figure S5. Exchange-correlation (covalent-like) interaction energies between atoms H_1-H_4, H_1-H_6, H_1-H_2 and H_1-H_5.

Figure S6. a) Evolution of the stabilization energy due to the electron delocalization within ring of 3 H_2 molecules as a function of r_s. b) Energy evolution of ring of three H_2 molecules at the imposed *D_{3h}* and *D_{6h}* symmetry point-group in black and red, respectively. The blue cross correspond to unconstraint H_6 system.

Figure S7. Plots of $s(\rho)$ for the $P6_3/m$ phase at 1 atm, 6, 25, 35, 50, 60, 75 and 100 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

Figure S8. NCI isosurfaces at different pressures for the P63/m phase using s = 0.2 a.u and colored over the range $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u.

Figure S9. Plots of $s(\rho)$ for the C2/c phase at 125, 150, 200 and 250 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

Figure S10. NCI isosurfaces at different pressures for the C2/c phase using s = 0.2 a.u and colored over the range $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u.

Figure S11. Plots of $s(\rho)$ for the Cmca-12 phase at 300 and 350 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

Figure S12. NCI isosurfaces at different pressures for the Cmca-12 phase using s = 0.2 a.u and colored over the range $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u.

Figure S13. Plots of s(ρ) for the Cmca phase at 400, 450 and 490 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

Figure S14. NCI isosurfaces at different pressures for the Cmca phase using s = 0.2 a.u and colored over the range $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u.

Figure S15. Plots of s(ρ) for the $I4_1/amd$ phase at 500, 750, 1000, 1500 and 2000 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

Figure S16. NCI isosurfaces at different pressures for the $I4_1/amd$ phase using s = 0.2 a.u and colored over the range $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.20$ a.u.

Table S3. Structures of the solid phases.

Figure S17. Evolution of a) the energy per proton, b) volume per proton, c) pV per proton term and d) the enthalpy per proton as function of the pressure.

Table S4. Cartesian coordinates calculated at the PBEPBE/6-311++G(d,p) level for the $3H_2$ molecule model.

Structural description of solid phases

Figure S18. Stack of layers of a) $P6_3/m$, b) C2/c, c) Cmca-12 and d) Cmca.

Figure S19. Description of the first coordination spheres of hydrogen, in the $P6_3/m$ phase at 100 GPa, for one H_2 system includes a) in the $(\vec{b},\vec{c})$ plane (nn, nnn and nnnn) and b) in the $(\vec{a},\vec{b})$ plane (nn, nnn, nnnn).

Figure S20. a) Description of the first coordination spheres of hydrogen (nn and nnn), in the C2/c phase at 250 GPa, for the three non-equivalent H_2 systems includes in the same layer. b) Geometric shapes when considering the nearest neighbor and the next nearest neighbor.

Figure S21. A layer of Cmca-12 phase at 350 GPa, description of the first coordination spheres of hydrogen (nn, nnn, and nnnn).

Figure S22. Description of the first coordination spheres of hydrogen, a) in the Cmca phase at 490 GPa (nn, nnn, nnnn) and b) in the $I4_1/amd$ phase at 500 GPa (nn, nnn).

NCI evolution under pressure

Figure S23. a-b) Main interactions scheme in $P6_3/m$. NCI analysis of c) the shape **A** and d) the shape **B** using s = 0.2 a.u and the following color scale: $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

Figure S24. a) Main interactions scheme b) The ring of 3 H_2 molecules, cut from hydrogen solid of C2/c symmetry for different pressures. NCI analysis using s = 0.2 a.u and the following color scale: $-0.2 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

Figure S25. a) Main interactions scheme b) The ring of 3 H_2 molecules, cut from hydrogen solid of Cmca-12 symmetry for different pressures. NCI analysis using s = 0.2 a.u and the following color scale: $-0.2 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

Figure S26. a) Main interactions scheme b) Variation of the Hydrogen local environment: NCI analysis using s = 0.2 a.u and the following color scale: $-0.2 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

Figure S27. a) Main interactions scheme b) Variation of the tetra-coordinated Hydrogen local environment: NCI analysis using s = 0.1 a.u and the following color scale: $-0.2 < \mathrm{sign}(\lambda_2)\rho < 0.2$ a.u. The value below shape corresponds to the pressure (GPa) and the electron density values of BCPs are represented in blue and italic.

Table S5. Classification of interactions delimited by characteristic electron density values (a.u.).

Table S1. Correlation between the radius d (pm) and the dimensionless Wigner-Seitz radius r_s, along with the evolution of NCI peaks.

r_s	d (Å) x10	$\lambda_2<0$		$\lambda_2>0$
2,47	250	-0,255	0	0
2,37	240	-0,255	0	0
2,28	230	-0,255	-0,0005	0
2,18	220	-0,255	-0,001	0
2,08	210	-0,255	-0,001	0
1,98	200	-0,256	-0,001	0,001
1,88	190	-0,256	-0,002	0,001
1,78	180	-0,256	-0,003	0,002
1,68	170	-0,256	-0,004	0,002
1,58	160	-0,257	-0,006	0,003
1,48	150	-0,257	-0,009	0,004
1,39	140	-0,258	-0,013	0,006
1,29	130	-0,259	-0,019	0,009
1,19	120	-0,259	-0,028	0,013
1,09	110	-0,256	-0,045	0,02
0,99	100	-0,245	-0,074	0,03
0,94	95	-0,23	-0,099	0,037
0,93	94	-0,226	-0,106	0,039
0,92	93	-0,221	-0,113	0,041
0,91	92	-0,214	-0,122	0,043
0,90	91	-0,205	-0,133	0,045
0,89	90	-0,191	-0,149	0,047
0,88	89	-0,173	-0,173	0,049
0,87	88	-0,177	-0,177	0,051
0,86	87	-0,182	-0,182	0,053
0,85	86	-0,186	-0,186	0,055
0,84	85	-0,191	-0,191	0,058
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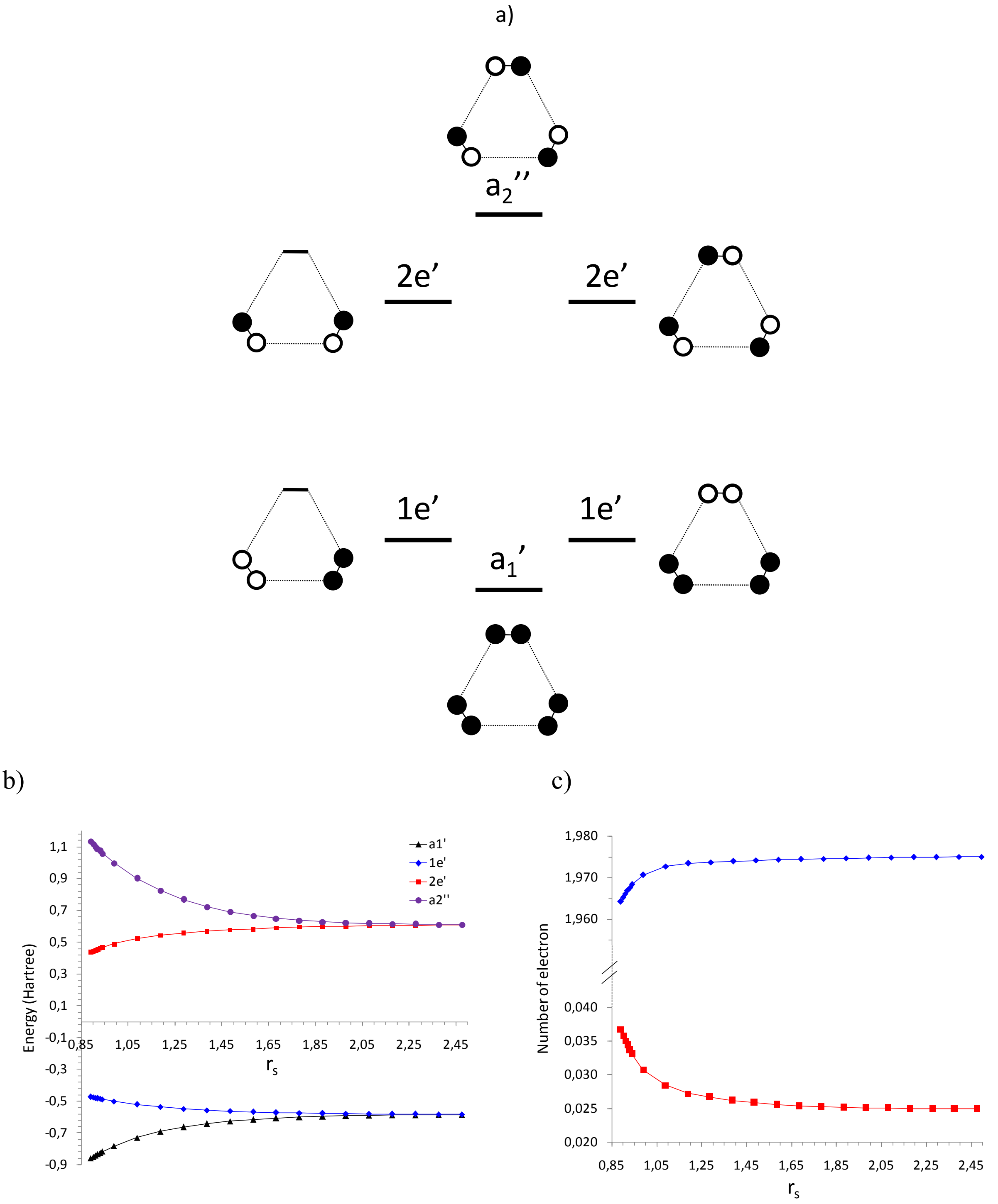
0,74	75	-0,249	-0,249	0,09



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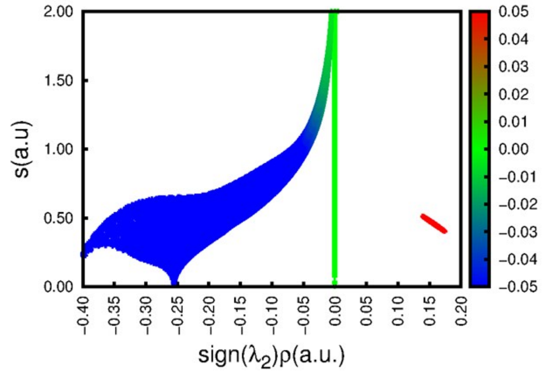 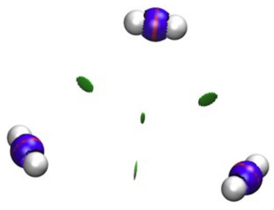	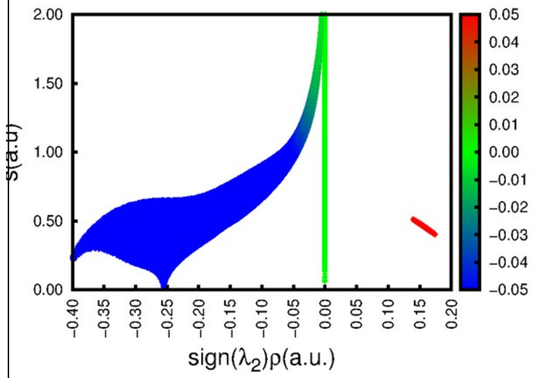 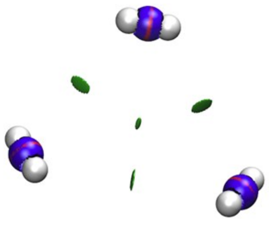
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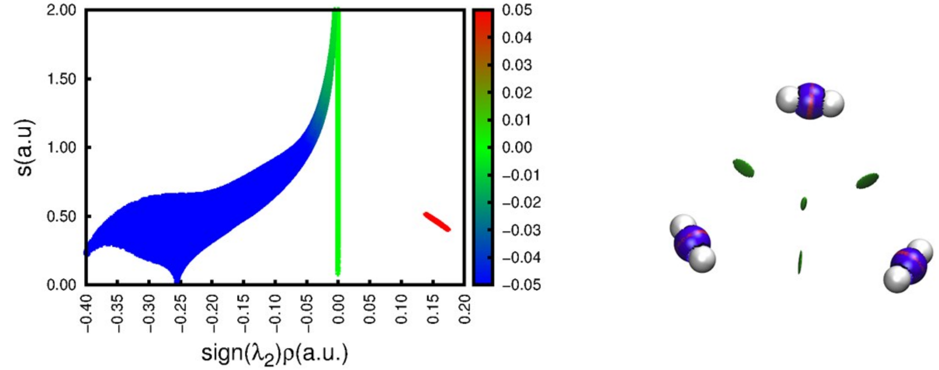

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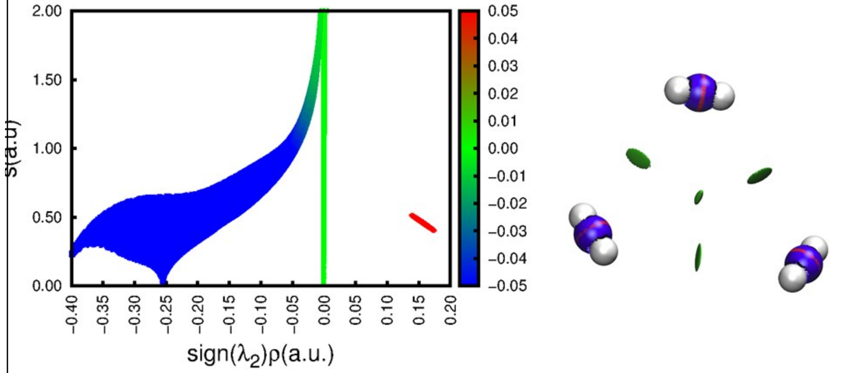

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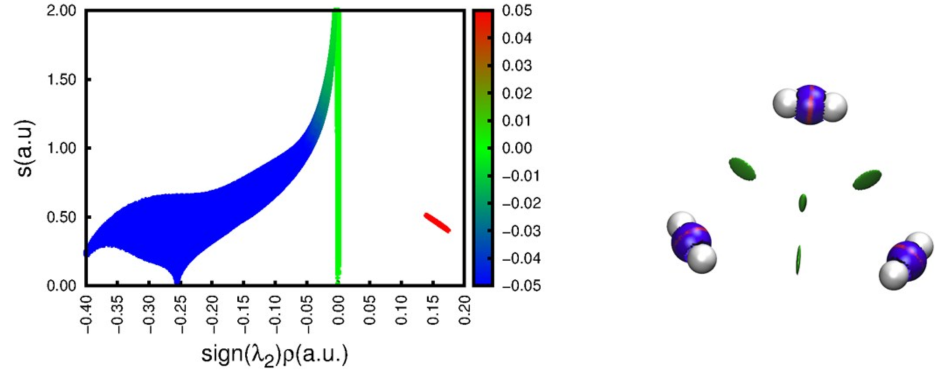

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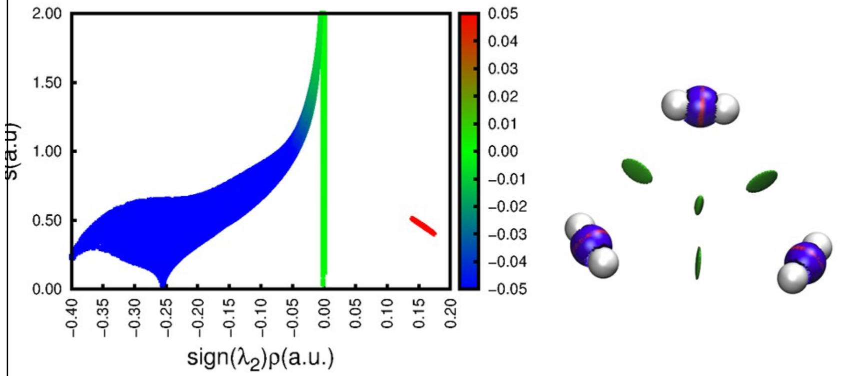

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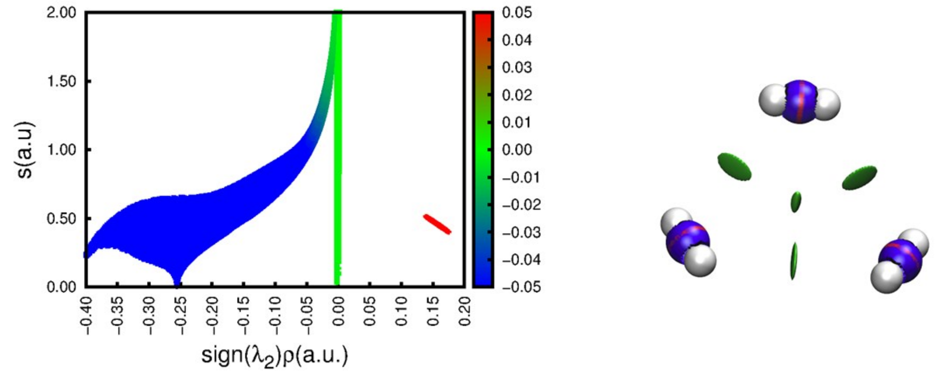

