Excited-state non-adiabatic quantum dynamics and its theoretical challenges

Zernike Institute for Advanced Materials

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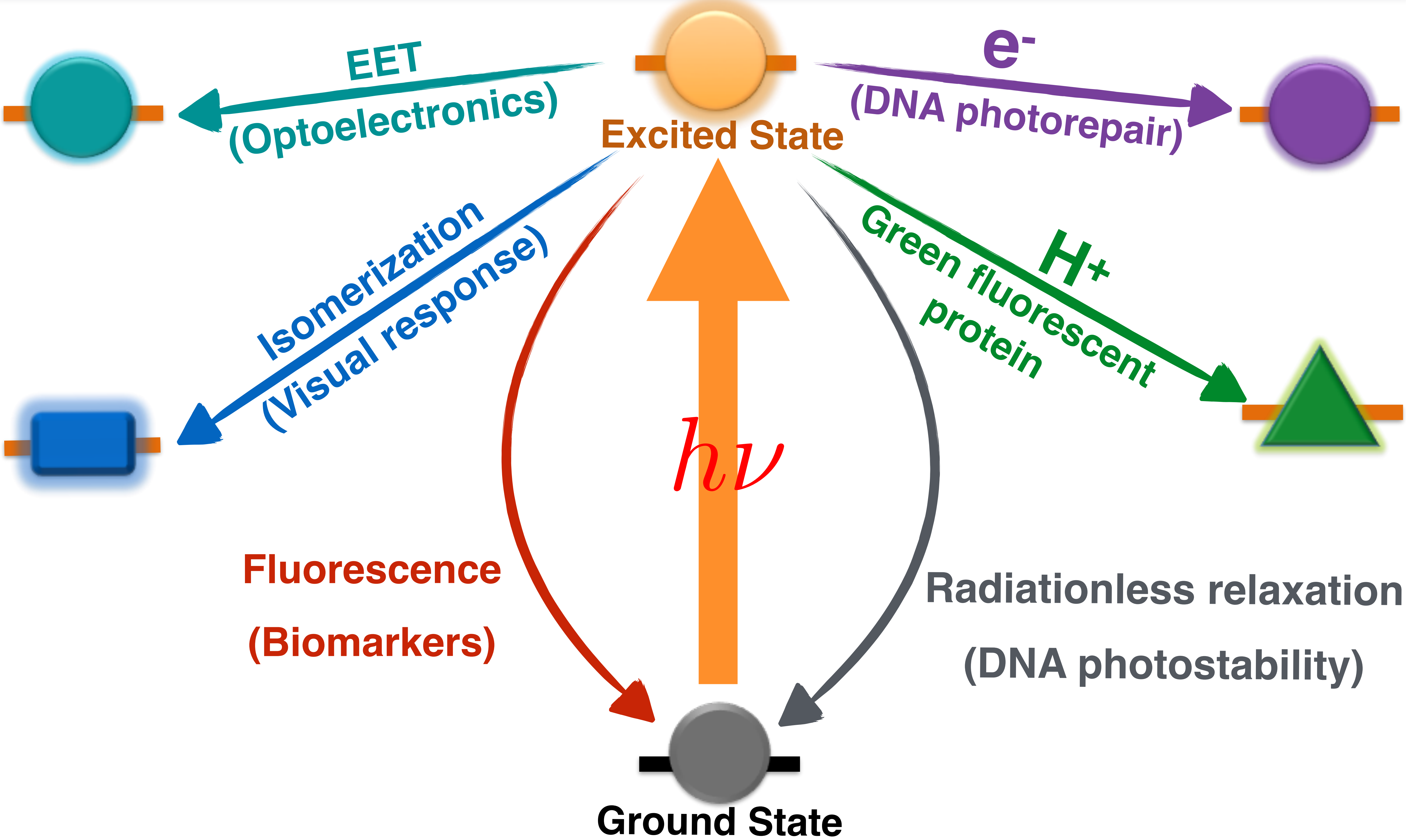
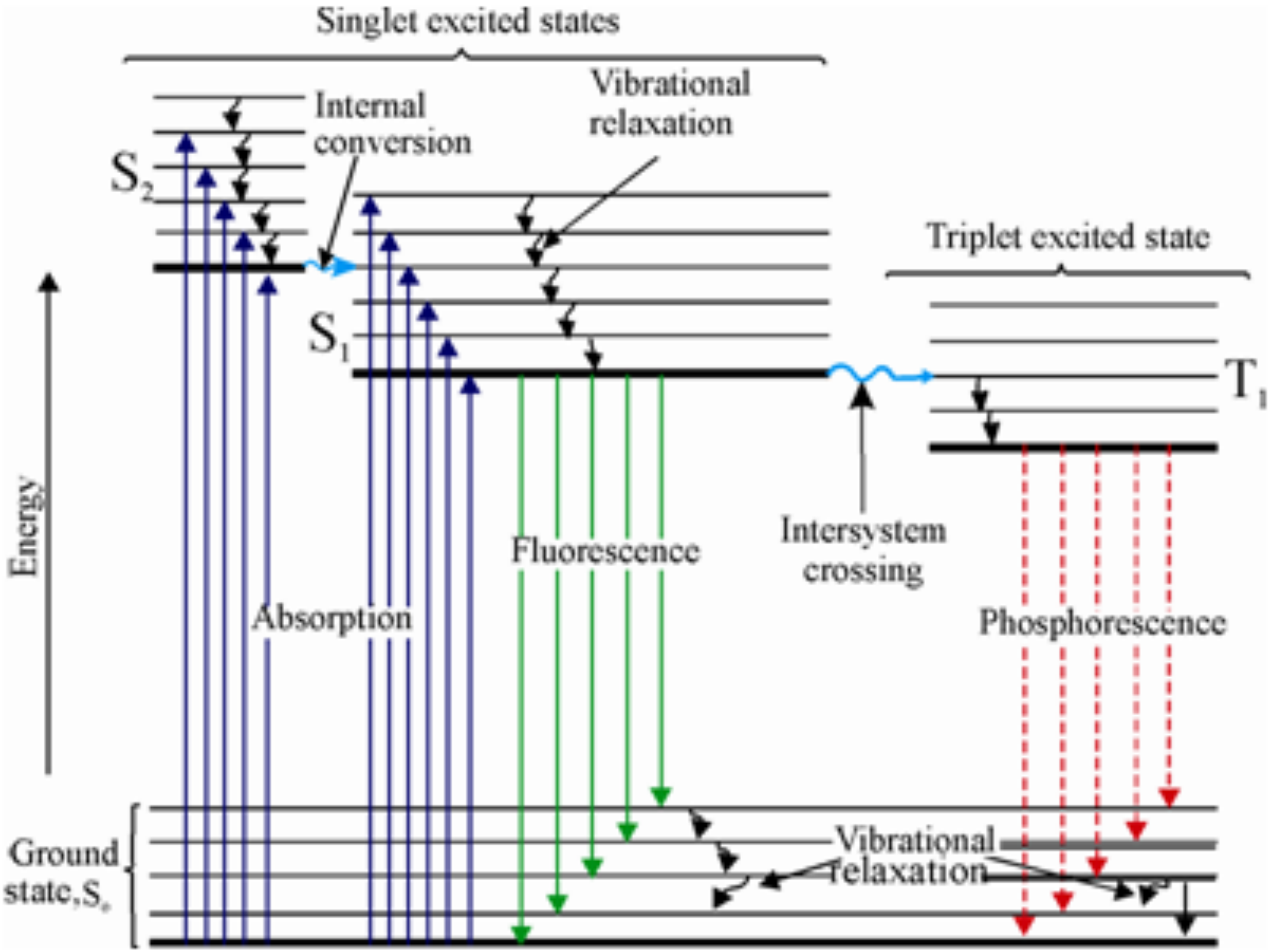
Photochemical processes in complex environment

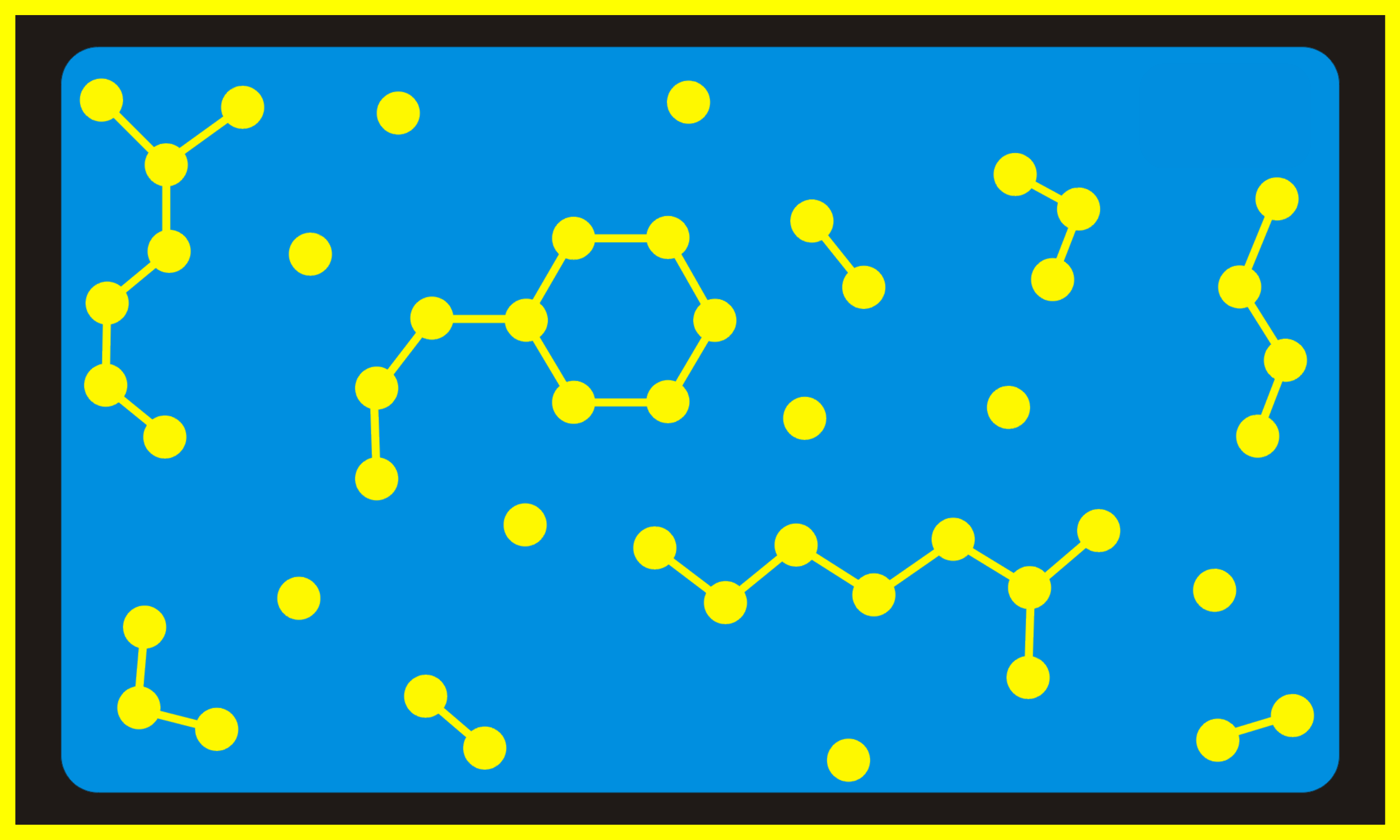


Jablonski diagram

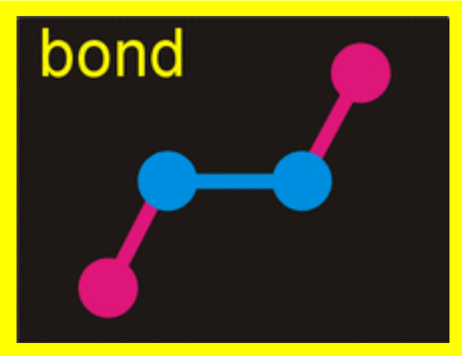


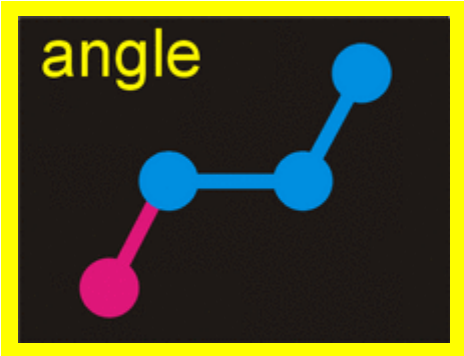
Molecular mechanics

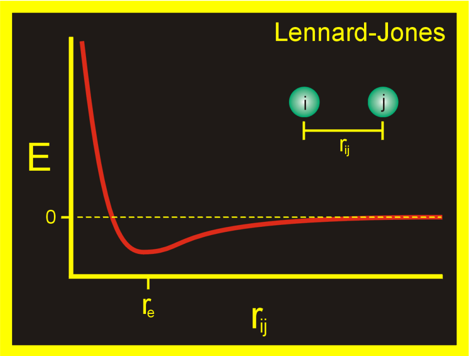
Newtonian equation of motion

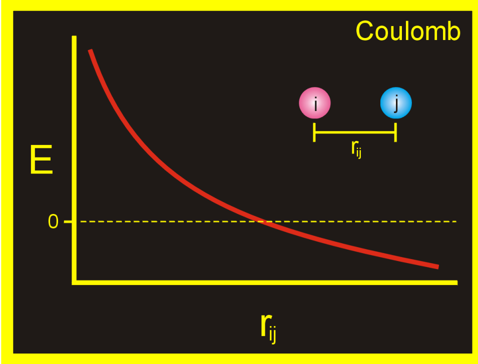


Classical force fields



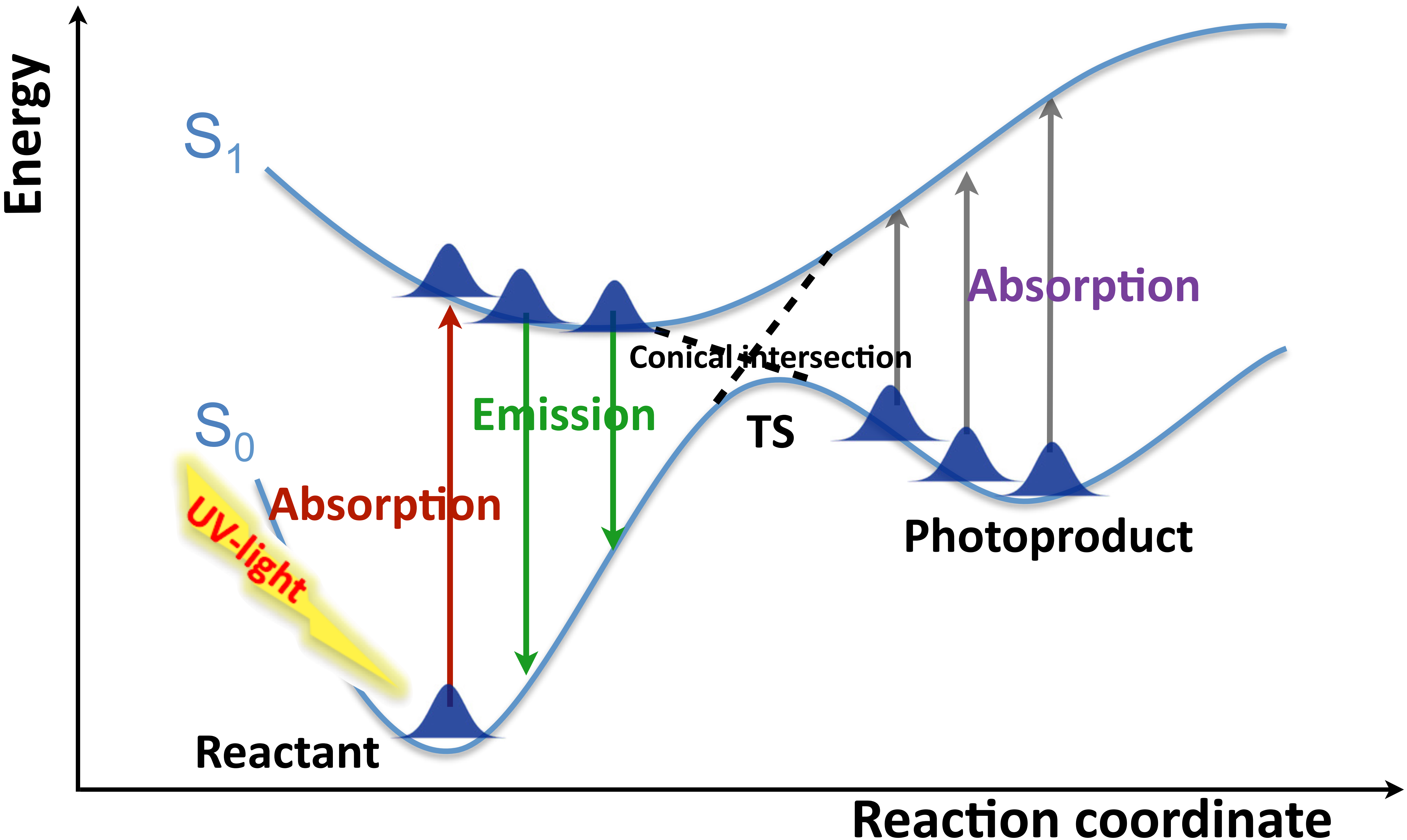




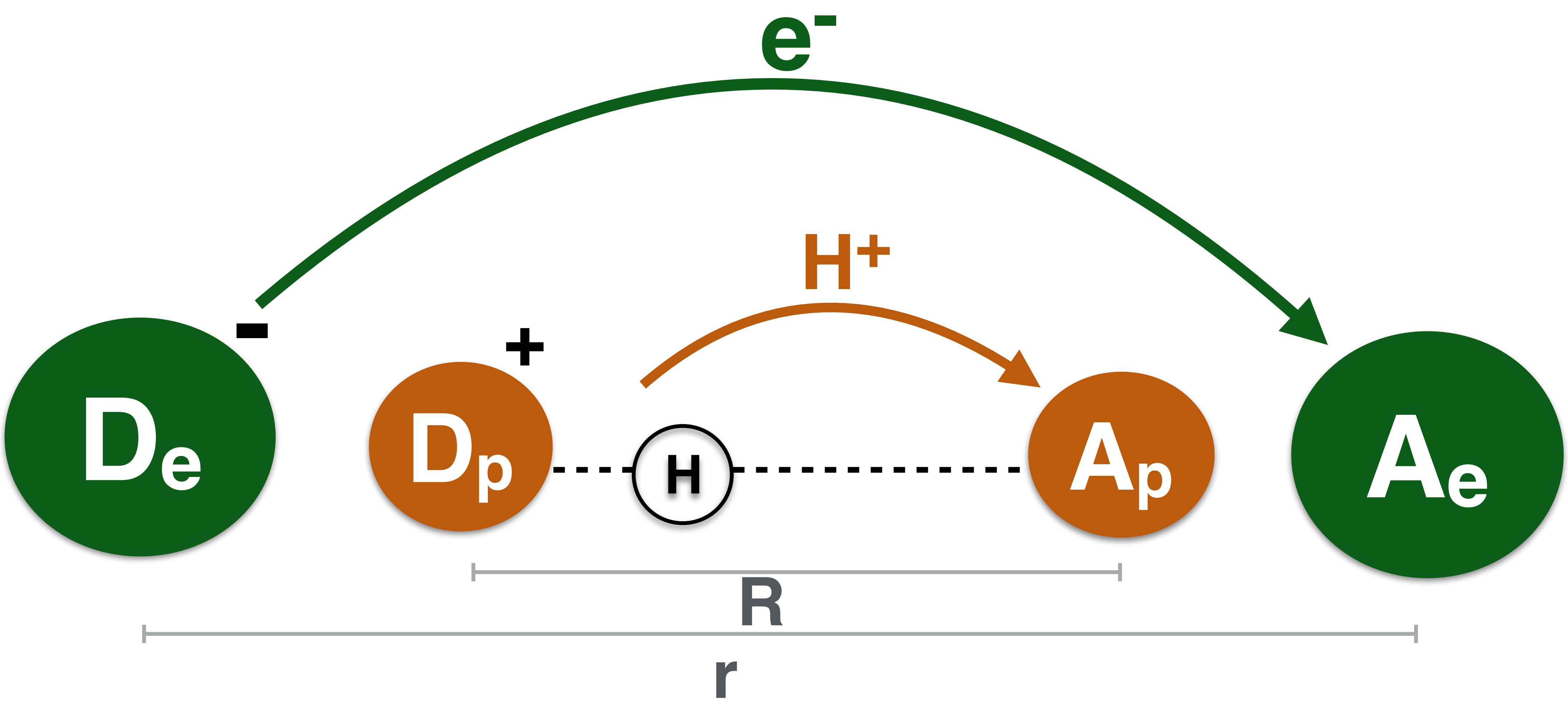


$v_b(r) = \frac{1}{2}k_b(r - r_0)^2$ $v_a(\theta) = \frac{1}{2}k_a(\theta - \theta_0)^2$ $v_d(\varphi) = k_d(1 + \cos(n\varphi - \varphi_0))$ $v_{ij}(r_{ij}) = \frac{C_{ij}^{(12)}}{r_{ij}^{12}} - \frac{C_{ij}^{(6)}}{r_{ij}^{6}}$ $v_c(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$

Theoretical challenges in quantum dynamics



Proton Coupled Electron Transfer (PCET)



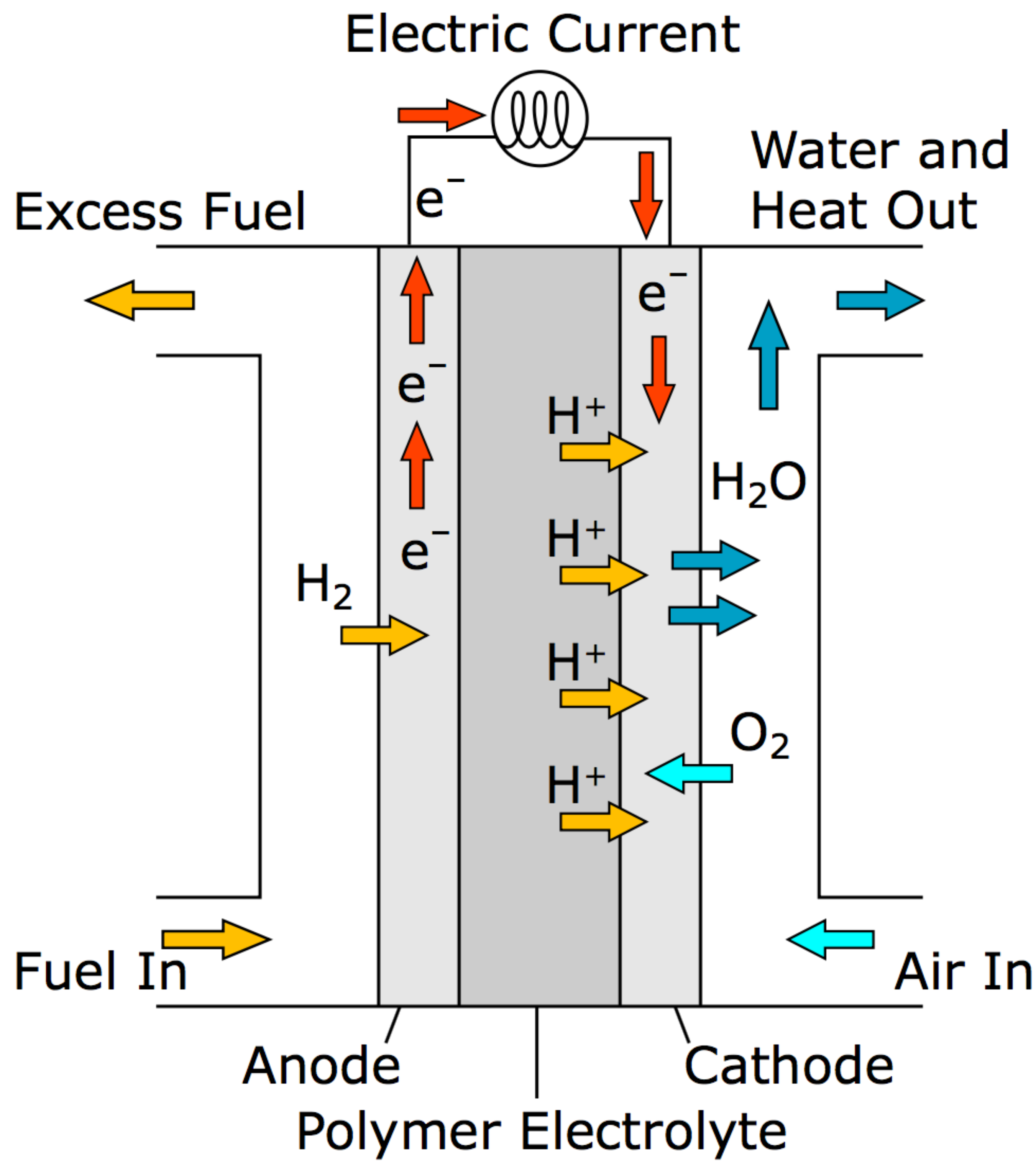
Importance of PCET

Biological processes

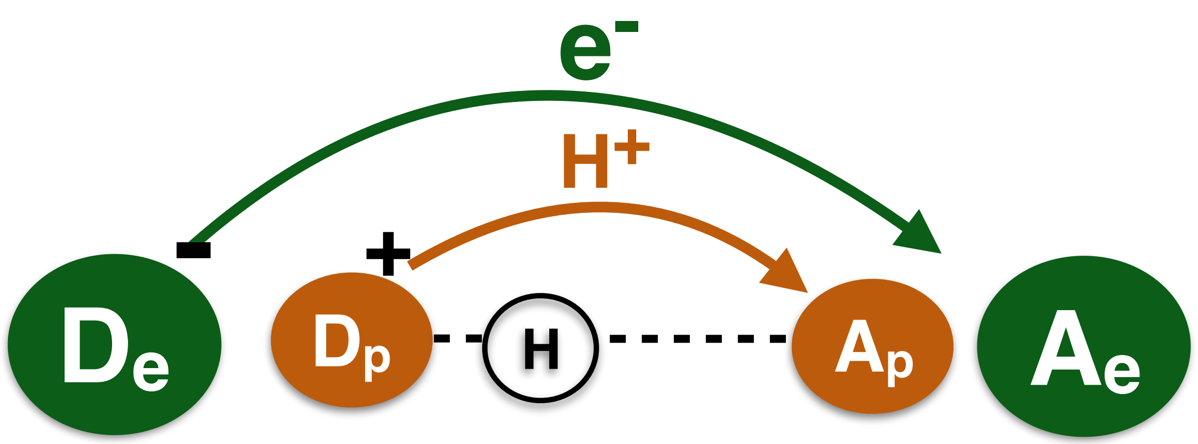
- Photosynthesis
- Respiration
- Enzymatic reactions
- Light-induced DNA repair

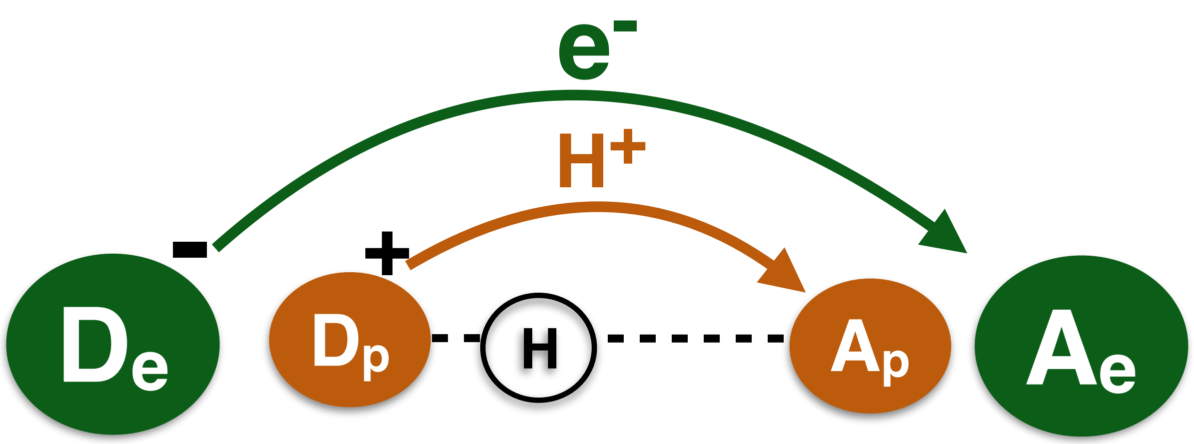
Electrochemical processes

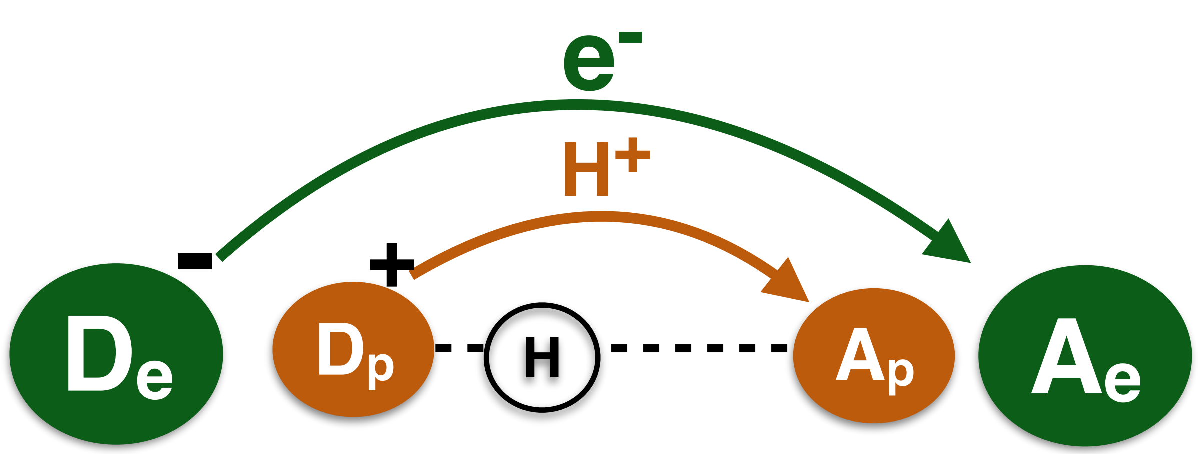
- Fuel cells
- Solar cells
- Energy devices

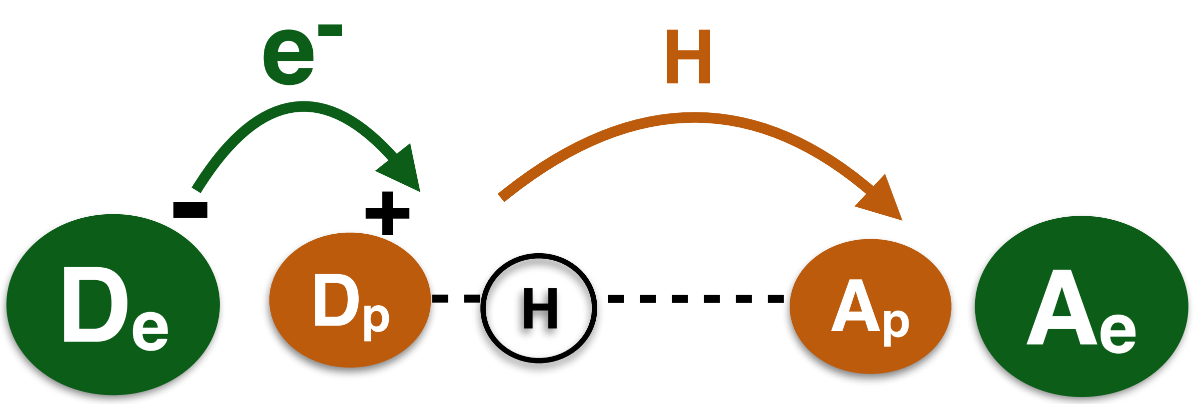


Sequential vs. Concerted

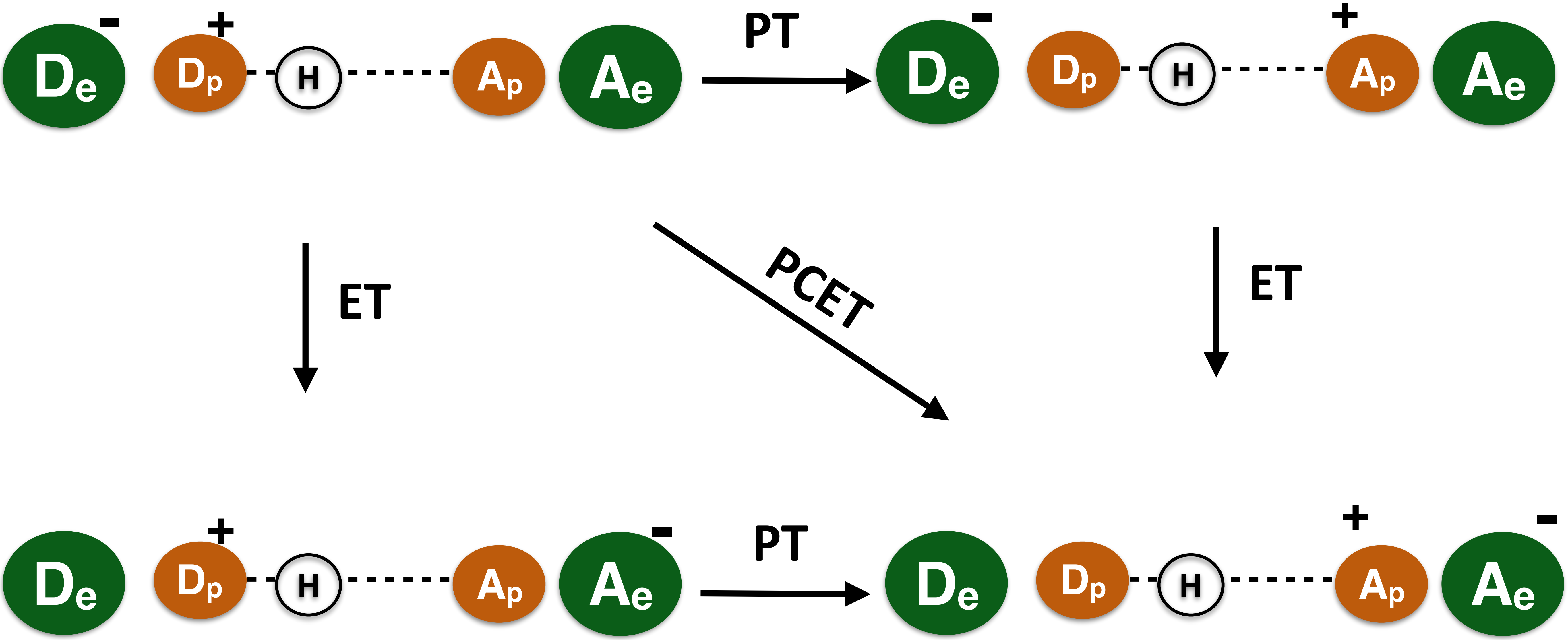






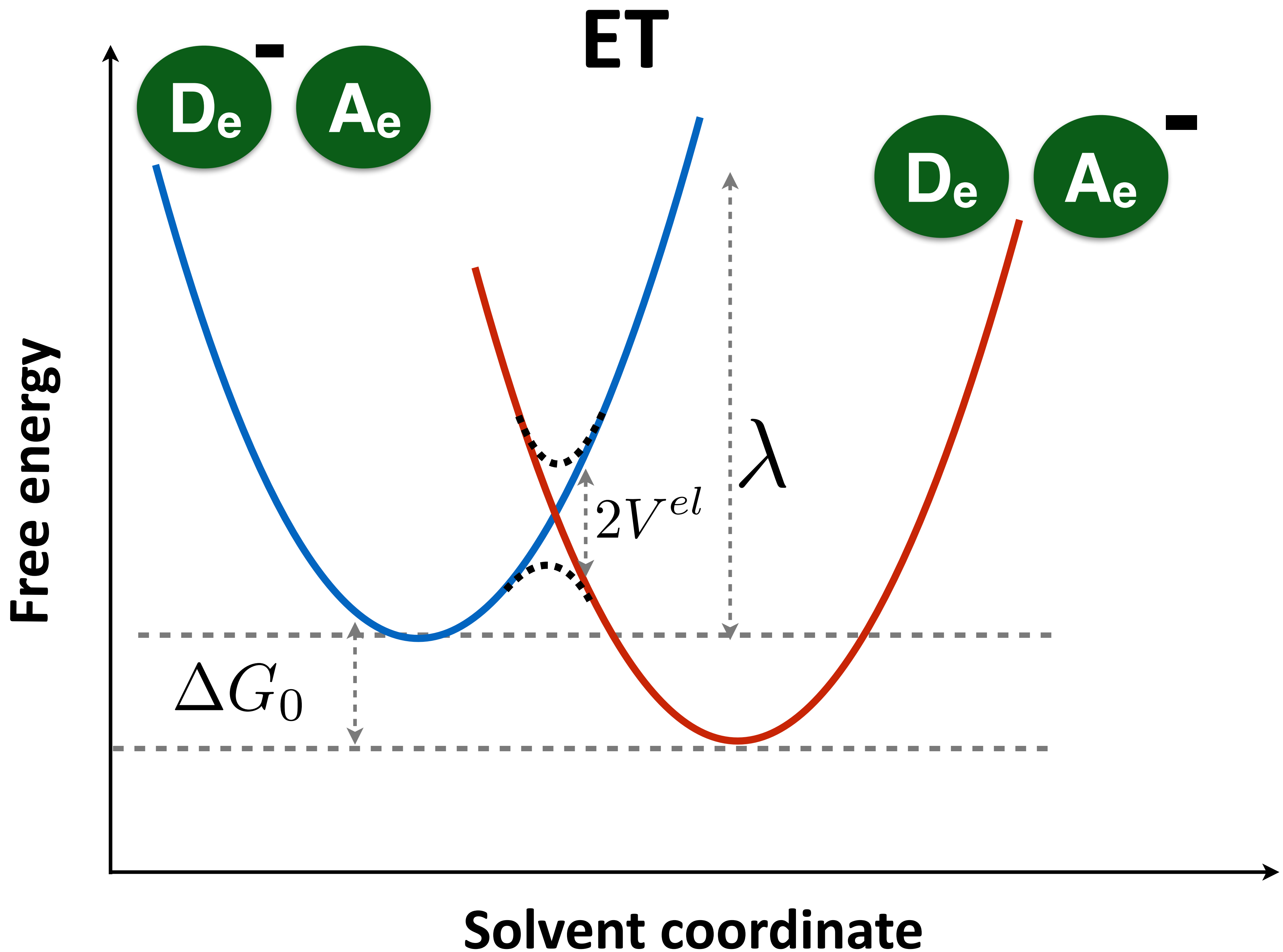


4 States



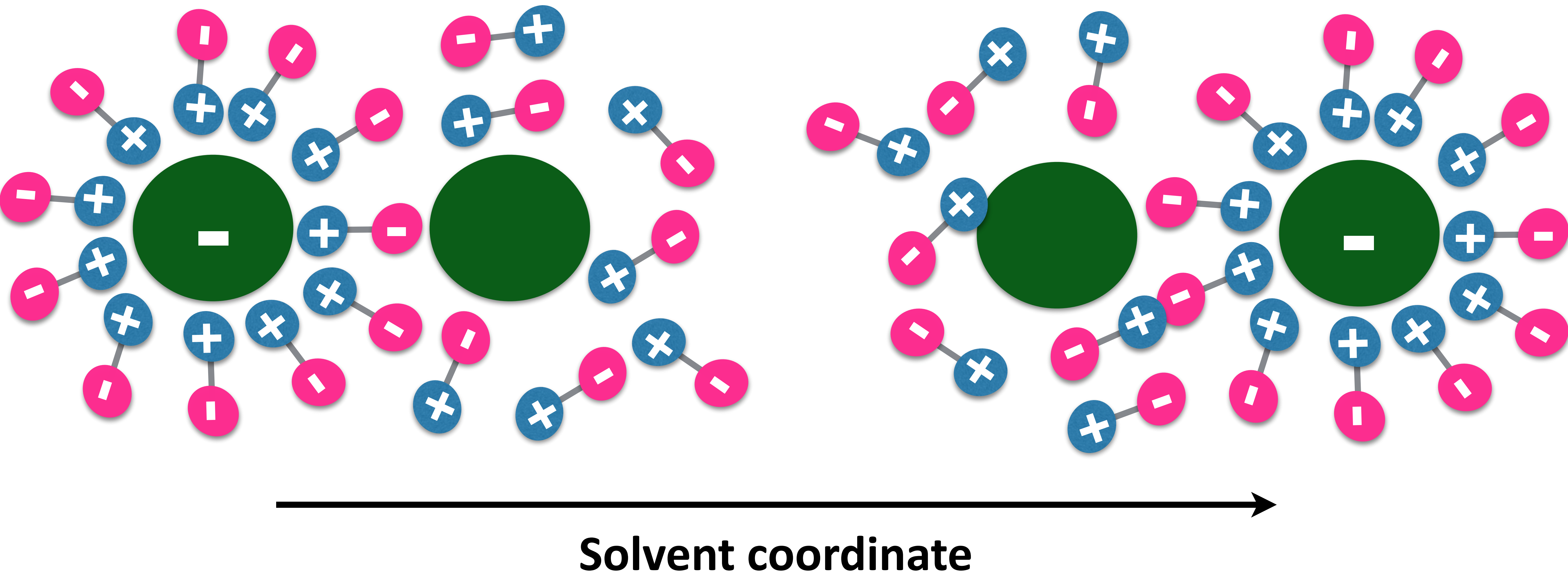
PCET avoids high energy charged intermediates

