Cs Adsorption and Related Reactive Dynamics in Frayed Edge of Micaceous Minerals

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Supported by T. Yaita's Project (Fukushima)
"Cs Adsorption-Desorption on Clay Minerals for Waste Reduction"

Discussion

T. Yaita, S. Suzuki, T. Ohnuki, T. Ikeda, T. Kitamura (JAEA)
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A. Nakao (Kyoto Pref. Univ.)
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A.Fujiwara, K. Mori (Ryoka)
K. Nishihara, K.Okazaki (Advance)

Outline

1, Objectives of Atomistic Calculation Studies

2, Models and Methods

3, Calculation Results

4, Conclusion

1, Objectives of Atomistic Calculation Studies

Goal of the Project: **Reduction of Huge Amounts of Wasted Soils**

Concepts & Method

Scientific Ideas

Radioisotopes of Cs

Decontamination

Wasted Soils

33 Cups of Tokyo Dome（MOE Test Cal.）

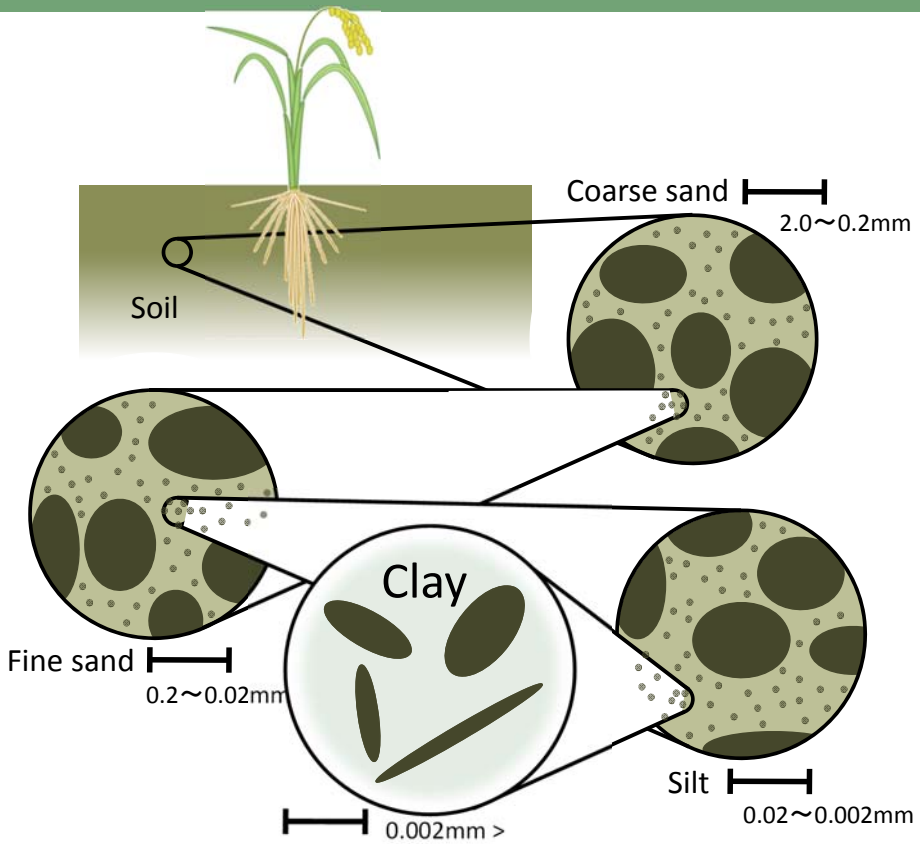
Conventional Insights：

- **Top of Soils (Depth 5～10㎝)**
- **Clay Minerals（Radius＜2μm）**
- **Micaceous Clay ⇒ Irreversible Ads.**

Atomistic Level Mechanism
（Role of Computational Science）

1, Objectives of Atomistic Calculation Studies

Soil：



Cs: Mainly Adsorbed in Clay (＜2μm) (＞90%)

1. Objectives of Atomistic Calculation Studies

Microscale Distribution of Cesium Sorbed to Biotite and Muscovite

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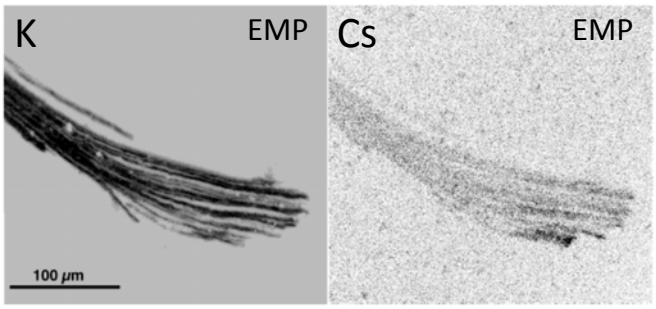
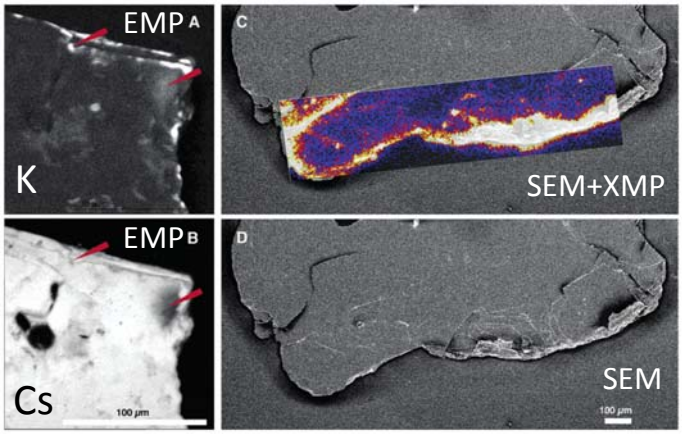
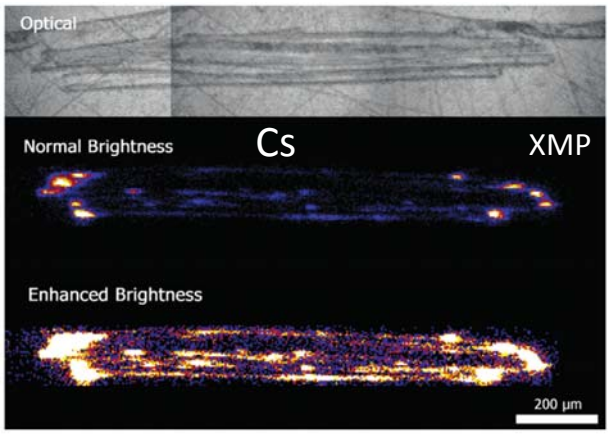
Pacific Northwest National Laboratory, Richland, Washington 99352, PNC-CAT and GSE-CARS, Argonne National Laboratory, Argonne, Illinois 60439