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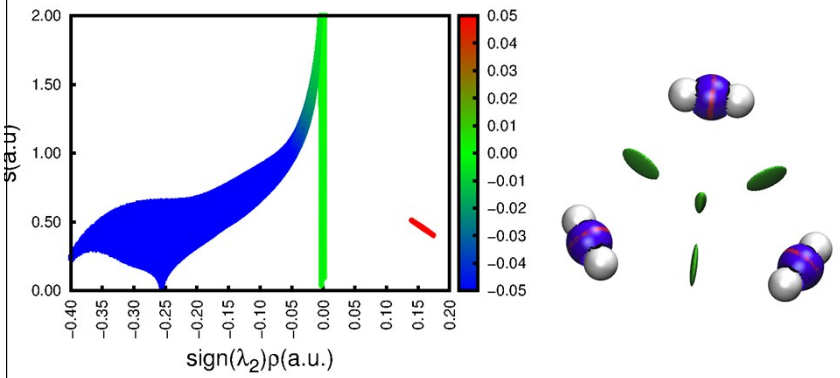

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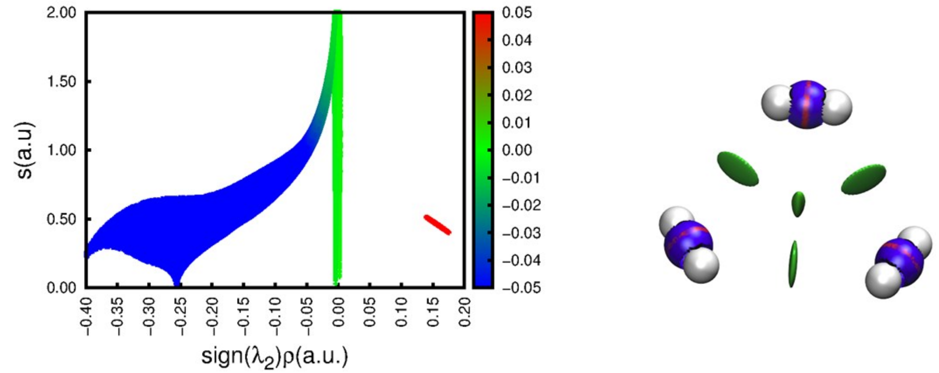

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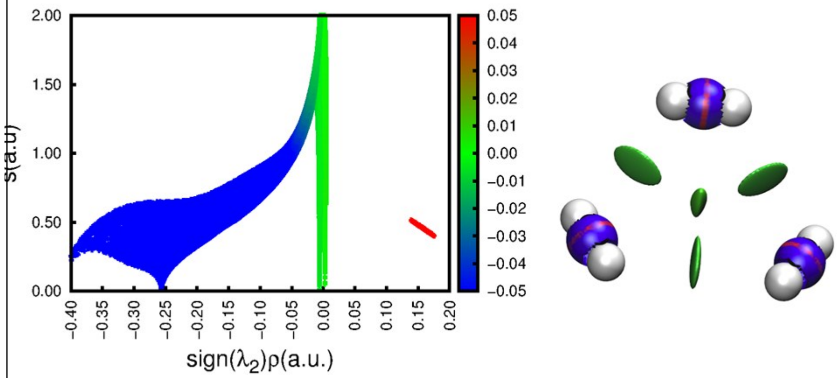

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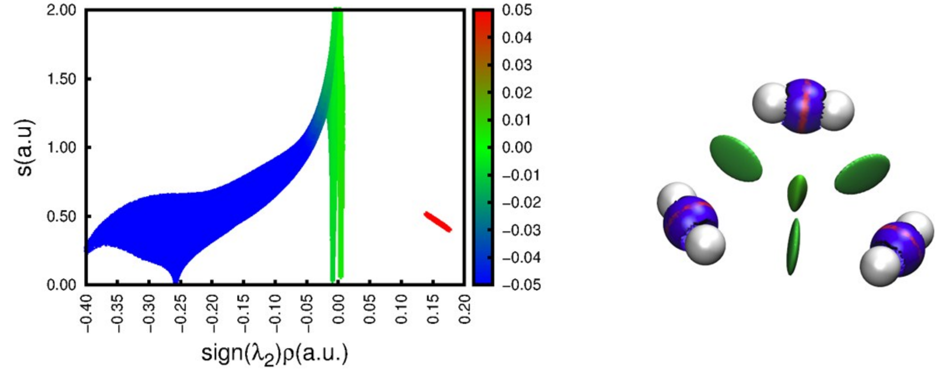

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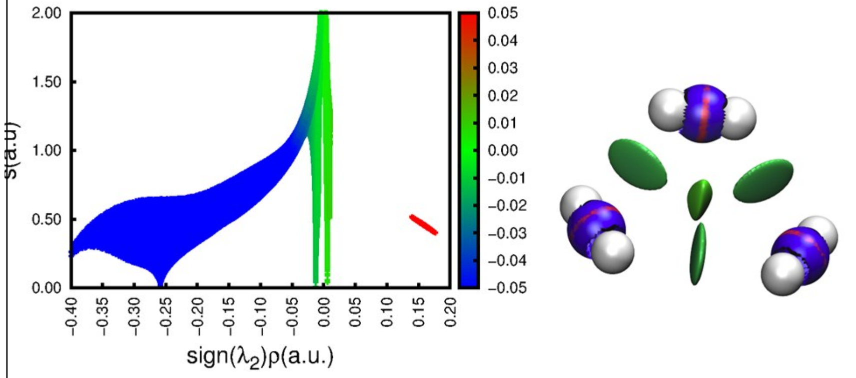

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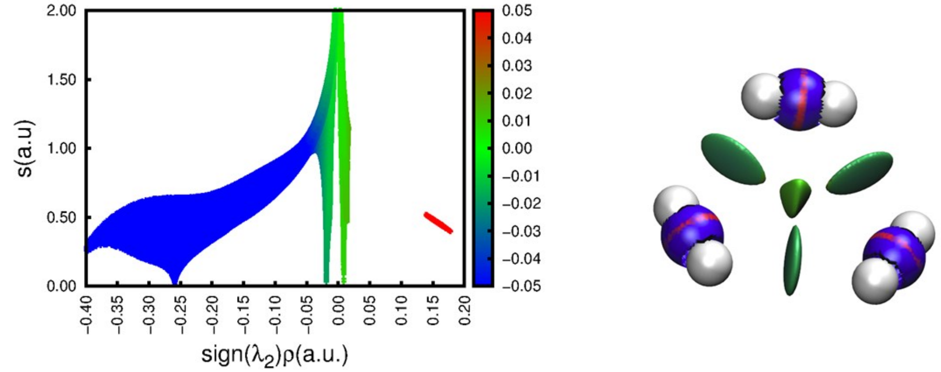

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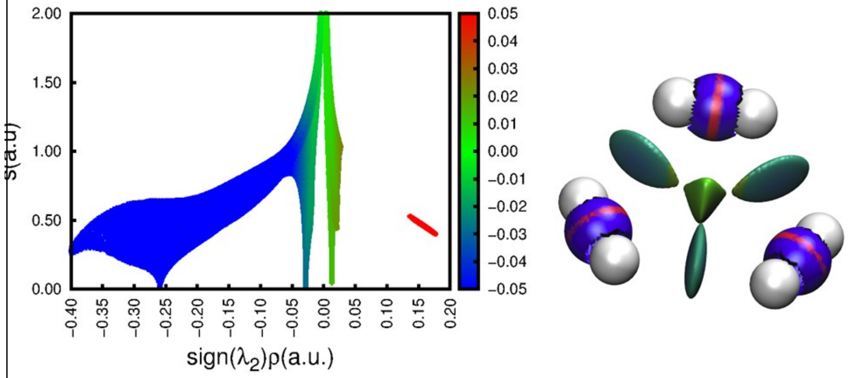

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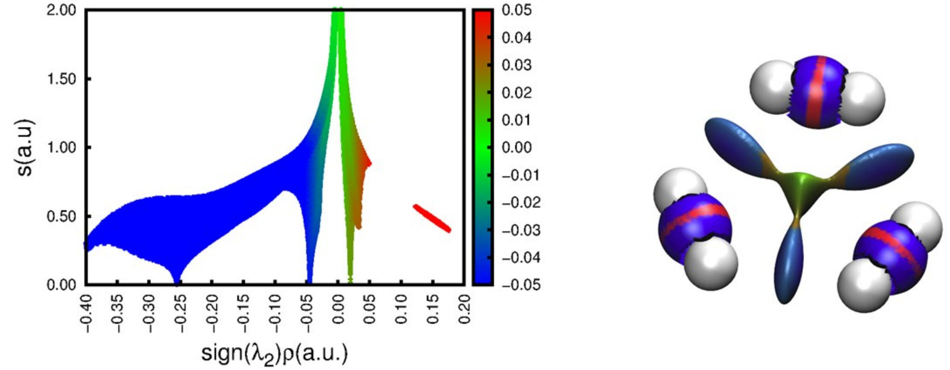

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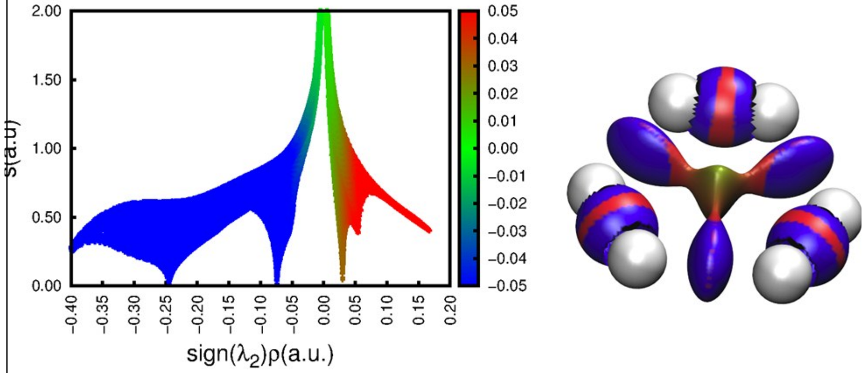

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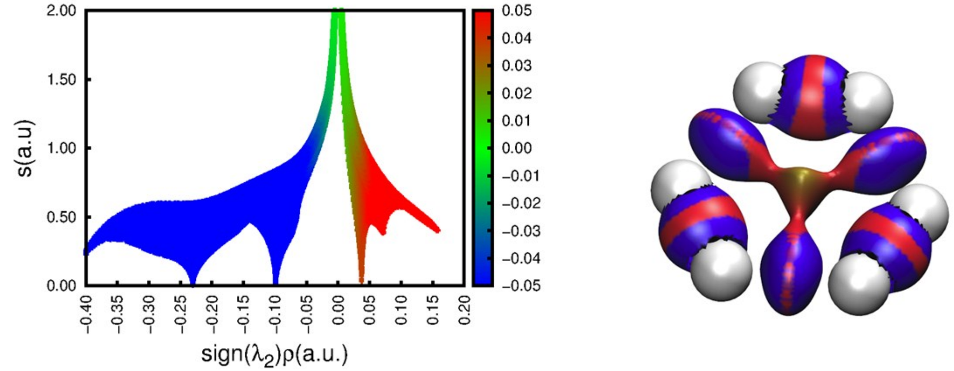

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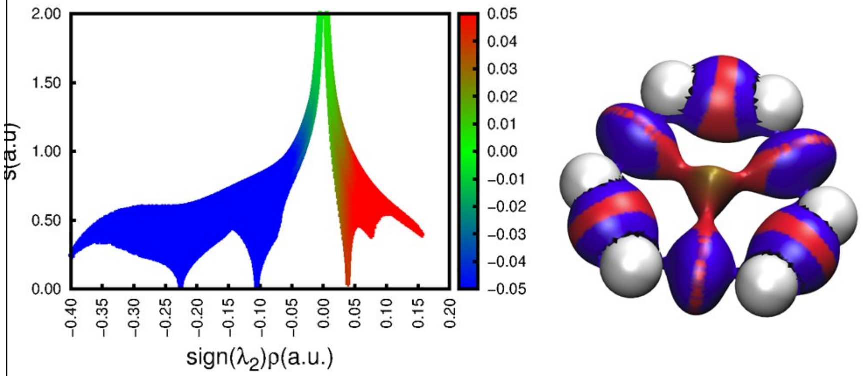

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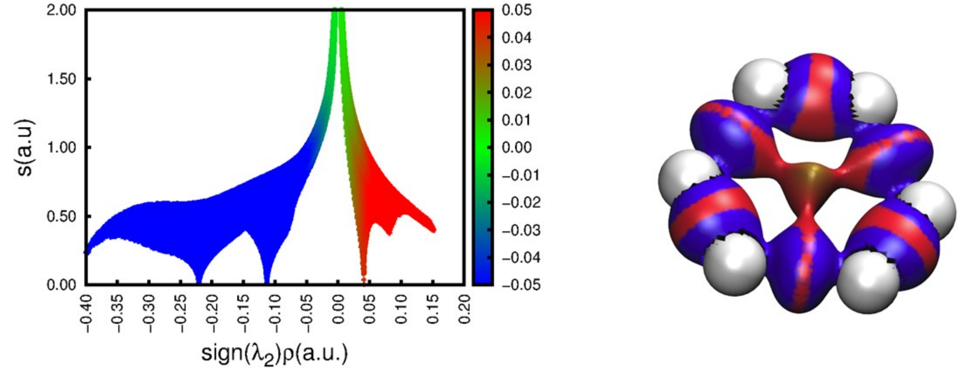

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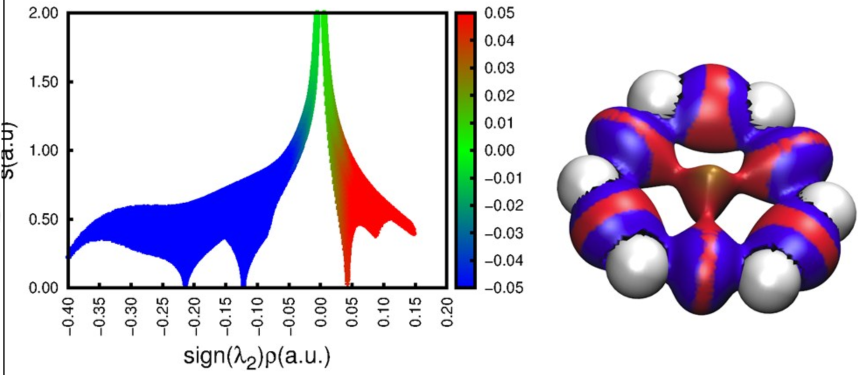

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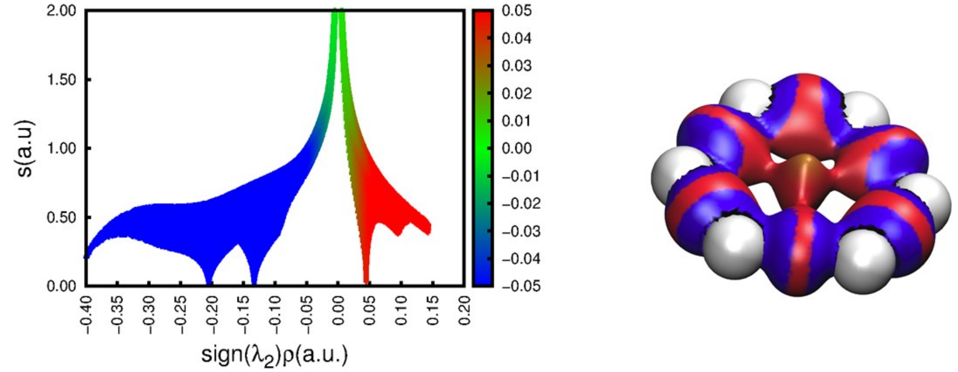

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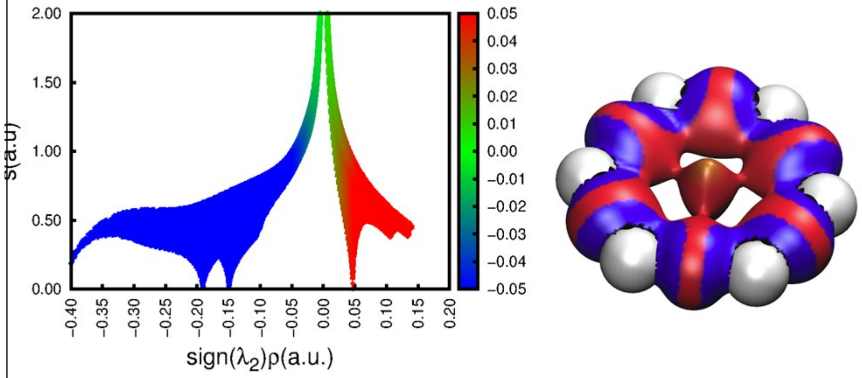

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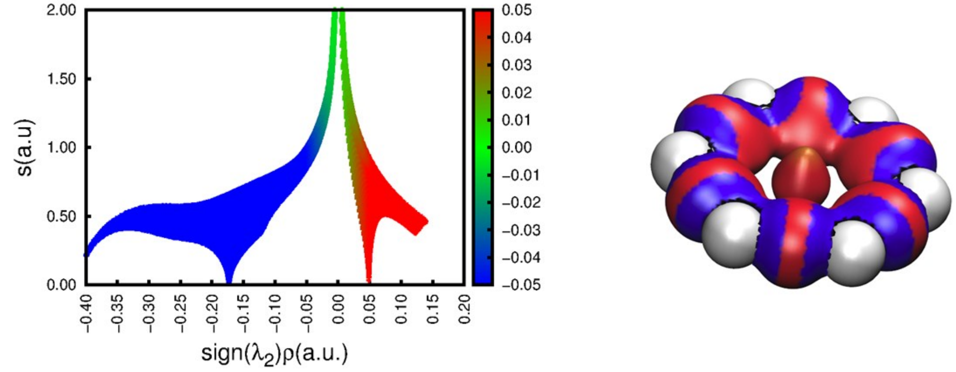

