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Oxygen Vacancies as Archetypal Intrinsic Defects in WO_3

Introduction

Crucial to selecting efficient photoabsorbers for water splitting is the thorough understanding of the **electronic properties of their surfaces and interfaces** with water and electrolytes, as well as of the effects of **intrinsic defects**. Tungsten trioxide (WO_3) is one promising photoabsorber [1,2,3,4]. By means of first-principles simulations, we investigate a realistic model of the experimentally most stable surface of WO_3 , which presents a **high concentration of oxygen vacancies**. We study the presence of **competing localized and delocalized charge configurations at finite temperature** and their influence on the properties of the material.

- [1] Q. Mi, Y. Ping, Y. Li, B. Cao, B.S. Brunschwig, P.G. Khalifah, G. Galli, H.B. Gray, and N.S. Lewis, *J. Am. Chem. Soc.* **134**, 18318 (2012)
- [2] Y. Ping, Y. Li, F. Gygi, and G. Galli, *Chem. Mater.* **24**, 4552 (2012)
- [3] Y. Ping, D. Rocca, and G. Galli, *Phys. Rev. B* **87**, 165203 (2013)
- [4] Y. Ping and G. Galli, *J. Phys. Chem. C* **118**, 6019 (2014)

Computational Approach

Our simulations are based on density functional theory (DFT) and employ **dielectric-dependent hybrid (DDH) functionals** [1,2] developed in Galli group. They explicitly include the **effect of spin** to explore both closed and open shell ground states. To study the effect of finite temperature on the electronic and charge transport properties, **molecular dynamics (MD) simulations** have been performed, using the Qbox code [3]. Electronic structure calculations beyond DFT, at the G_0W_0 level, are performed with the WEST code [4].

- [1] J.H. Skone, M. Govoni, and G. Galli, *Phys. Rev. B* **89**, 195112 (2014)
- [2] J.H. Skone, M. Govoni, and G. Galli, *Phys. Rev. B* **93**, 235106 (2016)

- [3] F. Gygi, *IBM J. Res. & Dev.* **52**, 137 (2008)
- [4] M. Govoni and G. Galli, *JCTC* **11**, 2680 (2015)

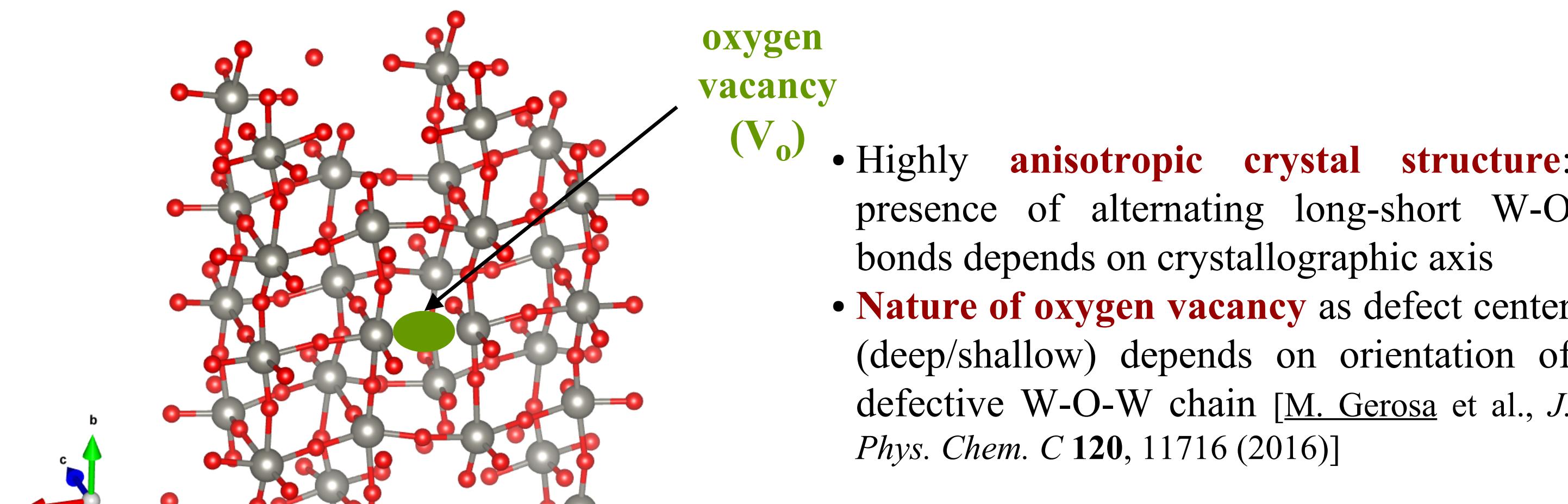
Qbox
First-Principles Molecular Dynamics

