

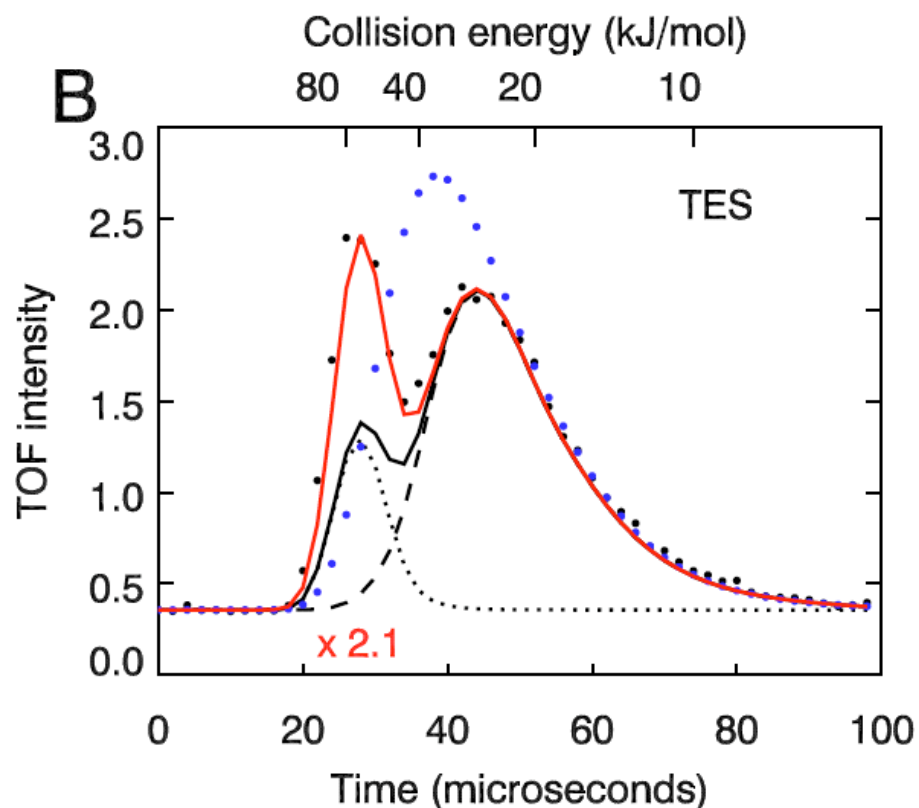


Reactions of H₂ with metal surfaces. Introduction sixth lecture.

**G.J. Kroes, Leiden Institute of Chemistry,
Leiden University.**

- **Outline:**
 - Experiments
 - Theoretical methods
 - **Theoretical results; comparison to experiment.**
 - H₂ + Cu(111): vibrationally inelastic scattering
 - H₂ + Cu(111): orientational dependence reaction
 - H₂ + Cu(100), Ru(0001): transferability SRP functional

$P(v=0 \rightarrow v=1, j=3)$, for $H_2 + Cu(111)$. $\theta_i = 15^\circ$, $T_s = 400$ K.



TOF spectra: info on $(v=0, j \rightarrow v=1, j=3)$.

Blue dots: Exp., velocity incident H_2 ($v=1, j=3$).

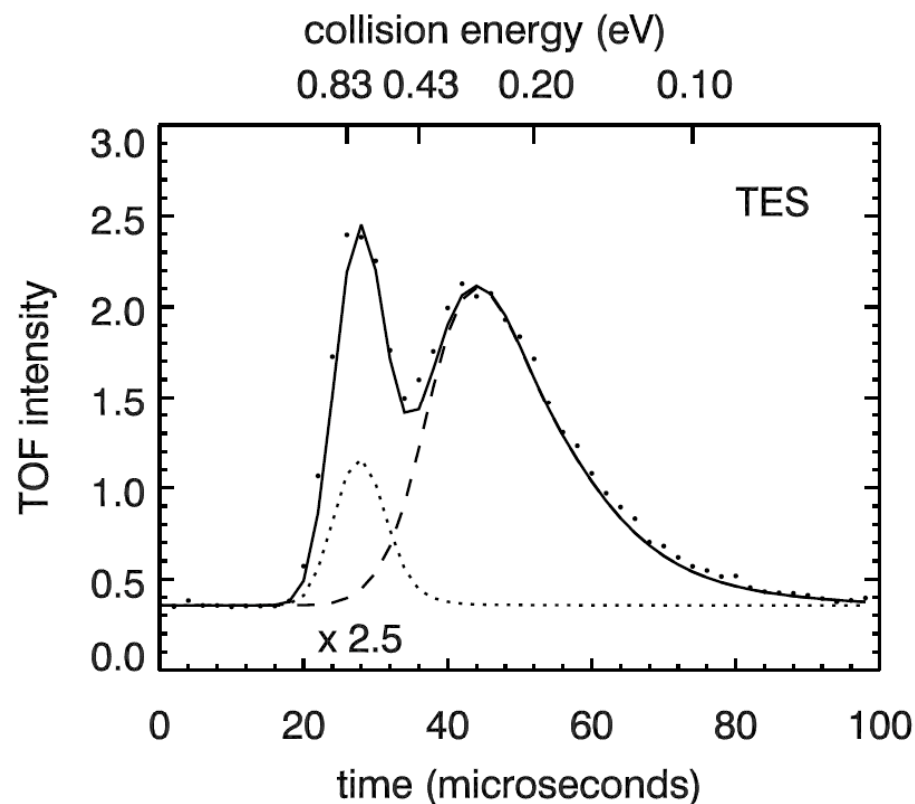
Black dots: Exp., scattered H_2 ($v=1, j=3$).

Long time “loss peak”:
reaction, vib. de-excitation.

Short time gain: vib. excitation.

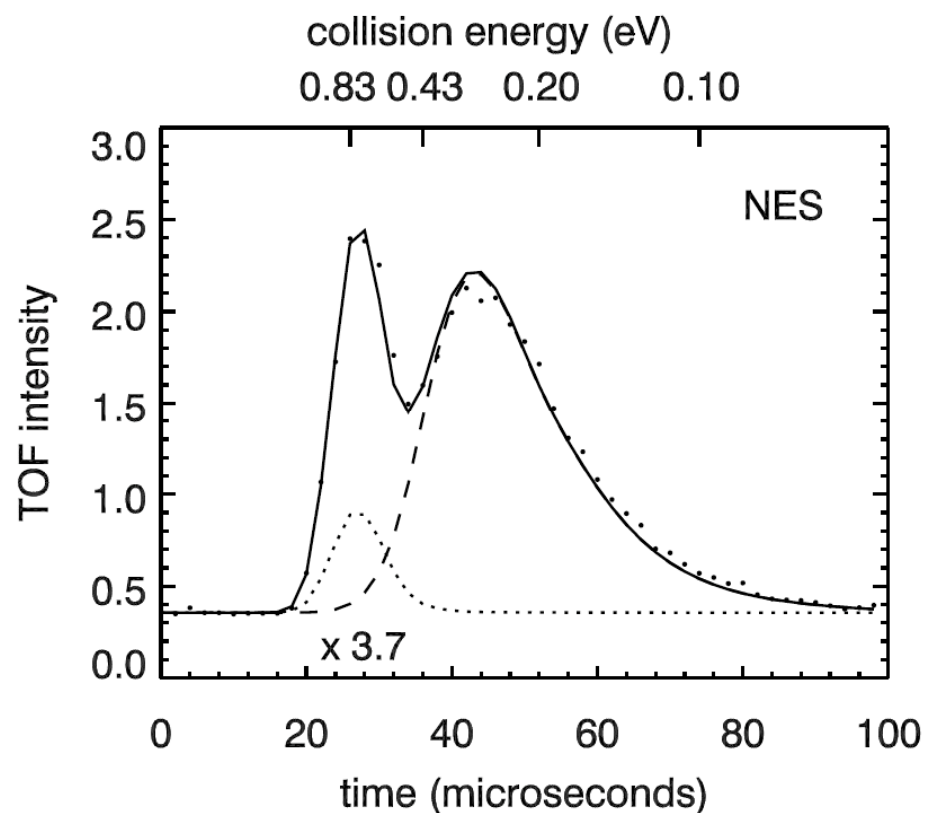
Calculations for normal incidence ($\theta_i = 0^\circ$). Total energy scaling (TES): $P(v=0 \rightarrow v=1, j=3)$ only depends on total KE. Rettner et al., Chem.Phys.175,157,1993; Kroes et al., PNAS 2010.

$P(v=0 \rightarrow v=1, j=3)$, for $H_2 + Cu(111)$. $\theta_i = 15^\circ$, $T_s = 400$ K.



Theory underestimates vibrational excitation by factor 2.5 assuming TES. Rettner et al., Chem.Phys.175,157,1993; G.J. Kroes et al., PNAS 2010.

