2013.10.8
Carl-Zeiss lecture
Jena

Raman spectroscopy: Variants and potentials

Hiro-o Hamaguchi

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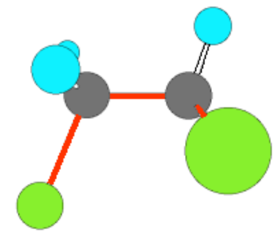
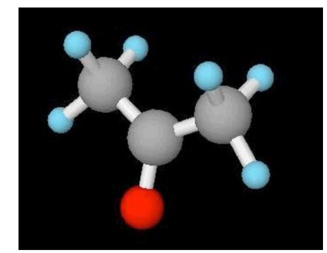
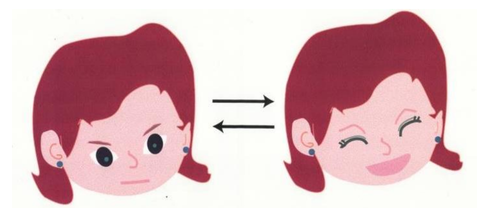
The University of Tokyo, Japan
Wseda University, Japan

Raman spectroscopy: Variants and potentials

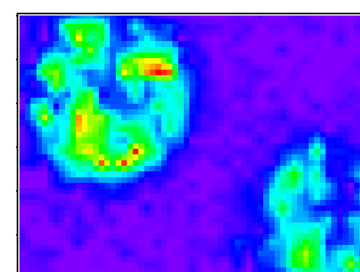
○ Raman brothers,
Raman, CARS/SRS, and SERS/TERS
What do they look at?
Hamaguchi's score sheet for Raman brothers

○ Raman spectroscopy in Japan
Discovery of rotational isomerism
Normal coordinate analysis



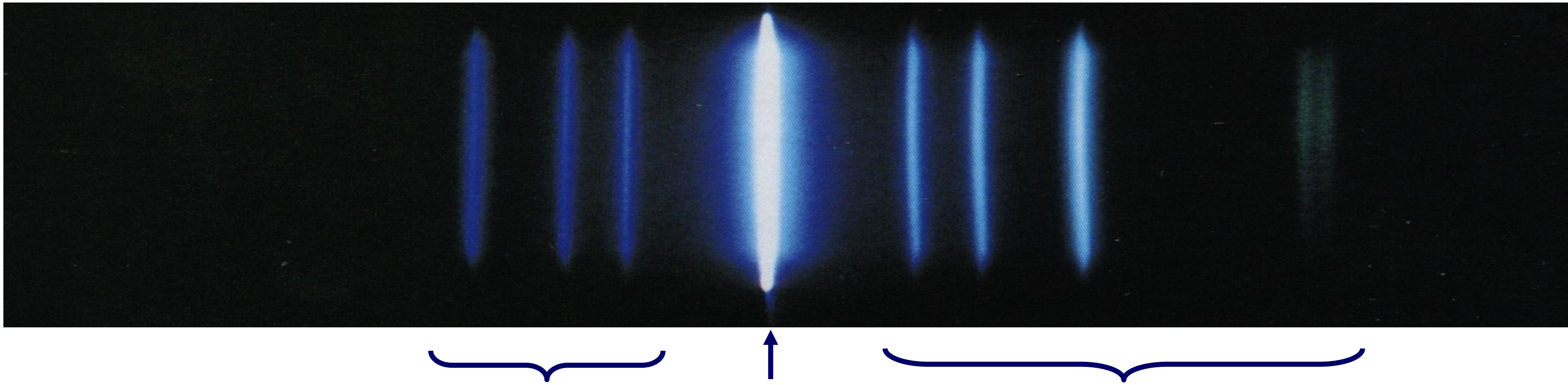
○ Time-resolved Raman spectroscopy
Dynamic polarization model of
chemical reactions



○ Raman microsepctroscopy of living cells

○ Tailor-made Raman spectroscopy

Raman Spectroscopy



Raman scattering :

Inelastic light scattering discovered by C. V. Raman in 1928

Raman spectroscopy:

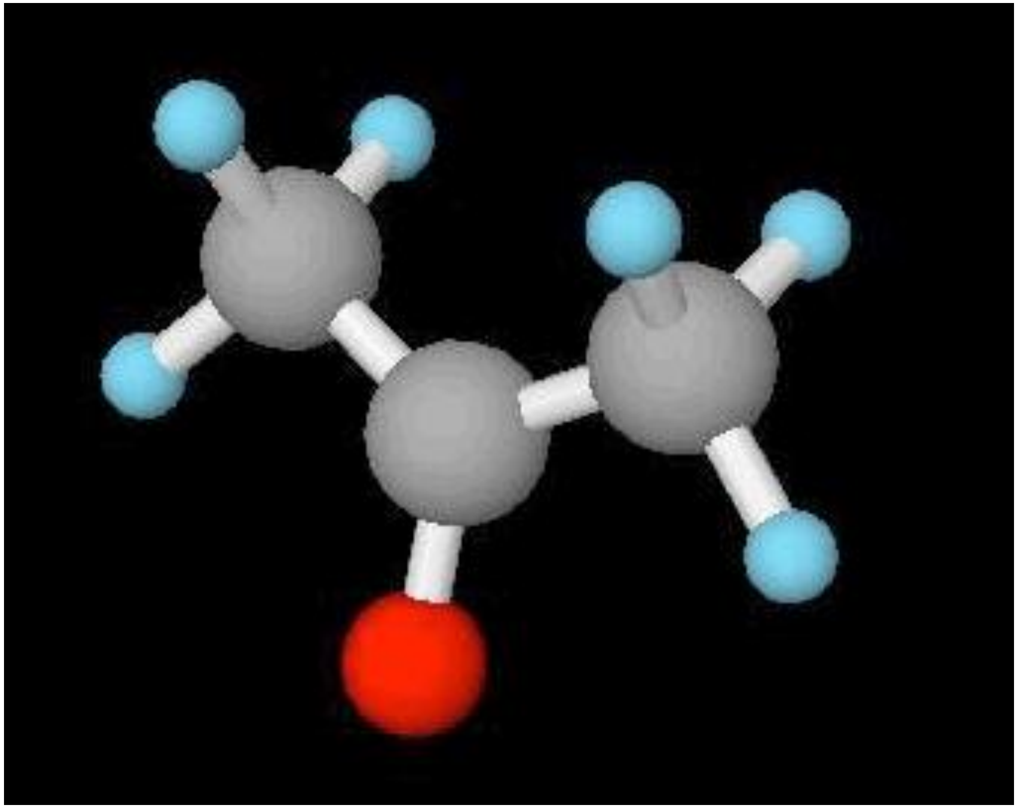
Spectroscopy utilizing Raman scattering

C. V. Raman (1888-1970)

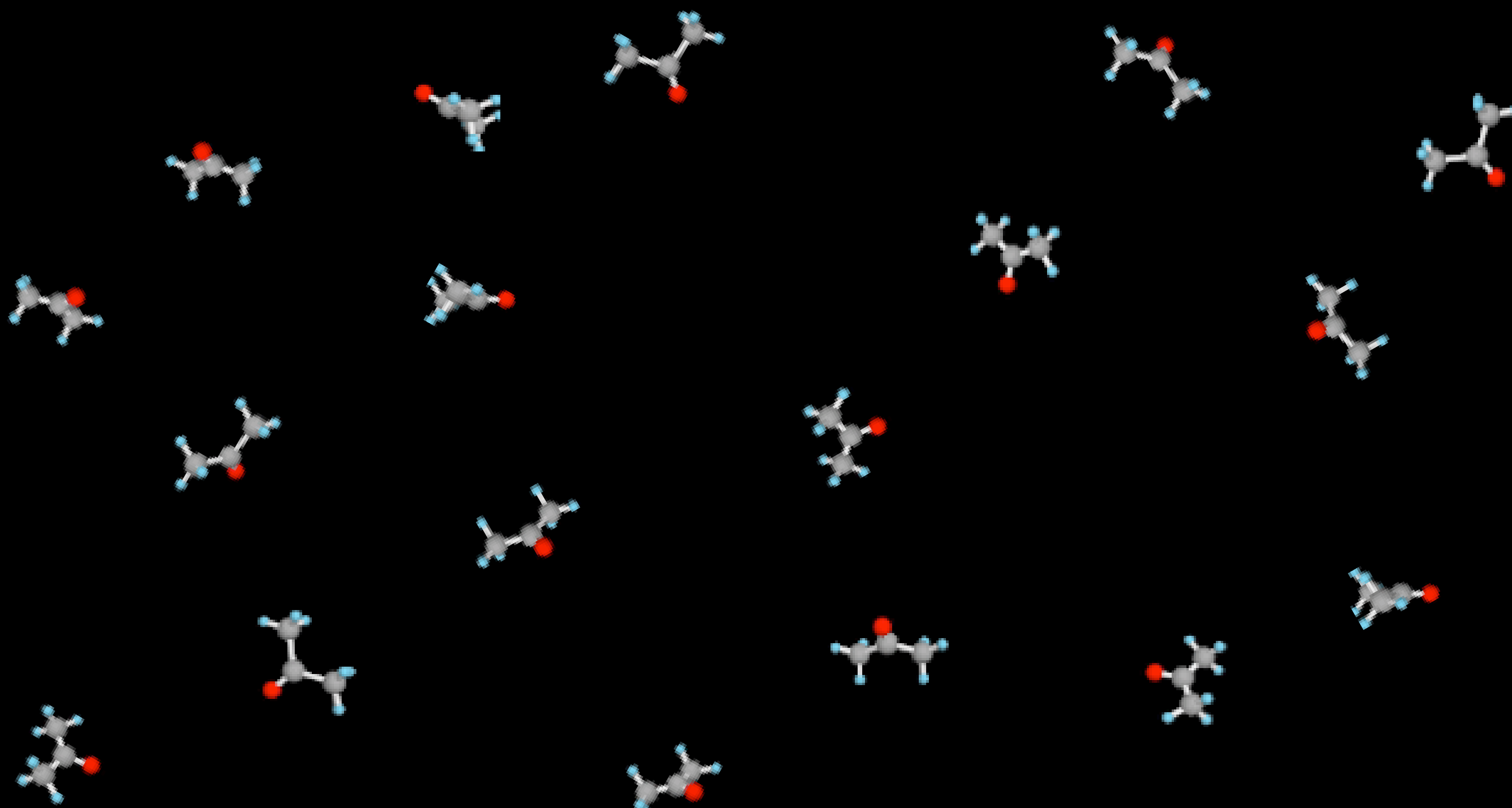
Raman Brothers: What do they look at?

Normal Mode of Vibration:

The Totally Symmetric C-C Stretch Mode of an Acetone Molecule

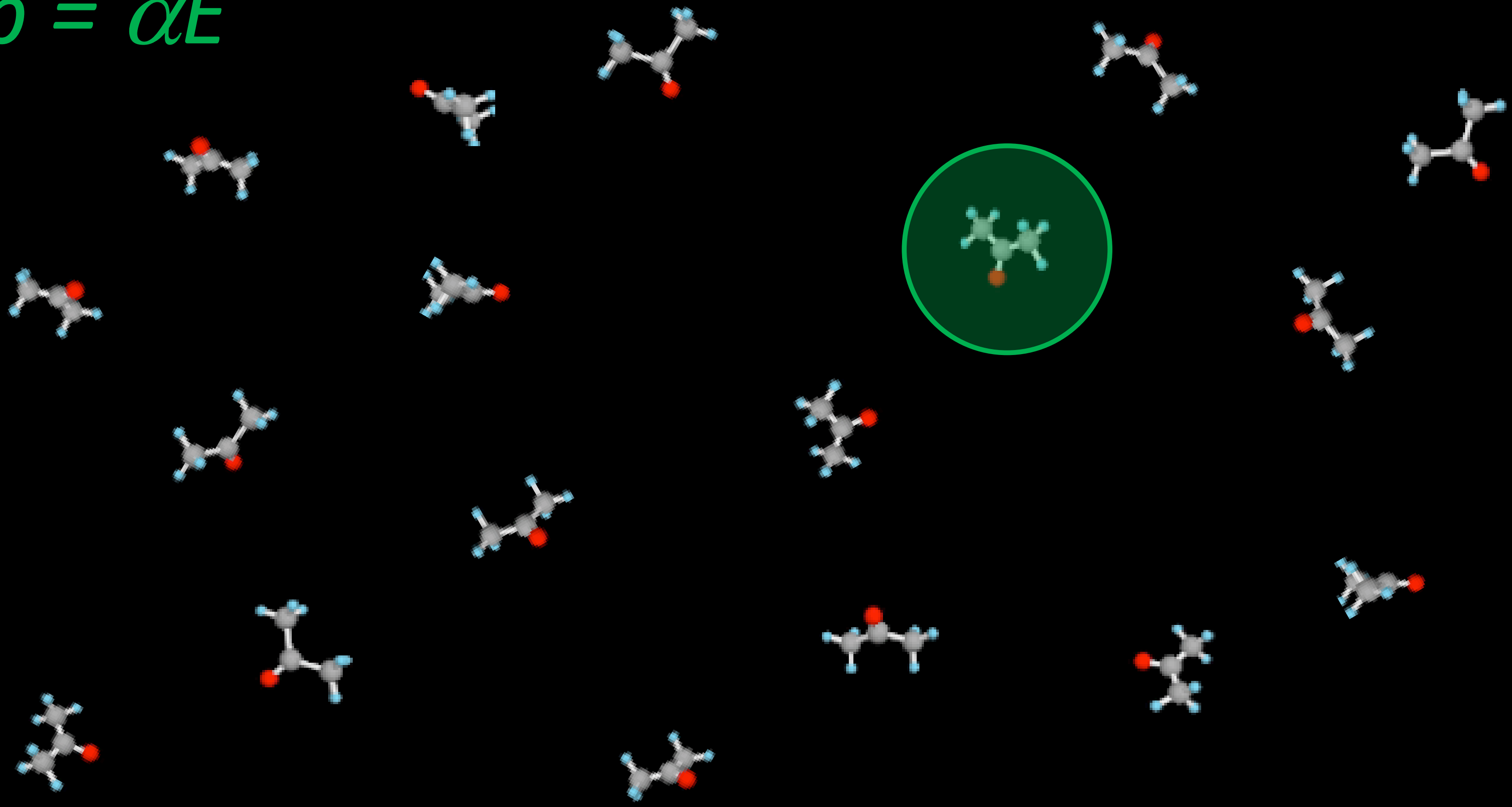


Vibrational Motions of Ensembles of Acetone Molecules

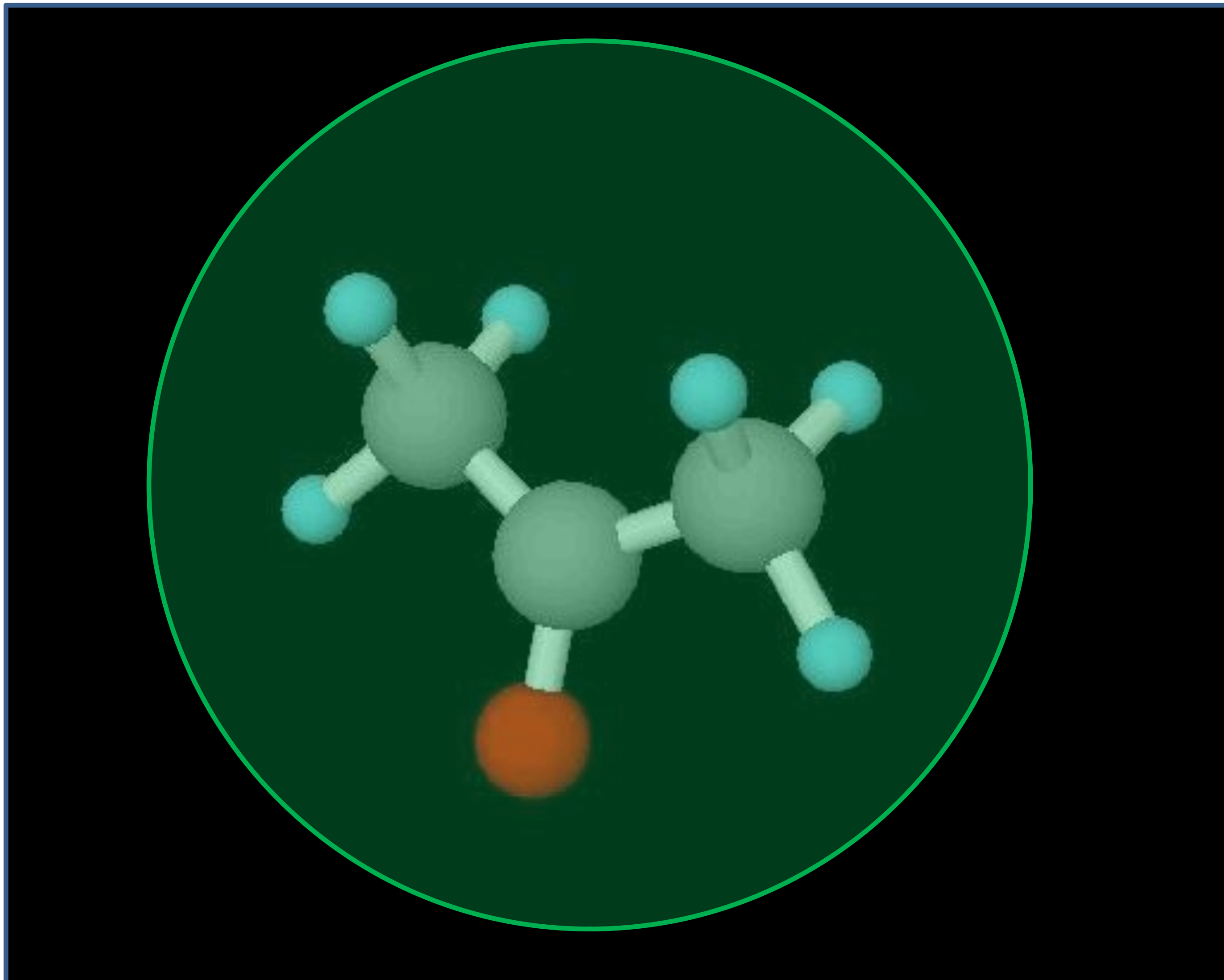


What Does Raman look at?