<http://qboxcode.org>

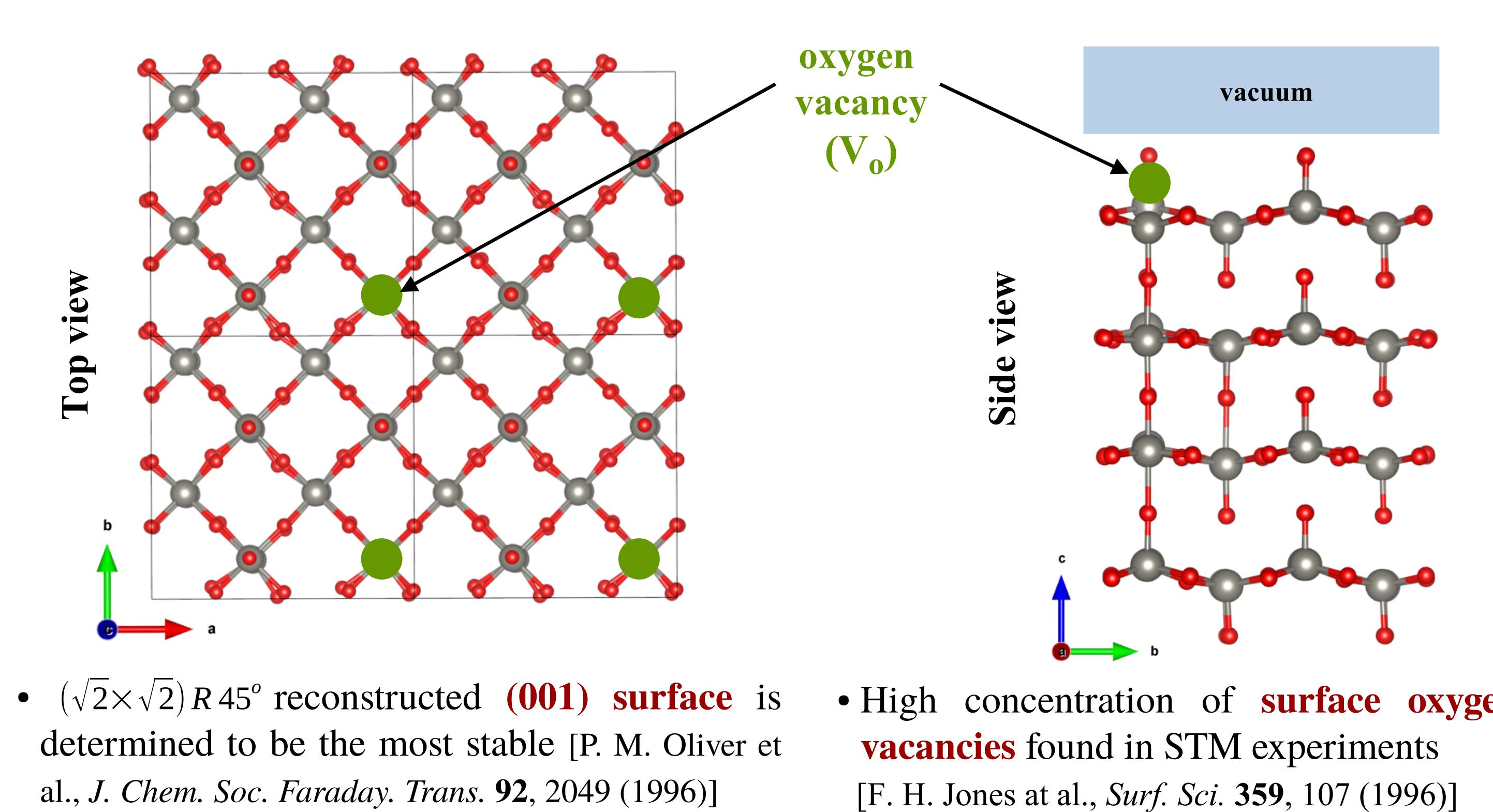
WEST!

