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Principal Investigator	**Jerzy Leszczynski**
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Technical Section

Technical Objectives

The “Proof of Concept for Efficient Application of Quantum-Chemical Techniques to Model Environmental Mercury Depletion Reactions Through Transition State Theory” project focuses on the study of the atmospheric reactions of mercury through modeling of atmospheric mercury depletion processes. Among the essential reactions for mercury depletion in the environment are redox reactions. The existence of mercury either in elemental (Hg^0) or in oxidized divalent Hg^{2+} forms affects mercury availability and mobility within the ecosystem. There are scientific debates on this issue and some proofs were also forwarded for both type of particles. The present project has proposed investigation on a simple electrochemical reaction on the hydrated forms of mercury using state of the art computational techniques to figure out the feasibility of the interconversion between the two forms of mercury. For this purpose, we mainly deal with the experimental studies of interaction between halogens with mercury, X_2/X (X= Cl, Br, and I) + $Hg^0_{(g)}$. [1]. We use the Transition State Theory (TST) to find the ways of mercuric halides formation in presence of water molecules (as water is present in upper atmosphere). Although we could locate the low barrier for the Hg—Br bond formation in presence of one water molecule, further increase of water molecules faced with the sampling difficulties caused by the relatively large number of degree of freedom. The formation of Hg—Cl and Hg—I bonds goes barrier-less, at least within classic TST. But, for reactions of active metals and halogens, the transition states could appear through the intersection of electronic terms of neutral and ionic species and caused by the electron transition from the metal atom to the halogen molecule. The classic TST is not valid for such cases. Important questions remain challenging for us: how does the interaction of water and solute ions affect the rate constants of mercury depletion? For this we need to study the microscopic mechanism of mercuric salt dissolution. Although the microsolvation model derived from salt-water cluster is not expected to quantitatively predict the liquid-phase solvation of the salts, it can be used to provide valuable insights into the interactions between the water, mercury ions, halogens and other oxidants. In this perspective, we have proposed an extension of studies to several other computational techniques, where the molecular dynamics trajectories of integrated tempering sampling simulations [2] are used to illustrate the microsolvation of mercury-halide ion pairs and to obtain valuable and reasonable thermodynamic characteristics.

Computational Approach

The computational approach includes:

1. The gas-phase and liquid-phase structural analyses for the compounds HgX^+, HgX_2, (X = Cl, Br, I,) with n=1-6 water molecules with density function theory calculations (M06) including intrinsic reaction coordinate calculations (IRC).
2. Frequency calculations to ensure whether the computed structures are minima on the respective potential energy surfaces. Localization of transition state.
3. The aqueous salvation energies calculations at the same M06 levels using a polarized continuum model with conductor-like screening reaction field (CPMC).
4. Relativistic SBKJC VDZ effective core potential (ECP) basis set of the atoms. The Hg basis sets were further augmented with optimized ***f*** (ξ = 1.10) and ***g*** (ξ = 1.40) polarization functions. The basis sets of all other elements were augmented with one ***d*** and one ***f*** polarization functions (C: ξ_d = 0.75, ξ_f = 0.80; N: ξ_d = 0.80, ξ_f = 1.00; O: ξ_d = 0.85, ξ_f = 1.40; S: ξ_d = 0.65, ξ_f = 0.55; Cl: ξ_d = 0.75, ξ_f = 0.70; Br: ξ_d = 0.338, ξ_f = 0.56; I: ξ_d = 0.266, ξ_f = 0.4075).
5. GAUSSIAN 09 codes.

Progress Statement Summary

The main objectives of the project were to find the efficient computational approaches to study atmospheric mercury depletion reactions (AMD). The careful literature search of AMD suggests that unlike in the gas-phase, the mercury in the upper atmosphere exists mostly as soluble mercuric ion Hg^{2+}(aq) and the reactivity of solvated mercuric ion affect significantly the atmospheric speciation of mercury. The reactivity of mercuric ion towards different halide ions was explored through electronic structure calculations combined with the calculation of Gibbs free energy of formation in aqueous solution using DFT level of theory (Table 1). A reasonable estimation of these thermochemical quantities is important as they could be subsequently used to compute the kinetics of several such reactions in aqueous medium. As can be seen from Table 1 the calculated values of ΔG^0 are quite close to the experimental data for the systems, where both mercury ion and halogen ion are hydrated. The calculated ΔG_{eq} in most of such cases is within 2-5 kcal/mol of the experimental data. The results show that with more rigorous quantum chemical approaches it is possible to calculate the thermochemical properties, which are accurate enough to analyze kinetics of such reactions.

