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The effect of oxygen impurities on a caesium-covered Mo(001) surface: insights from Molecular Dynamics simulations for negative ion sources.

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8th International symposium on Negative Ions, Beams and Sources , Padova Oct. 2-7 2022

Outline

- Molecular Dynamics Simulations of surface processes
- MD simulations for Negative Ion Sources
- Quick overview of obtained results for H^- production
- The role of impurity: Oxygen

Molecular Dynamics Simulations

- Molecular Dynamics simulations consist in the solution of motion equations for the system under study

  - Surface model
  - DFT calculations &Potential Energy Surface
  - Semiclassical Collisional Method

    - *Input*
      - Chemical composition and structure of the heterogeneous system
      - Interaction Potential Function between the species involved in the reaction

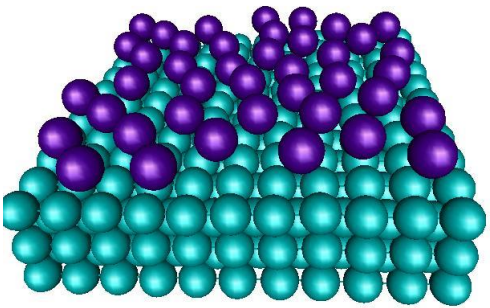
    - *Output*
      - Work function
      - Charge transfer
      - Surface Process probabilities
      - Reaction mechanism
      - Angular distributions
      - Roto-Vibrational distributions

Surface processes

A_{gas}+w		
	A_{gas}+w	*atomic elastic/inelastic scattering*
	A_{ads}+w	*atomic adsorption*
	$A^{\pm}$ +w	*ionic scattering*
$[AB(v_i; j_i)]_{gas}$ + w		
	$[AB(v_f; j_f)]_{gas}$ + w	*molecular elastic/inelastic scattering*
	$[AB(v_f; j_f)]_{gas}$ * w	*molecular adsorption*
	A_{ads}*w +B_{ads}*w	*molecular dissociative adsorption*
	A_{ads}*w + B_{gas}	*atomic adsorption/desorption*
	A_{gas} + B_{gas}+w	*atomic scattering*
A_{gas}+ B_{ads}*w	$[AB(v; j)]_{gas}$ + w	*Eley-Rideal atom recombination*
	$[AB(v; j)]_{ads}$ + w	*molecular adsorption*
	A_{gas}+ B_{ads}*w	*atomic adsorption/desorption*
	A_{ads}*w + B_{gas}	*atomic adsorption/desorption with exchange*
	A_{ads}*w +B_{ads}*w	*atomic adsorption*
	A_{gas} + B_{gas}+w	*atomic scattering*
A_{ads}*w+ B_{ads}*w	$[AB(v; j)]_{gas}$ + w	*Langmuir-Hinshelwood atom recombination*
	$[AB(v; j)]_{ads}$ + w	*molecular adsorption*
	A_{gas}+ B_{ads}*w	*atomic adsorption/desorption*
	A_{gas} + B_{gas}+w	*atomic scattering*

Caesiated Surface Model and Work function determination

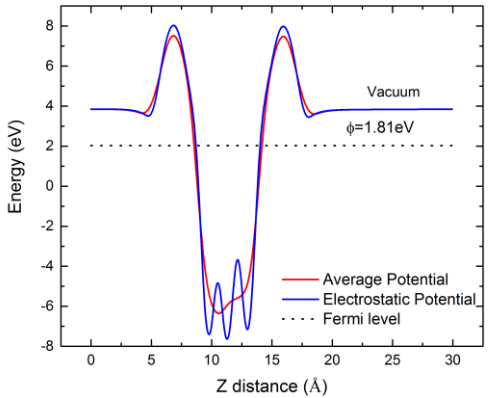
Negative ion generation yield is greatly enhanced by the evaporation of caesium because of the role played by Cs atoms in lowering the work function (ϕ) of metallic surfaces, although investigations on Cs-free sources are reported in the literature.



