"Interaction of water vapor with clean and contaminated ruthenium surfaces"

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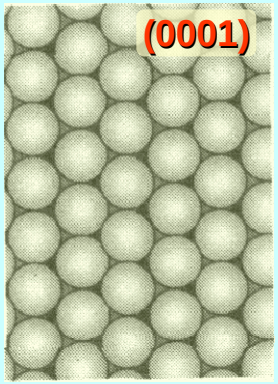
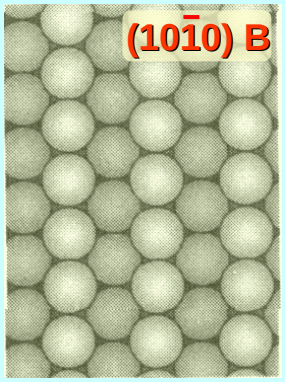
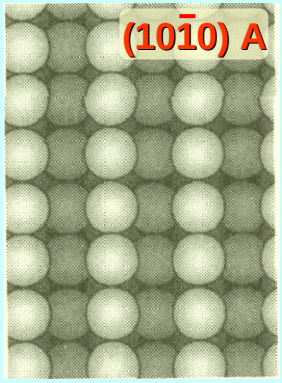
Outline

Atomic structure of Ru surfaces in some capping layers



(close packed)





(atomically rough)

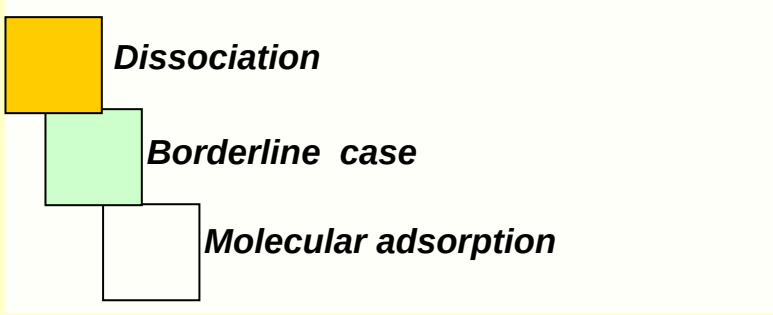
The (0001) and (10$\bar{1}$0) faces of an ideal *hcp* crystal – possible surfaces in capping layers

- **Interaction of H_2O with clean, O-covered and C-covered surfaces**
  focus on H_2O /Ru(10$\bar{1}$0), adsorption, desorption, reaction

- **Electron-stimulated surface processes**
  desorption, dissociation, oxidation; H_2O on Ru(0001)and Ru(10$\bar{1}$0)

Thermochemical predictions for stability of water on metal surfaces

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg



For borderline cases partial dissociation may occur

(Thiel and Madey,1987)

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Our main method: temperature programmed desorption (TPD)

*clean surface of sample,

*dose gas (H_2O)

*heat sample at linear rate (~ 2 to 5 K/s),

*measure desorption spectrum with mass spectrometer,

*determine energies, lifetimes (from peak temperatures)