Single electron transfer (ET)

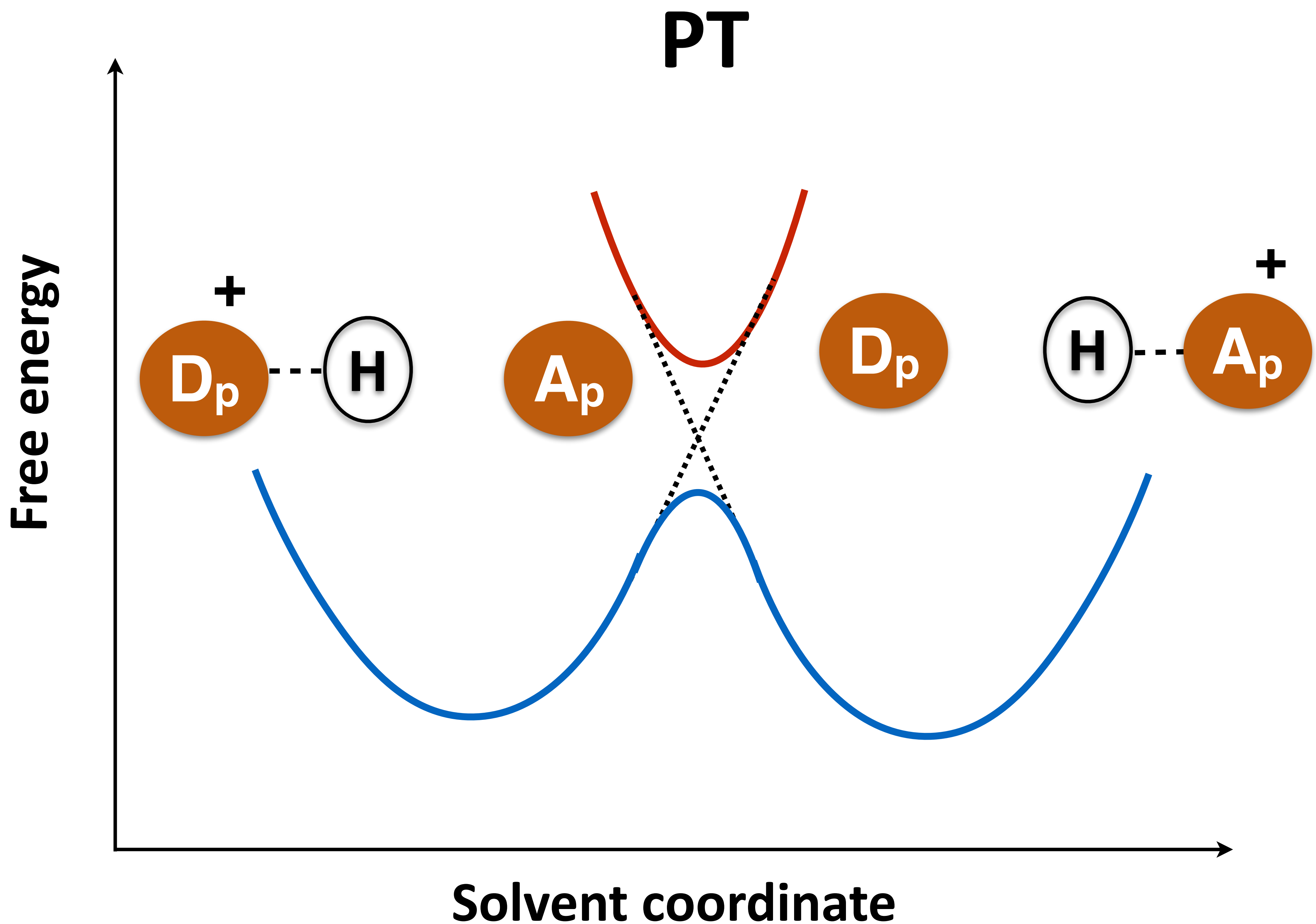


R. A. Marcus, Nobel Lecture, *Angew. Chem. Int. Ed. Engl.*, 32: 1111, **1993**.

Environment coordinate

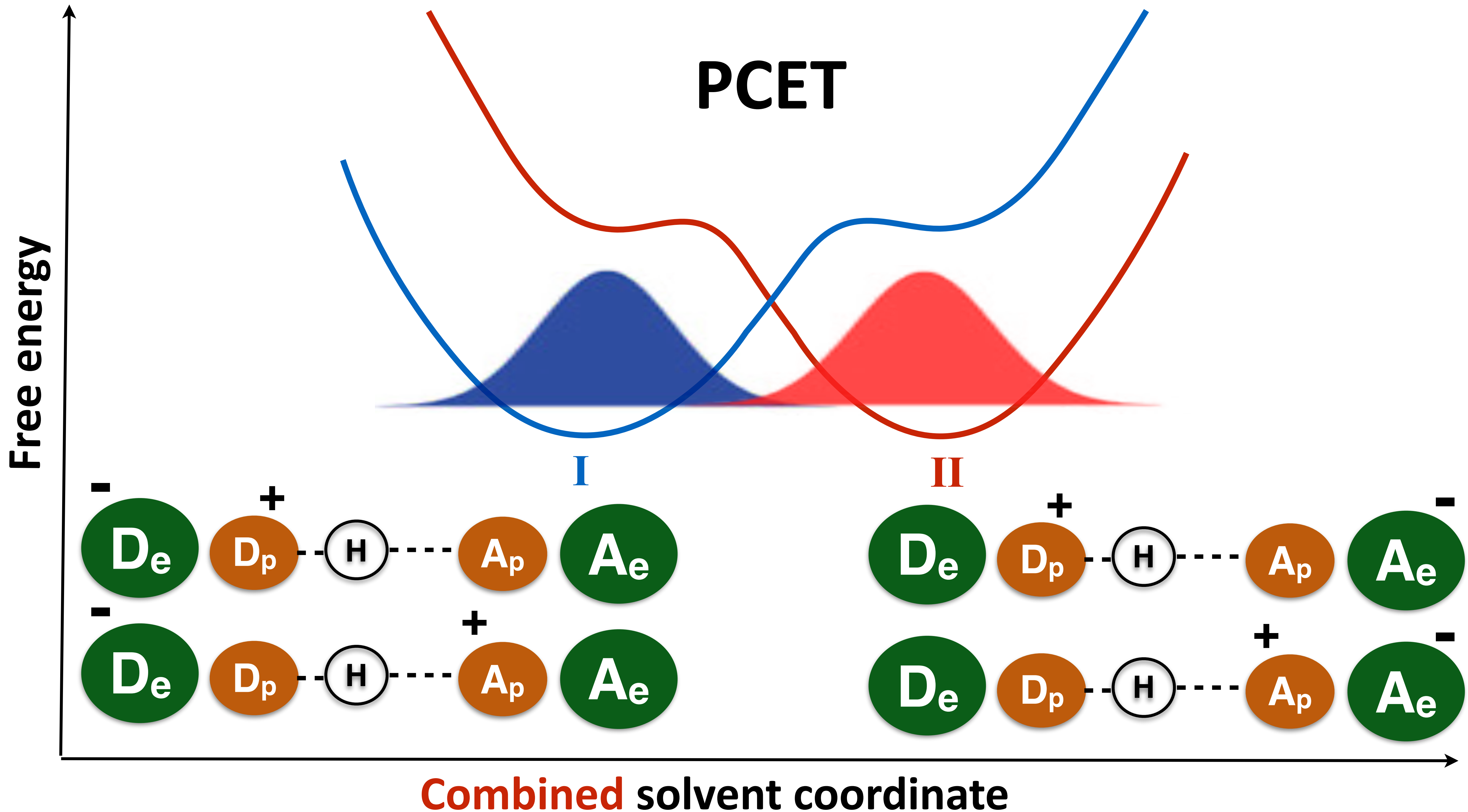


Single proton transfer (PT)



D. Borgis, J.T. Hynes, *Chem. Phys.*, 170, 315, **1993**.

Electron-proton vibronic states



S. Hammes-Schiffer, *J. Am. Chem. Soc.* 137, 8860-8871, **2015**.

Theoretical Challenges of PCET

Wide range of timescales

- Electrons
- Transferring protons
- Solute modes
- Environment electronic/nuclear polarization

fs → ps

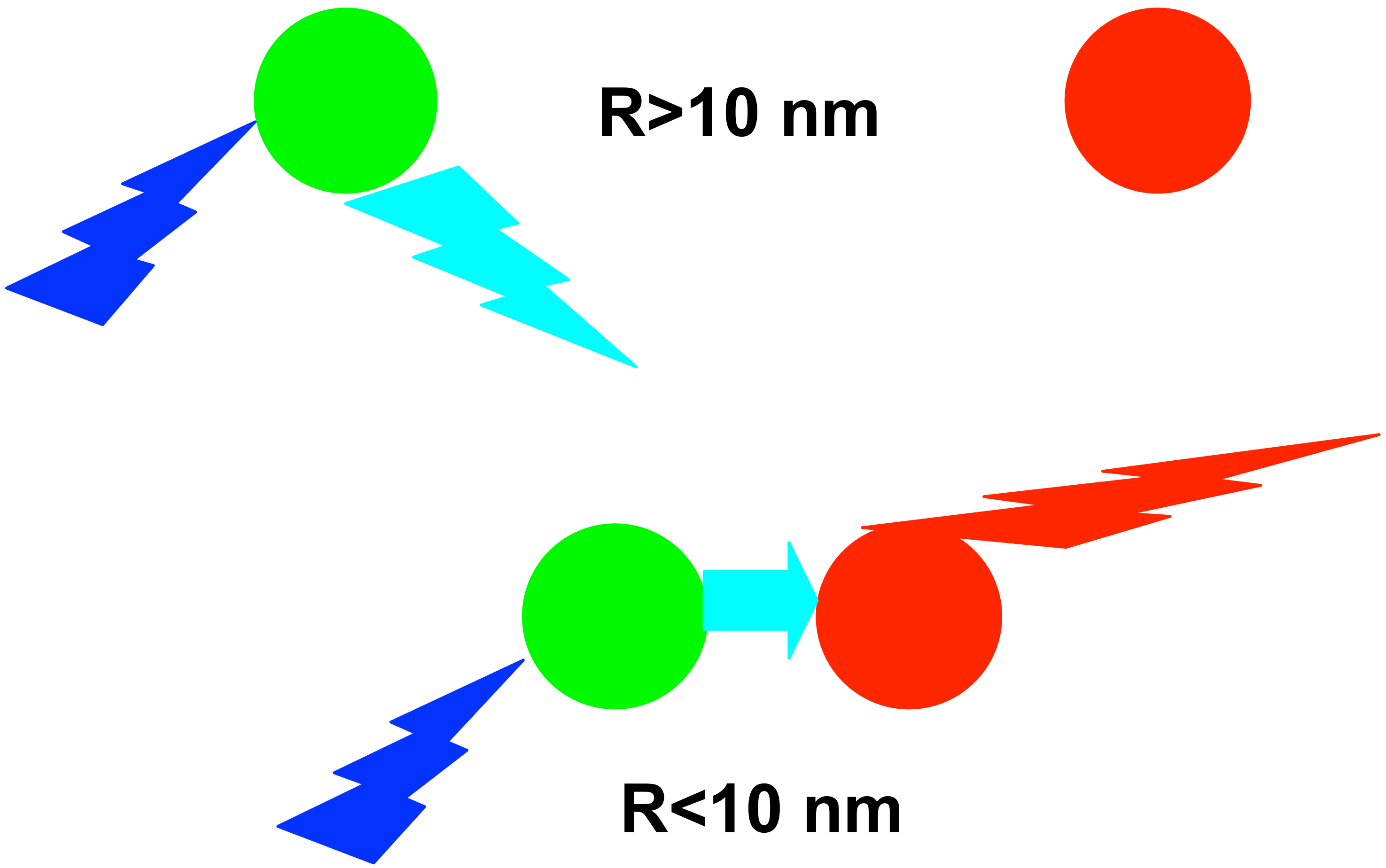
Quantum behavior of electrons and protons

- Hydrogen/proton tunneling
- Excited electronic/vibrational states
- Mixed electron-nuclear motion (non-adiabatic effect)

Role of the Environment

- Size of the system

Förster resonance energy transfer (FRET)



Förster resonance energy transfer (FRET)

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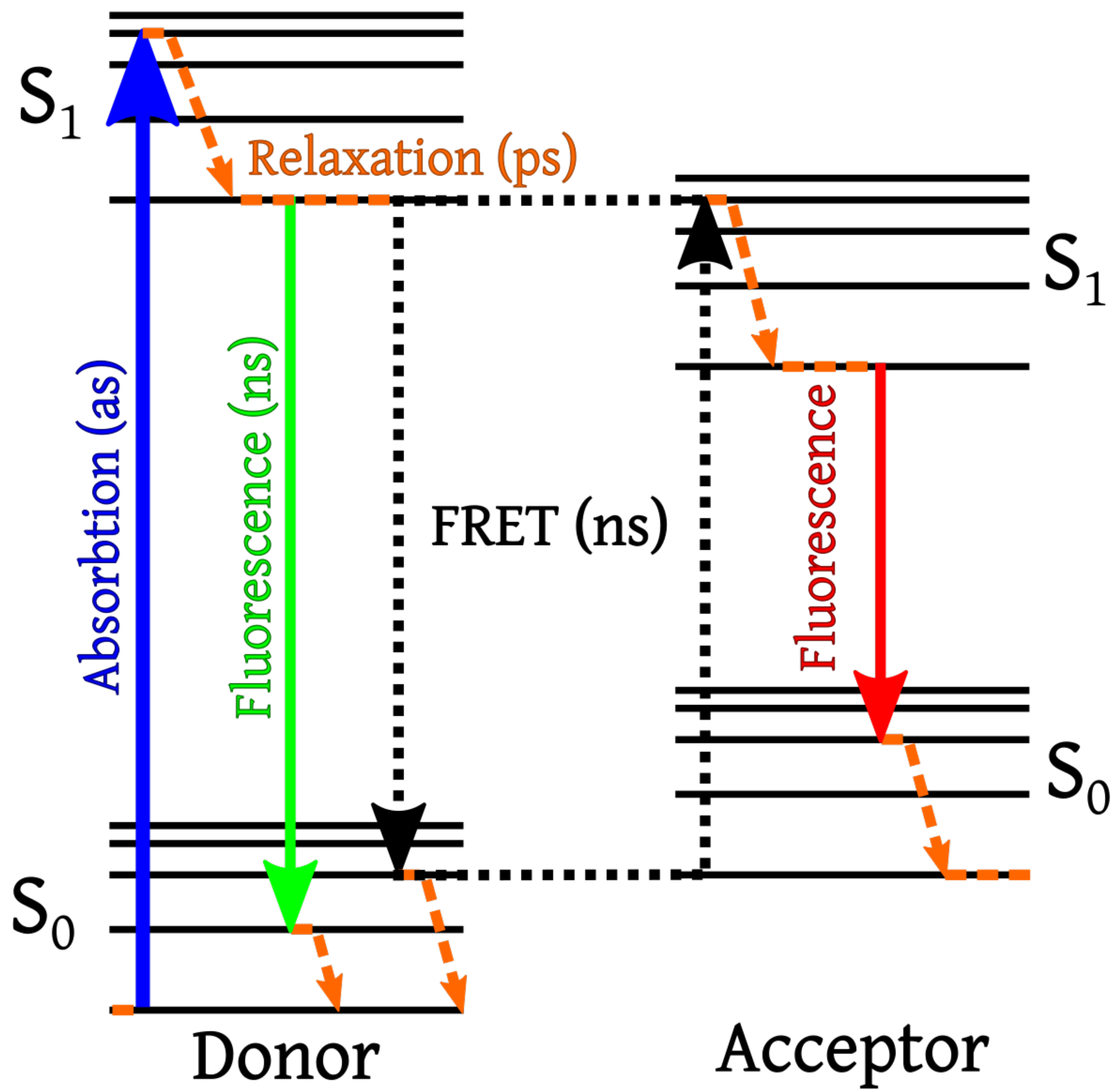
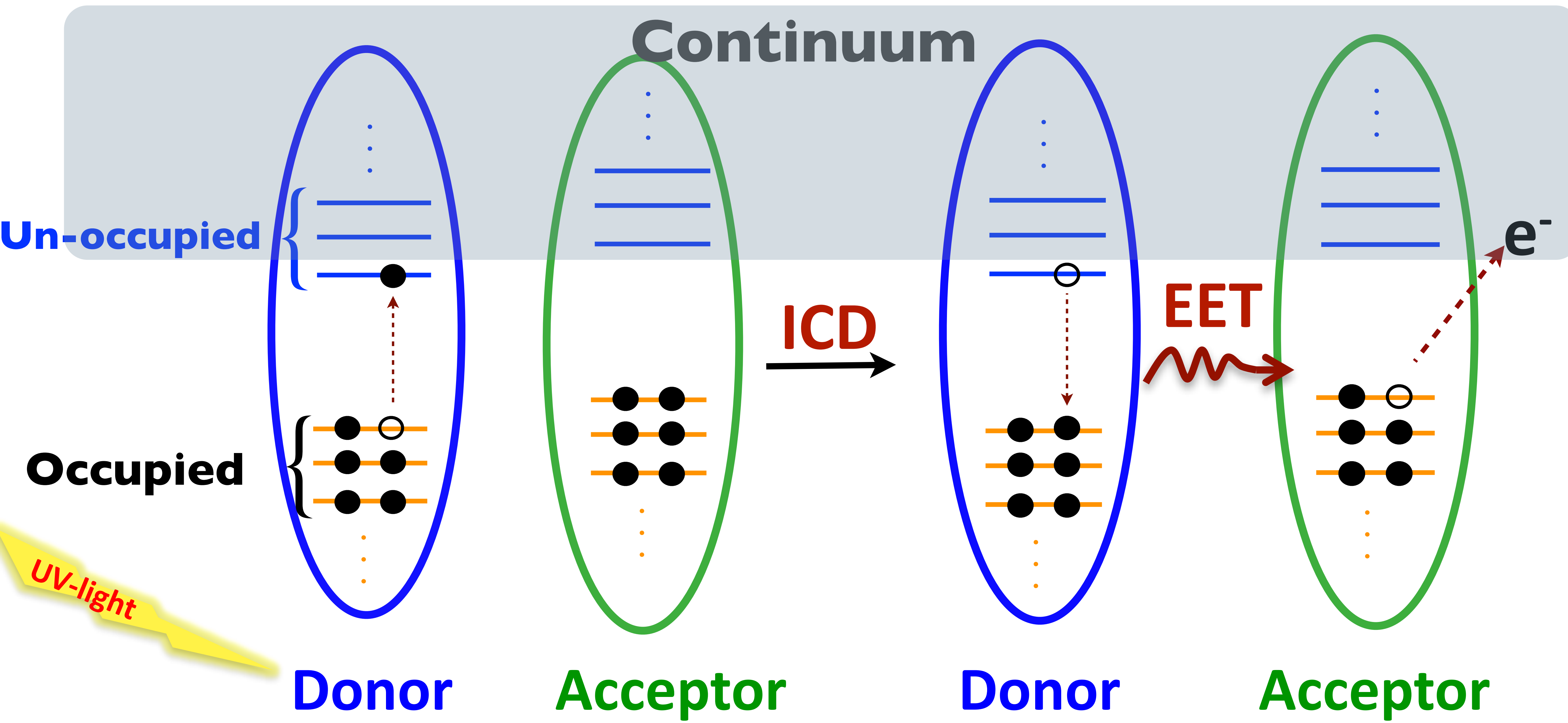
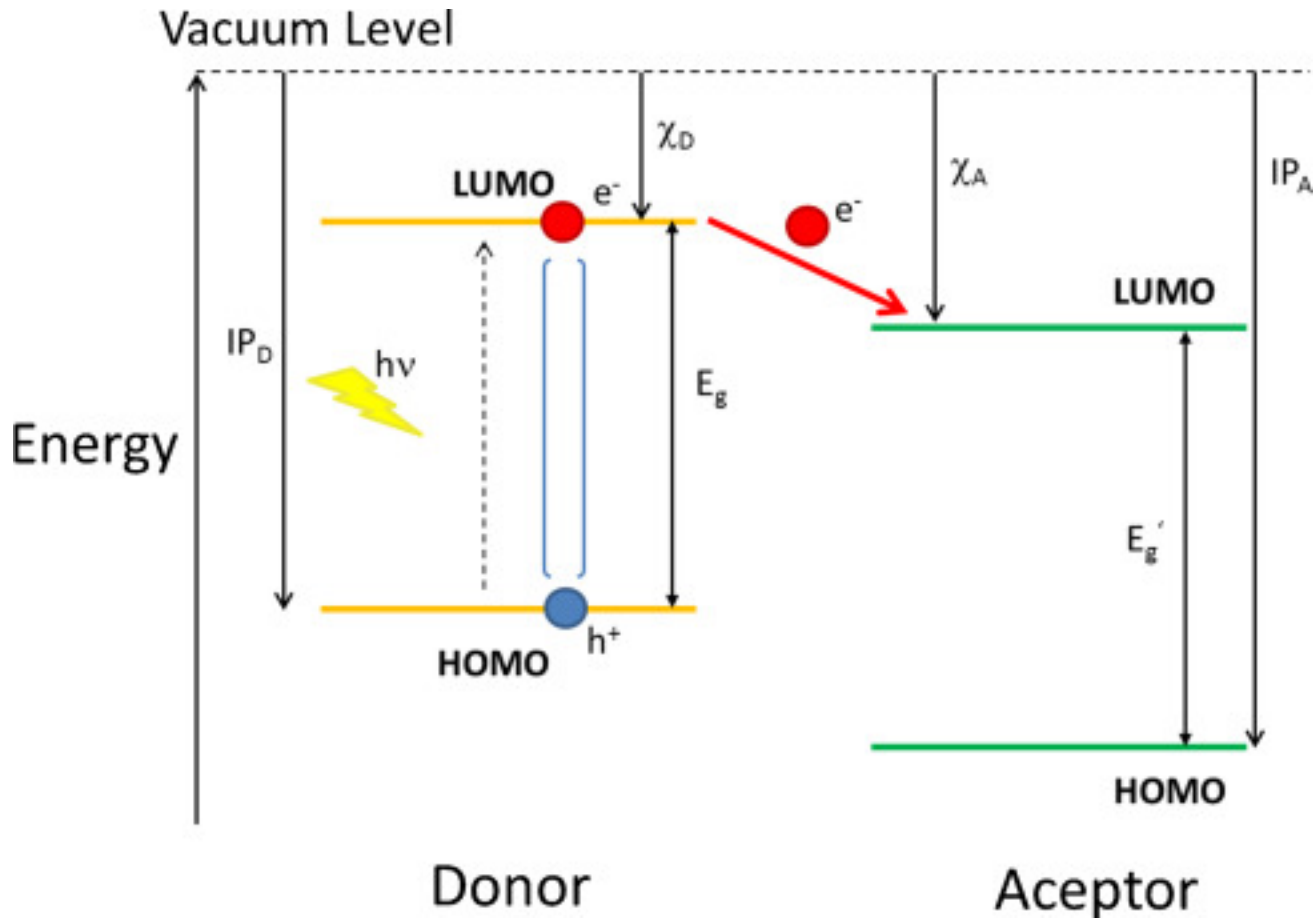


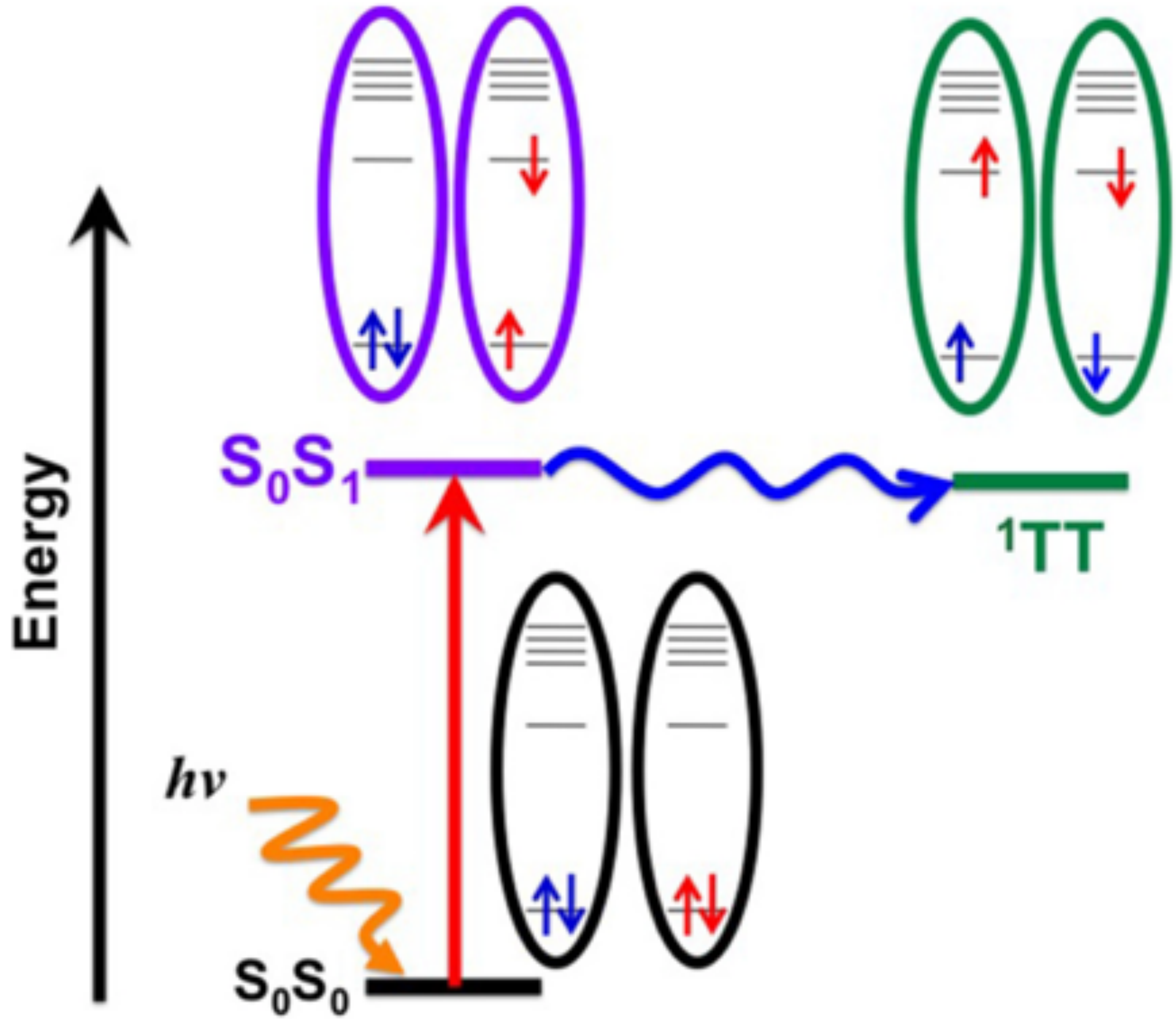
Intermolecular Coulombic decay



Organic photovoltaic cells



Singlet Fission



Photochemical processes in complex environments

Quantum dynamics

- Time-dependent Schrödinger eq. for nuclei
- Multi-configuration time-dependent Hartree and its multi-layer variant
- Explicit/model potential energy surfaces
- Variational multi-configuration Gaussian (vMCG)
- Highly accurate TR spectra

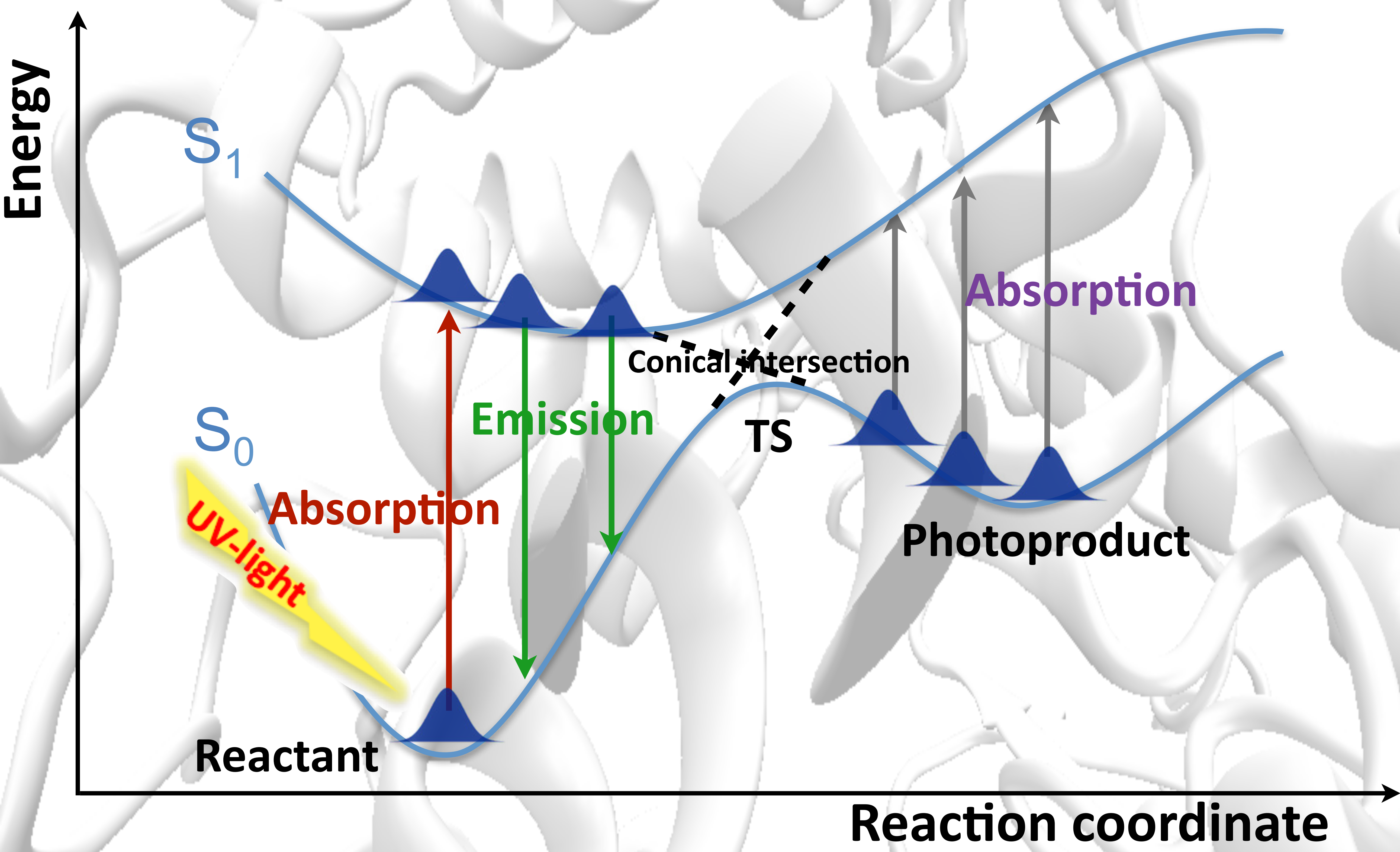
Quantum chemistry

- Time-independent Schrödinger eq. for electrons
- Ground and excited electronic states methods
- Explicit and implicit environmental methods
- Quantum mechanics/molecular mechanics (QM/MM)
- QM/Effective fragment potential

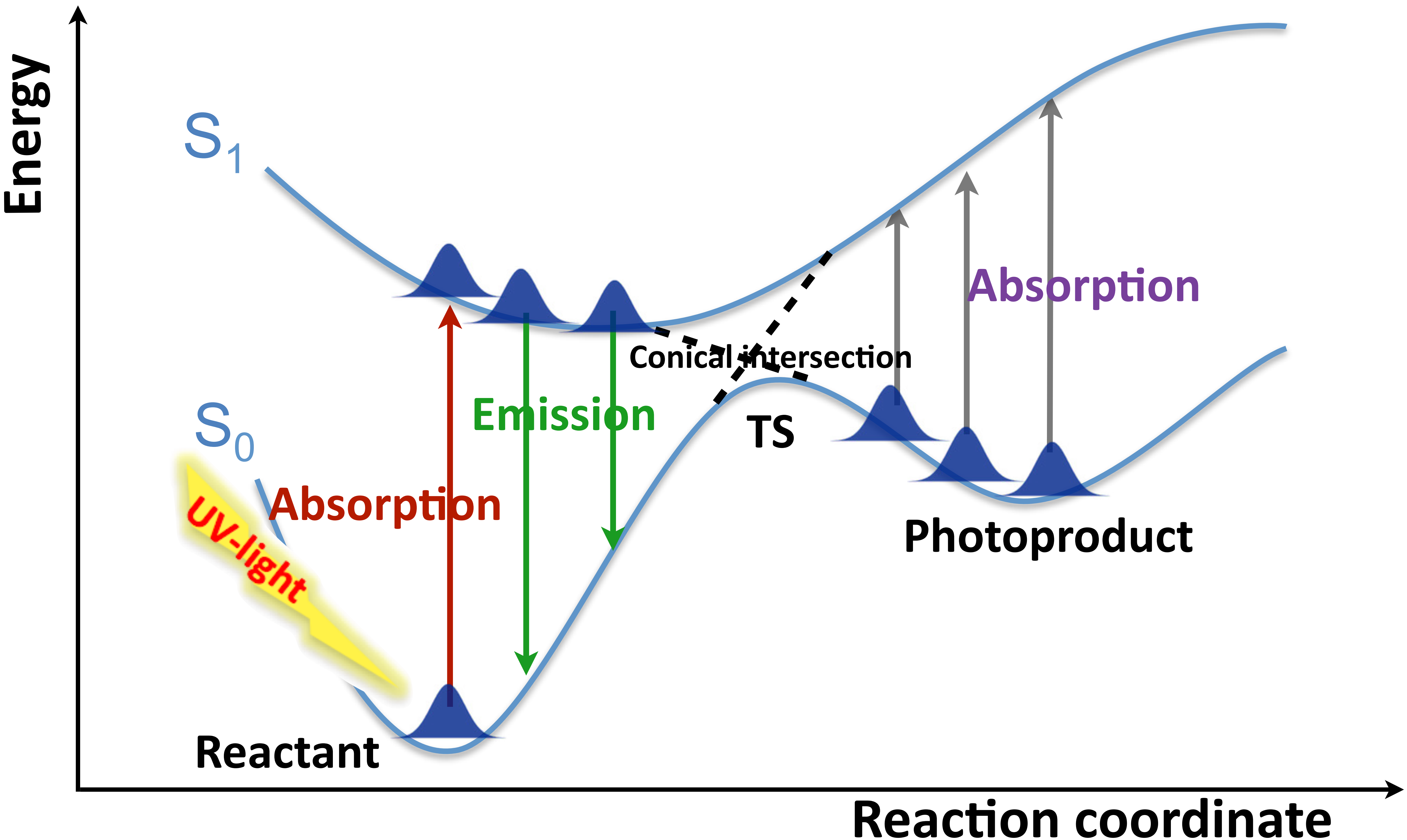
Time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

