Laser distillation as a tool to alleviate the effects of dissipation: the subsurface absorption of hydrogen in palladium

Jean Christophe Tremblay

Réunion plénière du GDR-ARCHES

Domaine du Mas Blanc, Alénya

October 3-6, 2011

Context

- **Our humble goals**
  - Study the vibrational relaxation of molecules in the vicinity of metallic surfaces
  - Perform state resolved dissipative vibrational dynamics of strongly coupled anharmonic systems *fully quantum mechanically*
- **Energy relaxation in dissipative environments**
  - Breakdown of the adiabatic Born-Oppenheimer approximation
- **Electron-hole pair coupling at metallic surfaces**
  - Chemisorption of gas-phase molecules on thin films produces chemicurrent
  - Scattering of vibrationally excited molecules on metal leads to emission of electrons
  - Reaction rates of chemical processes at surfaces slowed down by electronic friction

Hydrogen at metallic surfaces

- **Metals can be used to store hydrogen**
  - Subsurface and bulk absorption
  - Defined potential energy minima in the surface

- **Hydrogens in the subsurface are highly reactive**
  - e.g. alkene hydrogenation on a catalytic surface
  - Hydrogen coming out of the subsurface site have the right kinetic energy and direction for an optimally reactive collision
  - Hydrogens in the bulk are less reactive, more tightly bound

- **Can we populate selectively the subsurface to render a catalyst more active?**

A system of interest

- **Hydrogen on a Palladium (111) surface**
  - *Well localized* **minima above and below the surface**

    Ozawa, Arboleda Jr., Roman, Nakanishi, Dino and Kasai *J. Phys.: Condens. Matter* **19, (2007) 365214**
  - **Present a good catalytic activity**

    Kay, Peden and Goodman *Phys. Rev. B* **34 (1986) 817.**
  - **High quality potential energy surface available**

    Ozawa, Roman, Arboleda Jr., Dino, Nakanishi and Kasai *J. Appl. Phys.* **101, (2007) 123530**

- **How do we propose to manipulate the adsorbate?**
  - **Short and intense shaped laser pulses**

- **Some key challenges**
  - **Design of efficient and** *selective* **pulses**
  - **Dissipation of the energy from the adsorbate to the surface**

Some perspective

Molecular mechanics

- Classical particles
- Classical force fields

Ab initio molecular dynamics

- Classical EOMs
- Quantum mechanical forces

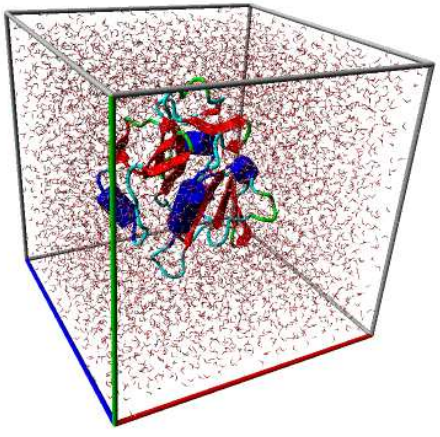
Hybrid QM/MM methods

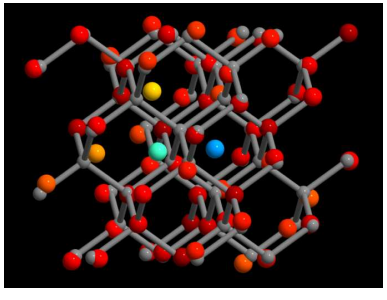
- QM reactive center
- Classical environment

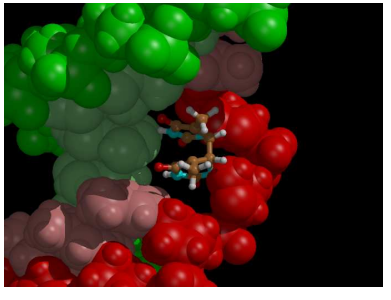
Quantum molecular dynamics

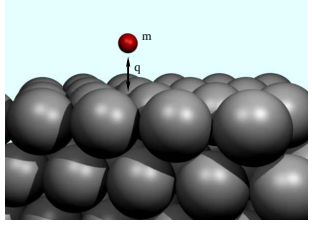
- non-local effects must be taken into account

