Complex Redox Chemistry on $RuO_2(110)$ – CO Oxidation

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† *Walter Ekardt – RIP*

Acknowledgements

- **Gerhard Ertl**
- Young Dok Kim
- Stefan Wendt
- Markus Knapp
- Karl Jacobi
- Hicham Idriss
- ...

CO oxidation: Prototypical catalytical reaction

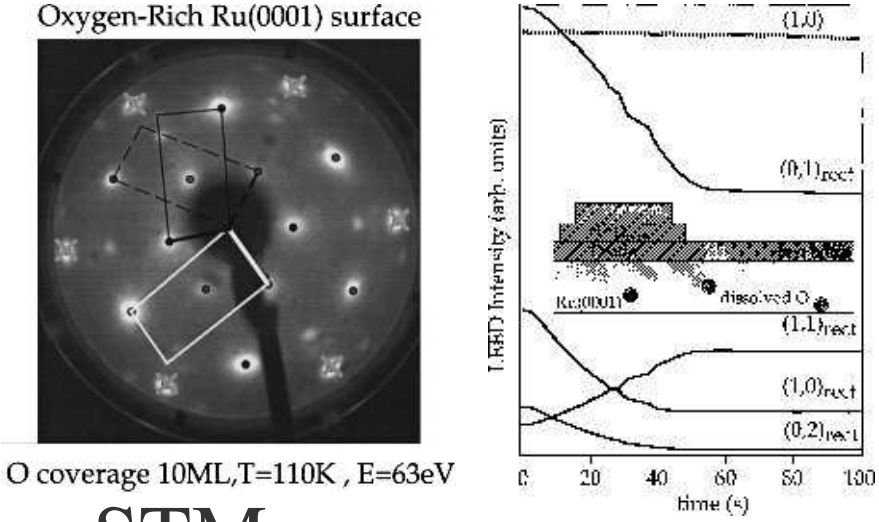
- CO+O/Ru(0001)
  - Poor catalyst as such
  - After oxygen dosis an excellent catalyst

- Material gap:
  - The active surface consists of *ruthenium oxide* (Over *et al; Science,* 2000)

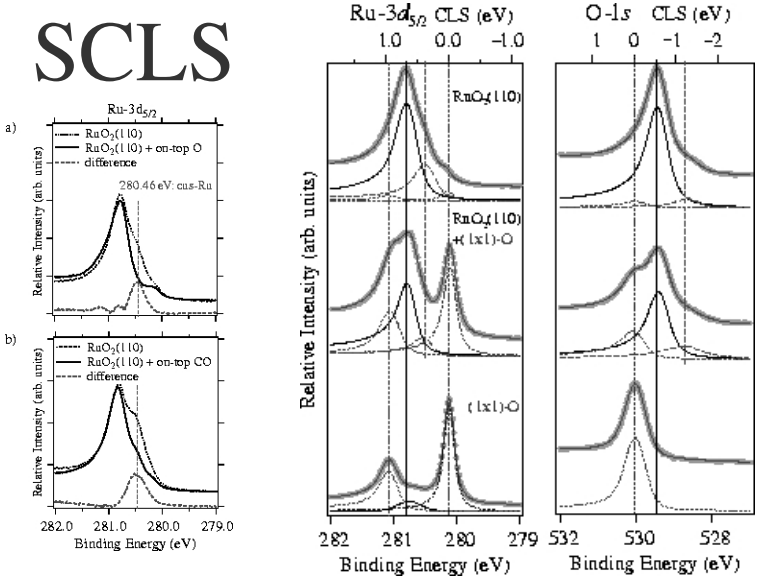
- (Pressure gap?
  - Zang & Kisch
  - New measurements by Jacobi *et al*)