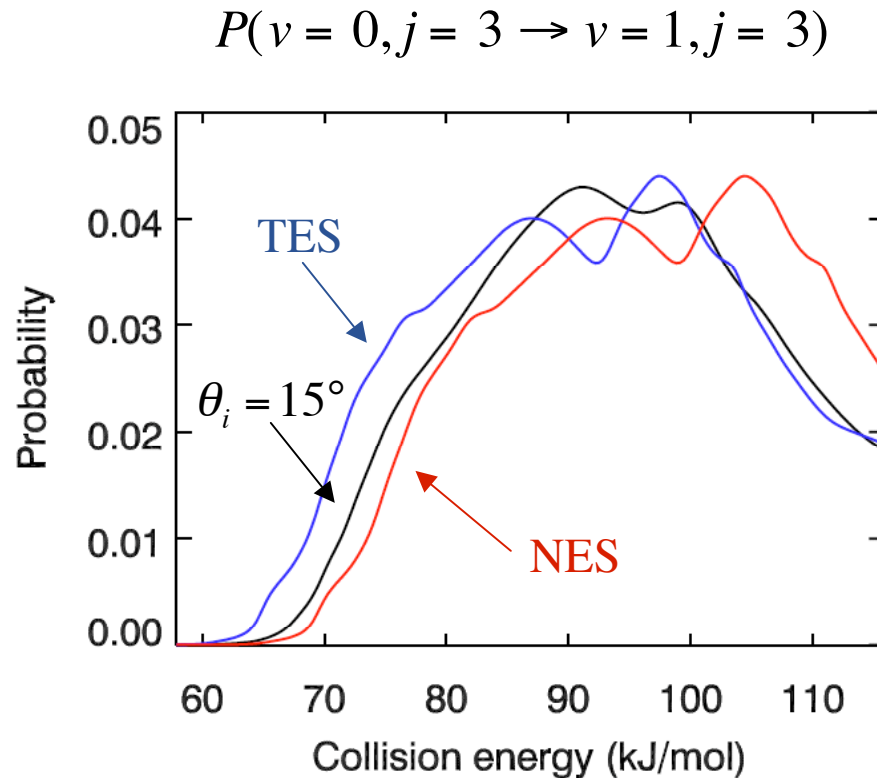
$P(v=0 \rightarrow v=1, j=3)$, for $H_2 + Cu(111)$. $\theta_i = 15^\circ$, $T_s = 400$ K.



Normal energy scaling (NES):
 $P(v=0 \rightarrow v=1, j=3)$ only depends
on normal component KE.

Theory underestimates vibrational excitation by factor 3.7
assuming NES. Rettner et al., Chem.Phys.175,157,1993; G.J.
Kroes et al., PNAS 2010.

Vibrationally inelastic scattering, $\theta_i = 15^\circ$. Scaling with E_i .



Calculations for normal incidence ($\theta_i = 0^\circ$).

Total energy scaling (TES):
 $P(v=0 \rightarrow v=1, j=3)$ only depends on total KE.

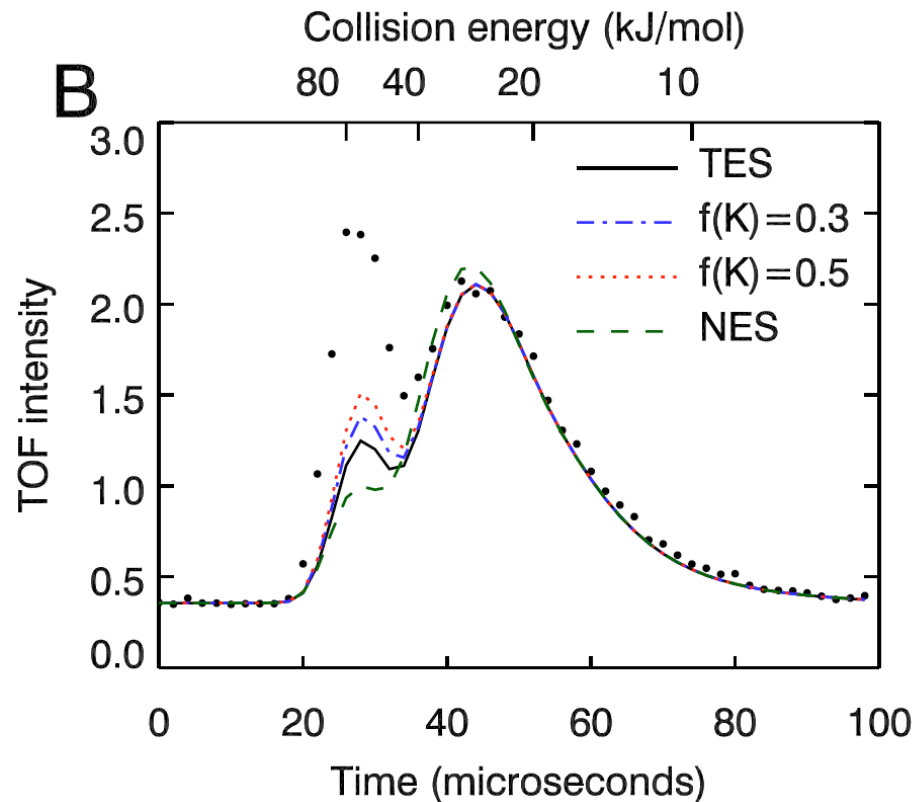
Normal energy scaling (NES):
 $P(v=0 \rightarrow v=1, j=3)$ depends on KE normal to surface.

Scaling with E_i intermediate between TES and NES.

Assuming intermediate scaling, **BOSS theory underestimates vibrational excitation by factor 3.1.**

Rettner et al., Chem.Phys.1993; Kroes et al., PNAS 2010.

Effects surface DOFs. I. Energy loss to surface.



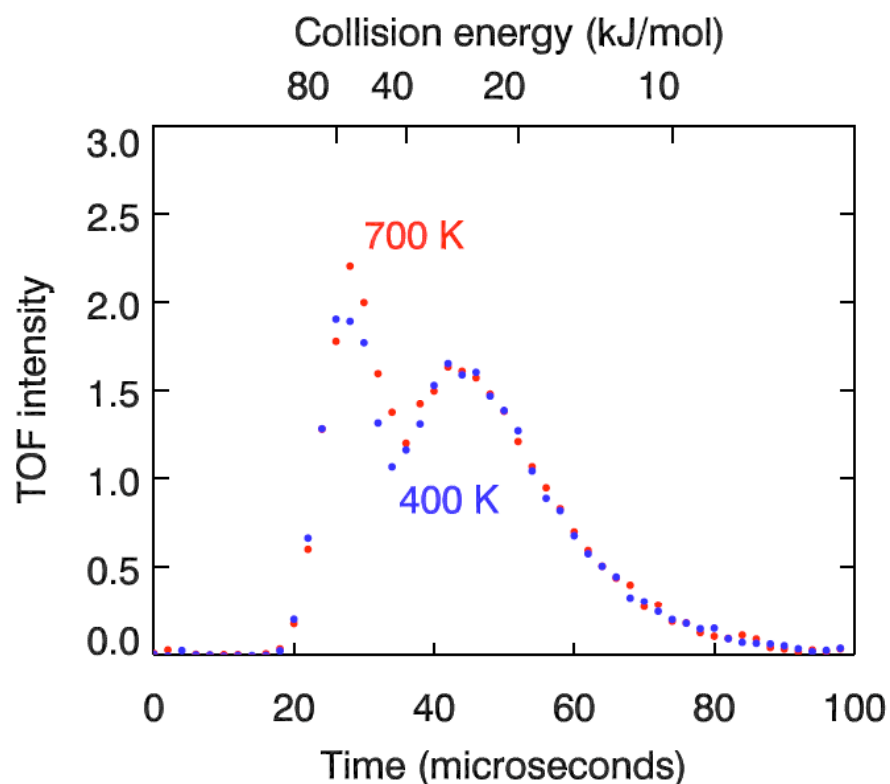
Exps. on $v=1 \rightarrow 0$ scattering of H_2 on Cu:
fraction $f(K)$ of available K lost to surface ($0.09 < f(K) < 0.35$).

Watts and Sitz, JCP114, 4171 (2001).

$$K' = [1 - f(K)] \left(K - [E_{v'j'} - E_{vj}] \right)$$

TOF intensity of the vib. exc. peak depends on $f(K)$.
 $f(K)=0.3$: theory underestimates $P(v=0 \rightarrow v=1, j=3)$ by factor 2.6.
Larger $f(K) \rightarrow$ better agreement experiment. Rettner et al.,
Chem.Phys.175,157,1993; Kroes et al., PNAS 2010.

Effects surface DOFs. II. Surface temperature.



$T_s = 400 \rightarrow 700$ K: vibrational excitation up by 20%.

BOSS calculations could underestimate $T_s=400$ K results by 27%.

Precise amount uncertain: how to extrapolate exp. to 0K?

Pure BOSS underestimates $P(v=0 \rightarrow v=1, j=3)$ by factor 3.1.

“Modified BOSS”: by factor ≤ 1.9 at 0 K.

