TITLE:	COMBINED THEORETICAL AND EXPERIMENTAL INVESTIGATION OF MECHANISMS AND KINETICS OF VAPOR-PHASE MERCURY UPTAKE BY CARBONACEOUS SURFACES
PIs:	Radisav D. Vidic (Environmental Engr.), vidic@engrng.pitt.edu, 412-624-1307 Eric V. Borguet (Chemistry), borguet+@pitt.edu, 412-624-8304 Karl J. Johnson (Chemical Engr.), karlj@engrng.pitt.edu, 412-624-5644
INSTITUTION:	University of Pittsburgh Department of Civil and Environmental Engineering Pittsburgh, PA 15261-2294
STUDENTS:	Seok-Joon Kwon Lindsey Munro
GRANT NO.:	DE-FG26-98FT40119
PERIOD OF PERFORMANCE:	September 1, 1998 – March 1, 2001 **DATE:** April, 2000

ABSTRACT

OBJECTIVE

The overall goal of this research program is to gain fundamental understanding of the important chemistry and physics involved in mercury adsorption on carbonaceous surfaces. This knowledge will then be used to optimize adsorption processes and operating conditions to maximize the uptake of mercury within the required contact time. An additional long-term benefit of this research is the basic understanding of the Hg adsorption process, which may facilitate the design of new adsorbents for more efficient and cost-effective removal of Hg from a variety of effluent streams. Molecular modeling of the adsorption of Hg on carbonaceous surfaces will greatly increase the insight into the physics of the adsorption process and combined with in situ rate measurements of mercury adsorption and desorption (conventional and pulsed laser) on graphite using linear and nonlinear optical probes with real time optical resolution have the potential to provide fundamental insight into the process of mercury uptake by carbonaceous surfaces. Besides accurate assessment of key parameters influencing adsorption equilibrium, fundamental understanding of the kinetics of mercury adsorption, desorption, and diffusion will be developed in this study. These key physical and chemical processes postulated through molecular modeling efforts and verified by in situ measurements will be utilized to select (or develop) promising sorbents for mercury control, which will be tested under dynamic conditions using simulated flue gas.

ACCOMPLISHMENTS TO DATE

Vacuum chamber for surface adsorption/desorption experiments with sample manipulator enabling cooling

to 90 K and heating to over 800 K at heating rates of up to 10 K/sec was designed and constructed. Additional features that were uniquely designed and constructed for this experimental system include apertured temperature programmed desorption (TPD) spectrometer and a differential reflectance (DR) spectrometer for real time monitoring of adsorption and desorption.

Sub-monolayer sensitivity of TPD and DR to adsorption and desorption on carbonaceous surface was demonstrated for a model system (acetone/graphite). Also, identification of monolayer, bilayer and multilayer adsorption states from TPD and determination of the heat of adsorption was successfully accomplished for the model system. Linear correlation between DR signal and TPD signal in sub-monolayer and multilyer regime was established and the *in-situ*, sub-monolayer sensitivity of DR was successfully used to distinguish between carbonaceous surface and sample support TPD spectral features. Mercury adsorption and desorption experiments providing initial estimate of heat of adsorption were recently accomplished and the sensitivity of DR to mercury adsorption on carbonaceous surface was established.

Accurate potentials for mercury-mercury and mercury-carbon interactions are needed to simulate the adsorption of mercury by activated carbon. Because pair interactions between the mercury atoms are most likely to dominate on the surface of the adsorbate and because Hg_2 is a weakly bound molecule, inclusion of highly accurate correlation and relativistic effects is required for successful modeling of this system.

Interatomic potential for two Hg atoms were fitted to CCSD(T) calculations of the dimer binding energy. Precision of a procedure in which the CCSD(T) calculations were carried out with a small (9s8p7d3f)/[7s6p4d3f] basis set and the effect of higher angular momentum functions (f3gh) was treated using Møller-Plesset perturbation theory was evaluated. The calculated binding energy (0.047 eV) and equilbrium separation (3.72Å) using this approach are in excellent agreement with experimental results. A variety of experimental properties, including the second virial coefficient, rotational and vibrational spectroscopic constants, and vibrational energy levels, have been calculated using this interatomic potential and agreement with experiment is good overall.

The importance of many-body effects between mercury atoms was examined by calculating the 3- and 4-body contributions to the energy for a 30 different geometries, including equilateral triangle, linear and bent structures for Hg_3 and tetrahedral structres for Hg_4. These calculations indicate that the many-body contribution is increasingly significant (~40% of trimer binding energy for equilateral triangle with r=3Å, 17% for r=3.5 Å CCSD(T) +G2 +5s,5p). Current investigations are focused on fitting a functional form to these results for use in simulations of the mercury graphite system.

Conference presentations
Lindsey Munro, J. K. Johnson, and K. D. Jordan, "Interaction Potentials for Mercury", American Conference on Theoretical Chemistry, Boulder, Colorado, Jun 27 - July 2, 1999.
Lindsey Munro, K. D. Jordan, and J. K. Johnson, "Development of an accurate intermolecular potential for mercury", American Institute of Chemical Engineers Annual Meeting, November 12-17, 2000, Los Angeles, California.

Papers
L. Munro, K. D. Jordan, and J. K. Johnson, "An Accurate Mercury Dimer Potential from Ab Initio", in preparation.