Interionic Force Model for Pentahalide Molecules and Higher Niobium-Based Halide Clusters

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Molecular bound states tend to become progressively more stable in the melts of polyvalent metal halides as the nominal valence of the metal increases. We examine in this work the case of pentavalent metal halides. First we propose a simple ionic model for the binding in several pentahalide clusters: the chlorides of Nb, Ta, Sb, and Mo and the bromides of Nb and Ta. The molecular monomers of these compounds have a D_{3h} trigonal-bipyramidal structure in the ground state, and we make use of data on equatorial bond lengths and breathing mode frequencies in the vapour to determine the main force-law parameters of the metal ion. We also find that the C_{4v} square-pyramidal structure is mechanically unstable against transformation into the D_{3h} shape. We then consider higher molecular clusters, *i. e.* the dimers of Nb pentahalides and the bound states formed by $NbCl_5$ with the chlorides of Cs, Al, Ga, and Sb. We propose structural models for all these stable clusters and compare their calculated vibrational frequencies with the available data from vibrational spectroscopy of mixed melts.

Key words: Ionic Clusters; Vapour Complexes; Molten Salts.