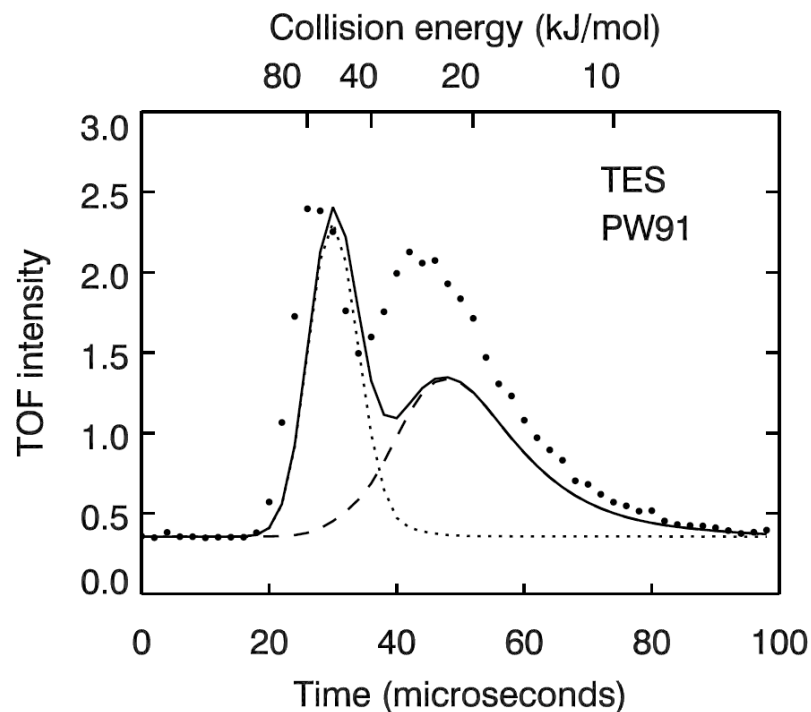
Disagreement predominantly due to neglect surface DOFs.

Rettner et al., Chem.Phys. 1993; Kroes et al., PNAS 2010.

Vibrationally inelastic scattering. $H_2 + Cu(111)$. Discrepancy due to BOSS model, not to PES.

1. PES describes effect vibrational pre-excitation on reaction.
2. SRP-DFT method not just “any semi-empirical method”.
3. Spectrum not reproducible with RPBE-PW91 SRP functional
4. Promoting effect T_s , effect energy loss on measured $P_{v=0 \rightarrow 1}$
5. PES accurately describes rotationally inelastic scattering.

SRP functional, $x=0$.
Kroes et al., submitted.



DFT is accurate for energetic and azimuthal corrugation PES.

functional	$E_b(\text{bth})$	$E_b(\text{ttb})$	ΔE
LDA	-21.1	8.1	29.9
PW91	46.8	74.1	27.3
PBE	46.0	73.2	27.2
revPBE	68.9	94.5	25.6
RPBE	74.4	99.7	25.3

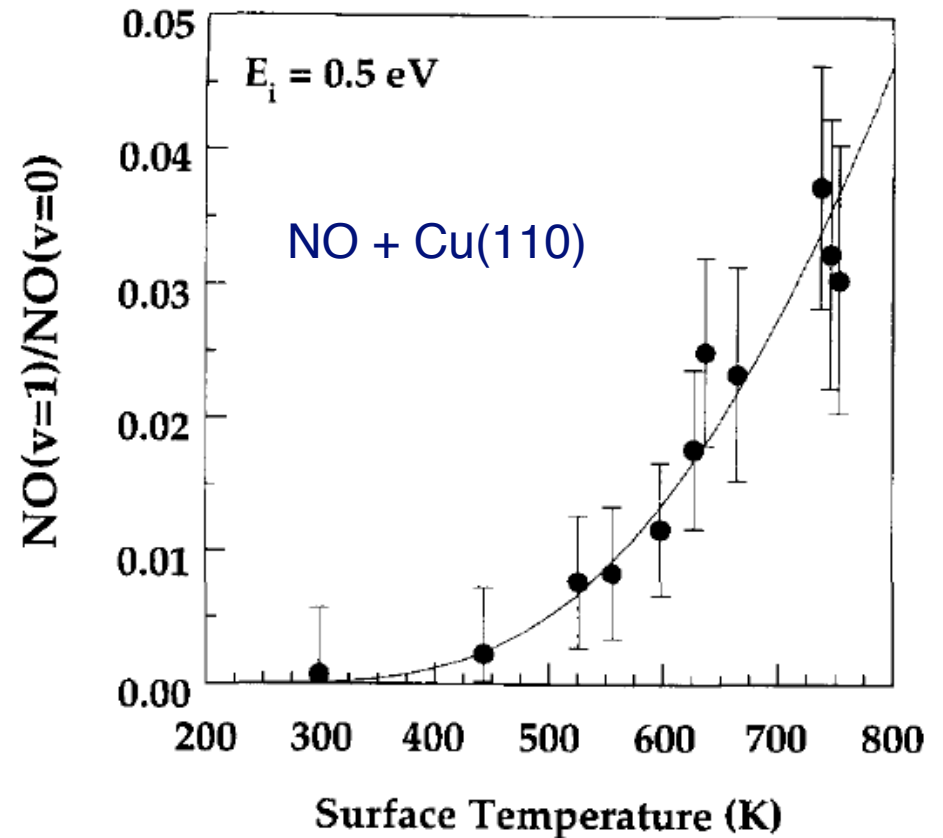
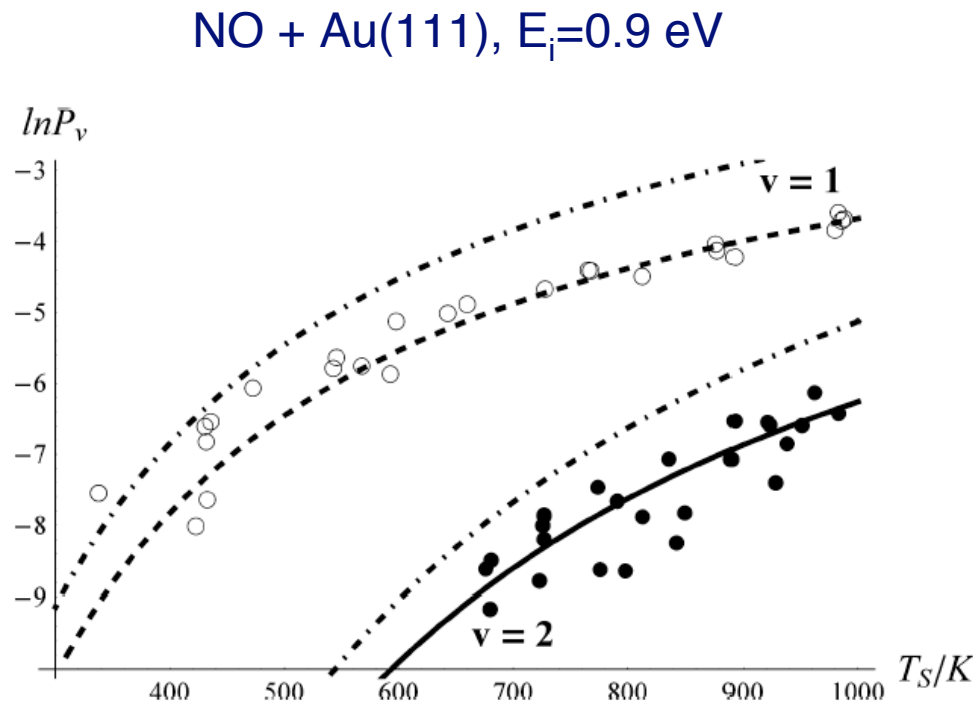
GGAs may give very accurate results for energetic corrugation of PES and for anisotropy of barrier heights.

Absolute values barrier heights strongly depend on functional.

functional	$E_b(\phi=90^\circ)$	$E_b(\phi=50^\circ)$	ΔE
LDA	-21.1	3.2	24.3
PW91	46.8	73.5	26.6
PBE	46.0	73.4	27.4
revPBE	68.9	96.9	28.0
RPBE	74.4	102.7	28.3

Mortensen et al., PRL95, 216401 (2005).
Kroes et al., PNAS 2010;

Missing vib. excitation H₂ on Cu(111) due to E→V transfer?



Not likely. $P(v=0 \rightarrow 1)$ for NO + metal at $T_s \approx 400$ K < 0.01 . Size needed: 0.10-0.15. NO + metal: **strong E→V coupling limit.**

Wodtke & Auerbach & co., Chem.Sci.1, 55, 2010;
Sitz & co., Surf.Sci.374, 191, 1997.

Missing vib. excitation H₂ on Cu(111) due to P→V transfer?
Extrapolating effect of T_s down to 0 K.

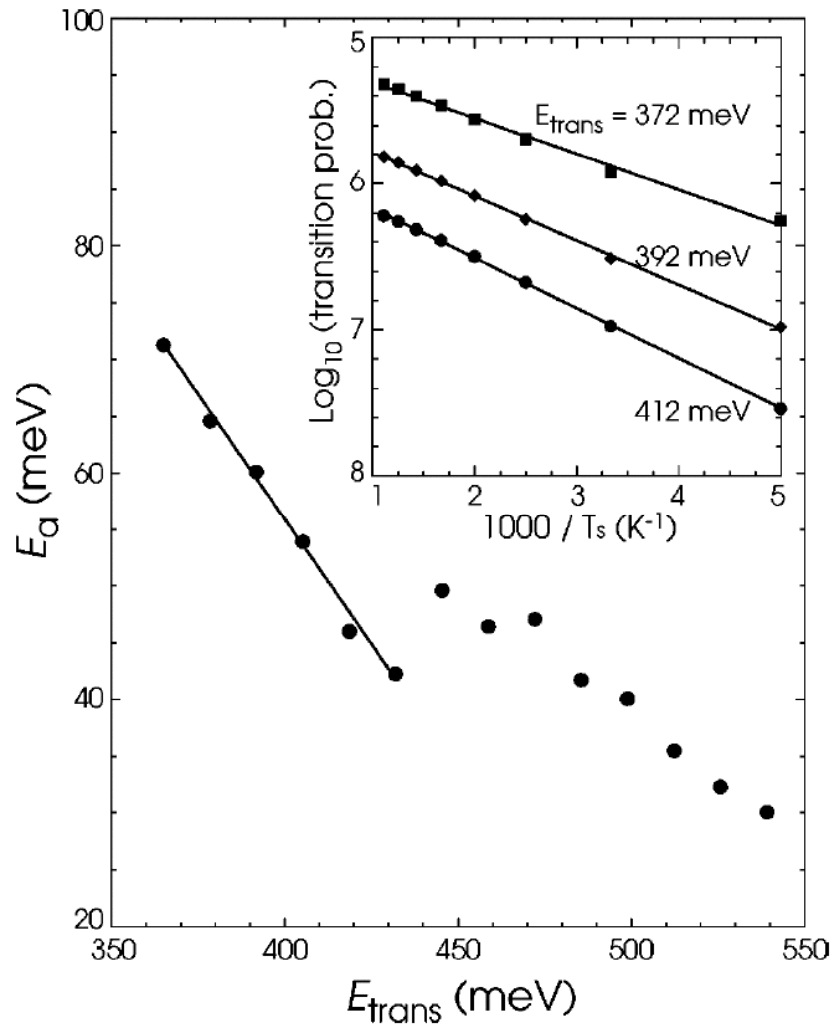
$$R(T_s) = R(0K) + B \exp(-E_a / kT_s)$$

Three unknowns.

