Non-Resonant Multi-Photon Transitions in Polyatomic Molecules

TP C3 and TP C1

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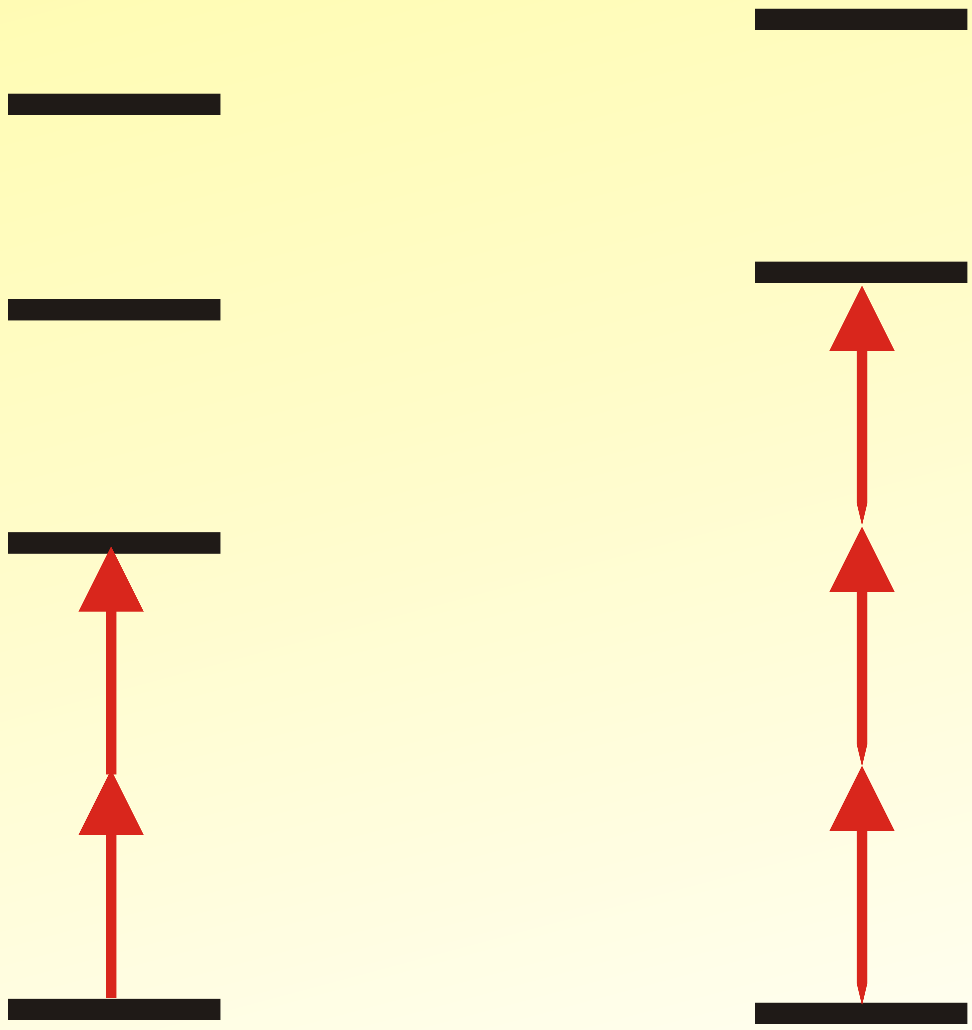
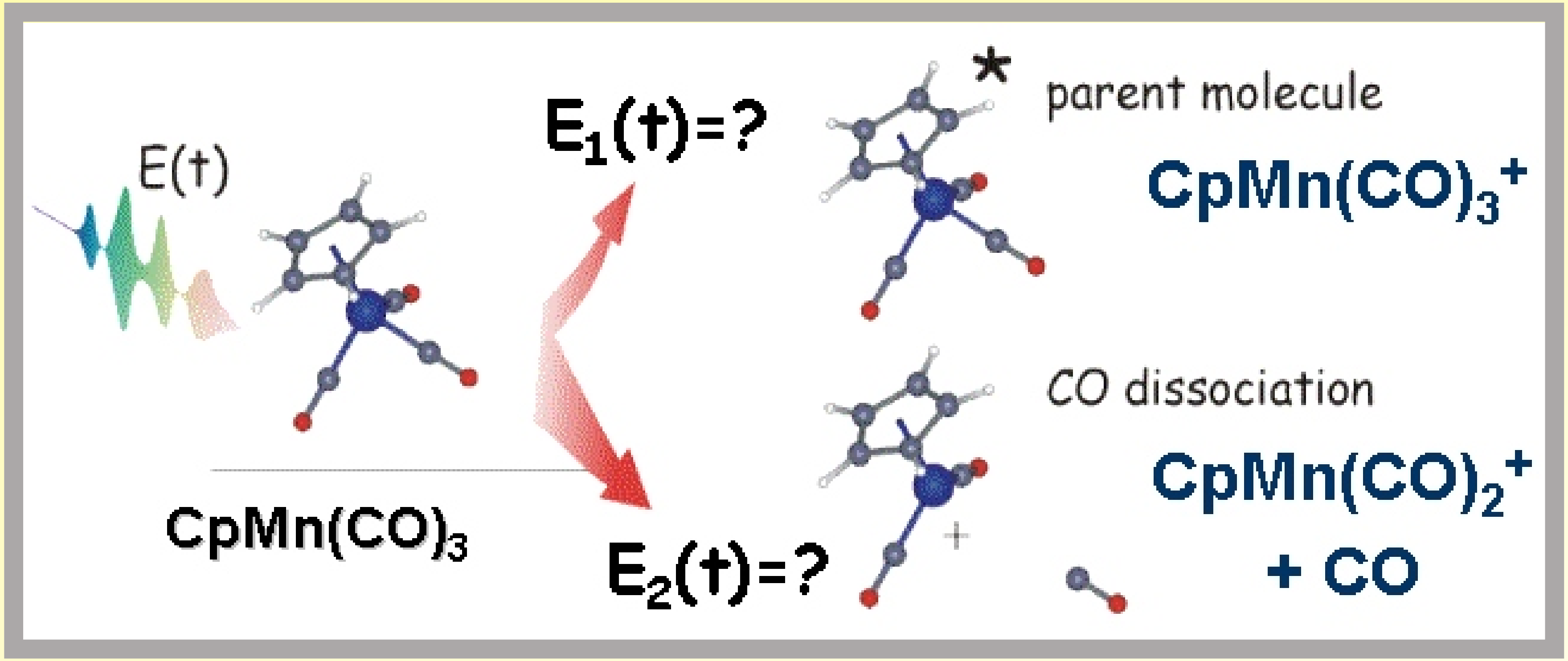
Non-Resonant Multiphoton Transitions (NMT)



