Time Resolved Spectroscopic Studies of Chemical Dynamics

Kelly Gaffney
PULSE Center Photon Science Division at SLAC
June 20, 2007
Chemistry… *Warner Bros. Style*

The mechanism!?! 
Embedded in $Q$ and $\omega_Q$

$$K = \frac{C_{prod}}{C_{reac}} = \exp(-\Delta G / kT)$$

$$k = \omega_Q \exp(-\Delta G^\dagger / kT)$$
Borrowing from the Discothèque
Stroboscopic Studies of Dynamics

**time delay**

**time**

Red is laser trigger
Blue is laser probe

**time**
Electronic Spectroscopy and Franck-Condon Principle

The Franck-Condon principle supposes momentum of nuclei conserved.

\[ \langle \psi_f | e \cdot \mu | \psi_i \rangle = \sum_f \frac{2 \pi}{\hbar} \langle \phi_f | e \cdot \mu | \phi_i \rangle \chi_f \chi_i \]

'vertical excitation' that project \( \chi_i \) onto \( \chi_f \)

Electronic Absorption Spectrum
Time Domain Picture of Spectroscopy

\[ I(\omega) \propto \sum_{w} \left< \chi_v \left| \phi_1 e \cdot \mu \phi_2 \right> \chi_w \left| \phi_2 e \cdot \mu \phi_1 \right> \chi_v \right> \delta(E_f - E_i - \omega) \]

replace delta function with Fourier transform

\[ I(\omega) \propto \int_{-\infty}^{\infty} dt \exp(-i(\omega - \omega_{21} - \omega_{vw})) \sum_{w} \left< \chi_v \left| \phi_1 e \cdot \mu \phi_2 \right> \chi_w \left| \phi_2 e \cdot \mu \phi_1 \right> \chi_v \right> \]

use \( H^{vib} \) to propagate on excited state potential

\[ I(\omega) \propto \int_{-\infty}^{\infty} dt \exp(-i(\omega - \omega_{21} - \omega_{v})) \left< \chi_v \left| \tilde{\mu}_{21} \exp(-iH^{vib}_2 t / \hbar) \tilde{\mu}_{21} \right| \chi_v \right> \]

define a wavepacket

\[ \exp(-iH^{vib}_2 t / \hbar) \tilde{\mu}_{21} \left| \chi_v \right> = \left| \Phi(t) \right> \]

time domain view of electronic absorption

\[ I(\omega) \propto \int_{-\infty}^{\infty} dt \exp(-i(\omega - \omega_{21} - \omega_{v})) \left< \Phi(0) \left| \Phi(t) \right> \right> \]

Time Domain Picture of Spectroscopy continued...

\[ I(\omega) \propto \int_{-\infty}^{\infty} dt \exp(-i(\omega - \omega_2 - \omega_v))\langle \Phi(0)|\Phi(t)\rangle \]
How Do We Access Molecular Dynamics?

Light Pulses → *intensity, phase, frequency, and polarization*

*Time resolved spectroscopy*
Monitors the time dependent evolution of any and all of these properties for a signal pulse generated by prior excitation pulses.
Pump Probe Spectroscopy

excited state population dynamics

\[ E = h \nu - \Delta \]

\[ E = h \nu \]

Stimulated Emission

Ground State Bleaching

\[ \Delta A < 1 \rightarrow \Delta A \propto \Delta n \]
Frequency Resolved Pump Probe Spectroscopy

Structural dynamics inferred from spectral dynamics...inference often ambiguous
Pump Probe Spectroscopy continued...

Complexity of Optical Transient Absorption

Multiplicity of chemical species
Multiplicity of electronic states
Time evolving absorptions

Structural dynamics inferred from spectral dynamics...inference often ambiguous
Polarization Resolved Pump Probe Spectroscopy measures transient dichroism

pump prepares $\cos^2\theta$ distribution

probed at magic angle and parallel to pump polarization

$$R(t) = \frac{S_{||}(t) - S_{ma}(t)}{2S_{ma}(t)}$$
Iodine Photodissociation and Geminate Recombination

* A Chemical Dynamics Case Study

Theoretical $I_2$ potential energy diagrams

X state frequency $\sim 210$ cm$^{-1}$

B state frequency $\sim 110$ cm$^{-1}$

Iodine Photodissociation and Geminate Recombination

A Chemical Dynamics Case Study

pre-dissociation

dissociation

geminate

recombination

vibrational cooling

Pre-Dissociation and Curve-Crossing Dynamics

Phase Shift in Excited State Absorption
Probes Delay in Dissociation

Decay of Ground State Bleach Provides Access to Time Scale for Vibrational Relaxation in Solution

CO Photo-dissociation from Myoglobin

...another case study

http://www.fizyka.umk.pl/~wiesiek/HEMOHIS.JPG
CO-Myoglobin Photo-Dissociation
Ultrafast Electronic Spectroscopy