$E_a(eV)$	B	$R(0K)$	$R(0)/R(400K)$
0.225	23.08	2.57	0.99
0.20	15.62	2.55	0.98
0.15	7.40	2.51	0.96
0.10	3.835	2.39	0.92
0.0558	2.62	2.08	0.8
0.05	2.57	2.00	0.77
0.0226	3.09	1.00	0.38
0.020	3.29	0.76	0.29

E_a value of 55.8 (22.6) meV reduces ratio “exp@0K”/theory by 20% (to 1, agreement theory experiment).

Missing vib. excitation H₂ on Cu(111) due to P→V transfer?
Extrapolating effect of T_s down to 0 K. II.



E_a values of 55.8 (22.6) meV:
consistent with values
calculated for ($v=0, j=0 \rightarrow$
 $v=1, j=0$) D_2 of 50 to 30 meV.
Range: 120 meV above the
threshold for $v=0 \rightarrow 1$ in D_2 .

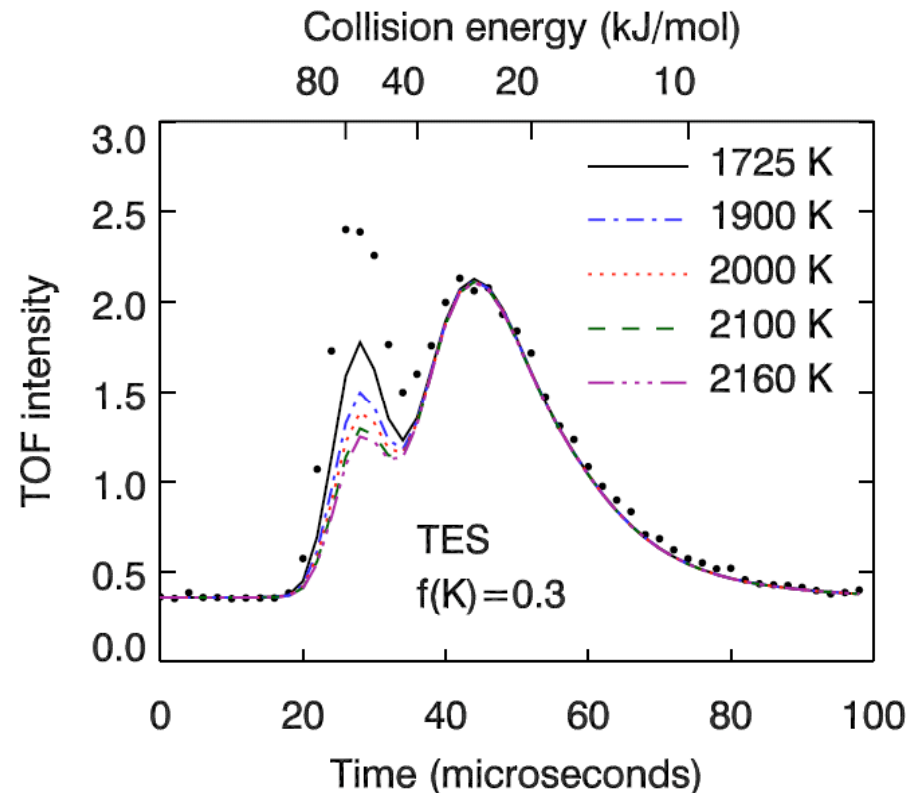
H₂ + Cu(111): obs. threshold
about 580 meV.

Peak in TOF spectrum occurs
at 770 meV (for $v=0 \rightarrow v=1, j=3$).

Wang, Darling, & Holloway,
JCP120, 2923, 2004.

Kroes et al., PNAS 2010.

Vibrationally inelastic scattering. $H_2 + Cu(111)$.
Uncertain effect nozzle temperature.

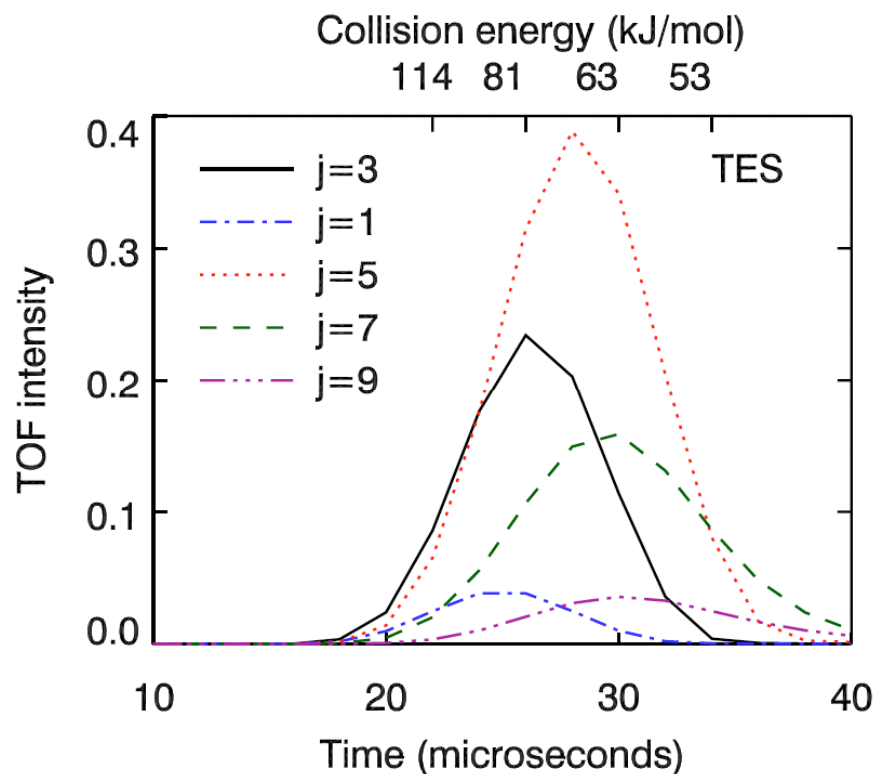


Experiments stated value of T_n , not its uncertainty.

Error 100 K changes contribution vibrational excitation by 6%.

Average energy beam, and of Maxwellian/supersonic beam, allow for even larger deviations. Kroes et al., PNAS 2010.

Vibrationally inelastic scattering. $H_2 + Cu(111)$. Which j -state within $v=0$ contributes most?



$j=5$ state contributes more than $j=3$ state.

However: $P(v=0, j=5 \rightarrow v=1, j=3) \approx P(v=0, j=5 \rightarrow v=1, j=3)$.

