Combining molecular dynamics and on-the-fly kinetic Monte Carlo to investigate radiation damage in solids

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Beyond Molecular Dynamics:
Long Time Atomic-Scale Simulations
March 26th - March 29th 2012

Overview

- **Introduction into radiation damage.**
  - Motivation.
  - Time-scale problem.
  - Requirement for atomistic simulation.
  - General methodology.

- **Applications:**
  - Simulating self-irradiation effects of plutonium[1-3].
    - Defect formation and migration in Ga-stabilised δ-Pu.
  - The effect of structure on radiation damage[4].
    - Comparison of radiation response of the rutile, brookite and anatase polymorphs of TiO_2.

[1] M Robinson, S D Kenny, R Smith, M T Storr, E McGee. Nucl. Inst. Meth. B **267** 18 (2009)

[2] M Robinson, S D Kenny, R Smith, M T Storr. Nucl. Inst. Meth. B **269** 21 (2011)

[2] M Robinson, S D Kenny, R Smith, M T Storr. J, Nuc. Mat. **423** 1-3 (2012)

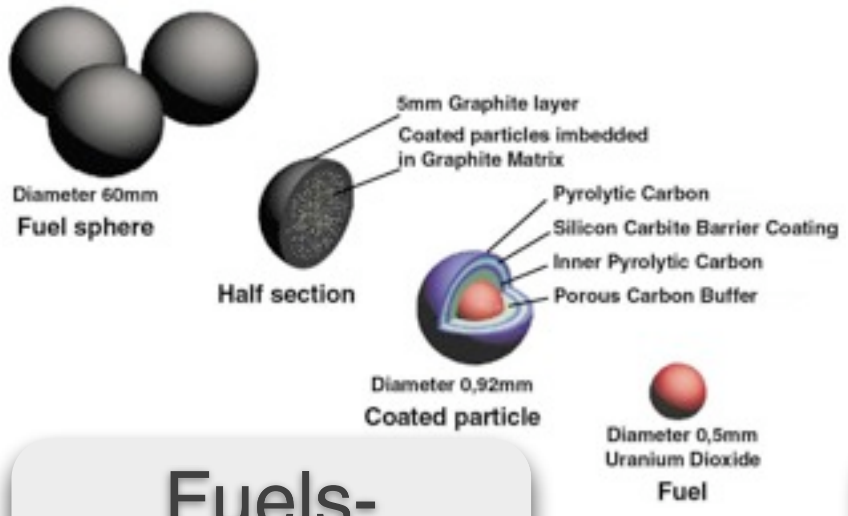
4 M. Robinson, N. A. Marks, K. R. Whittle and G. R. Lumpkin Phys. Rev. B **85** 10 (2012)

Curtin University

Introduction

- Materials for nuclear applications must all share one important property:

> *"The ability to maintain functionality during exposure to extreme levels of irradiation"*



Fuels- TRISO/UO_2

Waste forms - Synroc/ Oxide Ceramics

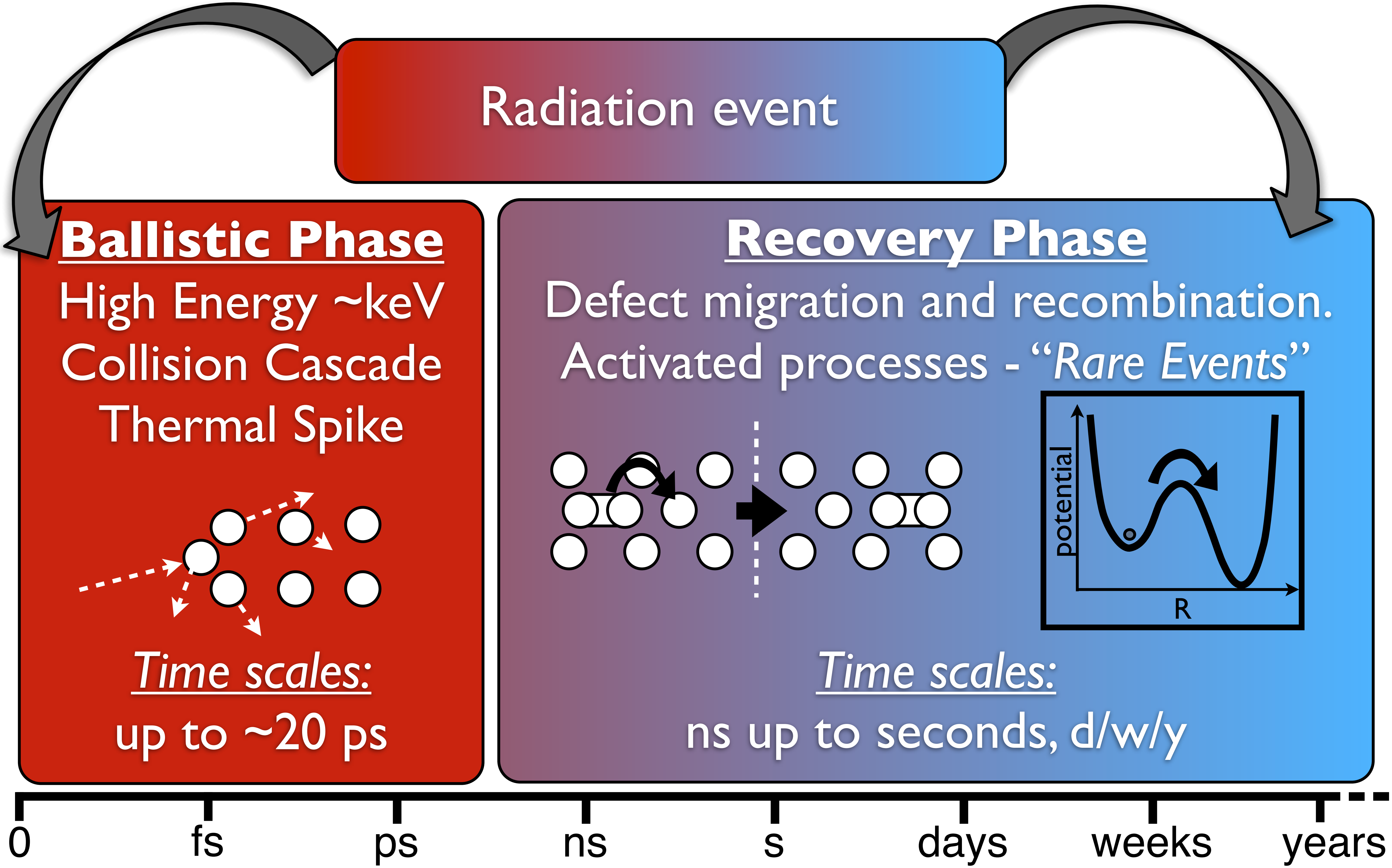
Reactor materials - ODS Steels

Fuel elements - Graphite

- Two key goals:
  - To develop new *'nuclear materials'* for future reactors or waste forms.
  - To determine the life expectancy and failure mechanisms of materials currently in service.
- Requires an in-depth understanding of the **atomistic processes** that attribute to macroscopic changes in properties.

[1] A Hirata, T Fujita, Y R Wen, J H Schneibel, C T Liu, and M W Chen, Nature Materials **10**, 922-926 (2011).

Time scale problem



Radiation event

Ballistic Phase

High Energy ~keV
Collision Cascade
Thermal Spike

Time scales:
up to ~20 ps

Recovery Phase

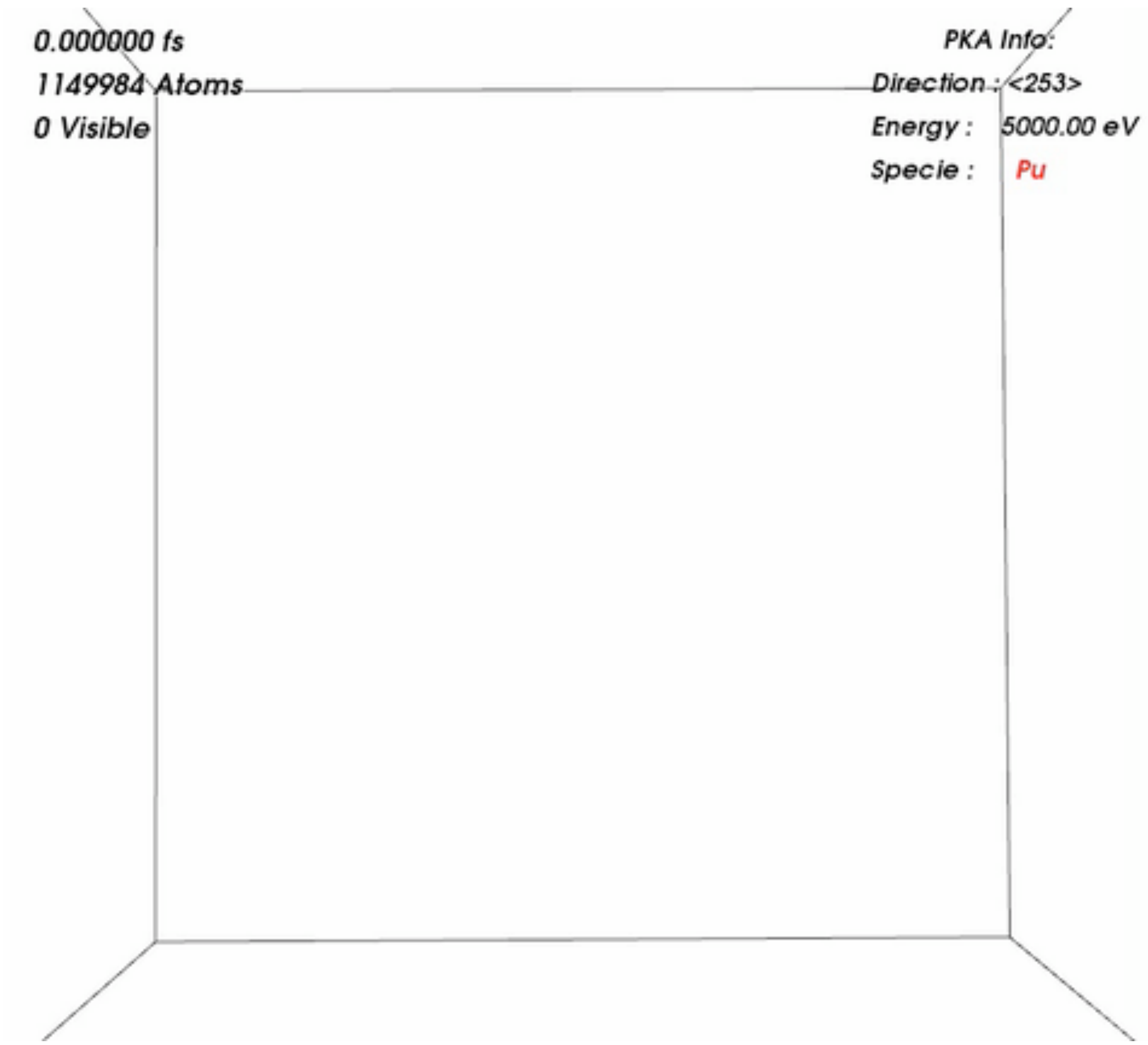
Defect migration and recombination.
Activated processes - "*Rare Events*"

Time scales:
ns up to seconds, d/w/y

but events may overlap...

Ballistic Phase

- Recoil event from a **Primary Knock-on Atom** (**PKA**)
- High energies, typically ~keV (dependent on the simulated process)
- Requires dynamics
  - *Ab initio* methods unsuitable.
- Requires atomistic lattice effects
  - Phase field or continuum models inappropriate.
- Molecular dynamics is well suited to modelling the ballistic phase:
  - Time-scales: ~*O* (ns)
  - Length scale: ~*O* (nm)
  - Ensembles (thermo/barostats)



Simulation: 5 keV cascade in fcc Pu @ 300 K. 1.1M atoms 15 ps

Molecular Dynamics

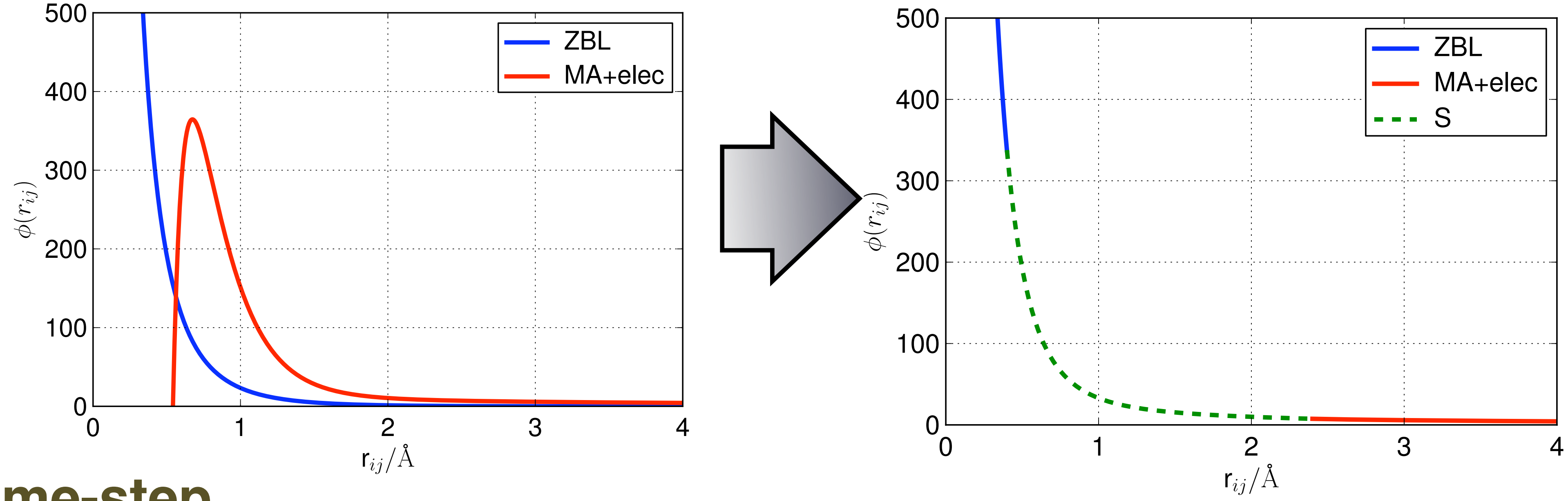
- Molecular Dynamics (MD) is a powerful tool that can be used to investigate the ballistic phase at the atomic level response.

- In addition, MD has allowed in depth studies into all areas of radiation damage
  - Self-irradiation effects (decay).
  - Ion implantation (e.g SWIFT heavy ion).
  - Sputtering.
  - Defect aggregation at grain boundaries or interfaces.
  - Dislocation dynamics and diffusion.
  - Bubble formation.

- Serves as an alternative to analytical models of defect production (KP, NRT) or models based on the binary collision approximation (SRIM)

Ballistic Phase

- Important requirements for modelling the ballistic phase using MD:
  - **Interatomic potential**
    - Must **depict nuclei-nuclei interactions** correctly - i.e. ZBL screened coulomb potential.



  - **Variable time-step**
    - Due to the **high atomic velocities**.
  - **Sampling**
    - Due to the **chaotic nature** of the atomic collisions, important to gain a high level of sampling of PKA **energies**, initial **directions** of impact, **thermal vibrations, atomic specie.**
  - **Defect analysis**
    - Vacancy/Interstitial (Frenkel pairs), Anti-sites, Dislocations, Schottky defects

Recovery Phase

- Modelling the recovery phase is made significantly harder by the highly inhomogeneous nature of the residual lattice:
  - After the ballistic phase, the remaining lattice is potentially **highly disordered**.
    - Frenkel pairs, voids, dislocations.
  - The presence of **impurities** or **fission products**.
    - Bubble formation (H,He,Xe,Kr).
  - Nuclear materials and fuels are typically **complex** and **multi-component**
    - Structural vacancies, partial occupancy (i.e. disordered Pyrochlores/Fluorites).
    - Interfaces or grain boundaries (ODS steels, fuel cladding).

- Removes the possibility of using on-lattice KMC due to the variation in local environment surrounding each defect.

Recovery Phase

- The recovery phase itself can be broken down into :
  - Transitions where the **end state is known**.
    - Examples:
      - Simple vacancy/interstitial hops.
      - Direct recombination.
    - Methods:
      - Climbing image NEB[1], String methods
  - Transitions where the **end state is unknown**
    - Examples:
      - Complex defect migration.
      - Long range recombination.
    - Methods:
      - Dimer[2], ART[3], RAT[4]
  - These techniques can also be used in on-the-fly KMC methods.
      - Migration and recombination pathways.

[1] G. Henkelman, B. P. Uberuaga, and H. Jónsson, The Journal of Chemical Physics **113**, 9901-9904 (2000).
[2] G. Henkelman and H. Jónsson, The Journal of Chemical Physics **111**, 7010-7022 (1999).
[3] G.T.Barkema and N Mouseau. Comp. Mat. Sci. **20** 3 (2001)
[4] L. J. Vernon, Modelling Growth of Rutile TiO2, Loughborough University, 2010.

Application 1

Simulating radiation damage in Ga-stabilised Pu.

Application - Ga stabilised Pu

- **Simulating radiation damage in Ga-stabilised δ-Pu.**
  - Understanding the aging due to self-irradiation in fcc plutonium.
  - FCC plutonium is unstable at RT so is alloyed with a small percentage of Ga (up to ~12%)

- Aim
  - To study the radiation response of Ga-stabilised Pu.
    - Cascade simulations, displacement threshold energy calculations
  - To investigate the effect of Ga on defect diffusion.
    - Transitions barrier calculations and OTF-KMC of defect migration.

Application - Ga stabilised Pu

- Methodology:
  - MD cascades
    - Modified Embedded Atom Method (**MEAM**) for PuGa[1,2] in **LBOMD**.
    - **0.2 - 10 keV** PKA energies.
    - 10 lattices equilibrated to **300K** for between 10-15 ps.
    - 12 PKA directions chosen from the FCC irreducible volume.
    - Thermal and periodic boundaries.
    - MD runs of 20 ps.
  - LTSD
    - Simple transitions, manual setup, MEP defined using CNEB.
    - Transition searches using Dimer/RAT methods
    - On-the-fly KMC - Dimer/RAT followed by CNEB

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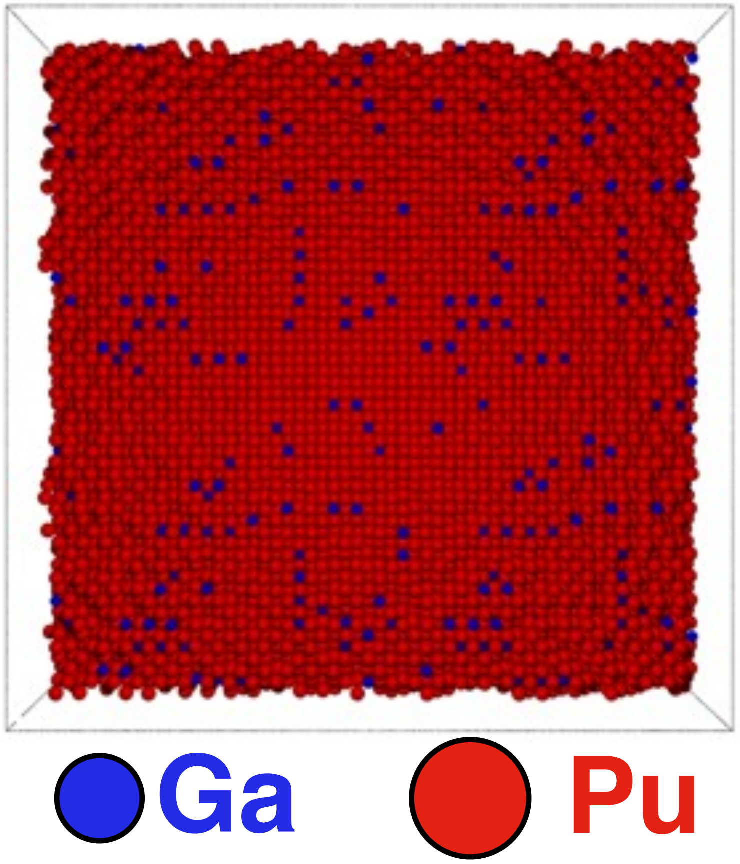
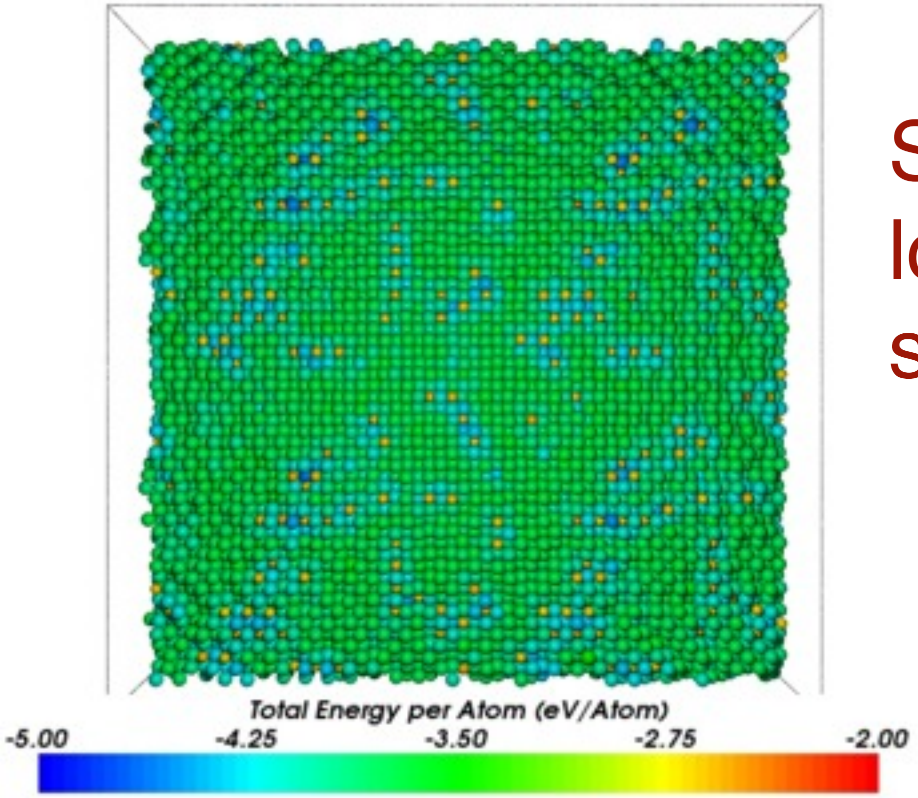
[1] M. I. Baskes, Physical Review B **62**, 15532-15537 (2000).

[2] M. I. Baskes, K. Muralidharan, M. Stan, S. M. Valone, and F. J. Cherne, JOM Journal of the Minerals, Metals and Materials Society **55**, 41-50 (2003).

Application - Ga stabilised Pu

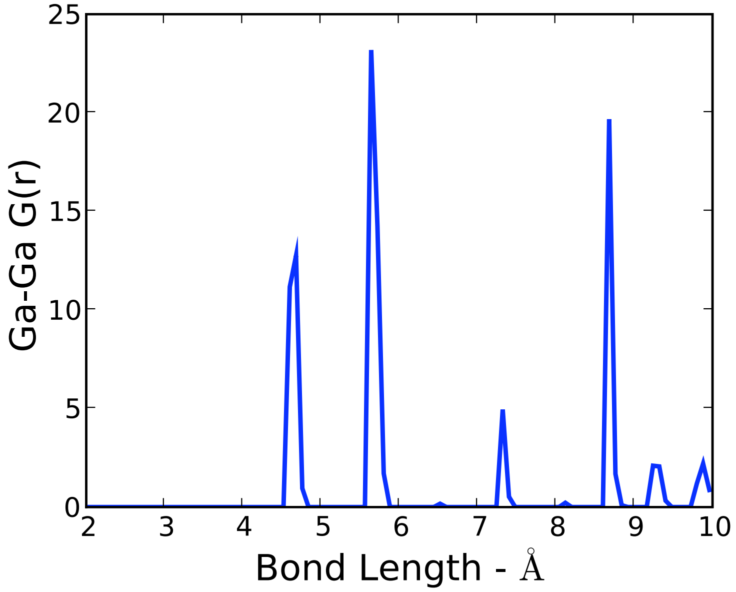
- **Lattice Structure**
  - FCC phase Pu with arbitrary 5% substitutional Ga.





