Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Oxygen chemistry of halogen-doped $CeO_2(111)$ – supplementary information

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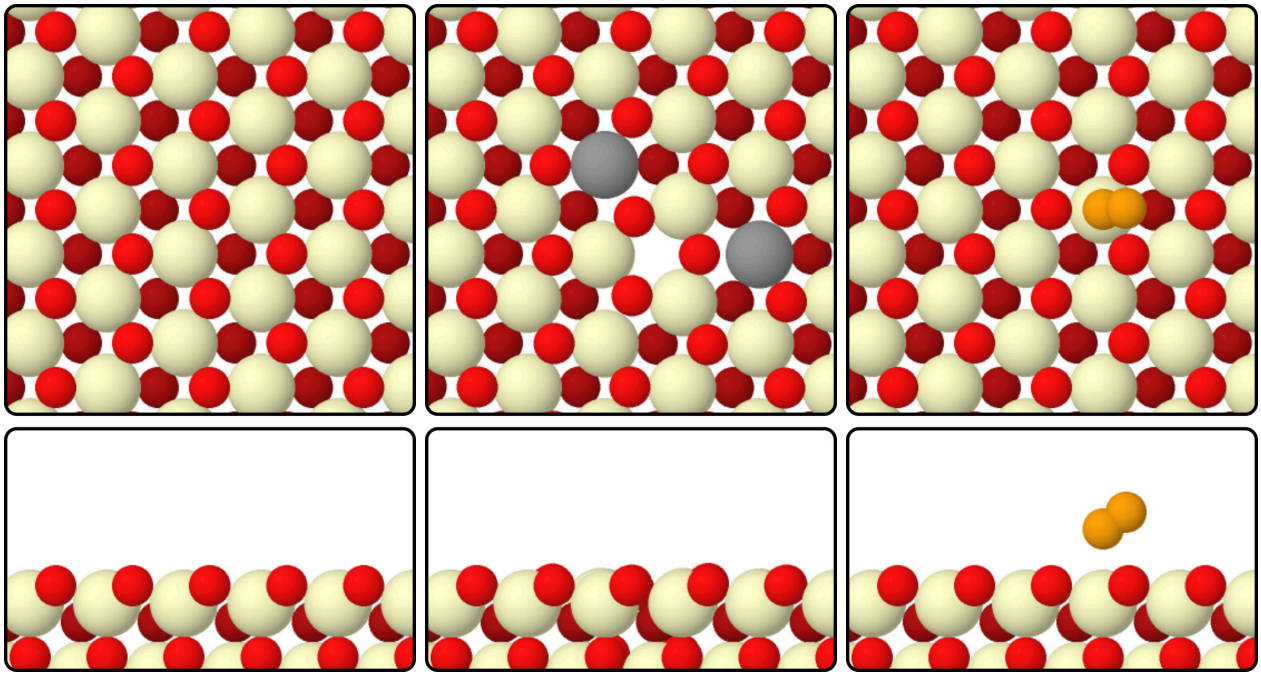
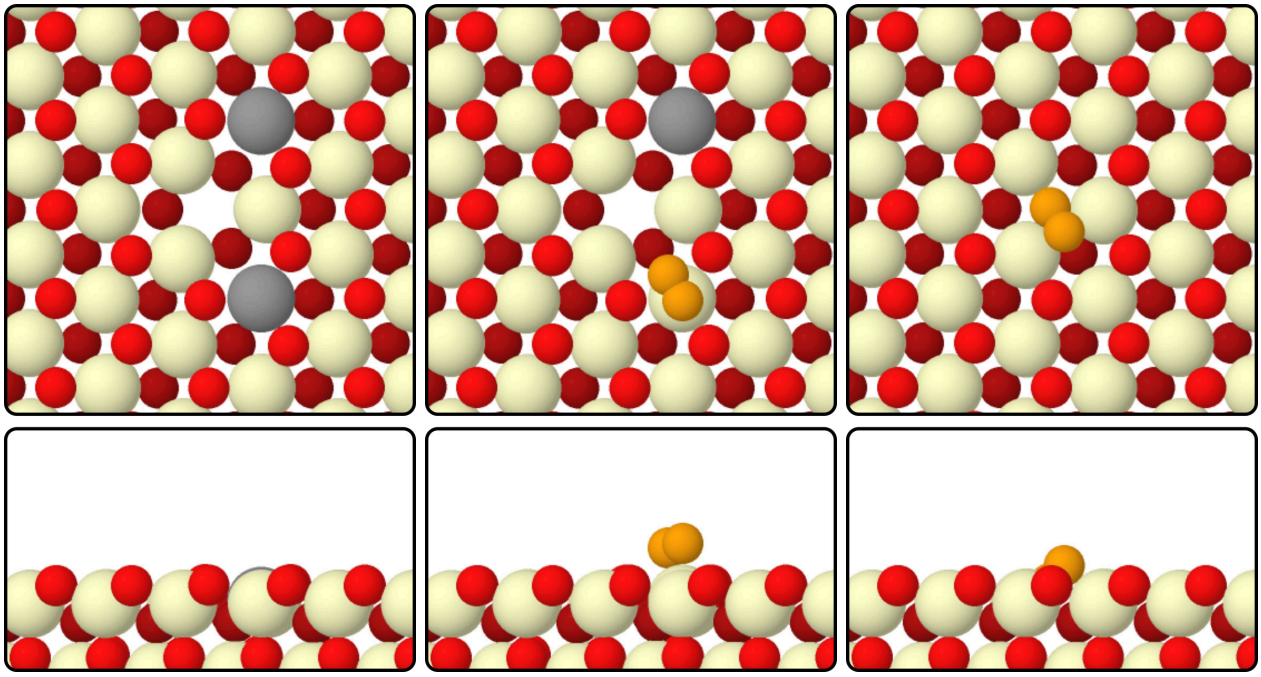


