Main Group Chemistry Beyond First Row: The Remarkable Chemistry of the Late p-Block Elements

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Frontiers in Chemical Physics and Analysis Seminar Series

Presented by…

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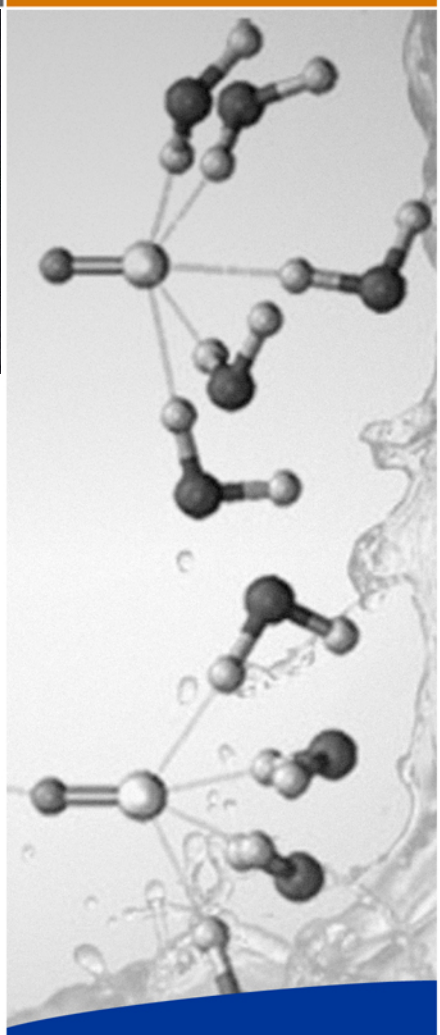
Abstract

Chemists have employed computational modeling to understand the structures, spectra, energetics and reactivities of the first row elements (Li–F) with great success. But, it has long been recognized that the chemistry of the main group elements in the second and subsequent rows of the *p*-block of the Periodic Table differs dramatically from that of their first row counterparts. This "first row anomaly" is well recognized in inorganic chemistry, and many reasons have been advanced to explain the difference.

One of the most striking differences between the first and subsequent row elements is the ability of the latter row elements to "expand their valence shell," forming *hypervalent* molecules such as PCl_5, SF_4/SF_6 and ClF_3/ClF_5. Recent studies of the fluorides of phosphorus, sulfur and chlorine revealed that (*i*) hypervalency was the result of a new type of bonding, *recoupled pair bonding*, that results when a pair of electrons in a lone pair orbital are recoupled to form a bond with a ligand using one of the electrons in the pair, (*ii*) recoupled pair bonding is common in non-hypervalent molecules, e.g., recoupled pair bonding leads to bound, low-lying excited $^4S^-$, $^2S^-$ and ^2D states in SF and the $^3B_1$ and $^3A_2$ excited states in SF_2, and (*iii*) recoupled pair bonding has a dramatic effect on the structure, spectra and energetics of the XF_n species The ability of electronegative ligands to recouple the electrons in the lone pair orbitals of second and higher row late *p*-block elements is a major factor in the anomalous behavior of these elements, including their unusual reactivities.

The seminar will introduce the basic features of recoupled pair bonding and illustrate how recoupled pair bonding affects the structure, spectra and bond energies of second row compounds.



Date: February 24

Location: EMSL Auditorium

Time: 2:30 pm