$RuO_2(110)$: Characterisation

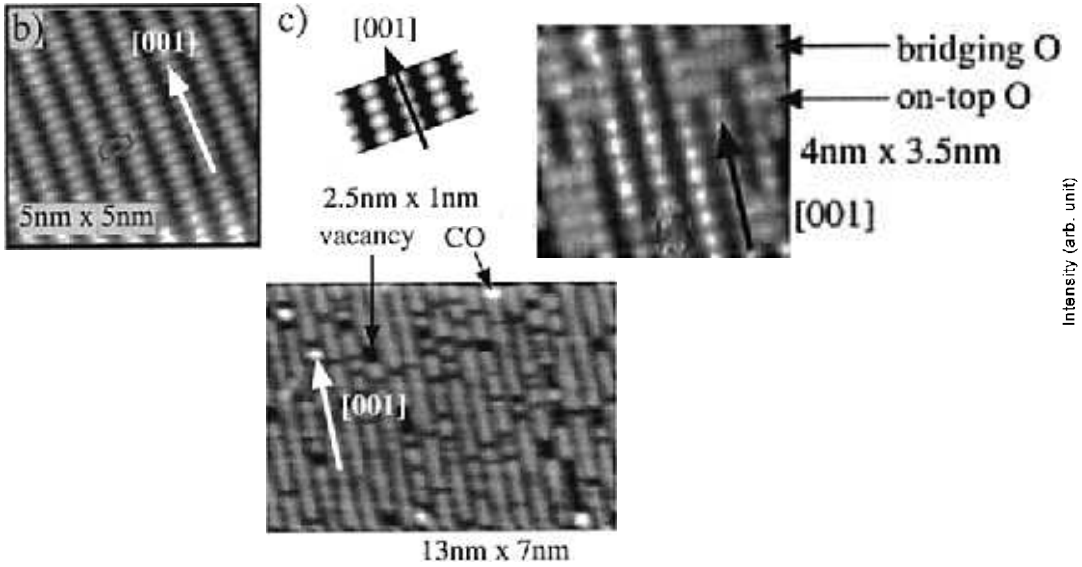
- LEED



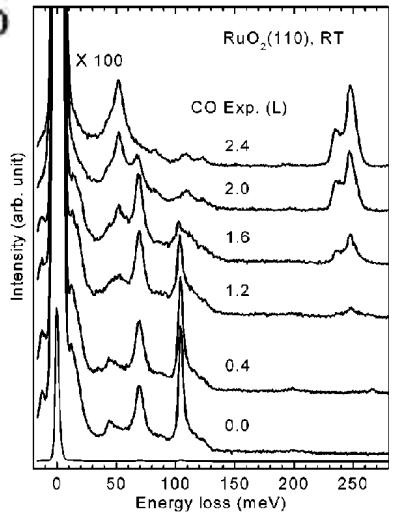
- SCLS



- STM



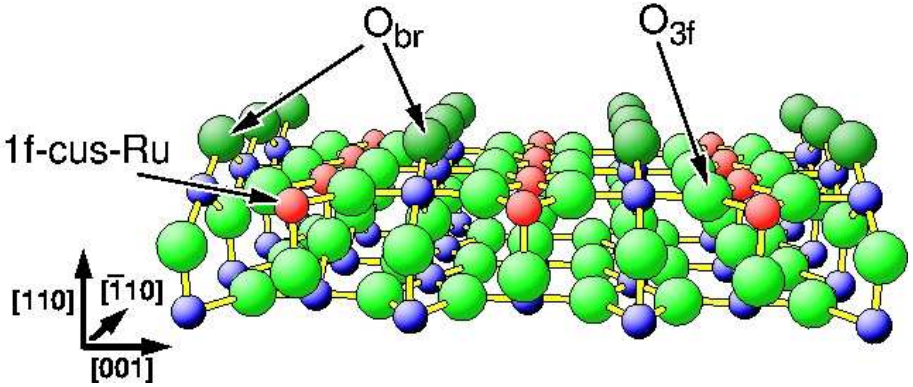
- HREELS



Jacobi *et al*

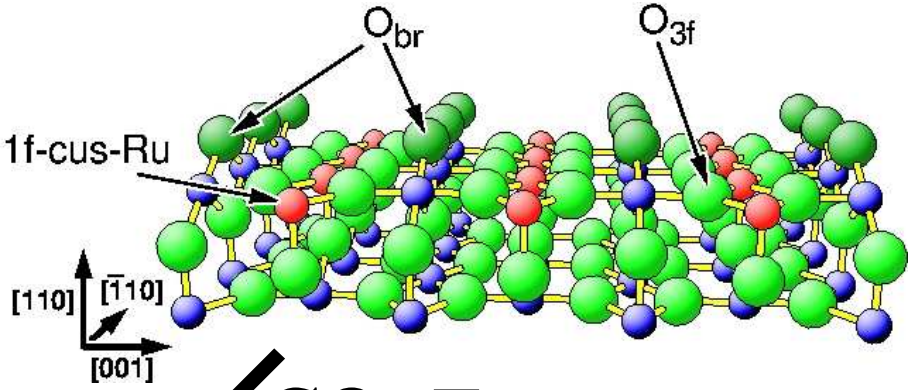
$RuO_2(110)$ terminations

s-$RuO_2(110)$



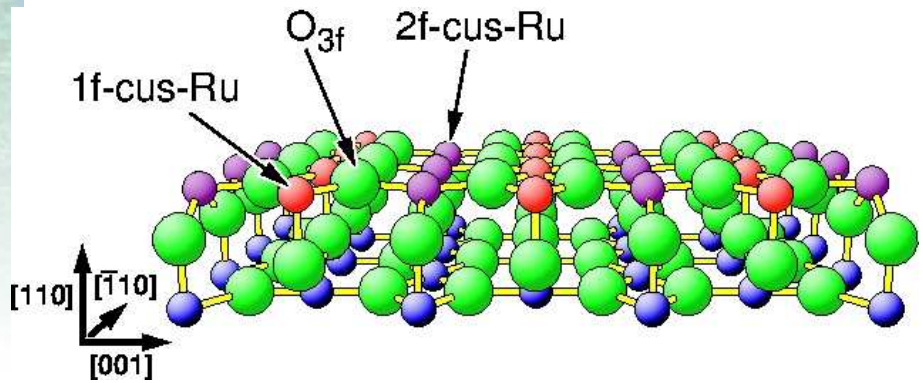
$RuO_2(110)$ terminations

s-RuO_2(110)



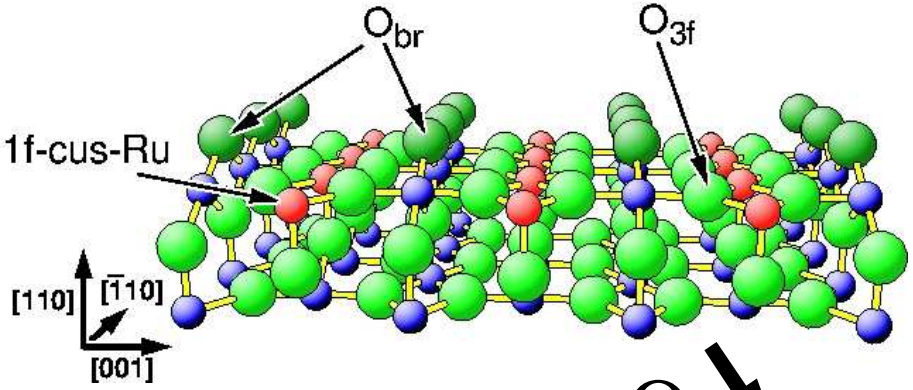
CO, *T*

r-RuO_2(110)



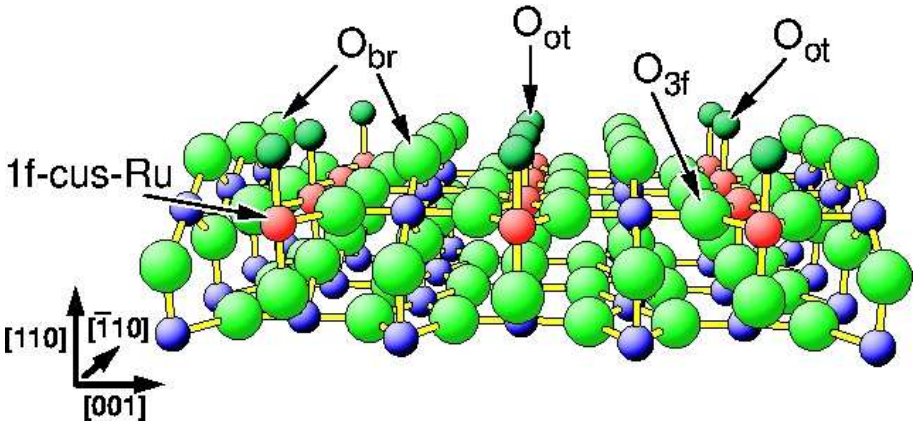
$RuO_2(110)$ terminations

s-RuO_2(110)



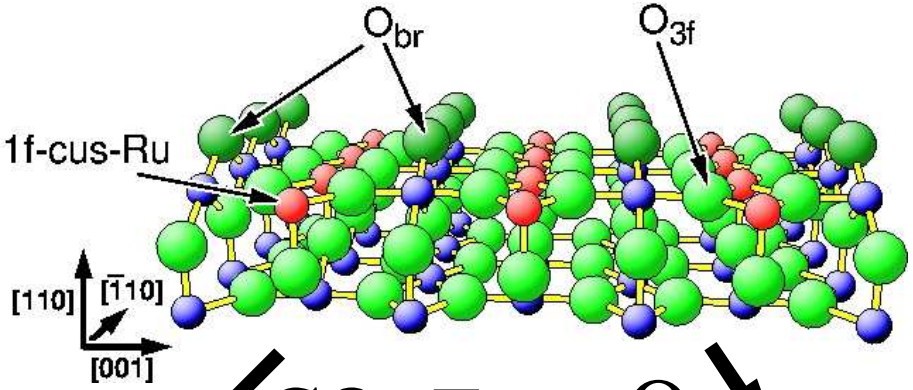
O_2

s-RuO_2(110)-$O_{on\text{-}top}$



$RuO_2(110)$ terminations

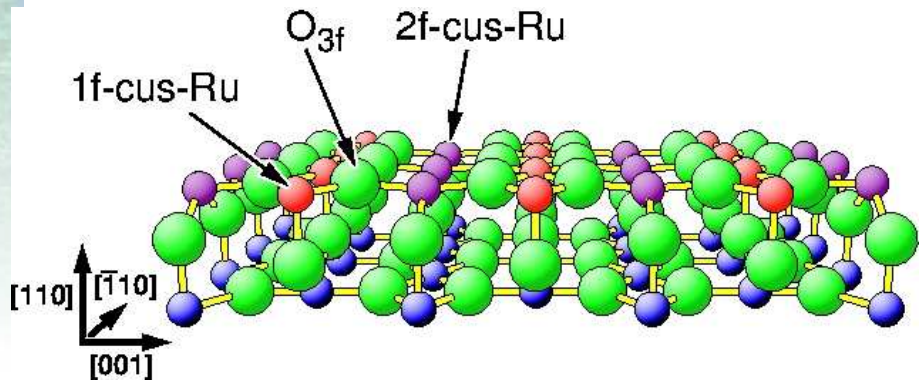
s-RuO_2(110)



