# *Ab initio molecular tier model for vibrational quantum dynamics*

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On 3/24-25/2017 @ RIKEN AICS (Kobe)

"International workshop on numerical methods and simulations for materials design and strongly correlated quantum matters"

# Collaborators

- Gerhard Stock
(Freiburg Univ.)
  - Tier model
  - Dynamic effect
on perturbation

- John E. Straub
(Boston Univ.)
  - Time-dependent
perturbation
  - Applications to
biomolecules

- Kiyoshi Yagi
(RIKEN)
  - Anharmonic
coefficient
calculations
  - VSCF/VCI
calculations

- Hiroto Kikuchi
(Nippon Medical School)
  - Enzymatic reactions
- Toshiya Takami   (Oita Univ.)
  - Controlling quantum dynamics
- Motoyuki Shiga (JAEA)
  - Quantum string method

**Alexander von Humboldt**
Stiftung / Foundation

科研費
K A K E N H I

# Contents

- Motivation: Why quantum dynamics in (bio)molecules?
  - Recent spectroscopic studies
  - Recent theoretical development
  - Our previous work
- Molecular tier model
  - "Economical" quantum modeling
  - Implementation
  - Applications: Three isomers of acetylbenzonitrile
- Summary
- Controlling quantum mechanical systems

# Why quantum dynamics in (bio)molecules?

- Harmonic approximation is sometimes enough
  - Classical and quantum completely agree each other
- There are residual anharmonic effects
  - Frequency shift
  - Energy flow (transfer)
- Bond vibrations (should) have quantum character
  - $k_B T$ ~ 200 cm-1

acetylbenzonitrile

ω ~ 2000 cm-1

ω ~ 3000 cm-1
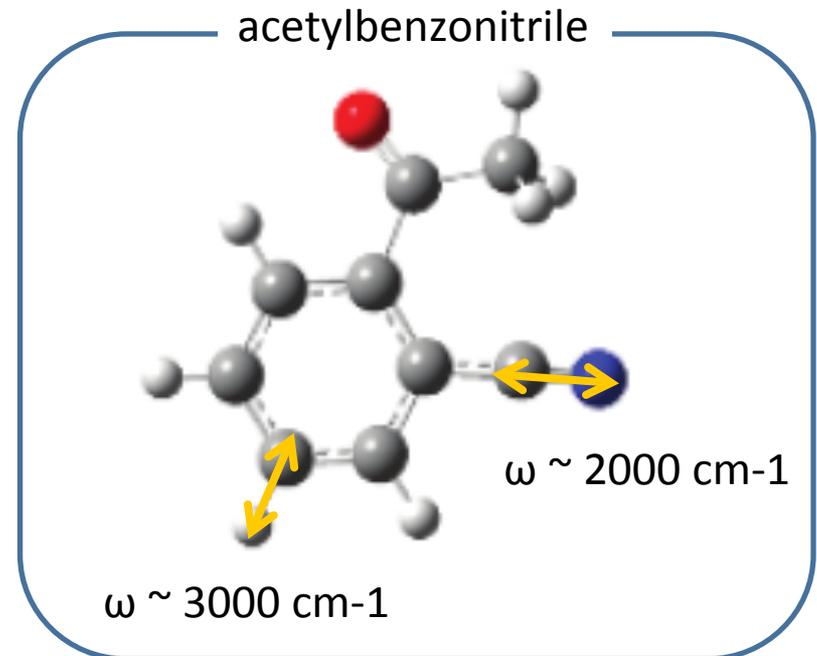
$$\frac{\hbar\omega}{k_B T} > 1$$ : Quantum behavior

$$\frac{\hbar\omega}{k_B T} < 1$$ : Classical behavior

# Recent advance in spectroscopy

>>> Vibrational energy flow experiment <<<

Isotopically labelled pump-probe experiment

Dual-frequency 2D-IR experiment
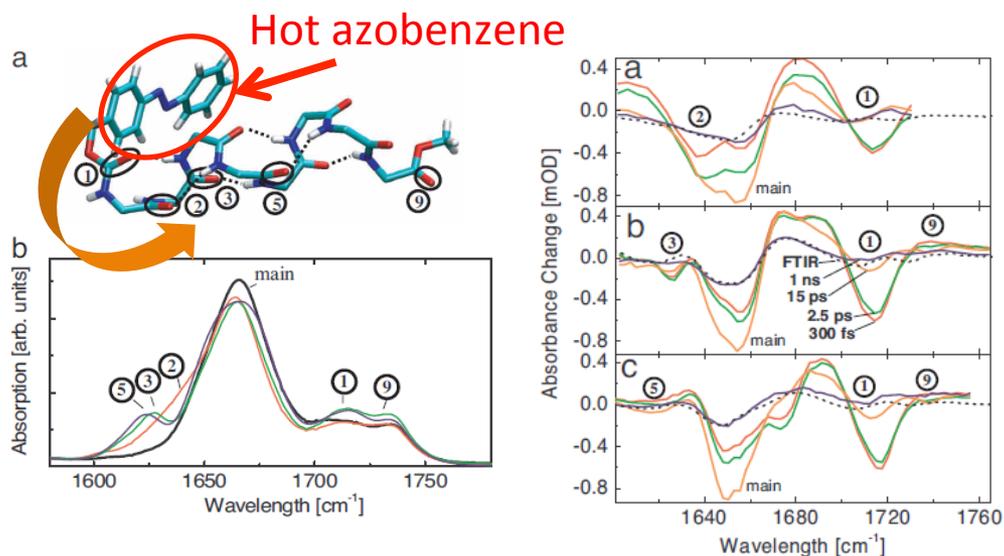


Botan, Backus, Pfister, Moretto, Crisma, Toniolo,
Nguyen, Stock, Hamm, PNAS **104**, 12749 (2007).
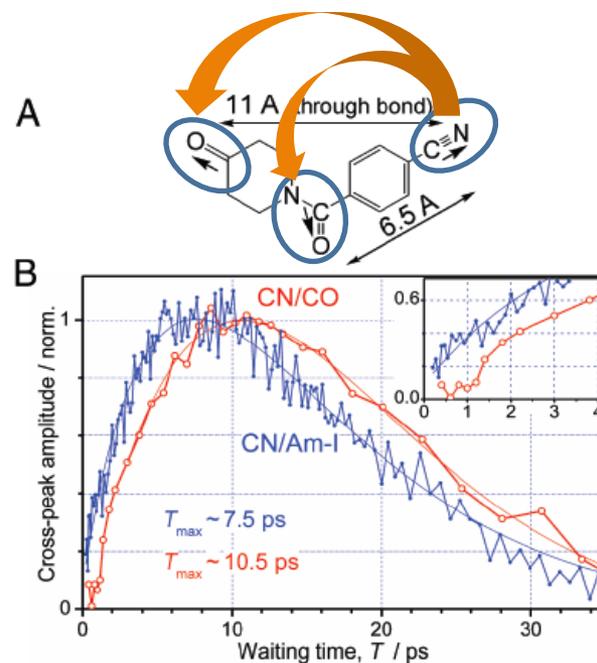
Rubtsov, Acc. Chem. Res. **42**, 1385 (2009).

# Further experiment on energy flow

Henrike M. Müller-Werkmeister, Yun-Liang Li, Eliza-Beth W. Lerch, Damien Bigourd, Jens Bredenbeck
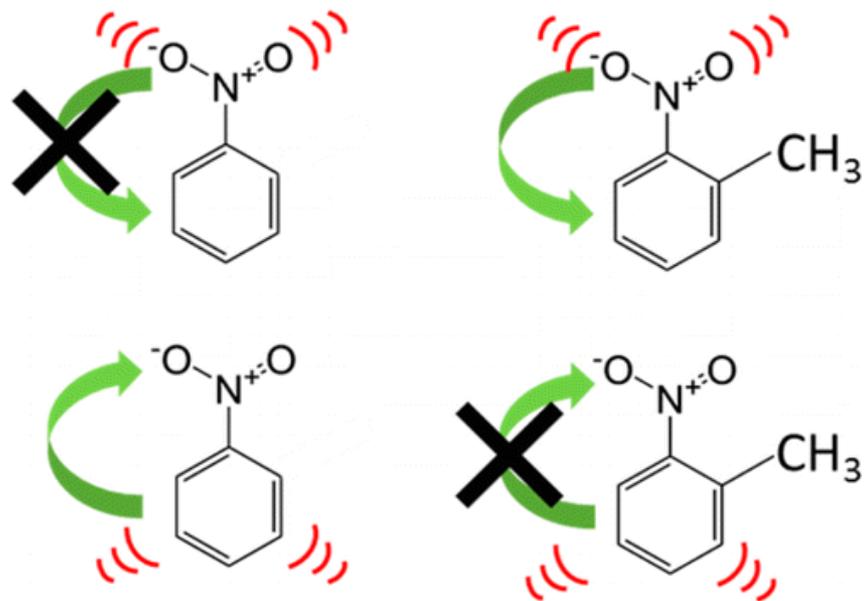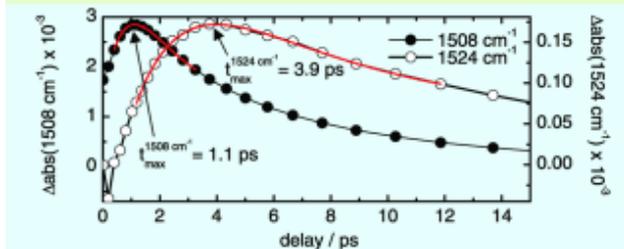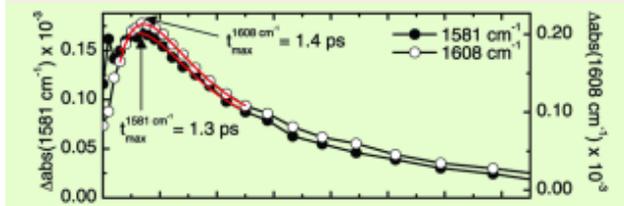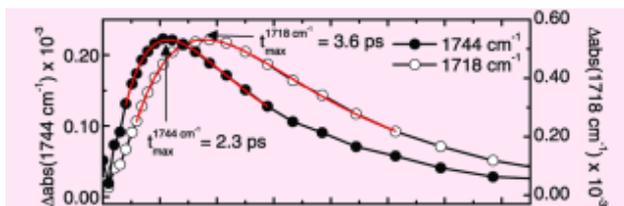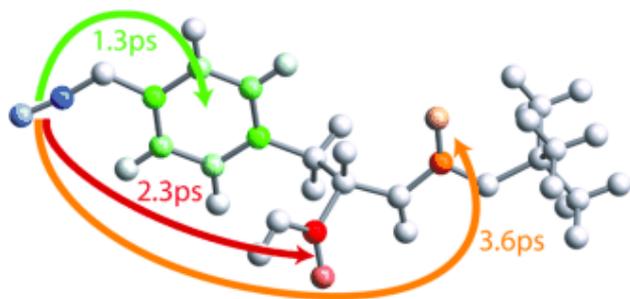
# Energy flow in molecular wire



Molecule

L    R

$j_q$

(a)

$h\nu$

(b)



(a) Waiting time / ps

$v = 1440 \pm 200$ m/s

$R_0 = 14.6 \pm 0.4$ Å

$T_{max}$ / ps    $I_{max}$

CH5-a    CH10-a    CH15-a

Chain length / Å

(b)

CH3-s    6 Å =>
0.42 ps

CH5-a    9 Å => 0.63 ps

N₃

CH10-a    16.5 Å => 1.15 ps

N₃

CH10-s    16.5 Å => 1.15 ps

N₃

CH15-a    24 Å => 1.7 ps

N₃

Ballistic transport of heat (phonon)
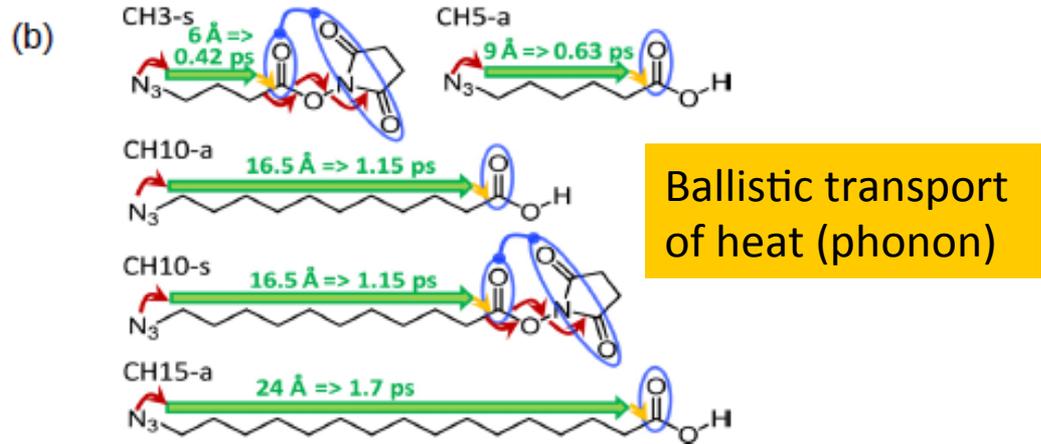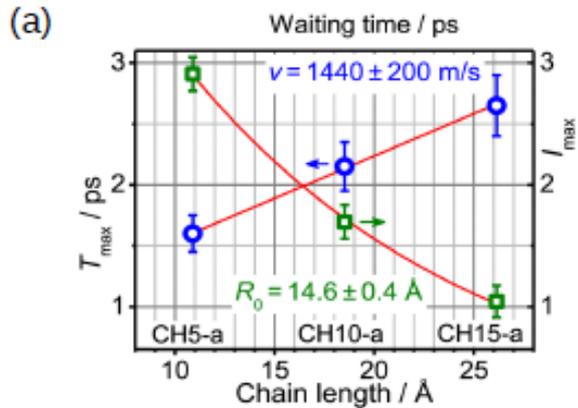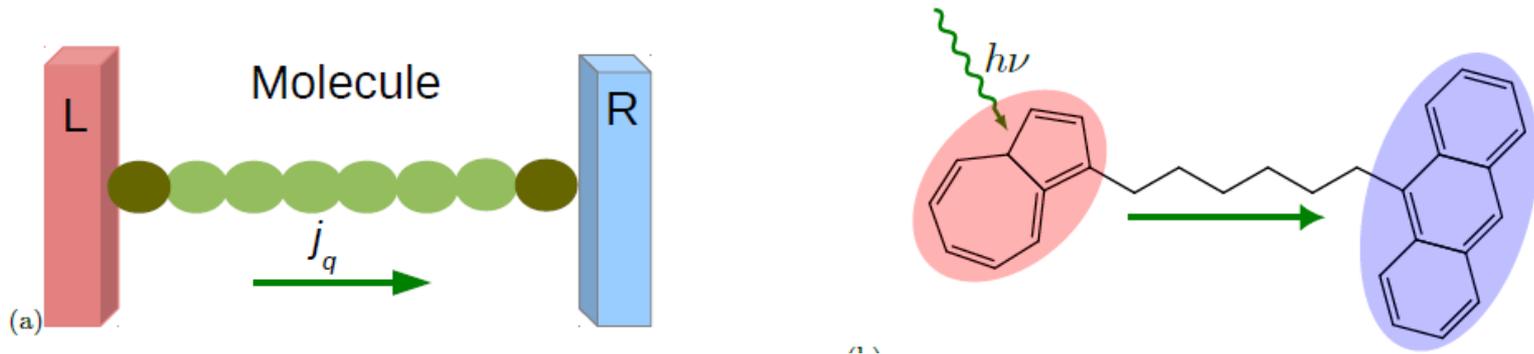
D. Segal and B. K. Agarwalla
Vibrational Heat Transport in Molecular Junctions
Annu. Rev. Phys. Chem. 2016. 67, 185-209.

