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

Supplementary Information

Emergence of novel hydrogen chlorides under high pressure

(Supplementary Materials)

Qingfeng Zeng[1,2*], Shuyin Yu[1,2], Duan Li[1,2], Artem R. Oganov[b,c,d], and Gilles Frapper[e]

[a]Science and Technology on Thermostructural Composite Materials Laboratory, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China
[b]International Center for Materials Discovery, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China
[c]Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, NY 11794-2100, USA
[d]Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region 141700, Russia
[e]IC2MP UMR 7285, Université de Poitiers - CNRS, 4, rue Michel Brunet TSA 51106 - 86073 Poitiers Cedex 9, France

*The author to whom the correspondence should be addressed to: Qingfeng Zeng
Email: qfzeng@nwpu.edu.cn

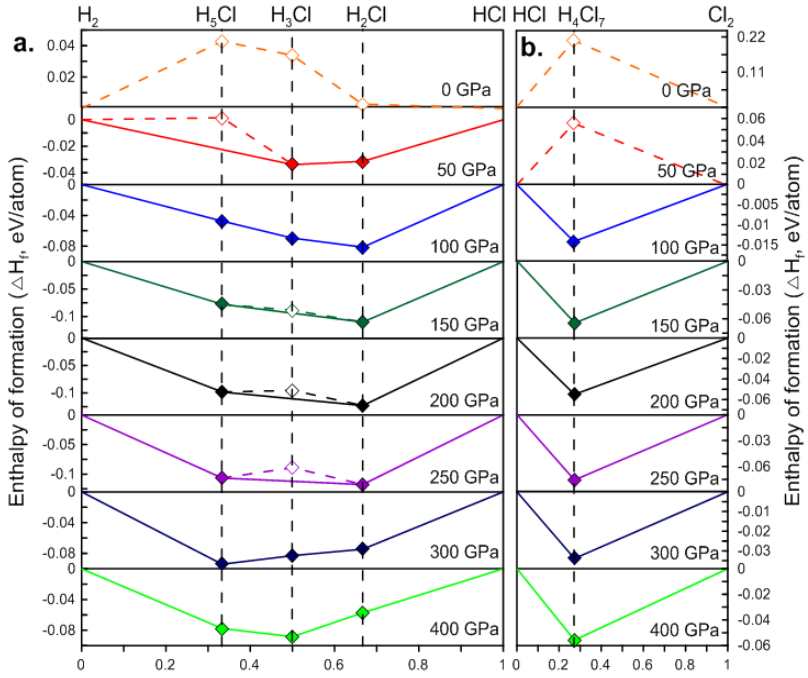


Figure S1 Phase stability of the H-Cl system considering decomposition into HCl + H_2 (a) and HCl + Cl_2.