Environ. Sci. Technol. **2004**, *38*, 1017−1023





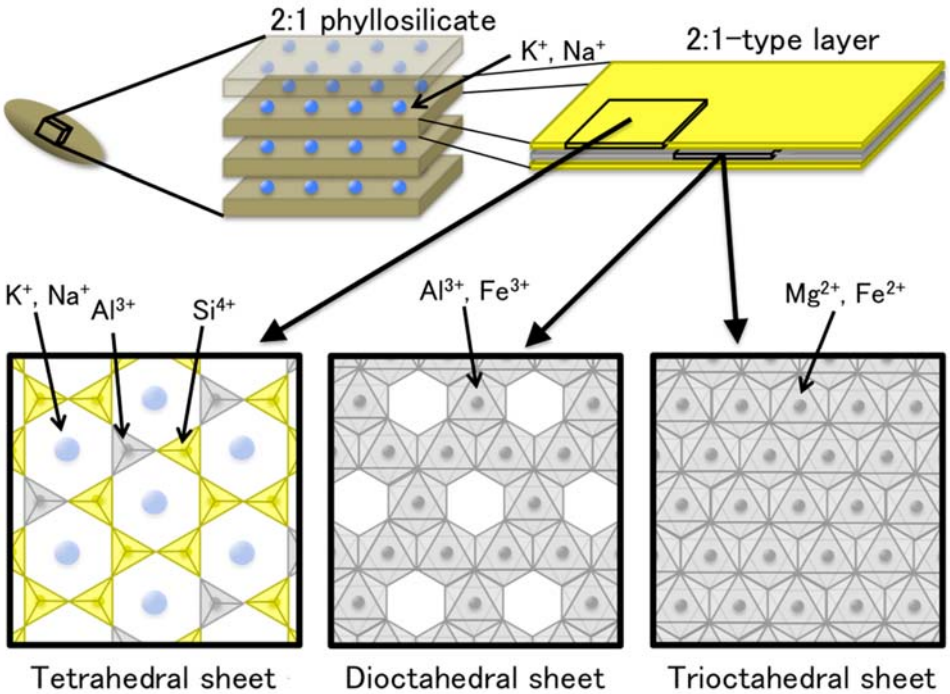


EMP : electron microprobe, SEM: scanning electron microscopy, XMP: X-ray microprobe

Frayed Edges of Micaceous Minerals ⇨ **Strong Affinity ?**

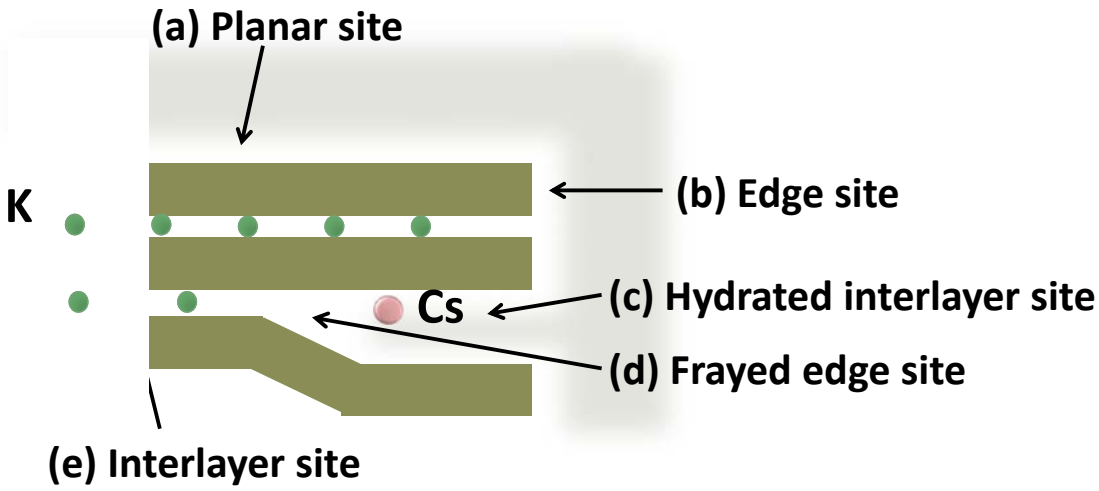
2. Models and Methods

Muscovite :



2. Models and Methods

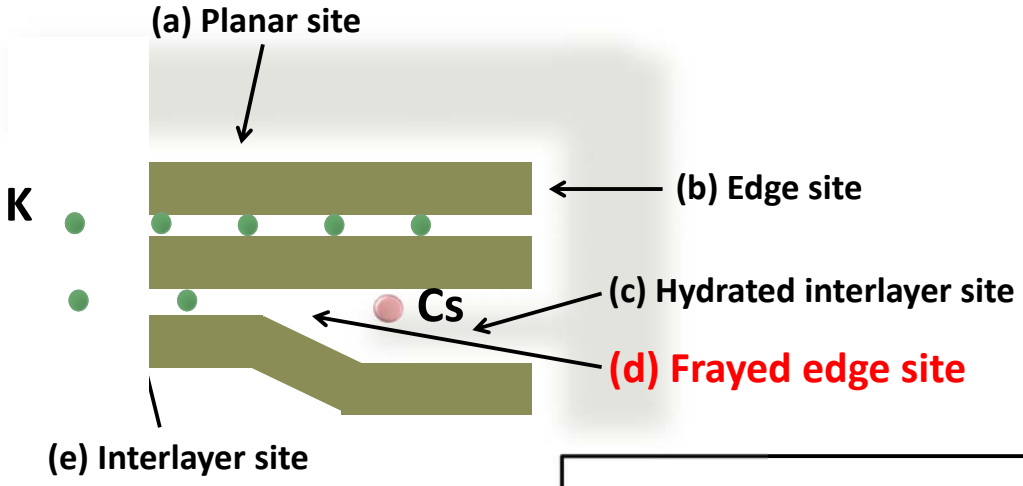
Adsorption Sites (Muscovite):



- Exchangeable Sites: (a)、(b)、(c)
- Irreversible Sites : (d)、(e)

2. Models and Methods

Adsorption Sites:



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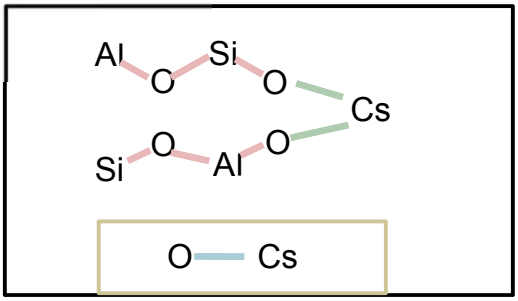
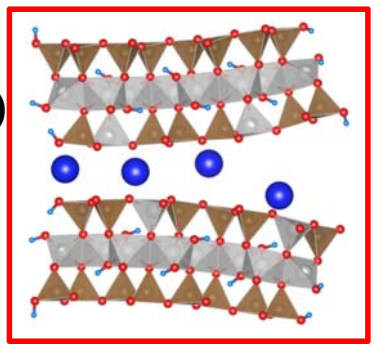


2. Models and Methods

Calculation Methods:

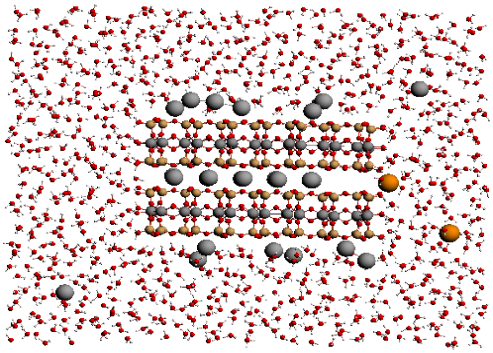
First-Principles Calculation



Target : Electrons (Electronic Structure)

- Interaction between atoms is calculated.
- Small System

Molecular Dynamics



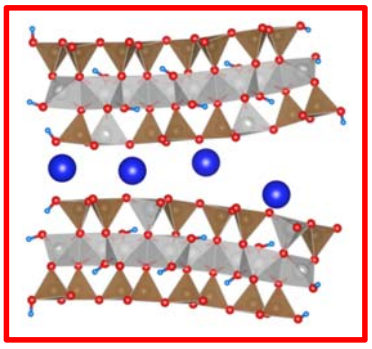
Target : Atoms & Molecules

- interaction between atoms is assumed as force potential
- Large System

2. Models and Methods

Calculation Methods:

First-Principles Calculation



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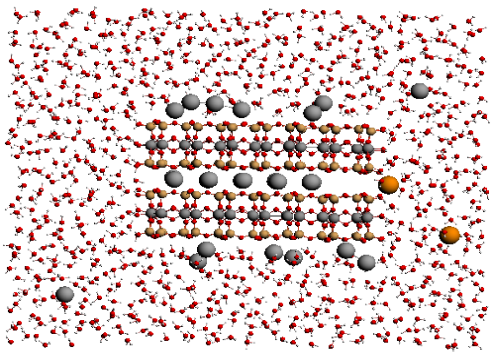
Molecular Dynamics



Target : Atoms & Molecules

- interaction between atoms is assumed as force potential
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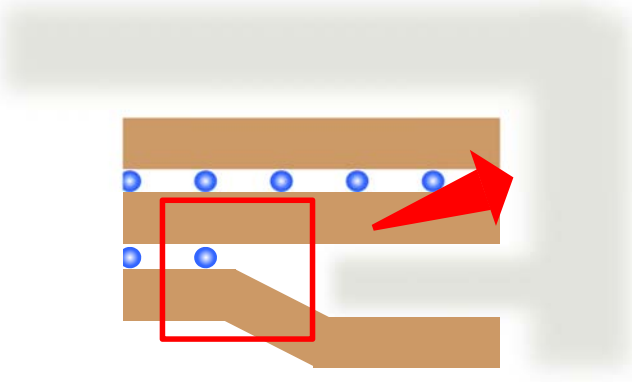
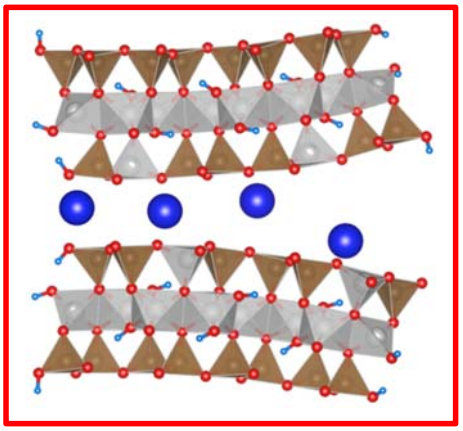
2. Models and Methods

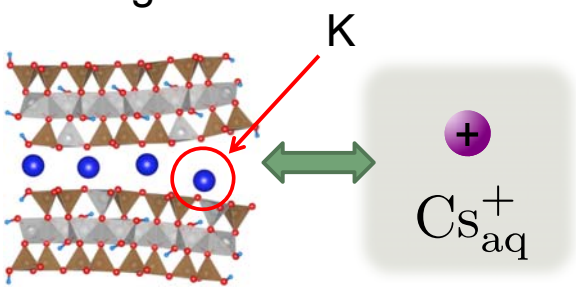
Frayed Edge Modeling:



Minimum System



Ion Exchange



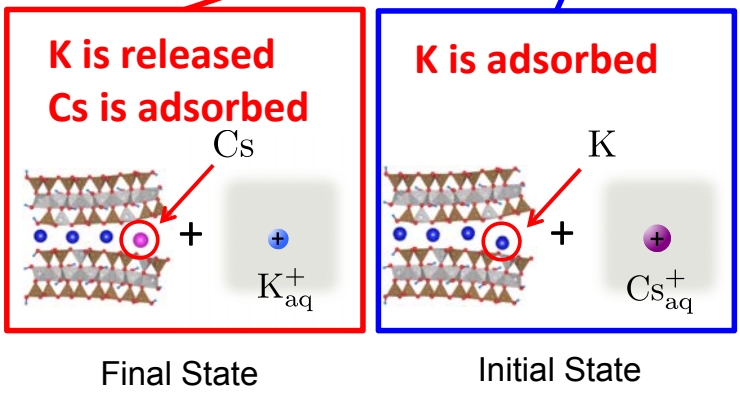
Hydration
Dehydration

Use Experimental Values

3, Calculation Results

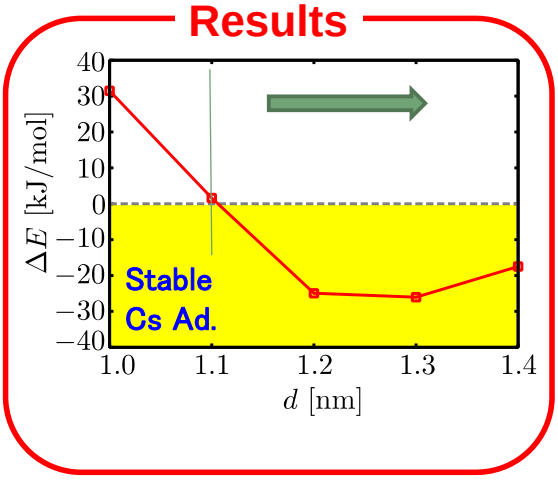
Ion Exchange Energy:

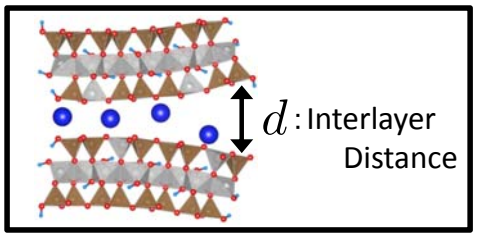
$$\Delta E(d) = E(\mathrm{Cs}, d) - E(\mathrm{K}, d)$$



Final State

Initial State





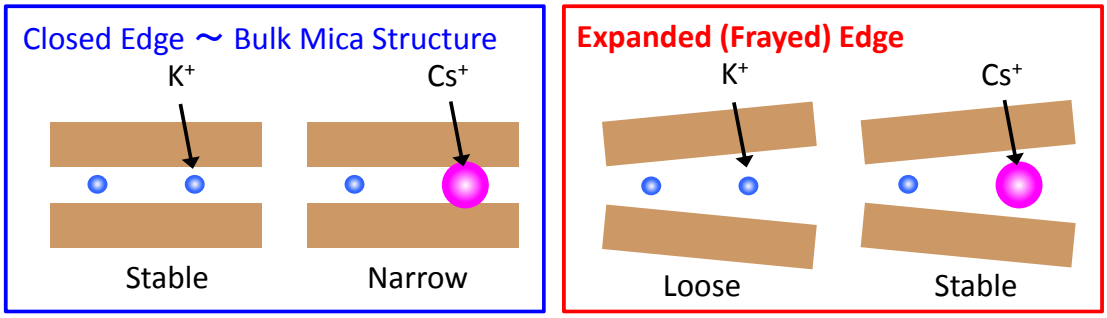
d > 1.1nm

Cs adsorption automatically occurs

ΔE_{max}(d) ~27KJ/mol

3, Calculation Results

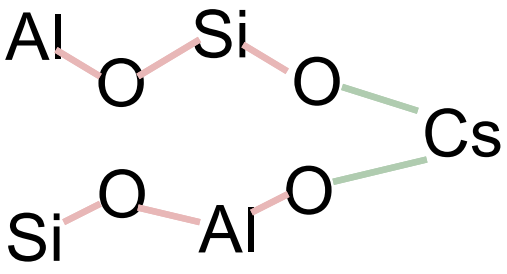
Simple Mechanism: Ion Radius Difference

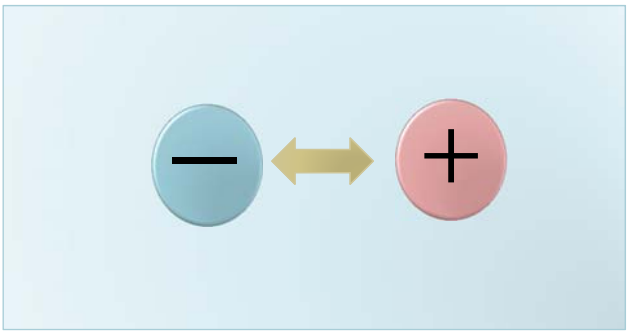


M. Okumura, H. Nakamura, M. Machida,
Journal of the Physical Society of Japan 82, 033802 (2013).

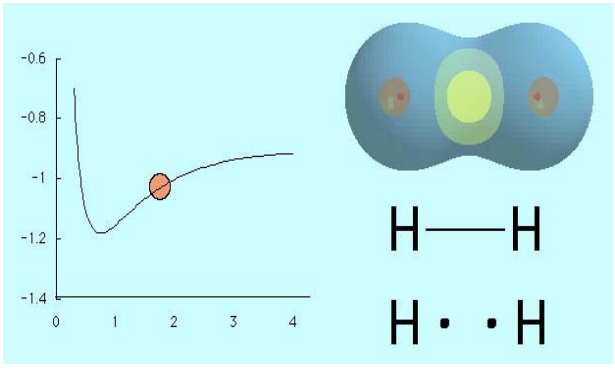
2. Models and Methods

Chemical Bond: Ionic Bond



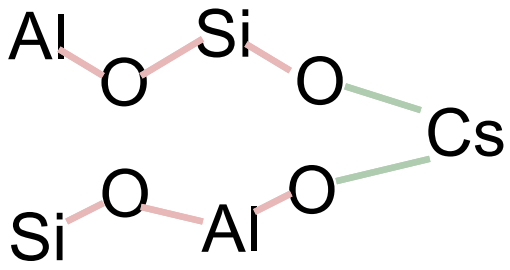


Covalent Bond

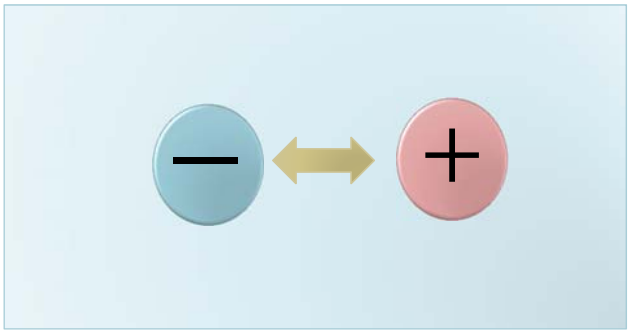


2. Models and Methods

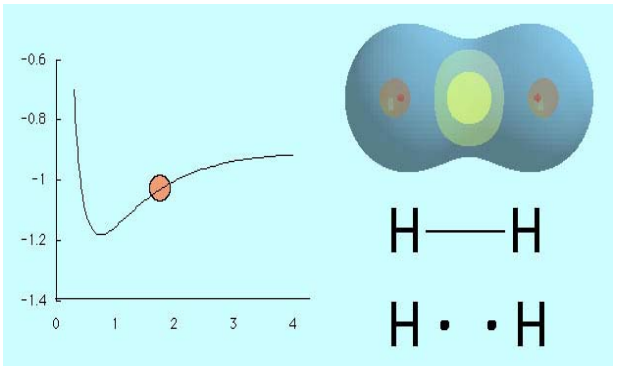
Chemical Bond:



Ionic Bond

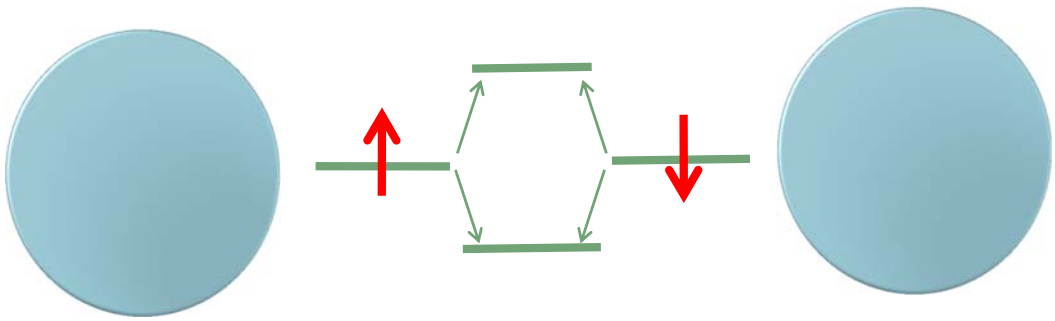


Covalent Bond



2. Models and Methods

Covalent Bond:



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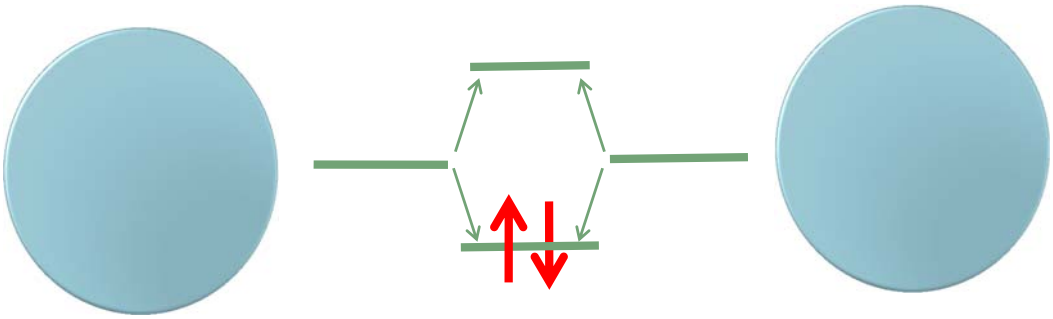

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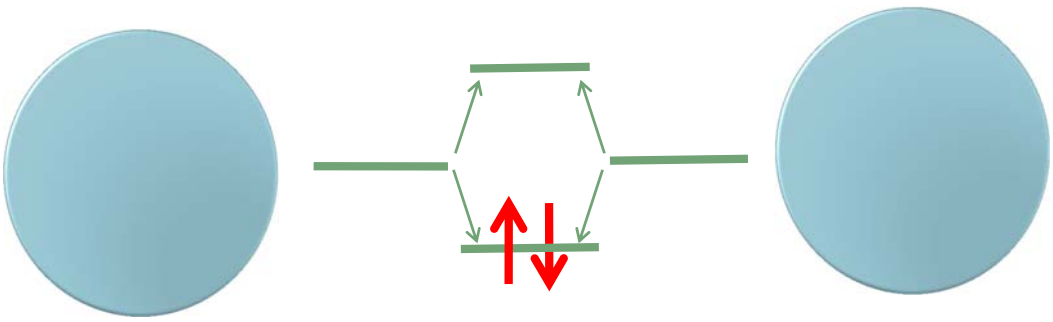
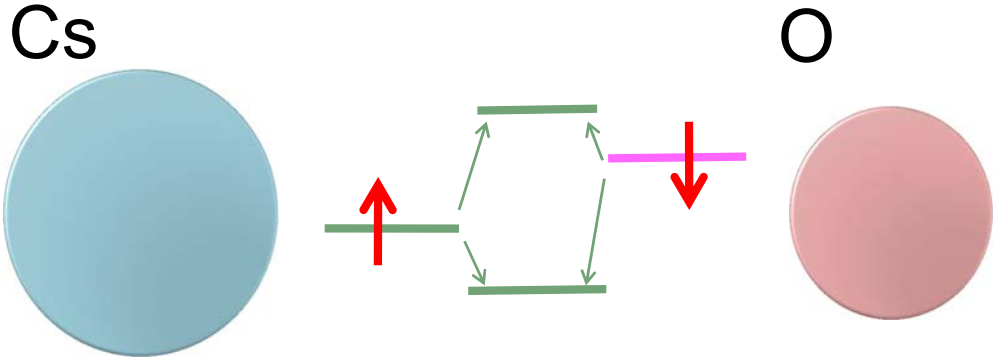
Covalent Bond:

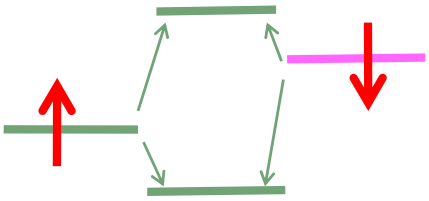




2. Models and Methods

Cs

[Kr].4d^{10}.5s^{2}.5p^{6} 6s^{1}



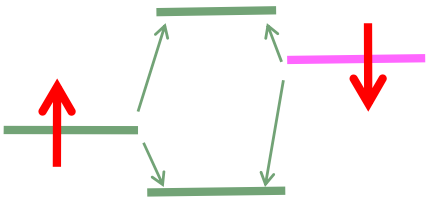
O

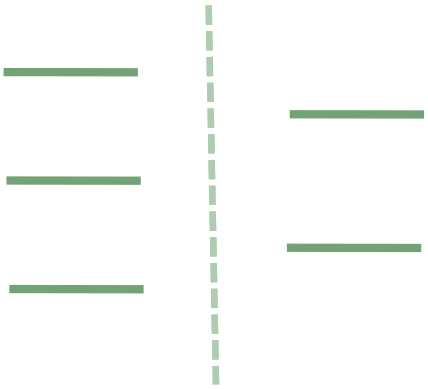
[He].2s^{2}.2p^{4}

2. Models and Methods

Cs

[Kr].4d^{10}.5s^{2}.5p^{6} 6s^{1}





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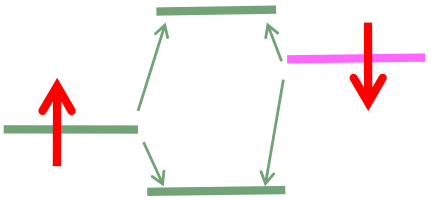
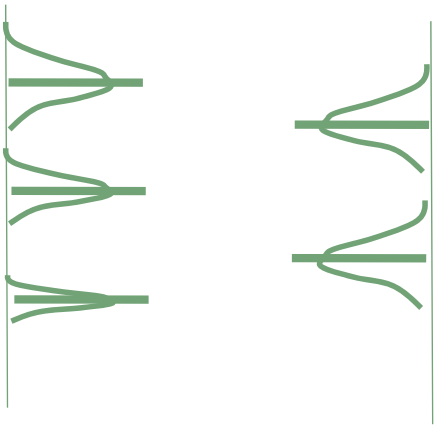
2. Models and Methods

