A LIGAND FIELD THEORY VIEW OF THE ELECTRONIC STRUCTURE OF CaX (X=F, Cl, Br, I, AND O)

ROBERT W FIELD, CHRISTOPHER CUMMINS, *Department of Chemistry, MIT, Cambridge, MA, USA*; MICHAEL HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA, USA*; GUY TAIEB[a], *Institut des Sciences Moléculaires d'Orsay, Université Paris-Sud, Orsay, France*.

The CaX family of diatomic molecules illustrates concepts developed by inorganic chemists to rationalize the properties of metal-centered complexes. The basic idea is that an atom or an atomic-ion is surrounded by ligands, and that the electronic properties of the complexes are dealt with in a model in which the central metal atom and the ligands are treated as retaining their separated atom or molecule properties perturbed by identifiable and quantifiable metal-ligand interactions. Ligand Field Theory is *semi-empirical* in the sense that it is a framework for building a systematic understanding of the properties of families of complexes from spectroscopic measurements of the properties of the separated species and the interactions between them. The electronic structures of the CaX molecules are described by atomic-ions-in-molecule ligand field models. The Ca atom is treated as Ca^+ with a single electron in the 4sσ , 4pσ or π, or 3dσ,π, or δ orbital For X=F, Cl, Br, and I, the ligand is a closed-shell halide ion. For X=O, the ligand is an open-shell O^- ion with a single hole in the pπ (π^{-1}) or $p\sigma$ (σ^{-1}) orbital. The building blocks of the electronic structure model are known by different names in the inorganic chemistry, small-molecule spectroscopy, and quantum chemistry communities. Fine structure (spin-orbit, spin-spin, spin-rotation, and lambda-doubling) and spectroscopic perturbation matrix elements (spin-orbit and L-uncoupling) report on the CaX electronic structure.

[a](ISMO-UMR 8214), Universite Paris Sud, Bat. 210