563 Mo atoms

41 Cs atoms

A. Damone et al. **2015** Plasma Phys. Control. Fusion, 57, 035005



ϕ for pure Mo is 4.36 eV

M.Rutigliano et al. **2017,** Surf. Scie., 664, 194–200

Molecular Dynamics simulations of surface processes involved in negative ion formation

2017
- Determination of H^- yield for caesiated surface
  M. Rutigliano, A. Palma, N. Sanna Surf. Scie. 2017

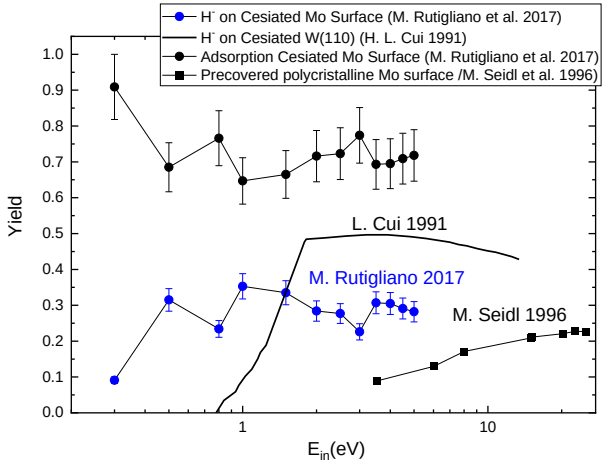
2018
- Determination of D^- yield for caesiated surface
  M. Rutigliano, A. Palma, N. Sanna Plasma Sources Sci. Technol. 2018

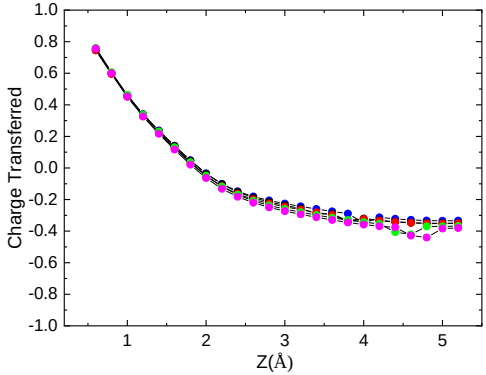
2019-2020
- Investigation on the role of impurities: oxygen
  A. Palma, N. Sanna, M.Rutigliano App. Surf. Sci. 2020

2021
- Investigation of the long-range interactions *via* DFT-D method on impurity interaction
  N. Sanna, M.Rutigliano, A. Palma Chem. Phys. Lett. 2021

2022
- MD simulations for O_2 interacting on caesiated surface
  M. Rutigliano, A. Palma, N. Sanna

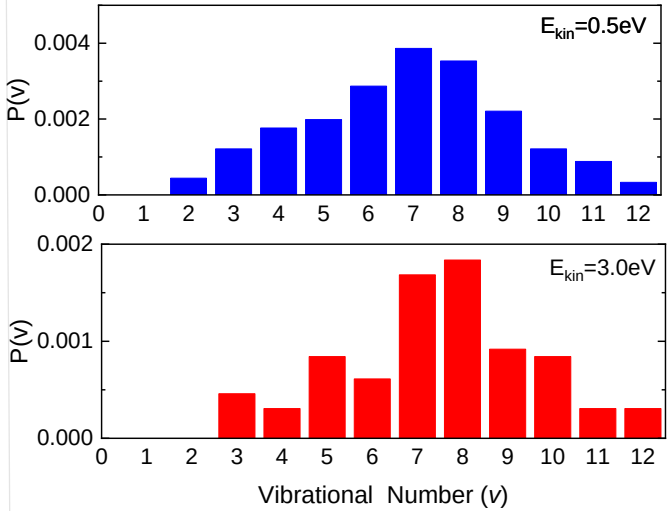
Determination of H^- yield for caesiated surface





