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SUPPORTING INFORMATION

High-pressure stabilization of argon fluorides

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I. Comparison of experimental and theoretical dissociation energies of F_2 and KrF_2 .

Table SI-1 gives the ZPE corrected dissociation energies (D_0) in eV obtained by means of molecular calculations employing three GGA methods (PBE,¹ revPBE², PW91³) and two hybrid functionals (HSE06,⁴ and B3LYP). The calculations were conducted using Gaussian09⁵ with the *cc-pVQZ* basis set. For each functional the geometry of the molecules was optimized.

	PBE	revPBE	PW91	HSE06	B3LYP	Exp.
F ₂	2.26	2.23	2.28	1.45	1.56	1.576
KrF ₂	2.25	2.24	2.29	1.04	1.13	1.017

As can be seen in the table above the GGA functionals severely overestimates the stability of both F_2 and KrF_2 while the hybrid functional (HSE06) yields results in good agreement with experiment.

These differences influence the calculated energy of formation of KrF_2 , $E_f(KrF_2)$, which by using a simple thermodynamic cycle can be related to $D_0(F_2)$ and $D_0(KrF_2)$:

$$E_f(KrF_2) = D_0(F_2) - D_0(KrF_2)$$

Using this equation and the data of Table SI-1 one can calculate the experimental value of $E_f(KrF_2)$ as equal to 53.0 kJ/mol. In comparison GGA functionals predict the energy of formation of KrF₂ as equal to 1.4 / -1.3 / -0.8 kJ/mol (for PBE/revPBE/PW91) while the values derived from HSE06/B3LYP are again much closer to experiment (39.1 / 42.2 kJ/mol).

II. Computational details

Periodic DFT calculations utilized the HSE06 hybrid potential, while the PBE exchange-correlation functional was used for comparative calculations. The projector-augmented-wave (PAW) method⁸ was used, as implemented in the VASP 5.2 code.⁹ The cut-off energy of the plane waves was set to 1200 eV with a self-consistent-field convergence criterion of 10⁻⁶ eV. Valence electrons were treated explicitly, while VASP pseudopotentials were used for the description of core electrons. In order to ensure proper treatment of valence electrons a 'hard' pseudopotential for fluorine (PAW radial cut-off of 1.1 Å) has been chosen. The k-point mesh was set at $2\pi \ge 0.06$ Å⁻¹, and was increased to $2\pi \ge 0.04$ Å⁻¹ for DOS calculations. All structures were optimized using a conjugate-gradient algorithm until the forces acting on the atoms were smaller than 5 meV/Å. The abovementioned parameters ensured convergence of the calculated enthalpy within 2 meV per atom. The enthalpies of formation of Ar_mF_n were calculated with respect to elemental Ar in either the *fcc* or *hcp* structure,¹⁰ as well as the α polymorph of F₂.¹¹ We note that above 50 GPa α -F₂ (C2/c space group) symmetrizes spontaneously to a Cmca structure which is analogous to the high-pressure polymorph of Cl₂.¹²

Structure visualization was performed with the *VESTA 3.1* software.¹³ Symmetry recognition was performed with the online program *FINDSYM*.¹⁴

III. Description of the structures and the pressure dependence of their enthalpy

Argon subfluoride: Ar₂F



We found the structure of *C2/m* symmetry (see above) to be the most stable polymorph in the 0-200 GPa pressure range; see the pressure dependence of the relative enthalpy (H_{rel}) above. This polymorph consists of a three-atom-thick layer of unbound Ar (white spheres = Ar) separated by a monolayer of ArF₂ molecules (blue spheres = Ar, red spheres = F). The Ar-F distances within the symmetric and linear F-Ar-F units (1.69 Å at 100 GPa) are comparable to those found in pure ArF₂ (1.66 Å at the same pressure). The shortest inter-/intralayer Ar···F contacts are 2.23 Å / 2.32 Å – more than 30 % longer than the Ar-F bond, and are comparable to what is found in pure ArF₂ at the same pressure (2.33 Å). The Ar···Ar contacts within the Ar layer span from 2.54 Å to 2.63 Å as compared to 2.61 Å found in pure Ar at the same pressure.

