超高速反応する分子の核波束実時間観測と励起状態ポテンシャル曲面のトポロジー

Real-Time Observation of Nuclear Wavepacket Motion of Reacting Molecules and Topology of Potential Energy Surfaces

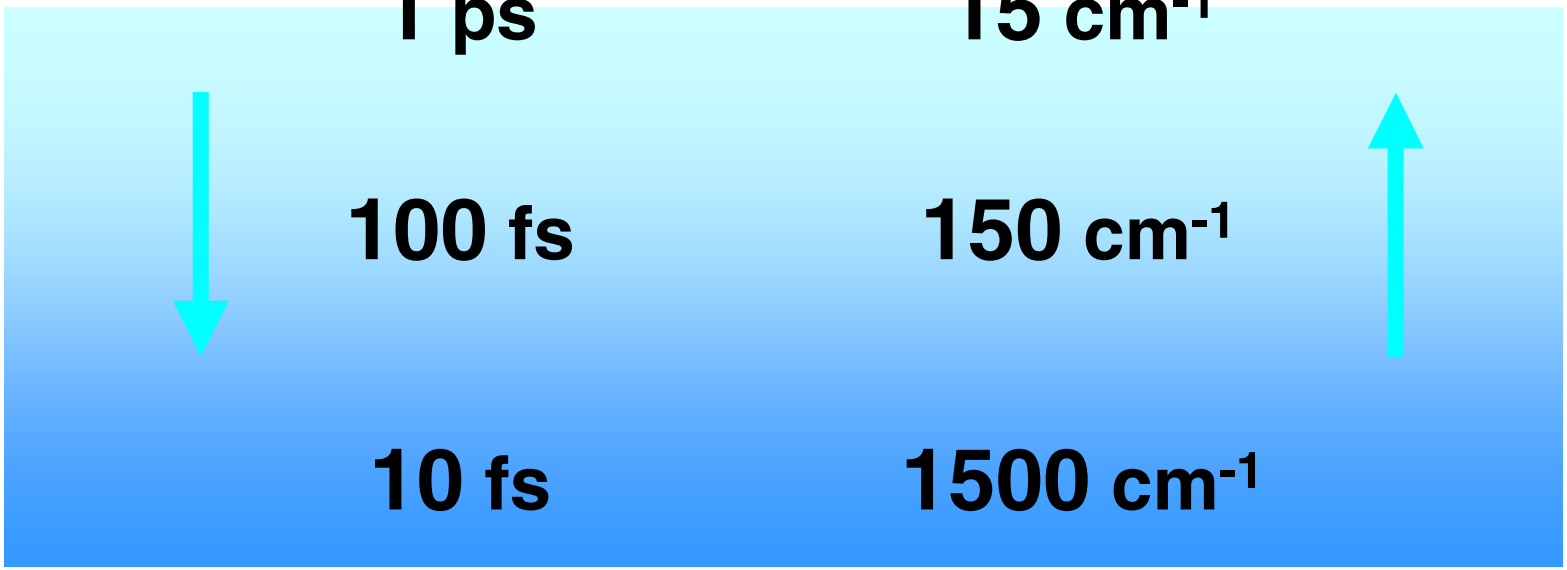
Molecular Spectroscopy Laboratory, RIKEN
JAPAN

Tahei TAHARA

ER研究会, July 9, 2007

The Band Width in Time and Energy

$$\Delta t \cdot \Delta \nu \geq R$$



for Gaussian

Observation of Nuclear Wavepacket Motion

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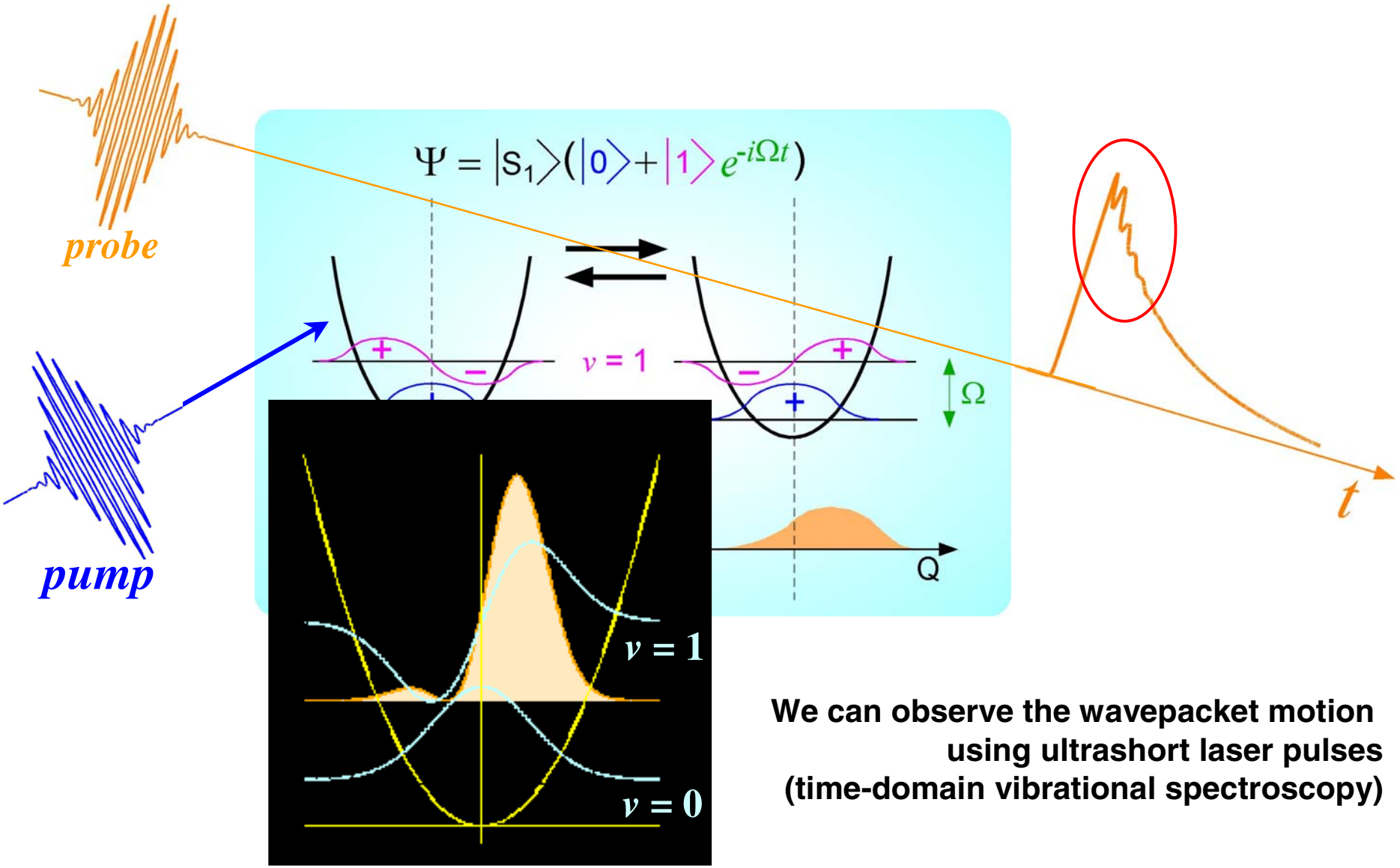
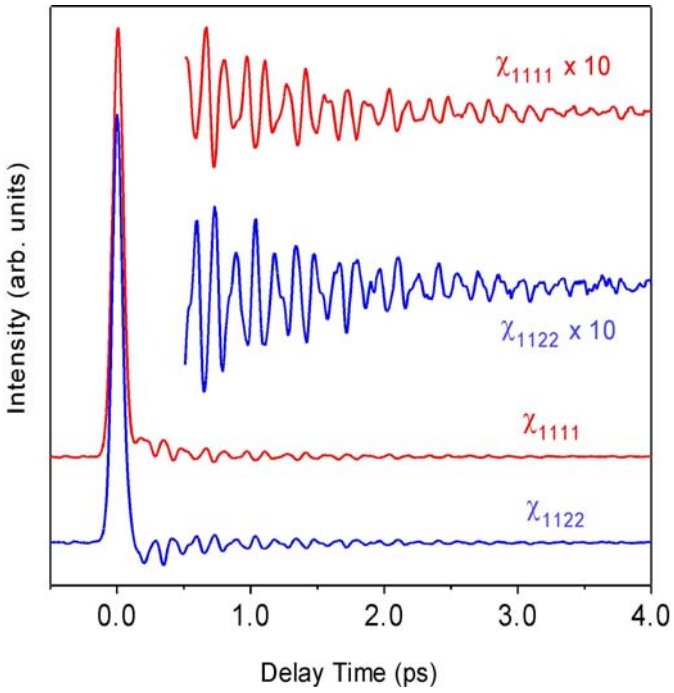


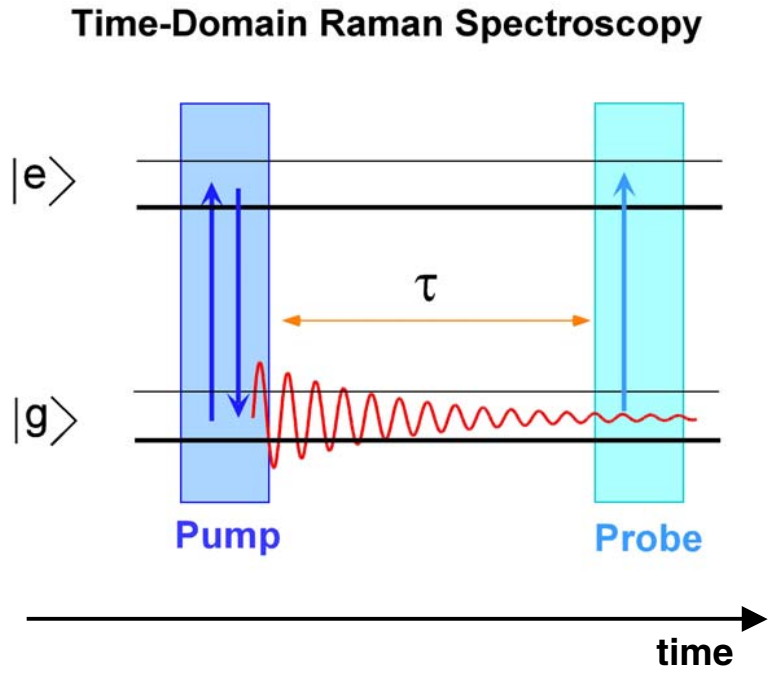
We can observe the wavepacket motion using ultrashort laser pulses (time-domain vibrational spectroscopy)

Time-domain vs Frequency domain

Heterodyned Impulsive Stimulated Raman of CCl_4

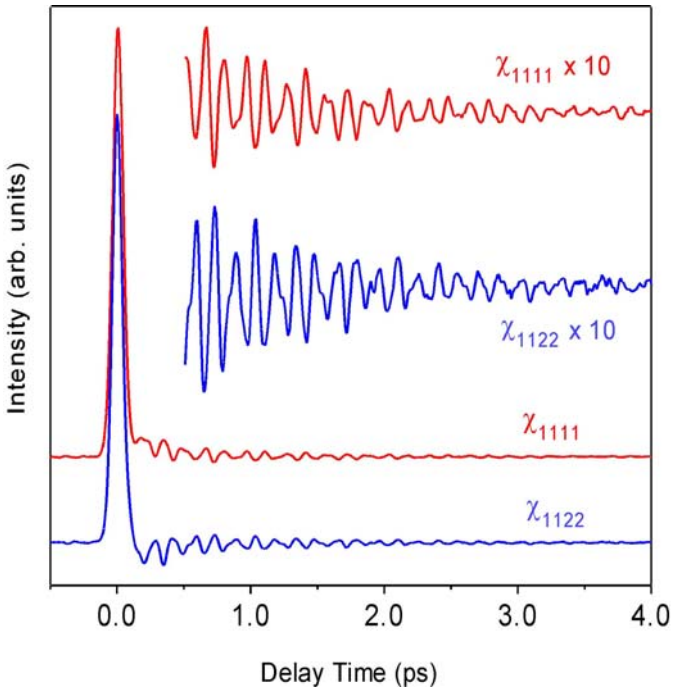


Matsuo and Tahara, CPL, 264, 636(1997)

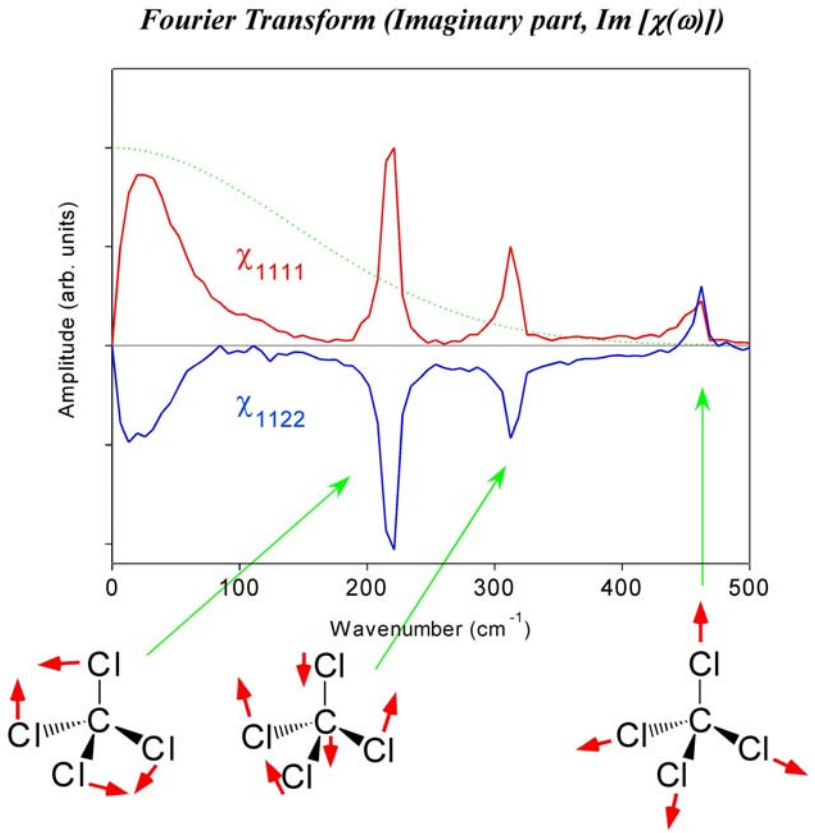


Time-domain vs Frequency domain

Heterodyned Impulsive Stimulated Raman of CCl_4



Matsuo and Tahara, CPL, 264, 636(1997)



Time-domain vibrational data is equivalent to frequency-domain data.

