Light, Molecules, Action!
Using light to power molecular devices

USING ULTRAFAST UV-VISIBLE AND X-RAY SPECTROSCOPY TO PROBE EXCITED STATE DYNAMICS IN PHOTOACTIVE MOLECULES.

Cobalamin (Vitamin B₁₂)
Photochemistry
Light is a versatile energy source

- Light (esp. laser light) can be shaped, timed, tuned, focused, aimed and delivered at a target as required.

- Spatial and temporal control of molecular activation.

Optically controlled molecular devices

- motors, switches, activators, junctions, memory, logic circuits, actuators, sensors, and delivery platforms.

Function is controlled by photochemistry

- Photon energy produces action via movement of charge, change in shape or cleavage of a bond – light activates a change in the chemical nature of a molecular system.
The photochemistry of cobalamins is of interest:

- Newly discovered $\text{B}_{12}$ based photoreceptor proteins use light to control gene activation and carotenoid synthesis.

- The upper group “R” can be replaced by a drug (e.g., a cancer drug) to allow photoactivated drug delivery.

- Reactive radicals can be produced with spatiotemporal control.

- Photoresponsive “anti-vitamins” allow control of biological availability.

- Molecular switches and sensors can be developed by designing appropriate ligands, “R”.

![B12 Analogs: Anti-Vitamins and Optical Control](image)
B₁₂ Photolysis

\[
\text{AdoCbl} + h\nu \xrightarrow{\varphi \approx 100\% \ (20\%)} \text{Ado}^* + \text{Cbl}^* \\
\text{EtPhCbl} + h\nu \xrightarrow{\varphi < 1\%} \text{EtPh}^* + \text{Cbl}^* \\
\text{HOCbl} + h\nu \xrightarrow{\varphi \approx 2\%} \text{OH}^* + \text{Cbl}^* \\
\text{H}_2\text{OCbl}^+ + h\nu \xrightarrow{\varphi \approx 2\%} \text{OH}^* + \text{H}^+ + \text{Cbl}^* \\
\text{CNCbl} + h\nu \xrightarrow{\varphi \leq 10^{-4}} \text{CN}^* + \text{Cbl}^*
\]

Photochemistry is controlled by the lowest singlet state (S₁) surface or by branching of states at higher energy, bypassing S₁ state barriers.
B₁₂ Spectra

Typical UV-Visible Spectra

Wavelength (nm)

280 380 480 580 680

ε (10³ M⁻¹ cm⁻¹)

γ-band region

αβ-band region

CNCbl
H₂OClb
AdoClb
Co–OH₂⁺
Co–OH
H₂OClb
HOCbl
EtPhClb
PhEtyClb

Co–R =

AdoClb
CNCbl
H₂OClb
HOCbl
EtPhClb
PhEtyClb
HOCl (B$_{12b}$) Photolysis

pH 10.3, 99+\% HOCl

\[ \text{HOCl} + h\nu \xrightarrow{\varphi=2\%} \text{OH}^* + \text{Cbl}^* \]

\( \lambda_{\text{exc}}: \)
- 269 nm
- 404 nm
- 535 nm
- 560 nm
- 575 nm

HOCbl (B$_{12b}$) Photolysis

$\tau_1 = 0.32 \pm 0.08$ ps
$\tau_2 = 5.50 \pm 0.17$ ps
HOCbl (B$_{12b}$) Photolysis

pH 10.3, 99+% HOCbl

HOCbl + $h\nu \xrightarrow{\varphi=2\% \lambda<300\text{nm}}$ OH$^+$ + Cbl$^*$

269 nm only:

$\varepsilon (10^3 \text{M}^{-1} \text{cm}^{-1})$

-6 0 6 12 18 24

Wavelength (nm)

$\Delta \varepsilon (10^3 \text{M}^{-1} \text{cm}^{-1})$

-0.250 -0.125 0.000 0.125 0.250

Wavelength (nm)

0.32 \pm 0.08 \text{ ps}
5.50 \pm 0.17 \text{ ps}

$\text{Cob(II)}$ $\sim$2\% yield

$\gg$ 100 \text{ ps}
HOCbl (B\textsubscript{12b}) Photolysis

The surfaces for three different electronic configurations define the lowest excited state surface for cobalamins. (Calculations: Kozlowski et al.)

Photochemistry is controlled by the lowest surface or by branching of states at higher energy.
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Photochemistry is controlled by the lowest surface or by branching of states at higher energy.
Antivitamin $B_{12}$ EtPhCbl

- Photo conditional “anti-vitamin” $B_{12}$.
- Metabolically inert.
- Optical control of biological availability.

$$\text{EtPhCbl} + h\nu \xrightarrow{\phi<1\%} \lambda<600nm \text{EtPh}^+ + \text{Cbl}^+$$

Antivitamin $\text{B}_{12}$ EtPhCbl

![Diagram of Antivitamin $\text{B}_{12}$ EtPhCbl]

- N$_\text{DMS}$($\text{Co}^{II}(\text{corrin})-\text{R}$) $\rightarrow$ {N$_\text{DMS}$($\text{Co}^{III}(\text{corrin})^{+} + \text{R}^{+}$)}
- IC $\rightarrow$ GS
- Co-N$_\text{Hx}$ bond
- Co-"R" bond
- MLCT $\rightarrow$ I
- LF $\rightarrow$ IV
- IC $\rightarrow$ GS

![Absorption Spectra of Antivitamin $\text{B}_{12}$ EtPhCbl]

Absorption Intensity

$\Delta A$ (mOD)

Wavelength (nm)

