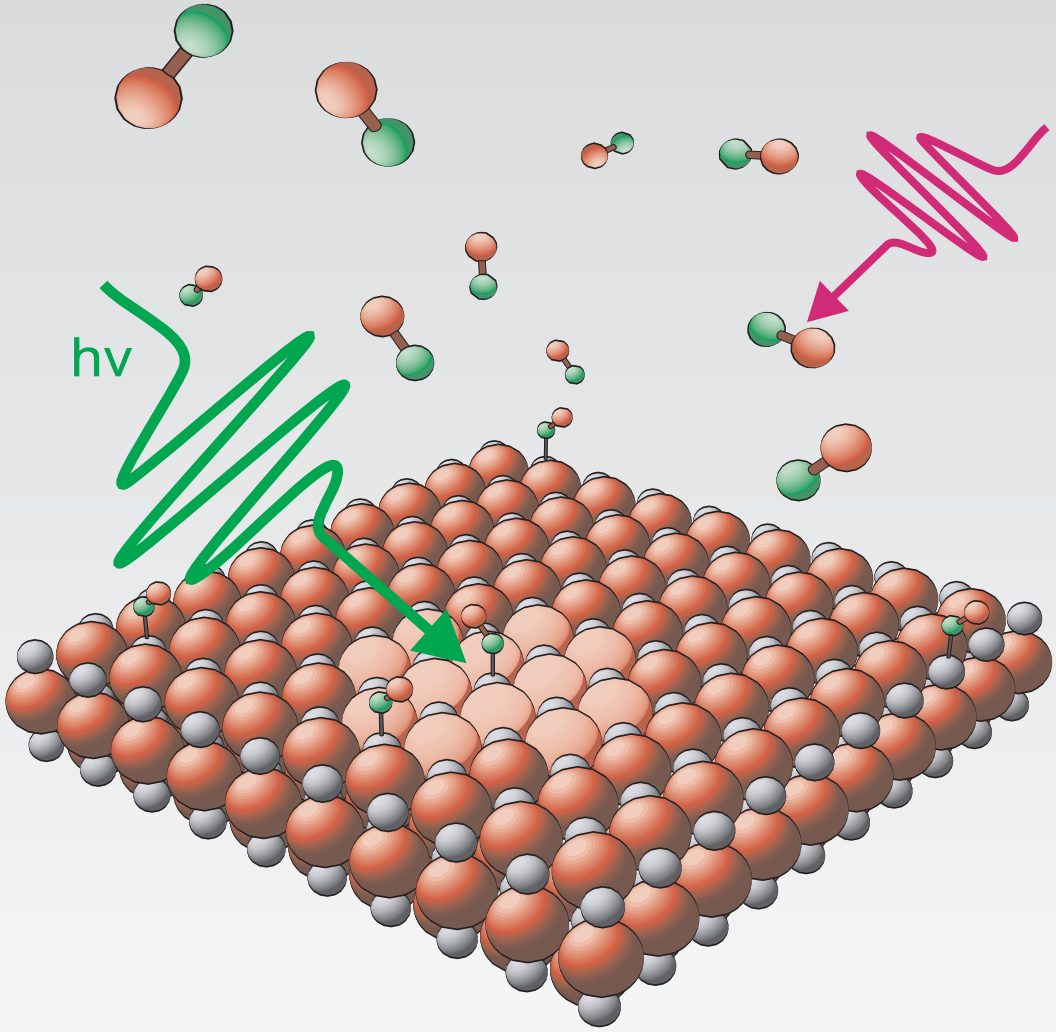
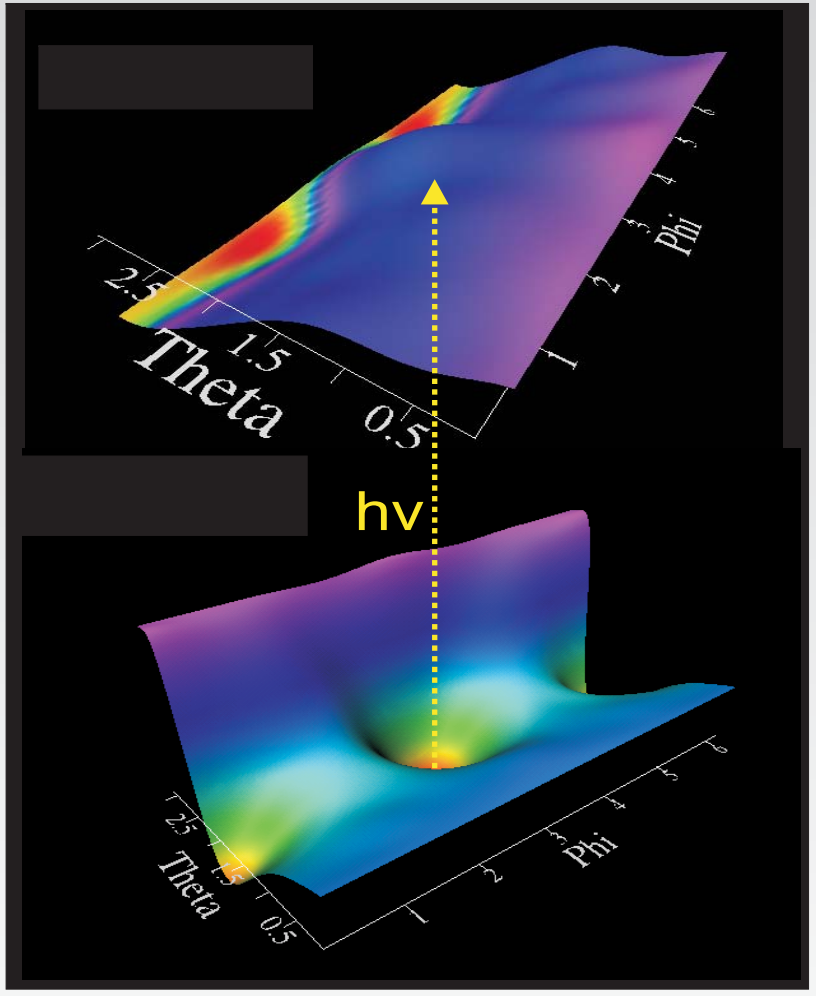
Photoinduced Dynamics at Surfaces

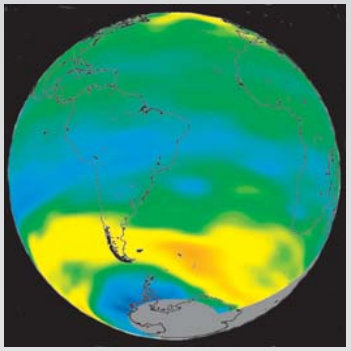




Thorsten Klüner
Theoretical Chemistry
University Oldenburg, Germany

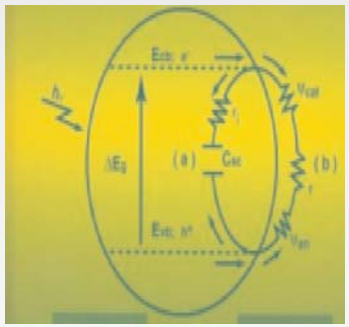
Why Surface Photochemistry ?

- Photochemical reactions at dust particles in our atmosphere



- Interstellar chemical reactions

- Heterogeneous photocatalysis (light acting as reagent)



Chemical reactions at surfaces under influence of light

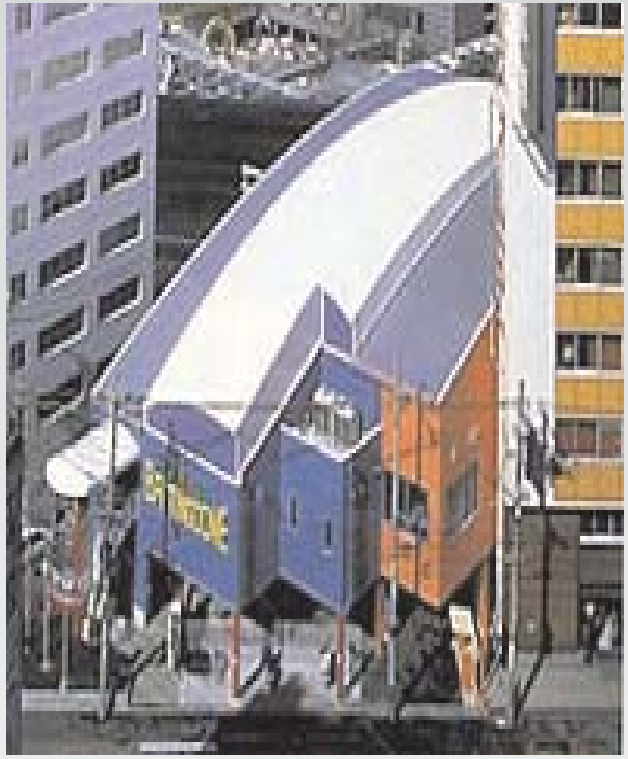
Photocatalysis: Titanium dioxide (TiO_2)

self-cleaning surfaces

anti-fog coating

anti-bacterial coating

Photocatalysis: Titanium dioxide (TiO_2)



self-cleaning surfaces

anti-fog coating

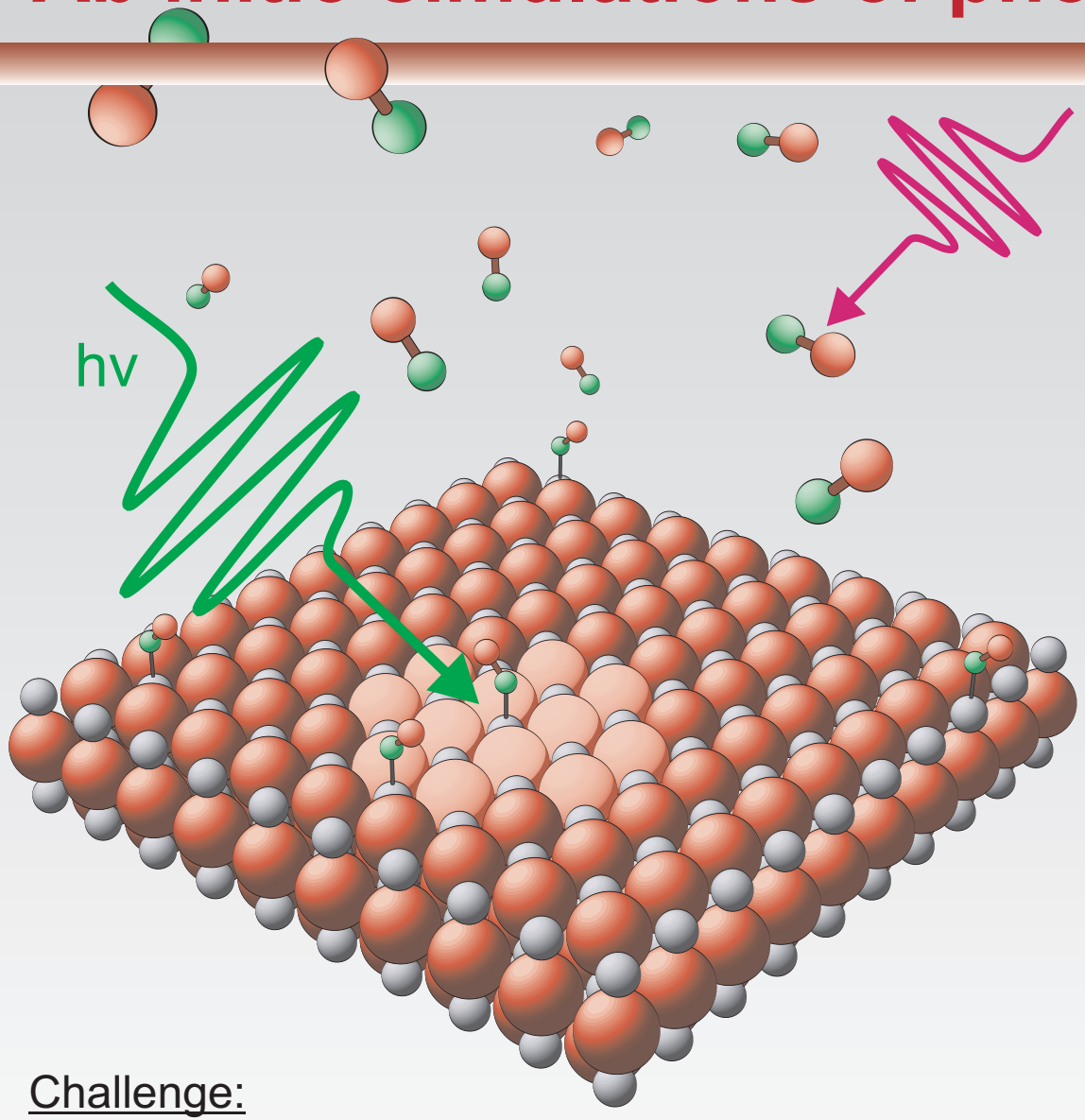
anti-bacterial coating

goal: micrscopic understanding of photochemical elementary processes on surfaces

by: reduction of intrinsic complexity of phenomenon under study

Ab initio simulations of photochemistry on surfaces

Ab initio simulations of photochemistry on surfaces



REDUCE COMPLEXITY!

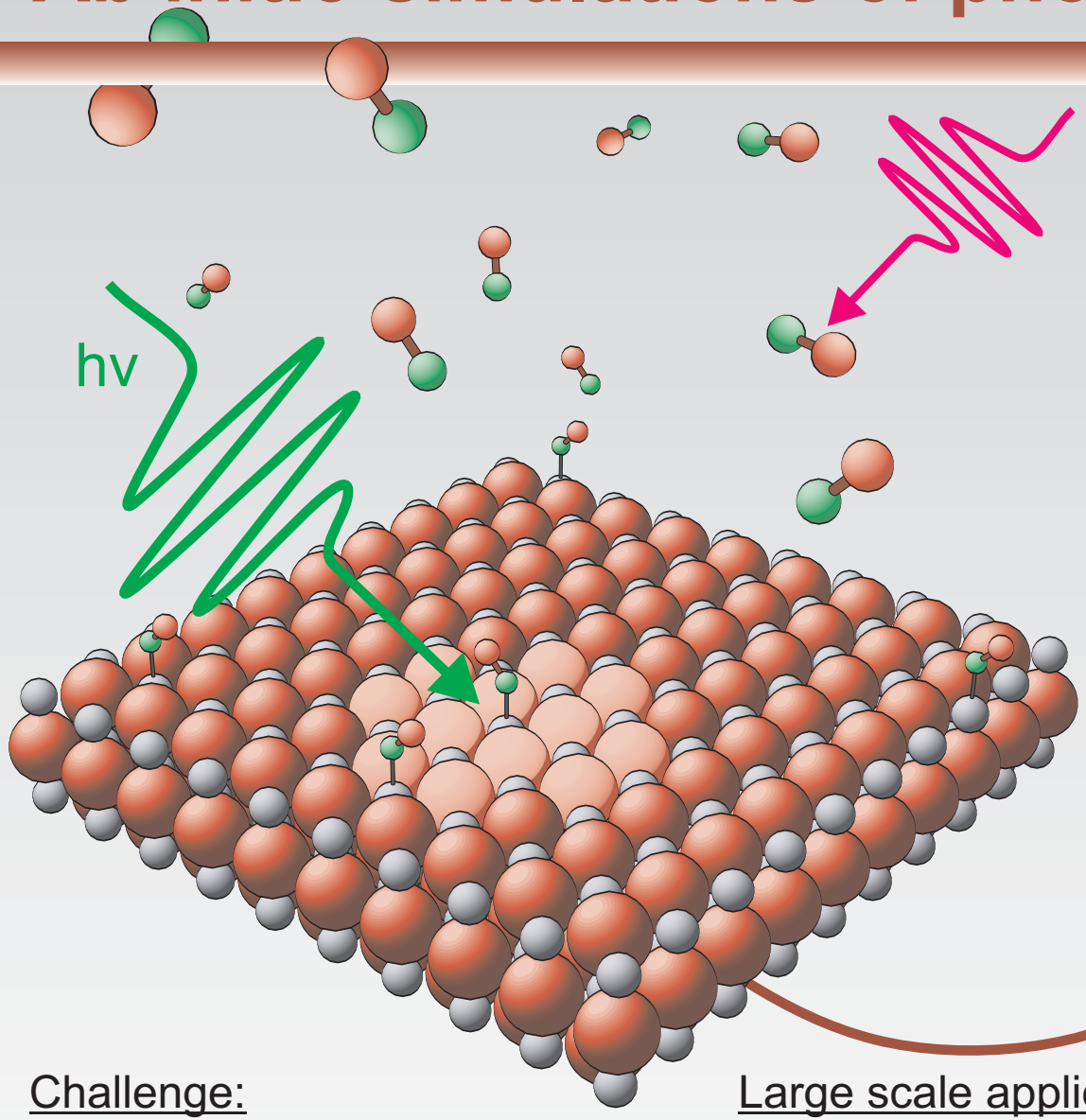
Challenge:

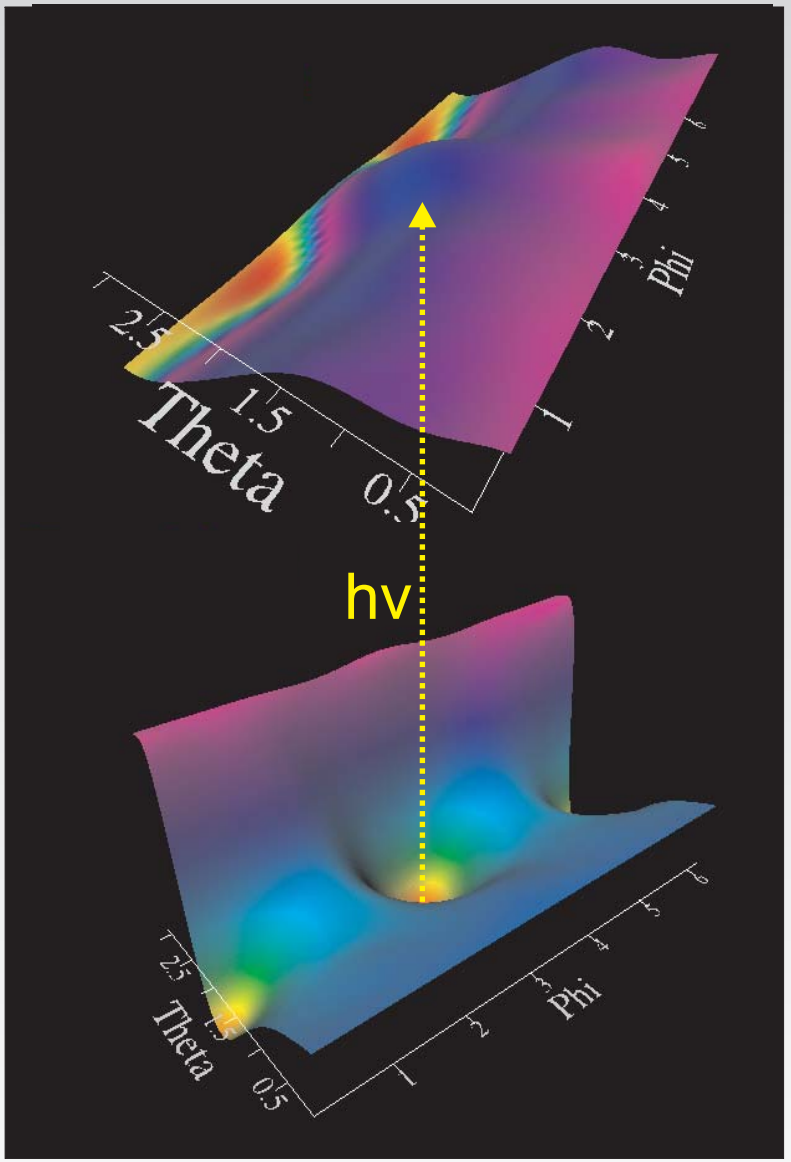
understanding of
1) surface photochemistry
2) surface spectroscopy

Simplest elementary reaction:

Laser-induced desorption of diatomic molecules from “simple” surfaces

Ab initio simulations of photochemistry on surfaces





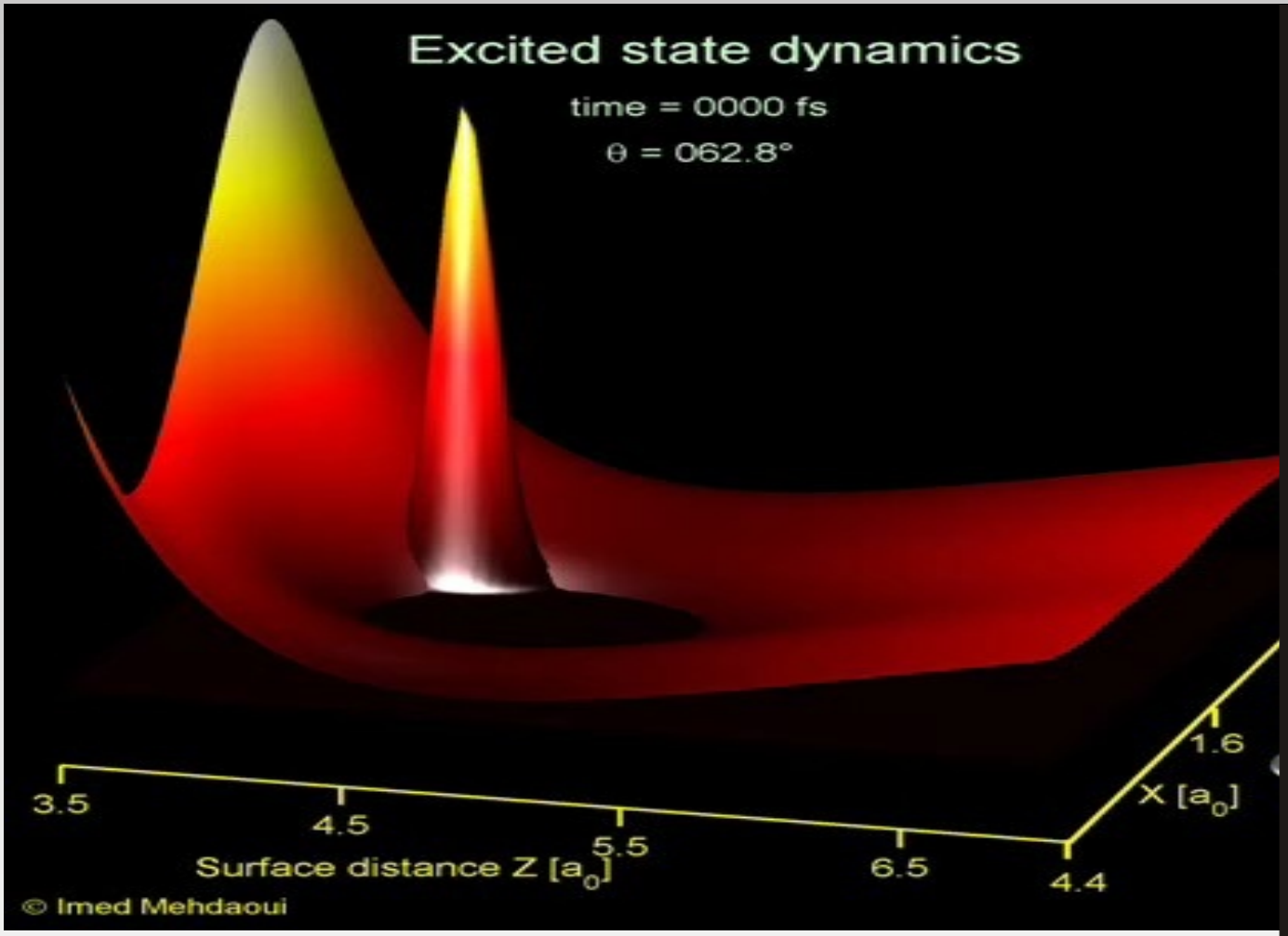
Challenge:

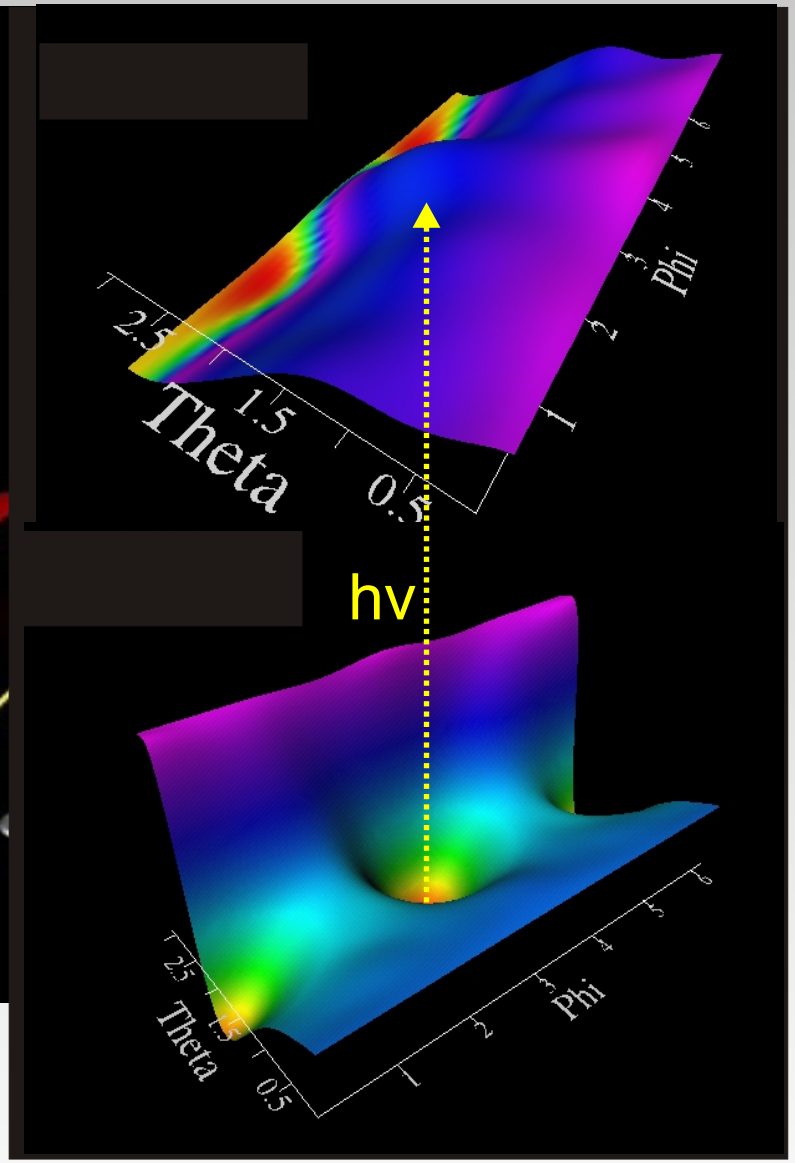
understanding of
1) surface photochemistry
2) surface spectroscopy

Large scale application:

high dimensional quantum dynamics
on ab initio potential energy surfaces

Ab initio simulations of photochemistry on surfaces





Challenge:

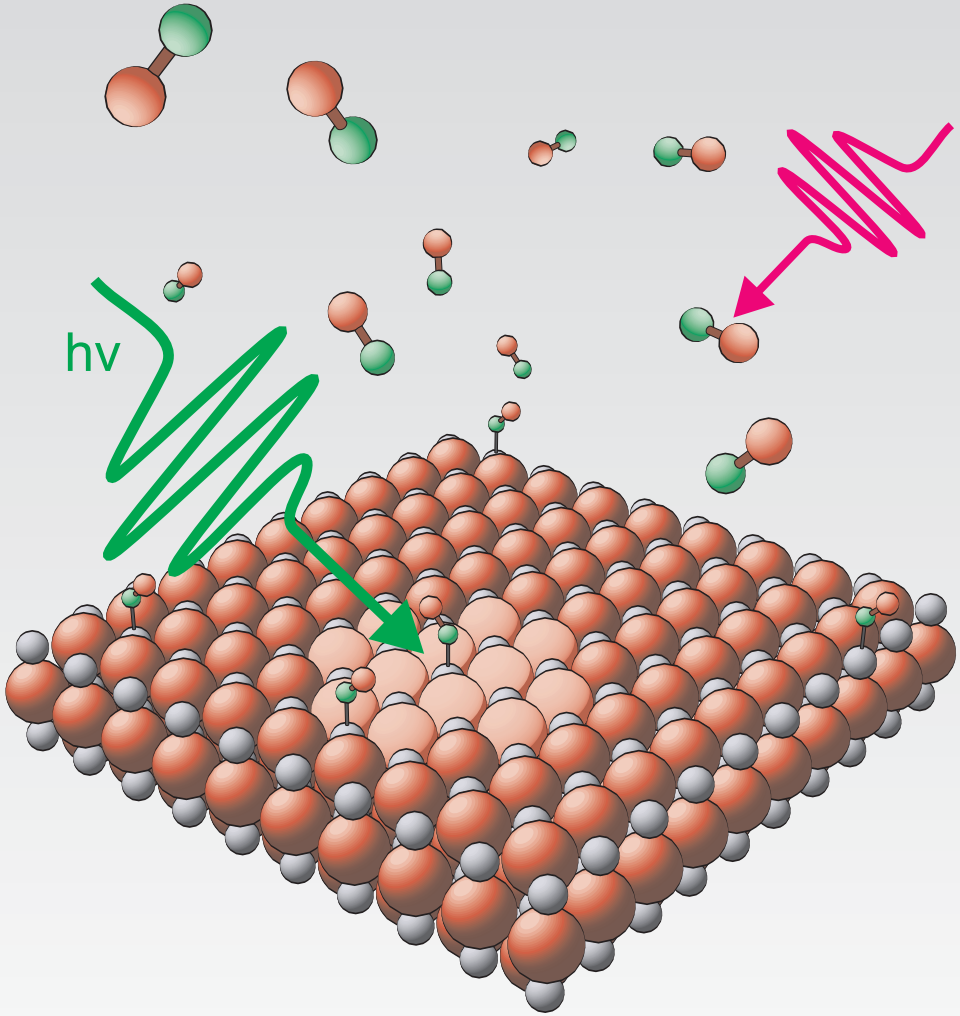
understanding of
1) surface photochemistry
2) surface spectroscopy

