

6. The Halogens and their Compounds

We now come to our coverage of Chapter 12, which deals with the Groups 17 and 18 elements, i.e. the halogens and the noble gases. The redox chemistry of the oxoacids and anions was discussed extensively in Chemistry 2810; I suggest you look back at your notes and to Chapter 6 (the redox chapter) to refresh this material in your mind.

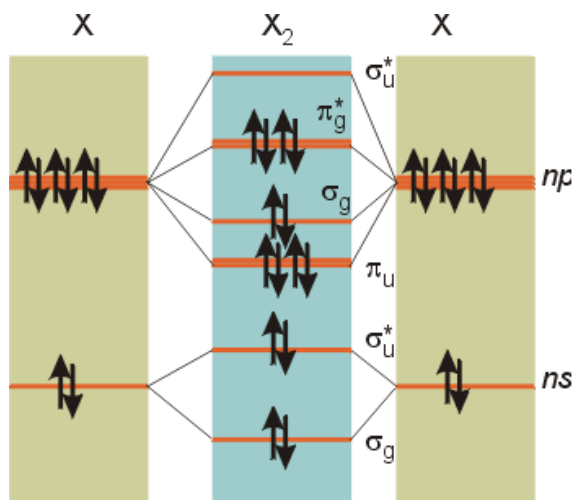
6.1 The elements

These are all diatomic molecular compounds. We have already discussed the MO structures of the first row diatomic molecules. Remember that F_2 was significant in having the sequence of MO filling be that of the so-called “first-order” bonding model. I.e. the electron configuration of difluorine is: $1s_g^2 1s_u^2 2s_g^2 1p_u^4 1p_g^4$.

In the case of dichlorine, and in fact all the heavier halogens too, the sequence of filling is that of the elements up to nitrogen in the 2nd row elements, i.e. the so-called “second-order” orbital sequence. This is shown in the diagram shown at the right. Hence for Cl_2 and the heavier elements, the electron configurations are: $1s_g^2 1s_u^2 1p_u^4 2s_g^2 1p_g^4$.

The colours of the halogens: fluorine pale yellow, chlorine yellow-green, bromine dark orange and iodine as purple vapour and as dark purple crystals are a direct result of the electronic structures. Absorption of visible light occurs by promotion of electrons from the $1p_g^4$ HOMO to the $2s_u$ LUMO. The colour change in going down the group involves a “red-shift”, i.e. a drop to lower wavelengths of absorbed light. This corresponds directly to the expected decrease in HOMO-LUMO gap on descending the periodic table, as the overlap that leads to bonding decreases due to the larger sizes of the valence orbitals.

Note the bond energies of the dihalogens, shown in Table 6.1



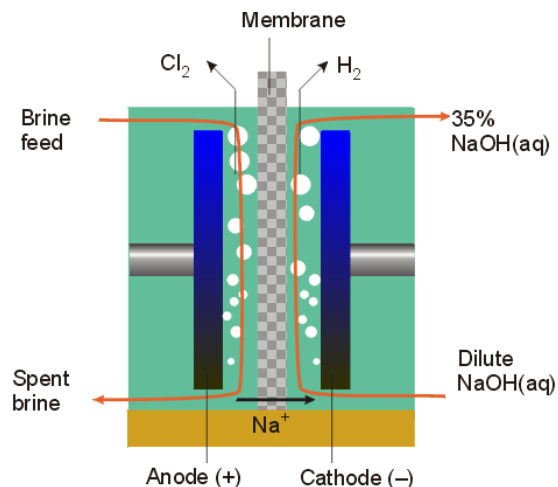
Bond	Bond Energy, kJ mol^{-1}
F_2	159
Cl	243
Br	193
I_2	151

We see that the bond energy of difluorine is anomalously low. It is not surprising therefore that many of the mechanisms for reaction of difluorine involve $F\bullet$ radicals. The bond energy of chlorine is substantially larger, and only diiodine has a lower bond energy among the halogens than does difluorine. This weakness is often attributed to the extent of repulsion between the lone pairs on adjacent atoms due to the very short bond in difluorine. However, molecular orbital theory provides a more cogent explanation: we know that p-bonds for the 2nd period elements are particularly effective. In difluorine, not only the bonding $1p_u$, but also the antibonding $1p_g$ orbitals are quadruply occupied. Hence we might expect a strong p-antibond as well as the strong p-bond – and we know already that antibonding always *more than cancels bonding overlap*.

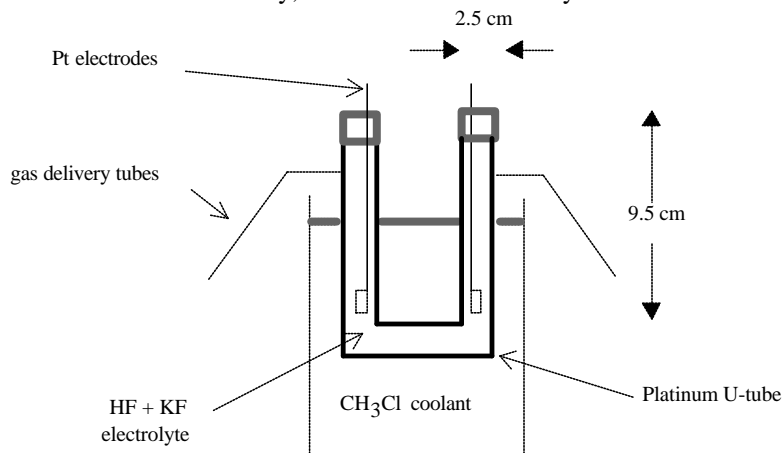
6.1.1 Isolation of the elements

The elements are produced by electrolysis (F_2 and Cl_2), or by reaction of Cl_2 with halides (Br_2 and I_2). The chemistry and electrochemistry of the chlor-alkali cell were discussed in great detail in Chemistry 2810, and I will not elaborate any further on this topic now. It remains a vital industrial preparative method, although the overall tonnage of elemental chlorine usage in industry is expected to fall as increasingly alternate technologies are developed, e.g. for preparation of potable water supplies and bleaching of paper pulp.

Pure F_2 was first prepared by the Frenchman Henri Moissan in 1886 using an electrolysis cell. It was one of the last of the common elements in the periodic table to be isolated as the free element. Chemists had been aware of the existence of the element from its compounds for many years beforehand, but the great reactivity of difluorine had prevented its isolation. Moissan's cell consisted of a small platinum U-



tube with fluorospar (mineral) stoppers which allowed for platinum electrodes and small delivery tubes. Originally he tried pure HF as the electrolyte and source of fluoride ion, but he later realized that the electrolysis reaction is catalysed by the presence of alkali metal fluorides. The ideal electrolyte is $\text{KF}\cdot 2\text{HF}$. This recipe remains the basis of the industrial preparation of fluorine to this day, with advances made only in the size and construction of the electrolytic cells.

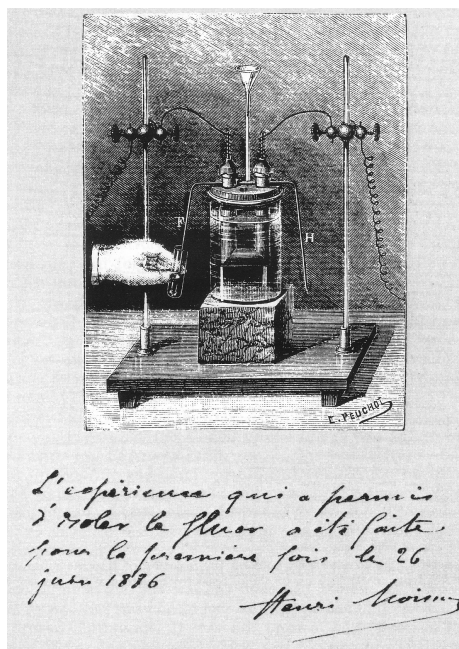


Schematic diagram of Henri Moissan's cell with which he discovered F_2 in 1886

The schematic diagram above shows the apparatus that Moissan built that allowed him to produce a stream of fluorine gas emanating from one of the gas delivery tubes. Reactions were performed in small platinum crucibles and deflagrating spoons containing other elements that were suspended in the gas stream. This diagram has been illustrated in a contemporary etching, which is shown in the picture at the right. The caption signed by Henri Moissan reads: *The experiment that permitted the isolation of fluorine for the first time on the 26th June, 1886.*

Modern industrial electrolytic cells for the production of F_2 are constructed from mild steel using a steel cathode and a carbon anode and a gas collector for the fluorine gas constructed of **monel**, an alloy of copper and nickel that shows high resistance to fluorine and is highly prized for this reason in all chemical work using elemental fluorine.

One of the big uses of F_2 remains the preparation of UF_6 , used in the ^{235}U enrichment procedure for nuclear fuels. Note that Canada is unique in using a power-generating reactor design based on natural uranium fuel (that is, fuel that does not require enrichment). Reactors of all other countries use partially enriched fuel, that is uranium dioxide that has an enhanced content of the ^{235}U compared to the major ^{238}U isotope. Of course, the ^{235}U is also used in manufacturing bombs. Hence the difficulty in distinguishing between peaceful and military uses of nuclear energy. Countries that purchase Canadian built CANDU reactors, however, have no excuse at all for building fuel enrichment facilities, which are large industrial installations that are easy to detect through ground-based and satellite intelligence surveillance.



