HZB Helmholtz Zentrum Berlin

Where are the electrons?

Charge transfer and dissociation from a femtosecond electronic-structure perspective

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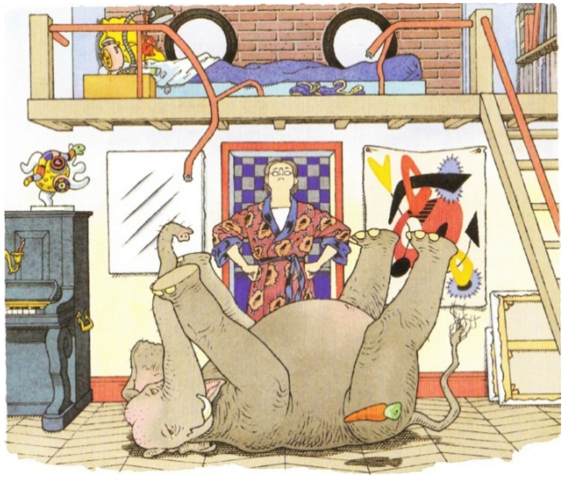
13th PSI Summer School 2014 – Exploring time, energy and length scales in condensed matter, Zug, August 2014

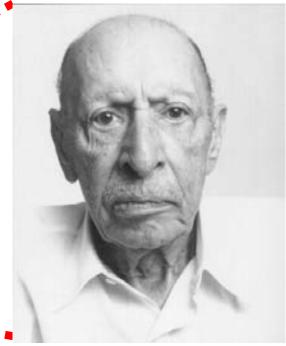
Outline

Part I What are we talking about? Some fundamentals…

Part II

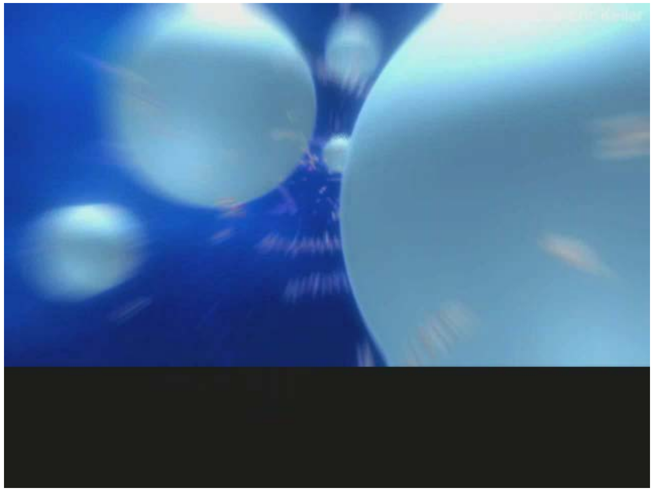


Part III



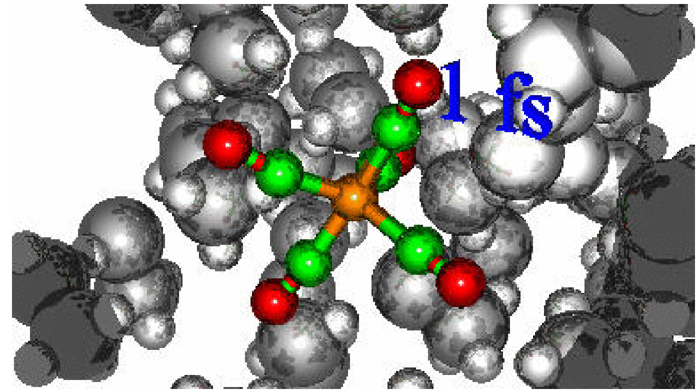
See the atoms move

Organic chemistry



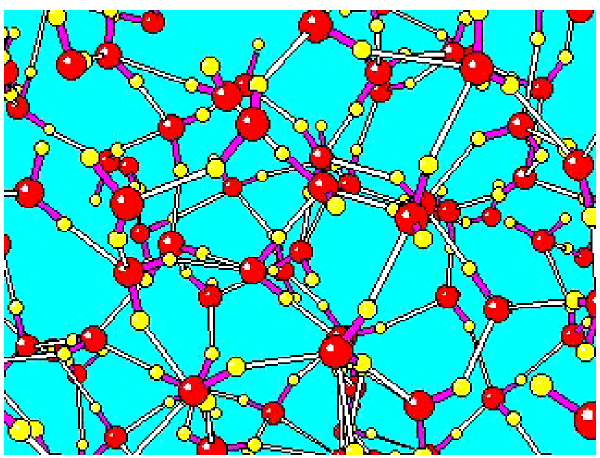
http://www.molecularmovies.com/

Photochemistry



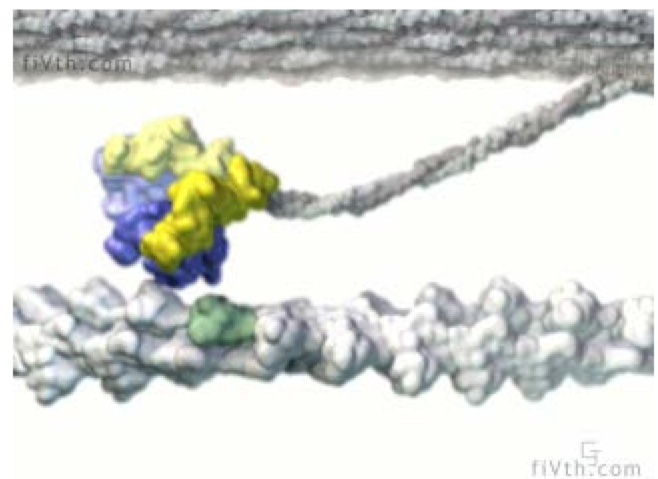
Michael Odelius, Stockholm University , Sweden

Water



Lars Ojamäe, Linköping University , Sweden

Molecular motors



http://www.molecularmovies.com/

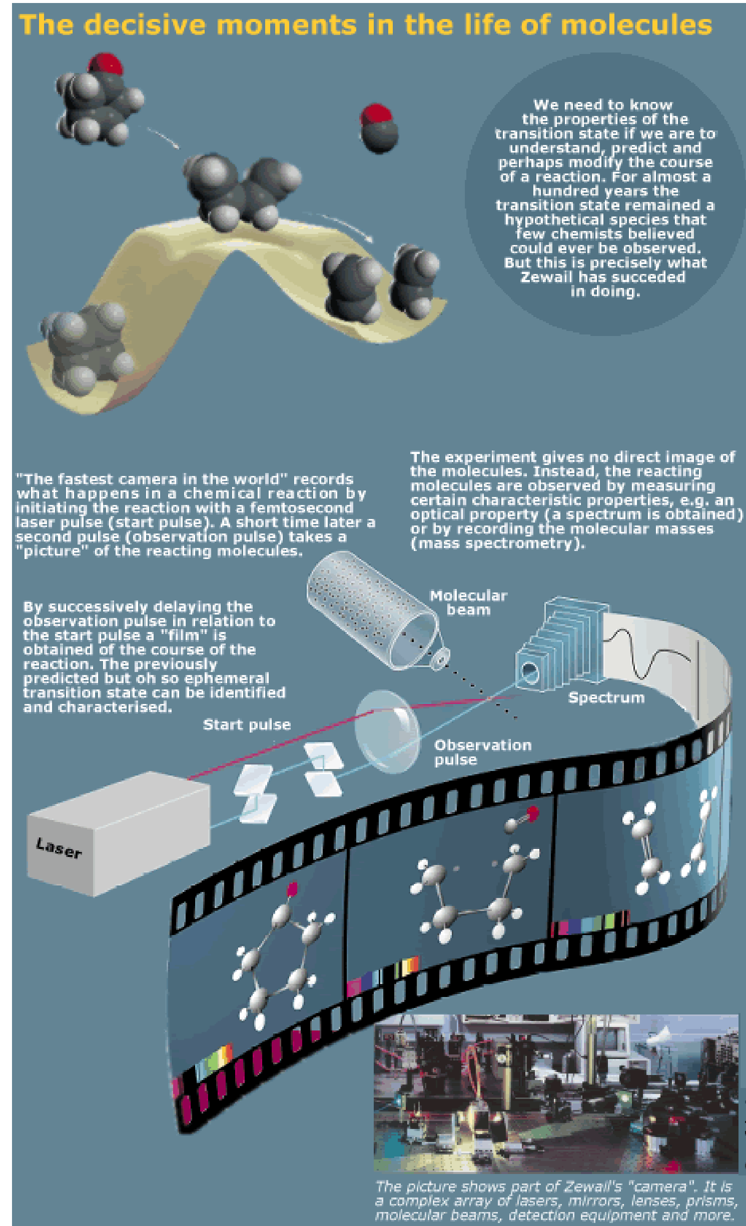
A. Zewail, Nobel price in Chemistry (1999)

„… for his studies of the transition states of chemical reactions using femtosecond spectroscopy.“

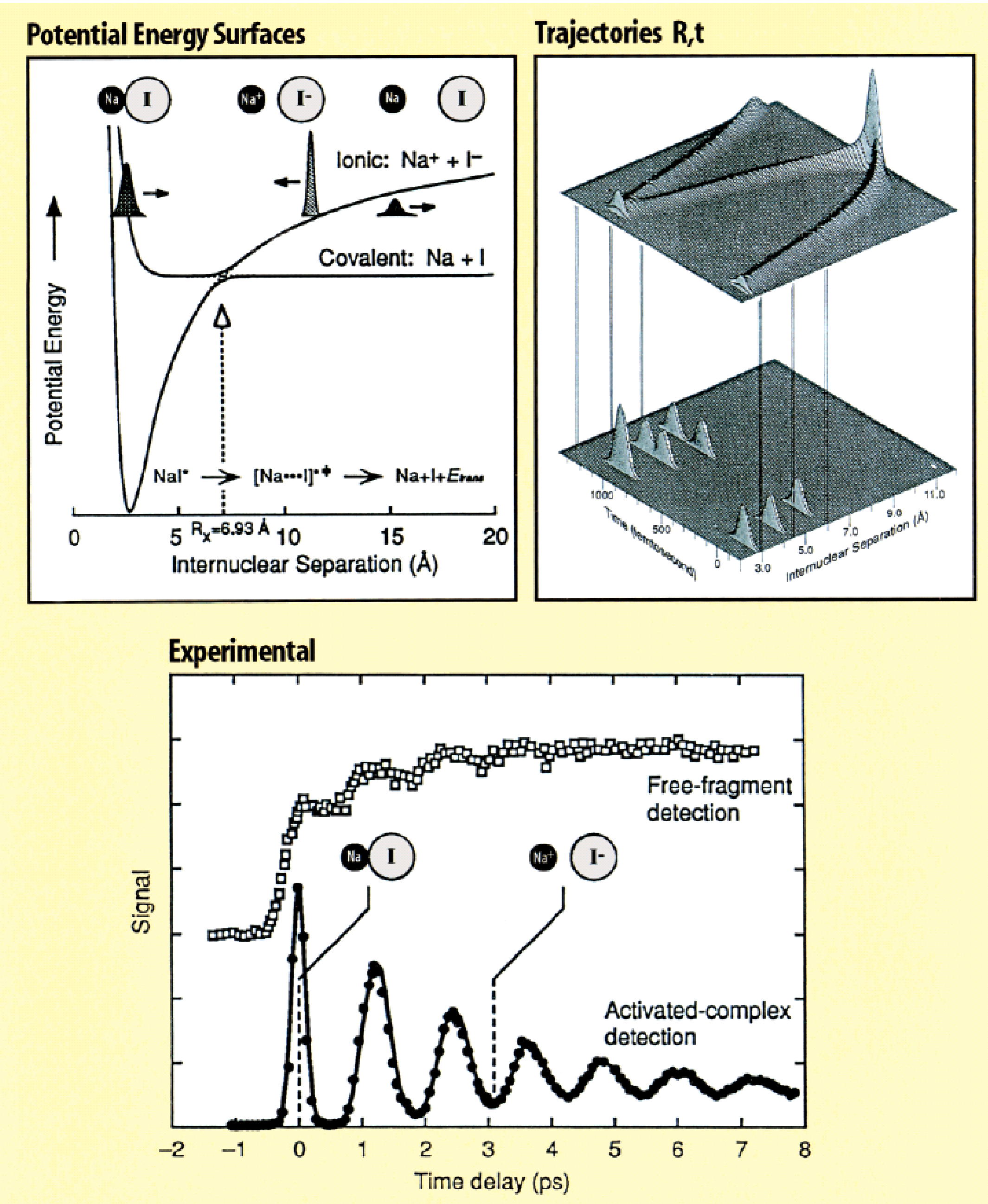
Nobel Lecture

http://nobelprize.org/nobel_prizes/chemistry/laureates/1999/zewail-lecture.html#

„Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond Using Ultrafast Lasers“



A textbook example for molecular dynamcis



A. Zewail

J. Phys. Chem. A **2000,** *104,* 5660−5694

Femtochemistry:
Atomic-Scale Dynamics of the Chemical Bond Using Ultrafast Lasers (Nobel Lecture)**

Ahmed H. Zewail*

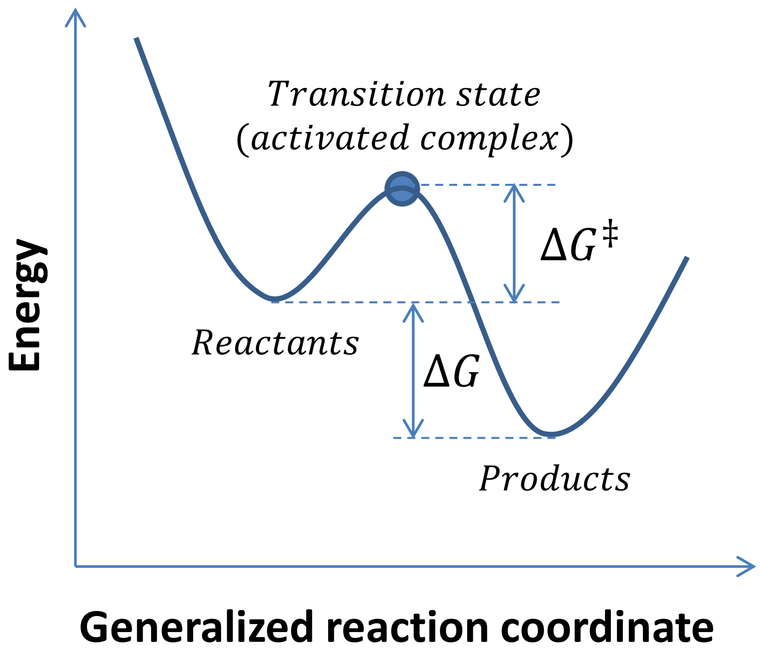
Angew. Chem. Int. Ed. **2000**, *39*, 2586 – 2631

Real-time tracking of nuclear dynamics (1000 m/s = 1 Å/100 fs)

Wait a second: What do we actually talk about?

Chemical dynamics deals with the atomic-scale view of the elementary steps of a chemical reaction (pico- to femtoseconds and Ångstrom).

This could be a triggered reaction (pump-probe) or a non triggered reaction (e.g. thermally activated). Most often, photoreactions (triggered) are studied!



Thermodynamics

$$K = \frac{[Products]}{[Reactants]} = e^{-\frac{\Delta G}{RT}}$$

Transition state theory

$$k = \upsilon \cdot e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

- **Thermodynamic properties of the transition state ($\Delta G^{\ddagger}$) and the collision frequency (υ) determine the reaction rate (k) (the kinetics) of thermal reactions**
- **The energy potential landscapes determine the reaction mechanisms (the dynamics) of photochemical reactions**

We talk about the atomic-scale dynamics of chemical interactions.

The Born-Oppenheimer Approximation

By neglecting the coupling of nuclear and electron motions we can treat the motion of nuclei and electrons independently.

Masses of electrons and nuclei are so different (10^4) **that the nuclei appear to be fixed while electrons are moving!**

Solve the Schrödinger equation for the **electrons in the static potential of the fixed nuclei** (Produktansatz).

The electronic part of the wavefunction depends on the nuclear distance BUT as a parameter, NOT as a variable!

$$\Psi_{molecule} = \Psi_e \cdot \Psi_n$$

$$\Psi_e = \Psi_e(r_e, R_n)$$

$$\Psi_n = \Psi_n(R_n)$$

Within the adiabatic approximation ("electrons follow nuclear motions instantaneously") we can solve the Schrödinger equation for Ψ_e at fixed R_n repeatedly for many R_n:

$$[T_e + V_e]\, \Psi_e(r_e, R_n=\text{const}) = E_e\, \Psi_e(r_e , R_n=\text{const})$$

By plotting the resulting set of solutions E_e versus R_n we build potential energy curves (surfaces, landscapes, depending on the number of parameters/reaction coordinates)

The potential energy curve **E_e versus R_n** corresponds to the electronic part of the total energy of the molecules plus the energy arising from repulsion of nuclei (sum of kinetic and potential energy of electrons plus potential energy of nuclei, vibrational and rotational energies are missing!)

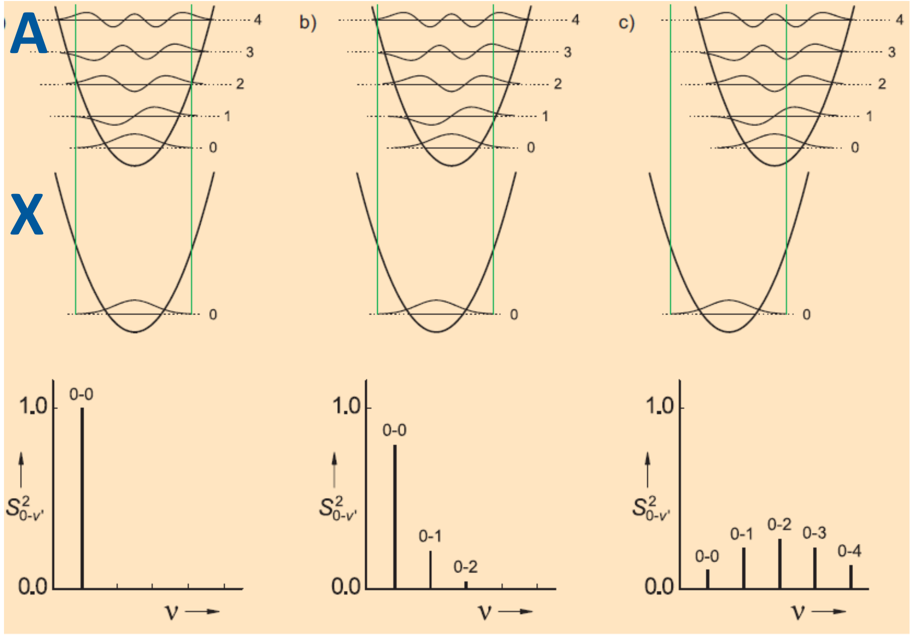
The Franck-Condon Principle

For the transition between state X and A with vibrational levels υ the transition probability (electronic dipole transition) is proportional to:

The **electronic dipole moment** times the **Franck-Condon factors**

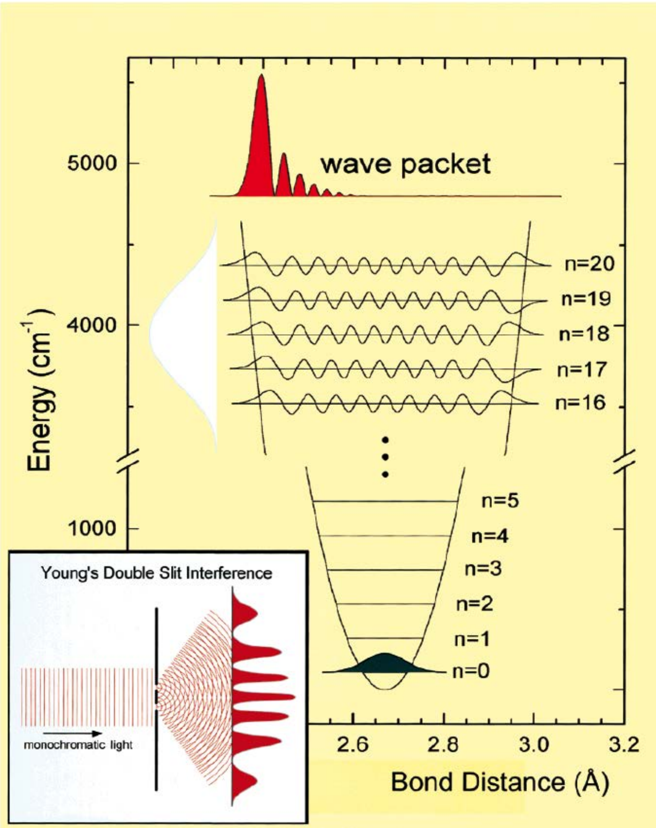
$$|\langle \Psi_e^A \mid d_e \mid \Psi_e^X \rangle|^2 \quad \cdot \quad |\langle \Psi_n^\upsilon \mid \Psi_n^0 \rangle|^2$$

$$|\int \Psi_e^A \, d_e \, \Psi_e^X \, dr_e|^2 \quad \cdot \quad |\int \Psi_n^\upsilon \Psi_n^0 \, dR_n|^2$$



