Optimal Control Theory

Applications to Polyatomic Systems

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Contents of the Talk

(1) the Optimal Control Theory - some extensions

(2) laser pulse control using non-resonant multi-photon transitions

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(4) accelartion of internal conversion in pyrazine

(5) excitation energy localization in chromophore complexes

Optimal Control Theory

Control functional

$$J[\mathbf{E}_c] = \mathcal{O}[\mathbf{E}_c] - \lambda(\frac{1}{2}\int_{t_0}^{t_f} dt\ \mathbf{E}_c^2(t) - I_0)$$

Functional equation determining the optimal pulse

$$\mathbf{E}_c(t) = \lambda \frac{\delta \mathcal{O}[\mathbf{E}_c]}{\delta \mathbf{E}_c(t)}$$

standard scheme of OCT with a target operator

$$\mathcal{O}[\mathbf{E}_c] = \langle \Psi(t;\mathbf{E}_c)|\hat{O}|\Psi(t;\mathbf{E}_c)\rangle$$

non-resonat multi-photon transitions, MCTDH

OCT for open system dynamics

$$\mathcal{O}[\mathbf{E}_c] = \mathrm{tr}\{\hat{\rho}(t;\mathbf{E}_c)\hat{O}\}$$

excitation energy localization in chromophore complexes (control of exciton dynamics)

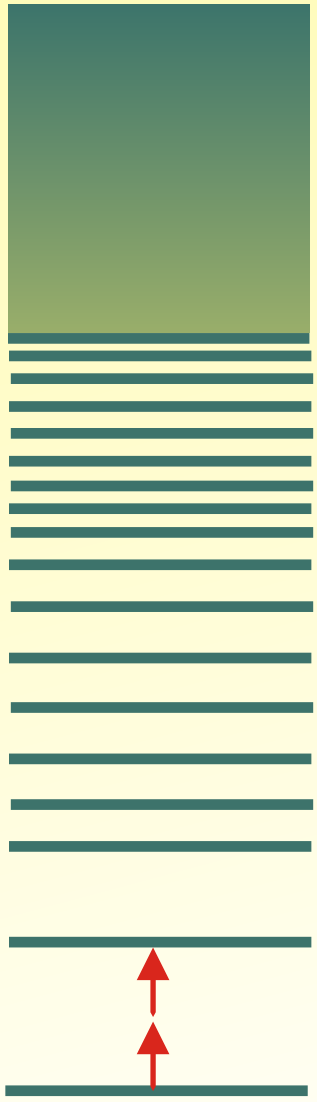
OCT with a target operator distributed in time and parameter space

direct optimization of transient probe pulse absoprtion in a pump probe scheme

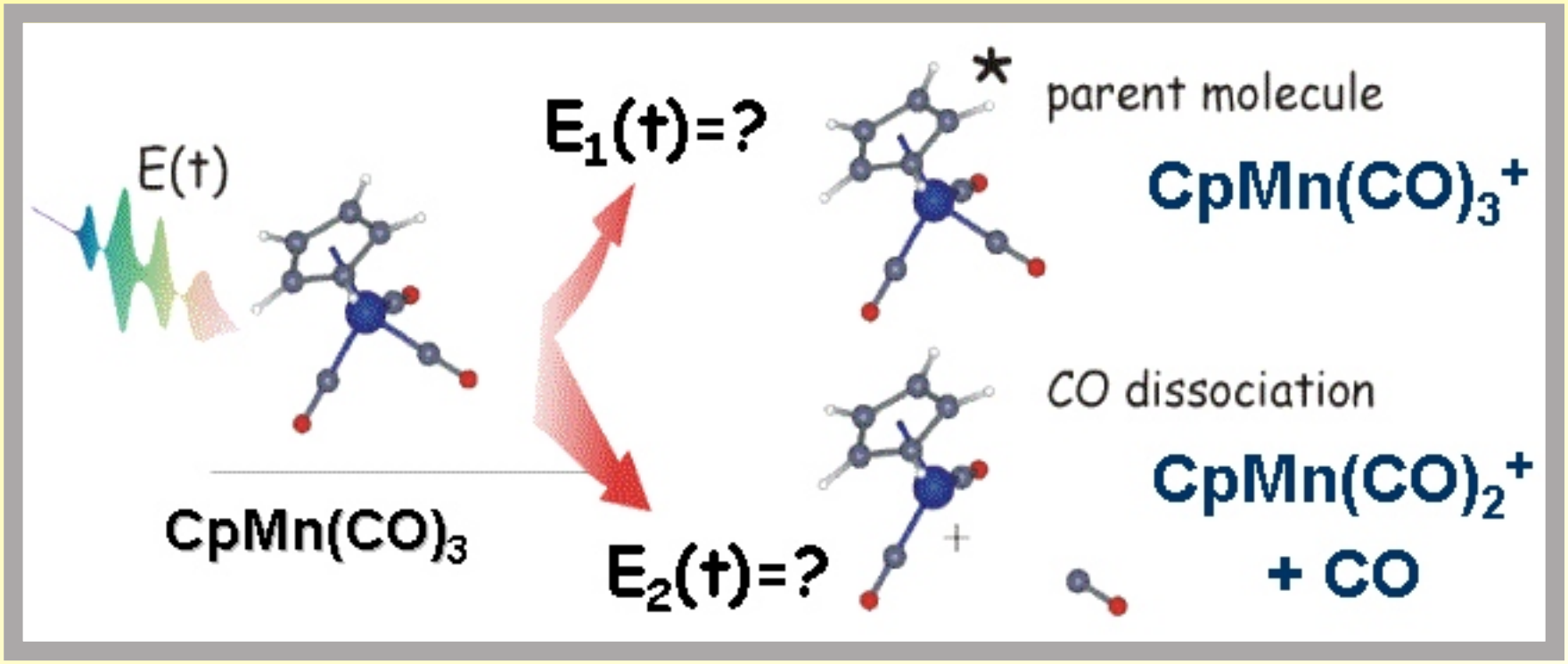
$$\mathcal{O}[\mathbf{E}_c] = \int_{t_0}^{\infty} dt \int dp \, \langle \Psi(t;p)|\hat{O}(t;p)|\Psi(t;p)\rangle$$

Optimal Control Theory for Non-Resonant Multi-Photon Transitions

$$\mathcal{O}[\mathbf{E}_c] = \langle \Psi(t;\mathbf{E}_c)|\hat{O}|\Psi(t;\mathbf{E}_c)\rangle$$



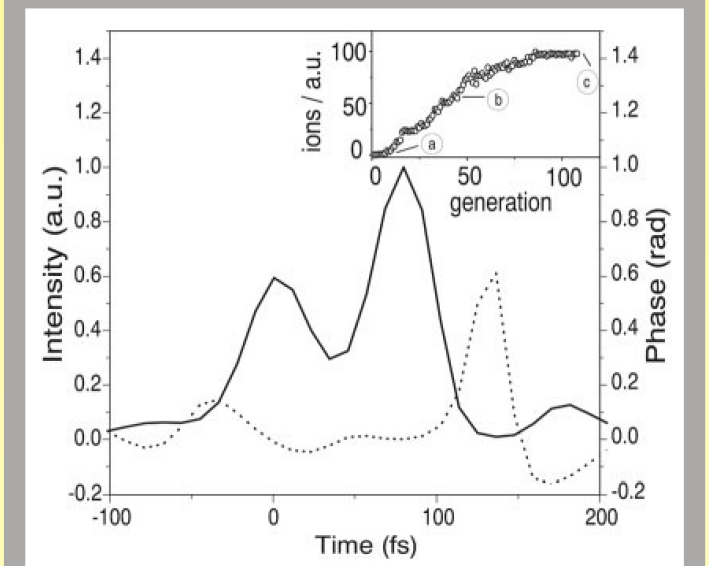
Fs-Laser Pulse Induced Ionization Versus Dissociation of an Organometallic Compound

