Chemical Dynamics

UNIVERSITÄT
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Universität Heidelberg

PHYSIKALISCH-
CHEMISCHES
INSTITUT

IWR
Interdisciplinary Center
for Scientific Computing

Center for
Quantum Dynamics

CAM
CENTRE FOR
ADVANCED
MATERIALS

Ultrafast X-ray Summer School 2019

QUESTION

I am a …

- 🟦 … a physicist.
- 🟢 … a chemist.
- ▲ … a biologist / life scientist.
- ⬟ … I still need to find out.

QUESTION

I mostly work as ...

- 🟦 ... an experimentalist.
- 🟢 ... a theoretician.
- ▲ ... both an experimentalist and a theoretician.

Outlook

- Introduction

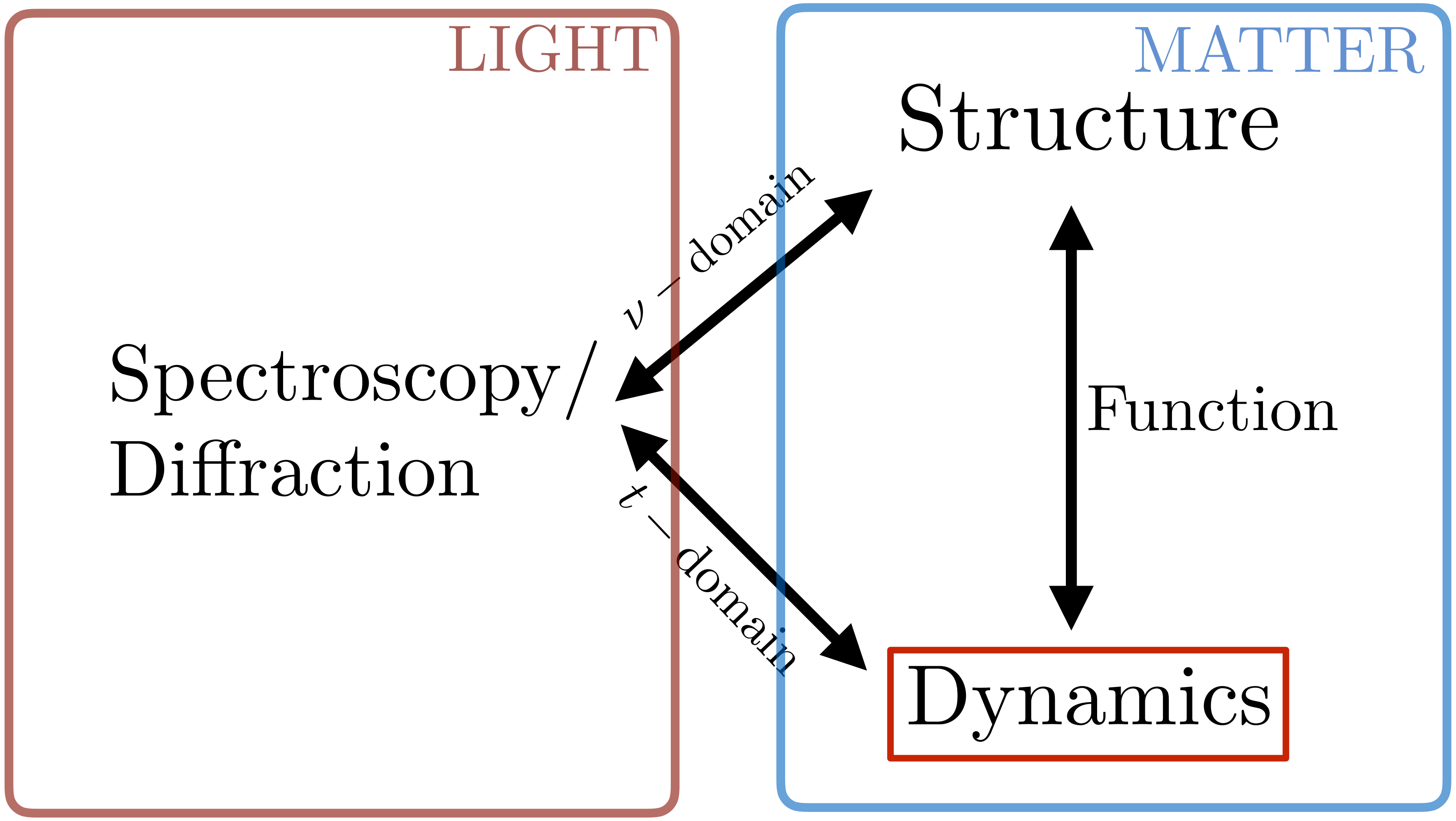
- From kinetics to dynamics of chemical processes

- Theoretical description of the structure and dynamics of molecules

- Time-dependent description of molecular spectroscopy

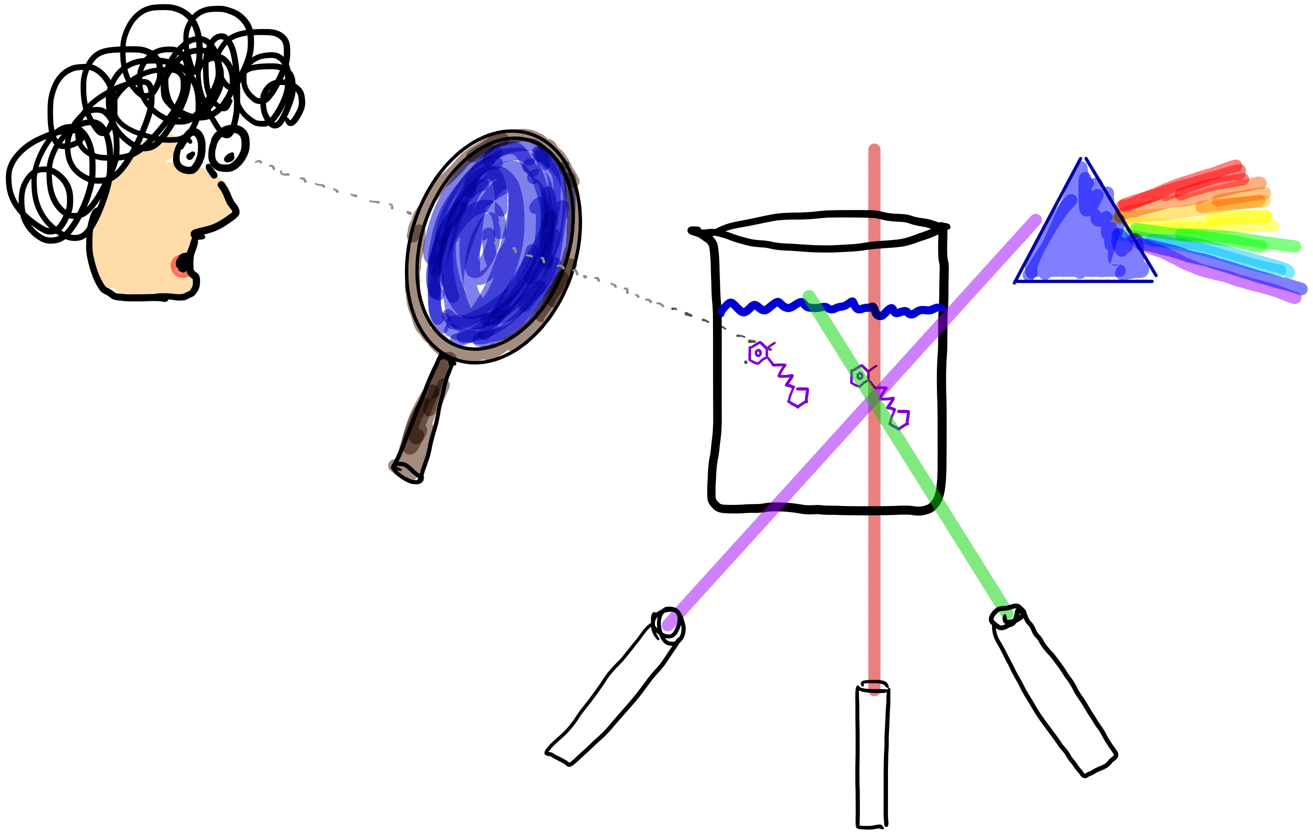
- Tracing chemical dynamics with (ultrafast) x-rays.
  Examples and applications.

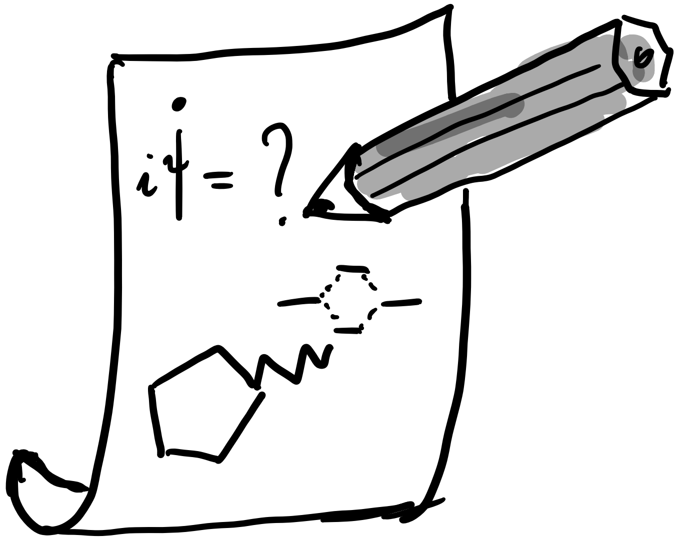
Chemical (Molecular Reaction) Dynamics

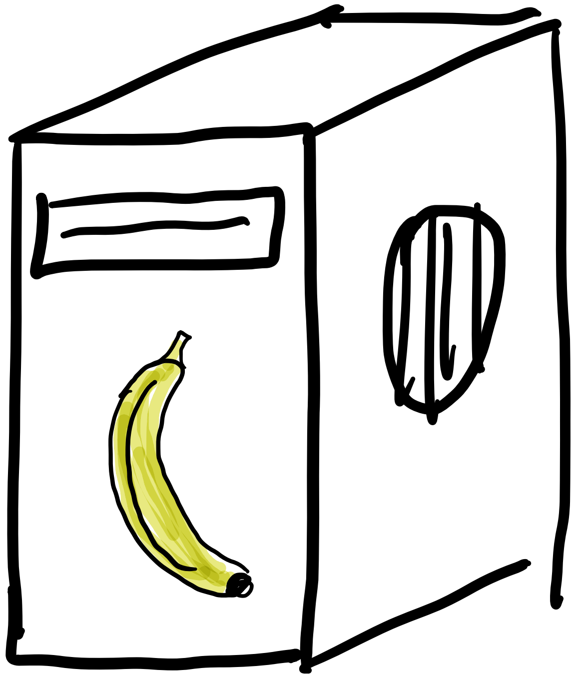


- Molecular level reaction mechanisms
- Elementary charge and energy transfer processes
- Means of probing them
- Means of controlling them

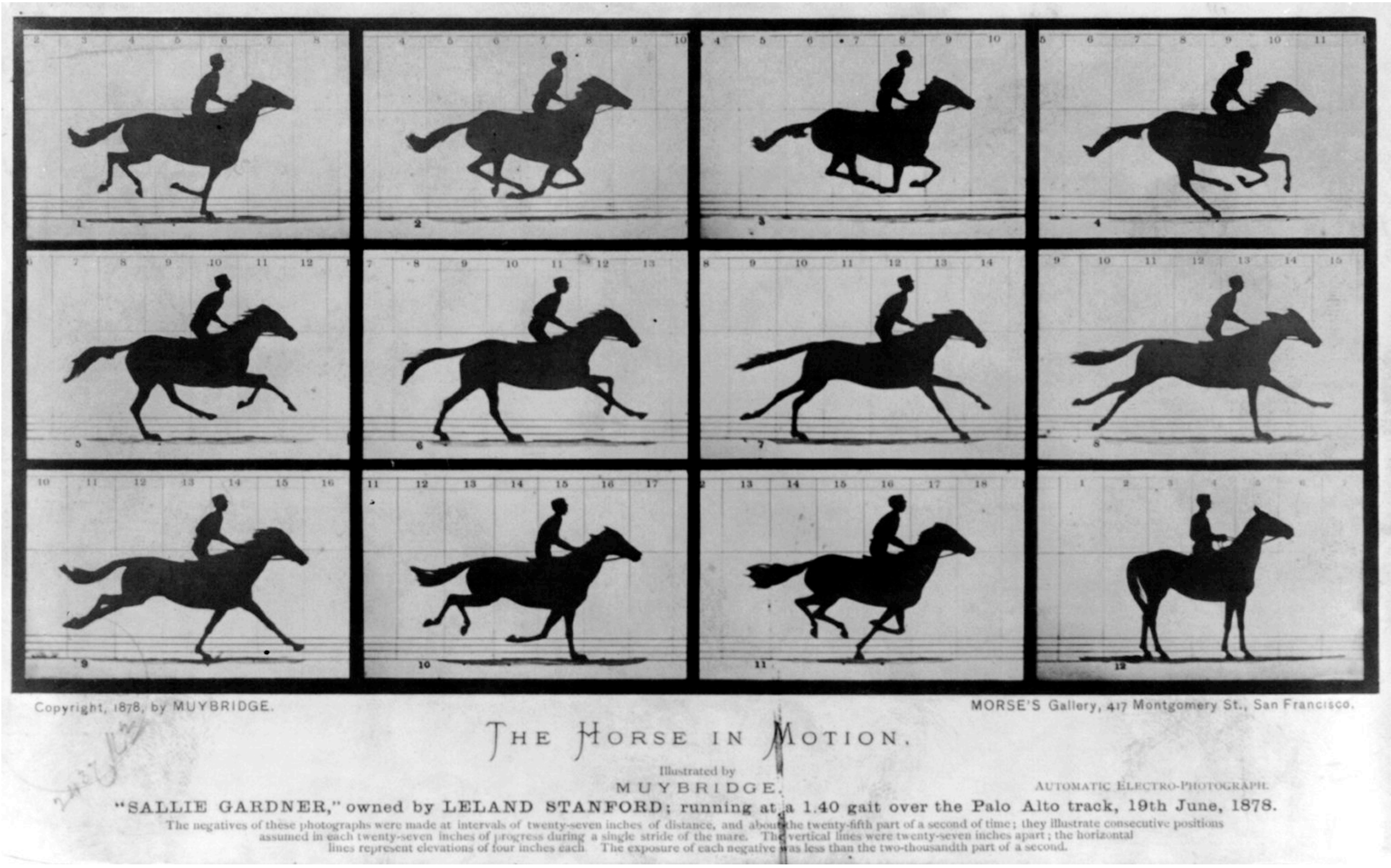
Chemical (Molecular Reaction) Dynamics







Time resolved measurements of kinetics and dynamics



Copyright, 1878, by MUYBRIDGE.

MORSE'S Gallery, 417 Montgomery St., San Francisco.

THE HORSE IN MOTION.

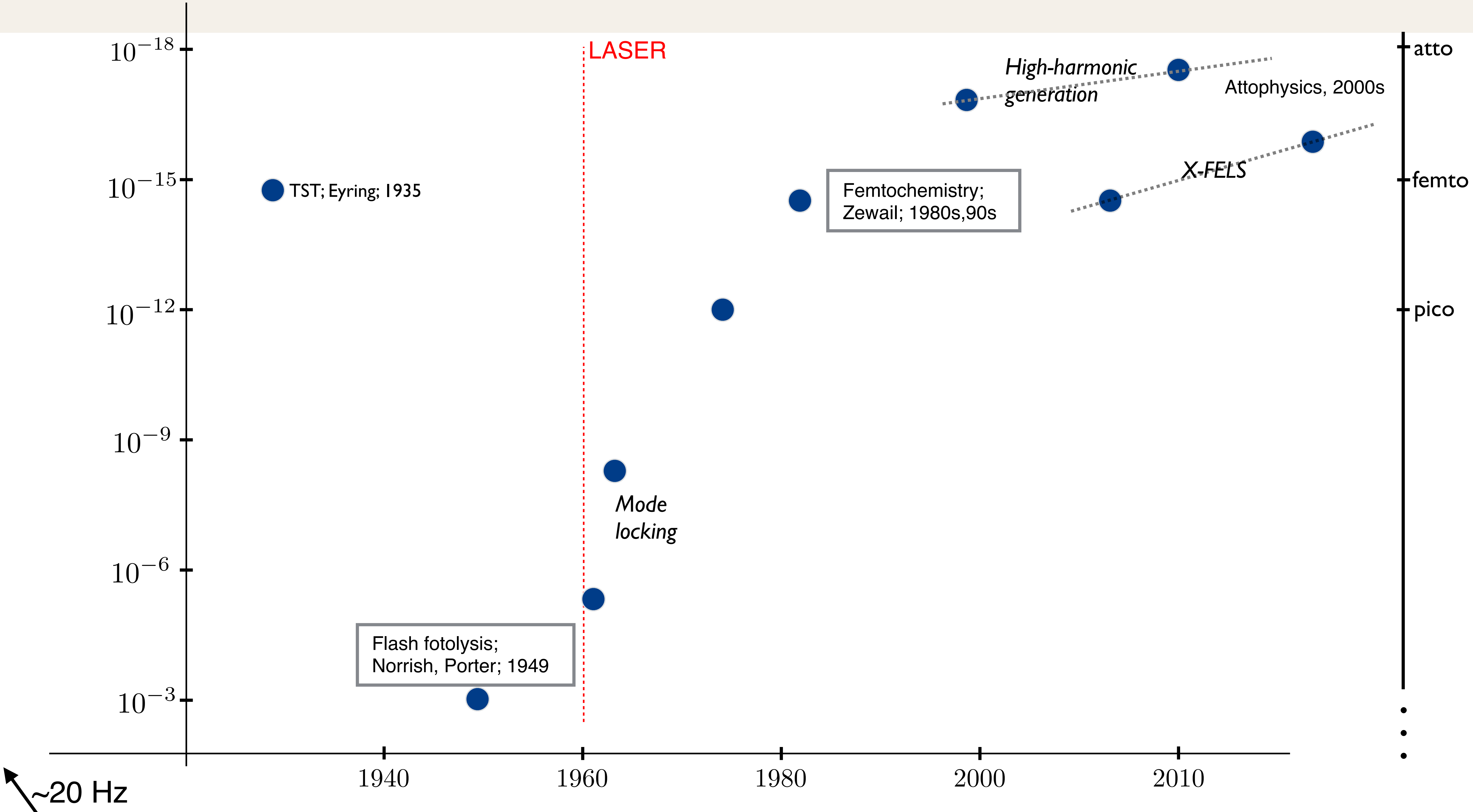
Illustrated by
MUYBRIDGE.

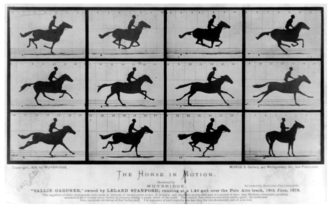
AUTOMATIC ELECTRO-PHOTOGRAPH.

"SALLIE GARDNER," owned by LELAND STANFORD; running at a 1.40 gait over the Palo Alto track, 19th June, 1878.

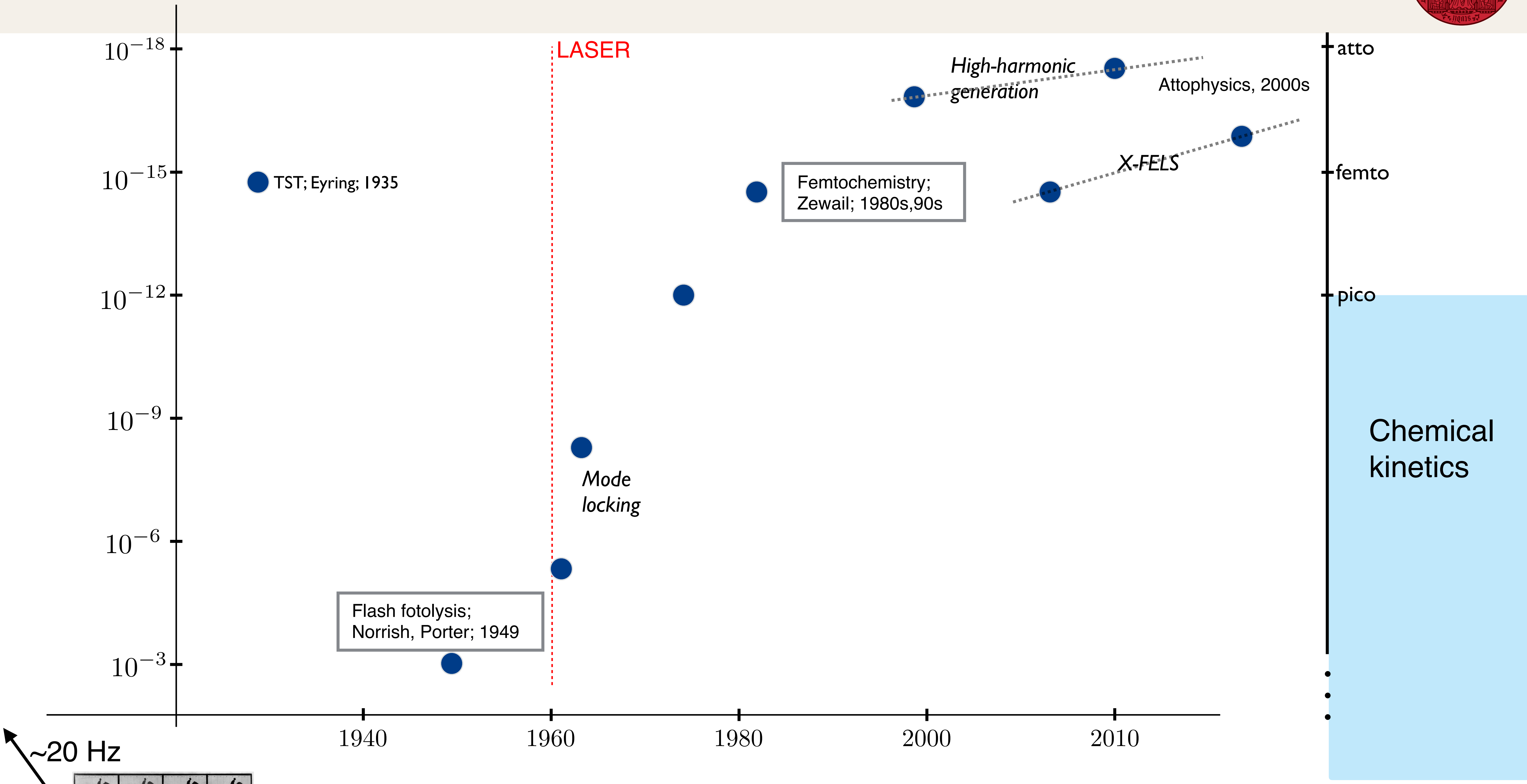
The negatives of these photographs were made at intervals of twenty-seven inches of distance, and about the twenty-fifth part of a second of time; they illustrate consecutive positions assumed in each twenty-seven inches of progress during a single stride of the mare. The vertical lines were twenty-seven inches apart; the horizontal lines represent elevations of four inches each. The exposure of each negative was less than the two-thousandth part of a second.

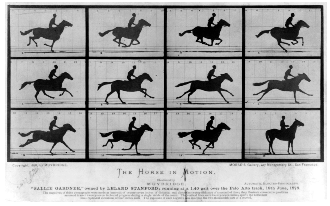
Time resolved measurements of kinetics and dynamics





Time resolved measurements of kinetics and dynamics





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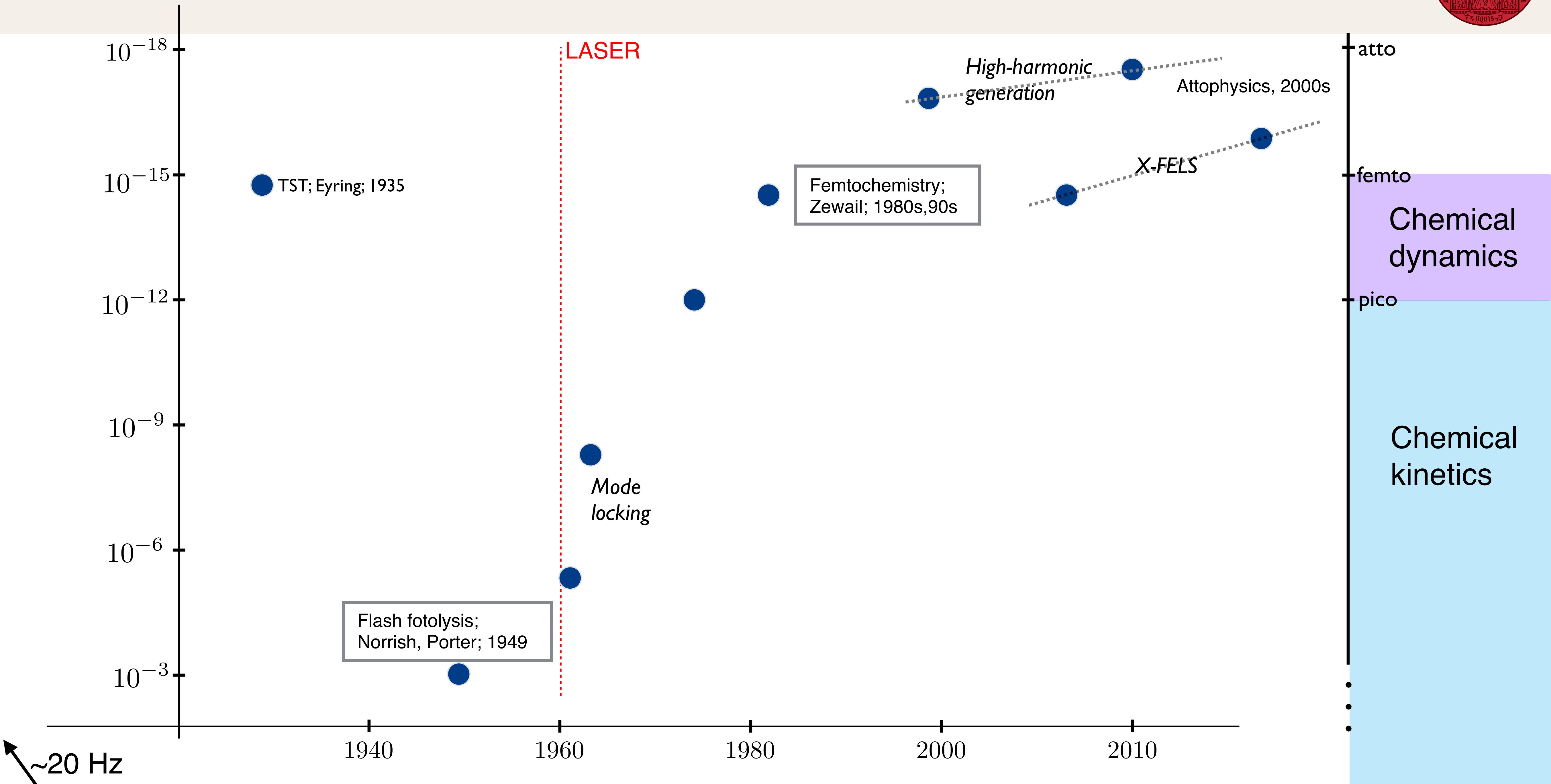

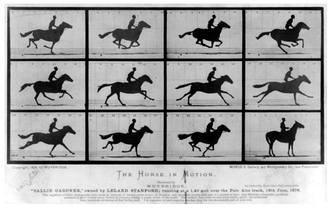

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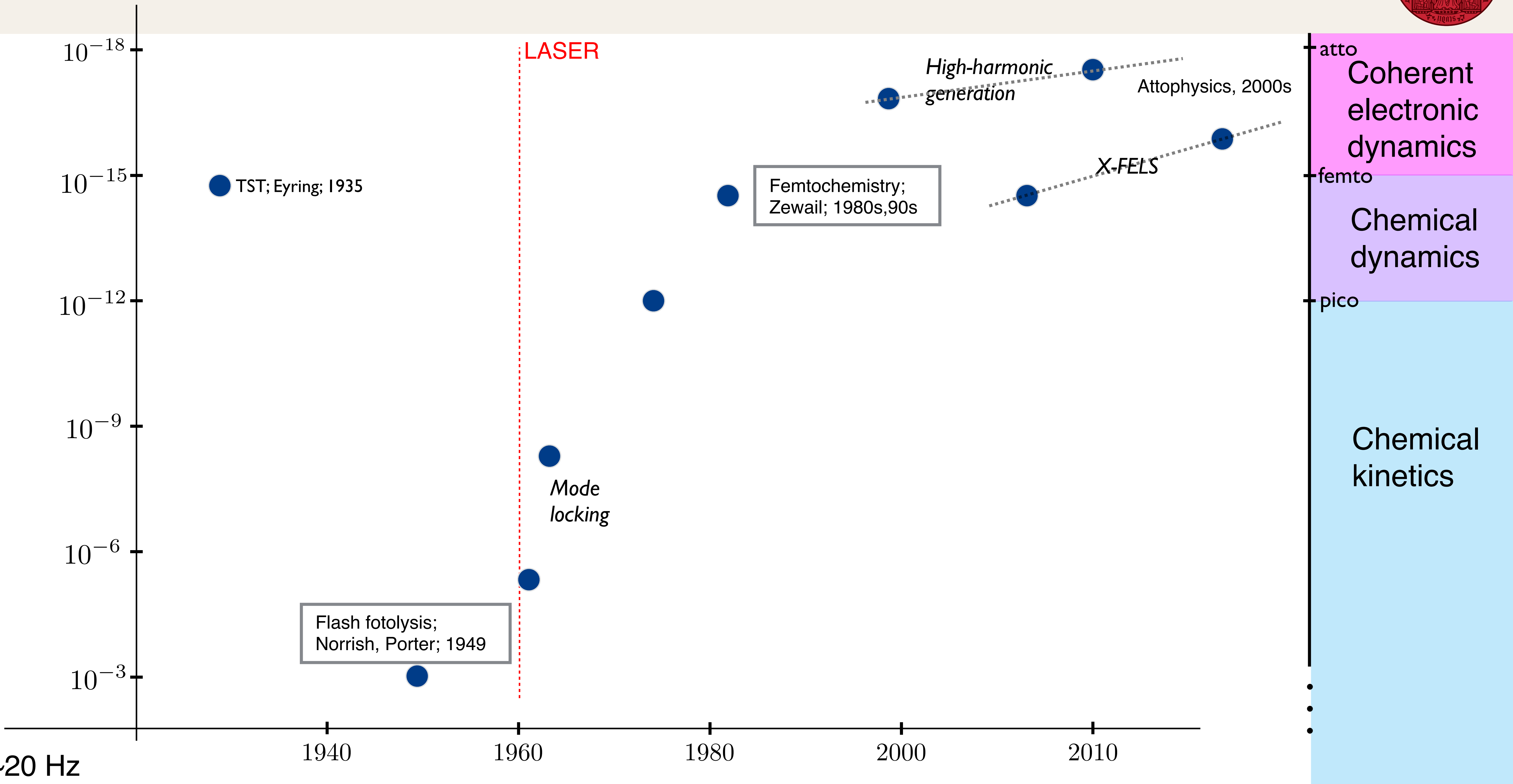
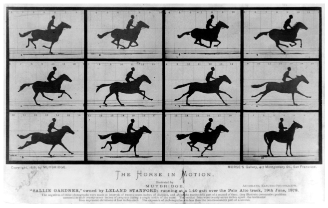
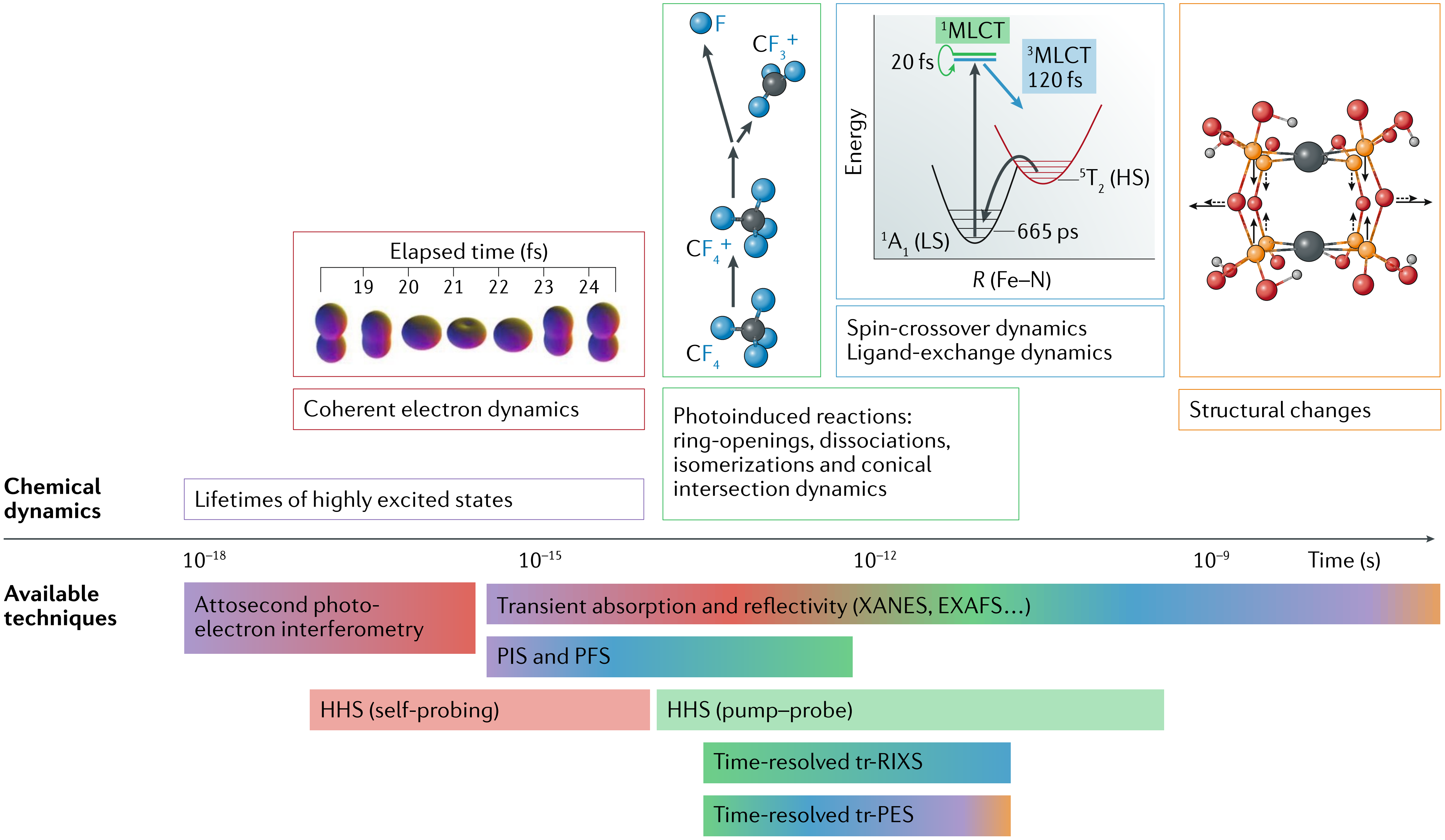


~20 Hz



Typical time-scales in Chemical Dynamics



Spin-crossover dynamics
Ligand-exchange dynamics

Coherent electron dynamics

Photoinduced reactions: ring-openings, dissociations, isomerizations and conical intersection dynamics

Structural changes

Chemical dynamics

Lifetimes of highly excited states

Available techniques

Attosecond photo-electron interferometry

Transient absorption and reflectivity (XANES, EXAFS…)

PIS and PFS

HHS (self-probing)

HHS (pump–probe)

Time-resolved tr-RIXS

Time-resolved tr-PES

The ultrafast X-ray spectroscopic revolution in chemical dynamics
Kraus, Zürch, Cushing, Neumark, Leone, Nat. Rev. Chem., **2**, 82 (2018)

From kinetics to dynamics of chemical processes

QUESTION

What is a transition state?