Theoretical challenges in quantum dynamics



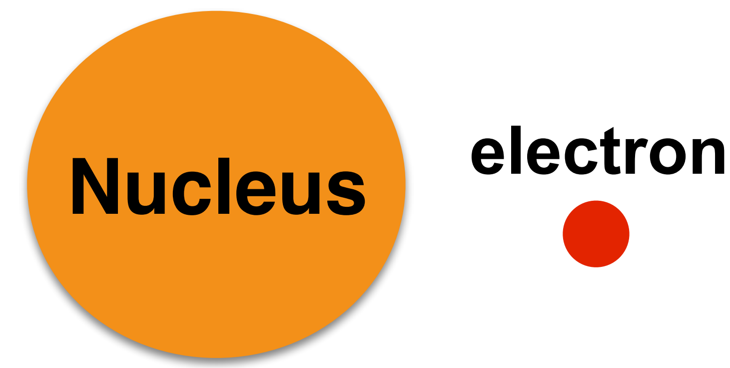
Theoretical challenges in quantum dynamics



Born-Oppenheimer approximation

- Technique to de-couple the motion of nuclei and electrons

$$H = T_e + T_N + U(r, Q)$$



- Exact eigenstates $\Psi(r, Q) = \sum_n \chi_n(Q)\Phi_n(r, Q)$

- Coupled equations for the expansion coefficients:

$$[T_N + V_n(Q) - E]\chi_n(Q) = \sum_m \widehat{\Lambda}_{nm}\chi_m(Q)$$

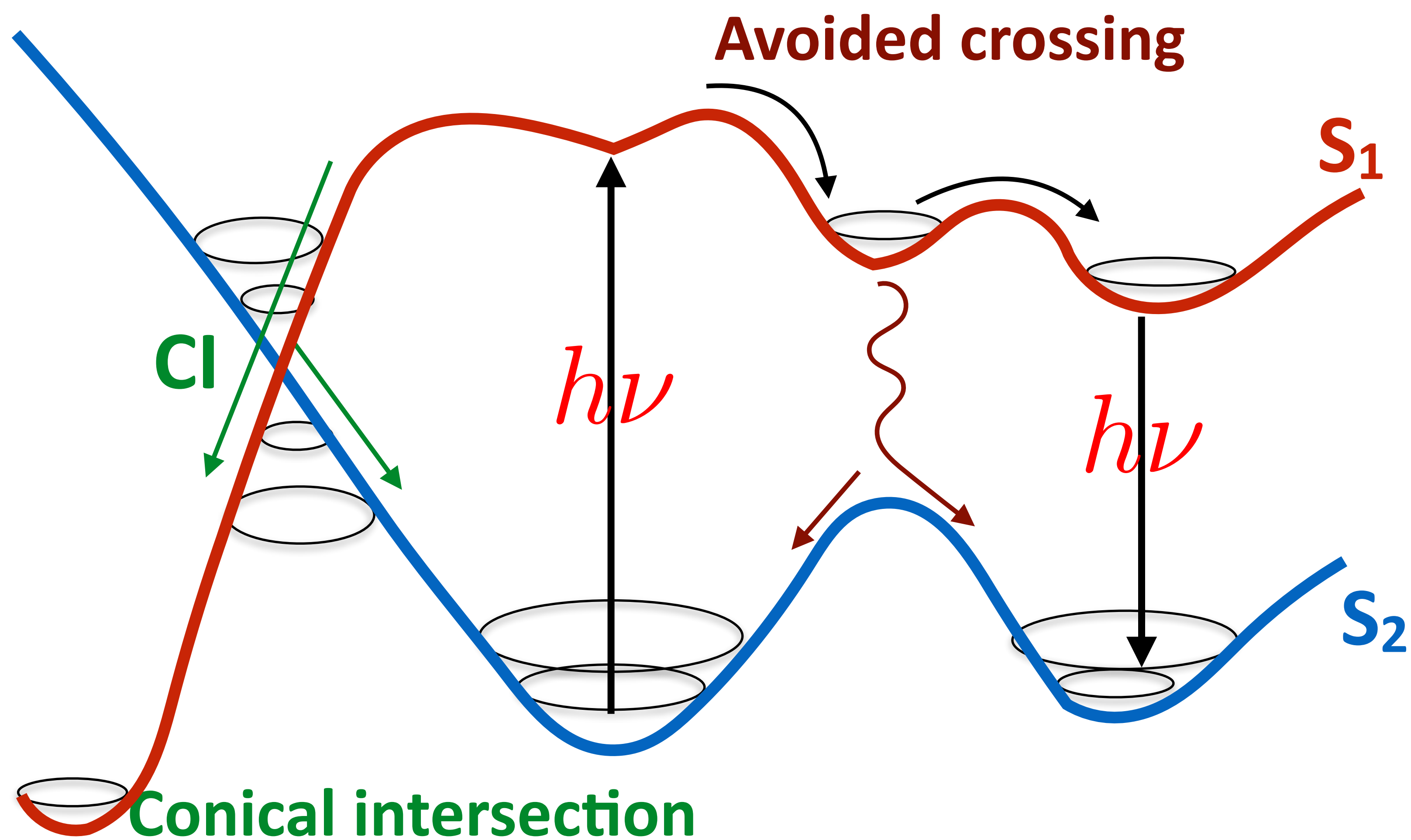
- Non-adiabatic operator

$$\begin{aligned}\hat{\Lambda}_{nm} &= \hbar^2 \sum_i \frac{1}{M_i} \langle \Phi_n | \frac{\partial}{\partial Q_i} | \Phi_m \rangle \frac{\partial}{\partial Q_i} + \langle \Phi_n | T_N | \Phi_m \rangle \\ &= \sum_{i=1}^{M} \frac{1}{M_i} F_{nm}^{(i)} \frac{\partial}{\partial Q_i} - G_{nm}\end{aligned}$$

Born-Oppenheimer app. & its breakdown

- Derivative coupling terms:

$$\mathbf{F}_{nm}(\mathbf{r},\mathbf{Q}) = \frac{\langle \Phi_n(\mathbf{r},\mathbf{Q}) | (\nabla H_e) | \Phi_m(\mathbf{r},\mathbf{Q}) \rangle}{V_m(\mathbf{r},\mathbf{Q}) - V_n(\mathbf{r},\mathbf{Q})}$$



Conical Intersection dimension

- 3N-6 for non-linear molecules

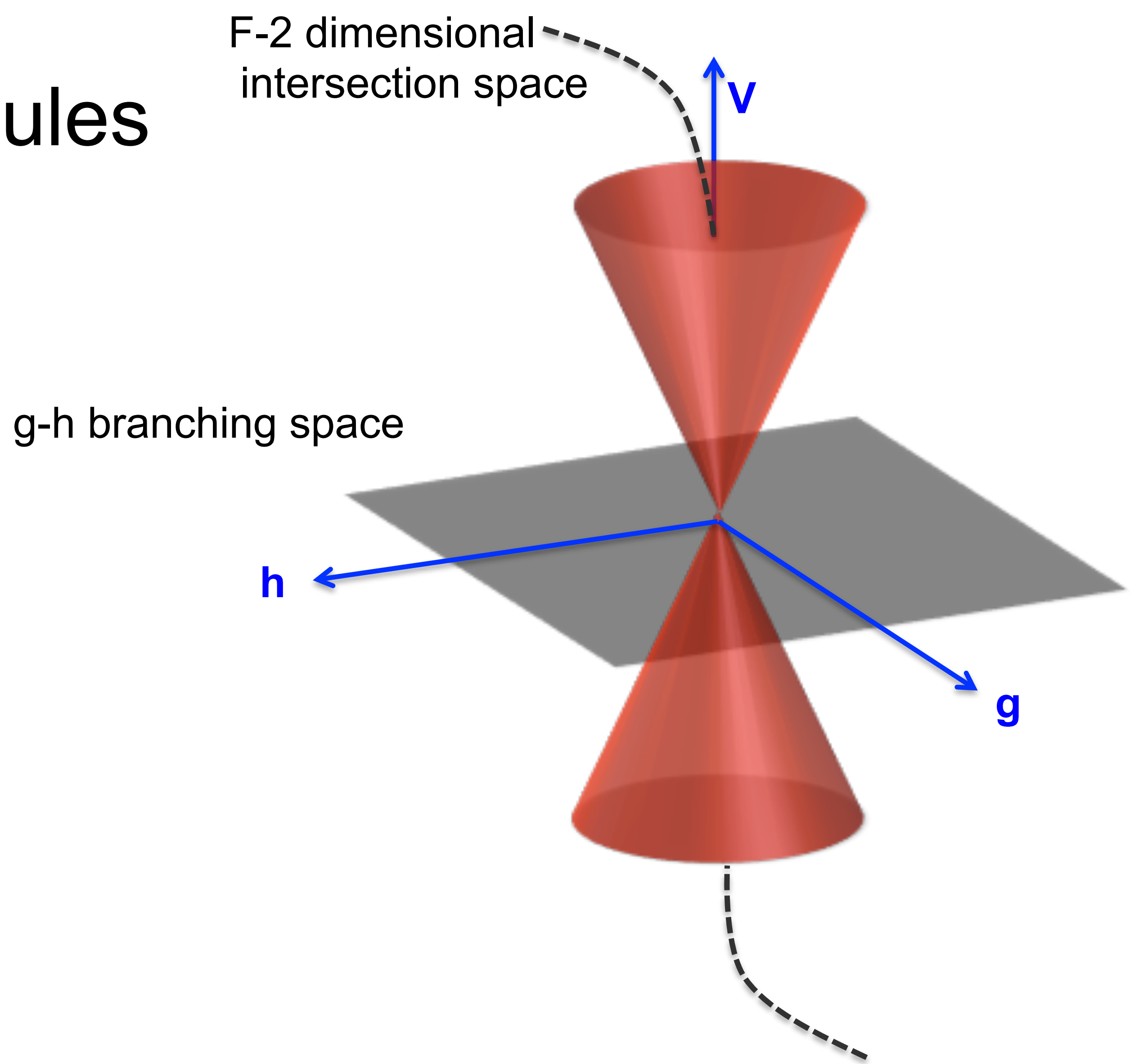
3N-6 - 2 = 3N - 8

- 3N-5 for linear molecules

3N-5 - 2 = 3N - 7

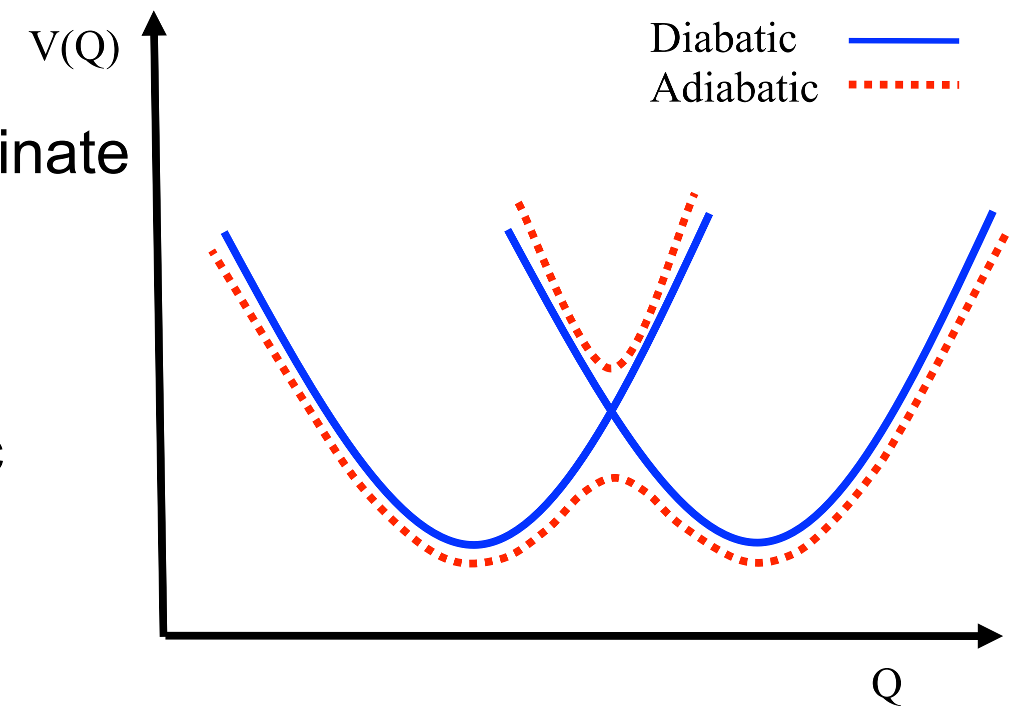
N=2

3 x 2 -5 -2 = -1



Diabatic representation

- Replace the adiabatic functions $\Phi(r,Q)$ by new functions $\phi(r,Q)$



- Smooth and slowly varying functions of the nuclear coordinate

$$F_{nm} \longrightarrow 0$$

Construction by a unitary transformation of the adiabatic electronic states within a suitable subspace:

Strictly diabatic
Quasidiabatic

$$\phi^{diabatic} = \mathbf{S}\Phi^{adiabatic}$$

- Coupled equations in the diabatic representation:

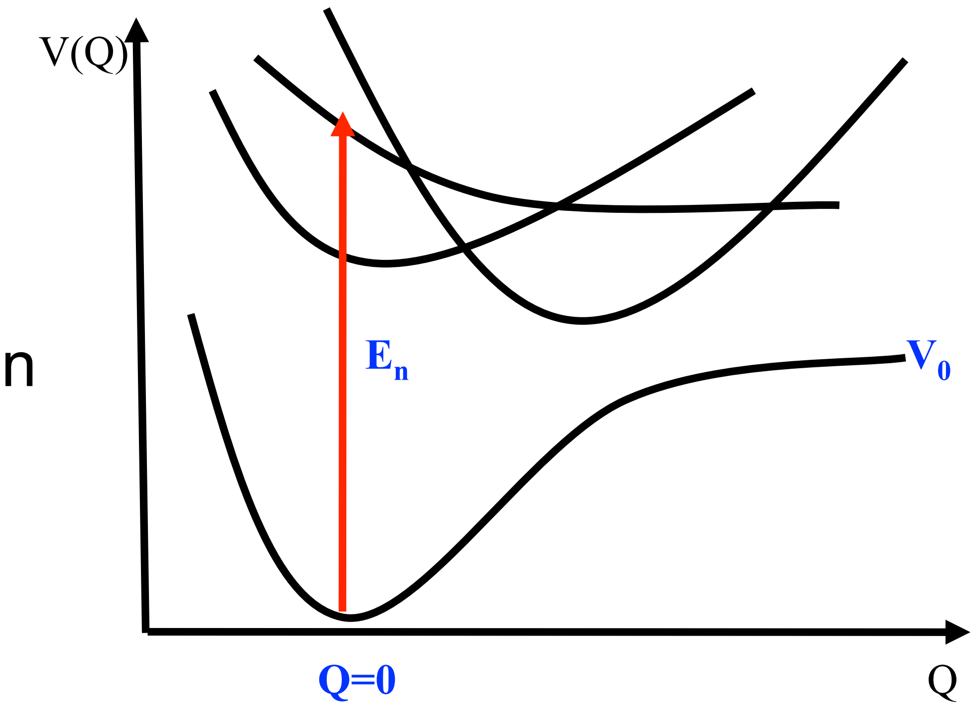
$$(T_N + W_{nn}(\mathbf{Q}) - E)\ \tilde{\chi}_n(\mathbf{Q}) = \sum_{n \neq m} W_{nm}(\mathbf{Q})\ \tilde{\chi}_m(\mathbf{Q})$$

Vibronic Coupling Model

- Matrix Hamiltonian in the diabatic basis:

$$H = T_N \mathbf{1} + \mathbf{W}(\mathbf{Q})$$

- Expanding $W(Q)$ about a reference nuclear configuration Q=0 , up to low-order terms in Q



$$W_{nn}(Q) = V_0(Q) + E_n + \sum_i k_i^{(n)} Q_i + \sum_{i,j} \gamma_{ij}^{(n)} Q_i Q_j + \cdots$$

$$W_{nm}(Q) = \sum_i \lambda_i^{(n,m)} Q_i + \cdots \qquad (n \neq m)$$

H. Köppel, W. Domcke, and L. S. Cederbaum, Adv. Chem. Phys. **57**, 59 (1984)

Coupling constants

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- Intrastate Coupling Constant $\kappa_i^{(n)} = \frac{\partial V_n(\mathbf{Q})}{\partial Q_i}|_{\mathbf{Q=0}}$
- Quadratic Coupling Constant $\gamma_i^{(n)} = \frac{\partial^2 \Delta V_n(\mathbf{Q})}{\partial Q_i^2}|_{\mathbf{Q=0}}$
- Interstate Coupling Constant $\lambda_i^{nm} = \sqrt{\frac{1}{8}\frac{\partial^2 (\Delta V_{nm})^2}{\partial Q_i^2}|_{\mathbf{Q=0}}}$
- 3 states problem

$$W_{eff}^{nm}(Q_i) = \begin{pmatrix} E_n & \lambda_i^{nm} Q_i \\ \lambda_i^{nm} Q_i & E_m \end{pmatrix} \qquad W_{eff}^{nml}(Q_i) = \begin{pmatrix} E_n & 0 & \lambda_i^{nl} Q_i \\ 0 & E_m & \lambda_i^{ml} Q_i \\ \lambda_i^{nl} Q_i & \lambda_i^{ml} Q_i & E_l \end{pmatrix}$$

Symmetry selection rule

- Symmetry selection rules:

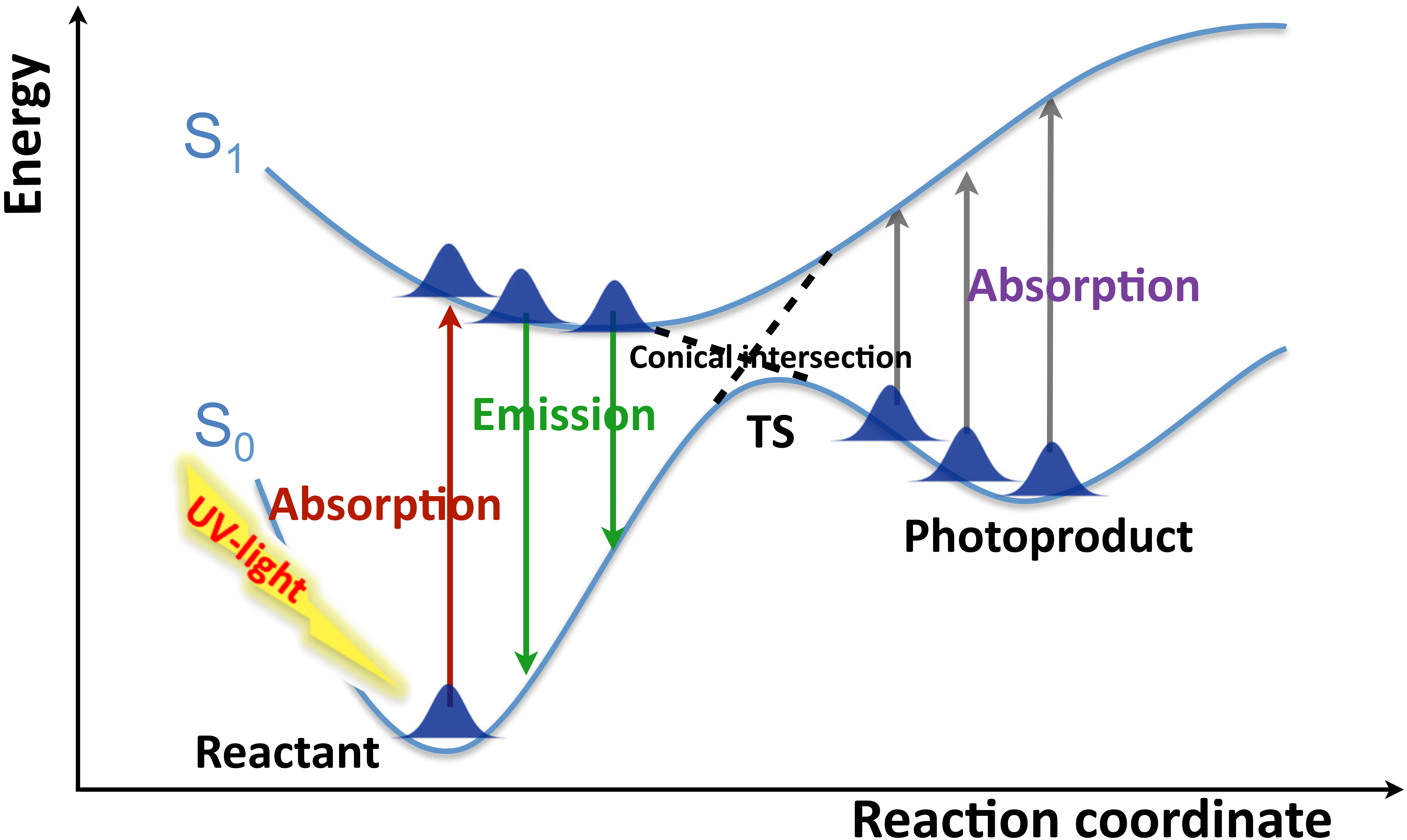
$$\Gamma_n \times \Gamma_{Q_i} \times \Gamma_m \supset \Gamma_A$$

2 states problem

- Vibronic coupling Hamiltonian for 2 states problem with N totally symmetric and M non-totally symmetric modes

$$H = (T_N + V_0)\mathbf{1} + \begin{pmatrix} E_1 + \sum_{i=1}^{N} \kappa_i^{(1)} Q_{gi} & \sum_{j=1}^{M} \lambda_j^{(1,2)} Q_{uj} \\ \sum_{j=1}^{M} \lambda_j^{(1,2)} Q_{uj} & E_2 + \sum_{i=1}^{N} \kappa_i^{(2)} Q_{gi} \end{pmatrix}$$

Theoretical challenges in quantum dynamics



Vibronic-coupling dynamics

Time-independent approach vs. Time-dependent approach

- Diagonalization of a Hamiltonian
- Eigenvalue problem

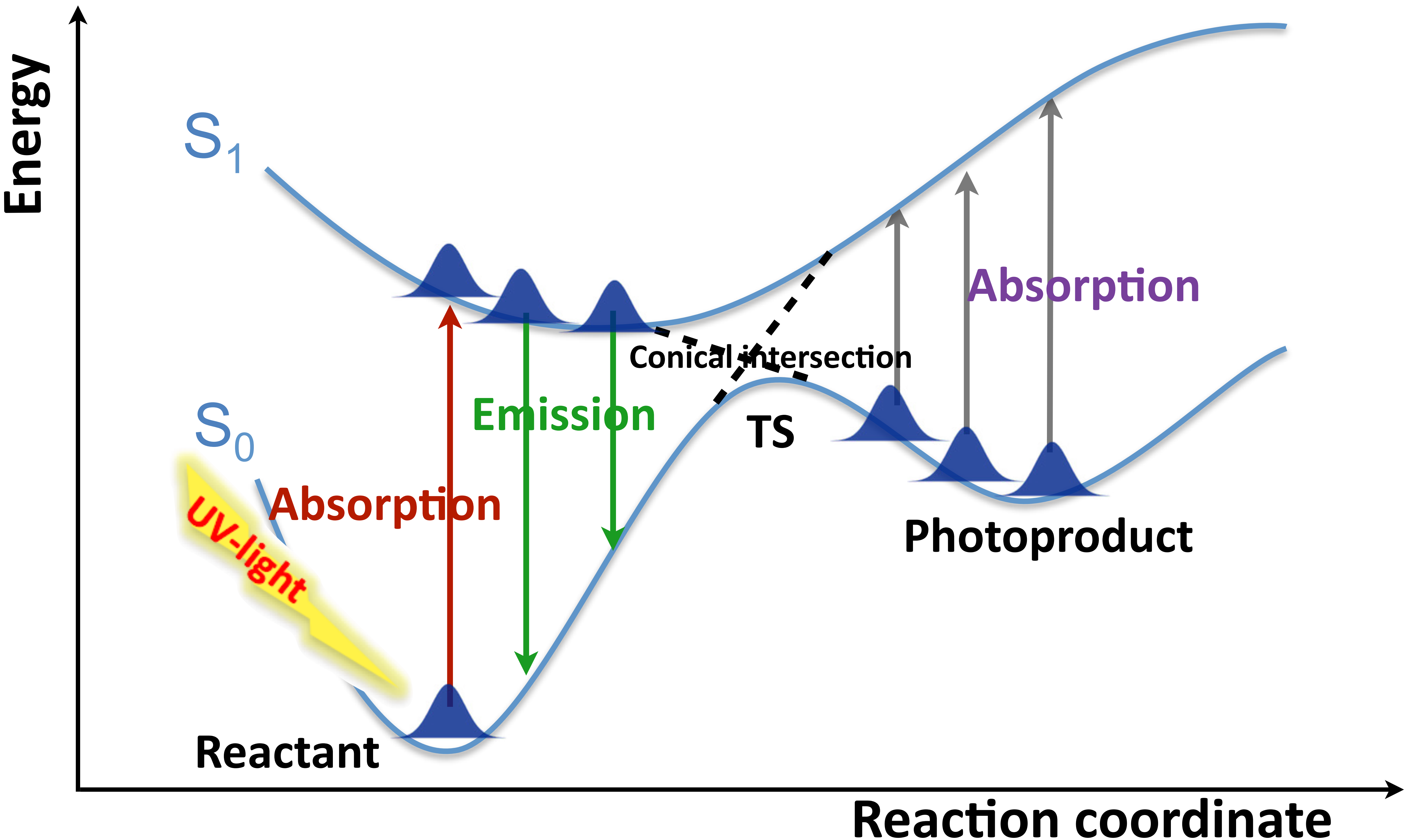
$$\hat{H}\,\Psi = E\,\Psi$$

- Propagation of a wavepacket
- Initial value problem

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\,\Psi$$

- Preparation of the initial wave packet
- Propagation of the wave packet
- Analysis of the propagated wave packet i.e. determining observable quantities

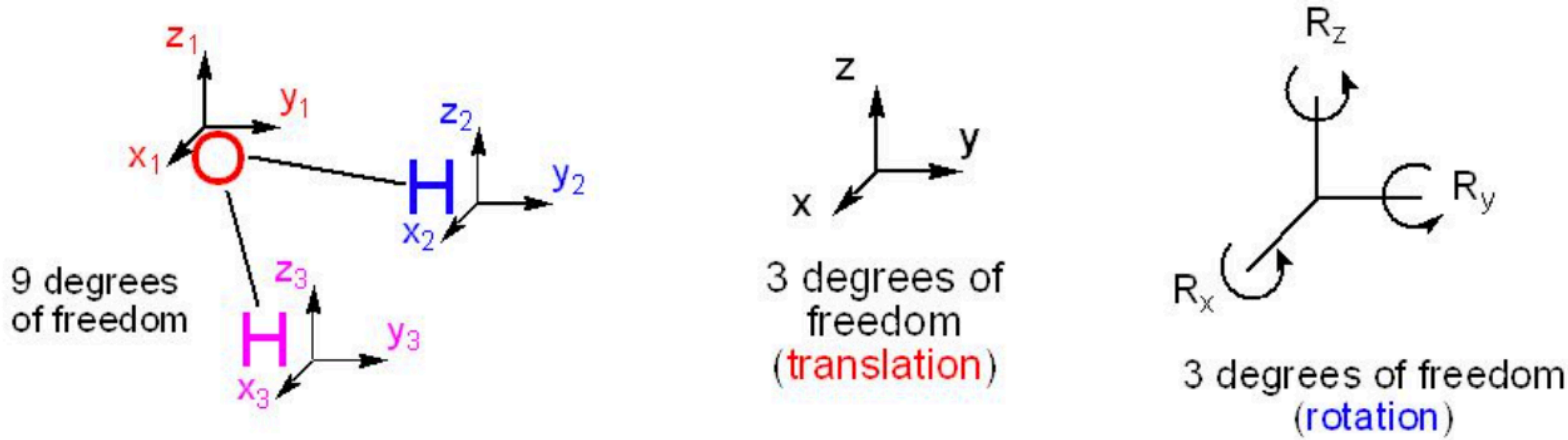
Theoretical challenges in quantum dynamics

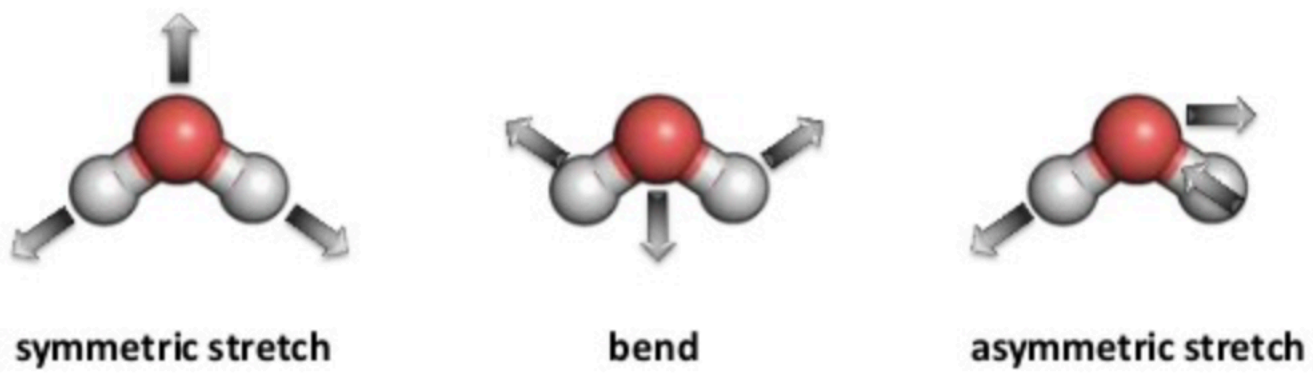


Degrees of freedoms (DOF)

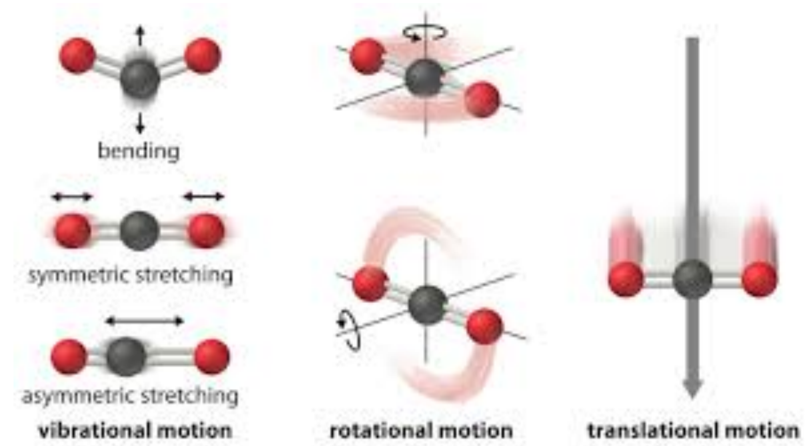
- 3N-5 for linear molecules
- 3N-6 for non-linear molecules

	Linear	Nonlinear
Translational	3	3
Rotational	2	3
Vibrational	**3N-5**	**3N-6**





This gets large very quickly !



Nuclear wave-packet propagation

- Exact methods

$$\Psi(Q_1,\dots,Q_f,t)=\sum_{j_1}^{N_1}\cdots\sum_{j_f}^{N_f}A_{j_1\dots j_f}(t)\prod_{\kappa=1}^{f}\chi_{j_\kappa}^{(\kappa)}(Q_\kappa)$$

- Time-dependent Hartree

$$\Psi(Q_1,\dots,Q_f,t)=A_{j_1\dots j_f}(t)\prod_{\kappa=1}^{f}\chi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

- Multi configuration time-dependent Hartree (MCTDH)

$$\Psi(Q_1,\dots,Q_f,t)=\sum_{j_1}^{n_1}\cdots\sum_{j_f}^{n_f}A_{j_1\dots j_f}(t)\prod_{\kappa=1}^{f}\chi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

U. Manthe, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. 97 , 3199 (1992)

Numerical effort

Increasing accuracy →

TDH ← **MCTDH** → **Standard method**

$n_1 = \ldots = n_f = 1$

$n_k \xrightarrow{approach} N_k$

$N \times f$

n^f

N^f

Example

TDH	MCTDH	Standard method
f=4, N=32: 6 kB	f=4, N=32, n=7: 620 kB	f=4, N=32: 48 MB
f=6, N=32: 9 kB	f=6, N=32, n=7: 32 MB	f=6, N=32: 48 GB
f=8, N=32: 12 kB	f=8, N=32, n=7: 1.03 GB	f=8, N=32: 48 TB

Mode combination

- Mode combination

$$\underbrace{(q_1, q_2}_{Q_1}, \underbrace{q_3, q_4, q_5}_{Q_2}, \underbrace{q_6}_{Q_3}, \cdots, \underbrace{q_{f-1}, q_f)}_{Q_p}$$

$$\Psi(Q_1, \ldots, Q_p, t) = \sum_{j_1}^{n_1} \cdots \sum_{j_p}^{n_p} A_{j_1 \ldots j_p}(t) \prod_{\kappa=1}^{p} \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t)$$

- Single Particle Functions (SPF)

$$\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) = \sum_{l_1=1}^{N_{1,\kappa}} \cdots \sum_{l_d=1}^{N_{d,\kappa}} c_{j_\kappa l_1 \ldots l_d}^{(\kappa)}(t)\, \chi_{l_1}^{(\kappa)}(q_{1,\kappa}) \cdots \chi_{l_d}^{(\kappa)}(q_{d,\kappa})$$

MCTDH equation of motion

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- Constrains

$$\langle \varphi_j^\kappa(0) | \varphi_l^\kappa(0) \rangle = \delta_{jl}$$

$$\langle \varphi_j^\kappa(t) | \dot{\varphi}_l^\kappa(t) \rangle = -i \langle \varphi_j^\kappa(t) | g^\kappa | \varphi_l^\kappa(t) \rangle$$

Constrain operator

- Time-dependent variational principle (Dirac Frenkel VP)

$$\langle \delta\Psi | \hat{H} - i\frac{\partial}{\partial t} | \Psi \rangle = 0$$

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

$$i\dot{\varphi}_j^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \sum_{k,l} {\rho_{j,k}^{(\kappa)}}^{-1} \langle \hat{\mathbf{H}} \rangle_{k,l}^{(\kappa)} \varphi_l^{(\kappa)}$$

Product representation of H

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- The computation of Hamiltonian matrix elements and mean-fields requires the evaluation of multi-dimensional integrals.