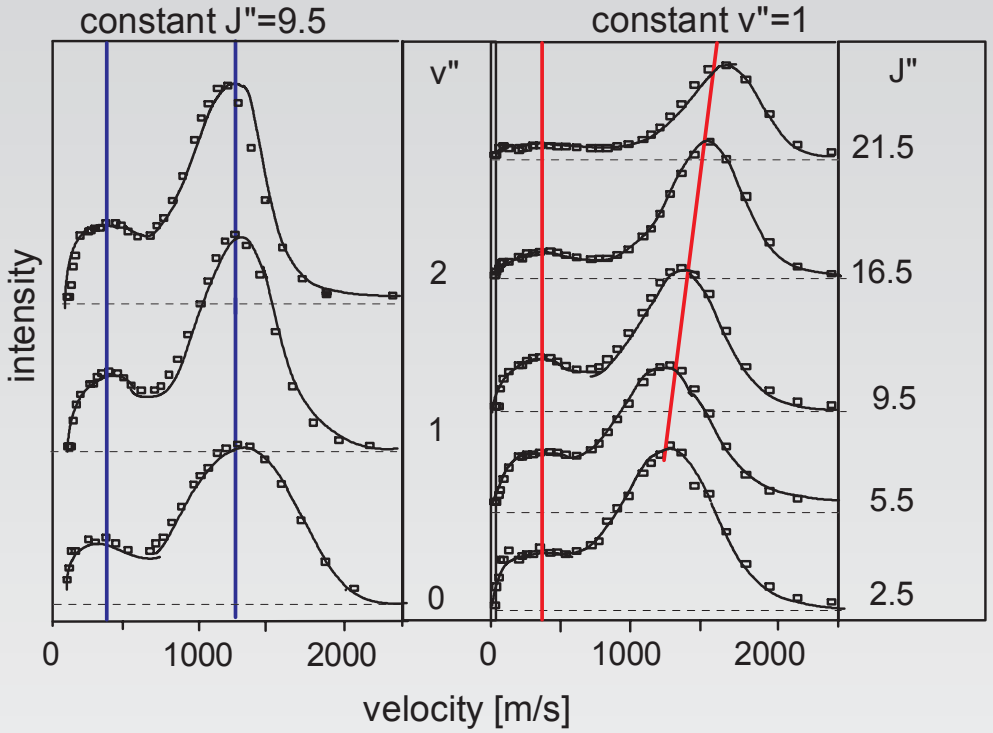
Large scale application:

high dimensional quantum dynamics
on ab initio potential energy surfaces

Photodesorption: NO/NiO(100)

Rempi-Experiment

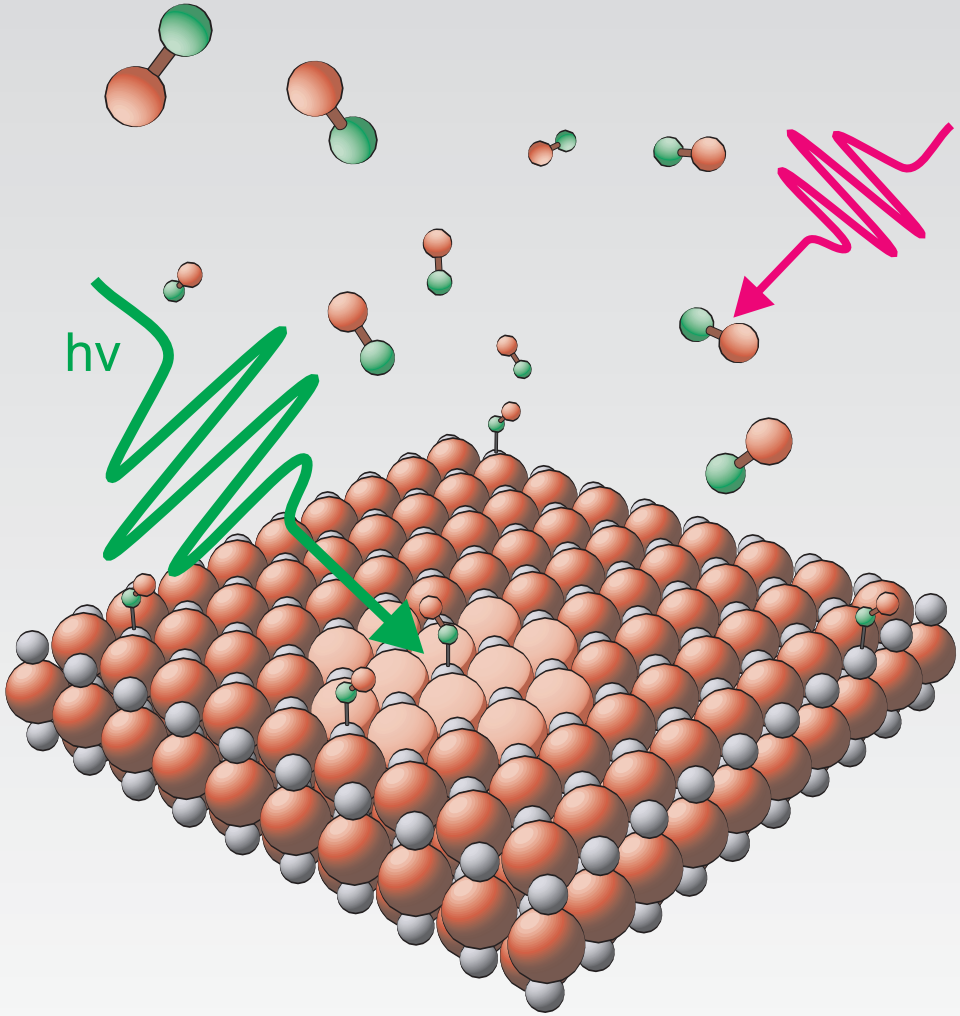


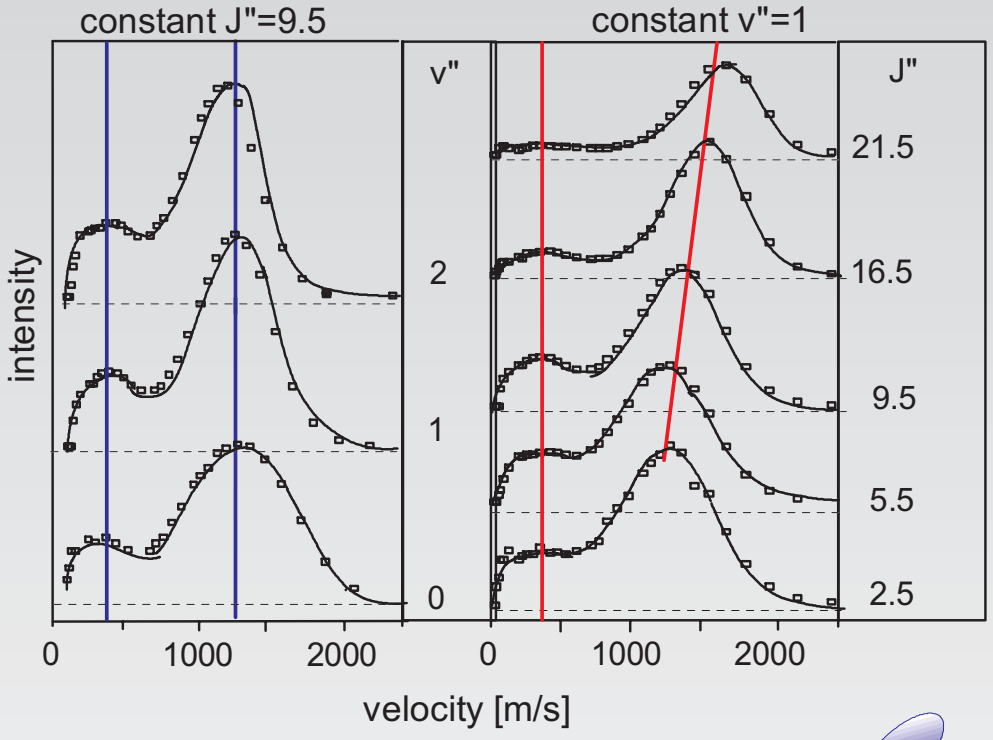


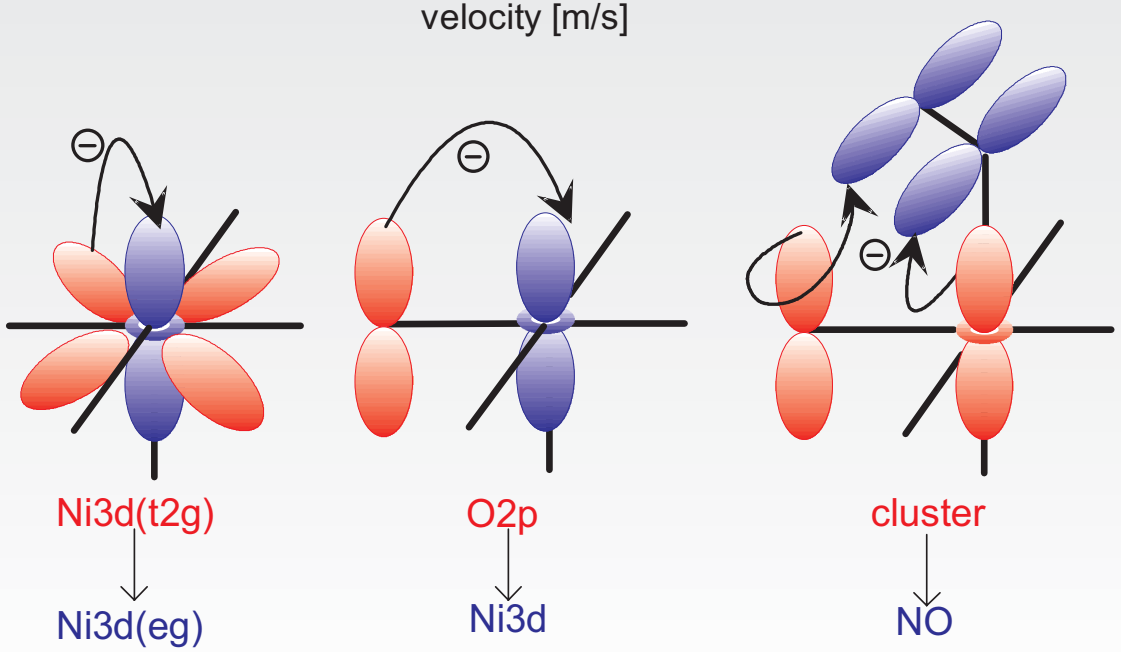
T. Mull et al., J. Chem. Phys. **96**, 7108 (1992)

Photodesorption: NO/NiO(100)

Rempi-Experiment

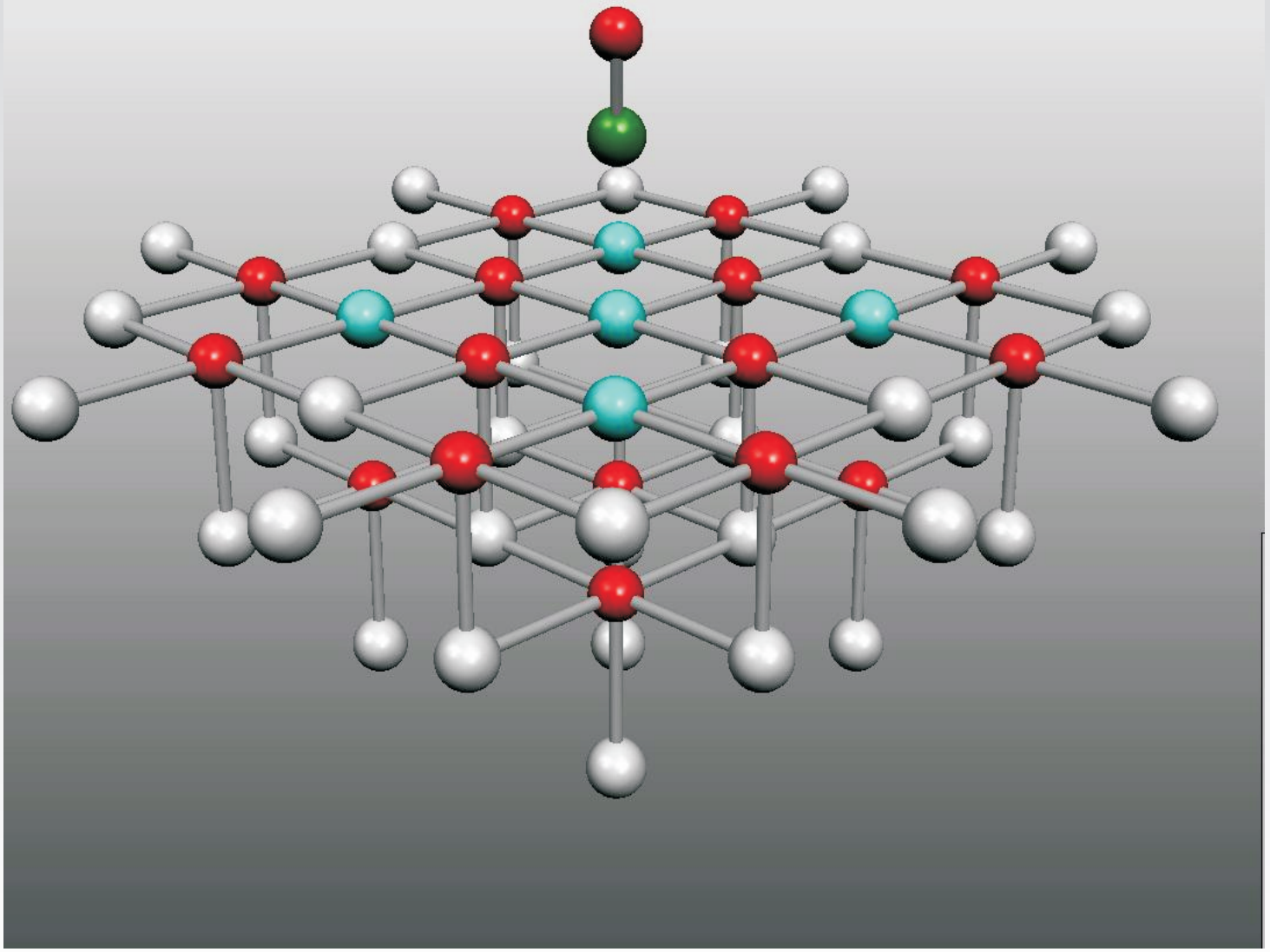






Photodesorption: NO/NiO(100)

$Ni_5O_{17}Mg_{33}^{42+}$/point charge field (not shown)



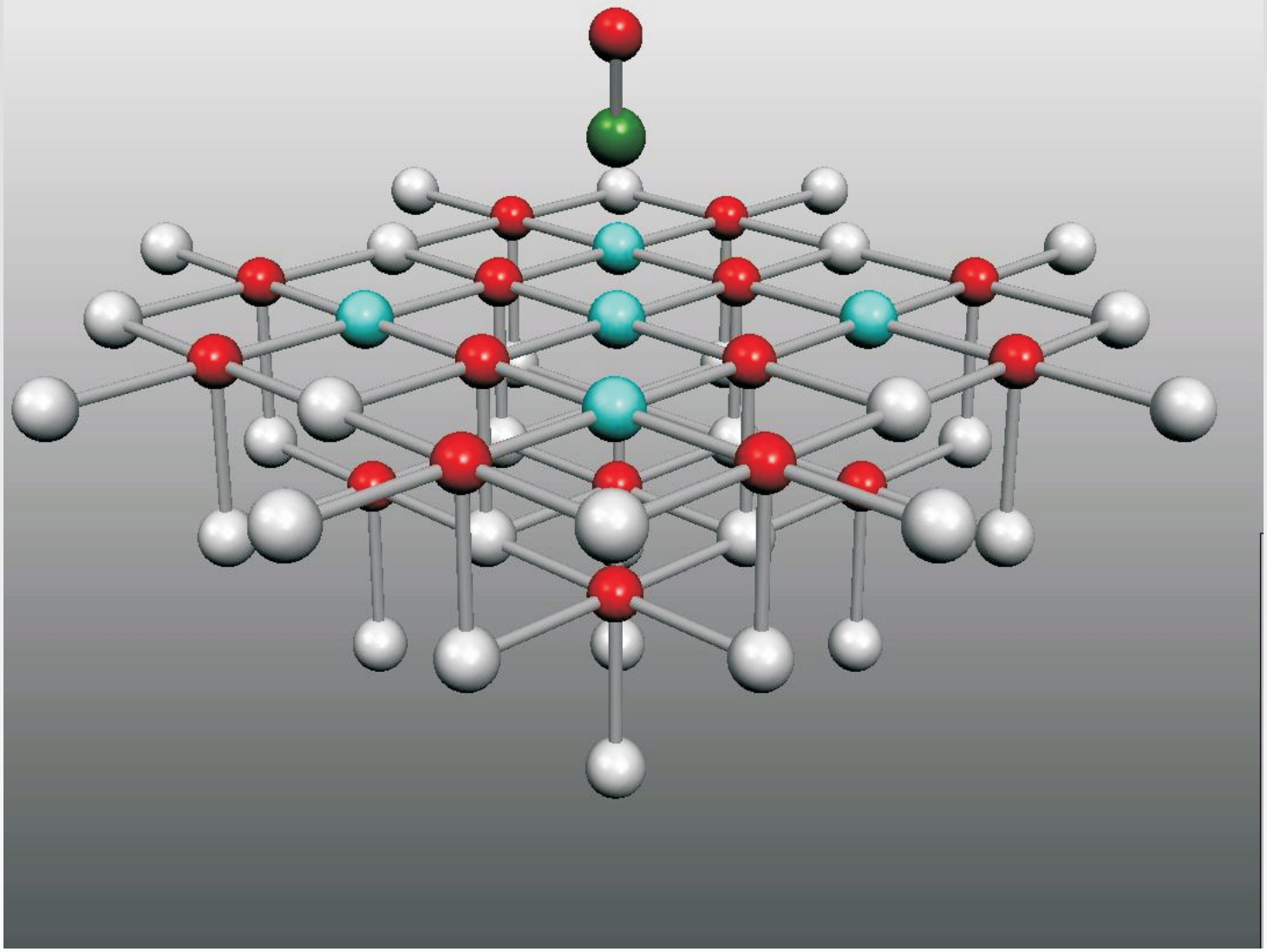
Cluster Models reliable for subtrates with localized electronic structure

~~DFT~~

Photodesorption: NO/NiO(100)

Cluster Models

$Ni_5O_{17}Mg_{33}^{42+}$/point charge field (not shown)



<u>Convergence studies</u>

- cluster size
- degrees of freedom
- basis set
- active space
- correlation model

systematic hierarchy
(CASSCF, CASPT-2
CCSD, CCSD(T))

for

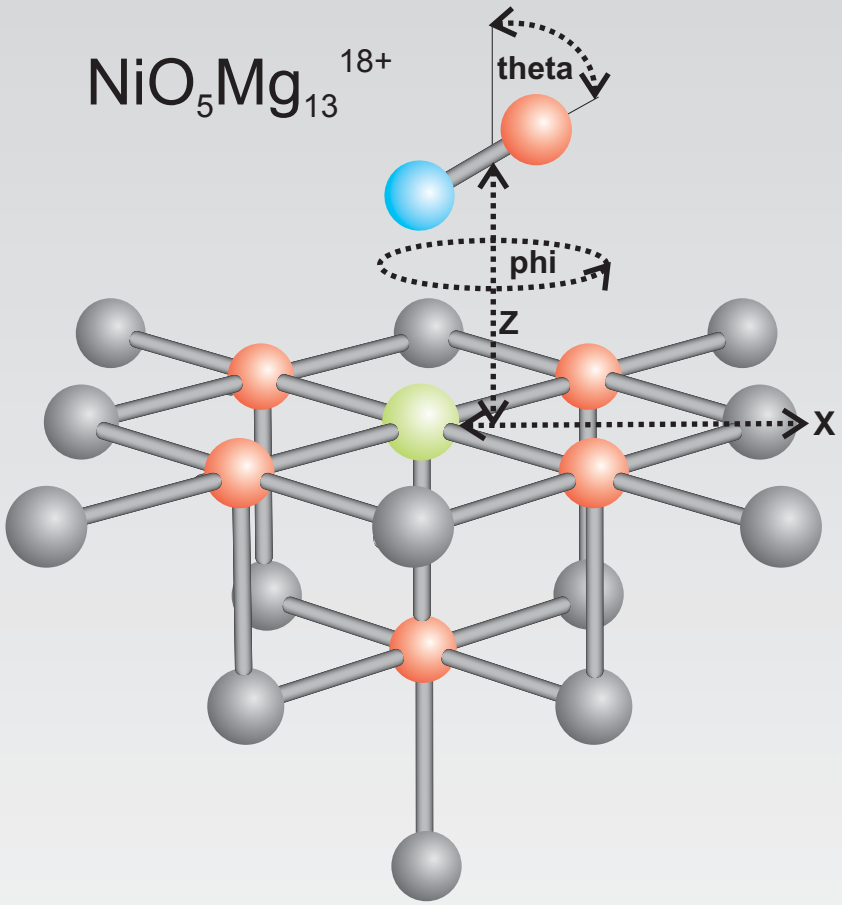
ground state

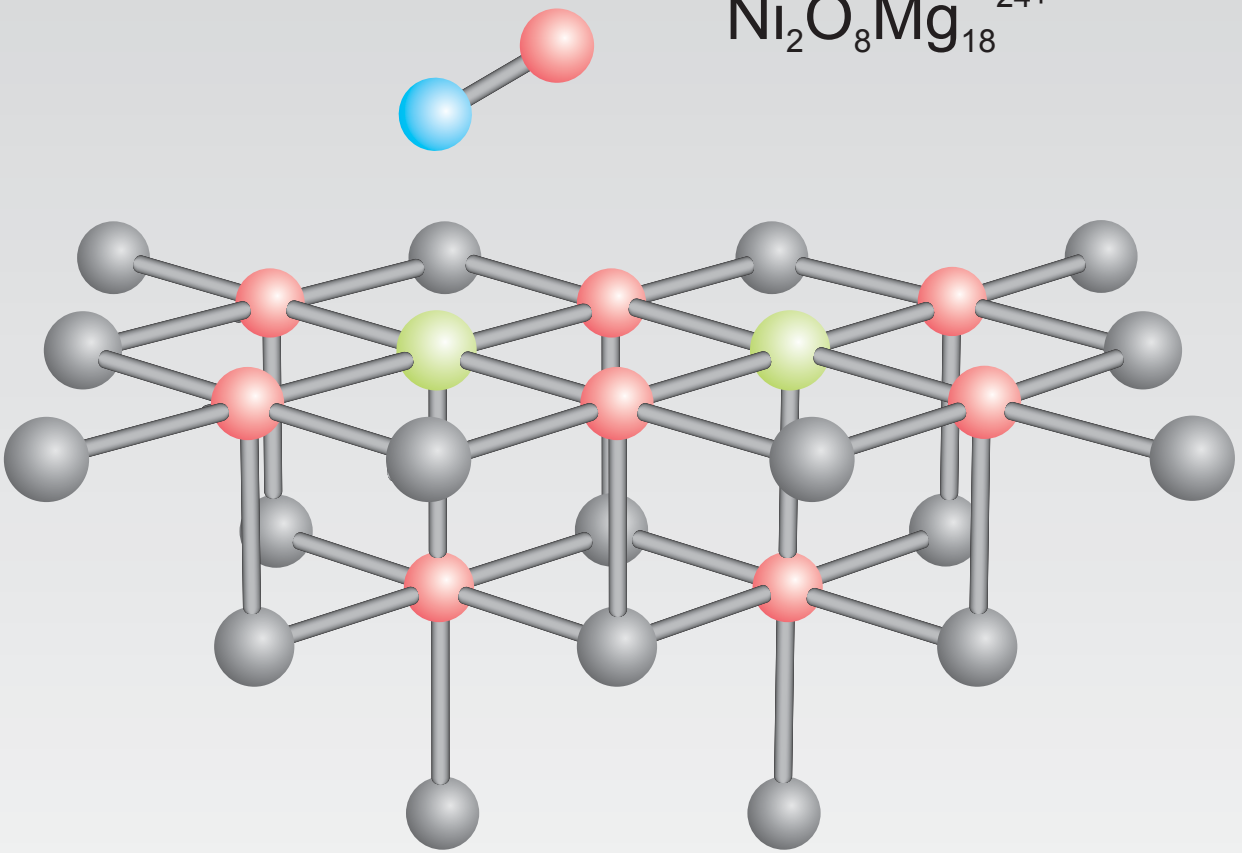
and

excited states

Photodesorption: NO/NiO(100)

Cluster Models





Ni O Mg N

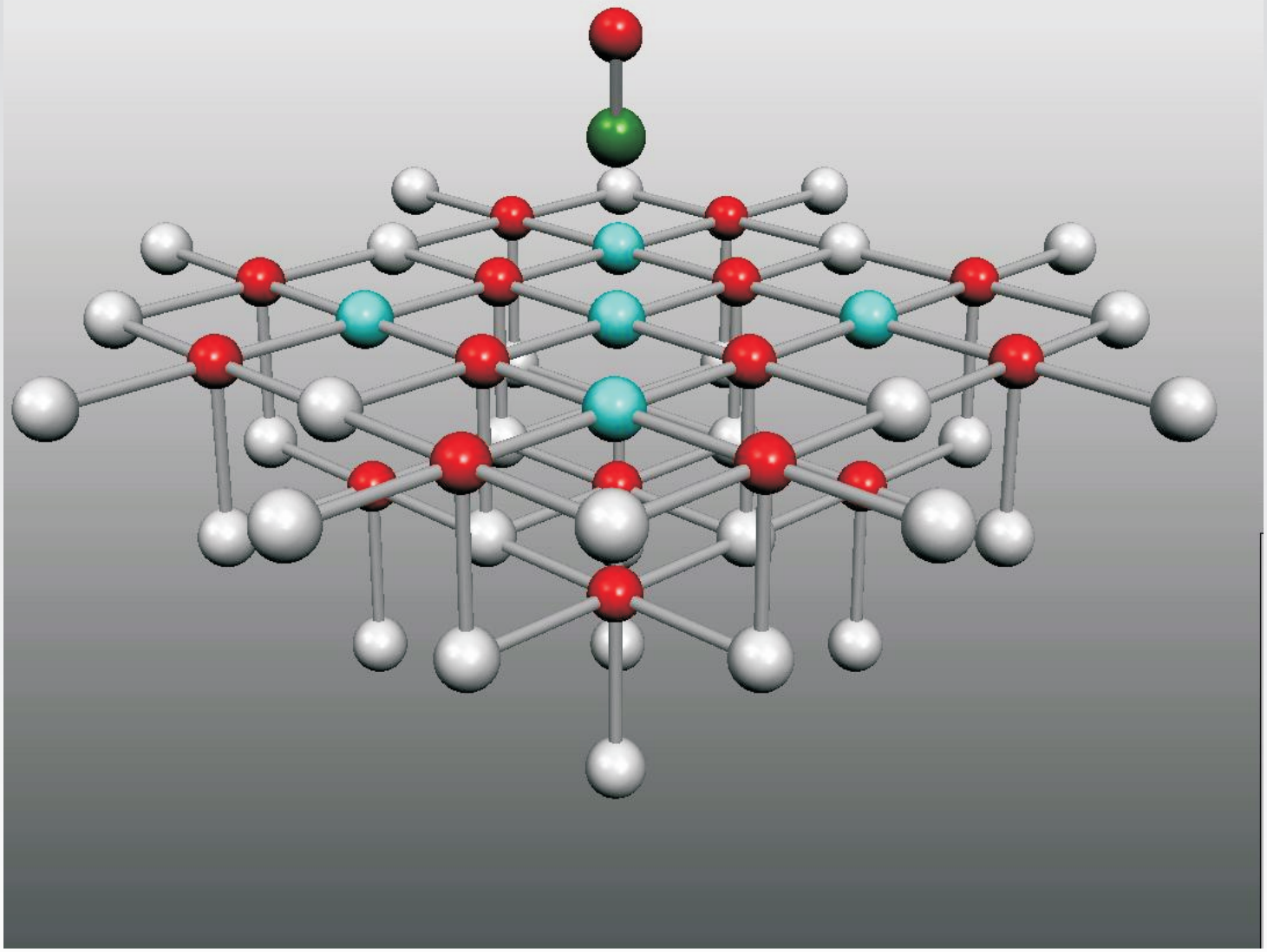
Point charge field not shown

Ground state: CASSCF/CASPT-2
Excited state: CASSCF/CI

Photodesorption: NO/NiO(100)

Cluster Models

$Ni_5O_{17}Mg_{33}^{42+}$/point charge field (not shown)



<u>Convergence studies</u>

- cluster size
- degrees of freedom
- basis set
- active space
- correlation model

systematic hierarchy
(CASSCF, CASPT-2
CCSD, CCSD(T))

for

ground state

and

excited states

NO/NiO(100)

Adsorption Energy

Cluster Model	Adsorption Energy/eV	
	CASSCF(2n+1,2n+1)	CASPT2
NO-$(NiO_5Mg_{13})^{18+}$/PCF	0.46 (0.37)	–0.34 (–0.70)
NO-$(Ni_2O_8Mg_{18})^{24+}$/PCF	0.46 (0.37)	–0.38 (–0.74)
NO-$(Ni_3O_{11}Mg_{23})^{30+}$/PCF	0.46 (0.37)	–0.41 (–0.79)
NO-$(Ni_5O_{17}Mg_{33})^{42+}$/PCF	0.46 (0.37)	–0.46 (–0.87)
experiment		–0.57

Results obtained with (smaller) basis set 1
Values without BSSE correction are in parentheses

NO/NiO(100)

Adsorption Energy

Cluster Model	Adsorption Energy/eV CASSCF(2n+1,2n+1)	CASPT2
NO-$(NiO_5Mg_{13})^{18+}$/PCF	0.46 (0.37)	–0.34 (–0.70)
NO-$(Ni_2O_8Mg_{18})^{24+}$/PCF	0.46 (0.37)	–0.38 (–0.74)
NO-$(Ni_3O_{11}Mg_{23})^{30+}$/PCF	0.46 (0.37)	–0.41 (–0.79)
NO-$(Ni_5O_{17}Mg_{33})^{42+}$/PCF	0.46 (0.37)	–0.46 (–0.87)
experiment		–0.57

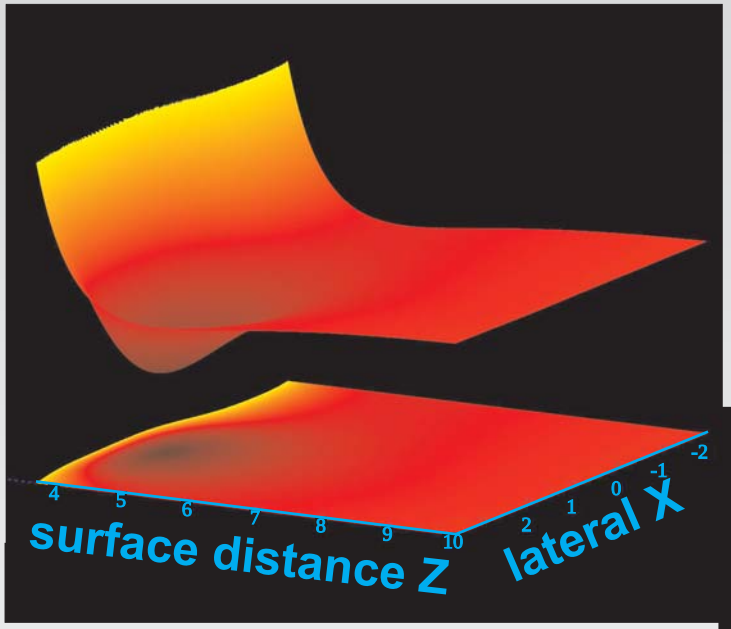
Results obtained with (smaller) basis set 1
Values without BSSE correction are in parentheses

One-particle basis error (see above): -0.07 eV
Zero point energy correction: +0.03 eV

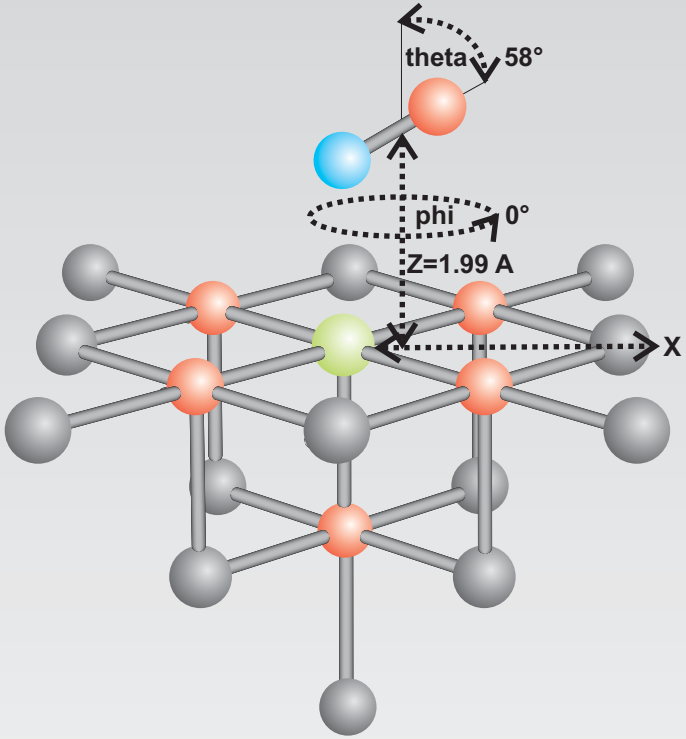
Best estimate of adsorption energy: -0.46 eV -0.07 eV +0.03 eV = -0.50 eV

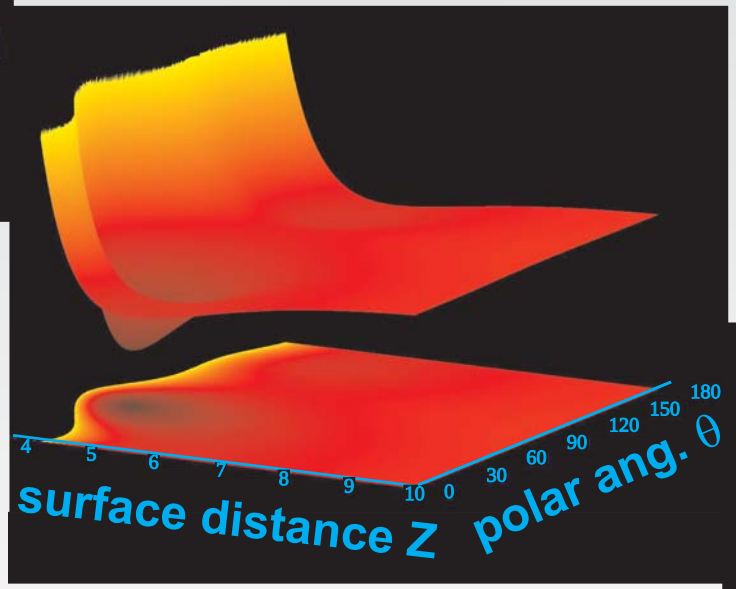
Photodesorption: NO/NiO(100)

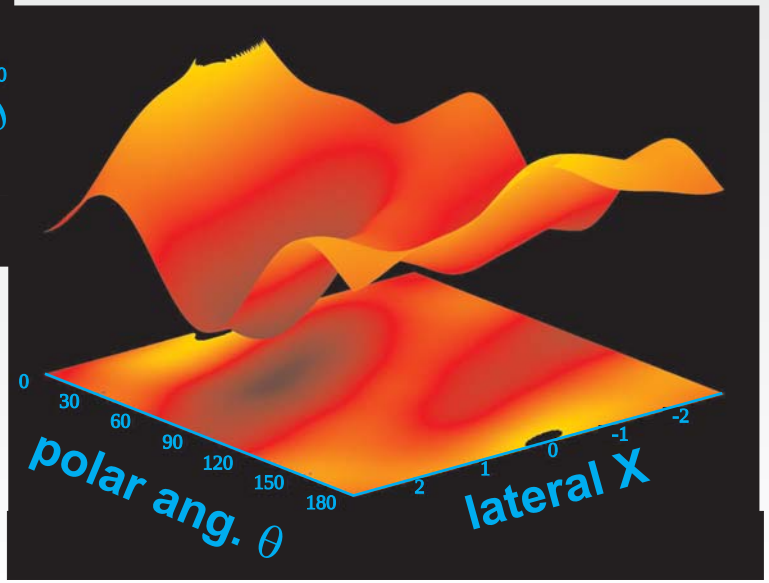
Ground state



CASSCF
CASPT-2

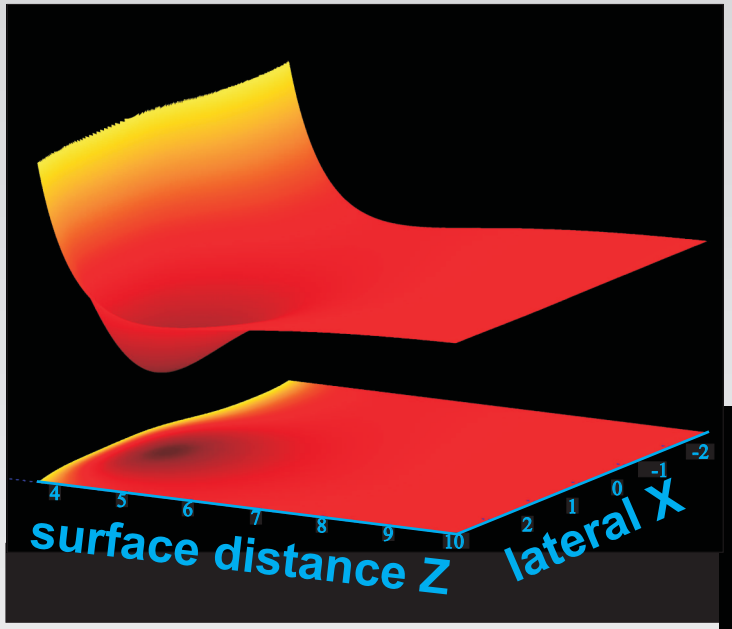




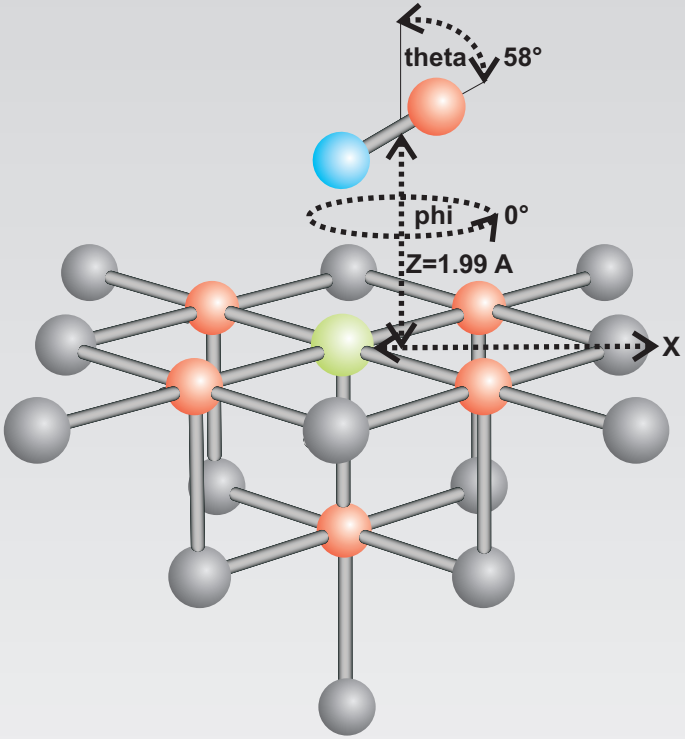


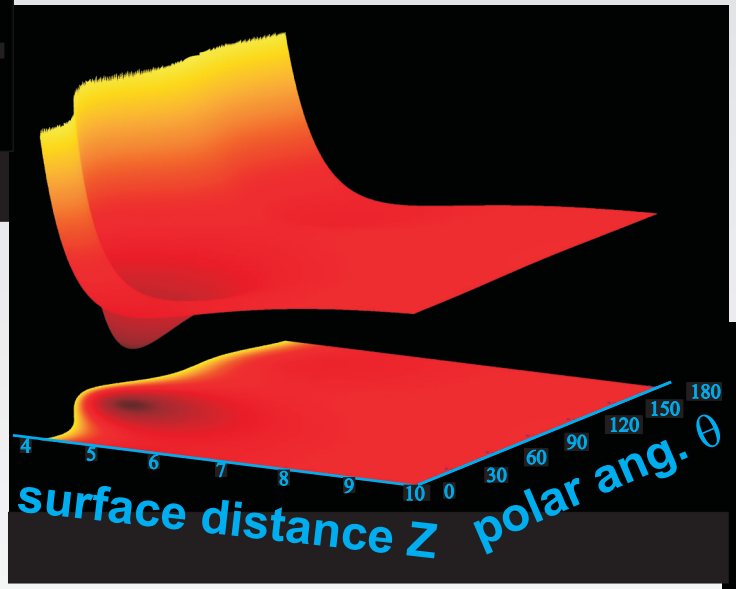
Photodesorption: NO/NiO(100)

Ground state



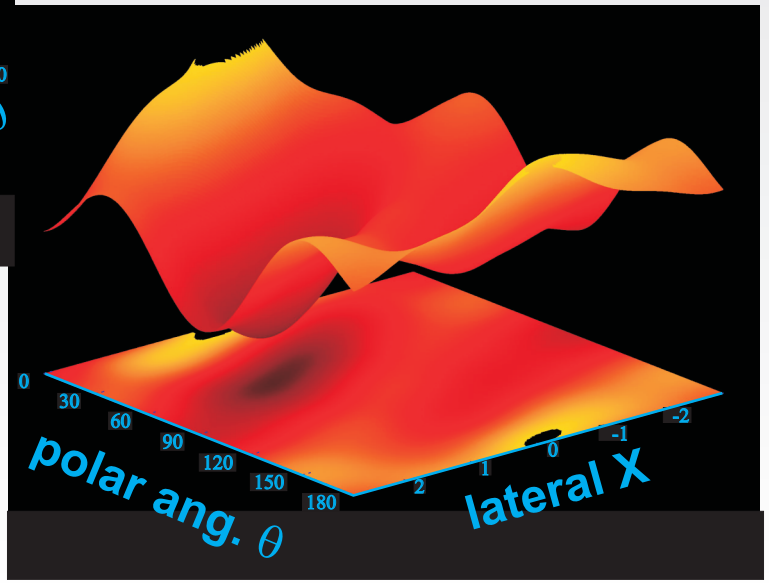
CASSCF
CASPT-2





PES global minimum:
Z=1.99 Å
theta=59°
Eads=0.50 eV

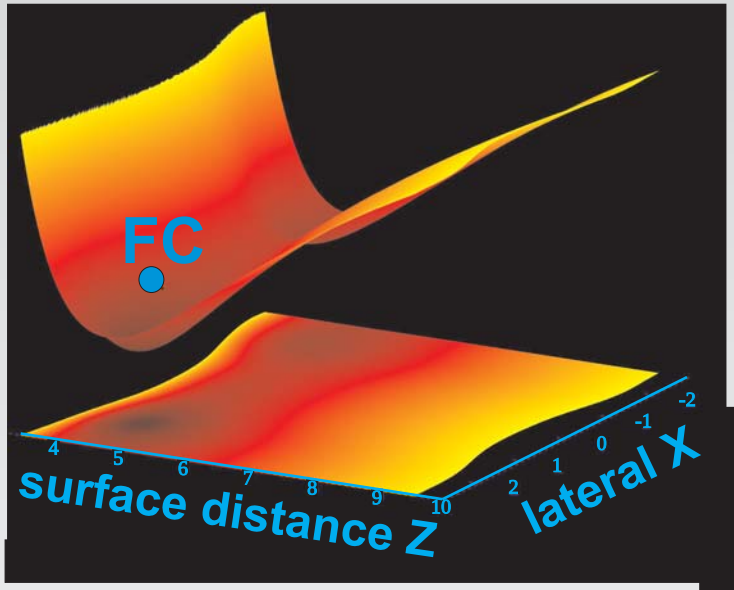
Experiment [1,2]:
Z=1.88 A
theta=61°
Eads=0.57 eV



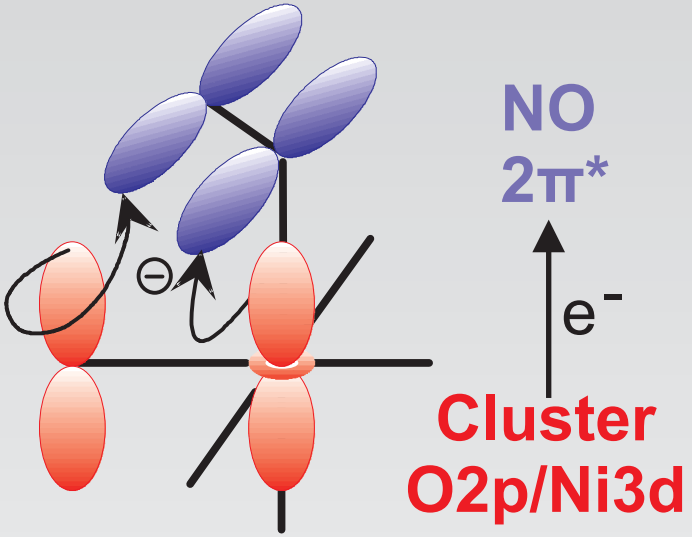
[1] R. Linday et al,
Surf. Sci. **425** L401 (1999)
[2] R. Wichtendahl et al.
Surf. Sci. **423**, 90 (1999)

Photodesorption: NO/NiO(100)

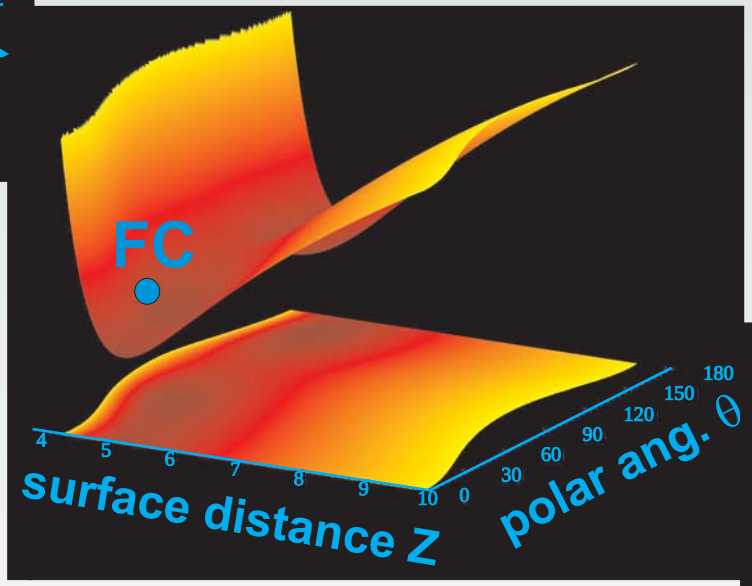
Excited state

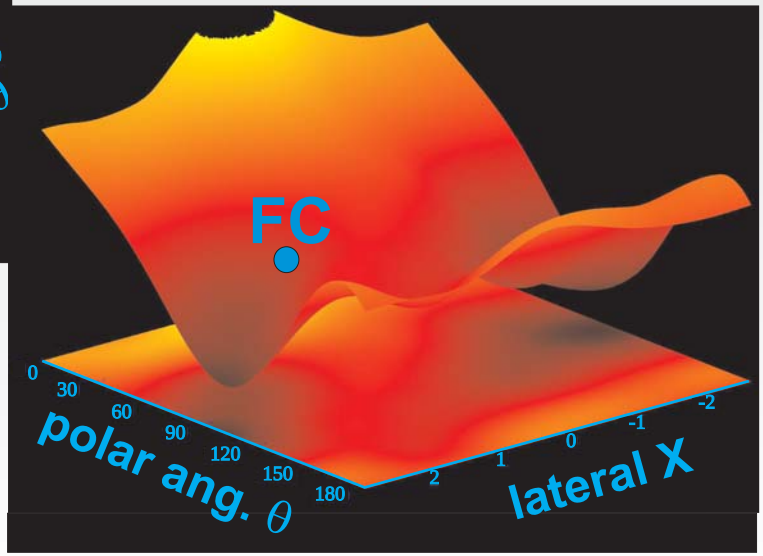


CASSCF/CI



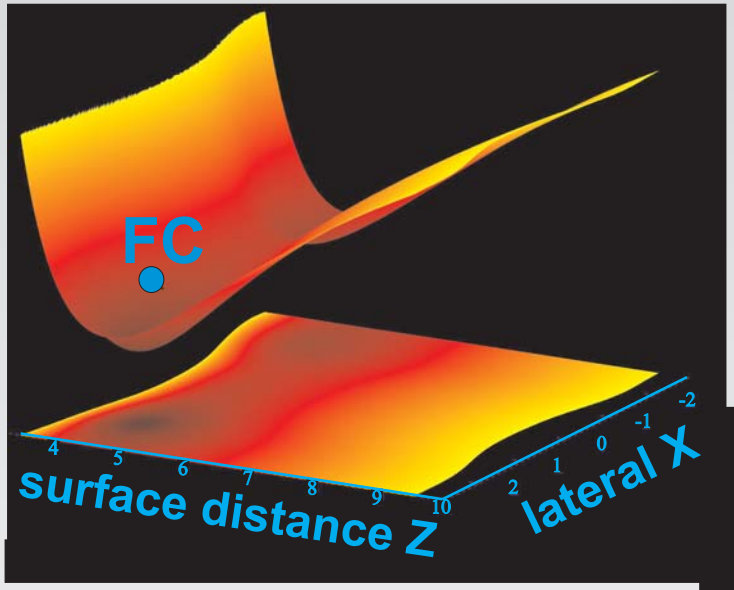
NO^--like intermediate



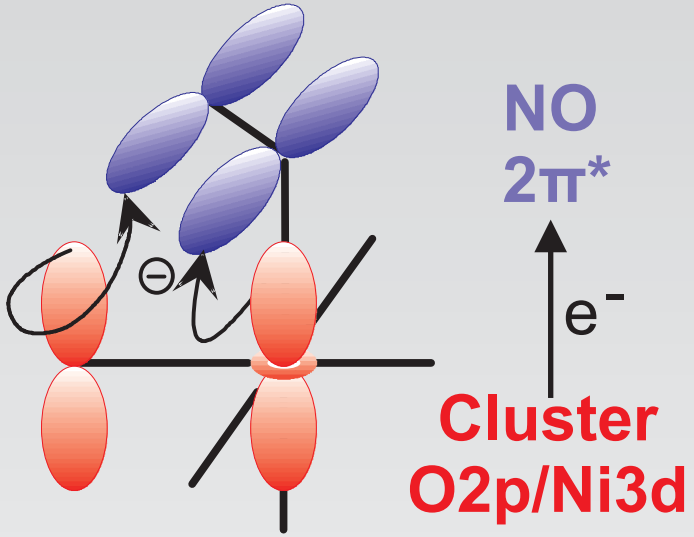


Photodesorption: NO/NiO(100)

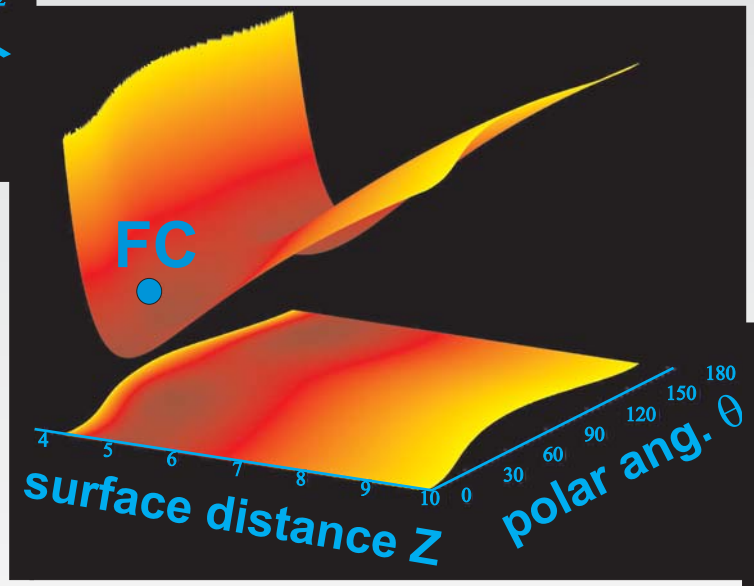
Excited state

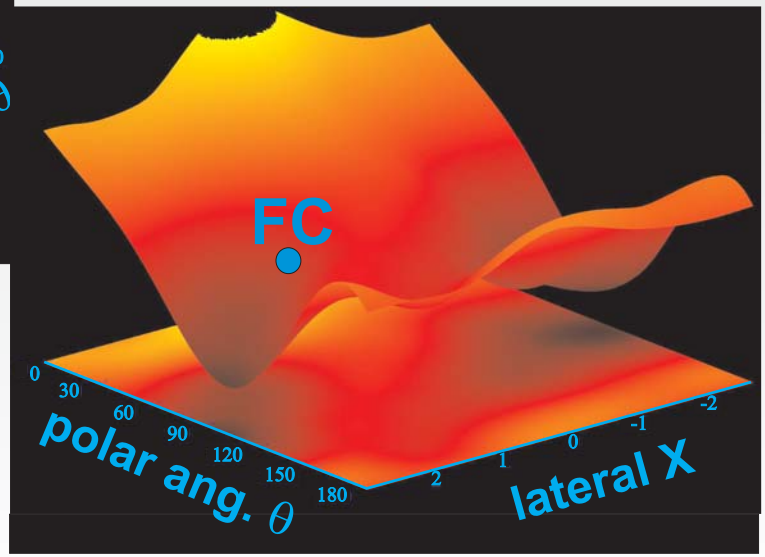


CASSCF/CI



NO^--like intermediate

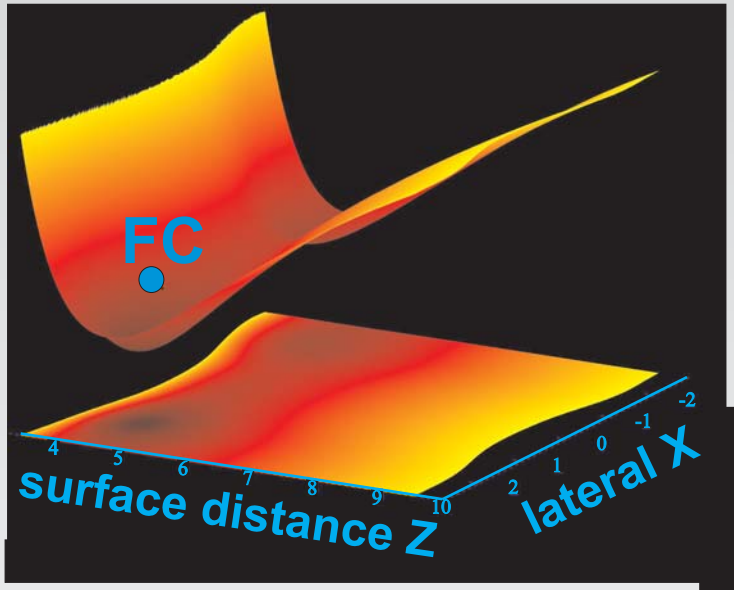




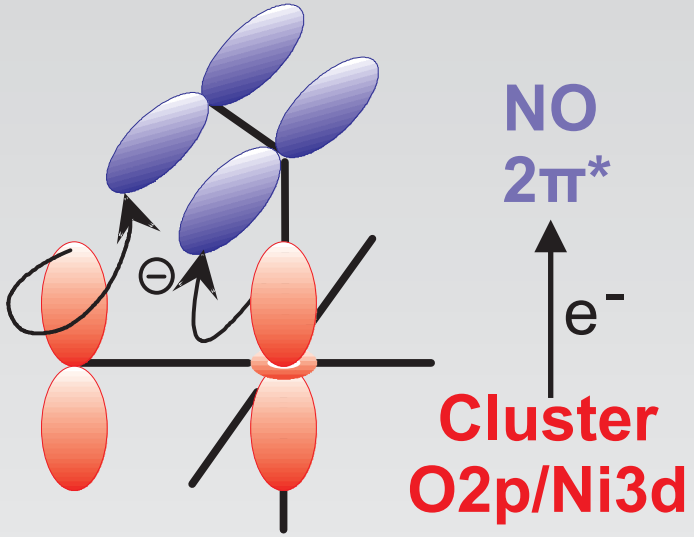
- Electrostatic forces dominate topology
- strong coupling of Z, X, and Θ

Photodesorption: NO/NiO(100)

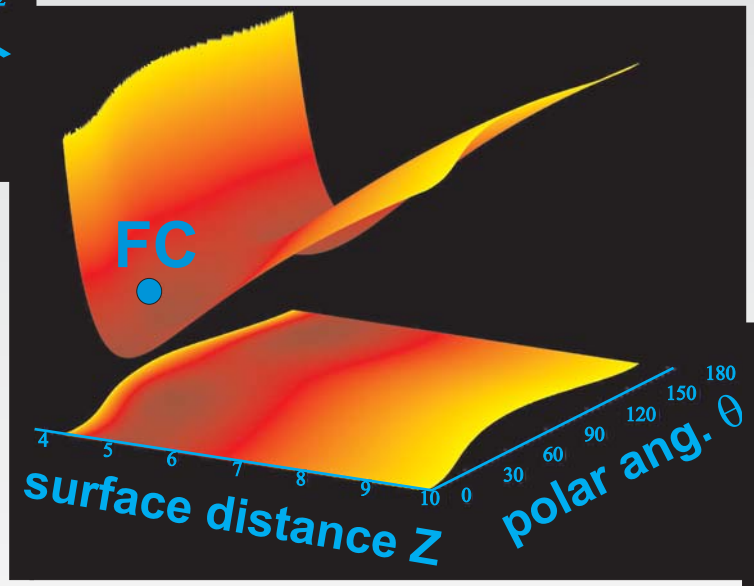
Excited state



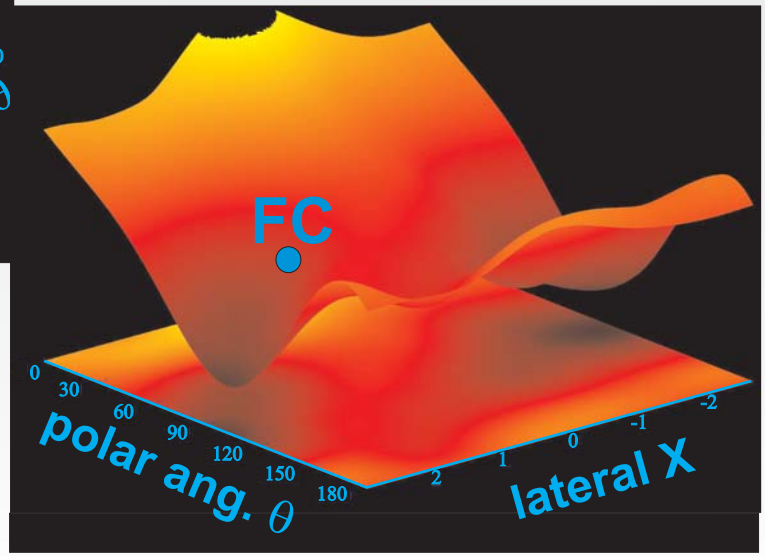
CASSCF/CI



NO^--like intermediate



- Electrostatic forces dominate topology
- strong coupling of Z, X, and Θ

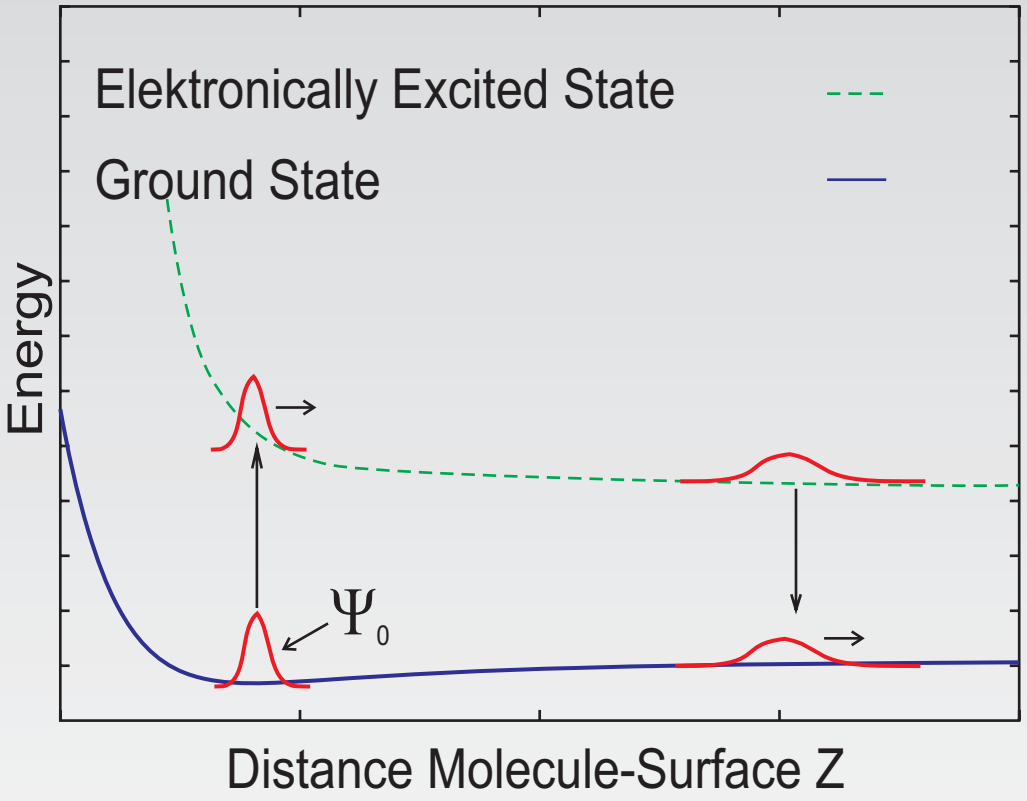


Ab initio potential energy surfaces: prerequisite for subsequent *quantum wave packet dynamics*