Franck-Condon factors

(Nuclear) Wavepackets



A. Zewail

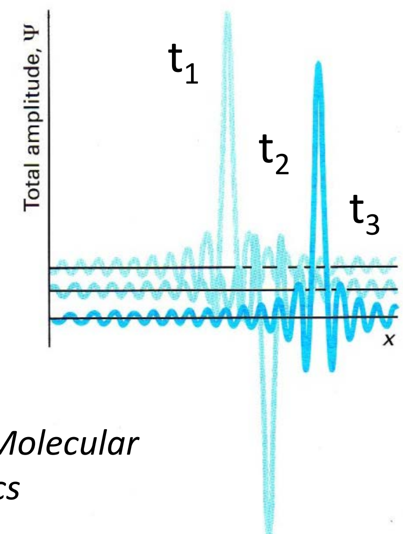
J. Phys. Chem. A **2000**, *104*, 5660−5694

- Coherent superposition of vibrational states
- Formation of a nuclear wavepacket
- The wavepacket is evolving in time (nuclei are moving)!
- Wavepackets to describe particles confined in space

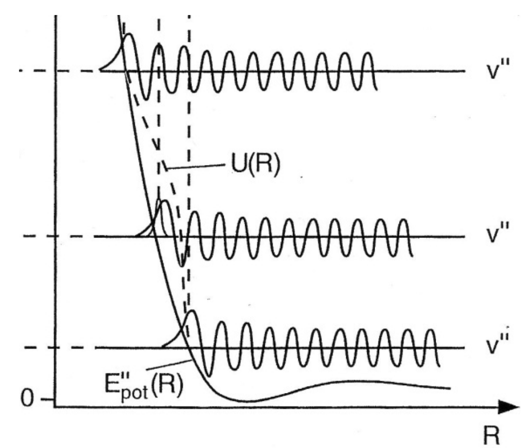
Superposing plane waves

$$\Psi(x,t) = (2\pi\hbar)^{-1/2}\int_{-\infty}^{+\infty} e^{i(p_x x - Et)/\hbar}\,\phi(p_x)\,dp_x$$

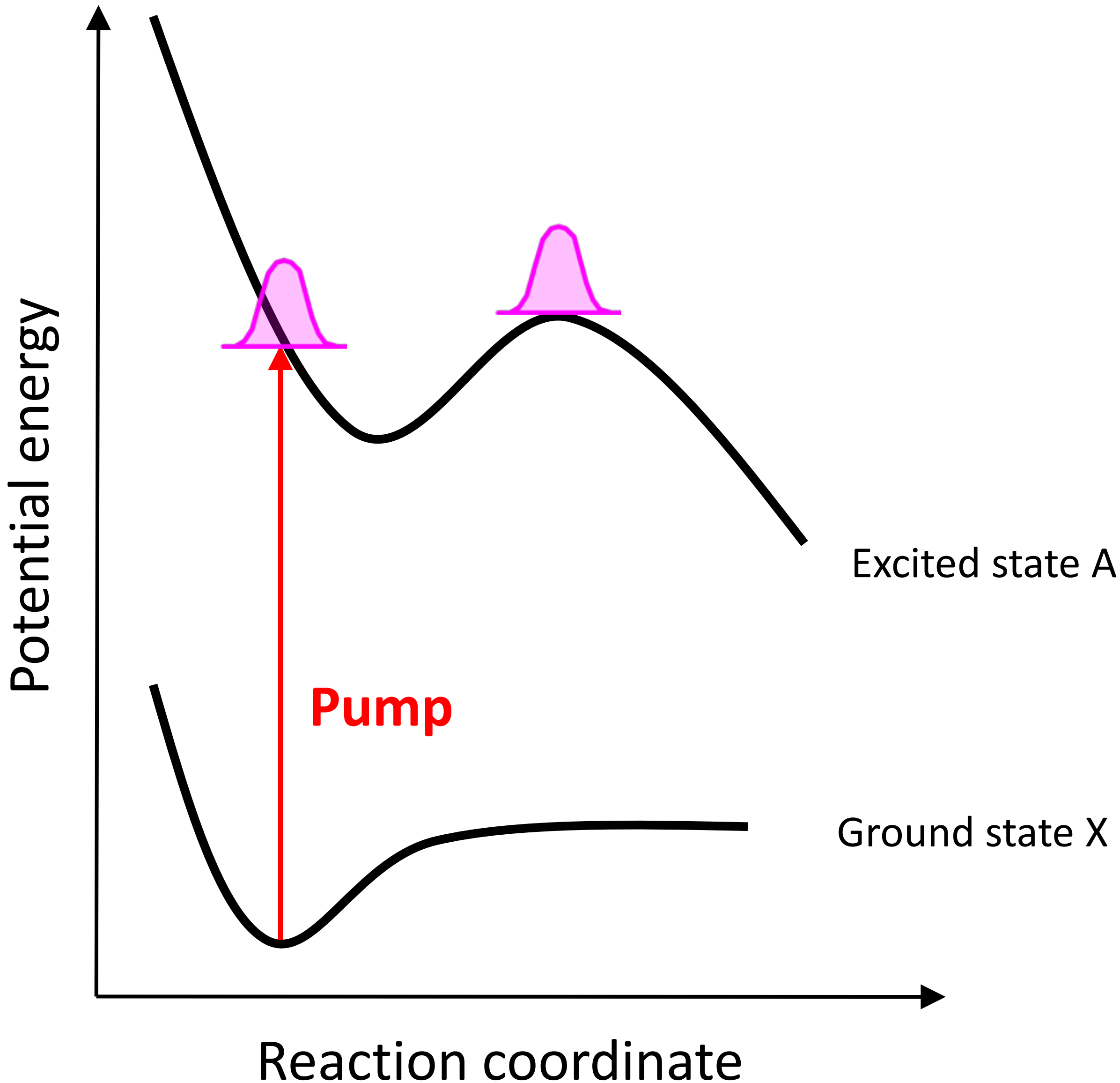
For free particles

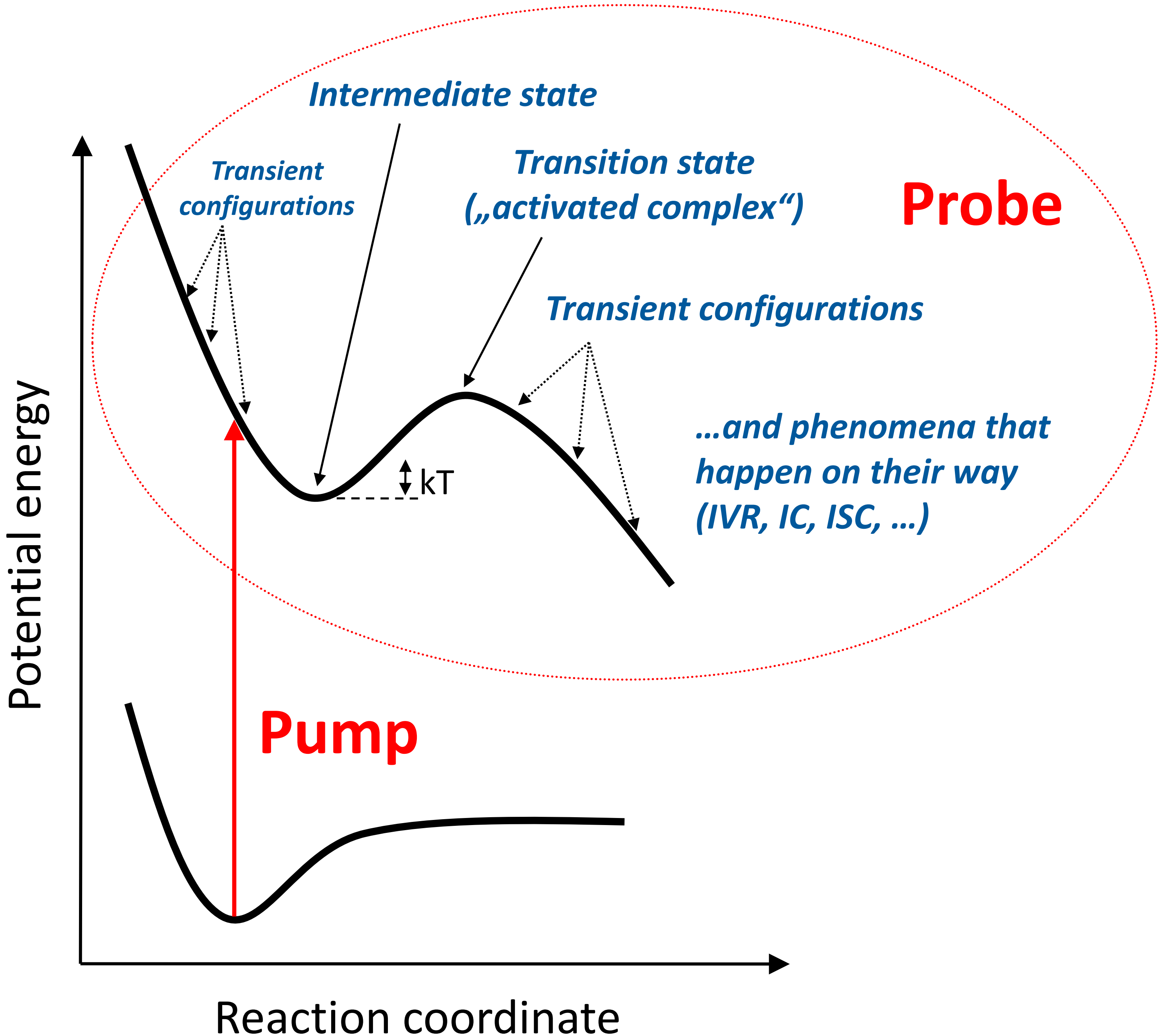


For dissociative states



Atkins, Friedman, Molecular quantum mechanics


Potential energy
Pump
Excited state A
Ground state X
Reaction coordinate

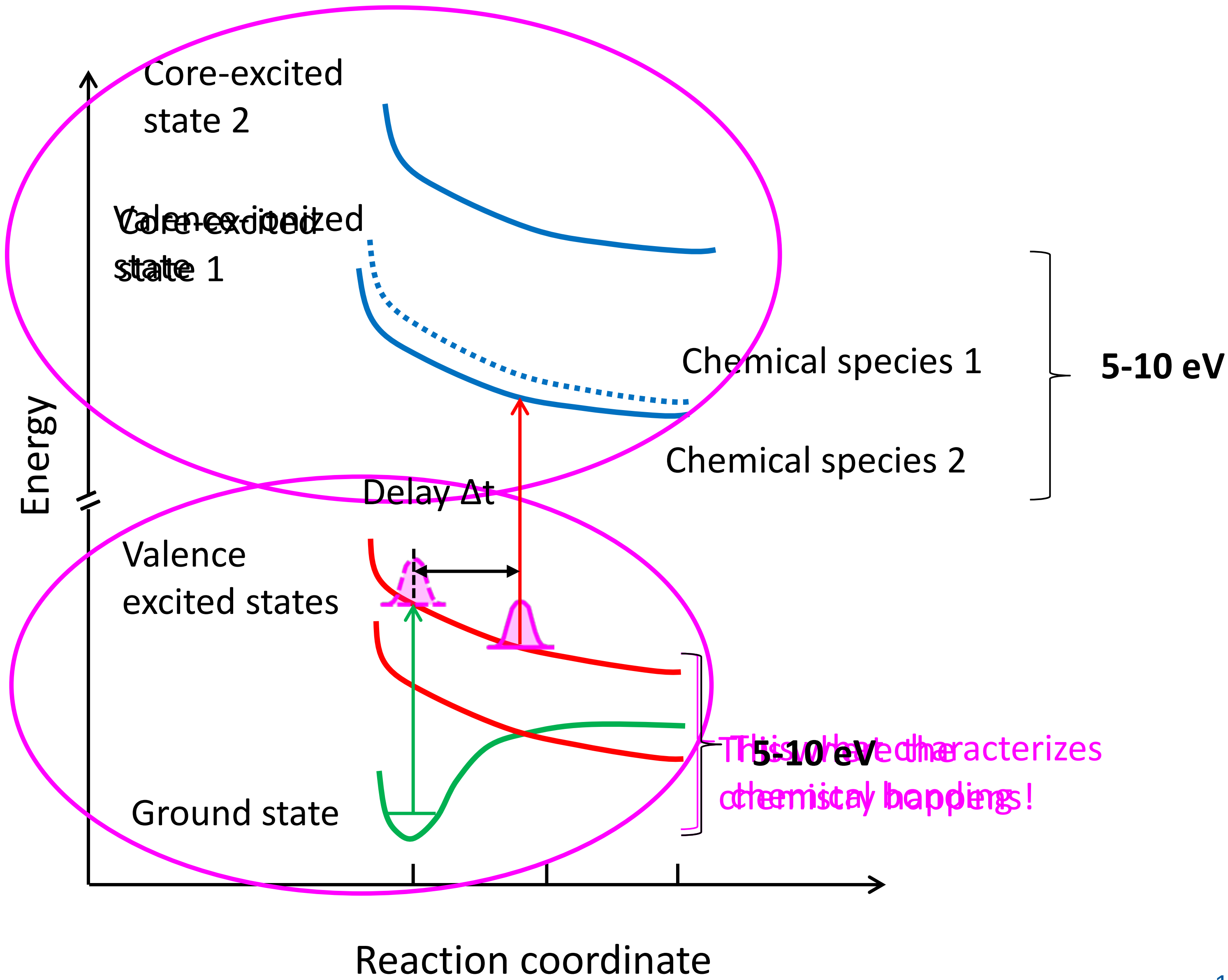


Intermediate state
Transient configurations
Transition state („activated complex“)
Probe
Transient configurations
…and phenomena that happen on their way (IVR, IC, ISC, …)
kT
Potential energy
Pump
Reaction coordinate

X-ray spectroscopy

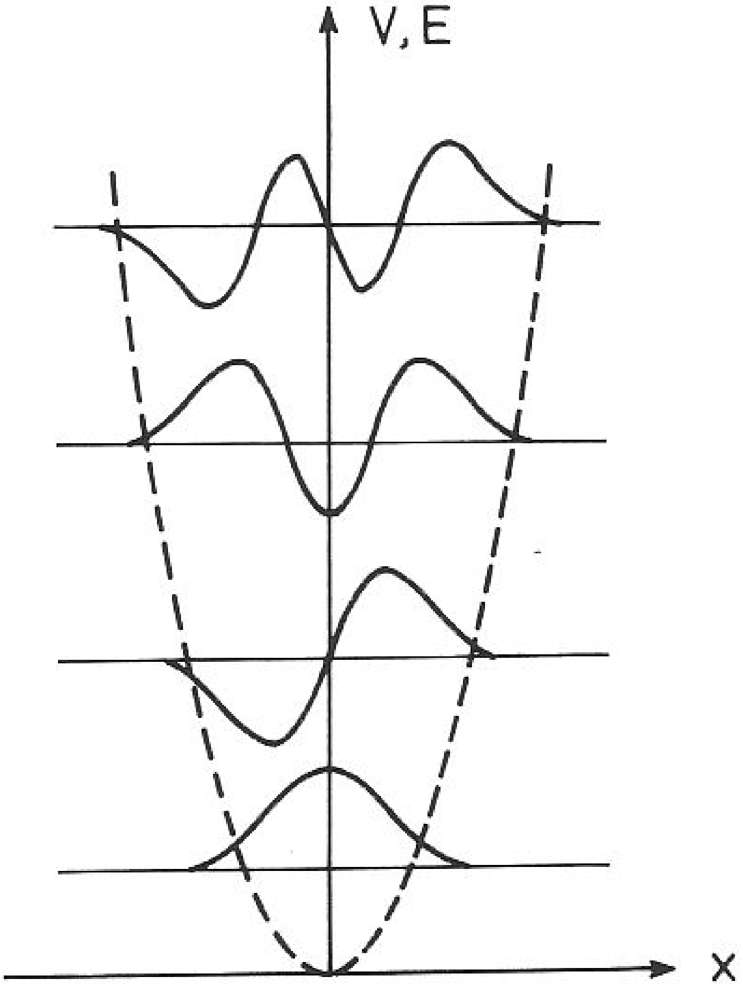
This „just“ the probing!

This is what we are interested in!

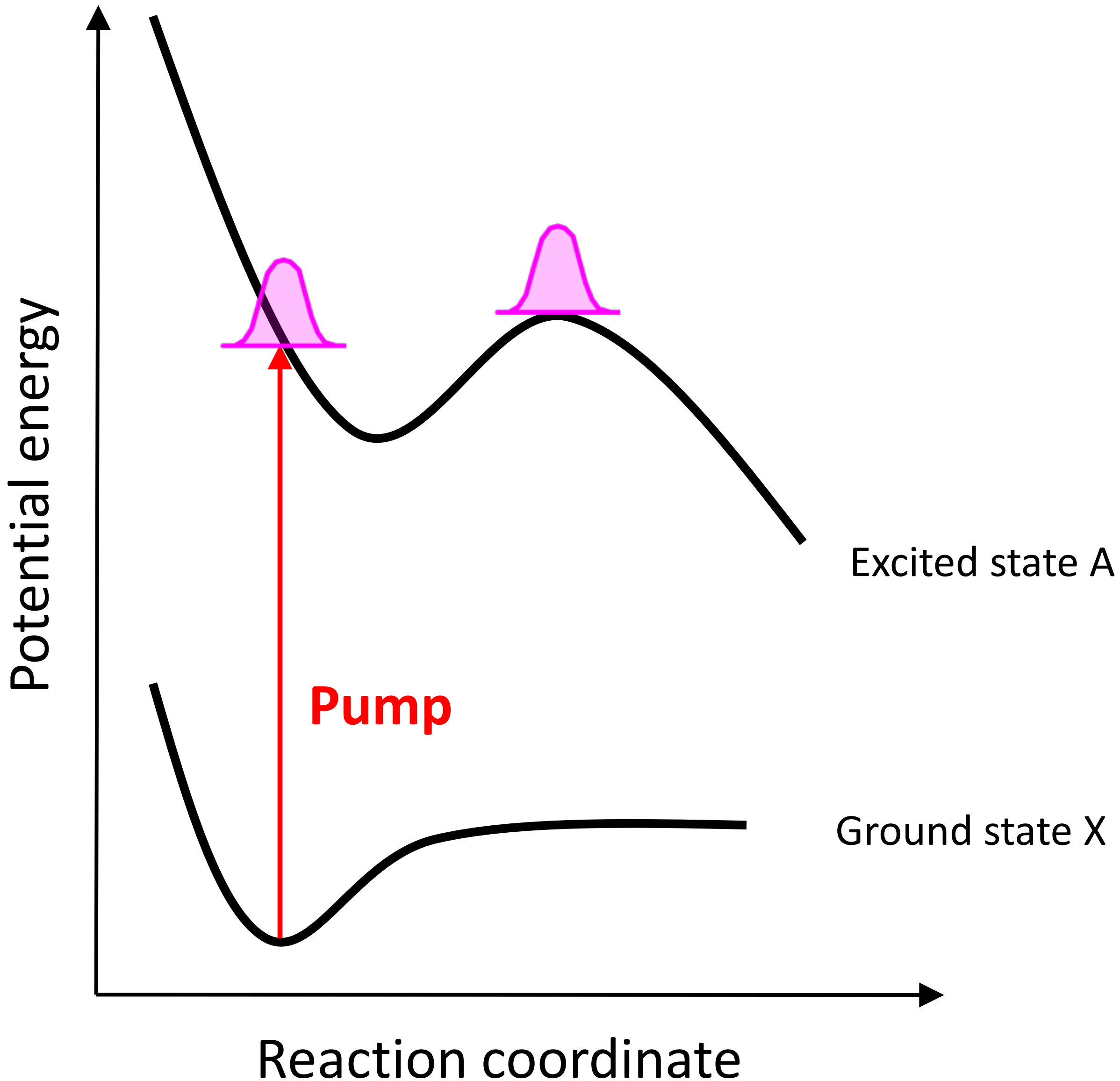


Quiz part I

How many drawings in one?



