Progress and problems in understanding the structure of vanadia and titania surfaces

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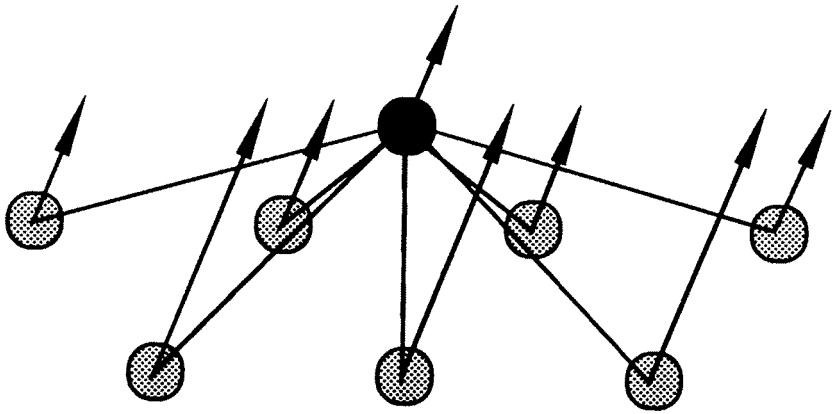
1. Methodology

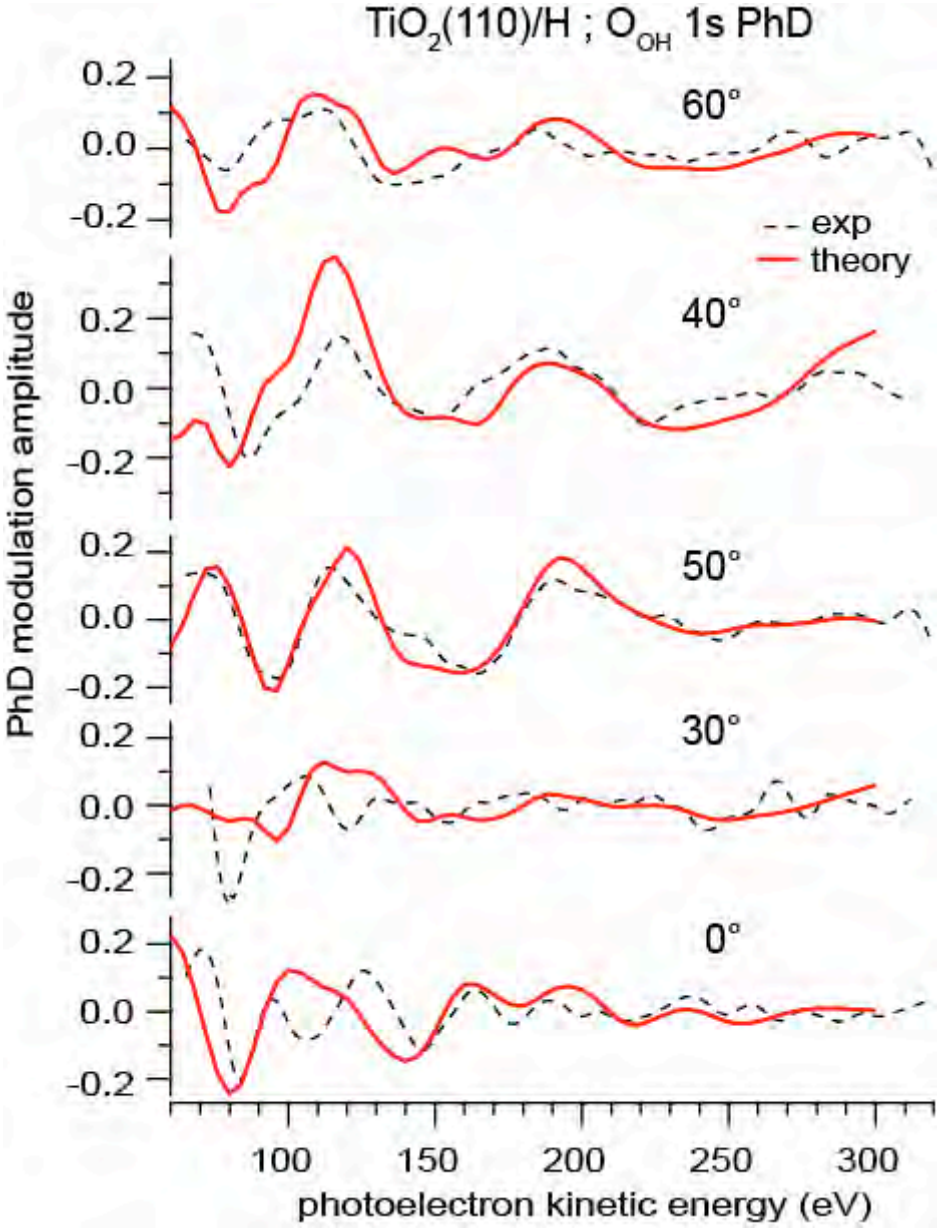
2. New results: vanadyl phthalocyanine; (glycine and) H on TiO_2(110)

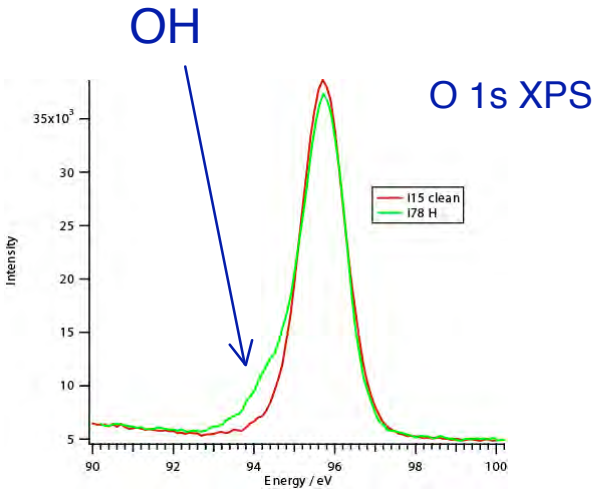
3. The V_2O_3(0001) clean surface – new insight from medium energy ion scattering?

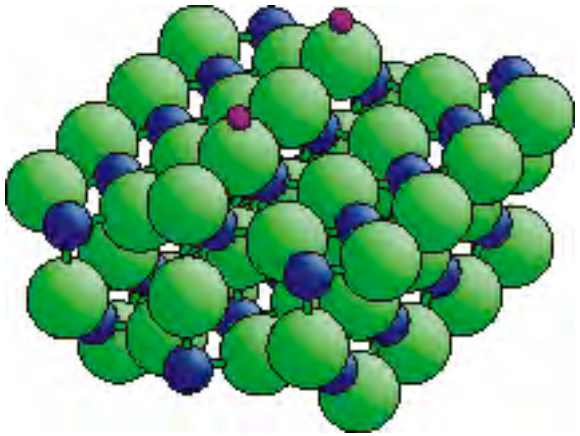
Scanned-energy mode photoelectron diffraction



Element-specific *and* ***chemical-state-specific local structure*** *through elastic scattering interferences of photoelectron wavefield*


TiO2(110)/H ; OOH 1s PhD
60°
40°
50°
30°
0°
exp
theory
PhD modulation amplitude
0.2
0.0
-0.2
100
150
200
250
300
photoelectron kinetic energy (eV)


OH
O 1s XPS
35x10³
30
25
20
15
10
5
Intensity
I15 clean
I78 H
90
92
94
96
98
100
Energy / eV



Recent PhD structure studies completed

- TiO_2(110) + H (also +(H+OH) in progress)
- TiO2(110) + glycinate *published*
- Vanadyl phthalocyanine on Au(111) *published*