The other two polymorphs (P-1 and C2/m (2)) are thermodynamically disfavored with respect to C2/m by more than 0.6 eV/f.u. in the whole pressure range. Most notably, structurally they contain chains characterized by [-F-Ar-Ar-] units (see below) with the Ar-Ar and Ar-F bond lengths of 2.34 Å and 2.02 Å, respectively (at 100 GPa).





The structure of C2/c symmetry (see above) is the most stable polymorph between 20 and 200 GPa (see the H_{rel} vs P plot above). It can be viewed as a mixture of slightly bent F-Ar-F units (F-Ar-F angle of 175.1°; Ar-F bond length of 1.68 Å at 100 GPa) and unbound Ar atoms (white spheres). The closest distance between an unbound Ar and F is 2.24 Å at 100 GPa. The length of Ar…Ar contacts ranges from 2.64 to 2.77 Å.

The *R-3m* polymorph (see below) is the ground state structure below 20 GPa. It contains, similarly to C2/c, a mixture of unbound Ar atoms (Ar…F contacts of 2.21 Å, Ar…Ar contacts of 3.48 Å at 100 GPa) and ArF₂ molecules (Ar-F bond length of 1.68 Å).



In contrast, a similar *R-3m* (2) structure (see above) contains chains of [-Ar-F-] stoichiometry (Ar-F bond length of 1.93 Å, nearest Ar···F/Ar···Ar contacts of 2.40 Å /2.65 Å). This structure is disfavored with respect to C2/c and *R-3m* by over 0.4 eV/f.u. in the whole pressure range studied.

Argon difluoride: ArF₂ (comparison of *Cmcm* and *I4/mmm*)

It's noteworthy to point that at 0 GPa *Cmcm* converges upon geometry optimization to the *I4/mmm* structure. This indicates a relation between the two polymorphs. Transforming the *I4/mmm* polymorph to a $\sqrt{2}x\sqrt{2}x1$ cell enables direct comparison with the *Cmcm* structure (see below). Both polymorphs consists of ArF₂ layers stacked along the *c* lattice vector in *I4/mmm* and the *a* lattice vector in *Cmcm*. While in the former structure the ArF₂ molecules are located on a square lattice, in *Cmcm* the movement of half of the these molecules along the *b* direction results in considerable shortening of two intra-layer Ar…Ar contacts at the expense of the other two. As a result of this distortion the *b* cell vector of *Cmcm* expands while *c* shortens compared to *a* and *b* in the $\sqrt{2}x\sqrt{2}x1$ cell of *I4/mmm*. Together with a small contraction along *a* this makes the volume of *Cmcm* approximately 1.5 % smaller than *I4/mmm* in the whole pressure range studied.



Below we show a comparison of the Ar \cdots Ar and F \cdots F distances in *Cmcm* (green line), *I4/mmm* (red) and pure Ar/F₂ (black dotted lines).





The structure of *C2/m* symmetry (see above, marked as *C2/m (2)* in order to distinguish it from yet another ArF₃ polymorph) is the most stable polymorph in the 0 – 200 GPa pressure range (see H_{rel} vs p plot above). It contains bent (176°) and slightly non-symmetric F-Ar-F units (1.64 Å / 1.69 Å at 100 GPa). These units, together with F₂ molecules (white spheres) are arranged into chains with [F-F…F-Ar-F…F-Ar-F] repeat units. The F-F distances of 1.34 Å are identical to those found in pure F₂. The intrachain F…F contacts (1.97/1.95 Å) are slightly shorter than analogous contacts in pure ArF₂ (2.04 Å) and F₂ (1.99 Å) at the same pressure. Distances between chains are 2.30 Å (Ar…F-F) and 2.24 Å (Ar-F…F-F).

Similarly to C2/m (2) the *P*-1 structure contains a mixture of ArF₂ and F₂ molecules (see below). At 100 GPa the ArF₂ units are bent (174°) and exhibit bond distances of 1.61 and 1.71 Å. The F-F bond length is 1.35 Å with shortest F…F/Ar…F contacts at 1.93 Å / 2.27 Å. Interestingly, the *P2*₁/*c* polymorph is isostructural with XeF₂·XeF₄¹⁵ and, at 100 GPa, contains both ArF₂ and ArF₄ units.