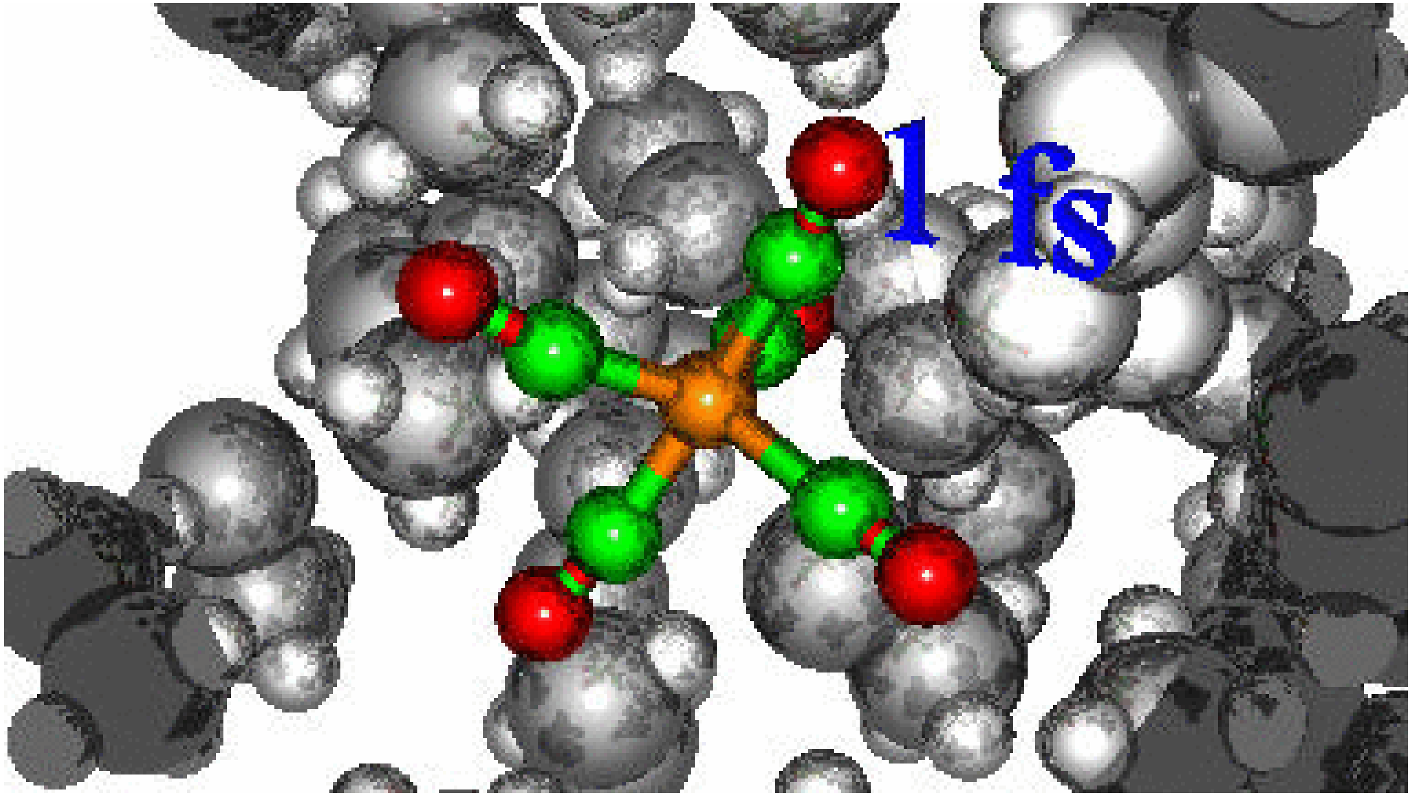
What is “wrong” here?



What time-resolution do I need to resolve molecular motion?

How fast do electrons move?

What do you see?



Outline

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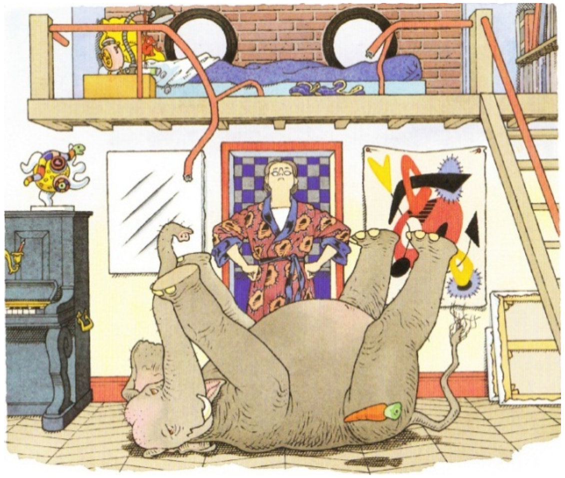
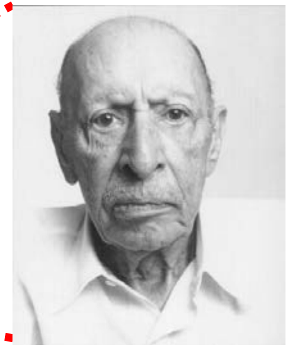
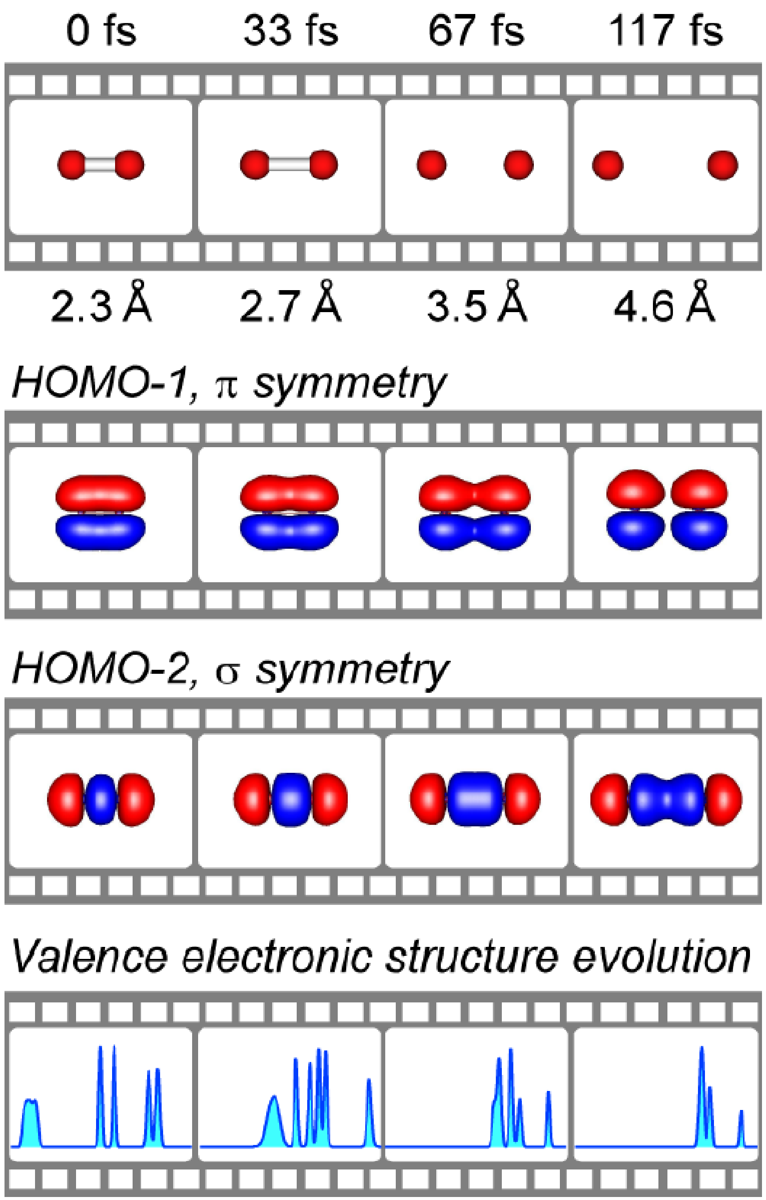
Part II

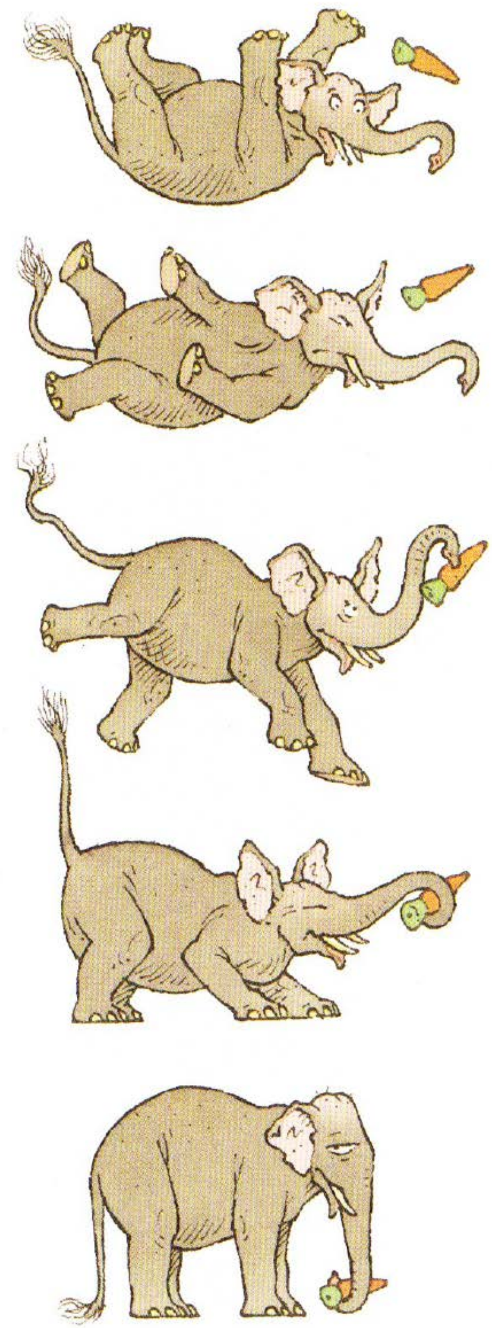


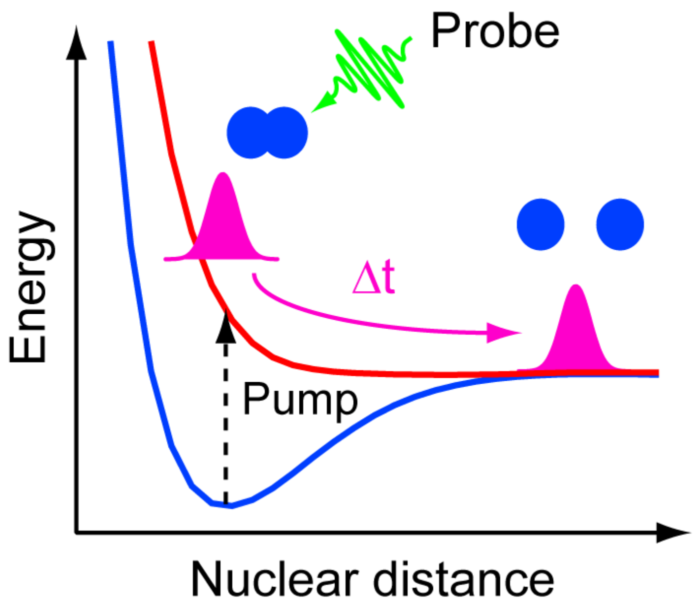
Part III

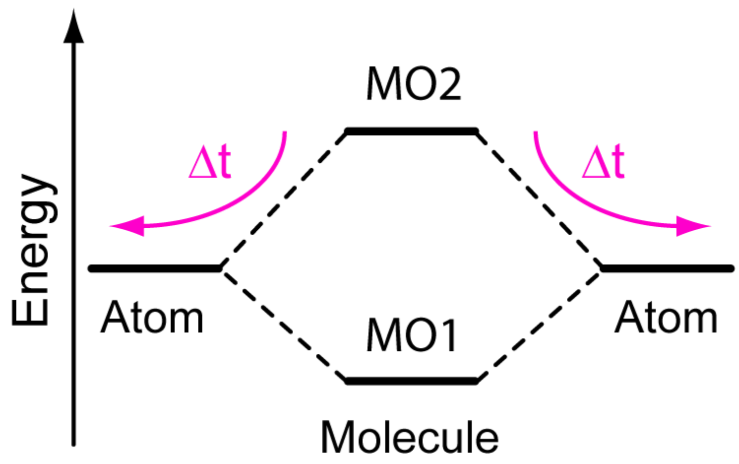


$$Br_2 + h\nu_{pump} \longrightarrow 2\,Br$$





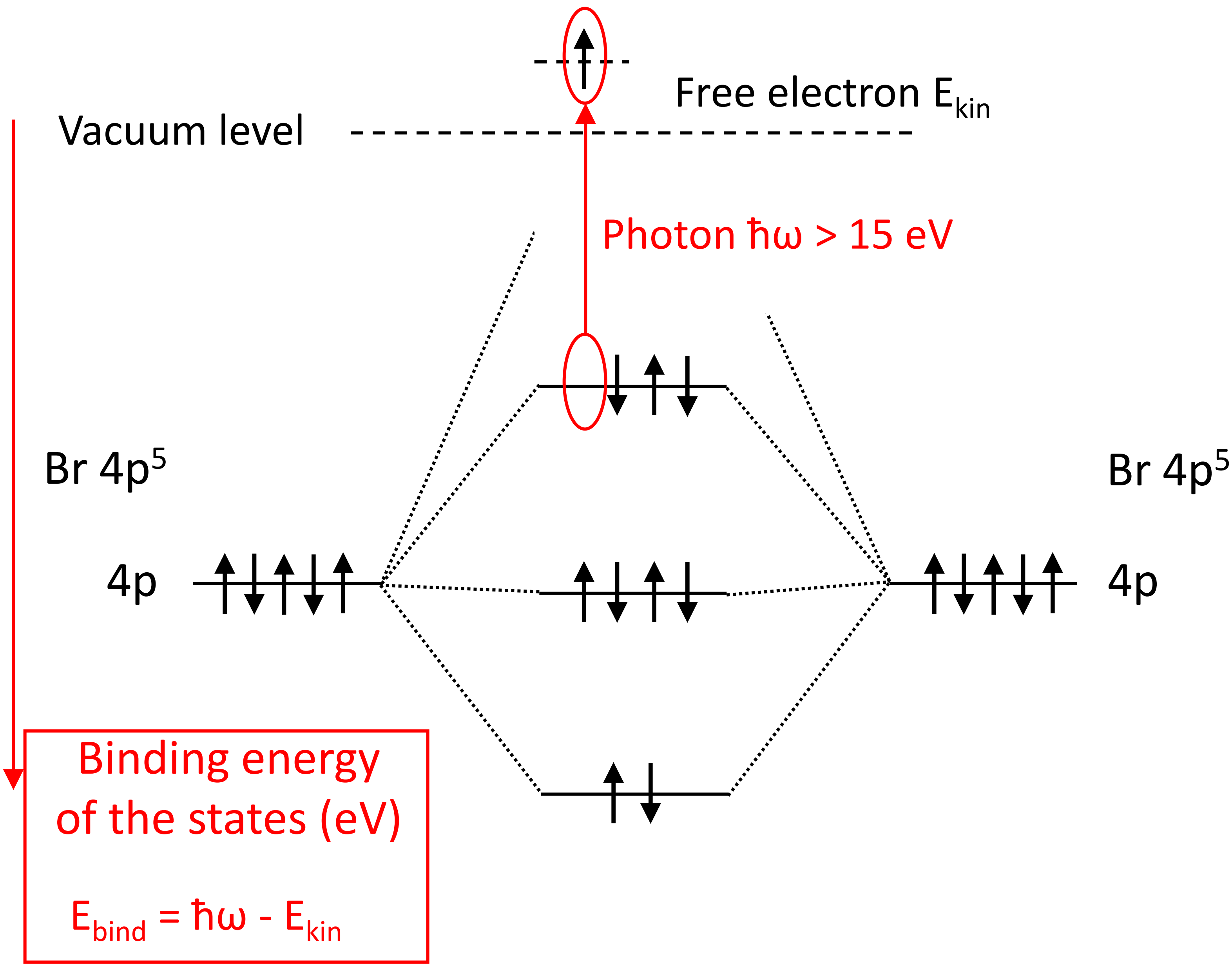




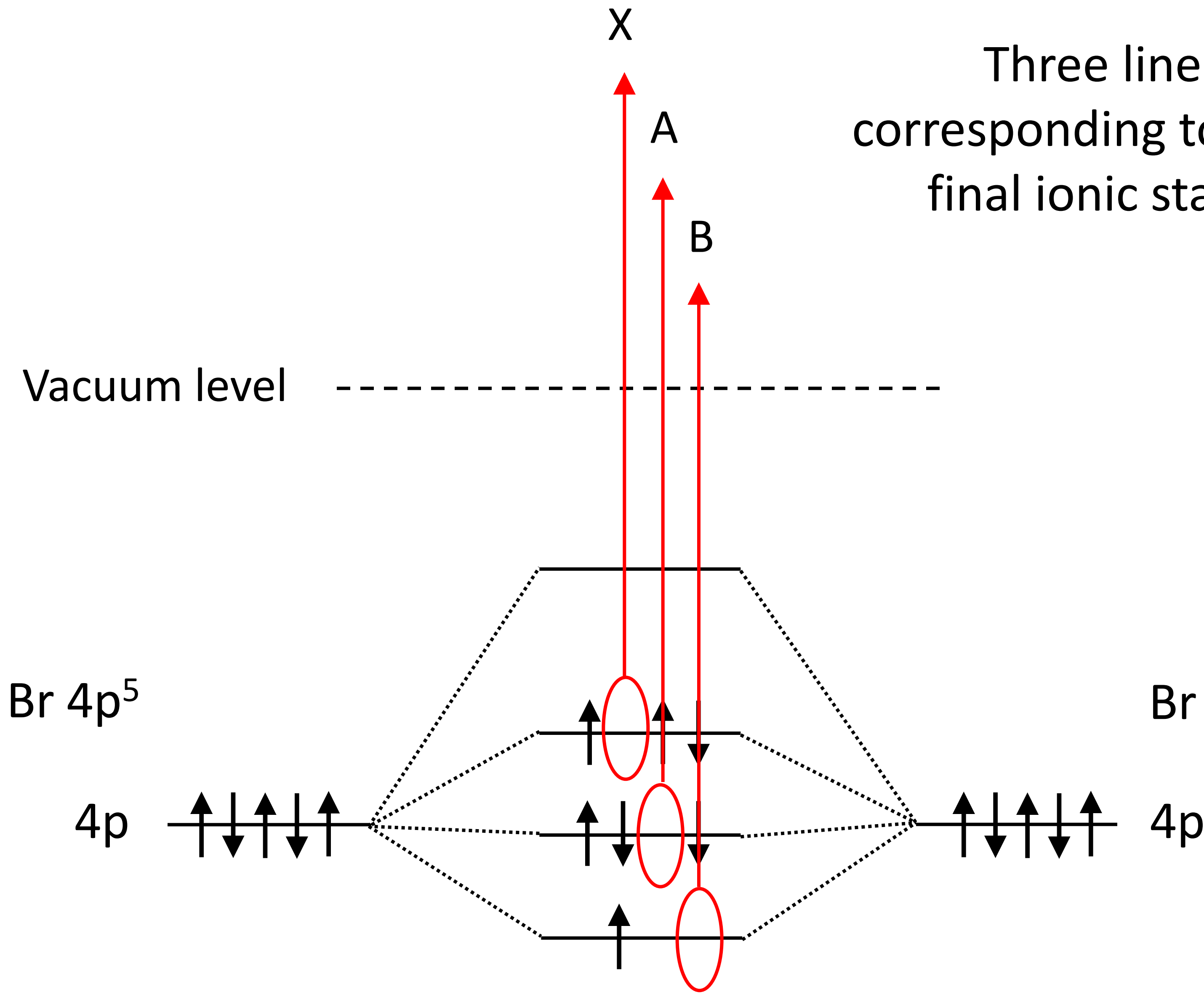
Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