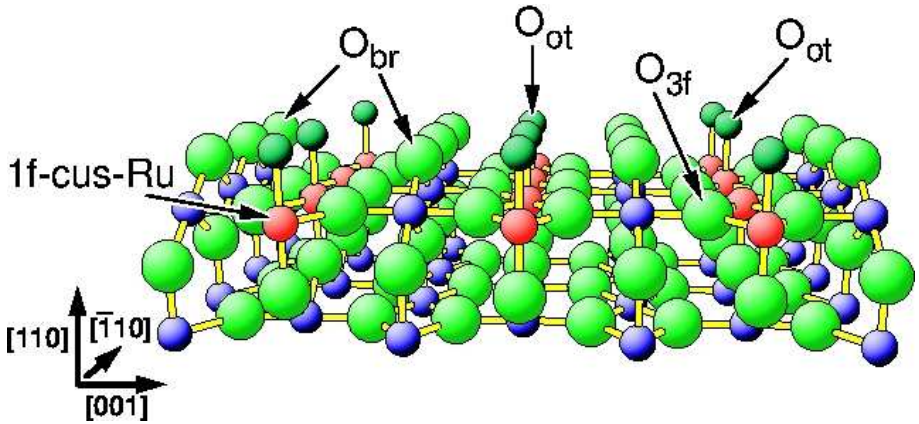
CO, *T*

O_2

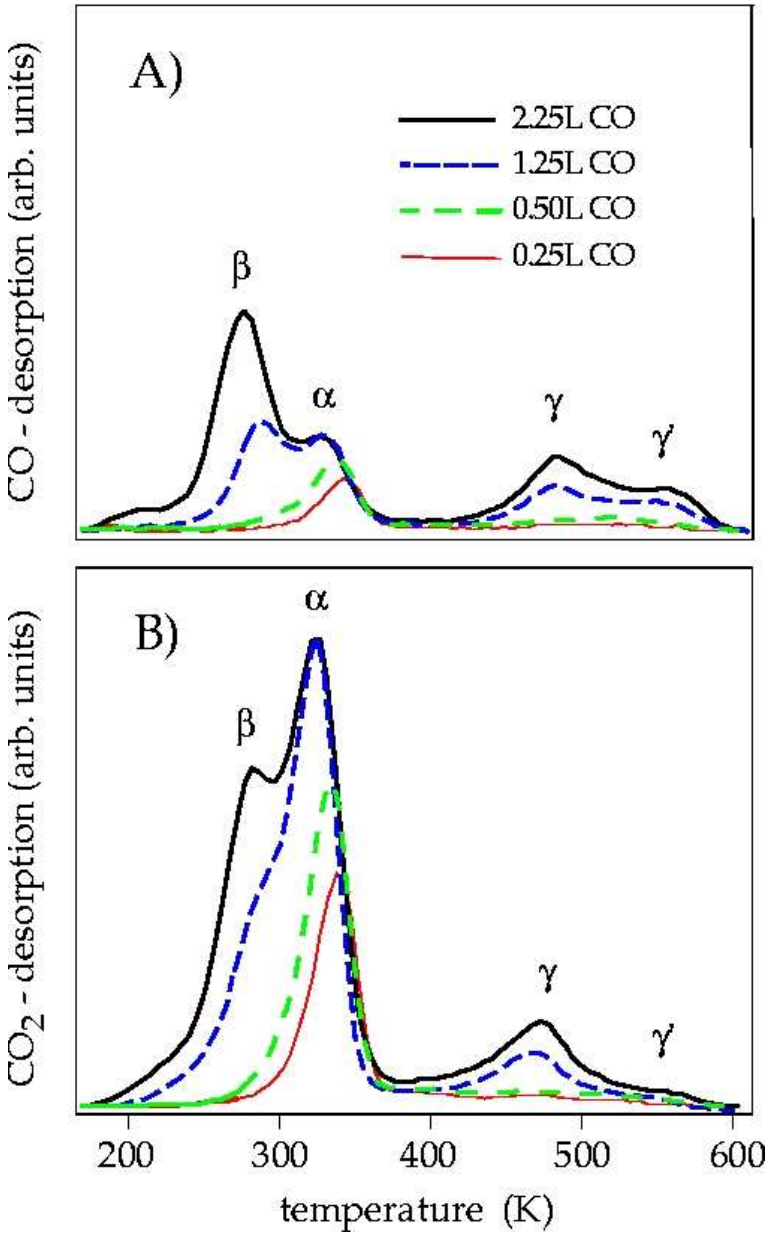
r-RuO_2(110)

