2013.11.14
Carl-Zeiss Lecture 3
IPHT Jena

Time-resolved Raman Spectroscopy

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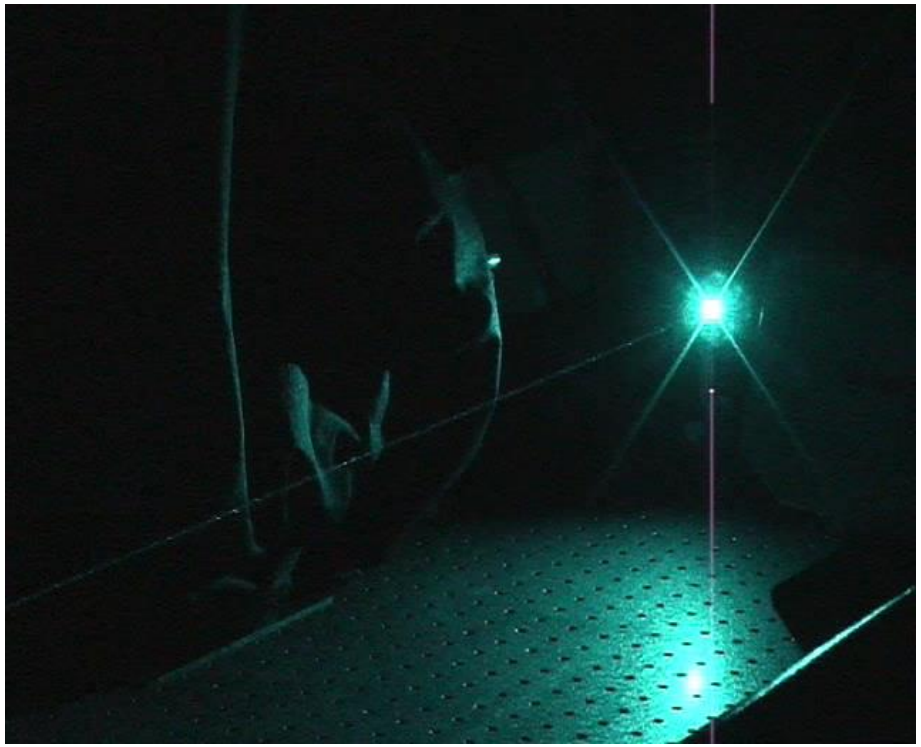
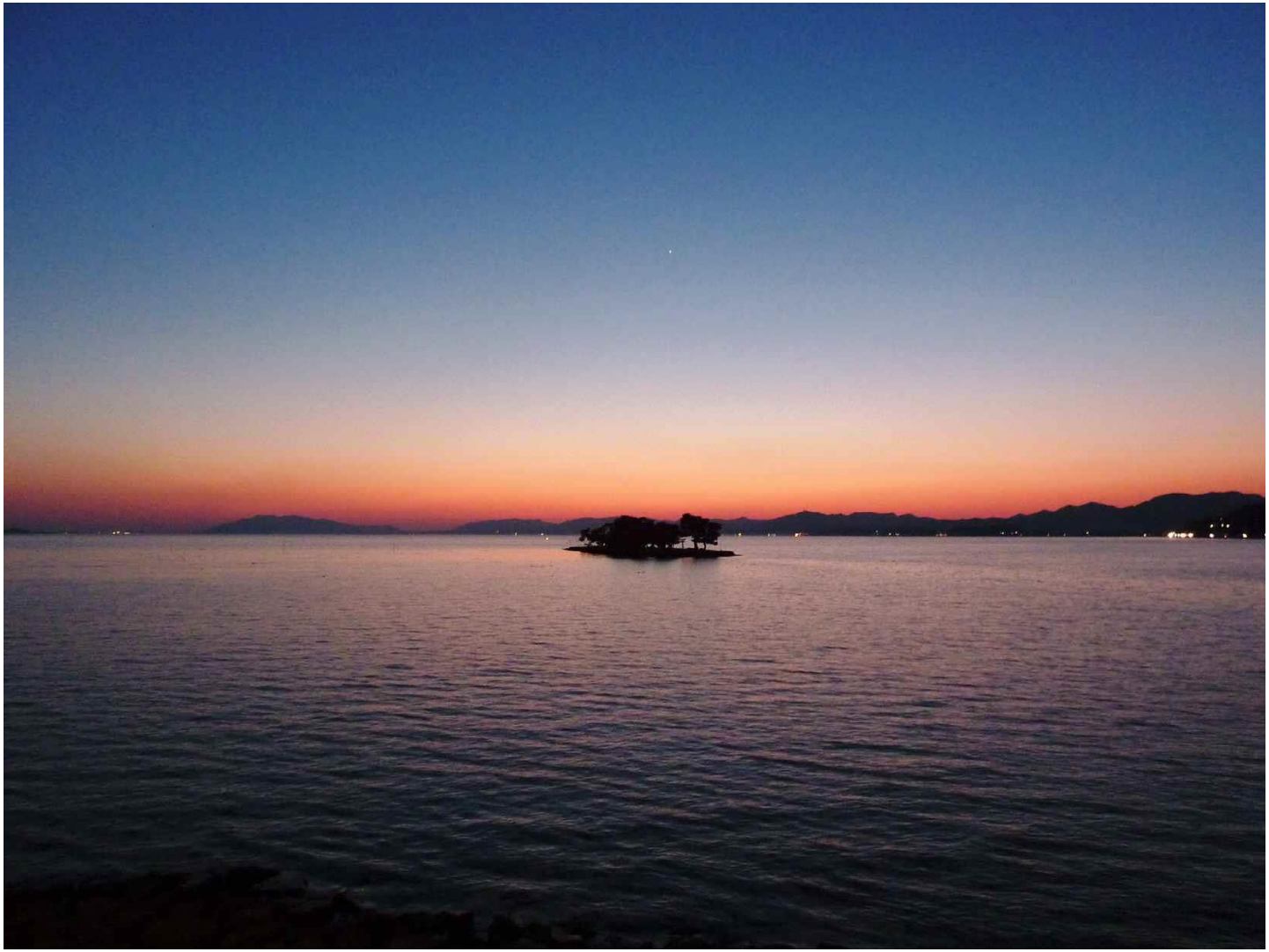
「諸行無常」

Nothing can last for ever



Time and Space: When？ Where？



Sun set at Shinjiko Lake. http://blogs.yahoo.co.jp/naru3075/41266684.html

Space

Time

10 cm — 10^{9} s

10 μm — 10^{3} s

1 μm — 10^{2} s

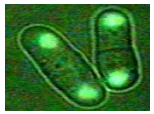
10 nm — 10^{-10} s

1 nm — 10^{-12} s

0.1 nm — 10^{-15} s

Organ

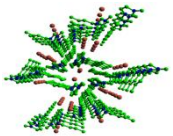
Cell



Organelle

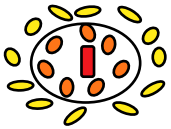
Biology

Ionic liquid

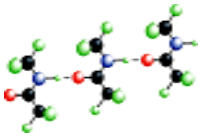


Liposome

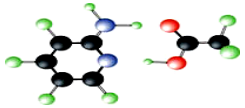
Solvation structure



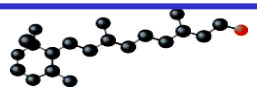
Aggregate



Complex



Molecule

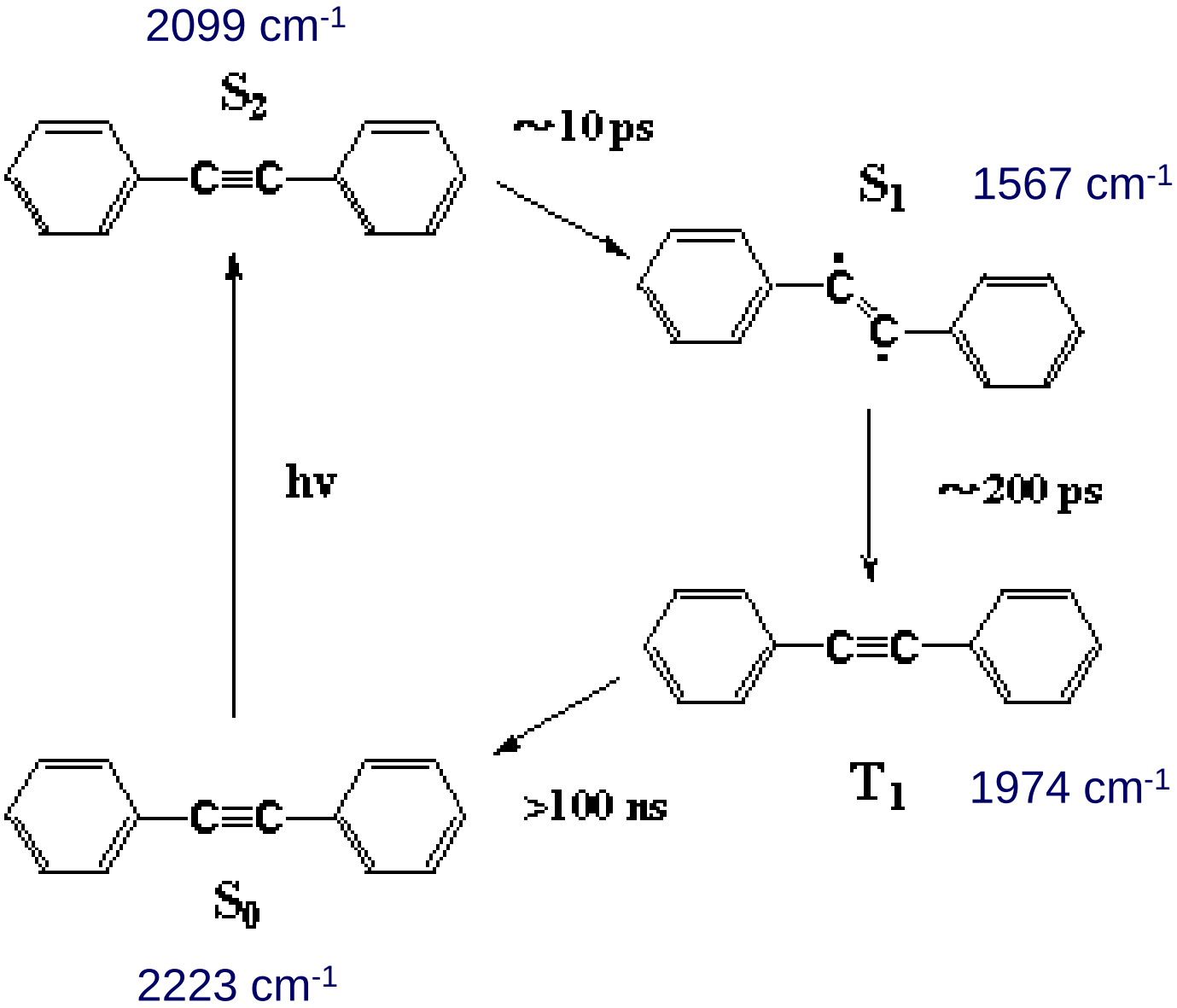


Atom

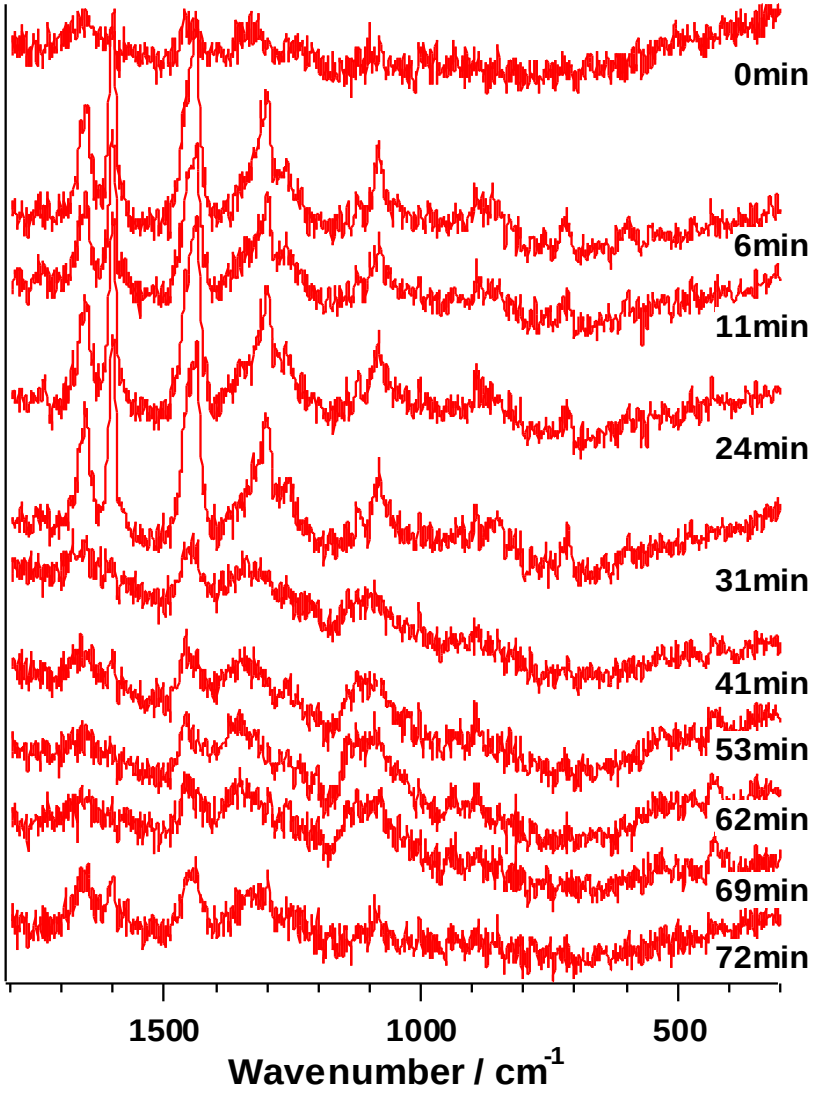
Chemistry

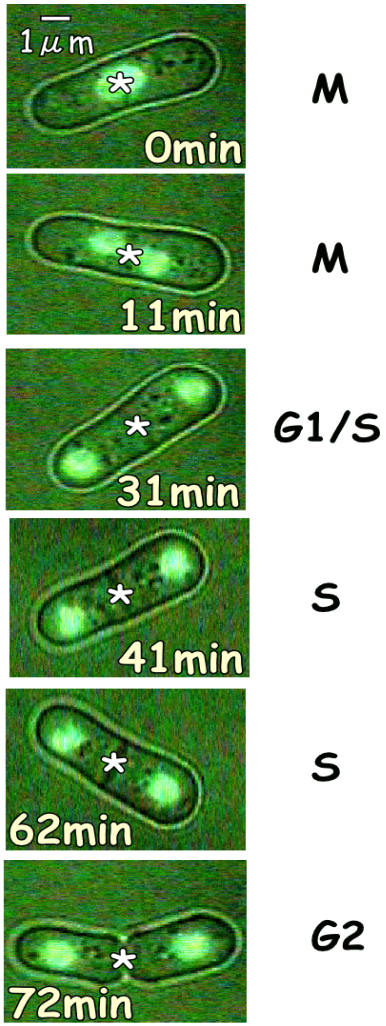
Physics

Structures of Diphenylacetylene in Different Electronic States



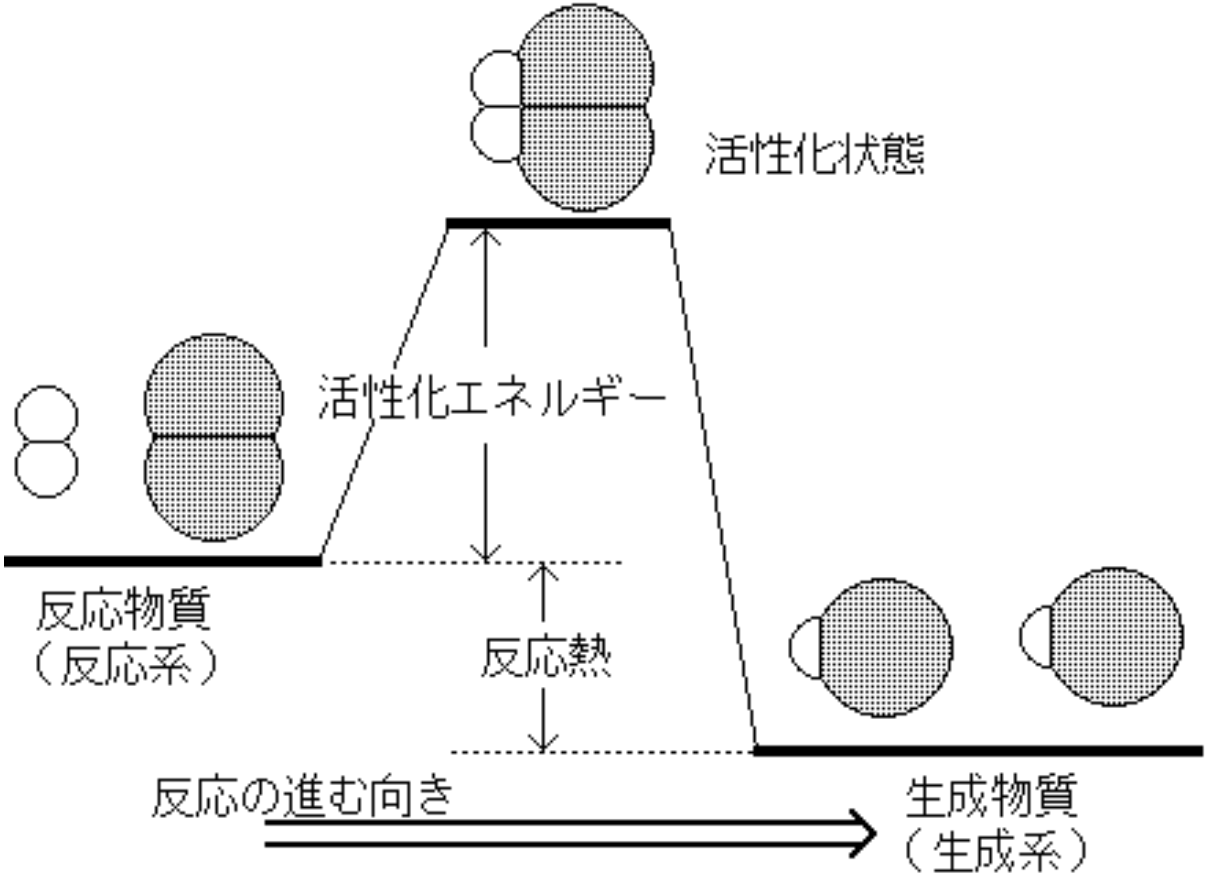
Time-resolved Raman Spectroscopy of a Dividing Yeast





Y-S Huang, T. Karashima, M. Yamamoto, H. Hamaguchi, *J. Raman Spectrosc.*, **34,** 1-3 (2003).

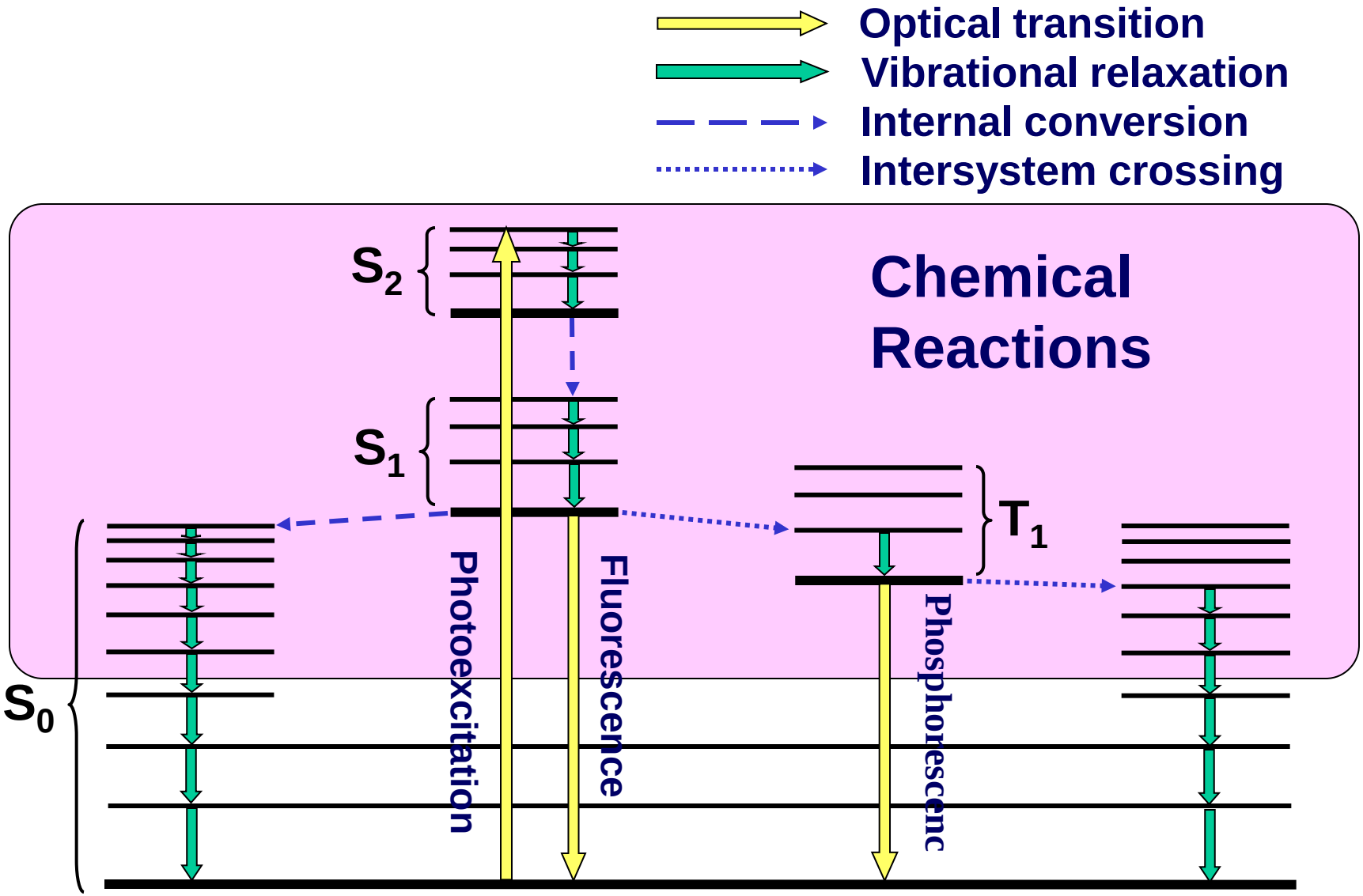
How Does Chemical Reaction Proceed?



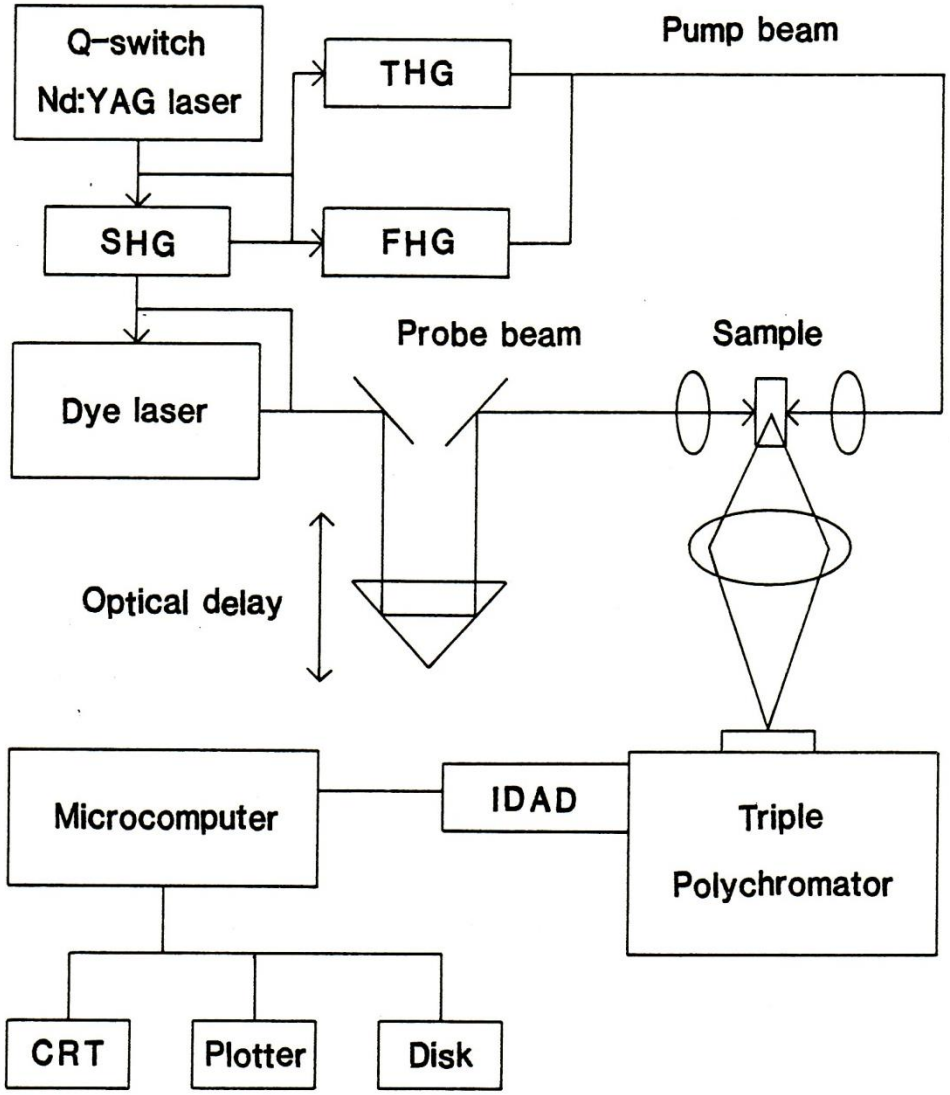
When？ Where？

http://www.ed.kanazawa-u.ac.jp/~kashida/ChemII/chapter1/sec1/c112.htm

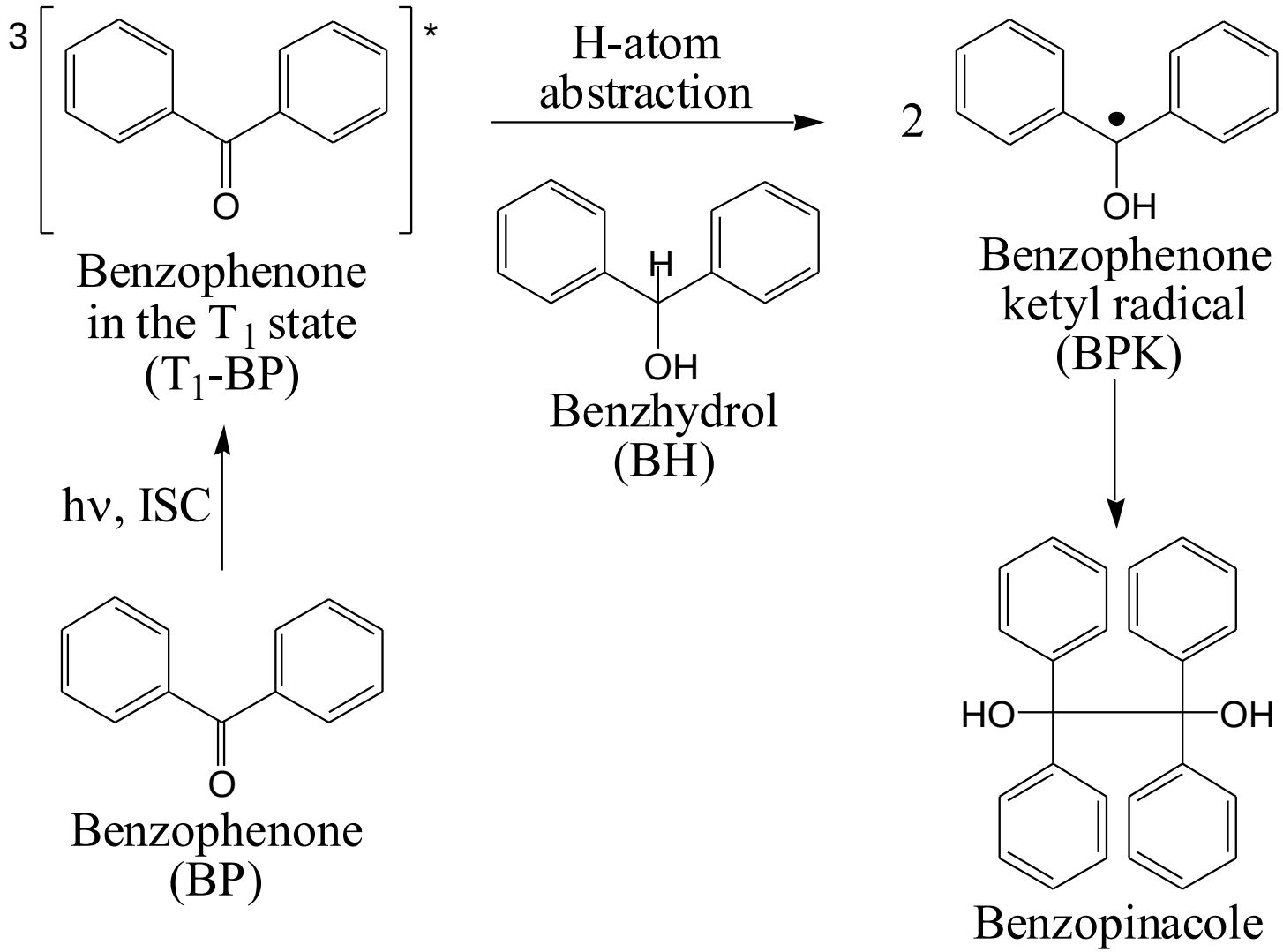
Photophysics and Photochemistry of Molecules



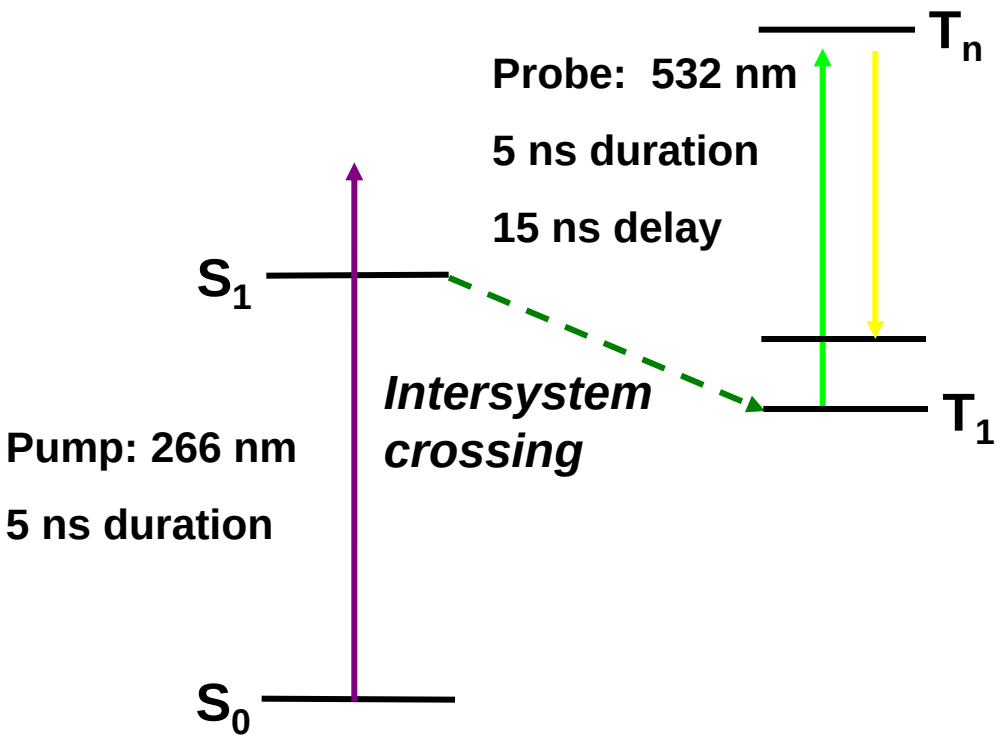
Nanosecond Transient Raman Spectrometer (1983)

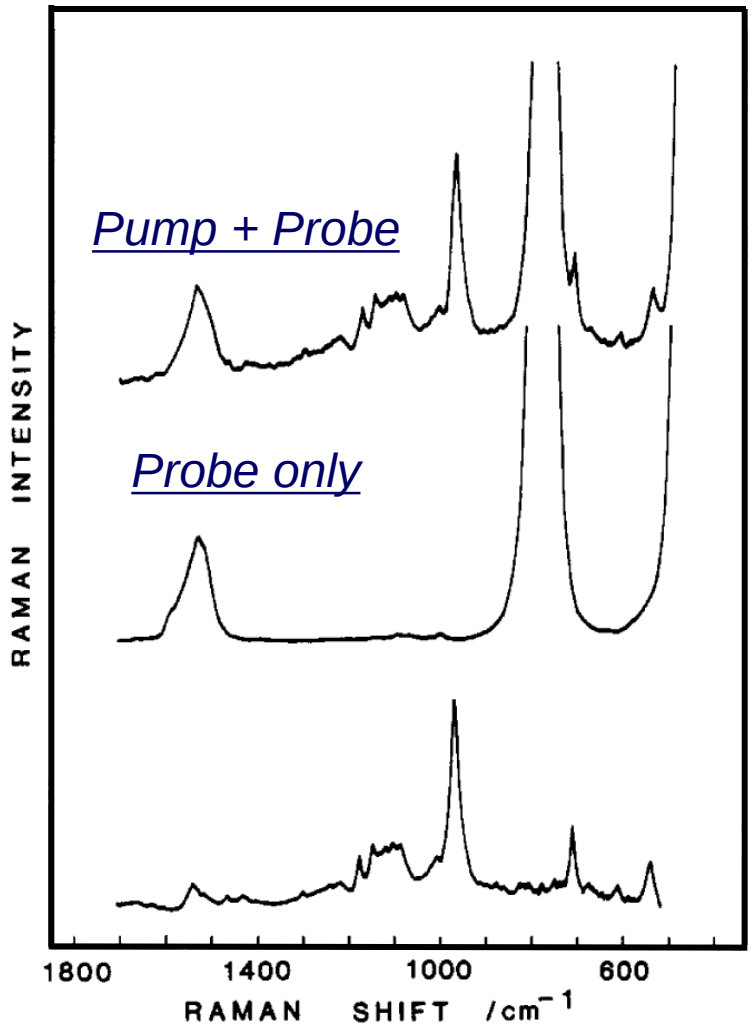


Photochemical Hydrogen Abstraction Reaction of Benzophenone



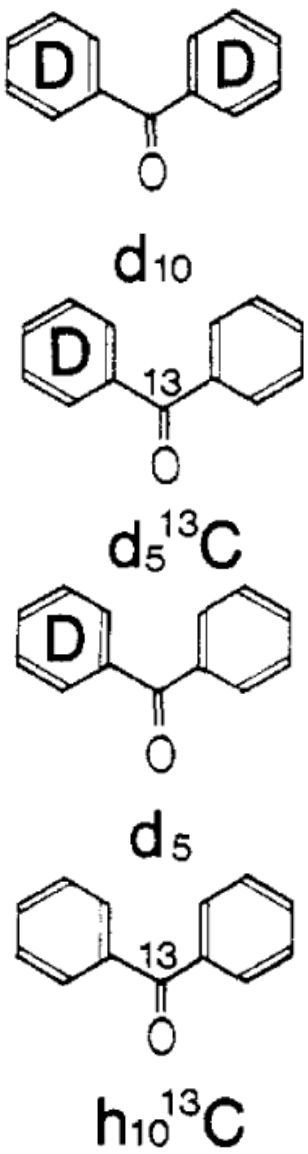
Nanosecond Time-resolved Raman Spectroscopy of BP in CCl_4

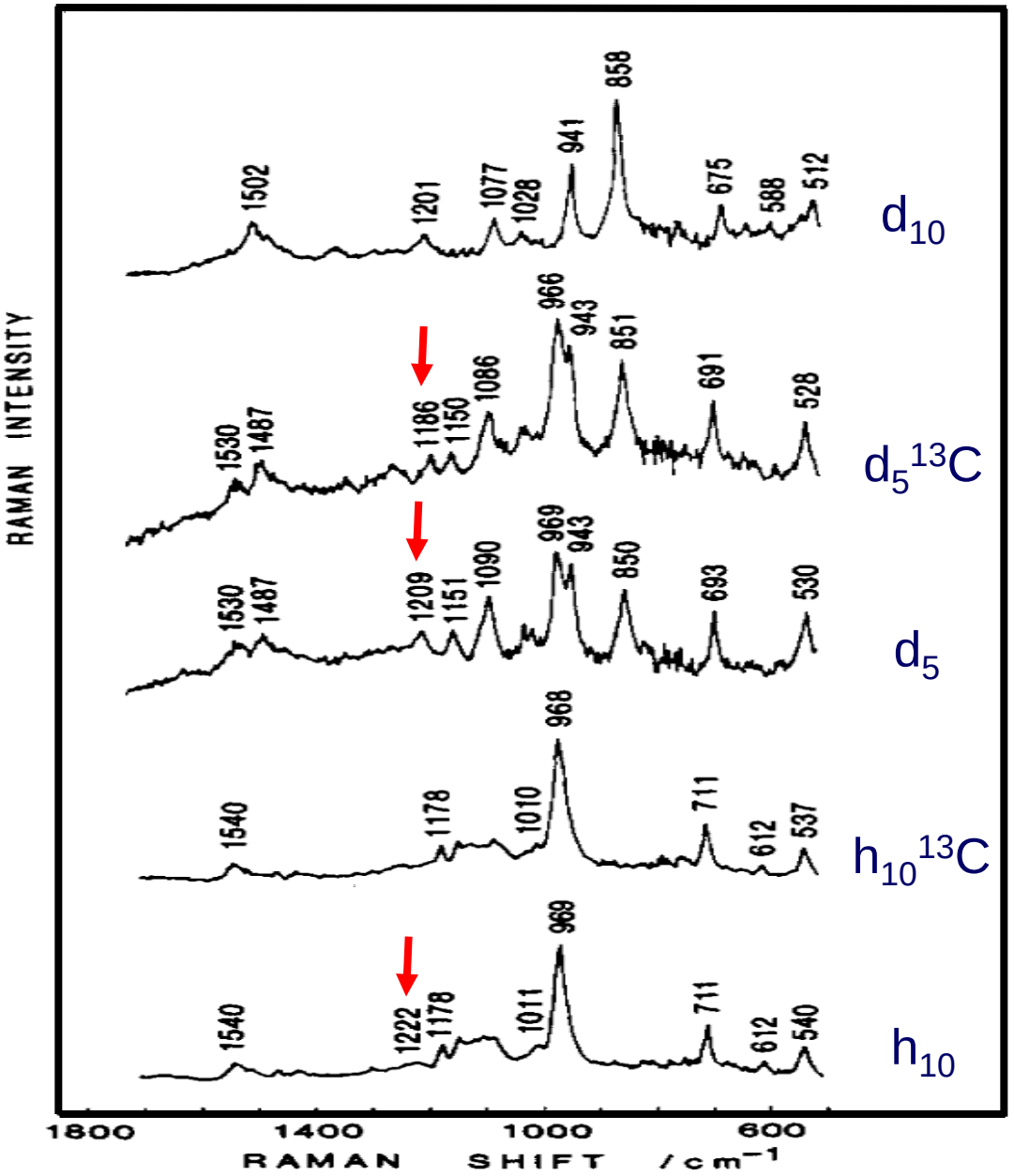




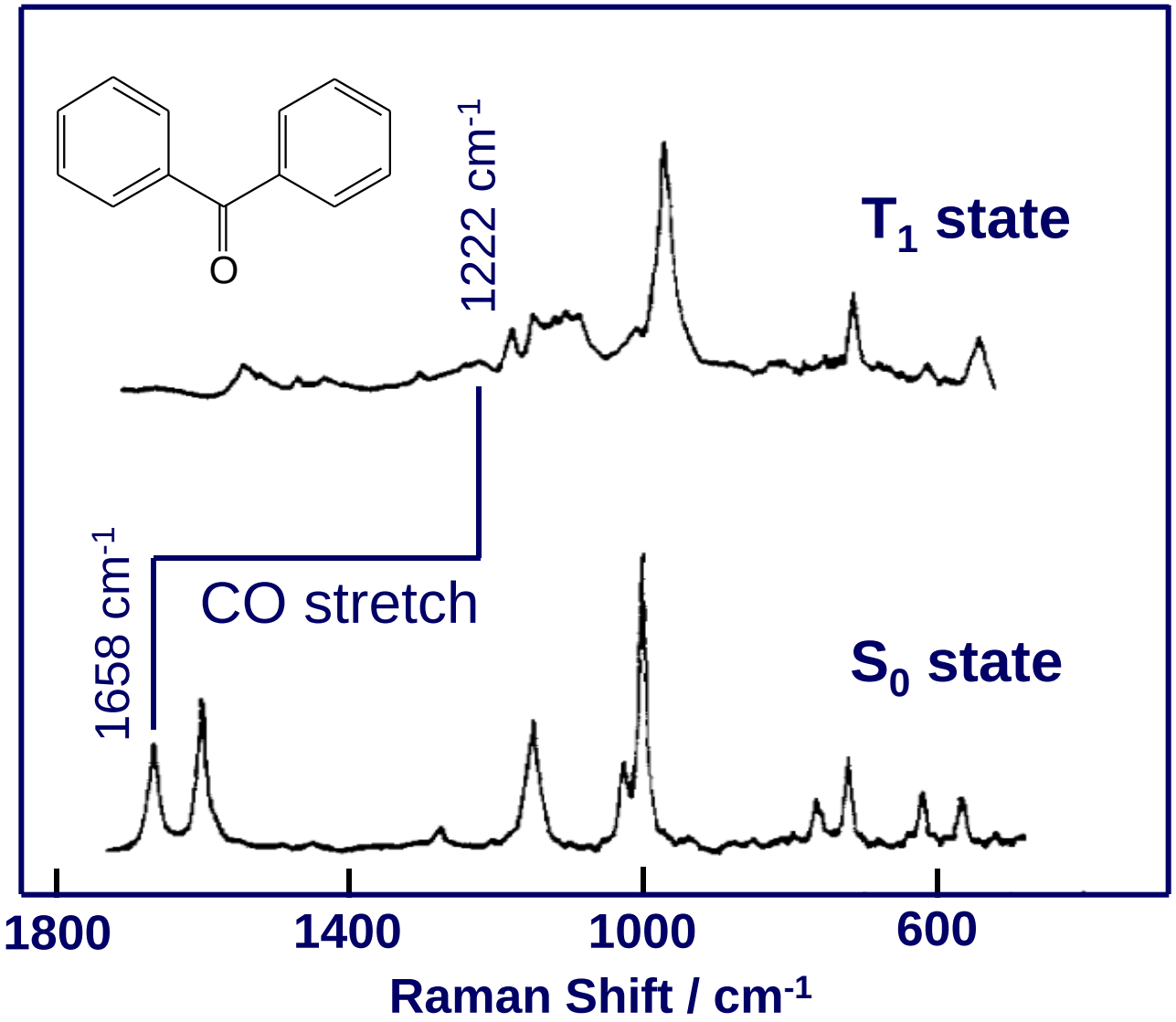
T. Tahara, H. Hamaguchi and M. Tasumi, JPC (1987).