Atomic and molecular orbitals of Br_2

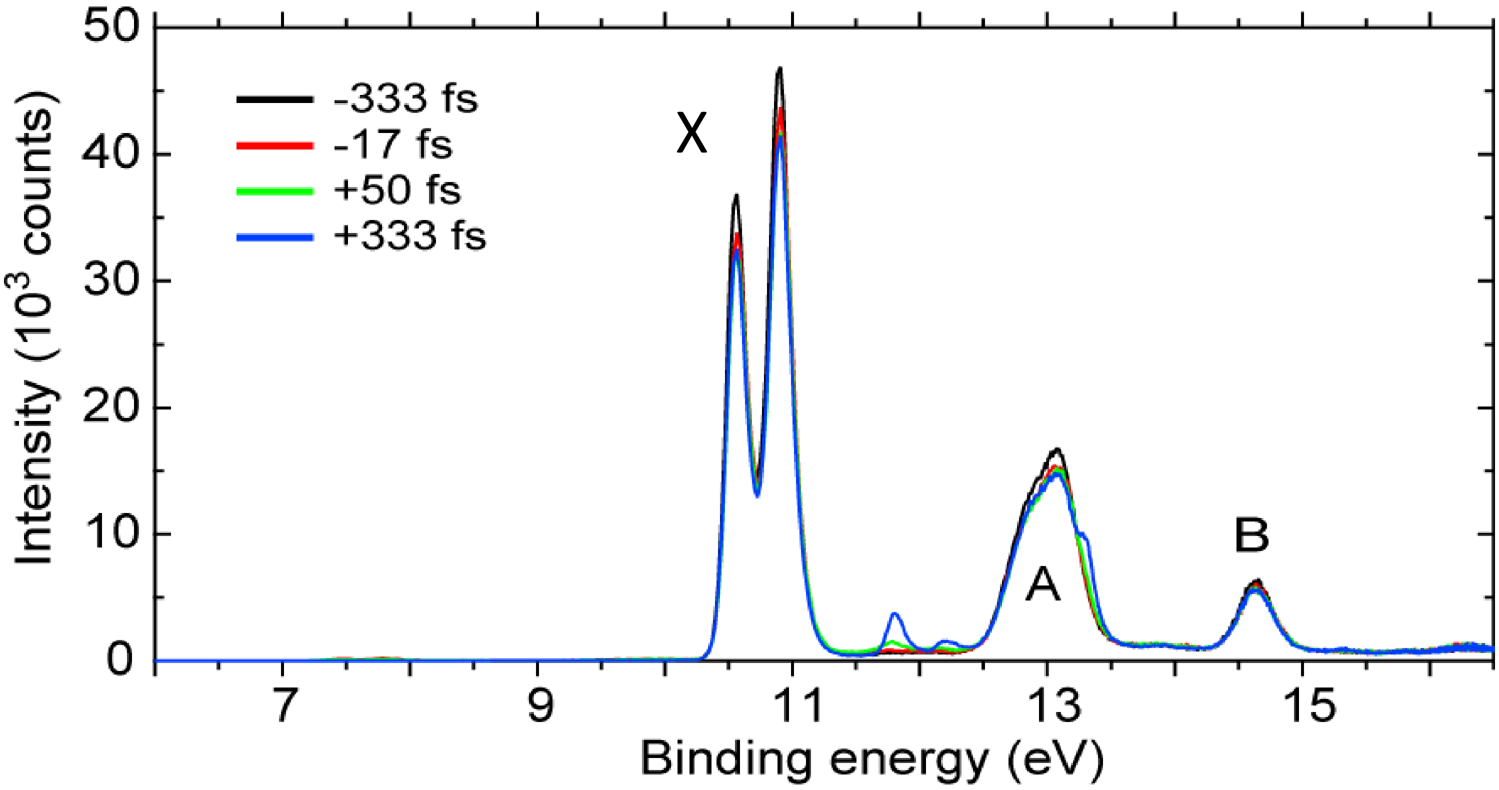
Photoelectron spectroscopy



Photoelectron spectroscopy of Br_2

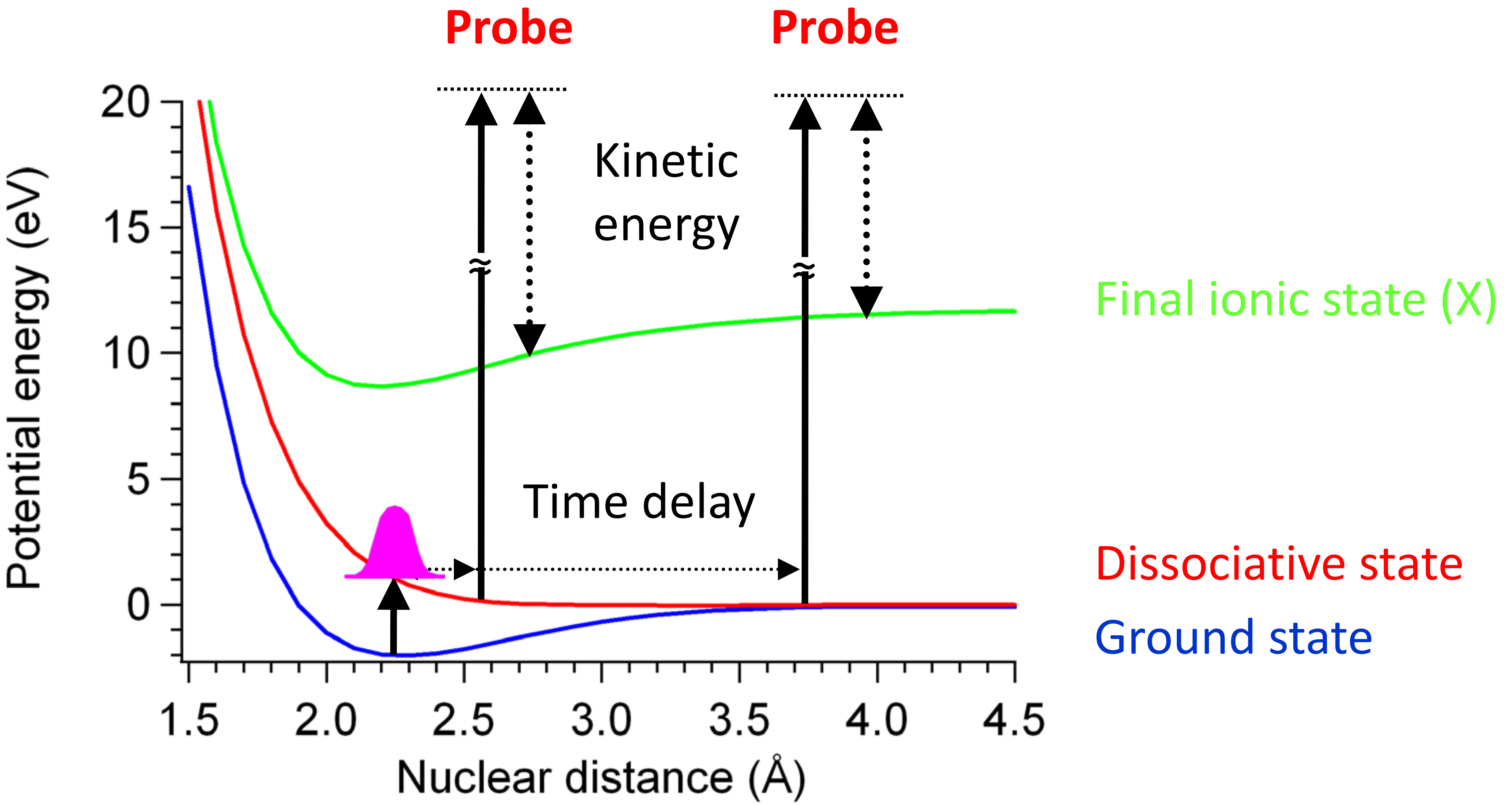


Three lines corresponding to three final ionic states



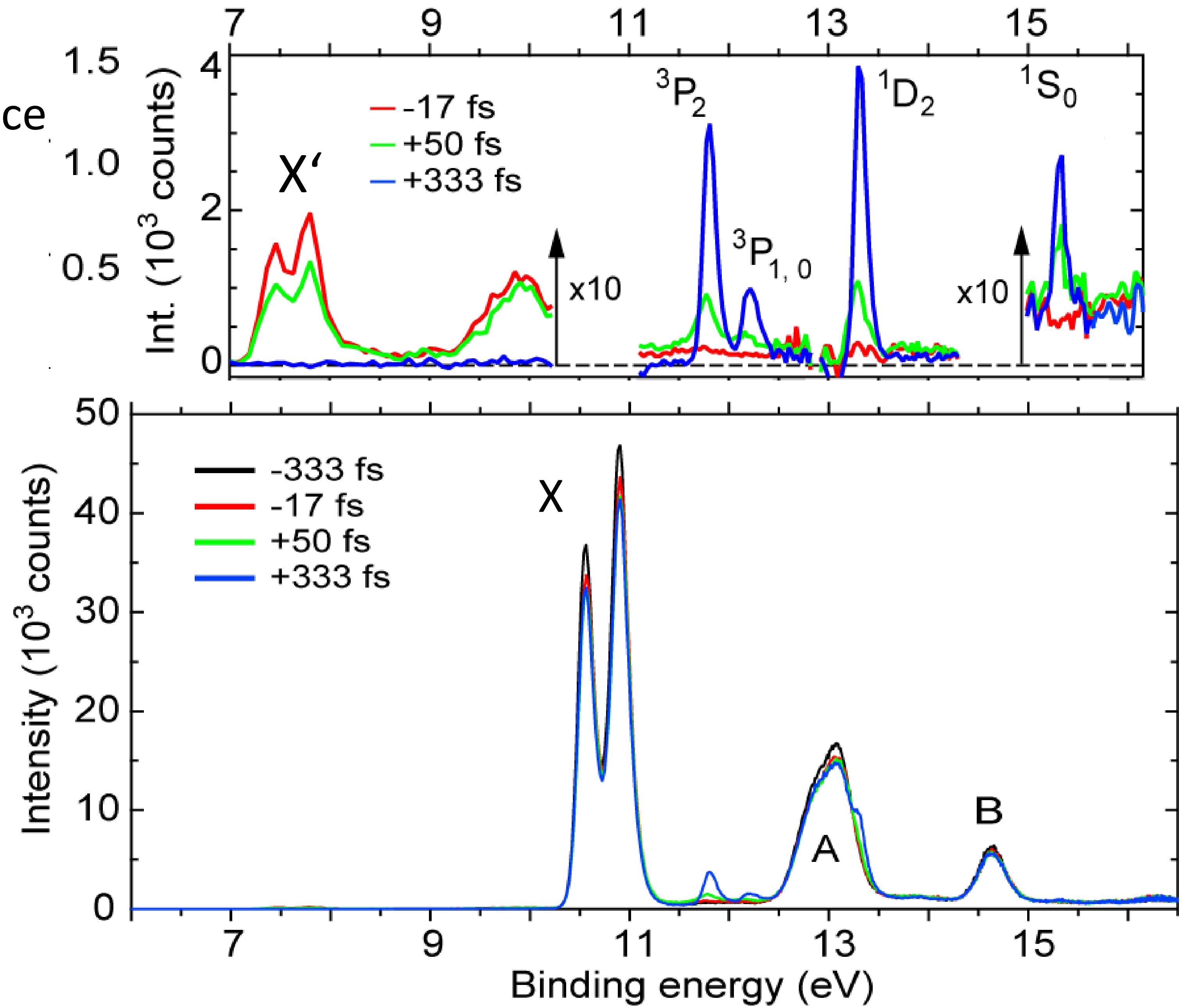
-333 fs
-17 fs
+50 fs
+333 fs
X
A
B
Intensity (10^3 counts)
Binding energy (eV)
0
10
20
30
40
50
7
9
11
13
15

Diatomic molecule (Br_2, calculated)

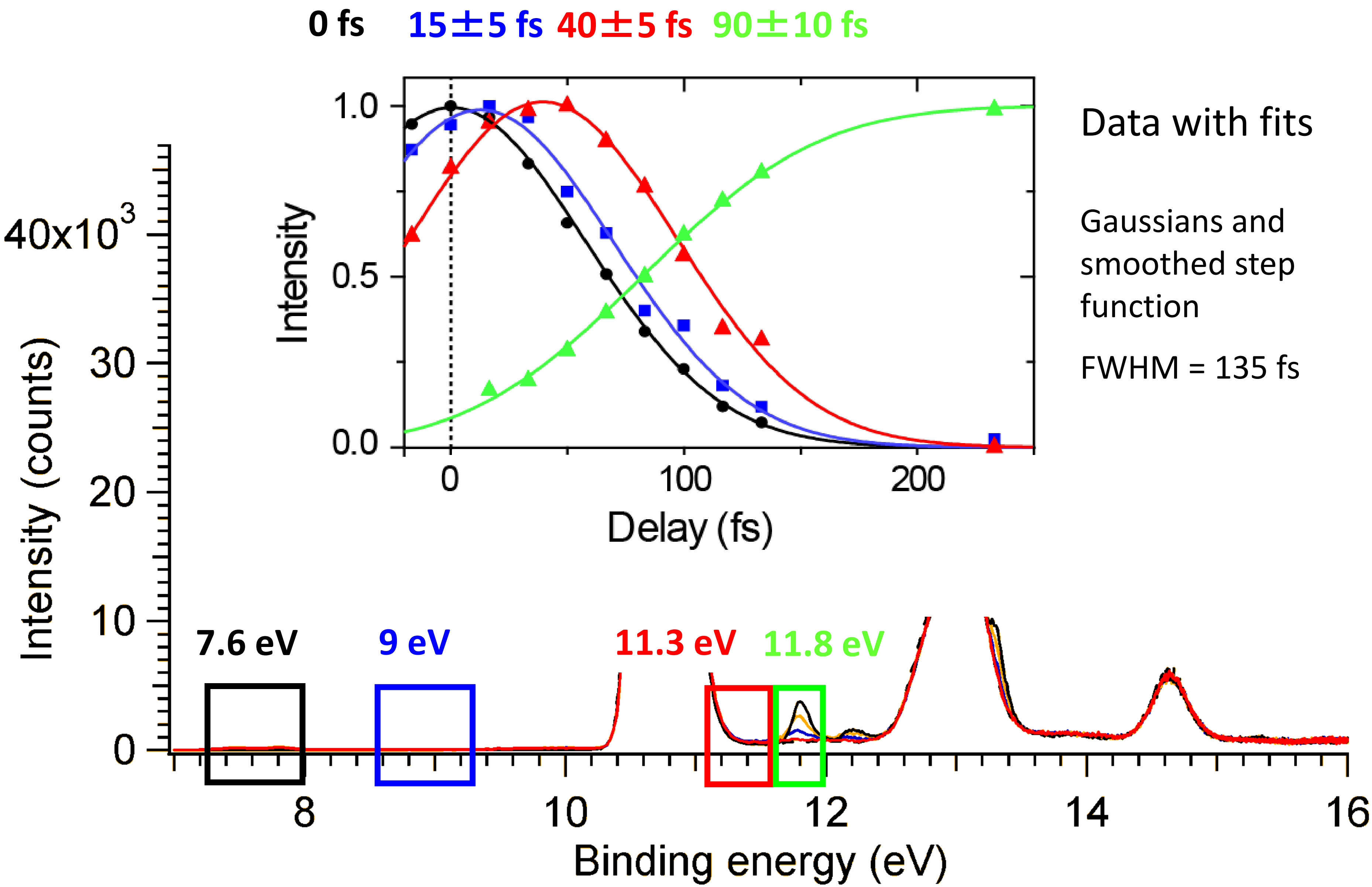


Pump (400 nm, 3.1 eV)

Difference spectra



Extracting valence state evolution

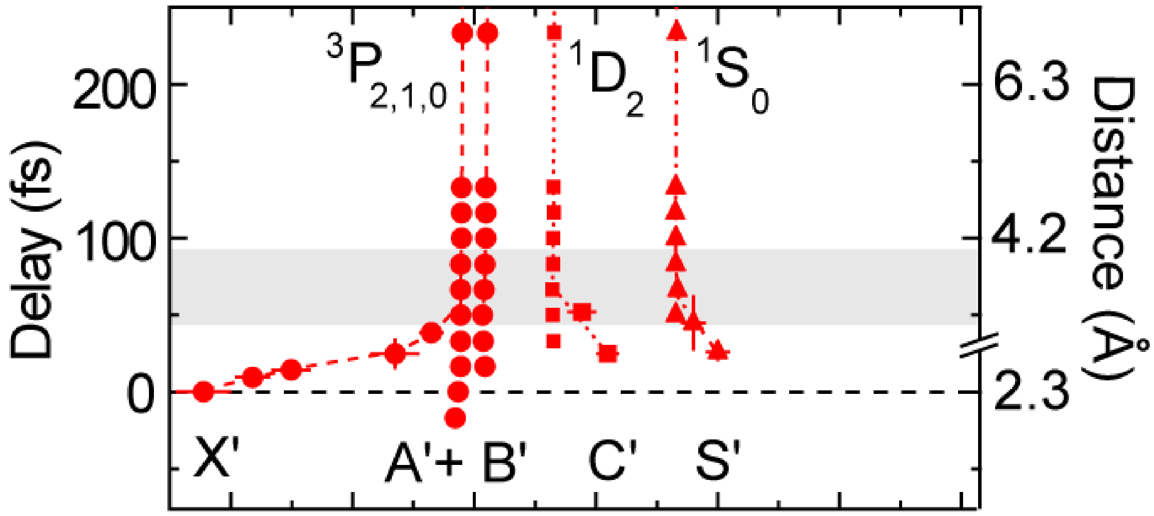


Data with fits

Gaussians and smoothed step function

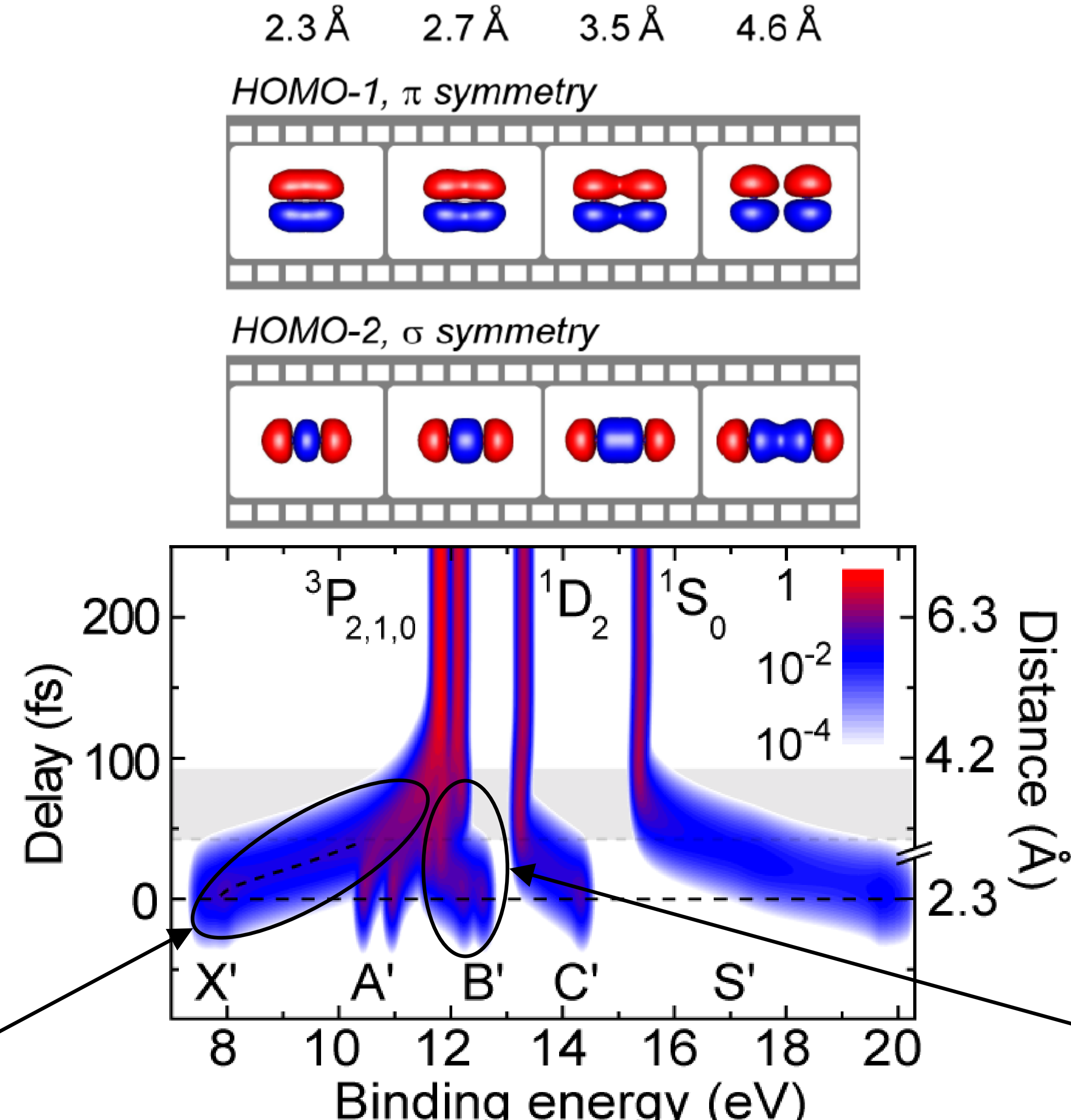
FWHM = 135 fs

Mapping valence electron rearrangements



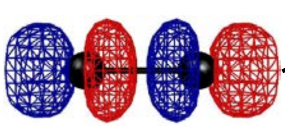
Wernet, Odelius, Godehusen, Gaudin,Schwarzkopf, Eberhardt, PRL **103**, 013001 (2009).

