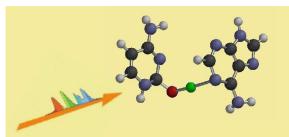


UP1: KONTROLIERTE LIGANDENABSPALTUNG VON METALLORGANISCHEN VERBINDUNGEN

L. González



AGENDA

- Control of competing ligand fragmentation
- Control of elementary biological processes
- Optimal control with non-resonant multiphoton transitions
- Inversion

COWORKERS

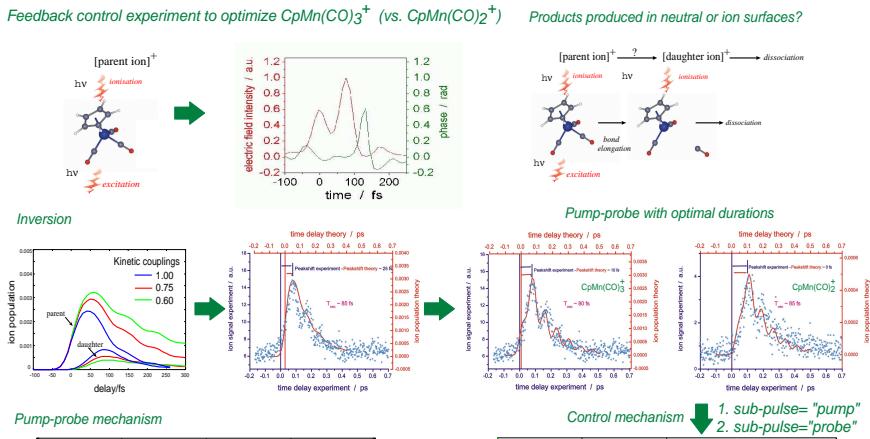
J. Full
D. Ambrosek
M. Oppel

COOPERATIONS

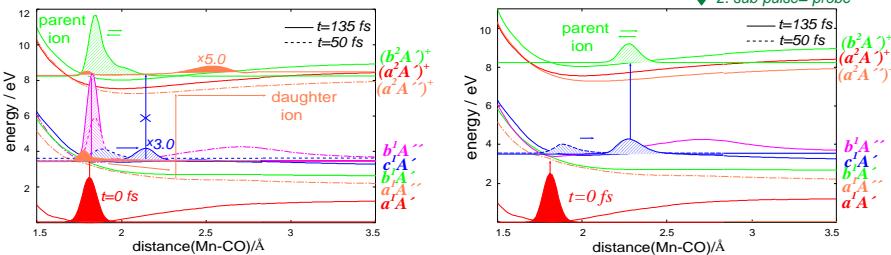
TP A1 (Wöste/Bernhardt/Lindinger)
TP C3 (May/Zimmermann)
TP C6 (Gross/Saenz)
C. Daniel (Strasbourg)
G. Paramonov (Minsk)
T. Seideman (Northwestern)
P. Hobza (Prag)

RESULTS

CONTROL via ANALYSIS and INVERSION



Pump-probe mechanism



PUBLICATIONS

J. Full, C. Daniel, L. González.
Ultrafast nonadiabatic laser driven dynamics of excited states of $\text{CpMn}(\text{CO})_3$. An ab initio quantum chemical and dynamical study. *Phys. Chem. Chem. Phys.* **5**, 87 (2003).

C. Daniel, J. Full, L. González, C. Lupulescu, J. Manz, A. Merli, S. Vajda, L. Wöste.
Deciphering the reaction dynamics underlying optimal laser fields. *Science* **299**, 536 (2003).

D. Ambrosek, M. Oppel, L. González, V. May.
Theory of ultrafast non-resonant multi-photon transitions: basics and applications to $\text{CpMn}(\text{CO})_3$. *Chem. Phys. Lett.* **380**, 536 (2003).

J. Full, L. González, J. Manz.
Neutral-to-ionic transition dipole couplings beyond Koopmans' picture. Applications to femosecond pump-probe spectroscopy. *J. Phys. Chem. Submitted*.

V. May, D. Ambrosek, M. Oppel, L. González.
Ultrafast non-resonant multiphoton transitions in molecular systems. I: Basic theory. To be submitted.

