Femtochemistry

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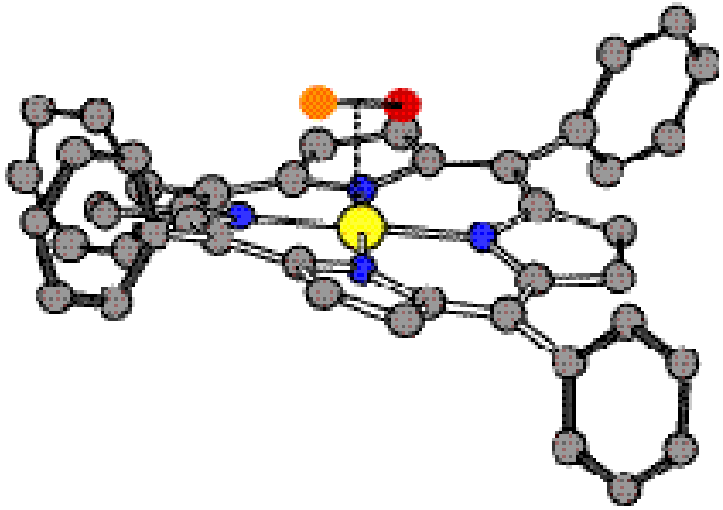
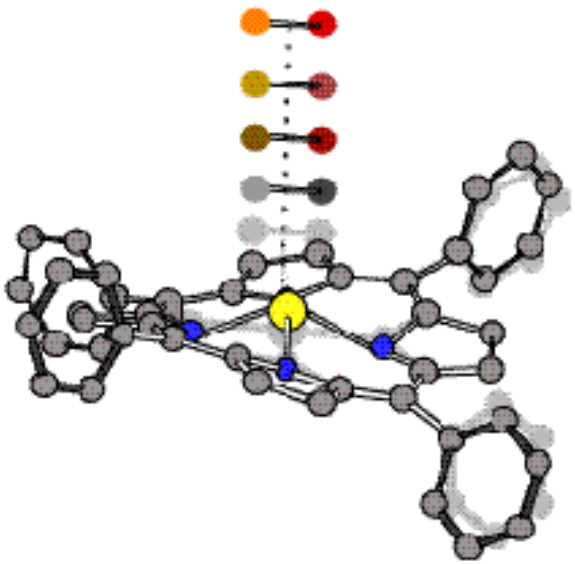


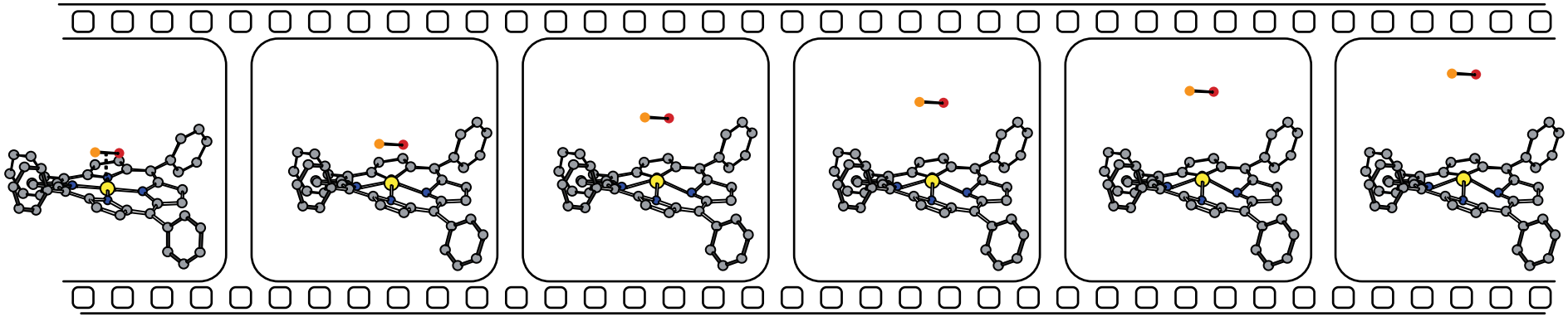
Description of static molecular properties in terms of bond lengths and angles has served us well.

Virtually every new discovery in biology and chemistry can be traced to a structure being solved.



Chemical transformations are about dynamics, i.e. rapid changes in bond lengths and bond angles.

What is needed is a tool that will make possible a simple connection between the static picture and its time evolution.



The ultimate goal of any molecular dynamics study is to produce a motion picture of the nuclear motions as a function of time.