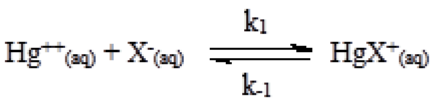
Table 1. Calculated $\mathbf{\Delta G^\circ_{aq}}$ (kcal/mol) for the micro-solvated $[HgX(H_2O)n]^+$ (X=Cl, Br, I and n=1-6) formation reactions due to vertical and equilibrium solvation of the respective solutes in aqueous solution at the M06/SBKJCVDZ ECP.

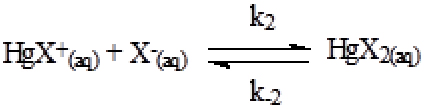
Experimental $\mathbf{\Delta G^\circ_{aq}}$ ($Hg^{++}_{(aq)} + Cl^{-}_{(aq)} \rightarrow HgCl^{+}_{(aq)}$) = **-9.22 kcal/mol.**

Experimental **ΔG°_{aq}** ($Hg^{++}_{(aq)} + Br^{-}_{(aq)} \rightarrow HgBr^{+}_{(aq)}$) = **-12.33 kcal/mol.**
Experimental **ΔG°_{aq}** ($Hg^{++}_{(aq)} + I^{-}_{(aq)} \rightarrow HgI^{+}_{(aq)}$) = **-17.46 kcal/mol.**

Reactions	ΔG°_{aq}, kcal/mol					
	X=Cl		X=Br		X=I	
	Vertical	Equilibrium	Vert.	Equil.	Vert.	Equil.
$Hg^{++}_{(aq)} + X^{-}_{(aq)} \rightarrow HgX^{+}_{(aq)}$	-35.77	-39.74	-37.98	-23.85	-41.95	-43.17
$[Hg(H_2O)]^{++} + X^{-}_{(aq)} \rightarrow [HgX(H_2O)]^{+}$	-26.28	-27.19	-29.46	--26.44	-31.72	-33.54
$[Hg(H_2O)_2]^{++} + X^{-}_{(aq)} \rightarrow [HgX(H_2O)_2]^{+}$	-30.95	-26.17	-33.21	-34.21	-36.75	-32.45
$[Hg(H_2O)_3]^{++} + X^{-}_{(aq)} \rightarrow [HgX(H_2O)_3]^{+}$	-30.27	-27.73	-31.53	-32.52	-37.52	-38.39
$[Hg(H_2O)_4]^{++} + X^{-}_{(aq)} \rightarrow [HgX(H_2O)_4]^{+}$	-33.35	-29.71	-33.43	-30.23	-44.22	-45.23
$[Hg(H_2O)]^{++} + [X(H_2O)]^{-} \rightarrow [HgX(H_2O)_2]^{+}$	**-10.42**	**-9.21**	**-13.32**	**-17.69**	**-17.09**	**-16.52**
$[Hg(H_2O)_2]^{++} + [X(H_2O)_2]^{-} \rightarrow [HgX(H_2O)_4]^{+}$	**-11.79**	**-16.24**	**-12.89**	**-13.1**	**-24.41**	**-22.32**
$[Hg(H_2O)_3]^{++} + [X(H_2O)_3]^{-} \rightarrow [HgX(H_2O)_6]^{+}$	**-11.35**	**-21.25**	**-17.24**	**-14.62**	**-20.32**	**-19.23**

The above observation paves way to consider that the mercury depletion reaction in the environment could be through reactions: $HgX_n^{q}(aq) + X^{-}(aq) \rightarrow HgX_n^{q-1}(aq)$. The general equilibration in such reactions could be described as follows:





These reactions are formation/dissociation of diatomic systems. Hence transition-state, reaction rate etc. cannot be studied through classis TST. Application of TST is hypothetically possible in such reactions if water molecule is considered as a third body species. The preliminary investigation at the DFT level using continuum solvation model has shown the existence of transition state for the $HgCl^{+}$ formation from Hg^{2+}, Cl^{-}, and H_2O. However, further analysis demonstrates that transition states in such kind of "hydrated" systems (with one and more water molecules) characterize the vibrations of water molecules rather than the mercury halide bond formation. However, just for the H_2O—Hg—Br system the small barrier (1.2 kcal/mol) was found within CPCM. The optimized structure of $HgBr^{+}\ldots H_2O$ complex is shown in Fig. 1. Two-dimensional contour mapping of the whole reaction surfaces was generated in gas-phase as well as under solvated condition using CPCM and shown in Fig.2. The structure of transition state is proven by the appropriate IRC calculations (Table 2) and frequency analysis at the same level of theory.

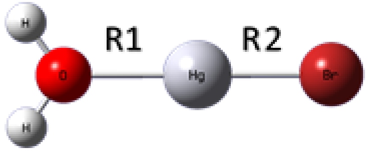


Fig. 1. Optimized structure of $HgBr^{+}\ldots H_2O$ molecular system.

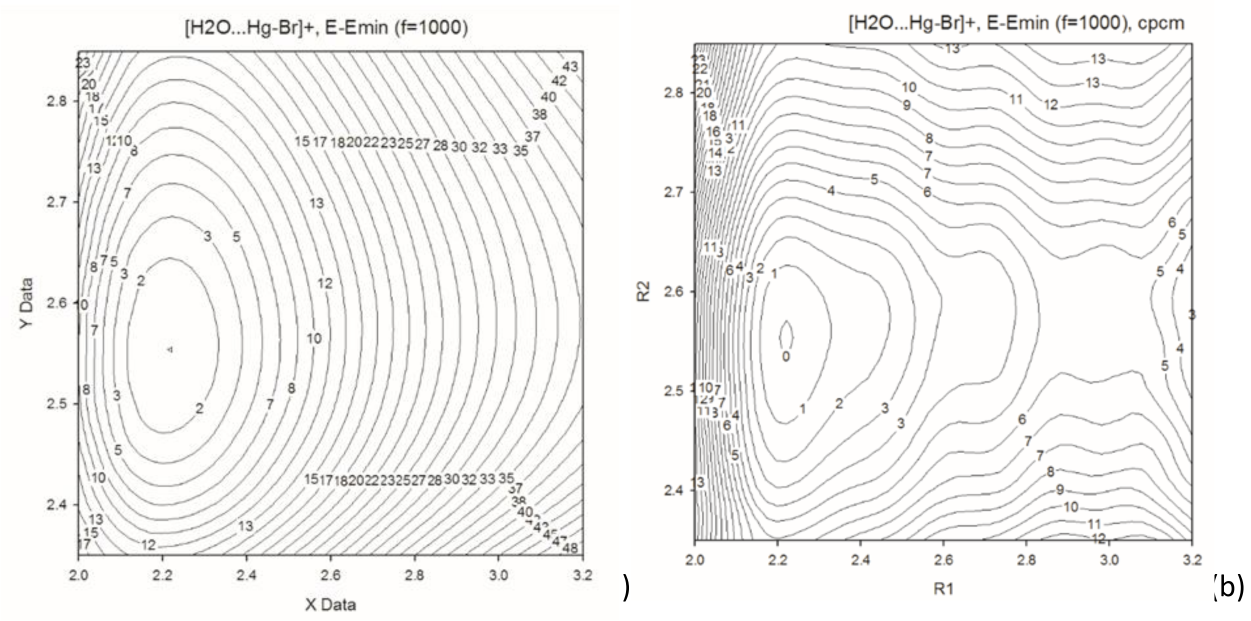


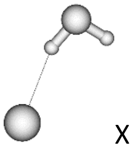
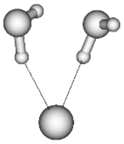
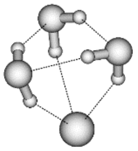
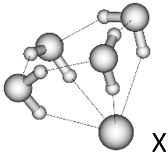
Fig.2. Computed gas-phase (a) and CPCM (b) energy surface of HgBr$^+$…H_2O molecular system as a function of r1 and r2 (Fig. 1) at the DFT/M06 level of theory. The surface (a) is devoid of any transition state. The surface (b) shows clear transition state.