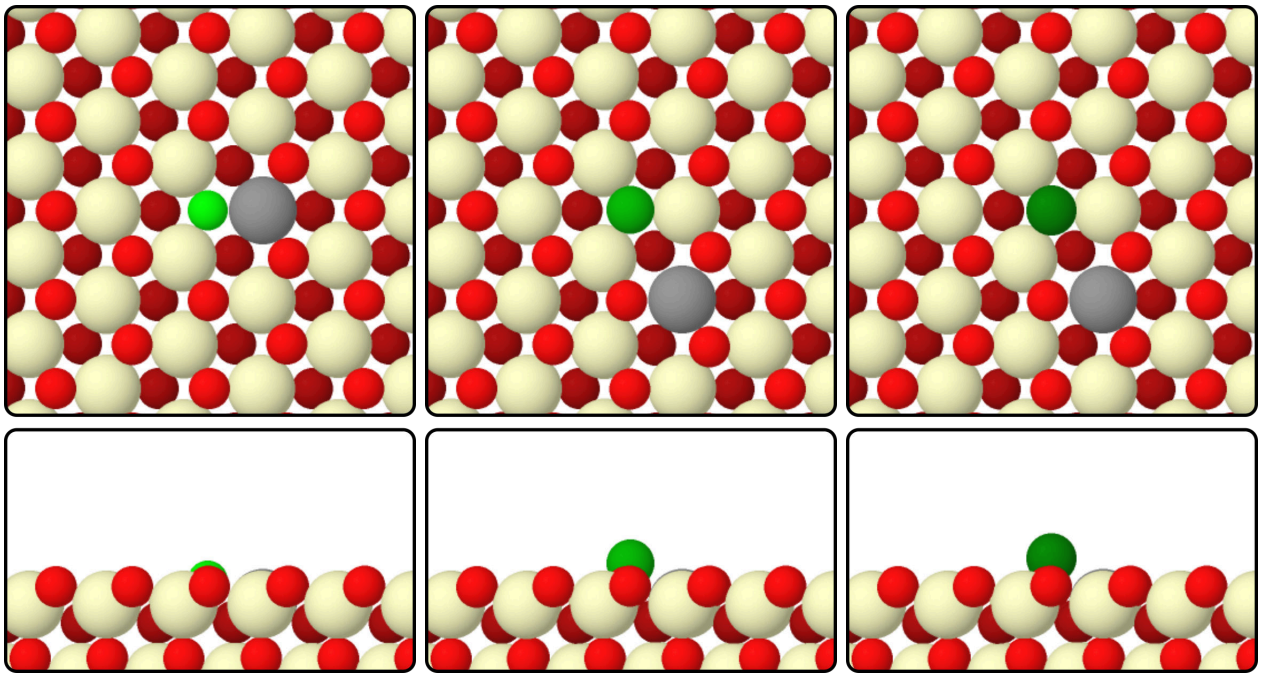
(a) (b) (c)