🟦 An unstable configuration of a molecule

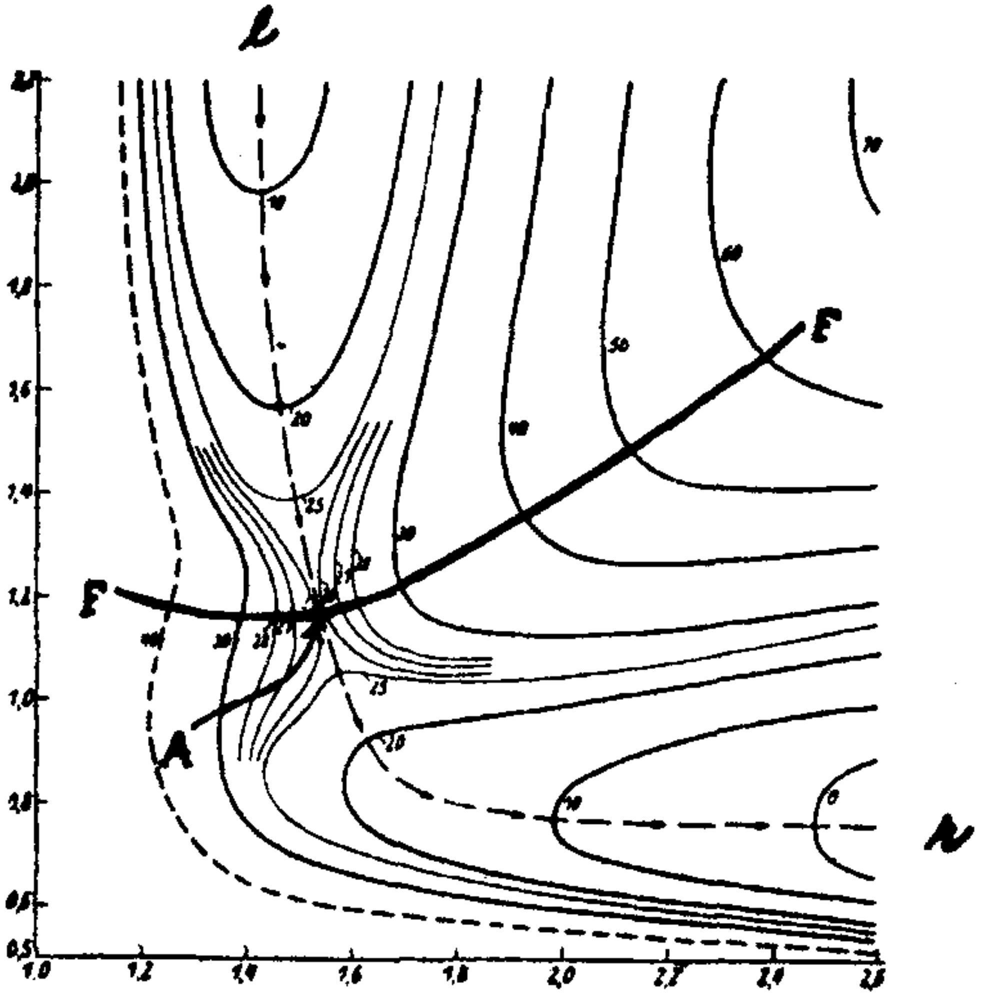
🟢 The maximum energy configuration along the minimum energy pathway connecting stable structures.

▲ A dividing surface in phase space along which recrossing is minimized.

⬟ All of the above.

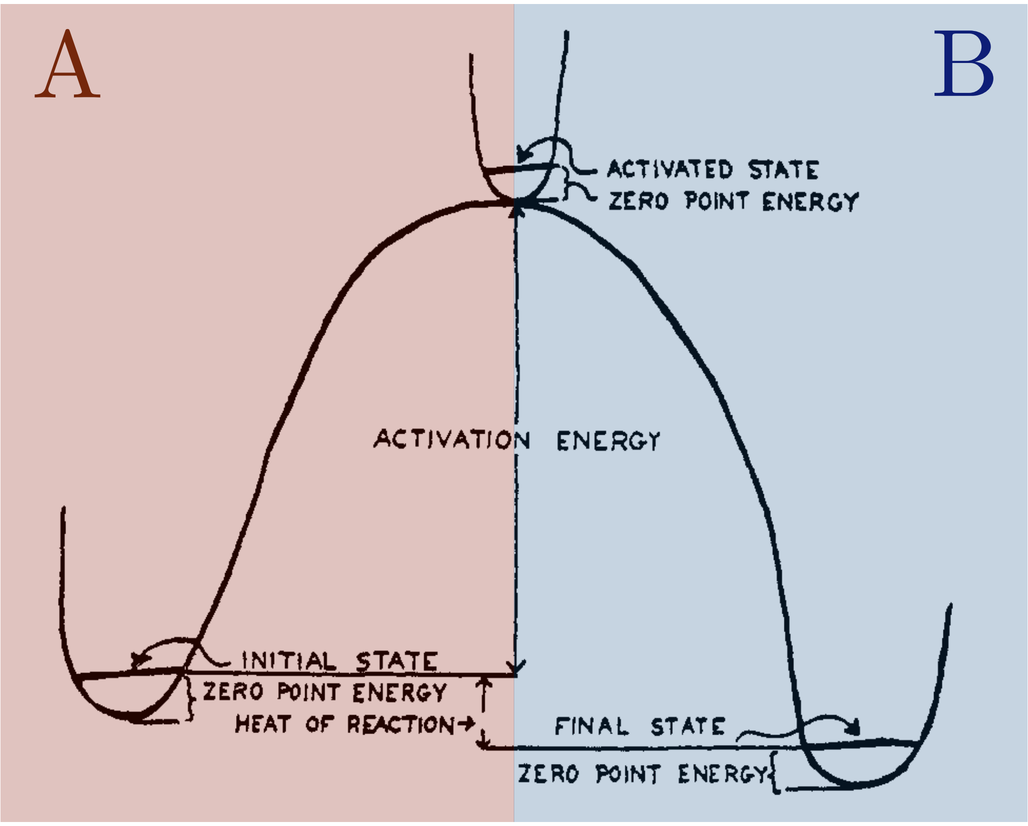
Fig. 1.—The regions (*l*) and (*r*), the activation point A and the surface F, in the section of the configuration space, corresponding to a linear configuration of the atoms H, H, Br. The ordinate is the distance of the two H atoms in A, the abscissa the distance of the middle H from the Br. The numbered lines are contour lines of the energy surface, constructed by Eyring and Polanyi for the reaction

$$H + HBr = H_2 + Br.$$



Wigner 1938

From kinetics to dynamics



$$\mathrm{A} \underset{\kappa_B}{\overset{\kappa_A}{\rightleftharpoons}} \mathrm{B}$$

$$\langle \Theta_A \rangle : \text{fraction of A}$$

$$\frac{d}{dt}\langle \Theta_B \rangle = \kappa_A \langle \Theta_A \rangle - \kappa_B \langle \Theta_B \rangle$$

$$\frac{d}{dt}\langle \Theta_A \rangle = \frac{d}{dt}\langle \Theta_B \rangle = 0$$

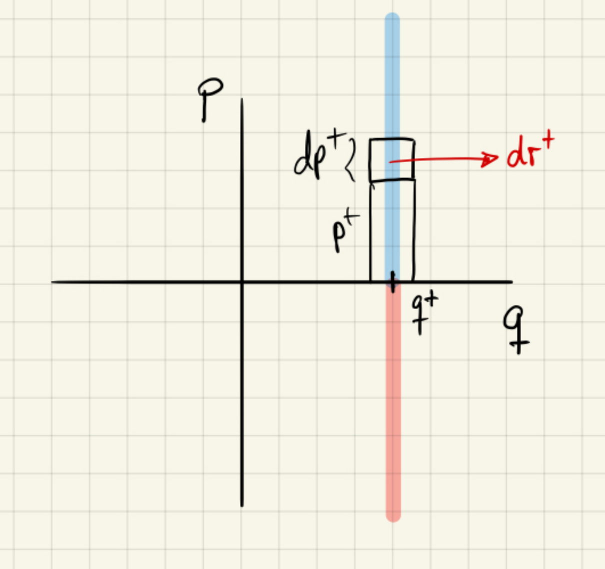
$$\frac{\langle \Theta_B \rangle}{\langle \Theta_A \rangle} = \frac{\kappa_A}{\kappa_B} = K_{\mathrm{eq}}$$

From kinetics to dynamics

Micro-canonical reaction rate in the energy shell E+dE

$$\boxed{\kappa(E) = \frac{N^{\ddagger}(E-\epsilon_0)}{h\rho(E)}}$$

ϵ_0: classical barrier



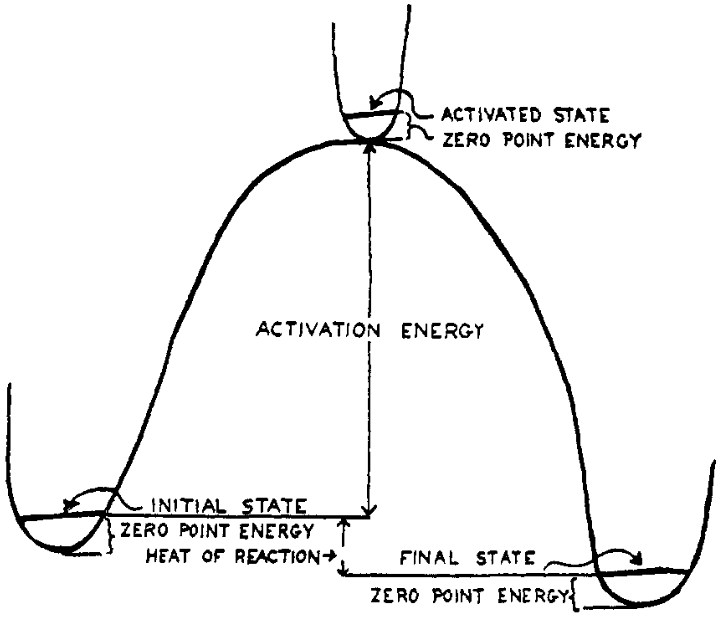
$$\Gamma^{\ddagger} = \int_0^{E-\varepsilon_0} d\Gamma^{\ddagger} = \frac{1}{h} N^{\ddagger}(E-\varepsilon_0) := \kappa(E)\,\rho(E)$$

$$\kappa(T) = \frac{1}{Q(T)} \int_0^{\infty} \kappa(E) e^{-E/KT} dE$$

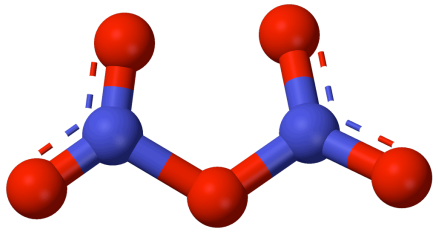
$$\kappa(T) = \frac{KT}{h} \frac{Q^{\ddagger}}{Q} e^{-\epsilon_0/KT}$$

$$T = 300 \text{ K} \implies \frac{KT}{h} = 6.25 \times 10^{12} \text{ s}^{-1}$$

$$\approx 160 \text{ fs per attempt}$$



From kinetics to dynamics



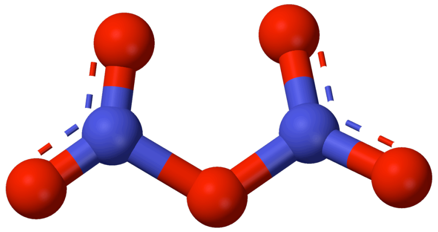
$$\xrightarrow{k[\mathrm{N_2O_5}]} \mathrm{NO_2} + \mathrm{NO_3}$$

$$-\frac{d[\mathrm{R}]}{dt} = k[\mathrm{R}]$$

Viggiano et al., *J. Chem. Phys.* **74** 6113 (1981)
Rate constants for the collisional dissociation of N2O5 by N2.

KJ Leidler, *J. Chem. Ed.* **61** 494 (1984)
The development of the Arrhenius Equation.

From kinetics to dynamics



$$\xrightarrow{k[N_2O_5]} NO_2 + NO_3$$

$$-\frac{d[R]}{dt} = k[R]$$

$$k(T)[s^{-1}] = A\,e^{-B/T}$$

S Arrehnius, Z phys. Chem. 4, 226 (1889)

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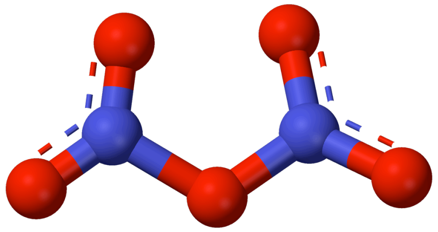

$$N_2O_5 \xrightarrow{k[N_2O_5]} NO_2 + NO_3$$

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$$\boxed{A} = 5.08 \times 10^{13} [s^{-1}]$$

$$\frac{1}{A} = \tau = 1.97 \times 10^{-14}\ [\mathrm{s}] \Rightarrow 19.7\ [\mathrm{fs}]$$

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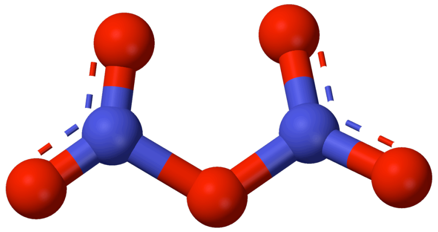

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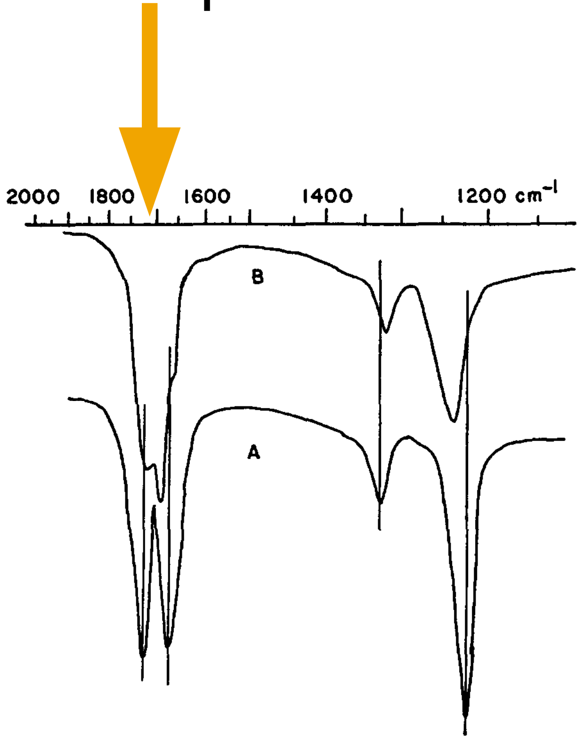
IR spectrum of N_2O_5



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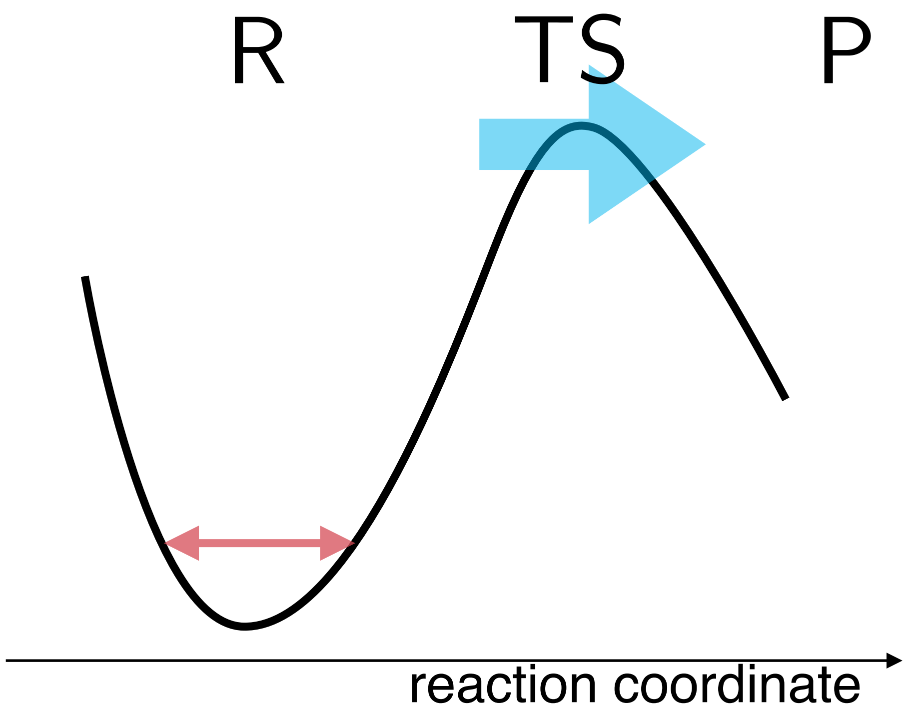
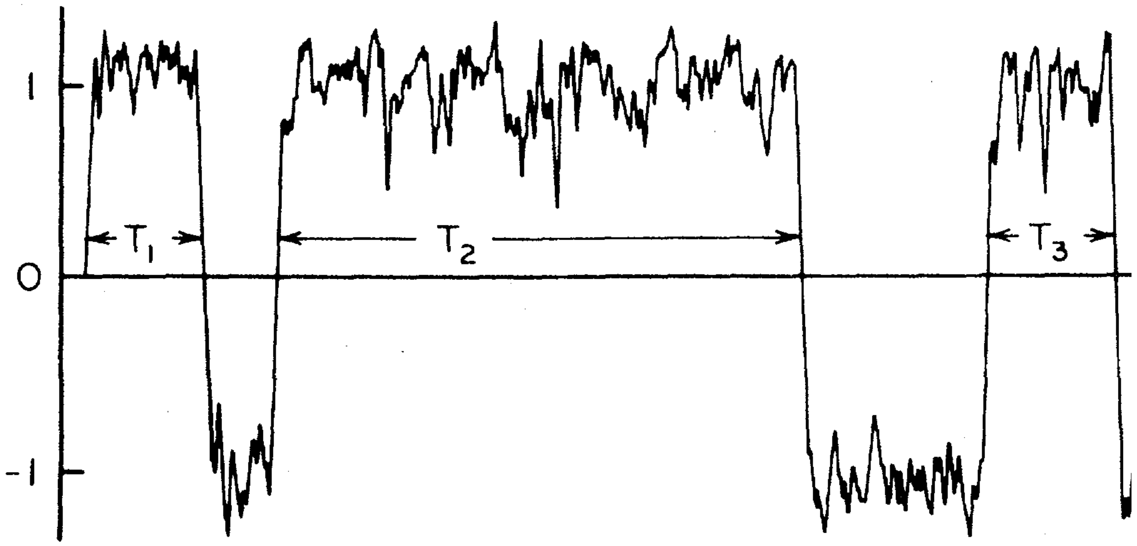
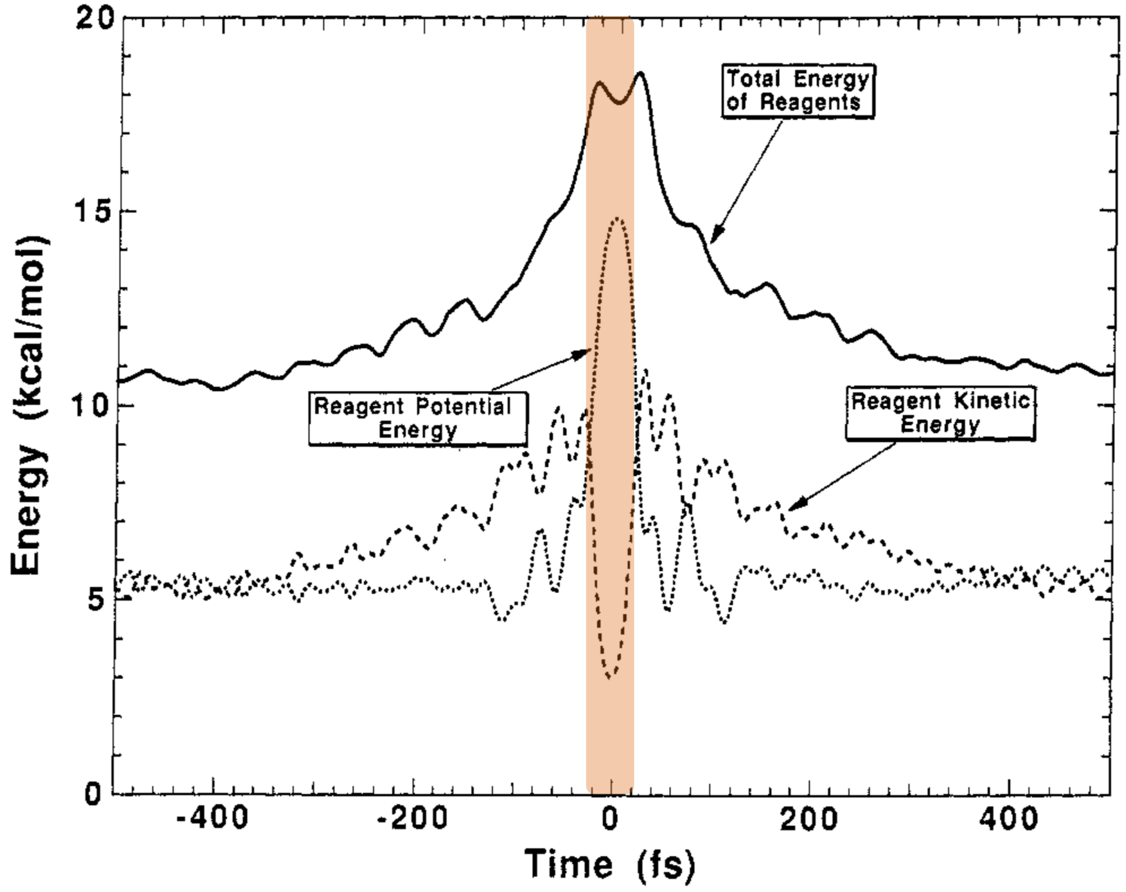
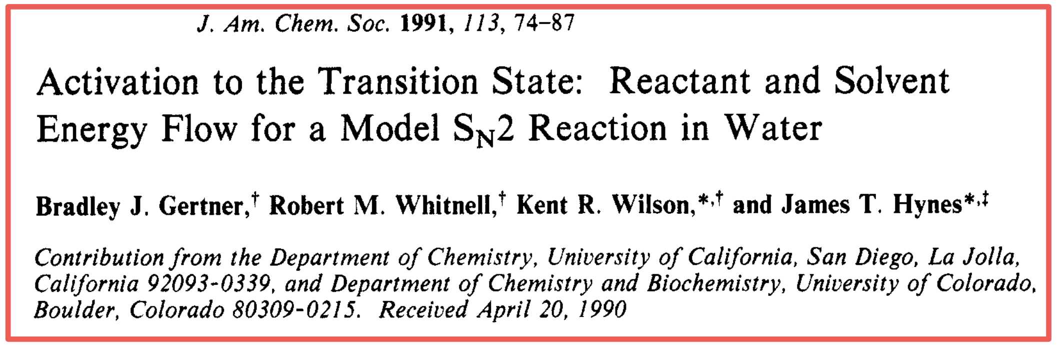
From kinetics to dynamics

- (Thermal) Chemical reactions are “rare events”.
- Once a reactive event starts, it proceeds very rapidly.







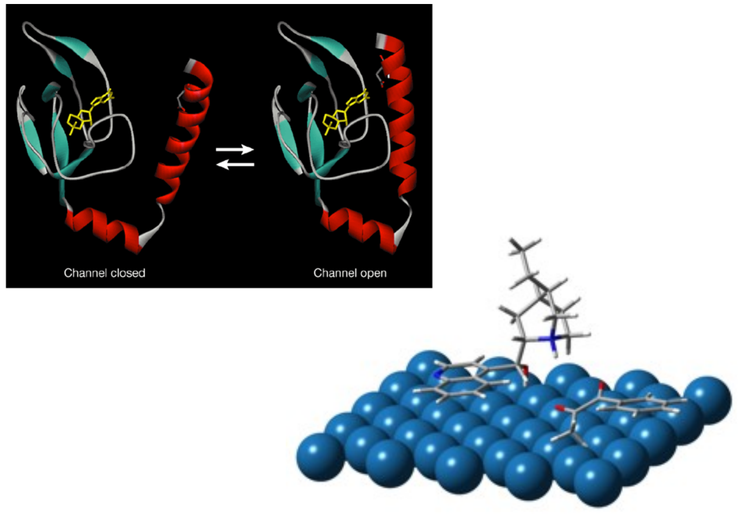

J. Am. Chem. Soc. **1991**, *113*, 74–87

Activation to the Transition State: Reactant and Solvent Energy Flow for a Model S_N2 Reaction in Water

Bradley J. Gertner,[†] **Robert M. Whitnell,**[†] **Kent R. Wilson,**[*,†] **and James T. Hynes**[*,‡]

Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92093-0339, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215. *Received April 20, 1990*

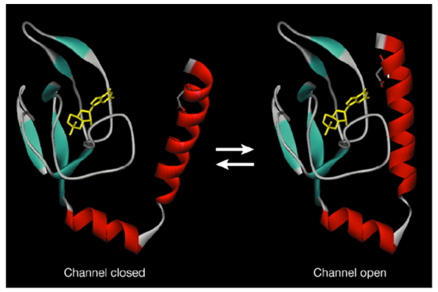
Fundamental reactive steps

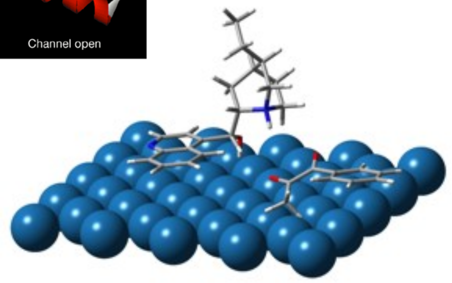


Fundamental reactive steps

- Thermally activated processes
  - A large part of chemistry and biology is here
  - The “trigger” problem

Fundamental reactive steps





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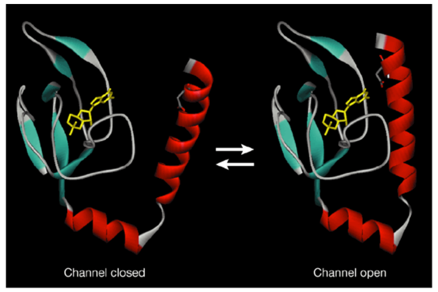
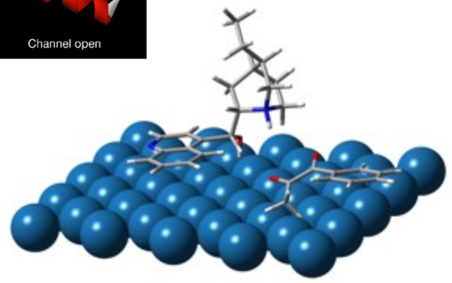
Ultrafast energy transfer to liquid water by THz pulses

PK Mishra, OV, R Santra
Angew. Chem. Int. Ed. **52**, 13685 (2013)
J. Phys. Chem. B **119**, 8080 (2015)
Phys. Rev. E **93**, 032124 (2016)

Fundamental reactive steps





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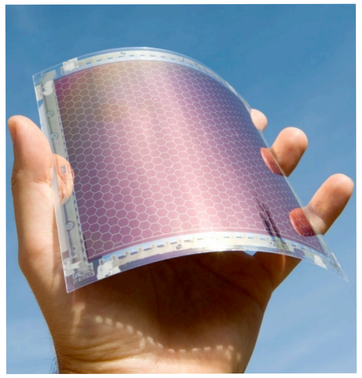
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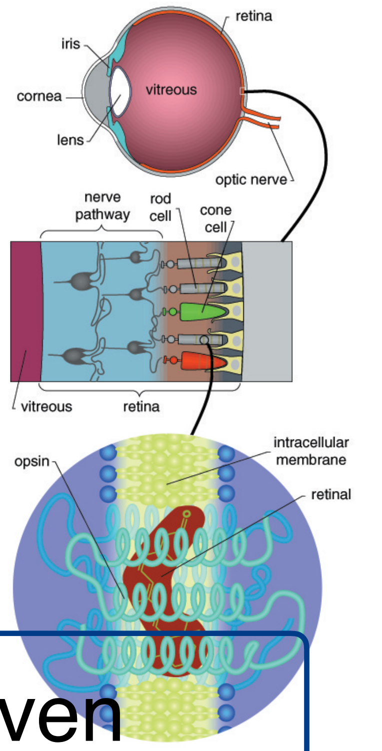

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- Light activated/driven processes
  - Photophysics/photochemistry
  - Light to energy conversion & charge separation
  - Pump-probe ultrafast spectroscopies

QUESTION

It is possible to define rates for photo-triggered processes:

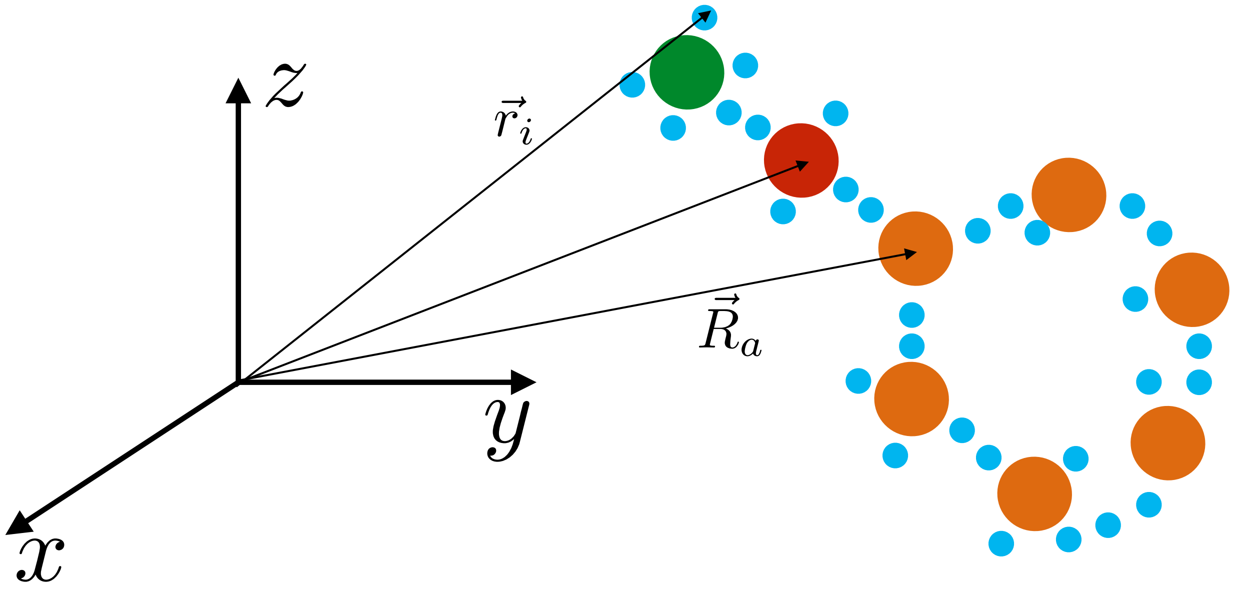
🟦 Always.

🟢 Never.

▲ It depends.