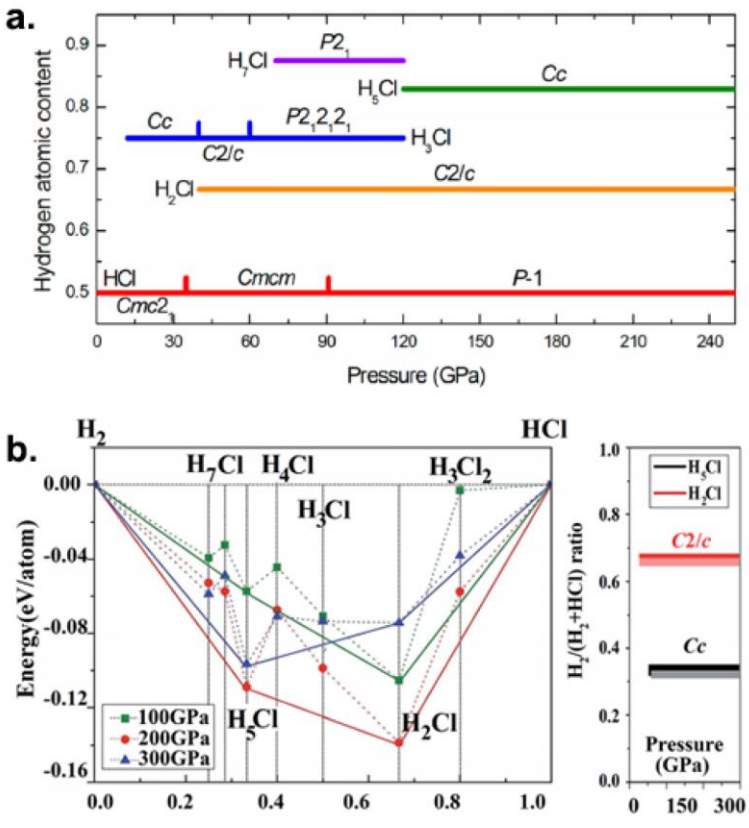
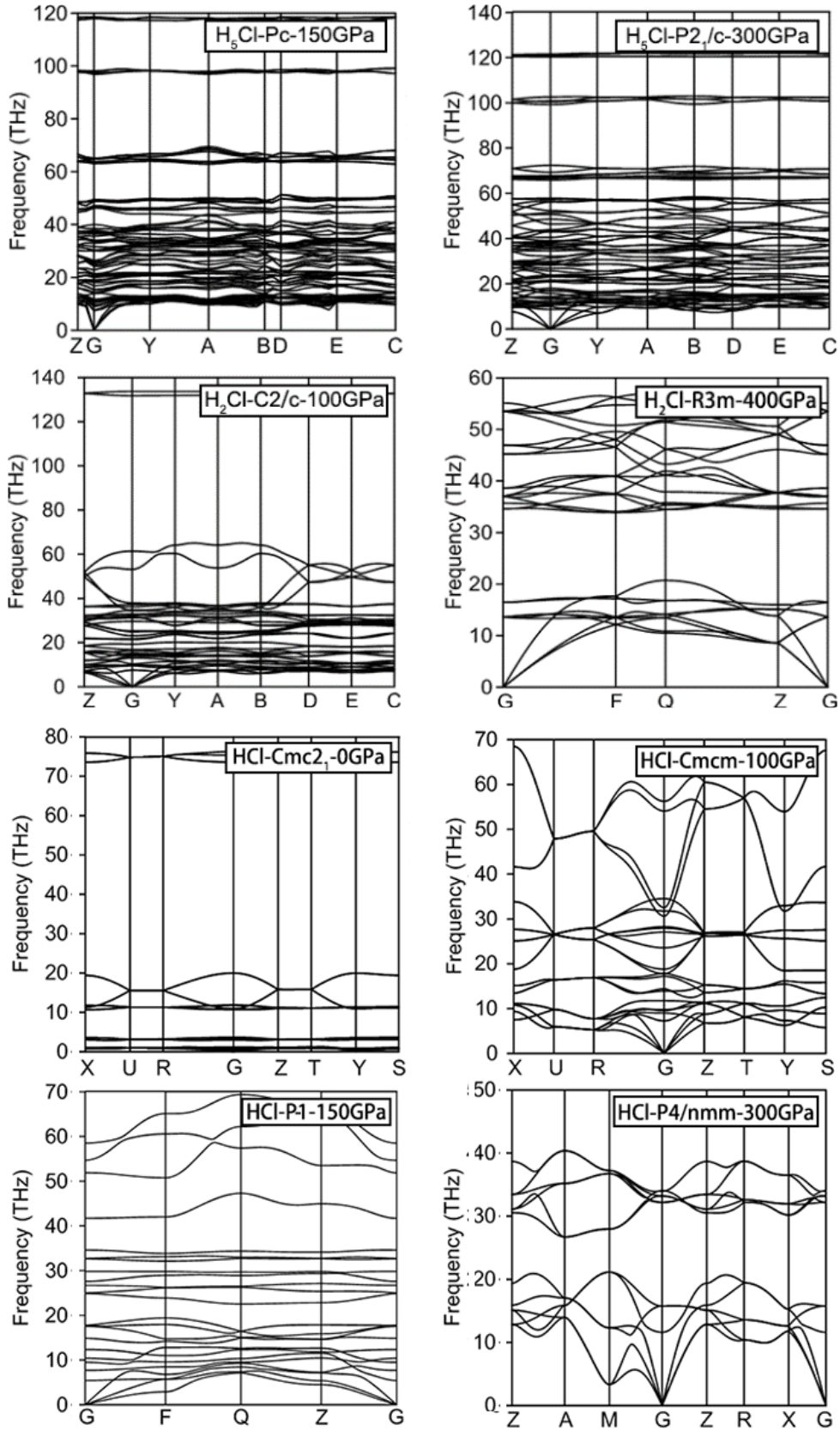


Figure S2 Previous studies of the phase stability of the H-Cl system (a) Duan et al. results[1] and (b) Wang et al. results[2].


H5Cl-Pc-150GPa
Frequency (THz)
Z G Y A B D E C
H5Cl-P21/c-300GPa
Frequency (THz)
Z G Y A B D E C
H2Cl-C2/c-100GPa
Frequency (THz)
Z G Y A B D E C
H2Cl-R3m-400GPa
Frequency (THz)
G F Q Z G
HCl-Cmc21-0GPa
Frequency (THz)
X U R G Z T Y S
HCl-Cmcm-100GPa
Frequency (THz)
X U R G Z T Y S
HCl-P-1-150GPa
Frequency (THz)
G F Q Z G
HCl-P4/nmm-300GPa
Frequency (THz)
Z A M G Z R X G