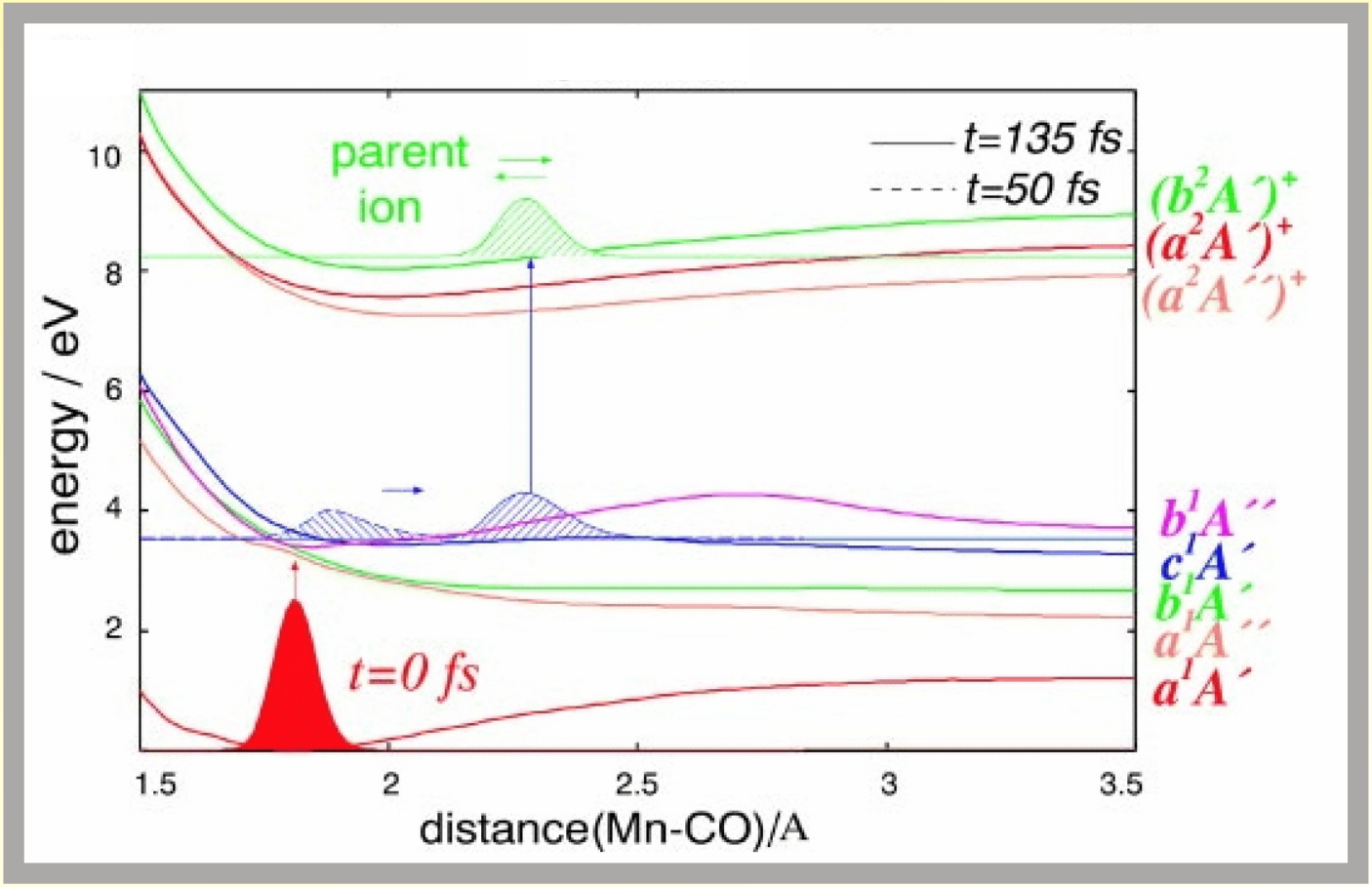


cyclopentadienyl manganese tricarbonyl

C. Daniel et al., Science, 299, 536 (2003)

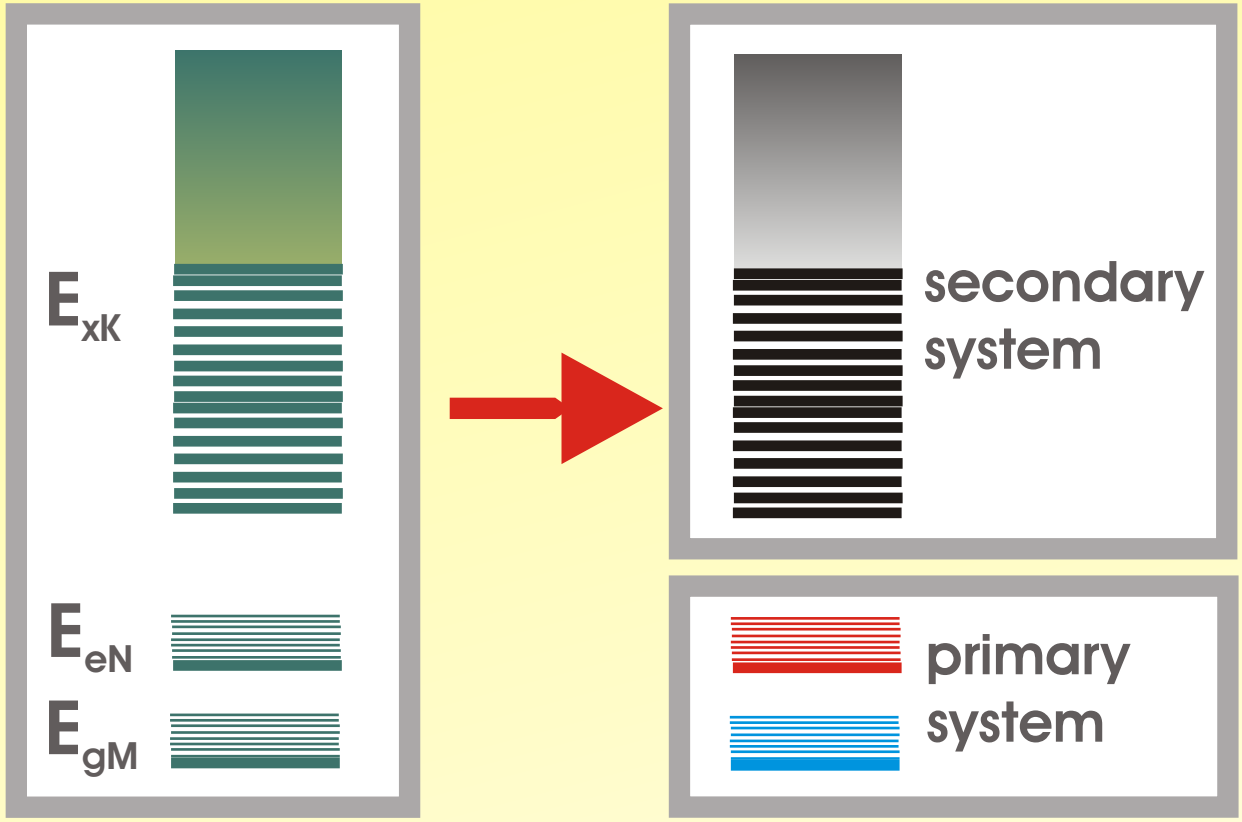
5-photon transition and the optimal pulse to form the parent ion





$a^1A' \rightarrow c^1A'$:
2PT at λ = 798.7 nm
85 fs
$c^1A' \rightarrow (b^2A')^+$:
3PT at λ = 801.12 nm

Removal of the Off-Resonant States



Effective Time-Dependent Schrödinger Equation

->time-nonlocal

->nonlinear with respect to the radiation field

$$i\hbar\frac{\partial}{\partial t}|\Psi_1(t)\rangle = H_1(t)|\Psi_1(t)\rangle - \int_{t_0}^{t} d\bar{t}\; K_{\mathrm{field}}(t,\bar{t})|\Psi_1(\bar{t})\rangle$$

$$K_{\mathrm{field}}(t,\bar{t}) = \mathbf{E}(t)\cdot\sum_{a,b}\mathbf{D}_{ab}(t,\bar{t};\mathbf{E})|\varphi_a\rangle\langle\varphi_b|\cdot\mathbf{E}(\bar{t})$$

integral kernel

Non-Resonant Two-Photon Transitions

The RWA and the SVA

Coupled Schrödinger-equations for the vibrational wave functions

$$i\hbar\frac{\partial}{\partial t}|\chi_g(0;t)\rangle = (H_g - \frac{1}{2}|E(t)|^2 d_{gg}^{(\mathrm{II})})|\chi_g(0;t)\rangle - \frac{1}{4}E^{*2}(t)d_{ge}^{(\mathrm{II})}|\chi_e(2;t)\rangle$$

$$i\hbar\frac{\partial}{\partial t}|\chi_e(2;t)\rangle = (H_e - 2\hbar\omega_0 - \frac{1}{2}|E(t)|^2 d_{ee}^{(\mathrm{II})})|\chi_e(2;t)\rangle - \frac{1}{4}E^{2}(t)d_{eg}^{(\mathrm{II})}|\chi_g(0;t)\rangle$$