Theoretical Description of the Structure and Dynamics of Molecules

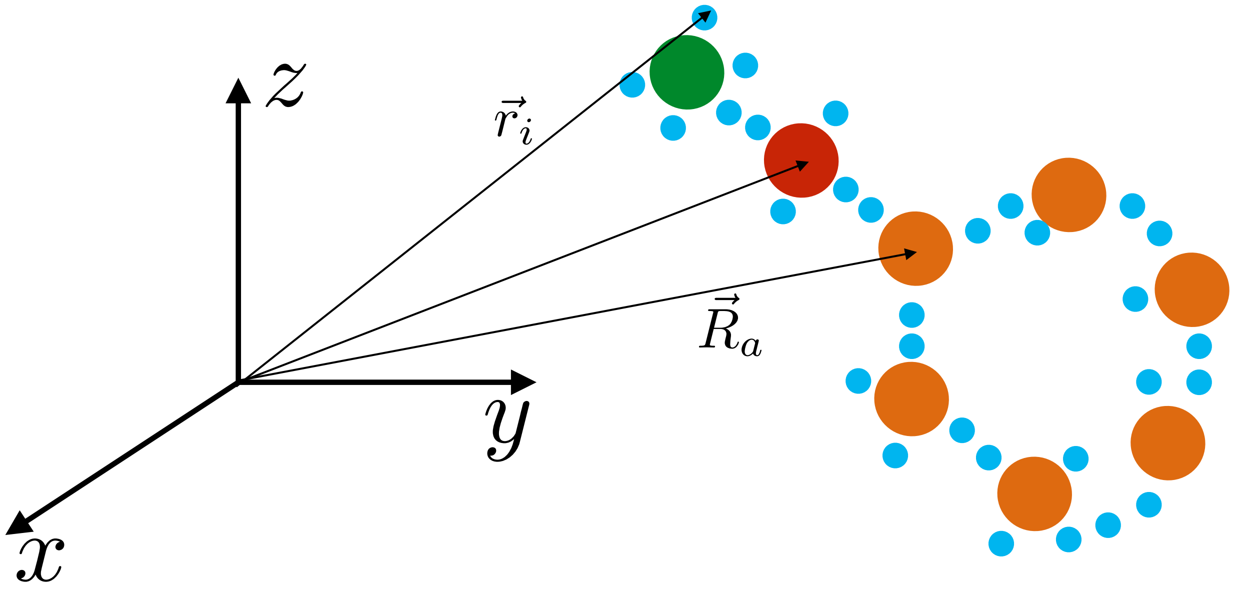
The molecular Hamiltonian



$$\hat{H}(\mathbf{r},\mathbf{R},t) = \sum_a -\frac{\hbar^2\vec{\nabla}_a^2}{2M_a} + \sum_{a>b}\frac{e^2 Z_a Z_b}{|\vec{R}_a-\vec{R}_b|} + \sum_i -\frac{\hbar^2\vec{\nabla}_i^2}{2m} + \sum_{j>i}\frac{e^2}{|\vec{r}_i-\vec{r}_j|} - \sum_{ai}\frac{e^2 Z_a}{|\vec{R}_a-\vec{r}_i|}$$
$$-\vec{E}(t)\left(\sum_a eZ_a\vec{R}_a - \sum_i e\vec{r}_i\right)$$

$$i\hbar\frac{\partial\Psi(\mathbf{r},\mathbf{R},t)}{\partial t} = \hat{H}\Psi(\mathbf{r},\mathbf{R},t)$$

The molecular Hamiltonian



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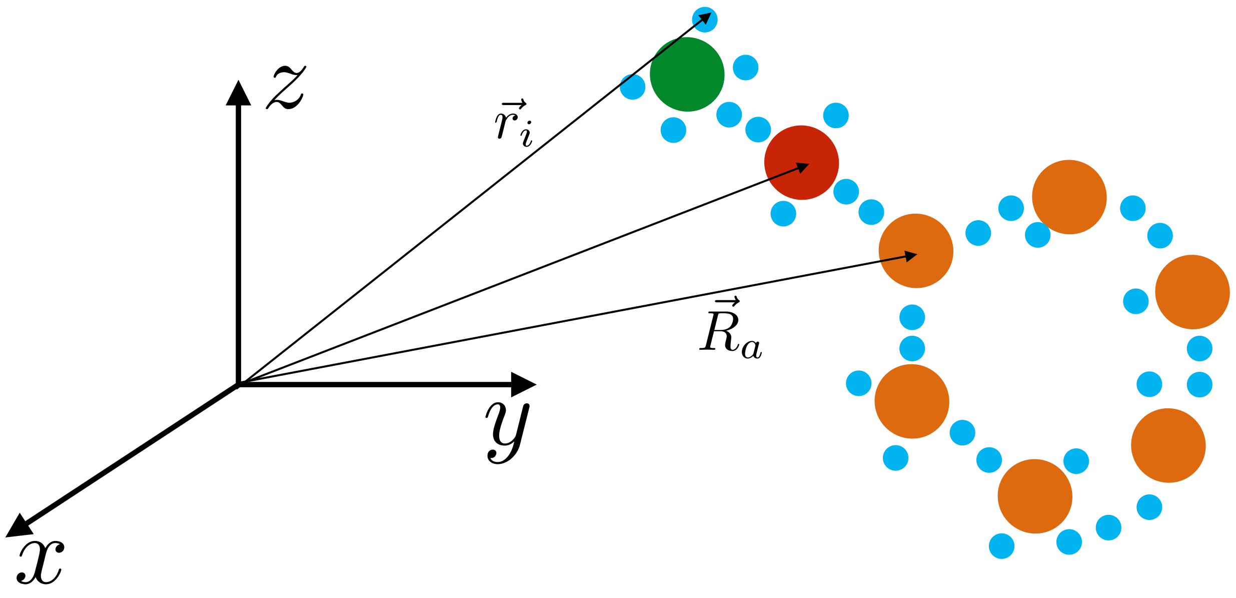
$$-\vec{E}(t)\left(\sum_a e Z_a \vec{R_a} - \sum_i e\vec{r}_i\right)$$

$$i\hbar\frac{\partial\Psi(\mathbf{r},\mathbf{R},t)}{\partial t} = \hat{H}\Psi(\mathbf{r},\mathbf{R},t)$$

The molecular Hamiltonian



$$\boxed{\hat{H}(\mathbf{r},\mathbf{R},t) = \hat{T}_N + \hat{H}_e - \vec{E}(t)\hat{\mu}}$$

$$\boxed{\hat{H}_e = \sum_i -\frac{\hbar^2\vec{\nabla}_i^2}{2m} + \sum_{j>i}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{ai}\frac{-e^2 Z_a}{|\vec{R}_a - \vec{r}_i|} + \sum_{a>b}\frac{e^2 Z_a Z_b}{|\vec{R}_a - \vec{R}_b|}}$$

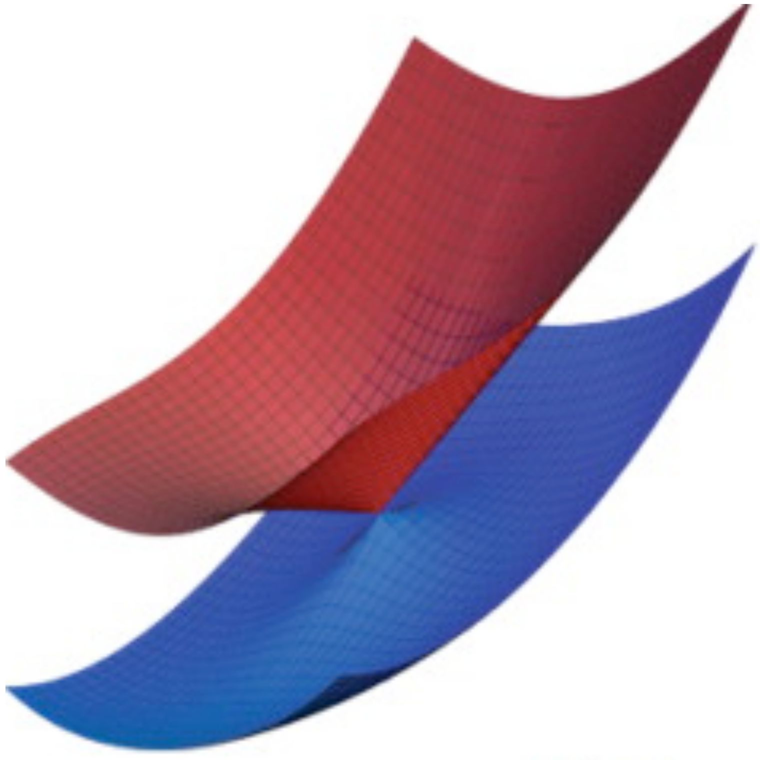
$$\boxed{\hat{H}_e\Phi_j(\mathbf{r};\mathbf{R}) = V_j(\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R})}$$

The molecular Schrödinger equation

$$\Psi(\mathbf{r},\mathbf{R},t) = \sum_i \chi_i(\mathbf{R},t)\Phi_i(\mathbf{r};\mathbf{R})$$

Plug into TDSE

$$i\hbar\frac{\partial\chi_j}{\partial t} = (T_N + V_j)\chi_j - \sum_{i\neq j}\Lambda_{ji}\chi_i$$



- Photo-acidity
- DNA photo-protection
- …

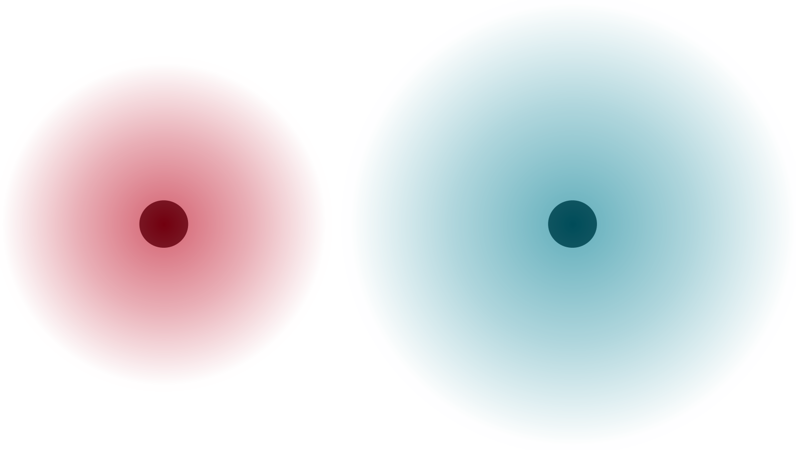
$$\Lambda_{ji} = \frac{1}{2M}\left(2\langle\Phi_j|\nabla\Phi_i\rangle\nabla + \langle\Phi_j|\nabla^2\Phi_i\rangle\right)$$

$$\langle\Phi_j|\nabla\Phi_i\rangle = \frac{\langle\Phi_j|(\nabla\hat{H}_{el})|\Phi_i\rangle}{V_i - V_j}$$

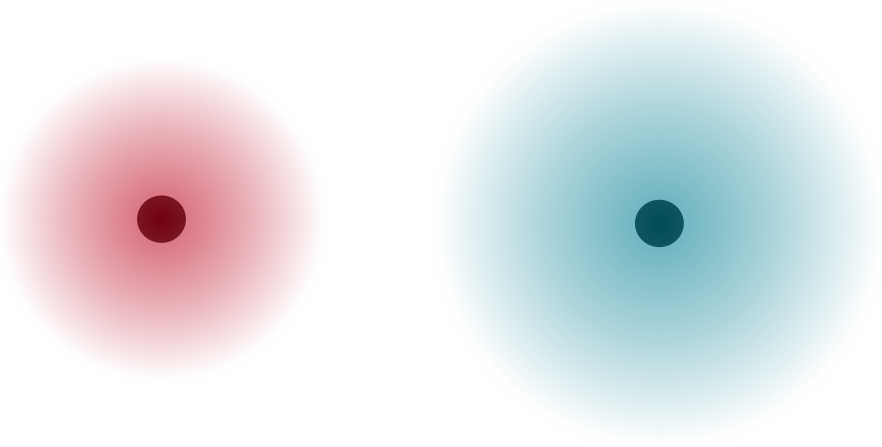
In **practical applications** it is often advantageous to use a **diabatic** representation.

M. Born and R. Oppenheimer, *Ann. Phys.*, **84**, 457 (1927)
M. Born and K. Huang, Book: *Oxford University Press*, [Appendix VIII] (1954)

Electron-nuclei coupling and correlation



Electron-nuclei coupling and correlation



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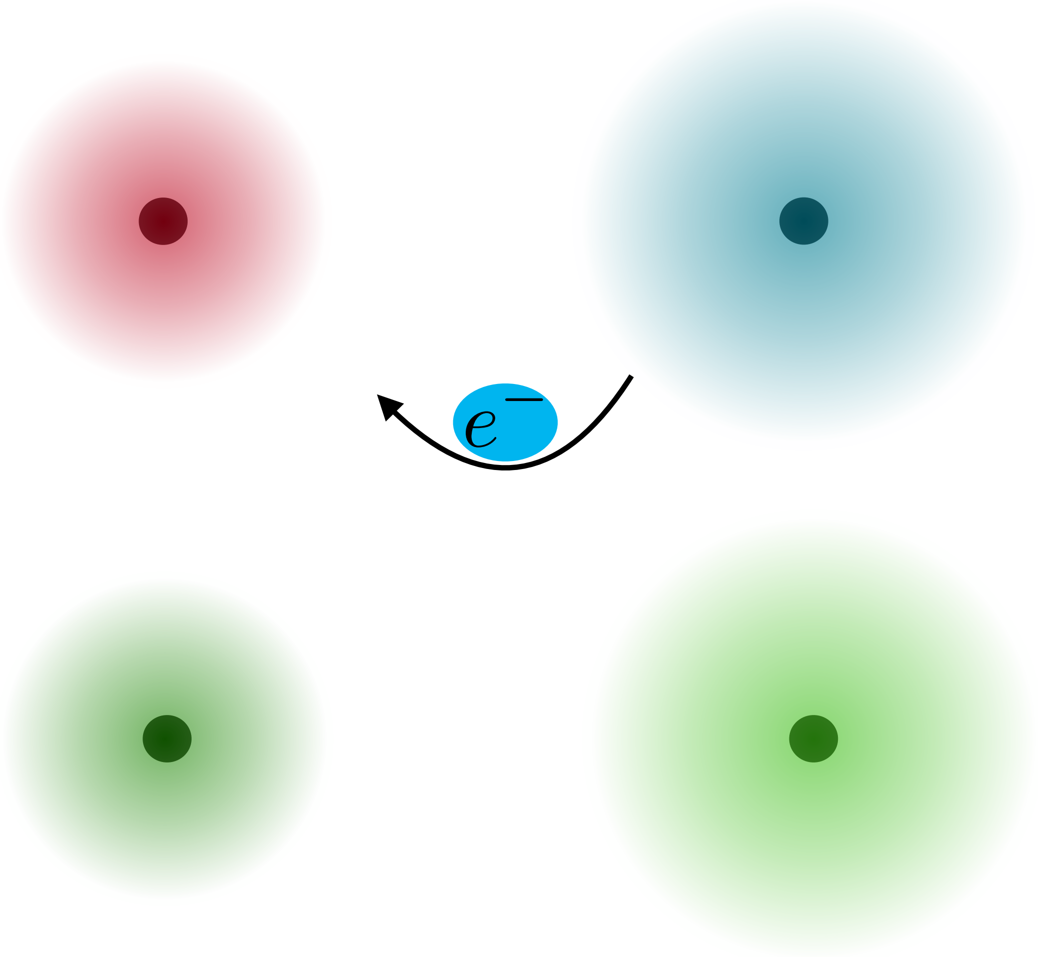
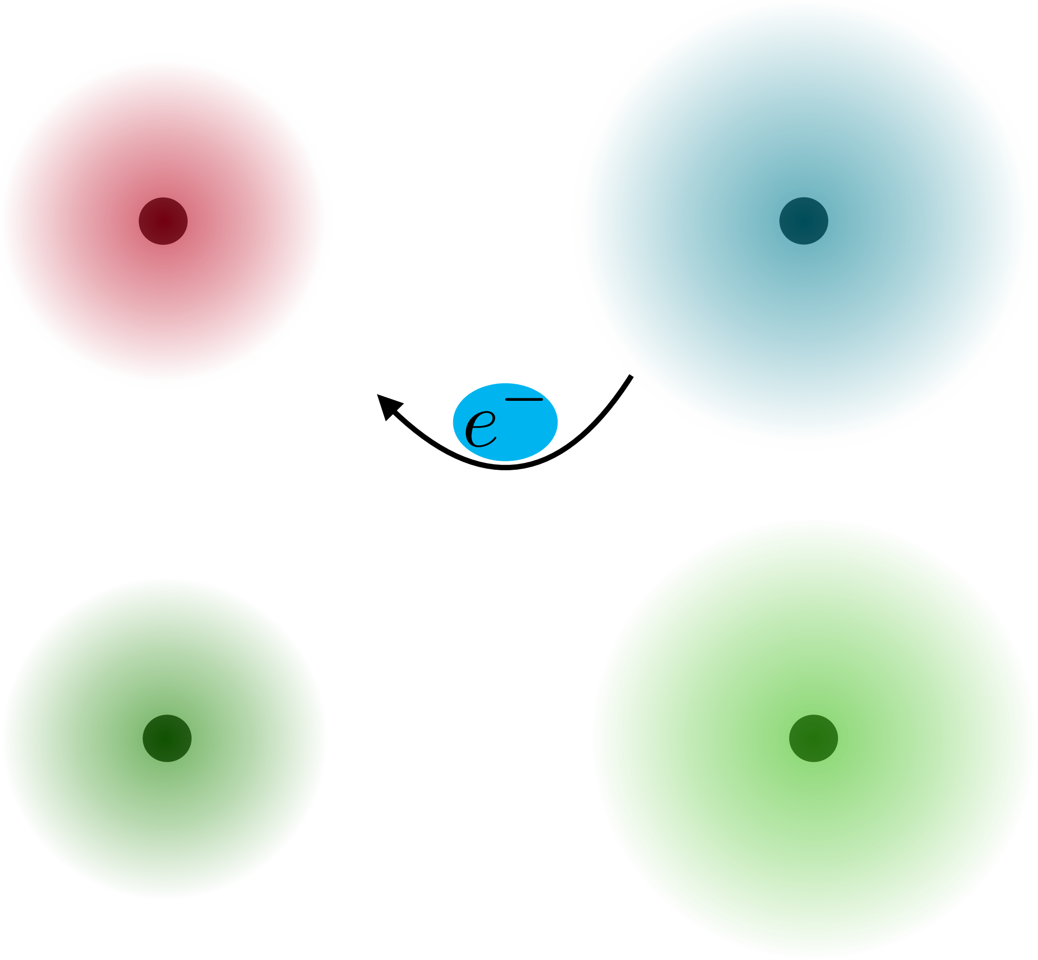
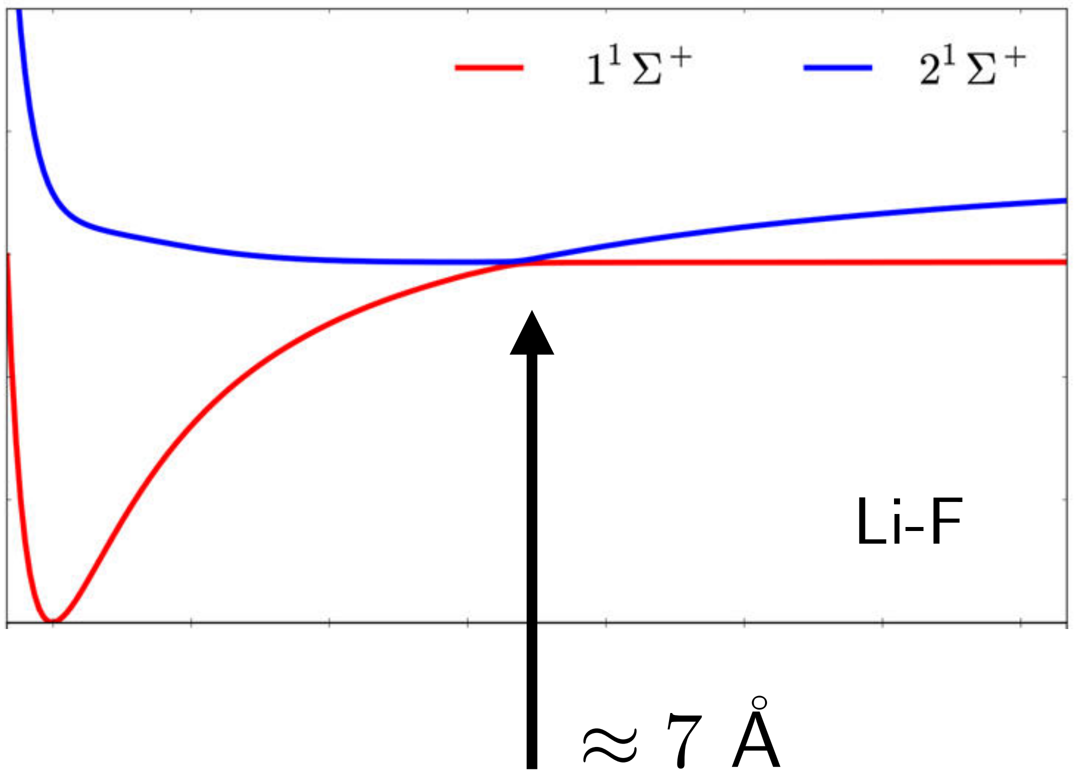
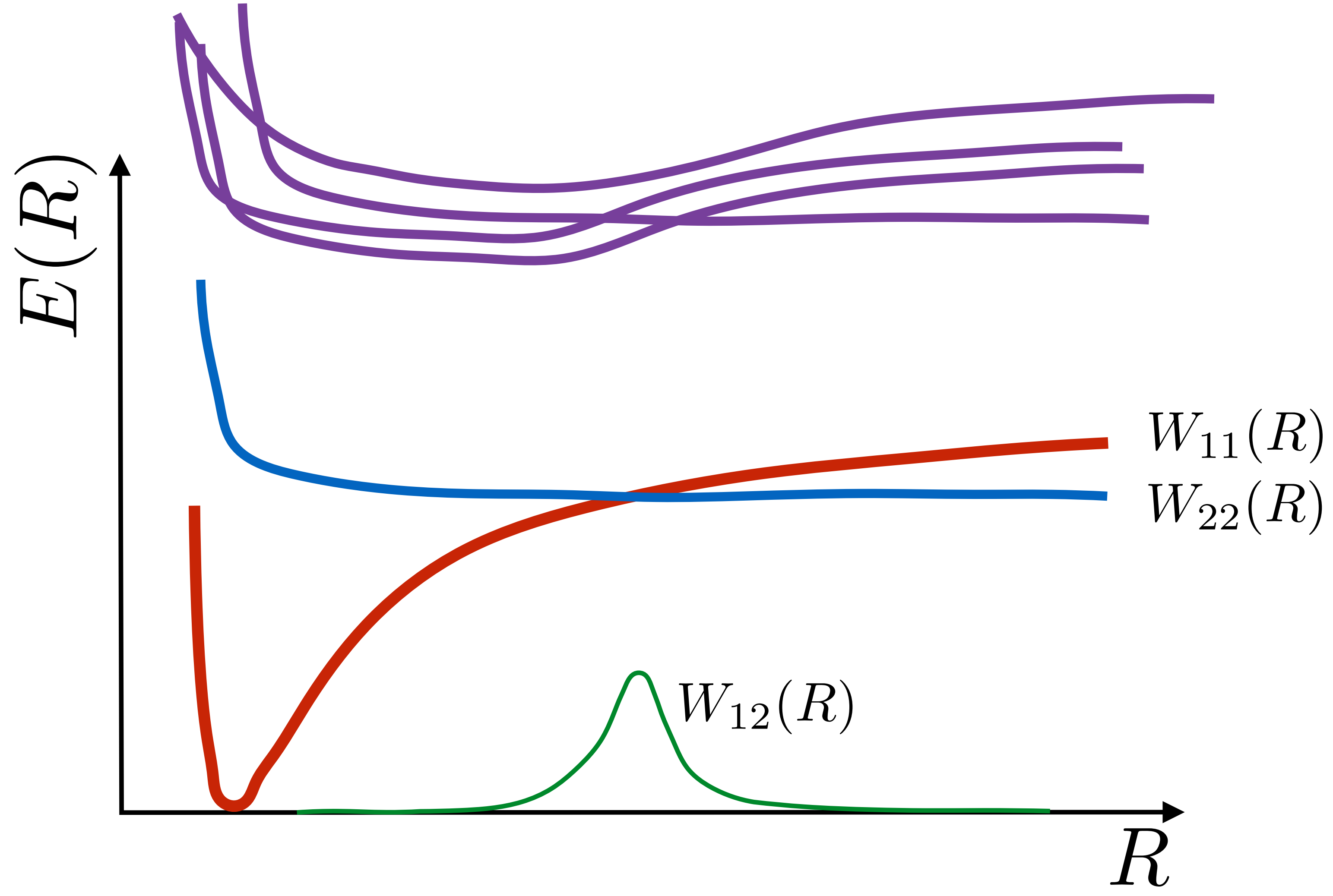


Electron-nuclei coupling and correlation





The group Born-Oppenheimer approximation



Non-adiabatic transitions to states outside the window of interest are neglected:

$$\Lambda_{1(2),k} \approx 0; \quad k \neq 1,2$$

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} \tilde{\chi}_1 \\ \tilde{\chi}_2 \end{pmatrix} = \left[\hat{T}_N \otimes \mathbf{1} + \begin{pmatrix} \hat{W}_{11} & \hat{W}_{12} \\ \hat{W}_{12} & \hat{W}_{22} \end{pmatrix}\right]\begin{pmatrix} \tilde{\chi}_1 \\ \tilde{\chi}_2 \end{pmatrix}$$

QUESTION

Why is the BO approximation so useful?

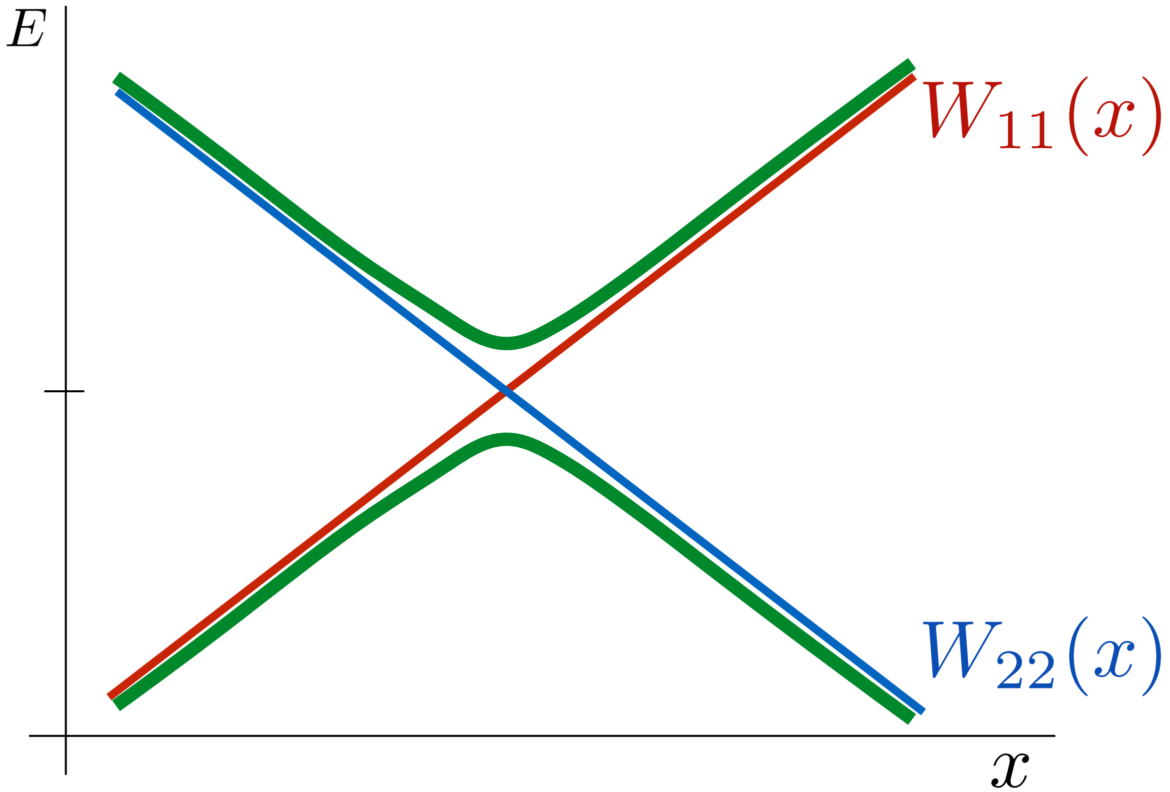
🟦 Because it decouples electronic and nuclear dynamics.

🟢 Because electrons and nuclei are treated on the same footing.

△ One can use it to draw Lewis structures.

⬟ Because when it breaks one can publish papers on it.

The Landau-Zener model for non-adiabatic transitions



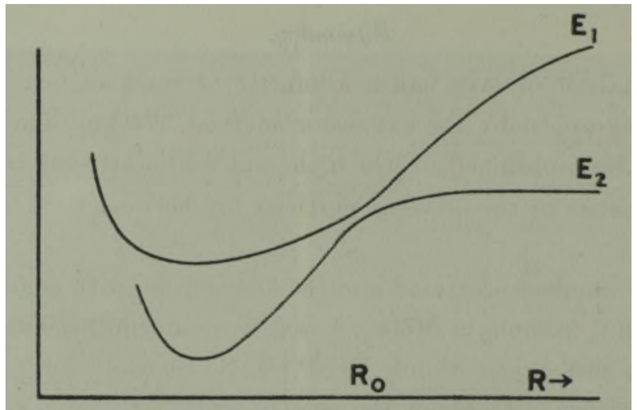


Fig. 1.—Crossing of polar and homopolar states.

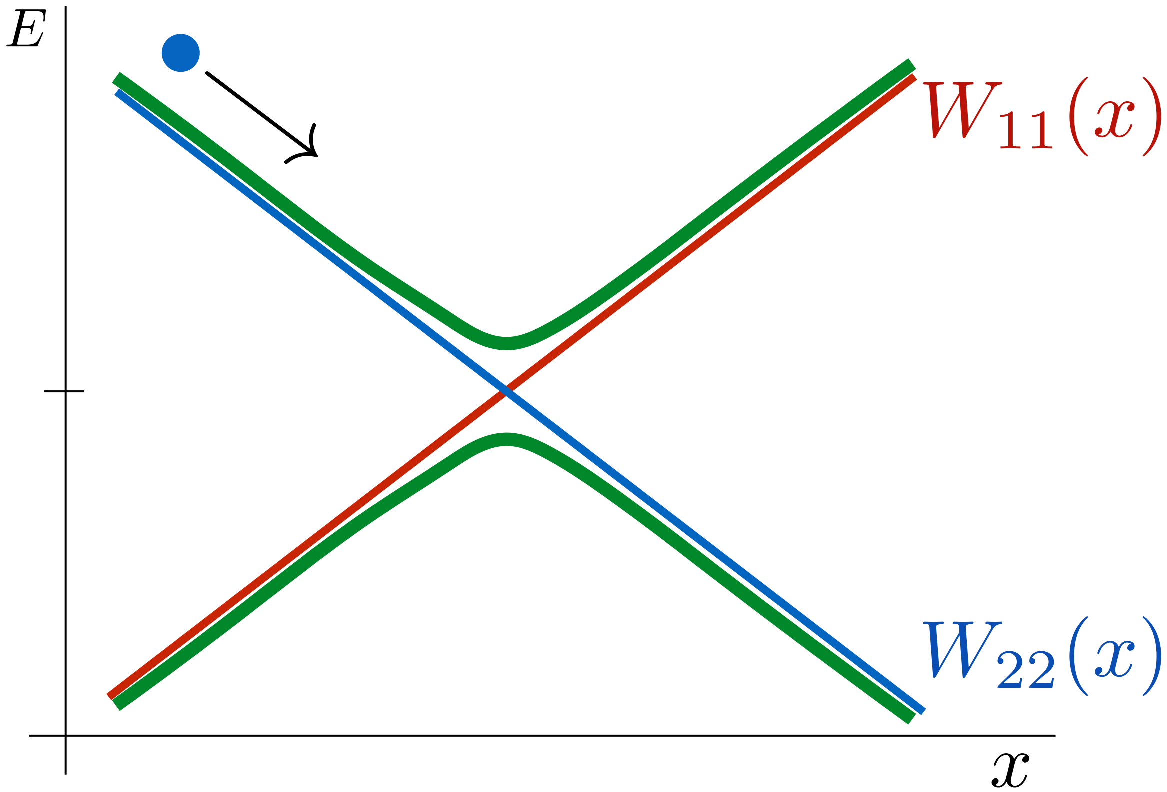
$$\left.\begin{array}{l} F_{12} = \dfrac{dW_{11}}{dx} - \dfrac{dW_{22}}{dx} = \text{const.} \\ v = \dot{x} = \text{const.} \end{array}\right\} \quad \begin{aligned} \frac{d}{dt}(W_{11} - W_{22}) &= F_{12}\, v \\ &= \alpha \end{aligned}$$

$$W_{12} = \text{const.}$$

The energy gap changes linearly with time.

Zener, C. *Proc. R. Soc. London A* **1932**, *137*, 696.
Landau, L. D. *Phys. Z.* **1932**, *2*, 46.
Wittig, C. *J. Phys. Chem. B* **2005**, *109*, 8428

The Landau-Zener model for non-adiabatic transitions



$$\mathbf{W}(t) = \begin{pmatrix} \alpha t/2 & W_{12} \\ W_{12} & -\alpha t/2 \end{pmatrix}$$

$$\dot{C}_1(t) = W_{12} C_2(t) \exp\left(-i/\hbar \int^t \alpha t' \, dt'\right)$$

$$\dot{C}_2(t) = W_{12} C_1(t) \exp\left(i/\hbar \int^t \alpha t' \, dt'\right)$$

Zener, C. *Proc. R. Soc. London A* **1932**, *137*, 696.
Landau, L. D. *Phys. Z.* **1932**, *2*, 46.
Wittig, C. *J. Phys. Chem. B* **2005,** *109*, 8428

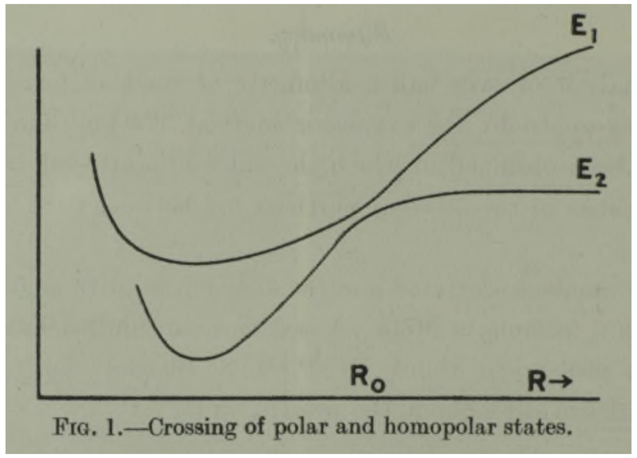


FIG. 1.—Crossing of polar and homopolar states.

$$C_1(-\infty) = 0$$

$$|C_2(-\infty)| = 1$$

$$P_{\text{nat}} = |C_2(\infty)|^2$$

$$P_{\text{nat}} = \exp\left(-2\pi \, \omega_{12} \, \tau_d\right)$$

$$\omega_{12} = \frac{|W_{12}|}{\hbar} \qquad \tau_d = \frac{|W_{12}|}{v|F_{12}|}$$

QUESTION

Fast atomic motion results in...

🟦 ... non-adiabatic transitions.

🟢 ... small probability that the electronic subsystem rearranges.

▲ ... break-up of the BO approximation.

⬟ ... that electrons cannot follow.