M.Rutigliano et al. **2017,** Surf. Scie.,664, 194–200

H^- formation mechanism and isotope effect



Surface *production*

more efficient than

Volume *production*

Isotopic effect is non-observed:

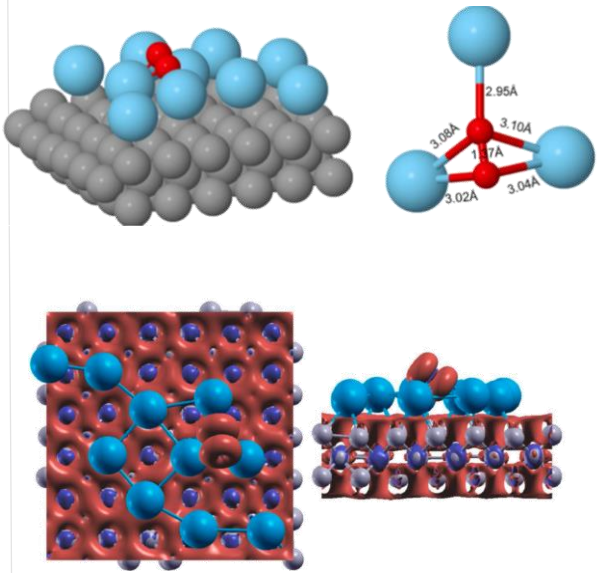
D behaves substantially like H

H atoms recombine on MoCs in v>5 → Dissociative attachement → Volume production

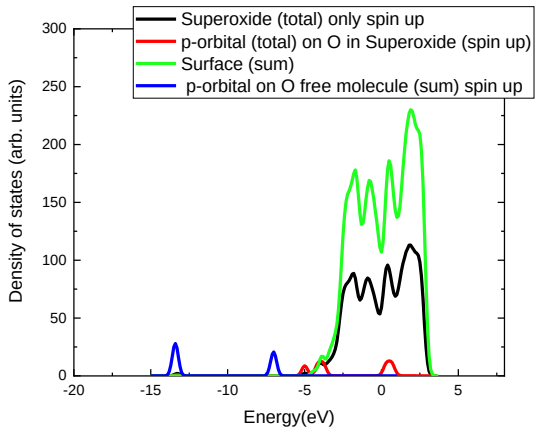
M. Rutigliano et al. **2018** Plasma Sources Sci. Technol. 27 075014
M. Rutigliano et al. **2018** Plasma Sources Sci. Technol. 27 115006

Investigation on the role of impurities: oxygen

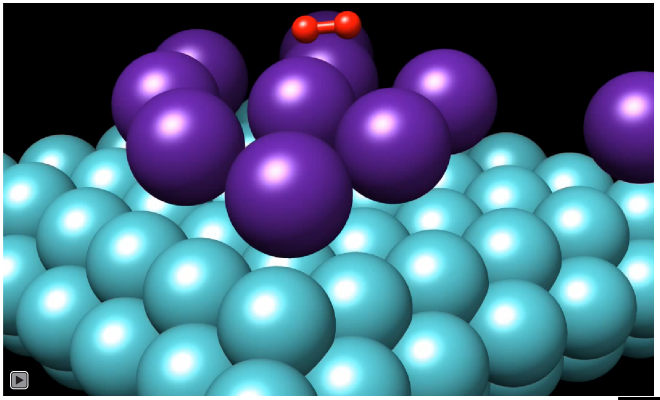
- By *ab initio* DFT calculations we have foreseen the formation of a stable caesium oxide structure on the surface. From an accurate multi-property analysis, we were able to claim that its geometrical and electronic features strongly resemble those typical of a CsO_2 superoxide compound.