Figure S1: **Structures related to the stoichiometric surface.** (a) The pristine surface. (b) A sub-surface oxygen vacancy. (c) An adsorbed oxygen molecule. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); grey – cerium(III); orange – oxygen molecule.



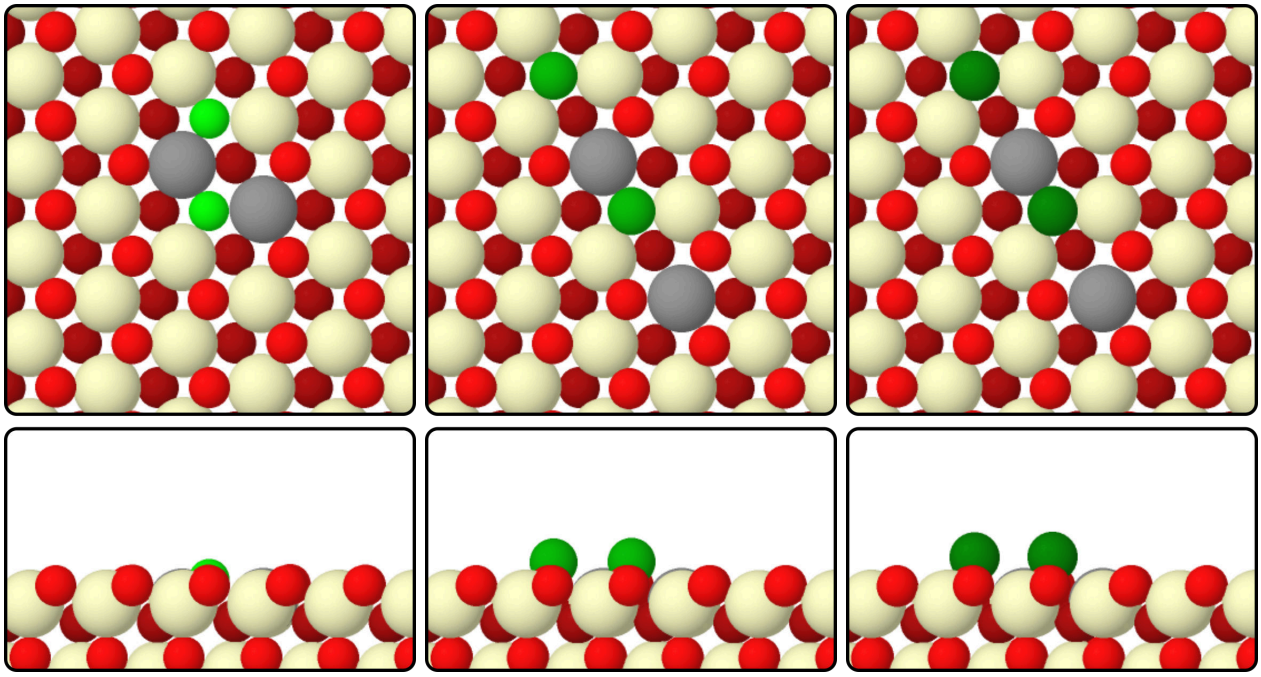
(a) (b) (c)

Figure S2: **Structures related to a surface oxygen vacancy.** (a) An isolated vacancy. (b) A superoxide molecule adsorbed in the vicinity of a vacancy. (c) A peroxide molecule in a vacancy. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); grey – cerium(III); orange – superoxide molecule in (b), peroxide molecule in (c).