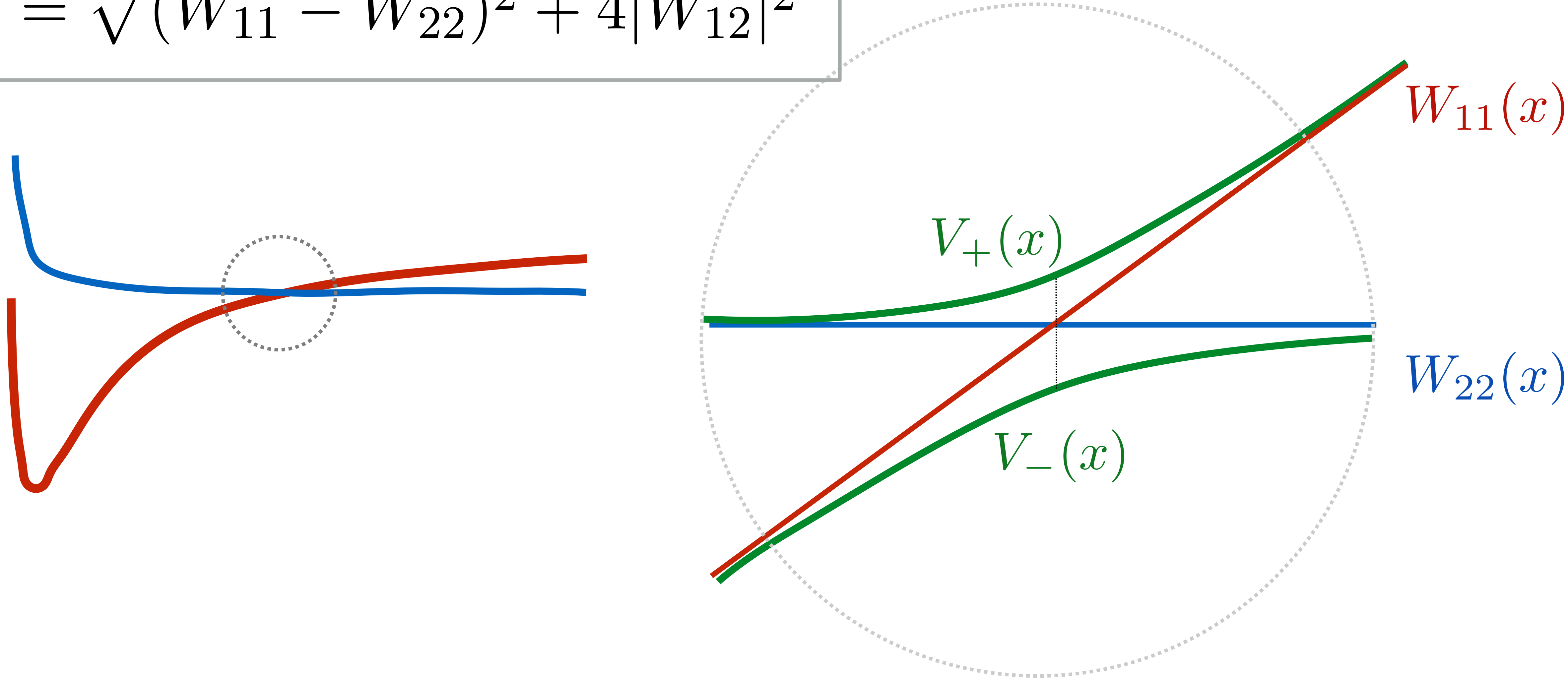
Curve crossings: non-crossing rule in diatoms

$$\mathbf{W} = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}$$

$$W_{ij} = \langle \Phi_i^{(d)} | H_{el} | \Phi_j^{(d)} \rangle$$

$$V_{\pm} = \frac{W_{11} + W_{22}}{2} \pm \frac{1}{2}\sqrt{(W_{11} - W_{22})^2 + 4|W_{12}|^2}$$

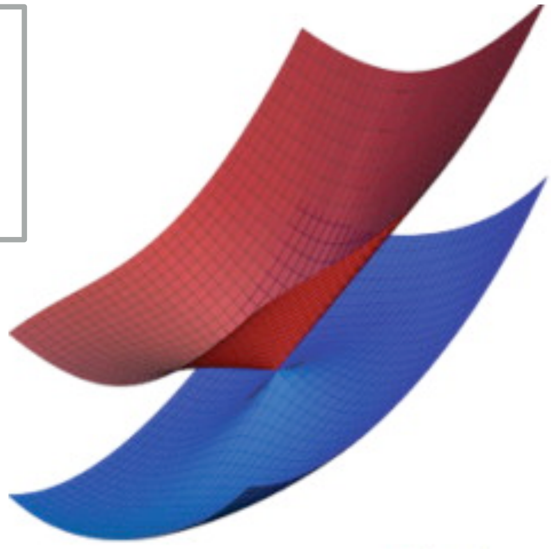
$$\Delta V = \sqrt{(W_{11} - W_{22})^2 + 4|W_{12}|^2}$$



Curve crossings: conical intersections

$$\mathbf{W} = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}$$

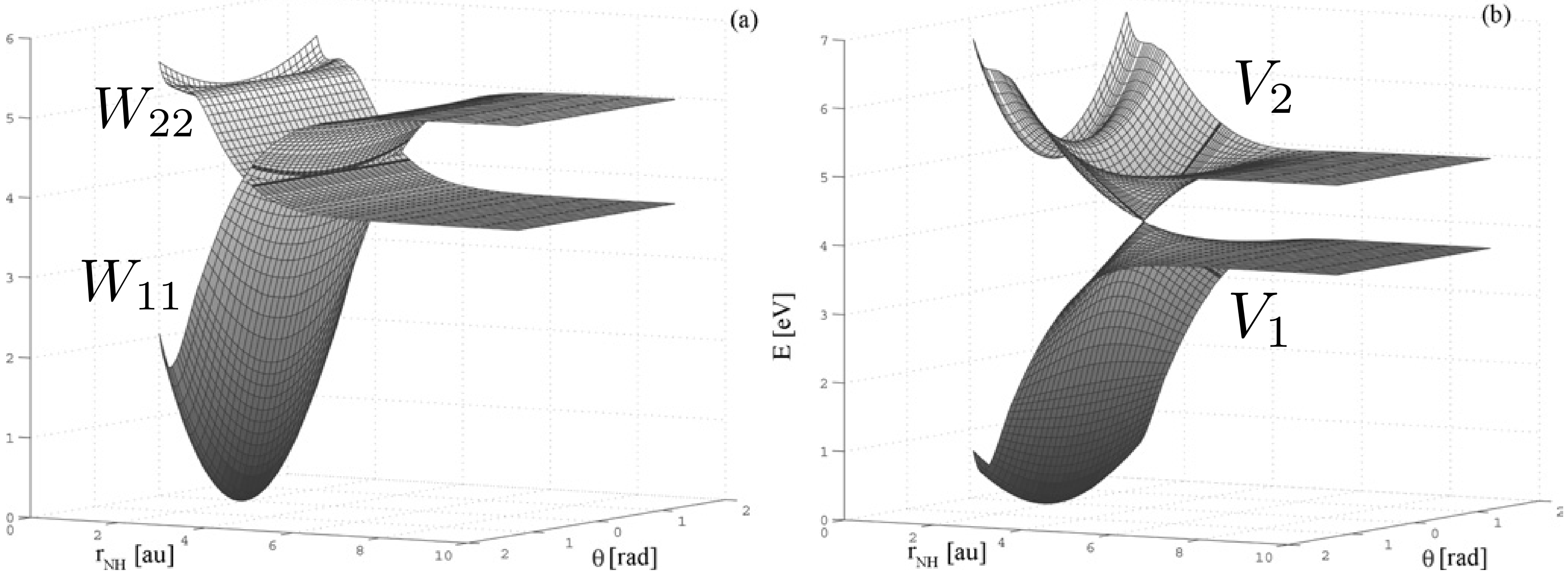
$$W_{ij} = \langle \Phi_i^{(d)} | H_{el} | \Phi_j^{(d)} \rangle$$



$$V_{\pm} = \frac{W_{11} + W_{22}}{2} \pm \frac{1}{2}\sqrt{(W_{11} - W_{22})^2 + 4|W_{12}|^2}$$

$$\Delta V = \sqrt{(W_{11} - W_{22})^2 + 4|W_{12}|^2}$$

Two conditions to satisfy: CI have dimensionality M-2



Adapted from *Faraday Discuss.* 2004, **127**, 283-293

Numerically solving the dynamics problem

$$\Psi(\mathbf{R},t) = \sum_J A_J(t)\Phi_J(\mathbf{R})$$

$$= \sum_{j_1,\ldots,j_f}^{N_1,\ldots,N_f} A_{j_1,\ldots,j_f}\varphi_{j_1}(R_1)\varphi_{j_2}(R_2)\cdots\varphi_{j_f}(R_f)$$

N^f configurations

Standard method

$$i\hbar\dot{A}_I = \sum_J \langle\varphi_I(\mathbf{R})|T+V(\mathbf{R})|\varphi_J(\mathbf{R})\rangle A_J$$

Time-dependent configurations:
- MCTDH
- Moving Gaussian basis

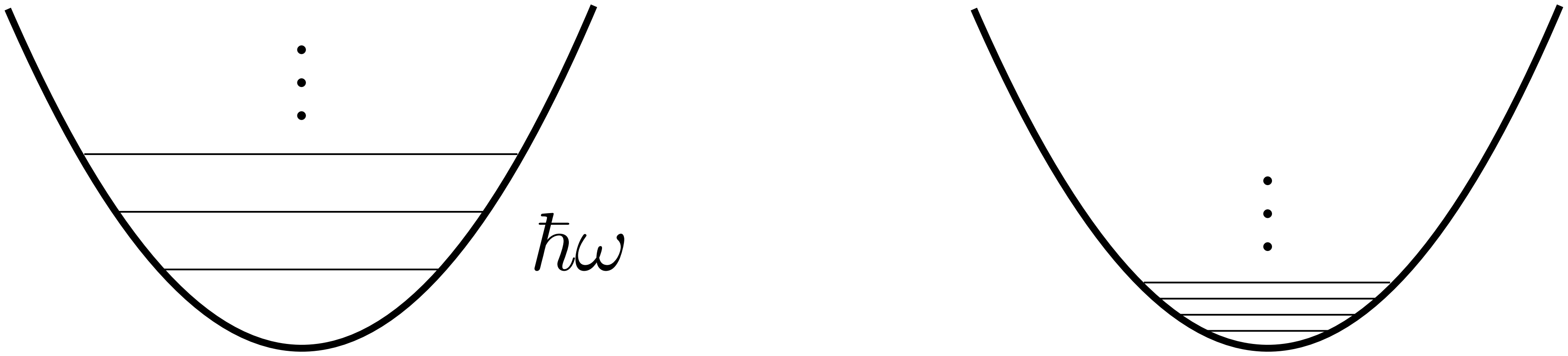
R. Kossloff, *J. Phys. Chem.* **92**, 2087 (1988)
C. Leforestier et al., *J. Comp. Phys.* **94**, 59 (1991)
M.H. Beck et al. *Phys. Rep.* **324**, 1, (2000)
M. Ben-Nun, T.J. Martinez, Adv. Chem. Phys. **121**, 439 (2002)
Worth et al. *J. Phys. Chem A* **107**, 621 (2003);

Nuclei can approximately be described classically ...

... when the energy scale of the problem is much larger than the nuclear energy level separations.

$$\boxed{\lambda = \frac{h}{mv}}$$

$$\boxed{\frac{1}{2}kx^2 \qquad \omega = \sqrt{\frac{k}{m}}}$$



Numerically solving the dynamics problem

Nuclear dynamics described classically:

Born-Oppenheimer

$$m_a \ddot{\vec{R}}_a = -\vec{\nabla}_a V_0(\mathbf{R}) \begin{cases} V_0(\mathbf{R}) = \langle \psi_{0;\mathbf{R}} | \hat{H}_e(\mathbf{R}(t)) | \psi_{0;\mathbf{R}} \rangle & \text{BOMD} \\ V_0(\mathbf{R}) = f(\mathbf{R}) = \sum\limits_{\text{bonds}} + \sum\limits_{\text{angles}} + \sum\limits_{\text{charges}} + \dots & \text{MM (mol. mech.)} \end{cases}$$

Non-adiabatic transitions

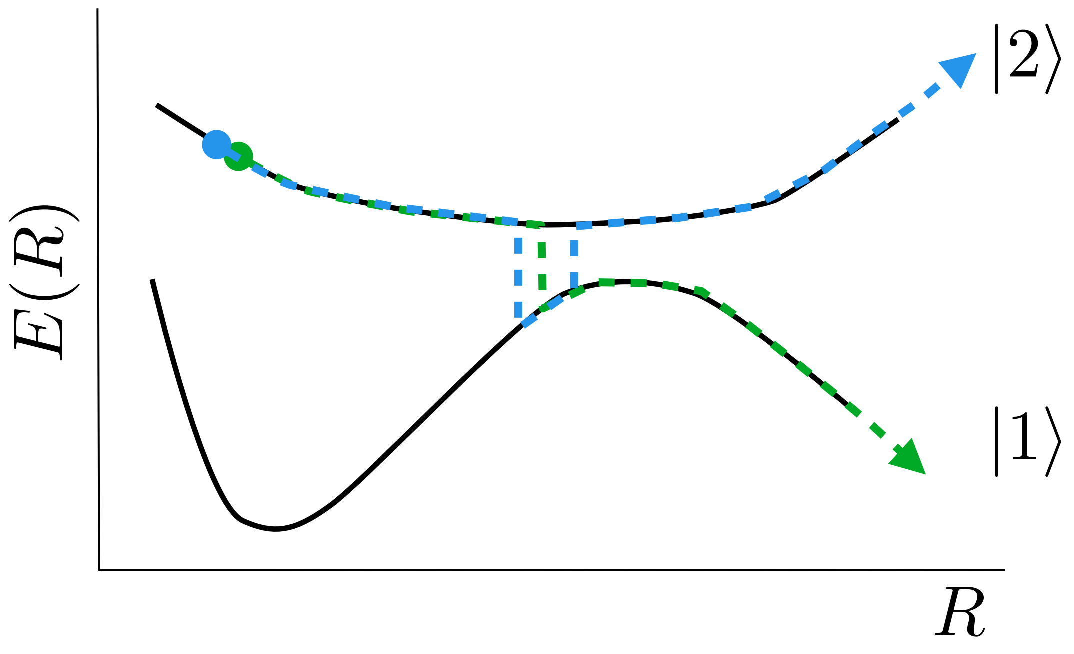
$$m_a \ddot{\vec{R}}_a = -\vec{\nabla}_a V_{\mathrm{x}}(\mathbf{R}) \begin{cases} V_{\mathrm{x}}(\mathbf{R}) = \langle \psi(t) | \hat{H}_e(\mathbf{R}(t)) | \psi(t) \rangle & \boxed{\text{Ehrenfest}} \\ V_{\mathrm{x}}(\mathbf{R}) = V_j(\mathbf{R}) & \boxed{\text{Surface-Hopping}} \end{cases}$$

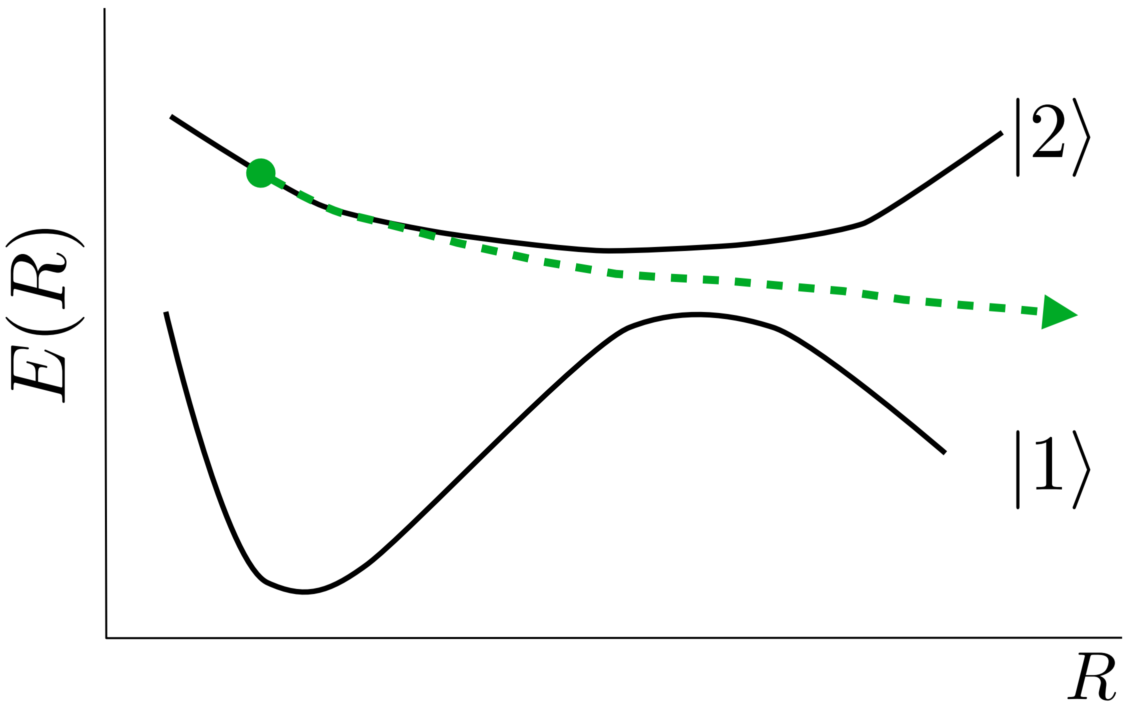
$$i\hbar |\dot{\psi}(t)\rangle = \hat{H}_e(\mathbf{R}(t)) |\psi(t)\rangle$$

$$\hat{H}_e(\mathbf{R}) |\psi_{j;\mathbf{R}}\rangle = V_j(\mathbf{R}) |\psi_{j;\mathbf{R}}\rangle$$

J. Tully, *J. Chem. Phys.* **93**, 1061 (1990)
M.D. Hack, D.G. Truhlar, *J. Phys. Chem. A* **104**, 7917, (2000)

Non-adiabatic dynamics with classical trajectories





$$m_a \ddot{\vec{R}}_a = -\vec{\nabla}_a V_j(\mathbf{R})$$

$$i\hbar \dot{c}_j(t) = \sum_i c_i(t) \left(V_i \delta_{ji} - i\hbar\, \dot{\mathbf{R}} \cdot \mathbf{d}_{ji} \right)$$

$$m_a \ddot{\vec{R}}_a = -\vec{\nabla}_a V_{\mathrm{x}}(\mathbf{R})$$

$$V_{\mathrm{x}}(\mathbf{R}) = \langle \psi(t) | \hat{H}_e(\mathbf{R}(t)) | \psi(t) \rangle$$

$$i\hbar |\dot{\psi}(t)\rangle = \hat{H}_e(\mathbf{R}(t)) |\psi(t)\rangle$$

J. Tully, *J. Chem. Phys.* **93**, 1061 (1990)
M.D. Hack, D.G. Truhlar, *J. Phys. Chem. A* **104**, 7917, (2000)

QUESTION

Nuclei can (sometimes) be approximated as classical particles when...

🟦 ...electrons are fast.

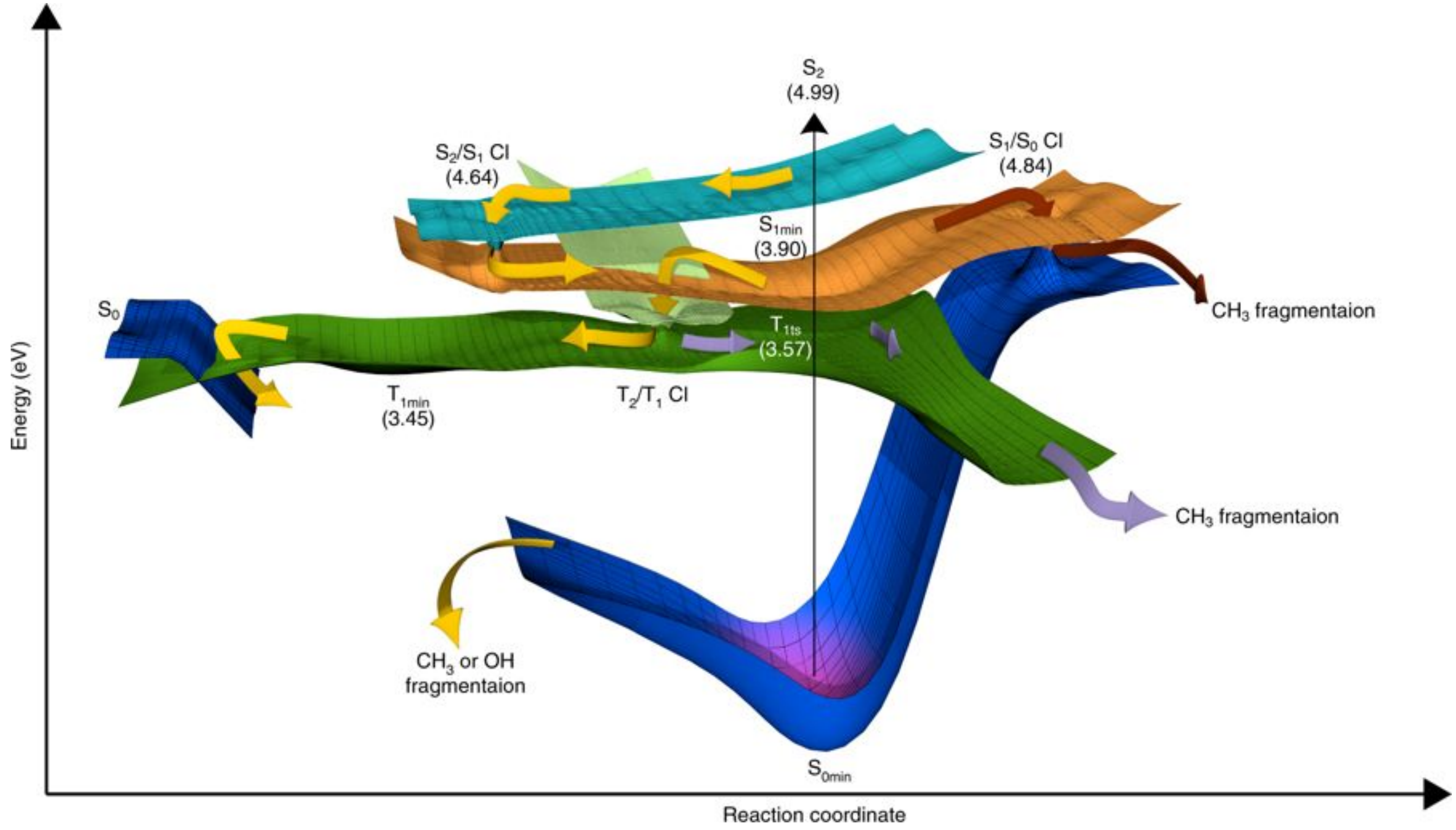
🟢 ...electrons are slow.

▲ ...nuclei have a large kinetic energy.

⬟ ...nuclei don't move.

Time-dependent Description of Molecular Spectroscopy

Nearly all we know about matter is through its interaction with light.
— Yoda.



Acetylacetone photodynamics at a seeded free-electron laser
R. J. Squibb et. al.
Nature Communications, **9**, 63 (2018)

Non-perturbative absorption spectrum

$$\sigma(\omega) = \frac{\#\text{ of photons absorbed at freq. } \omega \quad ①}{\#\text{ of photons per unit area at freq. } \omega \quad ②}$$

① From the total energy gained (lost) by the system at a given frequency:

$$N_a(\omega) = \frac{\Delta E(\omega)}{\hbar\omega}$$

② From classical electromagnetism:

$$\frac{N(\omega)}{A} = \frac{|\tilde{\epsilon}(\omega)|^2 c}{\hbar\omega}$$

$$\boxed{\sigma(\omega) = \frac{\Delta E(\omega)}{|\tilde{\epsilon}(\omega)|^2 c}}$$

where $\tilde{\epsilon}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \epsilon(t) e^{i\omega t} dt$ Back FT

So the task is to determine the energy exchanged with the EM field at each frequency.

Non-perturbative absorption spectrum

$$\boxed{E(t) = \langle \Psi(t) | \hat{H}(t) | \Psi(t) \rangle}$$

$$\boxed{\hat{H} = \hat{H}_0 - \hat{\mu}\epsilon(t)}$$

$$\boxed{\dot{E}(t) = \cancelto{0}{\langle \dot{\Psi}(t) | \hat{H} | \Psi(t) \rangle + \langle \Psi(t) | \hat{H} | \dot{\Psi}(t) \rangle} + \langle \Psi(t) | \frac{d\hat{H}}{dt} | \Psi(t) \rangle}$$

$$\boxed{\begin{aligned} \dot{E}(t) &= -\langle \Psi(t) | \hat{\mu} | \Psi(t) \rangle \dot{\epsilon}(t) \\ &= -P(t)\dot{\epsilon}(t) \end{aligned}}$$

Total energy increase:

$$\boxed{\Delta E = \int_{-\infty}^{\infty} \dot{E}(t) dt = \int_{-\infty}^{\infty} -P(t)\dot{\epsilon}(t) dt = -2\pi \int_{-\infty}^{\infty} -i\omega[\tilde{P}(\omega)]^* \tilde{\epsilon}(\omega) d\omega = \int_{-\infty}^{\infty} \Delta E(\omega) d\omega = \Delta E}$$

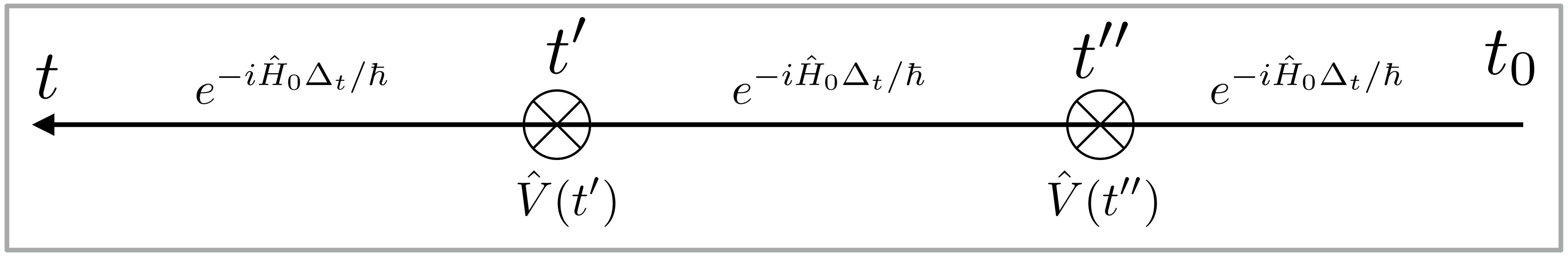
$$\boxed{\Delta E(\omega) = 2\pi i\, \omega [\tilde{P}(\omega)]^* \tilde{\epsilon}(\omega)}$$

Time-dependent perturbation theory

$$\boxed{\Psi(t) = \Psi^{(0)}(t) + \lambda\Psi^{(1)}(t) + \lambda^2\Psi^{(2)}(t) + \cdots}$$

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\Psi^{(0)}(t) &= H_0\Psi^{(0)}(t) \\
i\hbar\frac{\partial}{\partial t}\Psi^{(1)}(t) &= H_0\Psi^{(1)}(t) + V(t)\Psi^{(0)}(t) \\
i\hbar\frac{\partial}{\partial t}\Psi^{(2)}(t) &= H_0\Psi^{(2)}(t) + V(t)\Psi^{(1)}(t) \\
&\vdots
\end{aligned}$$

$$\begin{aligned}
\Psi^{(0)}(t) &= e^{-i\hat{H}_0(t-t_0)/\hbar}\Psi^{(0)}(t_0) \\
\Psi^{(1)}(t) &= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{-i\hat{H}_0(t-t')\hbar}\hat{V}(t')e^{-i\hat{H}_0(t'-t_0)\hbar}\Psi^{(0)}(t_0) \\
\Psi^{(2)}(t) &= \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{-i\hat{H}_0(t-t')\hbar}\hat{V}(t')e^{-i\hat{H}_0(t'-t'')/\hbar}\hat{V}(t'')e^{-i\hat{H}_0(t''-t_0)/\hbar}\Psi^{(0)}(t_0)
\end{aligned}$$



The case of a very short pulse

$$\epsilon(t) = a\,\delta(t) \quad\longrightarrow\quad \tilde{\epsilon}(\omega) = a/2\pi$$

Ideal short pulse.

$$P(t) = \langle\Psi(t)|\hat{\mu}|\Psi(t)\rangle = \Big(\langle\Psi^{(0)}(t)| + \langle\Psi^{(1)}(t)|\Big)\,\hat{\mu}\,\Big(|\Psi^{(0)}(t)\rangle + |\Psi^{(1)}(t)\rangle\Big)$$

$$|\Psi^{(1)}(t)\rangle = \frac{a}{i\hbar}e^{-i\hat{H}_0 t/\hbar}\hat{\mu}|\Psi^{(0)}(0)\rangle$$

First order TDPT

$$P(t) = 2\Re\left\{\langle\Psi^{(0)}(t)|\hat{\mu}|\Psi^{(1)}(t)\rangle\right\} = 2\Re\left\{\frac{1}{i\hbar}e^{iE_0 t/\hbar}\langle\Psi^{(0)}(0)|\hat{\mu}e^{-i\hat{H}_0 t/\hbar}\hat{\mu}|\Psi^{(0)}(0)\rangle\right\}\Theta(0)$$

$$\begin{aligned}\tilde{P}(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} P(t)e^{i\omega t}dt \\ &= \frac{1}{2\pi i\hbar}\int_{-\infty}^{\infty}\langle\Psi^{(0)}(0)|\hat{\mu}e^{-i\hat{H}_0 t/\hbar}\hat{\mu}|\Psi^{(0)}(0)\rangle e^{i(\omega_0+\omega)t}dt\end{aligned}$$

$$\sigma(\omega) = \frac{2\pi\omega}{\hbar c}\int_{-\infty}^{\infty} C(t)e^{i(\omega_0+\omega)t}dt$$

Wavepacket interpretation of 1-photon spectroscopy

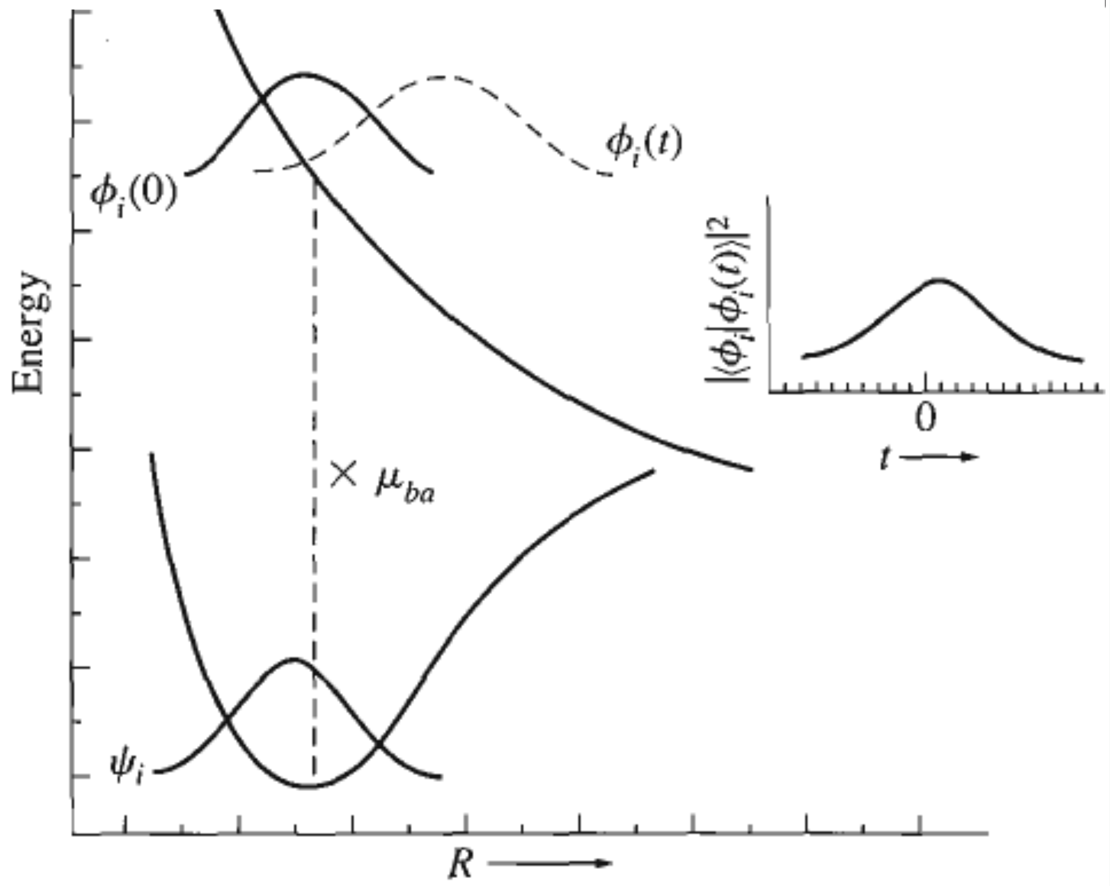


Figure 14.6 Wavepacket interpretation of the formula for the one-photon absorption spectrum, $\sigma(\omega_1)$ (Eq. 14.21). The state $\phi_i = \mu_{ba}\psi_i$ is a *wavepacket* on the excited electronic state potential and begins to move according to the Time-Dependent Schrödinger Equation. The absolute value squared of the autocorrelation function constructed from the overlap of $\phi_i(t)$ with $\phi_i(0)$ is shown in the inset. The Fourier transform of the autocorrelation function at frequency $\tilde{\omega}_1$ determines the absorption spectrum (see Eq. 14.21).

$$\sigma(\omega) \propto \omega \sum_j |\langle\Psi_j|\hat{\mu}|\Psi_0\rangle|\ \ \delta(\omega + \omega_0 - \omega_j)$$

$$\begin{aligned}\sigma(\omega) &\propto \omega \int_{-\infty}^{+\infty} \langle\Psi_0|\hat{\mu}e^{-\frac{i}{\hbar}\hat{H}_0 t/\hbar}\hat{\mu}|\Psi_0\rangle e^{i\omega t}dt \\ &\propto \omega\ 2\Re\left\{\int_0^{+\infty} \underbrace{\boxed{\langle\Psi_0|\hat{\mu}e^{-\frac{i}{\hbar}\hat{H}_0 t/\hbar}\hat{\mu}|\Psi_0\rangle}}_{C(t)} e^{i\omega t}dt\right\}\end{aligned}$$

Tannor D.J., *Introduction to Quantum Mechanics, A Time-Dependent Perspective*
University Science Books **2007**