<http://www.west-code.org/>

Bulk: Monoclinic Structure



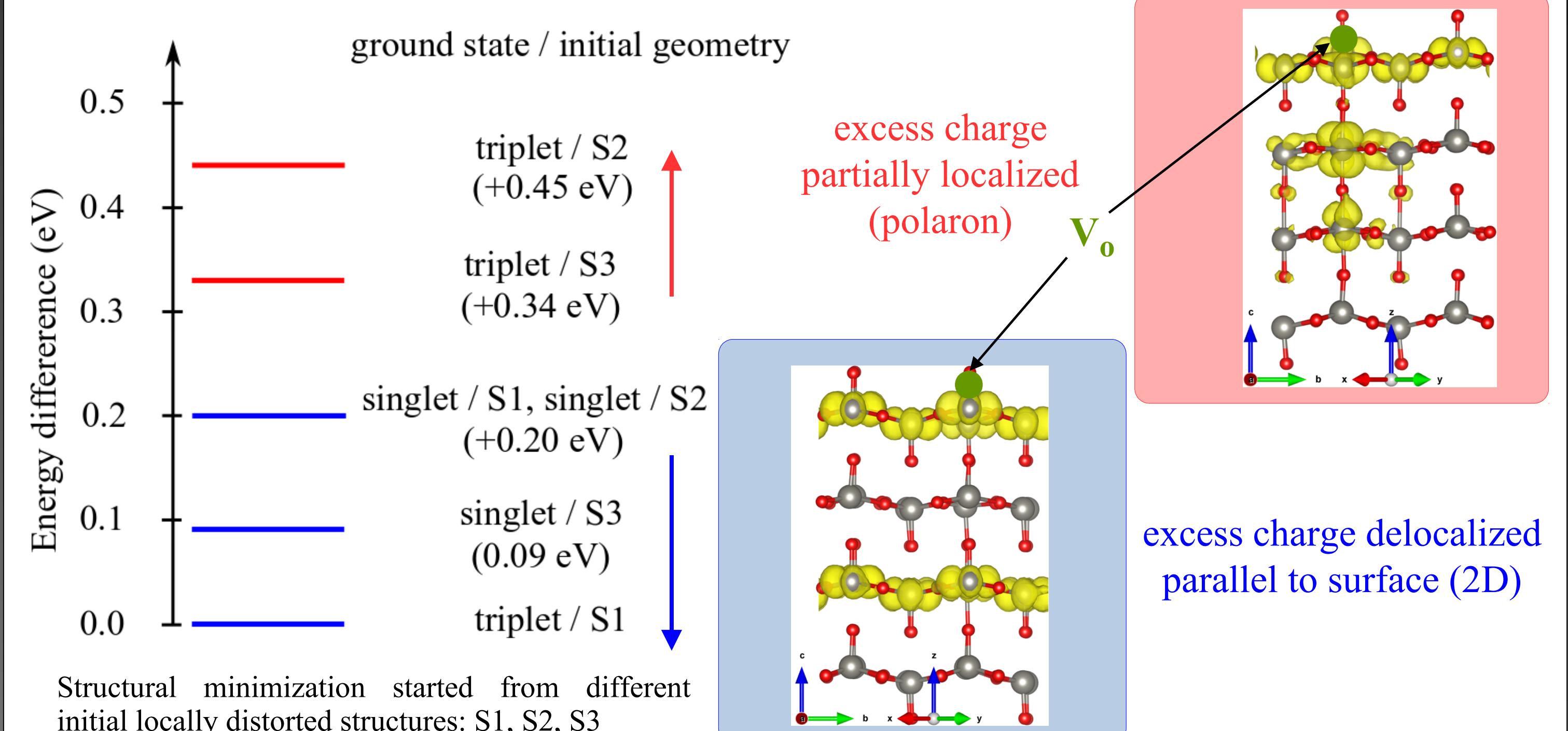
Structure of Substoichiometric Surface



