First-principles investigation of the adsorption of carbon dioxide, carbon mono-oxide and oxygen on $CsPbX_3$ (X= Cl, Br, I) surfaces.

Contact: **arpit.mishra@edf.fr**

A. Mishra[1,2], Ph. Baranek[1,2] and A. Postnikov[3]

1 EDF R&D, Economie, Fonctionnement et Etude des Systèmes Energétiques (EFESE), EDF Lab – Paris Saclay, 7 rue Gaspard Monge, F-91120 Palaiseau, France
2 Institut Photovoltaïque d'Ile de France (IPVF), 30 Route départementale 128, 91120 Palaiseau, France
3 Université of Lorraine, Institut Jean Barriol, Laboratoire de Chimie et Physique – Approche Multi-échelle des Milieux Complexes (LCP-A2MC), 1 Bd Arago, F-57078 Metz, France

Abstract

Organic-Inorganic halide perovskites offer a promising alternative to current Si-based technologies due to their ability to be produced at low cost and high efficiency. However, the major issue with these kind of perovskites is their stability in the presence of humid environment, carbon dioxide, carbon mono-oxide, oxygen, etc which may hinder their practical electroluminescence applications. To investigate this phenomenon, first-principles calculations (using CRYSTAL[1]) are used to study the adsorption of CO_2, CO and O_2 on $CsPbX_3$ (inorganic halide perovskite, where X= Cl, Br, I) surfaces.

Hybrid Functionals

- LDA and GGA functionals underestimate and overestimate the values of the band-gap respectively
- Perdew-Burke-Ernzerhof[2] functionals revised for solids (PBEsol) were incorporated along with certain percentage of Hartree-Fock exchange
- Hybrid functionals predict well the band-gap close to the experimental values

Type of Functional	Band Gap energy (eV)	Latt. Parameter (Å)
B3LYP	2.7032	6.0615
B3PW	2.5764	6.0068
B97H	2.6091	6.0146
PBE0	2.9146	5.9674
PBEsol_0	2.6236	5.8844
PBEsol_XC	1.5036	5.8815
PBE	1.8088	5.9943

Table 1

Table 1: The comparison of Band gap energy and Latt. Parameter calculations are done. The calculations are done using different functionals. All calculations are performed on bulk $CsPbBr_3$

Table 2: The comparison of Band gap energy and Latt. Parameter are made between values obtained form calculations and the experimental values. Band gap energy and Latt. Parameter calculations are done on $CbPbX_3$ (where X= Cl, Br, I) using hybrid functionals. In this case all calculations were performed on the bulk.

Compound	Hamiltonian	Latt. Parameter (Å)	Band gap (eV)
$CsPbCl_3$	$Hybrid_{PBEsol\_XC}$	5.659	2.91
		Exp: 5.660	**Exp: 2.86**
$CsPbBr_3$	$Hybrid_{PBEsol\_XC}$	5.884	2.20
		Exp: 5.883	**Exp: 2.30**
$CsPbI_3$	$Hybrid_{PBEsol\_XC}$	6.195	1.62
		Exp: 6.198	**Exp: 1.73**

Table 2

Adsorption of Molecules

- Depending on the type of termination the formation energy can be calculated as:

$E_{form} = mCsPbX_3 - nCsPbX_3 + PbX_2$ (with CsX termination)

$E_{form} = mCsPbX_3 - nCsPbX_3 + CsX$ (with PbX_2 termination)

11 layer slab was used with CsX (where X= Cl, Br, I) termination

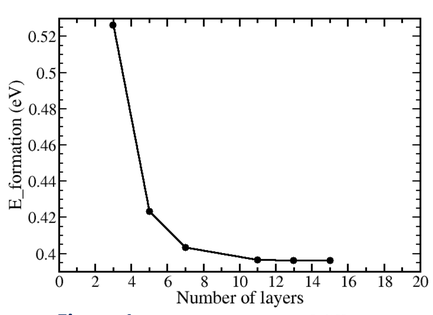


Figure 1: Formation energy of different layers of $CsPbBr_3$ surface with CsBr termination

- A slab model approach was taken into account. A (100) surface with different sizes (2, 4, 8, 9 times the lateral size of the minimal slab unit cell) of Supercell were constructed.
- CO_2, O_2 and CO molecule was introduced at some distance from the surface and the whole system is allowed to relax.
- After the optimization of the geometry, frequency calculations were done to search for the saddle points.

