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Interaction of $As(OH)_3$ -species with semiconducting mineral surface via proximity effect : A computational modeling study for Arsenic removal from ground water

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Abstract : Contamination of Arsenic species in groundwater and surface water is a serious health related issue across many parts of India, especially in Gangetic West Bengal. Arsenic (III) concentration is over 50 micrograms/liter is harmful for human body, and it is a major challenge to remove poisonous arsenic compounds from usable water in large scale across India. Removal of Arsenic (III) species from ground water can be performed by "proximity effect" mechanism. This works via presence of aqueous As (III) species in the "proximity" of semiconducting mineral surface in oxidizing environment via electron transfer-spin transfer mechanism. HF-DFT methods and B3LYP hybrid methods are employed in Gaussian 03 to calculate adsorption energies of $As(OH)_3$ on PbS-galena (100) surface, and results show that the co-adsorption of O_2 and As(III)-species on galena(100) surface occurs via electron exchange spin transfer mechanism. Singlet state of molecular oxygen is more favorable spin state when it remains co-adsorbed on galena along with As(III) species. This study will give insight into possible removal techniques of water soluble As(III) species from usable water.

***IndexTerms* - Hartree-Fock theory, B3LYP, co-adsorption, spin-flip, As(OH)3 , removal, oxidizing**

I. INTRODUCTION

Arsenic and its compounds are used in various medical applications including oncology treatment **[11],** in dermatotherapy **[9]**, and in the treatment of blood and bone marrow cancer like leukaemia **[7]**. Arsenic (III) species are also known to have carcinogenic effect upon exposure to human skin and body **[10]**. Movement of Arsenic (III) compounds in groundwater brings these harmful species in contact with human in many areas in the world **[6]**. As (III) species are more toxic and ore mobile compared to As(V) species. Arsenic (III) hydroxide. $As(OH)_3$ is the most abundant As(III) species present in groundwater and is a highly mobile species. Adsorption of $As(OH)_3$ on semiconducting mineral surfaces and subsequent oxidation to As(V) will lead to removal of mobile As(III) from groundwater. This oxidation of As(III) to As(V) in solution is often kinetically unfavourable.

Proximity effect via long range electron transfer can play a role in simultaneous adsorption of arsenic hydroxide and other oxidizing species such as O_2 or Fe3+ on conducting/semiconducting mineral surfaces **[3,8]**. Proximity effect is a mechanism that involves correlation of chemical reaction of one surface site with another one in neighbouring surface site via spin transfer, spin polarization, electron transfer and charge transfer mechanisms through the semiconducting mineral. This cause mobility an adsorption of a different species on the vicinity of semiconducting mineral surface. It is known that Arsenic species in oxidized state are less toxic than the reduced state, and it is important to understand the redox process involving various arsenic species present in ground water and earth's crust. Mineralogists showed that adsorption of arsenic species in reduced form on galena (PbS) surface involved complicated mechanism and does not occur via regular ligand exchange or via regular bond breaking or bond formation **[5]**. Adsorption percentage of $As(OH)_3$ on PbS surface increases with increasing pH but no inner metallic complex is formed during this process. This arises the question about the mechanism, and confirms that no direct bond formation takes place.

Inspired by many earlier studies **[1,2,4]**, a quantum mechanical approach is taken to study redox couple interaction with mineral surfaces, especially long-range interaction of As(III) species with semiconducting mineral surfaces in presence of oxidizing environment. Later this study is extended beyond semiconducting minerals and applied on minerals that are abundant of Earth's crust.

Proximity Effect: As briefly stated earlier, it is a phenomenon where chemical reactions of neighbouring surface sites promote electron exchange and spin exchange and/or transfer through the semiconducting mineral surface, which in turn cause movement of the other species that are present in the "proximity" of these surface sites. It has been already shown that semiconducting mineral surfaces like galena is oxidized via proximity effect **[3]**. In this paper, same analogy is followed to understand the mechanism of $As(OH)_3$ adsorption on galena (100) surface. It is to be noted that galena (PbS) itself is a reducing entity, but when an oxidizing species like O_2 is adsorbed on PbS surface, the adduct PbS-O_2 helps electron shuttling process through the mineral to the surface site, and converts the mineral as oxidizing agent. In this paper, oxygen atom and oxygen molecules are used as oxidizing agent.