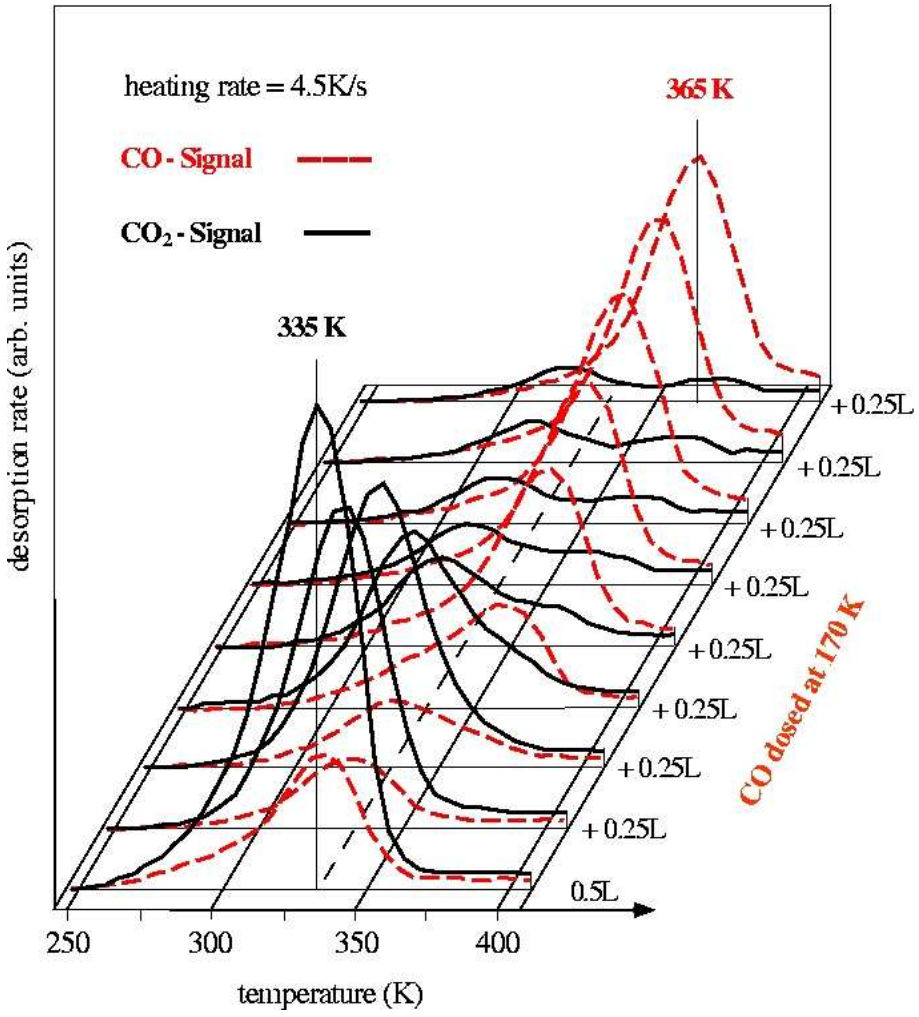


s-RuO_2(110)-$O_{on\text{-}top}$



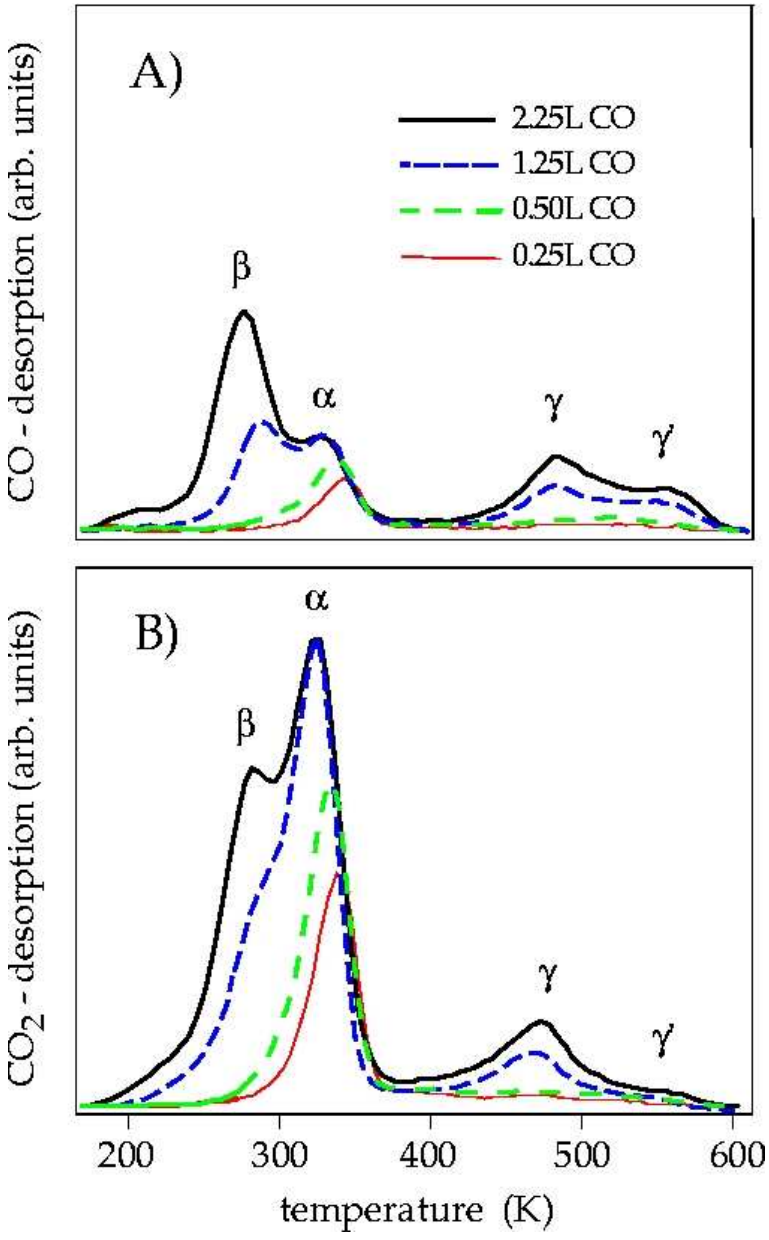
$CO+O/RuO_2(110)$: Experiments – TDS





Wendt *et al; Surface Science*, in print

$CO+O/RuO_2(110)$: Experiments – TDS

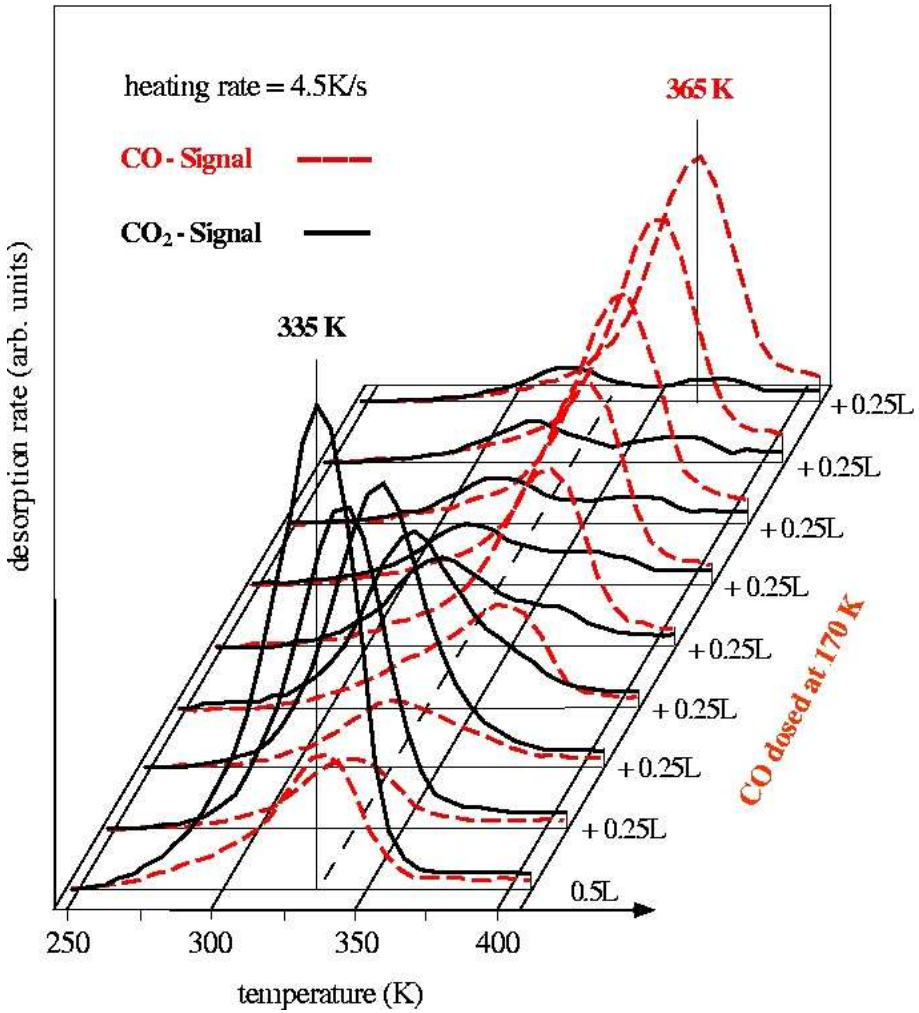


- CO adsorbed at low temperature (170 K) and the surface is heated
- The data agree with the elder measurements by Jacobi *et al* (*e.g.* Wang *et al; Surface Science,* 2001)
- Both desorption of CO and formation of CO_2 seen
- Four peaks found: α, β, γ and γ'
- Two regions: ~300 and ~500 K

Wendt *et al; Surface Science,* in print

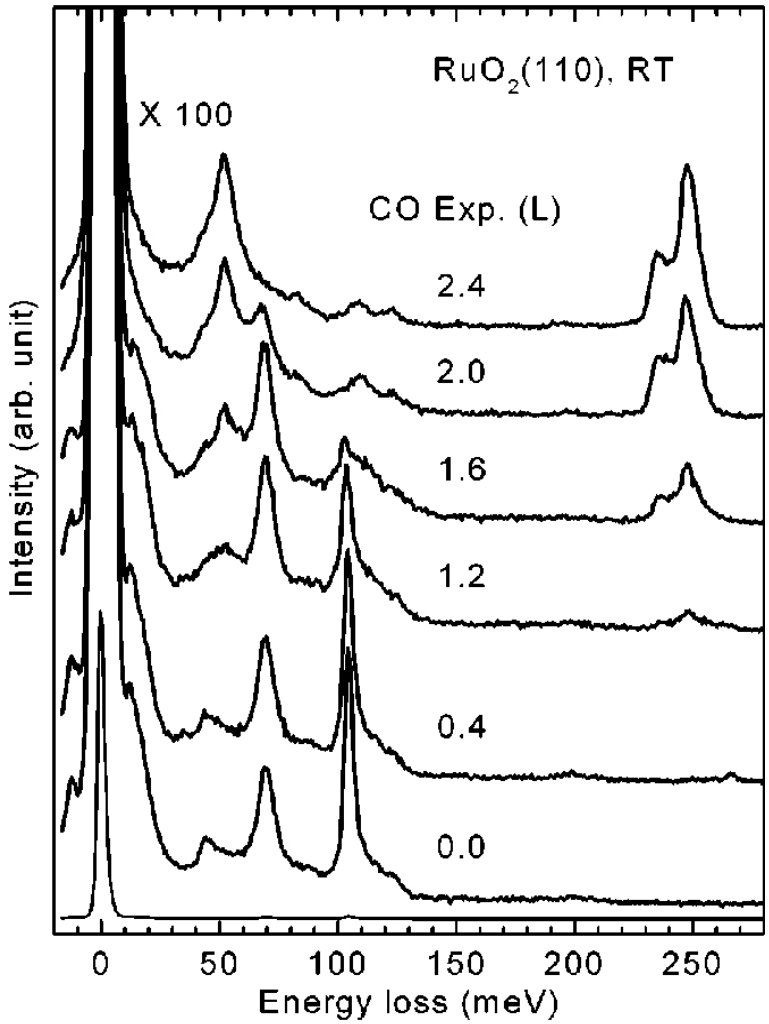
$CO+O/RuO_2(110)$: Experiments – TDS

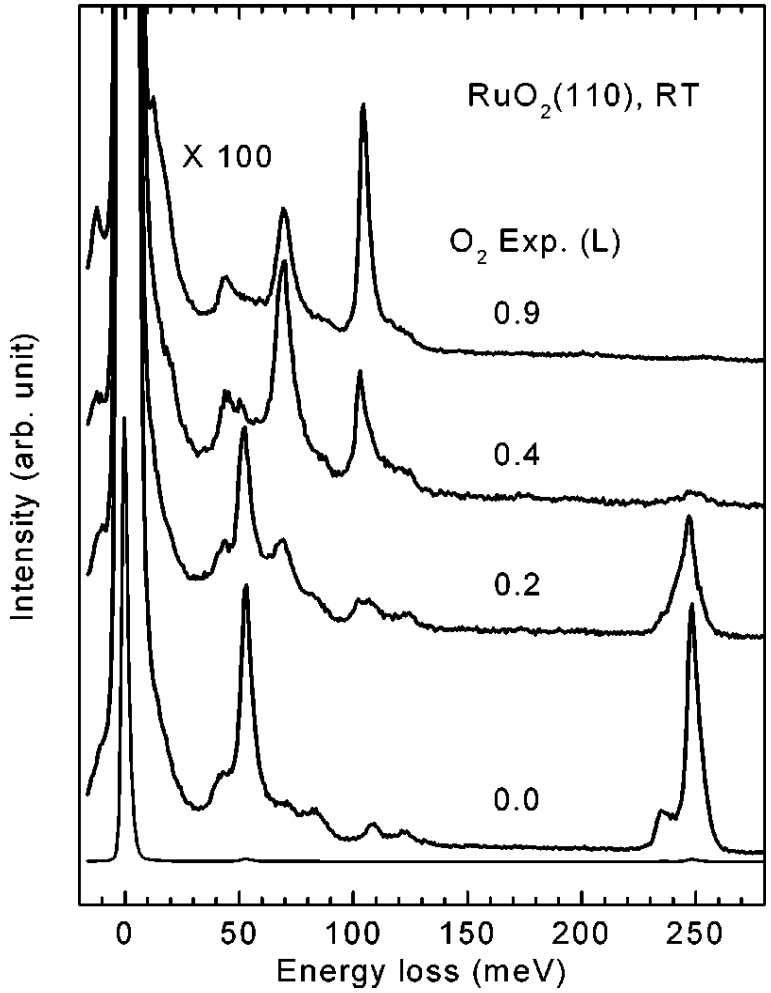
- CO adsorbed at low temperature (170 K), the surface is heated and more CO is adsorbed (at 170 K)
- The low temperature region shown
- Both desorption of CO and formation of CO_2 seen
- Formation of CO_2 reduces, desorption of CO increases
- Thus less (reactive) O found by CO



