

WILDE LAB.

[Hydrogen Transportation Mechanisms across Surfaces]

Department of Fundamental Engineering

Nanoscale Surface Physical Chemistry

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Absorption, Diffusion, and Catalysis at H₍₂₎-Exposed Surfaces

Atomic Scale Clarification of Hydrogen Penetration, Isotope Exchange, Catalytic Reaction Mechanisms

Hydrogen (H) absorption and diffusion in and desorption from metals and oxide nanoparticles and thin films are crucially important for the storage and purification of H₂ in clean energy technology (fuel cells, fusion) and for industrial hydrogenation catalysis. Our research clarifies the microscopic pathways along which gas phase H₂ dissociates at the surfaces and H atoms penetrate into the interior of metals and oxides, and why Pd-absorbed H is essential for olefin (C=C) hydrogenation catalysis on Pd. To aid the development of novel efficient hydrogenation catalysts and hydrogen storage materials, we investigate through isotope labeling and H/D exchange experiments at pure and modified palladium (Pd) surfaces how the H transport across the gas/solid interface depends on the surface structure and thereby becomes controllable at the atomic level. We also study H diffusion and phase transitions in oxide thin films and the fusion-related H isotope (H) retention in HI plasma-exposed tungsten.

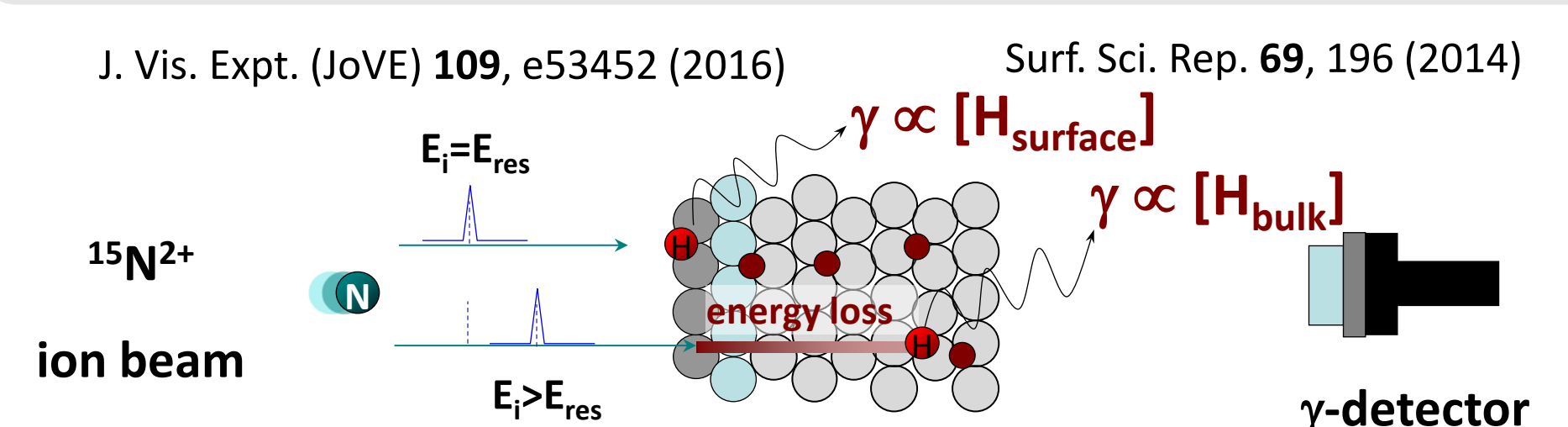
◆ Experimental Techniques & Key Information

- ✓ *Nuclear Reaction Analysis (NRA)*: Quantitative ▪ Non-destructive ▪ High-resolution - Hydrogen Depth Profiling ▪ Visualization of H-breathing by nanostructures ▪ Depth-resolved H stability analysis (diffusion, desorption, reaction)
- ✓ *Thermal Desorption Spectroscopy (TDS)*: Bonding stability of H species ▪ Hydrogen absorption kinetics ▪ Isotope (D) labeling ▪ Gas/surface/subsurface-H/D exchange mechanisms ▪ Kinetic isotope effects