Capturing molecules *in the process* of reacting has been a long-time dream

Femtosecond lasers are fast enough

BUT

Their greater than 200-nm wavelength does not allow for any spatial information

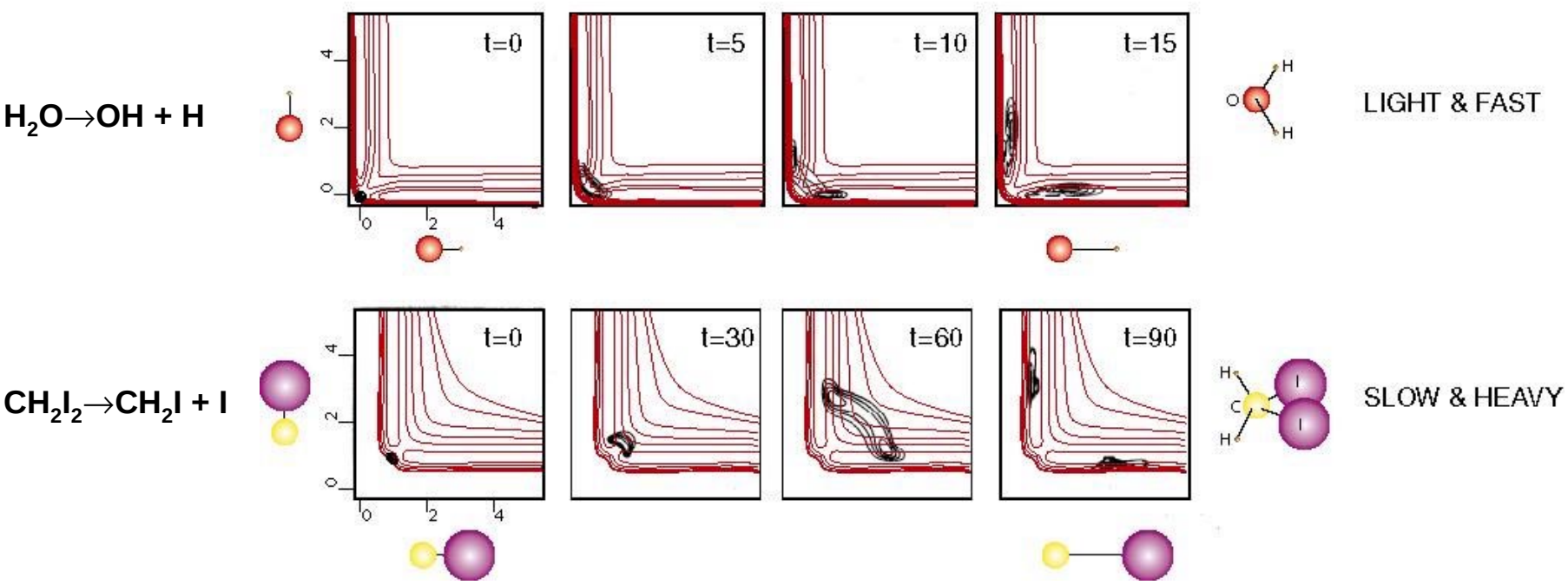
Spectroscopy of the transition state is an attempt to compensate for the inability of lasers to provide the spatially needed resolution

Ultrafast Electron Diffraction (UED) is the only experimental system that attempts to break that limit

Putting things in perspective

What are the time-scales?

What are the length-scales?



Time in femtoseconds, distance in Å

TIME

The very light systems require a time resolution of a few femtoseconds, while heavier ones can be studied with pulses a few hundred femtosecond long.

BOND LENGTH

The *LCLS* will make it possible to map out the nuclear motions with a resolution of 0.1 Å, which is clearly sufficient.

