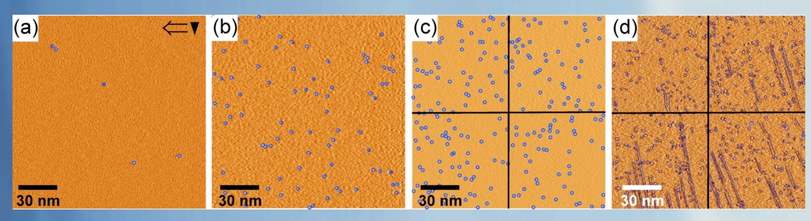
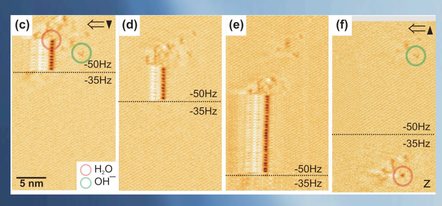
Water chemistry and manipulation on alkaline earth halide surfaces

Adam S. Foster[1,2], T. Trevethan[3], S. Hirth[4], F. Ostendorf[4], A. L. Shluger[3] and M. Reichling[4]
[1]Department of Physics, Tampere University of Technology, P.O. Box 692, 33101, Finland
[2]Helsinki University of Technology, Lab. of Physics, P.O. Box 1100, FIN-02015 HUT, Finland
[3]Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK
[4]Fachbereich Physik, Universität Osnabrück, Barbarastraße 7, 49076, Osnabrück, Germany
E-mail: adam.foster@tut.fi

Manipulation experiments

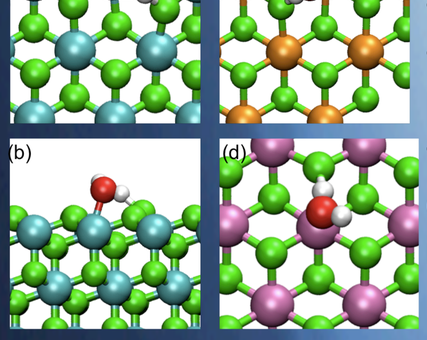


• AFM images as a function of time show the gradual deposition of water and the eventual manipulation of some of the resultant defects – similar defects seen in vacuum on a longer timescale.



• Controllable manipulation can be seen when approaching the tip closer to the surface. Only certain defects are moved.

CaF_2, SrF_2 and BaF_2



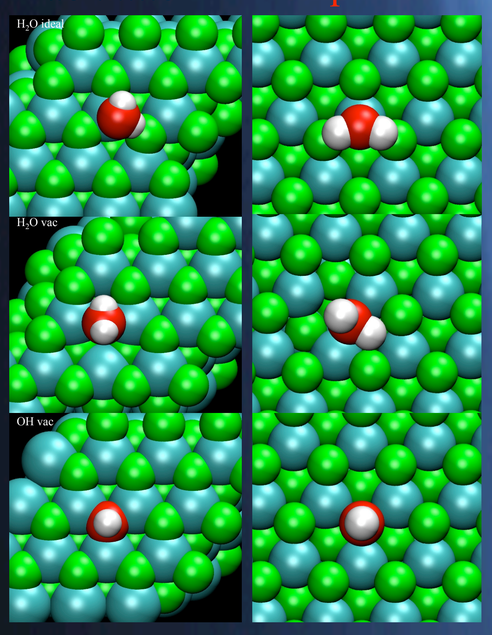
• We considered the properties of three alkali earth halides – we show that, as in experiments, water is more mobile on BaF_2.

Methods

• Bulk and surface calculations of defects and adsorbates initially made at first principles level (PBE-PAW-VASP) - including dipole and charge corrections.

• Diffusion paths and barriers of all adsorbates and defects calculated within this framework using the Climbing-NEB method.

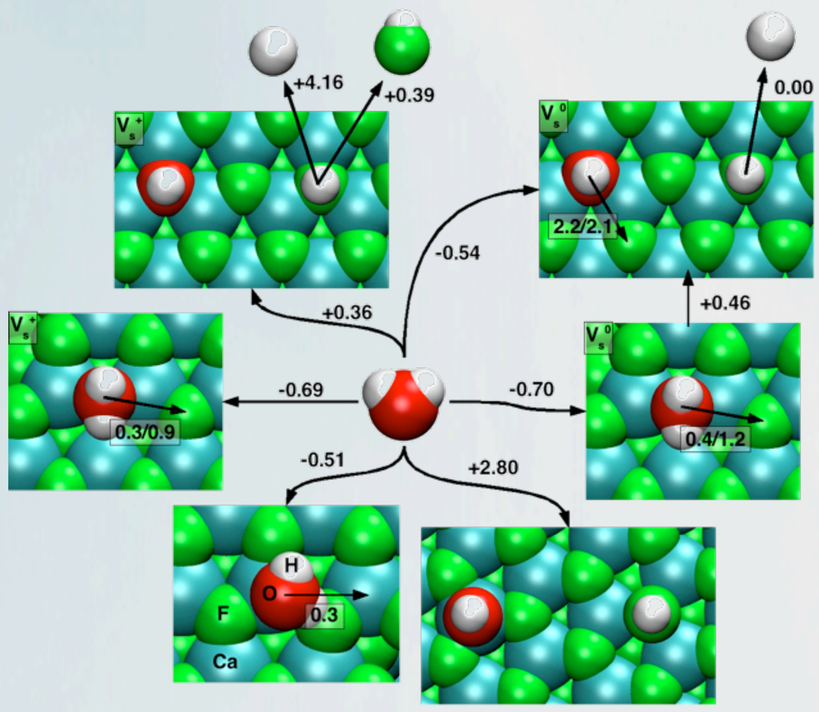
ab initio empirical



• For imaging and manipulation, empirical potentials were carefully checked against the first principles atomic structures and diffusion barriers (SCIFI).

