

Computational Approaches to the Development of Advanced Mercury Control Technologies



Alexander Calder:
The Mercury Fountain
Joan Miro Museum, Barcelona, Spain



Jan Steckel

National Energy Technology Laboratory

Mercury Control Technology Research and Development Program Review



Motivation for Theoretical Work

Macroscopic:

Activated Carbon + Hg

Coal + Hg
(spectroscopy)

Kinetic modeling, Hg
oxidation

Heterogeneous model
for Hg oxidation

Metal Hg sorbents

Atomistic description:

Hg – arene
interactions

Hg – arene
interactions

Gas phase *ab initio*
modeling of Hg
oxidation subreactions

Hg on metal surfaces

Hg on metal surfaces

This is no longer recommended:



From the website of Theodore Gray, the
maker of the Periodic Table
(www.theodoregray.com/PeriodicTable)

Computational Challenges, Theoretical Methods

- VDW \rightarrow covalent \rightarrow metallic w/size of Hg clusters
 - Subtle interplay between types of bonding
 - Requires method in which both are well described
 - Ψ based methods (CC or QMC)
 - Relativistic effects
 - Spin-orbit corrections
 - Methods not well developed, tested
 - \rightarrow “notorious”...
- **HF**
 - 1st approximation for wavefunction based methods
 - Will not model weakly bound systems.
 - **DFT**
 - Well known deficiency for dispersion interactions.
 - Might be ok for metallic interactions
 - **MP2**
 - Models dispersion and electron correlation for many compounds but not highly accurate for Hg₂
 - **CCSD(T)**
 - More accurate wavefunction-based technique
 - Need adequate basis set, high angular momentum functions

Software:

MOLPRO - Mol Phys. 74, 1245 (1991)

Gaussian03 – Frisch *et al.*, Gaussian Inc. (2003)

VASP – Vienna Ab Initio Simulations Package



Stuttgart *ab initio* pseudopotential for Hg

- Ion core = core electrons (60 or 78) plus nucleus
- Valence system treated in non-relativistic manner
- (For Hg) neutral atom used as the reference system for generating the pseudopotential
- All electron relativistic (Dirac-Fock), quasirelativistic (Wood-Boring) or non-relativistic calculations used for Hg atom to generate the pseudopotentials
- Contributions of most important relativistic operators are transferred to the pseudopotential
- Core-valence correlation accounted for by semi-empirical polarization potential (cpp) for 78 e⁻ pp

Nicklass, Dolg, Stoll, Pruess J. Chem. Phys. **102**, 8942 (1995).

Stoll, Metz, Dolg, J. Comput. Chem. **23**, 767 (2002).

Basis Sets

eCP78mwb ‘library’ basis: (4s4p1d)/[2s2p1d]

Kuechle, Dolg, Stoll, Pruess, Mol. Phys. 74, 1245 (1991).

eCP60mwb ‘library’ basis: (8s7p6d)/[6s5p3d]

Andrae, Häussermann, Dolg, Stoll, Pruess, Theor. Chim. Acta. 77, 123 (1990).

eCP60mdf ‘library’ basis: (8s8p7d)/[6s6p4d]

Häussermann, Dolg, Stoll, Pruess, Schwerdtfeger, Pitzer, Mol. Phys. 78, 1211 (1993).

Czuchaj basis set (eCP78mwb): (9s8p6d)/[8s6p3d]

Czuchaj *et al.* Chem. Phys. 214, 277 (1997).

Kirk Peterson (KAP) dz (eCP60mdf): (7s7p6d2f)/[4s4p3d2f]

Kirk Peterson in “Recent Advances in Electron Correlation Methodology” (ACS, 2003).

(This is part of a series, with TZ, QZ, etc., but DZ was all that we could manage with C₆H₆-Hg)