Mapping valence electron rearrangements

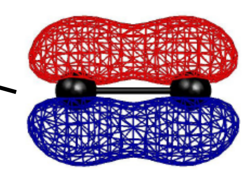


Theory

σ orbital

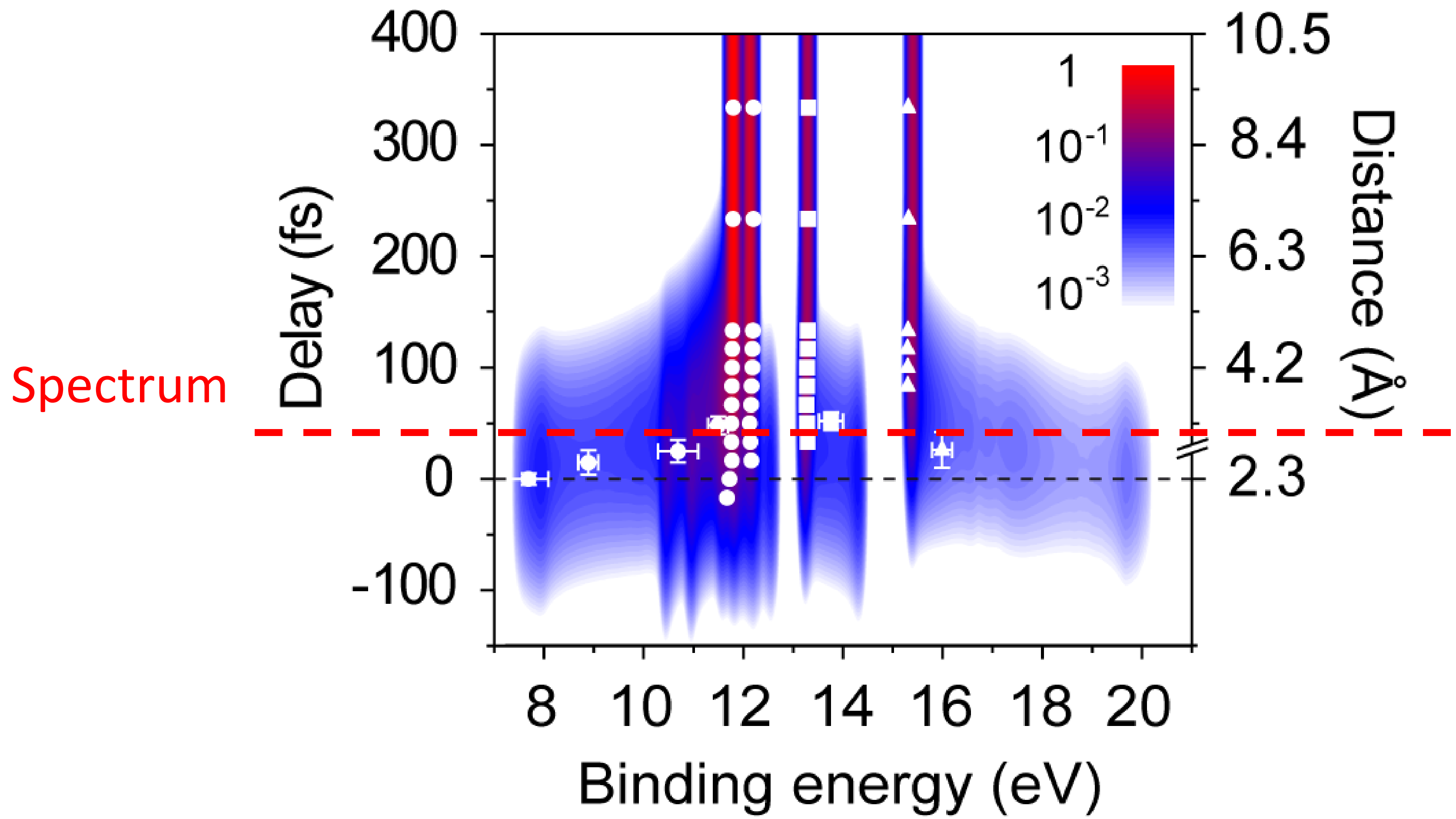


π orbital

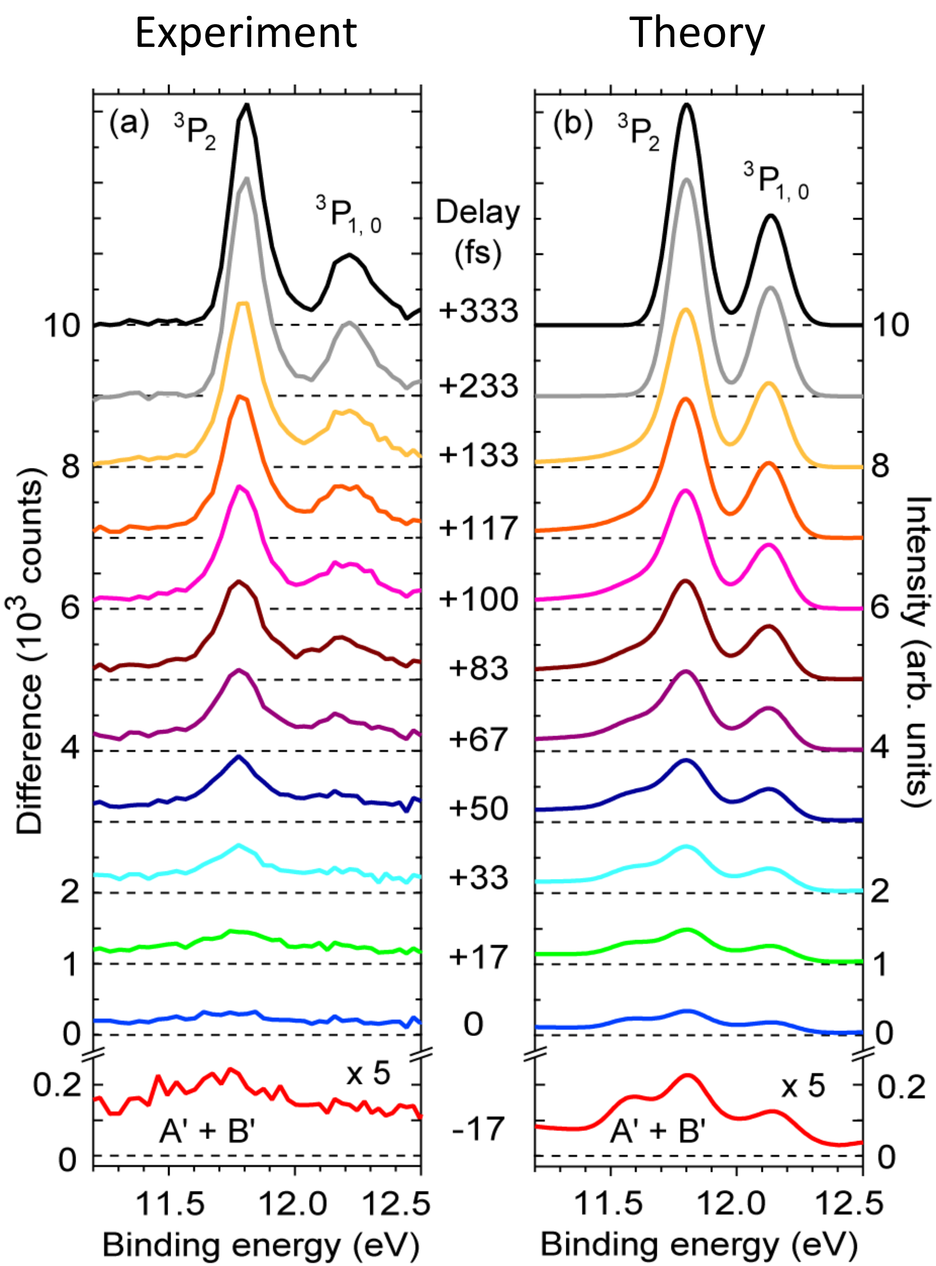


Direct comparison of experiment and theory

Pump/probe 60/120 fs



Spectral evolution from horizontal cuts

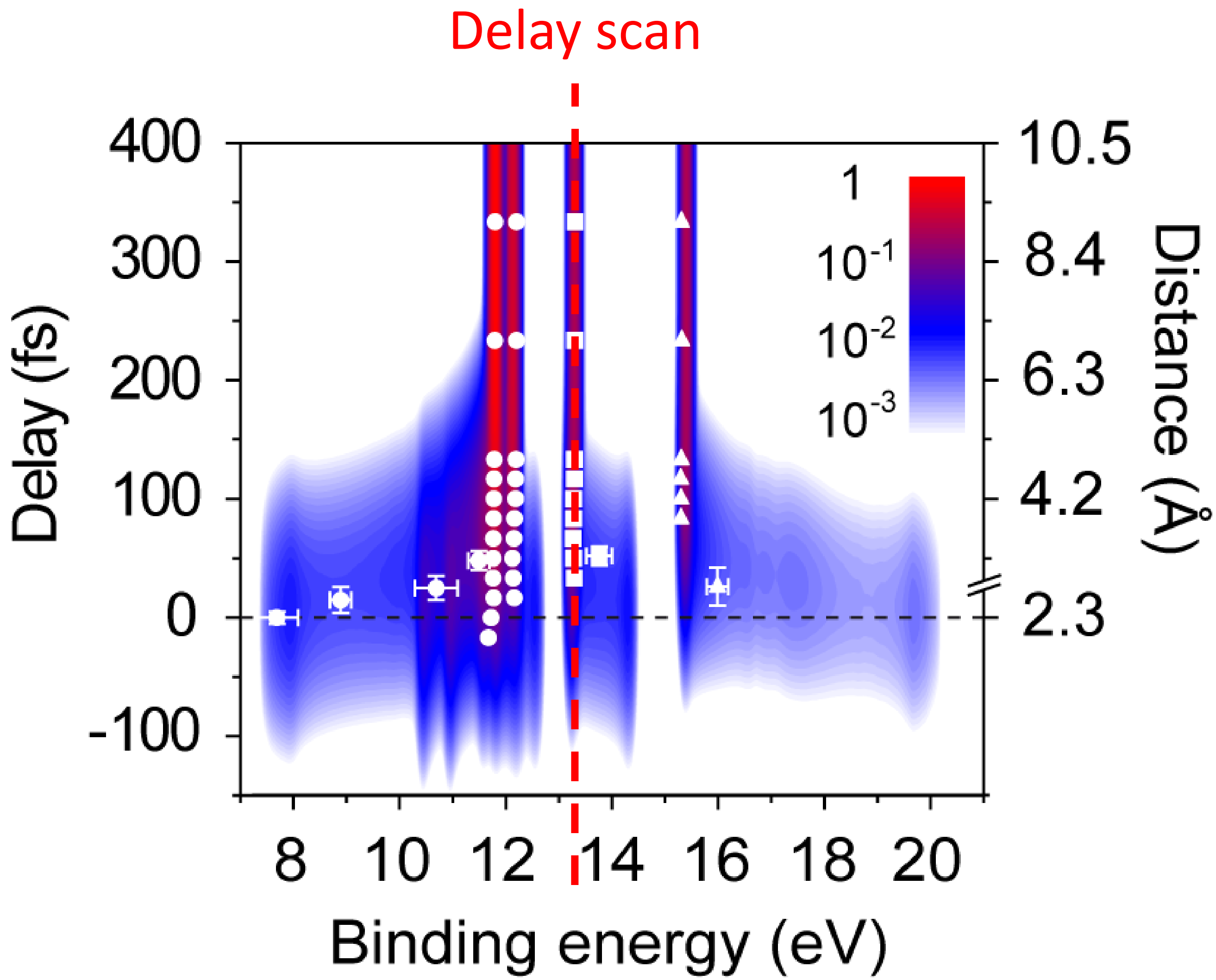


^3P of free atom

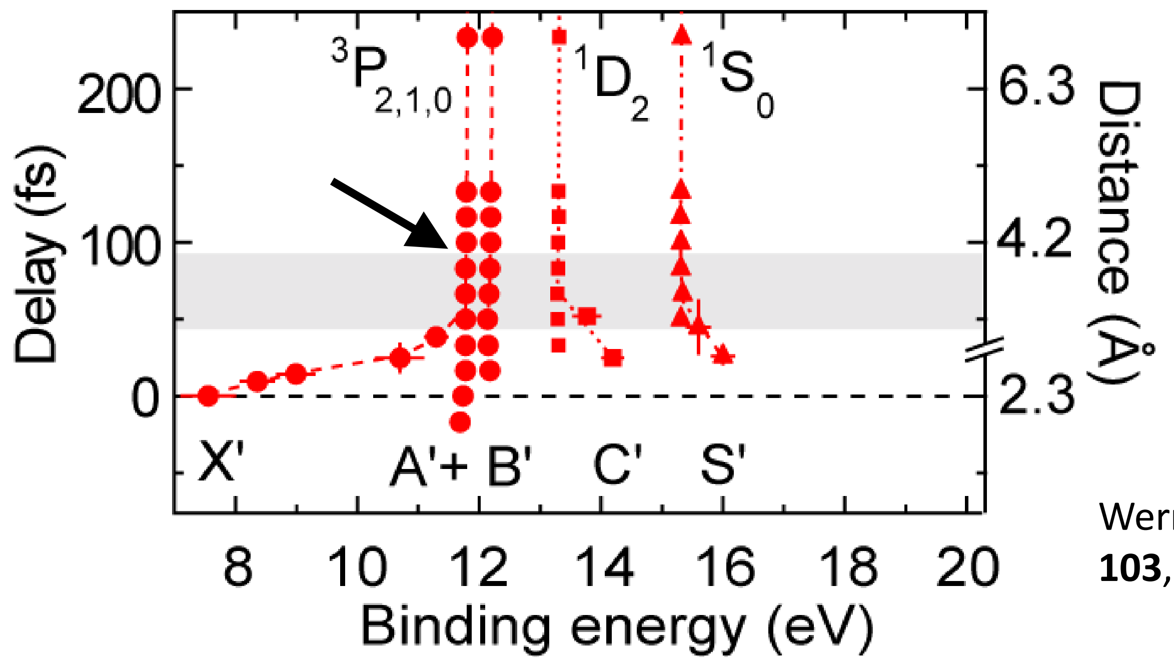
A' and B' of excited molecule

Direct comparison of experiment and theory

Pump/probe 60/120 fs



Mapping valence electron rearrangements

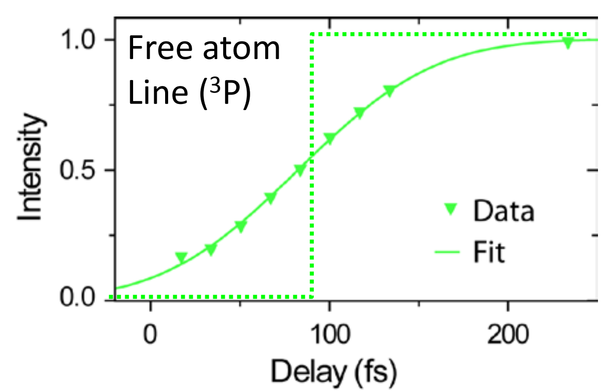


Wernet et al., PRL **103**, 013001 (2009).

After ~85 fs (~3.8 Å)

→ Free atom states arise

→ Dissociation complete



Note: R_e = 2.3 Å

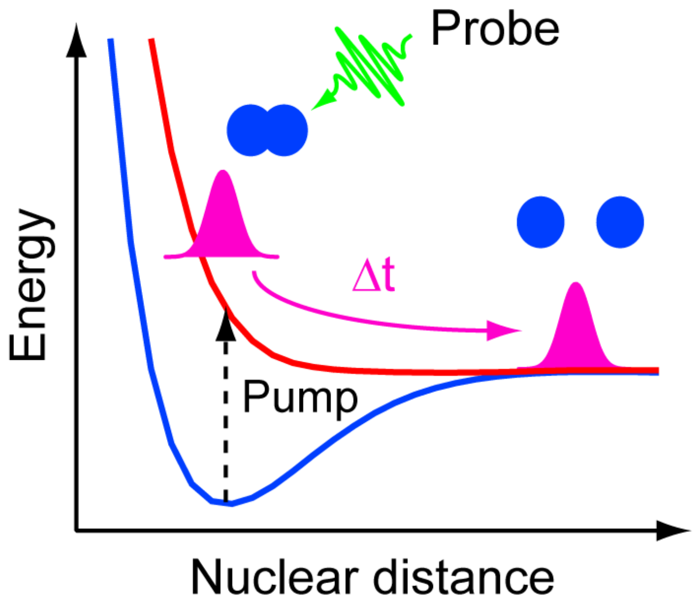
Dissociation time

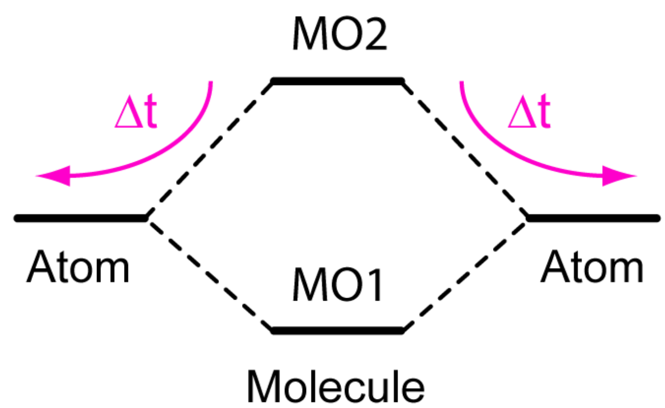
Method	*Time (fs)*	*Distance (Å)*
TRPES Wernet et al., PRL 103, 013001 (2009).	85	3.8
$2 \cdot R_e$ (R_e = 2.3 Å)	120	4.6
Laser femto-chemistry	140-200	5-6
Ion momentum imaging Li et al., PNAS 107, 20219 (2010)	140	5
Interferometry with high harmonics Wörner et al, Nature 466, 604 (2010).	300	8.5

Nugent-Glandorf et al., Phys. Rev. Lett. **87**, 193002 (01) , Nugent-Glandorf et al., J. Chem. Phys. 117, 6180 (02)
Strasser et al., J. Chem. Phys. **127**, 184305 (07)

Quiz part II

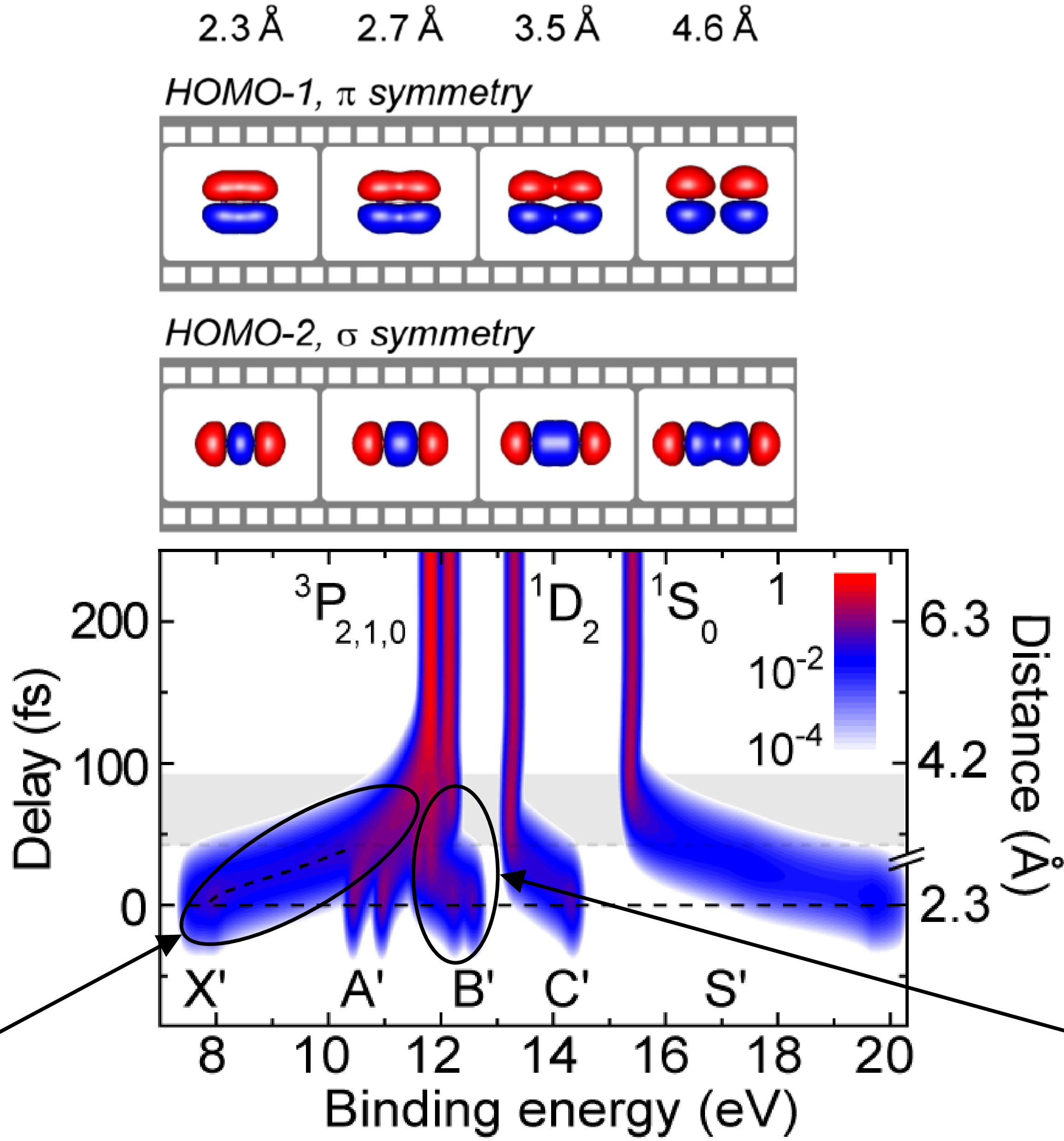
Which one applies? Detect the differences…





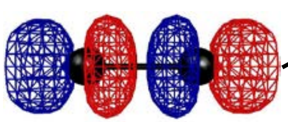
Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

What is fishy with this argument?

