Ultrafast Spectroscopic Methods:
Fundamental Principles and Applications in Photocatalysis

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MacMillan Group Meeting
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**Timescales of Molecular Events**

- **μs (10^{-6} s)**
  - diffusion at room temp.
  - • electron transfer
  - • energy transfer

- **ns (10^{-9} s)**
- **ps (10^{-12} s)**
- **fs (10^{-15} s)**

- **dF(CF_3) Fluorescence**

- **intersystem crossing**
  - S_n → ISC → T_n
  - S_0 →

- **bond vibrations**
Molecular Systems Studied with Ultrafast Spectroscopy

**short timescale processes**
- Energy transfer (EnT)
- Electron transfer (ET)
- Photoluminescence (PL)
- Internal conversion (IC)
- Intersystem crossing (ISC)
- Proton transfer
- Bond isomerization

**excited-state organometallic chemistry**

**materials science**

Outline for the Presentation

- **Basics of Transient Absorption Spectroscopy**
  - physical basis for observed spectral changes
  - experimental setup
  - data analysis

- **Case Study 1: Excited State Dynamics in a Photocatalytic Polymerization**
  - original hypothesis and revised mechanism

- **Case Study 2: Observation of an Ultrafast Energy Transfer Event**
  - Intro to TCSPC (time-correlated single photon counting)
  - excited-state lifetime measurements and TEAS measurements reveal EnT event

- **Case Study 3: Excited-State Conformational Changes in CuI Complexes**
  - physical basis for time-resolved fluorescence spectroscopy
  - experimental apparatus for ultrafast fluorescence measurements
Taking Snapshots of Ultrafast Molecular Dynamics

Flight can be reconstructed from multiple snapshots of the process taken at different delays.

Detector requirements:
- Fast shutter speed (short laser pulse)
- Short delays

Processed data

Images show different time stamps:
- $t = 0 \text{ s}$
- $t = 0.5 \text{ s}$
- $t = 1.0 \text{ s}$
- $t = 1.5 \text{ s}$
Experimental Setup and Hardware

Crucial Features

- spatial and temporal overlap of pump/probe
- short pulse duration
- short pulse delay (ps-μs timescale)
- stable, broad spectrum probe

pump
visible light

probe

- white light
- broadband IR
- XAS (X-ray Absorption)
- NMR

website of Mikas Vengris http://web.vu.lt/ff/m.vengris/
Origin of the Ground State Bleach (GSB) Feature

Pump

Probe

ES 1

ground state

red – blue

ΔA

300 400 500 600 700 800 900

a.u./OD

300 400 500 600 700 800 900

a.u./OD
Origin of the Excited State Absorption (ESA) Feature

Pump

Probe

$ES_1$

$ES_2$

$ES_1$

$ESA$

ground state

ground state
Origin of the Excited State Absorption (ESA) Feature

Excited State Absorption - positive signal in ΔA spectrum
Overview of Commonly Observed ΔA Features

GSB and SE features often overlap in wavelength - can be hard to distinguish within negative feature
Representation and Handling of 3-Dimensional Data

**contour plot/heat map**

**single-wavelength analysis**

- 530 nm (GSB)
- 700 nm (ESA)

**single-timepoint analysis**

- Multiple ways to visualize data
- Multiple single-timepoint traces may be most common

Glotaran Data Analysis Software
Kinetic Models for Excited State Decay

**branched model**

\[ k_1 \quad k_2 \]

\[ \text{[ester]} \]

**sequential model**

\[ h\nu \quad k_1 \quad k_2 \]

\[ \text{[ester]} \]

*more complicated combinations of these simple models can be invoked

*beware of overfitting: complex models can fit data well, but be unphysical

*choice of model precedes fitting process:
  some intuition or physical knowledge required

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Atom-Transfer Radical Polymerization with an Organic Photocatalyst

**Photocatalyst**

PC

\[ \text{Br} - \text{C} = \text{O} \text{Et} \]

**Initiator**

**Monomer**

\[ \text{Me} - \text{C} = \text{O} \text{Me} \]  

**Polymer**

\[ \text{EtO} - \text{C} - \text{Me} - \text{Me} - \text{Br} \]

**Photocatalyst**

PCH

\[ \begin{array}{c}
\text{N} \\
\text{Ph} \\
\text{N} \\
\text{Ph}
\end{array} \]

PCF

\[ \begin{array}{c}
\text{N} \\
\text{Ph} \\
\text{N} \\
\text{Ph} \\
\text{CF}_3
\end{array} \]

\[ \text{D} = 1.55 \]

**Superior dispersity (D = 1.17)**

**High initiation efficiency (I* = 69.5%)**

Bimolecular Excited-State Dynamics of PCF by TVAS and TEAS

triplet sensitizers do not quench PCF*

PCF* does not access T_n manifold by TVAS

MP• is generated by SET from S_1 state of PCF*
Excited State Electron Transfer Rates for PCF and PCH

PCF (Ar = 4-(CF$_3$)-phenyl)

PCH (Ar = phenyl)

$\text{PCF} \rightarrow \text{MBP} \rightarrow \text{PCH/F}^* + \text{Br}^-$

plots of $1/\tau$ v.s. [MBP] reveals $k_{PET}$ values for PCF and PCH

<table>
<thead>
<tr>
<th>PC</th>
<th>$k_{PET} \text{ (s}^{-1} \text{M}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCF</td>
<td>$3.9 \pm 0.2 \times 10^9$</td>
</tr>
<tr>
<td>PCH</td>
<td>$3.6 \pm 0.2 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Biexponential fit of the PET kinetics for PCH reveals static PET (within 7-17 ps) to MBP
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Time-Correlated Single Photon Counting (TCSPC)

