Ultrafast 1,3-Cyclohexadiene Ring-Opening Reactions: Dynamics and Control

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Aims and Goals …

Laser Control of Chemical Reactions

**Question:** Can we use optical pulse characteristics and environmental conditions to manipulate or control reaction dynamics in complex (condensed phase) environments?

**Approach:**

- Vary the environmental conditions – solvent, temperature, etc.
- Use ultrafast methods to monitor excited state dynamics
- Sculpt optical pulses using an acousto-optic modulator (AOM) or liquid crystal spatial light modulator (LC-SLM)

**Molecular Systems:**

- Cyclohexadiene
- $\alpha$-terpinene
- $\alpha$-phellandrene
- 7-dehydrocholesterol

Electrocyclic ring-opening, optical switches and biological chromophores.
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The initially prepared excited state population decays in approximately 21 fs accompanied by C=C bond elongation and twisting, internal conversion to the dark state occurs in approximately 35 fs accompanied by stretching of the C-C bond. The decay of the $2^1A$ state is ca. 80 fs accompanied by a much larger distortion from the near planarity of the initial chromophore. The reaction is described as “more or less ballistic” with negligible barriers along the reaction path.
Ultrafast X-Ray Probe of Ring-Opening

AMO14110 collaboration:

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Portions of this research were carried out at the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory. LCLS is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University.
Ultrafast X-Ray Probe of Ring-Opening

- LCLS pump probe experiment at 60 Hz
- Molecular beam (200mbar He, ~14 mbar CHD)
- UV: 266 nm, ~50fs, 50 µJ, 120 µm
- X-rays: 850 eV, ~70 fs, 30µmx50µm
- Weak focusing for x-rays
- Used post-processing
- Time resolution ~300 fs
- Time resolution principal limitation

High-Field Physics Chamber at AMO Endstation
Average ion kinetic energy release increases upon UV excitation

- X-ray fragmentation occurs in the weak-field regime, no resonances
- IR fragmentation: strong field, resonances
Production of H⁺ ion fragments increases upon UV excitation.

Subsequent exploration of the conformational space available.

Time dependence of total ion signal (VMI run)

Time dependence of H⁺ signal (TOF)

<150 fs

~ 1 ps
Early time-resolved x-ray fragmentation experiments are promising

- Ion count and ion kinetic energy change upon photoexcitation.
- Experiment is limited by time-resolution (and low statistics), but the technique has a potential for probing much shorter timescales (~5 fs)
- More detailed calculations of the evolution of core-excited species are needed.

The initial pulse interacts with the electronically excited molecule for no more than a few tens of femtoseconds.

Cyclohexadiene Photochemistry - Solution

Time delay (ps)

Heptane

Methanol

Wavelength (nm)

Time Delay (ps)
Cyclohexadiene Photochemistry - Solution

- Magnitude of trapping depends on solvent.
- Dynamics depend weakly on solvent (alcohols faster than alkanes)
Cyclohexadiene Photochemistry - Solution

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Oscillator Strength</th>
<th>Singlet Transition (nm)</th>
<th>Ground State Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHD</td>
<td>0.12</td>
<td>269</td>
<td>0</td>
</tr>
<tr>
<td>cZc</td>
<td>0.15</td>
<td>293</td>
<td>92.5</td>
</tr>
<tr>
<td>cZt</td>
<td>0.42</td>
<td>275</td>
<td>66.7</td>
</tr>
<tr>
<td>tZt</td>
<td>0.89</td>
<td>267</td>
<td>50.4</td>
</tr>
<tr>
<td>tEt</td>
<td>1.06</td>
<td>267</td>
<td>42.7</td>
</tr>
</tbody>
</table>
Cyclohexadiene Photochemistry – in 7-dehydrocholesterol


7-dehydrocholesterol (Provitamin D₃)
Absorption and fluorescence in n-heptane

- Quantum yield = \((2 \pm 1) \times 10^{-4}\)
- \(QY = (3 \pm 1) \times 10^{-4}\) in 2-butanol
- Estimated lifetime: 1.2 ± 0.6 ps in heptane, 1.7 ± 0.6 ps in 2-butanol
The lifetimes of the fast and slow component are constant across the visible region with similar spectral profiles.

