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Formation of Volatile Iodine from Cesium Iodide Aerosols: A DFT Study

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***Abstract*—**Periodic DFT calculations were performed to study the chemistry of CsI particles and the possible release of volatile iodine from CsI surfaces for nuclear safety interest. The results show that water adsorbs at low temperature associatively on the (011) surface of CsI, while water desorbs at higher temperatures. On the other hand, removing iodine species from the surface requires oxidizing the surface one time for each removed iodide atom. The activation energy of removing I_2 from the surface in the presence of two OH is 1,2 eV.

***Keywords*—**Aerosols, CsI, reactivity, DFT, water adsorption.

I. Introduction

CESIUM iodide (CsI) aerosols may be produced in important amounts after severe accident in nuclear power reactor [1], [2], and may be found in gaseous phase at low temperature conditions (<1000 K). Kinetic study at low temperature done in the frame of CANDU project showed that CsI is formed rapidly (0.1 sec) by interaction between Cs and I released from the fuel [2]. Gazeous chemistry of CsI has been studied experimentally and theoretically. Sudolská et al. [3] studied the interaction between cesium containing compounds with water molecules. Badawi et al. [4] calculated theoretically thermochemical properties of different cesium containing molecules in the gas phase including CsI. Standard enthalpy of CsI formation at 298 K was estimated to be -156.2 kj.mol^{-1} which is in good agreement with experimental values [5], [6]. However, the literature does not provide a lot of information (theoretical or experimental) about CsI aerosols reactivity. It is then consistent to extend the results obtained on aerosols with similar chemistry such as sodium chloride, NaCl, which is widely studied for atmospheric and marine interest [7], [8]. NaCl solid crystalizes in simple cubic structure [9] [10]. The (100) surface is its most stable surfaces shown by Bruno and coworkers The surface is formed of neutral layers containing alternating Na^+ and Cl^- ions.

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The adsorption of water on stable NaCl surfaces was studied theoretically by Yang et al. [11]. The most stable adsorption mode is a molecular one with water oxygen atom located on the top of Na^+ cation and hydrogen directed toward Cl^-. The adsorption energy is 370 meV. On the other hand, Cabrera et al. [12] examined monolayer adsorption of water on (100) surface of NaCl. Adsorption energy per one water molecule was calculated to be 415 meV which is decomposed in two interaction types: water-water and water-surface interaction. The latter becomes more important when the surface coverage increases.

To the best of our knowledge, the I_2 formation reaction mechanism has never been investigated even if its formation has been demonstrated experimentally. However, some hint may be extrapolated form studies on NaCl. The formation of HCl is only possible in presence of strong acids in the gaseous phase. The formation of Cl_2 is only possible in presence of oxidizing agent such as HNO_3 and water alone is not oxide chloride.

In this paper, we investigate chemical reactivity of CsI crystal and to propose reaction pathway leading to the formation of I_2 from our surface. The paper is organized as follows. Theoretical part and methodology are presented in Section II. Theoretical results are presented in Section III that is divided in three parts: Surface energy to know the most stable ones, water adsorption starting by one water molecule reaching one monolayer, and formation of iodine molecules from the stable surface and reaction mechanism leading to the formation of I_2. Finally, we present conclusions and perspectives.

II. Computational Details

All calculations were done using VASP (Vienna ab initio simulation package) [13], [14] which is based on periodic DFT calculations (density functional theory), using plane waves basis set and projector augmented wave method (PAW) [15]. Exchange-correlation energy was calculated using generalized gradient approximation (GGA) as parameterized by Perdew et al. [16]. Kohn-Sham equations were solved self-consistently until less than 10^{-5} eV difference between two consecutive steps. For surface calculations, the positions of ions in the four top layers were relaxed without any symmetry constraint until the forces between atoms become less than 0.03 eV/Å. The cutoff energy used is 450 eV while kpoint mesh was 3x3x3 and 3x3x1 for bulk and surface calculations, respectively.

