Structure and Vibrational Spectra of the Vapour Molecules Fe_2Cl_6 and $AlFeCl_6$

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Melting of aluminium and iron trichloride crystals is accompanied by a structural transition from octahedral to tetrahedral coordination of the metal ions, and a widely accepted interpretation of their liquid structure is that it mainly consists of strongly correlated dimeric units. Such Al_2Cl_6 and Fe_2Cl_6 molecules are stable in the vapour phase and coexist in gaseous mixtures together with $AlFeCl_6$ molecules. In this work we extend to Fe_2Cl_6 and $AlFeCl_6$ our earlier study of the ionic interactions in Al_2Cl_6 [Z. Akdeniz and M. P. Tosi, Z. Naturforsch. **54a,** 180 (1999)], using a model which accounts for ionic deformability through (i) effective valences and (ii) electrostatic and overlap polarizabilities. The main disposable parameters of the model are adjusted to the Fe–Cl bond length in $FeCl_3$ monomer molecule and to the Fe–Fe bond length and a bond-stretching frequency in the Fe_2Cl_6 molecule. The results are used to evaluate the structure of the $AlFeCl_6$ molecule, which has so far only been inferred from the observed Raman spectrum in mixed vapours. Extensive comparisons with data on molecular vibrational frequencies are also presented for Fe_2Cl_6 and $AlFeCl_6$.

Key words: Ionic Clusters; Molecular Vapours; Molten Salts.