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A hypervalent and cubically coordinated molecular phase of IF₈ predicted at high pressure†

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Up to now, the maximum coordination number of iodine is seven in neutral iodine heptafluoride (IF₇) and eight in anionic octafluoride (IF₈⁻). Here, we explore pressure as a method for realizing new hypercoordinated iodine compounds. First-principles swarm structure calculations have been used to predict the high-pressure and $T \rightarrow 0$ K phase diagram of binary iodine fluorides. The investigated compounds are predicted to undergo complex structural phase transitions under high pressure, accompanied by various semiconductor to metal transitions. The pressure induced formation of a neutral octafluoride compound, IF₈, consisting of eight-coordinated iodine is one of several unprecedented predicted structures. In sharp contrast to the square antiprismatic structure in IF₇⁻, IF₈, which is dynamically unstable under atmospheric conditions, is stable and adopts a quasi-cube molecular configuration with $R3$ symmetry at 300 GPa. The metallicity of IF₈ originates from a hole in the fluorine 2p-bands that dominate the Fermi surface. The highly unusual coordination sphere in IF₈ at 300 GPa is a consequence of the 5d levels of iodine coming down and becoming part of the valence, where they mix with iodine’s 5s and 5p levels and engage in chemical bonding. The valence expansion of iodine under pressure effectively makes IF₈ not only hypercoordinated, but also hypervalent.

1. Introduction

It is well known that the coordination number of atoms in compounds can greatly affect chemical properties and exploring new coordination motifs of elements is of importance to understand their chemical behavior and expand their applications. Iodine has, with the exception of astatine, the lowest electronegativity, the largest polarizability, and the largest atom size of the halogens. These properties and the ability to readily engage in hypercoordination, i.e. allowing for more atoms in its coordination sphere than what is predicted by the octet rule, combined with its low toxicity, make iodine distinct from the lighter p-block elements. The ability of iodine to engage in hypercoordination allows fabrication of compounds that are potential substitutes for transition metal-based catalysts. Commercially available hypercoordinated iodine compounds have shown promise for mild and highly selective oxidizing ability and environmentally benign catalysis.

The highest known coordination number in a neutral iodine fluoride compound is seven, in IF₇. Isoelectronic XeF₇⁻ and TeF₇⁻ have been synthesized. With the exception of some caged ions, higher coordination numbers in neutral main group compounds are, to the best of our knowledge, non-existent. XeF₈ has been shown unstable even under pressures reaching 200 GPa. Chemically, the limit in the coordination number of iodine can be rationalized from the atom’s seven valence electrons. Formally, the valence shell of iodine in IF₇ has 5e⁻/C₀ salt. The coordination geometry of IF₈⁻ is square antiprismatic. This kind of arrangement is commonly observed in different transition metal octafluorides, for example in TaF₈⁻, ReF₈⁻ and ZrF₈⁻.

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Does this mean that the quest for higher coordination numbers in neutral iodine fluorides is over?

We do not believe so. Pressure is known to fundamentally change the chemistry and structure by, for example, overcoming reaction energy barriers, shortening interatomic distances, and modifying atomic orbital energy levels. There are many examples of the utility of pressure in allowing remarkable new hypercoordinated compounds, for example H$i,I, XeF$_{6}, HgF$_{4}, Li$_3 Cs, CsF$_s, AuF$_{6}, Li$_2 Au, AH$_{x} (A = Sr, Ba), LaH$_{10}, and BaReH$_{9}.

To explore the effects of pressure and search for higher coordination numbers in iodine fluorides, we have performed an extensive structure search of selected stoichiometries of IF$_x$ ($x = 1/3, 1/2, 2/3, 1–12$) from 100 to 300 GPa using swarm-intelligence-based structural prediction calculations. Dynamical stability is an important criterion when predicting structural stability. The calculated phonon spectra of the predicted phases are shown in the ESI† and show no phonon modes with imaginary frequencies (Fig. S1†). The most notable of our predictions is the stabilization of a molecular IF$_8$ phase of R$3$ symmetry at 300 GPa. The cubic coordination geometry of this molecular solid is distinct from the square antiprismonic structure in IF$_8$. We will return to discuss this unprecedented iodine coordination sphere and its underlying electronic structure.