The *C2/c* structure (see below) contains ArF_2 units and bent chains of F atoms (white spheres) with a F-F distance of 1.65 Å at 100 GPa and a F-F-F angle of 159°. The *C2/m* structure also shown below contains chains characterized by a [F-Ar-F-F-Ar-F] repeat unit (F atoms, marked in white, inserted between two ArF_2 units) with Ar-F/F-F distances of 1.74 Å / 1.68 Å.





The structure of *C2/m* symmetry is the most stable polymorph of ArF_4 in the 0 – 200 GPa pressure range (see H_{rel} *vs* P plot above). It consist of linear and symmetric ArF_2 molecules (bond length of 1.66 Å at 100 GPa) and F₂ units (bond length of 1.34 Å). The packing of this *van der Waals* complex is such that the centers of mass of the two molecules form a distorted *NaCl*-type lattice. Each Ar atom is surrounded by 6 F₂ molecules and vice versa (Ar···F contacts at 2.33 Å). Additional Ar···F contacts are provided by second nearest ArF₂ molecules (Ar···F contact at 2.50 Å). The closes F···F contacts (Ar-F···F-F) are at 1.93 Å. As in the case of the other Ar_mF_n phases the molecular character of this structure is clearly visible, even at 100 GPa.

The second structure of C2/m symmetry (C2/m (2), see below) consist of two types of linear and symmetric ArF₂ units (bond lengths of 1.66 and 1.69 Å at 100 GPa) mixed with slightly elongated F₂ molecules (bond length of 1.39 Å). Shortest Ar…F and F…F contacts have a length of 2.16 Å and 1.85 Å, respectively.



Both I4/m and $P2_1/n$ contain ArF₄ molecules characterized by Ar-F bond lengths of 1.66 Å, and 1.64 Å, respectively at 100 GPa. At the same pressure the shortest Ar···F/F···F contacts are 2.43 / 2.10 Å for I4/m and 2.30 / 2.14 Å for $P2_1/n$. We note that $P2_1/n$ is isostructural with the ambient pressure structure of XeF₄,¹⁶ while I4/m has a structure analogous to the recently proposed high-pressure form of HgF₄.¹⁷

IV. Phonon stability

Phonon calculations are of interest both as guarantors of dynamical stability and with respect to the information such calculations may yield on the ease, or difficulty of motions in the structures considered

Dynamical stability of the enthalpically preferred structures has been assessed through phonon analysis, within the harmonic approximation using DFT with PBE parameterization to the density functional. Phonon dispersion curves were calculated using the finite-displacement method as implemented in the CASTEP code. We used sufficiently large super-cells, typically in the order of $3 \times 3 \times 3$ (or larger) in the interpolation of the force constants required for the accurate phonon calculations.

Our analysis reveals that all of the reported phases are dynamically stable within the pressure range corresponding to their thermodynamical stability. We note that for most of the structures we did observe negative frequencies at the low-pressure limit but those quickly stabilize upon pressure increase.

Below we show as an example the phonon dispersion curves for ArF_2 in the *Cmcm* structure optimized at 150 GPa.



V. ArF₂ synthesis from NF₃ and Ar



The figure above shows the pressure dependence of the enthalpy of formation of ArF_2 from a mixture of NF₃ and Ar (*i.e.* the enthalpy change associated with the reaction: $Ar + \frac{2}{3}NF_3 \rightarrow ArF_2 + \frac{1}{3}N_2$) calculated at the HSE06 level. As can be seen, the formation of ArF_2 and N_2 from the mixture of NF₃ and Ar is disfavored within the whole studied pressure range (0 – 200 GPa). A straightforward extrapolation to higher pressures indicates that this reaction should proceed spontaneously only above 300 GPa. In the calculations NF₃ has been assumed to adopt a recently proposed high-pressure structure.¹⁸ For N₂ below 60 GPa a $P4_12_12_1$ molecular structure¹⁹ has been assumed while above that pressure the polymeric cubic-gauche polymorph²⁰ was taken as the ground state.