They are converted to each other by Fourier transformation.

Why Time-Domain Measurement?

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Time-domain vibrational spectroscopy
is very powerful
to study excited-state molecules,
especially when
they have only very short lifetimes.

★ **We can get insight about**
reactive potential energy surfaces,
which are not simply harmonic! ★

Ultrafast reactions are weird special problems?

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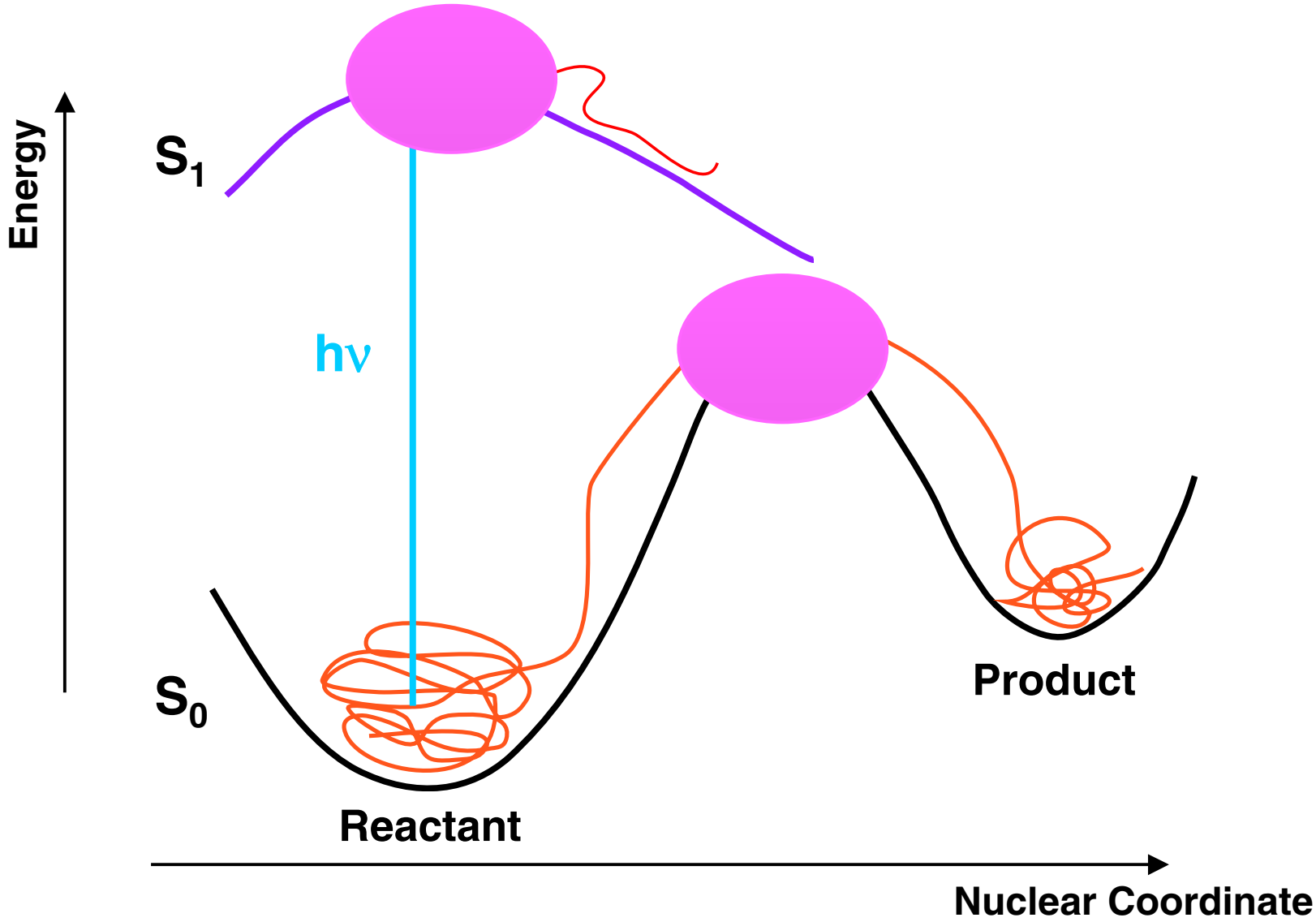

Nuclear Wavepacket Motion of Potential Energy Surface

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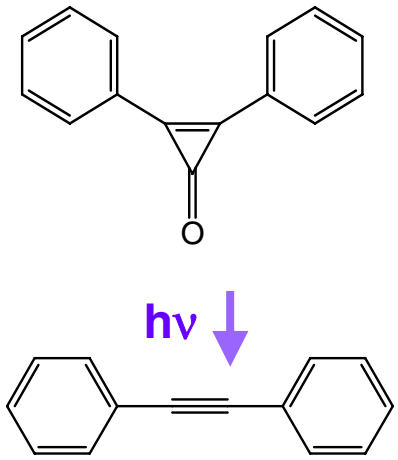
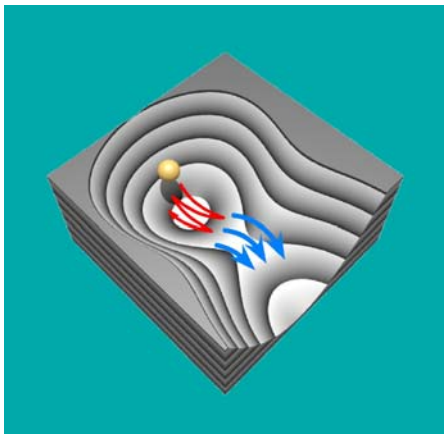
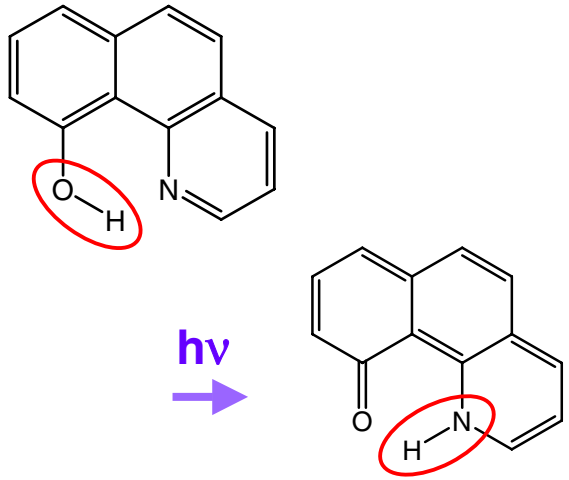
Photodissociation
Diphenylcyclopropenone

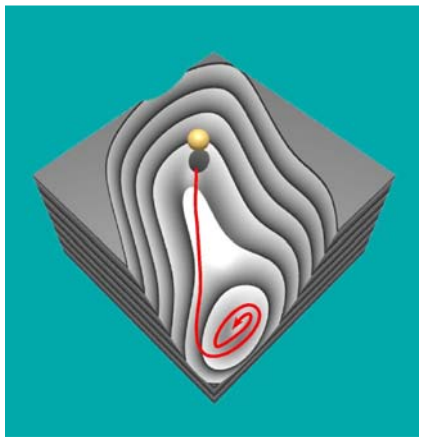




parallel

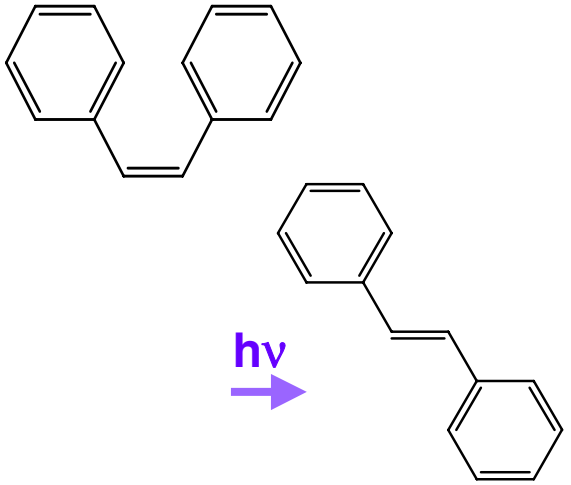
Excited-State Proton Transfer
10-Hydrobenzoquinoline

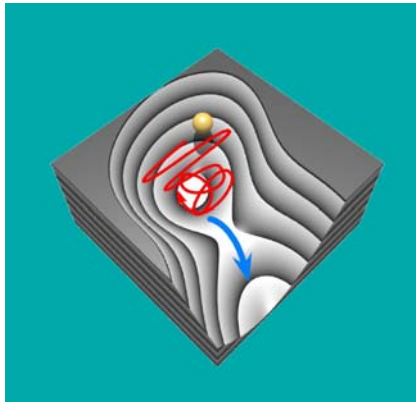




assist

Photoisomerization
cis-Stilbene





perpendicular

Observation of nuclear wavepacket motion of "reacting" short-lived excited states

- Photoisomerization of *cis*-stilbene
- Photo-induced structural change of bis(2,9-dimethyl-1,10-phenanthroline)copper (I)

Photoisomerization of *cis*-stilbene

Stilbene:
A Fundamental Molecule in Organic Photochemistry

Performance

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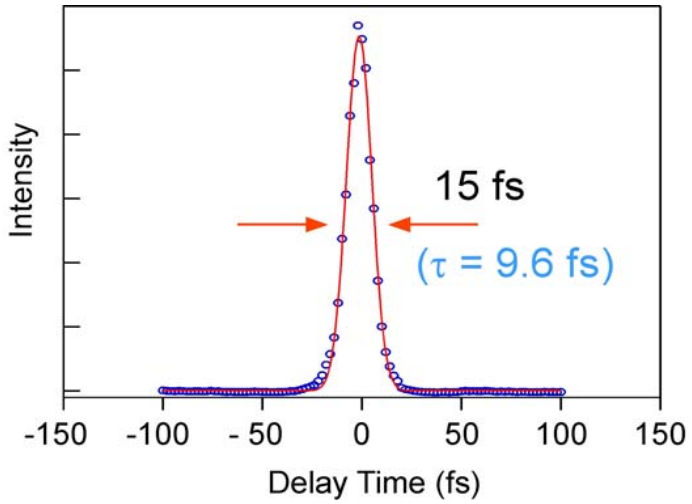
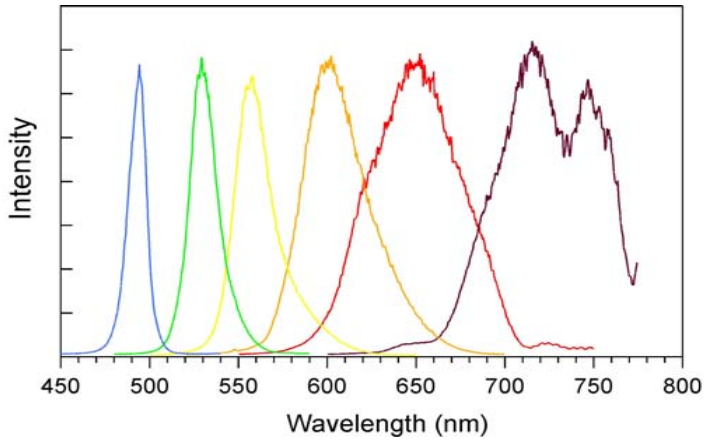