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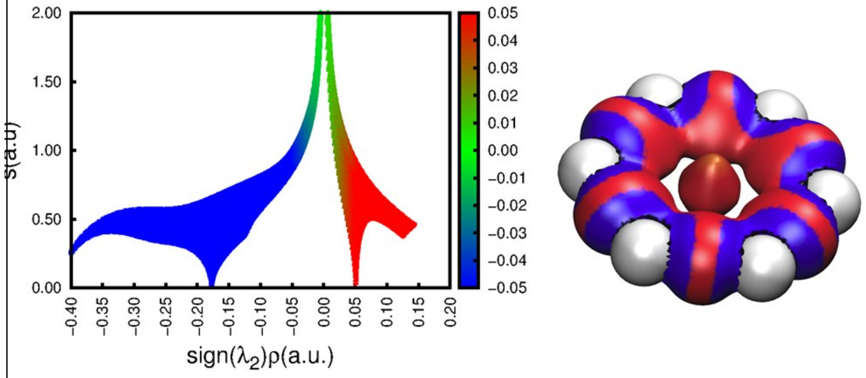

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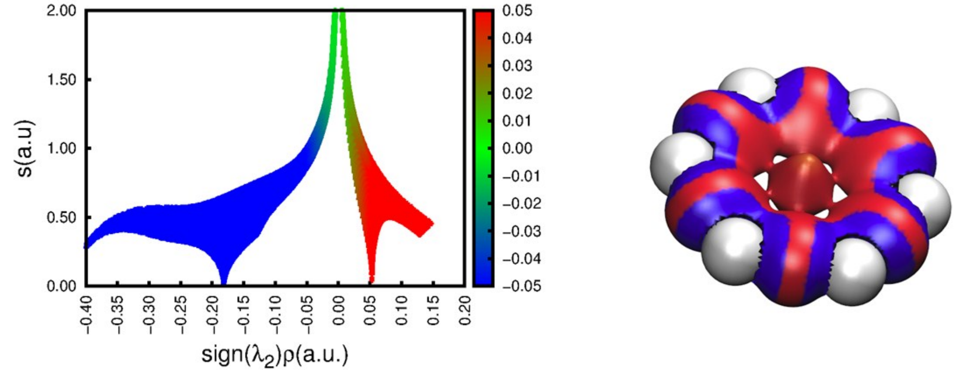

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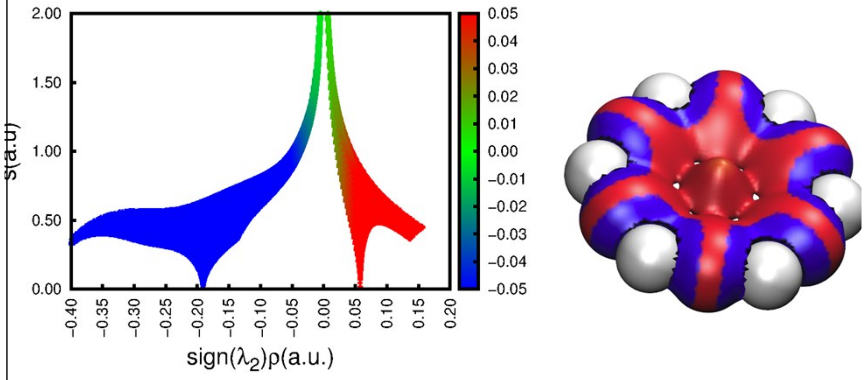

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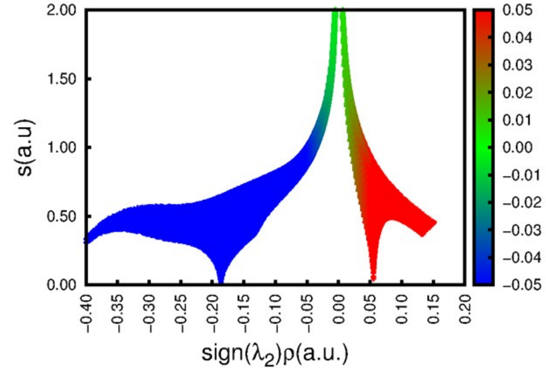
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1.00
0.50
0.00
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sign(λ_2)ρ(a.u.)
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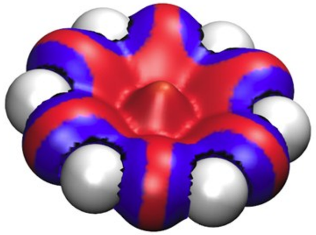

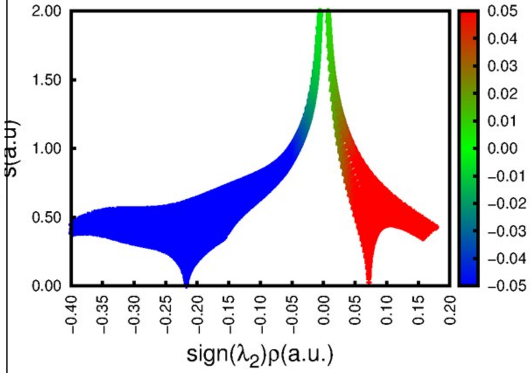
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1.50
1.00
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0.00
−0.40 −0.35 −0.30 −0.25 −0.20 −0.15 −0.10 −0.05 0.00 0.05 0.10 0.15 0.20
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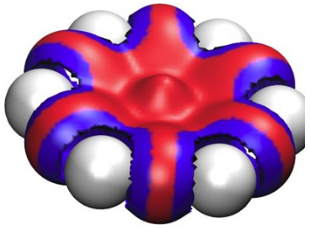

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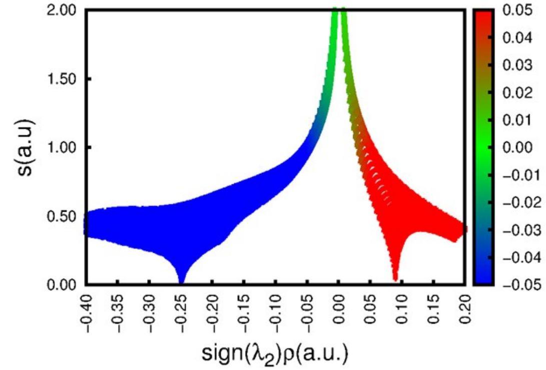
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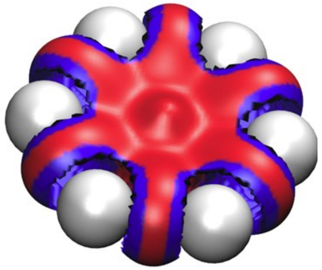

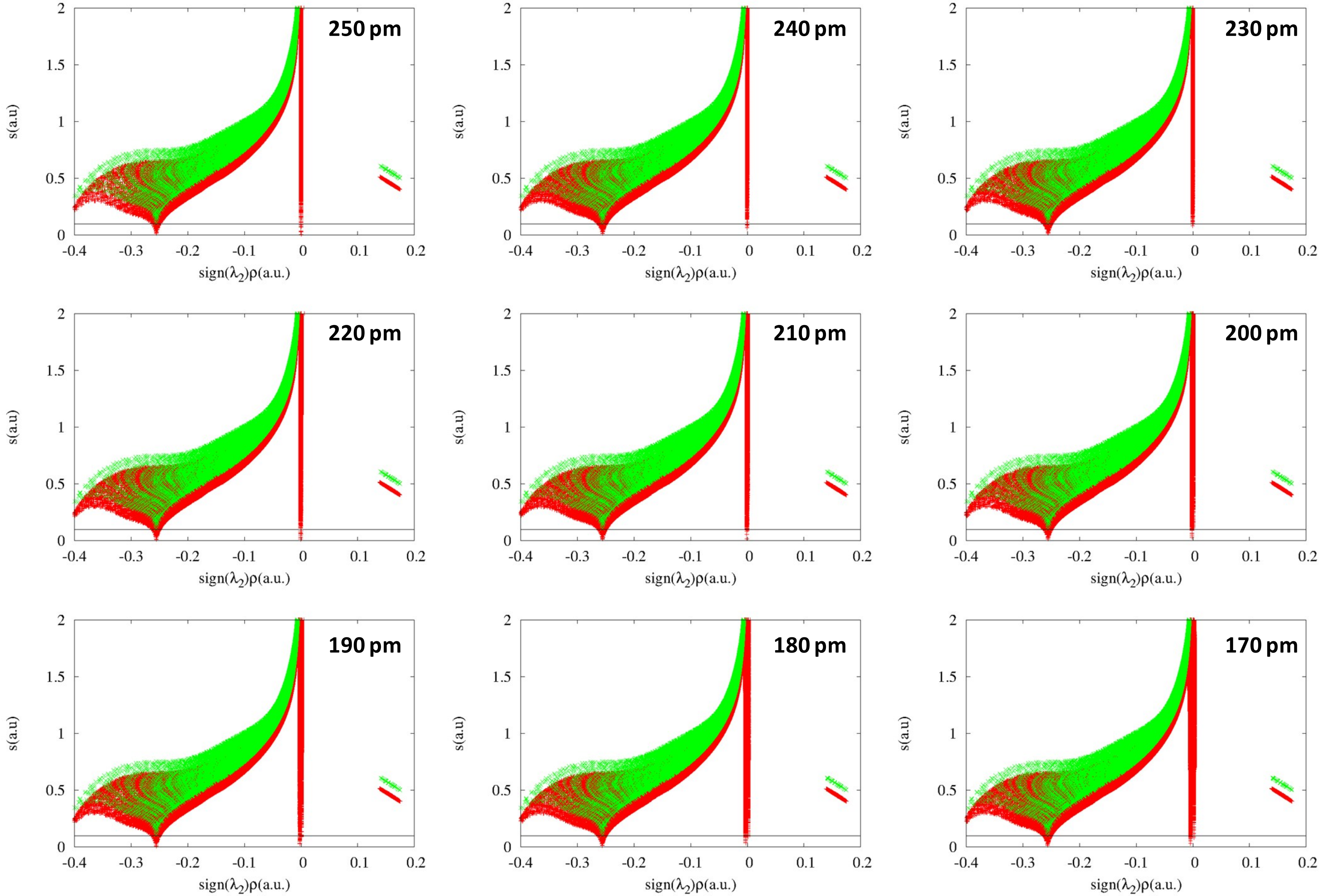
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220 pm
210 pm
200 pm
190 pm
180 pm
170 pm
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0.5
1
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2
sign(λ_2)ρ(a.u.)
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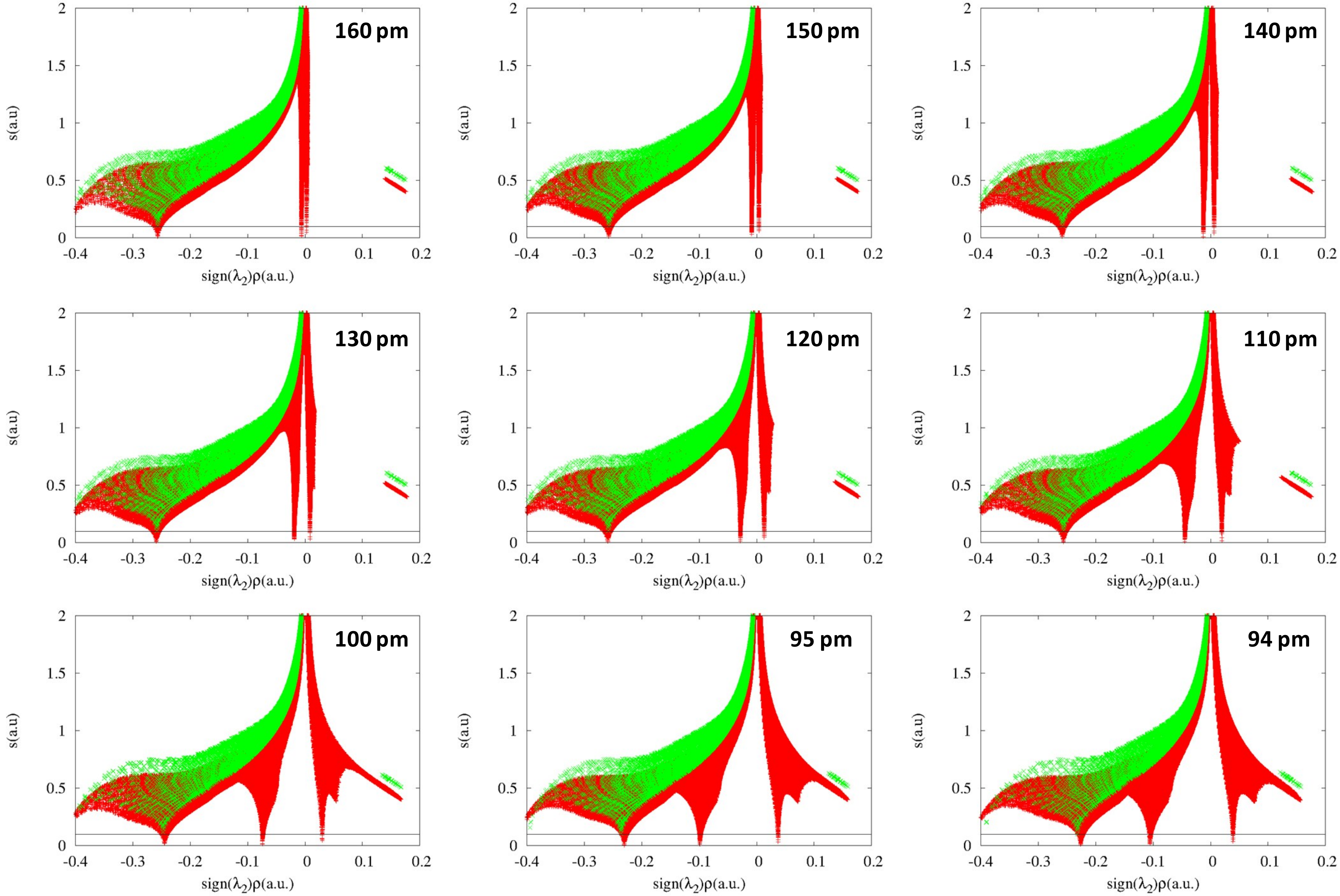
-0.3
-0.2
-0.1
0
0.1
0.2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95 pm
94 pm
s(a.u)
sign(λ2)ρ(a.u.)
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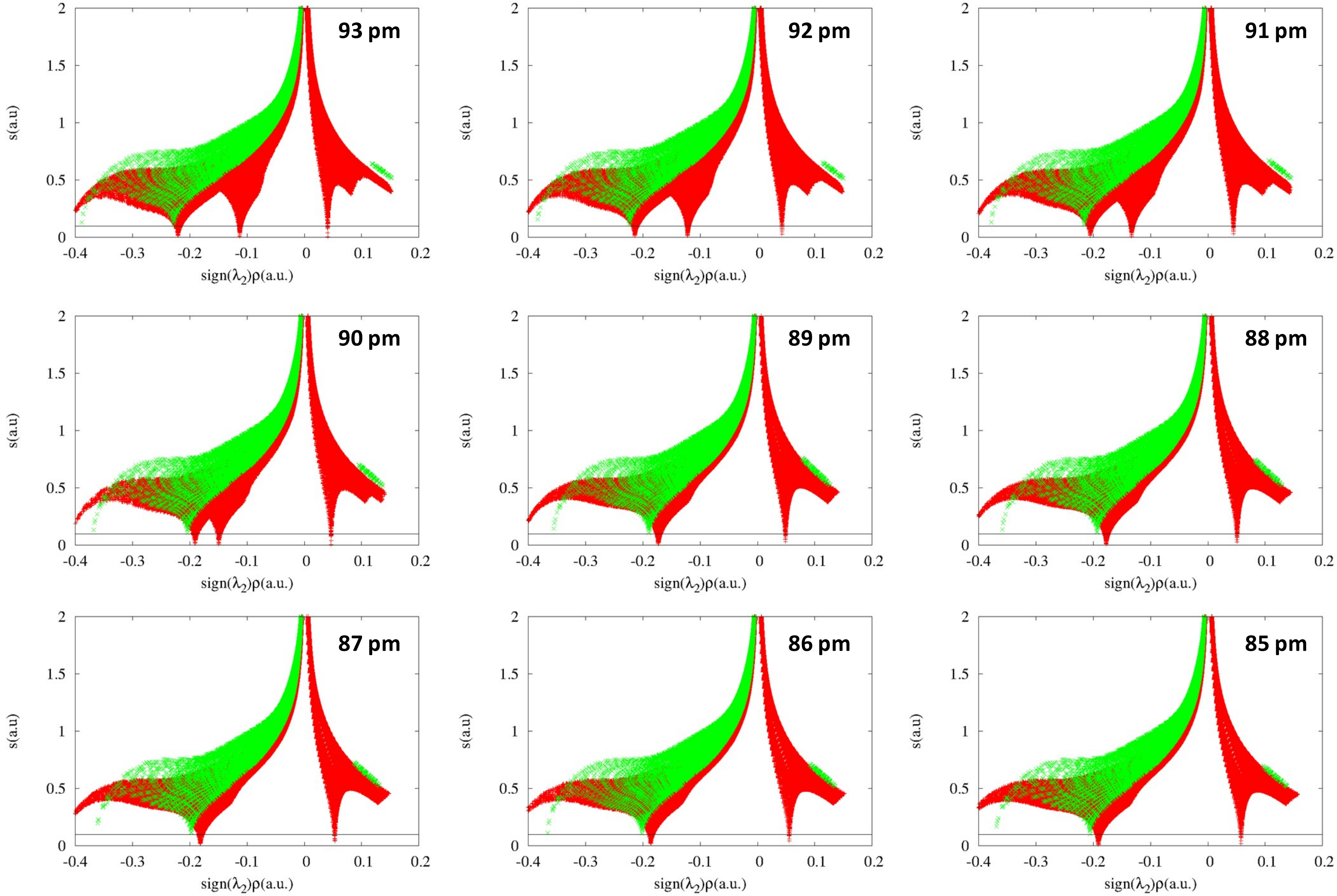
0.5
1
1.5
2
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2


