

# Chemical dynamics with ultrafast X-rays

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UXSS11, June 2011, DESY (Hamburg).

# What is “Chemical Dynamics”?

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**CHEMICAL DYNAMICS, INC.**



# What is “Chemical Dynamics”?

## The atomic-scale dynamics of chemical interactions.

Atomic-scale= „Ultrafast“ (pico- to femtoseconds) and „ultrasmall“ (Ångstrom)

Dynamics of chemical interaction = Chemical bonding as it changes during chemical reactions or elementary steps of chemical reactions.

The *reaction rate* (*rate constant k*) quantify the „speed“ of an overall reaction, e.g.,  $n A + m B \rightarrow C + D$ :

$$\frac{d[C]}{dt} = k(T)[A]^{n'}[B]^{m'}$$

[...] = concentration of ..., T = Temperature, n'/m' = reaction orders

**Chemical dynamics deals with the atomic-scale view of the elementary steps of a chemical reaction.**

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

# 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

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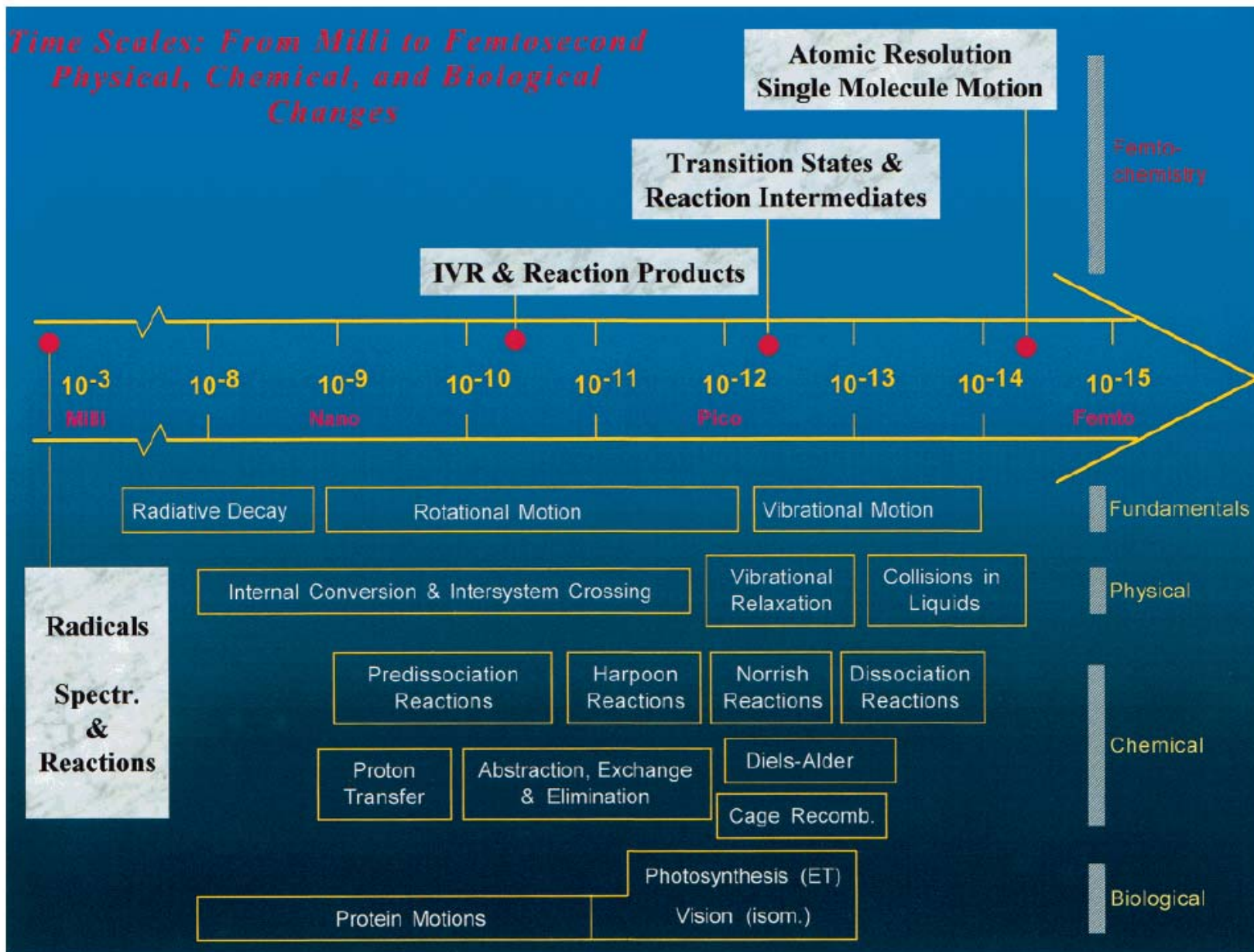
### **Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond†**

**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*

*Time Scales: From Milli to Femtosecond  
Physical, Chemical, and Biological  
Changes*



**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

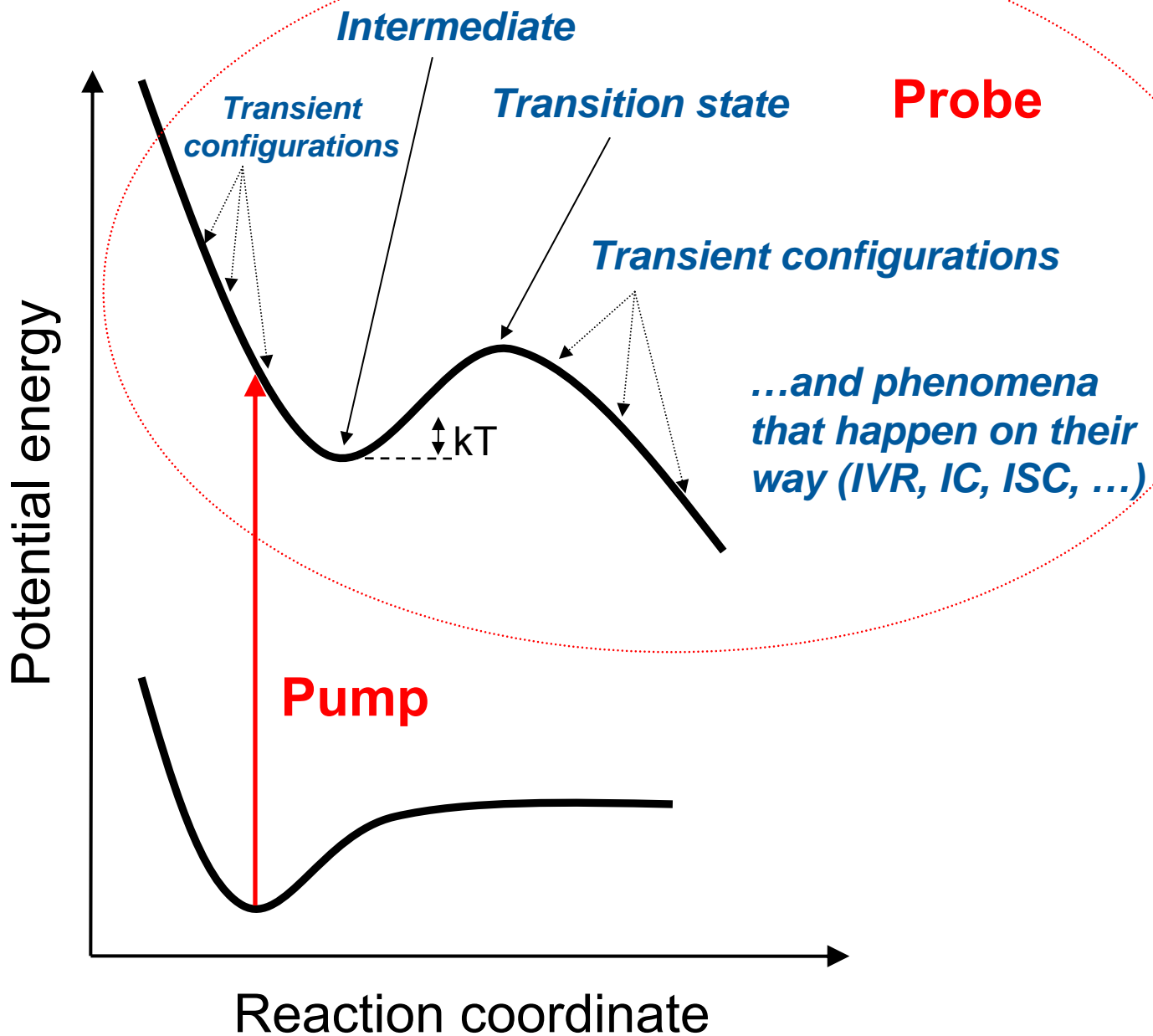
(see **EXTRA SLIDES** for more detailed explanations)

- 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



# Outline

- What is “Chemical Dynamics”?
- Nobel prizes in Chemistry (Zewail 1999, Ertl 2007) and the molecular movie
- Nat dynamics in the gas phase
- Fundamentals
  - Wavepackets
  - Born-Oppenheimer-Approximation
  - Franck-Condon factor and Franck-Condon-Principle
  - Molecular Orbitals
- Environments: Where chemical dynamics occurs
- X-ray methods: How to probe chemical dynamics
- Other methods (not using x-rays)
- Representative examples (subjective collection)
- Summary and conclusions



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

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



**The decisive moments in the life of molecules**

We need to know the properties of the transition state if we are to understand, predict and perhaps modify the course of a reaction. For almost a hundred years the transition state remained a hypothetical species that few chemists believed could ever be observed. But this is precisely what Zewail has succeeded in doing.

„The fastest camera in the world“ records what happens in a chemical reaction by initiating the reaction with a femtosecond laser pulse (start pulse). A short time later a second pulse (observation pulse) takes a “picture” of the reacting molecules.

The experiment gives no direct image of the molecules. Instead, the reacting molecules are observed by measuring certain characteristic properties, e.g. an optical property (a spectrum is obtained) or by recording the molecular masses (mass spectrometry).

By successively delaying the observation pulse in relation to the start pulse a “film” is obtained of the course of the reaction. The previously predicted but oh so ephemeral transition state can be identified and characterised.

The diagram illustrates the experimental setup and the reaction progress. A laser beam is split into a start pulse and an observation pulse. The start pulse initiates a chemical reaction, and the observation pulse captures the state of the molecules at a specific time. The resulting spectrum is recorded. The reaction progress is shown as a film strip with molecular models at different stages. A molecular beam is also shown entering the setup.

**Laser**, **Start pulse**, **Observation pulse**, **Molecular beam**, **Spectrum**

Foto: Caltech

The picture shows part of Zewail's “camera”. It is a complex array of lasers, mirrors, lenses, prisms, molecular beams, detection equipment and more.

# G. Ertl, Nobel price in Chemistry (2007)

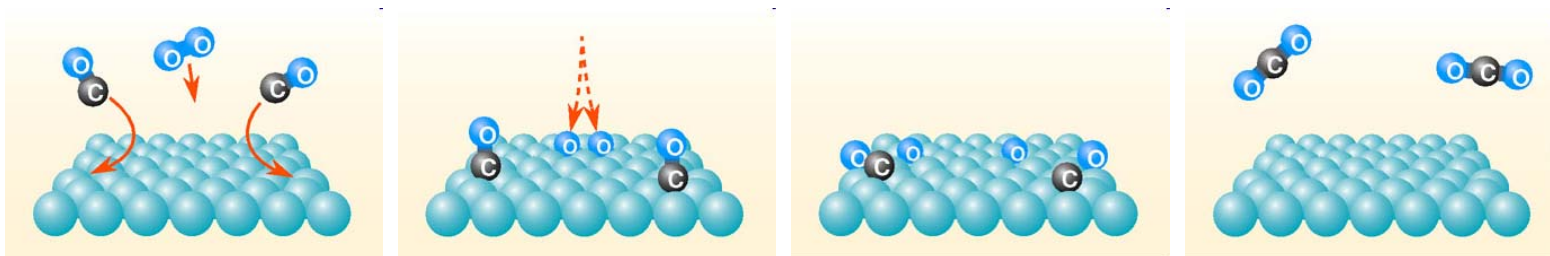
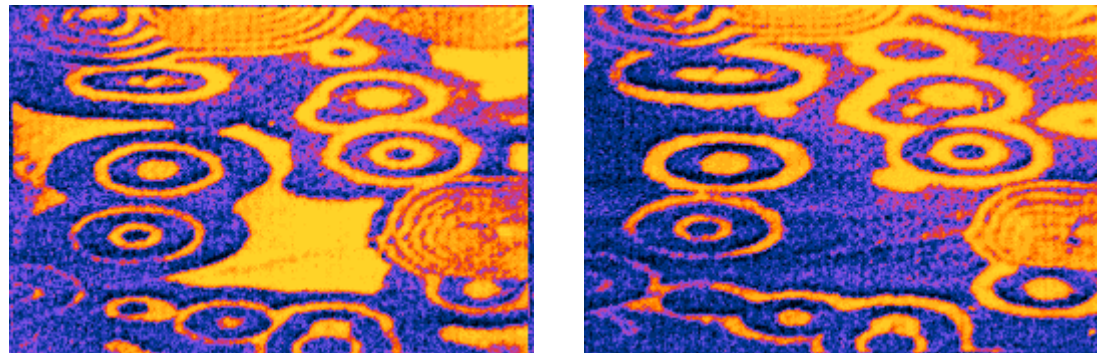
„...for his studies of chemical processes on solid surfaces.“

