OPEN-SYSTEM DENSITY MATRIX THEORY FOR SURFACE SCIENCE PROBLEMS

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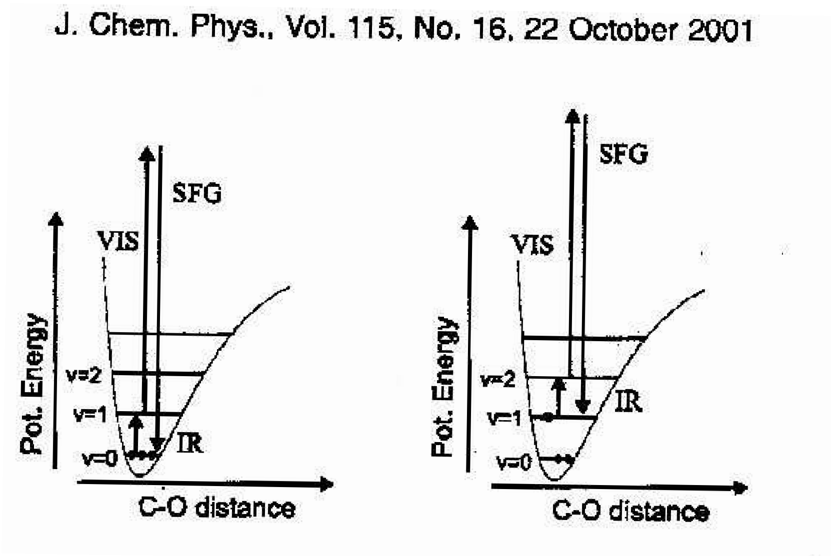
DISSIPATIVE PROCESSES AT SURFACES

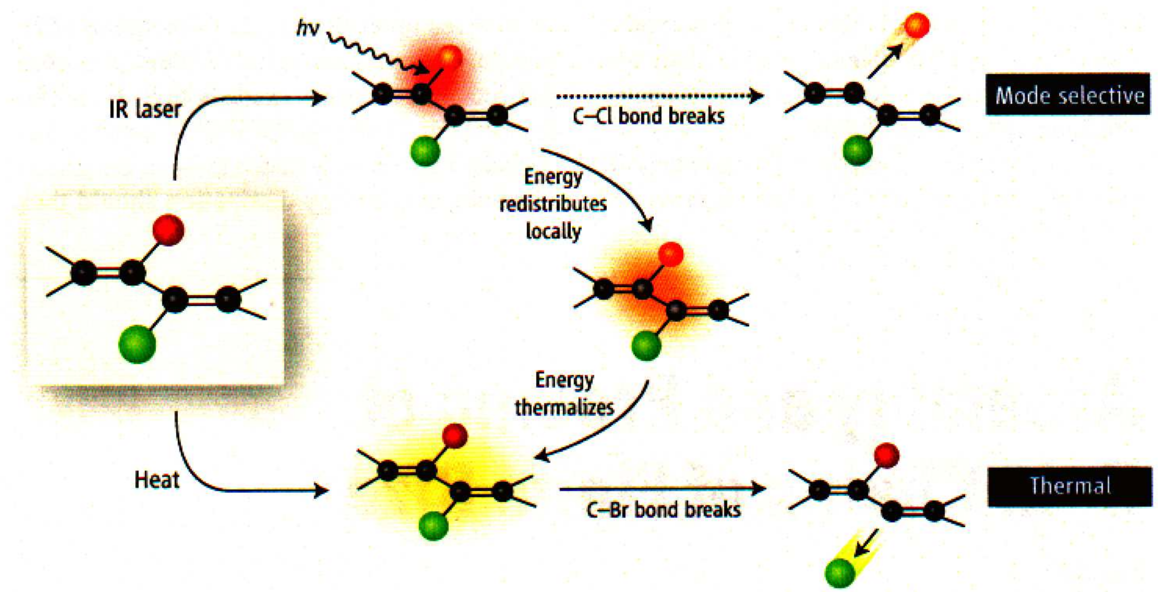
- **Spectroscopy**



Wolf, CO/Ru(0001), overtone excitation

- **Mode-selective chemistry**

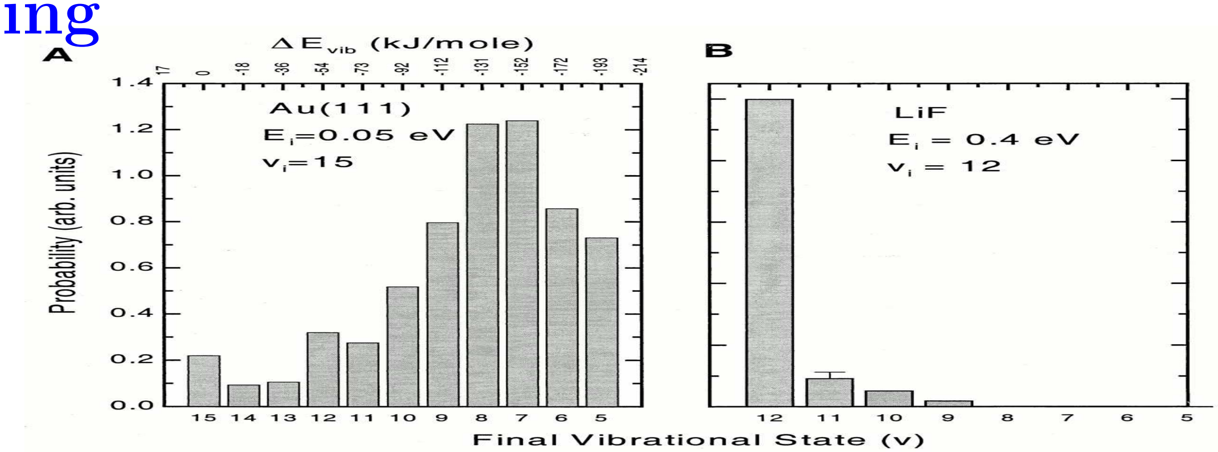
Cohen *et al.*, H/Si(111), Science **312**, 1024 (2006)



- **Molecule-surface scattering**

Huang *et al.*, Science **290**, 111 (2000)

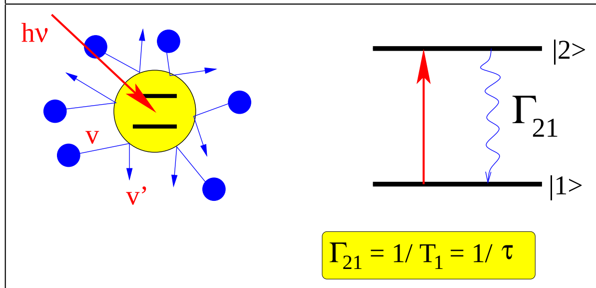
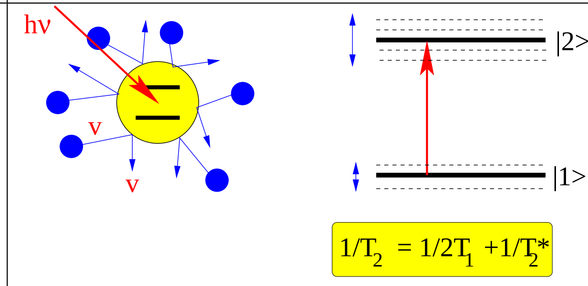
NO(v_i)+Au(111) $\rightarrow$ NO(v_f)+Au*(111)



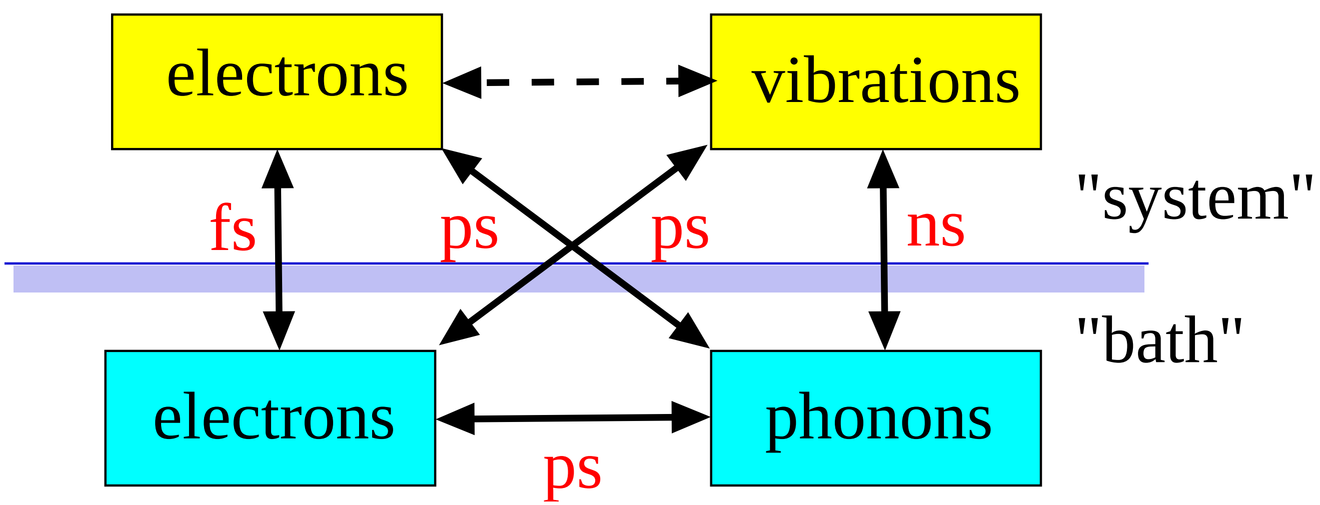
Problem: Vibrational energy relaxation and dephasing!

DISSIPATION AND RELAXATION AT SURFACES

- **General**

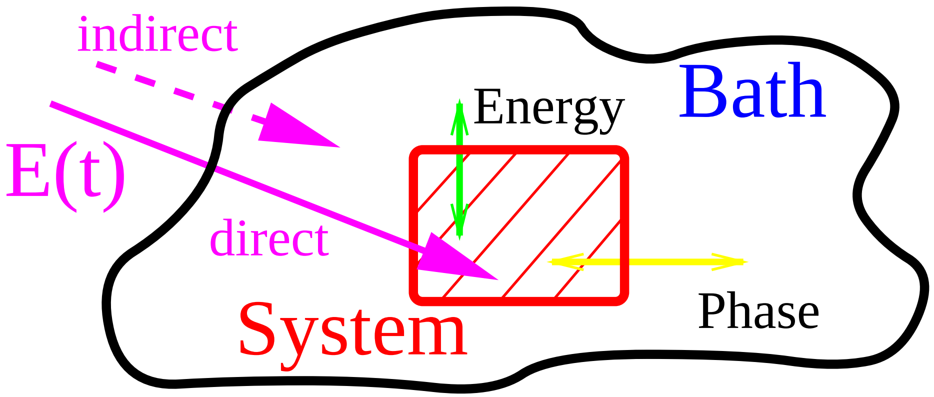
Energy relaxation	Phase relaxation
	
inelastic, timescale T_1 (τ) e.g., population transfer	elastic, timescale T_2 e.g., line broadening

- **Adsorbate energy relaxation times τ**



FULL DYNAMICS

- **The system-bath Hamiltonian**



$$\hat{H} = \underbrace{\left[\hat{H}_s(s) - \underline{\hat{\mu}}\underline{E}(t)\right]}_{\text{system}} + \underbrace{\hat{H}_{sb}(s, q_1, \ldots, q_N)}_{\text{system-bath}} + \underbrace{\hat{H}_b(q_1, \ldots, q_N)}_{\text{bath}}$$

- **The time-dependent Schrödinger equation**

$$\frac{\partial \Psi(s, q_1, \ldots, q_N, t)}{\partial t} = -\frac{i}{\hbar}\hat{H}\Psi(s, q_1, \ldots, q_N, t)$$

- **Methods**

  standard, MCTDH ("exact"), TDSCF (approximation)

MULTICONFIGURATION TD HARTREE: MCTDH

- **MCTDH wavefunction for distinguishable particles**

$$\Psi(q_1,\ldots,q_F,t) = \sum_J A_J(t)\,\psi_J(t)$$

total wavefunction

$$\psi_J(t) = \prod_{\kappa=1}^{F} \underbrace{\varphi^{\kappa}_{j_\kappa}(q_\kappa,t)}_{\text{SPFs}}$$

configurations

- **Variational principle $\Rightarrow$ MCTDH equations of motion**

Coefficients:

$$i\hbar\frac{\partial A_J}{\partial t} = \sum_L \langle\psi_J|\hat{H}|\psi_L\rangle A_L$$