- These multi-dimensional integrals may be written as a product of one-dimensional integrals, if the Hamiltonian satisfies the following product form:

$$\hat{H} = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{p} \hat{h}_r^{(\kappa)}$$

$$\langle \Phi_J | \hat{H} | \Phi_L \rangle = \sum_{r=1}^{s} c_r \langle \varphi_{j_1}^{(1)} | \hat{h}_r^{(1)} | \varphi_{l_1}^{(1)} \rangle \dots \langle \varphi_{j_p}^{(p)} | \hat{h}_r^{(p)} | \varphi_{l_p}^{(p)} \rangle$$

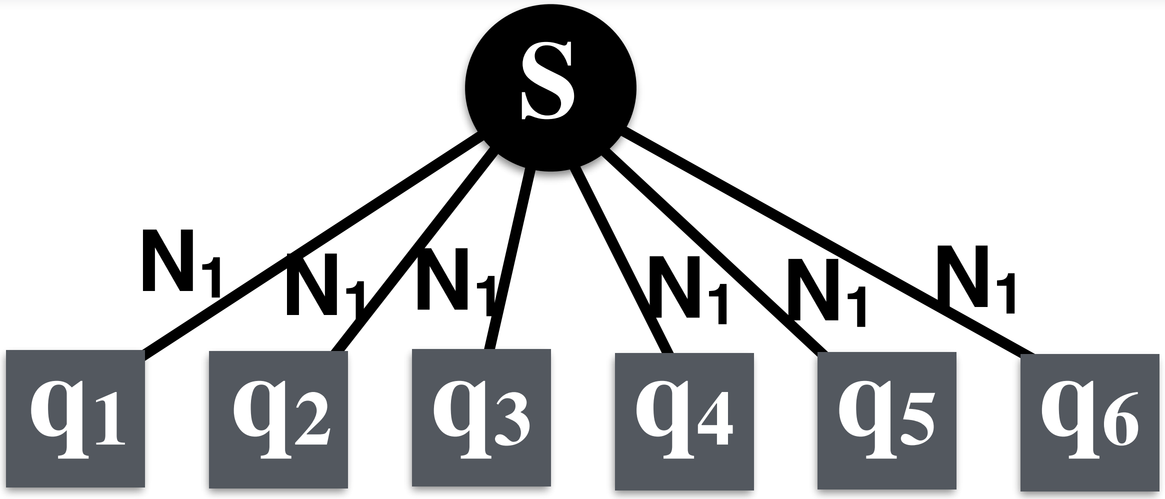
M.H. BECK, A. JÄCKLE, G. A. WORTH, and H.-D. MEYER. *Phys. Rep., 324:1, 2000*

Non-adiabatic problems: Multi-set algorithm

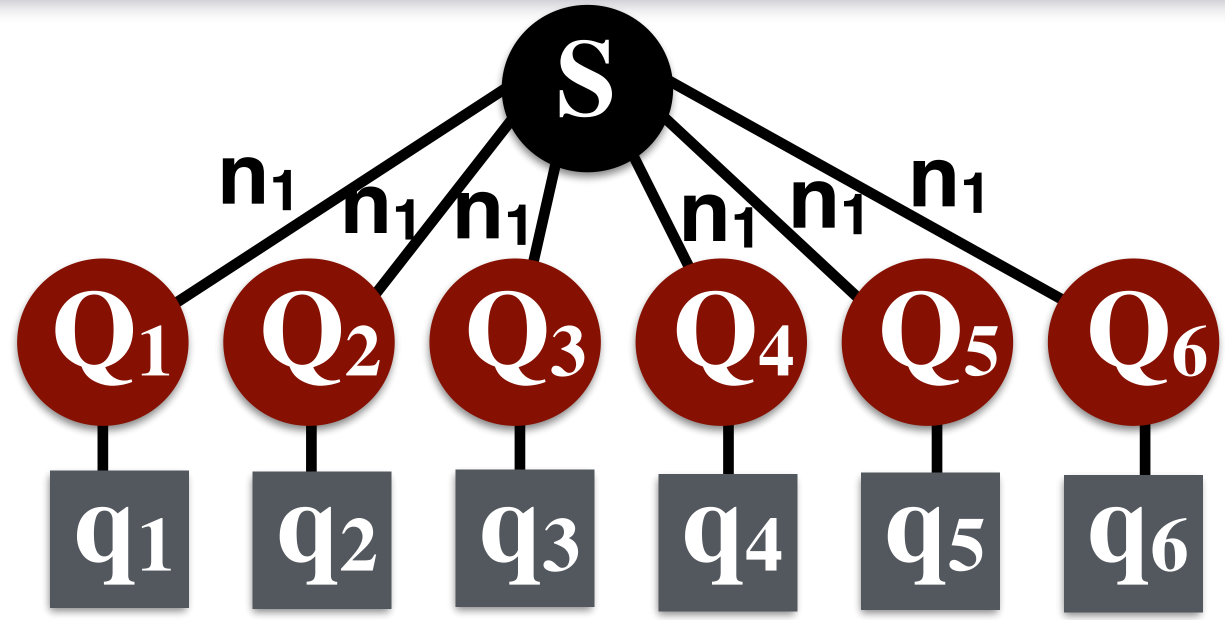
- Single-set vs Multi-set formulation

$$\Psi(Q_1,\ldots,Q_p,t) = \sum_{\alpha=1}^{\alpha} \sum_{j_1}^{n_1^{\alpha}} \cdots \sum_{j_f}^{n_p^{\alpha}} A_{j_1\ldots j_p}^{\alpha}(t) \prod_{\kappa=1}^{p} \varphi_{j_\kappa}^{(\alpha,\kappa)}(Q_\kappa,t)|\alpha\rangle$$

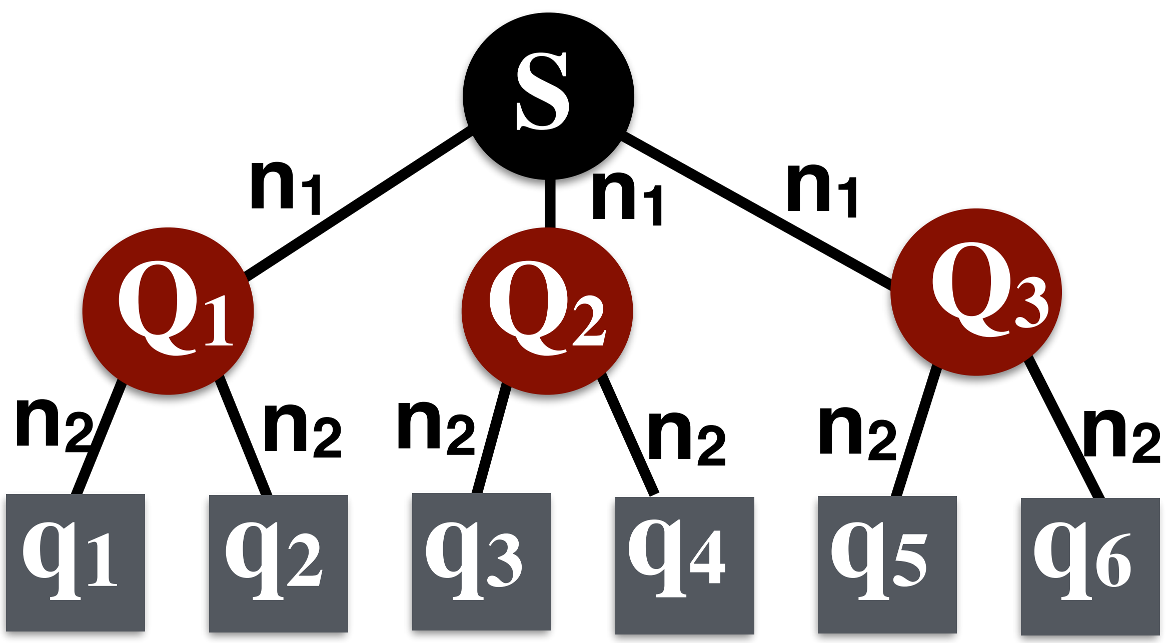
$$= \sum_{\alpha} \sum_{J} A_J^{(\alpha)} \, \Phi_J^{(\alpha)} |\alpha\rangle$$



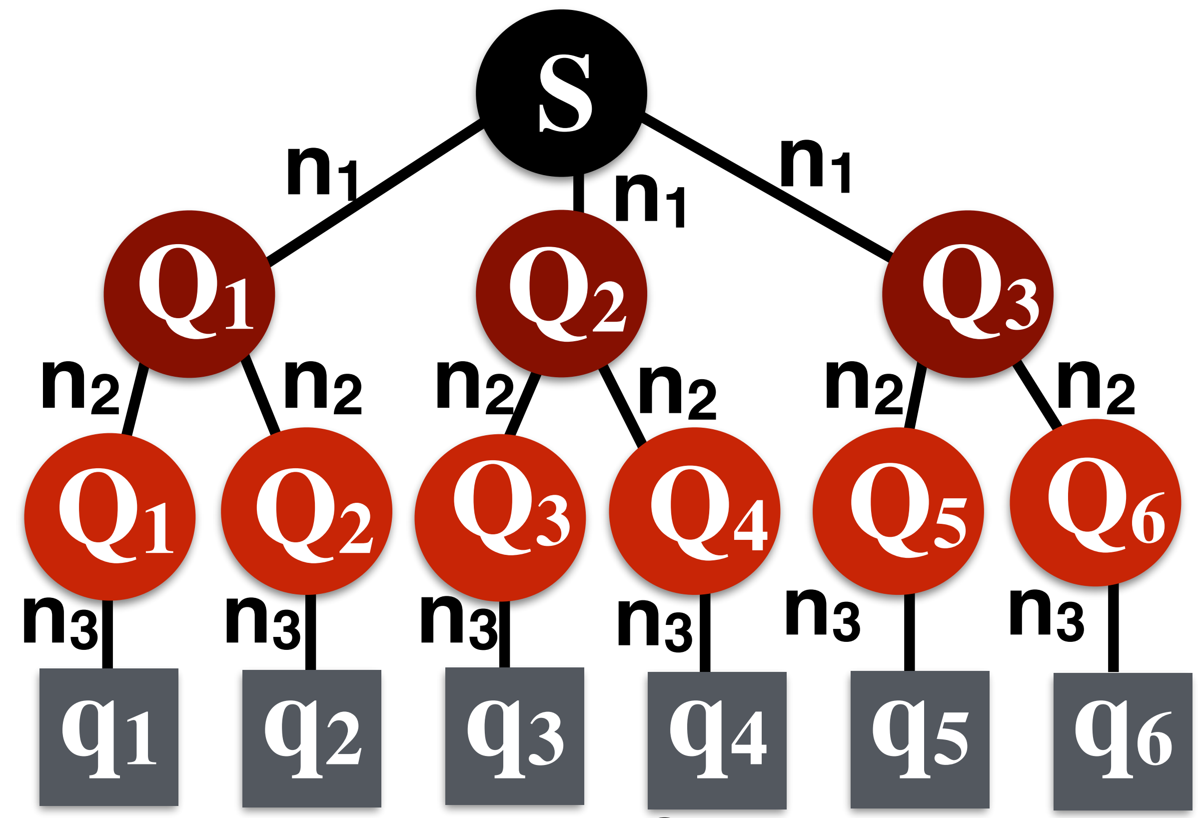
Exact method



MCTDH

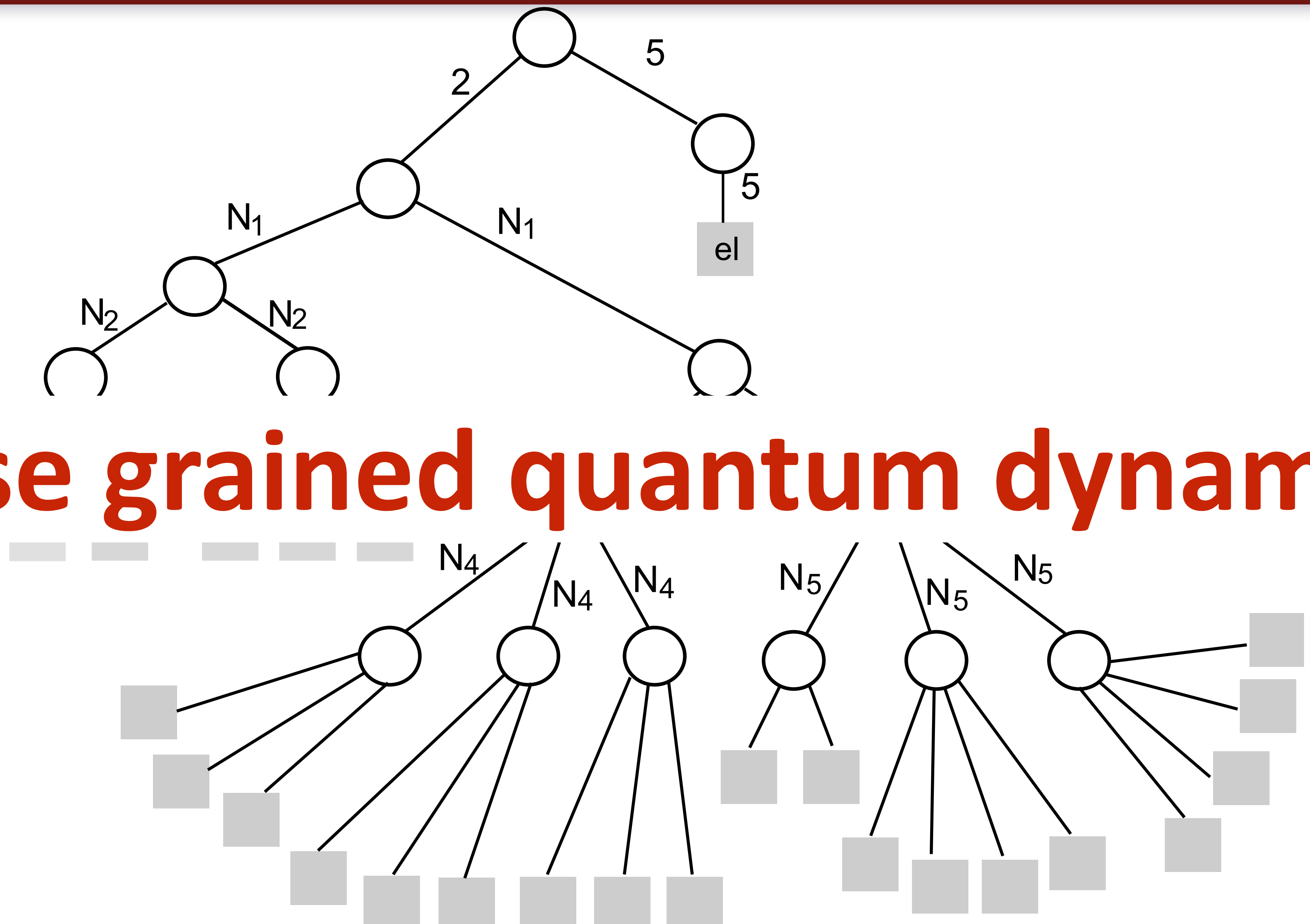


MCTDH-combined modes



ML-MCTDH

Pyrrole 24D, ML-MCTDH-tree



Corse grained quantum dynamics

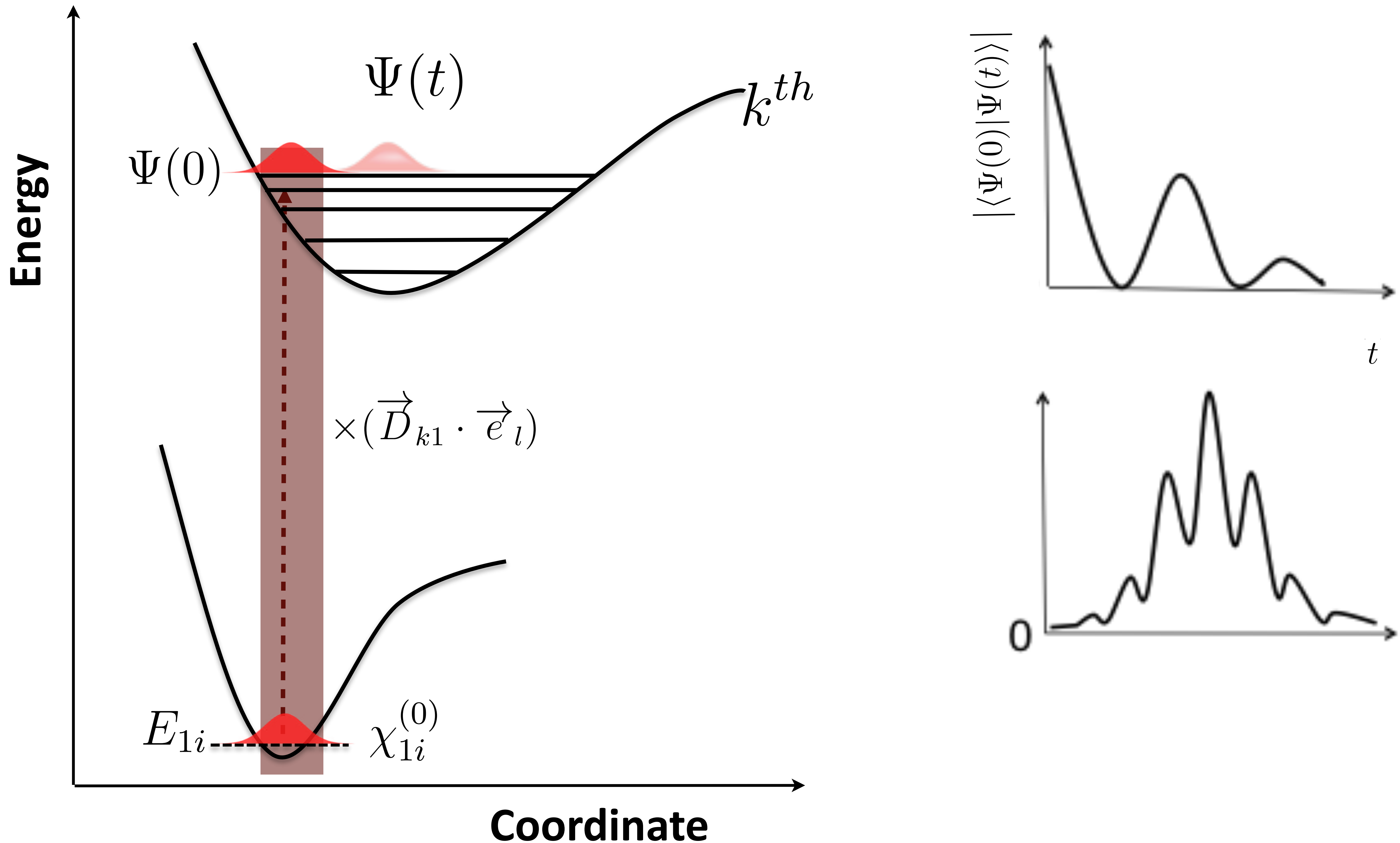
MCTDH (89 h) ML-MCTDH (15 min)

S. Faraji et al., *J. Chem. Phys*. 135, 154310, **2011**.

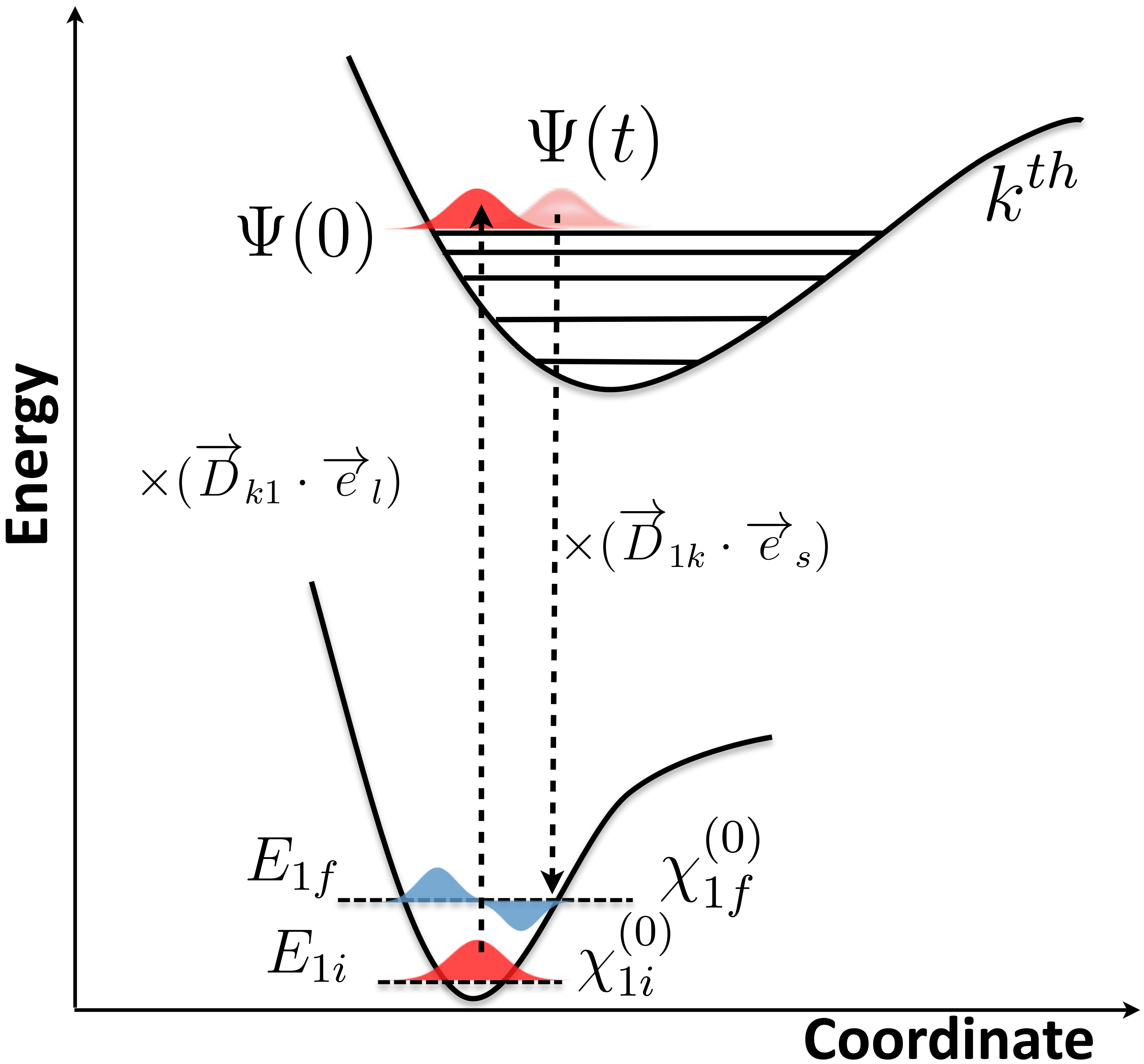
Dynamical observables

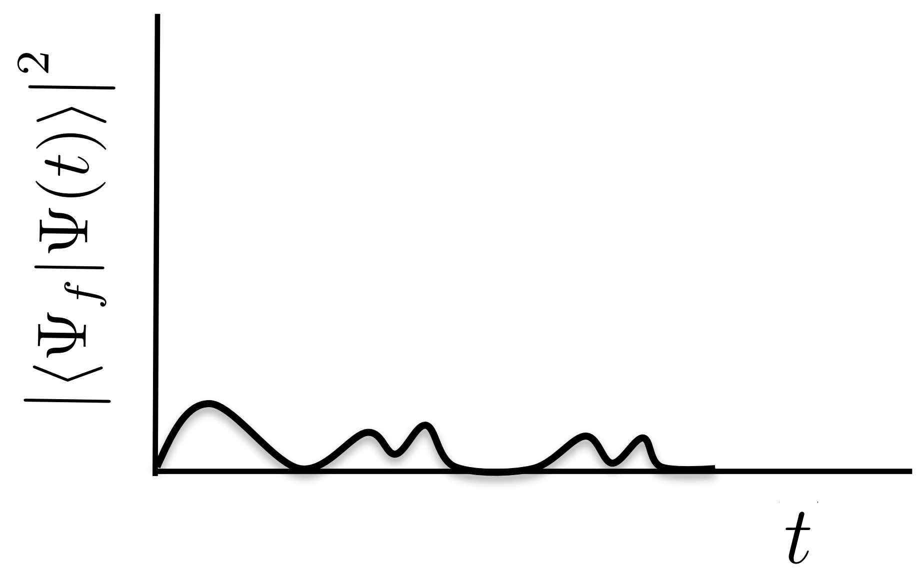
- Various spectra
- Electronic population
- Flux into a reaction channel
- Probability density along a coordinate
- ….

Absorption spectrum



Resonance Raman spectrum



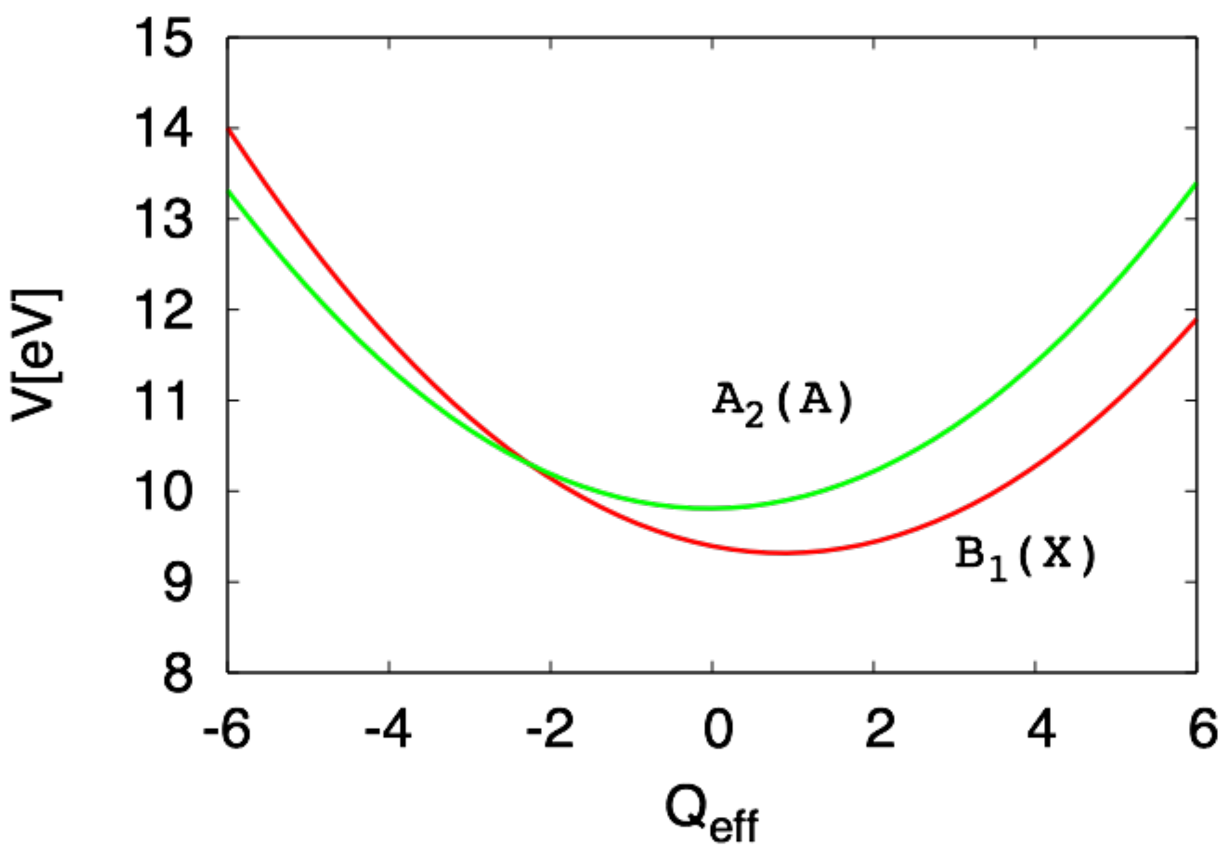


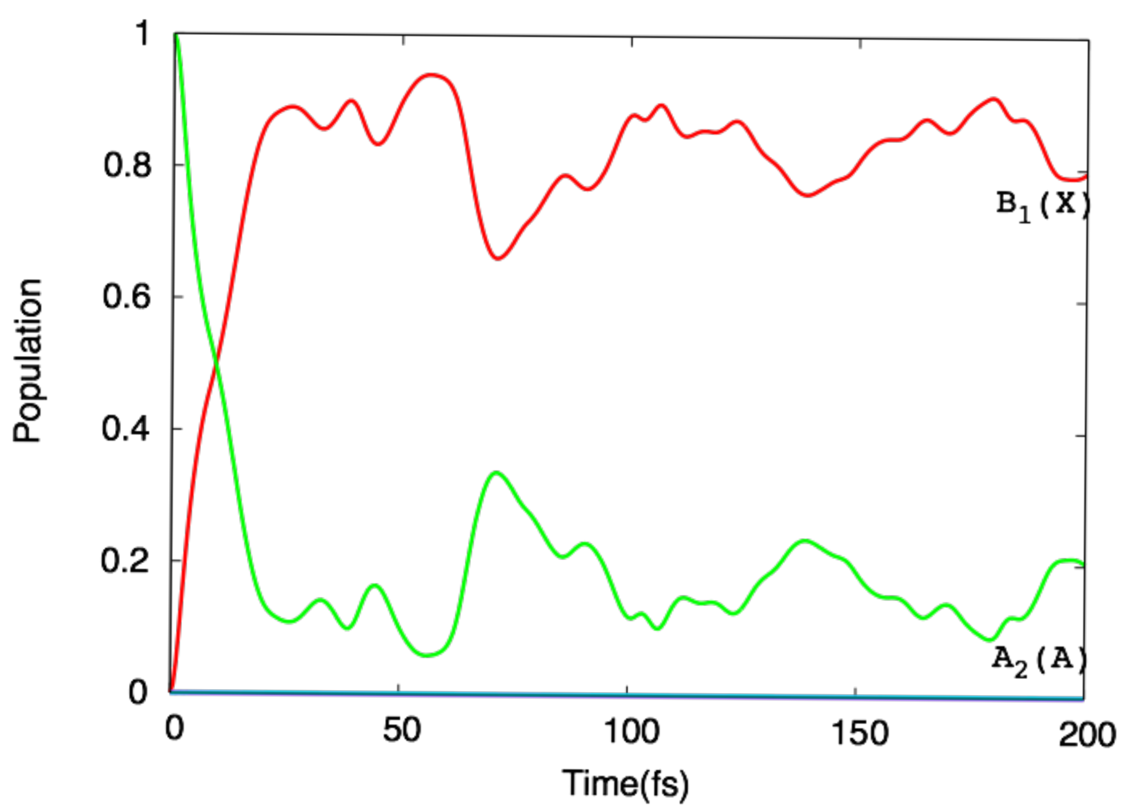
Diabatic electronic population

- Probability of the wavepacket being on one of the electronic surfaces.

$$P_\alpha^{(d)} = \|\Psi_\alpha\|^2$$

- Fluorescence dynamics





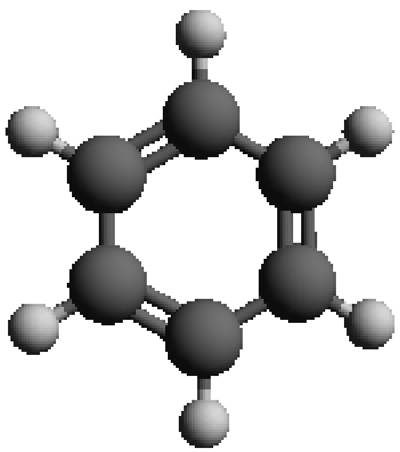
Current state of quantum dynamics

Collection of MCTDH calculations on vibrance coupling model potential

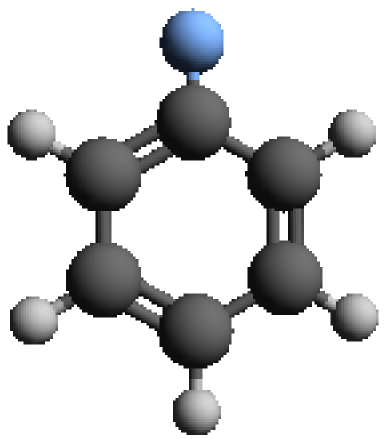
Process	System	Formula	f	e
Photo-excitation	pyrazine	$C_4H_4N_2$	24	2
	furan	C_4H_4O	13	4
	pyrrole	C_4H_5N	10 (24)	5
Photo-ionization	butatriene	$C_4H_4^+$	18	2
	allene	$C_3H_4^+$	15	3
	pentatetraene	$C_5H_4^+$	21	3
	benzene	$C_6H_6^+$	13	5
	monofluorobenzene	$C_6F_2H_5^+$	12(30)	5
	difluorobenzene	$C_6F_2H_4^+$	12(30)	5
	trifluorobenzene	$C_6F_2H_4^+$	12(30)	5
	cyclopropane	$C_3H_6^+$	14	4
	trifluoroacetonitrile	CF_3CN^+	12	5
	phenylacetylene	$C_8H_6^+$	24	4
	naphthalene	$C_{10}H_6^+$	29	6
	anthracene	$C_{14}H_{10}^+$	31	6
Photo-detachment	phenide	C_6H_5	27	2
	nitrate radical	NO_3	4	2

Fluorinated benzene radical cations

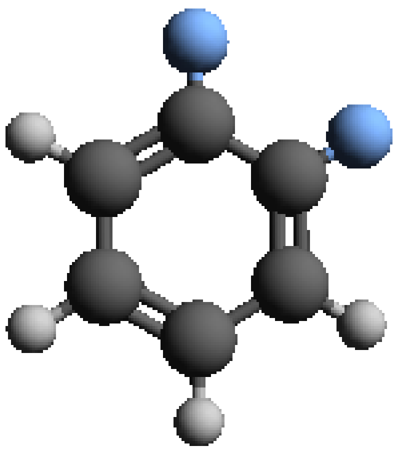
- Fluorescence



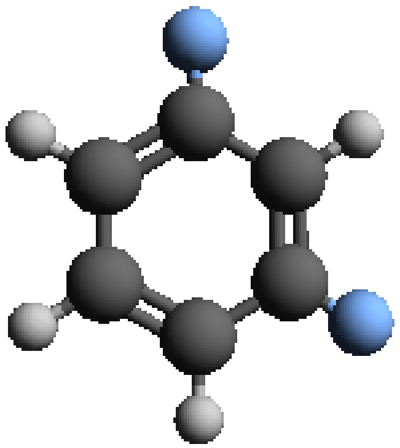
D_{6h}



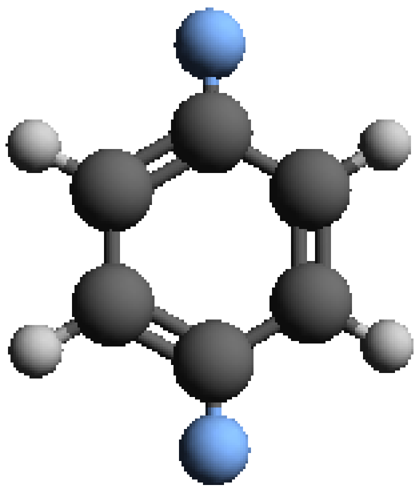
C_{2v}



C_{2v}
Ortho



C_{2v}
Meta



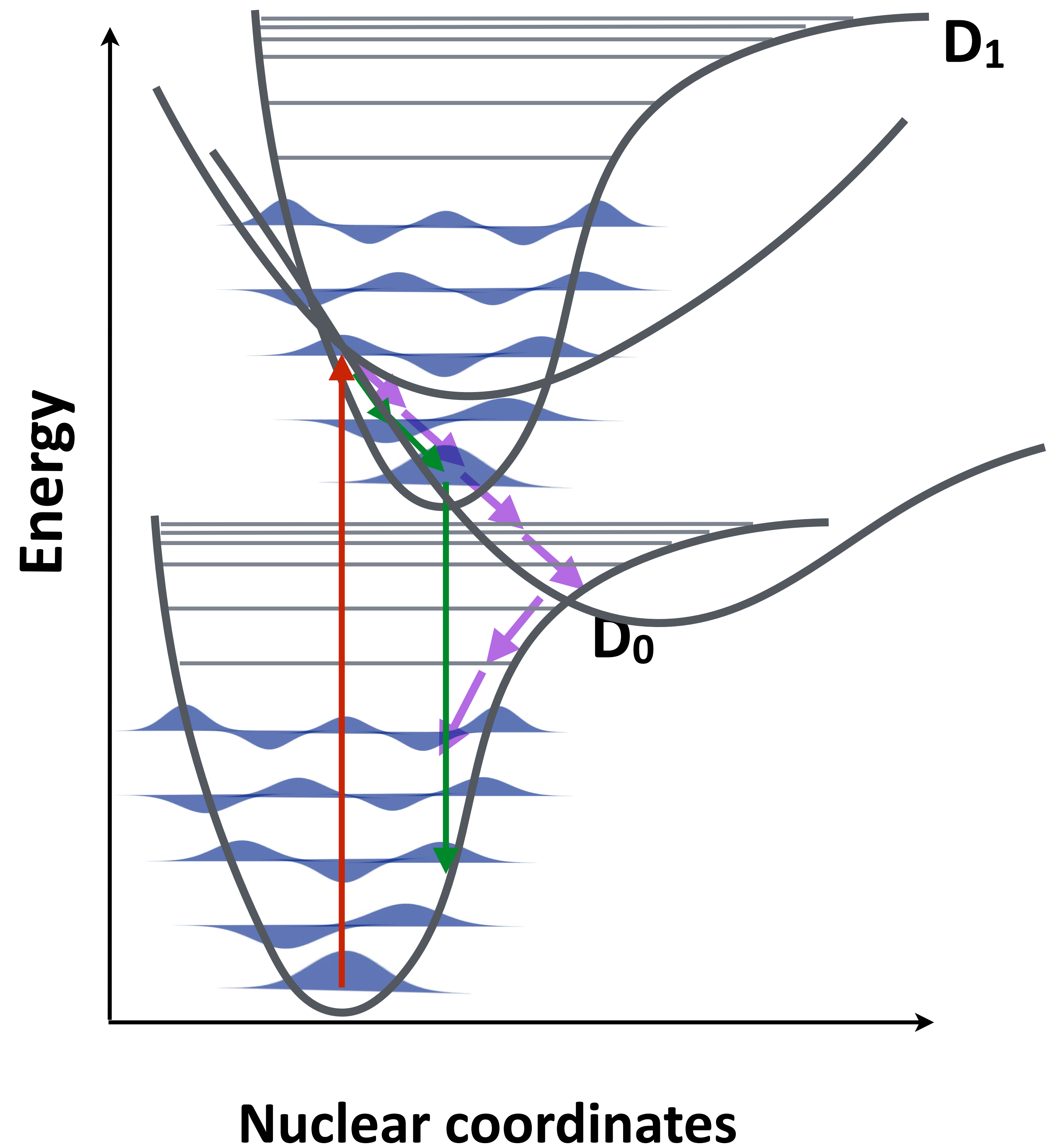
D_{2h}
Para

S. Faraji, H. Köppel, *J. Chem. Phys*. 129, 074310, **2008**.
S. Faraji, H-D. Meyer, H. Köppel, *J. Chem. Phys*. 129, 074311, **2008**.
S. Faraji, E. Gindensperger, H. Köppel, *Chem. Phys.*, 97, 239, **2010**.