$$p = \alpha E$$



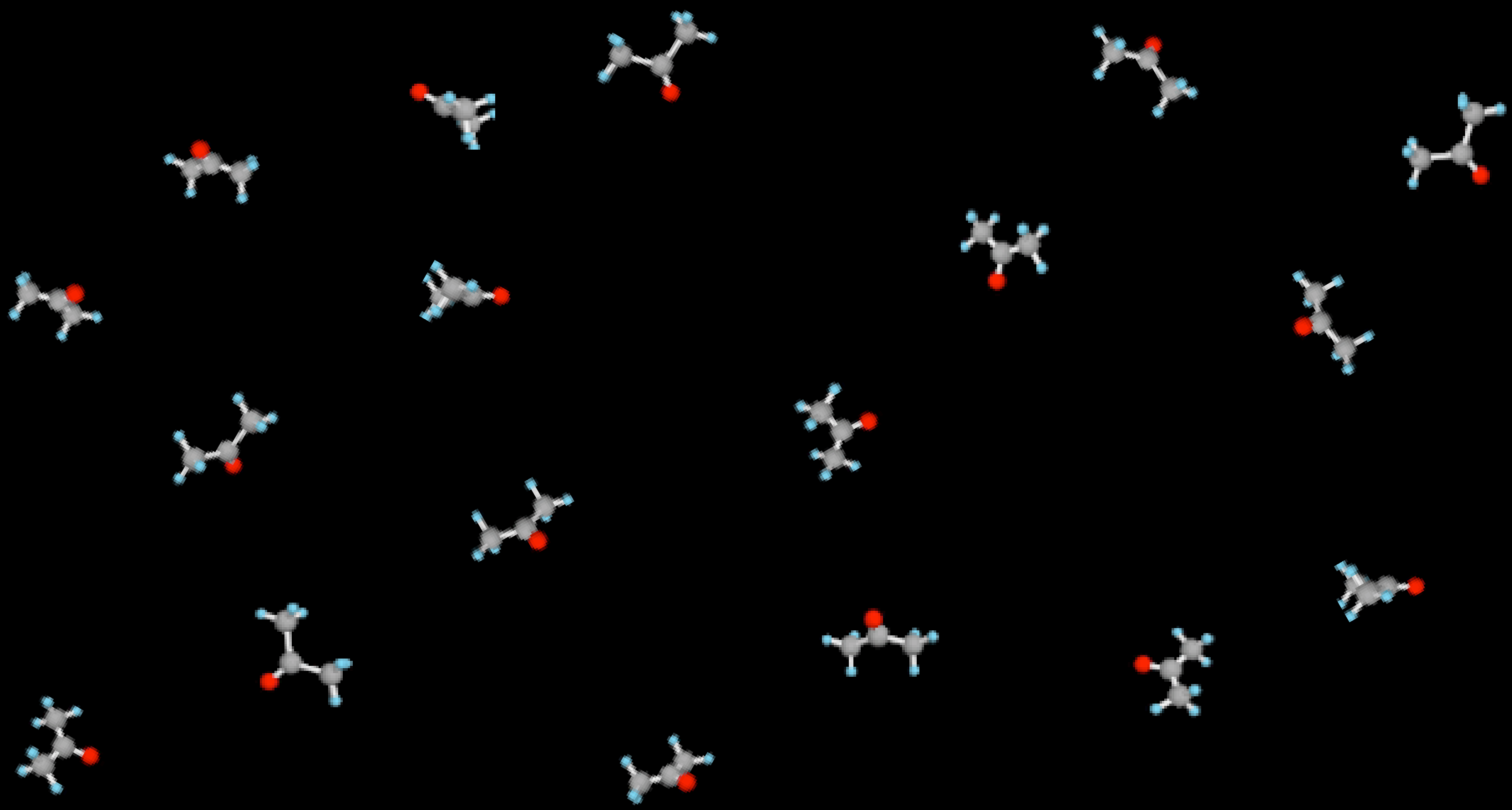
Raman Looks at a Normal Mode of Vibration.



Raman Gives a Molecular Fingerprint.