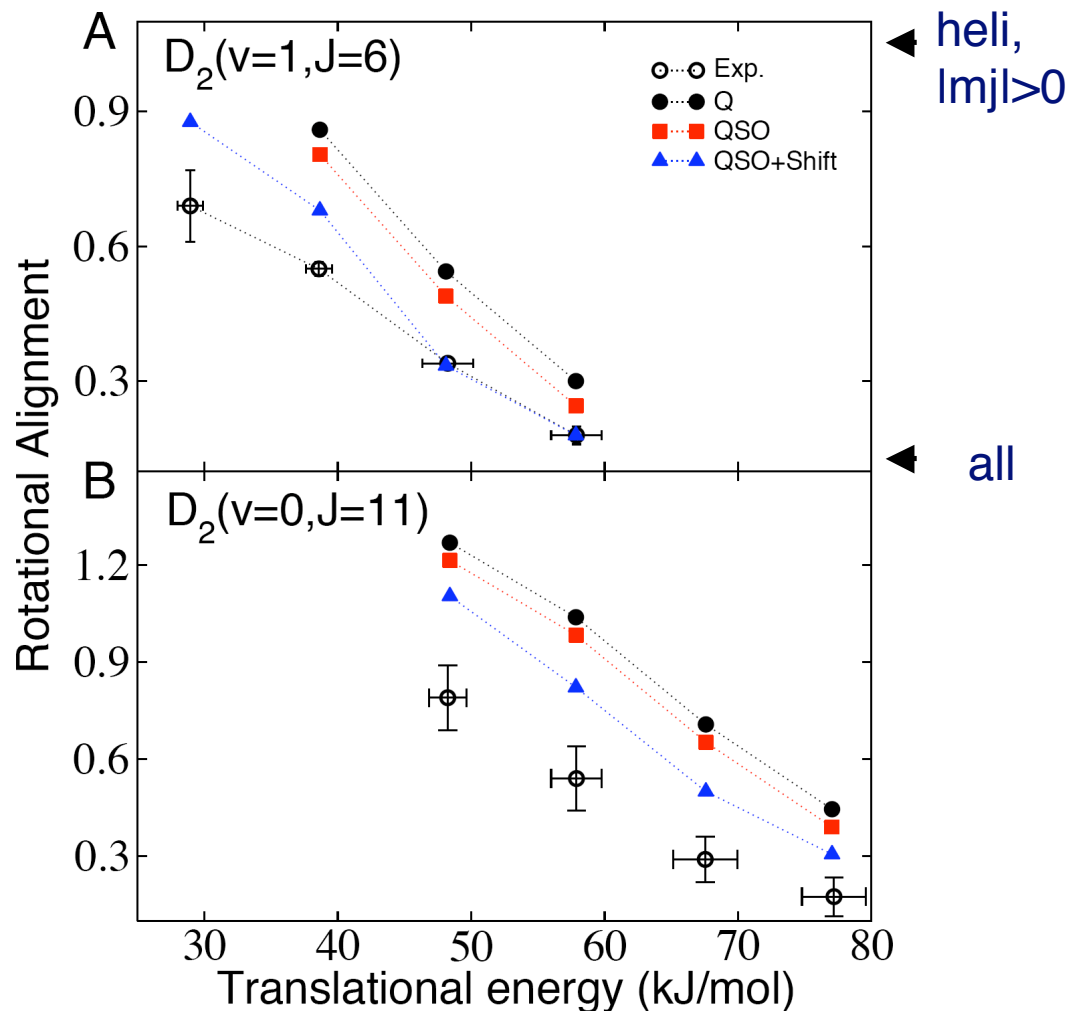
But: $P(v=0, j=5 \rightarrow v=1, j=3)$ peaks at lower E , where $I(\text{inc beam})$ is greater.

Accurate vibrational excitation probabilities cannot be determined assuming $j'=j$.

This had to be done originally to extract estimated $P(v=0 \rightarrow 1)$.

Rettner et al., Chem.Phys. 1993; Kroes et al., PNAS 2010.

Dependence reaction on orientation. $D_2 + Cu(111)$. $T_s=925$ K.



High T_s , effect T_s on results unknown!

Q theory: preference for helicopter reaction is **too large**.

Hou et al., Science 277, 80, 1997.

Diáz et al., PCCP 12, 6499, 2010.

$$A_0^{(2)}(j) = \frac{\sum_{m_j} R_{vjm_j}(E_i) \{3m_j^2 - j(j+1)\} / \{j(j+1)\}}{\sum_{m_j} R_{vjm_j}(E_i)}$$

AIMD calculations using a dynamic surface.

Ab Initio Molecular Dynamics (AIMD) calculations:

- VASP, forces on the fly
- 4 layers, 3 upper layers move according to $T_s = 925$ K
- 2 x 2 surface unit cell
- SRP48 functional used self-consistently:

$$E_{XC}^{SRP48} = xE_{XC}^{RPBE} + (1-x)E_{XC}^{PBE}, x = 0.48$$

reproduces barrier heights for 4 representative geometries to within 1.5 kJ/mol

- velocity Verlet method, $\Delta t = 0.5$ fs
- scattering if $Z > 6.1$ Å
- reaction if $r > 1.6$ Å or periodic image interaction

VASP SRP48 reproduces Dacapo SRP43 barrier heights.

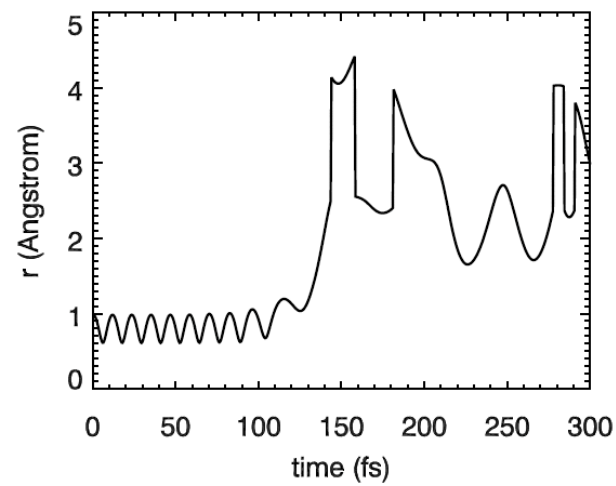
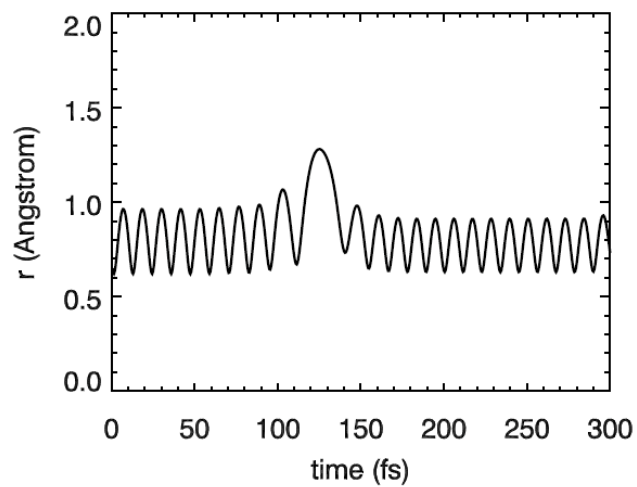
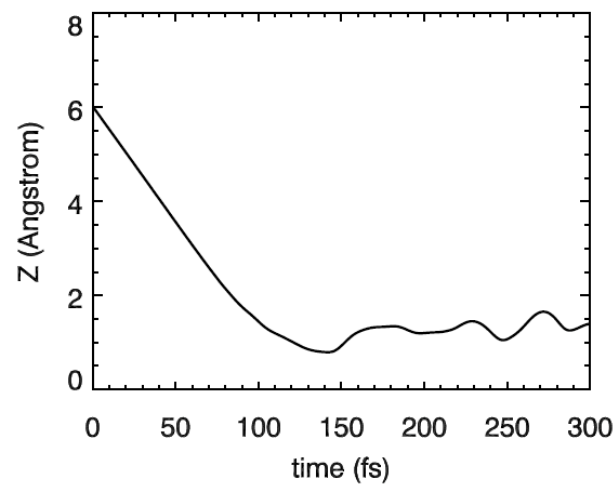
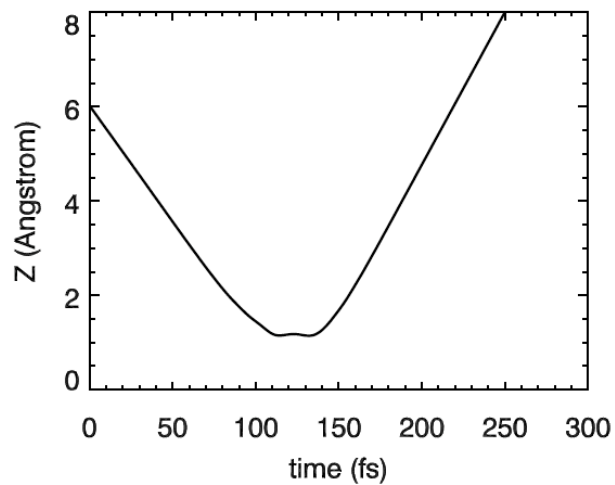
Geometry	SRP48	SRP
bth, $r=1.95 a_0$, $Z=2.20 a_0$	60.6	60.6
ttb, $r=2.64 a_0$, $Z=2.62 a_0$	84.6	86.0
fcc, $\phi=0$, $r=3.00 a_0$, $Z=2.40 a_0$	97.4	97.7
t2f, $\phi=0$, $r=2.40 a_0$, $Z=2.40 a_0$	74.1	74.3

DFT potential (kJ/mol) at SRP reaction barrier geometries.

SRP48 functional reproduces SRP values to within 1.5 kJ/mol.

G.J. Kroes et al., to be published.

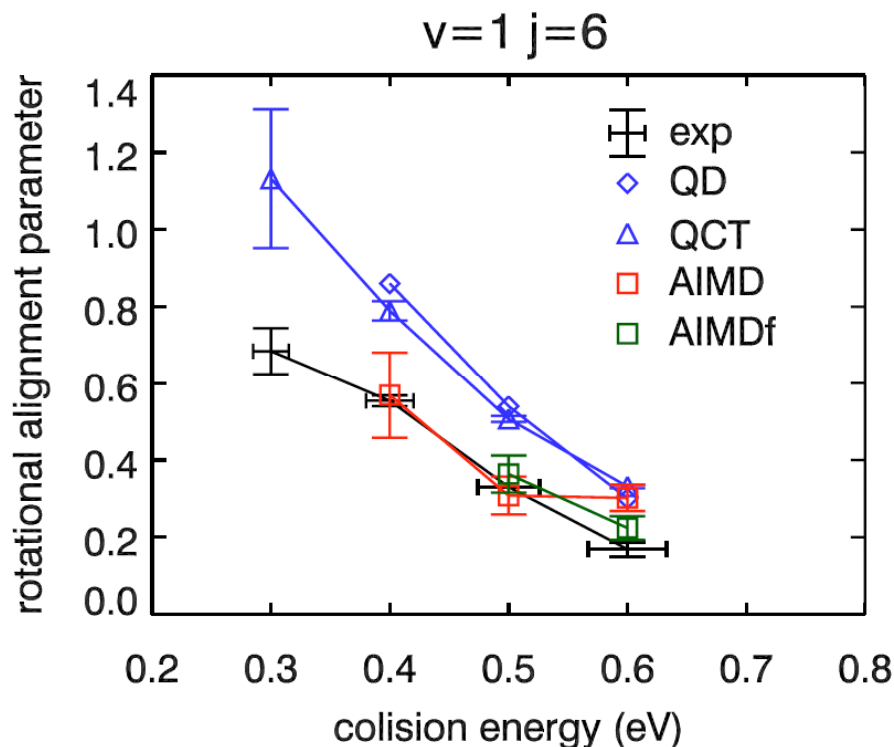
AIMD: illustrative trajectories.