Intermediates in Electrophilic Substitution

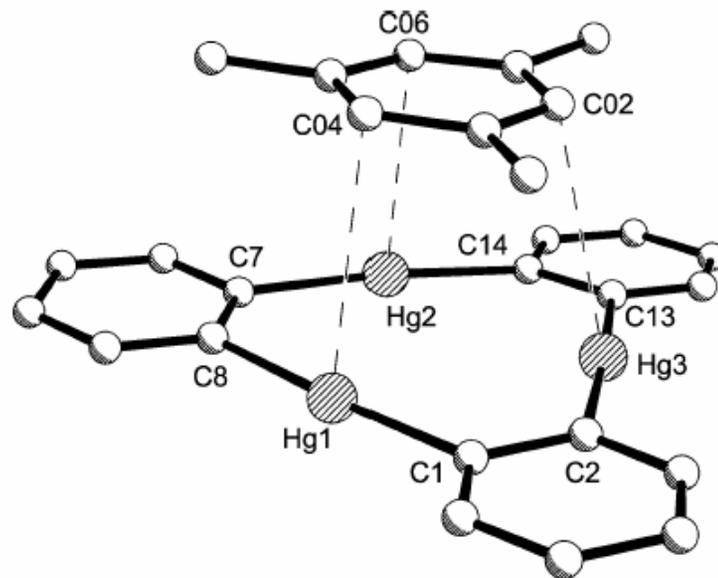
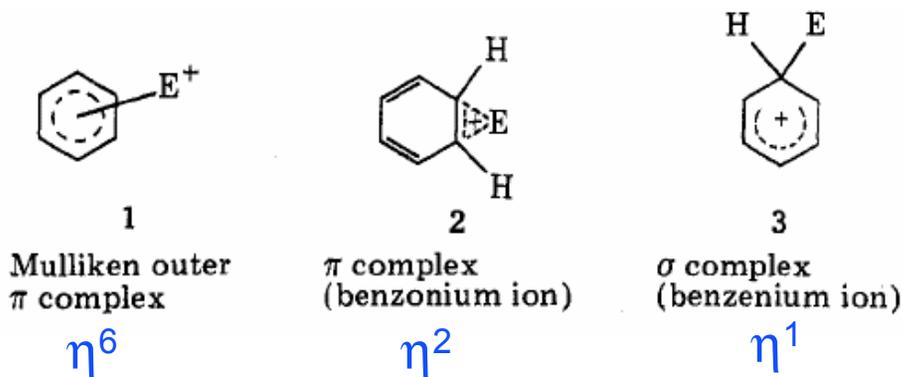
- Olah *et al.*: NMR study of mercuration of a series of arenes including benzene, toluene, mesitylene; conclusion was that intermediate undergoes rapid exchange of sigma and pi complexes.

J. Org. Chem. 41, 1983 (1976)

- Damude *et al.*: Isolation of a wide range of arene complexes of mercury; conclude that arenes bound to Hg in η^1 manner.