Ultrafast Electron Diffraction
H. Zewail

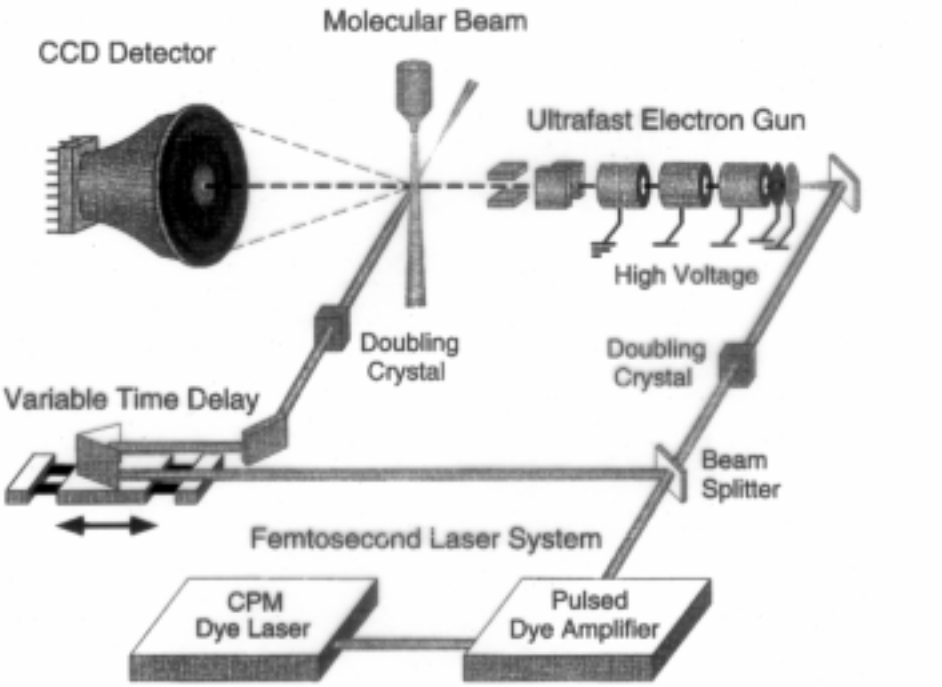
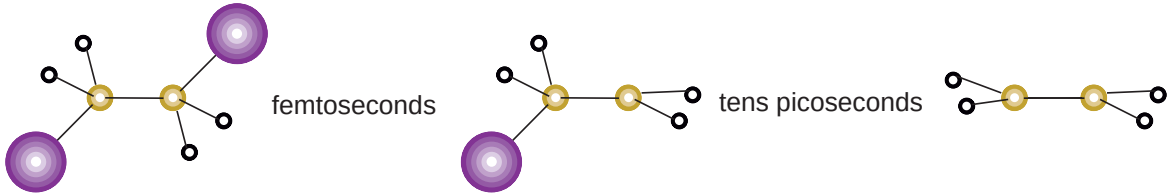
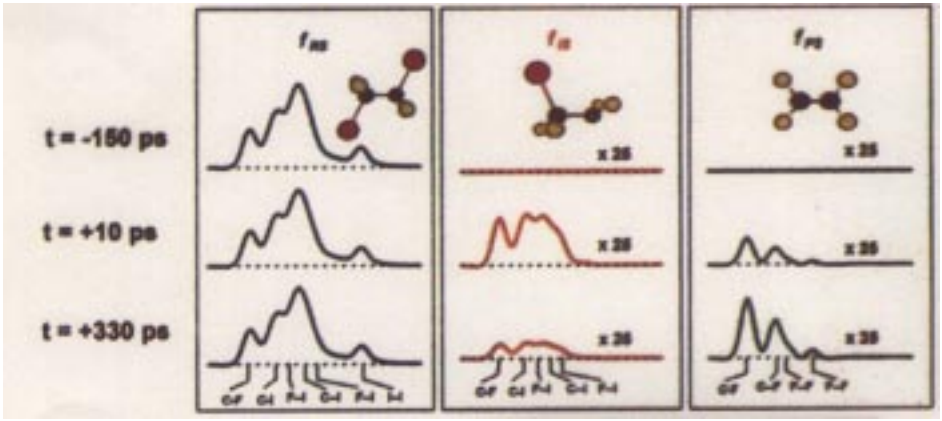


Fig. 1. A schematic of the experimental setup used here for ultrafast electron diffraction (UED).

UED CH_2I-CH_2I Photodissociation

LCLS





UED will never break the psec time limit because of the fundamental relationship between the number of electrons in the bunch and pulse length.

The *LCLS* is the only tool with the required temporal and spatial resolution

Comparison between Ultrafast Electron Diffraction (UED) and the *LCLS*

	Δt^1	Flux	Cross section^2	Rate Hz	Signal^3
UED	**10ps**	7000	10^7	1000	**$7\ 10^{13}$**
LCLS	**200fs**	$2\ 10^{12}$	1	100	**$2\ 10^{14}$**

