

## The possible existence of the $\text{CF}_5^-$ , $\text{CCl}_5^-$ , $\text{SiF}_5^-$ , $\text{SiCl}_5^-$ , $\text{GeF}_5^-$ , and $\text{GeCl}_5^-$ anions.

**Marzena Marchaj**, Sylwia Freza, Piotr Skurski

Department of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland  
Corresponding Author e-mail: marzena.marchaj@gmail.com

The possible existence of the  $\text{CF}_5^-$ ,  $\text{CCl}_5^-$ ,  $\text{SiF}_5^-$ ,  $\text{SiCl}_5^-$ ,  $\text{GeF}_5^-$ , and  $\text{GeCl}_5^-$  anions has been investigated using ab initio methods. The species containing Si and Ge as central atoms were found to adopt the  $D_{3h}$ -symmetry trigonal bipyramidal equilibrium structures whose thermodynamic stabilities were confirmed by examining the most probable fragmentation channels. The ab initio re-examination of the electronic stabilities of the  $\text{SiF}_5^-$ ,  $\text{SiCl}_5^-$ ,  $\text{GeF}_5^-$ , and  $\text{GeCl}_5^-$  anions (using the OVGF(full) method with the 6-311+G(3df) basis set) led to the very large vertical electron detachment (VDE) energies of 9.316 eV ( $\text{SiF}_5^-$ ) and 9.742 eV ( $\text{GeF}_5^-$ ), whereas smaller VDEs of 6.196 and 6.452 eV were predicted for the  $\text{SiCl}_5^-$  and  $\text{GeCl}_5^-$  species, respectively. By contrast, the high-symmetry and structurally compact anionic  $\text{CF}_5^-$  and  $\text{CCl}_5^-$  systems cannot exist due to the strongly repulsive potential predicted for the  $\text{X}^-$  ( $\text{F}^-$  or  $\text{Cl}^-$ ) approaching the  $\text{CX}_4$  ( $\text{CF}_4$  or  $\text{CCl}_4$ ). The formation of weakly bound  $\text{CX}_4 \cdots \text{X}^-$  ( $\text{CF}_4 \cdots \text{F}^-$  and  $\text{CCl}_4 \cdots \text{Cl}^-$ ) anionic complexes (consisting of pseudo-tetrahedral neutral  $\text{CX}_4$  with the weakly tethered  $\text{X}^-$ ) might be expected at low temperatures (approaching 0K), whereas neither  $\text{CX}_5^-$  ( $\text{CF}_5^-$ ,  $\text{CCl}_5^-$ ) systems nor  $\text{CX}_4 \cdots \text{X}^-$  ( $\text{CF}_4 \cdots \text{F}^-$  and  $\text{CCl}_4 \cdots \text{Cl}^-$ ) complexes can exist in the elevated temperatures (above 0K) due to their susceptibility to the fragmentation (leading to the  $\text{X}^-$  loss).