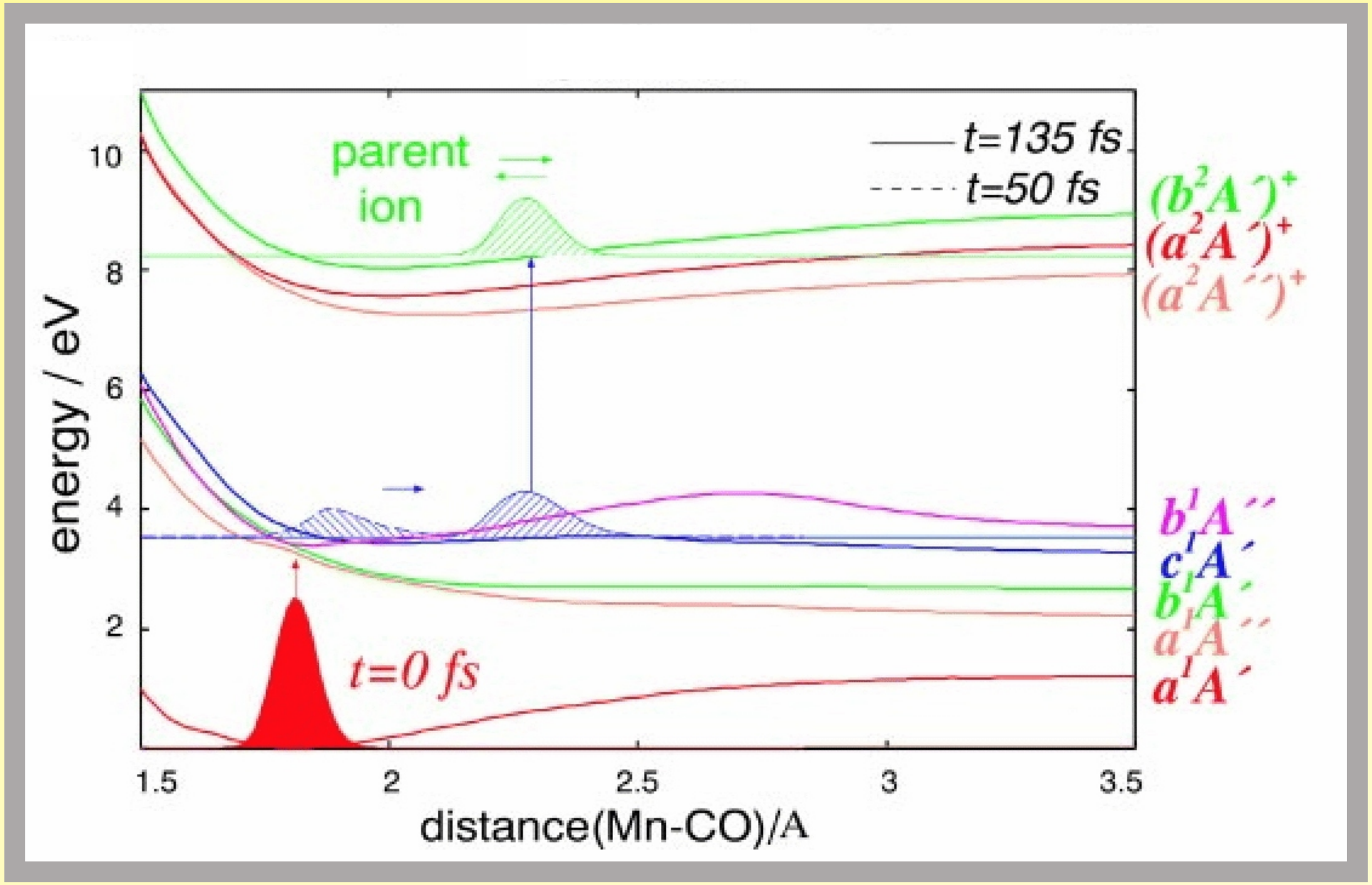
Motivation

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

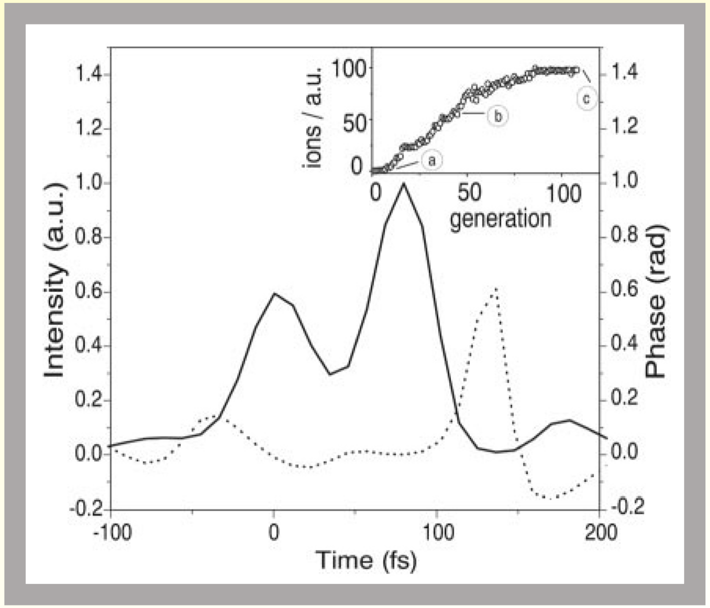
$a^1A' \rightarrow c^1A'$:

2PT at =798.7 nm

85 fs

$c^1A' \rightarrow (b^2A')^+$:

3PT at =801.12 nm

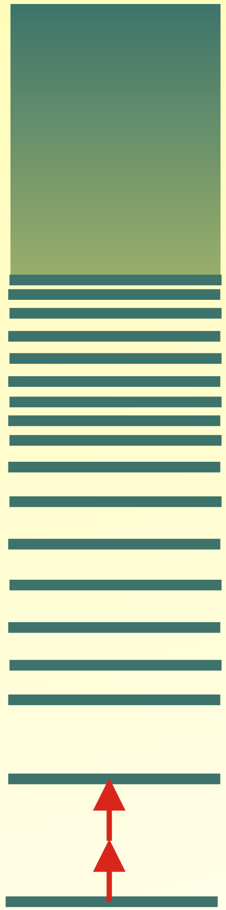


Basics of Non-Resonant Two-Photon Transitions

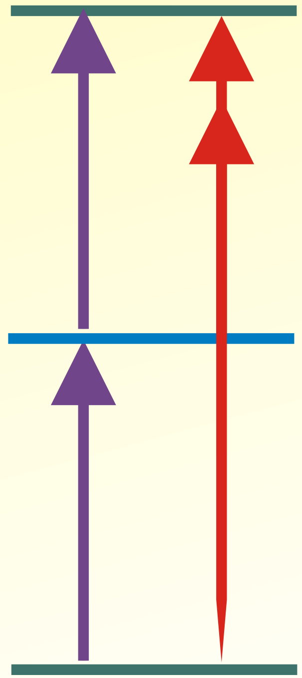
Excited state population after two-photon transition

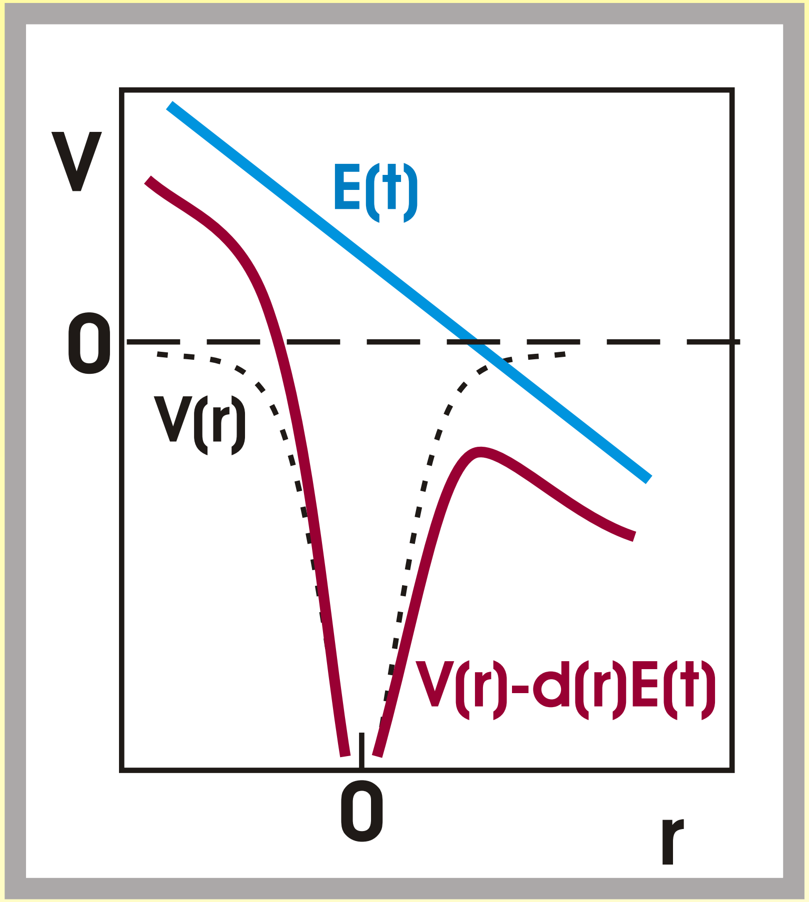
$$P_e \sim I_0^2 \,|\sum_x \frac{d_{ex}d_{xg}}{\omega_x-\omega_g-\omega_0}\left(\frac{1}{\omega_e-\omega_x-\omega_0}-\frac{1}{\omega_e-\omega_g-2\omega_0}\right)|^2$$

non-resonant transition



resonant transition





small (two-atomic) systems

solution of the complete time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(r,R,t) = [H_{\rm el}(r;R) + T_{\rm nuc} + V_{\rm nuc-nuc} - \mathbf{E}(t)\mathbf{d}(r,R)]\Psi(r,R,t)$$