Substoichiometric Surface: Electronic Structure and Localized Charges

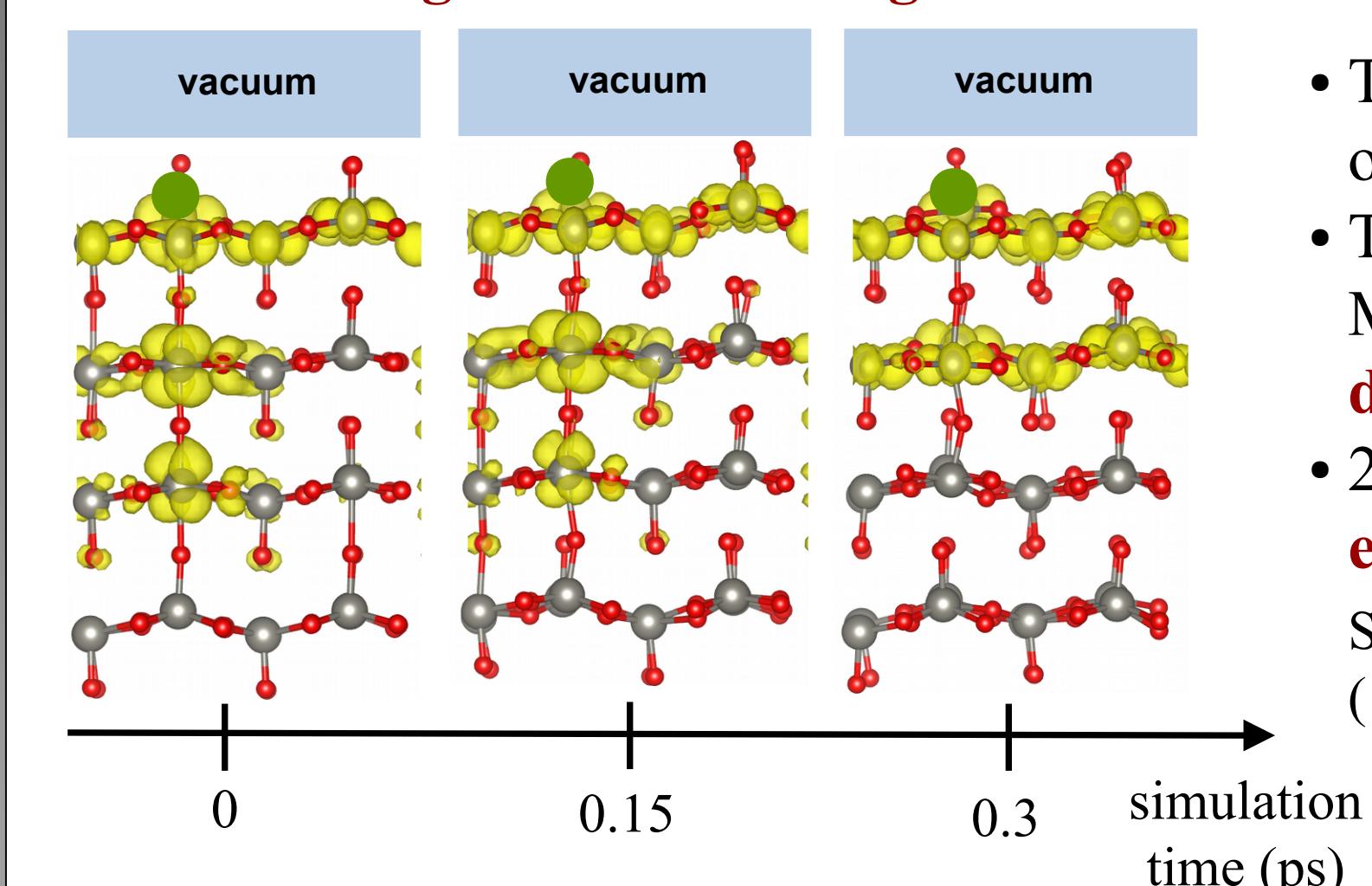
Corrugated Potential Energy Surface Sampled at 0 K