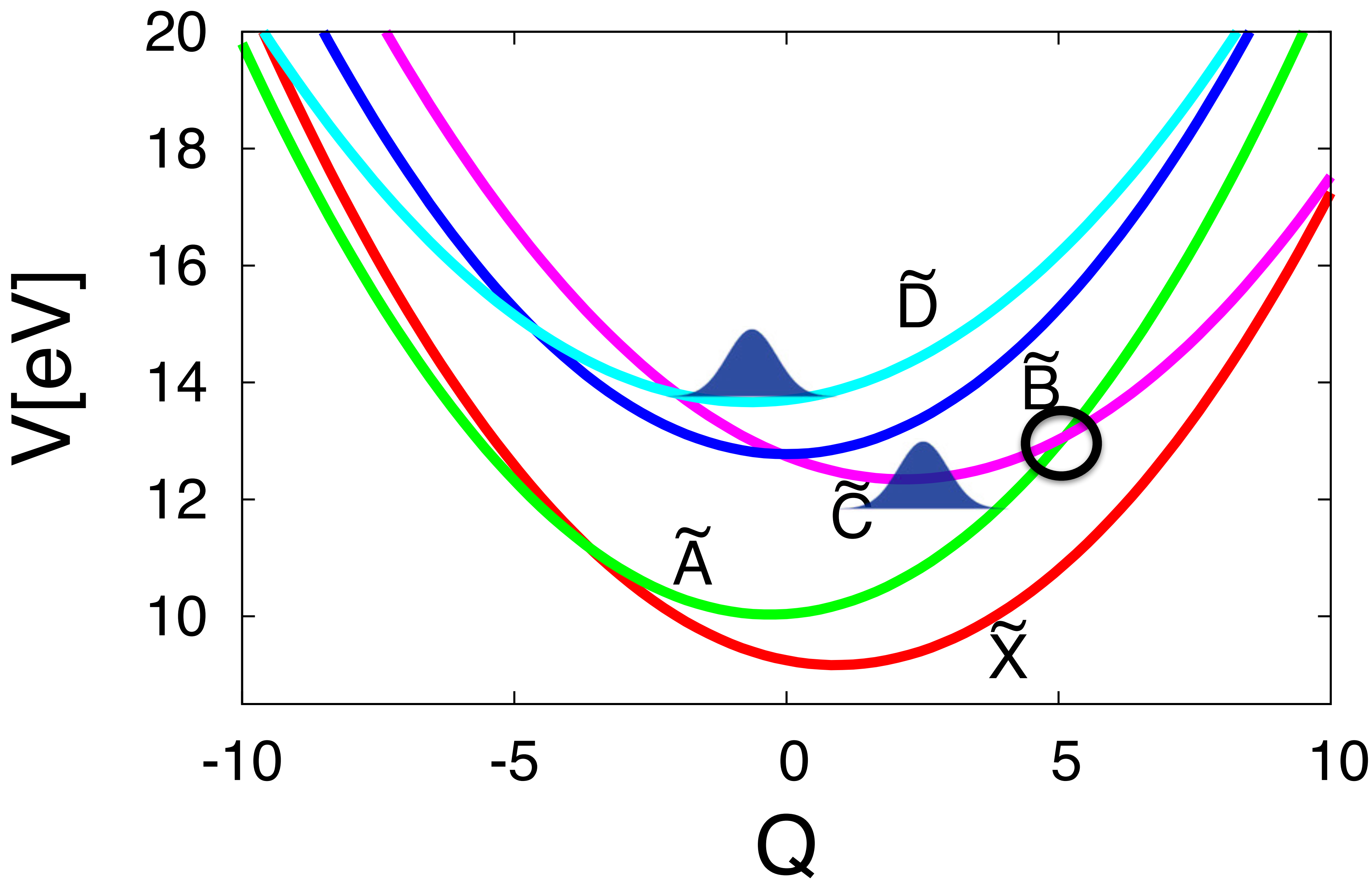
Radiative vs. non-radiative decays

- Fluorescence

- Internal conversion



Vibronic coupling model PESs and minima of conical intersection seams



Non-Fluorescent	**Ortho**	**13.07 eV**
Fluorescent	**Meta**	**13.65 eV**
Non-Fluorescent	**Para**	**13.08 eV**

Minima of conical intersection seams

Ortho

	$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$	9.14 *9.13*	9.62	25.63	13.92	13.64
$\tilde{A}$		9.62 *9.61*	28.97	**13.07**	13.57
$\tilde{B}$			12.66 *12.62*	12.70	12.96
$\tilde{C}$				12.44 *12.49*	13.05
$\tilde{D}$					12.87 *12.91*

Para

	$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$	8.96 *8.96*	9.97	31.13	15.53	19.53
$\tilde{A}$		9.87 *9.86*	23.98	**13.08**	19.29
$\tilde{B}$			12.60 *12.59*	12.62	14.31
$\tilde{C}$				12.30 *12.30*	13.65
$\tilde{D}$					13.58 *13.56*

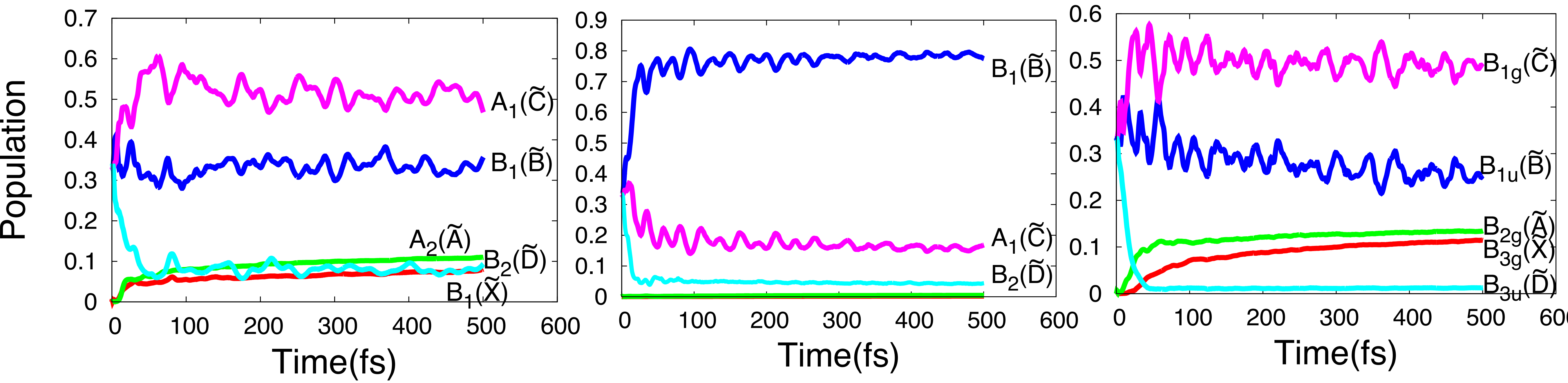
Meta

	$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$	9.19 *9.18*	9.62	21.47	14.68	13.84
$\tilde{A}$		9.61 *9.61*	21.13	**13.65**	14.18
$\tilde{B}$			12.61 *12.62*	12.74	13.09
$\tilde{C}$				12.60 *12.59*	13.16
$\tilde{D}$					13.08 *13.13*

Time-dependent electronic populations

Non- fluorescent — **Fluorescent** — **Non- fluorescent**

Ortho — **Meta** — **Para**



No population transfer to the GS

Transition dipole moment

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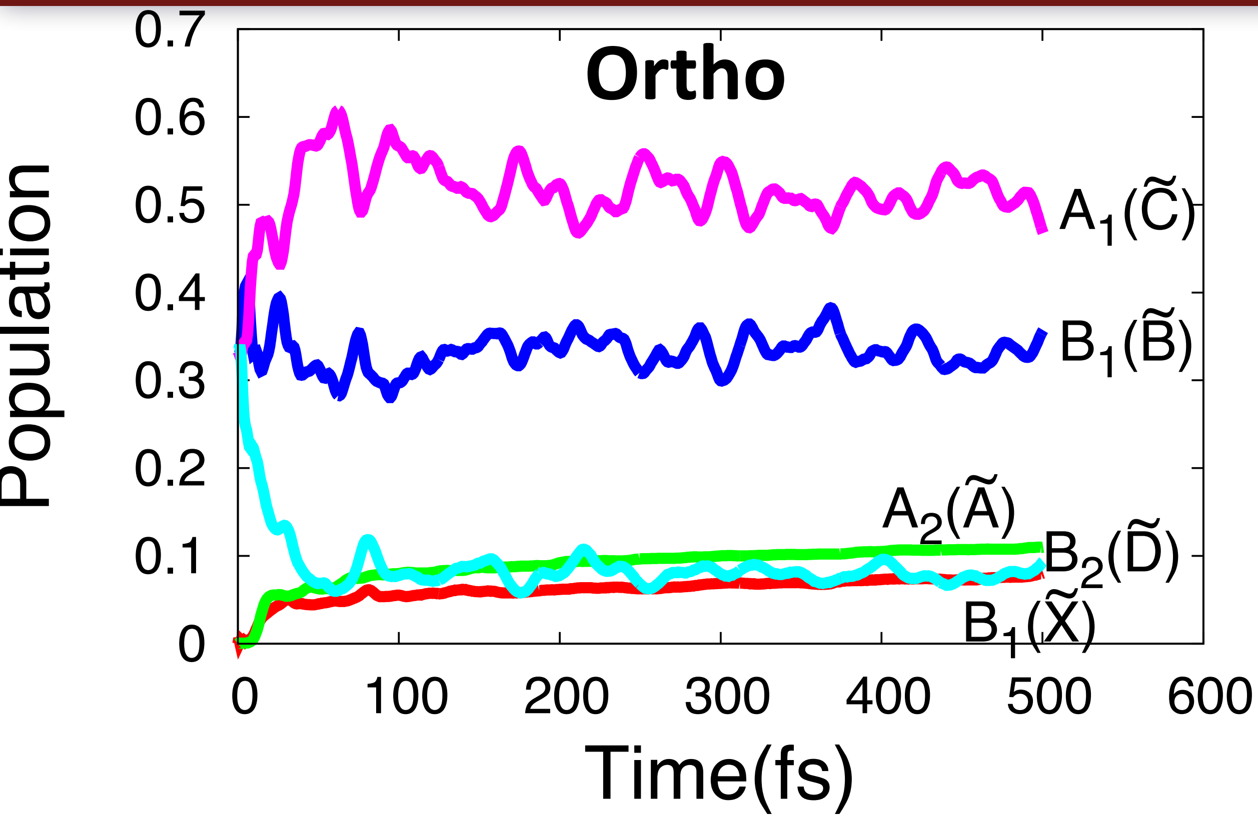
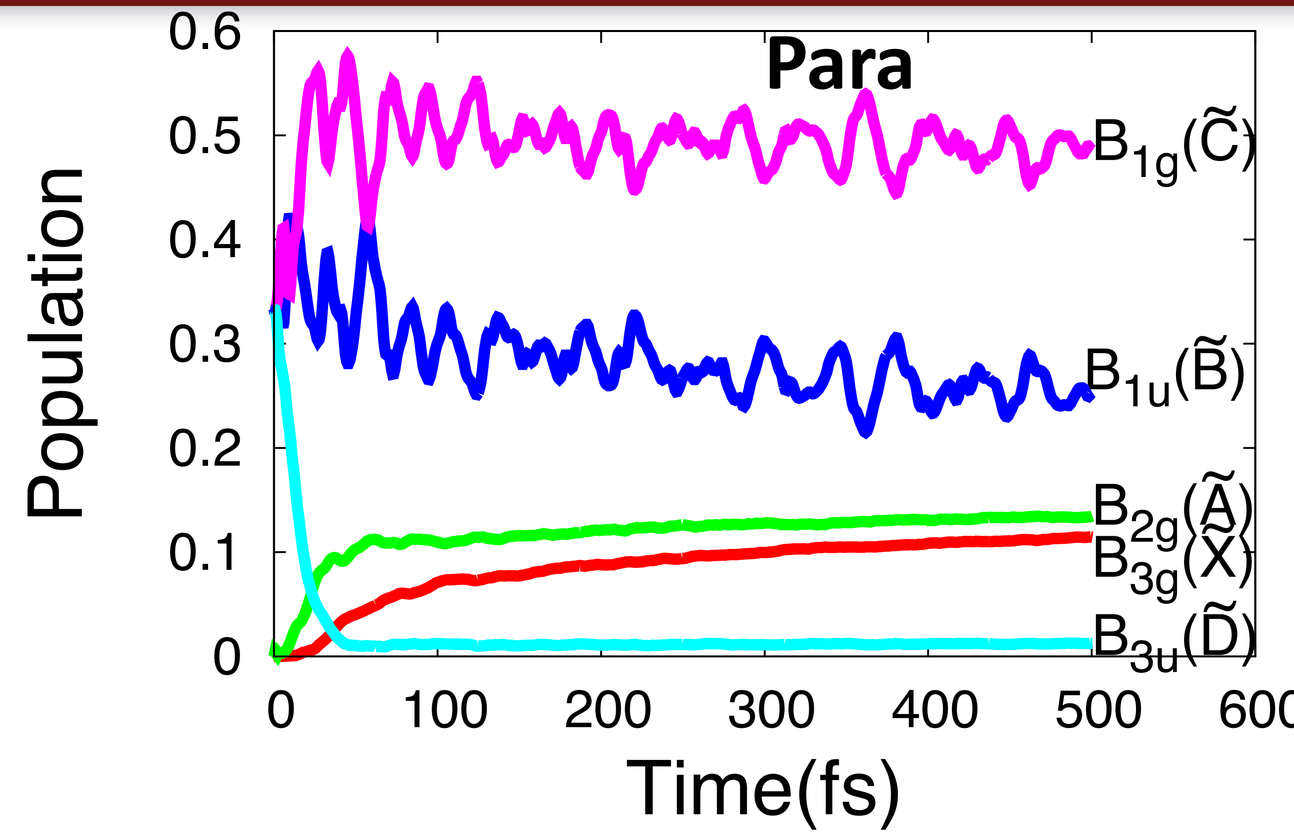
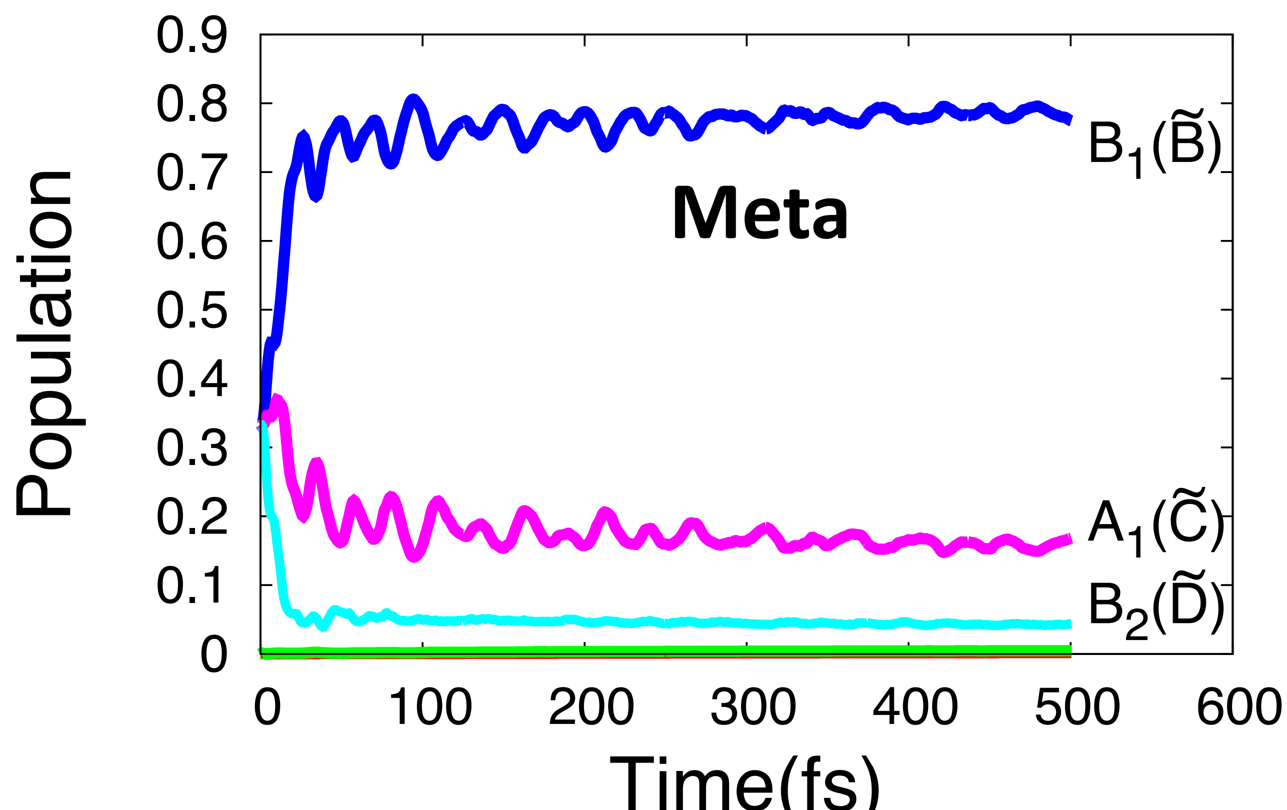
- Oscillator strengths of transition dipole moment between 5 electronic states

		$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
Mono	$\tilde{X}$	0.0935	-	0.000
	$\tilde{A}$	0.0552	0.000	-
1,2	$\tilde{X}$	0.0999	0.0001	-
	$\tilde{A}$	0.0644	-	0.0001
1,3	$\tilde{X}$	0.1002	-	0.0002
	$\tilde{A}$	0.0641	0.000	-
1,4	$\tilde{X}$	0.1282	-	-
	$\tilde{A}$	0.0474	-	0.000
1,2,3	$\tilde{X}$	0.0889	-	0.000
	$\tilde{A}$	0.0907	0.0002	-

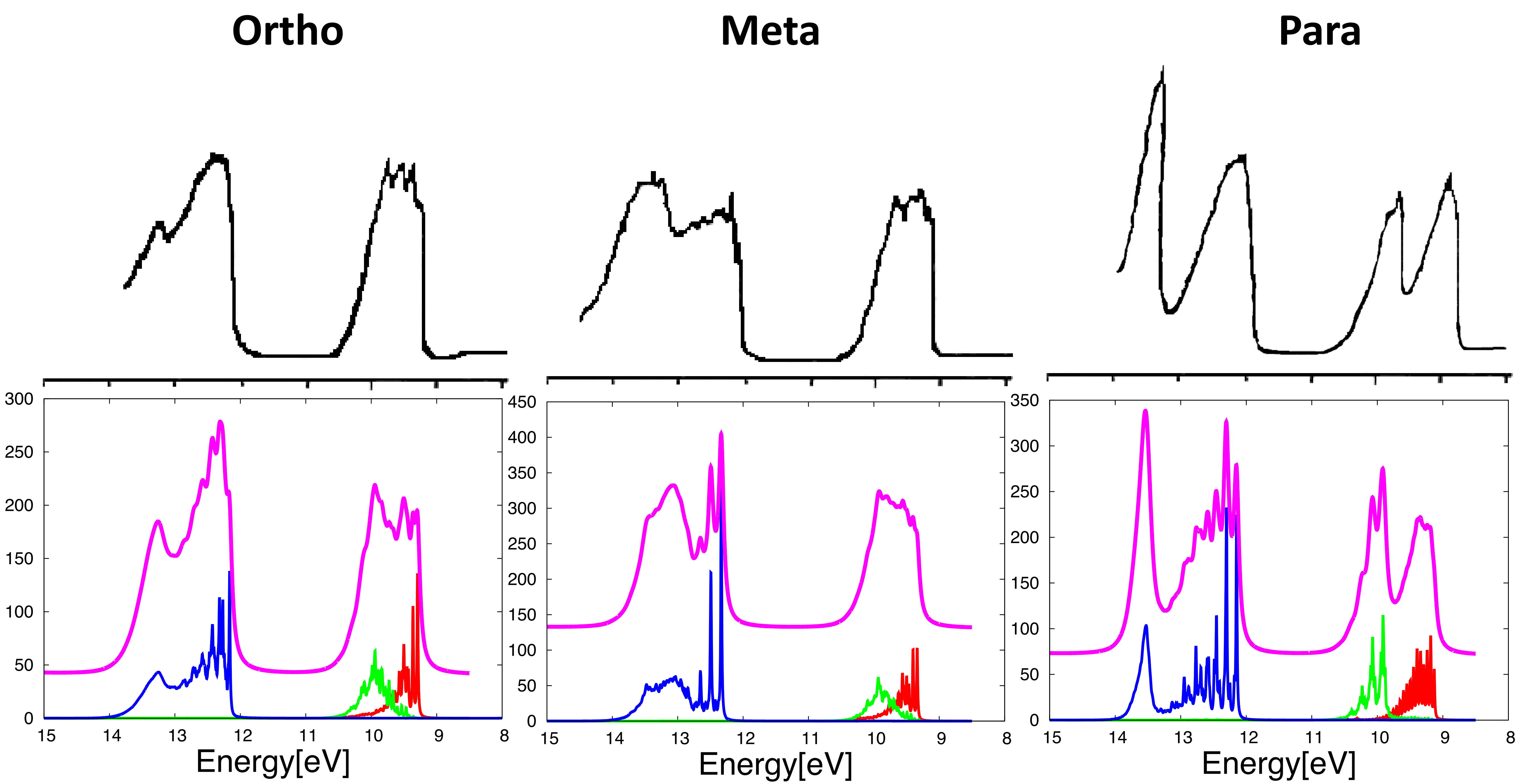
Time-dependent electronic populations





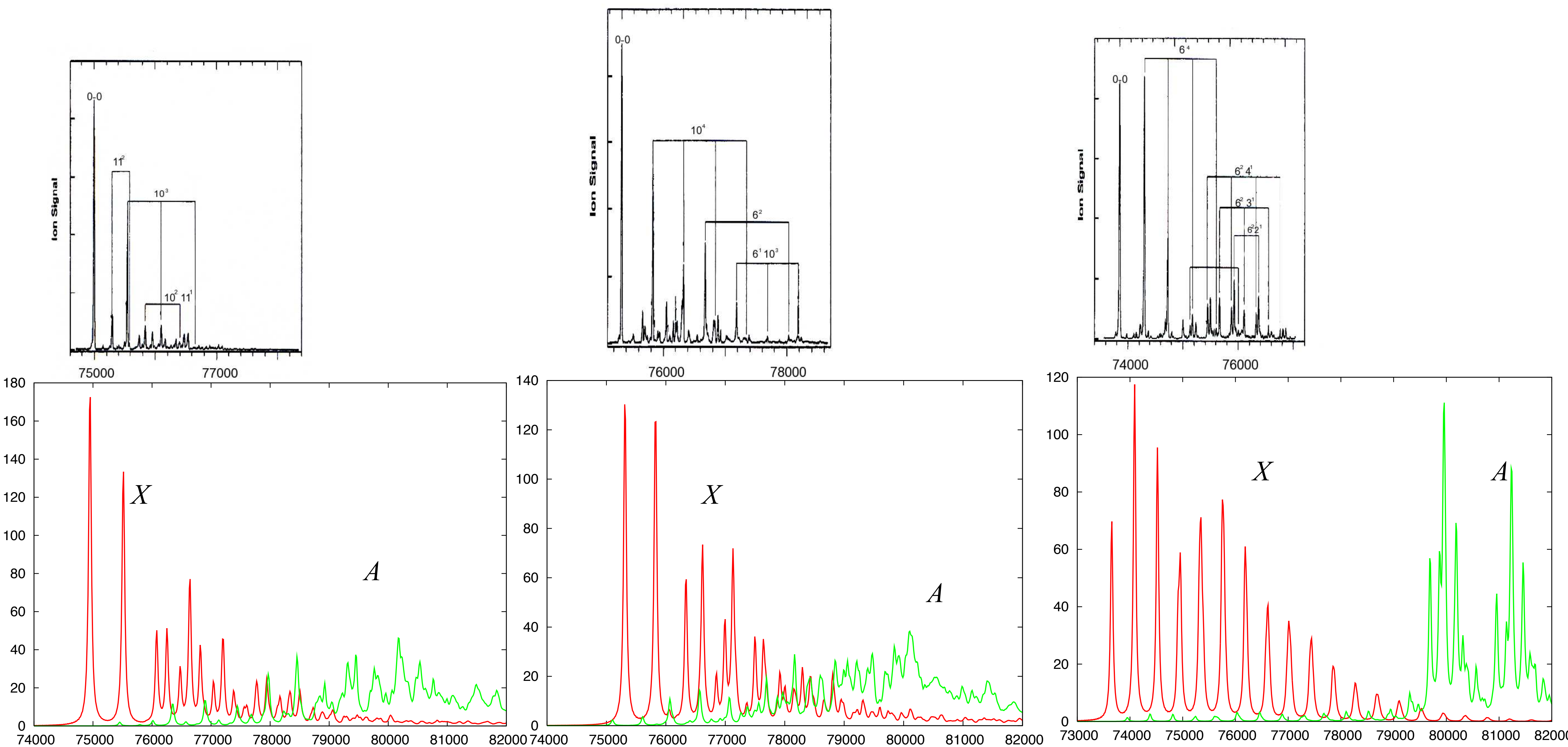


Photoelectron spectra

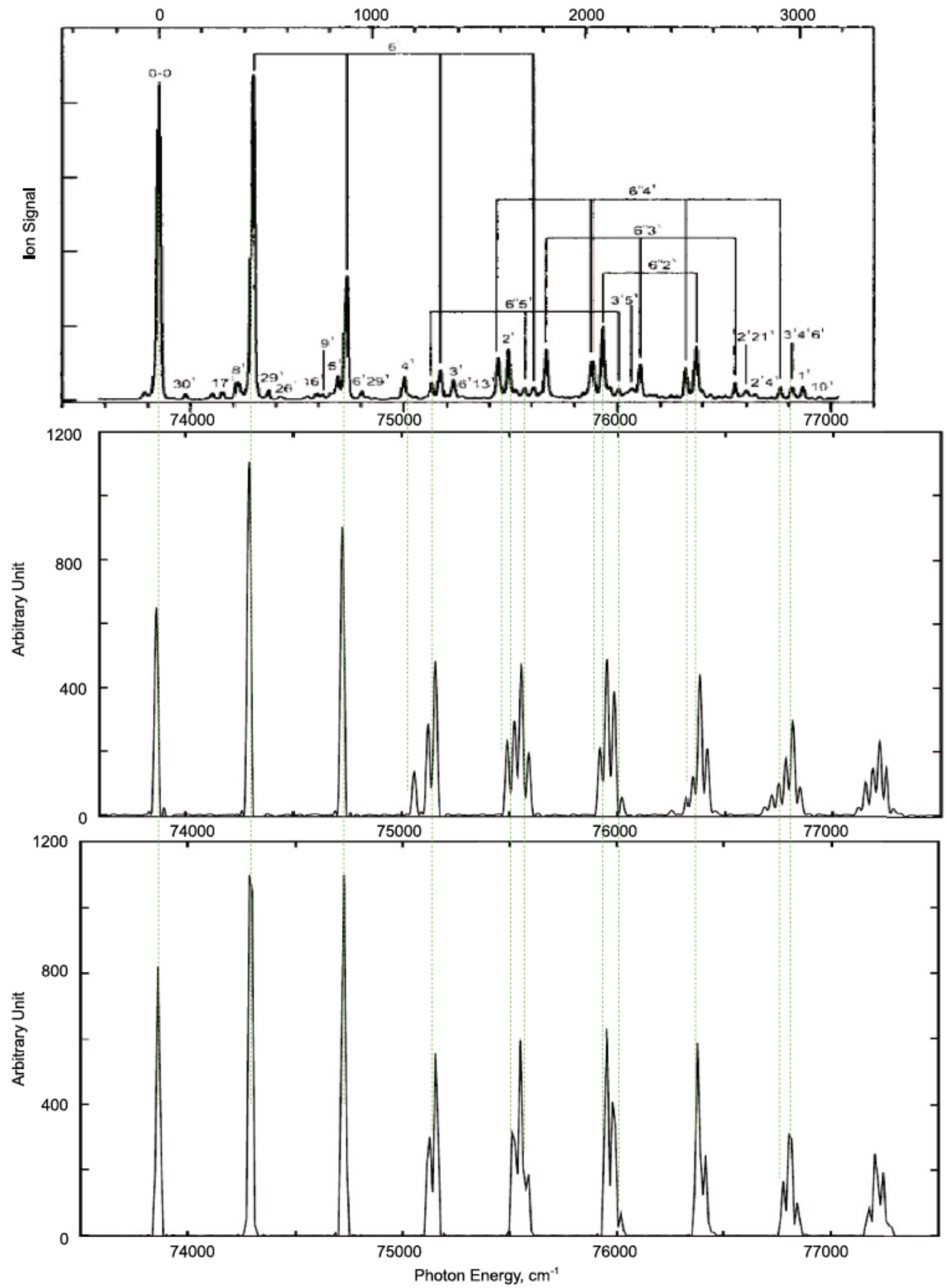


MATI spectra

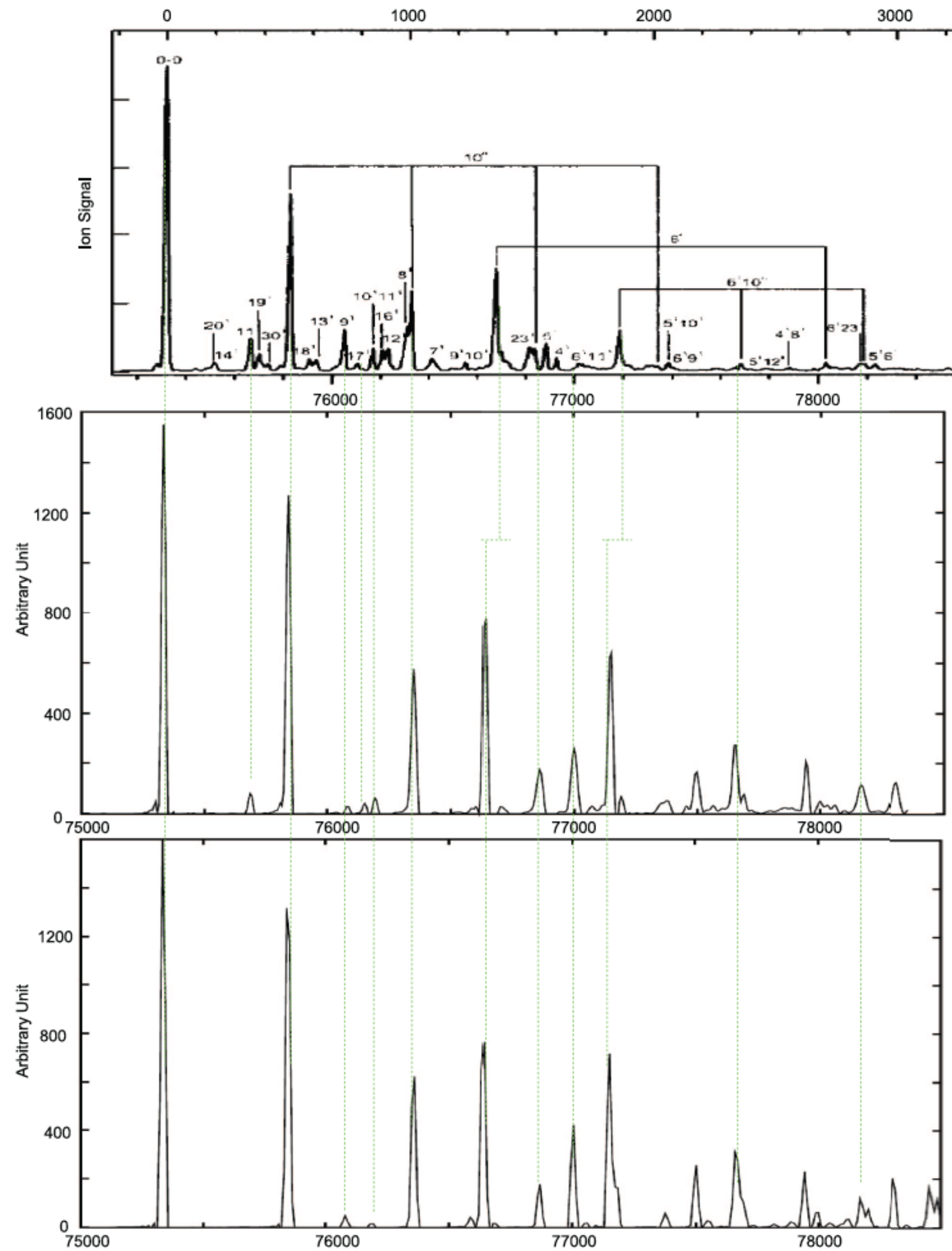
o-difluorobenzene m-difluorobenzene p-difluorobenzene



