crystals

MDPI

Supplementary Material: High-pressure reactivity of Kr and F_2 - stabilization of krypton in the +4 oxidation state

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1. Comparison of the performance of PBE, PBE+D3, and HSE06 methods

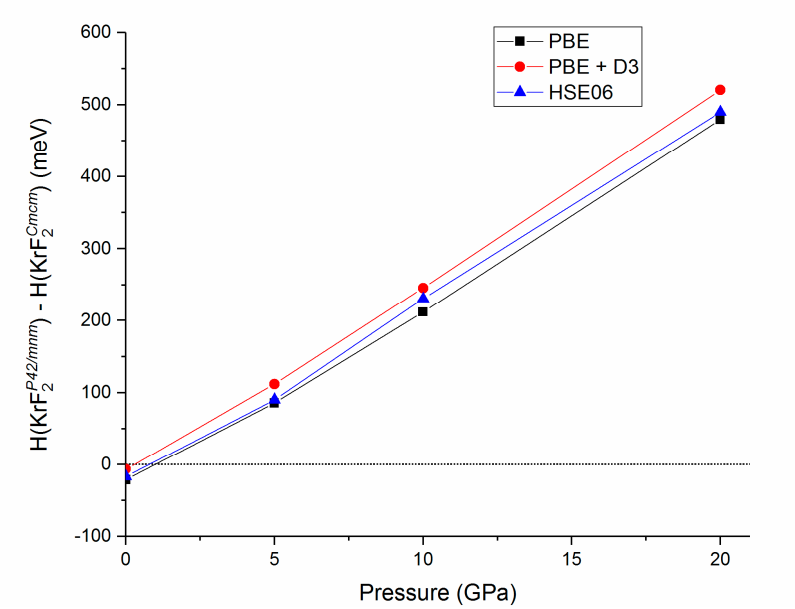


Figure S1. Comparison of the relative enthalpy of the ambient pressure *P4₂/mnm* structure of KrF_2 with respect to the high-pressure *Cmcm* structure obtained with three different computational methods (PBE, PBE+D3, HSE06).

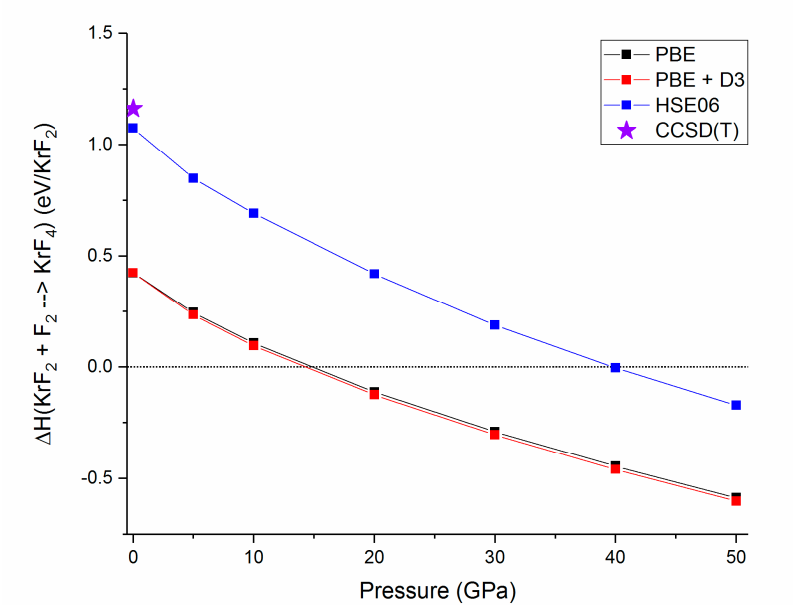


Figure S2. Comparison of the enthalpy change of the reaction $KrF_2 + F_2 \rightarrow KrF_3$ obtained with three different computational methods (PBE, PBE+D3, HSE06). The ambient pressure CCSD(T) value calculated with the use of data from Dixon et al. (ref. 55) is marked with a star.

2. Structure parameters of Kr_3F_2, KrF_2, and KrF_4

Table S1. Structure parameters of the most stable polymorphs of Kr_3F_2, KrF_2, and KrF_4.