II. METHODS

Adsorption of small molecules like $As(OH)_3$ and O_2 on semiconducting mineral surfaces are studied in this paper. The co-adsorption of 2 separate species on the mineral surface is believed to be occurring via electron transfer-spin transfer process with some redox chemistry involved. All the calculations done in this paper involves all electron quantum mechanistic approach. Calculations on PbS(100) were done on Pb16S16 cluster with 4-4-2 layer set up. Gaussian 03 programme is used to calculate adsorption energies. Both pure Hartree Fock (HF) and hybrid B3LYP (Becke, 3-parameter, Lee–Yang–Parr) functionals are used to compare the adsorption energy values. Hybrid functionals incorporate exact exchange from Hartree Fock and other exchange-correlations energy between electrons from other sources (generally Kohn-Sham orbitals).

Since adsorbates are charged species, and interactions with other charged species in neighbouring unit cell is to be avoided, henceforth a 16x16 galena cluster is chosen, to reduce computational time and edge effects of the mineral surface.

The later are described in **[3]**. The adsorption energy of $As(OH)_3$ on semiconducting PbS cluster in the presence and absence of an oxidizing species [O and O_2] are calculated in this paper.

To determine adsorption energy for an individual species during the co-adsorption process of As(III) species and oxidizing species on PbS surface, following set of equations are used:

ΔE1 = E(surface)+adsorbate-1+adsorbate-2 – [E(surface) + Eadsorbate-1 + Eadsorbate-2] (Equation-1)
ΔE2 = E(surface)+adsorbate-1 - [E(surface) + Eadsorbate-1] (Equation-2)
ΔE3= E(surface)+adsorbate-2 – [E(surface) + Eadsorbate-2] (Equation-3)
E(proximity) = ΔE1 – (ΔE2+ ΔE3) (Equation-4)

Hexagonal -c plane projection of Quartz crystal is studied as a mineral surface, as quartz is the most abundant mineral on earth crust. $As(OH)_3$, being water soluble, can come to contact of quartz in most abundant level, and thus study of interaction of water-soluble arsenic species with quartz will provide great insights in designing possible removal techniques of arsenic species from usable water.

III. RESULTS AND DISCUSSIONS

Results of all electron ab initio calculation of simultaneous adsorption of $As(OH)_3$ and oxidizing species on semiconducting mineral surfaces like galena has been studied and analysed here. Equation 2 and 3 shows calculation of single species on mineral surface in absence of any other oxidizing species on the vicinity of the surface site. Equation 1 calculate co-adsorption of both oxidizing and reducing species present on either side of the semiconducting mineral surfaces, and combining all these 3 equations, proximity effect energy is calculated for a particular set of oxidizing-mineral-reducing species.

Proximity effect on Adsorption of $As(OH)_3$ on PbS (100) surface under the influence of atomic Oxygen [O]

a) Hartree-Fock functionals calculation in Gaussian 03

ΔE1= E PbS(16-16).O.$As(OH)_3$ – [EPbS(16-16) + EO + E$As(OH)_3$] = 19.05 eV
ΔE2 = E PbS(16-16).$As(OH)_3$ - [EPbS(16-16) + E$As(OH)_3$] = 27.76 eV
ΔE3= E PbS(16-16).O – [EPbS(16-16) + EO] = 3.54 eV
E(proximity) = ΔE1 – (ΔE2 + ΔE3) = -12.25 eV

b) B3LYP hybrid functionals calculation in Gaussian 03

ΔE1= E PbS(16-16).O.$As(OH)_3$ – [EPbS(16-16) + EO + E$As(OH)_3$] = -40.0 eV
ΔE2 = E PbS(16-16).$As(OH)_3$ - [EPbS(16-16) + E$As(OH)_3$] = -20.14 eV
ΔE3= E PbS(16-16).O – [EPbS(16-16) + EO] = -3.27 eV
E(proximity) = ΔE1 – (ΔE2 + ΔE3) = -16.6 eV

We have obtained thermodynamically favourable (negative) proximity energy values for both Hartree-Fock and B3LYP-hybrid functional calculations, which mean that oxygen promotes the adsorption of $As(OH)_3$ on galena cluster. B3LYP takes into account electron correlation and exchange, that's why it has more negative value, which indicates stabilization of As(III) adsorption on galena more compared to HF approach. This trend is observed in other calculations as well. HF approach does not incorporate electron exchange via semiconductor, so proximity effect theory only works for B3LYP hybrid model. That is why adsorption energies in HF are all thermodynamically unfavourable or less favourable compared to B3LYP approach, which supports adsorption on mineral surface via proximity effect theory.