Our calculations were done on super cell formed of eight layers of CsI in which 10Å layers of vacuum were added

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between two consecutive layers. The lower part of the super cell was fixed to mimic bulk constraints while the rest kept free to relax to study the surface relaxation and reactivity.

Surface energies were calculated according to:

$$\gamma = (E_{slab} - nE_{bulk})/2A$$

where E_{slab}, E_{bulk} and A are energy of our cell, energy of the bulk unit cell and surface area, respectively. 'n' is the number of CsI units in the super cell.

Adsorption energy was calculated according to:

$$E_{ads} = E_{CsI} + n*E_{(H2O)gas} - E_{(CsI+\ H2O)}$$

where E_{CsI}, $E_{(H2O)gas}$, $E_{(CsI+\ H2O)}$ are the energies of the CsI exposed surface, gas phase water molecule and the whole system, respectively. 'n' is the number of adsorbed water molecules on the surface giving a positive value for exothermic adsorption.

To study the effect of temperature and pressure on the water adsorption, statistical thermodynamic model were used. Gibbs free energy was computer for the adsorbed water molecule on the surface:

$$\Delta_r G = [\Delta E_0 + \Delta E_{zpe(surface+molecule)} - n\sum\mu_{molecule}(T,p)]$$

where ΔE_0 is the electronic energy for the adsorption system at zero K, ΔE_{zpe} is the zero point energy and $n\mu_{molecule}$ is the chemical potential of the gas phase molecules, which can be expressed in:

$$\mu_{molecule}(T, p) = \mu^0(T) + RT\ln [P/P^0]$$

where $\mu^0(T) = \Delta[E_{zpe}(H_2O) + E_{vib}(0 \text{ to } T) + E_{rot} + E_{trans}] + RT - T(S_{vib} + S_{rot} + S_{trans})$.

For minimum energy path and computing the activation energies, Climbing Nudged Elastic Band (Cl-NEB) [17], [18] theory was used to find transition state between reactant and product. The transition state geometry is confirmed by vibrational frequency analysis.

III. Results and Discussion

The CsI crystal is simple cubic with space group Pm3m; the lattice parameter is a=456.67 pm [19] at room temperature. CsI primitive cell contains cesium atom at the corner (0,0,0) and iodine atom in the middle of the cell (a/2)(1,1,1).

A. Surface Structure and Stability

Surface energies were computed for the low indices surfaces: (001), (211), (210), (011) and (111).

Surface energies of (111) and (001) faces. These two faces are polar surfaces which terminate by one type of ions (either Cs^+ or I^-). Surface energies of the relaxed surfaces are 520 and 615 mJ/m^2 for (111) and (001) planes, respectively. For both planes we notice quiet low relative relaxation (~ 5%).

Surface energies of (011), (210) and (211) faces. These surfaces are non-polar ones which terminate by neutral layer (contains both Cs^+ and I^-). Surface energies of the relaxed surfaces are 193, 365 and 417 mJ/m^2 for (011), (210) and (211) planes respectively. The (211) plane shows the highest relative relaxation among others (20%).

From what we have shown, we conclude that (011) plane is the most stable surface of CsI. The stability order in the relaxed and rigid case is (011) < (210) < (211) < (111) < (001), in which surface energy of (011) and (210) planes are the lowest ones. Side and top view of the most stable surface (011) are presented in Fig. 1. Based on these calculations, the CsI nanoparticles will exhibit only the (011) surfaces.

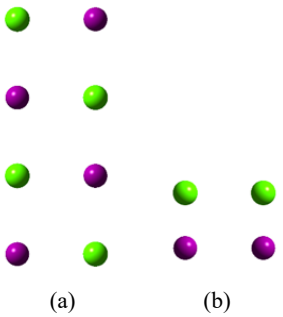


Fig. 1 Side (a) and top (b) view of the relaxed (011) plane (cesium in green and iodine in pink)

B. Adsorption of Water on (011) Stable Surface

Adsorption of One Water Molecule

Adsorption of water on the surface is studied in two modes: associative and dissociative one. For the former case, different orientations of the adsorbed water were studied to test the most stable geometry. While for the dissociative adsorption case, water molecule on surface was dissociated to one H+ and OH- group which interact with I- and Cs+ on the surface, respectively.

