Ultrafast dynamics of molecular systems with ultrashort optical and X-ray pulses

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Dynamics of molecular systems

Intramolecular charge transfer dynamics
Spin dynamics
Intramolecular vibrational relaxation
Solvation dynamics
Solute-solvent photochemical reactions

Photovoltaics

Magnetic Data storage

Photocatalysis
Ultrafast Intramolecular Relaxation

- Intramolecular energy redistribution and internal conversion at extremely short times.
- High frequency FC modes dump impulsively their energy to lower frequency ones (often optically silent)


- Valid for organic dyes


- Ultrafast Intersystem crossing: No «heavy-atom rule». DOS, SOC and structural dynamics play crucial role at ultrashort times


Kasha-Vavilov Rule (Disc. Faraday Soc. 1950) very robust!
I. Ultrafast photoelectron spectroscopy of charge transfer reactions: beating the Kasha-Vavilov rule

II. X-ray studies of Conical Intersections
Extreme-UV femtosecond source: Facility for photoelectron spectroscopy (ESCA) of liquid, gas and solid phases. Complementary to X-ray studies at the SLS and XFELs

VUV spectrometer

Liquid phase chamber

Electron spectrometer

Ellipsoidal mirror chamber

VUV steering chamber

Grating monochromator

High harmonic generation

Molecular beam end station

TR - ARPES end station

10 - 120 eV
40 fs pulses
10 kHz
Polarization control

Funding:

Aqueous Ferrioxalate

\[
[Fe^{III}(C_2O_4)_3]^{3-} + h\nu \rightarrow [(CO_2)Fe^{II}(C_2O_4)_3]^{3-} + CO_2 \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + CO_2 + CO_2^- 
\]

Parker & Hatchard, J. Phys. Chem. 1959
Straub et al. PCCP 2018
• **Initial events:**
  - How fast is the photoreduction?
  - How fast is the first \( CO_2 \) dissociation?
  - Does reduction trigger dissociation or vice-versa?
  - What is the role of the solvent?

Previous ultrafast visible, IR and X-ray absorption TA studies:
- No consensus on the reduction process (<140 fs to > 150 ps)
- No consensus on the initial \( CO_2 \) dissociation (<140 fs to 2 ps)
- No consensus on second \( CO_2 \) dissociation (2 ps to 1 ns)
- IR TA studies point to ~25-35% recovery of parent molecule in ~ 2 ps. Attributed to intramolecular relaxation.

Rentzepis and co-workers, Inorg. Chem. 2008
Suzuki and co-workers, Struct. Dyn. 2015
Vöhringer and co-workers, PCCP 2018
Ultrafast Vacuum ultraviolet (VUV) photoelectron spectroscopy of solutions

Winter and Faubel, Chem. Rev. 2006

Ojeda et al, PCCP 2017
Aqueous Ferrioxalate

Pump at 4.66 eV
Probe at 34 eV

$\tau_R < 30$ fs
(upper limit)

LAPE: Arrell et al., PRL 2016
- 25% of ferrous species are lost in 2 ps
- IR TA: partial (25-35 %) recovery of depleted parent molecule population in ca. 2 ps. Attributed to intramolecular relaxation.
- X-ray TA: <140 fs CO$_2$ dissociation and 2-3 ps relaxation time, attributed to dissociation of the second fragment (the CO$_2^-$ anion)
Aqueous Ferrioxalate

Photoreduction < 30 fs
Dissociation < 140 fs, QY 100%
Geminate recombination ~2 ps, 25-35%
Cage exit, 65-75%

Longetti et al, PCCP (in press)
Electronic cooling in <20 fs for non-symmetric modes.

Messina et al, JPCL (2015)
Conical intersections
Ab-initio multiple spawning (AIMS)
Method:
Conical Intersections

Conical Intersections

Use X-ray emission spectra (XES) rather than X-ray absorption
No photoinduced XES spectra available

- Only electron-impact XES available (Brammer et al, CPL 1984)
- Photoinduced XES recorded at ELETTRA. Resonant XES excited at ~285 eV. Non-resonant XES excited at ~310 eV
- Simulations using the DFT-ROCIS protocol and the RIXS module in ORCA (Coll. M. Odelius, Stockholm)
Non-resonant X-ray emission spectra

Resonant X-ray emission spectra

Ingle et al., J. Phys. B (submitted)
Very good agreement theory-experiment

Allows identifying which atoms contribute to the XES

Competition between dynamics through CI and core-hole lifetime of Carbon.
First, it should be mentioned that in XAS, the processes of ejection, backscattering, and interference are extremely fast. For inner shell electrons with ionization energies above 1 keV, these processes are mostly completed well within ~1 fs, as can be seen from the measured homogeneous line widths of the absorption edges. This means that XANES and EXAFS take a truly instantaneous snapshot of immobile atoms, even during a violent chemical reaction. Therefore, implementing ultrafast time-resolved XAS via the pump–probe scheme (Figure 1) is straightforward.

\[1 \text{ eV} = 1.52 \text{ fs}\]
<table>
<thead>
<tr>
<th>Method</th>
<th>Type of information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep-UV to visible probe (270-700 nm) Transient absorption</td>
<td>Electronic</td>
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<tr>
<td>Polychromatic Fluorescence up-conversion IR to UV (300 nm to 2 µm)</td>
<td>Electronic</td>
</tr>
<tr>
<td>Ps and fs X-ray (2 to 20 keV) absorption spectroscopy (XANES and EXAFS)</td>
<td>Electronic and geometric</td>
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<tr>
<td>Ps and fs X-ray emission and inelastic scattering spectroscopy (coll. XFEL)</td>
<td>Electronic, spin, momentum</td>
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<tr>
<td>Multidimensional TA Ultraviolet and coherent visible spectroscopies</td>
<td>Geometric, electronic and correlations</td>
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<tr>
<td>Deep-UV circular dichroism</td>
<td>Geometric and correlations</td>
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<td>Momentum, electronic</td>
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