Single-particle functions:

$$i\hbar\frac{\partial\varphi^{(\kappa)}_j}{\partial t} = \left(1-\hat{P}^{(\kappa)}\right)\sum_{k,l}\left(\hat{\rho}^{(\kappa)}\right)^{-1}_{j,k}\langle\hat{H}\rangle^{(\kappa)}_{kl}\varphi^{(\kappa)}_l$$

Meyer, Manthe, Cederbaum: CPL **165**, 73 (1990); JCP **97**, 3199 (1992)

MARKOVIAN REDUCED DENSITY MATRICES

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

$\uparrow$

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

Liouville-von Neumann

$\downarrow$ $\downarrow$

1. Bath approximation
2. Perturbation theory
3. Markov approximation

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

LvN open system

$\downarrow$

4. Secular approximation

$$\left(\frac{\partial \hat{\rho}_s}{\partial t}\right)_{D,mn} = \sum_{ij} R_{mnij}\ \rho_{s,ij}$$

Redfield

$$\left(\frac{\partial \hat{\rho}_s}{\partial t}\right)_D = \sum_k \left(\hat{C}_k \hat{\rho}_s \hat{C}_k^\dagger - \frac{1}{2}\left[\hat{C}_k^\dagger \hat{C}_k, \hat{\rho}_s\right]_+\right)$$

Lindblad

ENERGY RELAXATION AND (PURE) DEPHASING

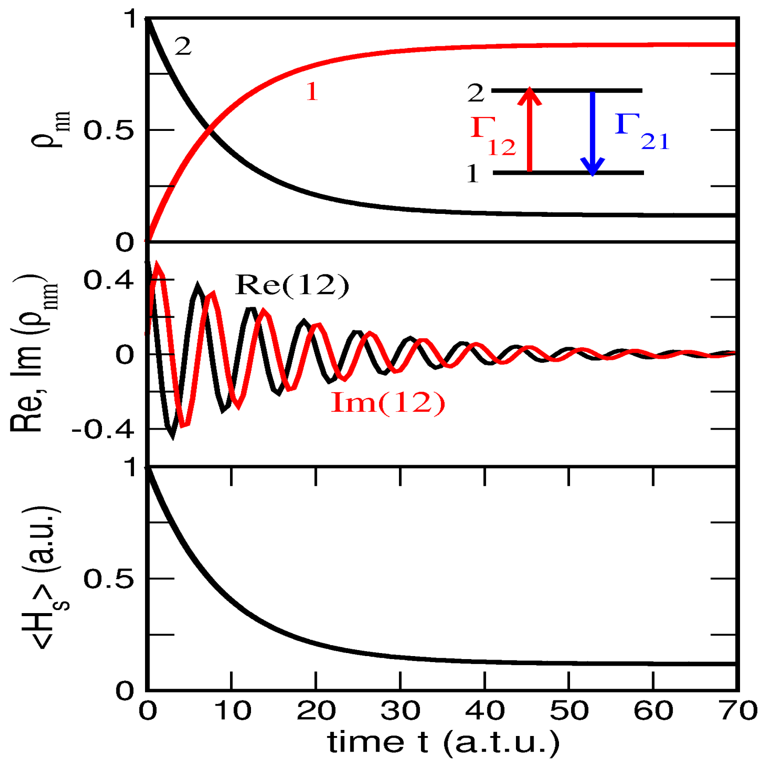
• Lindblad operators for a 2-level system

Energy (and phase) relaxation:

$$\hat{C}_1 = \sqrt{\Gamma_{2\to 1}}|1\rangle\langle 2|$$

$$\hat{C}_2 = \sqrt{\Gamma_{1\to 2}}|2\rangle\langle 1|$$

$$\Gamma_{1\to 2} = \Gamma_{2\to 1}\exp(-\hbar\omega_{21}/kT)$$ (detailed balance)

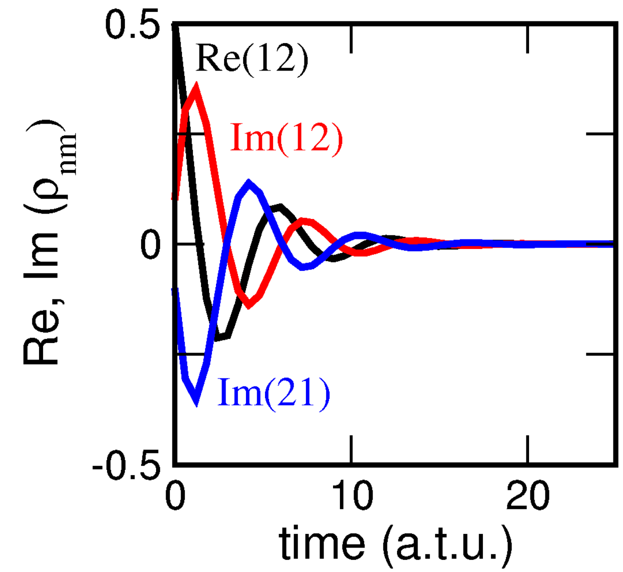


Pure dephasing:

$$\hat{C}_3 = \sqrt{\gamma^*_{12}}\,(|2\rangle\langle 2| - |1\rangle\langle 1|)$$

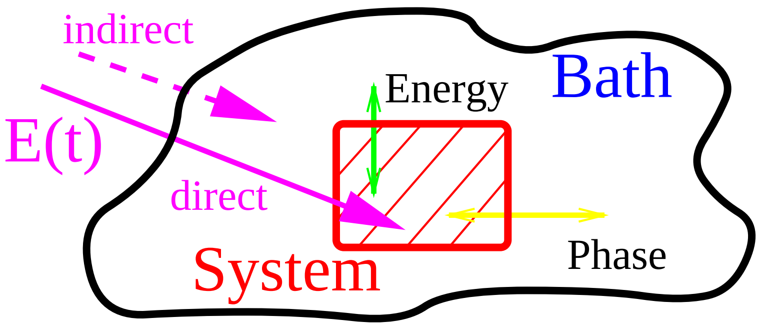
$$\gamma^*_{12} = \frac{1}{T_2^*}$$ (pure dephasing rate)

$$\gamma_{12} = \frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1}$$ (total dephasing rate)



REDUCED DYNAMICS

- **Open-system density matrix theory**



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

- **Lindblad form in system eigenstate representation**

Populations:

$$\frac{d\rho_{nn}}{dt} = \sum_p^N \underbrace{-\frac{i}{\hbar}\left[V_{np}(t)\rho_{pn} - \rho_{np}V_{pn}(t)\right]}_{\text{system-field}} + \sum_p^N \underbrace{\left[\Gamma_{p\to n}\rho_{pp} - \Gamma_{n\to p}\rho_{nn}\right]}_{\text{dissipation}}$$

Coherences:

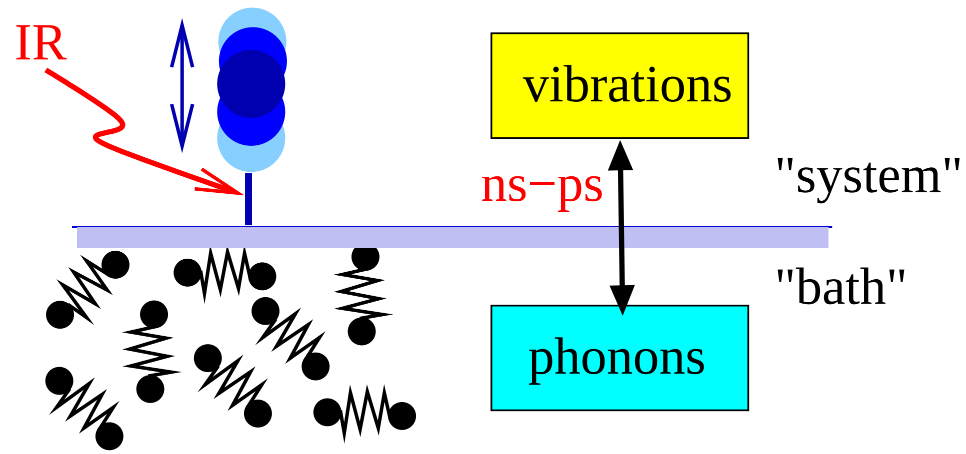
$$\frac{d\rho_{mn}}{dt} = -\frac{i}{\hbar}\left[(E_m - E_n) + \sum_p^N \left[V_{mp}(t)\rho_{pn} - \rho_{mp}V_{pn}(t)\right]\right] \underbrace{-\gamma_{mn}\,\rho_{mn}}_{\text{dephasing}}$$