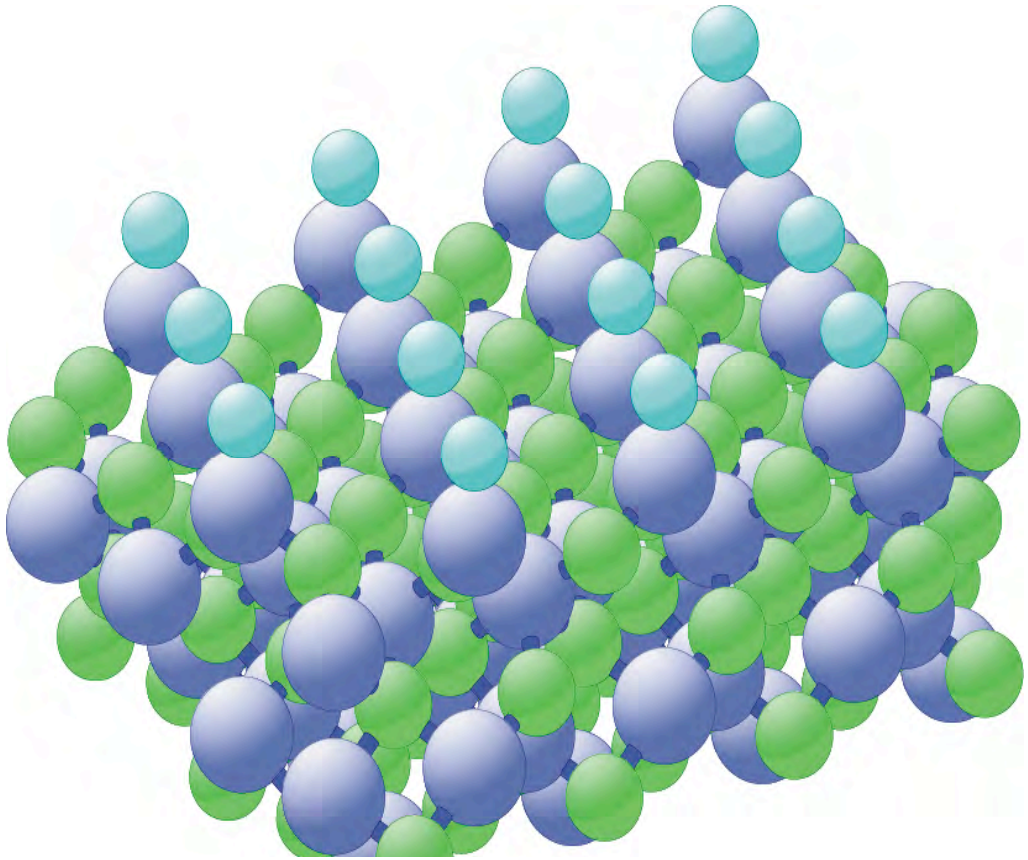
PhD structure studies unresolved

- V_2O_3(0001) + CO & + CH_3O(H)

PhD structure studies attempted

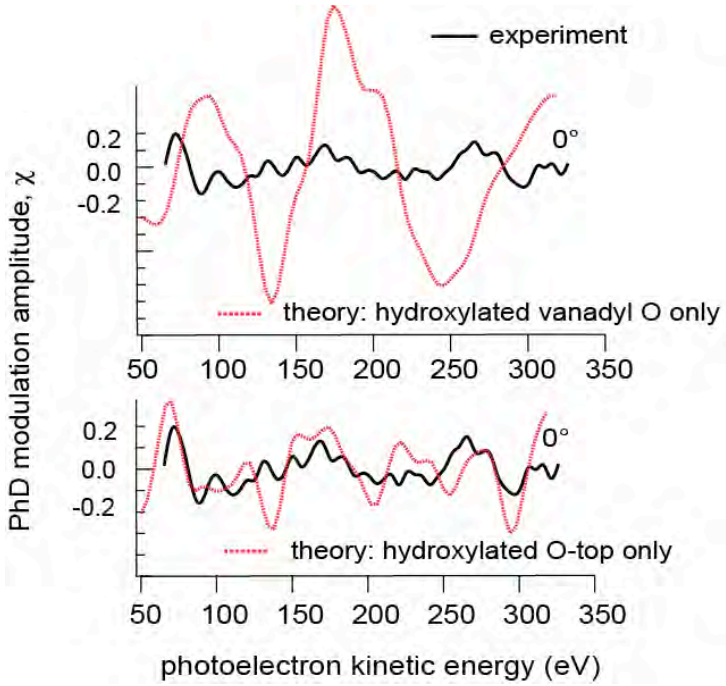
- V_2O_3(0001) + CH_3
- TiO_2 + CH_3
- Ru(0001) + CeO + V

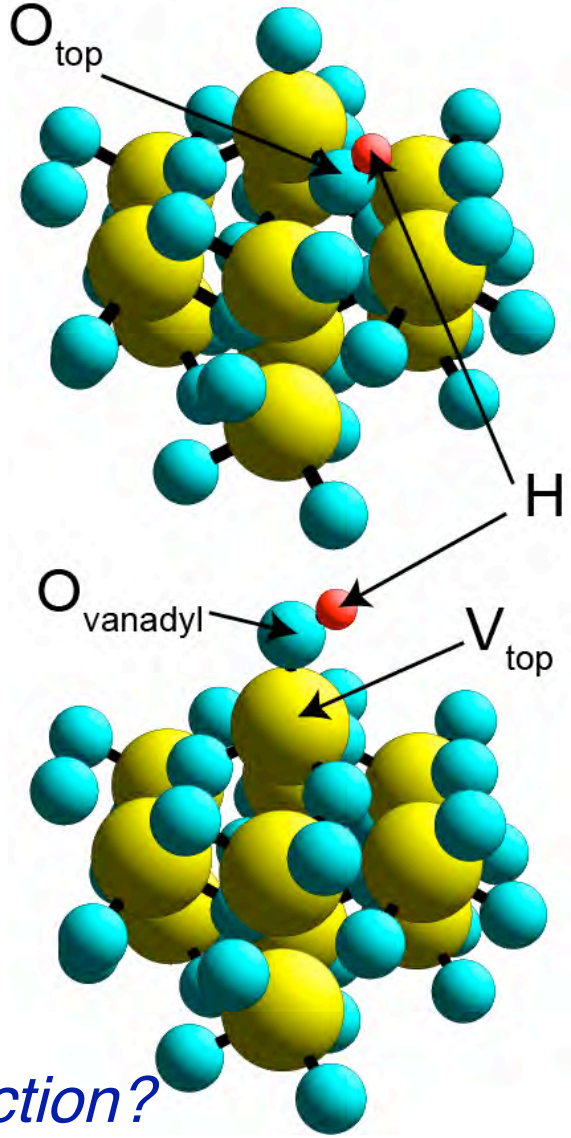
An old problem – the structure of $V_2O_3(0001)$:
V=O termination?



- LEED (Kuhlenbeck) favours V=O
- O 1s and V 2p PhD – ambiguous – half-metal or V=O
- O 1s PhD from hydroxylated surface shows OH is not atop V

Hydroxylation of $V_2O_3(0001)$ – which O atoms are hydroxylated?