# Vibration affects electron transfer
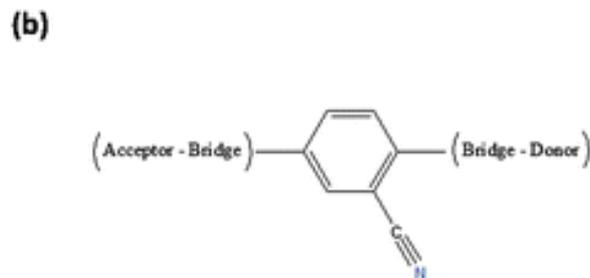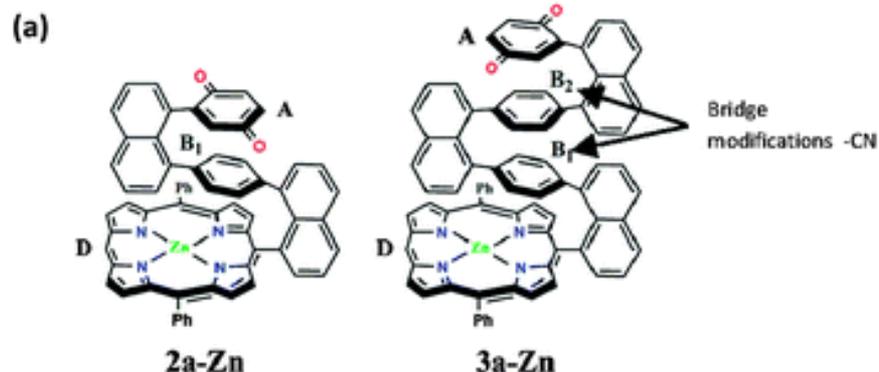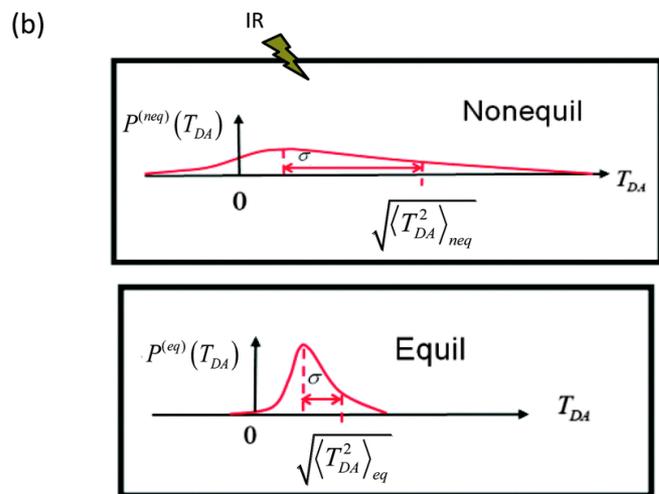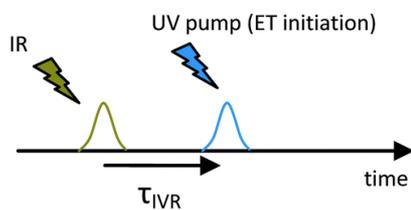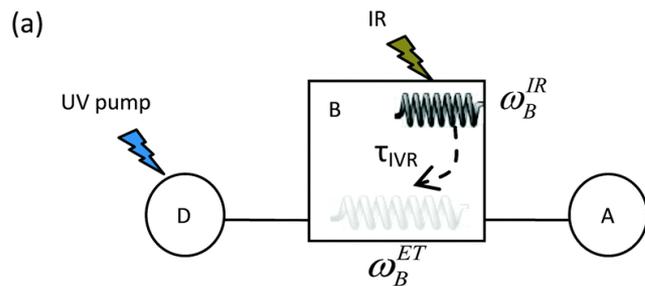


P. Antoniou, Z. Ma, P. Zhang, D. N. Beratan, and S. S. Skourtis, Phys. Chem. Chem. Phys. 17 (2015) 30854-30866

# Energy flow in a protein



Cytochrome c

# Recent theoretical development
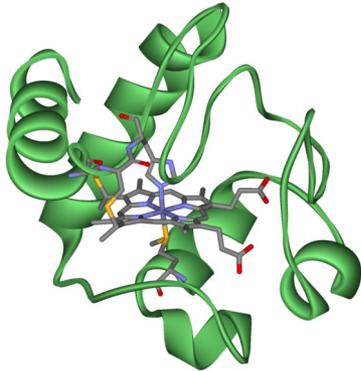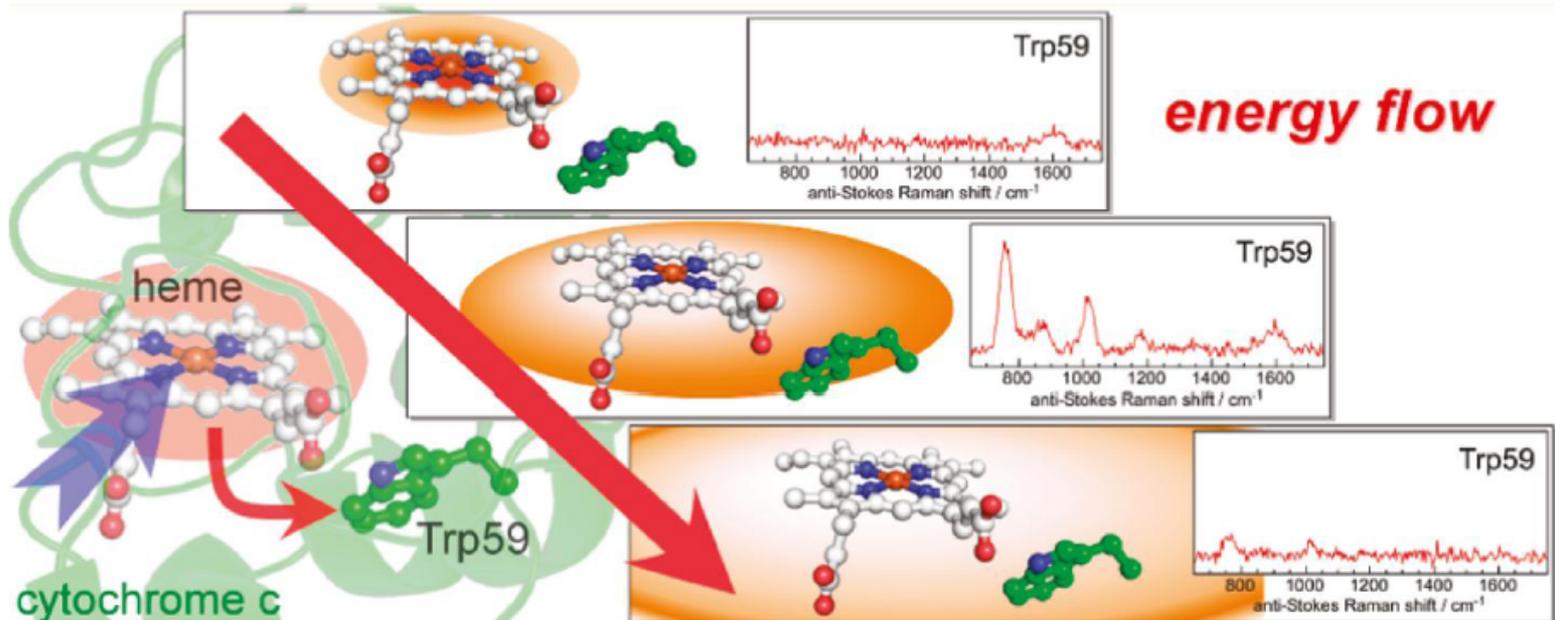
# Notice!

- I only consider quantum dynamics of molecular vibrations
  - Not electrons
    - Dynamics on an <span style="color:red">electronically ground state</span>
    - No nonadiabatic dynamics
  - No reaction (bond breaking or bond forming)
  - No conformational change
    - Vibrations around <span style="color:red">a single stable point</span> (basin)
- But it is still difficult!

# Basic strategy for quantum dynamics

- Represent a Hamiltonian and a wavefunction using some "basis" functions
- Solve the linear simultaneous equation (Schrodinger eq.) as an initial value problem
- If the basis function is good, the convergence is obtained for large number of basis functions
- Exponential wall for the degree of freedom!

$$\left| \Psi(t) \right\rangle = \sum_a C_a(t) \left| \phi_a \right\rangle$$

$$H_{ab} = \left\langle \phi_a \left| H \right| \phi_b \right\rangle$$
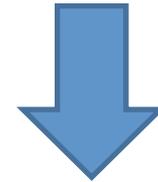
$$i\hbar \frac{\partial}{\partial t} \left| \Psi(t) \right\rangle = H \left| \Psi(t) \right\rangle$$

$$i\hbar \frac{\partial}{\partial t} C_a(t) = \sum_b H_{ab} C_b(t)$$

$$\left| \phi_a \right\rangle = \left| \varphi_{i_1} \right\rangle \left| \varphi_{i_2} \right\rangle \left| \varphi_{i_3} \right\rangle \cdots \left| \varphi_{i_N} \right\rangle$$

# VSCF/VCI method

K. Yagi:
Sindo code

- Clever way to select the basis functions

- Borrowing the concept from quantum chemistry calculation
  - Hartree method

- Integral for the mean potential is time-consuming
  - There are approximate ways to deal with it
  - N-mode representation

- Configuration interaction (CI) is applied for vibration
  - So called VCI

$$\Psi_{\mathbf{n}}^{\text{VSCF}} = \prod_{i=1}^{f} \phi_{n_i}^{(i)}(Q_i),$$

$$\left[ -\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \left\langle \prod_{j\neq i} \phi_{n_j}^{(j)} | V | \prod_{j\neq i} \phi_{n_j}^{(j)} \right\rangle \right] \phi_{n_i}^{(i)} = \epsilon_{n_i}^{(i)} \phi_{n_i}^{(i)}.$$

Configuration Interaction

$$\Psi_{\mathbf{n}}^{\text{VCI}} = \sum_{\mathbf{m}} C_{\mathbf{mn}} \Psi_{\mathbf{m}}^{\text{VSCF}}.$$

$$|\Psi(t)\rangle = \sum_{\mathbf{n}} \langle \Psi_{\mathbf{n}}^{\text{VCI}} | \Psi(0)\rangle e^{-iE_{\mathbf{n}}t/\hbar} |\Psi_{\mathbf{n}}^{\text{VCI}}\rangle.$$

H. Fujisaki, **K. Yagi**, K. Hirao, J.E. Straub, Chem. Phys. Lett. 443 (2007) 6

# Methods based on Path integral

## Single particle



**Classical Mechanics**

Classical Particle

**Quantum Mechanical Path Integral**

Ring Polymer

## Many particles



$x_1$
$x_2$
$x_3$
$x_4$
$\frac{1}{P}V(|\mathbf{x}_i - \mathbf{x}'_i|)$
$x'_1$
$x'_2$
$x'_3$
$x'_4$
$\frac{1}{2}m\omega_P^2(\mathbf{x}_{i+1} - \mathbf{x}_i)^2$

**"Isomorphism** between quantum theory and classical statistical mechanics of polyatomic fluids"

$$Z = \int d\mathbf{q}d\mathbf{p} \cdot \exp[-\beta H_{eff}]$$

$$H_{eff} = \left(\sum_{i=1}^{P}\frac{p_i^2}{2m_i}\right) + V_{eff}$$

$$V_{eff} = \sum_{i=1}^{P}\left[\frac{mP}{2\beta^2\hbar^2}(q_i - q_{i+1})^2 + \frac{1}{P}V(q_i)\right]$$
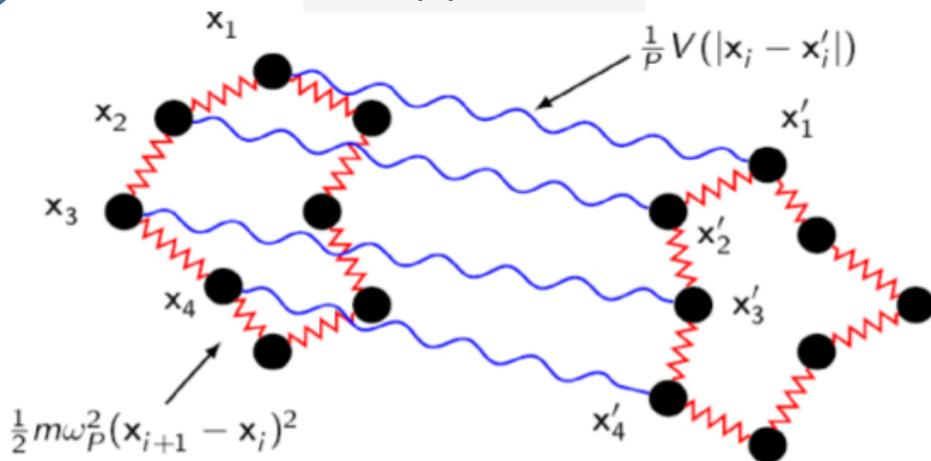
David Chandler and Peter G. Wolynes
J. Chem. Phys. 74, 4078 (1981)

