Ultrafast Processes in Matter

We have all of these wonderful tools, what can we do with them scientifically?

Study ultrafast processes in matter:

Atoms & Molecules
- Electron motion in atoms – formation of wavepackets
- Reaction dynamics in molecules
- Control of processes

Solids
- Electron dynamics
- Phonons
- Laser induced disordering

Biological
- Vision: Rhodopsin
- Photosynthesis
- Biomolecule dynamics
Ultrafast processes in atoms

Are there any interesting ultrafast processes in atoms? time scales tend to be slow ~ nanoseconds

But with an ultrafast pulse, it is possible to excite transitions simultaneously
The optical coherence of the pulse will result in quantum coherence amongst the transitions
When there are many transitions within the bandwidth, this yields a “wave packet”
Most easily achieved for high lying “Rydberg” states in an atom
Wave packets are interesting from the point of view of fundamental quantum mechanics
Connection between quantum and classical mechanics
A localized classical state is a wave packet of quantum states

\[ E_n = -\left[ \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, n = 1, 2, 3, \ldots \]
Observation of Spatially Localized Atomic Electron Wave Packets

John A. Yeazell and C. R. Stroud, Jr.
The Institute of Optics, The University of Rochester, Rochester, New York 14627
(Received 21 January 1988)

FIG. 3. Scheme of the experimental setup.
Manipulation of Rydberg states

Rydberg states can be manipulated by electric field pulse with a duration comparable to the “orbit” time.

These can be generated from ultrafast pulses using “terahertz generation” techniques.

Using these pulses, it is possible to produce a fully localized wave packet, very similar to a classical state.
Wavepackets: Revivals and Fractional Revivals

Wave packets spread due to unequal level spacing (anharmonicity)

For finite number of levels packet reforms: “revival”

\[ \cos[\omega_0 t] + \cos[(\omega_0 + \Delta)t] + \cos[(\omega_0 + 2\Delta + \delta)t] \] has a peak at \( t = \frac{2\pi}{\delta} \)

Revivals can occur in which the wave packet is split into parts -- nonclassical
Excitation of molecular wave packets

A short pulse can excite a wave packet in a molecule as well

Packet of internuclear distance (or bond length) of molecule

Corresponds to specific internuclear distance

Resulting motion can be monitored using a number of techniques

Excitation to a higher state that then fluoresces

Excitation to a higher state that dissociates

Mapping potential energy surface

Fluorescence-detected wave packet interferometry: Time resolved molecular spectroscopy with sequences of femtosecond phase-locked pulses

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J. Chem. Phys. 95 (3), 1 August 1991 0021-9606/91/151487-25$03.00 © 1991 American Institute of Physics 1487
Molecules: Transition states

Studies of chemical reactions used to focus on kinetics:

How fast does the reaction $AB + C \rightarrow A + BC$ proceed?

Using ultrafast techniques, it is possible to study reaction dynamics

Specifically consider an intermediate transition state

$AB + C \rightarrow [ABC]^\dagger \rightarrow A + BC$

What is $[ABC]^\dagger$ and how long does it exist?

Experiment at right shows reaction

[Dantus, Rosker, Zewail, J. Chem. Phys. 87, 2395 (1987)]

$ICN \rightarrow [I…CN]^\dagger \rightarrow I + CN$

Transition state is electronic excited state of molecule

Created by pump pulse

Probe pulse excites CN which then fluoresces

Transient state observable
Revivals in molecular motion

Just as for atomic Rydberg wave packets, molecular vibrational wave packets spread due to anharmonicity.

Anharmonicity tends to be weaker close to bottom of molecular potential versus high up in a Coulomb potential.

Again as for Rydberg wave packets it is possible to see revivals when the wavefunctions rephase.

Ultrafast Diffraction

These techniques provide information about atomic motion in a molecule

How can such information be obtained, leads one to ask, what is the relevant static measurement to consider?

- X-rays
  - Diffraction
  - Absorption

Also electron diffraction can also be useful (much stronger interaction)

Can ultrafast versions be developed to provide dynamic structural information?

Yes….

although challenging

also used for solids, better signals (next week)
**Generation of hard x-rays**

Hit solid or liquid target with high power pulse

Produces a plasma that radiates x-rays

Need fresh target every shot

Liquid moving target (wire)

Alternative

Synchrotron

“Slice” electrons from bunch

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**Generation of Femtosecond Pulses of Synchrotron Radiation**

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*Fig. 5. X-ray emission spectrum measured from a liquid-mercury target in a helium atmosphere at standard conditions. The spectrum is corrected for the detection efficiency of the x-ray CCD camera and the absorption of all materials in the x-ray beam’s path. For orientation, the positions of the iron and the chlorine K absorption edges are shown. No line emission is visible in the entire spectral range.*
Sample initially photo excited by laser pulse

Ultrafast x-ray absorption peak

Peak position is proportional to bond length

Shift to lower energy consistent with increasing Fe-C distance

Inconsistent with ionized product

Ultrafast tabletop laser-pump–x-ray probe measurement of solvated Fe(CN)$_6^{4-}$

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Ultrafast Electron Diffraction

Diffraction patterns from CHD

Changes in molecular structure can be inferred from diffraction pattern
Ultrafast electron diffraction from molecules

1,3-cyclohexadiene ring opening reaction to hexatriene upon excitation to the 1B2 electronic state. Diffraction images illustrate that structural observations of prototypical organic reactions can be made in real time, opening a new methodology to study chemical reaction dynamics.