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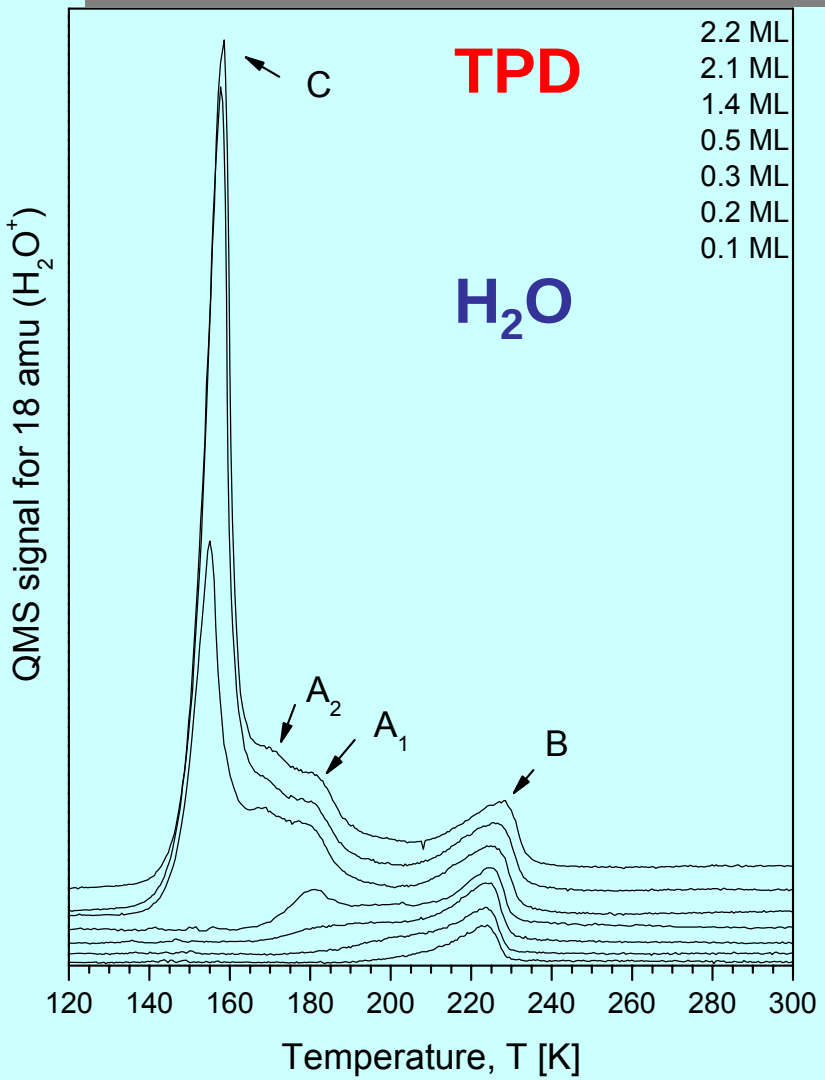
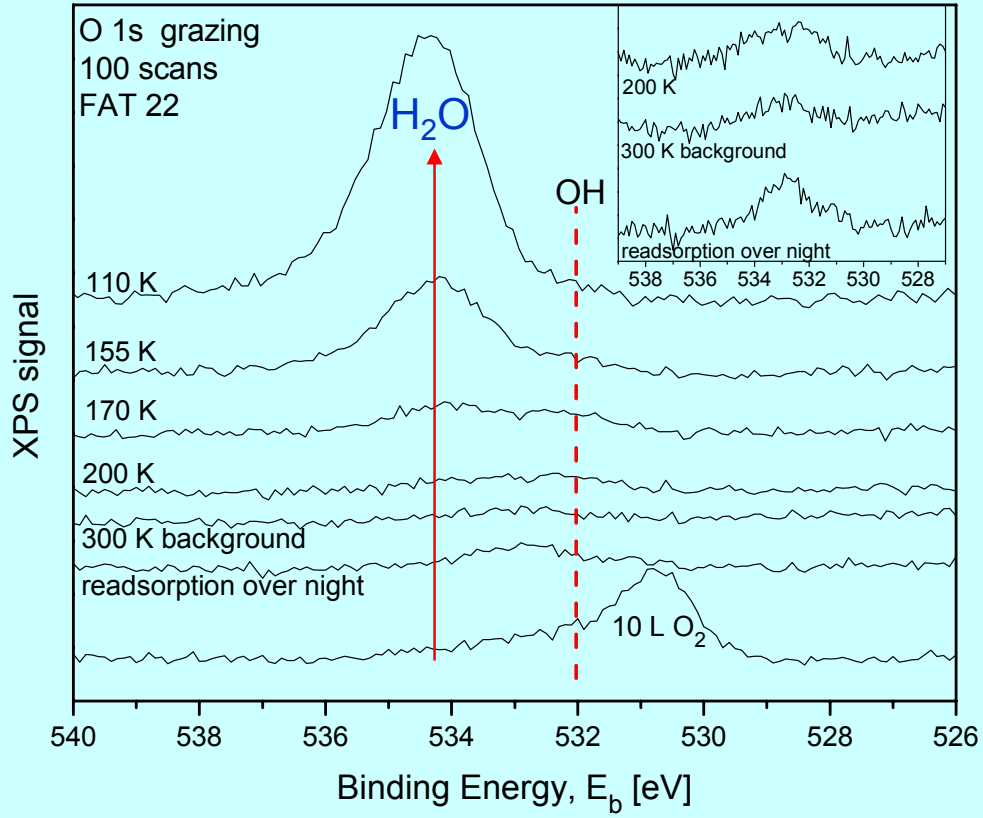
TPD of H_2O from clean Ru(10$\bar{1}$0)