# Quantum mechanical free energy

**Centroid density: Probability for finding the state around** $(\mathbf{c}_1, \cdots, \mathbf{c}_N)$

$$\rho(\mathbf{c}_1, \cdots, \mathbf{c}_N) = \left\langle \prod_{i=1}^{N} \delta\left(\frac{1}{P}\sum_{s=1}^{P}\mathbf{r}_{i,s} - \mathbf{c}_i\right) \right\rangle_{PI}$$

$$= Z^{-1} \lim_{P\to\infty} \left[ \prod_{i=1}^{N} \left(\frac{m_i P}{2\pi\beta\hbar^2}\right)^{\frac{3P}{2}} \int d\mathbf{r}_{i,1} \int d\mathbf{r}_{i,2} \cdots \int d\mathbf{r}_{i,P} \right] \exp\left(-\beta V_{eff}[\mathbf{r}]\right) \left[ \prod_{i=1}^{N} \delta\left(\frac{1}{P}\sum_{s=1}^{P}\mathbf{r}_{i,s} - \mathbf{c}_i\right) \right]$$

**Definition:** <span style="color:red">**Free energy for centroid variables**</span>

$$A(\mathbf{c}_1, \cdots, \mathbf{c}_N) \equiv \beta^{-1} \log \rho(\mathbf{c}_1, \cdots, \mathbf{c}_N)$$

**Free energy gradient ~ effective force (potential of mean force)**

$$\frac{\partial A}{\partial \mathbf{c}_i} = \frac{\left\langle \left[\frac{1}{P}\sum_{s=1}^{P}\frac{\partial V(\mathbf{r}_{i,s})}{\partial \mathbf{r}_{i,s}}\right] \prod_{i=1}^{N} \delta\left(\frac{1}{P}\sum_{s=1}^{P}\mathbf{r}_{i,s} - \mathbf{c}_i\right) \right\rangle_{PI}}{\left\langle \prod_{i=1}^{N} \delta\left(\frac{1}{P}\sum_{s=1}^{P}\mathbf{r}_{i,s} - \mathbf{c}_i\right) \right\rangle_{PI}} = \left\langle \left[\frac{1}{P}\sum_{s=1}^{P}\frac{\partial V(\mathbf{r}_{i,s})}{\partial \mathbf{r}_{i,s}}\right] \right\rangle_{\mathbf{c}_j = \frac{1}{P}\sum_{s=1}^{P}\mathbf{r}_{j,s} \text{ for all } j}$$

# Computational conditions

**System:  $N_2H_5^-$ ion,  RIMP2/SV(P)***

- **Bead #: $P$         =   1, 4, 8, 16, 32**

- **Polymer #: $L$     =    41**

- **Step #: $N_{step}$     =   500**

- **Cycle #: $M_{cycle}$ =    40**

*cf.*  **# of ab initio calculation: 32*41*500*40 = 26,240,000**

For ab initio calculations, we used *Turbomole*

[R. Ahlrichs, M. Baer, M. Haeser, H. Horn and Ch. Koelmel, *Chem. Phys. Lett.* 162, 165 (1989)]
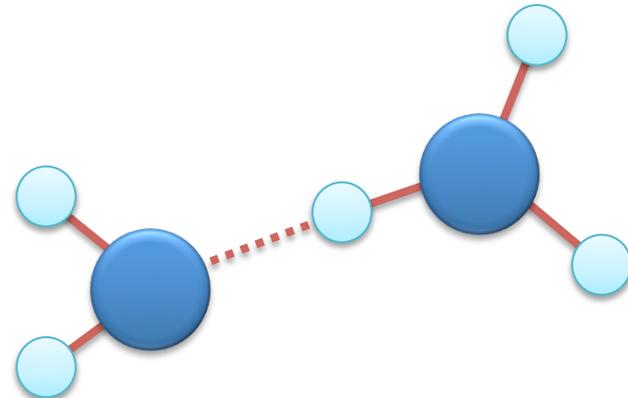
# Quantum string method
## (centroid intrinsic reaction coordinate)

M. Shiga

$$Q^{\text{Cent}} = \frac{1}{P} \sum_{S=1}^{P} Q^{(S)}$$

"Centroid variables" are used as coarse-grained variables

Quantum particle
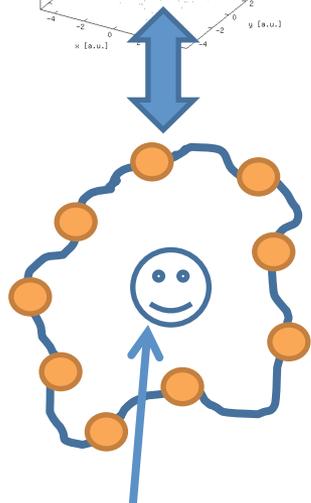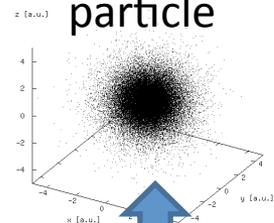
Small & solid atoms : classical coordinates
Large & transparent: quantum centroids

Centroid
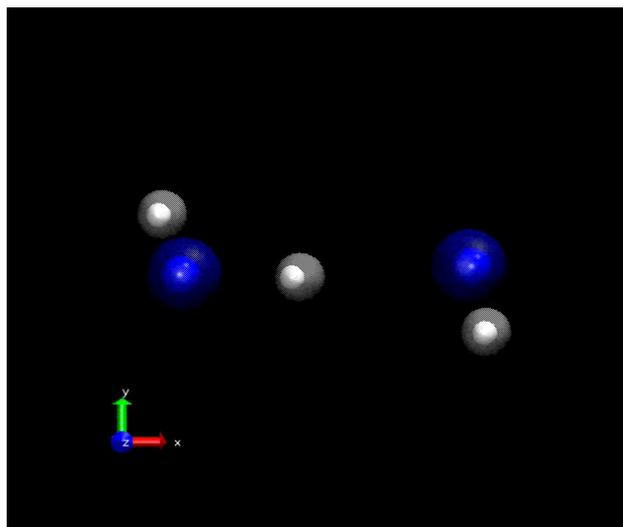
deprotonated ammonia dimer, $N_2H_5^-$

M. Shiga and H. Fujisaki,
J. Chem. Phys. 136, 184103 (2012)



classical $N_2H_5^-$
quantum $N_2H_5^-$

Quantum effects



kinetic T
potential V
entropy -TS
total
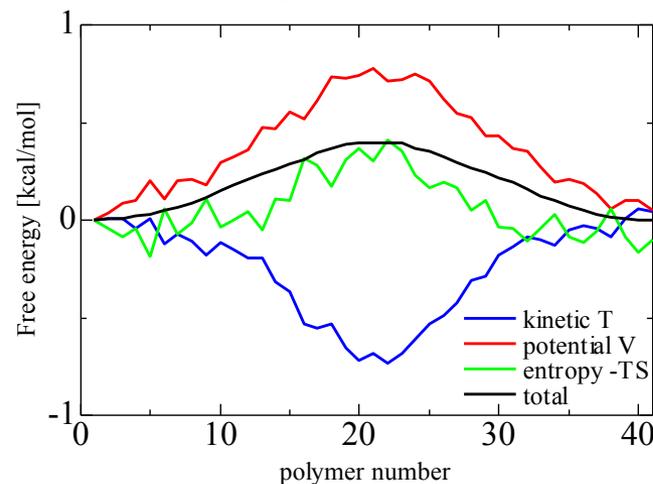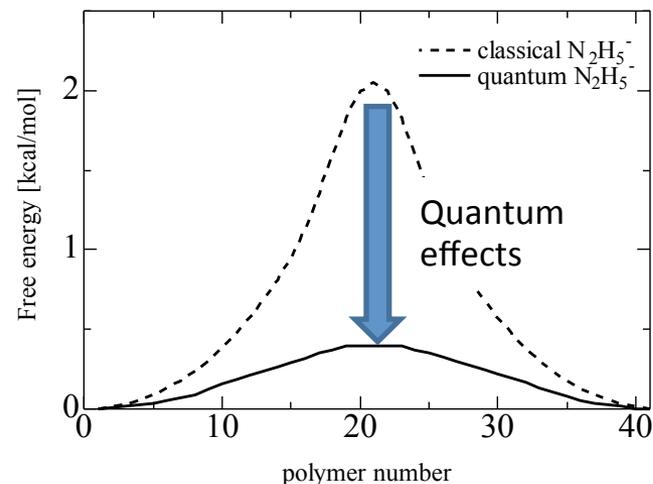
# Still difficult to treat quantum dynamics within path integral formalism

- Simplification of the model
  - System bilinearly coupled to a harmonic bath
- Perturbative expansion
- Semiclassical approaches
  - Use of bunches of classical trajectories with complex weight
  - Negative sign problem
    - Convergence is very slow
- Quasi-classical method
  - Neglect of phase information

$$\exp\left(iS/\hbar\right)$$

$t_A$

$t_B$

A

B

Any trajectory is possible!

$\exp\left(iS/\hbar\right)$

Only classical trajectory is allowed

$\exp\left(iS/\hbar\right)$

Only classical trajectory is allowed
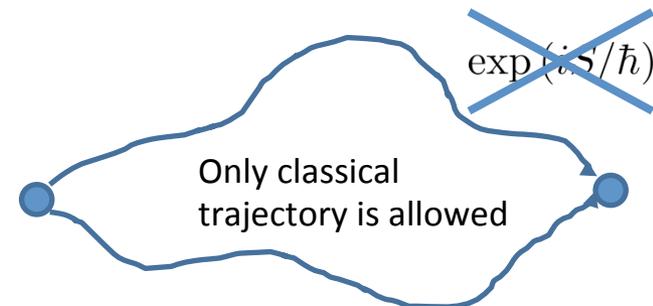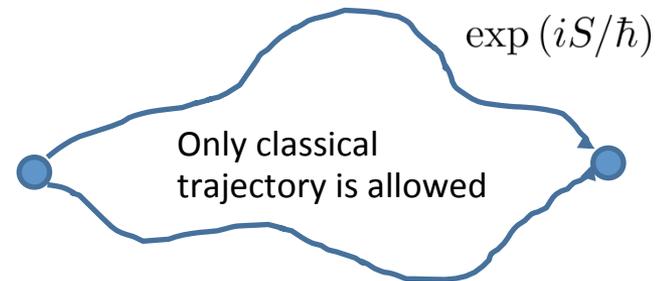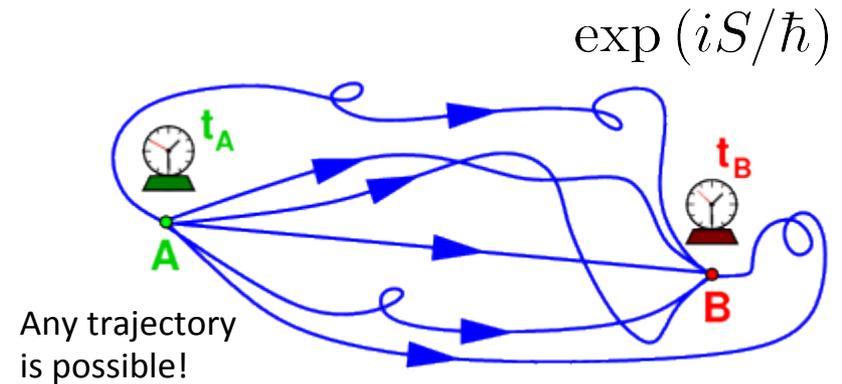
# Our previous attempts (2005~2010)

- **Chemical detail in vibrational energy relaxation**
  - Calculate anharmonicity of force fields or ab initio potential and regard them as perturbation
  - We used simply time-dependent perturbation theory
    - Short-time approximation
    - Some dynamic extension is possible
      - H. Fujisaki, G. Stock, J. Chem. Phys. 129, 134110 (2008)

$$H = H_S + H_B + V$$

$$H_S = \frac{p_S^2}{2} + \frac{\omega_S^2}{2} q_S^2$$

$$H_B = \sum_k \left( \frac{p_k^2}{2} + \frac{\omega_k^2}{2} q_k^2 \right)$$

Normal mode approx.

$$V = q_S F$$

$$F = \sum_{k,l} C_{Skl} q_k q_l$$

Anharmonic coupling

Reduced density matrix

$$\rho_{11}^S(t) \approx \exp[-s(t)]$$

$$s(t) = \frac{\hbar}{2} \sum_{k,l} \frac{(C_{Skl})^2}{\omega_S \omega_k \omega_l} \frac{1 - \cos(\omega_S - \omega_k - \omega_l)t}{(\omega_S - \omega_k - \omega_l)^2}$$

Fujisaki, Zhang, Straub, J.Chem.Phys.**124** (2006) 144910
Fujisaki, Straub, J. Phys. Chem. B **111** (2007) 12017.