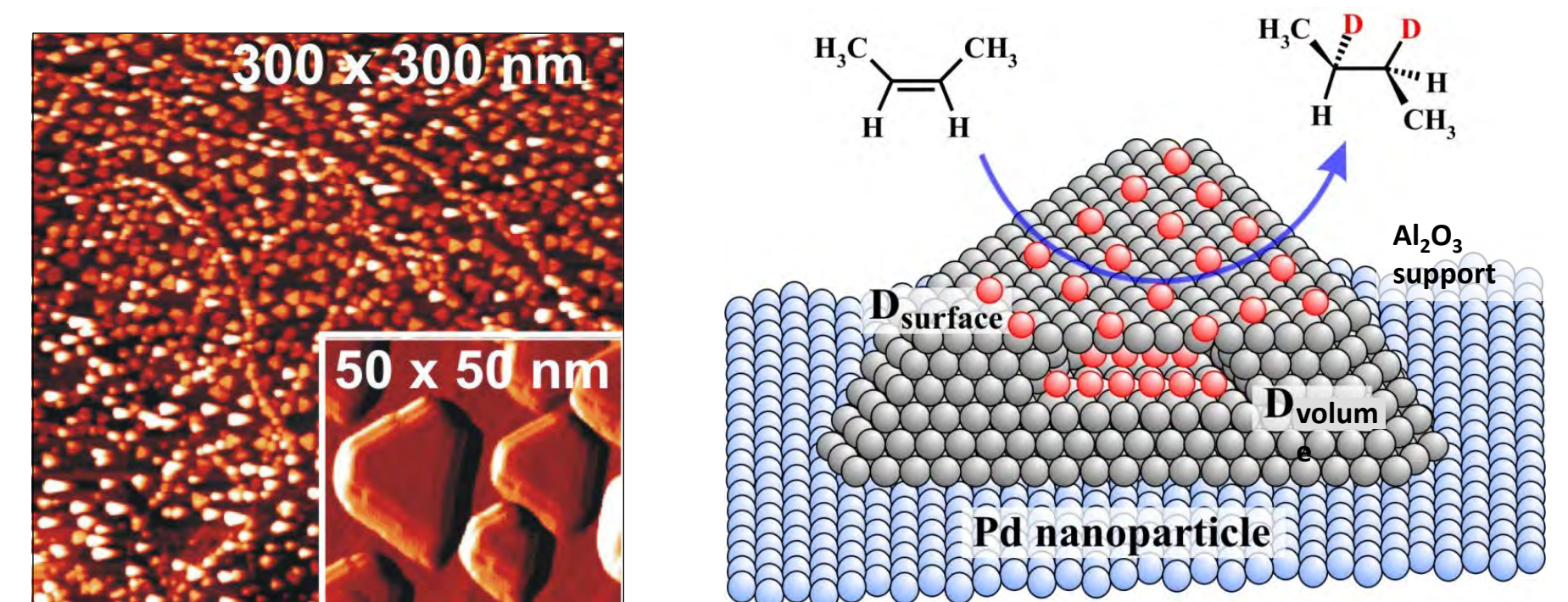
◆ Latest Research Topics

- ✓ *Hydrogen Storage & Retention* → H-Absorption/Release Mechanism
- ✓ *Hydrogenation Catalysis* → Reactivity of 'Subsurface-H'
- ✓ *(Photo)Catalysis* → H-Defect Interactions & Diffusion in CeO₂ and TiO₂

Principle of NRA $^{15}\text{N}(6.385\text{ MeV}) + ^1\text{H} \rightarrow ^{12}\text{C} + \alpha + \gamma(4.43\text{ MeV})$



Hydrogen in Pd nanocrystals: Essential in hydrogenation catalysis

 Angew. Chem. Int. Ed. **47**, 9289 (2008) Phys. Rev. B **77**, 113412 (2008)