In 2-butanol the decay of the total integrated intensity is biexponential with time constants of 0.56 ps (56%) and 1.8 ps (44%).
The Decay of the Excited State Absorption is Biexponential

In alkanes the slow component is blue-shifted about 4 nm. In alcohols it is blue-shifted about 13 nm.

Fast: 0.4 ps – 0.6 ps
Slow: 1.1 – 1.8 ps
Amplitudes 1:2 to 2:1, most ~ 1:1

In 2-butanol the decay of the total integrated intensity is biexponential with time constants of 0.56 ps (56%) and 1.89 ps (44%).

In heptane the integrated intensity decays with time constants of 0.61 ps (66%) and 1.32 ps (34%).
Bifurcation on the excited state surface. No change in electronic state.

- Anisotropy
- Spectrum
- Fluorescence

Similar excited state barriers, with different pre-factors.

External solvent dependent component, but also a ca. 2 kJ/mol intrinsic barrier.
Unravelling the details of vitamin D photosynthesis by non-adiabatic molecular dynamics simulations

Example trajectory of provitamin D excited state dynamics. Black: ground state, blue: $S_1$, green: $S_2$, red dots indicate the current state for which nuclear forces are calculated.

Unravelling the details of vitamin D photosynthesis by non-adiabatic molecular dynamics simulations

A set of 50 trajectories of the excited state dynamics of Pro. Black: ground state, blue: $S_1$, green: $S_2$, red dots indicate the current state for which nuclear forces are calculated.
DHC Excited State Calculations


Unravelling the details of vitamin D photosynthesis by non-adiabatic molecular dynamics simulations

Excited state decay of Pro (reactive trajectories: magenta, all trajectories: red, unreactive trajectories: yellow). The logarithm of the $S_1$ populations is plotted in solid lines. The linear fit of the curves is plotted in dashed lines.

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Excited state decay of Pro (reactive trajectories: magenta, all trajectories: red, unreactive trajectories: yellow). The logarithm of the $S_1$ populations is plotted in solid lines. The linear fit of the curves is plotted in dashed lines.
Experimental Setup for UV Excitation
- the AOPDF UV pulse shaper and transient absorption detection

University of Michigan, Ann Arbor
Chemistry and Physics
The effective decay is faster for positive chirp than for negative chirp.

\[ F_{\text{slow}} = \frac{A_{\text{slow}}}{A_{\text{slow}} + A_{\text{Fast}}} \]

TL : ~2\times10^{10} \text{ W cm}^{-2}
DHC – Manipulating Channels?


- The total amplitude increases for positive chirp
- The amplitude of the fast component increases for positive chirp
- The amplitude of the slow component decreases.

- Positive chirp increases excited state population? (not clear)
- Positive chirp modifies the branching between two pathways – perhaps between reactive and non-reactive trajectories.
Photoproduct Formation

Provitamin D₃ in 2-butanol solvent

400 nm focused into CaF₂ provides a continuum extending to 270 nm.

UV region shows strong two-photon absorption when pump and probe overlap, followed by weak excited state absorption, bleach of the ground state, and relaxation of the previtamin D₃ photoproduct.
Steady state photolysis experiments using the unfiltered output of a mercury arc lamp and a UV-VIS spectrometer. For excitation times longer than 10-15 s secondary products begin to appear.

- The previtamin D₃ spectrum can be estimated by adding DHC back to the difference until the vibronic structure is minimized.
Unravelling the details of vitamin D photosynthesis by non-adiabatic molecular dynamics simulations

300 K distribution of 63054 structures of previtamin D₃.

cZc conformation
tZc conformation
Unravelling the details of vitamin D photosynthesis by non-adiabatic molecular dynamics simulations

Kinetics of Product Formation

\[ \tau_1 = 1.8 \pm 0.25 \text{ ps} \]
\[ \tau_2 = 6.2 \pm 0.25 \text{ ps} \]
Solvent (In)Dependence

- The fast decay component is in good agreement with the decay of the visible ESA.
- The slow decay component is assigned to the cZc $\rightarrow$ cZt isomerization of the hot product.
- A small nonequilibrium population may be trapped and isomerize on a longer time scale.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta$ (mPa s)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>0.387</td>
<td>1.1 ± .45</td>
<td>5.1 ± .45</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.34</td>
<td>1.4 ± .45</td>
<td>8.5 ± .45</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.544</td>
<td>1.5 ± .60</td>
<td>5.4 ± .60</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>3.096</td>
<td>1.8 ± .25</td>
<td>6.2 ± .25</td>
</tr>
</tbody>
</table>
Like DHC, α-terpinene is weakly fluorescent. The QY is ~ an order of magnitude smaller than for DHC.

$$\varphi_{fl} \approx 2 \times 10^{-5}$$

Sharp peak is Raman scattering from the solvent.