Wendt *et al; Surface Science*, in print

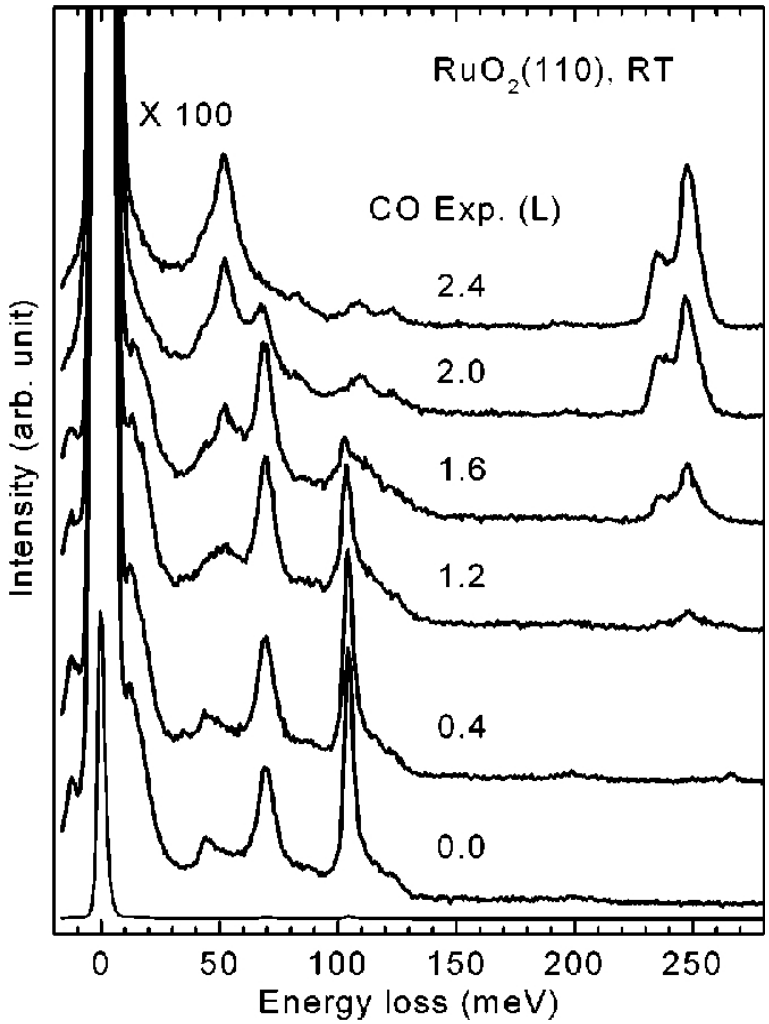
$CO+O/RuO_2(110)$: Experiments – HREELS: I





Fan *et al; JCP*, 2001

$CO+O/RuO_2(110)$: Experiments – HREELS: I

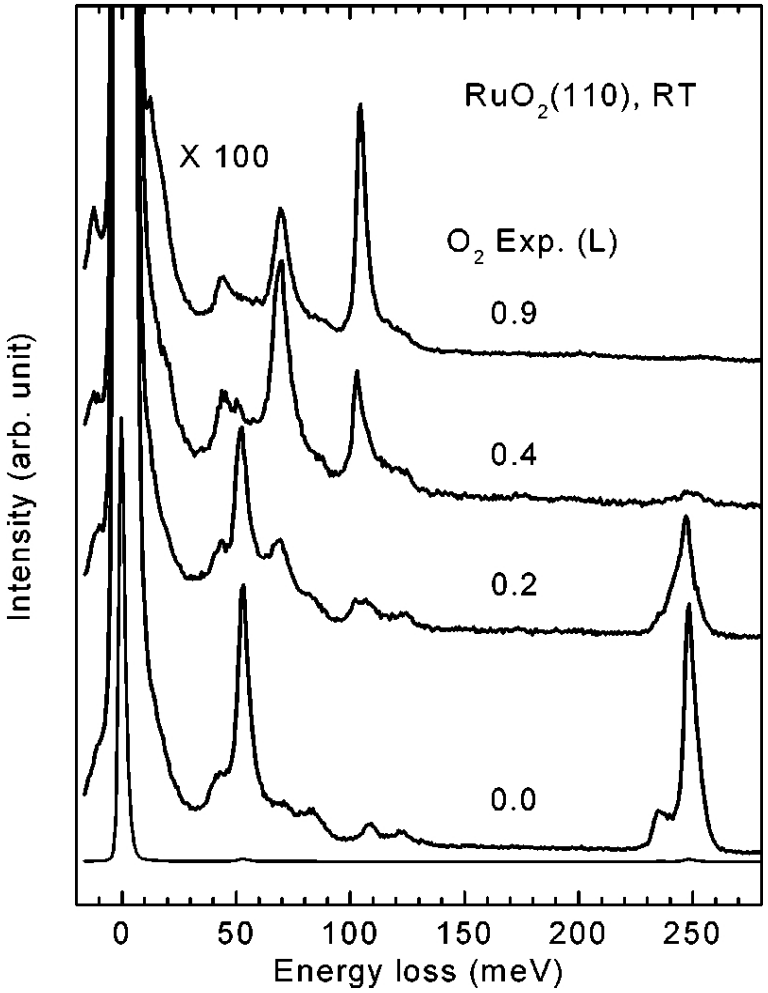


Fan *et al; JCP*, 2001

- The losses explained in Kim *et al, PRB* (2001)
- Starting from s-$RuO_2(110)$-$O_{on\text{-}top}$ (loss at 103 meV; O_{br} at 69 meV)
- Various exposures of CO let at room temperature
- The C-O mode appears, first $O_{on\text{-}top}$ and then O_{br} disappear
- Thus O consumed by exposed CO, in agreement with TDS

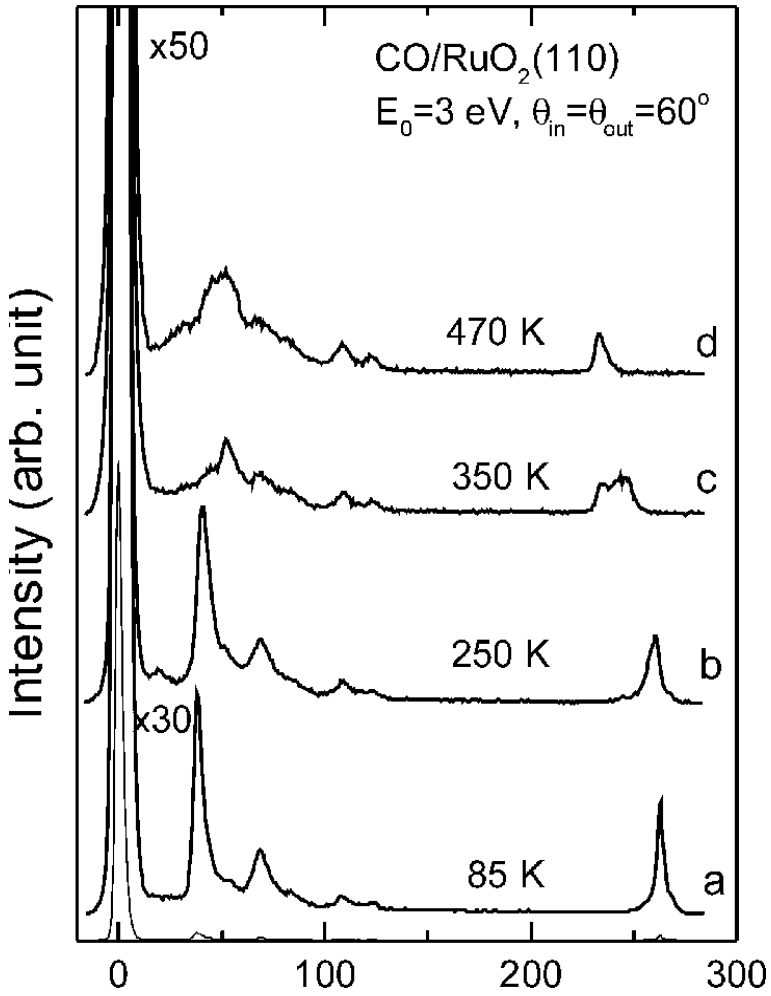
$CO+O/RuO_2(110)$: Experiments – HREELS: I

