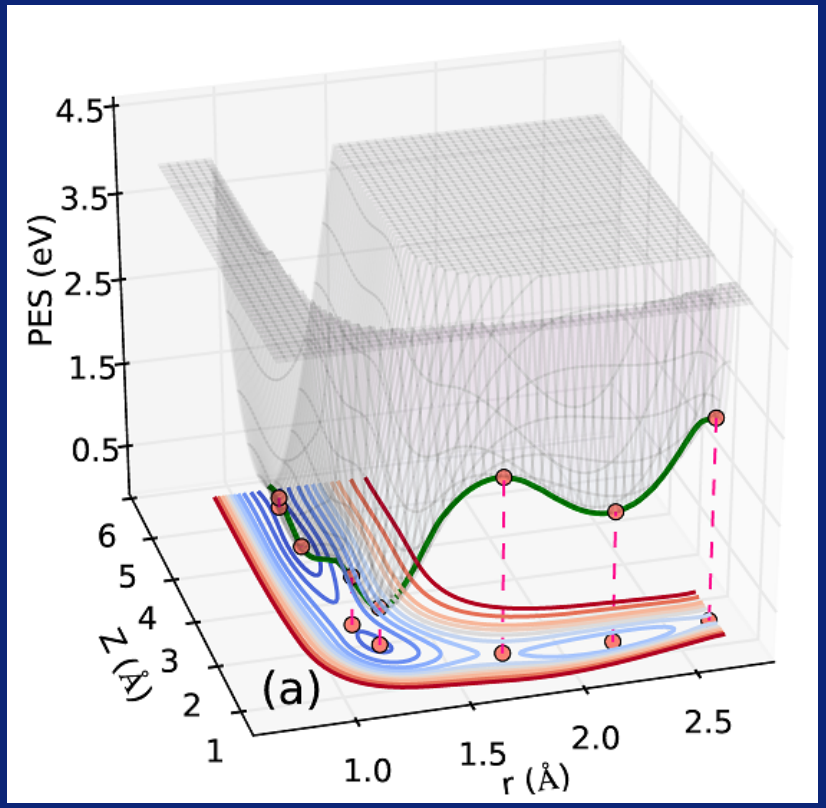
Machine learning in computational chemistry

Foundations and applications



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Winter School on
Theoretical Chemistry and Spectroscopy
Han-sur-Lesse, December 10 - 14

Contents

1) Neural Networks (NNs):
   Structure & “Learning” (1h)
   Hands-on: Training a simple NN (45 min)

2) NNs for potential energy surfaces:
   Coordinate representation (~45 min)
   Hands-on: (Re-)Fitting a potential energy surface for O_2@Pd(100) (~20 min + last night)

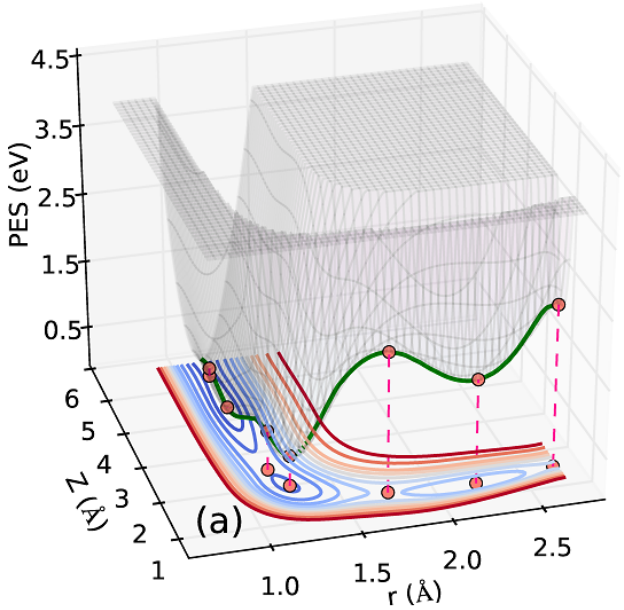
3) Applications in gas-surface dynamics (<1h)

Langevin dynamics 1: PESs

$$m\ddot{\boldsymbol{R}} = -\nabla V(\boldsymbol{R}) - \eta(\boldsymbol{R})\dot{\boldsymbol{R}} + F_{\text{random}}$$

potential energy surfaces (PESs)

electronic friction (EF)



I. Goikoetxea, J. Beltrán, **JM**, *et al.*, New J. Phys. **14**, 013050 (2012).
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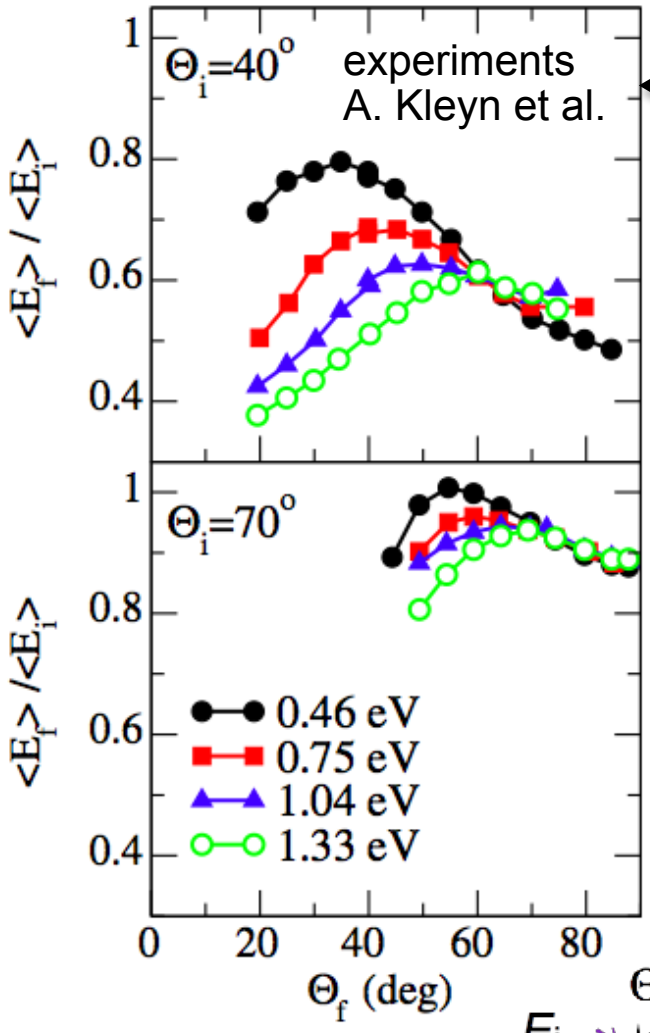
O_2 on Ag(111)



