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2440-6

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Treating non-adiabatic dynamics with the MCTDH method - from grid-based to direct dynamics

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Overview

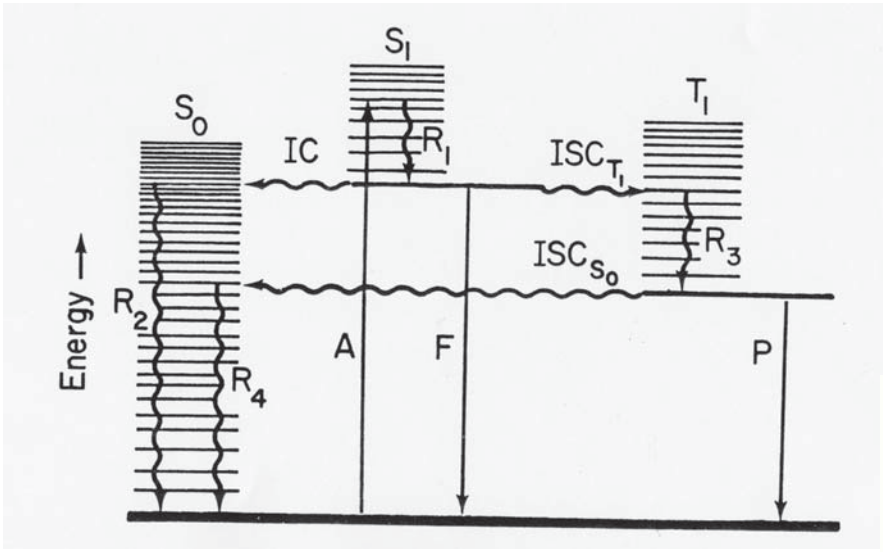
Aim is to study non-adiabatic photochemistry using full quantum dynamics simulations.

- Wavepacket Dynamics
  - The “standard method”
  - Multi-configuration time-dependent Hartree (MCTDH)
  - Extensions: G-MCTDH and vMCG
- The vibronic coupling model Hamiltonian
- Direct Dynamics

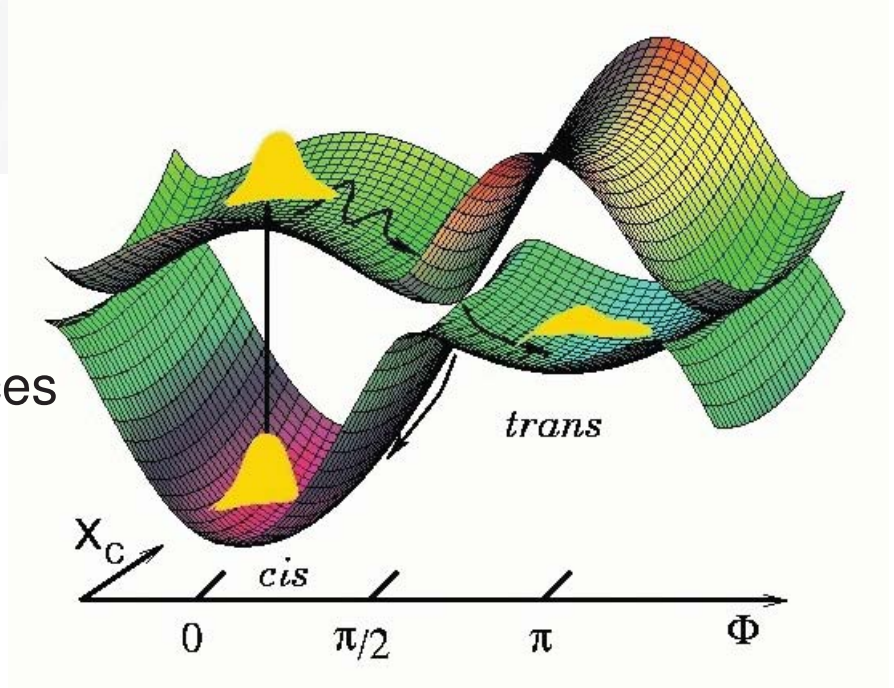
Collaborators:
Lenz Cederbaum and Hans-Dieter Meyer, Heidelberg
Irene Burghardt, Frankfurt
Mike Robb and Mike Bearpark, Imperial
Benjamin Lasorne, Montpellier
Helen Fielding, UCL

Birmingham:
Simon Neville
Gareth Richings
Charlotte Allan

Photochemistry: Basic Pictures

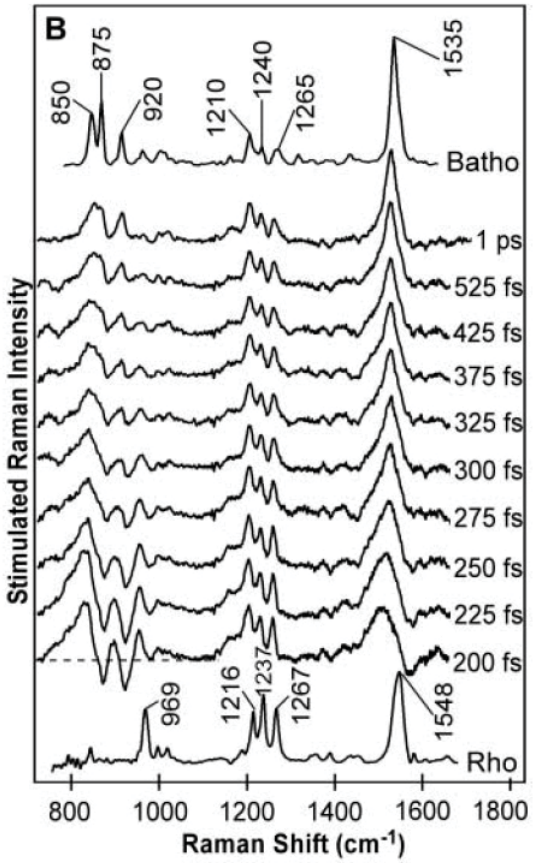


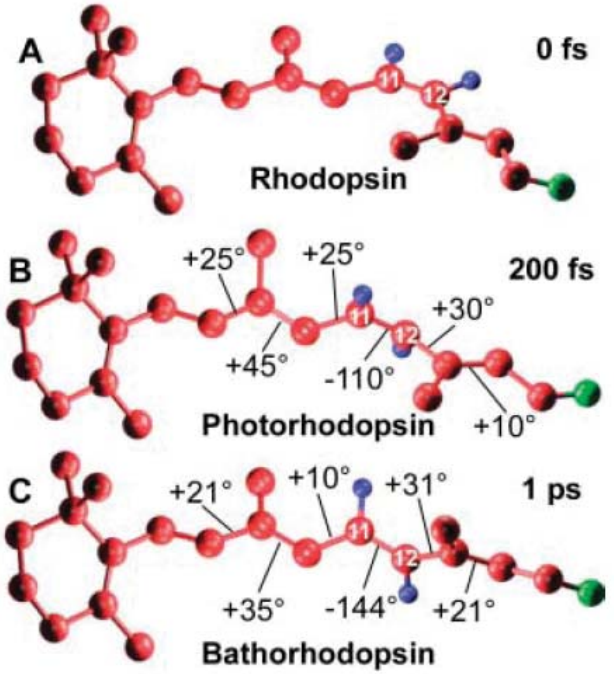
Jablonski Diagram



Evolution over Potential Surfaces

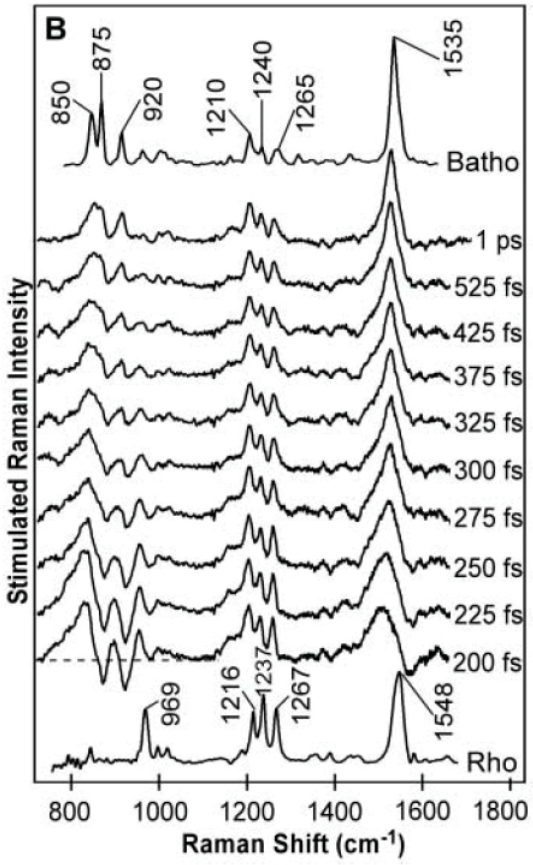
Time-resolved study - Rhodopsin

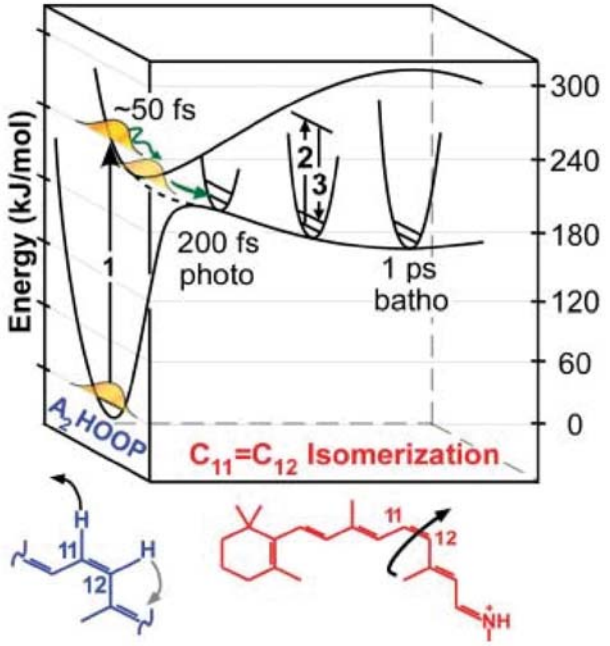




Kukura *et al* Science 310: 1006 (2005)

Time-resolved study - Rhodopsin





- Initial excitation - HOOP mode
- after 50 fs $S_1 \longrightarrow S_2$
- energy $\longrightarrow$ HT

Kukura *et al* Science 310: 1006 (2005)

The "Standard" Method

Solve TDSE

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

Nuclear wavefunction expanded in a basis set:

$$\Psi(q_1, \ldots, q_f, t) = \sum_{j_1=1}^{N_1} \ldots \sum_{j_f=1}^{N_f} A_{j_1 \ldots j_f}(t) \prod_{\kappa=1}^{f} \varphi_{j_\kappa}^{(\kappa)}(q_\kappa)$$

Variational equations of motion for A.