- **Rates Γ, γ: Perturbation theory, non-perturbative**

THIS TALK

- **Vibration-phonon coupling**

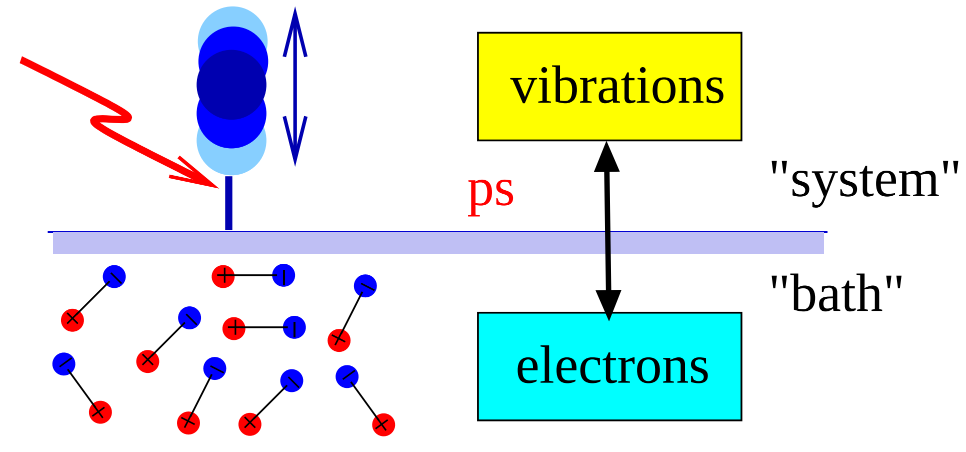
  H@Si(100): Mode-selective excitation



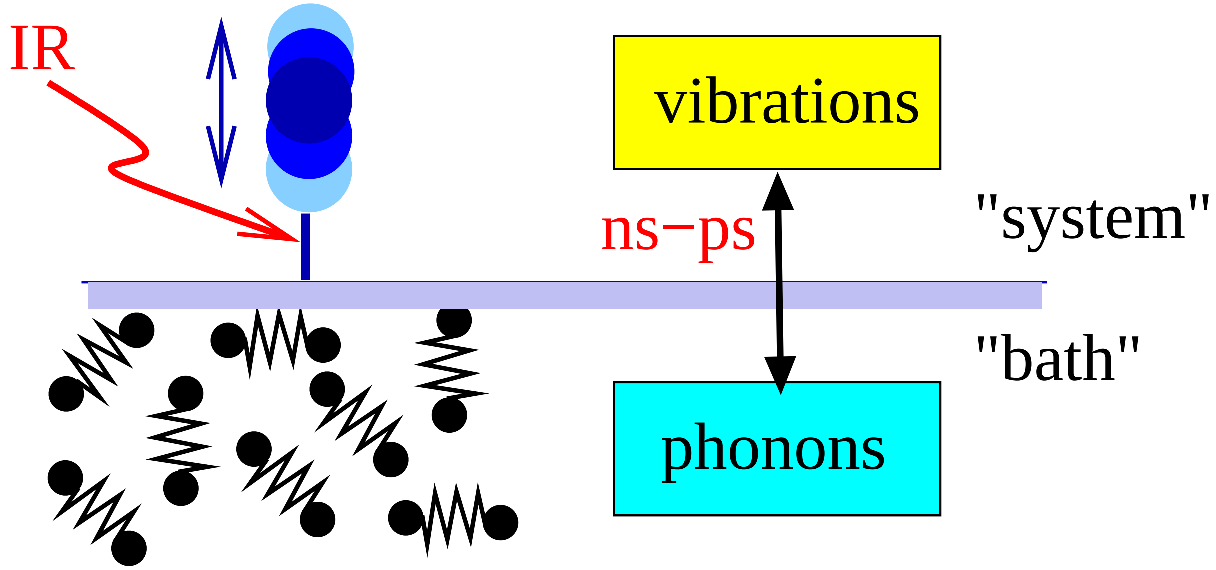
- **Vibration-electron coupling**

  CO@Cu(100): IR excitation

  NO/Au(111): Inelastic scattering



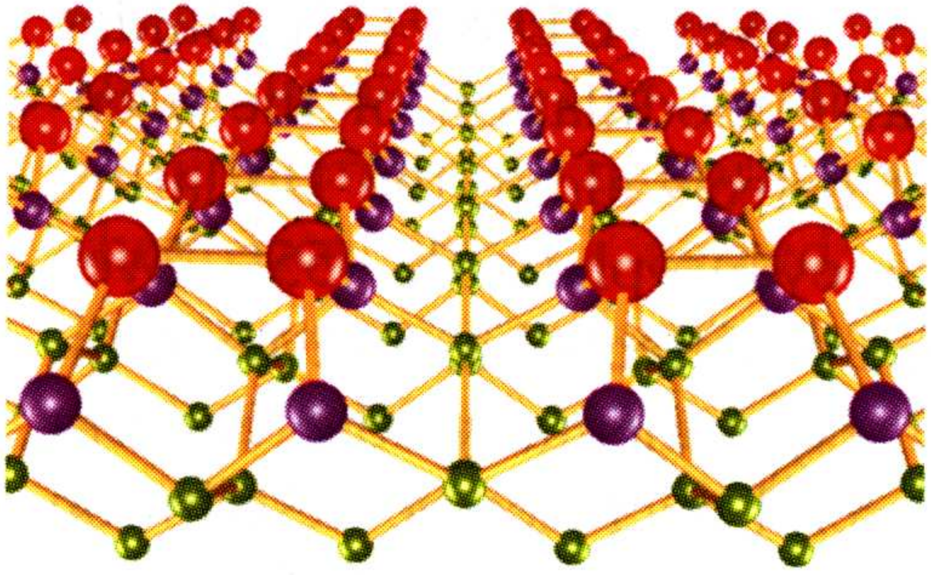
VIBRATION-PHONON COUPLING



- **System:** H:Si(100)

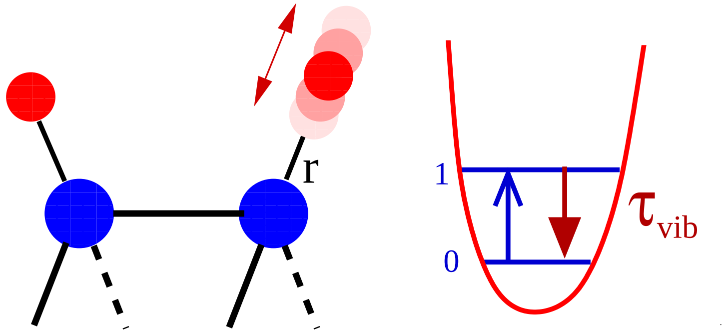
H/Si(100): VIBRATIONAL RELAXATION

- **The Si(100)-(2×1) surface**



- **Si-H stretching mode: Experiment**

Guyot-Sionnest (1995)



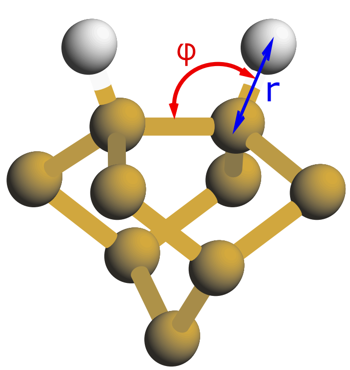
- T=300 K: τ_{vib}(H)= 1.2 ns
- Coupling of Si-H to phonons

H / Si(100): VIBRATIONAL RELAXATION

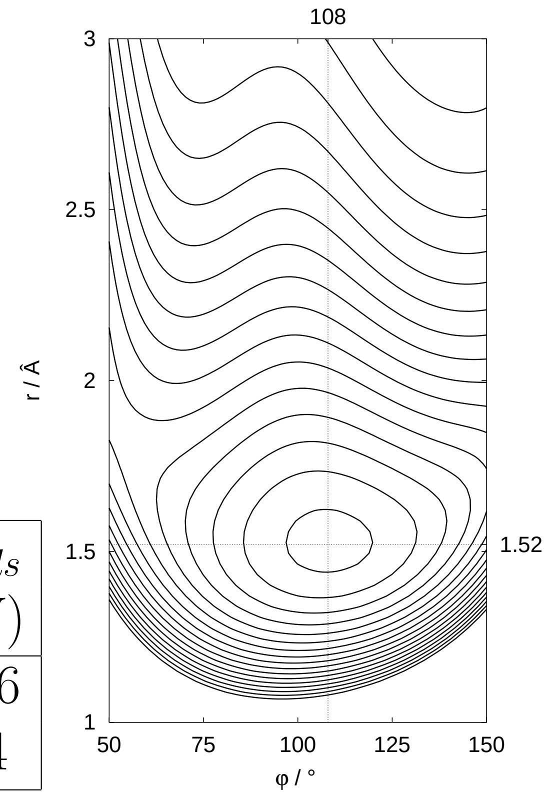
• A "system-bath" model

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

• 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	–

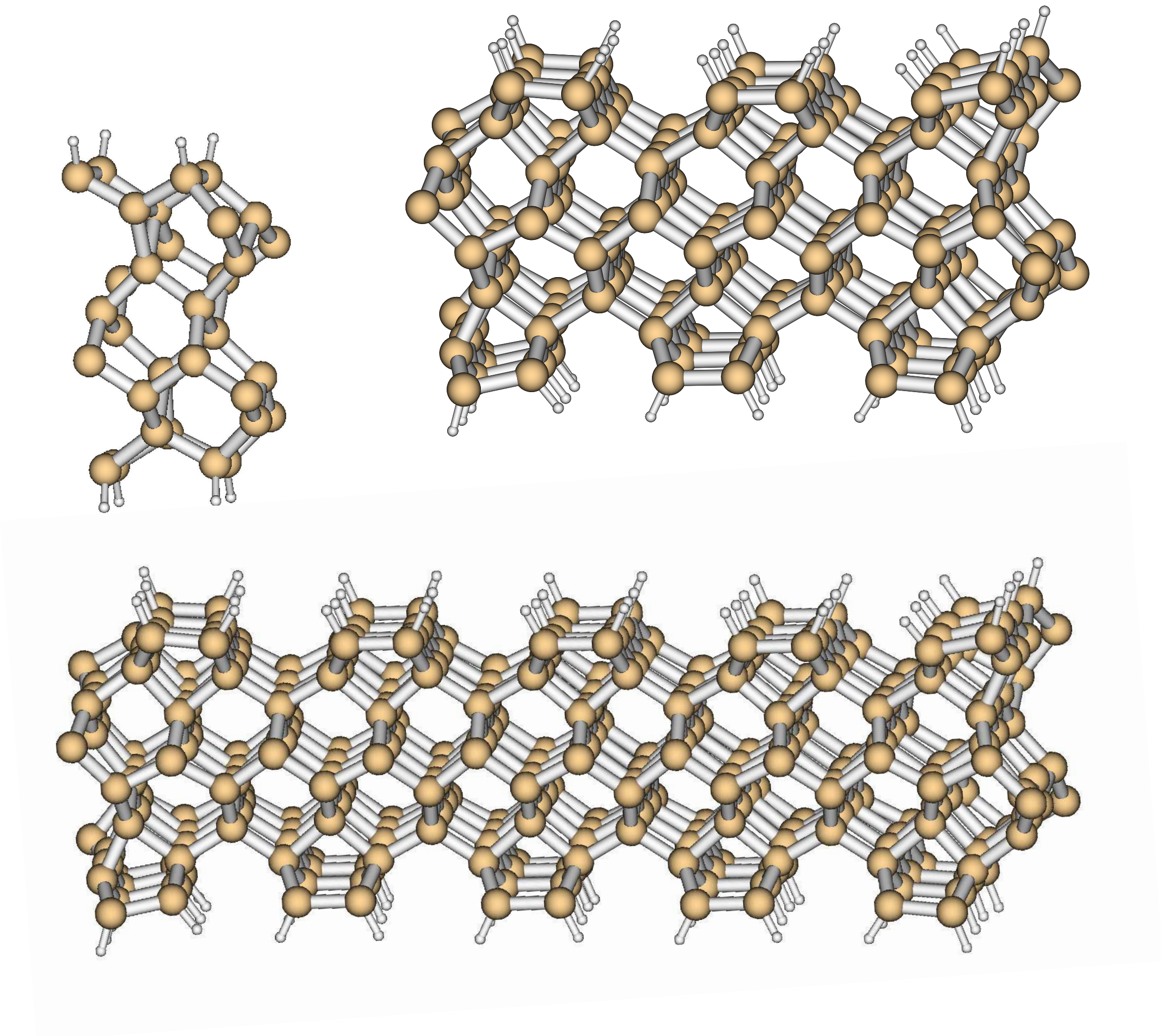
[1] I. Andrianov, PS, JCP **124**, 034710 (2006)

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

H/Si(100): VIBRATIONAL RELAXATION

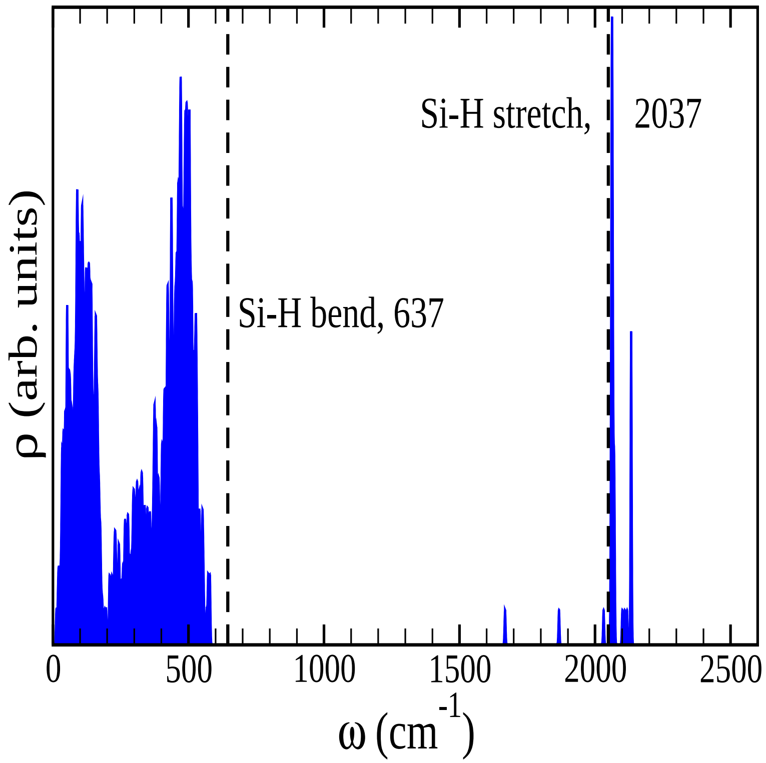
- **The "bath": Cluster models**

Bond-order Brenner force field[1]



- **Vibrational state density**

normal mode analysis (N_{at}=180)



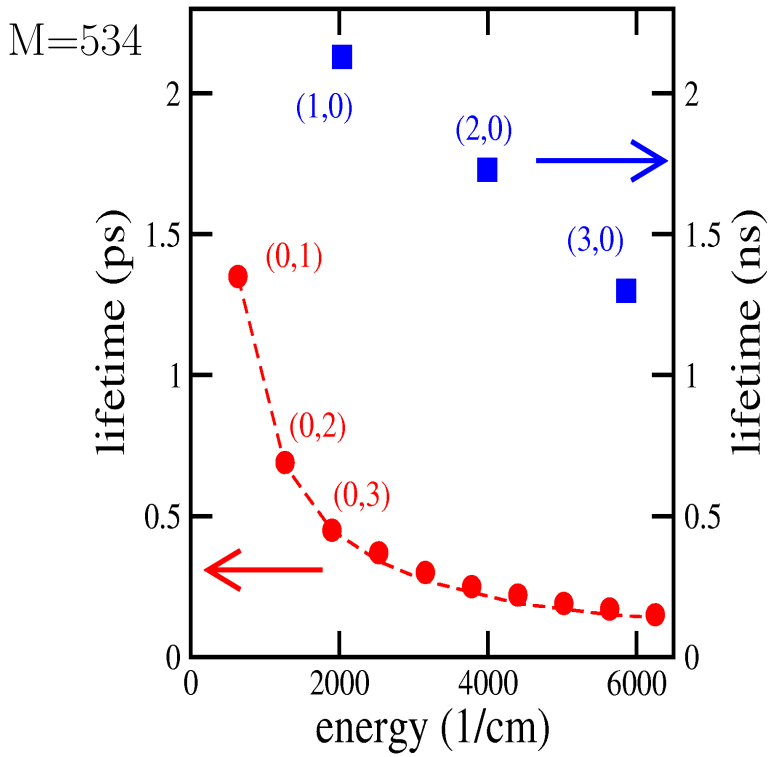
[1] D. Brenner, PRB **42**, 9458 (1990); A. Dyson, P. Smith, Mol. Phys. **96**, 1491 (1999)

H/Si(100): PERTURBATION THEORY

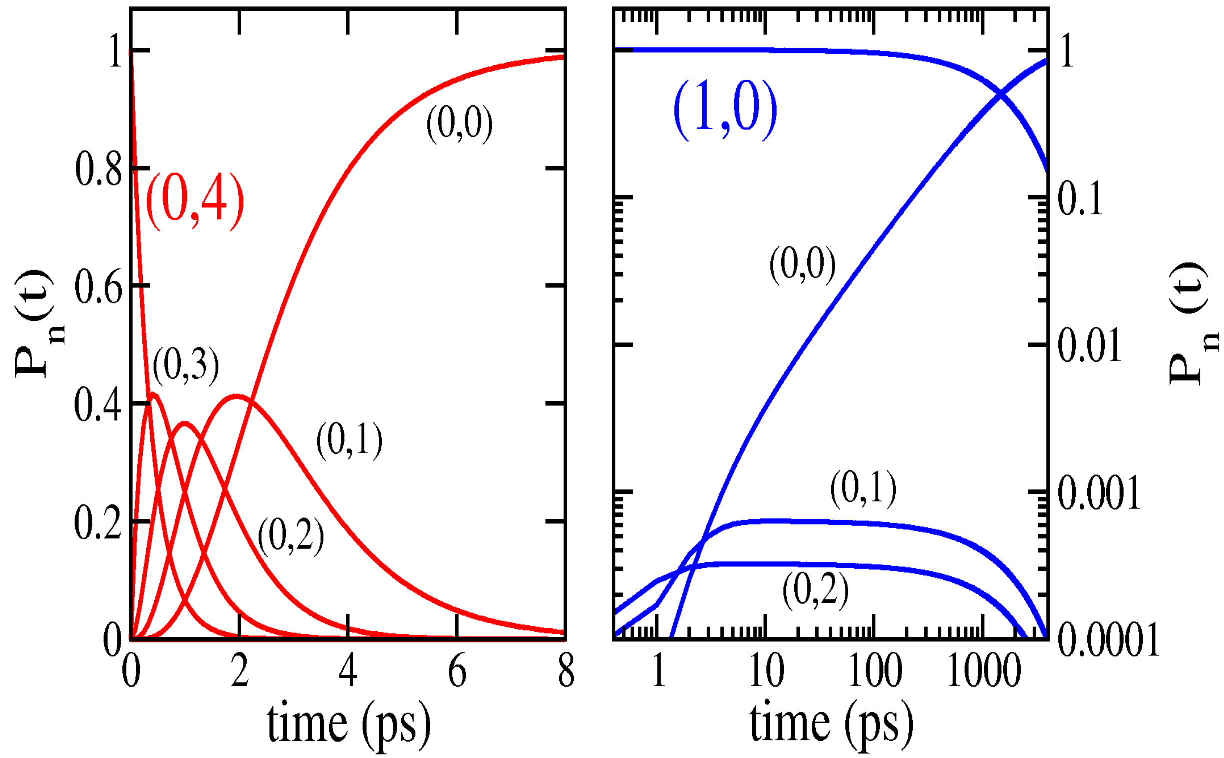
- **The Golden Rule of quantum mechanics**

$$\Gamma_{1\to 0} = \frac{2\pi}{\hbar} \sum_i \sum_f w_i(T)\,(1 - w_f(T))\,\left|\left\langle 0, f|\hat{H}_{sb}|1, i\right\rangle\right|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega_0)$$

- **Lifetimes (T=0)**



- **Decay mechanism:**

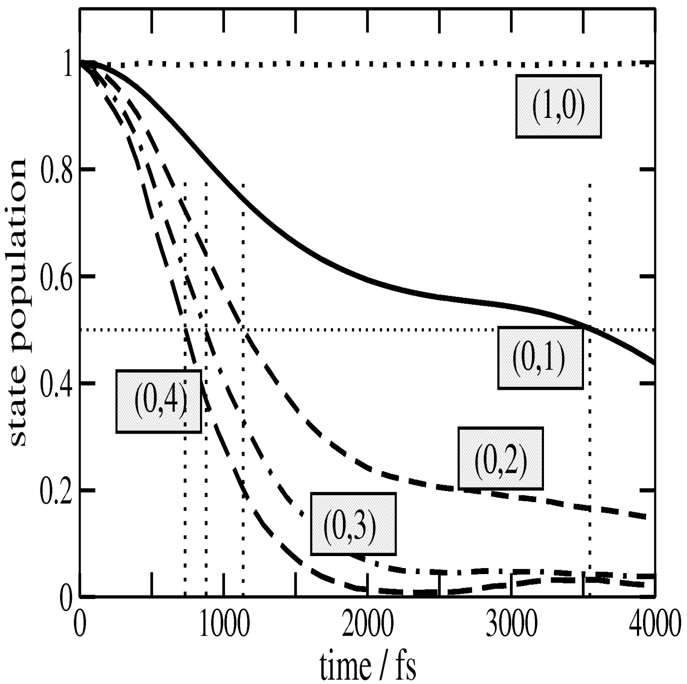


NON-PERTURBATIVE RELAXATION H:Si(100)

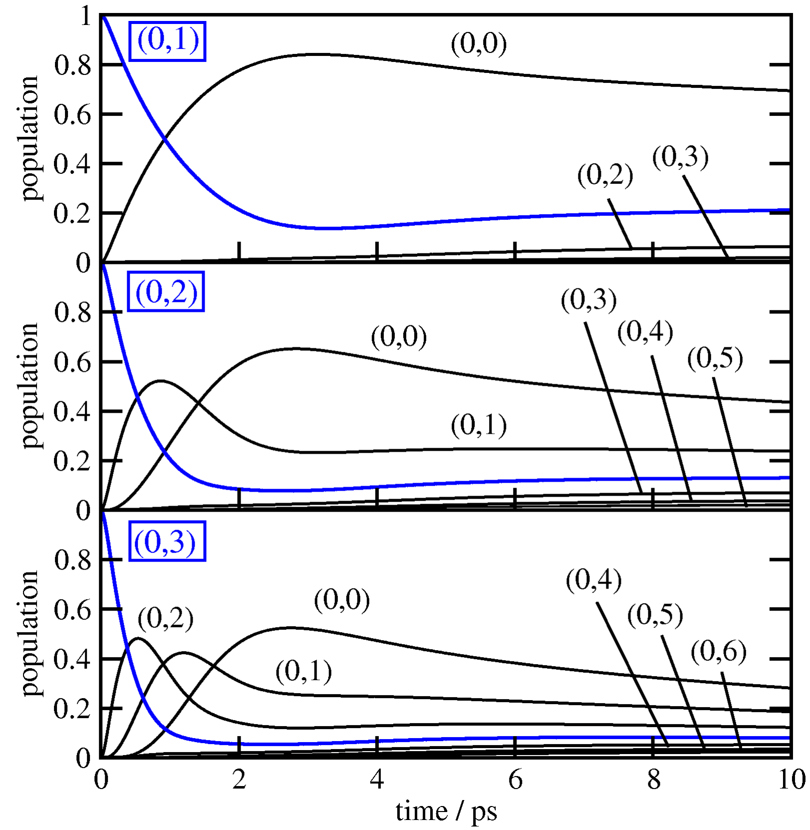
- Solve $i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$ by MCTDH or TDSCF for F=M+2 DOF

- **Relaxation of the bending mode: MCTDH and TDSCF**

MCTDH (M=50 oscillators)



TDSCF (M=534)



- **Half-life times $T_{1/2}$ of (0,1)**: Golden Rule: 0.94 ps, TDSCF: 0.92 ps

CPL **433**, 91 (2006), JPC C **111**, 5432 (2007)

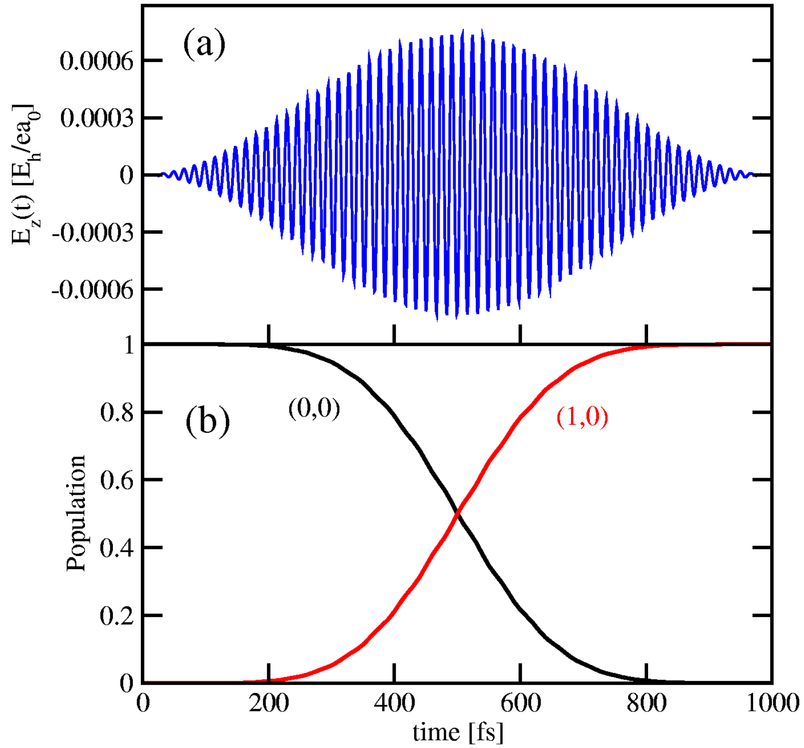
IR EXCITATION OF H:Si(100) WITH $\sin^2$ PULSES

$\sin^2$ pulse: $$V_{mn}(t) = -\mu_{mn}\, E_0 \sin^2\left(\frac{\pi t}{t_f}\right)\cos(\omega_0 t)$$

π pulse: $$E_0^{\pi} = \frac{2\pi\hbar}{t_f|\mu_{if}|}$$

- **Si-H stretch (1,0)**

$\omega_0 = \omega_r$, $t_f = 1$ ps

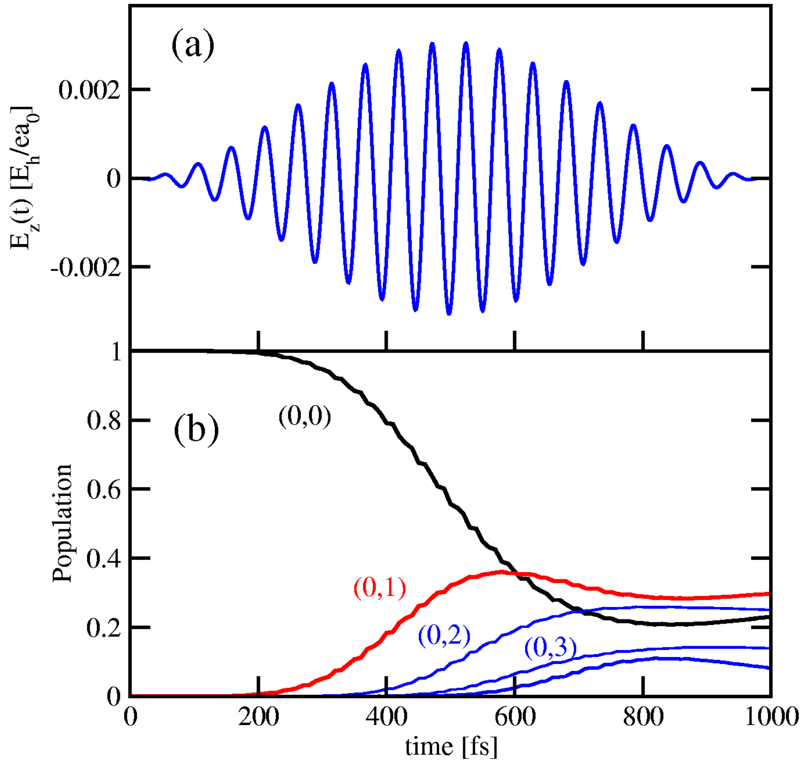


$\Longrightarrow$ mode- and state-selective

G.K. Paramonov, PS *et al.*, PRB **75**, 045405 (2007)

- **Si-H bend (0,1)**

$\omega_0 = \omega_\phi$, $t_f = 1$ ps

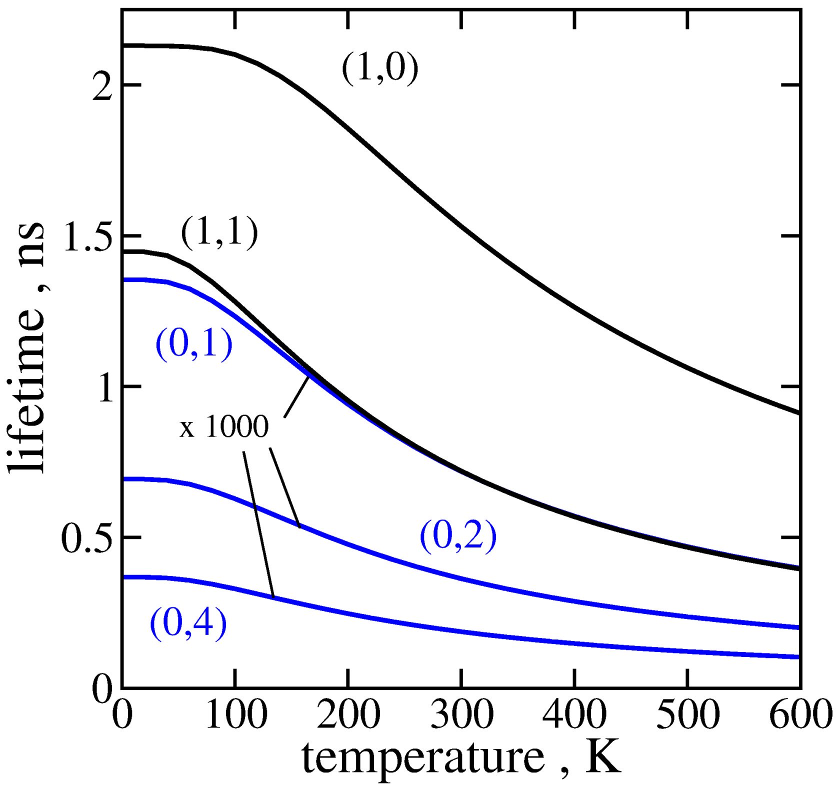


$\Longrightarrow$ mode-selective

TEMPERATURE EFFECTS: A PUZZLE

- **Reduced treatment**

  Golden Rule (M=534 oscillators)



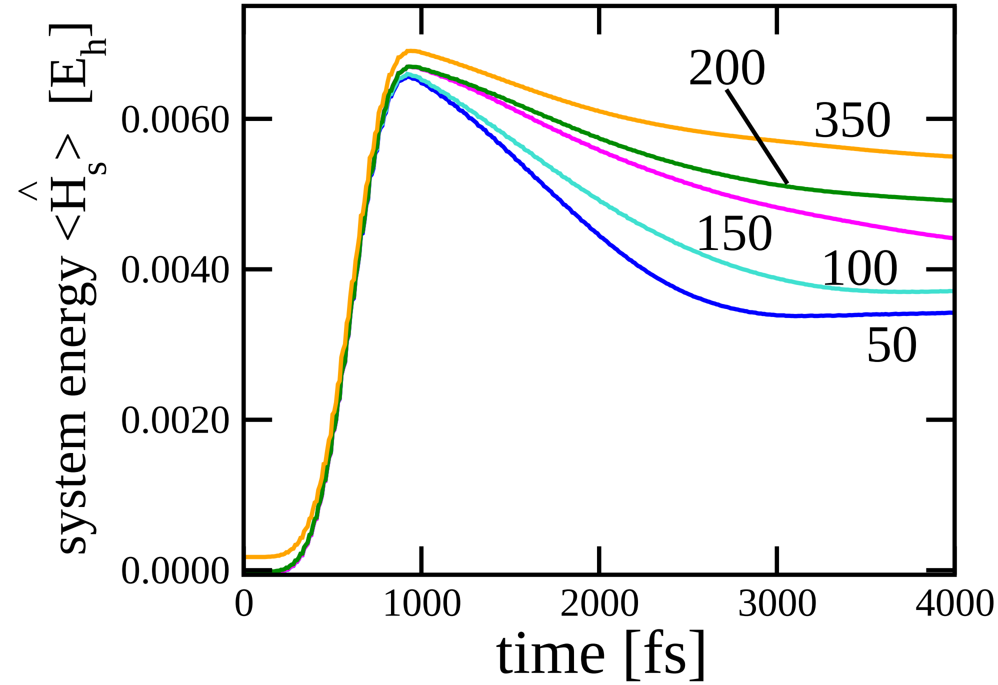
τ_{vib} goes down if T goes up

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

- **Full treatment**

  MCTDH (M=20)

  Random Phase Thermal Wavefunction Method



energy decay after IR (1 ps) (0,1) excitation

τ_{vib} goes up if T goes up

F. Lüder, M. Nest, PS, Theor. Chem. Acc., in press (2010)

RANDOM PHASE THERMAL WAVEFNCT METHOD

- **The method**

❶ create infinite-T wavefunction

$$|\Phi(\vec{\theta})\rangle = \frac{1}{\sqrt{L}} \sum_{l}^{L} e^{i\theta_l} |\phi_l\rangle$$

❷ propagate in imaginary time to $\beta/2$

$$\hat{\rho}(\beta) = \frac{1}{Z} e^{-(\beta/2)\hat{H}_0} \hat{I} e^{-(\beta/2)\hat{H}_0}$$

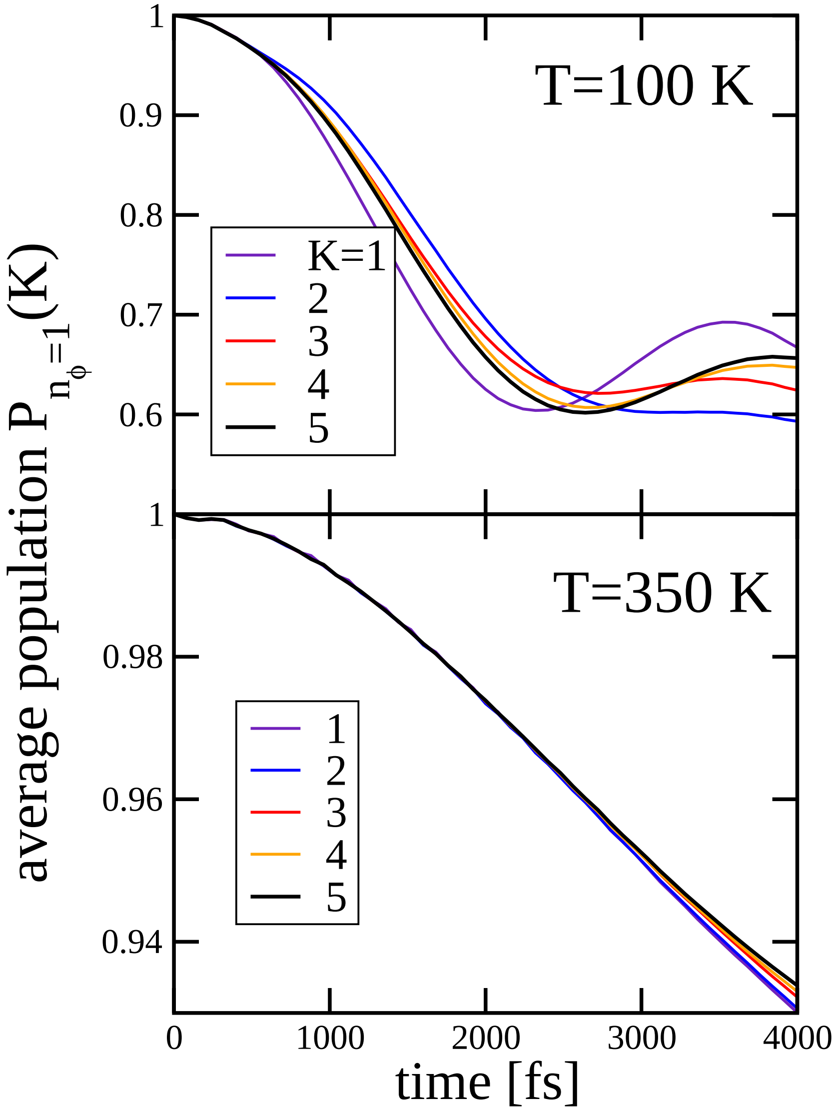
$$= \lim_{K\to\infty} \frac{1}{Z}\frac{1}{K} \sum_{k=1}^{K} |\Phi(\frac{\beta}{2}, \vec{\theta}_k)\rangle\langle\Phi(\frac{\beta}{2}, \vec{\theta}_k)|$$

❸ propagate in real time to time t

❹ repeat, average

Gelman, Kosloff, CPL **381**, 129 (2003)

- **Number of realizations K**

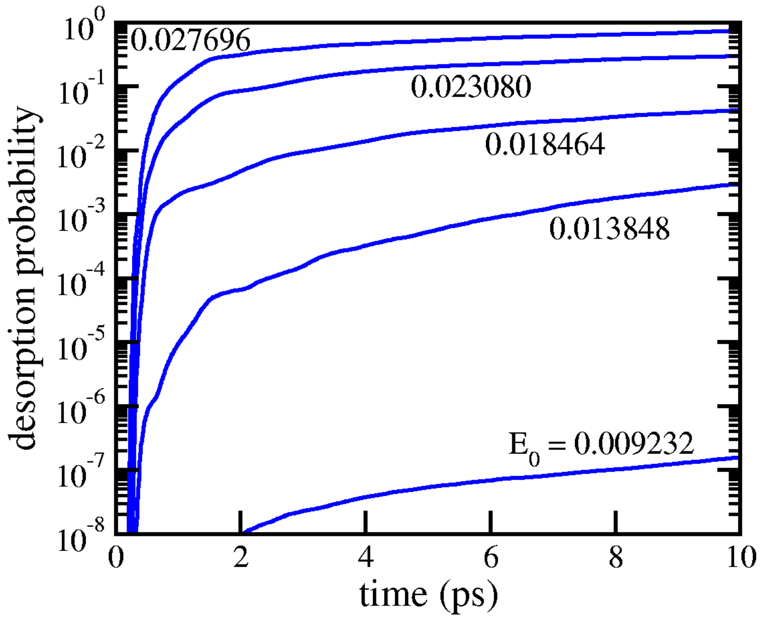


population decay H/Si(100), ϕ-mode

IR-PULSE DESORPTION OF H FROM H:Si(100)