# Applications: porphyrin + imizadole

QM potential: UB3LYP/6-31G(d)
Ground state: spin quintuplet



$v_4$

$v_7$

imizadole

Simulation data +
Exponential fit

Myoglobin

(A) $v_4$

(B) $v_7$
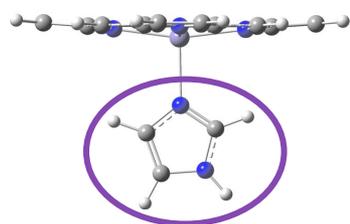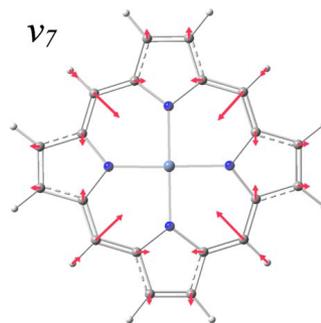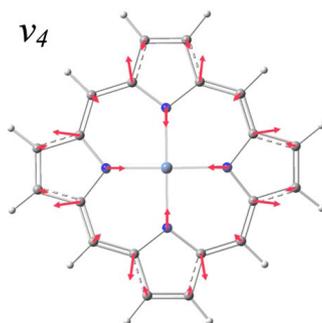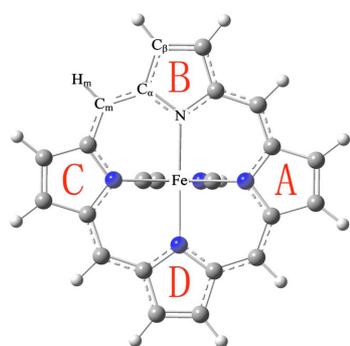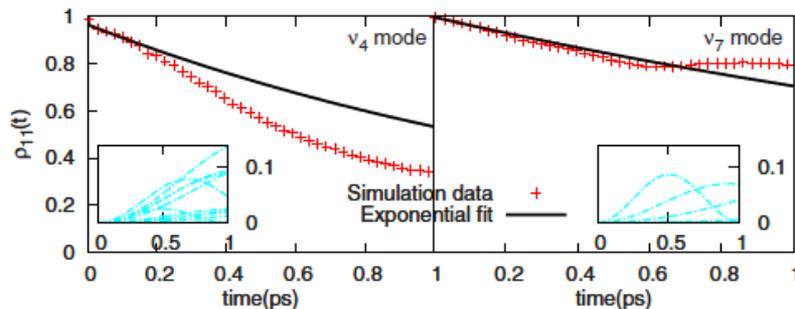
Zhang, Fujisaki, Straub, J. Chem. Phys. **130**, 025102 (2009).
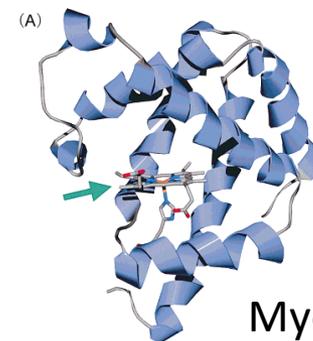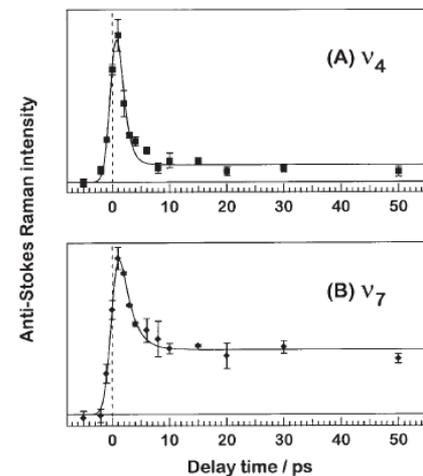
Mizutani, Kitagawa,
Chem. Rec. **1**, 258 (2001).

# What is lacking in previous studies?

- Just truncated ("model") molecule
  - Not "real" system!
  - We first should try QM/MM potential construction

- **Perturbation theory ~ short-time approximation**
  - Longer timescale is not captured
  - Power law decay
  - Energy flow into lower frequency modes
    - Functionally important motions
  - Quantum-classical correpondence?



porphyrin

Myoglobin
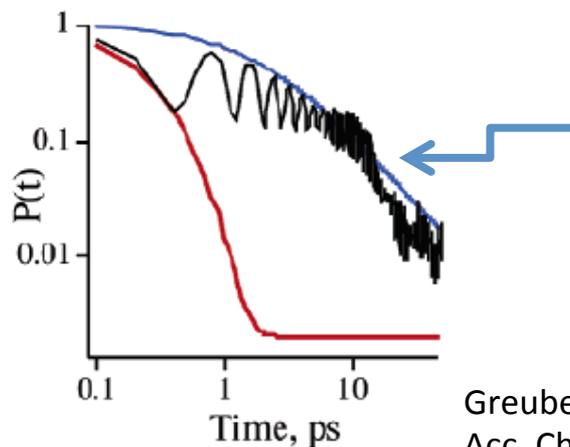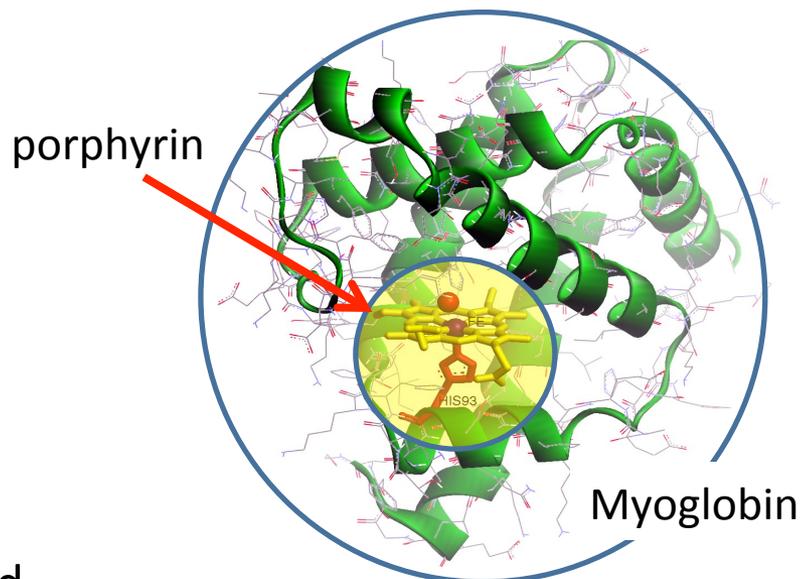


Highly excited bond vibration of methanol
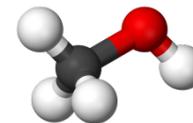
Greubele-Wolynes, Acc. Chem. Res. **37** (2004) 261

# Tier model for quantum systems

- "Graph theory" of quantum mechanics
  - Node: state (e.g. normal mode basis set)
  - Link (edge): interaction (e.g. due to anharmonic coupling)
- History
  - Seminal work
    - Sibert, Reinhardt, Hynes (1984)
  - Multi-photon excitation
    - Tietz, Chu (1981)
    - Chang, Wyatt (1985)
  - Energy flow problem for highly excited states
    - Logan, Wolynes (1990)
    - Stuchebrukhov, Marcus (1993)
    - Gruebele (1995~)
    - Leitner, Wolynes (1998~)

$$|i\rangle\rangle = |n_1^{(i)}, n_2^{(i)}, \ldots n_m^{(i)}\rangle$$

Parent node

1st tier

2nd tier

3rd tier

Anharmonic coupling

# Implementation (1)

Bowman @ Emory
Kiyoshi Yagi @ RIKEN
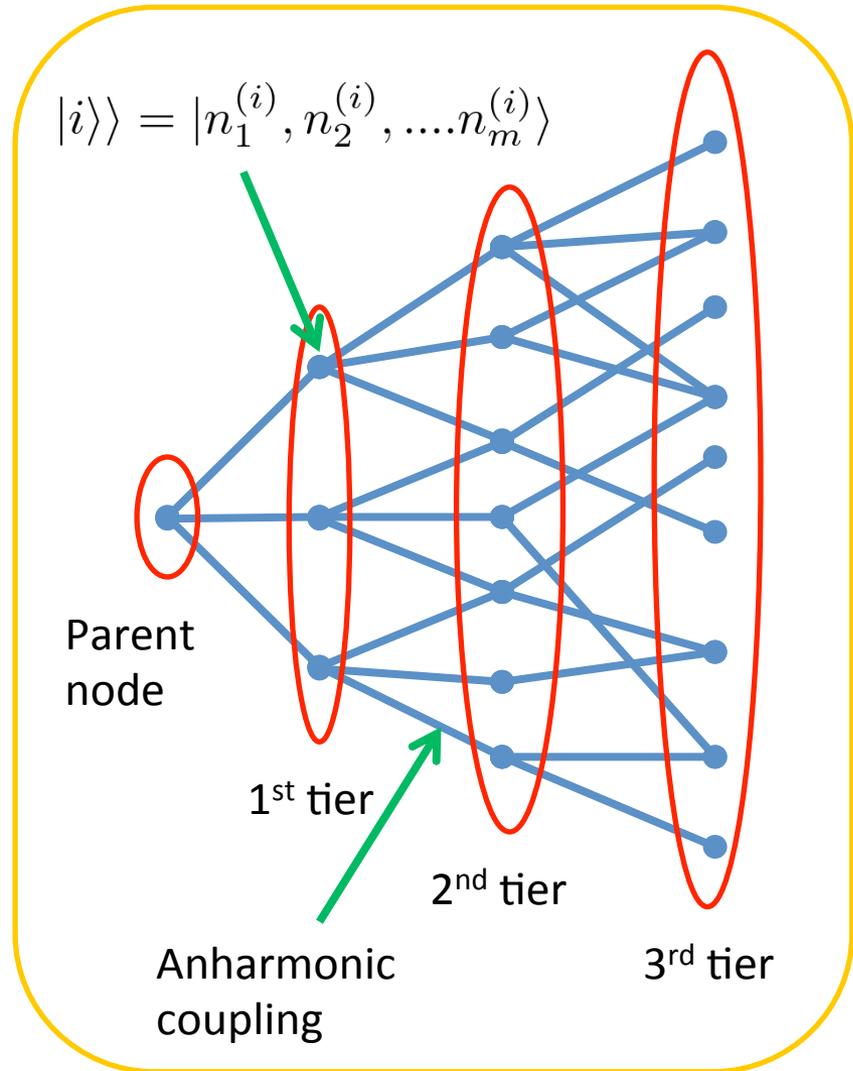
- Hamiltonian
  - Normal mode representation + anharmonic corrections

$$H = H_0 + V,$$

$$H_0 = \sum_k \left( \frac{p_k^2}{2} + \frac{\omega_k^2}{2} q_k^2 \right),$$

$$V = \frac{1}{3!} \sum_{ijk} C_{ijk} q_i q_j q_k$$

$$+ \frac{1}{4!} \sum_{ijkl} C_{ijkl} q_i q_j q_k q_l$$

  - We decide the mode space (lowest ~ highest modes)
  - Lowest modes are dangerous!

- 3 mode representation

$$V = V^{2\mathrm{MR}} + V^{3\mathrm{MR}},$$

$$V^{2\mathrm{MR}} = \frac{1}{2} \sum_{i \neq j} \left( C_{ijj} q_i q_j^2 + \frac{1}{3} C_{ijjj} q_i q_j^3 \right)$$

$$+ \frac{1}{4} \sum_{i<j} C_{iijj} q_i^2 q_j^2,$$

$$V^{3\mathrm{MR}} = \sum_{i<j<k} C_{ijk} q_i q_j q_k + \frac{1}{2} \sum_{i \neq j<k} C_{iijk} q_i^2 q_j q_k$$

  - Potential energy surface is calculated by quantum chemisty software (Gaussian)
  - We obtain the anharmonic coefficient using numerical differentiation of the potential or hessian matrix

# Implementation (2)

- State selection
  - For $q_i q_j^2$ term    Tier index
  $$\left|\cdots, n_i, \cdots, n_j, \cdots\right\rangle_\alpha$$
  $$\Rightarrow \left|\cdots, n_i + a, \cdots, n_j + b, \cdots\right\rangle_\beta$$
  integer
  - Resonance condition
  $$\text{If } \left|E_\alpha - E_\beta\right| < E_{th}$$
  $$\left(E_\alpha \simeq \sum_k \hbar\omega_k n_k\right)$$
  Then we accept the state
  $$\left|\cdots, n_i + a, \cdots, n_j + b, \cdots\right\rangle_\beta$$
  if it is not included in other tiers!
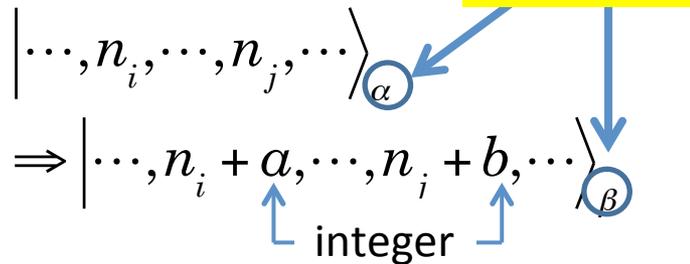
- Matrix elements
  - For $q_i q_j^2$ term
  $$\left\langle n_i \left| q_i \right| n_i + a\right\rangle \left\langle n_j \left| q_j^2 \right| n_j + b\right\rangle$$
  - Sum up over all terms if the Fermi resonance parameter
  $$\left|\frac{\left\langle \alpha |V| \beta\right\rangle}{E_\alpha - E_\beta}\right| > f_{th}$$
  - is above a threshold!