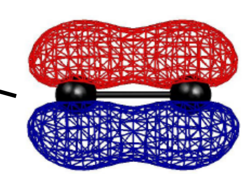


Theory

σ orbital



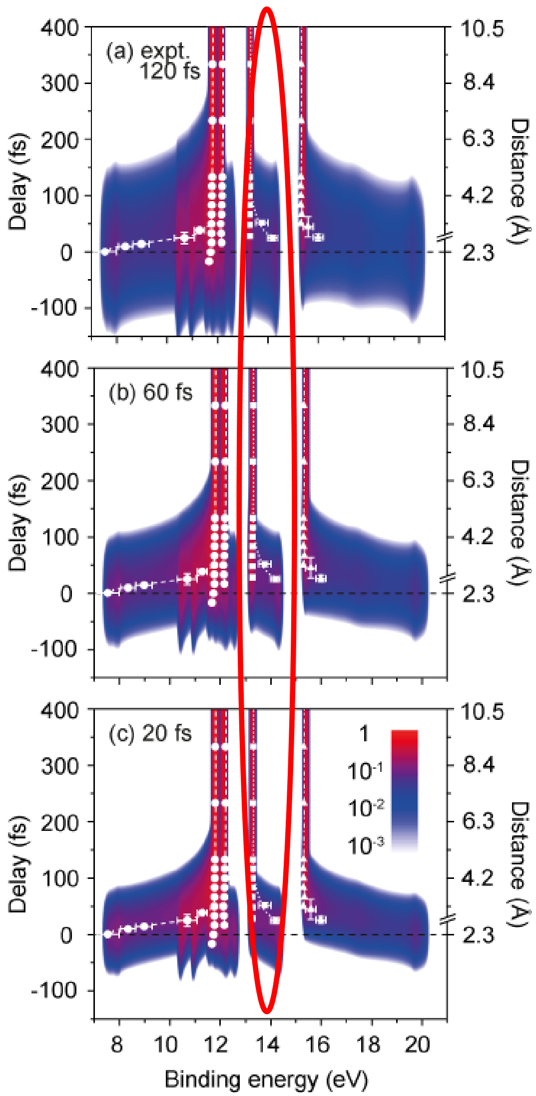
π orbital



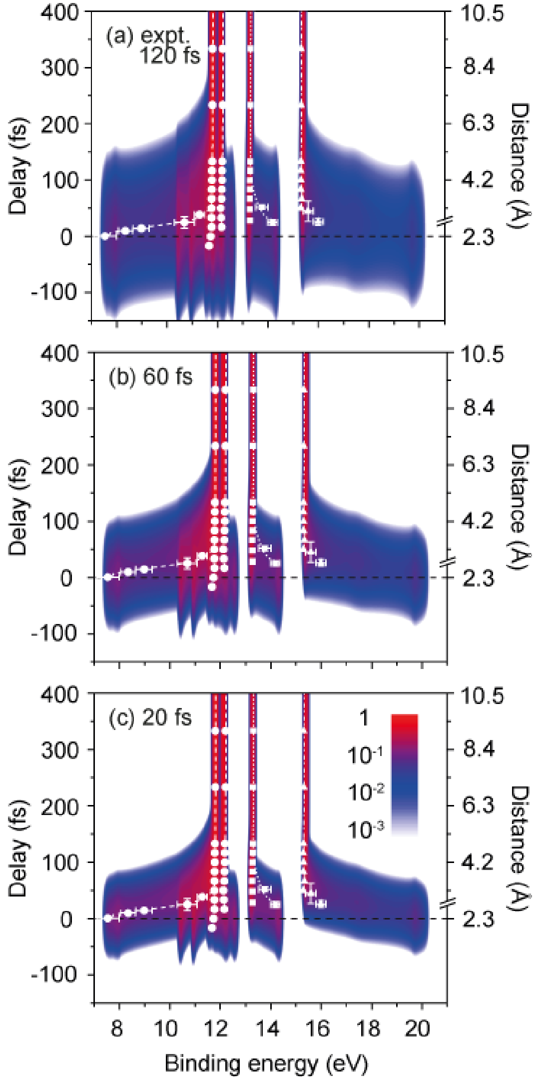
Dissociation time

Method	*Time (fs)*	*Distance (Å)*
TRPES Wernet et al., PRL 103, 013001 (2009).	85	3.8
$2 \cdot R_e$ (R_e = 2.3 Å)	120	4.6
Laser femto-chemistry	140-200	5-6
Ion momentum imaging Li et al., PNAS 107, 20219 (2010)	140	5
Interferometry with high harmonics Wörner et al, Nature 466, 604 (2010).	300	8.5

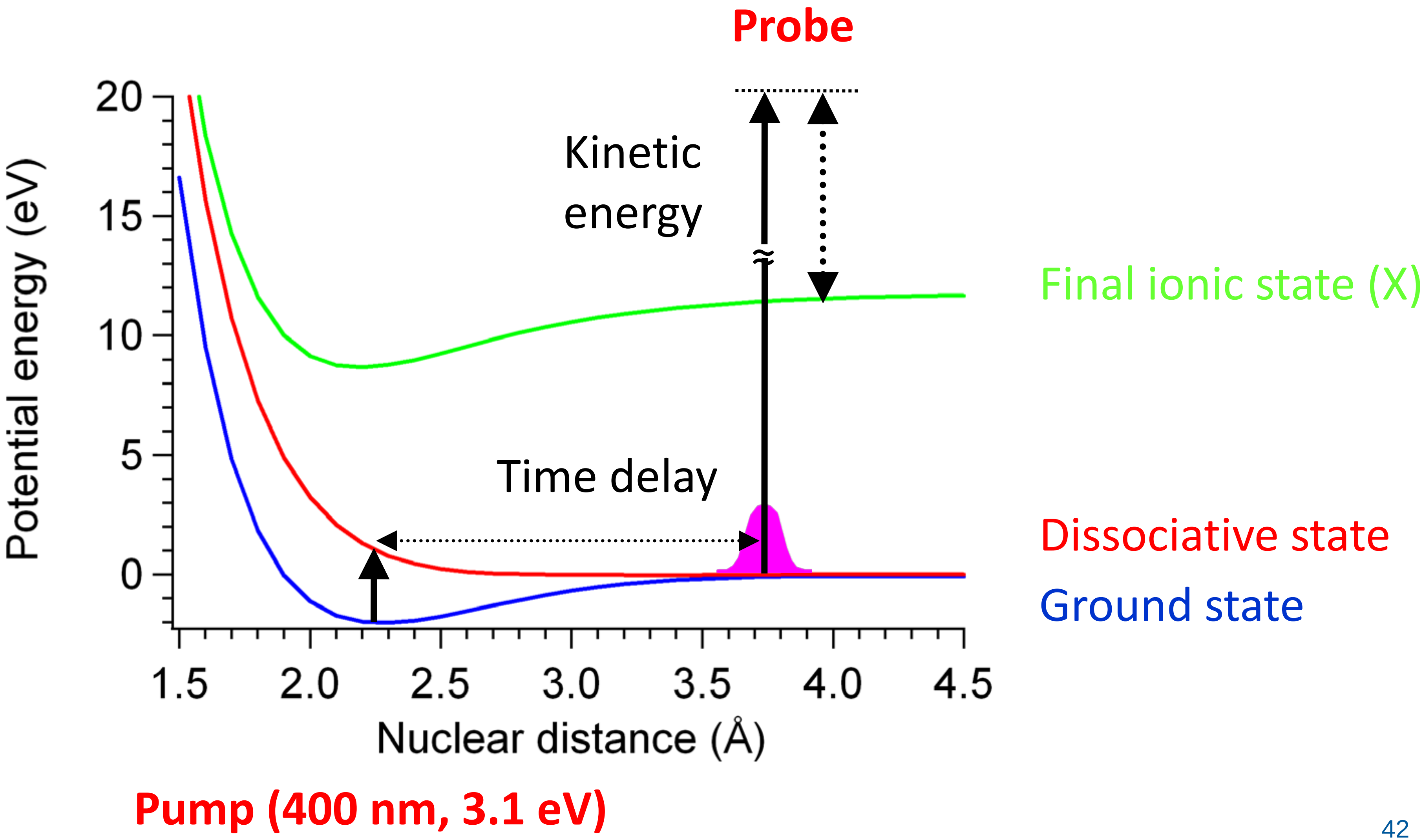
Does the temporal resolution influence the determination of the dissociation time?



Does the spectral resolution influence the determination of the dissociation time?



Diatomic molecule (Br_2, calculated)

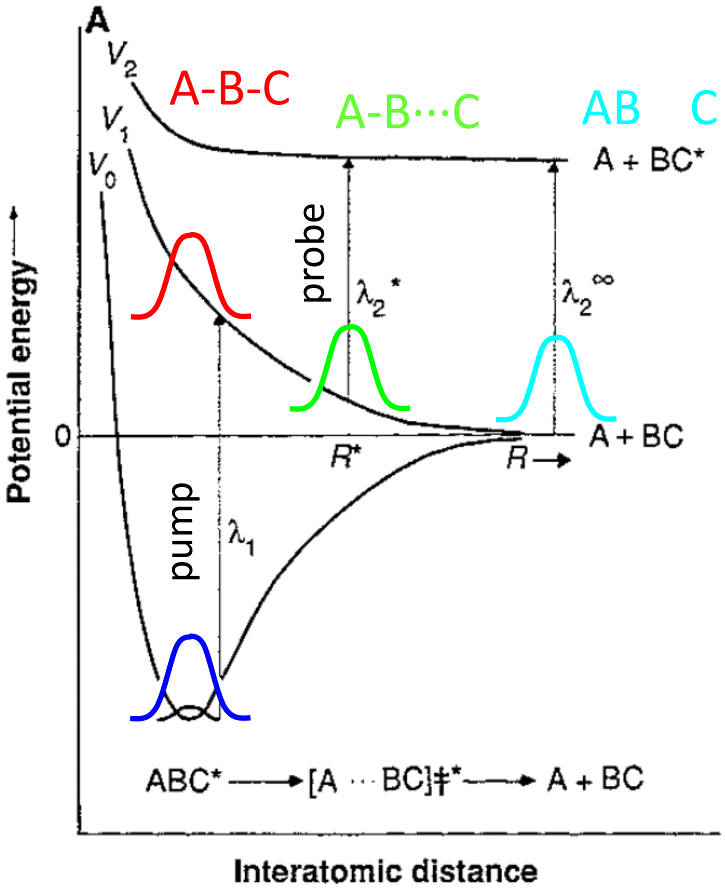


Dissociation time

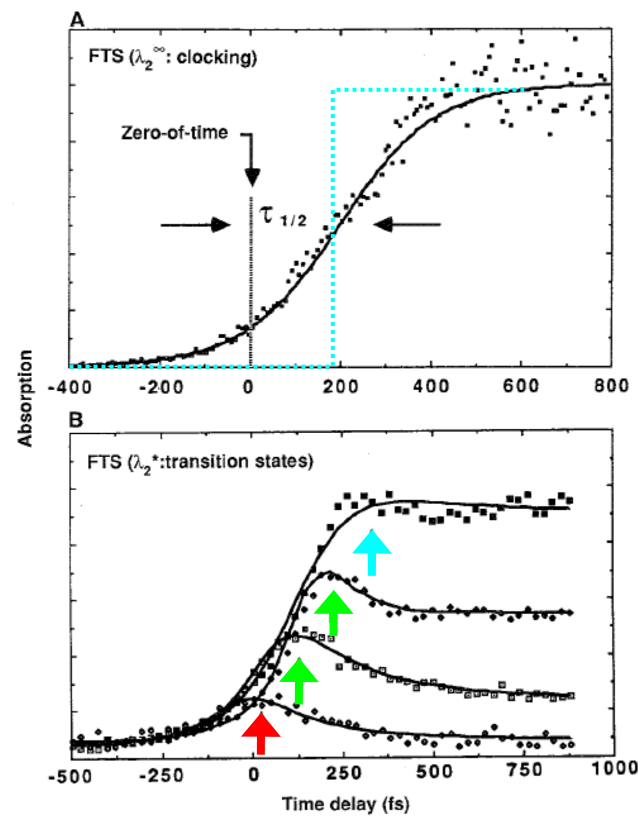
Method	*Time (fs)*	*Distance (Å)*	*Criterion*
TRPES Wernet et al., PRL 103, 013001 (2009).	85	3.8	Electronic structure
$2 \cdot R_e$ (R_e = 2.3 Å)	120	4.6	Common sense
Laser femto-chemistry	140-200	5-6	Dissociative state potential energy
Ion momentum imaging Li et al., PNAS 107, 20219 (2010)	140	5	Electronic structure
Interferometry with high harmonics Wörner et al, Nature 466, 604 (2010).	300	8.5	Electronic structure

Laser femtochemistry

A. Zewail, Laser femtochemistry, Science **242**, 1645 (1988).



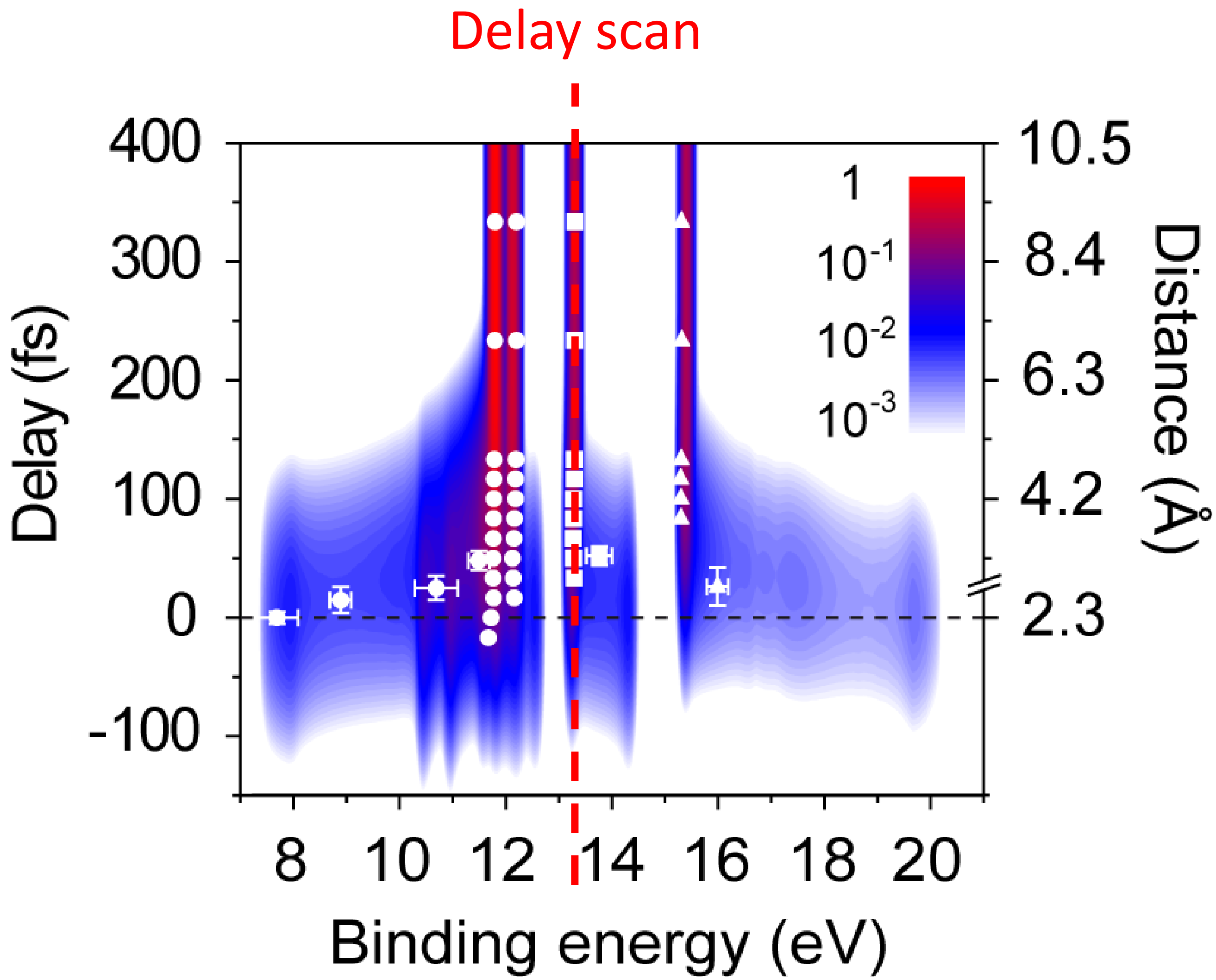
Experiment



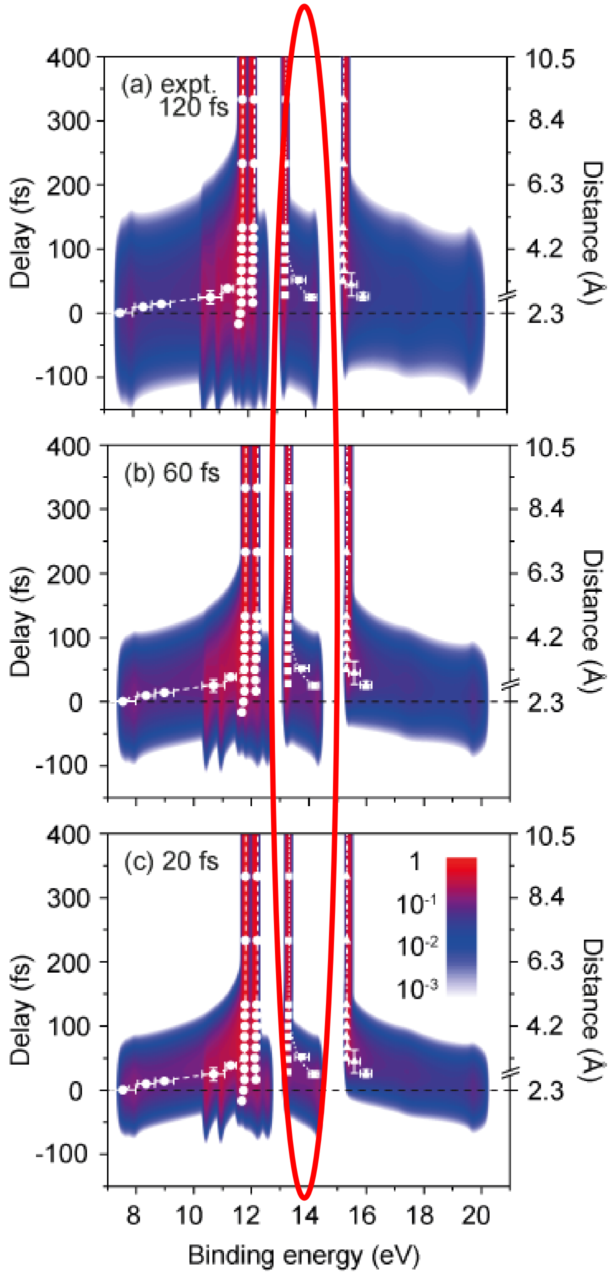
Real-time tracking of nuclear dynamics (1000 m/s = 1 Å/100 fs).

Direct comparison of experiment and theory

Pump/probe 60/120 fs



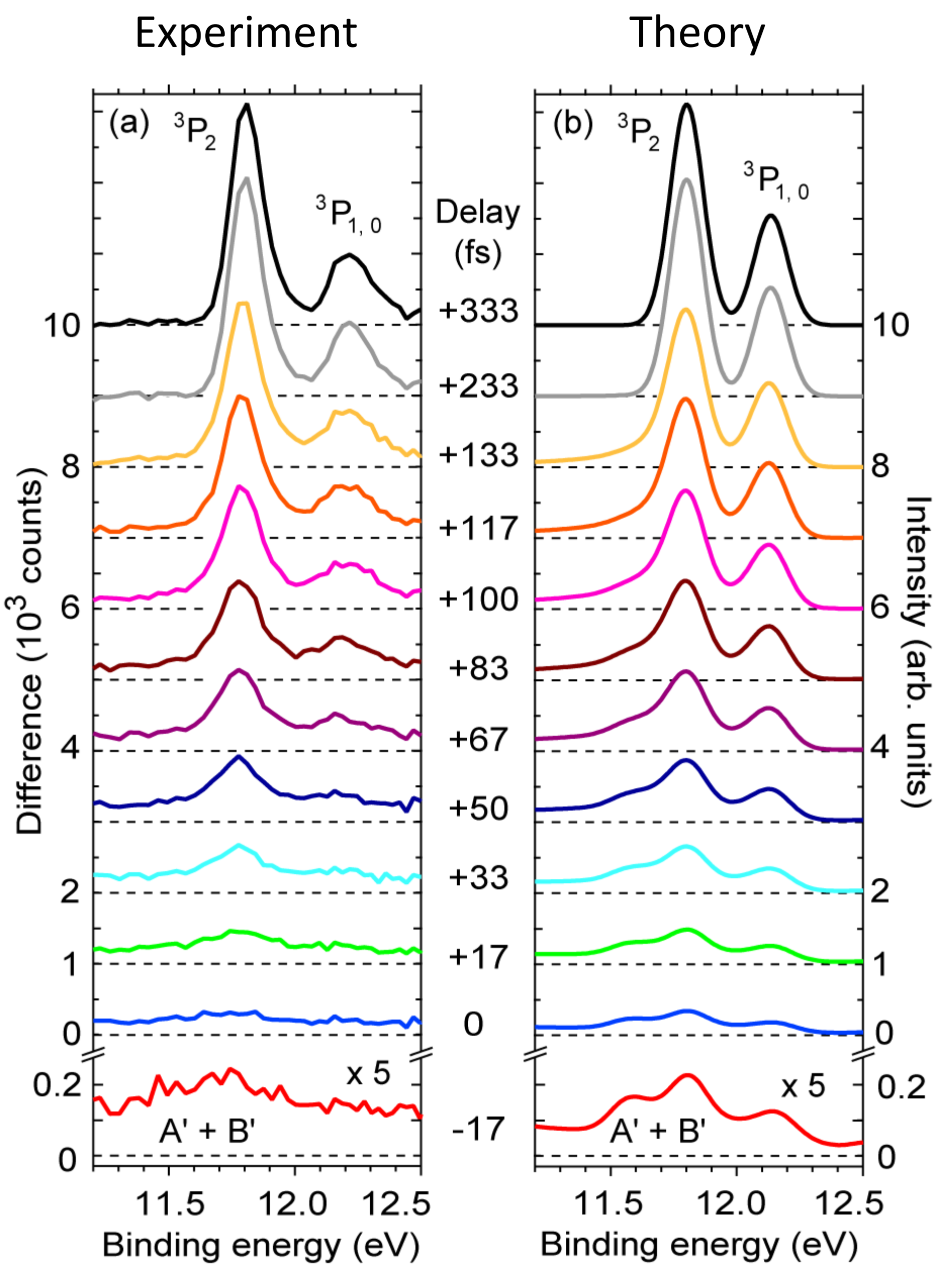
What time-resolution do we need?



