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On account of the rapid development of noble gas chemistry in the past half-century both xenon and krypton compounds can now be isolated in macroscopic quantities.1 The same though does not hold true for the next lighter group 18 element, argon, which forms only isolated molecules stable solely in low temperature matrices or supersonic jet streams. Here we present theoretical investigations into a new high-pressure reaction pathway which enables synthesis of argon fluorides in bulk and at room temperature. Our hybrid DFT calculations (employing the HSE06 functional) indicate that above 60 GPa ArF-containing molecular crystals can be obtained by a reaction between argon and molecular fluorine.

Introduction

Over fifteen years after the successful synthesis of HArF2 multiple other neutral Ar-containing molecules have been isolated and identified in both low-temperature matrices (e.g. ArBeS3 or Ar complexes with CUO4) and in supersonic jet streams (e.g. ArAuCl6). Nevertheless Ar compounds in bulk quantities are yet to be synthesized. Although the substantial stability of the ArF2 and ArH+ cations led to a speculation that ArX2+(MF5) salts (X = F, H; M = Sb, Au) could constitute viable synthetic targets5 to date such compounds have not been obtained.

The experimental pursuit for new connections of Ar has been aided by numerous theoretical predictions of possible new species, such as ArO4, 7 FBeAr+, 8 or ArBeSO4 to name just a few. Interestingly very little attention has been paid to the possible synthesis of ArF2. We note that XeF2 and KrF2 are both known and are some of the most stable noble-gas compounds in general. To the best of our knowledge ArF2 has not been synthesized up to now; we found only two theoretical investigations concerning this molecule dating back more than 25 years.10

It has been shown recently that high pressure (i.e. exceeding 1 GPa) can drastically alter chemical reactivity11 thus enabling synthesis of new compounds otherwise not attainable at ambient conditions—in particular chemical connections of noble gases.12 Indeed, multiple investigations concerning the high-pressure (HP) chemistry of xenon showed that at large compression this element reacts readily with silicon13 and even water ice.14 In addition, HP reactions of Xe with nickel and iron,15 AuF6 as well as elemental oxygen17 have been postulated on the basis of Density Functional Theory (DFT) calculations. However argon HP chemistry received less attention by theoreticians, although its melting curve18 and the high-pressure formation of molecular adducts with hydrogen were studied theoretically,19

Motivated by the possibility of stabilizing exotic noble gas containing species with the aid of high pressure (as exemplified by the predictions concerning the HP stabilization of HHeF2)20 we present theoretical investigations into a new high-pressure reaction pathway which enables synthesis of Ar connections with fluorine in bulk and at room temperature. With the use of an evolutionary algorithm we probe at selected pressures the potential energy surface (PES) of various ArnFn stoichiometries, and show that above 60 GPa both argon difluoride (ArF2) and a molecular complex of ArF2 and F2 (ArF2:F2=ArF4) can be synthesized from Ar and F2.

Computational details

Accurate prediction of chemical reactions requires methods that correctly describe the thermodynamic stability of all the reactants. This requirement is particularly hard to
fulfill for noble-gas compounds which often form hypervalent molecules. To ensure a correct description of the thermochemistry of the Ar/F$_2$ systems we tested several DFT methods based on the generalized-gradient approximation (GGA) and hybrid functionals by performing benchmark calculations for two molecules relevant to this study: F$_2$ and KrF$_2$ (a known analogue of the targeted ArF$_3$). We found that GGA methods fail to correctly describe the thermodynamic stability of these molecules while at the same time hybrid functionals yield results close to experiment†. Therefore, we consistently used the hybrid HSE06 functional‡ in calculation of both the geometry and enthalpy of Ar$_n$F$_n$ compounds, as well as the Ar and F$_2$ reaction substrates.

The candidate structure were identified with the use of the USPEX evolutionary algorithm§ coupled with the PBE functional. All of the selected best candidate structures were subsequently re-optimized at the HSE06 level. The evolutionary search for stable structures of Ar$_2$F and ArF$_n$ (n = 1 – 4) was performed at P = 100 and 200 GPa with 1, 2, and 4 formula units per cell. For more calculation details see ESI‡.

**Results and discussion**

The pressure dependence of the calculated enthalpies of formation of numerous Ar$_n$F$_n$ compounds (the so-called tie-line plot) is shown in Fig. 1. The results indicate that at approximately 60 GPa all of the considered argon fluorides (Ar$_2$F and ArF$_n$, n = 1 – 4) become thermodynamically more stable than the respective mixtures of Ar and F$_2$. At even larger pressures the convex hull is dominated by a well-developed minimum at $\frac{3}{4}$ F content (ArF$_2$ stoichiometry), which, as we will later show, corresponds to a molecular crystal composed of densely packed F-Ar-F units.

As noted, the enthalpy of formation of ArF$_2$ becomes negative above 58 GPa. In addition to ArF$_2$, a tetrfluoride, ArF$_4$, is also predicted to be stable (calculated pressure of formation equals to 54 GPa§§). The trifluoride, ArF$_3$, remains thermodynamically unstable in the whole pressure range studied (0 – 200 GPa); our calculation predict that ArF$_2$ would spontaneously decompose into ArF$_3$ and ArF$_4$. Similarly, both ArF and ArF are predicted to decompose into a mixture of Ar and F$_2$. The dominance of ArF$_2$ over multiple other Ar$_n$F$_n$ stoichiometries is evident upon inspection of their crystal structures†. Indeed, all of the obtained Ar$_n$F$_n$ structures contain isolated F-Ar-F units together with unbound Ar (in case of Ar$_2$F, ArF) or F$_2$ moieties (ArF$_3$ and ArF$_4$). Thus, the chemically meaningful stoichiometries of these molecular complexes are as follow: 2ArF$_2$ = 3Ar·ArF$_2$; 2ArF = Ar·ArF$_2$; 2ArF$_3$ = 2ArF$_2$·F$_2$; ArF$_4$ = ArF$_2$·F$_2$.

At ambient pressure (p ≈ 0 GPa) the lowest enthalpy structure of ArF$_2$ is a molecular crystal analogous to the high-temperature β phase of KrF$_2$ (P4$_{2}$/mncm); 25 at the same conditions, another polymorph – isostructural with the low temperature α form of KrF$_2$ (I4/mmmm)23 – is only 25 meV per formula unit (f.u.) higher in enthalpy. Both structures, shown in Fig. 2, contain linear and symmetric F-Ar-F molecules with bond lengths of 1.766 Å (P4$_{2}$/mncm) and 1.764 Å (I4/mmmm).

As pressure increases both P4$_{2}$/mncm and I4/mmmm destabilize with respect to a third polymorph of Cmcm symmetry. Already at 5 GPa this structure has the lowest enthalpy and it remains the most stable polymorph up to 200 GPa (Fig. 2). The Cmcm phase, similar to the theoretically predicted high-pressure form of XeF$_2$, 25 is also a molecular crystal. At the low-pressure limit (p = 5 GPa) it contains slightly bent F-Ar-F molecules (angle of 178.5°) albeit with fully symmetric Ar-F bonds (1.756 Å). Upon compression to 200 GPa the Ar-F bonds contract, by over 8 %, to 1.610 Å and remain symmetric. At the high-pressure limit, the ArF$_2$ molecules are more bent, although only slightly (173.9°). The molecular character of Cmcm is retained even at 200 GPa with the shortest intermolecular Ar···F contact (2.168 Å) being over 30 % longer than the intramolecular Ar-F bond. At 200 GPa the
closest F···F contact (1.951 Å) is considerably longer than the F-F bond in pure F₂ at the same pressure (1.342 Å).

The molecular character of the ArF₂ phases is evident also upon inspection of the electronic density of states (DOS) (Fig. 3). At 0 GPa the P₄/₂/mnm structure is characterized by a wide band gap of 5.6 eV. Further analysis of the partial electronic DOS clearly shows that the character of electronic states of ArF₂ molecules can be understood within the framework of the Rundle-Pimentel electron-rich three-centre model

26: one can identify states originating from bonding (σ, π), non-bonding (σ_n, π_n), and anti-bonding (σ*, π*) combinations of both s and p atomic orbitals. In agreement with the three-centre model the empty conduction band is derived from the σ* combination of p_z orbitals. We found that compression does not have any major impact on the band gap; it decreases only slightly, to 4.6 eV for Cmcm at 100 GPa (Fig. 4). Also the nature of the electronic states remains largely unchanged, with the separation between s and p states still clearly visible. We point that the partial DOS of both P₄/₂/mnm and Cmcm indicates no d orbital participation in the bonding, in analogy to what has been recently found for XeF₂.

Turning to ArF₄ we recall that up to 200 GPa the ground state polymorph of this compound (of C2/m symmetry) is a molecular complex‡ of ArF₂ and F₂. In this structure the molecules occupy positions on a distorted NaCl lattice. Extrapolation of our results to higher pressures indicates that a structure containing genuine ArF₄ units becomes the most

stable polymorph of ArF₂ only above 250 GPa. In other words, while oxidizing argon to the +2 oxidation state requires only 60 GPa, a fourfold increase in pressure is require to stabilize this atom in the +4 oxidation state. While very high, such pressures are already obtainable.