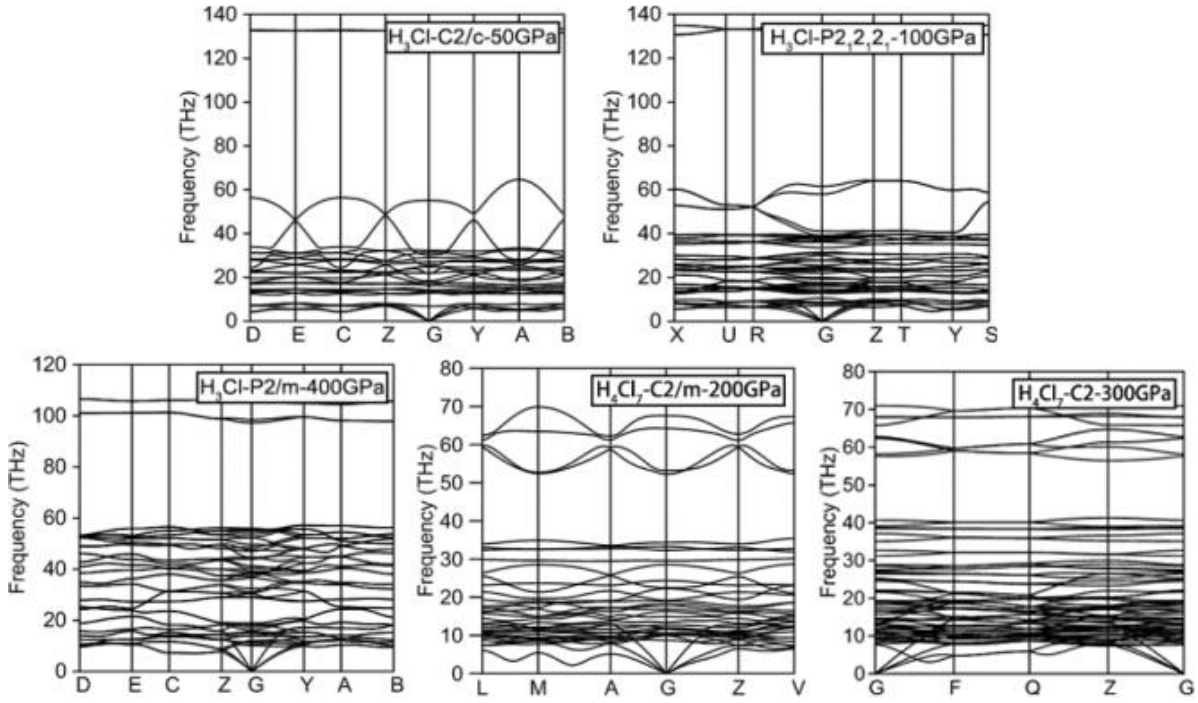


Figure S3 Phonon dispersion curves of the predicted H_xCl_y structures at selected pressures.

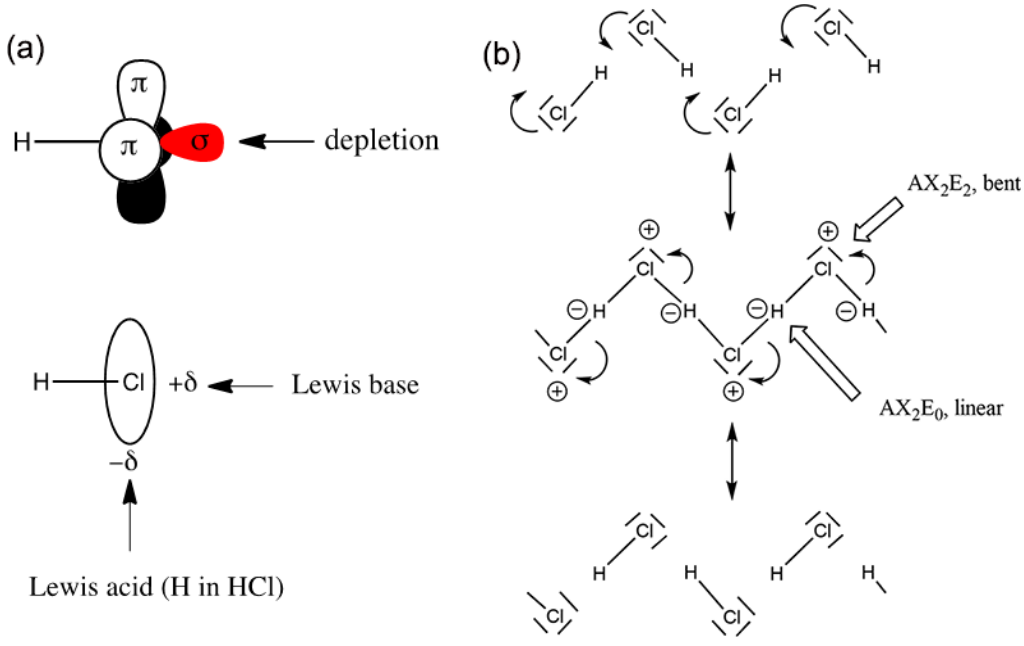
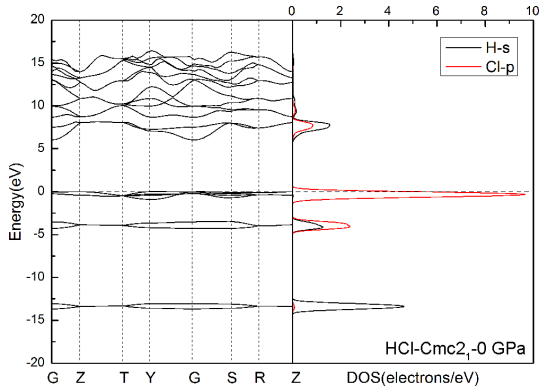
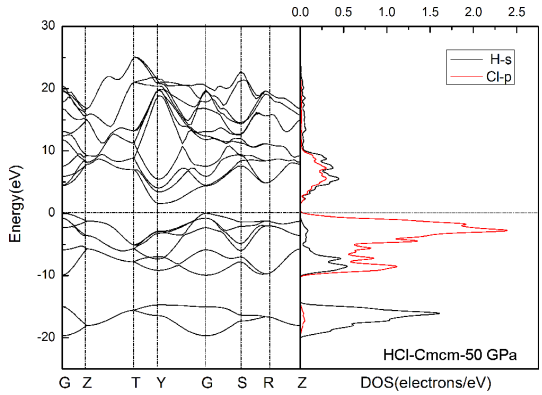
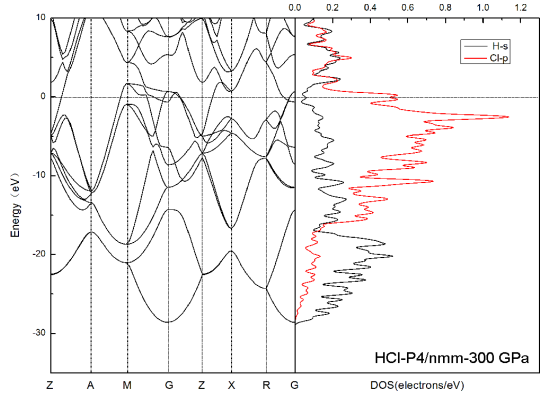
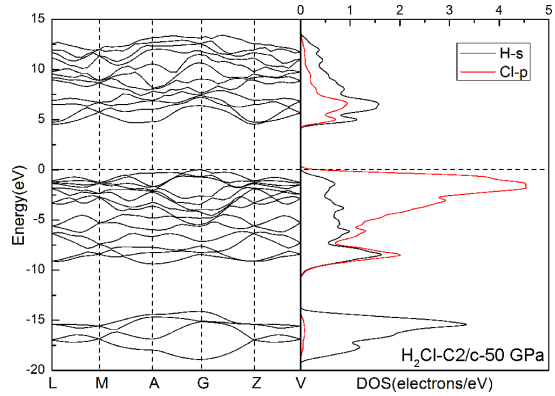