VI. Enthalpy-pressure curves obtained with PBE, HSE06 and HSE06 + D3 methods



Above we show the comparison of the pressure dependence of the relative stability of ArF_4 polymorphs computed with PBE¹, HSE06⁴, and HSE06 + D3.²¹ As can be easily seen the inclusion of the dispersion correction into HSE06 has little influence on the relative stability of ArF_4 phases. There are however considerable differences between the HSE06/HSE06+D3 results and PBE, the most striking being that at the PBE level structures containing genuine ArF_4 units (*I4/m* and *P2₁/n*) are much more stabilized with respect to polymorphs built of ArF_2 and F_2 molecules. In fact for PBE the *I4/m* polymorph is predicted to become the ground state structure of ArF_4 at 200 GPa, while at the same pressure HSE06/HSE06+D3 predicts it to be more than 0.5 eV/fu less stable than the $ArF_2 \cdot F_2 C2/m$ polymorph.

Differences between results obtained for PBE and HSE06 extend also to other stoichiometries. Below we show the comparison of the relative stability of different polymorphs of ArF_3 computed at the PBE (left) and HSE06 (right) level of theory.



The inclusion of Hartree-Fock exchange does not influence much the relative stability of the polymorphs containing ArF_2 and F_2 molecules (C2/m (2) and P-1). The most notable

differences are seen when comparing the stability of these structures with polymorphs characterized by a different bonding scenario. At the PBE level both C2/c (containing ArF₂ molecules and -F-F- chains) and C2/m (F-Ar-F₃-Ar chains) are much closer in enthalpy to C2/m (2) and P-1. The same applies to $P2_1/c$ containing ArF₂ and ArF₄ molecules. In fact the PBE picture at 200 GPa suggests that the C2/c structure (ArF₂ + -F-F- chains) is competitive in terms of enthalpy with C2/m (2) (ArF₂ + F₂). This is in stark contrast to HSE06 results at the same pressure which put C2/c over 0.6 eV/fu higher in enthalpy compared to C2/m (2).

As can be seen from the two previous examples inclusion of the dispersion correction into HSE06 does not influence much the relative stability of competing polymorphs. It also does not change the pressure required for the stabilization of ArF_2 and ArF_4 , as can be seen below from the pressure dependence of the enthalpy of formation of ArF_2 (left) and ArF_4 (right) calculated with HSE06 (full lines), HSE06+D3 (dotted lines), and PBE (dashed lines).



VII. D3 dispersion corrections for Ar, F₂, ArF₂ and ArF₂ at selected pressures

Ar	Absolut	Relative to <i>fcc</i>	
	fcc	hcp	hcp
0	-0.058	-0.059	-0.001
20	-0.172	-0.172	0.000
50	-0.217	-0.217	0.000
100	-0.266	-0.266	0.000
200	-0.331	-0.331	0.000

Values below are given in eV per formula unit

F ₂	Absolut	Relative to <i>C2/c</i>	
_	Cmca	C2/c	Cmca
0		-0.047	
20	-0.086	-0.087	0.000
50	-0.105	-0.105	0.000
100	-0.125	-0.125	0.000
200	-0.150		

AE	А	bsolute valu	Relative to Cmcm			
Arr ₂	Стст	I4/mmm	P4 ₂ /mnm	I4/mmm	P42/mnm	
0	-0.153	-0.156	-0.156	-0.003	-0.003	
20	-0.278	-0.276	-0.256	0.002	0.022	
50	-0.337	-0.333	-0.305	0.004	0.032	
100	-0.397	-0.392	-0.357	0.005	0.041	
200	-0.477	-0.471	-0.426	0.006	0.050	

A "E		Absolut	e values	Relative to C2/m				
Arr ₄	C2/m	C2/m (2)	I4/m	P2 ₁ /n	C2/m (2)	I4/m	<i>P2</i> ₁ / <i>n</i>	
0	-0.220	-0.187	-0.201	-0.207	0.032	0.019	0.013	
20	-0.358	-0.348	-0.376	-0.374	0.010	-0.018	-0.017	
50	-0.435	-0.426	-0.456	-0.449	0.009	-0.021	-0.014	
100	-0.513	-0.508	-0.536	-0.524	0.005	-0.023	-0.011	
200	-0.615	-0.612	-0.640	-0.624	0.032	0.019	0.013	





Above we show the comparison of the simulated x-ray diffraction pattern ($\lambda = 0.374$ Å) at 60 GPa of an equimolar mixture of *fcc* Ar and *Cmca* F₂ (blue line, stars mark reflexes originating from Ar), and ArF₂ in the *Cmcm* structure (green line). As can be seen the formation of ArF₂ should be clearly distinguishable by synchrotron x-ray diffraction, especially by the disappearance of strong peaks originating from *fcc* Ar.