The main driving force responsible for stabilization of both ArF₂ and ArF₄ with respect to Ar/F₂ mixtures is the volume reduction upon synthesis (7.5 and 5.1 % respectively, at 60 GPa). It’s noteworthy to mention that pressures below 100 GPa are now easily accessible by standard experimental techniques utilizing diamond anvil cells (DACs). Moreover despite the very reactive and corrosive nature of fluorine this element has already been compressed in a DAC in the past.

The use of elemental F₂ as an oxidizing reactant is essential as our simulations indicate that replacing F₂ by less chemically aggressive nitrogen trifluoride (NF₃) - which has been recently proposed as a fluorinating agent in high-pressure reactions

29 - increases the pressure of ArF₂ synthesis well over 200 GPa‡. The fact that the lowest enthalpy structures of ArF₂ and ArF₄ are molecular crystals indicates that inclusion of dispersion corrections

30,31 to the DFT hybrid functional may influence the thermodynamic stability of these phases. We have therefore calculated the so-called D3 correction

31 with Becke-Jonson damping

32 (using parameters given in ref. 33) for structures optimized with HSE06. For both ArF₂ and ArF₄ we found negligible differences in the pressure-enthalpy curves obtained with and without the dispersion corrections (see Fig. 2 and ESI‡). Although the values of these corrections reach up to ~0.5 eV (ArF₂) and ~0.6 eV (ArF₄) per f.u. at 200 GPa, the differences in these corrections between competing
polymorphs are much smaller and do not exceed 0.05/0.04 eV per f.u. for ArF2/ArF4. Given the fact that the differences in enthalpy between various ArF2 and ArF4 phases are of an order of 1 eV (i.e. two orders of magnitude larger) the inclusion of the dispersion correction does not lead to any noticeable differences in the relative stability of ArF2/ArF4 phases nor in the pressure dependence of their enthalpy of formation. Finally we would like to signal some important differences arising when the ArF system is calculated with the use of GGA (PBE functional) instead of the HSE06 hybrid functional. The energy of formation of an isolated ArF2 molecule from Ar and F2 calculated at the GGA/PBE level of theory is 116.3 kJ/mol, compared to a much larger value of 169.2 kJ/mol derived from the HSE06 calculations. Consequently GGA/PBE predicts a smaller synthesis pressure of ca 35 GPa for both ArF2 and ArF4. Underestimation of the pressure required for the stabilization of a particular compound might lead to errors in experiments, for example the synthesis might fail only because the pressure applied to the substrate mixture was not high enough. We also note that at the GGA/PBE level of theory ArnFn phases that exhibit unrealistic bonding scenarios (such as -F-F- chains) are much more stabilized with respect to structures containing ArF2 and F2 molecules than for HSE06 calculations. These differences, steaming most likely from the lack of non-local exact exchange contributions in PBE, are yet another example of the deficiencies of GGA when calculating highly correlated systems subject to large compression.34

Conclusions
In conclusion we predict the possibility of the high-pressure stabilization of ArF2-containing molecular crystals in macroscopic amounts and at room temperature. These compounds are the first examples of bulk systems containing covalently bonded argon. In case of ArF2 we show that its bonding can be described with the electron-rich three-centre model, similarly to what is found for XeF2 and KrF2. Along with recent predictions of the HP stabilization of CsF2 (n > 1)35 and HgF4,36 our work is another example of the potential of high-pressure fluorine chemistry in stabilizing exotic hypervalent molecules. This rapidly growing field is paralleled by research on matrix isolation studies conducted in a highly oxidizing environment.37

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Notes and references
§ Due to the large computational cost of the calculations employing the HSE06 functional we were not able to employ it during the USPEX runs.

§§ Our phonon calculations (ESI‡) indicate that the lowest enthalpy of formation of an isolated ArF2 molecule from Ar and F2 calculated at the GGA/PBE level of theory is 116.3 kJ/mol, compared to a much larger value of 169.2 kJ/mol derived from the HSE06 calculations. Consequently GGA/PBE predicts a smaller synthesis pressure of ca 35 GPa for both ArF2 and ArF4. Underestimation of the pressure required for the stabilization of a particular compound might lead to errors in experiments, for example the synthesis might fail only because the pressure applied to the substrate mixture was not high enough. We also note that at the GGA/PBE level of theory ArnFn phases that exhibit unrealistic bonding scenarios (such as -F-F- chains) are much more stabilized with respect to structures containing ArF2 and F2 molecules than for HSE06 calculations. These differences, steaming most likely from the lack of non-local exact exchange contributions in PBE, are yet another example of the deficiencies of GGA when calculating highly correlated systems subject to large compression.34

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