Hypervalent

Nature of the Chemical Bond with applications to catalysis, materials science, nanotechnology, surface science, bioinorganic chemistry, and energy

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Hypervalent compounds

It was quite a surprize to most chemists in 1962 when Neil Bartlett reported the formation of a compound involving Xe-F bonds.

But this was quickly followed by the synthesis of XeF₂ (from Xe and F₂ at high temperature and XeF₂ in 1962 and later XeF₆. Indeed Pauling had predicted in 1933 that XeF₆ would be stable, but no one tried to make it.

Later compounds such as ClF₃ and ClF₅ were synthesized. These compounds violate simple octet rules and are call hypervalent.
Noble gas dimers

Recall that there is no chemical bonding in He$_2$, Ne$_2$ etc.

This is explained in VB theory as due to repulsive Pauli repulsion from the overlap of doubly occupied orbitals.

It is explained in MO theory as due to filled bonding and antibonding orbitals.

<table>
<thead>
<tr>
<th></th>
<th>$R_e$ (Å)</th>
<th>$D_0$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$_2$</td>
<td>3.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Ne$_2$</td>
<td>[3.15]</td>
<td>0.05</td>
</tr>
<tr>
<td>Ar$_2$</td>
<td>3.758</td>
<td>0.24</td>
</tr>
<tr>
<td>Kr$_2$</td>
<td>4.03</td>
<td>0.36</td>
</tr>
<tr>
<td>Xe$_2$</td>
<td>4.36$^1$</td>
<td>0.53</td>
</tr>
</tbody>
</table>
Noble gas dimer positive ions

On the other hand the positive ions are strongly bound. This is explained in MO theory as due to one less antibonding electron than bonding, leading to a three electron bond for $\text{He}_2^+$ of 55 kcal/mol, the same strength as the one electron bond of $\text{H}_2^+$.

The VB explanation is less straightforward. We consider that there are two equivalent VB structures neither of which leads to much bonding, but superimposing them leads to resonance stabilization.

<table>
<thead>
<tr>
<th></th>
<th>$R_e$ (Å)</th>
<th>$D_0$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{He}_2^+$</td>
<td>1.081</td>
<td>54.5</td>
</tr>
<tr>
<td>$\text{Ne}_2^+$</td>
<td>(1.75)</td>
<td>30.0</td>
</tr>
<tr>
<td>$\text{Ar}_2^+$</td>
<td>(2.43)</td>
<td>30.7</td>
</tr>
<tr>
<td>$\text{Kr}_2^+$</td>
<td>(2.6)</td>
<td>26.5</td>
</tr>
<tr>
<td>$\text{Xe}_2^+$</td>
<td>(3.25)</td>
<td>23.7</td>
</tr>
</tbody>
</table>

Using $(\sigma_g) = L+R$ and $(\sigma_u) = L-R$.

Leads to (with negative sign):
Re-examine the bonding of HeH

Why not describe HeH as \((\sigma_g)^2(\sigma_u)^1\) where 
\((\sigma_g) = L+R\) and \((\sigma_u) = L-R\)

Would this lead to bonding?
The answer is no, as easily seen with the VB form, where the
right structure is 23.6-0.7=23.9 eV above the left.
Thus the energy for the \((\sigma_g)^2(\sigma_u)^1\) state would be +12.0 – 2.5 =
9.5 eV unbound at \(R=\infty\)
Adding in ionic stabilization lowers the energy by 14.4/2.0 = 7.2
eV (overestimate because of shielding), still unbound by 2.3 eV

\[
\begin{align*}
\text{He} & & \downarrow \uparrow \\
\text{H} & & - \\
\text{He}^+ & & \uparrow \uparrow \\
\text{H}^- & & 
\end{align*}
\]

\(\text{IP}=+24.6 \text{ eV}\) \(\text{EA} = 0.7 \text{ eV}\)
Examine the bonding of XeF

Consider the energy to form the charge transfer complex

\[ \text{Xe} \quad \text{F} \quad \rightarrow \quad \text{Xe}^+ \quad \text{F}^- \]

The energy to form \( \text{Xe}^+ \text{ F}^- \) can be estimated from

\[
E(A^+F^-) = E(A) + E(F) + IP(A) - EA(F) - \frac{14.4}{R(A)}
\]

Using \( IP(\text{Xe})=12.13 \text{eV}, \ EA(\text{F})=3.40 \text{eV}, \) and \( R(\text{IF})=1.98 \text{ A}, \)
we get \( E(\text{Xe}^+ \text{ F}^-) = 1.45 \text{eV} \) (unbound)

Thus there is no covalent bond for XeF, which has a weak bond of \( \sim 0.1 \text{ eV} \) and a long bond
Examine the bonding in XeF$_2$

The energy to form Xe$^+$F$^-$ is +1.45 eV

Now consider, the impact of putting a 2$^{nd}$ F on the back side of the Xe$^+$

Since Xe$^+$ has a singly occupied pz orbital pointing directly at this 2$^{nd}$ F, we can now form a covalent bond to it

How strong would the bond be?