Polyatomic systems

expansion with respect to some adiabatic electronic levels

$$\Psi(r, R, t) = \sum_a \chi_a(R, t)\varphi_a(r; R)$$

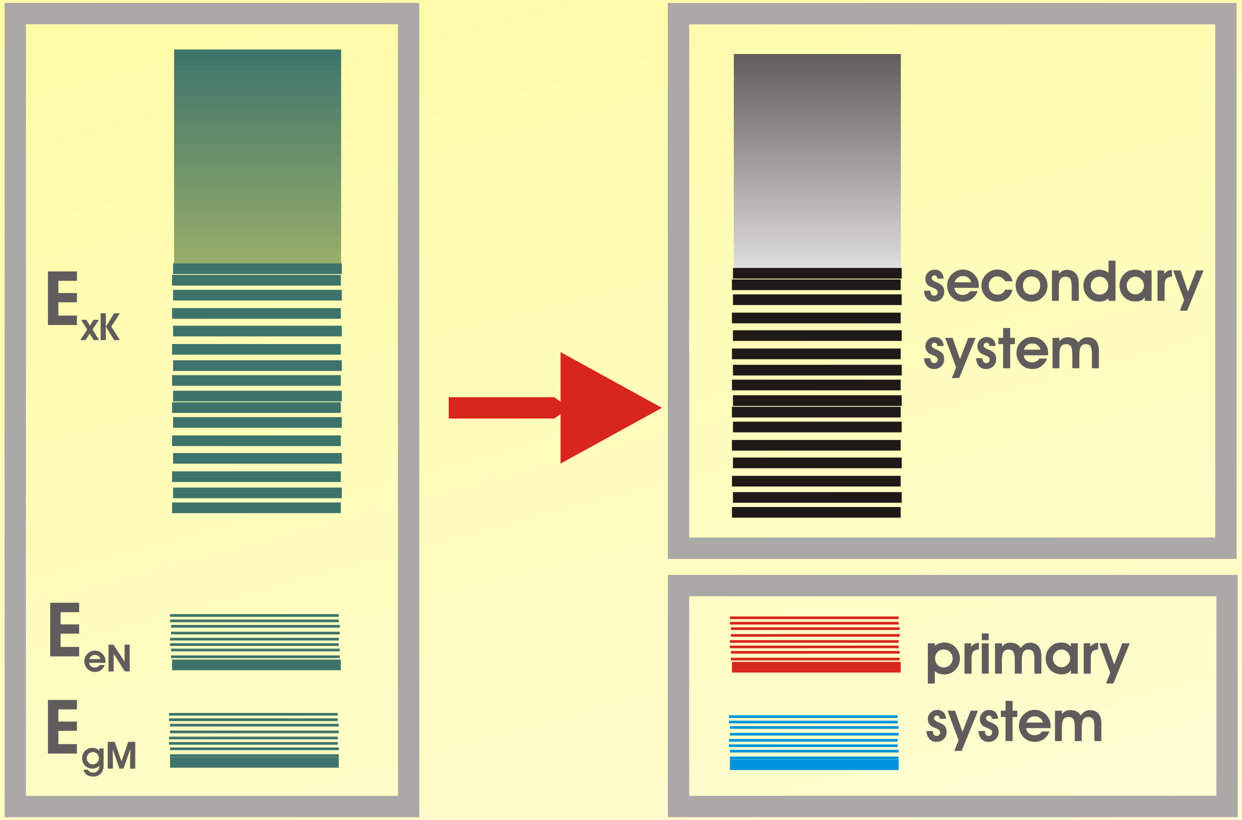
solution of coupled vibrational time-dependent Schrödinger equations

$$i\hbar\frac{\partial}{\partial t}\chi_a(t) = H_a\chi_a(t) + \sum_b [\Theta_{ab} - \mathbf{E}(t)\mathbf{d}_{ab}]\chi_b(t)$$

How to include the off-resonant levels?

Effective Schrödinger Equation

Removal of the Off-Resonant States



Effective Time-Dependent Schrödinger Equation

->time-nonlocal

->nonlinear with respect to the radiation field

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

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

integral kernel

two-photon coupling matrix

$$\mathbf{D}^{(\mathrm{II})}_{ab}(t-\bar{t}) = \frac{i}{\hbar}\int d\Omega\,\varrho(\Omega)\,\mathbf{d}(a,\Omega)\,e^{-i\Omega(t-\bar{t})}\,\mathbf{d}(\Omega,b)$$