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L$$

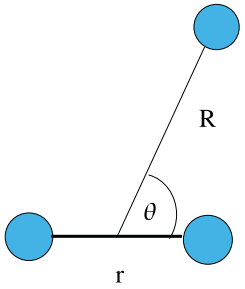
Use FFT or DVR basis set to circumvent f-dimensional integrals!
Computer memory $\sim N^f$

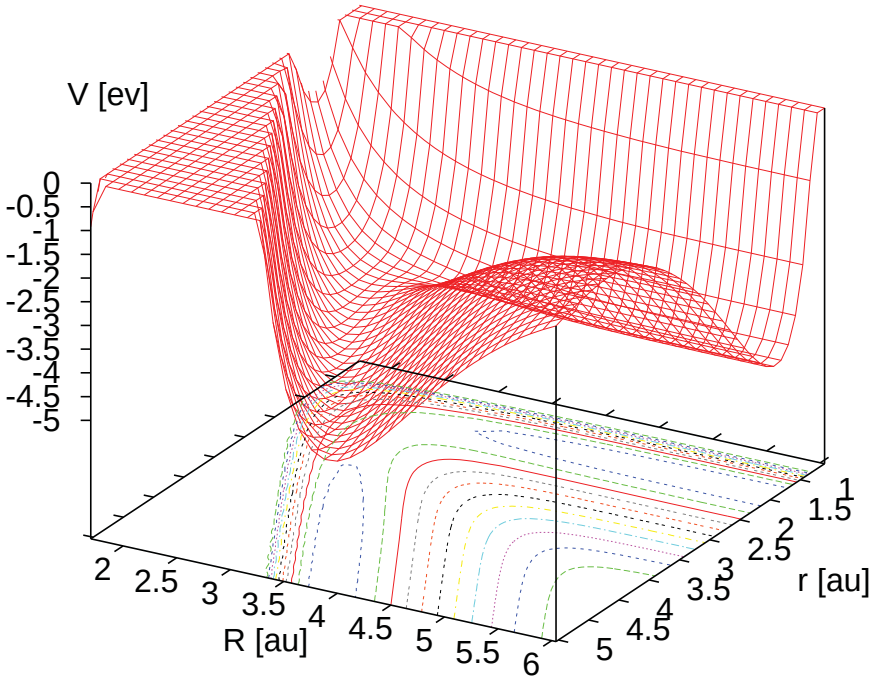
Kulander "Time-dependent methods for quantum dynamics", Elsevier, 1991

Kosloff, Ann. Rev. Phys. Chem. (94) **45**: 145

Wavepacket Dynamics

$$H + H_2 \longrightarrow H_2 + H$$





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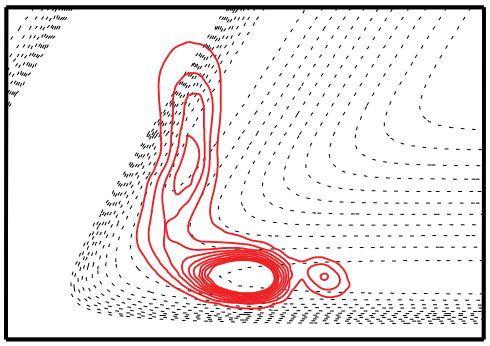

R

To solve the TDSE require:

- Potential surfaces
- Algorithm to propagate wavepacket
- Need to break the exponential barrier

The Multiconfiguration Time-Dependent Hartree (MCTDH) Method

$$\Psi(q_1,\ldots,q_f,t) = \sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_f} A_{j_1\ldots j_f}(t)\prod_{\kappa=1}^{f}\varphi_{j_\kappa}^{(\kappa)}(q_\kappa,t)$$

Variational equations for A and *single-particle functions* (SPFs) φ.

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L \\ i\dot{\varphi}^{(\kappa)} &= \left(1-P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle\mathbf{H}\rangle^{(\kappa)}\varphi^{(\kappa)} \end{aligned}$$

- non-linear equations of motion
- Computer memory $n^f + fnN$

Meyer, Gatti and Worth “Multidimensional quantum dynamics”, Wiley-VCH, 2009

Beck *et al* Phys. Rep. (00) 324:1

The Multiconfiguration Time-Dependent Hartree (MCTDH) Method

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- non-linear equations of motion
- Computer memory $n^p + pnN$
- A "particle" may be d-dimensional, $Q_i = (q_a, q_b, \ldots)$

Meyer, Gatti and Worth "Multidimensional quantum dynamics", Wiley-VCH, 2009

Beck *et al* Phys. Rep. (00) 324:1

A Simple Hamiltonian: The Vibronic Coupling Model

Assume diabatic basis: $\Psi(\mathbf{Q},\mathbf{r}) = \sum_\alpha \phi_\alpha(\mathbf{Q})\psi_\alpha(\mathbf{r};\mathbf{Q})$

$$\mathbf{H}(\mathbf{Q}) = \mathbf{T}(\mathbf{Q}) + \mathbf{W}(\mathbf{Q})$$

$$\hat{T}_\alpha + V^0_\alpha = \frac{\omega_i}{2}\left(\frac{\partial^2}{\partial Q^2} + Q^2\right)$$

$$\begin{aligned} W_{\alpha\beta} &= \langle\psi_\alpha|H_{el}|\psi_\beta\rangle \\ W_{\alpha\beta} &\approx V^0_\alpha\delta_{\alpha\beta} + \varepsilon_\alpha + \sum_i \underbrace{\frac{\partial}{\partial Q_i}\langle\psi_\alpha|H_{el}|\psi_\beta\rangle}\, Q_i + \ldots \end{aligned}$$

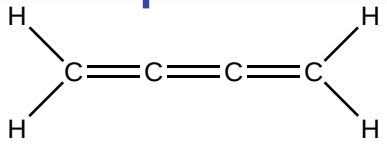
$$\kappa_i, \lambda_i \neq 0 \quad \textit{if} \quad \Gamma_\alpha \times \Gamma_i \times \Gamma_\beta \supseteq A_1$$

Köppel *et al* Adv. Chem. Phys. (1984) **57**: 59

Worth *et al*, Int. Rev. Phys. Chem. (08) **27**: 569

Butatriene photoelectron spectrum

18 modes $\mathrm{D_{2h}}$
$X^2\mathrm{B_{2g}}$; $A^2\mathrm{B_{2u}}$



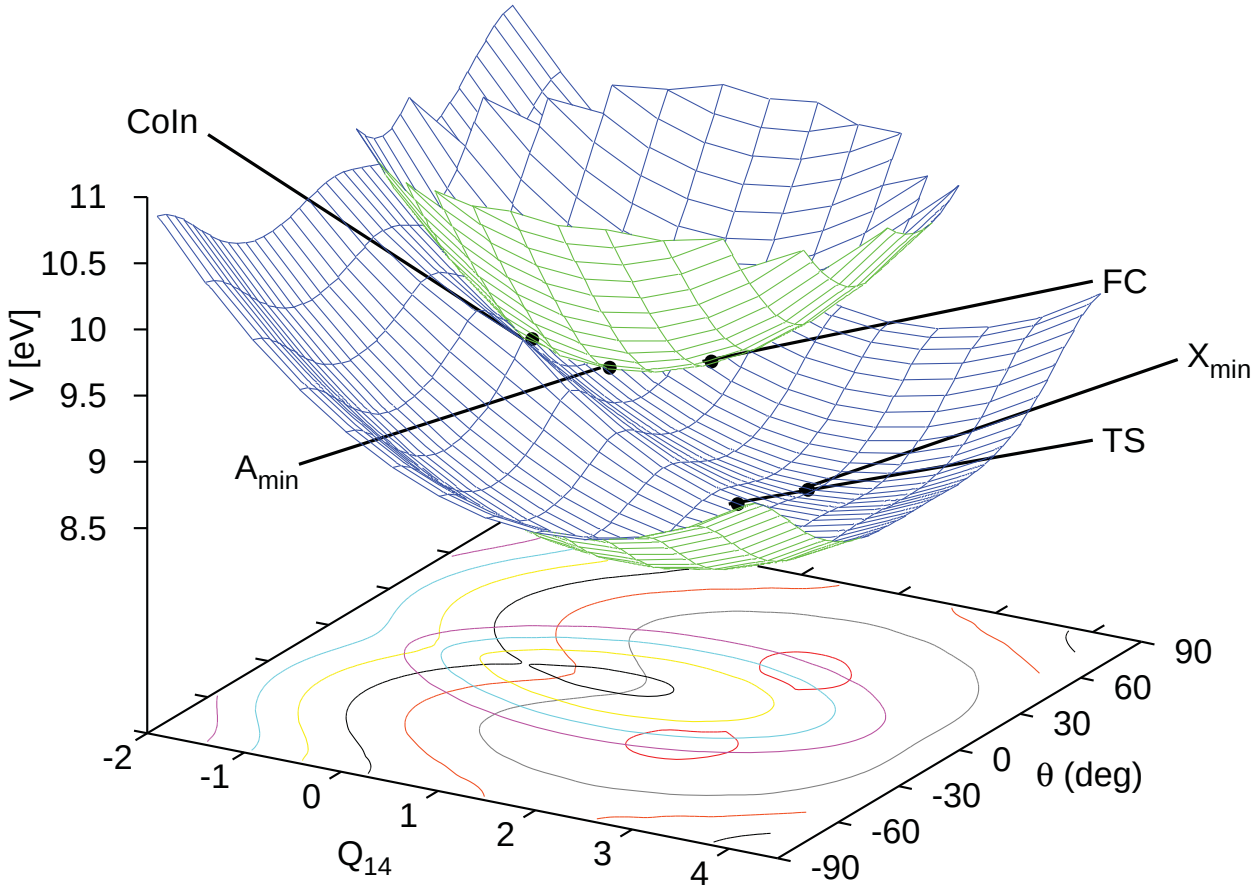
$$\mathbf{H} = \sum_i \frac{\omega_i}{2}\left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix}$$
$$+ \sum_{i\in \mathrm{A_g}}^{4} \begin{pmatrix} \kappa_i^{(1)} & 0 \\ 0 & \kappa_i^{(2)} \end{pmatrix} Q_i + \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} Q_{\mathrm{A_u}}$$
$$+ \ldots$$

$\langle\psi_\alpha|\frac{\partial H}{\partial Q_i}|\psi_\beta\rangle$ $\qquad$ $\mathrm{B_{2g}} \times \mathrm{B_{2u}} = A_u$

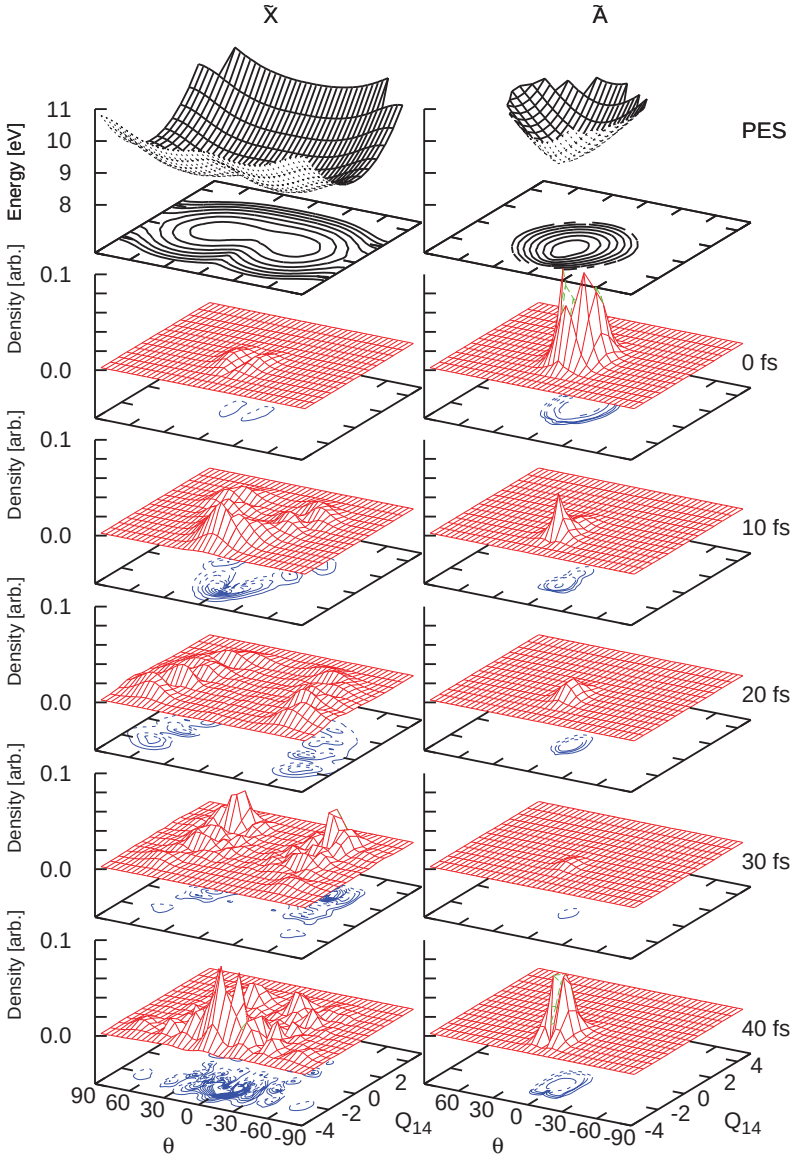
linear: 5 modes, 16 parameters
bilinear: 18 modes, 79 parameters

$$I(\omega) \sim \int_{-\infty}^{\infty} dt \langle \Psi(0) \mid \Psi(t)\rangle e^{i\omega t}$$

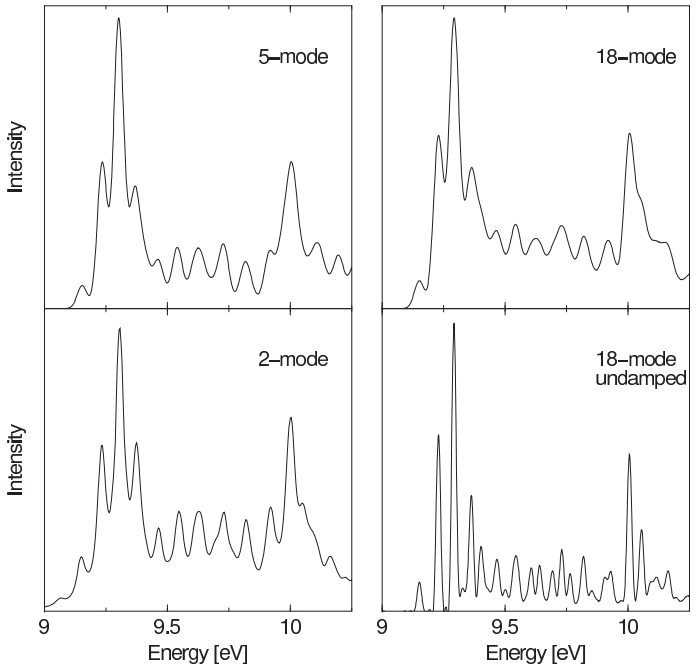
Butatriene Cation PES $\tilde{X}/\tilde{A}$



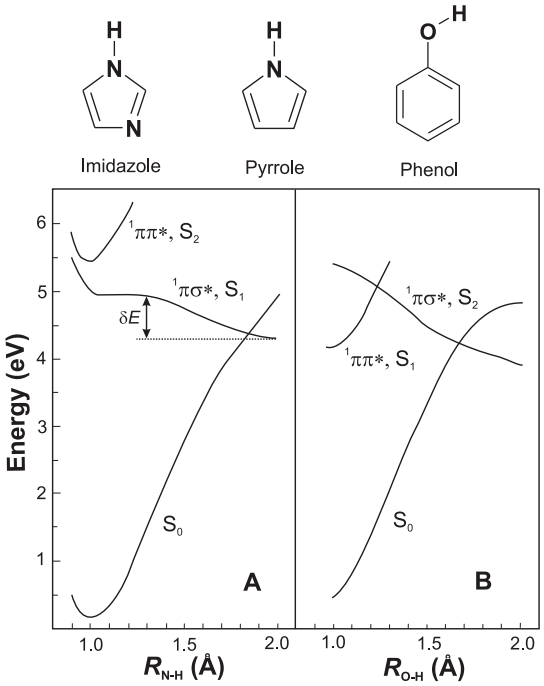
Butatriene Dynamics



N	MCTDH MB	standard MB
2	0.9	16.4
5	10.3	2.5×10^4
18	431.5	1.5×10^{17}



Pyrrole Photodissociation



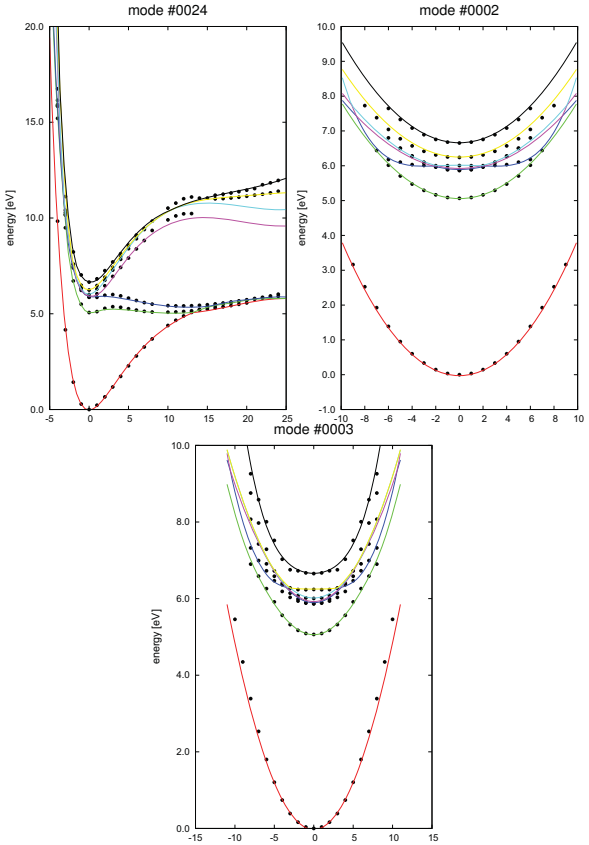
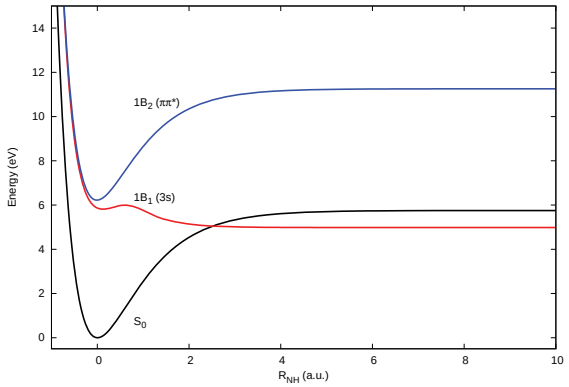


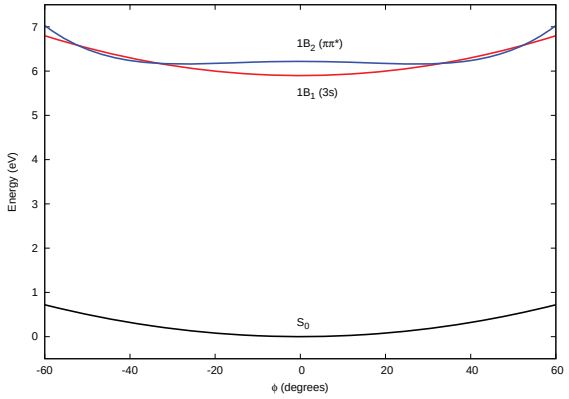
Figure 9: From top-to-bottom, left-to-right: fitted PESs for modes (i) ν_{24} (N-H stretch), (ii) ν_2 (ring torsion), (iii) ν_3 (ring torsion, out-of-plane C-H bend)

Ashfold *et al* Science (06) **312**: 1637

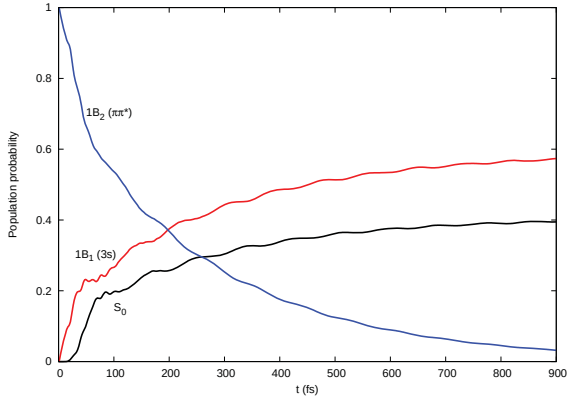
8-state MS-MR-CASPT2(8,8)/AVDZ+

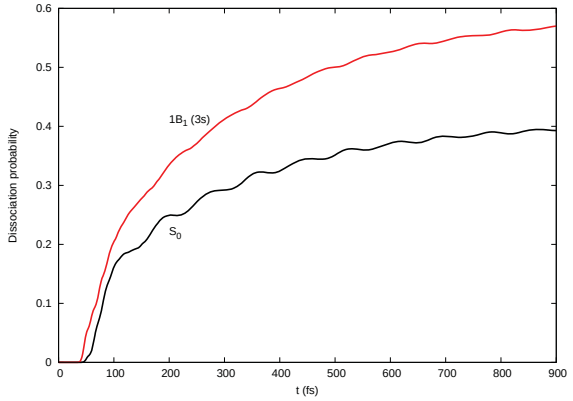
Pyrrole: 3-State 3-Mode Model





State populations





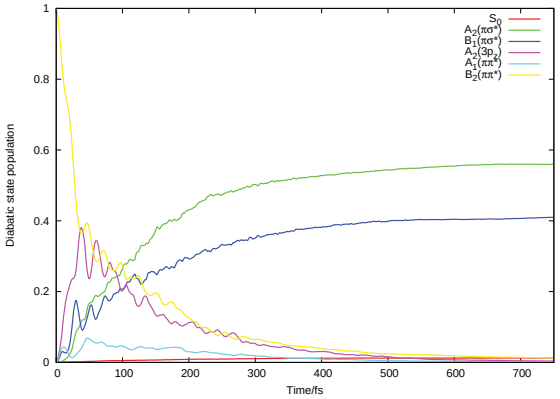
$\pi\pi^*$ coupled to upper $\pi\sigma^*$
upper $\pi\sigma^*$ coupled to S_0

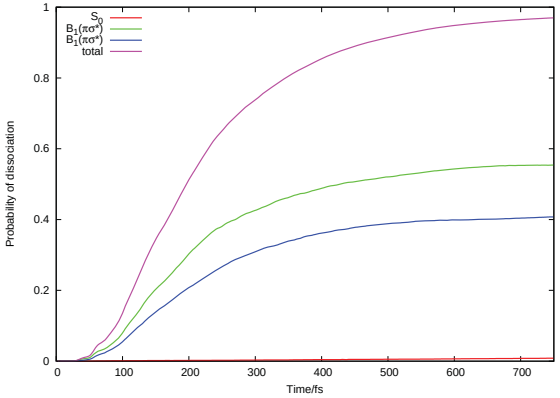
Flux

Pyrrole: 9-State 8(9)-Mode Model

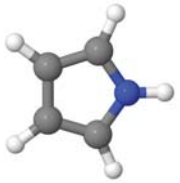
Ignoring ν_2

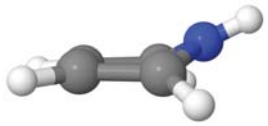
State populations





Flux



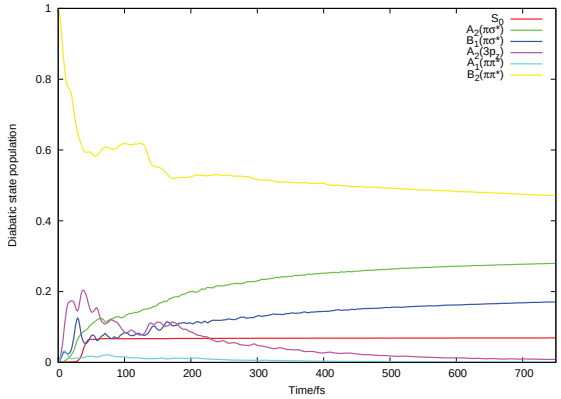


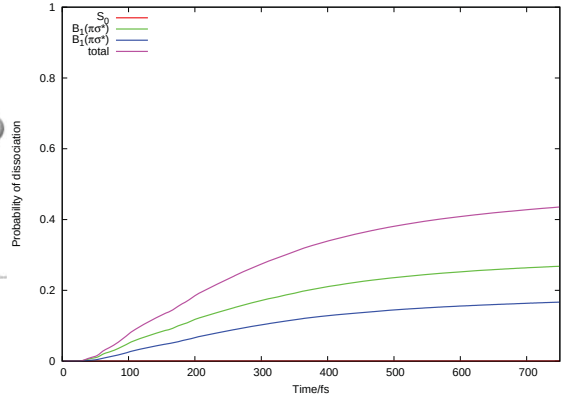
"Trapped"

"Geometry"

Including ν_2

State populations



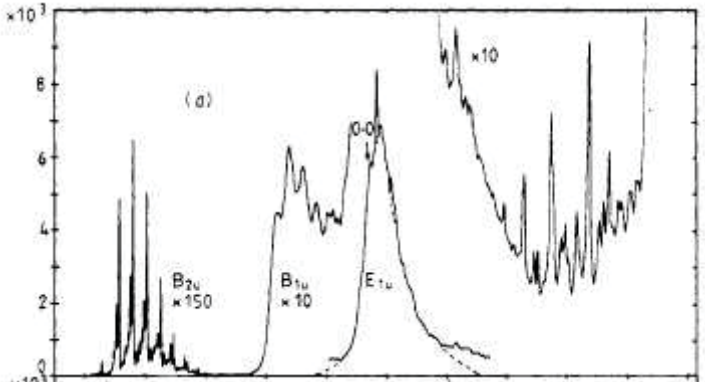


Flux

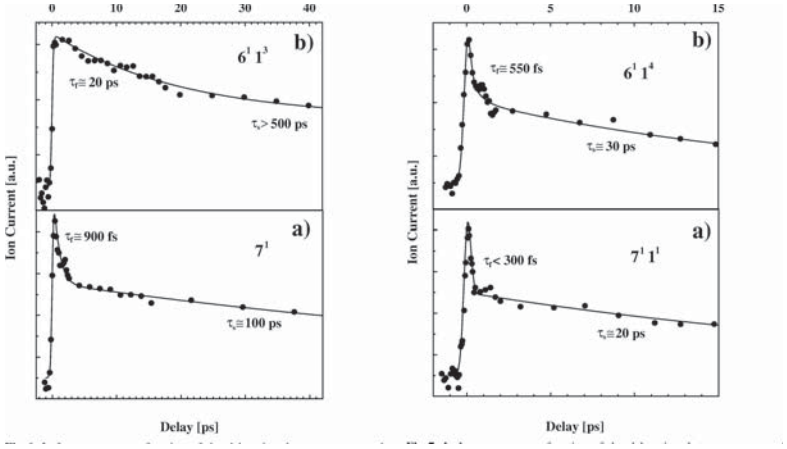
Benzene: Photophysics

Process	Quantum yield 253 nm	248 nm	242 nm	237 nm
Formation of photoproducts	0.016	0.022	0.024	0.037
Fluorescence	0.18	0.10	0	0
Formation of triplet (ISC)	0.6	0.6	0	0