Control Functional

$$J(t_f;E,E^*) = |\ \langle\chi_e^{(\mathrm{tar})}|\chi_e(t_f)\rangle\ |^2 - \frac{\lambda}{4}\int_{t_0}^{t_f} dt\ |E(t)|^4$$

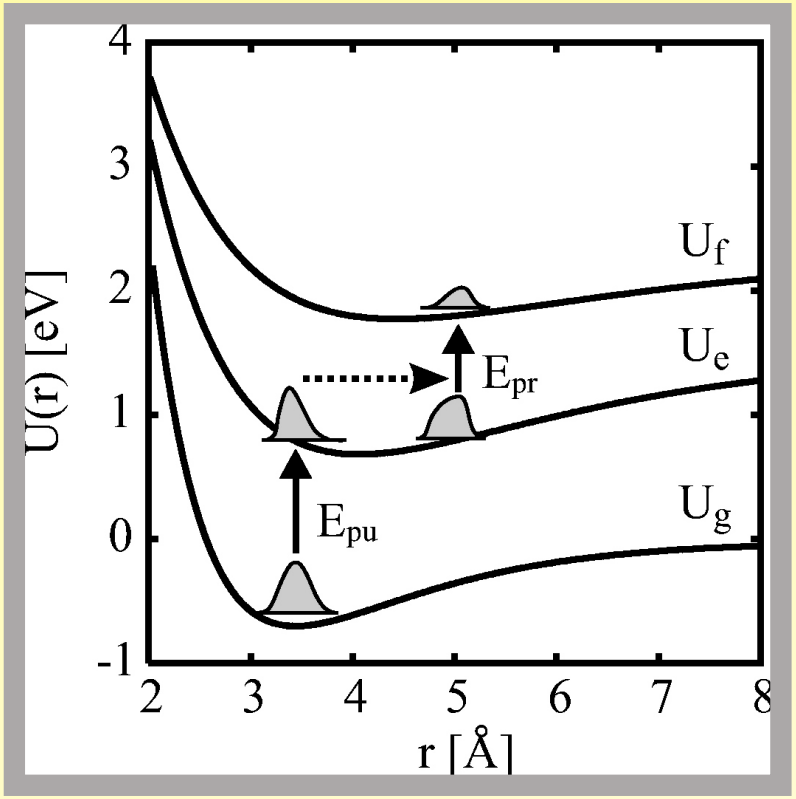
D. Ambrosek, M. Oppel, L. Gonzalez and V. M.
opt.comm. (special issue, submitted)

Direct Optimization of a Probe-Pulse Transient Absorption

$$\mathcal{O}[\mathbf{E}_c] = \int_{t_0}^{\infty} dt \int dp \, \langle \Psi(t;p) | \hat{O}(t;p) | \Psi(t;p) \rangle$$

Three level scheme for NaK

$1^1\ ^{1+}$-ground-state
$2^1\ ^{1+}$-first-excited states
$3^1\ ^{+}$-higher excited state



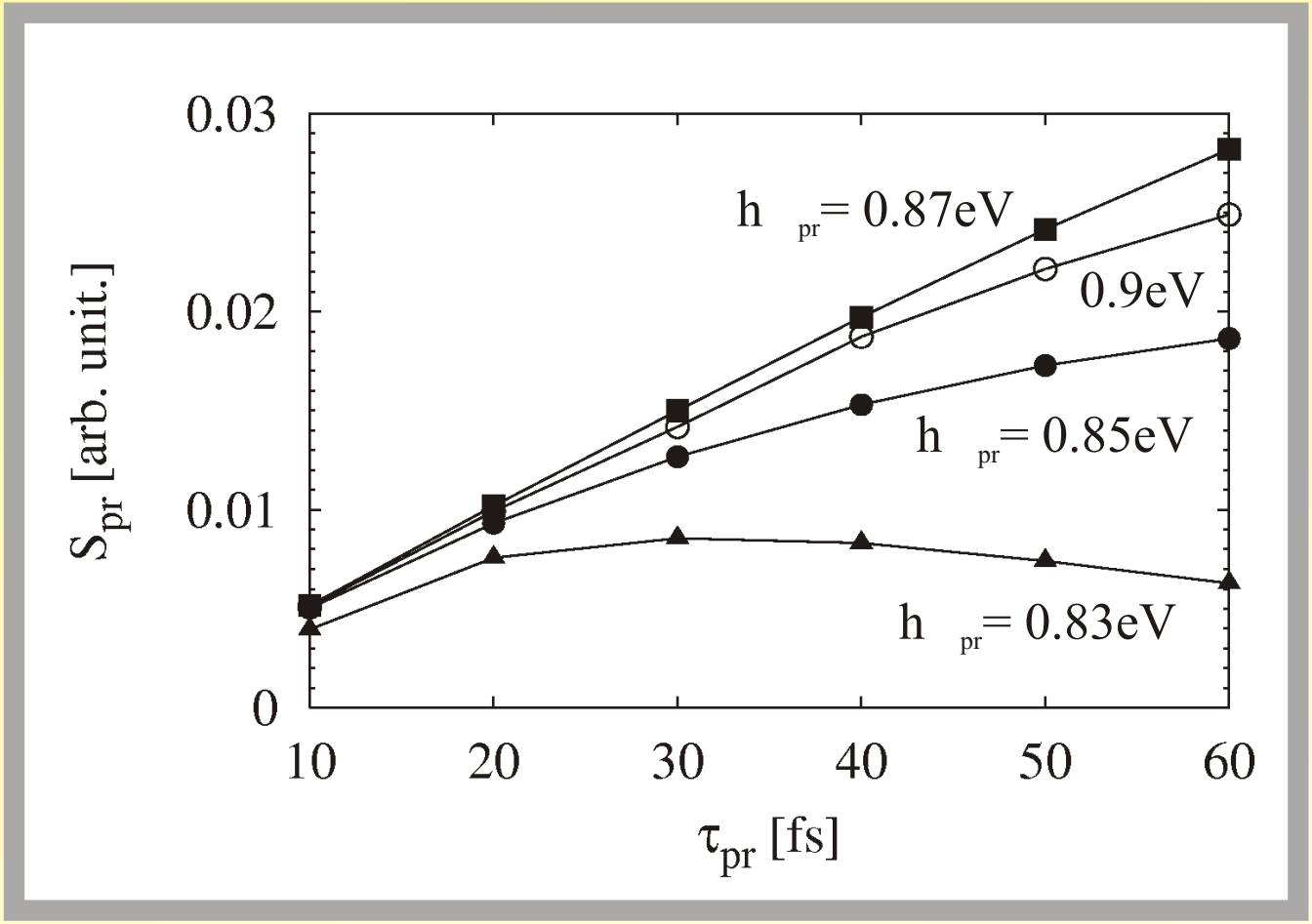
probe pulse
transient absorption signal

$$S_{\mathrm{pr}} = -\int dt\, \frac{\partial \mathbf{E}_{\mathrm{pr}}(t)}{\partial t} \mathbf{P}_{\mathrm{pr}}(t; \mathbf{E}_{\mathrm{c}})$$

