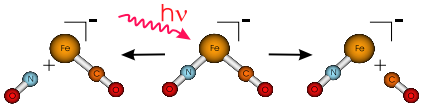
UP1: KONTROLLIERTE LIGANDENABSPALTUNG VON METALLORGANISCHEN VERBINDUNGEN

L. González, O. Kühn, M.Oppel



AGENDA

Ab initio quantum chemistry of excited electronic states
Nonadiabatic electron-nuclear dynamics
Laser pulse optimization

COWORKERS

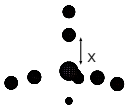
J. Full
Y. Zhao

COOPERATIONS

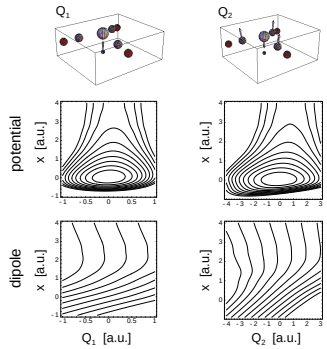
TP A1 (Wöste/Vajda/Bernhardt)
TP C3 (May/Zimmermann)
K. Seppelt (FU Berlin)
C. Daniel (Strasbourg)

RESULTS: $HCo(CO)_4 \longrightarrow HCo(CO)_3 + CO$

REACTION SURFACE HAMILTONIAN



- All-Cartesian approach
- DFT-B3LYP
- $R_{Co\text{-}CO}$= reaction coordinate
- two strongly coupled substrate modes



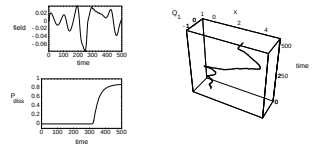
LOCAL LASER PULSE CONTROL

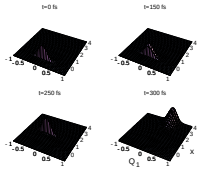
cost functional $\mathcal{J} = \sum_i \langle [\hat{p}_i \gamma_i - E(t)\, \partial\mu/\partial x_i]^2 \rangle$

γ_i<0 : damping
γ_i>0 : excitation

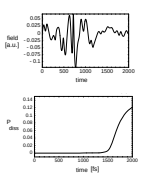
multidimensional control

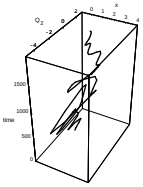
Co-H mode Q_1

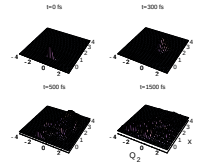




umbrella mode Q_2







PUBLICATIONS

Y.Zhao, O. Kühn,
Selective IR laser pulse control of H *and* CO *branching in the ground state photodissociation of* $HCo(CO)_4$.
Chem. Phys. Lett. 302, 7-14 (1999).

O. Kühn, J. Manz, Y. Zhao,
Ultrafast IR laser control of photodissociation: Single versus multi-pulse schemes.
Phys. Chem. Chem. Phys. 1, 3103-3110 (1999).

A. E. Orel, Y. Zhao, O. Kühn,
Laser driven ground state photodissociation of $HCo(CO)_4$*: An ab initio quantum molecular dynamics approach*
J. Chem. Phys. 112, 94-100, (2000).

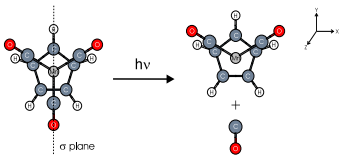
Y. Zhao, O. Kühn,
Competitive local laser control of phtotodissociation reaction $HCo(CO)_4$ -> $HCO(CO)_3$ + CO *in the electronic ground state*
J. Phys. Chem. A 104, 4882-4888 (2000).

J.Full, L. González, C. Daniel,
A CASSCF/CASPT2 and TD-DFT study of the low-lying excited states of η^5*-CpMn(CO)*$_3$
J. Phys. Chem. A 105, 184 (2001).

C. Daniel, J.Full, L. González, C. Kaposta, M. Krenz, C. Lupulescu, J. Manz, S. Minemoto, M. Oppel, P. Rosendo-Francisco, S. Vajda, L. Wöste,
Analysis and control of laser induced fragmentation processes in $CpMn(CO)_3$
Chem. Phys. (2001) in press.

FUTURE

MODEL SYSTEM



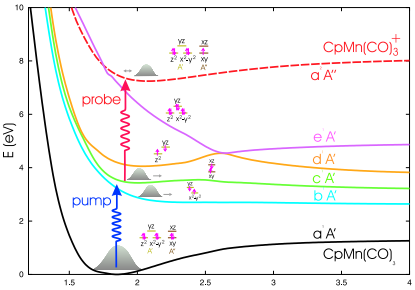
THEORY

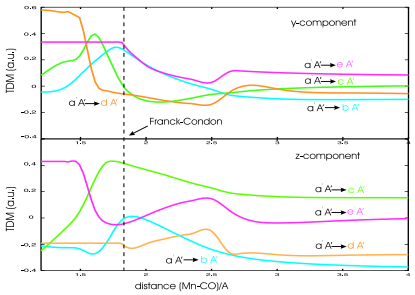
- CASSCF/MRCI potentials and dipole moments