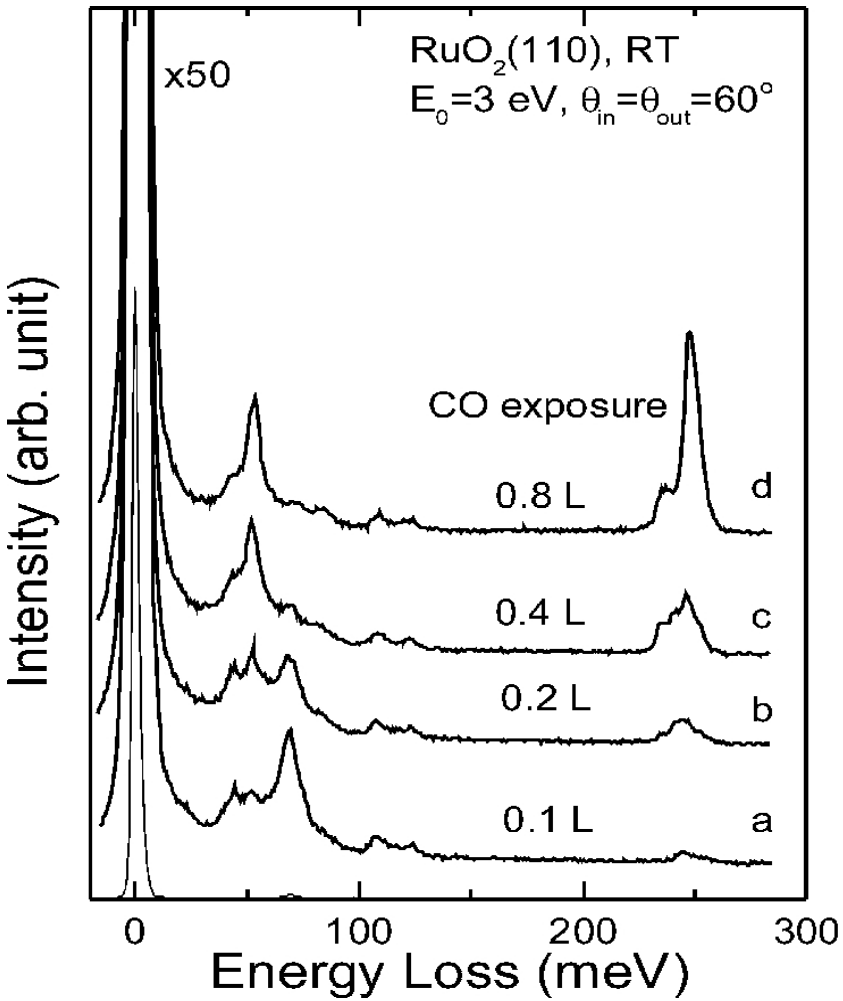
- Starting from r-RuO_2(110)-CO (losses at ~240 and 250 meV)
- Various exposures of O_2 let at room temperature
- The C-O mode disappears, first O_{br} and then $O_{on\text{-}top}$ reappear
- Thus s-RuO_2(110) and r-RuO_2(110)-$O_{on\text{-}top}$ recovered upon exposure to oxygen ➡ steady-state reaction at *"real"* conditions?!?



Fan *et al; JCP*, 2001

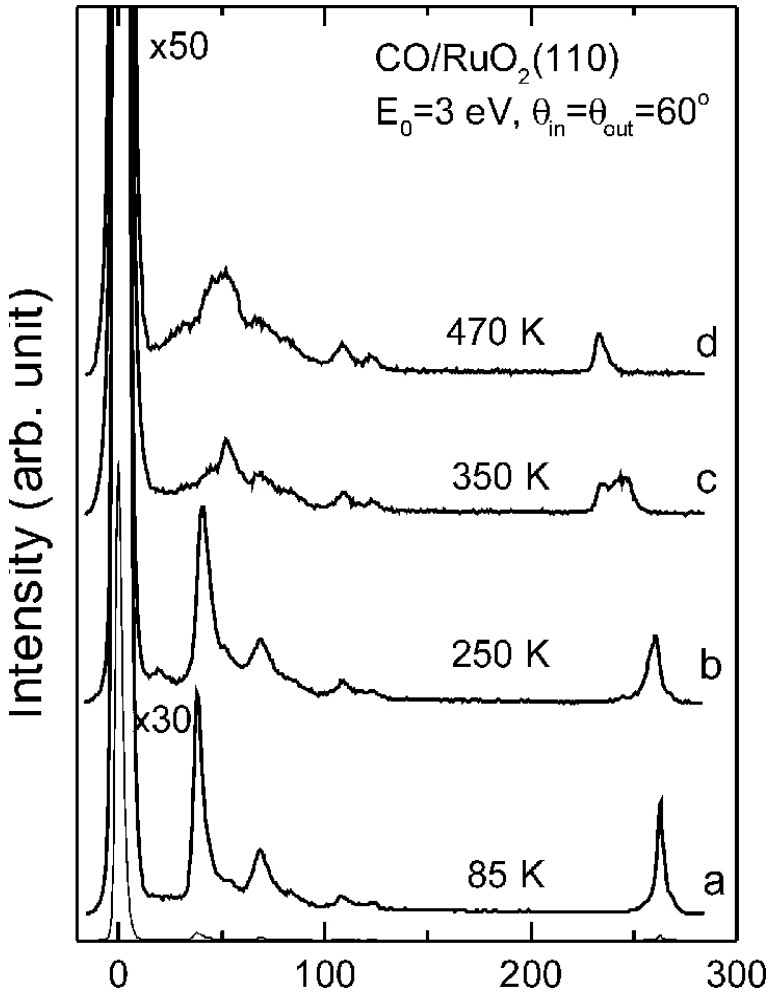
$CO+O/RuO_2(110)$: Experiments – HREELS: II





Wang *et al; Surface Science*, 2001

$CO+O/RuO_2(110)$: Experiments – HREELS: II



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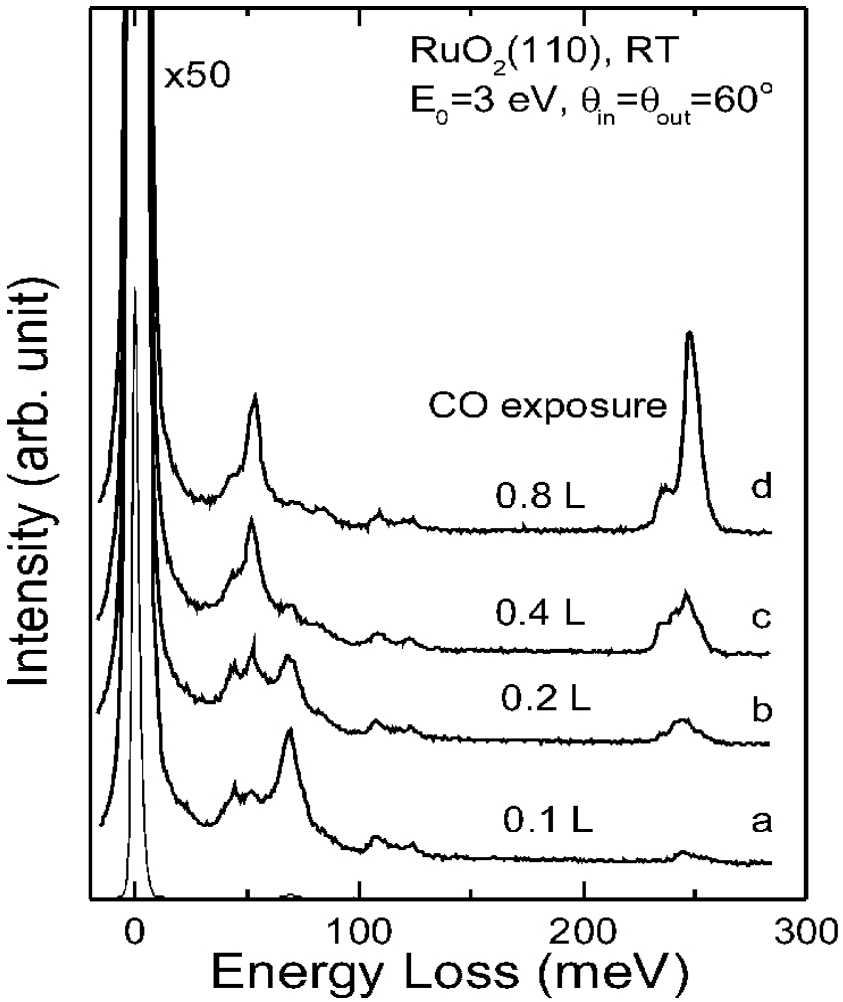
$CO+O/RuO_2(110)$: Experiments – HREELS: II