Cs

O





$[Kr].4d^{10}.5s^2.5p^6\,6s^1$

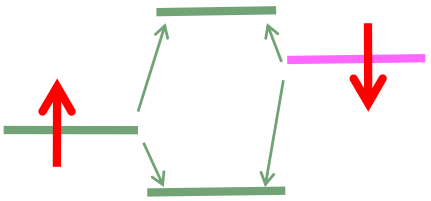
Density of State (E)

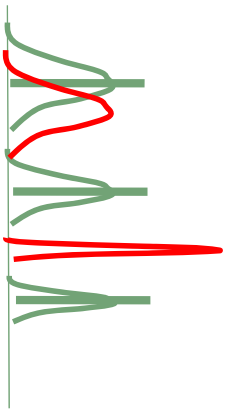
$[He].2s^2.2p^4$

2. Models and Methods

Cs

O





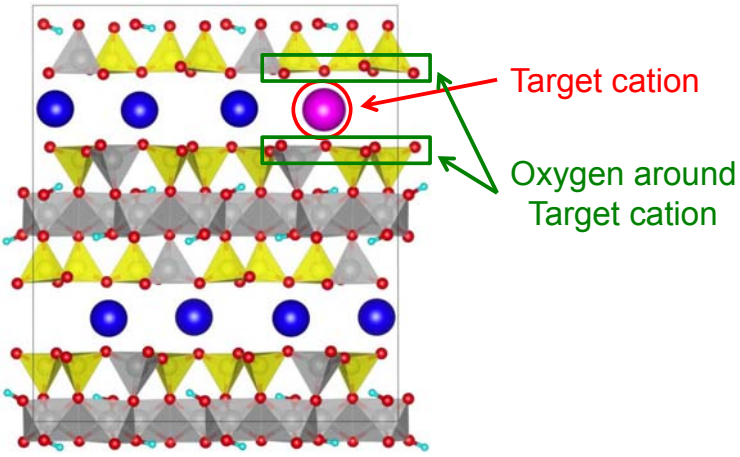
$[Kr].4d^{10}.5s^2.5p^6\,6s^1$

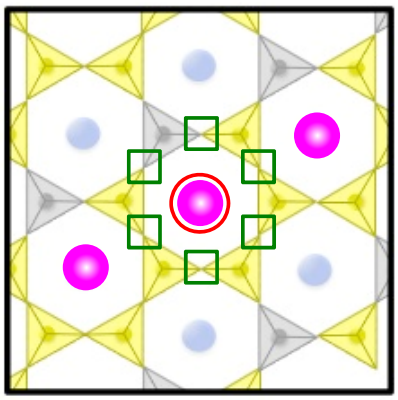
Density of State (E)

$[He].2s^2.2p^4$

3, Calculation Results

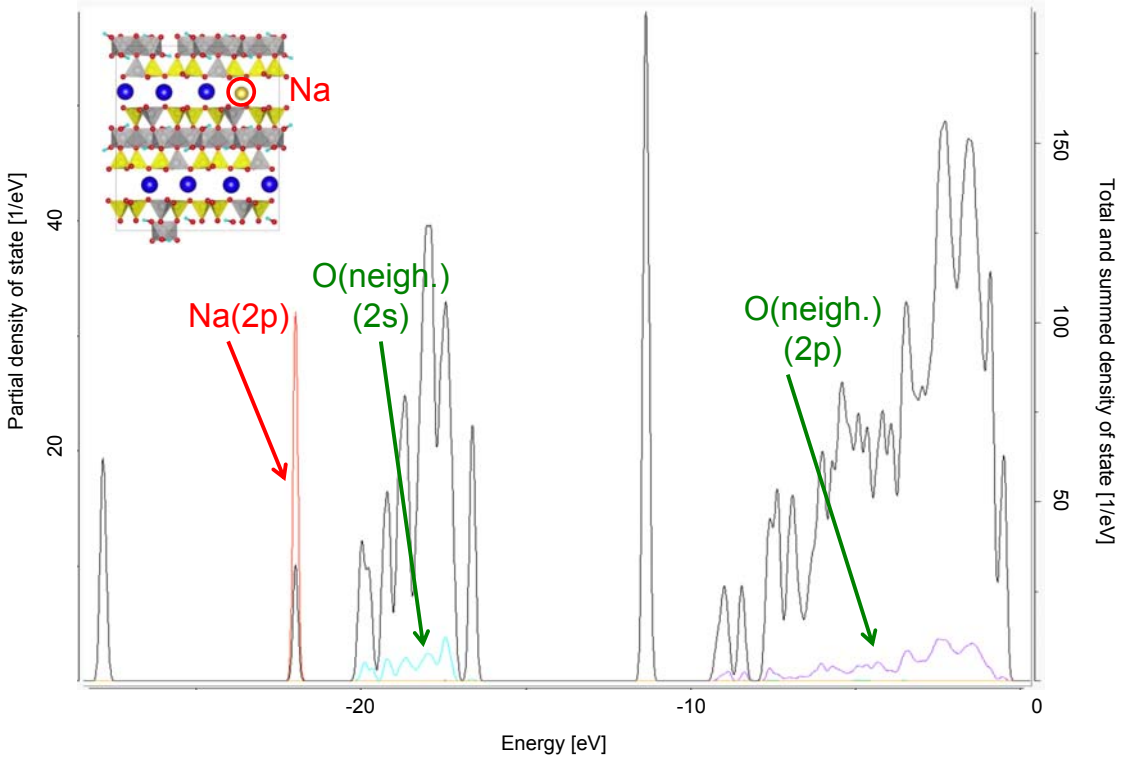
- **Muscovite ⇒ K is replaced with Cs**
- **Results ⇒ Density of States (E)**