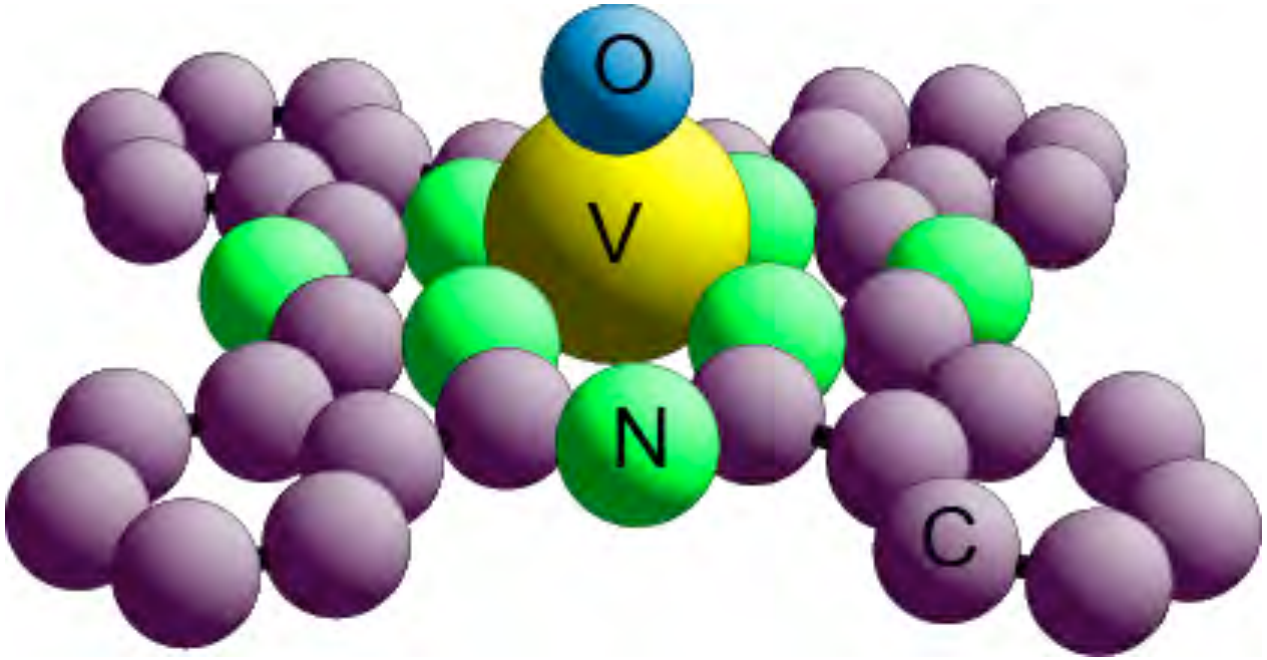


Normal emission O(H) 1s says NOT the vanadyl O

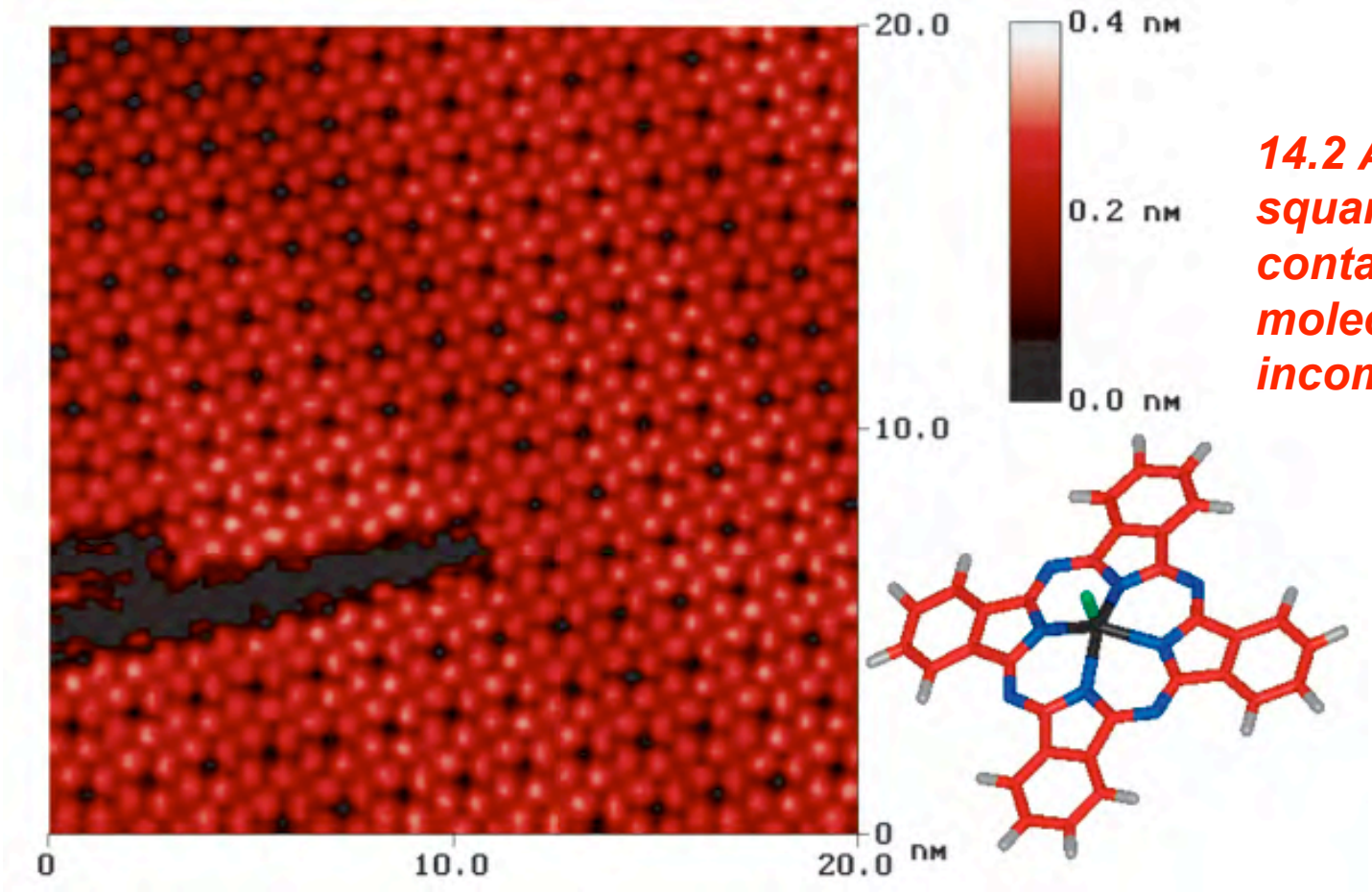
Is there a way of checking the PhD prediction?

Vanadyl phthalocyanine

VOPc

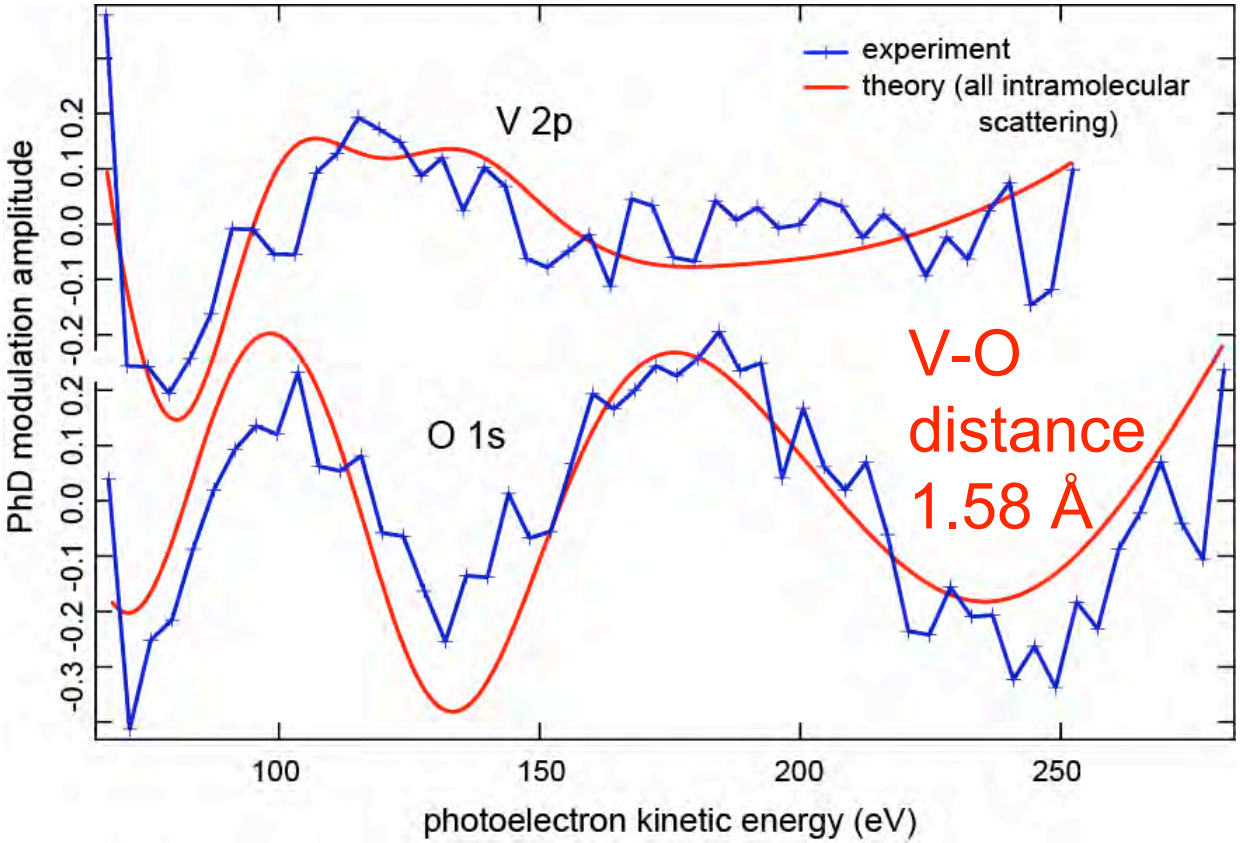


VOPc on Au(111) – STM *D.E.Barlow, K.W. Hipps, J. Phys. Chem. B 104 (2000) 59934*