Scattering

Reaction

Preliminary AIMD results, $v=1, j=6$.



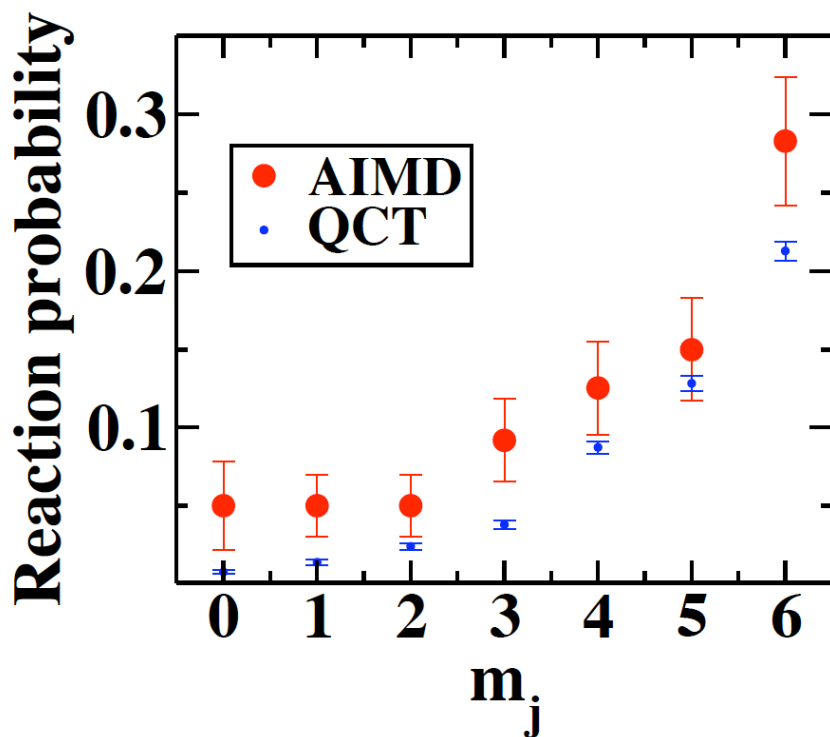
780 trajectories for each E_i .

QCT & AIMD error bars: 68% confidence intervals.

AIMD result agrees well with experiment for 0.4, 0.5 eV.
No large improvement for 0.6 eV.

Fixed surface AIMD results for 0.5 eV and 0.6 eV are puzzling!
Hou et al., Science 277, 80, 1997.

Why alignment parameter is lower for $v=1, j=6$ at 0.4 eV.



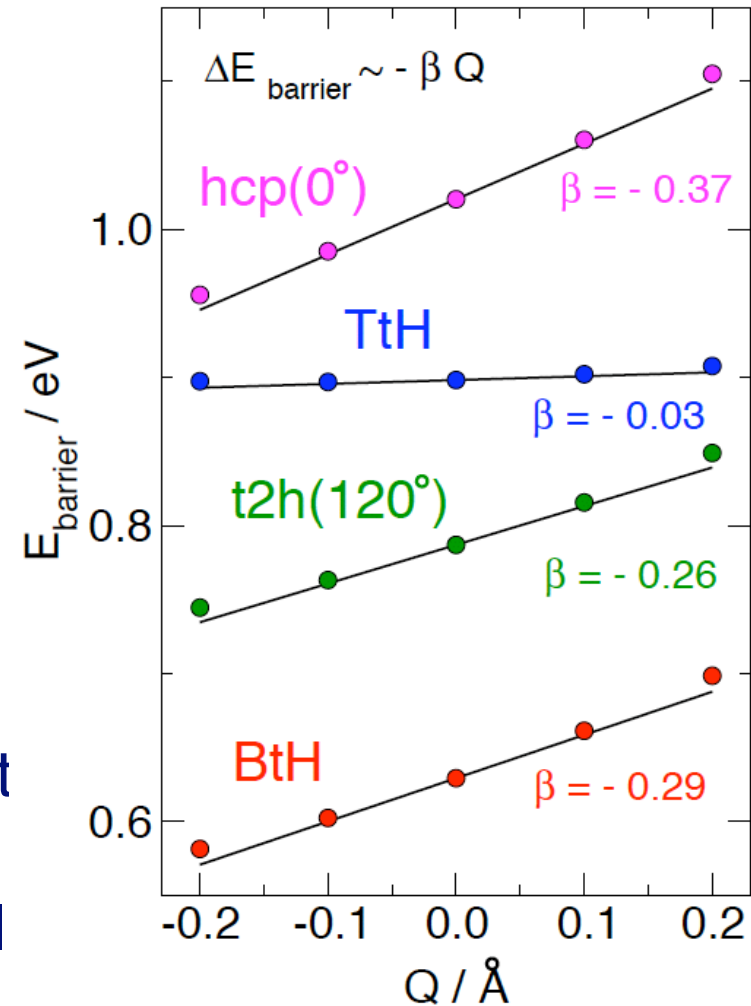
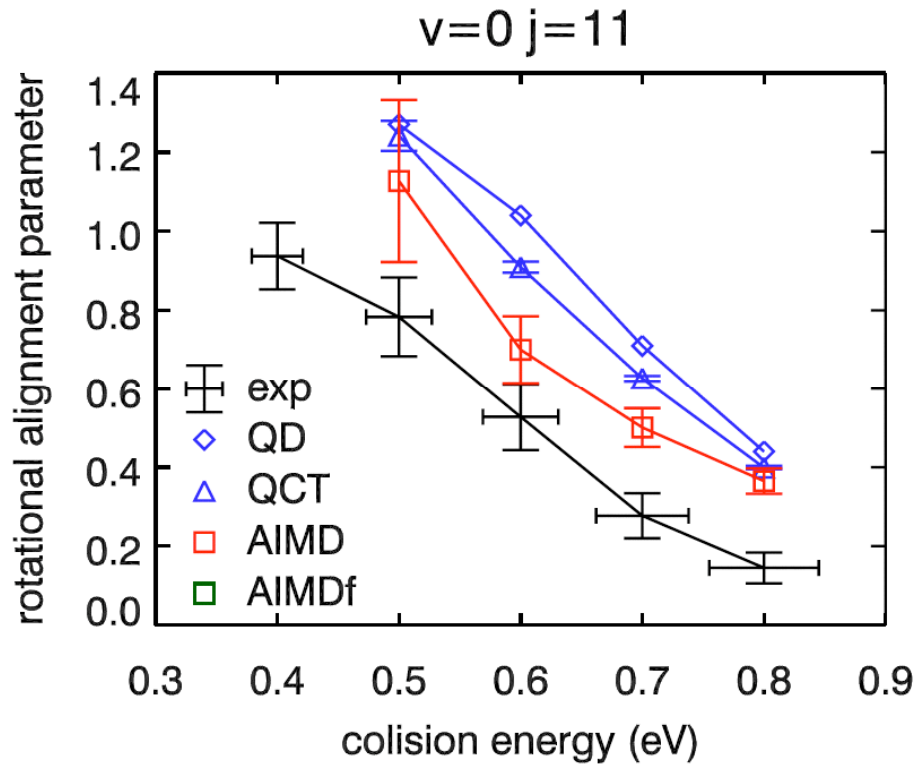
$$A_0^{(2)}(j) = \frac{\sum_{m_j} R_{vjm_j}(E_i) \{3m_j^2 - j(j+1)\} / \{j(j+1)\}}{\sum_{m_j} R_{vjm_j}(E_i)}$$

All AIMD reaction probabilities are higher.

This yields a zero contribution to the numerator, whereas the denominator becomes larger (larger average reaction probability).

To be published.

Preliminary AIMD results, $v=0, j=11$.



Improved agreement with experiment

Moving surface \rightarrow lower alignment:

- Smaller preference reaction parallel to rough surface
- E_b s decrease with d_{12} (up 2.7% from 0 to 925 K)

Hou et al., Science 277, 80, 1997; Bonfanti et al., PCCP 2011.

A hot surface exhibits lower barriers: SRP48 results.

geometry	SRP48, 925 K	SRP48, 0 K	SRP
bth	57.2	60.6	60.6
ttb	83.5	84.6	86.0

Barrier heights in kJ/mol for SRP molecular geometries.

For Cu, a_{3D} increases by 1.6% going from 0 to 925 K.

d_{12} increases by 2.7 %. Smaller than bulk interlayer spacing at low T (by 1.1%), bulk like close to 925 K.