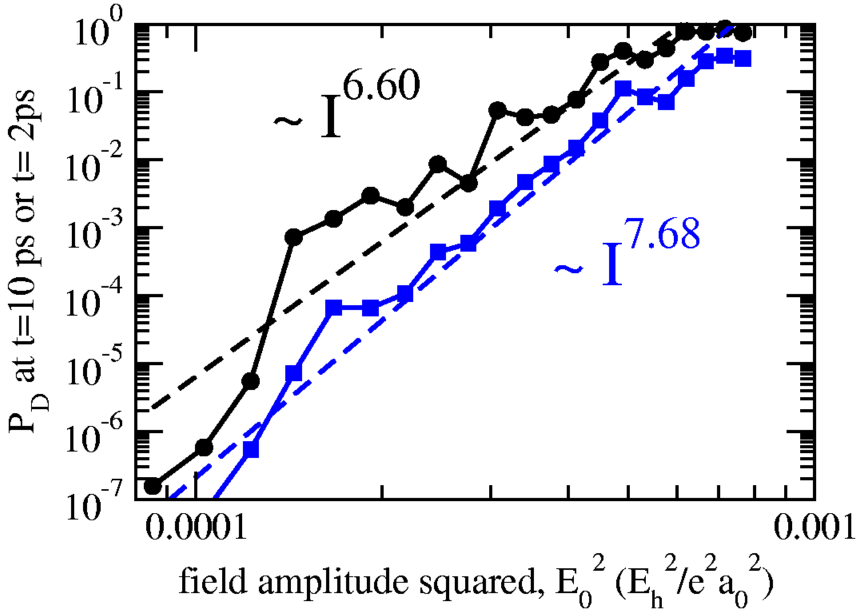
- **TDSCF model**
  - (534+2)-dimensional calculation
  - Plateau-type laser pulses, field strength E_0, 10 ps long, $\omega_0 = \omega_r < 0.1D$

- **Desorption**



desorption by mode-selective excitation

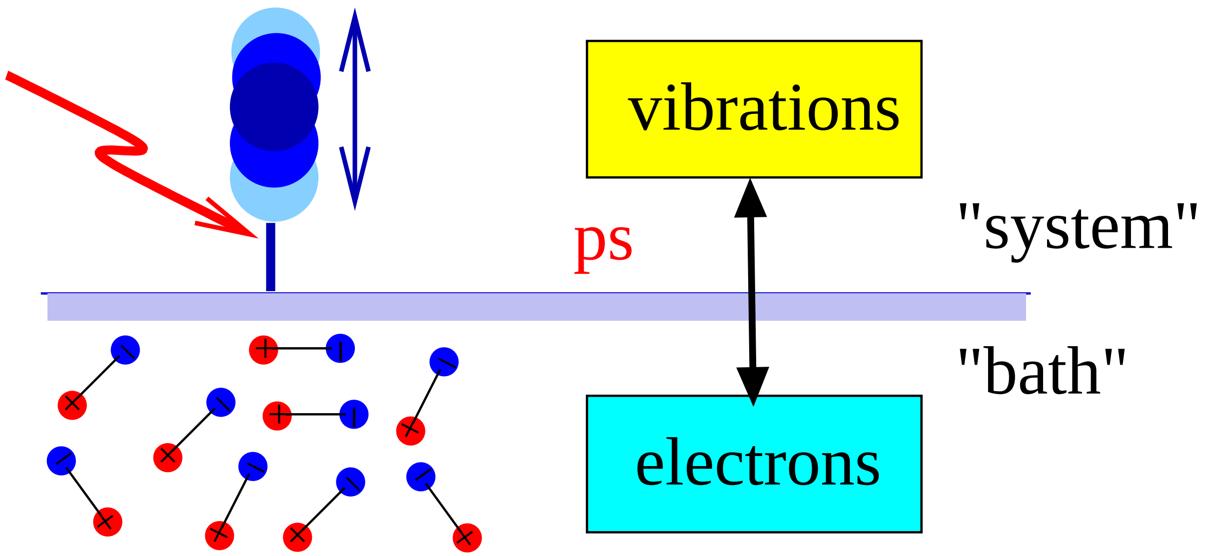
- **Scaling with intensity**



multi-photon process

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

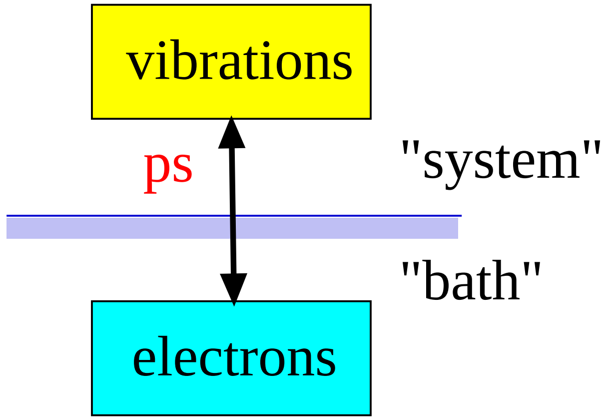
VIBRATION-ELECTRON COUPLING



- **System:** CO@Cu(100), IR excitation

VIBRATIONAL RELAXATION: Nonadiabatic Coupling

- **Problem**



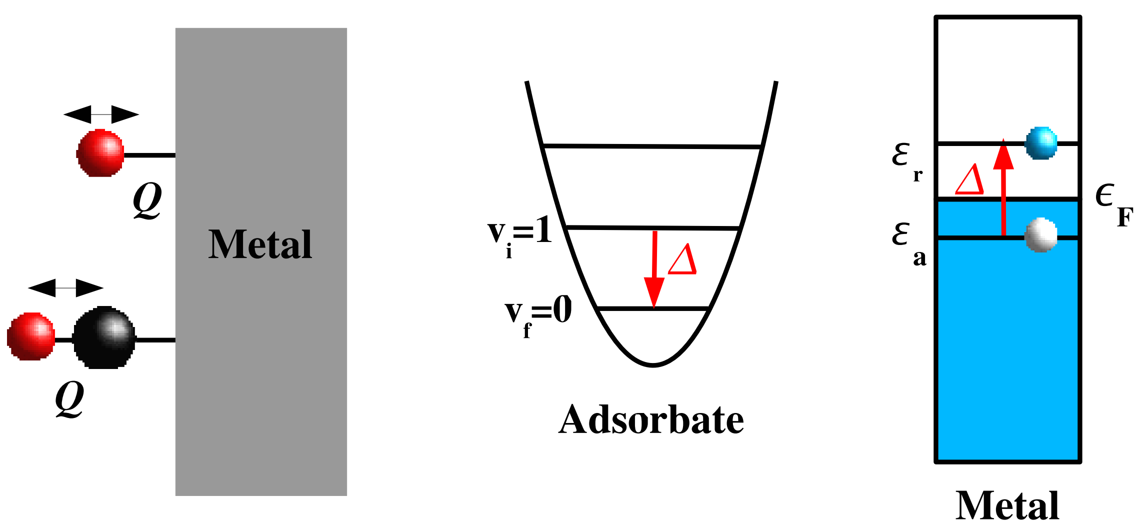
- **Theory**[1,2]

$$\Gamma_{n \to m} = \frac{2\pi}{\hbar} \sum_f \left| \langle m\, e_f | \hat{T}_{nuc} | n\, e_i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_{mn})$$

$$\langle m e_f | \hat{T}_{nuc} | n e_i \rangle = -\frac{\hbar^2}{\mu} \left\langle m | T^{(1)}_{fi}(Q) | \frac{\partial n}{\partial Q} \right\rangle_Q$$

❶ LCAO-MO cluster approach[1]

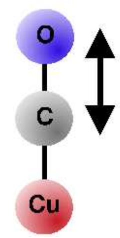
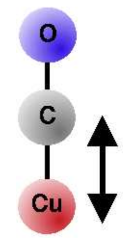
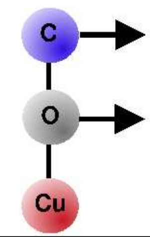
❷ Periodic DFT approach[2]

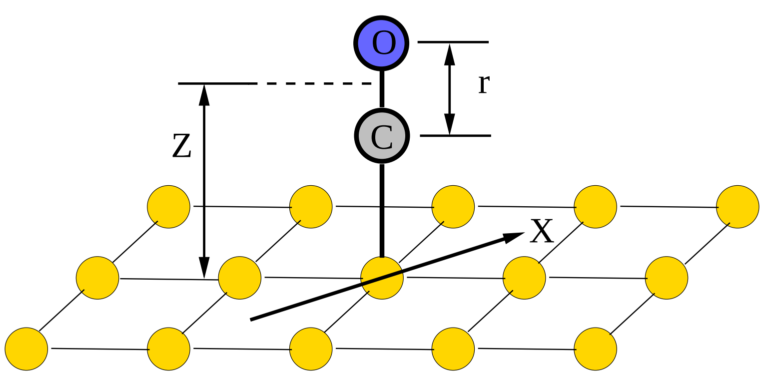


[1] Tully et al., PRB **46**, 1853 (1992)

[2] Lorente, Persson, Faraday Disc. **117**, 277 (2000)

CO/Cu(100): 3-MODE MODEL FOR IR EXCITATION

Mode	C–O stretch 	CO–Cu stretch 	frustrated translation 
	r: IR active	Z: IR active	X: 'dark'
ω [cm^{-1}]	2152	293	77
τ_{vib}^{el} [ps] @ 0 K	3.3	82	108
τ_{vib}^{tot} [ps] @ 10 K	1.7	22	14
@ 300 K	1.6	2.8	2.3
dipole μ_{01} [$\times 10^{-3}$ ea$_0$]	143.13	-38.00	0.00



- **Wave functions:** $\psi_{n_r,n_Z,n_X}(r, Z, X)$

Potential, lifetimes: Tully, Gomez, J. Vac. Sci. Technol. A **11**, 1914 (1993)

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:**

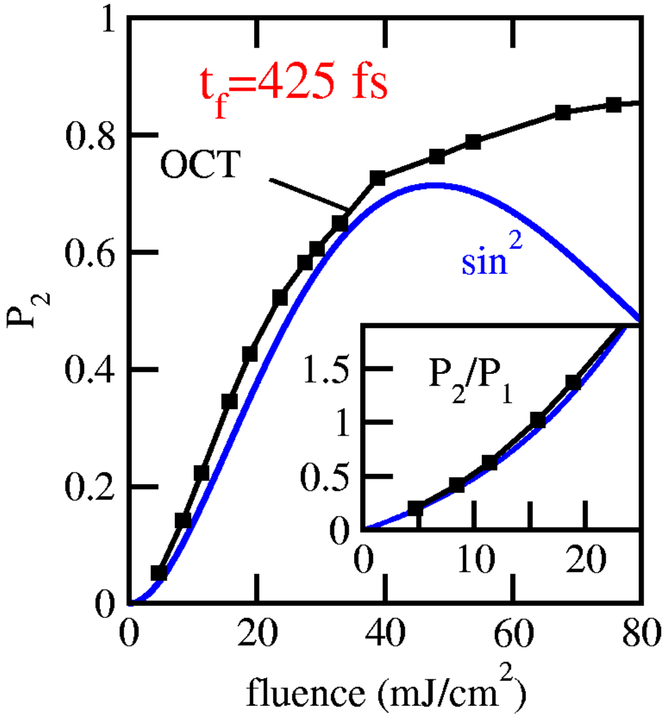
$$E(t) = -\frac{1}{\hbar\alpha(t)} \operatorname{Im}\langle\langle\hat{\sigma}(t)|\hat{\mu}|\hat{\rho}(t)\rangle\rangle$$

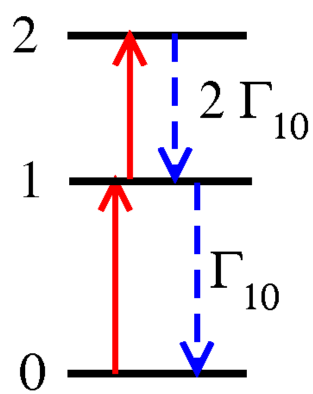
(1) Y. Ohtsuki *et al.*, JCP **109**, 9318 (1998); (2) Y. Ohtsuki *et al.* JCP **110**, 9825 (1999)

EXCITING THE r MODE: (0,0,0) → (2,0,0)