**Nobel Lecture** [http://nobelprize.org/nobel\\_prizes/chemistry/laureates/2007/ertl-lecture.html](http://nobelprize.org/nobel_prizes/chemistry/laureates/2007/ertl-lecture.html)

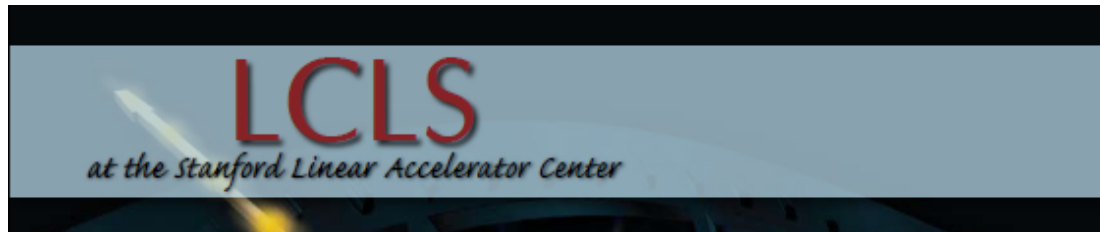
„Reactions at Surfaces: From Atoms to Complexity“



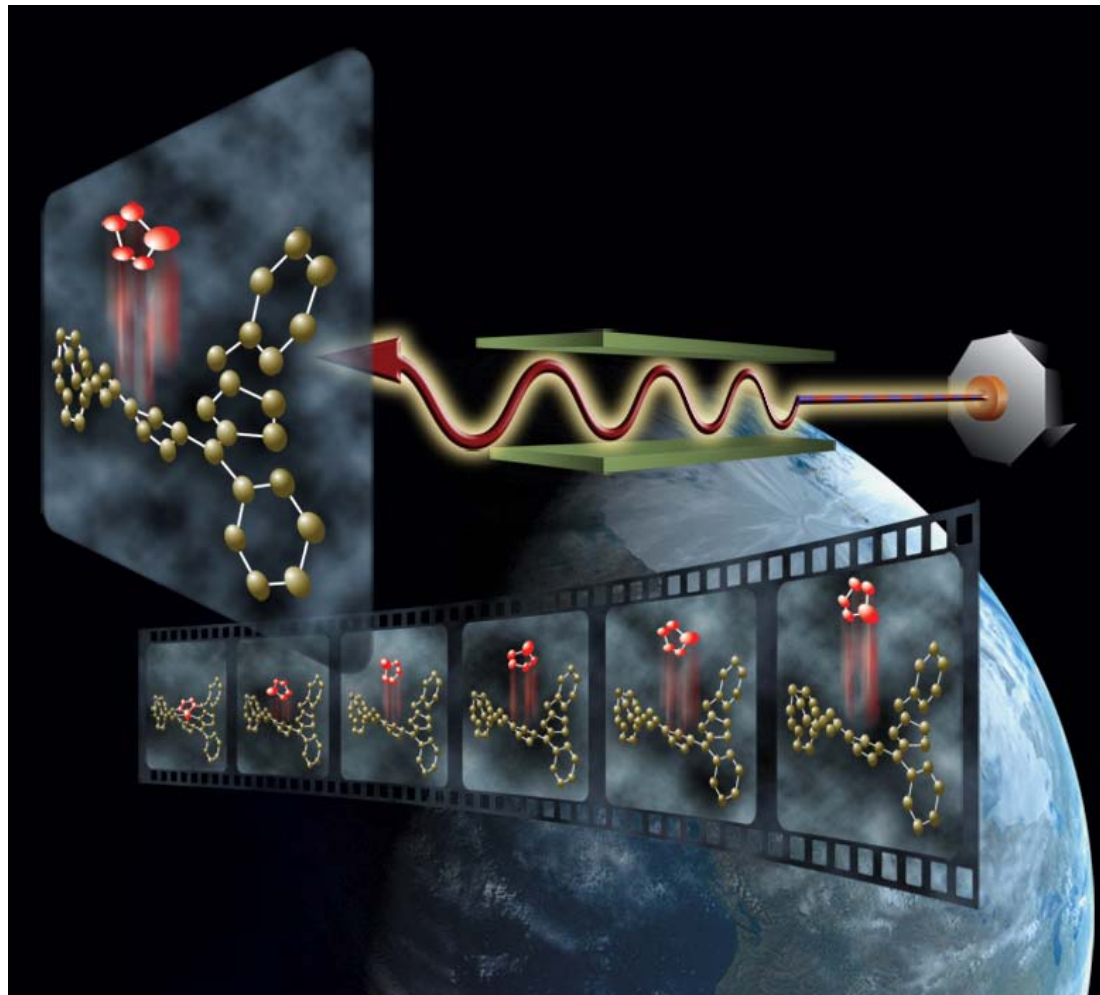
*Pattern formation on the surface (slow dynamics, reaction rates)*



# The molecular movie – LCLS (Stanford)

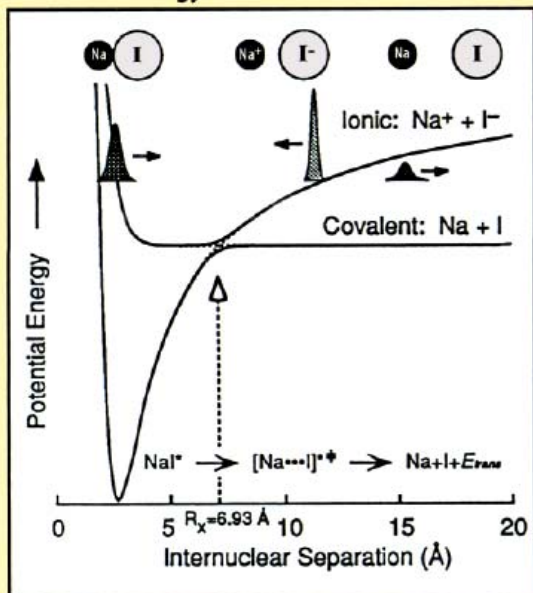


## LCLS Brochure

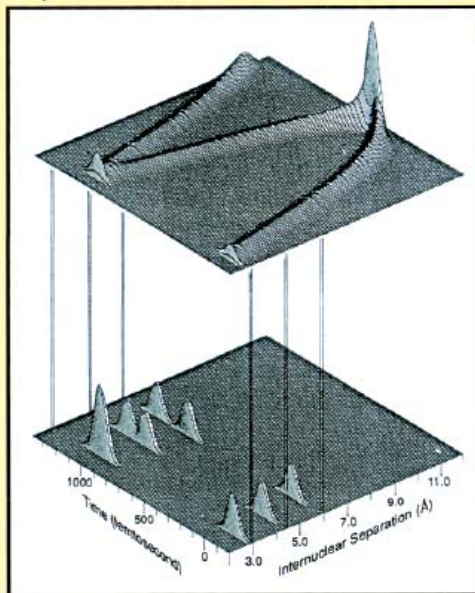


# NaI dynamics in the gas phase

## Potential Energy Surfaces



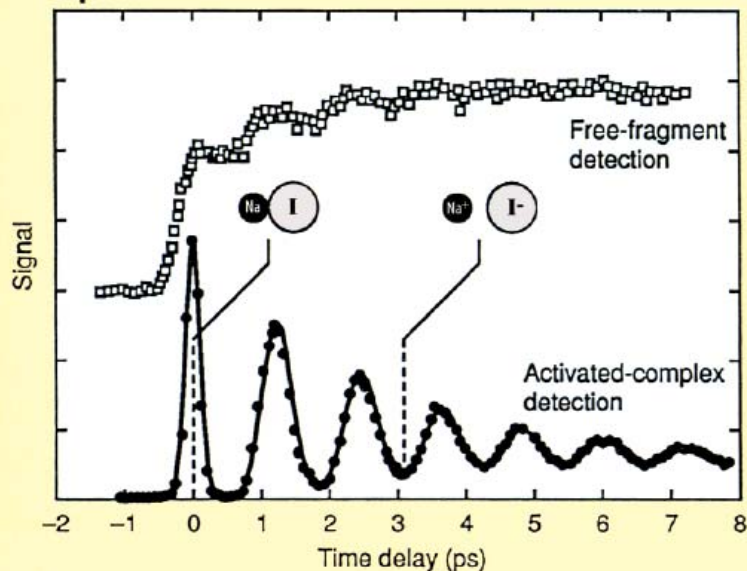
## Trajectories R,t



*A text-book example for chemical dynamics (A. Zewail)*

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

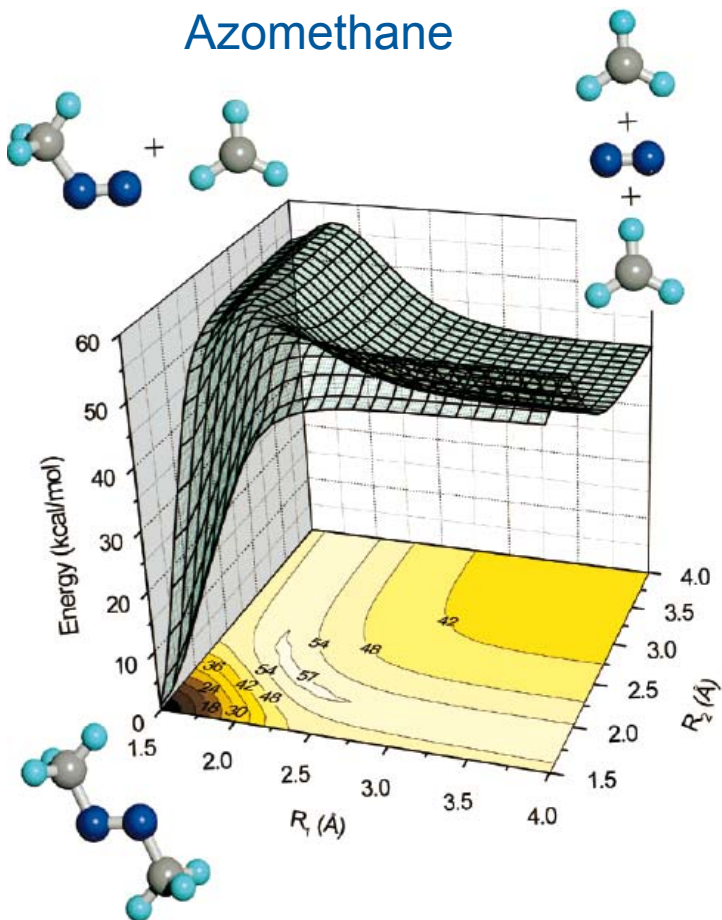
## Experimental



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

# More complicated cases...

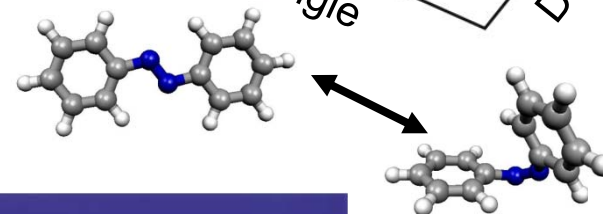
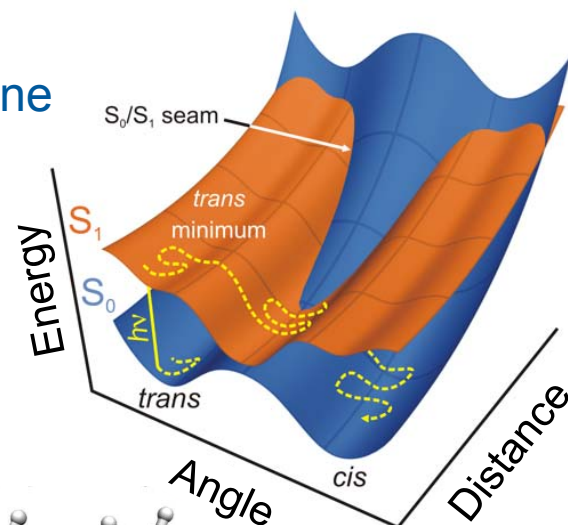
## Azomethane