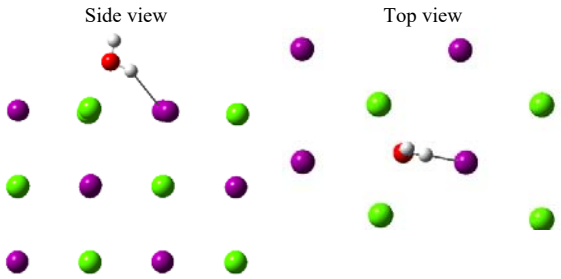


Fig. 2 Side and top views of the associative adsorption of water one (011) stable surface

In the associative case, water molecule was at 3 Å above the surface. Firstly, water molecule was parallel to the surface in which its oxygen atom located on top of Cs^+ to form O-Cs^+ interaction (O-Cs distance about 3.2 Å) while in the second one, the molecule was almost parallel to the surface with H-I interaction (H-I distance about 2.5 Å) (Fig. 2). Calculated adsorption energy of the two geometries was 306 and 510 meV, respectively which means that the major interaction between the water molecule and the surface is via hydrogen-iodide bond. On the other hand, dissociative adsorption was studied in which OH^- group located on top of Cs^+ at 2.8 Å, and

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one proton located at 1.7 Å on top of I^-. The adsorption energy was calculated to be -3.8 eV which is very endothermic suggesting that dissociative adsorption is energitically not possible. Moreover, if the OH group and the proton are near enough, the proton moves toward OH^- to reform water without any barriers

Adsorption of Half and One Monolayer of Water

Water molecules were added successively on the surface reaching coverage of half (Fig. 3 (a)) and one monolayer (Fig. 3 (b)) of water. When more than one water molecule is adsorbed on the surface, two types of interaction play a role in the most stable adsorption geometry: interaction between water molecules (ww) and between water molecule and the surface (ws). The following formulas were used to compute the interaction energies:

$$E_{ww} = n*E_{\text{one water molecule}} - E_{\text{water dimer}}$$
$$E_{ws} = E_{\text{adsorption}} - E_{ww}$$

Starting by half monolayer case, calculated adsorption energy was 2.2 eV in which ww and ws interaction energies are 0.6 and 1.6 eV, respectively. Two of the water molecules interact with the I atoms on the surface by hydrogen bond while other one on the top of Cs interacts by O-Cs bond and the last molecule interacts with its neighboring molecules at distance about 2.8 Å. For the one monolayer coverage, ww interaction increases up to an energy of 2.0eV while the total adsorption energy is 4.7 eV.

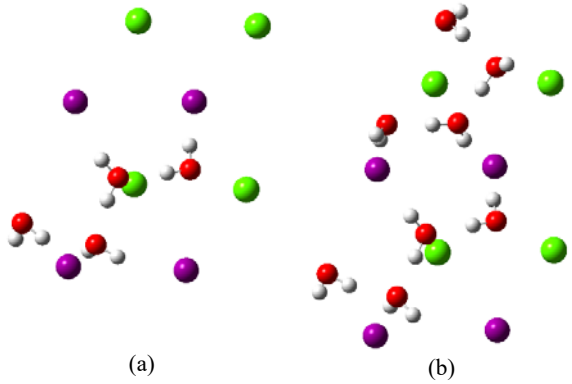


Fig. 3 Half (a) and one mono layer (b) of water on CsI (110) surface

C. Formation of Iodine Species

Many possible iodine species many be formed from the bare surface of CsI crystal (ex. I_2) or by interaction with other species (ex. IOH, IH). Firstly, we tried to release I_2 from bare surface of CsI. The reaction energy was about 4 eV which seems to be not possible. This conclusion is not surprising since removing I_2 will reduce Cs on the surface in which this process is chemically very improbable.

