Hypervalent Compounds

A DFT study on ClFx, Cl-O2, OCIO, and related species

Ke Xu and William A. Goddard III
Materials and Process Simulation Center, Beckman Institute (139-74), California Institute of Technology, Pasadena, California 91125

Hypervalent species are those with a central atom on which the number of valences exceeds that is allowed by the traditional theory but can nevertheless be thermodynamically stable, of which ClFx are a typical example. The structure of these species can be explained using a charge transfer GVB diagram, which naturally predicts the following consequences: the fluorine atoms that are ionic in some resonance structures should carry more negative charge, equatorial (semi-ionic) bonds should be longer than the normal axial one, and ClF7 should not have a stable structure.

DFT calculations were done on ClFx species to compare with experimental results, both of which were subsequently used together to validate this charge transfer GVB diagram explanation, which confirmed all the predictions given above. DFT calculations were also done for another hypervalent species Cl-O2, which gave adequate results for bond angles and bond lengths, but not as good bond energies or vibrational frequencies.