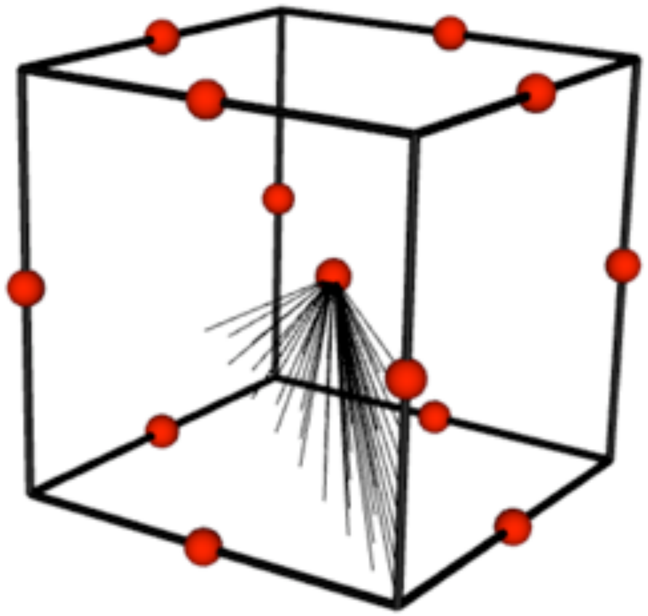
Substitutional Ga lowers the PE of surrounding Pu matrix

- Ga ordering determined using lattice Monte Carlo
  - Results in no 1st nearest neighbour (1NN) Ga-Ga bonds



Impact on LTSD techniques - resultant crystal structure highly inhomogeneous

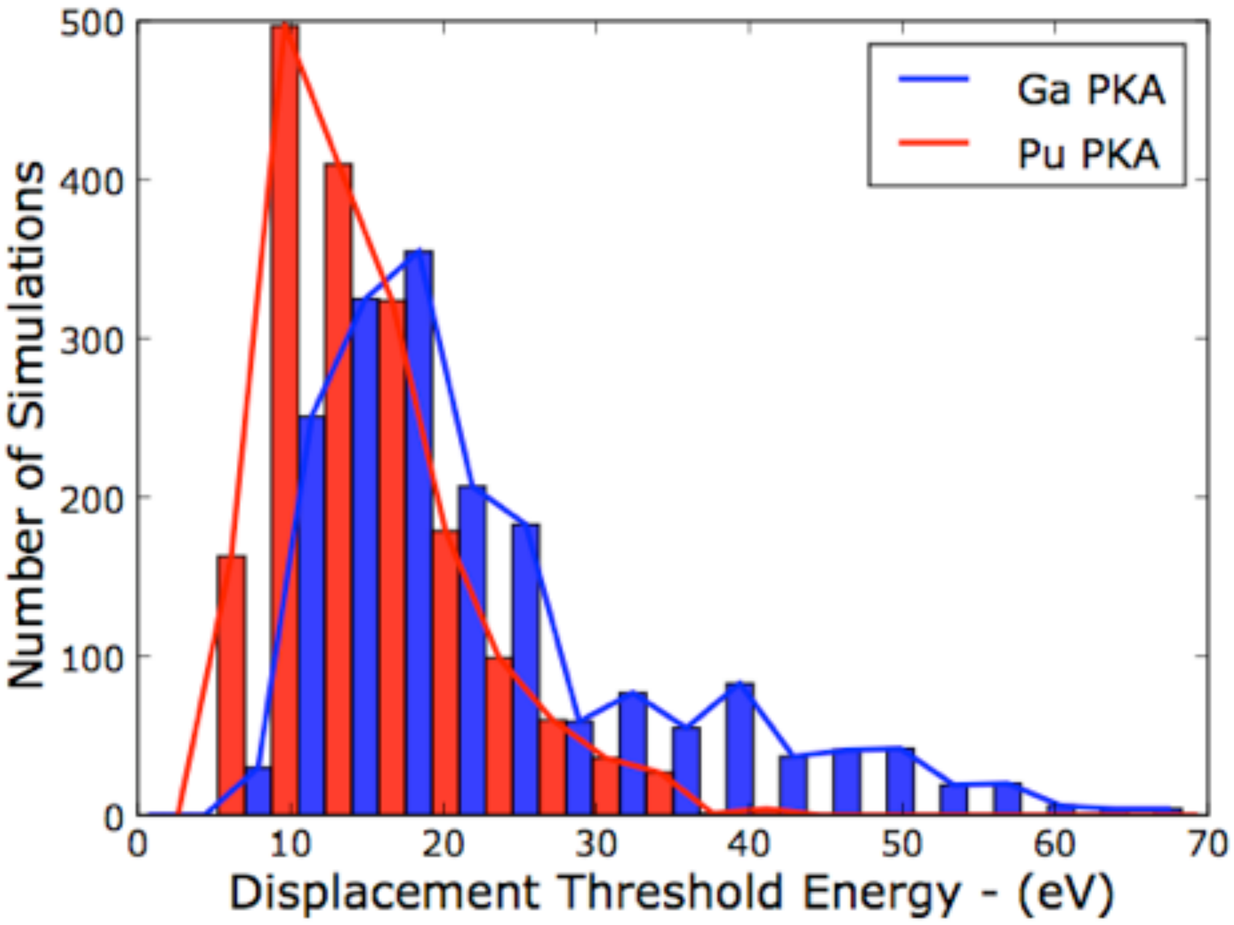
Application - Ga stabilised Pu



- **A first look at the ballistic phase**
- **The effect of Ga on: *Threshold displacement energy E_d.***

  "Minimum energy required to displace at atom as to create a Frenkel (vacancy-interstitial) Pair"

  - **Low energy cascades (< 200 eV) initiated in a irreducible volume.**



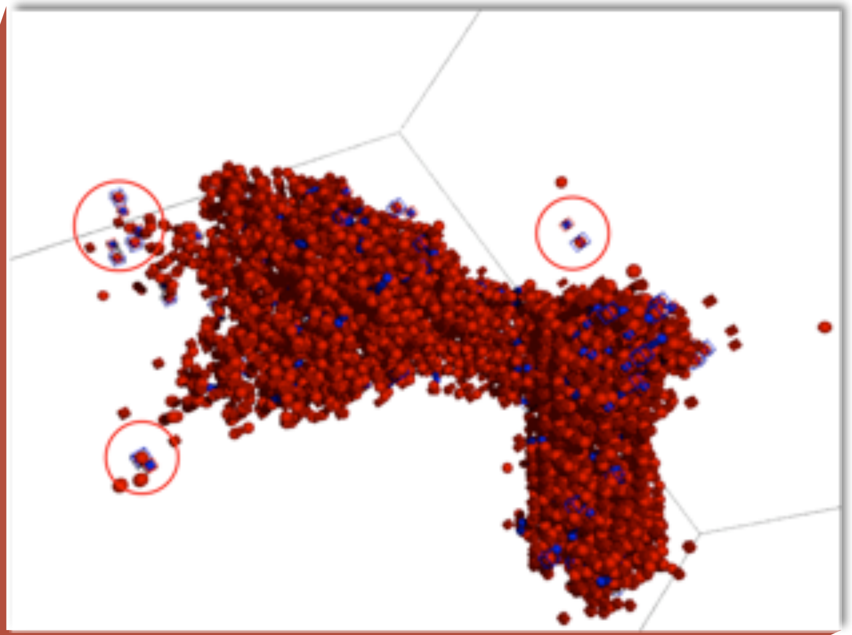
- Overall increase in E_d for the **Ga PKA**

Application - Ga stabilised Pu

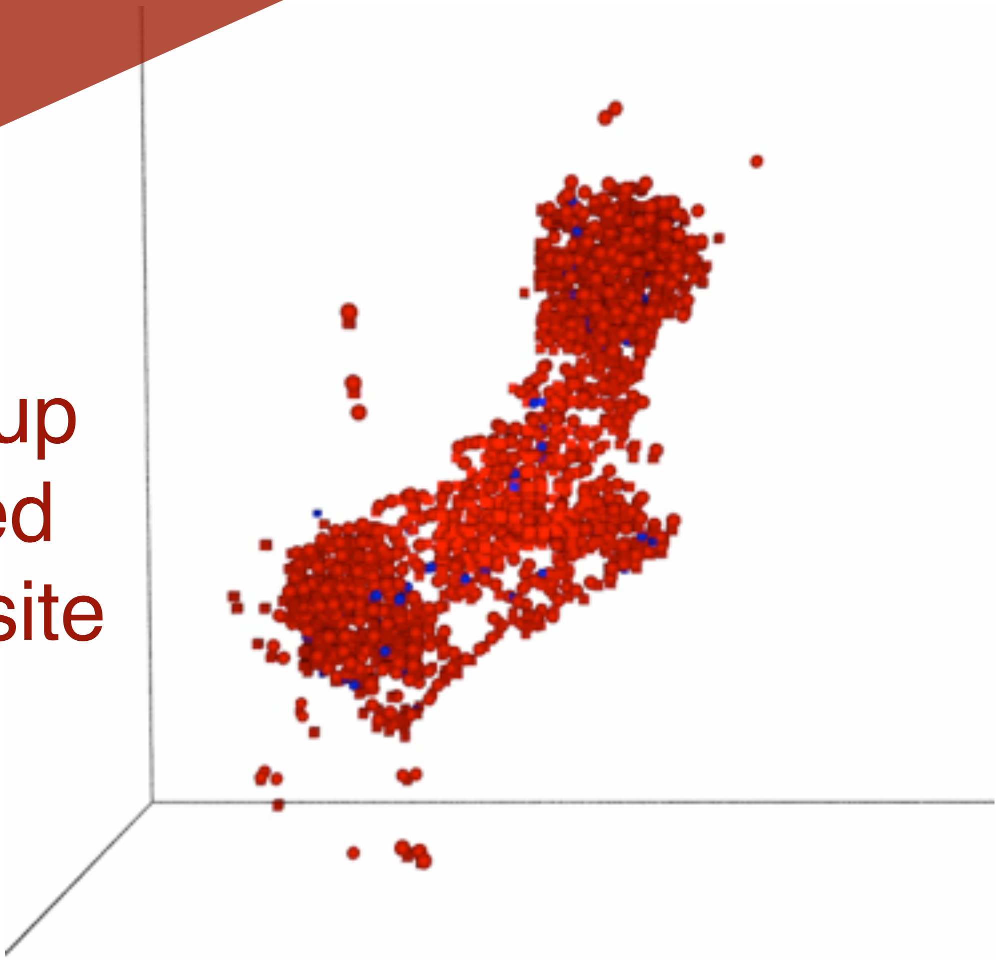
- **Cascade Results**

Pu 5 at. % Ga 5 keV Cascades Defect Analysis

	Ga	Pu	Mixed	Total
Constituents				
Vacancies	1	298	N/A	299
Interstitials	2	303	N/A	305
Anti-Sites	123	131	N/A	254
Defect Categories				
Lone Interstitials	0	246	N/A	246
Lone Vacancies	0	250	N/A	250
Lone Anti-Sites	8	19	N/A	27
1NN Di-Vacancies	0	1	0	1
2NN Di-Vacancies	0	2	0	2
Tri-Vacancies	0	1	0	1
1NN Di-Interstitials	0	11	0	11
2NN Di-Interstitials	0	2	0	2
Tri-Interstitials	0	0	0	0
1NN Di-Anti-Sites	0	0	95	95
2NN Di-Anti-Sites	0	0	1	1
Tri-Anti-Sites	0	0	0	0
Anti-site + Mono-Vacancies	0	2	0	2
Anti-site + Mono-Interstitials	2	0	0	2
Split-Interstitials	0	1	1	2
Split-Vacancies	0	4	1	5
Vacancy-Interstitials	0	12	0	12
Unclassified Tri-Defects	0	3	16	19



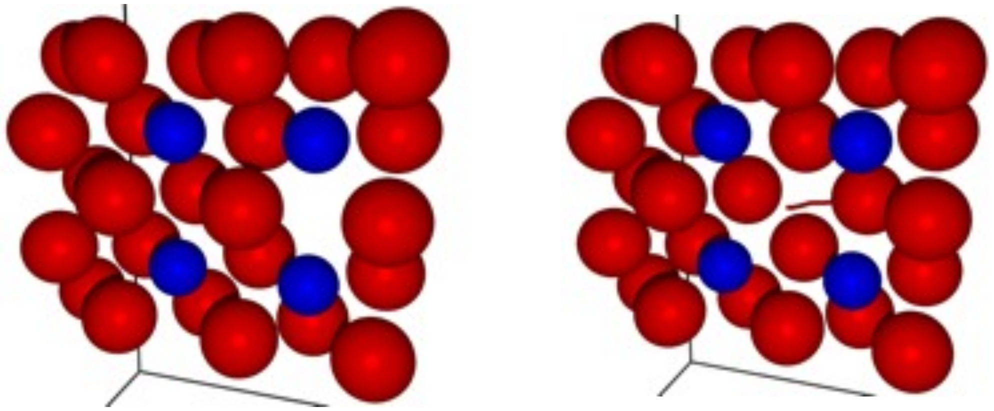
Large build up of 1NN mixed specie anti-site defects

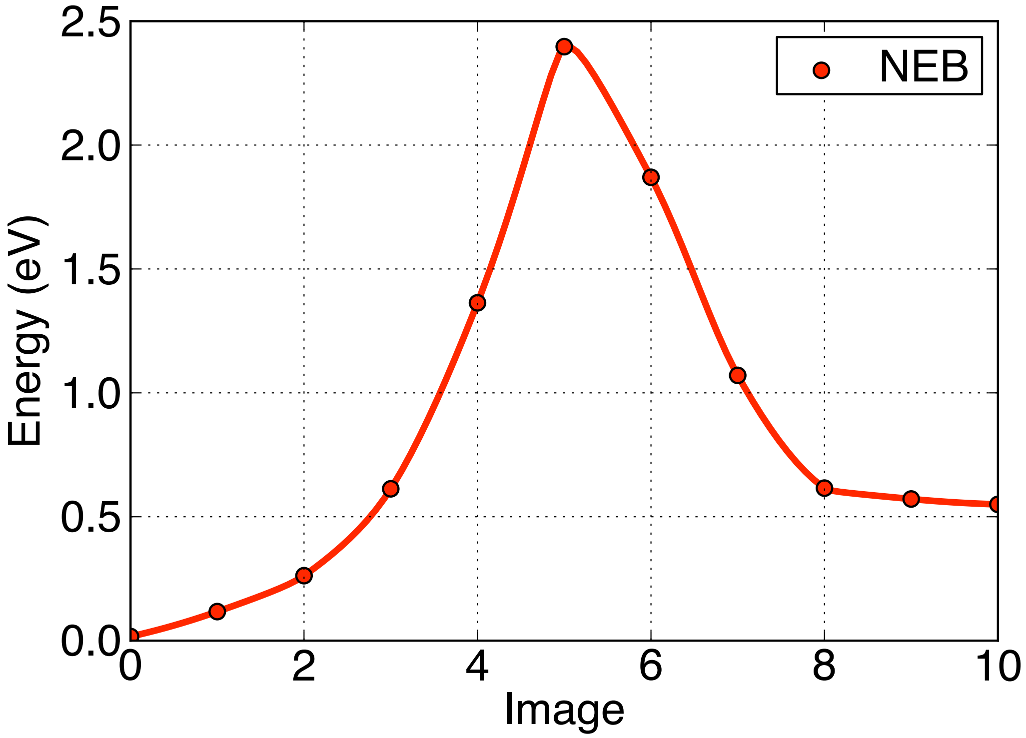


Application - Ga stabilised Pu

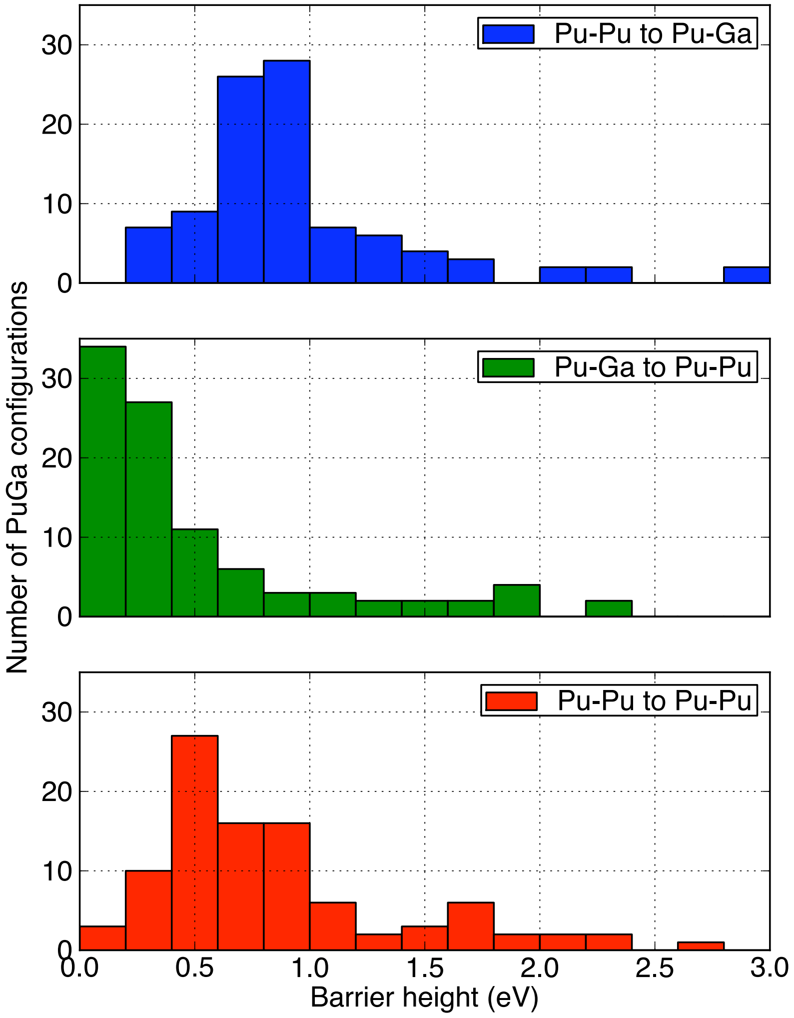
- **Simple Transition barrier results**
    - **(~ 25 different transitions in 100 PuGa lattices)**

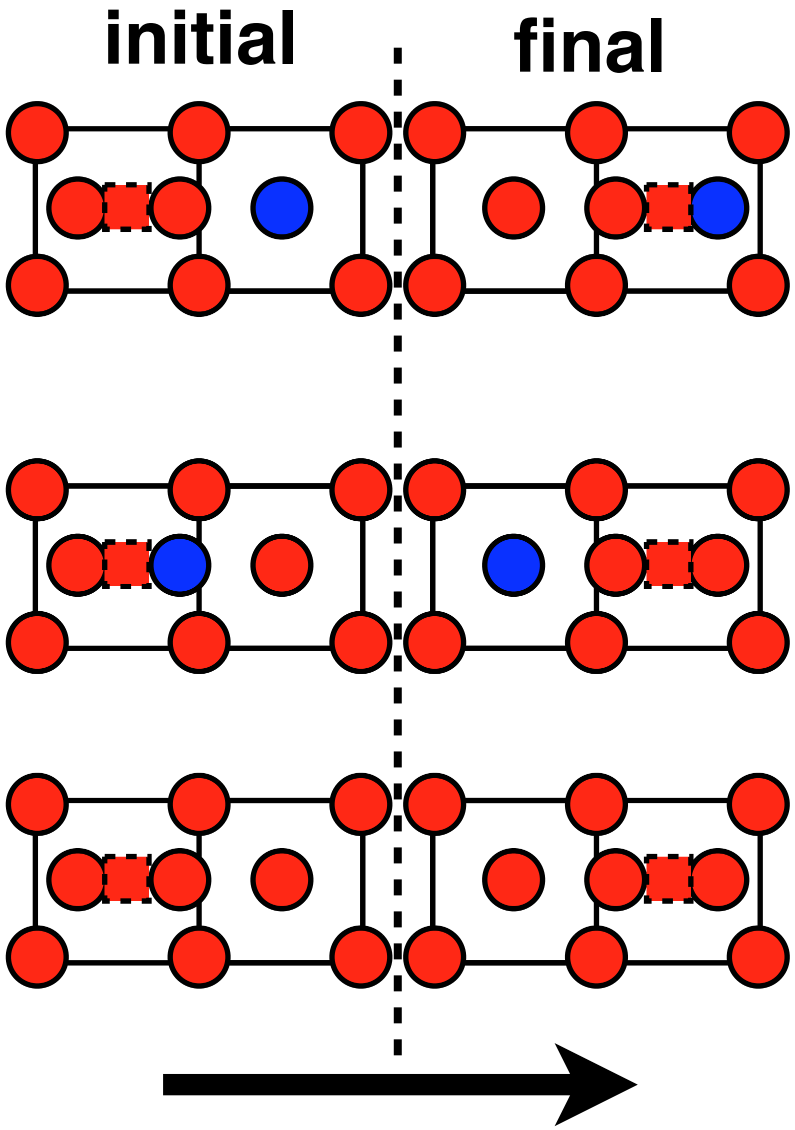
Mono-vacancy





<100> split-interstitials





- Interstitial barriers << vacancy barriers

- **The creation of vacancies by the displacement of Ga atoms is highly unfavourable.**

Application - Ga stabilised Pu

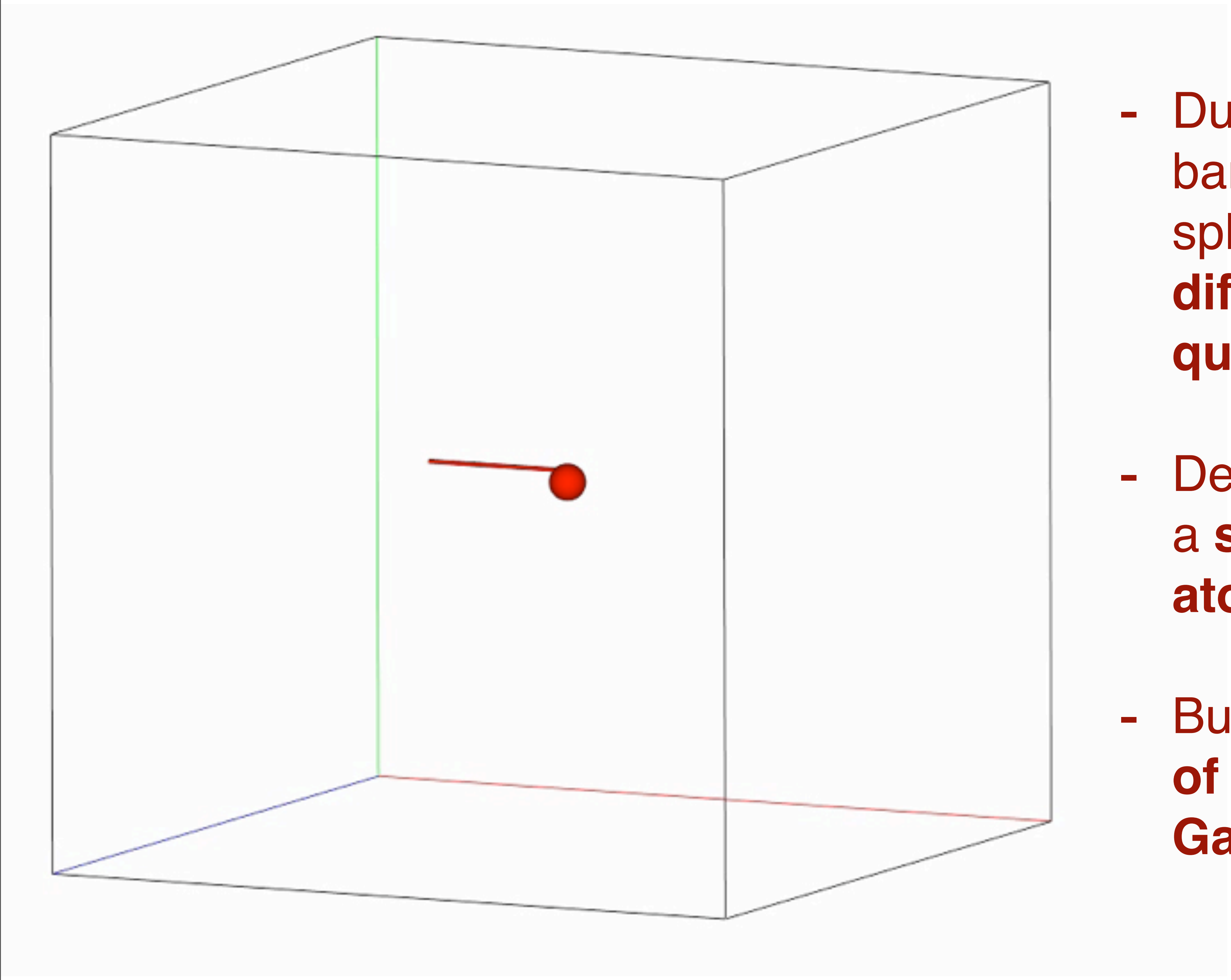
- **On-the-fly KMC of Pu split-interstitial**

- Due to the low energy barriers associated with split-interstitials, **diffusion occurs quickly** ~ns.
- Defect migrates through a **succession of Pu atomic replacements**
- But what about the **effect of the substitutional Ga** ? ...