J. Organomet. Chem. 181, 1 (1979).

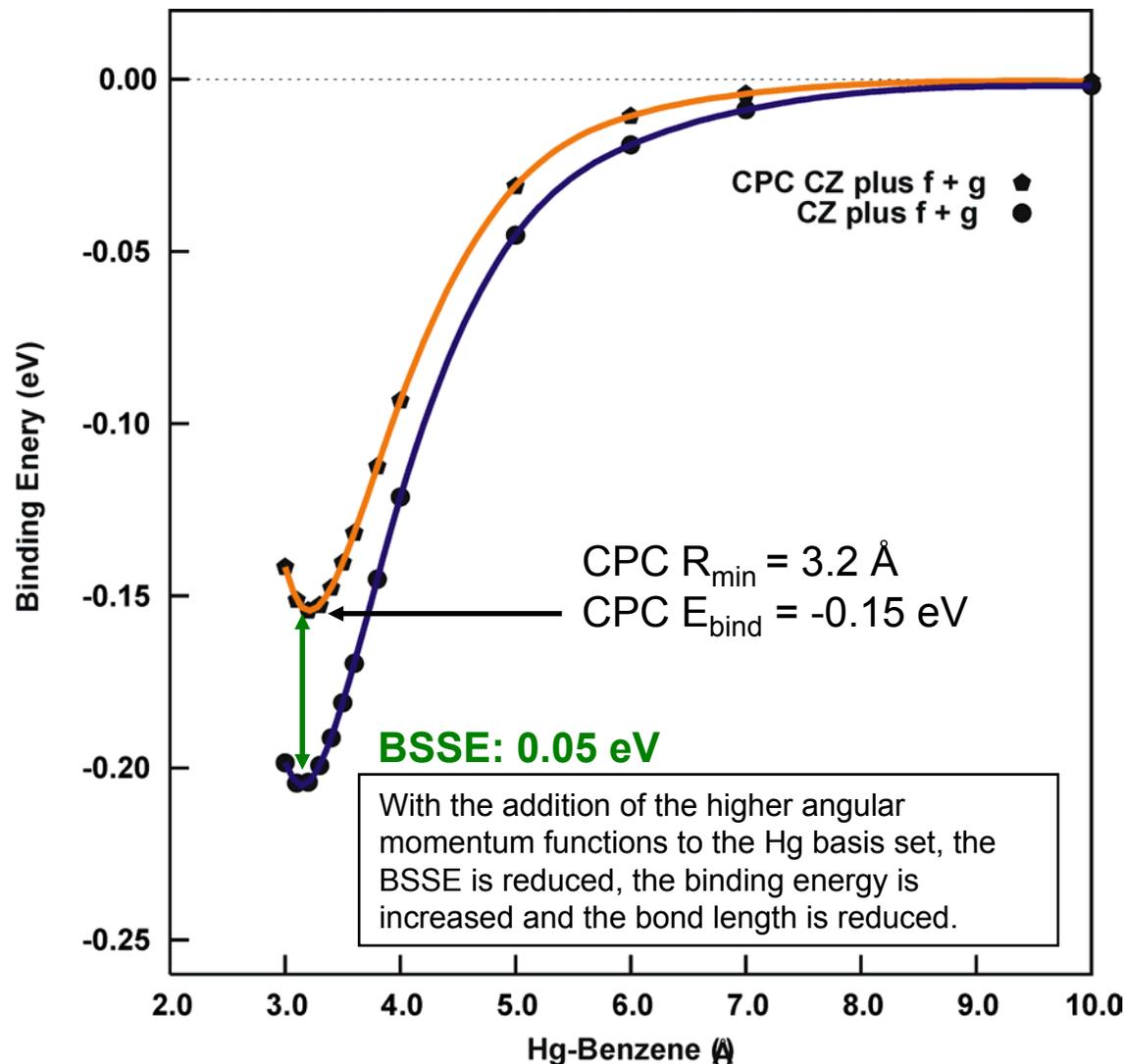
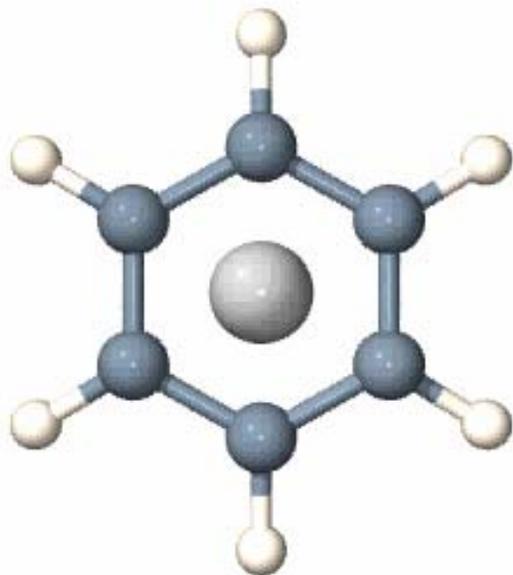
- Haneline: Methyl substituted benzene adducts of trimeric perfluoro-*o*-phenylene mercury
- Dalton 2686 (2003).



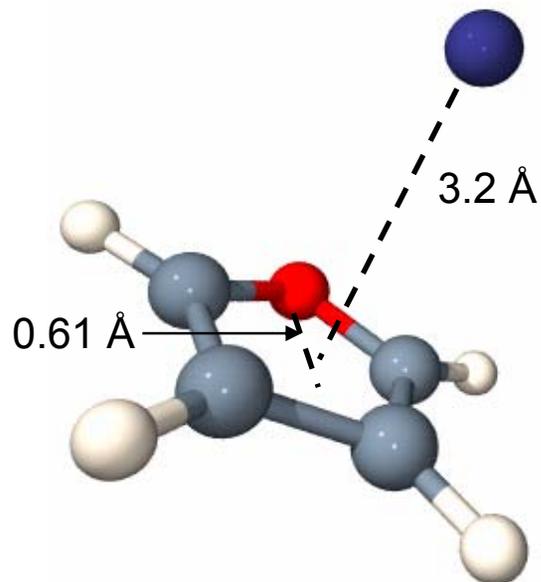
Hg - Benzene η^6 Interaction – *Improved Basis*

Potential Energy Plot

- CCSD(T)
- Single Point Energy Calculations
- Czuchaj basis set for Hg with the addition of 3f and 2g functions
- ~~VDZ~~ VTZ basis on benzene