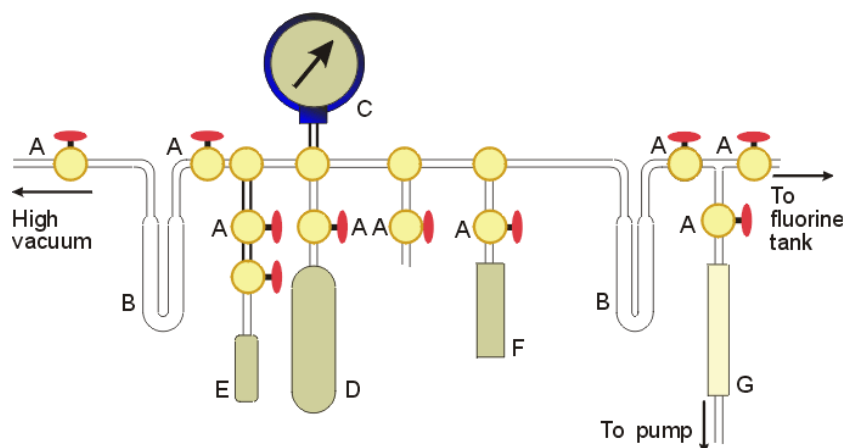
6.1.2 Special properties of fluorine

Elemental fluorine is extremely reactive. When Moissan first isolated it, this reactivity immediately became obvious. He observed: *Phosphorus ignited in the presence of this gas, producing phosphorus fluoride. Sulphur heated and melted rapidly. Carbon appeared to have no effect. Fused potassium chloride disintegrated when cold and gave off chlorine. Finally, crystallised silicon, washed by nitric acid and hydrofluoric acid, ignited on contact with this gas and burnt briskly, producing silicon fluoride. The platino-iridium electrode forming the positive pole was heavily corroded, while the platinum electrode of the negative pole was intact.*

Virtually every element reacts directly with elemental fluorine. In fact most elements will quite literally burn in a fluorine atmosphere. However, some metals in bulk form, if sufficiently pure, will oxidize on the surface in such a way that the initially formed fluoride layer forms a passive coating of metal fluoride on the surface. Nickel is the best at this self-passivation reaction. In this nickel resembles the stabilization of aluminum with oxygen, for which a thin layer of the metal oxide prevents further reaction in the absence of an initiator, such as a strong acid. Stainless steel with a high nickel content and as mentioned above, the alloy Monel, are all materials that can be successfully used to handle elemental fluorine. Nevertheless all work with elemental fluorine is hazardous and requires great caution and attention to every detail of the experiments.

Special vacuum lines constructed entirely of metals such as nickel and monel are required to work with elemental fluorine. A diagram of such a vacuum line is shown in the following figure:

Legend for fluorine vacuum line: (A) monel valves, (B) nickel U-traps for the condensation of gases, (C) monel pressure gauge, (D) nickel container for gas storage, (E) polytetrafluoroethylene reaction tube, (F) nickel reaction vessel, (G) nickel canister filed with soda lime (a mixture of sodium and calcium hydroxides) for neutralization of reactive HF which is a common by-product of fluorination reactions.



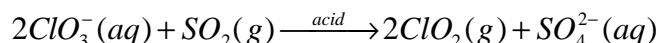
In addition to these metals that are self-passivating with fluorine, the use of fluorinated hydrocarbon plastics is also very common in fluorine chemistry. Teflon is the common trade name for **polytetrafluoroethylene**, while the more rigid Kel-F is **polychlorotrifluoroethylene**. Indeed, it would be fair to say that modern fluorine chemistry was revolutionized by the widespread availability of these specialty plastic products. Normally glass containers may not be used in fluorine chemistry. As Moissan already observed, silica burns in fluorine. Furthermore, HF is a common side-product when F₂ reacts with just about any hydrogen-containing compound, including water. HF strongly attacks glass. Hence Teflon and Kel-F are commonly used as glass-replacements in fluorine chemistry.

6.2 Halogen oxyacids and oxoanions

The oxyacids and their conjugate salt anions, the oxoanions, of the halogens form the most complete series of any of the elements. Of course, they are only possible for chlorine, bromine and iodine, as fluorine is *more electronegative* than oxygen. Chlorine and iodine form almost identical series of these compounds, but bromine is more difficult to ionize to the highest oxidation state (7), another consequence of the **scandide contraction**. However, an important difference exists for the periodic acid, which has the formula H₅IO₆, which corresponds to the formula HIO₄ + 2 H₂O. However, periodate which exists in basic media is still IO₄⁻.

There is a great deal to be learned from a careful study of the halogen oxyacids and their anions, especially the series shown in the diagram for chlorine. They are the most complete series of element-oxoanions known. Each is separated from the other by a change of two oxidation numbers for the central atom. The +7 state is highly reactive, and in particular anhydrous (pure) perchloric acid as well as many perchlorate salts are strong oxidizers. The explosive hazard of perchlorates was discussed in Chemistry 2810.

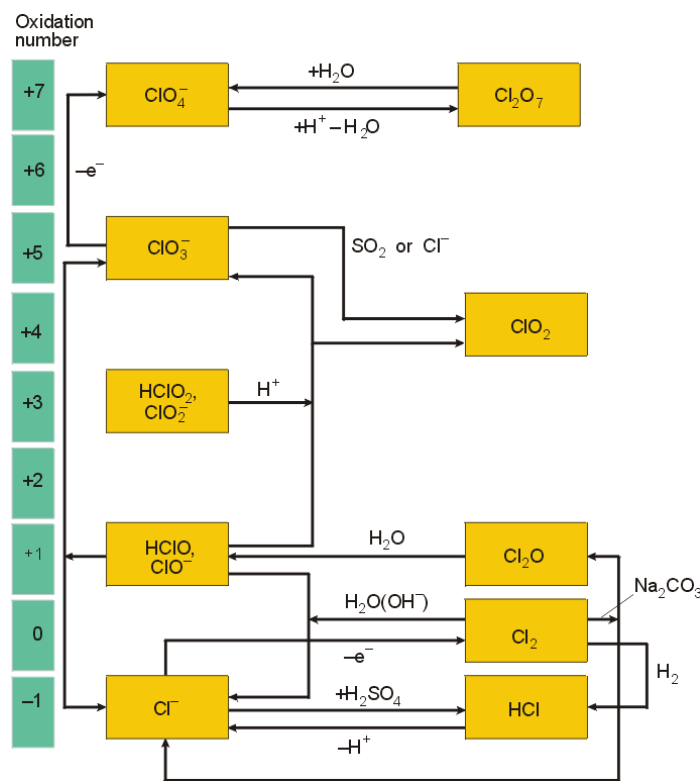
The interconversion of these oxy compounds was also discussed in Chemistry 2810 and rationalized using electrochemical data. There are also neutral oxygen compounds of chlorine involved in the redox cycles, including Cl₂O (a brown-yellow gas), ClO₂ (a yellow gas) and Cl₂O₇ (a colourless liquid). Those such as ClO₂ that belong to even oxidation states of chlorine are odd-electron compounds (free radicals). This species is produced in dilute form on a large scale as an oxidant for the bleaching of paper pulp. It is produced by the reaction of sulfur dioxide on chlorate salts by the reaction:



The diagram that follows summarizes the reactions involved in the interconversion of the halogen oxyacids. Many of the reactions are either disproportionation or comproportionation reactions.

OXYACIDS AND OXYANIONS OF CHLORINE

OX. ST.	+1	+3	+5	+7
ACIDS	hypochlorous $\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}:$	chlorous $\text{H}-\ddot{\text{O}}-\overset{+}{\text{Cl}}-\overset{-}{\text{O}}:$	chloric $\text{H}-\overset{+}{\text{O}}-\overset{+}{\text{Cl}}-\overset{-}{\text{O}}:$	perchloric $\text{H}-\overset{+}{\text{O}}-\overset{+}{\text{Cl}}-\overset{-}{\text{O}}-\overset{-}{\text{O}}:$
ANIONS	hypochlorite ClO^-	chlorite ClO_2^-	chlorate ClO_3^-	perchlorate ClO_4^-

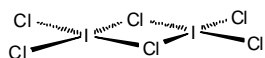


6.3 Chemistry of interhalogen compounds

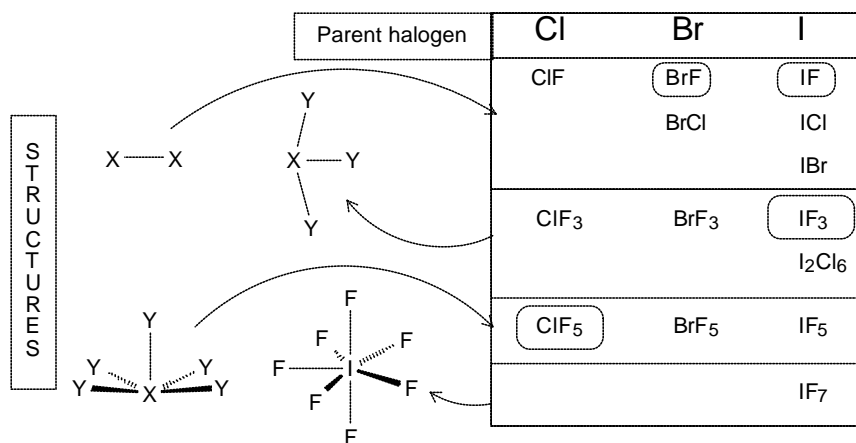
The halogens form derivatives of almost all the elements. Indeed, fluorine combines with *all* elements except helium argon and neon. So common, and so important, are the element halides, that halogen derivatives are discussed for all the other elements. Hence we will not deal with them in this section. An important class of compounds exists, however, in which *halogen elements are bonded to each other*. Such compounds (which may be neutral, anionic or cationic) are known as **interhalogens**.

In the laboratory for Chemistry 3810 we deal with interhalogen compounds in experiment #10. Each of the three compounds in this laboratory are examples of monpositive iodine, but they are prepared as neutral (IBr), anionic (ICl_2^-), as well as the cationic complex of I^+ with pyridine ligands. These simple compounds serve to illustrate the fascinating chemical behaviour of the interhalogen compounds.