CO-Myoglobin Photo-Dissociation
Ultrafast Vibrational Spectroscopy

\[
\frac{\Delta A^\perp}{\Delta A^\parallel} = \frac{4 - \sin^2 \theta}{2 + \sin^2 \theta}
\]
CO-Myoglobin Photo-Dissociation: CO Orientational Dynamics

Initial photolyzed configuration reached in ~2 ps

CO-Myoglobin Photo-Dissociation: time resolved crystallography

Electronic Excitation Driven Disorder in Semiconductors:
Transient Optical Reflectivity

ΔR dictated by change in $\varepsilon$

$\Delta \varepsilon_{\text{Drude}} \propto N_{e-h} \frac{1}{1 + i \frac{1}{\omega \tau}}$

Electronic Excitation Driven Disorder in Semiconductors

Intense laser excitation causes lattice instability

Femtosecond Disordering of InSb

biphasic dynamics: initial Gaussian decay followed by exponential decay
amplitudes provide dominant fluence dependent not time constants

\[ \tau_{111} = 340 \pm 80 \text{ fs} \]
\[ \tau_{220} = 240 \pm 80 \text{ fs} \]
Initial Dynamics Dictated by Thermal, Inertial Dynamics

Non-equilibrium Debye-Waller-like Factor:  \[ I_Q(t) = I_0 \exp(-Q^2 \Delta r^2(t)) \]

Franck-Condon Principle:  \[
\Delta r^2(t) = \frac{1}{3} \left\langle v^2 \right\rangle t^2 = \frac{kT}{M} t^2
\]

combining…  \[ I_Q = I_0 \exp\left(-\frac{t^2}{\tau_G^2}\right) \]  where  \[ \tau_G \equiv \frac{1}{k_G} \sqrt{\frac{M}{kT}} \]

predicted…  \[ \tau_{111} = 400 \text{ fs} \quad \text{and} \quad \tau_{220} = 260 \text{ fs} \]

measured…  \[ \tau_{111} = 340 \pm 80 \text{ fs} \quad \text{and} \quad \tau_{220} = 240 \pm 80 \text{ fs} \]

*inertial dynamics preserve memory of the crystal lattice, producing a disordered crystal not a liquid-like structure*
**Time Dependent rms Displacement**

\[ I_Q(t) = I_0 \exp(-Q^2 \Delta r^2(t)) \]

\[ \Delta r(t) = \left(3 \frac{\ln I_0 - \ln I(t)}{Q^2}\right)^{1/2} \]
Time Resolved Spectroscopic Studies of Chemical Dynamics

**what does it do well?**

- Can provide *solute’s-eye-view* of chemical dynamics when the *excited state potential energy surfaces are known*.

**…and not so well?**

- Provide unambiguous mechanisms for chemical reactions in more complex materials.
- Provide direct information about environmental changes – ‘solvation’ – that accompany a chemical transformation.
Characteristic Phenomena Lacking Robust Experimental Observation

- How does the solvent cage deform and relax during I$_2$ geminate pair recombination and vibrational cooling?
- How does the solvent shell transform during the photo-ionization of a simple solute – such as $\text{I}^- + h\nu \rightarrow \text{I} + \text{e}^-$?
- How does the protein environment channel the photo-excitation energy to a desired end product – such as the transmembrane proton gradient in bacteriorhodopsin?
- How to the charge and spin states of a metal center evolve in organometallic complexes?
Diffuse X-ray Scattering Studies of Chemical Dynamics in Solution

\[ \text{C}_2\text{H}_4\text{I}_2 + h\nu \rightarrow \text{C}_2\text{H}_4\text{I} + \text{I} \]

Protein Crystallography Studies of Photobiological Dynamics

Bacteriorhodopsin: A Photoiniated Membrane Proton Pump

Photoactive protein
Biological Function retained in Crystal
Ultrafast Structural Dynamics
\[ \Phi = 0.6 \quad \varepsilon = 60,000 \text{ M}^{-1}\text{cm}^{-1} \text{ at } 580 \text{ nm} \]
Hypothesized Structural Intermediates
but mechanism yet to be resolved

Bacteriorhodopsin Photocycle Initiated with all \textit{trans} to \textit{13-cis} Isomerization

Isomerization occurs within 500 fs

K intermediate forms with a 4 ps time constant

X-ray Spectroscopy Studies of Spin and Charge Dynamics

x-ray spectroscopy *atomic specific view of electronic structure*

non-resonant x-ray emission spectroscopy provides the easiest spectroscopic experiment from the source perspective

XANES $\Delta E \sim 50$ eV measurements and resonant emission viable… though source must be tuned to a specific edge.

EXAFS $\Delta E \sim 500$ eV measurements will require lasing while changing the electron beam energy… *viability yet to be determined.*
X-ray Emission Spectroscopy Primer

$K\beta_1$ intensity sensitive to spin multiplicity, ligand type, metal-ligand bond length

$K\beta'$ intensity sensitive to oxidation state