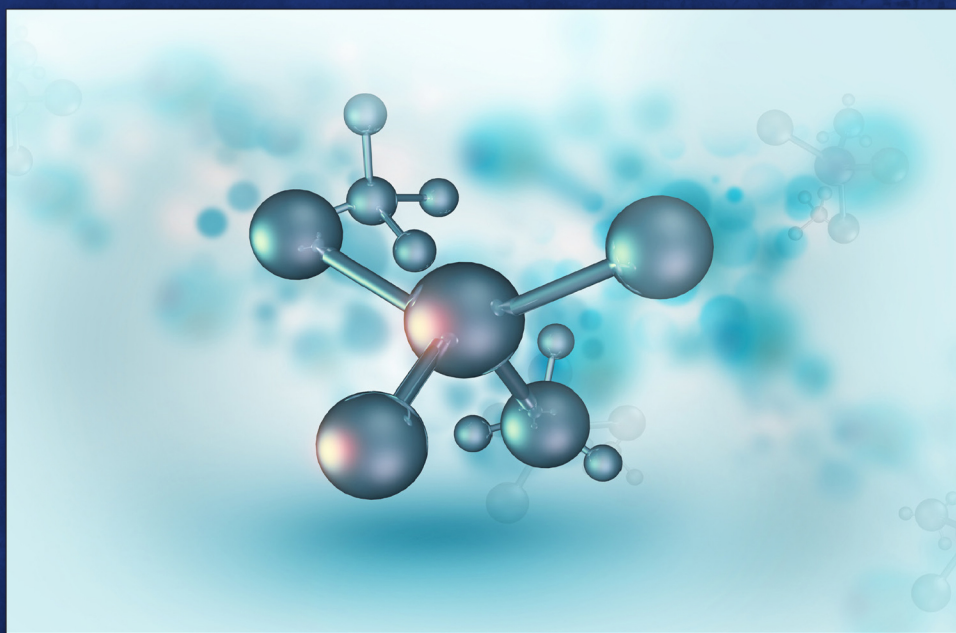


ATOMS, MOLECULES, AND CLUSTERS: STRUCTURE, REACTIVITY, AND DYNAMICS

SUPERHALOGENS AND SUPERALKALIS

BONDING, REACTIVITY,
DYNAMICS AND APPLICATIONS



Edited by
Pratim Kumar Chattaraj
Amrish Kumar Srivastava



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Contributors

Alexander I. Boldyrev

Department of Chemistry and
Biochemistry, Utah State University
USA

Pratim Kumar Chattaraj

Department of Chemistry, Birla
Institute of Technology
Ranchi, India

Jyotirmoy Deb

Department of Chemistry, Birla
Institute of Technology
Jharkhand, India

Ankit Kargeti

Department of Applied Sciences,
BML Munjal University
India

Abhishek Kumar

Department of Geology
Babasaheb Bhimrao Ambedkar
University,
India

Milan Milovanović

Faculty of Physical Chemistry
University of Belgrade

Neeraj Misra

Department of Geology, Babasaheb
Bhimrao Ambedkar University
India

Anton S. Pozdeev

Department of Chemistry and
Biochemistry, Utah State
University
USA

Tabish Rasheed

Department of Applied Sciences,
BML Munjal University
India

Ranajit Saha

Institute for Chemical Reaction
Design & Discovery (ICReDD)
Japan

Utpal Sarkar

Department of Physics, Assam
University
India

Shamoon Ahmad Siddiqui

Department of Physics, Faculty of
Science, Integral University
India

Ambrish Kumar Srivastava

Department of Physics, Deen Dayal
Upadhyaya Gorakhpur University
India

Harshita Srivastava

Department of Physics, Deen Dayal
Upadhyaya Gorakhpur University
India

Ruby Srivastava

Bioinformatics, CCMB-CSIR,
Hyderabad
India

Wei-Ming Sun

The Department of Basic Chemistry,
School of Pharmacy, Fujian
Medical University
P. R. China

Jitendra Kumar Tripathi

Department of Physics, Deen Dayal
Upadhyaya Gorakhpur University
India

Suzana Velickovic

University of Belgrade, Belgrade
Serbia

Filip Veljkovic

“VINCA” Institute of Nuclear
Sciences – National Institute of the
Republic of Serbia, University of
Belgrade, Belgrade
Serbia

4 Transition Metal Fluorides as Superhalogens

Shamoon Ahmad Siddiqui, Ankit Kargeti and Tabish Rasheed

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 Czaplá 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