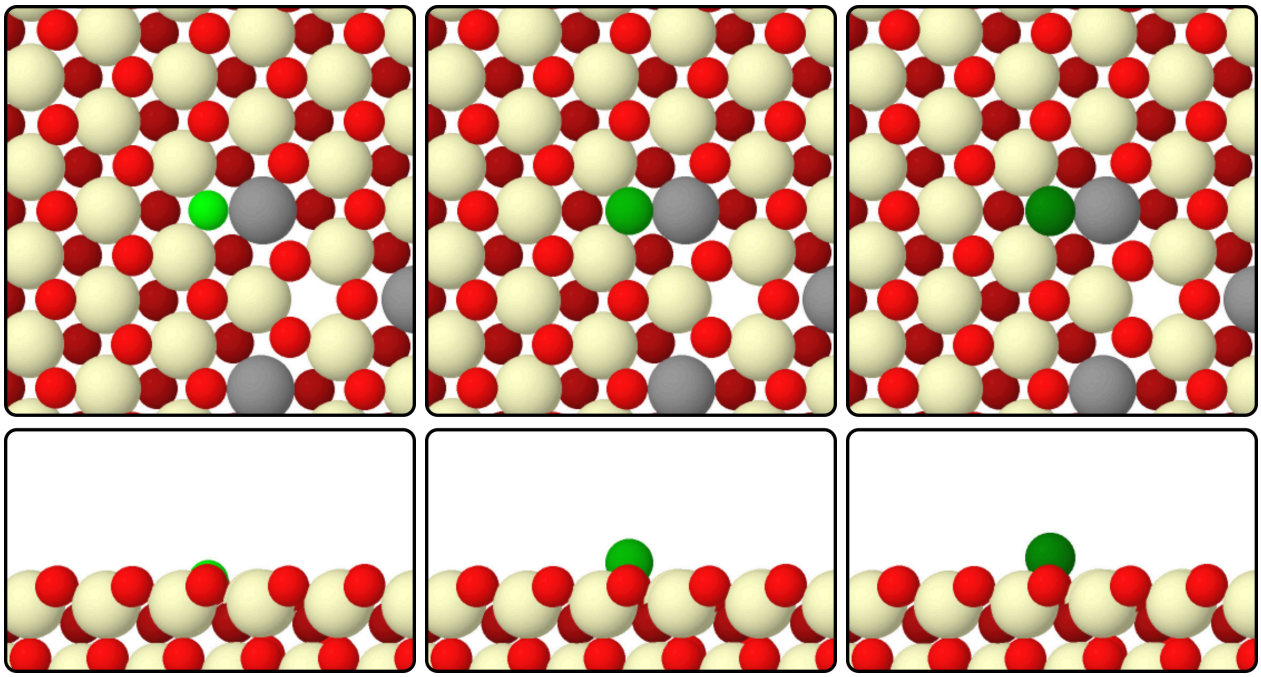
(a) (b) (c)

Figure S3: **A surface halogen impurity.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); grey – cerium(III); green – halogen.