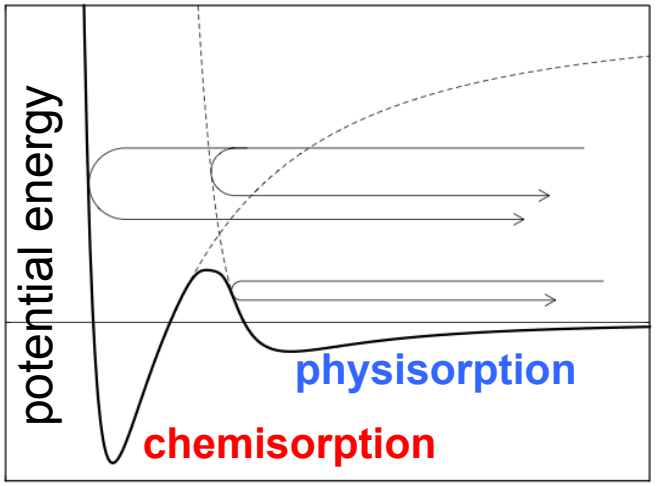
molecular scattering
(time-of-flight)
→ suggested interpretation:
double well in 1D

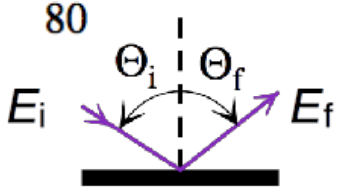
high energy loss

corrugated PES
(→ binary collisions)

low energy loss

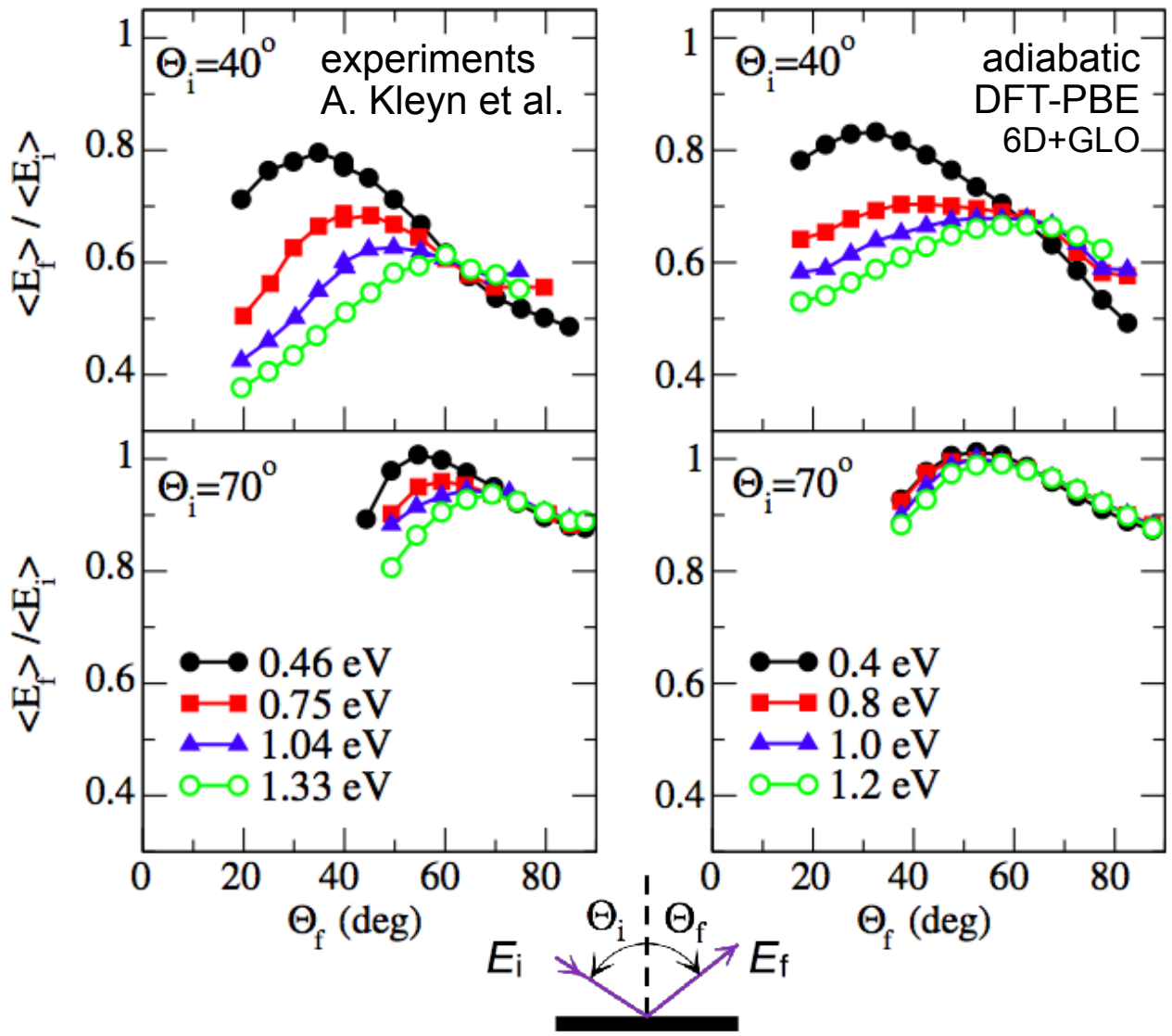
flat PES
($p_{||}$-conservation)





A. Raukema, R. J. Dirksen, and A. W. Kleyn,
J. Chem. Phys. **103** (1995) 6217.

O_2 on Ag(111)



vdW-tail absent
→ **no physisortion**

nevertheless(!)
accurately **reproducing**

✔ very low
sticking probability
$S_0(E_i < 1.0\ \text{eV}) < 10^{-7}$

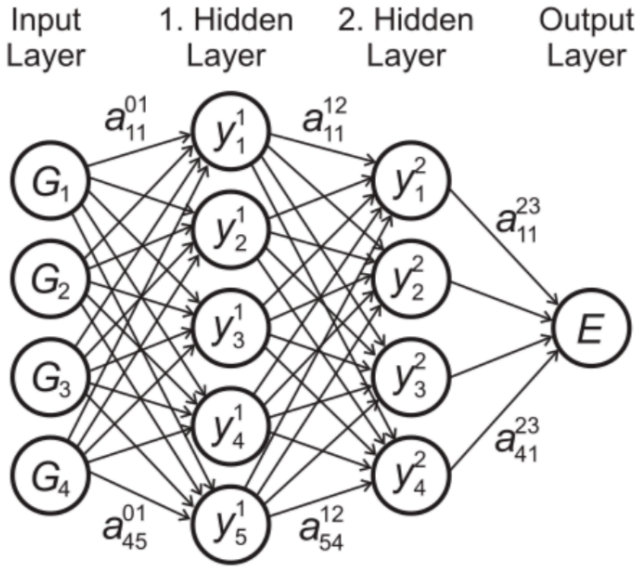
I. Goikoetxea, J. Beltran, **JM** *et al.*
New J. Phys. **14**, 013050 (2012).

