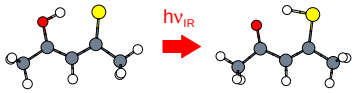
UP3: KONTROLLIERTER PROTONENTRANSFER IN DER KONDENSIERTEN PHASE

O. Kühn



AGENDA

Multidimensional coherent and dissipative quantum dynamics
Ultrafast spectroscopy of intramolecular hydrogen bonds
Design of optimal laser pulses for driving proton motion

COWORKERS

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M. Petkovic

COOPERATIONS

TP B2 Nibbering/Elsässer
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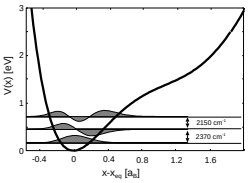
G. K. Paramonov (Minsk)
Y. Tanimura (Okazaki)
Y.-J. Yan (Hongkong)

RESULTS

PHTHALIC ACID MONOMETHYLESTER (PMME): DYNAMICS AND SPECTROSCOPY

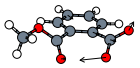
Cartesian Reaction Surface

- MP2 / 6-31+G(d,p)
- $R_{O1\text{-}H}$= reaction coordinate

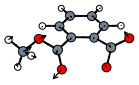


two strongly coupled substrate modes

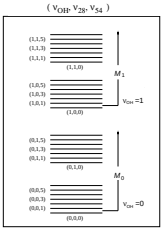
ν_{28} (1000 cm^{-1})

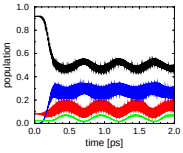


ν_{54} (70 cm^{-1})

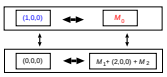


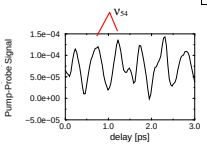
TDSCF-Dynamics

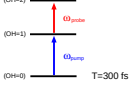




IVR patterns

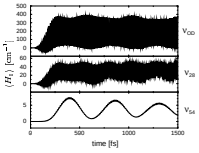




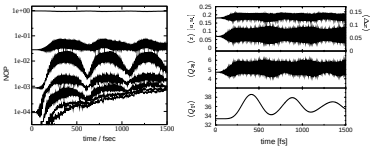


MCTDH-Dynamics

- 9-dimensional model
- mode combination
- natural orbital pop.: <10^{-3}



(ν_OD,ν_28) combined mode

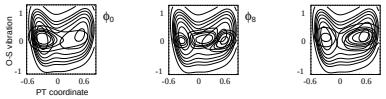


LASER CONTROL OF THIOACETYLACETONE

- goal: efficient driving of isomerization
  - simple pulse forms
  - robustness against energy and phase relaxation

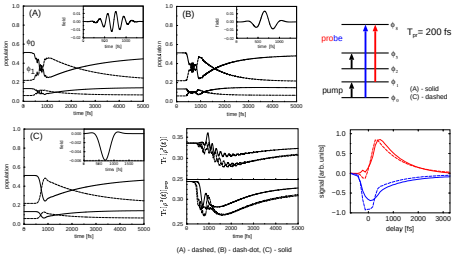
$$E(t) = E_0 \sin^2(t\pi/T)\cos(\Omega t) \qquad 0 \le t \le T$$

- two-dimensional relevant system plus heat bath



Dissipative Dynamics

regime: $\Omega \le (E_1 - E_0)/\hbar$



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FUTURE

CARTESIAN REACTION SURFACE HAMILTONIAN

$$H = \frac{\mathbf{P}_x^2}{2M_x} + V(\mathbf{x}) + \frac{1}{2}(\mathbf{P}_Q^2 + \mathbf{Q}\cdot\mathbf{K}(\mathbf{x})\cdot\mathbf{Q}) - \mathbf{f}(\mathbf{x})\cdot\mathbf{Q}$$

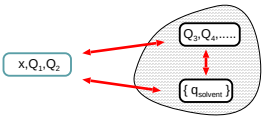
reaction coordinate	substrate normal modes	potential coupling
large amplitude motion anharmonicity	harmonic approximation mode-mode coupling	shift of oscillator PES

reference geometry

fixed	flexible
$\mathbf{R} - \mathbf{R}_0 = \mathbf{m}^{-1/2}\cdot\mathbf{U}\cdot\mathbf{Q}$	$\mathbf{R} - \mathbf{R}_0(\mathbf{x}) = \mathbf{R} - \mathbf{R}_0(\mathbf{x}) + \mathbf{m}^{-1/2}\cdot\mathbf{U}\cdot\mathbf{Q}$
proton motion in vicinity of potential minimum (PMME)	proton transfer in double minimum potential (SA)