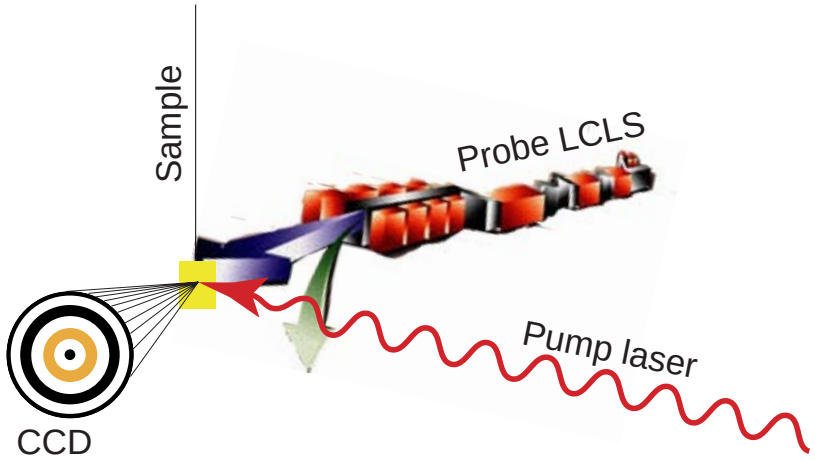
[1] time resolution; [2] relative crossection; [3] relative signals

The predicted signals are comparable but the *LCLS* time resolution is at least 50 times better.

Exp 1. Gas phase photochemistry

Exp 2. Condensed phase photochemistry

Exp 3. Dynamics in nanoparticles

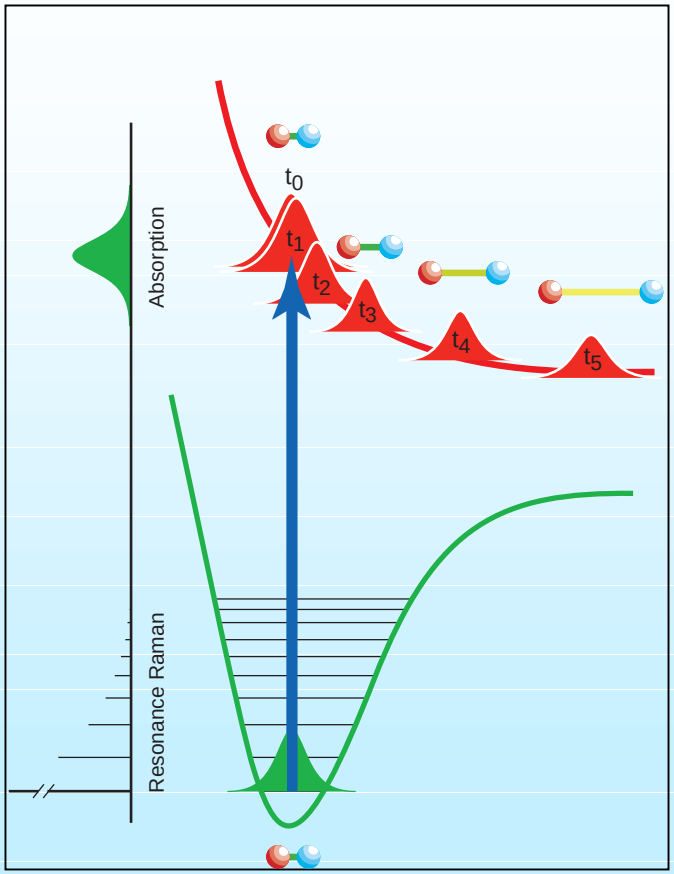


The femtochemistry experiments use an ultrafast laser to initiate the process and the *LCLS* beam as a probe

- **Time resolved diffraction**
- **Time resolved Mie scattering (small angle scattering)**

Experiment 1. Gas phase photodissociation reactions

LCLS



Photodissociation of an isolated diatomic molecule is the simplest of chemical reactions.