93 pm
92 pm
91 pm
90 pm
89 pm
88 pm
87 pm
86 pm
85 pm
s(a.u)
sign(λ_2)ρ(a.u.)
0
0.5
1
1.5
2
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2

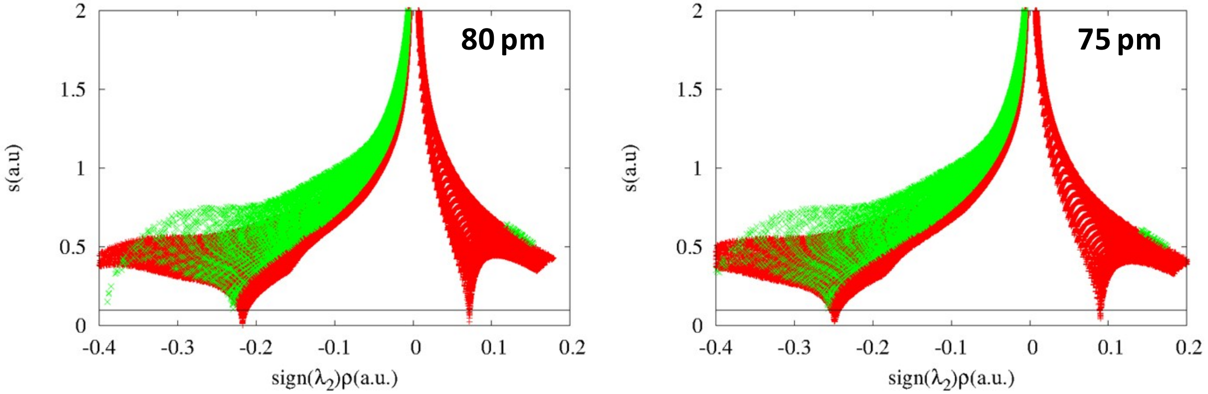


Figure S2. Superposition of plots s(ρ), those of $3H_2$ molecule model in red and those of isolated H_2 extracted from $3H_2$ in green. For the sake of clarity, the y-axis is shift of +0.1 a.u for the plot of isolated H_2.

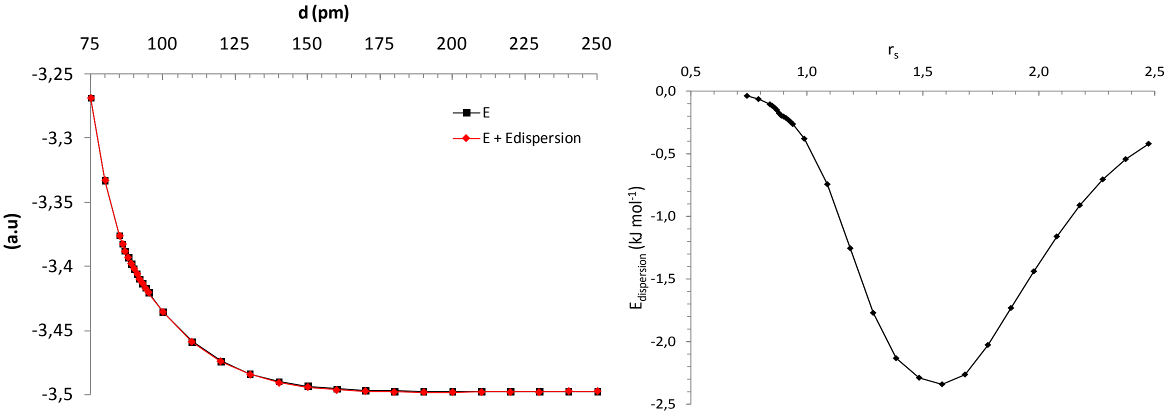


Figure S3. a) Energy evolution of $3H_2$ molecular model without and with the dispersion correction under compression. b) Dispersion energy as a function of r_s.

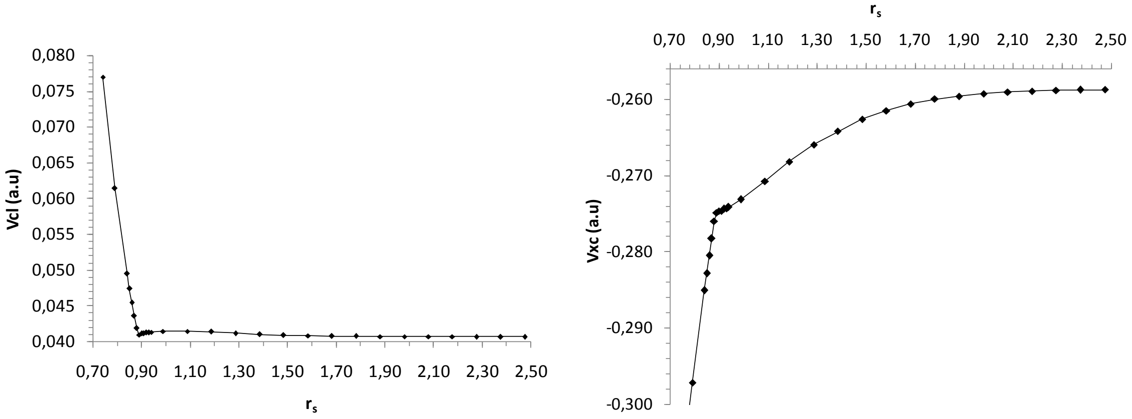

a)
b)

Figure S4. a) Total exchange-correlation (covalent-like) interaction energy for H_1. b) Total classical ionic-like interaction energy for H_1.

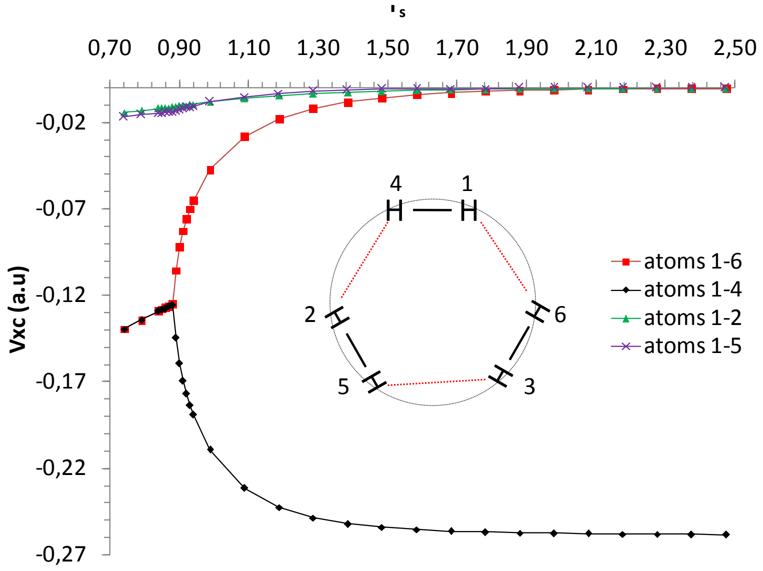


Figure S5. Exchange-correlation (covalent-like) interaction energies between atoms H_1-H_4, H_1-H_6, H_1-H_2 and H_1-H_5.

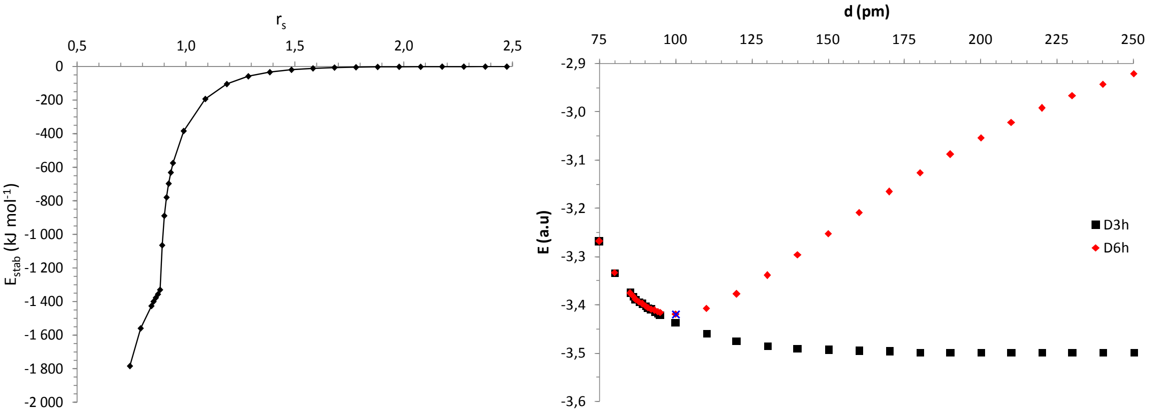


Figure S6. a) Evolution of the stabilization energy due to the electron delocalization within ring of 3 H_2 molecules as a function of r_s. b) Energy evolution of ring of three H_2 molecules at the imposed D_{3h} and D_{6h} symmetry point-group in black and red, respectively. The blue cross correspond to unconstraint H_6 system.

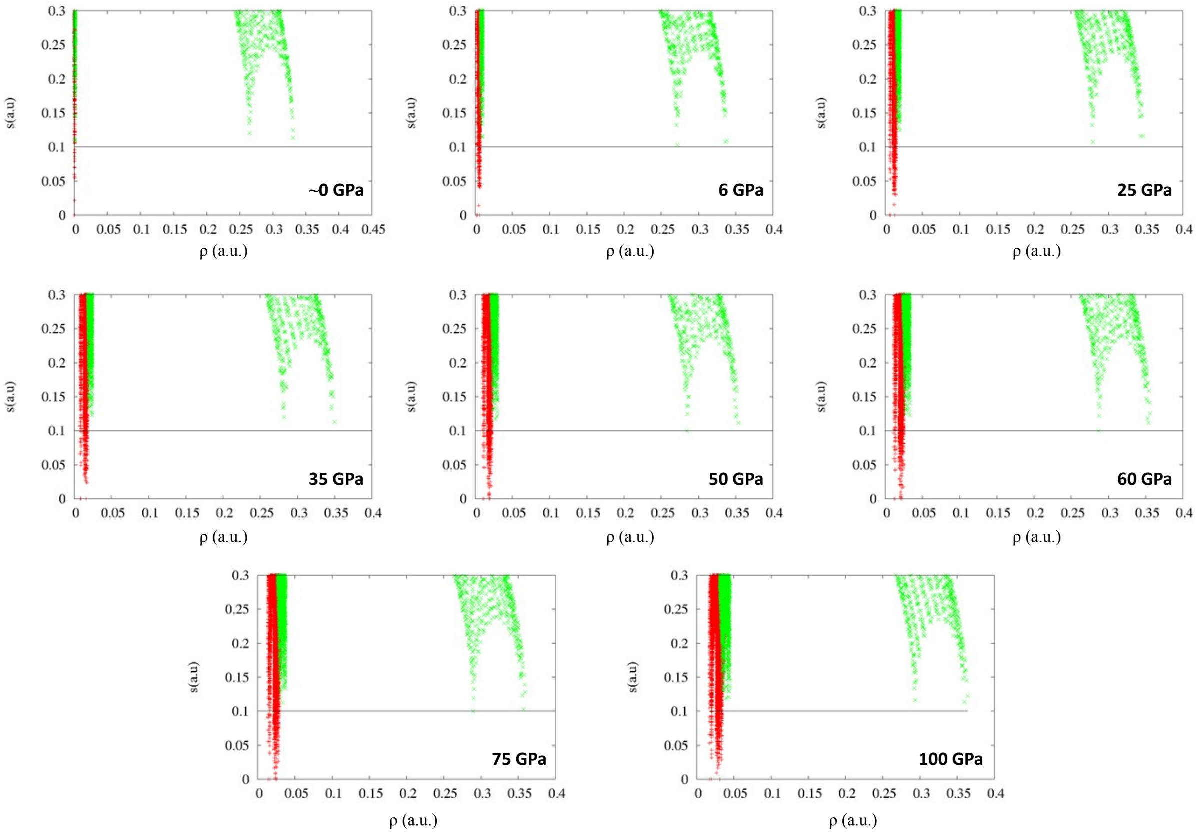
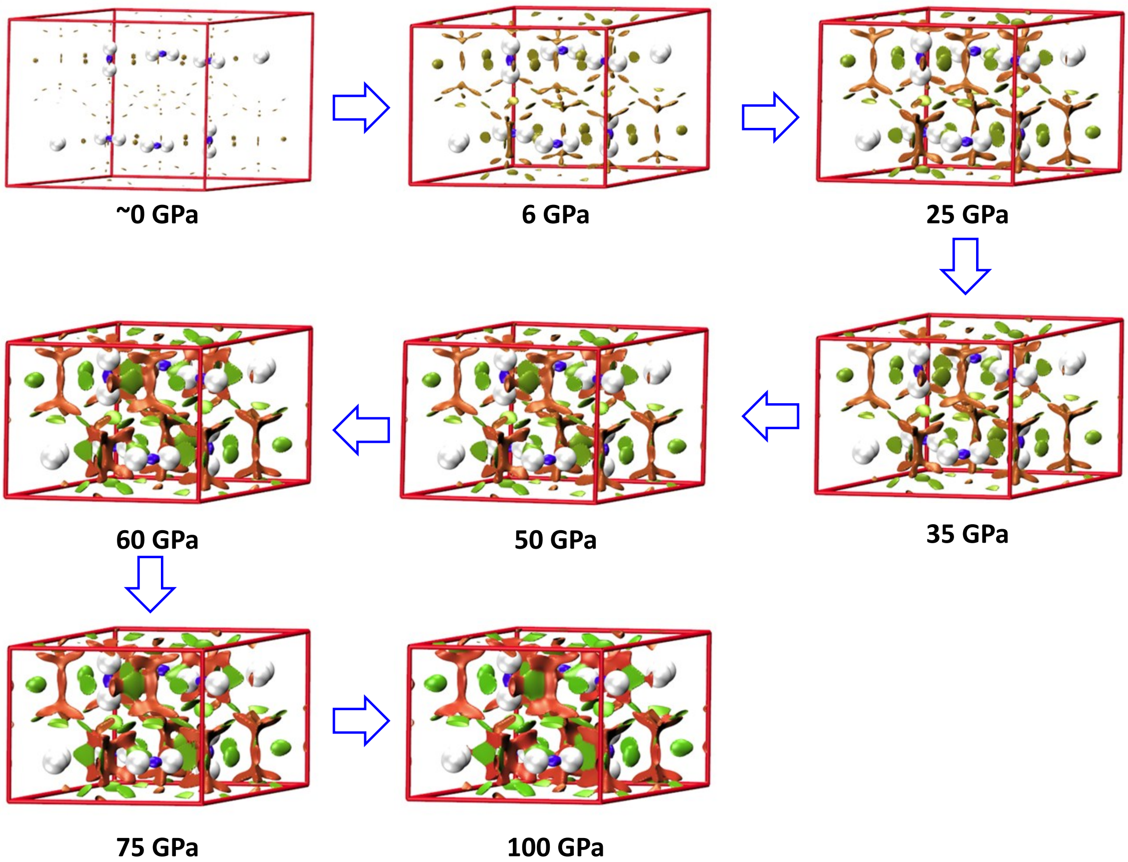


Figure S7. Plots of s(ρ) for the P6$_3$/m phase at 1 atm, 6, 25, 35, 50, 60, 75 and 100 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.



~0 GPa

6 GPa

25 GPa

35 GPa

50 GPa

60 GPa

75 GPa

100 GPa

Figure S8. NCI isosurfaces at different pressures for the P63/m phase using s = 0.2 a.u and colored over the range -0.20 < sign(λ_2)ρ < 0.05 a.u.

