A Quantum Chemical Treatment of the Chlorine Oxides

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The chlorine oxides, particularly chlorine monoxide (ClO) and chlorine peroxide (ClOOCl), are thought to be crucial participants in the catalytic destruction of ozone in the Antarctic polar vortex. Enthalpies of formation (0 K) and adiabatic ionization potentials are calculated for several chlorine oxide (Cl_xO_y) species, including the chlorine peroxide cation (ClOOCl+), using a modification of the HEAT thermochemical protocol. Specifically, the quadruples correction to the electronic energy of each species is modified, as the choice of basis set has a significant impact on the final enthalpy value for the chlorine-containing species. Calculated ionization potentials are compared to experimental photoionization spectra produced via photoionization mass spectrometry. A simulated absorption spectrum for chlorine peroxide is also constructed solely from theoretical calculations, using oscillator strengths and excitation energies obtained from equation-of-motion coupled-cluster (EOM-CC) techniques.