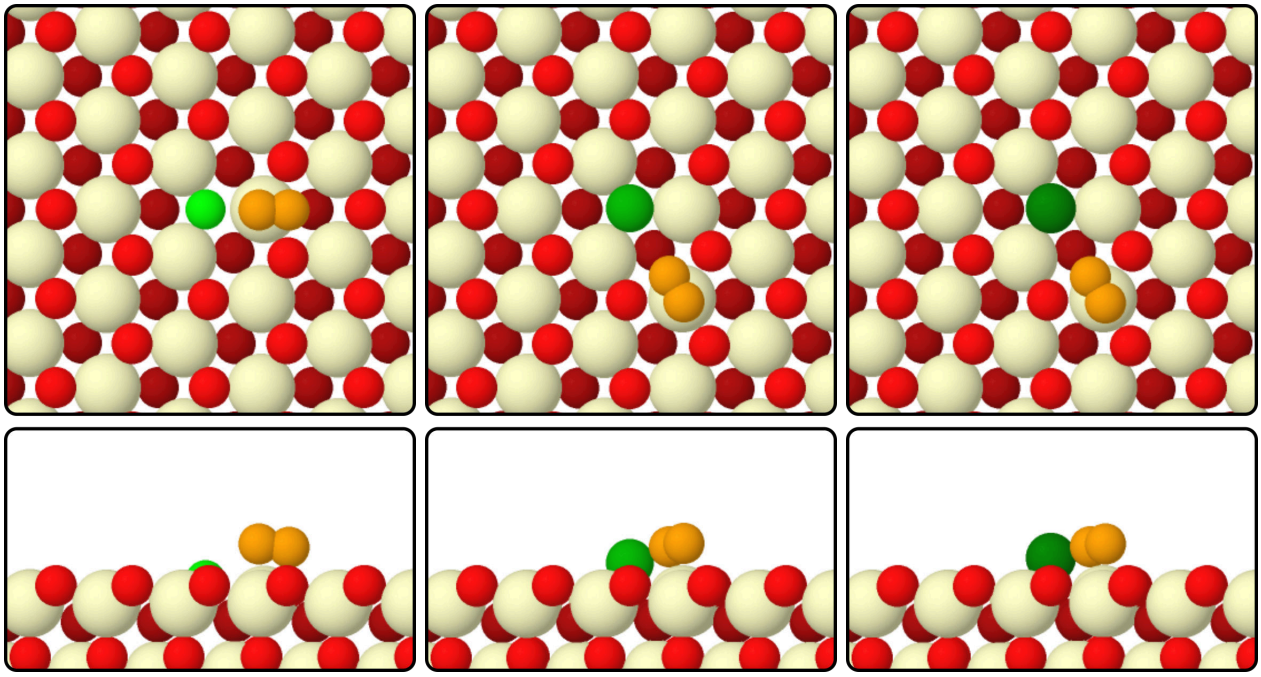
(a) (b) (c)

Figure S4: **A pair of surface halogen impurities.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); grey – cerium(III); green – halogen.



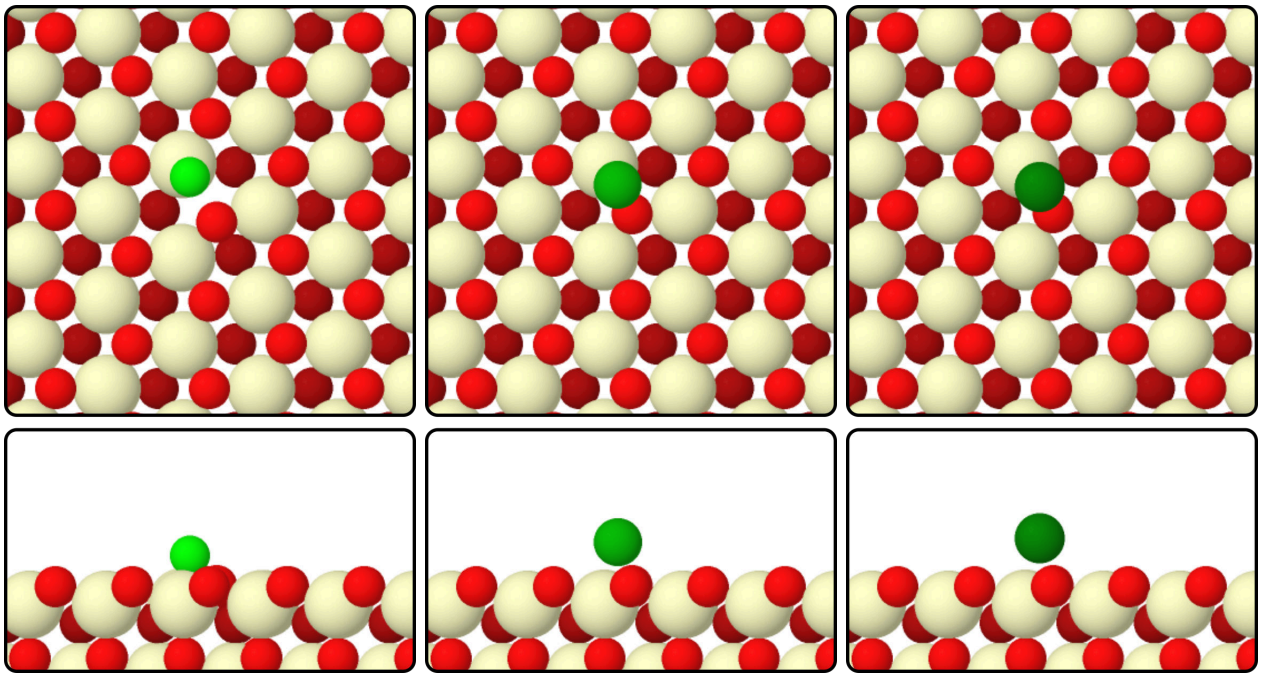
(a) (b) (c)