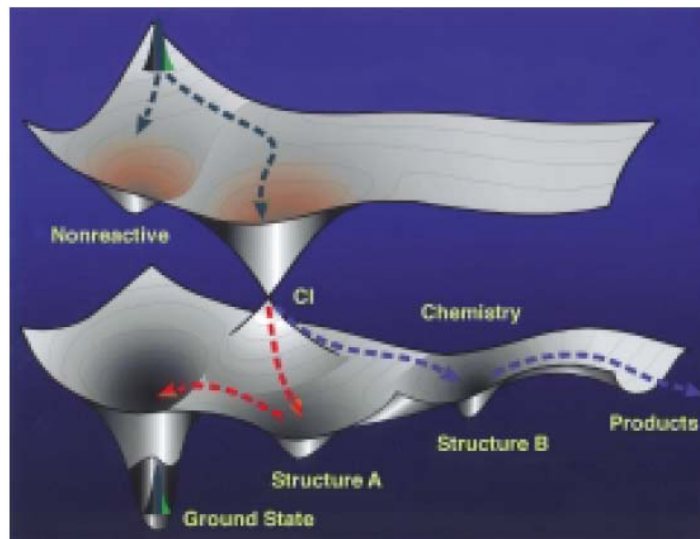
*J. Phys. Chem. A* 2000, 104, 5660–5694

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

## Azobenzene



## Generic



# Fundamentals: Wavepackets

A. Zewail

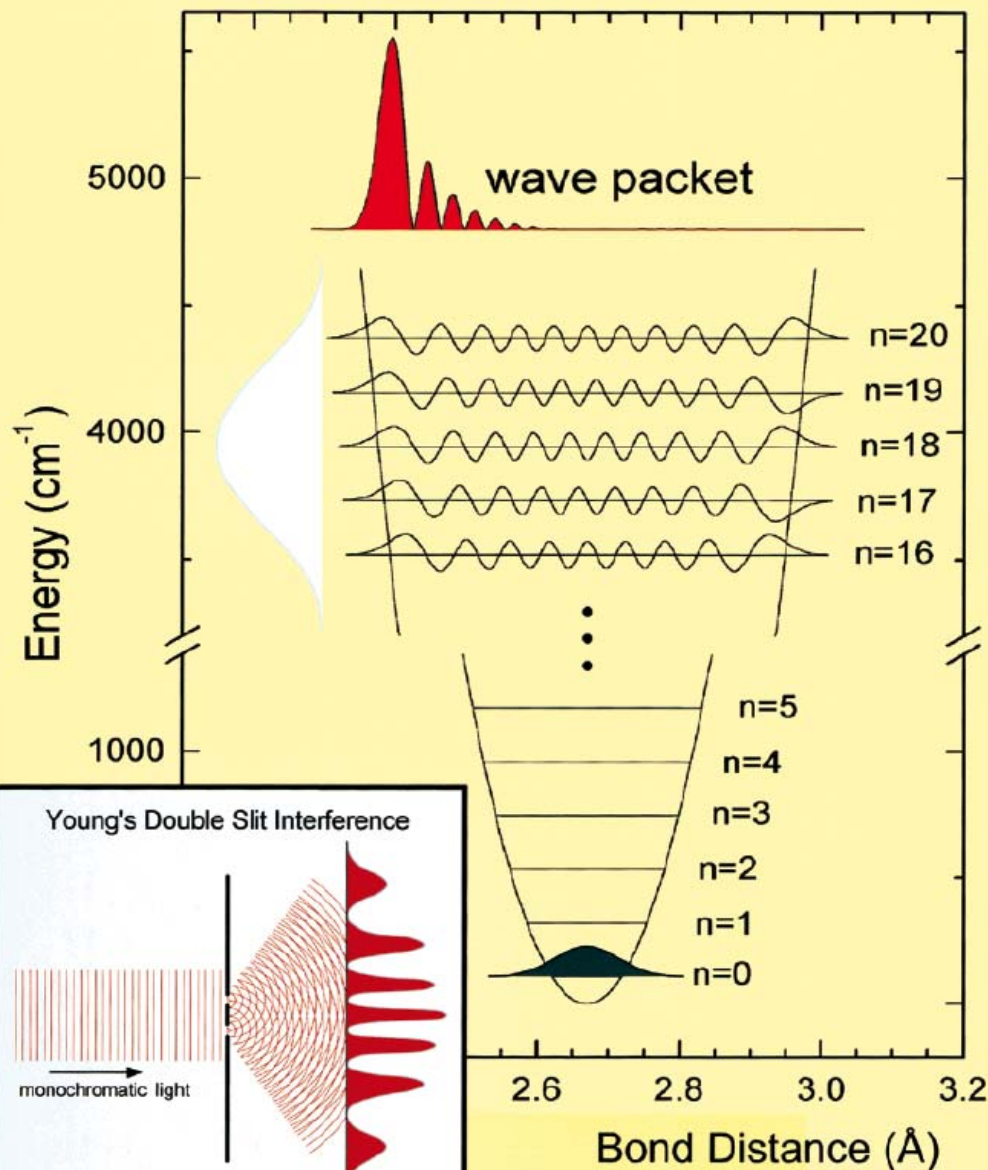
*J. Phys. Chem. A* 2000, 104, 5660–5694

Wavepacket description of the harmonic oscillator

Coherent superposition of vibrational states

The nuclear wavepacket is evolving (nuclei are moving)!

Equivalent: Short laser pulses, free electrons





# Fundamentals: Born-Oppenheimer Approximation

Masses of electrons and nuclei are very different → **Elektrons can follow the nuclear motions instantaneously!**

We don't need to solve the Schrödinger equation simultaneously for all particles in the systems (electrons and nuclei)

Instead: **Consider the nuclei as fixed** while solving the Schrödinger equation for the **electrons in the static potential of the fixed nuclei** (Produktansatz)

Repeat this for various nuclear distances

→ *The electronic part of the wavefunction depends on the nuclear distance BUT not as a variable but as a parameter!*

**The resulting set of solutions** (to the electronic part of the Schrödinger equation) **can be used to build potential energy curves** (surfaces, landscapes, depending on the number of parameters)

The potential energy curve corresponds to the electronic part of the total energy of the molecules plus the energy arising from repulsion of nuclei (vibrational and rotational energies are missing!)

# Fundamentals: Born-Oppenheimer Approximation

$$\Psi_{\text{molecule}} = \Psi_{\text{electrons}} \cdot \Psi_{\text{nuclei}}$$

Variable

$$\Psi_{\text{electrons}} = \Psi_{\text{electrons}}(r_{\text{electrons}}, R_{\text{nuclei}})$$

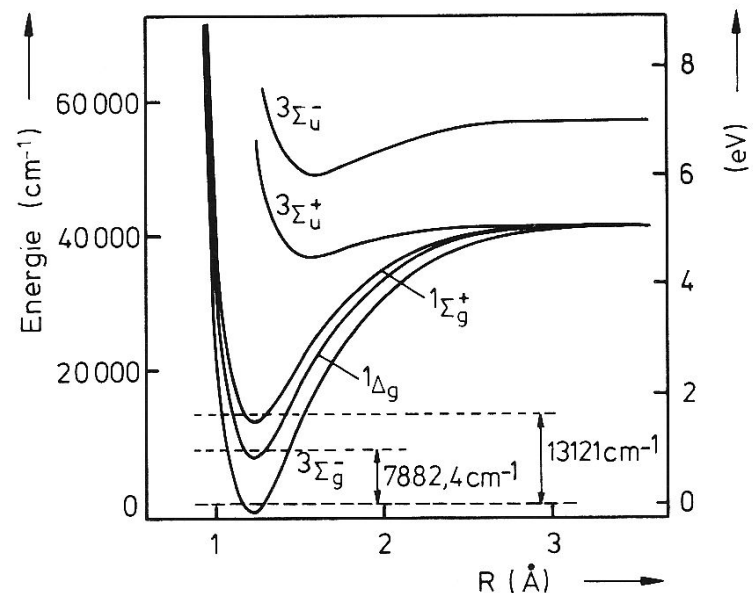
Parameter

$$\Psi_{\text{nuclei}} = \Psi_{\text{nuclei}}(R_{\text{nuclei}})$$

Variable

Solve the Schrödinger equation for  $\Psi_{\text{electrons}}$  at fixed  $R_{\text{nuclei}}$  and repeat for all  $R_{\text{nuclei}}$  to calculate the potential energy curves of the various electronic states

Example: O<sub>2</sub>

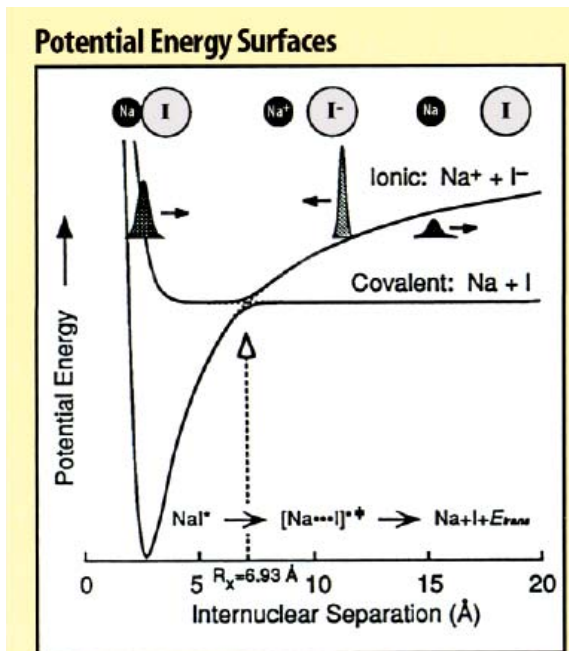




# Breakdown of the BO-Approximation

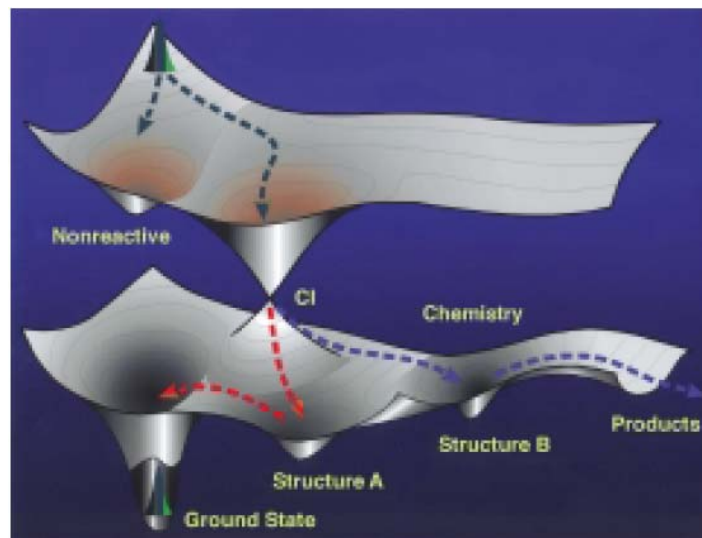
*Where potential energy curves meet*

NaI



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

Generic



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

# Environments: Where chemical dynamics occurs

- Gas phase
  - Low concentrations ( $10^{10}$ - $10^{13}$  molecules/cm<sup>3</sup>) 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<sup>3</sup>)
  - 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)

# 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*
  - At SLS/ESRF (ps): C. Bressler/XFEL, Hamburg, P. Glatzel/ESRF, Grenoble
  - At LCLS (fs): W. Wurth/Hamburg, A. Nilsson/Stanford and collaboration
  - At LCLS (fs): Ph. Wernet/HZB, Berlin, A. Föhlisch/HZB, S. Techert/MPI Göttingen and collaboration
  - [At FLASH (fs): M. Beye/HZB, A. Föhlisch/HZB, W. Wurth/Hamburg and collaboration]

# 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 PES → *Strong overlap with x-ray PES*
  - Special case of “laser femtochemistry”
- Electron scattering → *Hard to get fs pulses but high spatial resolution!*
  - A. Zewail/Caltech
  - D. Miller/Hamburg
- fs-IR spectroscopy → *Strong overlap with XAS/EXAFS (in terms of insight)*
  - E. Nibbering/MBI, Berlin, T. Elsaesser/MBI
  - R. Hochstrasser/Penn Chemistry, Pennsylvania
  - M. Fayer/Stanford University
  - P. Hamm/University of Zürich
  - H. Bakker/Amsterdam

## 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**

# Representative examples (subjective collection)

- Laser PES
  - **Gas phase:**
    - A. Stolow (Canada)
      - Recent papers
      - Review paper: A. Stolow et al., Chem. Rev. **104**, 1719 (2004).
    - Dan Neumark
    - Many others
  - **Surfaces/interfaces:**
    - H. Petek (Pittsburgh) → Petek et al., Science **288**, 1402 (2000).
    - C. B. Harris (Berkeley)
    - M. Wolf (Berlin)

# Representative examples (subjective collection)

- X-ray scattering
  - **Solutions:**
    - H. Ihee et al., Science **309**, 1223 (2005), Kim et al., Acta Cryst. A**66**, 270 (2010)
  - **Crystals:**
    - F. Schotte et al., Science **300**, 1944 (2003).
    - M. Woerner et al., J. Chem. Phys. **133**, 064509 (2010).
- Photoelectron spectroscopy (PES)
  - **Surfaces/Interfaces:** M. Bauer et al., Phys. Rev. Lett. 87, 025501 (2001)
  - **Gas phase:** S. Leone/Berkeley, O. Gessner/Berkeley
- Resonant Inelastic X-ray Scattering (RIXS)
  - **Solution:** Vanko et al., Angew. Chem. Int. Ed. **49**, 5910 (2010)
- Based on HHG sources (gas phase)
  - Gagnon et al., Science **317**, 1374 (2007)
  - Wörner et al., Nature **466**, 604 (2010)
  - Sansone et al., Nature **465**, 763 (2010)
- At FLASH
  - **Gas phase x-ray pump/x-ray probe:** Robert Moshhammer et al.

# Representative examples (subjective collection)

- Picosecond/Femtosecond XAS/EXAFS at synchrotrons
  - **Majed Chergui/Lausanne and Christian Bressler/XFEL, Hamburg** (ps and fs hard x-ray XAS/EXAFS)
  - **Munira Khalil, Nils Huse, Bob Schoenlein/Berkeley** (ps and fs hard and soft x-ray XAS/EXAFS)
  - **Philippe Wernet/HZB, Berlin** (ps soft x-ray XAS)
  - **Lin Chen/ Argonne et al.** (ps hard x-ray XAS/EXAFS)
  - ...