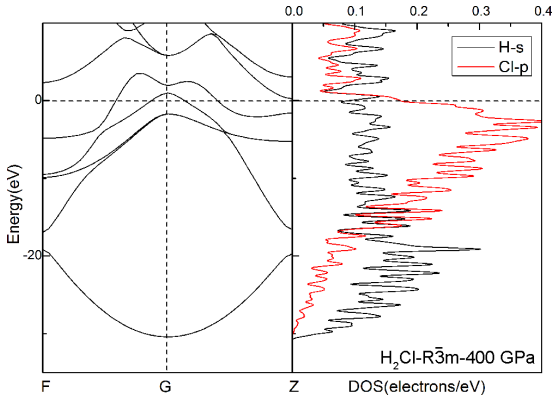
Figure S4 (a) Schematic illustration of the σ-hole concept applied to HCl. (b) Lewis resonance structures for the 1D zigzag HCl-chain.

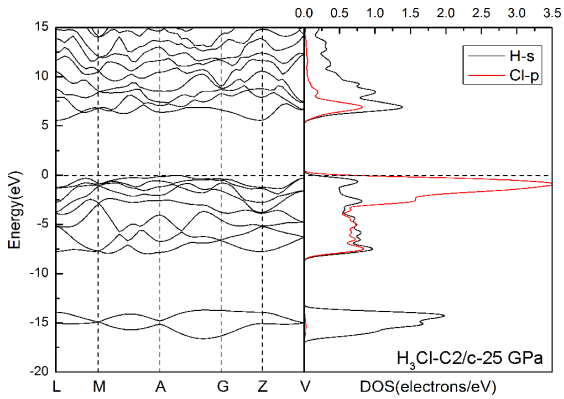

H-s
Cl-p
Energy(eV)
G Z T Y G S R Z
DOS(electrons/eV)
HCl-Cmc2$_1$-0 GPa

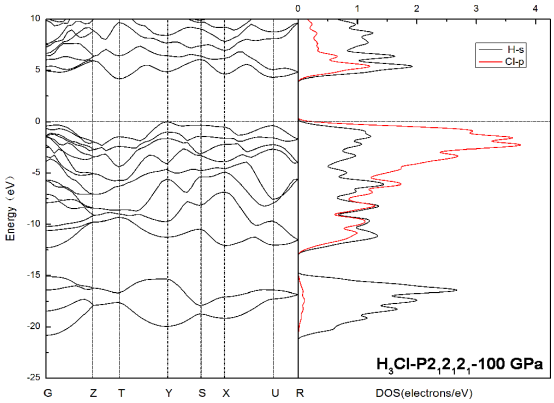

H-s
Cl-p
Energy(eV)
G Z T Y G S R Z
DOS(electrons/eV)
HCl-Cmcm-50 GPa

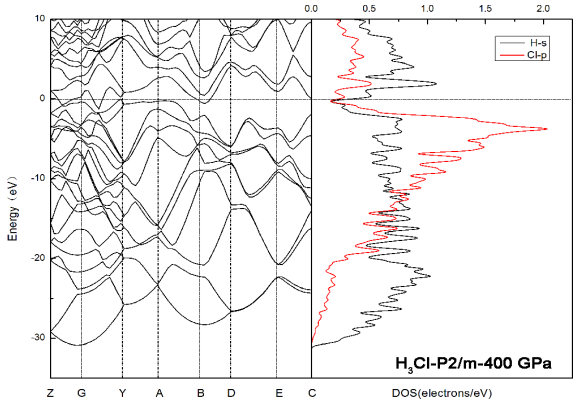

H-s
Cl-p
Energy (eV)
Z A M G Z X R G
DOS(electrons/eV)
HCl-P4/nmm-300 GPa


H-s
Cl-p
Energy(eV)
L M A G Z V
DOS(electrons/eV)
H$_2$Cl-C2/c-50 GPa


H-s
Cl-p
Energy(eV)
F G Z
DOS(electrons/eV)
H$_2$Cl-R$\bar{3}$m-400 GPa


H-s
Cl-p
Energy(eV)
L M A G Z V
DOS(electrons/eV)
H$_3$Cl-C2/c-25 GPa


H-s
Cl-p
Energy (eV)
G Z T Y S X U R
DOS(electrons/eV)
H$_3$Cl-P2$_1$2$_1$2$_1$-100 GPa


