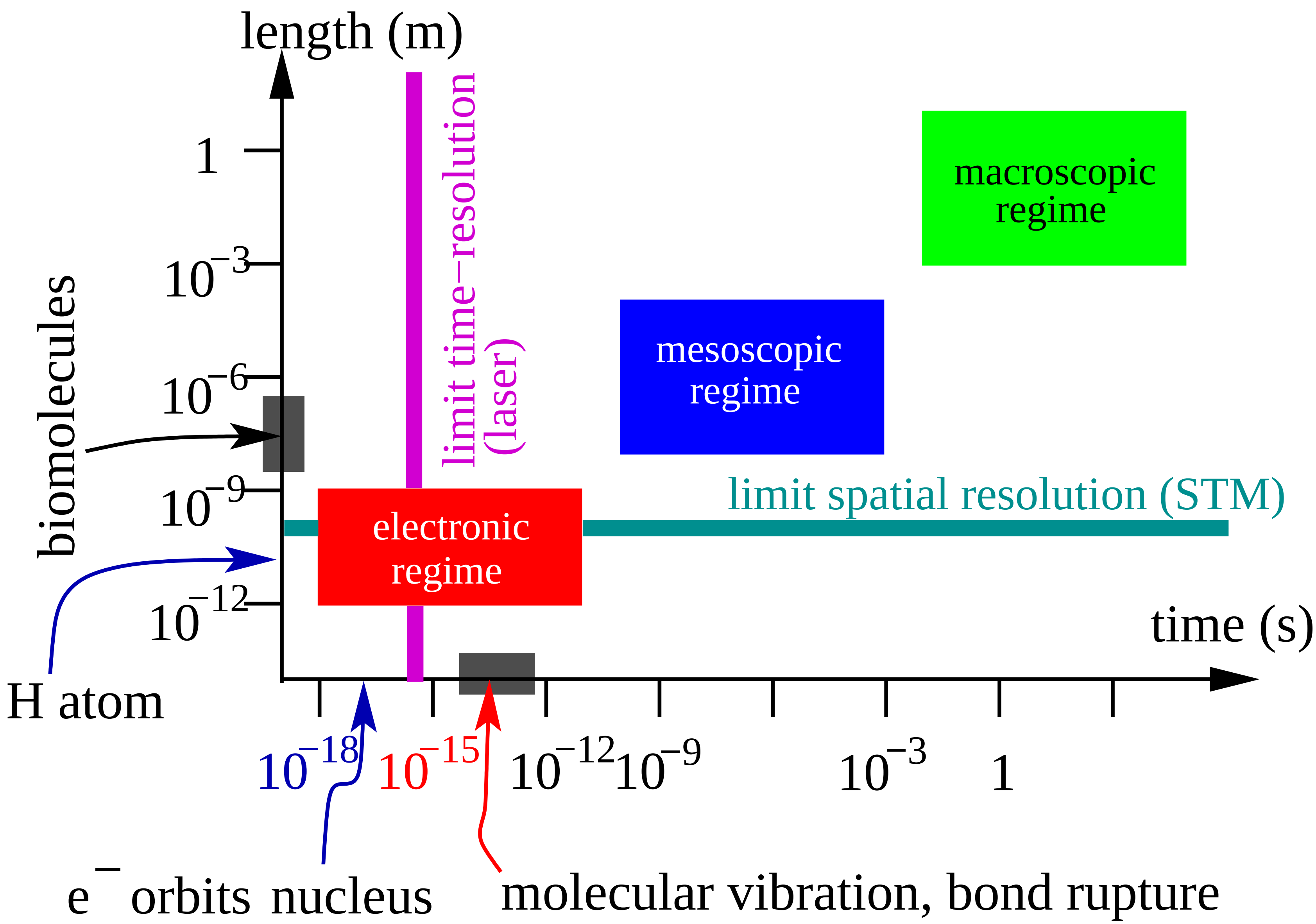
ELECTRON AND ATOM MOTION IN MOLECULES AND NANOSTRUCTURES

Peter Saalfrank

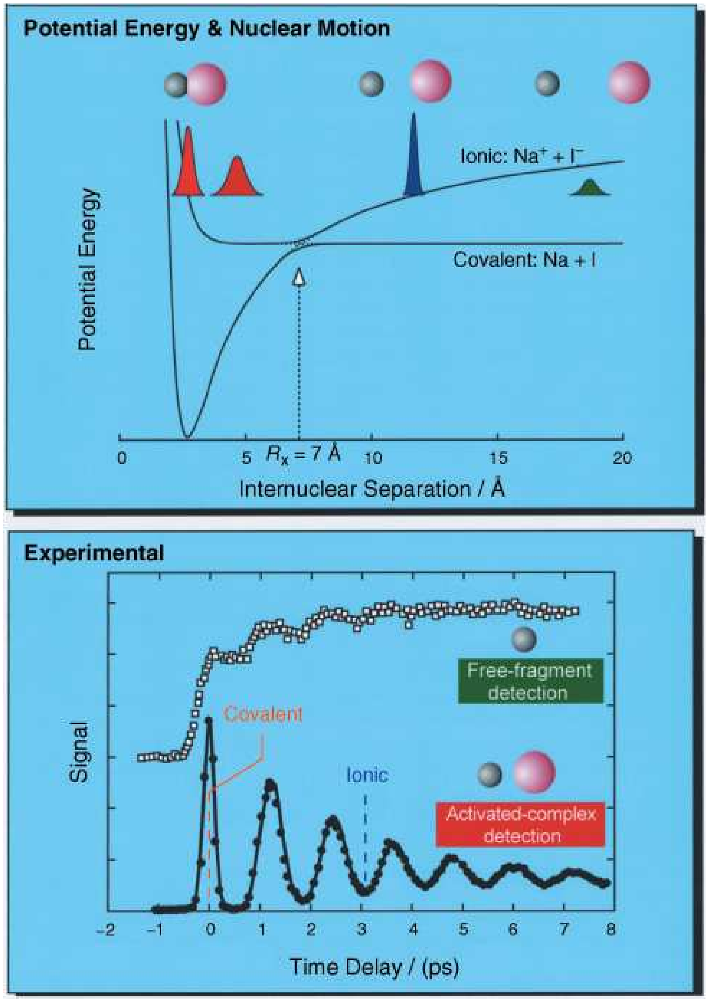
University of Potsdam, Germany

TIME- AND LENGTH-SCALES IN CHEMISTRY



ELECTRONS AND ATOMS IN MOTION

- **Atom motion**



Baskin, Zewail, J. Chem. Ed. **78**, 737 (2001)

femtosecond chemistry

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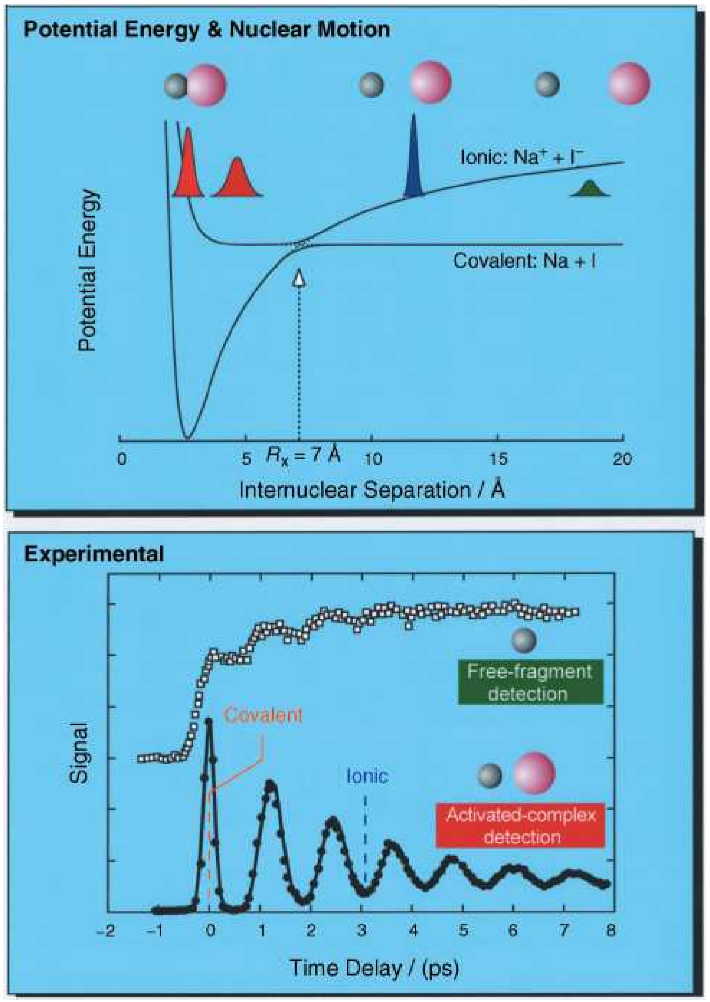
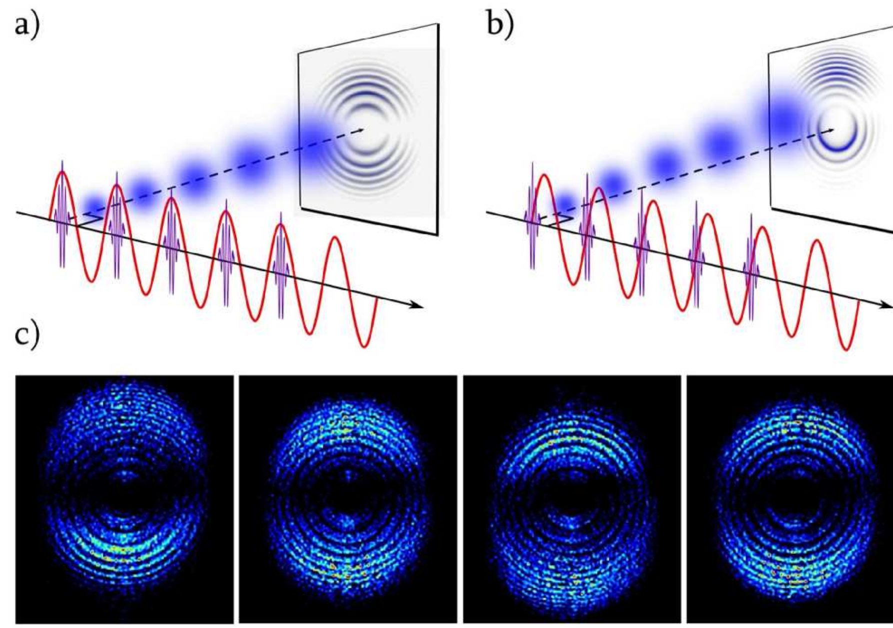


Baskin, Zewail, J. Chem. Ed. **78**, 737 (2001)

femtosecond chemistry

- **Electron motion**



Mauritsson *et al.*, PRL **100**, 073003 (2008)

http://www.youtube.com/

attosecond physics

Krausz, Corkum, . . .

- **Born-Oppenheimer separation**

OUTLINE

- **Laser-driven electron dynamics**

  Methods

❶ A simple example: H_2

❷ Charge transfer and transport in MIM contacts

❸ Charge transfer in molecular systems

❹ Dissipative electron dynamics

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- **Laser-driven electron dynamics**

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  ❶ A simple example: H_2

  ❷ Charge transfer and transport in MIM contacts

  ❸ Charge transfer in molecular systems

  ❹ Dissipative electron dynamics

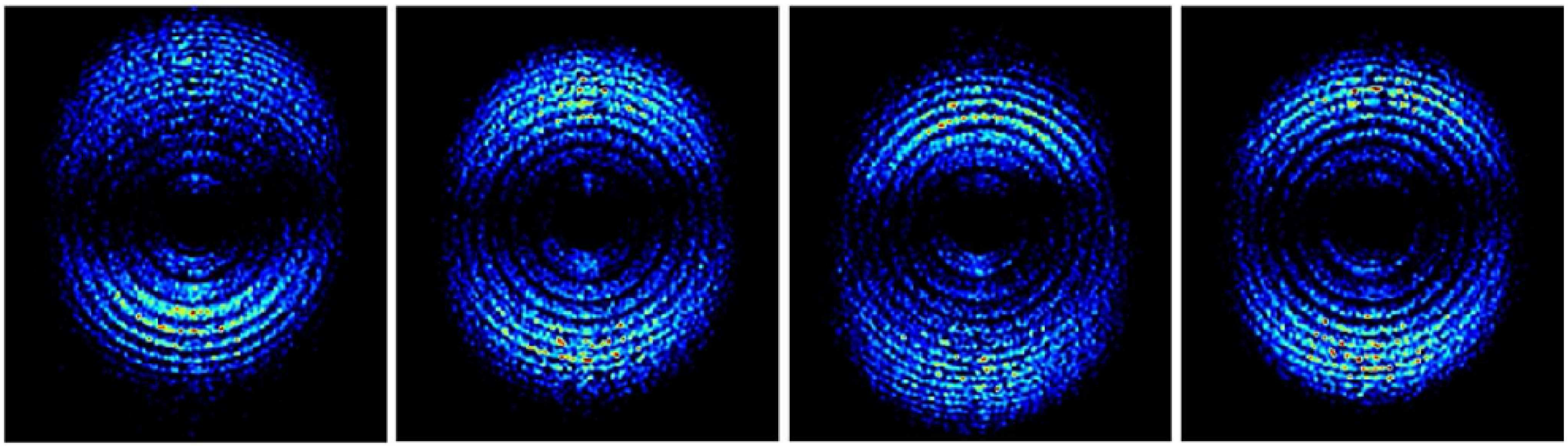
- **Nuclear dynamics with and without lasers**

  Methods

  ❶ An STM-driven switch: COD/Si(100)

  ❷ Vibrational relaxation and excitation: H/Si(100), CO/Cu(100)

LASER-DRIVEN ELECTRON DYNAMICS



LASERS AND ELECTRON DYNAMICS: METHODS

- **The N-electron time-dependent Schrödinger equation**

$$i\hbar \frac{\partial \Psi(\underline{x}_1, \ldots, \underline{x}_{\mathrm{N}}, t)}{\partial t} = \left[\hat{H}_{el}(\underline{x}_1, \ldots, \underline{x}_{\mathrm{N}}) - \underline{\hat{\mu}}\,\underline{E}(t) \right] \Psi(\underline{x}_1, \ldots, \underline{x}_{\mathrm{N}}, t)$$

$$\underline{\hat{\mu}} = -\sum_{i}^{N} \underline{r}_i + \sum_{A}^{N_A} Z_A \underline{R}_A$$

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- **Solution techniques**
  - One-electron approaches
  - Single-determinant methods
    - TD-HF: $\Psi(t) = \psi_0(t)$
    - TD-DFT: $\Psi(t) = \psi_0^{KS}(t)$
      - good for valence excitations ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$)
      - Rydberg states?
      - charge transfer states?
      - static correlation: conical intersections etc.?

LASERS AND ELECTRON DYNAMICS: METHODS

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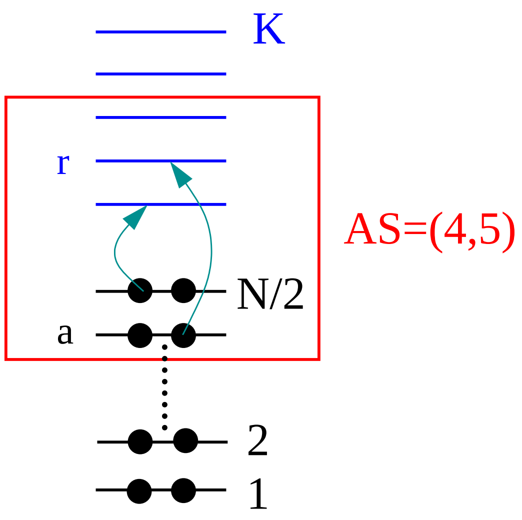
    - TD-DFT: $\Psi(t) = \psi_0^{KS}(t)$
  - Multi-determinant methods
    - TD-CI[1]: $\Psi(t) = C_0(t)\psi_0 + \sum_{ar} C_a^r(t)\psi_a^r + \sum_{ab,rs} C_{ab}^{rs}(t)\psi_{ab}^{rs} + \cdots$
    - TD-CASSCF[2]: $\Psi(t) = C_0(t)\psi_0(t) + \sum_{ar} C_a^r(t)\psi_a^r(t) + \sum_{ab,rs} C_{ab}^{rs}(t)\psi_{ab}^{rs}(t) + \cdots$



[1] Klamroth *et al.*, Appl. Phys. A **78**, 189 (2004); PRB **68**, 245421 (2003); Schlegel *et al.*

[2] Nest *et al.*, JCP **122**, 124102 (2005); PRA **73**, 023613 (2006); Scrinzi *et al.*; Kono *et al.*

LASERS AND ELECTRON DYNAMICS: METHODS

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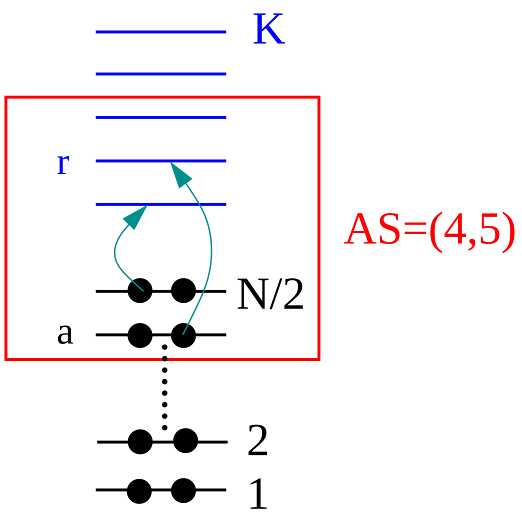


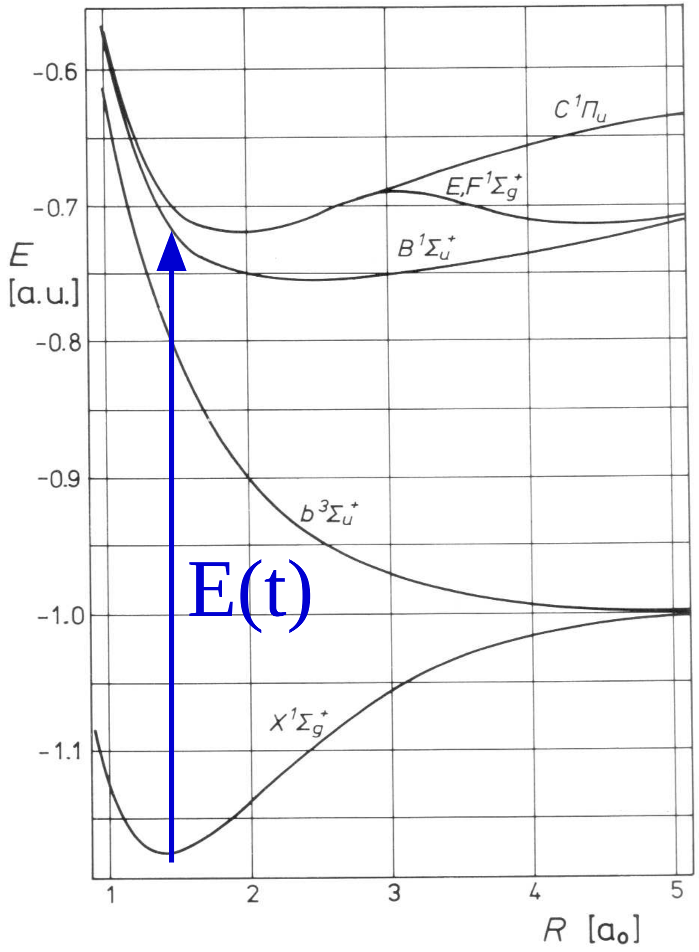
TD-CI: TD-CIS, TD-CIS(D), TD-CISD, ... TD-CISD··N=Full-CI (FCI)

TD-CASSCF(N,M): TD-CASSCF (N,N/2) = TD-HF, ..., TD-CASSCF(N,K)=FCI

A SIMPLE EXAMPLE: THE H_2 MOLECULE

- **TD-CISD (=FCI) treatment:** aug-cc-pV5Z; $|0\rangle \rightarrow |1\rangle$ laser excitation

  $\sin^2 \pi$ pulses $\boxed{E_z(t) = E_0 \sin^2(\pi t/2\sigma)\ \cos(\omega_{10} t)}$ with FWHM σ



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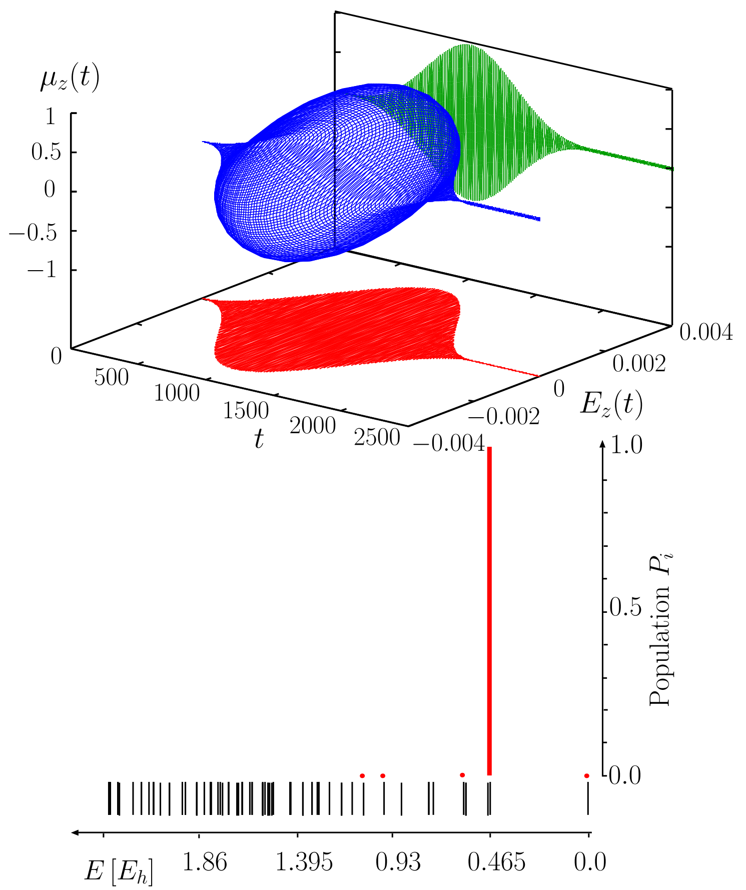
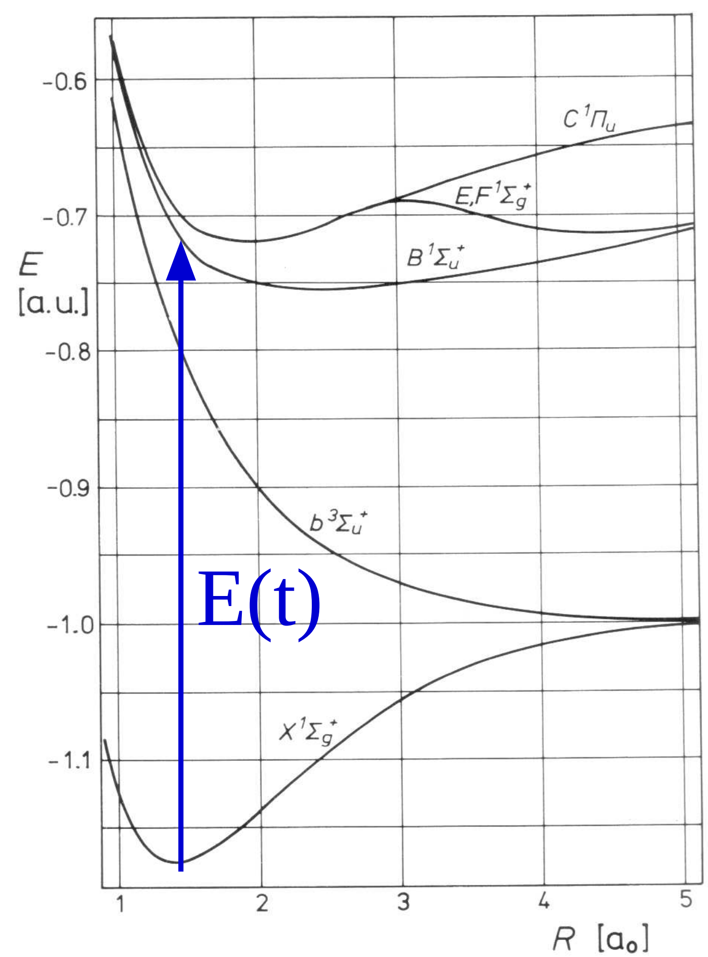
"long pulse": $\sigma = 1000\ \hbar/E_h$





single-photon, state-to-state

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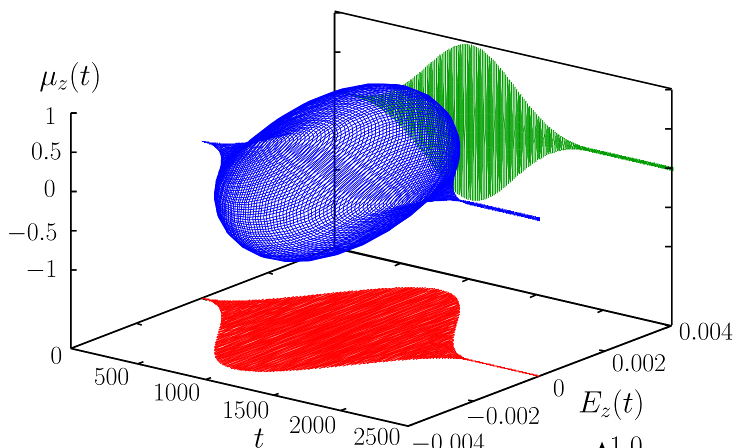
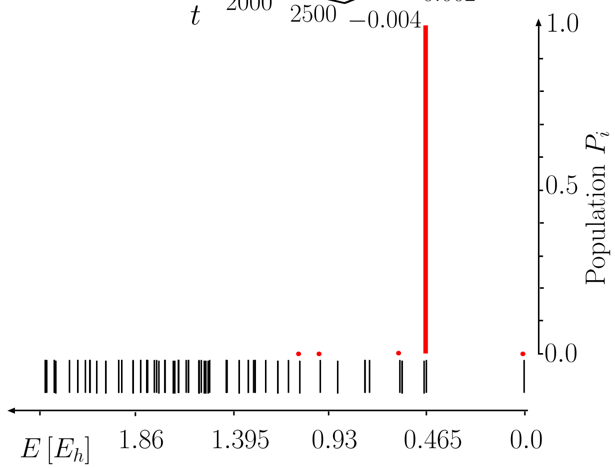
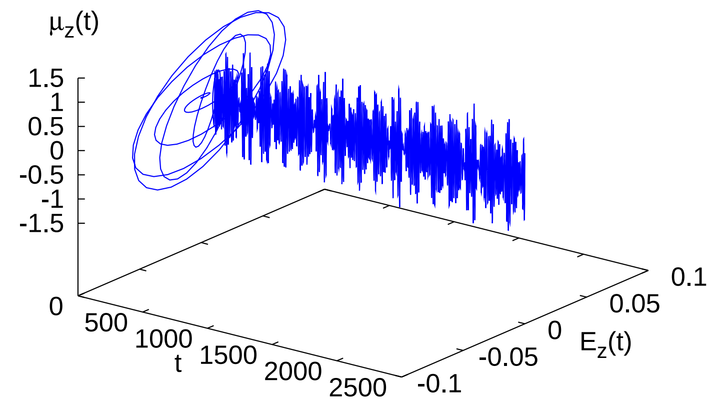
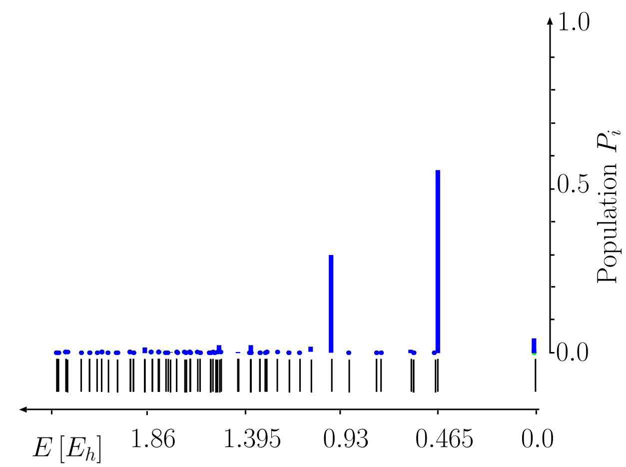




single-photon, state-to-state

"short pulse": $\sigma = 50\ \hbar/E_h$

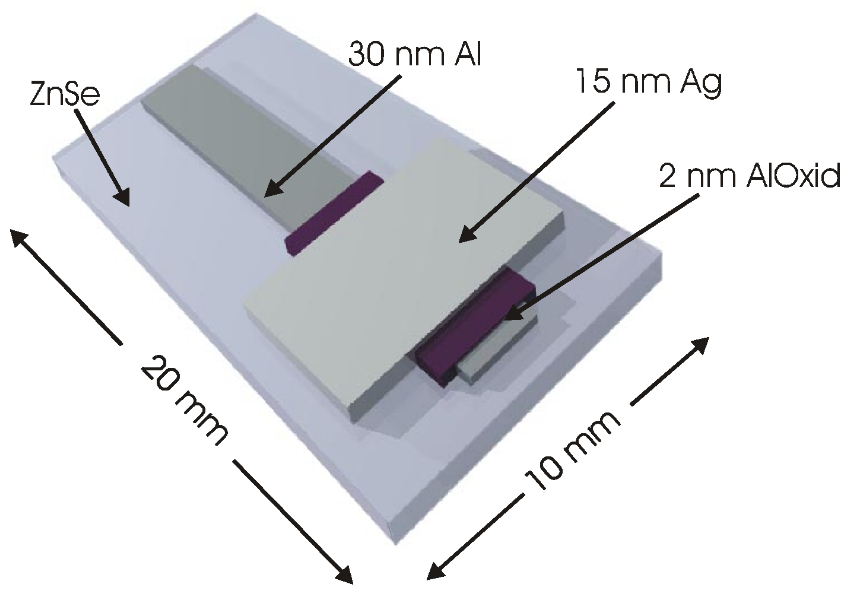




multi-photon, wavepacket

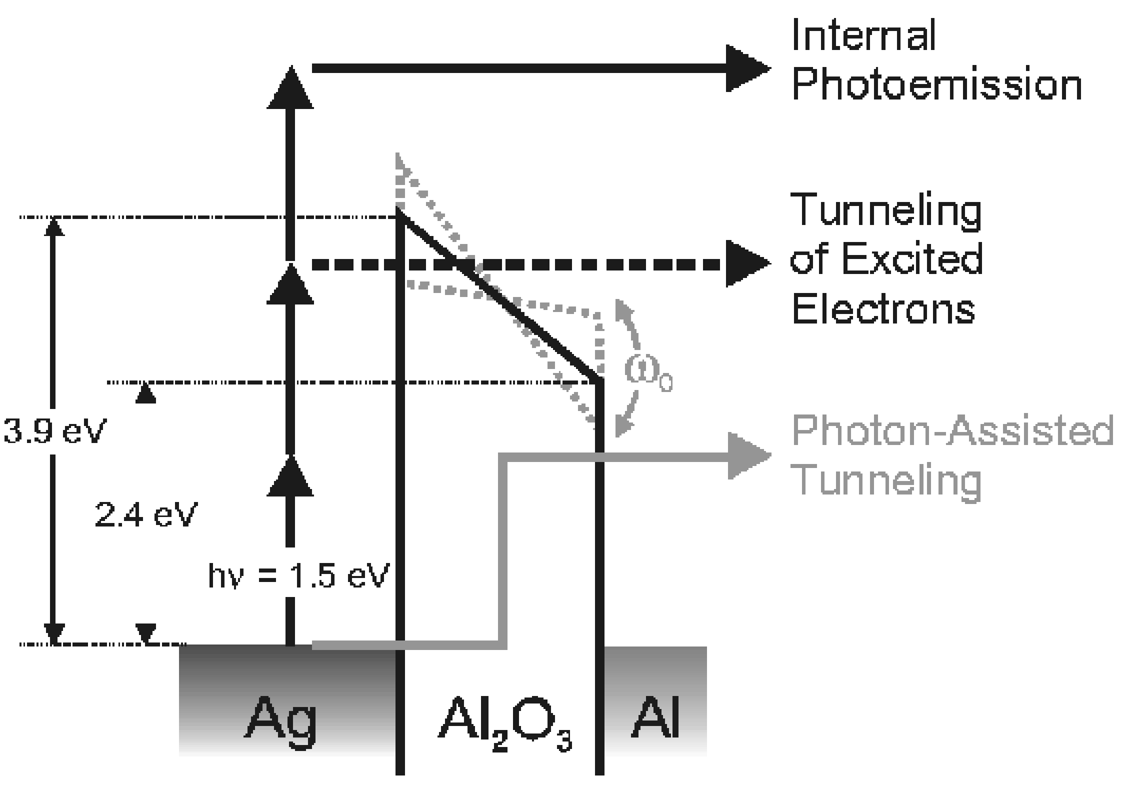
TRANSPORT: MIM JUNCTIONS

- Metal-Insulator-Metal junctions



- Possible processes

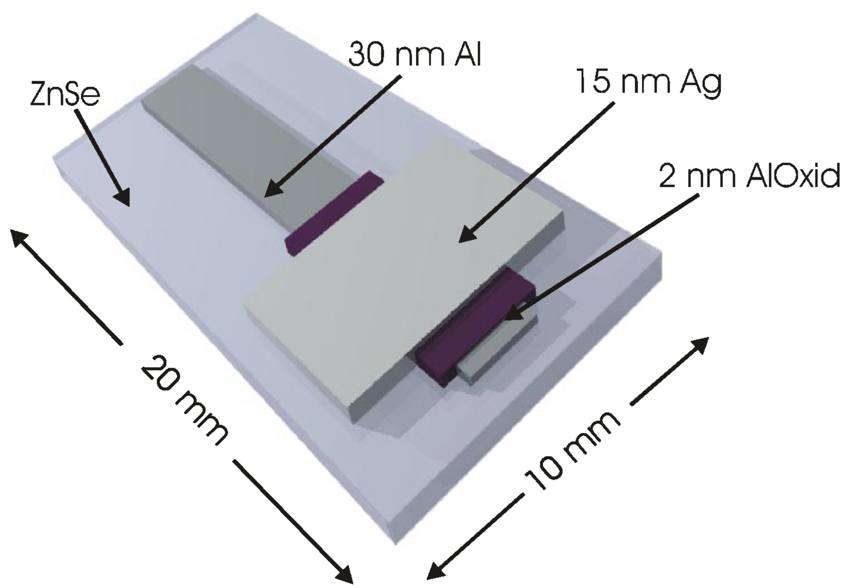
$(\hbar\omega = 1.5 \text{ eV})$



Klamroth et al., Appl. Phys. A (2003), PRB **61**, 245421 (2003)

TRANSPORT: MIM JUNCTIONS

- **Metal-Insulator-Metal junctions**

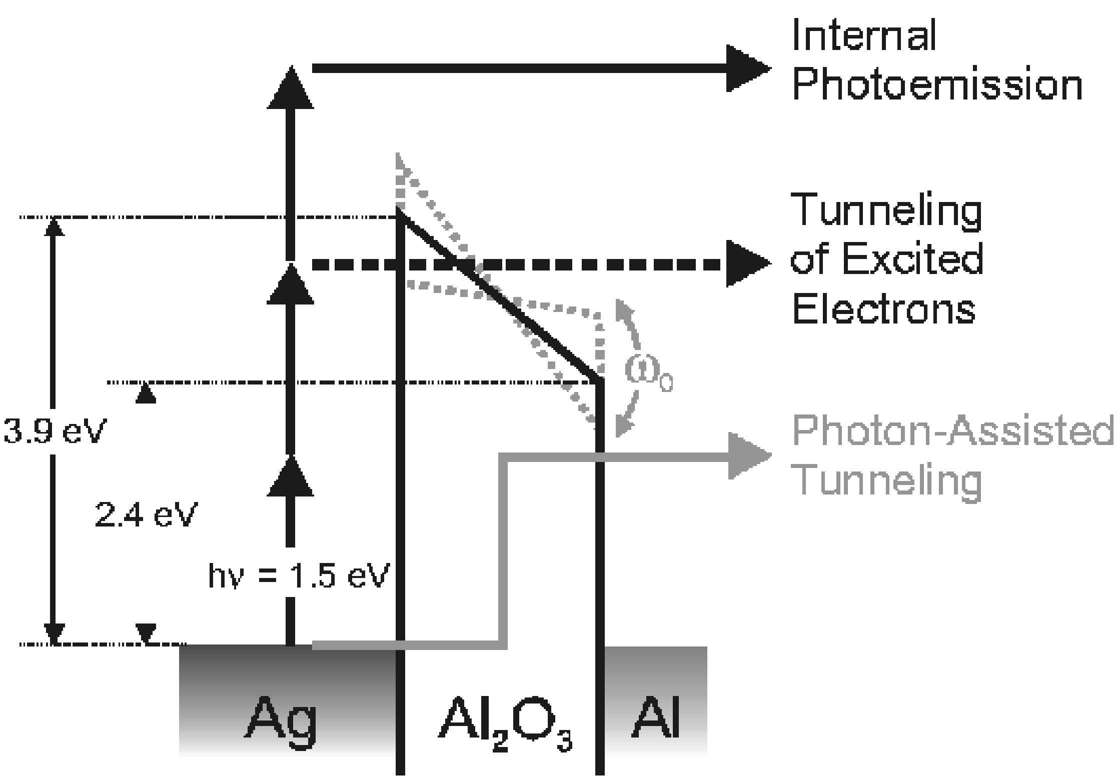


- **"Control parameters"**

1. bias V
2. laser pulses $E_z(t)$
3. film thickness

- **Possible processes**

($\hbar\omega = 1.5$ eV)

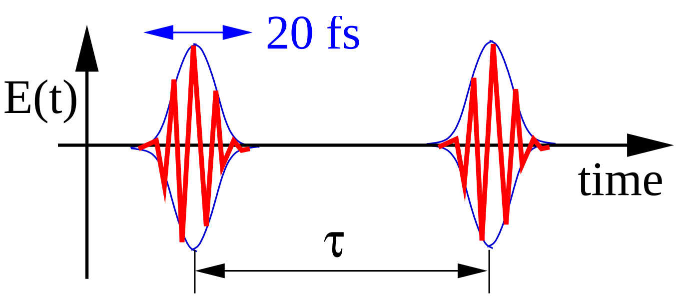


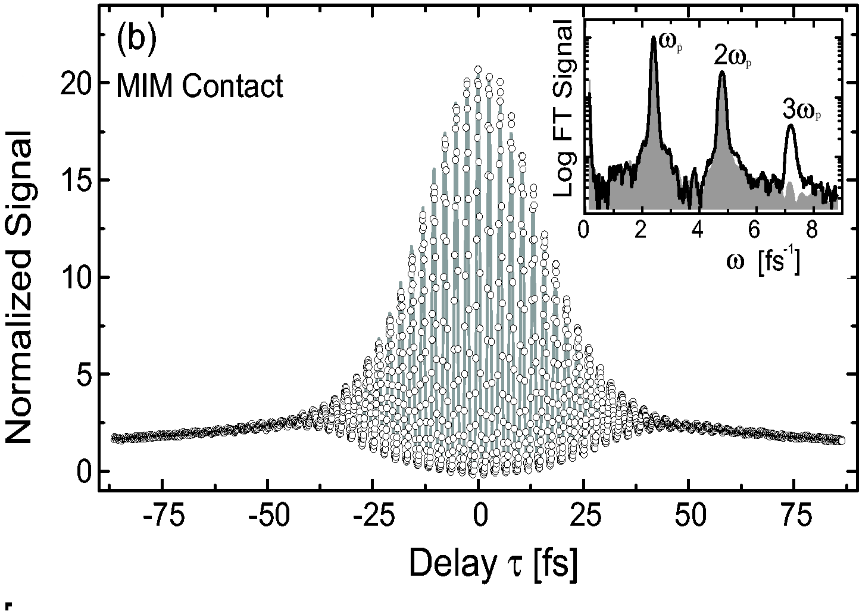
Klamroth et al., Appl. Phys. A (2003), PRB **61**, 245421 (2003)

TRANSPORT: MIM JUNCTIONS

- **Experiment: 2-pulse-correlation**

  Pfeiffer et al., Würzburg





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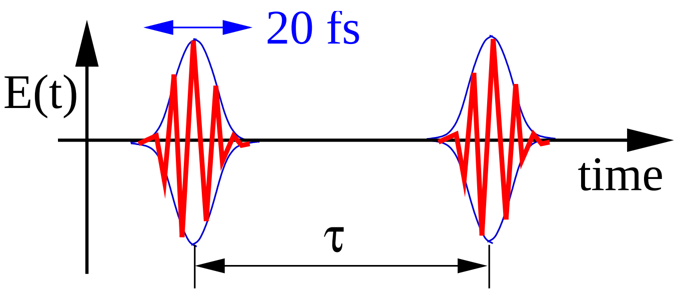
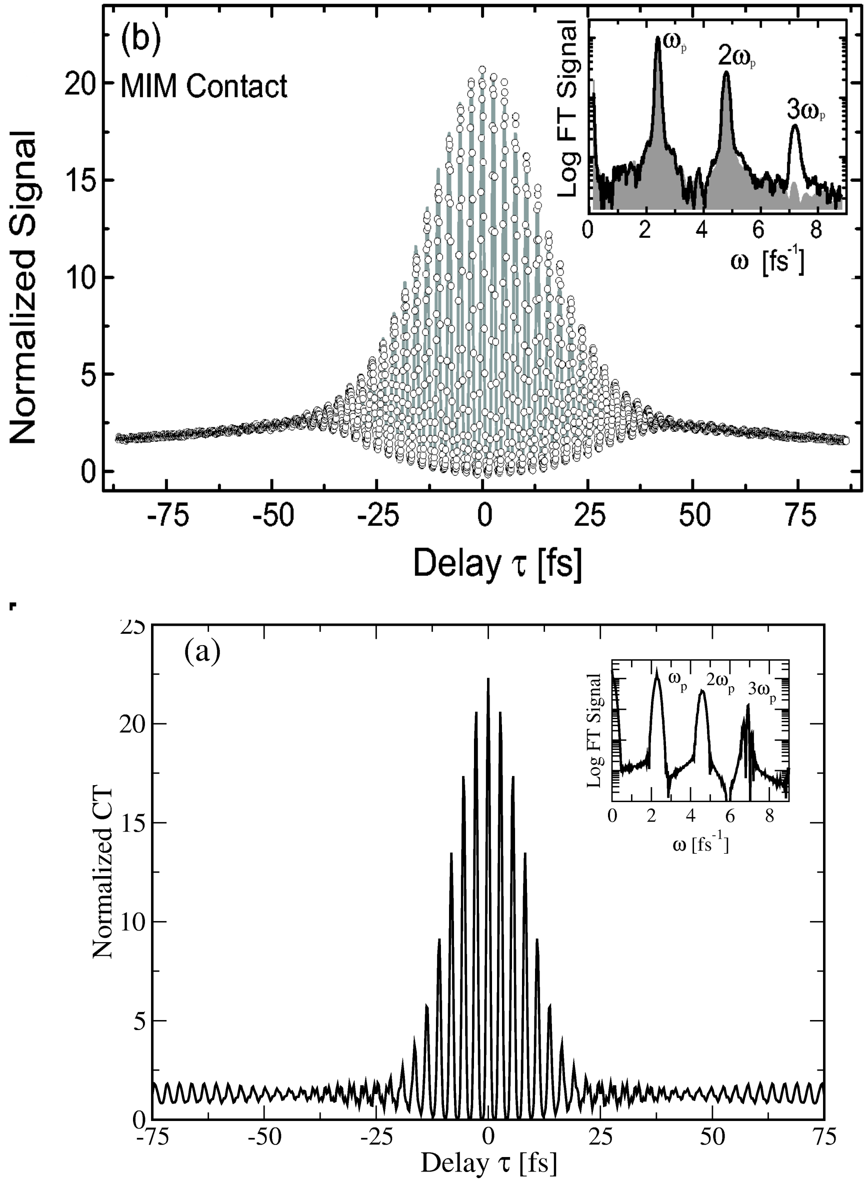
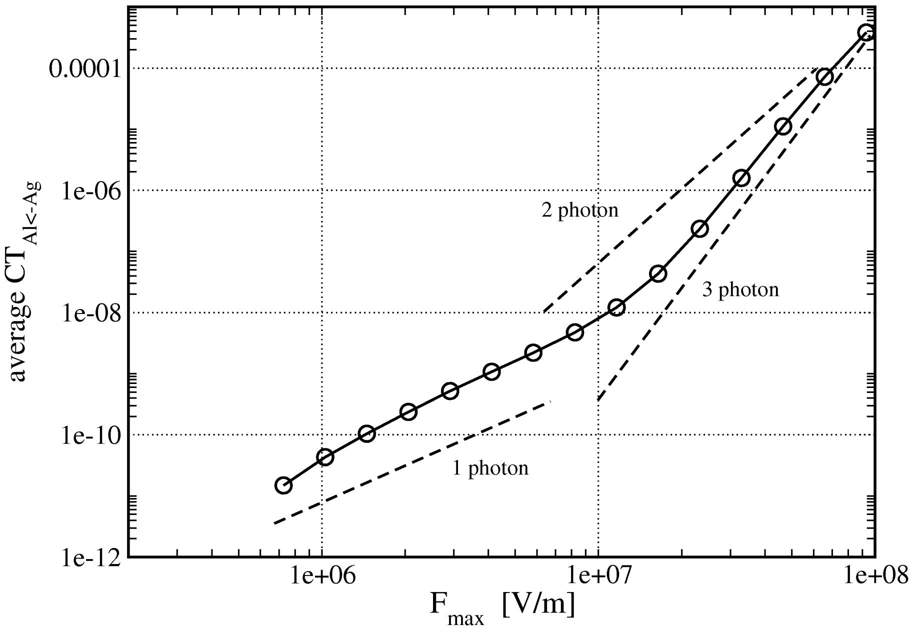




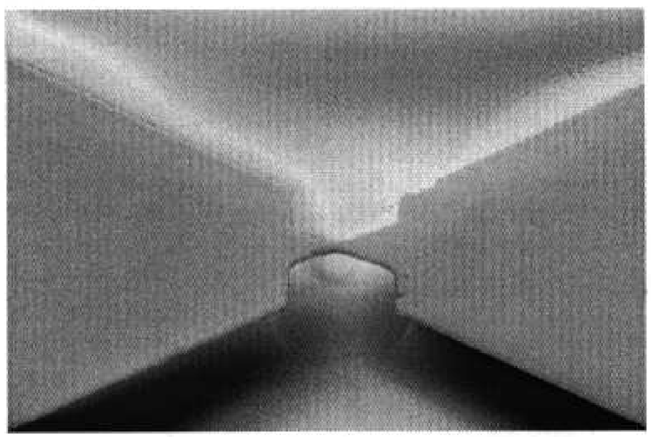
- **Theory**
  TD-CIS, 1D-Jellium

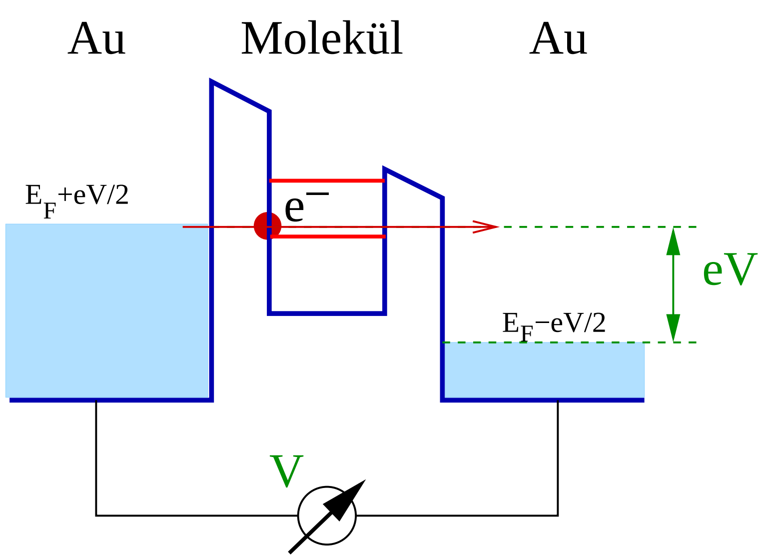


Klamroth et al., Appl. Phys. A (2003); PRB **61**, 245421 (2003)