Simulated time: 842.24 ns

Application - Ga stabilised Pu

- **On-the-fly KMC of Pu split-interstitial**



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Application - Ga stabilised Pu

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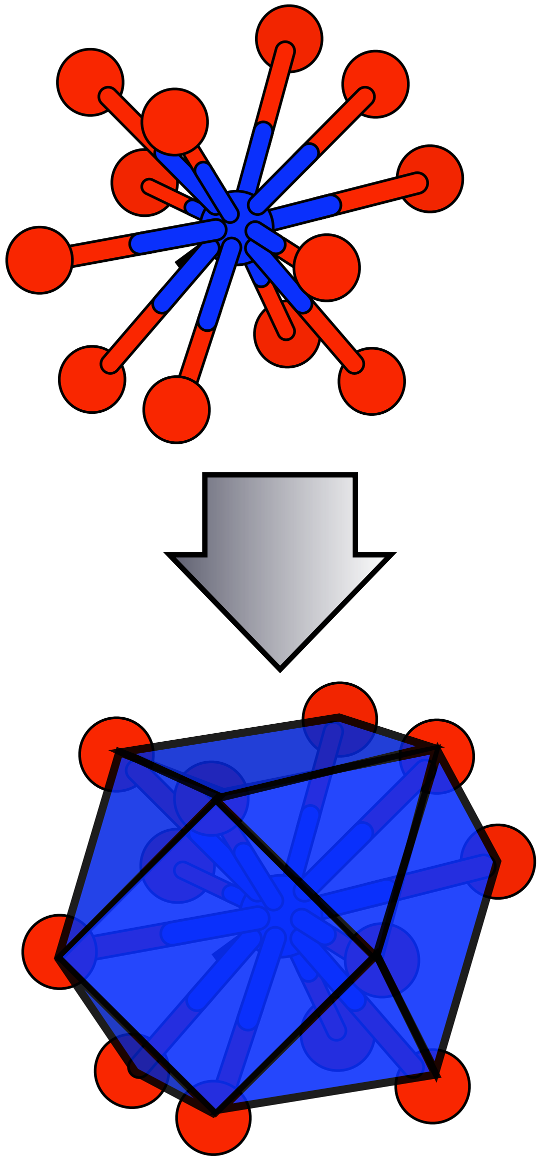
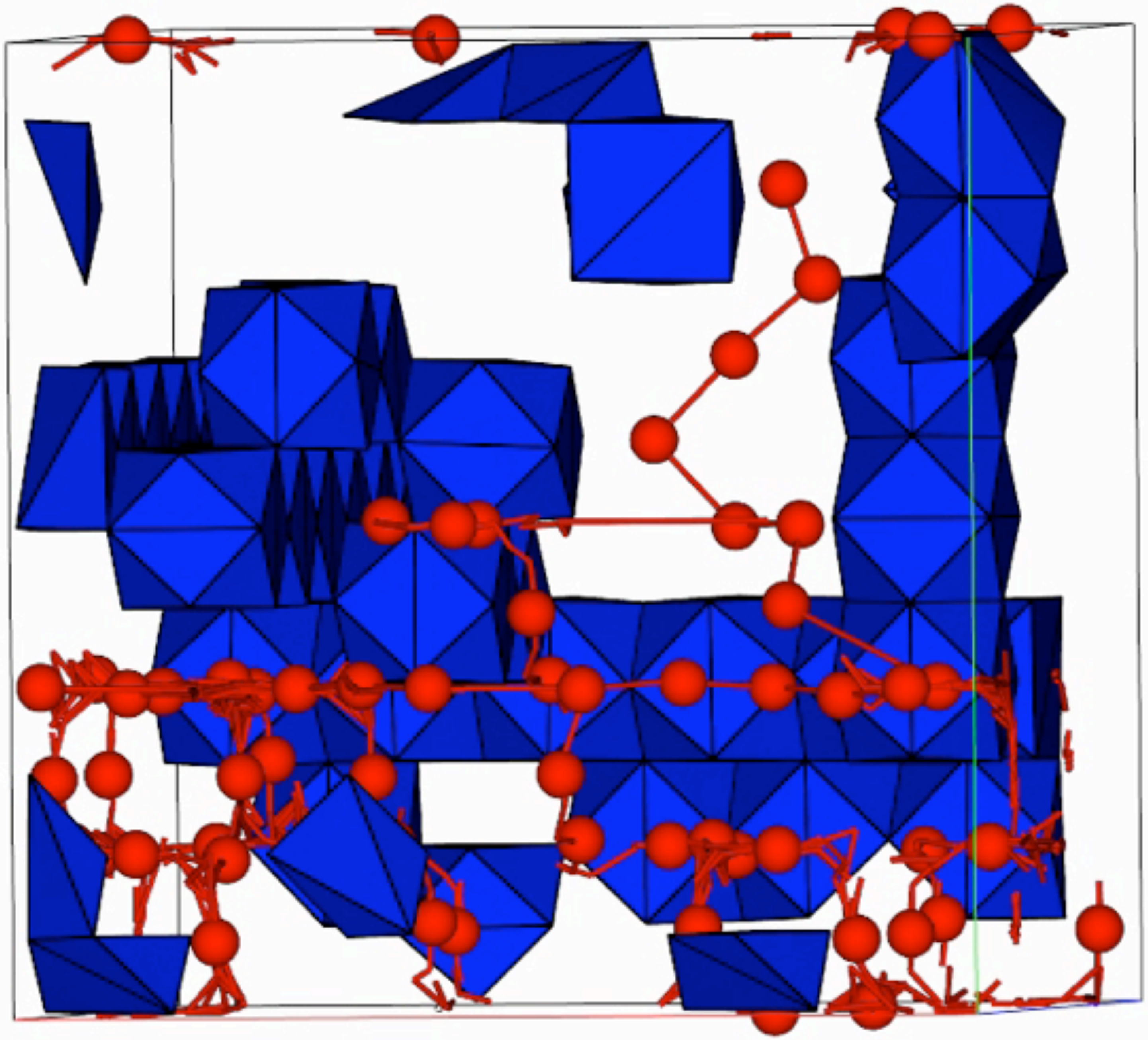
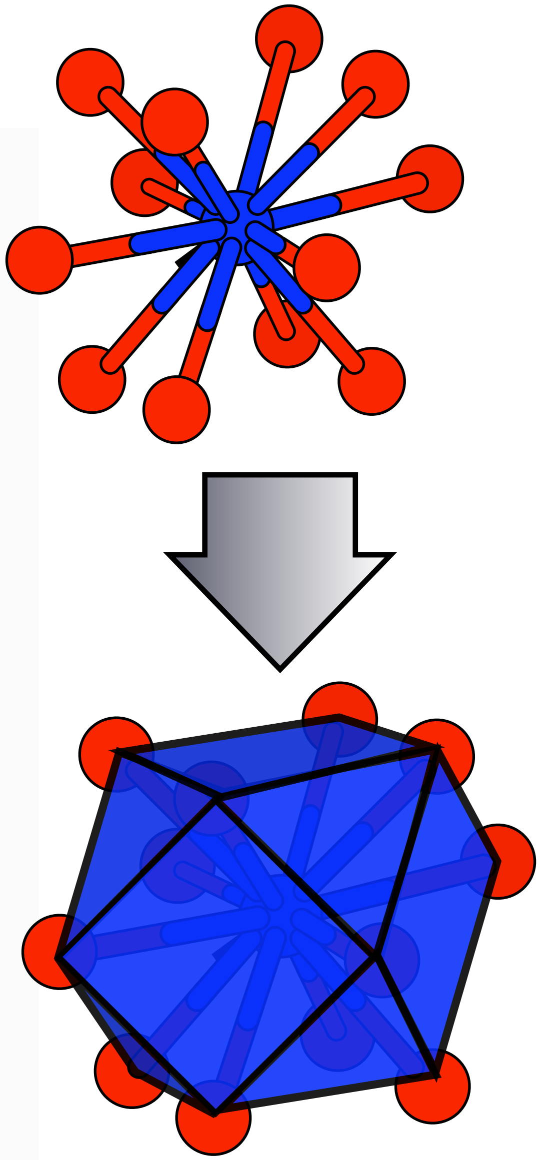


- By rendering the Ga-Pu polyhedra, it becomes clear that the **interstitial migration is confined to Pu rich regions.**

Application - Ga stabilised Pu

- **On-the-fly KMC of Pu split-interstitial**

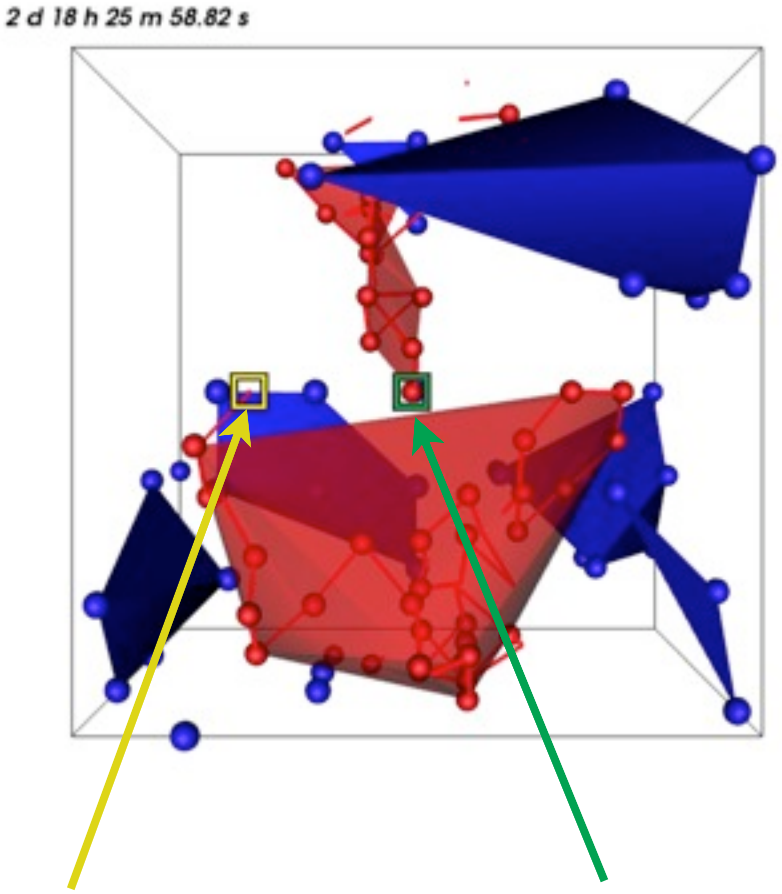




- By rendering the Ga-Pu polyhedra, it becomes clear that the **interstitial migration is confined to Pu rich regions.**

Application - Ga stabilised Pu

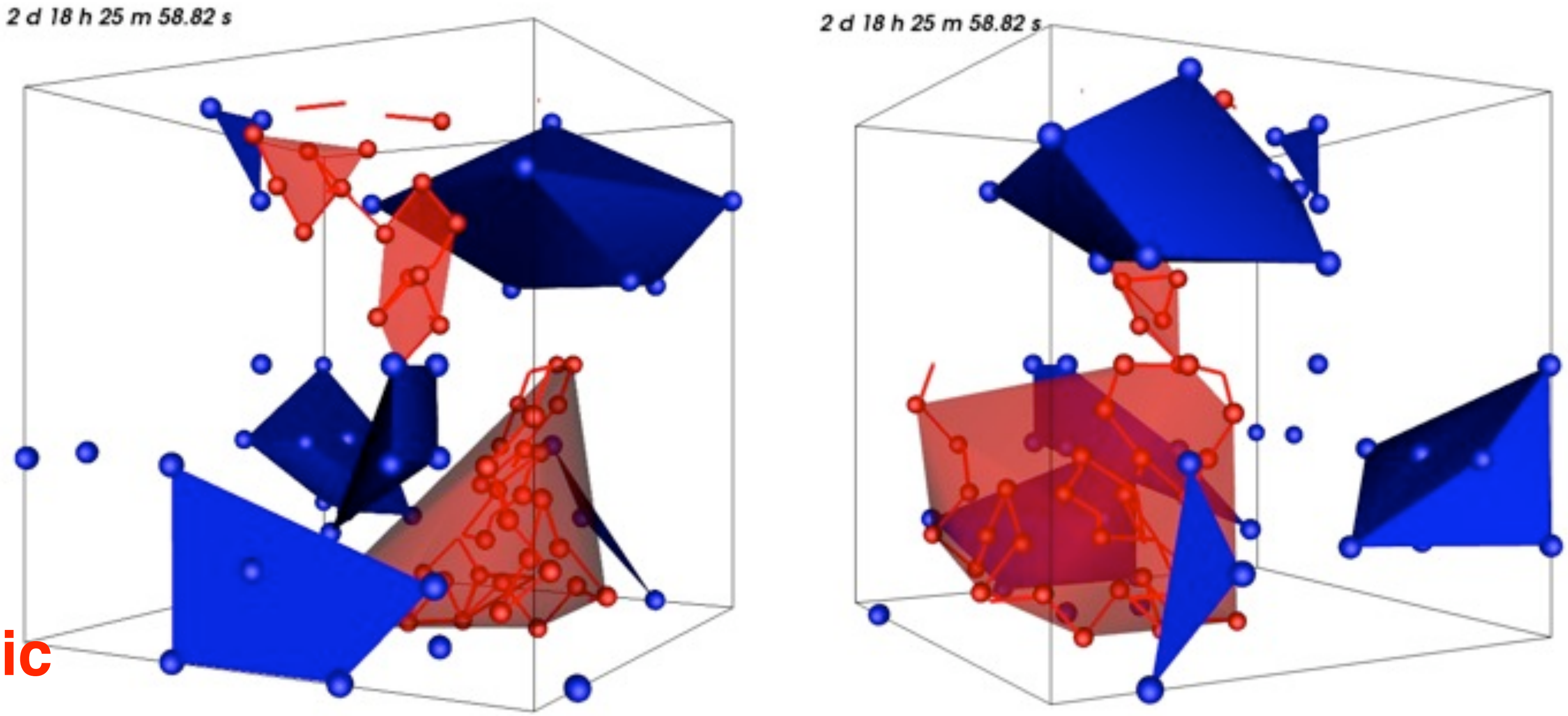
- **On-the-fly KMC of Pu mono-vacancy.**



Final mono-vacancy position

Initial mono-vacancy position

- The same is also true for vacancy migration, with the **migration pathway avoiding Ga-rich regions**.
- As the lowest energy barriers for vacancy transitions are higher than interstitial, the **time scale for migration is significantly increased.**



Ga rich regions

Regions containing atomic displacements

Application - Ga stabilised Pu

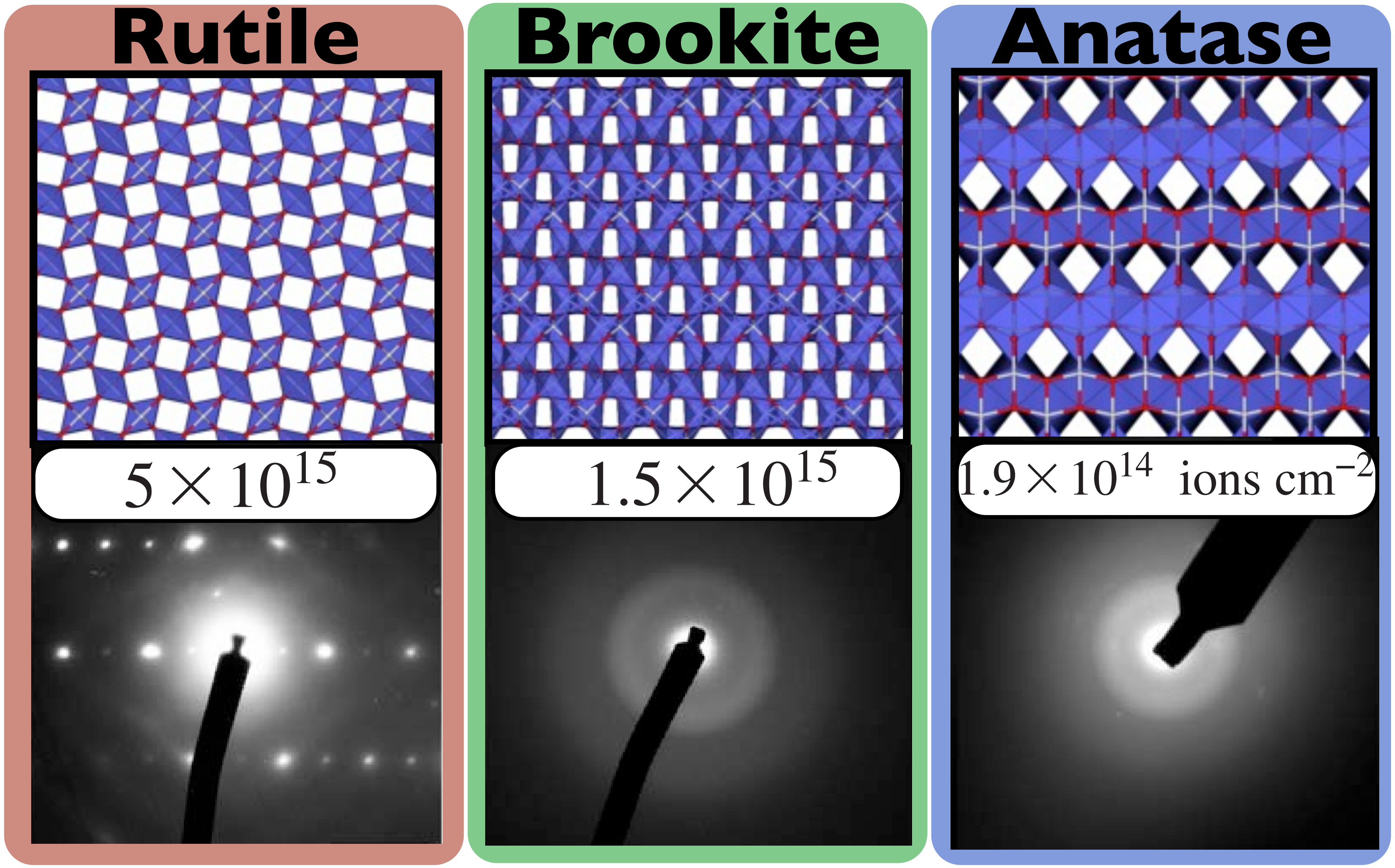
- **Conclusions:**
  - **We have built up a picture of radiation damage in Ga-stabilised Pu, showing the effect of Ga on:**
    - **Ballistic phase - Threshold displacement energies.**
      - **Higher value of E_d for the Ga PKA.**
    - **Ballistic phase - Cascade damage.**
      - **No outlying Ga defects**
      - **Build up of 1NN ‘anti-sites’ i.e. Pu-Ga switching during the cascade**
    - **Recovery phase - Transition barriers.**
      - **High energy barriers associated with introducing vacancies and interstitials intro Ga rich regions.**
    - **Recovery phase - Diffusion mechanisms.**
      - **Pu defect migrations is confined to Pu-rich zones, bounded by Ga-Pu polyhedra.**
- **TODO: Cascade overlap, effect of GB, varying at.% Ga, migration of complex defect structures. - *requires robust LTSD methods!***

Application 2

The effect of structure on radiation damage: A case study in TiO_2

Application - TiO_2

- **Rutile** application as a nuclear waste form, i.e. **Synroc**, and has a high tolerance to radiation damage.
- The **Anatase** and **Brookite** polymorphs behave differently with **Anatase** exhibiting a much **higher susceptibility** to radiation damage.



Increasing susceptibility to amorphisation

G. R. Lumpkin, K. L. Smith, M. G. Blackford, B. S. Thomas, K. R. Whittle, N. A. Marks, and J. Z. Zaluzec, Physical Review B **77**, 1-9 (2008).

Application - Ga stabilised Pu

- Aim
  - To study the low energy radiation response of the low pressure polymorphs of TiO_2
    - Reproduce trends found in experiments.
    - Investigate the atomic level differences in radiation response.
  - A transferable and generalised method of simulation and analysis of low energy radiation events.
    - As a method of calculating the threshold displacement energy, E_d.
    - To determine defect production mechanisms and recovery processes.
    - Quantitative insight into resultant defect structures.
    - To generate comparable results between crystal structures and/or potentials.

Application - TiO_2

- Methodology:
  - MD cascades
    - **Matsui-Akaogi (MA)** buckingham potential[1] with ZBL in the DL_POLY3 MD code.
    - Low energy cascades **< 200 eV**.
    - 10 lattices equilibrated to **300K** for between 10-15 ps.
    - 100 PKA directions chosen from a **uniform spherical distribution.**
    - Thermal and periodic boundaries.
    - MD runs of **20 ps**.
  - LTSD
    - Simple transitions, manual setup, MEP defined using CNEB.
    - Transition searches using Dimer/RAT methods
    - On-the-fly KMC - Dimer/RAT followed by CNEB

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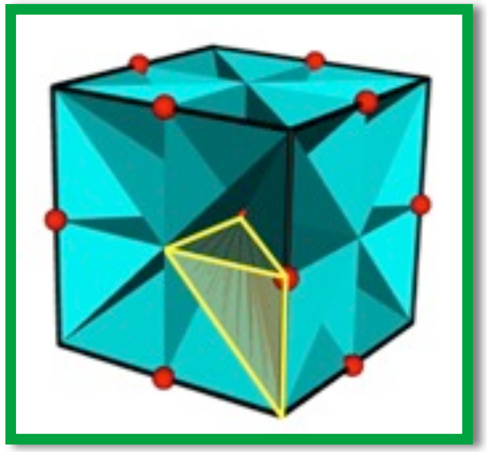
[1] M. Matsui and M. Akaogi, Molecular Simulation **6**, 239-244 (1991).

?

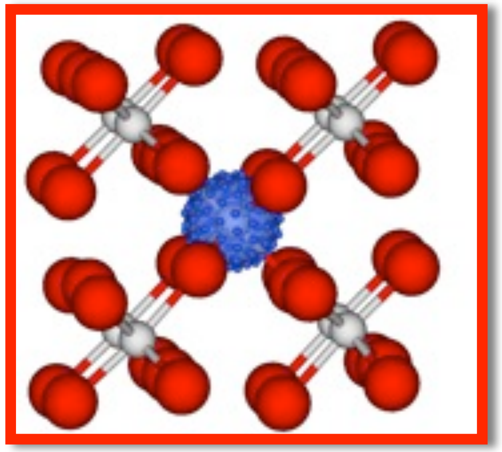
Application - TiO_2

- One of the goals was to produce a **generalized and transferable** methodology to study initial defect formation and extracting quantities such as threshold displacement energy E_d.
  - Main area to automate: the determination of **PKA directions**



irreducible unit e.g. fcc

x



unit sphere sampling

✓

The Thomson Problem

"Minimum energy configuration of point charges on the surface of a conducting sphere"

No analytical solution for large N, requires **numerical constrained minimisation.**

Application - TiO_2

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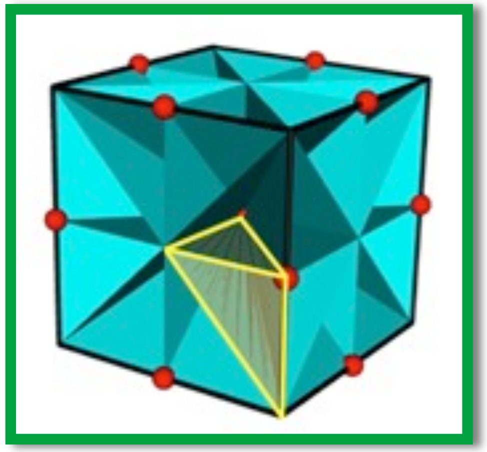

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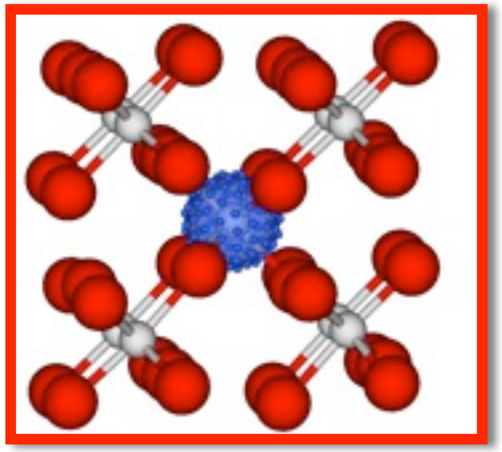

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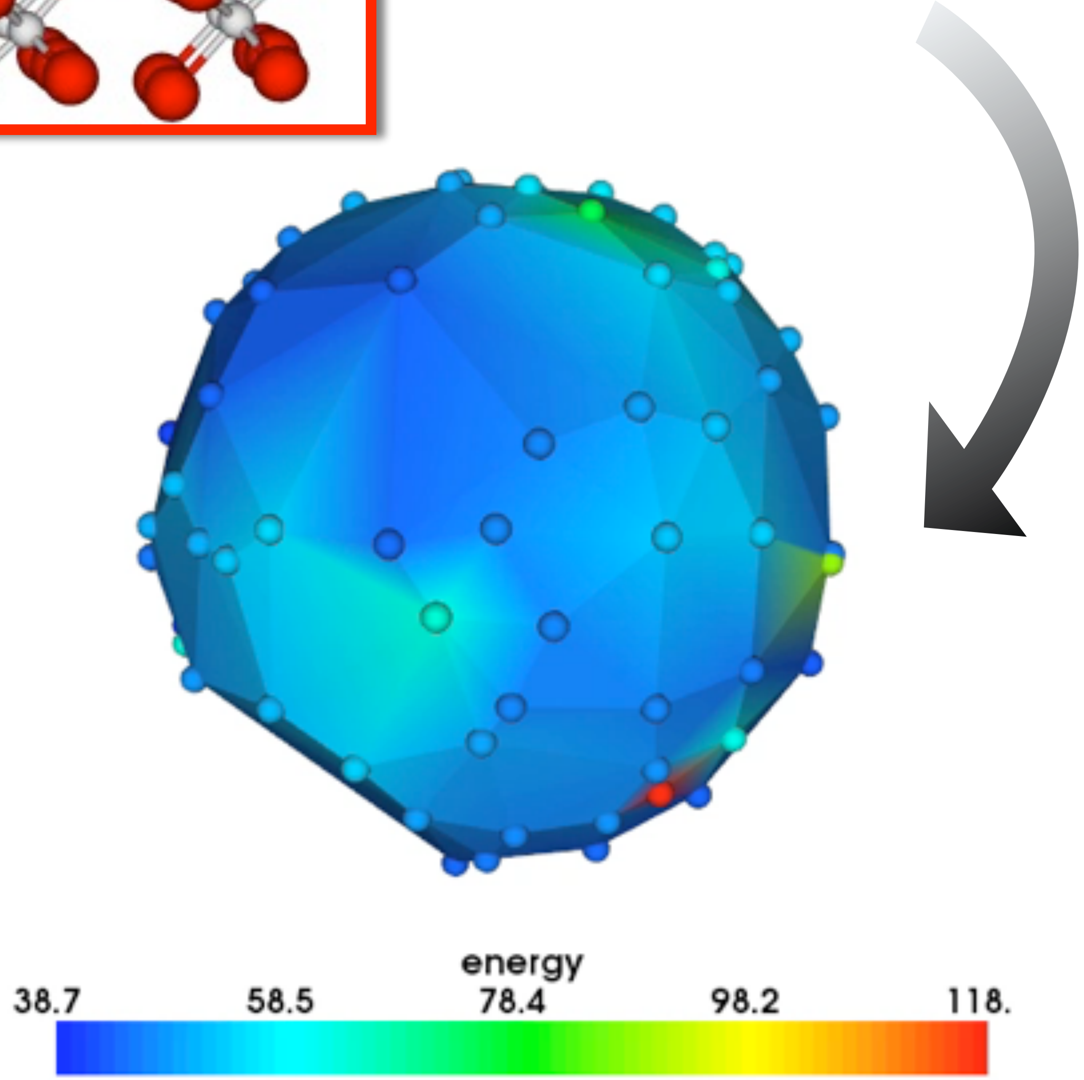


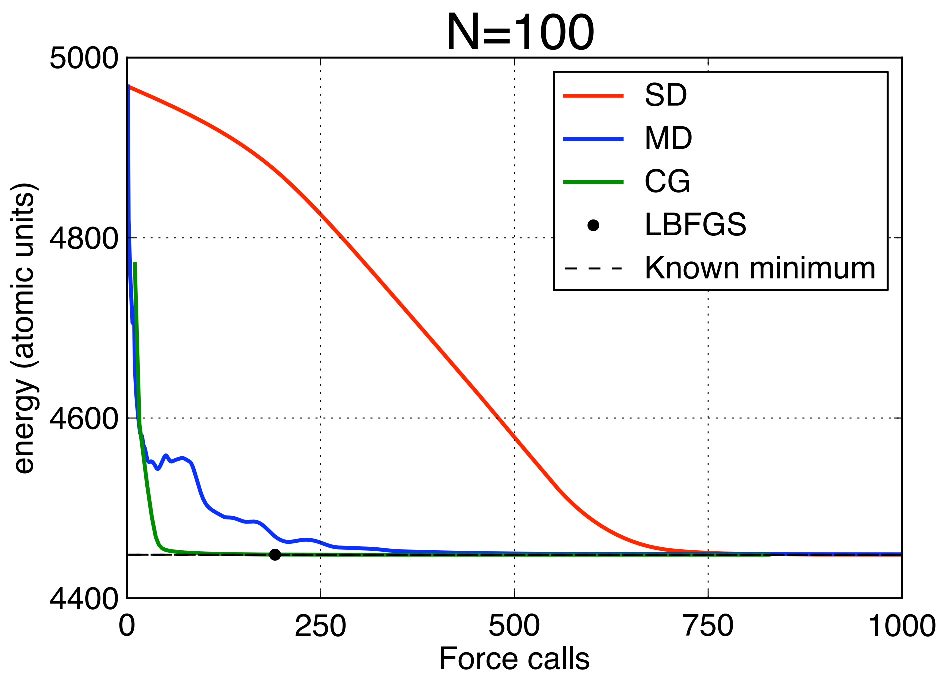
The Thomson Problem

"Minimum energy configuration of point charges on the surface of a conducting sphere"

