

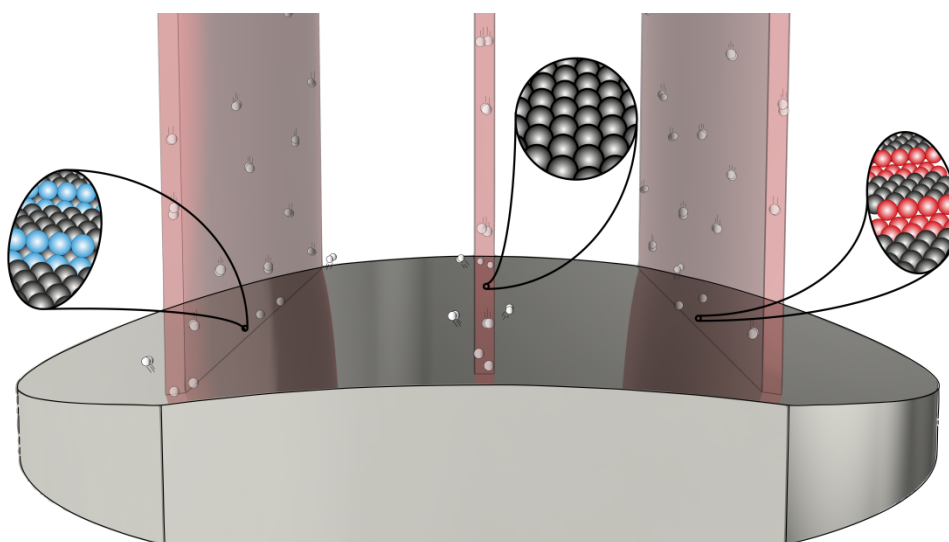
# Pt steps control H<sub>2</sub> and O<sub>2</sub> surface reactions in various ways

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Collisions of H<sub>2</sub> and O<sub>2</sub> molecules with Pt surfaces are relevant to actual heterogeneous (electro)catalysis. They also serve as model systems to develop improved theoretical methods to predicting chemical reaction dynamics and kinetics. We use Pt step type and step density variations to study how common defects on catalytic particles affects H<sub>2</sub> and O<sub>2</sub> sticking and dissociation. In Leiden, we use a *curved* surface approach. The curved surface of Pt single crystals yields a continuous variation in step density with spatial separation of step types. In combination with supersonic molecular beam techniques we unveil how the local corrugation of monoatomic steps controls single collision events. For H<sub>2</sub>, our studies resolved a 40-year old debate on the origin of defects dominating dissociation<sup>1</sup>. The predominant dissociation mechanisms are direct and elementary. Various dependencies of reactivity are inconsistent with a physisorbed, precursor-based model for H<sub>2</sub> dissociation. For O<sub>2</sub>, the opposite is true. Here, a physisorbed state is crucial to molecular sticking and subsequent reactions at low collision energies. At higher energies, the physisorbed state loses importance and direct adsorption into molecular chemisorbed states dominate reactivity. The latter conclusions required complementary experiments performed with dr. Kurahashi in Tsukuba, Japan. We used spin-rotation state-selected and aligned O<sub>2</sub> to determine how rotation parallel and perpendicular to the Pt(111) plane and the A- and B-type step direction affect trapping and dissociation on various 'flat' Pt single crystals.



<sup>1</sup> van Lent et al., *Science* **363**, 155–157 (2019)