- Quantum dynamics
  - Leap-frog method
    - Simple, stable and efficient
  $$\left|\phi(t + \Delta t)\right\rangle = \left|\phi(t - \Delta t)\right\rangle + \frac{2\Delta t}{i\hbar} H \left|\phi(t)\right\rangle$$

# Leap-frog method

- Classical leap-frog method

$$x(t + \Delta t) = x(t) + v(t + \Delta t / 2)\Delta t,$$

$$v(t + 3\Delta t / 2) = v(t + \Delta t / 2) + f(x(t + \Delta t))\Delta t$$
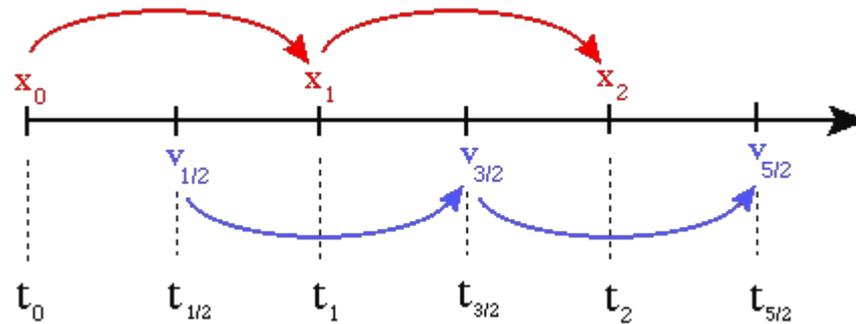


- Quantum leap-frog method

$$\left| \phi(t + \Delta t) \right\rangle = \left| \phi(t - \Delta t) \right\rangle + \frac{2\Delta t}{i\hbar} H \left| \phi(t) \right\rangle$$

Energy transfer observed with pump-probe and 2D-IR spectroscopy

Igor Rubtsov

for Acetylbenzonitrile (AcPhCN)

orth    meta

para
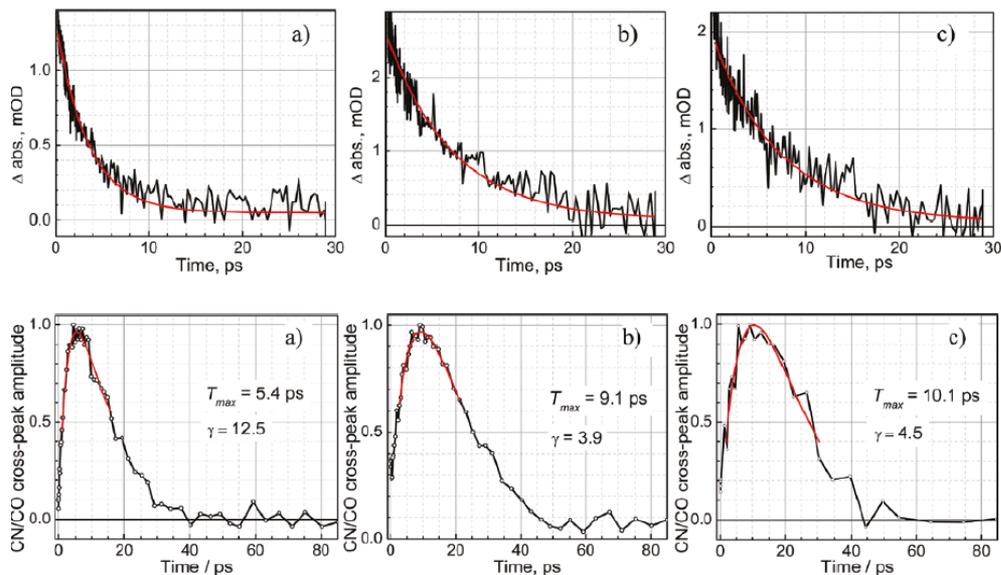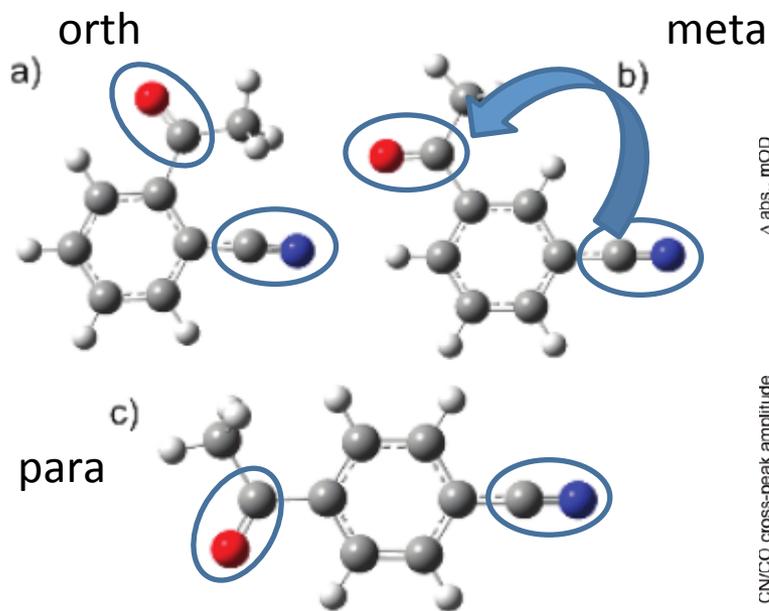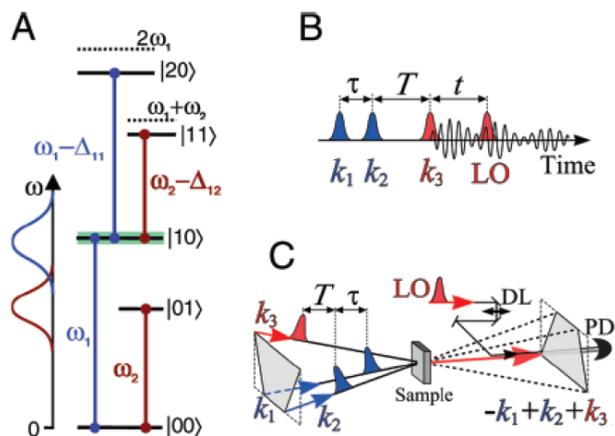
Kasyanenko, Tesar, Rubtsov, Burin, Rubtsov, J. Phys. Chem. B **115**, 11063 (2011).

# What to monitor? Normal mode energy and kinetic energy

- Normal mode energy of a molecule
  - High frequency: localized
  - Low frequency: delocalized

$$E_k(t) = \frac{1}{2} \langle \Psi(t) | \underbrace{(p_k^2 + \omega_k^2 q_k^2)} | \Psi(t) \rangle$$

Normal mode energy x 2

- Kinetic energy of an atom
  - "Thermo-meter"
  - Conversion between normal mode and kinetic energy is needed

$$E_{CO}^{kin}(t) = \frac{1}{2} \sum_{i,k} \mathcal{U}_{ik}^2 \, \hbar \omega_k n_k(t),$$

$\mathcal{U}_{ik}$ : orthogonal matrix for diagonalizing the hessian matrix

$n_k(t)$ : population on mode $k$ at time $t$

# Approximate calculation of quantum kinetic energy

- Normal mode conversion

$$P_i = \sum_k \mathscr{U}_{ik} p_k,$$

$$Q_i - Q_i^{eq} = \sum_k \mathscr{U}_{ik} q_k,$$

**Exact form**

$$E_i^{kin} = \frac{P_i^2}{2} = \frac{1}{2} \sum_{k,l} \mathscr{U}_{ik} \mathscr{U}_{il} \langle p_k p_l \rangle,$$

$$\langle p_k p_l \rangle = \sum_{\alpha,\beta} C_\alpha^*(t) C_\beta(t) \langle \alpha | p_k p_l | \beta \rangle.$$
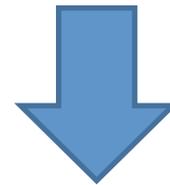
**Approximate form**

$$E_i^{kin} = \frac{1}{2} \sum_k \mathscr{U}_{ik}^2 \sum_\alpha |C_\alpha^*(t)|^2 \langle \alpha | p_k^2 | \alpha \rangle$$

$$= \frac{1}{2} \sum_k \mathscr{U}_{ik}^2 \hbar \omega_k \left( n_k(t) + 1/2 \right),$$

# Technical notes

- Calc. level: B3LYP(6-31G(d,p)) in implicit solvent (chroloform)
  - We can improve a bit more
  - No explicit solvent
- From $11^{th}$ through $47^{th}$ modes are included
  - Modes with less than 200 cm-1 or higher than CN vibrational frequency are excluded
  - Lowest modes are always dangerous for this type of calculations!
- Dimension of the resulting Hamiltonian matrix ~ 10000 (at most)
  - Convergence is checked

- CN harmonic frequency is scaled down according to higher level calculation and experiment
  - Stuchebrukhov, Marcus (1993)
  - Otherwise, oscillatory behavior
- For classical calculation
  - We just solve the Newton equation from an initial condition mimicking the CN mode excitation
  - Other modes initially have thermal energy with 300K
  - A small number of trajectories go out of the basin. Such a trajectory is excluded from the calculation
  - Normal mode energy and kinetic energy are defined to go along with quantum ones

# Numerical result: Convergence check
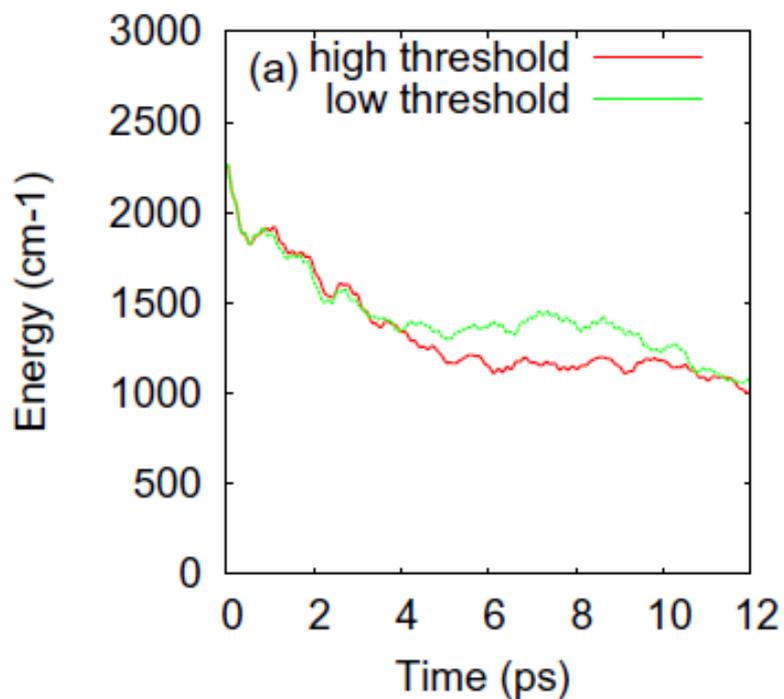


Low threshold: # of state ~ 10000
High threshold: # of state ~ 5000
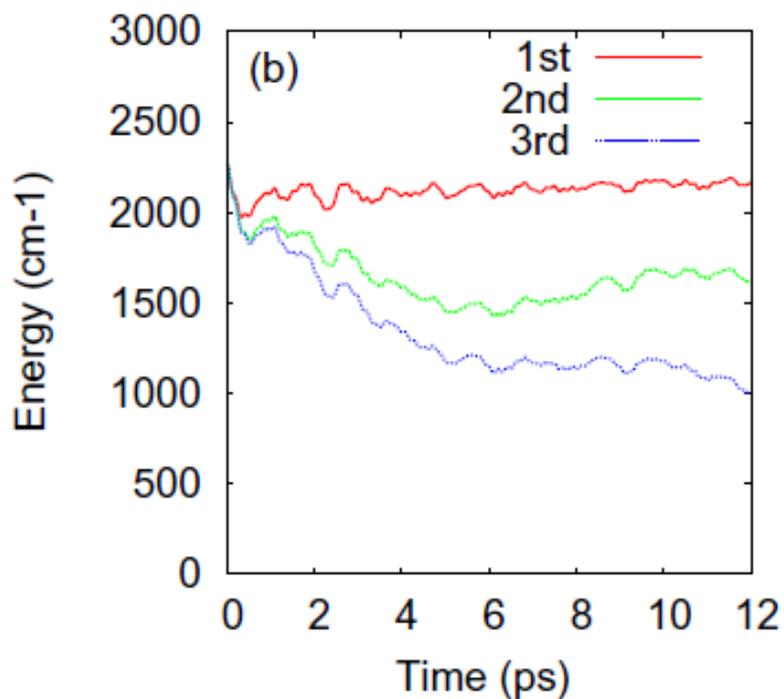
1) Subpicosecond: almost the same
2) $2^{nd}$ tier is not sufficient at all for describing relaxing behavior

H. Fujisaki, K. Yagi, H. Kikuchi, T. Takami, G. Stock, Chem. Phys. 482 (2017) 86.

# Comparison between quantum and classical dynamics
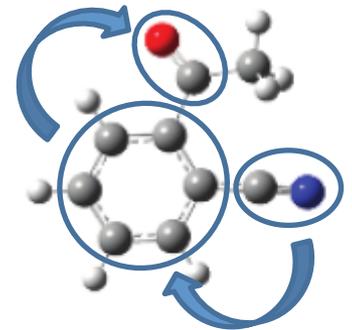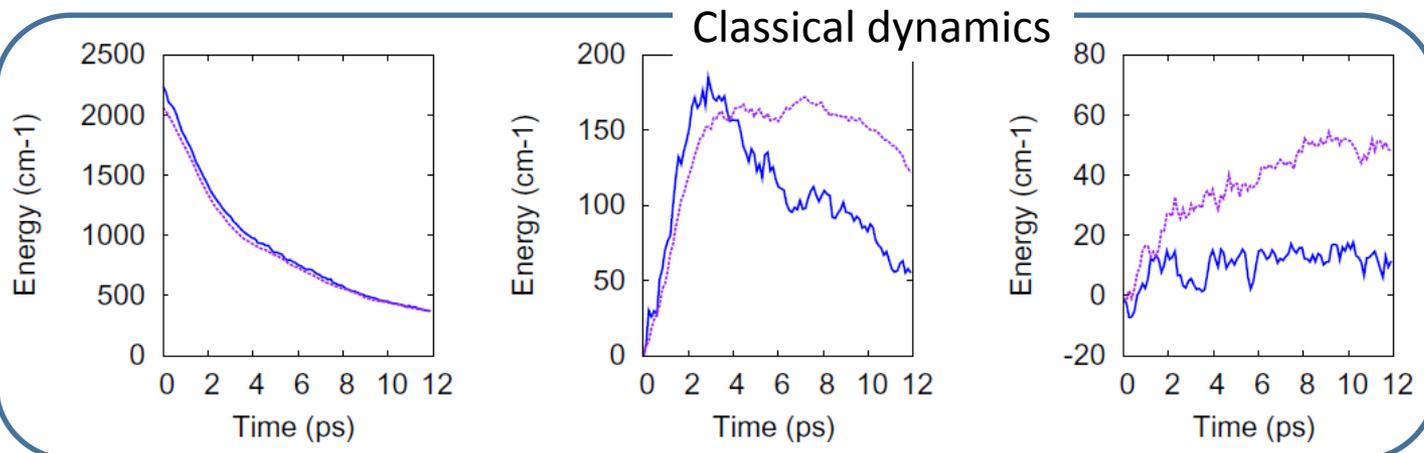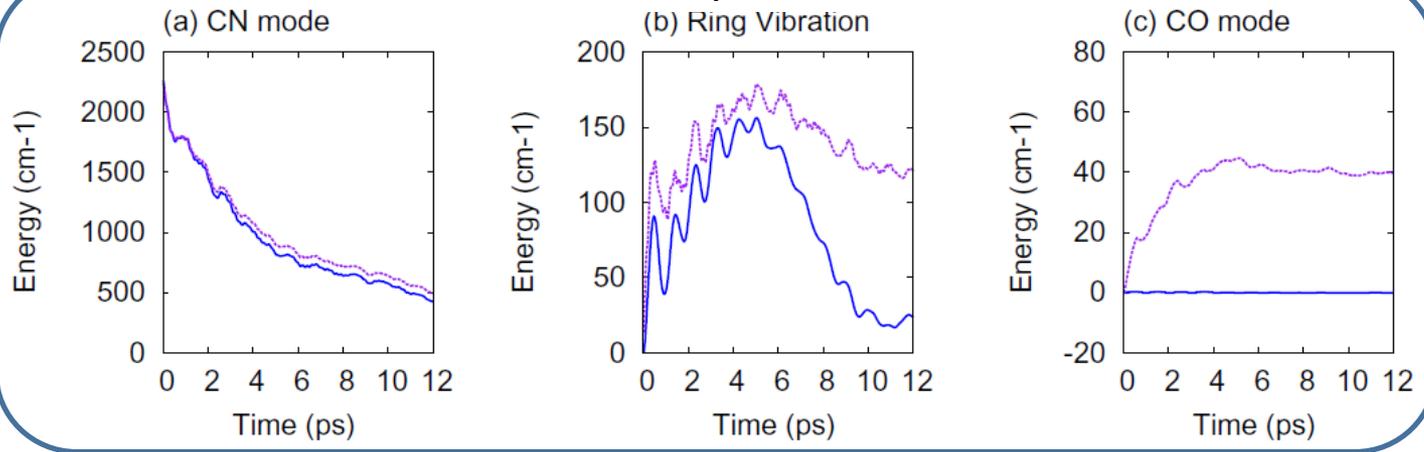
# Energy transfer between CN and CO bonds



(a) Relaxation time ~ 5 ps
In accord with exp.