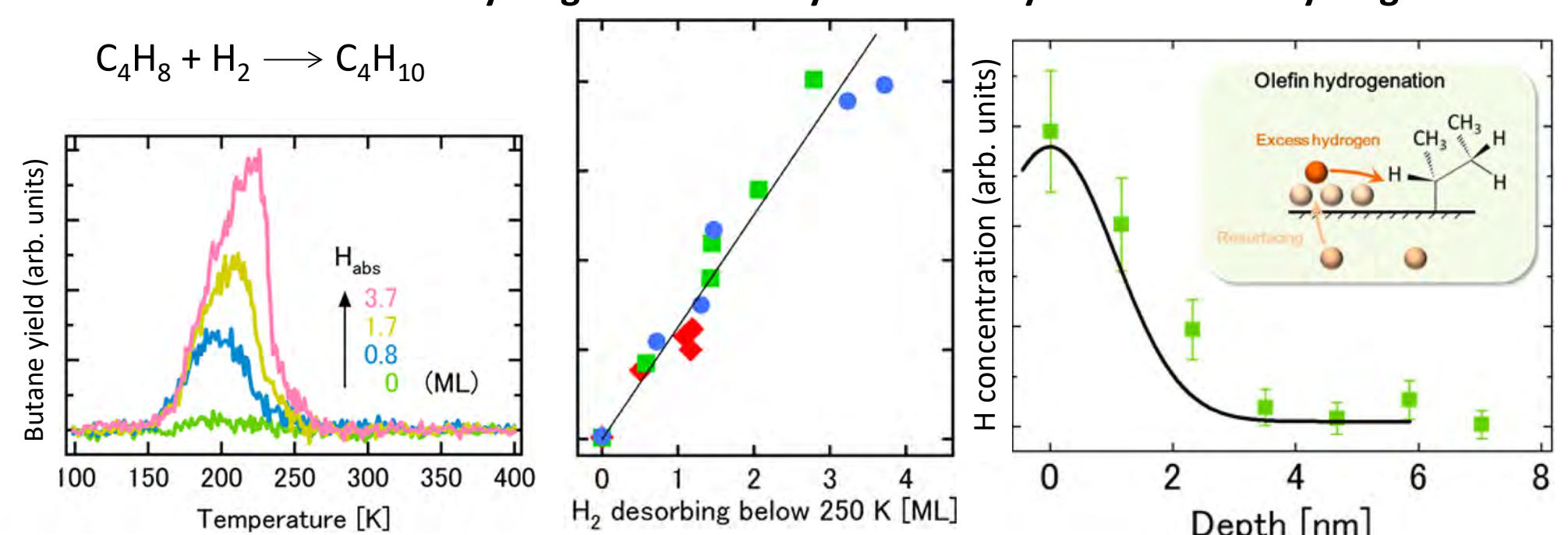
Model Hydrogenation Catalyst

=> Olefin (C=C) hydrogenation catalysis requires Pd-absorbed H !