NOPA

Tunability	500 – 750 nm
Pulse Duration	10 – 15 fs
Pulse Energy	10 μJ
Rep. Rate	1 kHz



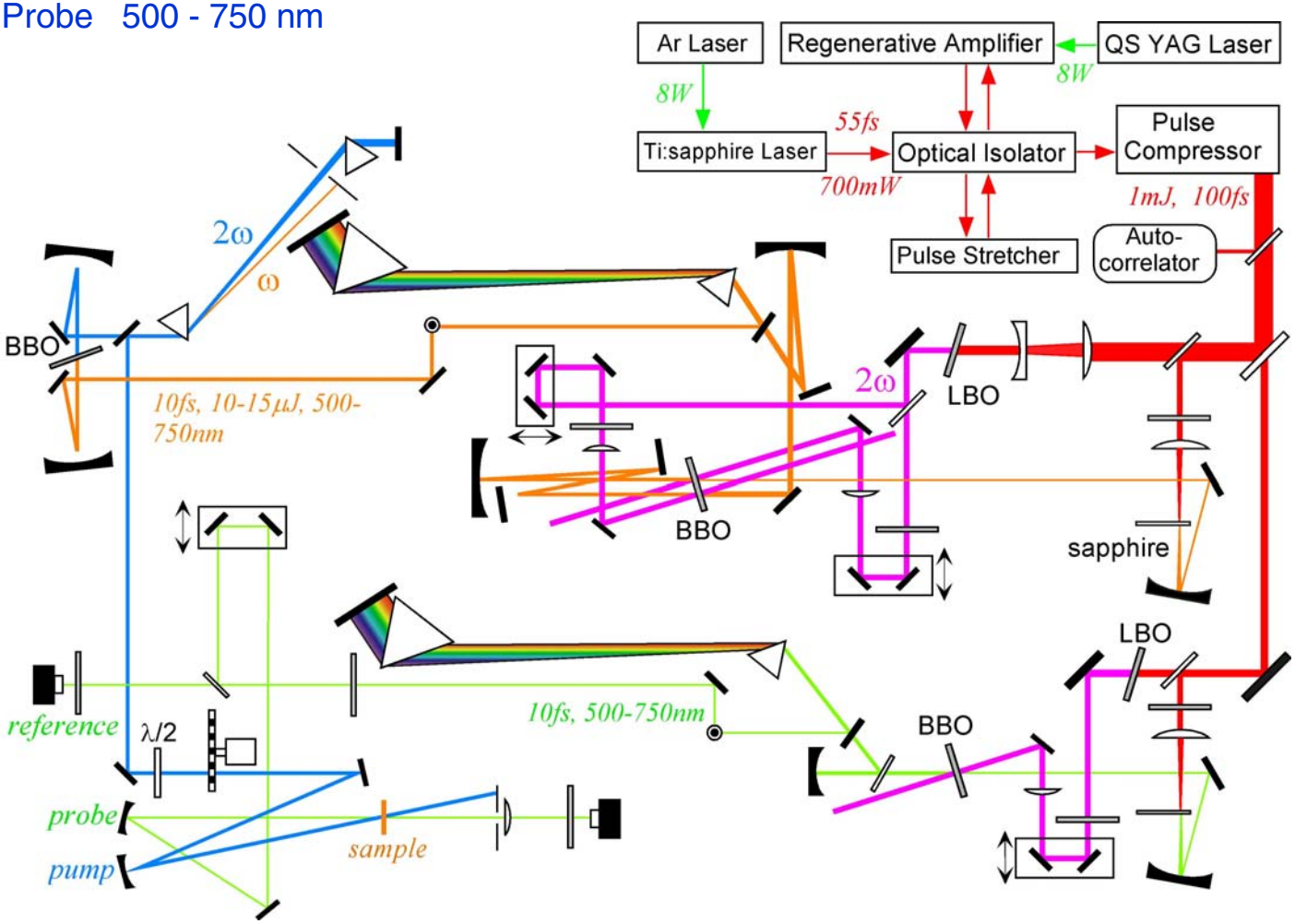
Two Color Pump-Probe Experiments

Pump	250 - 375 nm, 20 fs
Probe	500 - 750 nm, 10 - 15 fs
Time Resolution	30 fs
Sensivitity	0.03 mOD

Apparatus: Tunable Two-Color Pump-Probe Spectrometer based on NOPA

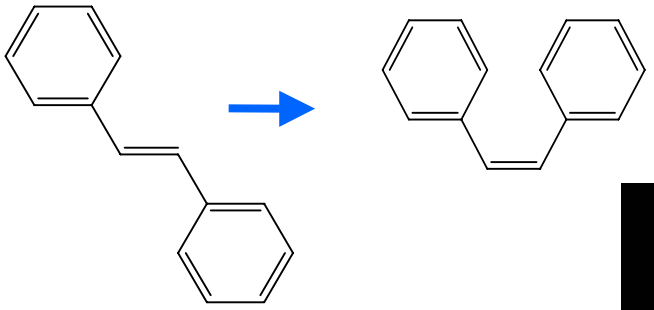
Tunability: Pump 250 - 375 nm
Probe 500 - 750 nm

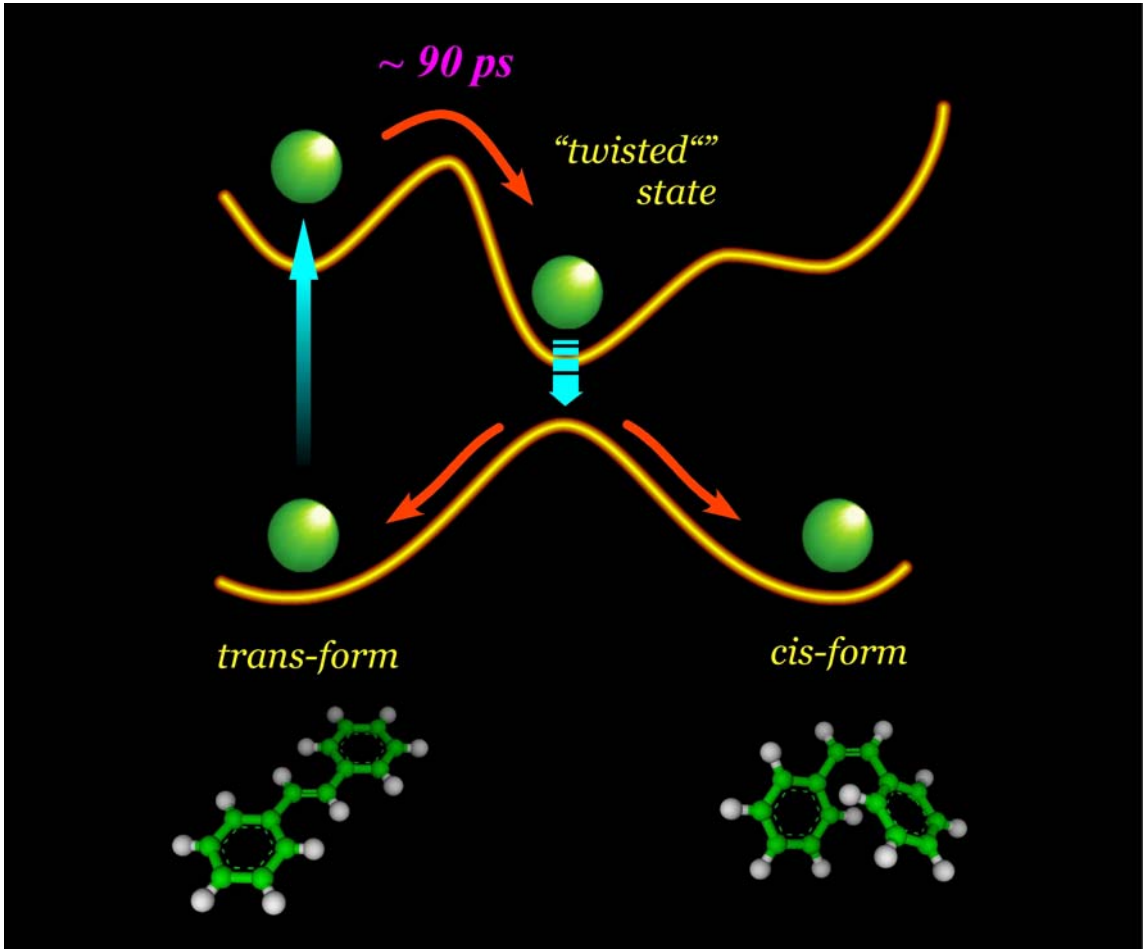
Riedle; Kobayashi; Cerullo & Silvestri



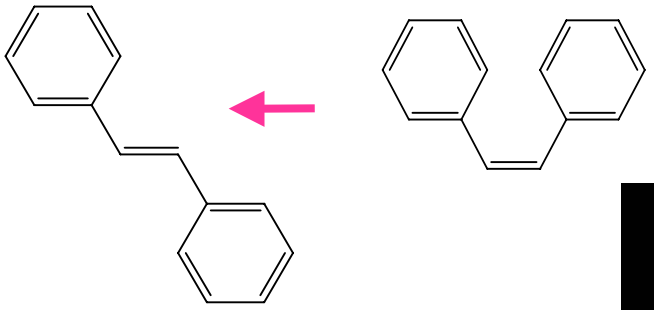
Time-Resolution of UV-vis Two Color Pump-Probe: 30 - 40 fs (Cross Correlation)