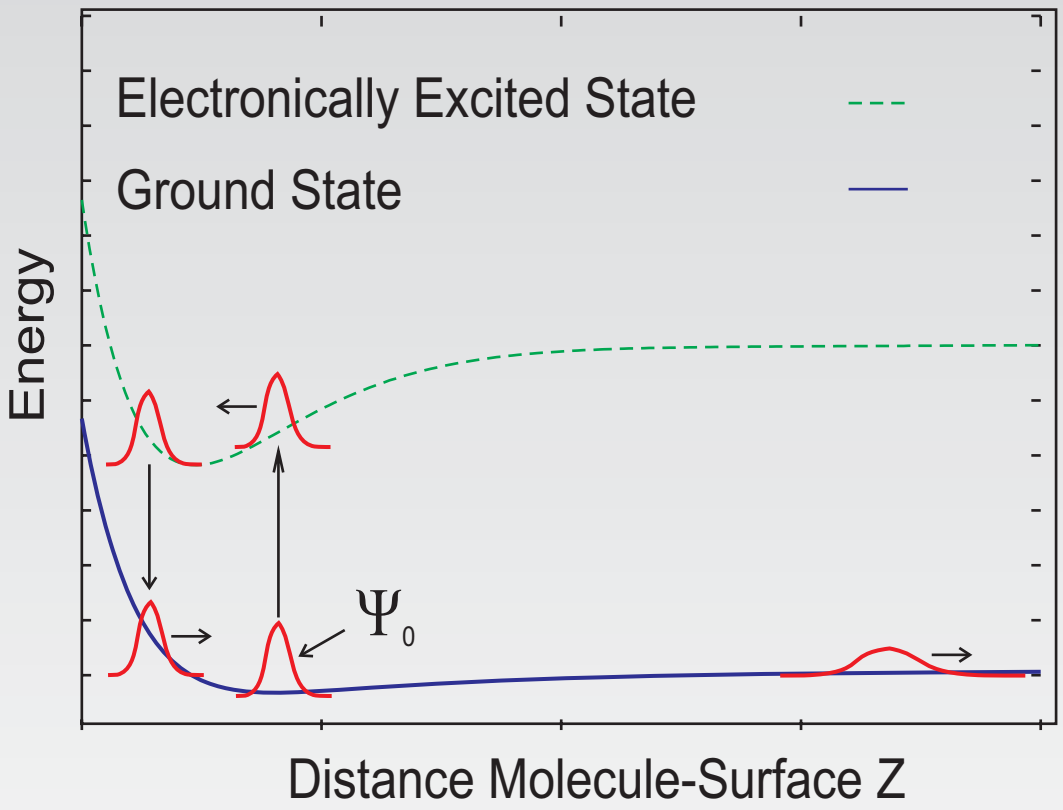
Quantum Dynamics

Desorption Mechanism

MGR Mechanism[9,10]



Antoniewicz Mechanism[8]



[8] P. R. Antoniewicz *Phys. Rev. Lett. B* **21**, 3811 (1980).
[9] D. Menzel und R. Gomer, *J. Chem. Phys.* **41**, 3311 (1964).
[10] P. A. Redhead, *Can. J. Phys.* **42**, 886 (1964).

Time dependent Schrödinger equation:

$$\hat{H}(q,t)\Psi(q,t) = i\hbar \frac{\partial}{\partial t}\Psi(q,t)$$

$$\Psi(q,t) = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\Psi(q,t=0)$$

→ Time evolution of nuclear wave function on potential surface

Quantum Dynamics

Wave Packet Calculations

Time dependent Schrödinger equation:

$$\hat{H}(q,t)\Psi(q,t) = i\hbar \frac{\partial}{\partial t}\Psi(q,t)$$

$$\Psi(q,t) = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\Psi(q,t=0)$$

→ Time evolution of nuclear wave function on potential surface

Hamiltonian

$$\hat{H}(Z,X,\theta,\phi) = -\frac{1}{2M}\frac{\partial^2}{\partial Z^2} - \frac{1}{2M}\frac{\partial^2}{\partial X^2}$$

$$-\frac{1}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$+\hat{V}(Z,X,\theta,\phi)$$

← Ab initio Potential Surface

Quantum Dynamics

Wave Packet Calculations

Time dependent Schrödinger equation:

$$\hat{H}(q,t)\Psi(q,t) = i\hbar\frac{\partial}{\partial t}\Psi(q,t)$$

$$\Psi(q,t) = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\Psi(q,t=0)$$

→ Time evolution of nuclear wave function on potential surface

Hamiltonian

$$\hat{H}(Z,X,\theta,\phi) = -\frac{1}{2M}\frac{\partial^2}{\partial Z^2} - \frac{1}{2M}\frac{\partial^2}{\partial X^2}$$

$$-\frac{1}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$+\hat{V}(Z,X,\theta,\phi)$$

← Ab initio Potential Surface

Stochastic Wave Packet Calculations:

Excitation-Deexcitation cycle (Jumping Wavepackets):

$$\Psi(t;t_n) = e^{-i\hat{H}_{gr}(t-t_n)} \cdot e^{-i\hat{H}_{ex}t_n} \cdot \Psi(0)$$

- FC-Excitation without explicit treatment of laser pulse

Quantum Dynamics

Wave Packet Calculations

Time dependent Schrödinger equation:

$$\hat{H}(q,t)\Psi(q,t) = i\hbar\frac{\partial}{\partial t}\Psi(q,t)$$

$$\Psi(q,t) = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\Psi(q,t=0)$$

→ Time evolution of nuclear wave function on potential surface

Hamiltonian

$$\hat{H}(Z,X,\theta,\phi) = -\frac{1}{2M}\frac{\partial^2}{\partial Z^2} - \frac{1}{2M}\frac{\partial^2}{\partial X^2}$$

$$-\frac{1}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$+\hat{V}(Z,X,\theta,\phi)$$

← Ab initio Potential Surface

Stochastic Wave Packet Calculations:

Excitation-Deexcitation cycle (Jumping Wavepackets):

$$\Psi(t;t_n) = e^{-i\hat{H}_{gr}(t-t_n)} \cdot e^{-i\hat{H}_{ex}t_n} \cdot \Psi(0)$$

- FC-Excitation without explicit treatment of laser pulse

Asymptotic Observables

$$A(t;t_n) = \left\langle \Psi(t;t_n)\middle|\hat{A}\middle|\Psi(t;t_n)\right\rangle$$

Quantum Dynamics

Wave Packet Calculations

Time dependent Schrödinger equation:

$$\hat{H}(q,t)\Psi(q,t) = i\hbar\frac{\partial}{\partial t}\Psi(q,t)$$

$$\Psi(q,t) = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\Psi(q,t=0)$$

→ Time evolution of nuclear wave function on potential surface

Hamiltonian

$$\hat{H}(Z,X,\theta,\phi) = -\frac{1}{2M}\frac{\partial^2}{\partial Z^2} - \frac{1}{2M}\frac{\partial^2}{\partial X^2}$$

$$-\frac{1}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$+\hat{V}(Z,X,\theta,\phi)$$ ← Ab initio Potential Surface

Stochastic Wave Packet Calculations:

Excitation-Deexcitation cycle (Jumping Wavepackets):

$$\Psi(t;t_n) = e^{-i\hat{H}_{gr}(t-t_n)} \cdot e^{-i\hat{H}_{ex}t_n} \cdot \Psi(0)$$

- FC-Excitation without explicit treatment of laser pulse

Asymptotic Observables

$$A(t;t_n) = \left\langle \Psi(t;t_n)\middle|\hat{A}\middle|\Psi(t;t_n)\right\rangle$$

Lifetime averaging: J.W. Gadzuk, Surf. Sci. 342, 345 (1995)

$$A(t;\tau) = \frac{\sum_{n=1}^{n_{max}} A(t;t_n)\exp\left(-\frac{t_n}{\tau}\right)}{\sum_{n=1}^{n_{max}} \exp\left(-\frac{t_n}{\tau}\right)}$$

- Exponential decay of excited state
- Equivalent scheme: density matrix propagation for open system

Parallelization

SGI Altix4700 HLRB II
Leibniz-Computing Centre
Munich

Parallelization

Parallelization

Supercomputer HLRB II (2007)

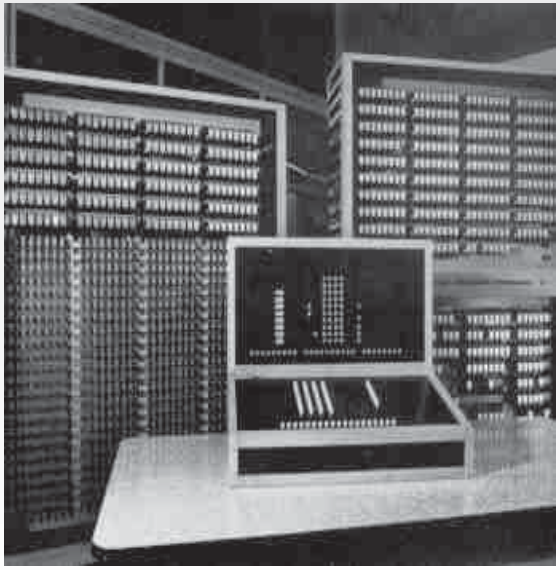
Processor clock: 1.6 GHz
Total number of cores: 9728
Total peak perf.: 62,3 TFlop/s
Total main memory: 39 TB
Total disk space: 600 TB
Total weight: 103 tons
Total electrical power: 1100 kVA

Parallelization

Supercomputer HLRB II (2007)

Processor clock: 1.6 GHz
Total number of cores: 9728
Total peak perf.: 62,3 TFlop/s
Total main memory: 39 TB
Total disk space: 600 TB
Total weight: 103 tons
Total electrical power: 1100 kVA

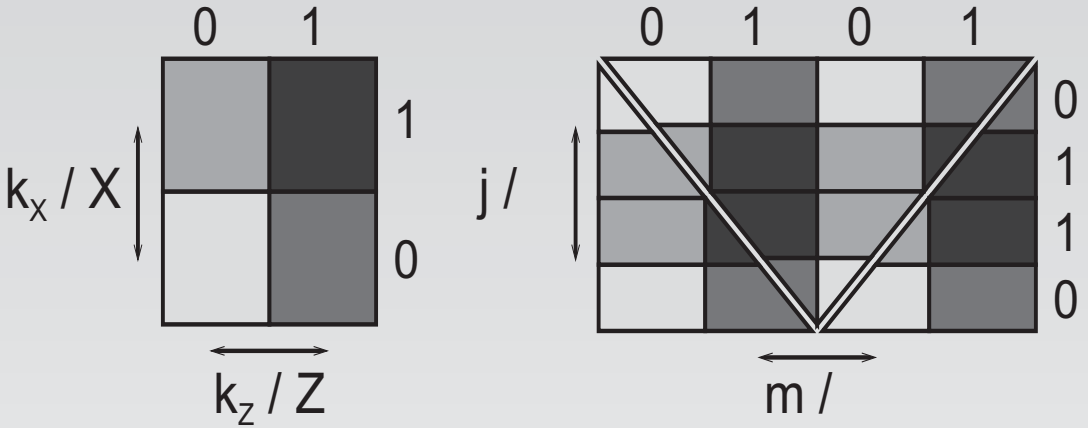
Factor: 10^{13}

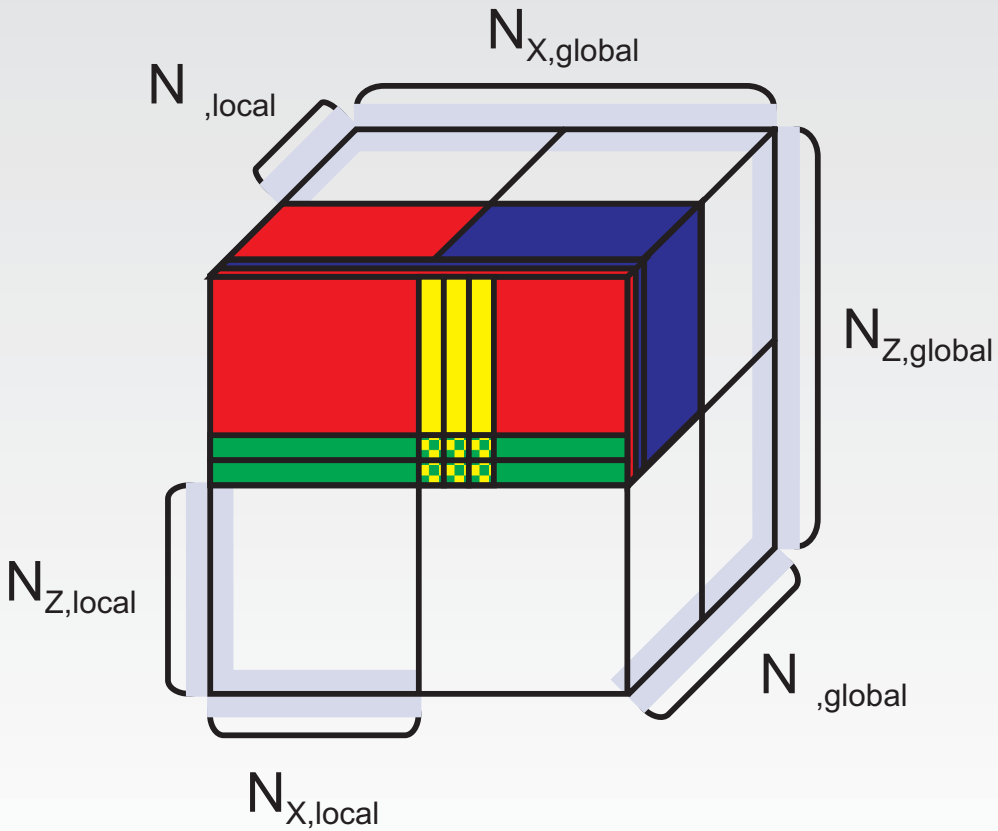


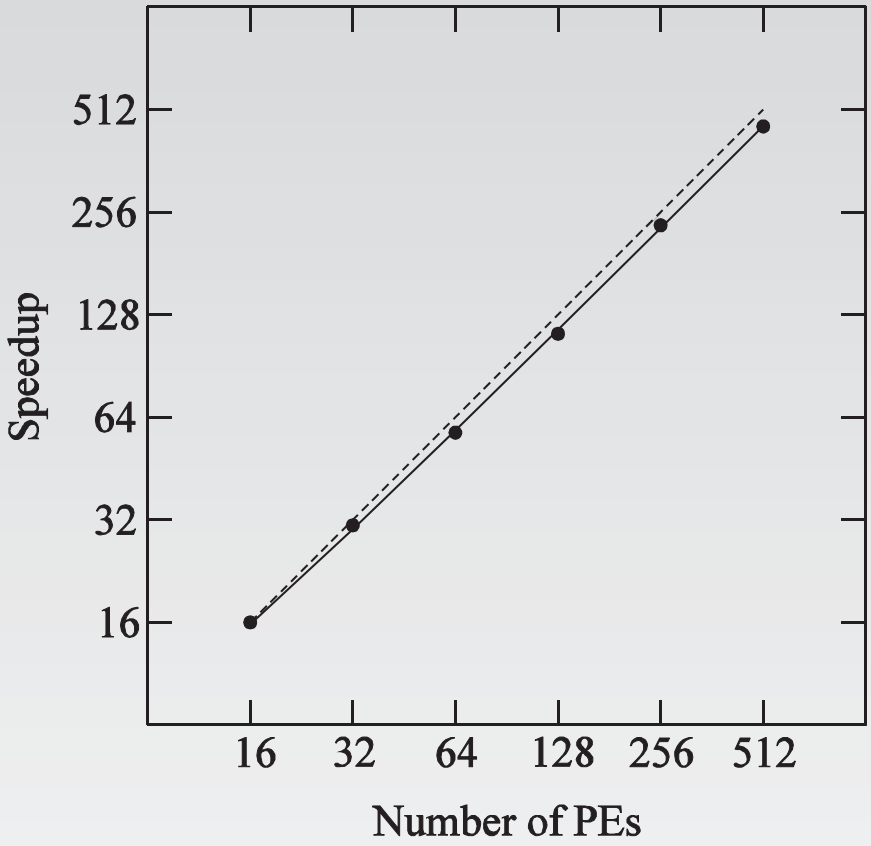
K. Zuse Z3 (1941)

Processor clock: 5,33 Hz
Total peak perf.: 3 Flop/s
Total main memory: 176 Byte

Speedup Analysis



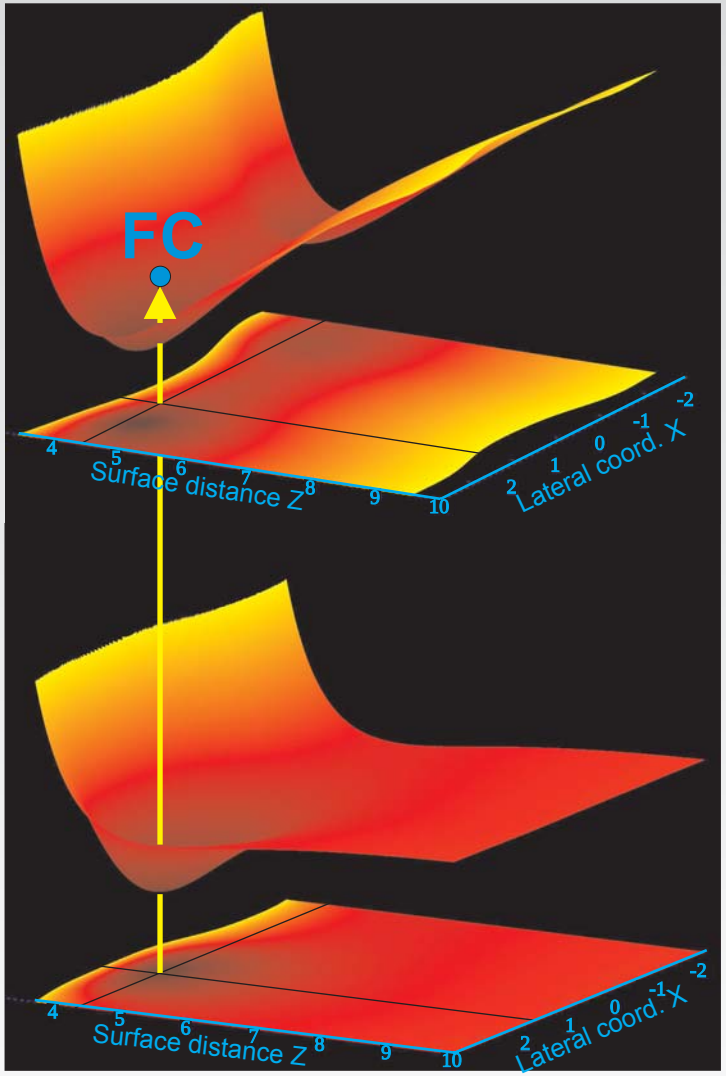


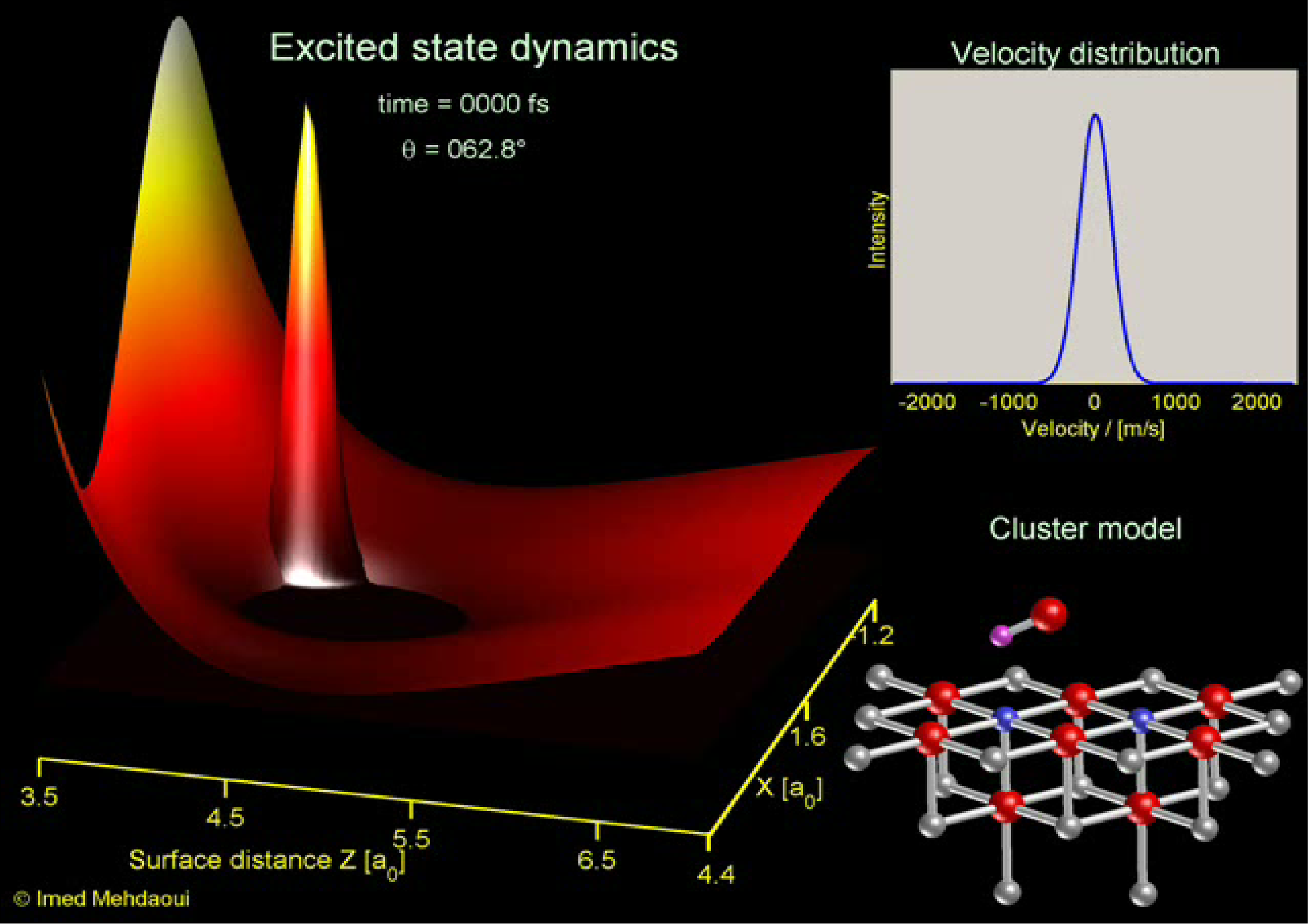


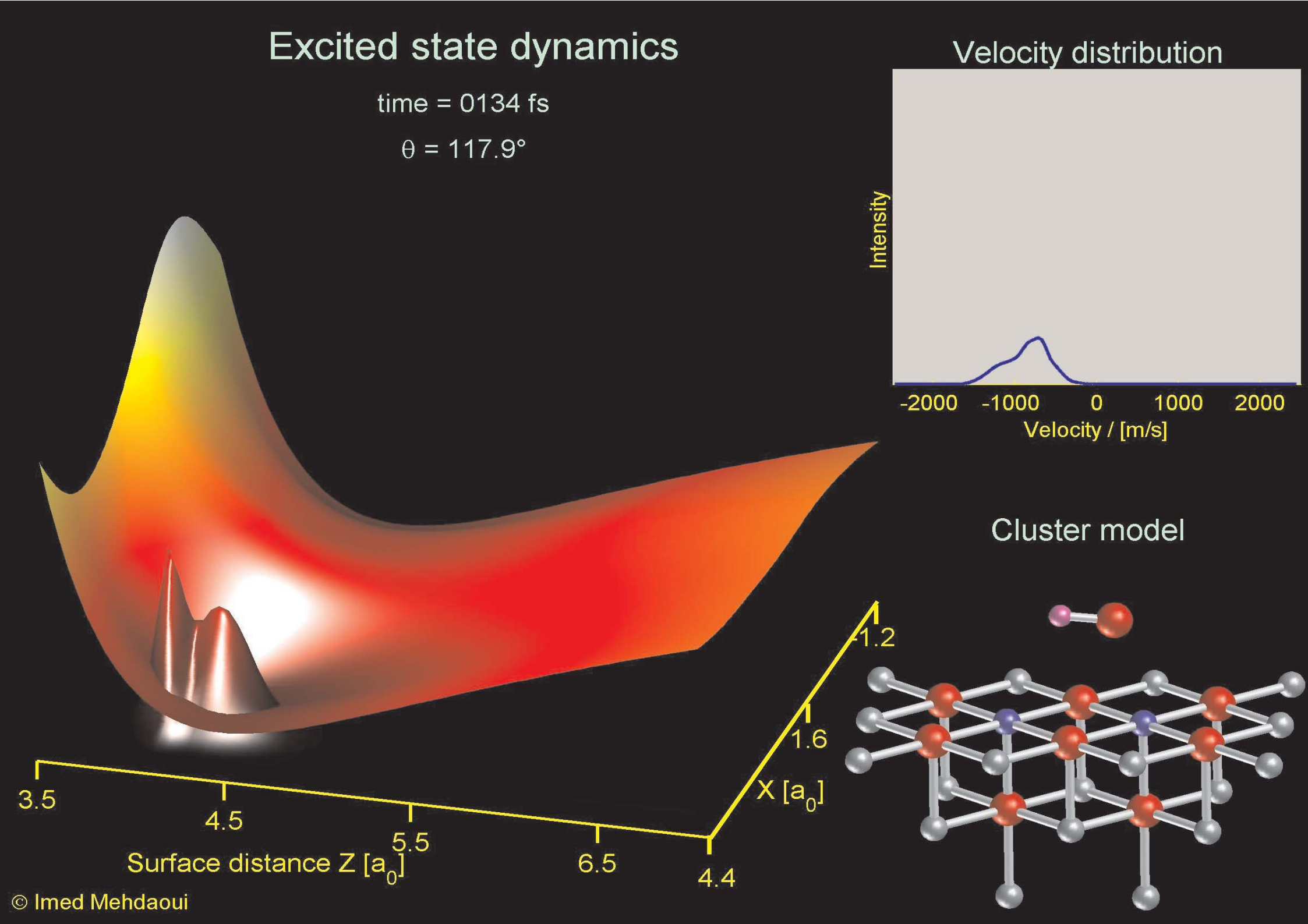
⇨ Study of 20 years on a 1 processor workstation takes two weeks on 512 processors (10^{10} DVR-basis functions)

Photodesorption: NO/NiO(100)