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\Psi_0\\ \Psi_1\\ \Psi_2\\ \Psi_3\\ \Psi_4\end{pmatrix} = \begin{pmatrix}H_{00} & H_{01} & H_{02} & H_{03} & H_{04}\\ H_{10} & H_{11} & H_{12} & H_{13} & H_{14}\\ H_{20} & H_{21} & H_{22} & H_{23} & H_{24}\\ H_{30} & H_{31} & H_{32} & H_{33} & H_{34}\\ H_{40} & H_{41} & H_{42} & H_{43} & H_{44}\end{pmatrix}\cdot\begin{pmatrix}\Psi_0\\ \Psi_1\\ \Psi_2\\ \Psi_3\\ \Psi_4\end{pmatrix}$$

$$H_{ii} = T_i + V_i^{adiab} - \vec{E}_{y/z}(t)\cdot\vec{\mu}_{ii}^{adiab}$$

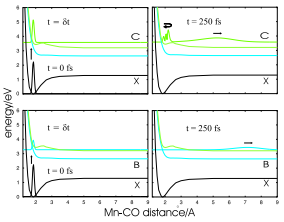
$$H_{ij} = -\vec{E}_{y/z}(t)\cdot\vec{\mu}_{ij}^{adiab} + H_{ij}^{diab}$$

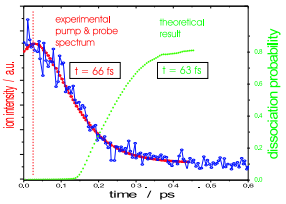




ANALYSIS

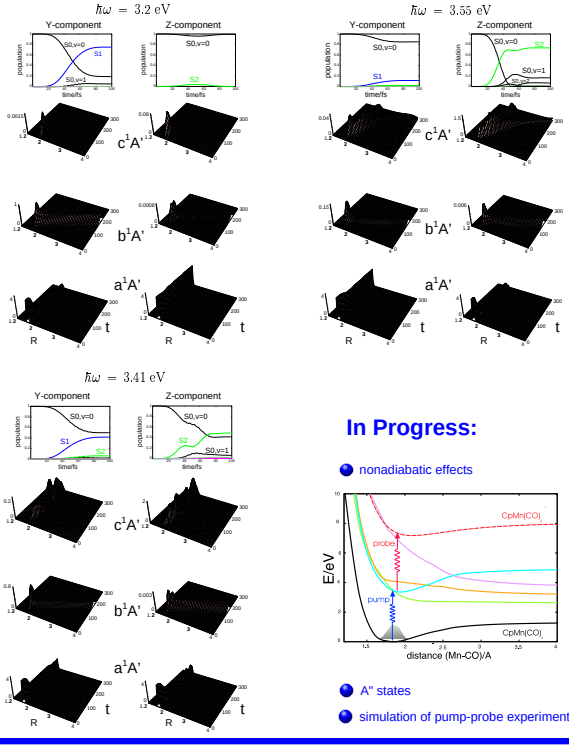
Wave packet dynamics after delta-pulse excitation: Dissociation time





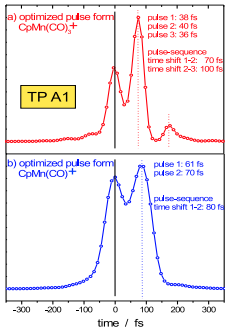
Laser-driven wave packet dynamics (36 fs, 8 TW/cm^2)

$$\vec{E} = \vec{E}_0 \cdot \cos\omega t \cdot s(t)$$



CONTROL

- simulation of a *feedback* control experiment:
  $CpMn(CO)_3^+$ vs. $CpMn(CO)_2^+$
  $CpMn(CO)_3^+$ vs. $CpMnCO^+$ (TP A1)



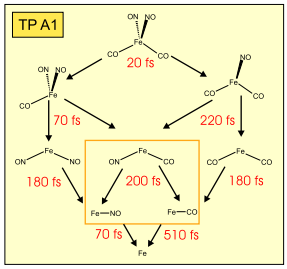
- control of fragmentation in different electronic states (TP A1)

$CpMn(CO)_3$ → $CpMn(CO)_2$ (b^1A') + CO
$CpMn(CO)_3$ → $CpMn(CO)_2$ (c^1A') + CO

- *Optimal control* theory:
  simulation of experimental pulse shaping (TP C3)

- competitive fragmentations

$FeNO^-$ + CO ← $FeNOCO^-$ → FeCO + NO^-



In Progress:

- nonadiabatic effects

- A'' states
- simulation of pump-probe experiments

References: B. A. Ruf, W. H. Miller, J. Chem. Soc. Faraday Trans. 2 84, 1523 (1988); Y. Chen, P. Gross, V. Ramakrishna, H. Rabitz, J. Chem. Phys. 102, 8001 (1995); R. S. Judson, H. Rabitz, Phys. Rev. Lett. 68, 1500 (1992); A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber, Science 282, 919 (1998).