Figure S5: **A sub-surface oxygen vacancy in the vicinity of a surface halogen impurity.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); grey – cerium(III); green – halogen.



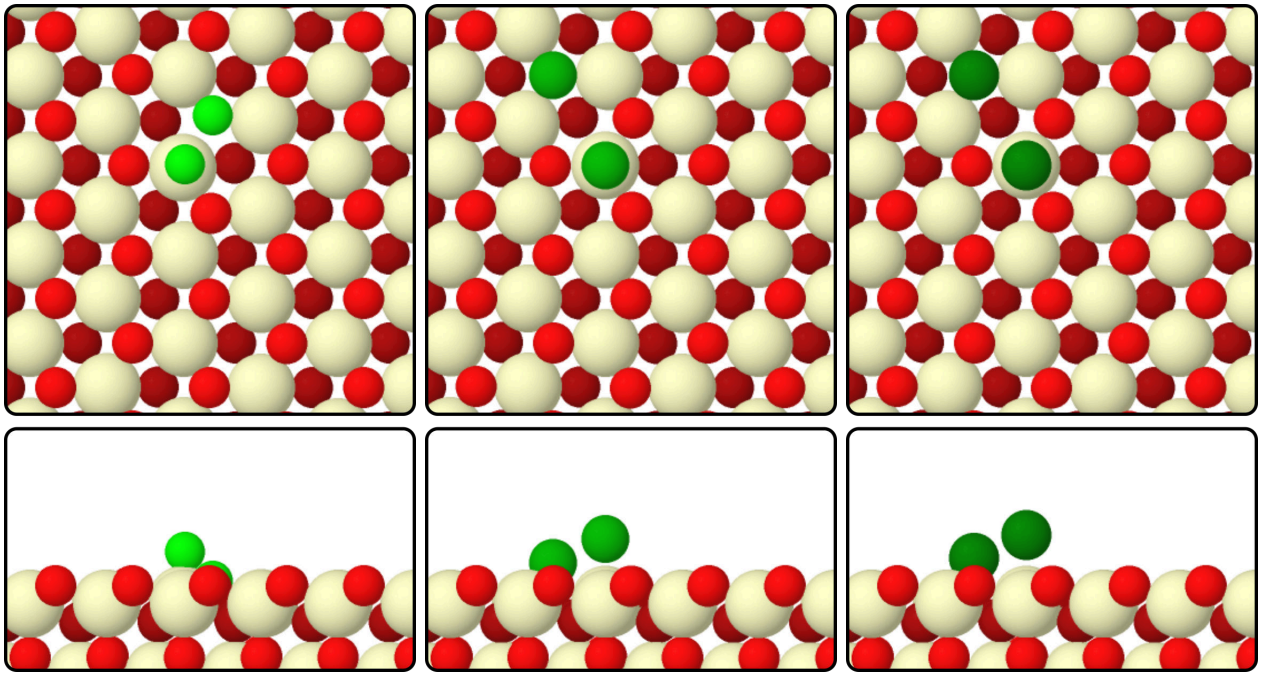
(a) (b) (c)

Figure S6: **A superoxide molecule adsorbed in the vicinity of a surface halogen impurity.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); green – halogen; orange – superoxide molecule.