Excitation

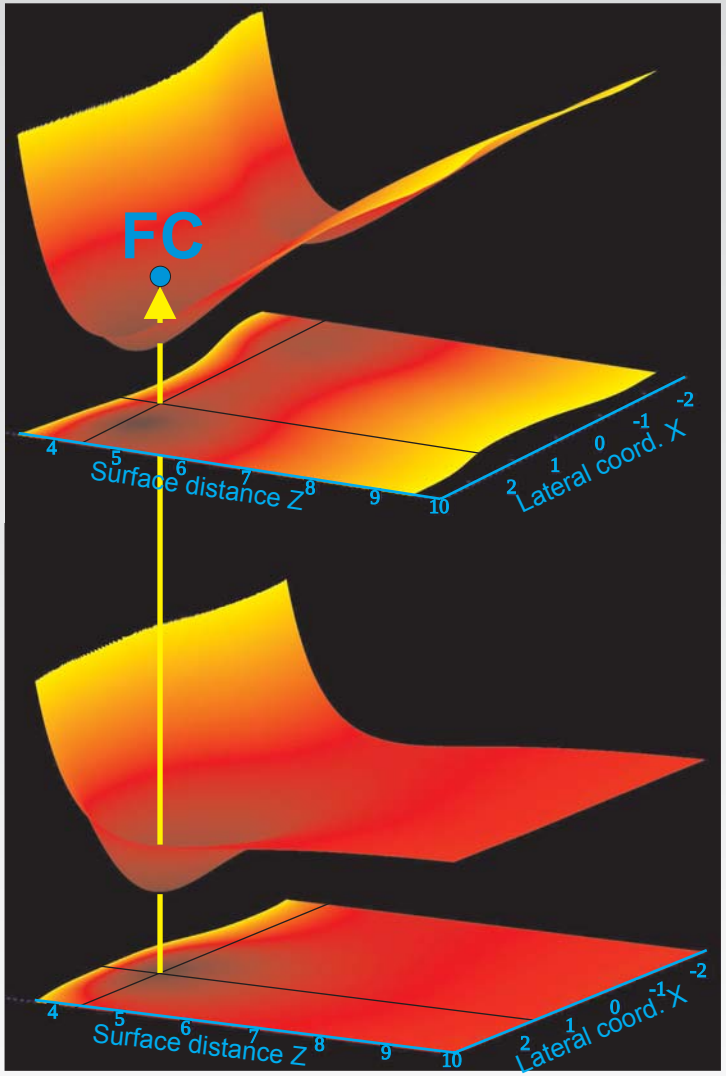



Excited state dynamics
time = 0000 fs
θ = 062.8°
Velocity distribution
Intensity
-2000
-1000
0
1000
2000
Velocity / [m/s]
Cluster model
1.2
1.6
X [a0]
3.5
4.5
5.5
6.5
4.4
Surface distance Z [a0]
© Imed Mehdaoui

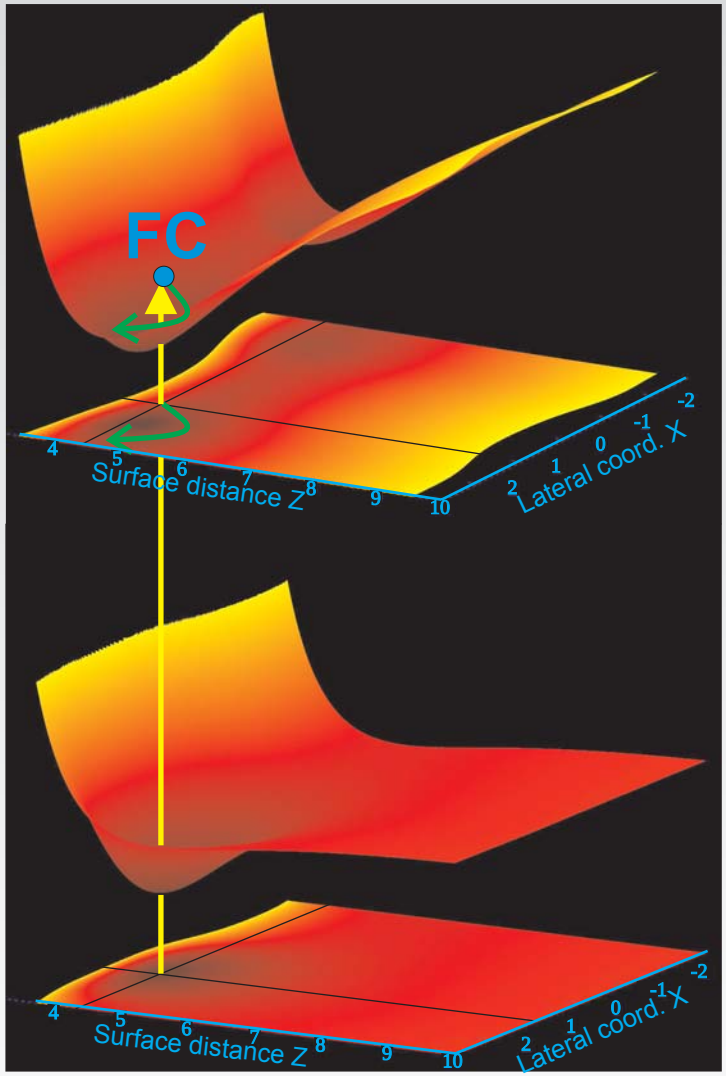

Excited state dynamics
time = 0134 fs
θ = 117.9°
Velocity distribution
Intensity
-2000
-1000
0
1000
2000
Velocity / [m/s]
Cluster model
3.5
4.5
5.5
6.5
4.4
Surface distance Z [a0]
1.2
1.6
X [a0]
© Imed Mehdaoui

Photodesorption: NO/NiO(100)

Excitation



Excited state propagation



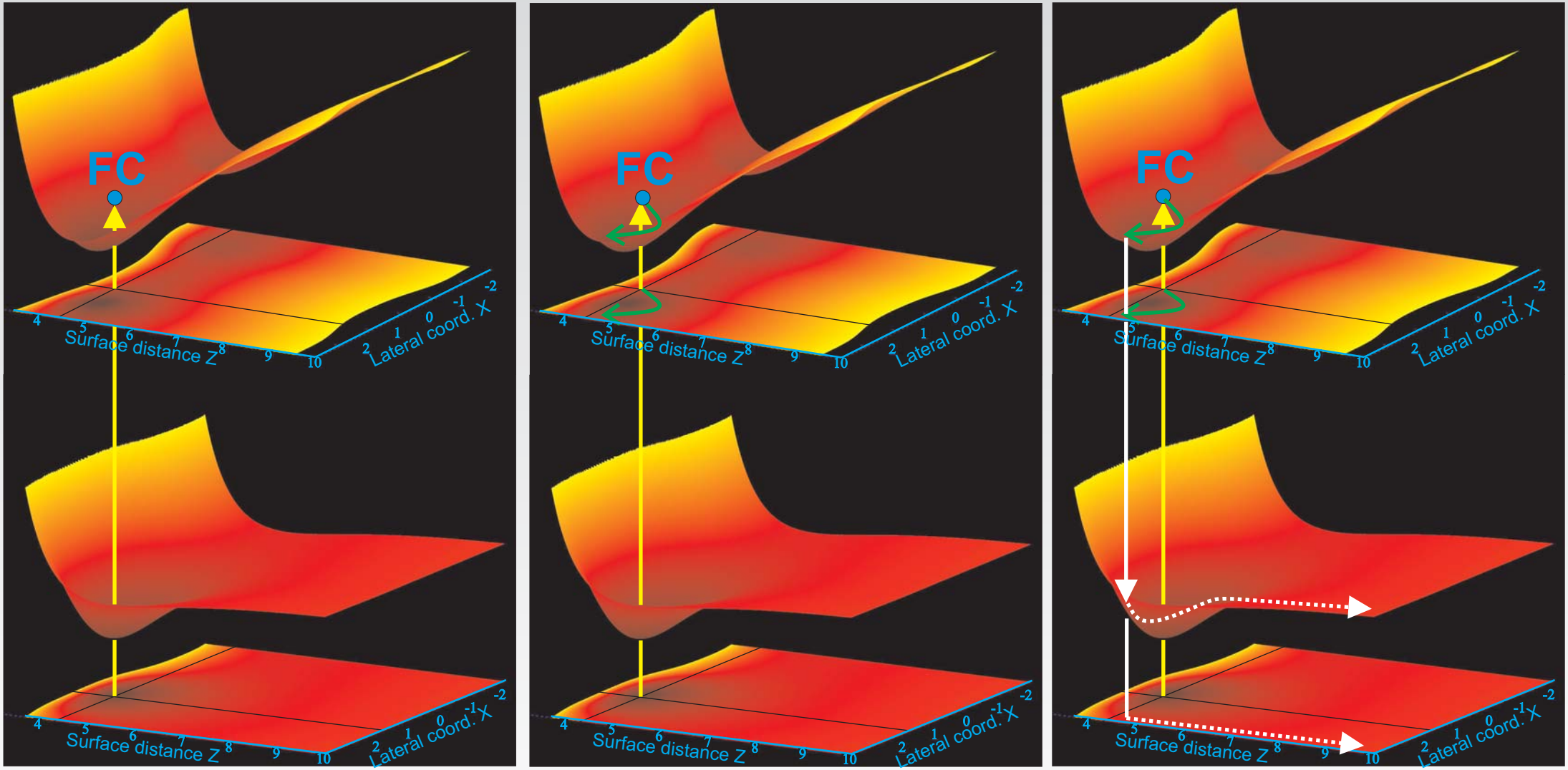
Photodesorption: NO/NiO(100)

Dynamics

Excitation

Excited state propagation

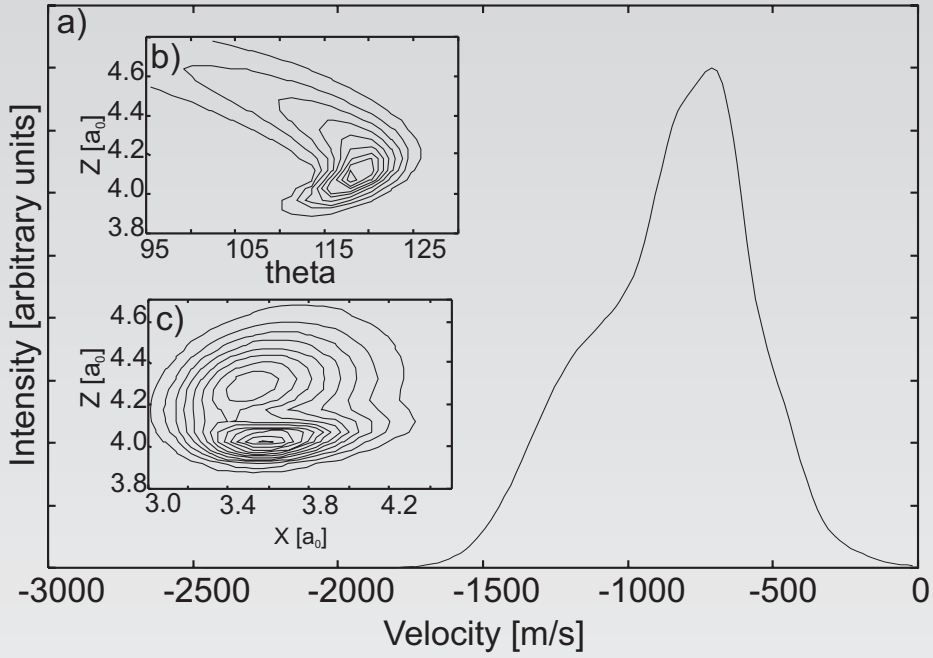
Relaxation and Ground state propagation

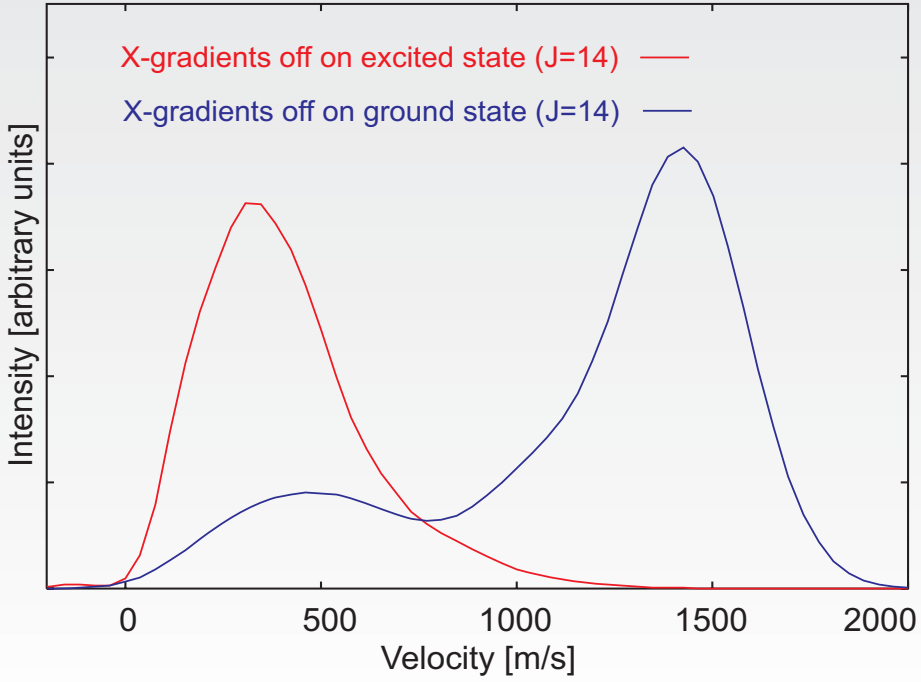


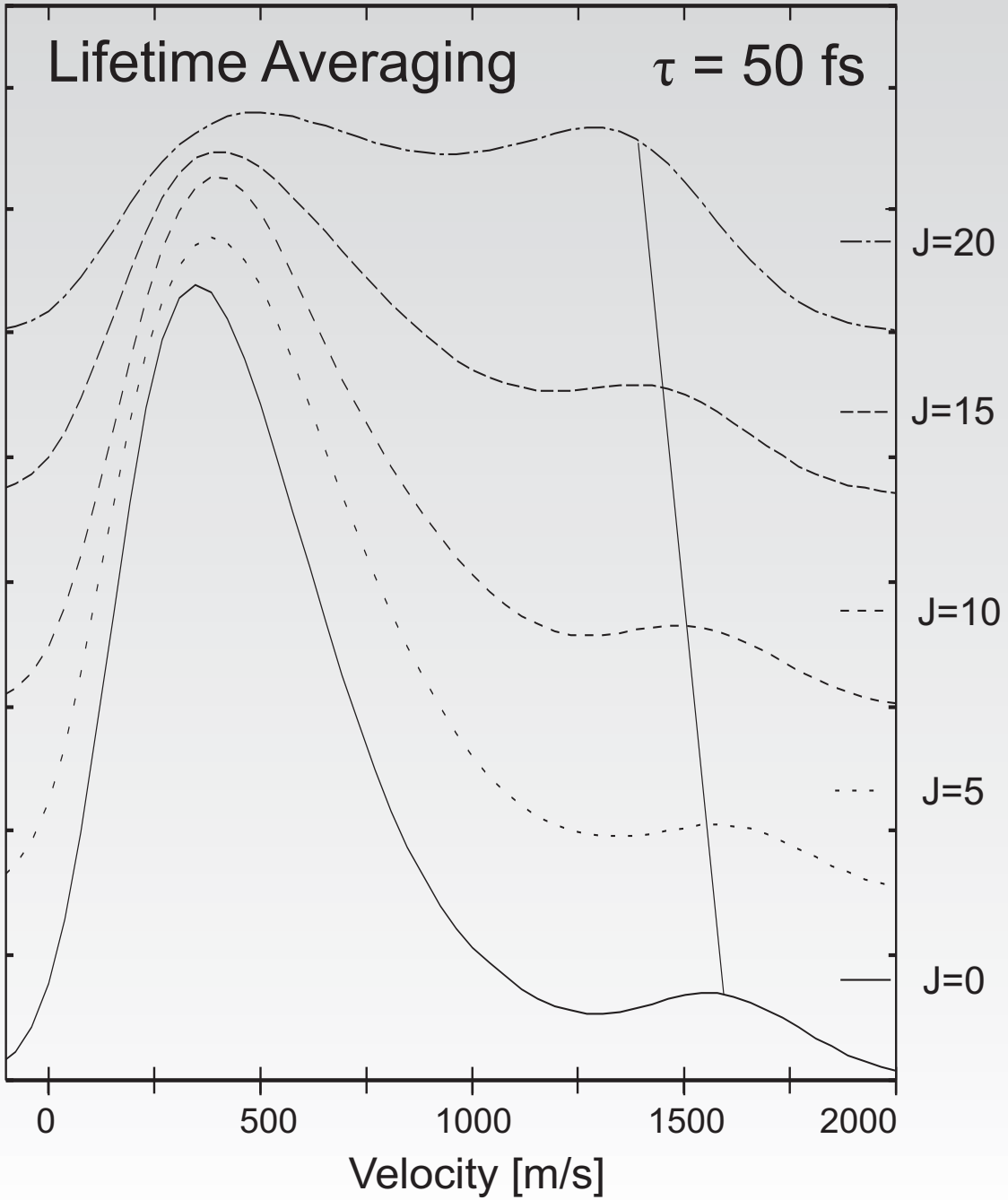
New desorption mechanism: Anti-Antoniewicz

Photodesorption: NO/NiO(100)

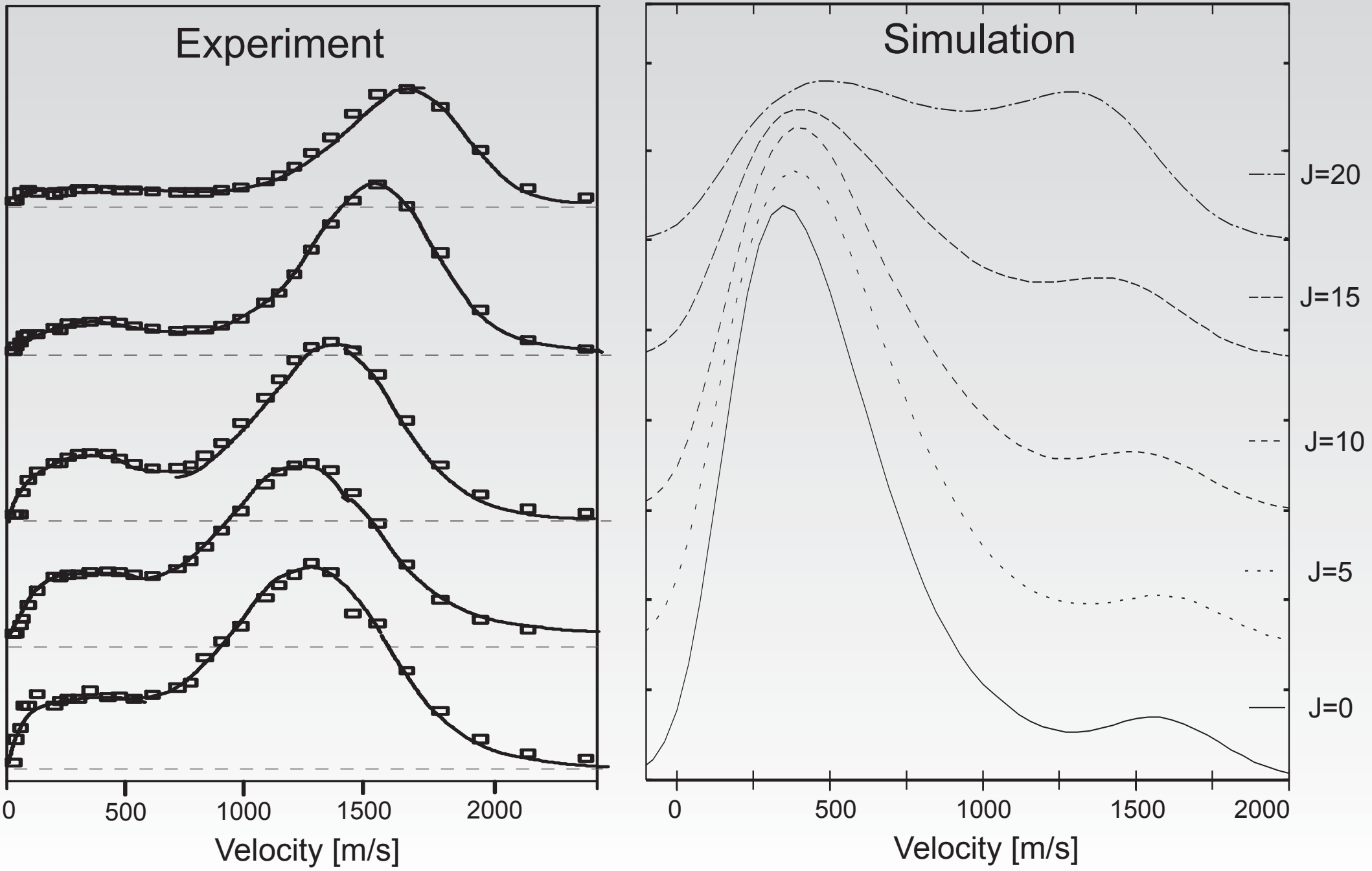
Results





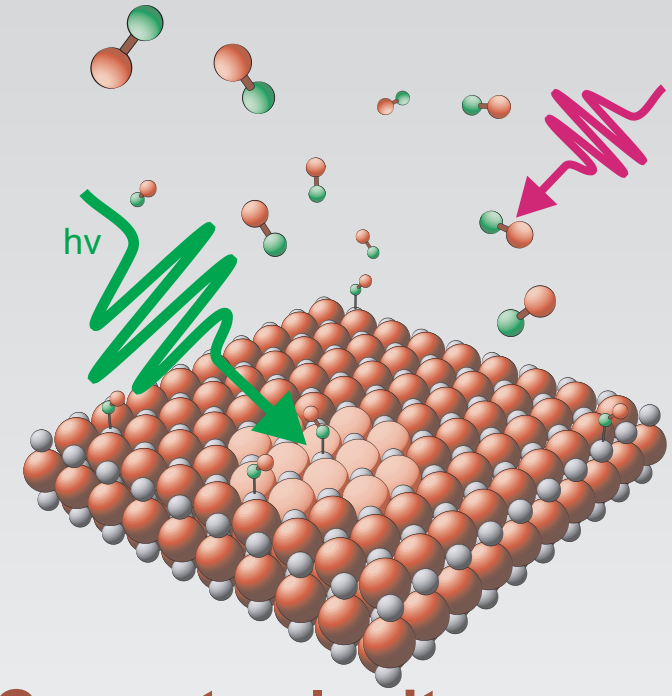


Photodesorption: NO/NiO(100)



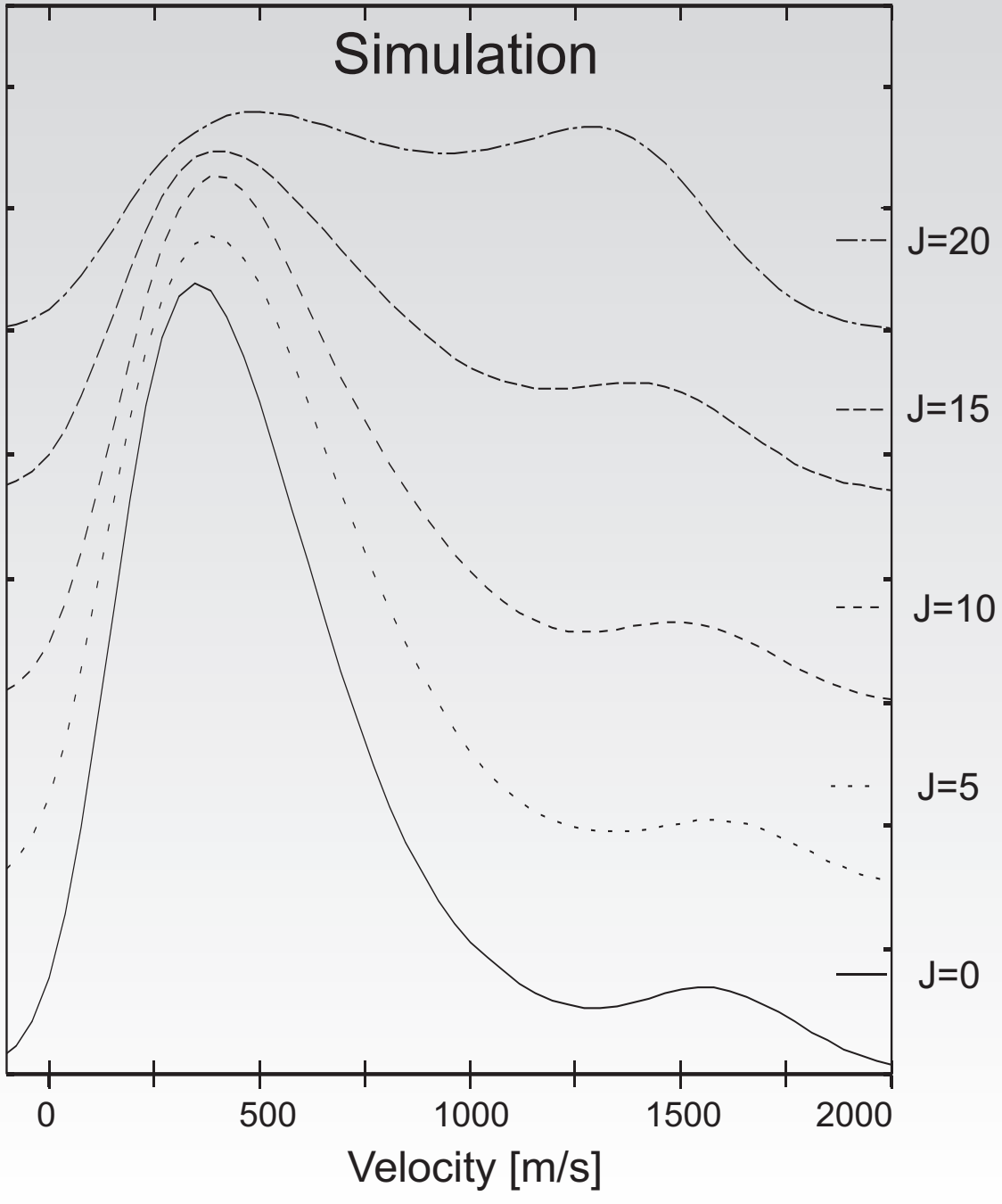
Photodesorption: NO/NiO(100)

Results



- Correct velocity range
- Bimodal distributions
- Wave packet bifurcation in lateral coordinate!
- New desorption mechanism (Anti-Antoniewicz)

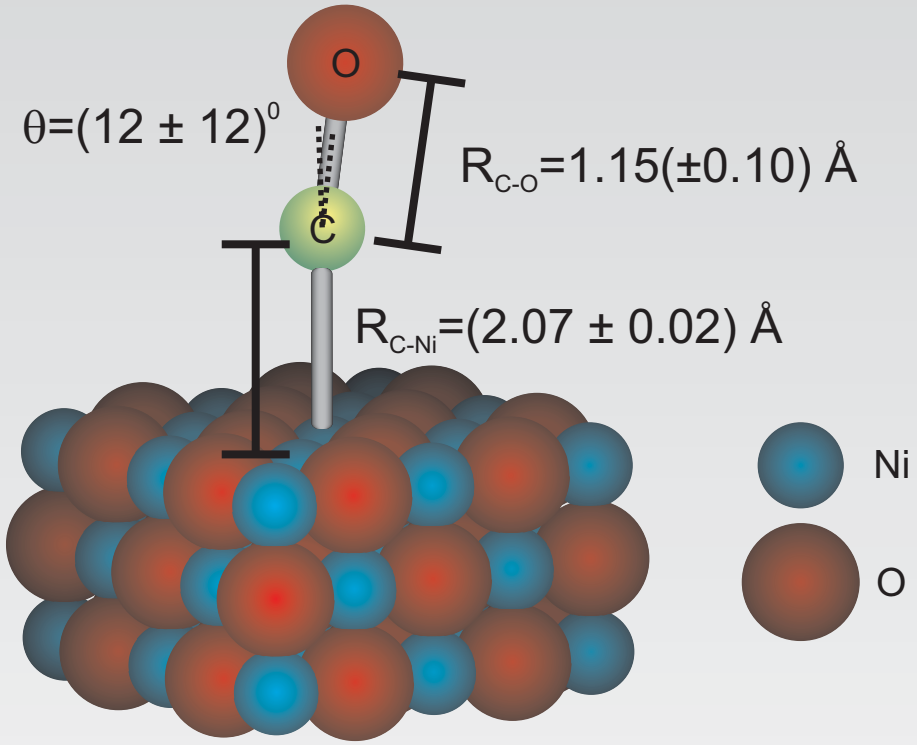
J. Phys. Chem. A **111**,13233 (2007)
Phys. Chem. Chem. Phys. **8**, 1584 (2006)
Chem. Phys. Lett. **415**, 150 (2005)



Photodesorption: CO/NiO(100)

Experiment and Theory

Experiment [1],[2]



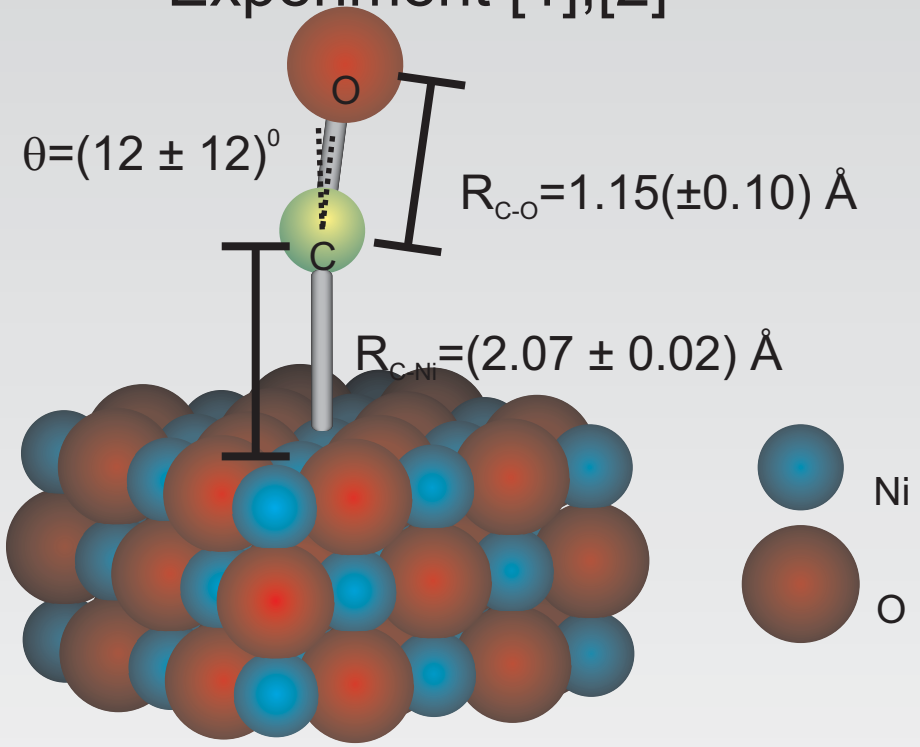
[1] J.-T. Hoeft et al. Phys. Rev. Lett. **87**, 8 (2001)
[2] R. Wichtendahl et al. Surf. Sci. **423**, 90 (1999)