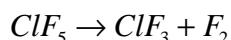
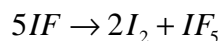
The structures of the interhalogens are accurately given by the VSEPR theory as shown in the scheme at right, including a rare example of a pentagonal bipyramidal molecule in IF_7 . (Although the evidence is that this compound has a slightly irregular structure, with inequivalent bond lengths in the pentagonal plane.) All are based on simple monomeric structures, with the *heavier* halogen as central atom, with the sole exception of " ICl_3 ", which is actually a chlorine-bridged dimer, as follows:

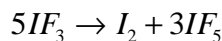


KNOWN INTERHALOGEN COMPOUNDS



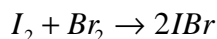
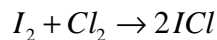
Those examples which are unstable compounds are enclosed in dashed boxes. They decompose by the following reactions



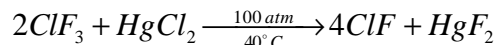


6.3.1 Synthetic routes to some interhalogens

ICl and IBr can be prepared by mixing the halogens in a suitable solvent, as done in experiment 10:

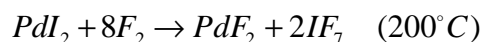
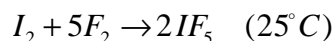
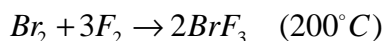


But this does not work for ClF, which is prepared by the following reaction:



Note the high pressures involved. I have performed this reaction when involved in a research project at the Free University of Berlin. We employed stainless steel autoclaves (pressure reactors) which could be heated and shaken in remote chambers in an autoclave room to protect from explosions caused by a rupture of the pressure relief disks that could occur if the pressure built up to too high a value. Note again the use of mercury (we saw this element earlier in the transmetallation synthesis of many element organometallics); it is an extremely versatile element in chemical synthesis.

The remaining halogen fluorides are mostly prepared by direct interaction of the elements, as shown by the following examples; but note the preparative route to IF₇.



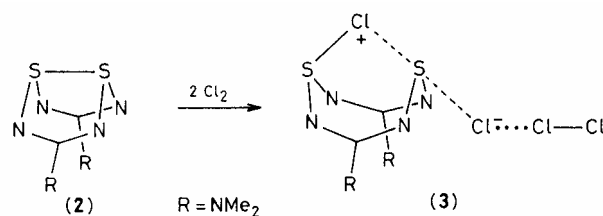
6.3.2 Halogen and interhalogen anions

The simple anions are perhaps the most commonly encountered for all the halogen elements. Closely related to the halogen anions F⁻, Cl⁻, Br⁻ and I⁻ are the molecular ions known as the **pseudohalides**. These are an important class of mononegative anions that mimic the chemistry of the halides. In a few cases, the corresponding neutral dimers also exist, i.e. what is often called a **pseudohalogen**. Some common examples of this class of compounds are in the following table.

Pseudohalide	Pseudohalogen	$E_{1/2}^0 (red.) / V$	Acid	pK_a^*
CN ⁻ cyanide	NCCN cyanogen	+0.27	HCN hydrogen cyanide	9.2
SCN ⁻ thiocyanate	NCSSCN dithiocyanogen	+0.77	HCNS hydrogen isothiocyanate	-1.9
OCN ⁻ cyanate			HCNO isocyanic acid	3.5
CNO ⁻ fulminate			HCNO fulminic acid	
NNN ⁻ azide			HNNN hydrazoic acid	4.92

* A. Alberta and E.R. Serjeant, The determination of ionization constants, London (1984).

The most common examples of an *interhalogen* anions is most definitely the triiodide ion, I₃⁻. The tribromide ion is also known, but trichloride is much less stable and is rarely encountered. While I was a post-doctoral researcher at the University of Guelph, however, I was involved on a project in which a student named Robert Reed isolated such an anion during a chlorination reaction. Indications of something unusual about this structure was the low C,H,N analytical data, and the tendency for the crystals to decompose with the smell of halogens. Fresh crystals were a beautiful rose-red colour, but on standing they tended to decolourize. The answer to the puzzle came from the X-ray crystal structure, which clearly shows the presence of an unsymmetrical trichloride ion in the crystal lattice.



Legend for the trichloride reaction and structure

In this reaction we were oxidizing a weak cross-ring sulfur-sulfur bond with molecular chlorine. Cl^+ was added to the sulfur in a reaction reminiscent of the cyclic bromonium ion of organic chemistry (addition to an alkene by molecular bromine). The counter ion should then have been Cl^- . Instead, we incorporated a second molecule of chlorine into the lattice, which combined with the Cl^- to form Cl_3^- . The lower picture is an example of an Oak Ridge Thermal Elipsoid Program output in which 3-D ellipsoids are drawn to indicate the region of space in which 30% of the electron density of each atom is found, as a result of molecular vibrations within the crystalline lattice. R.T. Boeré, et. al. *J. Chem. Soc., Chem. Commun.* (1985) 655

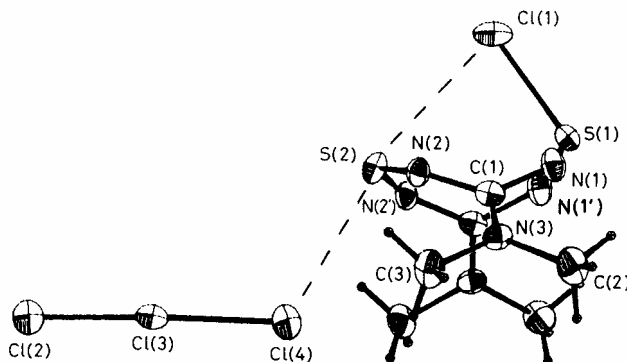
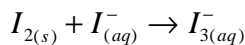
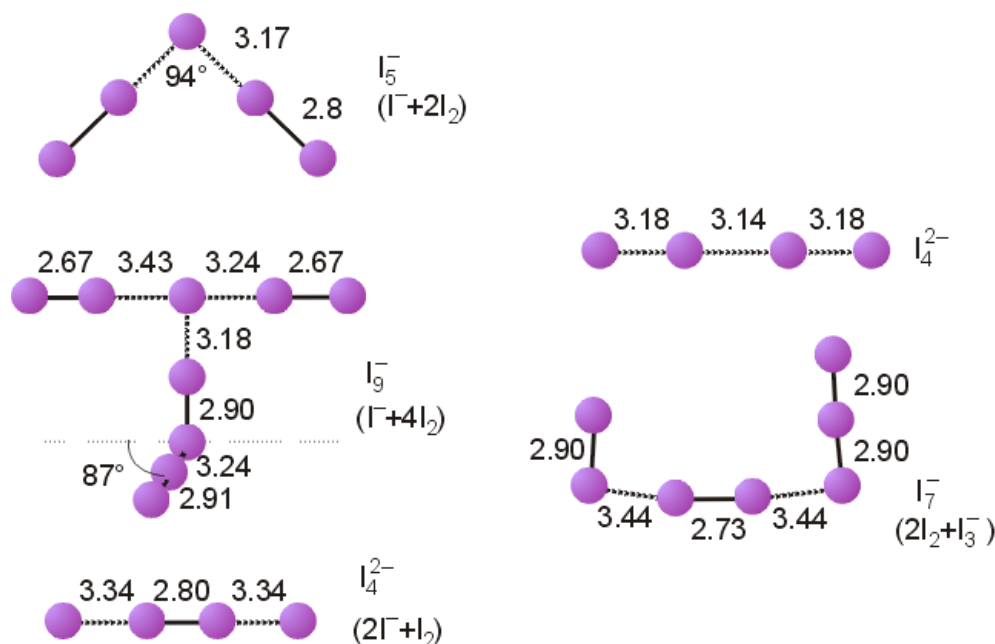


Figure 1. ORTEP drawing (30% probability ellipsoids) of a cation-anion pair in $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{Cl}_3]^-$. Selected bond lengths (in Å) and bond angles (in $^\circ$) are: S(1)–Cl(1) 2.290(3), S(1)–N(1) 1.542(6), N(1)–C(1) 1.363(7), N(2)–C(1) 1.366(7), N(3)–C(1) 1.277(7), N(3)–C(2) 1.501(7), N(3)–C(3) 1.487(8), S(2)–N(2) 1.514(5), S(2) \cdots Cl(1) 3.225(4), S(2) \cdots Cl(4) 3.160(4), Cl(4)–Cl(3) 2.393(4), Cl(3)–Cl(2) 2.183(4); N(1)–S(1)–N(1') 117.5(4), S(1)–N(1)–C(1) 131.0(5), N(1)–C(1)–N(2) 124.1(4), C(1)–N(2)–S(2) 135.0(4), N(2)–S(2)–N(2') 123.3(4), Cl(4)–Cl(3)–Cl(2) 177.7(2).

The tendency of trihalide anions to structurally distort is well documented, and is an indication of the very polarizable electron rich bonding in these systems. In classical wet analytical chemistry, triiodide is commonly used as an I_2 equivalent, essentially a way to solubilise the molecular iodine molecule in the highly polar solvent water:



We will consider the unique bonding situation in trihalide anions below. For iodine, it is also possible to go beyond triiodide and form polyiodide anions. The structures of these species persist only in the solid state, and critically depend on the identity of the counter ions. Some structures that have been determined for polyiodide anions are shown in the following diagram.



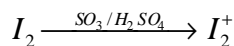
Some polyiodide salts exhibit electrical conductivity, which is thought to come from electron (or hole) hopping through a chain of iodine atoms in the solid state. This mechanism resembles that of proton migration through a hydrogen-bonded

array of molecules, either in the solid or in a liquid like water. It can be diagrammed by the picture shown at right, and means that Γ can pass rapidly through the matrix, but that the emerging iodide is *not* the same as the iodide that entered at the other end of the electrical circuit.

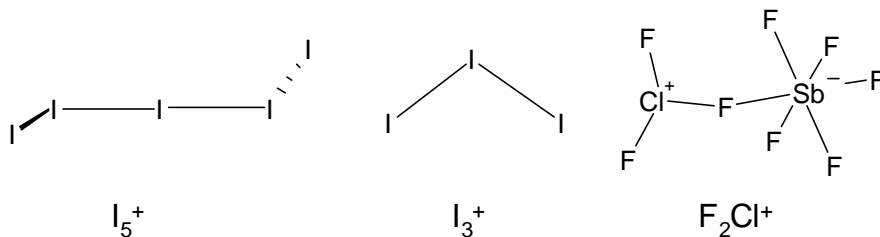
Finally, in the Chemistry 3810 laboratory, you also have the opportunity to prepare a mixed-halogen polyanion, ICl_2^- , which may be thought of as a complex of monpositive iodine with two chloride anions, given that in this case chlorine is more electronegative than iodine.