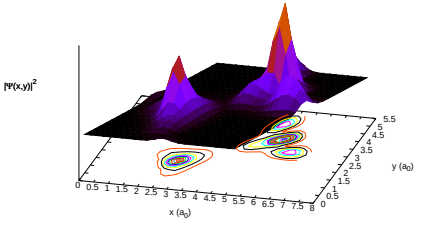
size





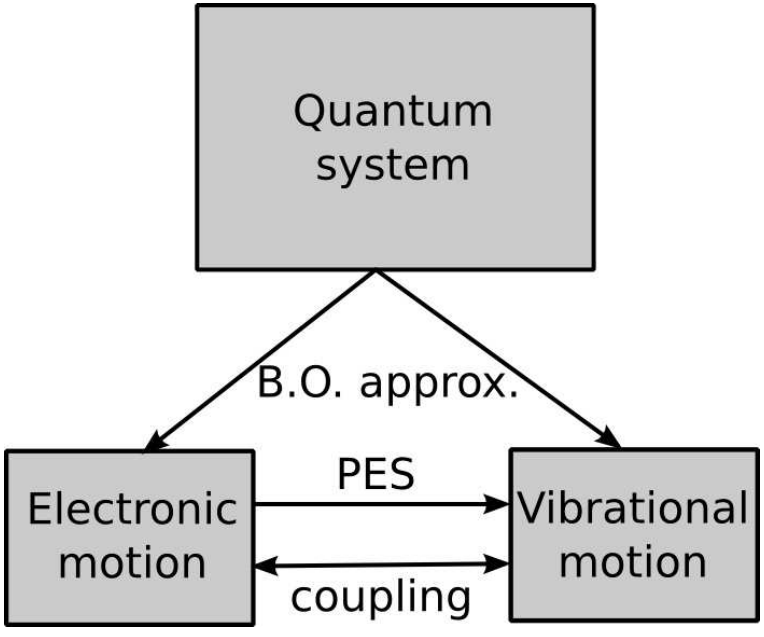


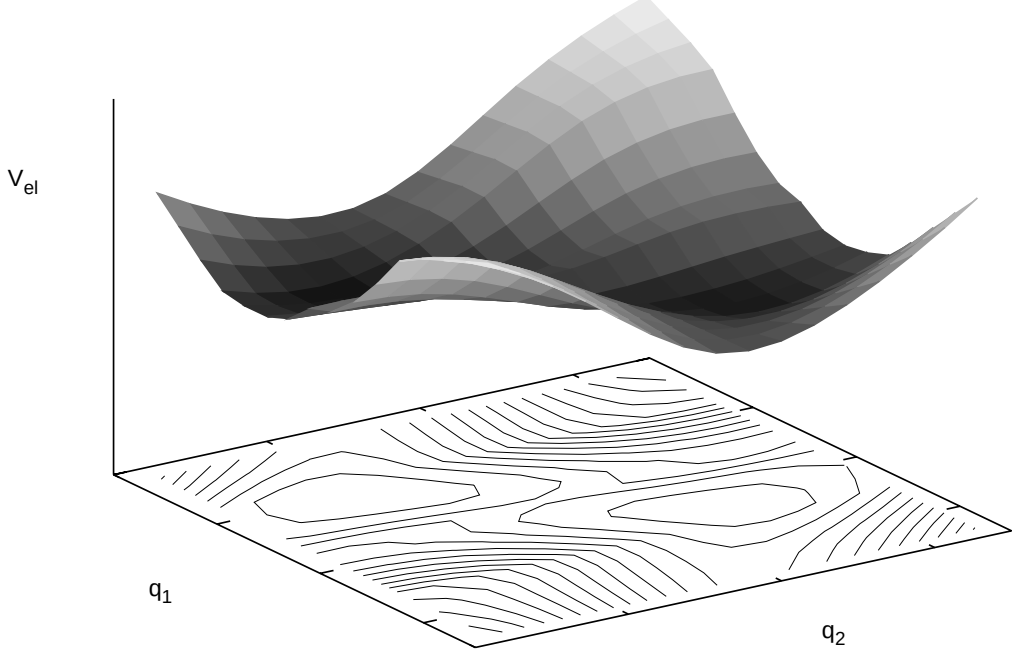


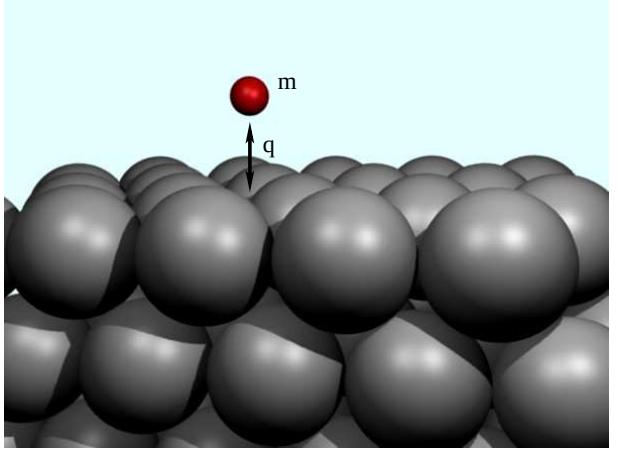


complexity

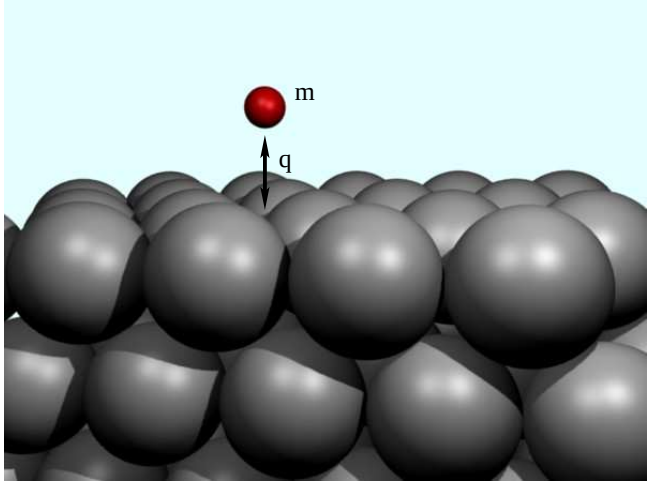
Born-Oppenheimer approximation

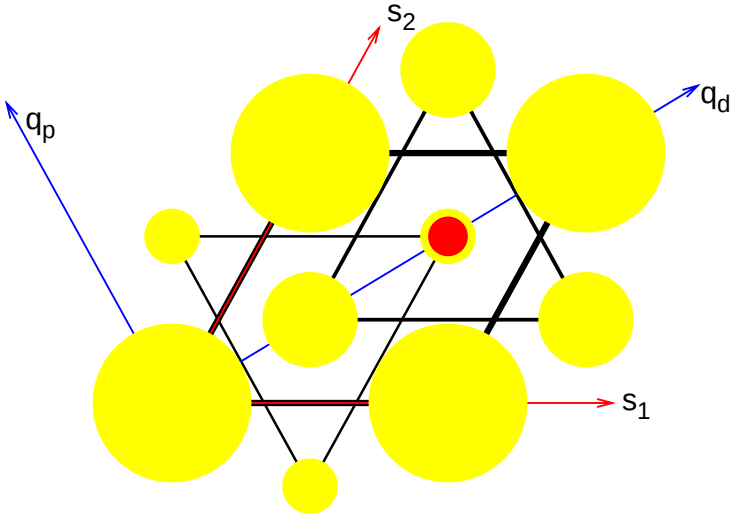






Vibrations of an hydrogen atom on palladium





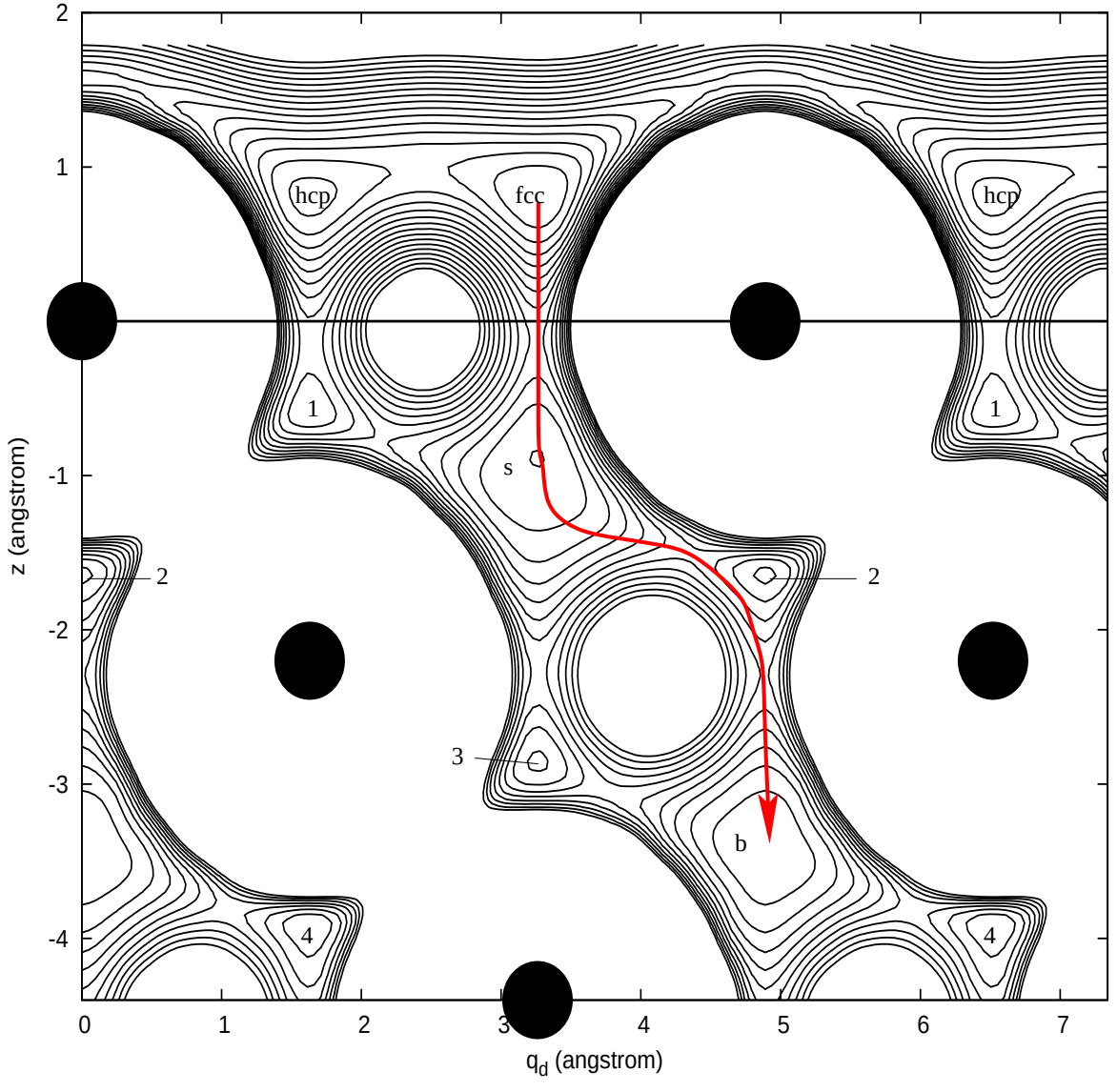
- **Field-free subsystem Hamiltonian**

$$\hat{H}_{sub} = -\frac{1}{2m}\left(\frac{1}{sin^2(\alpha)}\frac{\partial^2}{\partial s_1^2} - \frac{2cos(\alpha)}{sin^2(\alpha)}\frac{\partial^2}{\partial s_1 \partial s_2} + \frac{1}{sin^2(\alpha)}\frac{\partial^2}{\partial s_2^2} + \frac{\partial^2}{\partial z^2}\right) + V(s_1, s_2, z)$$

- **Extract its eigenvalues ϵ_n and eigenvectors $|n\rangle$**
  - **Multi-dimensional wave functions is a linear combination of simple functions**

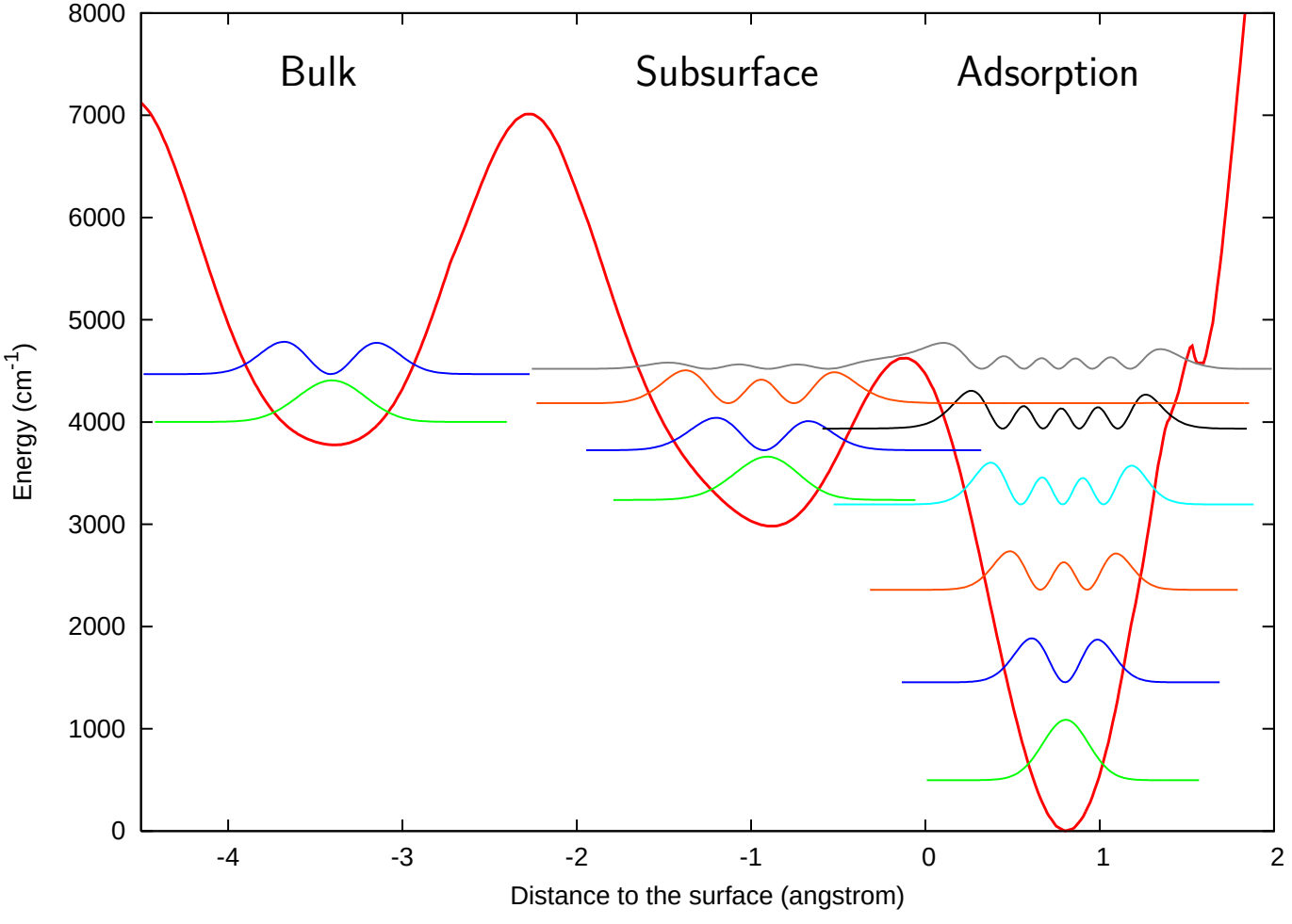
$$|n\rangle = \sum_{ijk} d_{ijk}^n \Phi_i(s_1)\Phi_j(s_2)\Phi_k(z)$$

1D reaction path Hamiltonian



- **Resurfacing barrier: 1600 cm^{-1}**
- **Bulk barrier: 3450 cm^{-1}**

The field-free, dissipation-free system eigenstates *in 1D*



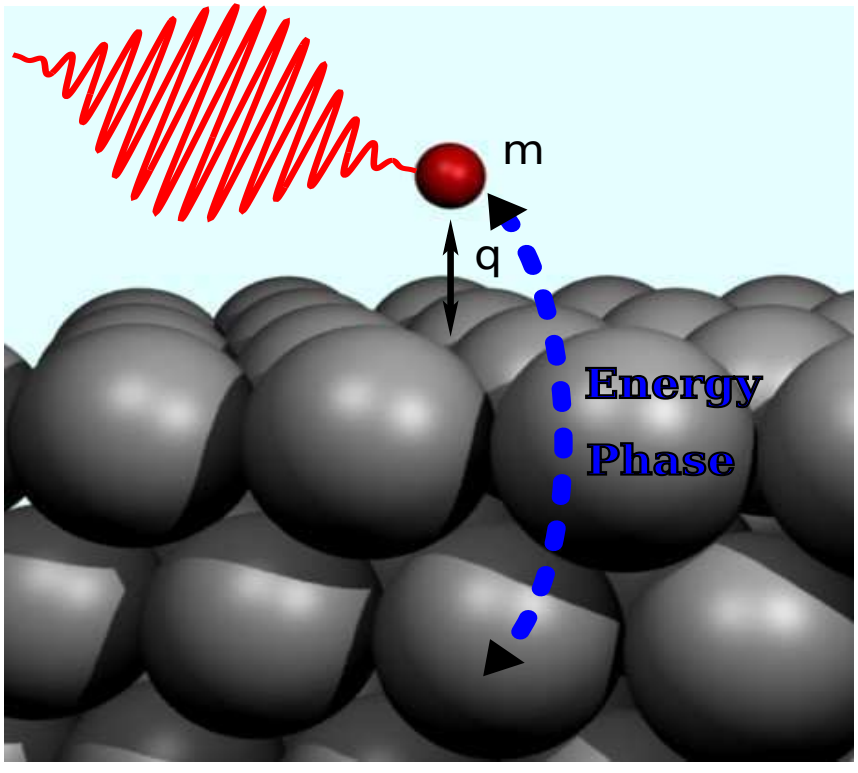
Assignment	Energy (cm^{-1})
$\mathrm{gs}^{(a)}$	0.0
$\nu_z^{(a)}$	957.6
$2\nu_z^{(a)}$	1861.8
$3\nu_z^{(a)}$	2696.7
$\mathrm{gs}^{(s)}$	2741.1
$\nu_z^{(s)}$	3686.5
$4\nu_z^{(a)}$	3438.2
$2\nu_z^{(s)}$	3686.5
$\left\{3\nu_z^{(s)} - 5\nu_z^{(a)}\right\}$	4148.6

- **500 sinc-DVR functions on the interval $[-4.5, 2]$Å**
- **Extraction of the lowest lying eigenpairs using the Lanczos algorithm**