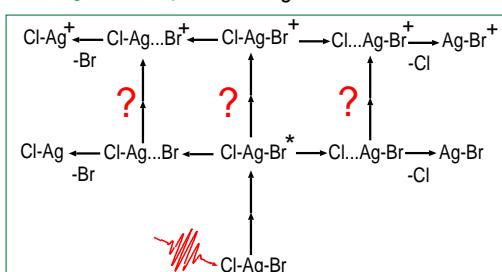
FUTURE

ANALYSIS and CONTROL

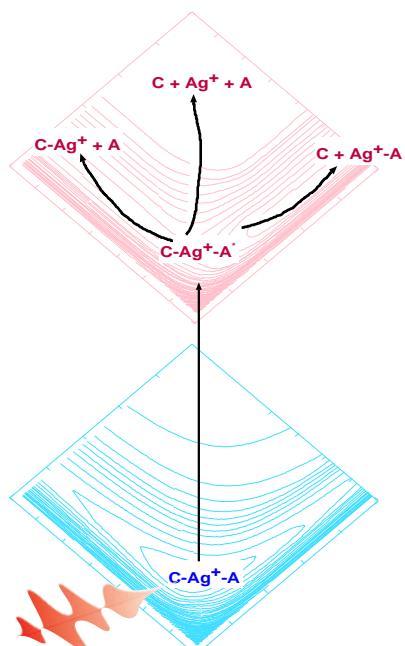
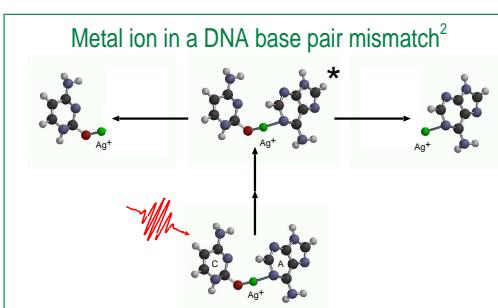
Control of competing ligand dissociation

Goal: Laser repairing of DNA mutation

Learning from simple: $\text{Cl}-\text{Ag}-\text{Br}$



to complex: Cytosine- Ag^+ -Adenine (or Purine)



THEORY

- 2d ab initio potential energy surfaces
- 2d non-adiabatic couplings
- 2d neutral-to-ionic transition dipole couplings

Non-resonant multi-photon transitions (NMT), TP C3

TDSE for the resonant state space (projection operator technique):
 $i\hbar \frac{\partial}{\partial(t)} |\Psi_{\text{res}}(t)\rangle = (\mathcal{H}_{\text{mol}} + \mathcal{H}_{\text{field}}(t)) |\Psi_{\text{res}}(t)\rangle + \int_0^t d\tau \mathcal{H}_{\text{field}}^{(\text{eff})}(t, \tau) |\Psi_{\text{res}}(\tau)\rangle$

Effective field Hamiltonian for a two photon transition:

$$\mathcal{H}_{\text{field}}^{(\text{II})} = -\mathbf{E}(t) \hat{\mu}^{(\text{II})} \mathbf{E}(t)$$

$$\mathbf{d}_{ab}^{(\text{II})} = \langle \varphi_a | \hat{\mu}^{(\text{II})} | \varphi_b \rangle = \langle \varphi_a | \hat{\mu} | \varphi(\bar{\Omega}) \rangle \varrho(\bar{\Omega}) \langle \varphi(\bar{\Omega}) | \hat{\mu} | \varphi_b \rangle$$

Effective TDSE with respect to the resonant electronic states:

$$\frac{\partial}{\partial t} |\chi_g(t)\rangle = -\frac{i}{\hbar} (\mathcal{H}_g - \mathbf{E}(t) \mathbf{d}_{ge}^{(\text{II})}) |\chi_g(t)\rangle + \frac{i}{\hbar} \mathbf{E}(t) \mathbf{E}(t) \mathbf{d}_{ge}^{(\text{II})} |\chi_e(t)\rangle$$

$$\frac{\partial}{\partial t} |\chi_e(t)\rangle = -\frac{i}{\hbar} (\mathcal{H}_e - \mathbf{E}(t) \mathbf{d}_{ge}^{(\text{II})}) |\chi_e(t)\rangle + \frac{i}{\hbar} \mathbf{E}(t) \mathbf{E}(t) \mathbf{d}_{eg}^{(\text{II})} |\chi_g(t)\rangle$$

Non-ZEKE transitions, G. Paramonov (Minsk) & TP C6

- discretization of continuum³
- semiclassical, perturbation theory (weak field)⁴

time-dependent Koopmans' picture (medium field)

$$D_i = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \rightarrow D_E = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \text{ion}$$

$$\Psi(t) = c_{\text{bound}}(t) e^{-iE_{\text{bound}}t/\hbar} (D_i) + e^{-iE_{\text{ion}}t/\hbar} (D_f(t))$$

$$i\dot{\Psi} = H\Psi$$

coupled equations for $c_{\text{bound}}(t)$ and $\theta(t)$ (3D) and nuclei (1D-3ND)

Optimal control theory with NMT+ non-ZEKE, TP C3