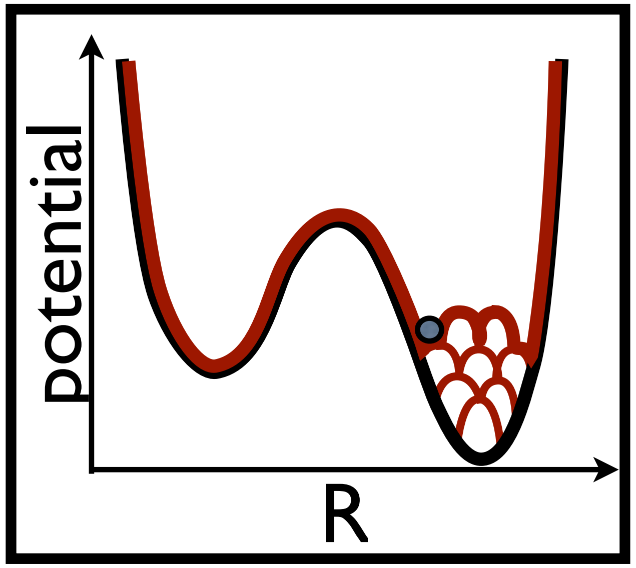
No analytical solution for large N, requires **numerical constrained minimisation.**

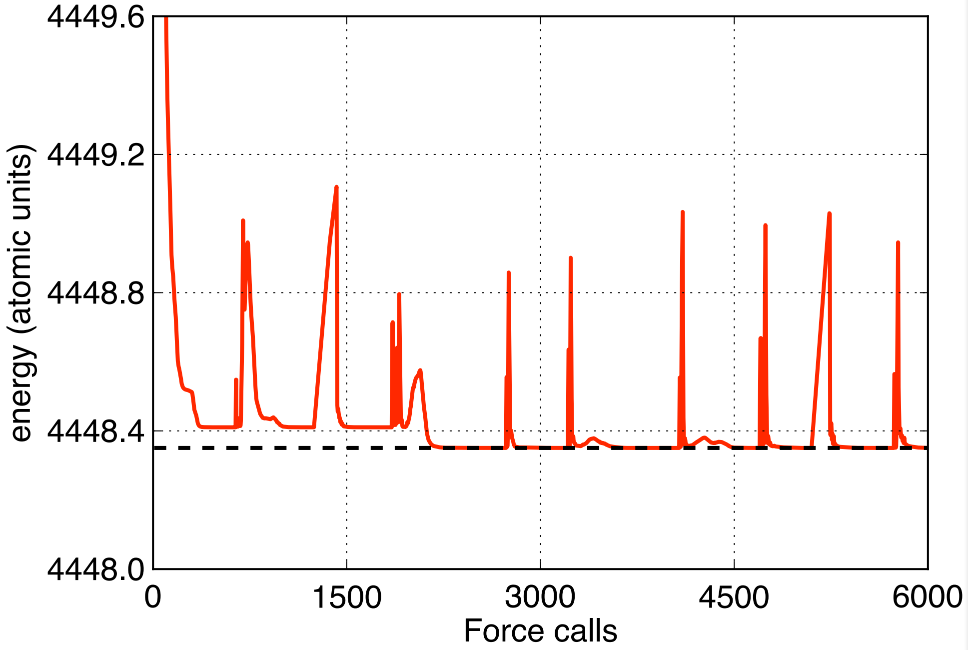
Application - TiO_2

- **Finding solutions to the Thomson Problem.**
  - Steepest Decent
  - MD
  - Conjugate Gradient
  - Broyden–Fletcher–Goldfarb–Shanno (BFGS & LBFGS)



- **Exponential Increase in local minima as N increases**
  - Requires basin-hopping techniques to find global minima.





Application - TiO$_2$

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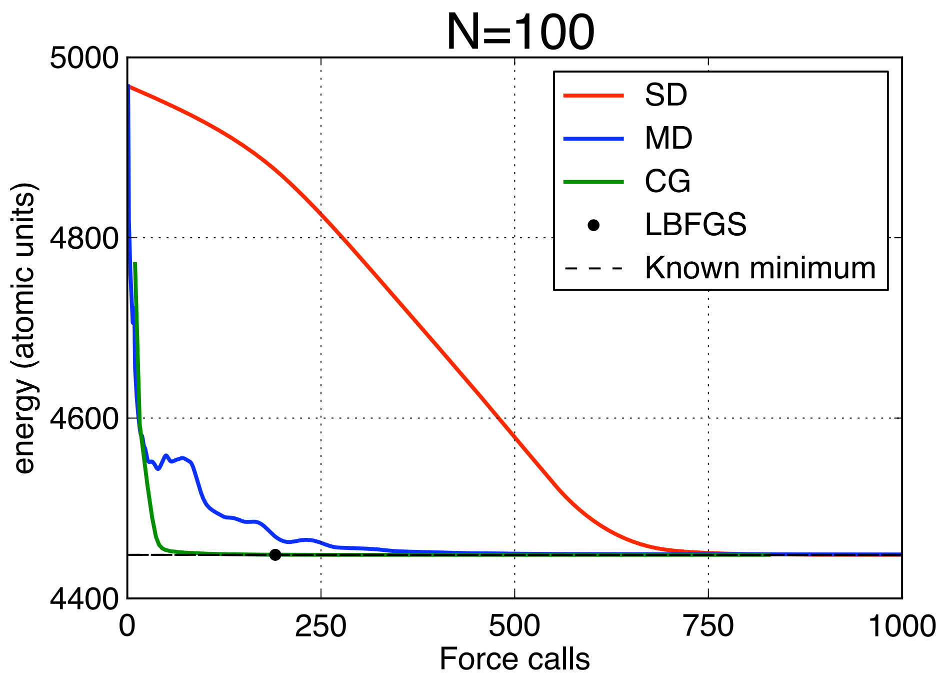

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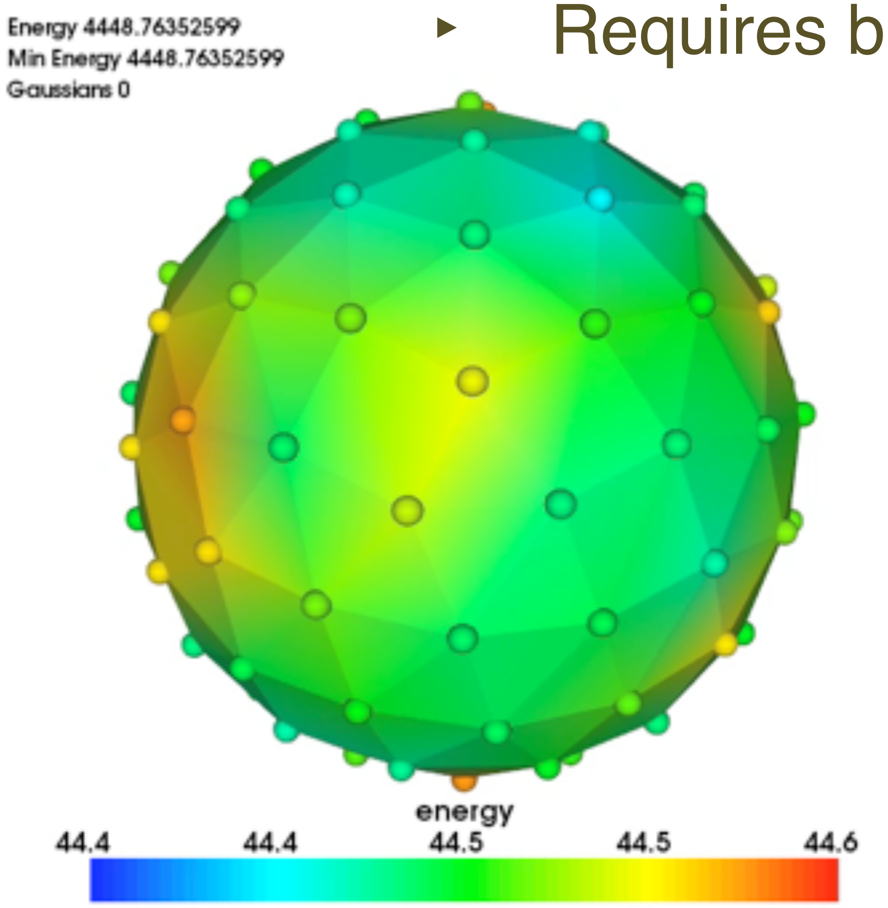
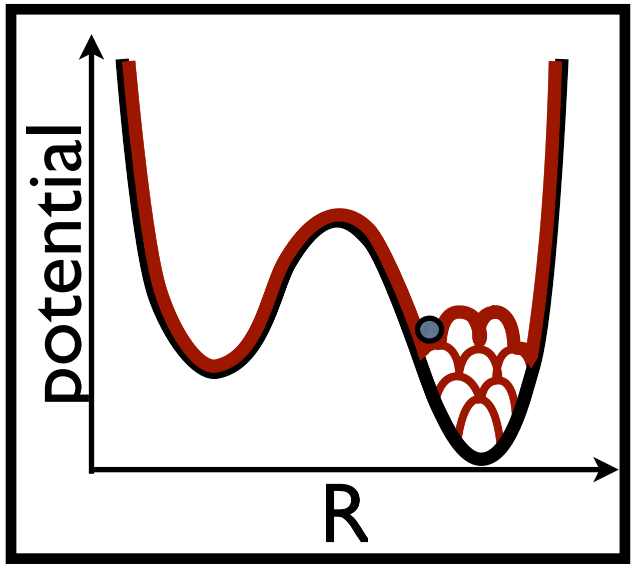
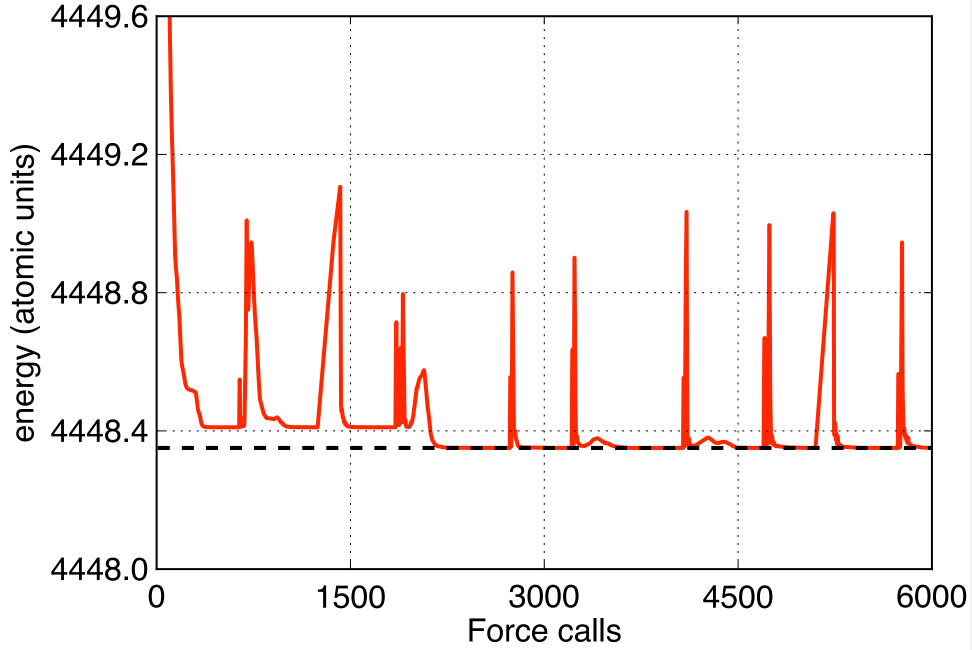
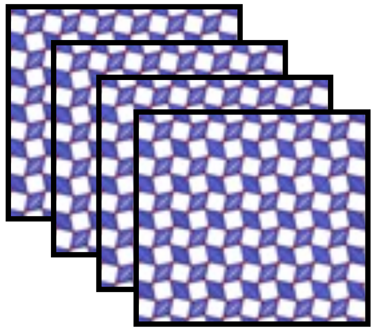






Application - TiO_2

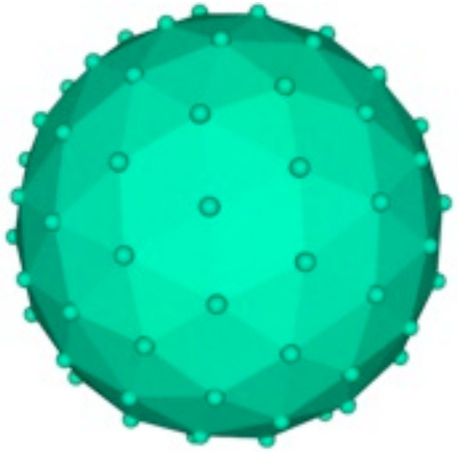


Relax and thermalise N_l lattices to T Kelvin.

MD

Determine unique PKAs: (Ti, O_I, O_{II})

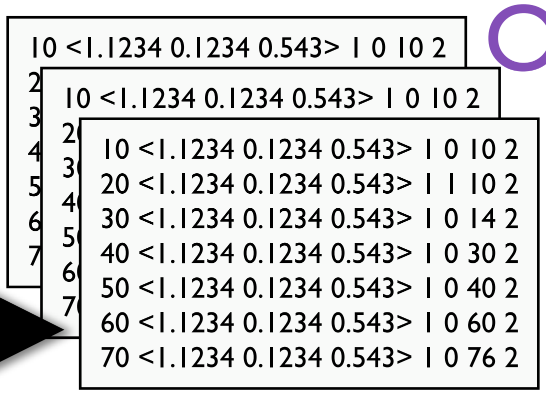
Choose E_{min}, E_{max} and step size ΔE.



Generate N_d PKA directions from solutions to the Thomson Problem

In each lattice, for each unique PKA, energy and direction, run MD collision cascades for t ps.

MD

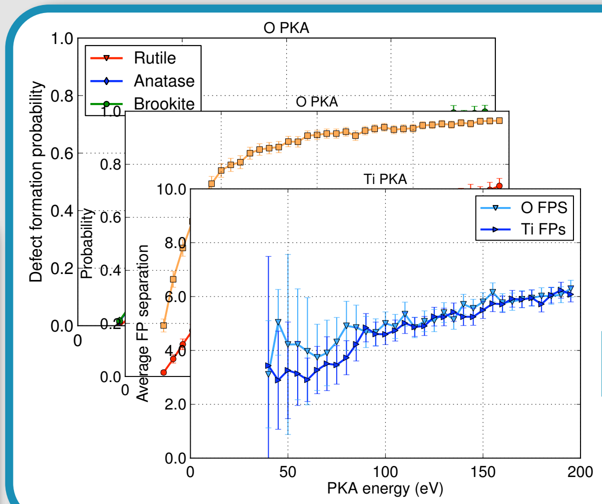


```
10 <1.1234 0.1234 0.543> 1 0 10 2
```

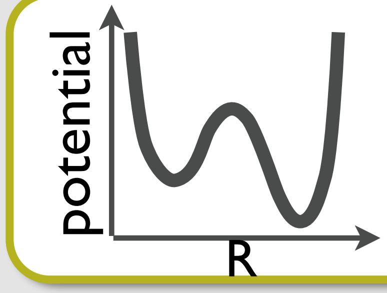
```
10 <1.1234 0.1234 0.543> 1 0 10 2
```

```
10 <1.1234 0.1234 0.543> 1 0 10 2
20 <1.1234 0.1234 0.543> 1 1 10 2
30 <1.1234 0.1234 0.543> 1 0 14 2
40 <1.1234 0.1234 0.543> 1 0 30 2
50 <1.1234 0.1234 0.543> 1 0 40 2
60 <1.1234 0.1234 0.543> 1 0 60 2
70 <1.1234 0.1234 0.543> 1 0 76 2
```

On-the-fly analysis: Frenkel pairs, replacements ...

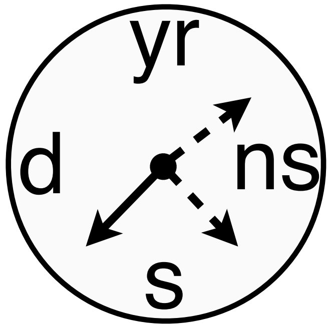


Post analysis: DFP, FP separations ...



Transition searches / OTF-KMC

LTSD

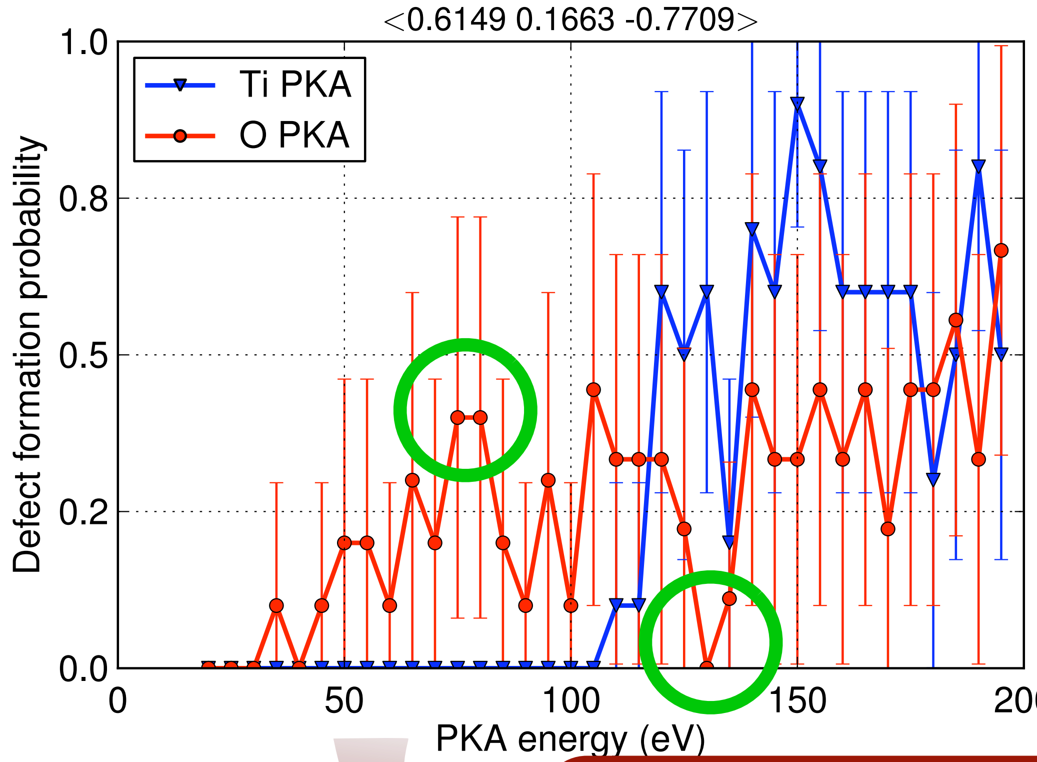


Analysis of **recovery time** as a function of PKA energy/specie

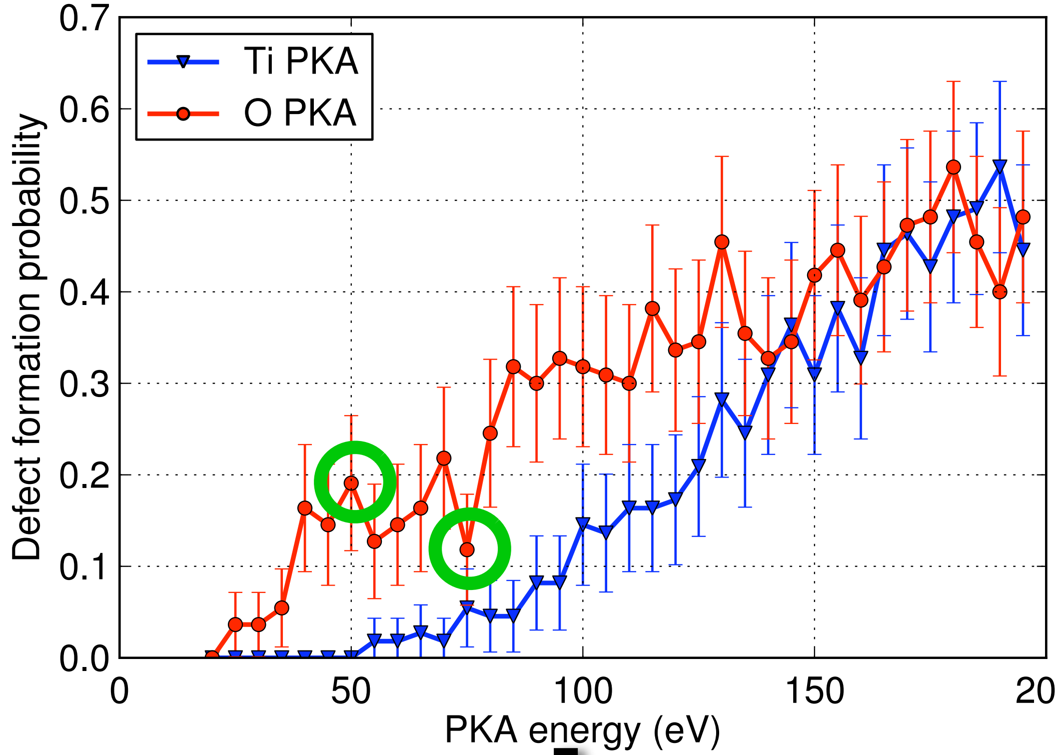
Application - TiO_2

- The importance of high sampling to generate representative results

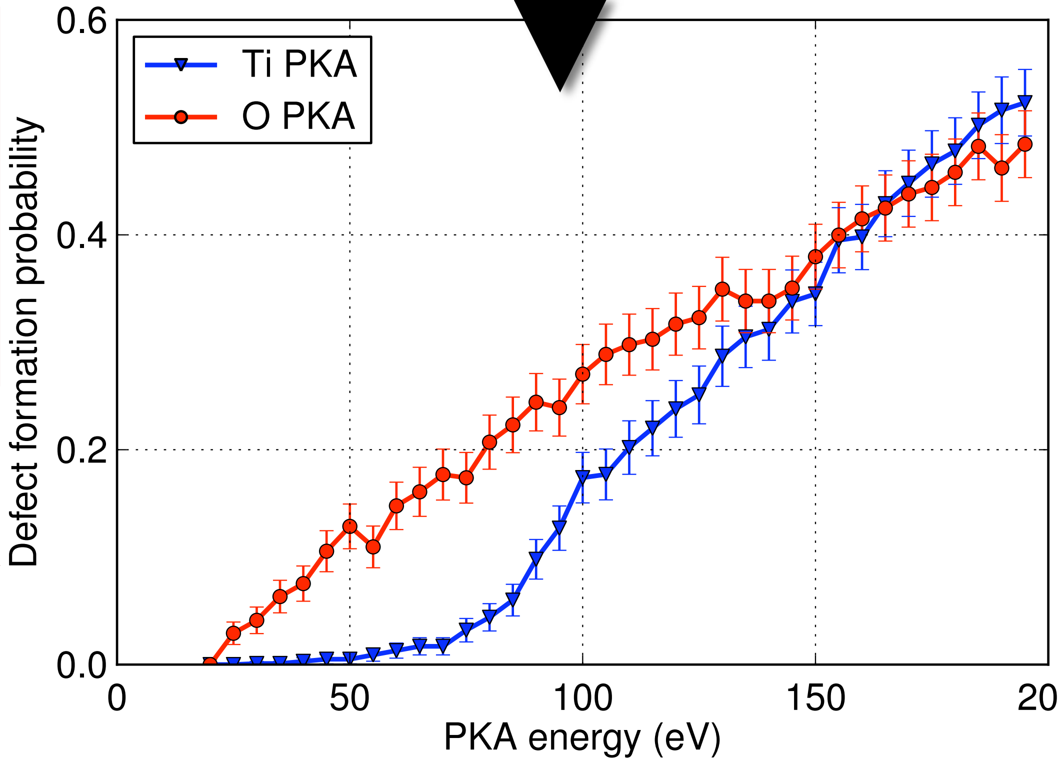
1 PKA direction = **720** MD simulations



10 PKA directions = **7200** MD simulations



The '*noise*' generated from sampling 1 PKA direction is significantly reduced as sampling increases.



100 PKA directions = MD **72000** simulations

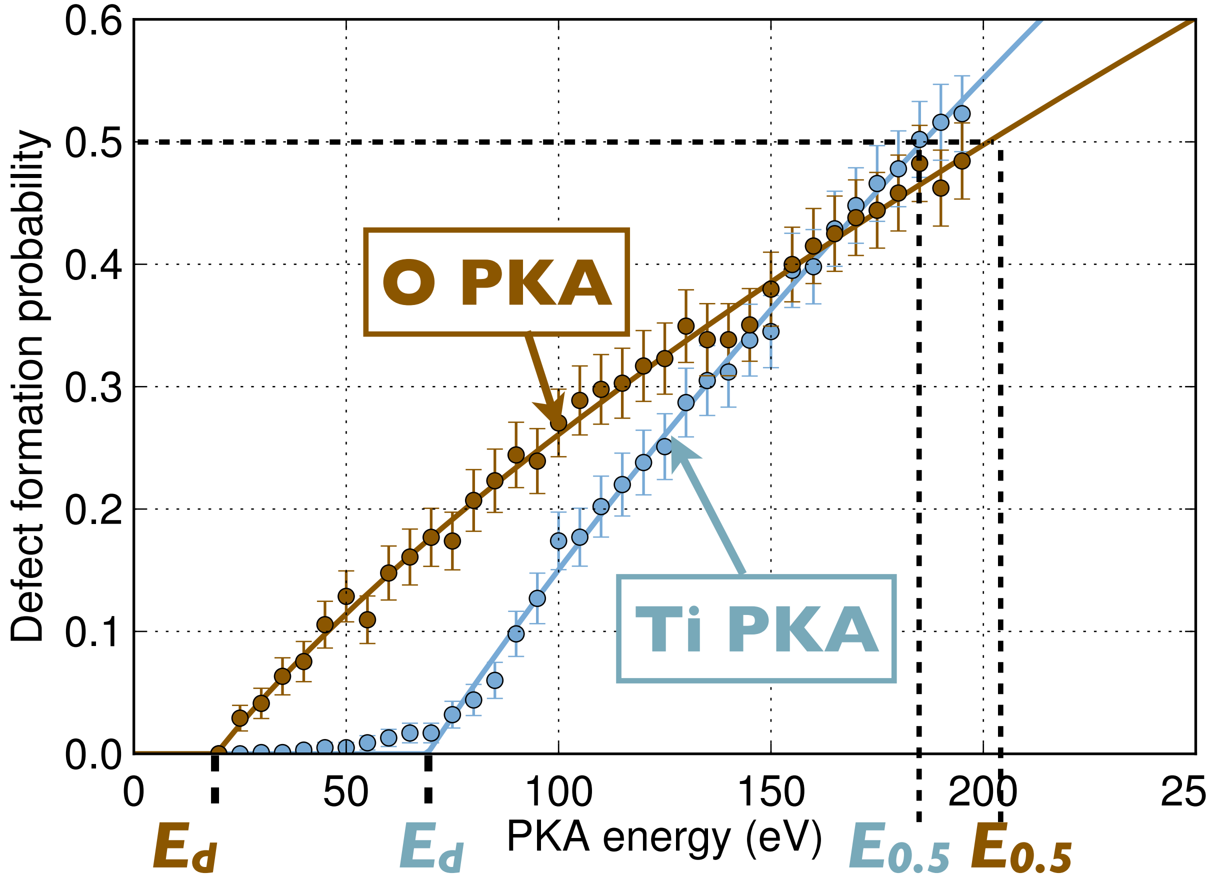
- **Defect formation probability (DFP)** - The probability of defect formation at a given PKA energy over all **directions** and **lattices**.