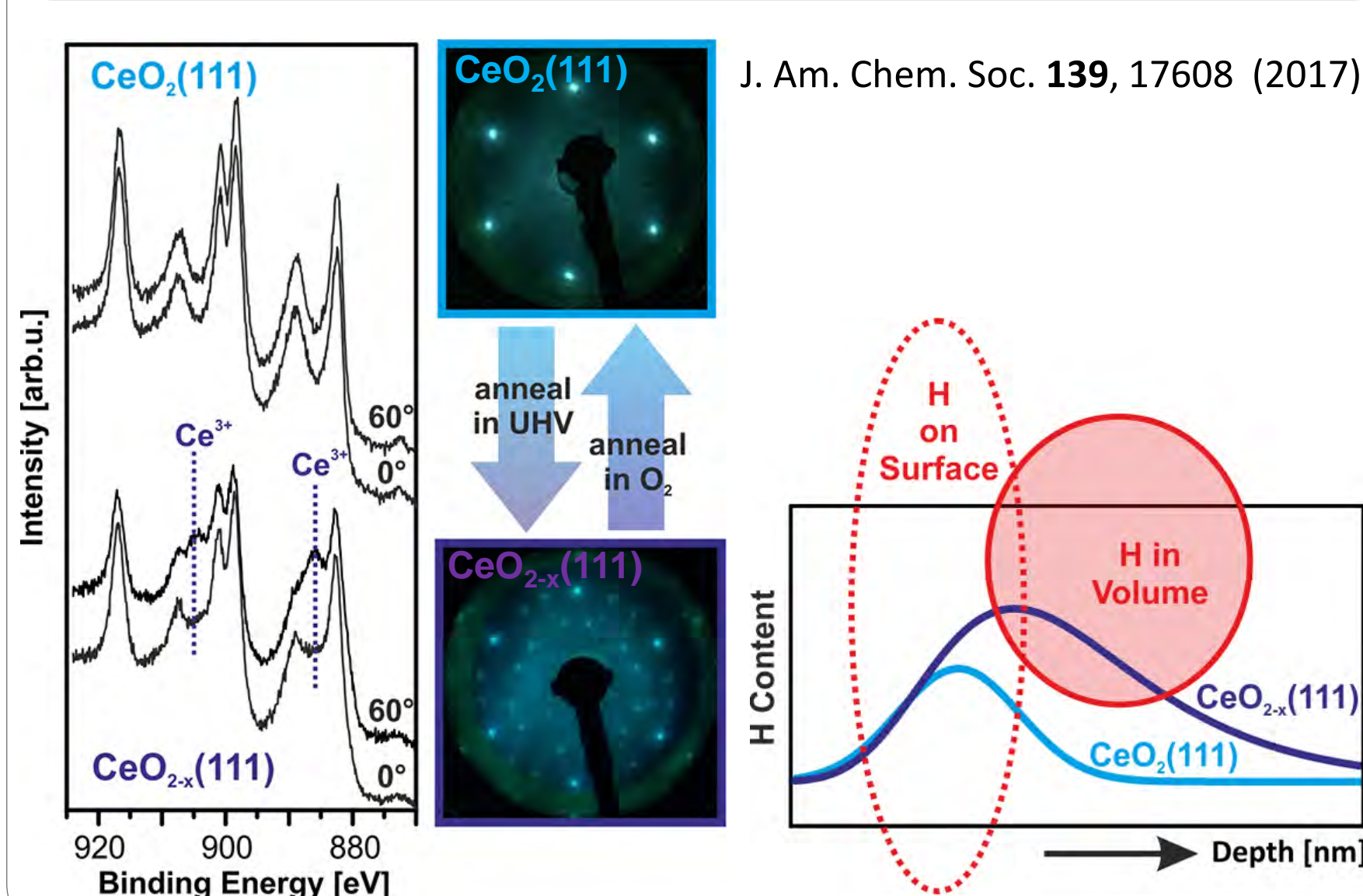
Resurfacing of Pd-absorbed H triggers hydrogenation catalysis