- TPD/Photoelectron diffraction
- Linear adsorption geometry
- Adsorption energy: 0.3 eV

Photodesorption: CO/NiO(100)

Experiment and Theory

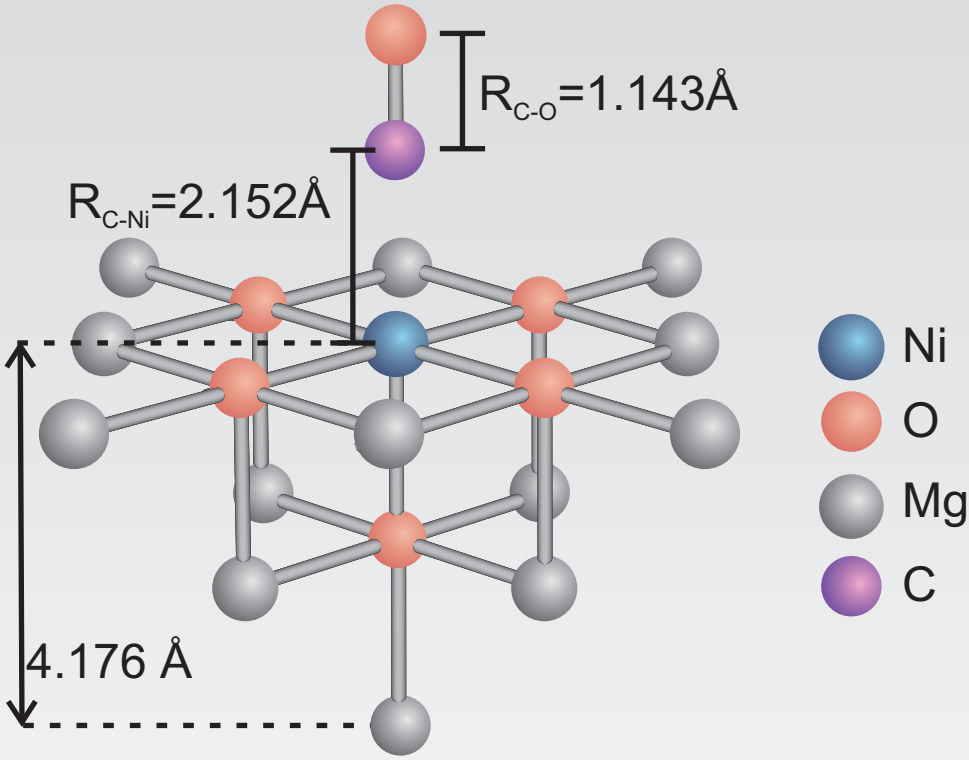
Experiment [1],[2]



[1] J.-T. Hoeft et al. Phys. Rev. Lett. **87**, 8 (2001)
[2] R. Wichtendahl et al. Surf. Sci. **423**, 90 (1999)

- TPD/Photoelectron diffraction
- Linear adsorption geometry
- Adsorption energy: 0.3 eV

Theory



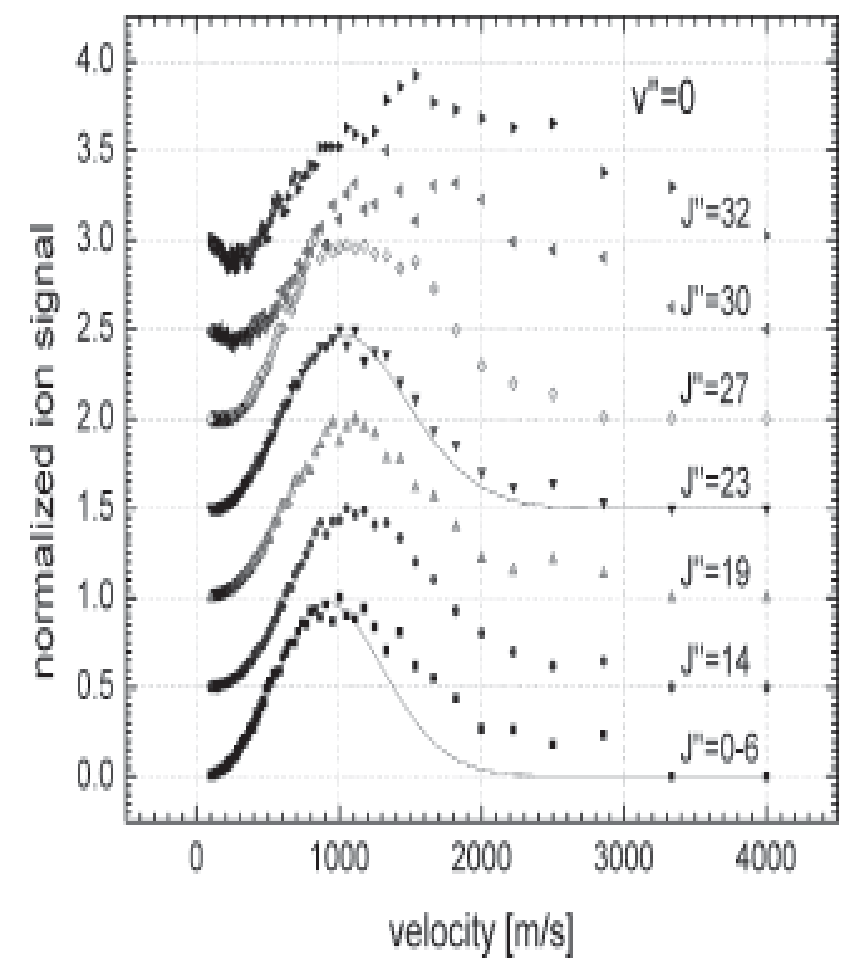
- CASSCF/CASPT-2 and CCSD(T)
- Linear adsorption geometry
- Adsorption energy: 0.24 eV

Good agreement between theory and experiment

Photodesorption: CO/NiO(100)

Experiment and Theory

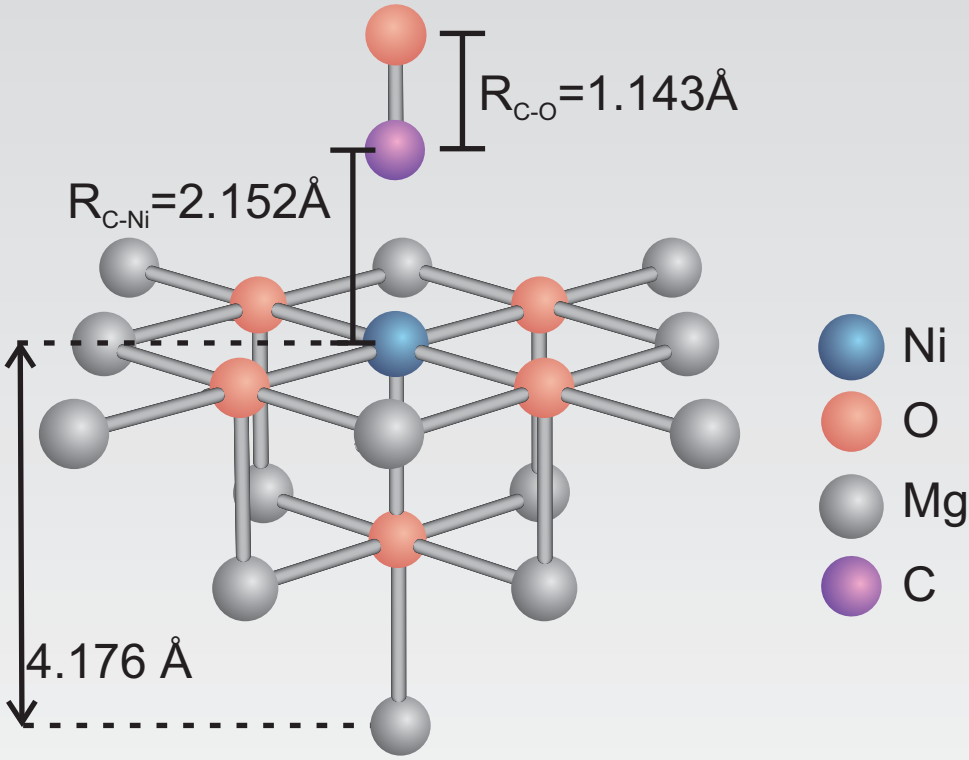
Laser Desorption Experiment



Monomodal distributions

B. Redlich et al,
Chem. Phys. Lett. **420**, 110 (2006)

Theory



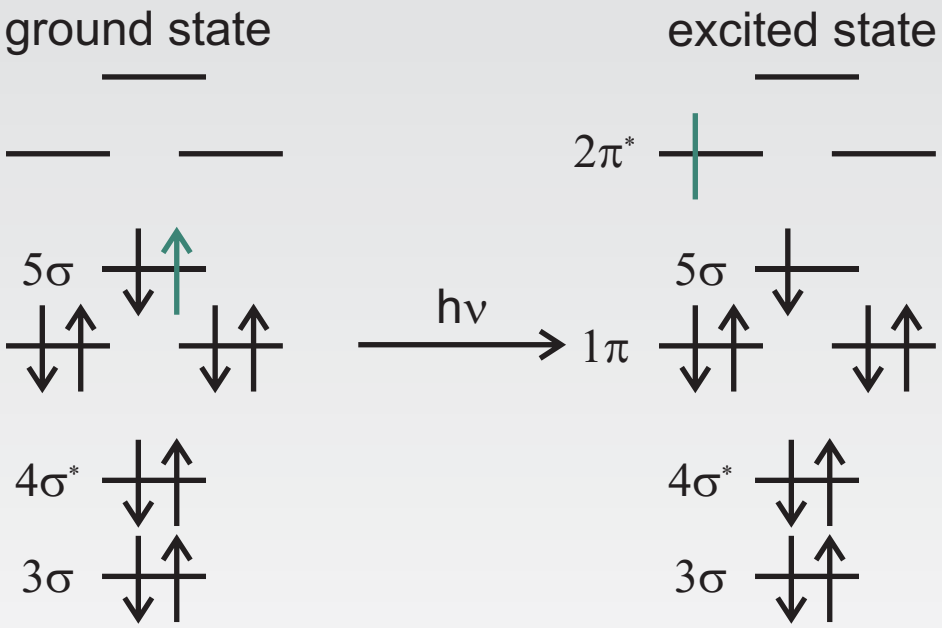
- CASSCF/CASPT-2 and CCSD(T)
- Linear adsorption geometry
- Adsorption energy: 0.24 eV

Agreement: theory and experiment

CO-internal-($5\sigma \rightarrow 2\pi^*$)-excitation

CO-internal-($5\sigma \rightarrow 2\pi^*$)-excitation

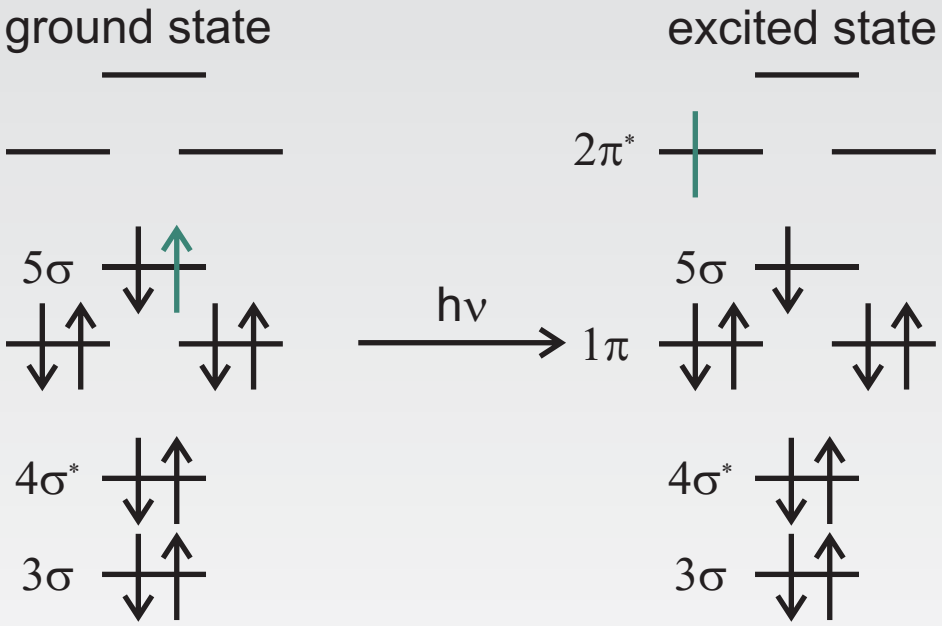
MO diagram für CO



.

CO-internal-($5\sigma \rightarrow 2\pi^*$)-excitation

MO diagram für CO



CO in gas phase

vertical excitation energy / eV

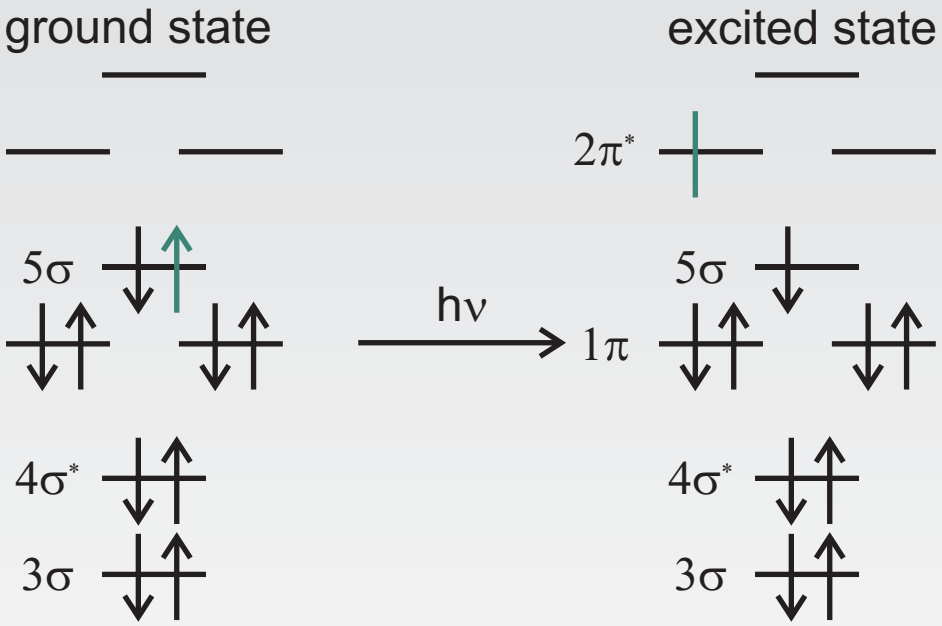
	CAS(2,3)		
state	CASSCF	CASPT2	Experiment[1]
$A^1\Pi$	9.52	8.22	8.51
$a^3\Pi$	6.36	6.02	6.32

[1] E. S. Nielson, P. JØrgensen und J. Odderhede, J. Chem. Phys. **73**, 6238 (1980).

Photodesorption: CO/NiO(100)

CO-internal-($5\sigma \rightarrow 2\pi^*$)-excitation

MO diagram für CO



CO in gas phase

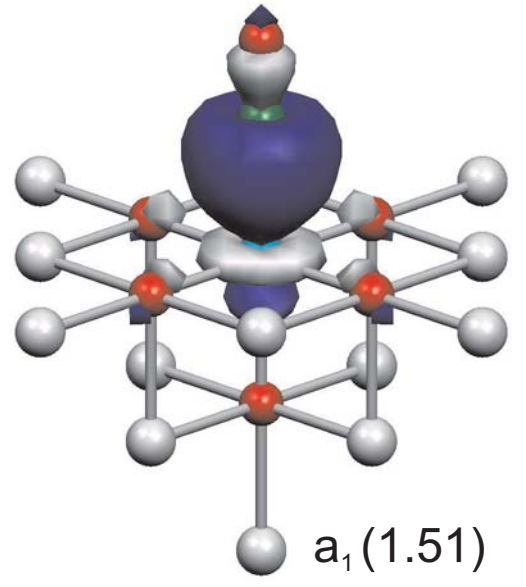
	vertical excitation energy / eV		
	CAS(2,3)		
state	CASSCF	CASPT2	Experiment[1]
$A^1\Pi$	9.52	8.22	8.51
$a^3\Pi$	6.36	6.02	6.32

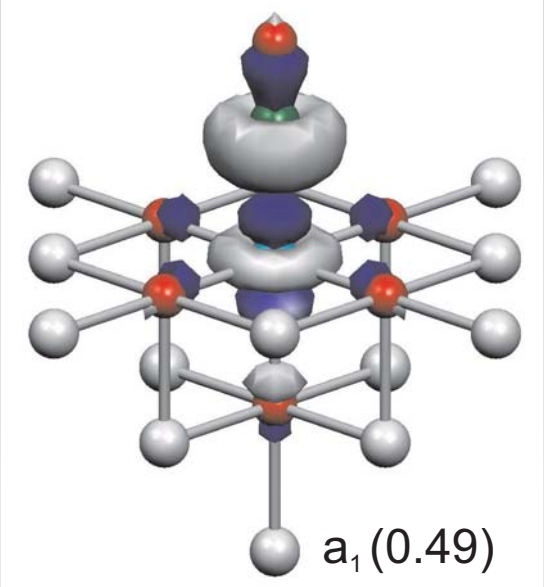
Laser energy: 4.66 eV

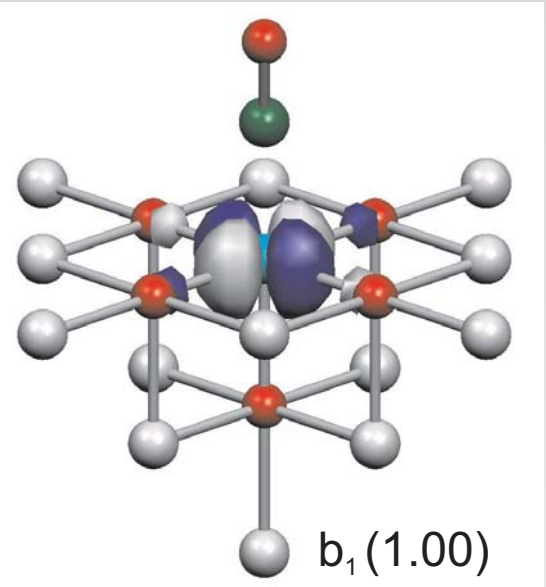
$5\sigma \rightarrow 2\pi^*$ excitation of CO-molecule?

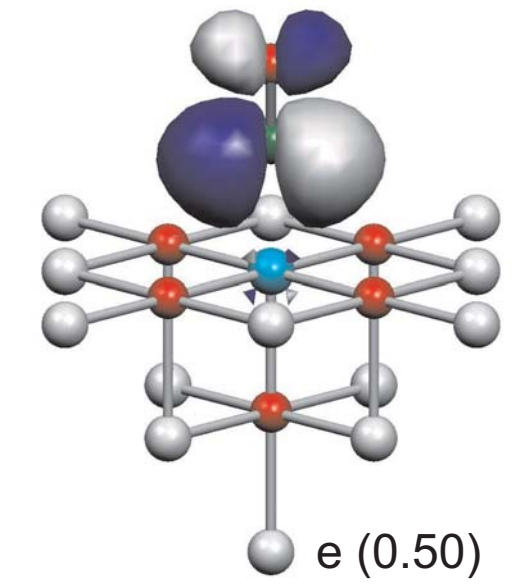
[1] E. S. Nielson, P. JØrgensen und J. Odderhede, J. Chem. Phys. **73**, 6238 (1980).

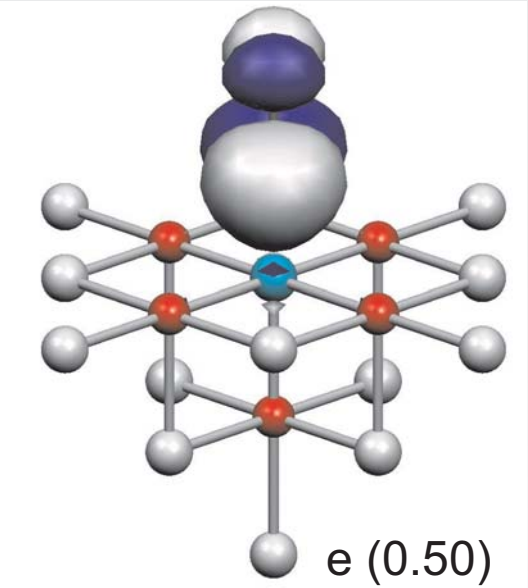
$CO\text{-}NiO_5Mg_{13}^{18+}$: CASSCF(4,5)/CASPT-2 *Active molecular orbitals*



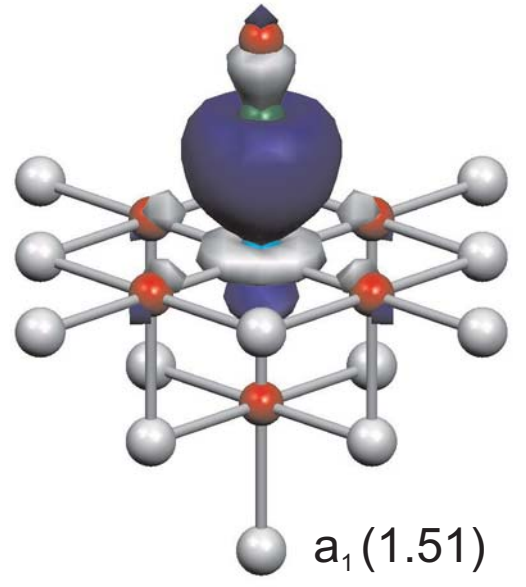


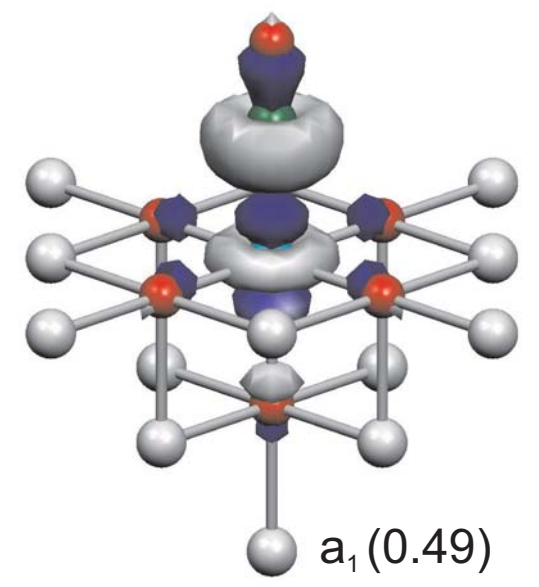


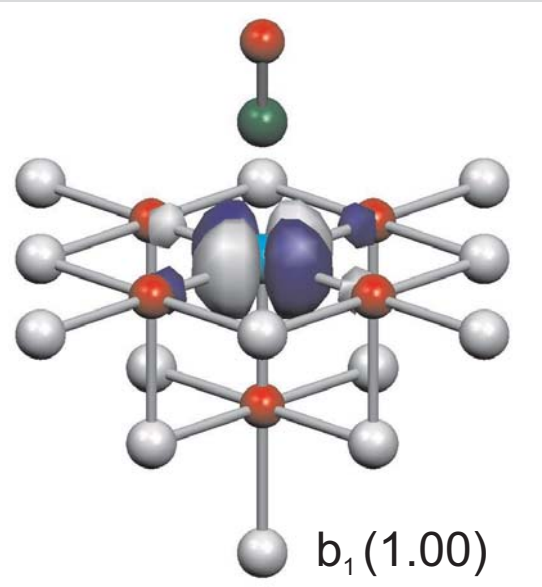


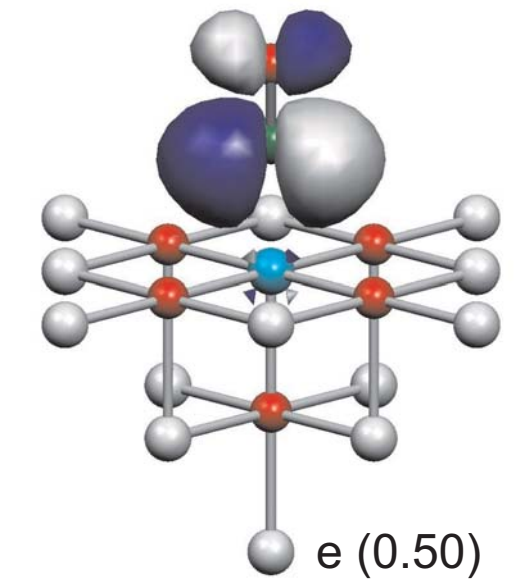


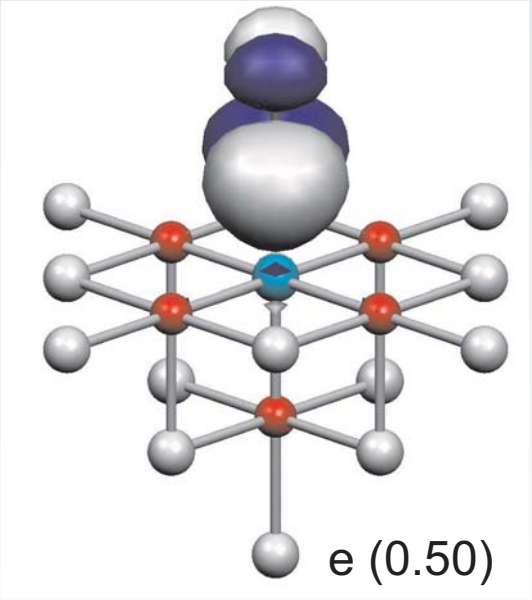
$CO\text{-}NiO_5Mg_{13}^{18+}$: CASSCF(4,5)/CASPT-2 *Active molecular orbitals*











Excitation energy / eV

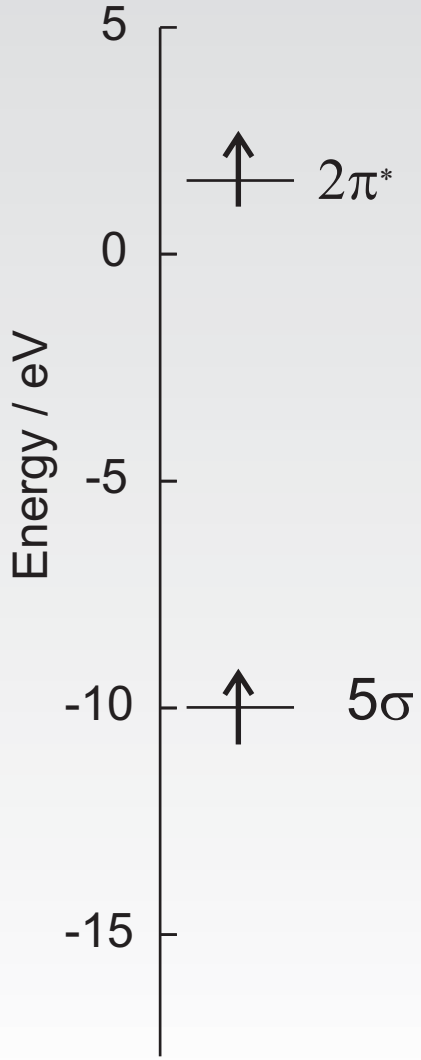
State	CAS(4,5) CASSCF	CAS(4,5) CASPT2
$\tilde{a}^5E$	6.88	6.18
$\tilde{A}^3E$	6.13	4.54
$\tilde{a}^1E$	5.90	4.34

Excellent agreement with experiment (4.66 eV)

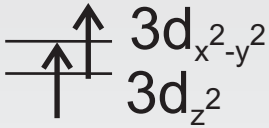
Photodesorption: CO/NiO(100)

Excitation Mechanism

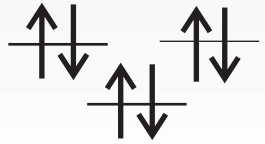
a) CO in gas phase
$a^3\Pi$-state



c) $NiO_5Mg_{13}^{18+}$/PCF



Ni^{2+} (d^8)



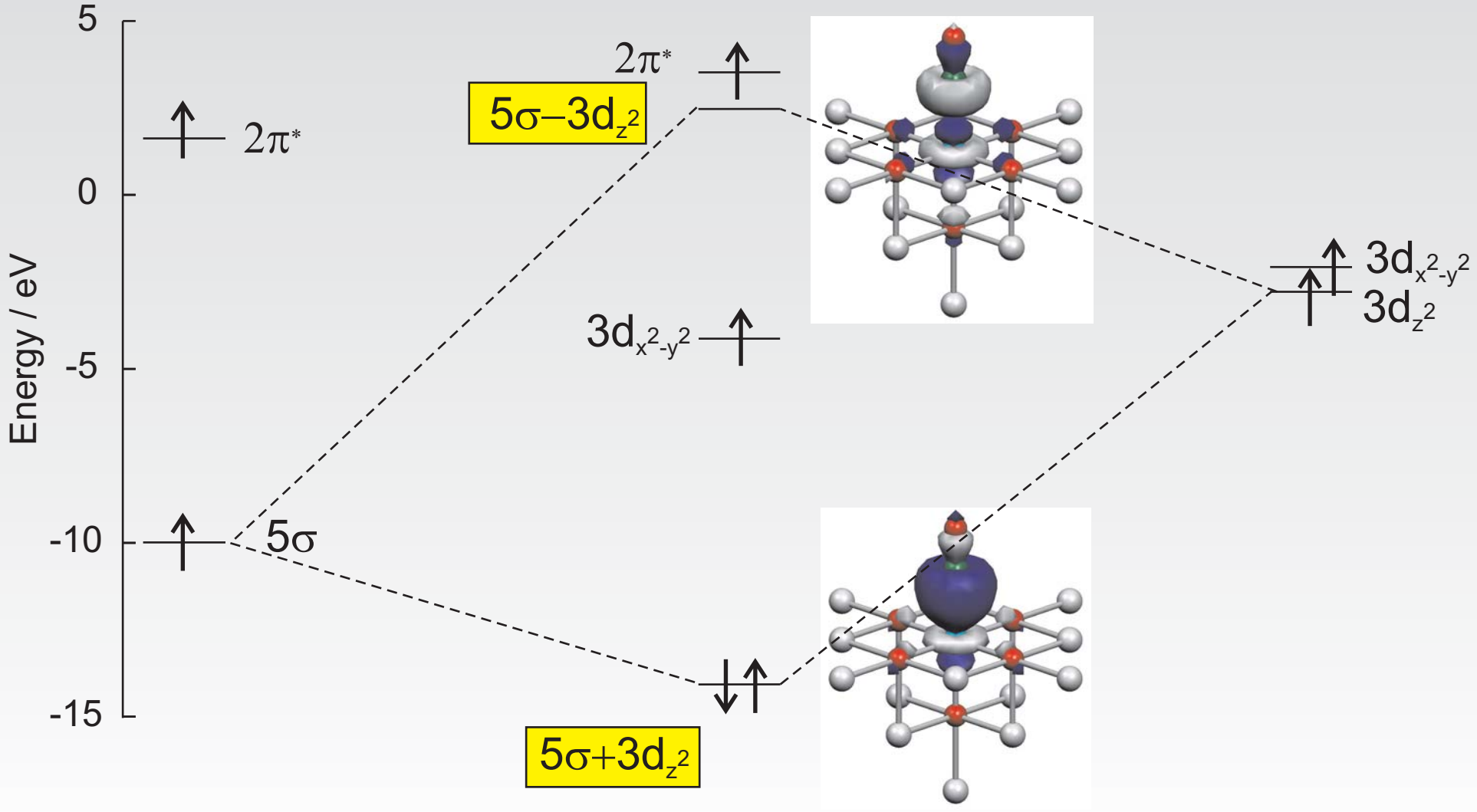
Photodesorption: CO/NiO(100)