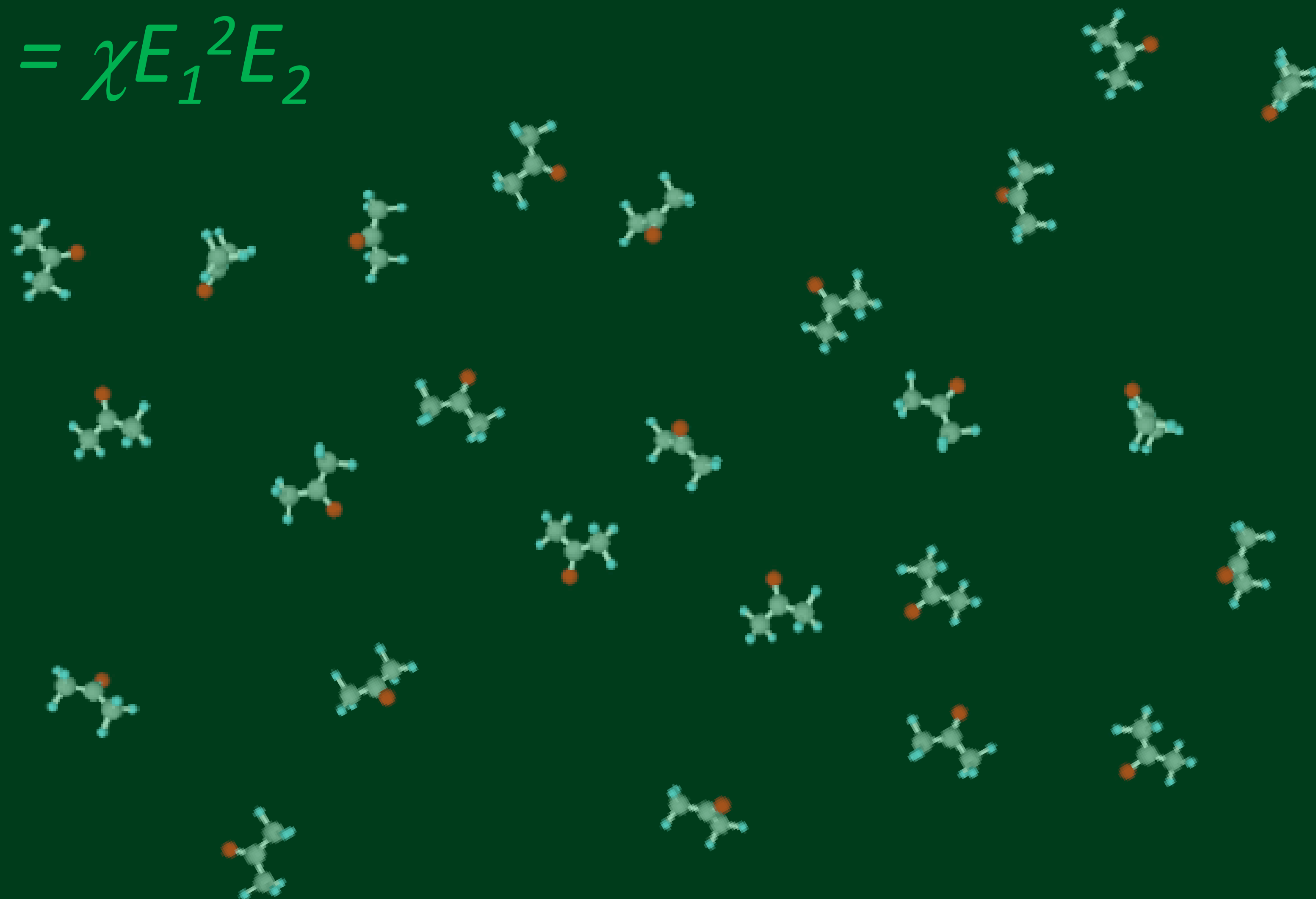
http://dailynewsagency.com

What Does CARS/SRS Look at?



CARS/SRS Looks at a Vibrational Coherence

$$p = \chi E_1^2 E_2$$



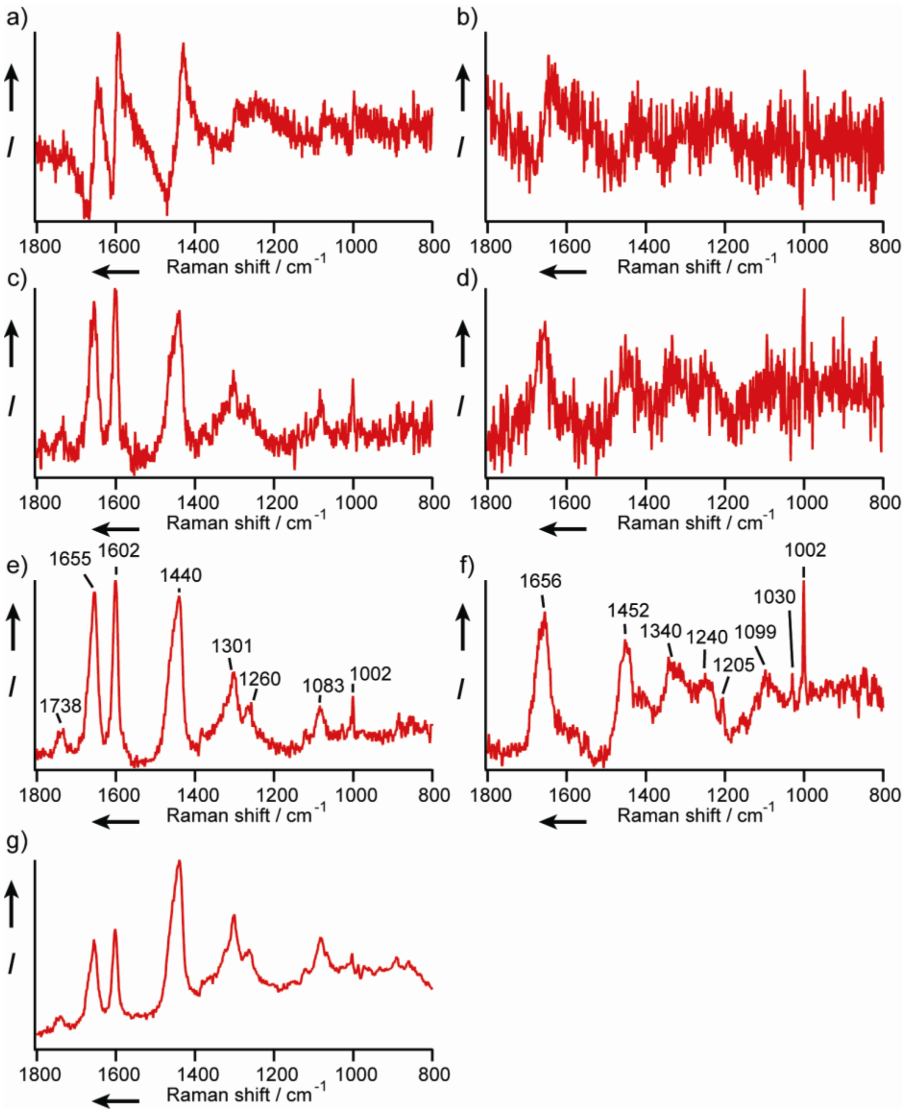
CARS Can Give a Molecular Fingerprint After Some Mathematical Treatments.