2. Results and discussion

2.1 Stability and crystal structures

The relative stabilities of the different binary compositions were estimated by calculating the enthalpy of formation at $T \rightarrow 0$ K and building the convex hull based on the most stable structures of the considered compositions (Fig. 1a). In Fig. 1a, the thermodynamically stable IF$_x$ structures are depicted as filled symbols, which resist decomposing into elemental solids or other stable compounds. Besides reproducing the known structures of IF$_x$ ($x = 3, 5, 7$) under ambient conditions, some unexpected compounds with stoichiometries of IF$_x$ ($x = 8, 10, 11, 12$) are predicted to become thermodynamically stable under high pressure. Note that these stoichiometries do not mean the same coordination number of fluorine around iodine. The maximal coordination number found is 8. The crystal structures of iodine fluorides that show stability in some part of the investigated pressure range are shown in Fig. 2. The stable structures will be discussed separately. All other considered stoichiometries, not shown in Fig. 2, have enthalpies that sit slightly above the solid line in Fig. 1a and are either unstable or metastable. Decomposition enthalpies with respect to stable IF$_x$ compounds and elemental solid I$_2$ or F$_2$ are shown in Table S1.†

A pressure-resolved phase diagram of iodine fluorides was built to facilitate experimental studies and is shown in Fig. 1b. At ambient pressure, the known molecular crystals of IF$_x$ ($x = 3, 5$ and 7) are reproduced (Fig. 2a, c, and f). Under compression, these molecular structures are predicted to undergo phase transitions and eventually transform into aggregated phases. For IF$_3$, the ambient pressure orthorhombic Pnma structure transforms to a monoclinic phase (space group P2$_1$/m) at 23 GPa (Fig. 2b). The P2$_1$/m phase contains a zigzag iodine chain, in which an I–I distance of 2.7 Å is nearly the same as that in the I$_2$ molecule at 1 atm. The IF$_3$ molecular phase is predicted to become unstable with respect to IF$_5$ and I$_2$ above 140 GPa. Under compression, C2/c-structured IF$_5$ is predicted to first transform to another molecular phase with P1 symmetry at 28 GPa (Fig. 2d) and subsequently into a non-molecular P2$_1$/m phase above 139 GPa (Fig. 2e). In contrast to IF$_5$, IF$_7$ directly transforms into a non-molecular P2$_1$/m phase at 20 GPa (Fig. 2g). Compared with the structures under near ambient conditions (Fig. 2c and f), the IF$_5$ and IF$_7$ molecular phases become gradually more distorted with compression. IF$_5$ is predicted to transform into an orthorhombic structure with Pnma symmetry, consisting of face-sharing 14-fold 1-F polyhedra (Fig. 2e) at 200 GPa. P2$_1$/m-structured IF$_7$ is similarly predicted to be structured as an edge-sharing 12-fold polyhedron (Fig. 2g) at 100 GPa.

2.2 Unexpected IF$_8$

We arrive next to the IF$_8$ stoichiometry. Here a new stable compound with R$3$ symmetry is predicted to be stable above 260
After examining the results of our structural searches, we found another IF₈ phase with a square antiprismonic structure (space group Pn₃n). However, the Pn₃n-structured IF₈ (Fig. S4†) is unstable with respect to the quasi-cubical IF₈ (i.e. R₃-structured IF₈) by 14.6 eV per formula unit. The large difference in enthalpy between the two structures can be attributed to a more favorable ππ-term for the R₃ structure and to the occupation of anti-bonding levels involving I 5d levels in the Pn₃n structure (details are provided in the ESI†)

2.3 Chemical bonding and electronic properties of IF₈

Under normal ambient conditions molecular IF₇ takes a pentagonal bipyramidal coordination and ionic IF₈⁻ a square antiprismonic coordination. The coordination sphere of these closed-shell molecules can be straightforwardly rationalized with simple valence shell electron-pair-repulsion (VSEPR) arguments, in which ligands maximize distances to their neighbors to minimize exchange, or Pauli repulsion. In contrast, molecular IF₈ is an electron deficient radical, with one hole in its valence p-shell. Under ambient conditions we are correct to expect such a structure to dissociate into IF₇ and an F atom. So how can IF₈ represent a stable composition under high compression, and why does it take its peculiar cubic structure?