IX. Structures at 100 GPa in VASP format

Ar₂F: *C2/m*

```
Ar2F C2/m

1.0000000000000000

2.6317679025856711 0.0205169133468514 -0.0067783704495711

0.2952694452150383 2.6161484786051941 0.0216582755996569

-0.7568925265286296 0.7906529856038799 8.9628699845093198

Ar F

4 2

Direct

0.1316876385533201 0.7812319411029461 0.4041335843421273

0.6994374775793027 0.2138163967575331 0.6112760562268866

0.5642926882880035 0.3486670929231793 0.1970087968412405

0.6322761037108952 0.2812645708941778 0.9041670833324362

0.0357985577360332 0.8774217665345337 0.0301307868057814

0.2288875341324467 0.6851062317876238 0.7782396924515298
```

ArF: *C2/c*

0.0190952492200864	-0.0270574552384793
4.7761099281347601	-0.0841548776620441
	0.0190952492200864 4.7761099281347601

ArF₂: *P4*₂/mnm

ArF2 P42/mnm		
1.00000000000000000		
3.5528674535750304	0.000000000000000	000000000000000000000000000000000000000
0.00000000000000000	3.55286745357503	0.0000000000000000000000000000000000000
0.00000000000000000	0.000000000000000	00 4.1574517544664937
Ar F		
2 4		
Direct		
0.00000000000000 0.0	000000000000000000000000000000000000000	0.0000000000000000
0.50000000000000 0.3	500000000000000000000000000000000000000	0.5000000000000000
0.3170546898444362 0.1	3170546898444362	0.0000000000000000
0.6829453101555638 0.0	6829453101555638	0.0000000000000000
0.1829453101555638 0.8	8170546898444362	0.5000000000000000
0.8170546898444362 0.1	1829453101555638	0.5000000000000000

ArF₂: *I4/mmm*

ArF2 I4/mmm		
1.000000000000000000		
2.9635279321443981	0.0000000000000000	0 0.000000000000000
0.00000000000000000	2.963527932144398	1 0.0000000000000000
0.000000000000000000	0.00000000000000000	0 5.4233655325590986
Ar F		
2 4		
Direct		
0.00000000000000 0.0	000000000000000000000000000000000000000	000000000000000000000000000000000000000
0.500000000000000 0	500000000000000000000000000000000000000).5000000000000000
0.000000000000000 0.0	000000000000000000000000000000000000000).3068324051682773
0.000000000000000 0.0	000000000000000000000000000000000000000	0.6931675948317226
0.500000000000000 0	500000000000000000000000000000000000000).8068324051682774
0.500000000000000 0	500000000000000000000000000000000000000).1931675948317228

ArF₂: Immm

ArF2 Immm			
1.00000000000000000			
2.5194985400075720	0.000000000000000000	0.0000000000000000000000000000000000000	
0.000000000000000000	3.495615271798198	85 0.0000000000000000	
0.0000000000000000000000000000000000000	0.000000000000000000	00 5.3586414273768943	
Ar F			
2 4			
Direct			
0.50000000000000 0.5	000000000000000000000000000000000000000	0.5000000000000000	
0.00000000000000 0.0	000000000000000000000000000000000000000	0.0000000000000000	
0.00000000000000 0.0	000000000000000000000000000000000000000	0.3102512957471044	
0.00000000000000 0.0	000000000000000000000000000000000000000	0.6897487042528956	
0.50000000000000 0.5	000000000000000000000000000000000000000	0.8102512957471044	
0.500000000000000 0.5	000000000000000000000000000000000000000	0.1897487042528956	