Absorption Spectrum



"Channel 3"



Clara *et al* Appl. Phys. B (00)71: 431

Benzene: Time-Resolved Spectra

Pump 243 nm
Probe:
260, 254, 235

Total Ion Count

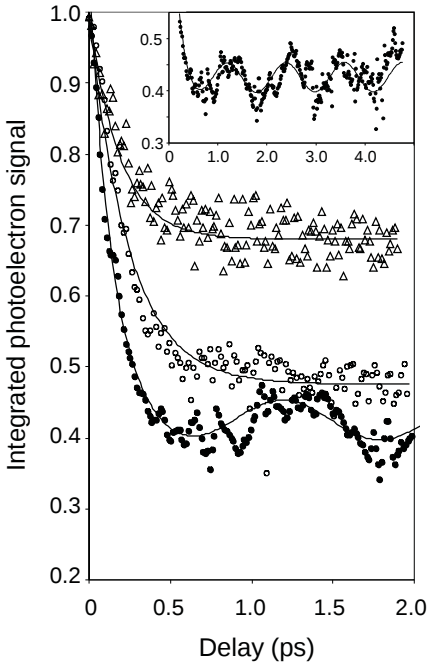


Photo-electron spectra

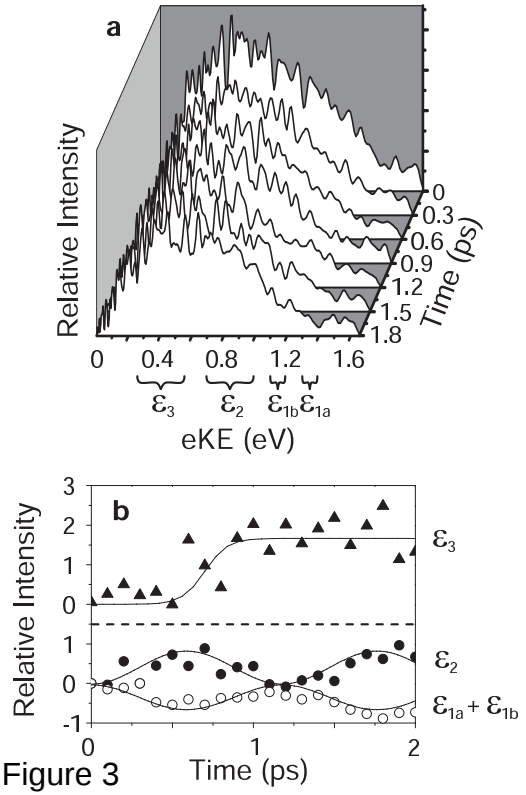
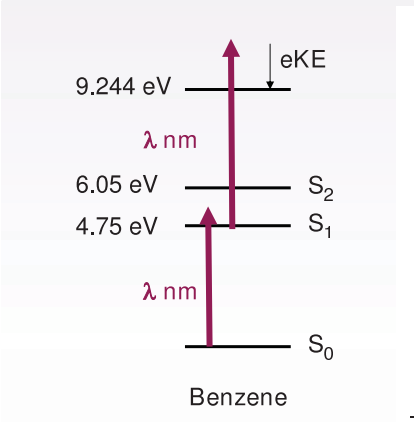


Figure 3

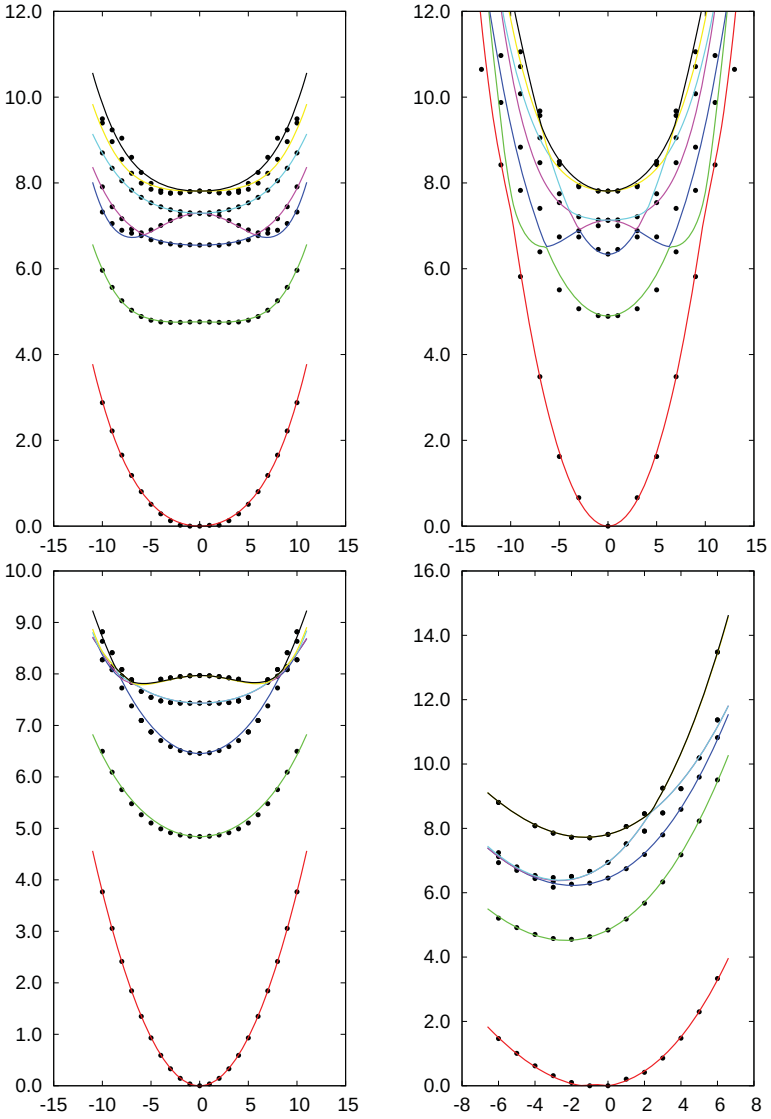


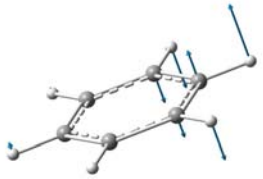
Decay 220 fs + 12 ps

Period 1.2 ps

Minns *et al* PCCP (10) **12**: 15607

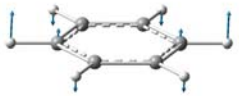
Benzene Potential Energy Surface Cuts

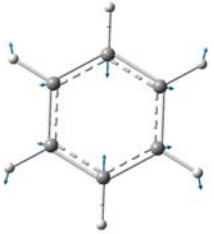




$\nu_4 + \nu_{16}$

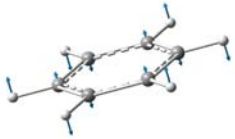
ν_{16a}

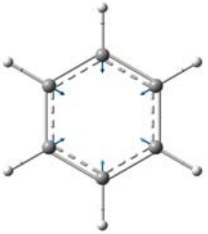




ν_{6a}

ν_4



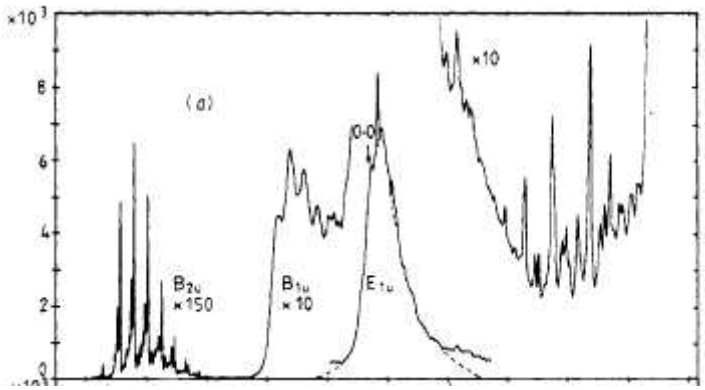


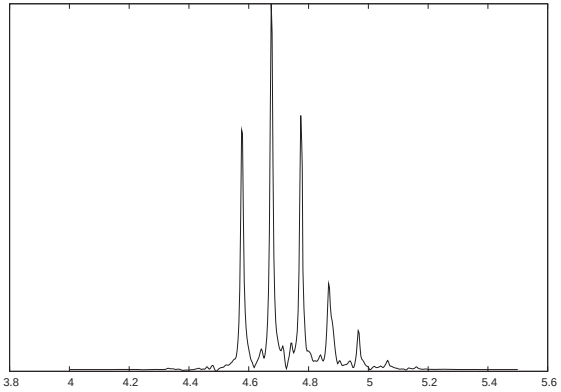
ν_1

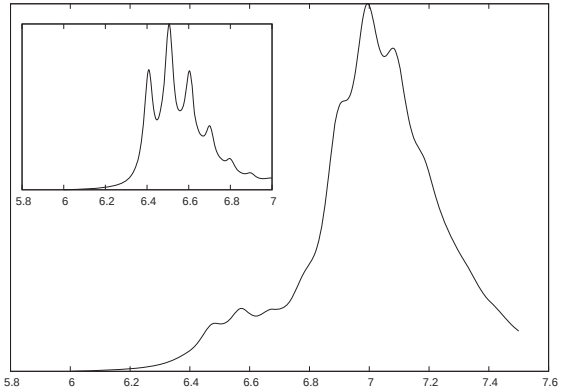
CASPT2 (6,6)/Roos

Simulated Absorption Spectra

5-state 8-mode model.