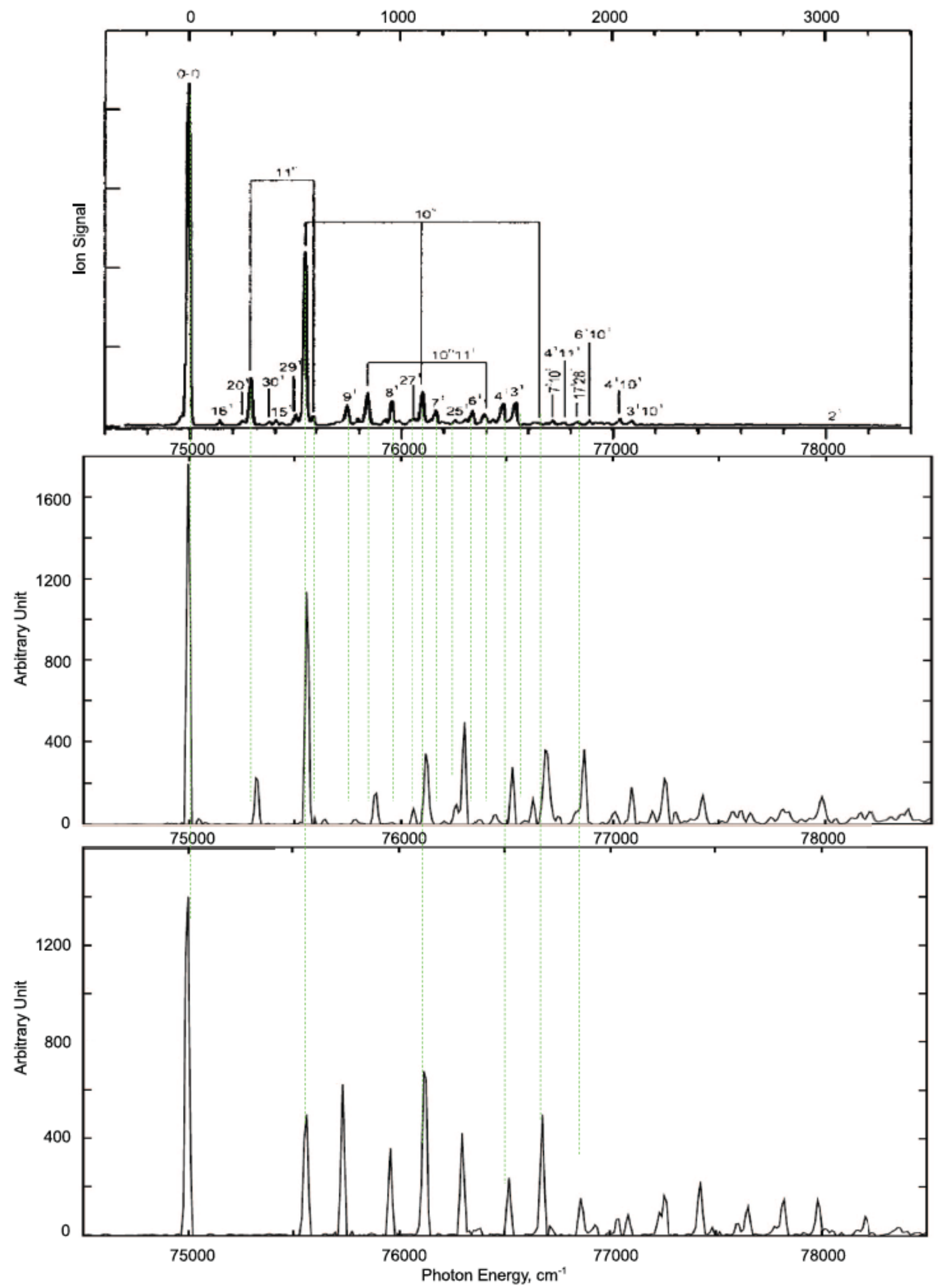
Full dimension 30 DOF



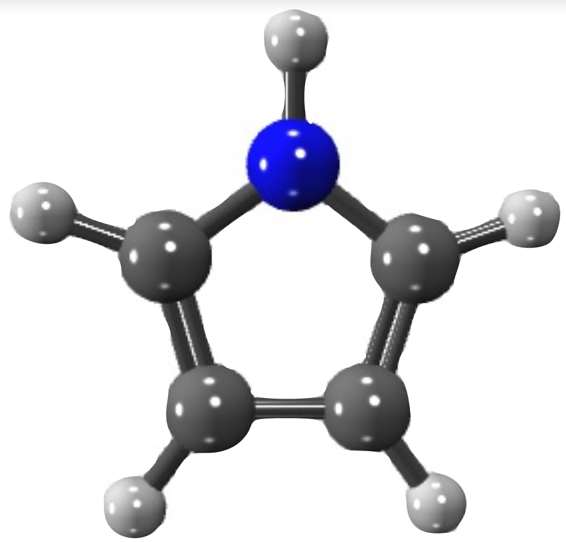
Full dimension 30 DOF



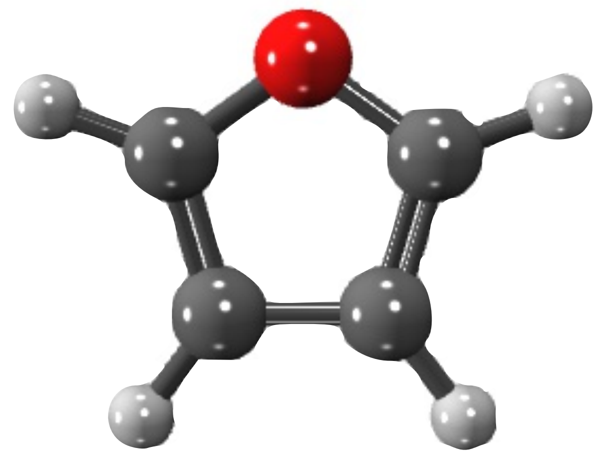
Full dimension 30 DOF



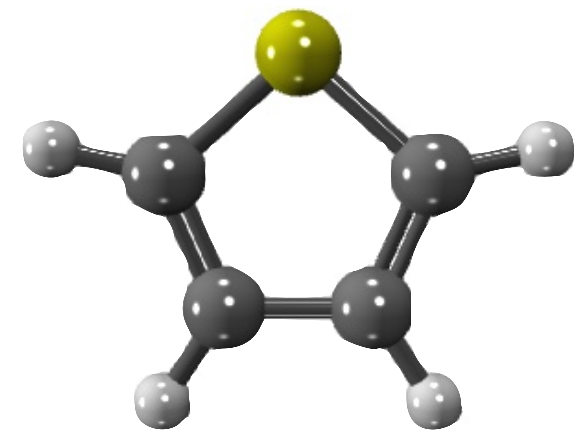
Heteroaromatic molecules



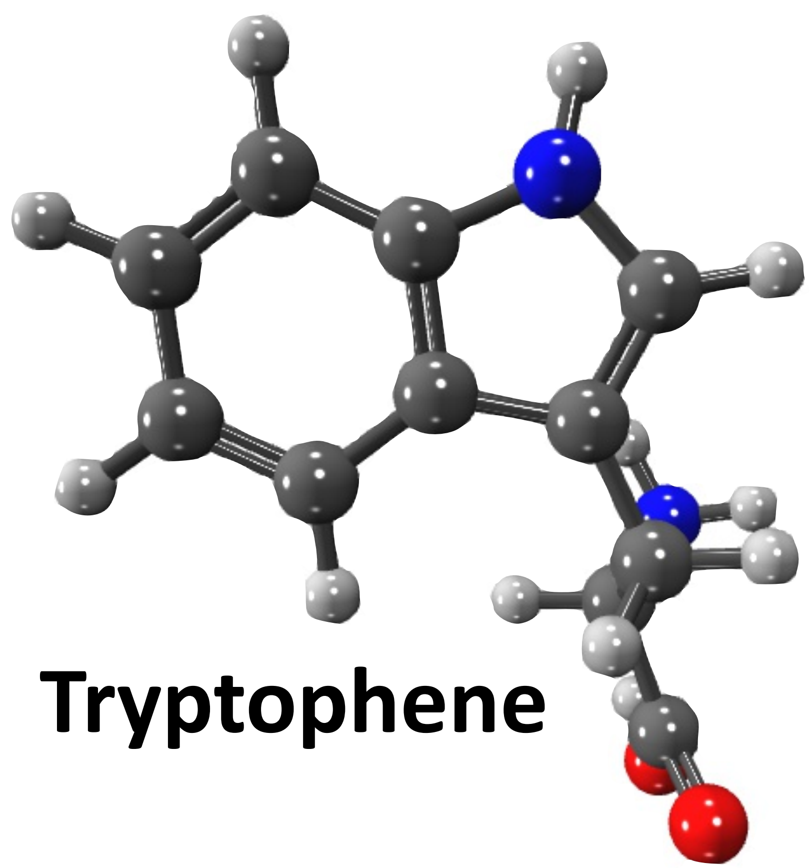
Pyrrole



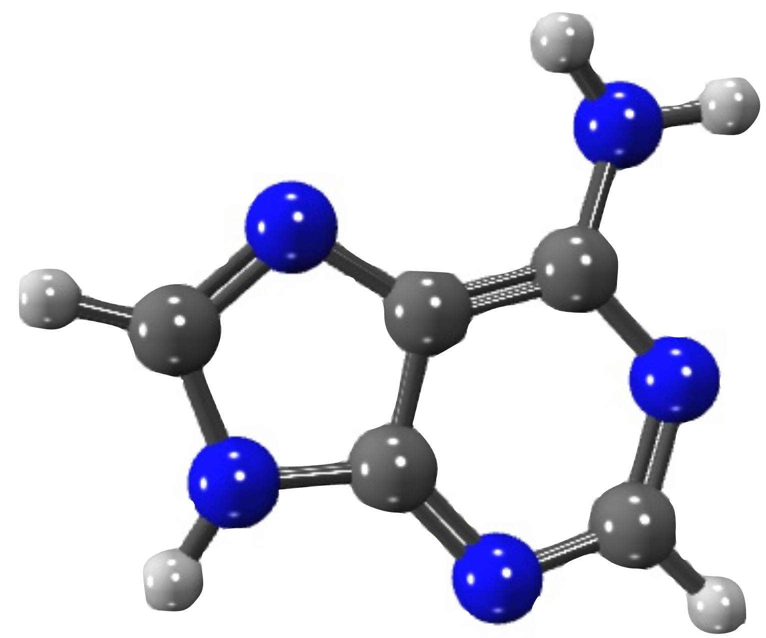
Furan



Thiophene

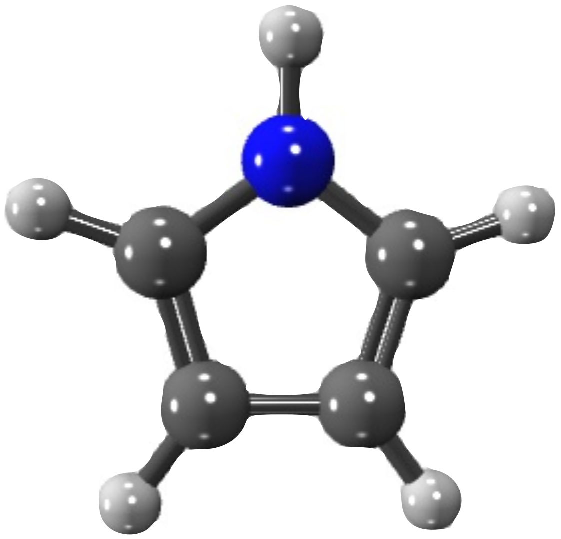


Tryptophene

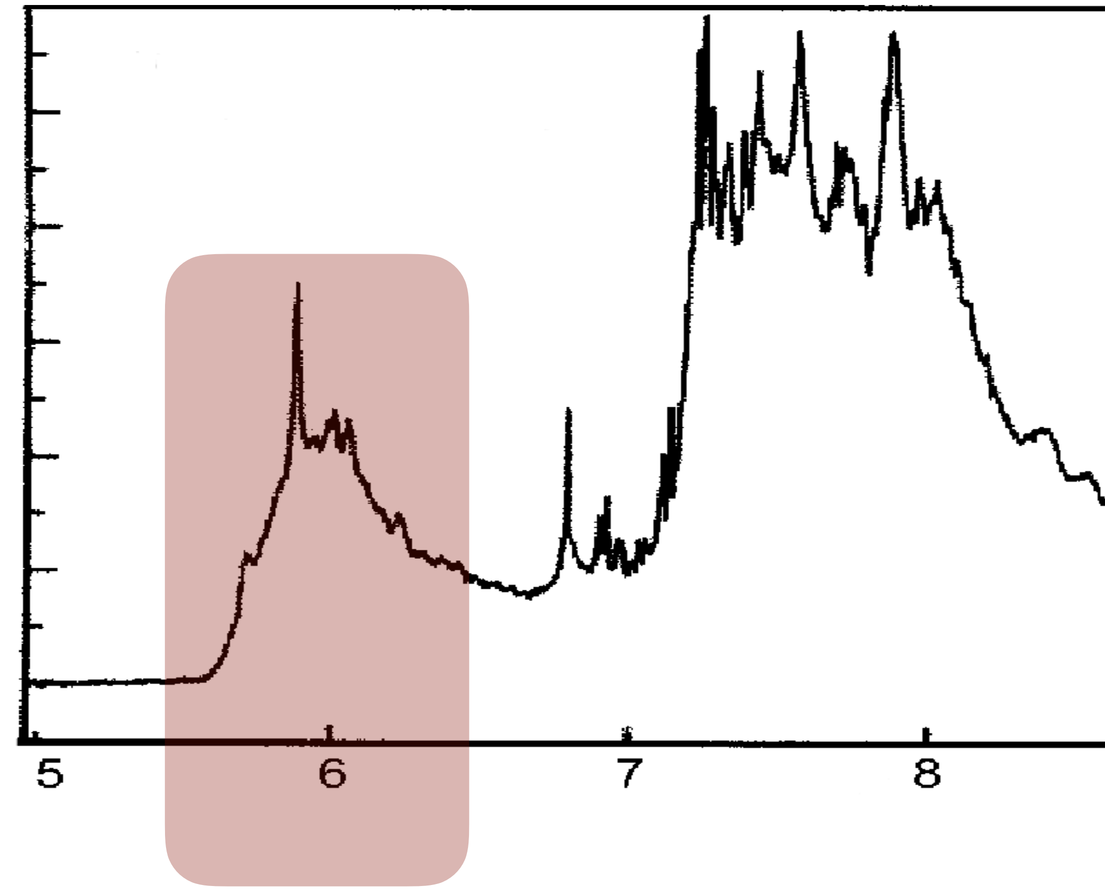


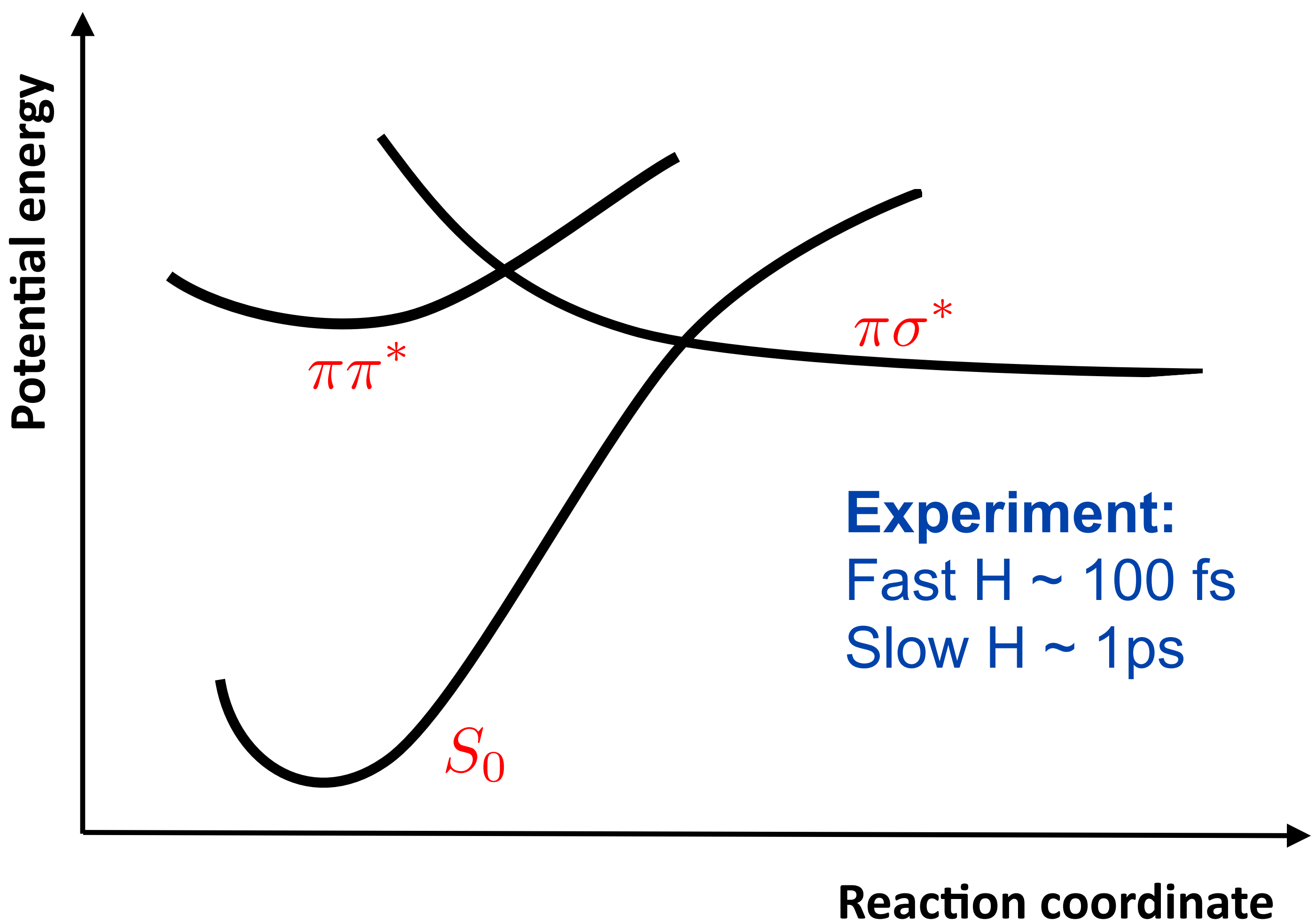
Adenine

Pyrrole



$$\Gamma_{vib} = 9A_1 + 3A_2 + 4B_1 + 8B_2$$



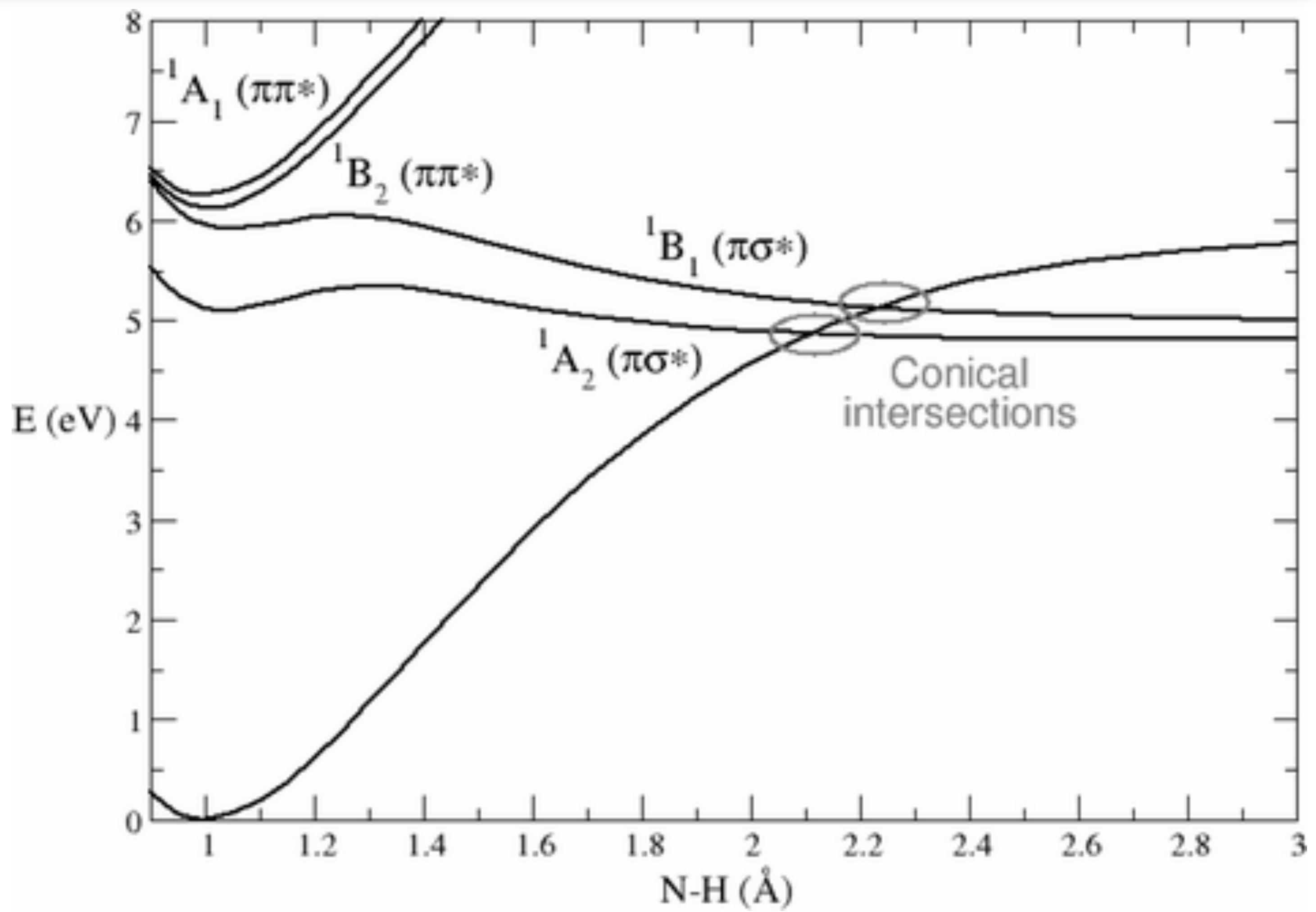


Experiment:
Fast H ~ 100 fs
Slow H ~ 1ps

A. L. Sobolewski and W. Domcke, Chem. Phys. 259, 181 (2000)

5 lowest electronic states

$B_2(\pi\pi^*)$	———	6.75 eV
$A_1(\pi\pi^*)$	———	6.55 eV
$B_1(\pi\sigma^*)$	———	6.12 eV
$A_2(\pi\sigma^*)$	———	5.33 eV
A_1	———	



A. L. Sobolewski and W. Domcke, Chem. Phys. 259, 181 (2000)

MR-CISD+Q/cc-pVDZ

CASSCF(5,6)

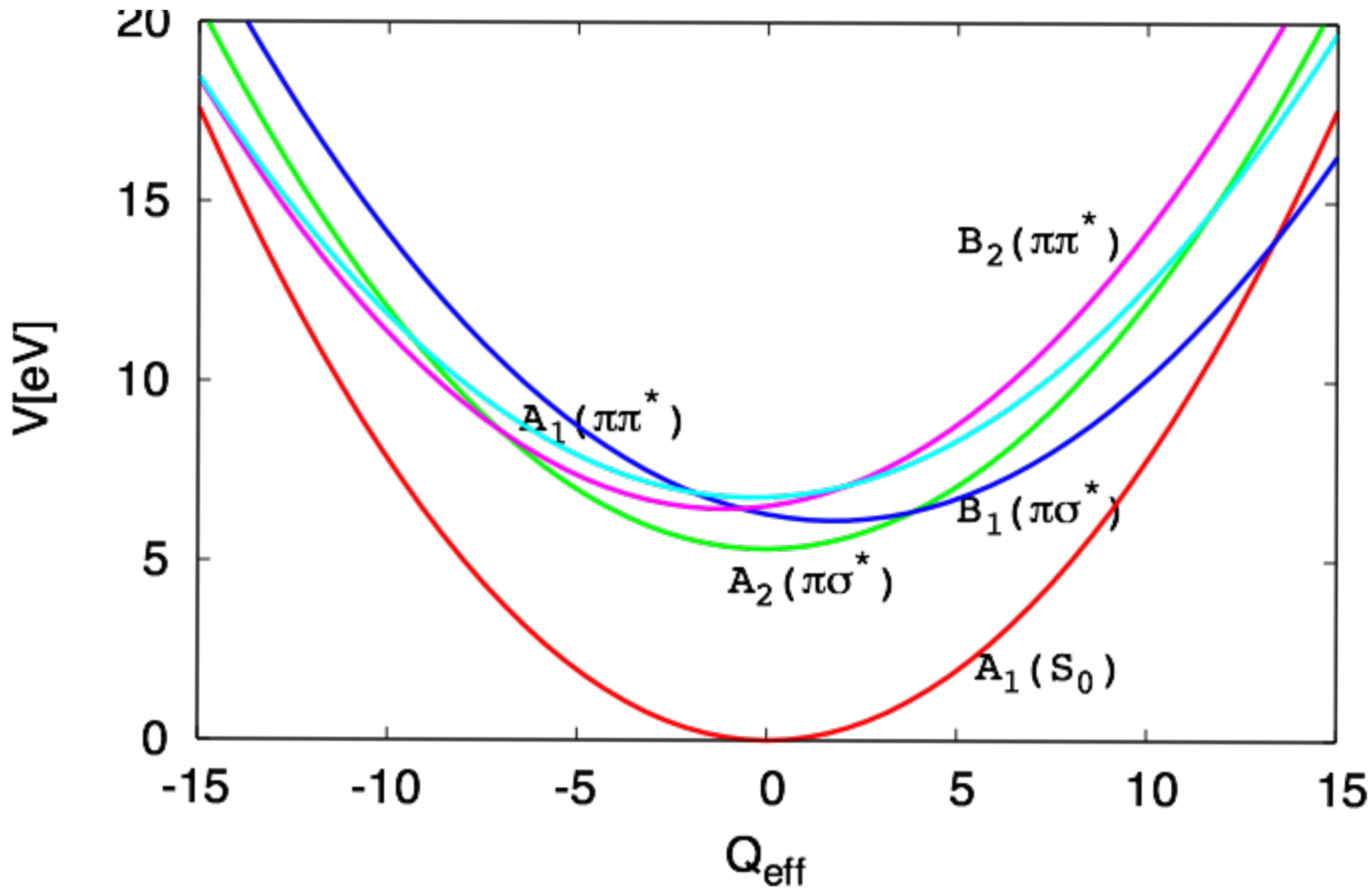
S. Faraji, M. Vazdar, V. S. Reddy, M. Eckert−Maksic, H. Lischka and H. Köppel, J. Chem. Phys. 135, 154310 (2011)

5x5 Vibronic Coupling Hamiltonian

$$\mathbf{H} = (T_N + V_0)\,\mathbf{1} + \mathbf{W}$$

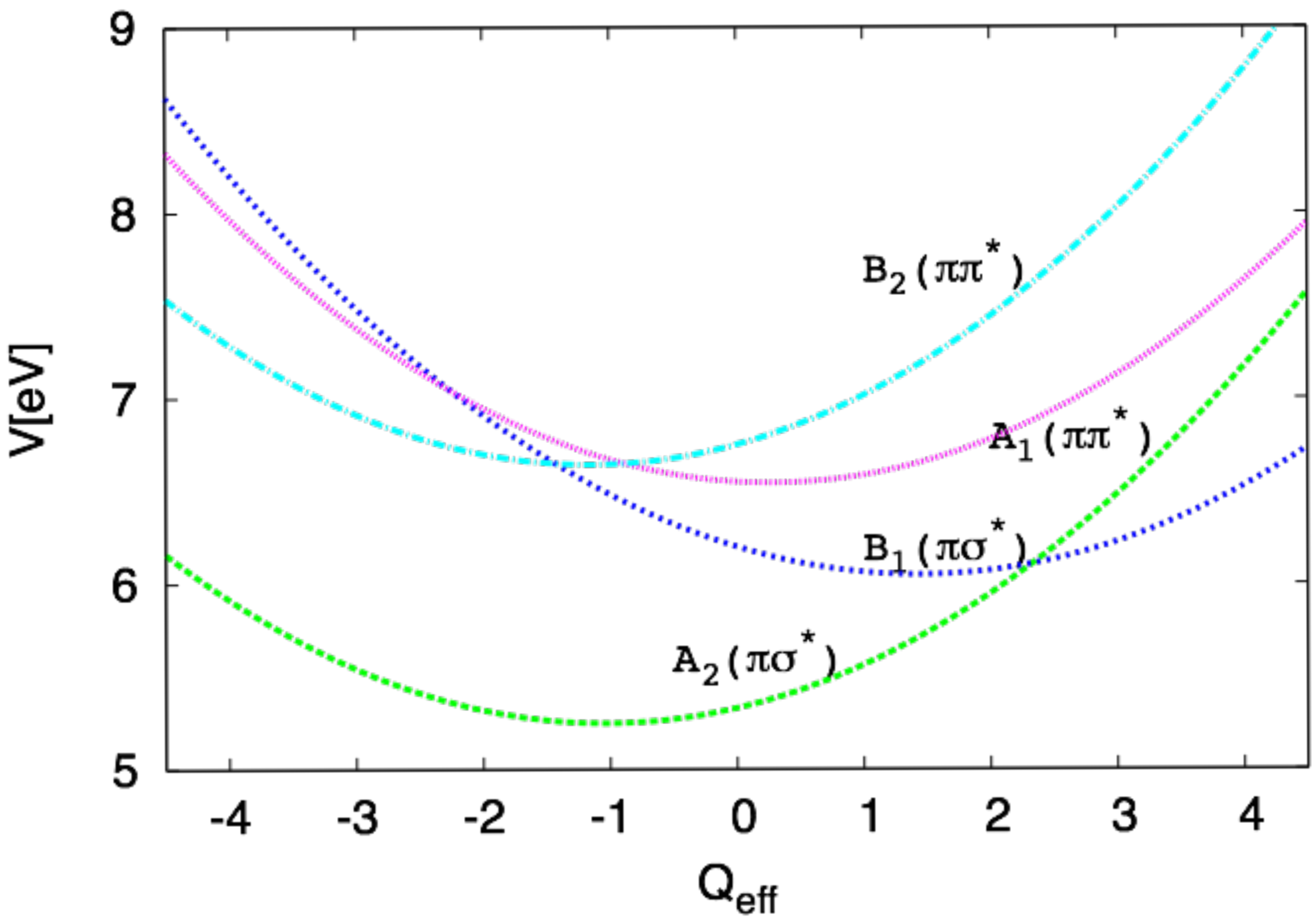
$$\mathbf{W} = \begin{pmatrix} W_0 & \lambda_{4/7}^{(0,1)} Q_{4/7} & \lambda_{6}^{(0,2)} Q_{6} & 0 & 0 \\ \lambda_{4/7}^{(0,1)} Q_{4/7} & W_1 & \lambda_{8,14,17}^{(1,2)} Q_{8,14,17} & \lambda_{4/7}^{(1,3)} Q_{4/7} & 0 \\ \lambda_{6}^{(0,2)} Q_{6} & \lambda_{8,14,17}^{(1,2)} Q_{8,14,17} & W_2 & \lambda_{3}^{(2,3)} Q_{3} & \lambda_{4/7}^{(2,4)} Q_{4/7} \\ 0 & \lambda_{4/7}^{(1,3)} Q_{4/7} & \lambda_{3}^{(2,3)} Q_{3} & W_3 & \lambda_{8,14,17}^{(3,4)} Q_{8,14,17} \\ 0 & 0 & \lambda_{4/7}^{(2,4)} Q_{4/7} & \lambda_{8,14,17}^{(3,4)} Q_{8,14,17} & W_4 \end{pmatrix}$$

Minima of conical intersection seams S0-S4



	S_0	S_1	S_2	S_3	S_4
$S_0(A_1)$	0.0	13.82	14.06	13.05	14.44
$S_1(A_2)$		5.01	6.04	6.49	9.28
$S_2(B_1)$			6.01	6.29	6.58
$S_3(A_1)$				6.25	6.57
$S_4(B_2)$					6.56

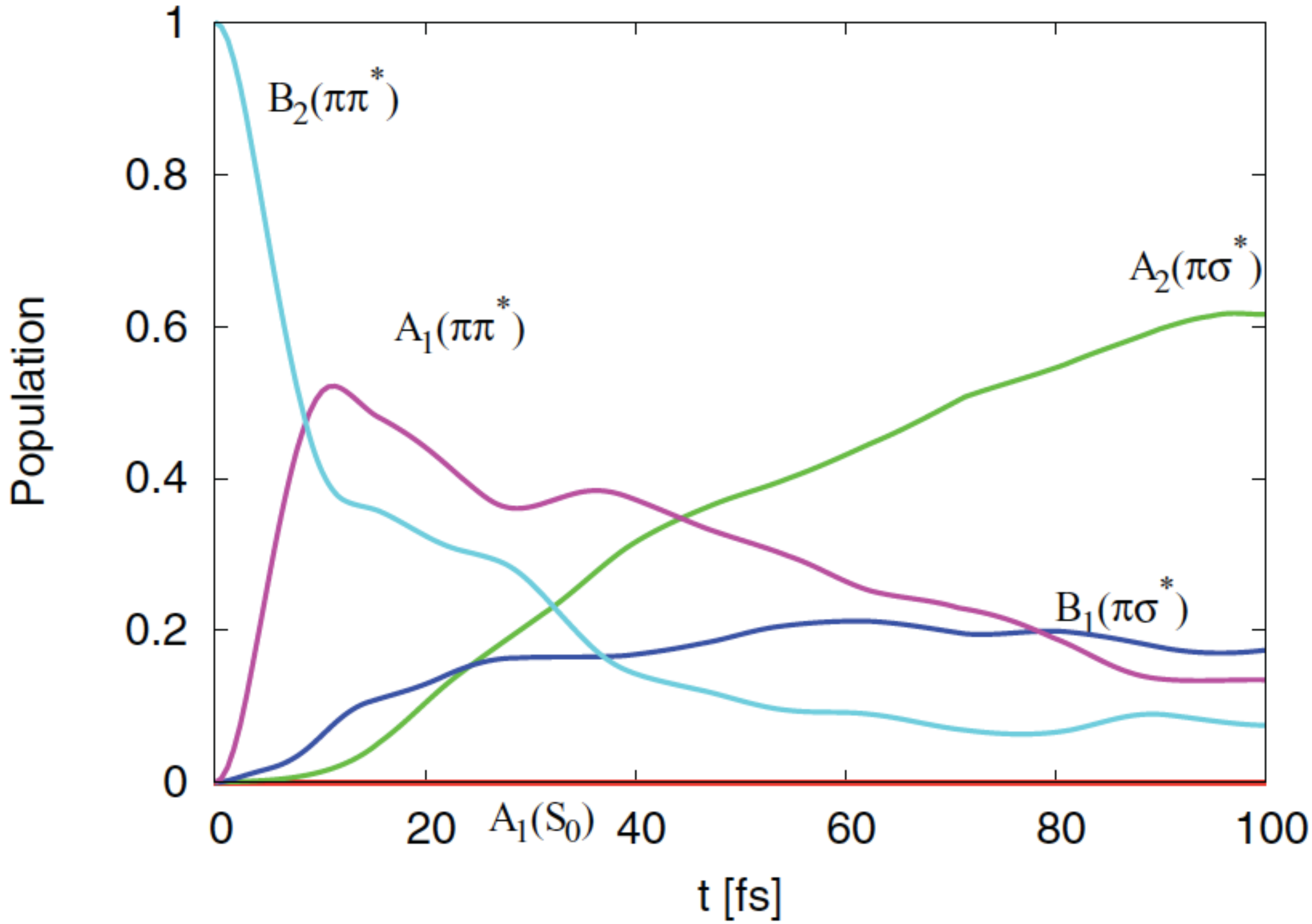
Minima of conical intersection seams S1-S2



	S_1	S_2	S_3	S_4
S_1	5.05	6.00	6.71	8.59
S_2		5.95	6.29	6.48
S_3			6.28	6.48
S_4				6.48

Time-dependent electronic populations

10 Mode, 5 States



Anharmonic treatment of mode 24

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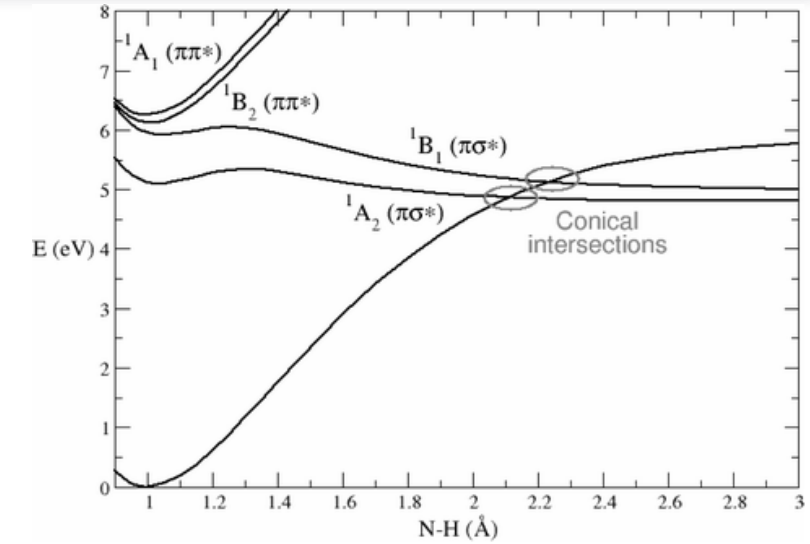
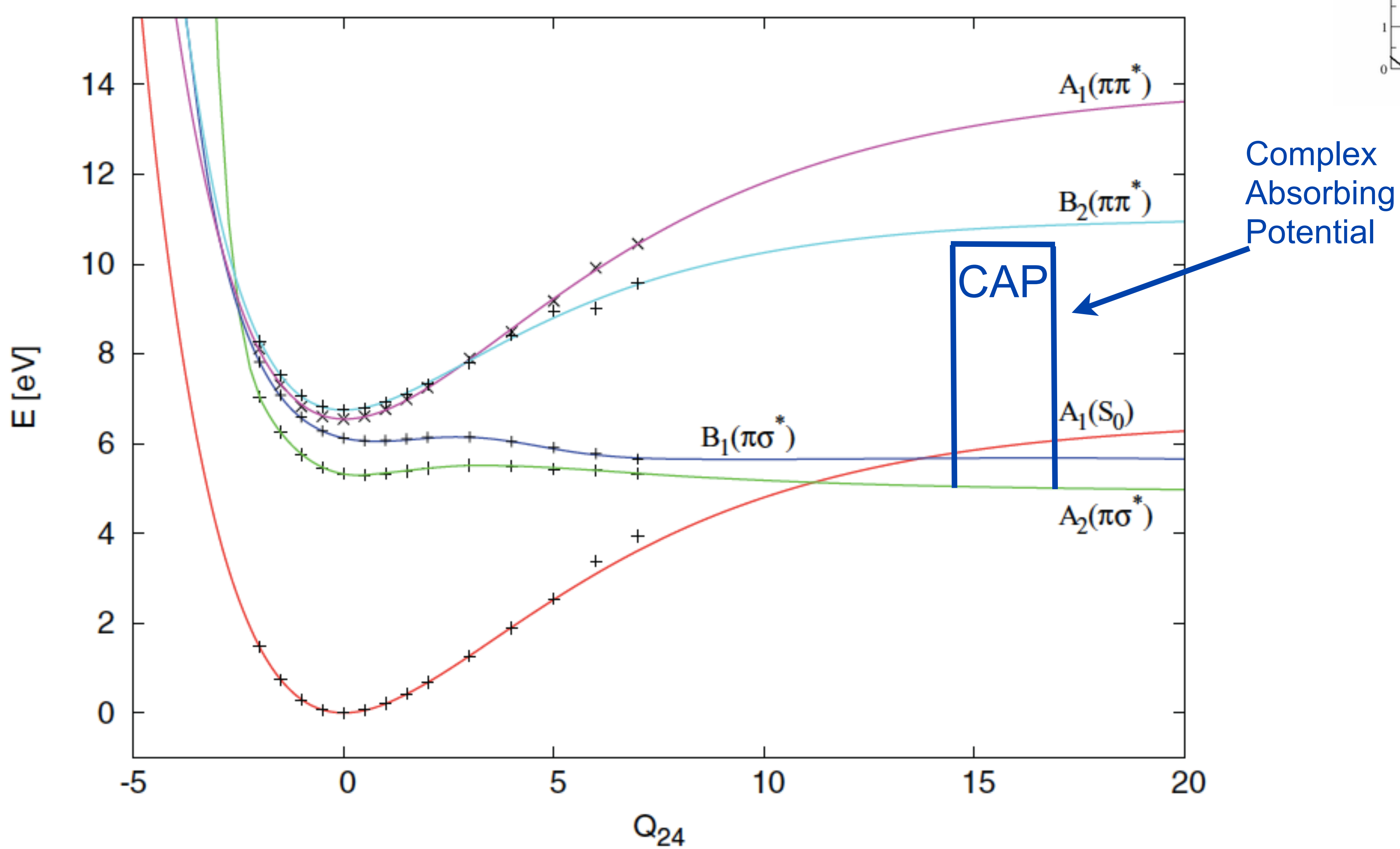
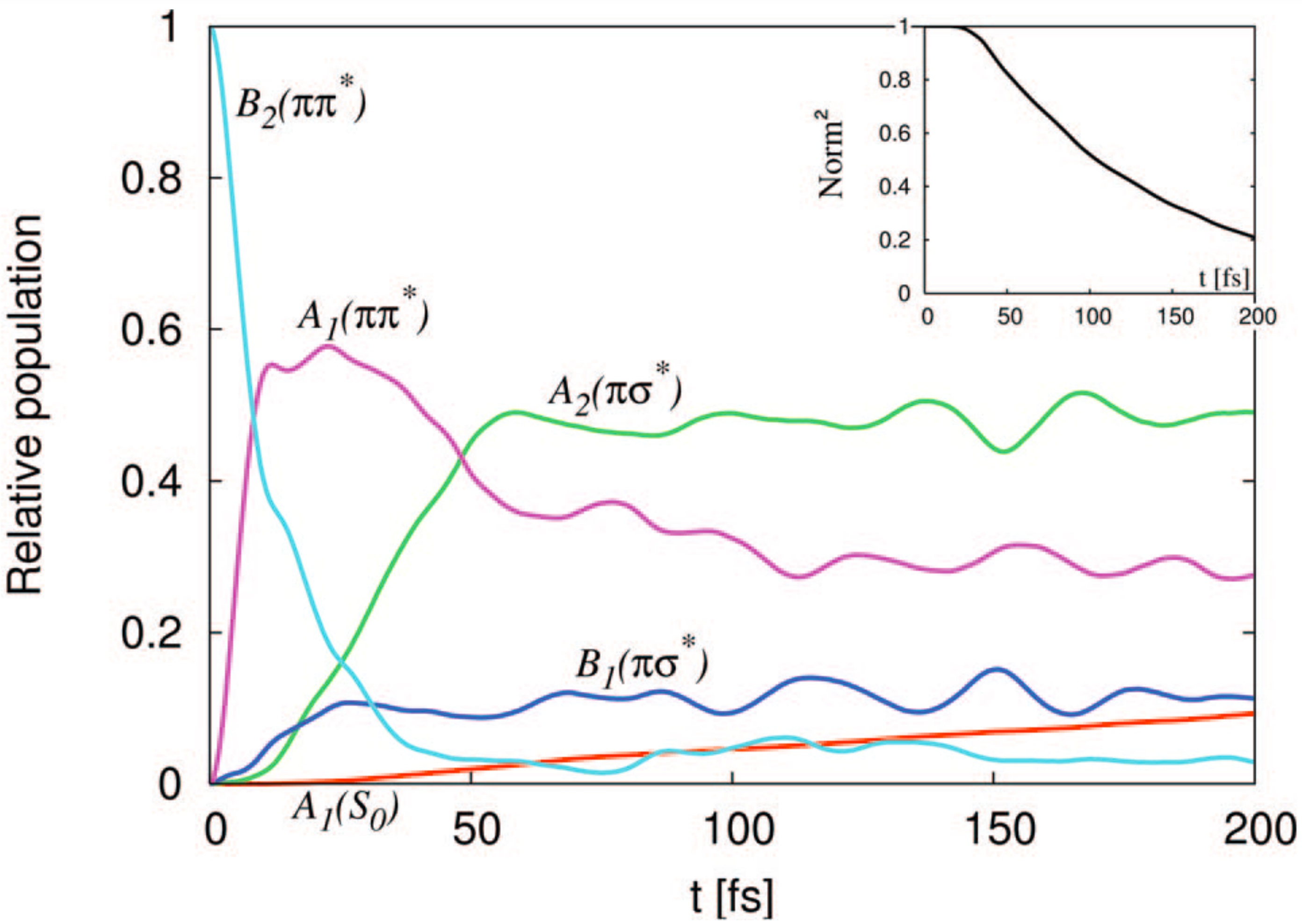
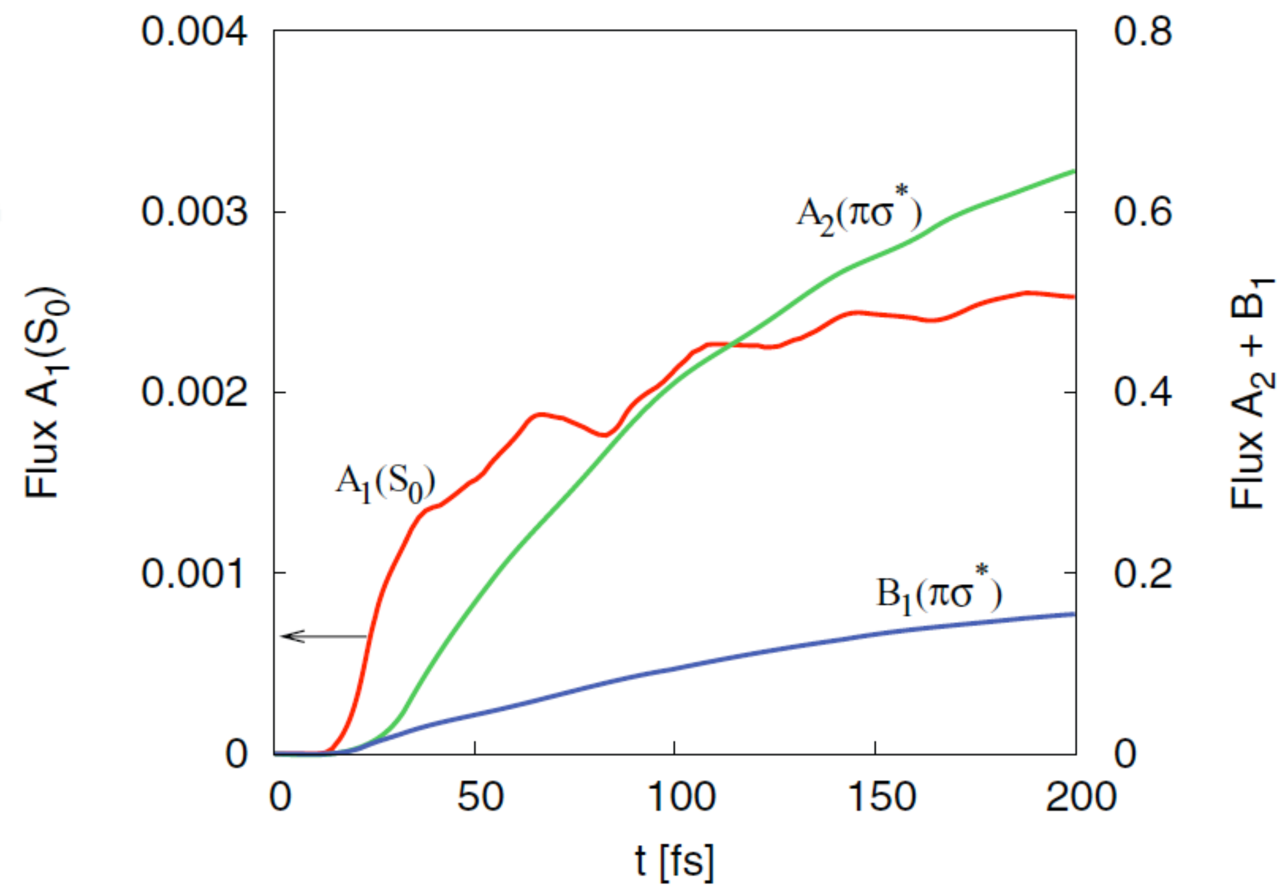