T_1 Raman Spectra of Isotopically Substituted Benzophenones





Raman Spectrum and Structure of T_1 Benzophenone



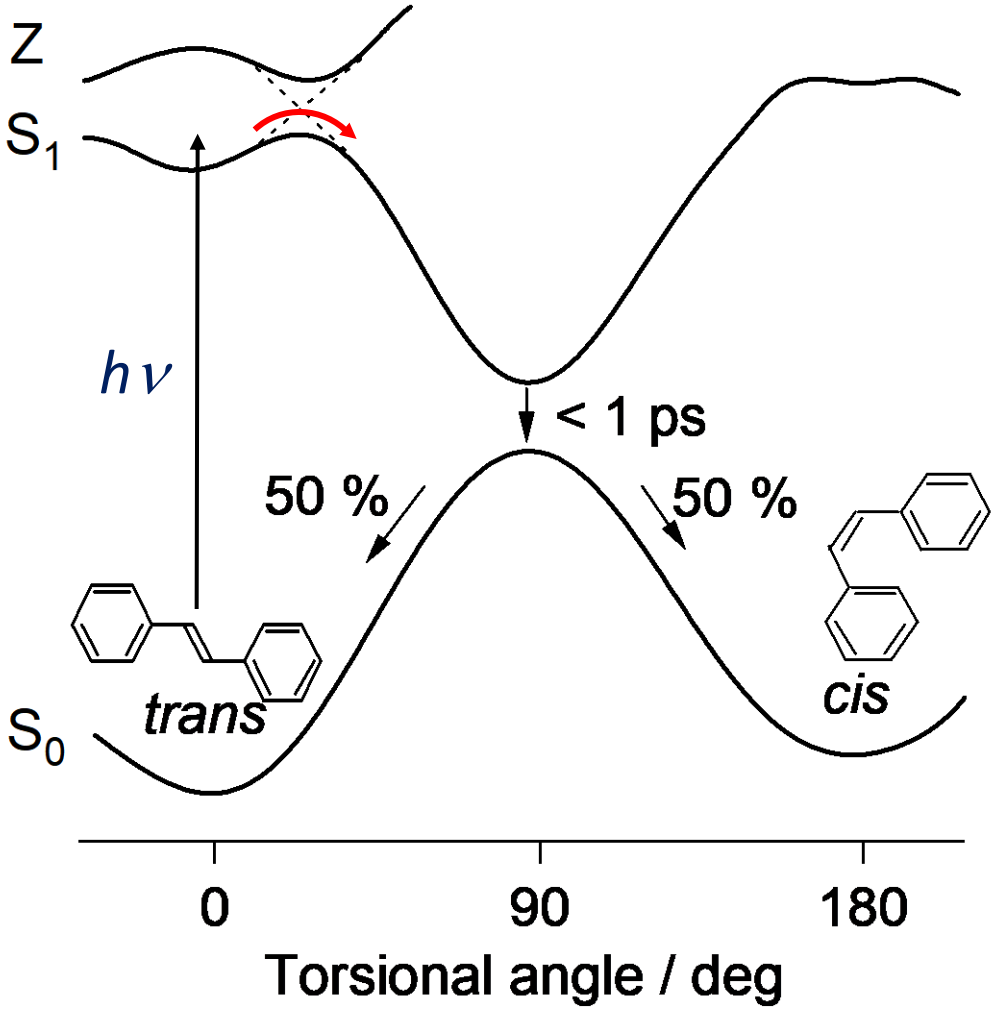
Photoisomerization of *Trans*-Stilbene

Why, when and how rotation occurs in the excited state?

Solvent-dependent isomerization rate

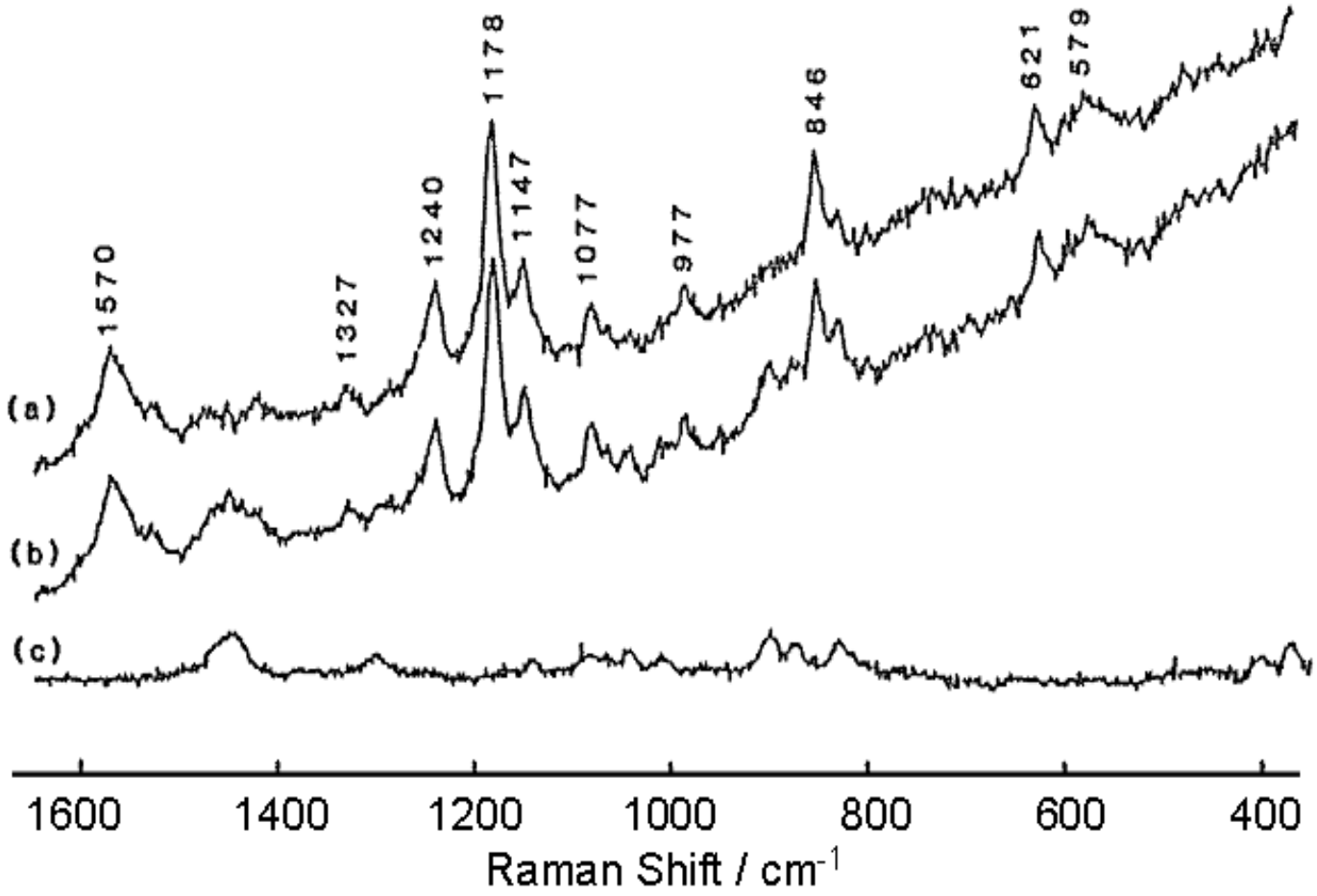
Hexane 70 ps

Dodecane 120 ps

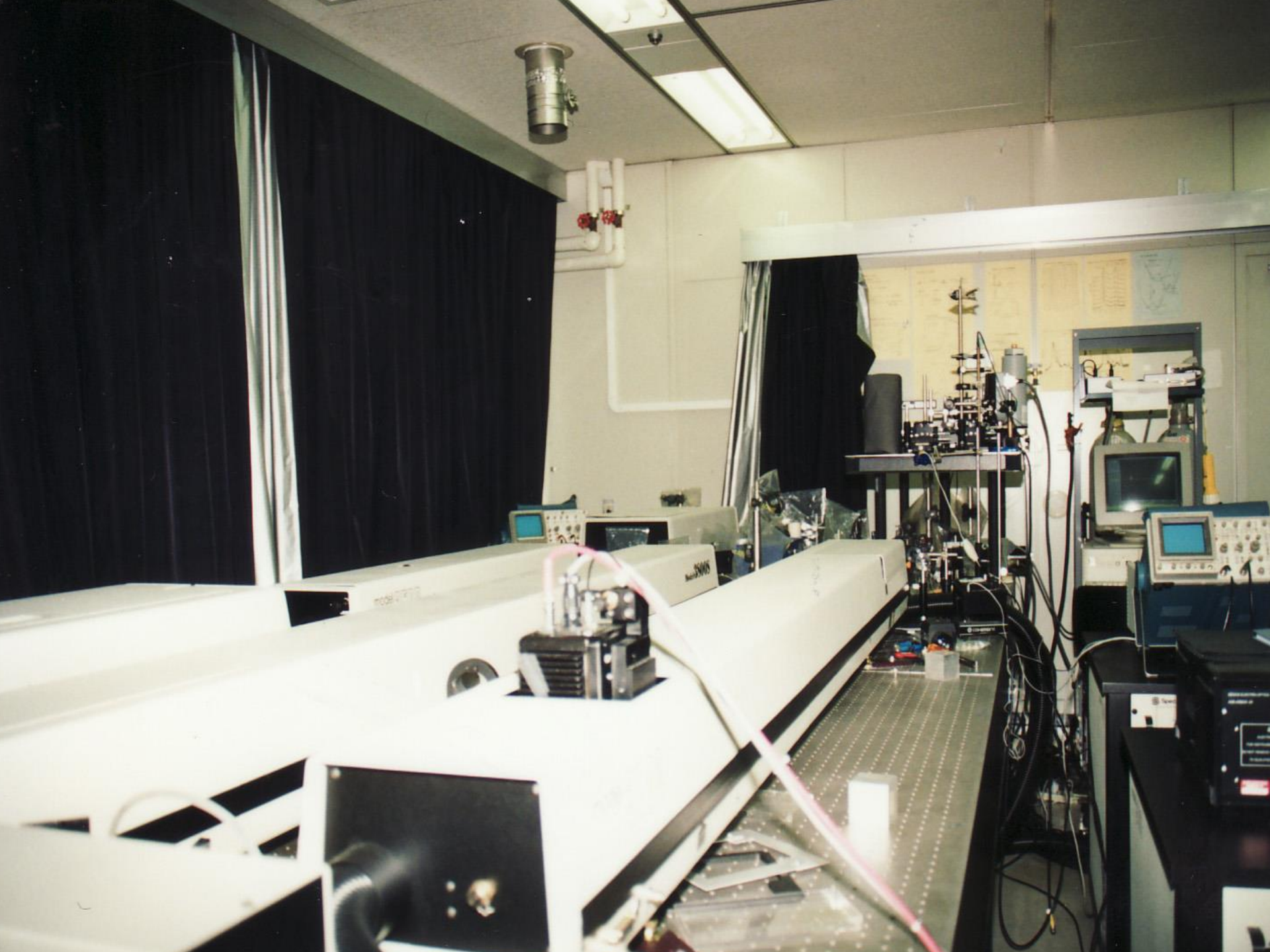


Probe solvent dependent structure and dynamics of S_1 trans-stilbene by time-resolved Raman spectroscopy

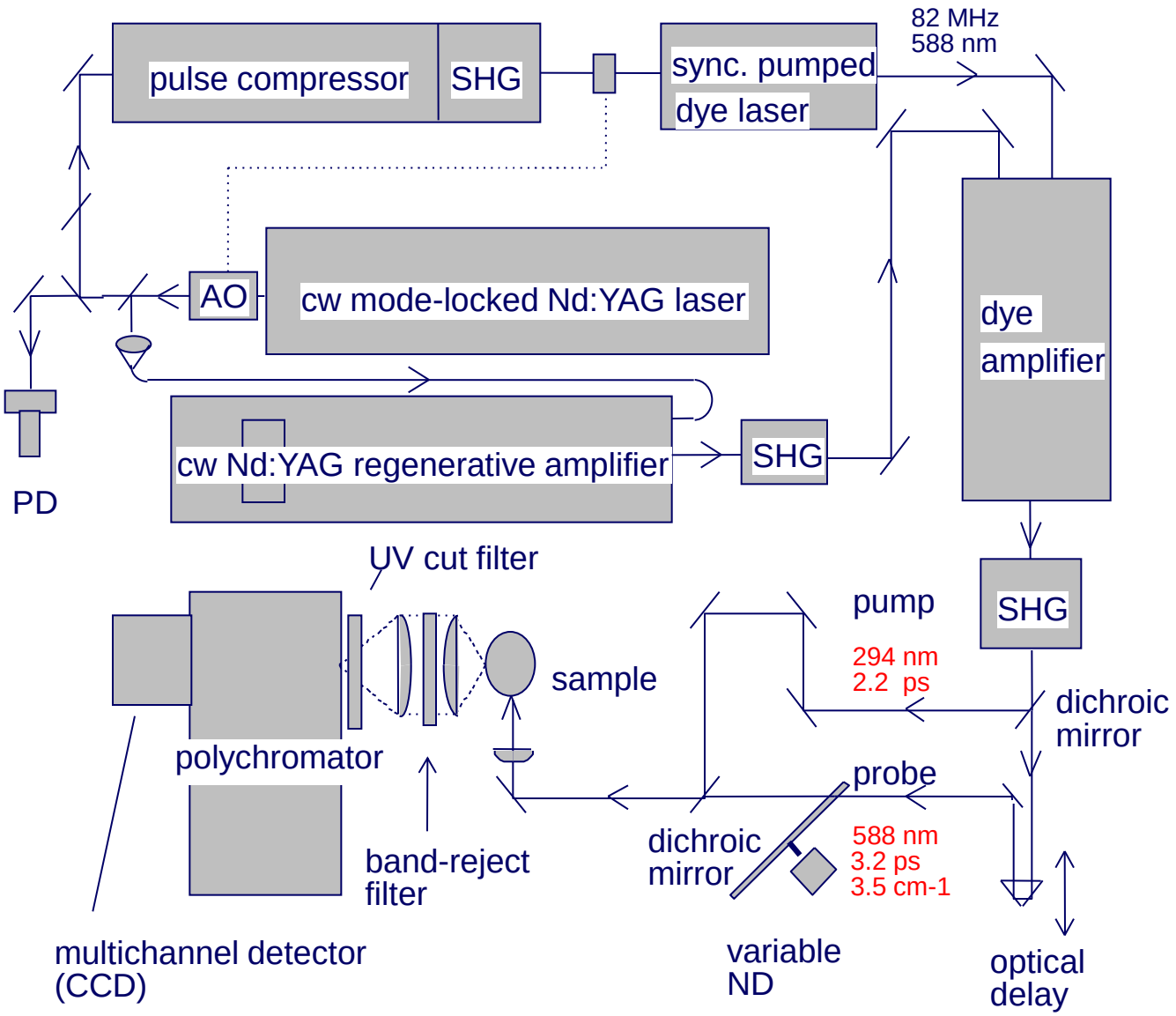
Nanosecond Transient Raman Spectrum of S_1 *Trans*-Stilbene (1983)

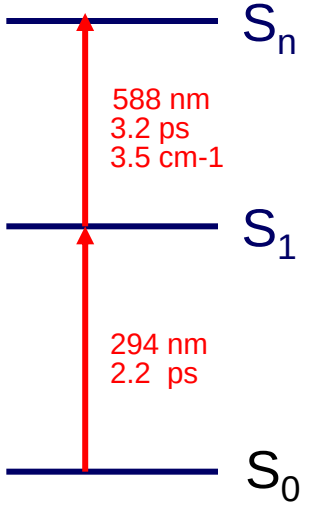


H. Hamaguchi, C. Kato, M. Tasumi, Chem. Phys. Lett., **100**, 3-7 (1983).



Picosecond Transform-limited Time-resolved Raman Spectrometer

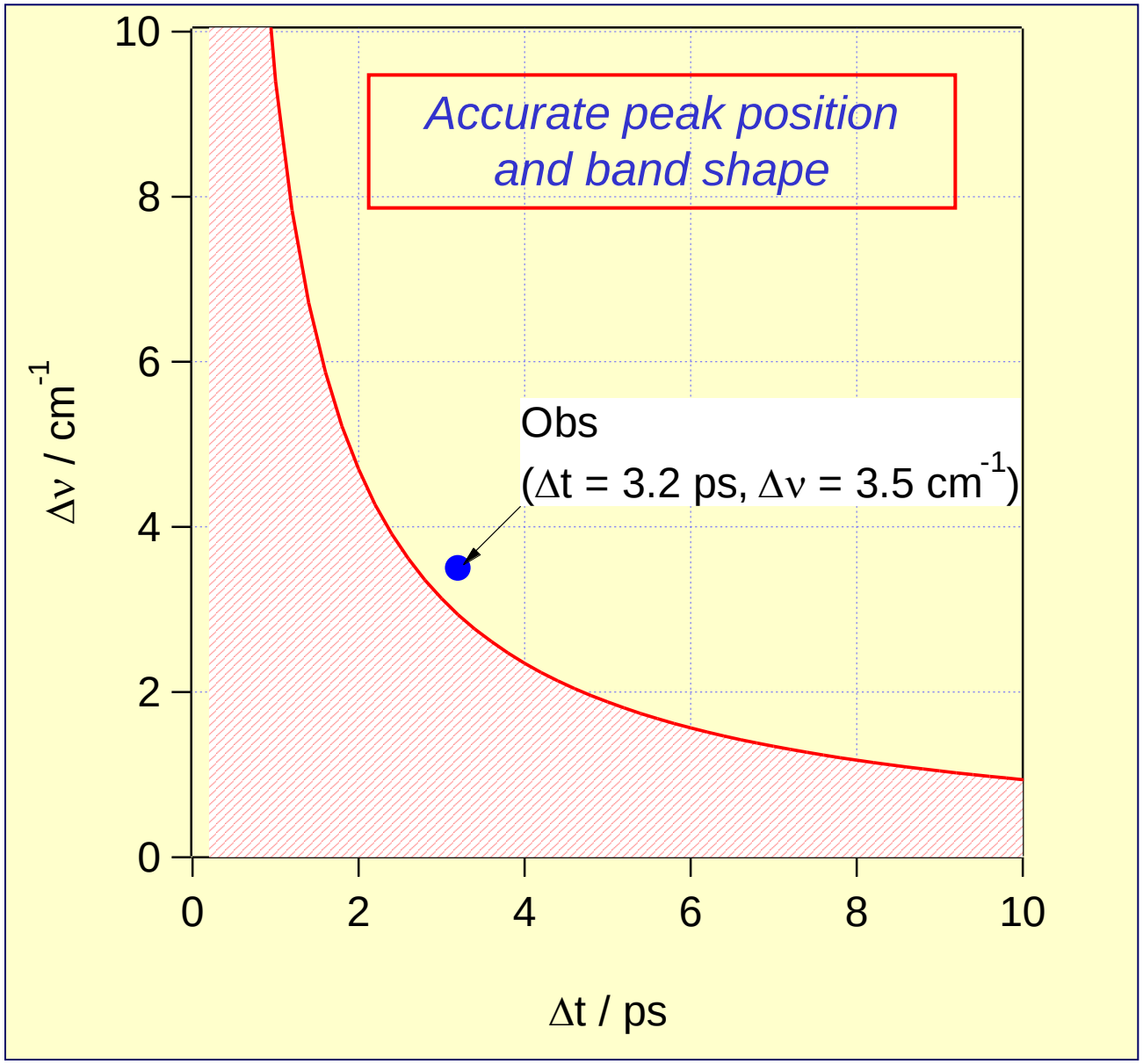




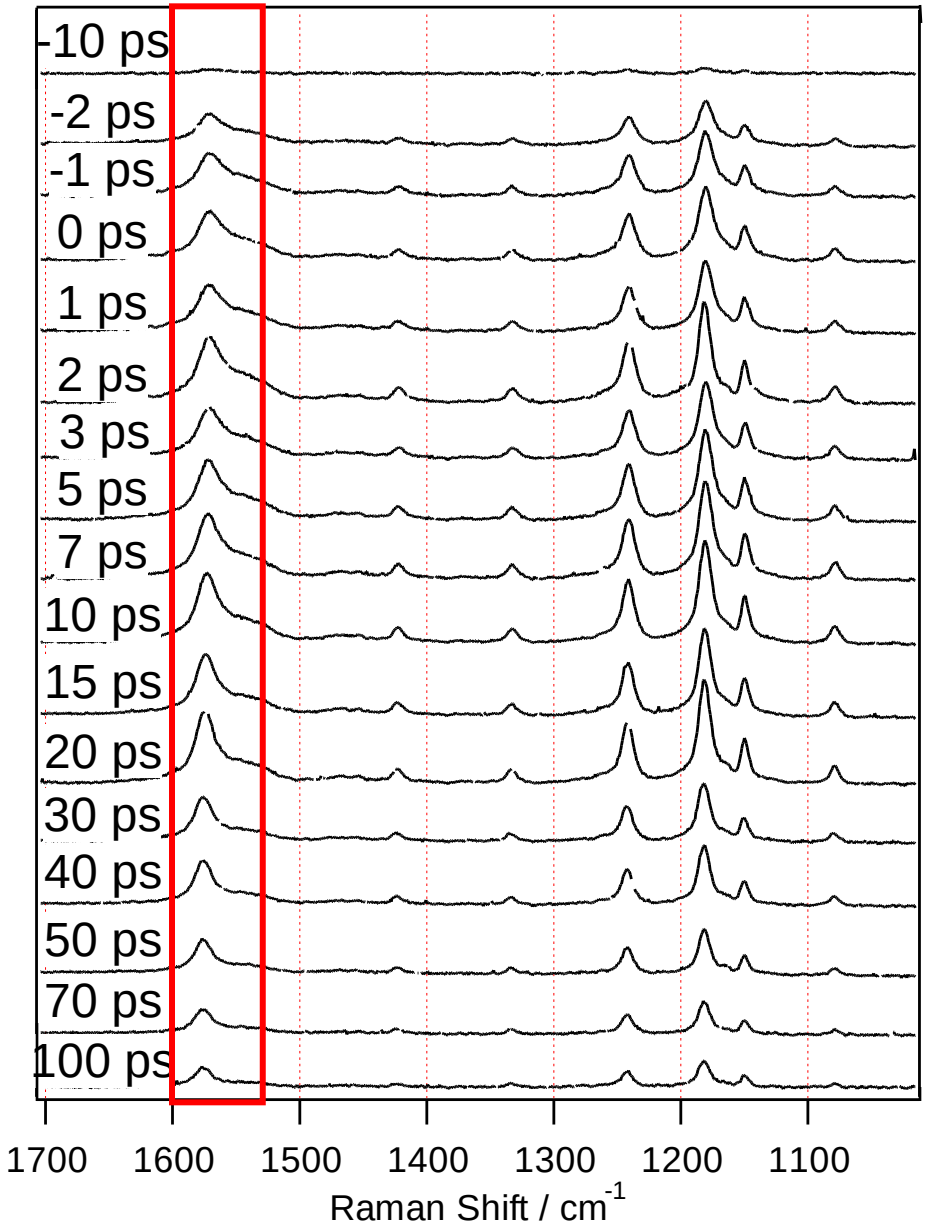
Trans-Stilbene

Iwata, Yamaguchi, and Hamaguchi, *Rev. Sci. Instrum.* **64**, 2140 (1993).

Picosecond Transform-limited Time-resolved Raman Spectroscopy



Picosecond Time-resolved Raman Spectra of S_1 *trans*-Stilbene in $CHCl_3$



Pump 294 nm
Probe 588 nm (0.1 mW)

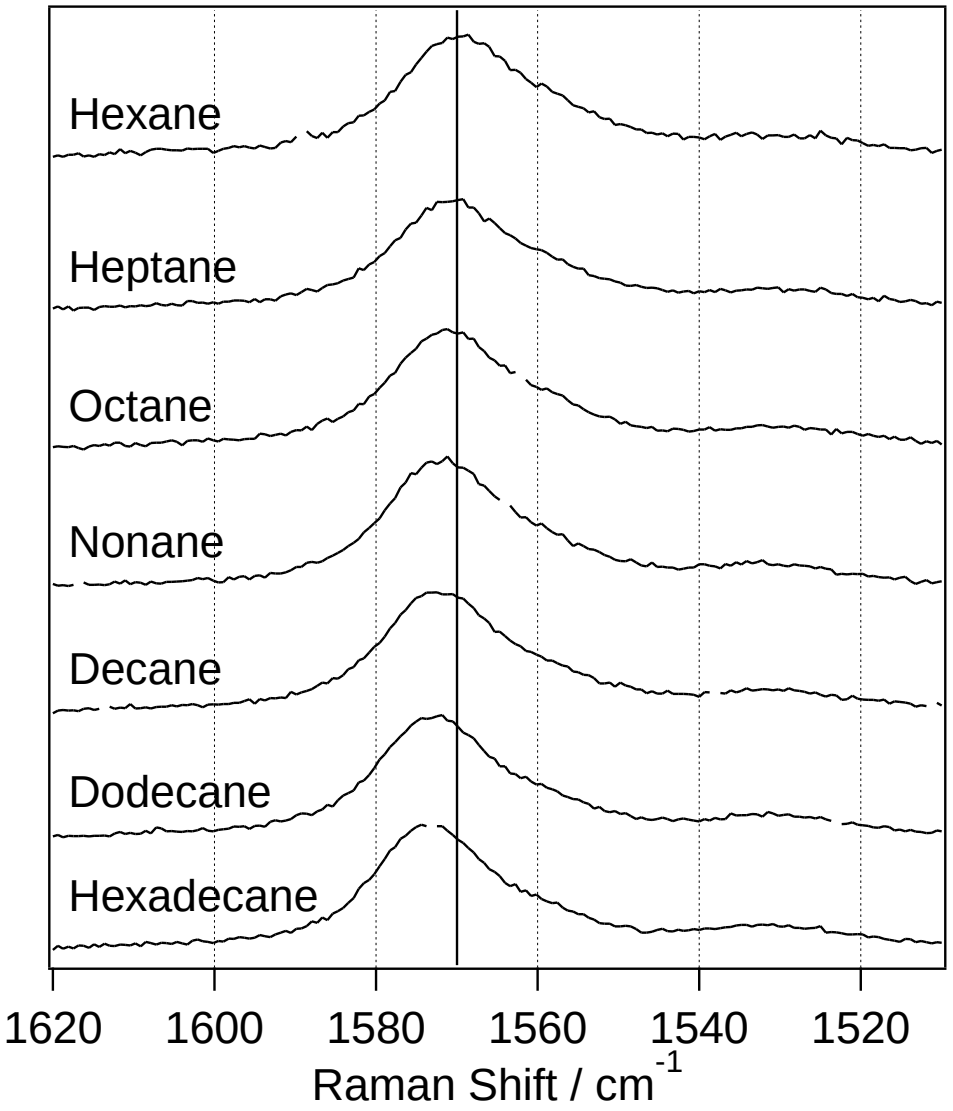
C=C stretch vibration

1560 cm^{-1}: double bond

Why rotation occurs

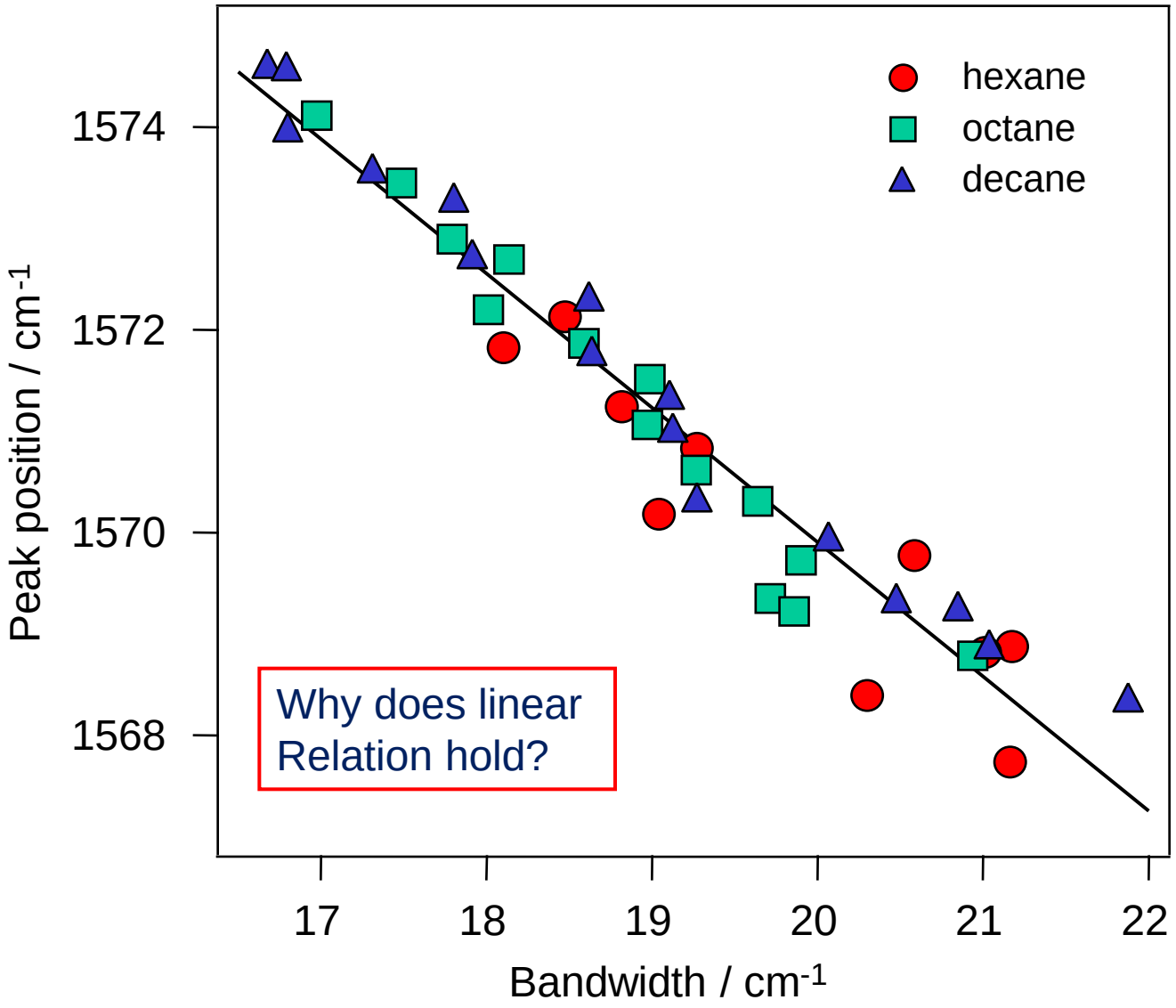
around a double bond ?

The C=C Stretch Raman Band of S_1 *trans*-Stilbene in Alkanes

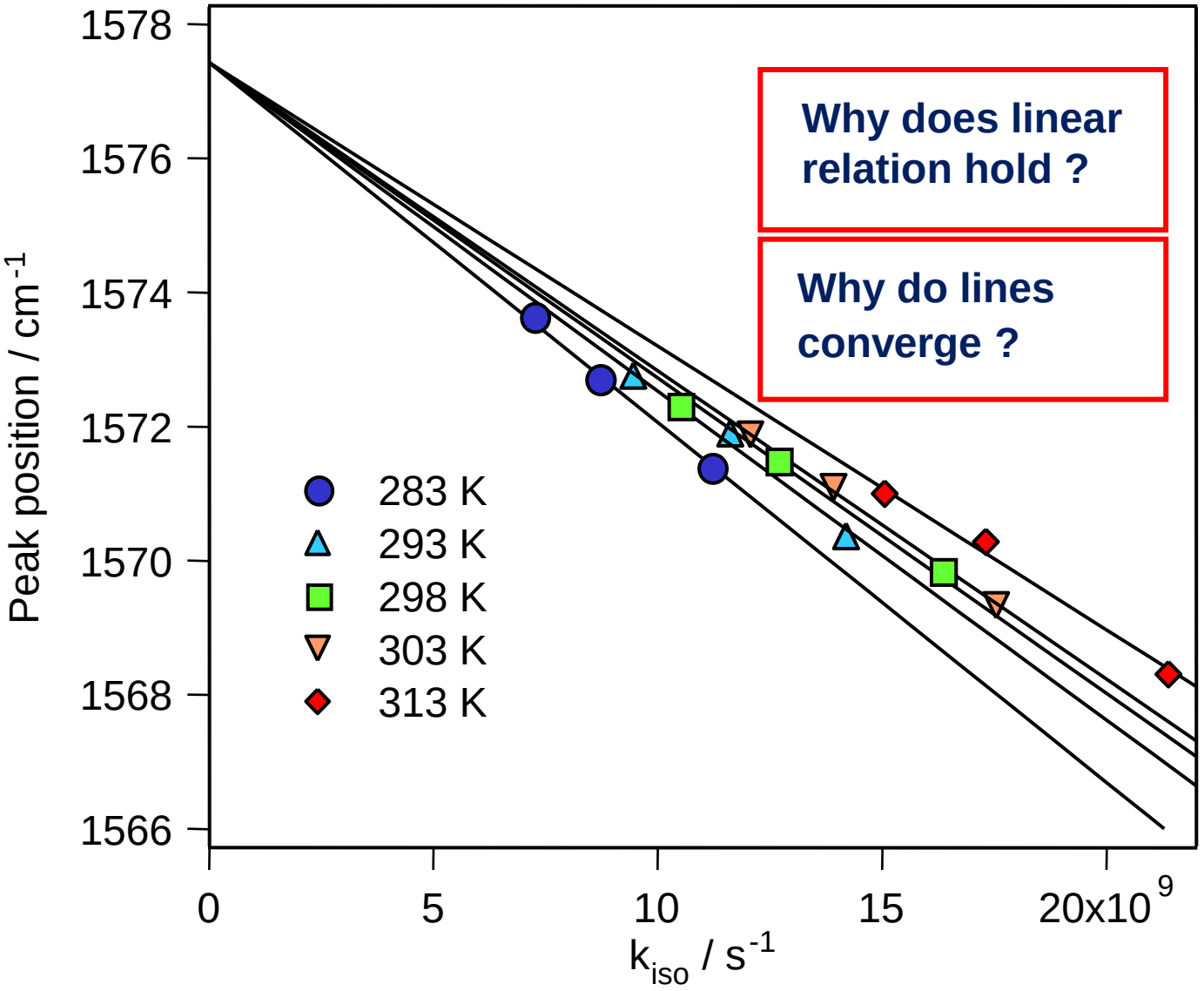


The peak position shifts to higher wavenumbers and the band width decreases on going from hexane to hexadecane. Why?

Peak Position vs Band Width of the C=C Stretch Raman Band of S_1 *trans*-Stilbene In Alakne Solvents at Different Temperatures

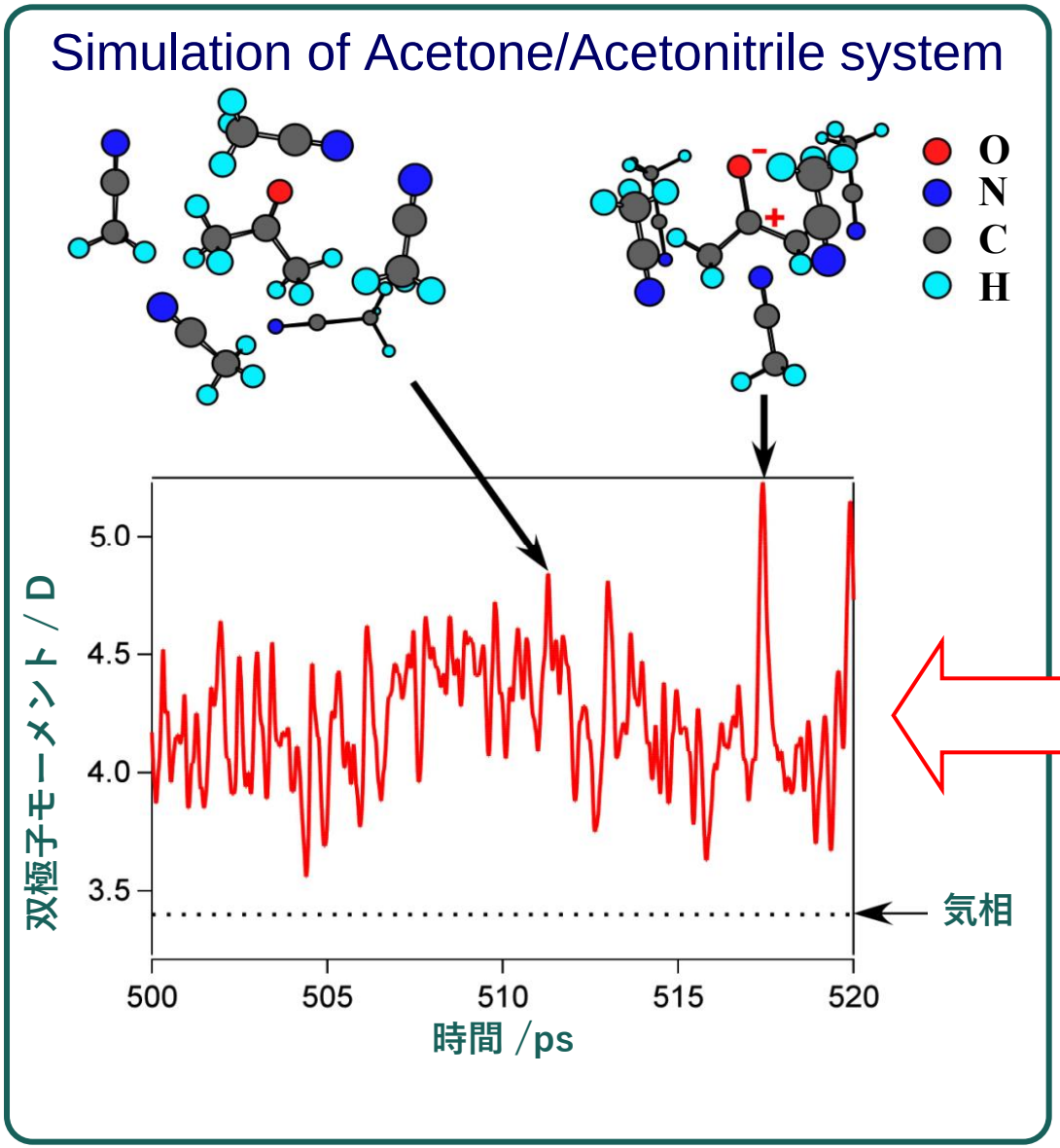


Peak Position of the C=C Stretch Raman Band vs the Isomerization Rate of S1 *trans*-Stilbene



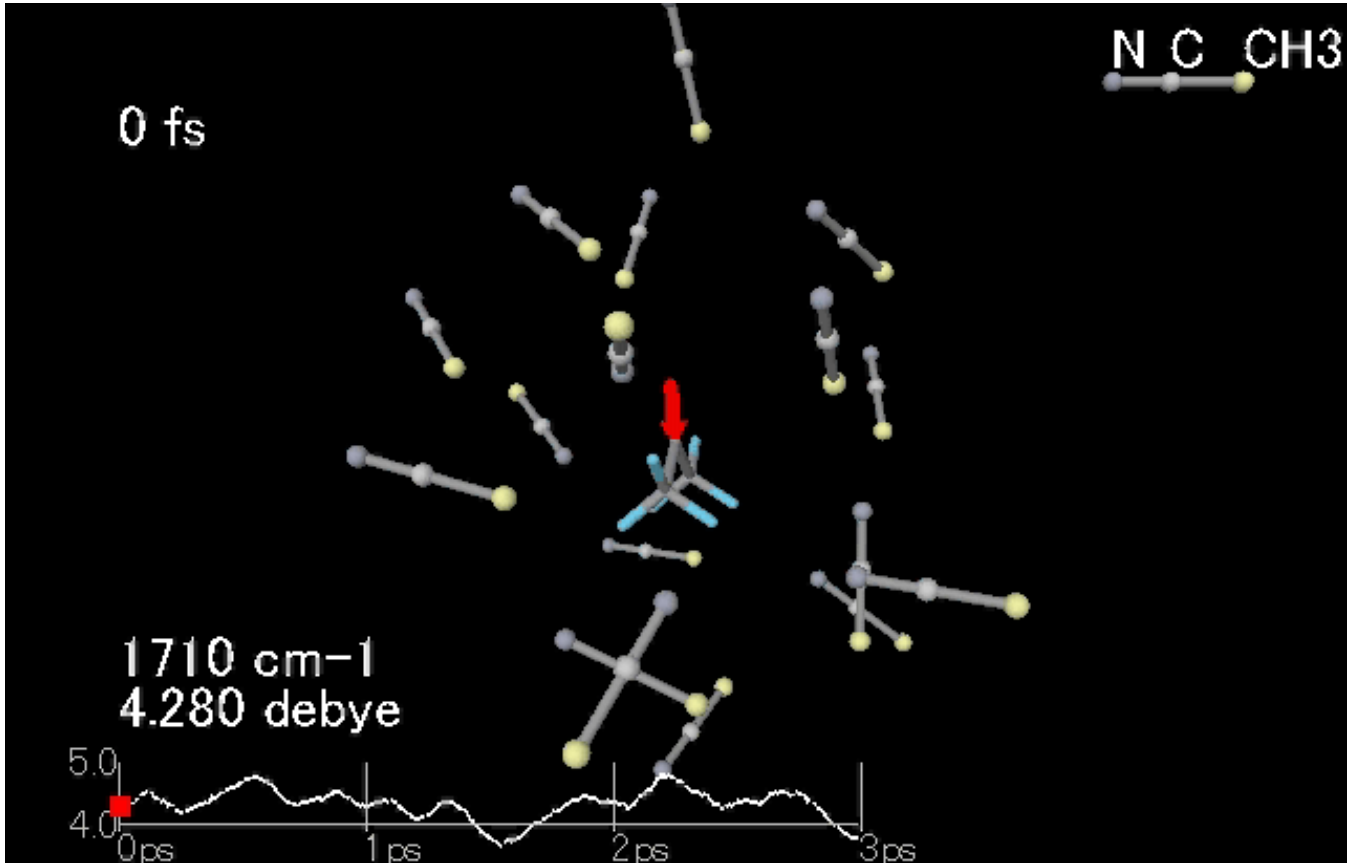
Theory of Vibrational Dephasing and Band Shape

Vibrational frequency is stochastically modulated in solution

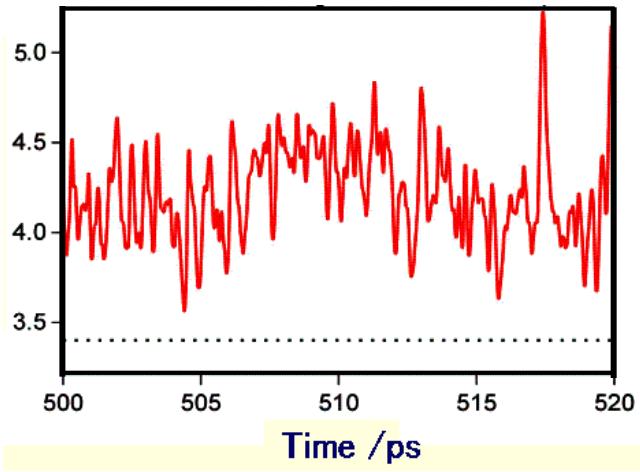


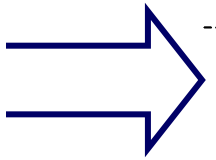
Solvent-induced dynamic polarization

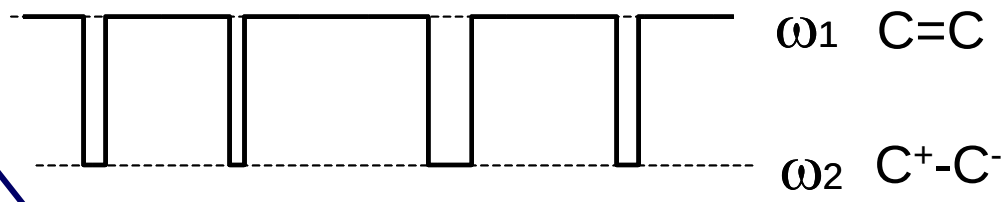
Solvent-induced Dynamic Polarization of Acetone in Acetonitrile



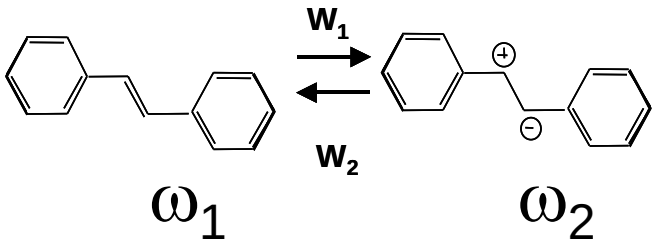
Formulation of Vibrational Band Shapes under Dynamic Polarization

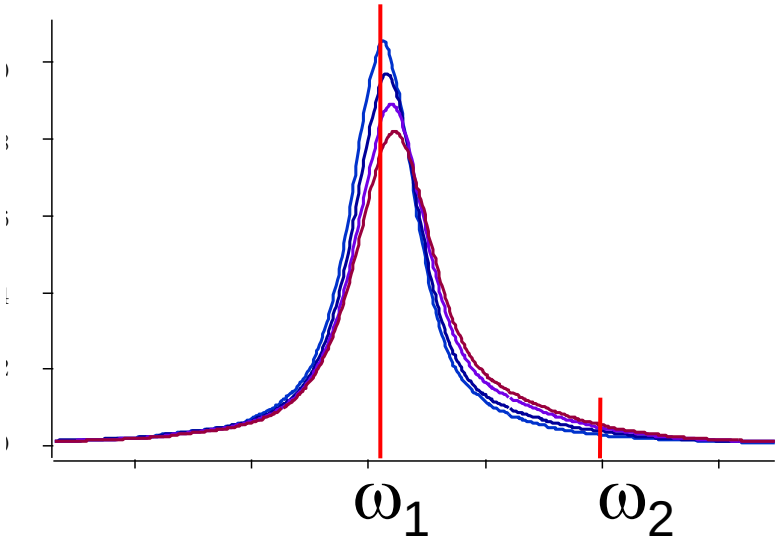






Modeling





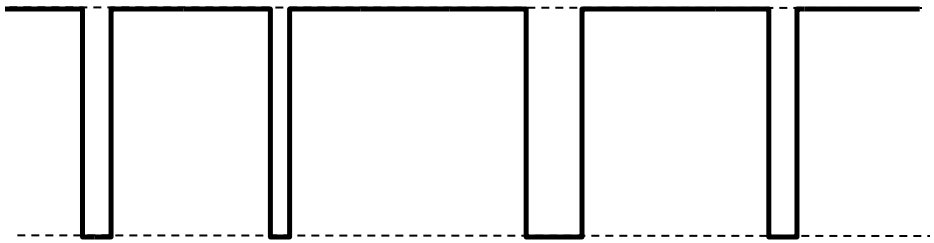
with no exchange — asymmetric exchange limit

- peak position : $\omega_1 \longrightarrow \omega_1 + \Delta\Omega \quad ; \quad \Delta\Omega = W_1\tau/\left(1+\tau^2\right)$
- band width : $\Gamma_0 \longrightarrow \Gamma_0 + \Delta\Gamma \quad ; \quad \Delta\Gamma = W_1\tau^2/\left(1+\tau^2\right)$

$\tau = (\omega_1-\omega_2)/W_2$

Extension of the Two Frequency Exchange Model

(a) Two Frequency Exchange Model



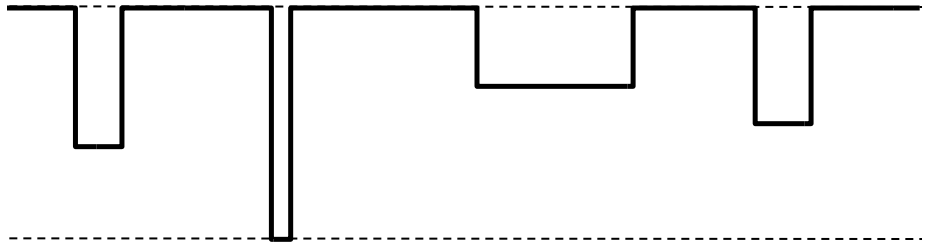
Hamaguchi *Mol. Phys*.**89**, 463 (1997).

$$\Delta\Omega = W_1\tau/(1+\tau^2)$$

$$\Delta\Gamma = W_1\tau^2/(1+\tau^2)$$

$$\Delta\Gamma / \Delta\Omega = \tau$$

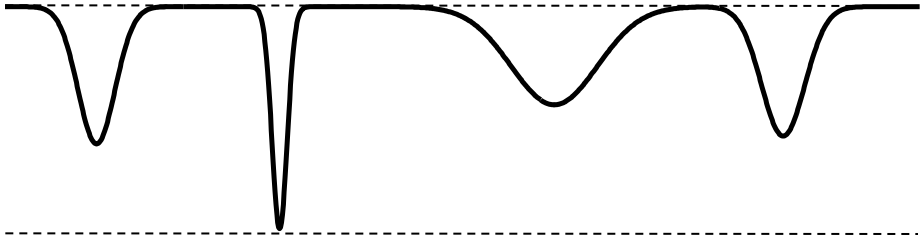
(b) Many Frequency Exchange Model



$$\Delta\Omega = W_1\sum_{\kappa=2}^{n}(W_{1\kappa}/W_1)\tau_\kappa/(1+\tau_\kappa{}^2)$$

$$\Delta\Gamma = W_1\sum_{\kappa=2}^{n}(W_{1\kappa}/W_1)\tau_\kappa{}^2/(1+\tau_\kappa{}^2)$$

(c) Continuous Frequency Modulation Model

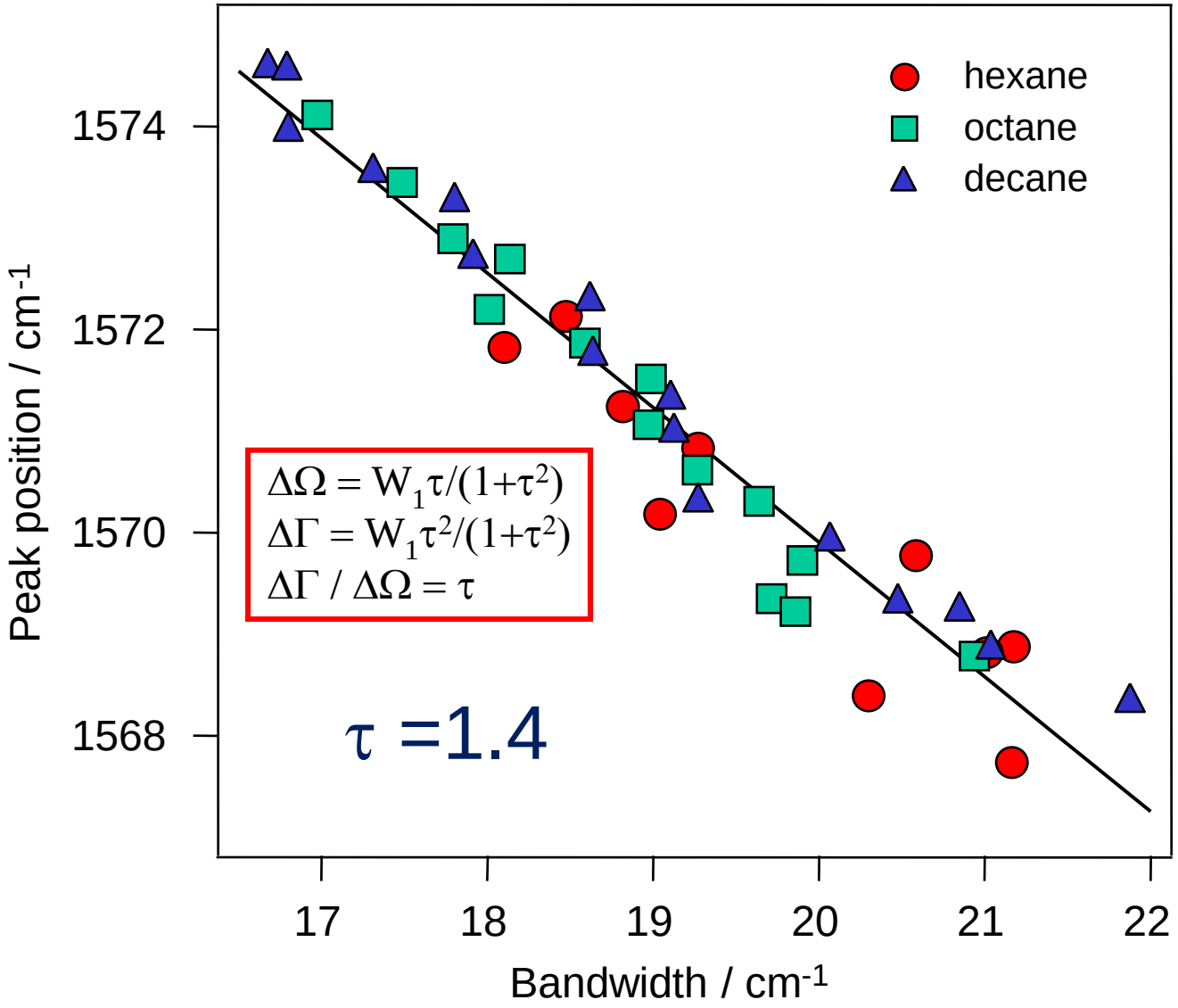


$$\Delta\Omega = \frac{W_1\int_{-\infty}^{0} G(\tau)\tau/(1+\tau^2)d\tau}{\int_{-\infty}^{0} G(\tau)d\tau}$$

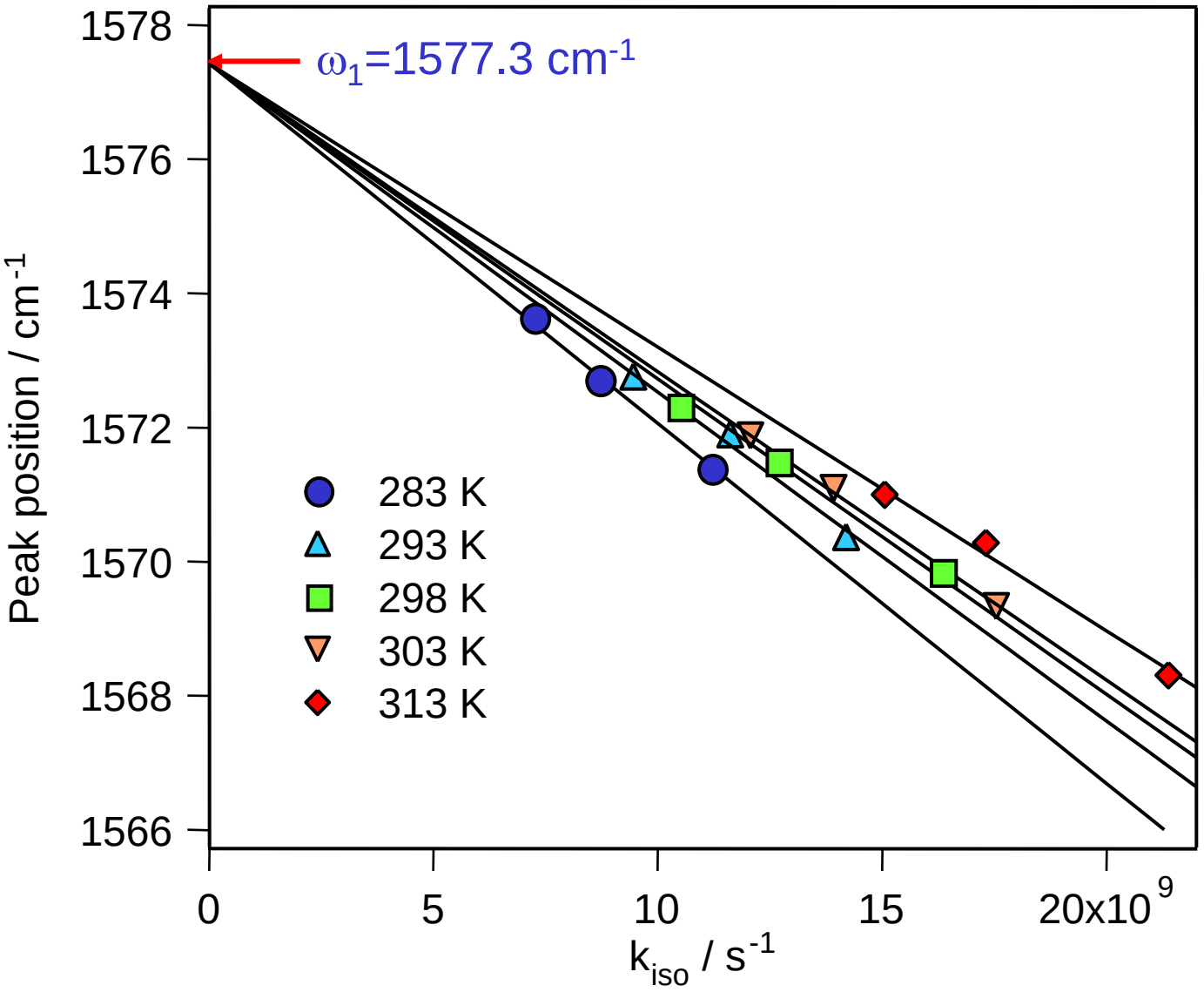
$$\Delta\Gamma = \frac{W_1\int_{-\infty}^{0} G(\tau)\tau^2/(1+\tau^2)d\tau}{\int_{-\infty}^{0} G(\tau)d\tau}$$

$$\Delta\Gamma / \Delta\Omega = \tau_{1/2}\ ;\ G(\tau)=\exp(-\ln 2\tau^2/\tau_{1/2}{}^2)$$

Peak Position vs Band Width of the C=C Stretch Raman Band of S_1 *trans*-Stilbene In Alakne Solvents at Different Temperatures



Peak Position of the C=C Stretch Raman Band vs the Isomerization Rate of S_1 *trans*-Stilbene



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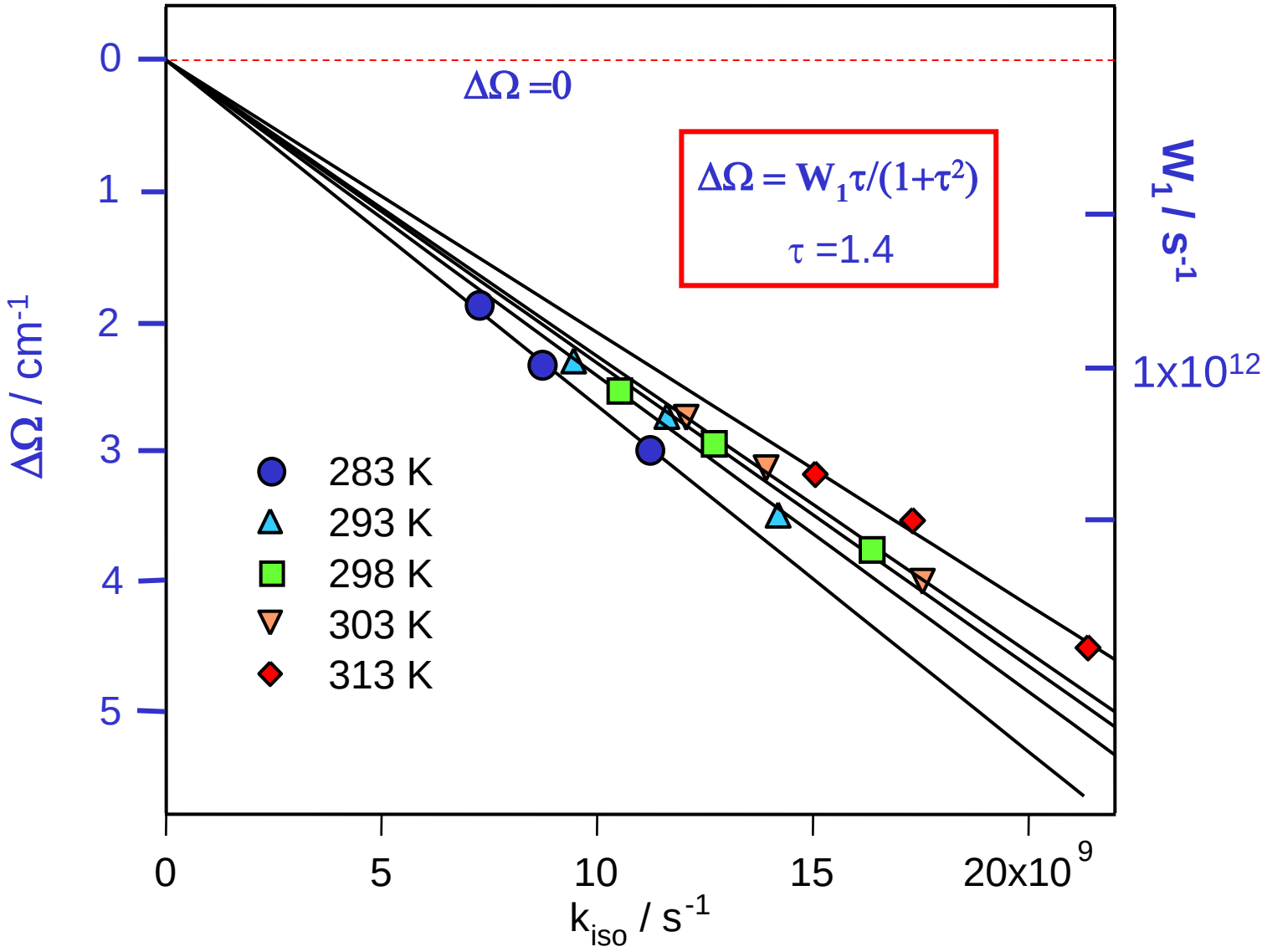

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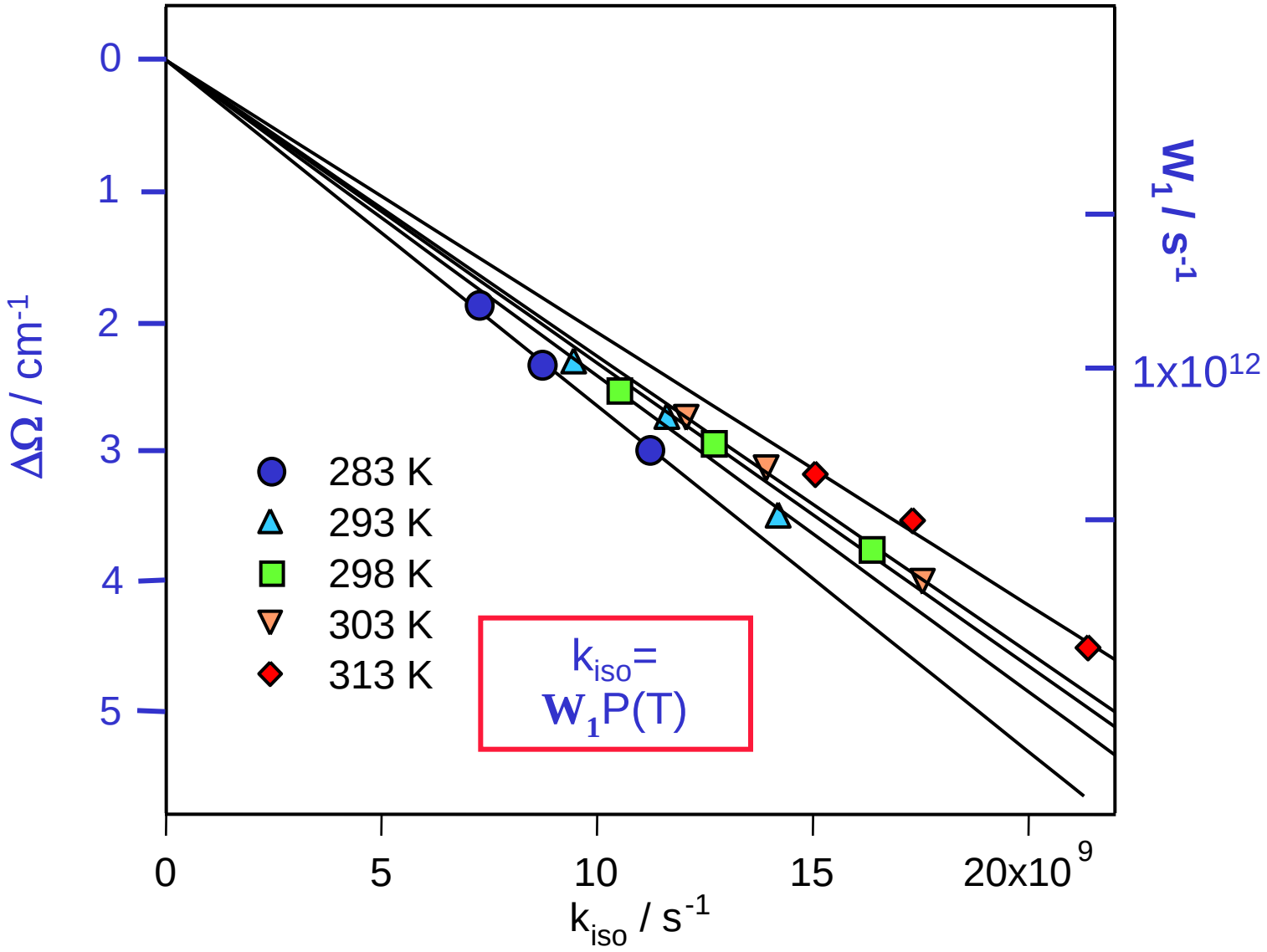
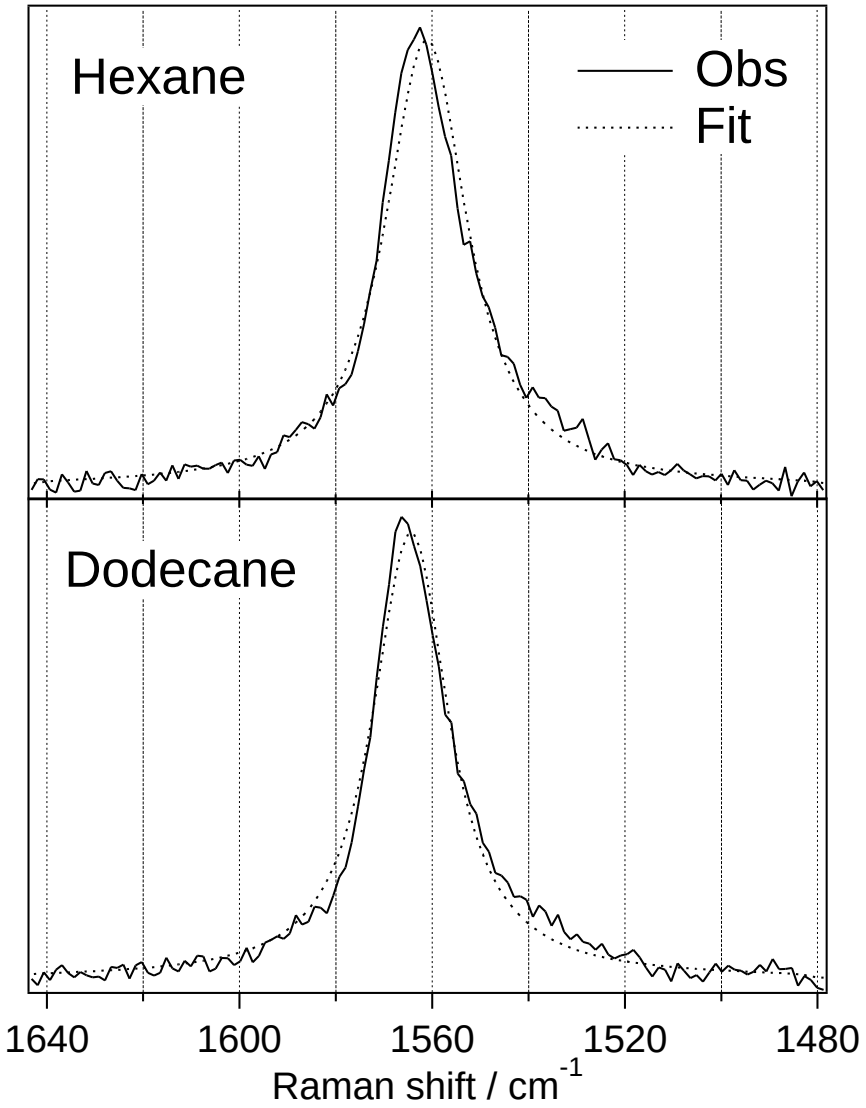
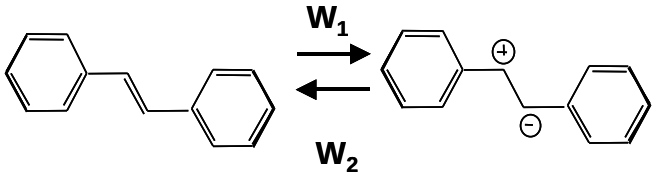


Fitting of the C=C Stretch Raman Band of S1 *trans*-Stilbene by the Two Frequency Exchange Model



W_1=2.7x10^{12} sec^{-1} (370 (fs)$^{-1}$)

$$\Delta\Omega = W_1\tau/(1+\tau^2)$$



W_1=1.5x10^{12} sec^{-1} (670 (fs)$^{-1}$)

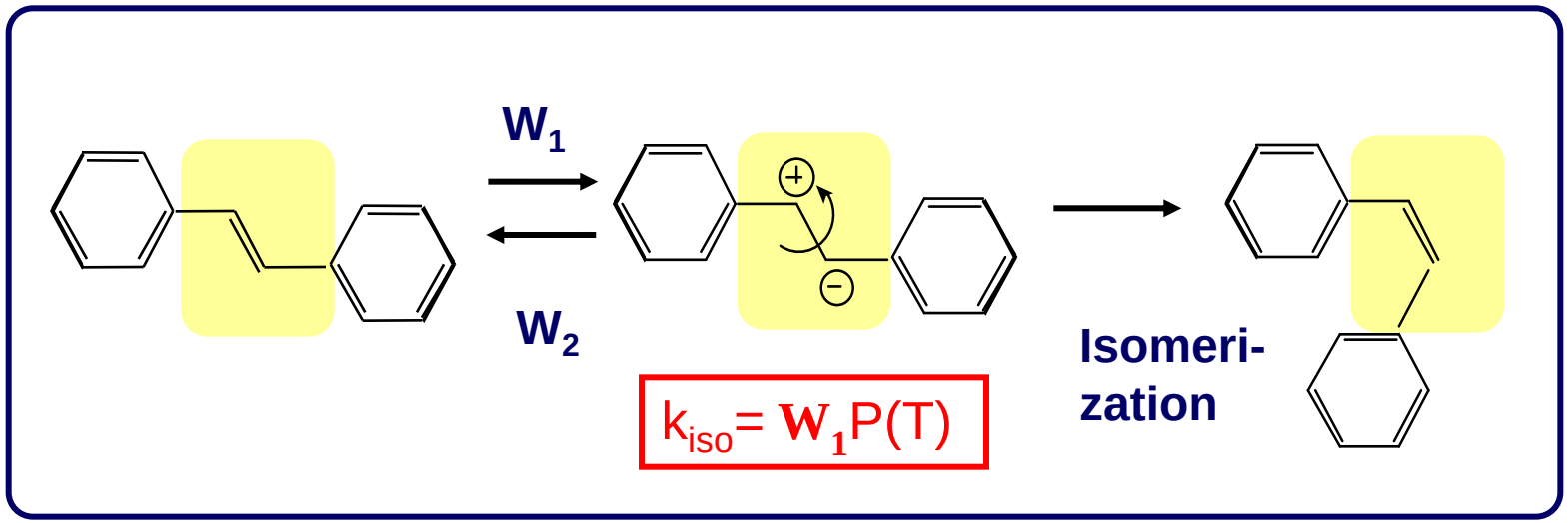
isomerization rate
Hexane 70 ps
Dodecane 120 ps

Dynamic Polarization Model of Isomerization

Hamaguchi, Iwata, *CPL* **208**, 465 (1993).

Deckert, Iwata, Hamaguchi, *J. Photochem. Photobiol*. **102**, 35 (1996).

Iwata, Ozawa, Hamaguchi, *JCP* **106**, 3614 (2002).



$k_{iso}=A\exp(-\Delta E/RT)$: Arrhenius formula

ΔE=3.5 kcal mol^{-1} (fluorecsence lifetime)

$k_{iso}=W_1P(T)$: Dynamic Polarization Model

ΔE=3.5~3.7 kcal mol^{-1} (Raman band shape)

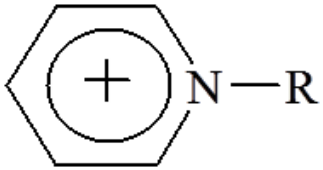
A new view on isomerization has come out of picosecond Raman spectroscopy !

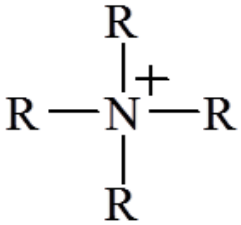
What Are Ionic Liquids?

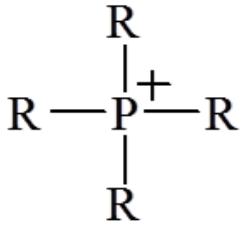
Liquids that are composed solely of ions

Ionic Liquids

Why are they liquids?
Green Solvents?
Liquid Structures?

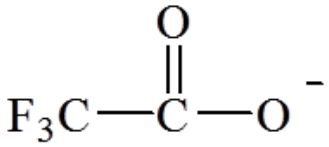


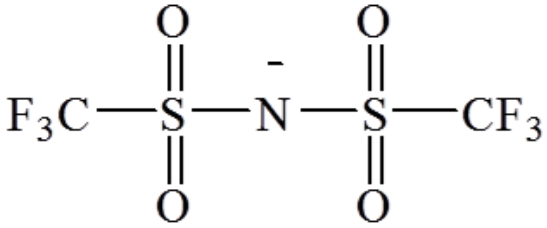




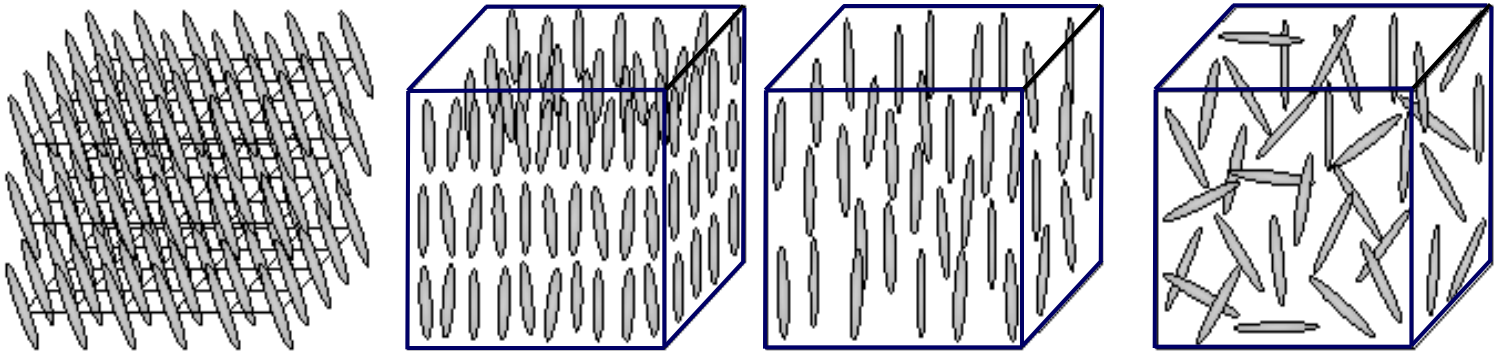
Cl^- Br^- I^-

BF_4^- PF_6^- $FeCl_4^-$





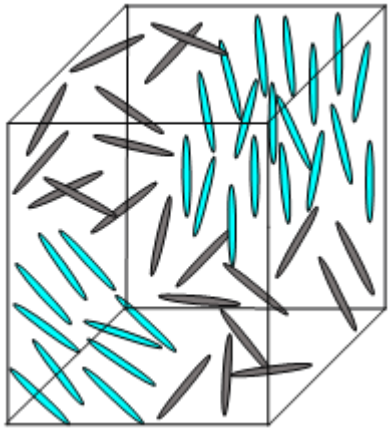
Are Ionic Liquids Really Liquids in the Conventional Sense?



Crystal Liquid Crystal Liquid

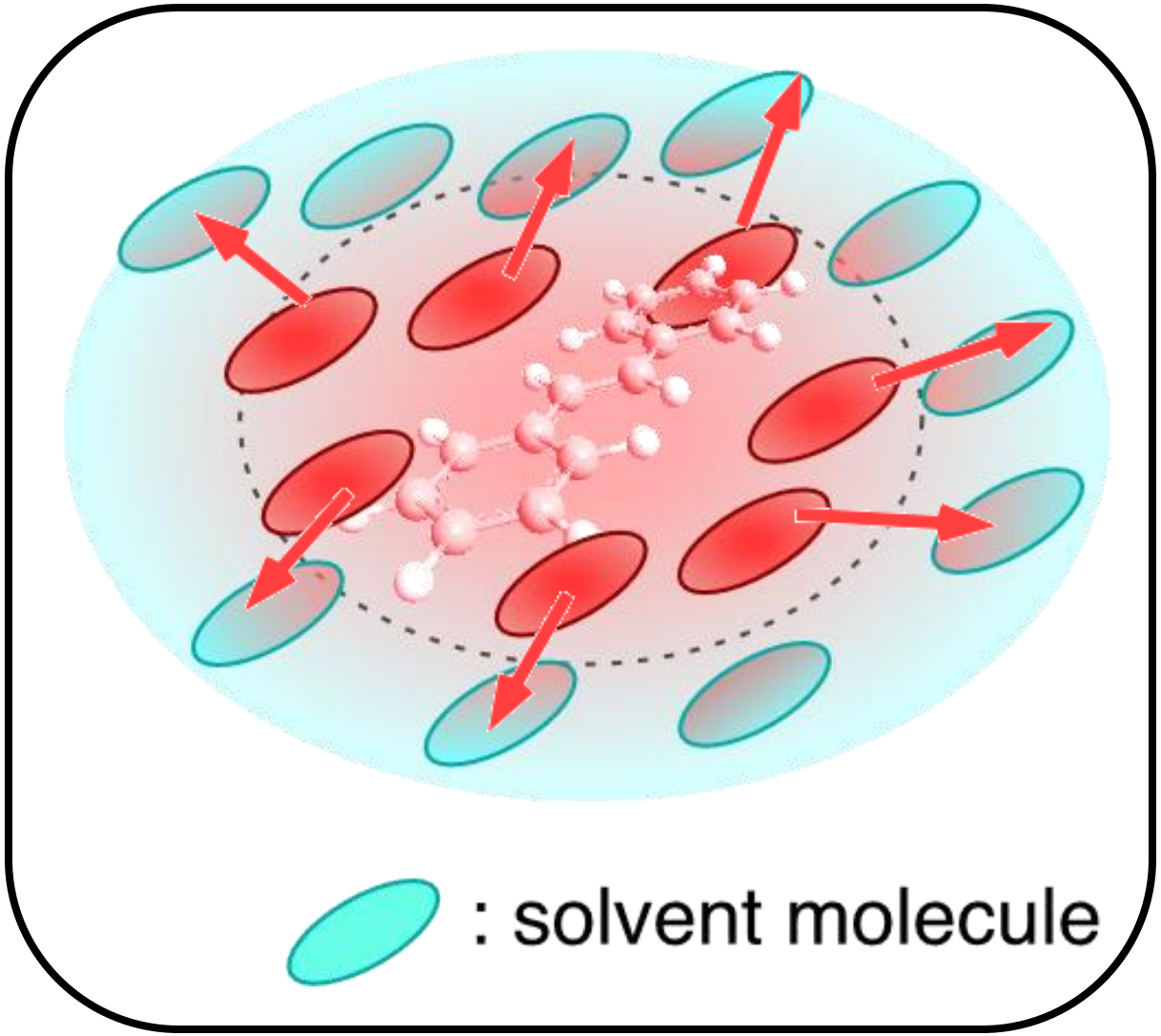
Known condensed phases of matter

Ionic Liquid ?



Transparent but heterogeneous fluid with well-defined local structures ?

Picosecond Energy Dissipation Dynamics of Photoexcited S_1 *Trans*-stilbene



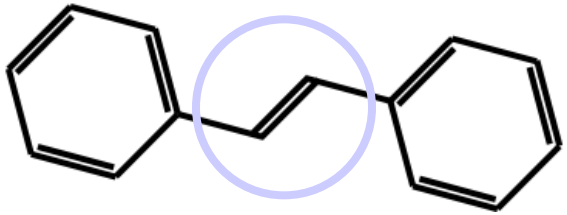
Picosecond Raman Thermometer with S_1 *trans*-stilbene

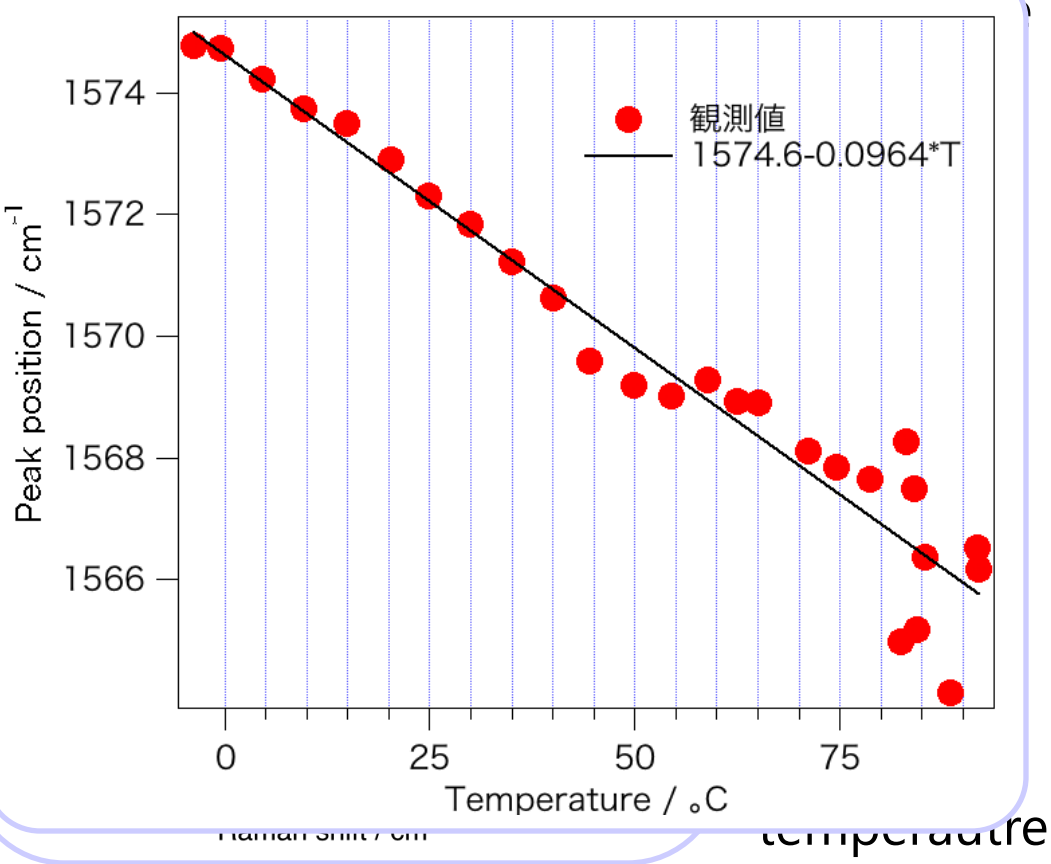
Transient Raman spectra

S_1 *trans*-stilbene at 50 ps

C=C str.

pump 294 nm probe 588 nm





Peak position

Temperature

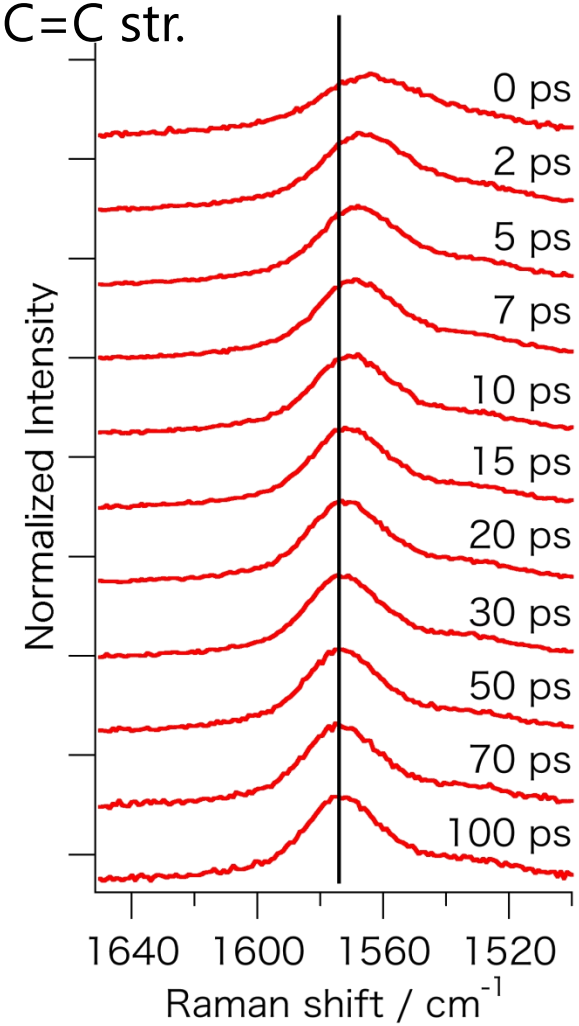
Raman thermometer

K. Iwata and H. Hamaguchi, *J. Phys. Chem. A*, **101**, 632 (1997)

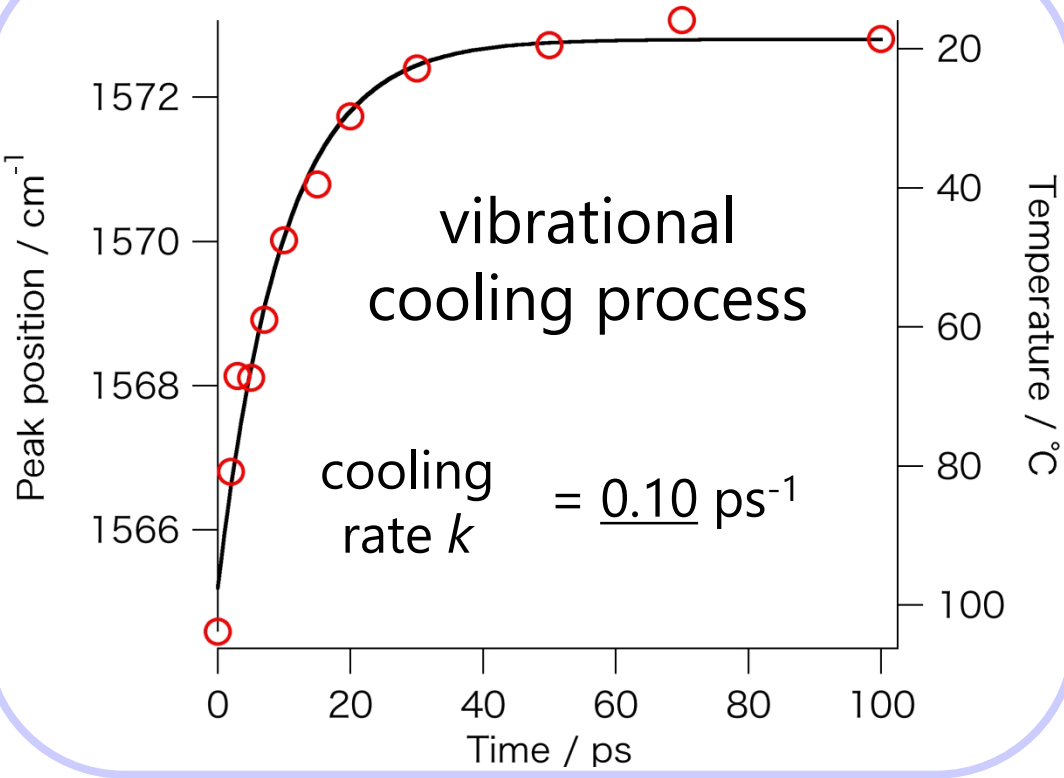
Vibrational Cooling Process of S_1 *Trans*-stilbene in Decane

Time-resolved Raman spectra

C=C str.

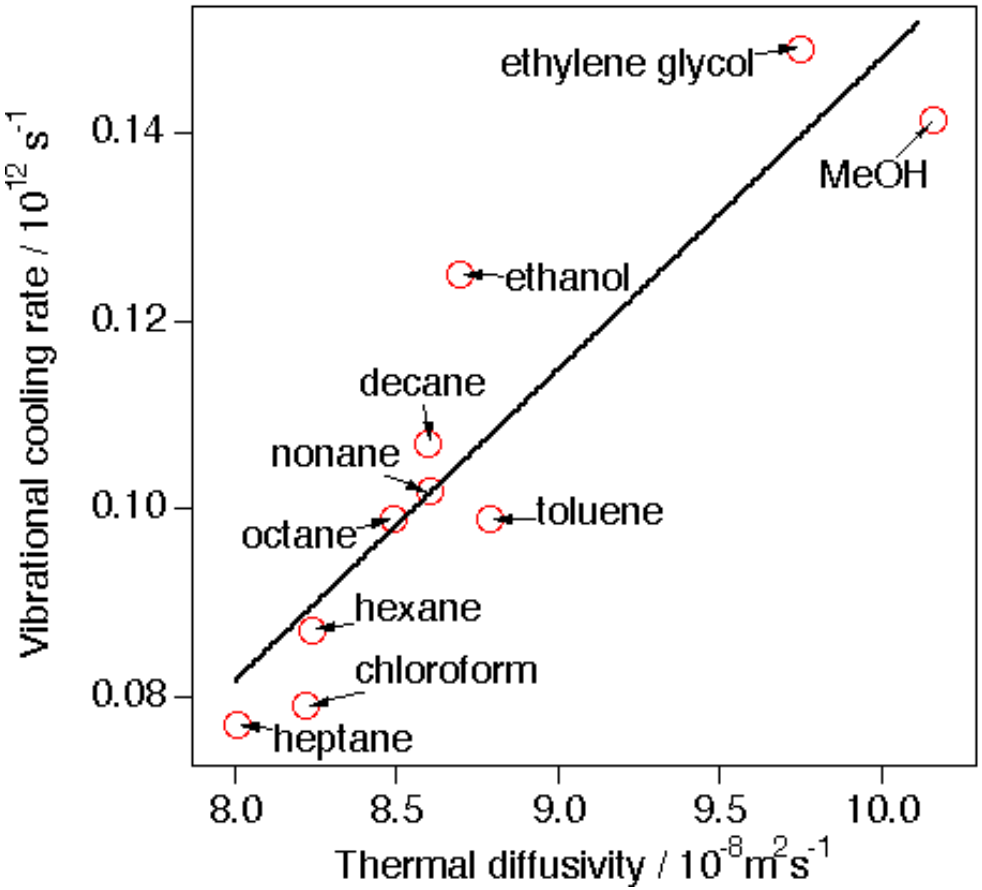


Peak shift to higher wavenumber → Cooling process



pump 296 nm probe 592 nm

Correlation between cooling rate and thermal diffusivity

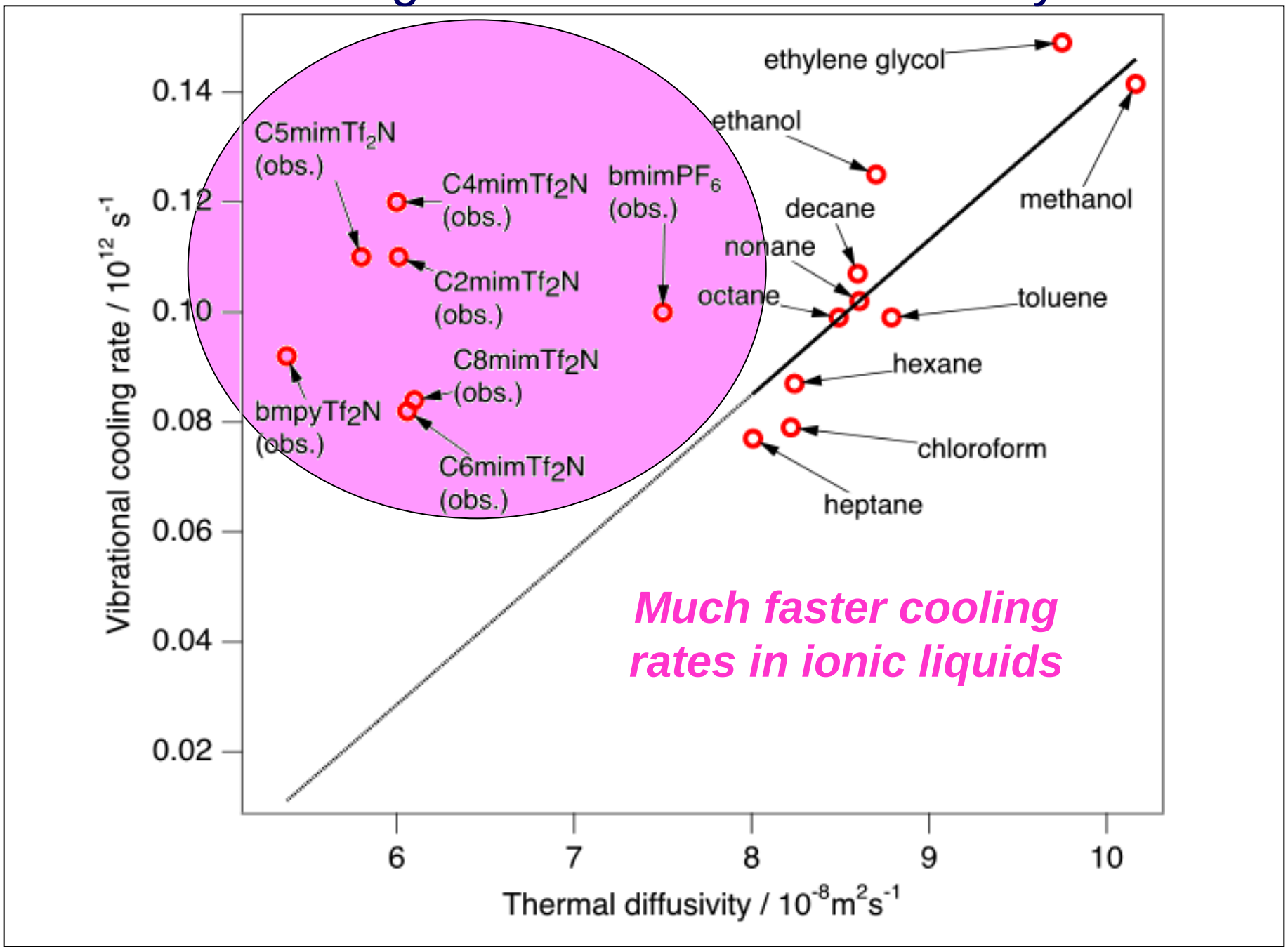


Cooling rate
(Ultrafast dynamics)

Thermal diffusivity
(Bulk property)

K. Iwata and H. Hamaguchi, *J. Phys. Chem. A*, **101**, 632 (1997).

Cooling Rate vs Thermal Diffusivity



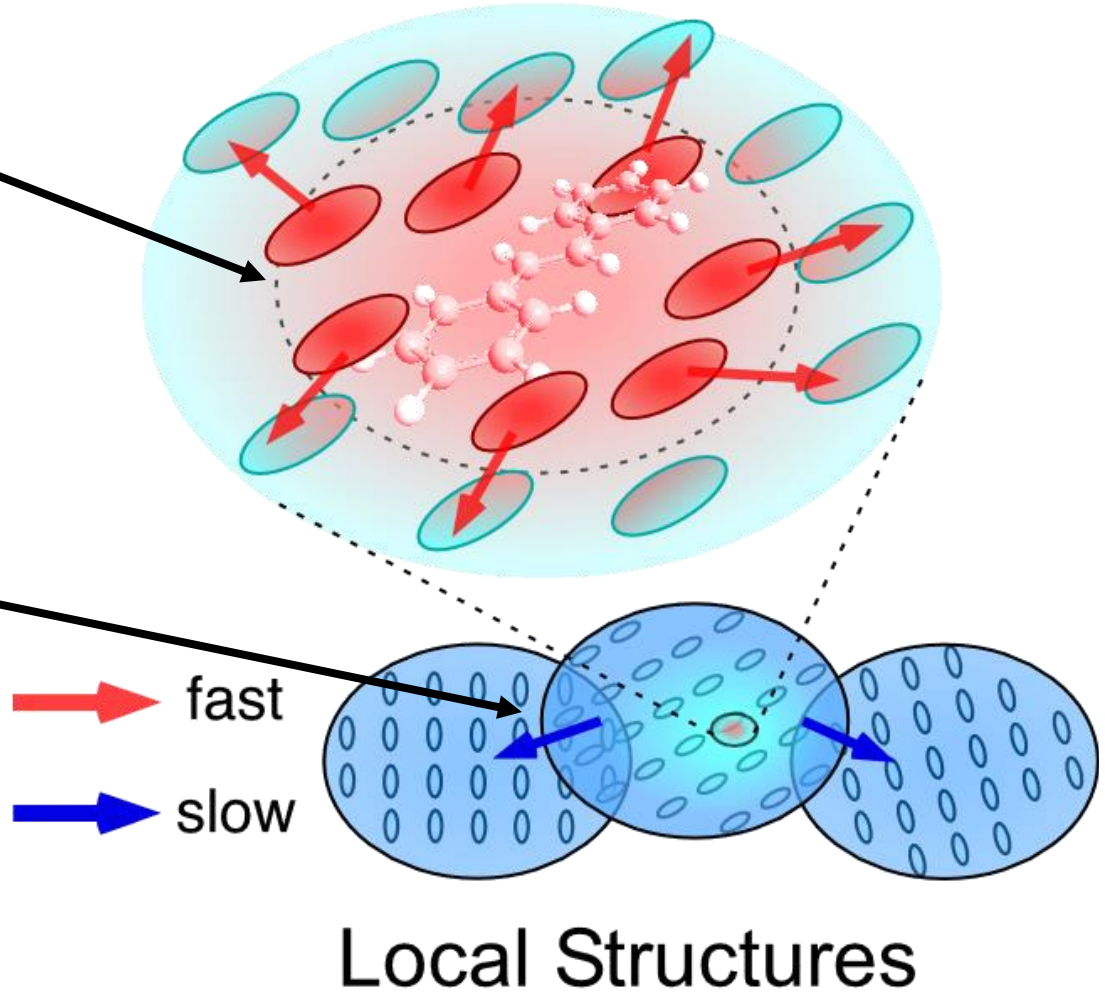
Macroscopic and Microscopic Thermal Diffusion in Ionic Liquids

Cooling rate
(microscopic)

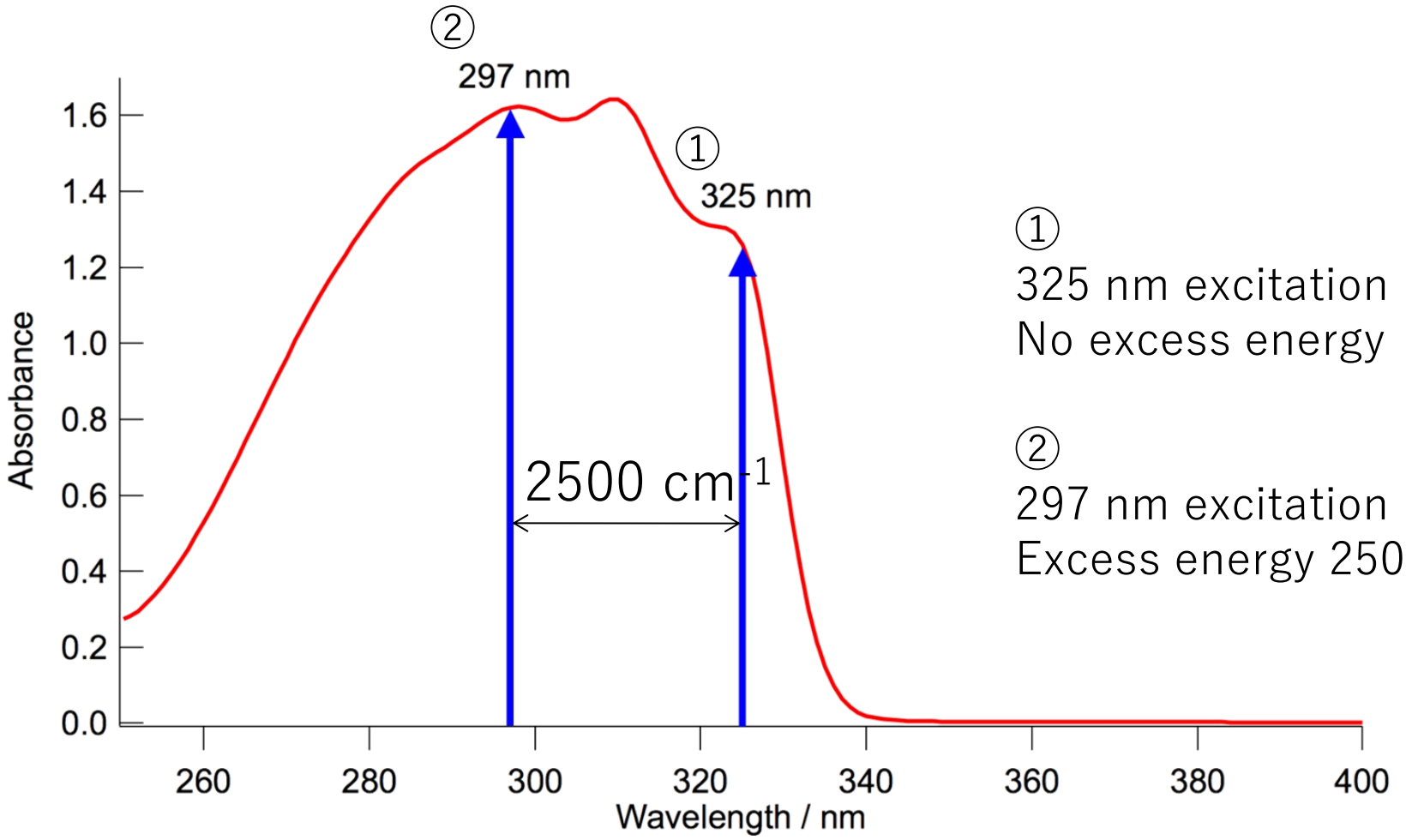
between molecules

Thermal diffusivity
(macroscopic)

between
"Local Structures"



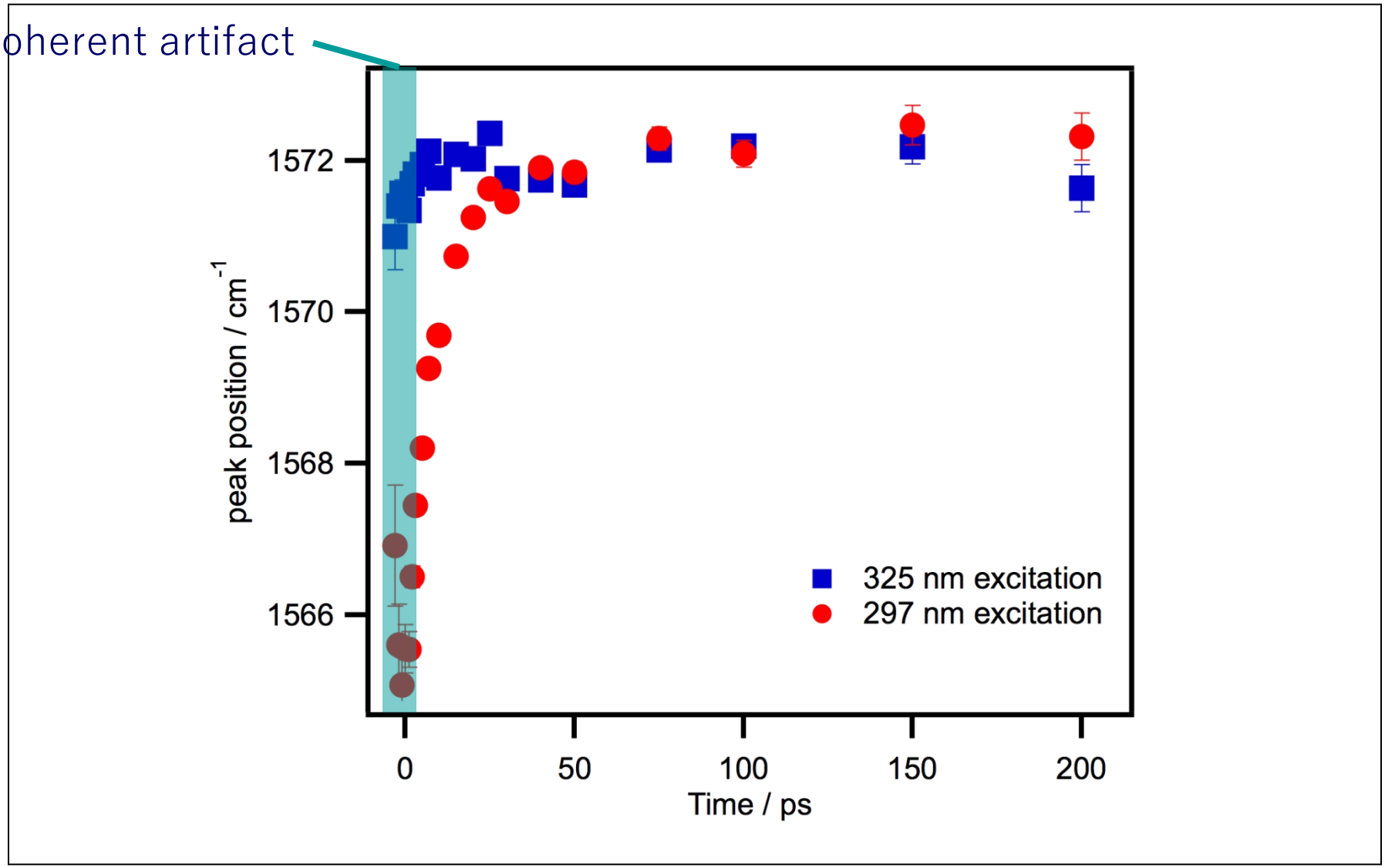
Absorption Spectrum of *trans*-stilbene in C_2mimTf_2N



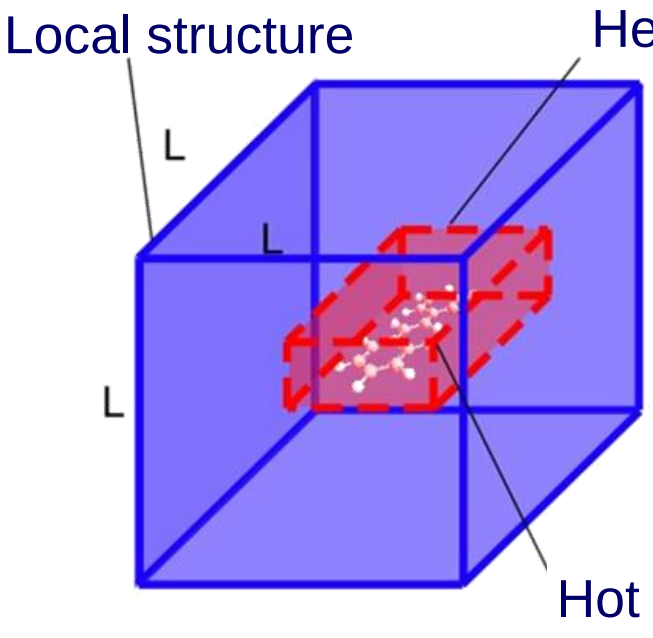
①
325 nm excitation ;
No excess energy

②
297 nm excitation ;
Excess energy 2500 cm^{-1}

Cooling Kinetics of S_1*trans*-stilbene in C_2mimTf_2N



Simulation of Heat Dissipation in an Ionic Liquid



Heat origin:
Hot S1 *trans*-stilbene + solvent

Temperature at the heat origin

$$\theta - T_{r.t.} = \frac{T_\Delta}{2}\{\sum_{n=-\infty}^{\infty}[\mathrm{erf}\{(a/2+nL)/(4D_{th}t)^{1/2}\}+\mathrm{erf}\{(a/2-nL)/(4D_{th}t)^{1/2}\}]\}$$

$$\times\{\sum_{n=-\infty}^{\infty}[\mathrm{erf}\{(b/2+nL)/(4D_{th}t)^{1/2}\}+\mathrm{erf}\{(b/2-nL)/(4D_{th}t)^{1/2}\}]\}$$

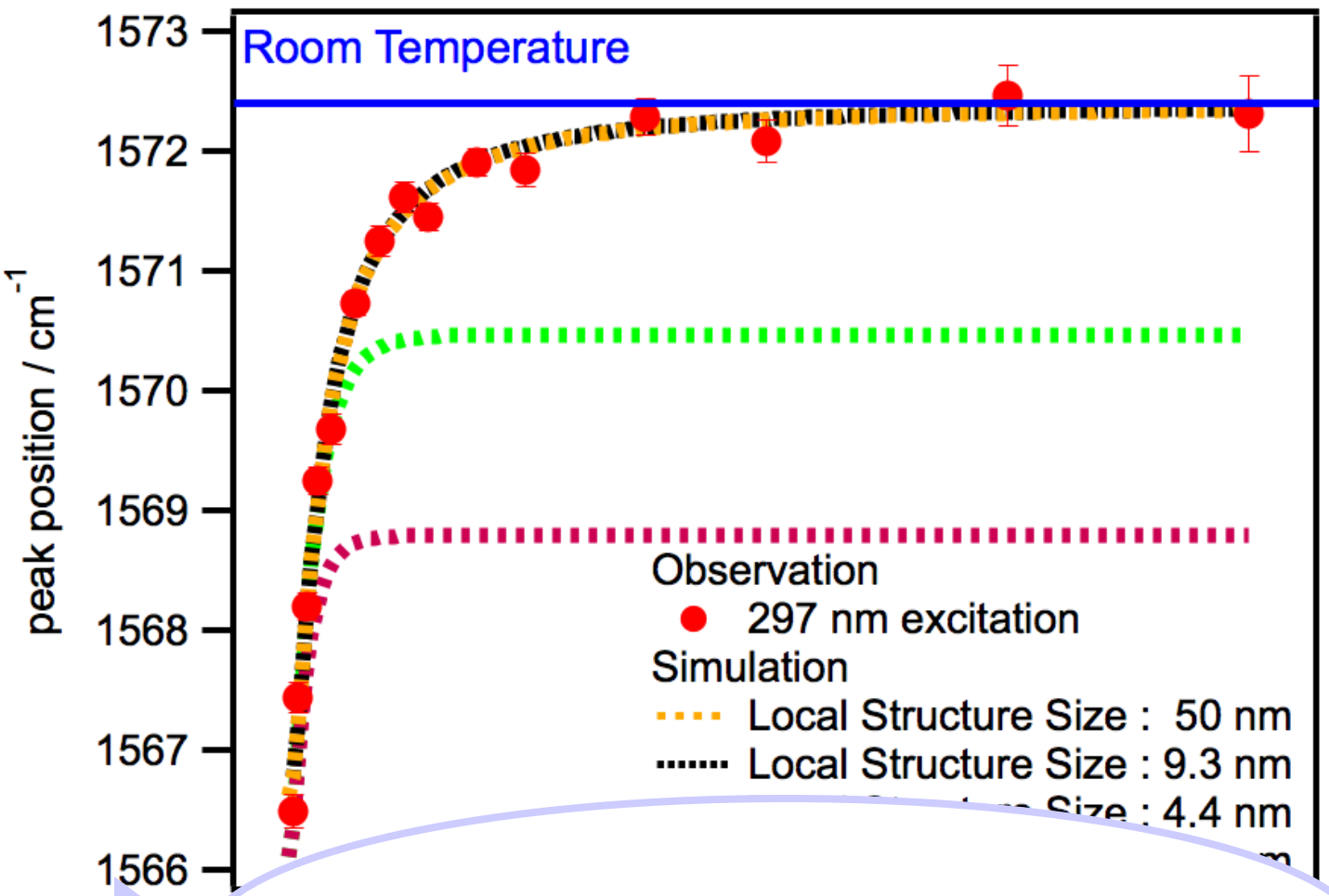
$$\times\{\sum_{n=-\infty}^{\infty}[\mathrm{erf}\{(c/2+nL)/(4D_{th}t)^{1/2}\}+\mathrm{erf}\{(c/2-nL)/(4D_{th}t)^{1/2}\}]\}$$

L: Size of Local Structure

a, b, c: Size of the heat origin

K. Iwata and H. Hamaguchi, *J. Phys. Chem. A*, **101**, 632 (1997)

Simulation of the Cooling Kinetics

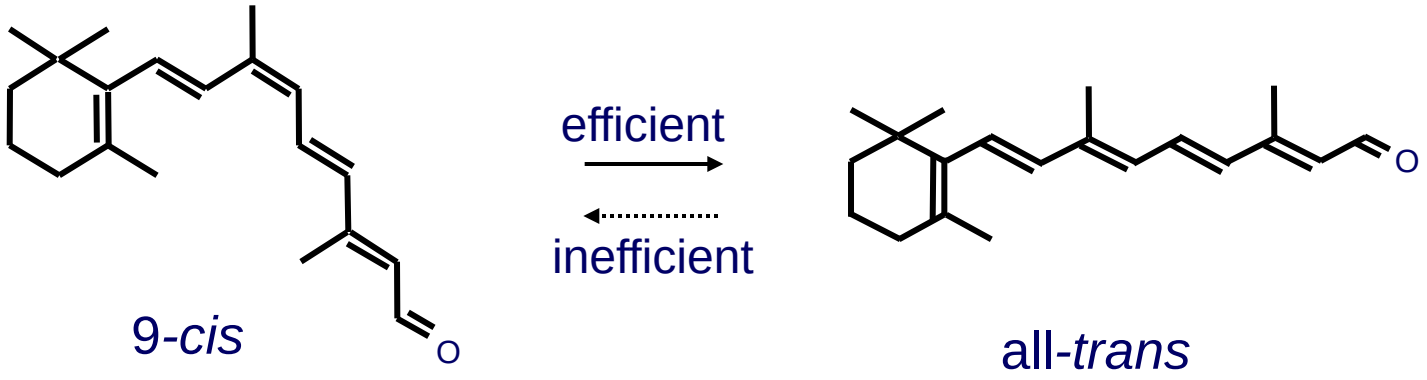


Size of local structure > 10 nm

Retinal: a prototype molecular system for

Photophysics ; closely lying excited states (S_3, S_2, S_1, T_1)

Photochemistry; photoisomerization



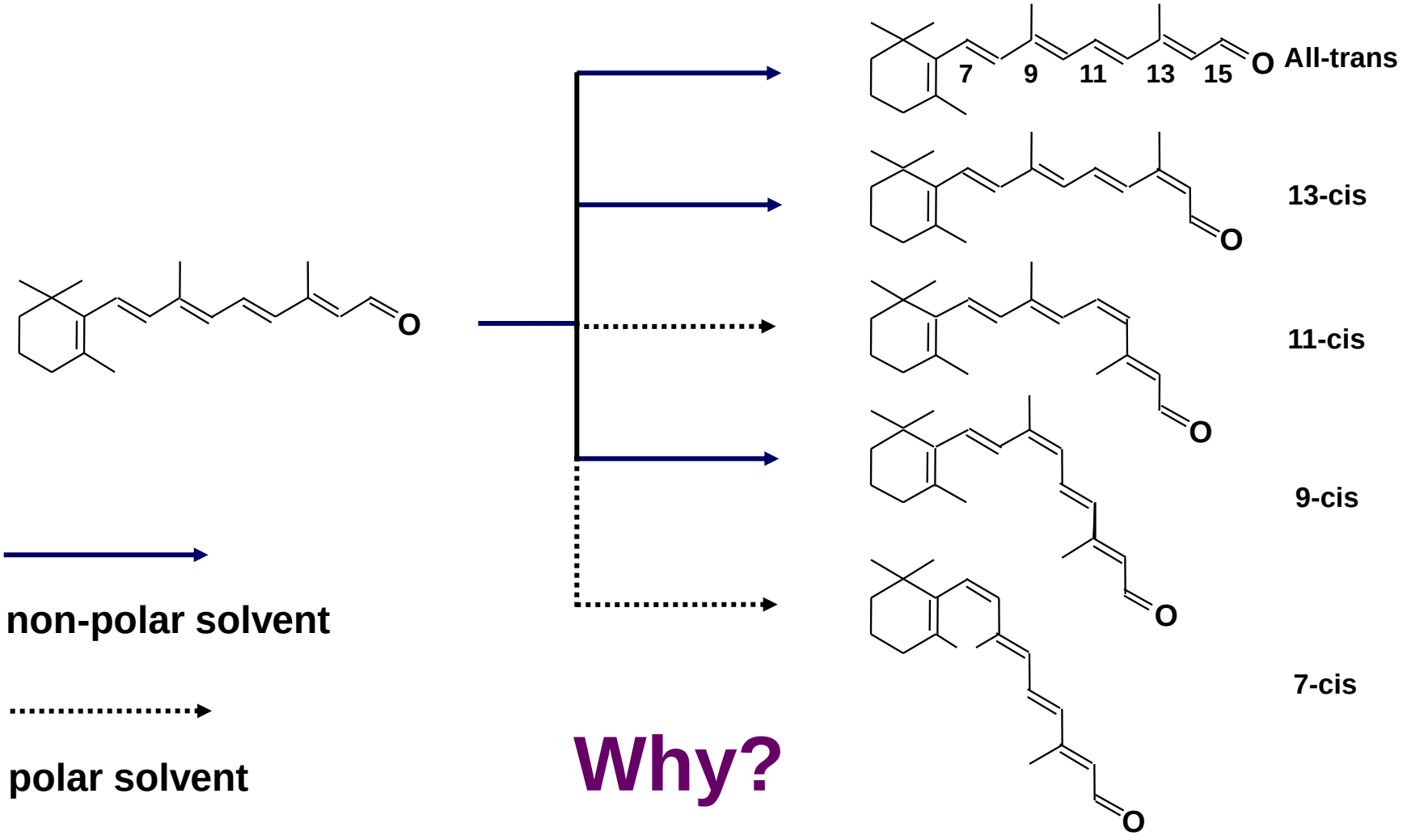
9-*cis* all-*trans*

- Asymmeric *trans-cis* photoisomerization
- Marked solvent effect

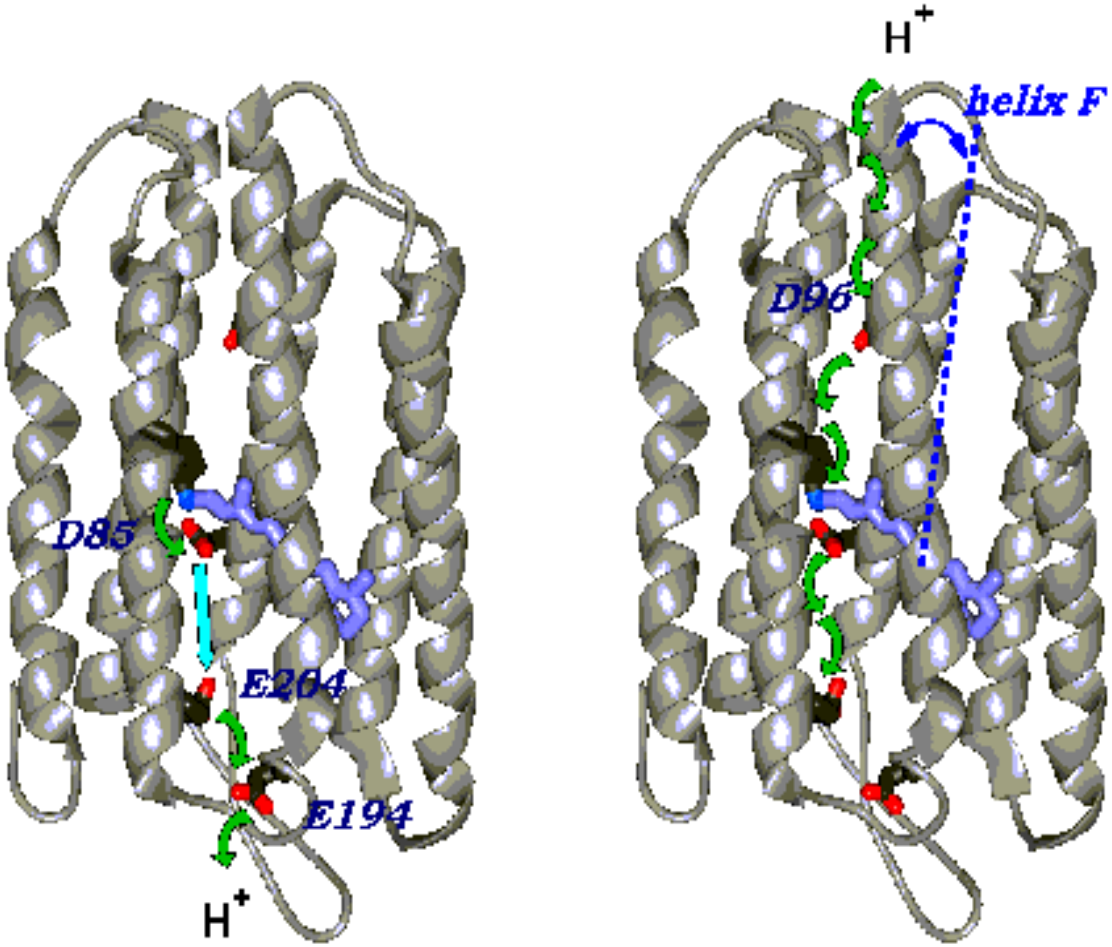
Photobiology; retinoid proteins

- Rhodopsin
- Bcteriorhodopsin
- Sensoryrhodopsin

Photoisomerization of All-*trans* Retinal



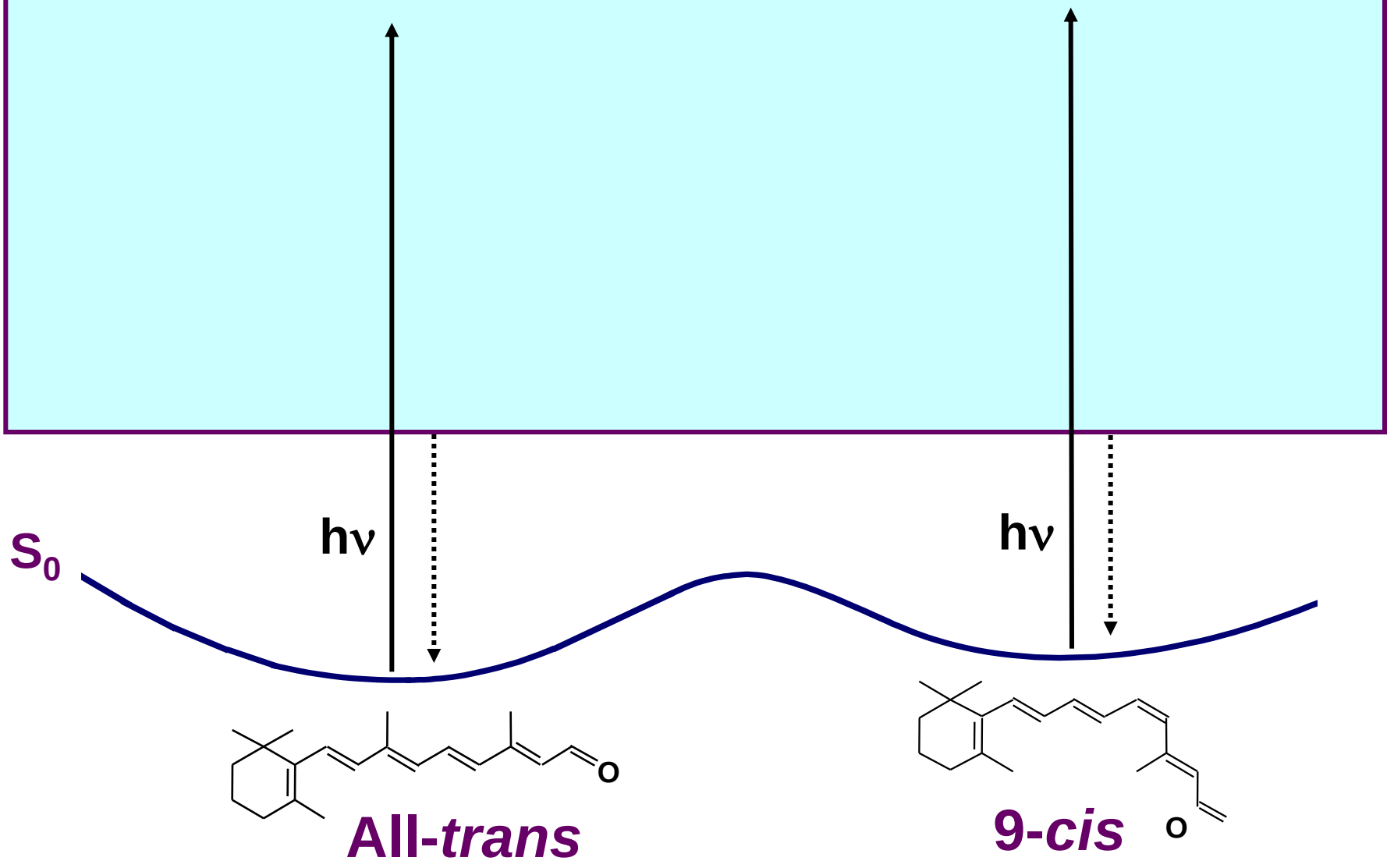
Proton Pumping by Bacteriorhodopsin



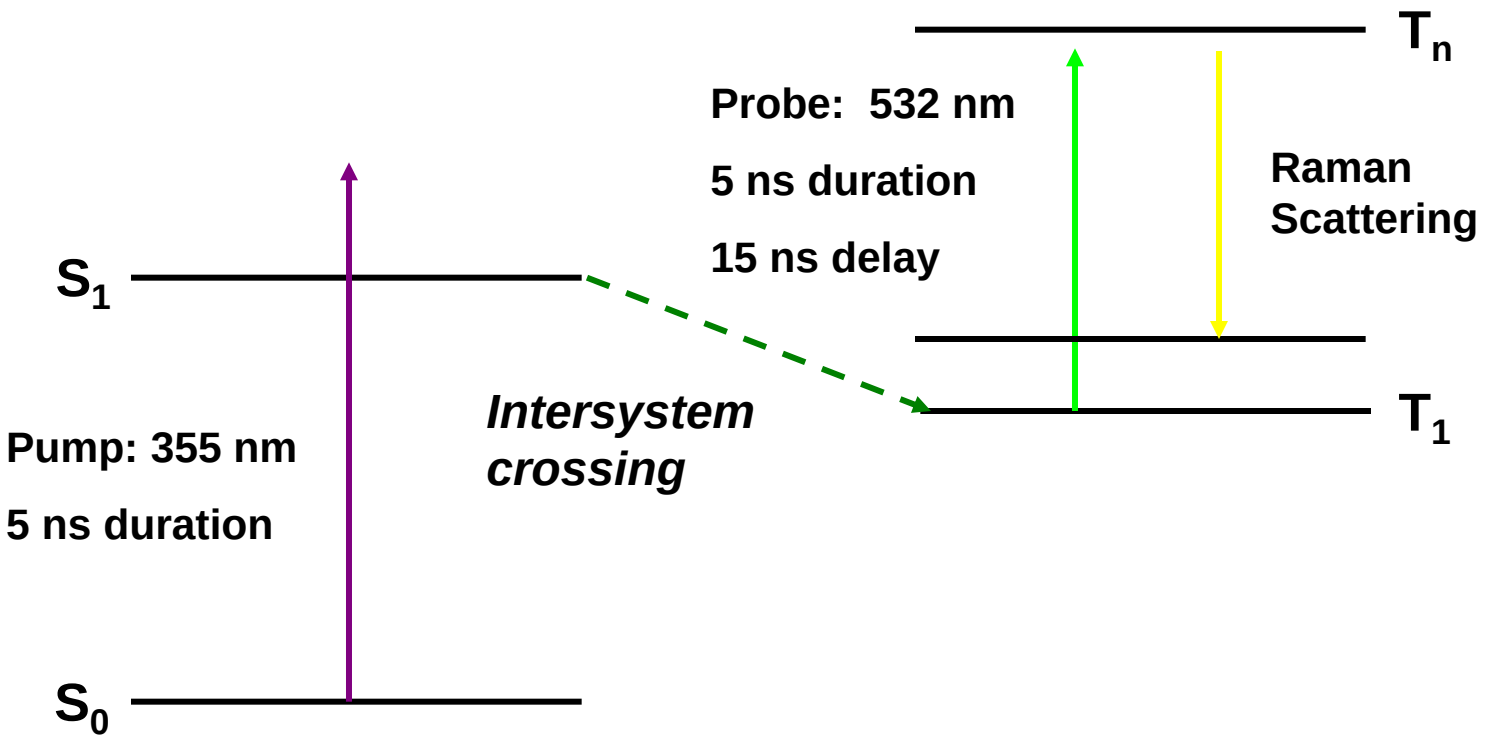
All-*trans* isomerizes to 13-*cis* exclusively. Why and How?

http://anx12.bio.uci.edu

What happens in the Excited electronic States of Retinal ?



Nanosecond Pump/Probe Time-resolved Raman Spectroscopy of Retinal Isomers



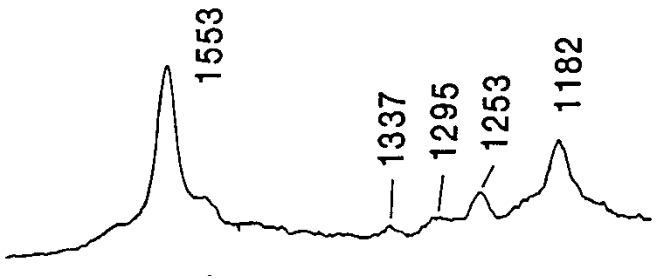
H. Hamaguchi, H. Okamoto,and M. Tasumi, Chem. Lett. **1984**, 549-550.

H. Hamaguchi, H. Okamoto, M. Tasumi, Y. Mukai, and Y. Koyama, Chem. Phys. Lett. **107**, 355-359 (1984).

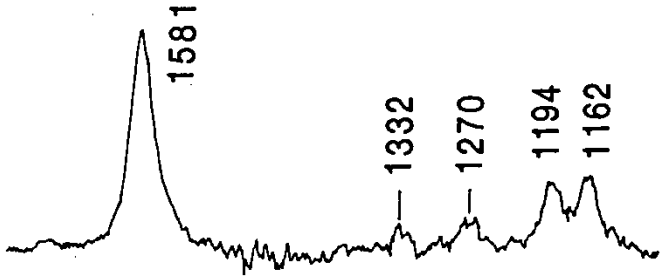
Raman Spectra of All-*trans*- and 9-*cis*-Retinal in the T_1 and S_0 States

All-*trans*-retinal

T_1 State



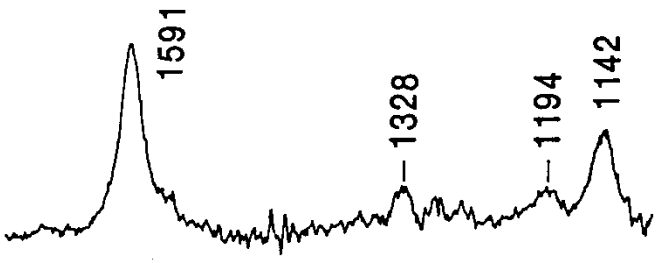
S_0 State



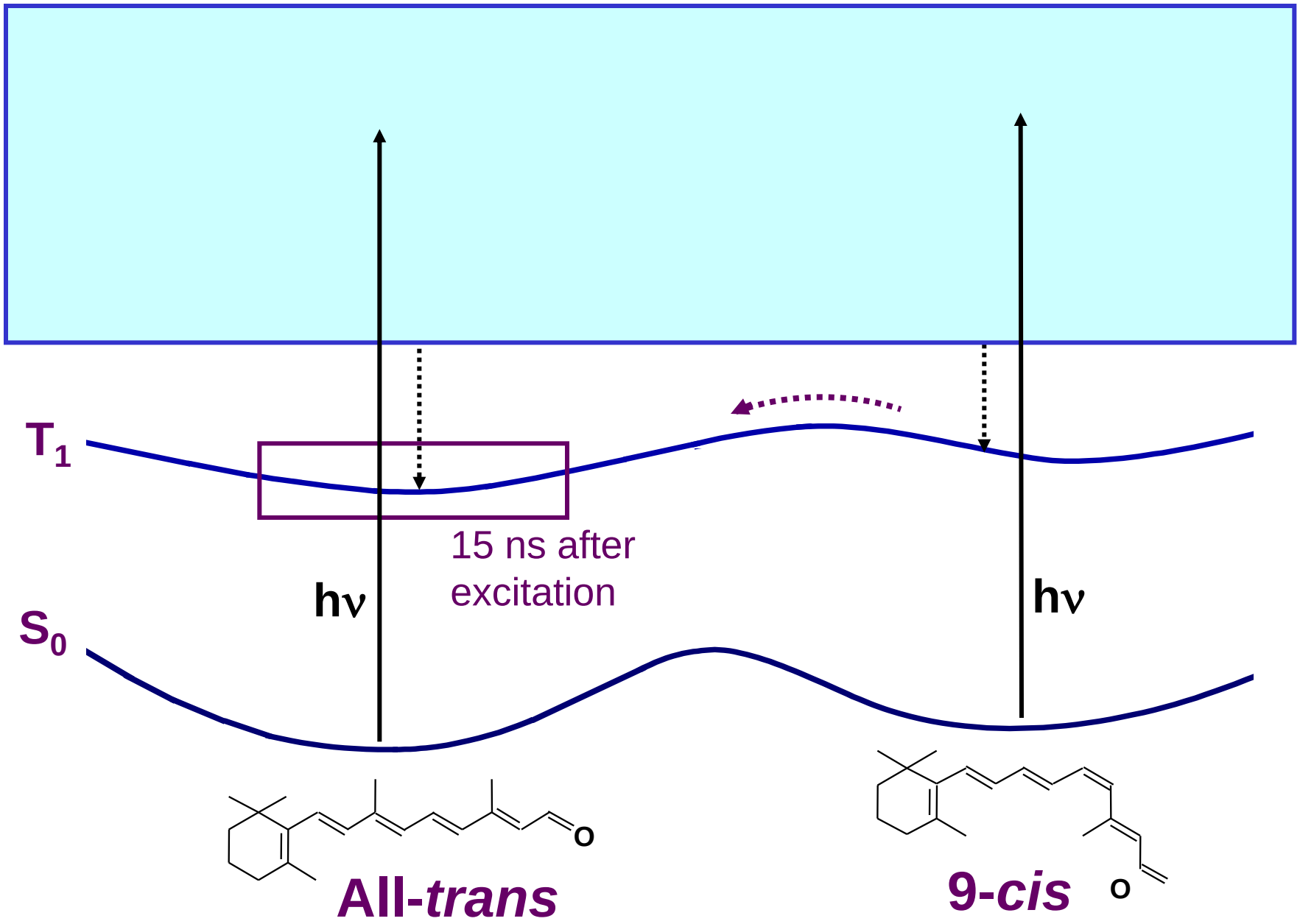
9-*cis*-retinal

T_1 State

S_0 State



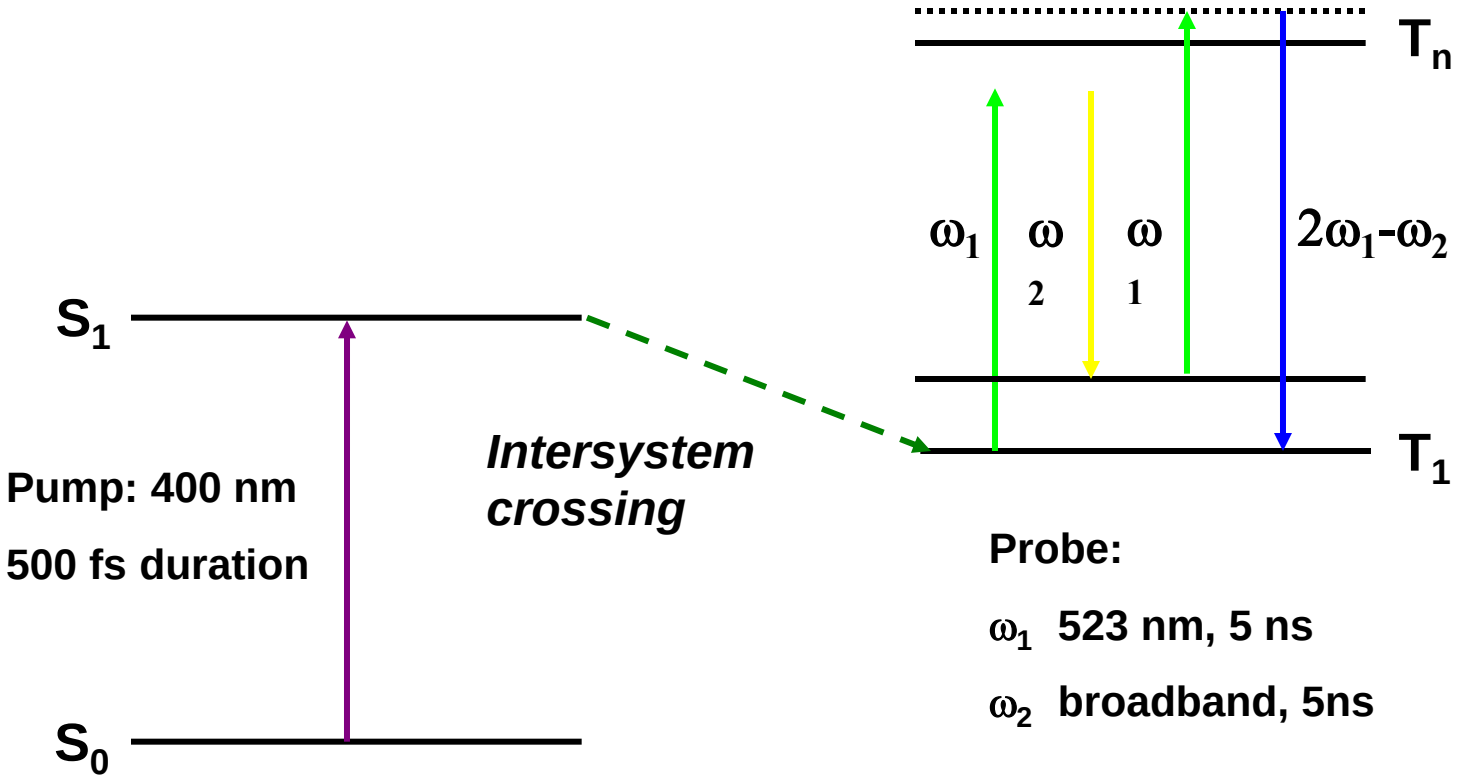
One-way Photoisomerization on the T_1 surface



All-*trans*

9-*cis*

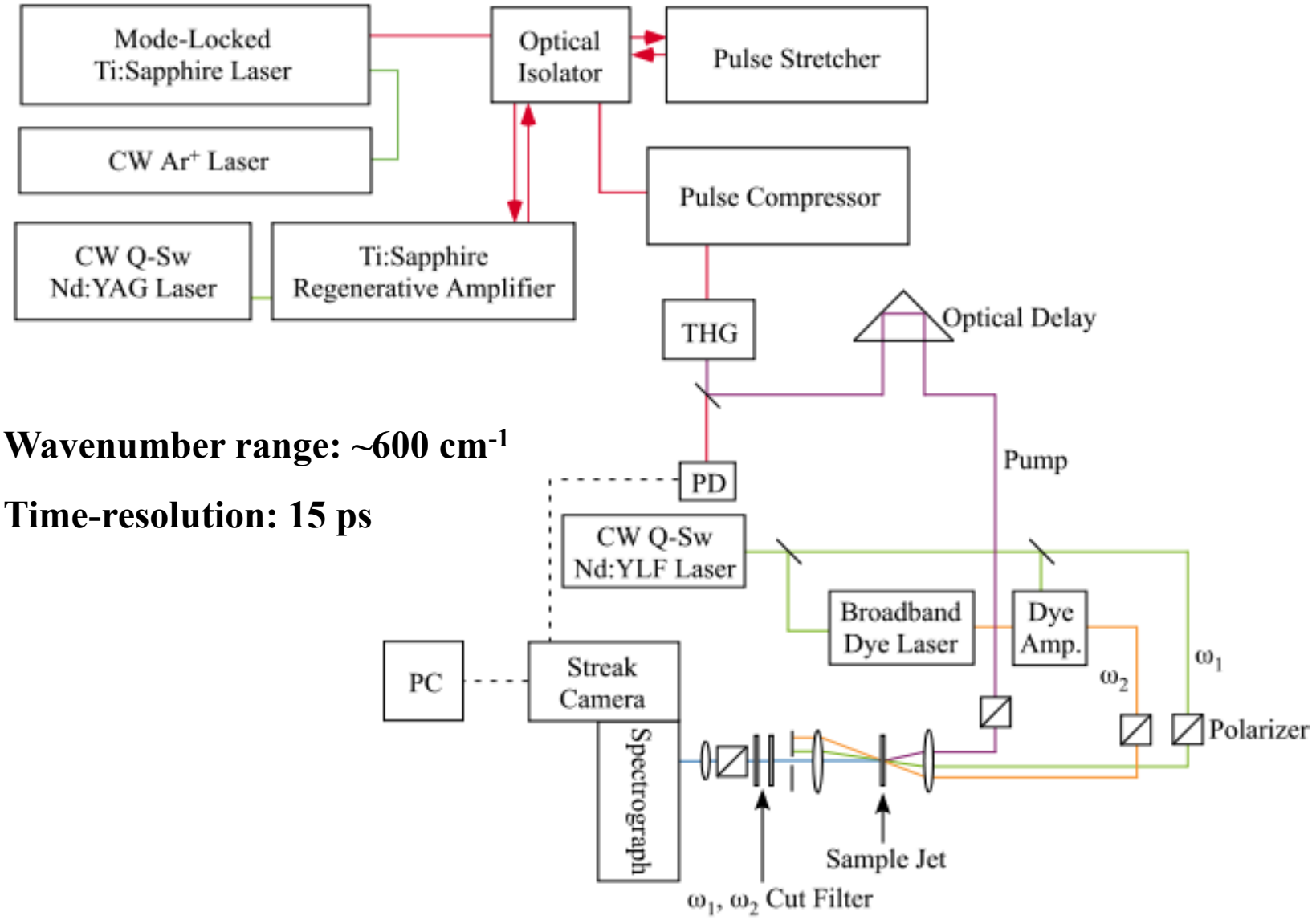
10 Picosecond Time-frequency Two-dimensional Multiplex CARS Spectroscopy of Retinal Isomers



T. Tahara, B. N. Toleutaev, and H. Hamaguchi, J. Chem. Phys. **217**, 369-374 (1994).

T. Tahara and H. Hamaguchi, Rev. Sci. Instru. **65**, 3332-3338 (1994).

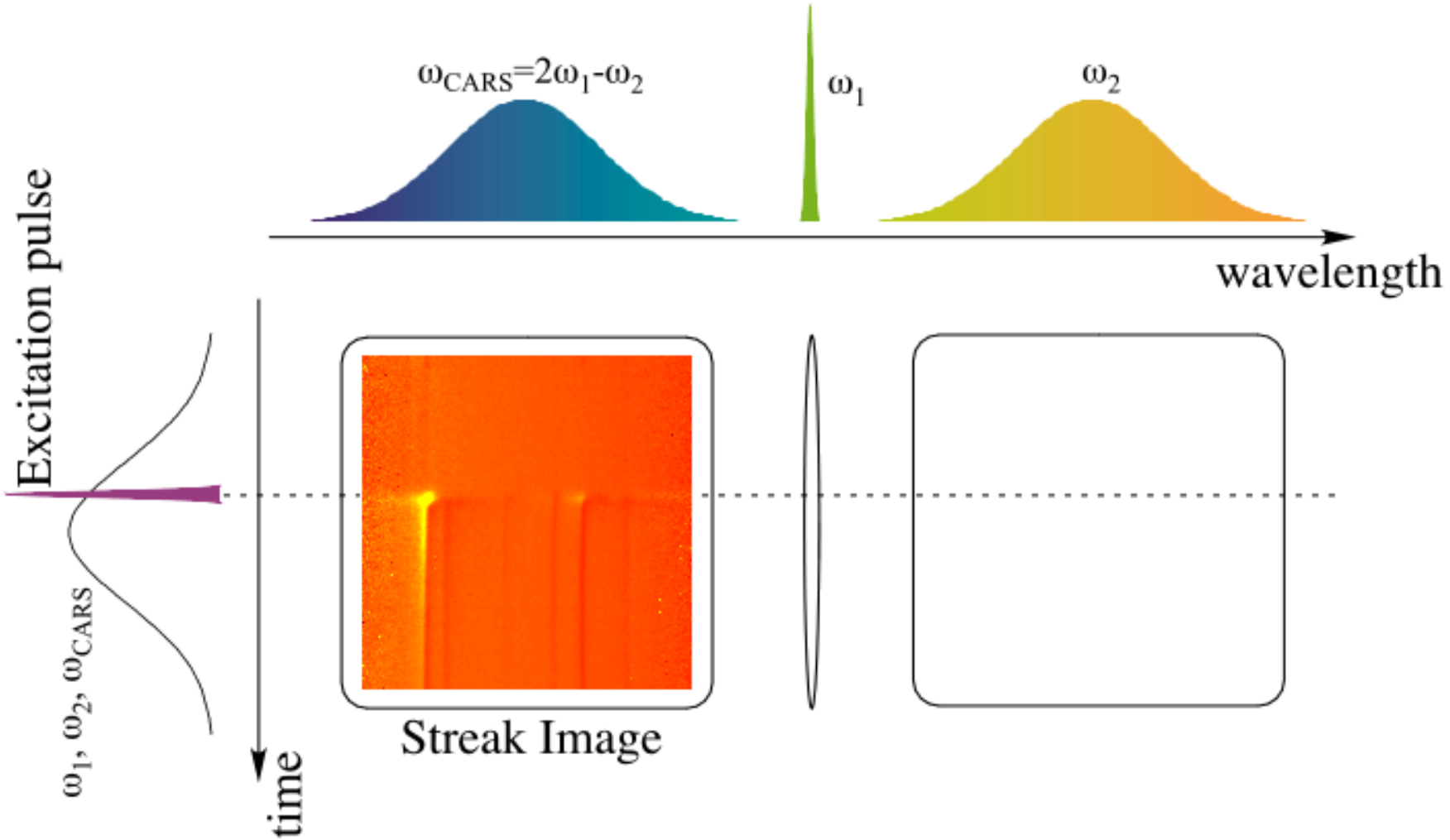
Experimental Setup for 2-D CARS Spectroscopy



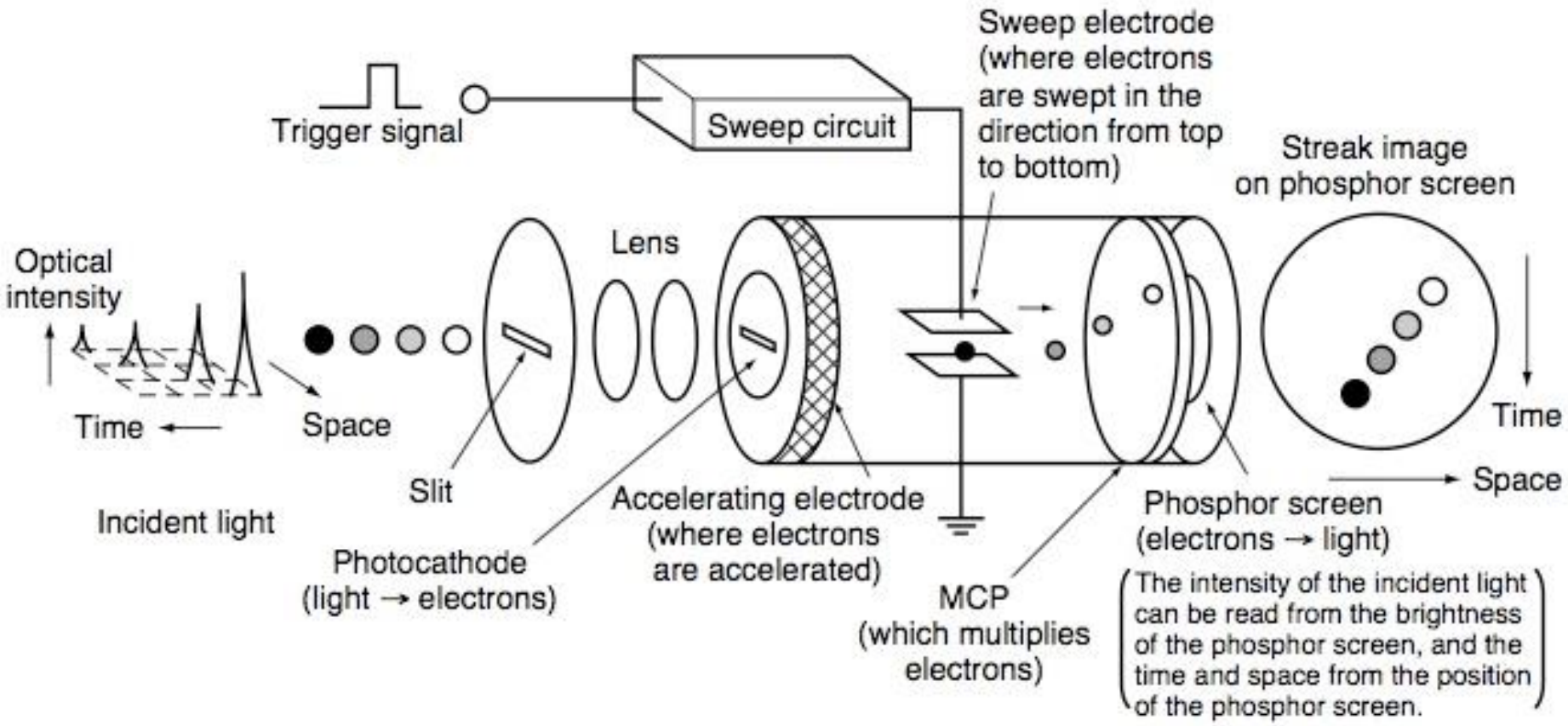
Wavenumber range: ~600 cm^{-1}

Time-resolution: 15 ps

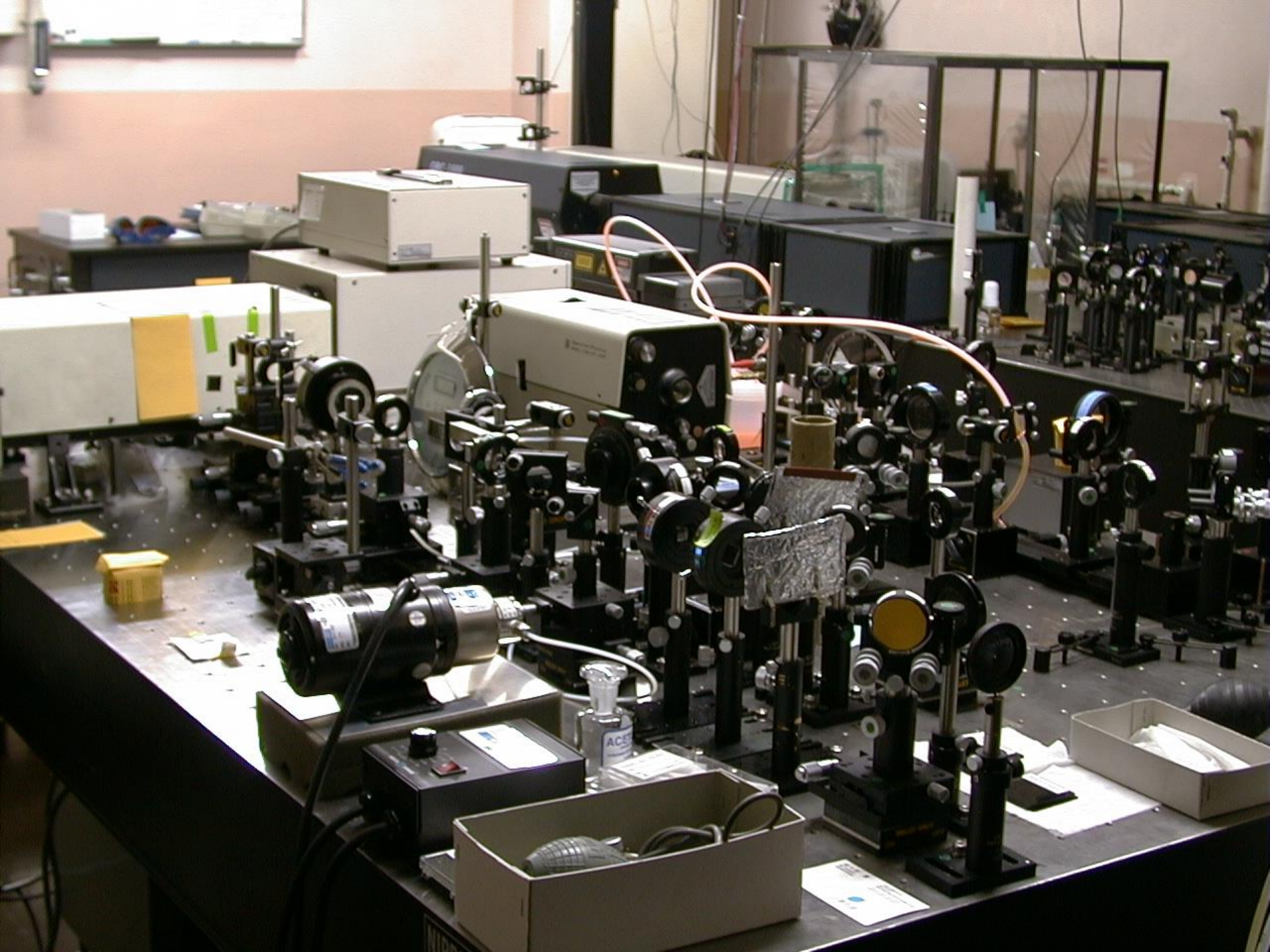
Picosecond Two-dimensional Multiplex CARS Spectroscopy (2-D CARS)



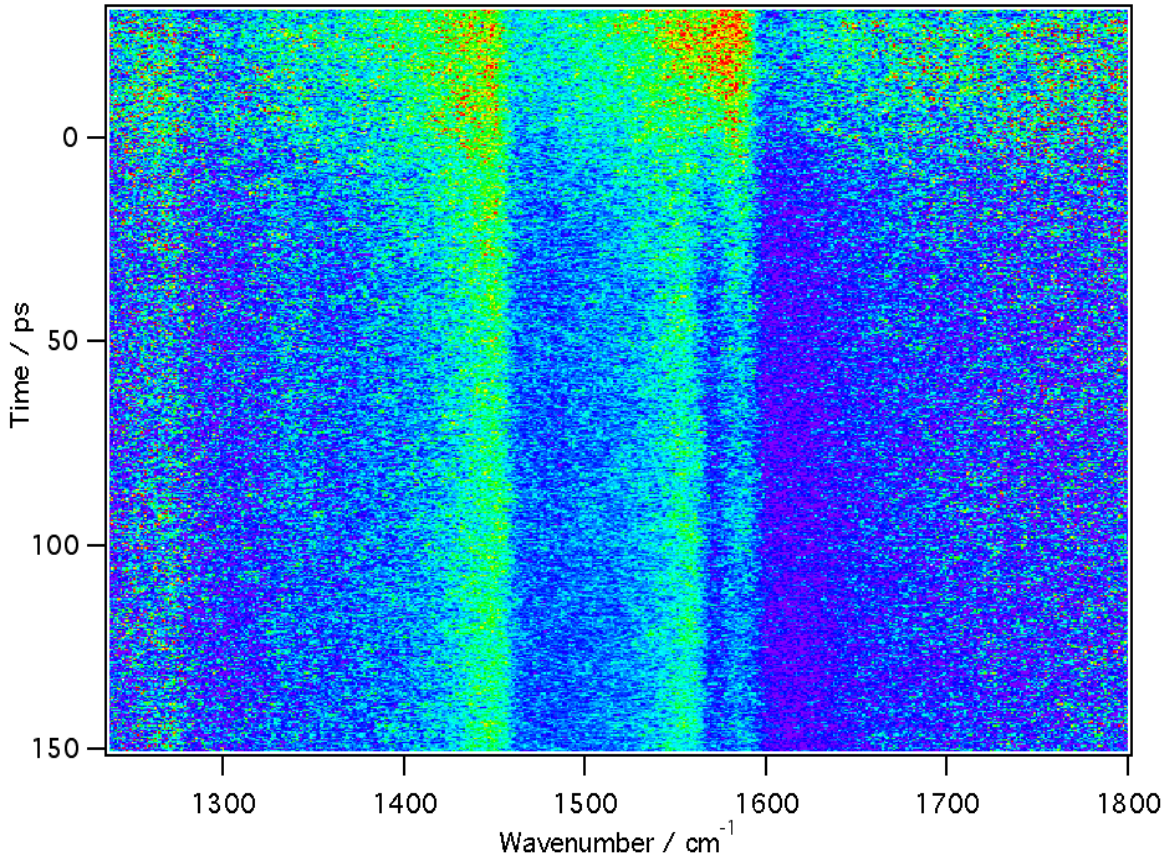
Operation Principle of a Streak Camera



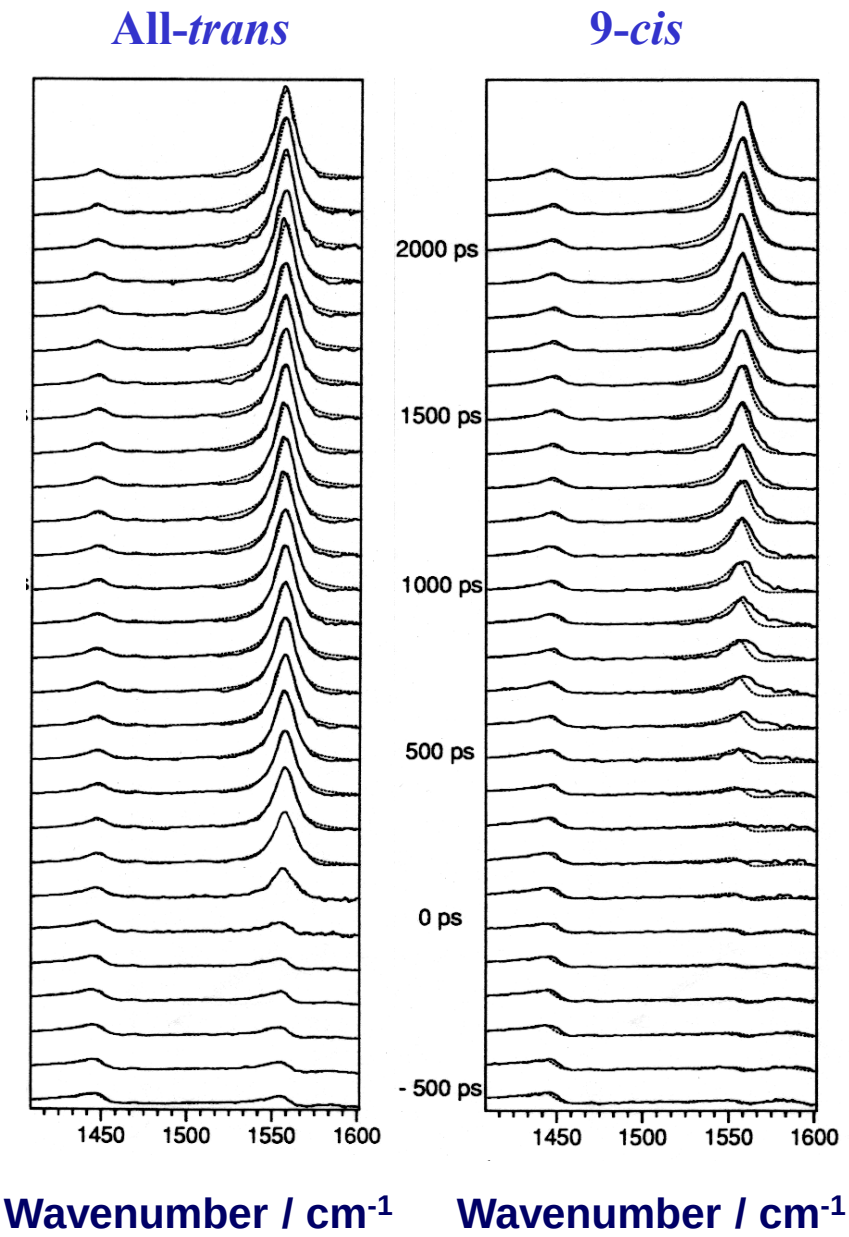
http://cvitae.org/content/view/180/895/



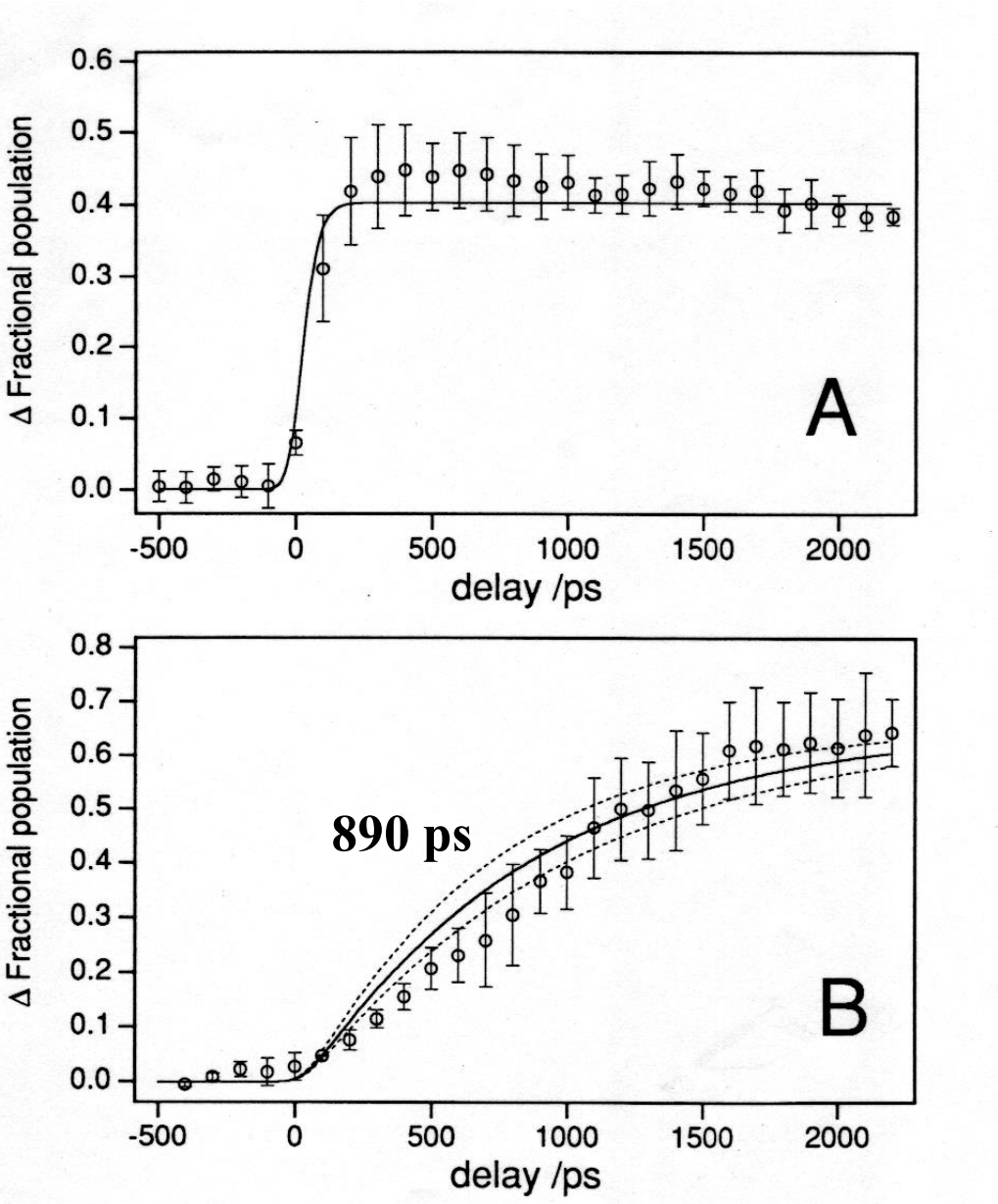
2-D CARS Image for All-trans-retinal in Cyclohexane



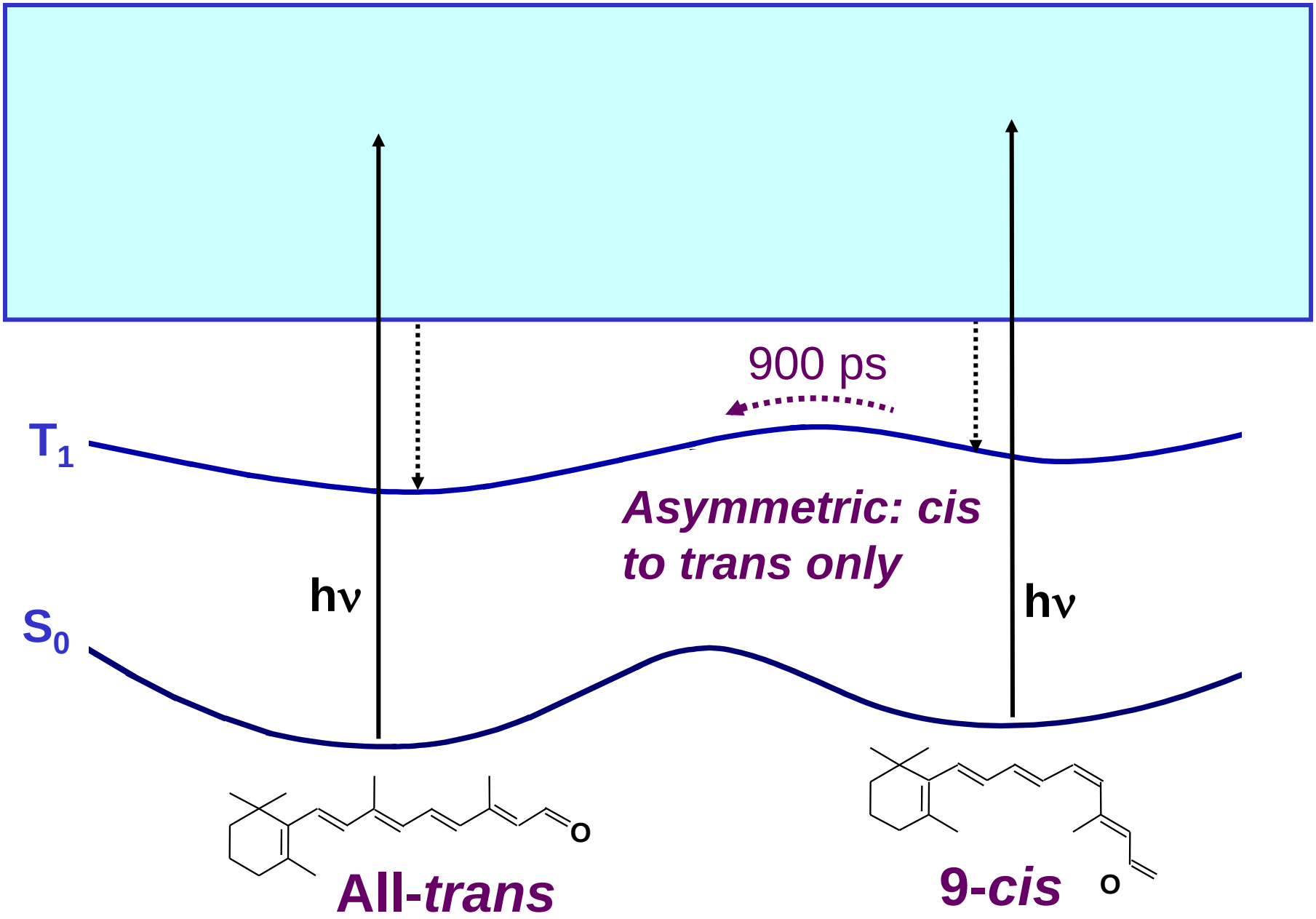
Picosecond Time-resolved CARS Spectra of Retinal Isomers in Cyclohexane



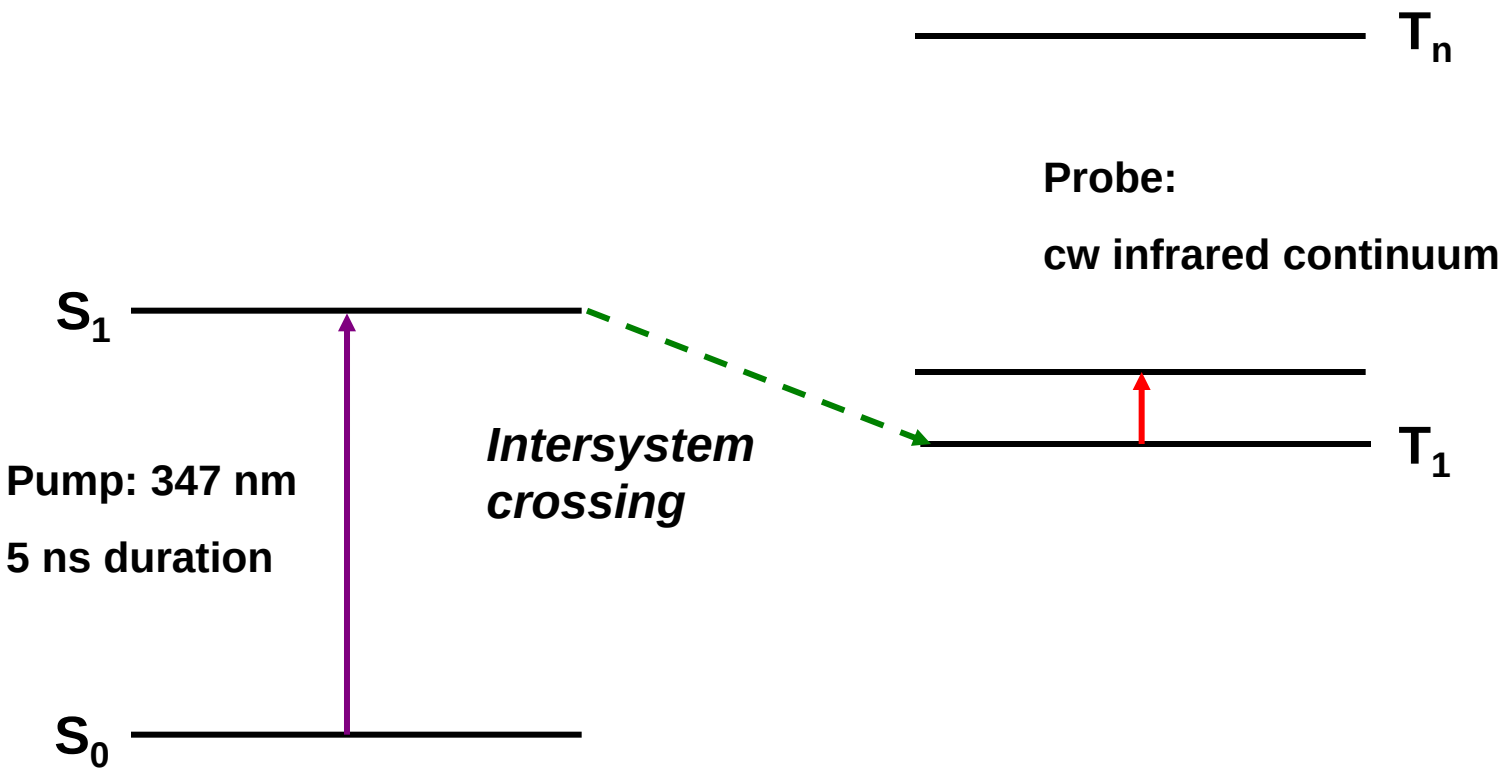
Population Rise of the All-trans T_1 State Monitored by CARS



Photoisomerization on the Triplet Potential Surface



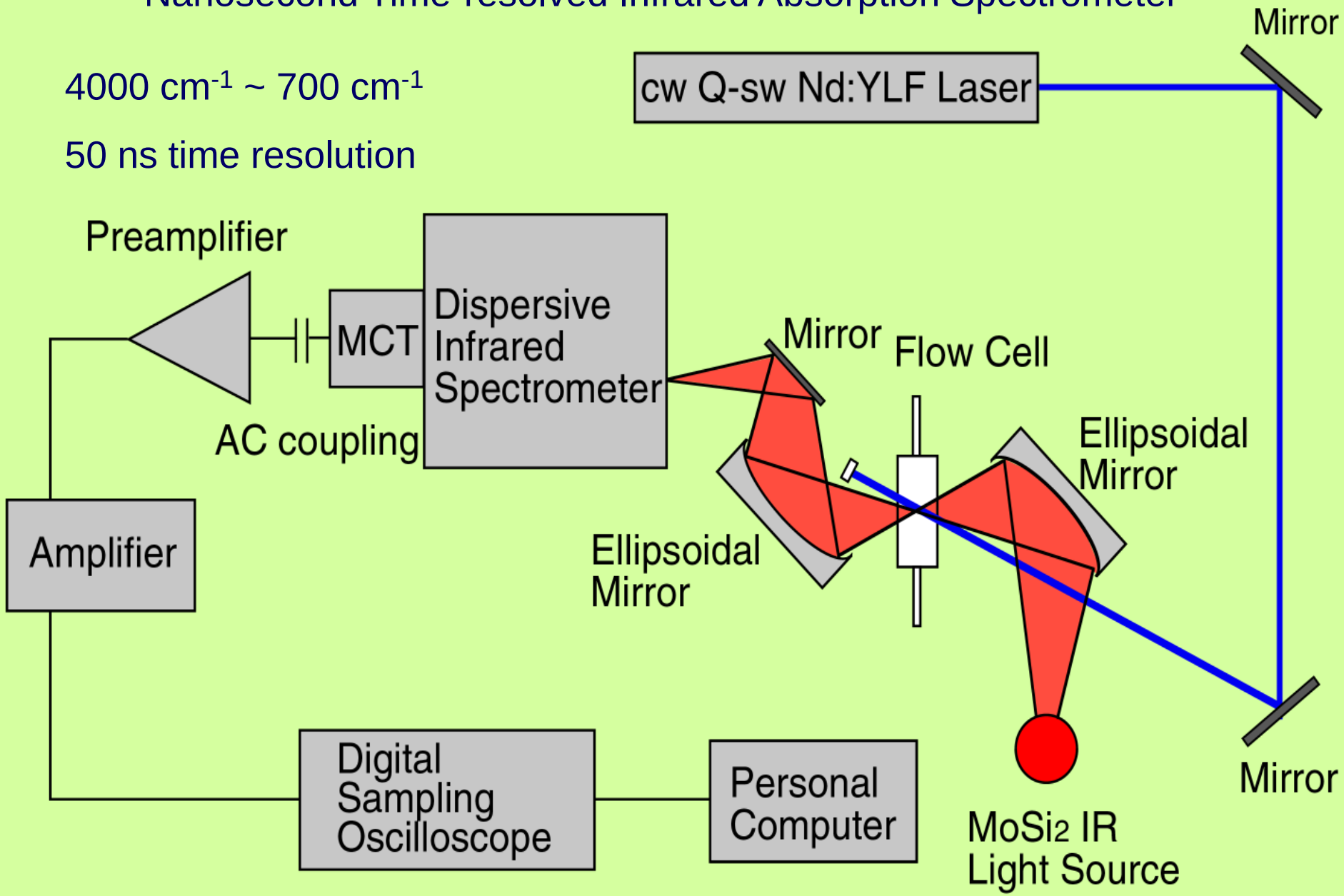
Nanosecond Pump/Probe Time-resolved Infrared Absorption Spectroscopy of Retinal Isomers



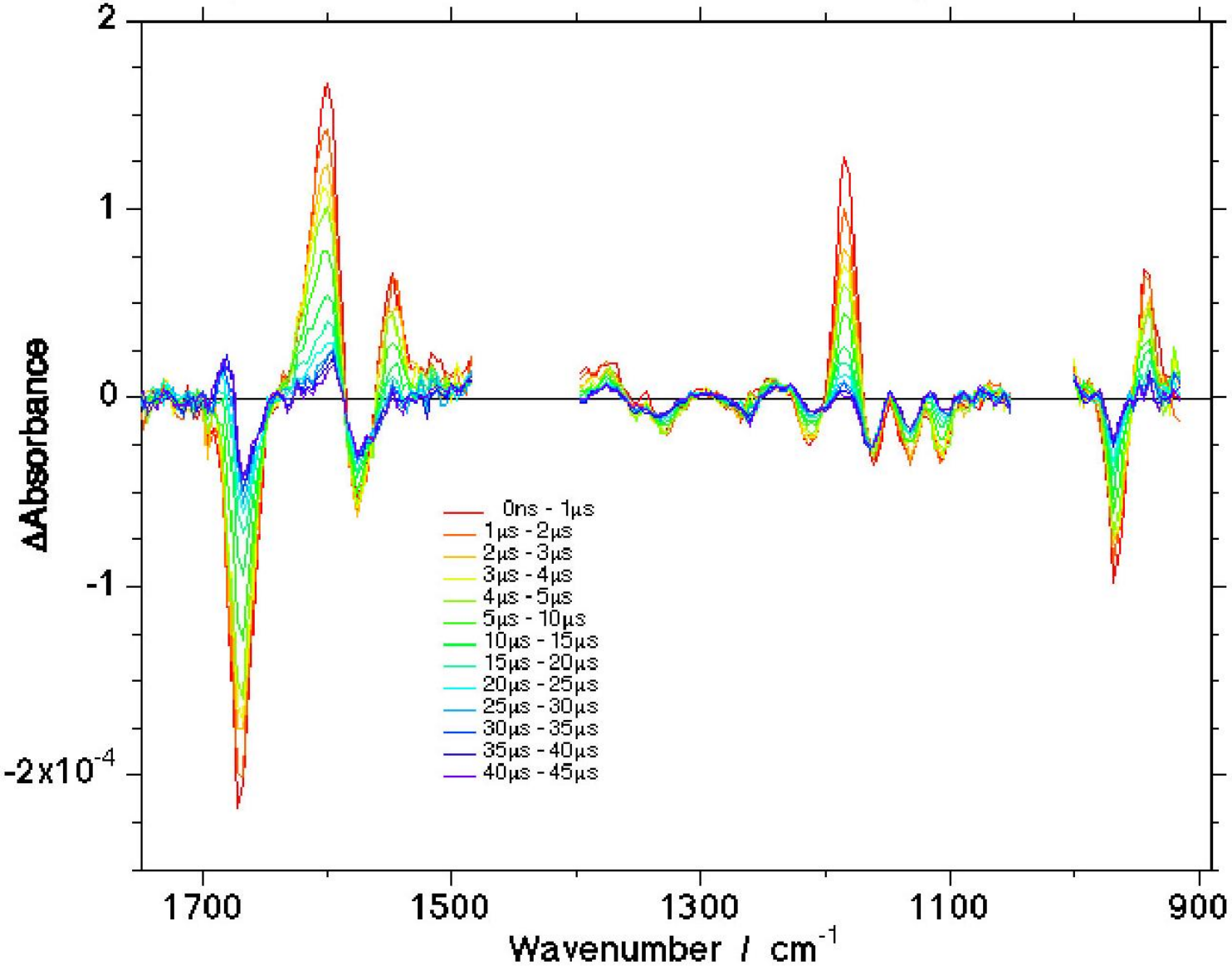
T. Yuzawa and H. Hamaguchi, J. Mol. Struct., **352**, 489-495.

T. Yuzawa and H. Hamaguchi, in preparation.

Nanosecond Time-resolved Infrared Absorption Spectrometer



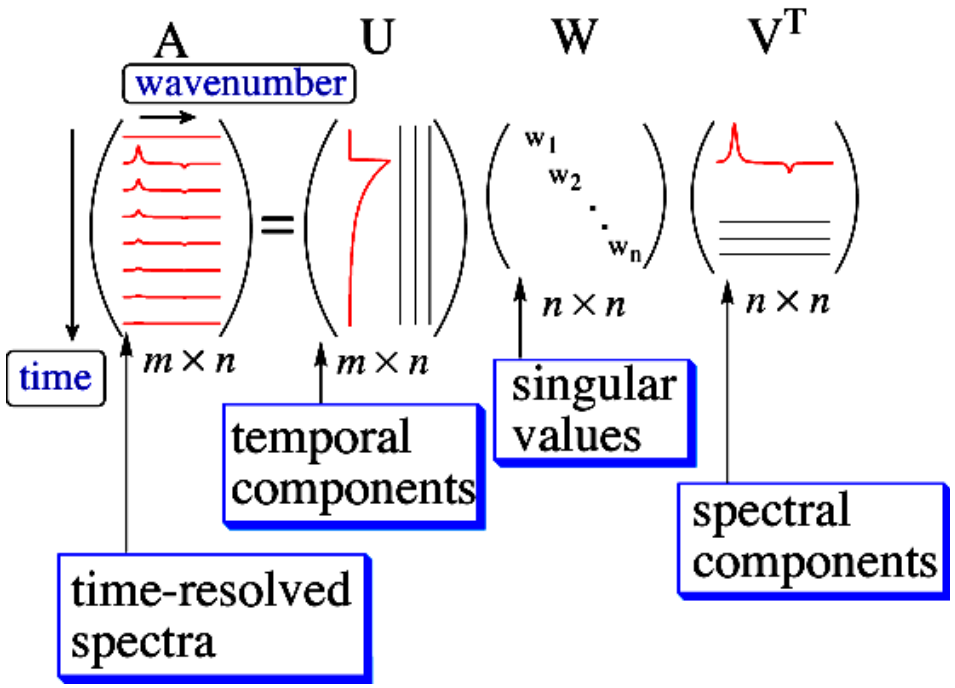
Time-resolved Infrared Absorption Spectra of Photoexcited All-*trans*-retinal in Cyclohexane



Singular Value Decomposition (SVD) Analysis

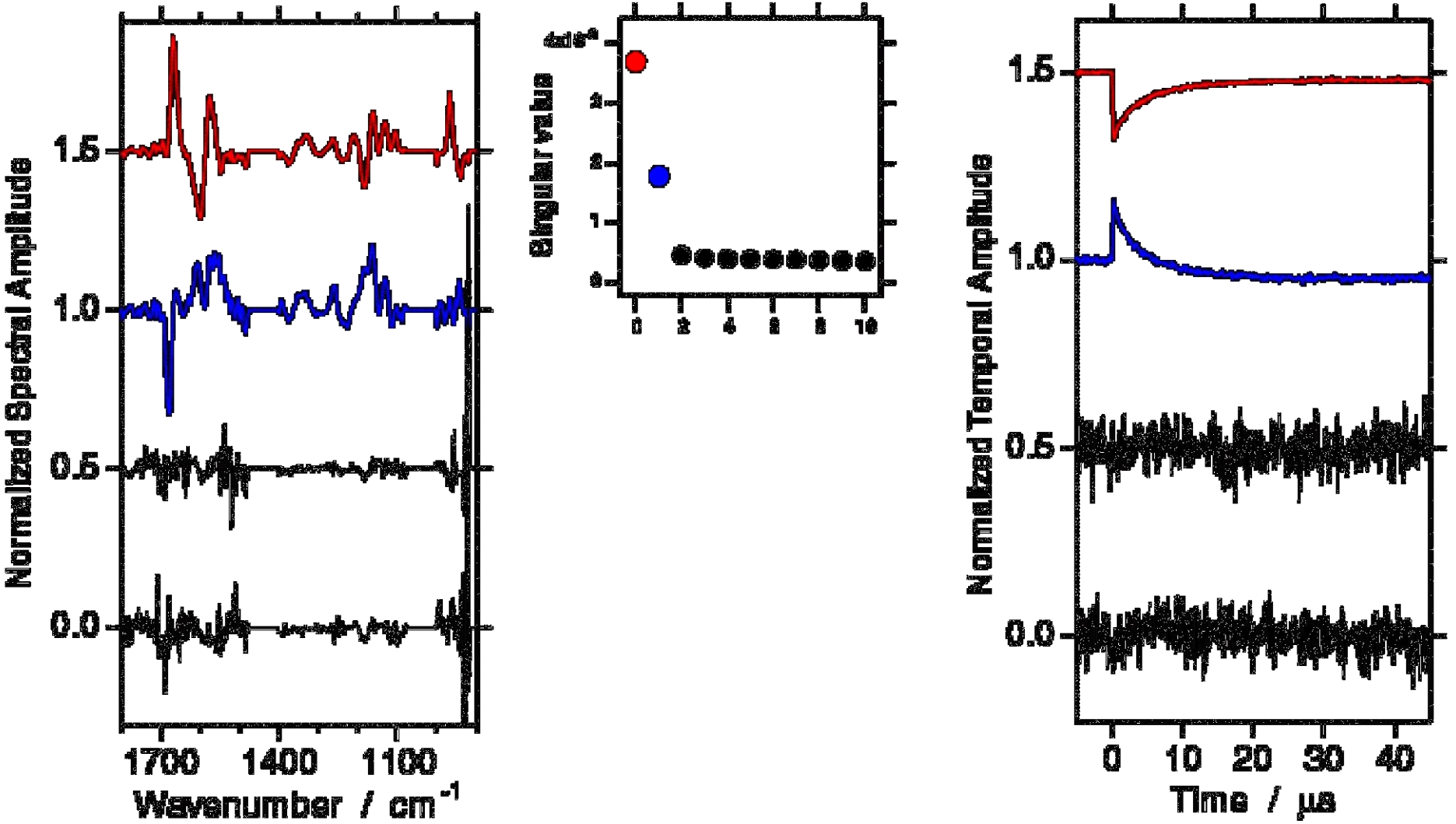
$$A = U\,W\,V^T$$

$$\begin{cases} U^T U = I & \text{column-orthogonal matrix} \\ V^T V = I & \\ W = \begin{pmatrix} w_1 & & & \\ & w_2 & & \\ & & \ddots & \\ & & & w_n \end{pmatrix} & \text{diagonal matrix} \end{cases}$$

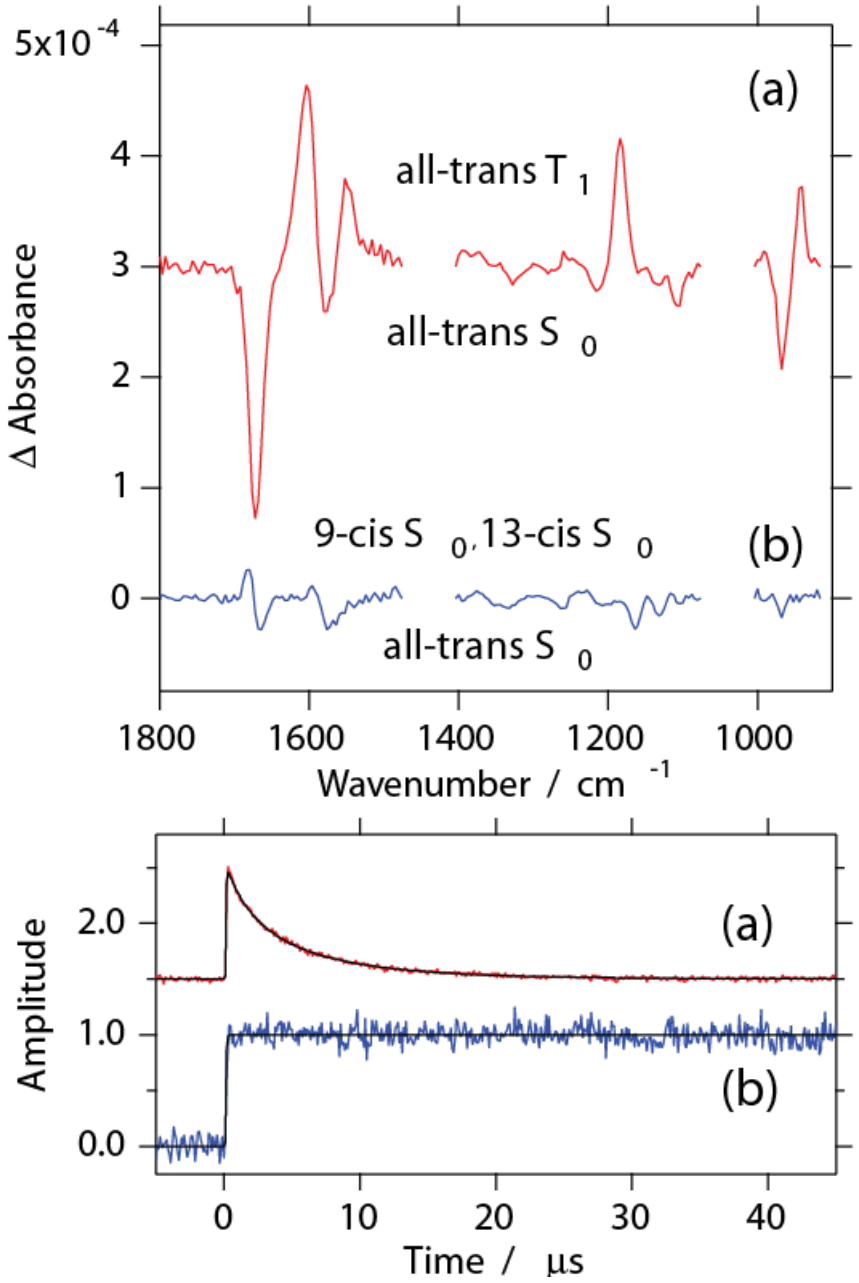


SVD Analysis of the Time-resolved Infrared Absorption Spectra of All-*trans* Retinal

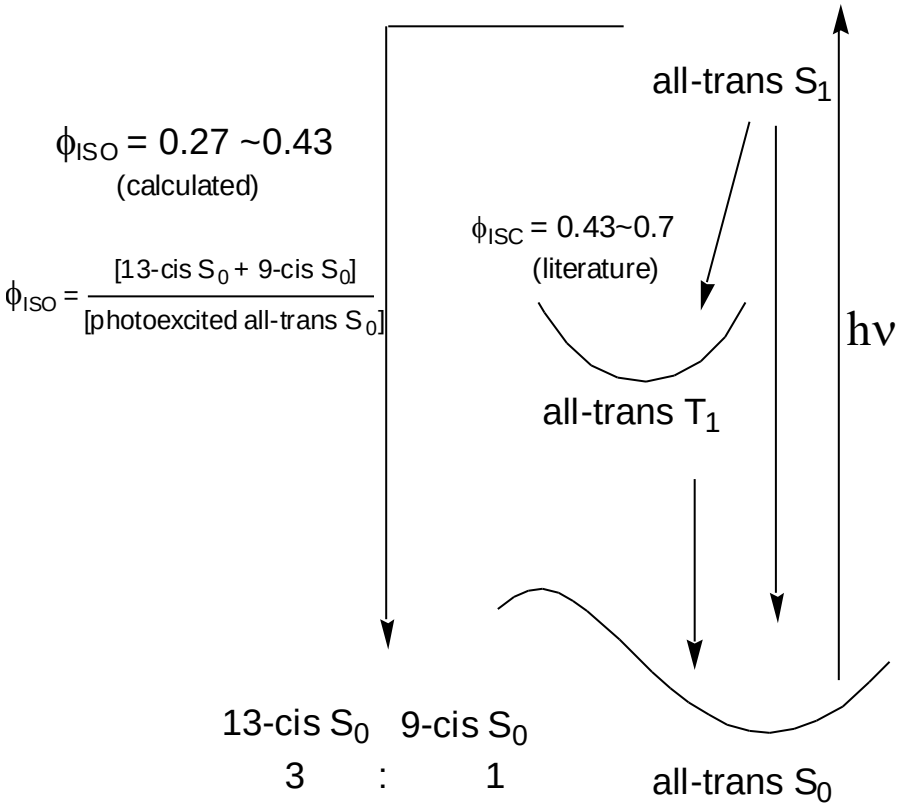
Spectral component ***Singular Values*** ***Temporal component***

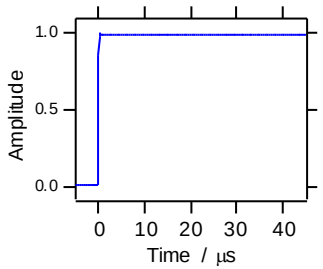


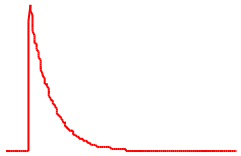
SVD Analysis of the Time-resolved Infrared Absorption Spectra of All-*trans* Retinal



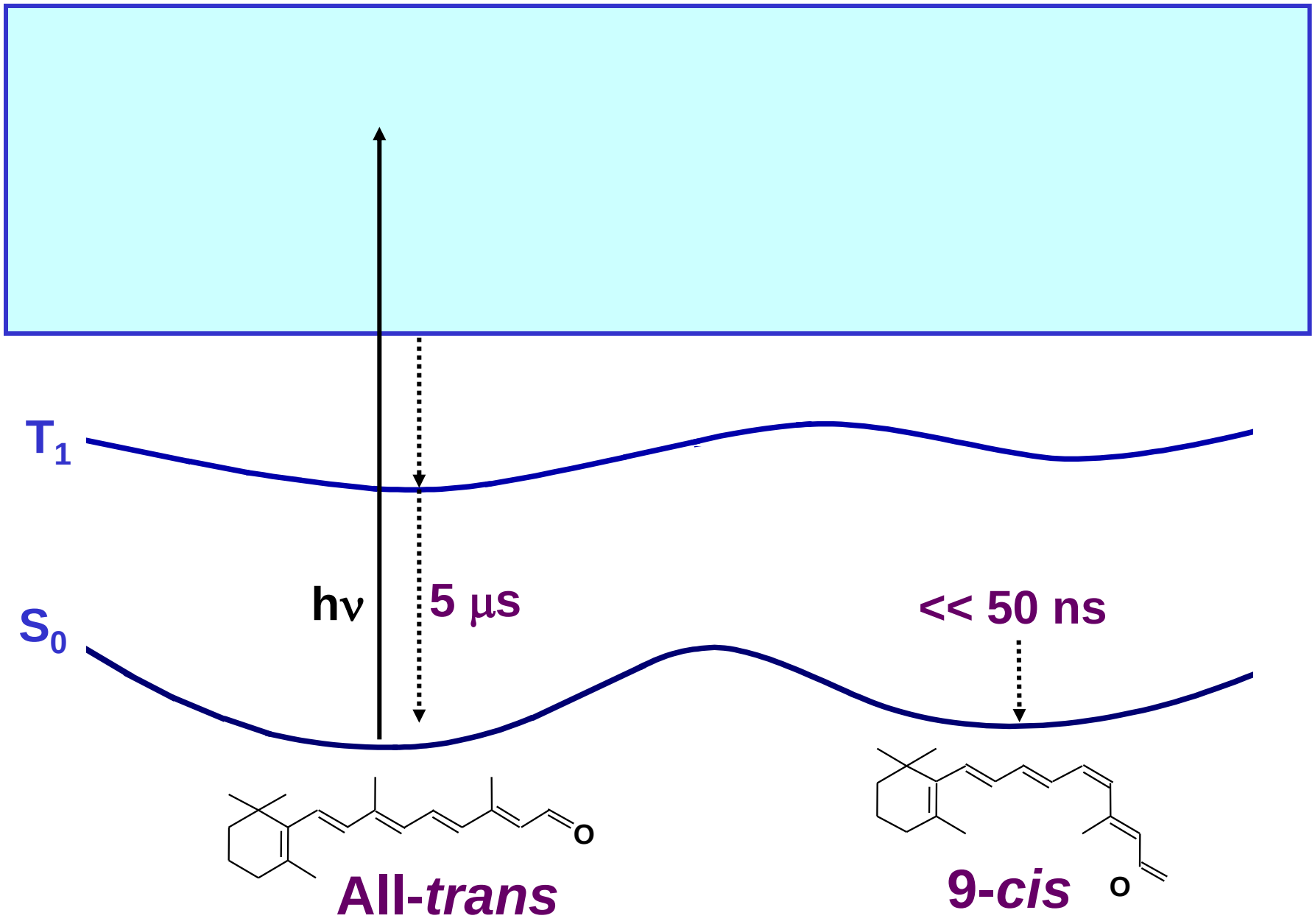
Photoisomerization Pathway of All-*trans*-retinal in Cyclohexane



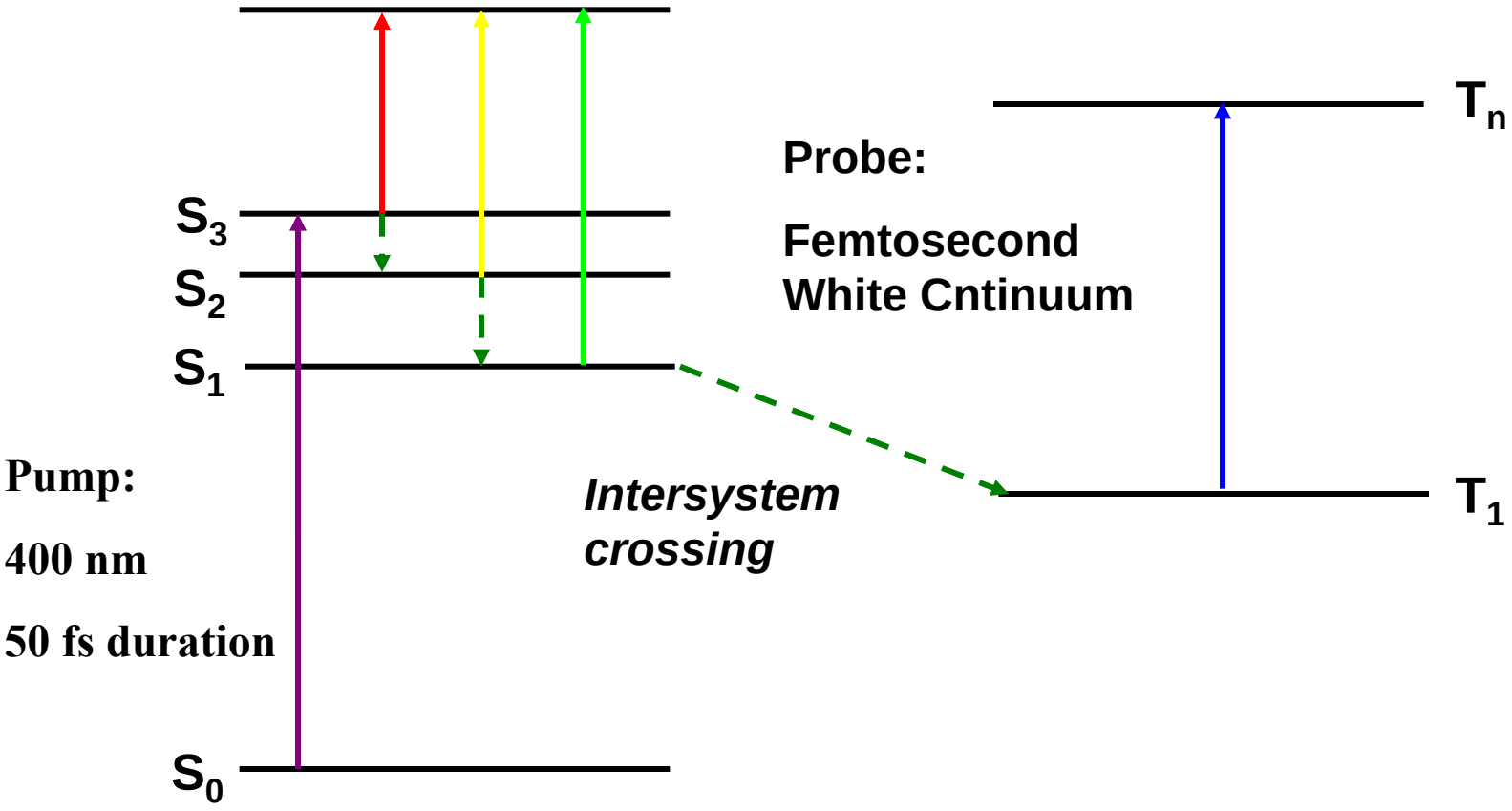




Two Relaxation Pathway of the Photoexcited All-*trans*-retinal



Femtosecond Pump/Probe Time-resolved Visible and Ultraviolet Absorption Spectroscopy of Retinal Isomers

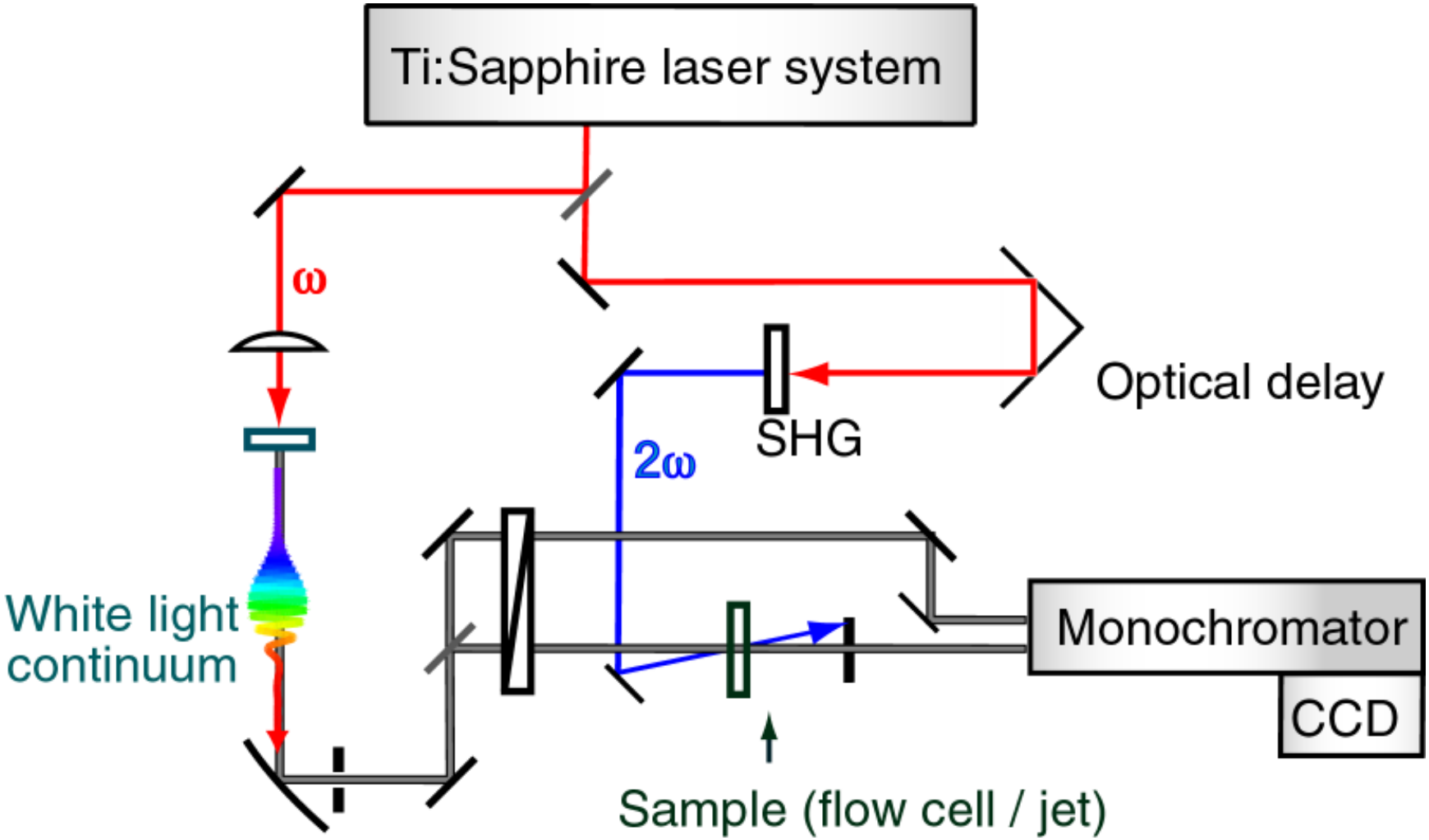


S. Yamaguchi and H. Hamaguchi, J. Mol. Struct. **379**, 87-92 (1996).

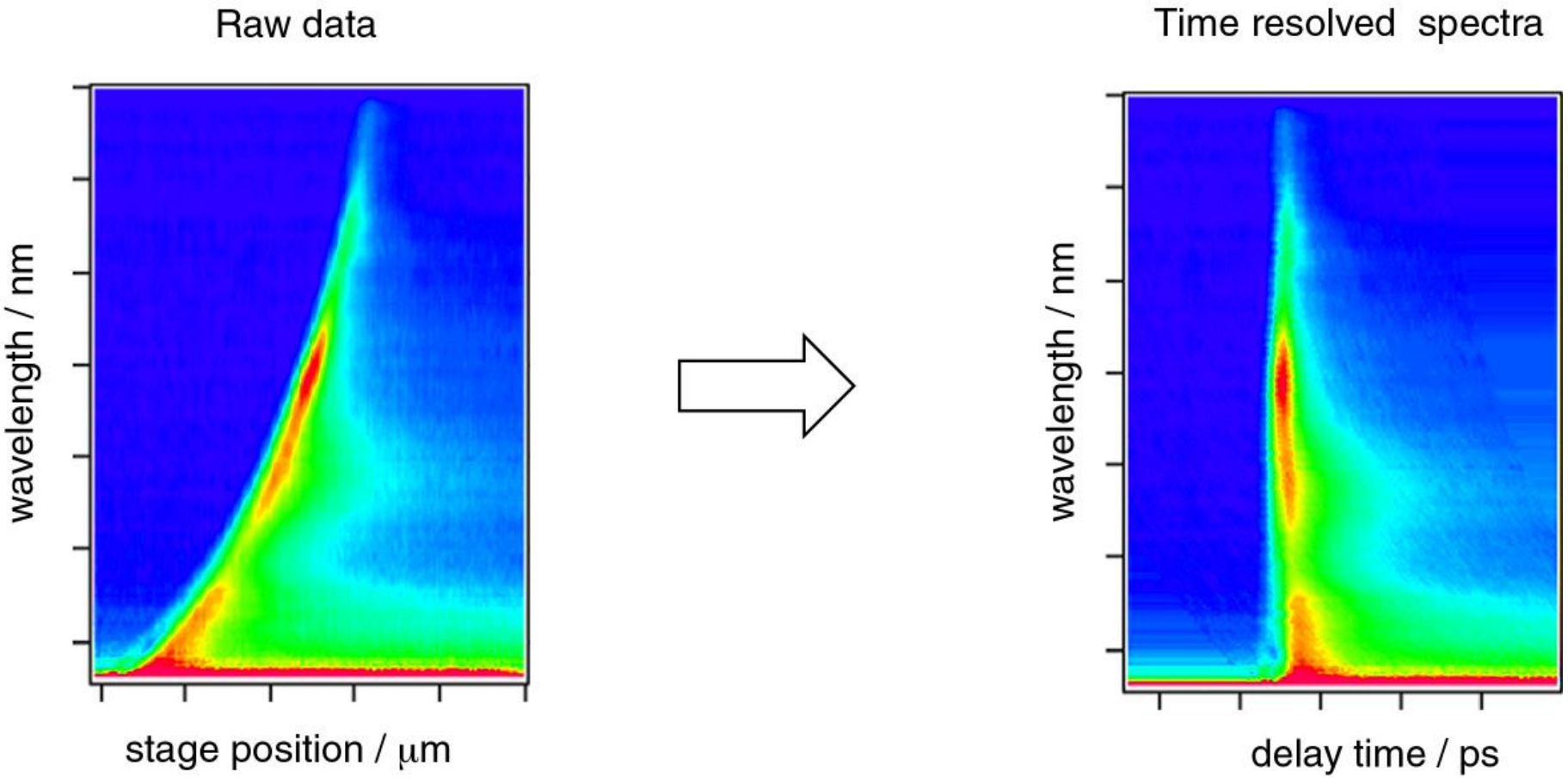
S. Yamaguchi and H. Hamaguchi, J. Chem. Phys. **109**, 1397-1408 (1998).

H. Minami and H. Hamaguchi, to be published.

Femtosecond Time-resolved Visible/Ultraviolet Absorption System

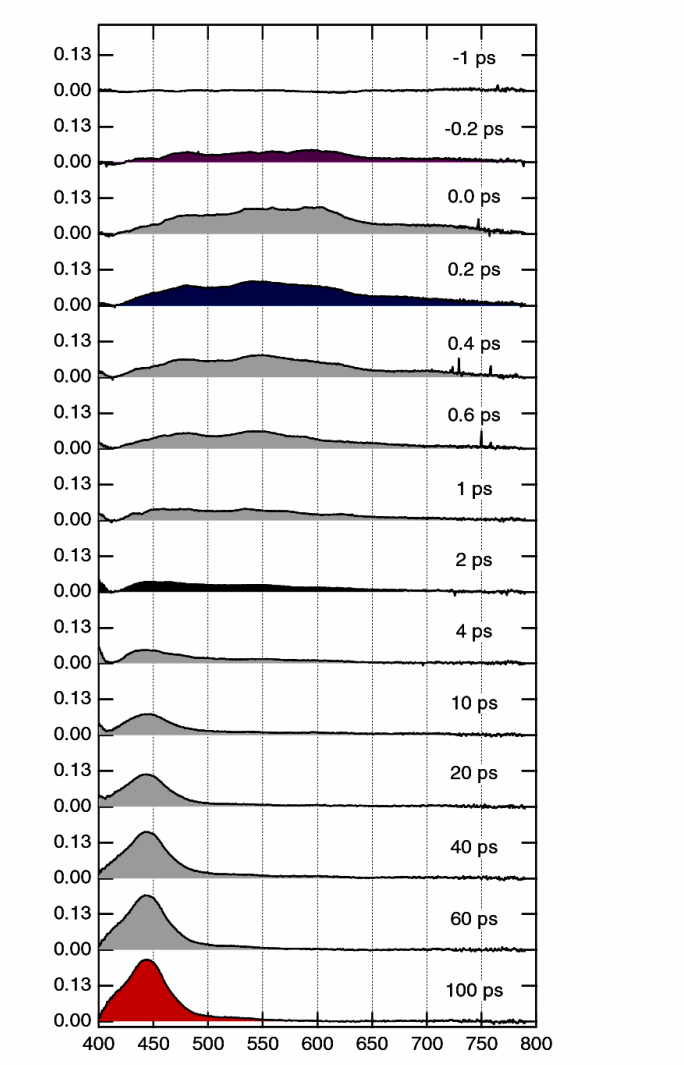


Chirp Correction for the Observed Femtosecond Time-resolved Absorption Spectra



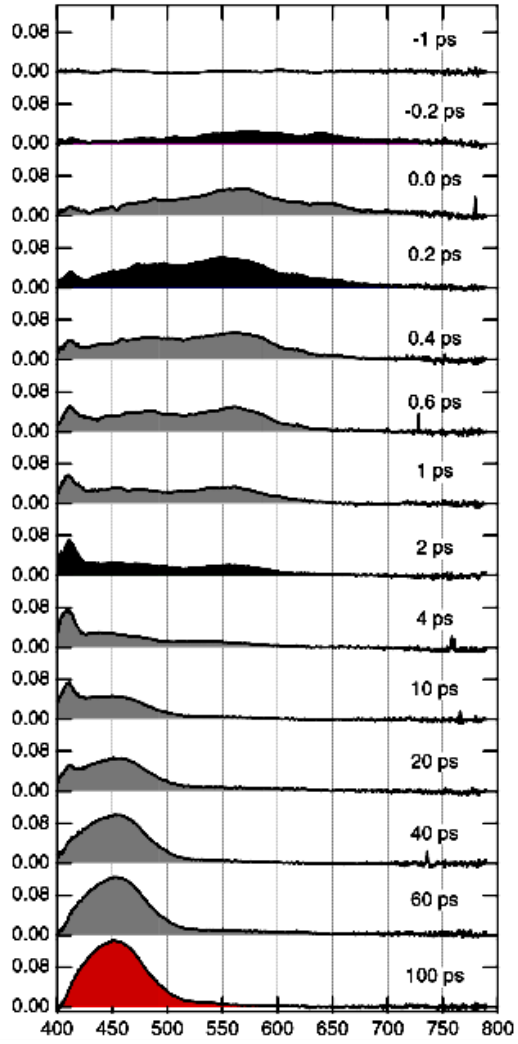
Femtosecond Time-resolved Visible Absorption Spectra in Hexane

All-*trans*



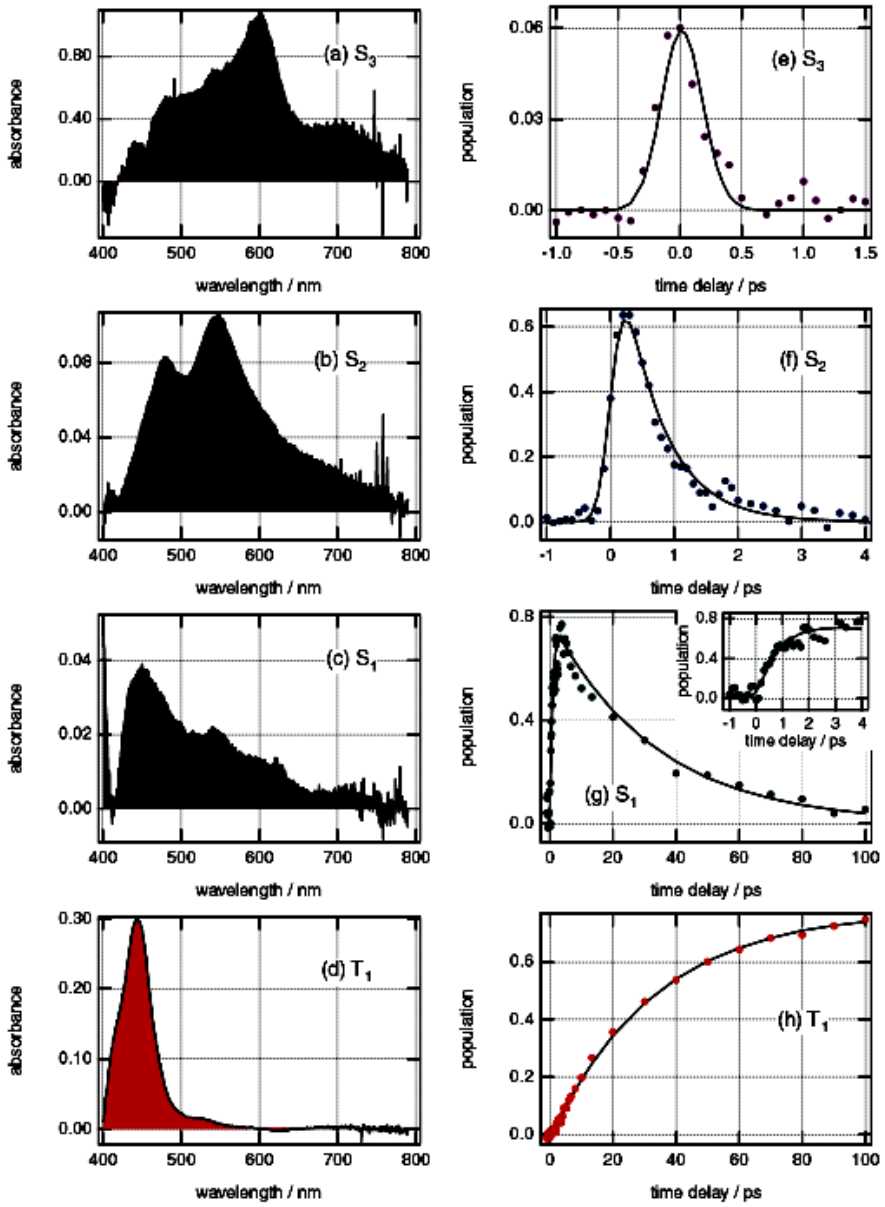
Wavelength / nm

9-*cis*

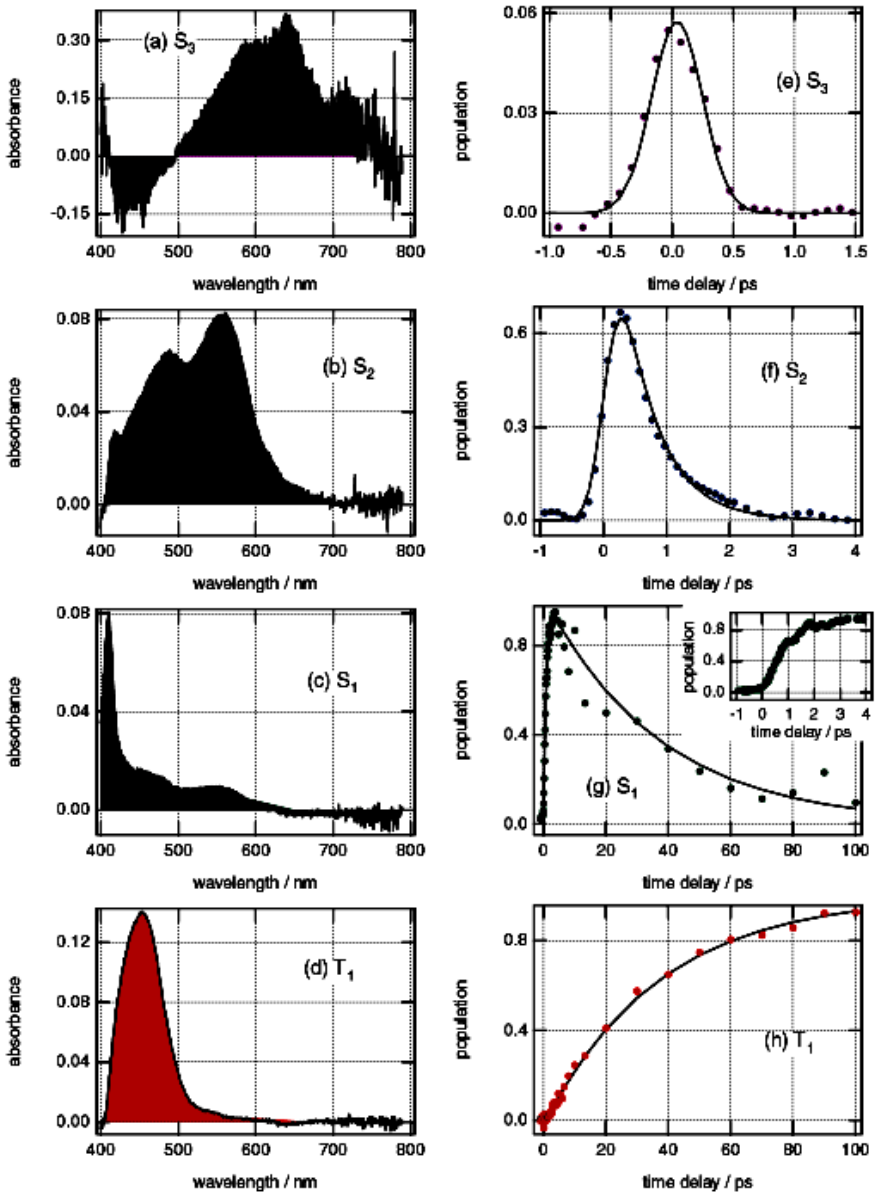


Wavelength / nm

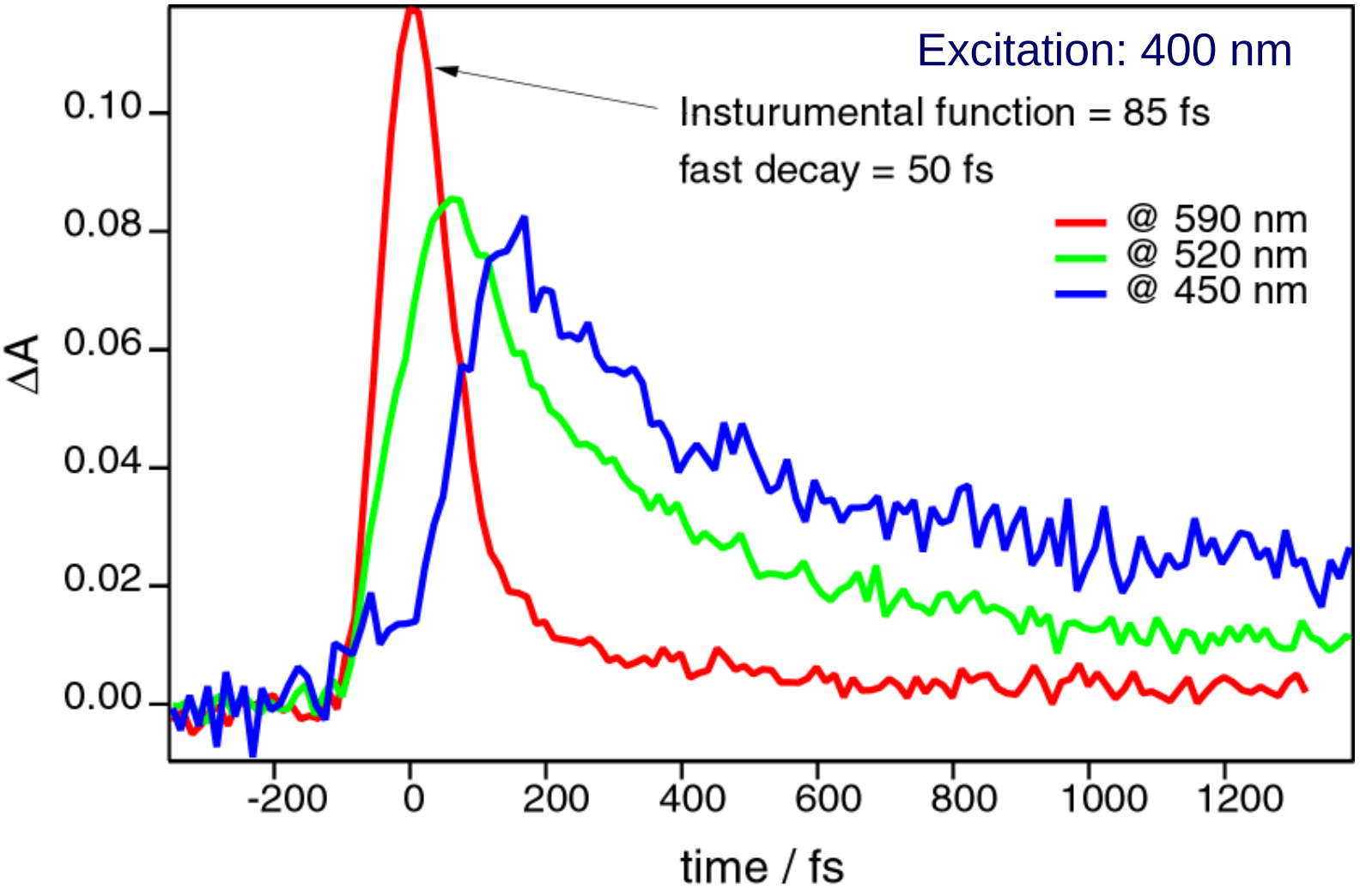
SVD Analysis for All-trans Retinal in Hexane



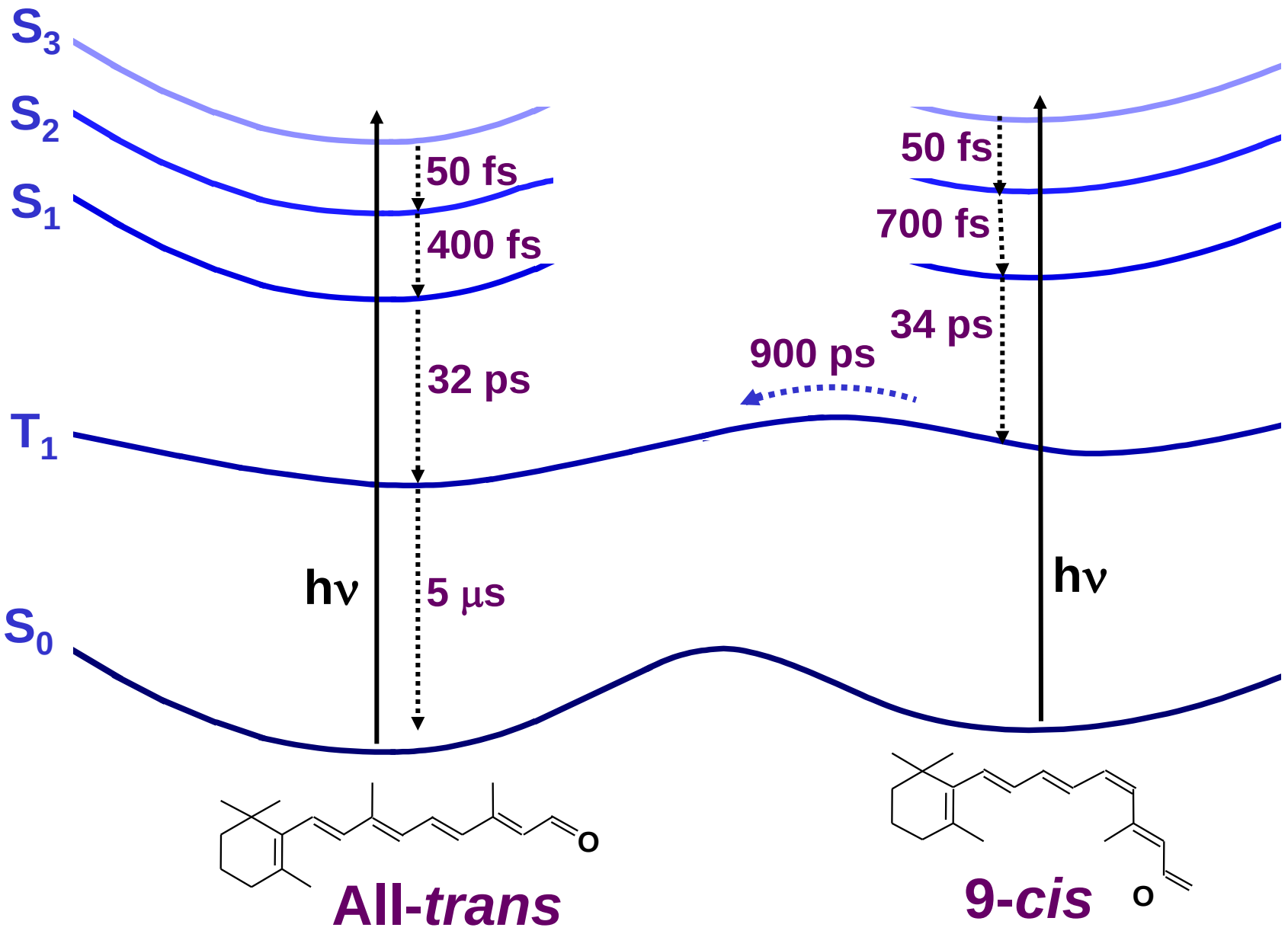
SVD Analysis for 9-cis Retinal in Hexane



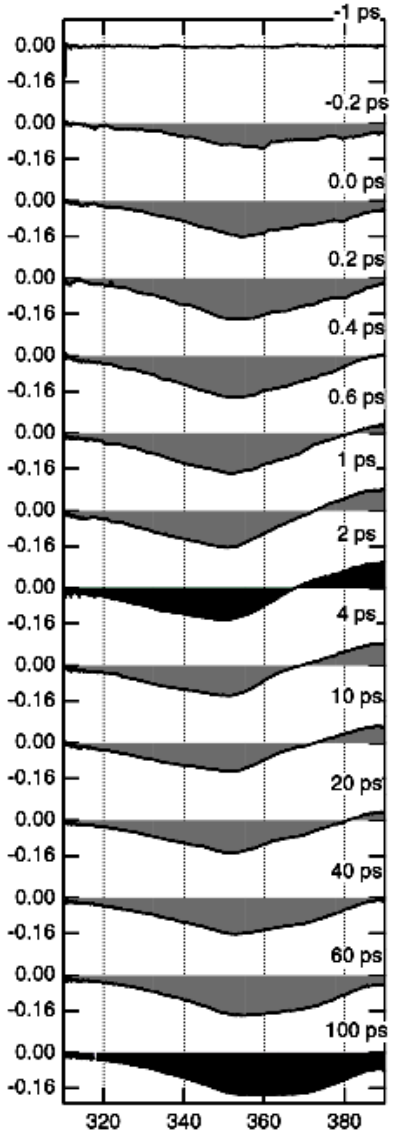
Cascading Decay Kinetics of Photoexcited All-trans-retinal in Heptane



Femtosecond Photoexcitation Dynamics of Retinal Isomers

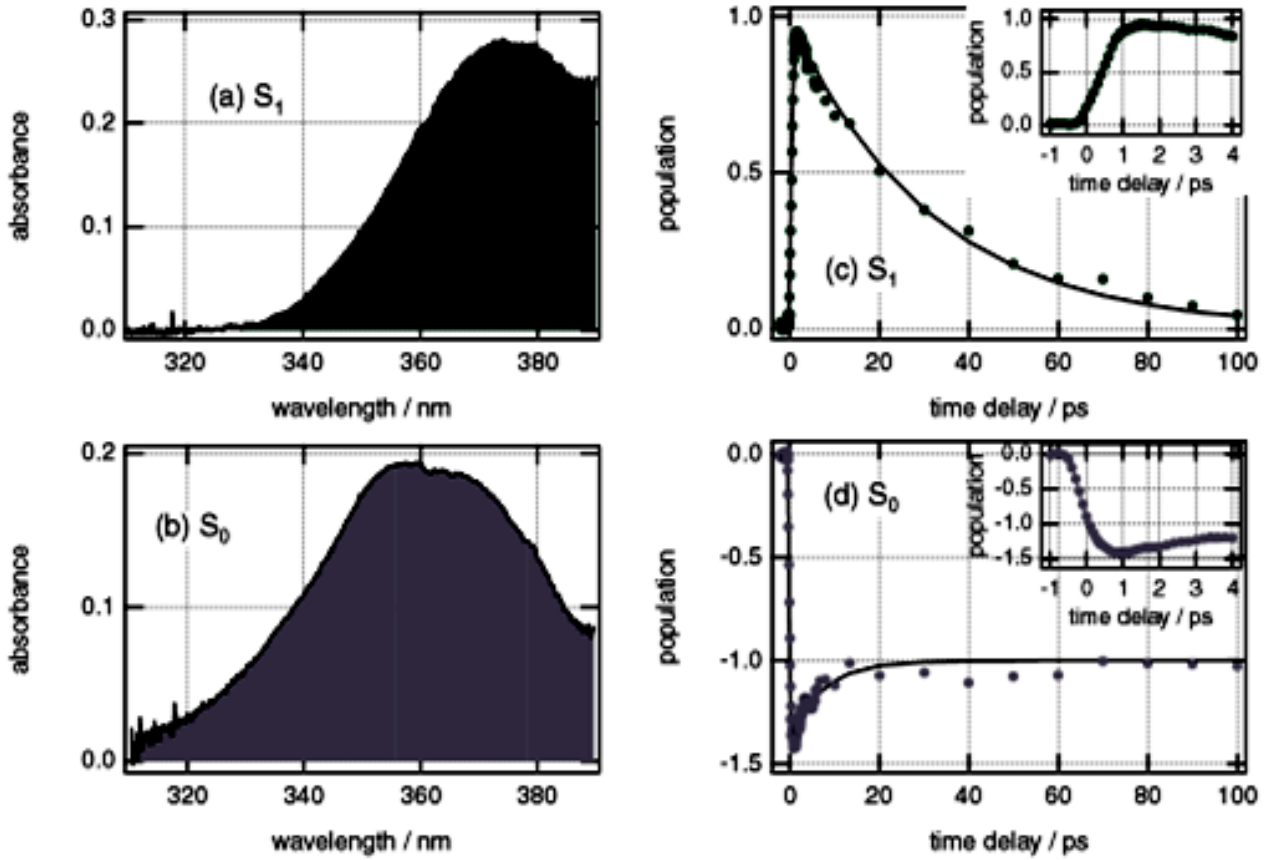


Femtosecond Time-resolved Ultraviolet Absorption Spectra of All-trans retinal in Hexane

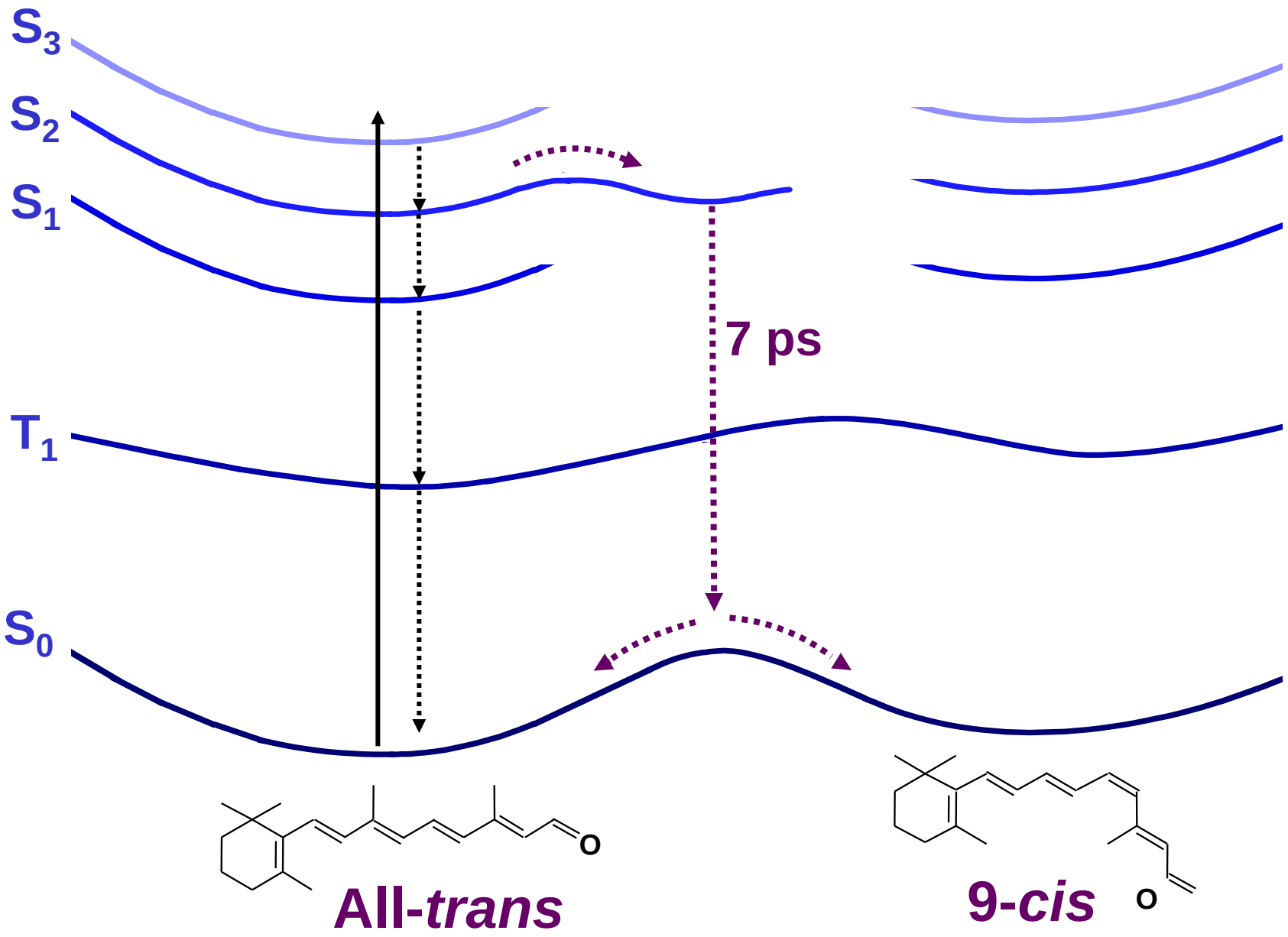


Wavelength / nm

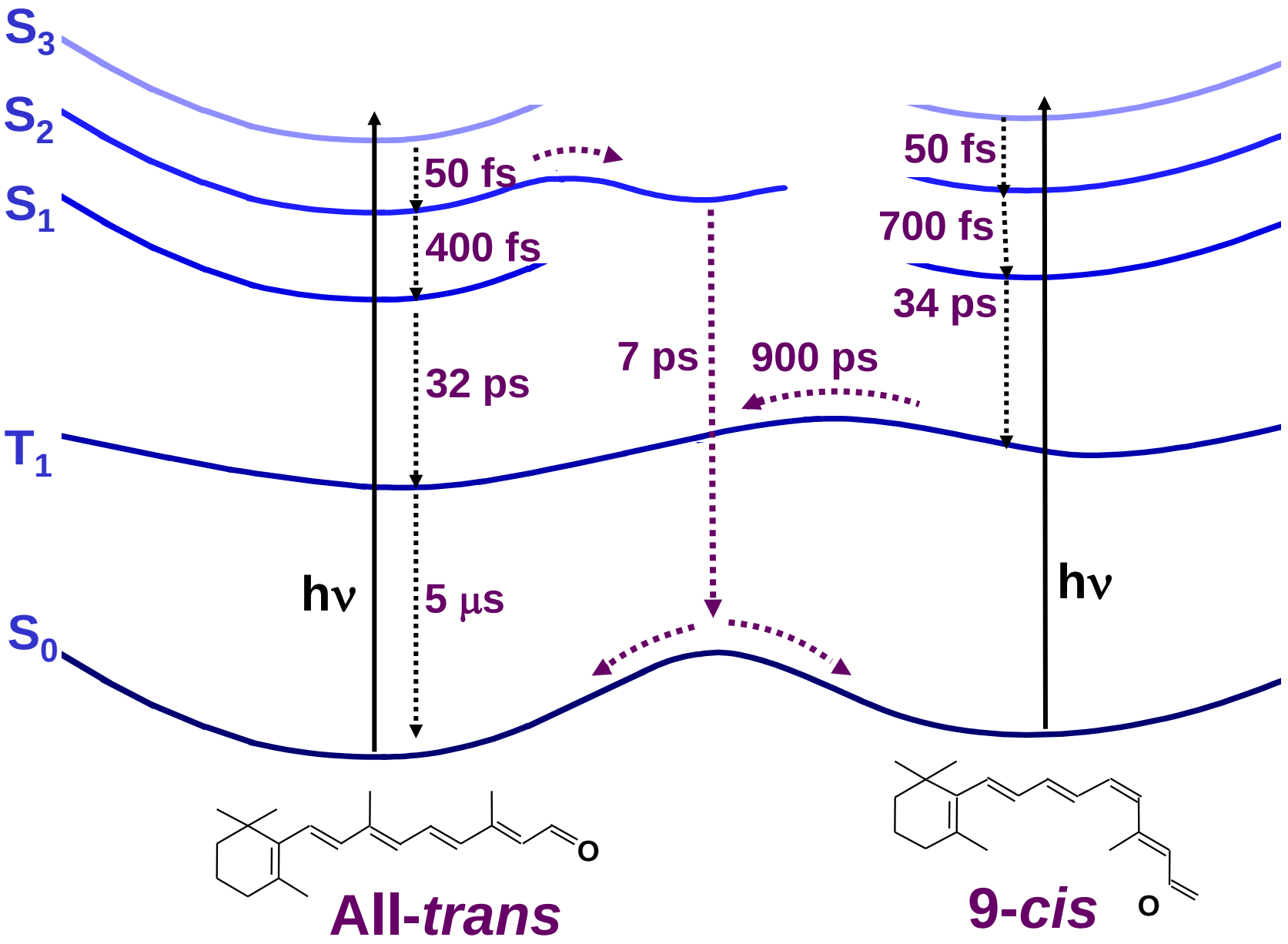
SVD Analysis of the Femtosecond Time-resolved Ultraviolet Absorption Spectra of All-trans-retinal in Hexane



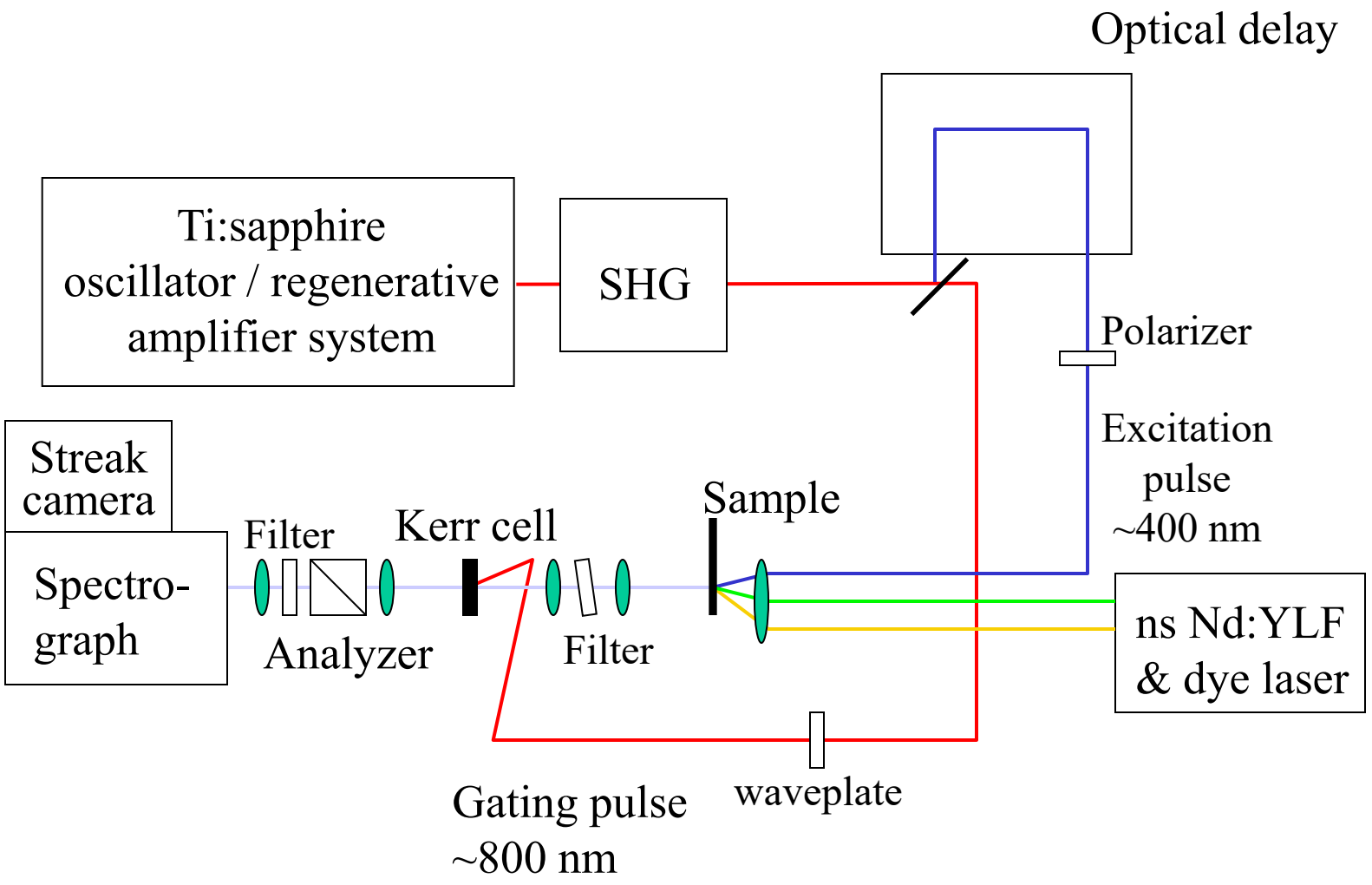
Trans to *Cis* Isomerization via the S2 state



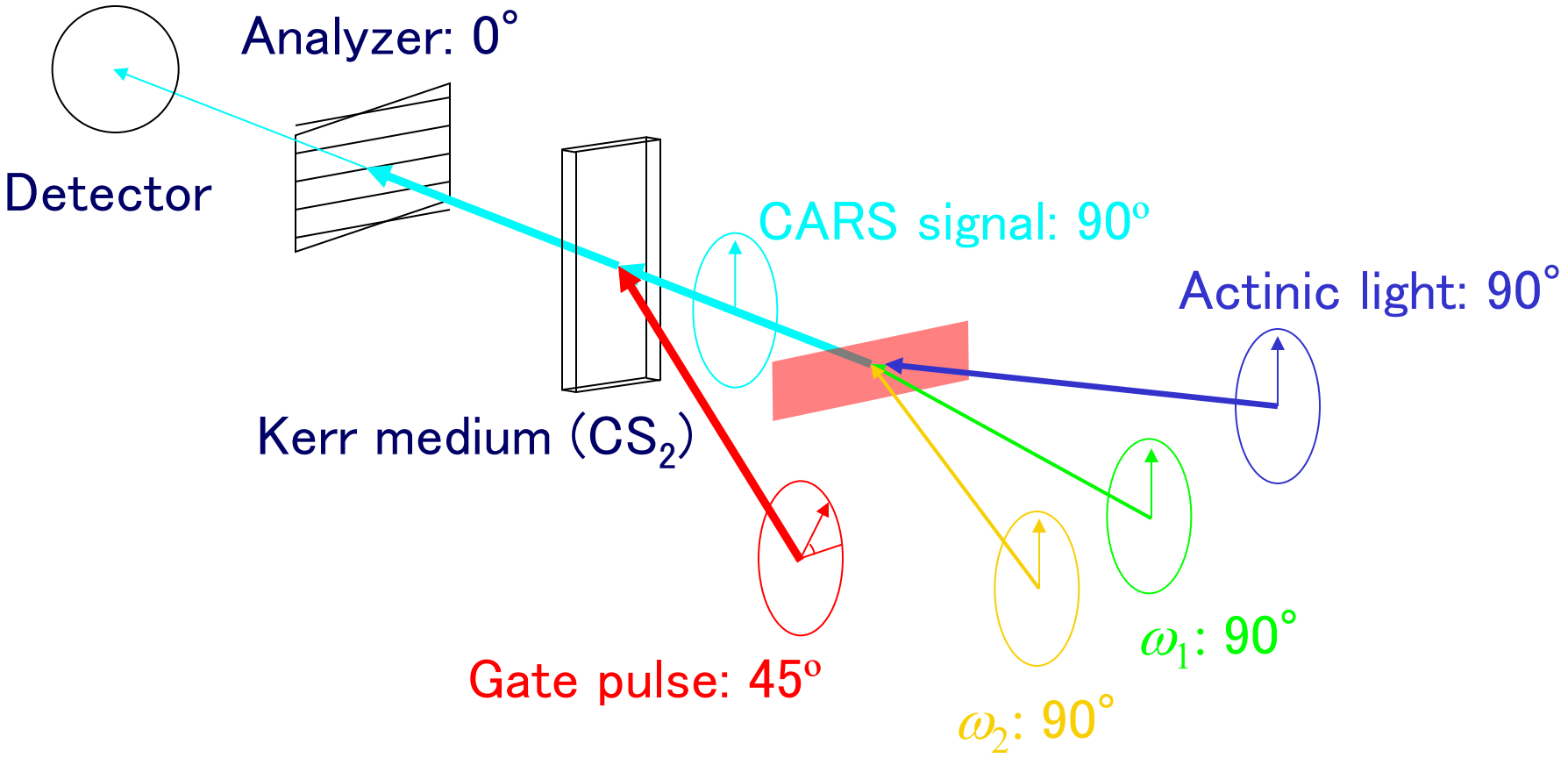
Photoisomerization Pathways and Dynamics of Retinal Isomers



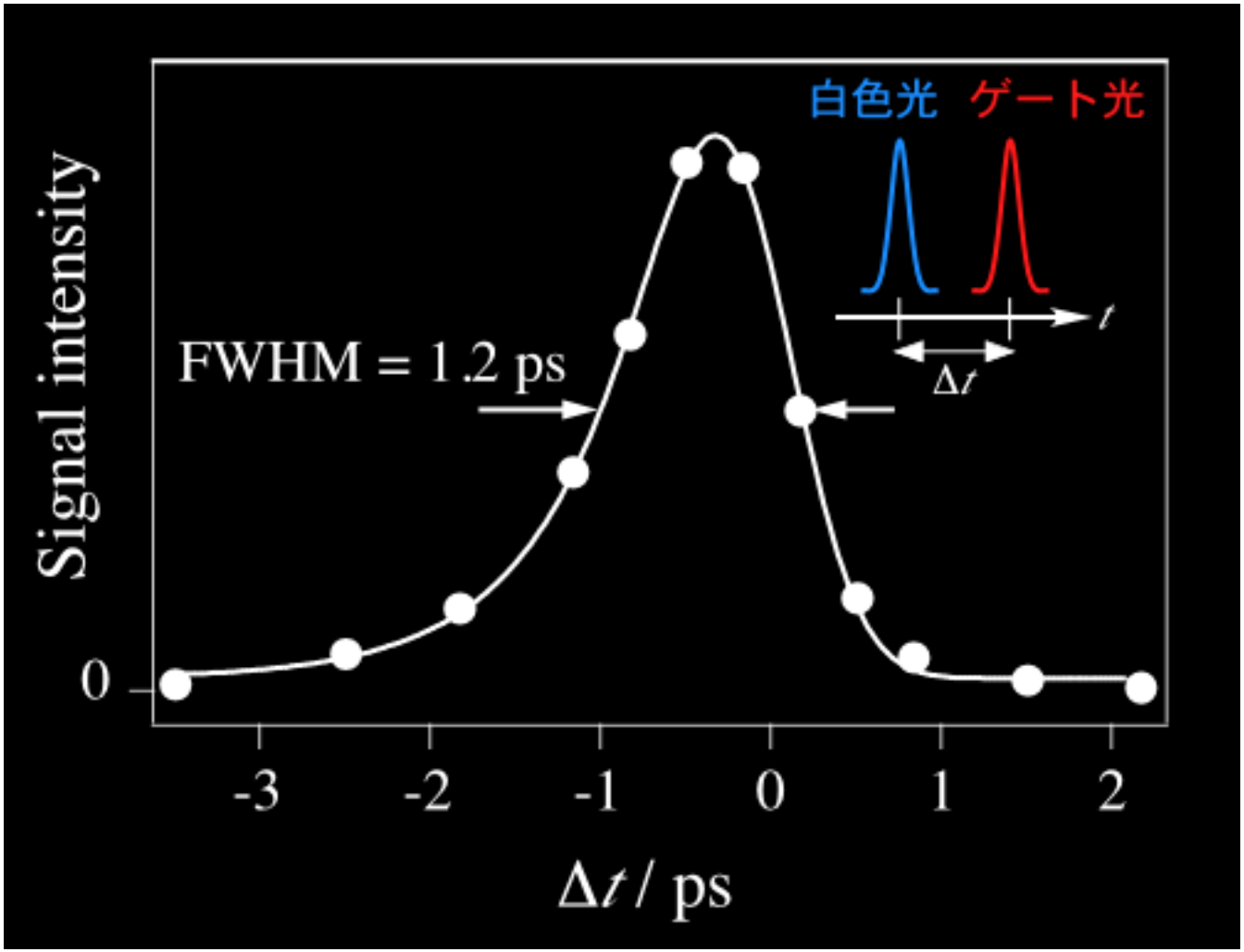
Picosecond Time-resolved 2-D CARS Spectroscopy with an Optical Kerr Gating



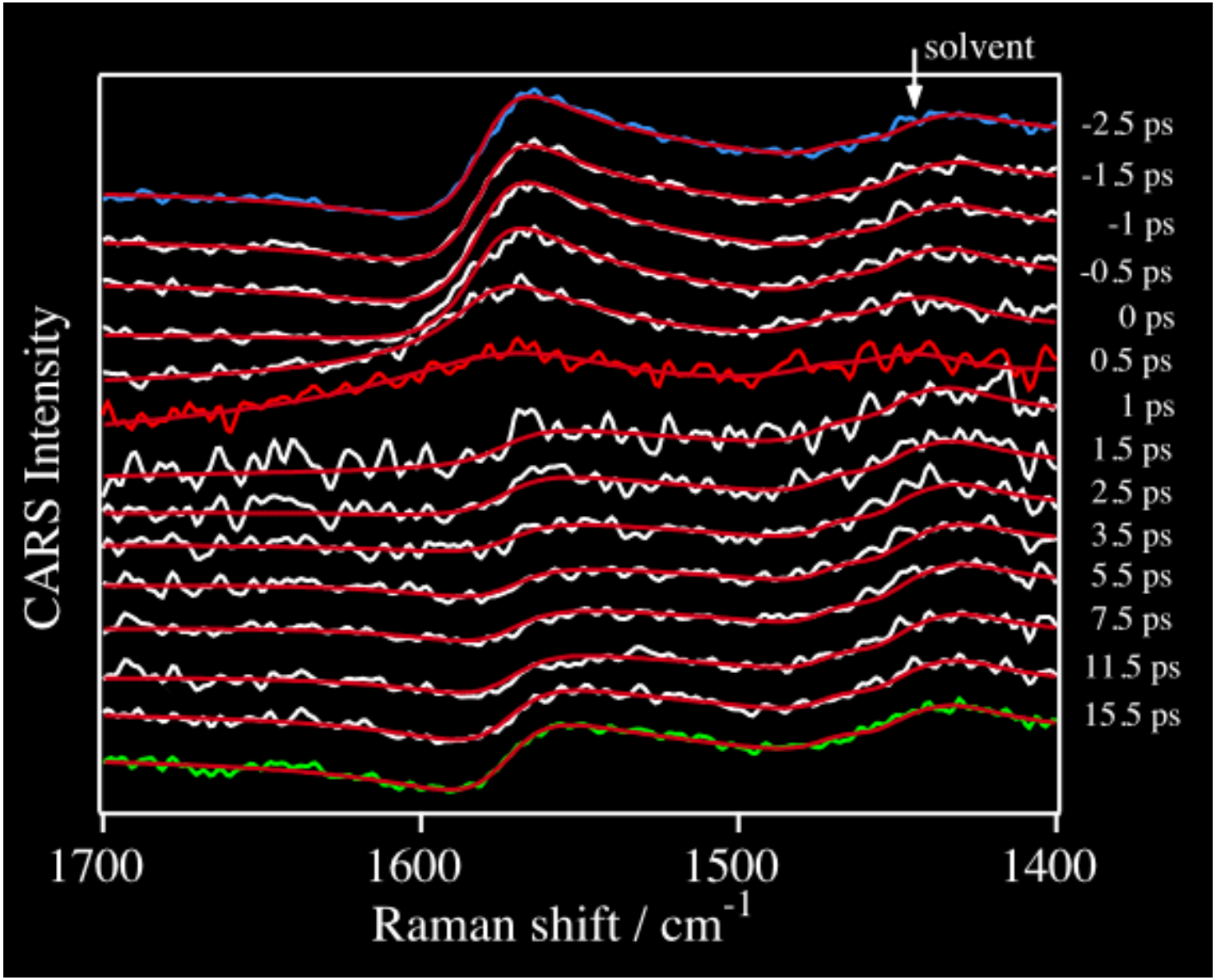
Optical Kerr Gating



Optical Kerr Gated Picosecond CARS Spectroscopy

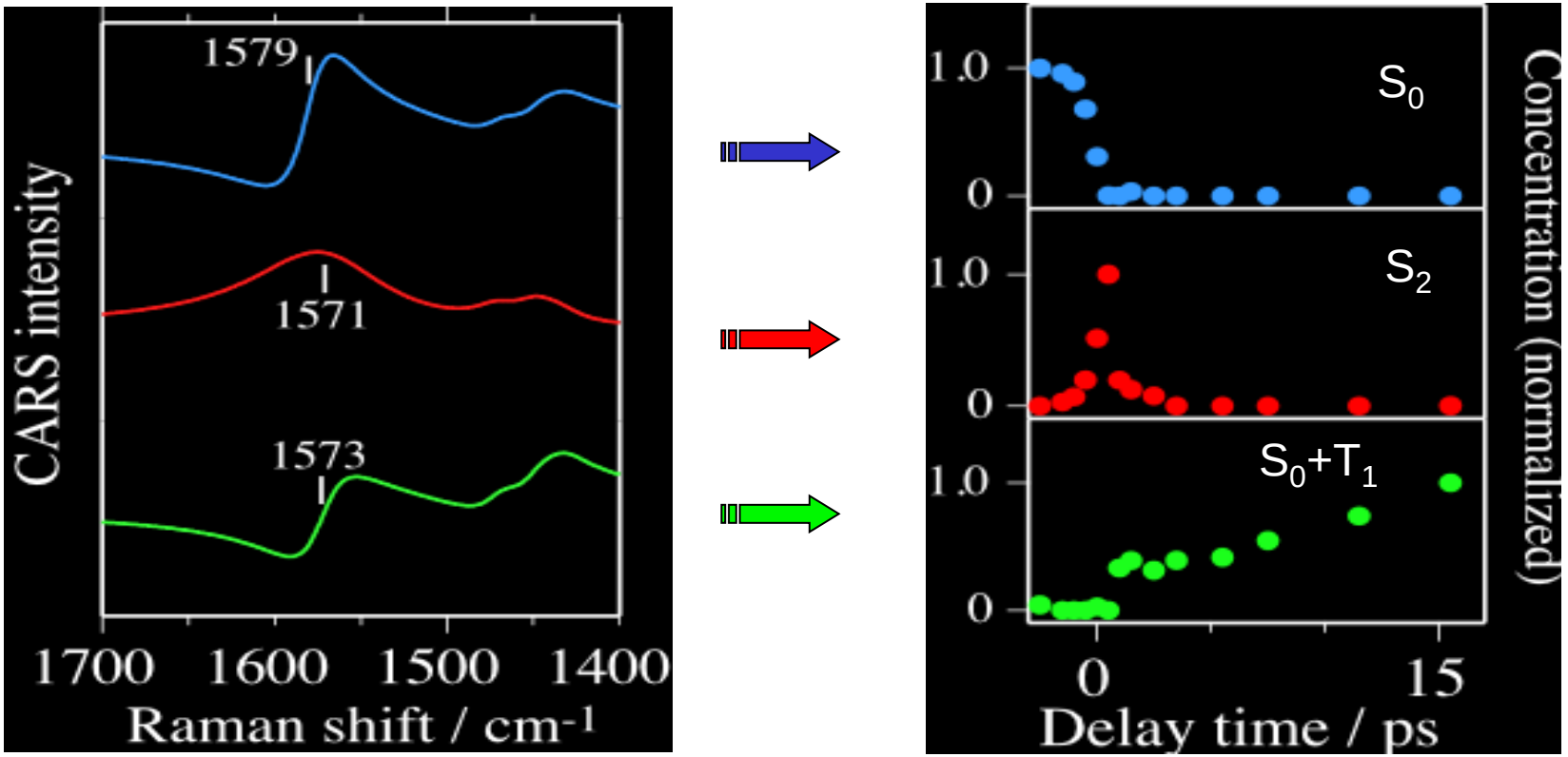


Picosecond Time-resolved CARS Spectra of Photoexcited All-*trans* Retinal in Ethanol : Simulation



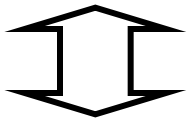
K. Ishii and H. Hamaguchi, Chem. Phys. Lett, **367**, 672 (2003).