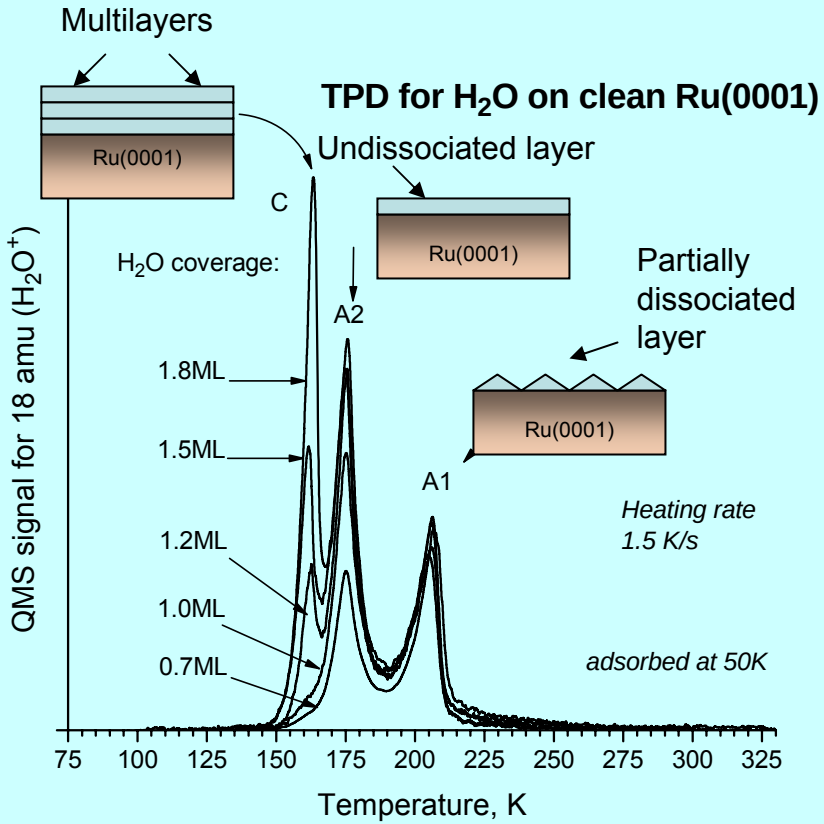
Evidence of dissociation

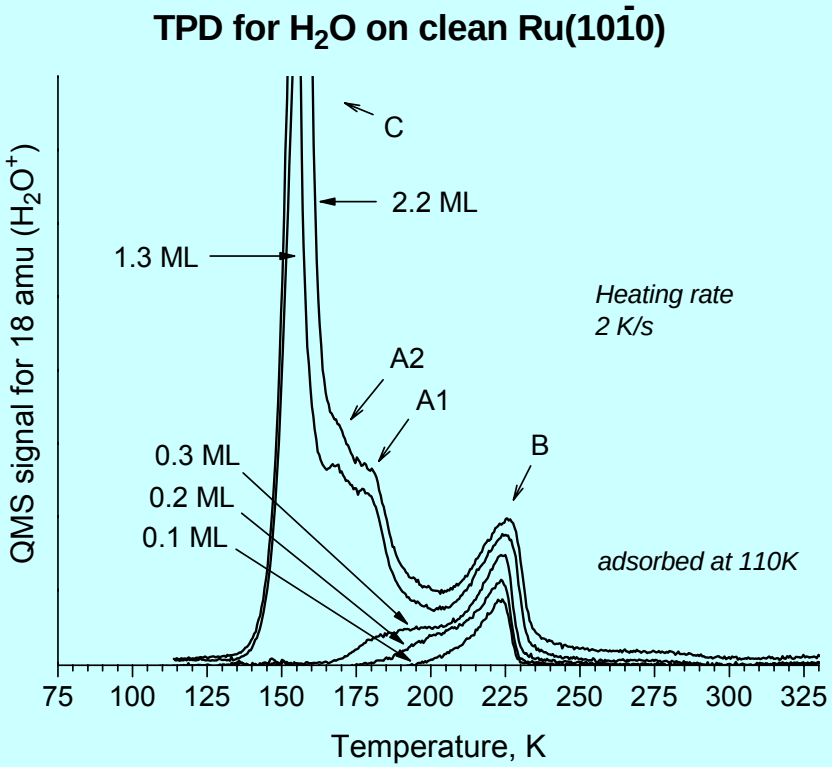
→ Supported by **XPS** data



H_2O adsorbs partially dissociated (TPD peak B) on Ru(10$\bar{1}$0)

TPD of water from two different Ru surfaces (0001) and $(10\bar{1}0)$





Highest T peaks correspond to recombination, $OH + H \rightarrow H_2O$

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Surface lifetime

Relevant for EUV mirror degradation:

- activation energies
- surface lifetimes
- coverages

Redhead eqn: $E_d = k_B T_{max}(\ln[\nu T_{max}/\beta] - 3.64)$

First order desorption: $\nu \sim k_B T/h \sim 1 \times 10^{13}\ s^{-1}$ **(assumed)**

Surface lifetime: $\tau = \nu^{-1} \exp(E_d/RT)$

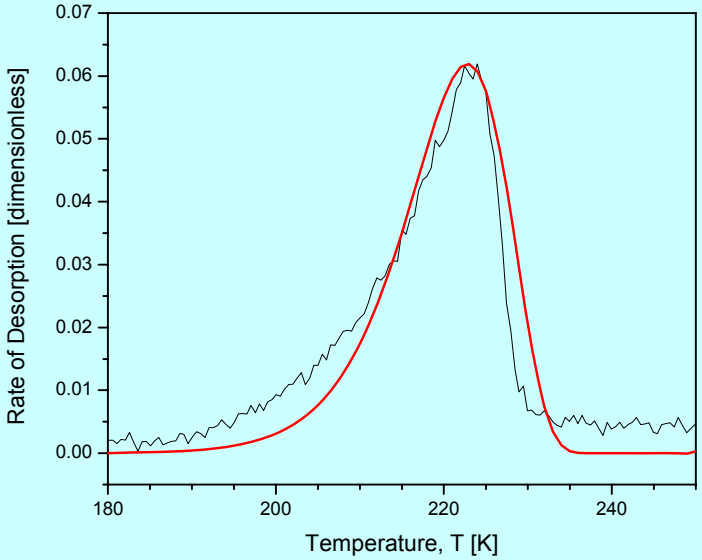
Coverage in ML: $\theta = 0.5 \times 10^6 \times p \times S \times \tau$

p in Torr, S sticking coefficient ~1

For H_2O

clean Ru (10$\bar{1}$0) surface	T (peak)	Activation energy E_d	Lifetime τ at T=300K	Coverage θ at 1×10^{-6} torr
estimation	225 K	0.60 eV	1.2 ms	6×10^{-4} ML
simulation	225 K	0.66 eV	0.4 ms	2×10^{-4} ML