CARS spectra

Imχ_3 spectra by MEM

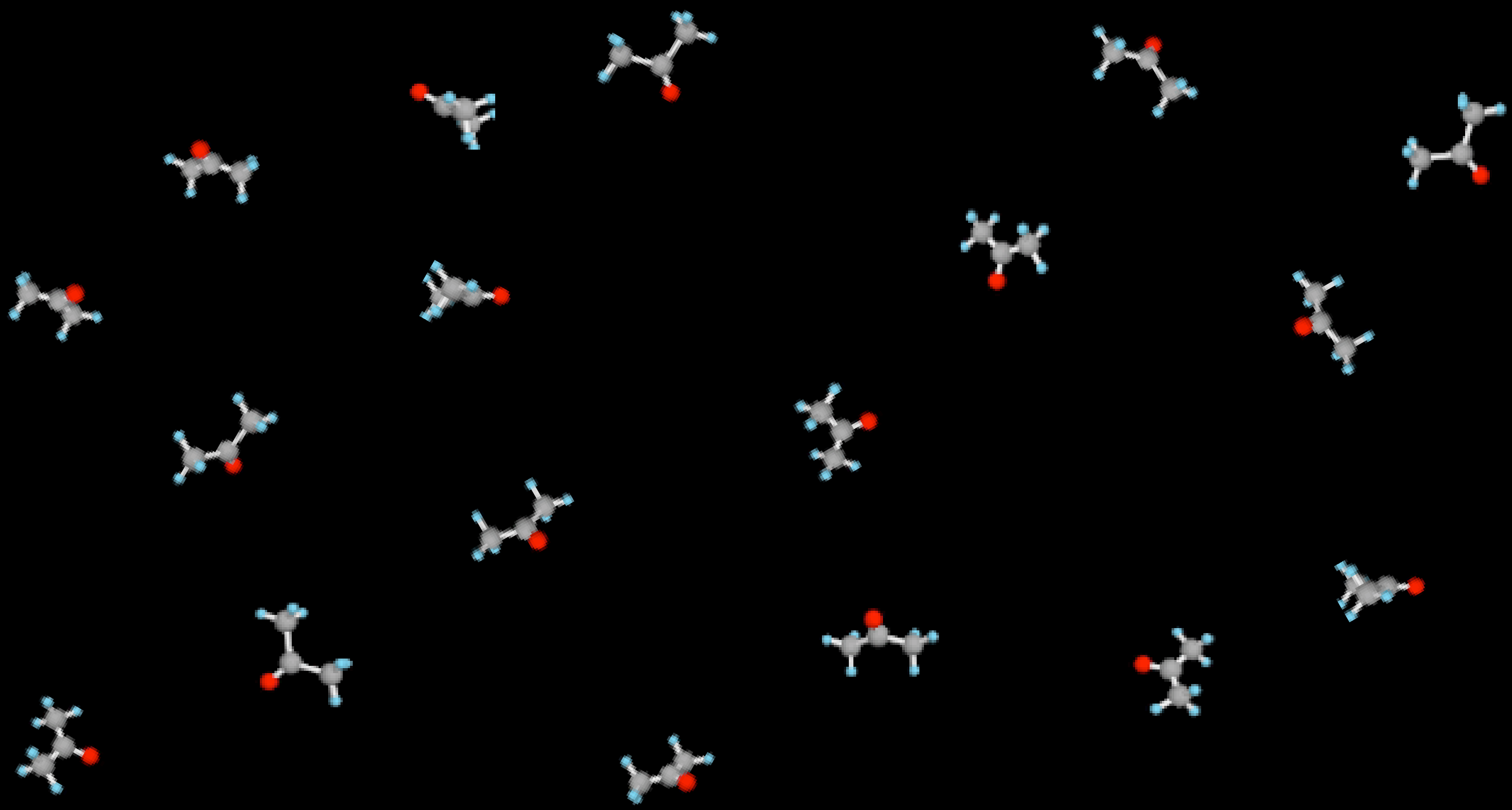
Imχ_3 spectra after SVD

Raman spectra

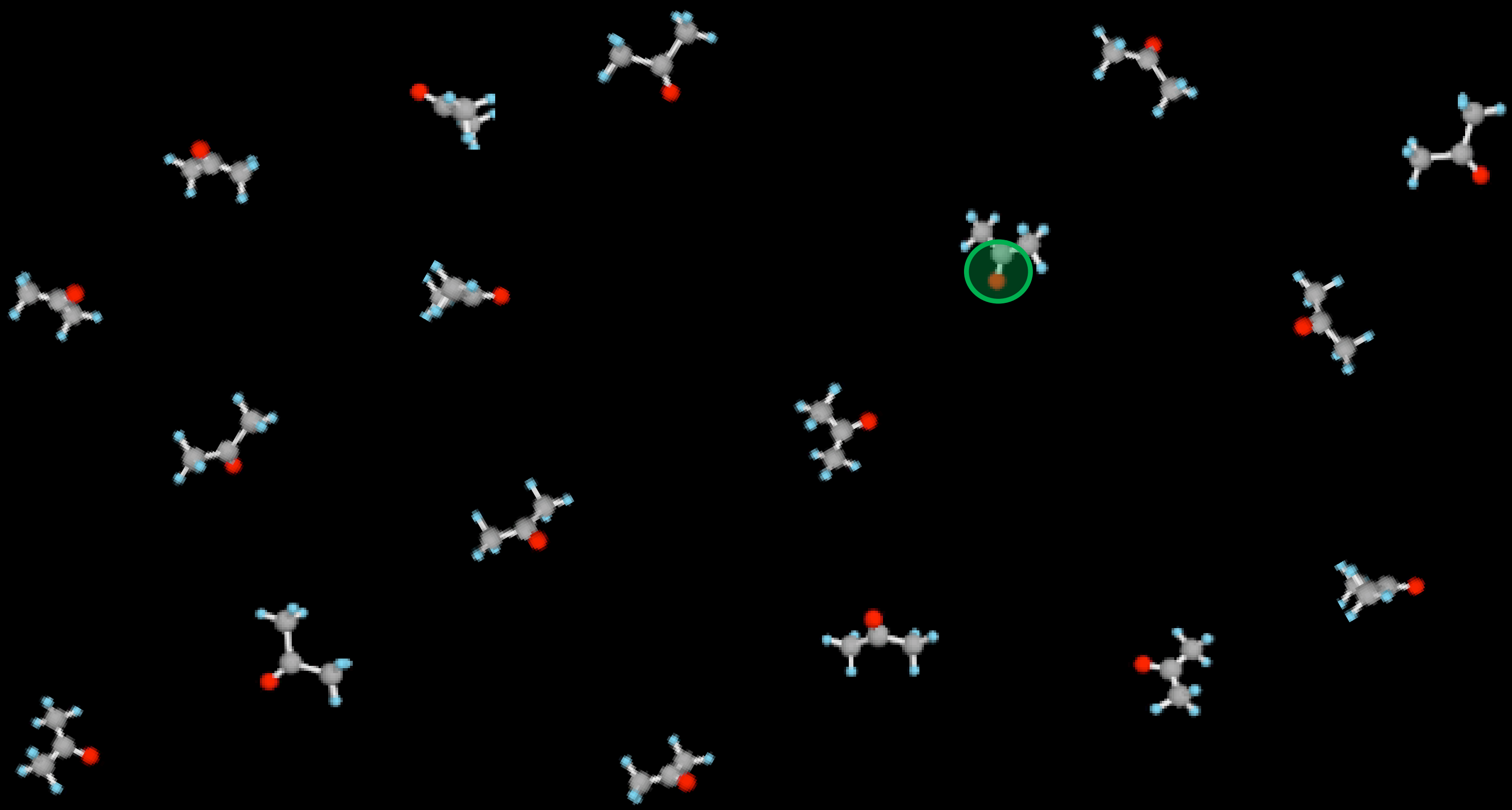


Okuno et al. Angewandte Chemie, *Angew. Chem. Int. Ed.*, **49**, 6773-6777 (2010).

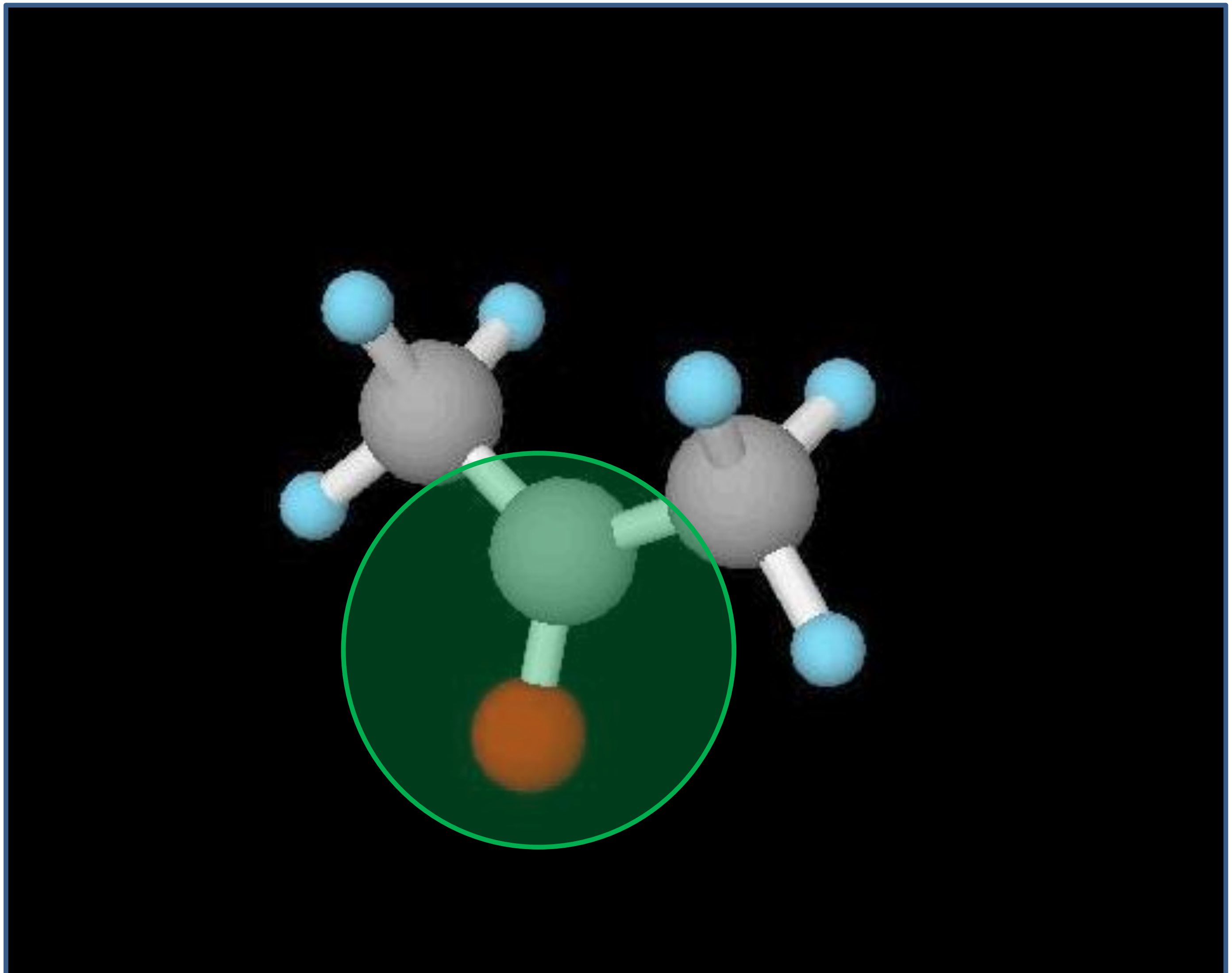
Vibrational Motions of Ensembles of Acetone Molecules



What Does SERS/TERS Look at?



SERS/TERS is Likely to Look at a Local Molecular Motion (May not be a Normal Mode)



SERS/TERS May not Give a Full Molecular Fingerprint.

http://dailynewsagency.com

Hamaguchi's Score Sheet for Ramans

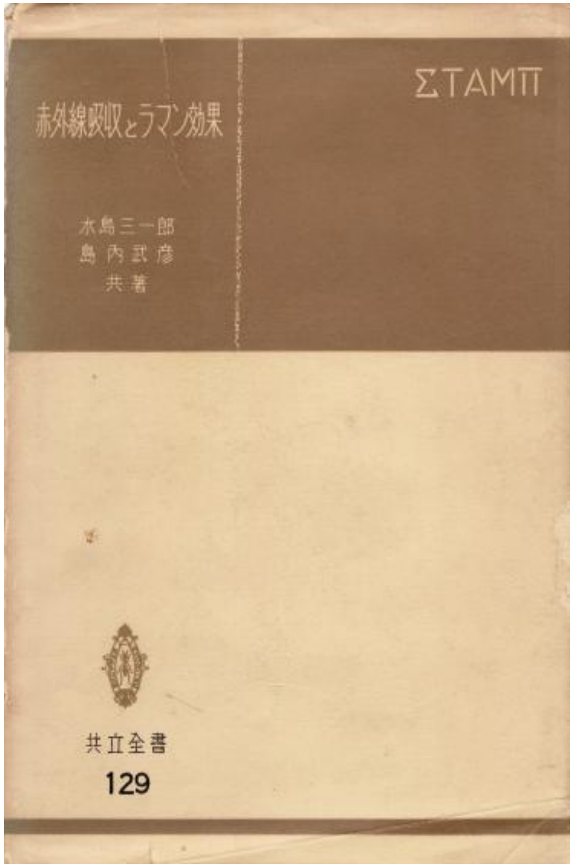
	Raman	CARS/SRS	SERS/TERS
Selection rule	Established	Established for homogeneous systems	Dependence on individual molecular orientation?
Polarization rule	Established	Established for homogeneous systems High polarization capabilities	Dependence on individual molecular orientation?
Information content	Molecular Fingerprint	Molecular fingerprint after mathematics	Molecular Fingerprint?
Sensitivity	Ensemble	Ensemble	Single molecule
Spatial resolution	$0.61\lambda/NA$ (500 nm)	$0.61\lambda/NA\sqrt{3}$ (300 nm)	Tip size (10 nm)
Time resolution	ps	ps	ps
Experimental difficulty	Fluorescence interference	Phase match/mismatch	Tip/substrate dependence

