Ab initio MO Calculations on the Structure and Raman and Infrared Spectra of $[Al_4O_2Cl_{10}]^{2-}$ Oxide in Chloroaluminate Melts

Rolf W. Berg

Department of Chemistry, Technical University of Denmark, Kemitorvet, Building 207,
DK-2800 Lyngby, Denmark

Reprint requests to Prof. R. W. B.; Fax: +45 45 88 31 36; E-mail: rwb@kemi.dtu.dk

Z. Naturforsch. **62a,** 157 – 168 (2007); received February 6, 2007

Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

The oxide complexation chemistry in molten tetrachloroaluminate salts and ionic liquids is discussed with respect to what possible structures may be formed in addition to $[AlCl_4]^-$: $[Al_2OCl_6]^{2-}$, $[Al_3OCl_8]^-$, $[Al_2O_2Cl_4]^{2-}$, $[Al_3O_2Cl_6]^-$ and $[Al_4O_2Cl_{10}]^{2-}$. *Ab initio* molecular orbital calculations are carried out on these various aluminium chloride and oxochloride ions, in assumed isolated gaseous free ionic state, by use of the Gaussian 03W program at the restricted Hartree-Fock (HF) level and with the 6-31+G(d,p) basis set. Without any pre-assumed symmetries and with tight optimization convergence criteria and by using the modified GDIIS algorithm, the model calculations generally converge. The structures and their binding energies are presented. The expected geometries are supported, with one exception perhaps being the $[Al_2OCl_6]^{2-}$ ion, that gave a linear Al-O-Al bonding system of staggered $AlCl_3$-groups (approximate D_{3d} symmetry), in analogy to the linear Al-O-Al geometry of the analogous $[Al_2OF_6]^{2-}$ ion, found previously. The calculations include determination of the vibrational harmonic normal modes and the infrared and Raman spectra (vibrational band wavenumbers and intensities), without any empiric adjustments of the harmonic force constants, using constants directly predicted from the Gaussian 03W program. Previously obtained IR absorption and Raman scattering spectra of melts are assigned, by comparing to the *ab initio* quantum mechanical vibrational analysis results. It is concluded that the small oxide content commonly found in basic and neutral tetrachloroaluminate melts, most probably consists of $[Al_4O_2Cl_{10}]^{2-}$ ions, and the vibrational spectra are given.

Key words: Raman and Infrared Spectroscopy; IR; Hartree-Fock; Tetrachloroaluminate; Ionic Liquid; Molten Salt.