We think that this can be explained in the following way: first, we know that the difference in electronegativity between F and I will not change meaningfully under high compression, and so we cannot expect a drastic change in the electronic structure for this reason. In atomic iodine, the 5d levels lie 8.2 eV above the 5p levels. Consequently, mixing, or hybridization, with 5d is not considered important for the chemical behavior of iodine under normal conditions. As we shall see, this changes under compression. To understand why, we take a molecular orbital (MO) perspective.

We know that for a cubic ligand field, the expected splitting of non-bonding d-orbitals is three (T₂g) – over – two (Eₕ). Work on 8-coordination by Burdett, Hoffmann and Fay (BHF) compared different coordination geometries using group theory arguments and extended Hückel calculations. Among other things, it was demonstrated that the Eₕ levels (the dₓ²−ᵧ² orbitals) should be non-bonding because they do not point along the bond axes of a cubic ligand field. However, the BHF work did not evaluate interactions that would occur with ligand p-levels in this specific coordination environment. The rarity of the cubic coordination sphere in nature is undoubtedly the reason for its near absence in the scientific literature.

To remedy the situation, we show in Fig. 3 the molecular orbital (MO) diagram for I 5s, 5p and 5d interacting with F 2p levels in a cubic (O₅ₙ symmetric) coordination geometry. This diagram is a sketch constructed from symmetry arguments applied to an isolated IF₈ molecule. The energy orderings have been predicted using DFT calculations on the different fragments in vacuum. Two orbital combinations, of A₁g and T₁u symmetry, predict the specific interactions of I 5s and 5p with the corresponding symmetry adapted MOs of the F₈ ligand cage. Assuming that the energy ordering shown in Fig. 3 is correct, five out of the six occupied MOs of these symmetries are I–F

![Diagram of molecular structures](image-url)
Fig. 3  Molecular orbital diagram showing orbitals of iodine mixing with the symmetry adapted ligand orbitals of the F₈ cage. Energies are not to scale. Approximate energy orderings were predicted using DFT calculations on frozen fragments of IF₈ and F₈ in vacuum. The energy levels of atomic I are known from experiment.⁷ Orbital symmetries responsible for I–F bonding are colored green for T₂g and Eₘ (I 5d), red for T₃u (I 5p) and black for A₁g (I 5s). One bonding combination of A₁g symmetry between I 5s and F 2s valence orbitals is omitted for clarity, as are the unoccupied orbitals.

bonding. The T₂g and Eₘ levels are noteworthy, as they predict the exclusive bonding interaction between the formally unoccupied I 5d levels and the F 2p ligand orbitals of the same symmetry. The designations of the MOs as bonding and anti-bonding are based on symmetry arguments, and this will not change under pressure. What might change is the relative importance of the MOs, their energy relative each other, and the degree of mixing of what are, under ambient conditions, unoccupied I 5d-levels. How can occupation of I 5d orbitals be possible under compression?

That orbitals of different kind can cross due to compression is well known.⁴⁵ Mao-Sheng Miao and Roald Hoffmann have given a nice explanation as to why orbitals can cross in compressed atoms.⁴⁶ In brief, orbitals that are smaller, and have fewer radial nodes, are less affected by compression. For a given principal quantum number, compression tend to increase level energies as s > p > d. In complex systems such as IF₈, the purely physical effect of pressure is one factor affecting level ordering. A positive charge on iodine also helps to decrease the energy of I 5d levels relative to the ligand F orbitals, and we will return to address the oxidation state of iodine. As we shall see, chemical interactions with F atoms play a key role for bringing down I 5d levels in IF₈.