PART ONE

System-bath dynamics

System-bath dynamics



- **Divide and conquer**
  - System + environment (or bath)
  - Their interaction (e.g. electron-hole pair creation, vibration-phonon coupling)
  - Neglect interaction of an external electric field with the bath

$$\hat{H}_{tot}(t) = \left(\hat{H}_s + \hat{H}_{ext}(t)\right) + \hat{H}_b + \hat{H}_{sb}$$

- **We are only interested in the dynamics of the subsystem**
- **Solution: Reduced density matrix**
  - Environment treated implicitely
  - Effect of the bath $\rightarrow$ non-unitary evolution of the system

Reduced density matrix for open systems

- **Total hamiltonian for a given system**

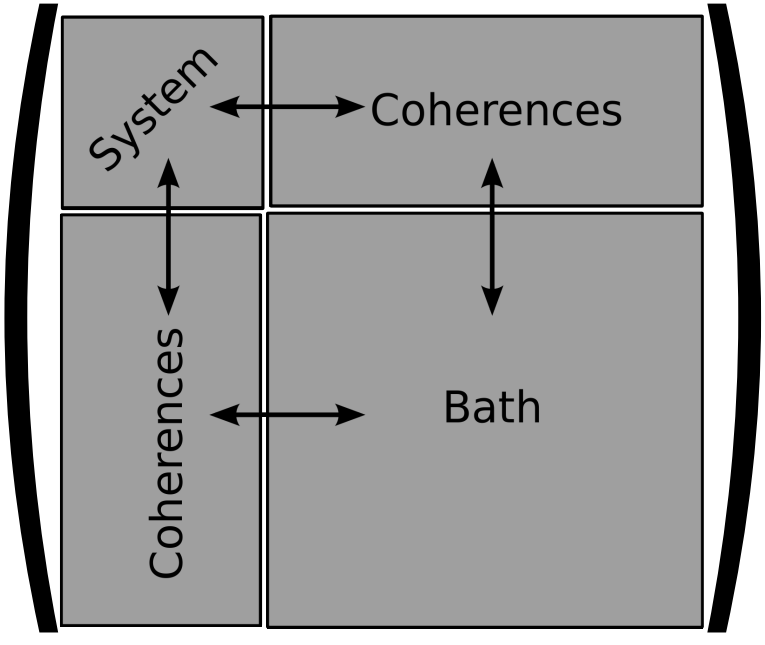
$$\hat{H}_{tot} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb}$$

- **Admits stationnary solutions**

$$\hat{H}_{tot}|\psi\rangle = E|\psi\rangle$$

- **Density matrix**

$$\hat{\chi} = |\psi\rangle\langle\psi| =$$



Reduced density matrix for open systems

- **Total hamiltonian for a given system**

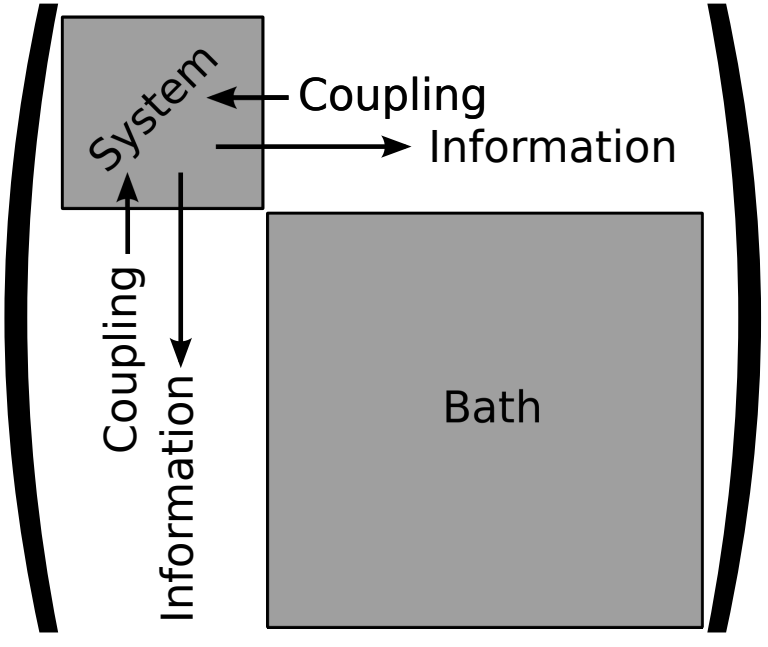
$$\hat{H}_{tot} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb}$$

- **Admits stationnary solutions**

$$\hat{H}_{tot}|\psi\rangle = E|\psi\rangle$$

- **Reduced Density Matrix**
  - **Trace out the bath**

$\hat{\chi} \longrightarrow$



Reduced density matrix formalism

- **System evolution characterized by the Liouville-von Neumann equation**

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

$\hat{H}(t) = \hat{H}_s - \hat{\mu} F(t)$ **and** $\mathcal{L}_D$ **is the dissipative Liouvillian**

- **Use the subsystem eigenstates to represent RDM**

$$\hat{\rho}(t) = \sum_{mn} \rho_{mn}(t) |m\rangle\langle n|$$

- **EOM are simple in the basis of eigenvectors of the subsystem**

$$\frac{\mathrm{d}\rho_{mn}(t)}{\mathrm{d}t} = -\frac{i}{\hbar}\omega_{mn}\rho_{mn}(t) + \frac{iF(t)}{\hbar}\sum_i (\mu_{mi}\rho_{in}(t) - \rho_{mi}(t)\mu_{in}) + \langle\langle m|\mathcal{L}_D\hat{\rho}|n\rangle\rangle$$

where $\omega_{mn} = (\epsilon_m - \epsilon_n)$**, and** $\langle\langle m|\mathcal{L}_D\hat{\rho}|n\rangle\rangle$ **represents the dissipation**

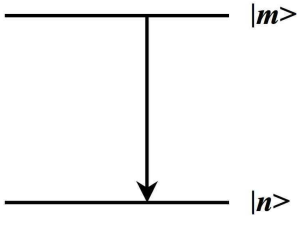
Semi-group treatment of dissipation

- **Lindblad semi-group formalism**
  - Ensures semi-positivity of $\hat{\rho}(t)$
  - Probabilistic interpretation of $\rho_{nn}(t)$

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

- **Energy relaxation**
  - Raising/lowering operators

$$\hat{C}_k \to \sqrt{\Gamma_{m\to n}}|n\rangle\langle m|$$



- **Phase relaxation**
  - Scaled Hamiltonian

$$\hat{C}_k \to \sqrt{\gamma^*}\hat{H}_s$$

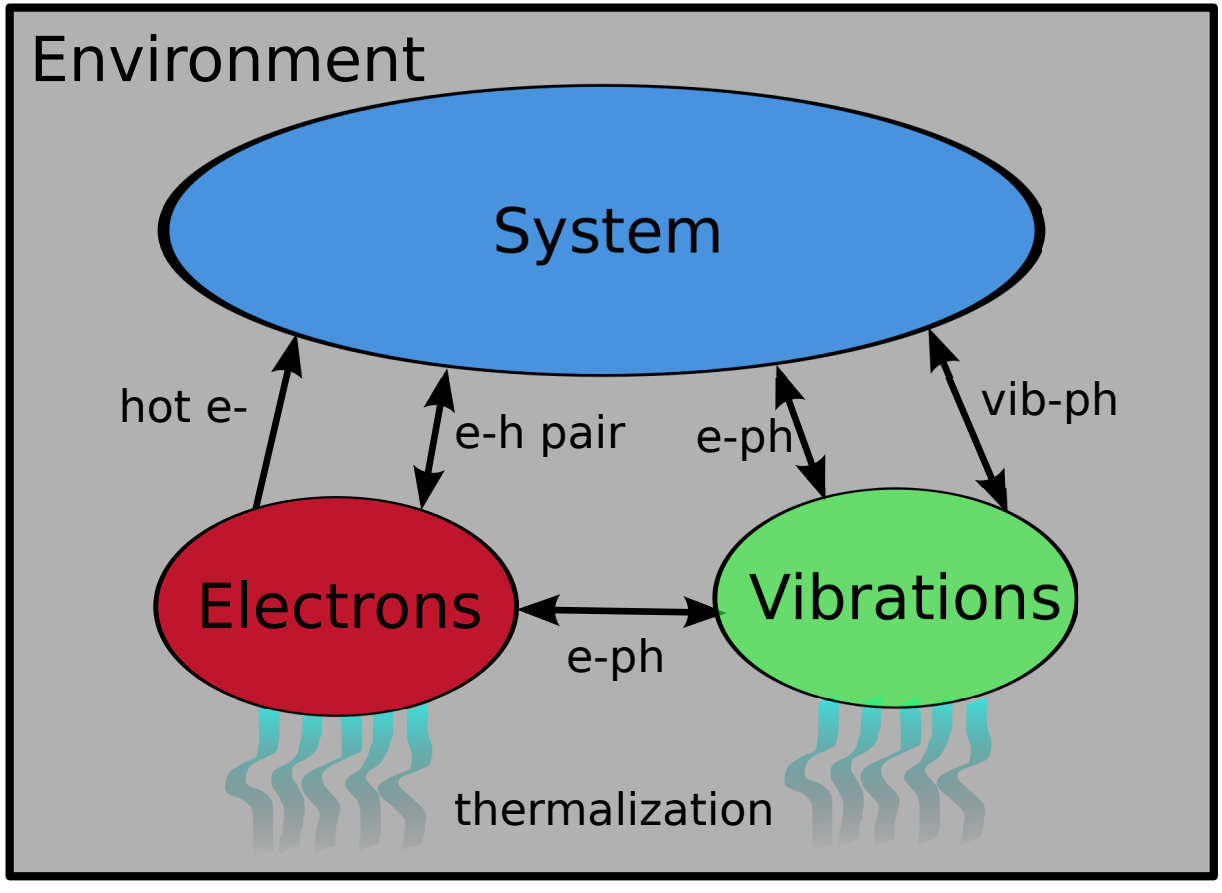
We set $\gamma^* = \Gamma_{1\to 0}$

- **Need the transition rates $\Gamma_{m\to n}$ $\longrightarrow$ problem-specific**