Non-Resonant Two-Photon Transitions

the RWA and the SVA

$$\mathbf{E}(t) = \frac{1}{2}\mathbf{n}E(t)e^{-i\omega_0 t} + \text{c.c.}$$

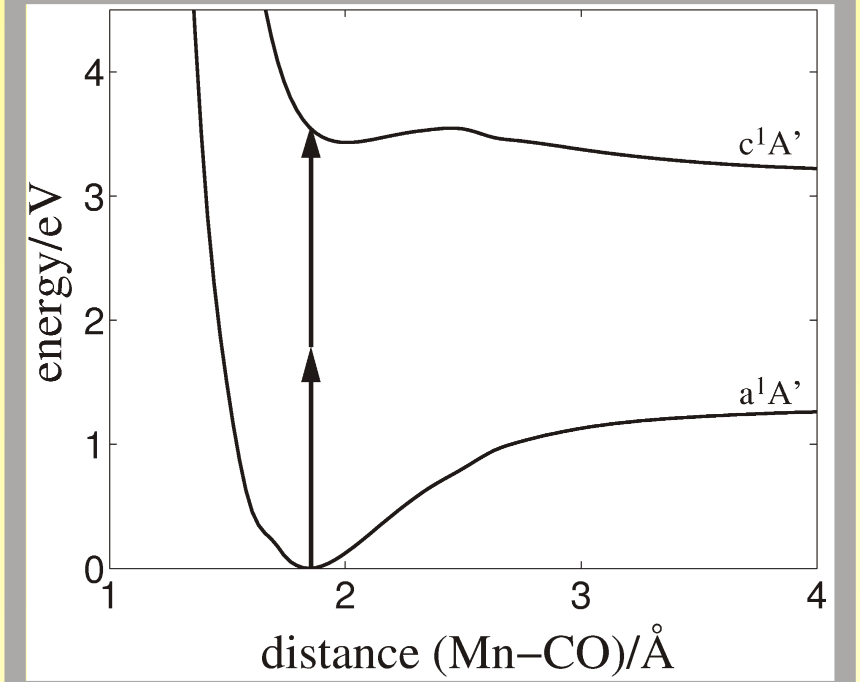
$$\chi_a(t) = \sum_n e^{-in\omega_0 t}\chi_a(n;t)$$

Coupled Schrödinger-equations for the vibrational wave functions

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

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

Two-level model for 2PT



Effective two-photon coupling matrix element

$$d_{ab}^{(\mathrm{II})} = \frac{1}{\hbar}\int d\Omega\,\frac{\varrho(\Omega)}{\Omega} d(a,\Omega)d(\Omega,b) \approx \frac{1}{\hbar}\bar{\rho} d_{\mathrm{eff}}^2$$

Some numbers:

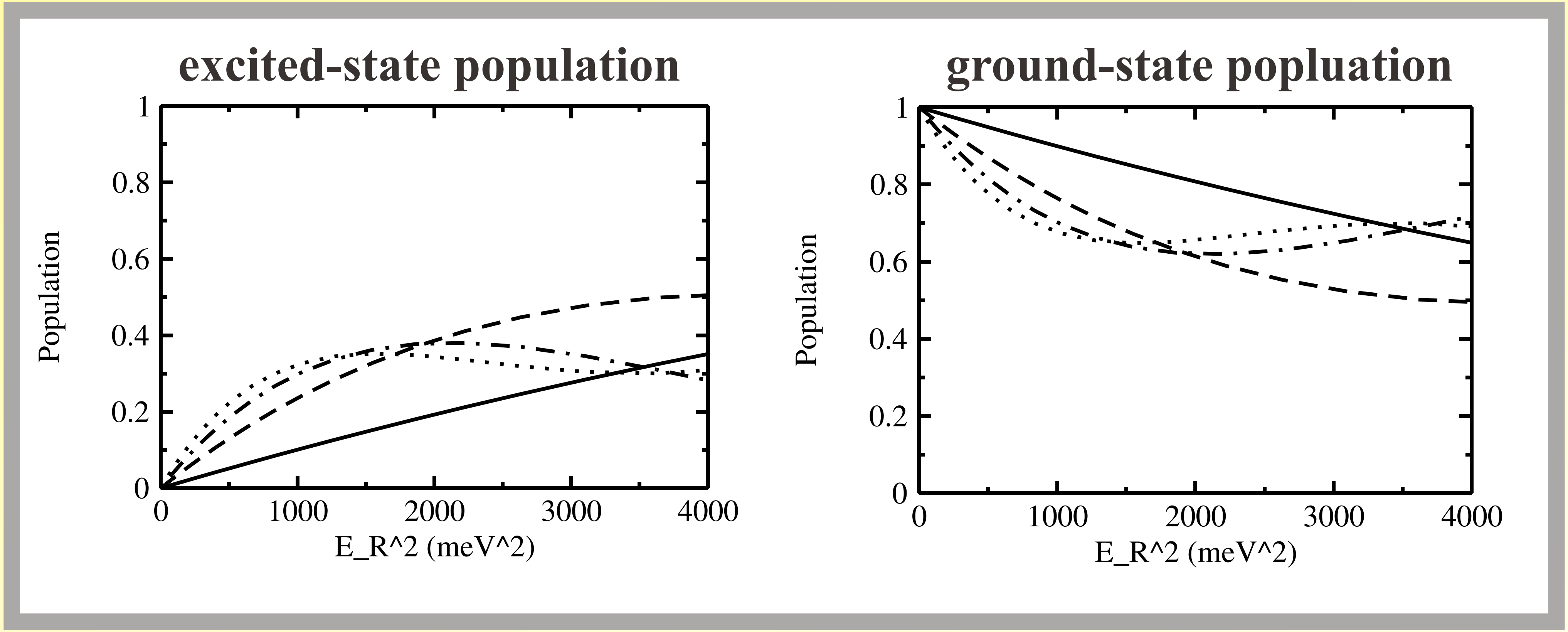
$\bar{\rho}/\hbar = 50/\mathrm{eV}$ $\qquad d_{\mathrm{eff}} = 1$ D