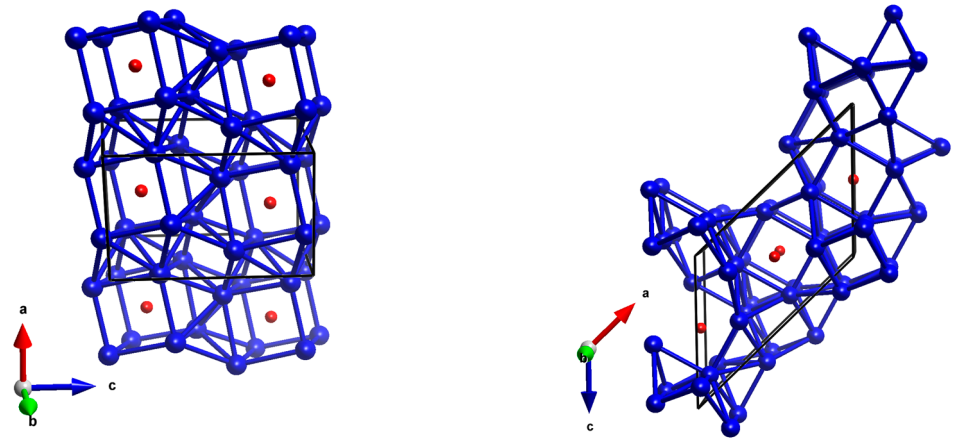
Compound Space group Pressure	a, b, c [Å]	α, β, γ [°]	Kr (x, y, z) Wyckoff site	F (x, y, z) Wyckoff site
Kr_3F_2 *P1* (1) 0 GPa	4.3541 6.8524 7.2714	111.41 97.94 99.37	Kr1: 0.2187 0.7392 0.2300 (1a) Kr2: 0.6126 0.0227 0.8602 (1a) Kr3: 0.8249 0.4557 0.5997 (1a)	F1: 0.0751 0.0006 0.3512 (1a) F2: 0.3624 0.4777 0.1087 (1a)
KrF_2 *Cmcm* (63) 50 GPa	6.04718 4.66210 4.48735	90 90 90	Kr1: 0.000 0.000 0.000 (4c)	F1: 0.1925 0.5223 0.0000 (8g)
KrF_4 *I4/m* (87) 50 GPa	4.6205 4.6205 4.1139	90 90 90	Kr1: 0.000 0.000 0.000 (2a)	F1: 0.6451 0.8113 0.0000 (8h)

3. Structures parameters of Kr_6F, Kr_4F, Kr_2F, and KrF

Table S2. Structure parameters of the most stable polymorphs of K_6F, Kr_4F, Kr_2F, and KrF.