(b) Rising time ~ 5 ps
Too fast or CO energy is too small (few %)
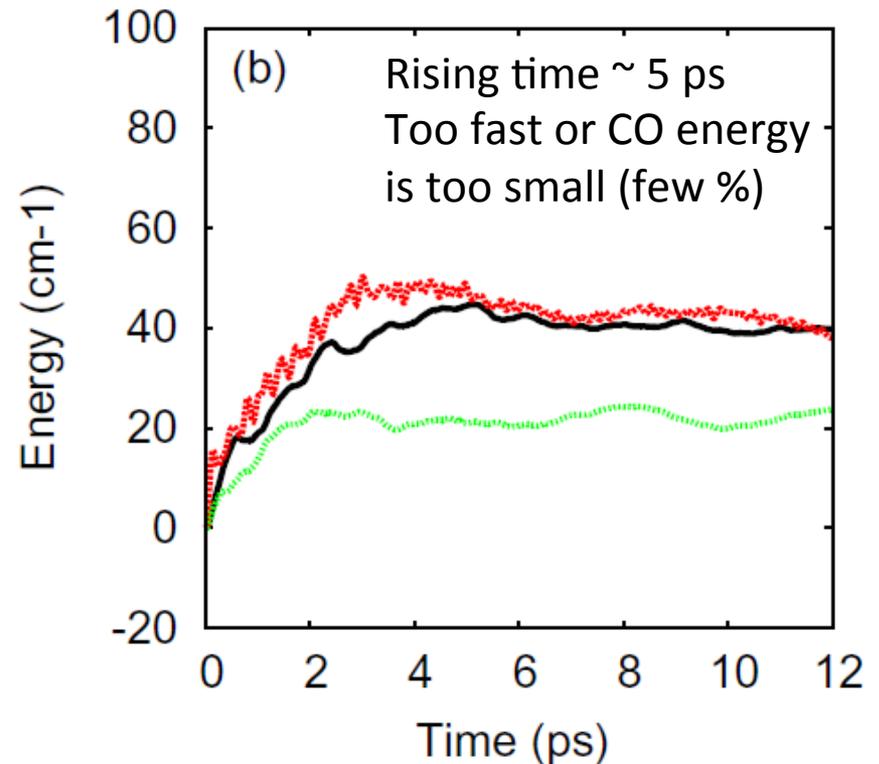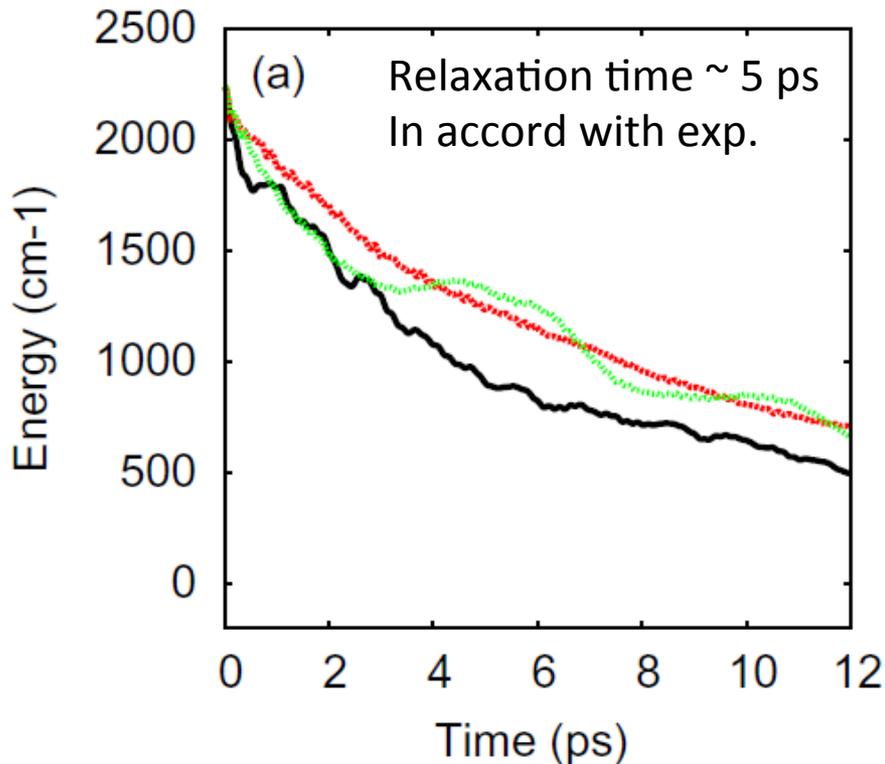
Explicit inclusion of solvent molecules Necessary!

H. Fujisaki, K. Yagi, H. Kikuchi, T. Takami, G. Stock, Chem. Phys. 482 (2017) 86.

# Mode selectivity of quantum energy flow

Red: Quantum energy exchange
Green: Classical energy exchange
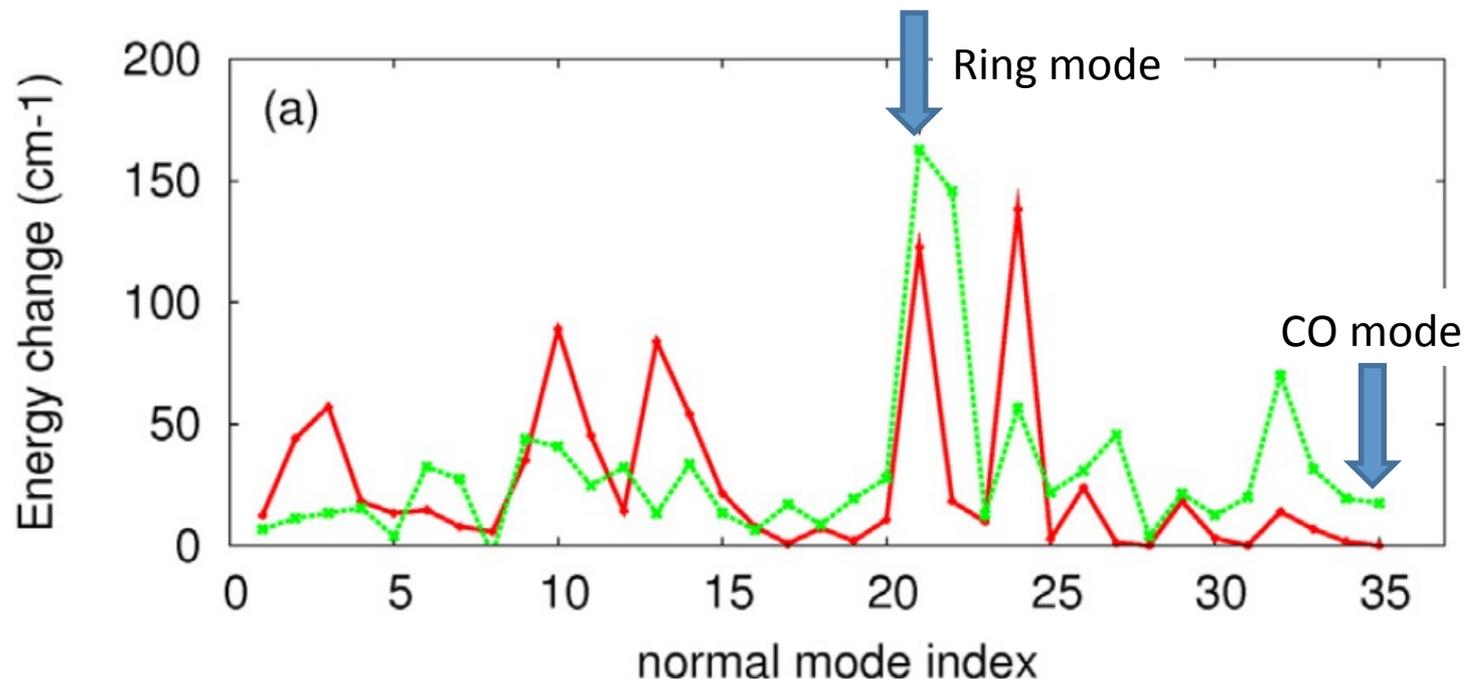
# AcPhCN + chroloform system should be considered

- Generate trajectories using MD code (amber)
- Take snapshots from them
- (Partially?) Optimize the cluster system
- Calculate the frequencies and anharmonic coefficients
- Construct the tier model
- Quantum dynamics calculation
  - Solute-solvent quantum energy transfer
  - Not yet done!
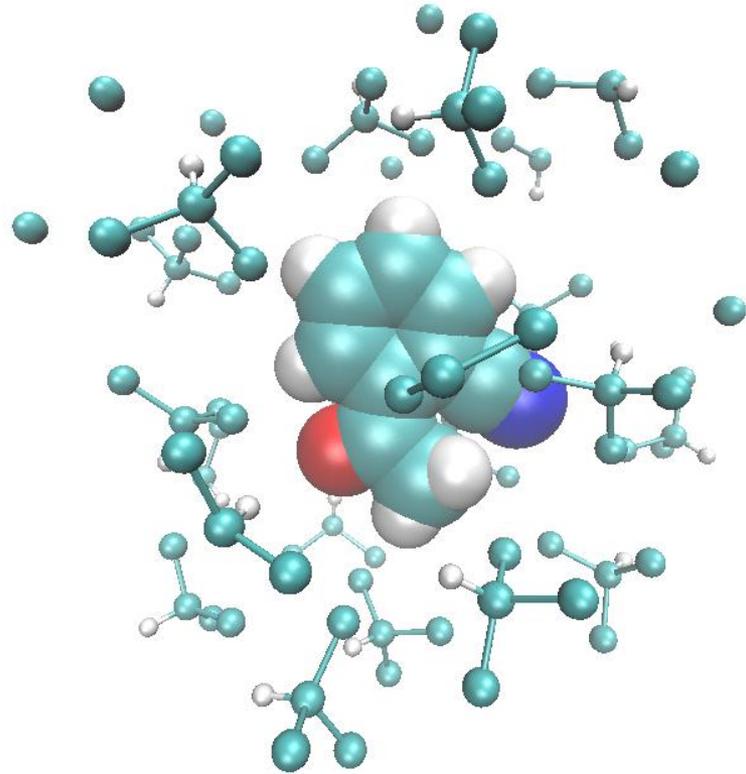
# *N*-methylacetamide + water cluster
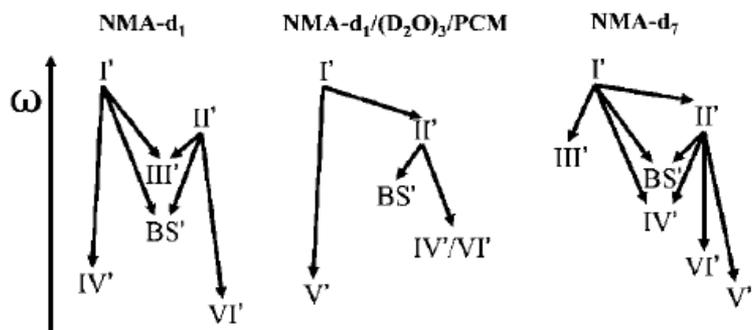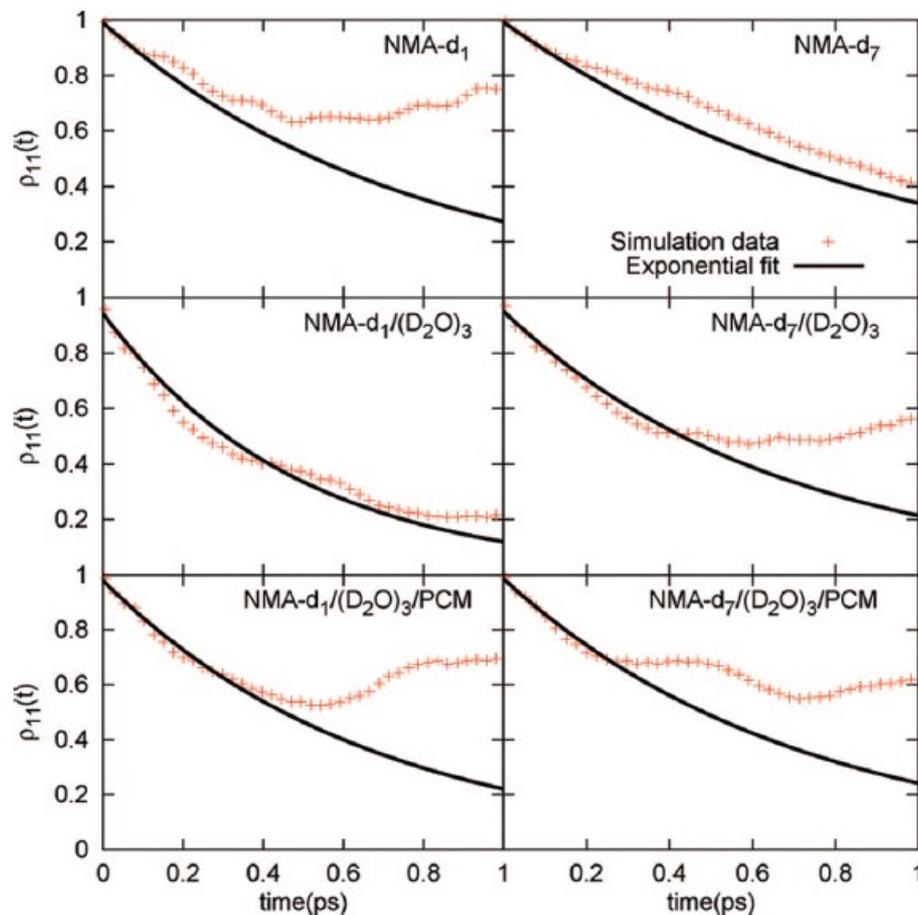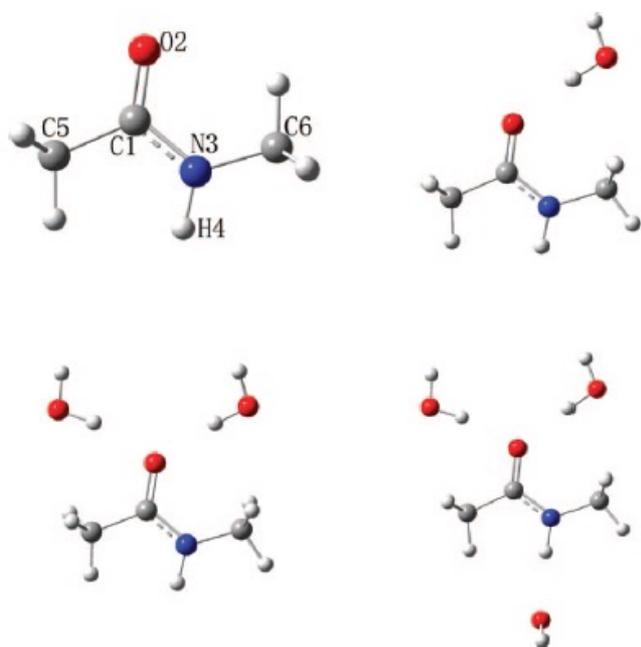
Y. Zhang, H. Fujisaki and J.E. Straub, J. Phys. Chem. A 113, 3051-3060 (2009).