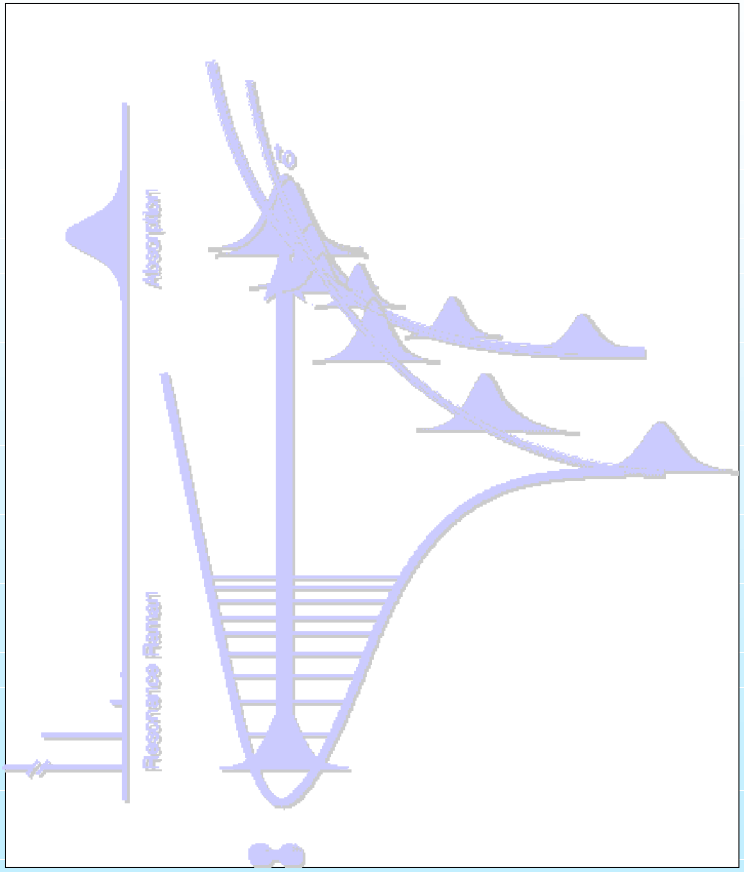
t=0 is easily defined

The initial wave-function is well defined

The wave-function remains localized throughout the reaction

The *LCLS* is ideally suited to investigate these reactions

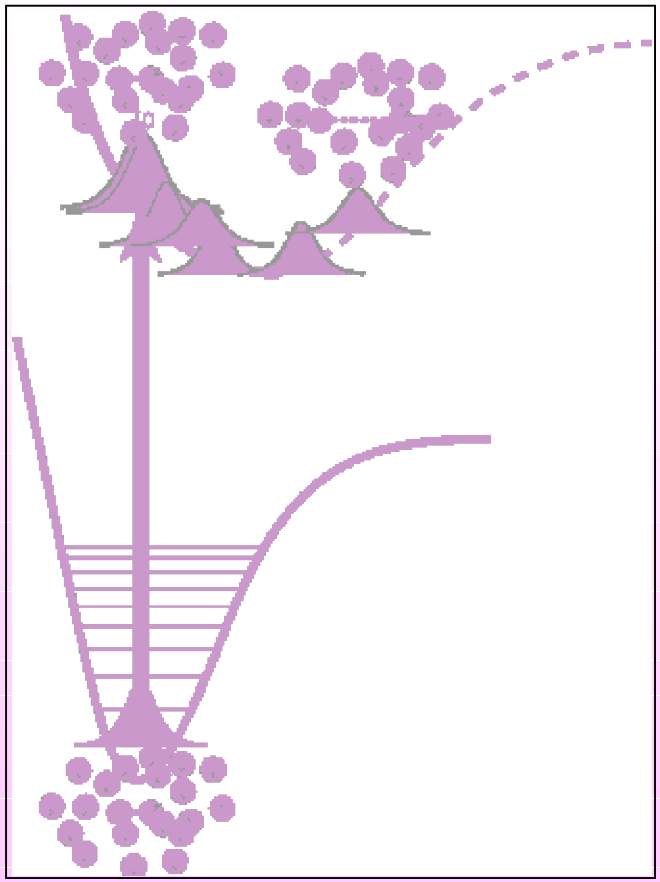
Nuclear and Electronic Coupling is Universal Phenomenon **LCLS**



The coupling between nuclear and electronic motion is a universal phenomenon that dominates almost all photochemistry.