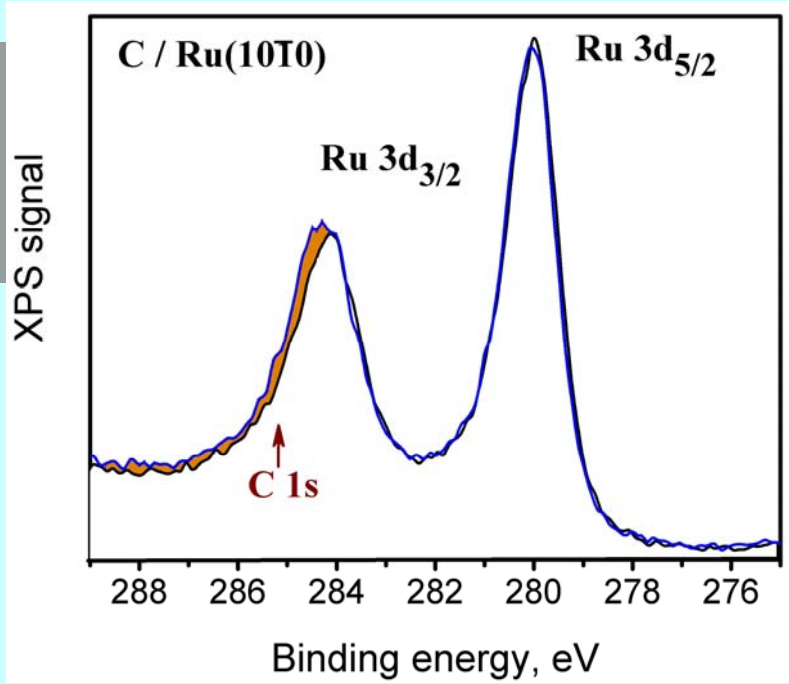
Pre-exponential factor in simulation:
$3 \times 10^{14}\ s^{-1}$



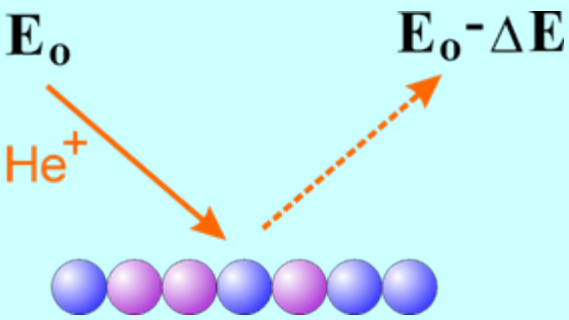
Surface lifetime of more reactive dissociation products is short, but may be long enough to cause radiation-induced chemical reactions

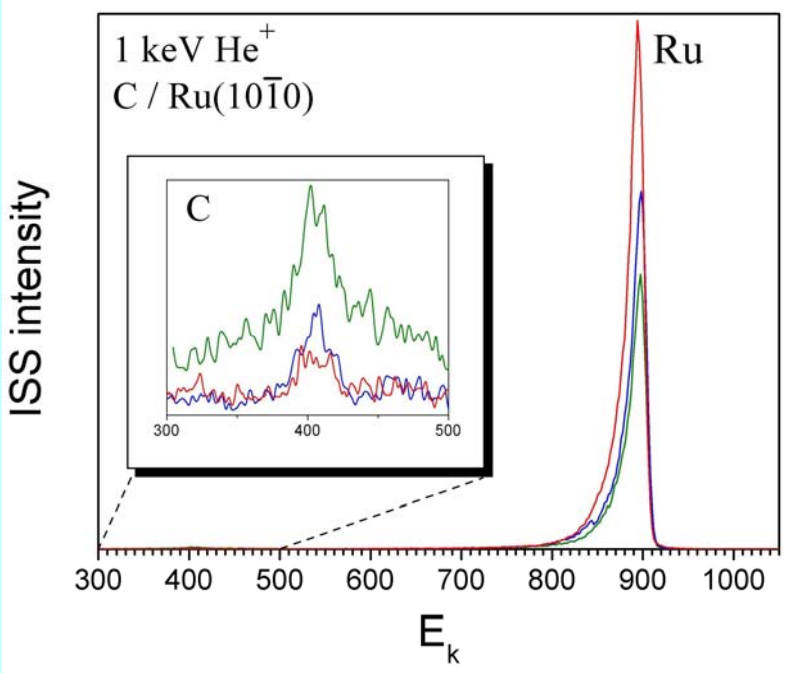
Detection of Carbon on Ru

Carbon growth may inhibit oxidation – but a carbon monolayer on Ru is hard to detect in XPS



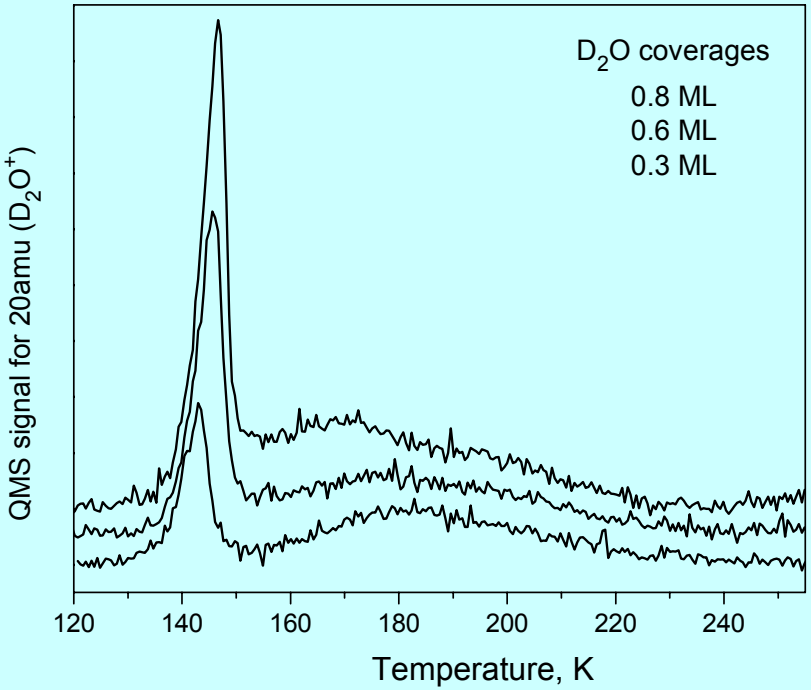
To measure onset of C reactions, a sensitive spectrometry is needed: low energy ion scattering (LEIS)



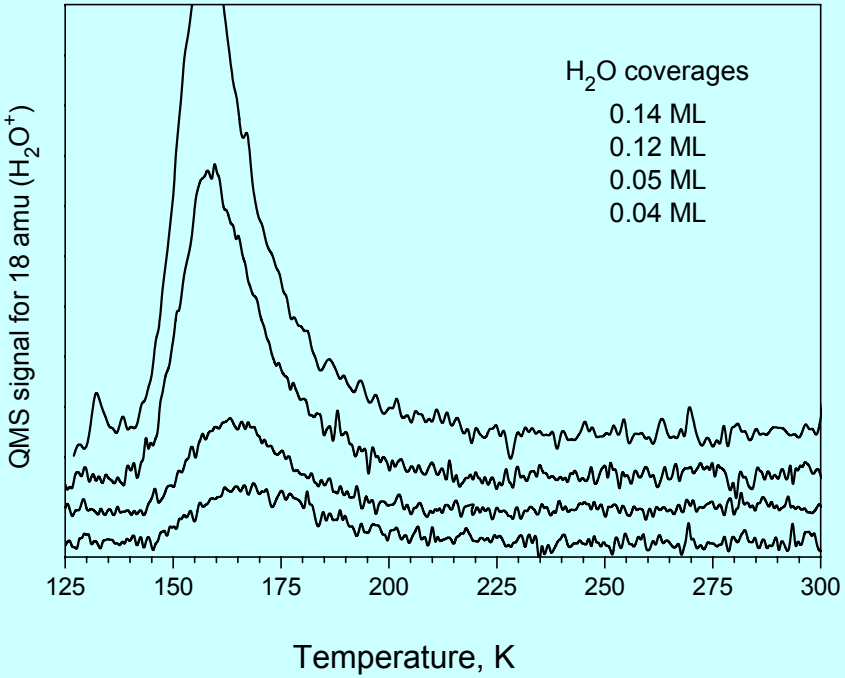


TPD of water from contaminated Ru

TPD of water from 80% **carbon-covered** Ru(1010)



TPD of water from **air - exposed** Ru(1010)



Binding energy and lifetimes of water on O-covered and C-covered surfaces less than on clean Ru ***(τ ~10^{-5} s)***

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Intermediate conclusions

- **Water adsorbs molecularly and dissociatively on Ru(10$\bar{1}$0), Ru(0001)**
- **Surface lifetimes short, < ms time scale**
- **Carbon, oxygen impurities cause decrease in H_2O binding energies, and surface lifetimes**

- **Next: Investigations on the influence of electron irradiation**

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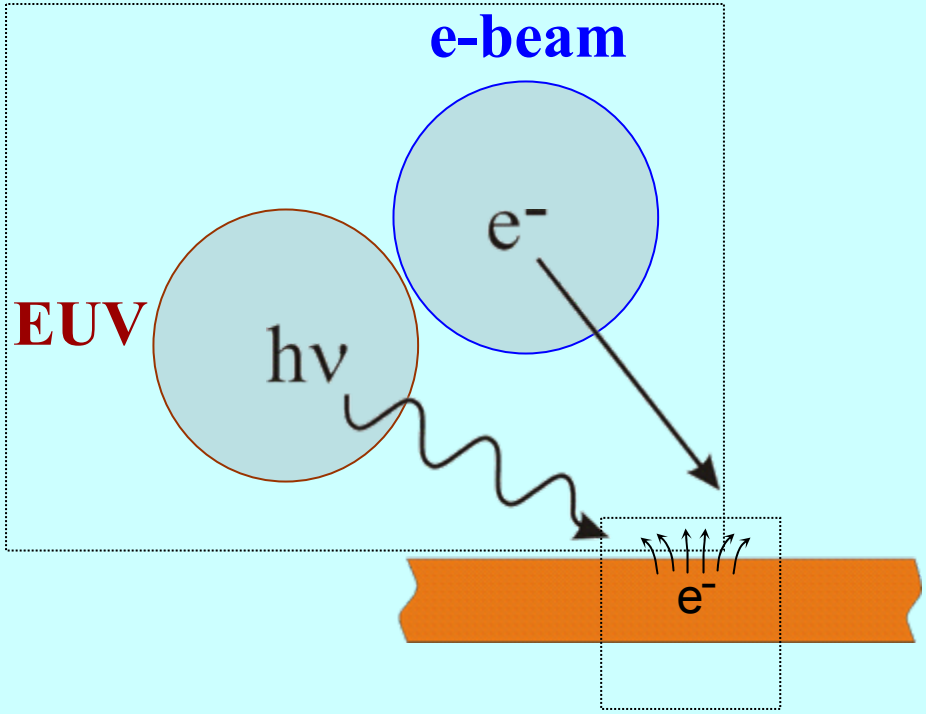
What do e-beams and EUV do to water on Ru?