H-s
Cl-p
Energy (eV)
Z G Y A B D E C
DOS(electrons/eV)
H$_3$Cl-P2/m-400 GPa

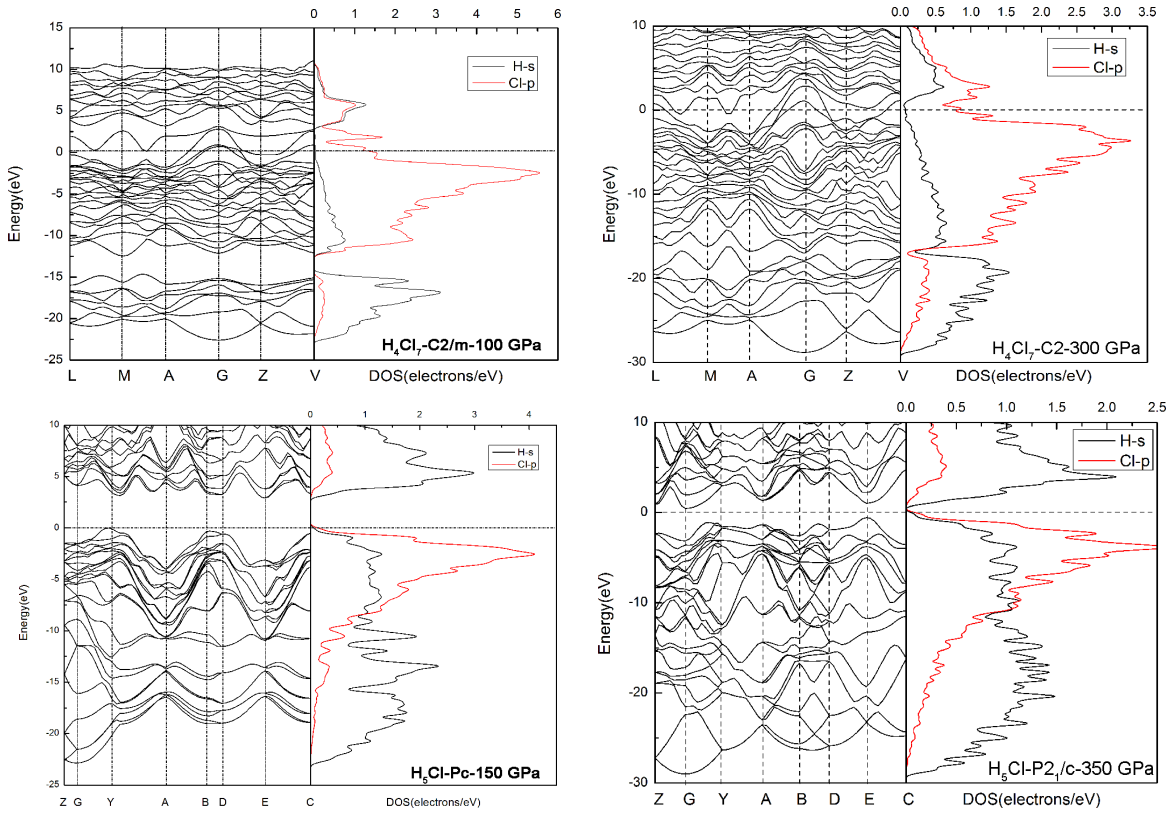


Figure S5 Band structures and density of states (DOS) of the predicted H_xCl_y structures at selected pressures.

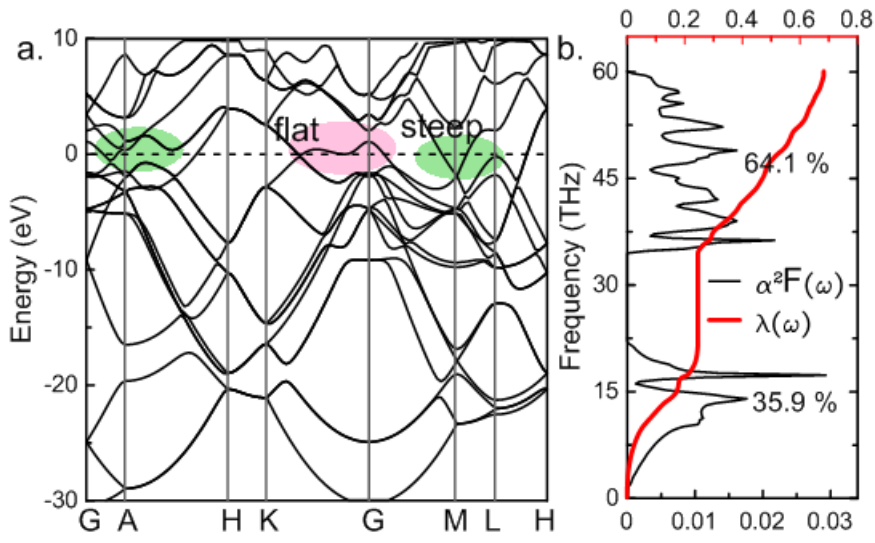


Figure S6 (a) Calculated band structure of R-3m H_2Cl at 400 GPa; (b) the Eliashberg phonon spectral function $\alpha^2F(\omega)$ and electron-phonon integral $\lambda(\omega)$ as a function of frequency at 400 GPa.

We note “the barriers for the internal proton transfer between the two H_2 units and the ones corresponding to the internal rotations of them are within 0.012 eV in energy. In gas phase, the H_5^+cation is best described as a H_2–H^+–H_2 (symmetric proton-bound dimer) with the H_2 units freely rotating around its C_2-axis.”, from Valdés et al.[3] In H_5Cl, the separation between H_3^+ and H_2 is reduced from roughly 1.4 Å (gas phase) to 1.1 Å (our calculated $P2_1/c$ phase at 350 GPa), thus the H_5^+cation could be described as H_3^+-H_2 unit. In the solid state, the local anionic environment maintains the H_5^+ planarity.