6.3.3 Halogen and interhalogen cations

Cations of halogens can form under strongly oxidizing conditions. For example, iodine is oxidized in fuming sulfuric acid to the blue paramagnetic diiodonium cation, I_2^+ .



Extensive work on the development of the chemistry of the iodine cations was done in Canada in the research lab of Prof. Jack Passmore at the University of New Brunswick in Fredericton. Among the structures he has obtained are the following:



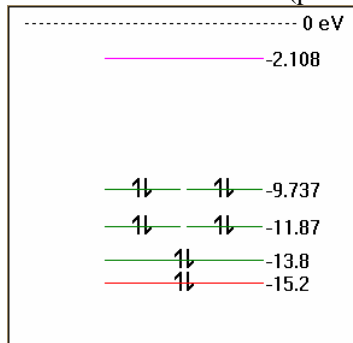
The last example is that of a mixed-halide cation, which is formed by the interaction of the powerful Lewis acid SbF_5 with the corresponding neutral chlorine fluoride ClF_3 . Chemistry of this type is dependent on the properties of a class of reagents known as **superacids**. Superacids are extremely strongly acidic, *non-aqueous* solutions of which fuming sulfuric acid was the original inspiration. A superacid normally contains a strong Brønsted acid as well as a powerful Lewis acid. In fuming sulfuric, the former is supplied by H_2SO_4 , while SO_3 functions as the latter.

6.3.4 Bonding in interhalogens

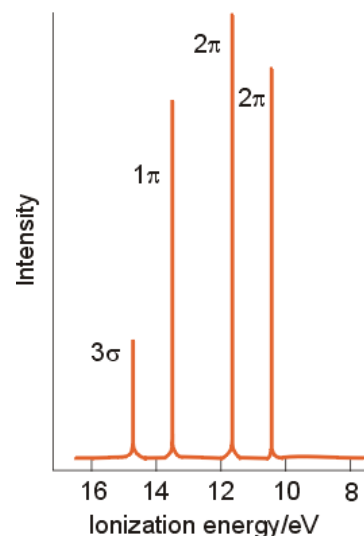
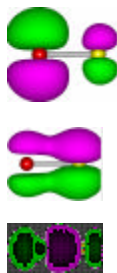
We have spoken at length in this course about the bonding in *electron-deficient* compounds such as the boron hydrides. A general theme for such compounds is the tendency to form dimers or clusters which can be thought of as measures of desperation: if the elements cannot gain sufficient electrons they somehow have to make do with what they have. The halogen and noble gas compounds we are now considering are, however, examples of (extreme) electron richness. Remember that in the dihalogens themselves, there is only a single empty orbital capable of accepting electrons, the $2s_{\text{v}}^*$ orbital. Yet halogens are noted charge acceptors, forming so-called **charge transfer complexes** with a wide variety of electron donors. This tendency can only be explained by the high electronegativity of the halogens, resulting in the fact that even the highest valence molecular orbital is *relatively* low lying in energy.

(A) Bonding in ICl

As our first example of bonding in electron-rich halogens, consider the simple interhalogen compound ICl . The UV-PES of this interhalogen is shown at right, and a PM3 MO calculation results (partial) at the left.



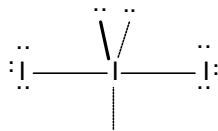
Energy Levels of upper MO's (orbital pictures for 3s, 1p and 2p.)



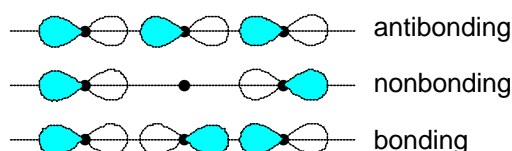
The photoelectron spectrum is complicated by the presence of **spin-orbit coupling**, which has the effect of splitting the ionization from the 2p level into two peaks. We take the average of these two peaks as the ionization energy. Agreement to the PM3 method is reasonable for this molecule. Above all, UV-PES establishes that the level ordering is that shown in the calculation, i.e. that the electron configuration is $1s^2 2s^2 3s^2 1p^2 2p^2$ rather than the order observed for the heavier dihalogens themselves which follow the “second-order” orbital sequence. You should confirm this by building the full MO diagram for ICl from the constituent atomic orbitals.

(B) Triiodide anion

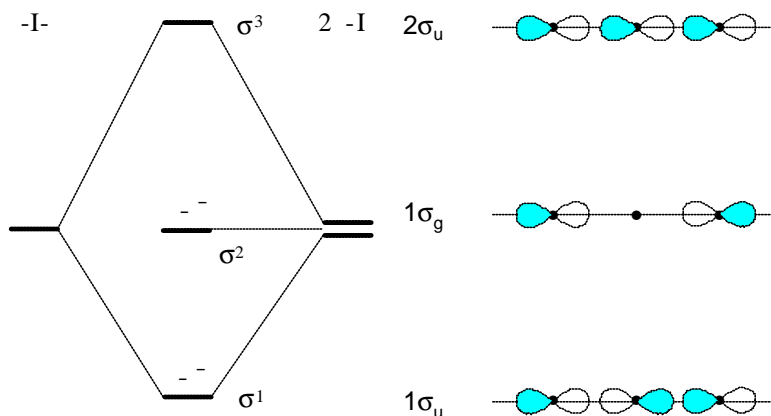
What structure is expected of I_3^- ? This is an important question, because most 3-atom molecules are indeed bent. However, I_3^- is a *linear* molecule. That is because it is based on the trigonal bipyramidal electron arrangement in the VESPR rationale of molecular structure:



To treat the bonding in a simple *on paper* fashion, we can make the approximation that each iodine uses a p_z orbital as its principal basis AO in bonding to its neighbours. We can test this hypothesis later by a full MO treatment using HyperChem. Now consider what this arrangement should look like, and what its symmetry properties will be. There is an obvious logical link to our simple H_3 structures done at the beginning of the course. The topology of the three p_z orbitals will then be:



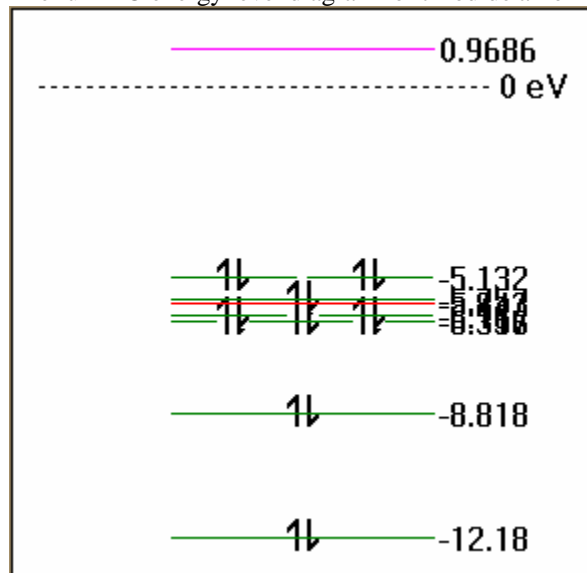
However, unlike the trihydrogen system where we used s orbitals, the bonding and antibonding combination of orbitals here will have s_u symmetry, while the non-bonding has s_g symmetry! The corresponding energy level diagram in which we combine the two terminal iodide anions to the central I^+ ion is then expected to be:



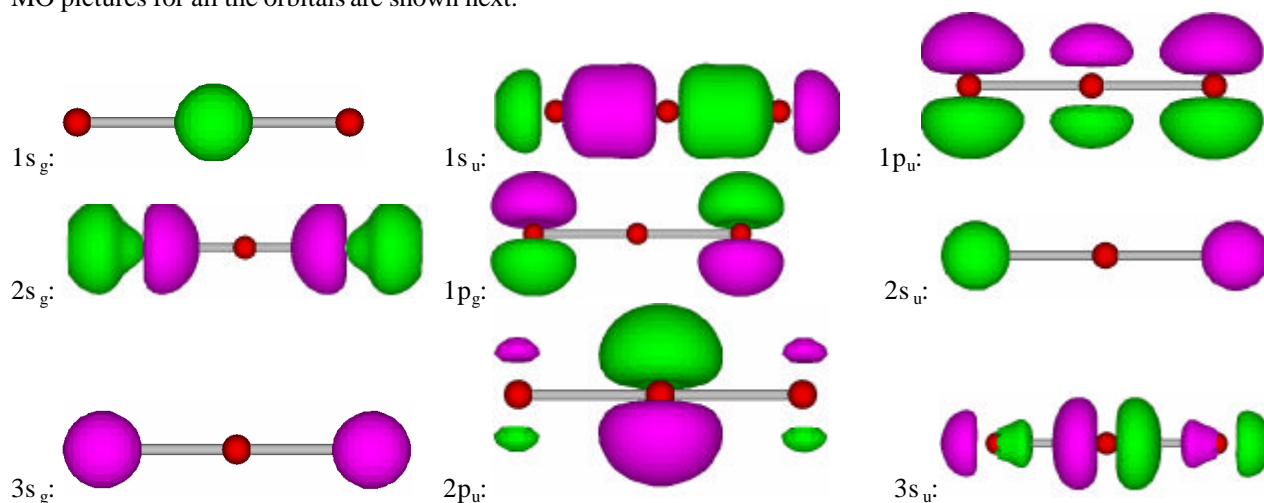
Filling this simple scheme with the four available electrons fills the bonding $1s_u$ and the non-bonding $1s_g$ molecular orbitals. What then is the bond order? There are only two electrons but three bonded atoms. The overall bond order is then 1 and the order *per bond* is $1/2$. This is then another example of a delocalized (3c,2e) bond, albeit of a different type from that observed in the bent bonds in B_2H_6 . Such bonds are extremely common among the halogens and noble gases. The ease with which triiodide anions can be distorted by their environment can be rationalized by such weak bonding.