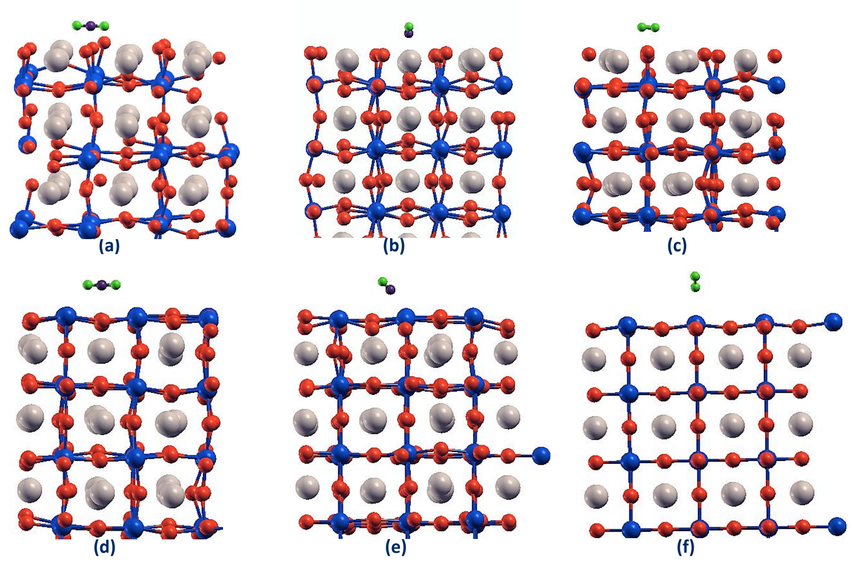
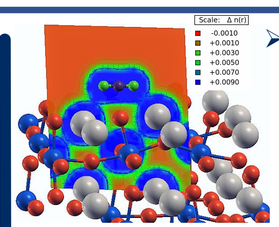


Figure 2: Adsorption of molecule CO_2, CO and O_2 on $CsPbBr_3$ surface. a, b and c has CsBr termination and molecule adsorbed is CO_2, CO and O_2 respectively. d, e and f has $PbBr_2$ termination with adsorbed molecule as CO_2, CO and O_2 respectively. Cs Pb Br C O

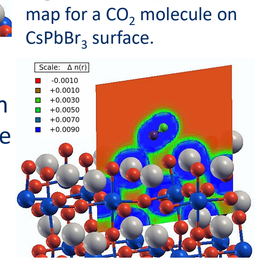


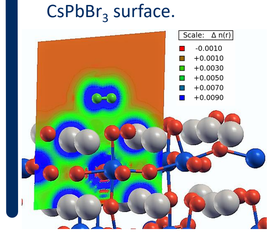
- Some charge transfer can be seen between CO_2 and the surface.

Figure 3: Charge density map for a CO_2 molecule on $CsPbBr_3$ surface.

- Some charge transfer can be seen between CO and the surface.

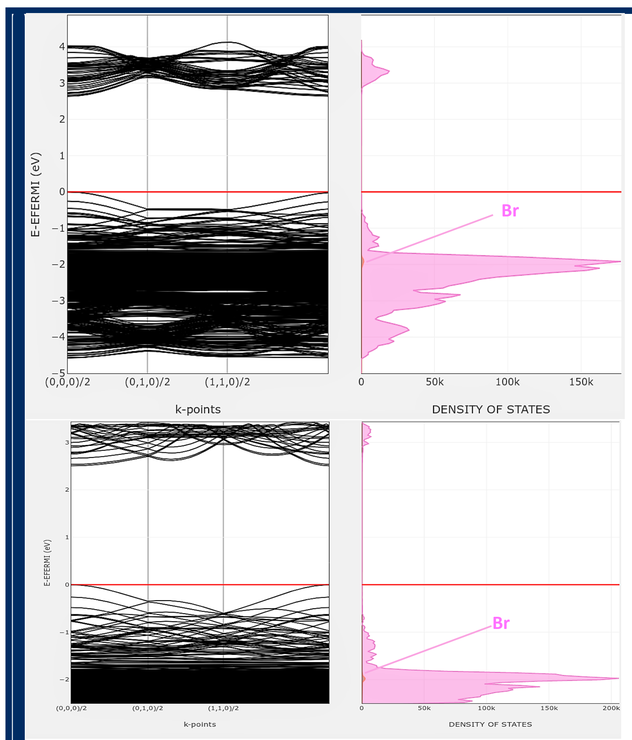
Figure 4: Charge density map for a CO molecule on $CsPbBr_3$ surface.