- **3-state model**

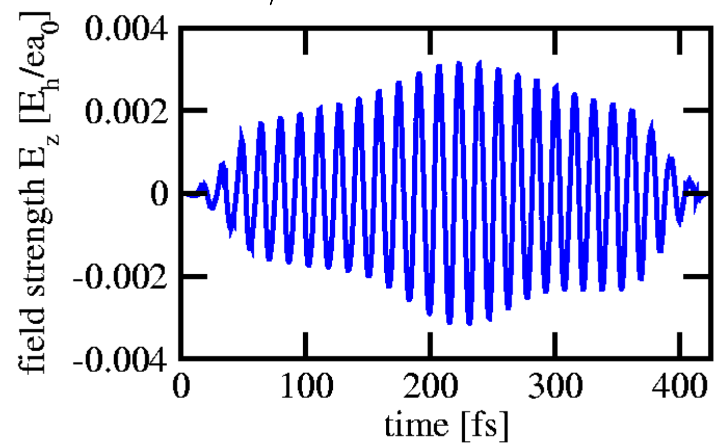
$\sin^2$ vs. OCT pulses; full dissipation; T=0

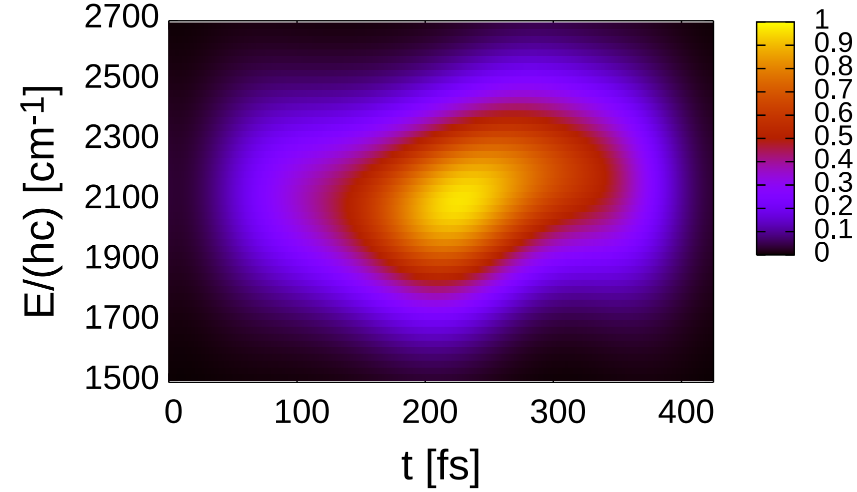




- **OCT field**

F = 68 mJ/cm^2





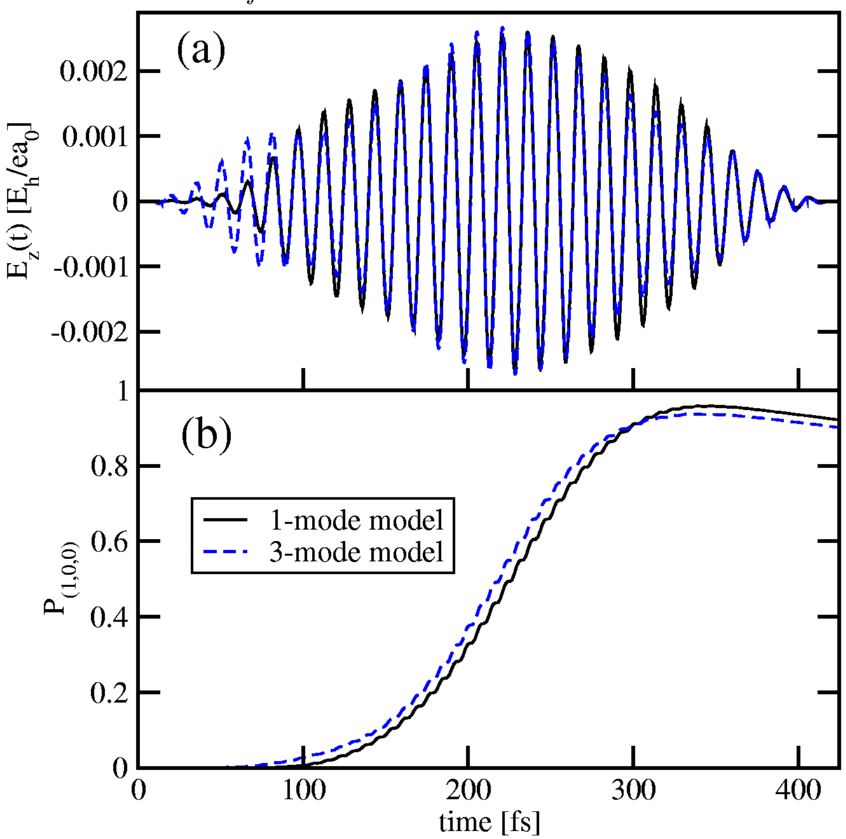
chirp!

Beyvers *et al.*, JCP **124**, 234706 (2006)

EXCITING THE r MODE → (1,0,0)

- **3-mode vs. 1-mode**

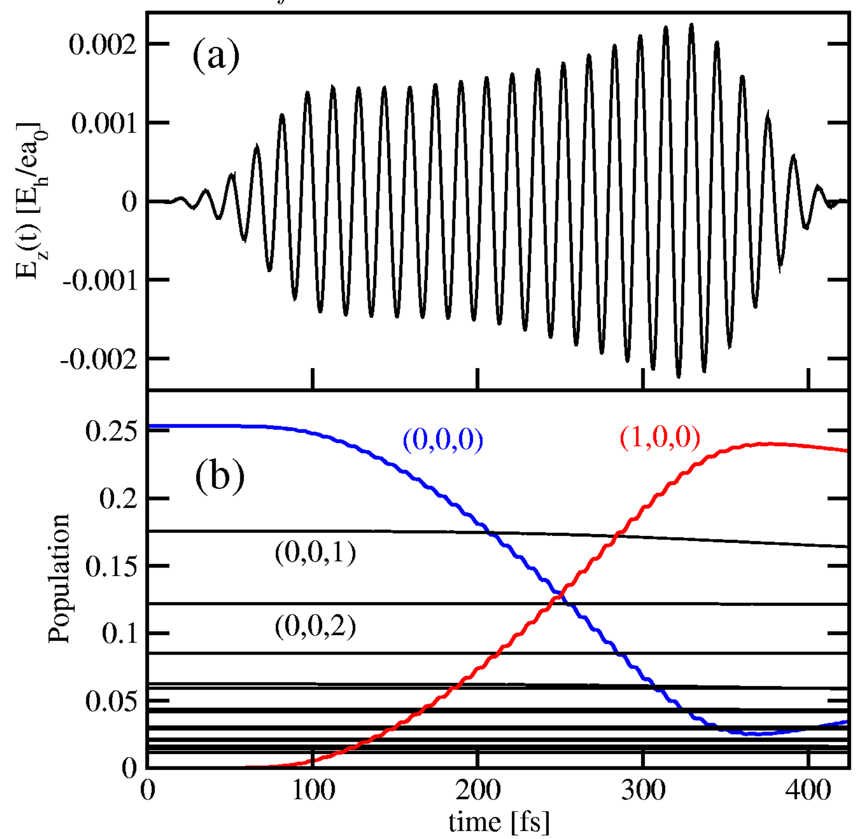
T=10 K; t_f=425 fs



weak intermode coupling

- **Temperature effects**

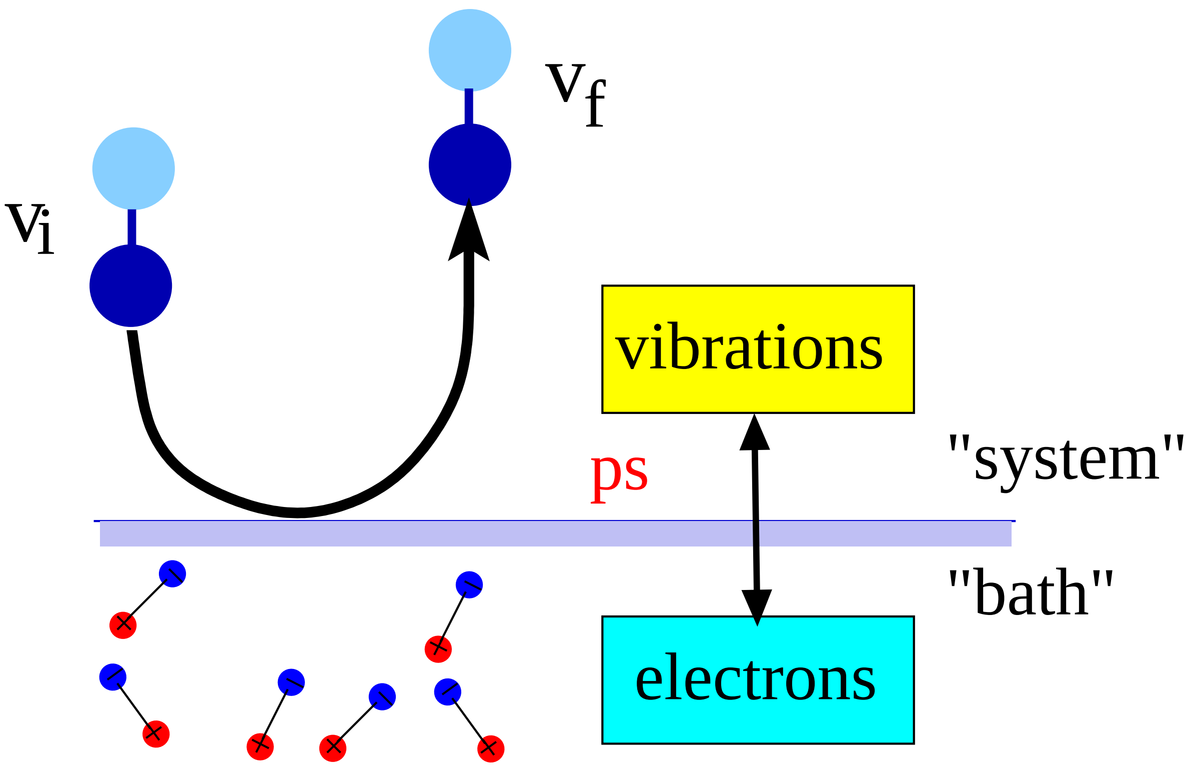
T=300 K; t_f=425 fs



limited control

limit: $\mathrm{P}_{max} = \rho_{00}(T)$ (=0.253)

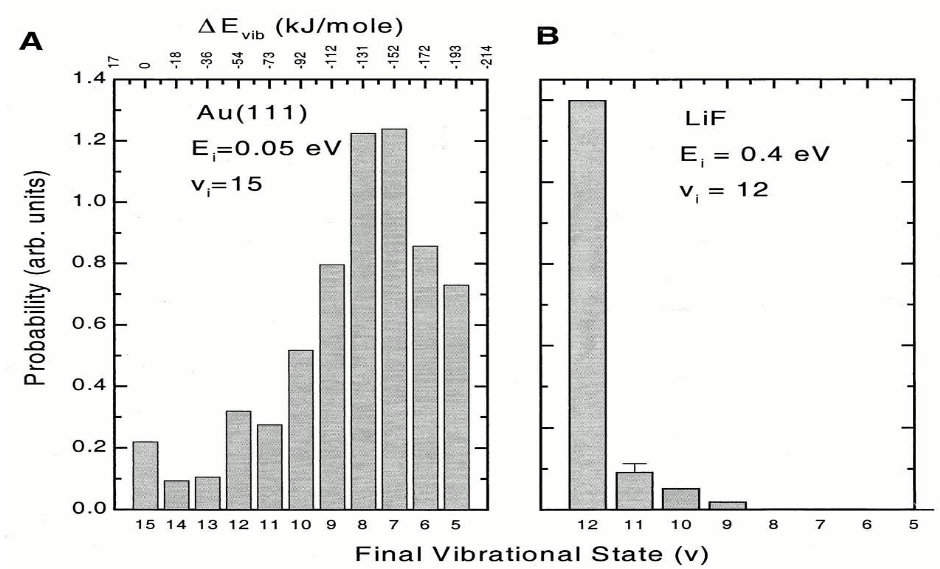
VIBRATION-ELECTRON COUPLING



- **System:** NO scattering at Au(111), vibrational relaxation

NO($v = 15$) SCATTERING FROM Au(111)