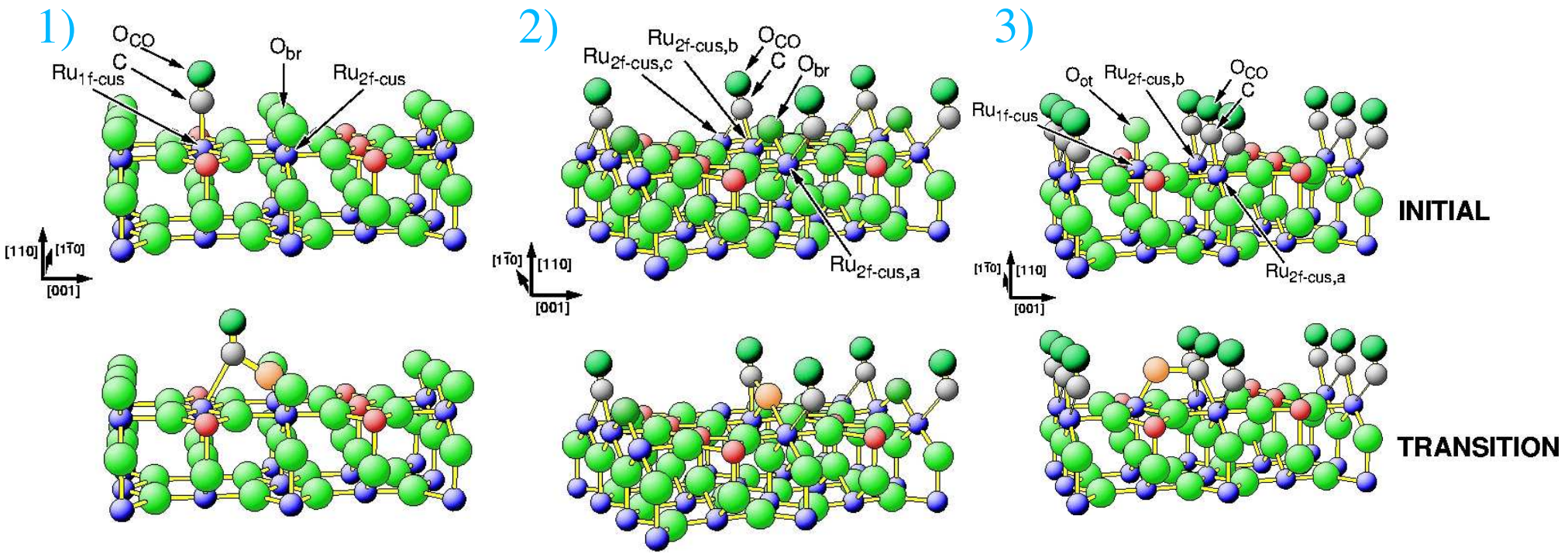
Wang *et al; Surface Science*, 2001

$CO+O/RuO_2(110)$: DFT
- method -

- DFT-KS/GGA (PBE)
- Plane waves (60 Ry)
- Pseudo potentials (Troullier-Martins)
- Super-cell / slab geometry (five double layers)
- Frequencies via force constants (finite differences)
- Reaction coordinate by a constant distance between C and O (Alavi *et al;* PRL, 1998)

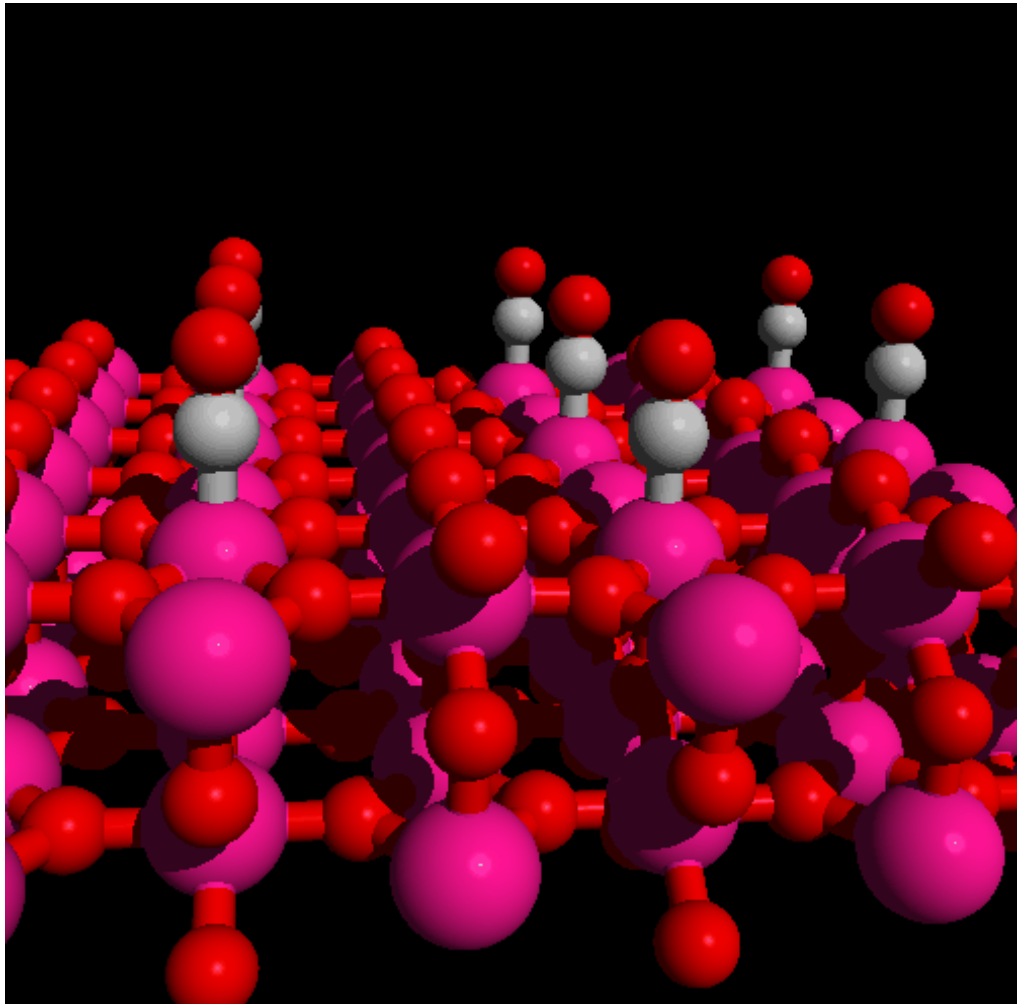
$CO+O/RuO_2(110)$: DFT
- reactions studied -

1) s-$RuO_2(110)$: $CO_{ot,\ 1f\text{-}cus} + O_{br}$
2) r-$RuO_2(110)$: $CO_{a\text{-}br,\ 2f\text{-}cus} + O_{br}$
3) r-$RuO_2(110)$: $CO_{a\text{-}br,\ 2f\text{-}cus} + O_{ot,\ 1f\text{-}cus}$