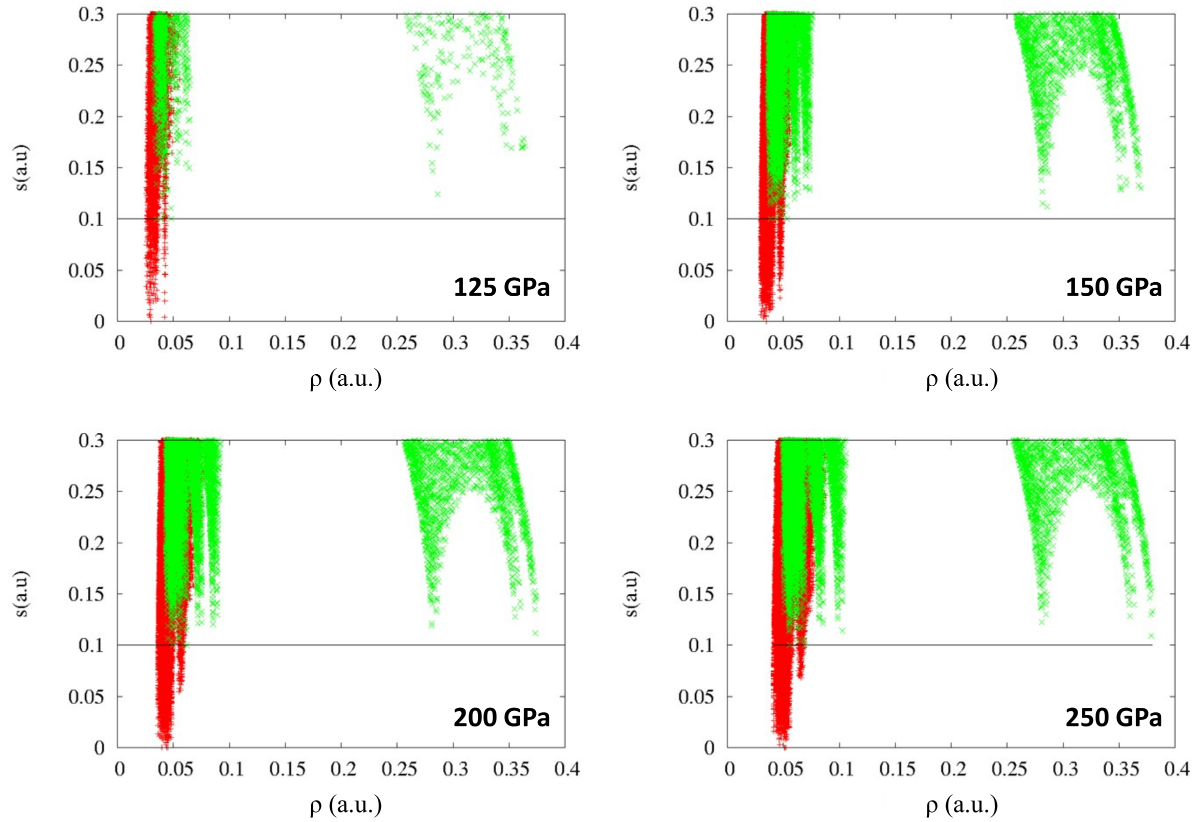


Figure S9. Plots of s(ρ) for the C2/c phase at 125, 150, 200 and 250 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

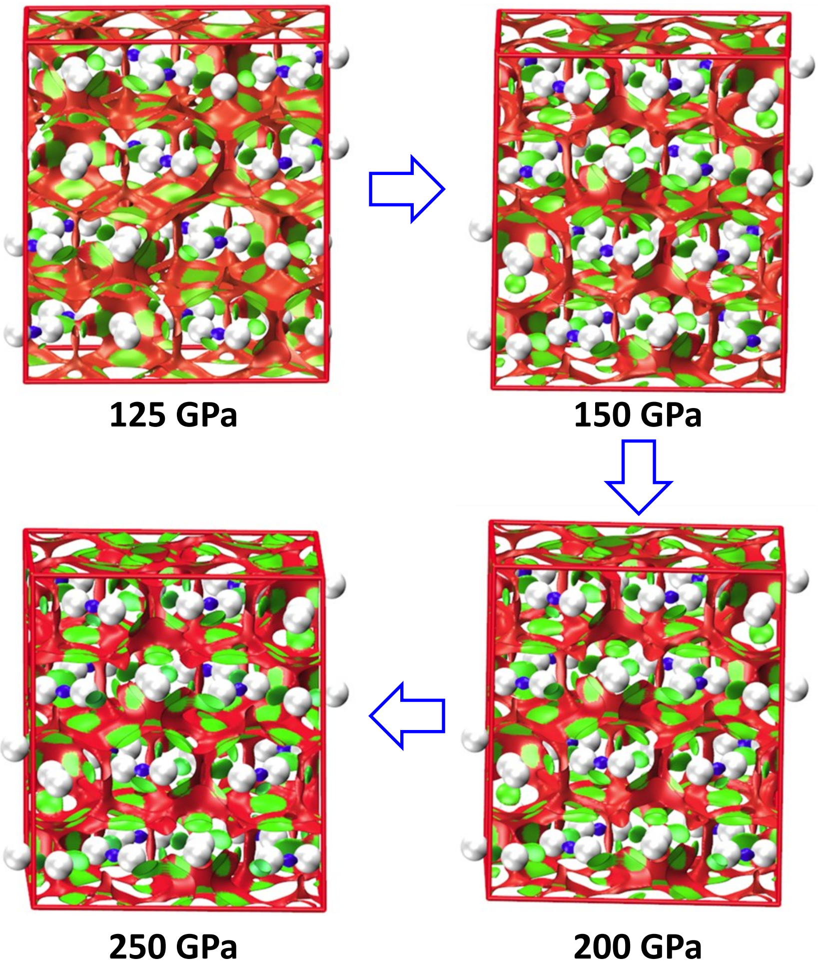


Figure S10. NCI isosurfaces at different pressures for the C2/c phase using s = 0.2 a.u and colored over the range $-0.20 < \text{sign}(\lambda_2)\rho < 0.05$ a.u.

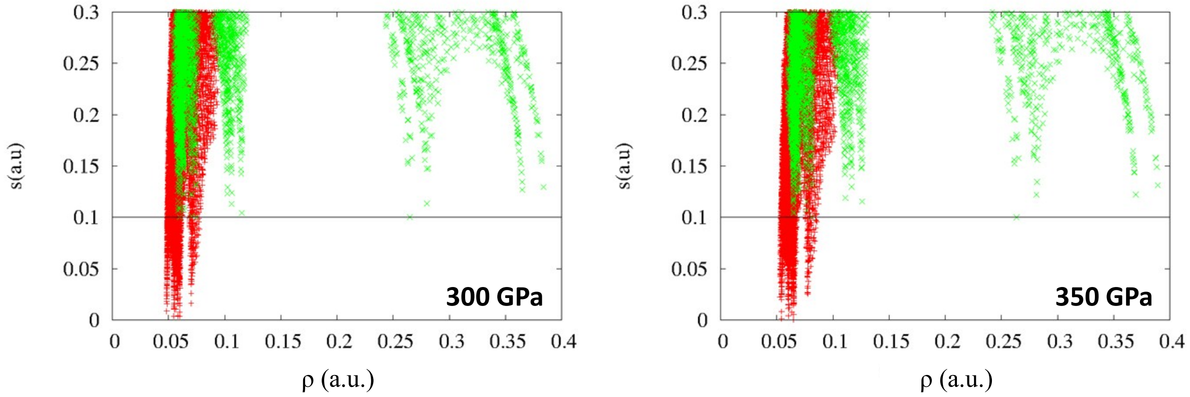


Figure S11. Plots of s(ρ) for the Cmca-12 phase at 300 and 350 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

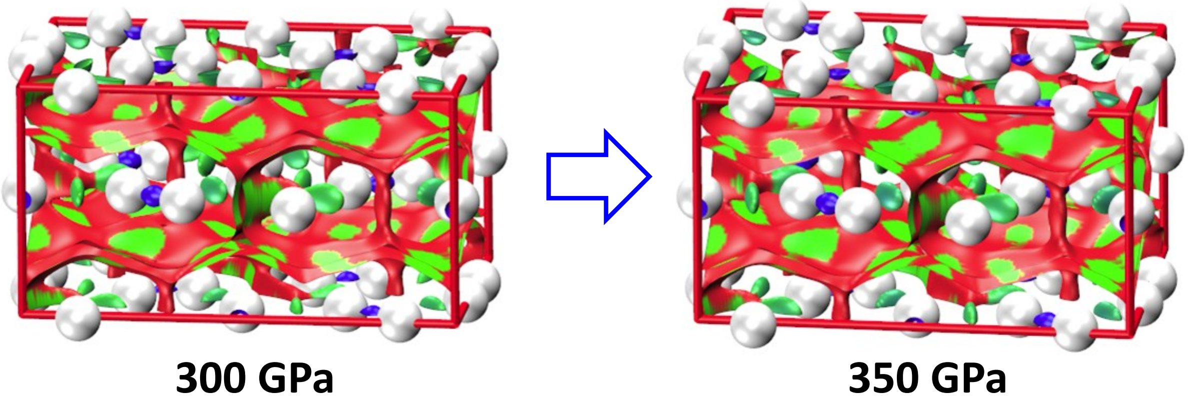


Figure S12. NCI isosurfaces at different pressures for the Cmca-12 phase using s = 0.2 a.u and colored over the range -0.20 < sign(λ_2)ρ < 0.05 a.u.

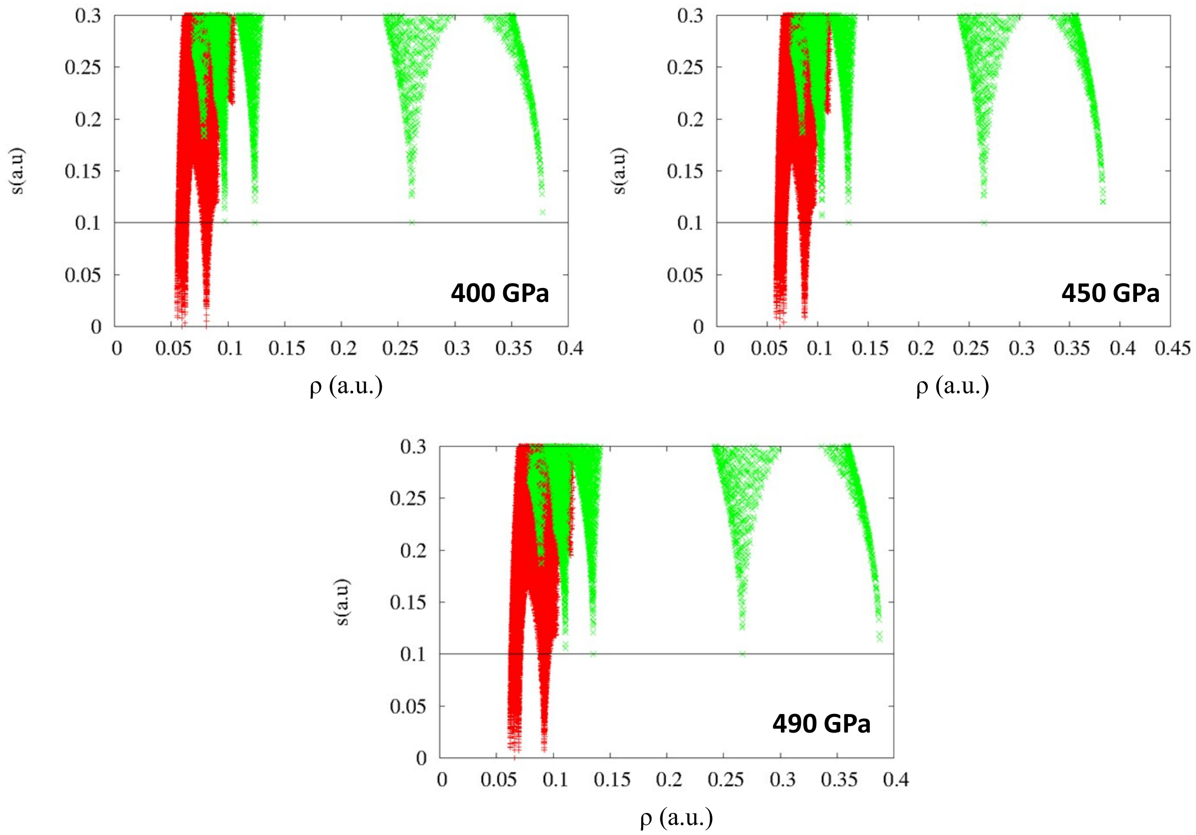


Figure S13. Plots of s(ρ) for the Cmca phase at 400, 450 and 490 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

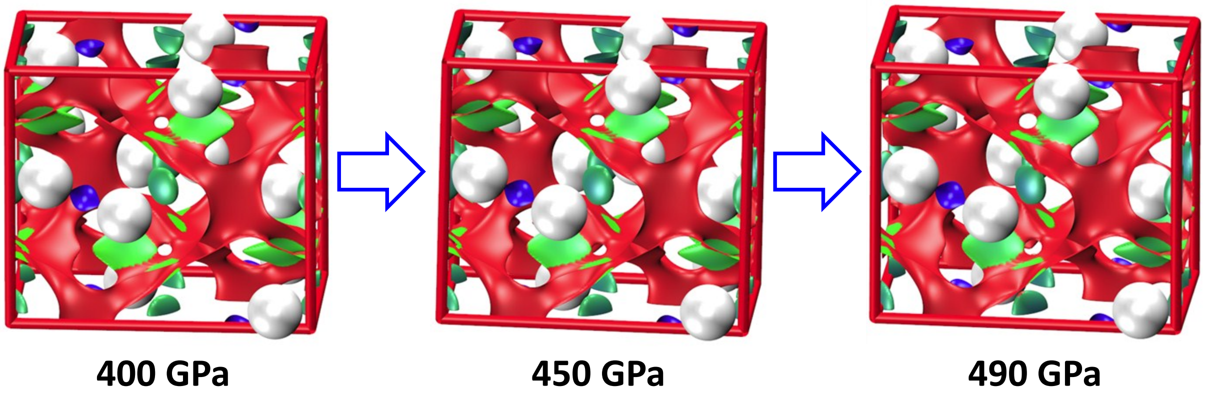


Figure S14. NCI isosurfaces at different pressures for the Cmca phase using $s = 0.2$ a.u and colored over the range $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u.

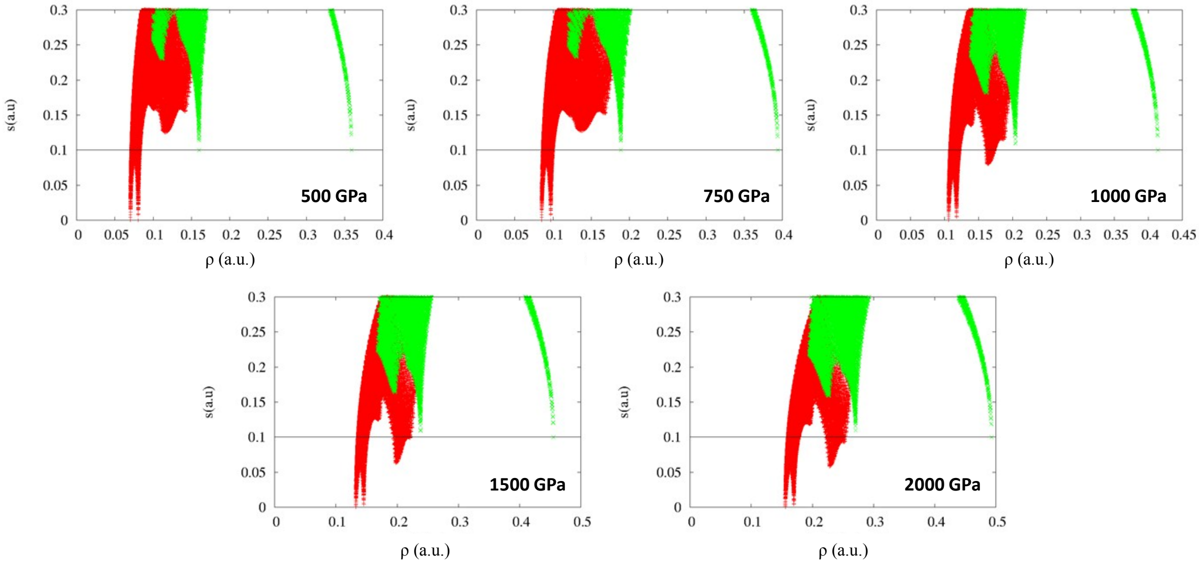


Figure S15. Plots of s(ρ) for the $I4_1/amd$ phase at 500, 750, 1000, 1500 and 2000 GPa using the following: $\lambda_2 < 0$ in green and $\lambda_2 > 0$ in red. For the sake of clarity, the y-axis for $\lambda_2 < 0$ is shift of +0.1 a.u.

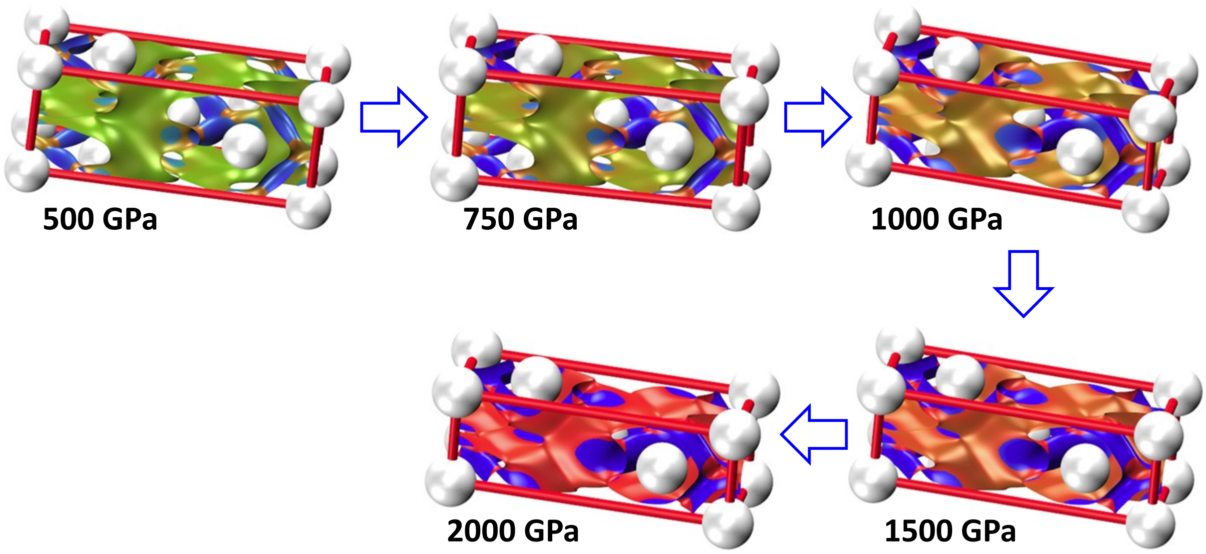


Figure S16. NCI isosurfaces at different pressures for the $I4_1/amd$ phase using s = 0.2 a.u and colored over the range $-0.20 < \text{sign}(\lambda_2)\rho < 0.20$ a.u.