Probably the same as for IF, which is 2.88 eV.

Thus we expect F--Xe$^+$F$^-$ to have a bond strength of $\sim$2.88 – 1.45 = 1.43 eV!

Of course for FXeF we can also form an equivalent bond for F--Xe$^+$--F. Thus we get a resonance, which we estimate below

We will denote this 3 center – 4 electron charge transfer bond as

\[ \text{F} \leftrightarrow \text{Xe} \rightarrow \text{F} \]
Estimate stability of XeF$_2$ (eV)

Energy form F Xe$^+$ F$^-$ at R=$\infty$

F-Xe$^+$ covalent bond length (from IF)

Energy form F Xe$^+$ F$^-$ at R=$R_e$

F-Xe$^+$ covalent bond energy (from IF)

Net bond strength of F--Xe$^+$ F$^-$

Resonance due to F$^-$ Xe$^+$--F

Net bond strength of XeF$_2$

| IP(A) | 12.130 |
| IP(A) - EA(F)$^f$ | 8.73 |
| $R(A^+ - F^-)$ | 1.977 |
| $E(A^+F^-) - E(A) - E(F)$ | 1.45 |
| $D(F - A^+)$ | 2.88$^a,d$ |
| $E(FA^+F^-) - E(A) - 2E(F)$ | 1.3 |

Resonance

Bond Energy (AF$_2$) | 2.7

Experiment$^g$ | 2.69

XeF$_2$ is stable with respect to the free atoms by 2.7 eV

Bond energy F$_2$ is 1.6 eV.

Thus stability of XeF$_2$ with respect to Xe + F$_2$ is 1.1 eV
The XeF$_2$ molecule is stable by 1.1 eV with respect to Xe + F$_2$

But to assess whether one could make and store XeF$_2$, say in a bottle, we have to consider other modes of decomposition. The most likely might be that light or surfaces might generate F atoms, which could then decompose XeF$_2$ by the chain reaction

\[
\text{XeF}_2 + F \rightarrow \{\text{XeF} + \text{F}_2\} \rightarrow \text{Xe} + \text{F}_2 + F
\]

Since the bond energy of F$_2$ is 1.6 eV, this reaction is endothermic by 2.7-1.6 = 1.1 eV, suggesting the XeF$_2$ is relatively stable.

Indeed XeF$_2$ is used with F$_2$ to synthesize XeF$_4$ and XeF$_6$.
Putting 2 additional F to overlap the Xe $p_y$ pair leads to the square planar structure, which allows 3 center – 4 electron charge transfer bonds in both the x and y directions.

The VB analysis indicates that the stability for XeF$_4$ relative to XeF$_2$ should be $\sim$ 2.7 eV, but maybe a bit weaker due to the increased IP of the Xe due to the first hypervalent bond and because of some possible F---F steric interactions.

There is a report that the bond energy is 6 eV, which seems too high, compared to our estimate of 5.4 eV.
Since XeF$_4$ still has a $pz$ pair, we can form a third hypervalent bond in this direction to obtain an octahedral XeF$_6$ molecule.

Indeed XeF$_6$ is stable with this structure.

Here we expect a stability a little less than 8.1 eV.

Pauling in 1933 suggested that XeF$_6$ would be stable, 30 years in advance of the experiments.

He also suggested that XeF$_8$ is stable.

However this prediction is wrong.
Using the same method as for XeF$_2$, we can estimate the binding energies for the other Noble metals. KrF$_2$ is predicted to be stable by 0.7 eV, which makes it susceptible to decomposition by F radicals.

RnF$_2$ is quite stable, by 3.6 eV, but I do not know if it has been observed.