## Femtosecond XANES Study of the Light-Induced Spin Crossover Dynamics in an Iron(II) Complex

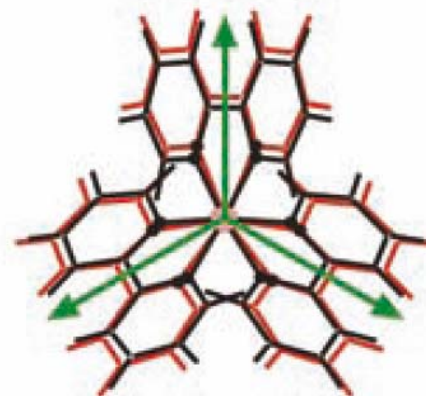
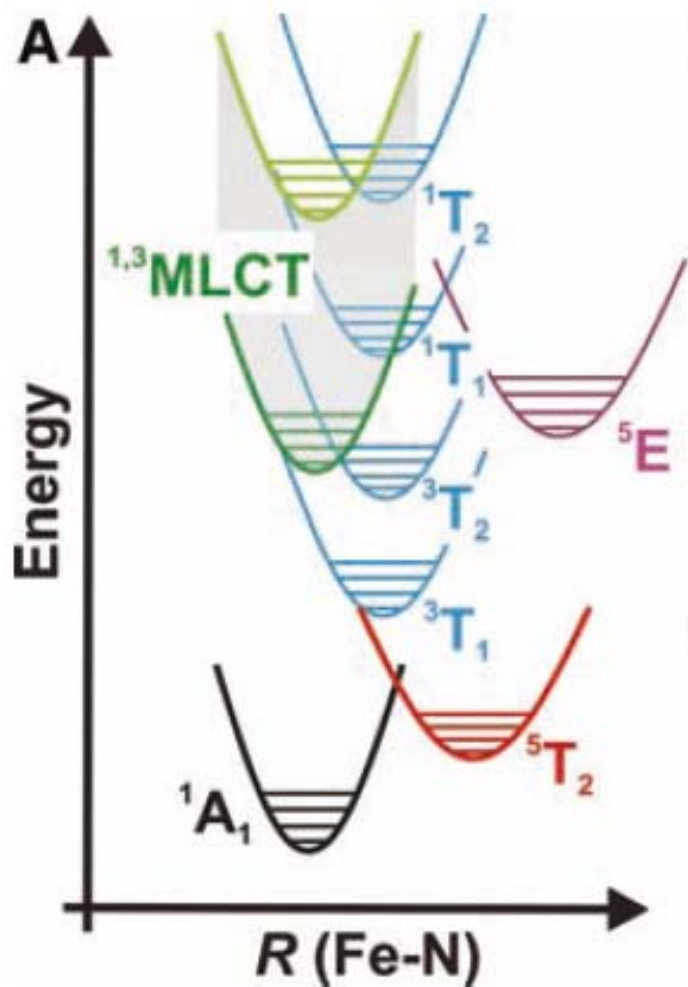
Ch. Bressler,<sup>1</sup> C. Milne,<sup>1</sup> V.-T. Pham,<sup>1</sup> A. ElNahas,<sup>1</sup> R. M. van der Veen,<sup>1,2</sup>  
W. Gawelda,<sup>1,2\*</sup> S. Johnson,<sup>2</sup> P. Beaud,<sup>2</sup> D. Grolimund,<sup>2</sup> M. Kaiser,<sup>1,2</sup>  
C. N. Borca,<sup>2</sup> G. Ingold,<sup>2</sup> R. Abela,<sup>2</sup> M. Chergui<sup>1†</sup>

[www.sciencemag.org](http://www.sciencemag.org) SCIENCE VOL 323 23 JANUARY 2009

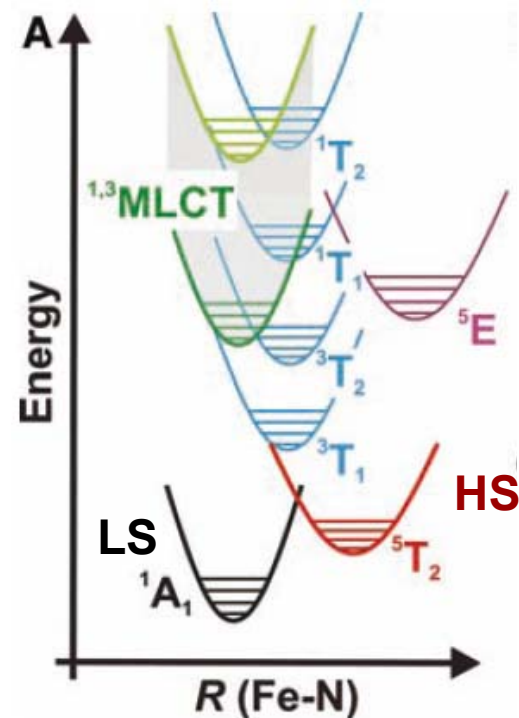
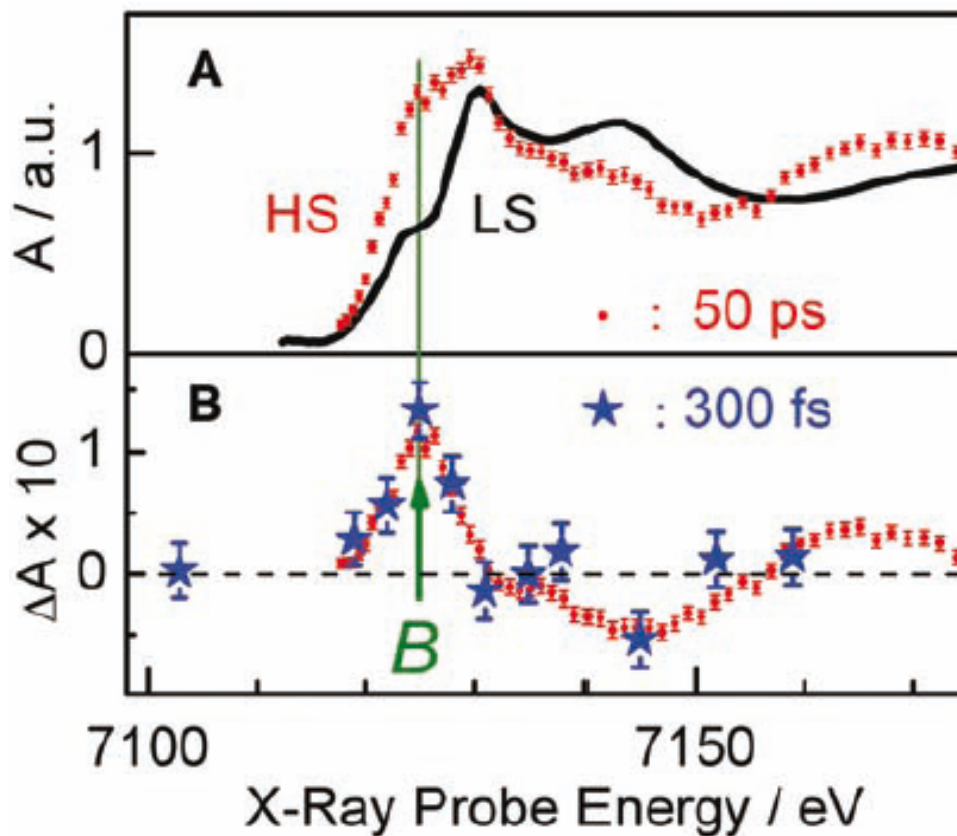
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# Representative examples (subjective collection)

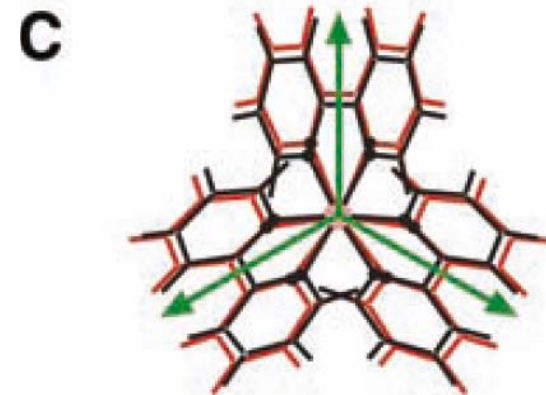
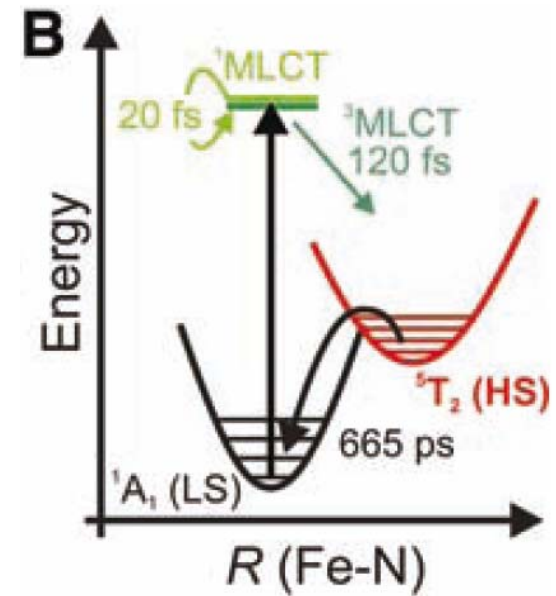
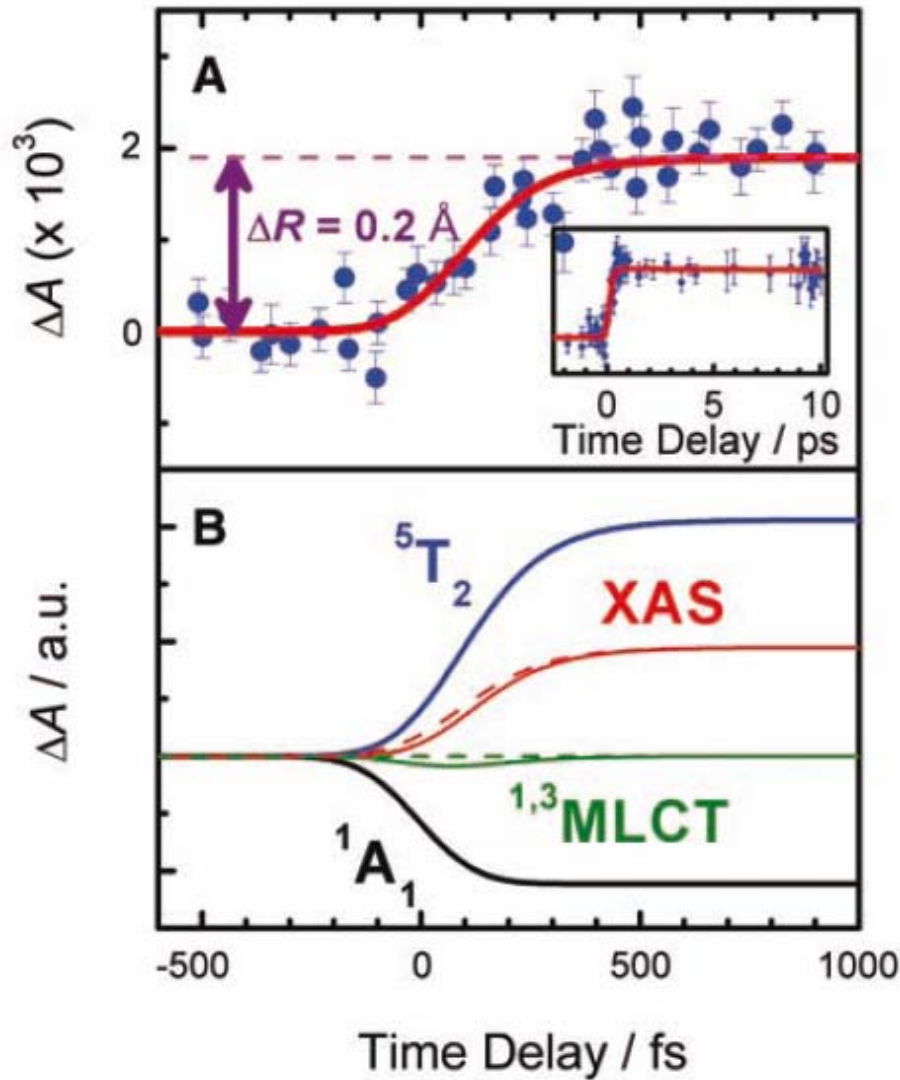
Iron(II)-tris(bipyridine) ( $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ )



# Representative examples (subjective collection)



# Representative examples (subjective collection)



→ Two-step ICS process

# Representative examples (subjective collection)

## Femtosecond Soft X-ray Spectroscopy of Solvated Transition-Metal Complexes: Deciphering the Interplay of Electronic and Structural Dynamics

Nils Huse,<sup>\*,†</sup> Hana Cho,<sup>†,‡</sup> Kiryong Hong,<sup>‡</sup> Lindsey Jamula,<sup>§</sup> Frank M. F. de Groot,<sup>⊥</sup> Tae Kyu Kim,<sup>\*,‡</sup> James K. McCusker,<sup>§</sup> and Robert W. Schoenlein<sup>†</sup>

<sup>†</sup>Ultrafast X-ray Science Laboratory, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