Wavepacket interpretation of 1-photon spectroscopy

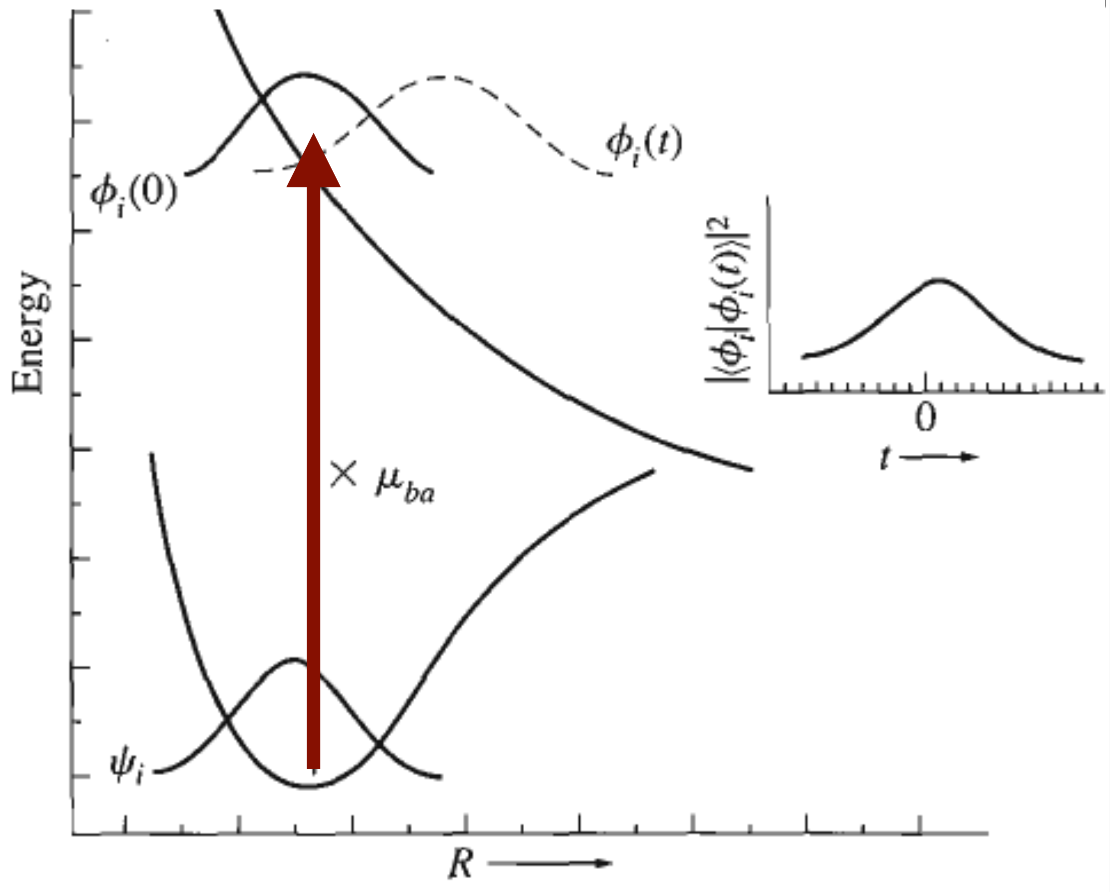


Figure 14.6 Wavepacket interpretation of the formula for the one-photon absorption spectrum, $\sigma(\omega_1)$ (Eq. 14.21). The state $\phi_i = \mu_{ba}\psi_i$ is a *wavepacket* on the excited electronic state potential and begins to move according to the Time-Dependent Schrödinger Equation. The absolute value squared of the autocorrelation function constructed from the overlap of $\phi_i(t)$ with $\phi_i(0)$ is shown in the inset. The Fourier transform of the autocorrelation function at frequency $\tilde{\omega}_1$ determines the absorption spectrum (see Eq. 14.21).

$$\sigma(\omega) \propto \omega \sum_j |\langle\Psi_j|\hat{\mu}|\Psi_0\rangle|\ \ \delta(\omega + \omega_0 - \omega_j)$$

$$\Downarrow$$

$$\sigma(\omega) \propto \omega \int_{-\infty}^{+\infty} \langle\Psi_0|\hat{\mu}e^{-\frac{i}{\hbar}\hat{H}_0 t/\hbar}\hat{\mu}|\Psi_0\rangle e^{i\omega t}dt$$

$$\propto \omega\ 2\Re\left\{\int_0^{+\infty} \underbrace{\langle\Psi_0|\hat{\mu}e^{-\frac{i}{\hbar}\hat{H}_0 t/\hbar}\hat{\mu}|\Psi_0\rangle}_{C(t)} e^{i\omega t}dt\right\}$$

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Wavepacket interpretation of 1-photon spectroscopy

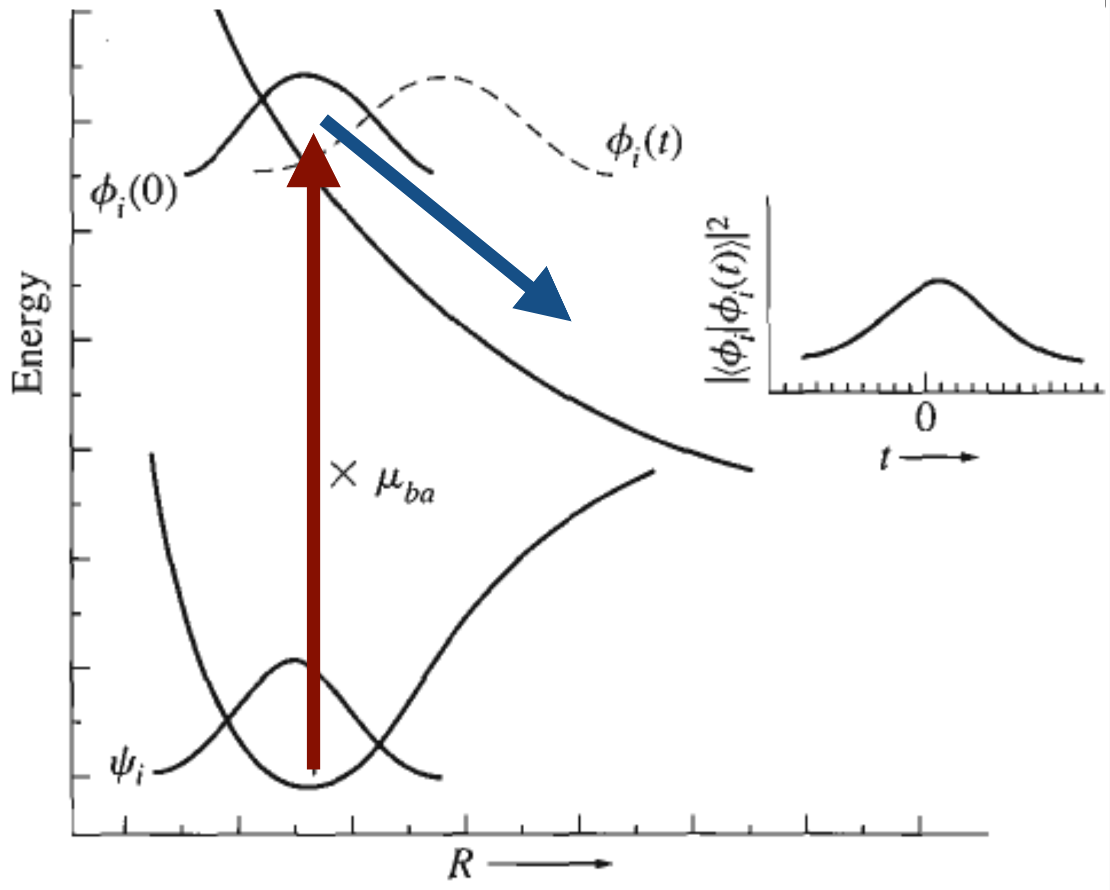

Figure 14.6 Wavepacket interpretation of the formula for the one-photon absorption spectrum, $\sigma(\omega_I)$ (Eq. 14.21). The state $\phi_i = \mu_{ba}\psi_i$ is a *wavepacket* on the excited electronic state potential and begins to move according to the Time-Dependent Schrödinger Equation. The absolute value squared of the autocorrelation function constructed from the overlap of $\phi_i(t)$ with $\phi_i(0)$ is shown in the inset. The Fourier transform of the autocorrelation function at frequency $\tilde{\omega}_I$ determines the absorption spectrum (see Eq. 14.21).

$$\sigma(\omega) \propto \omega \sum_j |\langle \Psi_j|\hat{\mu}|\Psi_0\rangle| \;\; \delta(\omega + \omega_0 - \omega_j)$$

$$\sigma(\omega) \propto \omega \int_{-\infty}^{+\infty} \langle \Psi_0|\hat{\mu} e^{-\frac{i}{\hbar}\hat{H}_0 t/\hbar}\hat{\mu}|\Psi_0\rangle e^{i\omega t} dt$$

$$\propto \omega\; 2\Re\left\{\int_0^{+\infty} \underbrace{\langle \Psi_0|\hat{\mu} e^{-\frac{i}{\hbar}\hat{H}_0 t/\hbar}\hat{\mu}|\Psi_0\rangle}_{C(t)} e^{i\omega t} dt\right\}$$

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Wavepacket picture of 1-photon spectroscopy

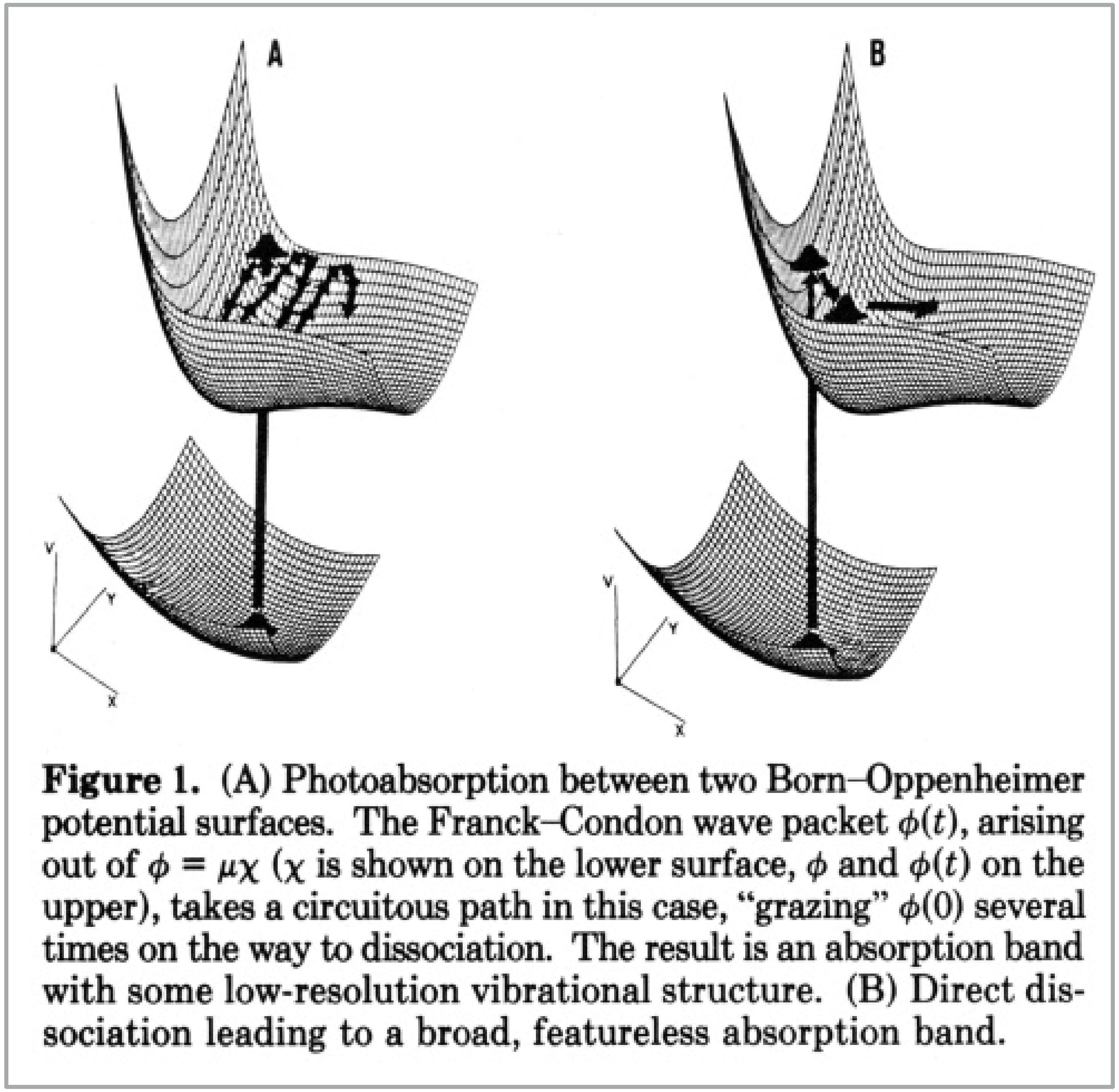

Figure 1. (A) Photoabsorption between two Born–Oppenheimer potential surfaces. The Franck–Condon wave packet $\phi(t)$, arising out of $\phi = \mu\chi$ (χ is shown on the lower surface, ϕ and $\phi(t)$ on the upper), takes a circuitous path in this case, "grazing" $\phi(0)$ several times on the way to dissociation. The result is an absorption band with some low-resolution vibrational structure. (B) Direct dissociation leading to a broad, featureless absorption band.

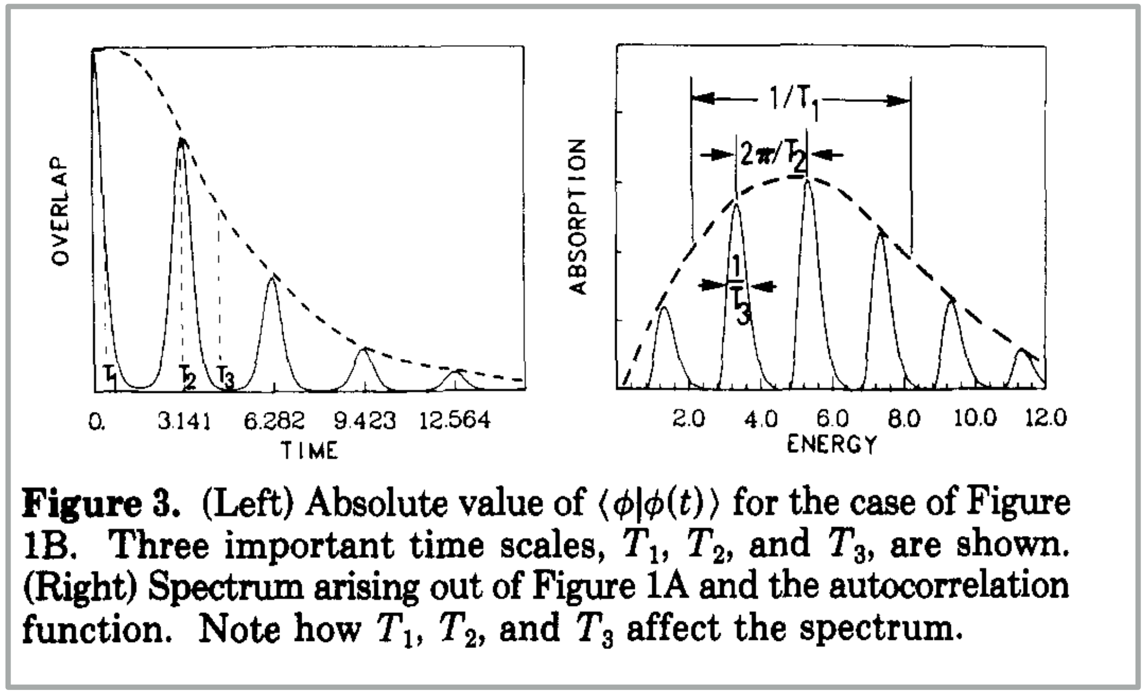

Figure 3. (Left) Absolute value of $\langle\phi|\phi(t)\rangle$ for the case of Figure 1B. Three important time scales, T_1, T_2, and T_3, are shown. (Right) Spectrum arising out of Figure 1A and the autocorrelation function. Note how T_1, T_2, and T_3 affect the spectrum.

- Shortest time-scale in C(t) defines total width of spectrum.

- Longest time-scale in C(t), its overall decay time, defines width of highest resolution features.

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Example: Photoabsorption spectrum of pyrazine

Molecular dynamics of pyrazine after excitation to the S_2 electronic state using a realistic 24-mode model Hamiltonian

A. Raab, G. A. Worth, H.-D. Meyer, and L. S. Cederbaum
Theoretische Chemie, Physikalisch–Chemisches Institut, Universität Heidelberg, INF 253,
D-69120 Heidelberg, Federal Republic of Germany

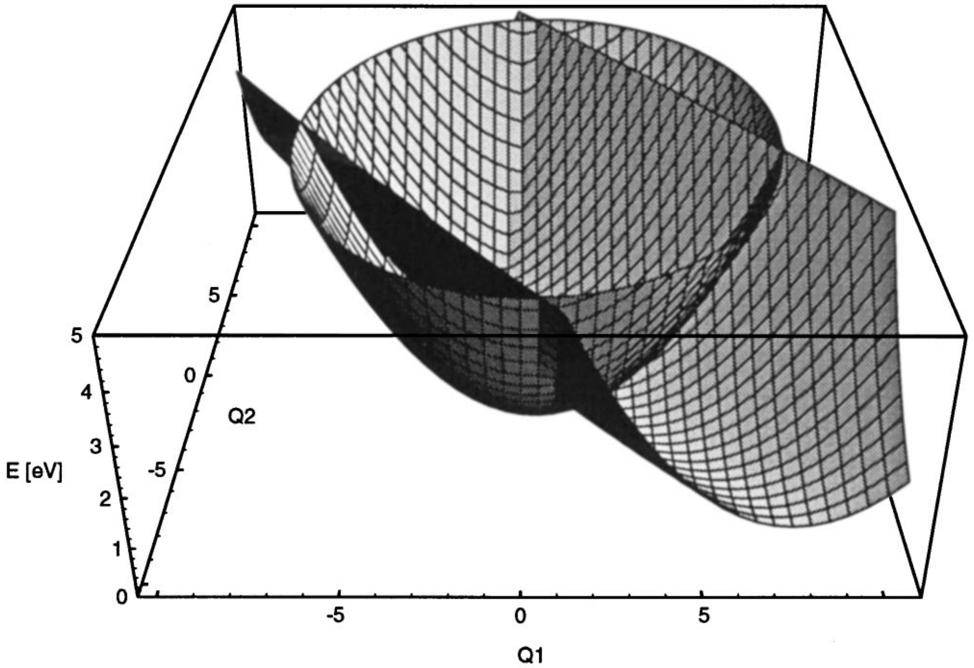
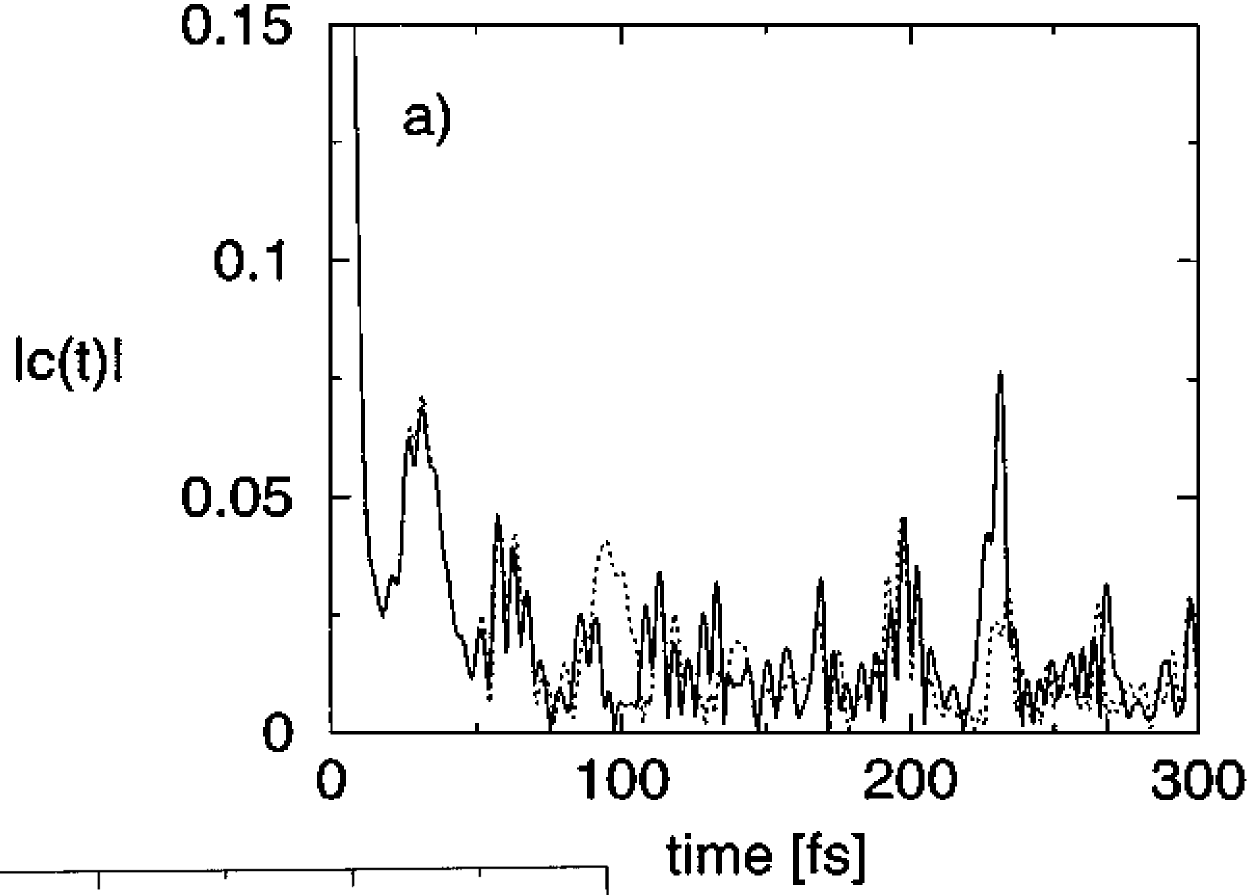
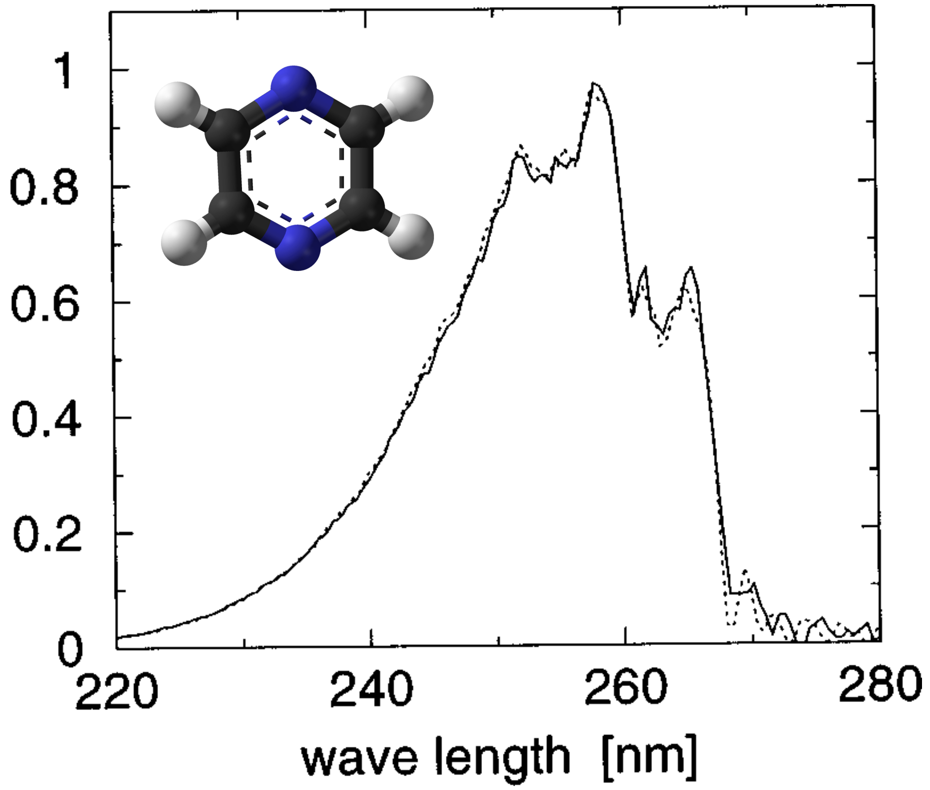


FIG. 1. The PES in dependence of the modes ν_{18b} and ν_{19b} ($Q1=Q_{18b}$, $Q2=Q_{19b}$, the remaining coordinates are set to zero): The S_2 PES is rather flat for $Q_{18b}=-Q_{19b}$ (the diabatic picture) leading to a rather interesting conical intersection with the S_1 PES. Note that the mode pair (ν_{18b}, ν_{19b}) belongs to the set G_2 [cf. Eq. (1)] and thus introduces a bilinear coupling.





QUESTION

Broad-band excitation results in wavepacket dynamics

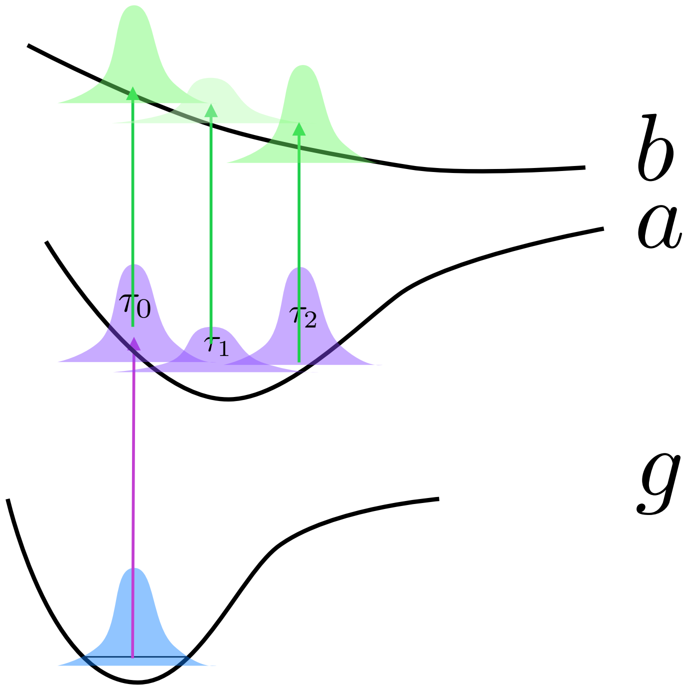
🟦 … always.

🟢 … only if the pulse is sufficiently intense.

▲ … only if the system has states spanning the given bandwidth.

⬟ … only if there is no observer.

Transient (x-ray) absorption spectrum



Pump and probe pulses do not overlap

Probe pulse is after pump pulse

Probe pulse is short

$$\sigma(\omega,\tau) = \frac{4\pi\omega}{\hbar c}\mathrm{Re}\left[\int_0^\infty dt\; e^{i\omega t}\langle\Psi_a(\tau)|e^{iH_a t/\hbar}\,\hat{\mu}_{ab}\,e^{-iH_b t/\hbar}\hat{\mu}_{ab}|\Psi_a(\tau)\rangle\right]$$

Lee, Pollard & Mathies, *Chem. Phys. Lett.* **163**, 11 (1989)

Transient (x-ray) absorption spectrum

Short time approximation:

$$\boxed{e^{iH_a t/\hbar}\,\hat{\mu}_{ab} \longrightarrow \hat{\mu}_{ab}\, e^{iH_a t/\hbar}}$$

$$\boxed{\begin{aligned} e^{iH_a t/\hbar}\, e^{-iH_b t/\hbar} &= e^{-i(H_b-H_a)t/\hbar} + \mathcal{O}(t^2) + \cdots \\ &\approx e^{-i(V_b-V_a)t/\hbar} \end{aligned}}$$

$$\sigma(\omega,\tau) = \frac{4\pi\omega}{\hbar c}\mathrm{Re}\left[\int_0^\infty dt\; e^{i\omega t - \Gamma t/\hbar}\langle\Psi_a(\tau)|\hat{\mu}_{ab}\, e^{-i(V_b-V_a)t/\hbar}\hat{\mu}_{ab}|\Psi_a(\tau)\rangle\right]$$

$$\sigma(\omega,\tau) = \frac{4\pi\omega}{c}\int d\mathbf{R}\;|\chi(\mathbf{R},\tau)|^2\;|\mu(\mathbf{R})|^2\;\frac{\Gamma}{\Gamma^2 + [V_b(\mathbf{R}) - V_a(\mathbf{R}) - \hbar\omega]^2}$$

(Lorentzian limit)

Lee, Pollard & Mathies, *Chem. Phys. Lett.* **163**, 11 (1989)

Tracing chemical dynamics with (ultrafast) x-rays. Examples and applications.

QUESTION

Why x-rays?

- 🟦 because they are fast.
- 🟢 because they oscillate a lot.
- ▲ because they have large specificity.
- ⬟ because they are intense.

Ultrafast x-ray light sources (accelerator based)

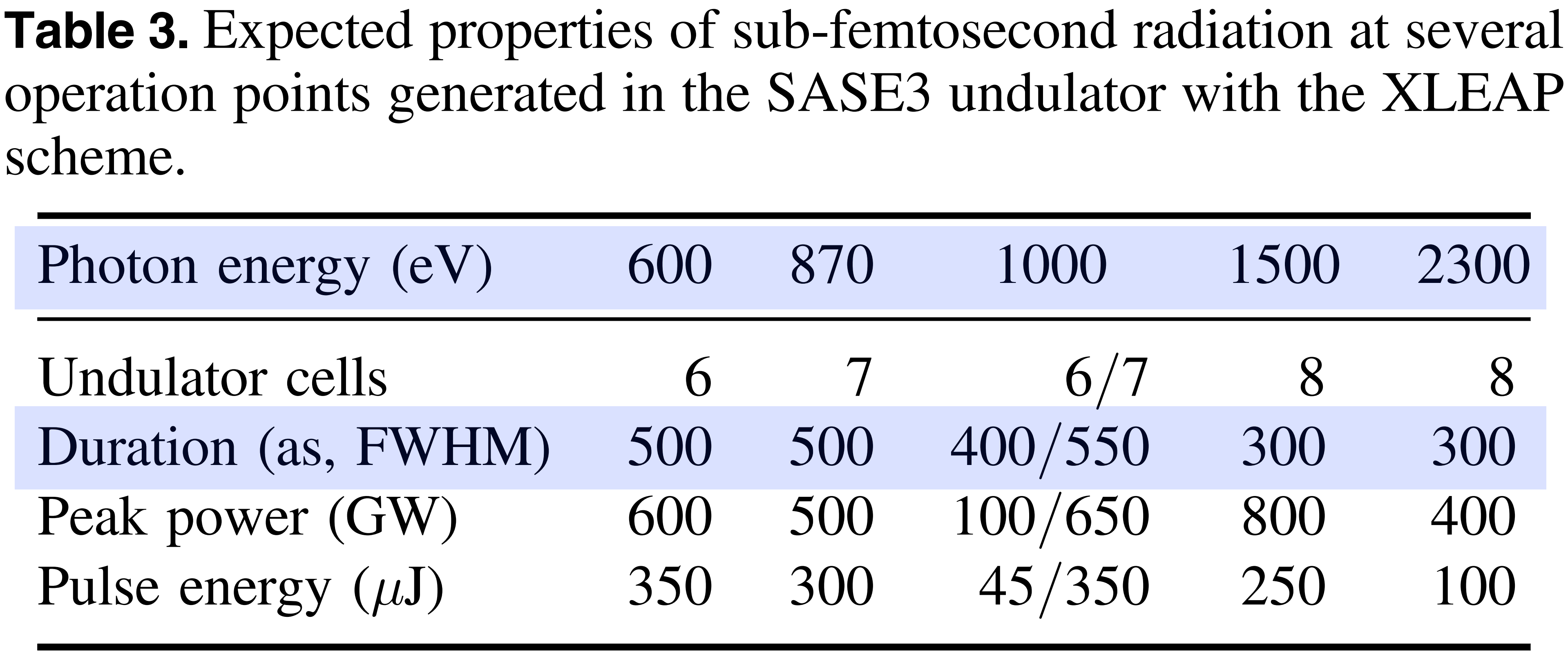
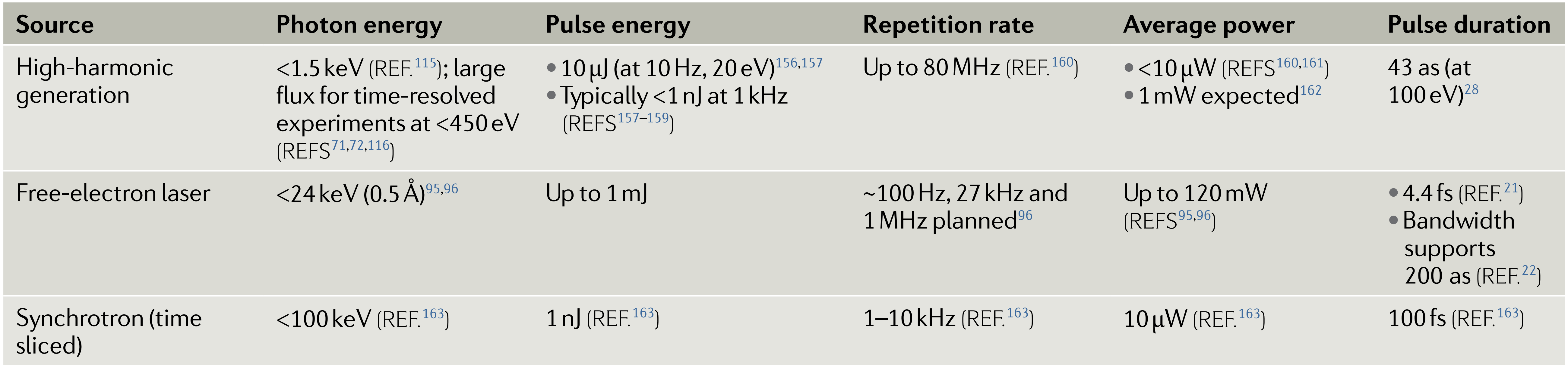


Table 3. Expected properties of sub-femtosecond radiation at several operation points generated in the SASE3 undulator with the XLEAP scheme.