We can now rationalize the linear geometry in I_3^- using these simple MO arguments, just as we did with a Walsh diagram for H_3^- . Remember that it is H_3^+ which is predicted to be triangular, but the presence of the electrons in the $1s_u$ orbital results in a linear geometry. Of course, in the true electronic structure of triiodide anion, there are many additional electrons of p symmetry that also contribute to the linear geometry. At the PM3 level of theory, amazingly, a picture very reminiscent of the above simple-minded bonding picture develops.

The full MO energy level diagram for triiodide anion in PM3 is:



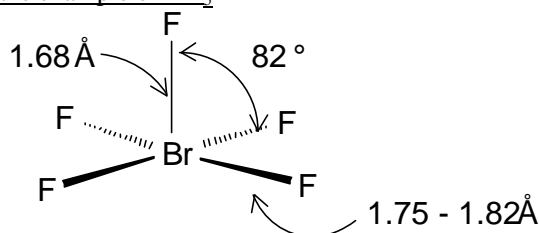
MO pictures for all the orbitals are shown next:



It is very clear that the orbitals $1s_u$ (-8.8 eV), $2s_g$ (-6.3 eV) and $3s_u$ (+1.0 eV) correspond almost directly to the “simple” picture developed above. Amazing to see is the extremely small involvement of the atomic s orbitals, which I can only explain by the large I—I distances of 2.73 Å in the geometry optimized structure, i.e. too far apart for effective $s-s$ overlap, but better suited to linear $p-p$ overlap. The charge distribution is also interesting, with +0.27 on the central atom, and -0.63 on each terminal atom.

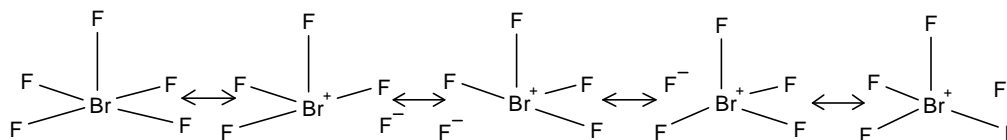
Finally, note that *there is nothing at all in the MO diagram to correspond to the three “lone pairs” surrounding the central atom in the VSEPR structure!* Indeed, there are many suggestions from calculation that the VSEPR theory is not a true theory of chemical bonding and structure. It is a very reliable method that returns correct structures, but should not be accorded a great deal of veracity beyond this utilitarian aspect.

The remaining MO's in triiodide (and remember that I have only provided a picture for *one* of every p orbital) correspond to the many lone pairs. In all there are 12 MO's of which 11 are filled. Of these, three correspond to the atomic s orbitals, and six to lone pairs of p -symmetry.

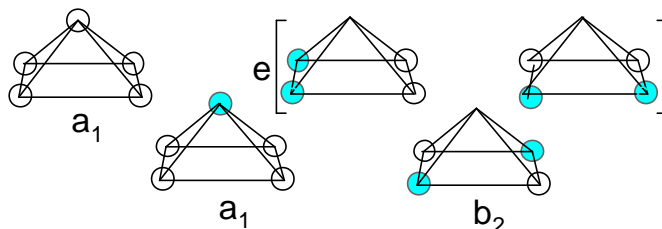
(C) Bonding in a “hypervalent” compound: the example of BrF_5 

The structure of BrF_5 is:

This is quite a remarkable structure. First of all, the atoms in the equatorial plane are actually bent *up* towards the axial fluorine, and not away from them. VSEPR rationalizes this result by pointing to a “lone-pair” on the Br that is large and needs more axial space. This, says the theory, causes the equatorial atoms to “bend up” out of the plane. Note also that the axial Br—F bond is considerably shorter than the four such bonds to the equatorial plane which are around 1.8 Å in length. Consider first a description of this structure using *electron precise Lewis structures*. Such structures *must* invoke so-called **no-bond resonance** to describe the bonding in this compound. Remember that the true Lewis diagram is a *hybrid* of all the contributing structures, so that the absence of a bond in any one of the five isomers does *not* imply that a bond is actually broken!

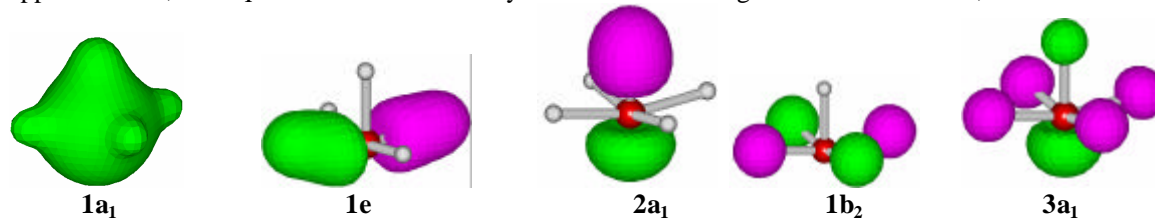


The full MO diagram of BrF_5 is extremely complex, and we will restrict ourselves in this course to a simplified *on paper* MO diagram that uses only *s*-like functions for the fluorine atoms. This can be calculated in HyperChem using a model BrH_5 molecule and by employing the extended Hückel MO method. First we need suitable SAO's for the five ligand *s* functions. These are not provided by the book, so we must make our own. These are modeled on the ones in the book for square planar geometry, but involve a different setting of the molecule w.r.t. the Cartesian coordinates. Here is such a set of SAO's:

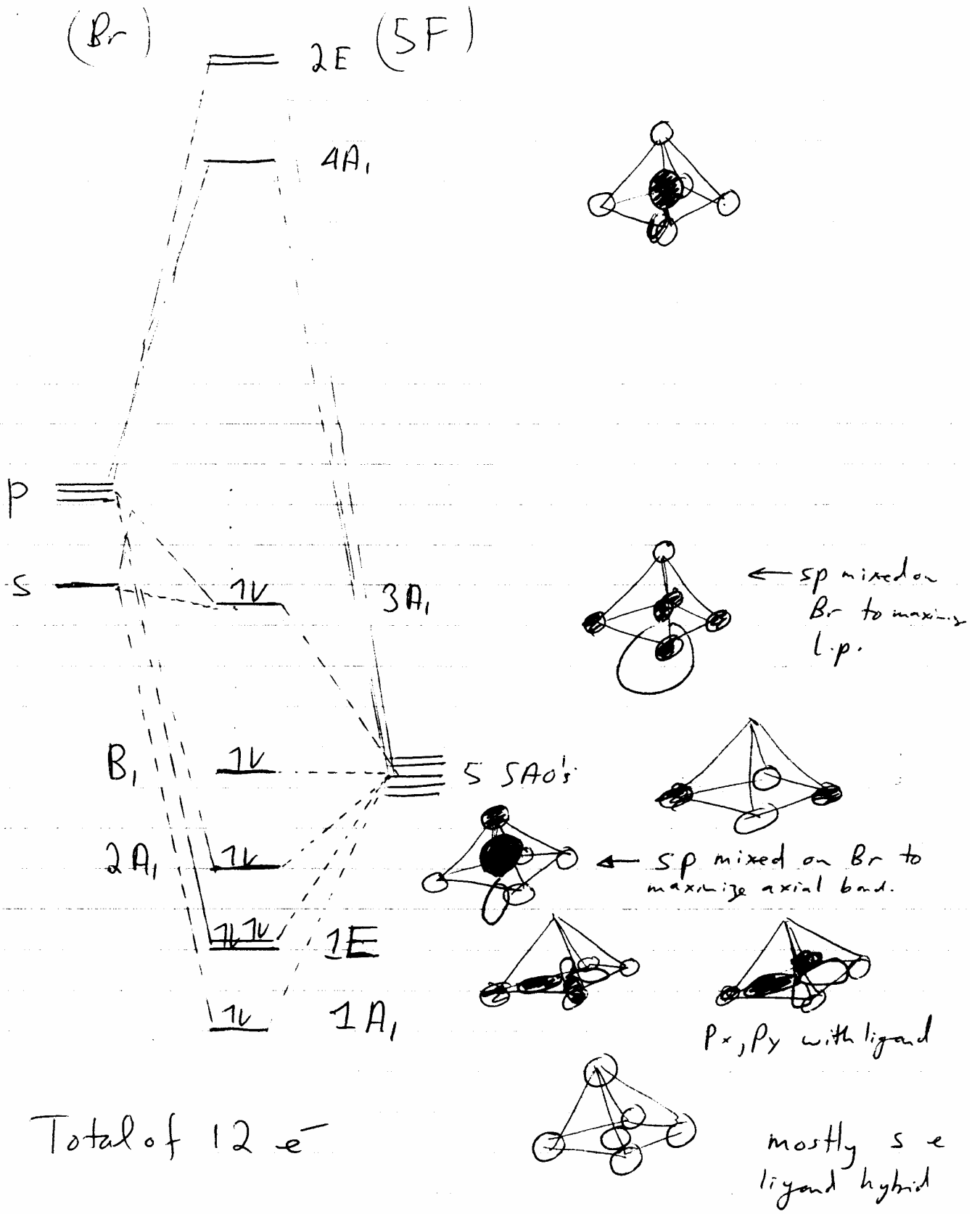


In this point group, the atomic orbitals transform as: *s* and p_z both transform as \mathbf{a}_1 , while p_x and p_y transform as a set as \mathbf{e} . Remembering that fluorine is considerably more electronegative than bromine, we are ready to combine the central atom AO and the ligand SAO's. This is done on the following page.

Now there are several points to consider in this bonding scheme. Note first of all that there is *no \mathbf{b}_2 component on bromine*. Hence the molecular \mathbf{b}_2 MO is at the exact energy of the ligand orbitals and is totally non-bonding. To a first approximation, the $2\mathbf{a}_1$ orbital is almost entirely dedicated to bonding in the axial direction, as shown in the HyperChem



plots. By contrast, $1\mathbf{a}_1$ and $1\mathbf{e}$ are largely bonding in the equatorial plane, and $3\mathbf{a}_1$ is almost non-bonding. Hence the bond order for the axial direction is essentially 1, while for the equatorial direction is overall 3, or only 0.75 per Br—F bond! This then rationalizes the observed much longer bond lengths for the equatorial bonds compared to the axial bond. In the full MO picture, it is also possible that there is a *p*-component to the axial bonds that is not available to the equatorial set. Finally, in detailed MO calculations on this system it has been shown that the small F—Br—F bond angles between the axial and equatorial site enables the $3\mathbf{a}_1$ MO to gain a small degree of bonding character in the axial direction, and this helps to rationalize these small bond angles. Remember that in the VSEPR explanation, the upwards bending of these bonds is explained by the large “lone pair” below the BrF_4 plane.