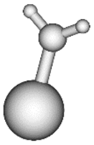
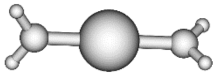
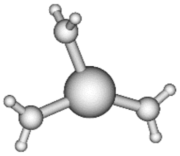
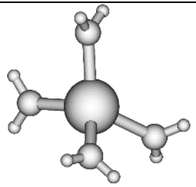
Table 2. Structural parameters of HgBr$^+$…H_2O molecular system and appropriate transitional state (TS).

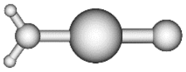
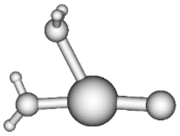
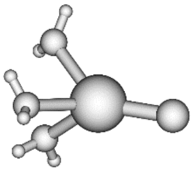
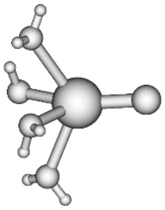
H_2O--Hg--Hal	OPT from IRC	IRC, reverse	TS	IRC, forward	OPT from IRC
O—Hg, ang.	2.96	2.96	2.99	2.96	2.96
Hg—Br, ang.	2.58	2.55	2.58	2.55	2.58
< O-Hg-Br, deg.	179.7	177.80749	180.0	177.73	179.73
Energy, a.u.	-184.20497472	-184.205926	-184.203026	-184.205926	-184.20497485
$E_{act,}$ kcal/mol			1.22		

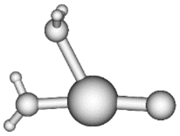
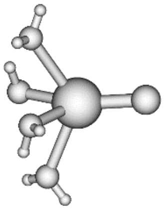
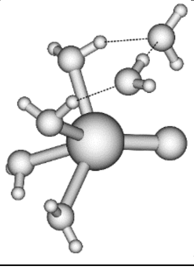
Increasing of number of water molecules faced with the sampling difficulties in Hg-Hal-H_2O molecular system caused by the large number of degree of freedom, which made further thermodynamic calculations undefinable. However, we obtained the DFT-optimized water clusters of mercuric halides (with water molecules, n=1-6), Table 3, which are consistent with other *ab initio* results [3].

Table 3. Optimized (in gas) surface (s) and interior (i) solvation geometries DFT calculated for Cl-, Br-, I- and mercury ions water clusters and for the mercuric halide ion water clusters; n is the number of water molecules.

$[X(H_2O)_n]^-$			
 X=Cl, Br,I	 X=Cl, Br,I	 X=Cl, Br,I	 X=Cl, Br,I
n=1	**n=2(s)**	**n=3(s)**	**n=4(s)**

$[Hg(H_2O)_n]^{++}$			
			
n=1	**n=2(i)**	**n=3(i)**	**n=4(i)**

$[Hg(H_2O)_n X]^+$			
 X=Cl, Br,I	 X=Cl, Br,I	 X=Cl, Br	 X=Cl, Br
n=1	**n=2**	**n=3**	**n=4**

$[Hg(H_2O)_n Cl(H_2O)_n]^+$			
 X=Cl, Br, I	 X=Cl, Br	 X=Cl	
n=1,1	**n=2,2**	**n=3,3**	

We concluded that the standard Transition State Theory is not applicable for evaluation of the Mercury depletion reactions. However, it is feasible to use the structures of hydrated mercuric-halide ion-pairs, Hg-Br, Hg-Cl to obtain the reliable thermodynamic data, from the cation-anion distance distribution over the range of temperatures. This could be done using integrated tempering sampling (ITS) classical MD simulations.

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3. Benjamin C. Shepler et al., J. Phys. Chem. A 2007, 111, 11342-11349.