Table S3. Structures of the solid phases.

Space group (n°) #atoms	Pressure (GPa)	Lattice parameters (Å, °)	Atomic coordinates[1] (fractional)
$P6_3/m$ (176) 16	1 atm	a=b=6.875 c=5.775 α=β=90.00 γ=120.00	H1 0.4461 0.6471 0.2500 H2 0.4788 0.1186 0.2500 H3 0.5833 0.4167 0.6850
	5	a=b=5.176 c=4.369 α=β=90.00 γ=120.00	H1 0.4426 0.6601 0.2500 H2 0.5059 0.1241 0.2500 H3 0.5833 0.4167 0.6646
	6	a=b=5.094 c=4.155 α=β=90.00 γ=120.00	H1 0.4443 0.6597 0.2500 H2 0.5091 0.1274 0.2500 H3 0.5833 0.4167 0.6602
	25	a=b=4.439 c=3.598 α=β=90.00 γ=120.00	H1 0.4507 0.6743 0.2500 H2 0.5181 0.1327 0.2500 H3 0.5833 0.4167 0.6470
	35	a=b=4.275 c=3.447 α=β=90.00 γ=120.00	H1 0.4481 0.6737 0.2500 H2 0.5255 0.1344 0.2500 H3 0.5833 0.4167 0.6427
	50	a=b=4.102 c=3.294 α=β=90.00 γ=120.00	H1 0.4483 0.6767 0.2500 H2 0.5304 0.1363 0.2500 H3 0.5833 0.4167 0.6380
	60	a=b=4.014 c=3.217 α=β=90.00 γ=120.00	H1 0.4488 0.6783 0.2500 H2 0.5329 0.1370 0.2500 H3 0.5833 0.4167 0.6356
	75	a=b=3.908 c=3.123 α=β=90.00 γ=120.00	H1 0.4489 0.6805 0.2500 H2 0.5361 0.1383 0.2500 H3 0.5833 0.4167 0.6323
	100	a=b=3.770 c=3.002 α=β=90.00 γ=120.00	H1 0.4484 0.6823 0.2500 H2 0.5417 0.1400 0.2500 H3 0.5833 0.4167 0.6280

C2/c (15) 48	125	a=3.189 b=5.518 c=6.526 α=γ=90.00 β=119.22	H1 0.0477 0.8329 0.3797 H2 0.9539 0.9538 0.3879 H3 0.9079 0.2225 0.3743 H4 0.0455 0.3309 0.3754 H5 0.7855 0.5884 0.3707 H6 0.5078 0.0715 0.3621
	150	a=3.115 b=5.387 c=6.364 α=γ=90.00 β=119.38	H1 0.5432 0.1713 0.3705 H2 0.4280 0.0473 0.3607 H3 0.9101 0.2768 0.3756 H4 0.0485 0.1649 0.3749 H5 0.7851 0.9119 0.3790 H6 0.0326 0.9284 0.3893
	200	a=2.999 b=5.185 c=6.115 α=γ=90.00 β=119.22	H1 0.4510 0.1771 0.3791 H2 0.5711 0.0475 0.3897 H3 0.0902 0.2763 0.3742 H4 0.9462 0.1594 0.3752 H5 0.2267 0.9122 0.3714 H6 0.9681 0.9289 0.3603
	250	a=2.911 b=5.033 c=5.928 α=γ=90.00 β=119.57	H1 0.8019 0.1812 0.3712 H2 0.6804 0.0467 0.3608 H3 0.1589 0.2763 0.3765 H4 0.3075 0.1560 0.3741 H5 0.0162 0.9124 0.3787 H6 0.2823 0.9300 0.3888
Cmca-12 (64) 24	300	a=2.558 b=4.755 c=2.870 α=β=γ=90.00	H1 1.0000 0.0037 0.1349 H2 0.0000 0.1318 0.4545 H3 0.0000 0.2675 0.3169
	350	a=2.499 b=4.653 c=2.816 α=β=γ=90.00	H1 0.5000 0.0051 0.6381 H2 0.5000 0.1314 0.9541 H3 0.5000 0.2709 0.8154
Cmca (64) 8	400	a=1.568 b=2.719 c=2.409 α=β=γ=90.00	H1 0.5000 0.3687 0.9348
	450	a=1.542 b=2.683 c=2.363 α=β=γ=90.00	H1 0.5000 0.3676 0.9330
	490	a=1.522 b=2.659 c=2.332 α=β=γ=90.00	H1 0.5000 0.3672 0.9304
$I4_1$/amd (141) 4	500	a=b=1.216 c=3.091 α=β=γ=90.00	H1 0.5000 0.5000 0.5000
	750	a=b=1.158 c=2.891 α=β=γ=90.00	H1 0.5000 0.5000 0.5000
	1000	a=b=1.073 c=2.954 α=β=γ=90.00	H1 0.5000 0.5000 0.5000
	1500	a=b=1.001 c=2.851 α=β=γ=90.00	H1 0.5000 0.5000 0.5000
	2000	a=b=0.956 c=2.737 α=β=γ=90.00	H1 0.5000 0.5000 0.5000

[1] Fractional coordinates of symmetry non-equivalent atoms.

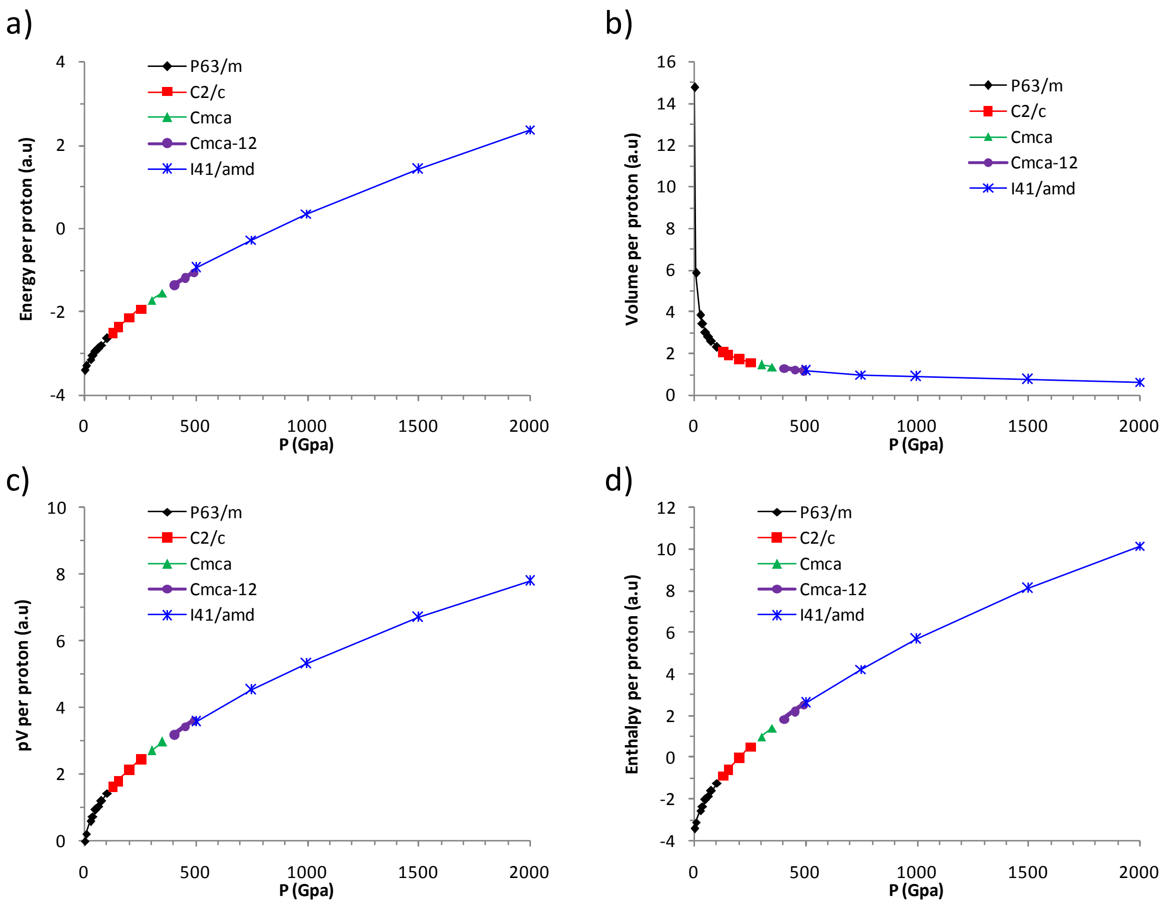


Figure S17. Evolution of a) the energy per proton, b) volume per proton, c) pV per proton term and d) the enthalpy per proton as function of the pressure.

Table S4. Cartesian coordinates calculated at the PBEPBE/6-311++G(d,p) level for the $3H_2$ molecule model.

d = 250 pm

H	0.37601700	2.47156000	0.00000000
H	-2.32844300	-0.91014000	0.00000000
H	1.95242500	-1.56142100	0.00000000
H	-0.37601700	2.47156000	0.00000000
H	-1.95242500	-1.56142100	0.00000000
H	2.32844300	-0.91014000	0.00000000

d = 240 pm

H	0.37602100	2.37036000	0.00000000
H	-2.24080300	-0.85953700	0.00000000
H	1.86478200	-1.51082400	0.00000000
H	-0.37602100	2.37036000	0.00000000
H	-1.86478200	-1.51082400	0.00000000
H	2.24080300	-0.85953700	0.00000000

d = 230 pm

H	0.37602100	2.26905500	0.00000000
H	-2.15306900	-0.80888400	0.00000000
H	1.77704800	-1.46017100	0.00000000
H	-0.37602100	2.26905500	0.00000000
H	-1.77704800	-1.46017100	0.00000000
H	2.15306900	-0.80888400	0.00000000

d = 220 pm

H	0.37601100	2.16762900	0.00000000
H	-2.06522700	-0.75817900	0.00000000
H	1.68921600	-1.40945000	0.00000000
H	-0.37601100	2.16762900	0.00000000
H	-1.68921600	-1.40945000	0.00000000
H	2.06522700	-0.75817900	0.00000000

d = 210 pm

H	0.37598800	2.06606700	0.00000000
H	-1.97726000	-0.70741900	0.00000000
H	1.60127300	-1.35864800	0.00000000
H	-0.37598800	2.06606700	0.00000000
H	-1.60127300	-1.35864800	0.00000000
H	1.97726000	-0.70741900	0.00000000

d = 200 pm

H	0.37593600	1.96435000	0.00000000
H	-1.88914500	-0.65660500	0.00000000
H	1.51320900	-1.30774500	0.00000000

H	-0.37593600	1.96435000	0.00000000
H	-1.51320900	-1.30774500	0.00000000
H	1.88914500	-0.65660500	0.00000000

d = 190 pm

H	0.37585200	1.86245400	0.00000000
H	-1.80085900	-0.60573000	0.00000000
H	1.42500600	-1.25672500	0.00000000
H	-0.37585200	1.86245400	0.00000000
H	-1.42500600	-1.25672500	0.00000000
H	1.80085900	-0.60573000	0.00000000

d = 180 pm

H	0.37570700	1.76035300	0.00000000
H	-1.71236400	-0.55480500	0.00000000
H	1.33665700	-1.20554900	0.00000000
H	-0.37570700	1.76035300	0.00000000
H	-1.33665700	-1.20554900	0.00000000
H	1.71236400	-0.55480500	0.00000000

d = 170 pm

H	0.37549500	1.65801200	0.00000000
H	-1.62362800	-0.50381800	0.00000000
H	1.24813300	-1.15419400	0.00000000
H	-0.37549500	1.65801200	0.00000000
H	-1.24813300	-1.15419400	0.00000000
H	1.62362800	-0.50381800	0.00000000

d = 160 pm

H	0.37517300	1.55539200	0.00000000
H	-1.53459600	-0.45278700	0.00000000
H	1.15942300	-1.10260600	0.00000000
H	-0.37517300	1.55539200	0.00000000
H	-1.15942300	-1.10260600	0.00000000
H	1.53459600	-0.45278700	0.00000000

d = 150 pm

H	0.37472300	1.45244000	0.00000000
H	-1.44521200	-0.40170100	0.00000000
H	1.07048900	-1.05073900	0.00000000
H	-0.37472300	1.45244000	0.00000000
H	-1.07048900	-1.05073900	0.00000000
H	1.44521200	-0.40170100	0.00000000

d = 140 pm

H	0.37416900	1.34907300	0.00000000
H	-1.35541600	-0.35049600	0.00000000

H	0.98124700	-0.99857600	0.00000000
H	-0.37416900	1.34907300	0.00000000
H	-0.98124700	-0.99857600	0.00000000
H	1.35541600	-0.35049600	0.00000000

d = 130 pm

H	0.37368300	1.24513500	0.00000000
H	-1.26516000	-0.29894800	0.00000000
H	0.89147700	-0.94618700	0.00000000
H	-0.37368300	1.24513500	0.00000000
H	-0.89147700	-0.94618700	0.00000000
H	1.26516000	-0.29894800	0.00000000

d = 120 pm

H	0.37376600	1.14030600	0.00000000
H	-1.17441700	-0.24646200	0.00000000
H	0.80065100	-0.89384400	0.00000000
H	-0.37376600	1.14030600	0.00000000
H	-0.80065100	-0.89384400	0.00000000
H	1.17441700	-0.24646200	0.00000000

d = 110 pm

H	0.37569900	1.03385200	0.00000000
H	-1.08319200	-0.19156200	0.00000000
H	0.70749300	-0.84229100	0.00000000
H	-0.37569900	1.03385200	0.00000000
H	-0.70749300	-0.84229100	0.00000000
H	1.08319200	-0.19156200	0.00000000

d = 100 pm

H	0.38332900	0.92361200	0.00000000
H	-0.99153600	-0.12983400	0.00000000
H	0.60820700	-0.79377800	0.00000000
H	-0.38332900	0.92361200	0.00000000
H	-0.60820700	-0.79377800	0.00000000
H	0.99153600	-0.12983400	0.00000000

d = 95 pm

H	0.39363400	0.86461100	0.00000000
H	-0.94559200	-0.09140800	0.00000000
H	0.55195800	-0.77320300	0.00000000
H	-0.39363400	0.86461100	0.00000000
H	-0.55195800	-0.77320300	0.00000000
H	0.94559200	-0.09140800	0.00000000

d = 94 pm

H	0.39700300	0.85205000	0.00000000

H	-0.93639800	-0.08221000	0.00000000
H	0.53939500	-0.76983900	0.00000000
H	-0.39700300	0.85205000	0.00000000
H	-0.53939500	-0.76983900	0.00000000
H	0.93639800	-0.08221000	0.00000000

d = 93 pm

H	0.40118400	0.83901800	0.00000000
H	-0.92720300	-0.07207300	0.00000000
H	0.52601900	-0.76694500	0.00000000
H	-0.40118400	0.83901800	0.00000000
H	-0.52601900	-0.76694500	0.00000000
H	0.92720300	-0.07207300	0.00000000

d = 92 pm

H	0.40659600	0.82527600	0.00000000
H	-0.91800800	-0.06051600	0.00000000
H	0.51141200	-0.76476000	0.00000000
H	-0.40659600	0.82527600	0.00000000
H	-0.51141200	-0.76476000	0.00000000
H	0.91800800	-0.06051600	0.00000000

d = 91 pm

H	0.41414400	0.81029900	0.00000000
H	-0.90881200	-0.04649000	0.00000000
H	0.49466700	-0.76380900	0.00000000
H	-0.41414400	0.81029900	0.00000000
H	-0.49466700	-0.76380900	0.00000000
H	0.90881200	-0.04649000	0.00000000

d = 90 pm

H	0.42695800	0.79228000	0.00000000
H	-0.89961300	-0.02638400	0.00000000
H	0.47265600	-0.76589600	0.00000000
H	-0.42695800	0.79228000	0.00000000
H	-0.47265600	-0.76589600	0.00000000
H	0.89961300	-0.02638400	0.00000000

d = 89 pm

H	0.44452100	0.77103900	0.00000000
H	-0.89000000	-0.00055300	0.00000000
H	0.44547900	-0.77048600	0.00000000
H	-0.44452100	0.77103900	0.00000000
H	-0.44547900	-0.77048600	0.00000000
H	0.89000000	-0.00055300	0.00000000

d = 88 pm

H	0.43988300	0.76217000	0.00000000
H	0.44011700	-0.76203500	0.00000000
H	-0.88000000	-0.00013500	0.00000000
H	0.88000000	-0.00013500	0.00000000
H	-0.44011700	-0.76203500	0.00000000
H	-0.43988300	0.76217000	0.00000000

d = 87 pm

H	0.43472600	0.75360000	0.00000000
H	-0.87000000	-0.00031700	0.00000000
H	0.43527400	-0.75328400	0.00000000
H	-0.43472600	0.75360000	0.00000000
H	-0.43527400	-0.75328400	0.00000000
H	0.87000000	-0.00031700	0.00000000

d = 86 pm

H	0.42972900	0.74493800	0.00000000
H	-0.86000000	-0.00031300	0.00000000
H	0.43027100	-0.74462500	0.00000000
H	-0.42972900	0.74493800	0.00000000
H	-0.43027100	-0.74462500	0.00000000
H	0.86000000	-0.00031300	0.00000000

d = 85 pm

H	0.42491900	0.73616900	0.00000000
H	-0.85000000	-0.00009400	0.00000000
H	0.42508100	-0.73607500	0.00000000
H	-0.42491900	0.73616900	0.00000000
H	-0.42508100	-0.73607500	0.00000000
H	0.85000000	-0.00009400	0.00000000

d = 80 pm

H	0.39998200	0.69283100	0.00000000
H	-0.80000000	-0.00002100	0.00000000
H	0.40001800	-0.69281000	0.00000000
H	-0.39998200	0.69283100	0.00000000
H	-0.40001800	-0.69281000	0.00000000
H	0.80000000	-0.00002100	0.00000000

d = 75 pm

H	0.37498300	0.64952900	0.00000000
H	-0.75000000	-0.00002000	0.00000000
H	0.37501700	-0.64950900	0.00000000
H	-0.37498300	0.64952900	0.00000000
H	-0.37501700	-0.64950900	0.00000000
H	0.75000000	-0.00002000	0.00000000

