Chapter 1. The Induced Deexcitation Model.

In complex scientific disciplines, such as chemistry, a command of the literature and an ability to recognize the common denominator of many apparently unrelated experimental observations often leads to the formulation of concepts and rules of broad applicability. One demonstration of how such a marriage of knowledge and intuition can bear offspring was given by Walsh, who, many years ago, recognized that many experimental facts, which were known at that time, could be explained in a self-consistent manner by assuming that the hybridization of a central atom (or core) depends on the electronic nature of the ligands attached to it and proposed the following rule: "If a Group X attached to Carbon is replaced by a more Electro-negative Group Y, then the Carbon Valency towards Y has more p Character than it had towards X."¹ We shall refer to this as Walsh's rehybridization rule. In recent times, this rule, in one form or another, has been applied to a variety of interesting chemical problems by many, most notably by Bent.²

An interesting application of Walsh's rehybridization rule, which is probably familiar to most chemists, is shown below:³,⁴

\[ \text{H}_3\text{C} \text{CH}_3 \quad \text{O} \quad \text{F} \text{F} \]

The angle decrease is ascribed to the increase of ligand electronegativity, which, allegedly, causes an increased utilization of the oxygen 2p AO's for bonding. The data shown below can also be rationalized in a similar fashion.⁴,⁵

\[ \text{Cl} \text{Cl} \quad \text{F} \text{F} \]

We now reexamine these concepts using MOVB theory.⁶
In a previous work, we applied MOVB theory to the problem of the stereochemistry of H2O and its derivatives. The salient features of our approach can be illustrated by reference to the conversion of Linear (L) to Bent (B) H2O. The appropriate bond diagrams are shown in Figure 1 and the subsystem convention is:

\[
\begin{array}{c|c|c}
  s, p_y, \sigma/4 & p_x, \sigma^*/2 & p_z/2 \\
\end{array}
\]

The energetic consequences of the L → B transformation are as follows:

\[
U (s, p_y, \sigma/4) \rightarrow H' (s, p_y, \sigma/4) \\
N (p_x, \sigma^*/2) \rightarrow N' (p_x, \sigma^*/2) \\
(p_z/2) \rightarrow (p_z/2)
\]

Clearly, the critical subsystem conversions are the first two. Specifically, the N → N' conversion acts in a manner which favors the maximum overlap L form. On the other hand, the U → H' conversion acts in an opposite sense favoring the B form which allows an electron pair to occupy the low lying 2s AO of the core atom. Since the deexcitation accompanying the U → H' conversion occurs over a large energy gap, \( \Delta E \), equal to a first approximation, to the energy difference between the 2s and 2p AO's of oxygen, the U → H' dominates the N → N' conversion and water ends up being bent.

We can now design systematically derivatives of H2O where the bending tendency is either diminished or enhanced. This can be done by tuning the U → H' conversion. The four electron-three orbital wavefunctions for the U and H' subsystems of H2O are shown in Figure 2. We recapitulate the conditions for the selective modification of the energetic advantage of H' over U: