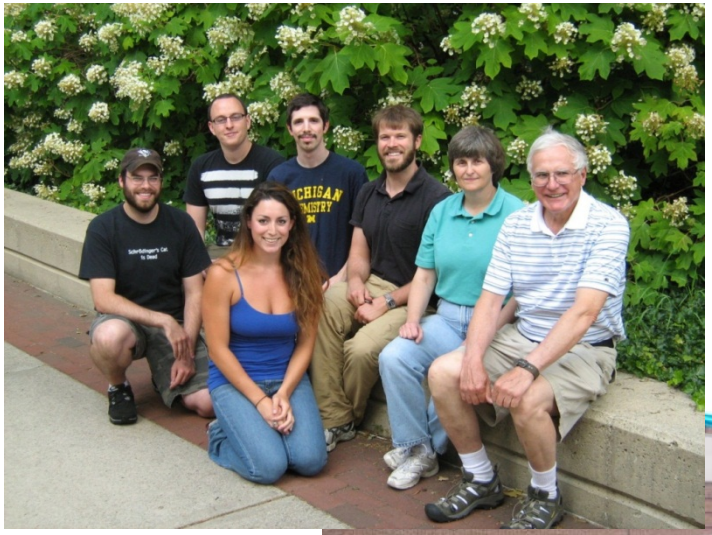
Ultrafast 1,3-Cyclohexadiene Ring-Opening Reactions: Dynamics and Control

Roseanne J. Sension

Chemistry, Physics, Applied Physics
University of Michigan, Ann Arbor, MI 48109

People:

Andrew Stickrath
Michael Orozco
Ahmasi Harris
Neil Anderson
Stuart Pullen
Elizabeth Carroll
Kuo-Chun Tang
Jian Peng
Aaron Rury
Broc Smith
Brenden Arruda
Edwin Najera
Ted Wiley
Ken Spears



Support for these projects came from the National Science Foundation

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:*** Electrocyclic ring-opening, optical switches and biological chromophores.
  - Cyclohexadiene
  - α-terpinene
  - α-phellandrene
  - 7-dehydrocholesterol

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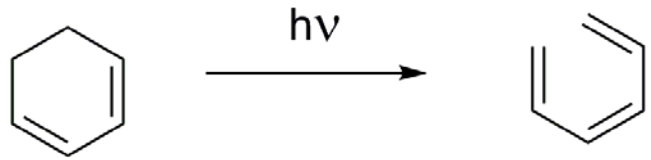

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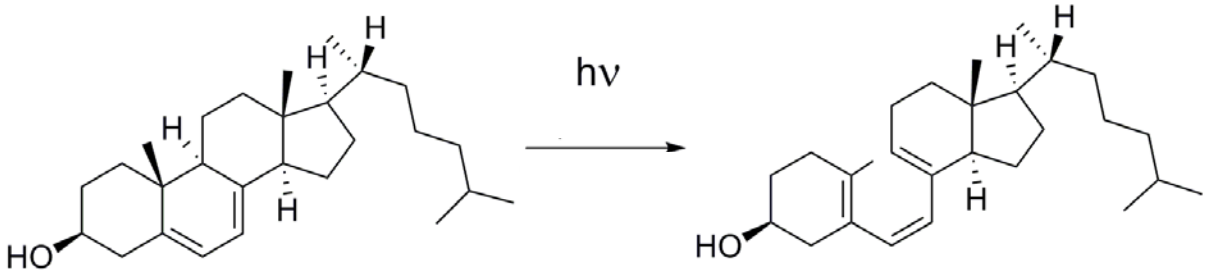

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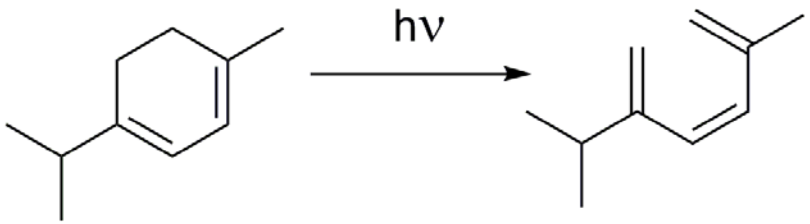

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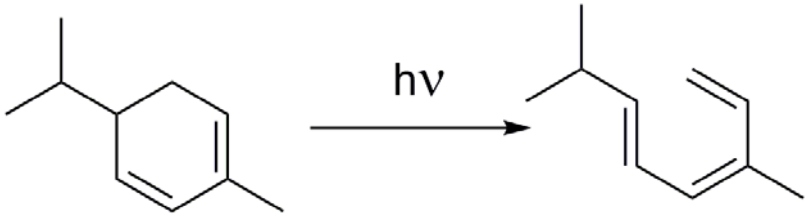


Cyclohexadiene Photochemistry - Gas

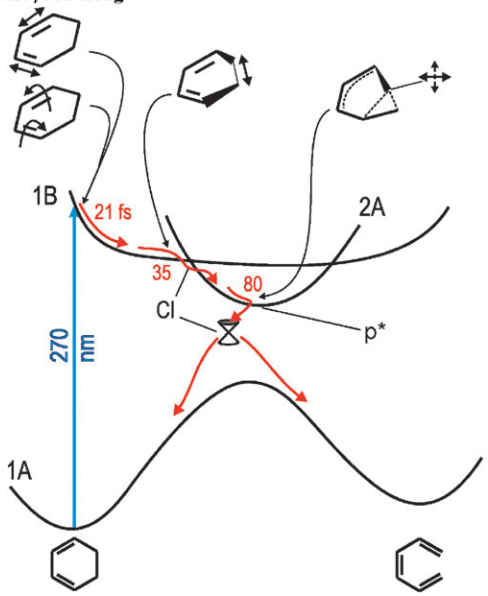
PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

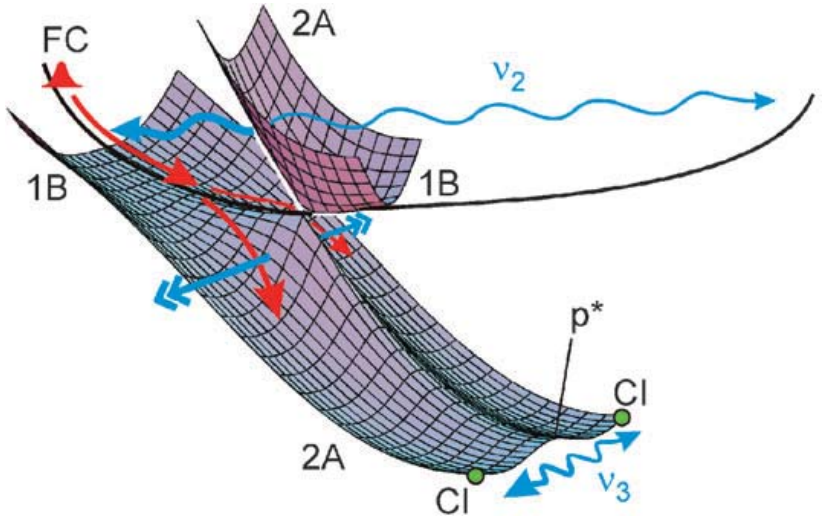
Cyclohexadiene ring opening observed with 13 fs resolution: coherent oscillations confirm the reaction path

K. Kosma, S. A. Trushin, W. Fuß* and W. E. Schmid

Received 14th August 2008, Accepted 13th October 2008
First published as an Advance Article on the web 6th November 2008
DOI: 10.1039/b814201g

Multiphoton ionization provides detection of the molecule along the reaction path.





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:

Vladimir S. Petrovic[1,2], spokesperson
Marco Siano[3]
James L. White[2,4]
Nora Berrah[5]
Christoph Bostedt[6]
John D. Bozek[6]
Douglas Broege[2,4]
Max Chalfin[1,2]
Ryan N. Coffee[6]
James Cryan[1,2]
Li Fang[5]
Joseph P. Farrell[1,2]
Leszek J Frasinski[7]
James M. Glownia[2,4]
Markus Guehr[2]
Matthias Hoener[5]
Holland David[8]
Jaehee Kim[1,2]
Todd Martinez[2,9]
Brian K. McFarland[2,4]
Jonathan P. Marangos[3]
Russell S. Minns[10]
Shungo Miyabe[2,9]
Sebastian Schorb[6]
Roseanne J. Sension[11]
Limor S. Spector[1,2]
Richard Squibb[7]
Hongli Tao[2,9]
Jonathan G. Underwood[10]
Philip H. Bucksbaum[1,2,4]

[1]Stanford University, Department of Physics, Stanford, CA
[2]The PULSE Institute, SLAC, Menlo Park, CA
[3]Blackett Laboratory, Imperial College London, UK
[4]Stanford University, Department of Applied Physics, Stanford, CA
[5]Physics Department, Western Michigan University, Kalamazoo, MI
[6]LCLS at SLAC National Accelerator Laboratory, Laser group, Menlo Park, CA
[7]Department of Physics, Imperial College London, UK
[8]Photon Science Department, Daresbury Laboratory, UK
[9]Stanford University, Department of Chemistry, Stanford, CA
[10]Department of Physics and Astronomy, University College London, UK
[11]Department of Chemistry, Department of Physics, University of Michigan, Ann Arbor, MI

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

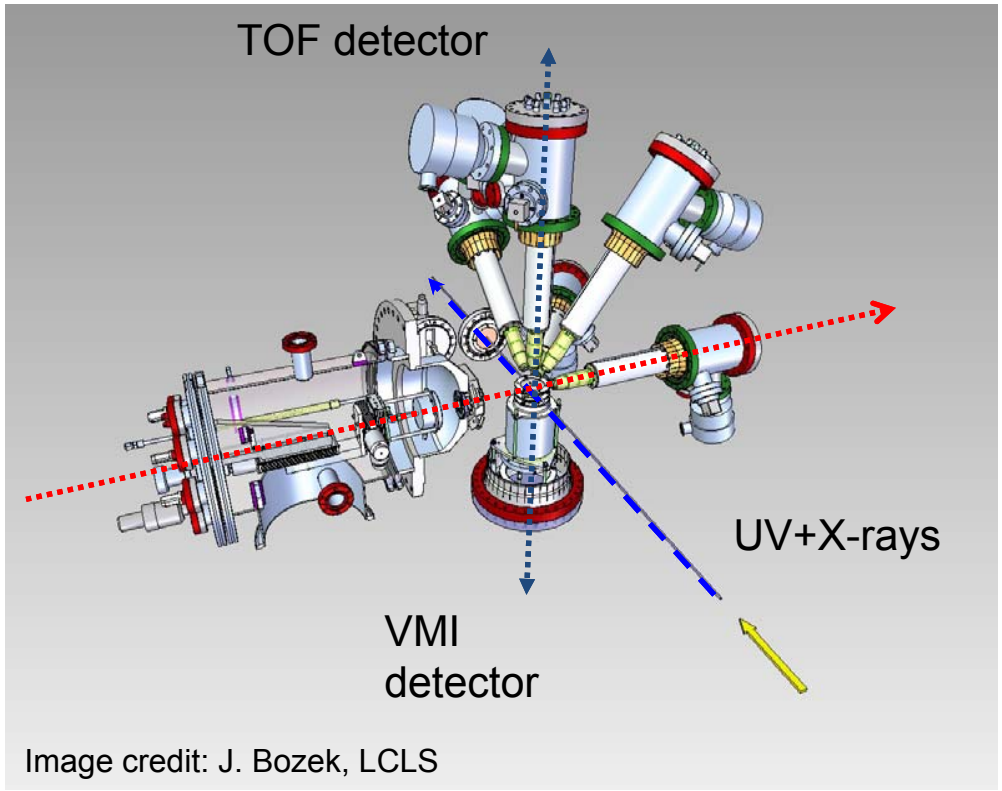
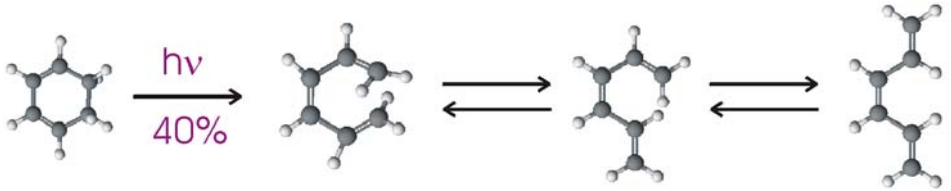


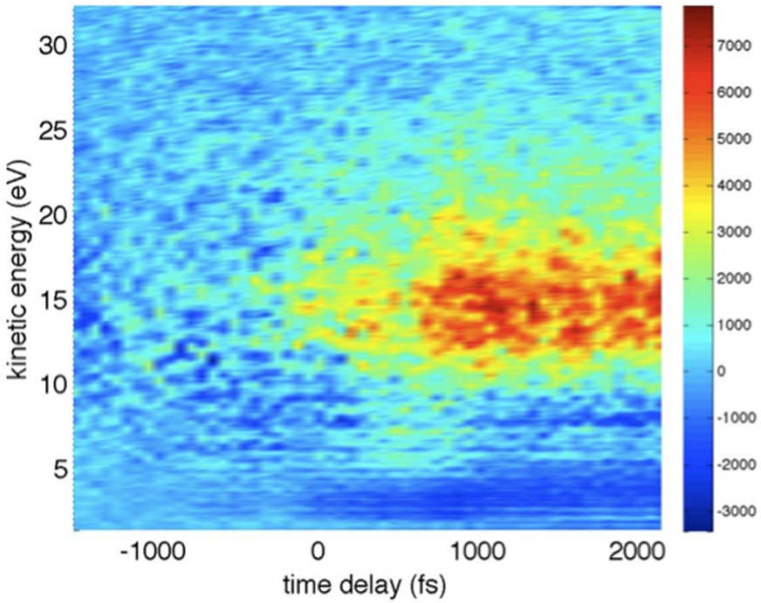
Image credit: J. Bozek, LCLS

- 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

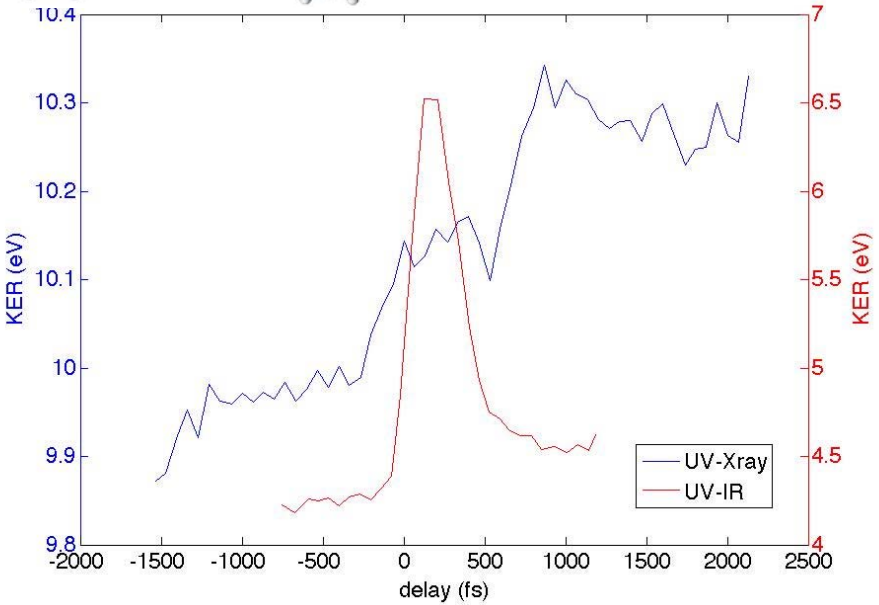
High-Field Physics Chamber at AMO Endstation

Average ion kinetic energy release increases upon UV excitation





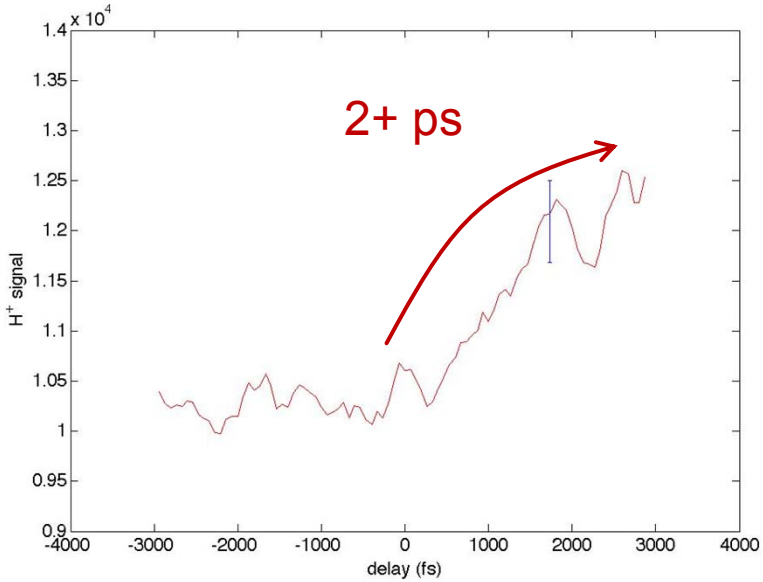
Time dependence of ion KER (difference plot)



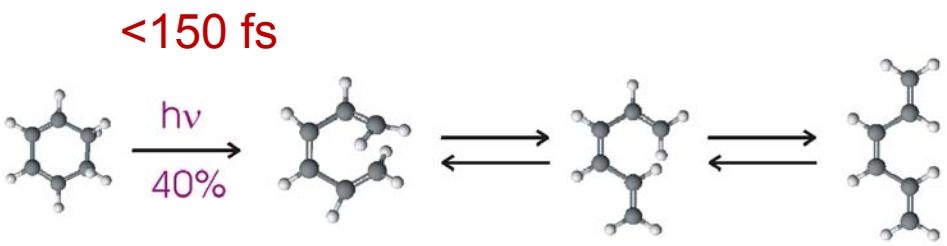
Time dependence of ion KER (x-ray/IR comparison)

- X-ray fragmentation occurs in the weak-field regime, no resonances
- IR fragmentation: strong field, resonances

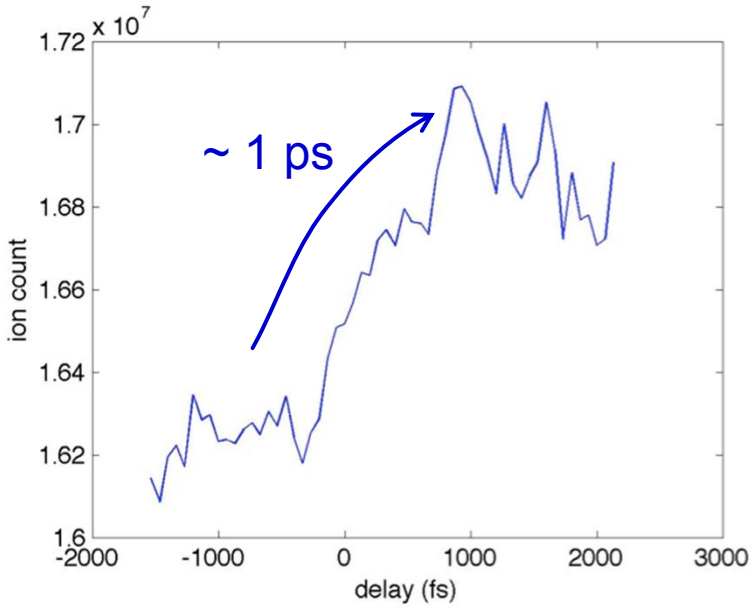
Production of H^+ ion fragments increases upon UV excitation



Time dependence of H^+ signal (TOF)

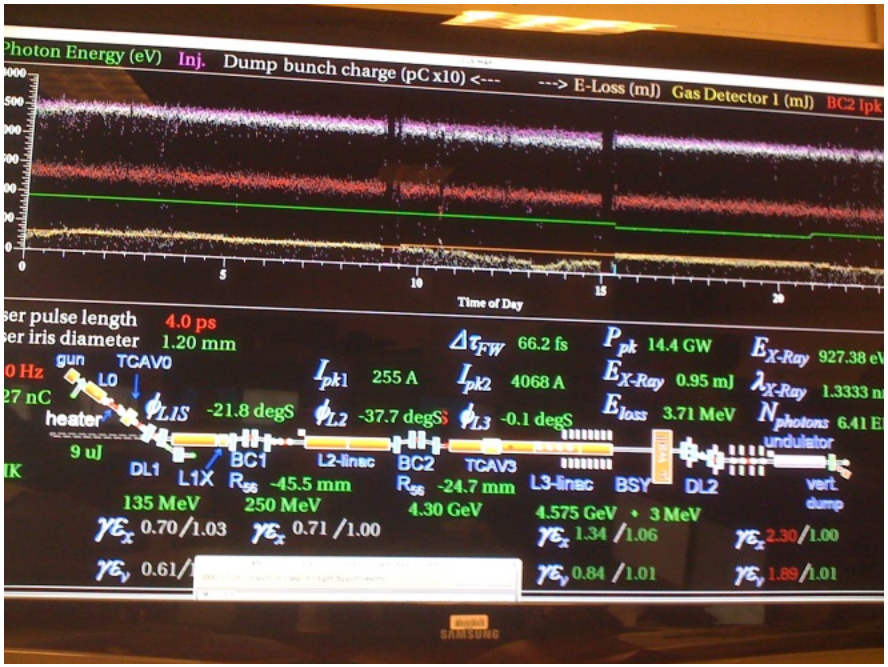


Subsequent exploration of the conformational space available.