✔ scattering

I. Goikoetxea, **JM** *et al.*
Phys. Rev. Lett. **112**, 156101 (2014).

N_2 on Ru(0001): HD-NNP

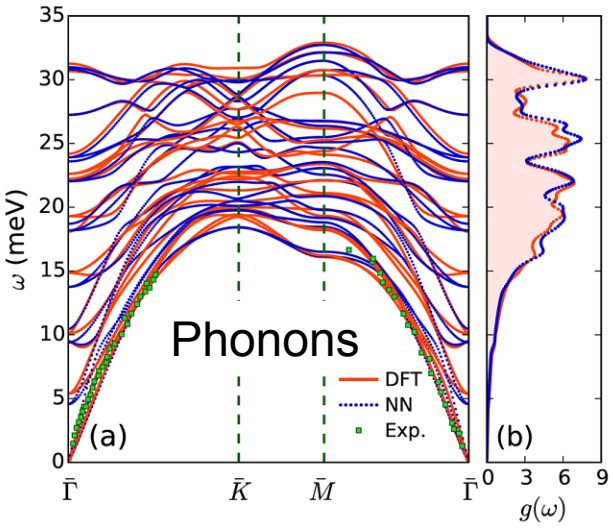
- A NNP that works for all supercells with different number of layers
- `RuNNer` code*
- Symmetry functions: G^2 and G^4; 2 hidden layers: 20 nodes
- More than 25000 training data set
- `VASP` code for DFT calculations with RPBE functional

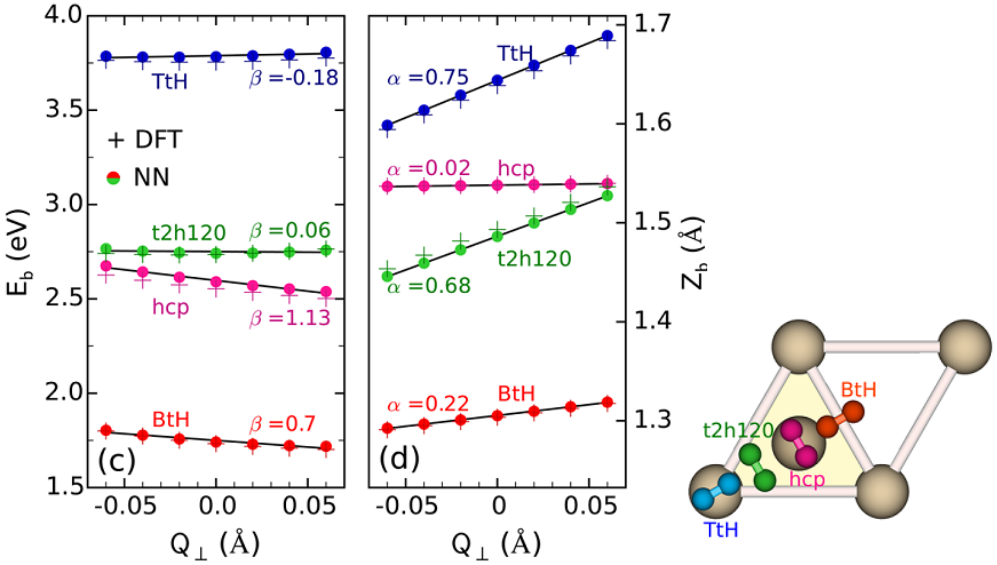


$$E = f_1^3(b_1^3 + \sum_{l=1}^{4} a_{l1}^{23} . f_l^2(b_l^2 + \sum_{k=1}^{5} a_{kl}^{12} . f_k^1(b_k^1 + \sum_{j=1}^{4} a_{jk}^{01} . G_j)))$$