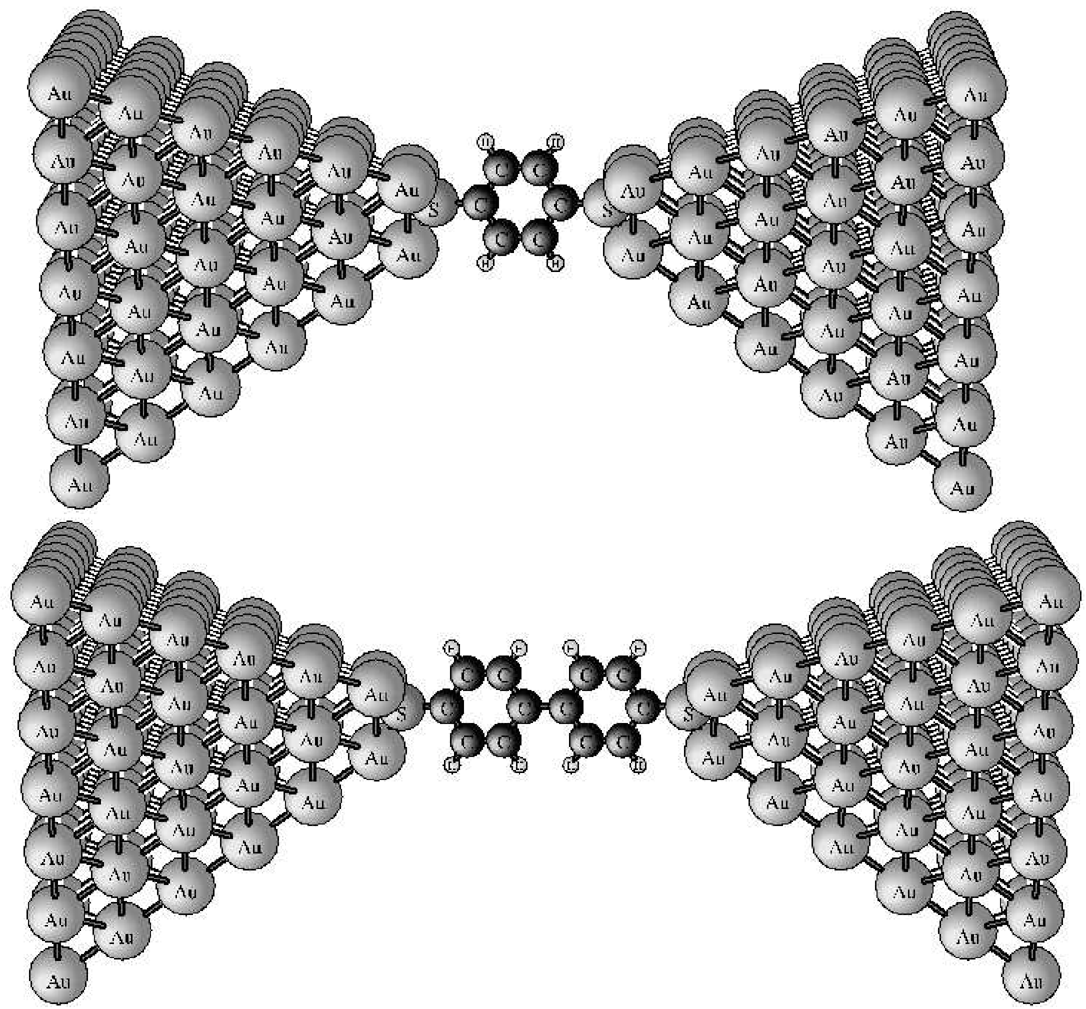
V-TRANSPORT: MOLECULAR JUNCTIONS

- Break junctions



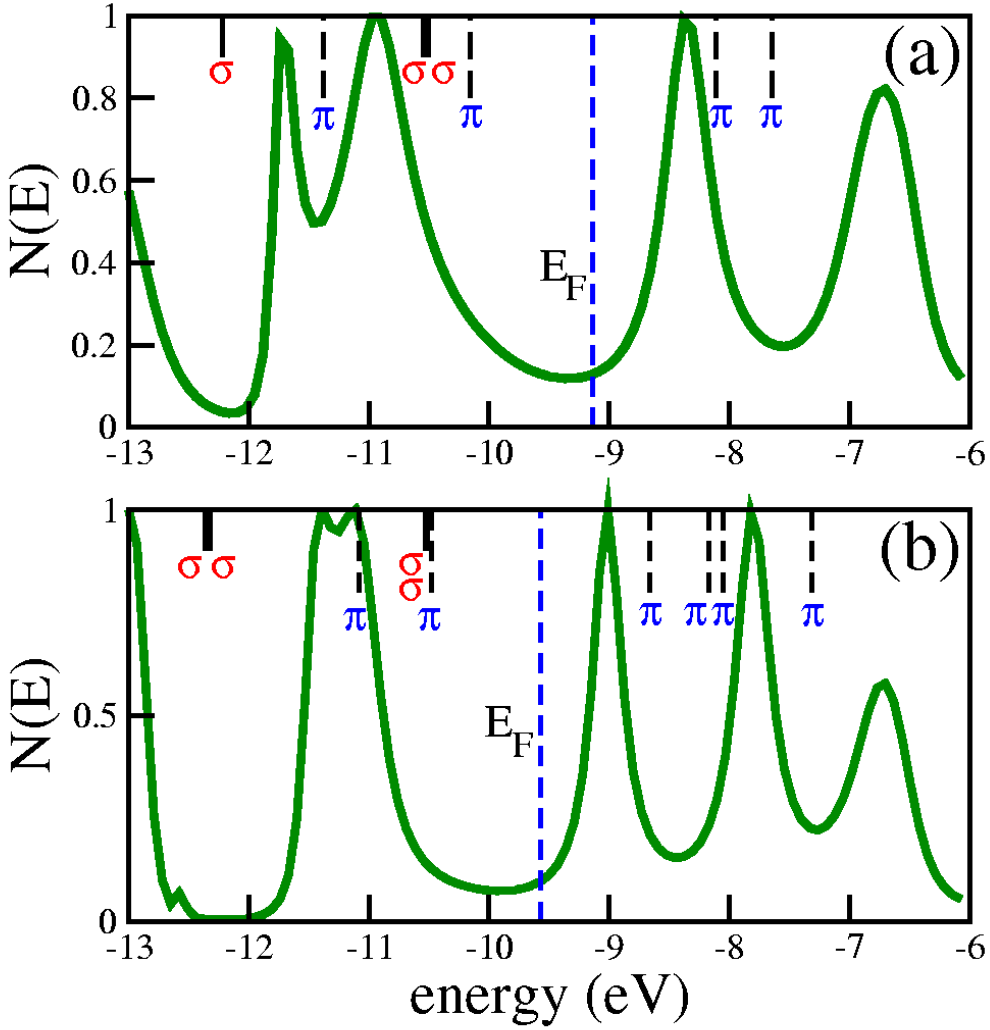


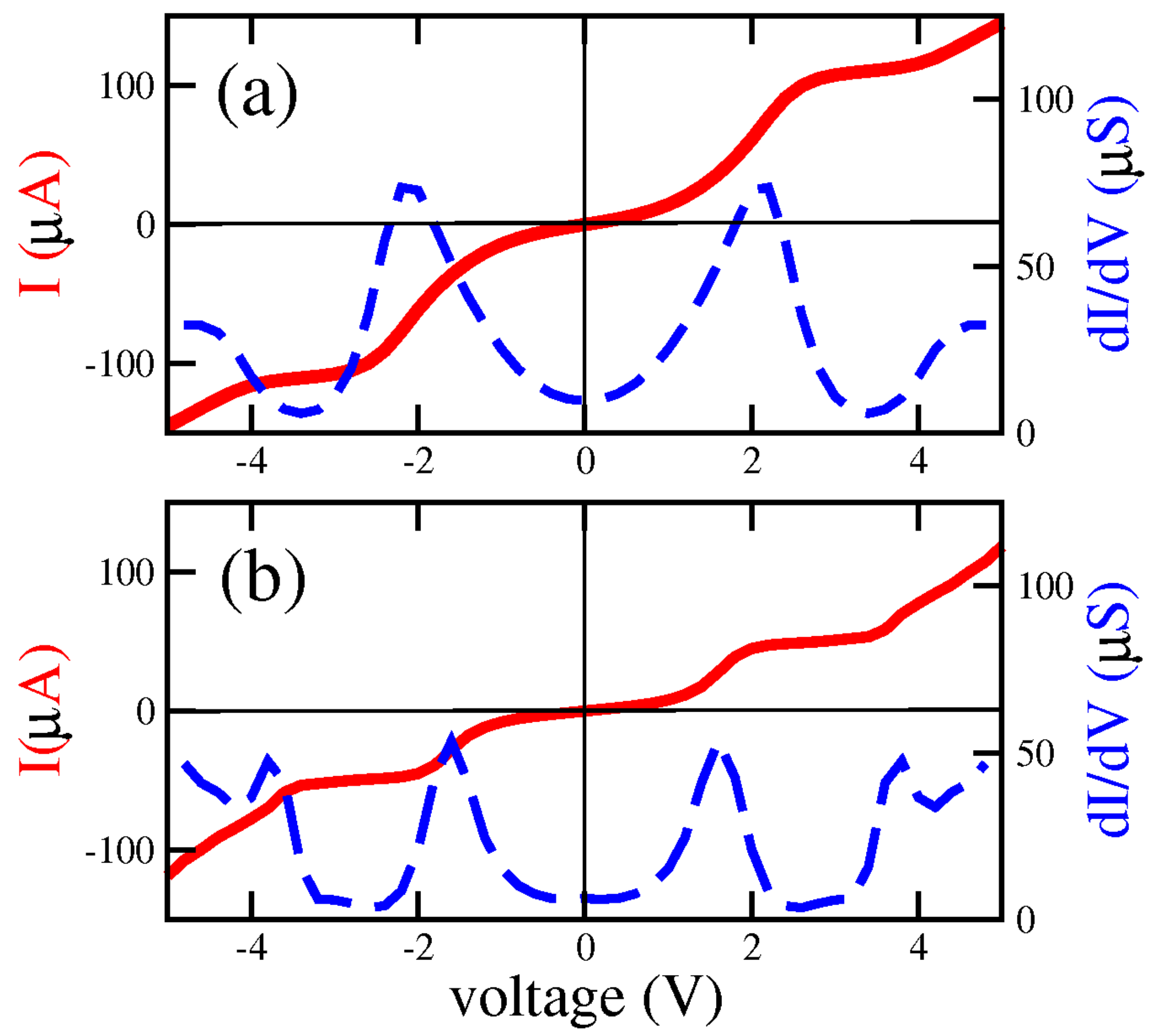
- Benzene-dithiolates



V-TRANSPORT: BENZENE-DITHIOLATES

- **Transmission N(E)**
- **I(V) curves**



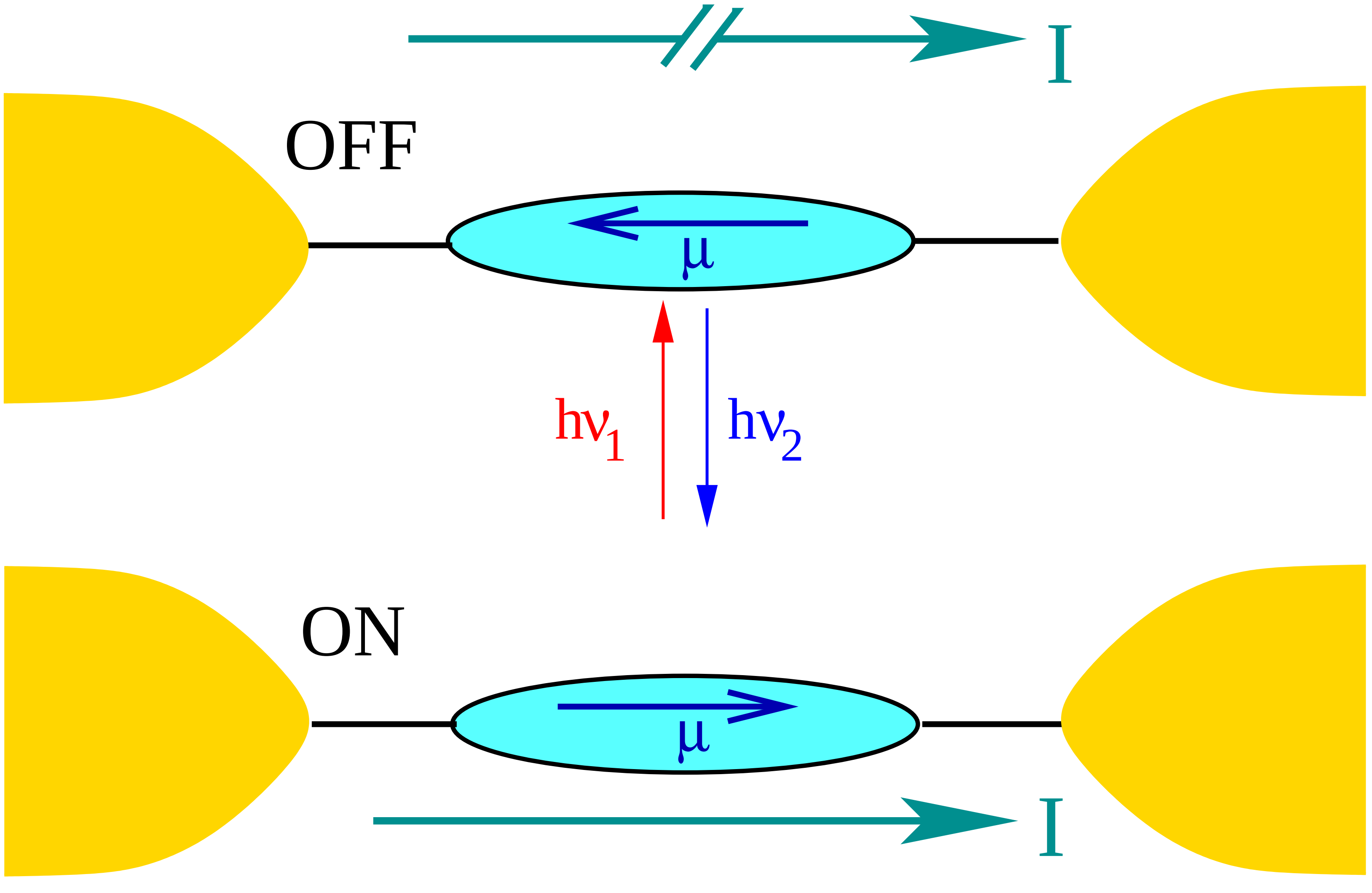


EHT Greens' functions with absorbing boundaries

Kopf, P.S., CPL **386**, 17 (2004)

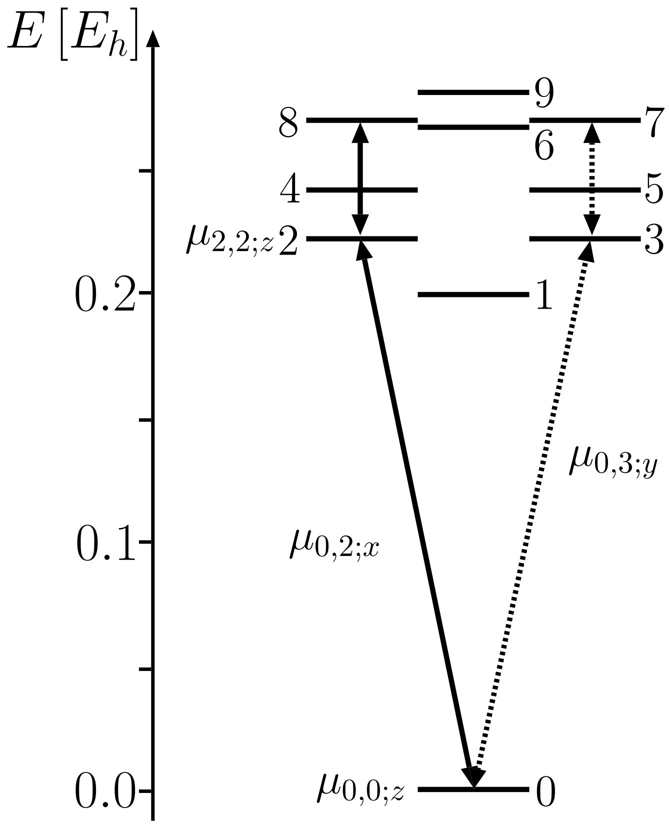
MOLECULAR JUNCTIONS: PHOTOSWITCHING

- **E.g., molecular dipole switch**



LiCN: A MOLECULAR DIPOLE SWITCH?

- **CIS(D) /6-31G* state energies:** $E_i^{\mathrm{CIS(D)}} = E_i^{\mathrm{CIS}} + E_i^{\mathrm{(D)}}$



- **Dipole moments:**

state	character	dipole μ_z (e a_0)
0	Li^+CN^-	-3.71
2/3	LiCN	+2.80
7/8	$Li^{\delta+}CN^{\delta-}$	-1.18

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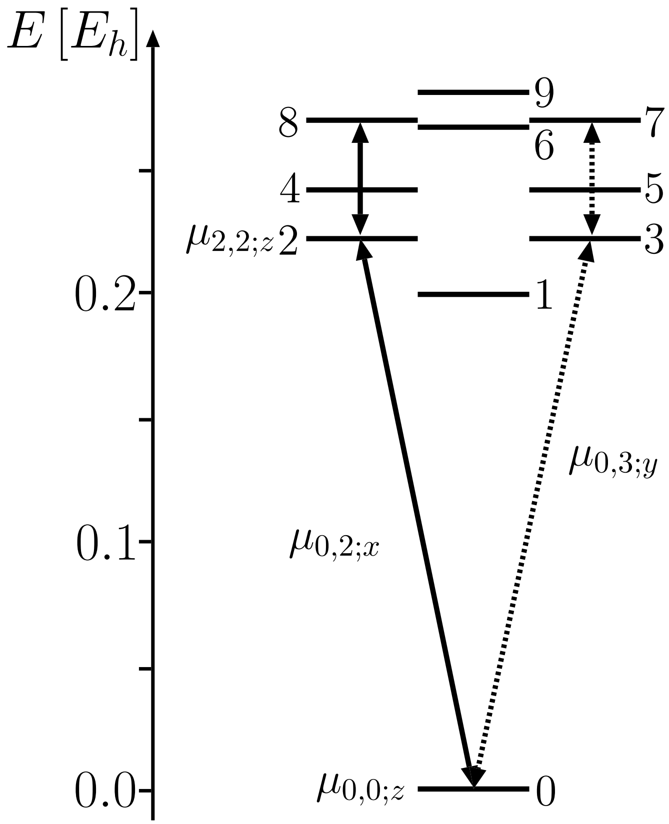

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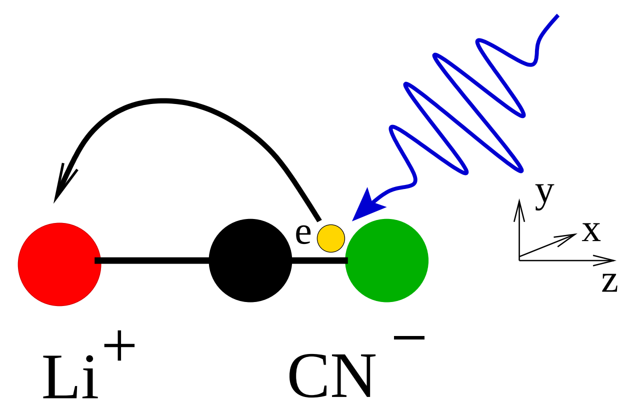
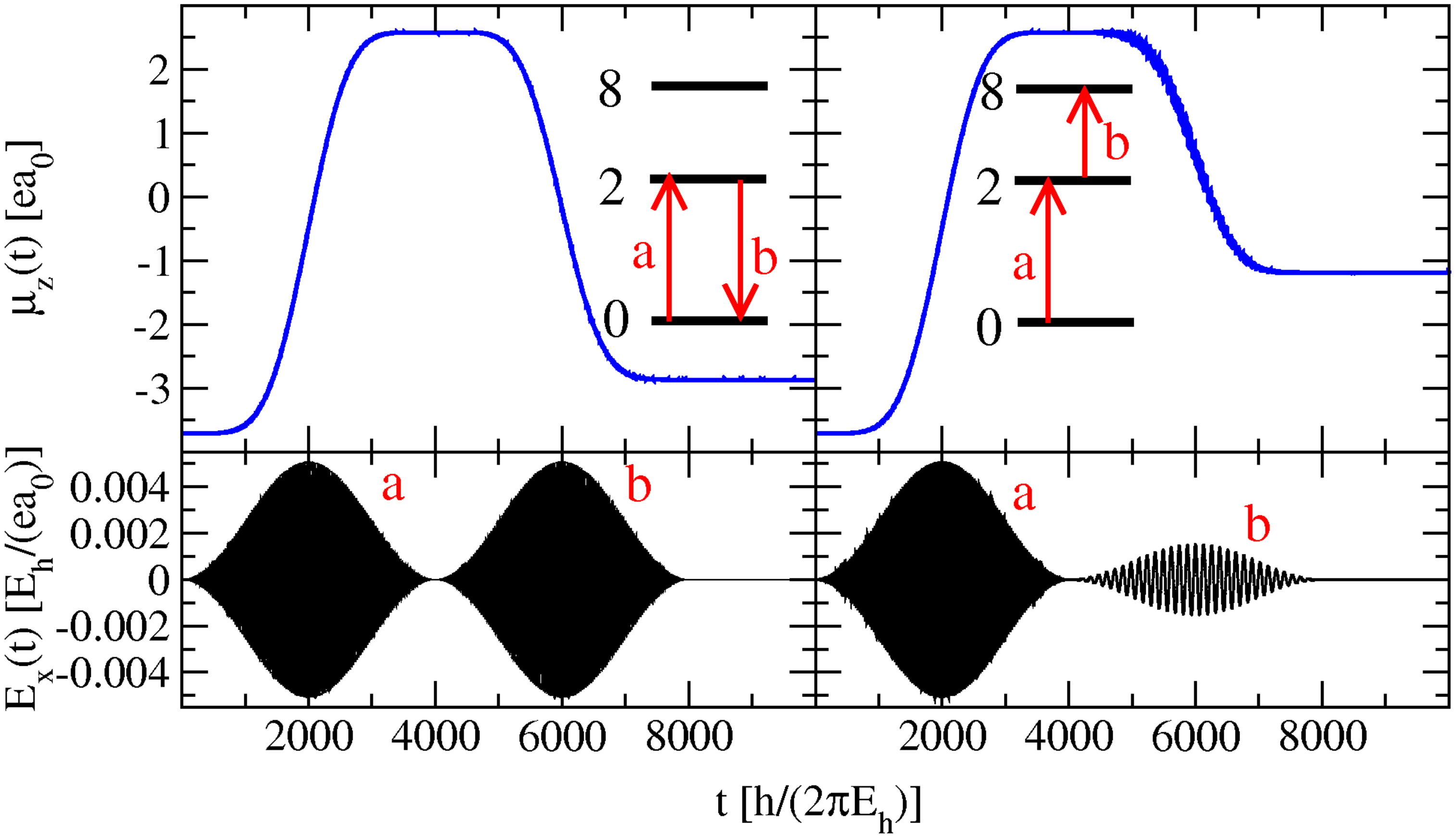


- **Goal: Laser-pulse controlled dipole switch**

LiCN: DIPOLE SWITCH

- **Switching sequences:** "Long" x-polarized π pulses



reversible and "branched switching"

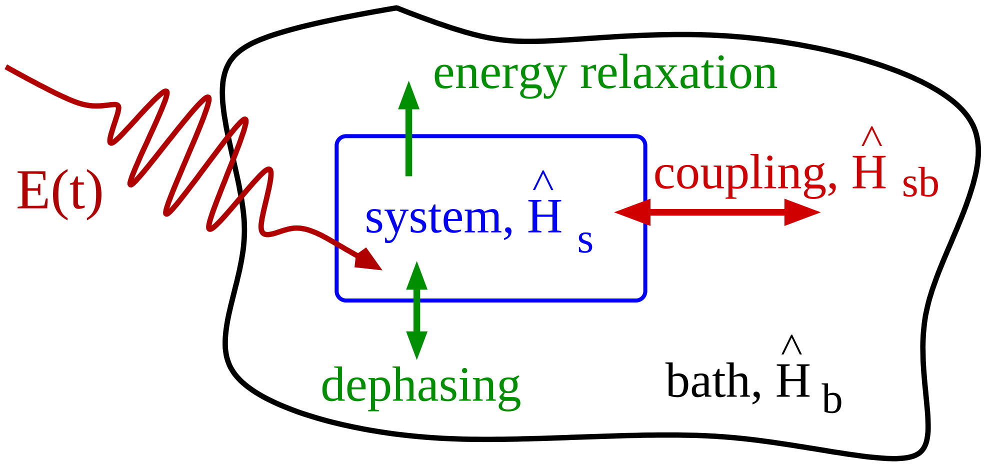
- **What about environmental effects (spontaneous emission)?**

P. Krause, T. Klamroth, PS, JCP **123**, 074105 (2005)

ELECTRON DYNAMICS IN AN ENVIRONMENT

- **Liouville-von Neumann equation for laser-driven electrons**

$$\frac{\partial \hat{\rho}_s}{\partial t} = \underbrace{-\frac{i}{\hbar}[\hat{H}_{el} - \underline{\hat{\mu}}\underline{E}(t), \hat{\rho}_s]}_{\text{system}} + \underbrace{\left(\frac{\partial \hat{\rho}_s}{\partial t}\right)_D}_{\text{dissipation}}$$



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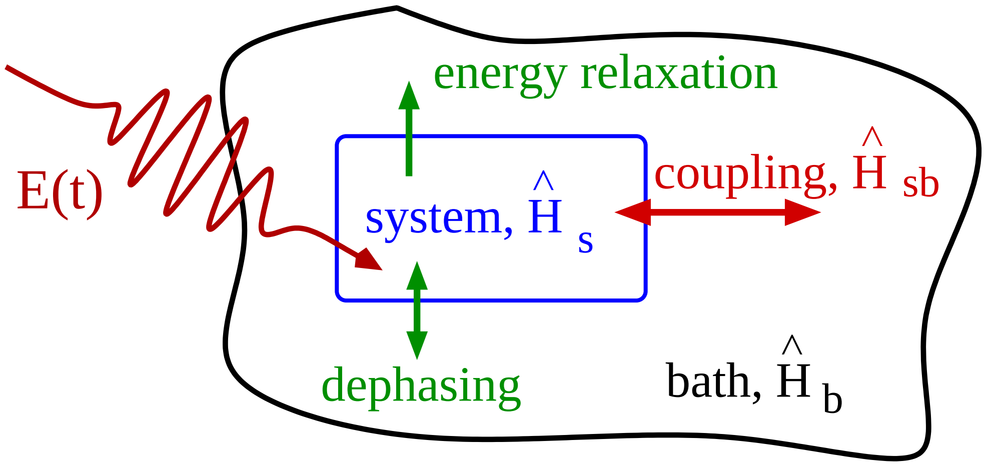
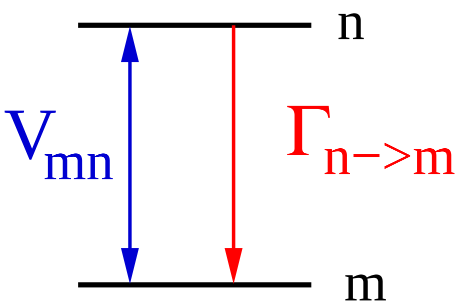


- **Lindblad dissipation, eigenstate basis**

Populations: Diagonal elements of $\hat{\rho}_s$

$$\frac{d\rho_{nn}}{dt} = \sum_p^N [-\frac{i}{\hbar}[V_{np}(t)\rho_{pn} - \rho_{np}V_{pn}(t)] + (\Gamma_{p\to n}\rho_{pp} - \Gamma_{n\to p}\rho_{nn})]$$



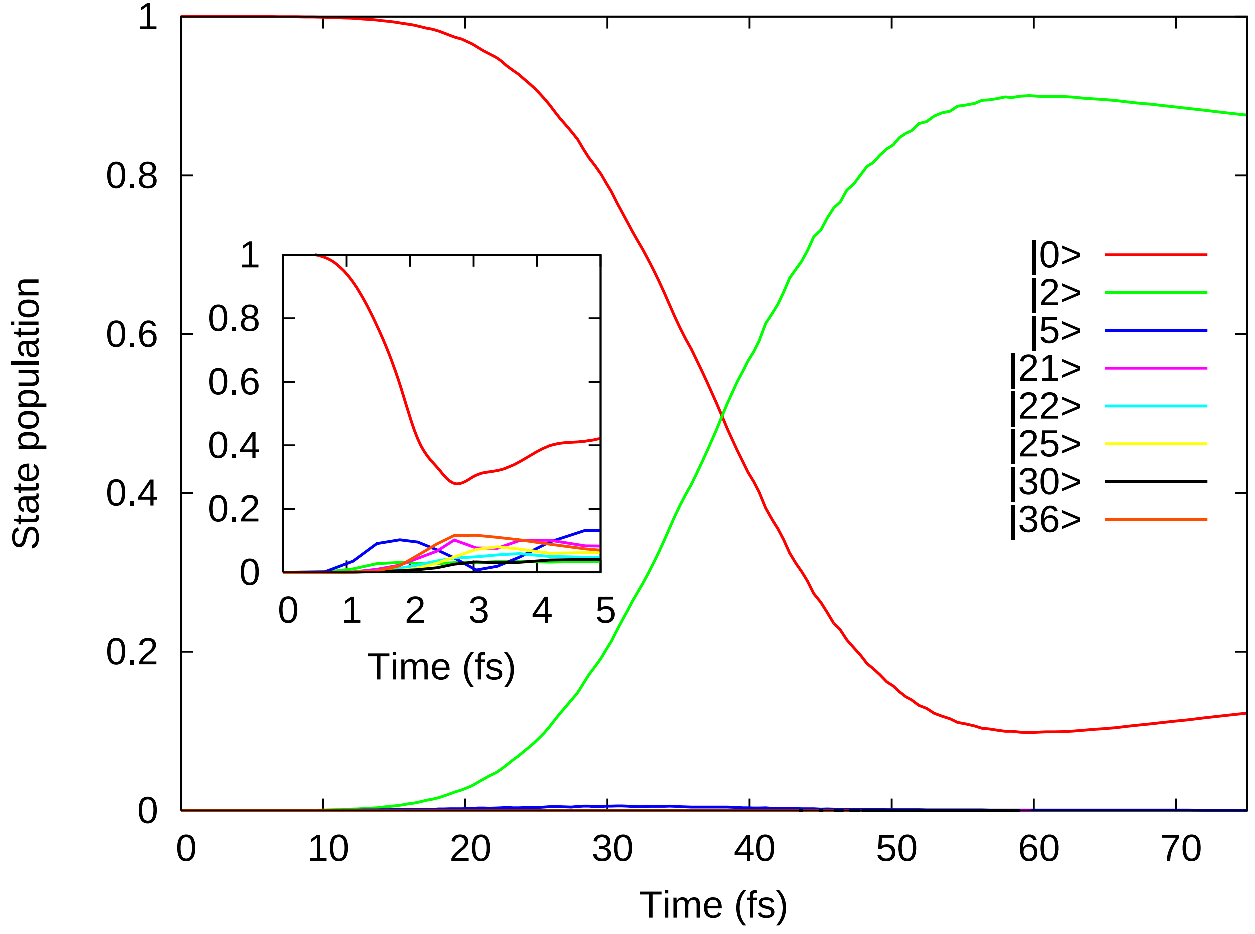
dipole coupling $V_{mn}(t) = -\underline{\mu}_{mn}\underline{E}(t)$