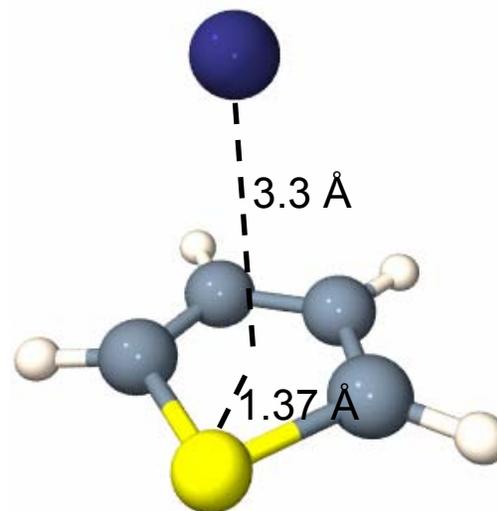


Hg η^5 Complexes: Furan and Thiophene



Furan:

CPC $E_{\text{bind}} = -0.13 \text{ eV}$



Thiophene:

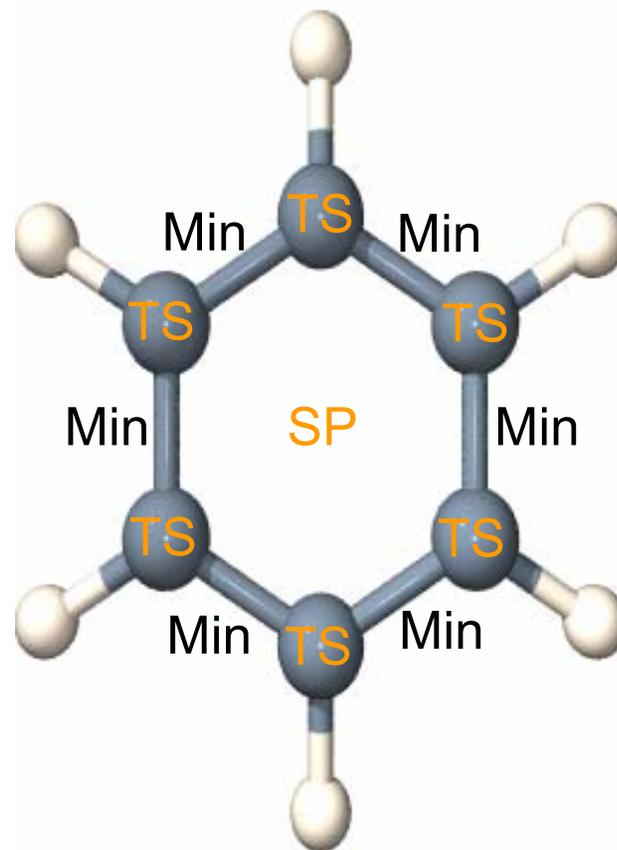
CPC $E_{\text{bind}} = -0.13 \text{ eV}$

CCSD(T), ecp78mwb, Czucaj plus f and g, VTZ

The presence of the heteroatom in the ring does not essentially change the interaction

(Benzene – Hg)⁺ Interaction

- Pi complex: η^2
minimum on the PES
 $E_{\text{bind}} = -2.18 \text{ eV}$
- Mulliken outer pi complex: η^6
Saddle point
 $E_{\text{act}} = 0.79 \text{ eV}$ (wrt pi)
- Sigma bonded configuration: η^1
TS
 $E_{\text{act}} = 0.3 \text{ eV}$ (wrt pi)



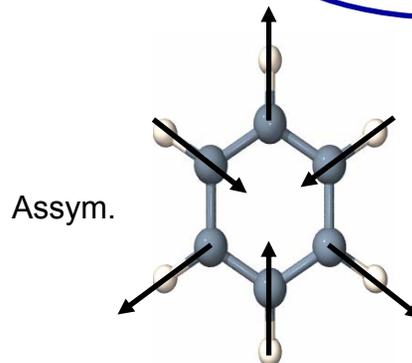
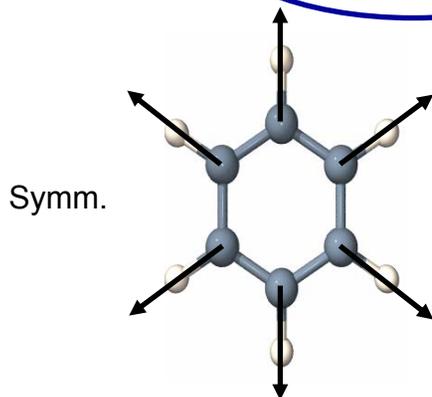
MP2, ecp60mdf, KAP DZ, 6-311G(d)