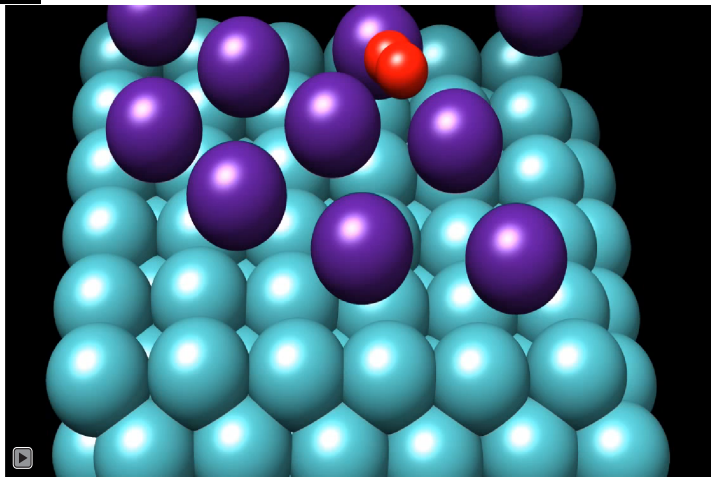


3D Electron Density map The red volume represents the excess of charge (positive value) while the blue one the depletion charge (negative value).



A. Palma et al., **2020**, Appl. Surf. Sci., 534, 147579

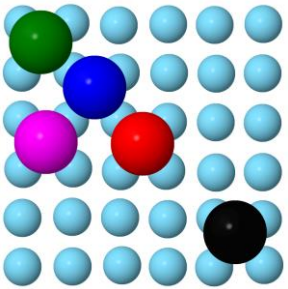


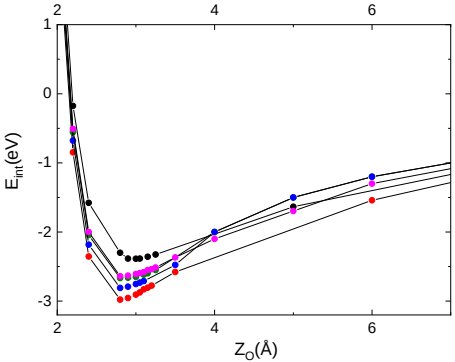


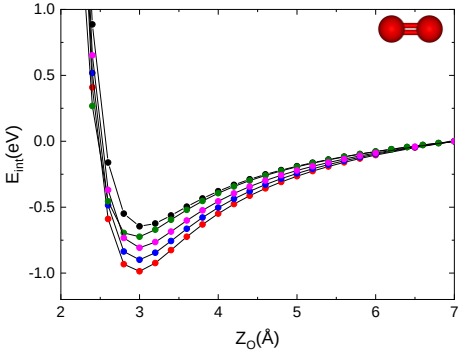
Effect for NIS

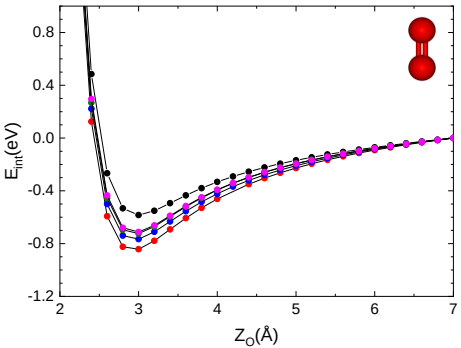
- Formation of superoxide-like CsO_2 compound on the caesiated surface can
  - Influence strongly the caesium work-function
  - Produce detrimental effects on:
    - negative ion yield
    - grid efficiency due to poisoning of the caesium component
  - Induce Cs consumption