$$\mathbf{P}_{\mathrm{pr}}(t) = n_{\mathrm{mol}} \langle \Psi(t; \mathbf{E}_{\mathrm{c}}, \mathbf{E}_{\mathrm{pr}}) | \hat{\mu} | \Psi(t; \mathbf{E}_{\mathrm{c}}, \mathbf{E}_{\mathrm{pr}}) \rangle - n_{\mathrm{mol}} \langle \Psi(t; \mathbf{E}_{\mathrm{c}}) | \hat{\mu} | \Psi(t; \mathbf{E}_{\mathrm{c}}) \rangle$$

probe pulse
polarization

Optimized Probe Pulse Transient Absorption Signal versus Probe Pulse Length



-> control pulse acts up to 1.5 ps

-> probe pulse is centered at 1.6 ps

A. Kaiser, and V. M., JCP 121, 2528 (2004), CPL 405, 339 (2005), CP (2005)

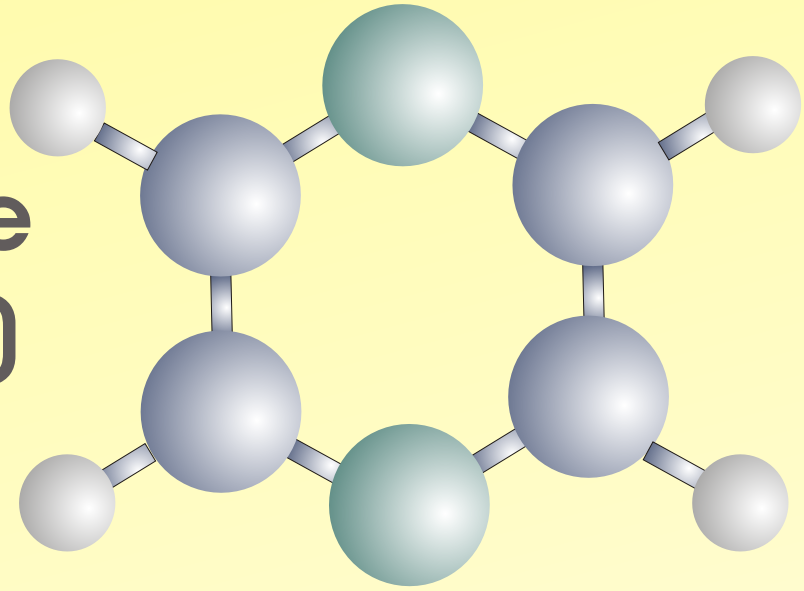
Laser Pulse Control of Vibrational Dynamics in Pyrazine

$$\mathcal{O}[\mathbf{E}_c] = \langle \Psi(t;\mathbf{E}_c)|\hat{O}|\Psi(t;\mathbf{E}_c)\rangle$$

plus

Multi Configuration Time-Dependent Hartree Method

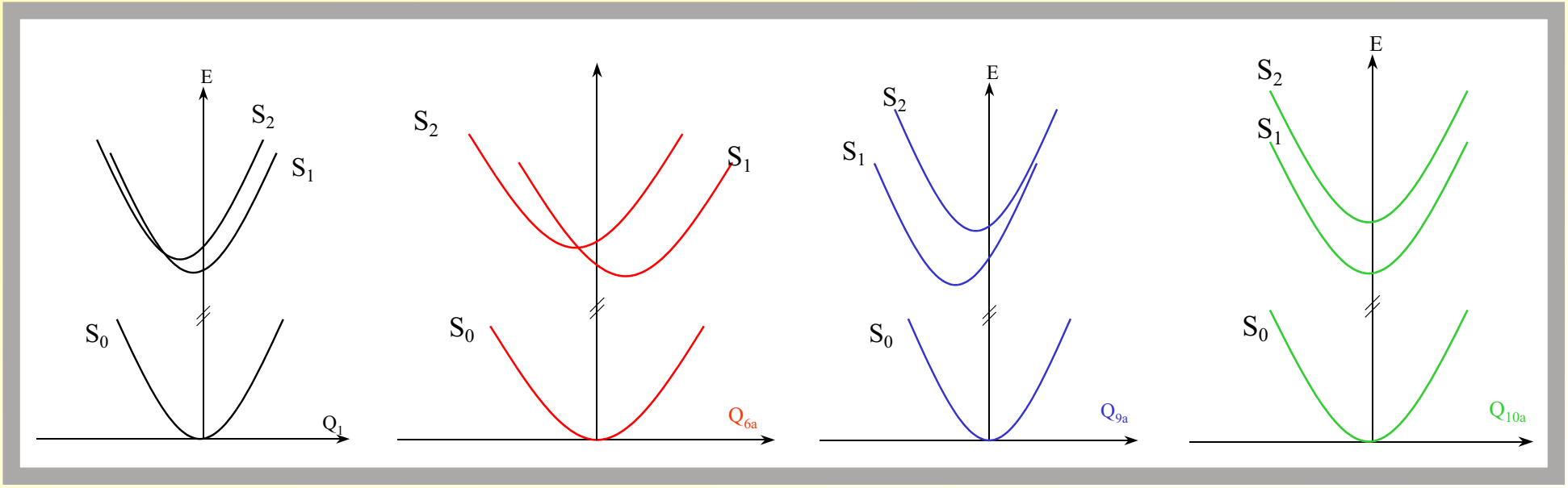
4-Mode Model of Pyrazine (vibronic coupling model)



Worth, Meyer, and Cederbaum,
JCP 109, 3518 (1998)