Total energy of competing states close in energy

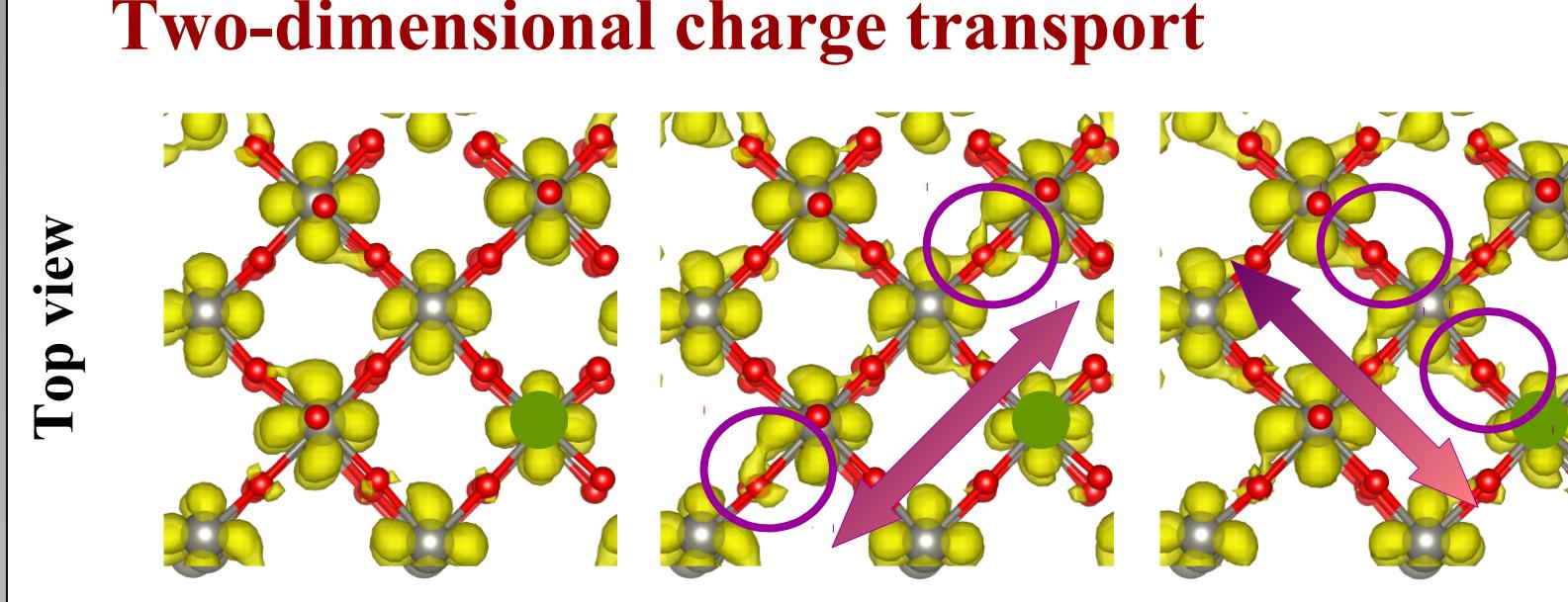


Charge Dynamics at Finite Temperature

Excess charge evolution along MD simulation



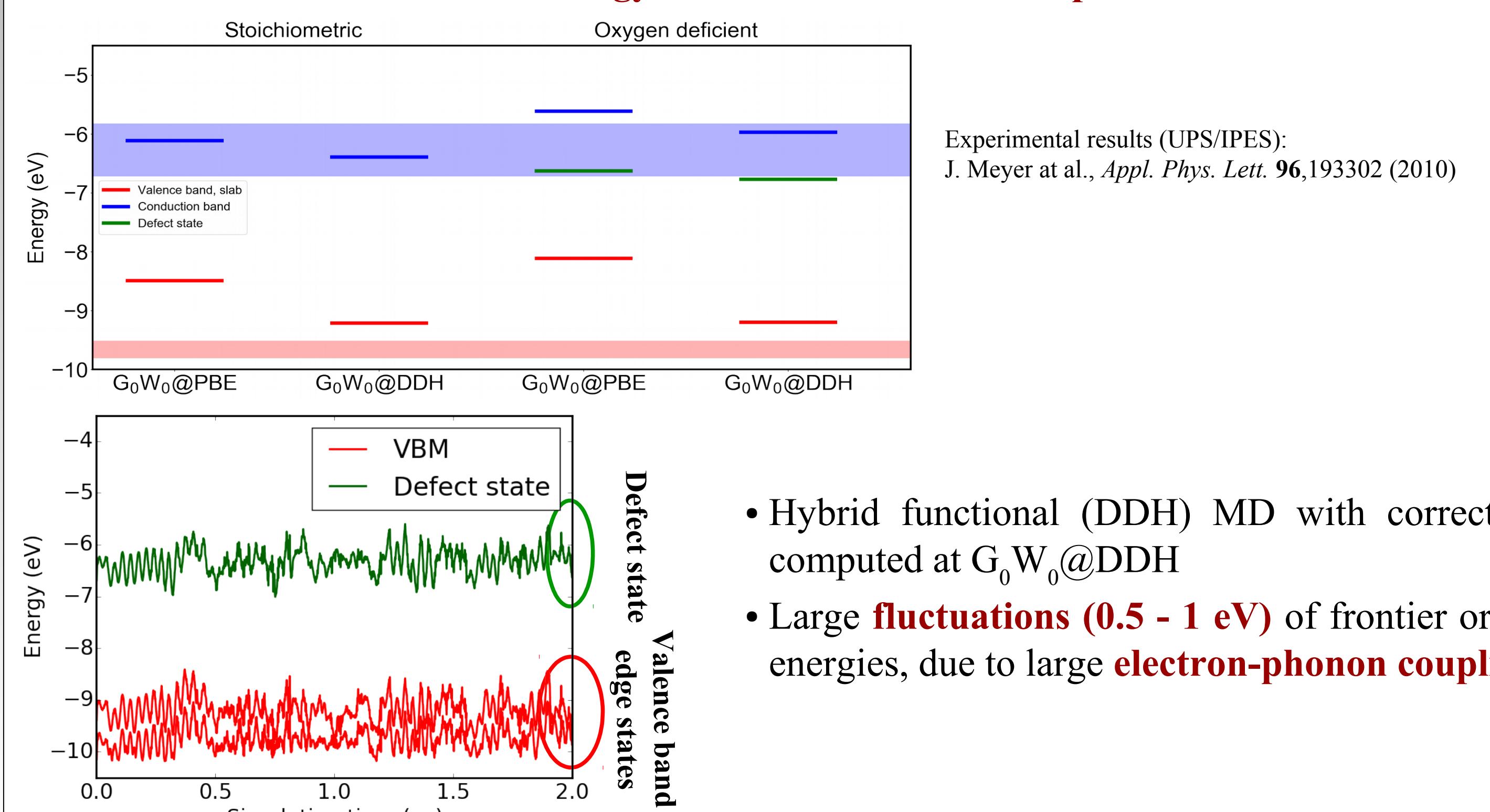
- The excess electrons occupy mainly 5d orbitals of W atoms **in the vicinity of the surface**
- Time evolution of excess charge distribution in MD simulations shows preference towards **2D delocalization**
- 2D delocalized states are found in **EPR experiments** on photoexcited WO_3 [O.F. Schirmer and E. Salje, *Solid State Comm.* **33**, 333 (1980)]



- Charge transport occurs mainly in the plane of the surface as **charge hopping** between 5d orbitals of adjacent W atoms through hybridization with 2p orbitals of bridging O atoms