PART TWO

Nonadiabatic effects via electronic friction

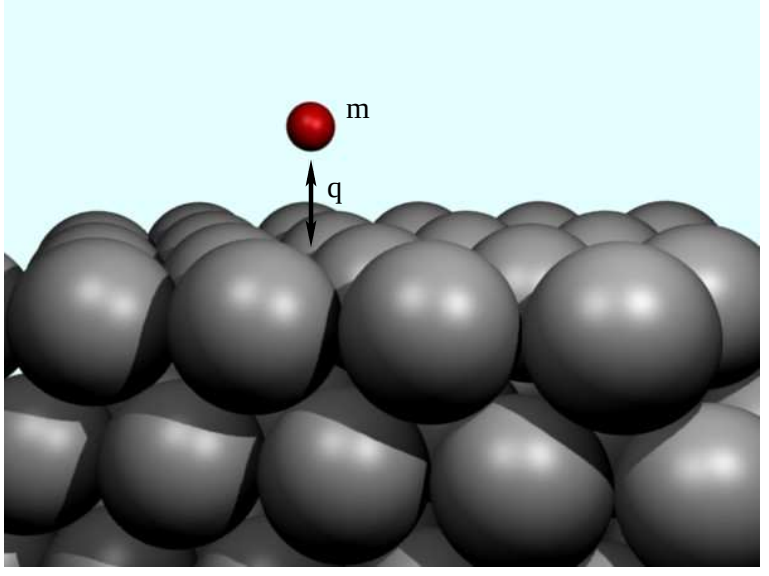
Types of couplings

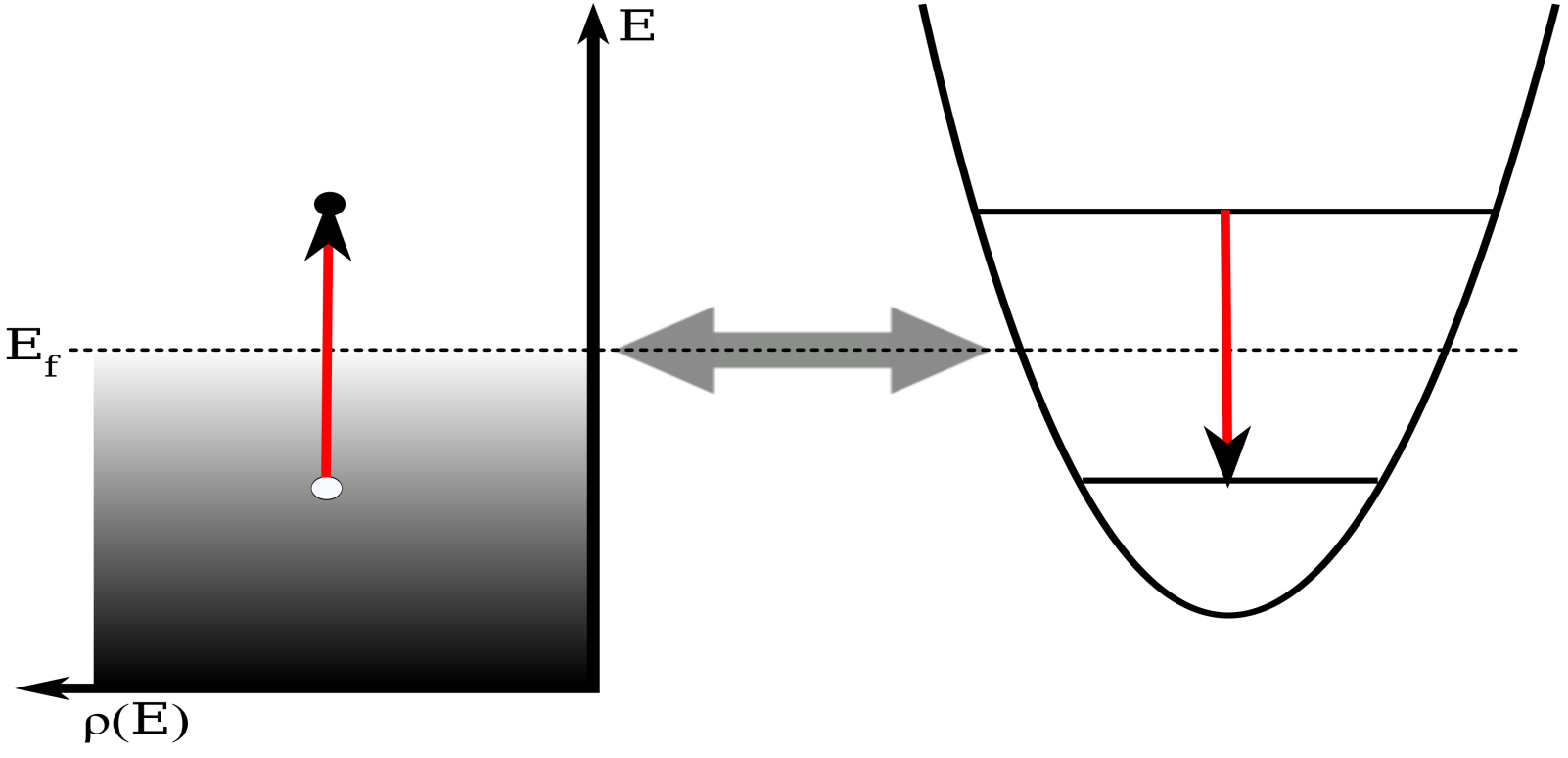


- **Non-adiabatic coupling $\rightarrow$ dominates for metallic environments**
- **Vibration-phonon coupling $\rightarrow$ dominates for semiconductors and bio-molecules**
- **Hot e^- $\rightarrow$ mediates indirect excitation via environment**

Nonadiabatic coupling of an adsorbate to a surface

- **Vibrational damping**





Position-dependent anharmonic electron-hole pair coupling model

- **Fermi's Golden rule**

$$\Gamma_{m\to n} = \frac{2\pi}{\hbar}\sum_f |\langle f|\hat{W}|i\rangle|^2 \delta(E_i - E_f)$$

- **Nonadiabatic coupling operator**

$$\hat{W} = \sum_{j=1}^{N} \frac{-\hbar^2}{2m_j}\left(\frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}\right)$$

  - **Factorize vibrational ($|n\rangle, |m\rangle$) and electronic parts ($|e_i,\rangle, |e_f\rangle$) of WF**

- **Separate treatment for each mode q**

$$\Gamma_{m\to n} = \gamma^{(q)} |\langle m|\rho_{embd}(x,y,z)\frac{\partial}{\partial q}|n\rangle|^2$$

where $\rho_{embd}(x,y,z)$ is the density of an atom embedded in a FEG

and $\gamma^{(q)}$ is the mode scaling constant

Embedding density models

1. Jellium model (or free lunch model)

$$\rho_{embd}(\vec{R}) = \rho_0 e^{-2\sqrt{2I}z}$$

where I is the metal work function and ρ_0 is the free metal density

2. Free metal density model

$$\rho_{embd}(\vec{R}) = \rho_{metal}(\vec{R})$$

– Requires a single periodic DFT calculation to generate the embedding density profile

3. Perturbed metal density model

$$\rho_{embd}(\vec{R}) = \rho_{calc}(\vec{R}) - \rho_{\infty}$$

– Requires many periodic DFT calculations to generate the embedding density profile

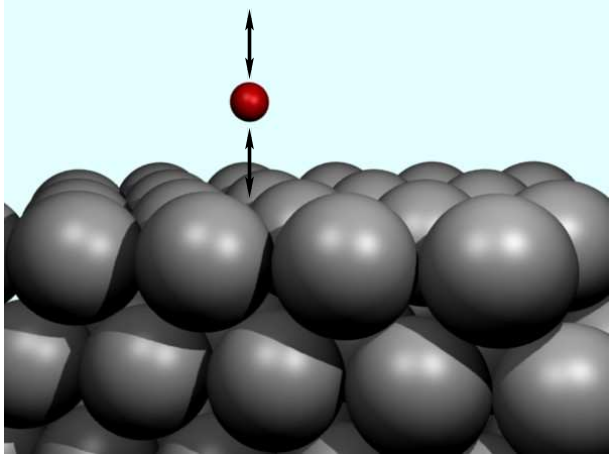
– Scaling chosen to fit the Persson lifetime at the equilibrium geometry

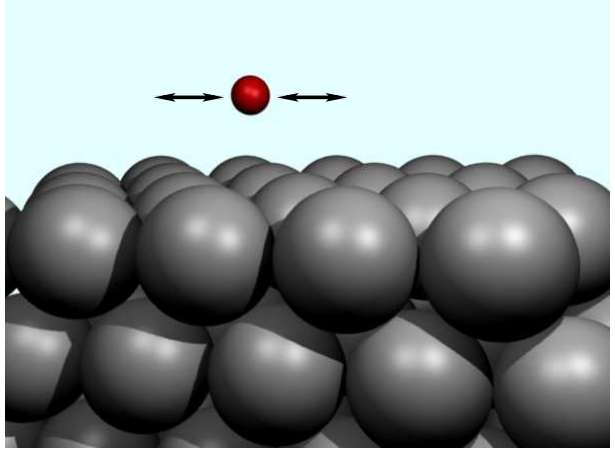
Lifetimes at different sites

Perpendicular mode

Model	fcc site / fs	hcp site / fs	Subsurface / fs	Bulk / fs
jellium	1348.7 fs	2512.7	389.0	366.9
metal	369.9	1190.8	373.2	349.8
perturbed	392.4	1269.6	525.5	450.8

$$\tau_z^{(f)} = 1/\Gamma_{persson}^{(f)} \simeq 393 \text{ fs}$$
$$\tau_z^{(s)} = 1/\Gamma_{persson}^{(s)} \simeq 417 \text{ fs}$$





Parallel mode

Model	fcc site / fs	hcp site / fs	Subsurface / fs	Bulk / fs
jellium	1130.4	1366.4	289.2	290.6
metal	326.5	395.4	278.9	277.4
perturbed	349.8	427.5	391.2	361.9

PART THREE

Design of control laser fields

Excitation mechanism

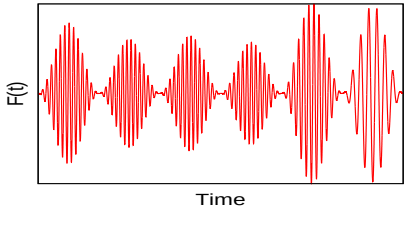
- **How do we want to steer the reaction in a controlled manner?**
  - **Interaction with short, intense laser field**

$$\hat{H}_{ext}(t) = -\vec{\mu}(\vec{R}) \cdot \vec{F}(\vec{R}, t) \sim -\vec{\mu}(\vec{R}) \cdot \vec{F}(t)$$

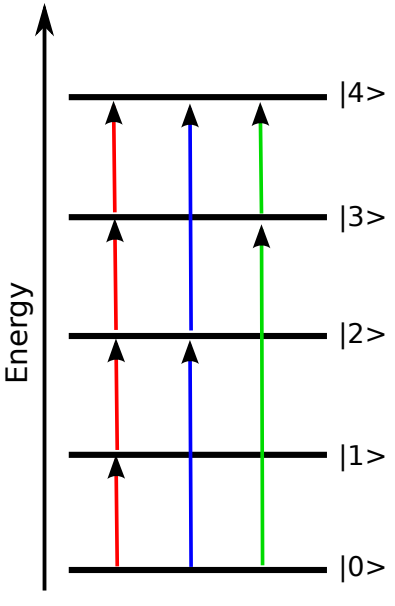
- **Rational pulses design**
  - **Series of π-pulses**

$$F_{ref}(t) = \sum_k F_{kz} U_k(t) \cos(\omega_k t) \quad ; \quad F_{kz} = \frac{2\pi\hbar}{t_p |\mu_k|} \quad ;$$

$$U_k(t) = \begin{cases} \sin^2\left(\frac{\pi(t-t_k)}{t_p}\right) & \text{for } t_k < t < t_k + t_p \\ 0 & \text{otherwise} \end{cases}$$



- **Reaction paths**



Excitation using guided locally optimal control theory

- **Define a cost functional**

$$J[F(t)] = \langle\langle \hat{G}(t_f)|\rho(t_f)\rangle\rangle - \int_0^{t_f} \frac{|F(t) - F_{ref}(t)|^2}{\hbar\alpha(t)} dt$$

- **Rewrite as a time-dependent function**

$$J[F(t)] = \int_0^{t_f} \frac{d}{dt}\left(\langle\langle \hat{G}(t)|\rho(t)\rangle\rangle\right) dt - \int_0^{t_f} \frac{|F(t) - F_{ref}(t)|^2}{\hbar\alpha(t)} dt + \langle\langle \hat{G}(0)|\rho(0)\rangle\rangle$$

- **Following a conventional variational procedure, we obtain**

$$F(t) = F_{ref}(t) - \hbar\alpha(t)\langle\langle \hat{G}(t)\hat{\mu}|\ \mathbf{Im}[\rho(t)]\rangle\rangle$$

- **A natural choice for the guiding function $\hat{G}(t)$**

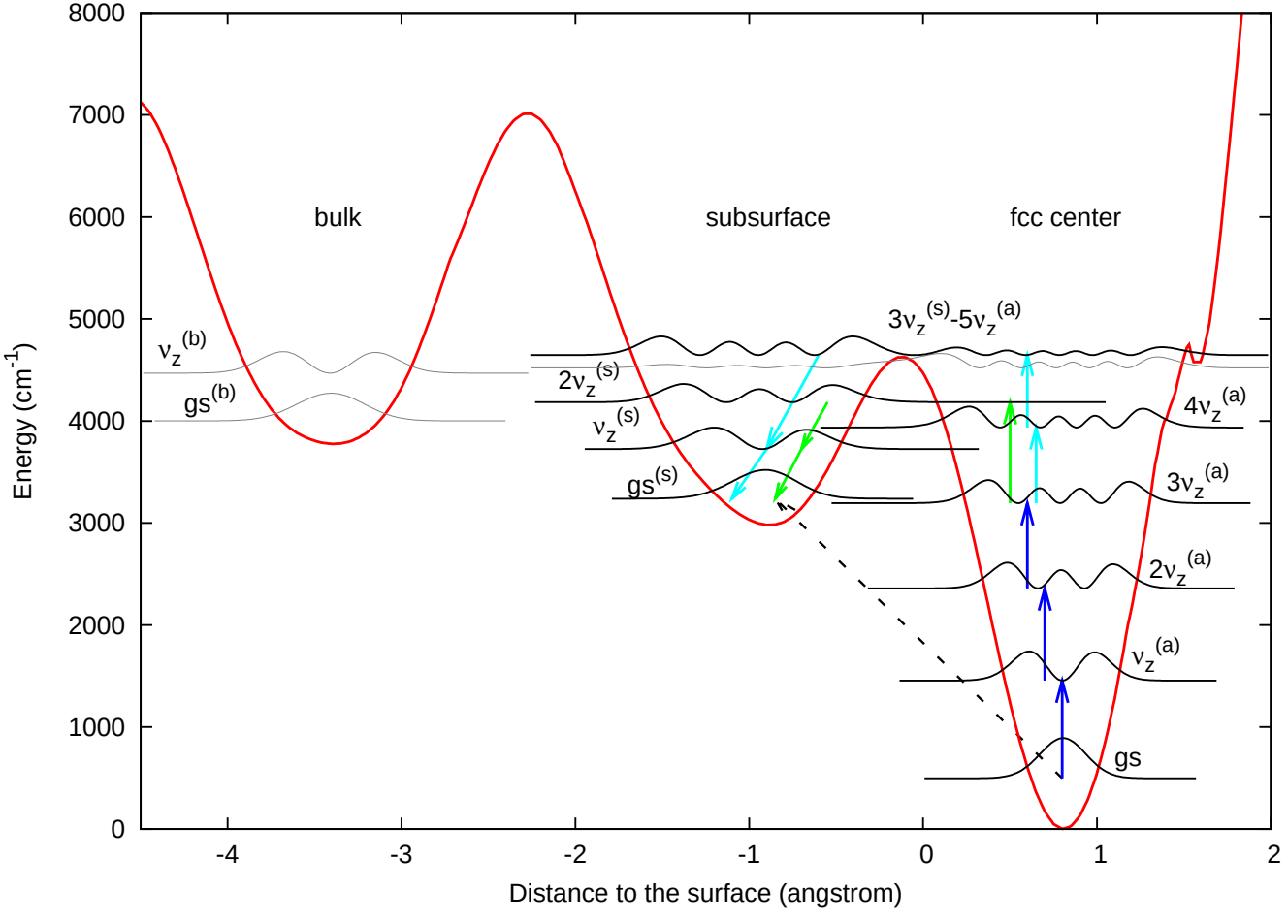
$$G(t) = \sum_{k=1}^{L} g_k(t) P_k$$

PART FOUR

Laser control of vibrational dynamics

Proposed excitation mechanism *in 1D*

- **Direct excitation not possible**
  - **Populate some intermediate state**
  - **Use energy relaxation as a dump mechanism**

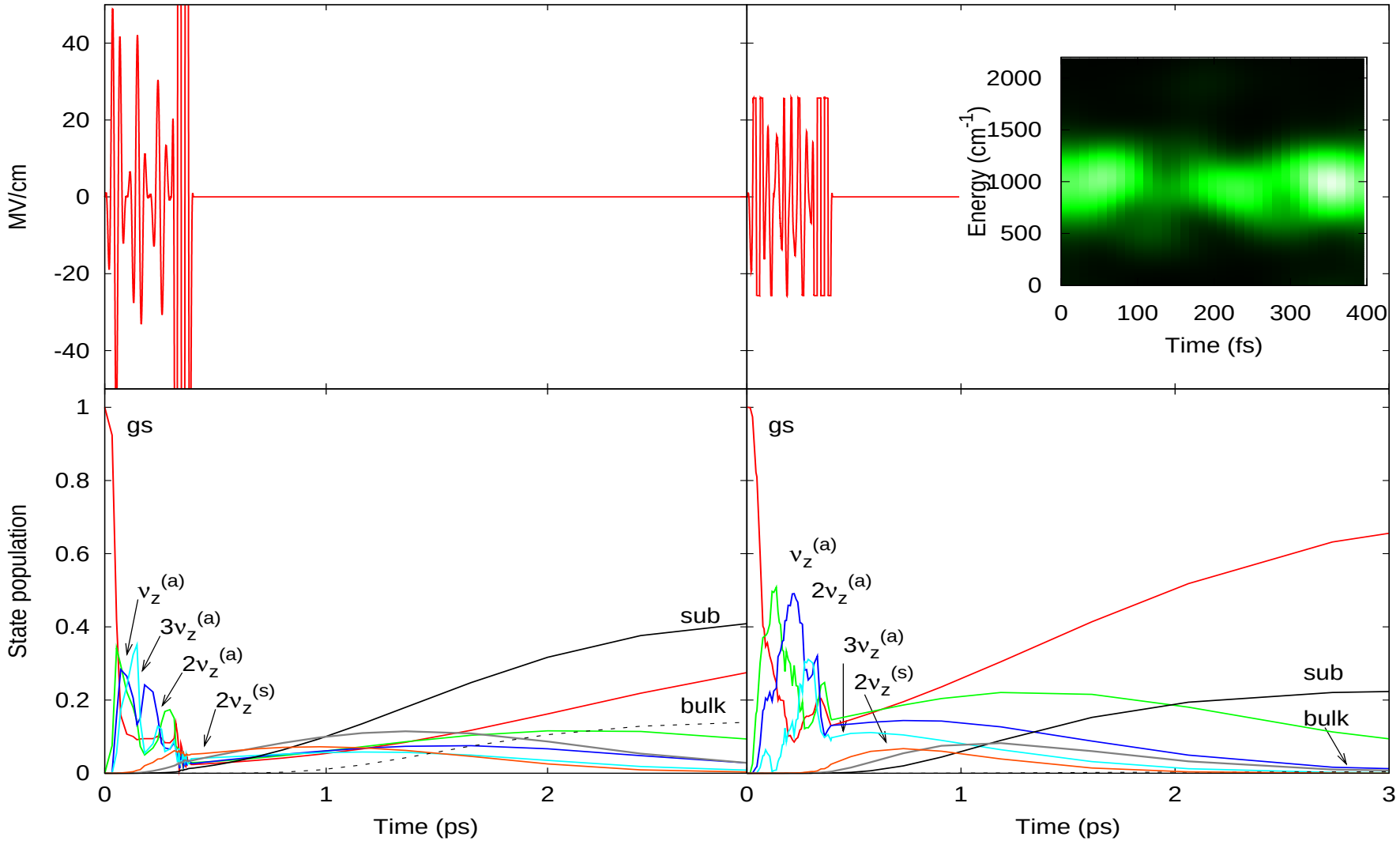


$$\tau_{m\to n} \sim \frac{1}{\Gamma_{m\to n}}$$

$$\tau^{(a)}_{1\to 0} = 867\text{fs}$$
$$\tau^{(a)}_{2\to 1} = 446\text{fs}$$
$$\tau^{(a)}_{3\to 2} = 313\text{fs}$$

$$\tau^{(s)}_{1\to 0} = 497\text{fs}$$
$$\tau^{(s)}_{2\to 1} = 265\text{fs}$$

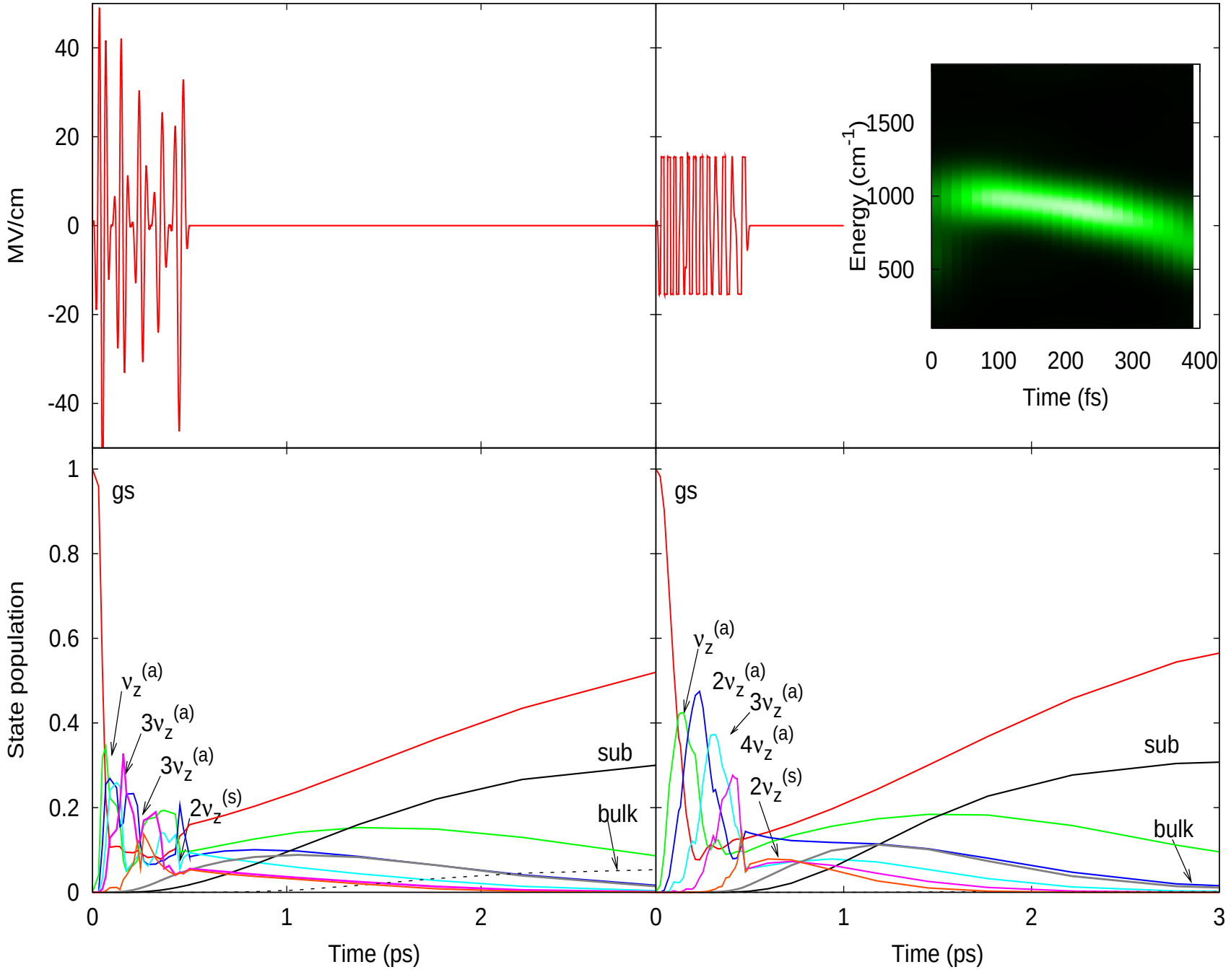
Excitation along reaction path 1



Series of non-overlaping π-pulses

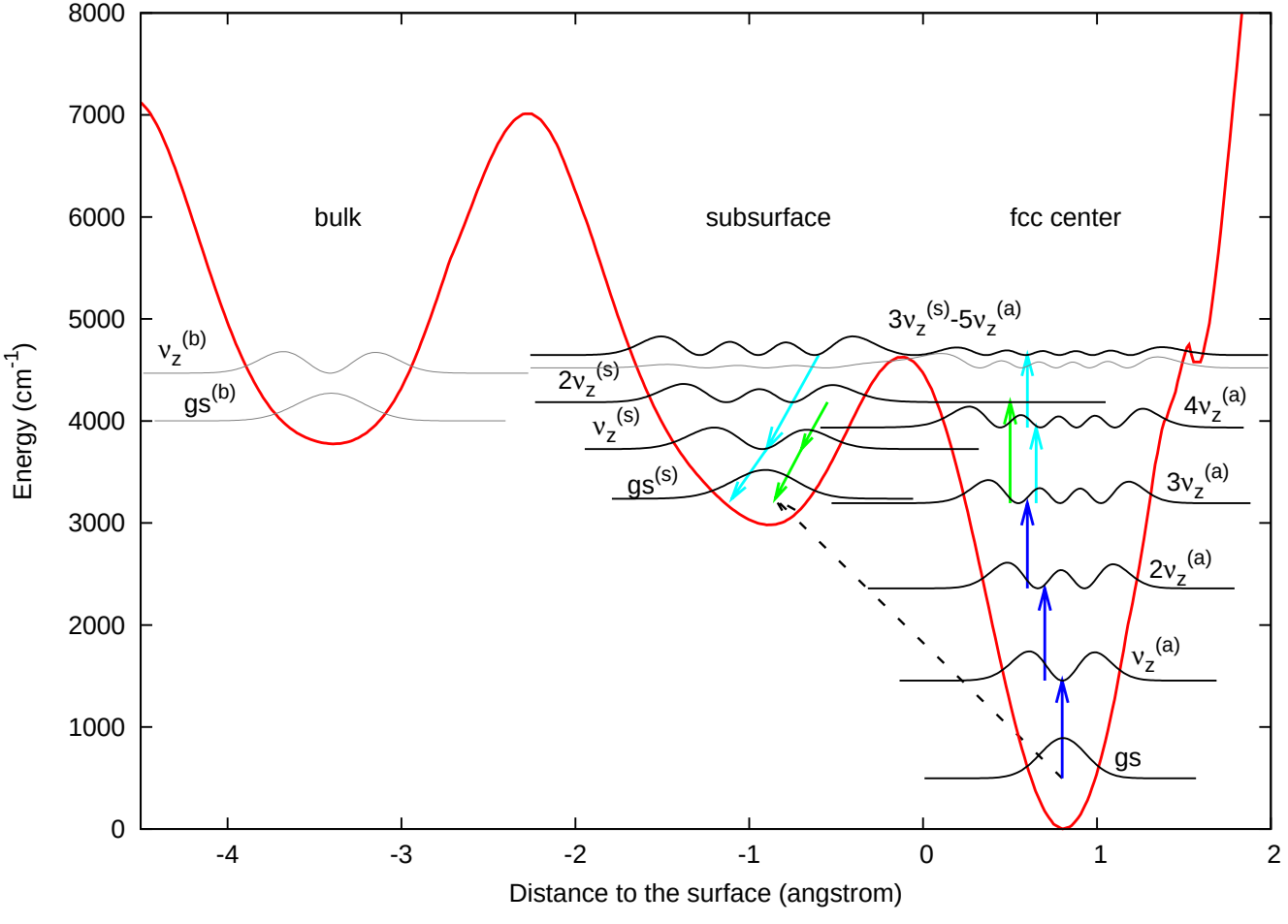
$$F(t) = \sum_k F_{0k} sin^2\left(\frac{\pi(t-t_k)}{\Delta t_k}\right) cos\left(\omega_k t\right) \;\; ; \;\; F_{0k} = \frac{2\pi\hbar}{\Delta t_k |\mu_k|}$$

Excitation along reaction path 2



Proposed excitation mechanism *in 1D*

- **Direct excitation not possible**
  - **Populate some intermediate state**
  - **Use energy relaxation as a dump mechanism**

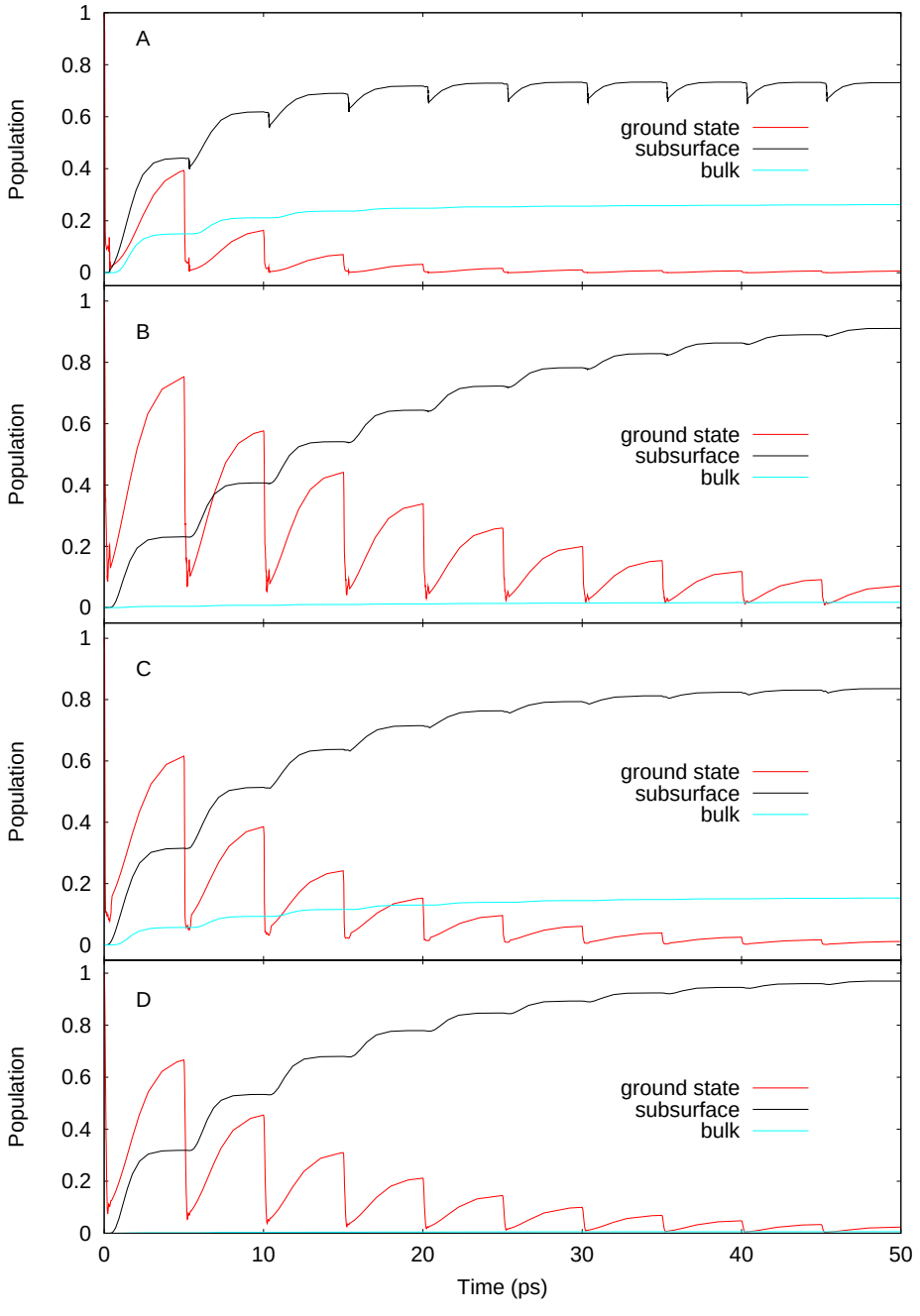


$$\tau_{m\to n} \sim \frac{1}{\Gamma_{m\to n}}$$

$$\tau^{(a)}_{1\to 0} = 867\text{fs}$$
$$\tau^{(a)}_{2\to 1} = 446\text{fs}$$
$$\tau^{(a)}_{3\to 2} = 313\text{fs}$$

$$\tau^{(s)}_{1\to 0} = 497\text{fs}$$
$$\tau^{(s)}_{2\to 1} = 265\text{fs}$$

Selective Subsurface Absorption by Laser Distillation (SSALaD)

