P-3

ON THE STRUCTURAL EFFECTS OF CF$_3$ GROUPS

Heinz Oberhammer

Universität Tübingen, Tübingen (F.R.G.)

Based on gas phase molecular structures for a series of molecules containing CF$_3$ groups, some general effects of these groups on the molecular geometries are observed. Systematic trends of CH$_3$/CF$_3$ substitution on bond lengths and bond angles are discussed. Variations of bond lengths upon CF$_3$ substitution are correlated with the "effective" electronegativity of the adjacent group. In sulfur compounds S-CF$_3$ bond lengths depend strongly on the sulfur oxidation number. The effect of CF$_3$ groups on the stereochemistry of trigonal bipyramidal molecules depends on the central atom. Examples for trifluoromethyl sulfur fluorides, trifluoromethyl fluoro phosphoranes and trifluoromethyl chloro phosphoranes are presented. Simple bonding models are suggested to rationalize the structural effects of CF$_3$ groups.

P-4

STRUCTURAL, VIBRATIONAL AND THERMODYNAMIC STUDIES OF PENTAFLUOROGERMANATE SALTS

T. Mallouk*, B. Desbat and N. Bartlett

Chemistry Department and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720 (U.S.A.)

The crystal structures of two A$^+$GeF$_5^-$ salts (A = XeF$_5$, ClO$_2$), coupled with vibrational studies of these and other salts (A = NO$_2$, SF$_3$, Bu$_4$N), show that the anion has at least four different structural forms. In XeF$_5^+$GeF$_5^-$ the anion consists of infinite chains of trans-bridged GeF$_6$ octahedra with a Ge–F–Ge angle of 141°; ClO$_2^+$GeF$_5^-$ contains cis-bridged chains with corresponding angles of 143° and 148°. The Raman and infrared spectra confirm earlier studies[1] that GeF$_5^-$ exists as a monomer of D$_{3h}$ symmetry in Bu$_4$N$^+$GeF$_5^-$. In NO$_2^+$GeF$_5^-$ a polymeric form different from those found in ClO$_2^+$GeF$_5^-$ and XeF$_5^+$GeF$_5^-$ must occur.

The enthalpies of formation of ClO$_2^+$GeF$_5^-$ and (SF$_3^+$)$_2$GeF$_6^{2-}$ (the structure of which will be described) were determined from lnK$_p$ vs. 1/T plots; from lattice energy evaluations of these salts (based upon a Madelung energy obtained by the method[2] of Bertaut) the first and second fluoride ion affinities of GeF$_4$ have been determined: ΔH(GeF$_4$(g) + F$^-$(g) = GeF$_5^-$(g)) = -101, ΔH(GeF$_5^-$(g) + F$^-$(g) = GeF$_6^{2-}$(g)) = +37 kcal mole^{-1}. Similar evaluations led to ΔH(BF$_3$(g) + F$^-$(g) = BF$_4^-$(g)) = -91, and ΔH(UF$_6$(g) + e$^-$ = UF$_6^-$(g)) = -133 kcal mole^{-1}.

1 I. Wharf and M. Onyszchuk, Can. J. Chem., 48, 2250 (1970).
2 F. Bertaut, J. Phys. Radium, 13, 499 (1952).