Structural description of solid phases

An arrangement in an *ABA* stacking is observed for the P63/m, Cmca-12 and Cmca phases in their pressure range of stability while that of C2/c is an *ABCDA* stacking (see **Figure S18**). $I4_1$/amd is a monoatomic phase whose protons are tetra-coordinated. Since each H_2 molecule and/or hydrogen interacts mainly with the nearest neighbors, we have chosen to focus our analyses on the solid phases using the first coordination spheres of each non-equivalent hydrogen. Note that in the $P6_3$/m, C2/c, Cmca-12 and Cmca phases, one hydrogen and its nearest neighbor (nn) form one H_2 molecule. For some structures, the considered farthest neighbors are the next next nearest neighbors (nnnn).

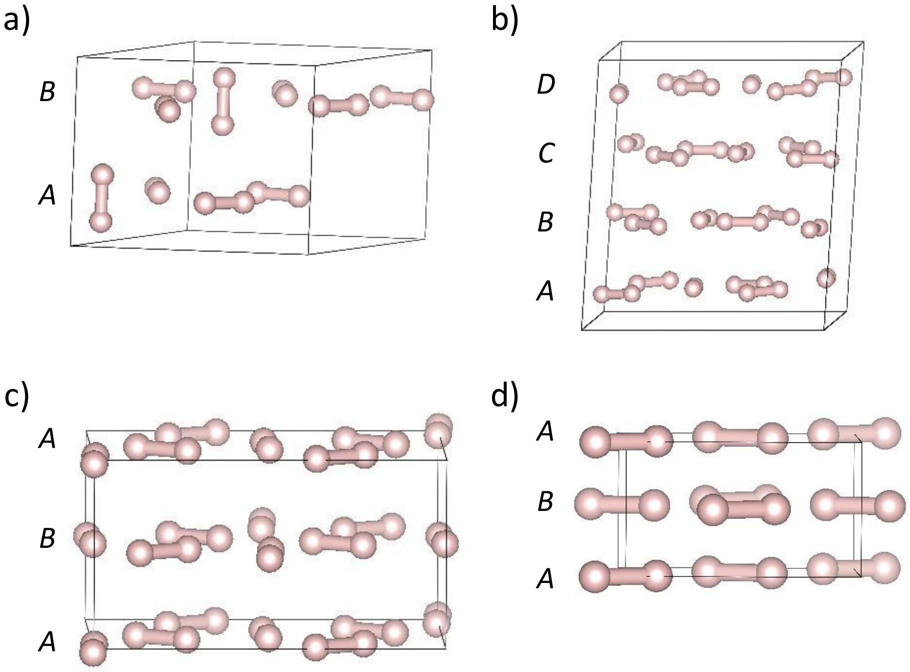


Figure S18. Stack of layers of a) $P6_3$/m, b) C2/c, c) Cmca-12 and d) Cmca.

The hydrogens are mono-coordinated in the $P6_3$/m phase, with two non-equivalent H_2 molecules in the cell. Their intramolecular distances differ slightly, one being 0.7326 Å in the $(\vec{b},\vec{c})$ plane and the other 0.7329 Å in $(\vec{a},\vec{b})$ plane (100 GPa). In the $(\vec{b},\vec{c})$ plane, each hydrogen has three next nearest neighbors (nnn) and also three neighbors in the third coordination sphere (not belonging to the same molecule) as shown in the **Figure 19 a)**. These distances are 1.495 and 1.575 Å, respectively. When considering the H_2 systems in the $(\vec{a},\vec{b})$ plane, the hydrogen atoms in each molecule (**Figure 19 b)**) are surrounded by two (one) second (third) nearest neighbors.

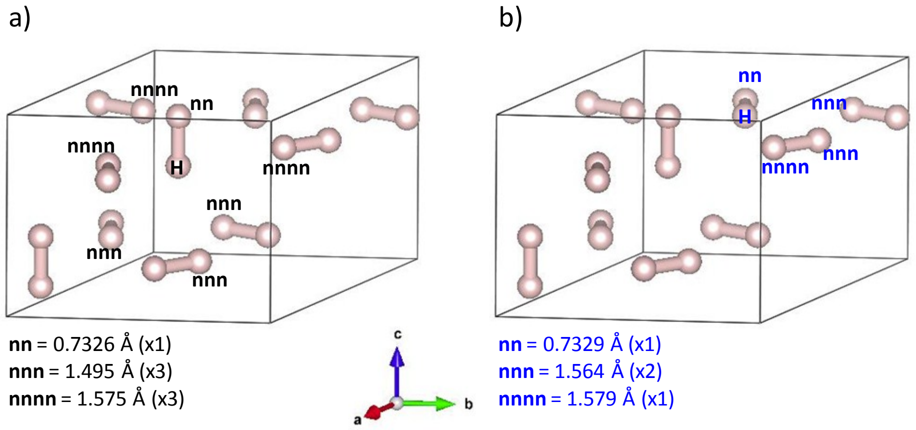


Figure S19. Description of the first coordination spheres of hydrogen, in the P6$_3$/m phase at 100 GPa, for one H_2 system includes a) in the $(\vec{b},\vec{c})$ plane (nn, nnn and nnnn) and b) in the $(\vec{a},\vec{b})$ plane (nn, nnn, nnnn).

In the C2/c phase, there are three non-equivalent H_2 molecules within each layer whose HH lengths are equal to ~0.752 Å for two of them and 0.748 Å for the other one (250 GPa). For the non-equivalent H_2 molecules, each hydrogen has one nearest neighbor as shown in **Figure 20 a)**. When considering all next nearest neighbors, a ring of 3H_2 molecules is found (**Figure 20 b)**).

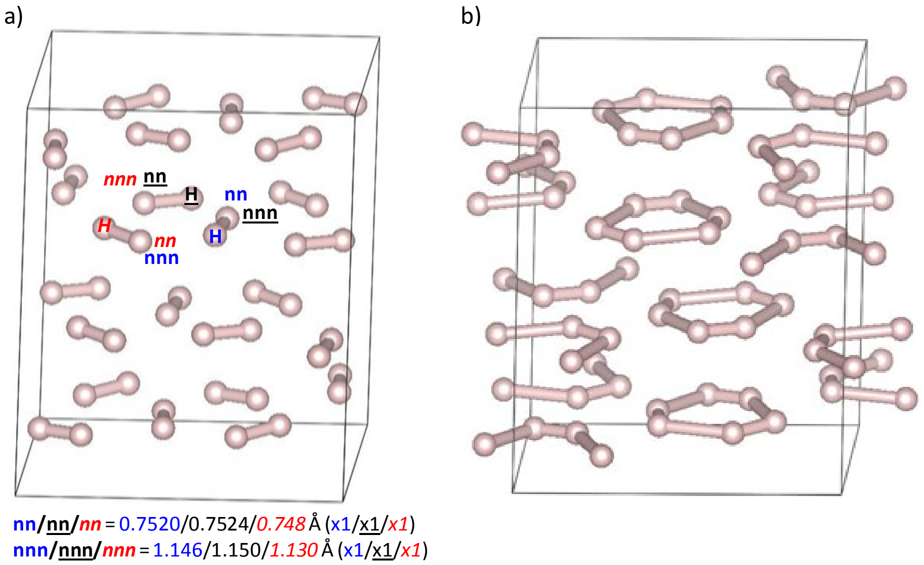
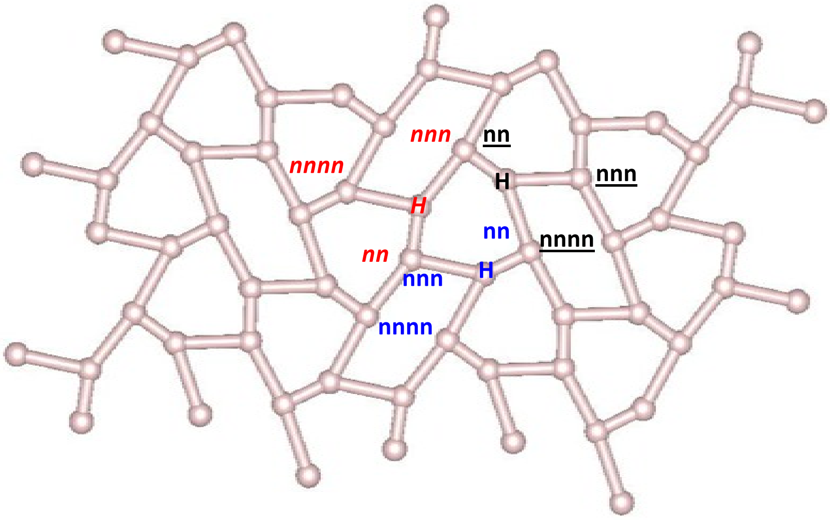


Figure S20. a) Description of the first coordination spheres of hydrogen (nn and nnn), in the C2/c phase at 250 GPa, for the three non-equivalent H_2 systems includes in the same layer. b) Geometric shapes when considering the nearest neighbor and the next nearest neighbor.

Similar to the P6$_3$/m and C2/c phase, hydrogens are also mono-coordinated in the Cmca-12 phase. Two equivalent H_2 systems (0.758 Å) and a non-equivalent one (0.779 Å) are localized in the same layer (350 GPa) as shown in **Figure S21**. In this phase, hydrogen atoms only have one nearest neighbor in its first three coordination spheres (nn, nnn and nnnn).

In its first coordination sphere, hydrogen is mono-coordinated in the Cmca phase, with all H_2 molecules being equivalent (0.777 Å at 350 GPa), as shown in **Figure S22**. Instead, hydrogen is di-coordinated in its second (nnn, 1.036 Å) and third coordination spheres (nnnn, 1.134 Å) in the Cmca-12 phase.



nn = **nn** = 0.758 Å (x1/x1)
nn = 0.779 Å (*x1*)

nnn = **nnn** = ***nnnn*** = 1.097 Å (x1/x1/*x1*)
nnn = 1.066 Å (*x1*)
nnnn = **nnnn** = 1.114 Å (x1/x1)

Figure S21. A layer of Cmca-12 phase at 350 GPa, description of the first coordination spheres of hydrogen (nn, nnn, and nnnn).

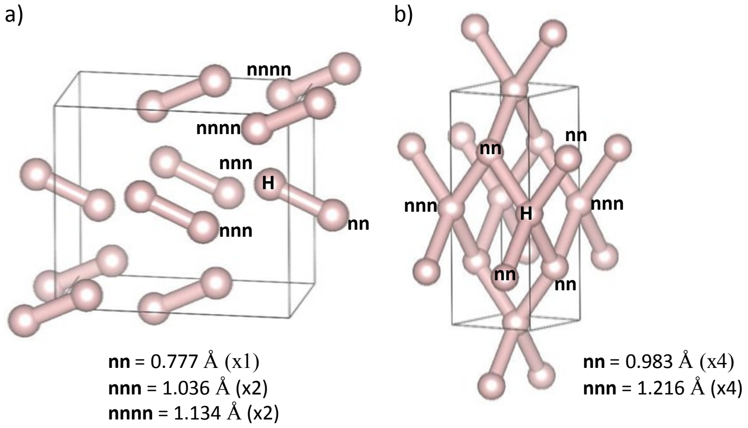


Figure S22. Description of the first coordination spheres of hydrogen, a) in the Cmca phase at 490 GPa (nn, nnn, nnnn) and b) in the $I4_1$/amd phase at 500 GPa (nn, nnn).

Alike the previous phases, $I4_1/amd$ is tetra-coordinated in its first and second coordination sphere (nn and nnn, respectively). For the first nearest neighbor, the corresponding shortest distance is equal to 0.983 Å (500 GPa). The distance of the next nearest neighbors is 1.216 Å.

NCI evolution under pressure

$P6_3/m$, P < 105 GPa.

The two covalent peaks associated with the non-equivalent H_2 molecules overlap at $\rho = 0.293$ a.u. The second nearest neighbors (3) (**Figure S23 a)**) are at a distance of 3.091, 2.159, 1.830, 1.659, 1.563, 1.495 Å at ~0, 6, 25, 50, 75 and 100 GPa, respectively. But the corresponding isosurfaces are not center between these hydrogens because of the polarization effect due to the hydrogen from the same H_2 molecule in the $(\vec{a},\vec{b})$ plane. Furthermore, two hydrogen molecules are forming a T shape in the solid, giving rise to a 3-H interaction (see **Figure S23b)**). Thus, the electron density of the associated BCP for the interaction **A** does not show the highest intermolecular density value (see Figure Y17 c) and d)). Instead, the NCI analysis reveals that the $H{\cdots}H_1H_2$ interaction is the strongest one with $dHH_1 = dHH_2 = 3.146$, 2.228, 1.925, 1.743, 1.647 and 1.575 Å at ~0, 6, 25, 50, 75 and 100 GPa, respectively. This is the reason why we have also chosen to consider this intermolecular interaction in our analysis.

Under pressure all interactions are strengthened. At very low pressure, intermolecular interactions are mainly van der Waals interactions considering the electron densities of associated BCPs very close to 0.0 a.u. The electron densities at 25 GPa have already reached a value of 0.02 a.u.. Thus, the transition van der Waals interactions → "strong" attractive interactions has already occurred (see below part entitled "**Correlation between P and $r_s(3H_2)$**").

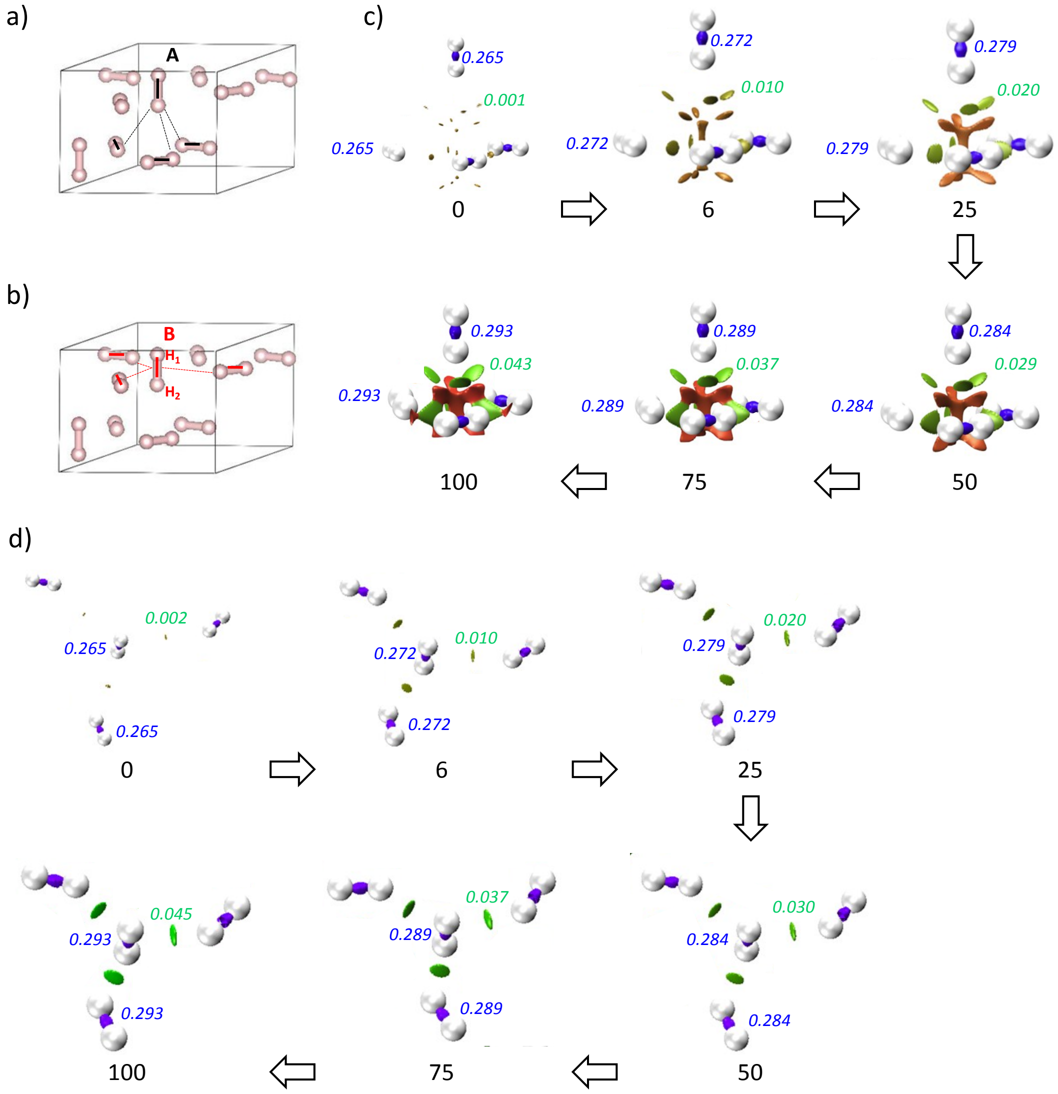


Figure S23. a-b) Main interactions scheme in $P6_3/m$. NCI analysis of c) the shape **A** and d) the shape **B** using s = 0.2 a.u and the following color scale: $-0.20 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

C2/c, 105 GPa < 270 GPa.