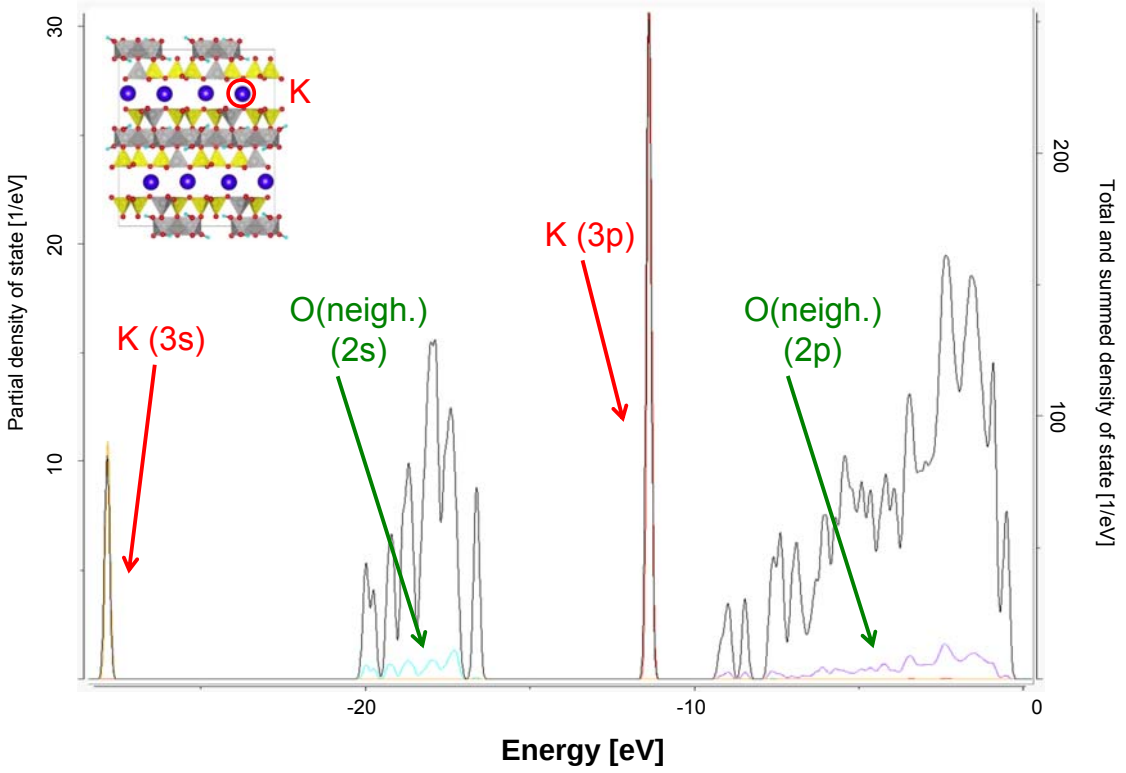


Tetrahedral sheet

3, Calculation Results



3, Calculation Results



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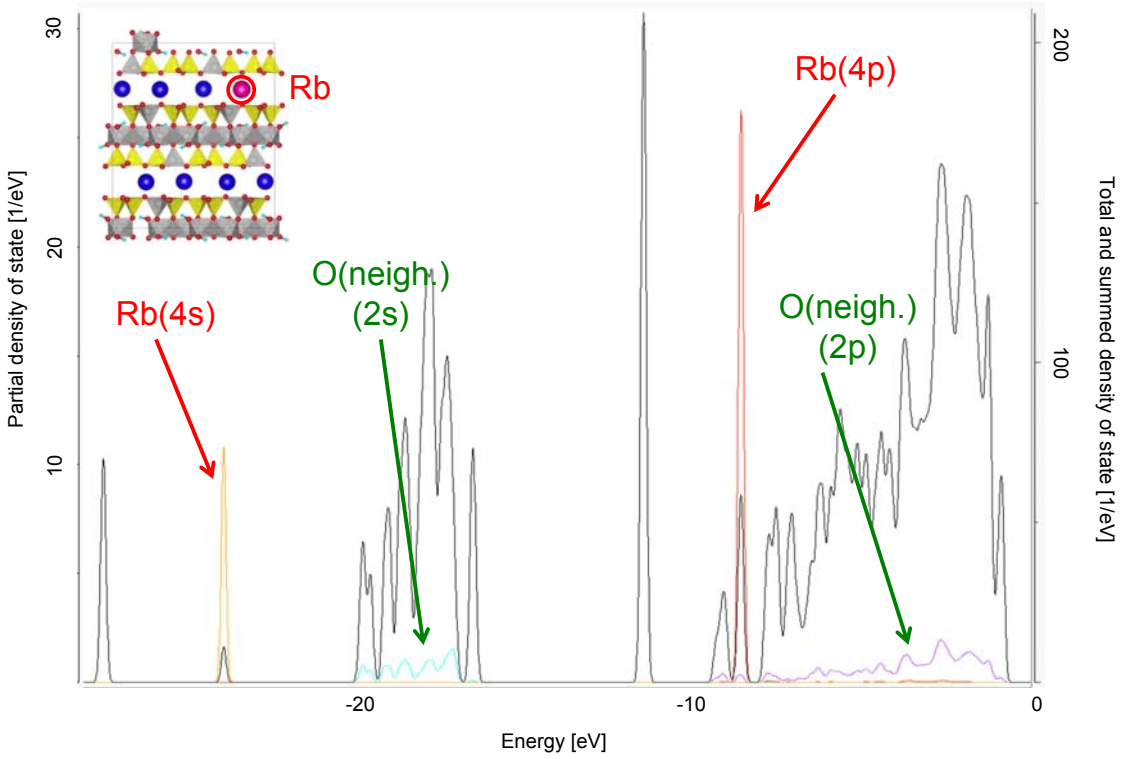