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Rn</th>
</tr>
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<tbody>
<tr>
<td>IP(A)</td>
<td>24.587</td>
<td>21.564</td>
<td>15.759</td>
<td>13.999</td>
<td>12.130</td>
<td>10.748</td>
</tr>
<tr>
<td>IP(A) - EA(F)$^f$</td>
<td>21.19</td>
<td>18.17</td>
<td>12.36</td>
<td>10.60</td>
<td>8.73</td>
<td>7.35</td>
</tr>
<tr>
<td>R(A$^+$ - F$^-$)</td>
<td>(1.3)</td>
<td>(1.41)</td>
<td>(1.73)</td>
<td>1.875$^e$</td>
<td>1.977</td>
<td>(1.98)</td>
</tr>
<tr>
<td>E(A$^+$F$^-$) - E(A) - E(F)</td>
<td>10.11</td>
<td>7.95</td>
<td>4.04</td>
<td>2.92</td>
<td>1.45</td>
<td>0.08</td>
</tr>
<tr>
<td>D(F - A$^+$)</td>
<td>(5.9)$^c$</td>
<td>1.60$^a$</td>
<td>2.62$^a$</td>
<td>2.55$^{a,d}$</td>
<td>2.88$^{a,d}$</td>
<td>(2.7)$^b$</td>
</tr>
<tr>
<td>E(FA$^+$F$^-$) - E(A) - 2E(F)</td>
<td>+4.2</td>
<td>+6.4</td>
<td>+1.4</td>
<td>+0.3</td>
<td>-1.4</td>
<td>-2.6</td>
</tr>
<tr>
<td>Resonance</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Bond Energy (AF$_2$)</td>
<td>-2.9</td>
<td>-5.3</td>
<td>-0.1</td>
<td>1.0</td>
<td>2.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Experiment$^g$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.95</td>
<td>2.69</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Based on bond energy of corresponding halogen-fluoride, e.g., D(IF) = 2.88 eV.

$^b$ An average of the values for Ar, Kr, and Xe.

$^c$ Based on D(HF).

$^d$ Experimental values are $D$(KrF$^+$) $\approx$ 2 eV and $D$(XeF$^+$) $\approx$ 1.6 eV.

$^e$ Experimental value is $R$(KrF$^+$) = 1.752 Å.

$^f$ Using EA(F) = 3.399.

$^g$ Cotton and Wilkenson, p. 587.
Since

\( \text{EA(Cl)} = 3.615 \text{ eV} \)

\( R(\text{XeCl}^+) = 2.32 \text{Å} \)

\( \text{De(} \text{XeCl}^+\text{)} = 2.15 \text{eV}, \)

We estimate that \( \text{XeCl}_2 \) is stable by \( 1.14 \text{ eV} \) with respect to \( \text{Xe} + \text{Cl}_2 \).

However since the bond energy of \( \text{Cl}_2 \) is \( 2.48 \text{ eV} \), the energy of the chain decomposition process is exothermic by \( 2.48-1.14=1.34 \text{ eV} \), suggesting at most a small barrier

Thus \( \text{XeCl}_2 \) would be difficult to observe
Halogen Fluorides, ClFₙ

The IP of ClF is 12.66 eV comparable to the IP of 12.13 for Xe.

This suggests that the px and py pairs of Cl could be used to form hypervalent bonds leading to ClF₃ and ClF₅.

We estimate that ClF₃ is stable by 2.8 eV.

Indeed the experiment energy for ClF₃ → ClF + 2F is 2.6 eV, quite similar to XeF₂. Thus ClF₃ → is endothermic by 2.6 - 1.6 = 1.0 eV

<table>
<thead>
<tr>
<th></th>
<th>ClF</th>
<th>ClH</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP(ClX)</td>
<td>12.66</td>
<td>12.75</td>
</tr>
<tr>
<td>IP-EA</td>
<td>9.26</td>
<td>9.35</td>
</tr>
<tr>
<td>R(ClF)</td>
<td>1.70 Å⁺ⁿ</td>
<td>1.70 Å⁺ⁿ</td>
</tr>
<tr>
<td>E(A⁺F⁻) - E(A) - E(F)</td>
<td>0.79</td>
<td>0.88</td>
</tr>
<tr>
<td>D(F - Cl⁺)</td>
<td>2.62</td>
<td>2.62</td>
</tr>
<tr>
<td>E[F(ClX)⁺F⁻] - 2E(F) - E(ClX)</td>
<td>-1.83</td>
<td>-1.74</td>
</tr>
<tr>
<td>Resonance</td>
<td>~1</td>
<td>~1</td>
</tr>
</tbody>
</table>

Stability of ClF₃ relative to ClF + 2F

Estimated 2.8 2.7
Experimental 2.6 2.7

¹ Experimental value for ClF₃
Geometry of ClF₃

As expected, the F-Cl-F three-center, four-electron bond is nearly linear (bond angle 175°). The reason why this angle is not linear has to do with the nonbonded interactions with the central ClF. The 3s lone pair on the Cl poaches out the back side as the ClF sigma bond is formed.