tuning modes

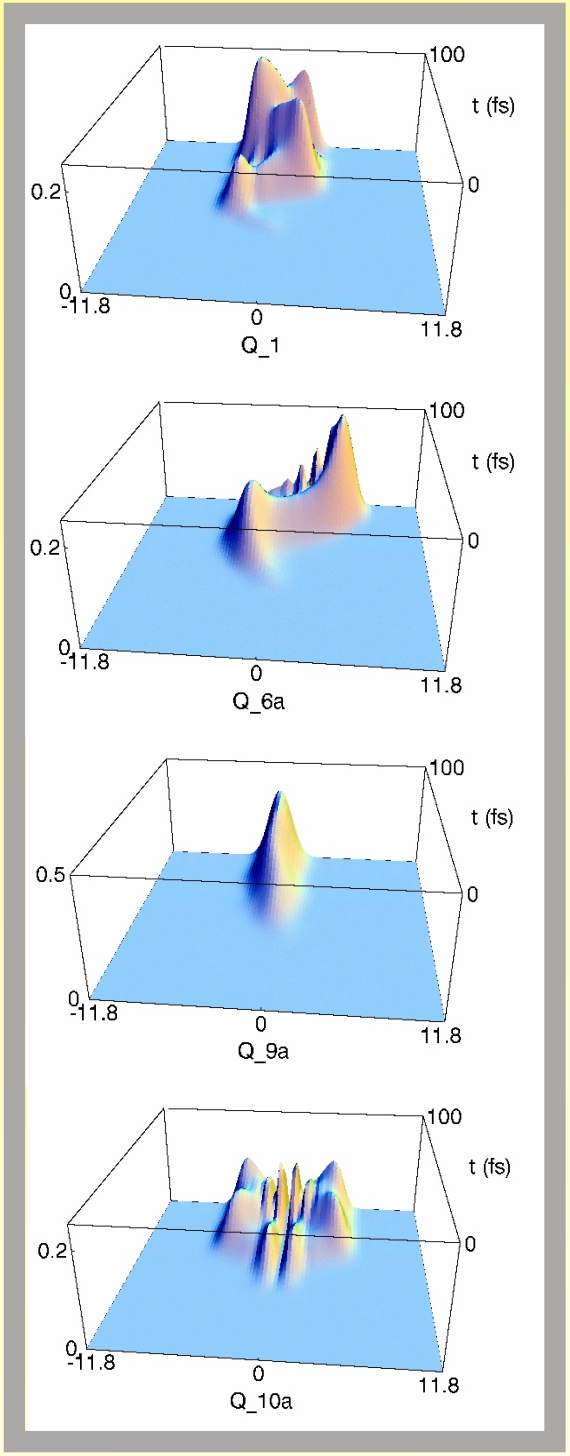
coupling mode



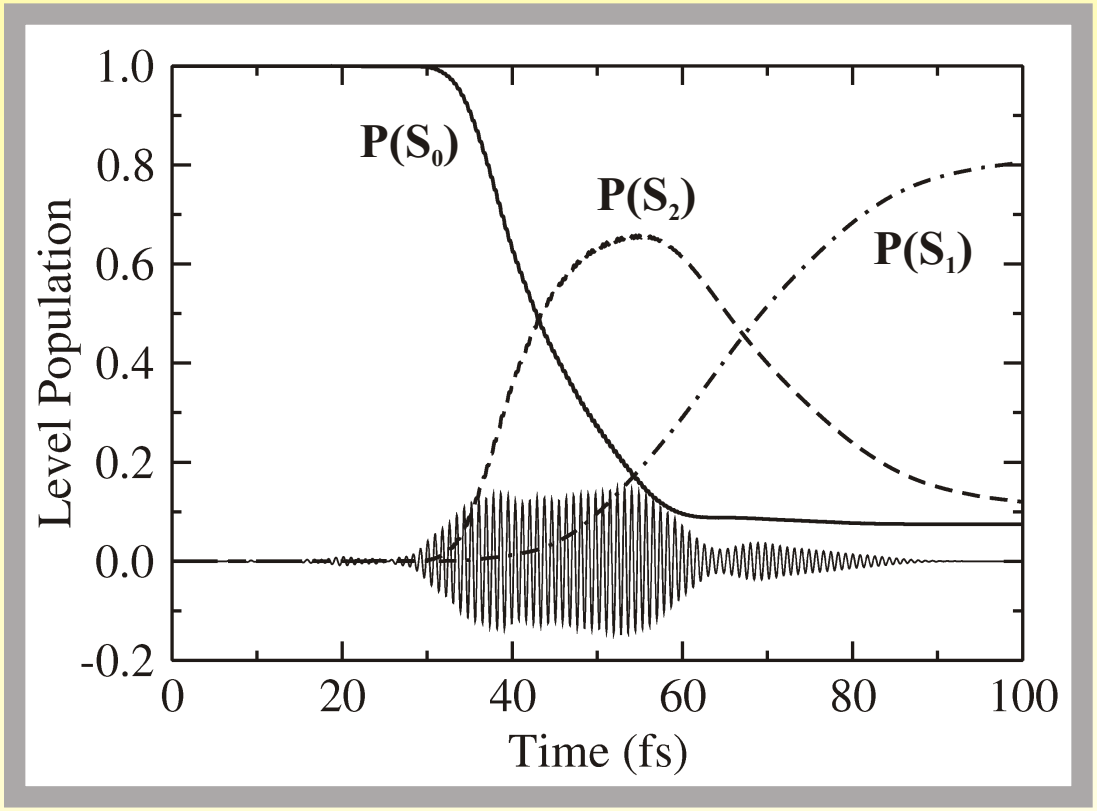
ring stretching

ring bending

out of plane



Optimization of the overall S_1-population



Reduced probability distribution of the four modes

$$P_{S_1}(Q_j, t) = \int dQ' \, |\chi_{S_1}(Q_1, Q_{6a}, Q_{9a}, Q_{10a}, t)|^2$$

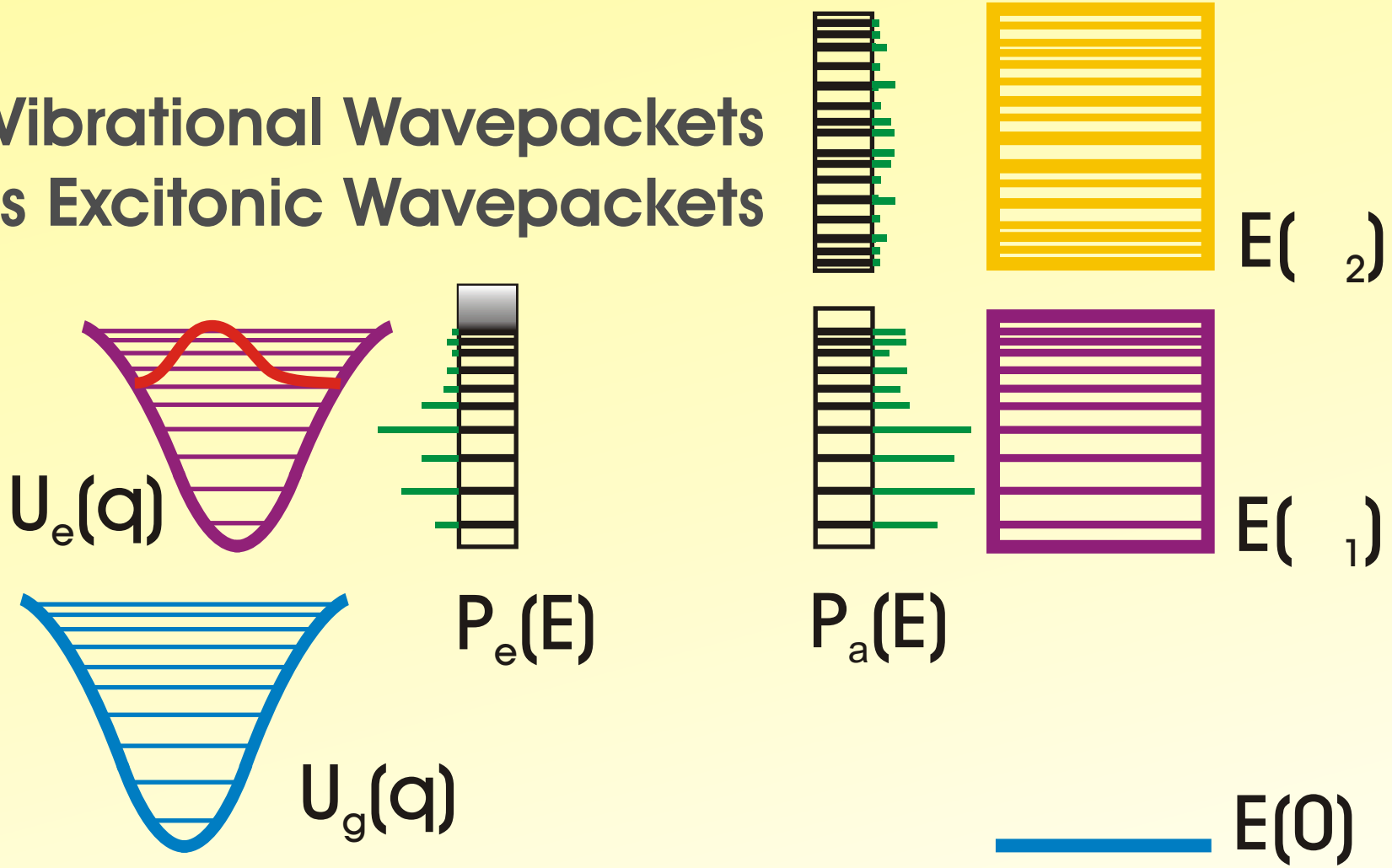
Excitation Energy Localization in a Pigment Protein Complex

$$\mathcal{O}[\mathbf{E}_c] = \mathrm{tr}\{\hat{\rho}(t;\mathbf{E}_c)\hat{O}\}$$

$$\mathcal{O}[\mathbf{E}_c] = \int_{t_0}^{\infty} dt \int dp \, \langle \Psi(t;p)|\hat{O}(t;p)|\Psi(t;p)\rangle$$