Time dependence of total ion signal (VMI run)

Early time-resolved x-ray fragmentation experiments are promising

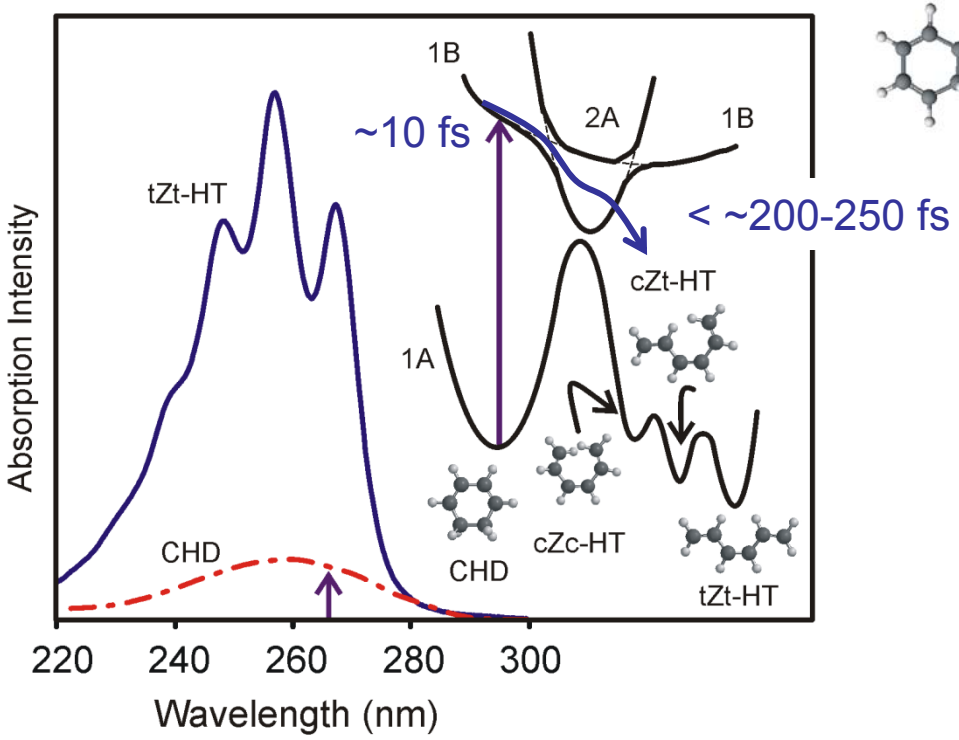


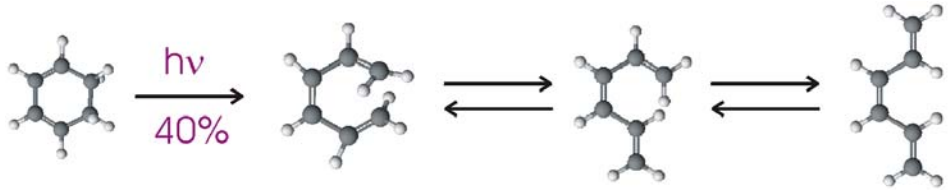
- Ion count and ion kinetic energy change upon photoexcitation.
- Experiment is limited by time-resolution (and low statistics), but the technique has a potential for probing much shorter timescales (~5 fs)
- More detailed calculations of the evolution of core-excited species are needed.

Petrovic, V. S.; Siano, M.; White, J. L.; Berrah, N.; Bostedt, C.; Bozek, J. D.; Broege, D.; Chalfin, M.; Coffee, R. N.; Cryan, J.; Fang, L.; Farrell, J. P.; Frasinski, L. J.; Glownia, J. M.; Gühr, M.; Hoener, M.; Holland, D.; Kim, J.; Martinez, T.; McFarland, B. K.; Marangos, J. P.; Minns, R. S.; Miyabe, S.; Schorb, S.; Sension, R. J.; Spector, L. S.; Squibb, R.; Tao, H.; Underwood, J. G.; Bucksbaum, P. H., **Transient x-ray fragmentation: Probing a prototypical photoinduced ring opening**., *Phys. Rev. Lett.*, 108, 253006, 2012.

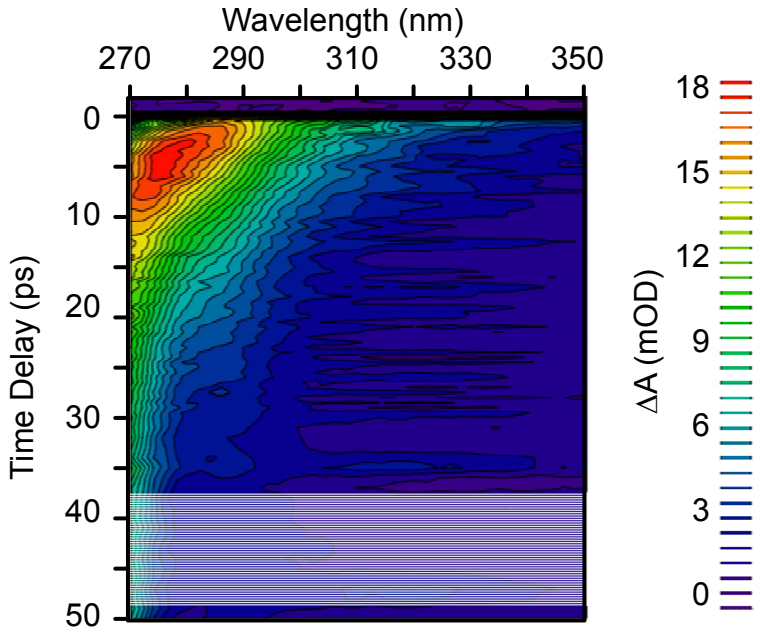
Cyclohexadiene Photochemistry - Solution

Anderson, N.A., Pullen, S.H., Walker II, L.A., Shiang, J.J., and Sension, R.J., 1998, J. Phys. Chem. A, 102, 10588-10598
Pullen, S.H., Anderson, N.A., Walker II, L.A., and Sension, R.J., 1998, J. Chem. Phys. 108, 556-563.
Harris, D.A., Orozco, M.B., and Sension R. J., 2006, J. Phys. Chem. A, 110, 9325-9333
S. Lochbrunner, W. Fuss, W. E. Schmid, and K. L. Kompa, 1998, J. Phys.Chem. A 102, 9334-9344.





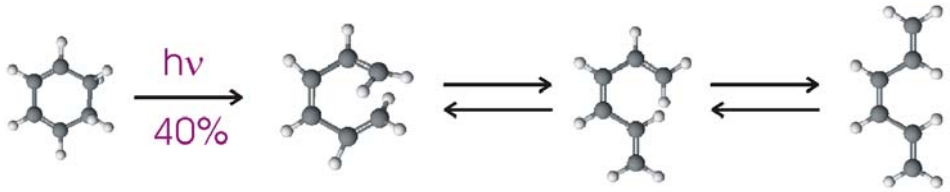
Relaxation in Heptane

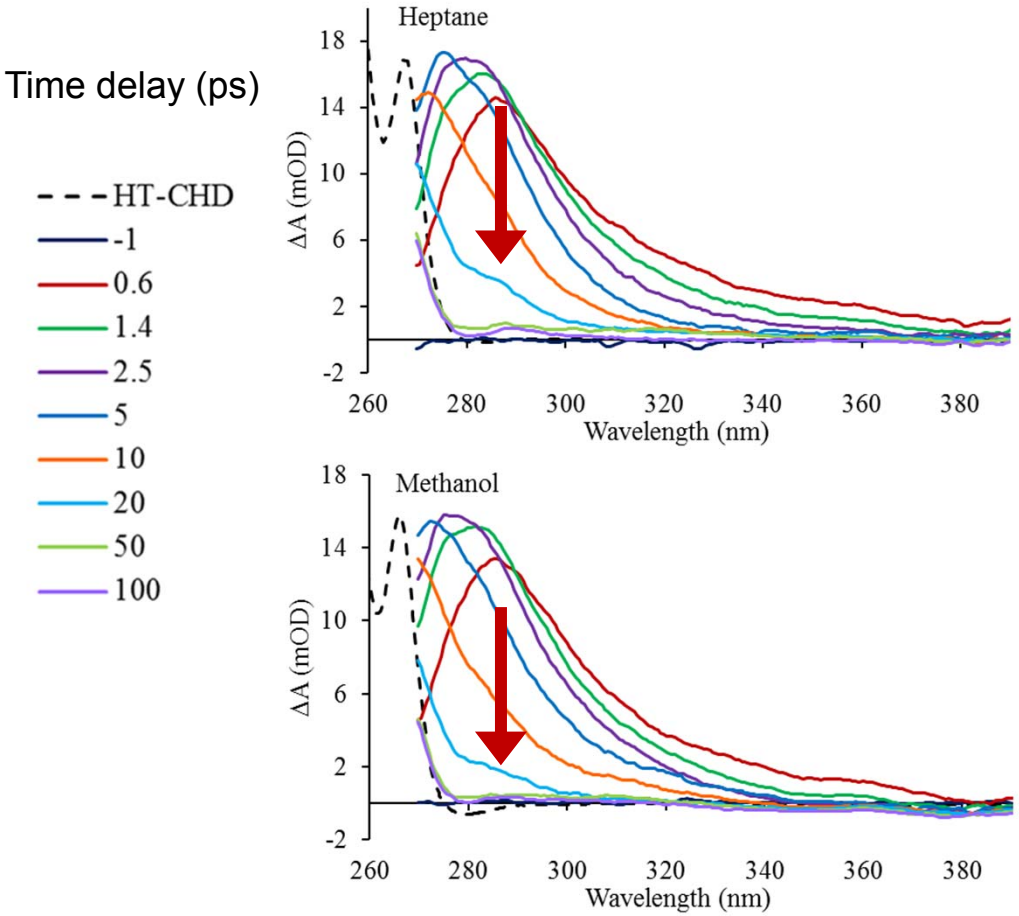


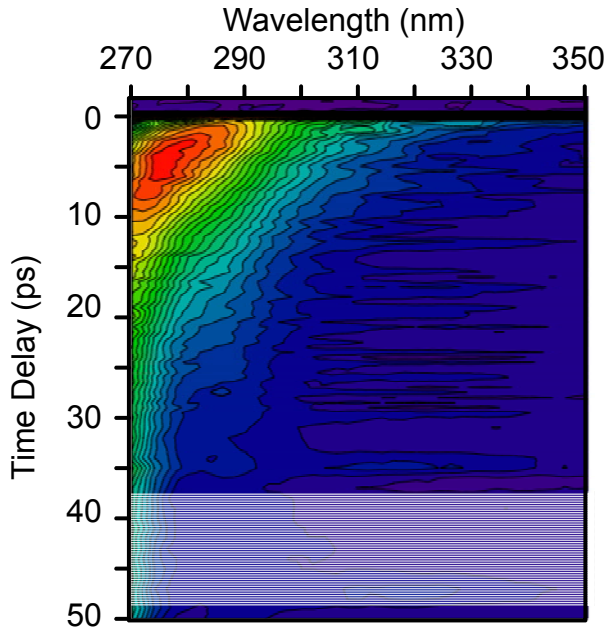
The initial pulse interacts with the electronically excited molecule for no more than a few tens of femtoseconds.

Trulson, M. O.; Dollinger, G. D.; Mathies, R. A. J. Chem. Phys. 1989, 90, 4274-4281.

Cyclohexadiene Photochemistry - Solution







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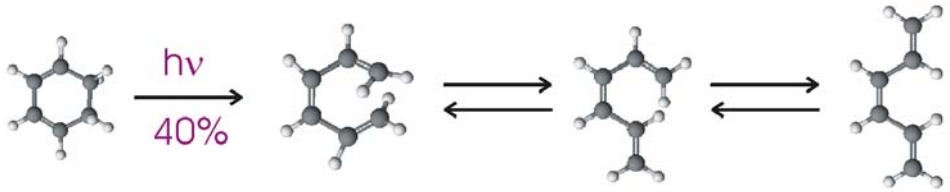
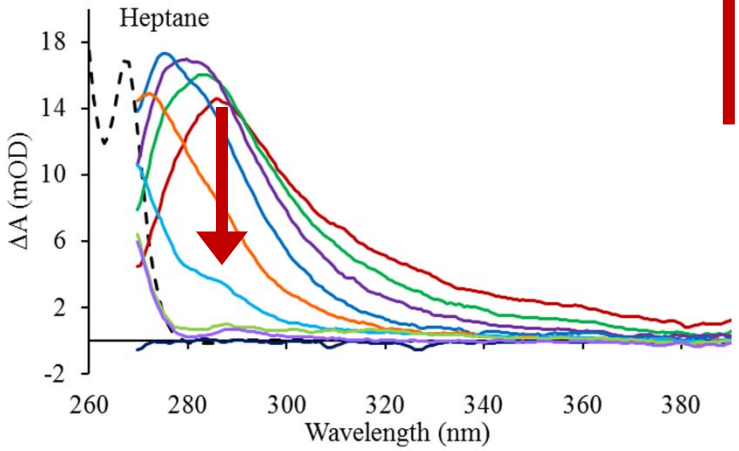
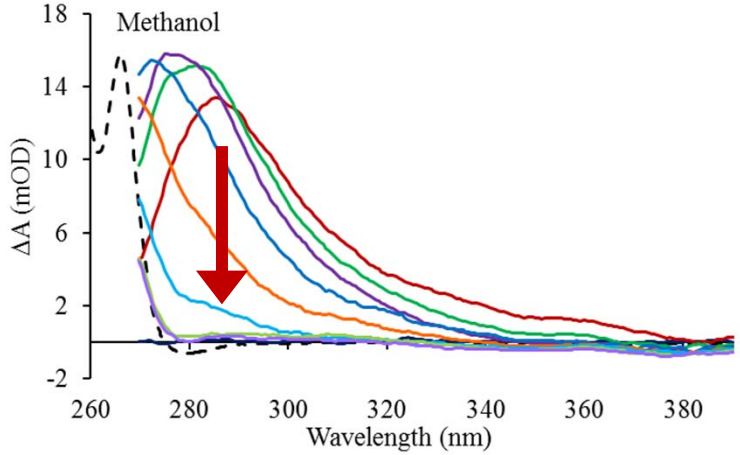
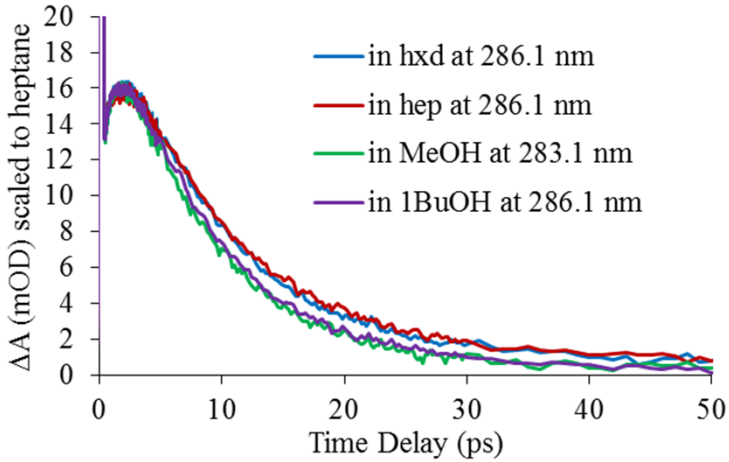


Time delay (ps)

HT-CHD
-1
0.6
1.4
2.5
5
10
20
50
100

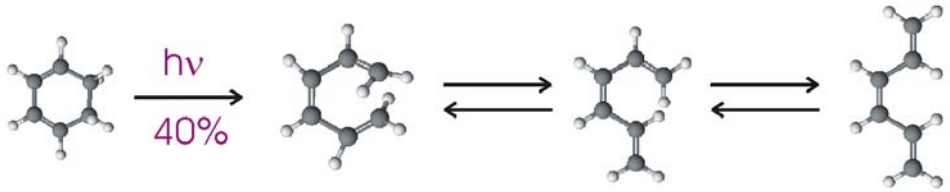


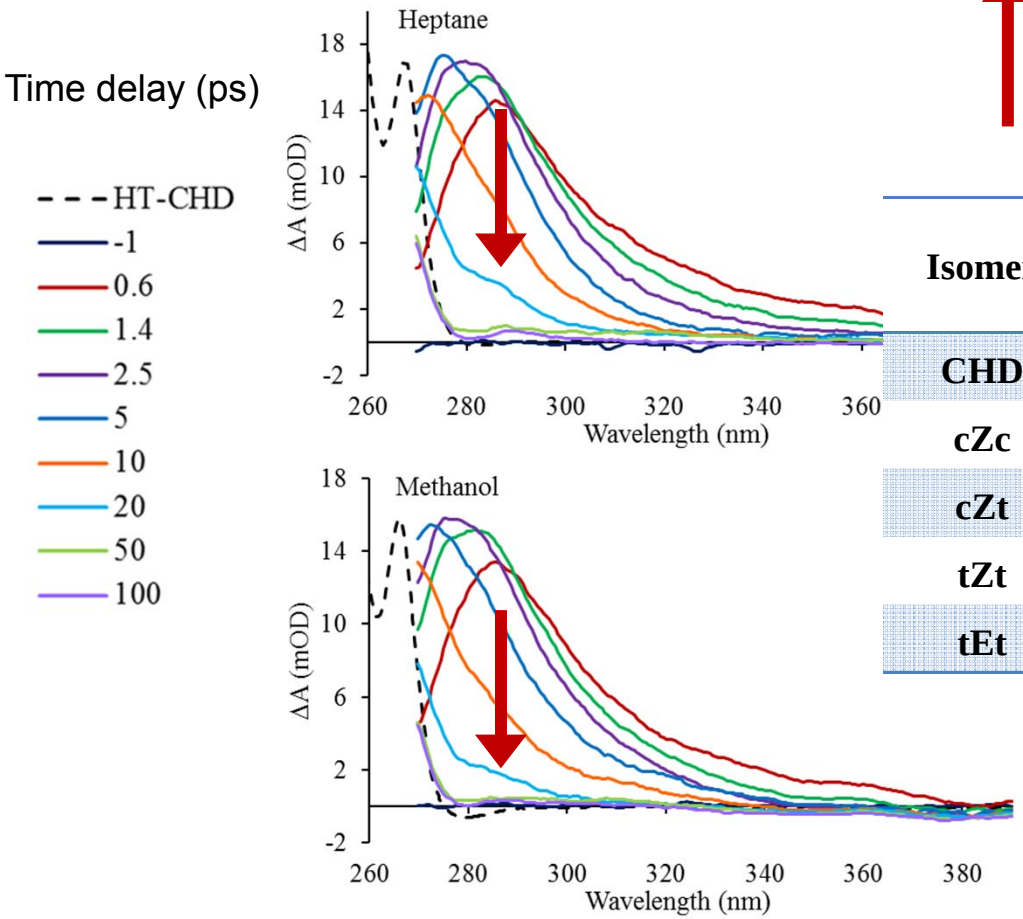




- Magnitude of trapping depends on solvent.
- Dynamics depend weakly on solvent (alcohols faster than alkanes)