First Observation of the key intermediate S_2

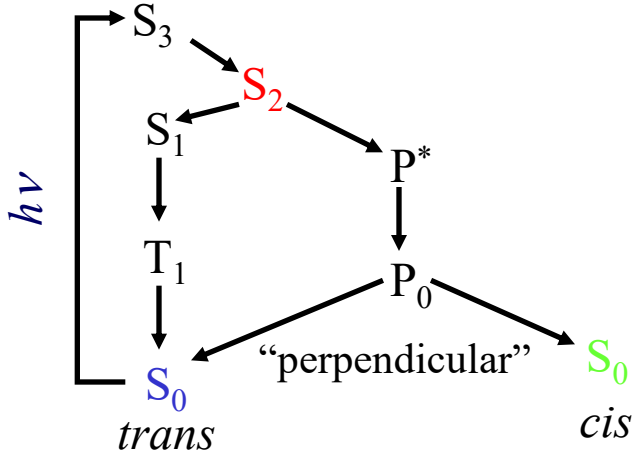


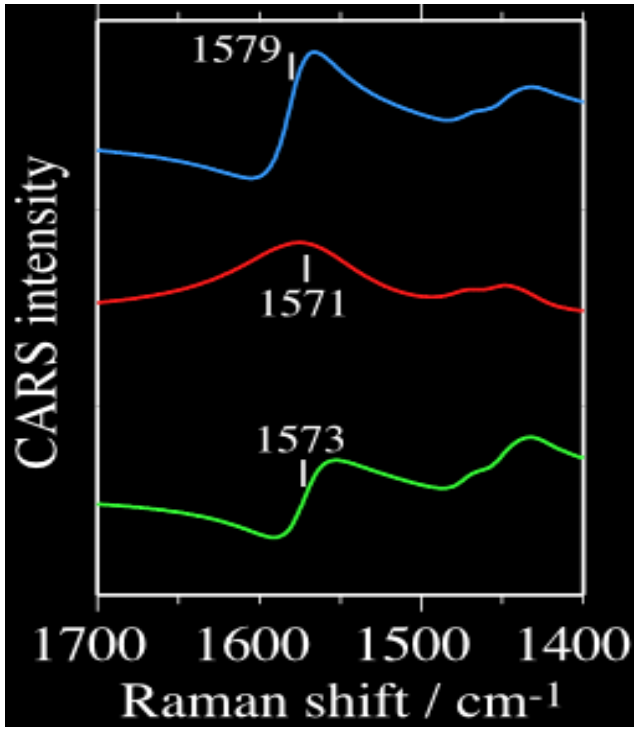
Large band width of the C=C band (100 cm^{-1})

Very fast vibrational dephasing



Dynamic polarization model of isomerization

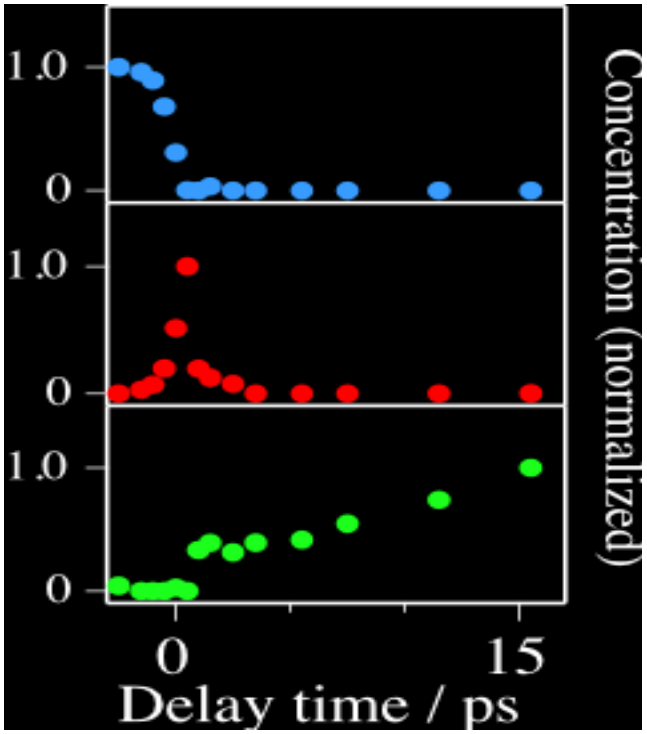


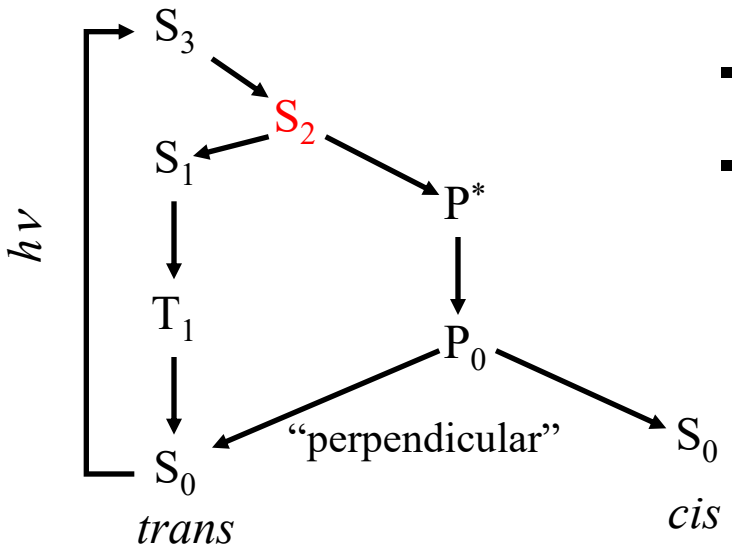


S_0の減少

S_2の生成、消滅

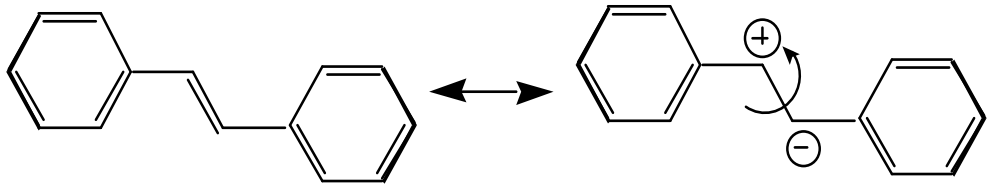
S_0の回復
Cis体の生成
T_1の生成





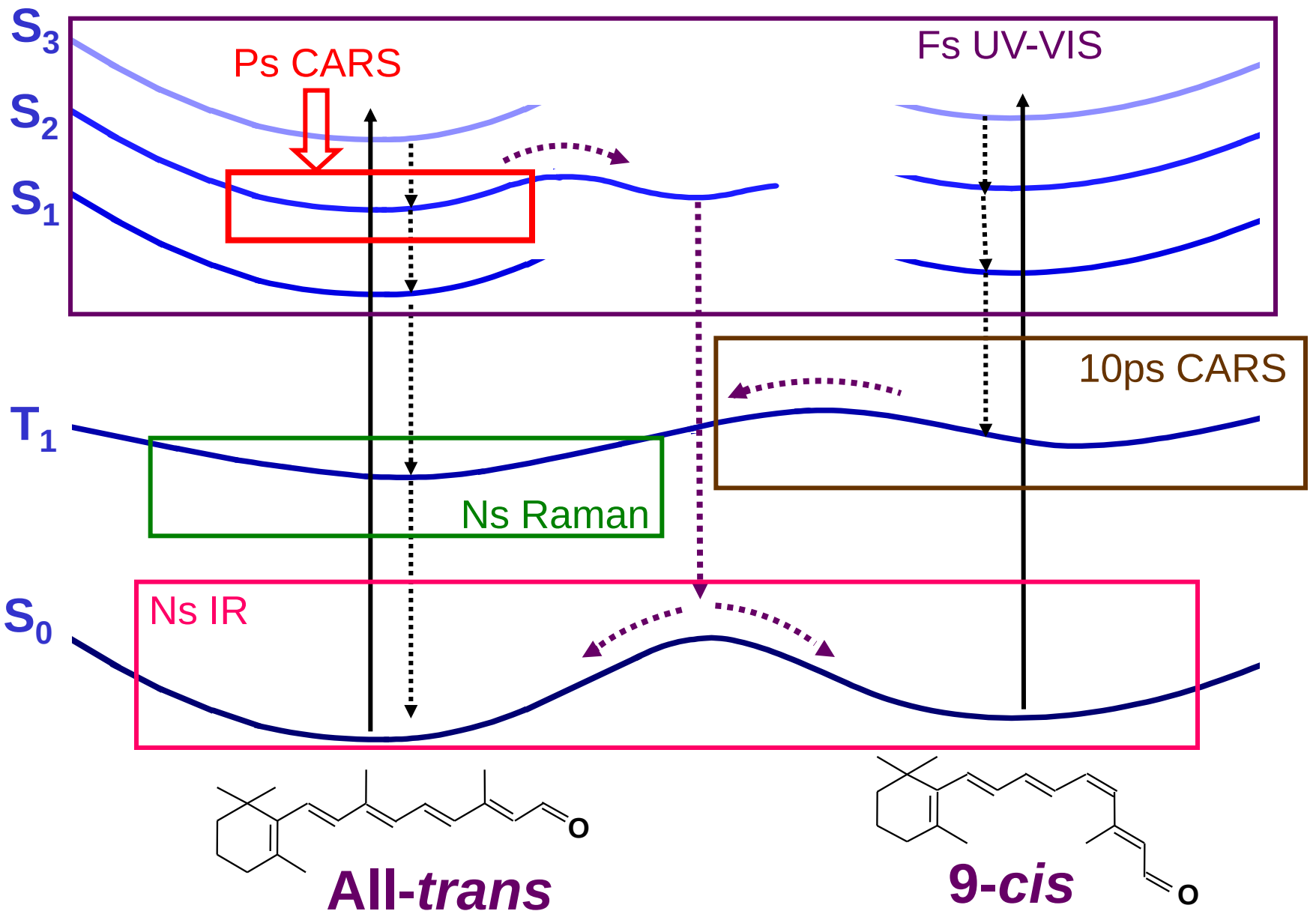
- S_2の振動スペクトル測定に初めて成功
- C=C伸縮バンドの顕著な広幅化(100cm^{-1})

異性化反応の動的分極理論と符合



動的分極

Time-resolved Spectroscopies Look at Photoisomerization of Retinal



All-*trans*

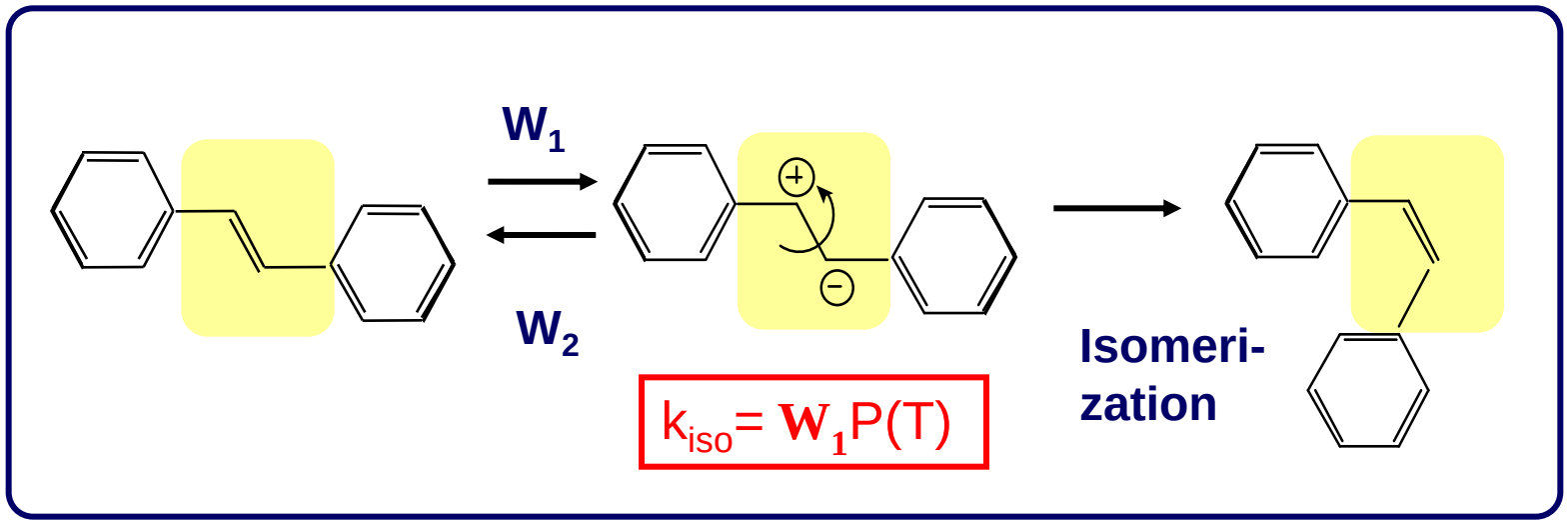
9-*cis*

Dynamic Polarization Model of Isomerization

Hamaguchi, Iwata, *CPL* **208**, 465 (1993).

Deckert, Iwata, Hamaguchi, *J. Photochem. Photobiol*. **102**, 35 (1996).

Iwata, Ozawa, Hamaguchi, *JCP* **106**, 3614 (2002).



k_{iso}=Aexp(-ΔE/RT) : Arrhenius formula

ΔE=3.5 kcal mol^{-1} (fluorecsence lifetime)

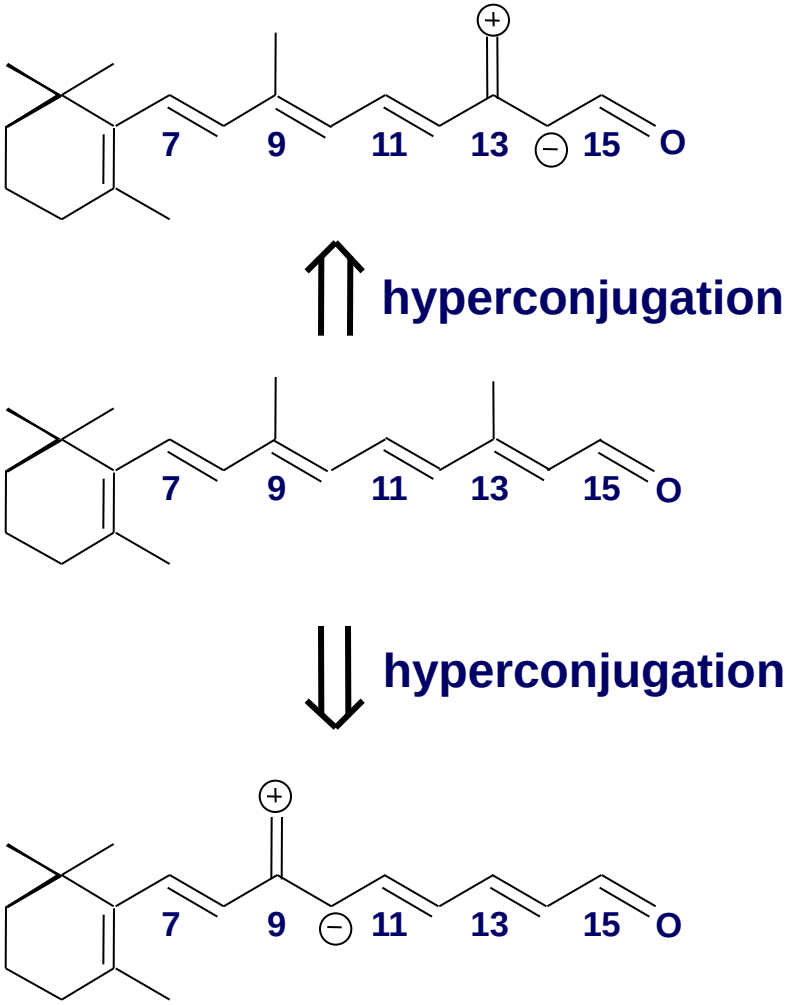
$k_{iso}=W_1P(T)$: Dynamic Polarization Model

ΔE=3.5~3.7 kcal mol^{-1} (Raman band shape)

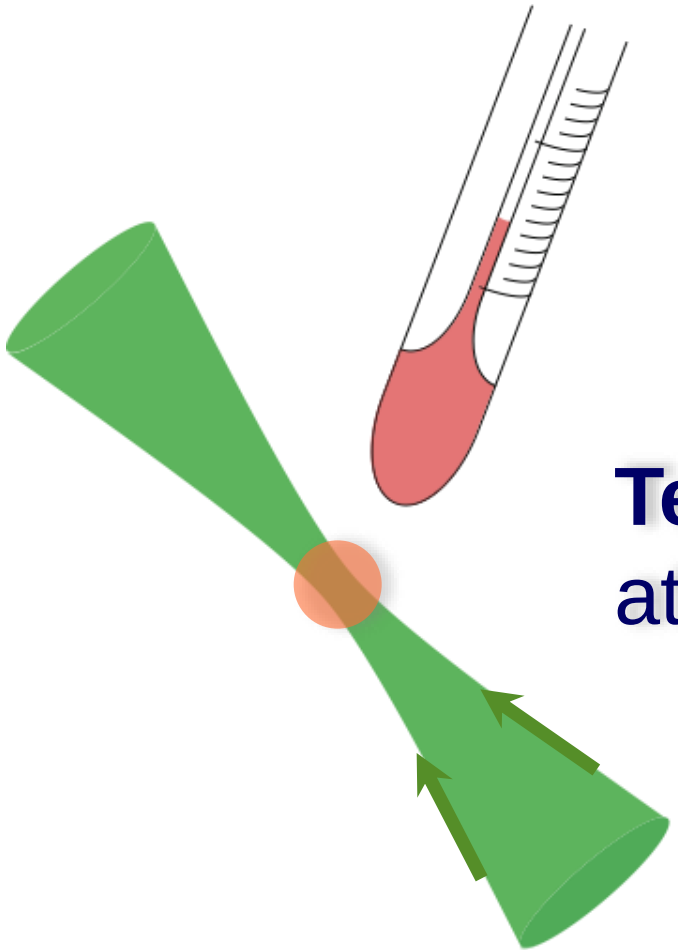
A new view on isomerization has come out of picosecond Raman spectroscopy !

Dynamic Polarization Model for the Retinal Photoisomerization

Why are 13-cis and 9-cis selected?

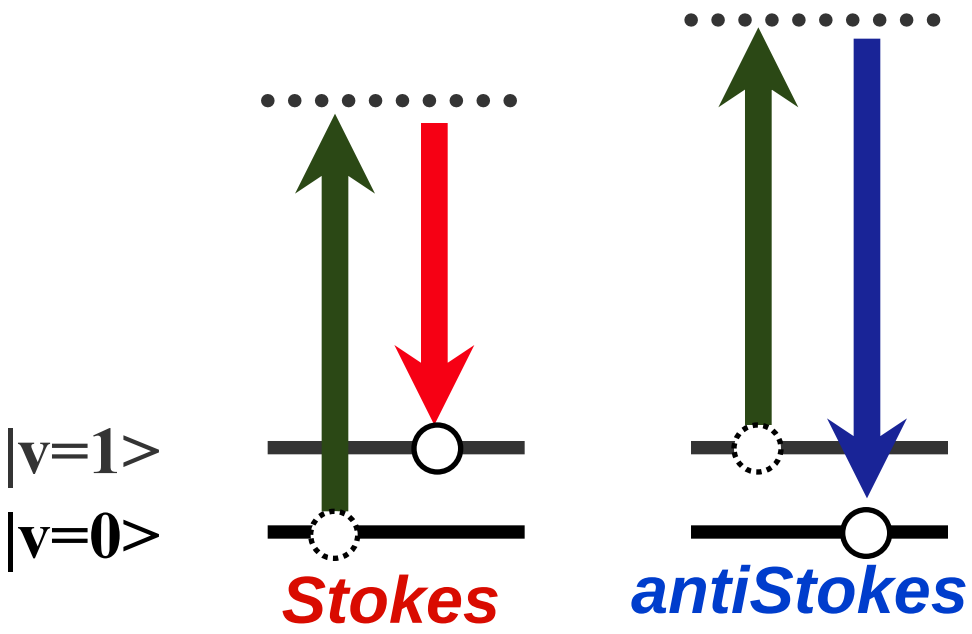


Absolute Temperature Determination with Stokes/anti-Stokes Raman spectroscopy



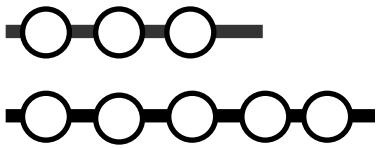
Temperature
at the laser focal spot?

Stokes/anti-Stokes Raman Scattering



Boltzmann factor

$$\exp\left[-\frac{\Delta E}{k_B T}\right]$$



Off-resonance Raman scattering

$$\frac{I_{\mathbf{antiStokes}}}{I_{\mathbf{Stokes}}} = \exp\left[-\frac{ch}{k_B T}\tilde{\nu}\right]\left(\frac{\tilde{\nu}_0+\tilde{\nu}}{\tilde{\nu}_0-\tilde{\nu}}\right)^3$$

Sensitivity Calibration with Standard Light

$$\mathbf{I^{obs}}\,[\tilde{\nu}] = \mathrm{Sensitivity}\,[\tilde{\nu}] \times \mathbf{I^{real}}\,[\tilde{\nu}]$$

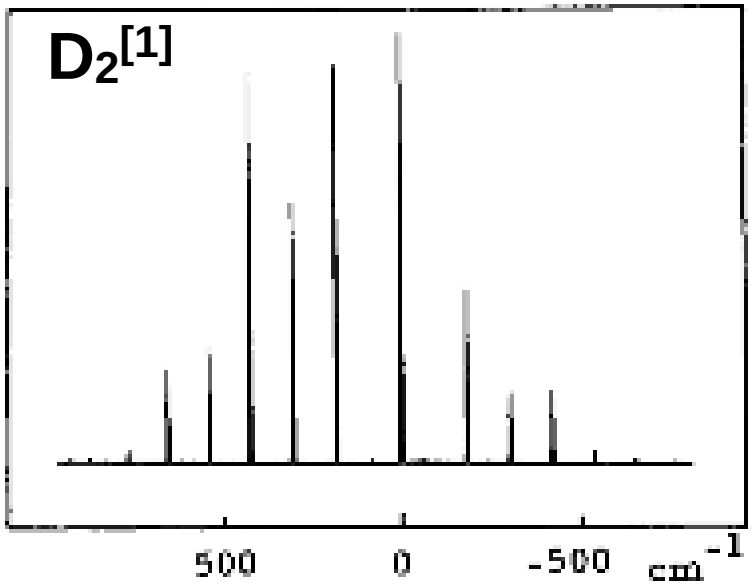
Accuracy of Sensitivity Calibration $>$ Accuracy of the Standard Intensity

Rotational Raman spectra as primary intensity standard

Previous study [1]
Sensitivity calibration with D_2

This study

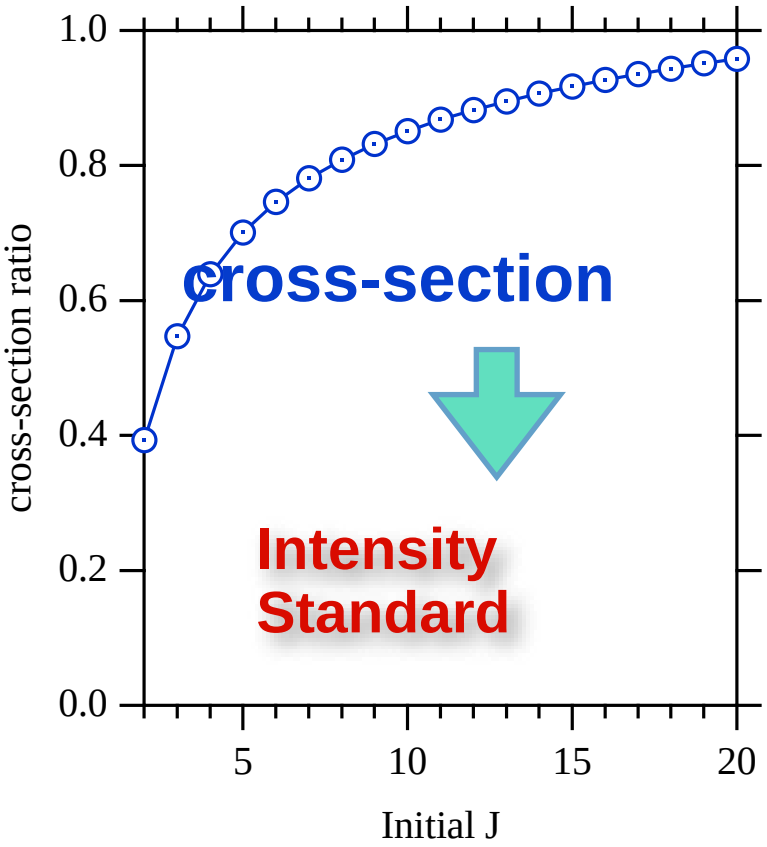
Sensitivity calibration with **N_2**
-200 ~ +200 cm^{-1}, 40 lines
Suitable for **low-frequency region**



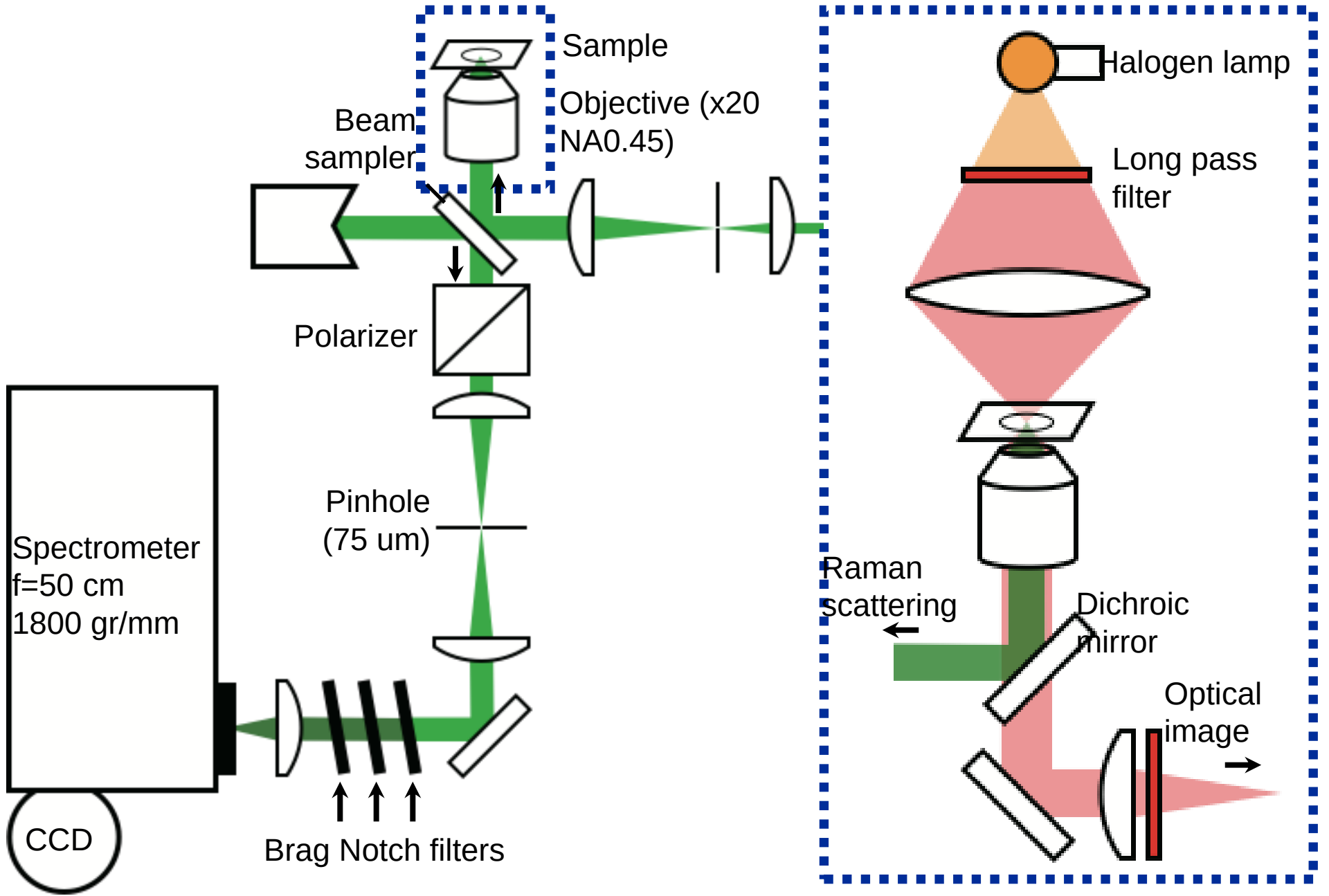
[1] H. Hamaguchi, I. Harada, T. Shimanouchi, Chem. Lett. 1974, 12, 1405-1410.

Calculated Raman Cross Section Ratios of N_2

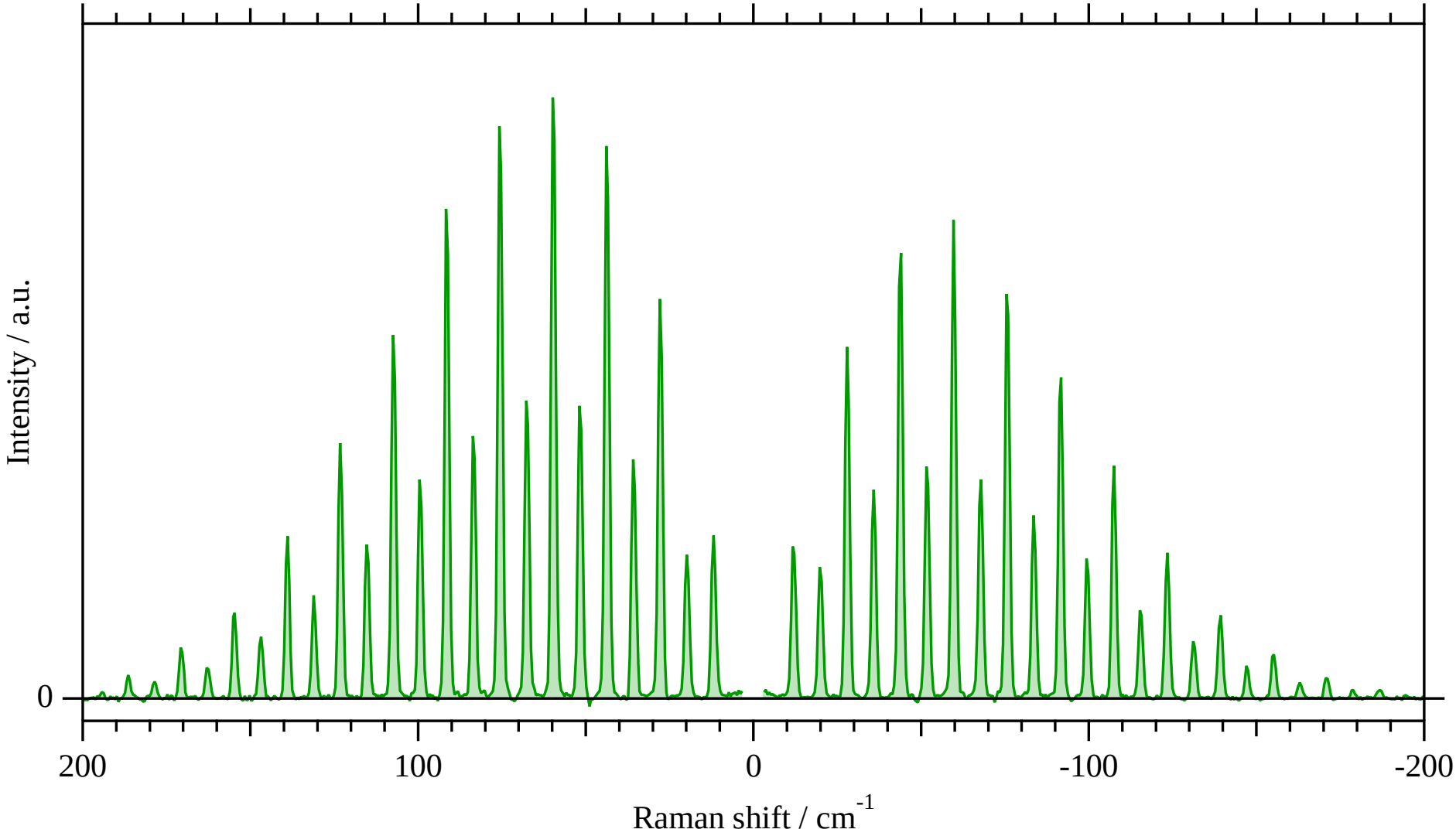
$$\frac{\sigma_{J\to J-2}}{\sigma_{J\to J+2}} = \left(\frac{\tilde{\nu}_0 - \tilde{\nu}_{J\to J-2}}{\tilde{\nu}_0 - \tilde{\nu}_{J\to J+2}}\right)^3 \times \frac{J(J-1)(2J+3)}{(J+1)(J+2)(2J-1)} \times \left|\frac{\langle 0;J|\gamma|0;J-2\rangle}{\langle 0;J|\gamma|0;J+2\rangle}\right|^2$$



Low Frequency Raman Microspectrometer

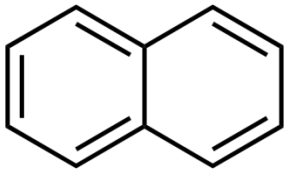


Rotational Raman Spectrum of N_2

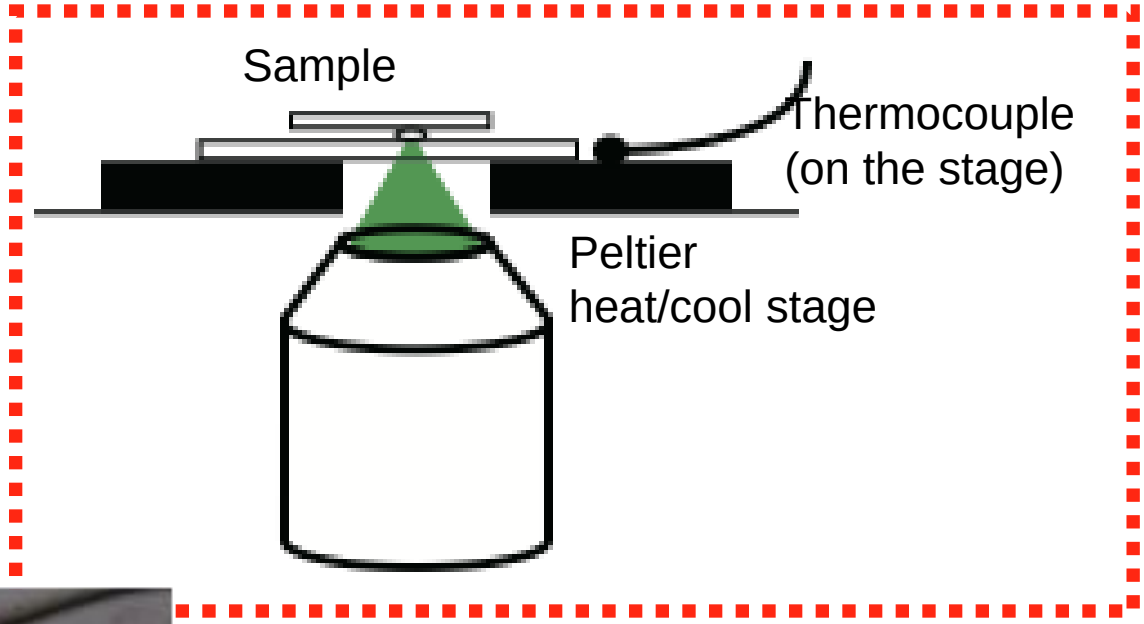


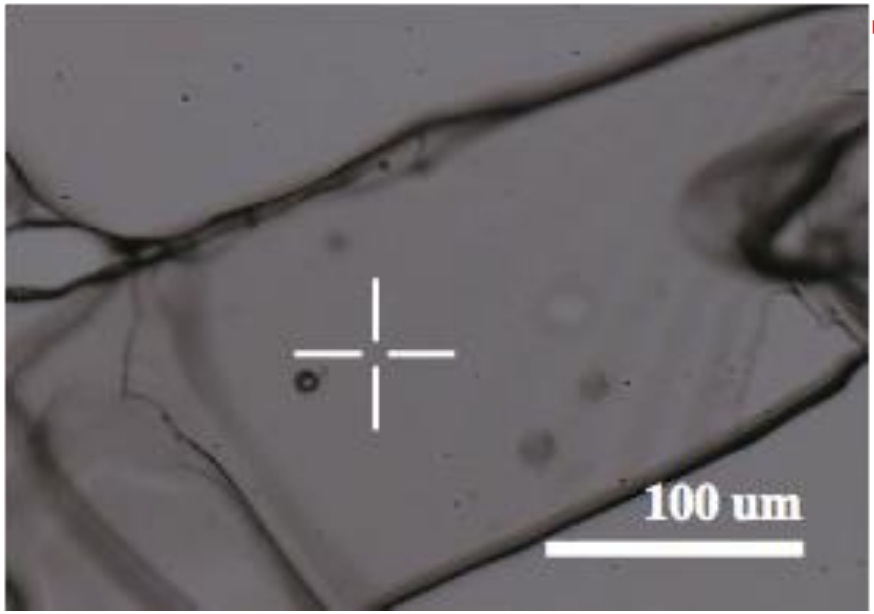
532 nm, 20 mW, x 20 Objective,
exposure: 30 min, resolution: 1.3 cm-1
Background (glass, air) was subtracted

Trace Naphthalene Melting



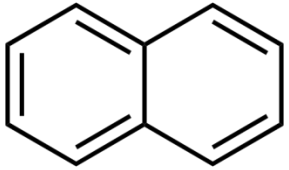
Naphthalene
Mp. 353 K (80 ° C)





532 nm, 4 mW, x 20 Objective
Exposure: 0.1 sec
Cycle: **0.22 sec** / spectrum
Heat speed: **20 K / min**
(on the heat stage)

Low-frequency Raman Spectrum of Naphthalene



solid

532 nm, 4 mW, x 20 Objective,
exposure: 80 sec

Coefficient values ± one standard deviation
w_0 =284.08 ± 0.483
w_1 =0 ± 0

Temperature determination
(-30 to -170 cm^{-1})

$$I_{\mathbf{Stokes}} \times \left(\frac{\tilde{\nu}_0 + \tilde{\nu}}{\tilde{\nu}_0 - \tilde{\nu}}\right)^3 \times \exp\left[-\frac{ch}{k_B T}\tilde{\nu}\right]$$

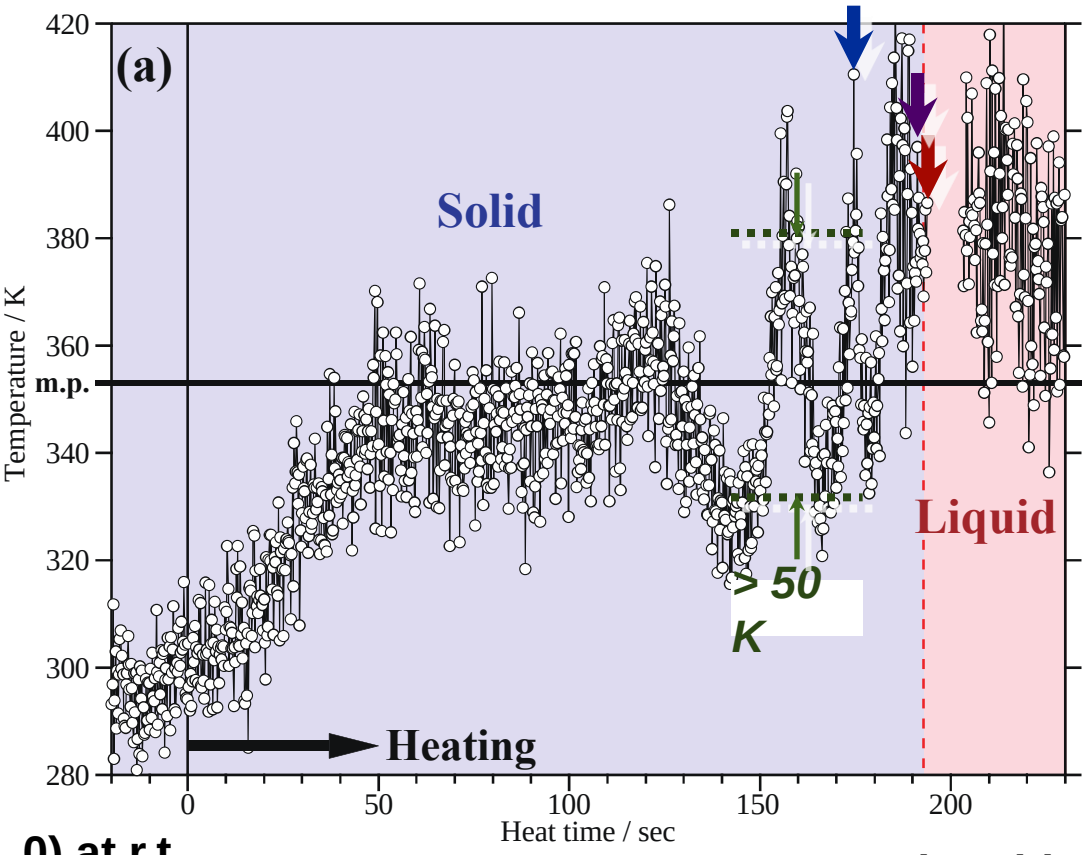
Intensity

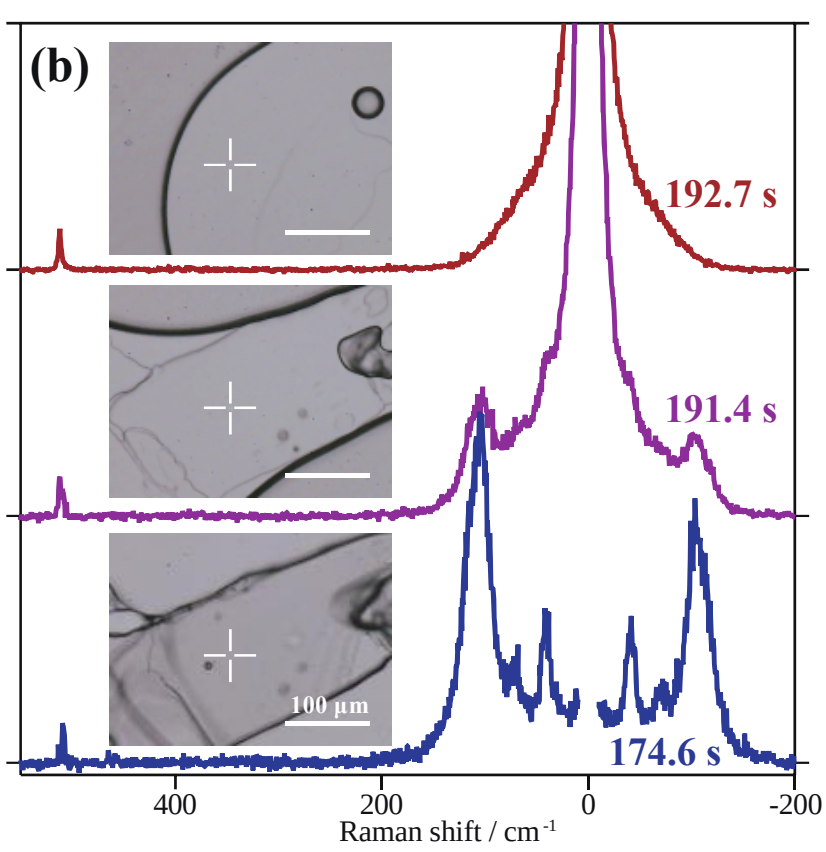
0

400 200 0 -200

Raman shift / cm^{-1}

Unusual Thermal Behavior before Melting





0) at r.t.
(< 0 s)

1) increasing to m.p.
(0~50 s)

2) plateau
(50~120 s)

3) fluctuation
(120 ~ 192 s)

4) melting
(192.7 s~)

Local temperature fluctuation just before melting?