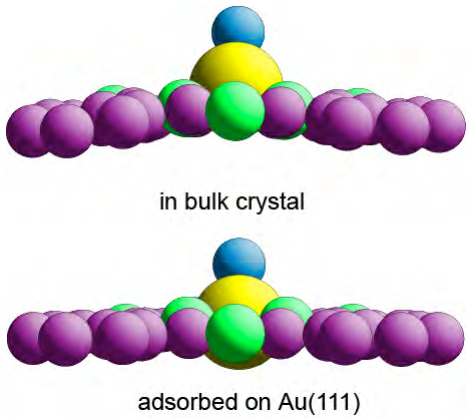


14.2 Å x 14.2 Å square unit mesh containing one molecule – incommensurate!

VOPc on Au(111) – O 1s and V 2p
PhD – normal emission



Intramolecular scattering only

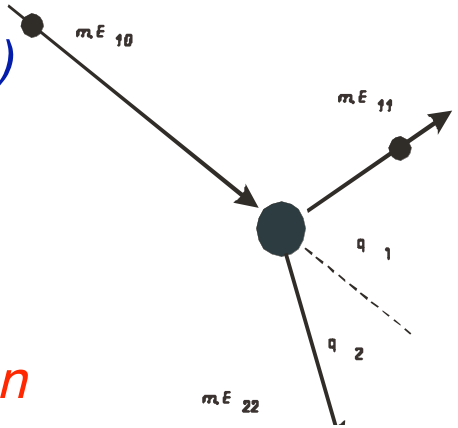


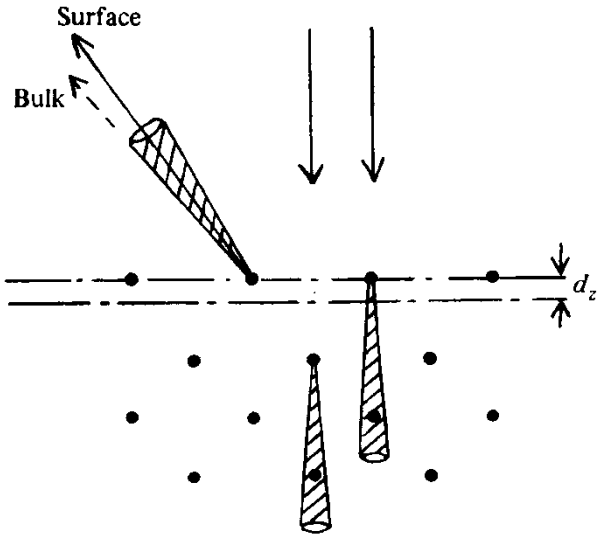
Medium Energy Ion Scattering (MEIS)

Scattered ion energy determined by:

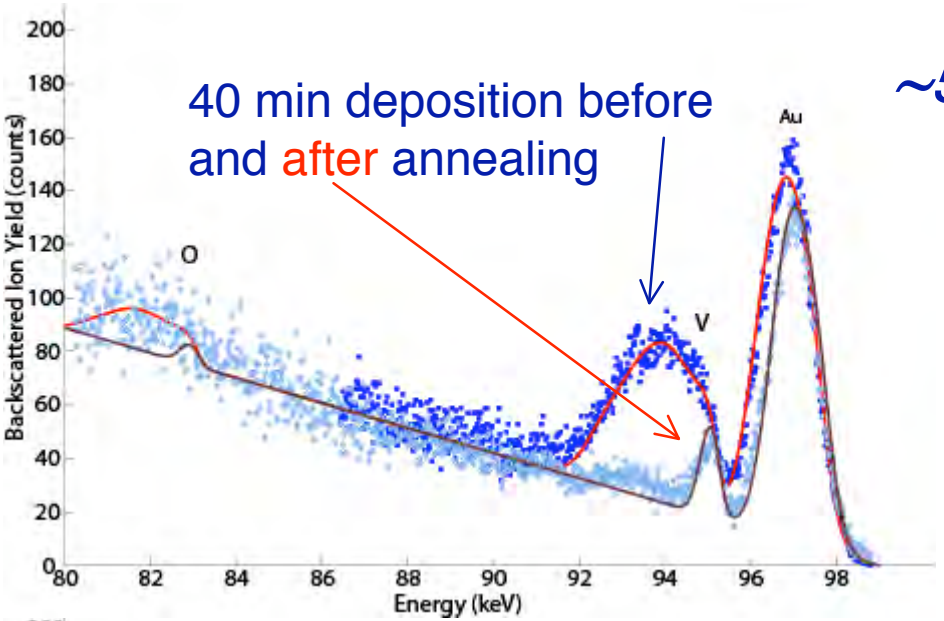
- *elastic scattering recoil energy loss (binary collision) - depends on mass of scatterer*
- *inelastic energy loss which is proportional to the path through the solid*

HENCE *depth-resolved compositional information*

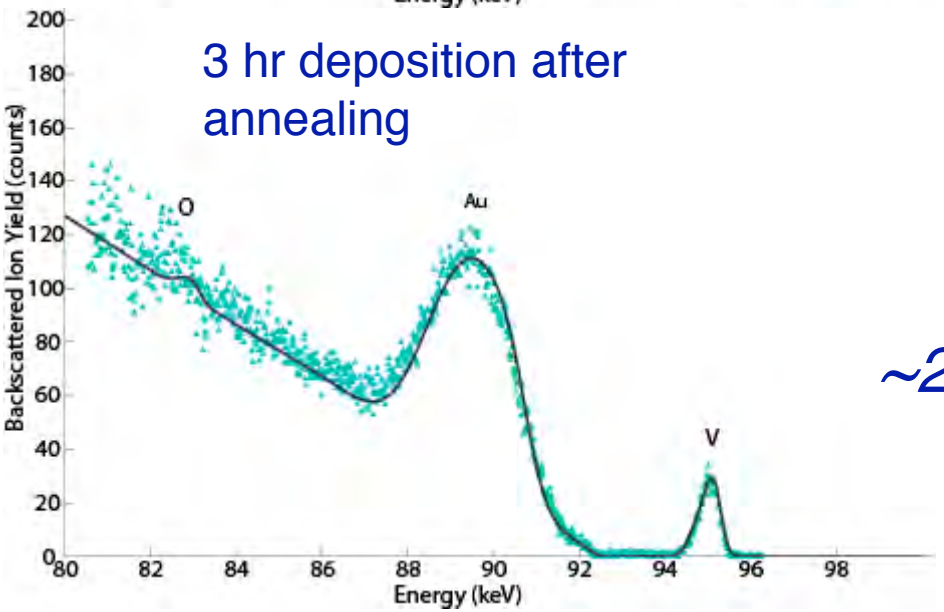




- *Elastic shadowing gives surface specificity*
- *Same effect in outgoing ions ('blocking') gives structural information*