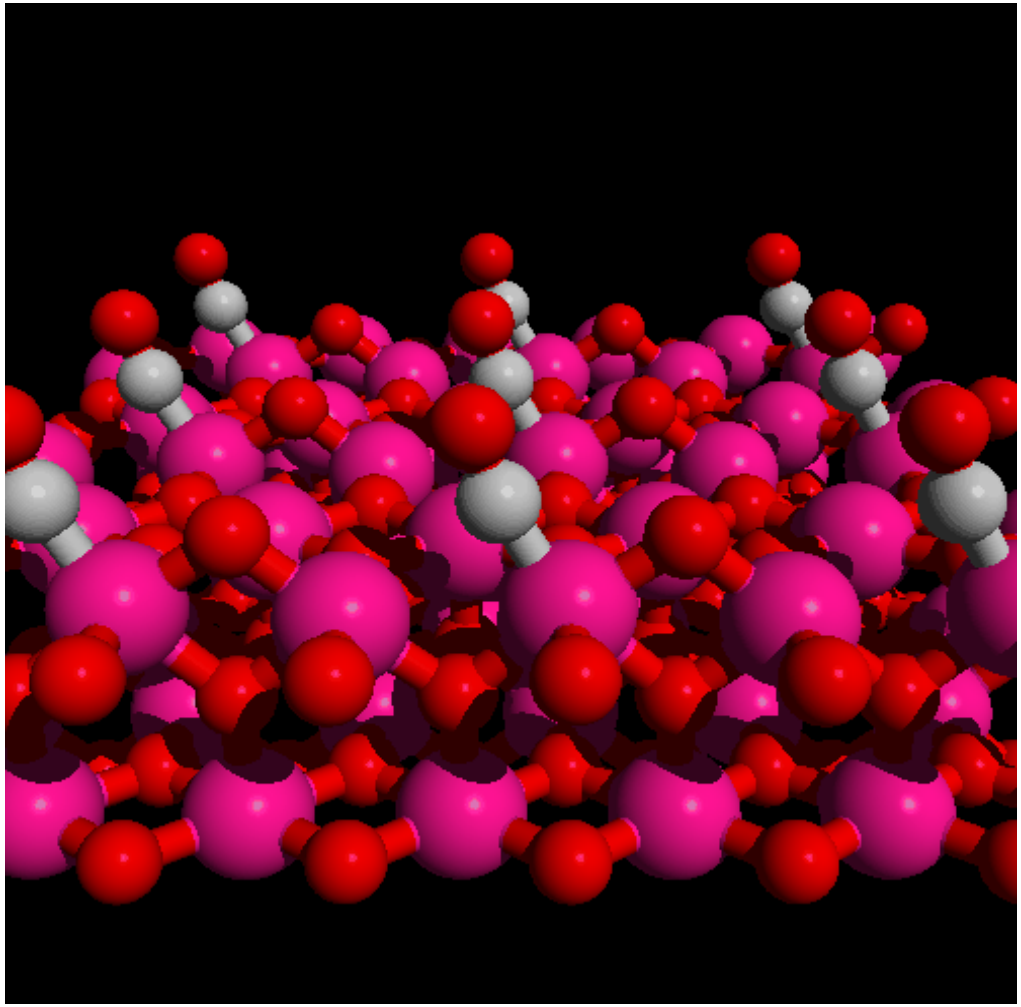
$CO+O/RuO_2(110)$: DFT

- reaction 1) -



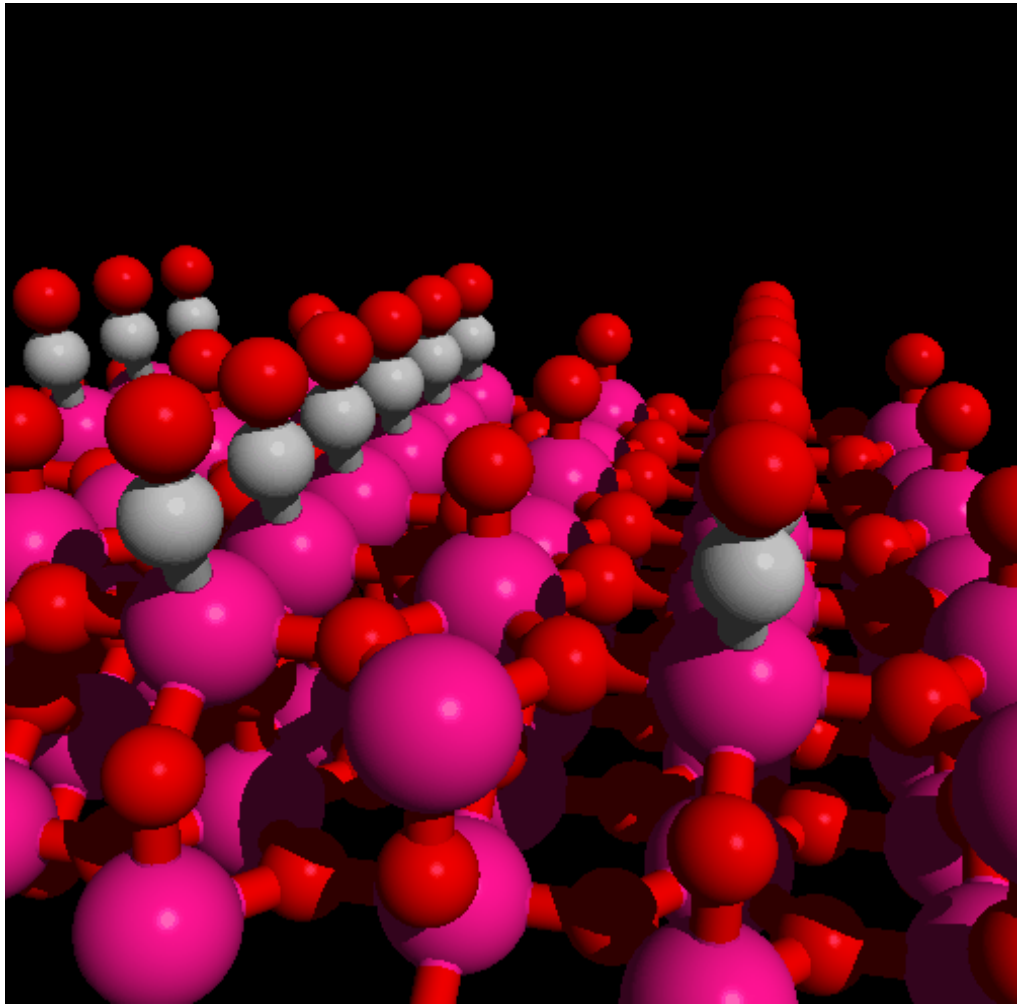
$CO+O/RuO_2(110)$: DFT

- reaction 2) -



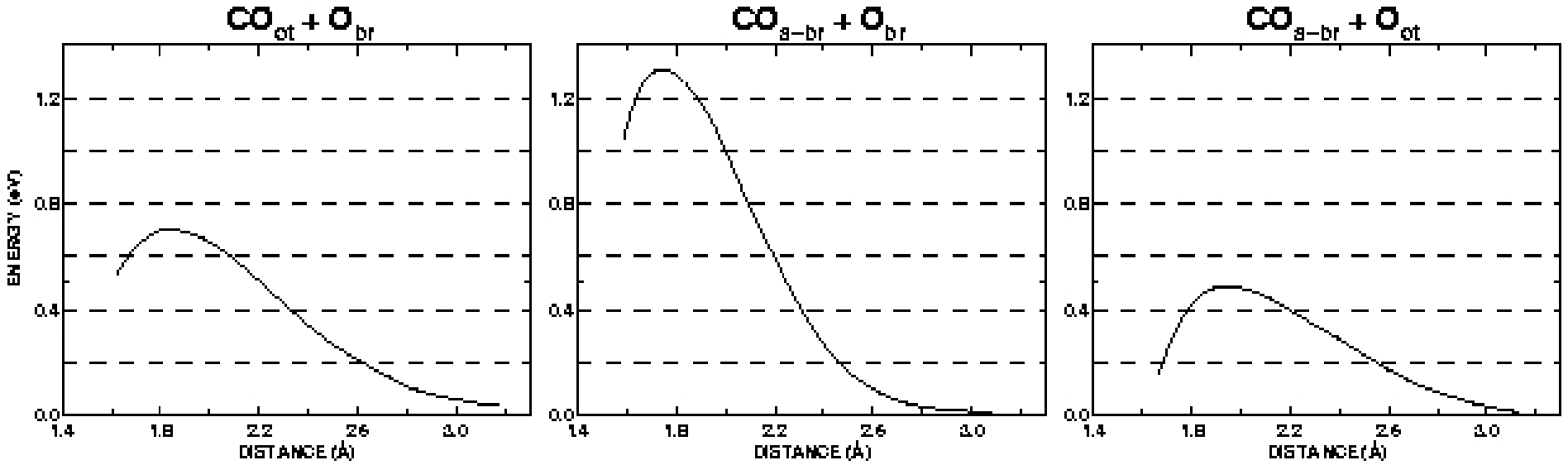
$CO+O/RuO_2(110)$: DFT

- reaction 3) -



$CO+O/RuO_2(110)$: DFT

- reaction barriers & geometries -



	HREELS	*DFT*
O_{br}	69	63
$O_{on\text{-}top}$	103	99
$CO_{on—top,\ 1f\text{-}cus}$	262; 39	258; 47
$CO_{a\text{-}br,\ 2f\text{-}cus}$	235, 245; 52	247; 46, 55
$CO_{s\text{-}br,\ 2f\text{-}cus}$		238; 50

$CO+O/RuO_2(110)$: DFT

- diffusion -

	HREELS	*DFT*
O_{br}	69	63
$O_{on\text{-}top}$	103	99
$CO_{on—top,\ 1f\text{-}cus}$	262; 39	258; 47
$CO_{a\text{-}br,\ 2f\text{-}cus}$	235, 245; 52	247; 46, 55
$CO_{s\text{-}br,\ 2f\text{-}cus}$		238; 50

$CO+O/RuO_2(110)$: DFT

- frequencies -

	HREELS	*DFT*
O_{br}	69	63
$O_{on\text{-}top}$	103	99
$CO_{on—top,\ 1f\text{-}cus}$	262; 39	258; 47
$CO_{a\text{-}br,\ 2f\text{-}cus}$	235, 245; 52	247; 46, 55
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$CO+O/RuO_2(110)$: DFT
- activation energies -

- A'la Hu *et al:*
  - Which constituent of reaction needs most energy to reach the transition state?

	HREELS	***DFT***
O_{br}	69	63
$O_{on\text{-}top}$	103	99
$CO_{on—top,\ 1f\text{-}cus}$	262; 39	258; 47
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Conclusions

- Fassen Sie alle relevanten Punkte zusammen
- Machen Sie den Zuhörern erneut die Bedeutung der Punkte klar