Cyclohexadiene Photochemistry - Solution

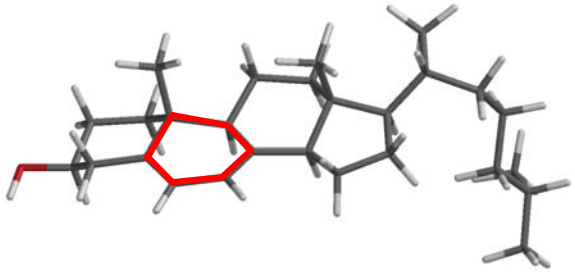


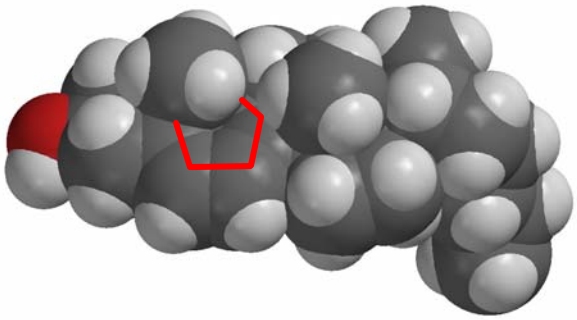


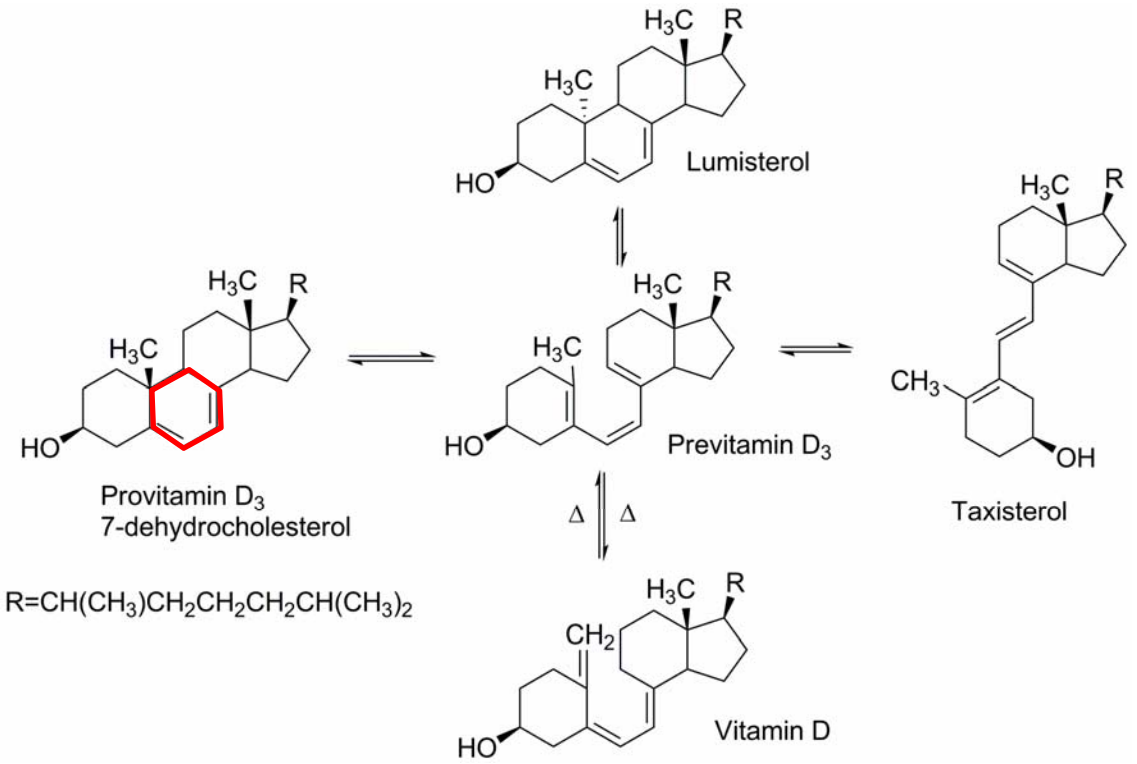
Isomer	Oscillator Strength	Singlet Transition (nm)	Ground State Energy (kJ/mol)
CHD	0.12	269	0
cZc	0.15	293	92.5
cZt	0.42	275	66.7
tZt	0.89	267	50.4
tEt	1.06	267	42.7

Cyclohexadiene Photochemistry – in 7-dehydrocholesterol

K.-C. Tang, A. Rury, M. B. Orozco, J. Egendorf, K. G. Spears and R. J. Sension, J. Chem. Phys. 2011, 134, 104503.
Anderson, N.A., and Sension, R.J., 2002 ACS Symposium Series 820, pp. 148-158.
Anderson, N.A., Shiang, J.J., Sension, R.J., 1999, J. Phys. Chem. A, v 103 (50), pp. 10730-10736
Fuss, W., Hofer, T., Hering, P., Kompa, K. L., Lochbrunner, S., Schikarski, T., Schmid, W. E. J. Phys. Chem. 1996, 100, 921-927.







7-dehydrocholesterol (Provitamin D_3)

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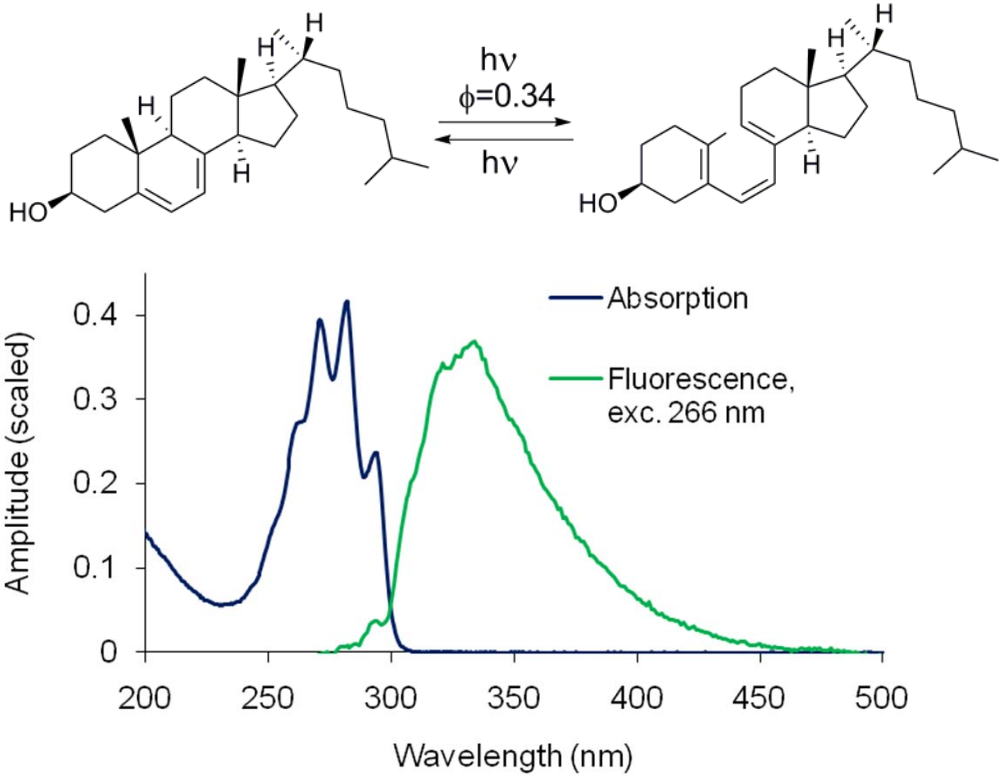
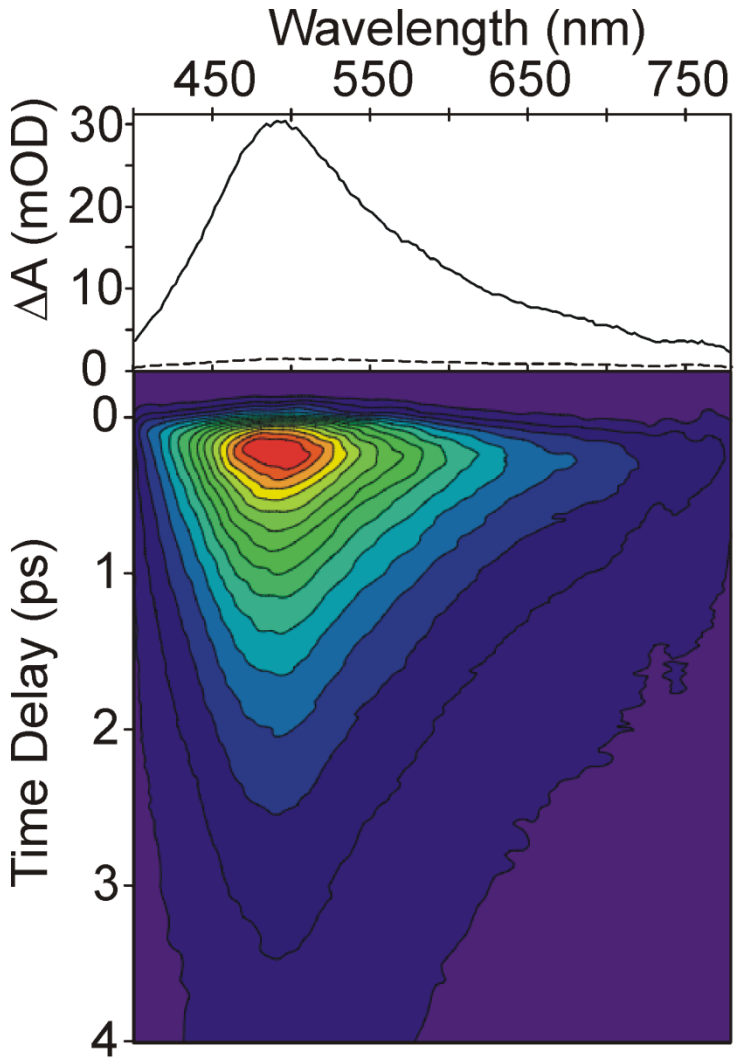


Absorption and fluorescence in n-heptane

- Quantum yield = $(2 \pm 1)\times10^{-4}$
- QY = $(3 \pm 1)\times10^{-4}$ in 2-butanol
- Estimated lifetime: 1.2 ± 0.6 ps in heptane, 1.7 ± 0.6 ps in 2-butanol



The Decay of the Excited State Absorption is Biexponential

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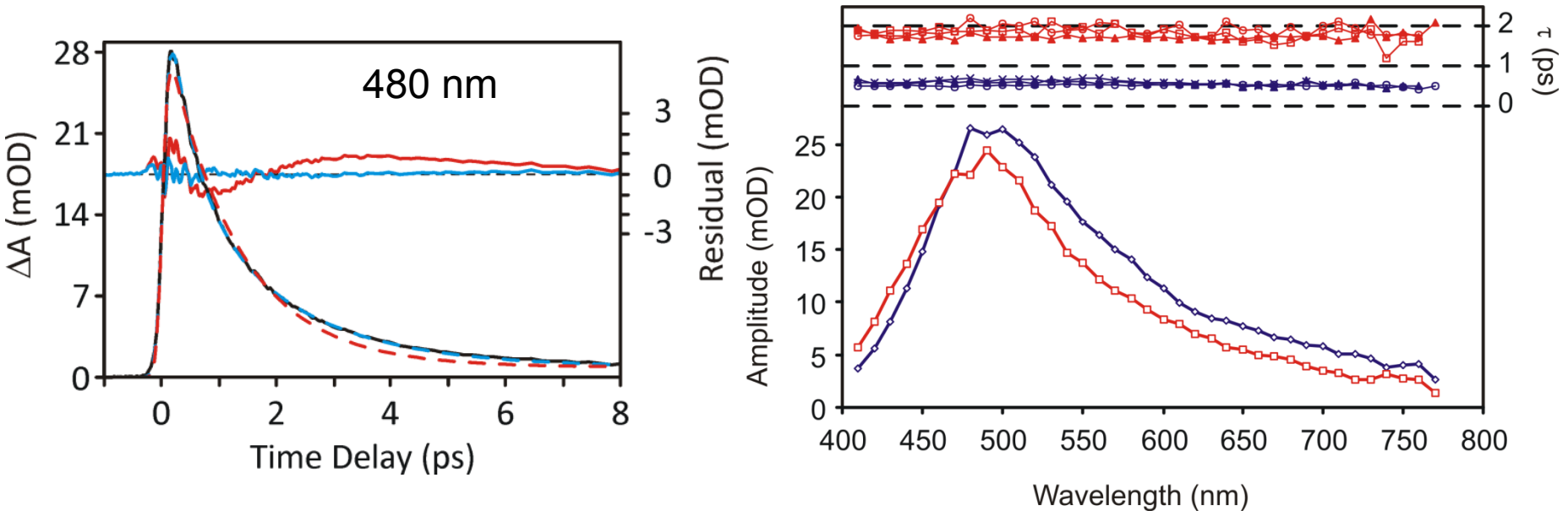

The lifetimes of the fast and slow component are constant across the visible region with similar spectral profiles.

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%).

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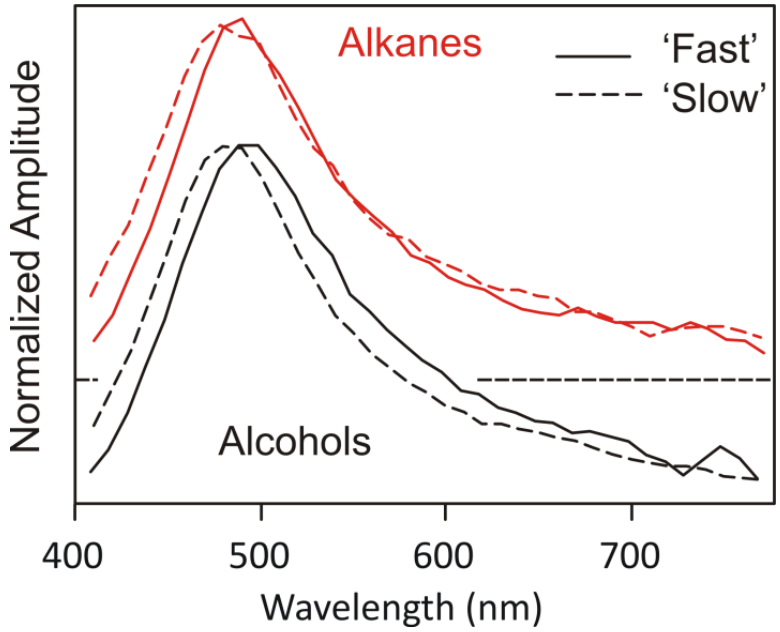


In alkanes the slow component is blue-shifted about 4 nm. In alcohols it is blue-shifted about 13 nm.

Fast: 0.4 ps – 0.6 ps

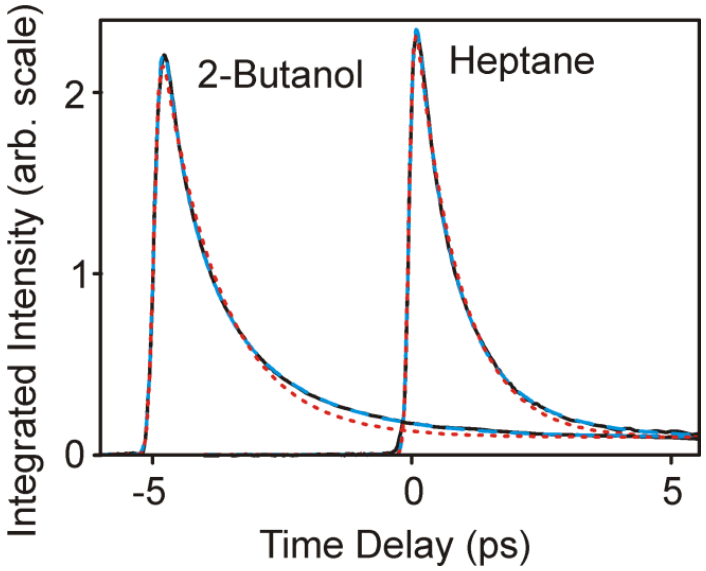
Slow: 1.1 – 1.8 ps

at ~29 C

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%).

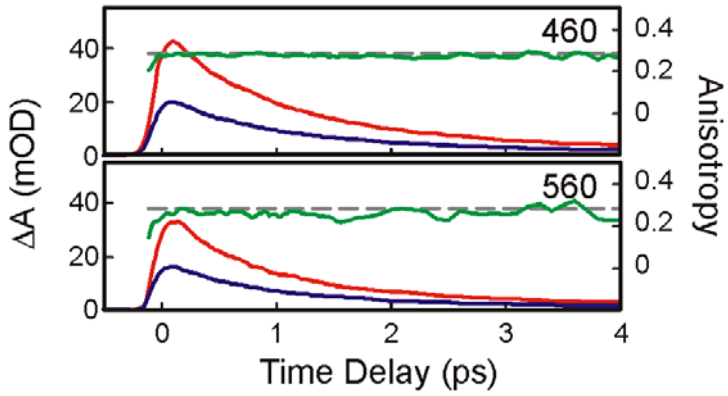


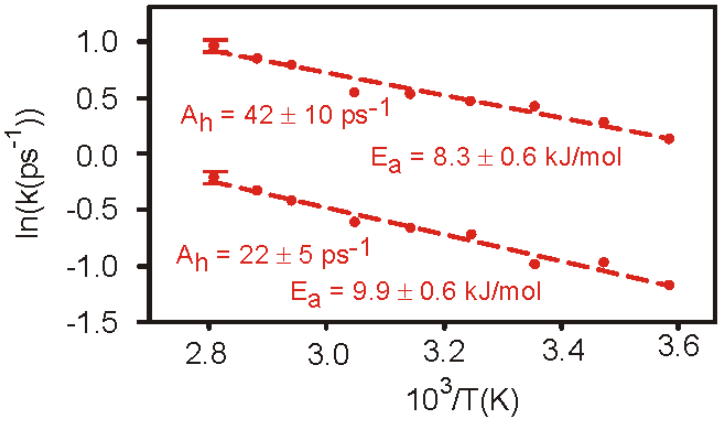
DHC Excited State Decay

K.-C. Tang, A. Rury, M. B. Orozco, J. Egendorf, K. G. Spears and R. J. Sension, J. Chem. Phys. 2011, 134, 104503.

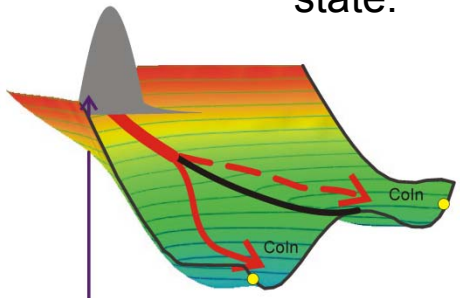
$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = \frac{2}{5}\left\langle P_2\left(\cos\theta(t)\right)\right\rangle$$

$$P_2(x) = \frac{1}{2}\left(3x^2 - 1\right)$$

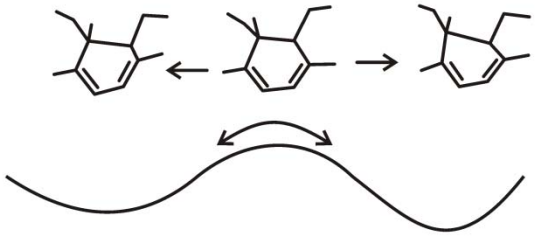




Bifurcation on the excited state surface. No change in electronic state.



- Anisotropy
- Spectrum
- Fluorescence

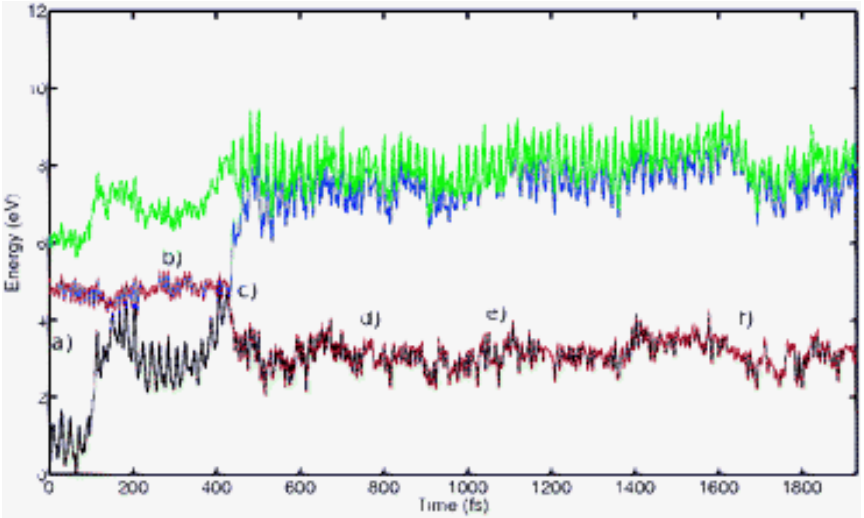


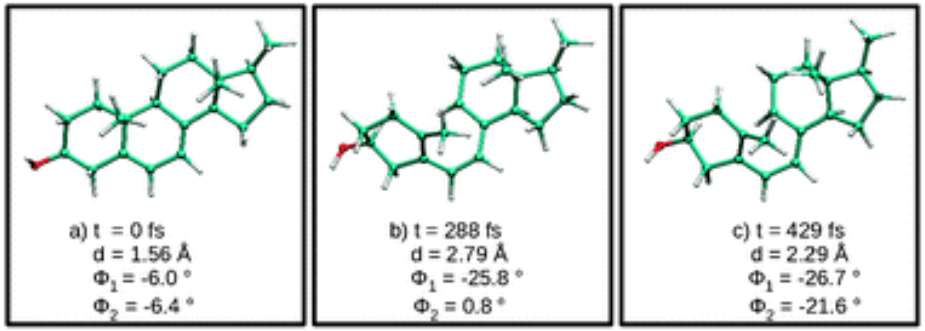
- Similar excited state barriers, with different pre-factors.
- External solvent dependent component, but also a ca. 2 kJ/mol intrinsic barrier.

DHC Excited State Calculations

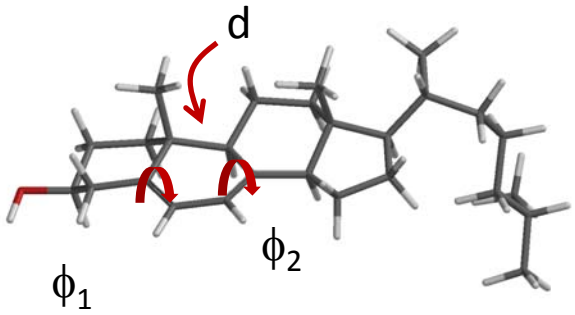
E. Tapavicza, A. M. Meyer and F. Furche, 2011, Phys. Chem. Chem. Phys. 13, 20986.

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.



DHC Excited State Calculations

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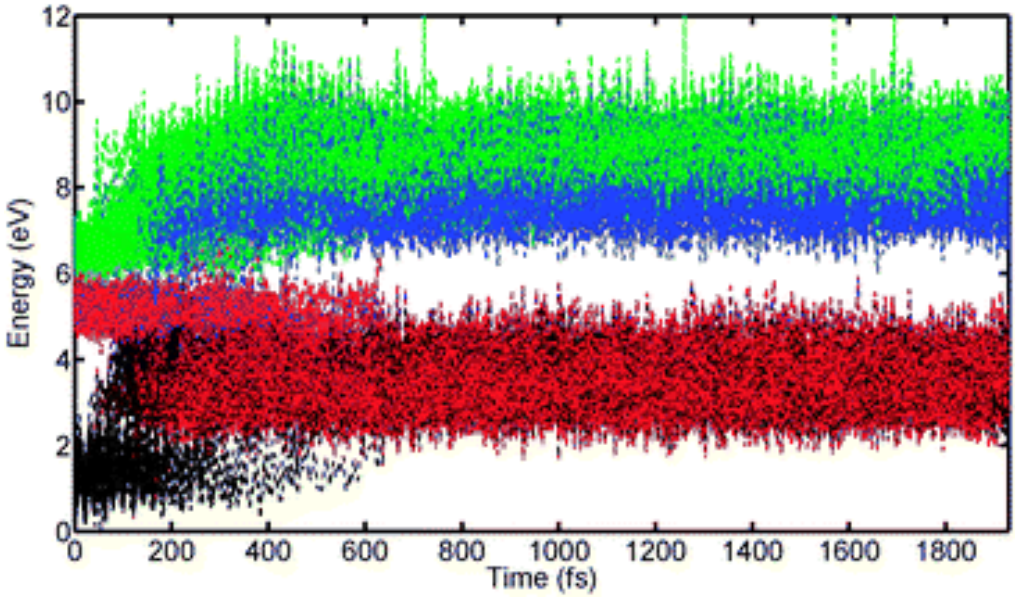
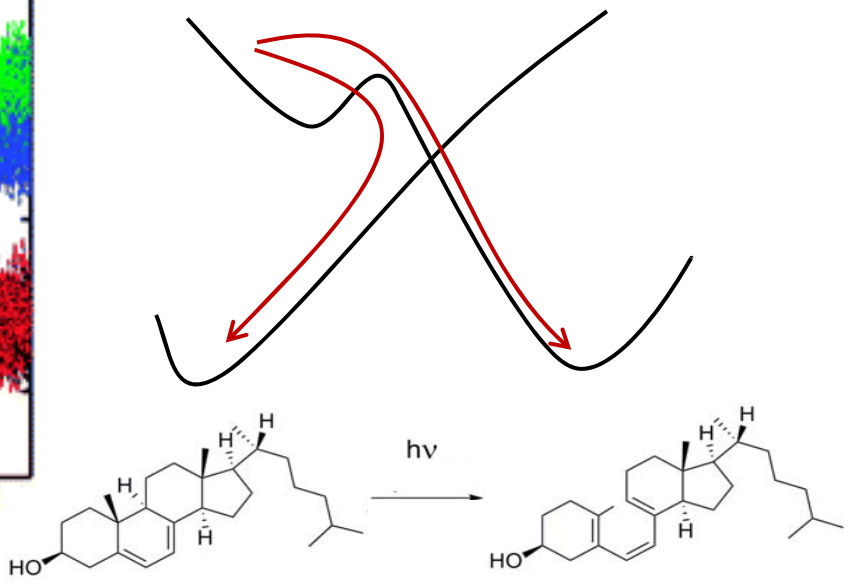


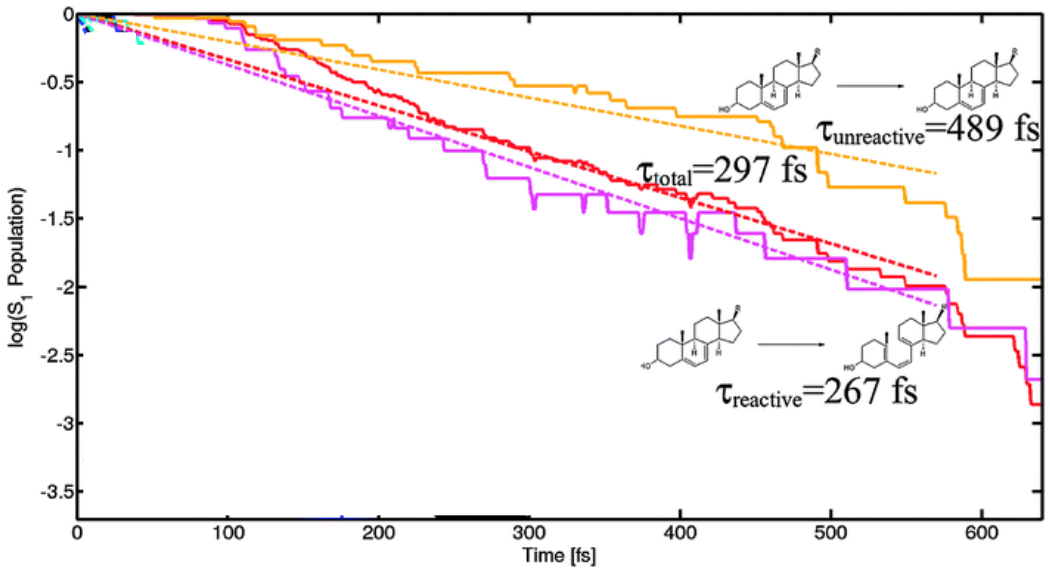


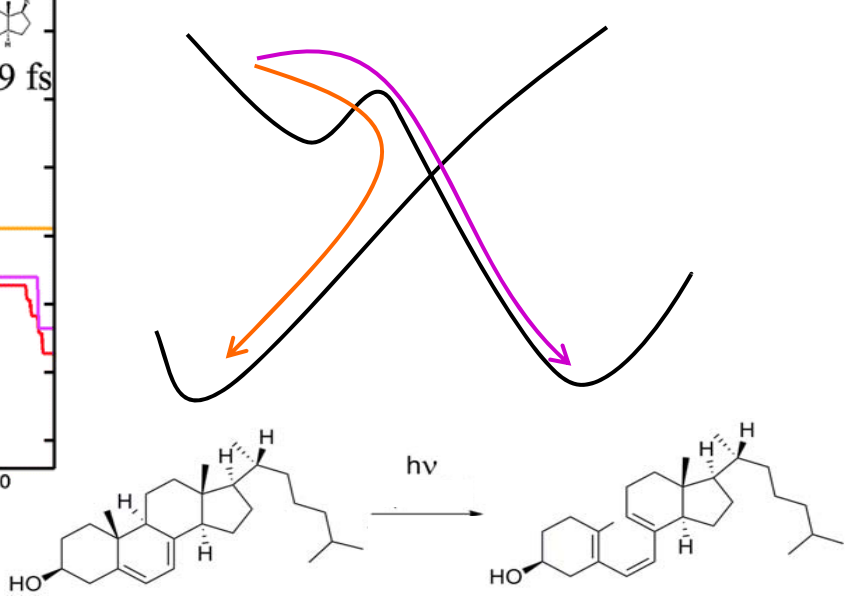
A set of 50 trajectories of the excited state dynamics of Pro. Black: ground state, blue: S_1, green: S_2, red dots indicate the current state for which nuclear forces are calculated.

DHC Excited State Calculations

E. Tapavicza, A. M. Meyer and F. Furche, 2011, Phys. Chem. Chem. Phys. 13, 20986.

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



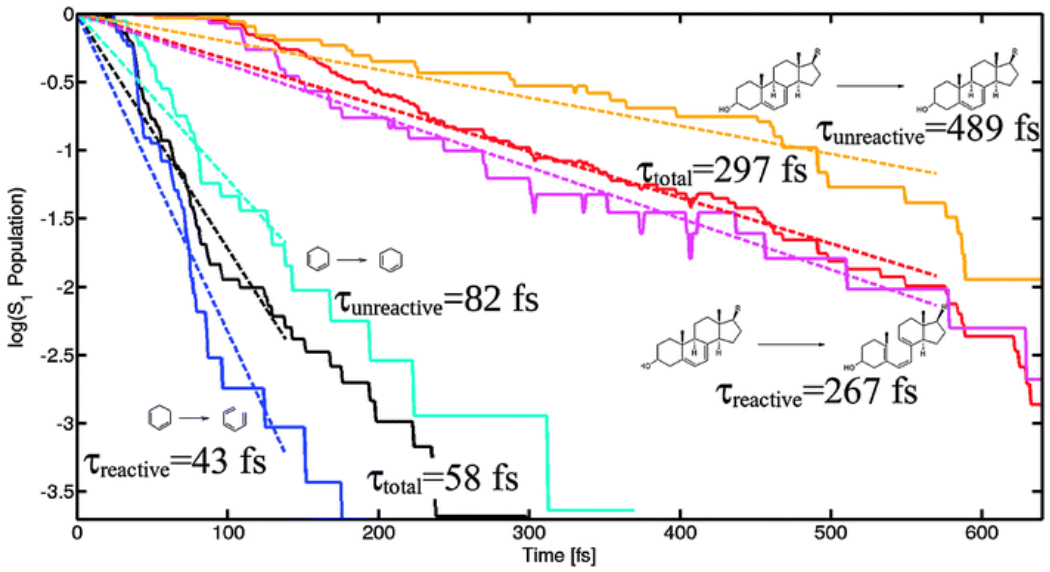


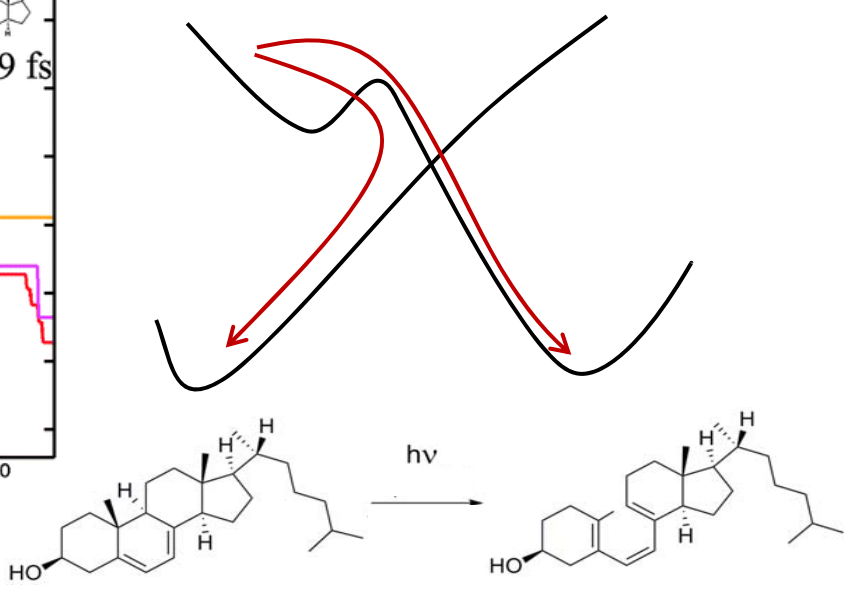
Excited state decay of Pro (reactive trajectories: magenta, all trajectories: red, unreactive trajectories: yellow). The logarithm of the S_1 populations is plotted in solid lines. The linear fit of the curves is plotted in dashed lines.

DHC Excited State Calculations

E. Tapavicza, A. M. Meyer and F. Furche, 2011, Phys. Chem. Chem. Phys. 13, 20986.

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

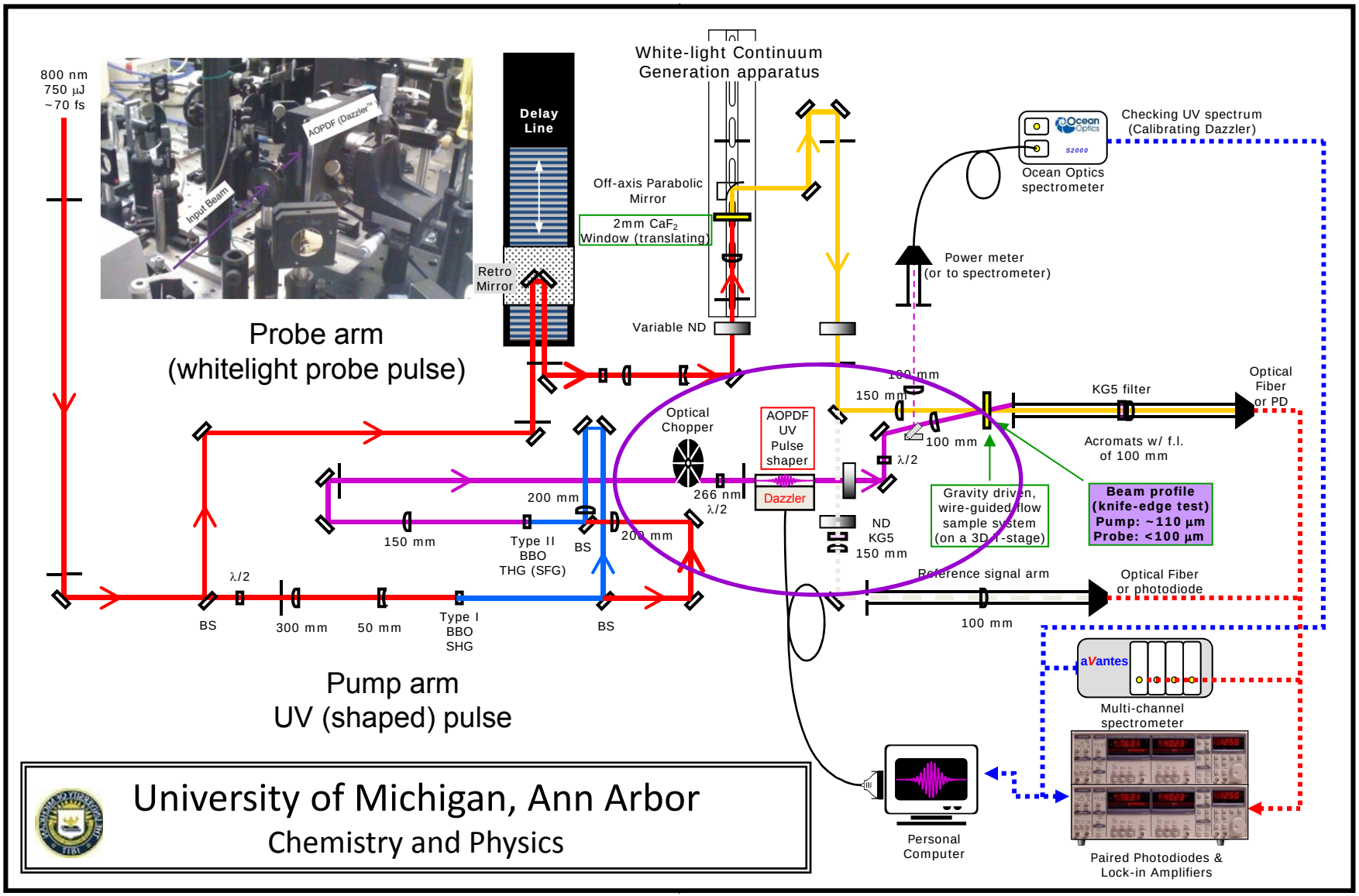




Excited state decay of Pro (reactive trajectories: magenta, all trajectories: red, unreactive trajectories: yellow). The logarithm of the S_1 populations is plotted in solid lines. The linear fit of the curves is plotted in dashed lines.

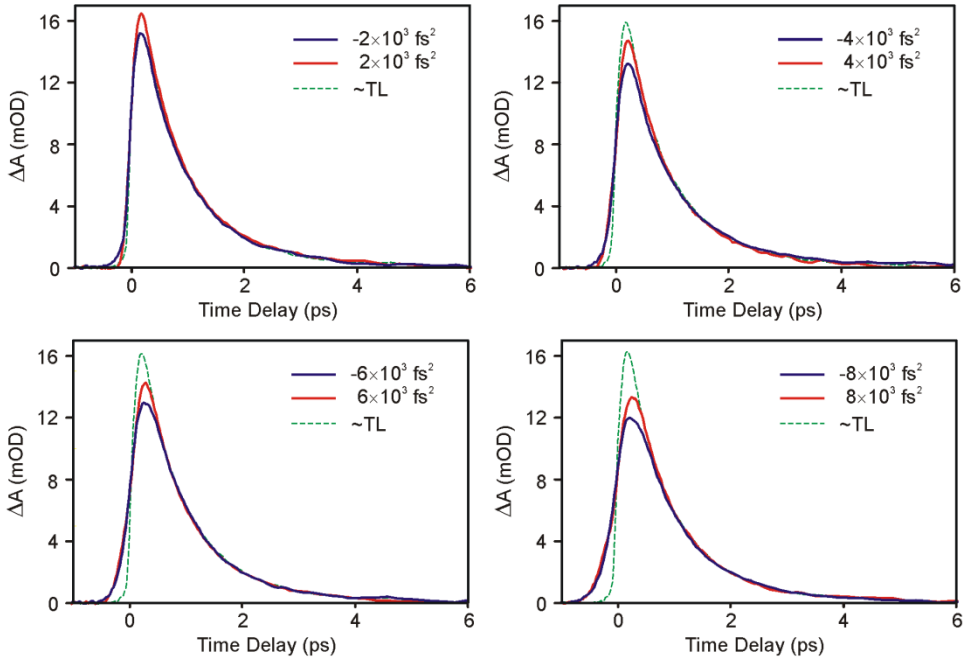
Experimental Setup for UV Excitation

- the AOPDF UV pulse shaper and transient absorption detection

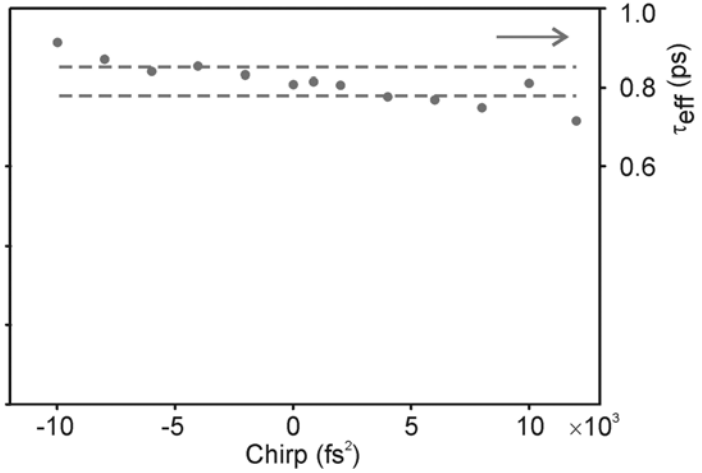


Systematic Variation of Linear Chirp

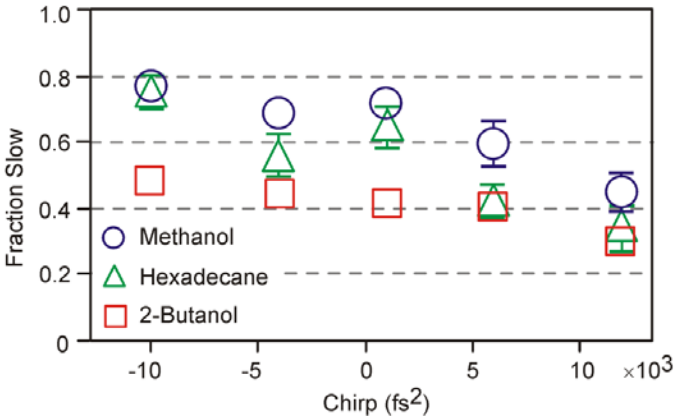
Tang, K.-C., and Sension, R. J. , 2011, Faraday Discussion, 153, 117-129.



TL : ~2×10^{10} W cm^{-2}



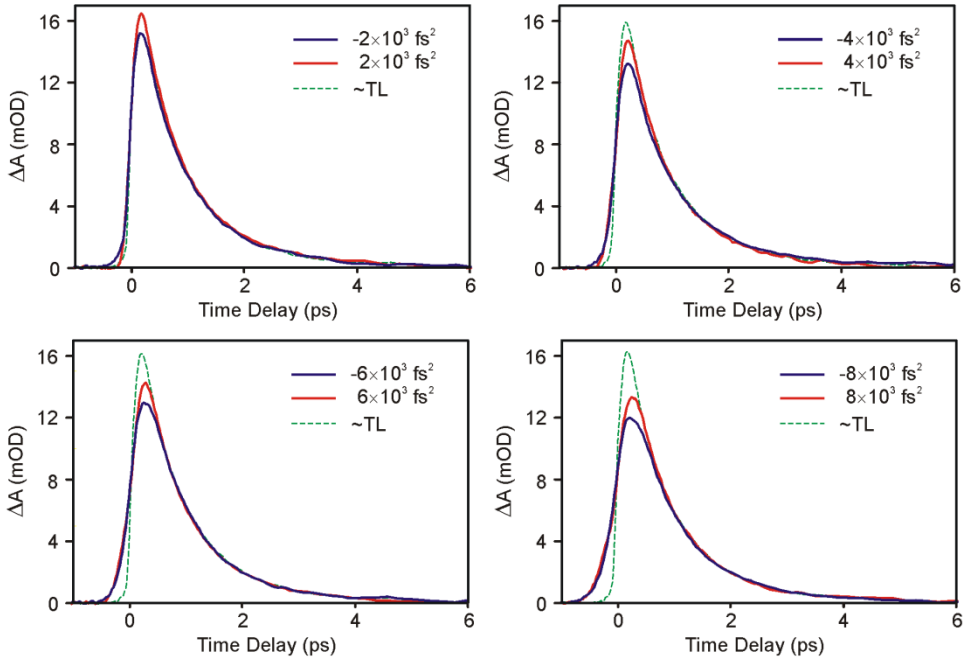
The effective decay is faster for positive chirp than for negative chirp.

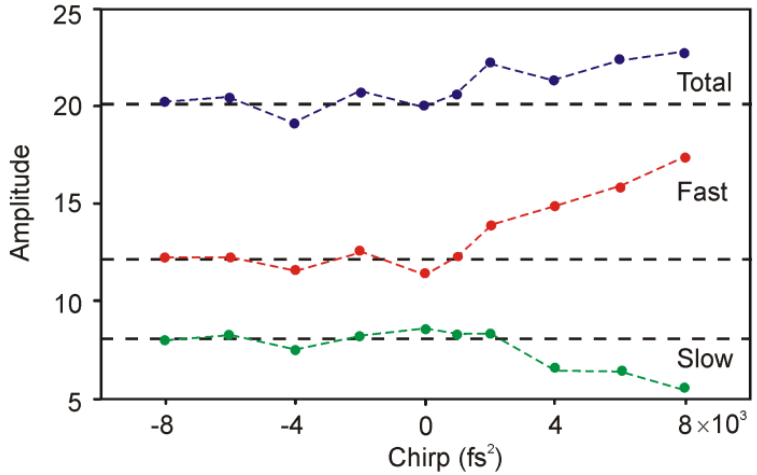


$$F_{slow} = \frac{A_{slow}}{A_{slow} + A_{Fast}}$$

DHC – Manipulating Channels?

Tang, K.-C., and Sension, R. J. , 2011, Faraday Discussion, 153, 117-129.



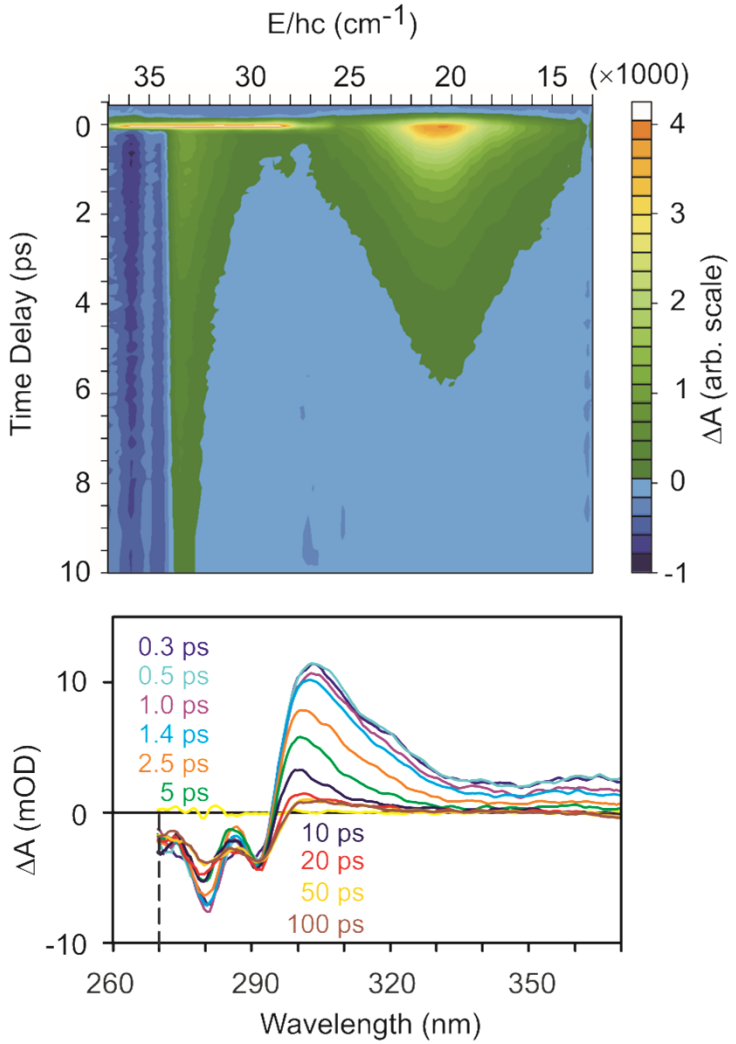


- The total amplitude increases for positive chirp
- The amplitude of the fast component increases for positive chirp
- The amplitude of the slow component decreases.

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

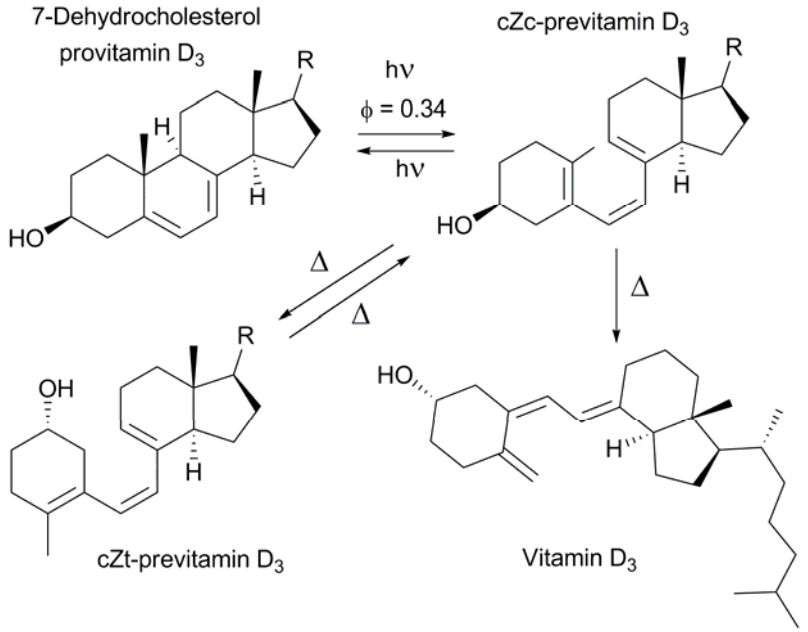
Photoproduct Formation

Provitamin D_3 in 2-butanol solvent

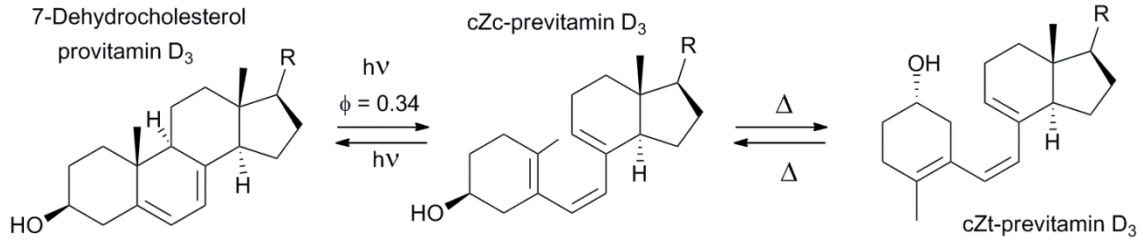


400 nm focused into CaF_2 provides a continuum extending to 270 nm.

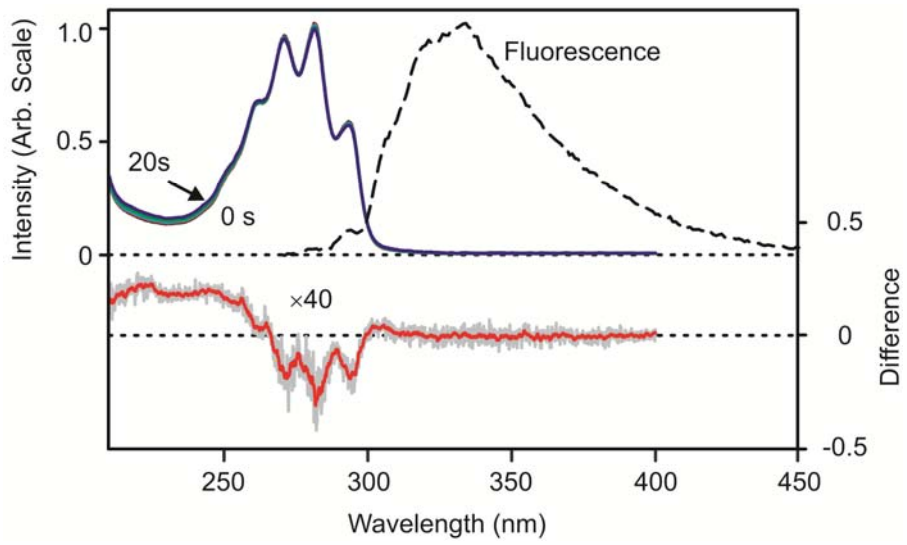
UV region shows strong two-photon absorption when pump and probe overlap, followed by weak excited state absorption, bleach of the ground state, and relaxation of the previtamin D_3 photoproduct.

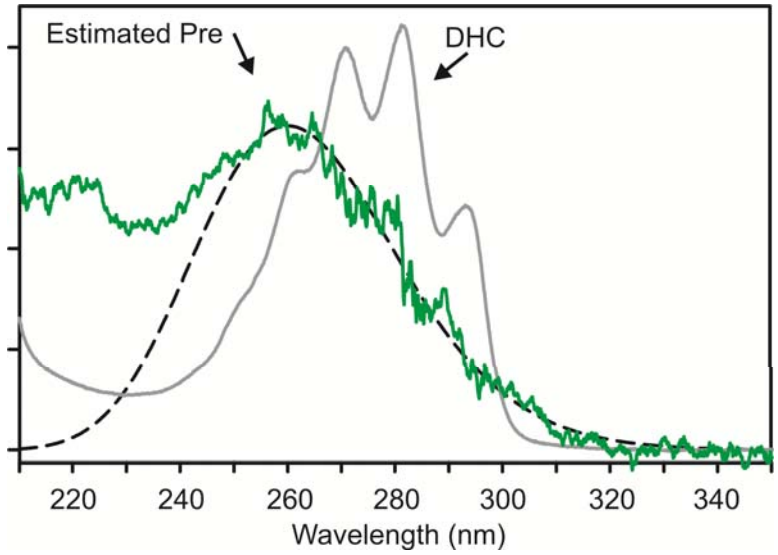


Steady State Photolysis of DHC



n-heptane



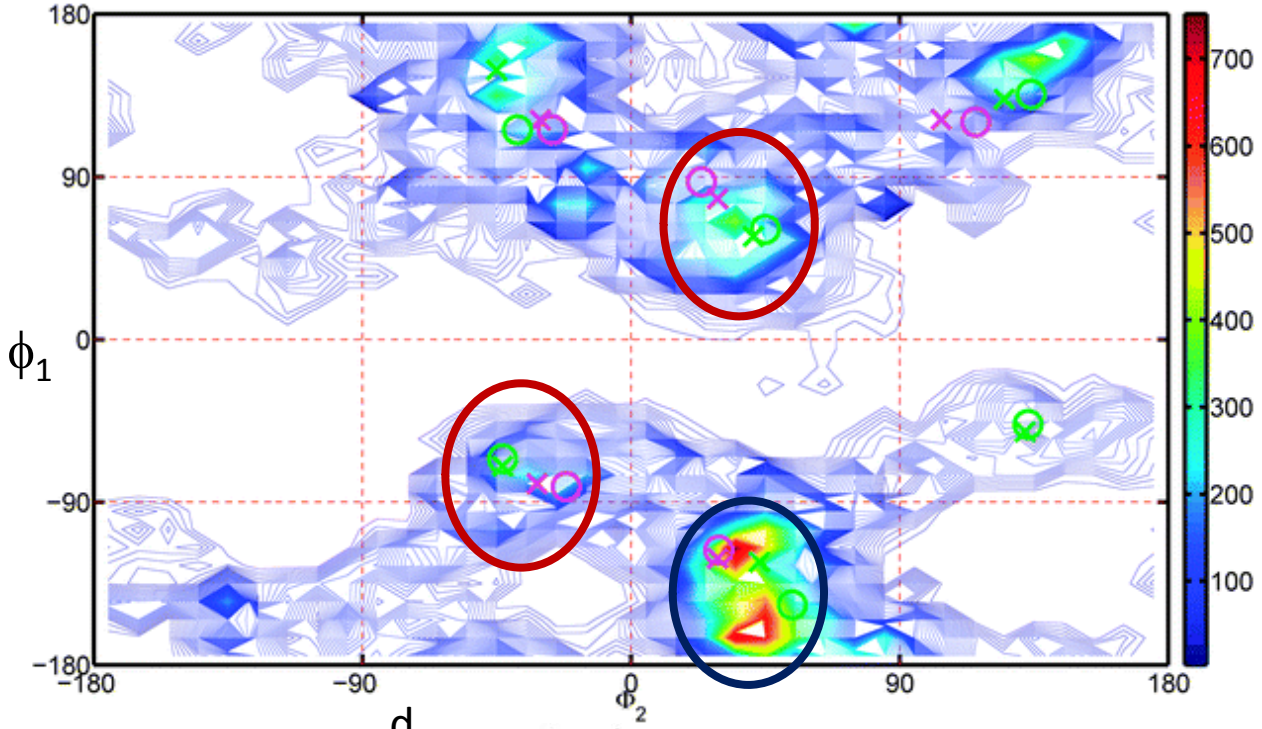


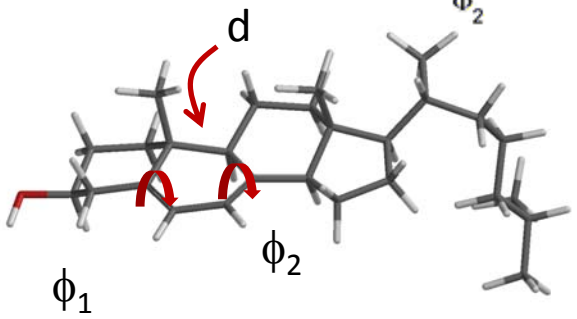
- Steady state photolysis experiments using the unfiltered output of a mercury arc lamp and a UV-VIS spectrometer. For excitation times longer than 10-15 s secondary products begin to appear.
- The previtamin D_3 spectrum can be estimated by adding DHC back to the difference until the vibronic structure is minimized.