J. Behler and M. Parrinello, Phys. Rev. Lett. 98, 146401 (2007)
J. Behler, J. Chem. Phys. 134, 074106 (2011)

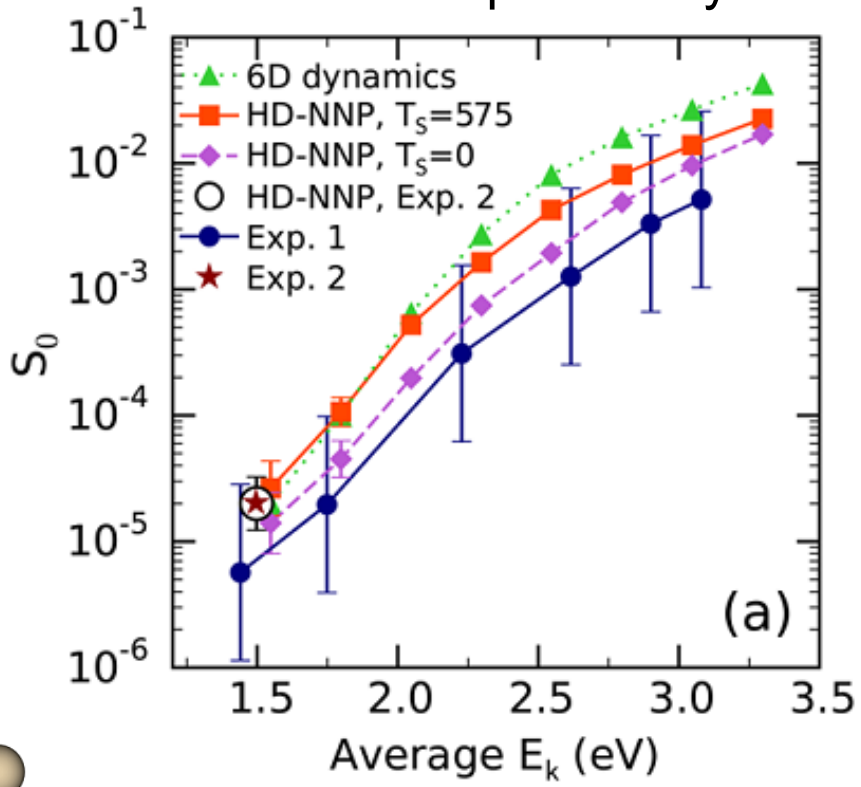
N_2 on Ru(0001): fully mobile surface





Electronic and mechanical coupling

Reaction probability

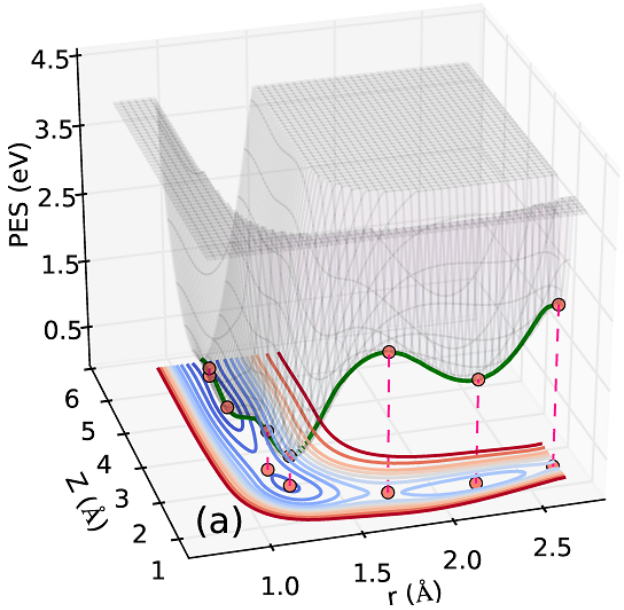


K. Shakouri, J. Behler, **JM**, and G.-J. Kroes,
J. Phys. Chem. Lett. **8**, 2131 (2017)
J. Phys. Chem. C (2018) DOI: 10.1021/acs.jpcc.8b06729

Langevin dynamics 2: EF

$$m\ddot{\boldsymbol{R}} = -\nabla V(\boldsymbol{R})$$

potential energy surfaces (PESs)



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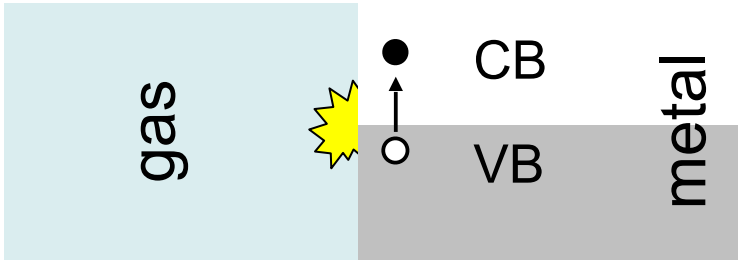
K. Shakouri, J. Behler, **JM**, *et al.*, J. Phys. Chem. Lett. **8**, 2131 (2017).

$$-\eta(\boldsymbol{R})\dot{\boldsymbol{R}} + \boldsymbol{F}_{\text{random}}$$

electronic friction (EF)



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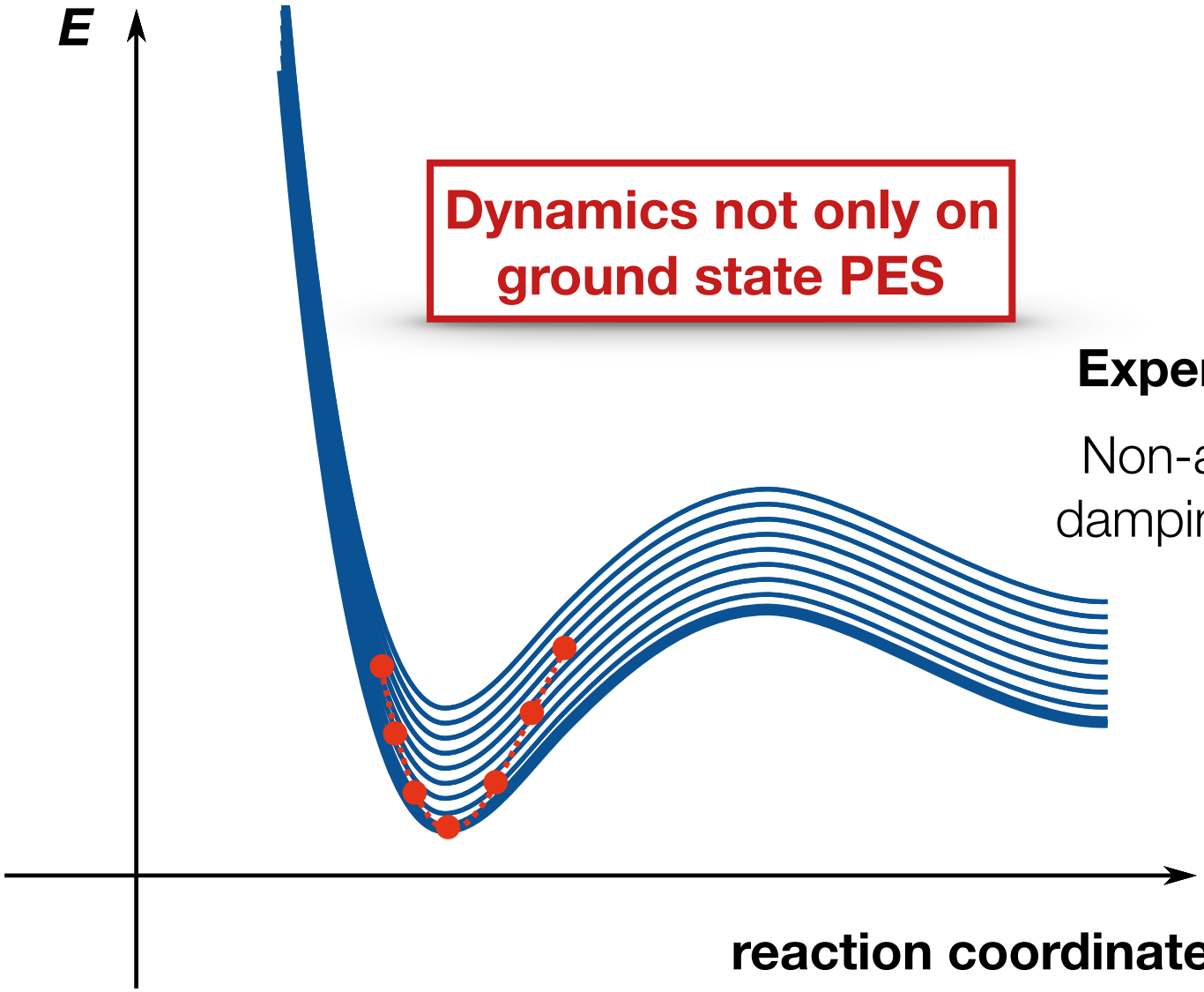
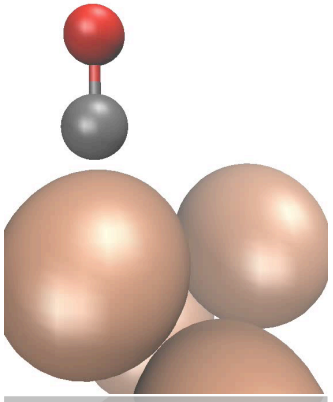
Beyond Born-Oppenheimer