Photon energy (eV)	600	870	1000	1500	2300
Undulator cells	6	7	6/7	8	8
Duration (as, FWHM)	500	500	400/550	300	300
Peak power (GW)	600	500	100/650	800	400
Pulse energy (μJ)	350	300	45/350	250	100

Overview of options for generating high-brightness attosecond x-ray pulses at free-electron lasers and applications at the European XFEL
S Serkez *et al.*, *J. Opt..*, **20**, 024005 (2018)

Ultrafast x-ray light sources



Source	Photon energy	Pulse energy	Repetition rate	Average power	Pulse duration
High-harmonic generation	<1.5 keV (REF.[115]); large flux for time-resolved experiments at <450 eV (REFS[71,72,116])	• 10 μJ (at 10 Hz, 20 eV)[156,157] • Typically <1 nJ at 1 kHz (REFS[157–159])	Up to 80 MHz (REF.[160])	• <10 μW (REFS[160,161]) • 1 mW expected[162]	43 as (at 100 eV)[28]
Free-electron laser	<24 keV (0.5 Å)[95,96]	Up to 1 mJ	~100 Hz, 27 kHz and 1 MHz planned[96]	Up to 120 mW (REFS[95,96])	• 4.4 fs (REF.[21]) • Bandwidth supports 200 as (REF.[22])
Synchrotron (time sliced)	<100 keV (REF.[163])	1 nJ (REF.[163])	1–10 kHz (REF.[163])	10 μW (REF.[163])	100 fs (REF.[163])

The ultrafast X-ray spectroscopic revolution in chemical dynamics
Kraus, Zürch, Cushing, Neumark, Leone, Nat. Rev. Chem., **2**, 82 (2018)

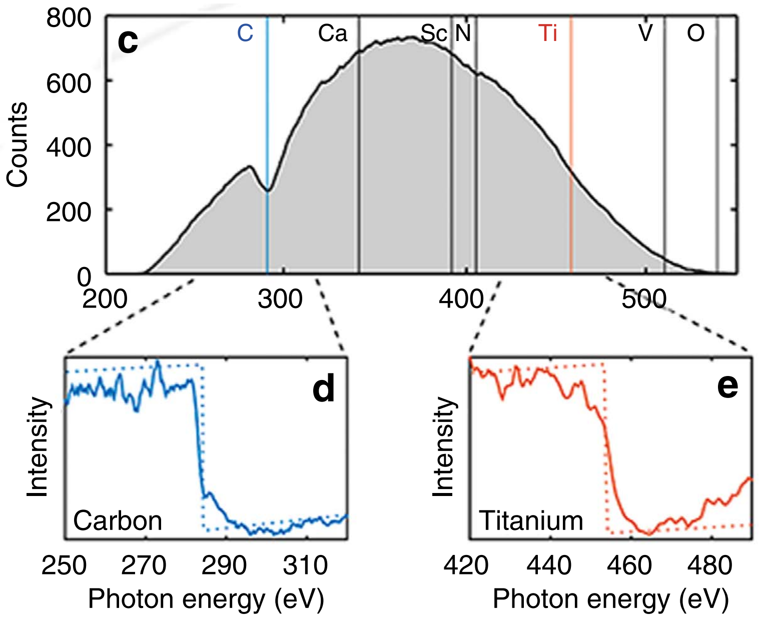
Ultrafast x-ray light sources ("table top")

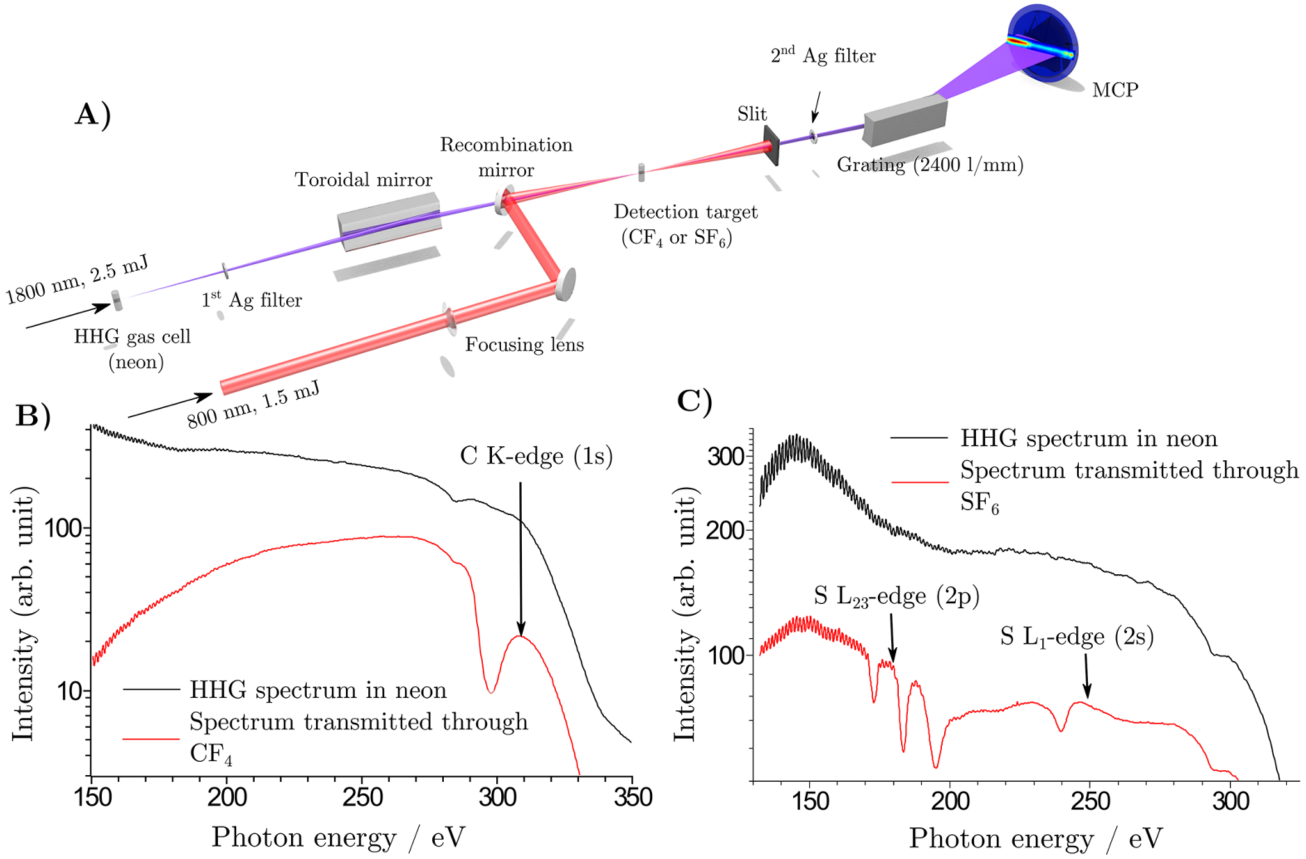
ARTICLE

Received 6 Nov 2015 | Accepted 31 Mar 2016 | Published 11 May 2016 DOI: 10.1038/ncomms11493 OPEN

0.5-keV Soft X-ray attosecond continua

S.M. Teichmann[1], F. Silva[1], S.L. Cousin[1], M. Hemmer[1] & J. Biegert[1,2]





0.5-keV Soft X-ray attosecond continua
SM Teichmann et al. Nat. Commun. ***7****, 11493 (2016)*
Time-resolved x-ray absorption spectroscopy with a water window high-harmonic source
Y. Pertot et al. *Science*, **355**, 264 (2017)

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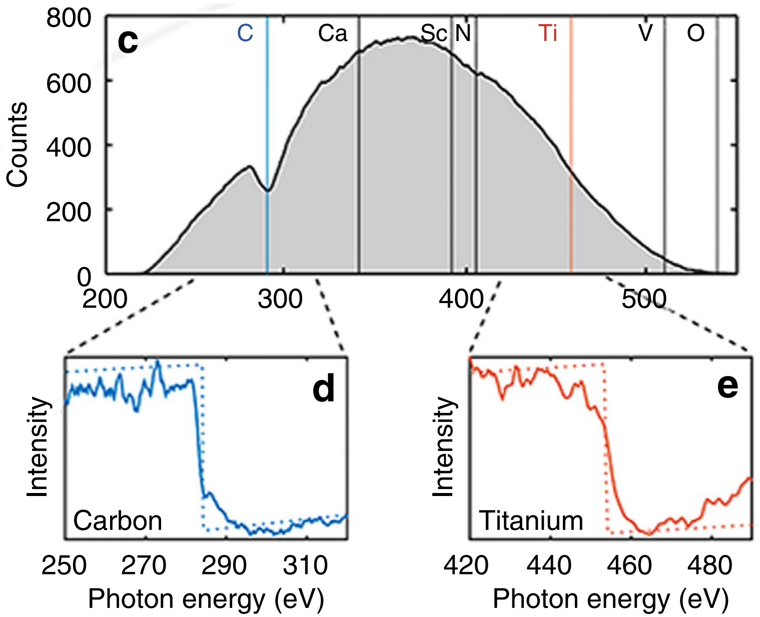

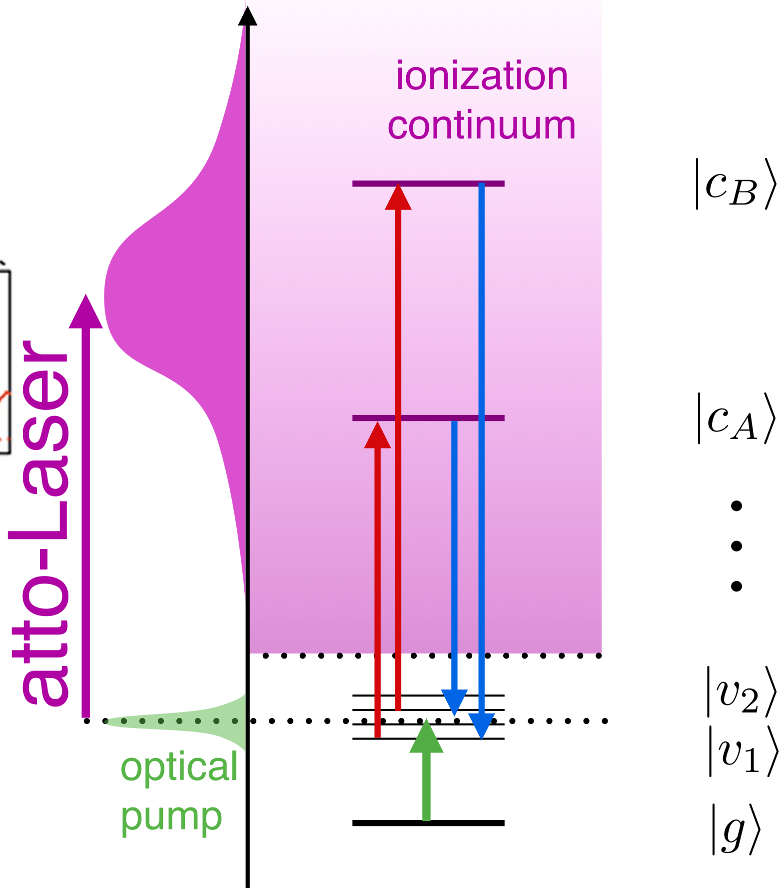

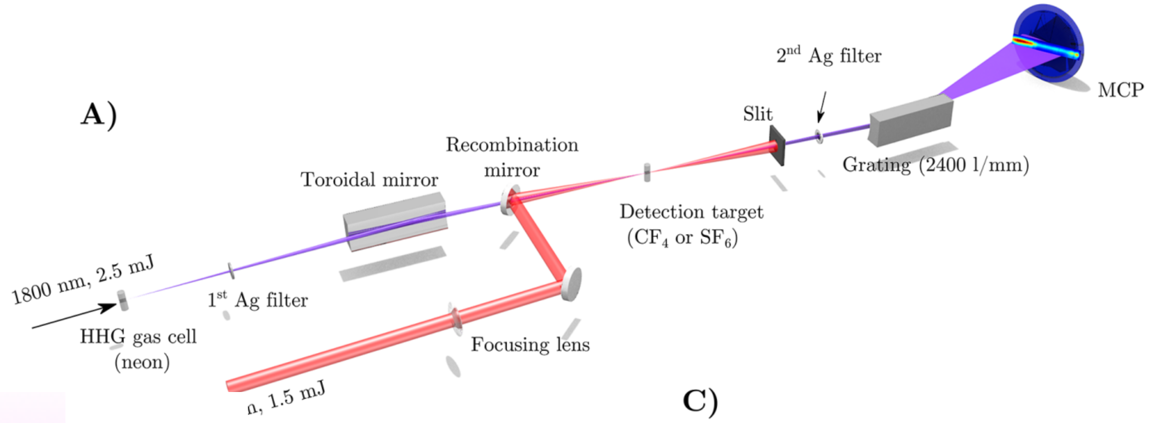

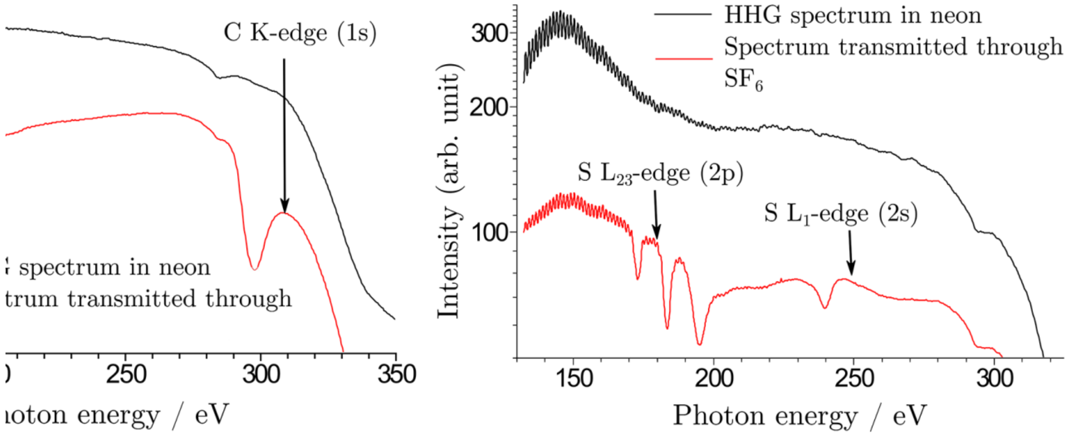

0.5-keV Soft X-ray attosecond continua
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Time-resolved x-ray absorption spectroscopy with a water window high-harmonic source
Y. Pertot et al. *Science,* **355**, 264 (2017)

Chemical reactions: what do we want to know?

- Nuclear configuration.
- Electronic configuration.
- Electronic state populations.
- Electronic coherences.
- Lifetimes, durations.

Overview of (TR) x-ray techniques

- (TR)-XAS: XANES / EXAFS (Near edge and extended edge absorption)
  Core electrons are excited to the valence shell near an edge or several eV. above an edge.

- (TR)-RIXS (Resonant inelastic x-ray scattering)
  Core electrons are excited to the valence shell. The core shell is refilled by an electron from another shell and the emitted electron is detected.

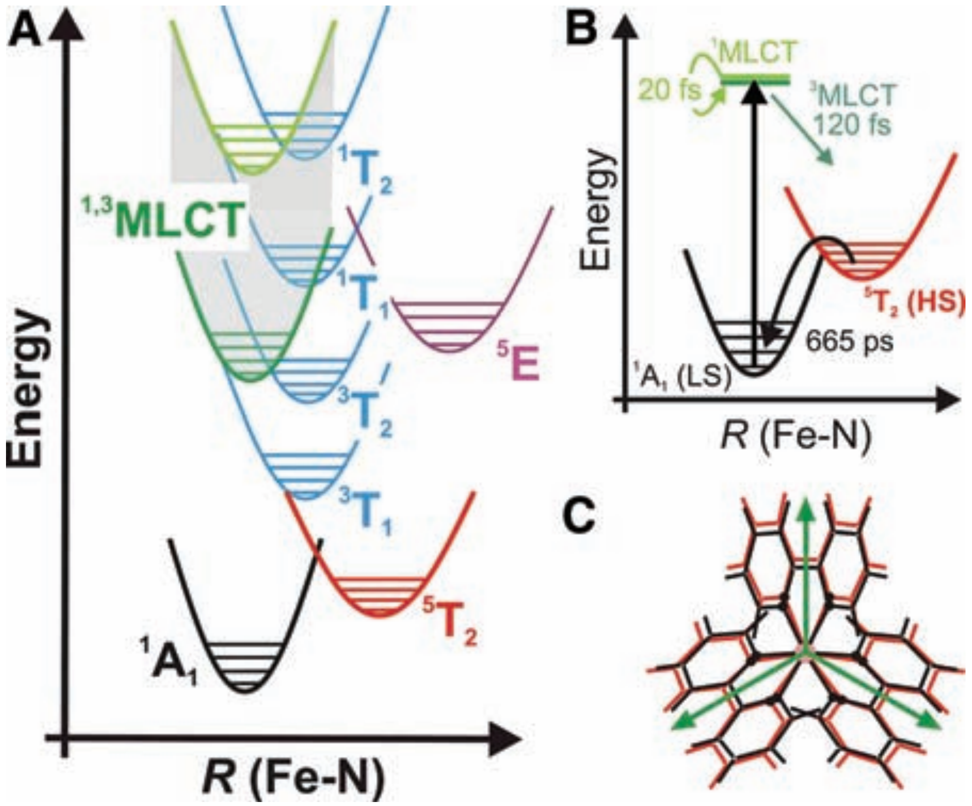
- (TR)-PES (Photoelectron spectroscopy)
  Core electrons are ionized into the continuum and their energy and/or momentum vector detected.

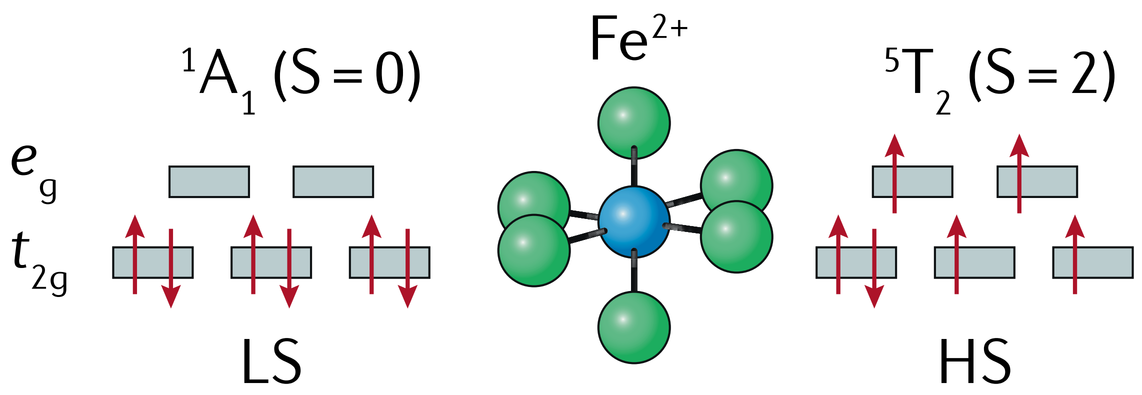
- Photofragmentation spectroscopy.
  A system previously excited by an XUV or x-ray pulse is further ionized by a short probe pulse (IR, XUV,...). Fragments are measured as a function of the time delay.

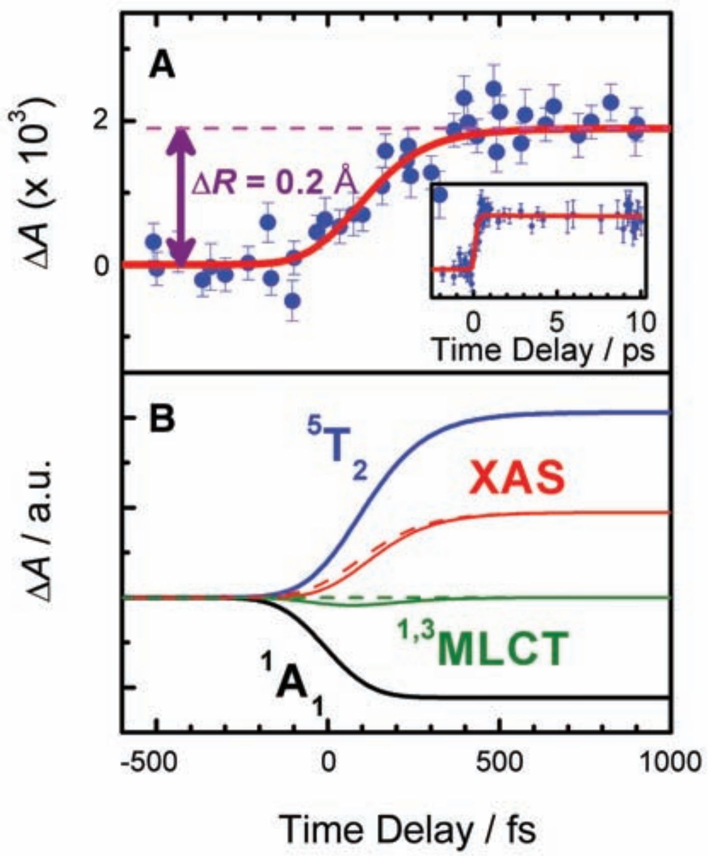
- (TR)-X-ray diffraction
  Diffraction of x-rays at a molecule reveals structural information, possibly time resolved.

The ultrafast X-ray spectroscopic revolution in chemical dynamics
Kraus, Zürch, Cushing, Neumark, Leone, Nat. Rev. Chem., **2**, 82 (2018)

Time-resolved XANES of spin-crossover dynamics



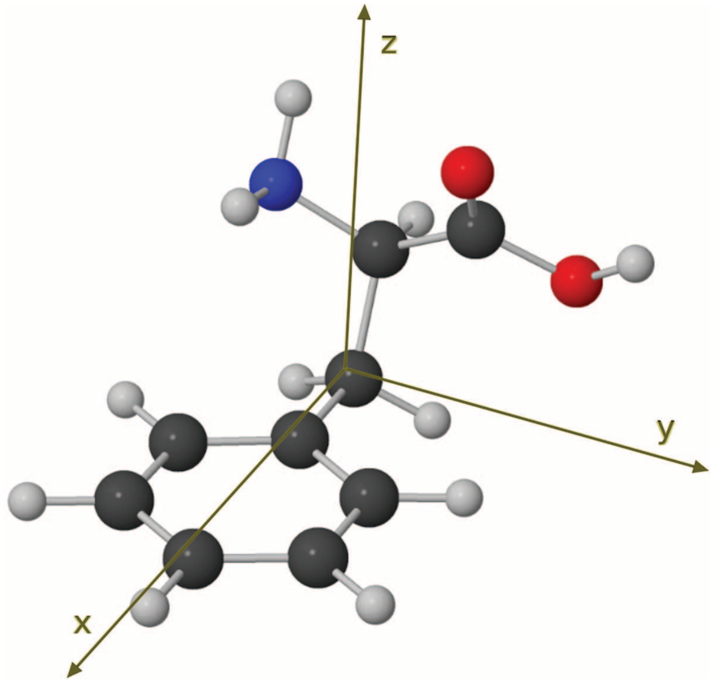


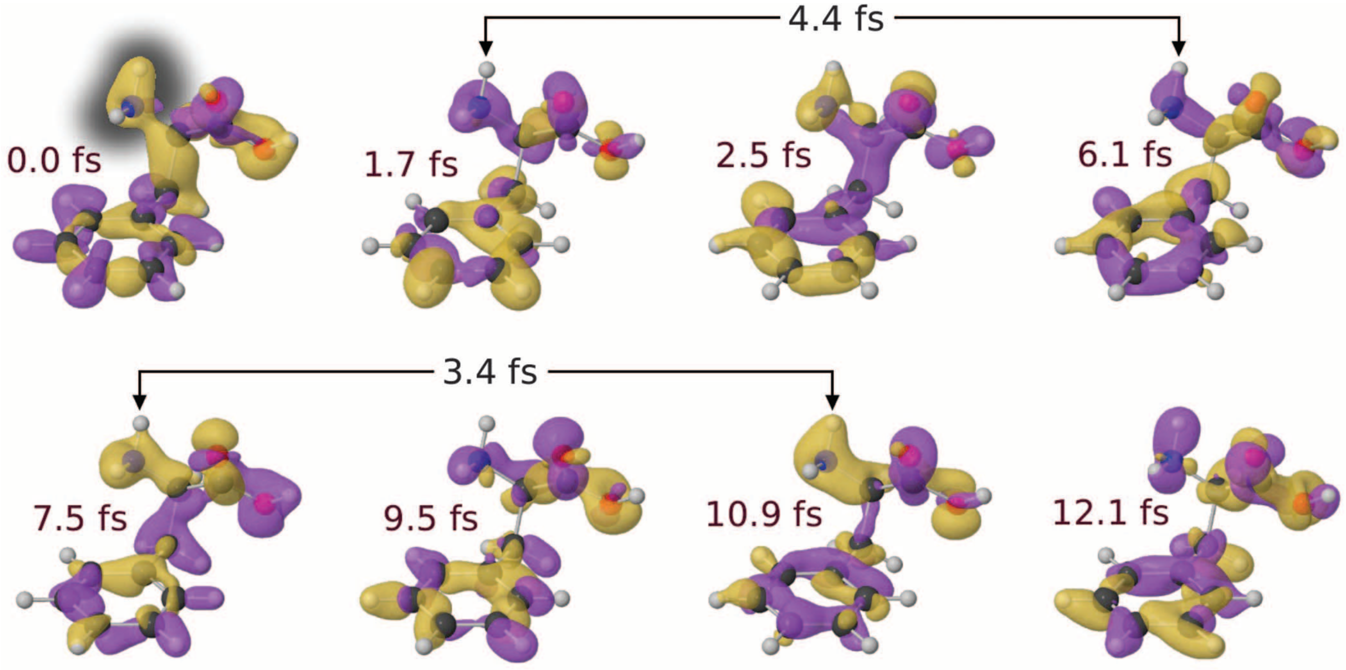


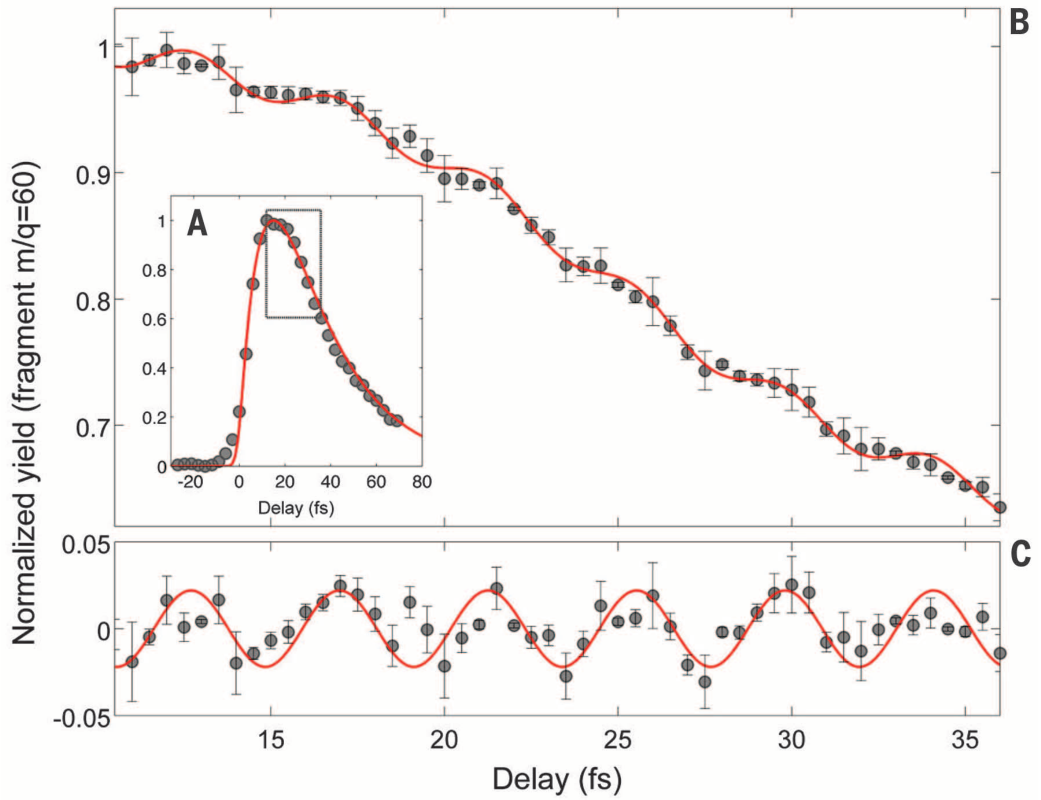
- 400 nm laser excitation followed by Fe K-Edge x-ray probe at about 7.2 kEv.
- Conversion from low spin to high spin can be followed in the modulation of the x-ray absorption
- Experiments @ Swiss Light Source.

Femtosecond XANES Study of the Light-Induced Spin Crossover Dynamics in an Iron(II) Complex
Ch. Bressler et al. *Science*, **323**, 489 (2009)

Electronic coherence in atoms and molecules



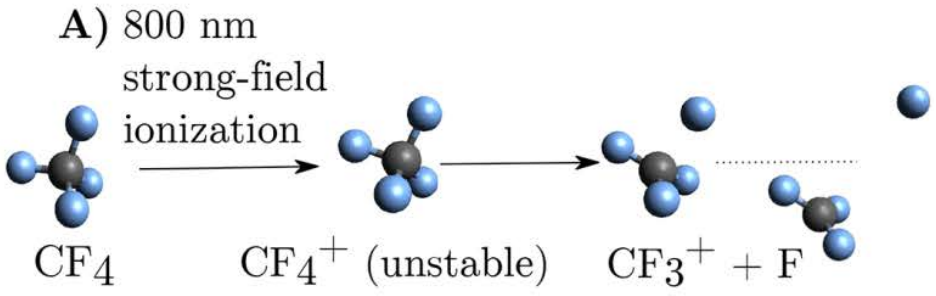


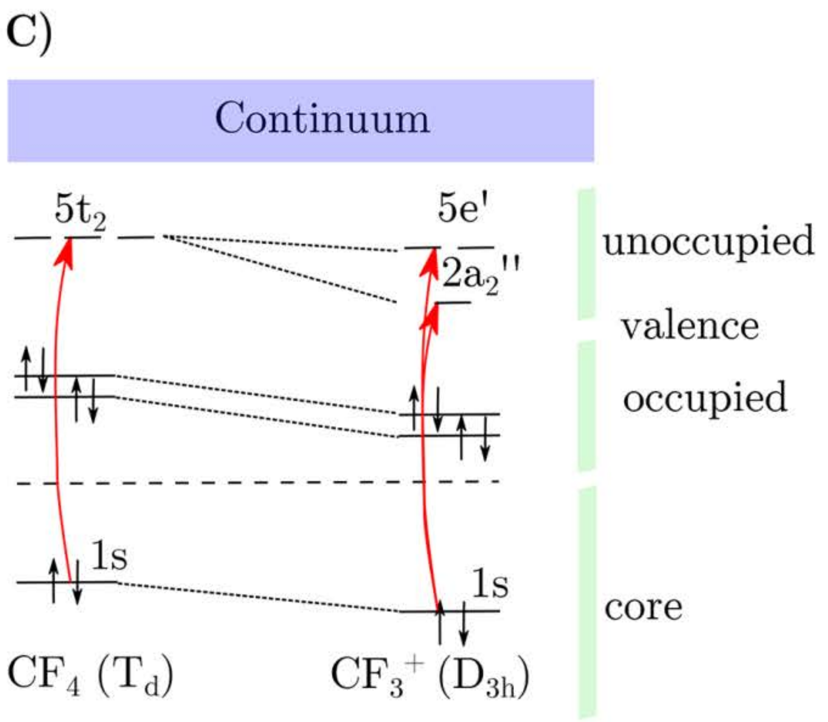


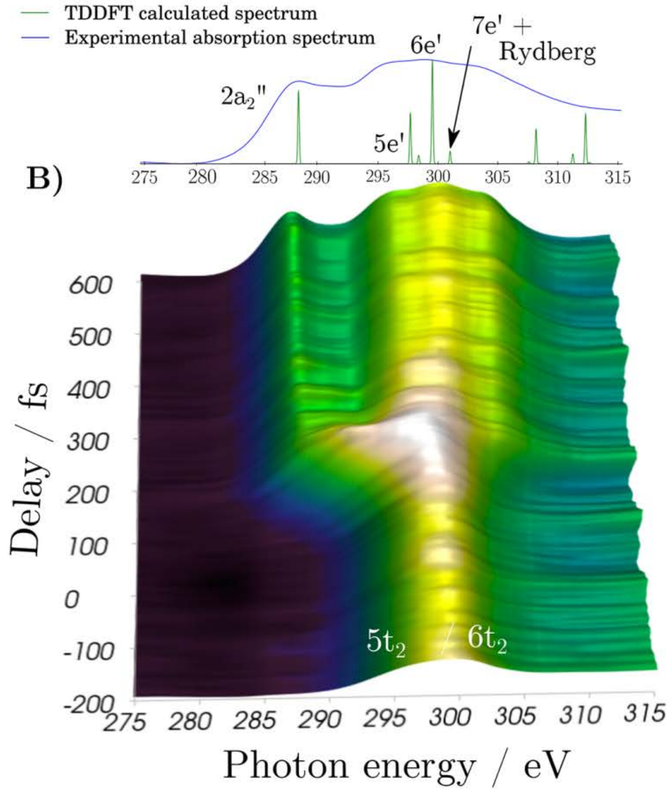
- An attosecond pulse starts electronic and vibrational dynamics in the molecule. Electrons rearrange.
- A delayed IR pulse fragments the molecule. Fragments detected as a function of the pump-probe delay inform about the systems dynamics.

Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses
F. Calegari et al. *Science,* **346**, 336 (2014)

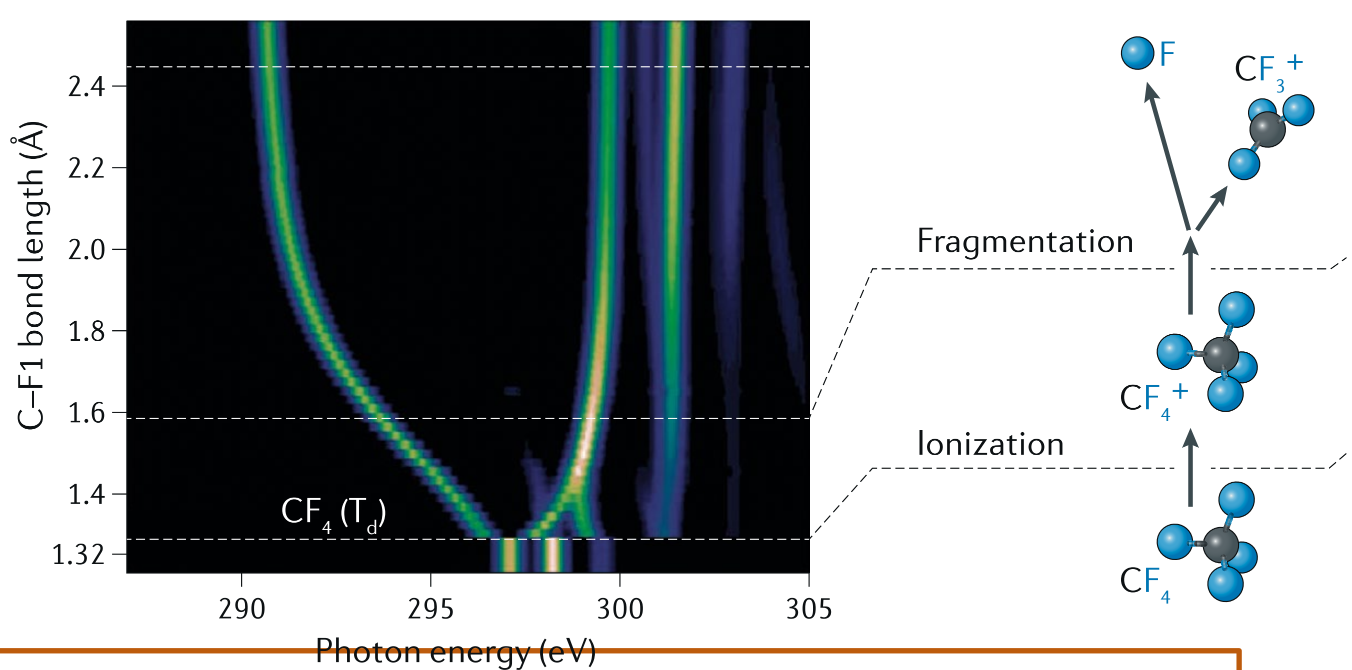
Chemical reactions followed by soft x-ray spectroscopy





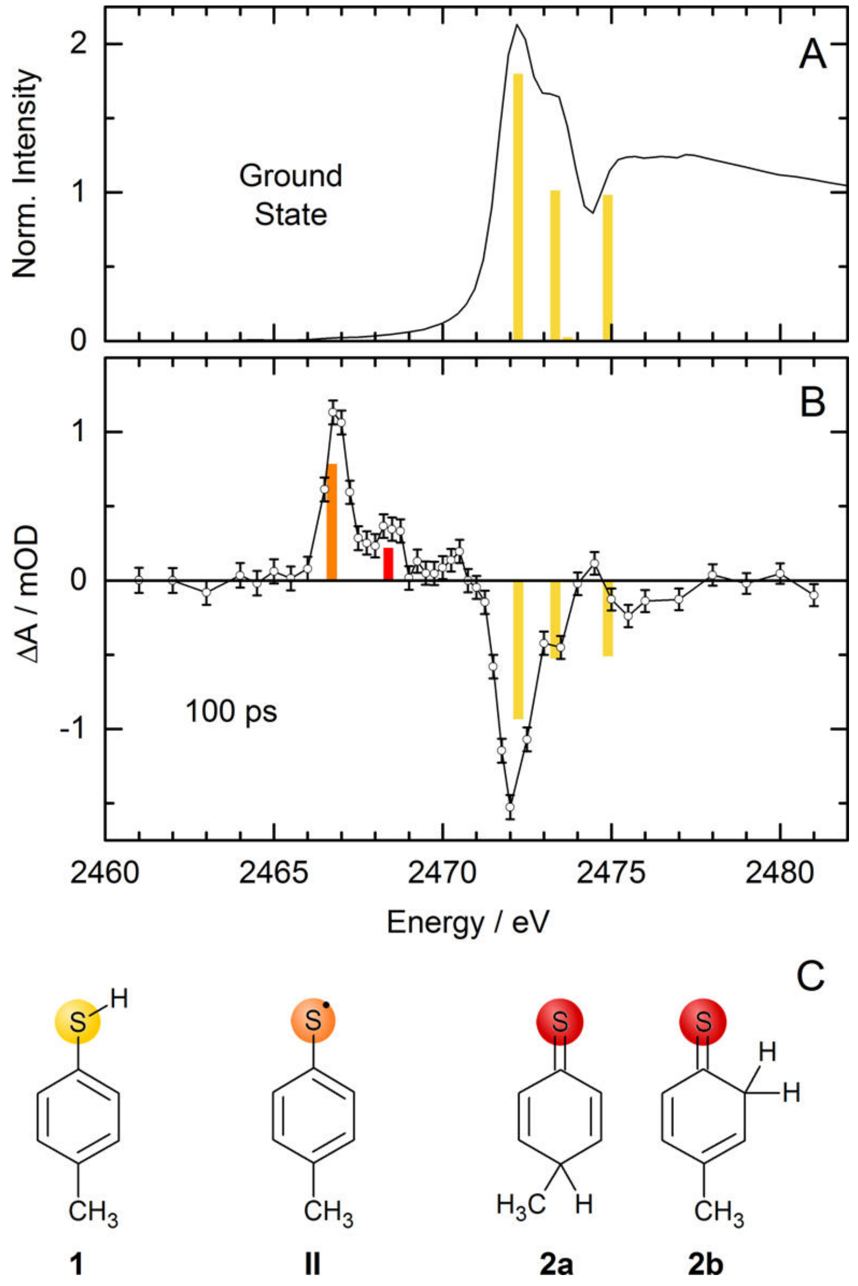


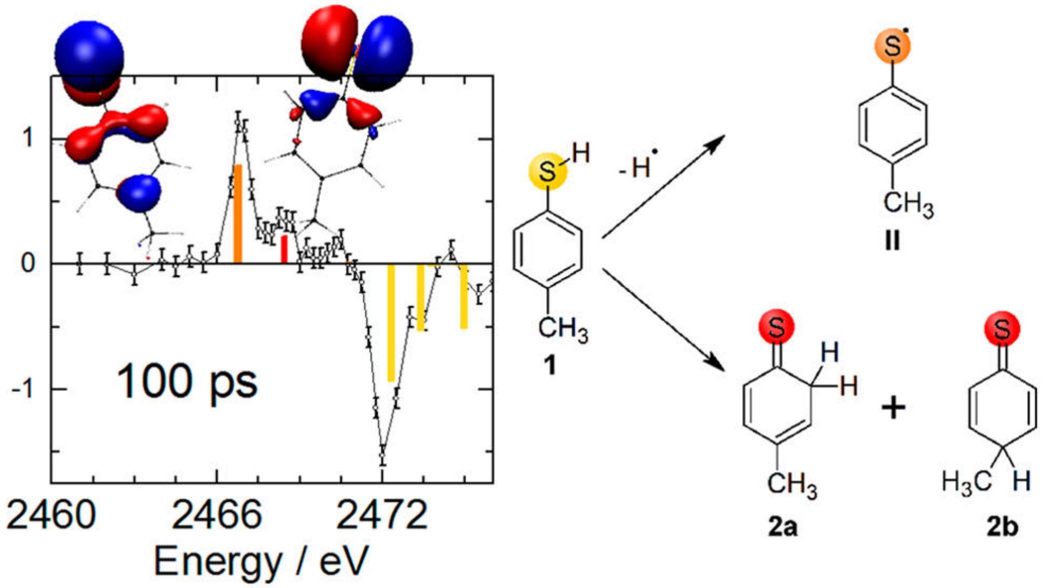
- A mid IR pulse ionizes CF4 into its cationic ground state. The molecule undergoes ultrafast fragmentation.
- A delayed XUV pulse probes the system at the Carbon K-edge. The transmitted XUV pulse is dispersed and analyzed.



Time-resolved x-ray absorption spectroscopy with a water window high-harmonic source
Y. Pertot et al. *Science*, **355**, 264 (2017)

Photochemistry of sulfurated molecules

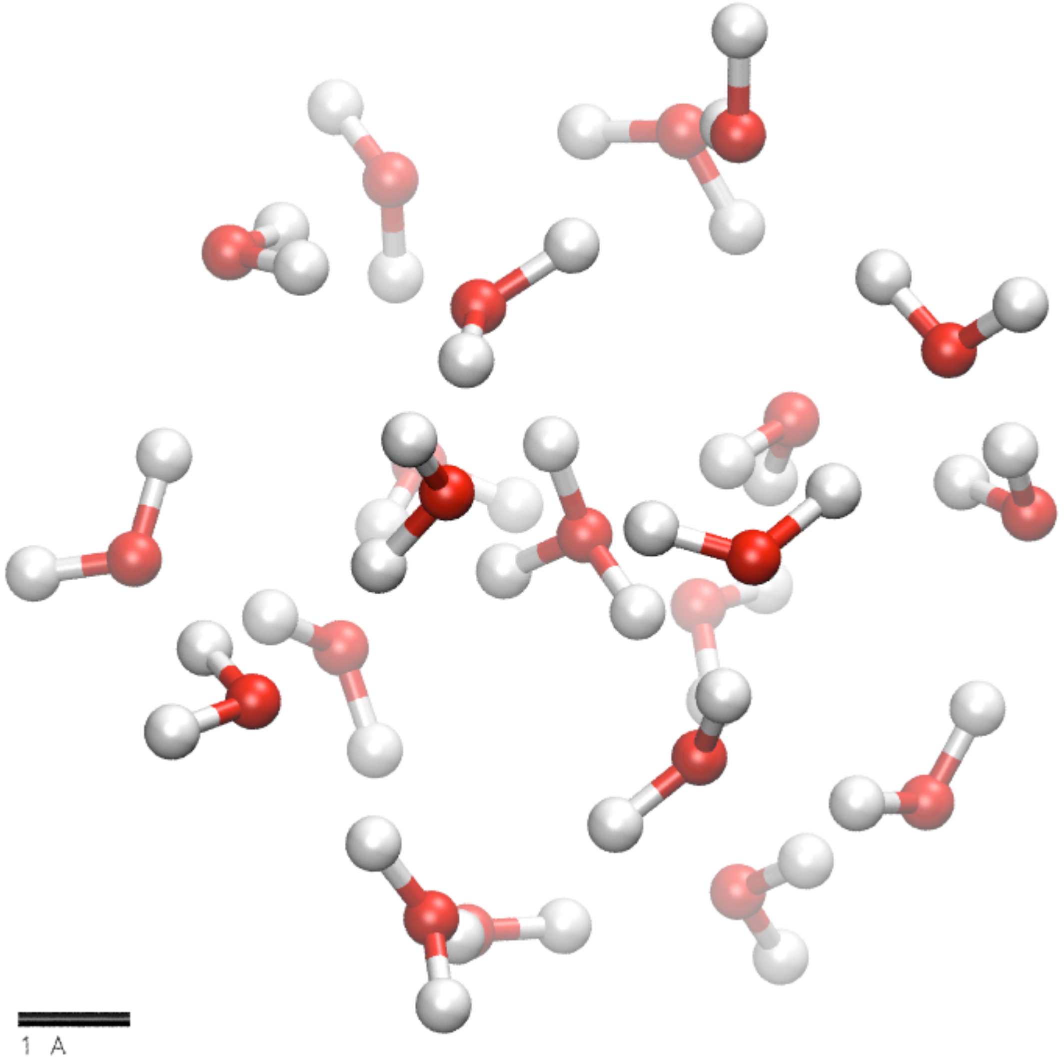


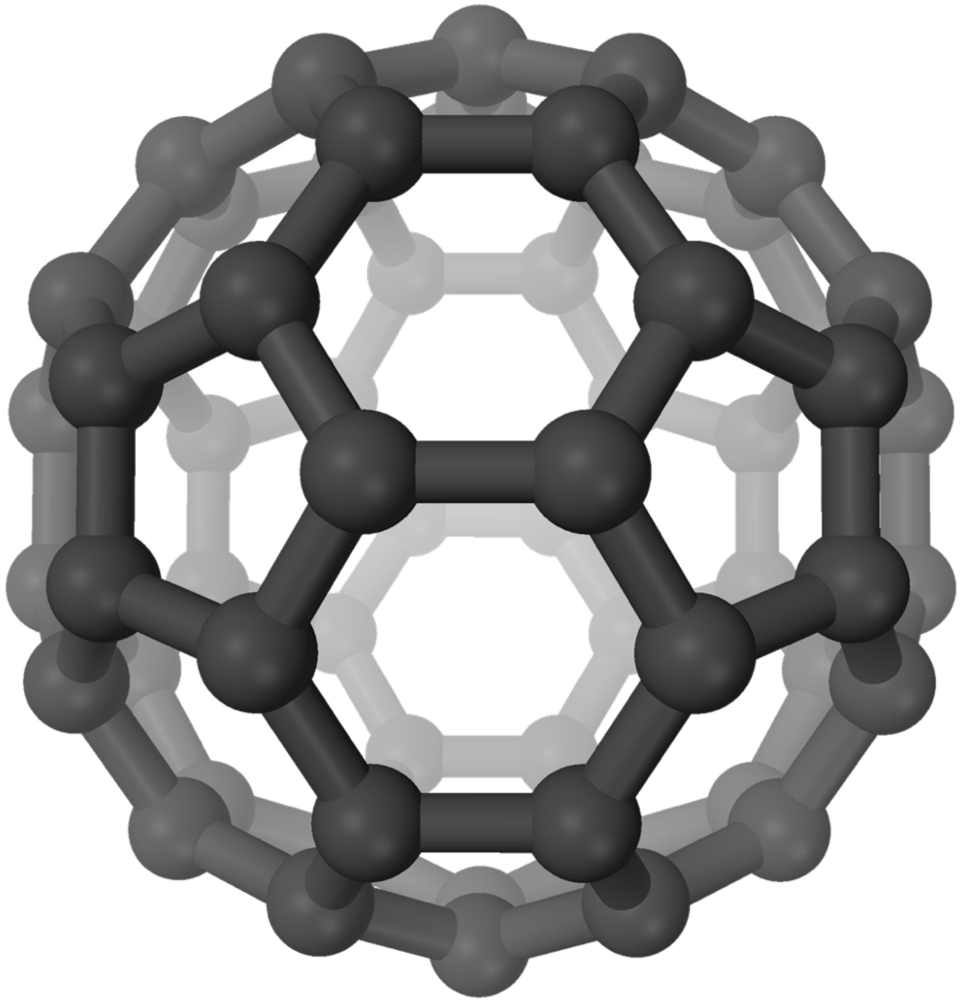


- A Thiol molecule is illuminated with laser light at 267 nm. Isomerization and appearance of radical species follow.
- These are probed by time-resolved X-ray absorption at the sulfur K-edge with a resolution of 70 ps.
- Experiments @ Advanced Light Source.

Light-Induced Radical Formation and Isomerization of an Aromatic Thiol in Solution Followed by Time-Resolved X-ray Absorption Spectroscopy at the Sulfur K-Edge
M. Ochmann *et al.* , *J. Am. Chem. Soc,* 2017, **139**, 4797

$H^+(H_2O)_{21}$

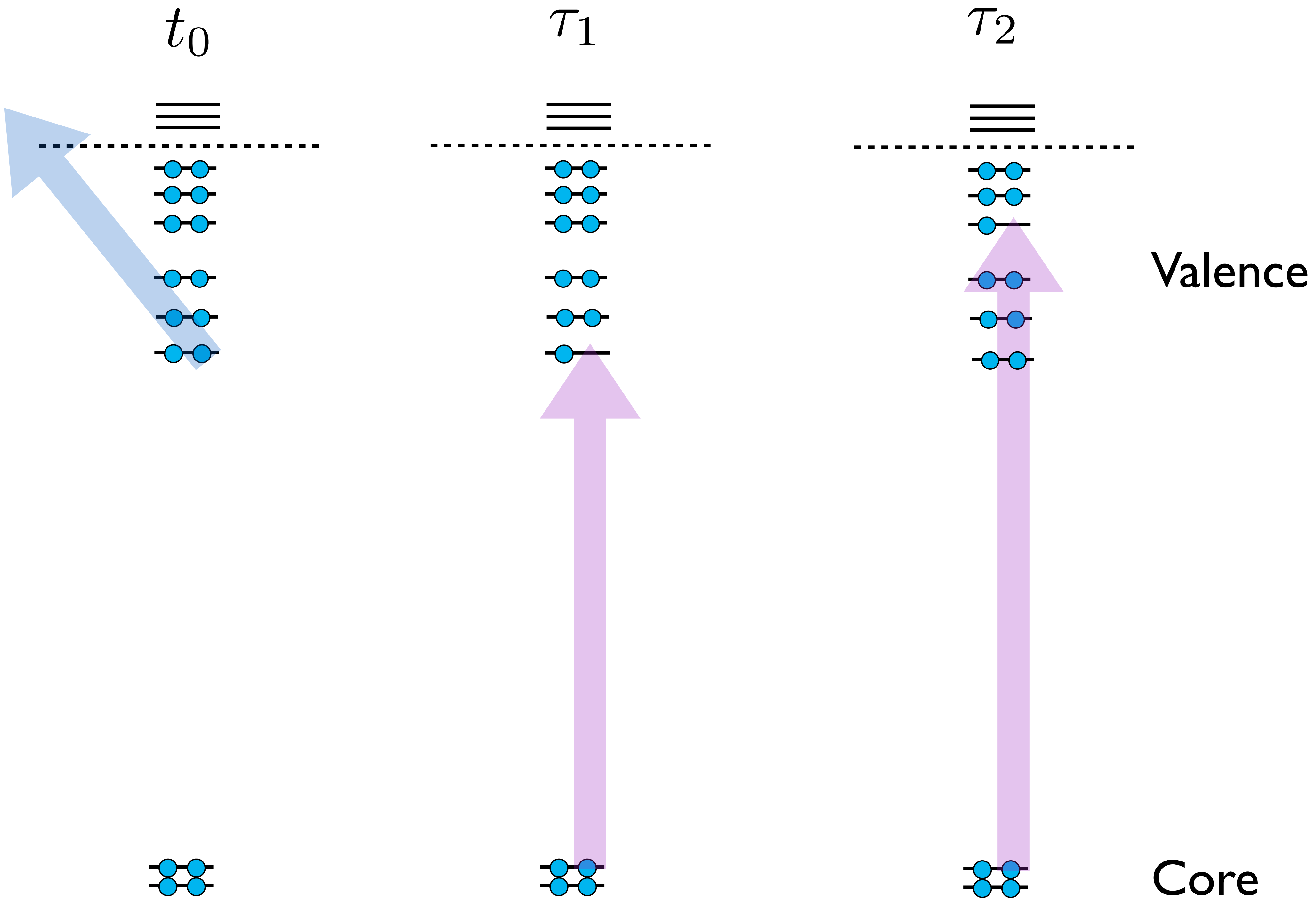




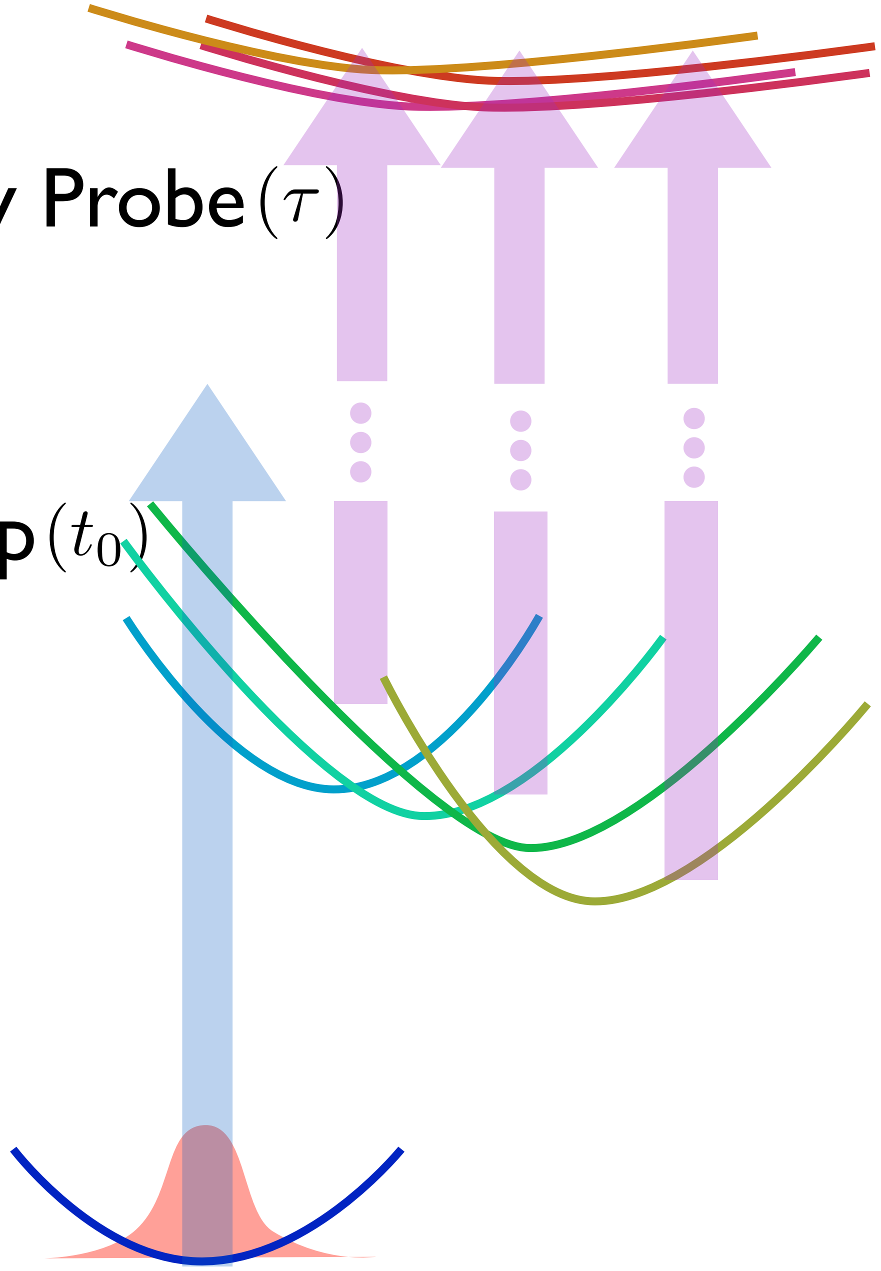
Core-level transient absorption spectroscopy as a probe of electron hole relaxation in photoionized H+(H2O)n
Z Li, ME Madjet, OV, R Santra, *Farad. Disc.* **171**, 457 (2014)

Transient x-ray absorption spectrum

XUV pump - X-ray probe



Transient x-ray absorption spectrum



1s-shell to valence excitation (N-1)

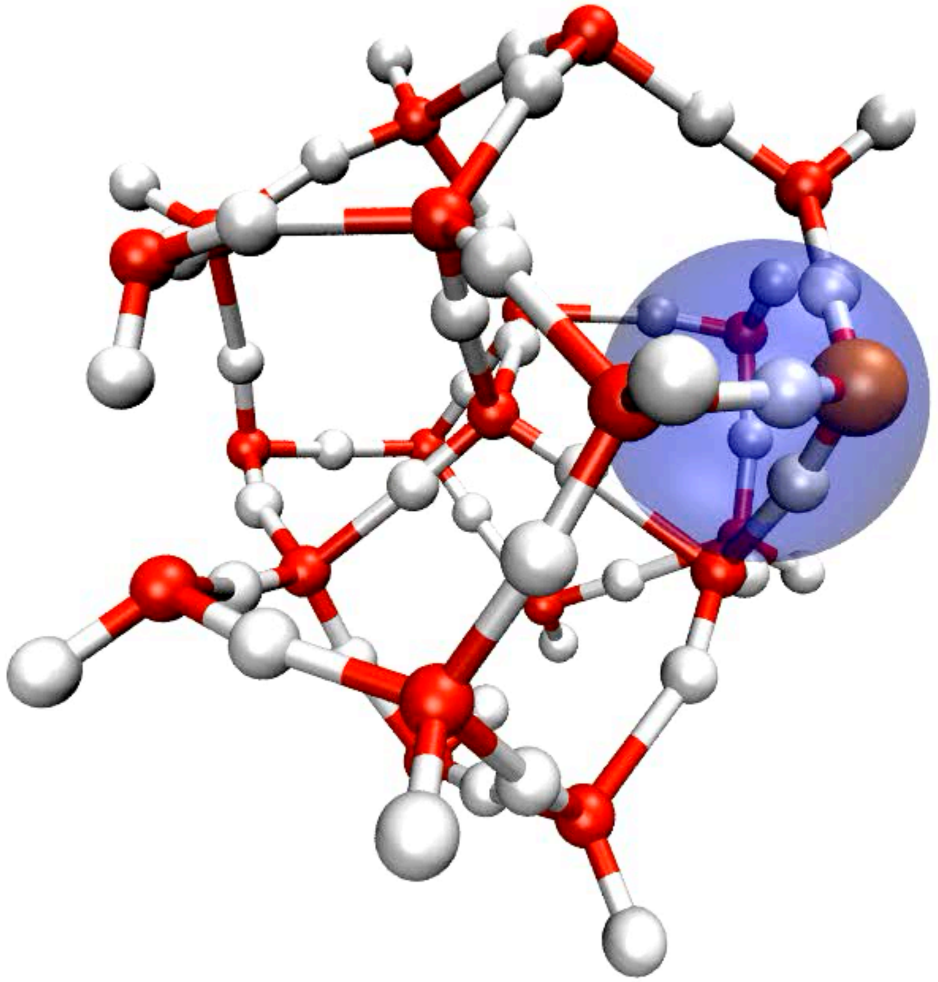
X-ray Probe (τ)

XUV Pump (t_0)

Outer-valence hole (N-1)

Ground State (N)

Ultrafast proton-hole motion



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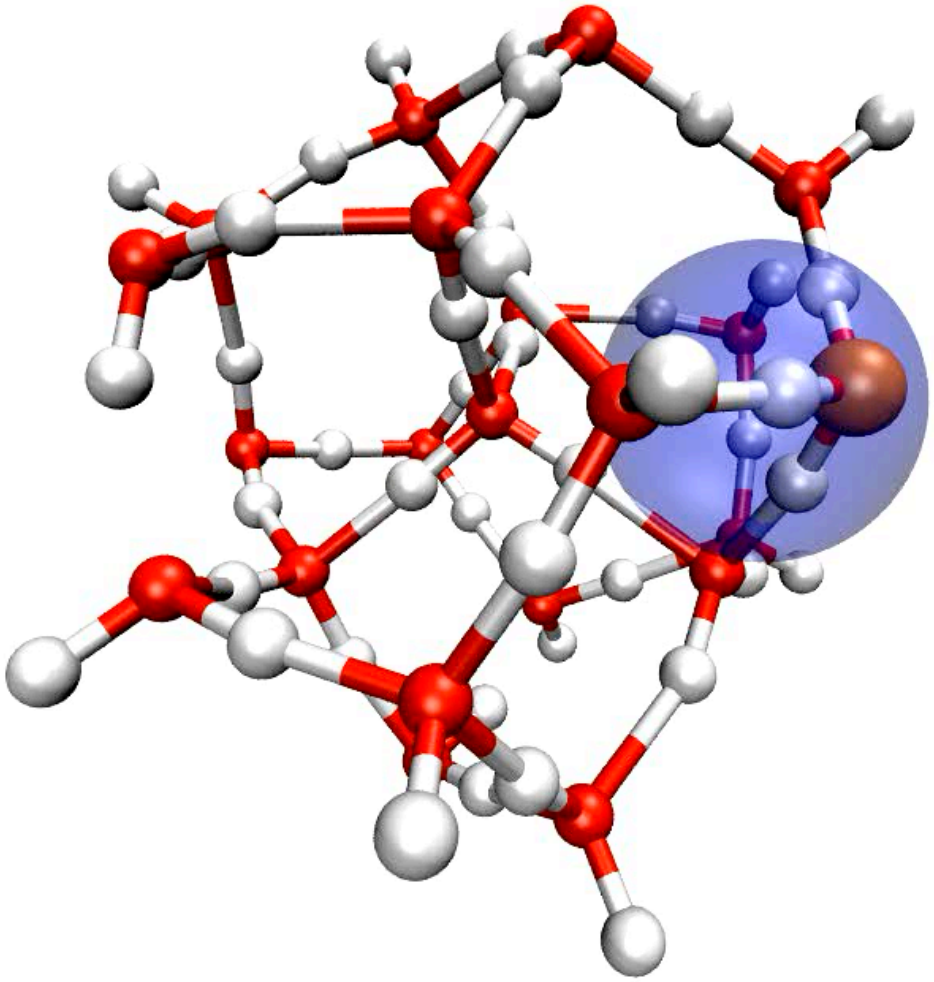

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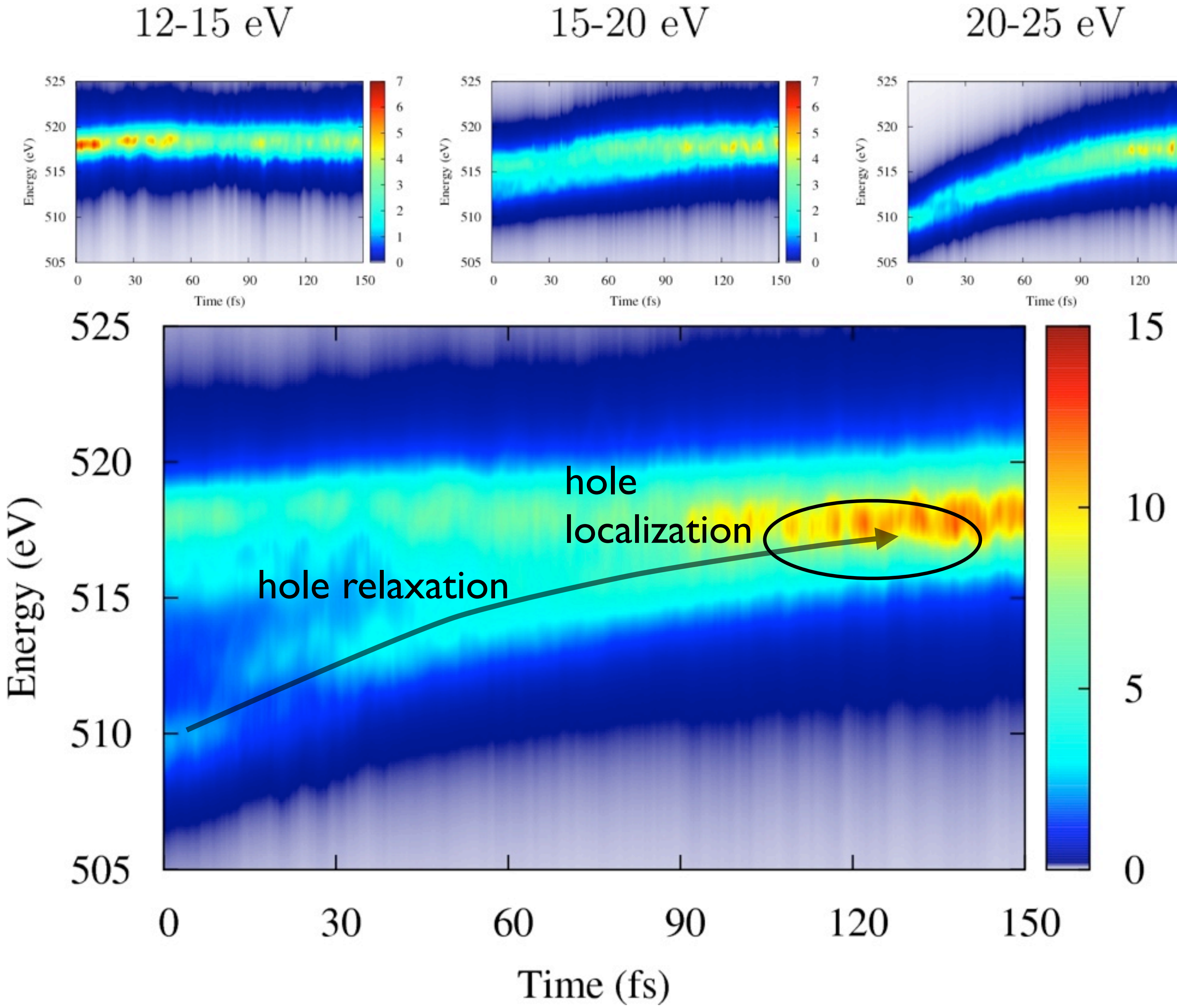

Core-level transient absorption spectroscopy as a probe of electron hole relaxation in photoionized H+(H2O)n
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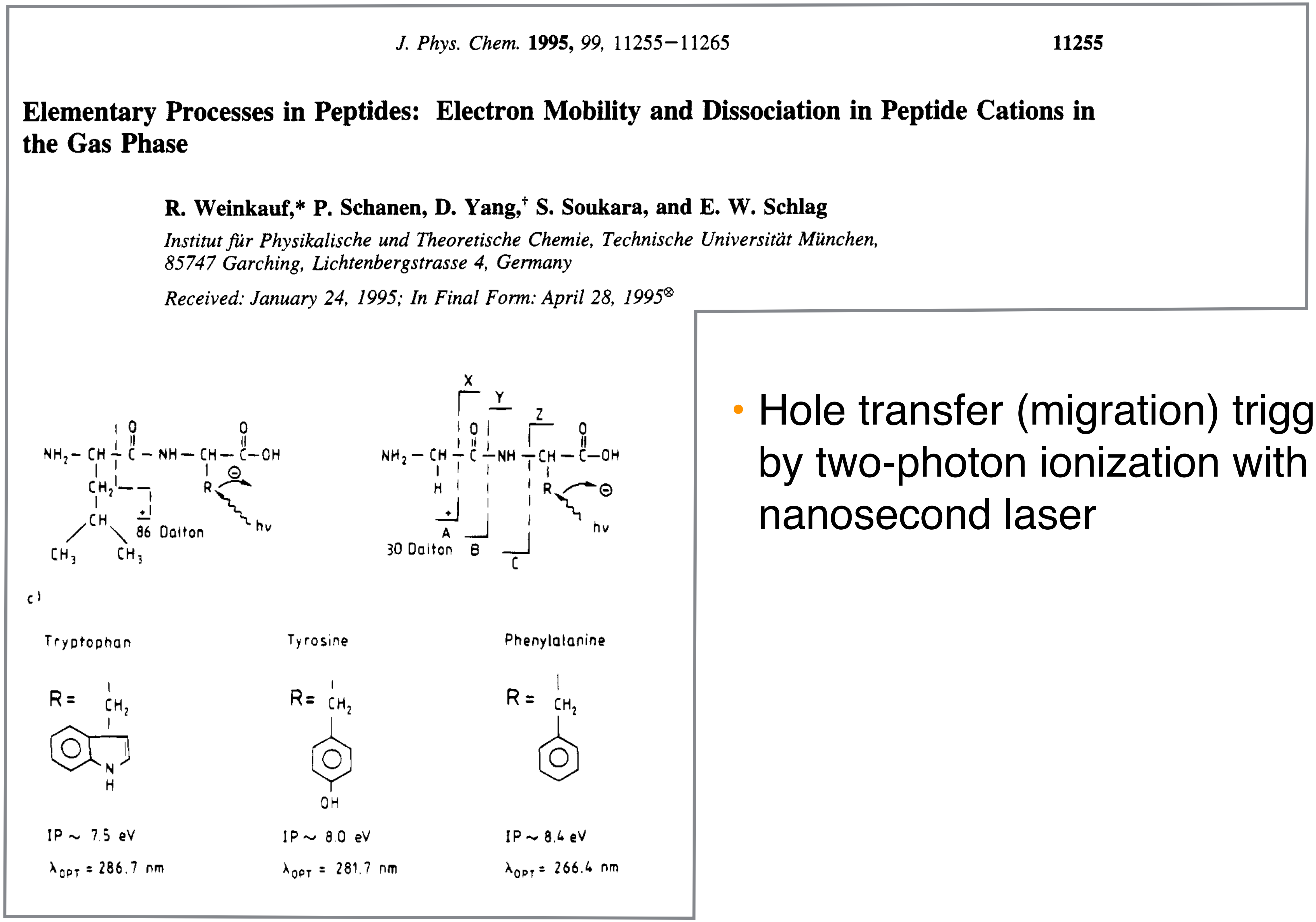
Charge transfer/migration: experiment