Primary irradiation sources:

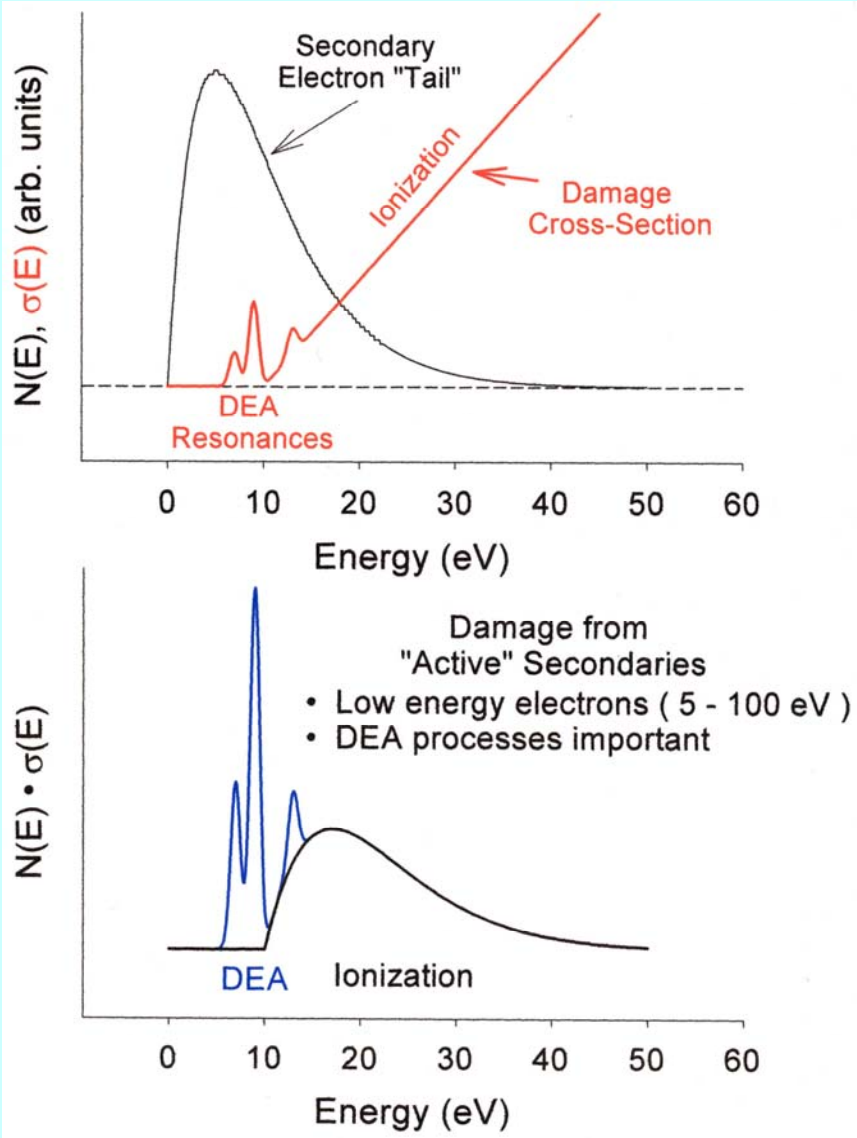


Secondary irradiation source:
photo- and secondary electrons

Our goal → to quantify beam damage in water layer on Ru

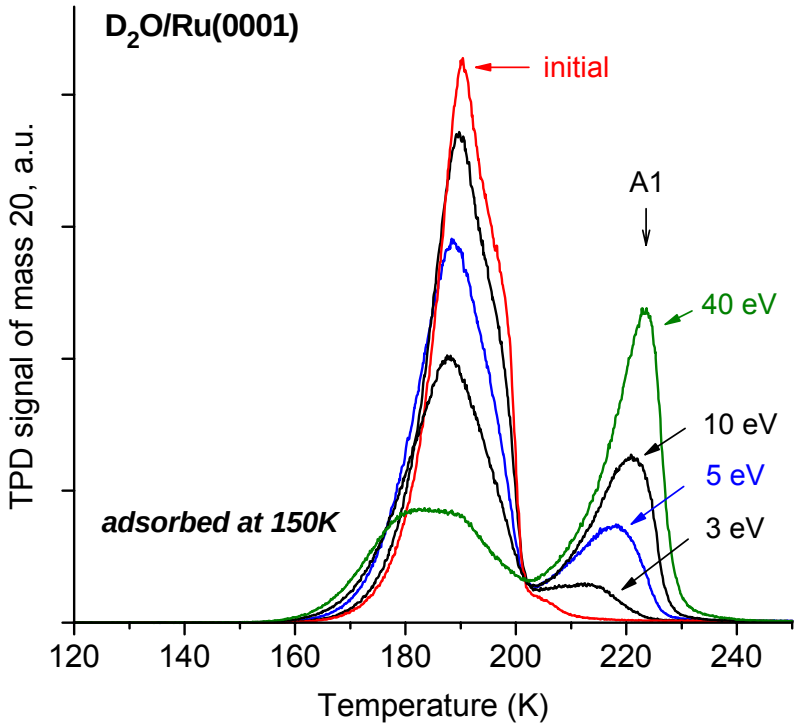
Importance of low energy "secondary" electrons in e^- and hν irradiation