Band edge positions

"Static" band structure and energy fluctuations at finite temperature



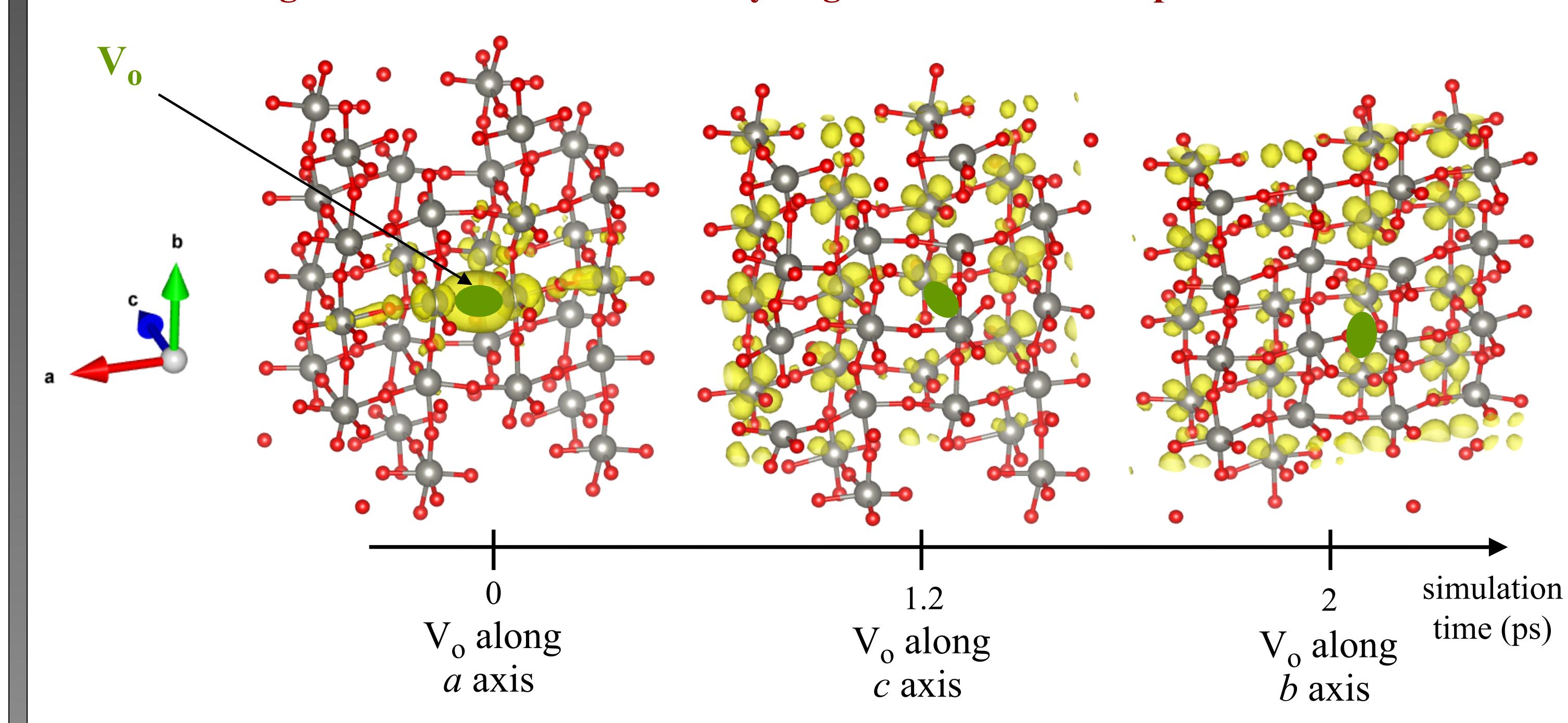
Molecular Dynamics Simulation of Bulk Oxygen Vacancy

Competition of Localized and Delocalized Excess Charges

Different first-principles studies have shown that oxygen vacancies can lead to localized or delocalized excess charge configurations, depending on the **position of the defect center** [1] and the **vacancies concentration** [2,3]. Thus, controversy still exists as to which of these configurations represent the most important effect in the real material. **Dynamical and finite temperature effects** need to be taken into account to gain insight into the nature of the defect.