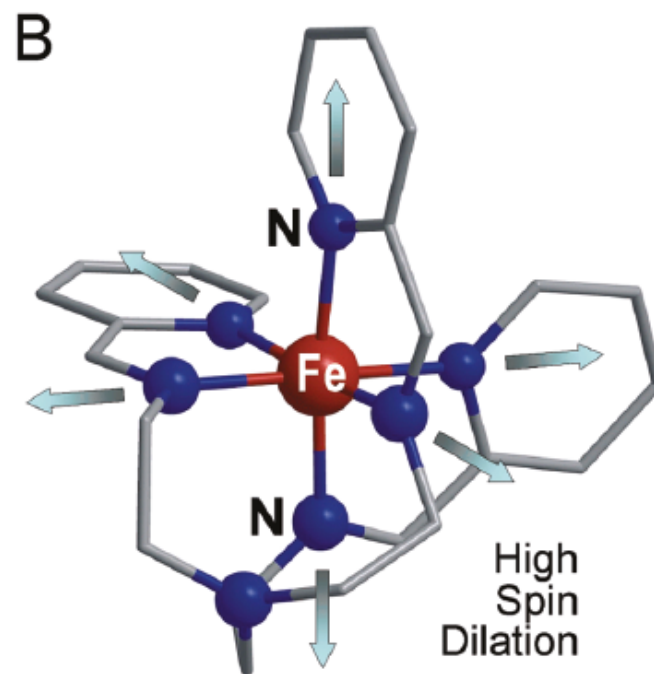
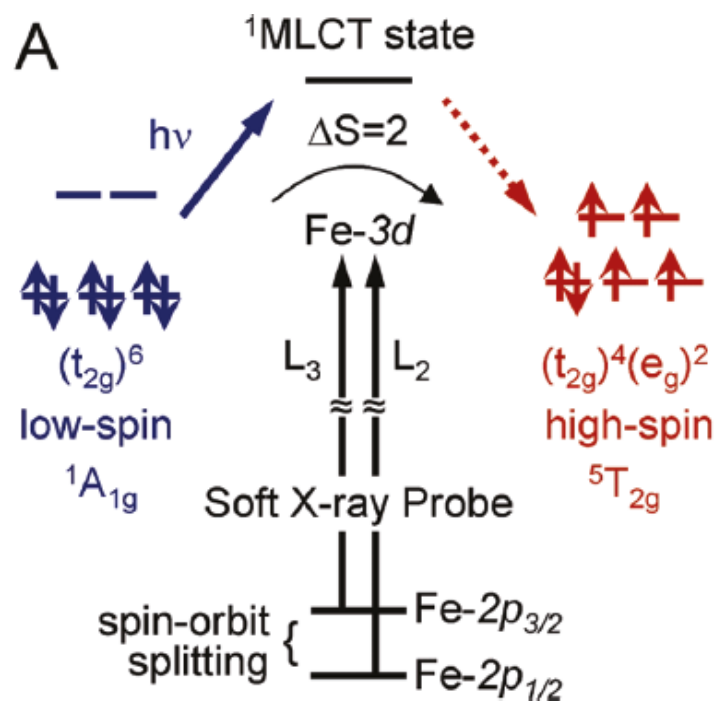
<sup>‡</sup>Department of Chemistry and Chemistry Institute of Functional Materials, Pusan National University, Busan 609-735, Republic of Korea

<sup>§</sup>Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States

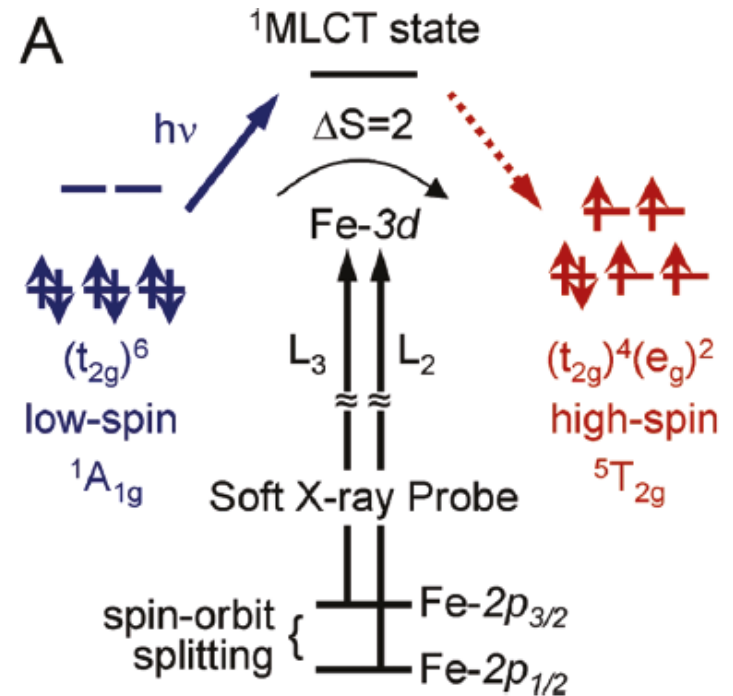
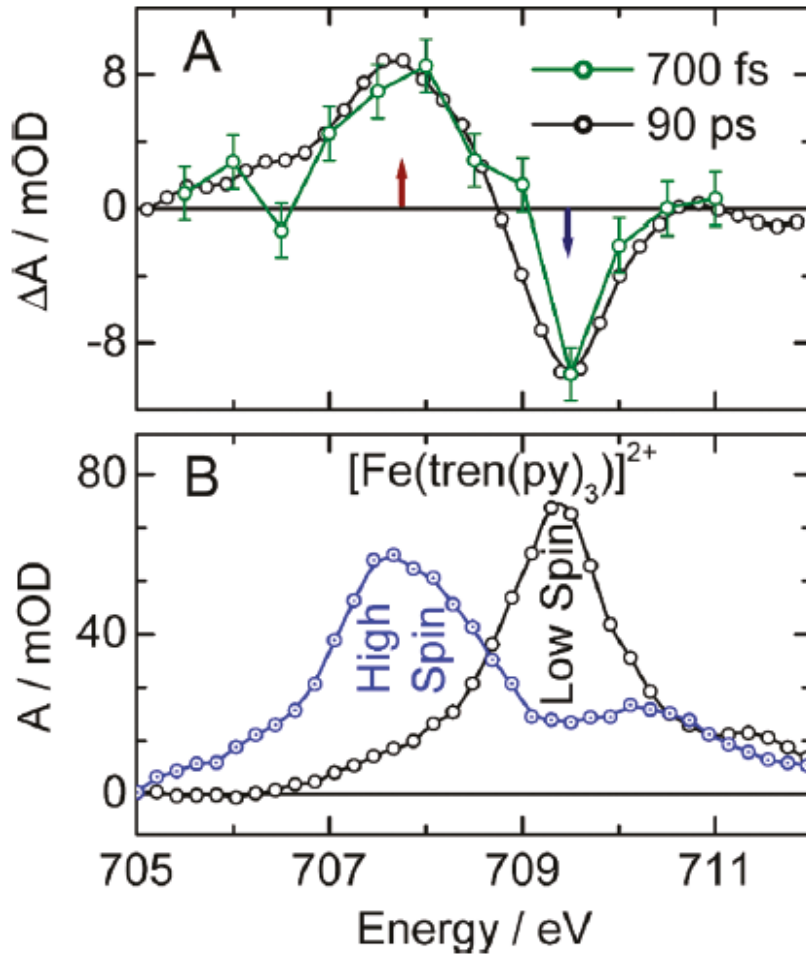
<sup>⊥</sup>Department of Chemistry, Utrecht University, 3584 Utrecht, Netherlands

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*Letters*

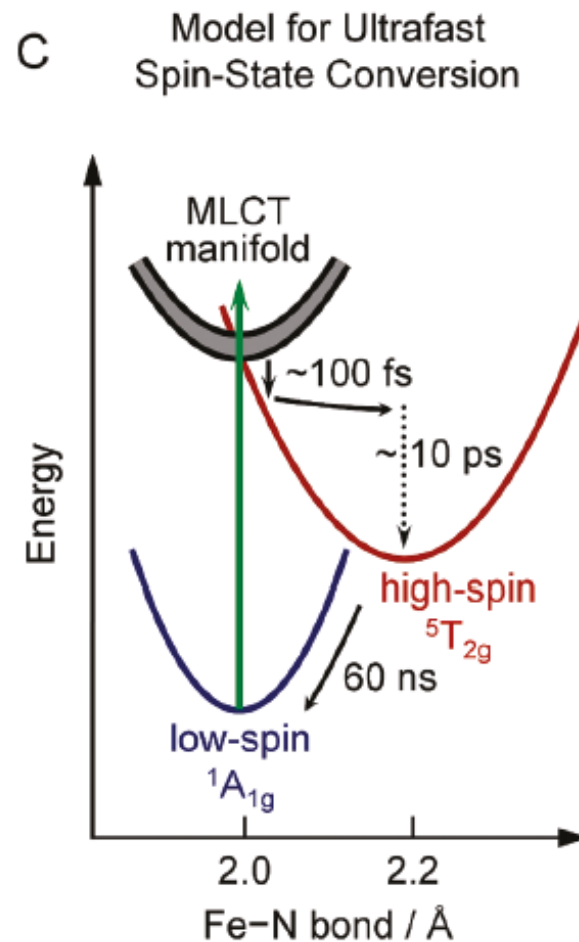
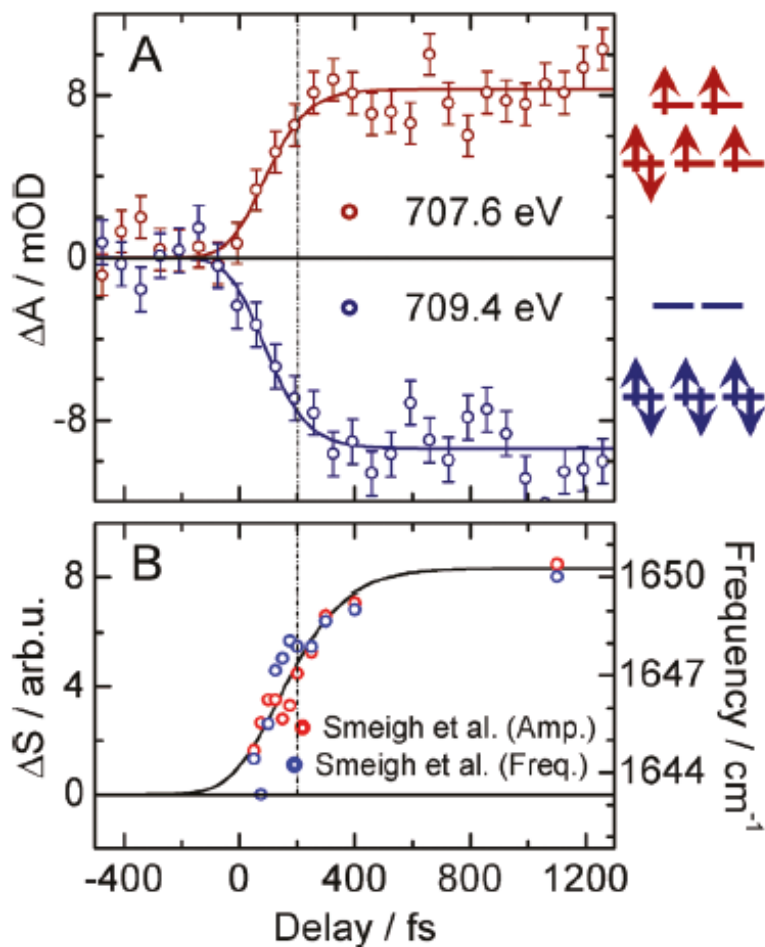
# Representative examples (subjective collection)