energy relaxation rates $\Gamma_{n\to m}$

dephasing enters $\dot{\rho}_{mn}$ *via* dephasing rates γ_{mn}

DISSIPATIVE MANY-ELECTRON DYNAMICS

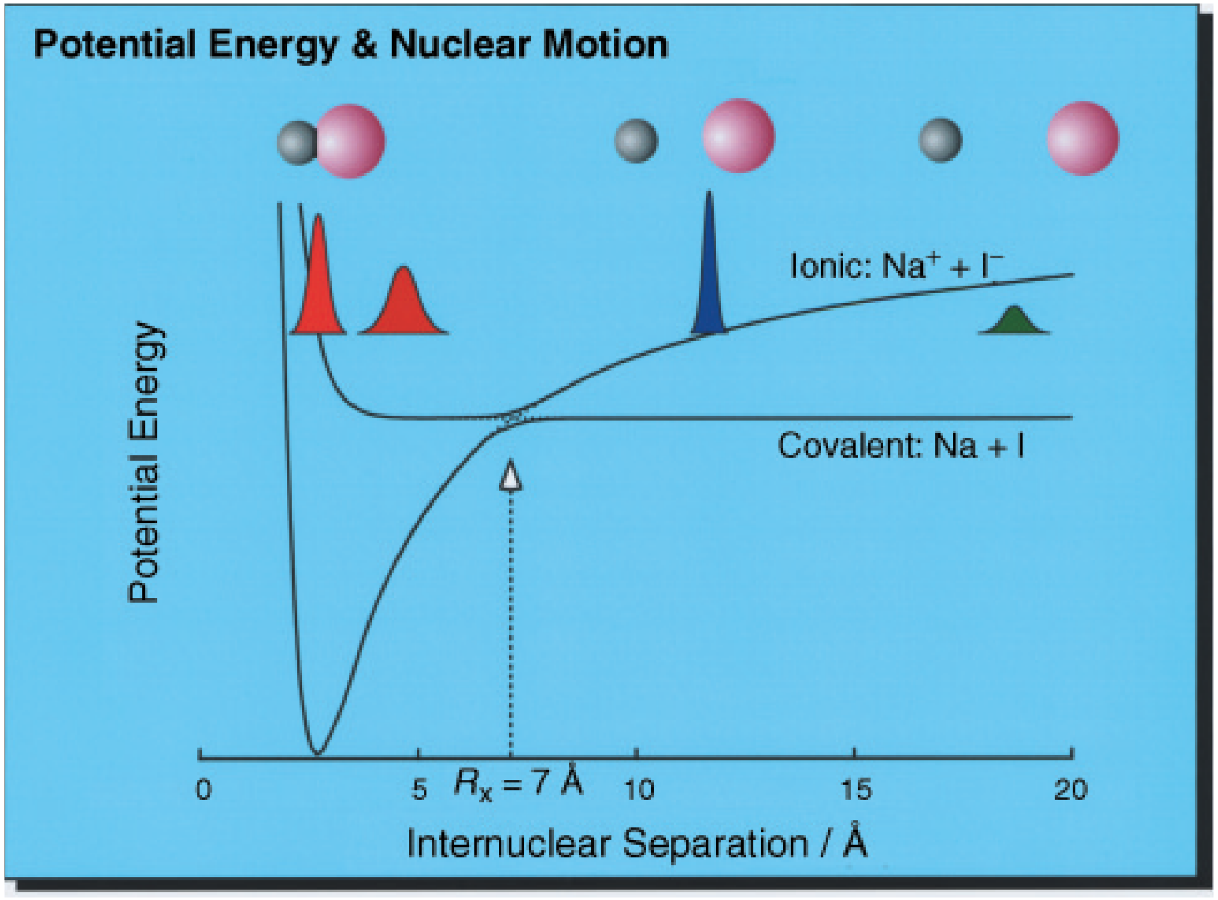
- **Switching of LiCN:** $\Gamma^{-1}_{2\to0} = 430$ fs; 5 and 75 fs π pulses



short pulses needed, less selective

J.C. Tremblay, T. Klamroth, PS, JCP **129**, 084320 (2008)

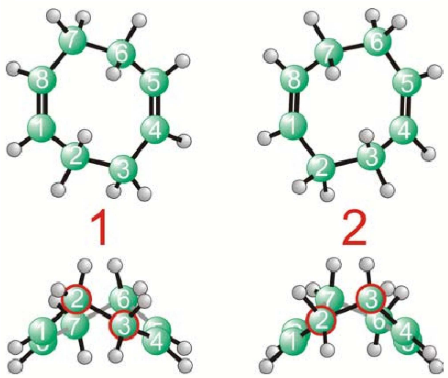
NUCLEAR (ATOM) DYNAMICS

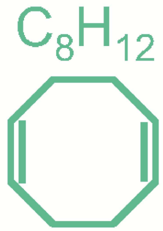


SWITCHING AGAIN: COD ON Si(100)

- **STM-induced conformational switching at low T**

1,5-cyclooctadiene





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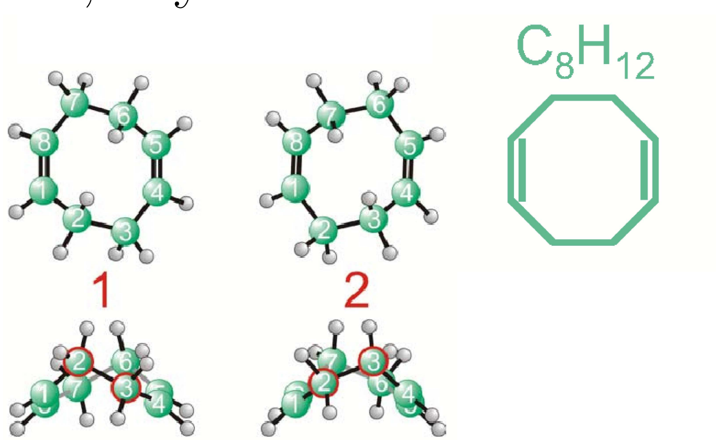

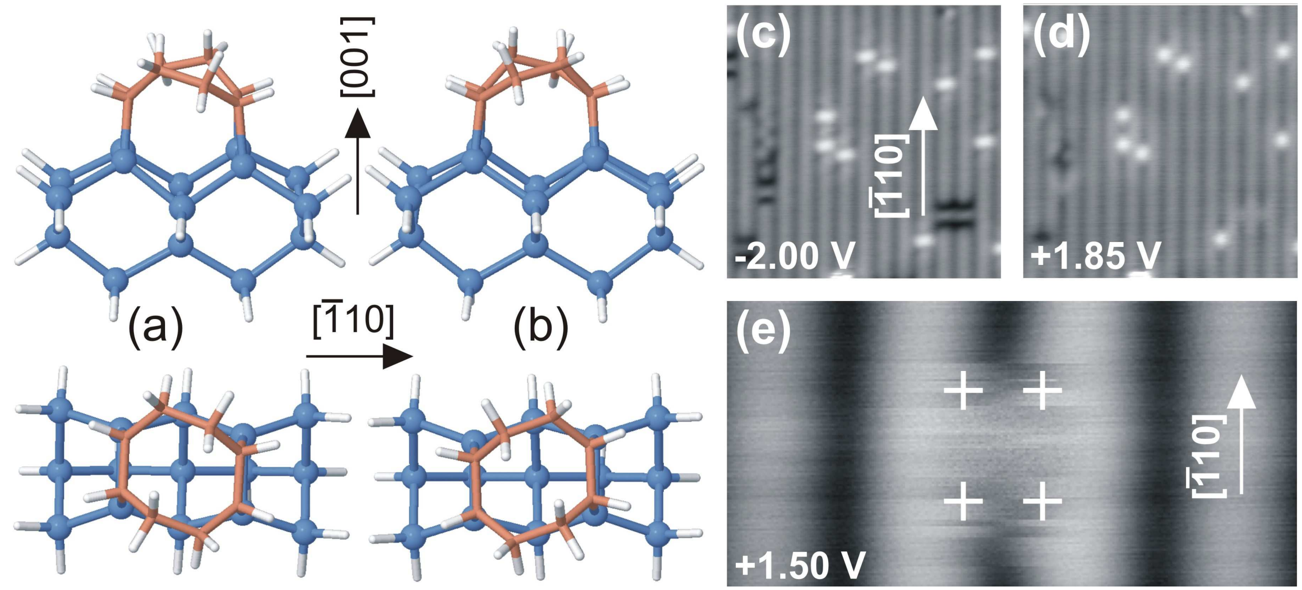

COD@$Si_{15}H_{16}$ cluster, B3LYP-6/31G*

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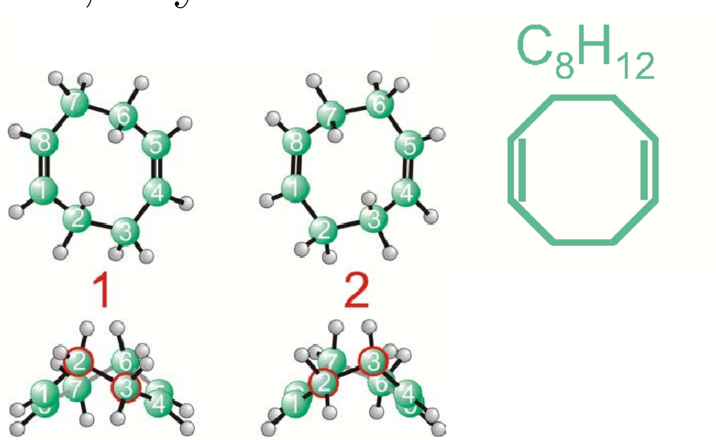
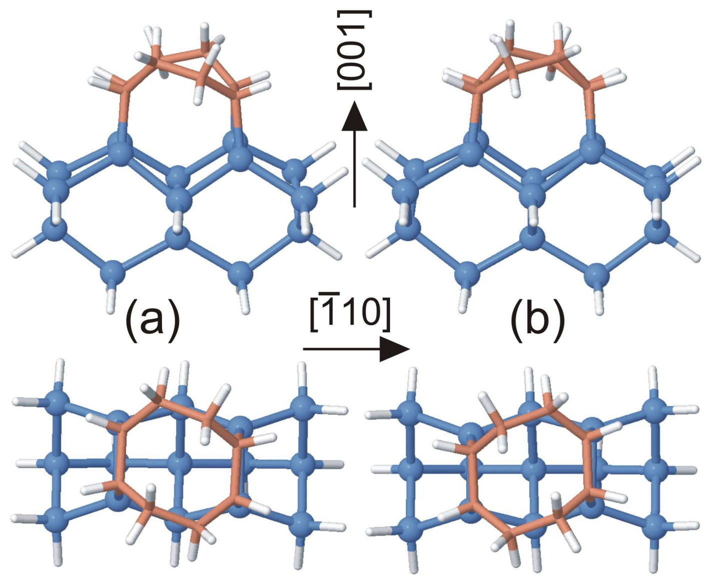
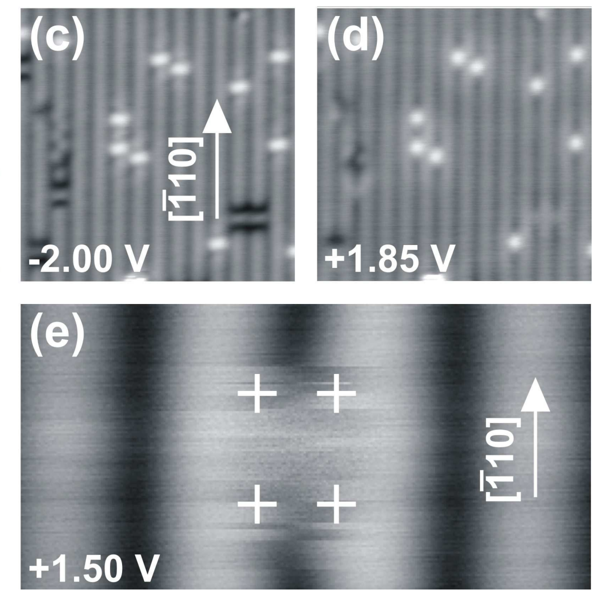
1,5-cyclooctadiene







COD@$Si_{15}H_{16}$ cluster, B3LYP-6/31G*

Experiment[1]:

- switching at $T = 5$ K
- rate $R_{sw}(+1.5\text{V}, 0.7\text{nA}) \approx 3.7$ Hz
- $R_{sw} \propto I$
- inelastic electron tunneling (IET)?

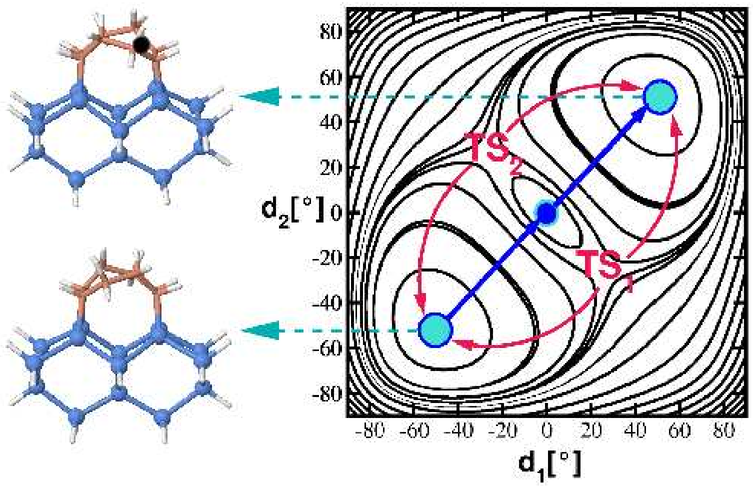
Theory:

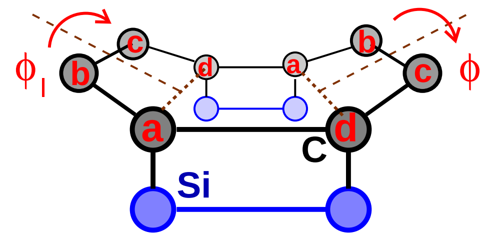
- Activation energy $E_a = 0.179$ eV
- Eyring: $R_{sw}^{therm}(5\text{K}) < 10^{-100}$ s^{-1}

[1] Nacci, Fölsch, PRB **77**, 121405(R) (2008)

COD@Si(100): MODEL AND THEORY

- **Ground state:** B3LYP/6-31G* cluster model





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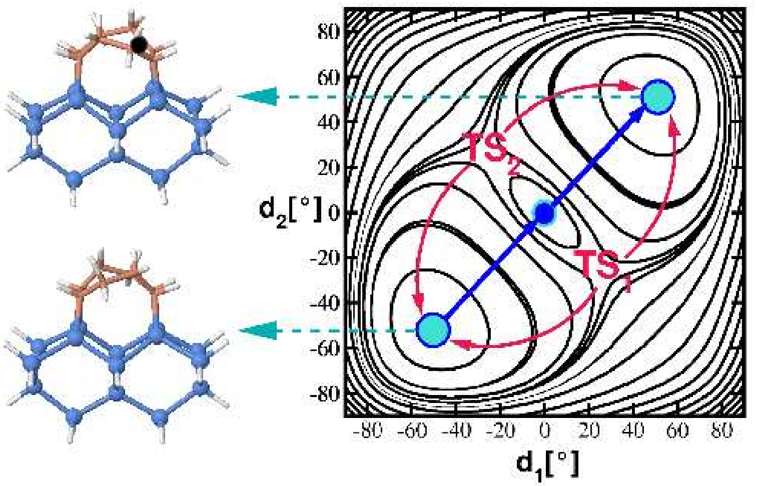
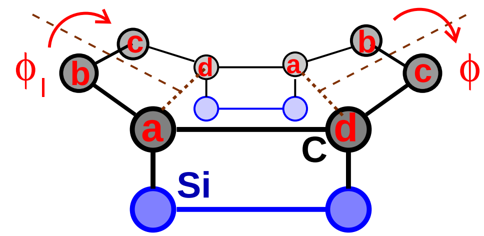
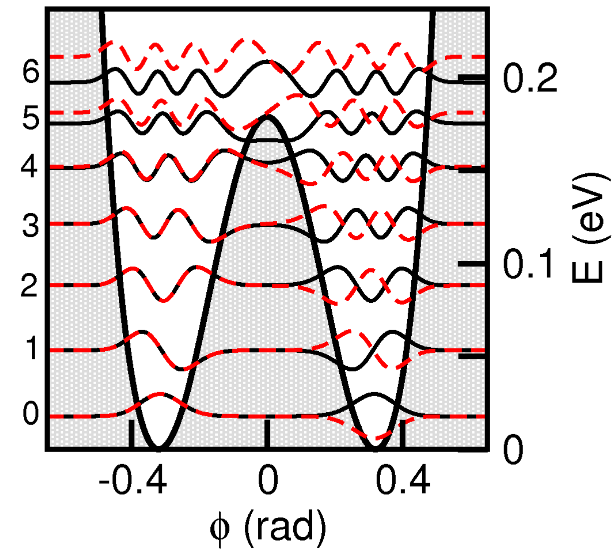




1D: $\phi = 1/2(\phi_l + \phi_r)$



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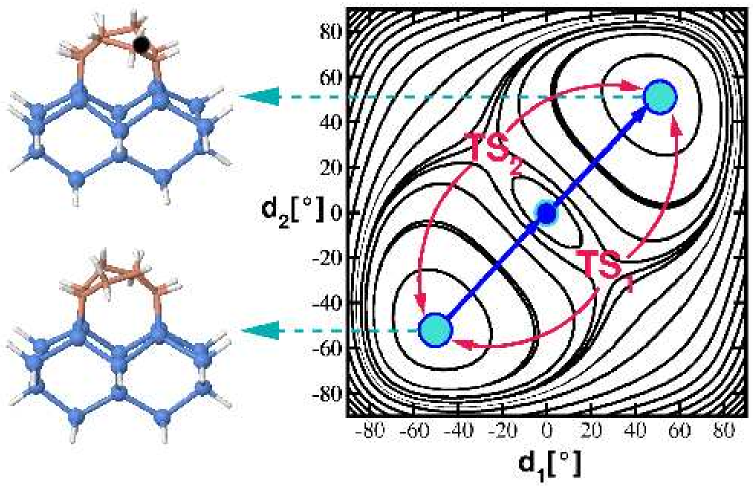
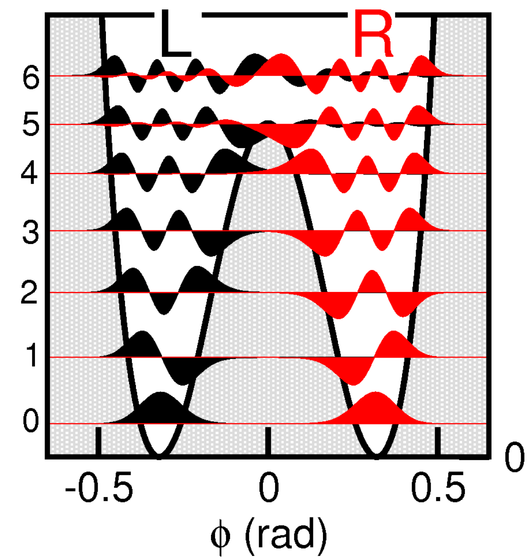


Left
Right



- **Use *localized* basis:** $|n_{L,R}\rangle = 1/\sqrt{2}(|n_+\rangle \pm |n_-\rangle)$