Frequencies of Benzene Breathing Mode

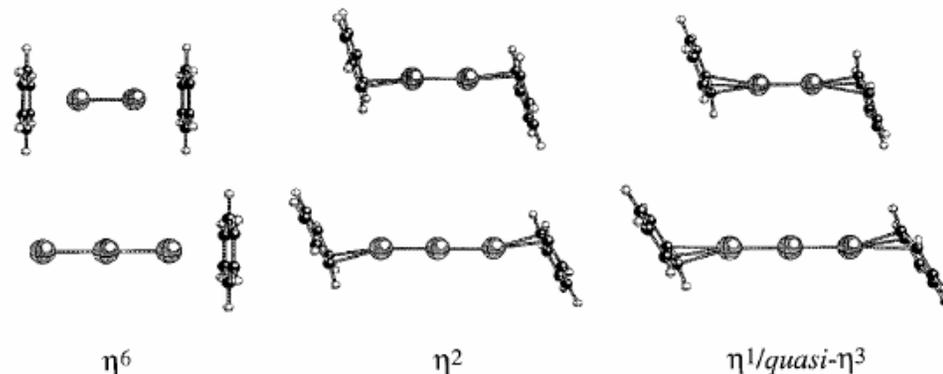
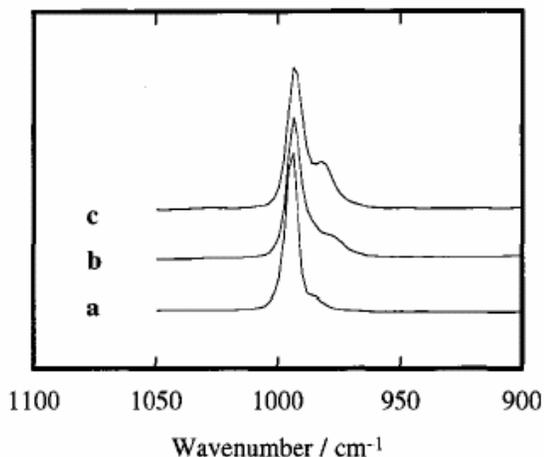
Level of theory: MP2

6-311G(d) ecp60mdf DZ KAP

| C ₆ H ₆ | | C ₆ H ₆ -Hg η ⁶ Min | | C ₆ H ₆ -Hg ⁺ η ⁶ SP | | C ₆ H ₆ -Hg ⁺ η ² Min | | C ₆ H ₆ -Hg ⁺ η ¹ TS | |
|-------------------------------|-----------|--|-----------|--|-----------|---|-----------|--|-----------|
| freq (cm ⁻¹) | rel. int. | freq (cm ⁻¹) | rel. int. | freq (cm ⁻¹) | rel. int. | freq (cm ⁻¹) | rel. int. | freq (cm ⁻¹) | rel. int. |
| Symm. → 1014 | inactive | 1012 | 2.2 | 992 | 1.3 | 989 | 20 | 994 | 0.06 |
| Assym. → 1013 | inactive | 1016 | 0.1 | 984 | 0.3 | 1008 | 1.4 | 1013 | 0.4 |



B3LYP ($\text{Hg}_2\text{Cl}_2/\text{GaCl}_3/\text{C}_6\text{H}_6$), Ulvenlund *et al.*



- a) Neat benzene
- b) Hg_2^{2+} in $\text{Hg}_2\text{Cl}_2/\text{GaCl}_3/\text{C}_6\text{H}_6$
- c) Hg_3^{2+} in $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{GaCl}_3/\text{C}_6\text{H}_6$