- 13 ps
- 247 ps
Antivitamin B$_{12}$ EtPhCbl

\[
\text{IC} \xrightarrow{\text{N$_{\text{DMSO}}$}} \left\{\text{Co}^{II}(\text{corrin})-\text{R}\right\} \xrightarrow{\text{N$_{\text{DMSO}}$}} \left\{\text{N$_{\text{DMSO}}$}-\text{Co}^{II}(\text{corrin})]^{+} + \text{R}^{+}\right\}
\]

\[
\text{Co-N$_{\text{NIX}}$ bond} \xrightarrow{\text{III}} \text{LF} \xrightarrow{\text{IV}} \text{IC} \xrightarrow{\text{IC}} \text{GS} \xrightarrow{\text{IC}} \text{GS} \xrightarrow{\text{N$_{\text{DMSO}}$}} \left\{\text{N$_{\text{DMSO}}$}-\text{Co}^{I}(\text{corrin})]^{+} + \text{R}^{+}\right\}
\]

\[
\text{Co-"R" bond}
\]

\[
\begin{align*}
\text{Intensity} & \quad \text{Wavelength (nm)} \\
\text{pH 1} & \quad \text{pH } \sim 7
\end{align*}
\]

\[
\Delta A \text{(mOD)}
\]

\[
\frac{9\%}{\text{Base Off Yield}}
\]
Coenzyme B$_{12}$: AdoCbl

In Ethylene Glycol
Coenzyme B$_{12}$: AdoCbl

In Water (~pH 7)
Vitamin B₁₂: CNCbl

- **Absorbance**
  - Wavelength (nm):
    - 250, 325, 400, 475, 550, 625, 700, 775, 850
  - γ-band
  - αβ-band

- **Chemical Structures**
  - [Co^{II}(corrin)]⁻
  - N_{DMAB}-[Co^{II}(corrin)]⁻ + R⁺
  - N_{DMAB}-[Co^{II}(corrin)]⁻ + R⁺
  - Co-N \__{DMAB} bond
  - Co-“R” bond

- **Graphs**
  - ΔA (mOD)
    - Wavelength (nm): 280 to 530
    - Time Delay (ps): -5 to 20
  - ΔA (mOD)
    - Wavelength (nm): 300 to 530
    - Time Delay (ps): -0.6 to 1.2

- **Chemistry Symbols**
  - IC
  - GS
  - MLCT
  - LF
  - X
  - I
  - II
  - III
  - IV
Vitamin B\textsubscript{12}: CNCbl
Vitamin $\text{B}_{12}$: CNCbl

Femtosecond XANES of Vitamin B$_{12}$
Polarized XANES of Electronically Excited Vitamin B$_{12}$

- X-ray absorption near edge structure
- Sensitive to electronic and structural changes.

Optical excitation is along “x”.
Perpendicular in-plane direction is “y”.
The “z” direction is out-of-plane.

Probe at the cobalt K-edge excited Co 1s electrons.

Measuring the difference signal across the near edge region.

\[ \Delta S = S_{\text{Laser On}} - S_{\text{Laser Off}} \]

Perpendicular difference signal.
Excited State XANES

\[ \Delta S_{\parallel/\perp} = S_{\text{Laser On}} - S_{\text{Laser Off}} \]

Parallel

\[ \Delta S_{\text{isotropic}} = \Delta S_{\parallel} + 2\Delta S_{\perp} \]

Perpendicular

\[ S_{ES} = \Delta S_{\text{isotropic}} + \alpha S_{GS} \]
Excited State XANES
Comparison with Simulation


Co-C≡N  1.857  2.216
Co-N_{imd}  2.054  2.275
Polarized XANES
Comparison with Simulation

\[ \Delta S_{∥} = 0.6 \Delta S_x + 0.2 \Delta S_y + 0.2 \Delta S_z \]
\[ \Delta S_{⊥} = 0.2 \Delta S_x + 0.4 \Delta S_y + 0.4 \Delta S_z \]

\[ \Delta S_x = 2 \Delta S_{∥} - \Delta S_{⊥} \]
\[ \Delta S_{y+z} = 3 \Delta S_{⊥} - \Delta S_{∥} \]
Structural changes around the Co atom.

- With pulse: modest ring changes. \((\pi^1\pi^1)\)
- \(\tau_1 = 0.11\) ps: Axial bond elongation.
  \(\rightarrow((\pi/d)^1(\pi^*/d_{xy}+n^*/\sigma^*d_{z2})^1)\)
- \(\tau_2 = 0.26\) ps: Corrin ring/axial relaxation
  \(\rightarrow(\pi^1(\sigma^*d_{z2})^1)\)
- \(\tau_3 = 6.2\) ps: Excited state population decay.
  \(\rightarrow(\pi^2)\)
- Ultrafast XAS and UV-Vis combine to give picture of the structural and electronic dynamics on the excited state surface.
Acknowledgements

**Students:**
- Ted Wiley
- Nick Miller
- Laura Kiefer
- William Miller
- Jon Elrod
- Anushka Gupta

**Collaborators:**
- Pawel Kozlowski (Univ. Louisville)
- Bernhard Kräutler (Univ. of Innsbruck)
- Kevin Kubarych
- Ken Spears
- Jim Penner-Hahn
- Aniruddha Deb

**Synthesis of novel designed compounds**

**Theoretical simulation and prediction**
- Roberto Alonso-Mori
- James M. Glownia
- Jake Koralek
- Marcin Sikorski
- Diling Zhu

**Spectroscopic and Physical measurements**

**Development of light sources**

**Funding:**
- NSF
- SLAC National Accelerator Laboratory

**Our group,**
- Jim Penner-Hahn
- Kevin Kubarych

**LCLS Beamline scientists**