Excitation Mechanism

a) CO in gas phase
$a^3\Pi$-state

b) CO / $NiO_5Mg_{13}^{18+}$/PCF
$\tilde{A}^3E$-state

c) $NiO_5Mg_{13}^{18+}$/PCF



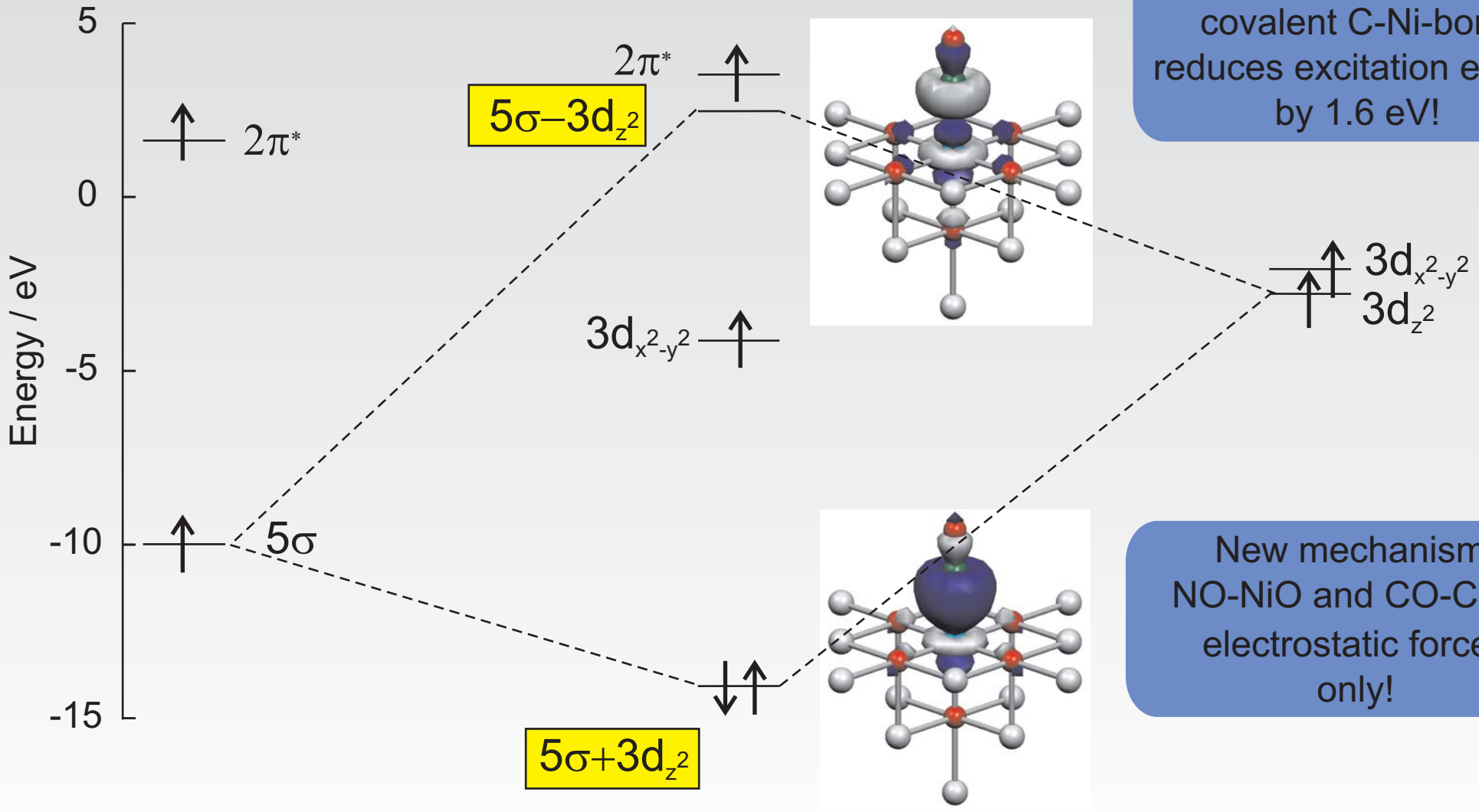
Photodesorption: CO/NiO(100)

Excitation Mechanism

a) CO in gas phase
$a^3\Pi$-state

b) CO / $NiO_5Mg_{13}^{18+}$/PCF
$\tilde{A}^3E$-state

c) $NiO_5Mg_{13}^{18+}$/PCF

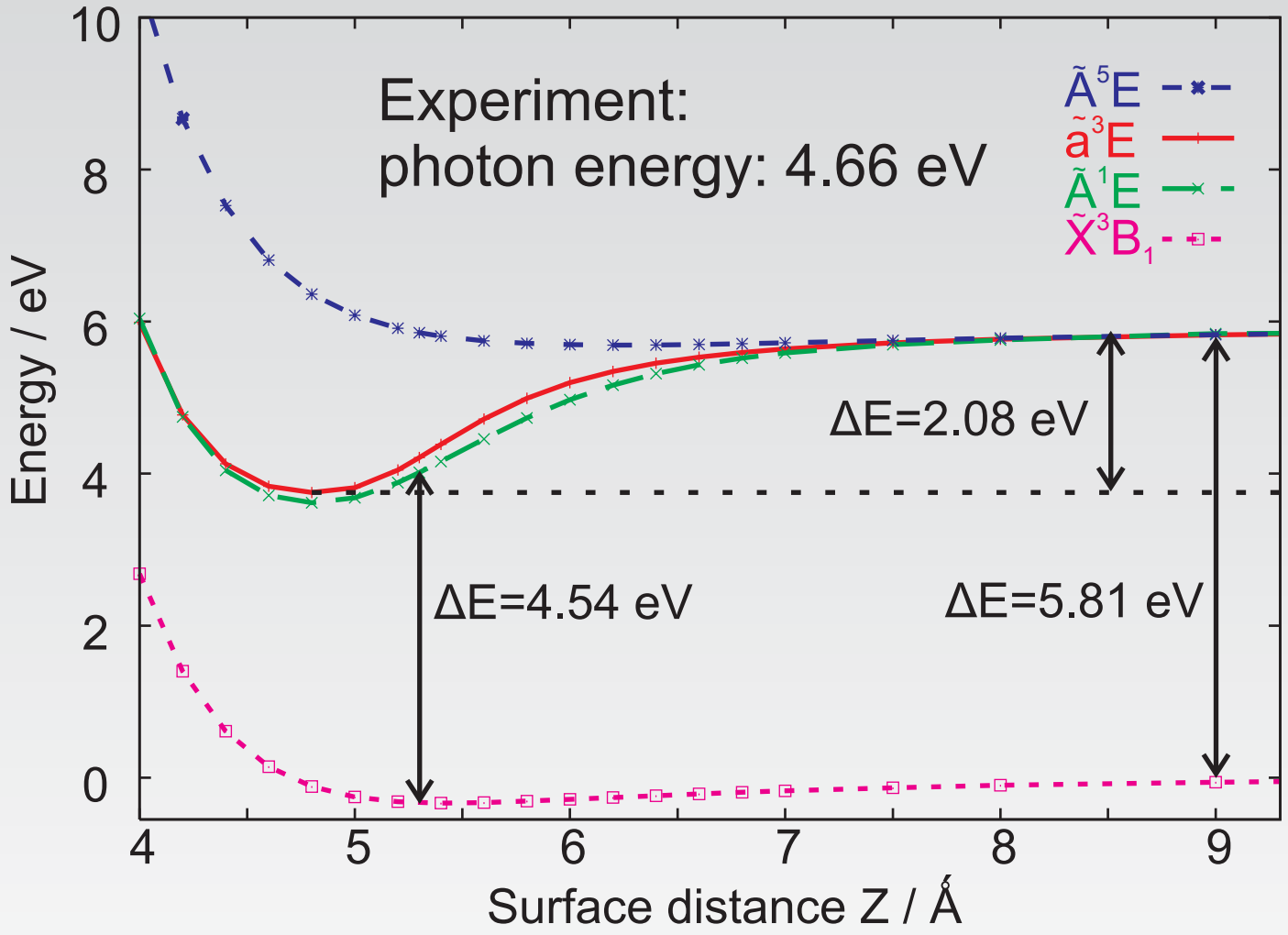


Formation of covalent C-Ni-bond reduces excitation energy by 1.6 eV!

New mechanism! NO-NiO and CO-Cr_2O_3 electrostatic forces only!

$CO\text{-}NiO_5Mg_{13}^{18+}$: CASPT-2

Excitation energies



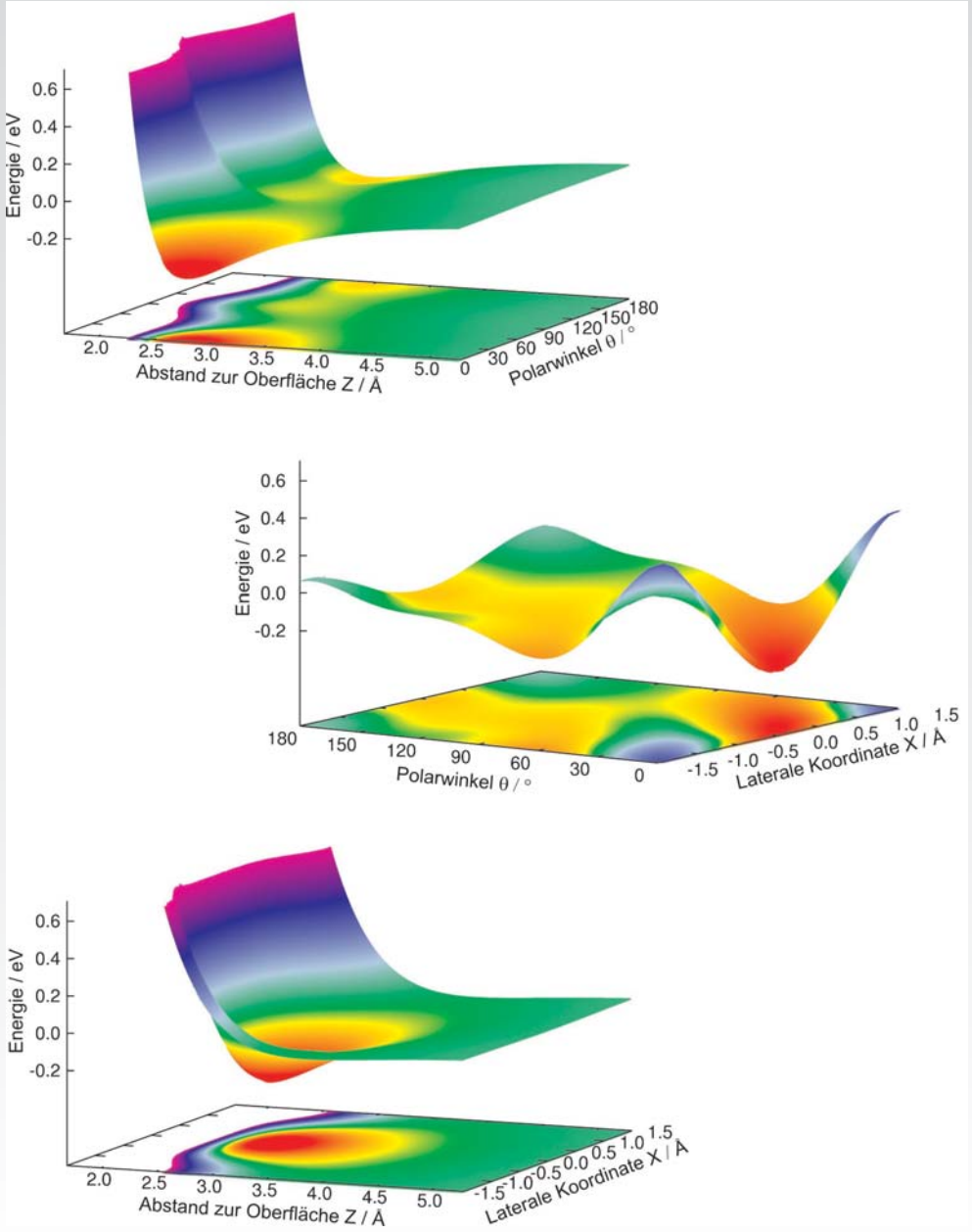
Excited state involved: $\tilde{a}^3E$

Antoniewicz-like desorption scenario

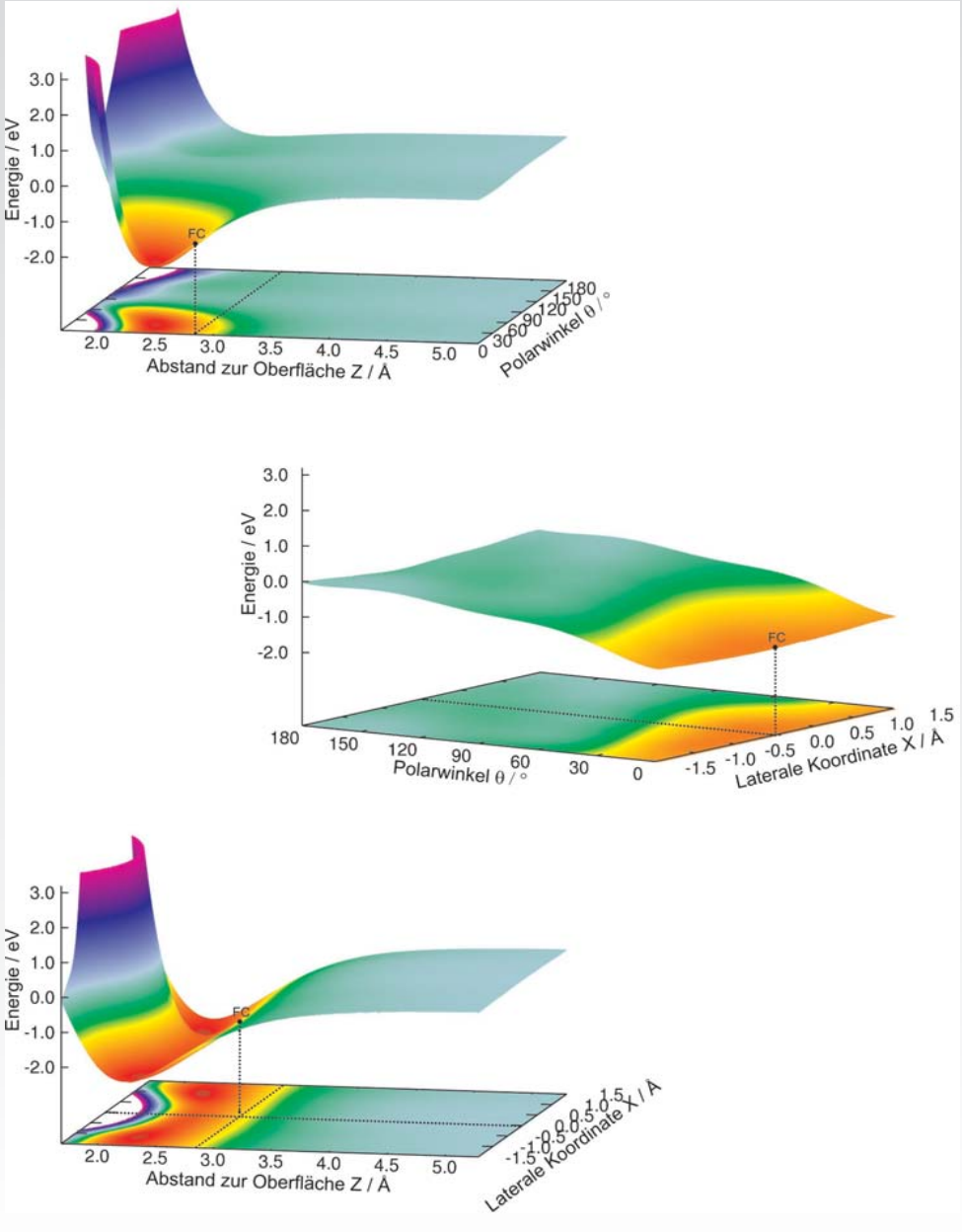
System: CO/NiO(100)

3D-Potential Energy Surfaces

Ground State



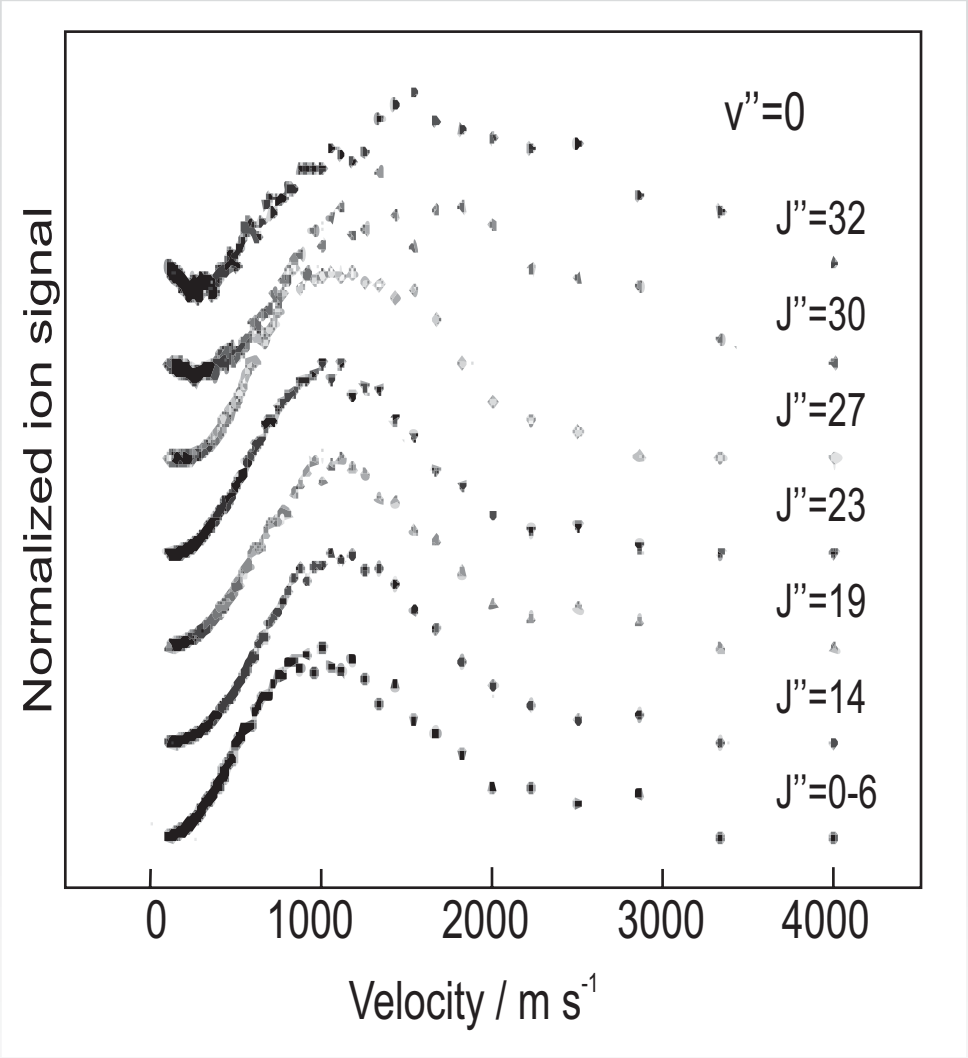
Excited State



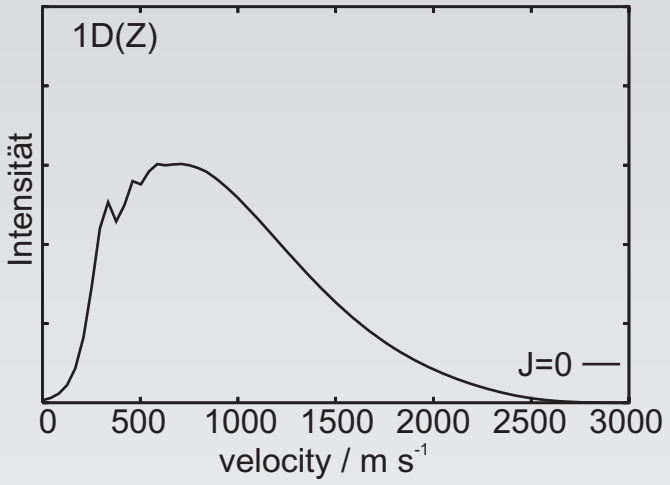
Photodesorption: CO/NiO(100)

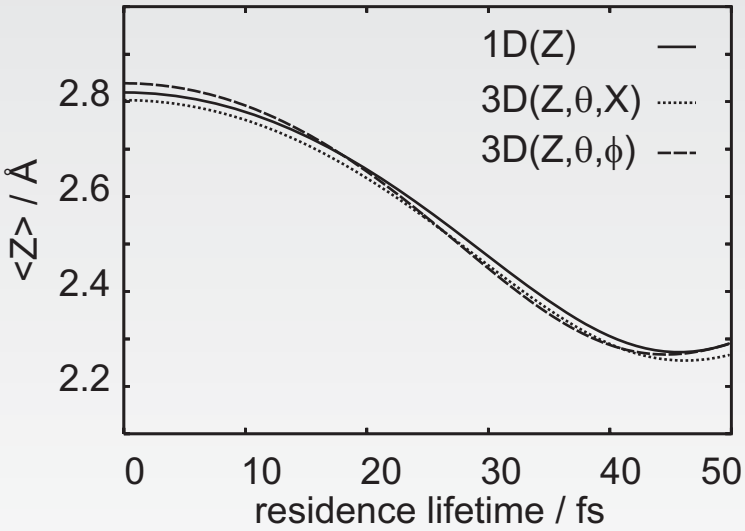
Results

Experiment[1]



Theory



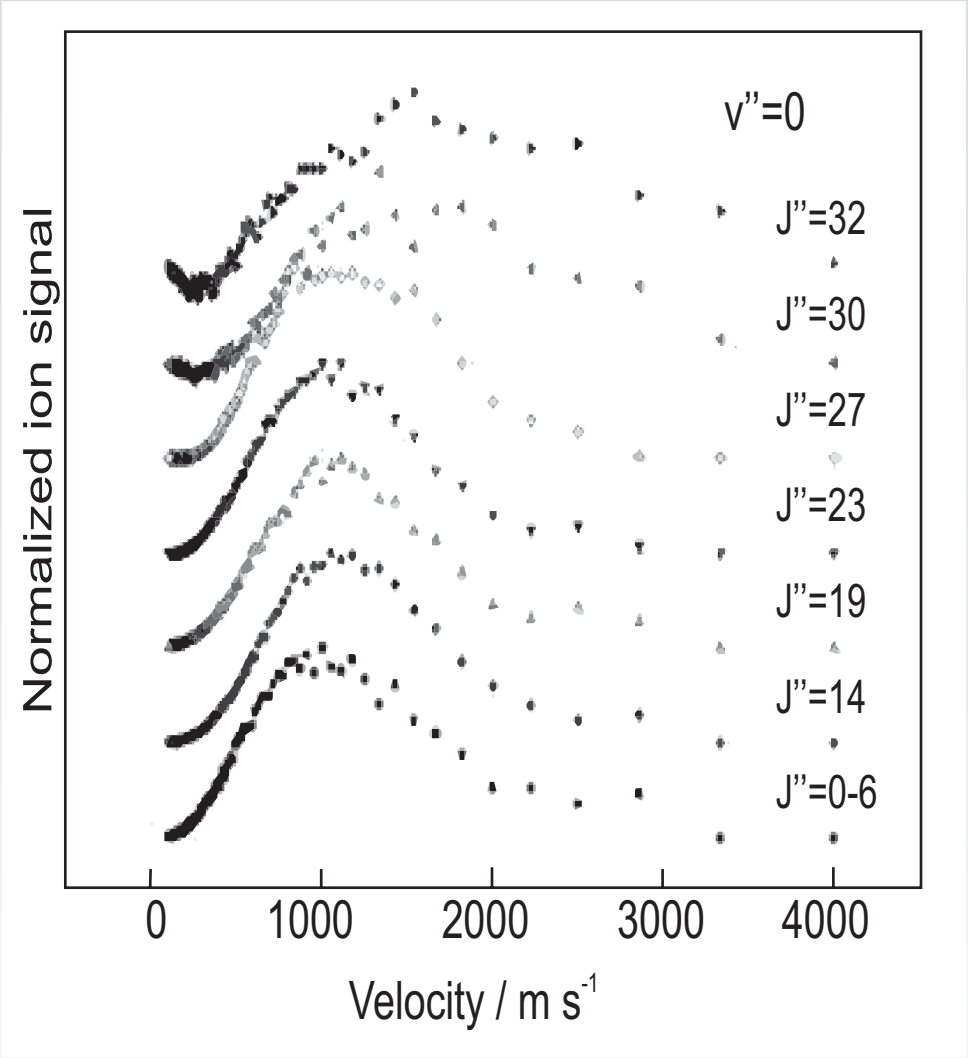


[1] B. Redlich, A. Kirilyuk, T. Holger, G. von Helden, G.Meijer und H. Zacharias, *Chem. Phys. Lett.* **420**, 110 (2006).

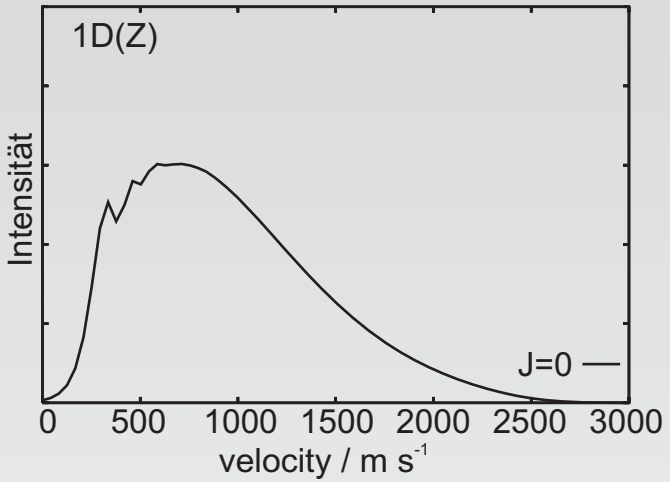
Photodesorption: CO/NiO(100)

Results

Experiment[1]



Theory



Results:

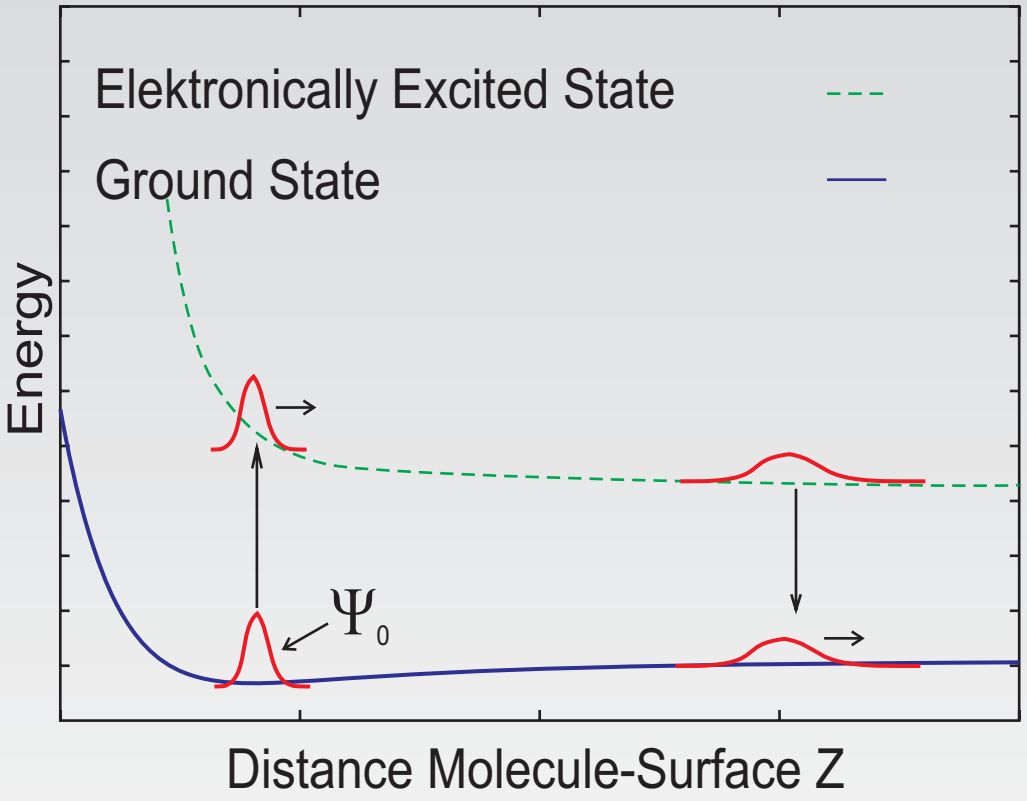
- Good agreement with experiment
- $CO(5\sigma \rightarrow 2\pi^*)$ excited state
- Antoniewicz mechanism due to covalent Ni-C bond in excited state
- Resonance lifetime 4-12 fs
- 1D-calculations sufficient

[1] B. Redlich, A. Kirilyuk, T. Holger, G. von Helden, G.Meijer und H. Zacharias, *Chem. Phys. Lett.* **420**, 110 (2006).