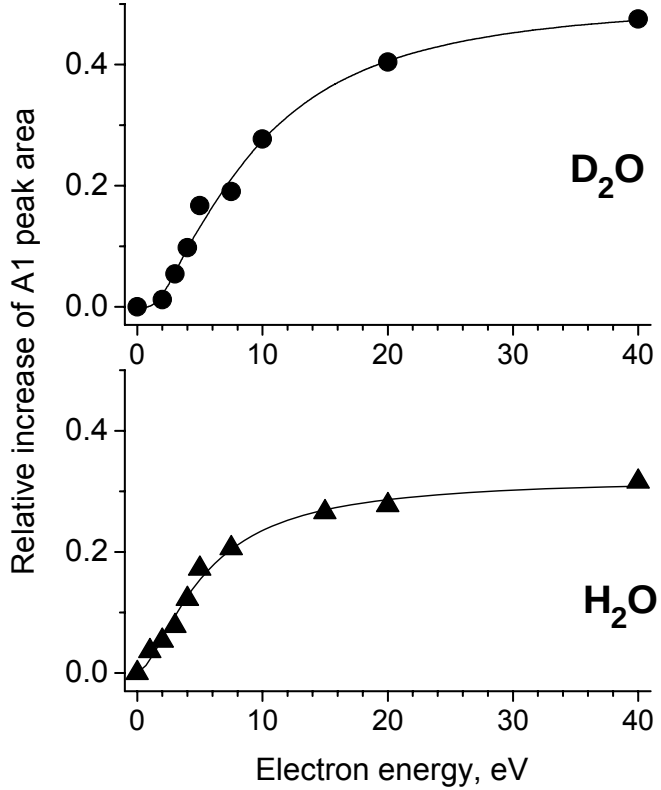
- Low-energy processes are particularly important, but not well-understood.
- At low energies (0-10 eV), dissociative electron attachment (DEA) resonances, and excited state (exciton) formation.
- At higher energies, dipolar dissociation (DD) & dissociative ionization (DI) contribute



T. M. Orlando and D. Meisel, Chapter 17, 2001, ACS Symp. Series 778

Electron-induced dissociation of water/Ru(0001): threshold measurements





Beam damage causes growth of the A1 TPD peak: dissociation into D + OD

Threshold energies are in the range 0 ~ 2eV

(Faradzhev et al.,Chem. Phys. Lett. 415 (2005) 165)

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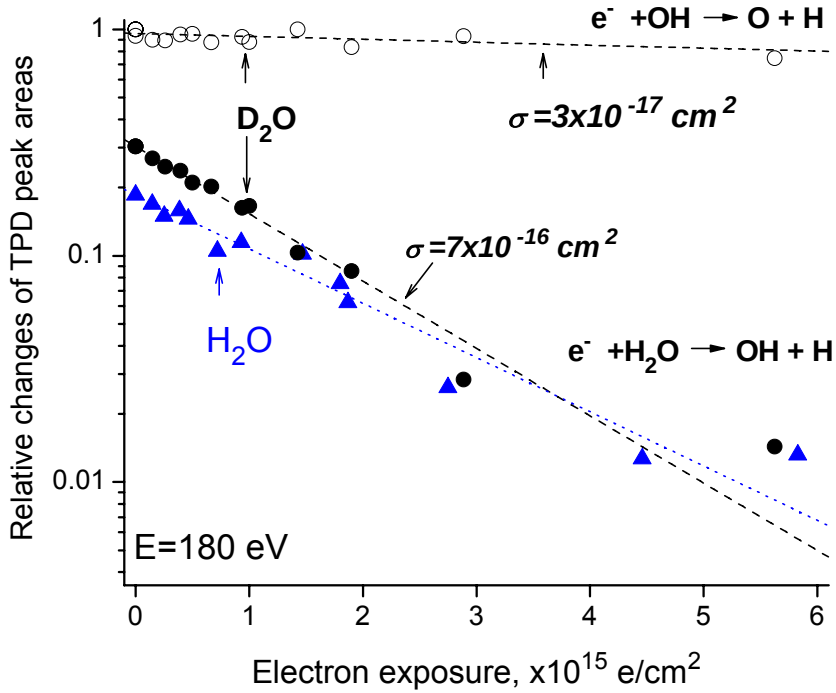
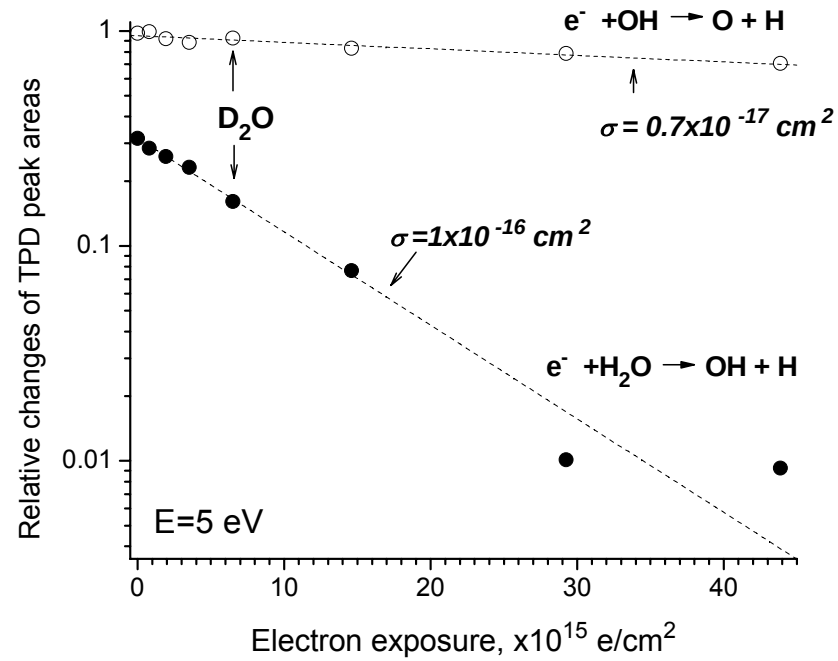
Electron-induced dissociation of water/Ru(0001): cross section measurements