- No charge transfer can be seen between O_2 and the surface.

Figure 5: Charge density map for a O_2 molecule on $CsPbBr_3$ surface.



- Band gap plays a crucial role in defining the electronic properties
- With the introduction of pollutants the band gap can be affected
- Band gap changes by +13% upon the introduction of CO_2
- CO_2 has no major contribution in the DOS

Figure 6: Band Structure and density of states (DOS) and projection of *sp* orbitals for Cs, Pb, Br, C and O (PDOS) for $CsPbBr_3$ surface (on the left) plotted along the high symmetry points

- Band gap changes by +7% upon the introduction of CO.
- CO has no major contribution in the DOS

Figure 7: Band Structure and density of states (DOS) and projection all atomic orbitals for C, O, Cs, Br (PDOS) for $CsPbBr_3$ surface with CO (on the left) plotted along the high symmetry points.

- Band gap, with the introduction of O_2 changes by +10%.
- The appearance of supplementary states in the band structure could affect the photoluminescence properties

Figure 8: Band Structure and density of states (DOS) and projection of all atomic orbitals for Cs, O, Br, (PDOS) for $CsPbBr_3$ surface with O_2 (on the left) plotted along the high symmetry points.

Type of Molecule	$CsPbCl_3$ CsCl termination Ads En (eV)	$CsPbCl_3$ $PbCl_2$ termination Ads En (eV)	$CsPbBr_3$ CsBr termination Ads En (eV)	$CsPbBr_3$ $PbBr_2$ termination Ads En (eV)	$CsPbI_3$ CsI termination Ads En (eV)	$CsPbI_3$ PbI_2 termination Ads En (eV)
CO_2	-1.281	-0.948	-1.490	-1.288	-3.304	-3.551
CO	-1.274	-1.013	-1.473	-1.372	-2.909	-3.719
O_2	-1.158	-0.039	-1.417	-0.048		-3.589

Table3: Adsorption energy (in eV) comparison of CO_2, CO and O_2 on $CsPbX_3$ (X= Cl, Br, I) surface with both type of termination i.e. CsX and PbX_2. The calculations were performed on the surface supercell. The 11 layer surface was multiplied by $2\sqrt{2}$ in x and y direction to make a surface supercell.

- Adsorption energy is calculated using the formula:
  - $E_{ads} = E_{BulkwithCO_2} - nE_{BulkwithoutCO_2} - E_{CO_2}$
- The negative adsorption energy indicates the adsorption is occurring between the molecule and $CsPbX_3$ surfaces.
- Mulliken population analysis was done to monitor the charge transfer between the molecule and $CsPbX_3$ surface.

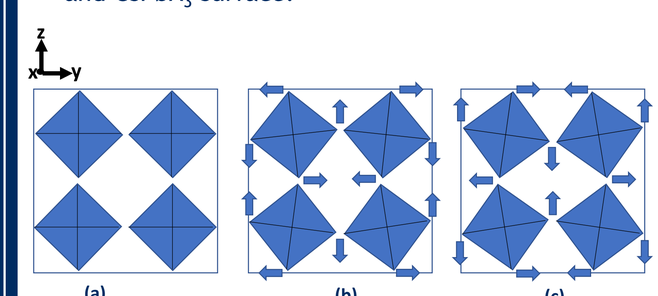


Figure 9: Three phases observed in $CsPbX_3$ surface, cubic (a), orthorhombic (b) and tetragonal (c).In b and c displacement field resulting in the corresponding phase transition. The diagram can be seen perpendicular to the zx plane.

- Octahedral tilting instabilities occurs in inorganic halide perovskites at high temperature[3]
- Octahedral tilting can play a role in affecting the adsorption energy of the pollutants

Conclusions

- Hybrid functionals appear better for the calculations of halide perovskites
- Band gaps are affected upon the introduction of CO_2 CO and O_2
- No electron transfer takes place between CO_2 molecule and $CsPbX_3$ surface.
- CO_2 CO and O_2 physisorb on $CsPbX_3$ surface
- Negative value of adsorption energies for $CsPbI_3$ > $CsPbBr_3$ > $CsPbCl_3$
- CsX termination is more reactive the PbX_2 in case of CsPbCl and CsPbBr

Future Perspectives

- Investigating the effects of same pollutants with organic halide perovskites (MAPI)
- Investigating ionic migration in MAPI using DFT

Acknowledgement

- We would like to thank the ANRT (French national association for research and technology) for its financial support within the CIFRE agreement 2018/0068 (industrial convention for training through research)

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