J. Phys. Chem. 1995, 99, 11255–11265 11255

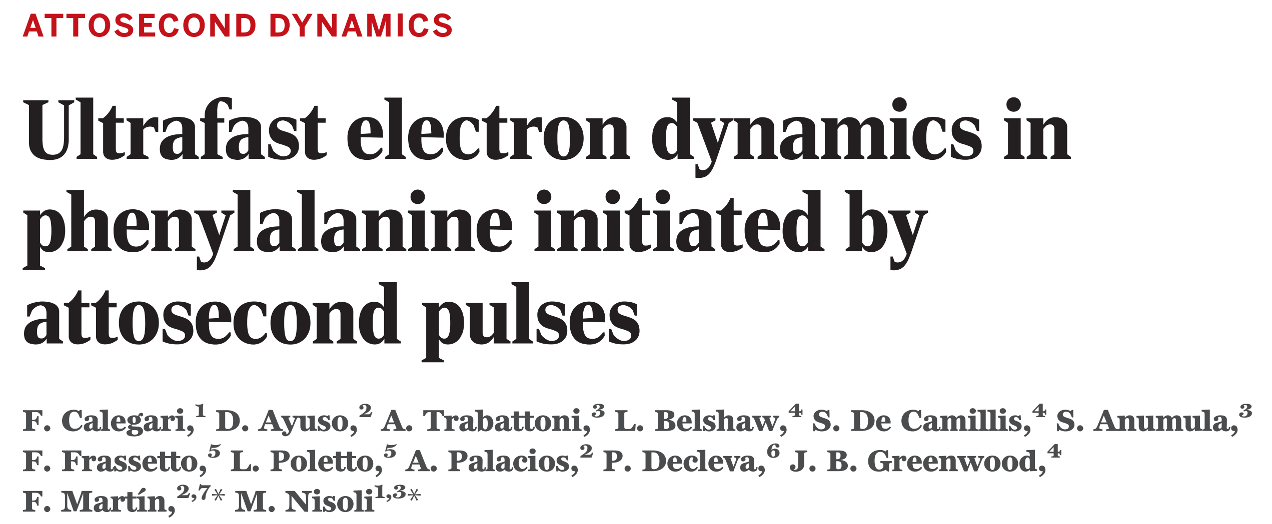
Elementary Processes in Peptides: Electron Mobility and Dissociation in Peptide Cations in the Gas Phase

R. Weinkauf,* P. Schanen, D. Yang,† S. Soukara, and E. W. Schlag
Institut für Physikalische und Theoretische Chemie, Technische Universität München, 85747 Garching, Lichtenbergstrasse 4, Germany

Received: January 24, 1995; In Final Form: April 28, 1995⊗

- Hole transfer (migration) triggered by two-photon ionization with a nanosecond laser

Charge transfer/migration: experiment

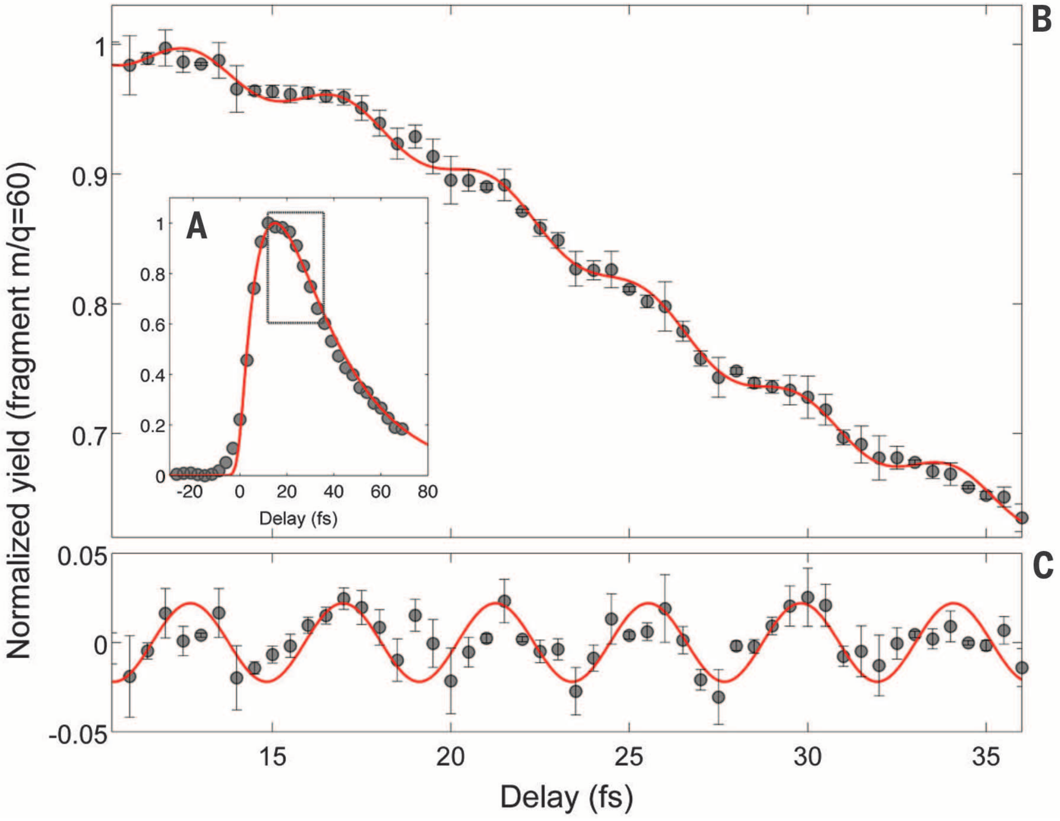


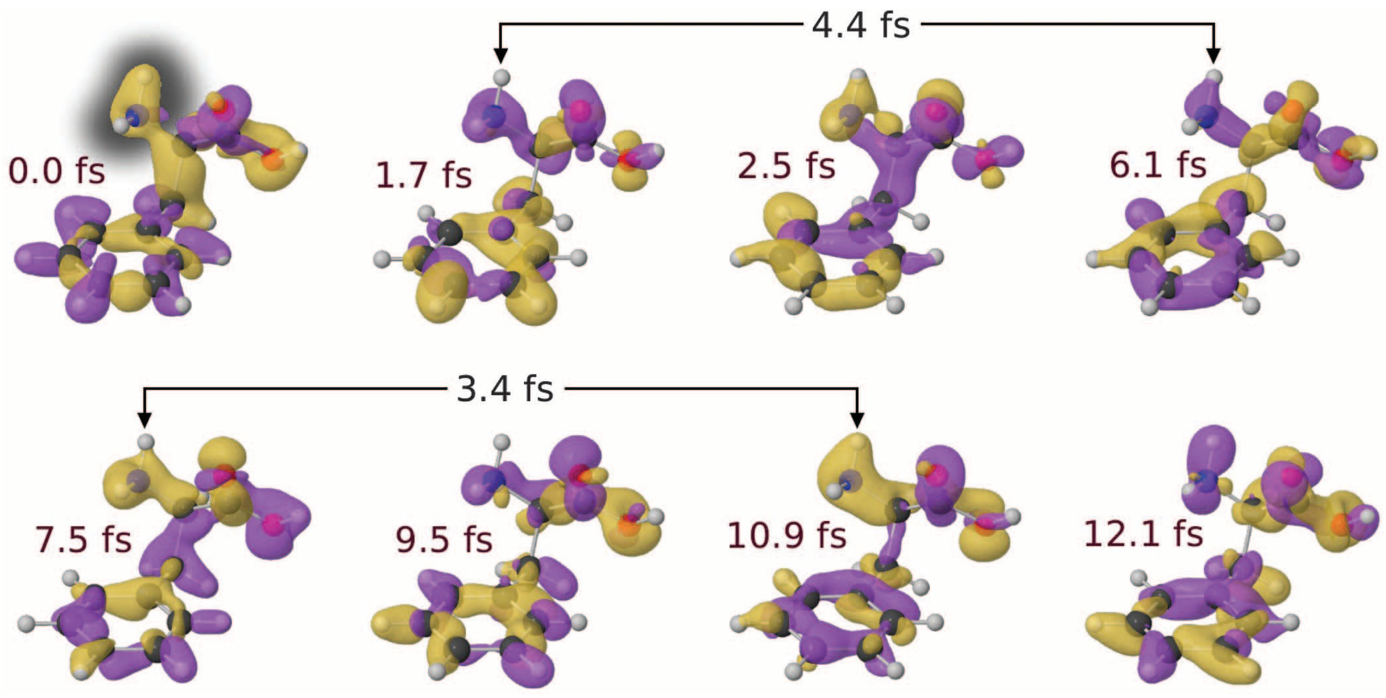
ATTOSECOND DYNAMICS

Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses

F. Calegari,[1] D. Ayuso,[2] A. Trabattoni,[3] L. Belshaw,[4] S. De Camillis,[4] S. Anumula,[3]
F. Frassetto,[5] L. Poletto,[5] A. Palacios,[2] P. Decleva,[6] J. B. Greenwood,[4]
F. Martín,[2,7]* M. Nisoli[1,3]*

- XUV (sub 300 as) pump-VIS/NIR probe
- Oscillations in the yield of some fragments persists for more than 30 fs.



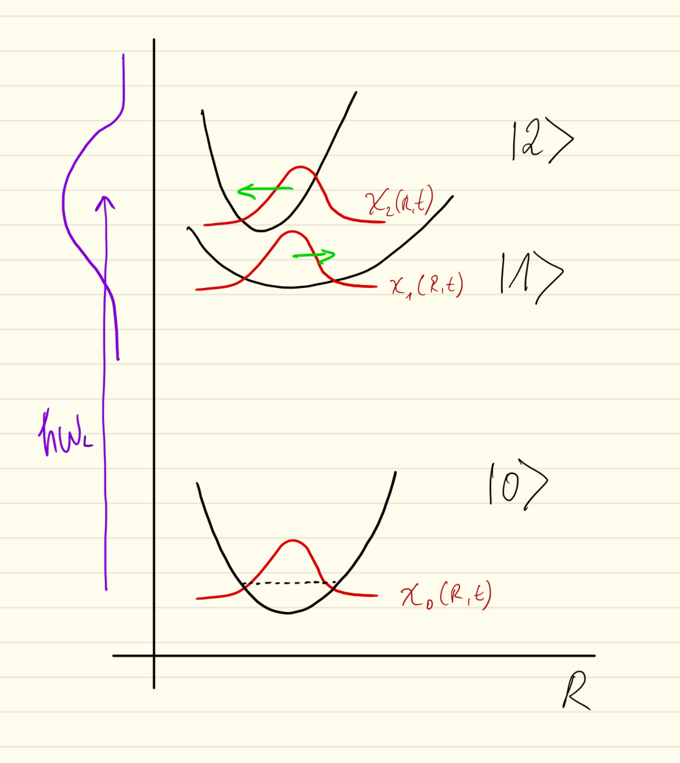


Science **346**, p. 336 (2014)

Electronic decoherence due to nuclear motion

$$\Psi(R,r,t) = \sum_j \chi_j(R,t)\psi(r;R)$$

Born-Huang

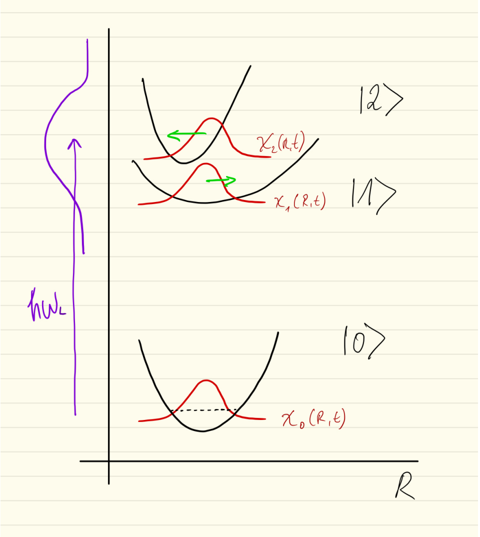


Electronic coherences <=> nuclear wave packet overlaps

$$\rho_{ji}(t) = \langle\chi_j(R,t)|\chi_i(R,t)\rangle$$

$$\langle\hat{O}(r)\rangle = \sum_j \rho_{jj}O_{jj} + \sum_{j>i} 2\mathrm{Re}\{\rho_{ji}\}O_{ji}$$

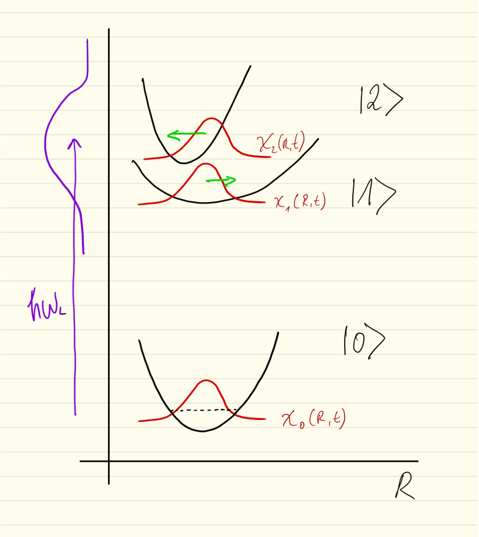
Fully quantum description of electronic decoherence



- Full dimensional
- Exact at short times

Electronic decoherence following photoionization: Full quantum-dynamical treatment of the influence of nuclear motion
C Arnold, OV, R Santra, *PRA* **95**, 033425 (2017)

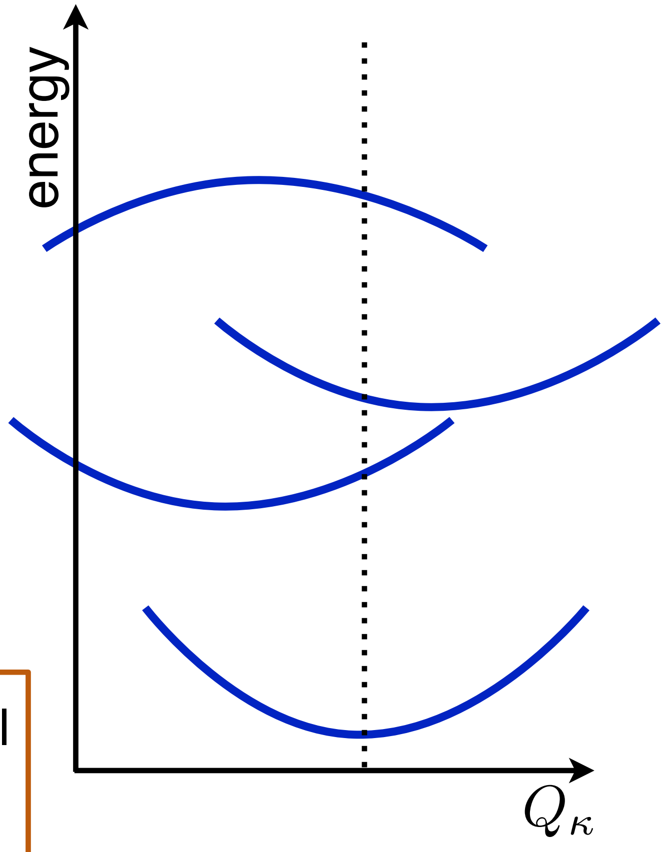
Fully quantum description of electronic decoherence



- Full dimensional
- Exact at short times

Hamiltonian: second order expansion of all relevant PES:

$$\hat{H} = \sum_{\kappa=1}^{f} \frac{\hbar\omega_j}{2}\left(\frac{\partial^2}{\partial Q_\kappa^2} + Q_\kappa^2\right) \otimes \mathbf{1} + \sum_j \left(\Delta E^{(j)} + \sum_{\kappa=1}^{f} g_\kappa^{(j)} Q_\kappa + \sum_{\kappa\lambda}^{f} \gamma_{\kappa\lambda}^{(j)} Q_\kappa Q_\lambda\right) \otimes |j\rangle\langle j|$$



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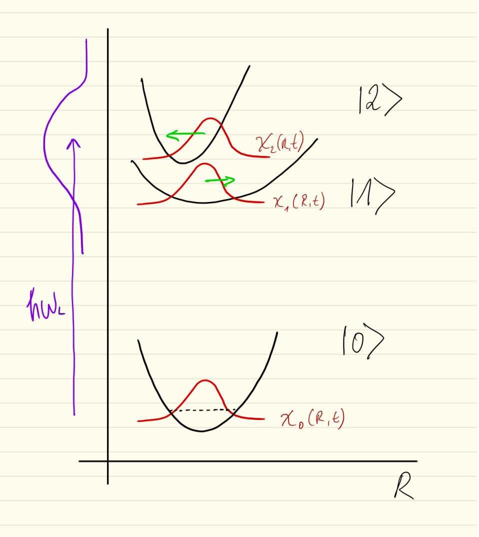

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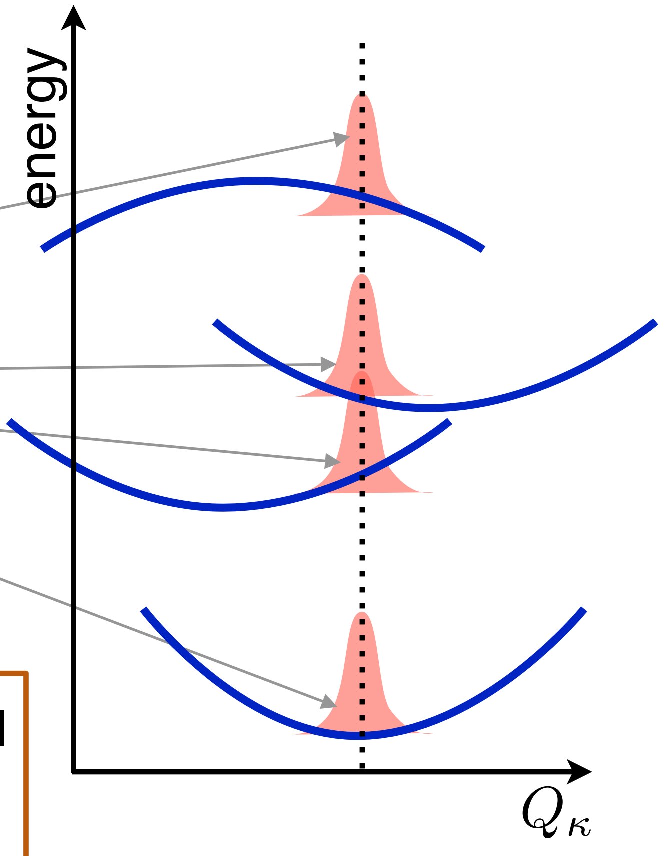
Initial wavefunction:

$$\Psi(\vec{Q},0) = \sum_j \sqrt{p_j} \left[\prod_{\kappa=1}^{f} \chi_\kappa^{(j)}(Q_\kappa,0)\right] |j\rangle$$

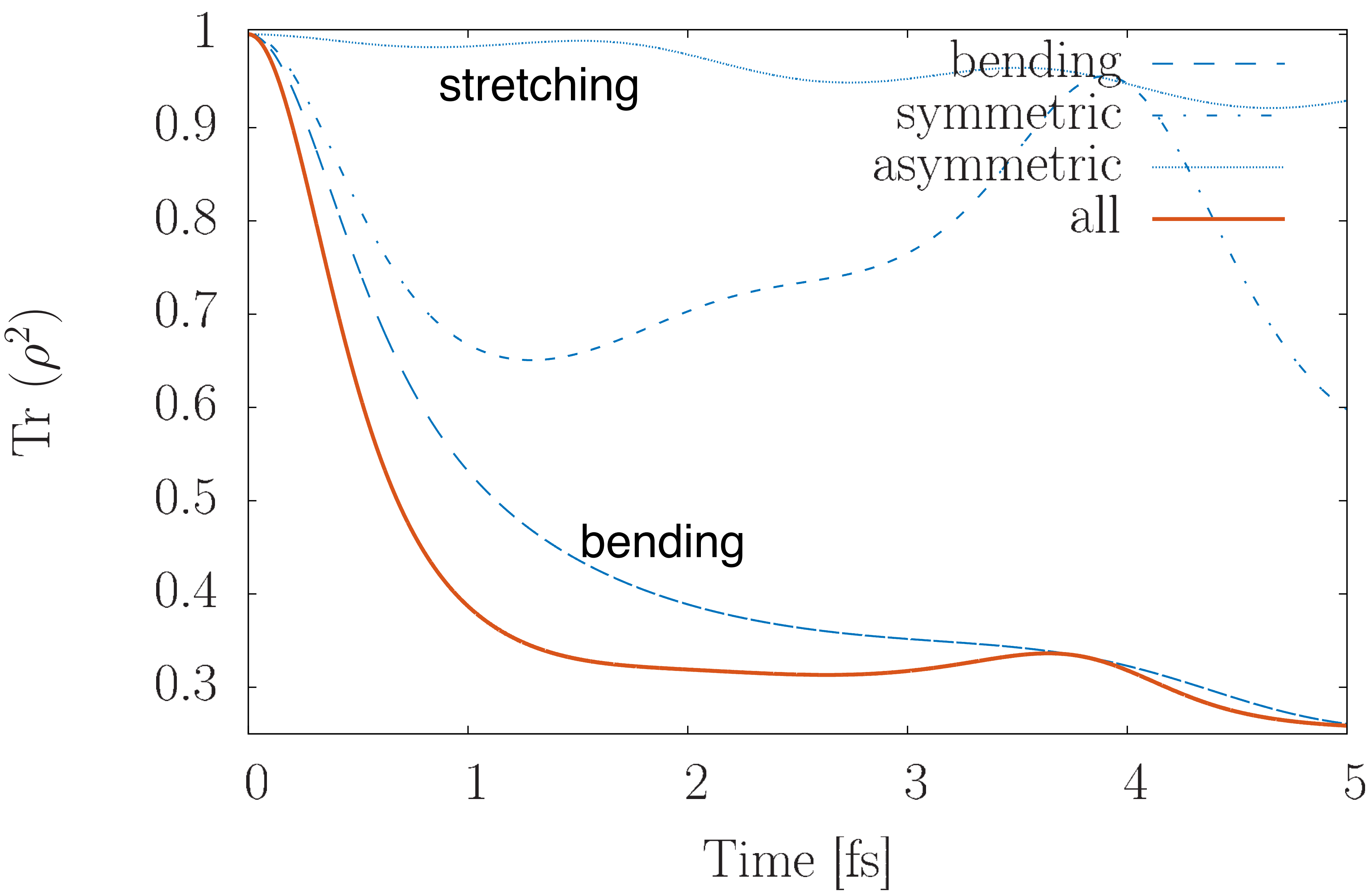


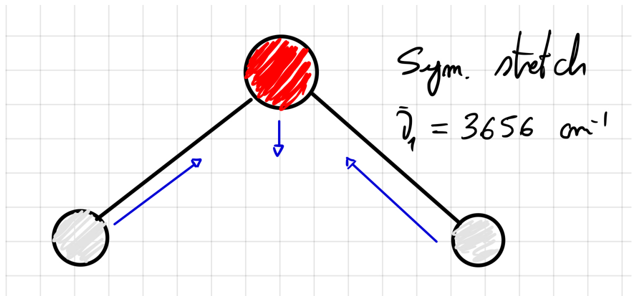
Electronic decoherence following photoionization: Full quantum-dynamical treatment of the influence of nuclear motion
C Arnold, OV, R Santra, *PRA* **95**, 033425 (2017)

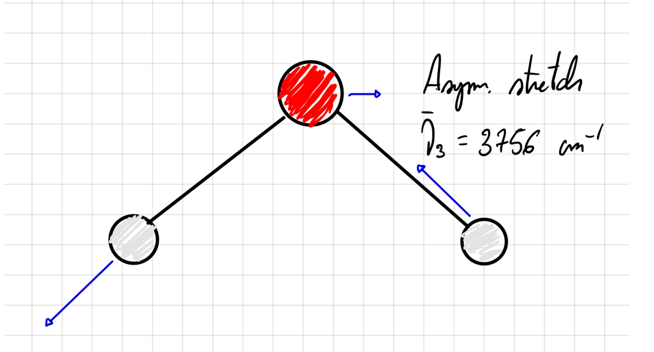
Electronic decoherence in water cation

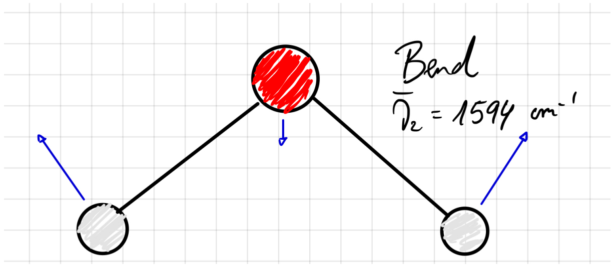
- 4 lowest cationic states equally populated

$$\Psi(\mathbf{Q},0) = \chi_1(Q_1,0)\chi_2(Q_2,0)\chi_3(Q_3,0)\frac{1}{\sqrt{4}}\left(|1\rangle + |2\rangle + |3\rangle + |4\rangle\right)$$





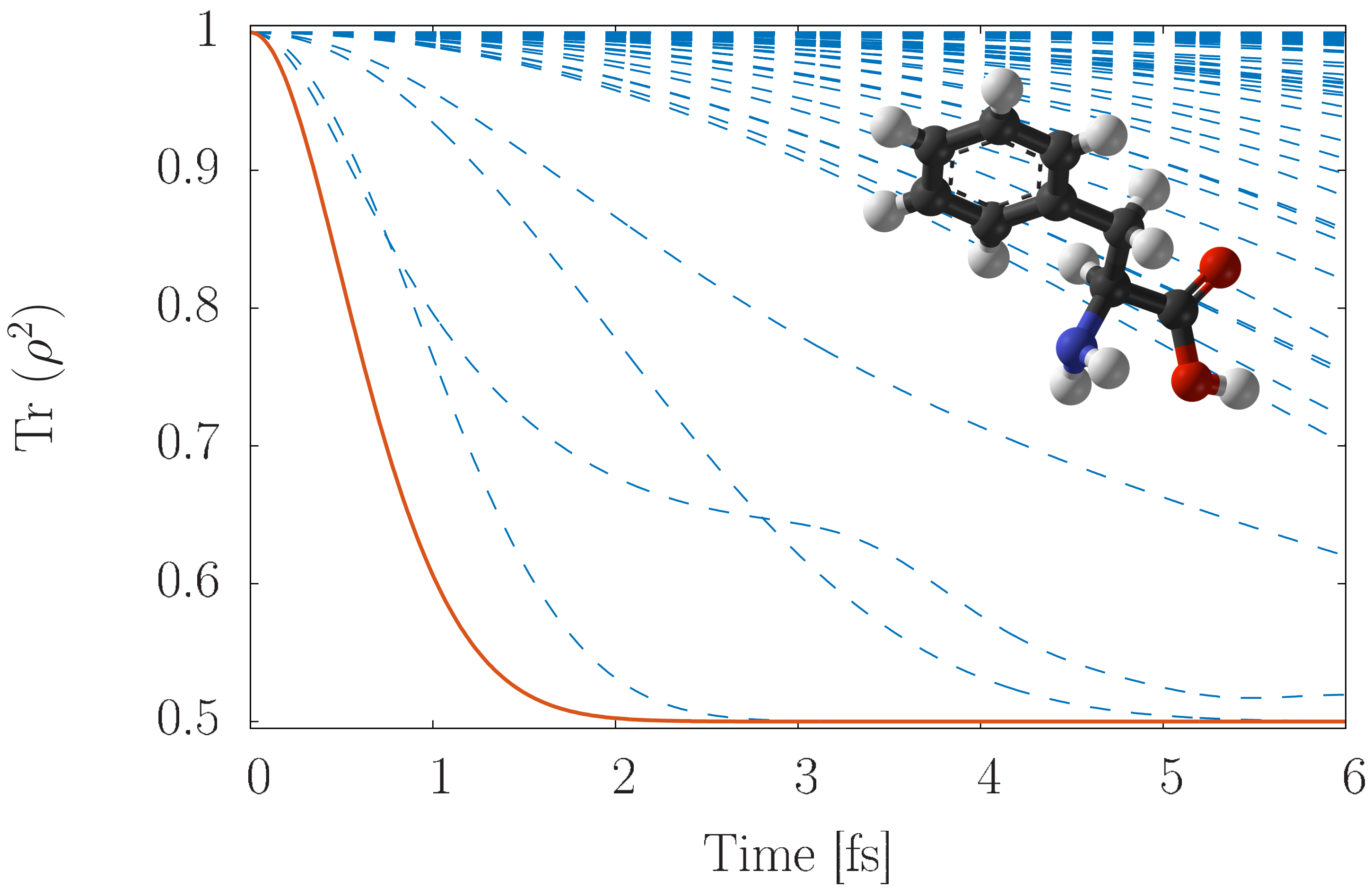




Electronic decoherence following photoionization: Full quantum-dynamical treatment of the influence of nuclear motion
C Arnold, OV, R Santra, *PRA* **95**, 033425 (2017)

Electronic decoherence in *phenilananine* cation

- 63 D molecular system
- Linear superposition of X and A cationic states



- Decoherence is not due to the fast modes (C-H)

- Skeletal low frequency modes mostly responsible for electronic decoherence

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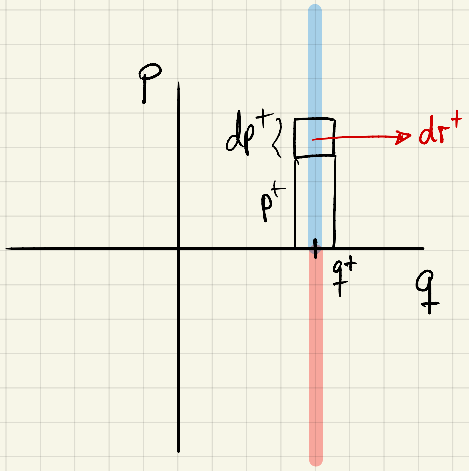
Microcanonical rate derivation:

①



Our goal is to compute the differential of rate passing through the little box in phase space.

The rate is the density of states per unit length along the reaction coordinate × the velocity v^+ at the crossing point.

From normalization of a phase space volume $N = \frac{\Delta q \cdot \Delta p}{h}$.

Hence, the number of states in a box of sides Δq around q^+ and dp^+ is $dN^+ = \frac{\Delta_q \, dp^+}{h}$,

Finally, the differential density is $\rho^+ = \frac{dN^+}{d\Delta_q} = \frac{dp^+}{h}$

The transition state has energy $E-\varepsilon_0$, where ε_0 is the classical barrier and E the total energy.

②

The energy of the activated complex is divided into translational energy ε_T and internal energy on all other DOF, ε_I

$$E-\varepsilon_0 = \varepsilon_T + \varepsilon_I$$

$$d\Gamma^+ = \boxed{\rho_I^+(\varepsilon_I)} \cdot \boxed{\rho^+(\varepsilon_T)} \cdot v^+(\varepsilon_T)$$

$$= \rho_I^+(\varepsilon_I) \cdot \frac{\boxed{v^+(\varepsilon_T)\, dp^+}}{h} \rightarrow d\varepsilon_T$$

$$d\Gamma^+ = \rho_I^+(\varepsilon_I) \frac{d\varepsilon_T}{h}$$

$$\boxed{\Gamma^+} = \int_0^{E-\varepsilon_0} \rho_I^+(\varepsilon_I) \frac{d\varepsilon_T}{h} = \int_{E-\varepsilon_0}^{0} \rho_I^+(\varepsilon_I) \frac{-d\varepsilon_I}{h}$$

$$= \int_0^{E-\varepsilon_0} \frac{1}{h} \rho_I^+(\varepsilon_I)\, d\varepsilon_I = \boxed{\frac{1}{h} N^+(E-\varepsilon_0)}$$

* State density per unit energy along perp. dir. to trans. state.

* State density per unit length along react. coord.

$$\frac{d\varepsilon_T}{dp} = \frac{d}{dp}\left(\frac{p^2}{2m}\right) = \frac{p}{m} = v$$

Calculation of the canonical rate expression

③

We have determined the total microcanonical rate. The rate constant corresponds to the total rate divided by the number of states of reactants at energy E → $\rho(E)$

$$r^{+}(E) = k(E)\,\rho(E)$$

$$k(E) = \frac{N^{+}(E-\varepsilon_0)}{\rho(E)} \; ; \qquad \rho(E) = \frac{dN(E)}{dE} .$$

- The thermal rate constant is now given by a Boltzmann average

$$k(T) = \frac{1}{Q(T)} \int_{\varepsilon_0}^{\infty} k(E)\, e^{-\beta E}\, dE$$

$$= \frac{k_B T}{h} \, \frac{Q^{+}(T)}{Q(T)} \cdot e^{-\beta \varepsilon_0} .$$

Absorption spectrum for a very short pulse (1)

Short (δ) pulse absorption spectrum.

①

Start from $\boxed{\Delta E(\omega) = 2\pi i \omega \left[\tilde{P}(\omega)\right]^* \tilde{\mathcal{E}}(\omega)}$, the energy gain at frequency ω.

For $\mathcal{E}(t) = \delta(0) \xrightarrow{IFT} \boxed{\tilde{\mathcal{E}}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\delta(0)\,dt = \frac{1}{2\pi}}$.

The TD polarization in first order PT reads

$$P(t) = 2\,\mathrm{Re}\left\{\langle \psi^{(0)}(t)|\hat{\mu}|\psi^{(1)}(t)\rangle\right\}$$

$$= 2\,\mathrm{Re}\left\{\frac{1}{i\hbar} e^{iE_0 t/\hbar} \langle \psi^{(0)}(0)|\hat{\mu}\, e^{-i\hat{H}_0 t/\hbar}\hat{\mu}\,|\psi^{(0)}(0)\rangle e^{i\omega t}\right\}\theta(0)$$

where $\theta(0)$ is the Heaviside function since $P(t)$ is causal and therefore different than 0 only after the pulse.

Absorption spectrum for a very short pulse (2)

②

Now we introduce $\bar{P}(t) = \begin{cases} P(t) & \text{for } t>0 \\ P(-t)^* & \text{for } t<0 \end{cases}$ such that $\bar{P}(t) = P(-t)^*$

The IFT can now be taken on $\bar{P}(t)$ without needing to take the real part times 2.

$$\boxed{\tilde{P}(\omega) = \frac{1}{2\pi i\hbar}\int_{-\infty}^{\infty} e^{iE_0 t/\hbar} \underbrace{\langle\psi^{(0)}(0)|\hat{\mu}\, e^{-i\hat{H}_0 t/\hbar}\,\hat{\mu}|\psi^{(0)}(0)\rangle}_{C(t)} e^{i\omega t}\, dt}$$

Finally $\Delta E(\omega) = \frac{\omega}{2\pi\hbar}\int_{-\infty}^{\infty} C(t)\, e^{i(\omega_0+\omega)t}\, dt$

and $\sigma(\omega) = \frac{\Delta E(\omega)}{|\tilde{\mathcal{E}}(\omega)|^2 \cdot c} = \frac{2\pi\,\omega}{\hbar \cdot c}\int_{-\infty}^{\infty} C(t)\, e^{i(\omega_0+\omega)t}\, dt$