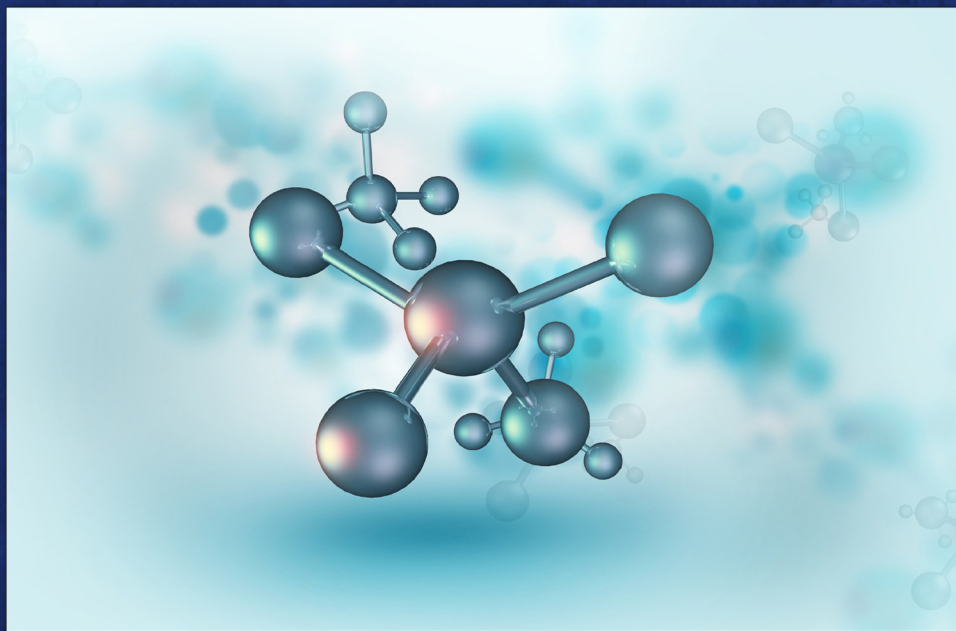


ATOMS, MOLECULES, AND CLUSTERS: STRUCTURE, REACTIVITY, AND DYNAMICS

SUPERHALOGENS AND SUPERALKALIS

BONDING, REACTIVITY,
DYNAMICS AND APPLICATIONS



Edited by
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4 Transition Metal Fluorides as Superhalogens

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4.1 INTRODUCTION

Superhalogens are unique chemical species that have electron affinity (EA) and vertical detachment energy (VDE) values exceeding the corresponding values of halogens. These complexes have EA values greater [1] than those of even the most electronegative atom in periodic table, namely Cl (3.617 ± 0.003 eV) [2,3]. These molecular systems are of particular interest to scientists both from theoretical and practical viewpoints. The basic concept of superhalogens was initially introduced by Gutsev and Boldyrev in 1981 [4]. Since then, they have garnered wide attention amongst researchers over the past few decades. These highly electronegative species can be used to design novel complex compounds having quite interesting properties. The high oxidizing capability of superhalogens, which had been pointed out much earlier [5] has numerous potential industrial applications. Systems with high EA values play an important role in the synthesis of novel compounds as well. For example, the novel salts LiAuF_6 and LiPtF_6 have been synthesized by Graudejus et al. [6] using solutions of AuF_4^- or PtF_6^{2-} as precursors. Superhalogens can also be used for developing organic superconductors [7] and their hydrogenation leads to the formation of superacids [8]. These superacids have useful applications in chemical industry. Srivastava et al. [9] and other research groups [10,11] have published articles on the usage of superhalogens as building blocks of superacids. Marcin Czapla et al. [12] have predicted the largest VDE complexes that are $[\text{SbF}_6(\text{HF})_{12}]^-$, $[\text{AsF}_6(\text{HF})_{12}]^-$ and $[\text{AlF}_4(\text{HF})_{12}]^-$ with values 14.03 eV, 14.03 eV and 13.96 eV, respectively, reported in literature so far. Freza and Skurski [13] calculated the electron binding energy of $[\text{H}_{12}\text{F}_{13}]^-$ species as 13.87 eV, which is almost three to four times higher than the chlorine atom with 3.62 eV. Recently, superhalogens have also been found to be useful for designing of safe electrolytic salts for lithium-ion batteries [14] and efficient materials for hydrogen storage [15].

The molecular structures of superhalogens generally consist of a metal atom at the centre surrounded by peripheral electronegative atoms such as fluorine (F), chlorine (Cl), oxygen (O), *etc.* Gutsev and Boldyrev [4] proposed the formula