COD@Si(100): MODEL AND THEORY

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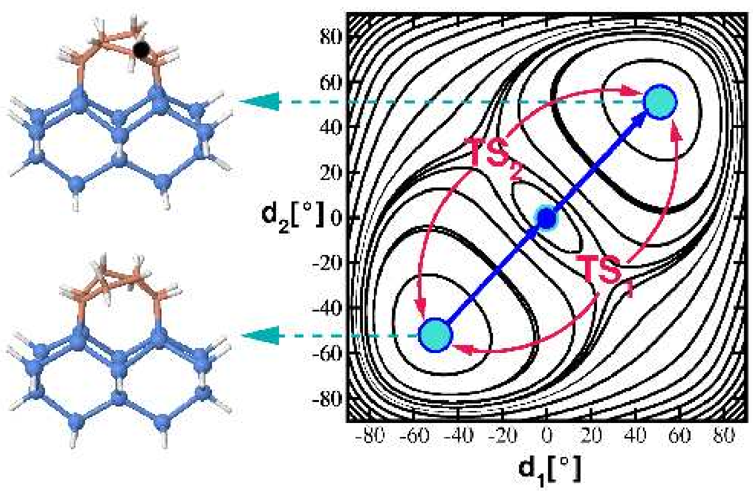
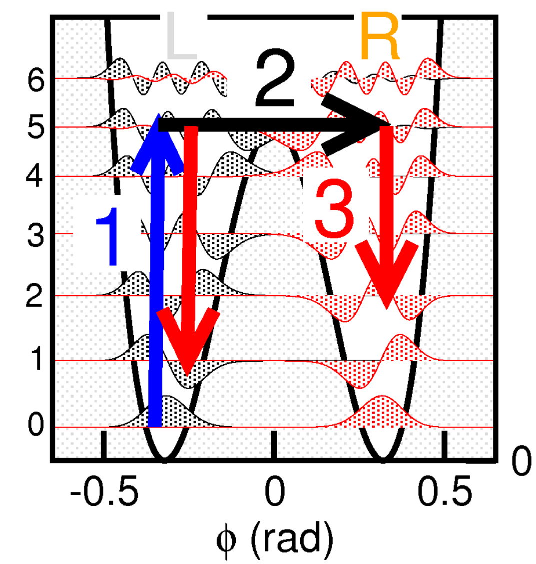


Start in $|0_L\rangle$:

1. excitation
2. tunneling
3. relaxation



- **LvN equation in *localized* state basis**

$$\frac{d\rho_{nn}}{dt} = \sum_p \left[-\frac{i}{\hbar} \underbrace{\left(H_{np}\rho_{pn} - \rho_{np}H_{pn} \right)}_{\text{tunneling}} + \underbrace{\left(\Gamma_{p\to n}\rho_{pp} - \Gamma_{n\to p}\,\rho_{nn} \right)}_{\text{excitation, relaxation}} \right]$$

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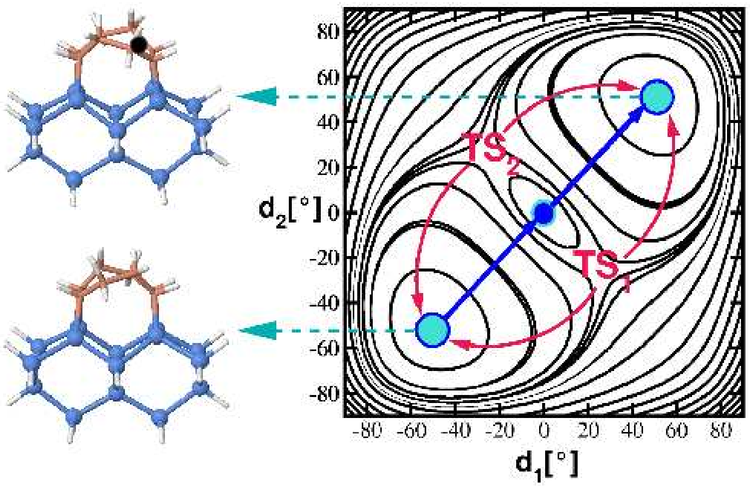

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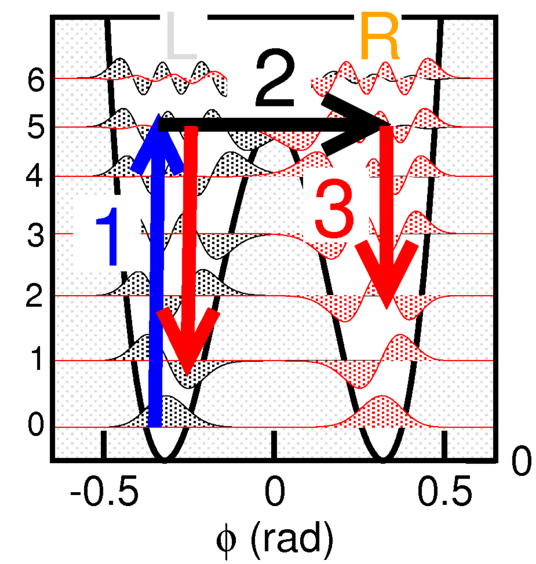

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$$\Gamma_{i\rightarrow f} = \Gamma^{relax}_{i\rightarrow f} + \Gamma^{IET}_{i\rightarrow f}(I,V)$$

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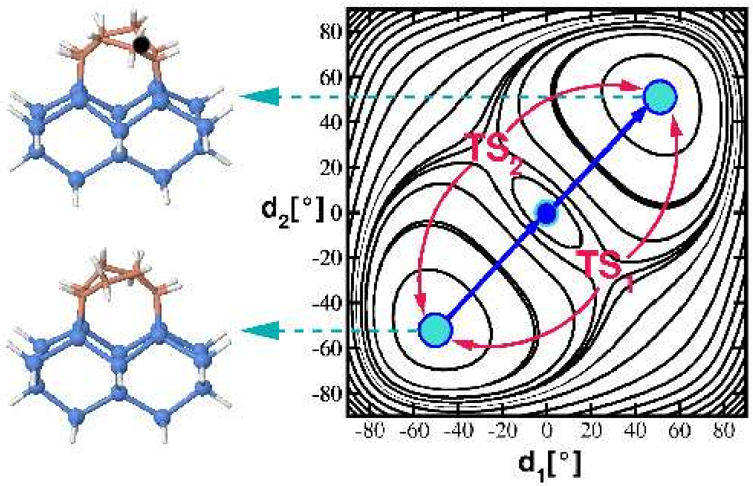

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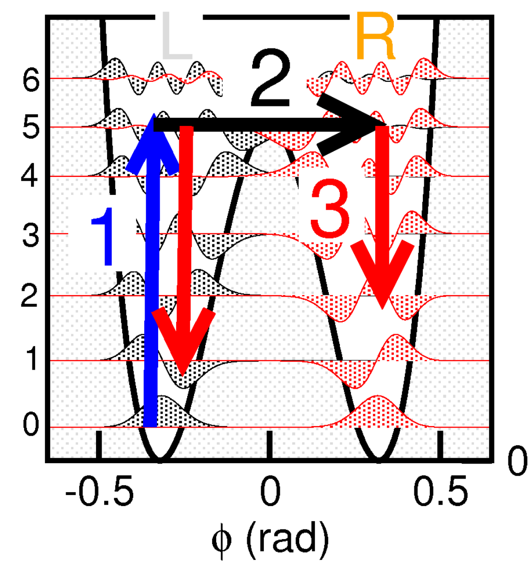

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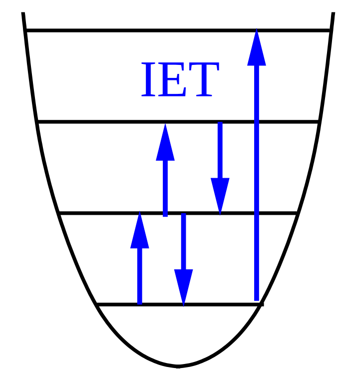

Persson, Demuth, Solid State Commun. **57**, 769 (1986)

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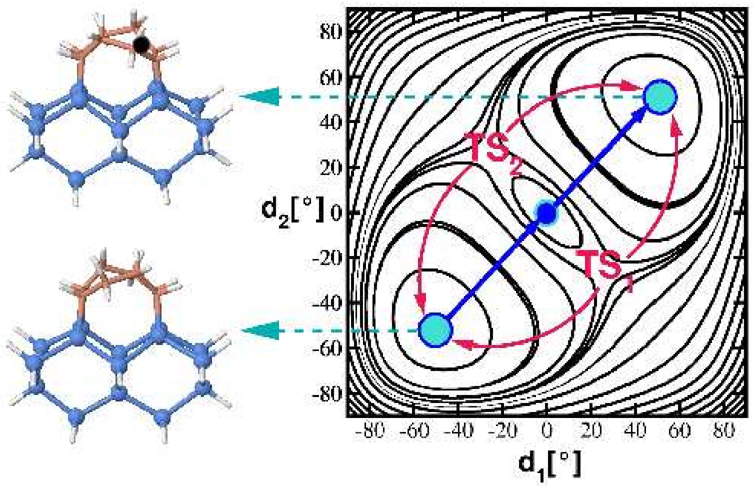

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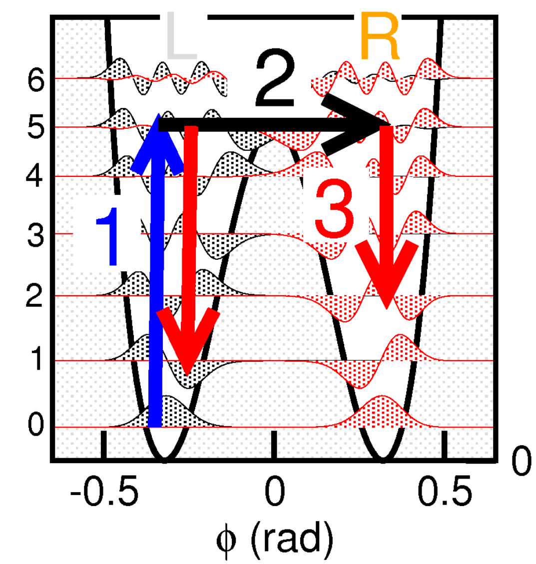

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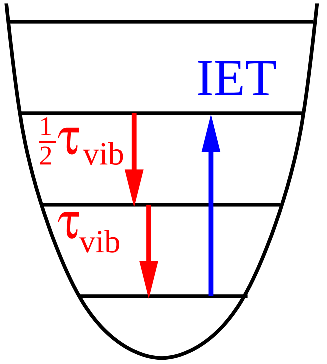

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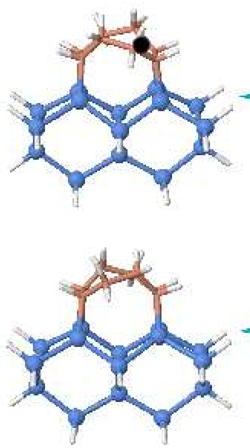

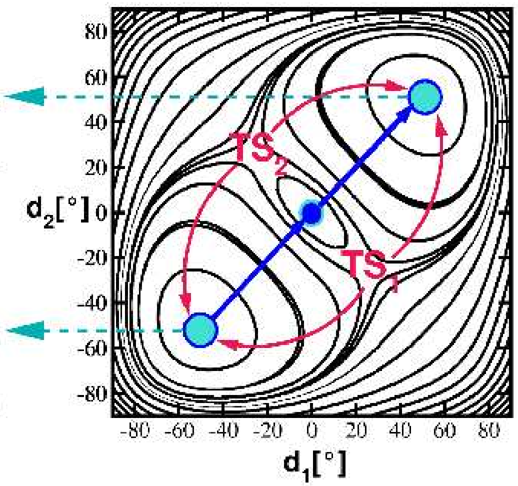

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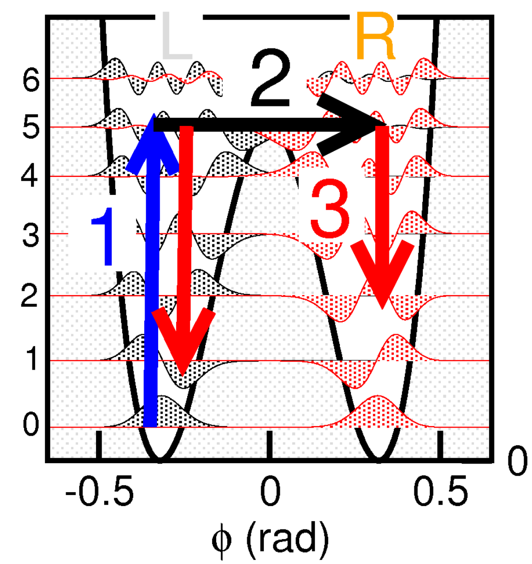

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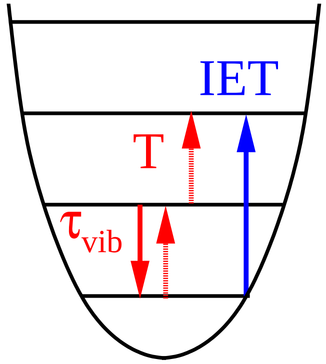
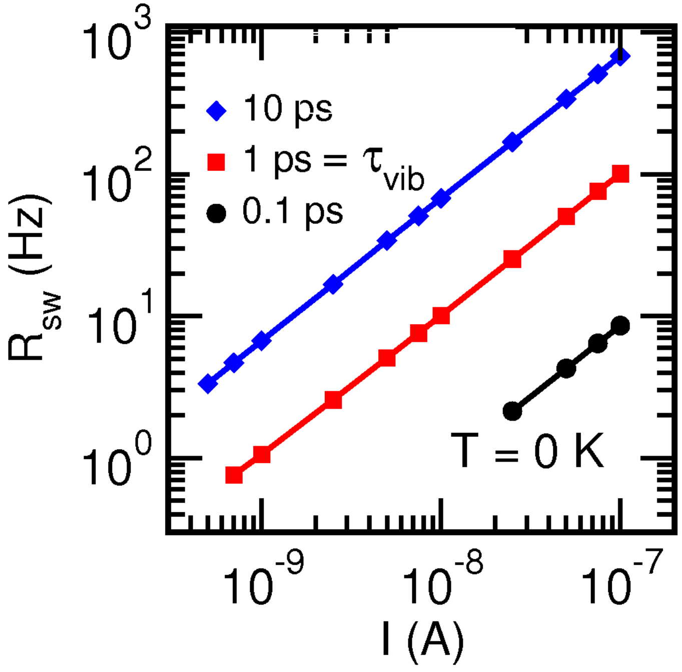
finite T: also $\uparrow$



COD@Si(100): RESULTS

- **Switch rate: $T = 0$**



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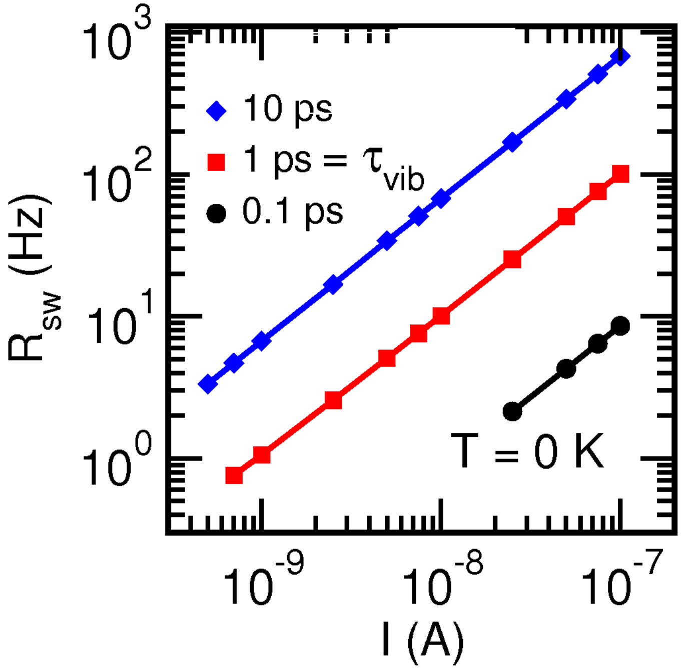

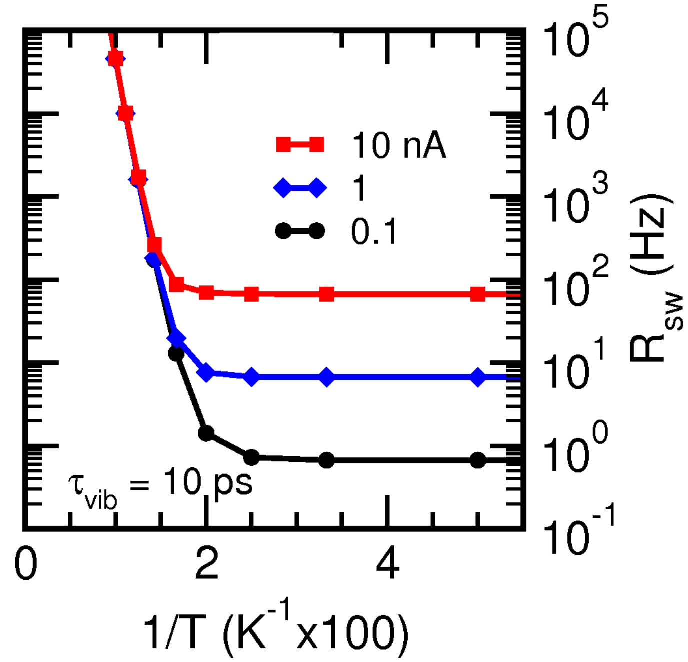

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COD@Si(100): RESULTS

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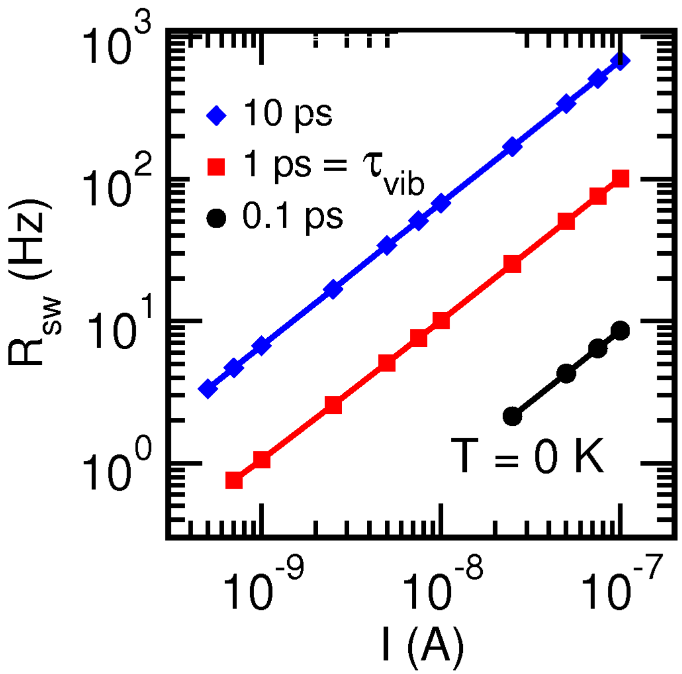
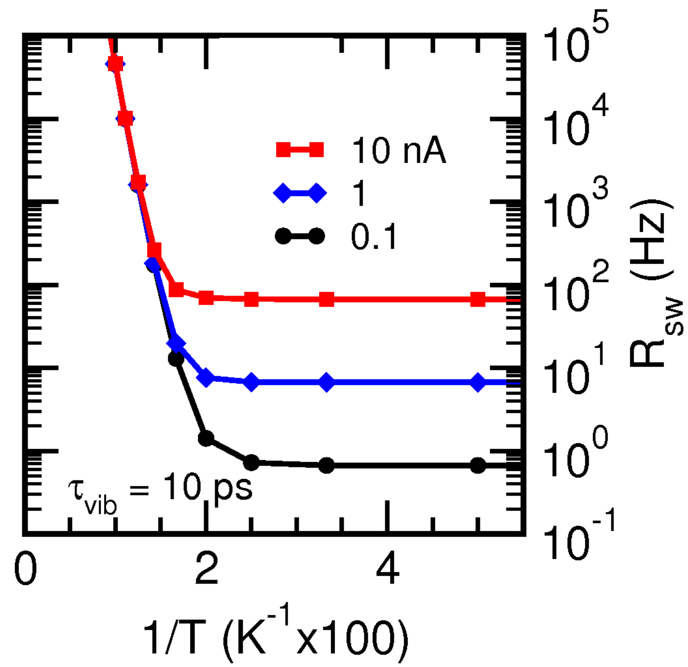
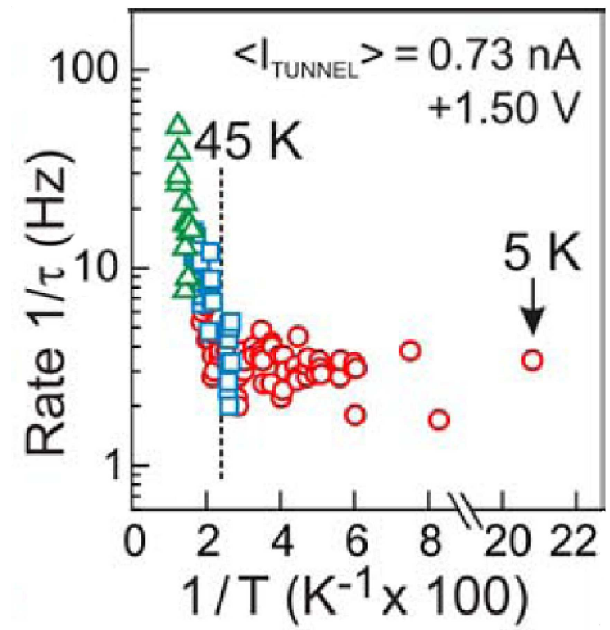
- **Experiment**







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I-controlled switching from *classical* to *quantum* regime

Nacci, Fölsch, Zenichowski, Klamroth, Dokic, Saalfrank, Nano Letters **9**, 2996 (2009)

CAN WE CALCULATE τ_{vib}?