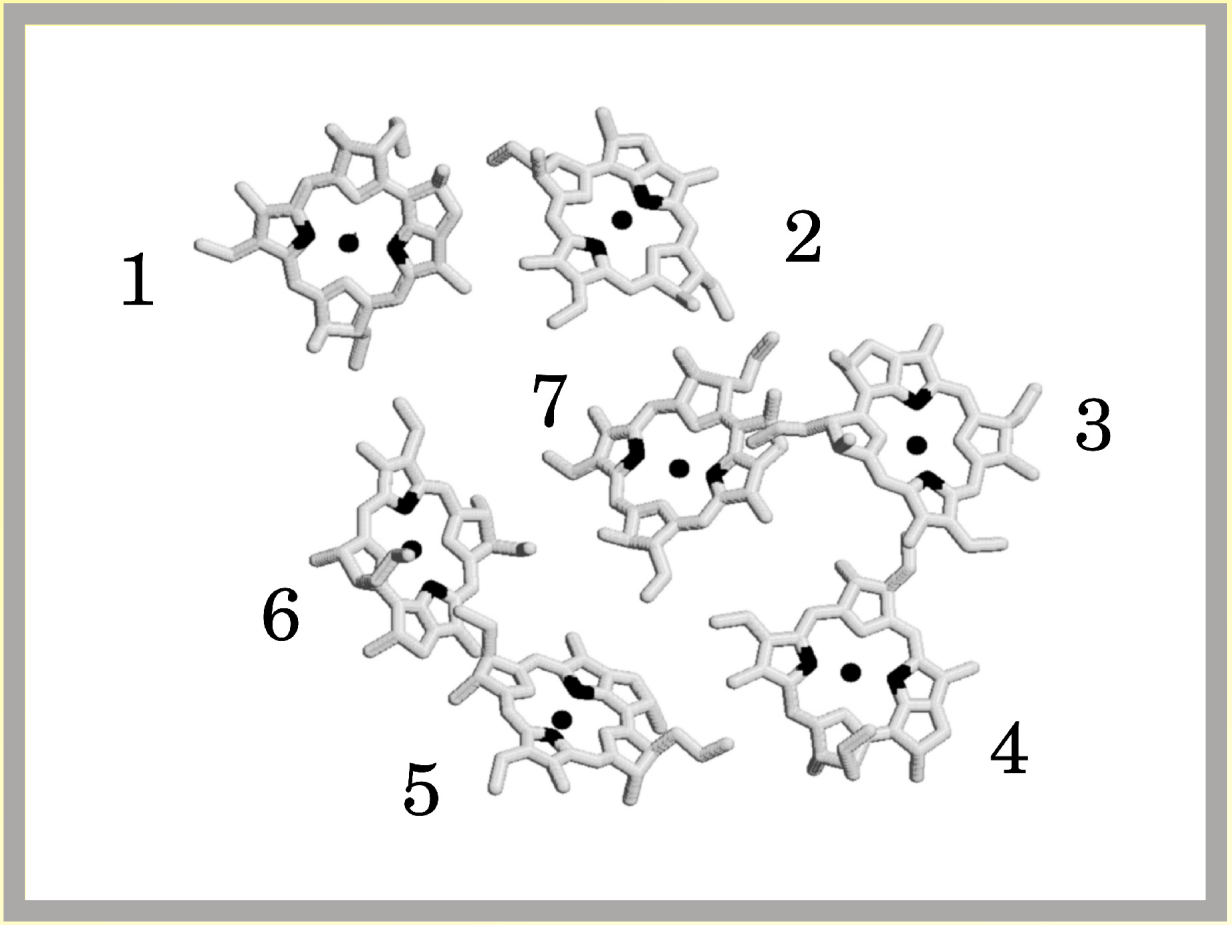
Excitation Energy Localization via the Formation of Excitonic Wavepackets

Vibrational Wavepackets versus Excitonic Wavepackets



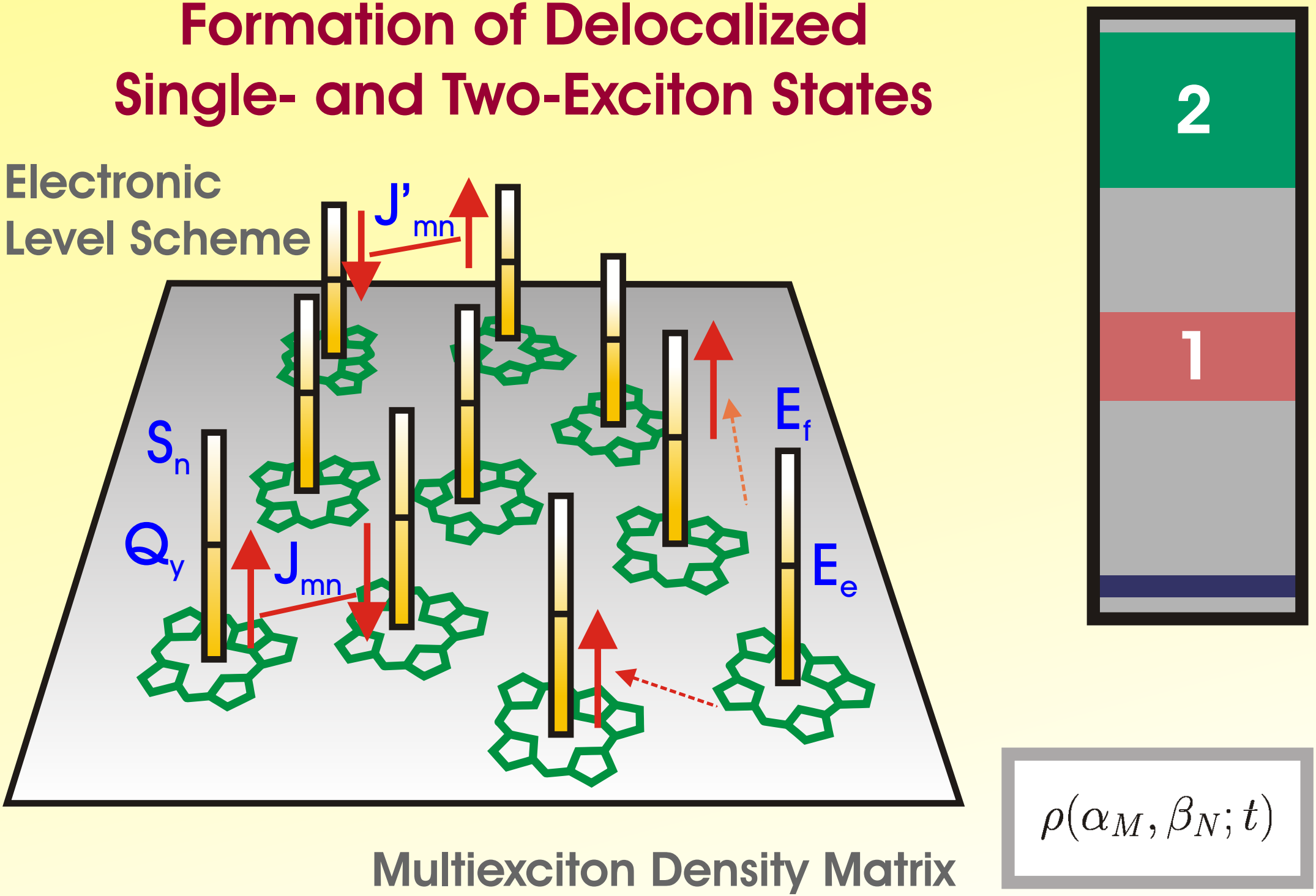
The study of particular relaxation pathways may become possible!

The monomeric FMO-complex



-> two-exciton states
-> excitation energy disspation
-> structural and energetic disorder
-> control using circular polarized laser pulses