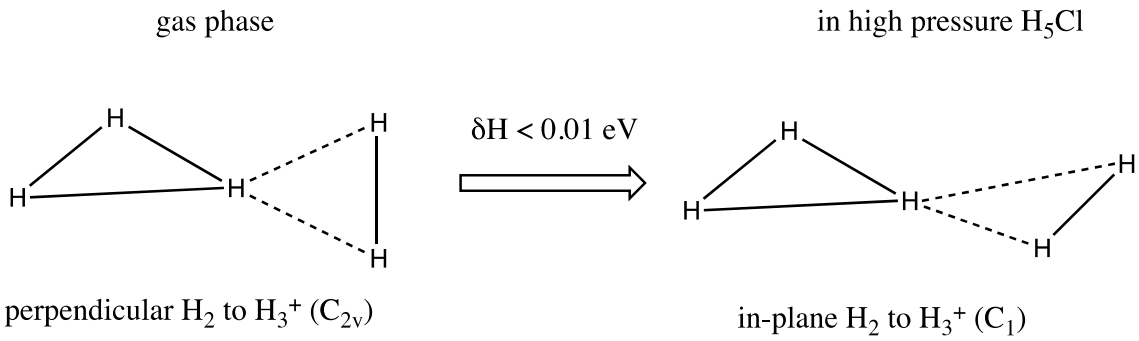


Figure S7 Gas phase and solid-state encapsulated H_5^+ clusters.

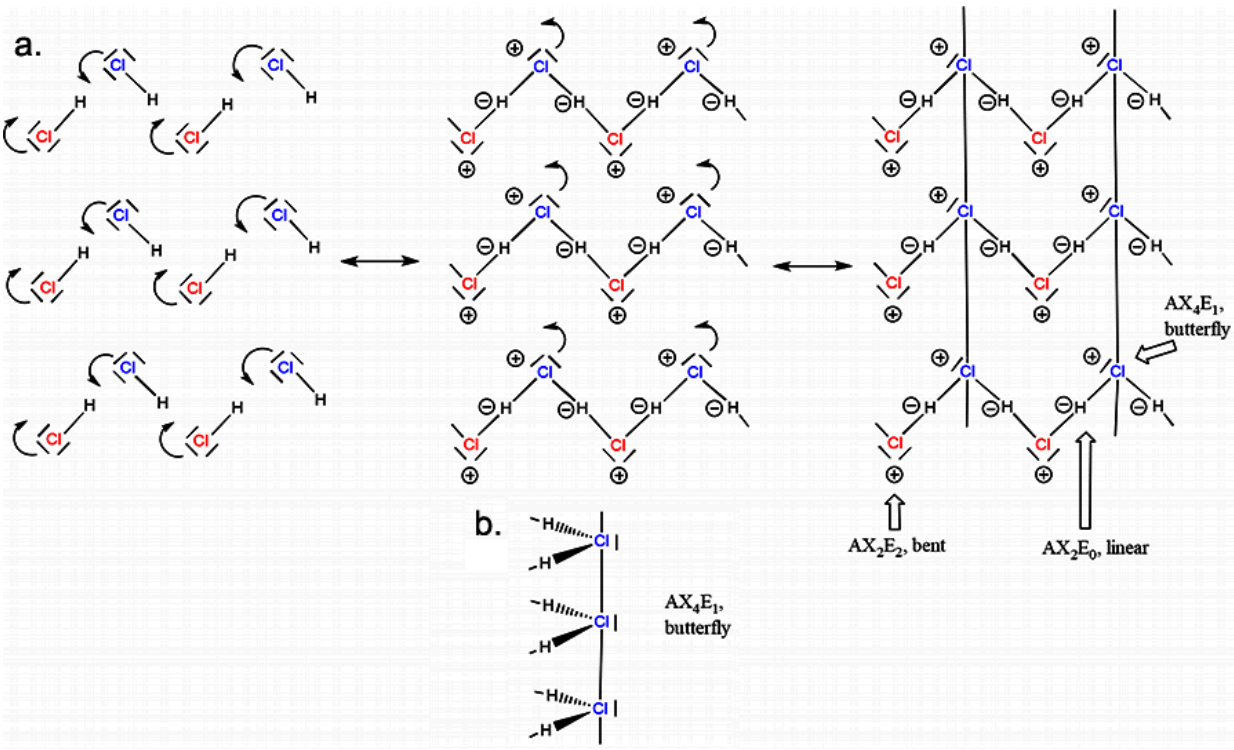


Figure S8 (a) Linked 1D zigzag HCl-chains in C2 H_4Cl_7 with assigned formal charges and VSEPR AX_nE_m notation (A, central atom; X, ligand and n its number; E, lone pairs and m its numbers; n+m is the steric number). (b) Butterfly structure of 4-coordinate chlorine centers in C2 H_4Cl_7 (blue, 4-coordinate chlorine atoms ; red, 2-coordinate chlorine atoms).

Table S1 The calculated lattice parameters, atomic coordinates, enthalpies for the predicted stable structures of H-Cl system at selected pressures.