• Very good agreement in structures and H_2O diffusion barrier (few %) – OH diffusion barrier underestimated by 30 %, but fully captures qualitative difference to H_2O.

Adsorption and diffusion



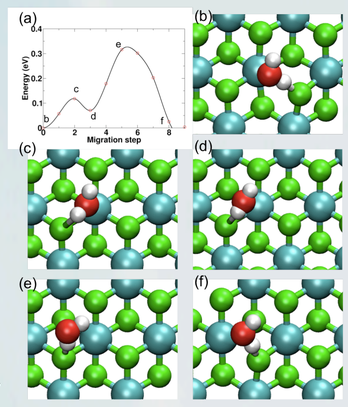
• We use first principles calculations to characterize the barriers for adsorption, reaction and migration on the surface.

• Water is too mobile on the ideal surface and must adsorb at vacancies.

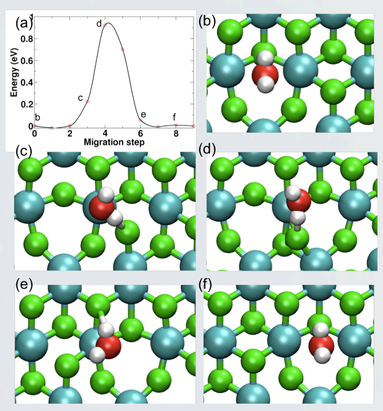
• Initial immovable species are OH groups at neutral F-centres.

• Over time, charged vacancies diffuse to the surface and trap molecular water – the manipulable species in images.

Diffusion paths



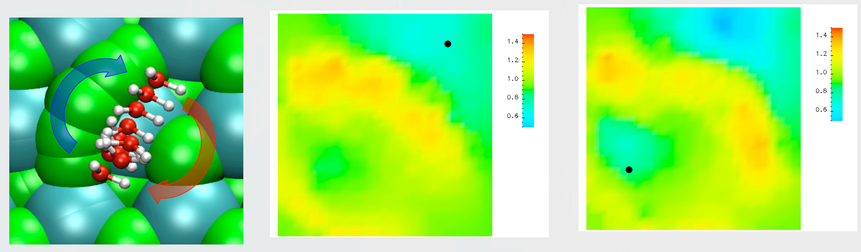
• Water diffuses by pivoting around a surface fluorine ion.



• Water also reduces the barrier for vacancy diffusion on the surface.

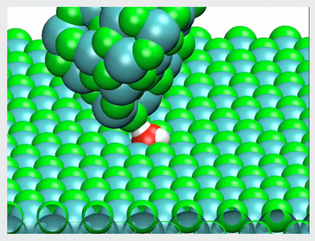
Mechanism of manipulation

• Plots of the barrier as a function of tip height demonstrate the influence of the tip on the barrier and identify the areas of maximum manipulation probability – irreversible?



• Key low barrier area appears already at about 0.45 nm – repulsion of fluorine under the tip makes vacancy part of diffusion easier, while H-F attraction aids molecular motion.

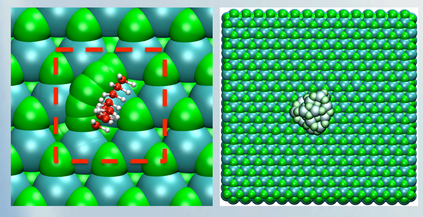
• Closer to the surface, the tip can act as part of the molecule's diffusion path.



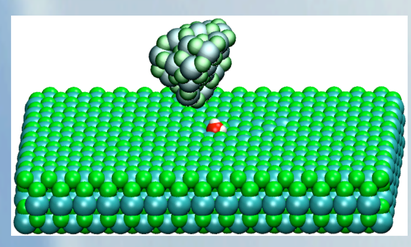
Modelling manipulation

• Barrier for water diffusion calculated at each tip position on a 7000 point grid, covering the area around the path and from 0.6 to 0.2 nm tip-surface distance.

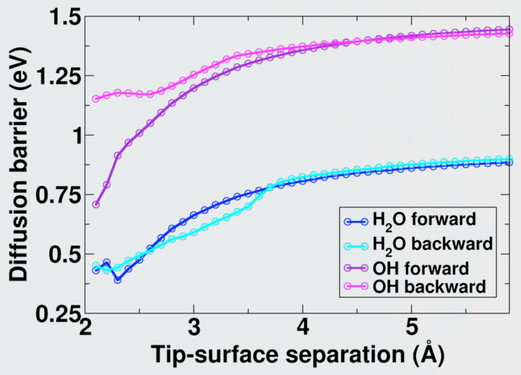
• Manipulation experiments generally have contrast characteristic of imaging Ca - negatively terminated tip.



• Oxide tips interact too strongly with water and cannot reduce the barrier before desorption.



• Annealed a large CaF_2 cluster to form a realistic tip contaminated by the surface – F termination.



• Tip clearly reduces barrier and H_2O is highly mobile at small tip-surface separations.

• What is mechanism of defect generation?

• Why does water remain in defects?