# Representative examples (subjective collection)

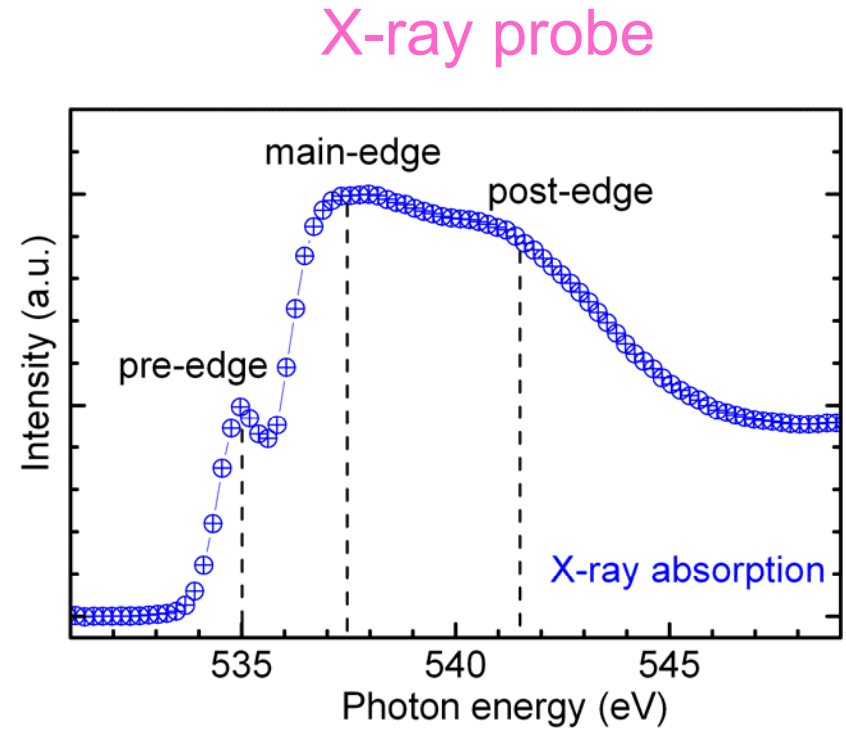
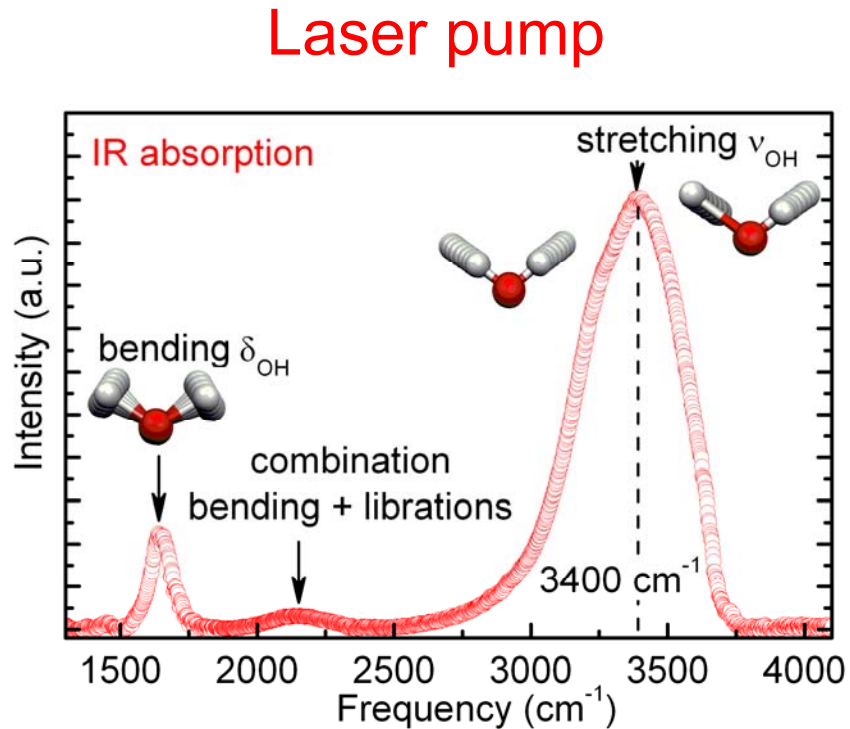
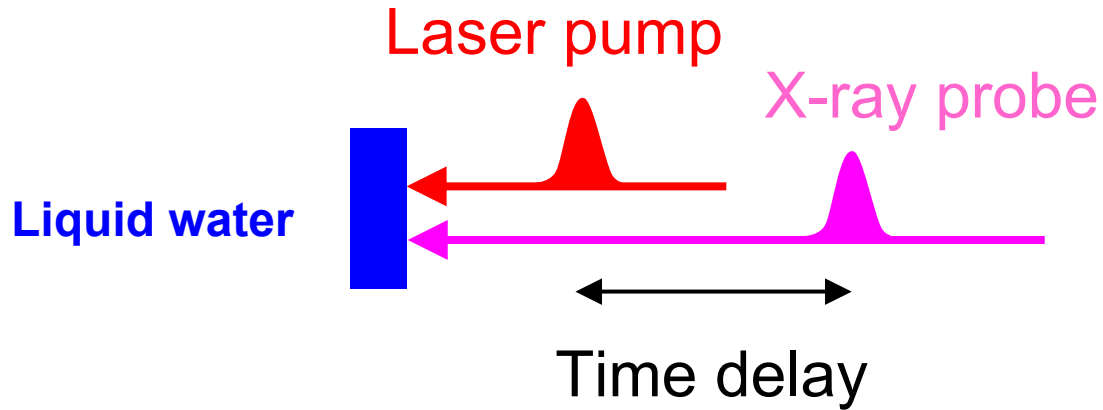


# Representative examples (subjective collection)

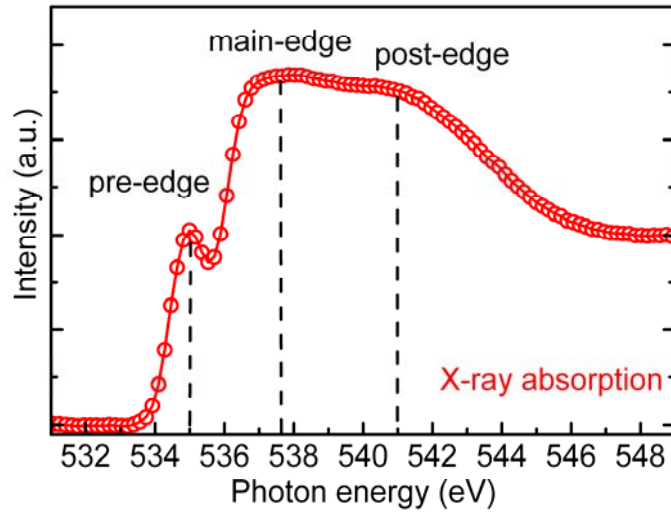




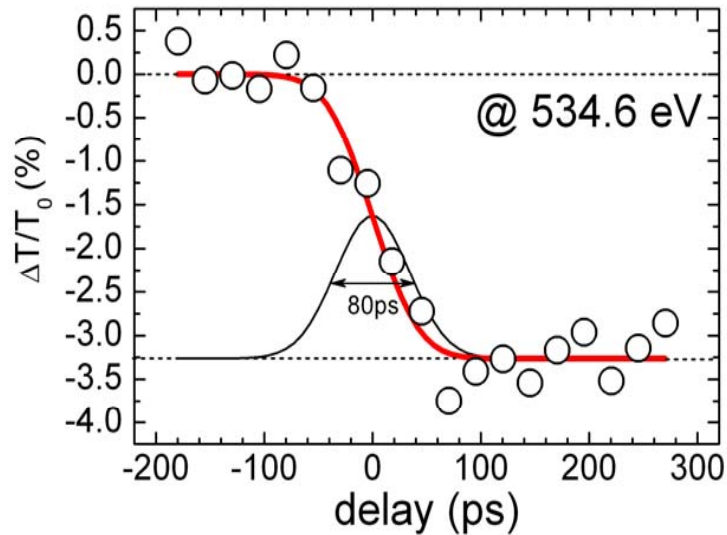
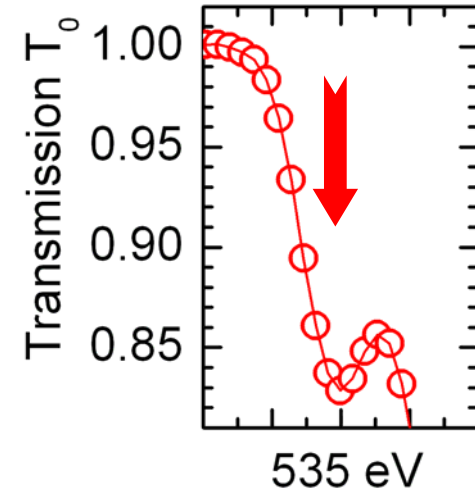
# Representative examples (subjective collection)



# Representative examples (subjective collection)



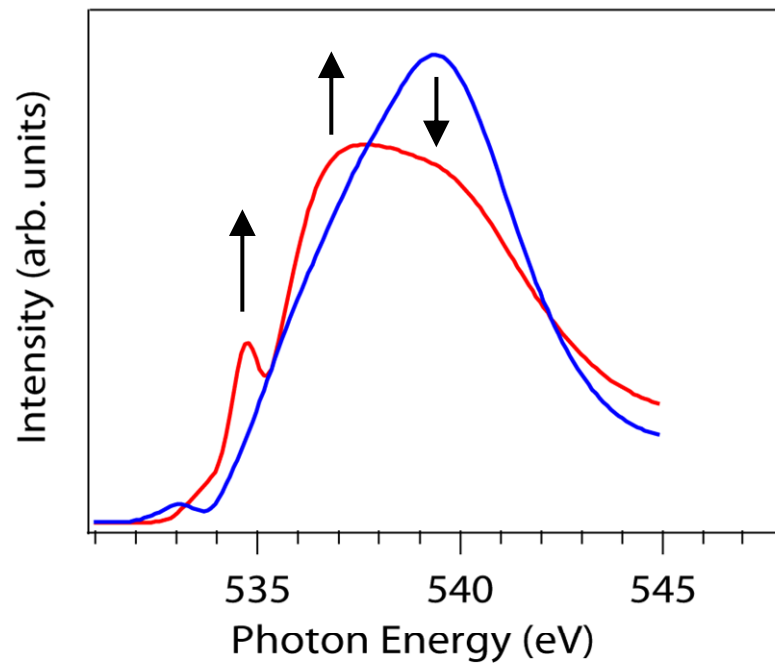
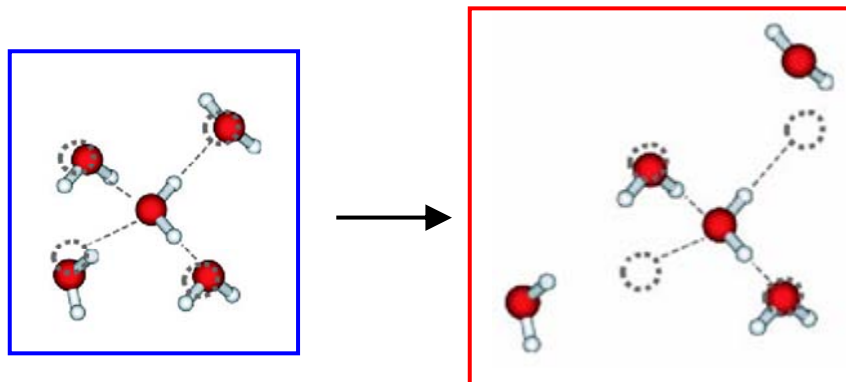
$$\text{XAS} = -\ln(T)$$



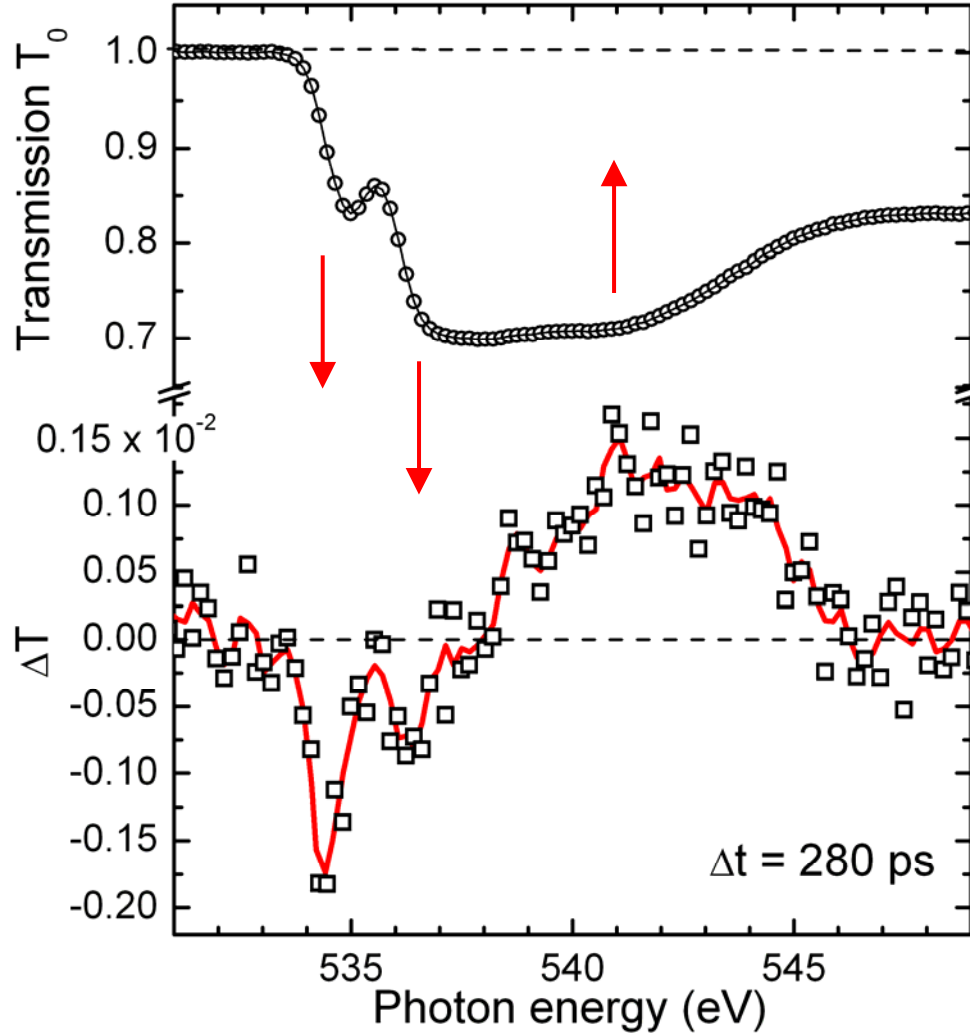
**T jump of 20 K**

# Representative examples (subjective collection)

Calculated absorption spectra



# Representative examples (subjective collection)



Wernet et al., Appl. Phys. A **92**, 511 (2008).