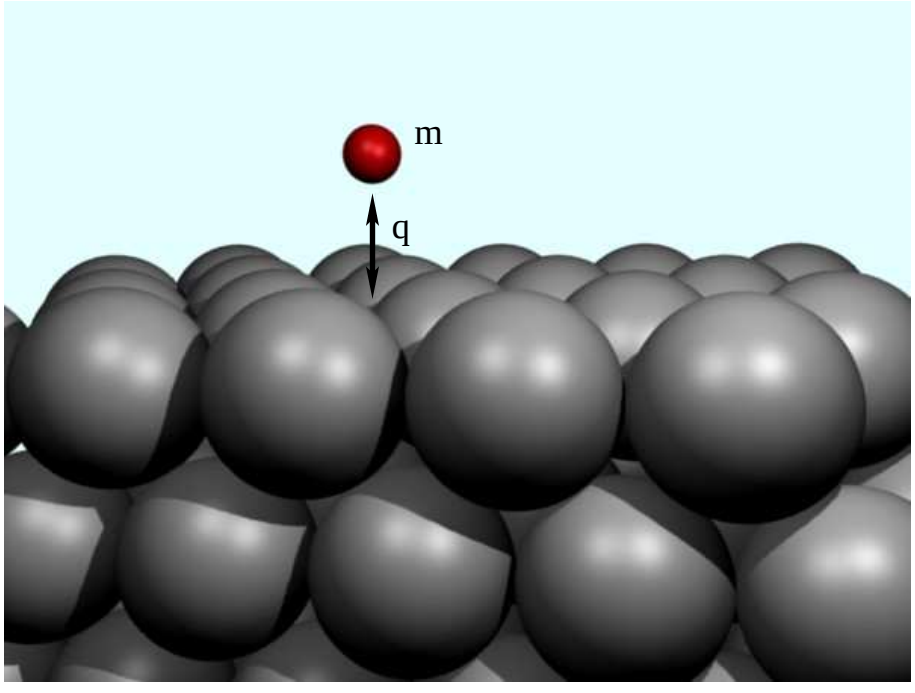


Transfer efficiency

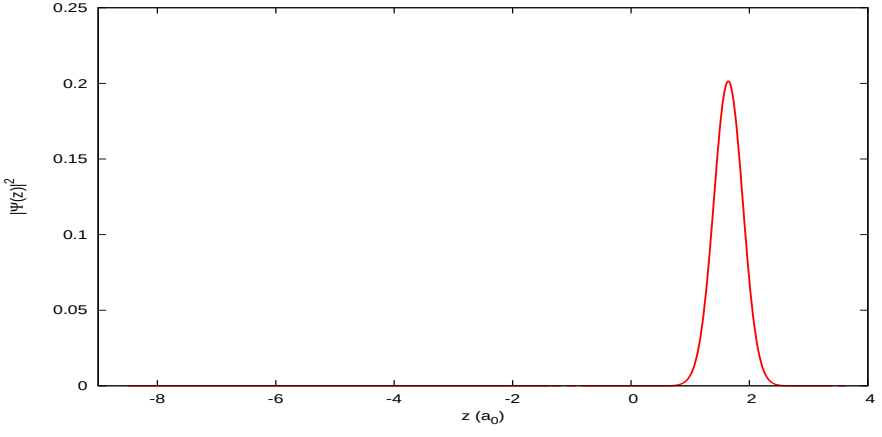
$$P(t) = P_0\left(1 - e^{-Rt}\right)$$

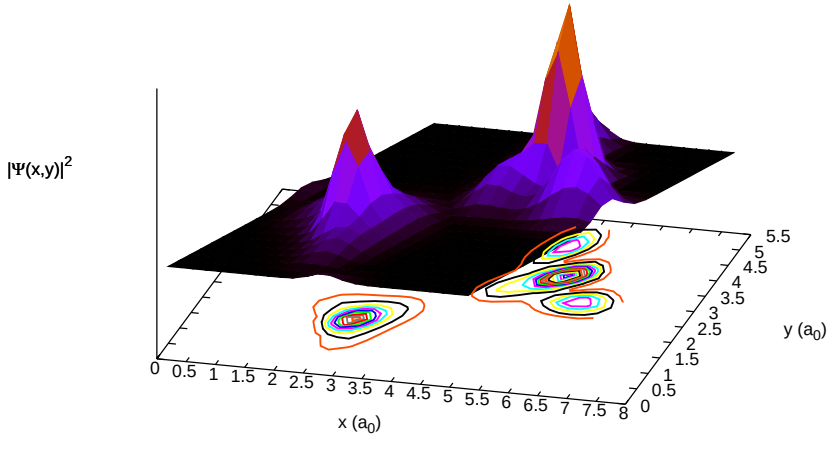
Simulation	P_0 (%)	R (ps^{-1})
RP1, rational	71.8	0.198
RP1, optimized	97.7	0.054
RP2, rational	84.1	0.095
RP2, optimized	99.0	0.077

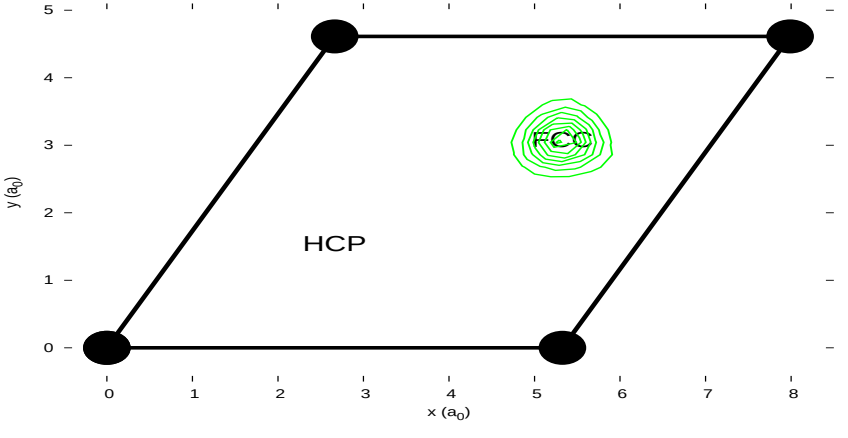
Three-dimensional wave-function



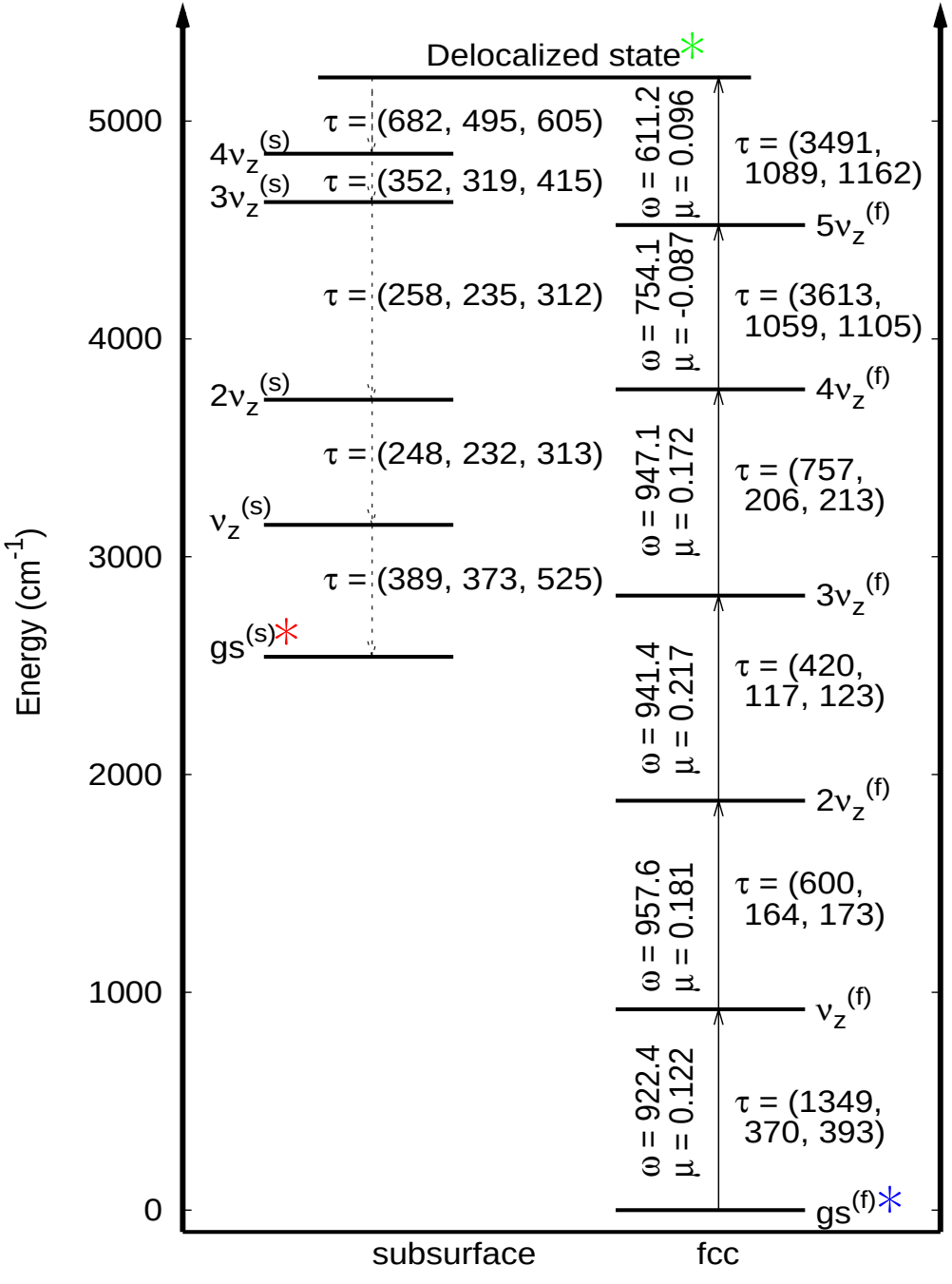
Assignment	Energy (cm^{-1})
$gs^{(f)}$	0.0
$gs^{(h)}$	288.3
$gs^{(s)}$	2540.5
$\nu_{qp}^{(f)}$	717.4
$\nu_z^{(f)}$	922.4