Dynamics not only on ground state PES



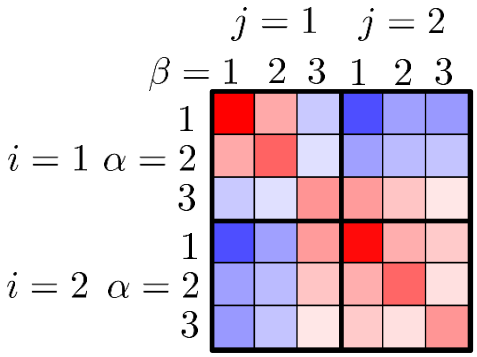
Experimental evidence

Non-adiabatic vibrational damping on metal surfaces

Orbital Dependent Friction

- Electron phonon couplings

$$g_{i\alpha}^{kab}(\vec{R}) = \left\langle \psi_{ak}(\vec{R}) \left| \frac{\partial V_{KS}(\vec{R})}{\partial R_{i\alpha}} \right| \psi_{bk}(\vec{R}) \right\rangle$$

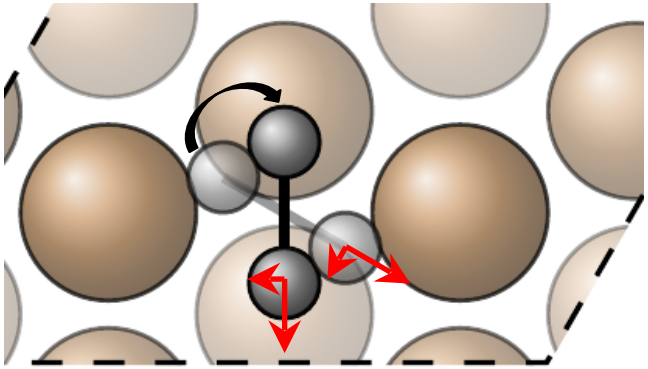


- Fermi's golden rule-like expression

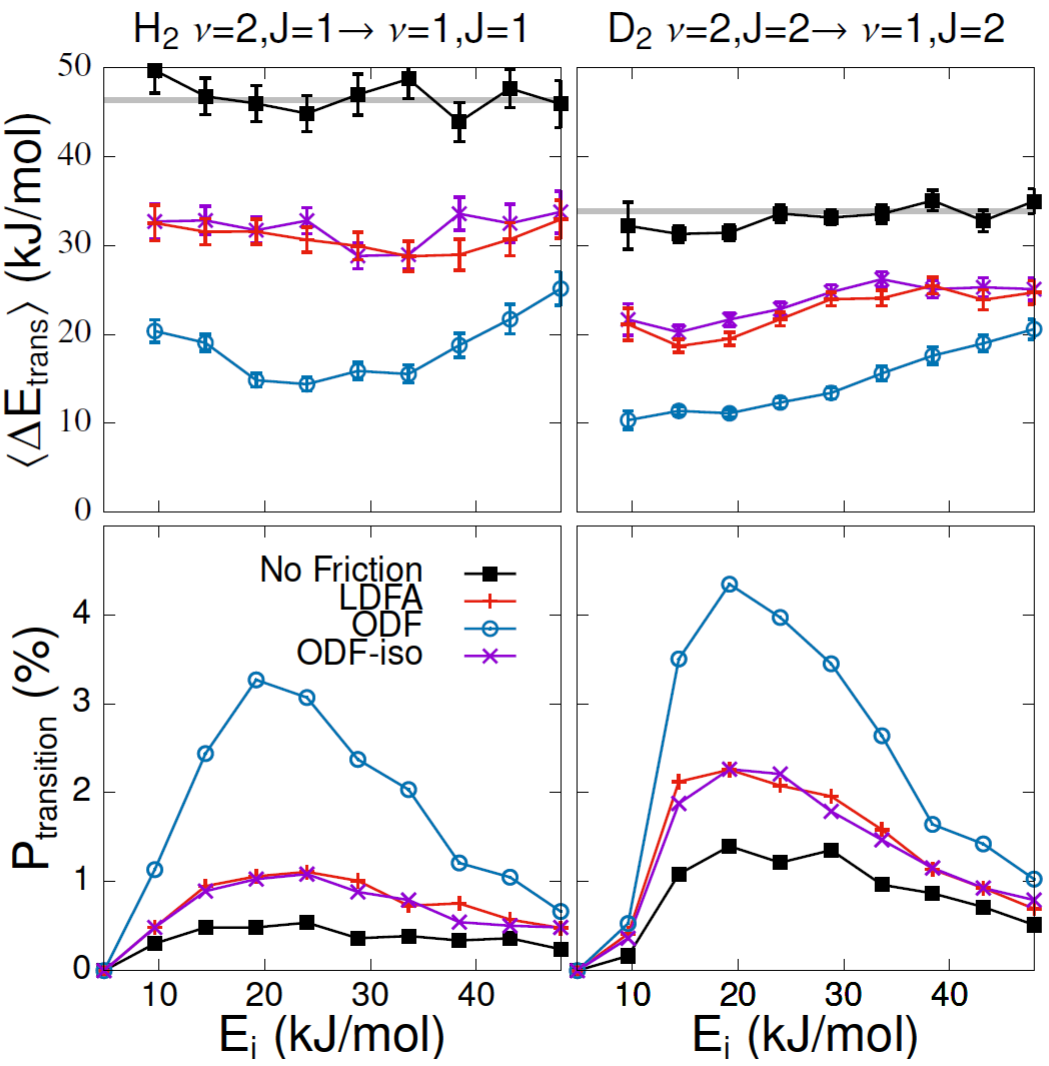
$$\eta_{i\alpha j\beta}^{\mathrm{ODF}}(\vec{R}) = h \sum_{abk} g_{i\alpha}^{kab}(\vec{R}) g_{j\beta}^{kab}(\vec{R})^{*} \delta(\epsilon_{ak} - \epsilon_F)\delta(\epsilon_{bk} - \epsilon_F)$$