Gavrila et al., Appl. Phys. A **96**, 11 (2009).

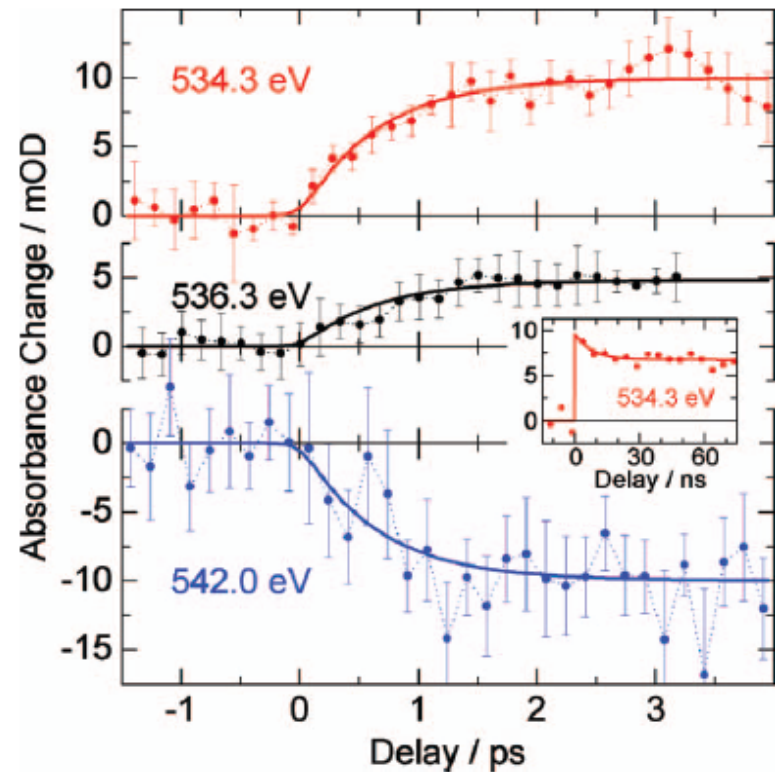
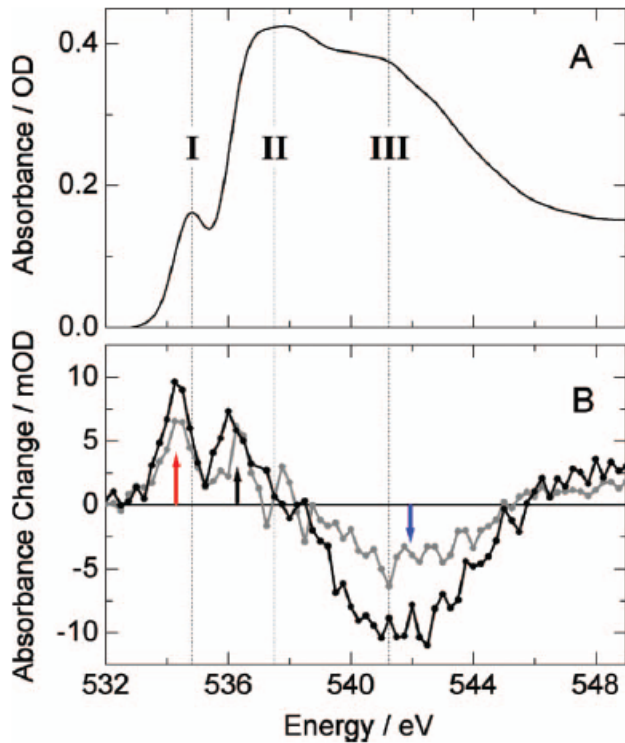
Confirmed by Huse et al., PCCP **11**, 3951 (2009).

# Representative examples (subjective collection)

THE JOURNAL OF CHEMICAL PHYSICS 131, 234505 (2009)

## Ultrafast conversions between hydrogen bonded structures in liquid water observed by femtosecond x-ray spectroscopy

Haidan Wen,<sup>1,a)</sup> Nils Huse,<sup>2,a),b)</sup> Robert W. Schoenlein,<sup>2,3</sup> and Aaron M. Lindenberg<sup>1,4,b)</sup>



Same time scale as in fs IR spectroscopy  
(thermalization within 700 fs)

# Summary and conclusions

- Chemical dynamics... **The atomic-scale dynamics of chemical interactions**
- ...with ultrafast x-rays **Fundamental aspects of elementary reactions**
- Ask yourself: **Why x-rays?**



## *The dreams:*

- **Map nuclei and electrons during chemical reactions**
  - Record the molecular movie
  - Both from the nuclei's and electrons' perspective
- **Study systems relevant for energy production and catalysis**
  - Master artificial photosynthesis (water splitting)
  - Elucidate and avoid rate-limiting steps → Insight-driven design of new catalysts



# EXTRA SLIDES

# 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)

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

## FEATURE ARTICLE

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### Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond<sup>†</sup>

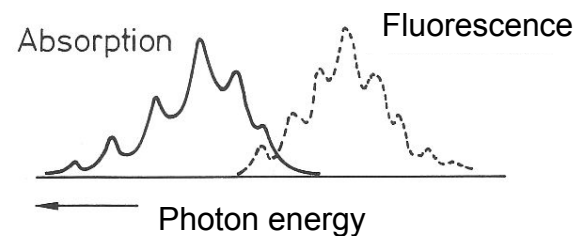
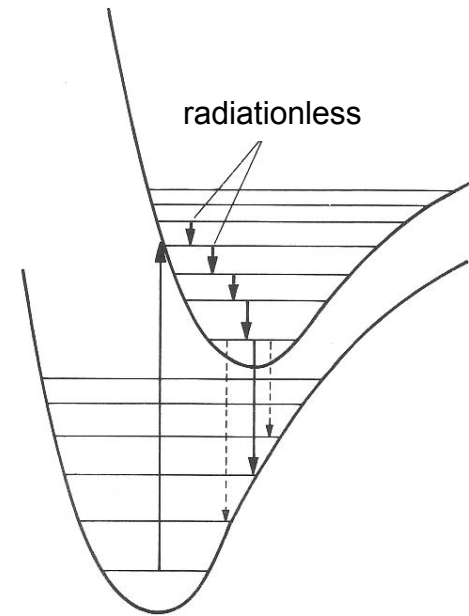
Ahmed H. Zewail

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

*Received: April 18, 2000*

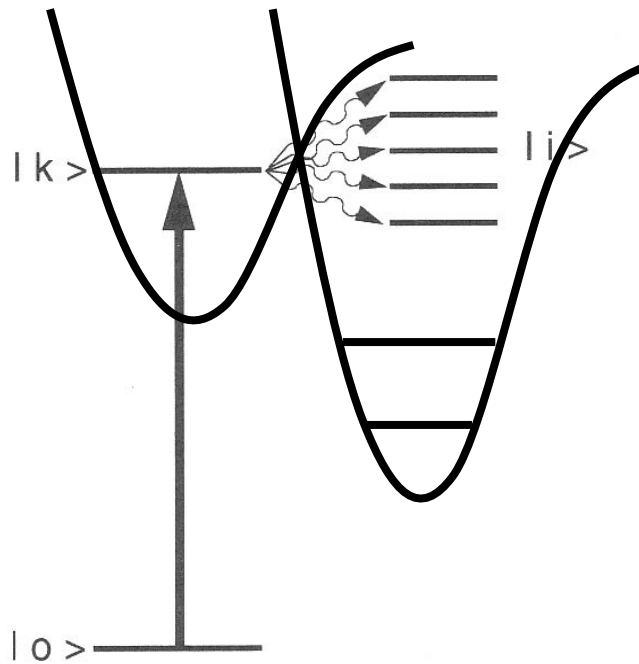
# Intramolecular vibrational redistribution (IVR)

- 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 respect to the temperature of the medium



# Internal conversion (IC)

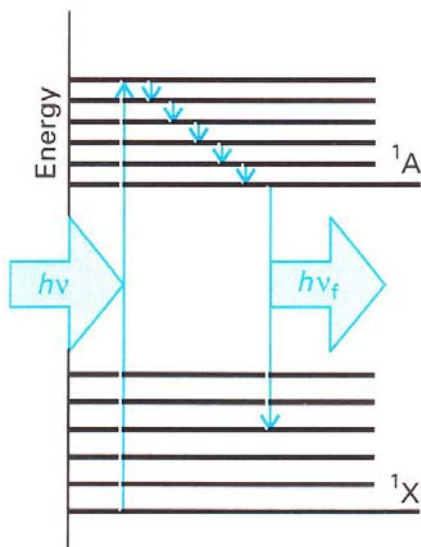
- Conversion from electronic into vibrational energy within one molecule
- Radiationless transition within one molecule
- Usually occurs on a time scale of fs to ps
- Mediated by vibronic coupling (see figure) between different electronic states of the same molecule



Model for vibronic coupling

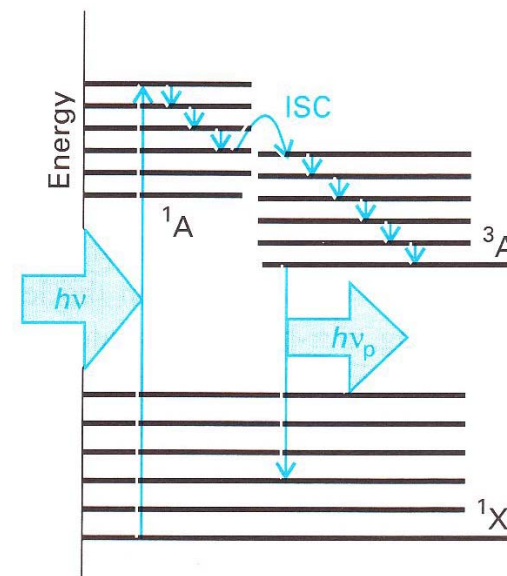
# Intersystem crossing (ISC)

- 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  $\mu$ s
- 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.

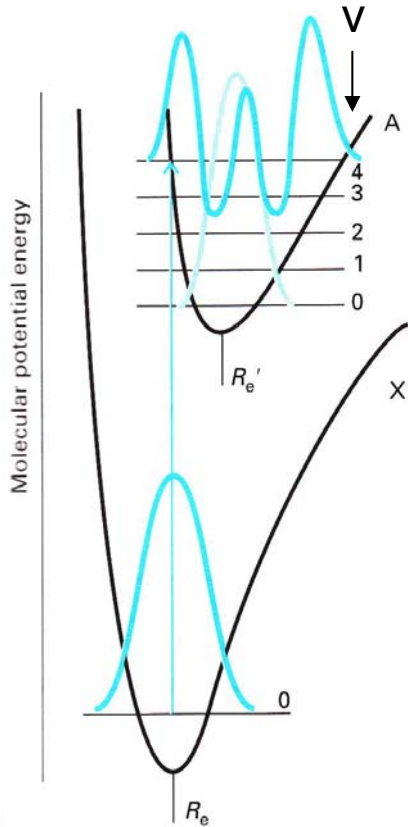
*From: Atkins, Friedman, Molecular quantum mechanics*



**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.

# Fundamentals: Franck-Condon factor

## Electronic transitions



$$\Psi_{\text{molecule}} = \Psi_{\text{electrons}} \cdot \Psi_{\text{nuclei}}$$

Variable

$$\Psi_{\text{electrons}} = \Psi_{\text{electrons}}(r_{\text{electrons}}, R_{\text{nuclei}})$$

Parameter

$$\Psi_{\text{nuclei}} = \Psi_{\text{nuclei}}(R_{\text{nuclei}})$$

Variable

Transition probability (electronic transition):

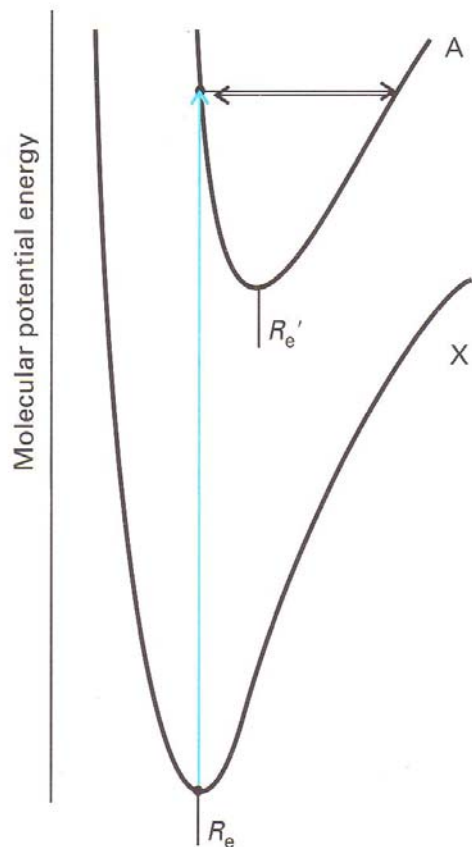
prop. to **electronic dipole moment** · **Franck-Condon factor**

$$\left| \int \Psi_{\text{electrons}}^X d_{\text{el}} \Psi_{\text{electrons}}^A d_{\text{electrons}} \right|^2$$

$$\left| \int \Psi_{\text{nuclei}}^v d_{\text{nuc}} \Psi_{\text{nuclei}}^0 d_{\text{nuclei}} \right|^2$$

# Fundamentals: Franck-Condon principle

## Electronic transitions



**Fig. 11.9** The classical basis of the Franck–Condon principle in which the molecule makes a vertical transition that terminates at the turning point of the excited state. The nuclei neither change their locations nor accelerate while the transition is in progress.