Note (Fourier-transform limited pulses):

$$\Delta t_{FWHM} \times \Delta E_{FWHM} = 1.85 \text{ eV fs}$$

Spectral evolution from horizontal cuts



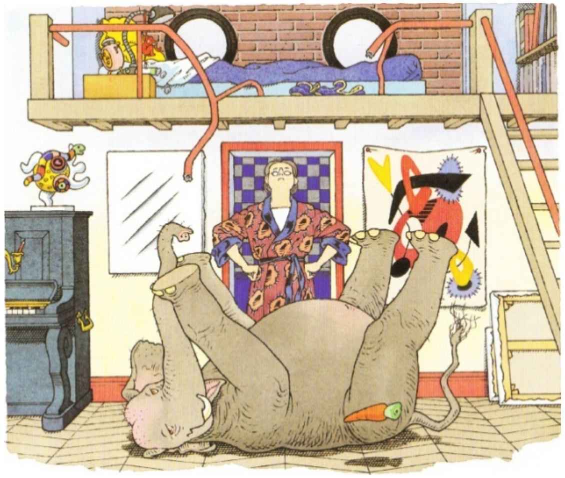
^3P of free atom

A‘ and B‘ of excited molecule

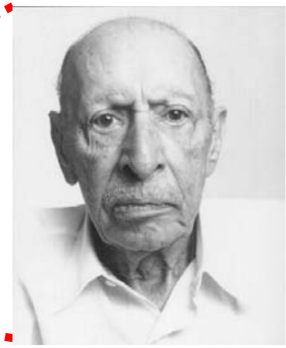
Outline

Part I What are we talking about? Some fundamentals…

Part II



Part III



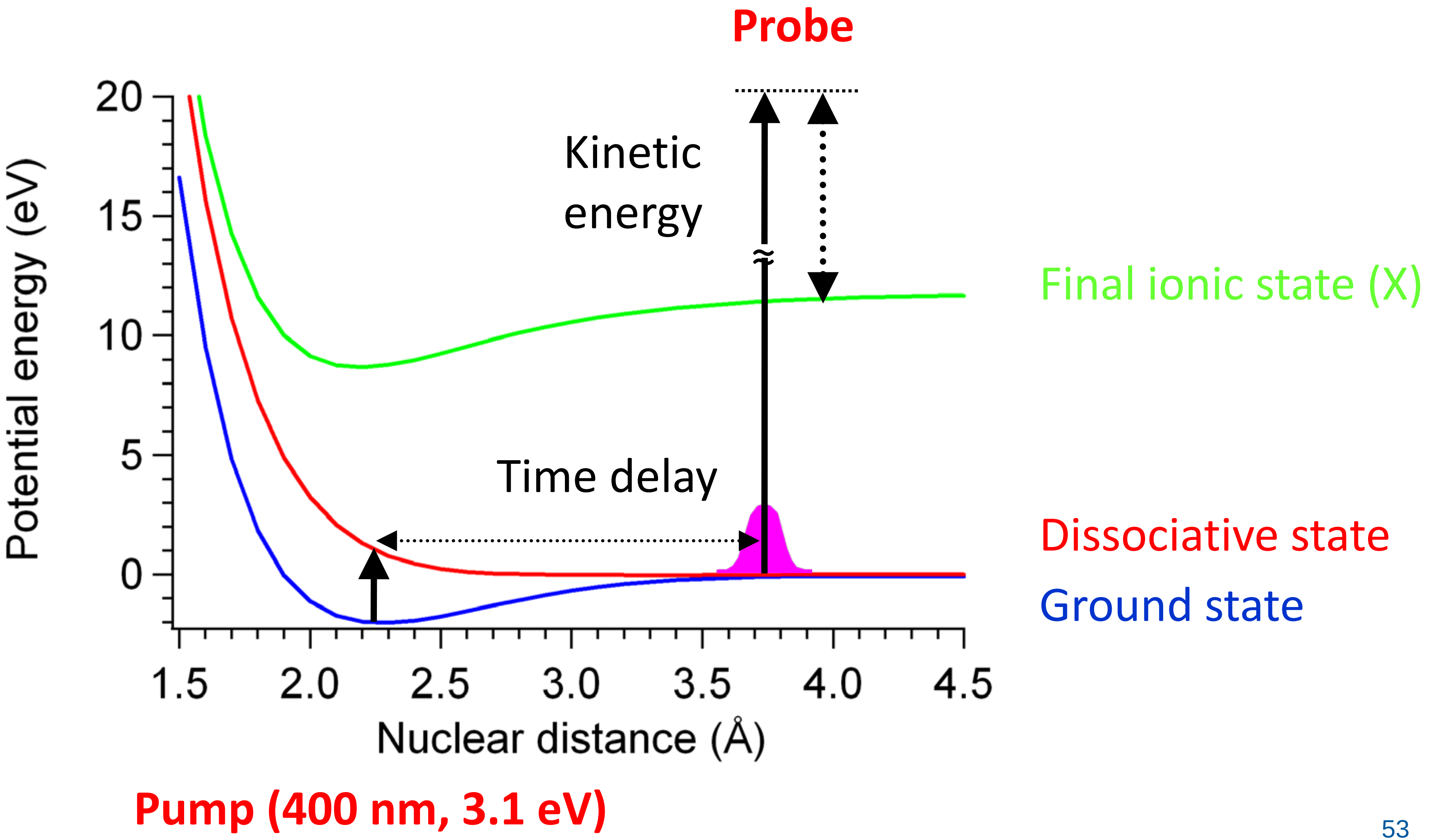
Richard Avedon – *Photographs 1946-2004*

Shibuya Hachiko crossing, Tokio – Photographed from Starbucks (2009)

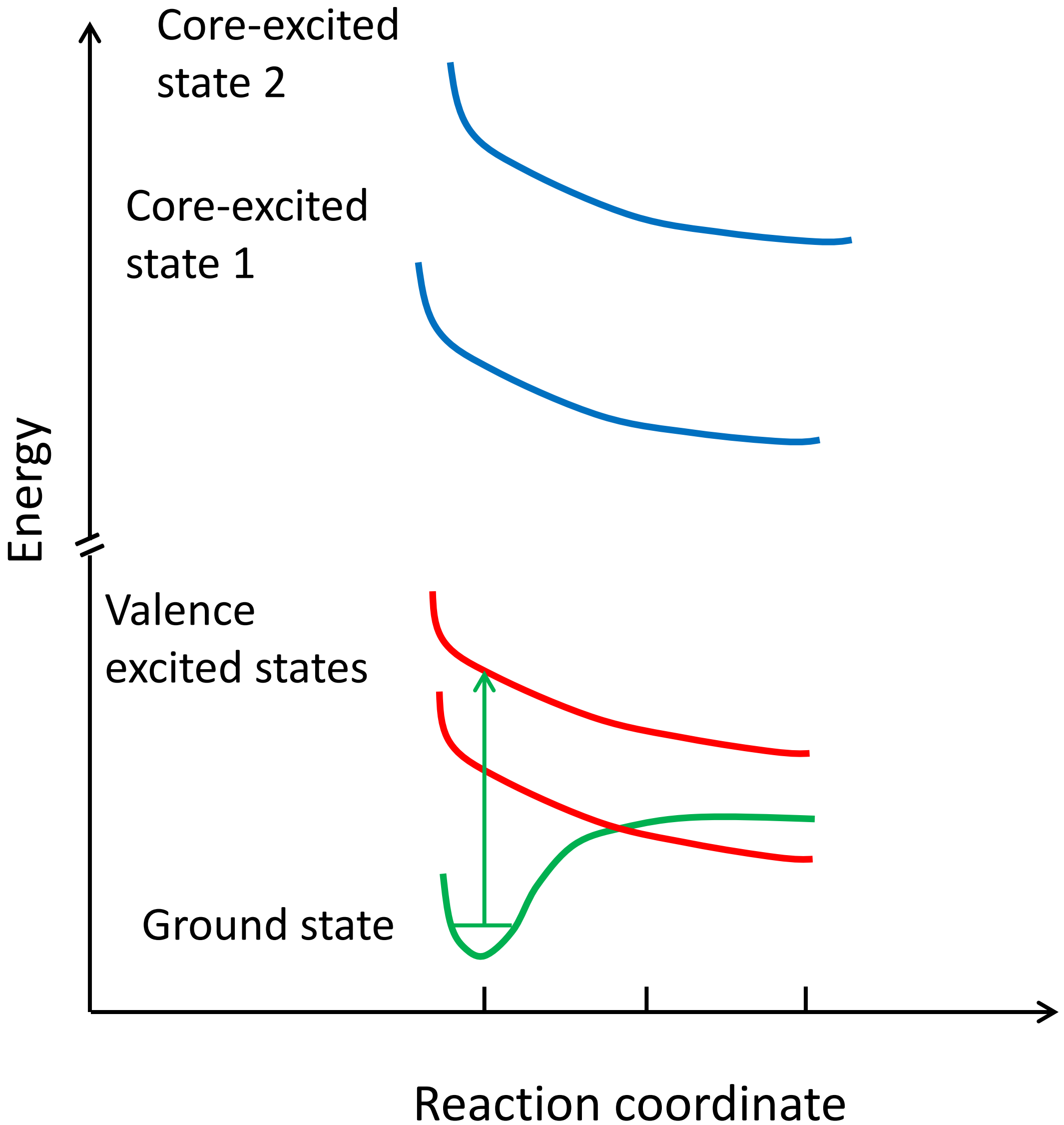
Shibuya Hachiko crossing, Tokio – Photographed from Starbucks (2009)

Quiz part III

Diatomic molecule (Br_2, calculated)



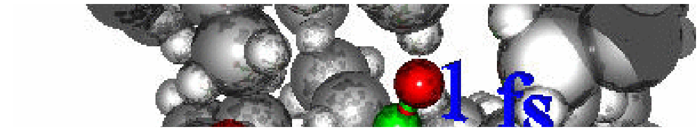
Where are the arrows for XAS and RIXS



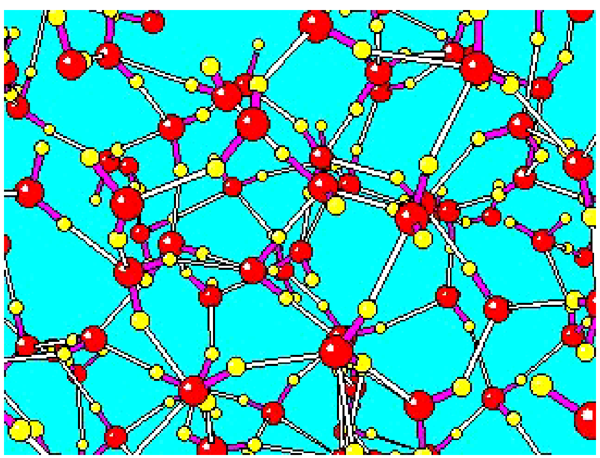
See the atoms move

Organic chemistry

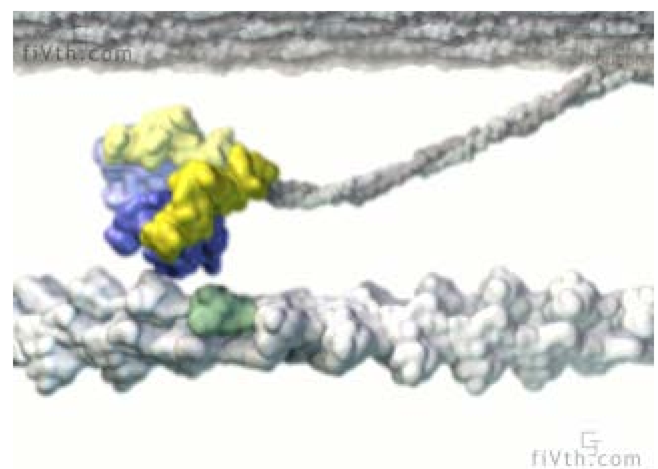
Photochemistry



But don‘t forget the electrons!



Lars Ojamäe, Linköping University , Sweden



http://www.molecularmovies.com/

Some extra slides

Chemical and thermodynamic equilibrium 1

Chemical equilibrium:

$Reactants \rightleftarrows Products$ e.g.: $A + B \rightleftarrows C + D$

$$Rate = \frac{d[Products]}{dt} \ \alpha \ [Reactants]$$

α: Proportional to

[…]: Concentration of …

e.g. $Rate = \frac{d[C]}{dt} \alpha \ [A] \cdot [B]$ (neglecting stochiometry and reaction order)

Proportionality constant k (rate konstant):

$$Rate = k \ \cdot [Reactants]$$

The rate (the rate konkstant) quantifies the speed/the efficiency of the reaction.

Chemical and thermodynamic equilibrium 2

$$Rate\ forward = Rate\ backward$$

$$k_{forward} \cdot [Reactants] = k_{backward} \cdot [Products]$$

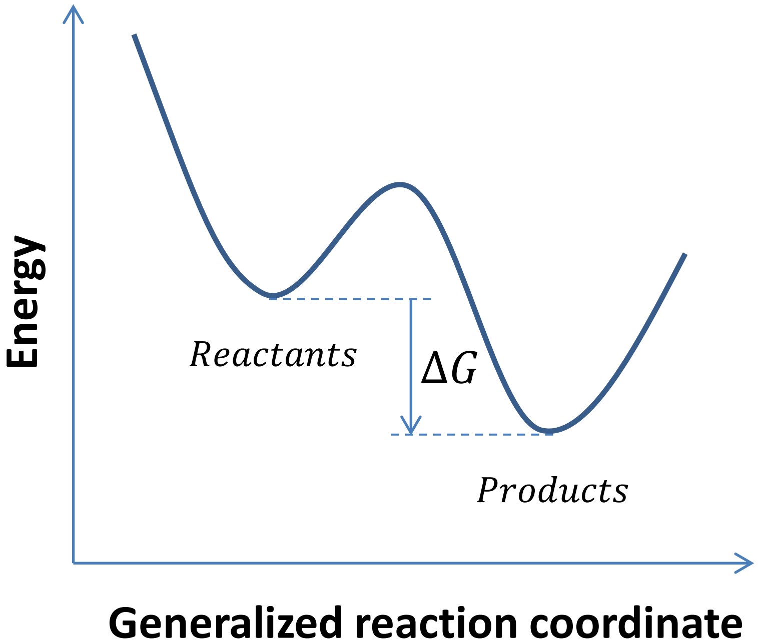
$$\Rightarrow \frac{k_{forward}}{k_{backward}} = \frac{[Products]}{[Reactants]} \equiv K$$ Equilibrium constant

Thermodynamic equilibrium:

$$\Delta G = -RT \cdot lnK$$

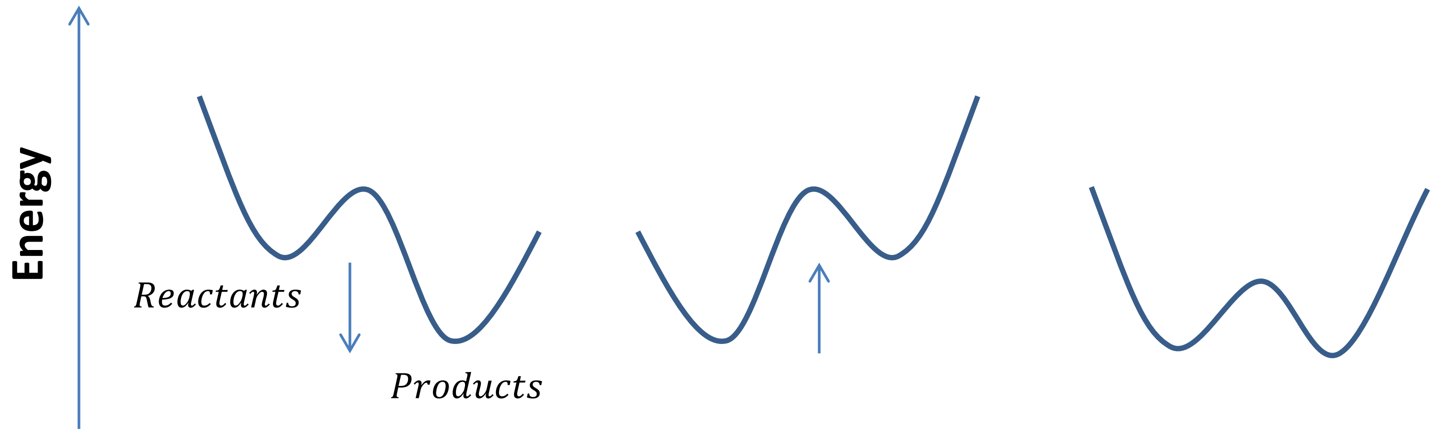
$$\Rightarrow \boxed{K = \frac{[Products]}{[Reactants]} = e^{-\frac{\Delta G}{RT}}}$$

with $\Delta G = G(Products) - G(Reactants)$



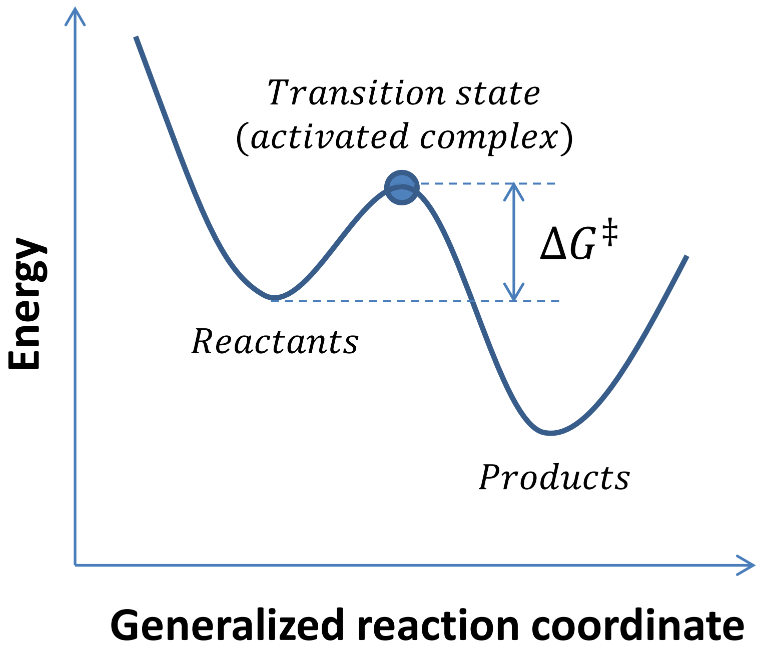
Chemical and thermodynamic equilibrium 3

$$K = e^{-\frac{\Delta G}{RT}}$$ with $\Delta G = G(Products) - G(Reactants)$



$\Delta G < 0$	$\Delta G > 0$	$\Delta G = 0$
$K \gg 1$	$K \gg 1$	$K = 1$
Energy is released	Energy is consumed	

Transition state theory 1



$$\Delta G^{\ddagger} = G(transition\ state) - G(Reactants)$$

$$Reactants \rightleftarrows Transition\ state \ \rightarrow Products$$

$$Rate = \ \upsilon \ \cdot [Transition\ state]$$

υ: Crossing frequency (frequency of crossing the barrier)

Collision frequency (for treatment within collision theory)

Neglecting molecular orientation (steric effects)

Transition state theory 2

With $Rate = k \cdot [Reactants]$ it follows:

$\upsilon \cdot [Transition\ state] = k \cdot [Reactants]$

Or

$$k = \upsilon \cdot K = \upsilon \cdot \frac{[Transition\ state]}{[Reactants]}$$

Sometime called the Eyring equation.

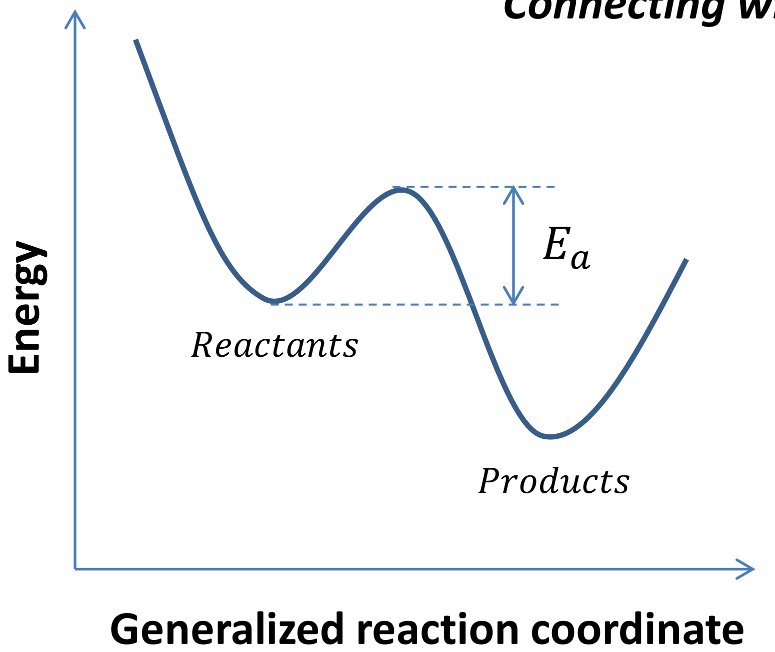
With $K = e^{-\frac{\Delta G^{\ddagger}}{RT}}$ we arrive at:

$$k = \upsilon \cdot e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

Sometime called the Eyring equation.