 J. Phys. Chem. C **120**, 11481 (2016)

Mechanism of olefin hydrogenation catalysis driven by Pd-dissolved hydrogen

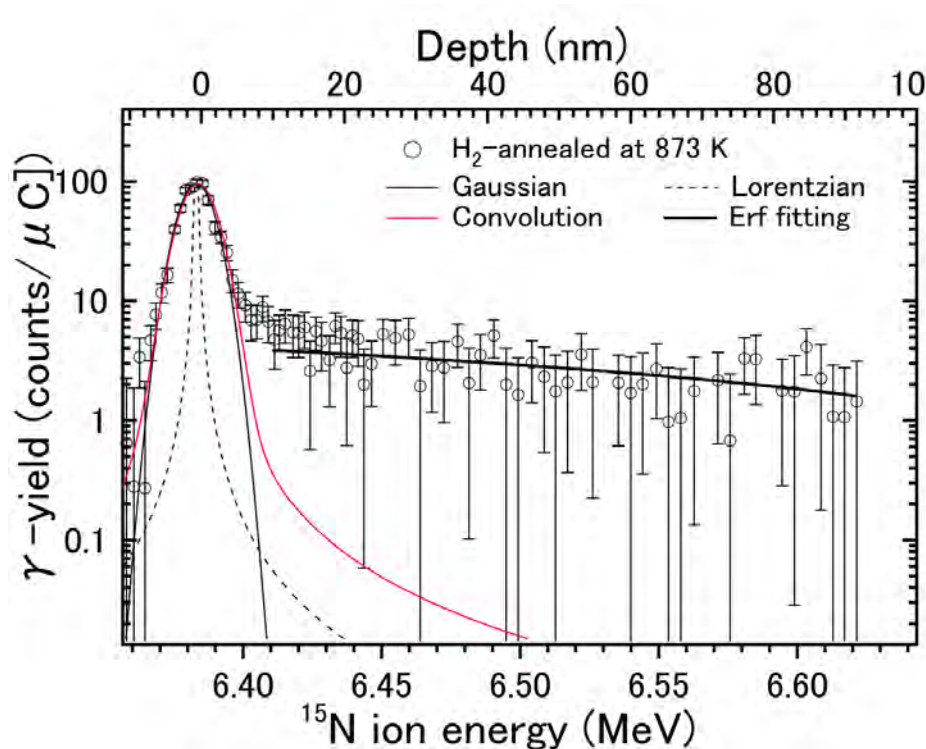


O-vacancies stabilize subsurface H in reduced CeO_{2-x}

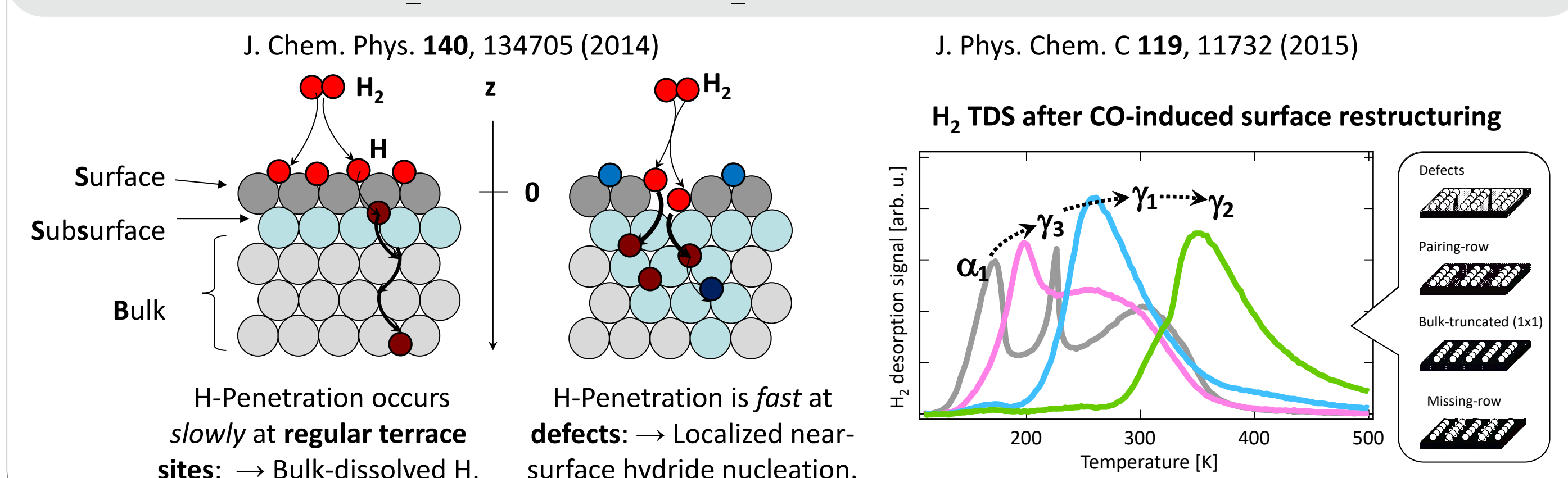


Accelerated phase transition and H-diffusion in TiO₂ films

 J. Phys. Chem. C **122**, 23026 (2018)

 H-diffusion profile in TiO₂ thin film:
All Rutile at 873-973 K!


Structure-sensitive H₂ absorption and H₂ desorption temperature control at Pd(110)



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