We can use the MO diagram in Fig. 3 to understand that as the volume of the F₈ cage decreases, as it will under compression, the overlap between I and F-based orbitals will naturally increase. Of course, iodine atoms and F₈ are just fictional references here – what matters are the IF₈ orbitals. Because the occupied T₂g and Eₘ MOs of IF₈ are all I–F bonding, these MOs will come down in energy relative to the other MOs as the pressure mounts and overlaps increase. The same goes for the I–F bonding A₁g and T₃u orbitals, which, together with the T₂g and Eₘ set, are predicted to drive the stabilization of the high symmetry cubic coordination under high pressure. Put differently, participation of I 5d, and the cubic coordination geometry, can be rationalized by symmetry facilitated bonding interactions with the ligand framework, which become increasingly pronounced as the volume of the system decreases (Fig. S5†). The ligand coordination is essential for bringing down the d-orbitals of iodine. There is, for example, no participation of I 5d levels in similarly compressed elemental iodine (Fig. S6†). There are, as the MO diagram shows, also simultaneous F–F interactions of both bonding and antibonding character in IF₈. However, as we shall see and quantify, I–F bonding interactions are significantly larger than F–F interactions, which largely cancel out under compression.

How does this analysis fit with the predicted R3 structure of IF₈ at 300 GPa? Remarkably well, as it turns out. First, our crystal orbital Hamilton populations (COHPs) confirm the predominately molecular character of the electronic structure, already inferred by the predicted bond lengths. The integrated COHP up to the Fermi level between iodine and its 8 nearest neighbors (F₁ & F₂) is −6.4/−6.2 eV, which is indicative of strong bonding interactions. In contrast, iodine’s interactions with its third nearest neighbor (F₃) is estimated as −0.7 eV, which clearly suggests that R3-structured IF₈ can be viewed predominately as a molecular crystal. The integrated COHPs between F₁–F₁, F₁–F₂ and F₁–F₃ are 0.06, 0.07 and −0.14 eV, respectively (F₃ refers to an F atom in the nearest neighboring IF₈ unit). That F–F bonding and anti-bonding interactions within the IF₈ molecule largely cancel out, but are destabilizing overall, is in qualitative agreement with the MO diagram in Fig. 3. Bonding between IF₈ molecules (I–F₃ and F₁–F₃) comes out as exclusively stabilizing in the COHP analysis (Fig. 4c and S4c†).

At 300 GPa, iodine’s 5d band penetrates well into the valence region, where it undergoes a significant dispersion and mixes both with the 5s and 5p levels of iodine, and with the valence shell of fluorine (Fig. 4b). Our COHP analysis clearly shows significant bonding interactions involving d-levels below the Fermi level (Fig. 4c). The only anti-bonding interactions observed near the Fermi level are of I 5s–F 2p and F 2p–F 2p character, in good agreement with the schematic MO analysis of the IF₈ molecule in Fig. 3. The only other anti-bonding states identified in the COHP are due to overlap with F 2s, which we omitted from Fig. 3 for clarity.

What about the metallic character of the material? That the R3-structured IF₈ shows metallicity (Fig. 4) is expected from the
fact that it’s a molecular solid of an open-shell molecule. In contrast, the $P_2/m$-structured IF$_7$, a molecular solid of a closed-shell molecule, is a semiconductor (Fig. S7†). We did perform an in silico experiment by artificially adding one electron to the IF$_8$ unit cell (the negative charge being compensated by a smeared out positive background charge in our program). The result of the extra electron is a material with semiconducting character that exhibits a similar Projected Density of States (PDOS) distribution (Fig. S8†). In IF$_8$, the Density of States (DOS) at the Fermi-level is dominated by the F 2p-bands. That the Fermi level should be dominated by F 2p is expected, and is also in good agreement with our MO analysis of the isolated IF$_8$ molecule (Fig. 3), which predicts the highest occupied level to be a pure F 2p–F 2p antibonding level of $E_u$ symmetry. Spin-polarized calculations on the $R^3$ phase of IF$_8$ shows that the material is not magnetic (Fig. S9†).