# Summary I

- <span style="color:cyan">Quantum dynamics simulations</span> are needed to understand and interpret recent time-resolved spectroscopic experiments
- To go beyond the previous study using perturbation theory, we developed a molecular tier model with chemical detail
  - Applications to acetylbenzonitrile
  - <span style="color:red">Second and third as well as first tiers are important!</span>
    - <span style="color:darkblue">Simple perturbation approach is not enough for this system</span>
  - <span style="color:red">Partly agrees with Rubtsov's experiment</span>
- Further analysis and refinement is needed
  - To include <span style="color:red">the solvent effects</span>, we need a cluster model
  - <span style="color:red">Multiresolution</span> idea to construct a "cheap" potential for a large molecular system
  - Better ways to construct state space
    - Matrix product state (MPS)?

# Relation to (quantum) chaos

- Highly excited molecules (or nuclei) are <span style="color:red">"quantum chaotic"</span>
  - Classically corresponding dynamics is chaotic
    - Scattered phase space portrait
  - Energy-level statistics well described by Wigner distribution
    - Similar to Random matrix system
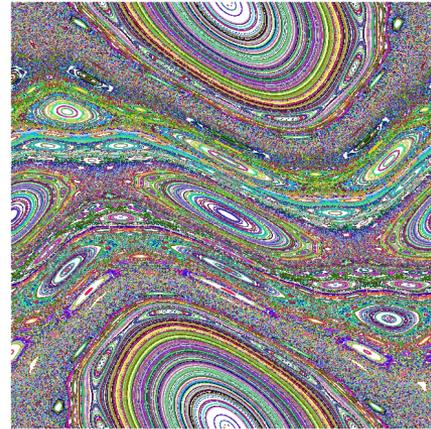
Phase space structure of a kicked rotor (classicalchaos system)

https://sieste.wordpress.com/2012/04/21/phase-space-plot-of-the-kicked-rotor/

Wigner distribution

Nonadiabatic chaos system

H. Fujisaki and K. Takatsuka, Phys. Rev. E 63, 066221 (2001)
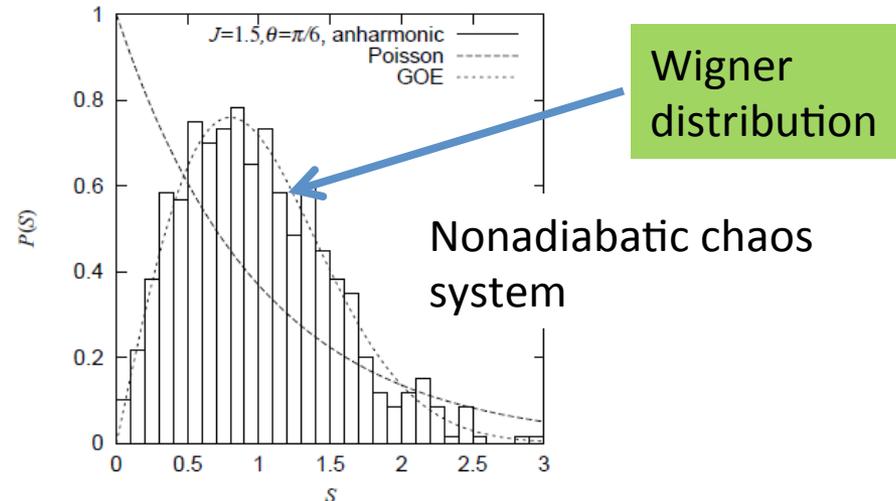
# "Chaos" in atoms and molecules

Chaos-driven dynamics in spin-orbit-coupled atomic gases

Nonadiabatic chaos
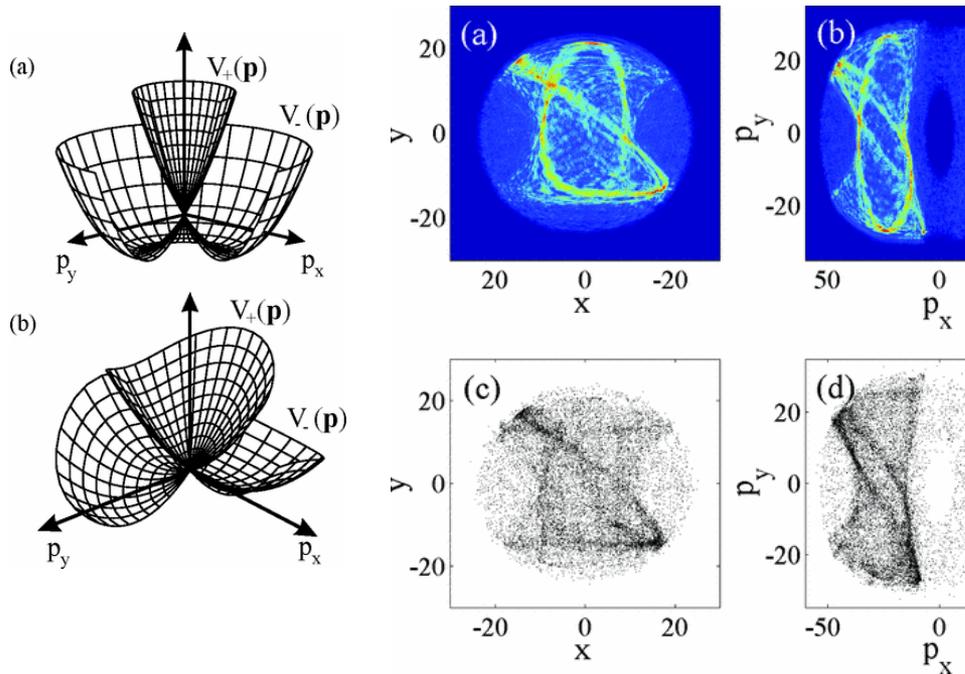


J. Larson, B.M. Anderson, and A. Altland, Phys. Rev. A 87, 013624 (2013)

Nonadiabatic coupling Is strong

intermediate

weak
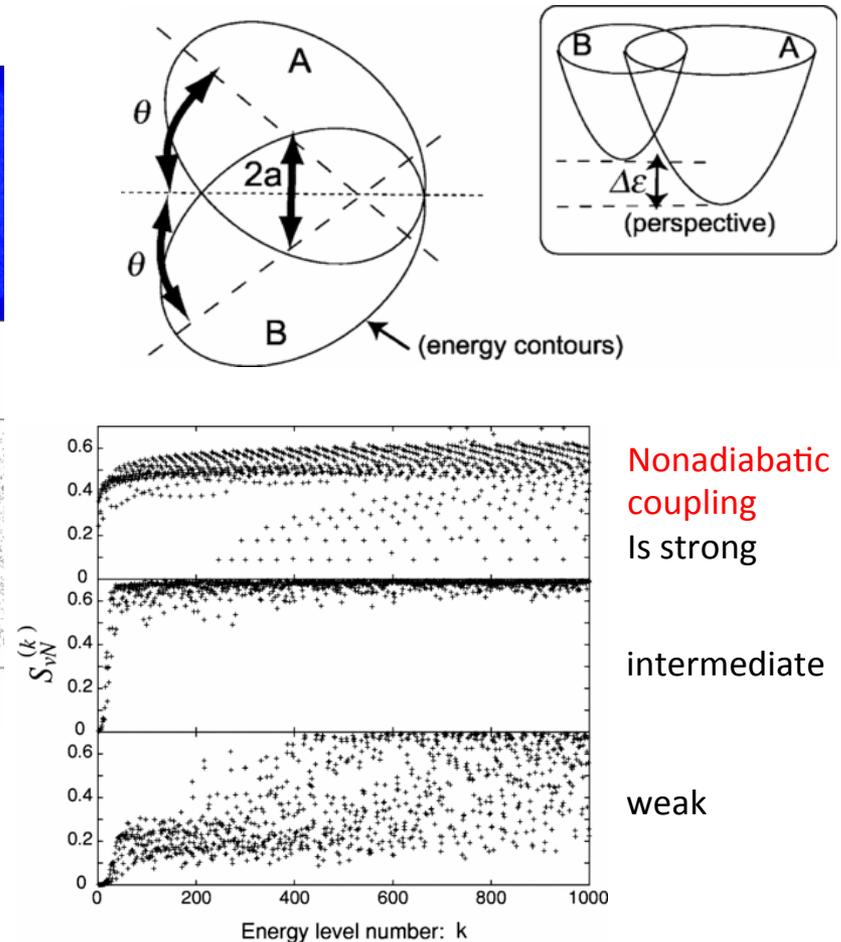
H. Fujisaki, Phys. Rev. A 70, 012313 (2004)

# Controlling quantum dynamics



- Laser shaping technology has been developing in experiment
  - Femtochemistry (Zewail)
  - Modulation of time and frequency component of a laser pulse
- Population inversion
  - Basic concept: π-pulse
  - Rabi oscillation between two quantum states
- General methods for control
  - Genetic algorithm (machine learning)
  - Optimal control theory
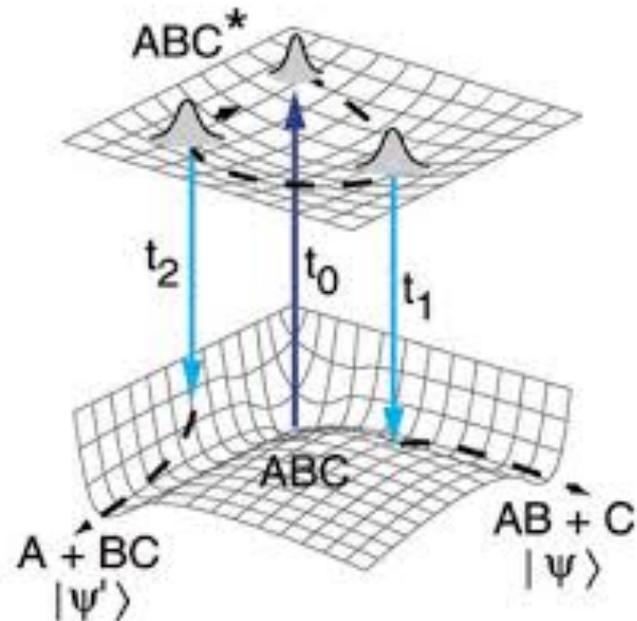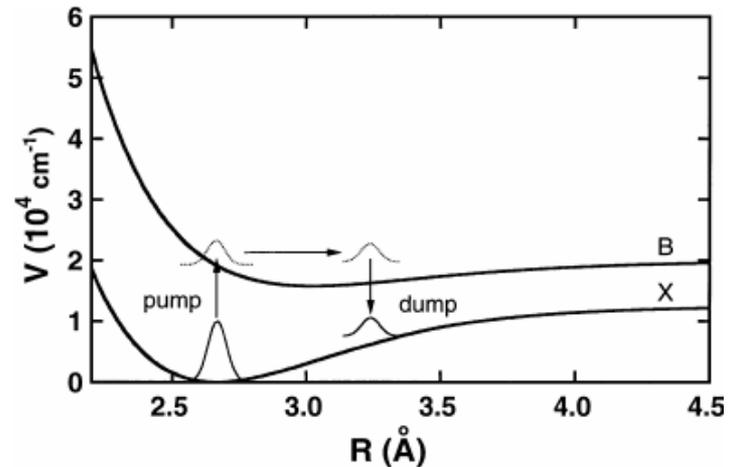
# System and problem to be studied

T. Takami

The Hamiltonian with an external (Laser) field $\varepsilon(t)$:

$$H[\varepsilon(t)] = H_0 + \varepsilon(t)V$$

$H_0$ : unperturbed Hamiltonian of a molecule
$V$ : dipole interaction between molecule and Laser