~50 A

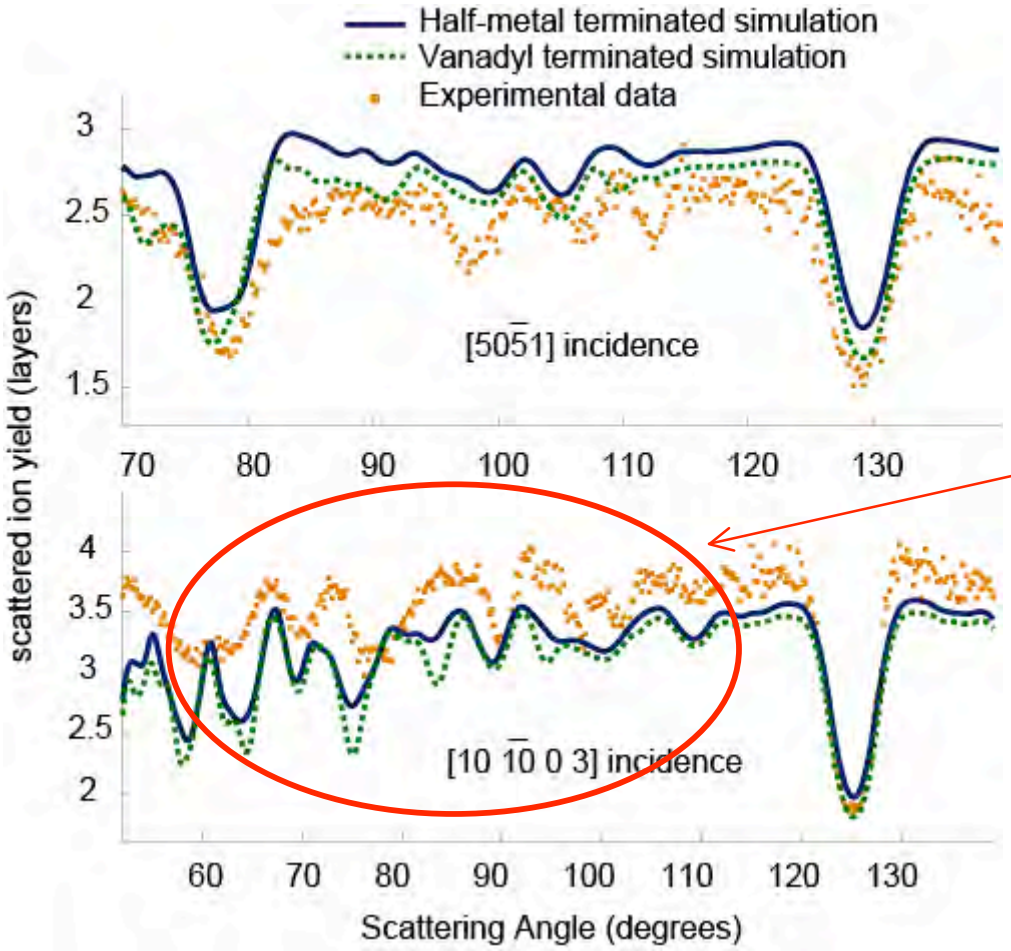


~200 A

Characterisation of film growth and ordering

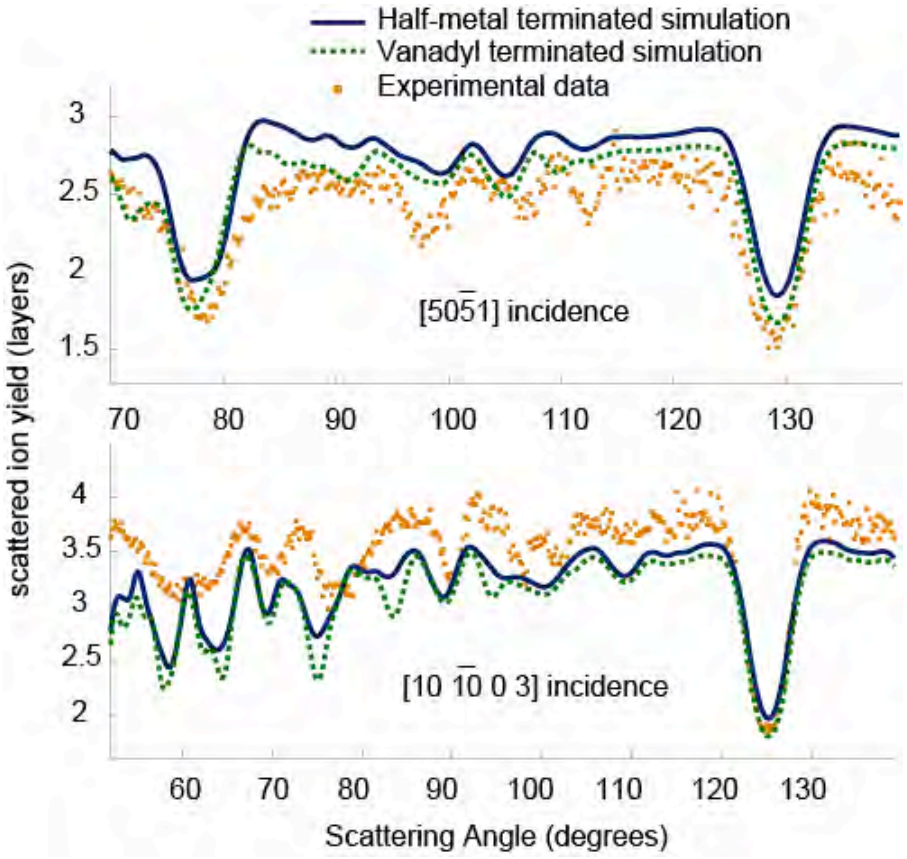
100 keV H^+ MEIS

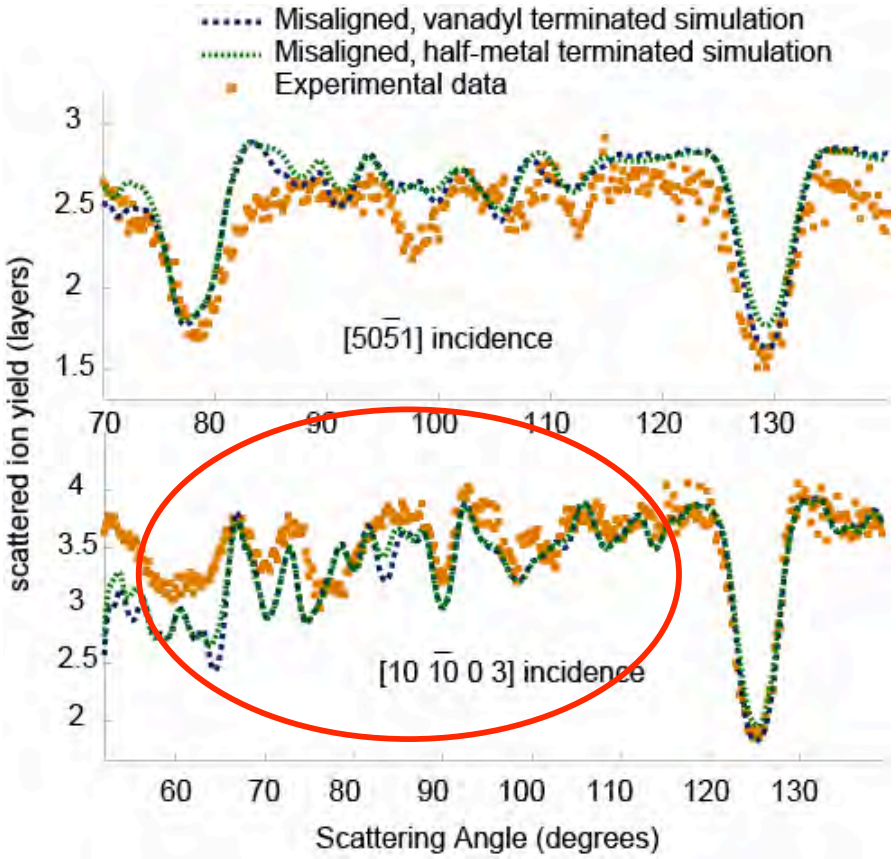
MEIS blocking curves from $V_2O_3(0001)$



Very poor fit!