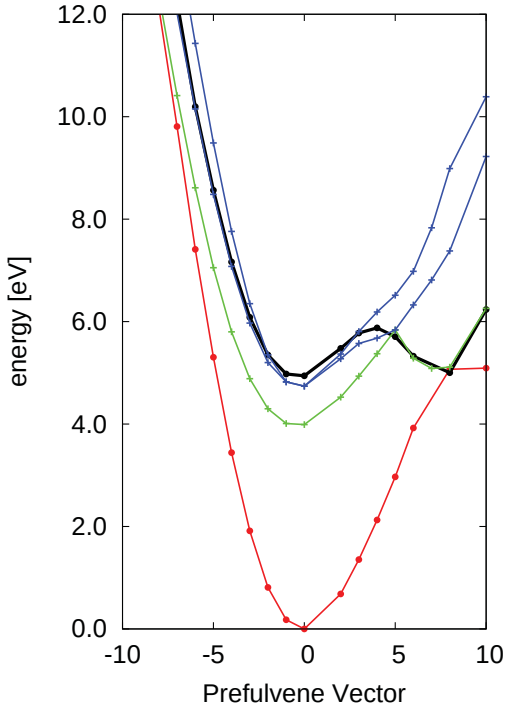
B_{2u} $B_{1u} + E_{1u}$

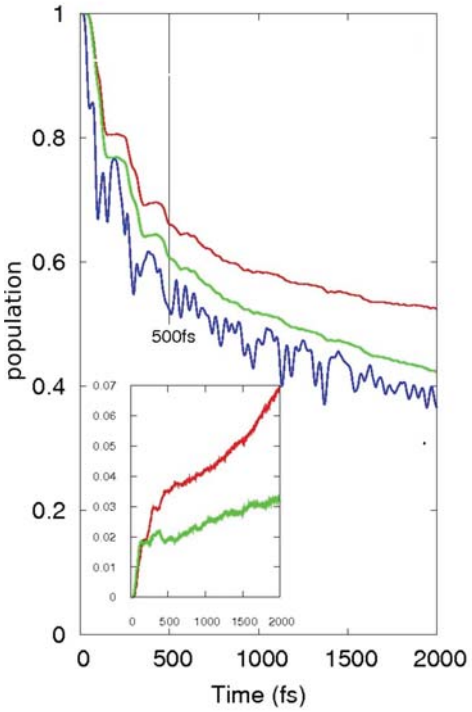
JCP (09) 131: 064303

Importance of Triplet States and ISC

Need SOC between states: $\langle {}^3\Psi | H_{SO} | {}^1\Psi \rangle$
At FC point, S_1 / T_2 coupling zero. In general SOC small ($< 5\ \mathrm{cm}^{-1}$)

5-state model (S_0, S_1, T_1, T_2)





$S + T$ (red)
S_1 (green)
S_1 *FC* (blue)

T populations (inset)

Higher Dimensions: The G-MCTDH Method

$$\Psi(Q_1,\ldots,Q_f,t)=\sum_{j_1=1}^{n_1}\ldots\sum_{j_f=1}^{n_f}A_{j_1\ldots j_f}(t)\prod_{\kappa=1}^{f-n}\varphi_{j_\kappa}^{(\kappa)}\prod_{\kappa=n+1}^{f}g_{j_\kappa}^{(\kappa)}$$

Replace single-particle functions with Gaussian functions and propagate parameters

$$g_j(\mathbf{x},t)=\exp\left(\mathbf{x}^T\mathbf{a}_j\mathbf{x}+\mathbf{x}^T\boldsymbol{\xi}_j+\eta_j\right)$$

- Need more GFs than SPFs,
- **BUT** set of parameters smaller than no. of grid points
- spatially unrestricted

DISADVANTAGES

- Non-orthogonal basis set - numerically difficult
- Efficiency requires approximate integral evaluation
  LHA $V=V(x_0)+V'(x-x_0)+V''(x-x_0)^2$
  - no longer converges on exact result

The Variational Multi-configurational GWP Method

In limit of only GWP basis functions: vMCG

$$\Psi(\mathbf{x}, t) = \sum_J A_J g_J(\mathbf{x}, t)$$

Related to Heller, Metiu etc.

$$\Psi(\mathbf{x}, t) = \sum_j g_j(\mathbf{x}, t)$$

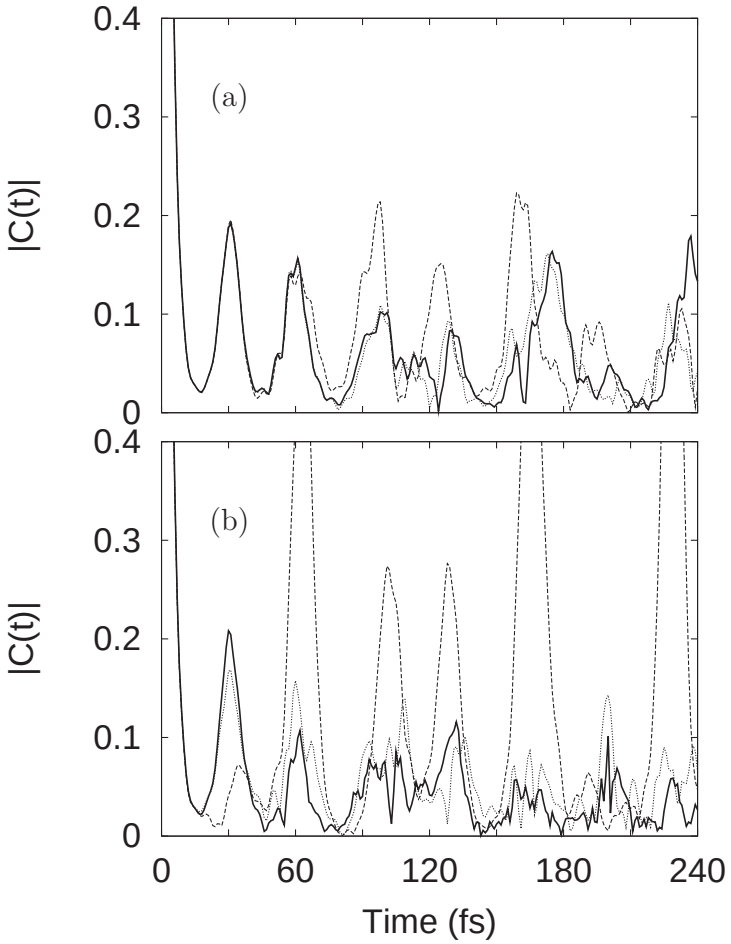
$$g_j(x) = \exp \tfrac{1}{\hbar}(-a_j(x - x_j)^2 + ip_j(x - x_j) + i\gamma_j)$$

where a_j is the width, γ_j the phase, and x_j, p_j are the position and momentum of the centre of the function. Centres x_j, p_j follow classical trajetories.

vMCG GWPs coupled and follow non-classical trajectories

vMCG propagation

The autocorrelation function for a 4-mode 2-state model after vertical excitation to the upper state



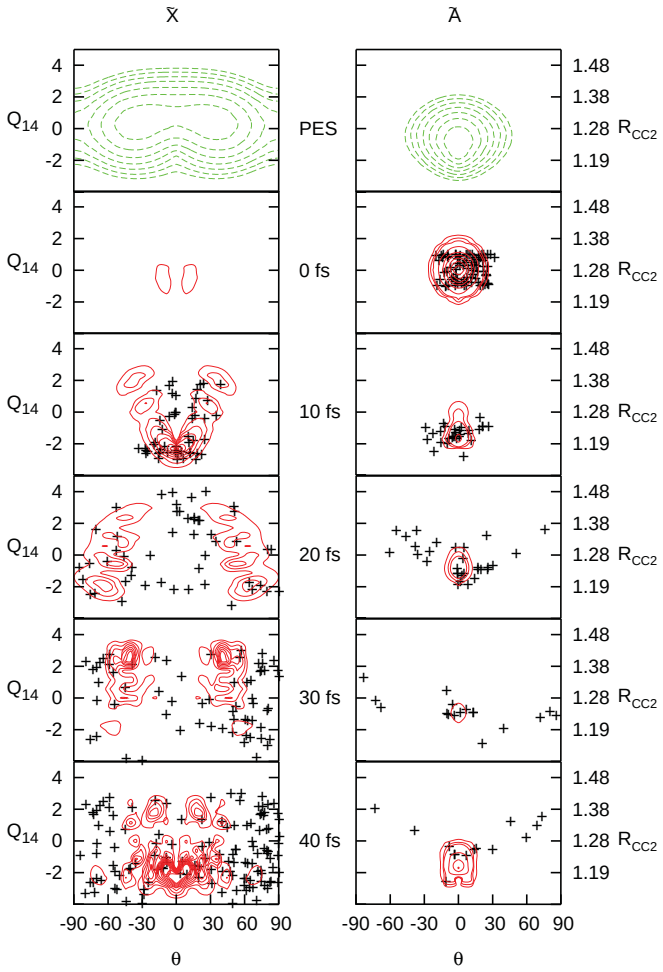
(a) vMCG
40 (dashed), 120 (dotted) and 160 GWPs (bold line)

(b) classical GWPs
160 (dotted), 3794 (dashed) and 94320 (bold line) GWPs.