Rabi energy (in eV): $E_{\mathrm{R}} = d_{\mathrm{eff}} E \rightarrow 2.08\ [d(\mathrm{D})] \times [E(10^9\mathrm{V/cm})]$

two–photon transition Rabi energy:

$E_{\mathrm{R}}^{(\mathrm{II})} = \bar{\rho}/\hbar \times E_{\mathrm{R}}^2 \qquad \Rightarrow 50/\mathrm{eV} \cdot 10^{-2}\ \mathrm{eV} \cdot 10^{-2}\ \mathrm{eV} = 5 \cdot 10^{-3}\ \mathrm{eV}$

Overall electronic level population P_e and P_g after ultrashort laser pulse excitation



full lines: 20 fs
dashed lines: 40 fs
dashed-dottel lines: 60 fs
dotted lines: 80 fs

harmonic PES:
E_{vib} = 40 meV, E = 0.123 eV
E_{eg} =3.43eV, $2E_{photon}$ = 3.46 eV

Optimal Control Theory

Control Functional

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

Nonlinear Equation Determining the Optimal Pulse

$$E^2(t) = \mathcal{E}(t) =$$

$$i \frac{d_{ge}^{(\mathrm{II})}}{\hbar \lambda} [\langle \chi_e(t_f; \mathcal{E}) | \chi_e^{(\mathrm{tar})} \rangle \langle \vartheta_g(t; \mathcal{E}) | \chi_e(t; \mathcal{E}) \rangle$$

$$- \langle \chi_e^{(\mathrm{tar})} | \chi_e(t_f; \mathcal{E}) \rangle \langle \chi_g(t; \mathcal{E}) | \vartheta_e(t; \mathcal{E}) \rangle]$$