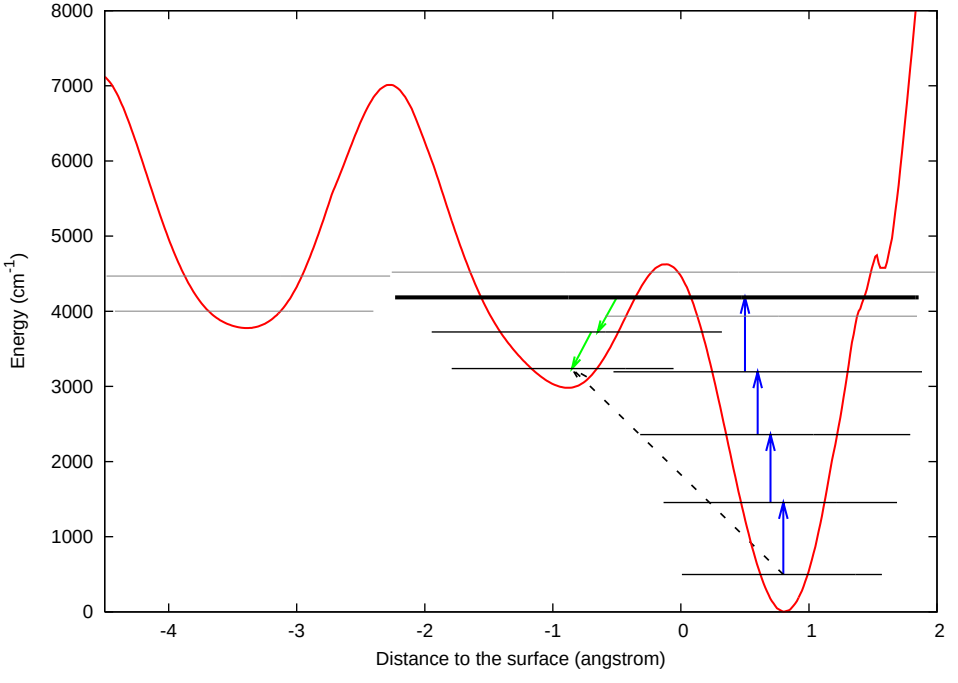




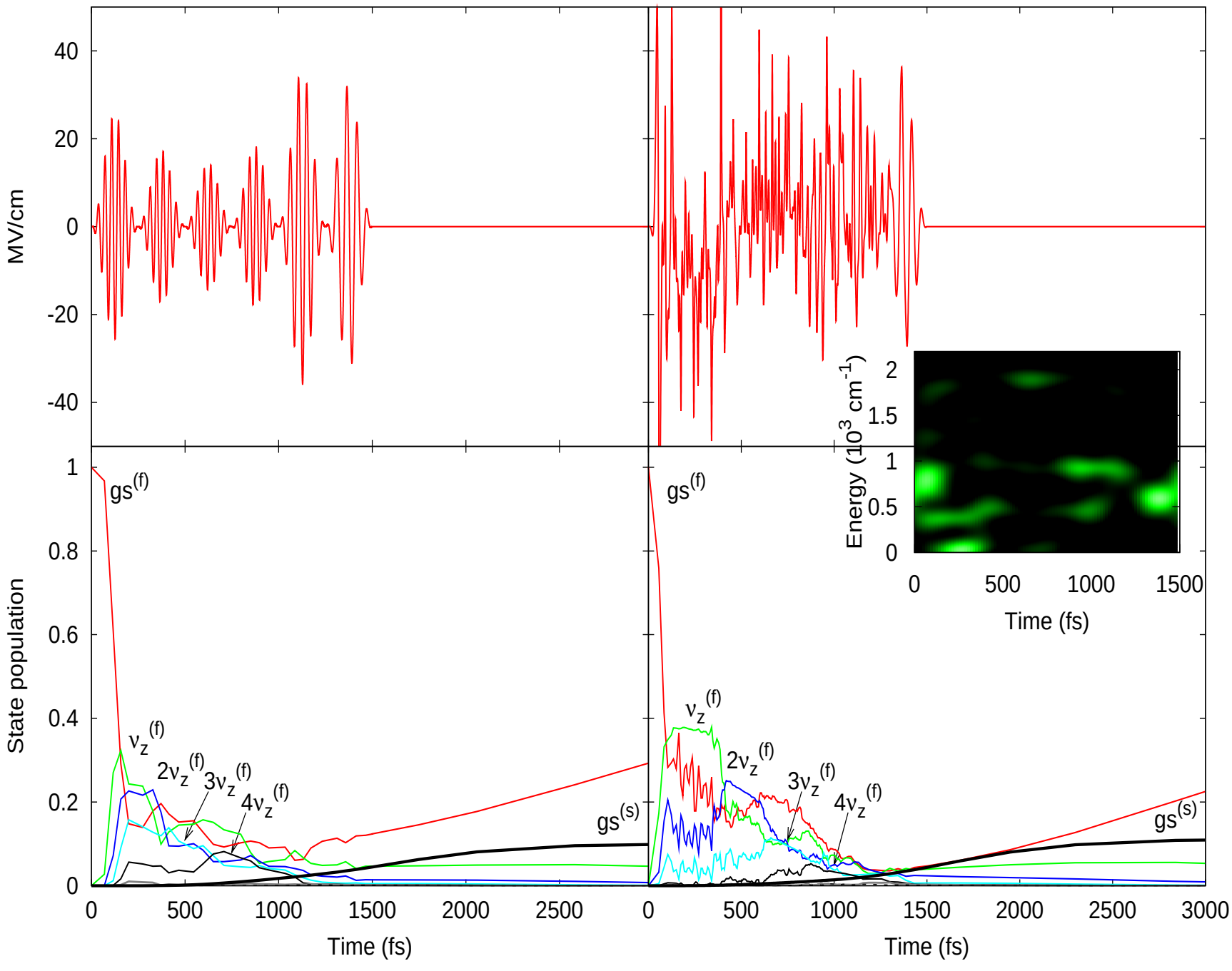


Proposed excitation mechanism

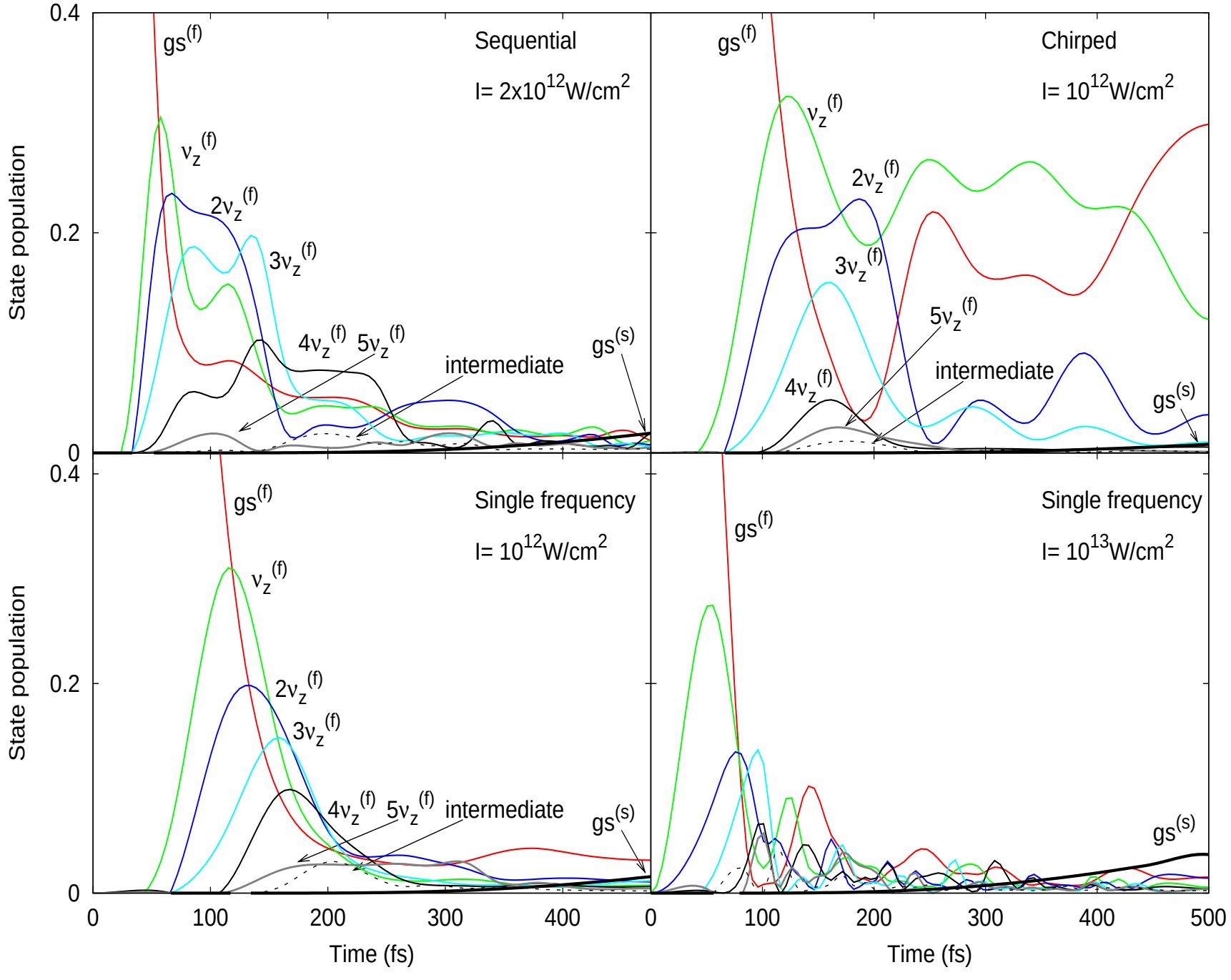




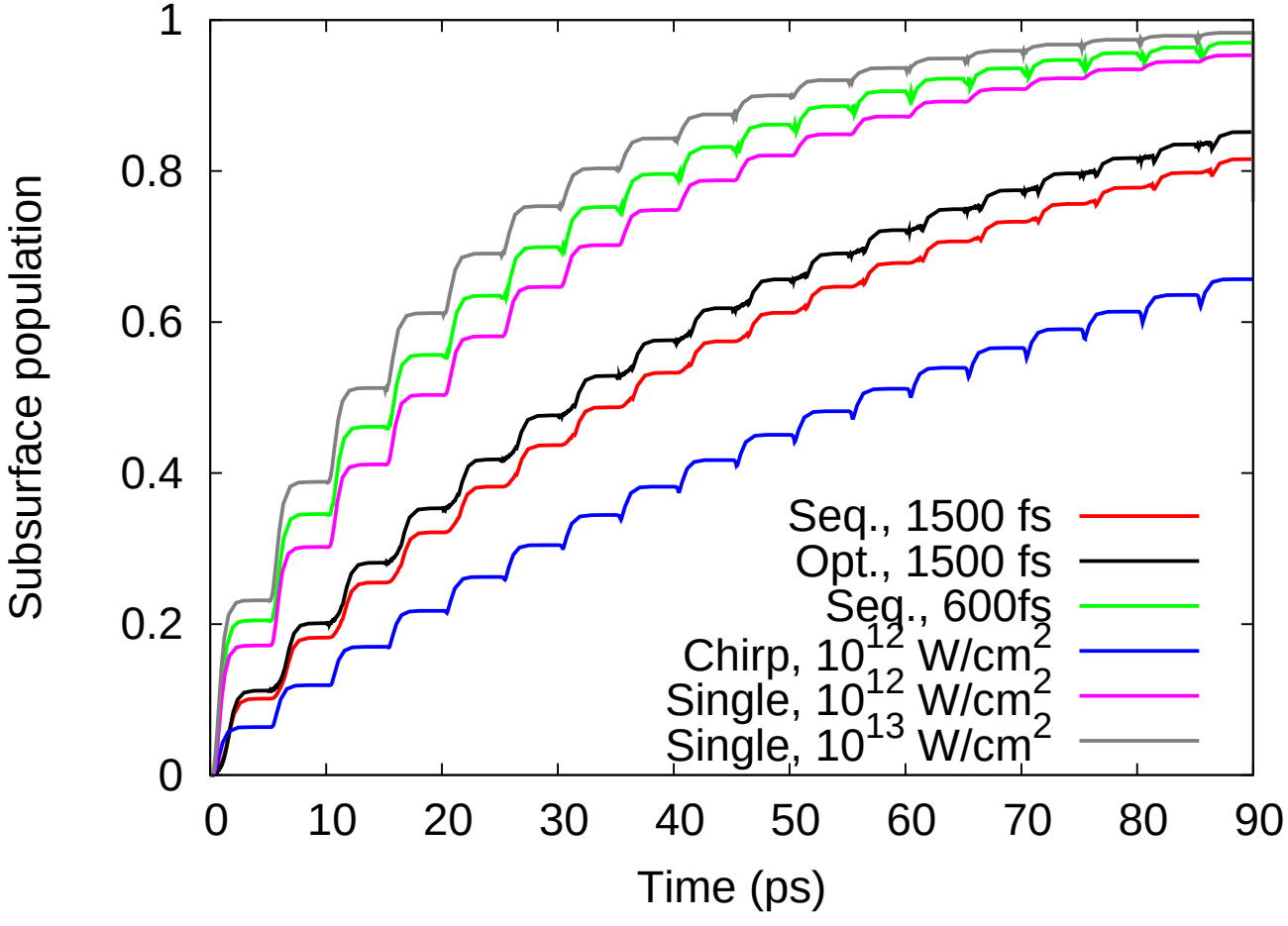
Excitation using long pulses



Excitation using short rational pulses



Selective Subsurface Absorption by Laser Distillation (SSALaD)



Transfer efficiency

$$P(t) = P_0\left(1 - e^{-Rt}\right)$$

Simulation	P_0 (%)	R (ps^{-1})
Sequential, 1500 fs	98.1	0.0197
Optimized, 1500 fs	98.1	0.0222
Sequential, 600 fs	99.1	0.0412
Chirped, 10^{12} W/cm^2	96.7	0.0126
Single, 10^{12} W/cm^2	99.3	0.0353
Single, 10^{13} W/cm^2	99.2	0.0482

Conclusion and outlook

- **State-resolved anharmonic transition rate model**
  - Position dependence relies on definition of good embedding density
  - Anharmonicity included via multi-D integration of vibrational WF
  - Scaling can be related to existing *ab initio* models
- **Application to state-resolved dynamics**
  - Laser-induced selective subsurface absorption of H in Pd(111)
  - Influence on the short-term population dynamics
  - Laser distillation achieves complete target population, but with different rates
- **Future work**
  - Perform optimal control simulations to maximize transfer rate
  - Study STM-induced bulk-to-subsurface transition
  - Investigate possibility of isotope separation

Acknowledgement

Funding agencies $$$

- Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT)
- Sonderforschungbereich 450 (SFB 450) of the Deutsche Forschungsgemeinschaft (DFG)

Personal and technical support

- Prof. Hideaki Kasai and Nobuki Ozawa for their H/Pd(111) potential energy surface
- Dr. Serge Monturet for periodic density calculations
- The group of Prof. Peter Saalfrank in Potdsam

Thank you for your attention!!!