Proximity effect on adsorption of $As(OH)_3$ on galena (100) in presence of molecular oxygen [O_2]

Singlet O_2 molecule

a)) Hartree-Fock functionals calculation in Gaussian 03

ΔE1= E PbS(16-16).O_2(s).$As(OH)_3$ – [EPbS(16-16) + EO_2(s) + E$As(OH)_3$] = 30.75 eV
ΔE2 = E PbS(16-16).$As(OH)_3$ - [EPbS(16-16) + E$As(OH)_3$] = 27.76 eV
ΔE3= E PbS(16-16).O_2(t) – [EPbS(16-16) + EO_2(t)] = 4.90 eV
E(proximity) = ΔE1 – (ΔE2 + ΔE3) = -1.91 eV

b) B3LYP hybrid functionals calculation in Gaussian 03

ΔE1= E PbS(16-16).O_2(s).$As(OH)_3$ – [EPbS(16-16) + EO_2(s) + E$As(OH)_3$] = -14.42 eV
ΔE2 = E PbS(16-16).$As(OH)_3$ - [EPbS(16-16) + E$As(OH)_3$] = -20.14 eV
ΔE3= E PbS(16-16).O_2(t) – [EPbS(16-16) + EO_2(t)] = 14.97 eV
E(proximity) = ΔE1 – (ΔE2 + ΔE3) = -9.25 eV

Triplet O_2 molecule
a) Hartree-Fock functional calculations in Gaussian 03
$\Delta E1$= E PbS(16-16).O_2(s).As$(OH)_3$ – [EPbS(16-16) + EO_2(s) + EAs$(OH)_3$] = 27.76 eV
$\Delta E2$ = E PbS(16-16).As$(OH)_3$ - [EPbS(16-16) + EAs$(OH)_3$] = 27.76 eV
$\Delta E3$= E PbS(16-16).O_2(t) – [EPbS(16-16) + EO_2(t)] = 2.72 eV
E(proximity) = $\Delta E1$ – ($\Delta E2$ + $\Delta E3$) = -2.72 eV

b) B3LYP functional calculations in Gaussian 03
$\Delta E1$= E PbS(16-16).O_2(s).As$(OH)_3$ – [EPbS(16-16) + EO_2(s) + EAs$(OH)_3$] = -13.61 eV
$\Delta E2$ = E PbS(16-16).As$(OH)_3$ - [EPbS(16-16) + EAs$(OH)_3$] = -20.14 eV
$\Delta E3$= E PbS(16-16).O_2(t) – [EPbS(16-16) + EO_2(t)] = 6.75 eV
E(proximity) = $\Delta E1$ – ($\Delta E2$ + $\Delta E3$) = -0.22 Ev

Spin flip occurs during co-adsorption of oxygen molecule and As(III) species on galena (100) surface (Figure 1). Oxygen molecule, as it approaches to the galena surface to induce proximity effect on the mineral surface to cause movement of As(III) species, flips the spin and go from triplet state (when away from surface) to singlet state (when close towards the surface

IV. CONCLUSION

It is evident from this study that oxidizing natural environment around semiconducting mineral surfaces like galena induce electron exchange, electron correlation and spin exchange through the mineral which facilitates movement and adsorption of As$(OH)_3$ species on semiconducting mineral surfaces. More thermodynamically favourable result obtained via B3LYP hybrid mode over classical HF-DFT mode emphasizes this fact even more. This hypothesis needs to be proved for other naturally occurring oxidizing species like Fe(III) oxides and hydroxides, and more quartz like abundant mineral of earth's crust can be studied for enhanced proximity effect. Spin states of oxidizing species and oxides are also needed to be studied to see their effect on inducing proximity effect on mineral surfaces.

Figure

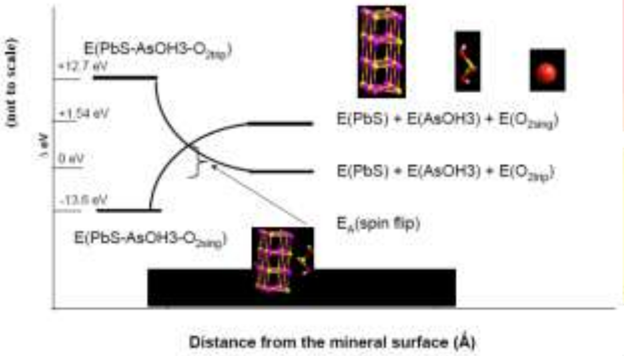

Figure 1: Effect of spin transfer during co-adsorption of As$(OH)_3$ and O_2 molecule on galena (PbS) (100) surface

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