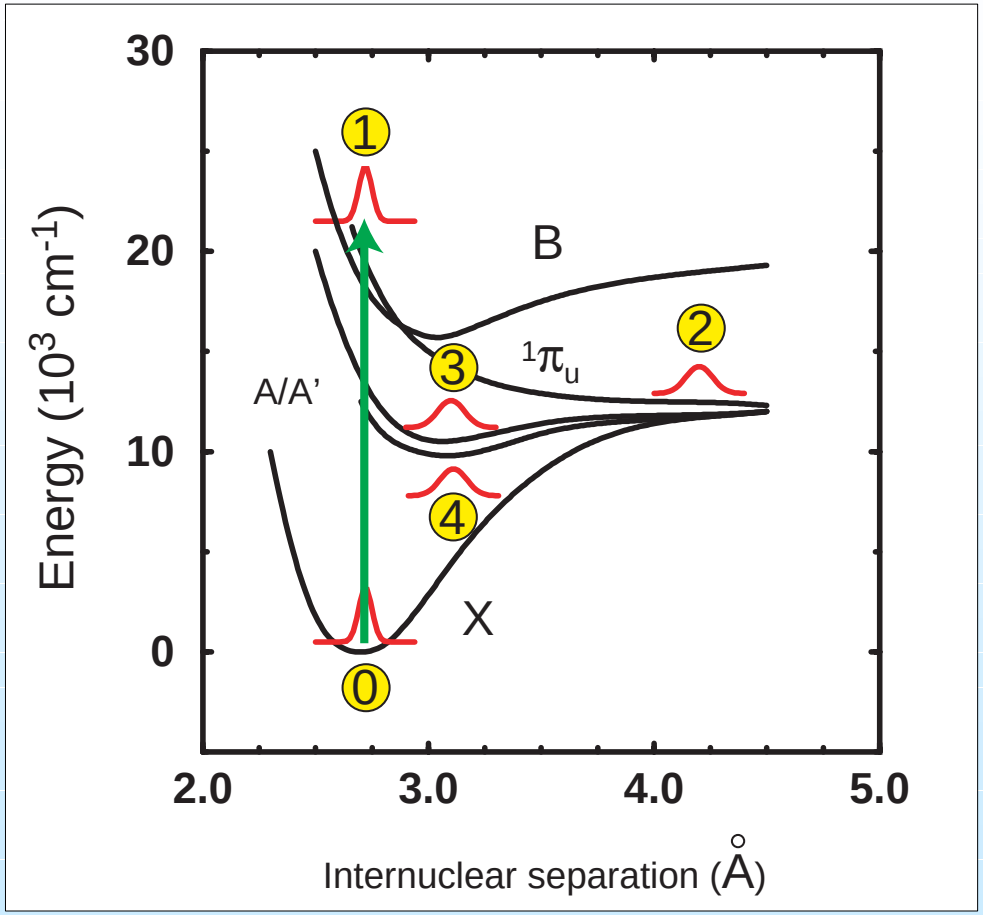
It is essential that we develop an intuitive picture of this behavior

LCLS **will make it possible to directly observe this complex motion.**



The solvent cage changes the dynamics and provides a means to study recombination reactions.

I_2 in dichloromethane (Neutze *et al.*)