Phase	P GPa	Space group	Lattice parameters (Å, °)	Atomic coordinates (fractional)		H eV/atom
H_5Cl	150	Pc (7)	a=2.818 b=2.817 c=10.297 β=106.7	H(2a)	(0.241, 0.102, 0.641)	1.144
				H(2a)	(0.544, 0.340, 0.787)	
				H(2a)	(0.818, 0.218, 0.575)	
				H(2a)	(0.220, 0.324,0.786)	
				H(2a)	(0.354, 0.747, 0.882)	
				H(2a)	(0.563, 0.397, 0.540)	
				H(2a)	(0.430, 0.104, 0.826)	
				H(2a)	(0.534, 0.074, 0.533)	
				H(2a)	(0.230, 0.366, 0.632)	
				H(2a)	(0.627, 0.756, 0.891)	
				Cl(2a)	(0.068, 0.264, 0.967)	
				Cl(2a)	(0.810, 0.259, 0.217)	
	350	$P2_1/c$ (14)	a=3.620 b=3.621 c=4.767 β=111.9	H(4e)	(0.700, 0.702, 0.505)	4.599
				H(4e)	(0.225, 0.462, 0.073)	
				H(4e)	(0.568, 0.808, 0.127)	
				H(4e)	(0.905, 0.690, 0.907)	
				H(4e)	(0.725, 0.512, 0.617)	
				Cl(4e)	(0.240, 0.874, 0.249)	
H_3Cl	50	C2/c (15)	a=3.282 b=8.669 c=3.186 β=91.9	H(8f)	(0.577, 0.068, 0.169)	-0.882
				H(4c)	(0.750, 0.250, 0.500)	
				Cl(4e)	(0.500, 0.640, 0.750)	
	100	$P2_12_12_1$ (19)	a=5.668 b=4.302 c=2.997	H(4a)	(0.310, 0.159, 0.417)	0.688
				H(4a)	(0.257, 0.073, 0.603)	
				H(4a)	(0.983, 0.124,0.227)	
				Cl(4a)	(0.584, 0.123, 0.027)	
	400	P2/m (10)	a=3.678 b=2.615 c=4.554	H(2n)	(0.705, 0.500, 0.841)	7.095
				H(2n)	(0.580, 0.500, 0.441)	
				H(2n)	(0.062, 0.500, 0.431)	
				H(2m)	(0.080, 0.000, 0.059)	
				H(2m)	(0.795, 0.000, 0.341)	
				H(2m)	(0.438, 0.000, 0.931)	
				Cl(2n)	(0.763, 0.500, 0.161)	
				Cl(2m)	(0.263, 0.000, 0.339)	
H_2Cl	100	C2/c (15)	a=6.946 b=5.405 c=4.376 β=129	H(8f)	(0.030, 0.502, 0.855)	1.332
				H(4e)	(0.000, 0.835, 0.750)	
				H(4e)	(0.500, 0.671, 0.750)	
				Cl(8f)	(0.324, 0.333, 0.324)	
	400	R-3m (166)	a=2.569, b=2.569 c=5.033, γ=120	H(3m)	(0.333, 0.667, 0.561)	8.897
				Cl(-3m)	(0.333, 0.667, 0.167)	
HCl	10	$Cmc2_1$ (36)	a=5.014, b=4.384 c=4.600	H(4a)	(0.500, 0.456, 0.001)	-2.166
				Cl(4a)	(0.500, 0.241, 0.207)	

	100	Cmcm (63)	a=3.880, b=3.747 c=3.867	H(4b) Cl(4c)	(0.000, 0.500, 0.500) (0.500, 0.000, 1.000)	2.724
	150	P-1 (2)	a=2.586, b=4.232 c=4.510, α=88.9 β=89.6, λ=87.3	H(2i) H(2i) Cl(2i) Cl(2i)	(0.751, 0.263, 0.089) (0.196, 0.997, 0.290) (0.461, 0.267, 0.360) (0.088, 0.251, 0.843)	4.772
	300	P4/nmm (129)	a=2.814, b=2.814 c=2.348	H(2a) Cl(2c)	(0.000, 0.000, 0.000) (0.500, 0.000, 0.699)	9.747
H_4Cl_7	100	C2/m (12)	a=7.918 b=4.471 c=9.339 β=147.7	H(8j) Cl(4i) Cl(4i) Cl(2c) Cl(4f)	(0.284, 0.250, 0.872) (0.162, 0.500, 0.990) (0.265, 0.500, 0.759) (0.500, 0.500, 0.500) (0.250, 0.250, 0.500)	3.992
	300	C2 (5)	a=7.109 b=4.101 c=8.280 β=149.0	H(4c) H(4c) Cl(4c) Cl(4c) Cl(4c) Cl(2b)	(0.281, 0.569, 0.863) (0.020, 0.292, 0.849) (0.358, 0.314, 0.500) (0.000, 0.345, 0.500) (0.251, 0.587, 0.501) (0.251, 0.861, 0.761)	12.233

Table S2 The calculated enthalpies at selected pressures of the predicted H_xCl_y structures.