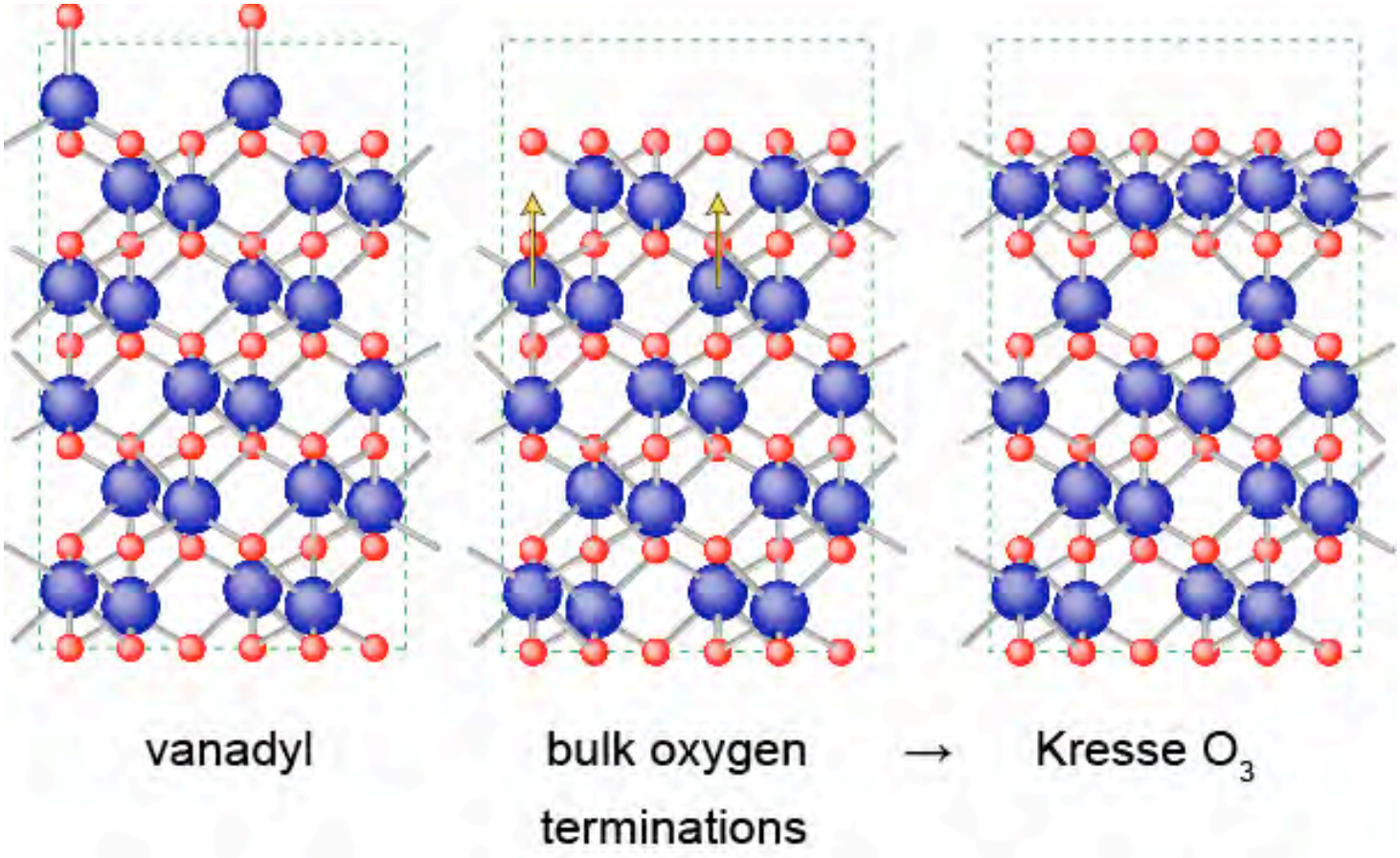
MEIS blocking curves from $V_2O_3(0001)$





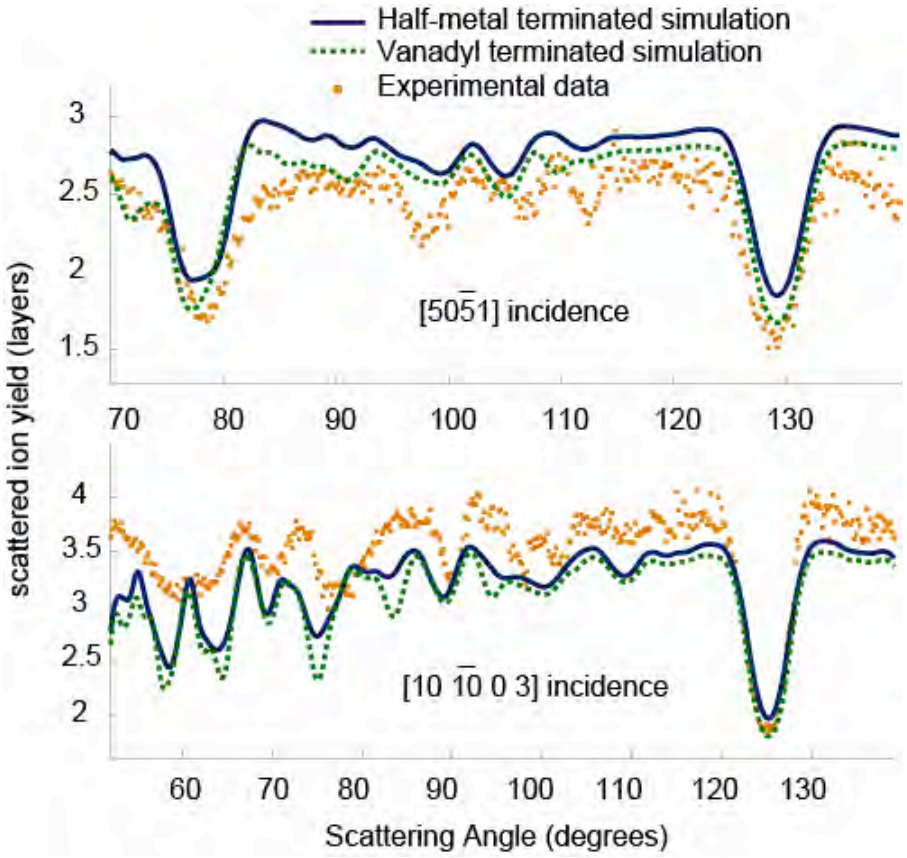
Film misalignment **might** account for the discrepancies

An alternative interpretation – the Kresse O_3 model

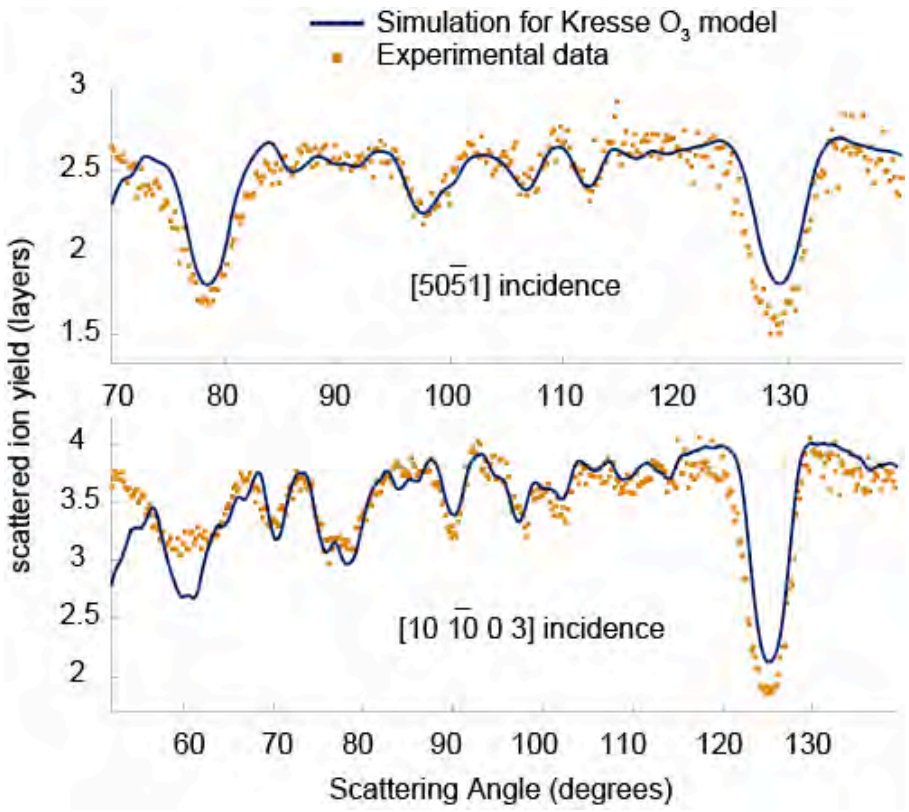


V moves up by ≥ 2 Å!