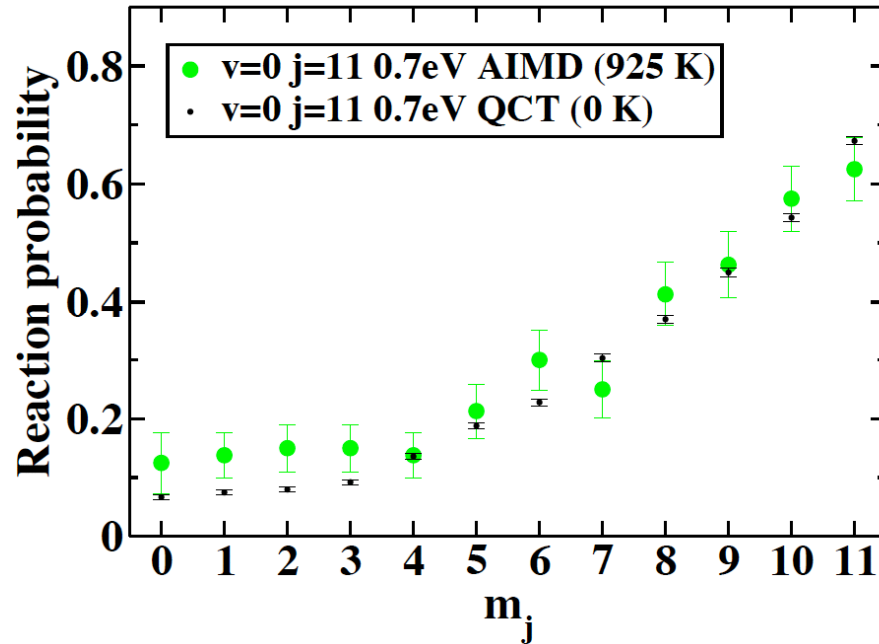
G.J. Kroes et al., to be published.

MEIS: Chae & Gustafson, Phys.Rev.B.54, 14082 (1996).

F.R. Kroeger, J.Appl.Phys.48, 853 (1977).

Leksina & Novikova, Sov.Phys.-Solid State 5, 798 (1963).

Why alignment parameter is lower for v=0,j=11 at 0.7 eV.

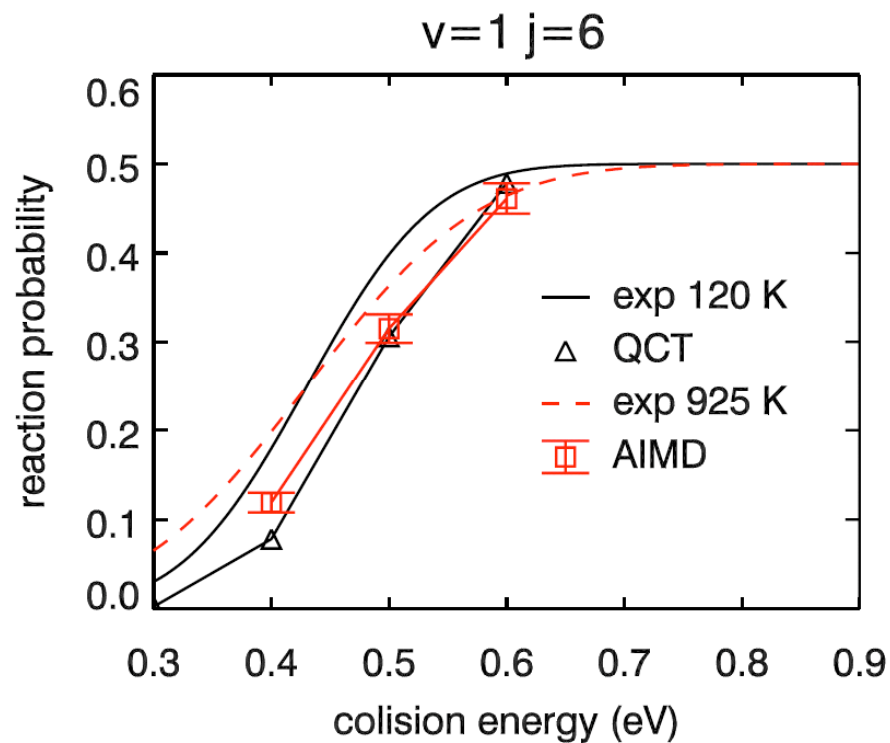


$$A_0^{(2)}(j) = \frac{\sum_{m_j} R_{vm_j}(E_i) \{3m_j^2 - j(j+1)\} / \{j(j+1)\}}{\sum_{m_j} R_{vm_j}(E_i)}$$

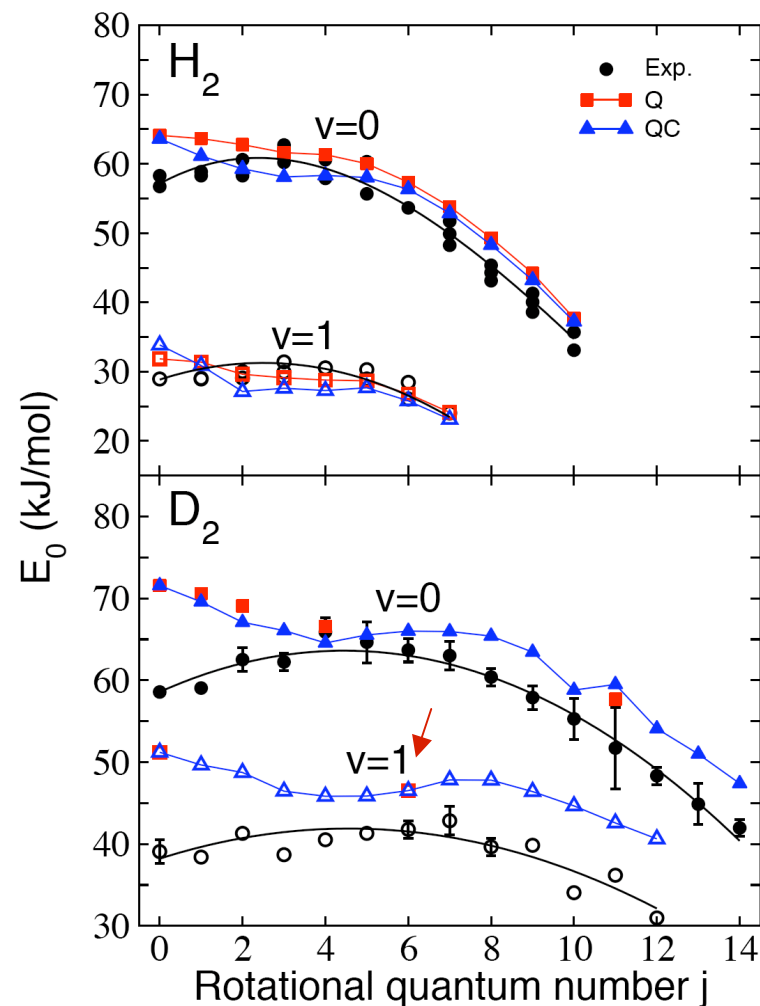
AIMD reaction probabilities are **higher for cartwheeling states**. This yields a **negative** contribution to the numerator, **and** the denominator becomes larger (larger average reaction probability).

To be published.

Preliminary AIMD results, reaction probability, $v=1, j=6$.



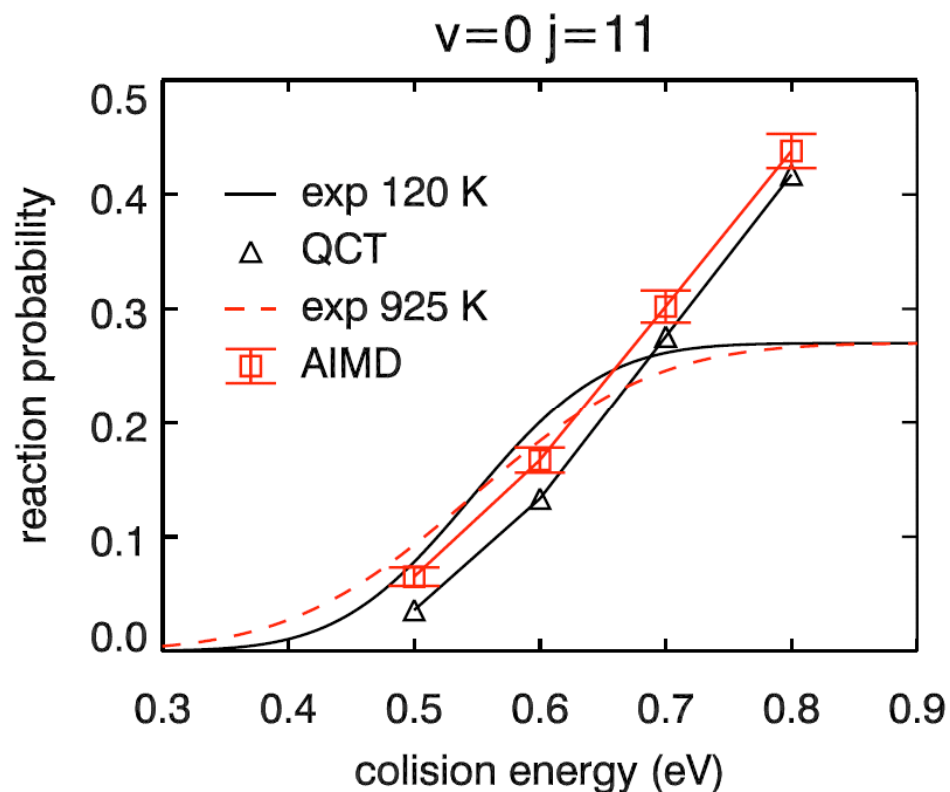
Reaction probability curve broadens somewhat. Agrees with experiment.