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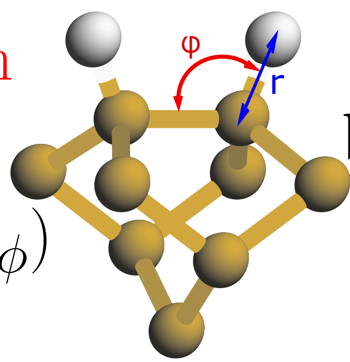
H / Si(100): VIBRATIONAL RELAXATION

- **A “system-bath” model for H on Si(100)**

$$\hat{H} = \underbrace{\hat{T} + V(r,\phi)}_{\hat{H}_s} + \underbrace{\sum_{i=1}^{M} \underbrace{\lambda_i(r,\phi)\; q_i}_{\text{1-phonon}} + \frac{1}{2}\sum_{i,j=1}^{M} \underbrace{\Lambda_{ij}(r,\phi)\; q_i q_j}_{\text{2-phonon}}}_{\hat{H}_{sb}} + \underbrace{\sum_{i=1}^{M} \left(\frac{\hat{p}_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} q_i^2 \right)}_{\hat{H}_b}$$

- **The model**

The system

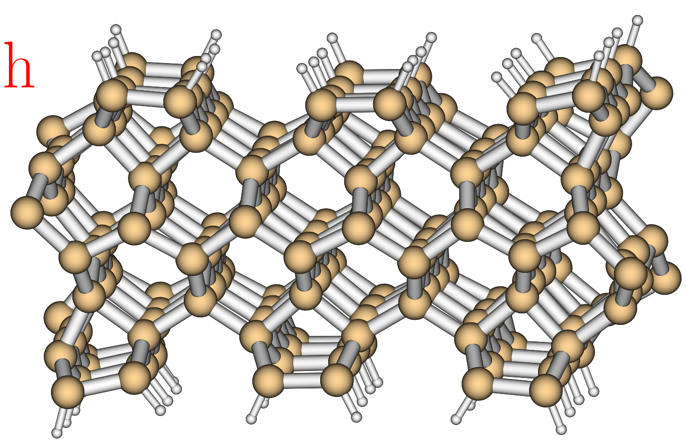


stretching mode r

bending mode ϕ

states (n_r, n_ϕ)

The bath



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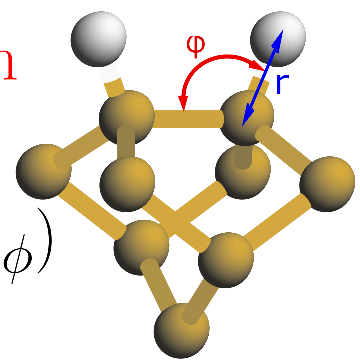

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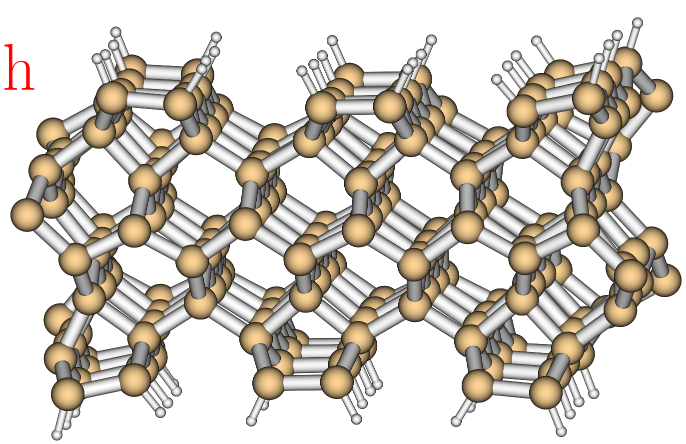
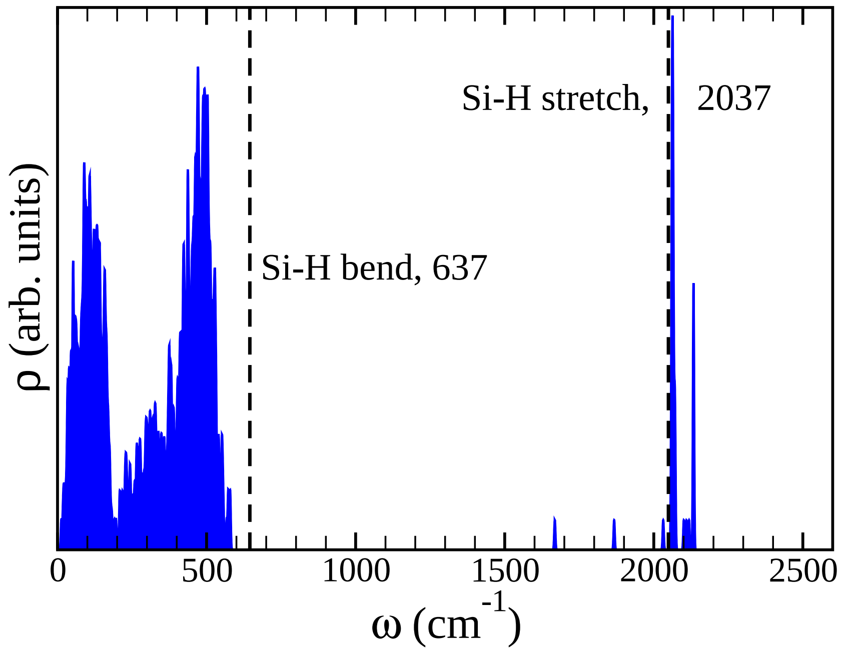


- **Vibrational state density**

normal mode analysis (N_{at}=180, FF[1])



[1] force field: D. Brenner, PRB **42**, 9458 (1990); NMA: I. Andrianov, PS, JCP **124**, 034710 (2006)

H/Si(100): PERTURBATION THEORY

- **The Golden Rule of quantum mechanics**

$$\Gamma_{n\to m} = \frac{2\pi}{\hbar} \sum_i \sum_f w_i(T)\,(1 - w_f(T))\,\left|\left\langle m, f|\hat{H}_{sb}|n, i\right\rangle\right|^2 \delta(\varepsilon_f^{ph} - \varepsilon_i^{ph} - \hbar\omega_{nm})$$

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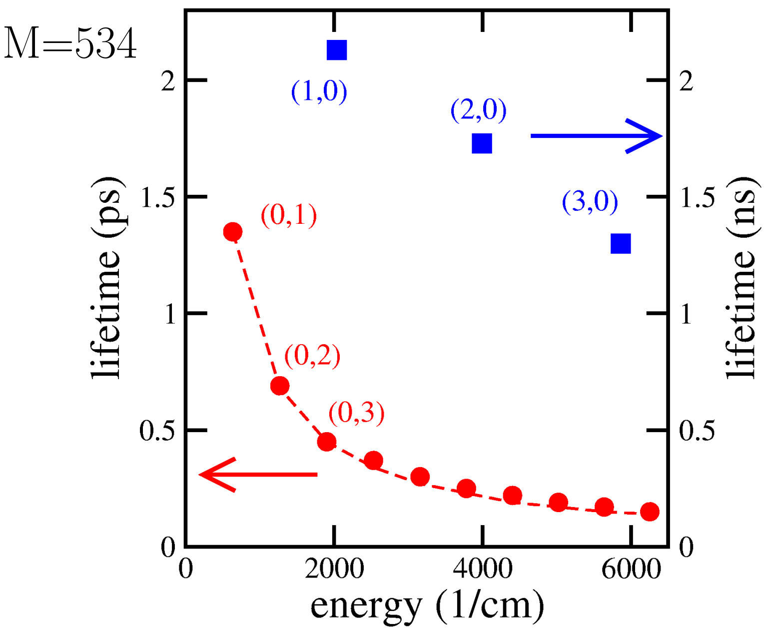
- **Lifetimes (T=0)**



- stretch mode: $\tau_{vib} = \Gamma^{-1}_{1\to 0} =$ ns
- bending mode: ps
- $\Gamma_{n\to m} \approx {\tau_{vib}}^{-1}\, n\, \delta_{m,n-1}$: $\Delta n = -1$
- exponential population decay

Non-perturbative RELAXATION H:Si(100), MCTDH

- Solve $i\hbar\frac{\partial\Psi}{\partial t} = (\hat{H}_s + \hat{H}_b + \hat{H}_{sb})\Psi$ with Multi Configuration TD Hartree method[1]
- Wavefunction:

$$\Psi(q_1 \ldots q_F, t) = \sum_{j_1}^{n_1} \cdots \sum_{j_F}^{n_F} A_{j_1 \cdots j_F}(t) \Phi_{j_1 \cdots j_F}(t)$$

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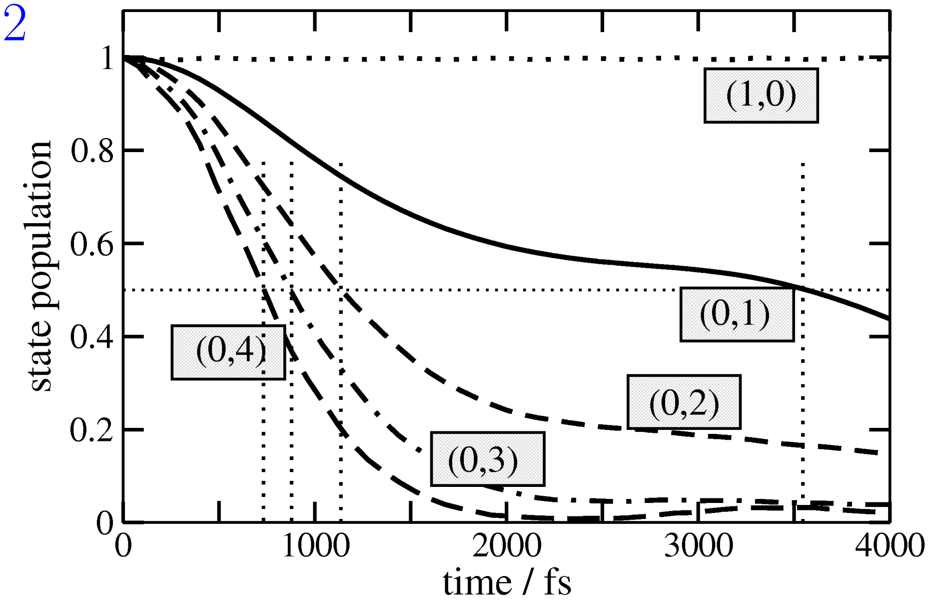
- **"Relaxation" dynamics**[2]

  (50+2 DOF)

  - non-exponential decay
  - recurrences



- **Alternatives: TD-SCF**[3] **and LCSA**[4]

[1] Meyer *et al.*, JCP **97**, 3199 (1992)

[2] I. Andrianov, PS, CPL **433**, 91 (2006)

[3] Paramonov, Andrianov, PS, J. Phys. Chem. C **111**, 5432 (2007)

[4] Martinazzo, Nest, PS, Tantardini, JCP **125**, 194102 (2006)

H/Si: IR MODE-SELECTIVE CHEMISTRY

Science **312**, 1024 (2006):

Desorption of H from Si(111) by Resonant Excitation of the Si-H Vibrational Stretch Mode

Zhiheng Liu,[1,2] L. C. Feldman,[2,3] N. H. Tolk,[2] Zhenyu Zhang,[3,4] P. I. Cohen[1*]

Past efforts to achieve selective bond scission by vibrational excitation have been thwarted by energy thermalization. Here we report resonant photodesorption of hydrogen from a Si(111) surface using tunable infrared radiation. The wavelength dependence of the desorption yield peaks at 0.26 electron volt: the energy of the Si-H vibrational stretch mode. The desorption yield is quadratic in the infrared intensity. A strong H/D isotope effect rules out thermal desorption mechanisms, and electronic effects are not applicable in this low-energy regime. A molecular mechanism accounting for the desorption event remains elusive.

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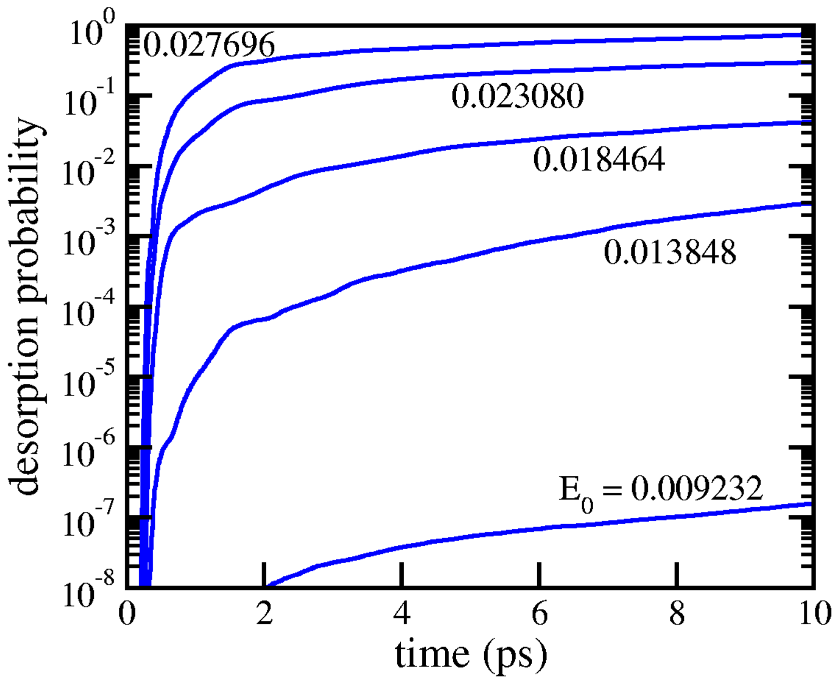
- **TD-SCF model: IR-desorption of H from Si(100)**



(534+2 DOF)

desorption by mode-selective excitation

G.K. Paramonov, I. Andrianov, PS, J. Phys. Chem. C **111**, 5432 (2007)

SUMMARY

- **Electron dynamics**

❶ correlated wavefunction-based many-electron methods

❷ ultrashort pulses:
multi-photon processes and electronic wavepackets

❸ transport

❹ dissipation

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- **Nuclear (atom) dynamics**

  ❶ open-system density matrices and system-bath Schrödinger equations

  ❷ applications to surface and nano science

  ❸ single molecules: switching conformations, and quanticity

  ❹ mode-selectivity despite of decoherence

THANKS TO ...

- ... **the group:**

- ... **the sponsors:**
  - Deutsche Forschungsgemeinschaft

    SFB 450, SFB 658, SPP 1145, UniCat, Sa 547/7
  - FCI
  - BMBF
  - AvH

t-DEPENDENT CONFIGURATION INTERACTION

• TD-CIS (Singles)

1. **Field-free Hartree-Fock**

$$\hat{f}(1)\phi_a(1) = \varepsilon_a \phi_a(1)$$

$$\phi_a = \sum_{\mu}^{K} d_{\mu a}\varphi_\mu$$

2. **Field-free CIS**

$$\underline{\underline{H}}_0\, \underline{D}_i = E_i \underline{D}_i$$

$$\psi_i = \underbrace{D_{i,0}\,\psi_0}_{\text{HF ground state}} + \sum_{a=1}^{N/2} \sum_{r=N/2+1}^{K} \underbrace{D^r_{a,i}\, {}^1\psi^r_a}_{\text{singlet excitations}}$$

3. **TD Schrödinger equation with field**

$$\Psi(t) = \sum_i C_i(t)\psi_i$$

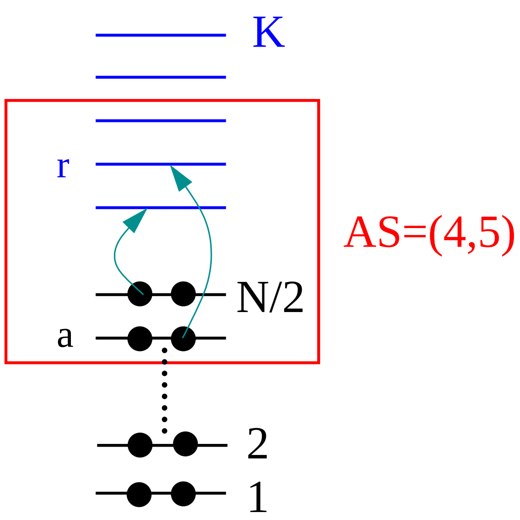
$$i\hbar\dot{\underline{C}}(t) = \underline{\underline{H}}(t)\,\underline{C}(t)$$

$$\hat{H} = \hat{H}_{el} - \underline{\hat{\mu}}\,\underline{E}(t) \qquad ; \qquad \psi(0) = \psi_0$$

• Extensions

- TD-CISD, TD-CIS(D)[1], . . . , FCI
- TD-CASSCF (=MCTDHF)

  - TD-CASSCF (N,M):
    N electrons in M spatial orbitals



  - TD-CASSCF (N,N/2): TD-HF
  - TD-CASSCF (N,K): FCI

[1] M. Head-Gordon *et al.*, CPL **219**, 21 (1994)

CIS(D) METHOD

- **Perturbative treatment of double-excitations**

$$E_i^{(D)} = -\frac{1}{4}\sum_{\text{abrs}} \frac{\left(u_{\text{ab},i}^{\text{rs}}\right)^2}{\left(\Delta_{\text{ab}}^{\text{rs}} - E_i^{CIS}\right)} + \sum_{\text{ar}} D_{\text{a},i}^{\text{r}} v_{\text{a},i}^{\text{r}}$$