SYSTEM-BATH APPROACH

relevant system
=
reaction coordinate
+
important substrate modes



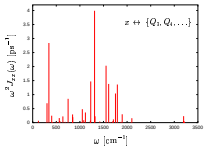
relaxation rates

$$k_{\alpha\delta} = \sum_{mn} S_{\alpha\delta}^{(m)} S_{\delta\alpha}^{(n)} \omega^2 \left(N_{\mathrm{BE}}(\omega)+1\right) \left[J_{mn}(\omega) - J_{mn}(-\omega)\right]$$

spectral densities

$$J_{mn}(\omega) = \pi \sum_i g_i^{(m)} g_i^{(n)} \delta(\omega - \omega_i)$$

- intramolecular interactions
  - ab initio reaction surface
- intermolecular interactions
  - model spectral densities
  - classical molecular dynamics (GROMACS)



QUANTUM DYNAMICS

Coherent Case

- Multiconfiguration Time-Dependent Hartree Approach

$$\Psi(x, Q_1, Q_2, \ldots; t) = \sum_{j_0 j_1 \ldots} A_{j_0 j_1 j_2 \ldots j_N}(t)\, \phi_{j_0}(x;t)\phi_{j_1}(Q_1;t)\ldots\phi_{j_N}(Q_N;t)$$

- Frenkel-Dirac variational principle
- coupled equations for coefficients $A_j(t)$ and single particle functions $\phi_j(t)$

Dissipative Case

- Quantum Master Equation in Markov approximation

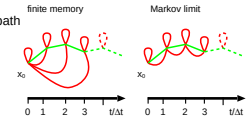
$$\frac{\partial}{\partial t}\rho(t) = \left[-i\mathcal{L} - \mathcal{R}\right]\rho(t)$$

$\mathcal{L}$: Liouville superoperator
$\mathcal{R}$: relaxation superoperator
→ spectral densities

- Path integral approach

$$\rho(x_N^+, x_N^-; t_N) = \int dx_0^+ \ldots dx_{N-1}^+ \rho(x_0^+, x_0^-; t_0)\, I(x_0^\pm, \ldots, x_N^\pm; \Delta t) \prod_{j=1}^{N} K(x_j^\pm, x_{j-1}^\pm)$$

- mapping to single reaction coordinate plus bath
- free propagator $K(x_j^\pm, x_{j-1}^\pm)$
- influence functional $I(x_0^\pm, \ldots, x_N^\pm; \Delta t)$
- iterative tensor propagator scheme



INFRARED SPECTROSCOPY

Response function formalism

$$P(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^\infty dT_3 dT_2 dT_1 E(t-T_3)E(t-T_3-T_2)E(t-T_3-T_2-T_1)\, R^{(3)}(T_3, T_2, T_1)$$

- third-order dipole correlation function

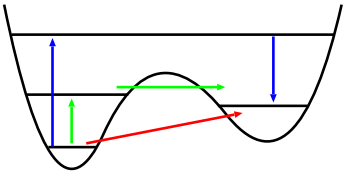
$$R^{(3)}(T_3, T_2, T_1) = \mathrm{Tr}\{\mu\, \mathcal{G}(T_3)\,|\,\mu, \mathcal{G}(T_2)\,|\,\mu, \mathcal{G}(T_1)\,|\,\mu, \rho_{\mathrm{eq}}]]]\}$$

- density matrix evolution with propagator $\mathcal{G}(t)$ in state representation
- phase matching conditions

→ Infrared pump-probe and two-dimensional spectroscopy

LASER CONTROL

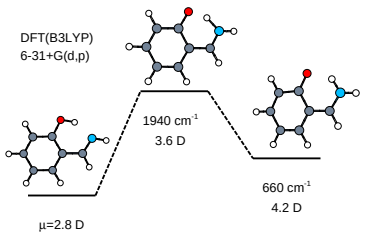
scenarios
- above barrier pump-dump
- tunneling or direct transition
- pre-excitation + tunneling or direct transition



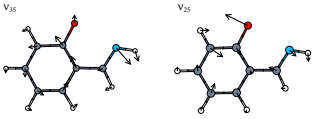
MODEL SYSTEMS

PMME in condensed phase

Proton transfer in Salicylaldimine (SA)



- strongly coupled modes



ω = 337 cm^{-1}
$\Delta E_{\mathrm{isomp}}(R_{OH}$=1.1A) = 45 cm^{-1}

ω = 861 cm^{-1}
$\Delta E_{\mathrm{isomp}}(R_{OH}$=1.1A) = 265 cm^{-1}

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