Interaction Potentials for O and O_2

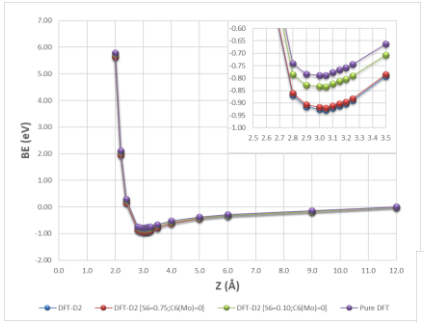


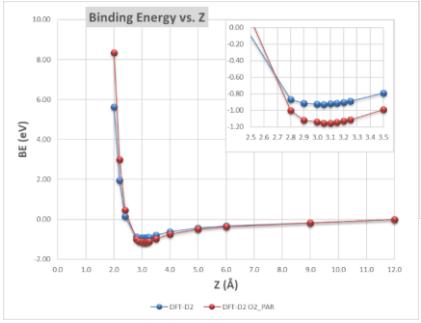


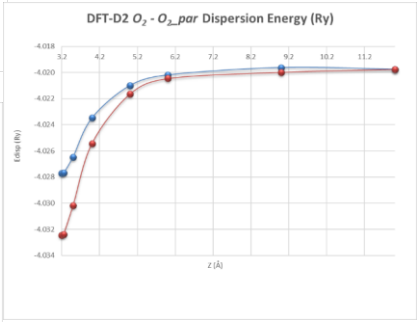


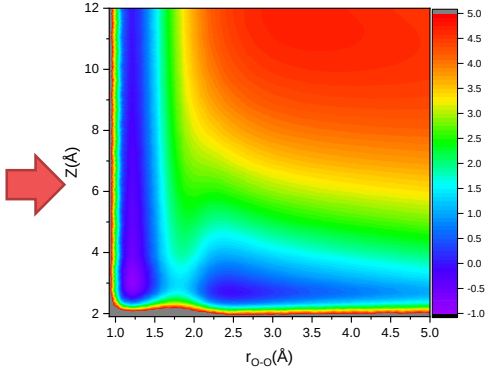


Investigation on the long range interaction *via* DFT-D methods on impurity interaction









N. Sanna et al., **2021**, Chem. Phys. Lett. 773, 138603

MD simulations for O,O_2 interacting on caesiated surface model

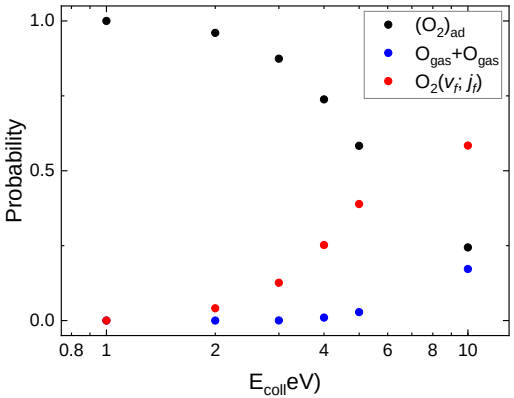
Case I. O interaction

The results of MD simulations for oxygen atoms colliding with kinetic energy (E_{kin}) up to 5.0 eV highlighted the **oxidation** of the exposed **caesium** topmost **layer**.
The totality of the trajectories ends with the adsorption of the oxygen atom on the surface.
From the trajectory analysis, it emerges that the impinging atom, independently on the impact site, is accelerated toward the surface where it remains trapped in the adsorption well.
The process seems to be independent of the kinetic energy of impinging oxygen atom and, therefore, only attributable to the strong chemical interaction between the species.

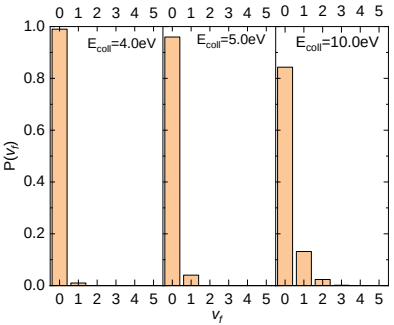
M.Rutigliano et al. **2022** work in preparation