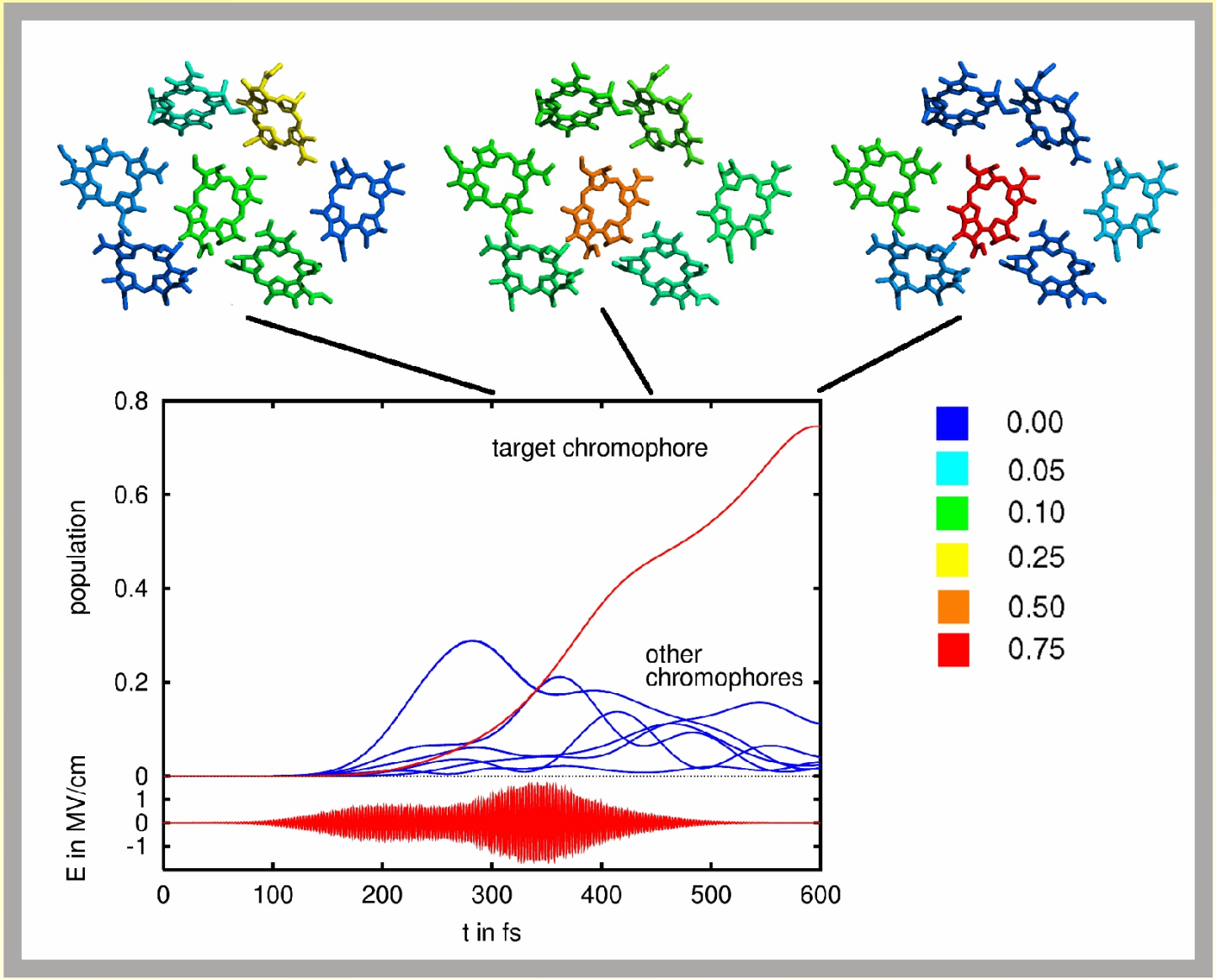
Formation of Delocalized Single- and Two-Exciton States



Multiexciton Density Matrix

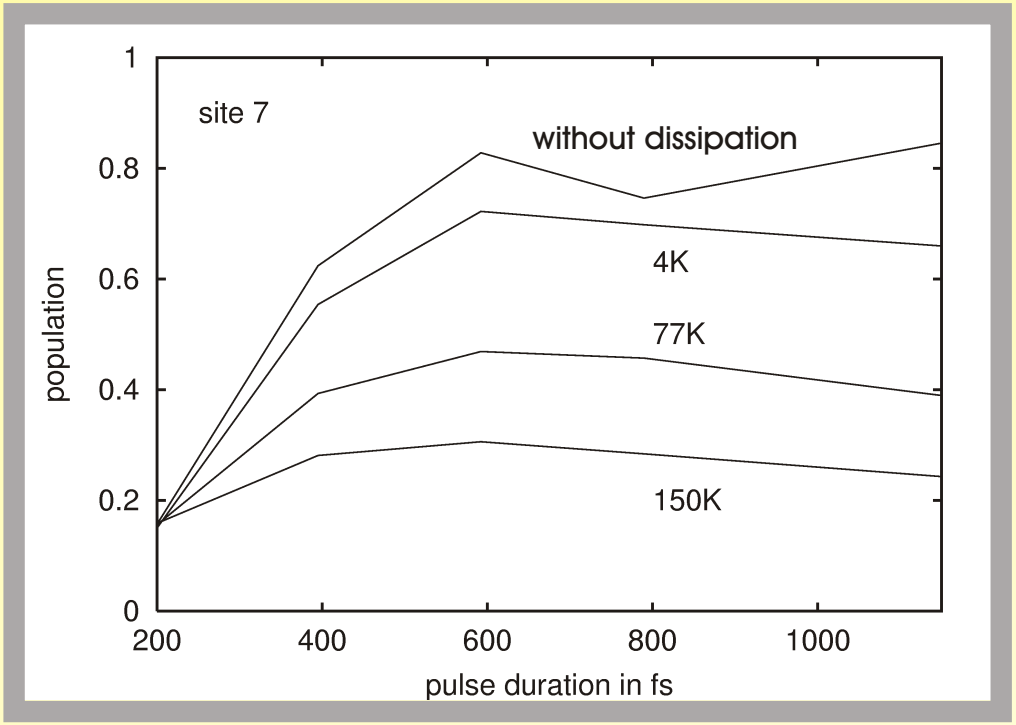
$$\rho(\alpha_M, \beta_N; t)$$

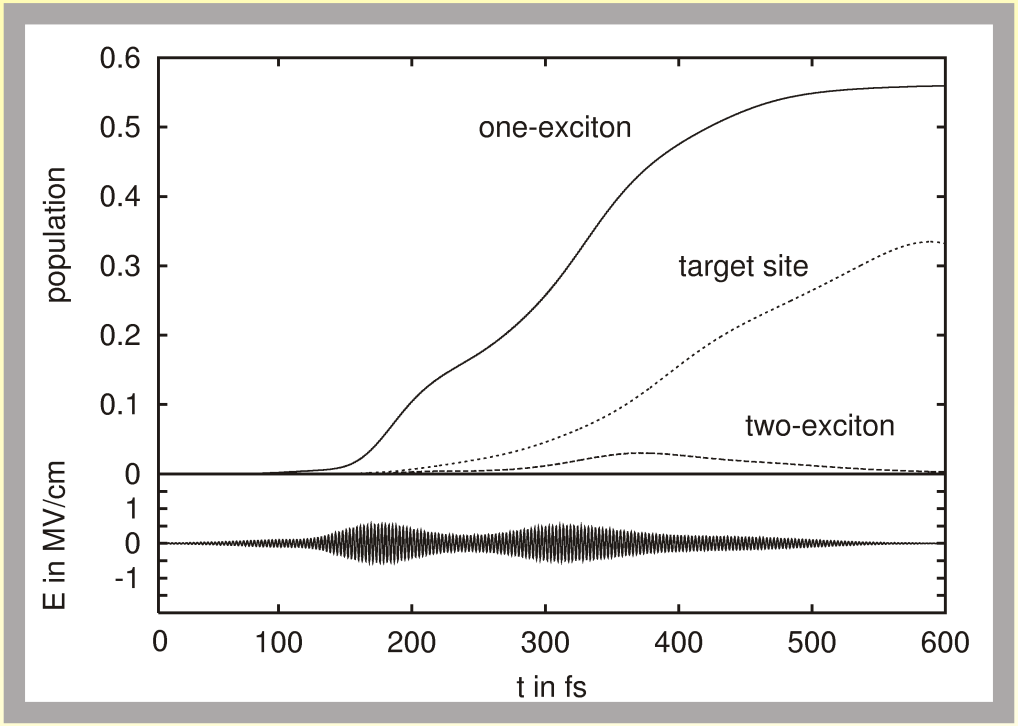
Laser Pulse Excitation Energy Localization in the FMO-Complex