Other reactions were studied by dissociating water molecule on the surface into OH and one proton which interacts with Cs and I, respectively. This dissociation and formation of HI to gas phase requires more than 4 eV which is very endothermic so not probable from thermodynamical view. Forming IOH from surface requires about 2.5 eV which is also very endothermic reaction and not probable.

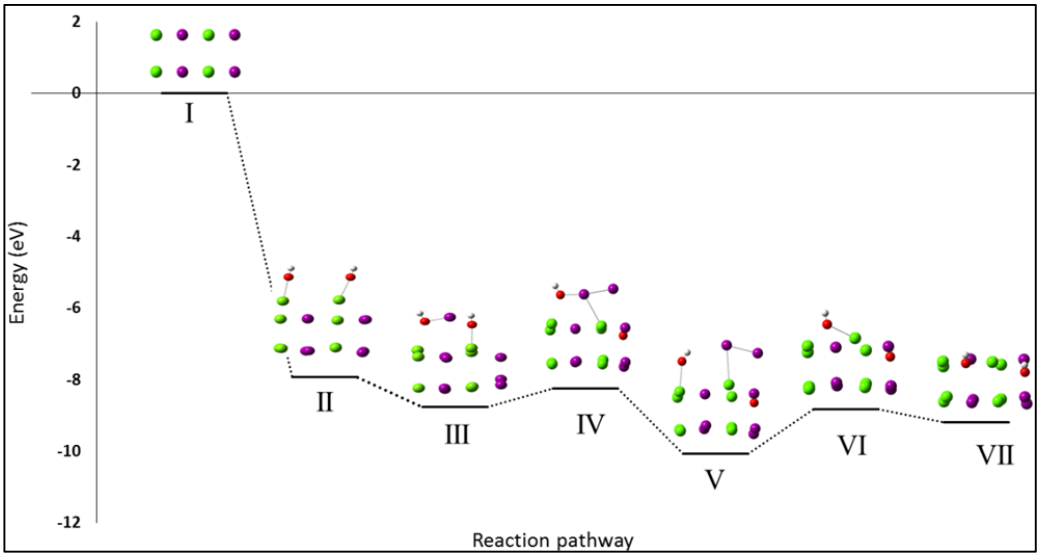


Fig. 4 Reaction pathway leading to the formation of I2 including two OH groups

As shown above, in agreement with results available on NaCl System, removing iodide requires oxidation of the surface. One of the possible oxidants is OH° since it can be produced by water radiolysis which exists in important amounts after a severe accident in nuclear power plant. Reaction pathway was studied including oxidizing the surface by one OH, but again this reaction pathway contains very endothermic steps. We conclude that removing I_2 requires oxidizing surface two times i.e. adding two OH. The reaction pathway followed is shown in Fig. 4. In first step we moved one I from the surface to the top of neighbor Cs (I to II) which is exothermic steps costs about 1 eV. Later, we added two OH on the surface while this steps is very exothermic (ΔE= 8.2eV). In the following steps we formed I_2 on the surface

which interacts with OH (V), this step is endothermic and its calculated activation energy is 0.4 eV. Next step is breaking the bond of I_2 with the OH (VI) which is also endothermic step with activation energy 0.7 eV. Finally, we removed the I2 to gas phase (VII) which is non activated step and moving OH from the surface to the place of removed iodide atoms (VIII).

IV. Conclusion

For nuclear safety interest, computational analysis was performed to study the chemistry of CsI crystal in gas phase especially the possible formation of I_2. Adsorption of water on the surface is an associative one with energy about 0.5 eV and the major interaction is the hydrogen bond between water and iodide on the surface. This adsorption happens at low temperature while at higher ones the water desorbs. Adding more water molecules will weaken the interaction with surface and will enhance interaction between water molecules. Formation of species containing iodine from the surface is not probable in the absence of an oxidant. Removing I_2 to gas phase requires oxidation the surface twice by two OH groups. The activation energy for this process is about 1.2 eV.

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