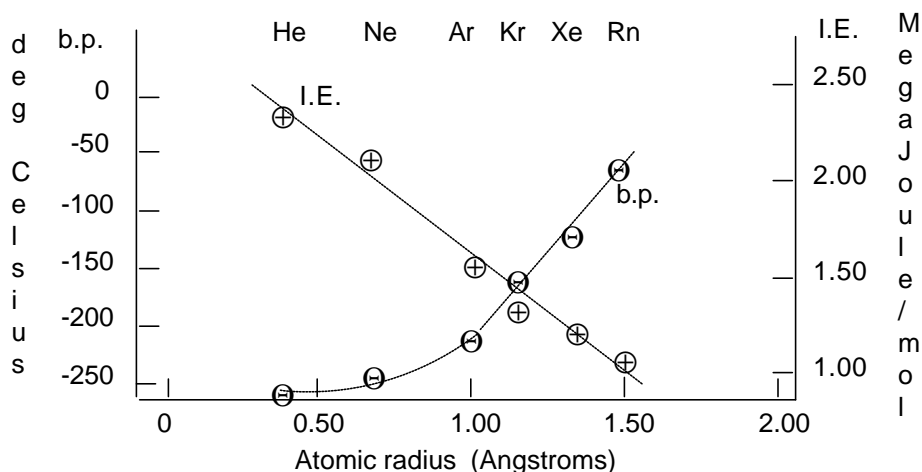


7. Noble Gas Compounds

The noble gases were once sought to be entirely *inert*. This false conclusion was obtained after many failed attempts at reacting them with all kinds of reagents, including strong oxidizers. Today they are called **noble**, indicating their strong preference for the elemental form, although compounds of xenon and krypton – the heaviest among them – are now well known. To this day despite a great deal of effort, no chemical compounds of argon, neon or helium have ever been proven.

7.1 Physical properties of noble gases

The noble gases all exist in nature as colourless, monatomic gases. They are ideal models systems for many theories of atomic properties and physical behaviour. We will consider only their boiling points and ionization energies:



Boiling point and ionization energy of the noble gases

The boiling point is plotted against the size of the atom. Since the only possible attraction between noble gas atoms are London dispersion forces, we see how these forces increase with increasing atom size. For the larger atoms, the relationship becomes linear.

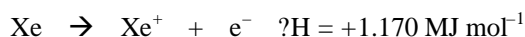
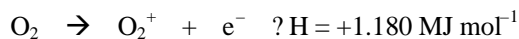
Ionization energy is critical in whether bonds to other chemical elements are possible. Note the highly linear correlation between the size of the atoms and the first I.E. Radon has the lowest I.E., but it is too intensely radioactive to have a chemistry - any possible products would tend to be destroyed by the radiolysis occurring in solutions of Rn.

7.2 Discovery of the noble gas compounds

In the general bonding situation, the atoms bonded will not be of the same type. If atom A and atom B are bonded to one another, and for point of argument, A is the more electronegative element, then the bonding interaction will look as follows:

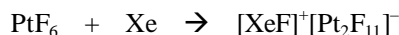
The story of how noble gas chemistry started is intriguing history. In fact, chemists had tried unsuccessfully for a long time to induce reactivity, especially in Xe. Soon after his discovery of F_2 , Henri Moissan received samples of noble gases from their discoverer, Lord Rayleigh. Even in an electric spark chamber, no reaction was found to occur.

Neil Bartlett, working at UBC as a young professor was performing experiments with PtF_6 , a highly coloured strong oxidant. When his student damaged the vacuum line in which the work was done, a different coloured compound (a solid) formed at the crack in the line. This was hypothesized and later proved to be the PtF_6^- salt of O_2^+ . Bartlett considered the following data:



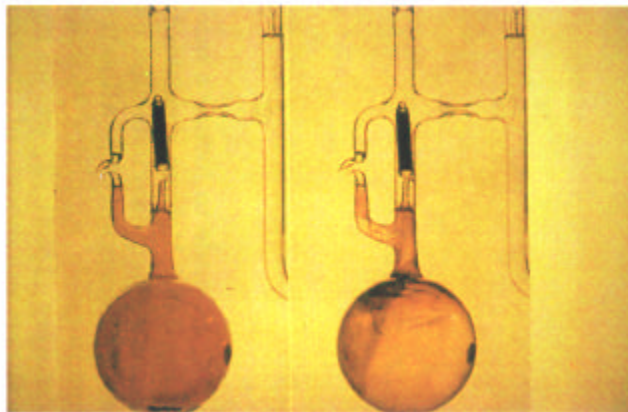
If PtF_6 could oxidize molecular oxygen, it should also be able to oxidize xenon, reasoned Bartlett. He did the experiment, and a rapid reaction leading to a solid product ensued.

The reaction that seems to occur is the following:



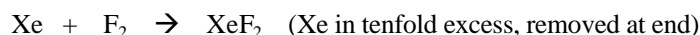
The exact nature of this complicated product has never been established, but the report published by him opened a floodgate of experiments in this area.

Re-enactment of Bartlett's historic first reaction of xenon with PtF_6 .



7.2.1 Known xenon fluorides and oxyfluorides

Most xenon compounds are fluorides, since fluorine is the most electronegative element, and is best able to supply the energy needed to ionize the hard-to-oxidize xenon atom. Direct interaction of the elements with heat and/or pressure, or else under UV light leads to three products as follows:



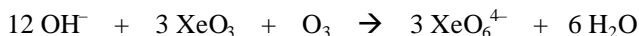
All three xenon fluorides are colourless solids. The structures of XeF_2 and XeF_4 fit the VSEPR predictions, while XeF_6 does not (see problem assignment.)

Hydrolysis of XeF_6 yields both OXeF_4 and XeO_3 . The latter is viciously explosive. Recently a better preparation of the useful OXeF_4 has been reported:



A slight excess of XeF_6 is used to prevent side reactions. The excess xenon hexafluoride is trapped by the produced NaF , and the prep. separates the gaseous products OXeF_4 and FNO_2 by a trap-to-trap distillation, the former being stopped by a dry ice bath (-78°C).

Oxidation of XeO_3 in solution using ozone leads to a rare example of a compound with an oxidation state of +8:



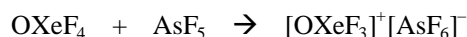
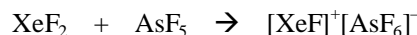
XeO_4 is an unstable and explosive gas! What should its structure be?

7.2.2 Pseudo-halide xenon compounds

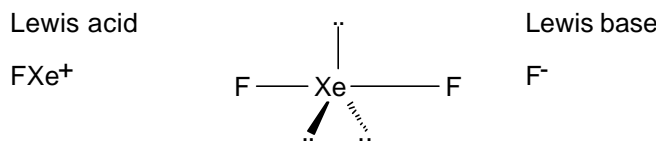
The highly electronegative ligands $^-\text{OTeF}_5$ and $^-\text{OSeF}_5$ can replace from two to six fluorine atoms on a xenon molecule, leading to solid compounds.

7.2.3 Lewis basicity of xenon fluorides

The bonding in xenon fluorides is weak, and charge separation occurs quite readily, leading to the loss of F^- and the formation of cations, e.g.



In these reactions, it is most useful to think of the neutral fluorides as acid/base adducts:



7.2.4 Recent chemistry of xenon cations

The cations of the type FXe^+ have been found to be potent Lewis acids in themselves. This has allowed the preparation of a number of new types of xenon compounds, including:



Many of these were prepared for the first time in Canada by Prof. Schrobilgen at McMaster University in Hamilton. Another recent discovery has been the first stable Xe-C bond, also in a cation, $\text{C}_6\text{F}_5\text{-Xe}^+$. This was first made by Frohn's group in Germany.

7.2.5 Known krypton compounds

Krypton has a much higher ionization energy than Xe, and until recently the only known krypton derivatives were Kr^{2+} fluorides, e.g. KrF_2 . All these krypton compounds are very unstable.

Recently Schrobilgen demonstrated the first Kr-N bond in $\text{HC}=\text{N}-\text{Kr}-\text{F}^+$, prepared by the reaction:



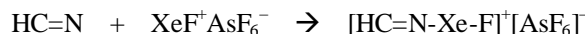
HF is also the solvent, and the reaction occurs at -60°C . The product is a white solid. On warming to room temperature it explodes with a flash of bright light.

7.3 Multinuclear NMR characterization of noble gas compounds

As we have seen, some of these newer noble gas compounds are quite unstable; thus $\text{HC}=\text{N}-\text{Kr}-\text{F}^+$ decomposes above -50°C . How can we be sure the compound has really been prepared? For example, all attempts to prepare $\text{Kr}(\text{OTeF}_5)_2$ have failed – only decomposition products have been unambiguously identified.

Solution NMR studies, often on the actual reaction mixtures, have proven very important for the characterization of these compounds. In fact, the success of this chemistry is at least in part a direct result of the useful NMR properties of ^{19}F (100%), ^{129}Xe (28%), $^{14,15}\text{N}$, ^{125}Te , etc. As an example of the application of these highly multinuclear NMR techniques, consider the spectra recently published for $\text{HC}=\text{N}-\text{Xe}-\text{F}^+$ by A.A.A. Emara and Gary J. Schrobilgen, *Inorg. Chem.* (1992) 31, 1323-1332.