B. Brüggemann, and V. M., JPC B 108, 10529 (2004)

Excitation Energy Localization at Chromophore m=7

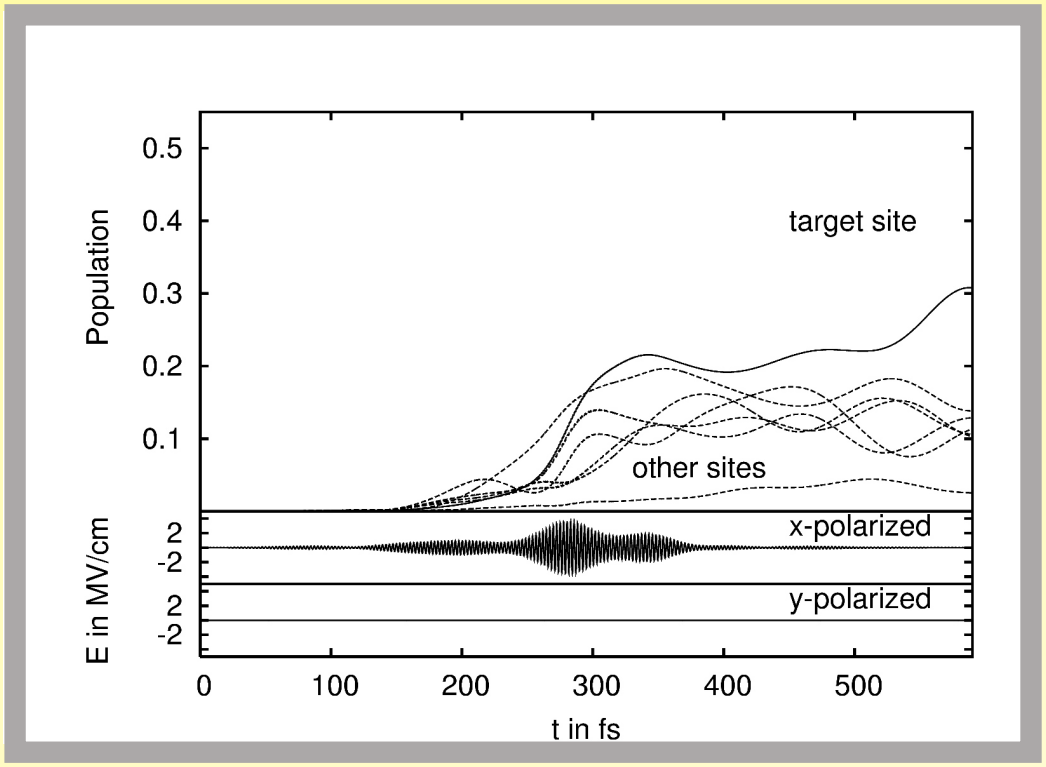


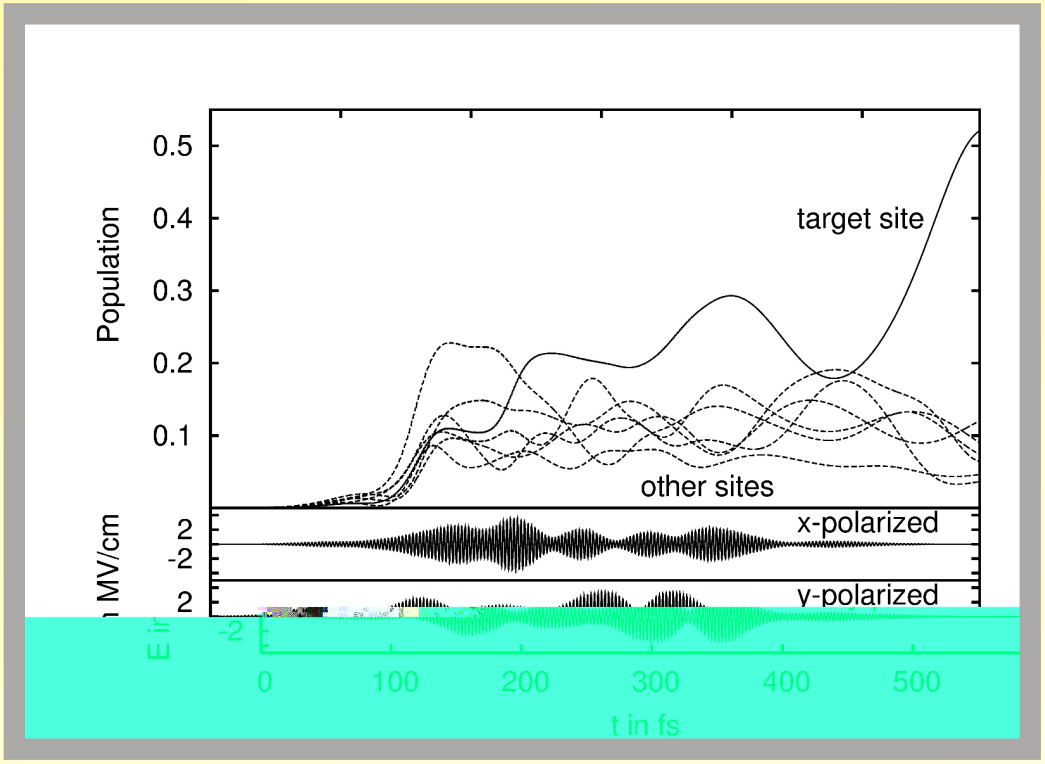


in dependence on
- the control pulse length
- temperture

- including two-exciton states
- at a temperature of 4 K

Linear versus circular polarization of the control pulse





-> 10 randomly oriented complexes
-> energetic disorder of 100 cm^{-1}
-> 4 K
-> neglect of two-exciton levels

Acknowledgment

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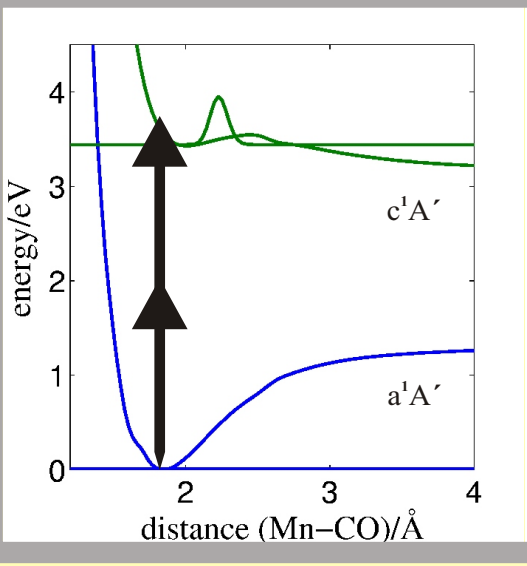
Luxia Wang (Berlin)
DFG (Sfb 450)

Appendix

Control yield of simple wave packet formation



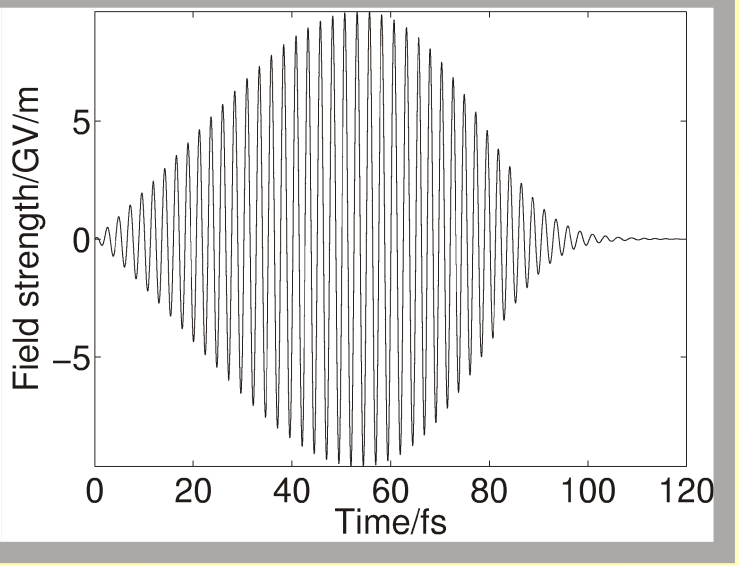


TABLE I: The yield $\mathcal{Q}$, the renormalized yield q, the maximum $E_{\max}$ of the field–strength (in GV/m) and the related intensity $I_{\max}$ (in GW/cm^2) for different used penalty factors λ (in 10^{12} fs (GV/m)^4) of the described control scheme

$\mathcal{Q}$	q	$E_{\max}$	$I_{\max}$	λ
0.68	0.82	58.1	3.02	3
0.29	0.74	42.2	2.19	12
0.0049	0.72	14.7	0.76	19
0.0009	0.72	9.6	0.50	20