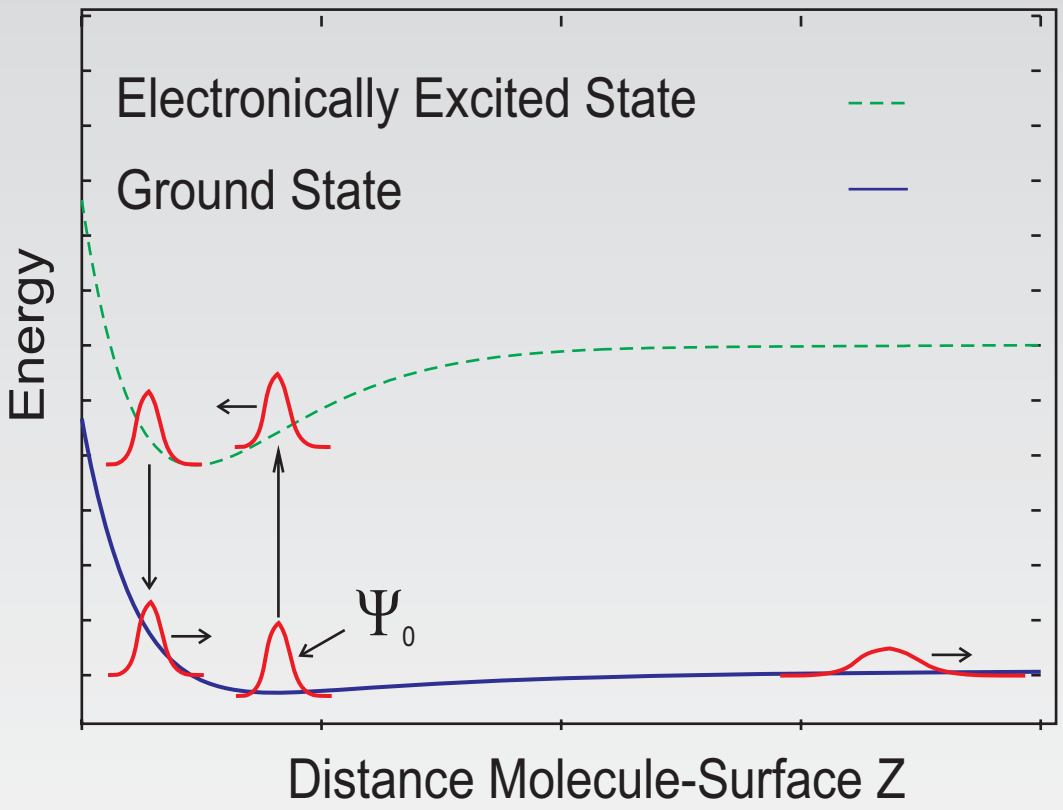
Quantum Dynamics

Desorption Mechanism

MGR Mechanism[9,10]



Antoniewicz Mechanism[8]

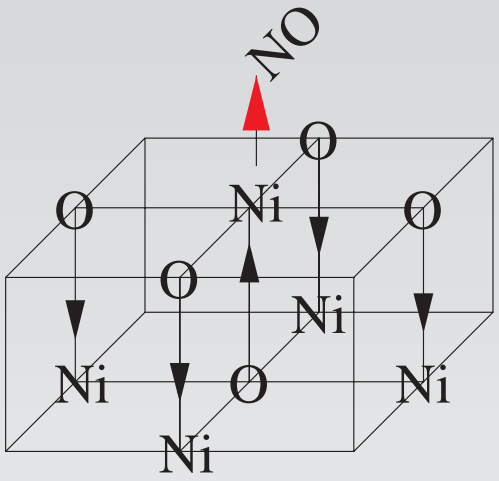


[8] P. R. Antoniewicz *Phys. Rev. Lett. B* **21**, 3811 (1980).
[9] D. Menzel und R. Gomer, *J. Chem. Phys.* **41**, 3311 (1964).
[10] P. A. Redhead, *Can. J. Phys.* **42**, 886 (1964).

Surrogate Hamiltonian Method

- Separation of the total system Hamiltonian:

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} + \hat{H}_{SF}(t) + \hat{H}_{BF}(t)$$



- *implicit* description of the bath: TLS

- representative bath modes are included in the description:

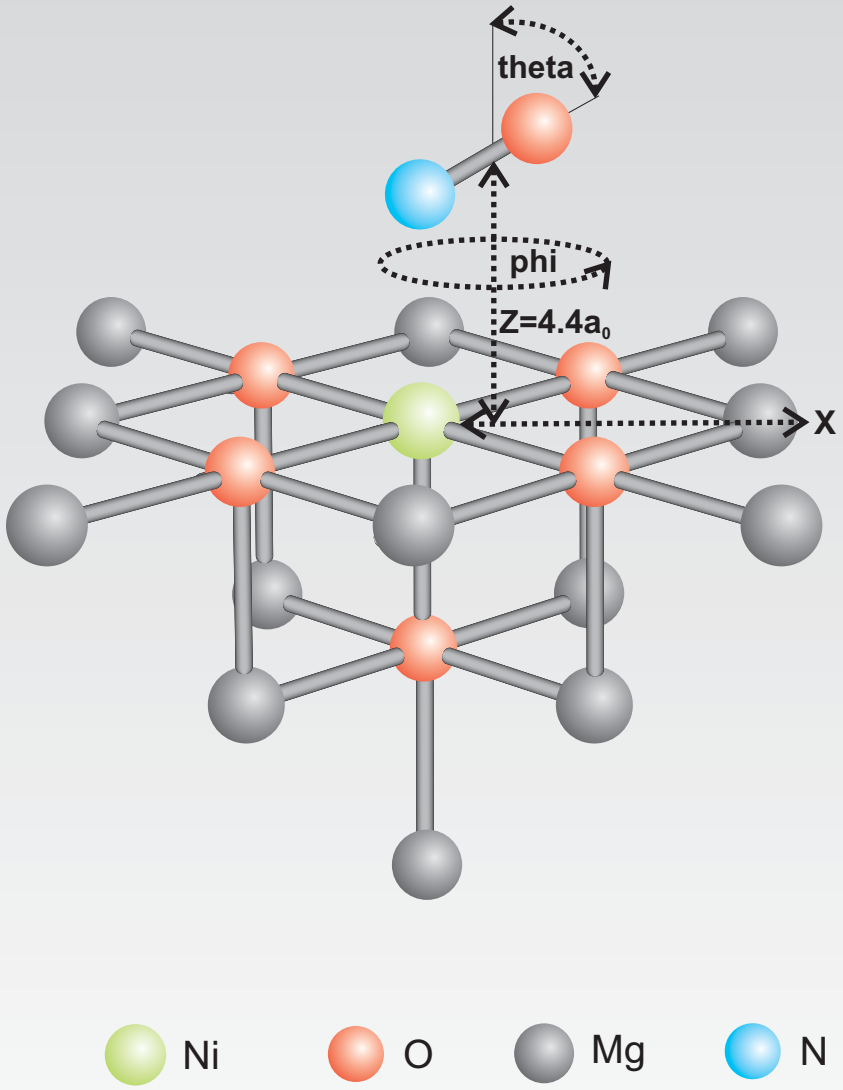
$$\hat{H}_B \approx \sum_{k=1}^{\infty} \hat{\tilde{n}}_k^{true} \longrightarrow \sum_{k=1}^{N} \hat{n}_k^{rep}$$

Gains	Costs
• well-suited for ultrafast events • controllable approximation	• enormous numerical effort

Reference: R. Baer and R. Kosloff, J.Chem.Phys. **106**, 8862 (1997)

Surrogate Hamiltonian Method

NO/NiO(100): system



$$\hat{H}_S = \begin{pmatrix} \hat{T} + V_g(Z,\vartheta) & 0 \\ 0 & \hat{T} + V_e(Z,\vartheta) \end{pmatrix}$$

$$\hat{H}_{SF} = \begin{pmatrix} 0 & E(t)\hat{\mu}_{tr} \\ E^*(t)\hat{\mu}_{tr} & 0 \end{pmatrix}$$

$$f = \frac{2}{3} E_{fi} |\mu_{fi}|^2 \qquad \mu_{tr}(Z) = \sqrt{\frac{3}{2}\frac{\exp(-Z)}{0.15}}$$

$$E(t) = E_0 \exp\left(-\frac{(t - t_{max})^2}{2\sigma_P^2}\right) \exp\left(i\omega_L t\right)$$

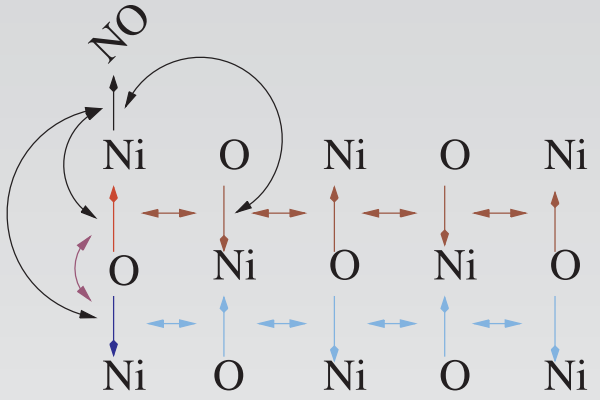
Surrogate Hamiltonian Method

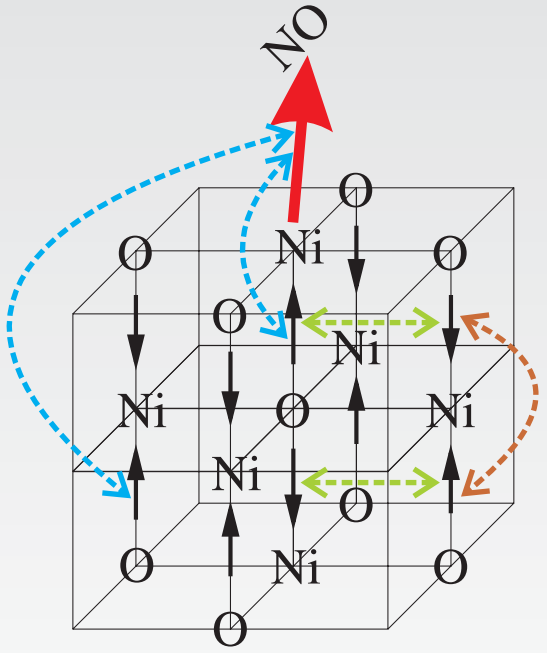
NO/NiO(100): bath

$$\hat{H}_B = \varepsilon \sum_i \hat{\sigma}_i^+ \hat{\sigma}_i + \frac{\eta}{\log(N)} \sum_{ij(NN)} \left(\hat{\sigma}_i^+ \hat{\sigma}_j + \hat{\sigma}_j^+ \hat{\sigma}_i \right)$$

$$\hat{H}_{SB} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \sum_i \hat{V}_i (\hat{\sigma}_i^+ + \hat{\sigma}_i)$$

$$\hat{V}_i = \hat{\vec{\mu}}_S \cdot \hat{\vec{E}}_i = \frac{\hat{\vec{\mu}}_S \cdot \hat{\vec{\mu}}_i}{|\hat{\vec{r}}_i|^3} - 3\frac{(\hat{\vec{\mu}}_S \cdot \hat{\vec{r}}_i)(\hat{\vec{\mu}}_i \cdot \hat{\vec{r}}_i)}{|\hat{\vec{r}}_i|^5}$$





$\hat{\sigma}_i^+$ ..... creation-

$\hat{\sigma}_i$ ..... annhilation-

} operators for the i-th TLS

- Bath parameters:

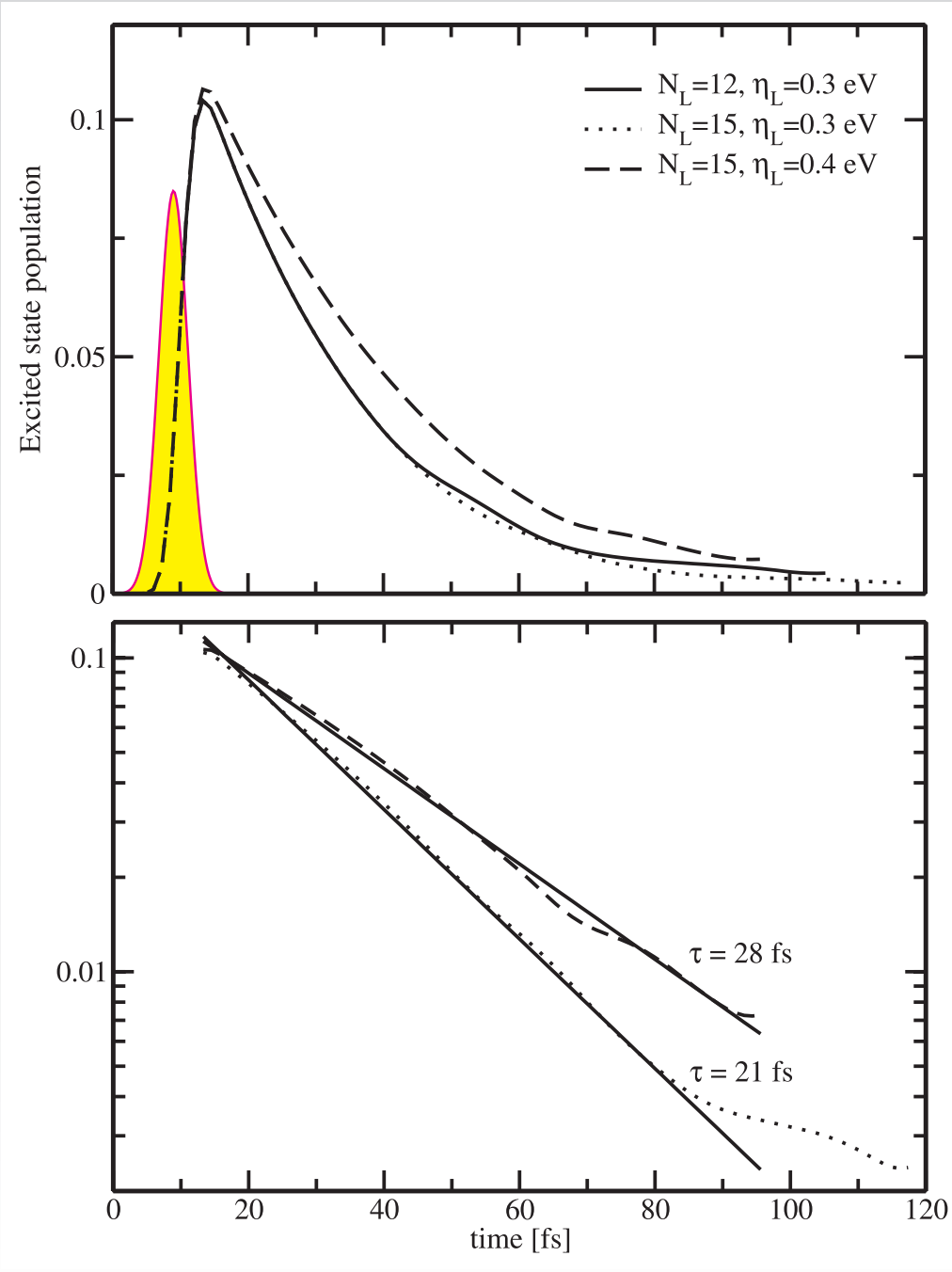
ε ..... energy of the bath dipoles

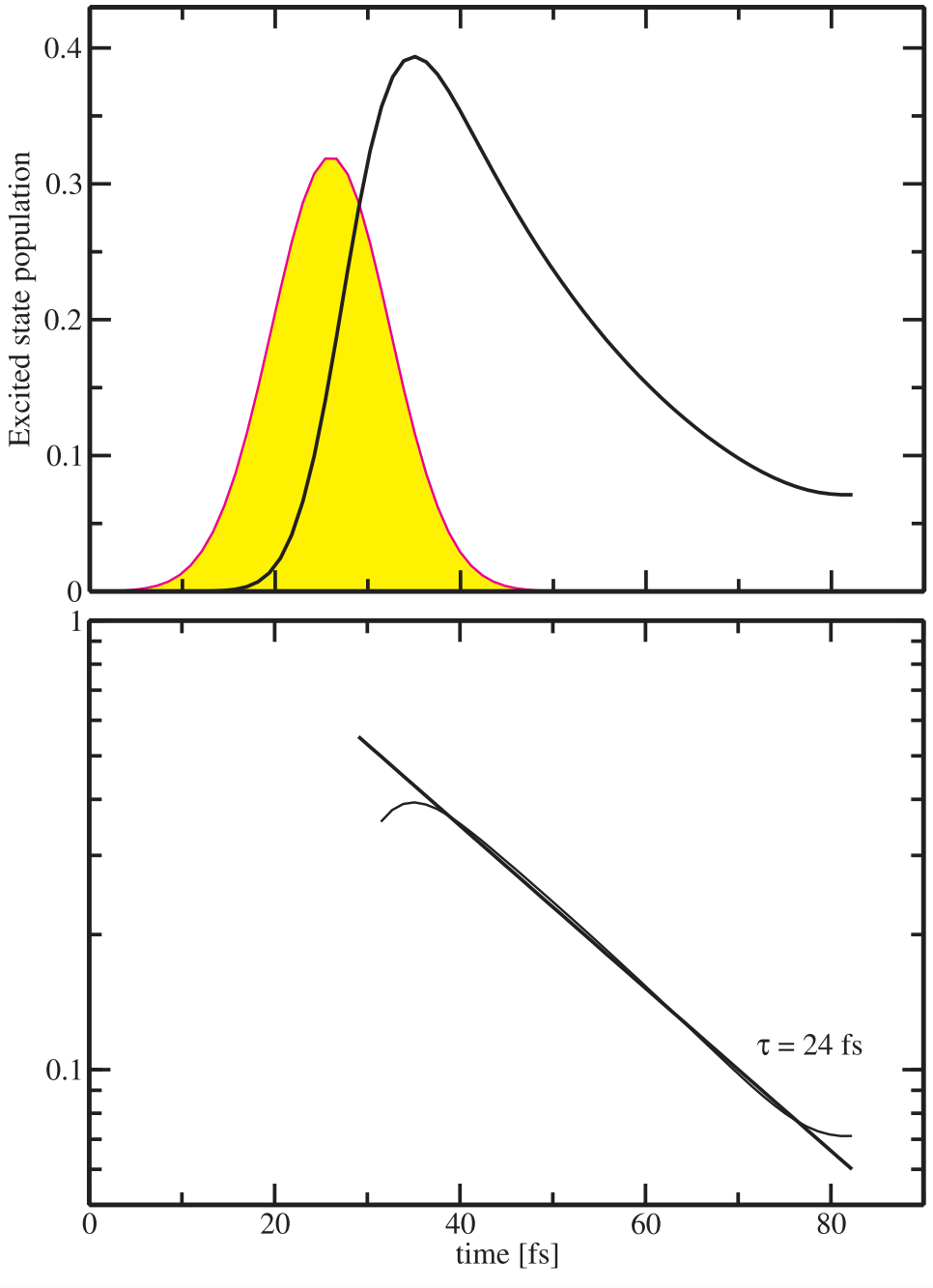
η ..... parameter for the nearest-neighbour-interaction of the bath dipoles

} from EELS or CI-calculations

Surrogate Hamiltonian Method

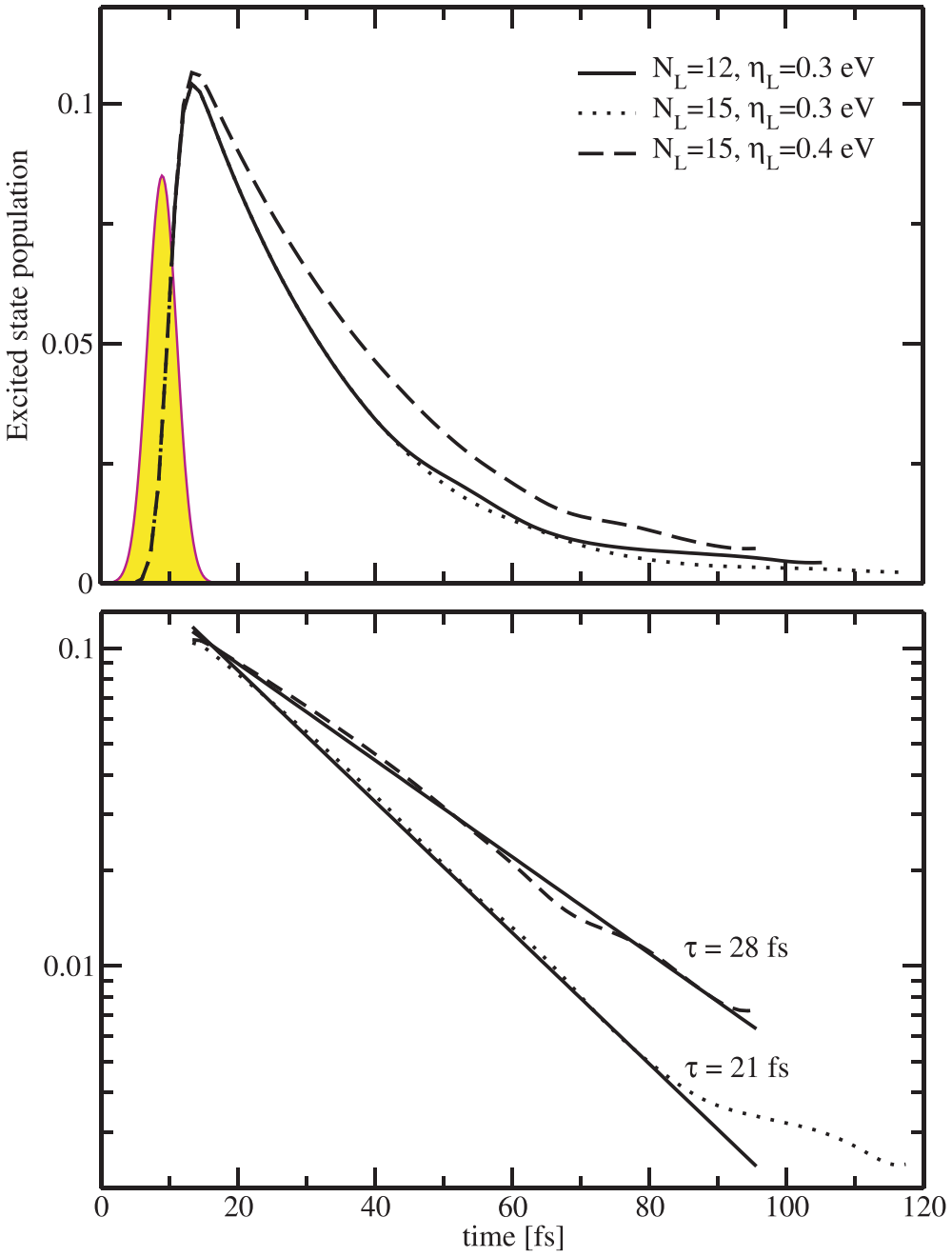
Excited state dynamics





Surrogate Hamiltonian Method

Excited state dynamics



Resonance lifetimes obtained agree with resonance liftetimes in previous stochastic wave packet calculations

Achievement:
ab initio simulation of surface photochemistry including non-adiabatic decay

Optimal Control of Quantum Dissipation

Minimization of dissipation by optimizing external field

Time-dependent OCT

Maximize functional J, i.e. $\delta J = 0$

$$J = \int_0^T dt \left\langle \psi(t) \middle| \hat{\Theta}_t \middle| \psi(t) \right\rangle - \alpha \int_0^T dt \, \frac{\varepsilon^2(t)}{s(t)}$$

$$- 2\Im \left[\int_0^T dt \left\langle \lambda(t) \middle| i \frac{\partial}{\partial t} - [\hat{H} - \hat{\mu}\varepsilon(t)] \middle| \psi(t) \right\rangle \right]$$

Optimal Control of Quantum Dissipation

Minimization of dissipation by optimizing external field

Time-dependent OCT

Pulse design equations:

$$i\frac{d}{dt}\left|\psi(t)\right\rangle = (\hat{H} - \hat{\mu}\varepsilon(t))\left|\psi(t)\right\rangle$$

$$\left|\psi(0)\right\rangle = \left|\phi\right\rangle \qquad \hat{\Theta}_t = \mathrm{tr}_B\{\left|\phi_{ref}(t)\right\rangle\left\langle\phi_{ref}(t)\right|\} \otimes \hat{I}_B$$

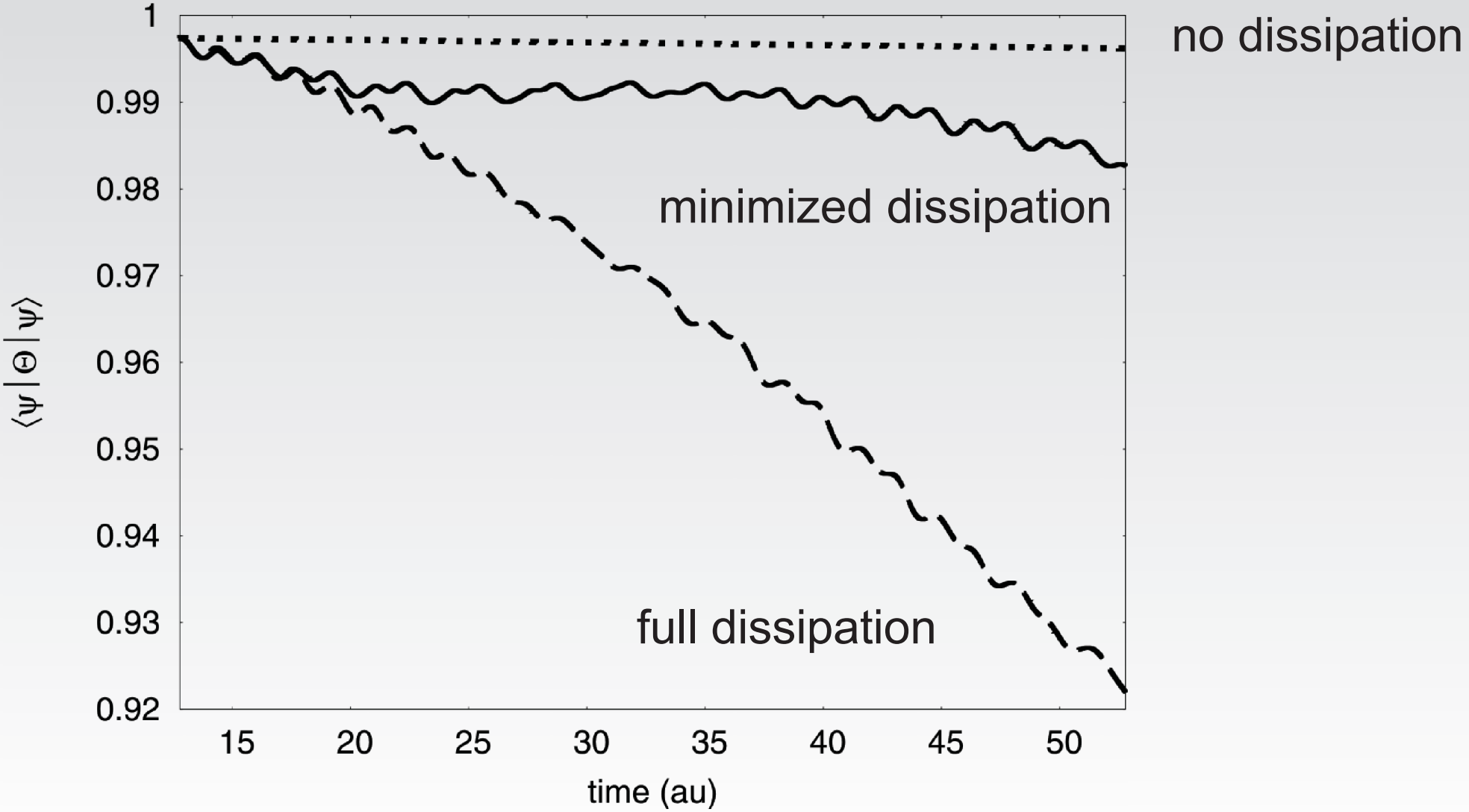
$$i\frac{d}{dt}\left|\lambda(t)\right\rangle = (\hat{H} - \hat{\mu}\varepsilon(t))\left|\lambda(t)\right\rangle - i\hat{\Theta}_t\left|\psi(t)\right\rangle$$

$$\varepsilon(t) = -\frac{s(t)}{\alpha}\Im\left\langle\lambda(t)\right|\hat{\mu}\left|\psi(t)\right\rangle$$

Optimal Control of Quantum Dissipation

Minimization of dissipation by optimizing external field

Time-dependent OCT



Acknowledgements

Carl von Ossietzky University Oldenburg

Theoretical Chemistry

Erik Asplund, Matthias Mehring,
Heiko Haman , Wai Leung Yim
Jan Mitschker, Imed Mehdaoui

Hideaki Aizawa*, Stefan Borowski*,
Sören Dittrich*, Amel Laref*,
Christiane Koch*,
Dominik Kröner*, Merle Krueger*,
Doron Lahav*, Michail Pykavy*,
Stephan Thiel* (*former members)

Funding

German Science Foundation
German Israeli Foundation
Volkswagen Foundation
Hanse-Wissenschaftskolleg
Fonds der Chemischen Industrie
Alexander von Humboldt foundation
High-Performance Computing Center Stuttgart