Burghardt *et al* JCP (08) **129**: 174104

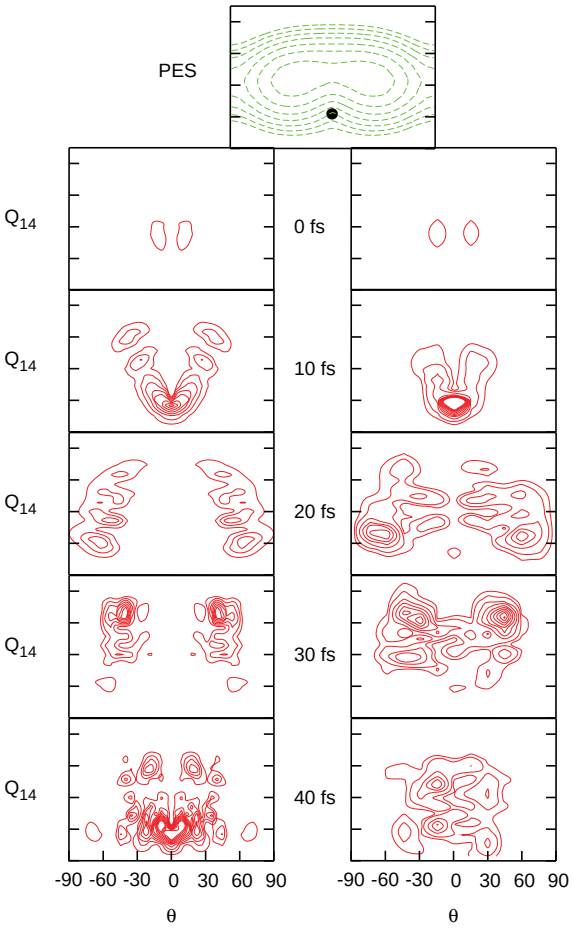
Butatriene: MCTDH v TSH v vMCG

80 Trajectories



Worth *et al* JPC A **107**: 621 (2003)

32 GWPs



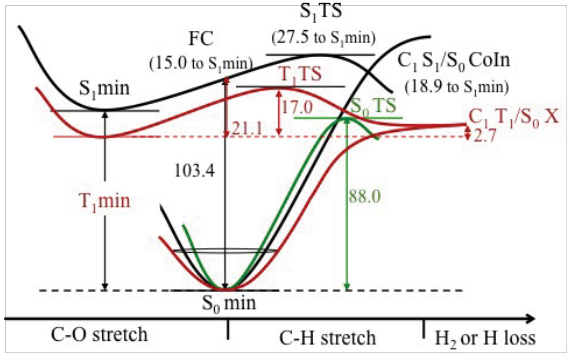
Worth *et al* Farad. Discuss. **127**: 307 (2004)

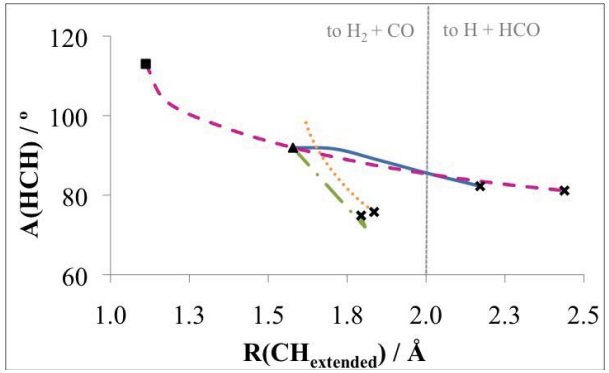
Direct Dynamics

Calculate PES (LHA) directly using quantum chemistry program.

- Store results in a database (energy, gradient, Hessian)

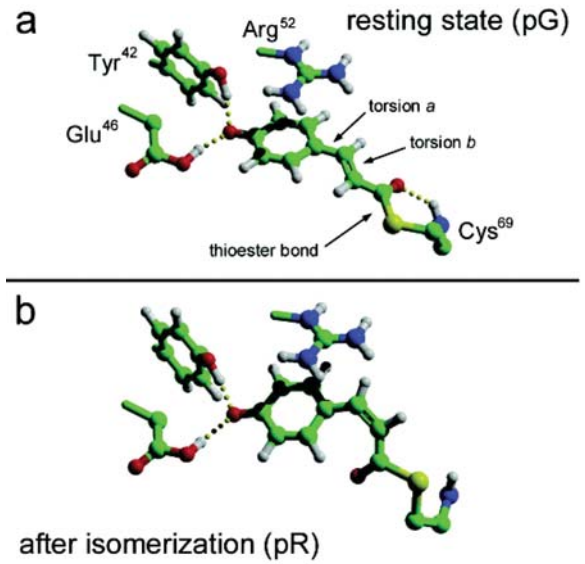
Formaldehyde Photochemistry





Araujo *et al* JPC (09) **131**: 144301

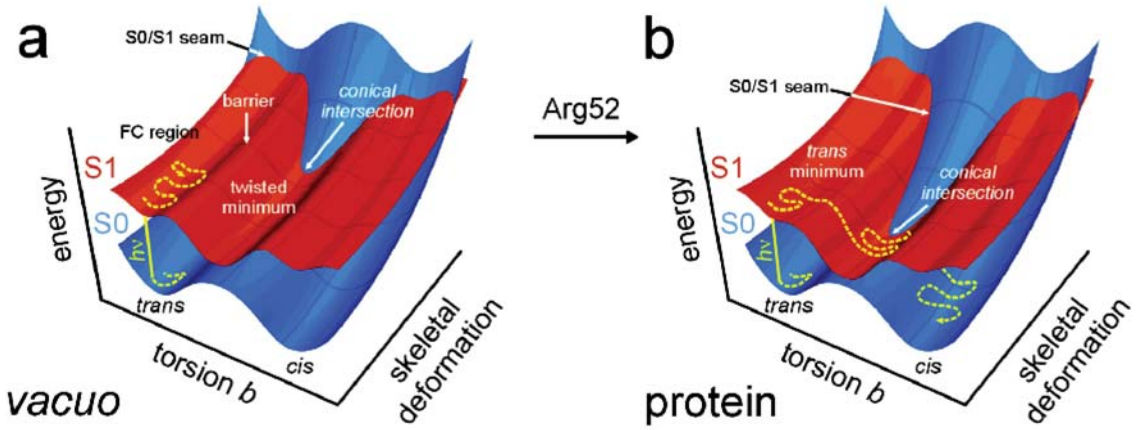
Non- Adiabatic Photochemistry: Environmental Effects



Photoactive yellow protein

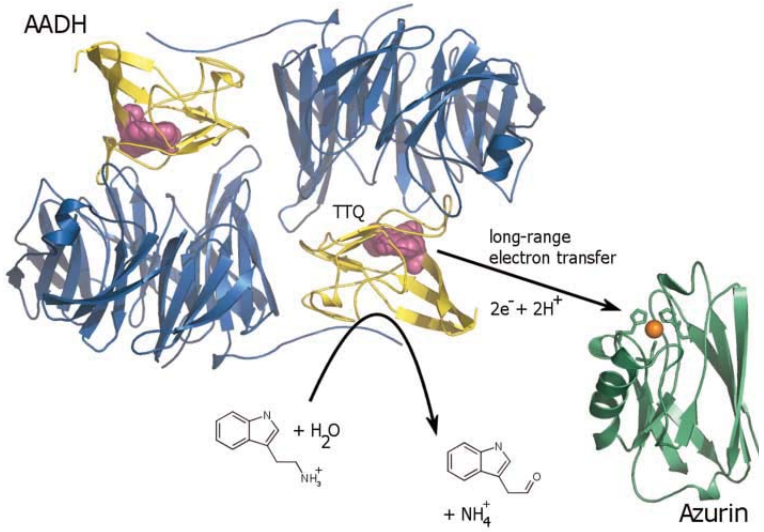
- CAS(6,6)/3-21G + GROMOS
- 14 trajectories
- trajectory surface hopping

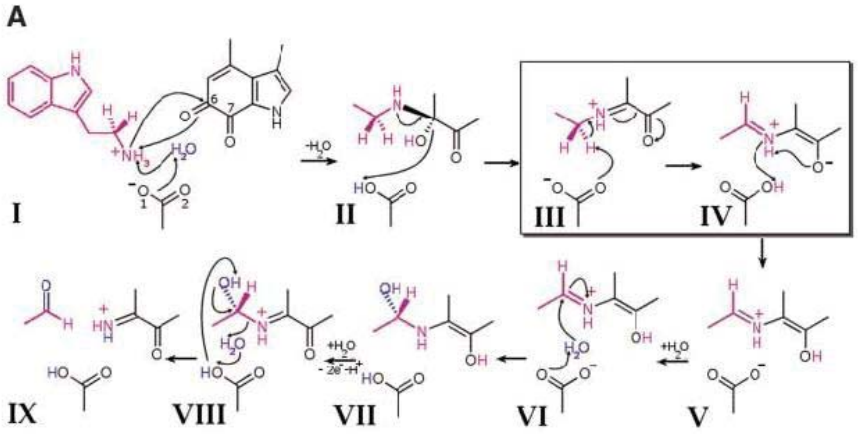
Groenhof *et al* JACS (04) **126**: 4228