### Classical version 1/2:

Electrons are much lighter than nuclei  
Electronic transitions occur at fixed nuclear positions  
(Careful: this is often wrongly denoted the **Franck-Condon principle**)

Positions and speed of motion of the nuclei does not change DURING the transition

→ Electronic transitions occur in the potential energy diagram vertically (at fixed nuclear distance)

# Fundamentals: Franck-Condon principle

## Electronic transitions

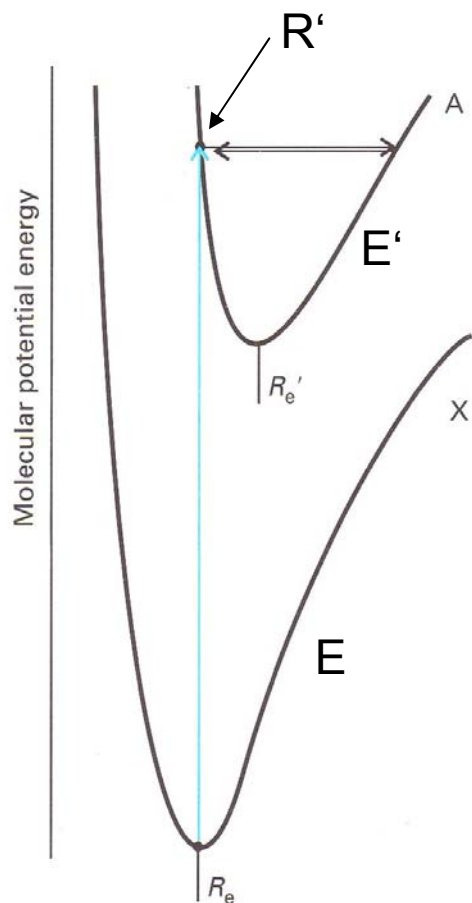


Fig. 11.9 The classical basis of the Franck-Condon principle in which the molecule makes a vertical transition that terminates at the turning point of the excited state. The nuclei neither change their locations nor accelerate while the transition is in progress.

### Classical version 2/2:

The vertical transition occurs at  $R'=R_e$  (when the nuclei are at rest at the turning points)

Starting from  $R_e$  where the vertical line for the transition meets the  $E'$  curve ( $R'=R_e$ )

In this classical picture, the nuclei are most of the time at the turning points, hence the transition probability is largest for transitions to these points

**Note:** Of course (once the transition is over) the nuclei are reacting to the new electron distribution with new positions (with vibrations according to where in  $E'$  they are)

# Fundamentals: Franck-Condon principle

## Electronic transitions

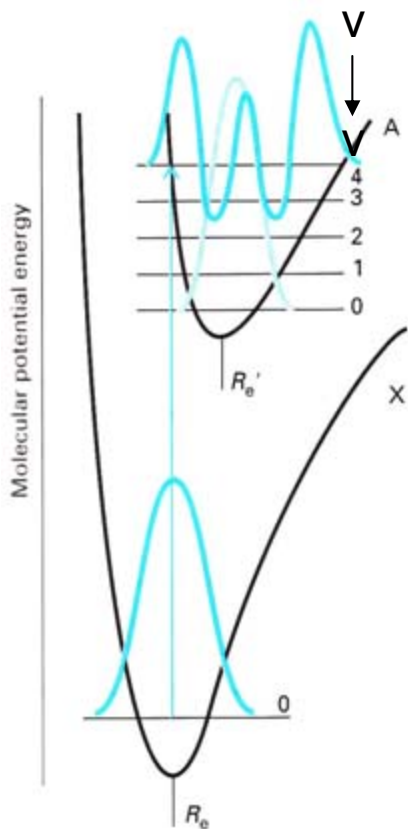


Fig. 11.10 The quantum mechanical version of the Franck-Condon principle. The molecule makes a transition from the ground vibrational state to the state with a vibrational wavefunction that most strongly resembles the initial vibrational wavefunction.

Transition probability (electronic transition):

prop. to **electronic dipole moment** · **Franck-Condon factor**

$$\left| \int \Psi_{\text{electrons}}^X d_{\text{el}} \Psi_{\text{electrons}}^A d_{\text{electrons}} \right|^2$$

$$\left| \int \Psi_{\text{nuclei}}^v d_{\text{nuc}} \Psi_{\text{nuclei}}^0 d_{\text{nuclei}} \right|^2$$

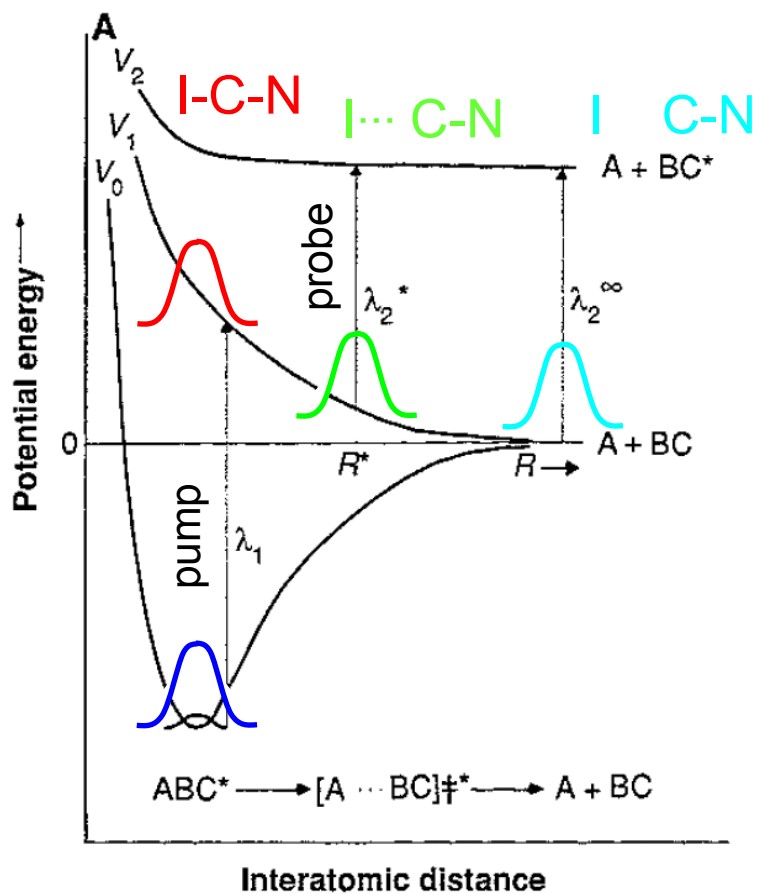
Maximum transition probability at maximum overlap of the nuclear wavefunctions in ground and excited electronic states

Consistent with classical version (see enhanced intensity of the nuclear wavefunctions at the turning 'points)

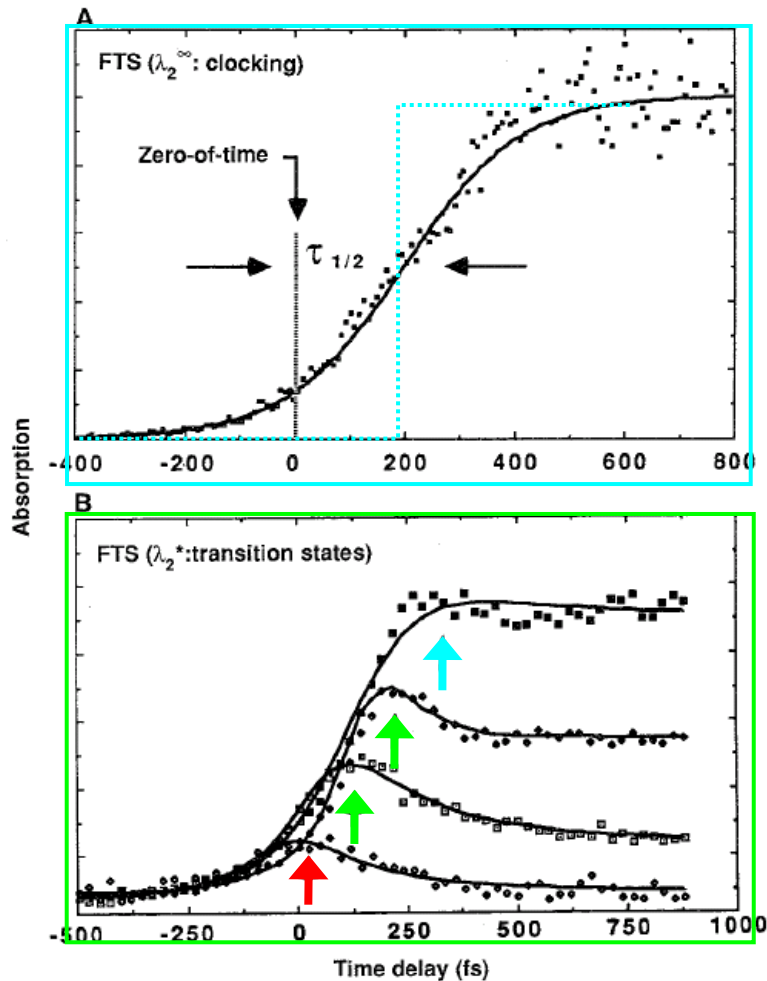
The FC factor is larger than 0 for a series of vibrational transitions.



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



### Experiment



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

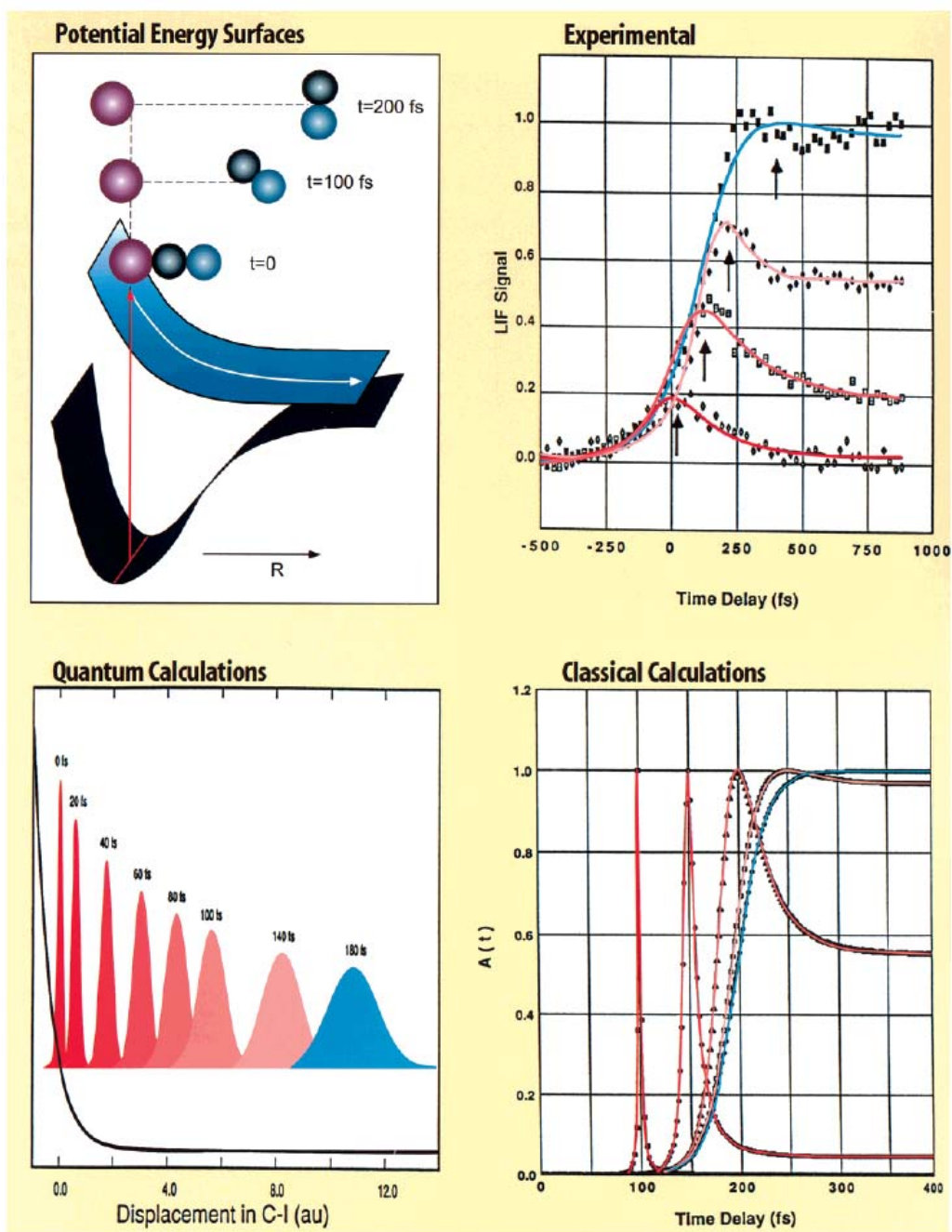


Figure 6. Femtochemistry of the ICN reaction, the first to be studied. The experimental results show the probing of the reaction in the transition-state region (rise and decay) and the final CN fragment (rise and leveling) with precise clocking of the process; the total time is 200 fs. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown. Reference 41.