Kinetics of Product Formation

E. Tapavicza, A. M. Meyer and F. Furche, 2011, Phys. Chem. Chem. Phys. 13, 20986.

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





300 K distribution of 63054 structures of previtamin D_3.

cZc conformation

tZc conformation

Kinetics of Product Formation

E. Tapavicza, A. M. Meyer and F. Furche, 2011, Phys. Chem. Chem. Phys. 13, 20986.

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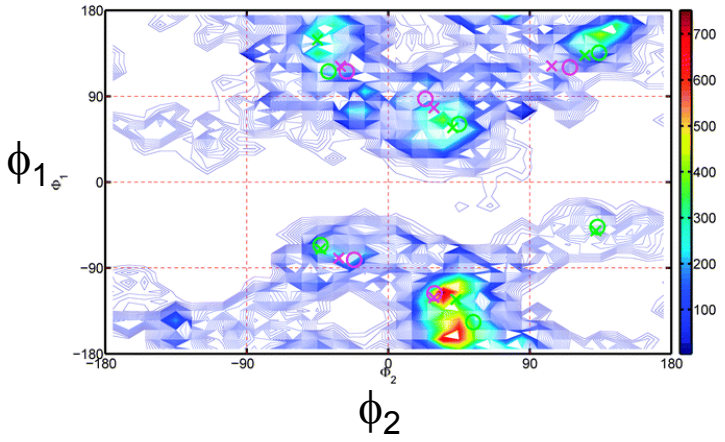
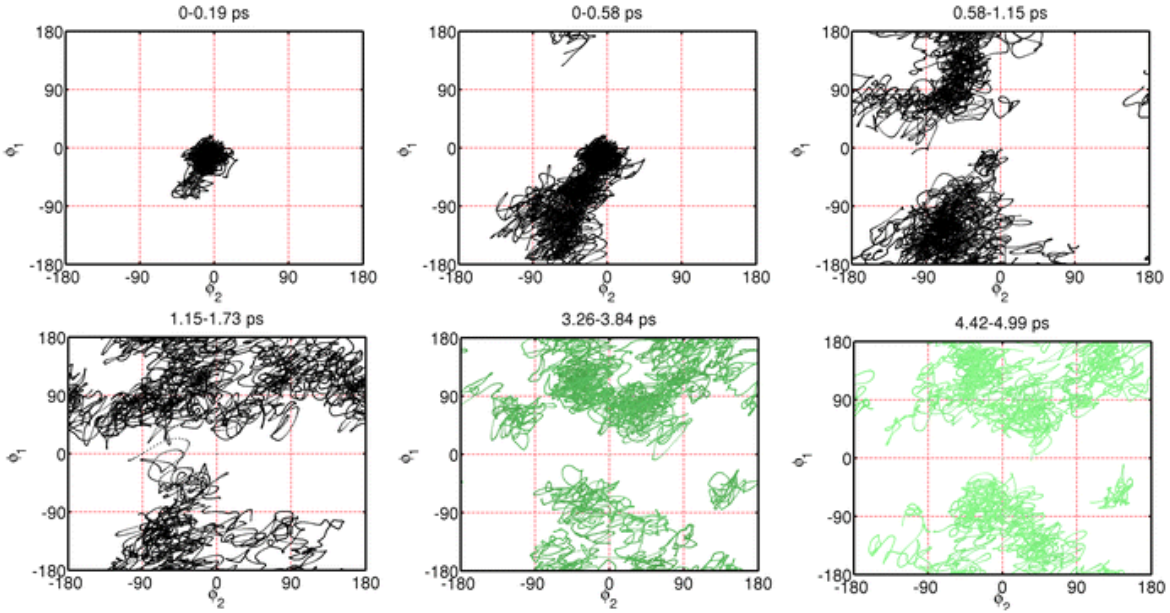
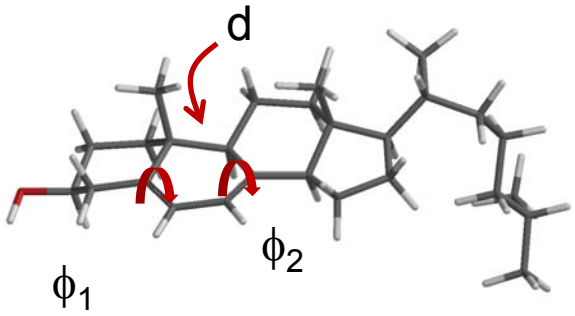
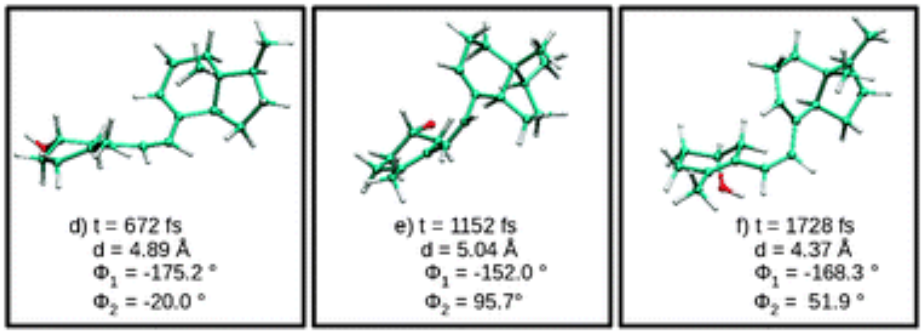
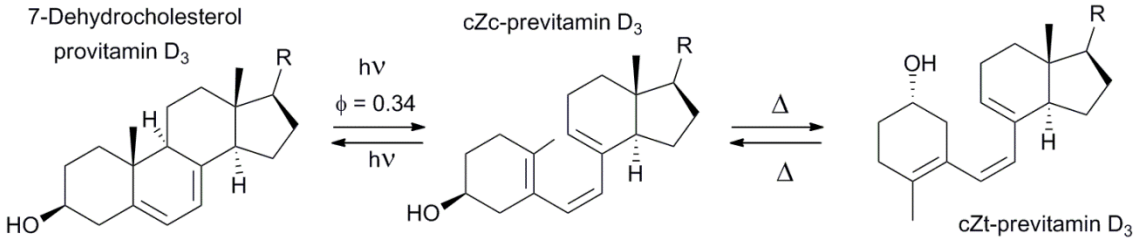


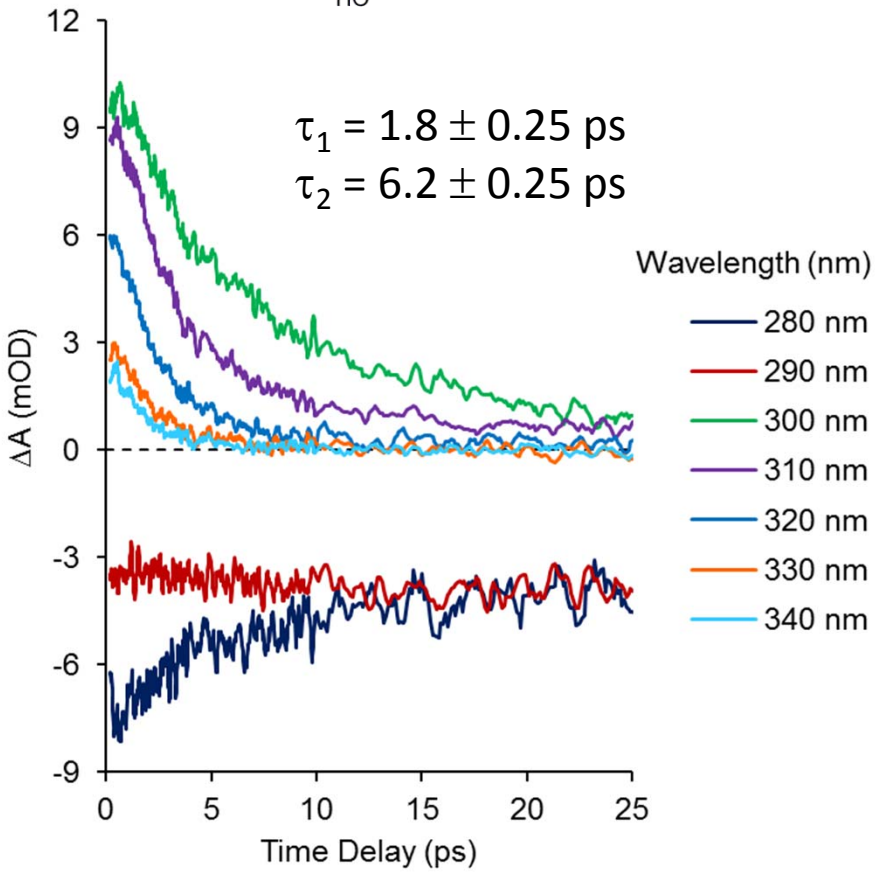


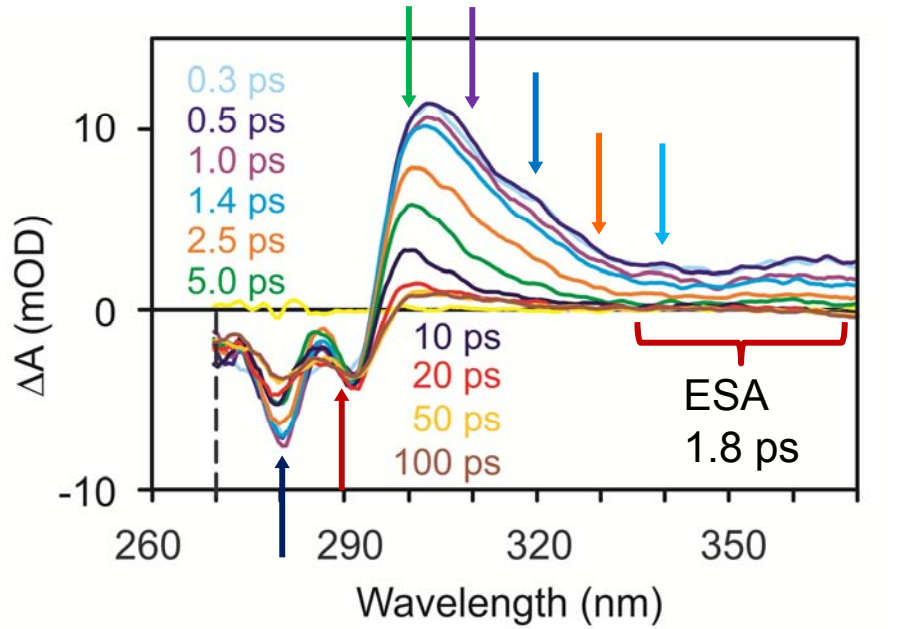




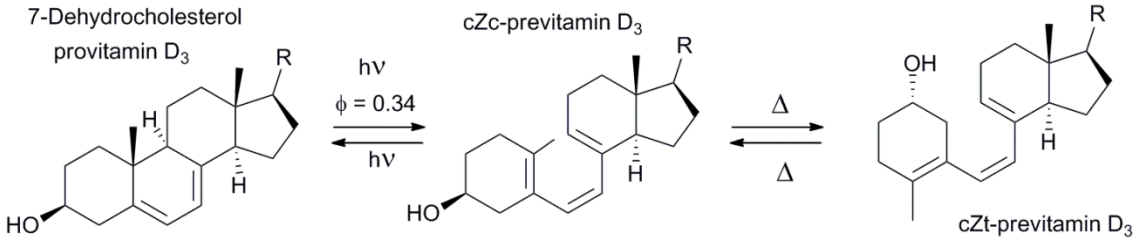
Kinetics of Product Formation



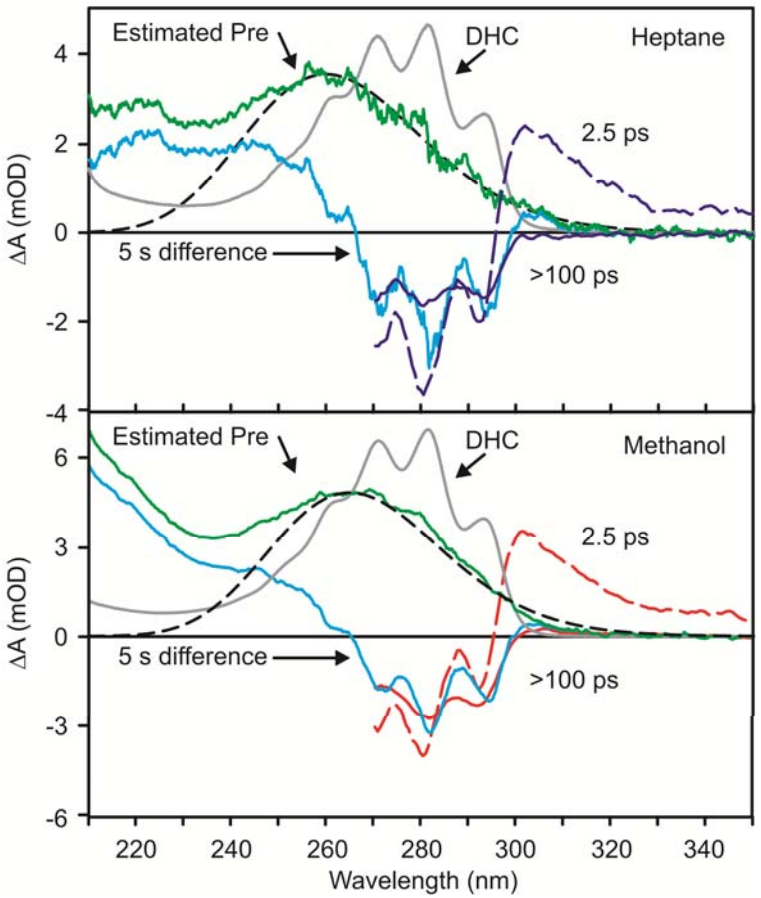




Solvent (In)Dependence

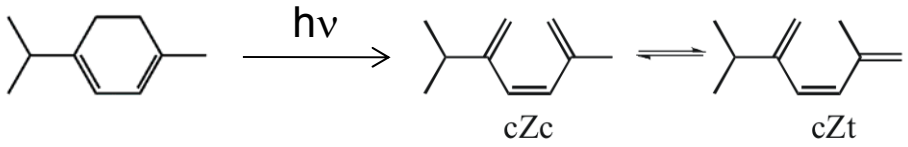


Solvent	η (mPa s)	τ_1 (ps)	τ_2 (ps)
Heptane	0.387	1.1 ± .45	5.1 ± .45
Dodecane	1.34	1.4 ± .45	8.5 ± .45
Methanol	0.544	1.5 ± .60	5.4 ± .60
2-Butanol	3.096	1.8 ± .25	6.2 ± .25



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

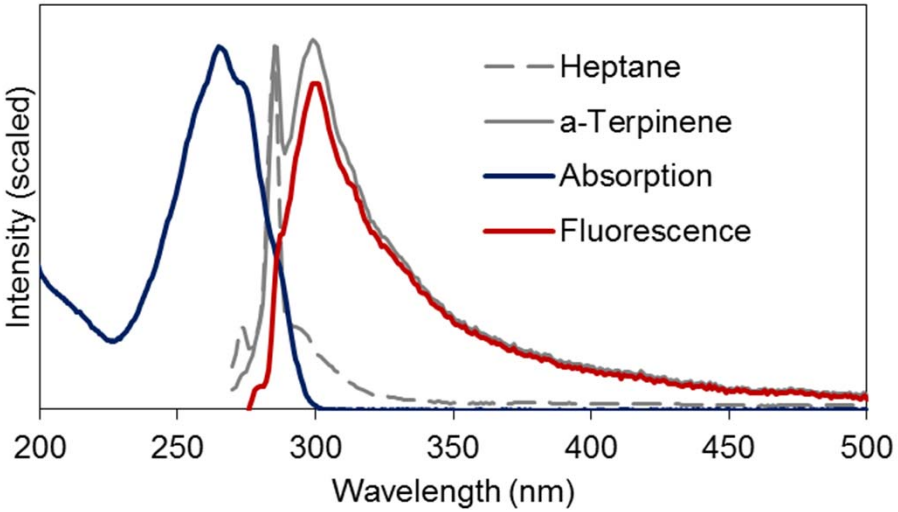
α-terpinene



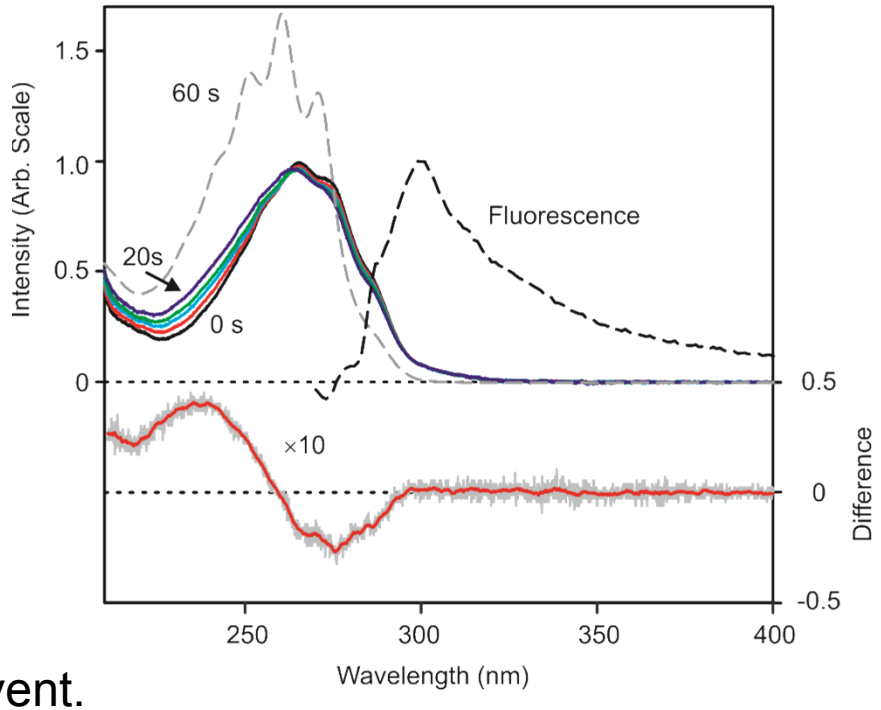
B. Arruda, J. Peng, B. Smith, K. G. Spears, and R. J. Sension "Photochemical Ring-Opening and Ground State Relaxation in α-Terpinene with Comparison to Provitamin D3" Submitted to J. Phys. Chem. B

Like DHC, α-terpinene is weakly fluorescent. The QY is ~ an order of magnitude smaller than for DHC.

φ_{fl} =~2×10^{-5}



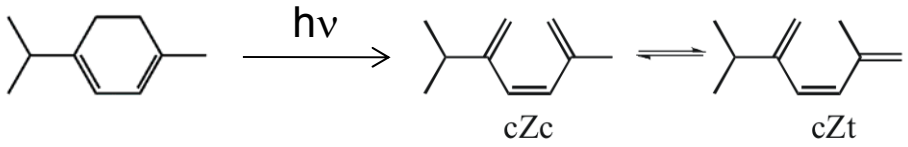
Steady state photolysis



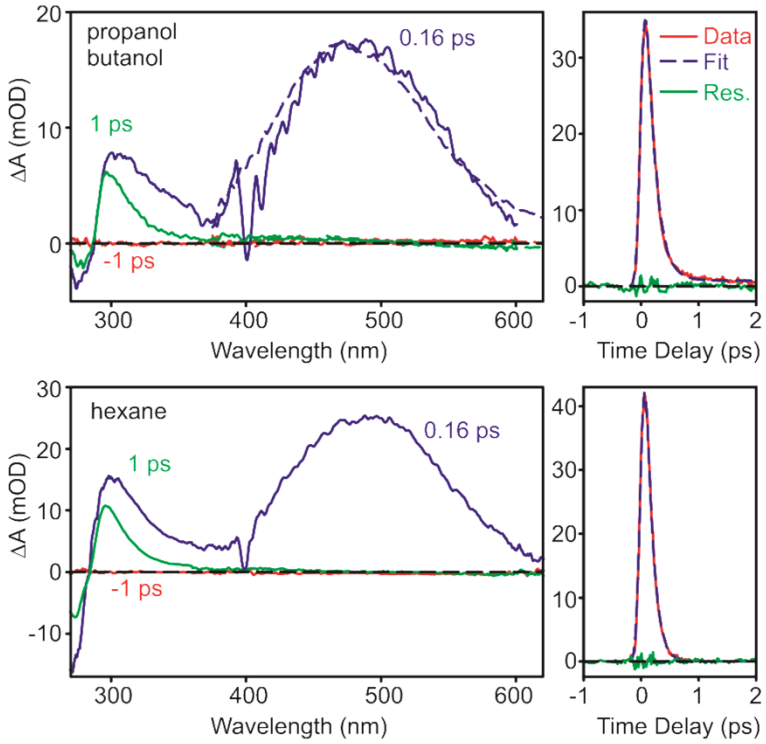
Sharp peak is Raman scattering from the solvent.

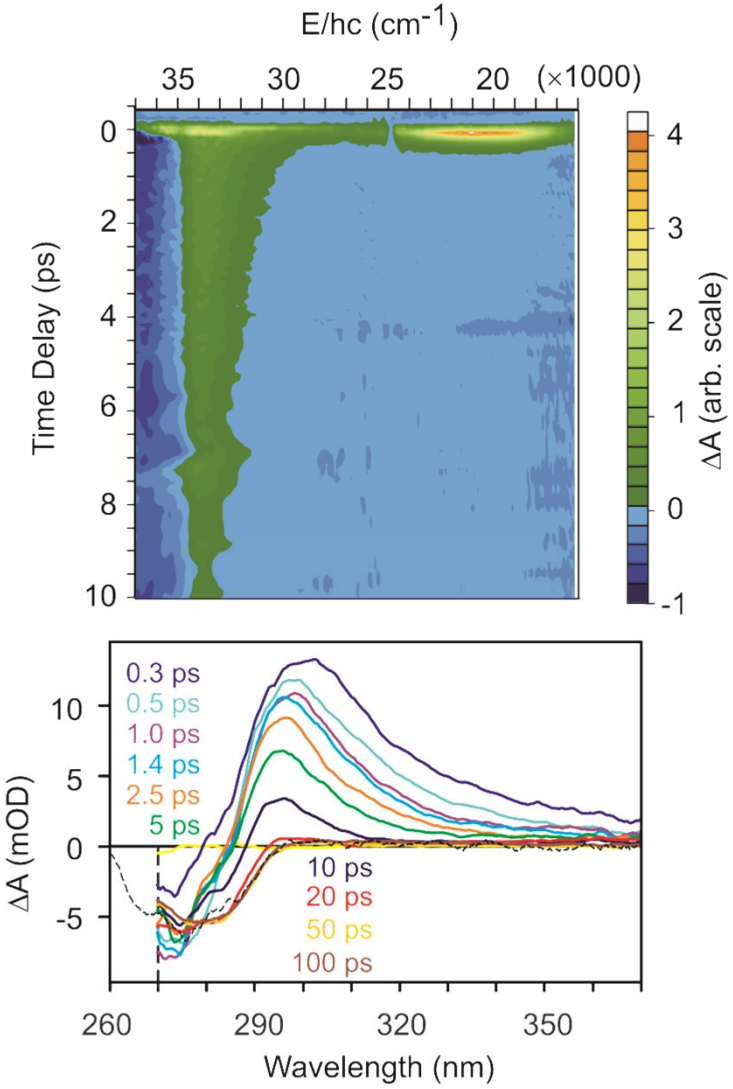
Slight variation in excitation wavelength allows separation of fluorescence and Raman.

α-terpinene



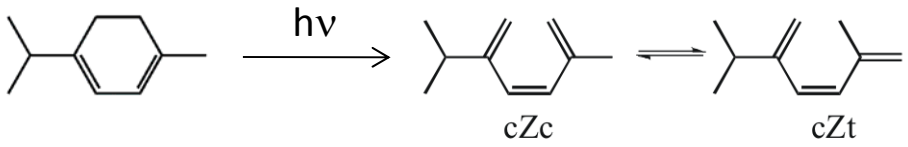
Excited state absorption following excitation of α-terpinene at 266 nm.





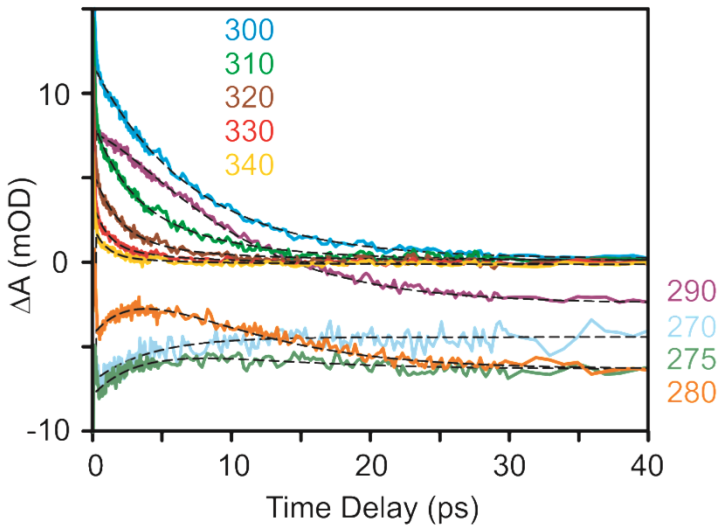
τ ~ 0.12 ps in n-hexane, 0.16 ps in 1-butanol

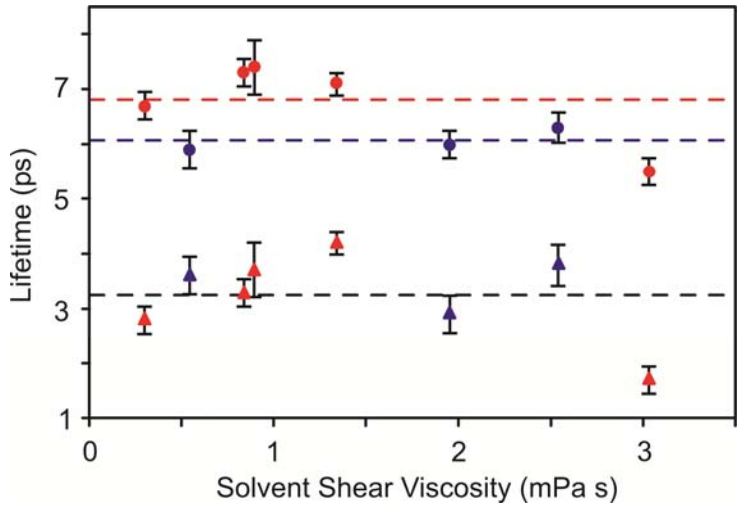
α-terpinene



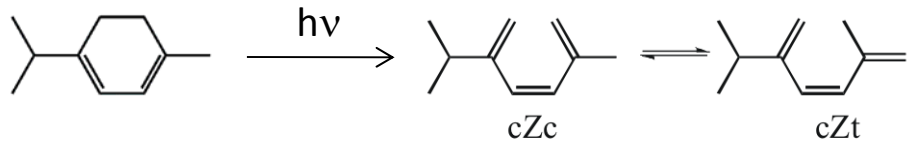
Solvent	η (mPa s)	τ_1 (ps)	τ_2 (ps)
Hexane	0.300	2.8 ± .25[d]	6.7 ± .25
Decane	0.838	3.3 ± .25	7.3 ± .25
Dodecane	1.34	4.2 ± .20	7.1 ± .20
Hexadecane	3.03	1.7 ± .25	5.5 ± .25
Cyclohexane	0.894	3.7 ± .50	7.4 ± .50
Methanol	0.544	3.6 ± .35	5.9 ± .35
1-Propanol	1.95	2.9 ± .25	6.0 ± .25
1-Butanol	2.54	3.8 ± .27	6.3 ± .27

The relaxation of the signal in the UV is similar to that observed for provitamin D_3. There is only a small solvent dependence.





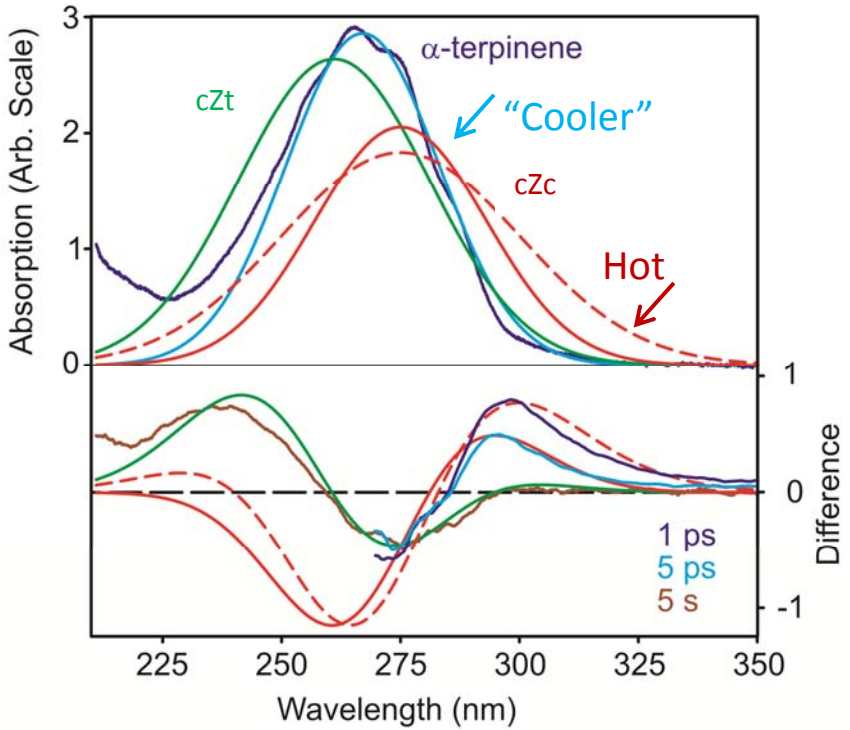
α-terpinene

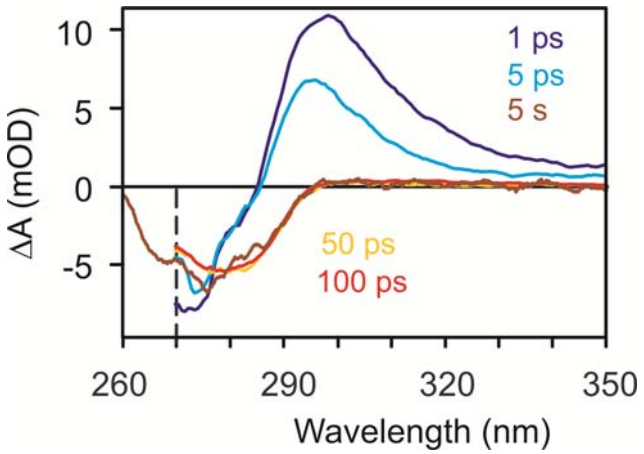


Isomer	Oscillator Strength	Singlet Transition (nm)	Ground State Energy (kJ/mol)
α-terpinene	0.22	278	0
cZc	0.12	282	100
cZt	0.38	265	94
tZc	0.25	269	99
tEt	0.84	271	62

TDDFT Calculation, 6-311**G(d,p) basis set and the B3LYP density functional

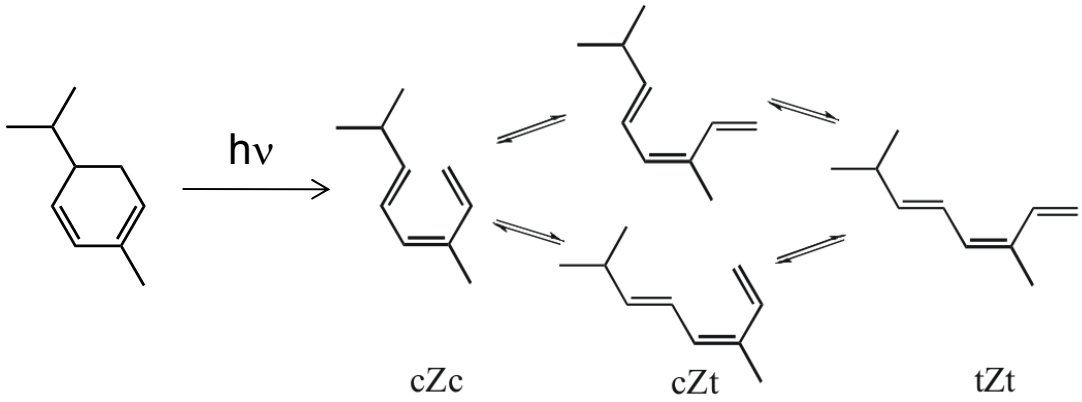
The data are well modeled by narrowing (thermal cooling) and isomerization.

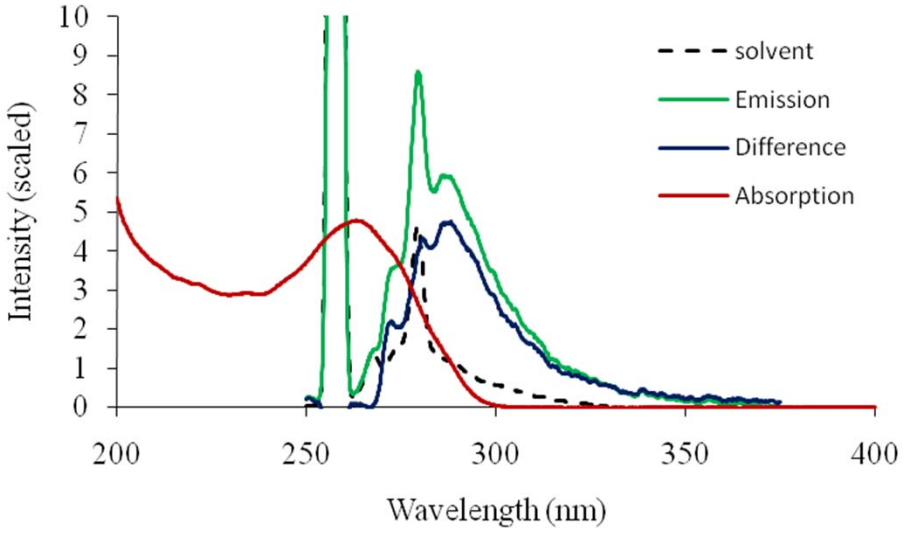




50 and 100 ps spectra resemble steady state cZt spectrum.

Cyclohexadiene Photochemistry – in α-phellandrene





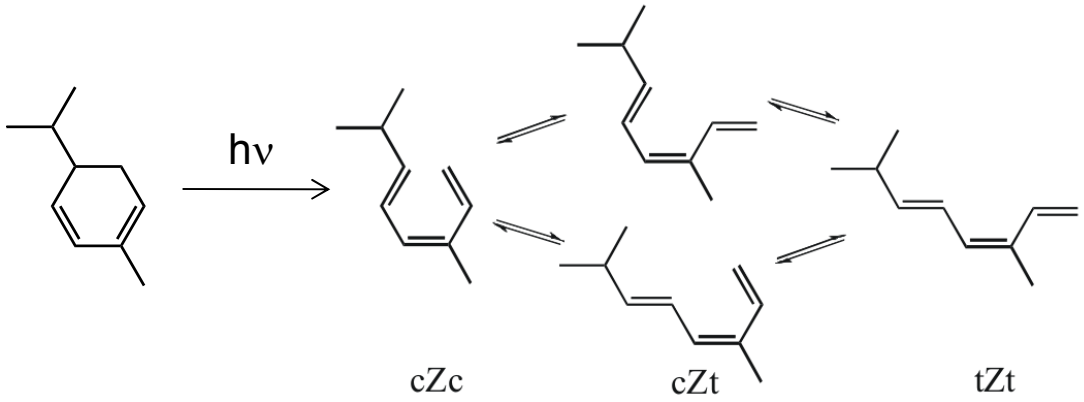
The absorption (red) and fluorescence (blue) in heptane.

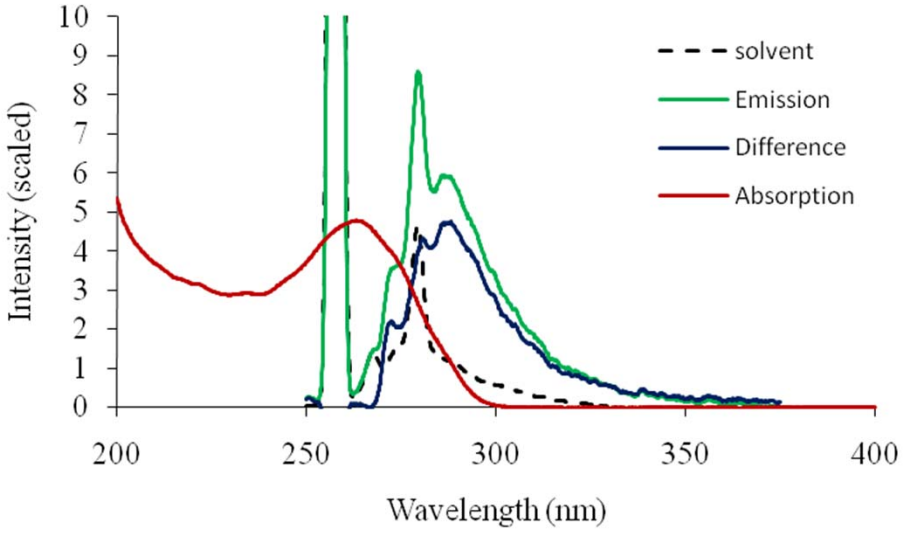
The sharp line in the fluorescence is a Raman line from the solvent.

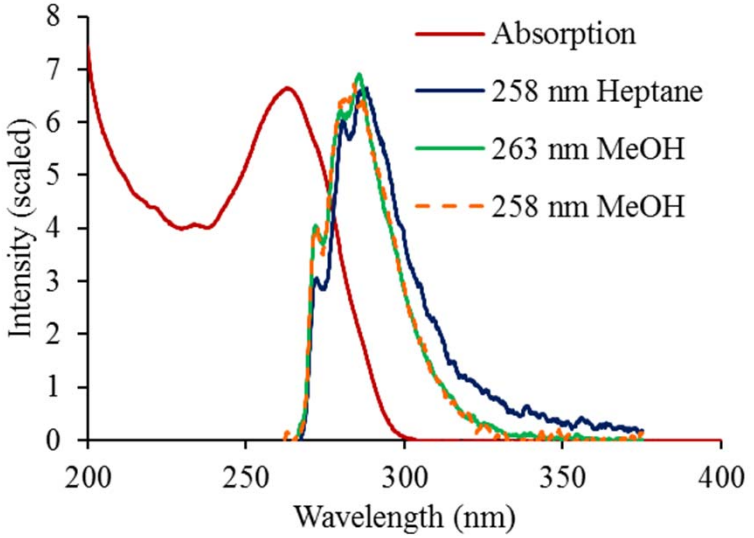
QY ~ 10^{-5} (somewhat smaller than α-terpinene, but measureable)

B. Arruda, E. Najera, B. Smith, K. G. Spears, and R. J. Sension, Manuscript in preparation.

Cyclohexadiene Photochemistry – in α-phellandrene

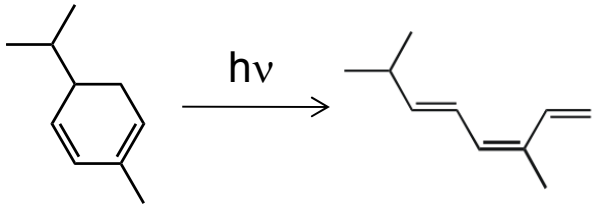


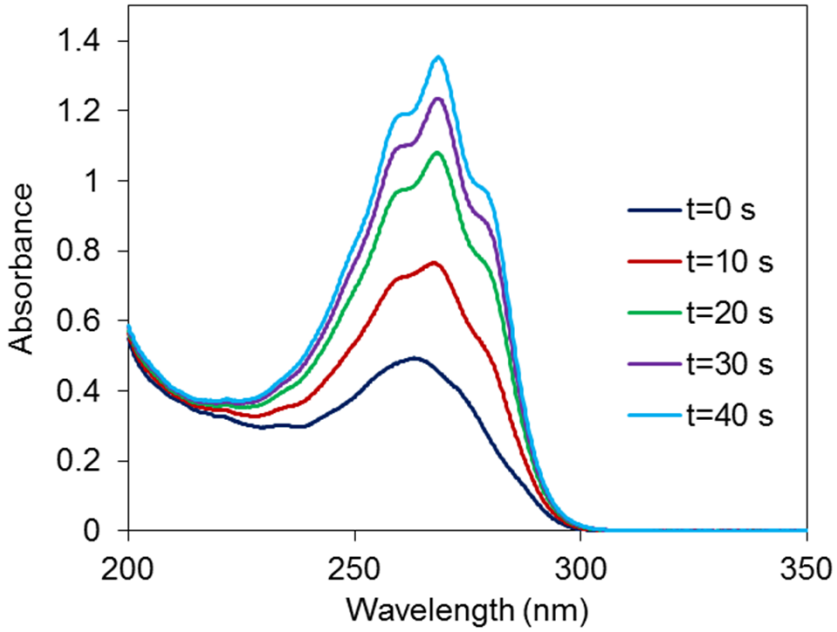




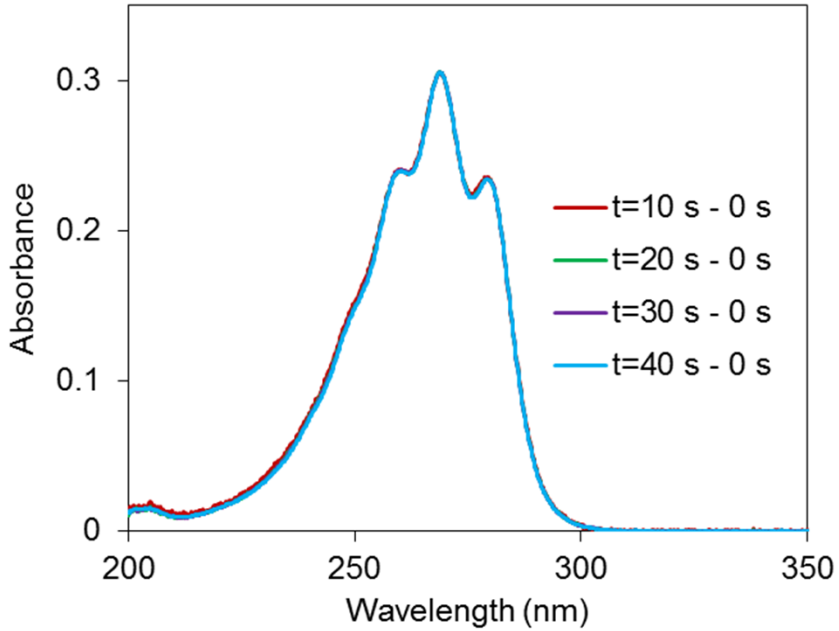
Steady state photolysis of α-phellandrene

Steady state photolysis in heptane





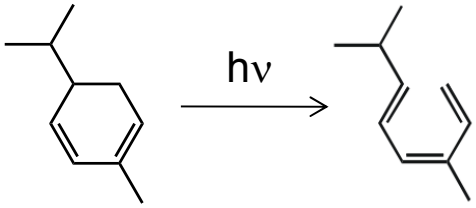
Steady state difference spectrum
tZt - α-phellandrene



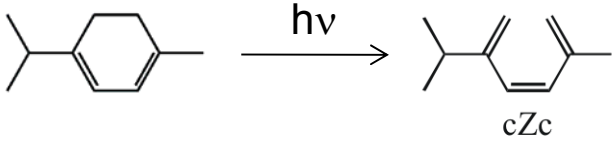
Within a scale factor the difference spectrum is constant for the first 40 or 50 seconds.

Secondary products involving cis-trans double bond isomerization begin to accumulate at longer times.

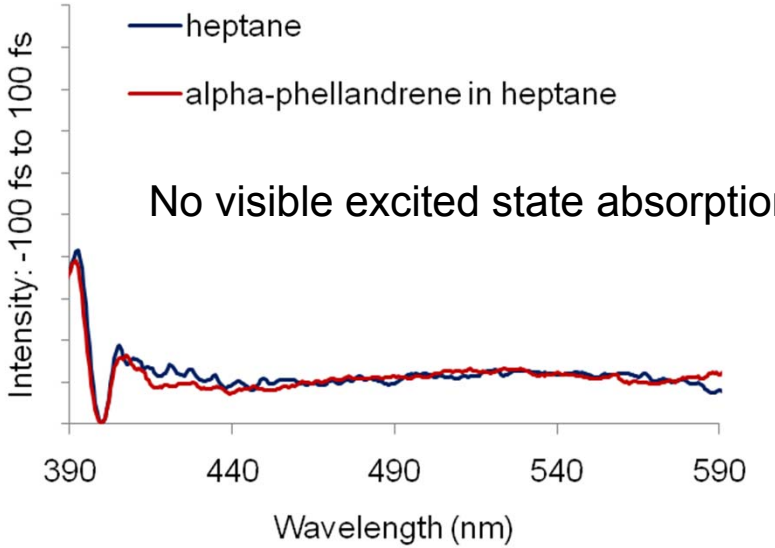
Excited state absorption of α-phellandrene

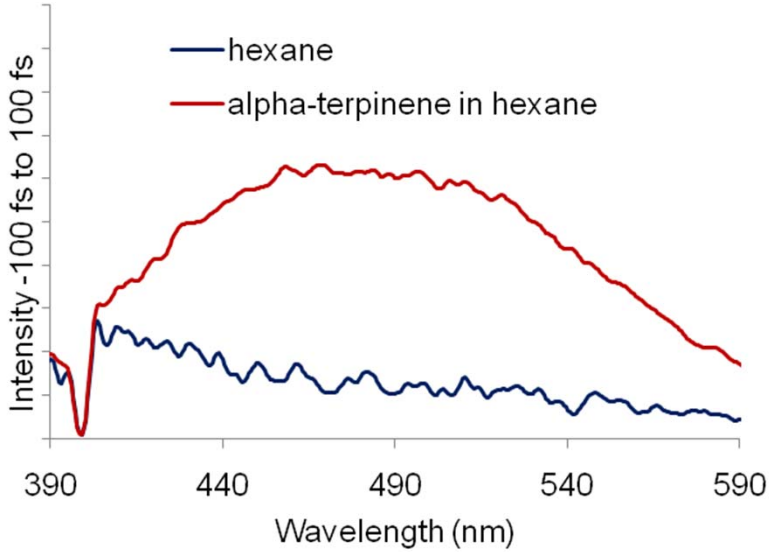


cZc



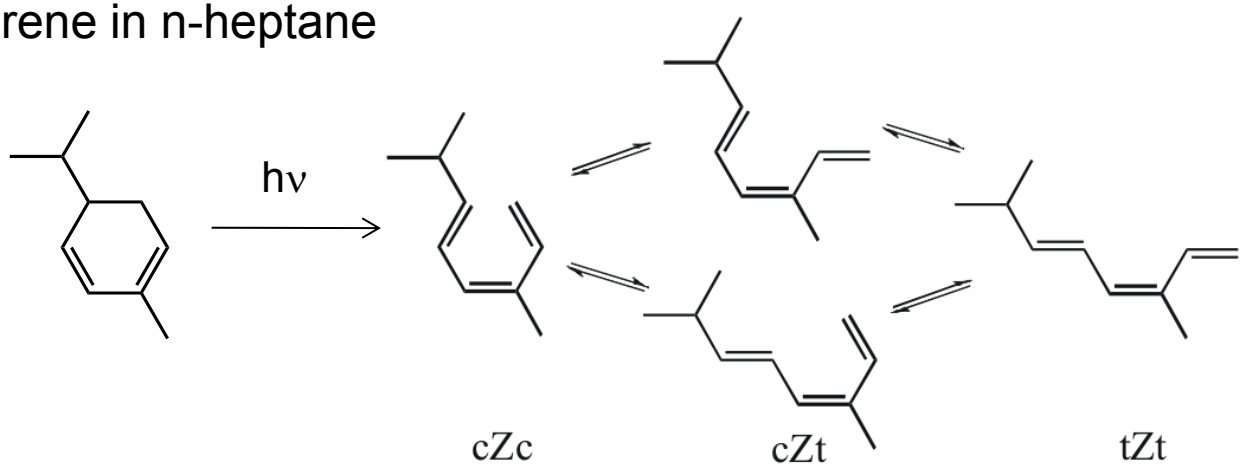
cZc



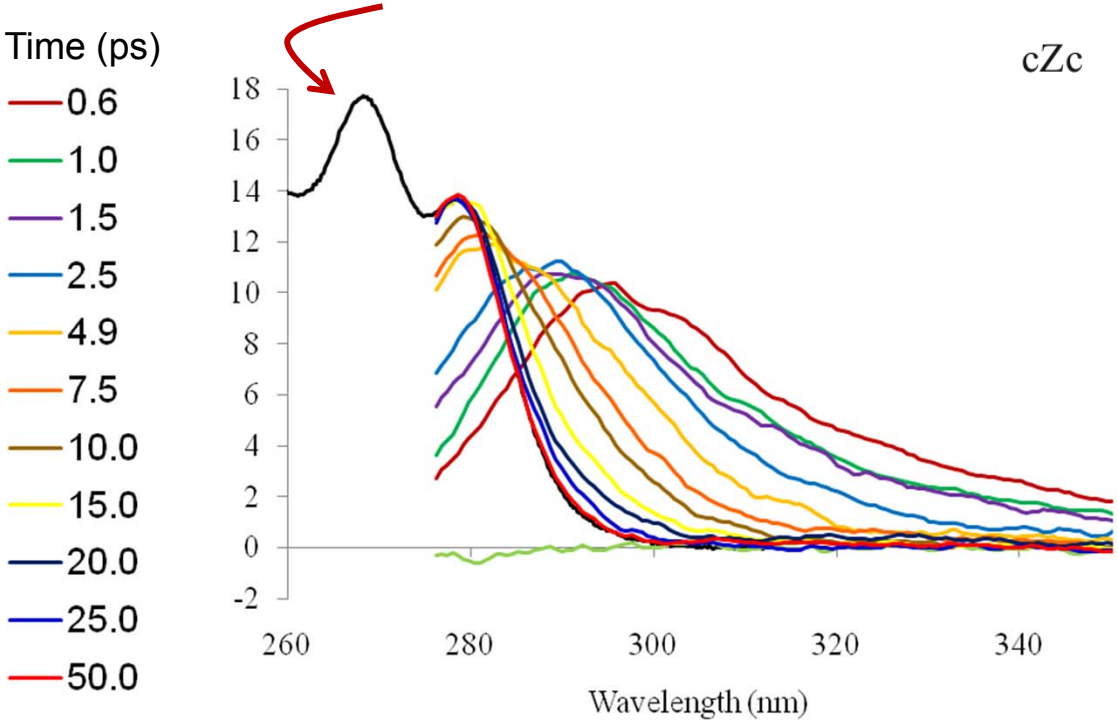


Photoproduct Formation - α-phellandrene

Excitation of α-phellandrene in n-heptane



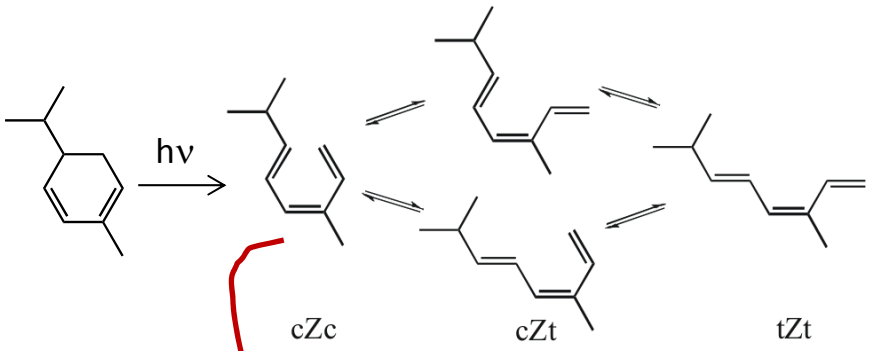
Steady state difference spectrum

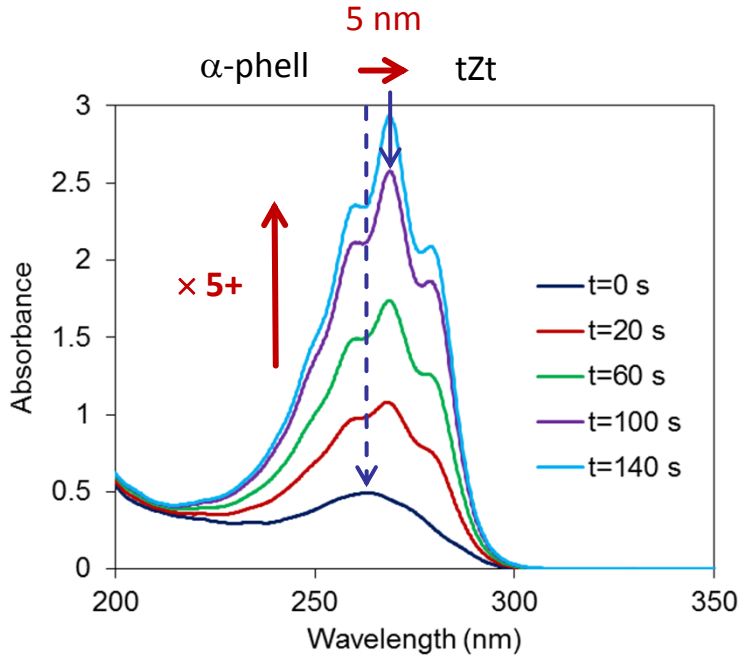


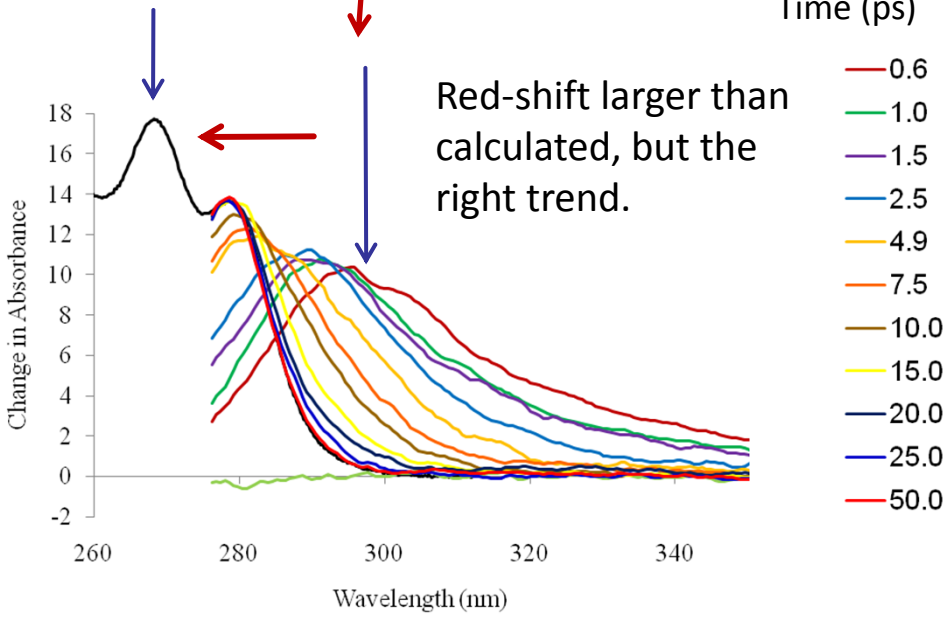
The product spectrum red-shifts and converges on the steady state result within about 50 ps.

Photoproduct Formation - α-phellandrene

Isomer	Oscillator Strength	Singlet Transition (nm)	Ground State Energy (kJ/mol)
α-phell	0.09	272	0
cZc	0.17	290	75
cZt	0.49	283	52
tZc	0.39	284	49
tZt	0.98	280	35



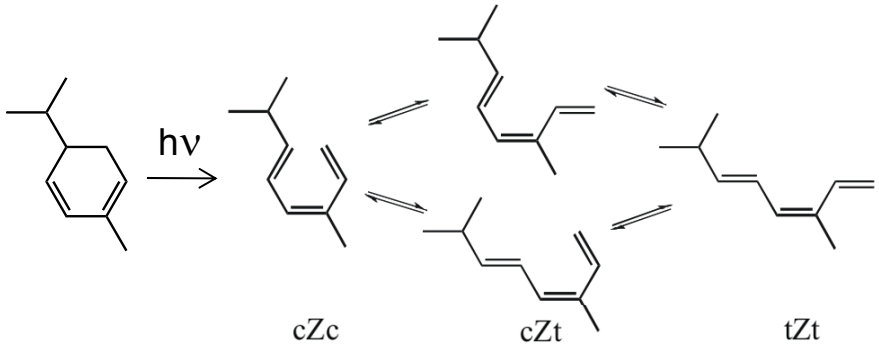


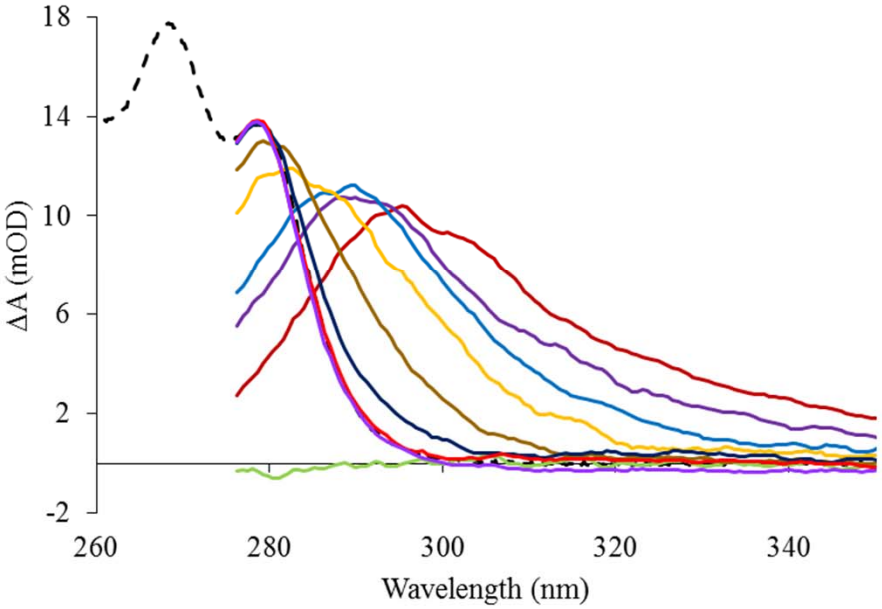


Red-shift larger than calculated, but the right trend.

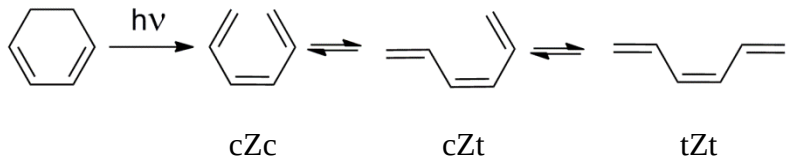
Comparison of α-phellandrene and CHD

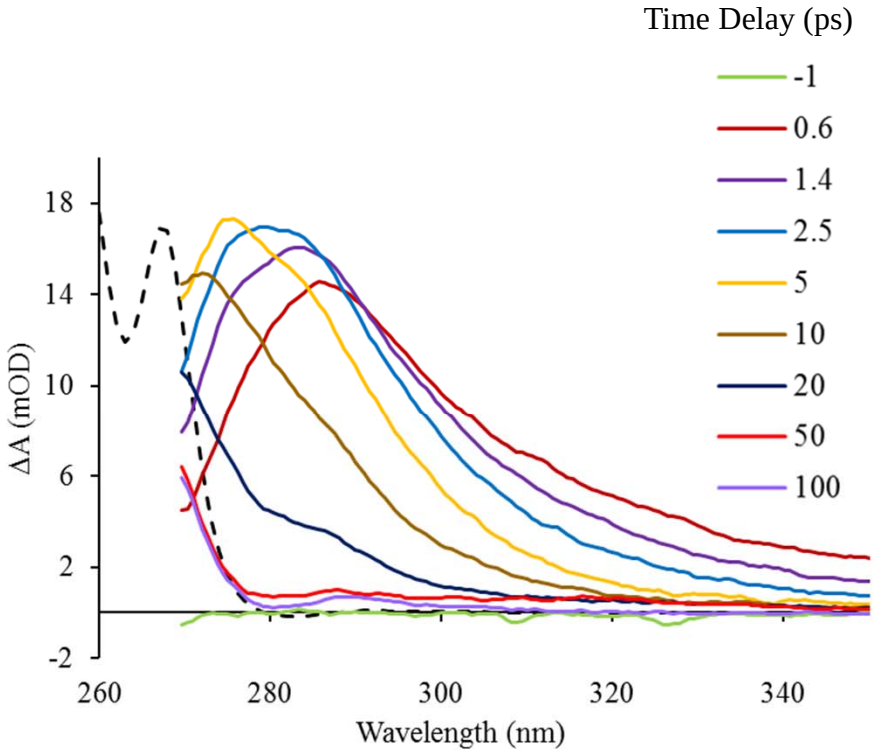
α-Phellandrene in n-heptane





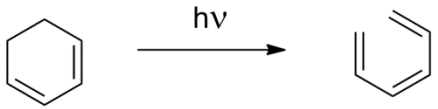
Cyclohexadiene in n-heptane



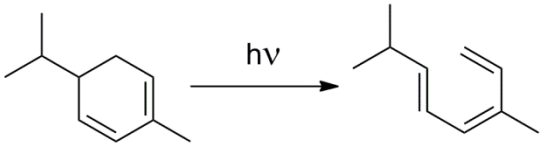


Summary

CHD

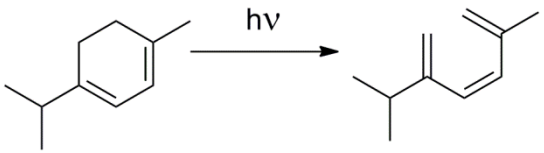


α-phellandrene

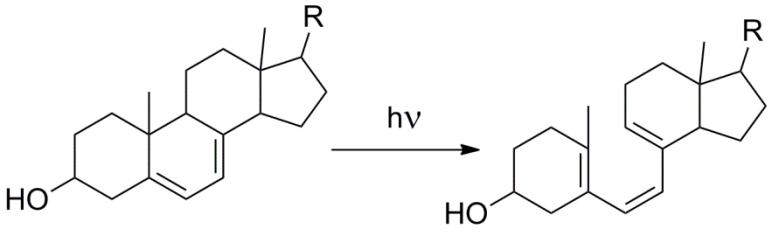


- No visible excited state absorption
- Fluorescence QY≤10^{-5} α-phell; ~10^{-6} CHD
- Ground state dynamics diffusive relaxation
- Multiphoton control possible CHD

α-terpinene



DHC



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