R. Maurer et al., Phys. Rev. B 94, 115432 (2016) & references therein

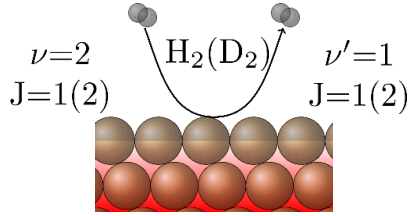
- no "chemically intuitive" functional form
  - NN fit(s) of 21 functions of 6 variables
  - positive definiteness
    → Cholesky decomposition
  - challenge: symmetry inherent to tensor transformations intertwines tensor elements



H_2 on Cu(111): fingerprint observables



$$\Delta E = \Delta E_{vib} + \underbrace{\Delta E_{rot}}_{=0} + \Delta E_{trans}$$



LDFA: scalar friction
obtained from atoms-in-jellium modell
("local-density friction approximation")

ODF-iso: scalar friction
obtained from "isotropicalization"
of ODF tensor

P. Spiering and **JM**
J. Phys. Chem. Lett. **9**, 1803 (2018).

Summary & Conclusions

- PES construction based on NNs:
  - specific coordinates for particular application domains
    (and further developments, e.g. PIP-NN)
  - some of-the-shelf implementations are nowadays
    available for “high-dimensional” schemes
- O_2 on Ag(111):
  - $>10^7$ trajectories allow to study reactive and scattering events
  - simple picture (“physisorption+chemisorption wells”) disputed
- N_2 on Ru(0001):
  - motion of surface atoms included → insights into phonons!

- NN-fits for electronic friction tensors have allowed to predict “fingerprints” for competing models
  (first application: H_2 on Cu(111))

Acknowledgements

Geert-Jan Kroes

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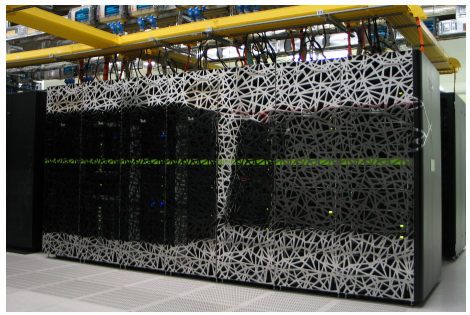
VENI
VIDI
VICI

NWO
Netherlands Organisation for Scientific Research



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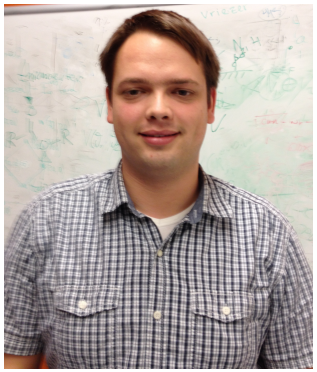

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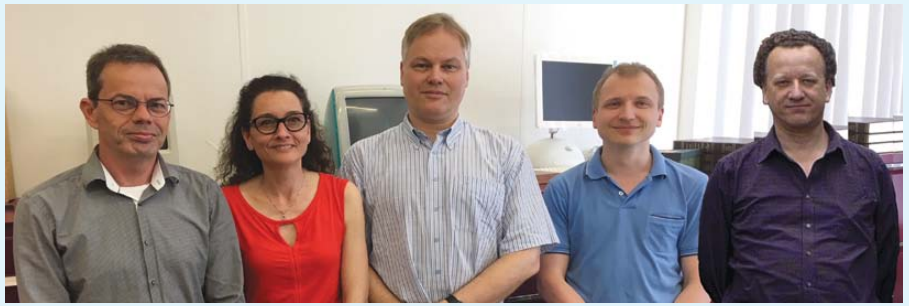
Thank you very much for your attention!

Division Computational & Theoretical Chemistry

Kick-off meeting: March 26, 2019 Amsterdam

Division Computational & Theoretical Chemistry



CTC-Board (fltr): Evert Jan Meijer, Célia Fonseca Guerra, Matthias Bickelhaupt, Jörg Meyer and Gerrit Groenenboom

Kick-off meeting
March 26, 2019, Amsterdam

This meeting aims to gather and unite the computational and theoretical chemists of the Netherlands.