1 → 2 300fsec

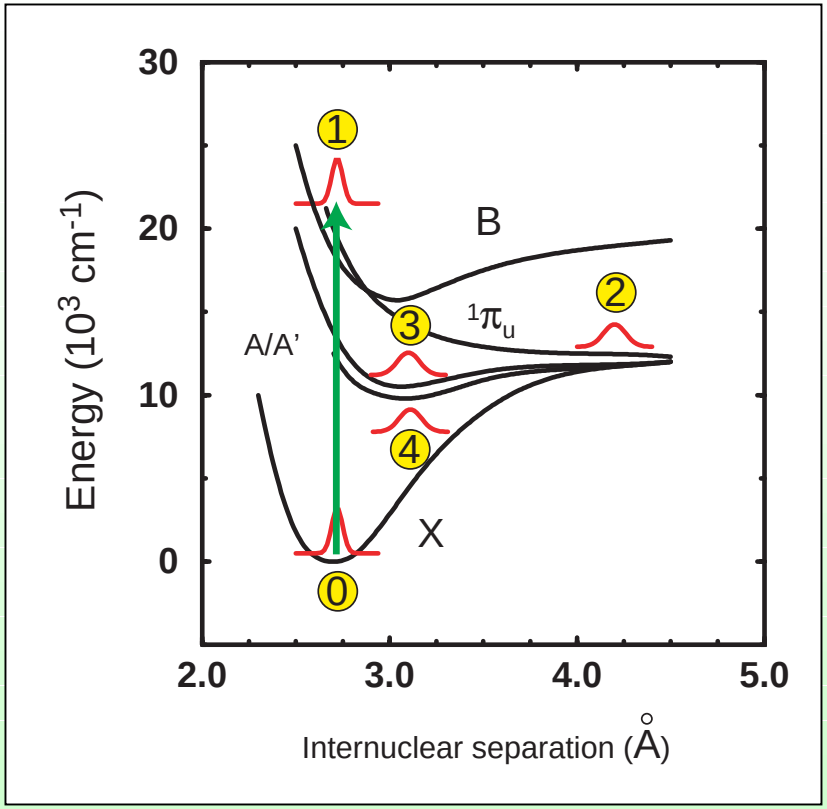
2 → 3 100psec

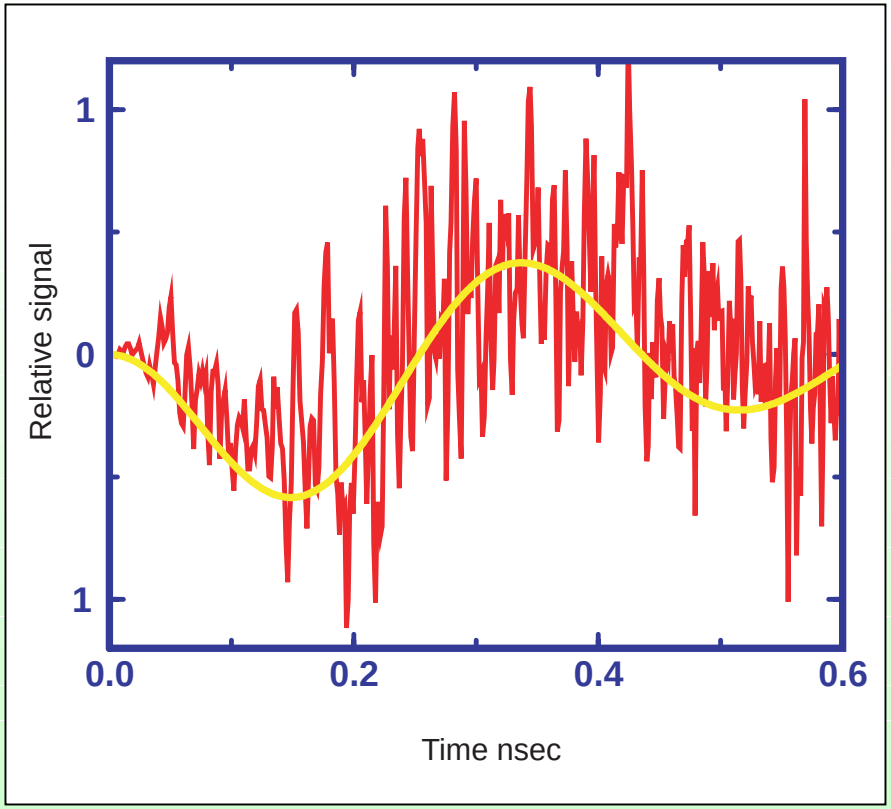
3 → 4 200psec

4 → 0 200psec

Diffuse X-ray scattering with 80 psec time resolution from European Synchrotron Radiation Facility

I_2 in dichloromethane (Neutze *et al.*)





Nanoparticles

Semiconductors and metal nanocrystals also known as quantum dots possess unique size-dependent electronic and optical properties that result from quantum size confinement of charge carriers and very large surface to volume ratios.

These properties hold great promise for applications in areas such as microelectronics, electro-optics, photocatalysis, and photoelectrochemistry. They are also particularly attractive, because of their large surface area and fast charge transport properties, for photovoltaics and photo-degradation of chemical wastes and pollutants.

The size distribution problem

Under most experimental conditions size dependent properties tend to be masked by the presence of a wide size distribution. The high intensity of the *LCLS* will make it possible to conduct experiments on *single particles*.