MEIS blocking curves from $V_2O_3(0001)$

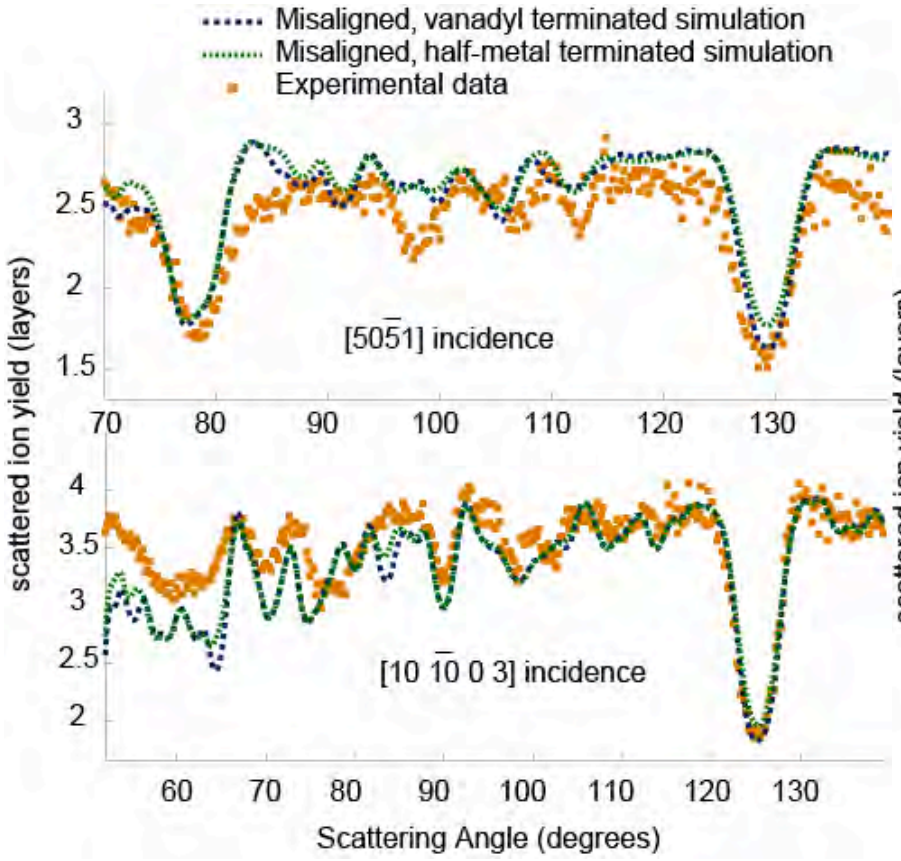


Vanadyl & half-metal models

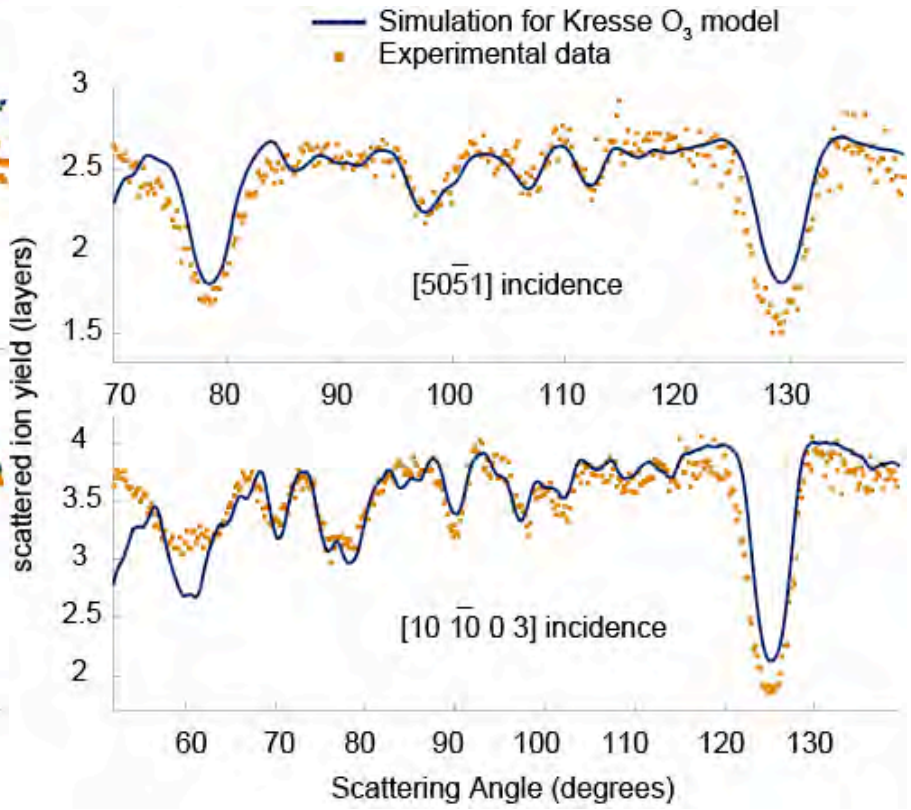


Kresse O_3 model

MEIS blocking curves from $V_2O_3(0001)$



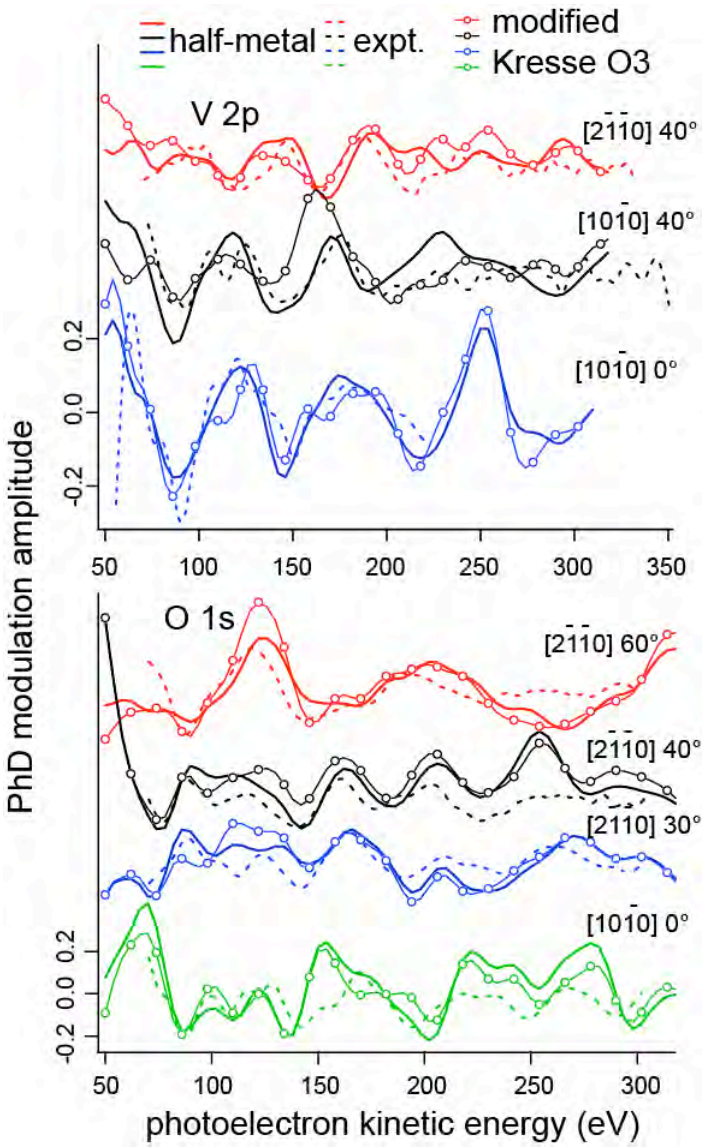
Misaligned vanadyl & half-metal models

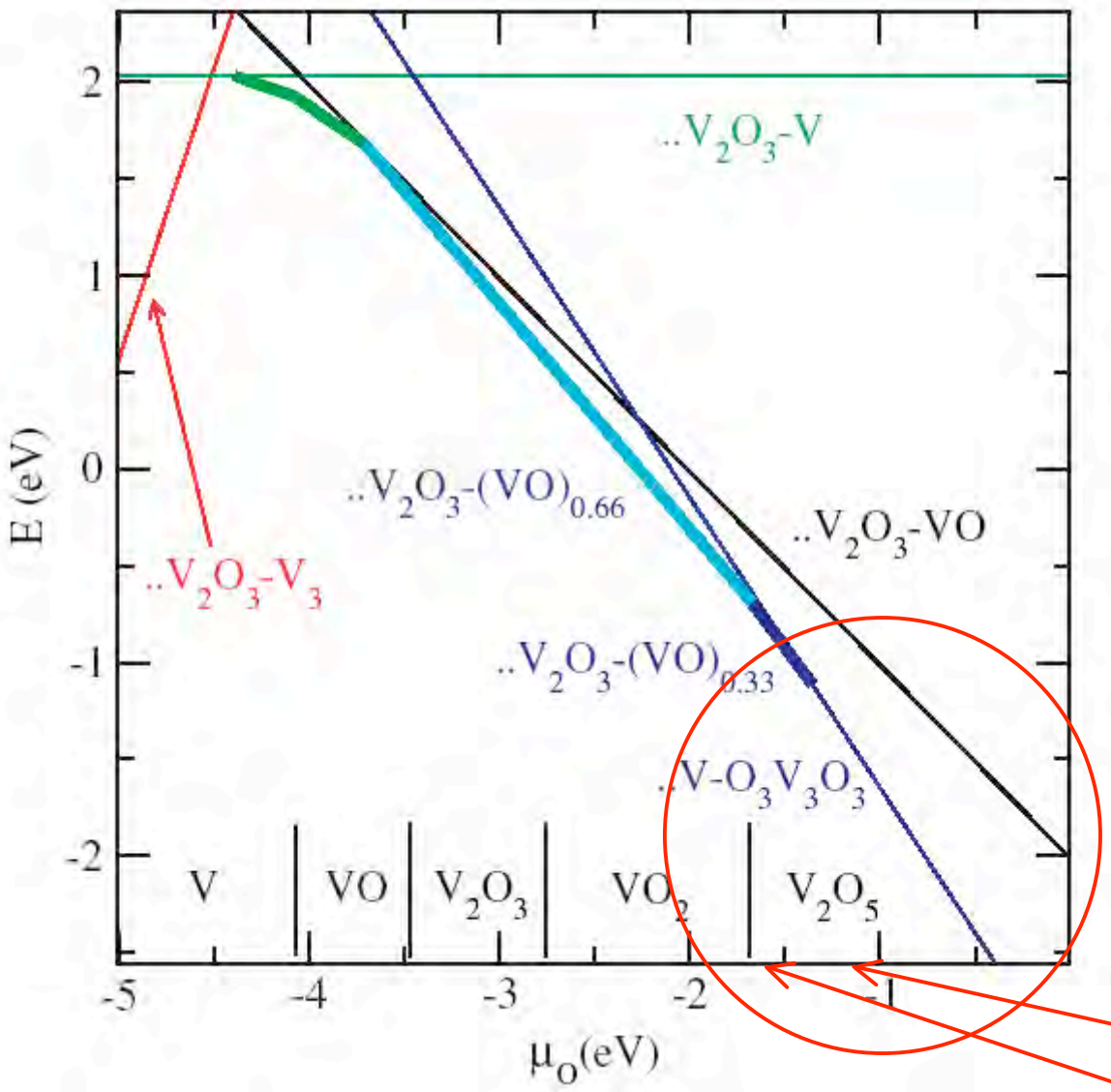


Kresse O_3 model

Is the old PhD data compatible with the Kresse O3 structure?

- OH on V_2O_3 – yes (O 1s only)
- Clean V_2O_3 – yes – IF displaced V atoms is moved back down by 0.5 Å

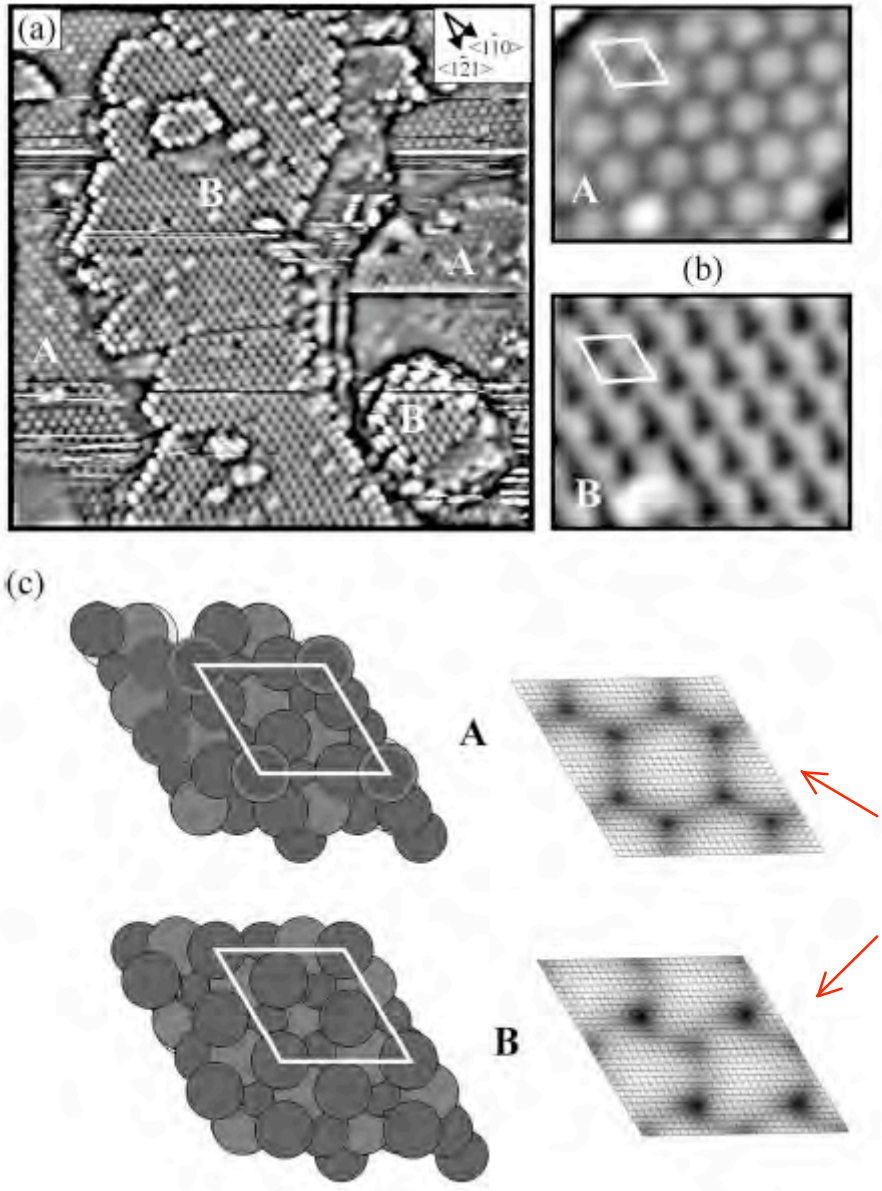




Kresse *et al.* SS 555 (2004) 118:

'The oxygen rich termination, on the other hand, is stable already for an oxygen chemical potential of -2.0 eV, which is actually realizable under typical UHV conditions.'……..The thermodynamics …. favours the VO termination, when the surface is in thermal equilibrium with bulk V2O3, and the O3 termination under typical oxygen rich ambient or even not too reducing UHV conditions.'

@ 10^{-7} mbar O_2
T ~340°C
T ~520°C



Surnev *et al.* SS 495 (2001) 91:

For the oxygen pressure employed [2x10^{-7} mbar] … two V_2O_3(0001) terminations with almost equal formation energies are found in the DFT calculations. In .. Model A the ..surface is terminated by V=O …. In Model B the surface is terminated by three O atoms per unit cell as in the bulk.

STM simulations