min

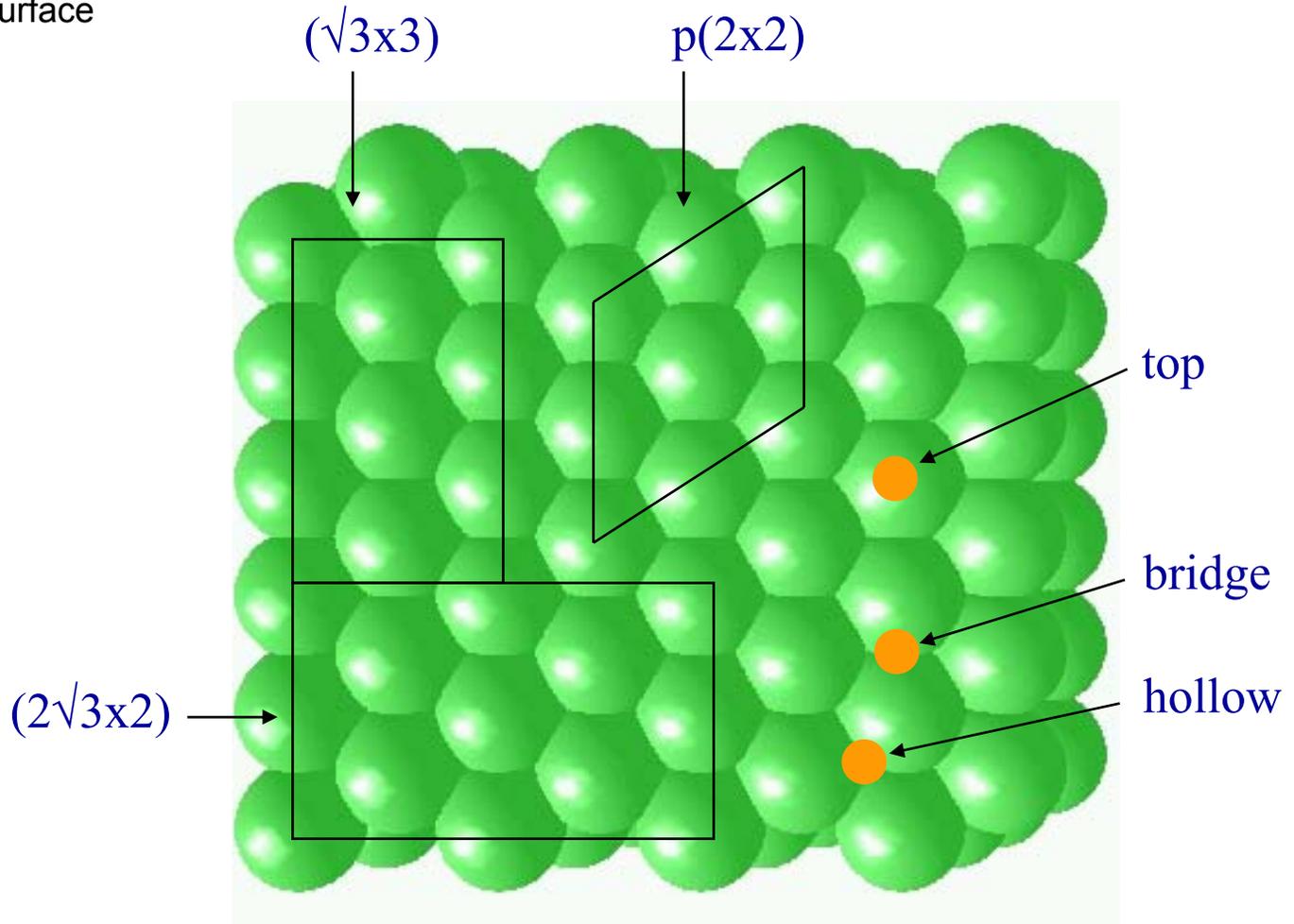
B3LYP Optimized structures of benzene with Hg_2^{2+} and Hg_3^{2+}

Raman Spectroscopy: totally symmetric band at 991 cm^{-1} is split and new peak appears at 978 for $\text{Bz}_2\text{-Hg}_2^{2+}$ and 982 cm^{-1} for $\text{Bz}_2\text{-Hg}_3^{2+}$.