Control yield of simple wave packet formation

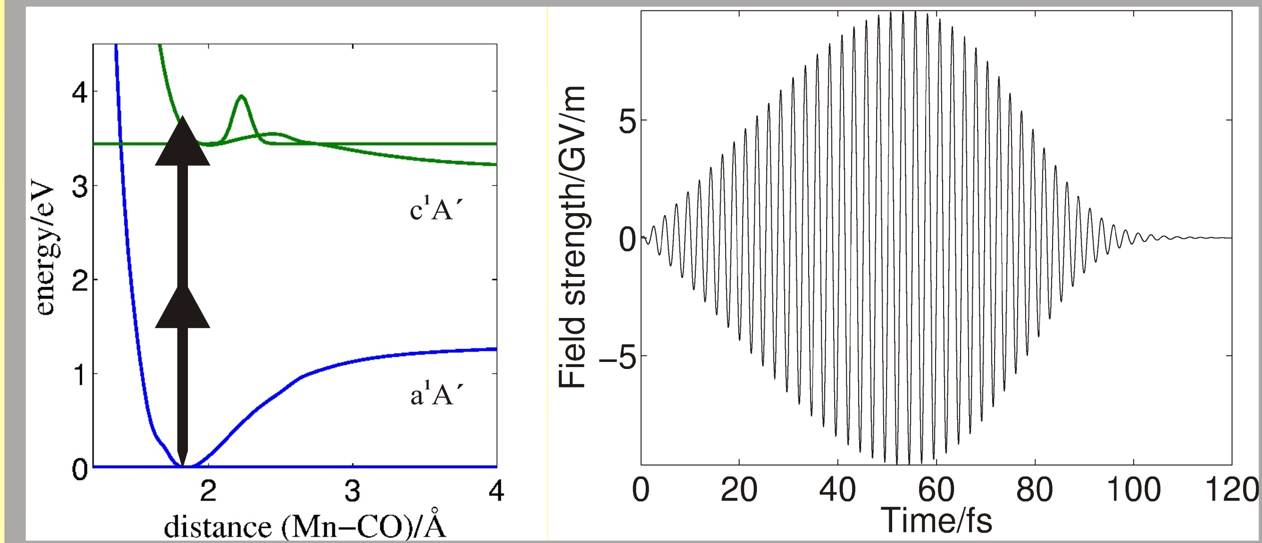
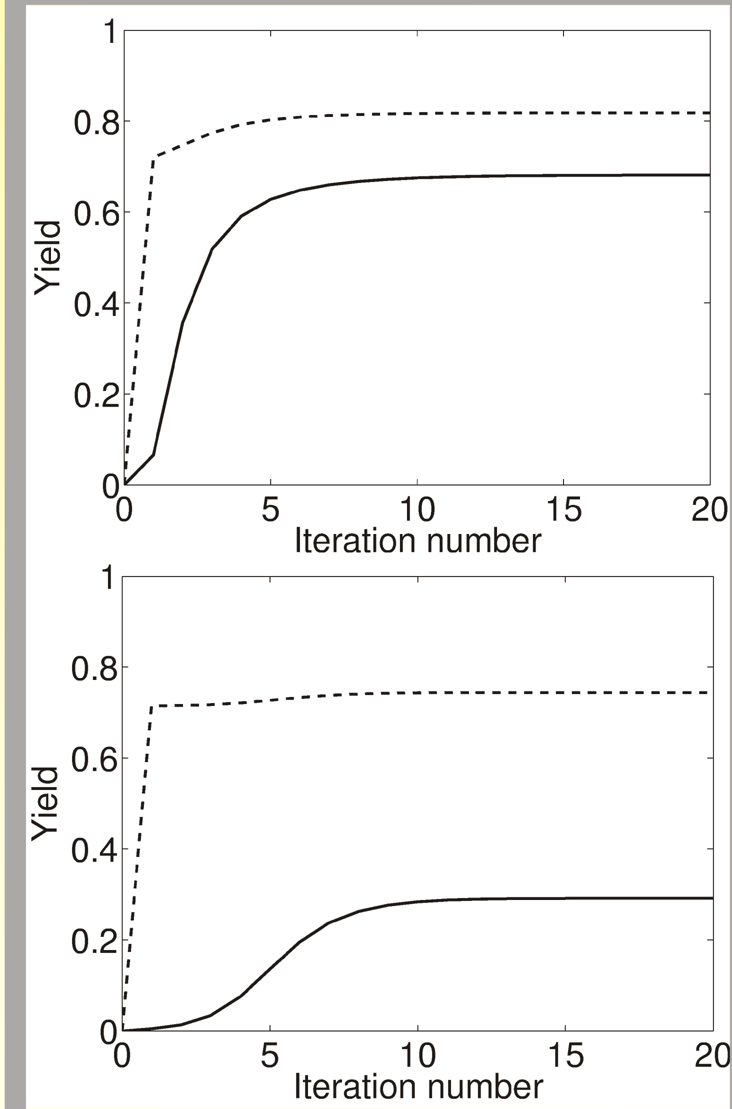


TABLE I: The yield $\mathcal{Q}$, the renormalized yield q, the maximum $E_{\max}$ of the field–strength (in GV/m) and the related intensity $I_{\max}$ (in GW/cm^2) for different used penalty factors λ (in 10^{12} fs (GV/m)^4) of the described control scheme

$\mathcal{Q}$	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



Laser Pulse Control of a Non-Resonant Two-Photon-Three-Photon Transition