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Becoming a member of the division?
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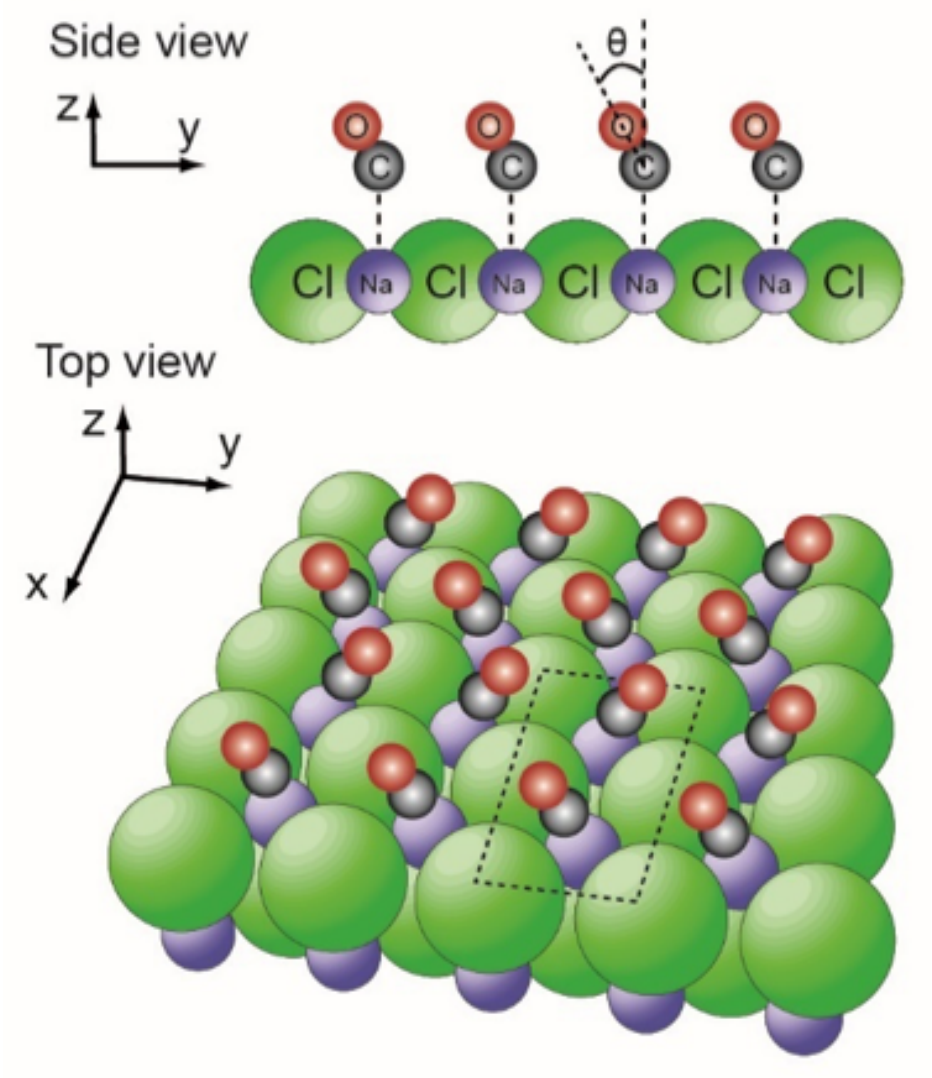
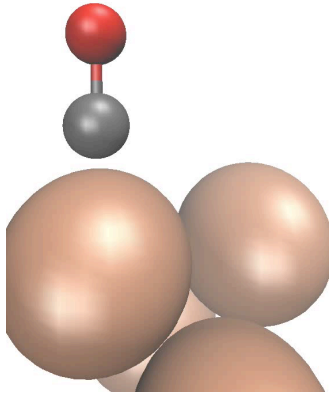
CO@NaCl(100) (1)





The Sommerfeld ground-wave limit for an adsorbed molecule at a surface

L. Chen, J. A. Lau, D. Schwarzer, J. Meyer, V. B. Verma, A. M. Wodtke

DOI: 10.1126/science.aav4278

CO@NaCl(100) (2) - “State changes”

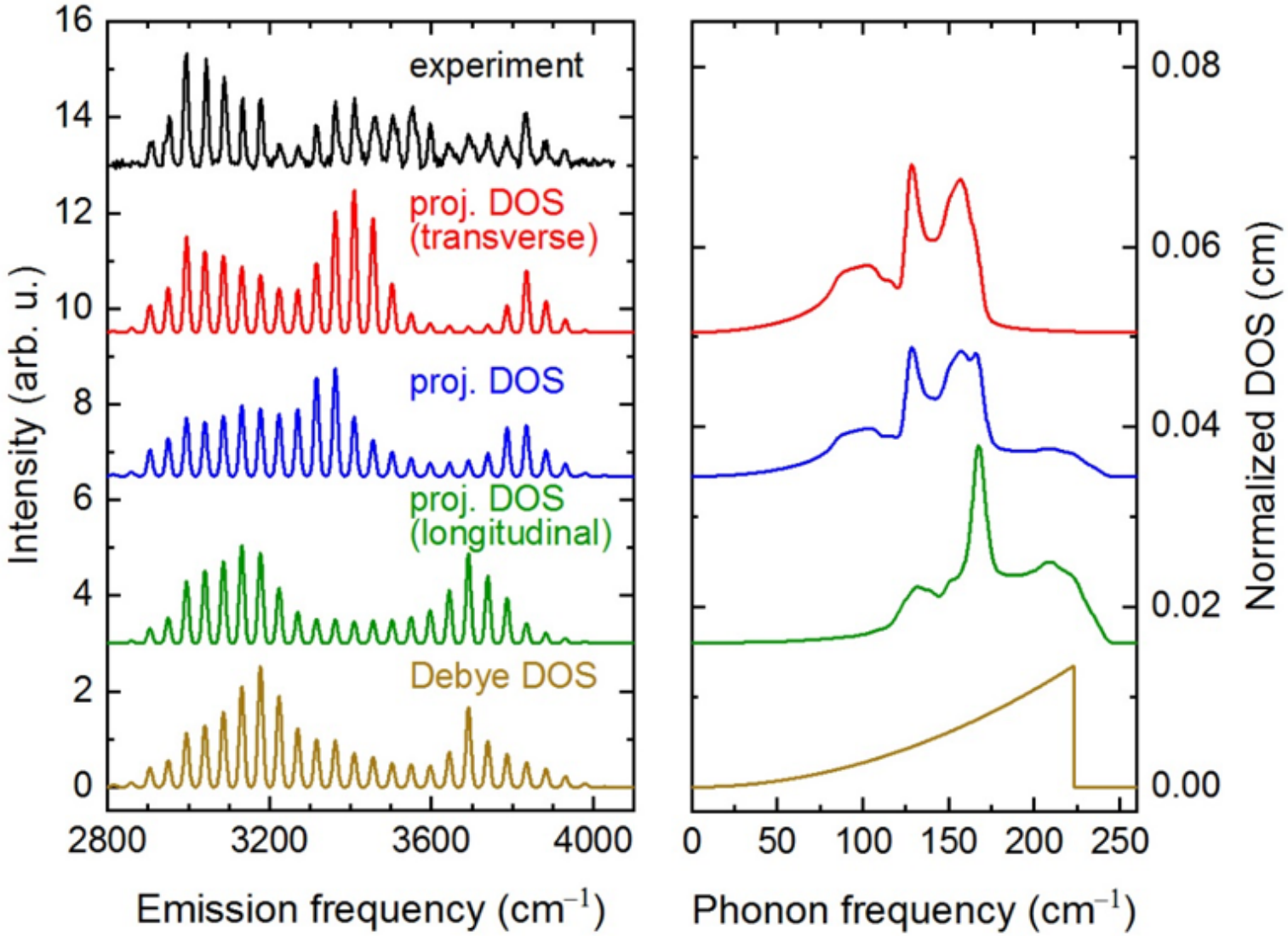
- Pooling

$$\begin{aligned}
CO(1) + CO(1) &\rightarrow CO(2) + CO(0) && + \Delta\varepsilon(2) \\
CO(2) + CO(1) &\rightarrow CO(3) + CO(0) && + \Delta\varepsilon(3) \\
&\vdots && \vdots \\
CO(v) + CO(1) &\rightarrow CO(v+1) + CO(0) && + \Delta\varepsilon(v+1)
\end{aligned}$$