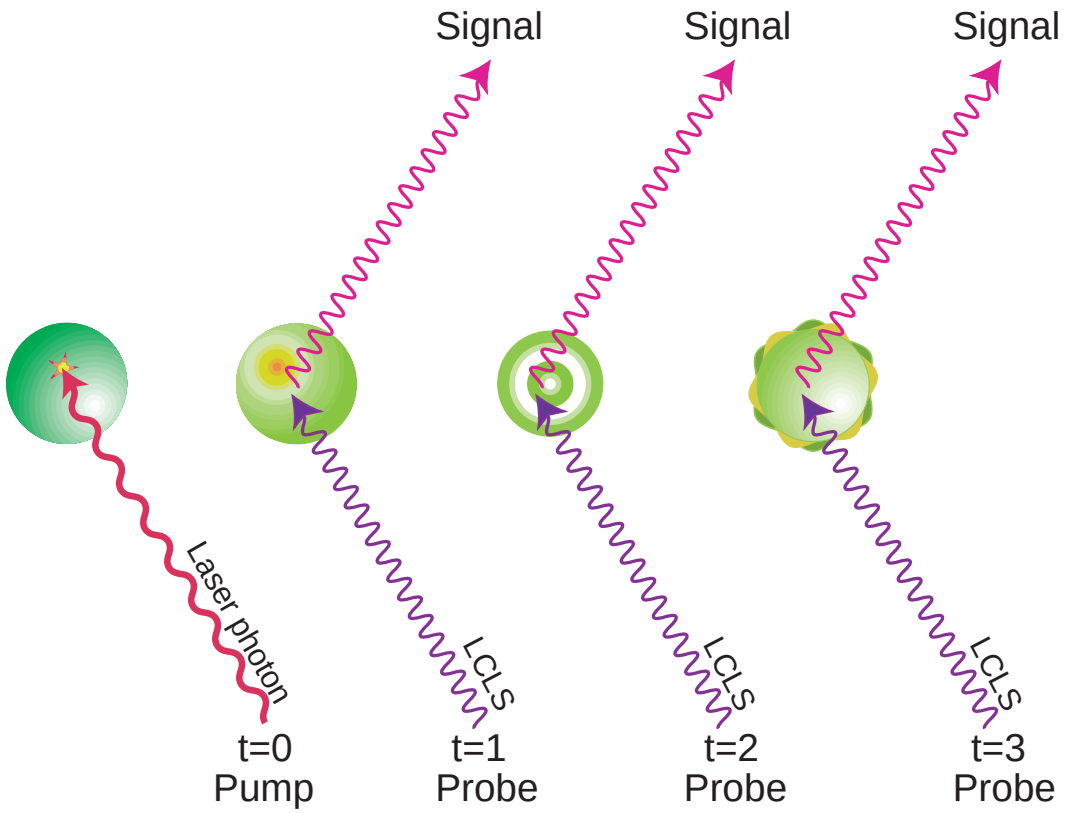
The solvent effect

Under most experimental conditions the high surface to volume ratio results in extreme sensitivity to solvent. To provide for a controlled, reproducible, well defined, inert environment, with low scattering background particles will be isolated in Ne crystals for study.

Melting a single nanoparticle

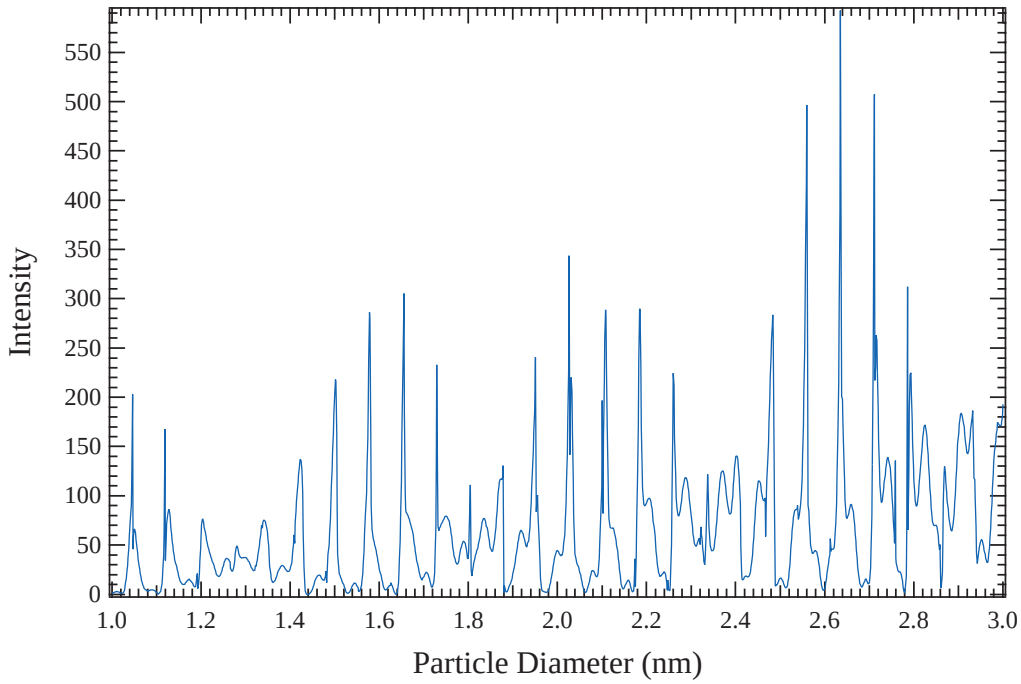
Experiment 3. Vibrations in nanoparticles

LCLS



The time evolution of the Mie scattering spectrum at 1.5 Å will make it possible to map out internal particle vibrational modes as well as surface capillary modes of a single nanoparticle.

Mie scattering spectrum at 1.5 Å



Simulated scattering intensity at a single angle as a function of particle size. A similarly rich spectrum is obtained for a fixed particle size as a function of scattering angle.

Mie spectra are extremely sensitive to changes in particle size and shape.

The *LCLS* is the only tool that will, in the foreseeable future, make it possible to observe nuclear motion during a reaction in real time.

The *LCLS* can be applied to a wide range of problems in the field of chemistry, some of which were touched upon here, from the most fundamental photodissociation reaction, to the more applied problem of characterizing the properties of nanoparticles.