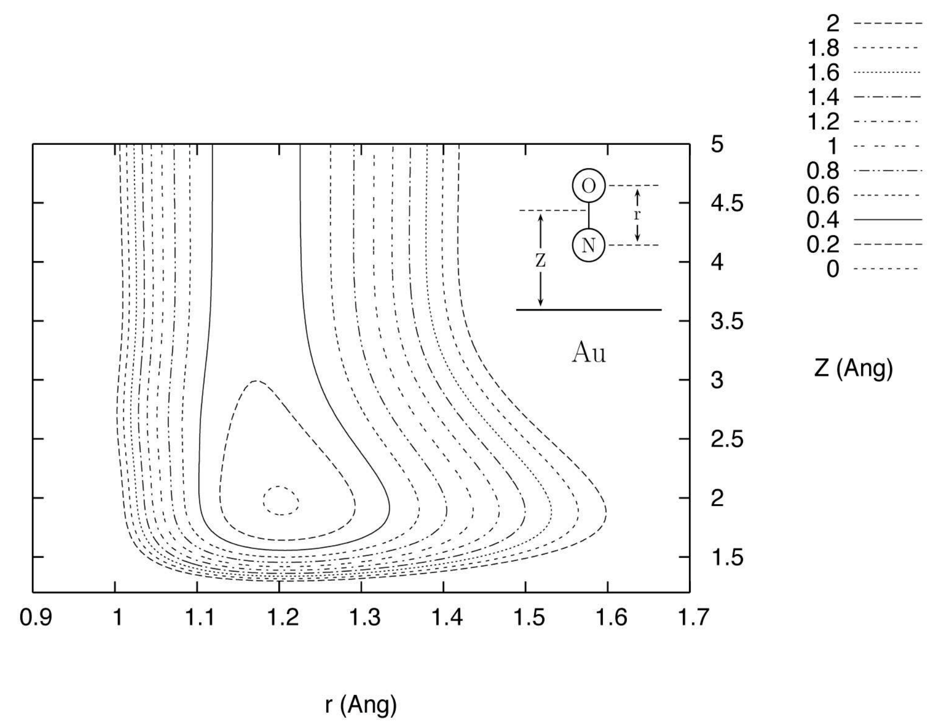
- **Experiment**[1]



- 7-8 vibr. quanta loss on Au (1.5 eV)
- coupling to electron-hole pairs
- Au/Cs surfaces: exoelectron emission

- **Model**

two-mode density matrix model with electronic friction



periodic DFT calculation

[1] Huang *et al.*, Science **290**, 111 (2000)

COUPLED-CHANNEL DENSITY MATRIX METHOD

- **The CCDM method**[1]

$$\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)] + \mathcal{L}_D\hat{\rho}(t)$$

$$\hat{\rho}(Z,Z') = \sum_{u,v}^{K} \hat{\rho}_{u,v}(Z,Z')|u\rangle\langle v|$$

unbound Z: grid representation
bound r: eigenstate representation

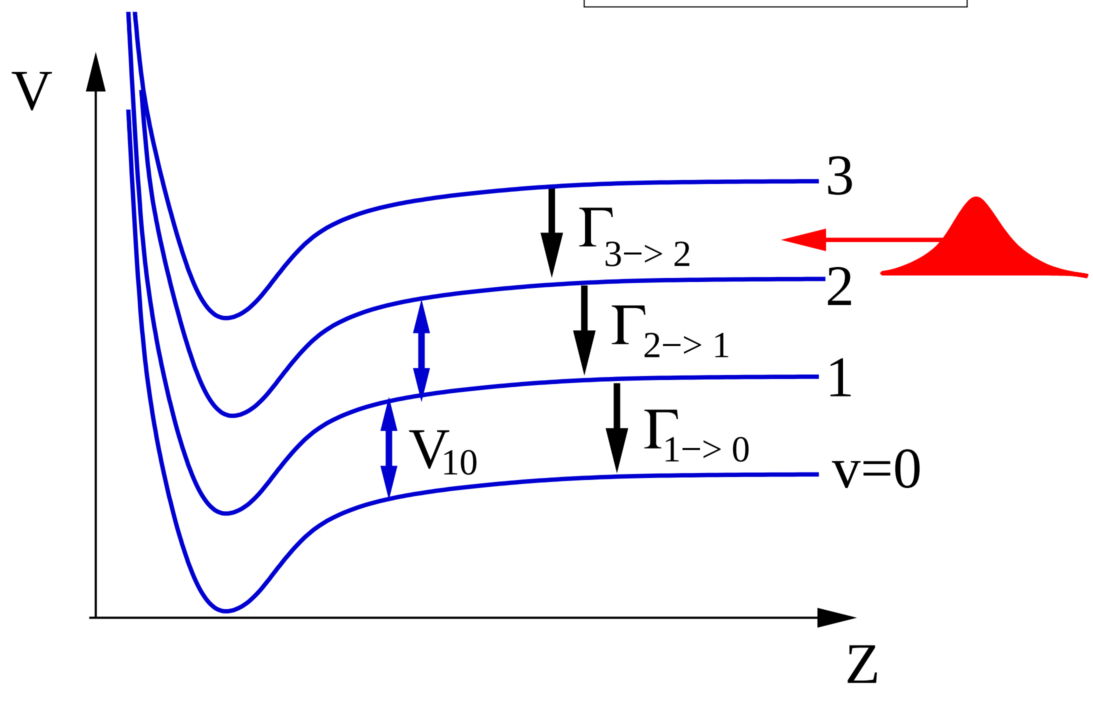
$\Longrightarrow$ K coupled 1D LvN equations

- **Electronic friction**

$$\mathcal{L}_D\hat{\rho}(t) = \sum_{u,v} C_{u,v}\hat{\rho}C^{\dagger}_{u,v} - \frac{1}{2}[C^{\dagger}_{u,v}C_{u,v}, \hat{\rho}]_+$$

$$C_{u,v} = \sqrt{\Gamma_{v\to u}(Z)}|u\rangle\langle v|$$

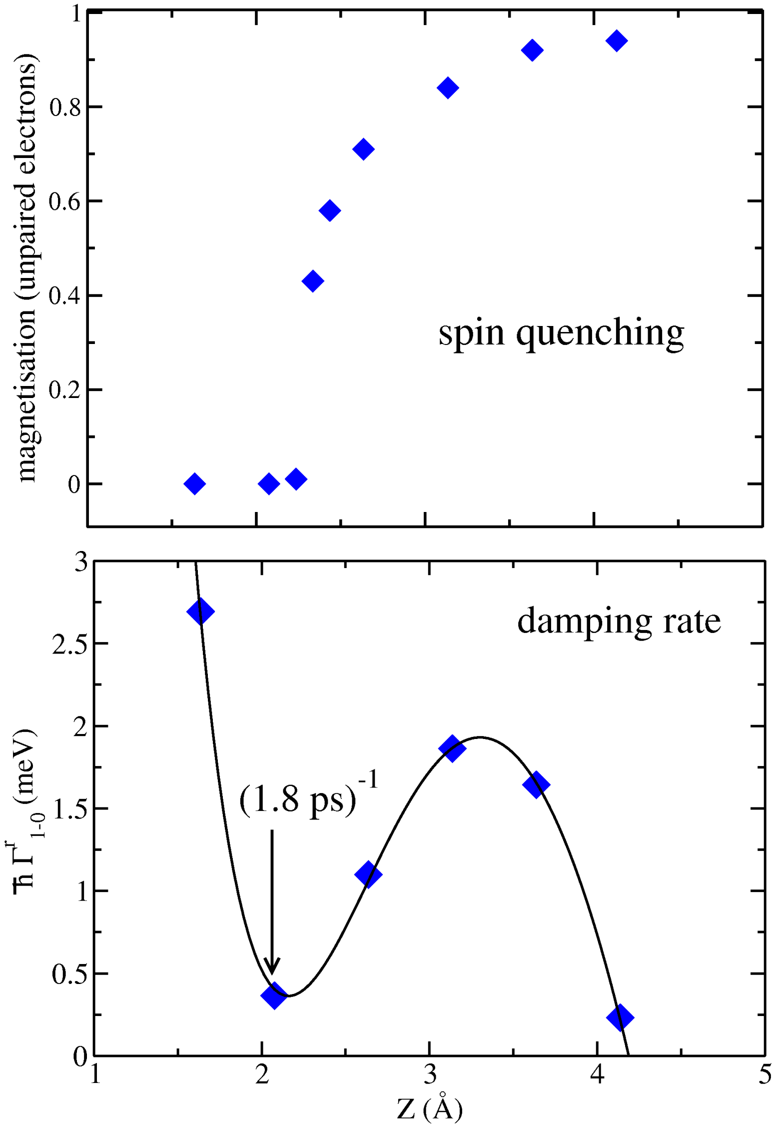
coordinate-dependent transition rates
from periodic DFT: $\Gamma_{v\to v-1} = v\Gamma_{1\to 0}$



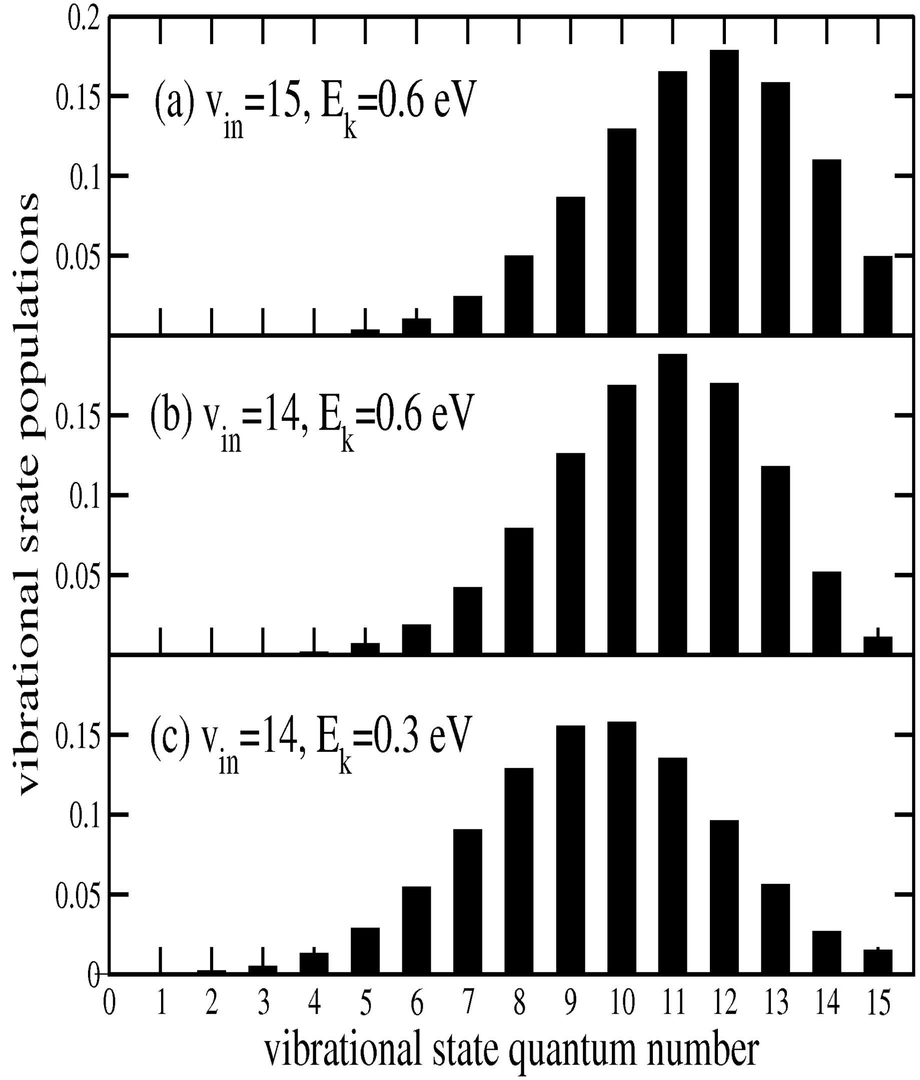
[1] Pesce, PS, CP **219**, 43 (1997); JCP **108**, 3045 (1998)

RESULTS

- Vibrational damping



- Vibrational relaxation



electronic friction accounts for vibrational relaxation

S. Monturet, PS, submitted (2010)

SUMMARY, OUTLOOK

- **Methods**
  - open-system density matrix theory
  - perturbation theory
  - wavepacket propagation
  - quantum chemistry
  - optimal control theory

- **Systems**
  - H@Si(100)
  - CO@Cu(100)
  - NO@Au(111)

- **Applications**
  - Vibration-phonon coupling
  - Vibration-electron coupling
  - State-selective vibrational excitation
  - Vibrational relaxation during scattering

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