Transition state theory 3

Connecting with the Arrhenius equation



$$k = A \cdot e^{-\frac{E_a}{RT}}$$

E_a is the activation energy.

What is A (besides an experimental parameter)?

Does A have a physical meaning?

Can E_a be calculated?

Transition state theory gives answers:

- A could be the collision frequency: $A = \upsilon$
- A could be the collosion frequency including a factor ρ accounting for steric effects (such as the relative orientation of molecules): $A = \upsilon \cdot \rho$
- $E_a = \Delta G^{\ddagger}$ can be calculated

Transition state theory 4

Limitations

- Its original goal was to calculate absolute rate konstants („absolute-rate theory“).
- TST turned out to be more successful in calculating the thermodynamic properties of the transition state from measured rate constants (calculating the Gibbs energy $\Delta G^{\ddagger}$ as well as the enthalpy and entropy).
- TST neglects the possibility of tunneling through the barrier (it assumes that the reaction does not occur unless particles collide with enough energy to form the transition structure).
- TST can fail for high temperatures when high vibrational modes are populated and transition states far from the lowest energy saddle point are formed.
- TST assumes that intermediates (reactants and products, see above, of elementary steps in a multi-step reaction) are long-lived (reaching a Boltzmann distribution of energies) and thus TST fails for short-lives intermediates.
- TST generally fails for photochemical reactions (that are determined by the energy potential landscape rather than the thermodynamics properties of TSs).

Femtochemistry (A. Zewail)

Femtochemistry:
Atomic-Scale Dynamics of the Chemical Bond Using Ultrafast Lasers
(Nobel Lecture)**

Ahmed H. Zewail*

Angew. Chem. Int. Ed. **2000**, *39*, 2586–2631

5660 *J. Phys. Chem. A* **2000,** *104,* 5660–5694

FEATURE ARTICLE

Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond†

Ahmed H. Zewail

Arthur Amos Noyes Laboratory of Chemical Physics, Laboratory for Molecular Sciences, California Institute of Technology, Pasadena, California 91125

Received: April 18, 2000

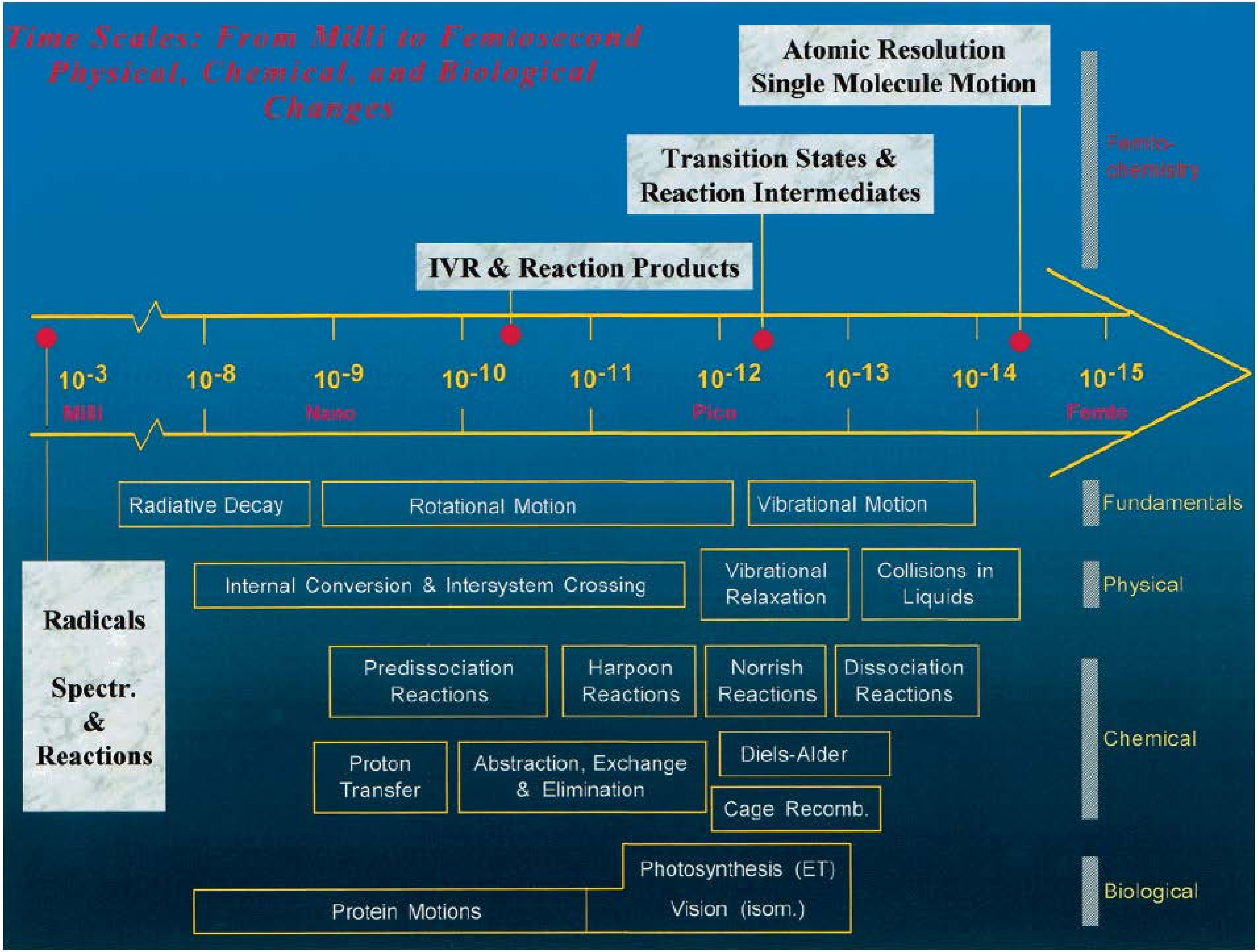


Figure 2. Time scales. The relevance to physical, chemical, and biological changes. The fundamental limit of the vibrational motion defines the regime for femtochemistry. Examples are given for each change and scale.

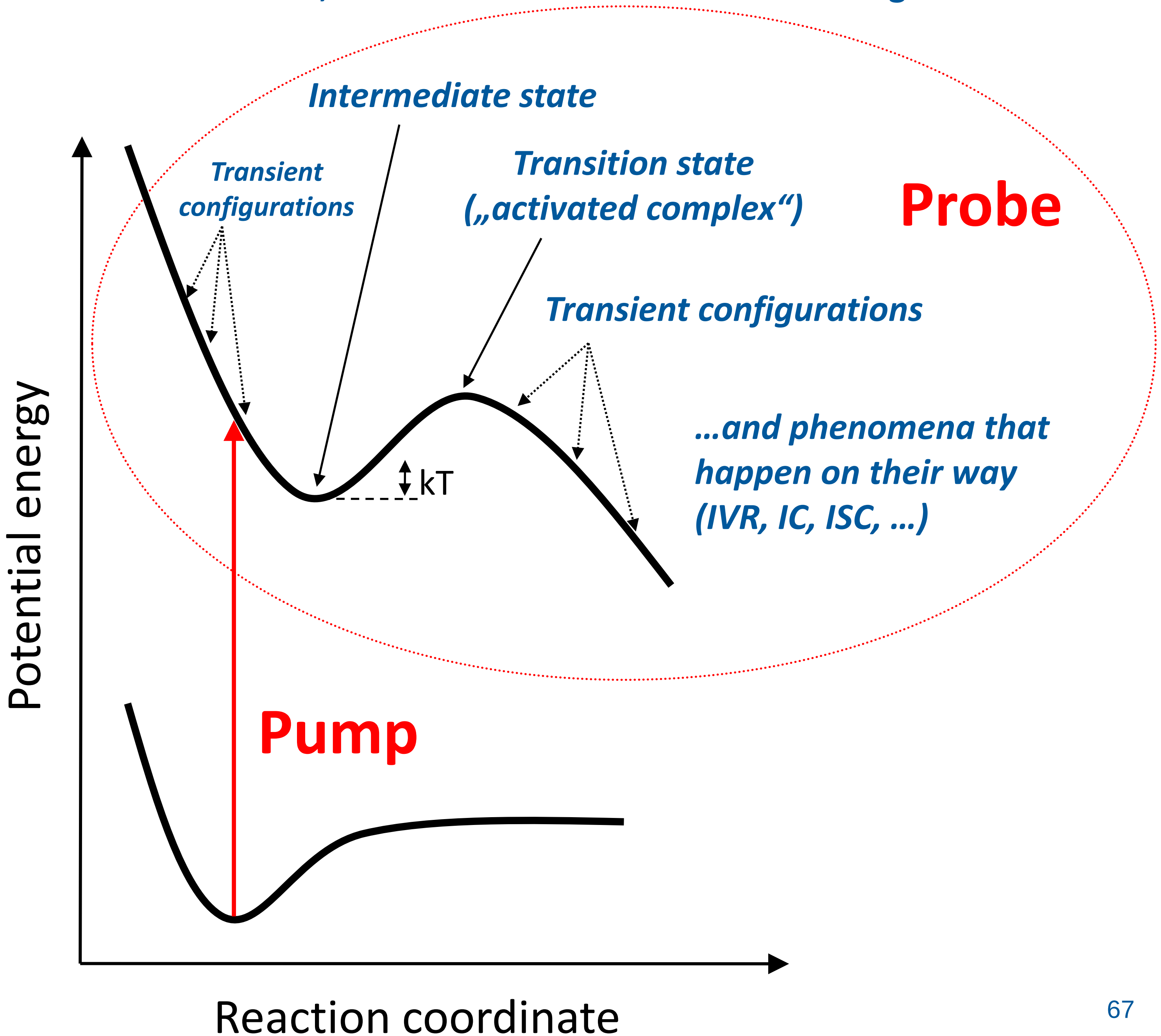
Important technical terms
(see EXTRA SLIDES for more detailed explanations)

- Reaction intermediate (next slide)
- Transition state (next slide)
- Transient species (next slide)
- Intramolecular vibrational redistribution (IVR)
  - **Redistribution of vibrational energy within one electronic state of the molecule**
- Internal conversion (IC)
  - **Conversion from electronic into vibrational energy within one molecule (vibronic coupling)**
- Intersystem crossing (ISC)
  - **Change of multiplicity of the molecule (e.g. change from singlet to triplet)**

See the IUPAC (International Union of Pure and Applied Chemistry) Gold Book:
http://goldbook.iupac.org/index.html

See the review paper by I. Hertel and W. Radloff:
Rep. Prog. Phys. 69, 1897 (2006).

Reaction intermediates, transition states and transient configurations



Reaction intermediates

Reaction intermediate / intermediate / reactive intermediate:

- Most chemical reactions occur in a step wise fashion with more than one elementary step
- *Reaction intermediate* =
  - **Molecular entity formed from the reactants or preceding intermediates in each step (except for the last one)**
  - **With a lifetime appreciably longer than a molecular vibration corresponding to a local potential energy minimum of depth greater than kT**
  - **Reacts further to give the directly observed products of the reaction (last step)**
- Are usually *short lived* and seldom isolated
- Need to be distinguished from *transition states* (through their lifetime)

Transition states

Transition states:

- The state through which the molecule must pass as it changes from reactants or intermediates to products or another set of intermediates
- The state corresponding to the highest energy along the corresponding reaction coordinate (nuclear distance e.g.)
- The molecules goes through *transient states* / *transient species* / *transient configurations* as they pass the transition state
- This often involves bond breaking and making
- See also *transition state theory*, *transition state method*, *activated complex* (slightly different from the transition state)

See also:

5660 *J. Phys. Chem. A* **2000,** *104,* 5660–5694

FEATURE ARTICLE

Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond†

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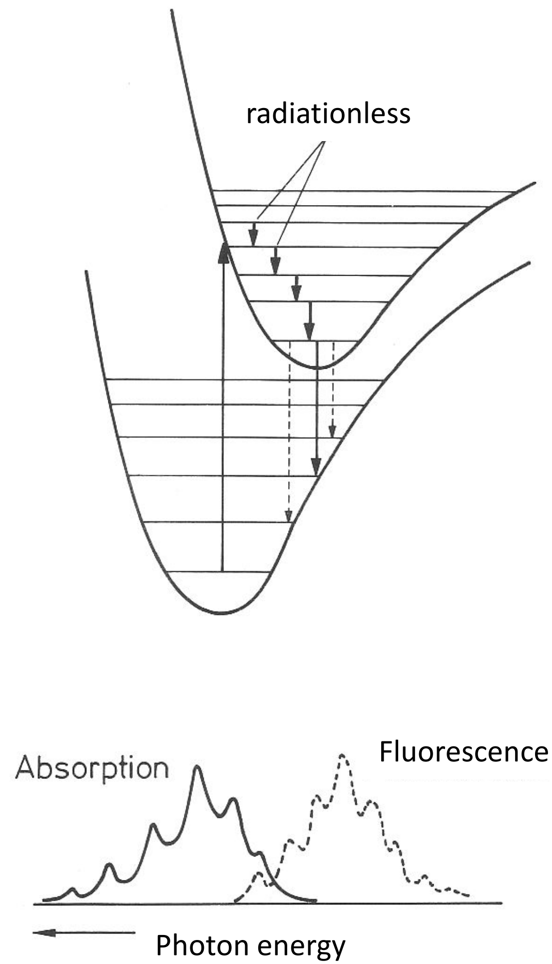
Received: April 18, 2000

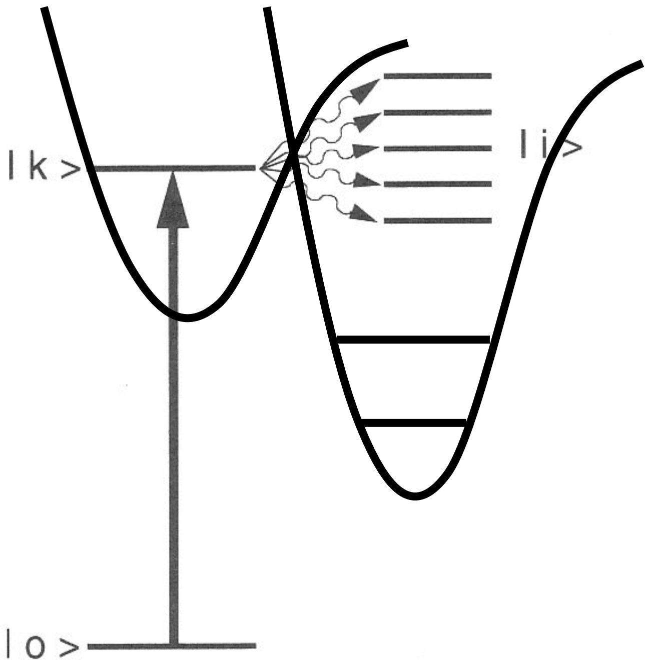
Intramolecular vibrational redistribution (IVR)

- Redistribution of vibrational energy within one electronic state of the molecule
- IVR leads from the initially populated vibrational states (e.g. a particular stretch vibration) to a broad distribution of vibrational energy equilibrated over all vibrational degrees of freedom (e.g. all stretch and bend vibrations)
- Usually occurs on a time scale of ps to ns
- Can be described by coupled anharmonic oscillators which exchange energy
- IVR is a sequence of radiationless transitions
- IVR leads to the fact that the fluorescence is red-shifted compare to the absorption (see figure)
- If the molecule is embedded in a medium (e.g. a liquid), IVR is faster than in the isolated molecule and leads to a thermalization with respec to the temperature of the medium



Internal conversion (IC)

- Conversion from electronic into vibrational energy within one molecule
- Radiationless transition within one molecule
- Usually occurs on a time scale of fs to ps
- Mediated by vibronic coupling (see figure) between different electronic states of the same molecule



Model for vibronic coupling

Intersystem crossing (ISC)

- Change of multiplicity of the molecule (e.g. change from singlet to triplet)
- Radiationless transition within one molecule
- Usually occurs on a time scale of ps to µs
- Mediated by spin-orbit coupling (often/fast when heavy atoms are present)
- Often results in phosphorescence (see figures comparing fluorescence and phosphorescence)

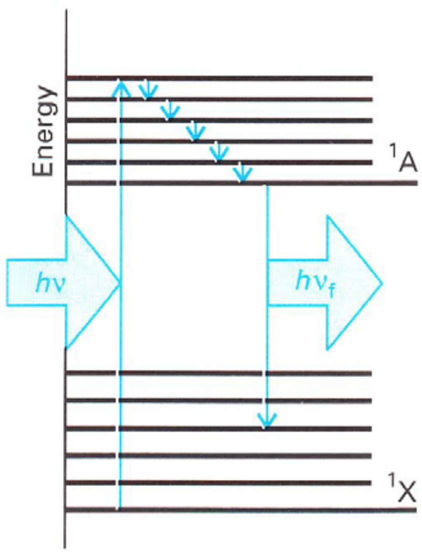


Fig. 11.21 The mechanism of fluorescence. The vibrational relaxation is non-radiative.

From: Atkins, Friedman, Molecular quantum mechanics

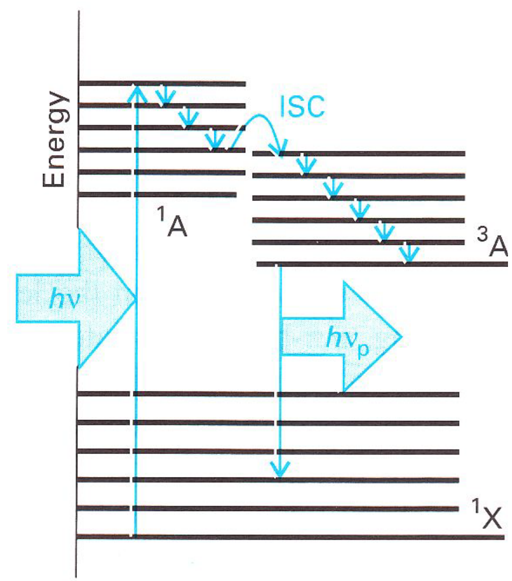


Fig. 11.22 The mechanism of phosphorescence. The vibrational relaxation is non-radiative; ISC stands for intersystem crossing, and is induced by spin–orbit coupling.

Environments: Where chemical dynamics occurs

- Gas phase
  - **Low concentrations (10^{10}-10^{13} molecules/cm^3) limits the set of methods**
  - **Elementary reactions, “simple” systems, isolated systems**
  - **Hard to get certain molecules into the gas phase (biomolecules e.g.)**
- Liquids
  - **Solutes (note the higher concentrations than in the gas phase: 1 mol/l corresponds to approximately 10^{20} molecules/cm^3)**
  - **Solvents (hydrogen-bond dynamics, collective phenomena)**
  - **Their interactions**
- Bio-molecules
  - **Special case (depending on sample preparation in the gas phase, in solution or in solids)**
- Surfaces/interfaces
  - **Often treated in a specialized community due to very different sample preparation in vacuum**
  - **Very few x-ray methods applied to chemical dynamics on surfaces (W. Wurth/Hamburg, A. Nilsson/Stanford)**
- Rarely: In solids (e.g. crystals, rare gas matrices)

Other methods (not using x-rays)

- "Laser femtochemistry" → ***Sets the stage!***
  - **Pump-probe methods with laser/optical/IR/THz wavelengths**
  - **Detecting ions, fluorescence etc.**
- Laser photoelectron spectroscopy → ***Strong overlap with x-ray PES***
  - **Special case of "laser femtochemistry"**
- Electron scattering → ***Hard to get fs pulses but high spatial resolution!***
  - **Gas phase**
  - **Surfaces**
- fs-IR spectroscopy → ***Strong overlap with XAS/EXAFS (in terms of insight)***
  - **Liquids**
  - **Surfaces**

Why x-rays?

Why x-rays?

Why x-rays for studying chemical dynamics?

- X-ray absorption spectroscopy (XAS/XANES/NEXAFS) and Extended X-ray Absorption Fine Structure (EXAFS)
  - **Element and chemical state selective ("chemical shift")**
  - **Local (starts from a core level which is well localized in space)**
  - **Symmetry sensitive (dipole selection rule implies sensitivity to orbital symmetry)**
  - **Combines sensitivity to electronic and geometric structures**
- X-ray scattering
  - **Structural probe with atomic scale resolution (both in time and space)**
  - **Global view (e.g. solute and solvent)**
- Photoelectron spectroscopy (PES)
  - **See XAS/EXAFS**
  - **In contrast to laser PES: Reach all possible ionic final states (complete picture)**
- Resonant Inelastic X-ray Scattering (RIXS)
  - **See XAS/EXAFS**

Study fundamental aspects of elementary reactions

X-ray methods: How to probe chemical dynamics

- X-ray absorption spectroscopy (XAS/XANES/NEXAFS) and Extended X-ray Absorption Fine Structure (EXAFS) → ***Mostly hard x-rays***
  - **Liquids**
  - **Bio-molecules**
  - **[Surfaces/interfaces]**
- X-ray scattering → ***Exclusively hard x-rays (so far only ps time resolution)***
  - **Liquids**
  - **[Gas phase, future at FELs (holography from within)?]**
- Photoelectron spectroscopy (PES) → ***Mostly laser and VUV wavelengths***
  - **Gas phase**
  - **Surfaces/interfaces**
  - **[Liquids]**
- Resonant Inelastic X-ray Scattering (RIXS) → ***Well suited for liquids***
  - **Liquids**
  - **Solids/surfaces/interfaces**
  - **Not yet for gas phase and bio-molecules (target density)**