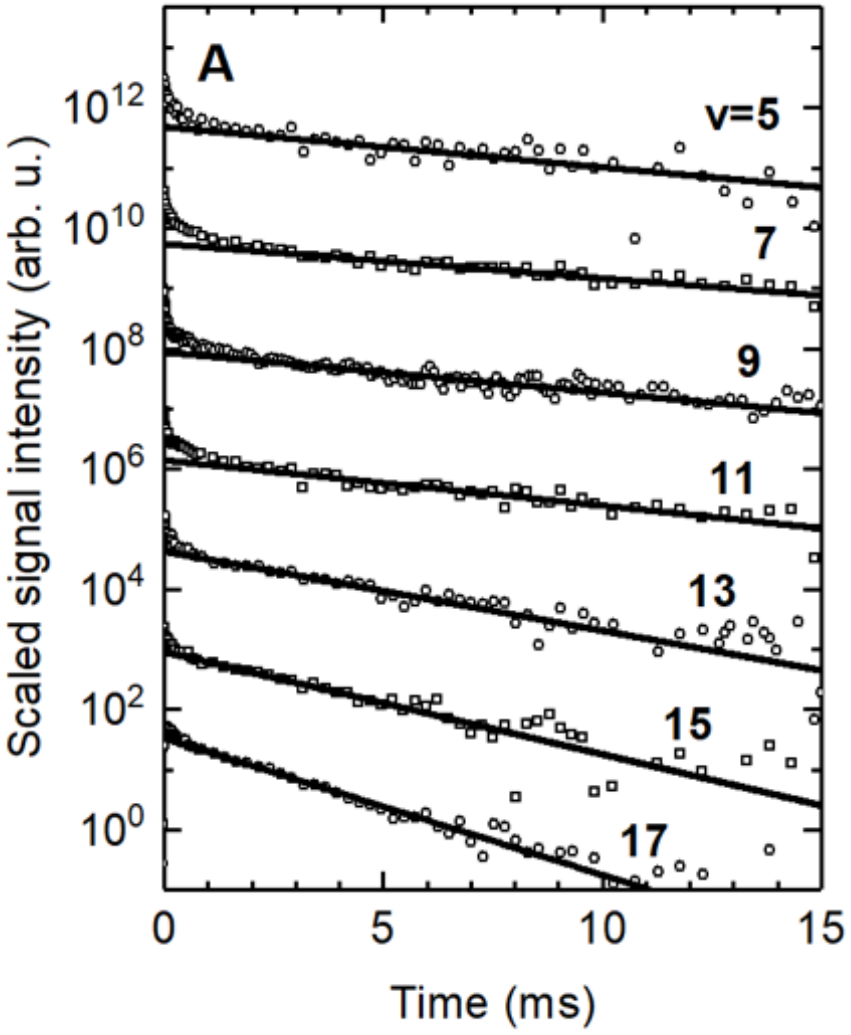
- Dissipation

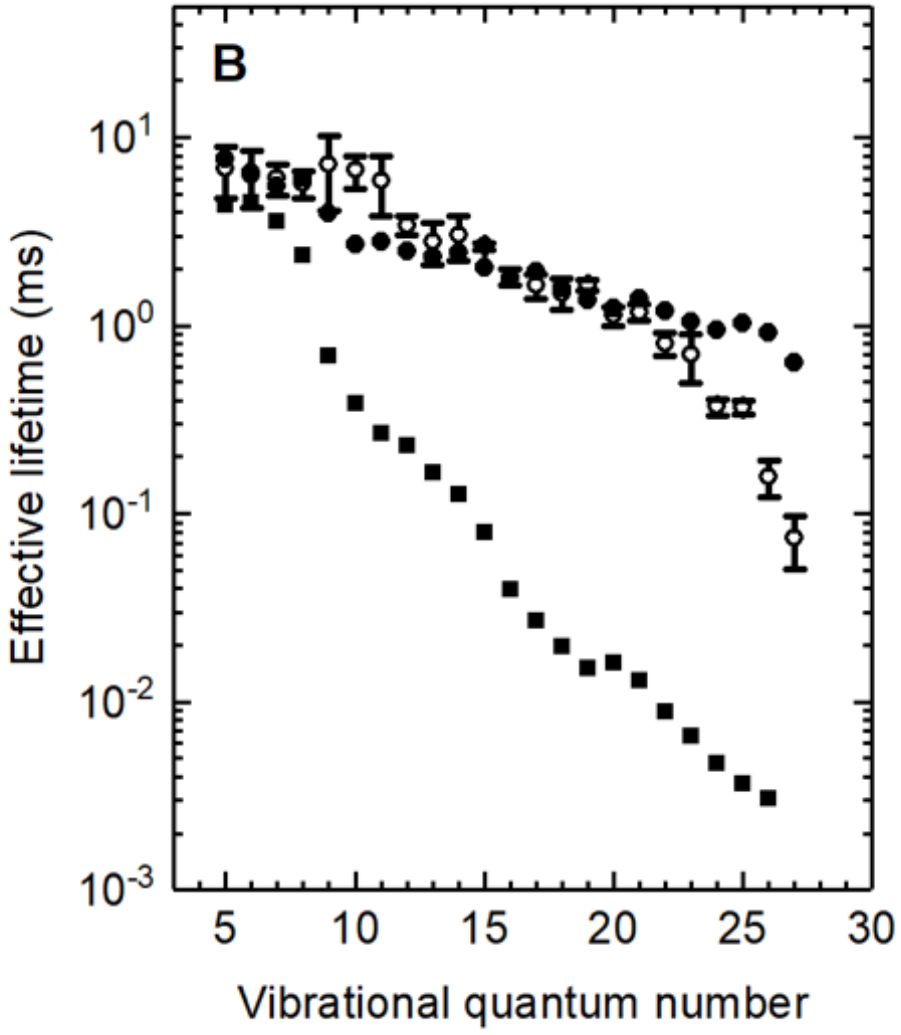
$$CO(v') \rightarrow CO(v'-1) + \Delta E_{phonon}$$

CO@NaCl(100) (3) - Phonons



CO@NaCl(100) (4) - Lifetimes





CO@NaCl(100) (5) - Theories…