384f An Ab Initio Investigation of Mercury Oxidation in Combustion Flue Gases

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Understanding the oxidation pathways of mercury in the flue gases of coal combustion is instrumental to its capture due to the water-soluble nature of oxidized mercury. The model developed in this work is based on theoretical rate constant calculations for the following mercury oxidation reactions involving chlorine species:

Hg + Cl + M -> HgCl + M (1) Hg + HCl -> HgCl + H (2) Hg + Cl2 -> HgCl + Cl (3) Hg + Cl2 + M -> HgCl2 + M (4) HgCl + HCl -> HgCl2 + H (5) HgCl + Cl2 -> HgCl2 + Cl (6) HgCl + Cl +M -> HgCl2 + M (7)

Transition state theory was used to calculate bimolecular rates and RRKM theory was used for the rate calculations involving the unimolecular reactions. Due to mercury having 80 electrons, the most recently developed effective core potentials which include relativistic effects have been used for mercury. Ab initio calculations were carried out using Gaussian98 software at both the QCISD and B3LYP levels of theory using relativistic Stuttgart and SBJK pseudopotentials. The choice of method and basis set combination was validated through a detailed comparison of theoretical geometry and heats of reaction predictions to experimental data available in the literature. A Chemkin derived model was developed based upon the theoretical predictions. The model predicts that mercury cannot be oxidized homogeneously unless chlorine levels are greater than 700 ppm.