*Error bars represent 95% confidence interval in SEM

Application - TiO_2

- **Quantitative analysis of the ballistic phase:**
  - DFP as a function of PKA energy

Rutile



$$DFP(E_{pka}) = \begin{cases} 0 & \text{if } E_{pka} \leq E_d \\ \frac{1}{\beta}({E_{pka}}^{\alpha} - {E_d}^{\alpha}) & \text{if } E_{pka} > E_d \end{cases}$$

Polymorph	**O PKA**		**Ti PKA**	
	E_d	$E_{0.5}$	E_d	$E_{0.5}$
Rutile	**19**	201	**69**	186
Brookite	**19**	105	**31**	120
Anatase	**15**	121	**39**	115

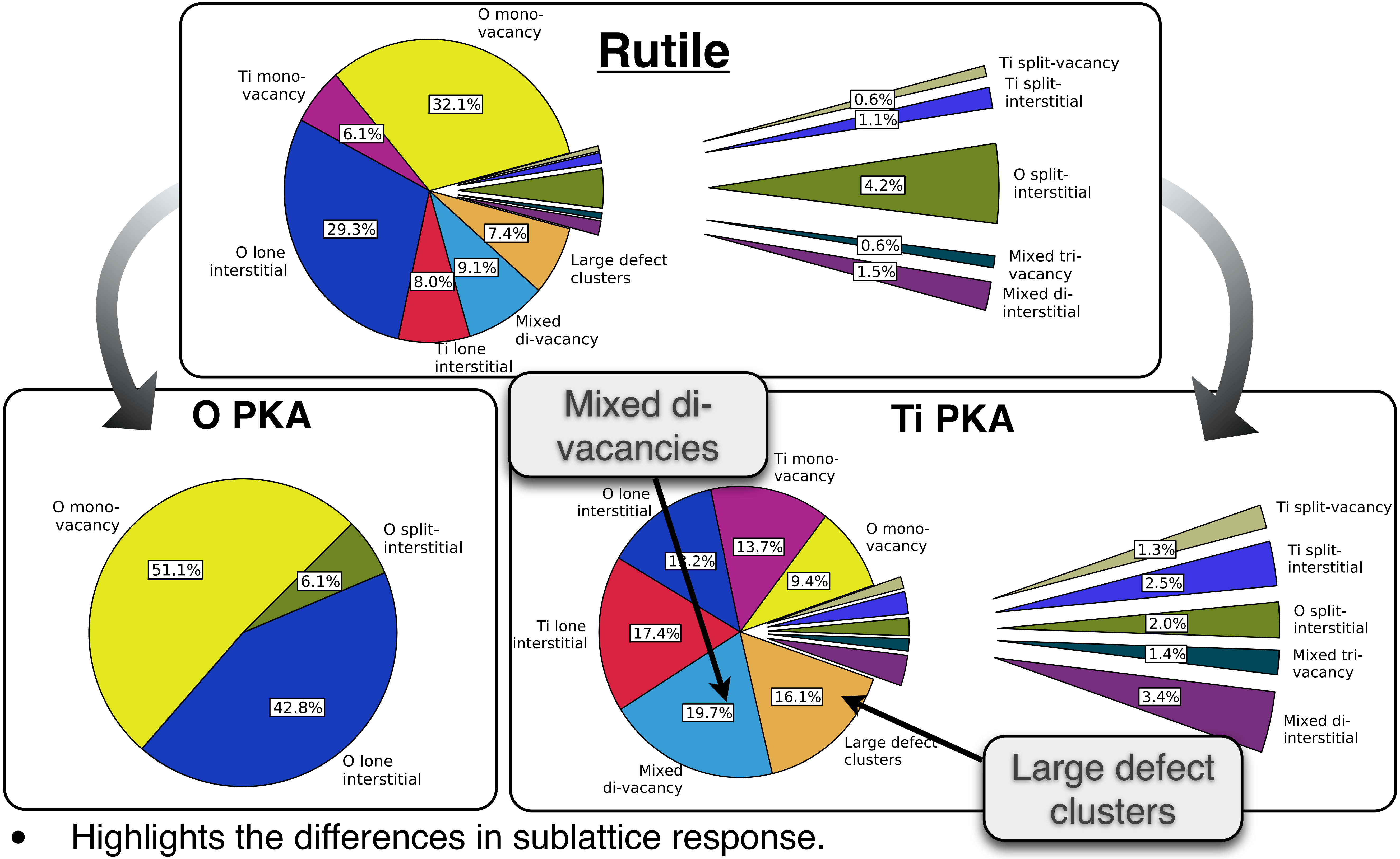
*Energies in eV

*$E_{0.5}$ - the energy required to achieve 50% DFP

- Defect formation is **probabilistic over a large energy range**, up to at least **300-400 eV**.
- Although the **E_d is lower for O**, defect formation is more probable from Ti displacements at higher energies.
- **Defect formation requires more energy** in **Rutile** over the energy range studied - particularly from Ti PKAs.

Application - TiO2

- **Taking an in-depth look into Rutile - Defect cluster analysis**



Rutile

O PKA

Ti PKA

- Highlights the differences in sublattice response.
- Provides a good foundation for studies of defect migration and FP recombination *i.e. KMC*

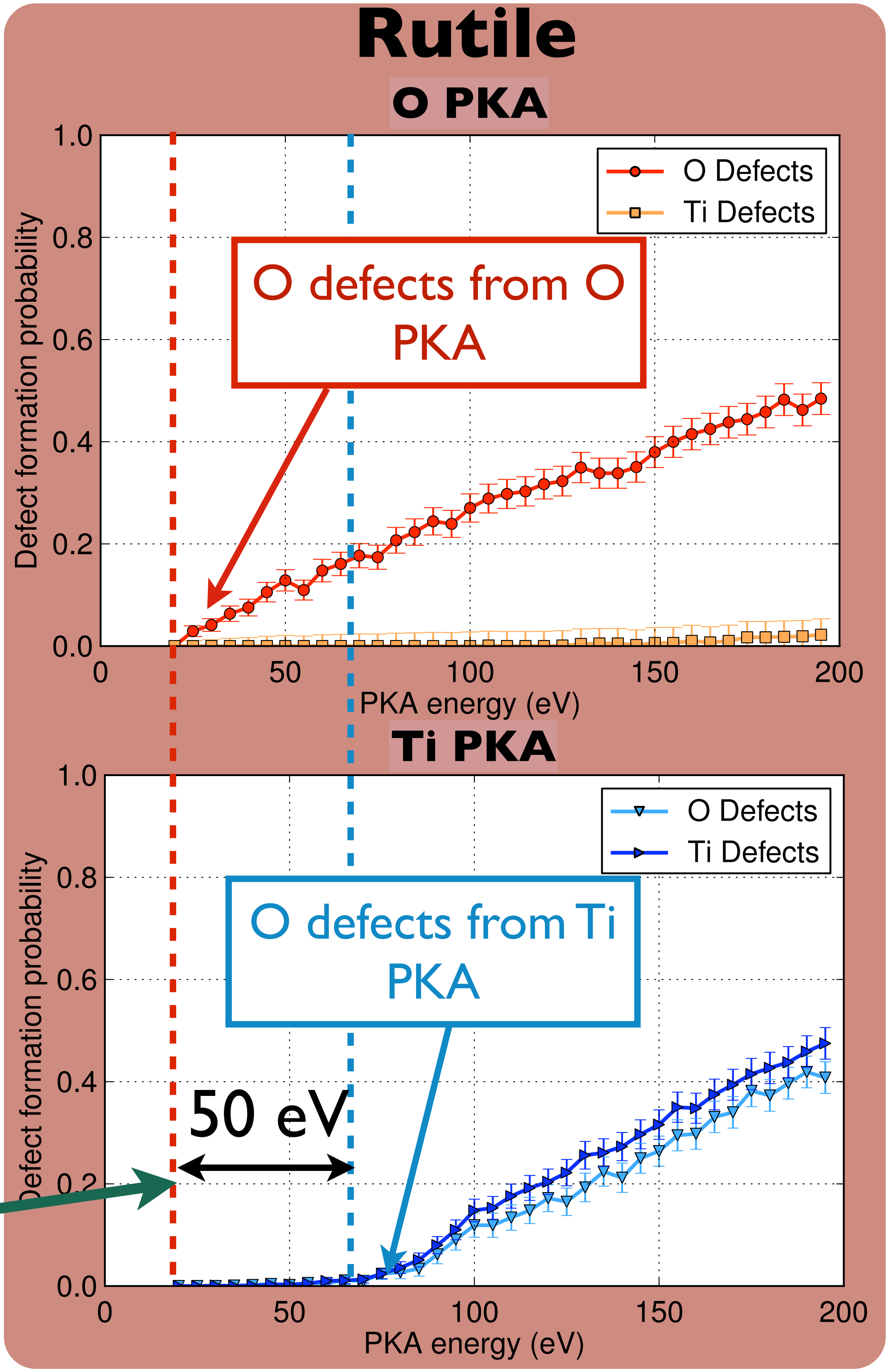
Application - TiO_2

- **DFP** categorised by the **atomic specie** of the defects.

Across all polymorphs

- ◉ Predominantly O defects created by O PKAs.
- ◉ Even proportion of Ti and O defects from Ti PKAs

- **Implications for TRCS (or other methods that rely on anion vacancies)**
  - Method traditionally only detects **first emission** i.e. **O defects from O PKAs**
  - **Second emission** relating to **O defects from Ti PKAs.**
    - *Only if energy gap is sufficiently large



Curtin University

Application - TiO_2

- **Quantitative analysis of the ballistic phase - Comparison with experiment:**
  - Experimental values of E_d for the O PKA are significantly lower than observed from the MD simulations, for example:
    - **TEM**
      - ~ 33 eV[1]
    - **TRCS** (Time-resolved Cathodoluminescence Spectroscopy)
      - ~ 39 eV rutile 45-50 eV for other oxides[2].
- **Reasons for discrepancies**
  - **TEM** -
    - Relies on observable defect structures (saturation of point defects)
    - Always overestimate E_d.
  - **TRCS** -
    - Displaces O atoms with electron beam - observes decay of excited F-centers.

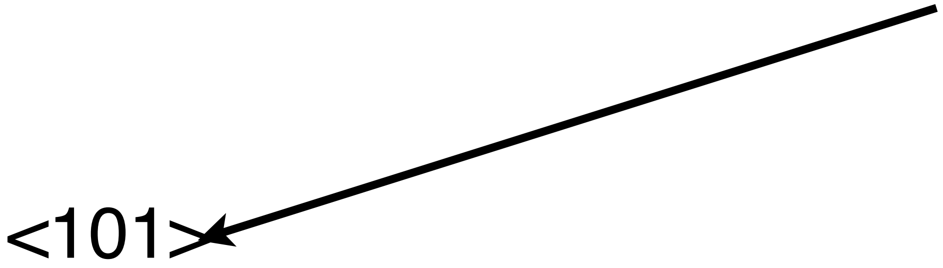
---

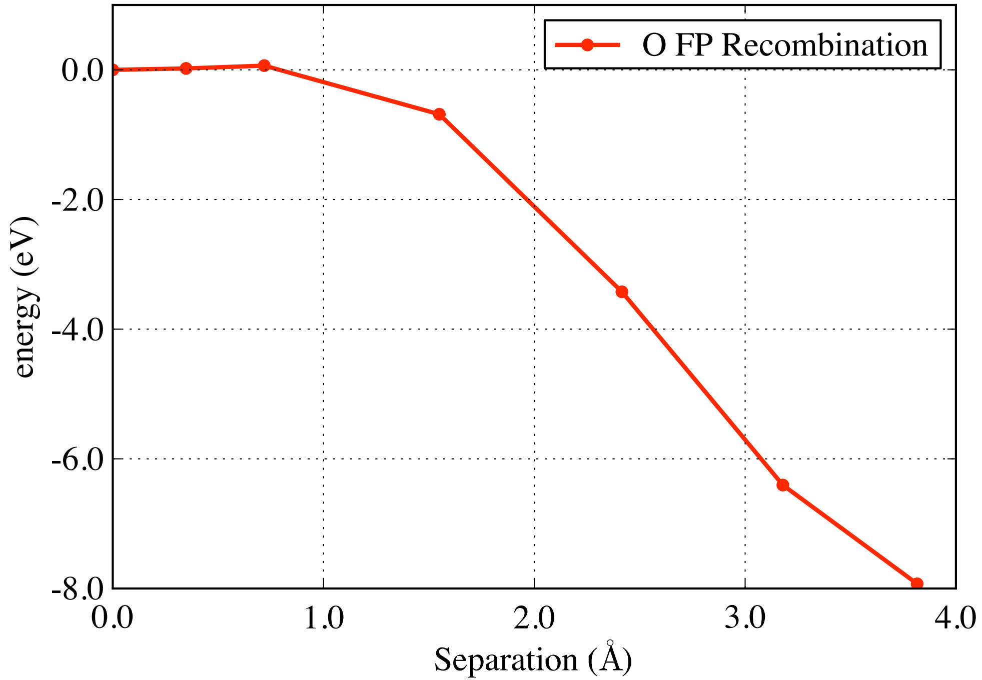
[1] E. C. Buck, Radiation Effects and Defects in Solids **133**, 141-152 (1995).

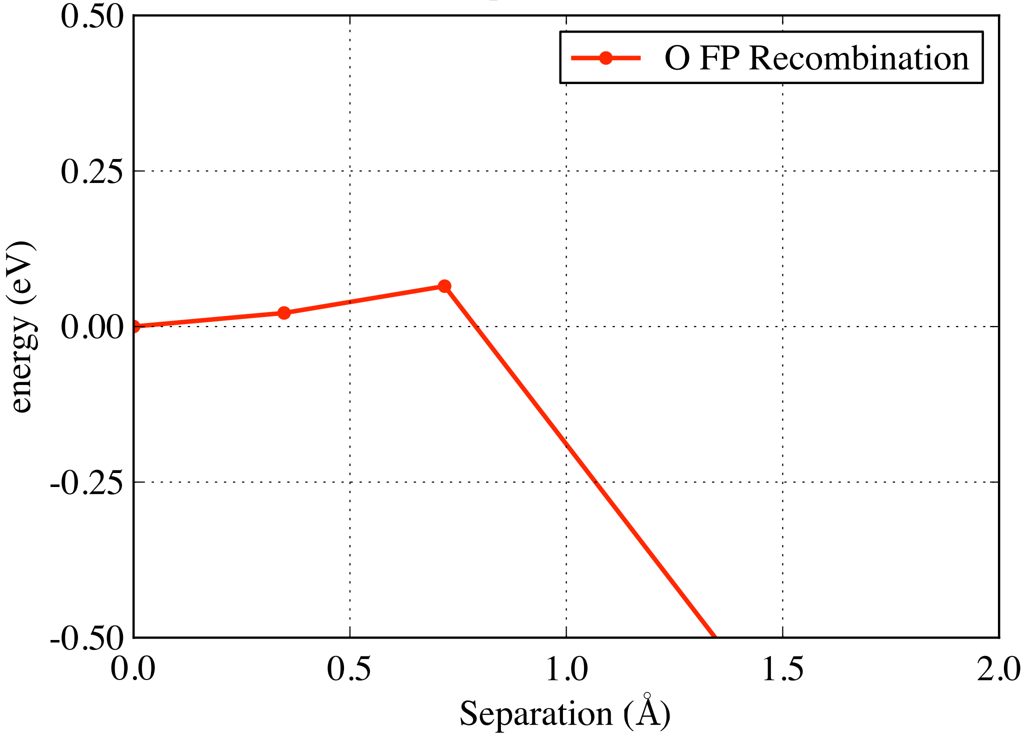
[2] K. L. Smith, R. Cooper, M. Colella, and E. R. Vance, Materials Research Society Symposium Proceedings **663**, 373–380 (2001).

Application - TiO_2

- **What can happen in 25 ns? (Rutile)**
  - **Simple O Frenkel pair annihilation - separation around 4 Å**







Single barrier process **0.07 eV**

- At *small* separations O FP recombination occurs on the ps time scale.
- At what separation do we see a marked increase in FP recombination barrier?

Application - TiO$_2$

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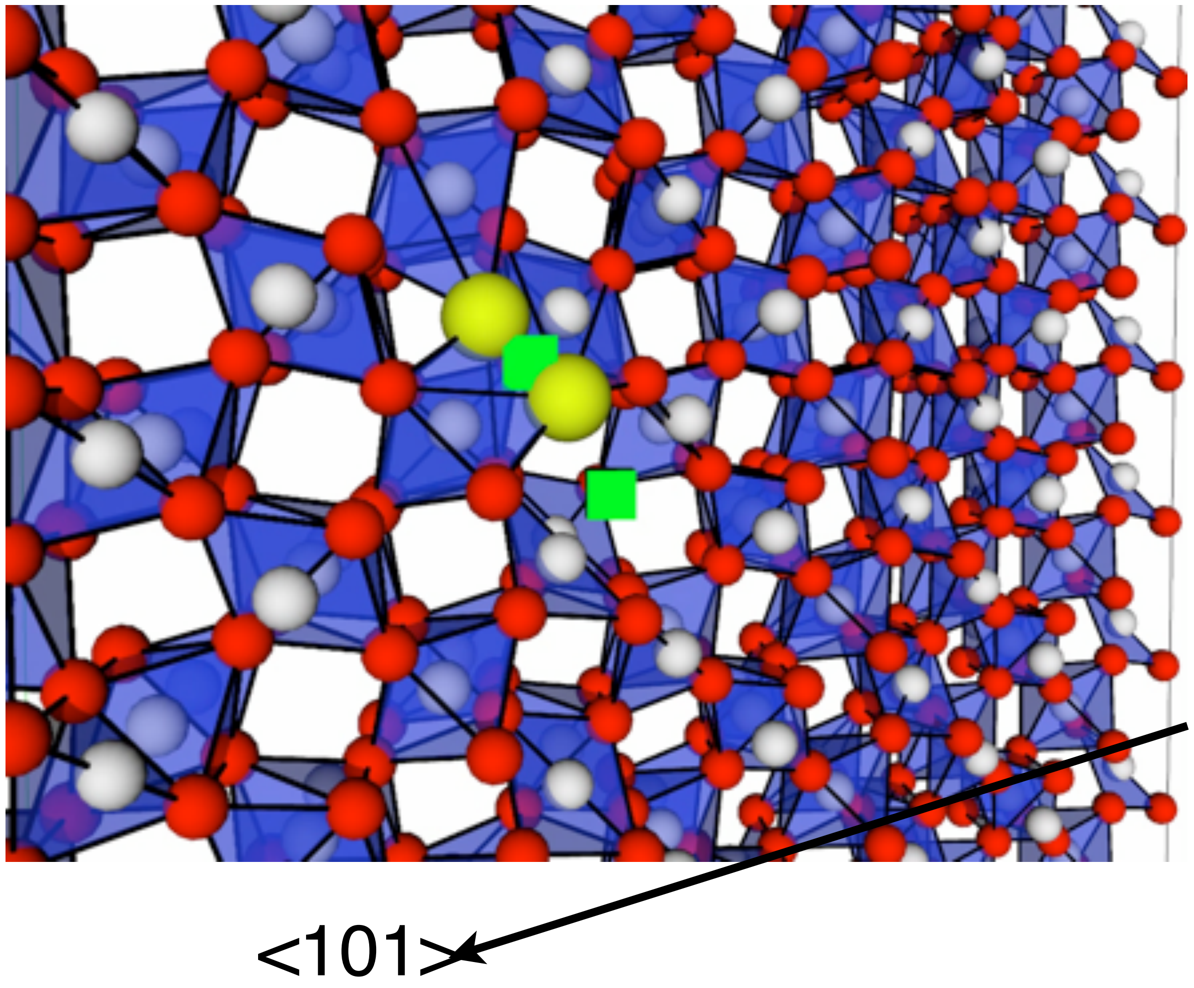
  - **Simple O Frenkel pair annihilation - separation around 4 Å**



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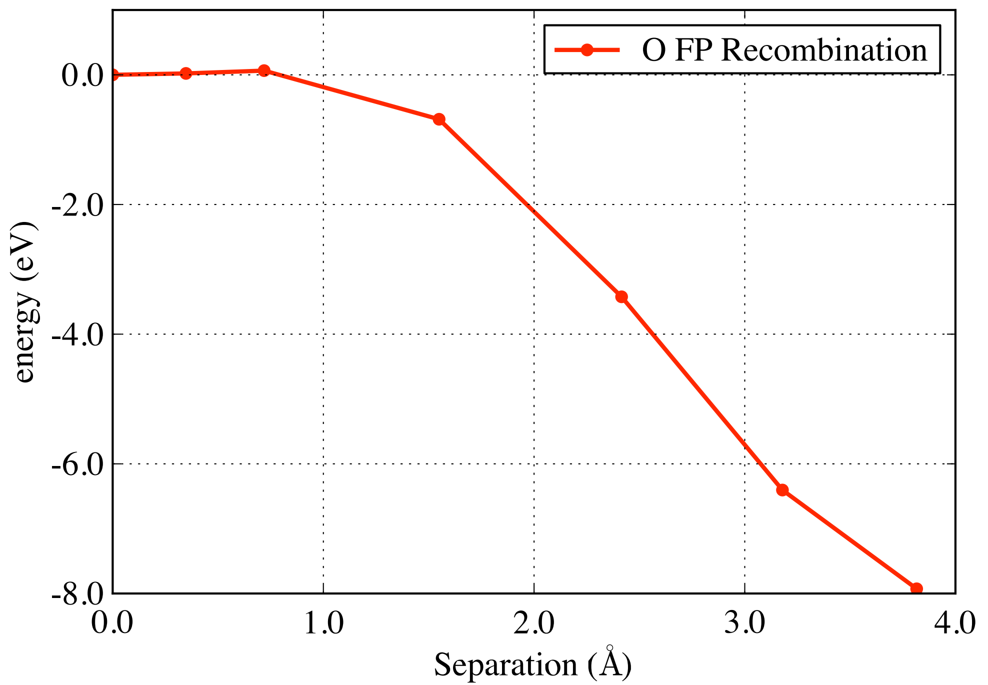
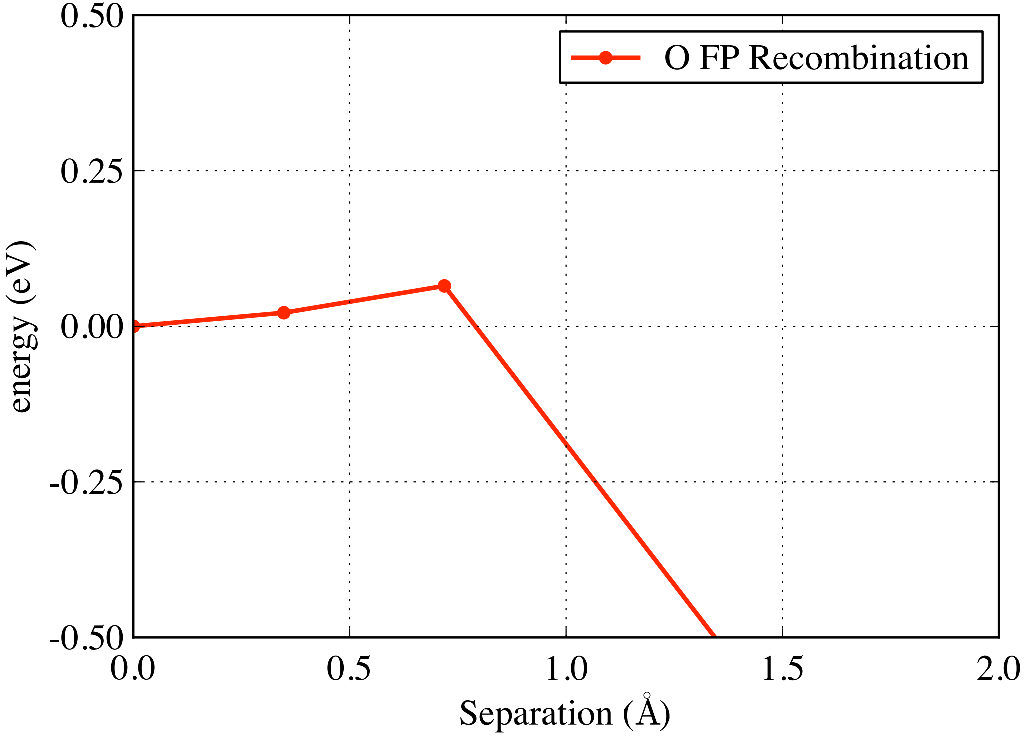
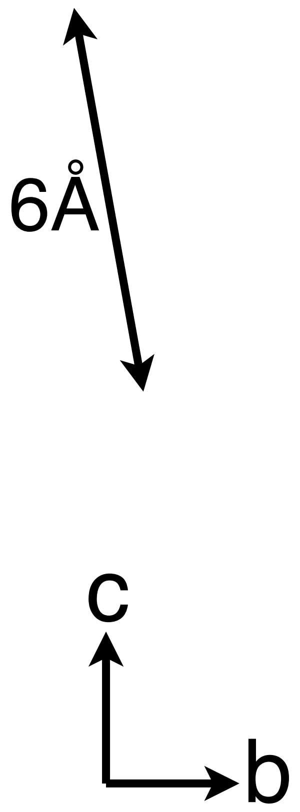