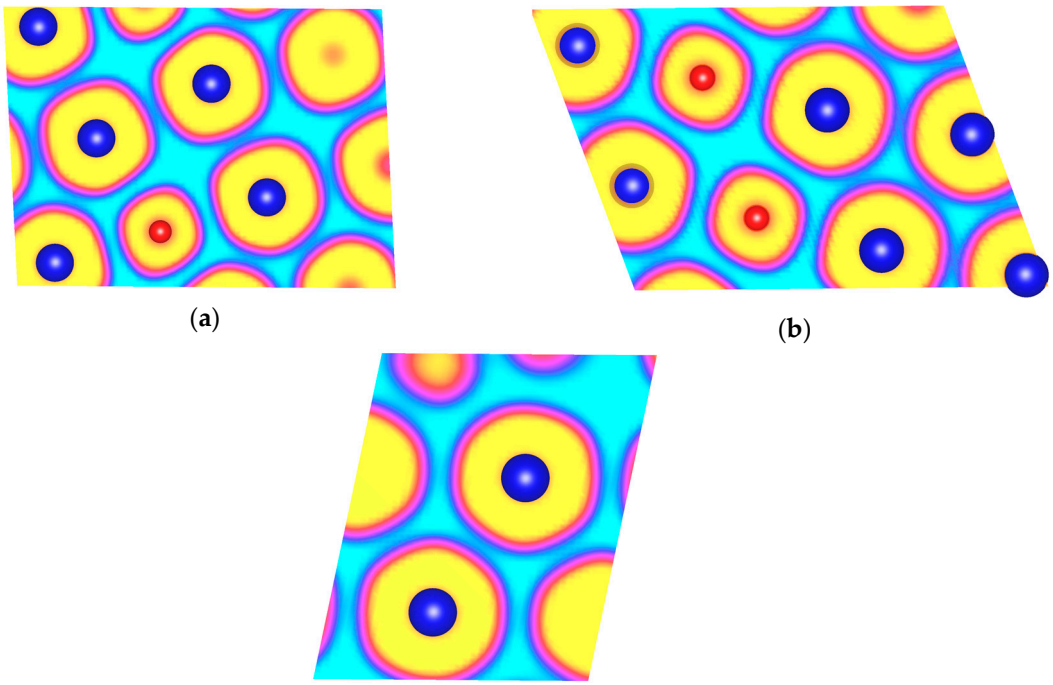
Compound Space group Pressure	a, b, c [Å]	α, β, γ [°]	Kr (x, y, z) Wyckoff site	F (x, y, z) Wyckoff site
Kr_6F *P–1* (2) 150 GPa	4.8663 4.9297 7.3985	81.21 87.79 84.45	Kr1: 0.8152 0.6734 -0.090 (2i) Kr2: 0.1542 0.8086 0.6203 (2i) Kr3: 0.5825 0.0811 0.690 (2i) Kr4: 0.0564 0.2678 0.7507 (2i) Kr5: 0.7089 0.1522 0.0272 (2i) Kr6: 0.6700 0.6105 0.5667 (2i)	F1: 0.4326 0.4769 0.8226 (2i)
Kr_4F *C2/m* (12) 150 GPa	9.3271 2.6789 6.6300	90 134.09 90	Kr1: 0.7295 0.0000 0.3084 (4i) Kr2: -0.0782 0.000 0.1456 (4i)	F1: 0.0000 0.5000 0.5000 (2d)
Kr_2F *I4/mcm* (140) 150 GPa	5.3779 5.3779 4.4173	90 90 90	Kr1: 0.3352 0.8352 0.0000 (8h)	F1: 0.0000 0.0000 0.2500 (4a)
KrF *P2/m* (10) 150 GPa	3.9663 2.2891 4.0543	90 90.16 90	Kr1: 0.7411 0.5000 0.7520 (2n)	F1: 0.2371 0.0000 0.7470 (2m)

4. Structures and ELF function for Kr_6F and Kr_4F at 150 GPa



(**a**) (**b**)

Figure S3. (**a**) The *P–1* structure of Kr_6F at 150 GPa; (**b**) the *C2/m* structure of Kr_4F at 150 GPa.



(**a**) (**b**)

(**c**)

Figure S4. The ELF function at 150 GPa for: (**a**) the *P–1* structure of Kr_6F; (**b**) the *C2/m* structure of Kr_4F; (**c**) the hcp structure of Kr. Yellow color depicts ELF values above 0.9, cyan – below 0.1, while magenta corresponds to values of 0.4.

5. Electronic band gaps of Kr_mF_n compounds at 150 GPa.

Table S3. Calculated band gaps (in eV) for the lowest enthalpy structures of Kr_mF_n compounds at 150 GPa.

Phase	Type	Band gap
Kr	Atomic (3D)	3.42
Kr_6F		metallic
Kr_4F		metallic
Kr_2F	2D	metallic
KrF	1D	metallic
KrF_2	Molecular (0D)	1.02
KrF_4		2.30
F_2		1.80

6. Comparison of F_2 and Kr geometries.

Table S4. Comparison of the experimental and calculated (PBE method) crystal structures of α-F_2 and Kr at ambient pressure.

		Exp (ref. 67, 68)	PBE
F_2	a (Å)	5.5	5.825 (+5.9 %)
	b (Å)	3.28	3.432 (+4.6 %)
	c (Å)	7.28	7.015 (–3.6 %)
	β (°)	102.17	102.55
	R(F-F)	1.49	1.428 (–4.2 %)
	R(F···F)	2.82	2.778 (–1.5 %)
Kr	a (Å)	5.638	6.396 (+13.4 %)