- **Example: H_2**

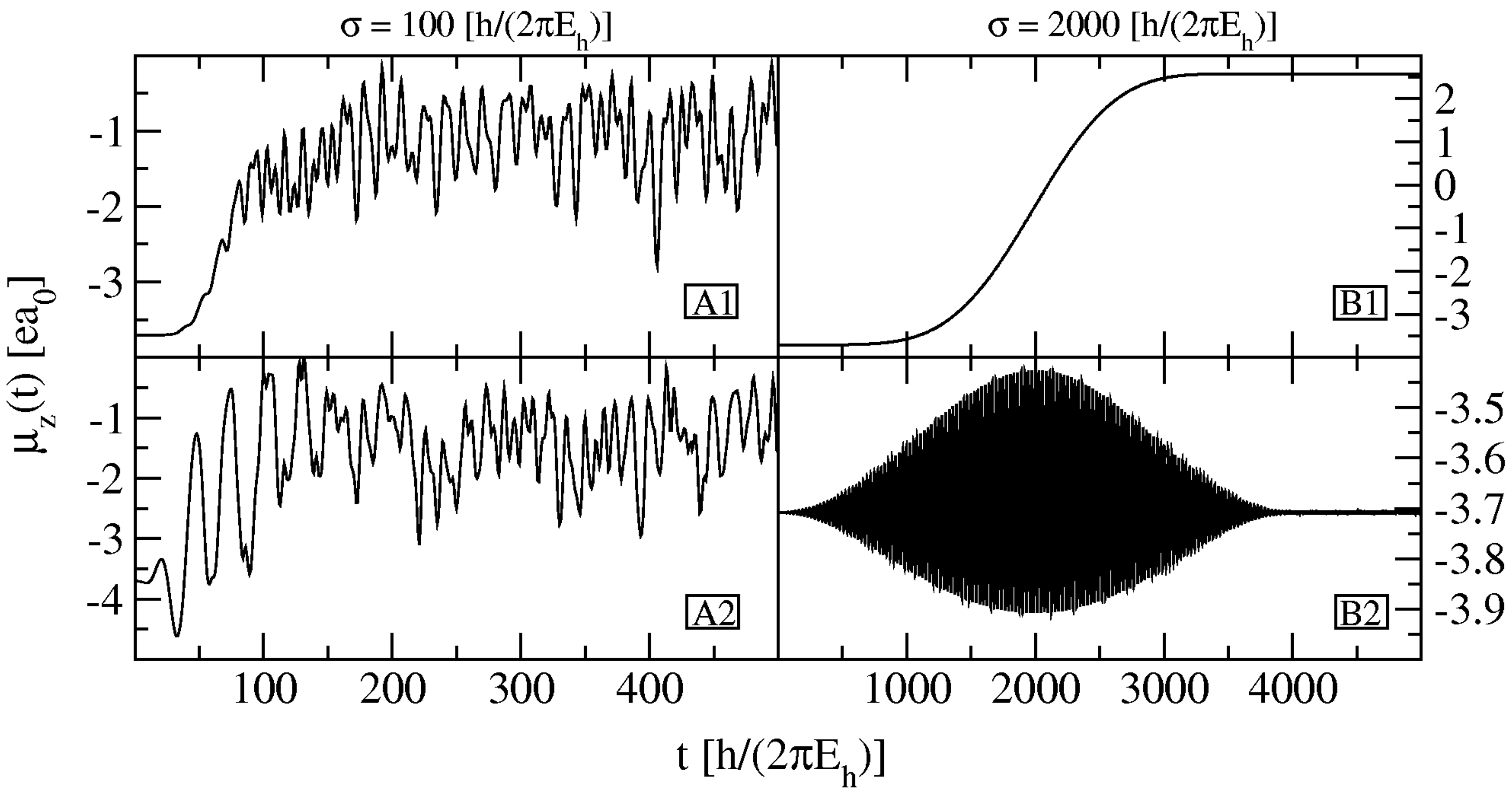
aug-cc-pV5Z	CIS	CIS(D)	CISD	"exact"
E_0 (E_h)	-1.1336	-1.1673	-1.1742	-1.178

Head-Gordon *et al.*, CPL **219**, 21 (1994)

LiCN: TD-CIS(D) CALCULATIONS

• Dipole moments

$\sin^2$ laser pulses: $E_x(t)$, $E_z(t)$



$E_x(t)$

$E_z(t)$

dipole switch with "long", x-polarized pulse

P. Krause, T. Klamroth, PS, JCP **123**, 074105 (2005)

MOLECULAR JUNCTIONS: THEORY

- **Landauer transport theory**

$$I(V) = \frac{2e}{h} \int_{E_F-\frac{eV}{2}}^{E_F+\frac{eV}{2}} N(E,V)\,dE$$

- **N(E): Miller-Seideman**

$$N(E) = \frac{1}{\hbar^2}\mathrm{Tr}[\underline{\underline{\Gamma}}^L \underline{\underline{G}}(E) \underline{\underline{\Gamma}}^R \underline{\underline{G}}^\dagger(E)]$$

- **LCAO-MO approach**

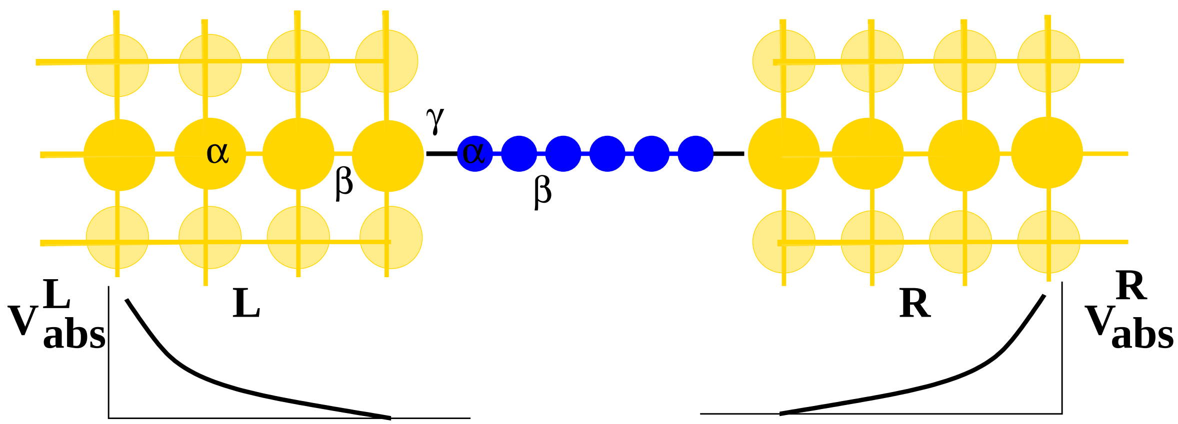
$$\underline{\underline{G}}(E) = \left[E\underline{\underline{S}} - (\underline{\underline{H}} - \frac{i\hbar}{2}(\underline{\underline{\Gamma}}^L + \underline{\underline{\Gamma}}^R)) \right]^{-1}$$

$$\begin{aligned} \underline{\underline{H}} &= \text{Hamiltonian matrix} \\ \underline{\underline{S}} &= \text{overlap matrix} \\ \underline{\underline{\Gamma}}^{L/R} &= \text{left / right absorbers} \end{aligned}$$

Kopf, P.S., CPL **386**, 17 (2004)

MOLECULAR JUNCTIONS: TESTING

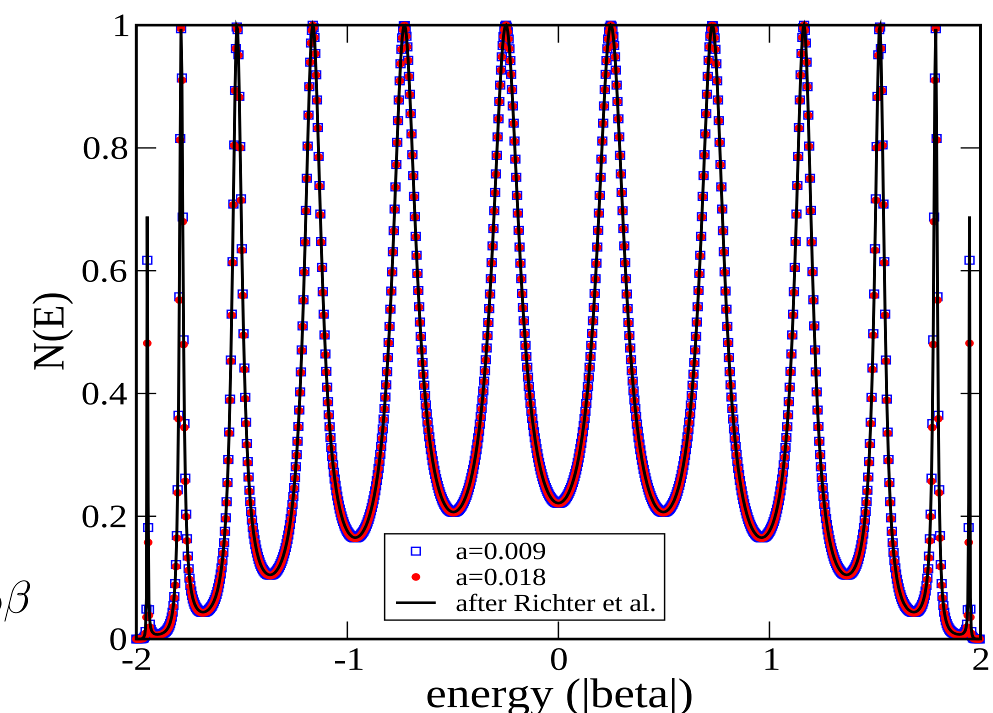
- **Quasi-1D Hückel (tight binding) model**



- **Transmission N(E)**

$$\begin{aligned} \hbar\Gamma^{L/R}_{ij} &= \delta_{ij} V^{L/R}_{abs}(\underline{r}_i) \\ \text{absorbers:} \quad V^R_{abs} &= a(z-z_0)^n \end{aligned}$$

$N = 12,\ N_L = N_R = 100,\ n = 4,\ \gamma = 0.5\beta$



REDUCED DENSITY MATRIX (RDM) THEORY

$$\langle \hat{A} \rangle(t) = \mathrm{tr}\{\hat{\rho}(t)\ \hat{A}\}$$

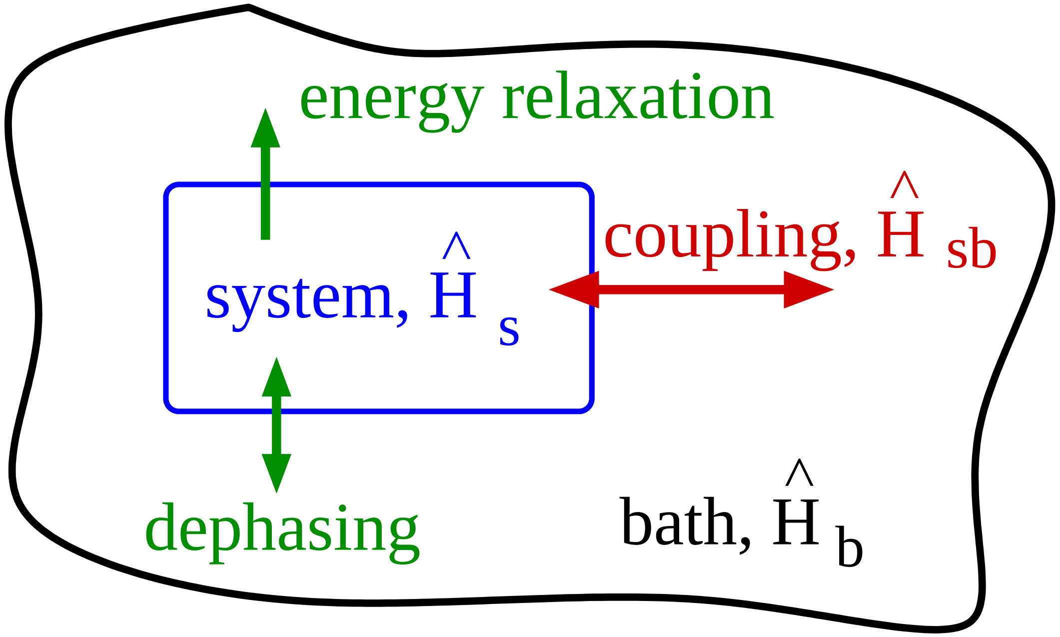
$$\uparrow$$

Liouville-von Neumann eq.

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_s + \hat{H}_b + \hat{H}_{sb}, \hat{\rho}\right]$$

$$\hat{\rho} = \sum_n w_n(T)|\psi_n\rangle\langle\psi_n|$$

density operator



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$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_s + \hat{H}_b + \hat{H}_{sb}, \hat{\rho}\right]$$

$\downarrow$ reduced density matrix: $\hat{\rho}_s = \mathrm{tr}_b \hat{\rho}$

$\downarrow$ approximations, e.g. Markov:

$\downarrow$ $\dot{\hat{\rho}}_s(t) = f[\hat{\rho}_s(t)]$

$$\frac{\partial \hat{\rho}_s(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_s, \hat{\rho}_s\right] + \left(\frac{\partial \hat{\rho}_s}{\partial t}\right)_D$$

LvN open system

$\downarrow$

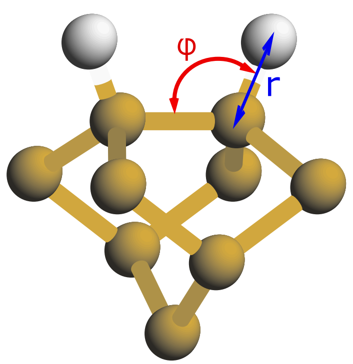
Redfield, Lindblad theories

H / Si(100): VIBRATIONAL RELAXATION

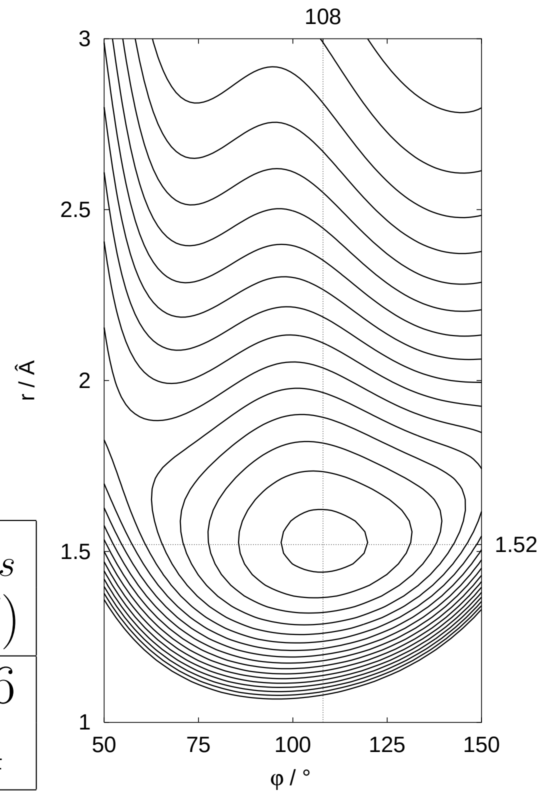
- **A "system-bath" model for H on Si(100)**

$$\hat{H} = \underbrace{\hat{T} + V(r,\phi)}_{\hat{H}_s} + \underbrace{\sum_{i=1}^{M} \underbrace{\lambda_i(r,\phi)\; q_i}_{\text{1-phonon}} + \frac{1}{2}\sum_{i,j=1}^{M} \underbrace{\Lambda_{ij}(r,\phi)\; q_i q_j}_{\text{2-phonon}}}_{\hat{H}_{sb}} + \underbrace{\sum_{i=1}^{M}\left(\frac{\hat{p}_i^2}{2m_i} + \frac{m_i\omega_i^2}{2} q_i^2\right)}_{\hat{H}_b}$$

- **The system**



	r_0 (Å)	ϕ_0 (deg)	E_{ads} (eV)
Here[1]	1.52	108	3.46
Lit.[2]	1.50	111	3.4



- **System modes**

n	(n_r, n_ϕ)	E_n^{the} (cm^{-1})	E_n^{exp} (cm^{-1})
1	(0,1)	637	645
2	(0,2)	1271	–
3	(0,3)	1903	–
4	(1,0)	2037	2097
5	(0,4)	2523	–
6	(1,1)	2661	–

[1] I. Andrianov, PS, JCP **124**, 034710 (2006)

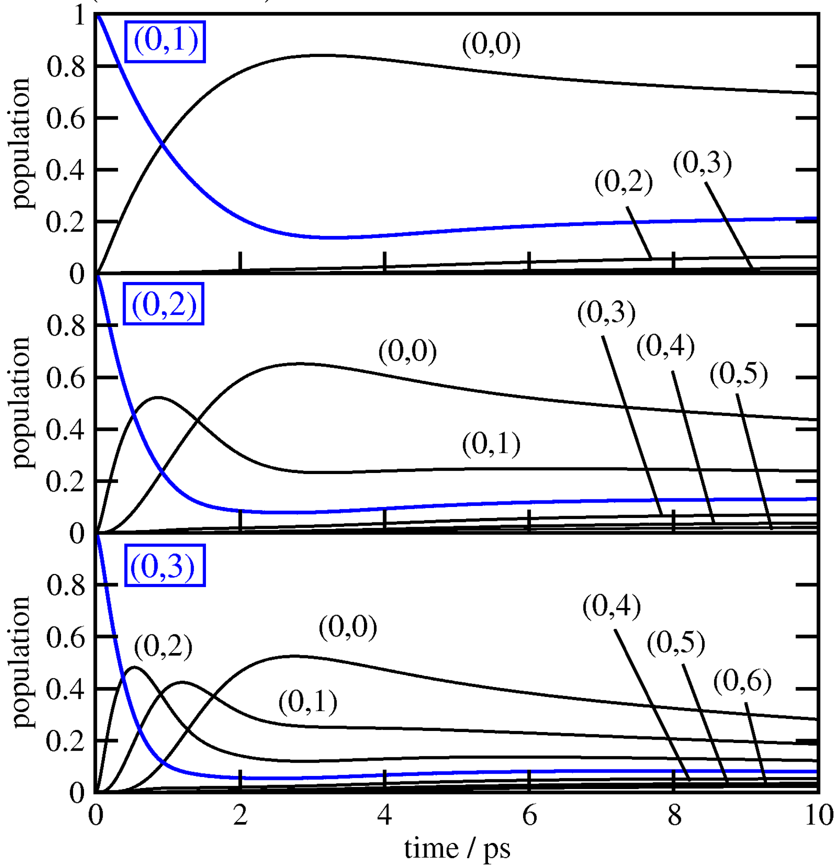
[2] Stokbro et al., Surf. Sci. **415**, L1037 (2000)

RELAXATION H:Si(100), TD-SCF

- Solve $i\hbar\frac{\partial\Psi}{\partial t} = (\hat{H}_s + \hat{H}_b + \hat{H}_{sb})\Psi$ with TD Self Consistent Field method
- Wavefunction: $\Psi(r, \phi, q_1, \ldots, q_M, t) = \Phi_s(r, \phi, t)\ \Pi_{i=1}^{M}\chi_i(q_i, t)$

• "Relaxation" dynamics

(M=534)



• Half-life times $T_{1/2}$

state	TD-SCF $M = 534$ (ps)	PT $M = 534$ (ps)	MCTDH $M = 50$ (ps)
(0,1)	0.92	0.94	3.54
(0,2)	0.48	0.48	1.13
(0,3)	0.34	0.33	0.87

Paramonov, Andrianov, PS, J. Phys. Chem. C **111**, 5432 (2007)

OPTIMAL CONTROL IN AN OPEN SYSTEM[(1),(2)]

- **Liouville-von Neumann equation:**

$$i\hbar\frac{\partial}{\partial t}|\hat{\rho}(t)\rangle\rangle = (\mathcal{L}_H + \mathcal{L}_D)|\hat{\rho}(t)\rangle\rangle$$ forward from $t = 0, |\hat{\rho}(0)\rangle\rangle = |\hat{\rho}_0\rangle\rangle$

- **Maximize constrained target functional:**

$$J = \langle\langle\hat{O}|\hat{\rho}(t_f)\rangle\rangle - \int_0^{t_f}\alpha(t)|E(t)|^2\mathrm{d}t - \int_0^{t_f}\mathrm{d}t\langle\langle\hat{\sigma}(t)|\frac{\partial}{\partial t} + \frac{i}{\hbar}[\mathcal{L}_H + \mathcal{L}_D]|\hat{\rho}(t)\rangle\rangle$$

- **Solve in addition to LvN equation:**

$$i\hbar\frac{\partial}{\partial t}|\hat{\sigma}(t)\rangle\rangle = (\mathcal{L}_H + \mathcal{L}_D)^\dagger|\hat{\sigma}(t)\rangle\rangle$$ backward from $t = t_f, |\hat{\sigma}(t_f)\rangle\rangle = |\hat{O}\rangle\rangle$

- **Field:**

$$E(t) = -\frac{1}{\hbar\alpha(t)}\,\mathrm{Im}\langle\langle\hat{\sigma}(t)|\hat{\mu}|\hat{\rho}(t)\rangle\rangle$$

(1) Y. Ohtsuki *et al.*, JCP **109**, 9318 (1998); (2) Y. Ohtsuki *et al.* JCP **110**, 9825 (1999)