Ulvenlund, Schwerdtfeger *et al.* Eur J. Inorg. Chem. 1999

Surface Cells and Adsorption Sites

fcc metal: (111) surface



Hg Adsorption on Au(111) and Pt(111)

Plane-wave DFT, 280 eV cutoff, ($\sqrt{3}\times 3$) surface cell

4 layers, 24 Au or Pt atoms in supercell, Two layers fixed at bulk positions, 4 x 6 x 1 k point mesh

| Pt(111) | E_{bind} (PW91) | | E_{bind} (PW91) | | |
|---------|--------------------------|----------------------|--------------------------|-------|-------|
| | | | LDA | PW91 | Exp |
| fcc | -0.33 | Bulk Properties: | | | |
| hcp | -0.33 | Bulk modulus (Gpa) | 310 | 239 | 278 |
| bridge | -0.28 | Cohesive E (eV) | -7.52 | -6.05 | -7.52 |
| top | -0.13 | Lattice Constant (Å) | 3.99 | 3.92 | 3.92 |

| Au(111) | E_{bind} (LDA) | | E_{bind} (LDA) | | | | |
|---------|-------------------------|----------------------|-------------------------|-------|-------|------|------|
| | | | LDA | PW91 | PBE | Exp | Wang |
| fcc | -0.64 | Bulk Properties: | | | | | |
| hcp | -0.64 | Bulk modulus (Gpa) | 189 | 137 | 136 | 170 | 185 |
| bridge | -0.58 | Cohesive E (eV) | -4.40 | -3.21 | -3.28 | -3.8 | -4.4 |
| top | -0.36 | Lattice Constant (Å) | 4.06 | 4.17 | 4.17 | 4.07 | 4.07 |

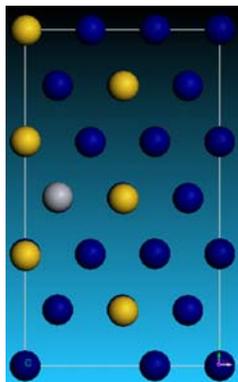
LDA, Wang *et al.* PRB 2004



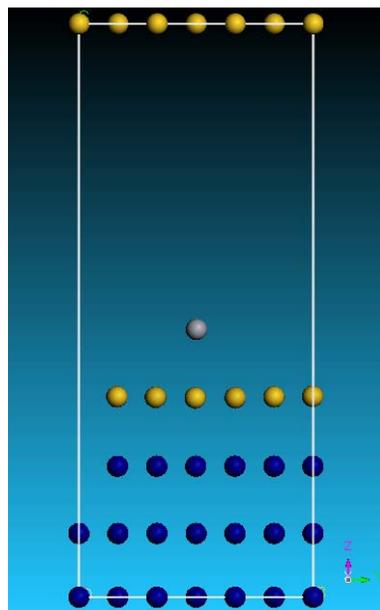
Hg-Au Exchange on the Au(111) Surface

Starting Structure
Hg at fcc site
on Au(111) surface

Top view:



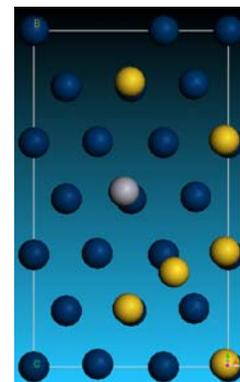
Side view:



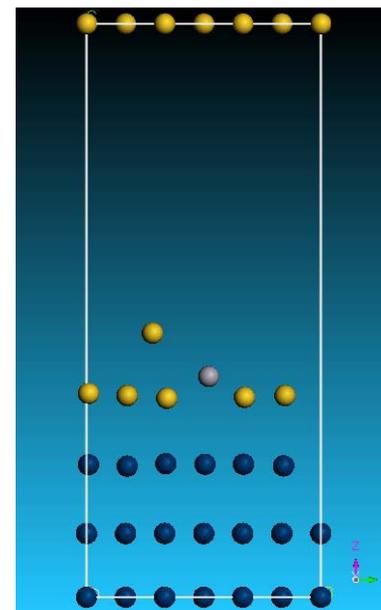
$E_{\text{rxn}} = 0.8 \text{ eV}$
(LDA)

Ending Structure
Hg has exchanged
with one of the top
layer Au atoms.