## Boundary Conditions:

$|\Phi_0\rangle$ : initial state
$|\Phi_T\rangle$ : target state
$T$ : total target time

**Target State**

$2\Delta_d$

Steered by an External Field

**Initial State**

$2\Delta_c$

Energy

## Problem:

Obtain an external field $\varepsilon(t)$
to steer $|\Phi_0\rangle$ at $t = 0$ to $|\Phi_T\rangle$ at $t = T$.
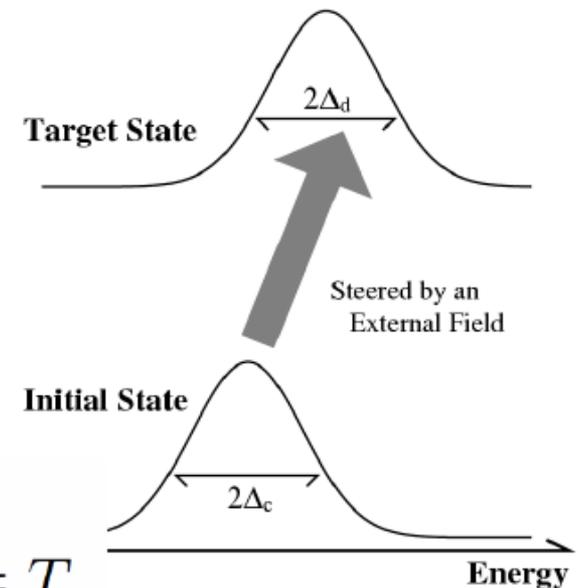
# Optimal control theory (OCT)

T. Takami

In quantum mechanics, we can use the **OCT** to obtain an external field $\varepsilon(t)$ for controlling quantum states[2,5,6,7]. According to the method of Zhu-Botina-Rabitz[7], the external field $\varepsilon(t)$ is obtained by maximizing the functional

$$J(|\phi(t)\rangle, |\chi(t)\rangle, \varepsilon(t)) = |\langle\phi(T)|\varphi_f\rangle|^2$$
$$-\alpha \int_0^T dt\, |\varepsilon(t)|^2 - 2\mathrm{Re}\left[\langle\phi(T)|\varphi_f\rangle \int_0^T dt\, \langle\chi(T)|\frac{\partial}{\partial t} + iH[\varepsilon(t)]\,|\phi(t)\rangle\right] \quad (1)$$

- $T$: final time, $\alpha$: penalty factor, $\varepsilon(t)$: external field
- $|\phi(t)\rangle$, $|\chi(t)\rangle$: quantum states
- Boundary conditions: $|\phi(0)\rangle = |\phi_i\rangle$, $|\chi(T)\rangle = |\phi_f\rangle$

and the expression is

$$\varepsilon(t) = \frac{1}{\alpha\hbar}\mathrm{Im}\left[\langle\phi(t)|\chi(t)\rangle\,\langle\chi(t)|\frac{\partial H(t)}{\partial\varepsilon(t)}|\phi(t)\rangle\right] \quad (2)$$

[6] J. Manz, K. Sundermann, R. de Vivie-Riedle, Chem. Phys. Lett. **290**, 415 (1998).
[7] W. Zhu, J. Botina, and H. Rabitz, J. Chem. Phys. **108**, 1953 (1998).

# A kicked rotor in an external field

T. Takami

Kicked rotor system is widely used in classical and quantum study of chaos. We construct a model of the kicked rotor system interacting with an external field, and show the results by our field.

**Standard map**[12]:

$$p' = p + \frac{K}{T}\sin q, \qquad q' = q + Tp' \qquad (13)$$

Hamiltonian of **Kicked Rotor**:

$$H_{\mathsf{KR}}(K;t) = \frac{1}{2}\hat{p}^2 + \frac{K}{\tau}\cos\hat{q}\sum_n \delta(t - n\tau) \qquad (14)$$

For simplicity, we chose $\hbar = 2\pi M/\tau N$ (**rational**). We introduce an **Interaction Hamiltonian** by

$$H_I(t) = \varepsilon(t)\cos(\hat{q} + \delta_\varepsilon) \qquad (15)$$

and study dynamics of the system

$$H(t) \equiv H_{\mathsf{KR}}(K;t) + H_I(t). \qquad (16)$$
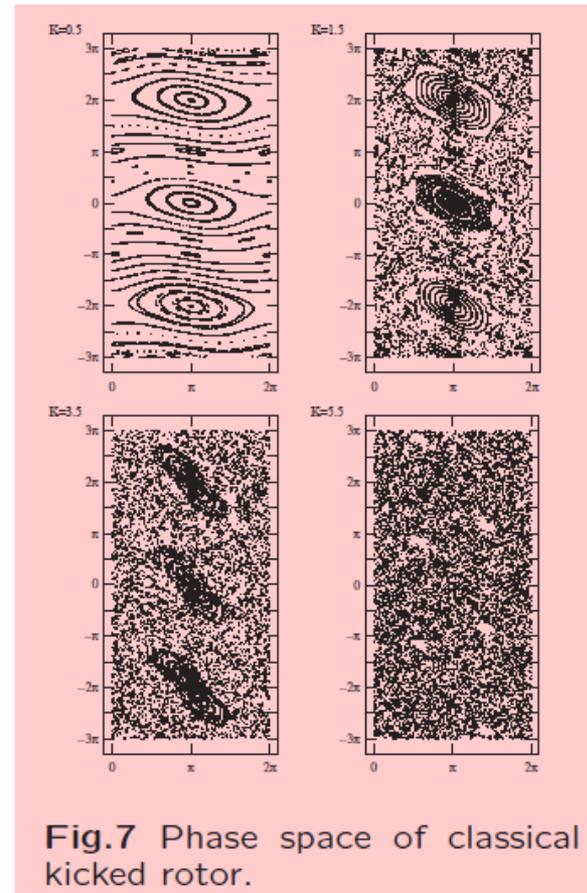


**Fig.7** Phase space of classical kicked rotor.

[12] A.M. Ozorio de Almeida, *Hamlitonian Systems: Chaos and Quantization*, Cambridge (1988).

# Optimal control of a kicked rotor

T. Takami

The optimal field is obtained by Zhu-Botina-Rabitz scheme[7].

[7] W. Zhu, J. Botina, and H. Rabitz, J. Chem. Phys. **108**, 1953 (1998).
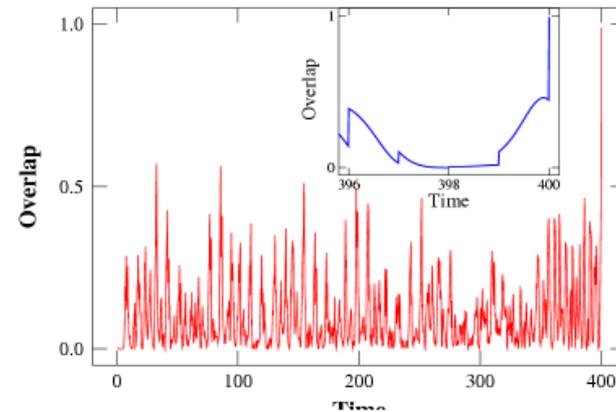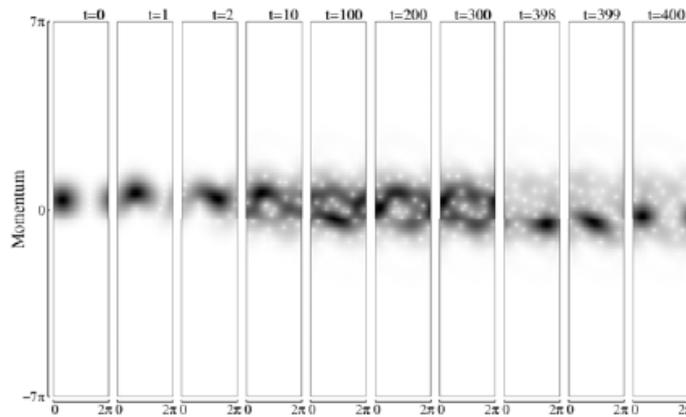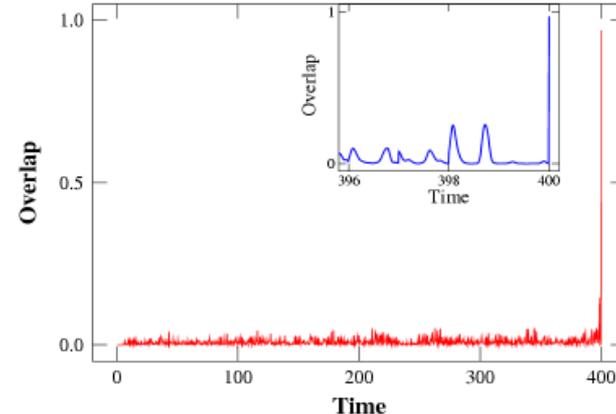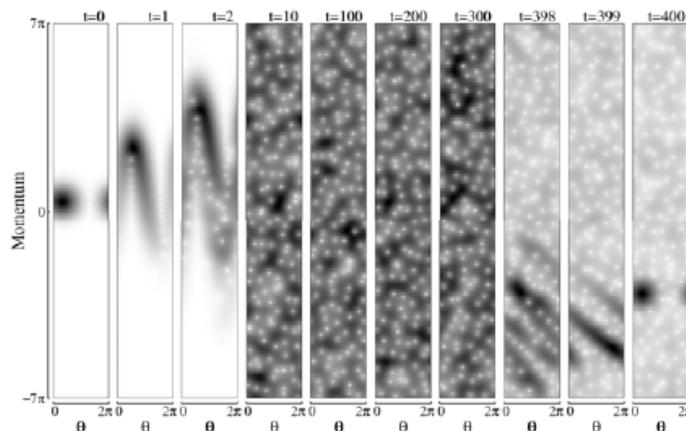


[9] T. Takami, H. Fujisaki, and T. Miyadera, Adv. Chem. Phys. **130A**, 435 (2005).

# An analytic field applied to a kicked rotor

T. Takami

$$\varepsilon(t) = \frac{\hbar\Omega}{|V|^2}\left[e^{-i\alpha}\langle\phi_0(t)|\hat{V}|\chi_0(t)\rangle + \text{c.c.}\right]$$

In the right figure, we show the final overlap by our analytic field, where the initial and final states, $|\Phi_0\rangle$, $|\Phi_T\rangle$, are minimum uncertainty packets.

For the strong chaos $K > 5$, the final overlaps tend to be almost 1 when the target time is long, while the field does not work for the weakly chaotic case $K = 3$.

This is because the interaction operator becomes a band matrix, which comes from the quantum localization of this system.

When we consider the steering between wave packets, it is expected that our field works if $\hbar$ is small enough since the minimum uncertainty packets are confined within the banded structure.



Fig.8 Final overlaps in quantum kicked rotor with $\hbar = 0.172$ driven by the analytical optimal field.
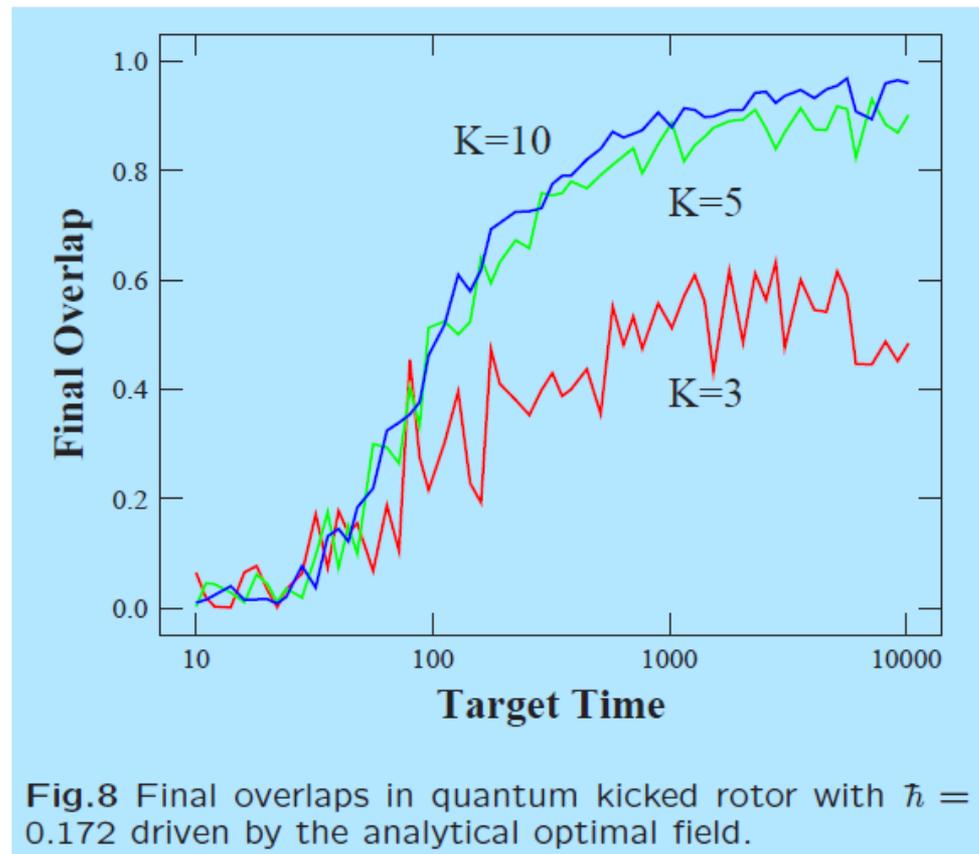
# References on this talk

- Vibrational quantum dynamics
    - H. Fujisaki, K. Yagi, H. Kikuchi, T. Takami, and G. Stock, Chem. Phys. 482 (2017) 86.
    - M. Shiga and H. Fujisaki, J. Chem. Phys. 136, 184103 (2012)
    - H. Fujisaki, Y. Zhang, and J.E. Straub, Adv. Chem. Phys. 145, 1-33 (2011).
    - Y. Zhang, H. Fujisaki, and J.E. Straub, J. Chem. Phys. 130, 025102 (2009).
    - T. Takami and H. Fujisaki, J. Mod. Opt. 56 (2009) 822-830.
    - T. Takami, H. Fujisaki, and T. Miyadera, Adv. Chem. Phys. 130A, 435 (2005)