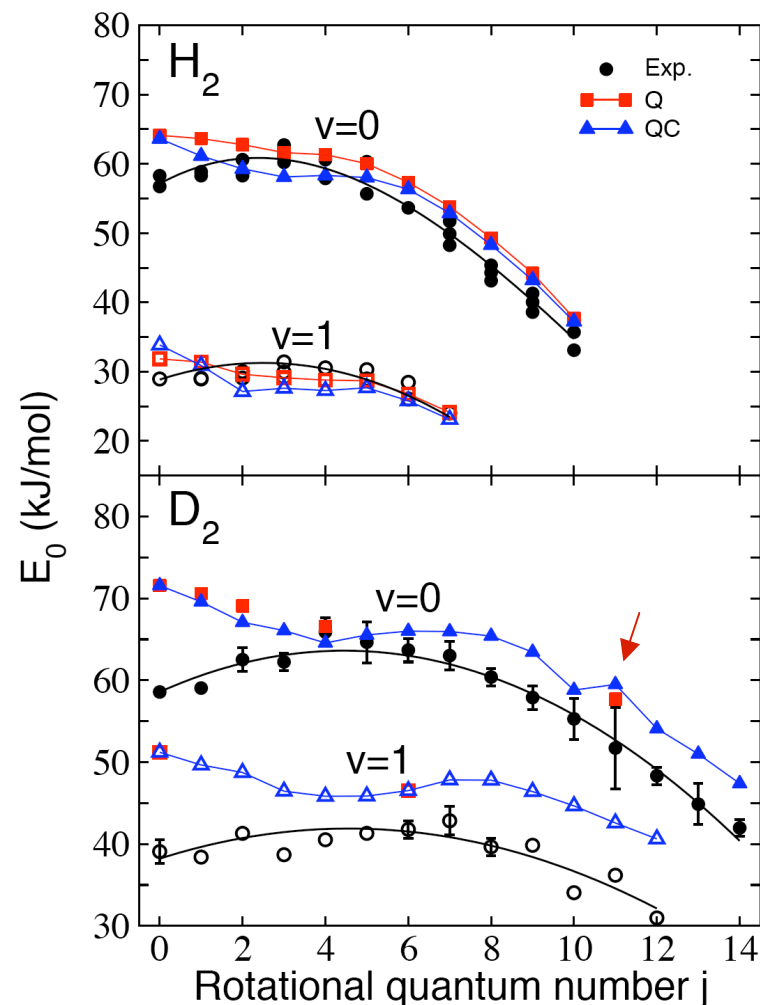
E_0 in better agreement with experiment.

Michelsen et al., JCP98, 8294, 1993; to be published.

Preliminary AIMD results, reaction probability, $v=0, j=11$.



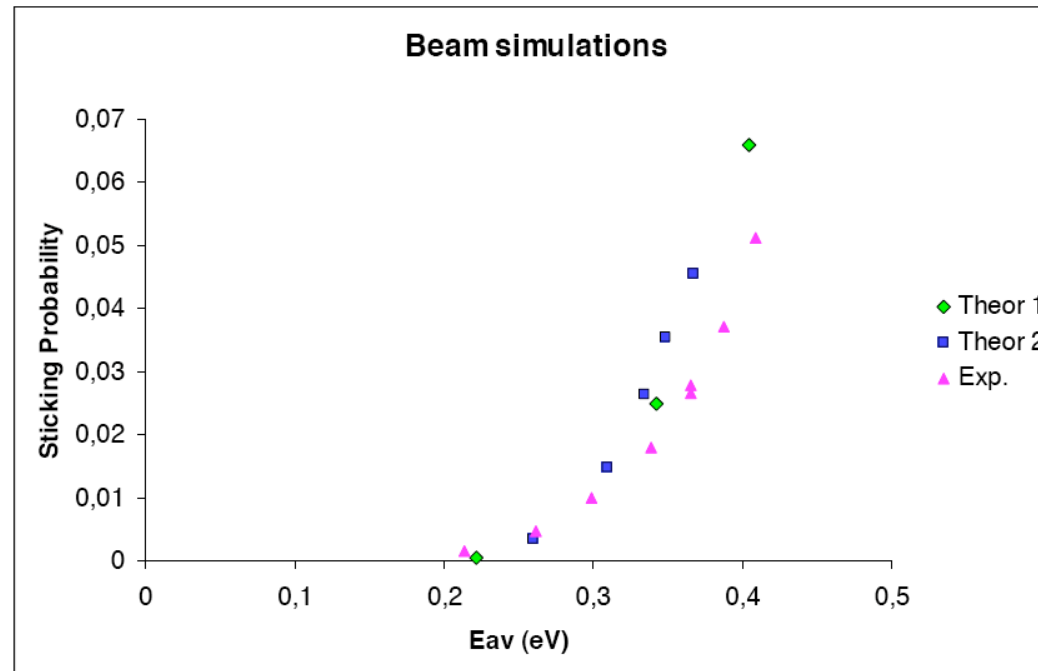
Reaction probability mainly increases with T_s .



E_0 and overall curve in better agreement with experiment.

Michelsen et al., JCP98, 8294, 1993; to be published.

Transferability SRP functional $H_2 + Cu(111)$ to $H_2 + Cu(100)$. Preliminary results.



$T_s = 190$ K

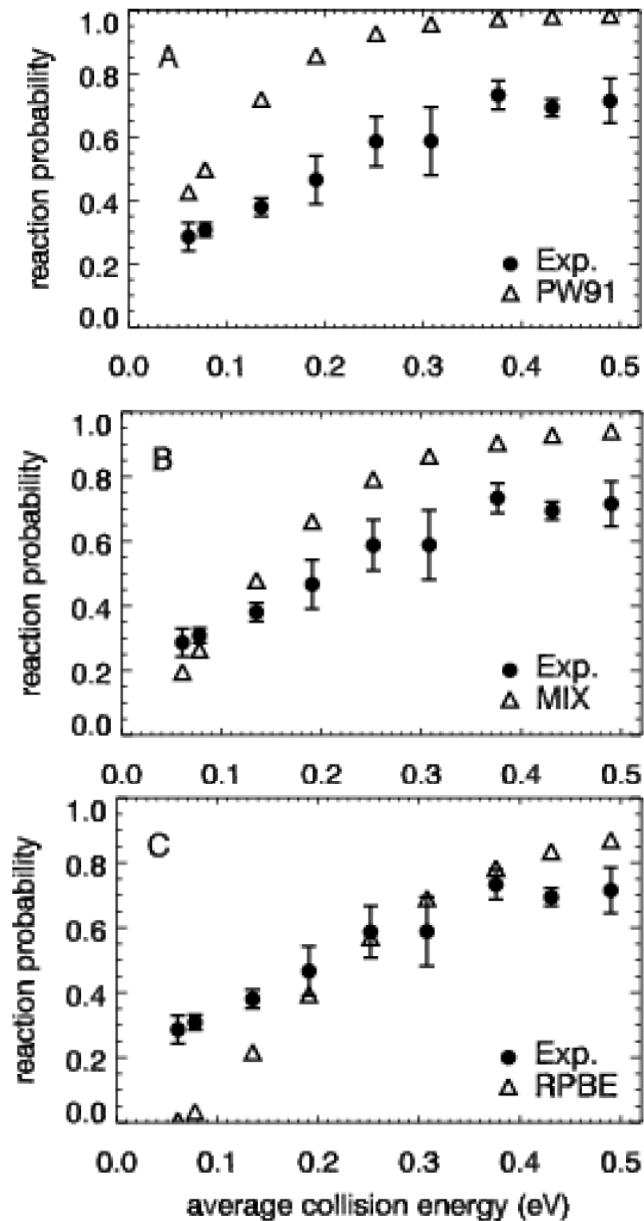
SRP functional ($x=0.43$) reproduces exps. on $H_2 + Cu(100)$ with chemical accuracy (to within 43 meV).

SRP functional transferable to different copper face!

Anger, Winkler, and Rendulic, Surf.Sci. 220, 1989, 1.

L. Sementa et al., in preparation.

SRP functional $H_2 + Cu(111)$ transferable to $H_2 + Ru(0001)$?



SRP functional $H_2 + Cu(111)$ does not describe $H_2/Ru(0001)$ well.

Diffraction in $H_2/Ru(0001)$ likewise not well described.

SRP functional not transferable to H_2 -metal surface system with low, early barriers.

PW91 and RPBE results do not straddle experiment.

Groot et al. JCP127, 244701, 2007.
P. Nieto et al., submitted to PCCP.

Conclusions lecture 6 H₂-metal reactions.

H₂ + Cu(111): BOSS model not accurate for contribution of **vibrational excitation** to measured TOF spectra.

Reasons: energy loss to surface and effect T_s not yet modeled. Probably result of neglecting phonons.

AIMD calculations allowing surface motion yield improved agreement for orientational dependence reaction.

Also increased agreement for (v,j) resolved reaction D₂.

SRP functional H₂/**Cu(111)** transferable to H₂/**Cu(100)**.
Not to H₂/**Ru(0001)**.

C. Díaz et al., Science 326, 832 (2009); PCCP 12, 6499, 2010.
Kroes et al., PNAS 2010.