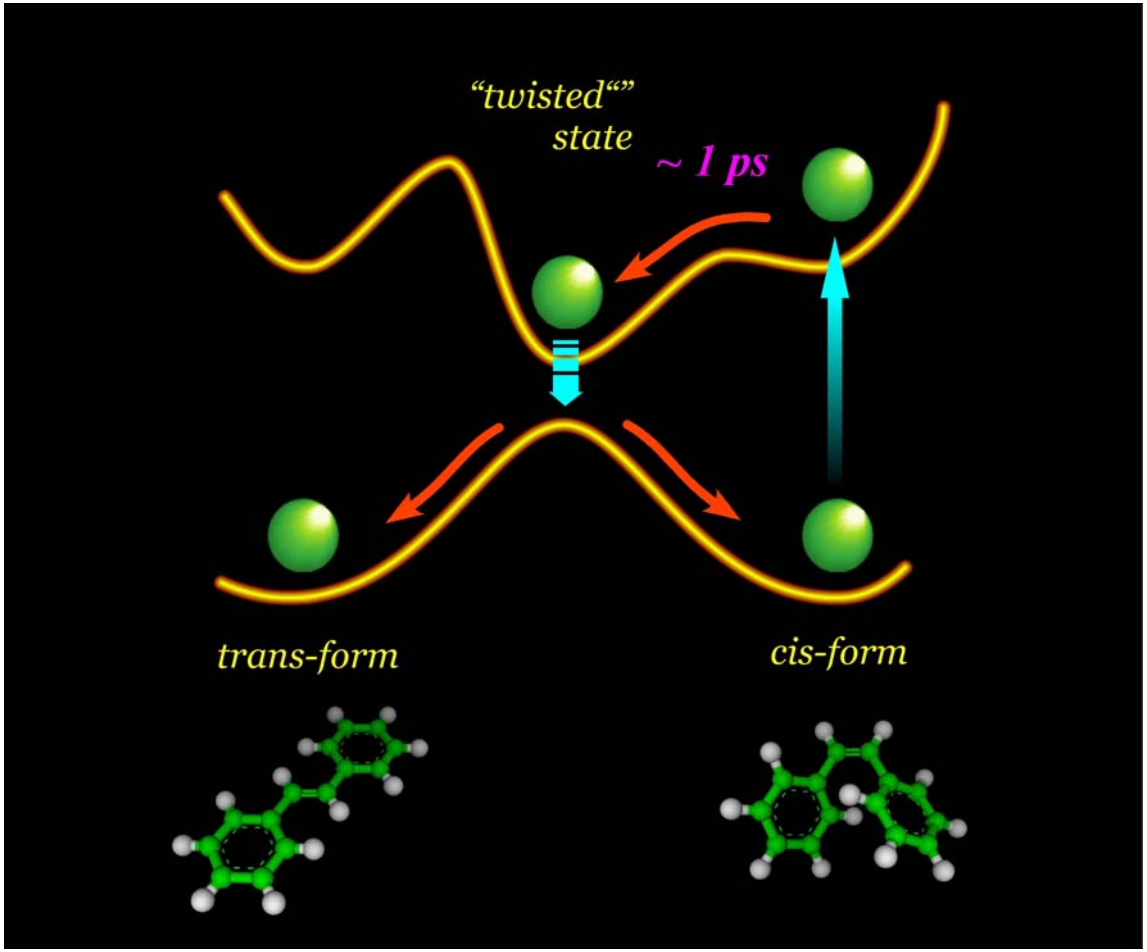
Photoisomerization of Stilbene





Photoisomerization of Stilbene





Absorption Spectra of *cis*-Stilbene

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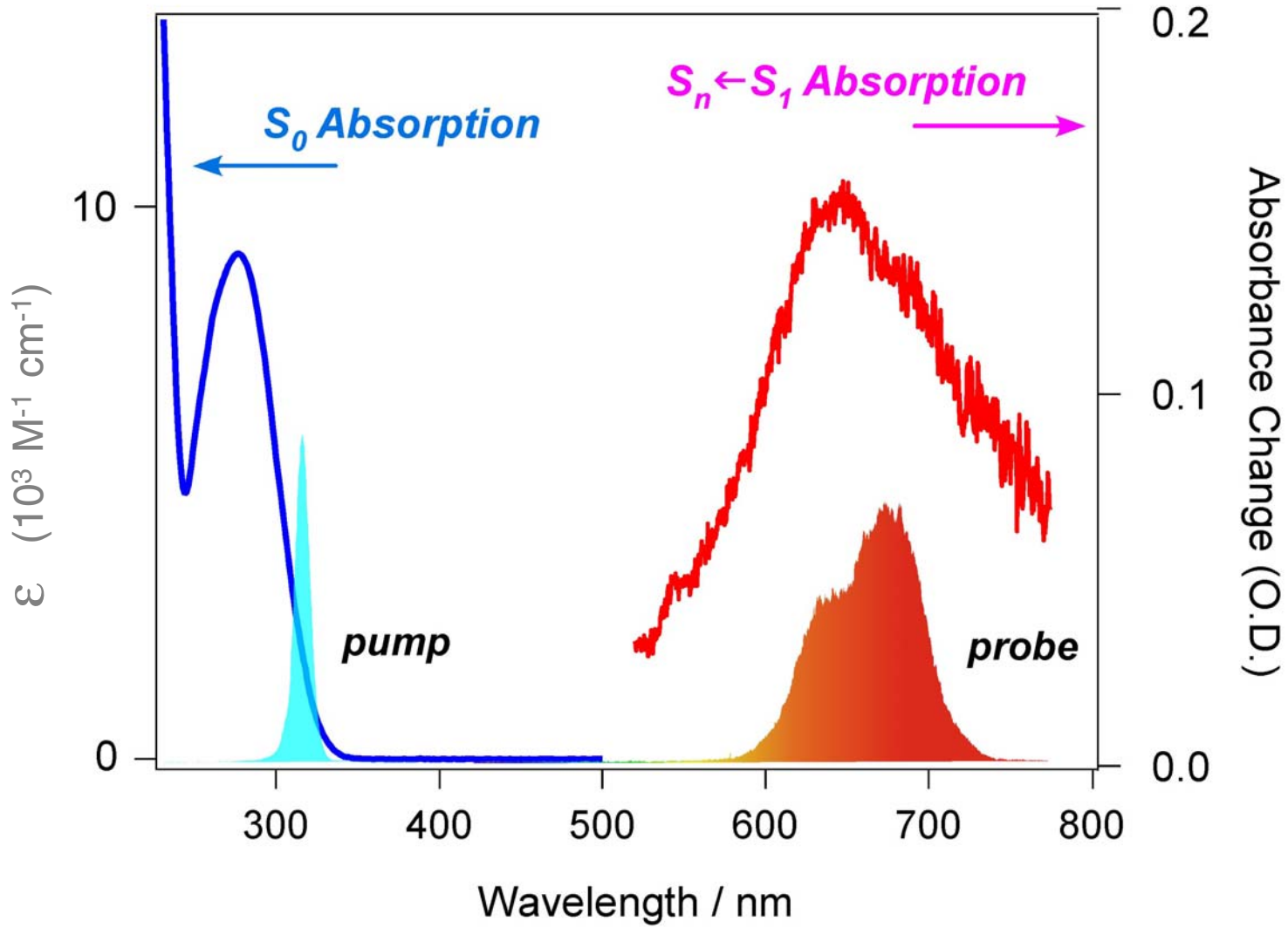
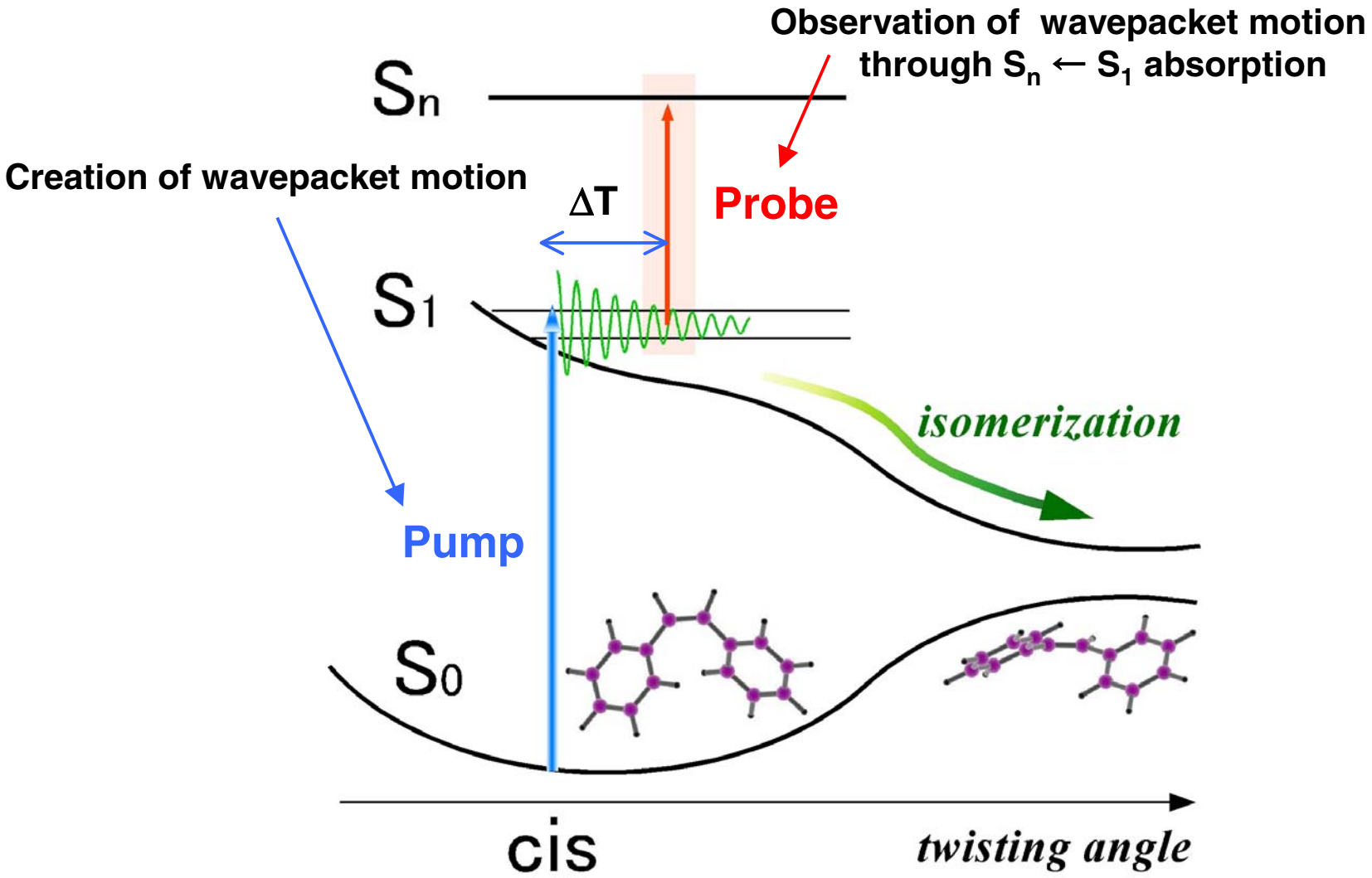


Observation of Pump-Induced Wavepacket Motion of S_1 *cis*-Stilbene



Time-Resolved Absorption Signal of *cis*-Stilbene

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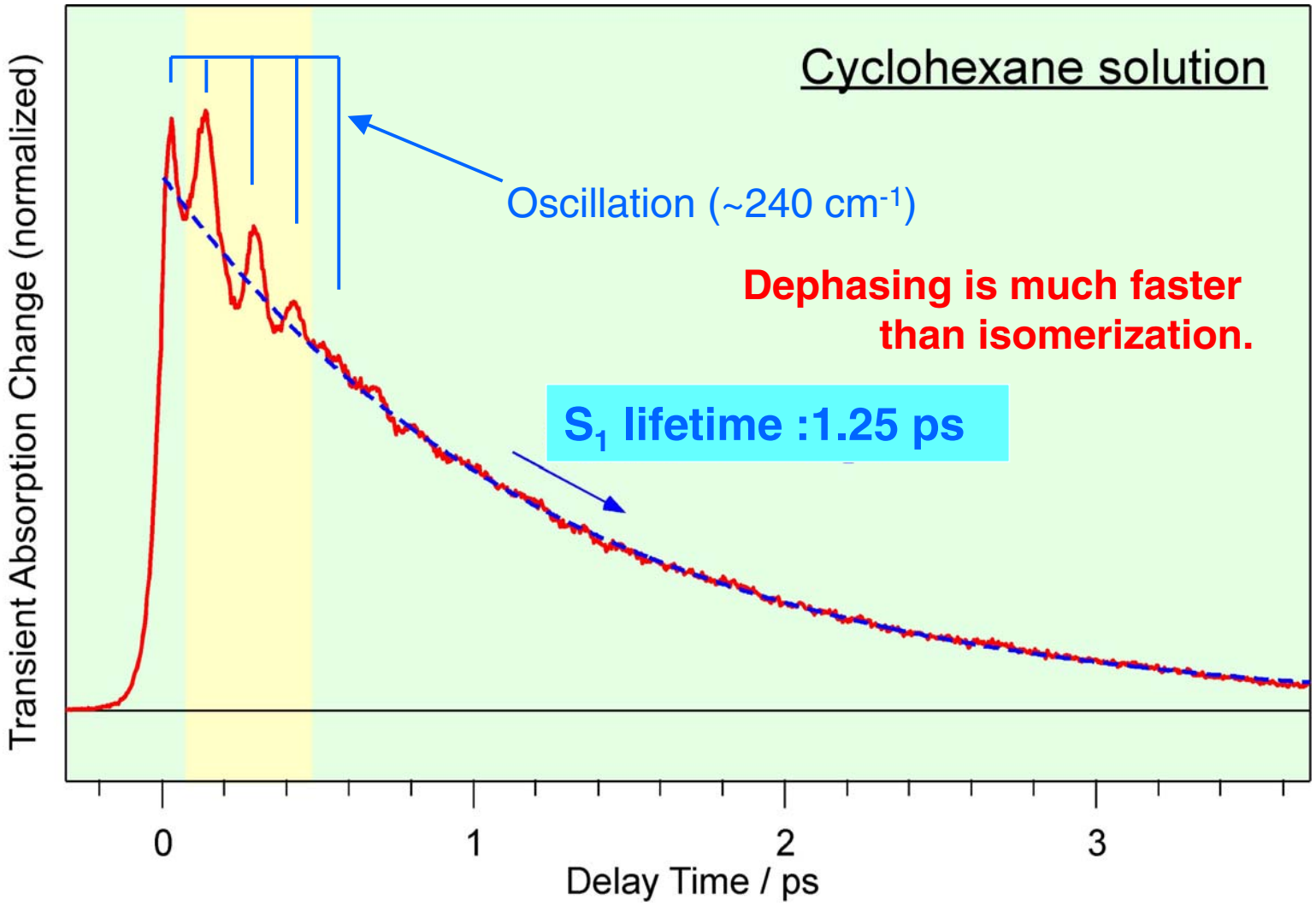
pump 315 nm; probe 660 nm; 5×10^{-3} M



Time-Resolved Absorption of *cis*-Stilbene

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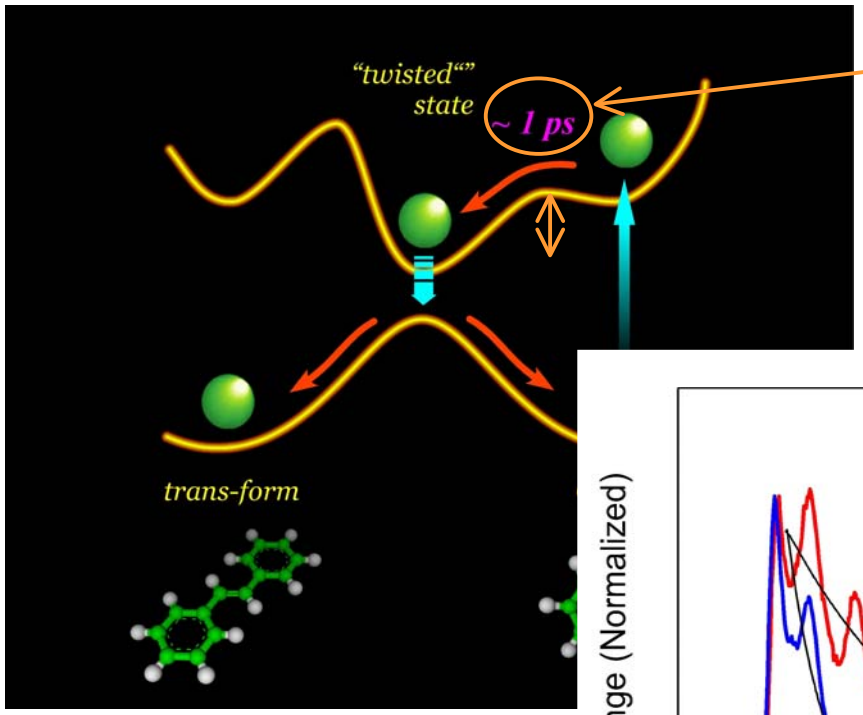
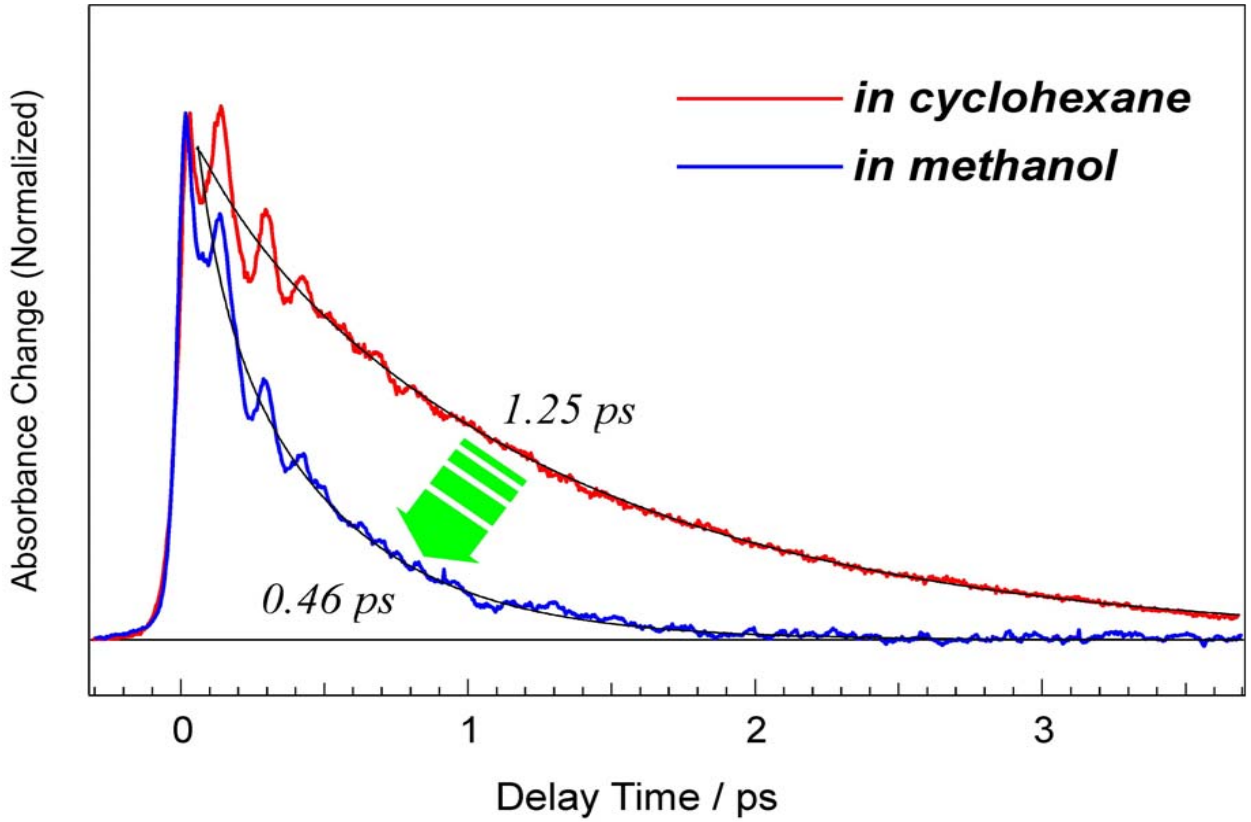


The isomerization rate significantly depends on the solvent.

The observed wavepacket motion is not directly correlated to the reaction coordinate.



Decay of Vibrational Coherence of S_1 cis-Stilbene

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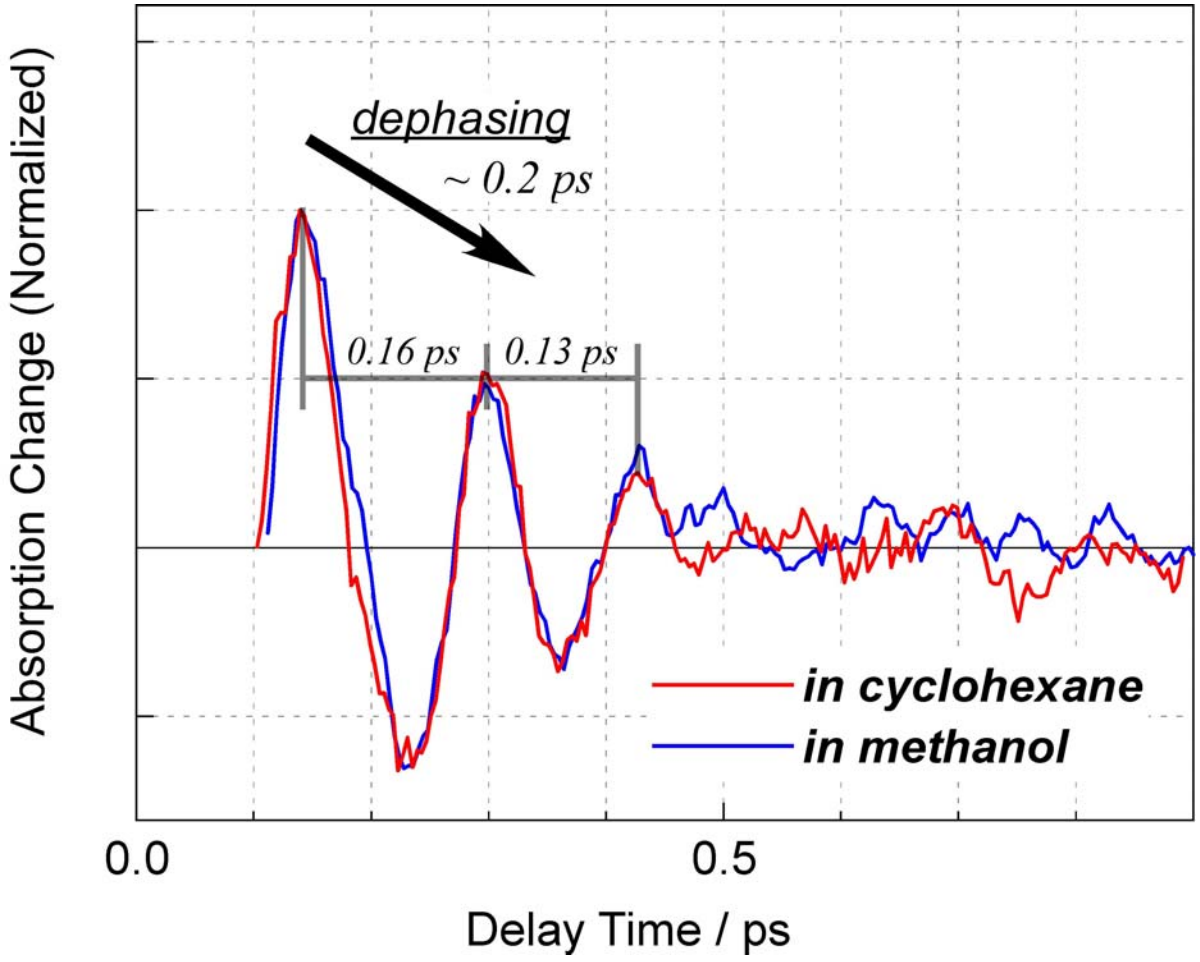

The wavepacket motion is insensitive to the change of solvent.

Wavepacket Motion in Photoisomerization of *cis*-Stilbene

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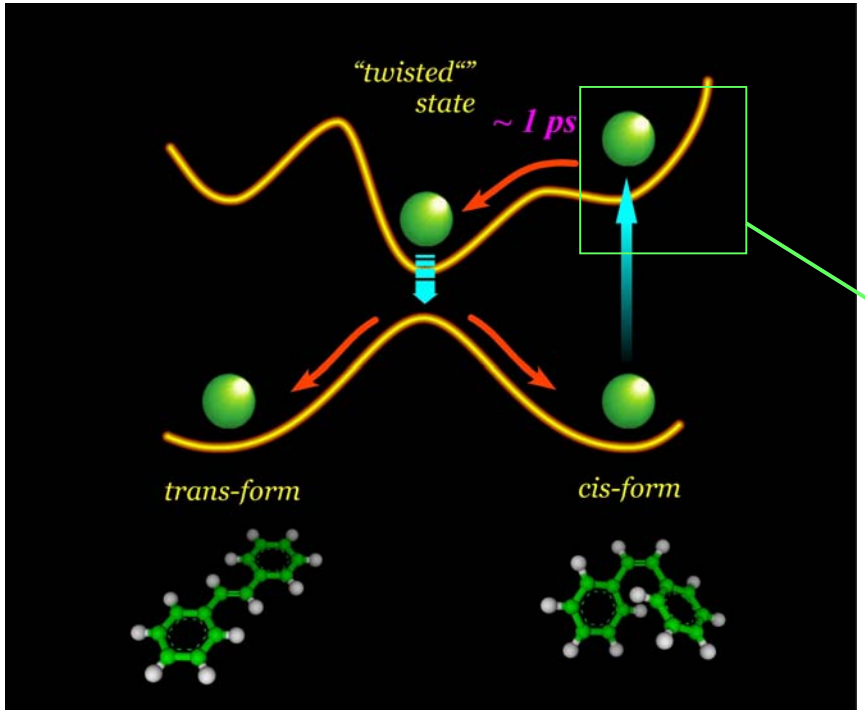

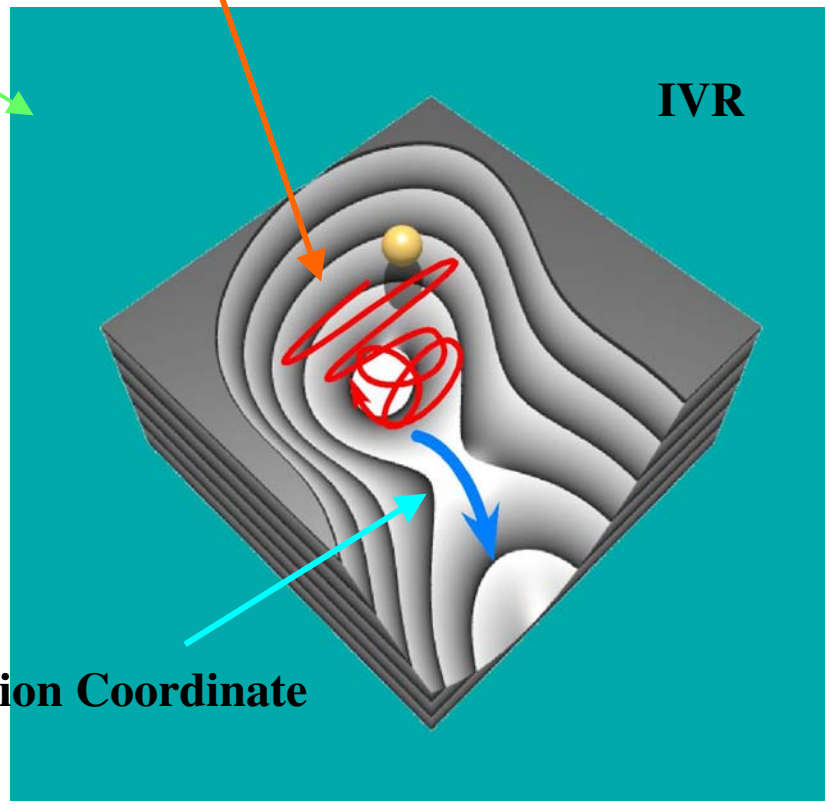

The observed wavepacket motion is "perpendicular" to the reaction coordinate.