ArF₂: Cmcm

0.0000000000	0.0000000000
4.3297319412	0.0000000000
0.0000000000	4.0454907417
0.999996364	0.000000000
0.354463607	0.50000000
0.499996394	0.000000000
0.854463637	0.500000000
0.517789245	0.000000000
0.836670816	0.50000000
0.517789245	0.000000000
0.836670816	0.500000000
0.017789185	0.000000000
0.336670756	0.500000000
0.017789185	0.000000000
0.336670756	0.500000000
	0.00000000000000000000000000000000000

ArF₃: *C2/m (2)*

ArF3	C2/	m 2																		
1.00	0000	0000)00(000	000															
6.	1472	.909	9416	5614	483	8	0.0	000	000	000	000	000	00	0.0	088	390	827	099	820)9
0.	0000	0000)00(000	000	0	3.7	829	947	579	961	434	40	0.0)000	000	000	000	000	00
-0.	5881	004	130	617	671	0	0.0	000	000	000	000	00	00	5.	168	395	183	977	323	36
Ar	F																			
4	12																			
Direc	et																			
0.62	2768	311	820	468	76	0.0	000)00(000	000	000)()	0.70)32	665	386	92	1769)	
0.37	231	688	179	531	25	0.0	000)000)000	000	000)0	0.29	967	334	613	078	323()	
0.12	2768	311	820	468	75	0.5	000	000)00	000	000)0	0.70	32	665	386	92	1769)	
0.87	7231	688	179	531	24	0.5	000)000)00(000	000	00	0.29	967	334	613	078	3230))	
0.37	7910	927.	462	184	30	0.0	000	000	000	000	000	00	0.8	28	952	804	.420	981e	5	
0.67	210	072^{-1}	537	815	70	0.0	000	1000	000	000	000	0	0.19	20	047	195	57()183	ŝ	
0.02	7910	072. 077	467	184	30	0.0			000	000		0	0.10	28	0 <i>47</i> 052	804	420) 2814	5	
0.07	0000	072^{-1}	402 537	215 215	70	0.5				000		0	0.0	271)]2 0/17	105	57(1183	2	
0.12	1009	0/2	000	625	25	0.5				000		0	0.10	770	047 655	570	160	$\frac{110}{112}$, ,	
0.00	0100	903 004	029	055	74	0.0				000		0	0.5	179 100	211	J/C 171	520	7134 1060	2	
0.12	100	090	970 020	504 625	-74	0.0						0	0.42	220	544 (55	421 570	330	1900 1120	s n	
0.30		903	029	033	23	0.5						10	0.5	19	000	3/8 401	40	1132	2	
0.62	8891	096	970	364	-75	0.5	000	1000		000	000)0	0.42	220	344 710	421	530	1868	5	
0.09	1598	494	872	395	96	0.0	000	1000)000	000	000)0	0.9:	500	/19	943	59.	3073	3	
0.90)401	502	127	603	79	0.0	000)000)00(000	000)0	0.0^{2}	199	279	796	406	5974	1	
0.59)598	497	872	396	21	0.5	000)000)00	000	000)()	0.95	500	719	943	593	3073	3	
0.40)401	505	127	604	-04	0.5	000)000)00(000	000)()	0.04	199	279	796	400	5974	1	

ArF₄: *C2/m*

ArF4	C2/m						
6.0	09261009	8523741′	0.0000	0000000000	00 0.	00138361	65031531
0.0	00000000	0000000	0 3.8229	9349365086	09 0.	0000000	00000000
-1.	84882694	1202649	2 0.0000	0000000000	00 3	.08543250	56405805
Ar	F						
2	8						
Direc	t						
0.00	00000000	000000	0.0000000	000000000	0.000	00000000	00000
0.50	00000000	000000	0.5000000	000000000	0.000	00000000	00000
0.42	14471963	662007	0.0000000	000000000	0.5780	522155962	21698
0.57	85528336	5338017	0.0000000	000000000	0.4213	377844037	78302
0.92	14471663	661983	0.5000000	000000000	0.5780	522155962	21698
0.07	85528036	5337993	0.5000000	000000000	0.4213	377844037	78302
0.80	50334457	732227	0.0000000	000000000	0.1950	003206072	27299
0.19	49665542	267774	0.0000000	000000000	0.8049	996808927	72678
0.30	50334457	732227	0.5000000	000000000	0.1950	003206072	27299
0.69	49665542	267773	0.5000000	000000000	0.8049	996808927	72678

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