- Method of choice for determining excited state lifetimes of luminescent molecules with lifetimes as low as 10 ns
- Requires 1-6 hours per experiment, depending on phosphorescence intensity

Wei, L.; Yan, W.; Ho, D. Sensors 2017, 17, 2800.
Energy Transfer Between Transition Metal Centers

\[
\text{Ir}^* + \text{Ni} \xrightarrow{h\nu} \text{EnT} \xrightarrow{\text{relax}} \text{Ir} + \text{Ni}^*
\]

**inverted kinetics**

\[k_{\text{relax}} \gg k_{\text{EnT}}\]

**Ni* cannot be observed**

If \(k_{\text{relax}} > 10^9 \text{ s}^{-1}\), we cannot observe the build up of Ni* since \(k_{\text{EnT}}\) is diffusion-limited.

Observation of Partial Quenching of Excited-State Iridium

\[ \phi_{PL} = 0.17 \pm 0.02 \]
\[ \tau = 640 \text{ ns} \pm 60 \text{ ns} \]

\[ \phi_{PL} = 0.011 \pm 0.002 \]
\[ \tau = 650 \text{ ns} \pm 70 \text{ ns} \]

anomalous lowered photoluminescence with unchanged lifetime (\(\tau\))

**proposed mechanism**

- \(\text{EnT}\) quenches excited state
- \(\text{EnT}\) must compete with IC
- requires \(\text{EnT}\) to be on ps timescale

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Observation of Ultrafast EnT from Ir(ppy)$_2$(phen) to CoCp

Excited state dynamics of Ir-Co complex mirrors that of isolated Co center: implies Ir–Co EnT
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Photophysics of Excited-State Cu(I)(phen) Complexes

- Large Stokes shift
- Excited-state lifetime modulated by phenanthroline substituents

**Cu(I)(dmphen)₂PF₆**

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{abs} (nm)</th>
<th>λ_{PL} (nm)</th>
<th>Φ_{PL} \times 10^4</th>
<th>τ (ns)</th>
<th>ΔG{sub}^{*} (eV)</th>
<th>E_{1,2}</th>
<th>E_{yy}^{*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(phen)₂(PF₆)</td>
<td>458 (6880)</td>
<td>–</td>
<td>–</td>
<td>&lt;10</td>
<td>–</td>
<td>0.19</td>
<td>–</td>
</tr>
<tr>
<td>Cu(dmp)₂(PF₆)</td>
<td>454 7950</td>
<td>740</td>
<td>2.3</td>
<td>85</td>
<td>2.04</td>
<td>0.64</td>
<td>–1.4</td>
</tr>
<tr>
<td>Cu(dpp)₂(PF₆)</td>
<td>448 (3440)</td>
<td>715</td>
<td>9.7</td>
<td>250</td>
<td>1.99</td>
<td>0.58</td>
<td>–1.4</td>
</tr>
<tr>
<td>Cu(bcp)₂(PF₆)</td>
<td>478 (13 200)</td>
<td>765</td>
<td>1.5</td>
<td>70</td>
<td>1.98</td>
<td>0.58</td>
<td>–1.4</td>
</tr>
</tbody>
</table>

- *Excited state is characterized as MLCT, and quenched by ET and EnT mechanisms*
- *Structurally related Cu(I) complexes have been implicated in photocatalytic transformations*
Molecular Basis for Time-Resolved Fluorescence Spectroscopy

- Time resolution of detector technology does not permit this approach to measuring fast dynamics
- Two solutions are often implemented: an optical Kerr shutter, and photon upconversion
Experimental Setup for Time Resolved Fluorescence via Upconversion

**photon upconversion setup**

\[ I_{\text{upconv}}(t) \sim I_{\text{gate}}(t) \times I_{\text{fluorescence}}(t) \]

\[ \frac{1}{\lambda_{\text{recorded}}} = \frac{1}{\lambda_{\text{fluorescence}}} + \frac{1}{\lambda_{\text{gate}}} \]

**gate pulse** + **fluorescence** must overlap

gate pulse takes slices out of **fluorescence** signal

website of Mikas Vengris http://web.vu.lt/ff/m.vengris/
Steady-State and Time-Resolved Emission Spectra of Cu(I)(dmphen)$_2$PF$_6$

- steady-state absorption
- sub 50 fs fluorescence
- sub 100 ns fluorescence
- steady-state fluorescence

$S_0 - S_n$ Transitions

- $S_2$
- $S_1$
- $S_0$

Lower oscillator strength at 550 nm, but higher fluorescence intensity: branching kinetics?

Excited-State Dynamics of Cu\(^{I}\)(dmphen)\(_2\)PF\(_6\) by Fluorescence Upconversion

branching model fits fluorescence decay kinetics and reveals long-lived flattened \(S_1\) state

Useful References and Reviews on Ultrafast Measurements


- Good primer on TEAS, and time-resolved fluorescence spectroscopies: http://web.vu.lt/ff/m.vengris/

- Review on fitting data from ultrafast measurements:
  *Biochimica et Biophysica Acta (BBA) - Bioenergetics* 2004, 1657, 82–104.

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**textbooks**

* Molecular Fluorescence: Principles and Applications
* Modern Molecular Photochemistry of Organic Molecules
* Femtosecond Laser Pulses: Principles and Experiments

**tripletes and fluorescence**  
**everything photophysics**  
**ultrafast laser pulses**