Because of significant mixing of $s$, $p$ and $d$ levels of iodine, we can conclude that a valence expansion of iodine has occurred. This implies that the IF$_8$ molecule, predicted to exist in the crystalline state at 300 GPa, is not only hyper-coordinated but also hypervalent. Expansion of iodine's valence space is here a consequence of additional energy levels being available for bonding, not a classification based on the fact that the number of ligands around iodine exceeds seven. Our bonding and density of states analyses are based on orbital projection methods, which differ slightly depending on the program used. Even though these methods are not exact, in that they do not recover all of the electron density, all approaches that we tested (see the Fig. S10†) do support the general conclusion that there is a valence expansion and that the I 5d levels are essentially equally populated. The $d_{yz}$ orbital does appear to be slightly more populated on average, which may explain the small structural deviation from a perfect cube (Table S4†).

What about the oxidation state of iodine? Because the predicted $R^3$ phase of IF$_8$ is metallic, a formal ionic extrapolation is not possible. If we nonetheless consider each F ligand as $F^–$ and remove one electron from the ligands due to the radical character (the F 2p hole), the oxidation state of iodine in IF$_8$ becomes +VII. Our best estimate of the total iodine orbital occupation in IF$_8$ corresponds to an atomic charge of +3.8, when calculated using a Mulliken-type approach. The relative occupation of the $I-based orbitals is $s^1p^6d^1$. We must stress that these values are approximate and sensitive to the internal basis set used in the projection scheme. Nevertheless, the orbital-based charge is in strikingly good agreement with a separately calculated QTAIM charge of +4.0 on iodine (see the ESI†). Combined, the orbital and charge density analyses, and the Electron localization Function (ELF, Fig. S11†) suggest a rather large degree of covalency in IF$_8$, and the presence of strong polar covalent and hypervalent bonds.

3. Conclusion

First-principles swarm structural search calculations have been employed to explore the phase stabilities and structures of I–F compounds under high pressure. Pressure favors the stabilization of fluoride-rich compounds (IF$_4$ = 3, 5, 7, 8, 10, 11, and 12) rather than iodine-rich compounds. Several I–F compounds are predicted to undergo pressure-induced molecular to extended phase transformations, accompanied by semiconductor to metal transitions. We have focused our analyses on a predicted $R^3$ phase of IF$_8$, where pressure stabilizes a unique cubical molecular structure. The predicted cubical coordination geometry is unique in main group chemistry, where square antiprismatic octa-coordination is common. The molecular crystal has an electron-deficient electronic structure that causes it to be metallic. Various molecular orbital and crystal orbital
projection-based analyses support a conclusion that the electronic and geometric structure of IF₈ is a consequence of valence expansion of iodine.

4. Computational details

Searches for I–F binary compounds were performed with the CALYPSO structure prediction method, while allowing for up to 4 formula units per unit cell. The predictive accuracy of this methodology has been repeatedly demonstrated on various systems, from elemental solids to binary and ternary compounds. The Vienna Ab initio Simulation Package (VASP) code and the Perdew–Burke–Ernzerhof functional in the generalized gradient approximation were adopted to perform structural relaxations within the framework of density-functional theory (DFT). The electron–ion interactions were represented by means of the all-electron projector augmented-wave method with 5s²5p⁵ and 2s²2p⁵ treated as the valence electrons of I and F atoms, respectively. A plane-wave basis set cutoff of 950 eV and the Monkhorst–Pack scheme with a dense k-point grid spacing of 2π × 0.032 Å⁻¹ in the Brillouin zone were used to converge energies to less than 1 meV/atom. To ensure the validity of the pseudopotentials used, the equation of state of IF₈ was also calculated using the full-potential WIEN2k code, with nearly identical results to the VASP calculations (Fig. S12). Phonon calculations were performed using a superscel approach with the finite displacement method using Phonopy. The Electron Localization Function (ELF) was used to estimate the degree of electron localization. Crystal Orbital Hamilton Population (COHP) analyses were performed using the LOBSTER program. Van der Waals (vdW) interactions were included using the optB88-vdw approach. DFT calculations on molecular fragments were made using Gaussian 16, revision B.01.

Conflicts of interest

The authors declare no competing financial interest.

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