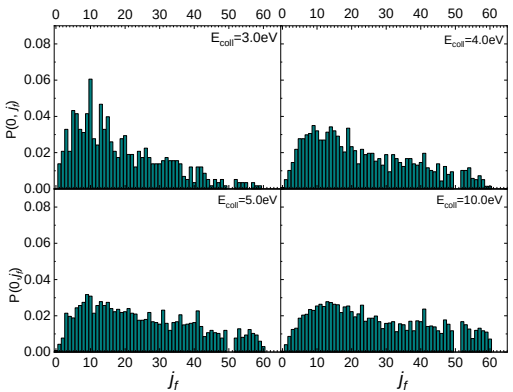
Case II. $O_2(0,1)$ interaction

$O_2(0,1)$ + MoCs ----> ″products″



$O_2(0,1)$ + MoCs ----> $O_2(v_f j_f)$





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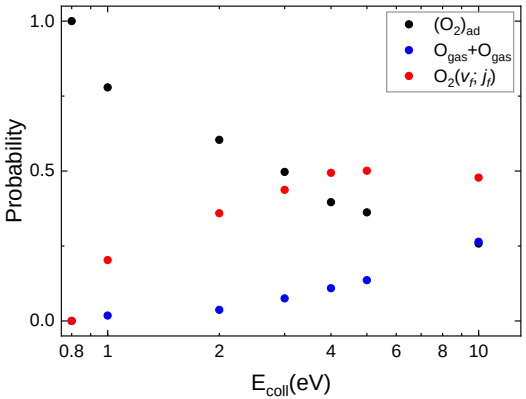
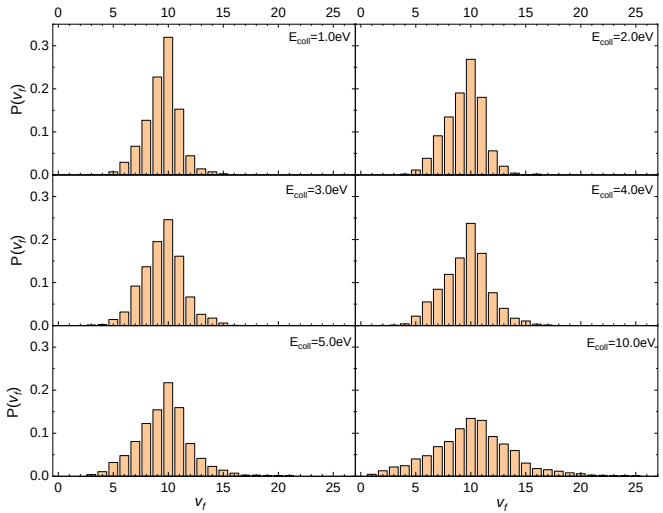
Case III. $O_2(10,1)$ interaction

$O_2(10,1)$ + MoCs ----> ″products″



$O_2(10,1)$ + MoCs ----> $O_2(v_f,j_f)$



M.Rutigliano et al. **2022** work in preparation

Implications for negative ion production

- Molecules inelastically scattered rotationally excited but colder translationally.
- Interaction of these molecules with plasma species distributes this energy through collisions with the possibility of making accessible processes that otherwise would not be.
- Cs layer oxidation for atomic or molecular oxygen adsorption imply a charge flux toward the Cs top layer modifying its properties and efficiency.
- Detrimental effect of molecular oxygen interaction can be attenuated if molecules are vibrationally excited suggesting that molecular internal energy transfer can be a candidate as a “tool” to limit oxide formation and preserve the functionality of the caesiated material grid.

Take-home message

- Atomistic simulations can help to better understand and foresee micro-/macroscopic processes occurring at the plasma-wall interface
- Obtained results are based on structural and chemical properties of wall material as well as on the impinging particle energy
- Atomic and molecular collisional data can be useful for kinetic models
- Determined values are in agreement with the same quantities, determined experimentally or by other types of calculation, reported in the literature

Thank You for Your Kindly Attention!