(14.11)

As the two new F atoms bond to the Cl to form the three-center bond, the F p orbitals overlap the Cl 3s pair. In order to avoid this problem, the two new F's rotate toward the center F slightly.
We estimate that $\text{ClHF}_2$ is stable to ClH + 2F by 2.7 eV. This is stable with respect to ClH + F2 by 1.1 ev. But $D(\text{HF}) = 5.87$ eV, $D(\text{HCl})=4.43$ eV, $D(\text{ClF}) = 2.62$ eV. Thus $\text{F}_2\text{ClH} \rightarrow \text{ClF} + \text{HF}$ is exothermic by 1.4 eV. $\text{F}_2\text{ClH}$ has not been observed.
The ClF$_5$ molecule (14.9) has an additional doubly-occupied p orbital not yet used for bonding. Thus, ClF$_5$ is expected to be strongly bound and to have the geometry

![ClF$_5$ structure](image)

of a square pyramid with the four equatorial F's involved on the two three-electron $\sigma$ bonds nearly in the same plane as the Cl. Indeed, this is the case with $F_{eq}$ClF$_{ax}$ angle being 86.5°.

We have now used up the three Cl p orbitals and hence (correctly) do not expect any more F's to bond to the Cl.

Considering negative ions, Cl$^-$ is analogous to Xe but with a very low IP (3.6 eV). Thus ClF$_2^-$ and ClF$_4^-$ are expected to be linear and square planar, respectively. (ClF$_6^-$ is not stable).
BrF$_n$ and IF$_n$

Br forms BrF$_3$ and BrF$_5$ compounds analogous to ClF$_3$ and BrF$_3$ with similar structure. In addition to BrF$_2^-$ and BrF$_4^-$, Br$^-$ also forms a stable BrF$_6^-$. 

I forms all the above compounds observed for Br but also forms IF$_7$. Clearly the bonding is more complicated for IF$_7$. 
SF₂ has the structure

leading to an FSF bond angle of (102°). Thus there is a p pair available for making a three-center σ bond to two fluorines. Indeed, SF₄ has the expected structure

leading to an FSF bond angle of (102°). Thus there is a p pair available for making a three-center σ bond to two fluorines. Indeed, SF₄ has the expected structure

where the S 3s pair pooches to the left.
SF₆ has an octahedral geometry with six equivalent bonds. Sometimes this structure is rationalized in terms of sp³d² hybrid orbitals; however, calculations do not find such a large amount of d character in the orbitals.

The VB rationalization for octahedral SF₆ would be to assume that S is promoted from (3s)²(3p)⁴ to (3s)⁰(3p)⁶ which would lead to 3 hypervalent bonds in the x, y, and z directions.

With an “empty” 3s orbital, the EA for SF₆ would be very high
PF₃ and PCl₃ have pyramidal geometries with bond angles of (102°) and (102°), respectively; however, PF₅ is also stable and leads to a trigonal bipyramidal geometry.

The VB view is that the PF₃ was distorted into a planar geometry, leading the 3s lone pair to become a 3pz pair, which can then form a hypervalent bond to two additional F atoms to form PF₅.
Donor-acceptor bonds to oxygen

\( \text{PCl}_3 \) forms a very strong bond to oxygen that can be viewed as bonding the P lone pair to the excited form of oxygen having two doubly-occupied p orbitals and one empty orbital.

There is lots of charge transfer toward the oxygen so that one might also view this in terms of charge transfer.
The simple VB description of ozone is, where the terminal $p_{\pi}$ electrons are not doing much.

This is analogous to the $s$ system in the covalent description of XeF2.

Thus we can look at the $p$ system of ozone as hypervalent, leading to charge transfer to form...
Consider bonding $\text{H}_2\text{C}$ and two N atoms. One form (diazirine) is

however, the bad bond angles tend to destabilize this form. A second form (called diazomethane) can be envisioned in terms of the three pieces

leading to

Thus, by ionizing the central N we obtain four orbitals that can form covalent bonds leading to two double bonds. The outer N has available a singly-occupied orbital for this electron allowing stabilization of the charge.
Application of hypervalent concepts

Origin of reactivity in the hypervalent reagent o-iodoxybenzoic acid (IBX)

Enhancing 2-iodoxybenzoic acid reactivity by exploiting a hypervalent twist
Hypervalent iodine assumes many metallic personalities

**Hypervalent I alternative**

**Oxidations**

\[
\text{CrO}_3/\text{H}_2\text{SO}_4
\]

**Radical cyclizations**

\[
\text{SnBu}_3\text{Cl}
\]

**Electrophilic alkene activation**

\[
\text{HgCl}_2
\]

**C–C bond formation**

\[
\text{Pd}(\text{OAc})_2
\]

This remarkable chemistry of iodine can be understood in terms of hypervalent concepts.

stop