The C2/c solid hydrogen contains rings of $3H_2$ molecules as the main molecular motif and unlike our molecular model does not have any particular symmetry (**Figure S24**). Over all, this “$3H_2$” ring has similar interactions as those revealed previously in the isolated system in imposed D_{3h} symmetry. BCPs electron density values reveal that intermolecular interactions in this rings are stronger than the ones existing within the C2/c structure and in agreement with the H···H lengths.

Under compression (125 → 250 GPa), the electron densities at BCPs associated with intermolecular interactions increases from ~0.06 to ~0.10 a.u. The same trend is observed for the BCPs associated with the steric clashes within this irregular ring (0.034 → 0.050 a.u for 125 → 250 GPa).

The NCI analyses reveal also that two successive layers interact together by attractive interactions other than van der Waals. Indeed, (*i*) the electron density of BCP associated to the strongest intermolecular interaction H···H is equal to 0.048, 0.053, 0.062 and 0.069 a.u at 125, 150, 200 and 250 GPa, respectively; and (*ii*) the electron density range of these stabilizing interactions is of [0.035, 0.048], [0.039, 0.053], [0.045, 0.062] and [0.051, 0.069] (a.u), respectively. Note that the interactions between the layer *B* with the top layer *C* (noted *BC*) and the bottom layer *A* (noted *AB*) are non-equivalent because of the nature of the stack (see **Figure S9**). Moreover, intermolecular interactions within *AB* and *CD* are the same nature. Same for those within *BC* and *DA*.

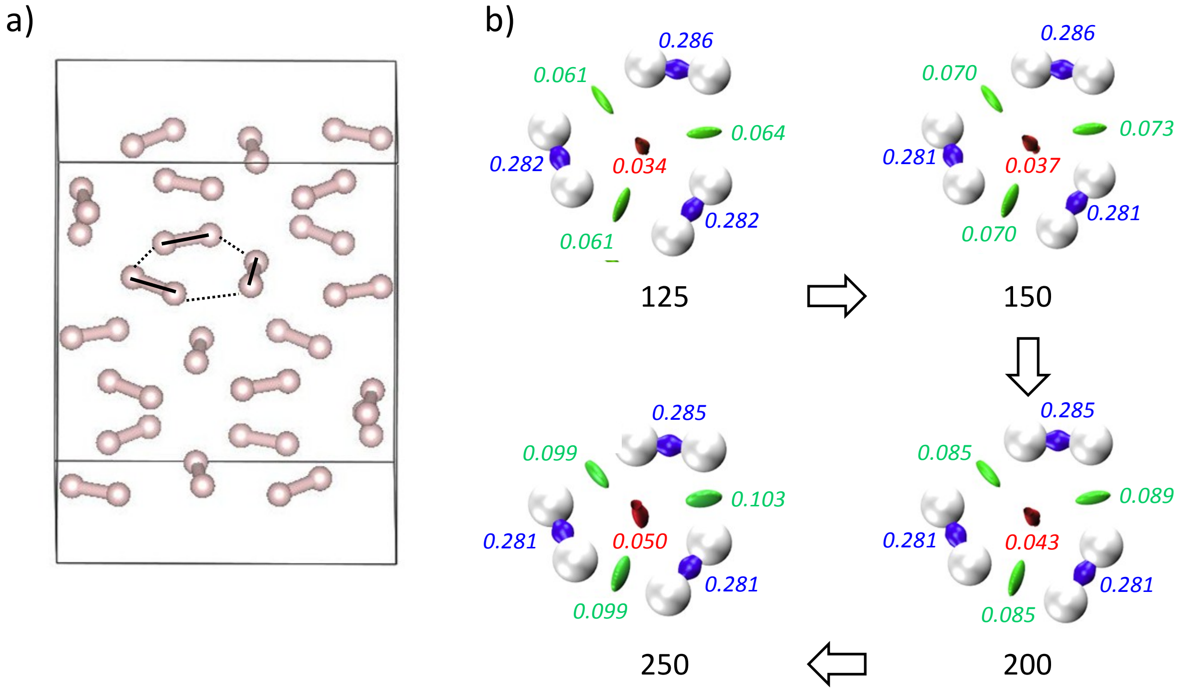


Figure S24. a) Main interactions scheme b) The ring of 3 H_2 molecules, cut from hydrogen solid of C2/c symmetry for different pressures. NCI analysis using s = 0.2 a.u and the following color scale: -0.2 < sign(λ_2)ρ < 0.05 a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

Cmca-12, 270 GPa < P < 385 GPa.

Figure S25 shows a similar motif for Cmca-12 to that of C2/c even if one of intermolecular interactions does not correspond to second next nearest neighbor (nnn) but to next (nnnn). There is a 3-molecular cycle, though in this case there are two equivalent H_2 systems and a non-equivalent one (instead of the 3 of them being equivalent). Thus, a gap is observed between the electron density of the associated BCPs (0.281 for the 2 equivalent H_2 molecules and 0.263 a.u. for the non-equivalent one, both at 350 GPa). Furthermore, these intermolecular interactions are also the strongest ones within this phase. Two successive layers interact through strong attractive interactions ($0.065 < \rho < 0.077$ a.u at 350 GPa) but weaker that those within same layer ($0.082 < \rho < 0.281$ a.u at 350 GPa) as observed within the C2/c phase.

Under compression, the trends observed for the $3H_2$ motif are similar to those of C2/c phase and the molecular model. The electron density range of BCPs associated to attractive intermolecular interactions between layers becomes larger ([0.058, 0.071] → [0.065, 0.077] for 300 → 350 GPa).

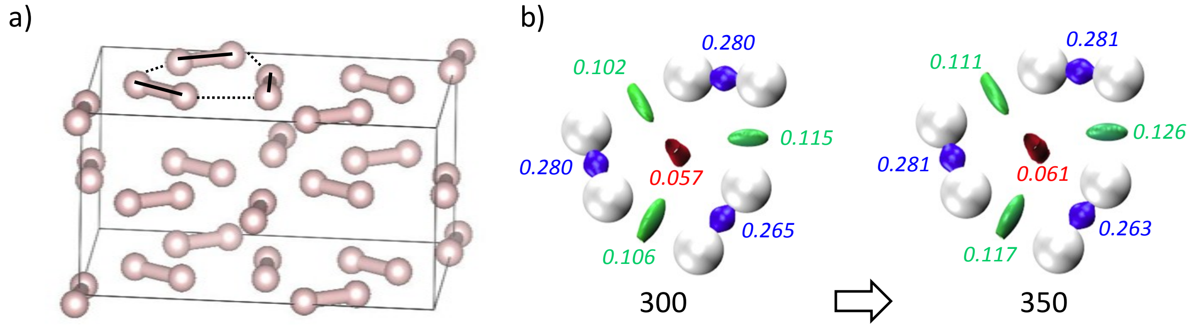


Figure S25. a) Main interactions scheme b) The ring of 3 H_2 molecules, cut from hydrogen solid of Cmca-12 symmetry for different pressures. NCI analysis using s = 0.2 a.u and the following color scale: $-0.2 < \mathrm{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

Cmca, 385 < P < 490 GPa.

Within this structuration, hydrogen is mono-coordinated **(Figure S26 a)**). Under pressure, the associated HH length decreases (0.780, 0.778 and 0.777 Å at 400, 450 and 490 GPa, respectively). Accordingly, the electron density of the associated BCPs slightly increases (**Figure S26 b)**). Hydrogens have two closest second neighbors, each of them belonging to a different H_2 unit. Resulting interactions are favorable and strengthen under compression: distances evolve as 1.063→1.045→1.036 Å for 400→450→490 GPa, respectively. However, this also yields a slight strengthening of the repulsion within the 4-member cycles (**Figure S26 b)**).

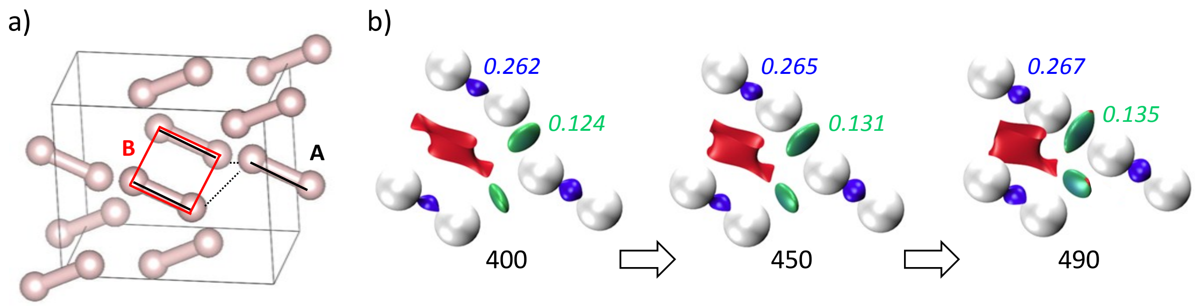


Figure S26. a) Main interactions scheme b) Variation of the Hydrogen local environment: NCI analysis using s = 0.2 a.u and the following color scale: $-0.2 < \text{sign}(\lambda_2)\rho < 0.05$ a.u. The value below shape corresponds to the pressure (GPa) and the absolute electron density values of BCPs are represented in italic (blue and green for intra- and inter- molecular bonds, respectively).

I4$_1$/amd, 490 GPa < P.

At pressures greater than 490 GPa, hydrogen is tetra-coordinated in a distorted tetrahedron environment (**Figure S27 a)**). The evolution of these interactions is shown in **Figure S27 b)** for P = 500, 750, 1000, 1500 and 2000 GPa, where first neighbors distances are 0.983, 0.926, 0.913, 0.871 and 0.835 Å, respectively. This geometrical criterion reveals the strengthening of these H···H interactions in agreement with the NCI analyses (**Figure S27 b)**). Keep in mind that the value for the isolated H_2 molecule is 0.256 a. u., so the values found here indicate that these interactions are already strong at 500 GPa. Indeed, from 500 to 2000 GPa, the electron density of associated BCPs increase from 0.160 to 0.271 a.u.

Due to the high density of this phase, important steric interactions appear with the next nearest neighbors. These are shown in **Figure S27 a)** as 4-member rings, where BCPs are at ca. 0.07 and ca. 0.08 a.u (500 GPa).

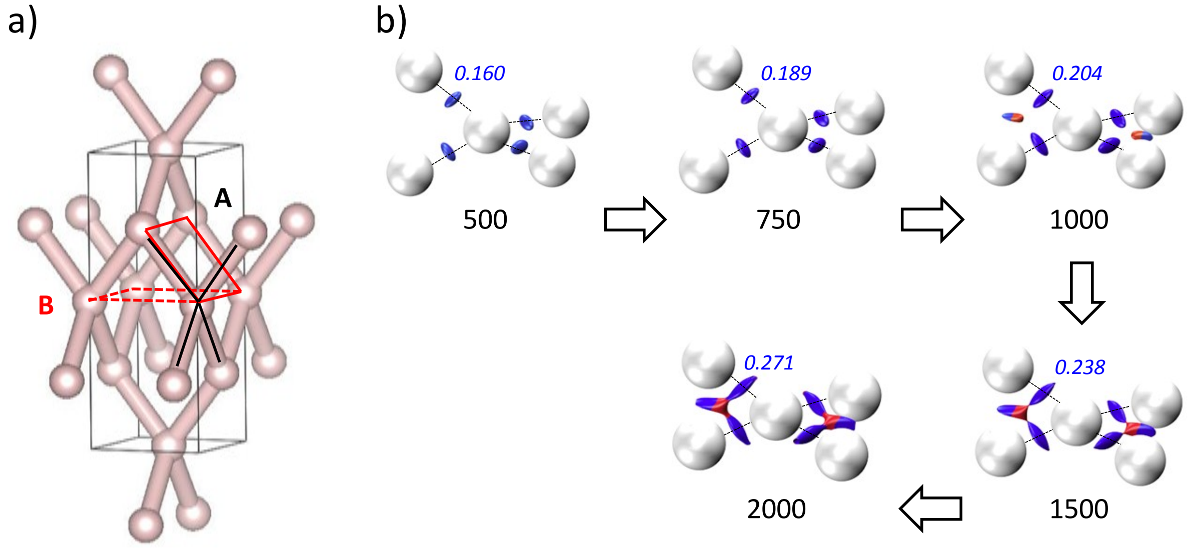


Figure S27. a) Main interactions scheme b) Variation of the tetra-coordinated Hydrogen local environment: NCI analysis using $s = 0.1$ a.u and the following color scale: $-0.2 < \mathrm{sign}(\lambda_2)\rho < 0.2$ a.u. The value below shape corresponds to the pressure (GPa) and the electron density values of BCPs are represented in blue and italic.

Table S5. Classification of all interactions delimited by characteristic electron density values (a.u.). * stands for a NCI interaction not related to an electron density BCP.

Systems	Covalent bond	Attractive interactions	Repulsive interactions
P63/m			
1 atm	0.265	0.001 ≤ ρ ≤ 0.002	0.0 ≤ ρ ≤ 0.001
5 GPa	0.271	0.007 ≤ ρ ≤ 0.009	0.002 ≤ ρ ≤ 0.005
6 GPa	0.272	0.008 ≤ ρ ≤ 0.010	0.002 ≤ ρ ≤ 0.006
25 GPa	0.279	0.017 ≤ ρ ≤ 0.020	0.006 ≤ ρ ≤ 0.014
35 GPa	0.282	0.020 ≤ ρ ≤ 0.025	0.008 ≤ ρ ≤ 0.017
50 GPa	0.284	0.024 ≤ ρ ≤ 0.030	0.010 ≤ ρ ≤ 0.022
60 GPa	0.287	0.027 ≤ ρ ≤ 0.033	0.014 ≤ ρ ≤ 0.028
75 GPa	0.289	0.030 ≤ ρ ≤ 0.037	0.017 ≤ ρ ≤ 0.033
100GPa	0.293	0.035 ≤ ρ ≤ 0.045	0.017 ≤ ρ ≤ 0.033
C2/c			
125 GPa	0.286; 0.282	0.035 ≤ ρ ≤ 0.064	0.027 ≤ ρ ≤ 0.042
150 GPa	0.286; 0.281	0.039 ≤ ρ ≤ 0.073	0.030 ≤ ρ ≤ 0.047*
200 GPa	0.285; 0.281	0.045 ≤ ρ ≤ 0.089	0.036 ≤ ρ ≤ 0.055*
250 GPa	0.285; 0.281	0.051 ≤ ρ ≤ 0.103	0.041 ≤ ρ ≤ 0.064*
Cmca-12			
300 GPa	0.280; 0.265	0.058 ≤ ρ ≤ 0.115	0.048 ≤ ρ ≤ 0.070*
350 GPa	0.281; 0.263	0.065 ≤ ρ ≤ 0.126	0.053 ≤ ρ ≤ 0.078*
Cmca			
400 GPa	0.262	0.079* ≤ ρ ≤ 0.124	0.055 ≤ ρ ≤ 0.081
450 GPa	0.265	0.085* ≤ ρ ≤ 0.131	0.059 ≤ ρ ≤ 0.087
490 GPa	0.267	0.089* ≤ ρ ≤ 0.135	0.062 ≤ ρ ≤ 0.092
$I4_1$/amd			
500 GPa	0.160	0.112*	0.070 ≤ ρ ≤ 0.117*
750 GPa	0.189	0.131*	0.085 ≤ ρ ≤ 0.138*
1000 GPa	0.204	0.161*	0.106 ≤ ρ ≤ 0.163*
1500 GPa	0.238	0.196*	0.133 ≤ ρ ≤ 0.198*
2000 GPa	0.271	0.227*	0.156 ≤ ρ ≤ 0.228*