Water chemistry and manipulation on alkaline earth halide surfaces

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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.

• We considered the properties of three alkali earth halides – we show that, as in experiments, water is more mobile on BaF₂.

• 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.

• 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 H₂O diffusion barrier (few %) – OH diffusion barrier underestimated by 30 %, but fully captures qualitative difference to H₂O.

CaF₂, SrF₂ and BaF₂

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

• Water diffuses by pivoting around a surface fluorine ion.

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Methods

Adsortion 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.

• Water diffuses by pivoting around a surface fluorine ion.

• 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.

• 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?

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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 CaF₂ cluster to form a realistic tip contaminated by the surface – F termination.

• Tip clearly reduces barrier and H₂O is highly mobile at small tip-surface separations.

• What is mechanism of defect generation?

• Why does water remain in defects?