Time-dependent electronic populations



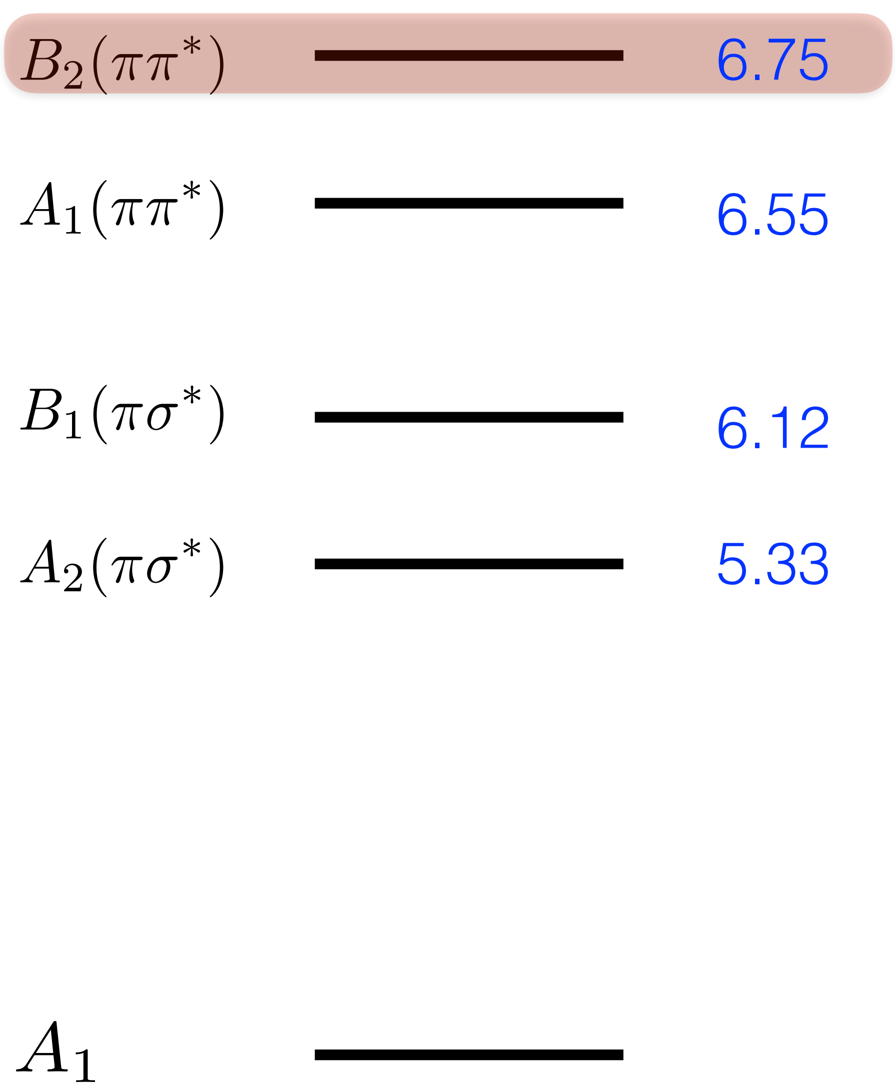
Population transfer to S_0

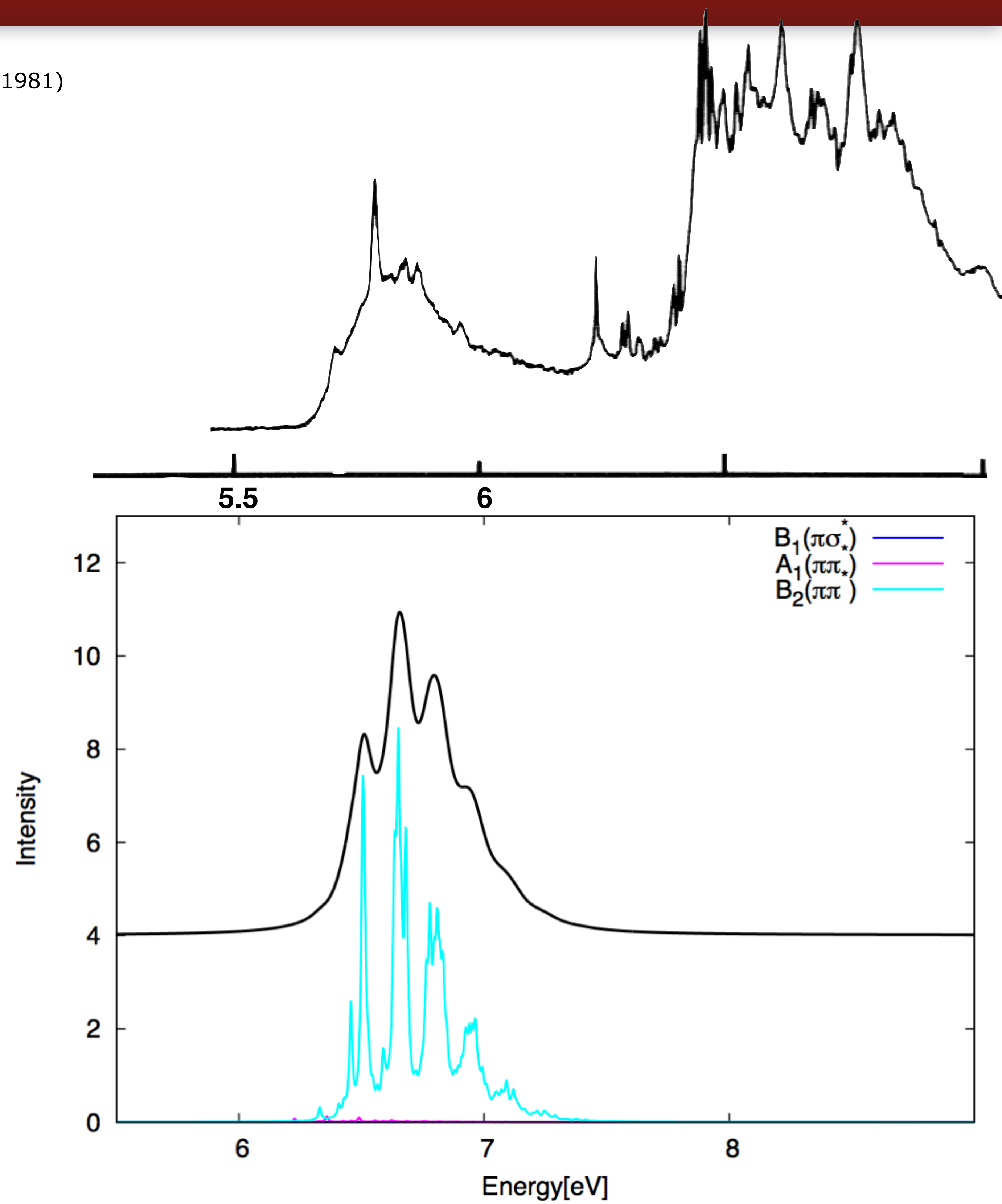


Experiment:
Fast H ~ 100 fs
Slow H ~ 1ps

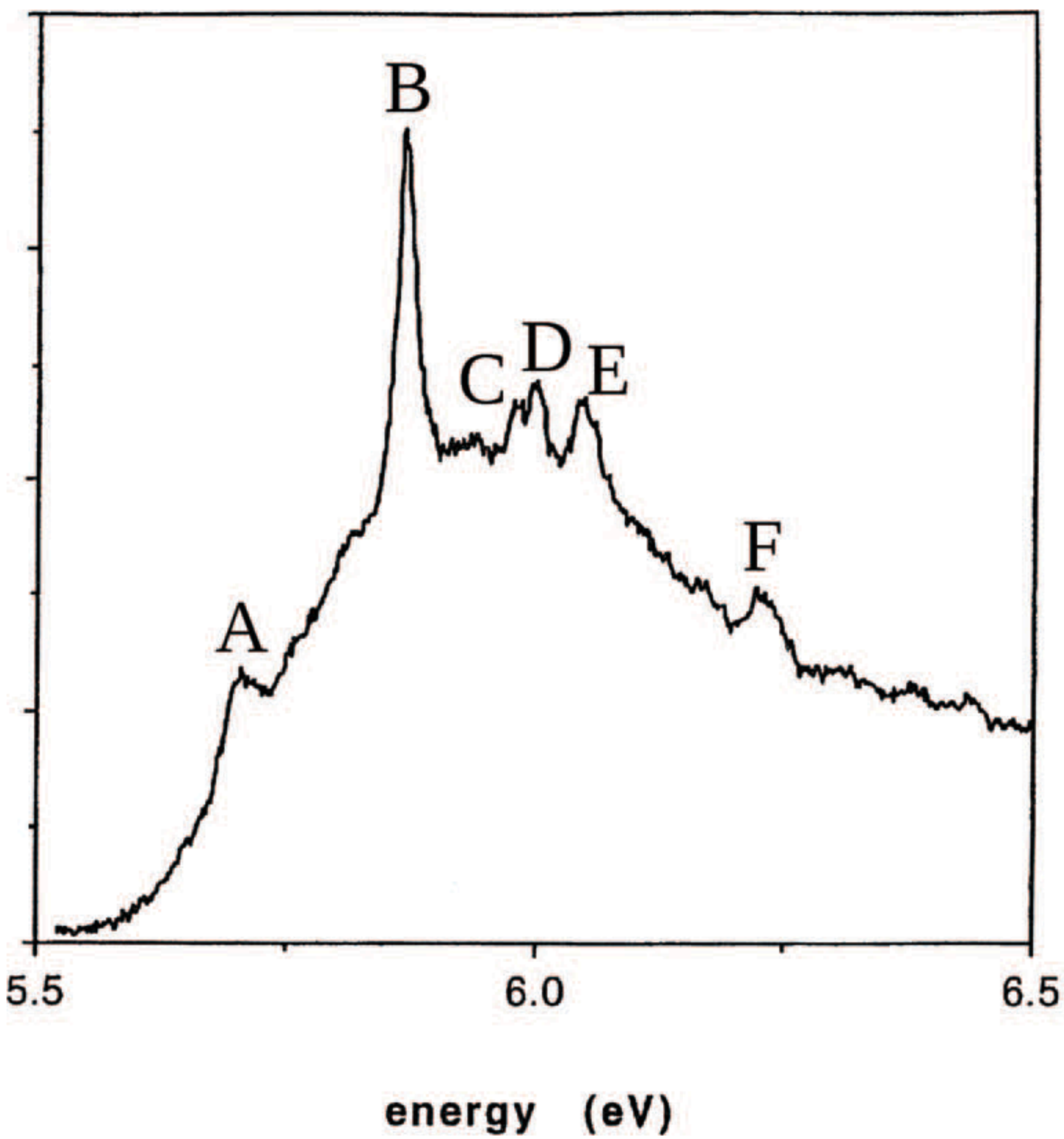
Absorption spectrum

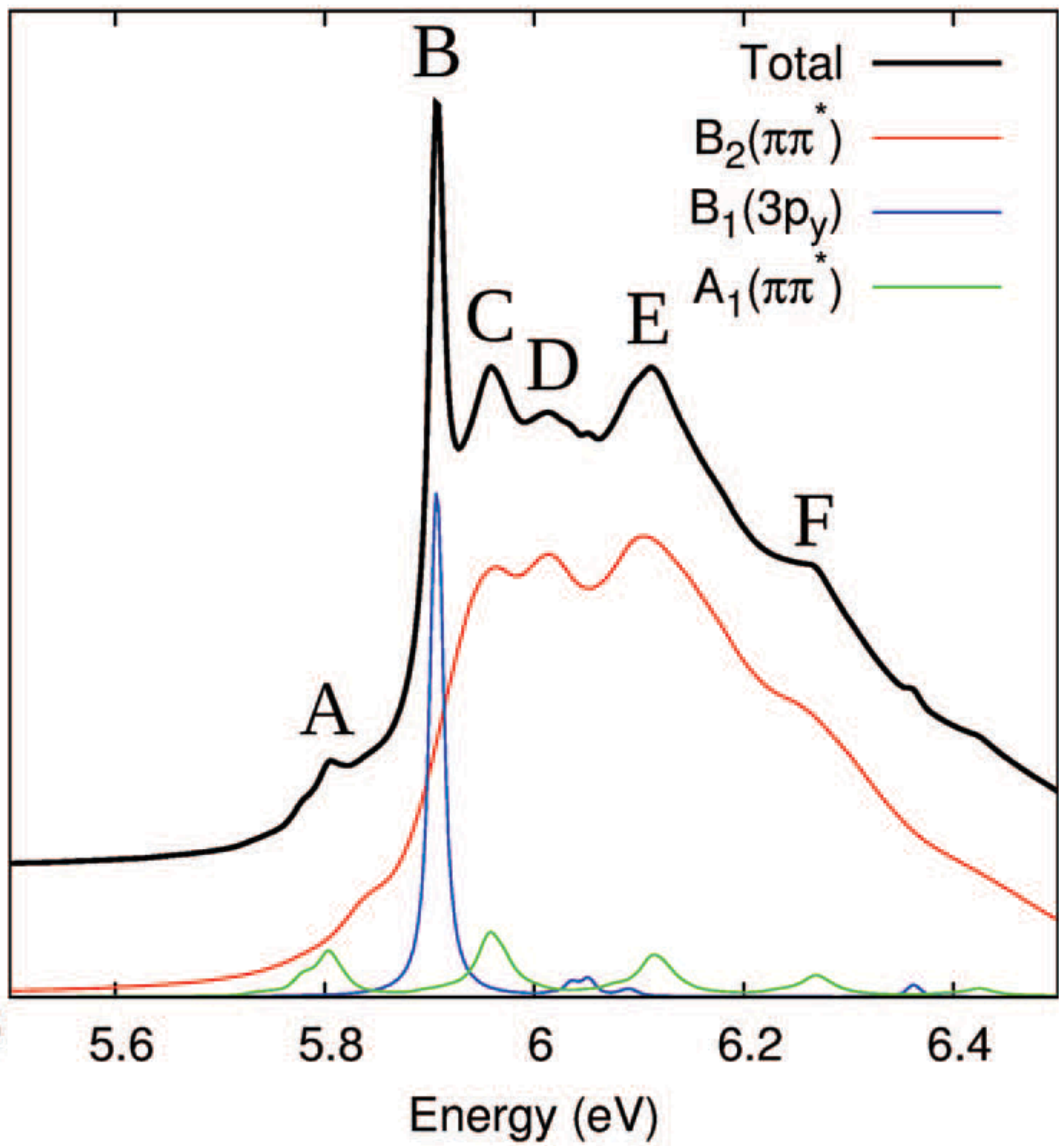
G. Bieri, L. Asbrink, and W. von Niessen, J. Electron Spectrosc. Relat. Phenom. **23**, 281 (1981)





Graham Worth's group





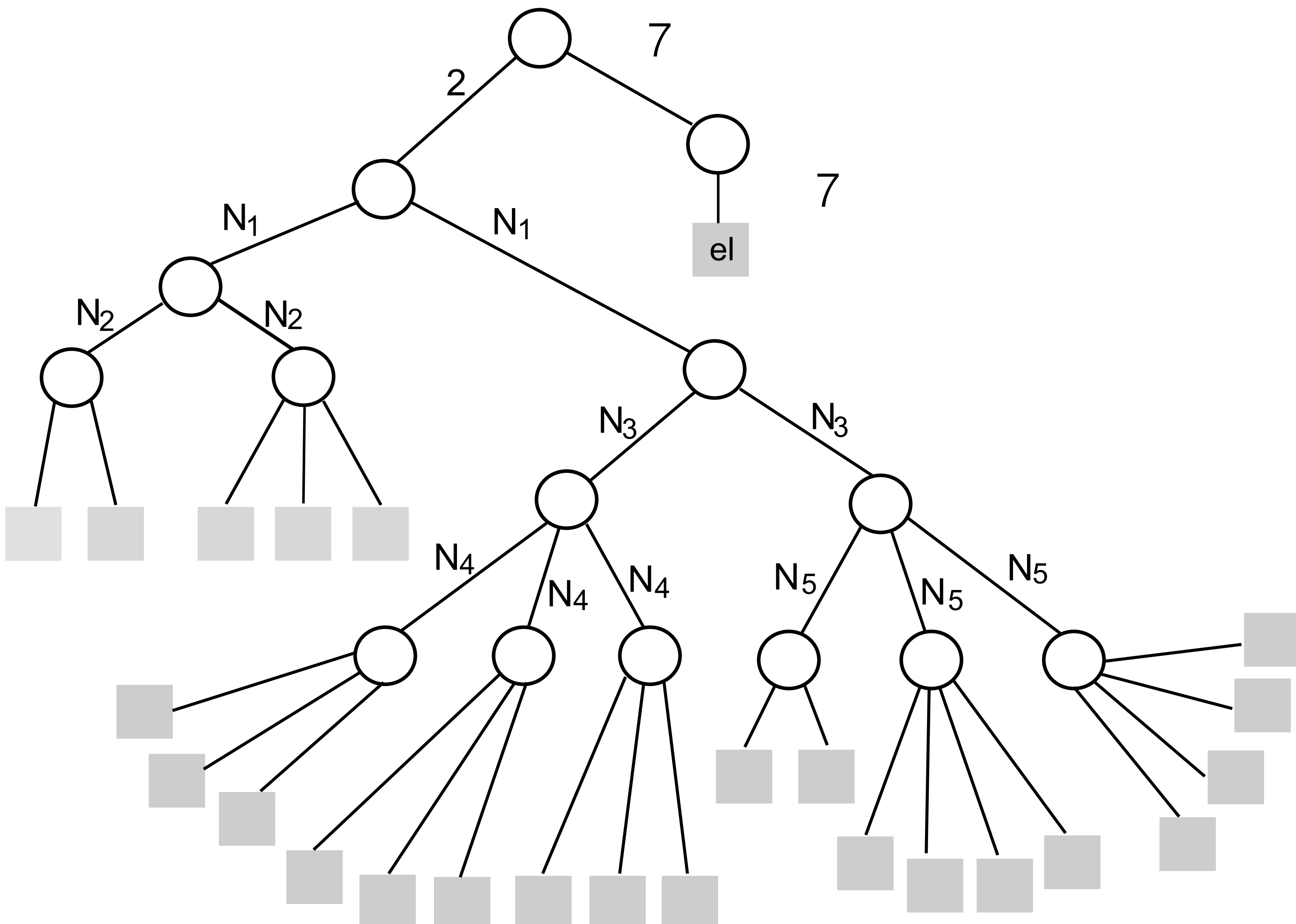
S. P. Neville and G. A. Worth, J. Chem. Phys. 140, 034317 (2014).

State	MRCI+Q	CASSCF & EOM-CCSD	EOM-CCSD
$B_2(\pi\pi^*)$	6.75 eV	6.24 eV	6.26 eV
$A_1(\pi\pi^*)$	6.55 eV	6.01 eV	6.15 eV
$B_1(3P_y)$		6.00 eV	6.00 eV
$A_2(3P_z)$		5.87 eV	5.91 eV
$B_1(\pi\sigma^*)$	6.12 eV	5.86 eV	5.87 eV
$A_2(\pi\sigma^*)$	5.33 eV	5.06 eV	5.14 eV
A_1			

Re-visit LVC(+Q) model Hamiltonian

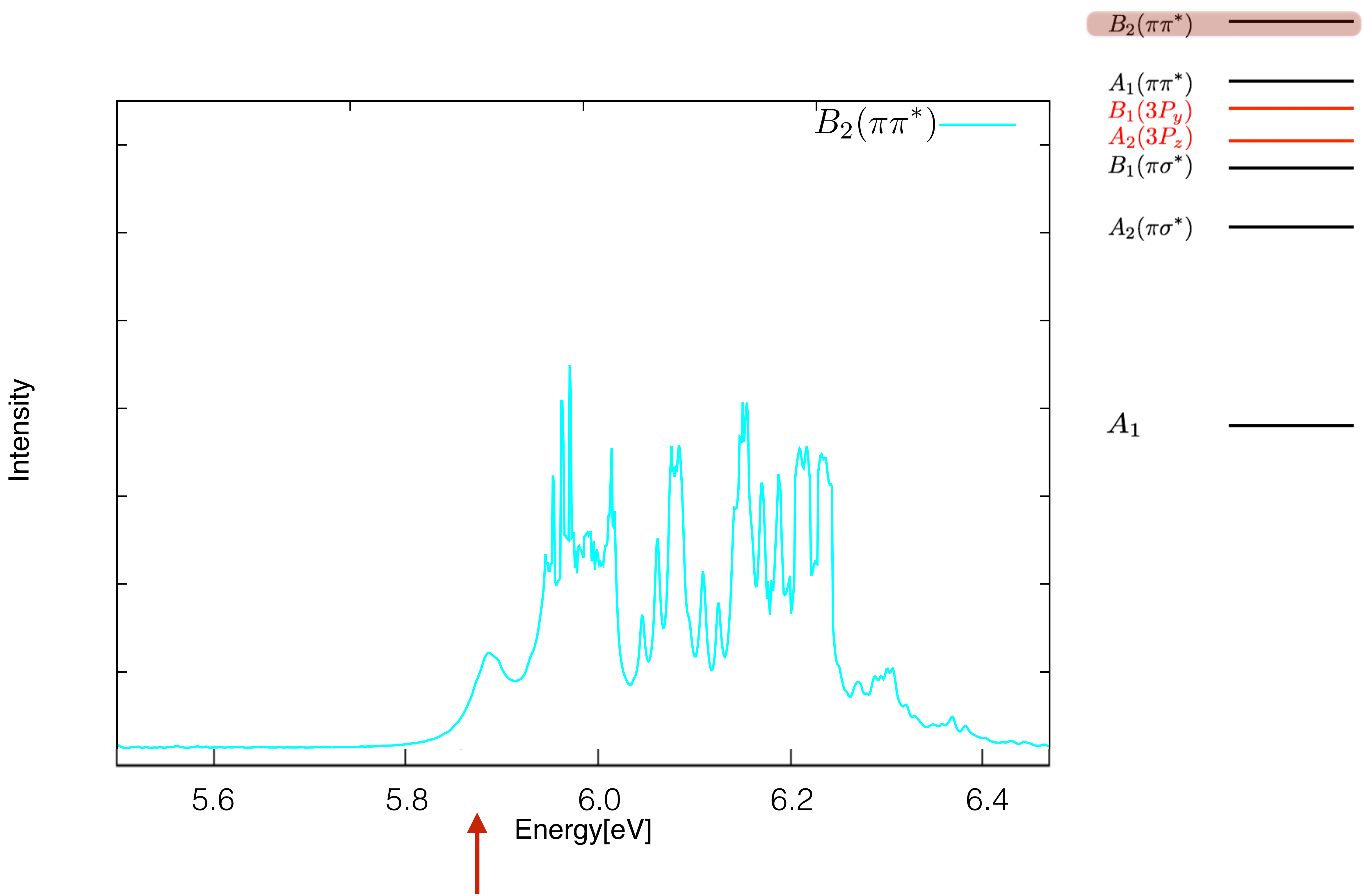
- 7x7 model Hamiltonian (S_0, S_1-S_6)
- Same anharmonic treatment of N-H normal coordinate
- Same CAP
- 24 vibrational mode (full dimension)

Pyrrole 24D, ML-MCTDH-tree



MCTDH (289 h) ML-MCTDH (11.5 h)

Absorption spectrum



Absorption spectrum

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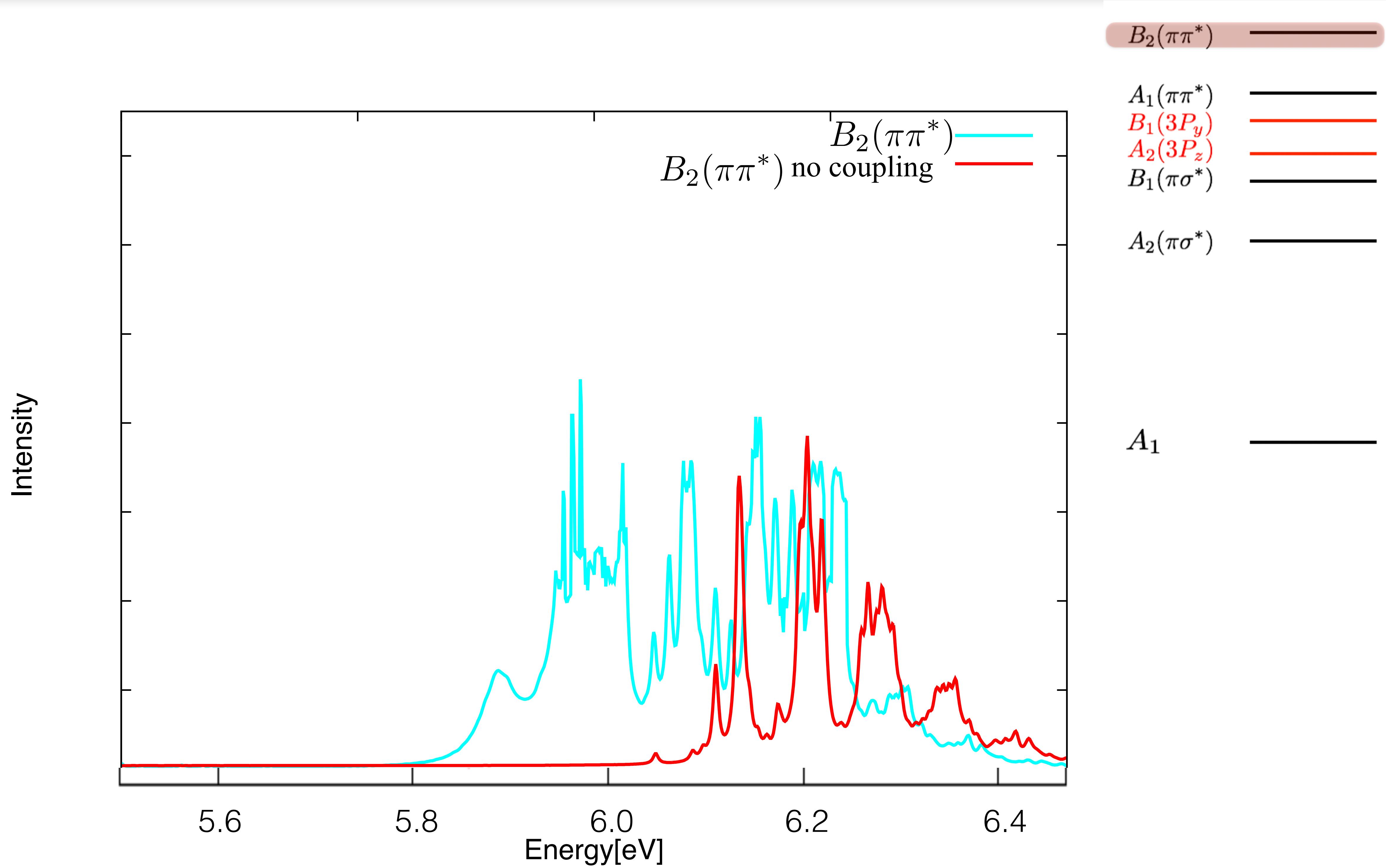
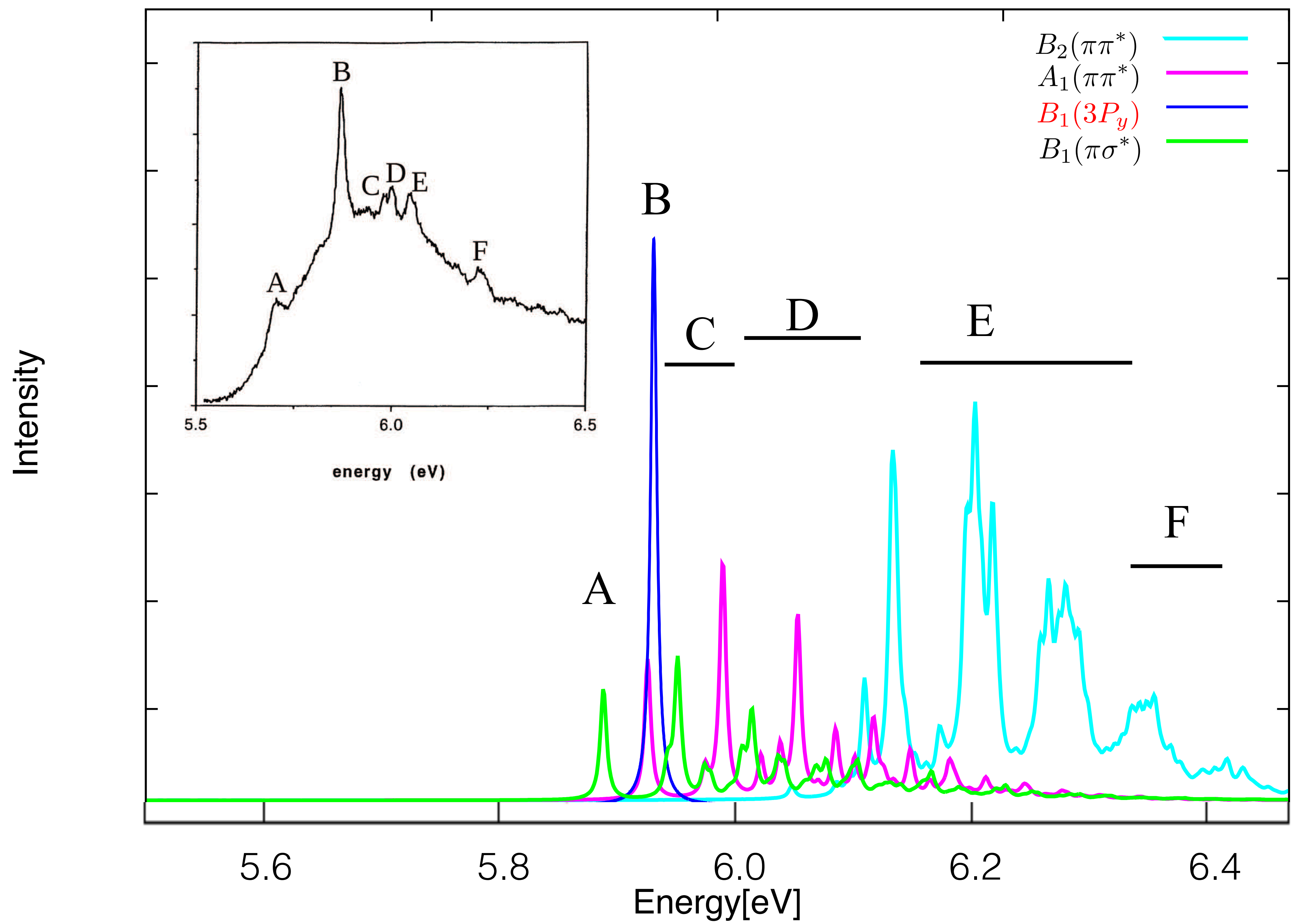
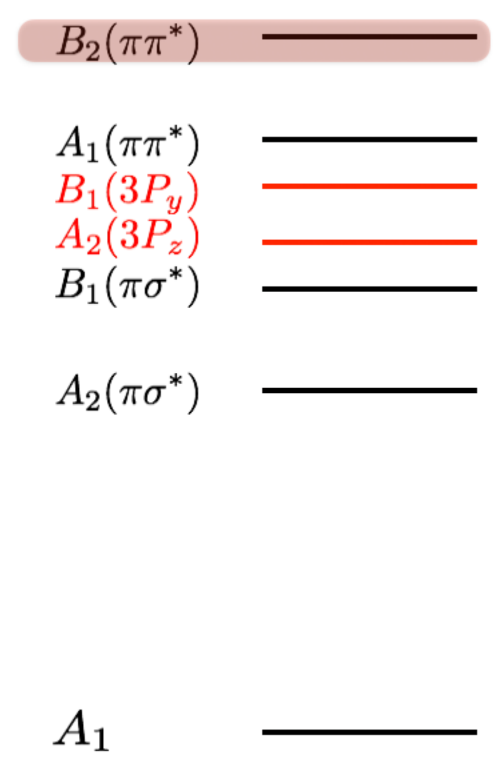


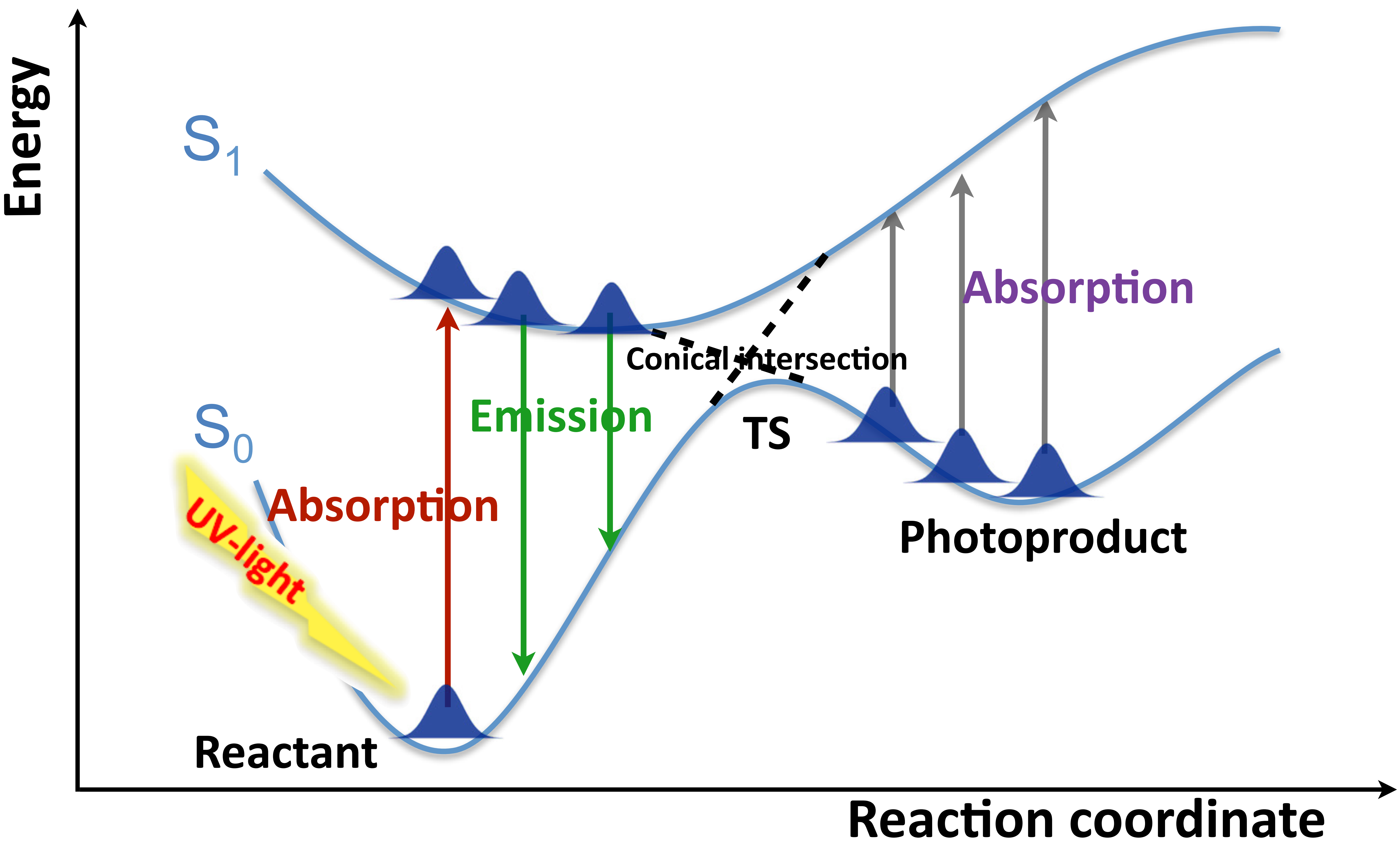
Absorption spectrum

No coupling





Theoretical challenges in quantum dynamics



Gaussian based MCTDH

- MCTDH

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

- Gaussian based MCTDH (G-MCTDH)