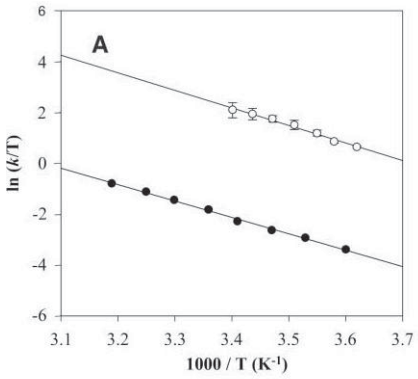
Proton Tunneling in Enzymes

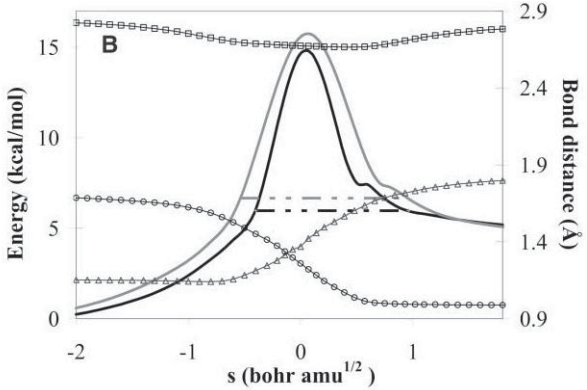
Aromatic Amine Dehydrogenase (AADH)





$$\Delta G^{\ddagger}_{exp} = 12.7\,\mathrm{kcal mol}^{-1}$$
$$\Delta G^{\ddagger}_{cal} = 13.2\,\mathrm{kcal mol}^{-1}$$
$$\Delta G^{\ddagger}_{tun} = -4.9\,\mathrm{kcal mol}^{-1}$$

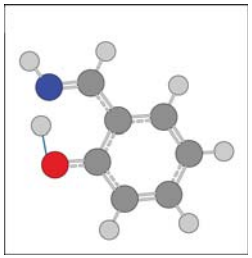




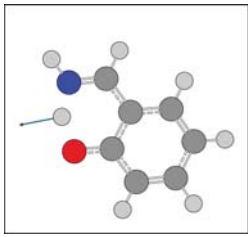
Masgrau *et al* Science **236**: 312 (2006)

Proton Transfer: Salicylaldehyde

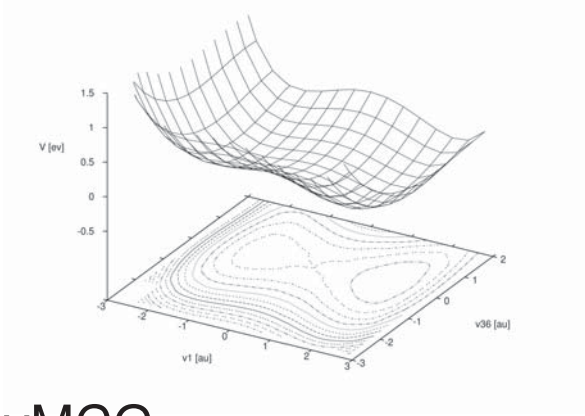
Barrier height 18 kJmol^{-1} (0.19 eV). Create wavepacket by displacing PT mode ν_1 to give 9.0 kJmol^{-1}(0.09 eV)



ν_1

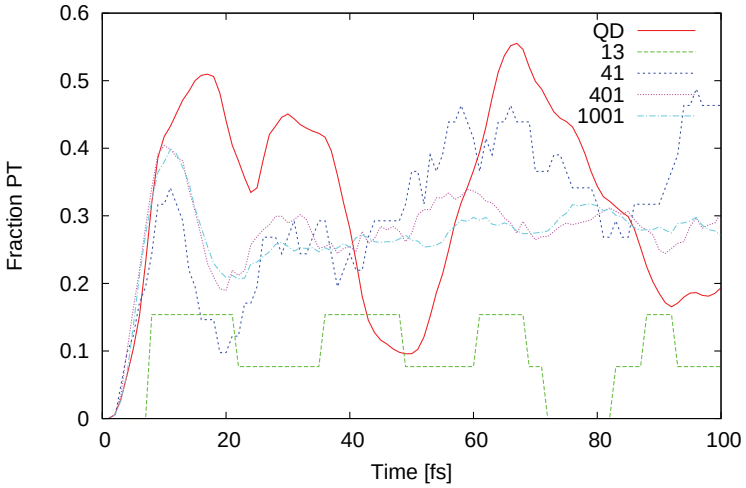


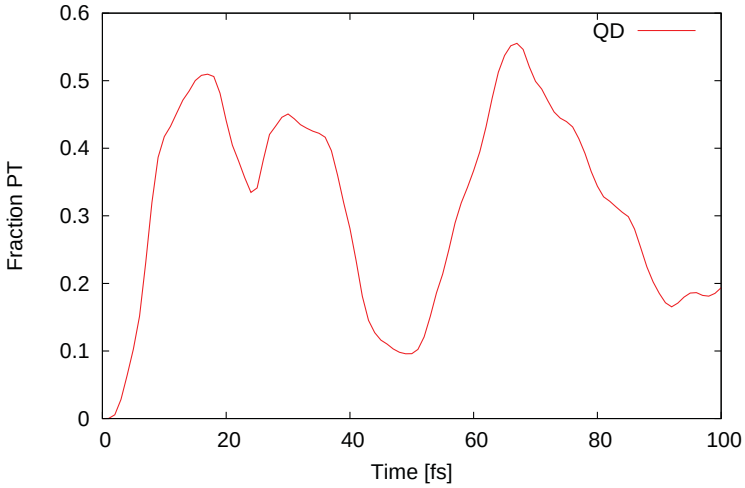
ν_{36}



Swarm of Trajectories

vMCG





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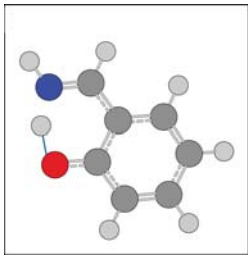
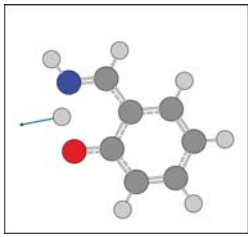
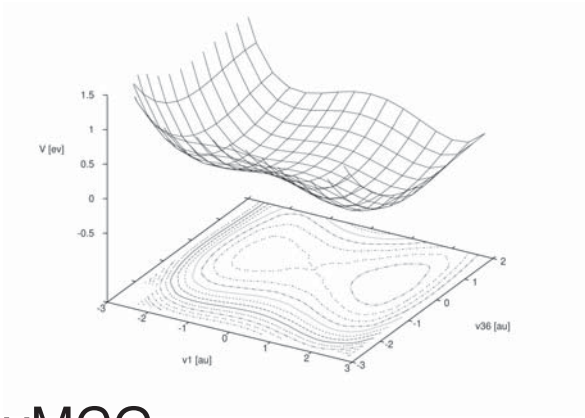


ν_1

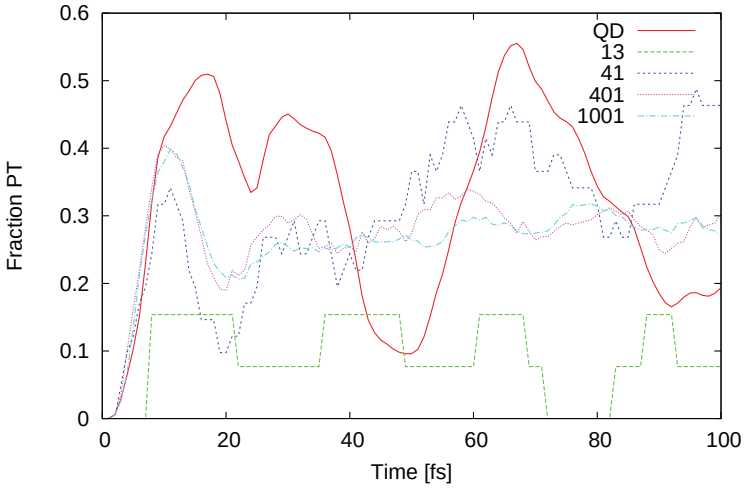


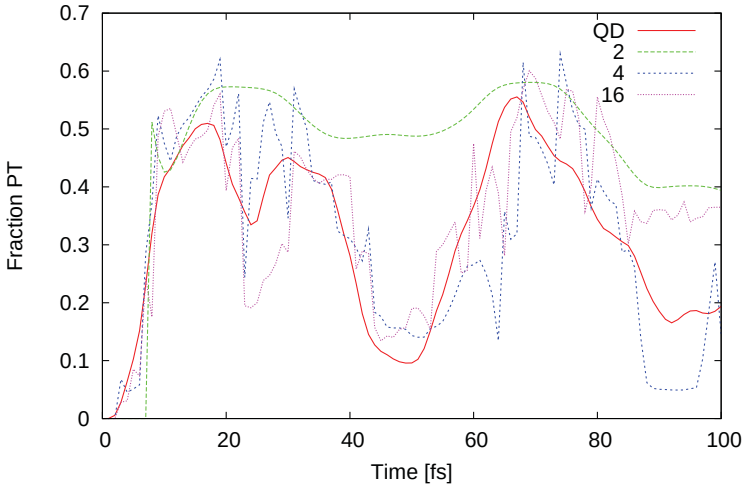
ν_{36}



Swarm of Trajectories

vMCG





Summary

Standard Wavepacket dynamics:

- Exponential increase in computer resources $\sim N^f$
  - 4-6 modes usual limit

MCTDH:

- Wavefunction more compact – scales with $n^p + pnN^d$
  - ca 20 modes possible
- Converges on exact result
- Starting point for further approximations
- together with the vibronic model Hamiltonian able to study multi-mode effects in non-adiabatic systems

Need:

- increase algorithm power to add “environment” explicitely
  - G-MCTDH
- better / more flexible potentials to study photochemistry
  - direct dynamics