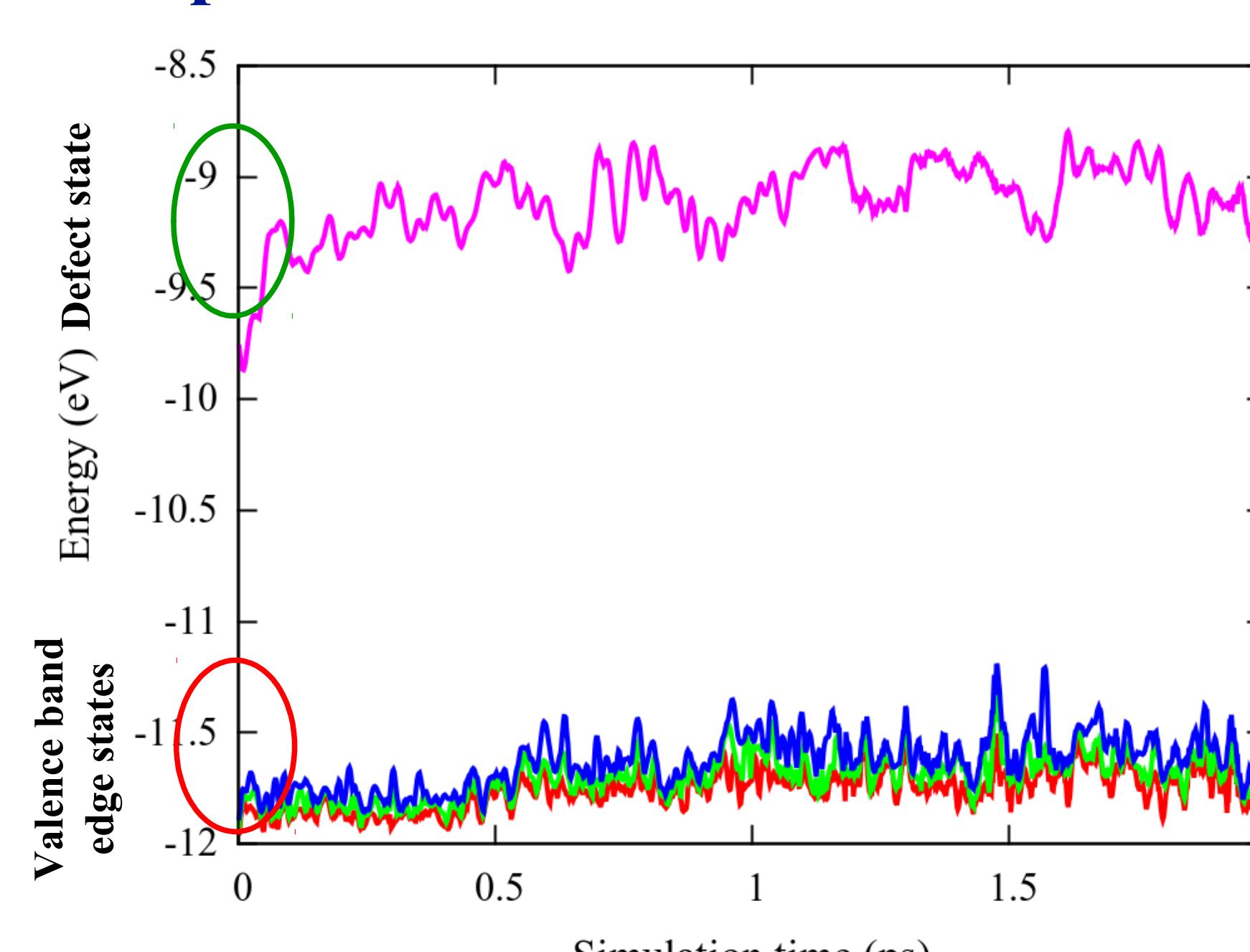
- [1] M. Gerosa, C. Di Valentini, G. Onida, C.E. Bottani, and G. Pacchioni, *J. Phys. Chem. C* **120**, 11716 (2016)
- [2] F. Wang, C. Di Valentini, and G. Pacchioni, *Phys. Rev. B* **84**, 073103 (2011)
- [3] W. Wang, A. Janotti, and C. Van de Walle, *J. Mater. Chem. C* **4**, 6641 (2016)

Excess charge delocalization and vacancy migration at finite temperature



- Starting from a localized excess charge configuration, **planar delocalization occurs** in a similar pattern as found for the surface
- The **vacancy migrates** in the crystal, occupying inequivalent sites, over the course of the MD simulation

Temperature Effects on Band Structure



- Gap state retains same character irrespective of the oxygen vacancy position and the localization properties of the excess charge
- Finite temperature fluctuations of frontier orbital energies are smaller than for the defective surface

Acknowledgments

This work was supported by NSF under the NSF-CCI center NSF-CHE-1305124. We acknowledge computational time provided by the University of Chicago Research Computing Center; by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program; and by Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract No. DE-AC02-06CH11357.