Pump-Induced Wavepacket Motion in S_1 *cis*-Stilbene

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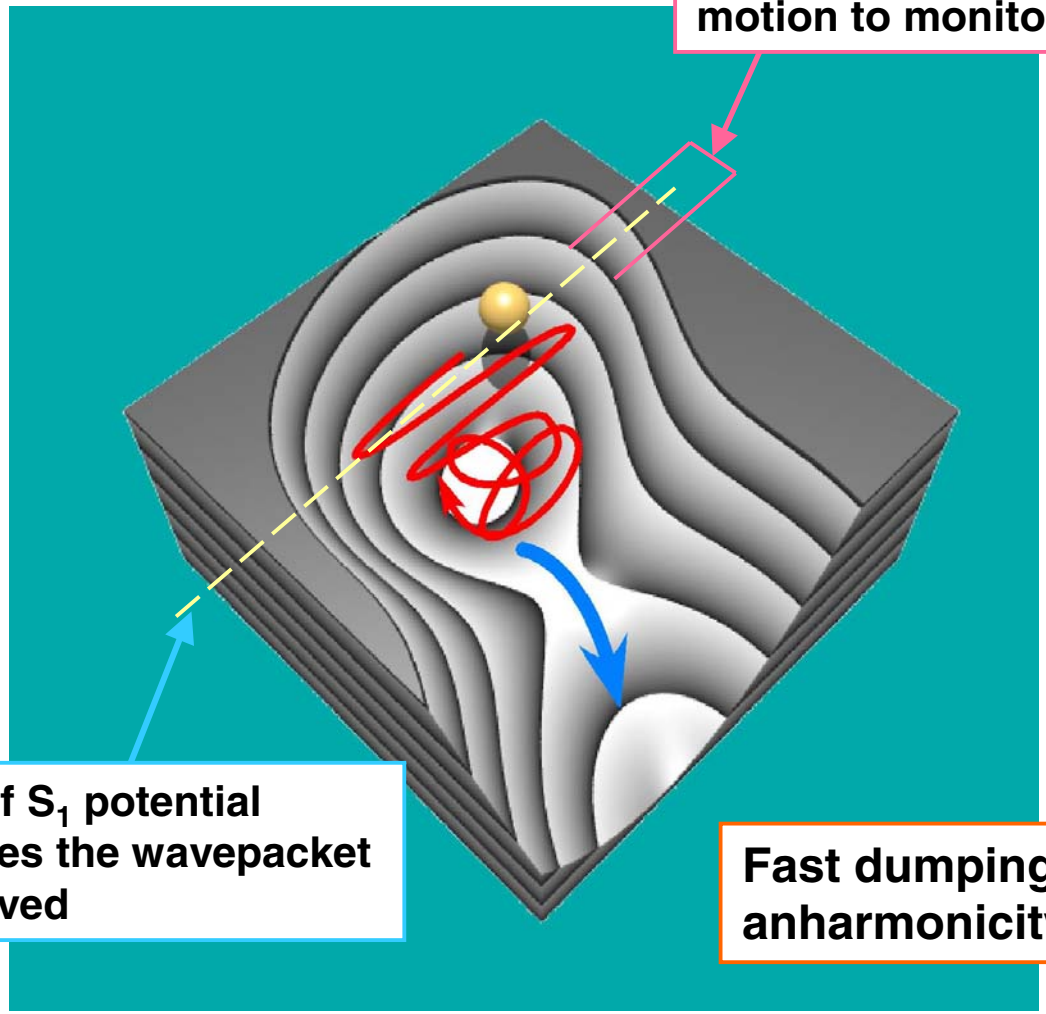
S_1 potential

Dumping time ~ 200 fs:
Time window for the wavepacket motion to monitor the S_1 potential



A curvature of S_1 potential that determines the wavepacket motion observed

Fast dumping indicates high anharmonicity of the potential

Observation of Raman-Induced Wavepacket Motion in S_1 *cis*-Stilbene

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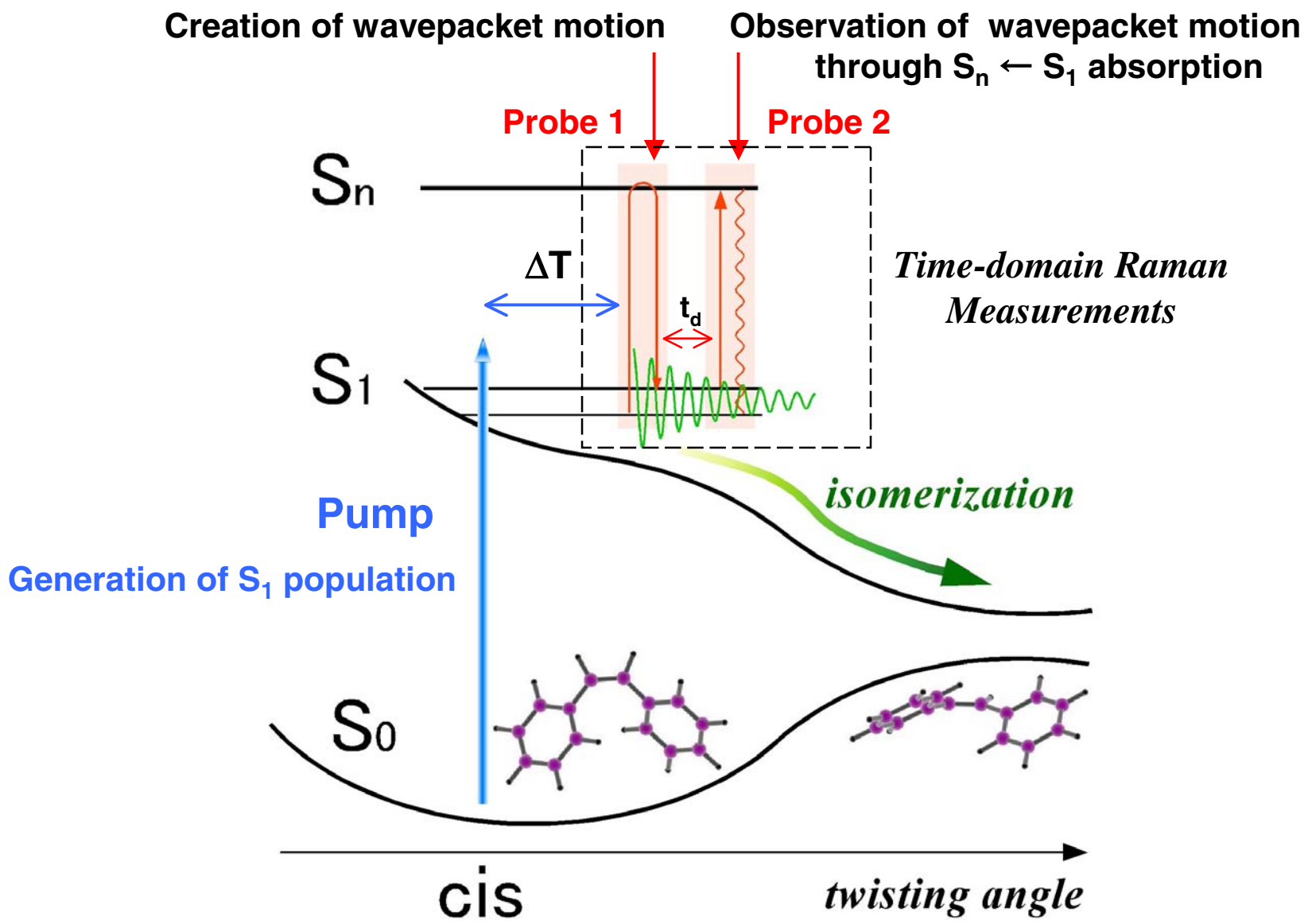

Observation of Raman-Induced Wavepacket Motion in S_1 *cis*-Stilbene

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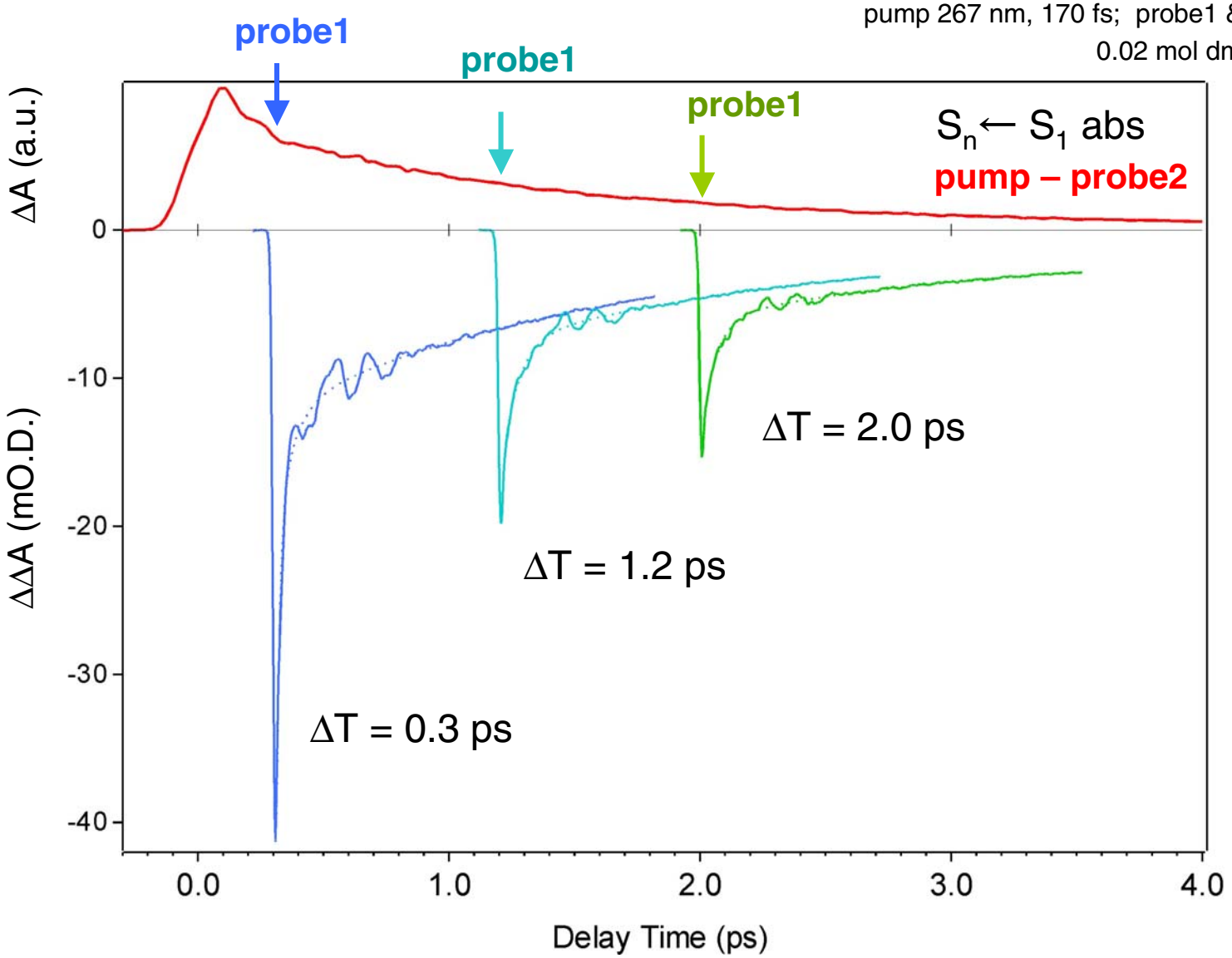
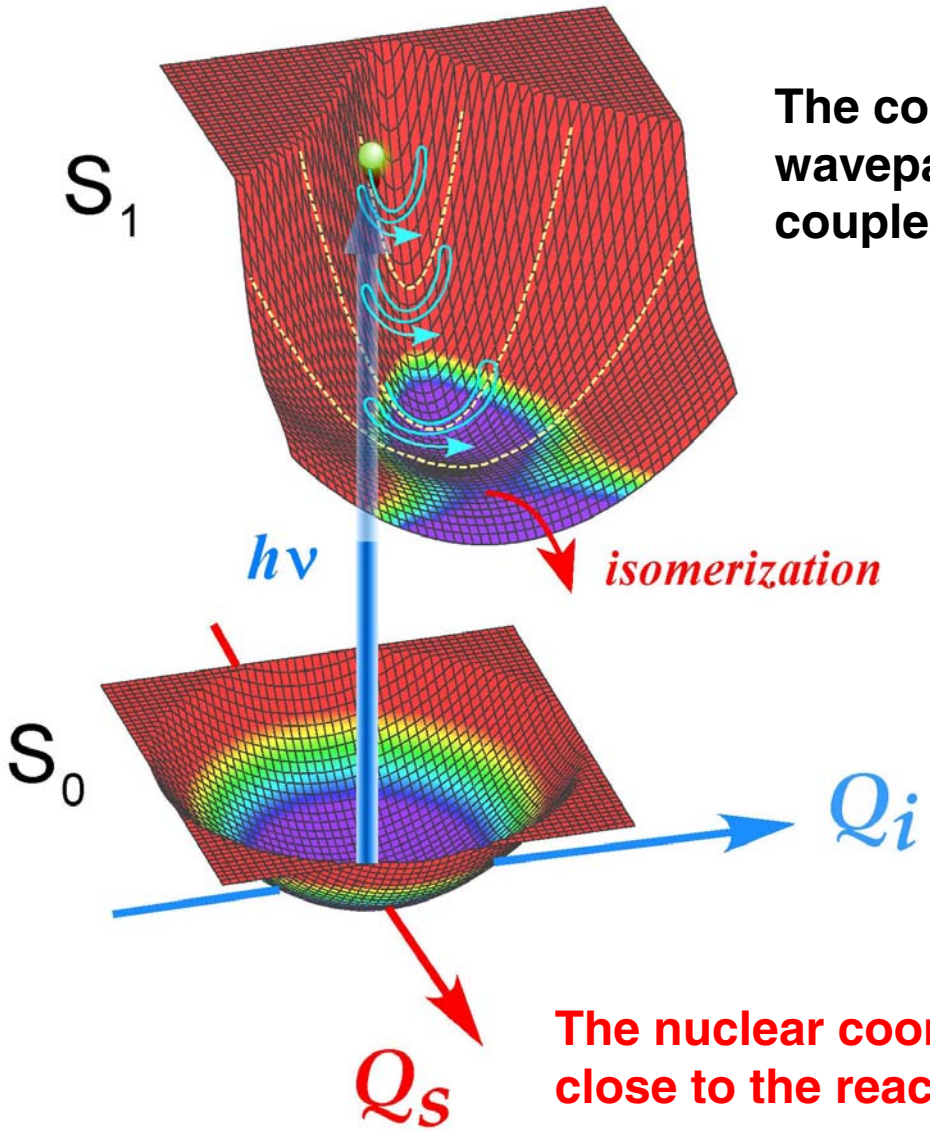
pump 267 nm, 170 fs; probe1 & 2 620 nm, 11 fs