Phase	P (GPa)	H (eV/atom)	Phase	P (GPa)	H (eV/atom)
HCl					
$Cmc2_1$	0	-3.12808	Cmcm	0	-3.0641
	10	-2.16641		25	-1.1123
	25	-1.11587		50	0.3257
	30	-0.80518		70	1.3408
	50	0.325667		100	2.7235
	70	1.340723		150	4.7771
P-1	75	1.5863	P4/nmm	150	4.9172
	100	2.7249		200	6.7570
	125	3.7809		250	8.4143
	150	4.7715		275	9.1894
	175	5.7079		300	9.9336
	200	6.5970		350	11.3653
	250	8.2543		400	12.7205
H_2Cl					
C2/c	25	-1.5985	R-3m	250	5.6675
	50	-0.4884		275	6.2420

	100	1.3322		300	6.8031
	150	2.8864		350	7.8762
	200	4.2806		400	8.8975
	250	5.5623			
	300	6.7582			
	350	7.8852			
H_3Cl					
Cc[1]	0	-3.25711	C2/c	10	-2.5444
	10	-2.5618		25	-1.8430
	25	-1.84537		50	-0.8823
	50	-0.88228		75	-0.0497
	75	-0.04969		100	0.7044
$P2_12_12_1$	30	-1.6303	P2/m	250	4.3253
	50	-0.8789		275	4.8128
	75	-0.0556		300	5.3002
	100	0.6883		350	6.2202
	125	1.3759		400	7.0949
	150	2.0204			
	200	3.2116			
	250	4.3036			
	300	5.3177			
H_5Cl					
Cc[1]	50	-1.1765	Pc	75	-0.5529
	100	0.0592		100	0.0586
	150	1.1438		125	0.6194
	200	2.1119		150	1.1438
	250	2.9987		200	2.1119
	300	3.8240		250	2.9988
	400	5.3346		300	3.8243
				350	4.6005
$P2_1/c$	230	2.6526			
	250	2.9988			
	270	3.3352			
	300	3.8234			
	350	4.5991			
	400	5.3343			
H_7Cl					
$P2_1$[1]	50	-1.4378			
	100	-0.2587			
	150	0.7241			
	200	1.5951			

H_4Cl_7					
C2/m	50	1.2604	C2	100	4.0064
	100	3.9920		250	10.4140
	150	6.3430		275	11.3380
	200	8.8610		300	12.2335
	300	12.2355		325	13.1032
	325	13.1071		350	13.9496
	350	13.9552		400	15.5098

Table S3 The calculated zero-point energies (ZPE) for the predicted stable H_xCl_y structures at selected pressures.

Phase	Space group	P (GPa)	ZPE (eV/atom)	Phase	Space group	P (GPa)	ZPE (eV/atom)
H_4Cl_7	C2/m	70	0.1130	H_2Cl	C2/c	50	0.1847
		100	0.1151			100	0.1916
		200	0.1295			200	0.2053
		275	0.1477			275	0.2157
	C2	275	0.1480		R-3m	275	0.1510
		300	0.1504			300	0.1626
		400	0.1560			400	0.2092
HCl	$Cmc2_1$	0	0.1107	H_3Cl	C2/c	25	0.1673
		10	0.1157			30	0.1707
		25	0.1236			50	0.1880
		30	0.1255		$P2_12_12_1$	50	0.1865
	Cmcm	30	0.1193			75	0.1962
		50	0.1250			100	0.2077
		100	0.1394			125	0.2138
		150	0.1539		P2/m	275	0.2114
	P-1	100	0.1421			300	0.2184
		125	0.1484			400	0.2403
		150	0.1536	H_5Cl	Pc	100	0.2228
		175	0.1581			200	0.2417
	P4/nmm	250	0.1282			350	0.2699
		300	0.1472		$P2_1/c$	350	0.2712
		400	0.1750			400	0.2755

Table S4 Bond lengths (in Å) in H-Cl based molecular species.

Compounds	PAW-PBE[4]	B3PW91[5]	PBE-PBE[5]	CCSD(T)[5]	Exp.	Bond order
H_2 ($^1\Sigma_g$ $D_{\infty h}$)	0.750	0.745	0.751	0.743	0.741[6]	1
H_2^+ ($^2\Sigma_g$ $D_{\infty h}$)	1.134	1.110	1.132	1.058	-	0.5
H_3^+ ($^1A_1'$ D_{3h})	0.887	0.880	0.889	0.875	-	
H_5^+ ($^1A_1$ C_{2v})	-	0.790	0.797	0.761	-	
	-	0.790	0.797	0.811	-	
	-	1.134	1.146	0.964	-	
	-	1.136	1.142	1.374	-	
Cl_2 ($^1\Sigma_g$ $D_{\infty h}$)	1.992	2.002	2.020	2.020	1.988[6]	1
Cl_3^- ($^1\Sigma_g$ $D_{\infty h}$)	2.332	2.320	2.345	2.328	2.426[7]	0.5
HCl ($^1\Sigma_g$ $C_{\infty v}$)	1.284	1.282	1.291	1.279	1.274[6]	1
$ClHCl^-$($^1\Sigma_g$ $D_{\infty h}$)	1.570	1.569	1.578	1.560	1.56[8],1.57[9,10]	0.5

References

[1] Duan D, Huang X, Tian F, et al. J. Phys. Chem. A, 2015, 119(45):11059.

[2] Wang Z, Wang H, Tse J S, et al. Chem. Sci., 2014, 6(1):522-526.

[3] Valdés, Álvaro, and Rita Prosmiti., Phys. Chem. Chem. Phys., 13: 6217-6224 (2014).

[4] Plane-wave method using the VASP code at the PAW-PBE level of theory. The molecular species are put in a 10×10×10 Å cell. Only the Γ-point is considered.

[5] The aug-cc-pvTZ triple-zeta basis set with polarization and diffuse functions was used as implemented in GAUSSIAN 09 code.

[6] Gas phase values from NIST http://webbook.nist.gov.

[7] http://www.colby.edu/chemistry/webmo/Cl_3^-.html

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[9] Ward B. H., Granroth G. E., Abboud K. A., Meisel M. W. and Talham, D. R., Chem. Mater., 10, 1102-1108 (1998).

[10] Atwood J. L., Inorg. Chem., 29, 467-470 (1990).