This compound was prepared between -10 and -20°C in anhydrous HF solution by the reaction:



BrF_5 can also be used as a solvent for this salt, with the distinction that it has a significantly higher viscosity. Scalar coupling to ^{14}N is quadrupole collapsed in this solvent because of the rapid relaxation. However, in HF solution, molecular motion is rapid enough that in this linear (i.e. highly symmetric) molecule, scalar coupling to ^{14}N is observed.

A feature of the synthetic method is that the researchers were able to employ 99% enriched samples of $\text{H}-^{13}\text{C}=\text{N}$ and $\text{H}-\text{C}=\text{N}$. The spectra therefore are of the three distinct xenon cation species $^1\text{H}-^{12}\text{C}=\text{N}-^{129}\text{Xe}-^{19}\text{F}^+$, $^1\text{H}-^{13}\text{C}=\text{N}-^{129}\text{Xe}-^{19}\text{F}^+$, and $^1\text{H}-^{12}\text{C}=\text{N}-^{129}\text{Xe}-^{19}\text{F}^+$. All possible scalar couplings between the nuclei in these various samples were measured. The constants varied from 2.6 Hz for $^4\text{J}(^{19}\text{F}-^1\text{H})$ to 6161 Hz for $^1\text{J}(^{19}\text{F}-^{129}\text{Xe})$.

During lecture we will go over the spectra shown here. We will interpret the spectra in detail, and consider the nuclear interactions that occur and their interpretation in terms of chemical structure.

Multinuclear NMR spectra of various HCN-Xe-F⁺ ions

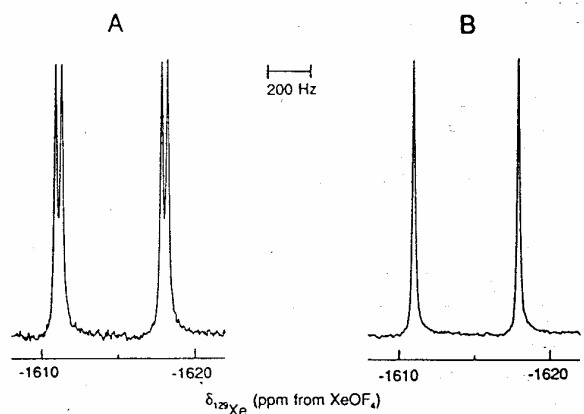
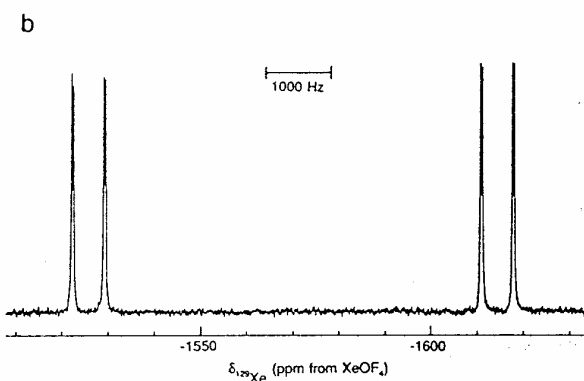
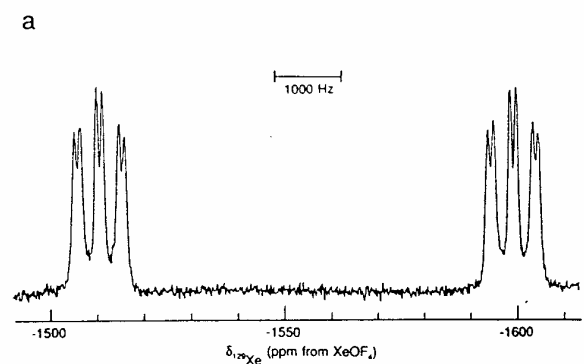


Figure 1. ²⁹Xe NMR spectra (69.563 MHz) of HC≡NXeF⁺AsF₆⁻: (a) 99.2% ¹³C-enriched sample recorded in HF solvent at -10 °C; (b) 99.5% ¹⁵N-enriched sample recorded in BrF₃ at -50 °C. Expansion A shows proton coupling, and expansion B is ¹H]-decoupled.

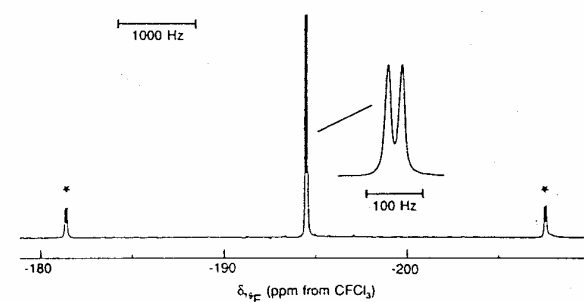


Figure 2. ¹⁹F NMR spectrum (235.361 MHz) of 99.5% ¹⁵N-enriched HC≡NXeF⁺AsF₆⁻ recorded in BrF₃ solvent at -50 °C. Asterisks denote ¹²⁹Xe satellites.

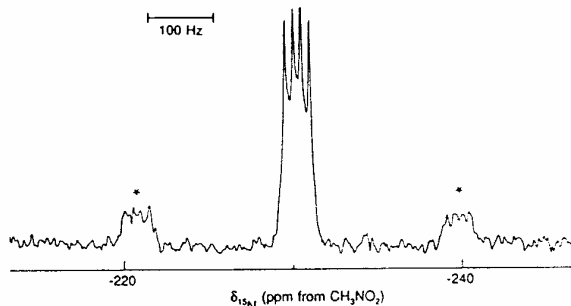


Figure 3. ¹⁵N NMR spectrum (25.347 MHz) of 99.5% ¹⁵N-enriched HC≡NXeF⁺AsF₆⁻ recorded in BrF₃ solvent at -50 °C. Asterisks denote ¹²⁹Xe satellites.

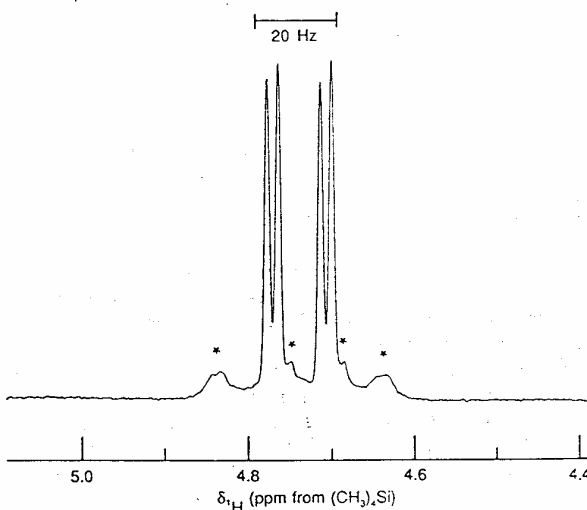


Figure 4. ¹H NMR spectrum (200.133 MHz) of 99.5% ¹⁵N-enriched HC≡NXeF⁺AsF₆⁻ recorded in BrF₃ solvent at -50 °C. Asterisks denote ¹²⁹Xe satellites.

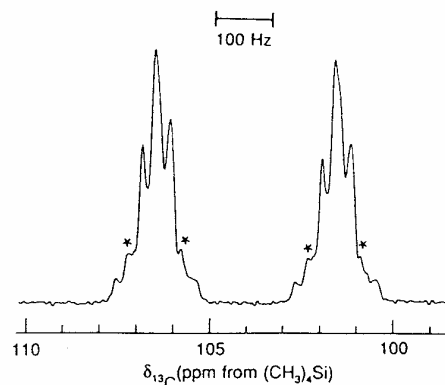
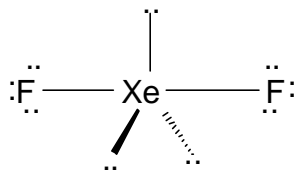


Figure 5. ¹³C NMR spectrum (62.915 MHz) of 99.2% ¹³C-enriched HC≡NXeF⁺AsF₆⁻ recorded in HF solvent at -10 °C. Asterisks denote ¹²⁹Xe satellites.

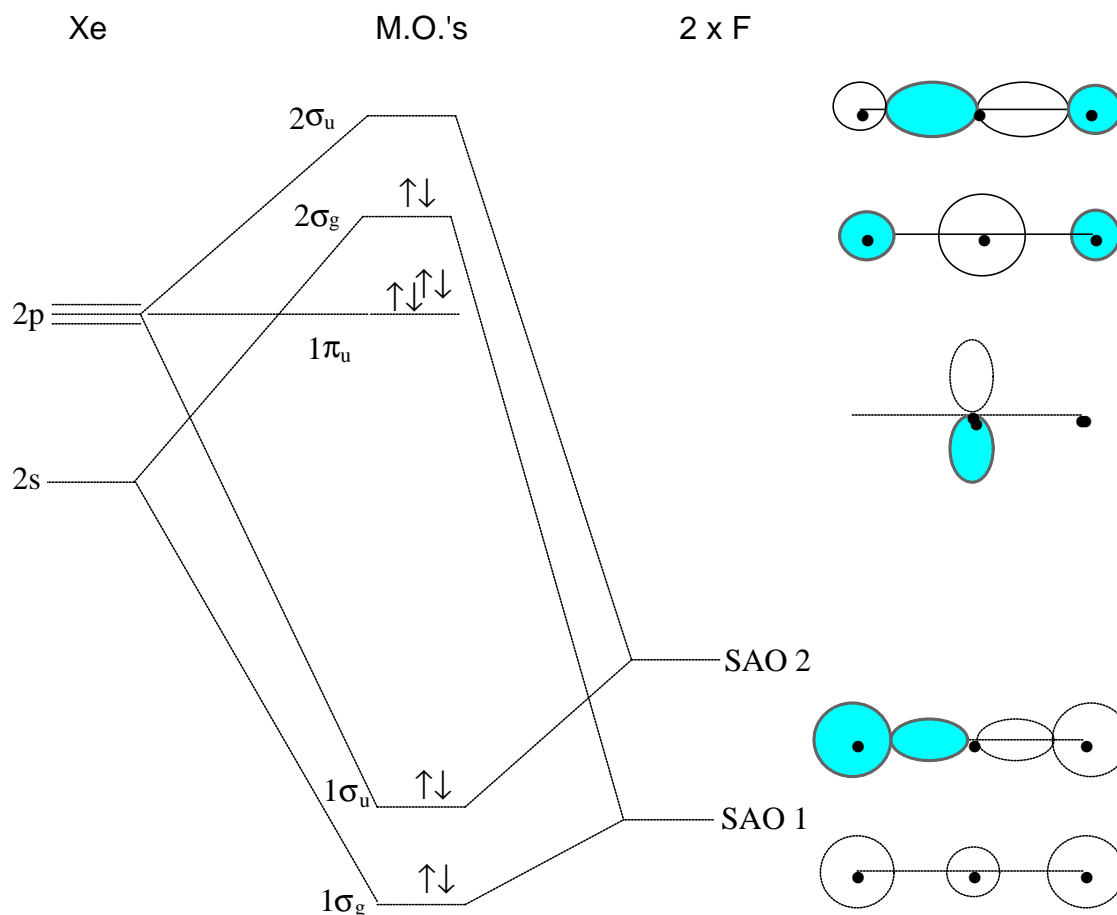
7.4 Bonding in noble gas compounds: XeF₂ as an example