Top view:

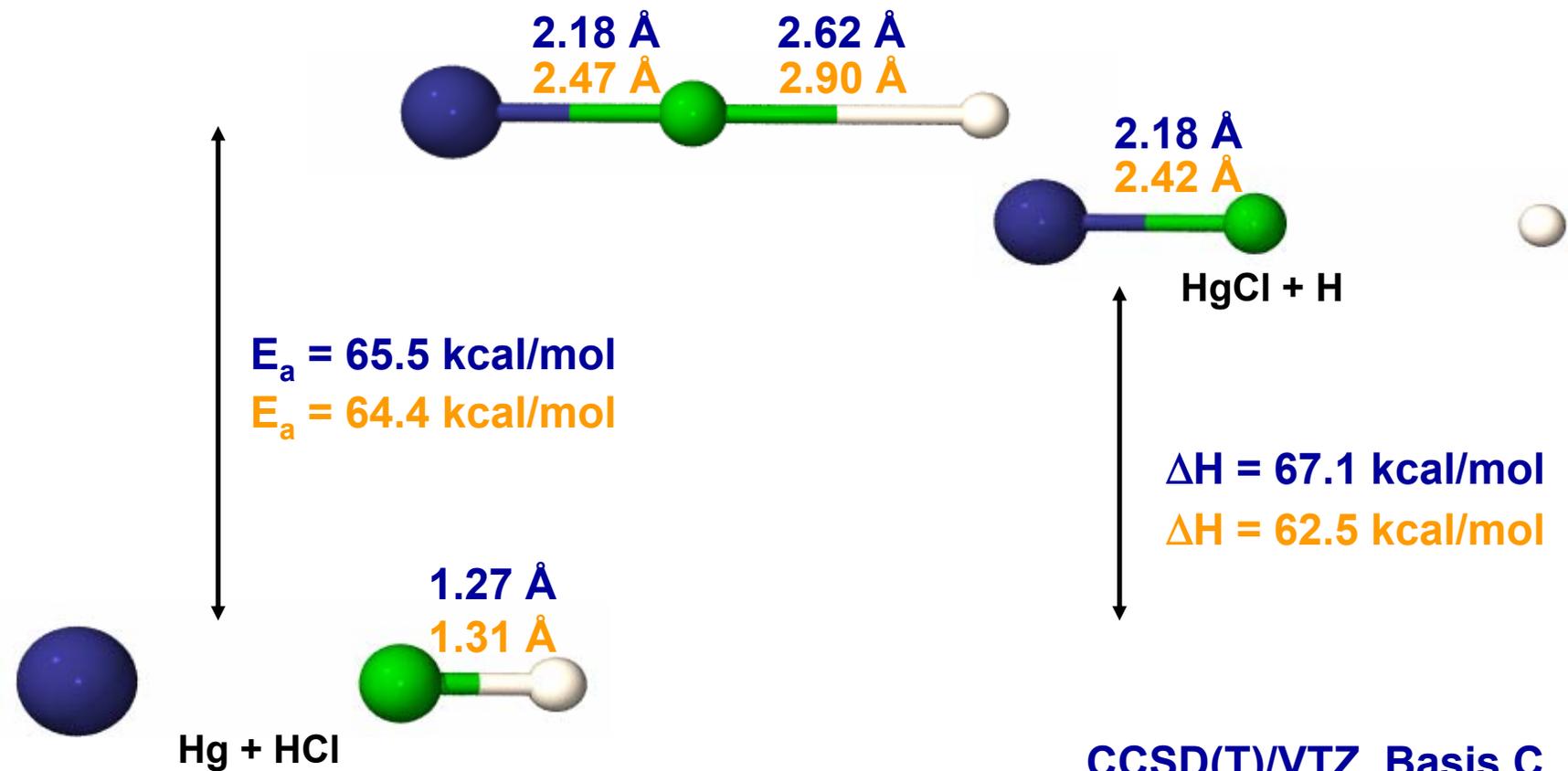


Side view:



Hg Oxidation

Transition State



CCSD(T)/VTZ, Basis C
MP2/QCI, Li *et al.*



Conclusions

- Basis sets published for Hg are either not adequate for CCSD(T) calculations on weakly bound complexes or too computationally demanding.
- η^6 Interaction between benzene and Hg with binding energy of 0.15 eV, Hg 3.2 Å from the plane of the ring
- Analogous η^5 interactions exist for furan and thiophene
- Heteroatom does not influence the η^6 interaction

- (Hg-benzene)⁺ complex predicted at MP2 level with strong binding energy of – 2.18 eV for the η^2 interaction
- Analogous compounds predicted for (Hg-furan)⁺ and (Hg-thiophene)⁺
- Essentially no barrier for Hg to move around the ring
- Changes in the IR spectrum of coal seen when Hg is added may be due to the formation of the (Hg-benzene)⁺ complex.

- Au not well-described by GGA functionals.
- Hg binds to both Pt(111) and Au(111) with a preference for the hcp and fcc hollow sites.