0.02 mol dm^{-3} in hexadecane



Mutlidimensional S_1 Potential of S_1 *cis*-Stilbene



The coordinate of the observed nuclear wavepacket motion, Q_i, is anharmonically coupled with another coordinate, Q_s.

$$\frac{\partial}{\partial Q_S}\left(\frac{\partial^2 V}{\partial Q_i^{\,2}}\right)=\frac{\partial k_{Q_i}}{\partial Q_S}$$ is significant.

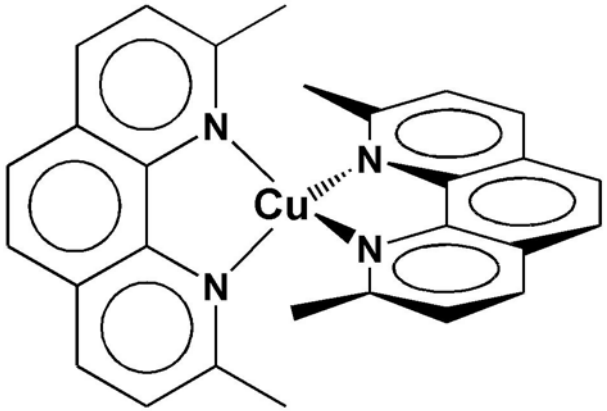
The vibrational coordinate of the wavepacket motion observed

The nuclear coordinate close to the reaction coordinate

Photoinduced Structural Chage (Jahn-Teller Distortion) of Cu complex

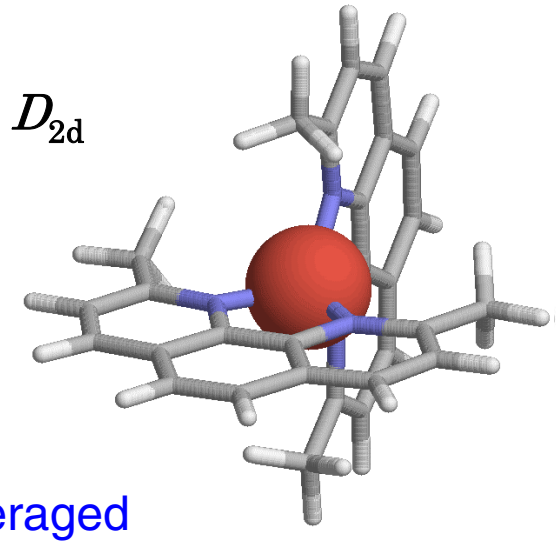
Bis(2,9-dimethyl-1,10-phenanthroline)copper (I):
A Fundamental Molecule in Inorganic Photochemistry

Bis(2,9-dimethyl-1,10-phenanthroline)copper (I):

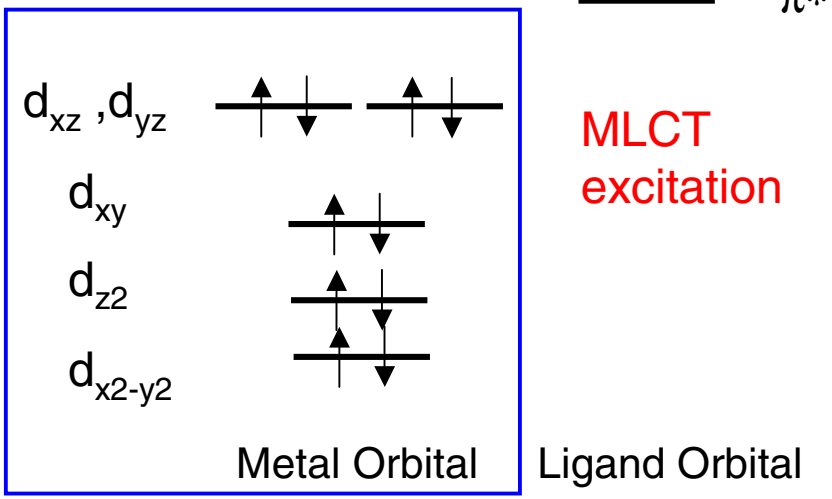


$[Cu(I)(dmphen)_2]^+$

Flattening distortion takes place.



- ☺ **Promising as the photocatalyst and photosensitizer in solar energy conversion**
- ☺ **Candidate for molecular switch**
- ☺ Real-time observation of **Jahn-Teller Distortion**



Femtosecond Time-Resolved Fluorescence Spectra

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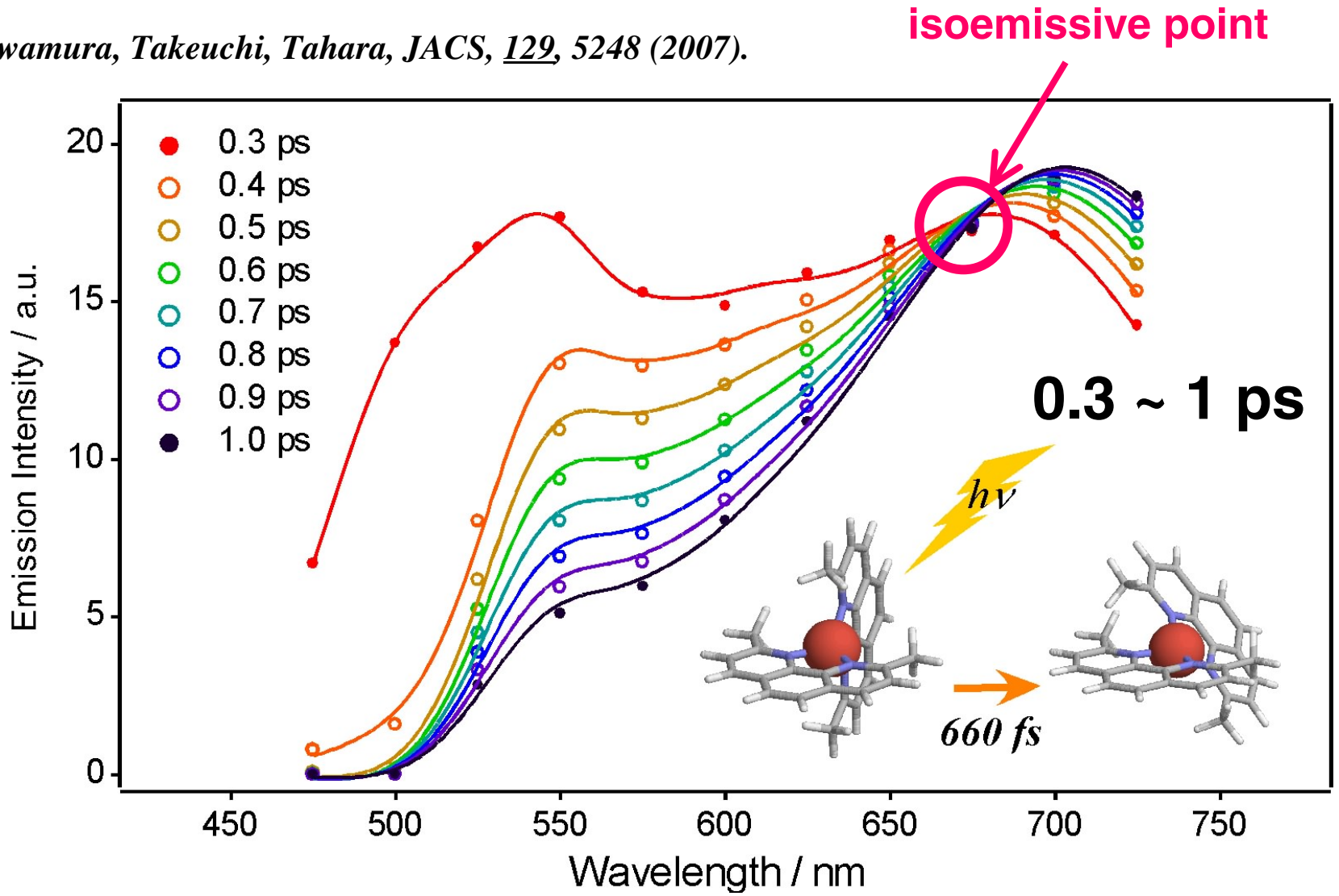
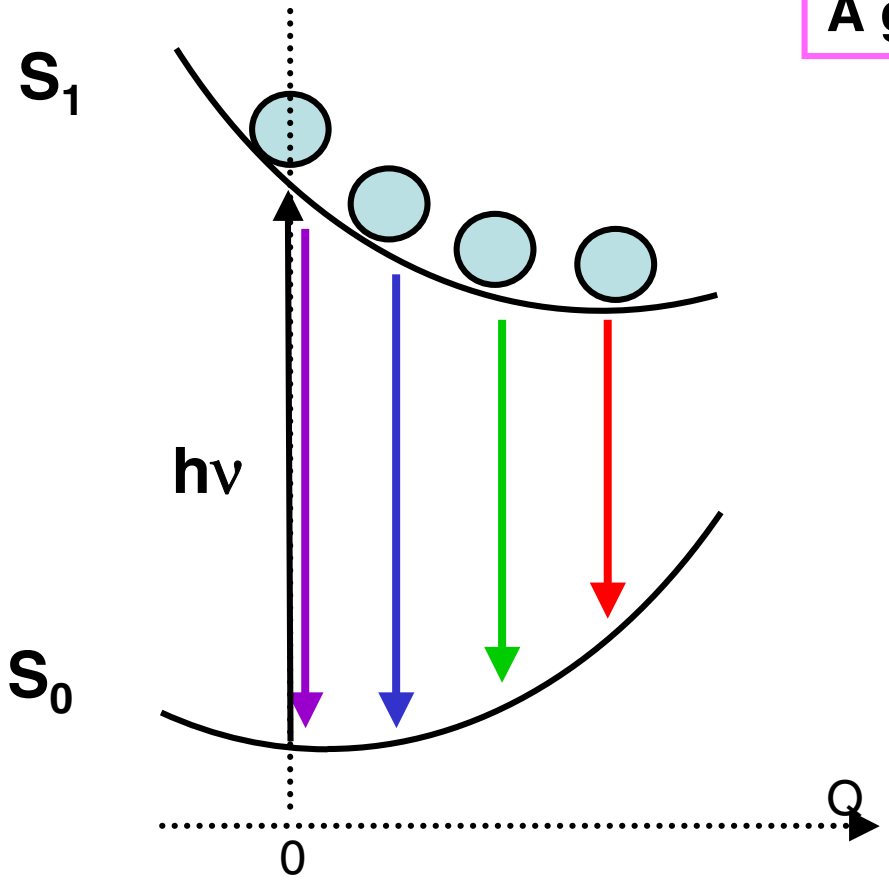
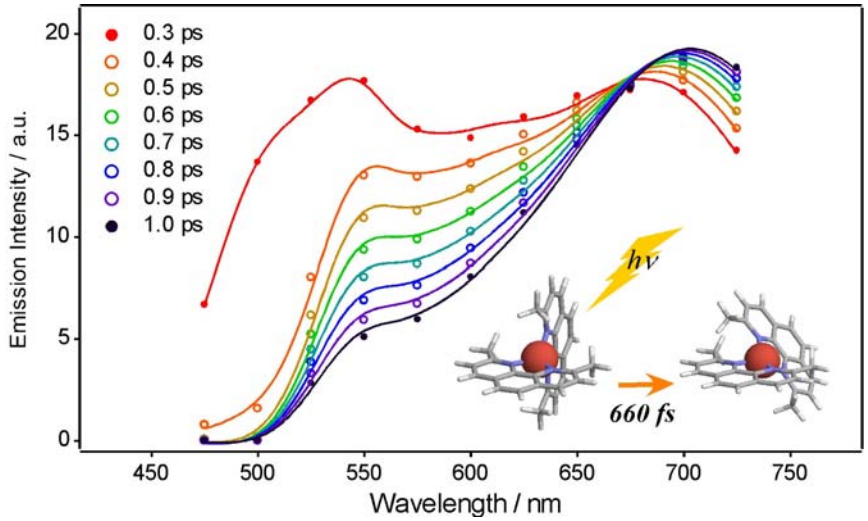
Iwamura, Takeuchi, Tahara, JACS, 129, 5248 (2007).