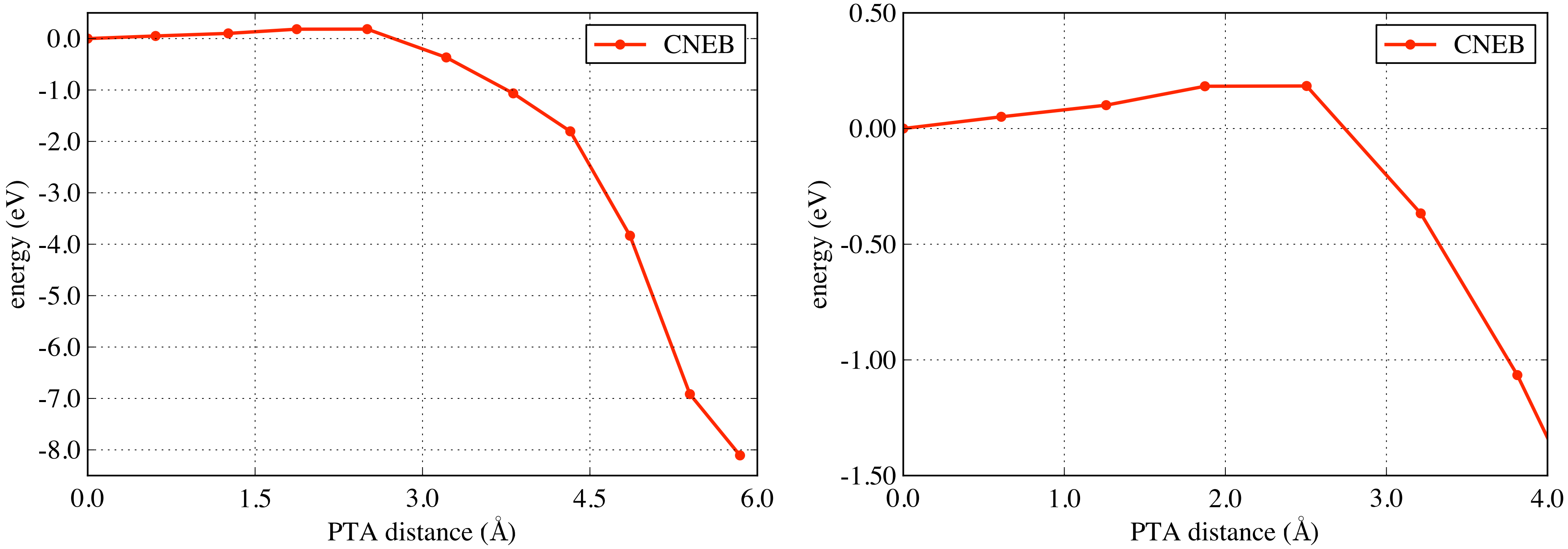
Single barrier process
0.07 eV

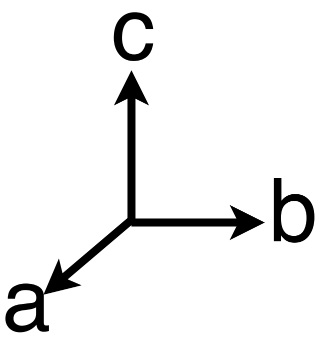
Application - TiO_2

- **O Frenkel pair annihilation - separation of around 6 Å.**



Migration along the c-axis

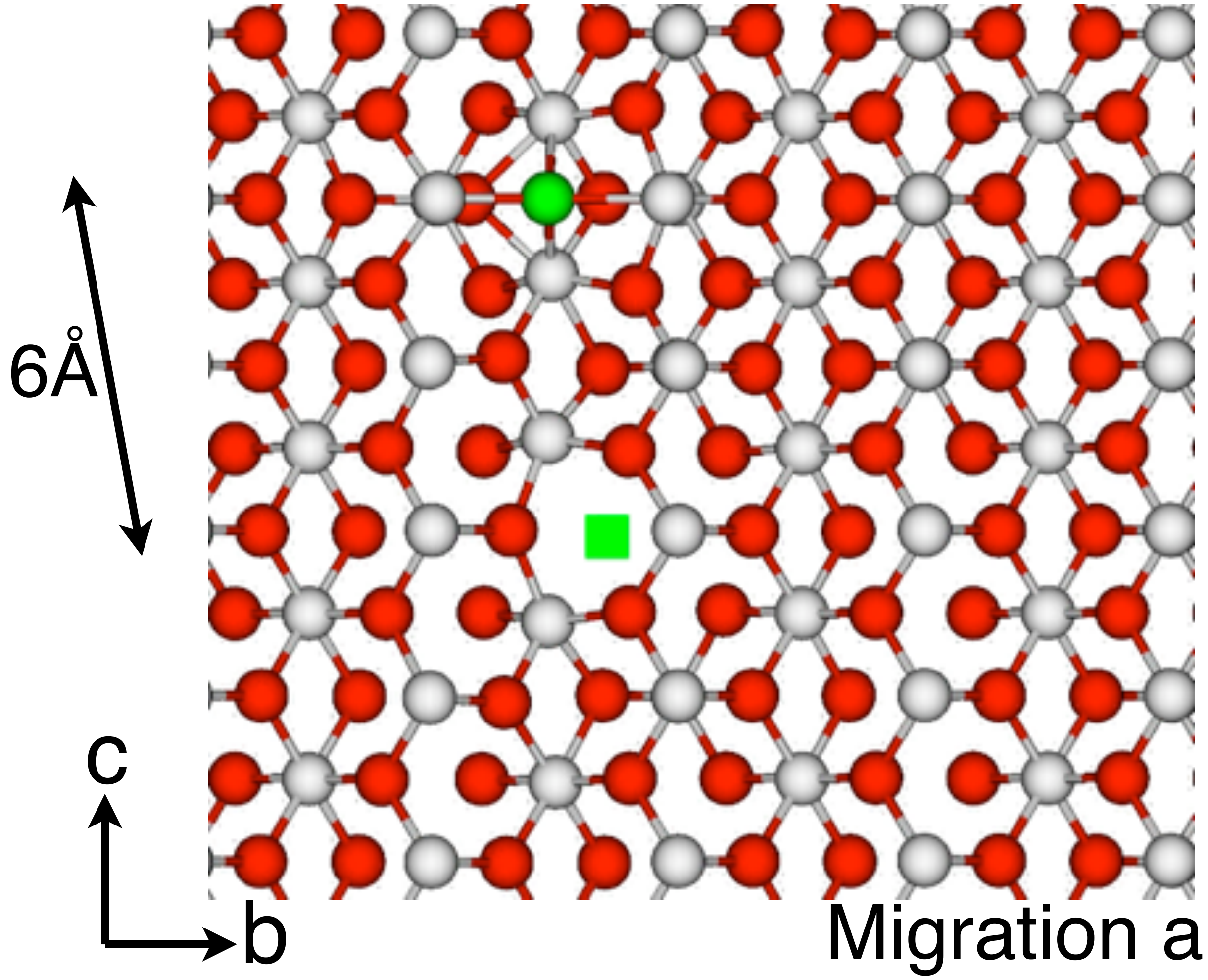


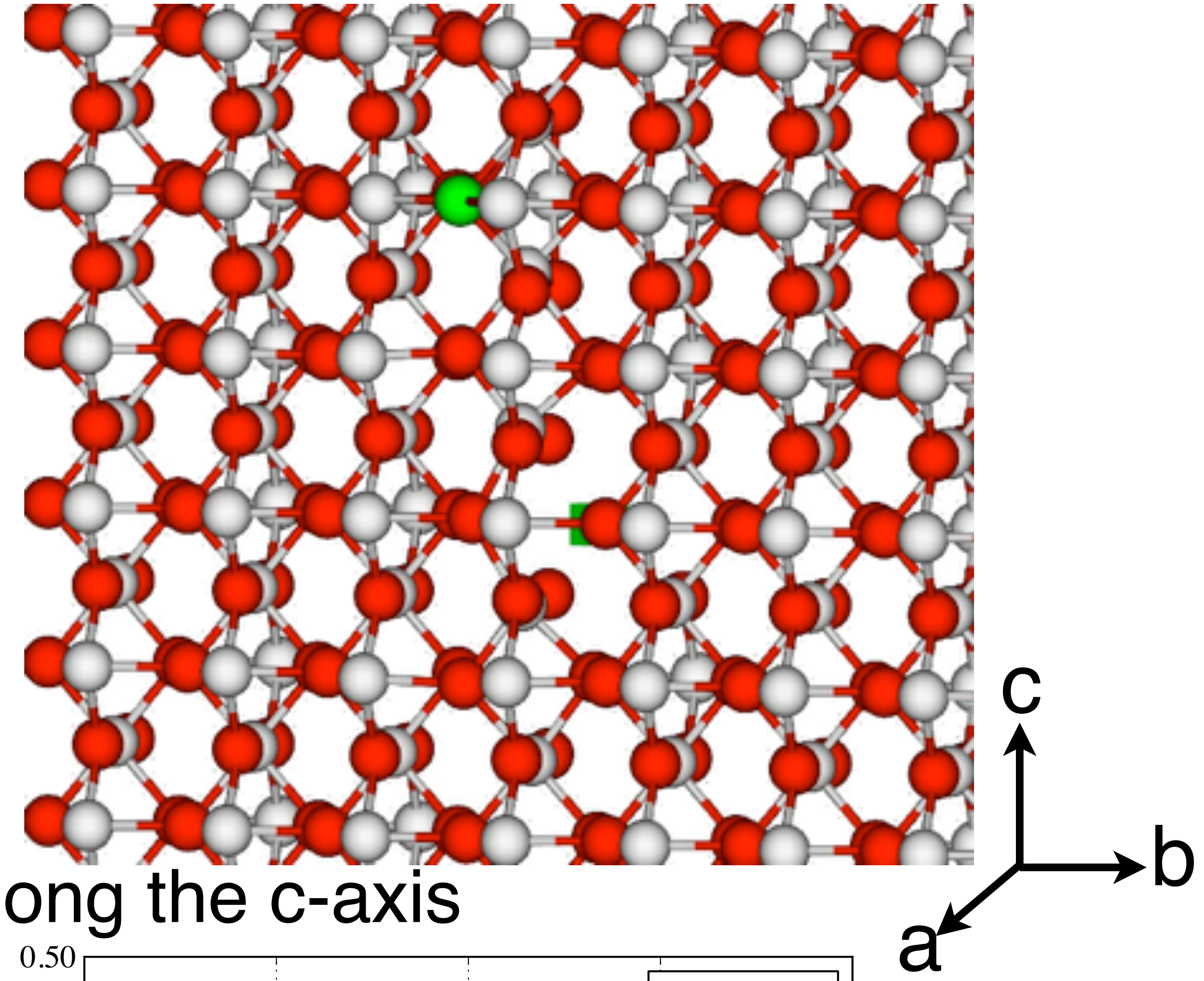


Single
barrier
process
0.18 eV

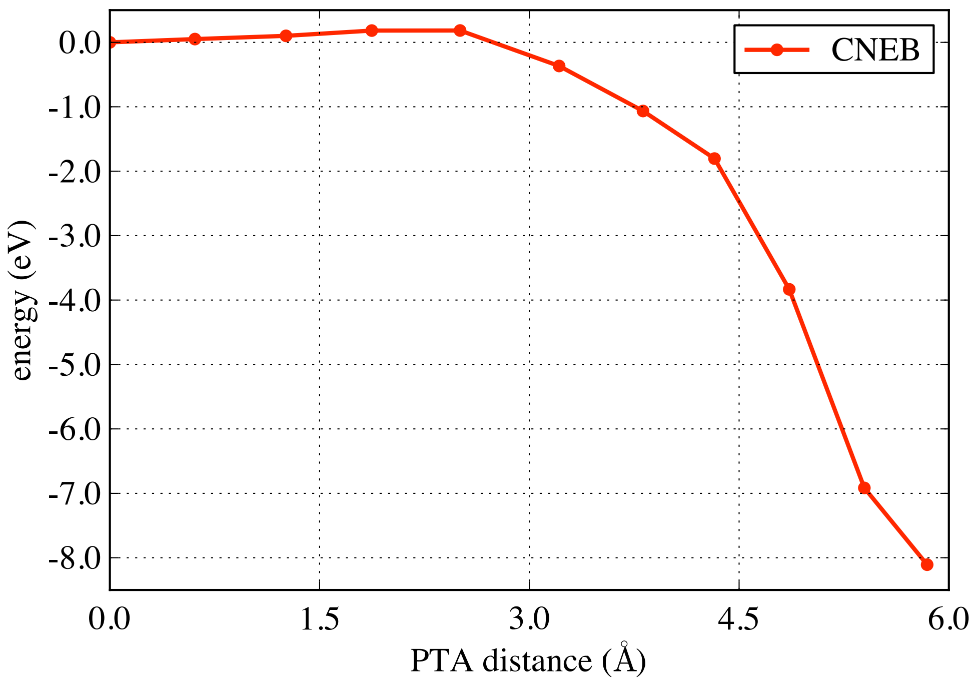
Application - TiO_2

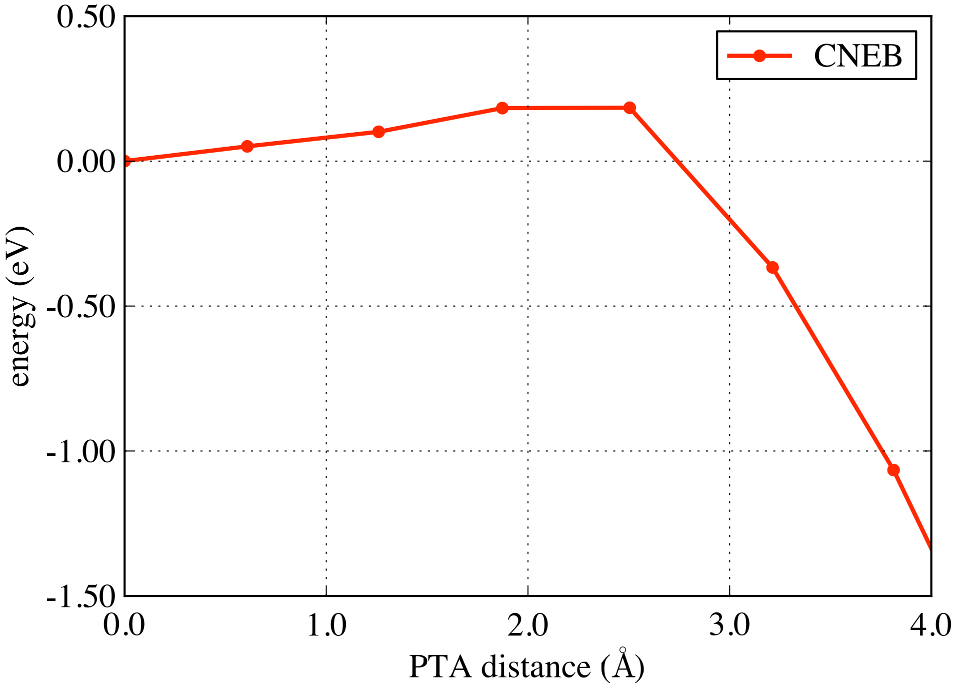
- **O Frenkel pair annihilation - separation of around 6 Å.**





Migration along the c-axis

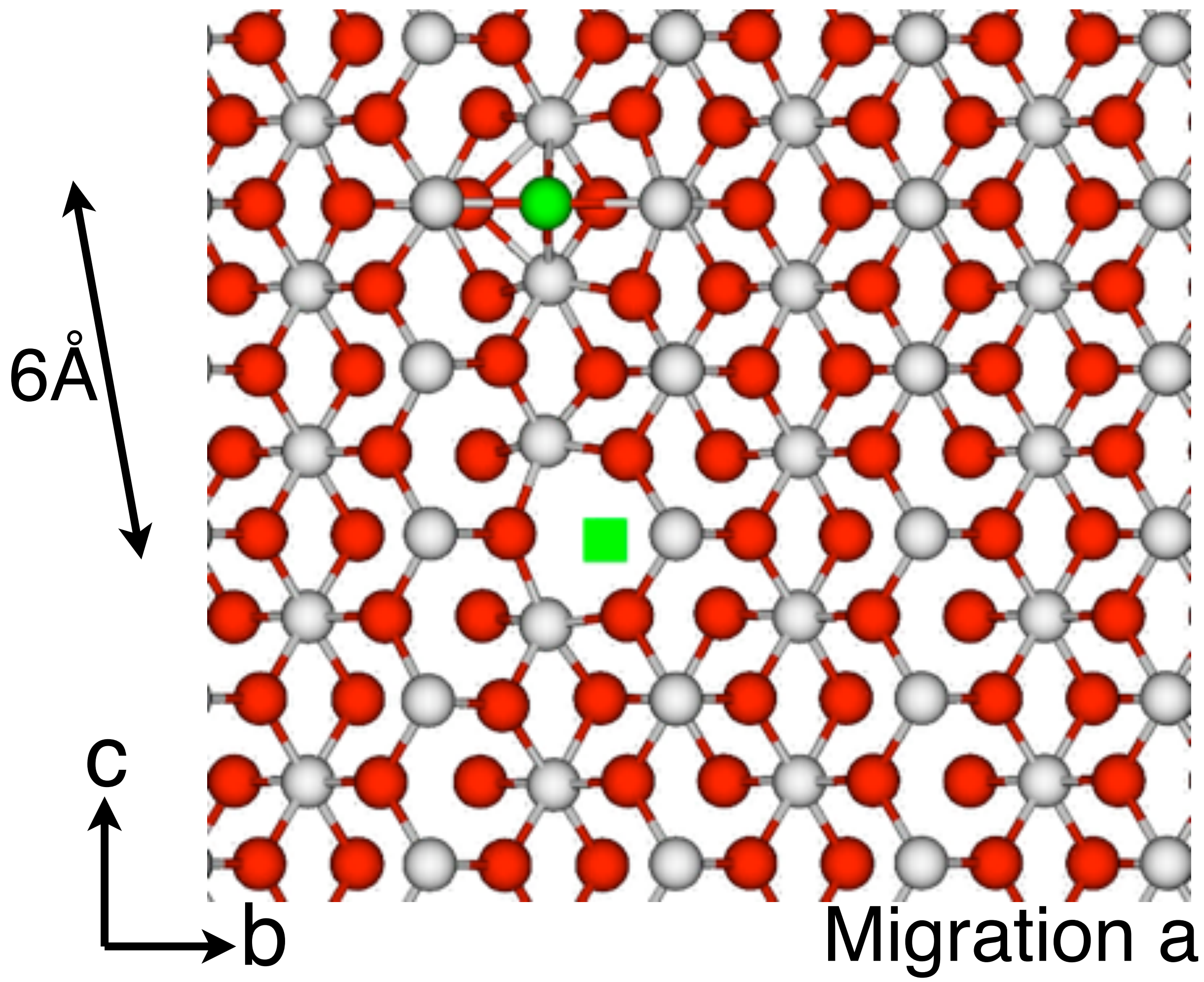


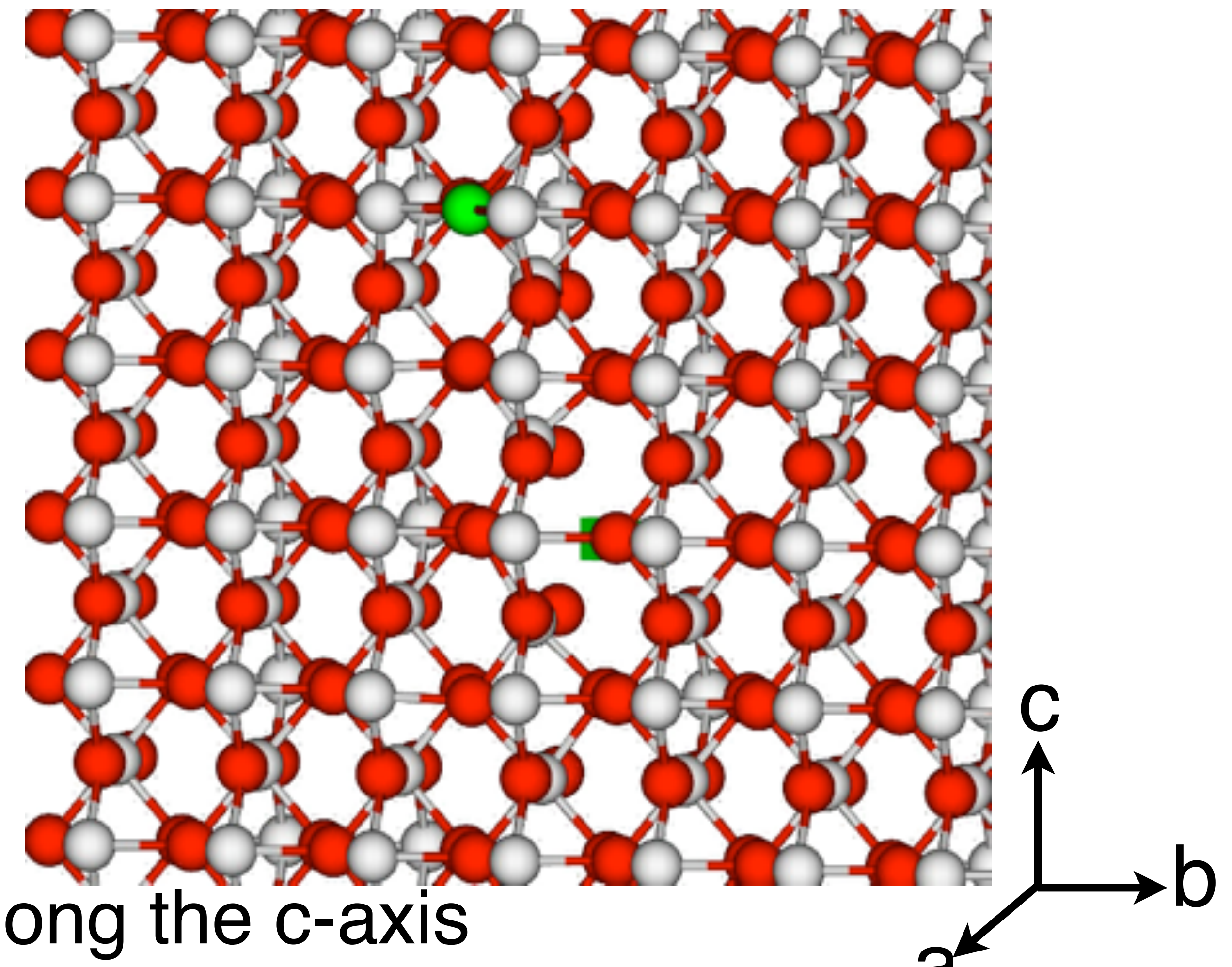


Single barrier process **0.18 eV**

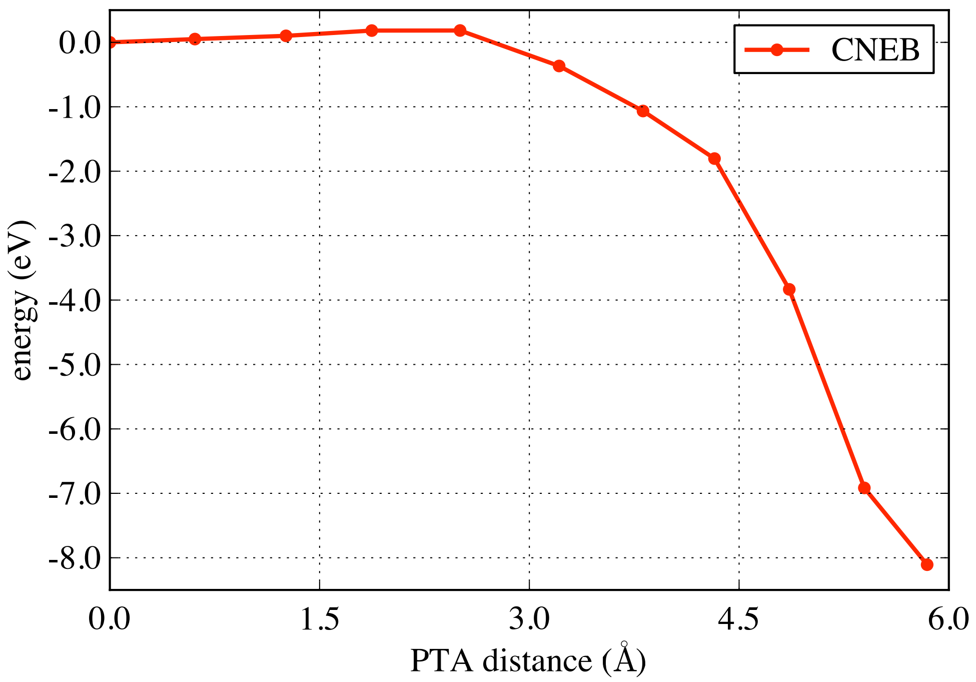
Application - TiO_2

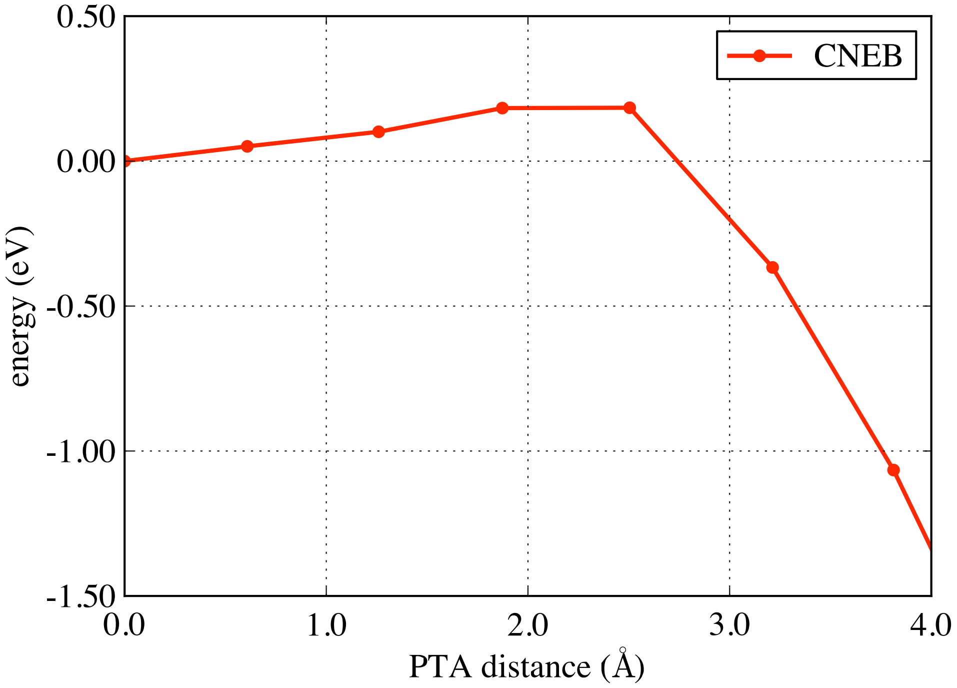
- **O Frenkel pair annihilation - separation of around 6 Å.**