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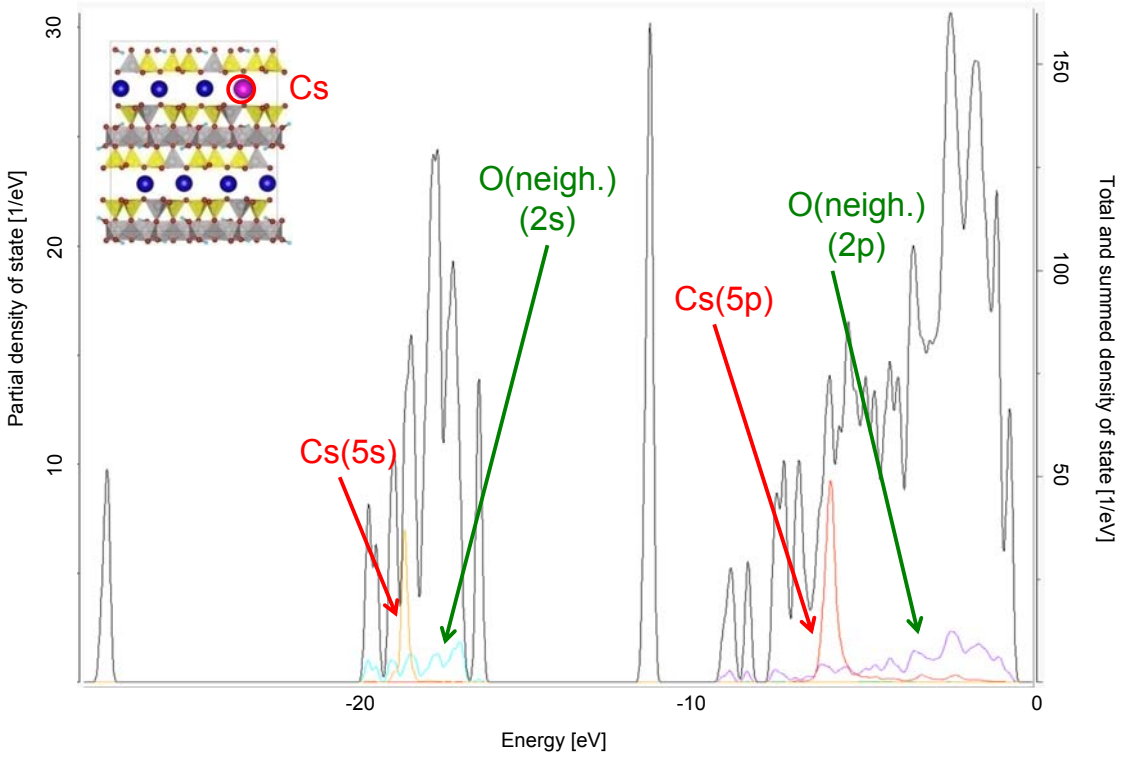

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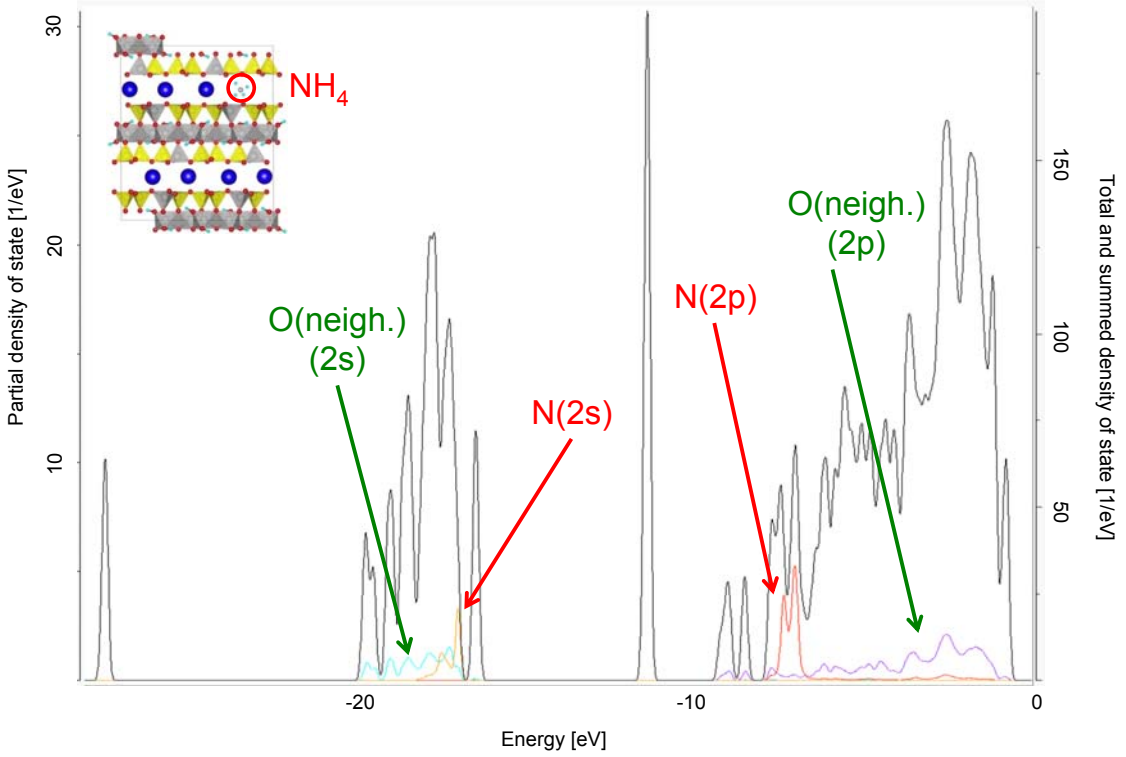


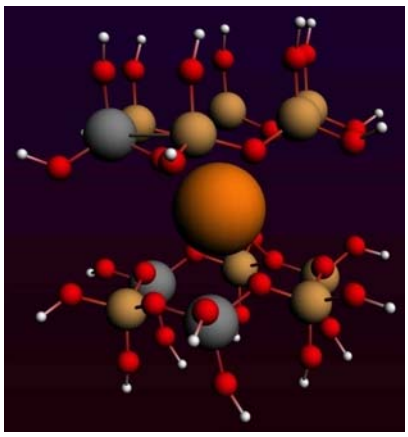
3, Calculation Results

Mechanism for Covalent Bonding:

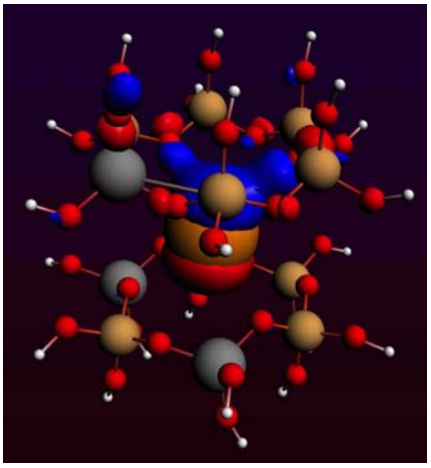
Cs Nuclear Charge is relatively large

Inner orbital is strongly contracted

Cs (5s, 5p) Energy Levels ~ O(2s,2p) levels



Atomic Orbital



Molecular Orbital

4, Conclusion

1, The frayed edge site really shows strong affinity for Cs

The mechanism: **Ion radius difference**

Interlayer distance of the frayed Edge ~ Cs diameter

2, Cs-Oxygen chemical bond is partly covalent.

Cs(5s5p) ~ O(2s2p): Energy levels are overlaped

Ionic+Covalent **Bonding Character is more strong**

Future Tasks:

Cs desorption → Simulation for the Chemical Bond (Cs-O) Cut