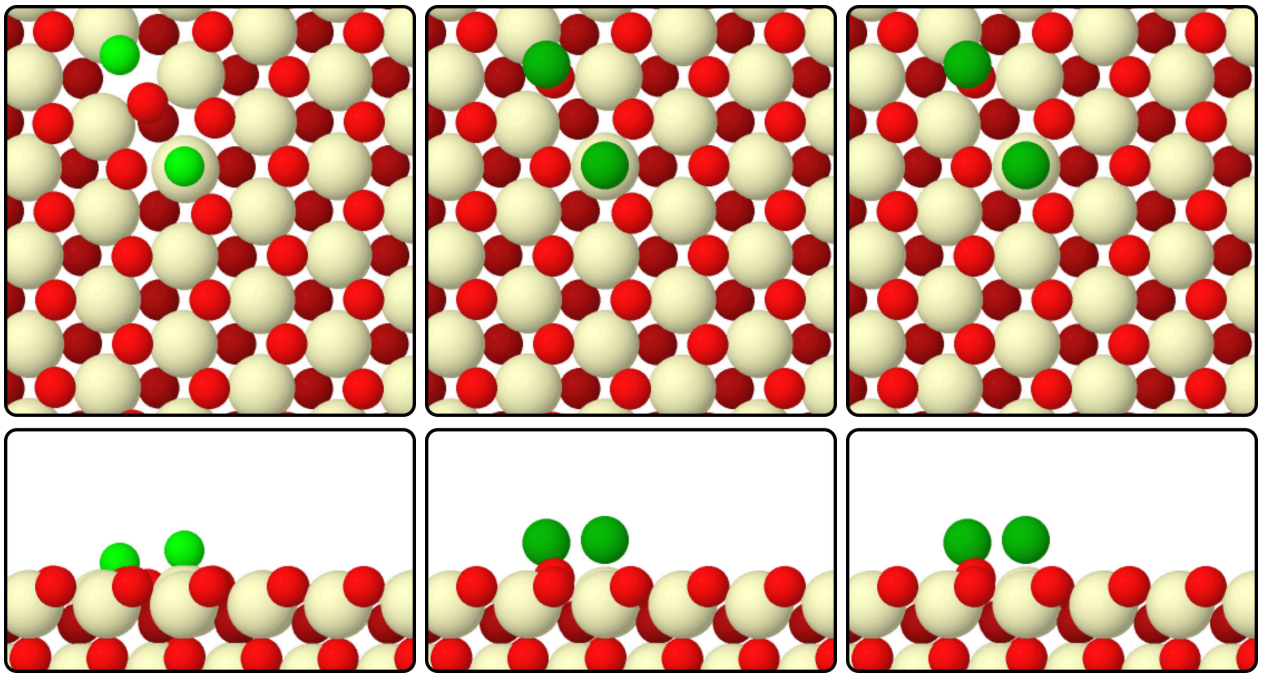
(a) (b) (c)

Figure S7: **A halogen atom adsorbed on the stoichiometric surface.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); green – halogen.



(a) (b) (c)

Figure S8: **A halogen atom adsorbed in the vicinity of a surface halogen impurity.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); green – halogen.



(a) (b) (c)

Figure S9: **A pair of halogen atoms adsorbed on the stoichiometric surface.** (a) Fluorine. (b) Chlorine. (c) Bromine. Colour scheme: bright red – surface oxygen; dark red – sub-surface oxygen; off-white – cerium(IV); green – halogen.