Migration along the c-axis



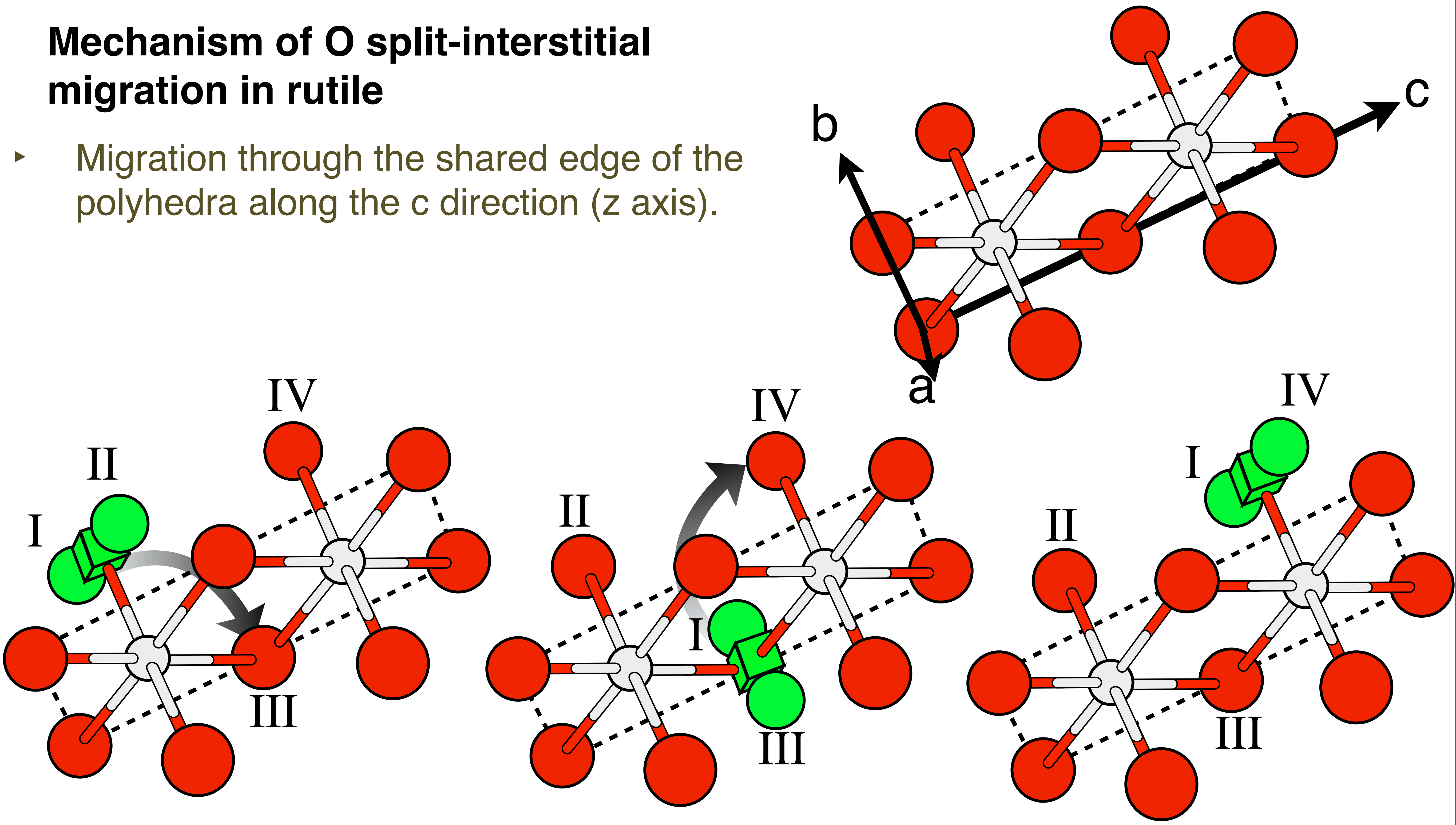


Single barrier process **0.18 eV**

Application - TiO$_2$

Mechanism of O split-interstitial migration in rutile

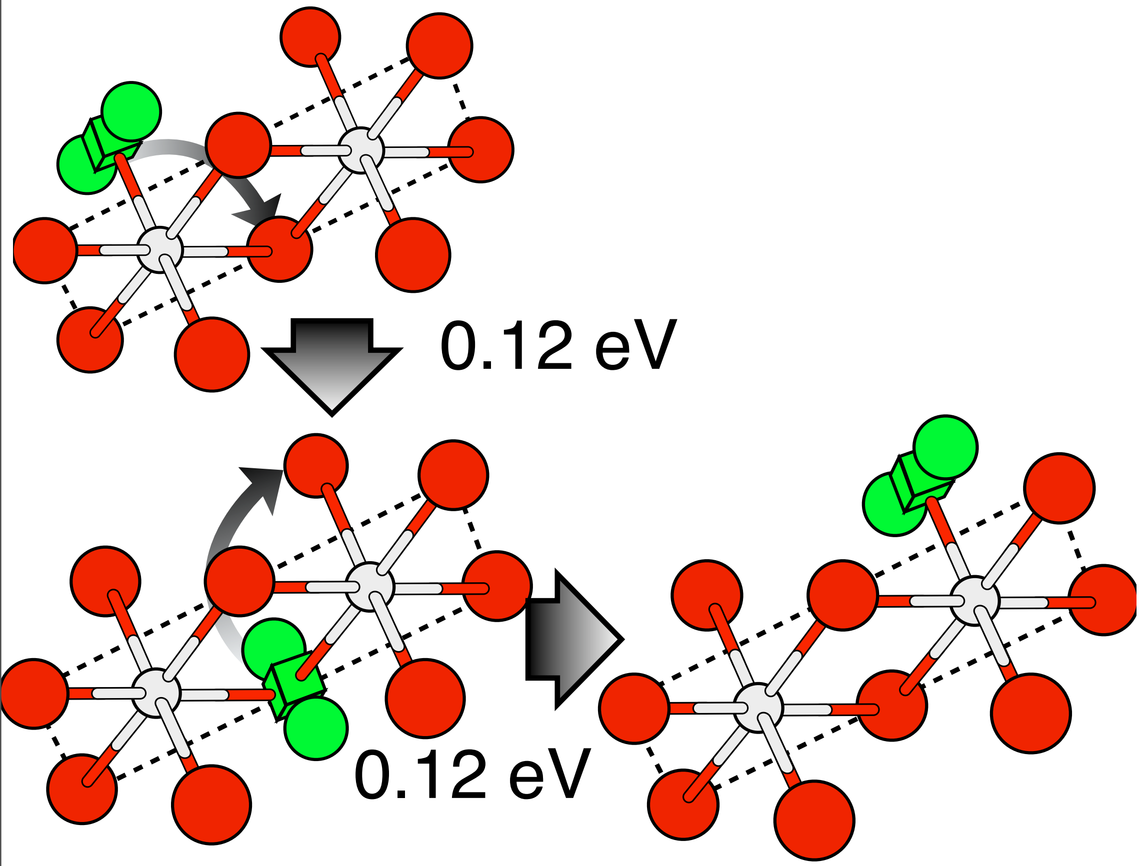
- Migration through the shared edge of the polyhedra along the c direction (z axis).



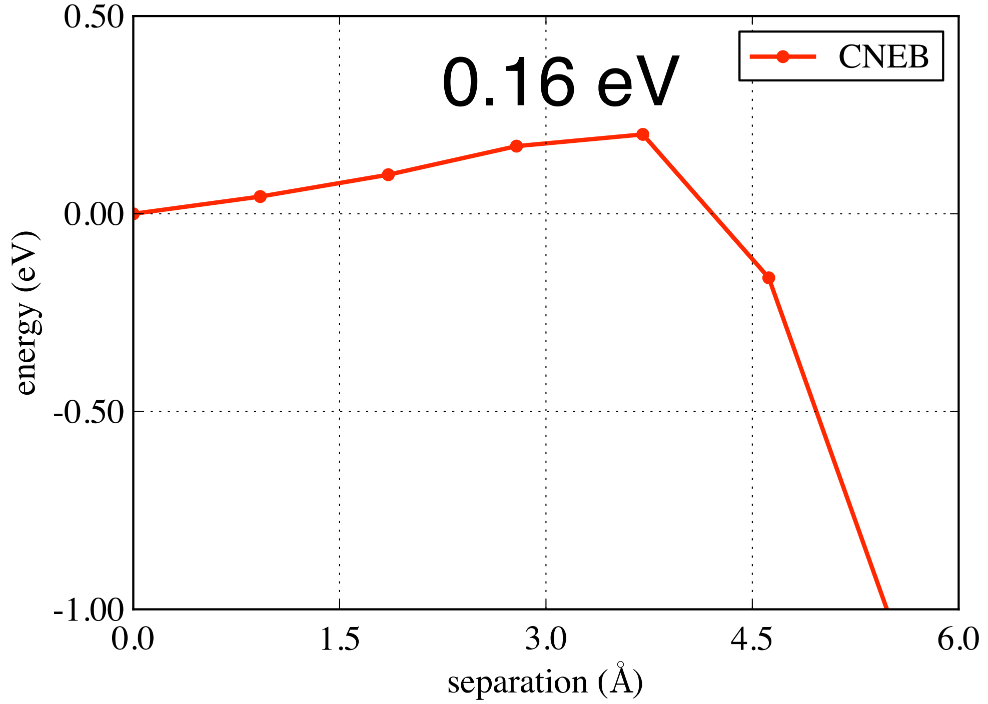
- **TODO: Is this migration possible in anatase and brookite?**

Application - TiO_2

- In bulk the transition is a **two stage process** with barriers around 0.12 eV.



- In the presence of a local vacancy, the mechanism has a very low single barrier for annihilation.



Application - TiO_2

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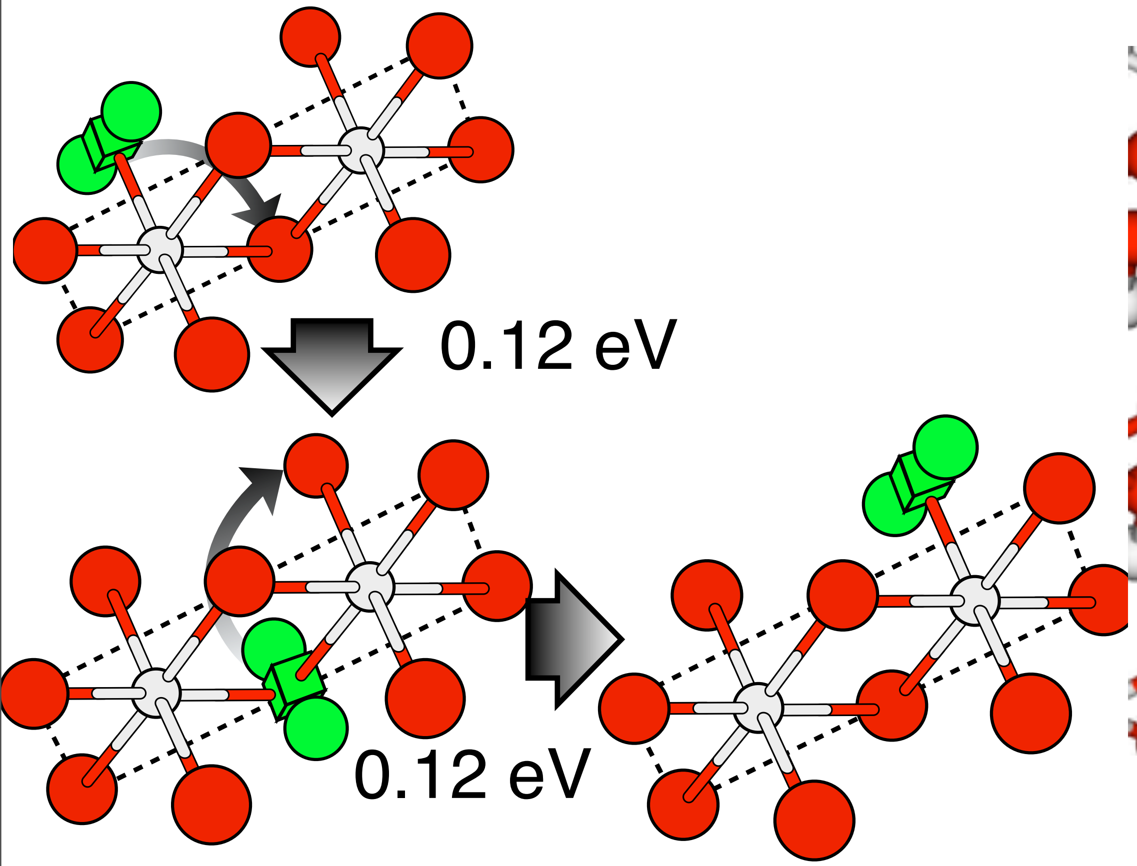

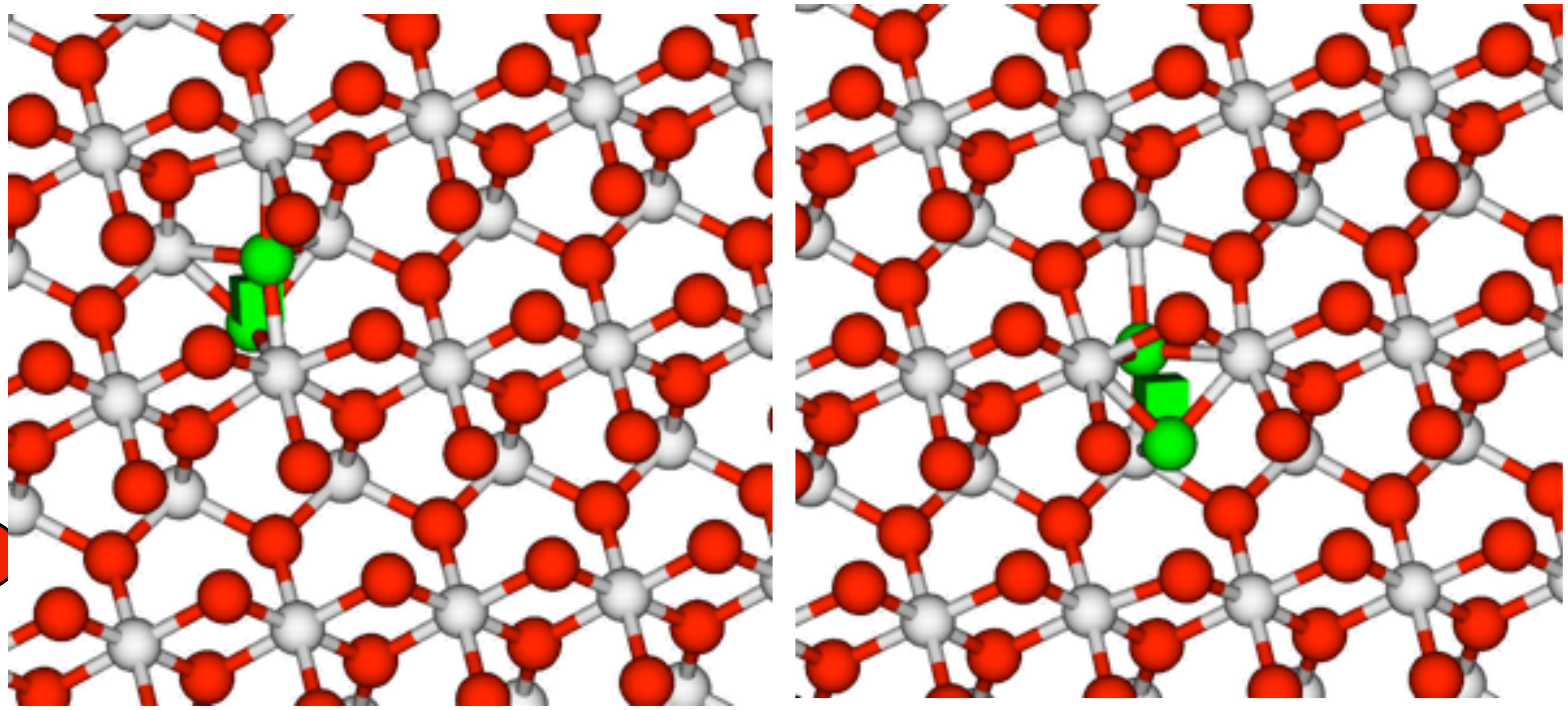

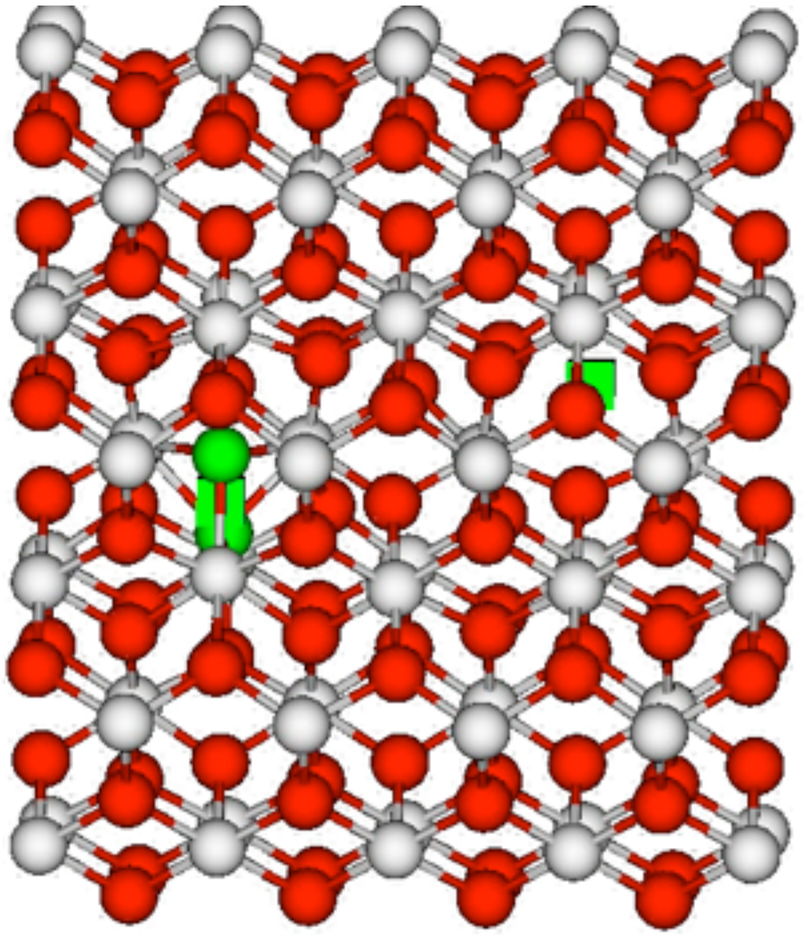

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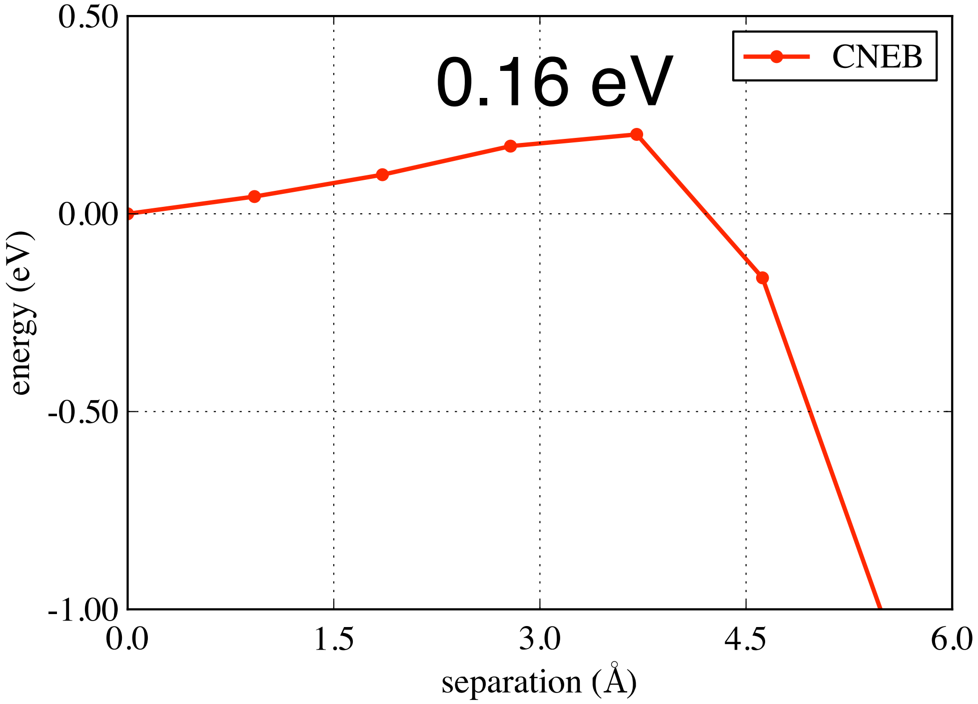

Application - TiO_2

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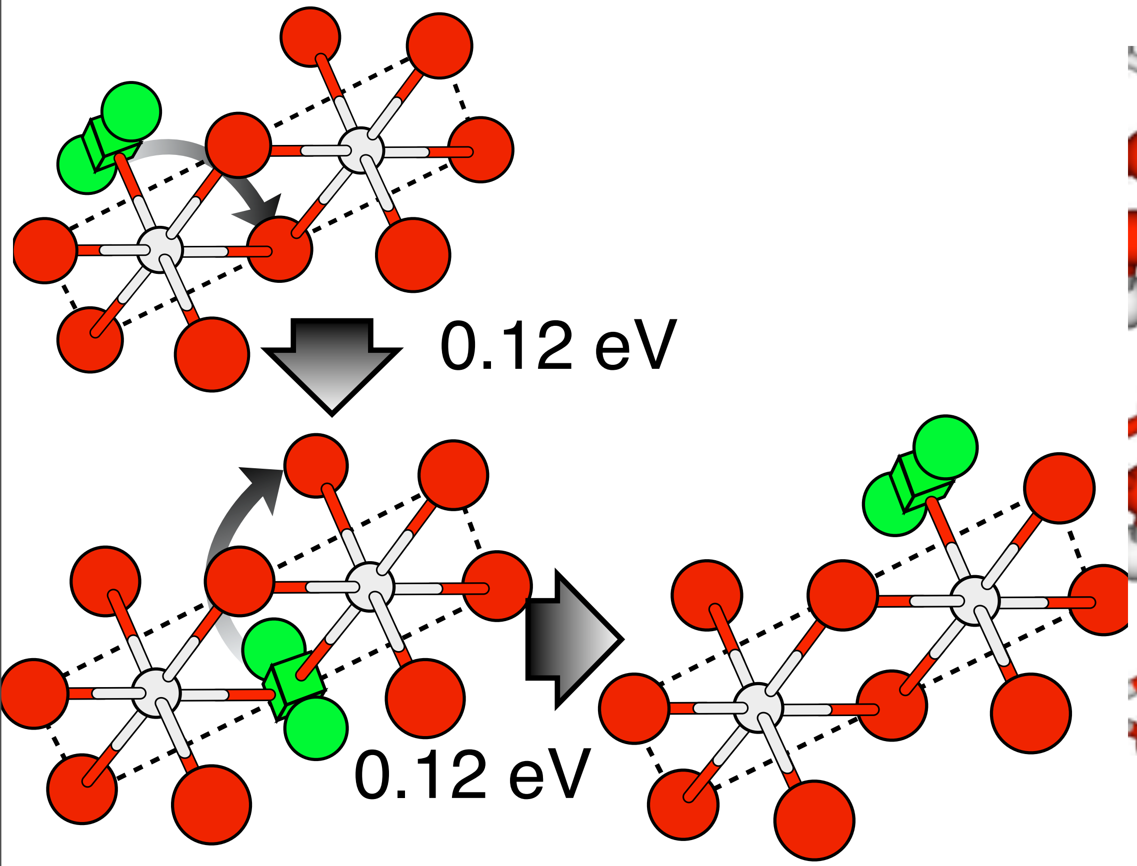