Fluorescence Spectral Change Corresponding to Flattening Distortion

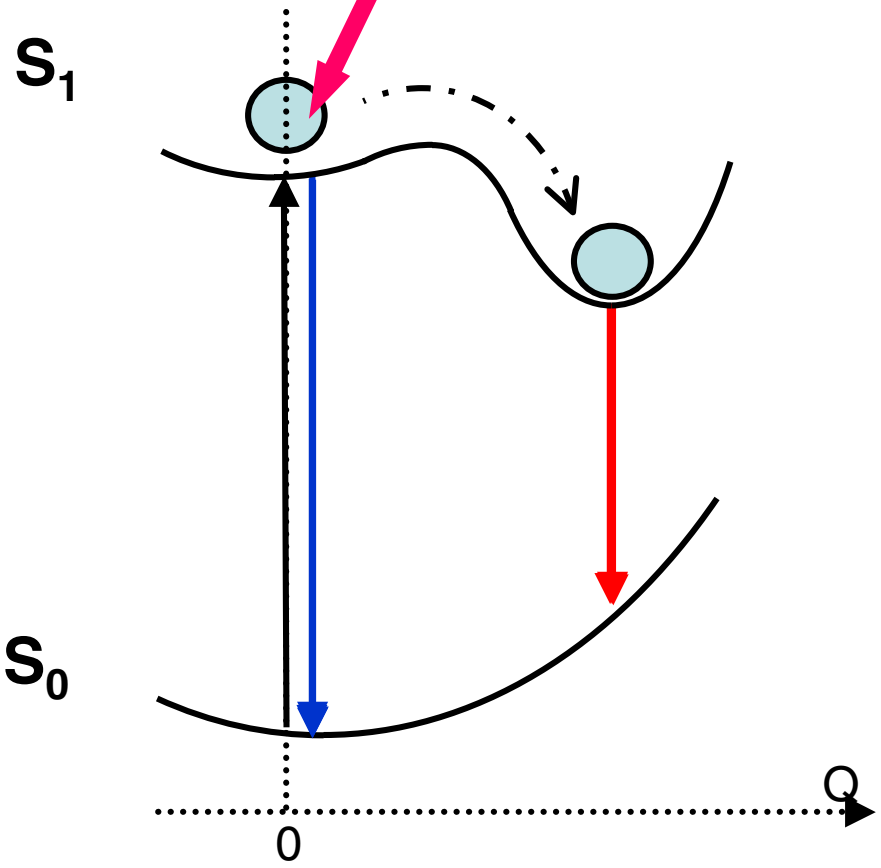
A gradual spectral shift is expected.

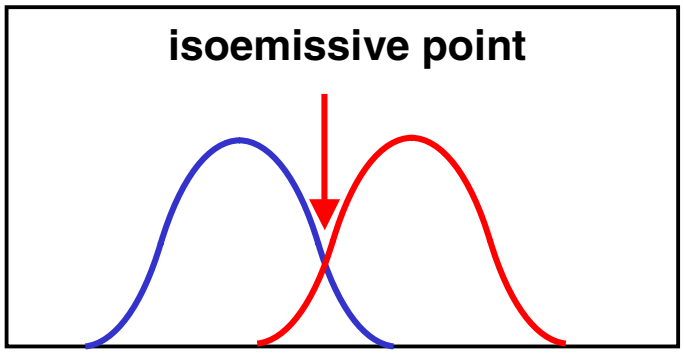


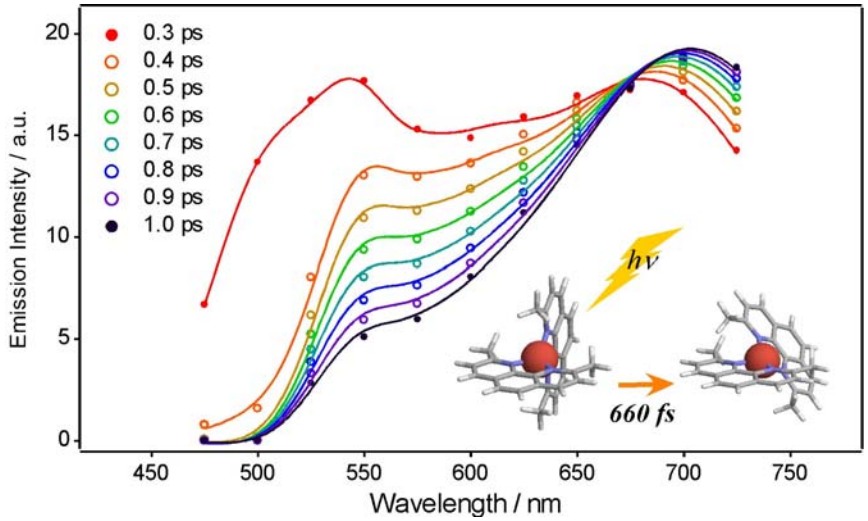


Fluorescence Spectral Change Corresponding to Flattening Distortion

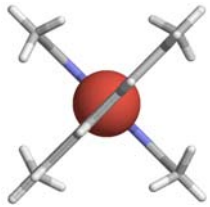
The data suggests “a hollow” on the S_1 potential at the perpendicular configuration.







A Realistic Potential Curve of the Jahn-Teller Distortion



D_{2d}

$^1B_2$ (S_2)

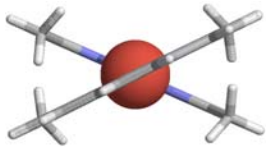
45 fs

Flattening Distortion

$^1A_2$ (S_1)

660 fs

($^1B_1$)



D_2

7.4 ps

T_1

Hollow ?

$h\nu$

If there is a bound state,
we should observe vibrations.

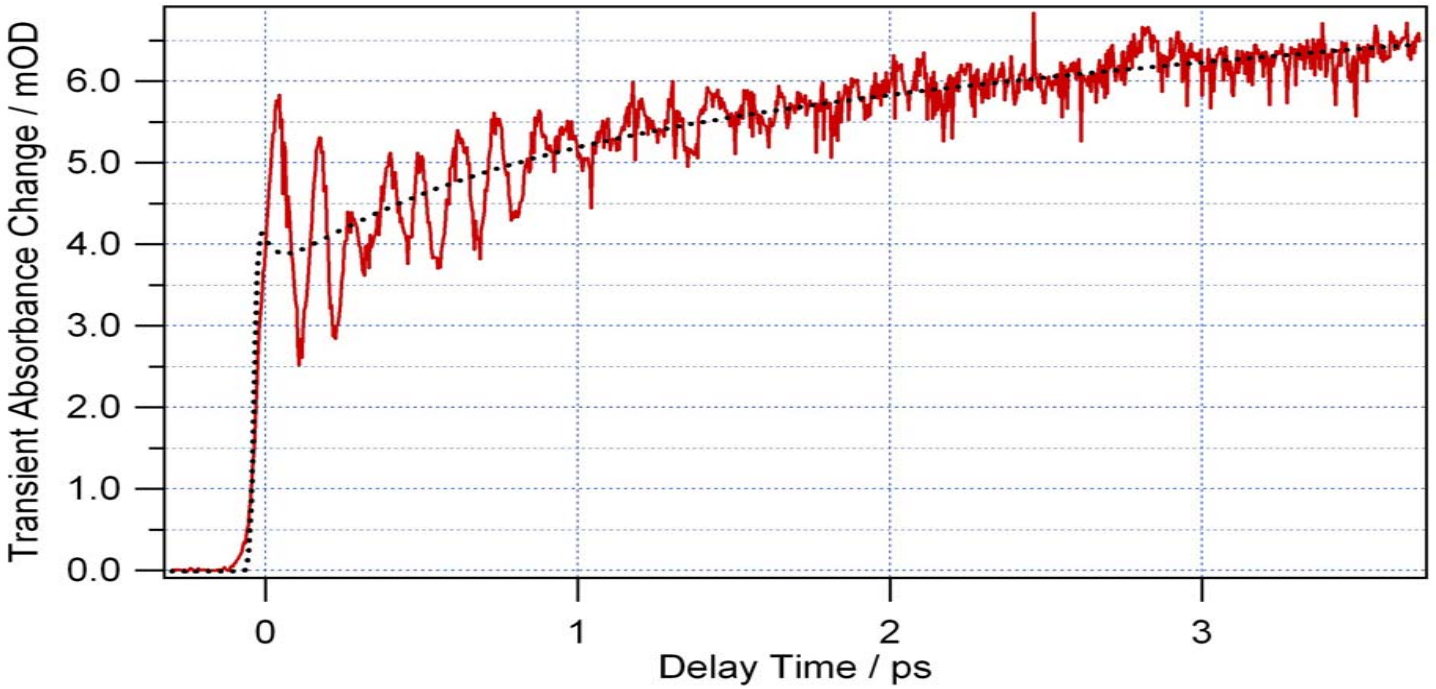
S_0

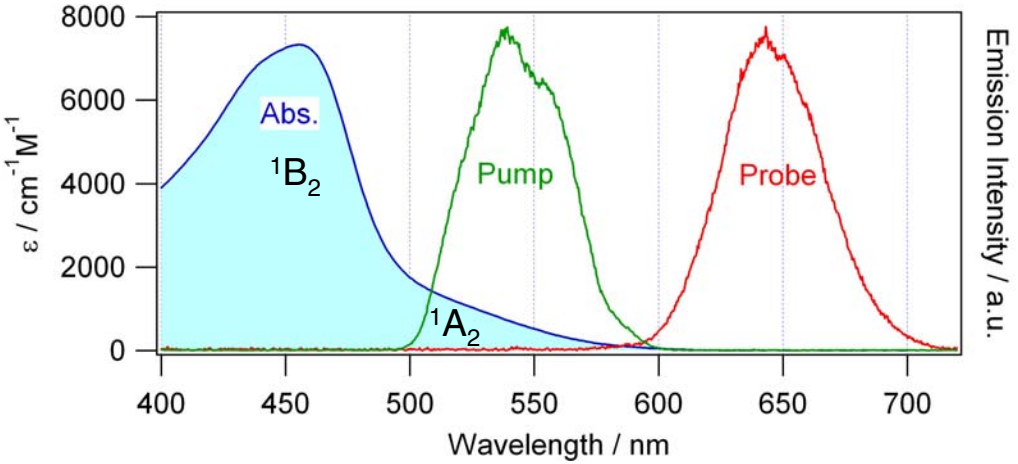
90°

dihedral angle

Ultrafast Pump-Probe Signal of $[Cu(dmphen)_2]^+$

pump 550 nm; probe 650 nm; 7×10^{-2} M in dichloromethane





Ultrafast Dynamics of Photo-Induced Flattening of $[Cu(dmphen)_2]^+$

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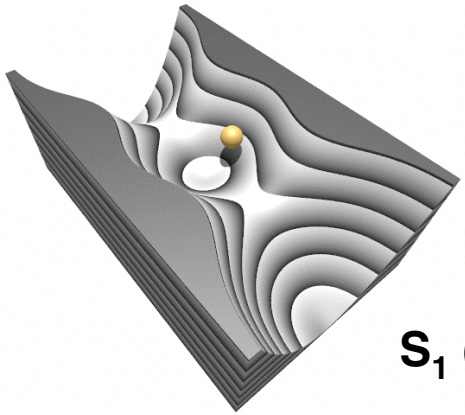
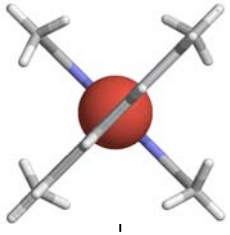
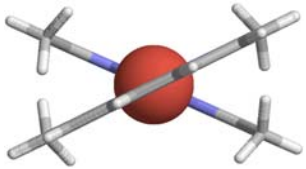




D_{2d}



D_2

S_1 ($^1A_2$)

660 fs

Flattening distortion (b_1)

A hollow on the S_1 potential

S_0

θ

90°

Direct Information on Structural Change

- **Pulse width > 100 fs (or 1 ps)**

  Structural Information of Short-Lived Transients

- **Pulse width < 100 fs (or 1 ps)**

  Direct Observation on Coherent Motion

Seeing what we could not see before creates new science.

Collaborators

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