XeF₂ is a linear molecule by the VSEPR method:

7.4.1 A first order MO description of bonding in XeF₂

The simple picture which was developed for linear HBe-H can be used for XeF₂ as well, except that in this case the ligands are more electronegative than the central atom. The atomic orbitals transform as s_g, s_u, and p_u. The appropriate SAO's are s_g and s_u. A simple first-order diagram results:



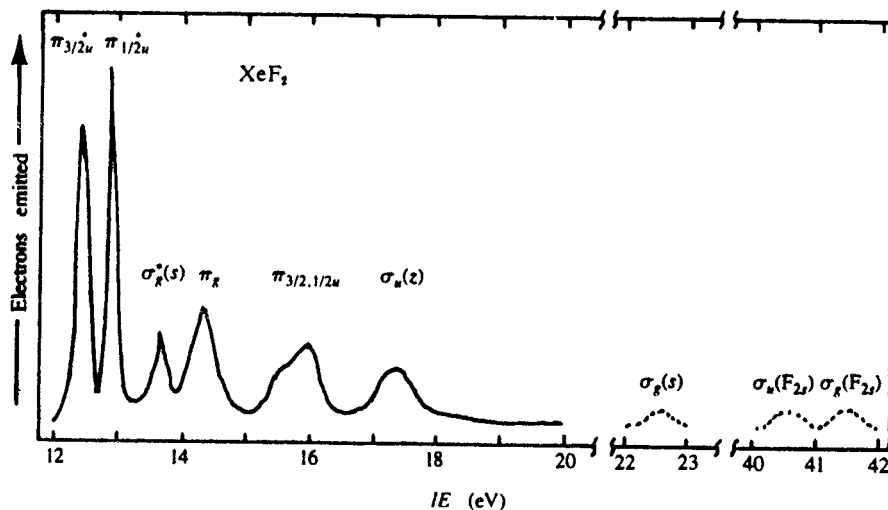
What is the bond order in this molecule? The only orbital that is net bonding is 1s_u! The total BO = 1, and each bond therefore has a bond order of 1/2. We can describe XeF₂ quite accurately as a linear molecule with a single (3c,2e) linear bond; note this is exactly what we concluded for I₃⁻! The thermochemical bond energy is correspondingly small: about 125 kJ mol⁻¹. Compare this to the single bond in H₂ with an energy of over 450 kJ mol⁻¹.

We have noted the great similarity to the bonding in I₃⁻. Actually a better analogy is IF₂⁻, which is exactly isoelectronic. This does not exist, although ICl₂⁻ does. Note however that IF₂⁺ does exist. Why should it form? Answer: remove electrons from the antibonding orbitals and thereby increase BO to 2!

This also makes the Lewis Acid/Base character of XeF₂ much easier to understand, vis-à-vis I₂ and I. We are not surprised at the ability of this compound to readily form XeF⁺ in solution in the presence of suitable fluoride ion acceptors.

7.4.2 UV-PES corrected MO description

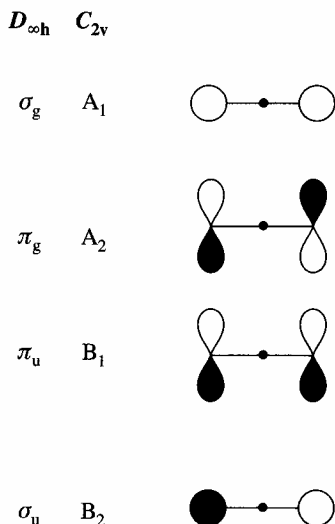
We can try to assess the correctness of this model with UV-PES.



Photoelectron spectrum of XeF_2 . Adapted with permission from C.R. Brundle, M.B. Robin, and G.R. Jones, *J. Chem. Phys.* 52: 3383 (1970).

To fully understand the peaks in the PES we must, of course take into account the non-bonded electrons, which we have omitted in our MO treatment for simplicity. This is done on the accompanying sheet using the energy scale of the photoelectron spectrum.

Procedure: consider the SAO's for the p -type atomic orbitals on the fluorine atoms, i.e. p_g and p_u shown in the following SAO table from the text book:

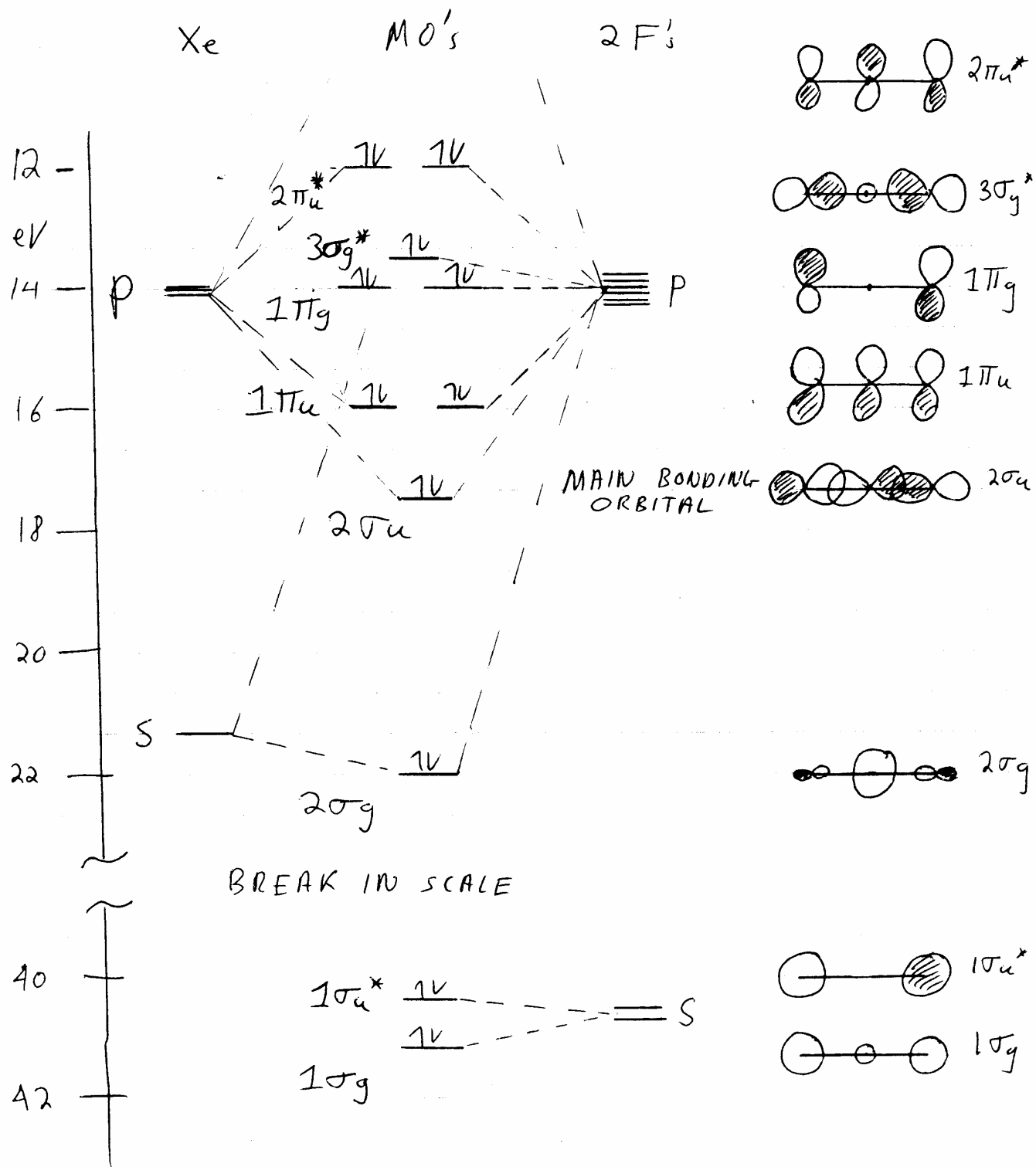


This leads to an important difference in the nature of the p non-bonded orbital in XeF_2 , since there is now an SAO which is of the correct symmetry to interact with the p_u AO. However, in fact, as the diagram shows, both the bonding and antibonding combination of these orbitals are occupied, so that the net effect on the bonding in the molecule is zero. Also there is still a totally non-bonding p orbital, i.e. p_g .

Make sure that you can sketch this interaction! Which of the Xe atomic orbitals are involved here?

Thus we may conclude that the omission of ligand lone-pair orbitals does not materially affect our interpretation of the bonding molecular orbitals in XeF_2 . However, they must be included for a full assignment of the ionizations showing up in the UV-PES of this electron rich molecule.

Consider this "corrected" diagram. Note also that of the two possible fluorine s orbitals, it is in fact the p_z orbitals that bond to Xenon. The deeply buried F s orbitals are found at very low energy (40 & 42 eV ionization potentials.)



The END – Chemistry 3810 Lecture Notes in 2003