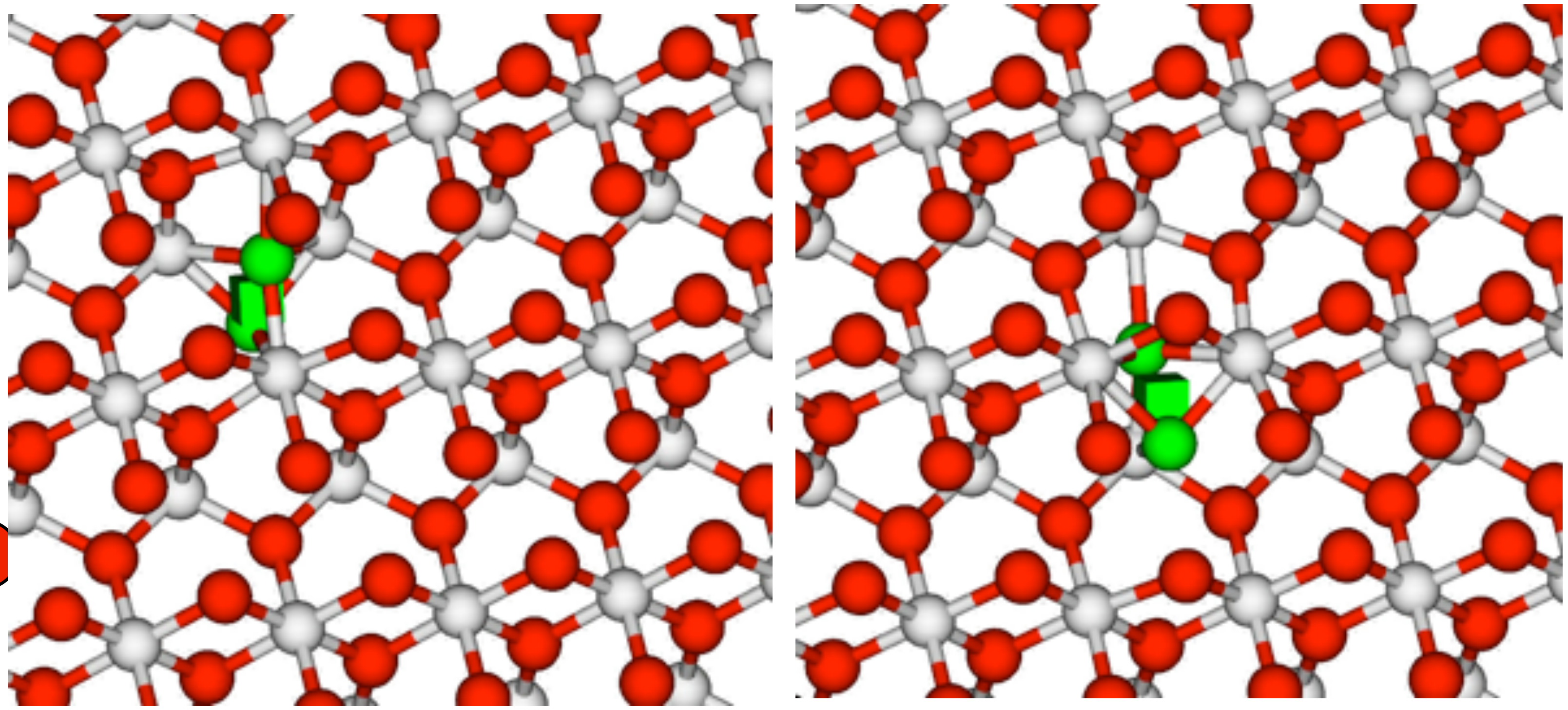

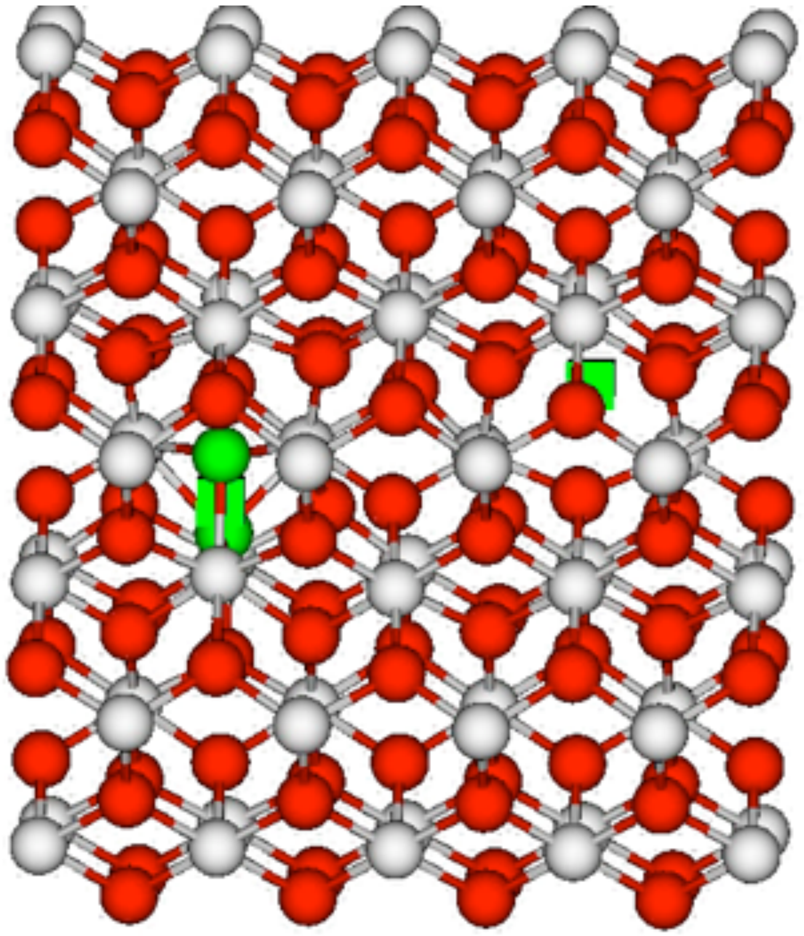

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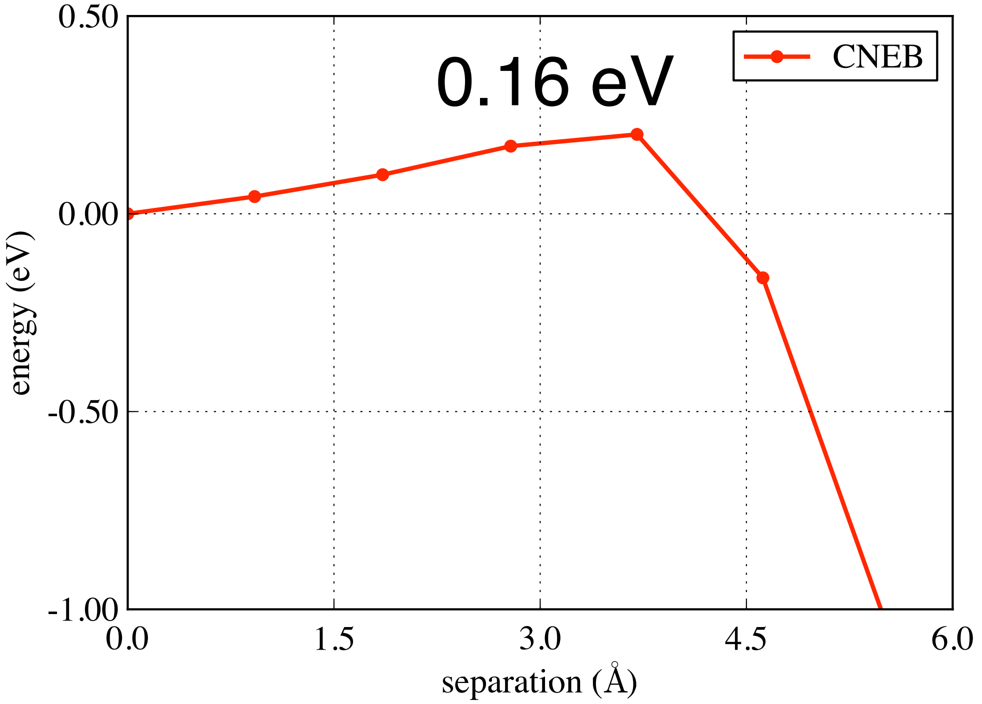

Application - TiO$_2$

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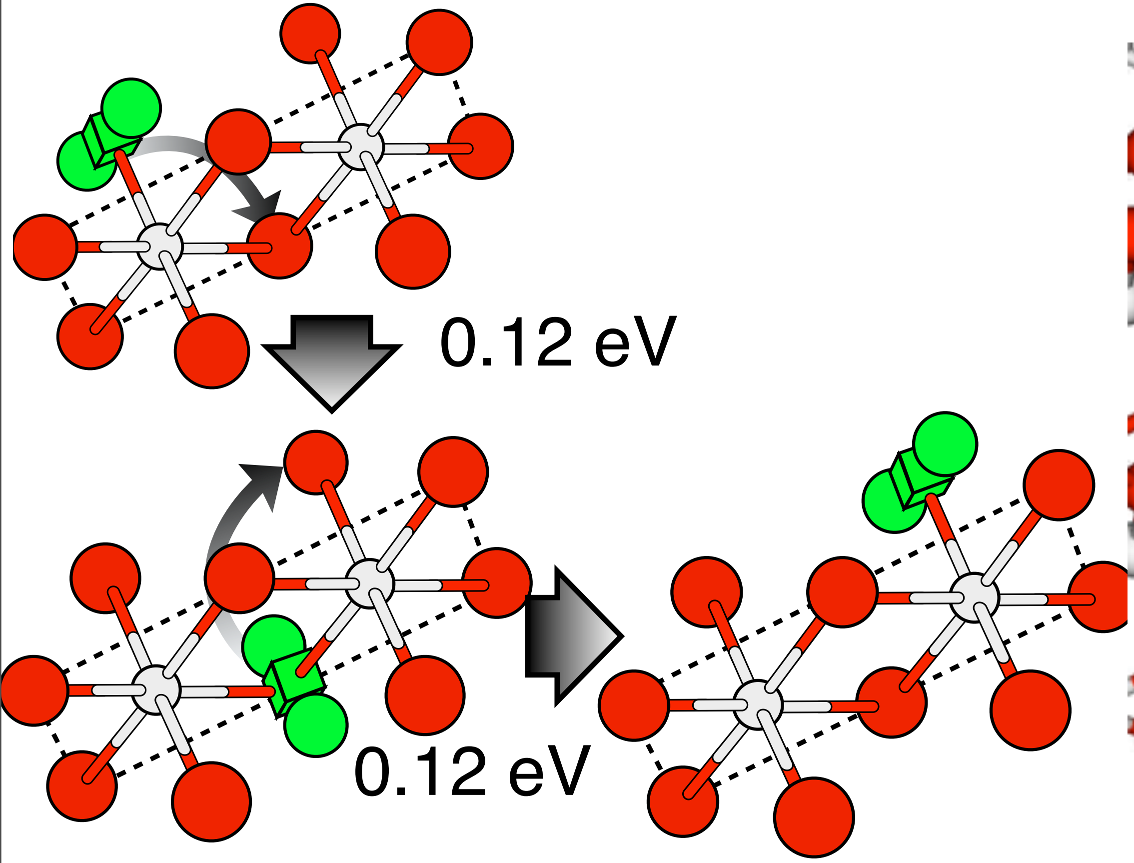

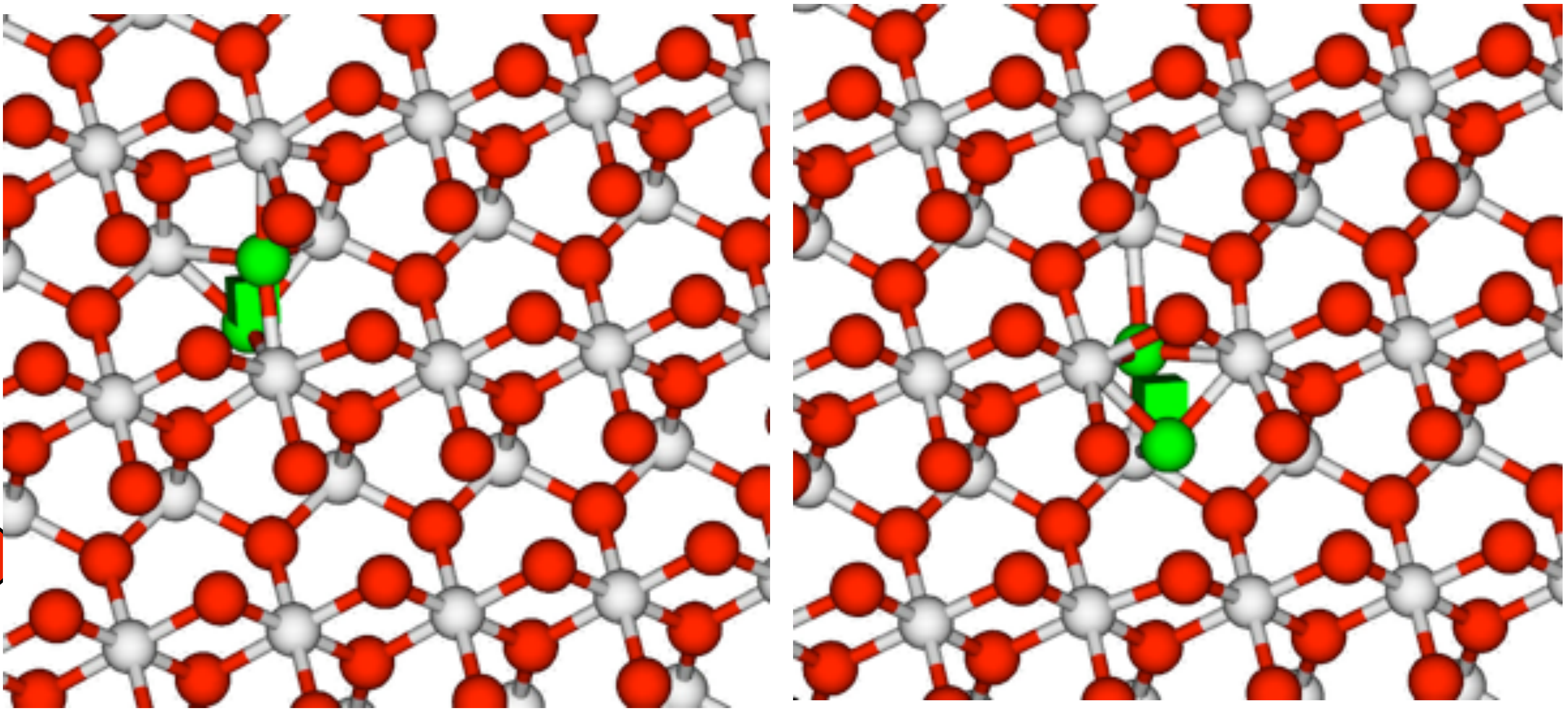

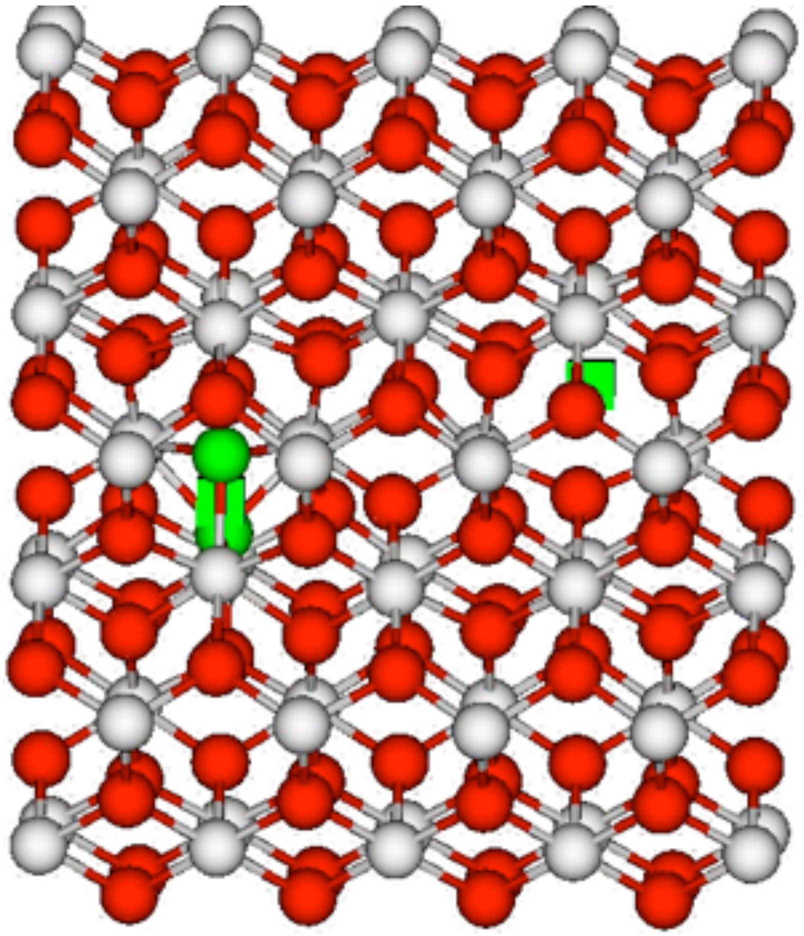

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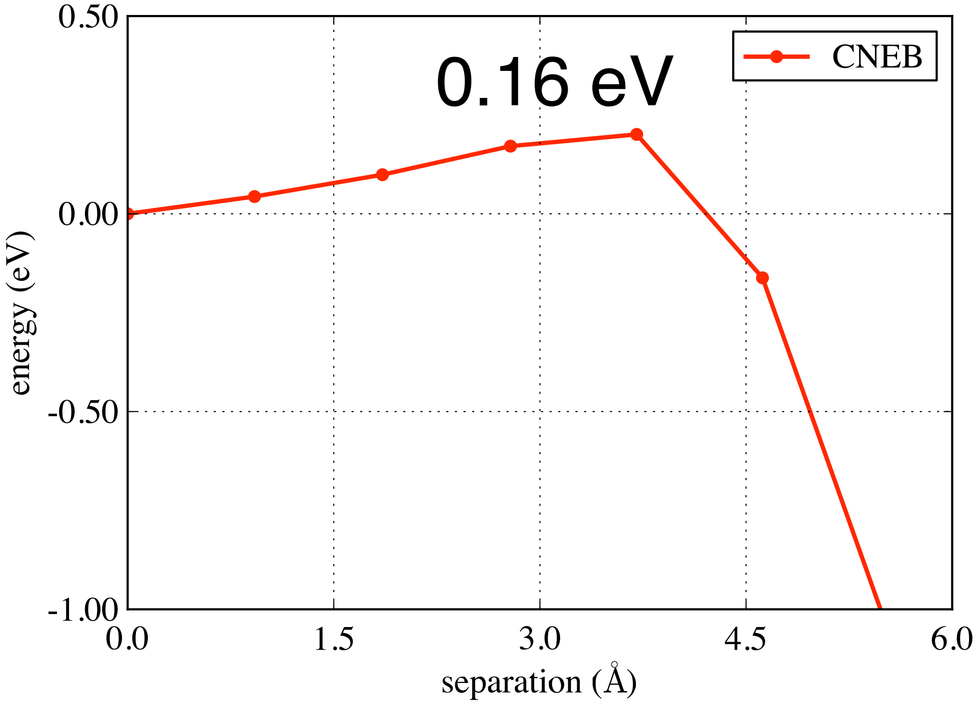
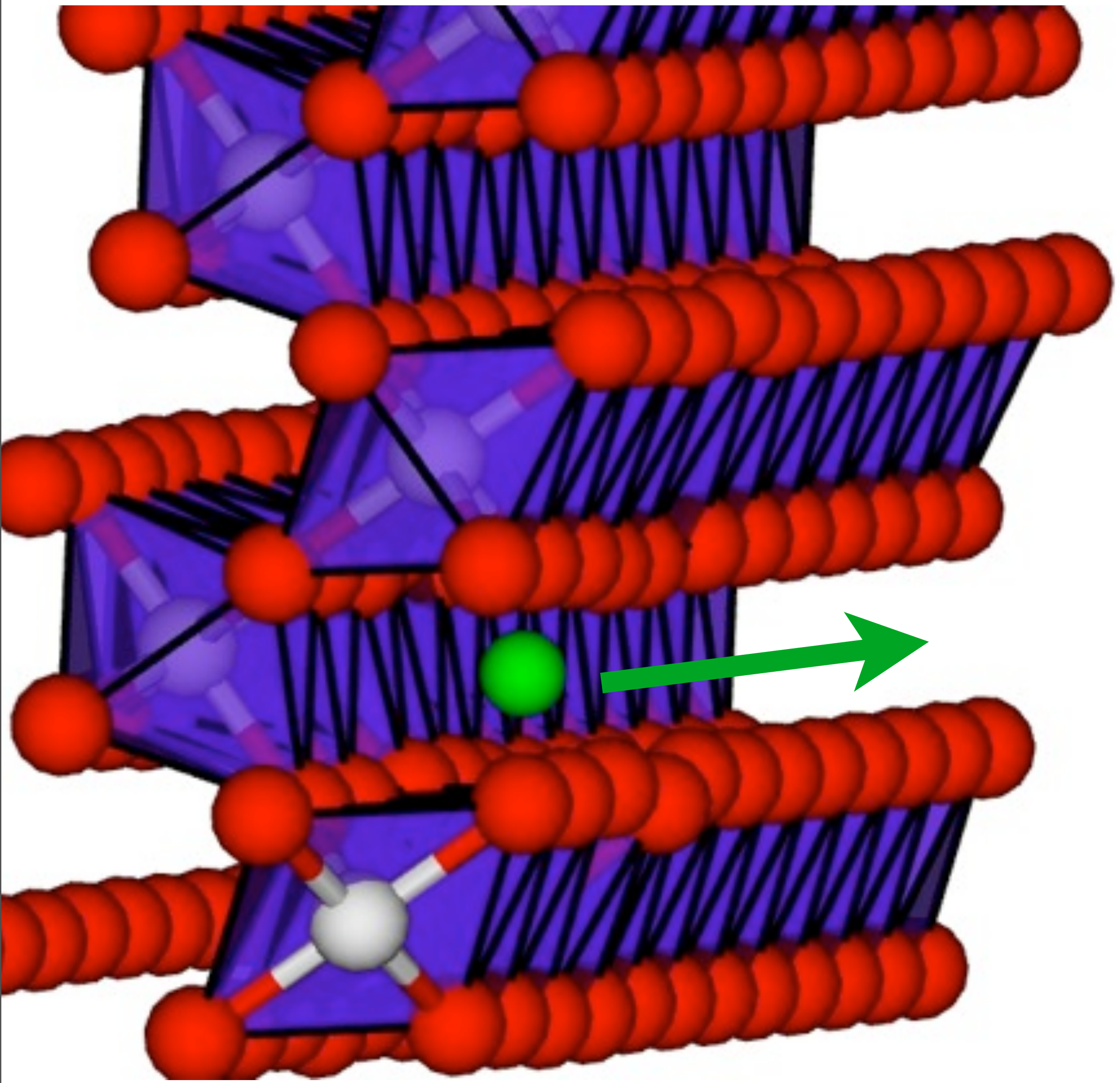
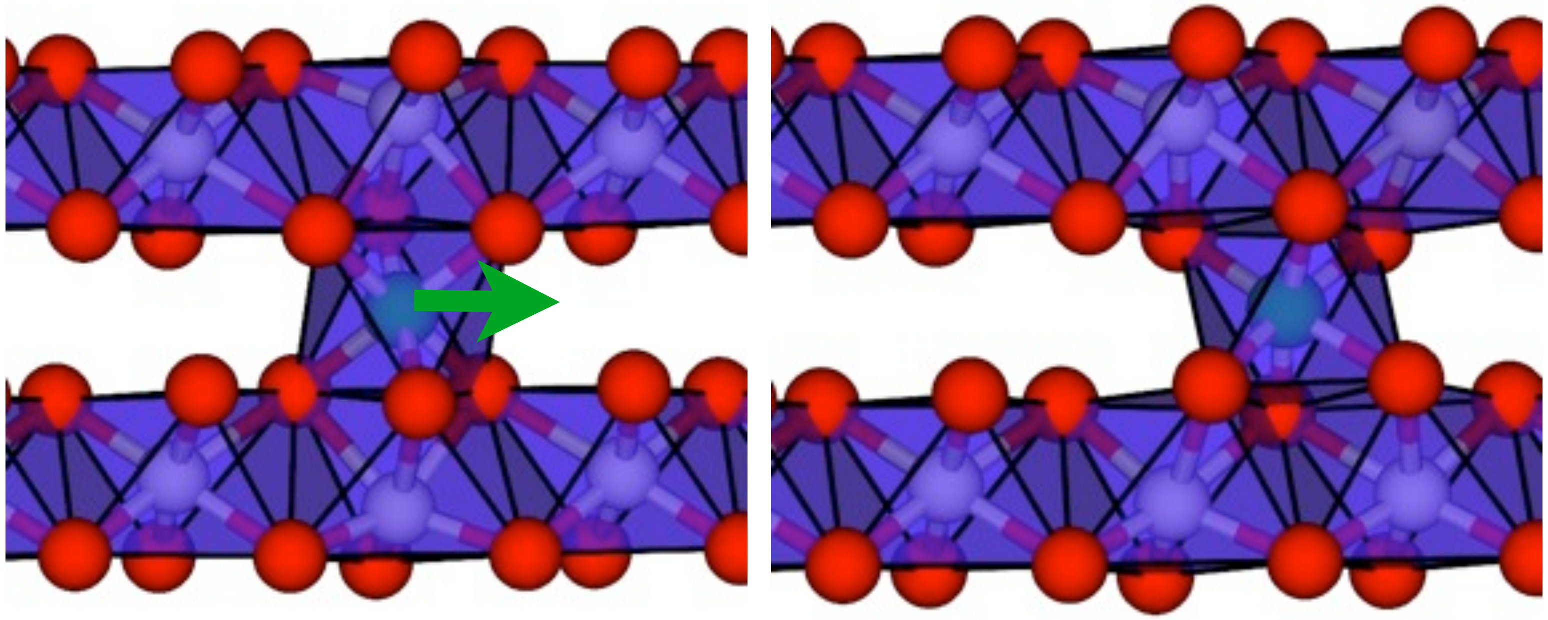


Application - TiO_2

- In contrast, Ti octahedral interstitials migrate at much higher barrier down the Z-axis channels.



  - Migration passes through 2 symmetrically equivalent octahedral sites with a barrier of **0.85 eV**



- Unlike the O split-interstitials that migrate through a concerted motion, the mechanism for the Ti interstitial is a simple linear transition.

Application - TiO_2

- **Current conclusions:**
  - **Ballistic phase - Displacement threshold energy**
    - Reiterates the probabilistic nature of defect formation at low energy
    - O values of E_d were found to be lower than experimental, but can be attributed to low energy recombination barriers.
  - **Ballistic phase - Quantitative defect cluster analysis**
    - Different response from each sublattice, O PKA generates strictly O defects, Ti PKA produces a multitude of defects
    - Representative defect proportions useful for future long time scale simulations
  - **Recovery phase - Transition barriers / Diffusion mechanisms**
    - Relatively long range and low barrier O FP recombination transitions.
    - O split-interstitial migration along the rutile c-axis, with very low energy barriers.
- **TODO:**
  - **The effect of the connectivity of the TiO_6 polyhedra on defect migration:**
    - **Is migration impeded by change from edge to corner sharing?**
    - **Is the presence of the z-axis channel in rutile the main factor behind its increase in tolerance ?**
  - **Full scale OTF-KMC in each polymorph on the resultant defect clusters - particularly the di-vacancies and di-interstitials.**

Requirements for Future Work

- A **robust method** of accessing time-scales beyond MD.
  - Automated
  - Handle multiple complex defect structures
  - Highly disordered lattices
  - Large systems (as PKA energy increases)

Thanks to …

Loughborough University

Curtin University

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