The "fast" process corresponds to *partial dissociation* to H + OH

The "slow" process includes desorption & *full dissociation* to O + H

(Faradzhev et al., Chem. Phys. Lett. 415 (2005) 165)

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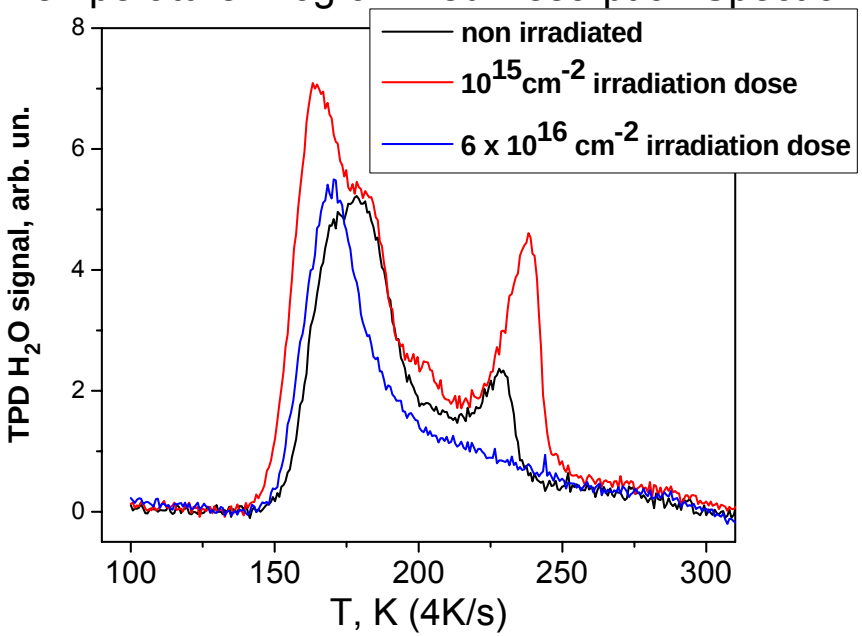
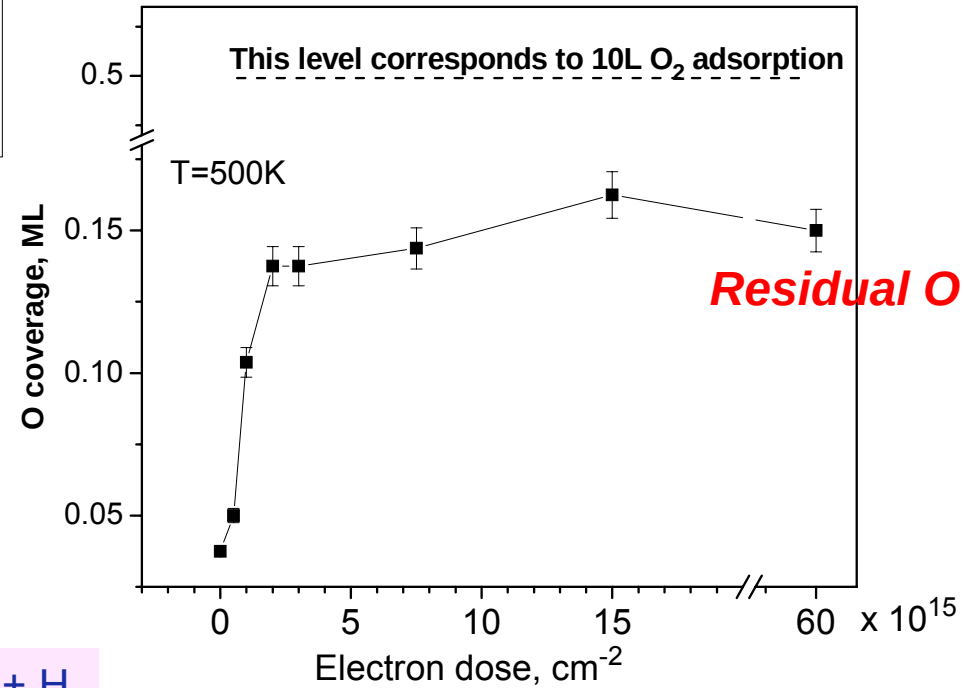
On Ru(10$\bar{1}$0), similar effects for electron-induced dissociation of H_2O

- Bombard ~2ML **H_2O** with 100 eV electrons
- Thermally desorb all **H_2O (TPD)**, measure residual **O using LEIS**

Temperature Programmed Desorption Spectra



Low Energy Ion Scattering of O accumulation



Evidence for 2 steps: $e^- + H_2O \rightarrow OH + H$

$e^- + OH \rightarrow O + H$

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Summary

- Water adsorbs molecularly and dissociatively on Ru($10\bar{1}0$), Ru(0001)
- Surface lifetimes short, < ms time scale
- Carbon, oxygen impurities reduce water binding energy, lifetimes
- Thresholds for e^- - induced dissociation low, a few eV
- Electron - induced dissociation processes on Ru include

***fast*:** $e^- + H_2O \rightarrow H + OH$

slow: $e^- + OH \rightarrow O + H$

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Thank you!