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

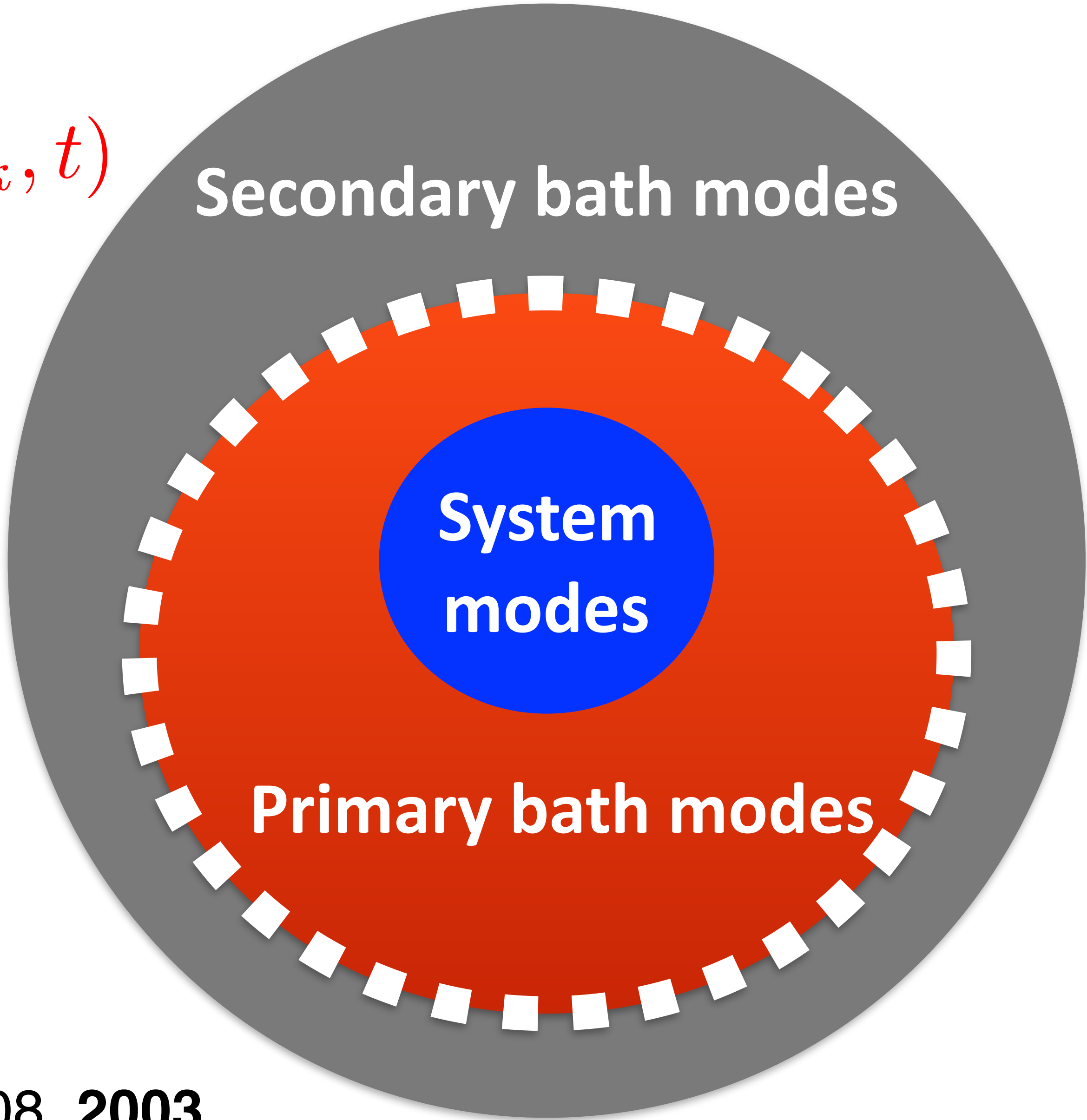
- Variational multi-configuration Gaussian (vMCG)

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

Gaussian based hybrid method: G-MCTDH

$$\Psi(Q,t) = \sum_J A_J(t)\Phi_J(Q,t)$$

$$\Phi_J(Q,t) = \prod_{\kappa=1}^{m} \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) \prod_{\kappa=m+1}^{f} g_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$



- Quantum-semiclassical MCTDH
- System-bath formalism

G. Worth, I. Burghardt, *Chem. Phys. Lett.*, 368, 502, 508, **2003**.
G. Worth, I. Burghardt, *Int. Rev. Phys. Chem.*, 34, 269, **2015**.

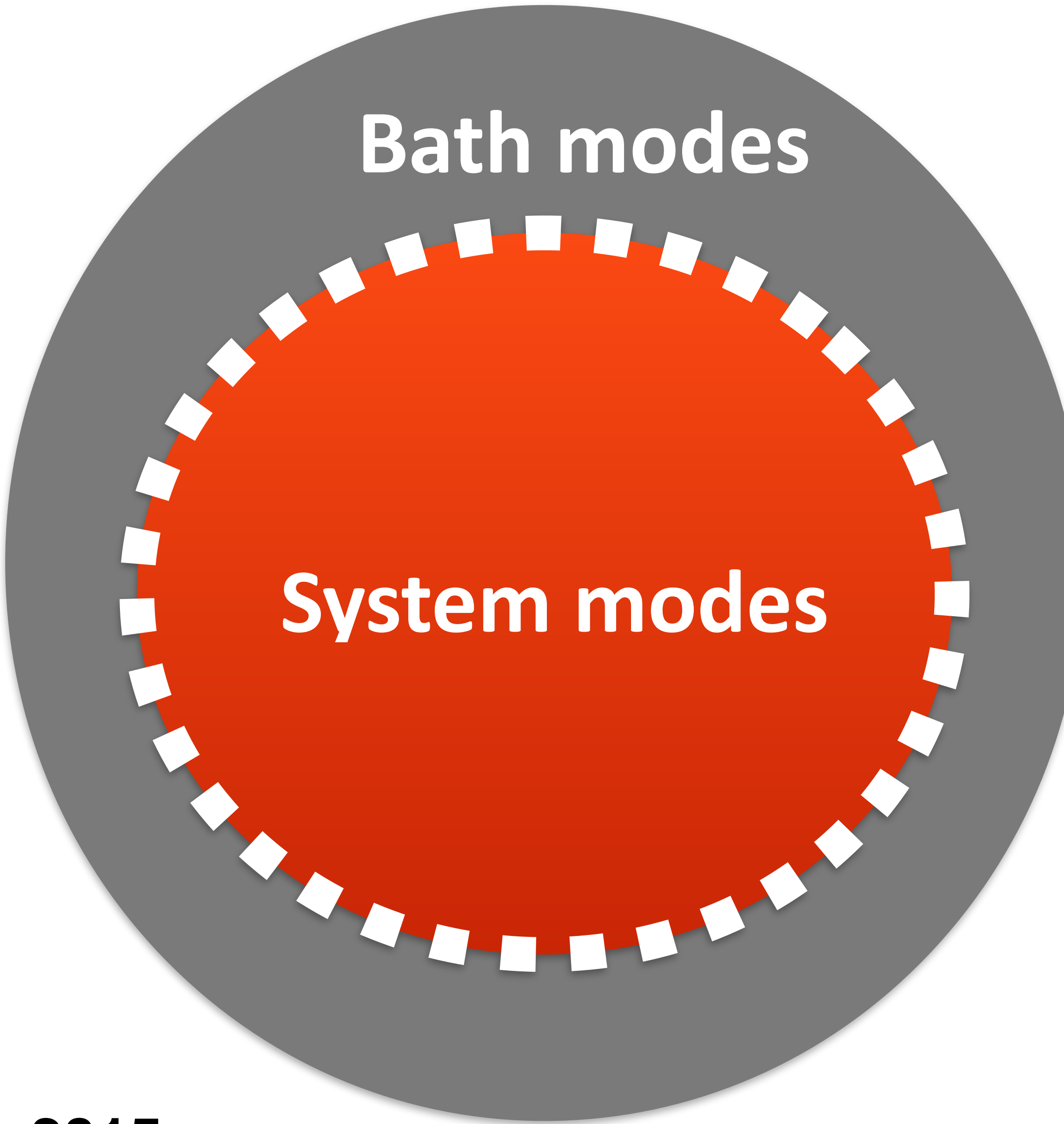
Variational multi-configurational Gaussian (vMCG)

$$\Psi(Q,t) = \sum_J A_J(t)\Phi_J(Q,t)$$

$$\Phi_J(Q,t) = \prod_{\kappa=1}^{f} g_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

$$\Psi(\mathbf{Q},t) = \sum_{j=1}^{n} A_j(t) \;\; g_j(\mathbf{Q},t)$$

- System-bath formalism
- **On-the-fly quantum dynamics**



G. Worth, I. Burghardt, *Int. Rev. Phys. Chem.*, 34, 269, **2015**.

Type of Gaussian

$$g_{j_\kappa}^{(\kappa)}(Q_\kappa, t) = \exp\left[Q_\kappa^T \; \zeta_j^\kappa(t) \; Q_\kappa \; + \; \xi_j^\kappa(t) Q_\kappa \; + \; \eta_j^\kappa(t)\right]$$

$$\Lambda_j^\kappa(t) = (\; \underbrace{\zeta_j^\kappa(t)}_{\text{width}}, \; \underbrace{\xi_j^\kappa(t)}_{\text{center}}, \; \underbrace{\eta_j^\kappa(t)}_{\text{phase}} \;)$$

- Thawed Gaussian(TG)
- Separable Gaussian (SG)
- **Frozen Gaussian (FG)**
- Semi-classical motion of Gaussian center in phase-space
- Analytical integrals, localized functions, fair memory requirement

Equation of motions for G-MCTDH

- Dirac-Frankel variational principle $$\langle \delta\Psi | H - i\frac{\delta}{\delta} | \Psi \rangle = 0$$

- EOM for expansion coefficients $$i\mathbf{S}\dot{\mathbf{A}} = [\mathbf{H} - i\boldsymbol{\tau}]\,\mathbf{A}$$

- EOM for SPFs $$i\dot{\boldsymbol{\varphi}}_j^{(\kappa)} = (\hat{1} - \hat{P}^{(\kappa)})\boldsymbol{\rho}^{(\kappa)^{-1}} \langle \hat{\mathbf{H}} \rangle^{(\kappa)} \boldsymbol{\varphi}^{(\kappa)}$$

- EOM for Gaussian parameters $$i\mathbf{C}^{(\kappa)}\dot{\boldsymbol{\Lambda}}^{(\kappa)} = \mathbf{Y}$$

Two-layer formalism

$$\Psi(\mathbf{Q},t) = \sum_J A_J(t)\, \Phi_J(\mathbf{Q},t) = \sum_J A_J(t) \prod_{\kappa=1}^{f} \chi_{j_\kappa}^{(\kappa)}(\mathbf{Q}_\kappa, t)$$

$$\chi_{j_\kappa}^{(\kappa)}(\mathbf{Q}_{\kappa_1}, t) = \sum_L B_{j,L}^{(\kappa)}(t)\, G_L^{(\kappa)}(\mathbf{Q}_\kappa, t) = \sum_L B_{j,L}^{(\kappa)}(t) \prod_{\mu=1}^{f^{(\kappa)}} g_{l_\mu}^{\kappa,\mu}(\mathbf{Q}_{\kappa,\mu}, t)$$

Multi-layer formalism

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- **M-layer formalism**

$$\Psi(\mathbf{Q},t) = \sum_J A_J^{[1]}(t)\ \Phi_J^{[1]}(\mathbf{Q},t) = \sum_J A_J^{[1]}(t) \prod_{\kappa_1=1}^{f^{[1]}} \chi_{j_{\kappa 1}}^{[1](\kappa_1)}(\mathbf{Q}_{\kappa_1},t)$$

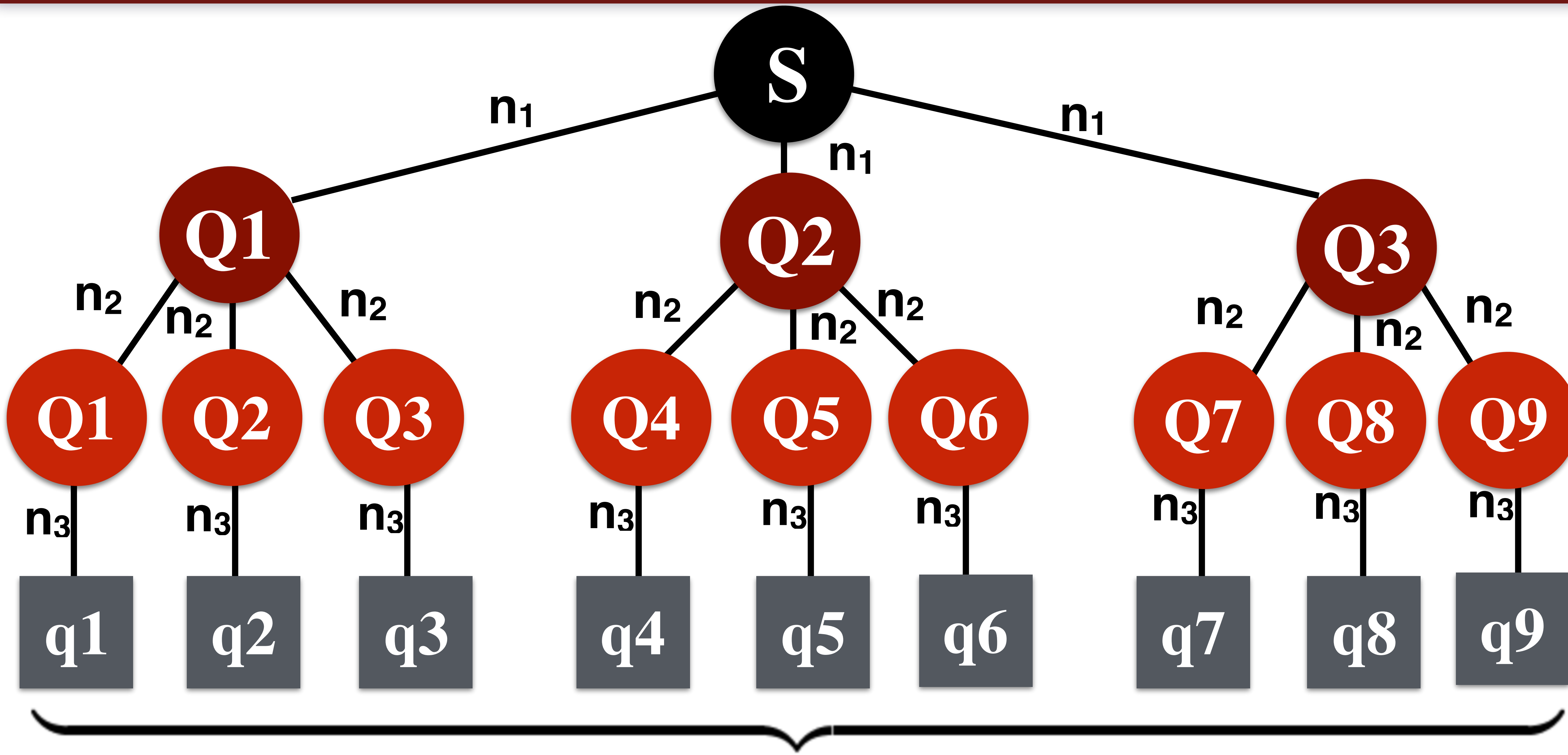
$$\chi_j^{[m-1](\mu_{m-1})}(\mathbf{Q}_{\kappa_{(m-1)}},t) = \sum_L A_{j,L}^{[m](\mu_{m-1})}(t)\ \Phi_L^{[m](\mu_{m-1})}(\mathbf{Q}_{\kappa_{(m-1)}},t)$$

$$= \sum_L A_{j,L}^{[m](\mu_{m-1})}(t) \prod_{\kappa_m=1}^{f_{\mu_{m-1}}^{[m]}} \chi_{l_{\kappa_m}}^{[m](\mu_m)}(\mathbf{Q}_{\kappa_m,\mu_{m-1}},t)$$

- **Last (Mth) layer is represented as FGs**

$$\chi_{l_{\kappa_M}}^{[M](\mu_M)}(t) = g_{l_{\kappa_M}}^{(\mu_M)}(\Lambda_{l_{\kappa_M}}^{(\mu_M)}(t))$$

Multi-layer vMCG is a MUST !



Frozen Gaussian

T. J. Martinez et al, *J. Phys. Chem. A*.104, 5161, **2000**.
G. Worth, I. Burghardt, *Chem. Phys. Lett.*, 368, 502, 508, **2003**.
G. Worth, I. Burghardt, *Int. Rev. Phys. Chem.*, 34, 269, **2015**.

Multi-scaling quantum dynamics

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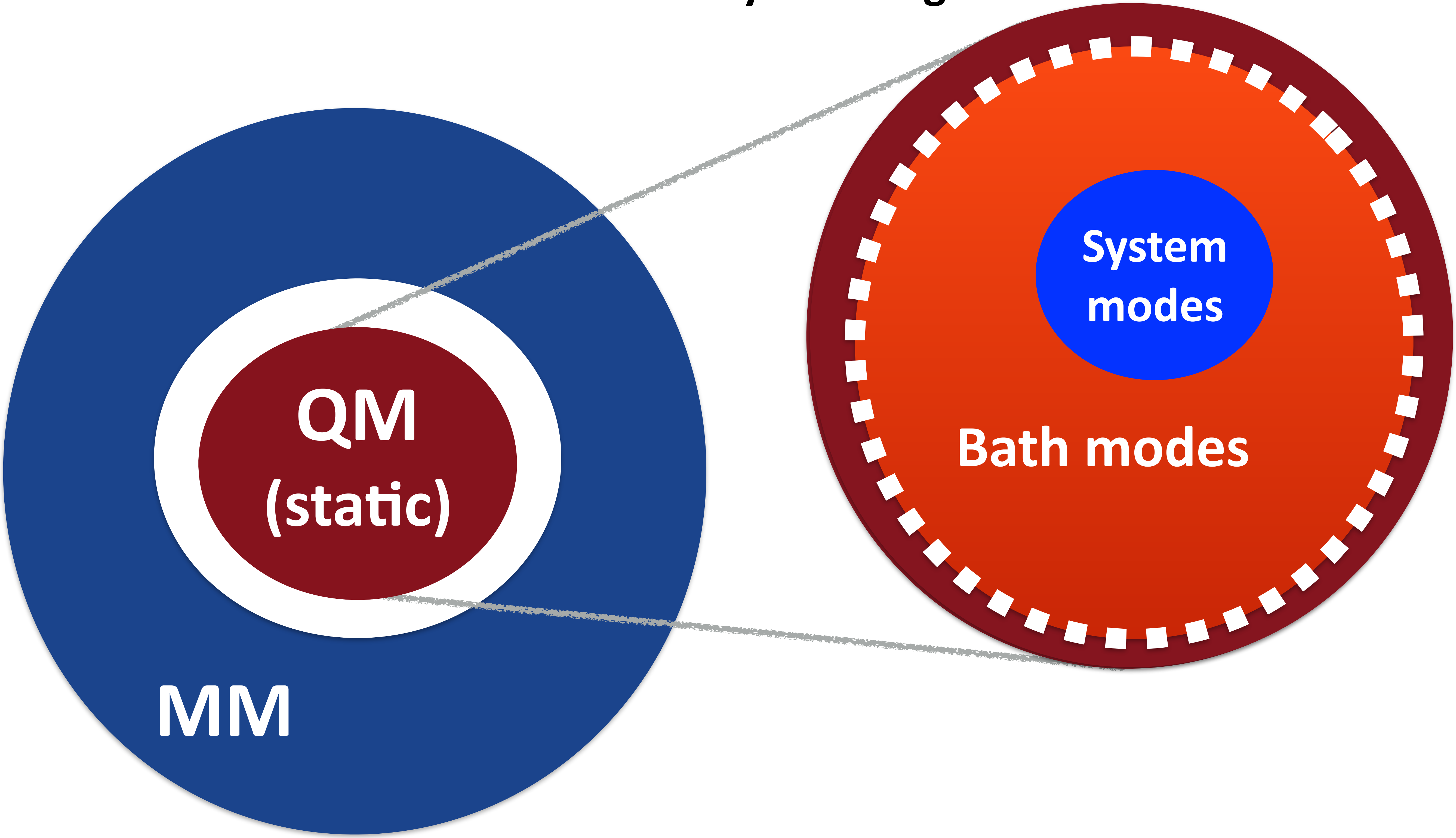
As accurate as necessary & as large as needed

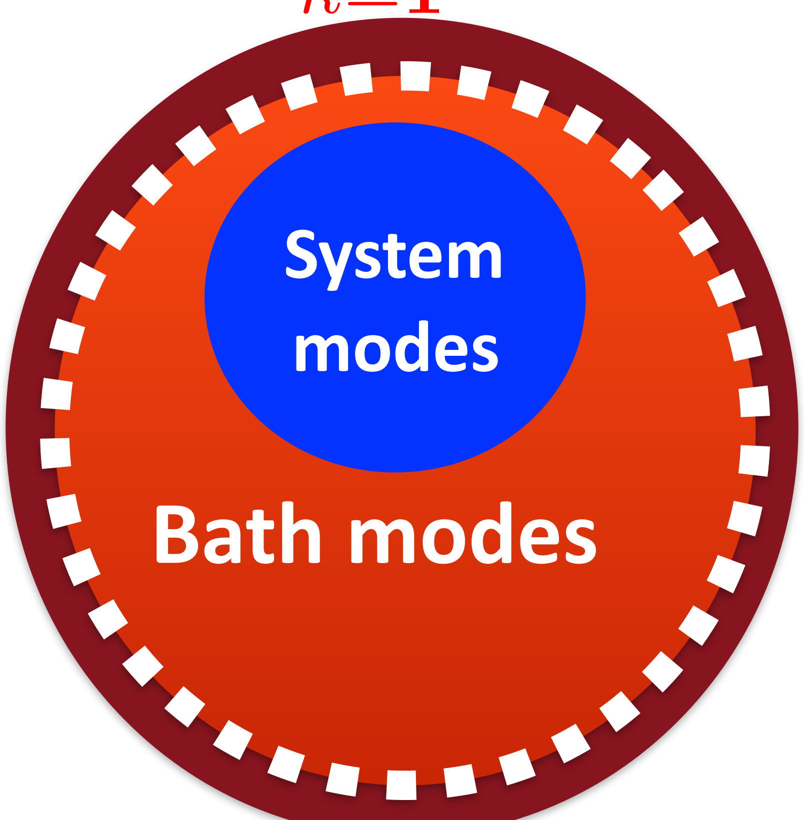


On-the-fly-quantum dynamics

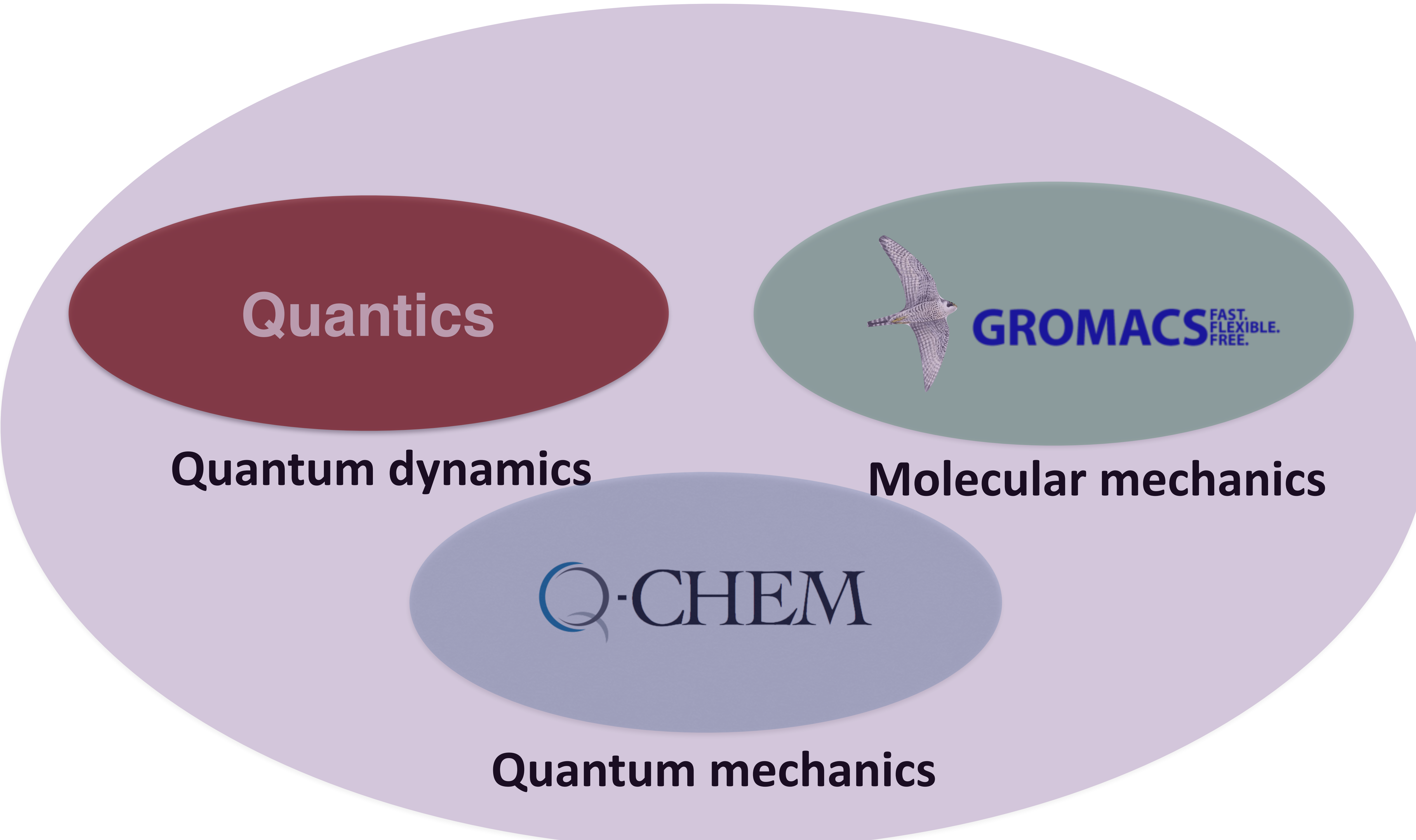
$$\Psi(Q,t)=\sum_{J} A_J(t)\quad \Phi_J(Q,t)$$

$$\Phi_J(Q,t)=\prod_{\kappa=1}^{m}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)\prod_{\kappa=m+1}^{f} g_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

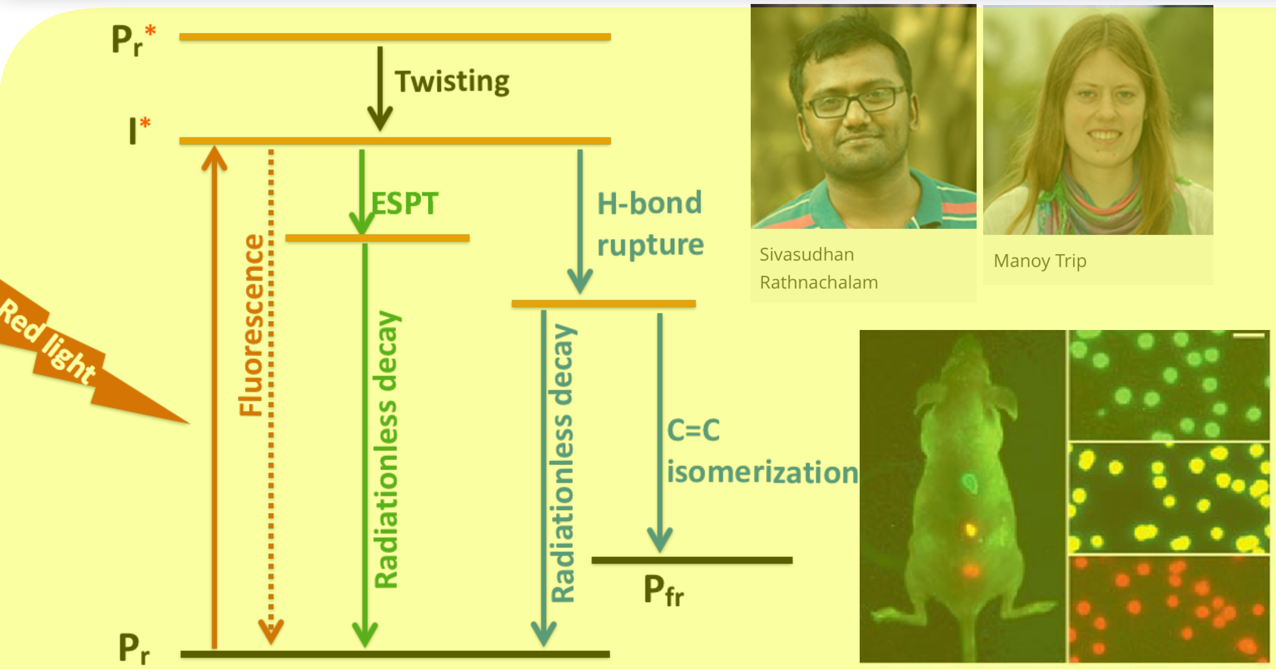
$$\Phi_J(Q,t)=\prod_{\kappa=1}^{f} g_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$



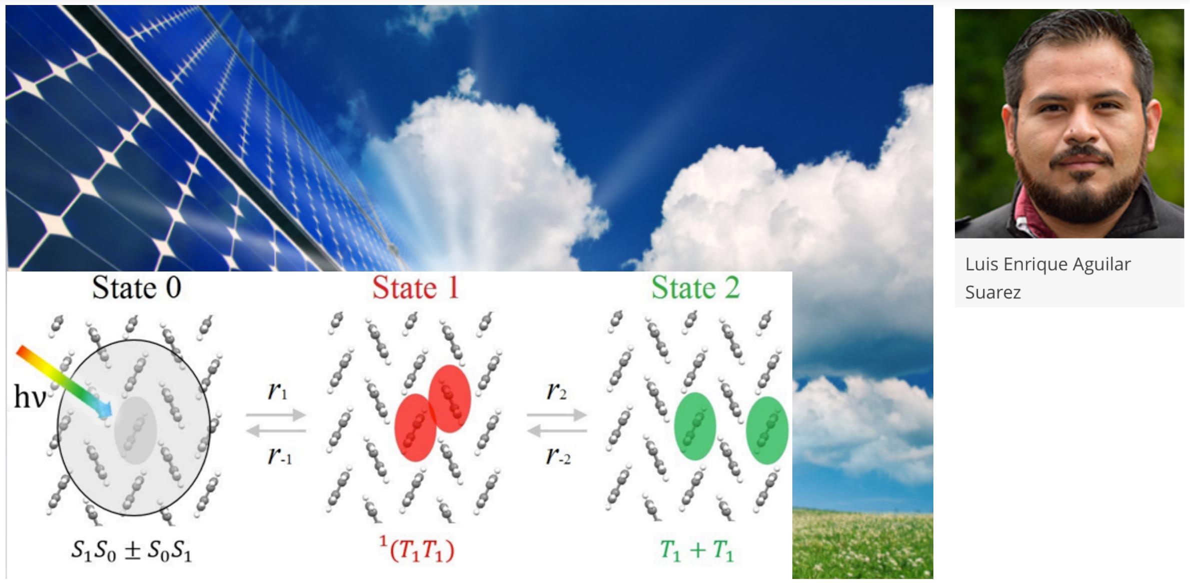
Software infrastructure



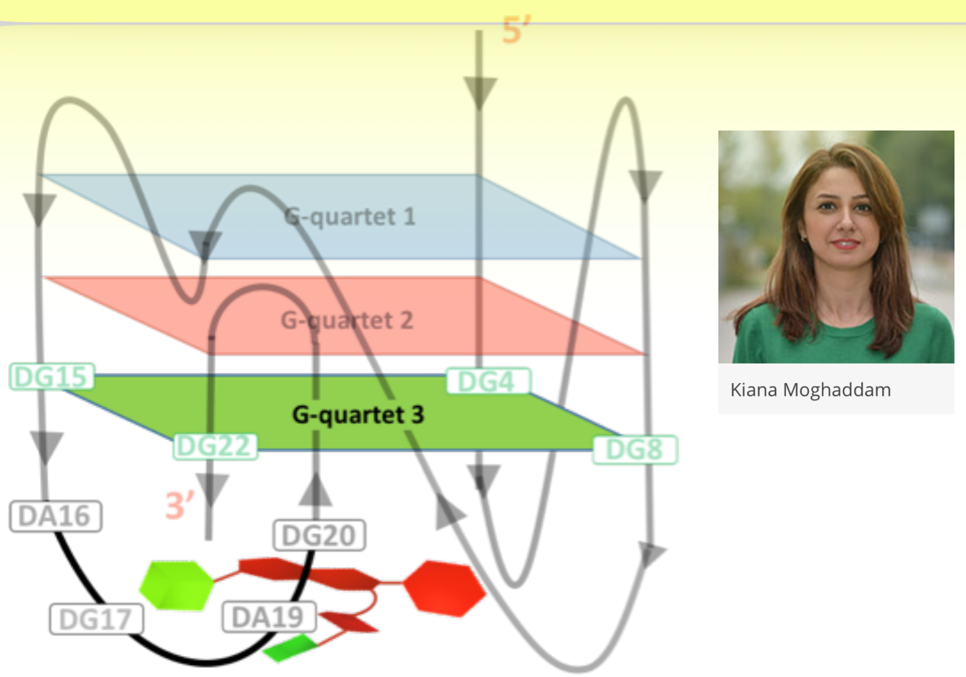
On-going projects



Biomarkers for labeling/tracking cancer cells



Singlet Fission in molecular solids



DNA G-quadroplex and cancer therapy

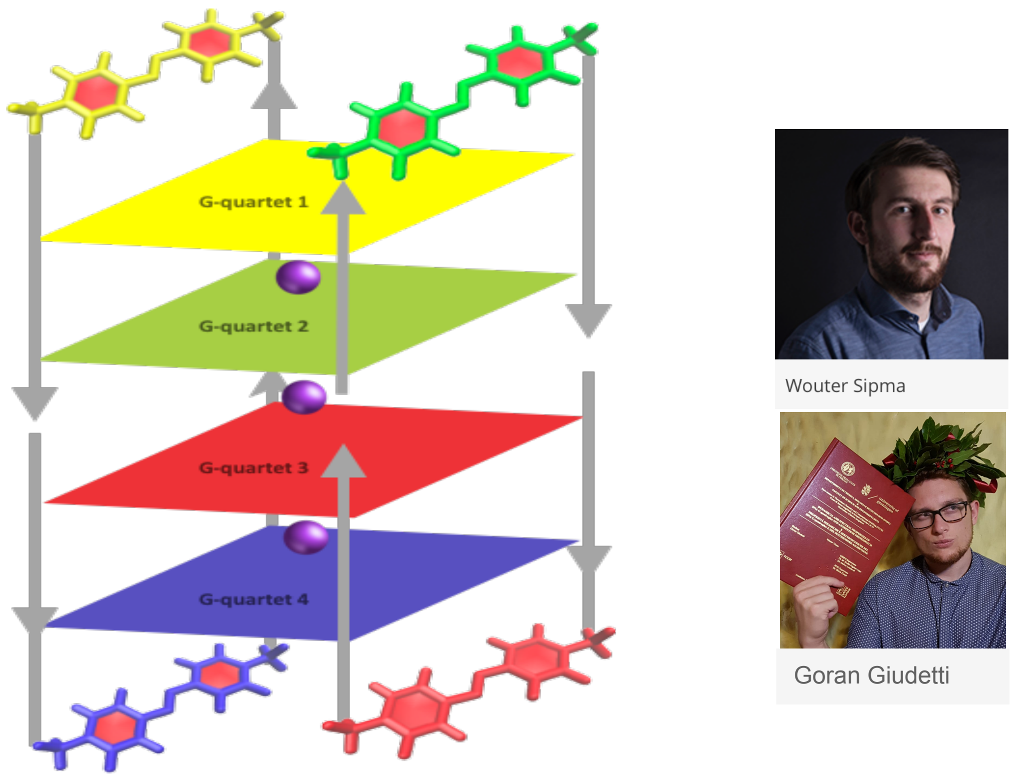


Photo-switchable DNA in nano technology