Slight variation in excitation wavelength allows separation of fluorescence and Raman.
Excited state absorption following excitation of $\alpha$-terpinene at 266 nm.

$\tau \sim 0.12$ ps in n-hexane, 0.16 ps in 1-butanol.
The relaxation of the signal in the UV is similar to that observed for provitamin D$_3$. There is only a small solvent dependence.
The data are well modeled by narrowing (thermal cooling) and isomerization.

50 and 100 ps spectra resemble steady state cZt spectrum.

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<tr>
<td>α-terpinene</td>
<td>0.22</td>
<td>278</td>
<td>0</td>
</tr>
<tr>
<td>cZc</td>
<td>0.12</td>
<td>282</td>
<td>100</td>
</tr>
<tr>
<td>cZt</td>
<td>0.38</td>
<td>265</td>
<td>94</td>
</tr>
<tr>
<td>tZc</td>
<td>0.25</td>
<td>269</td>
<td>99</td>
</tr>
<tr>
<td>tEt</td>
<td>0.84</td>
<td>271</td>
<td>62</td>
</tr>
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TDDFT Calculation, 6-311**G(d,p) basis set and the B3LYP density functional
Cyclohexadiene Photochemistry – in $\alpha$-phellandrene

The absorption (red) and fluorescence (blue) in heptane.

The sharp line in the fluorescence is a Raman line from the solvent.

QY $\sim 10^{-5}$ (somewhat smaller than $\alpha$-terpinene, but measurable)

Cyclohexadiene Photochemistry – in α-phellandrene
Steady state photolysis of \( \alpha \)-phellandrene

Steady state photolysis in heptane

\[
\begin{array}{c}
\text{Steady state difference spectrum} \\
tZt - \alpha\text{-phellandrene}
\end{array}
\]

Within a scale factor the difference spectrum is constant for the first 40 or 50 seconds.

Secondary products involving cis-trans double bond isomerization begin to accumulate at longer times.
Excited state absorption of $\alpha$-phellandrene

No visible excited state absorption.
Photoproduct Formation - $\alpha$-phellandrene

Excitation of $\alpha$-phellandrene in n-heptane

The product spectrum red-shifts and converges on the steady state result within about 50 ps.
### Photoprodut Formation - α-phellandrene

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<tr>
<td>α-phell</td>
<td>0.09</td>
<td>272</td>
<td>0</td>
</tr>
<tr>
<td>cZc</td>
<td>0.17</td>
<td>290</td>
<td>75</td>
</tr>
<tr>
<td>cZt</td>
<td>0.49</td>
<td>283</td>
<td>52</td>
</tr>
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<td>35</td>
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Red-shift larger than calculated, but the right trend.
Comparison of α-phellandrene and CHD

α-Phellandrene in n-heptane

Cyclohexadiene in n-heptane

Time Delay (ps)
-1 0.6 1.4 2.5 5 10 20 50 100

\( \Delta A \) (mOD)

Wavelength (nm)
Summary

CHD

\[ \begin{align*}
\text{CHD} & \xrightarrow{hv} \text{CHD} \\
\text{\(\alpha\)-phellandrene} & \xrightarrow{hv} \text{\(\alpha\)-phellandrene} \\
\text{\(\alpha\)-terpinene} & \xrightarrow{hv} \text{\(\alpha\)-terpinene} \\
\text{DHC} & \xrightarrow{hv} \text{DHC}
\end{align*} \]

- No visible excited state absorption
- Fluorescence QY \( \leq 10^{-5} \) \(\alpha\)-phell; \( \sim 10^{-6} \) CHD
- Ground state dynamics diffusive relaxation
- Multiphoton control possible CHD

- Strong visible excited state absorption
- Weak fluorescence, QY \( \sim 10^{-5} \) a-terp, \( \sim 10^{-4} \) DHC
  - \( \tau_{\text{ESA}} = \tau_{\text{Fluor}} \)
- Ground state cZc \( \rightarrow \) cZt isomerization \( \sim 5-8 \) ps.
- Chirp influences ES dynamics, control?