- Raman is HH's first choice for advanced applications.

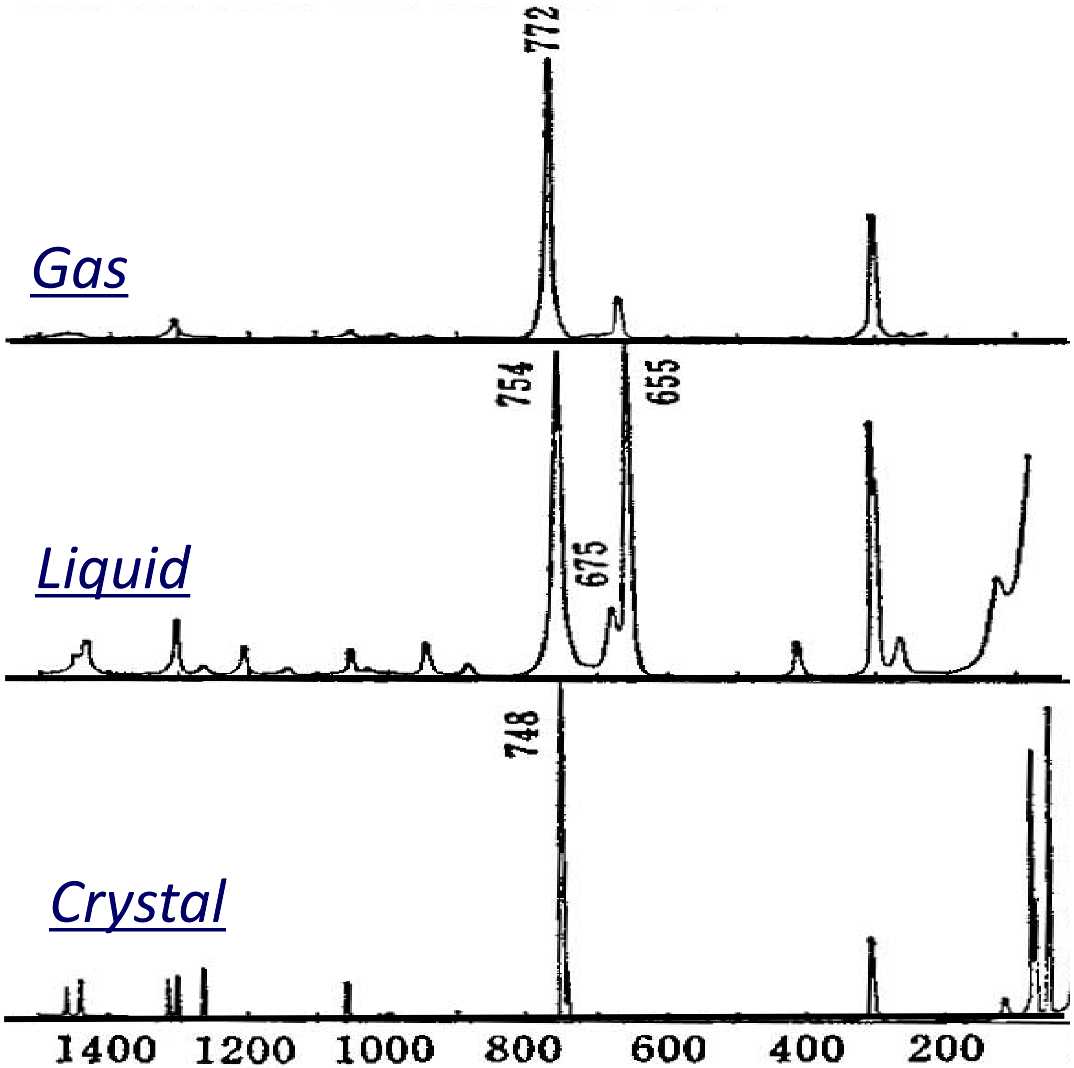
- CARS/SRS surpasses Raman for its polarization capabilities.

- SERS/TERS excels in sensitivity and spatial resolution. Its information content yet to be clarified.

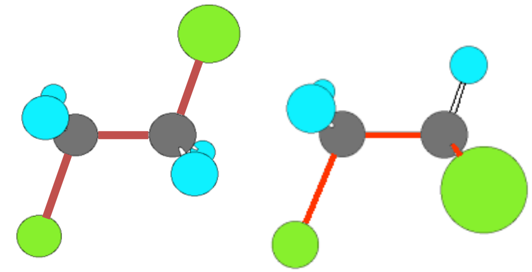
Raman Spectroscopy atTokyo

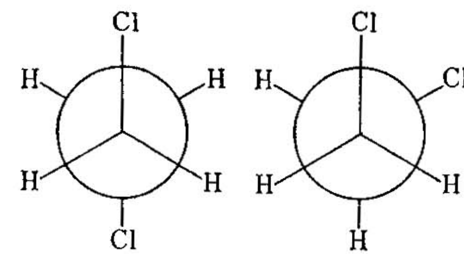


Discovery of the Rotational Isomerism



Trans *Gauche*





S. Mizushima
(1899-1983)

Raman Spectra are letters from the molecule

Vibrational Raman spectra are molecular fingerprints

Professor Takehiko Shimanouchi (1916-1980)

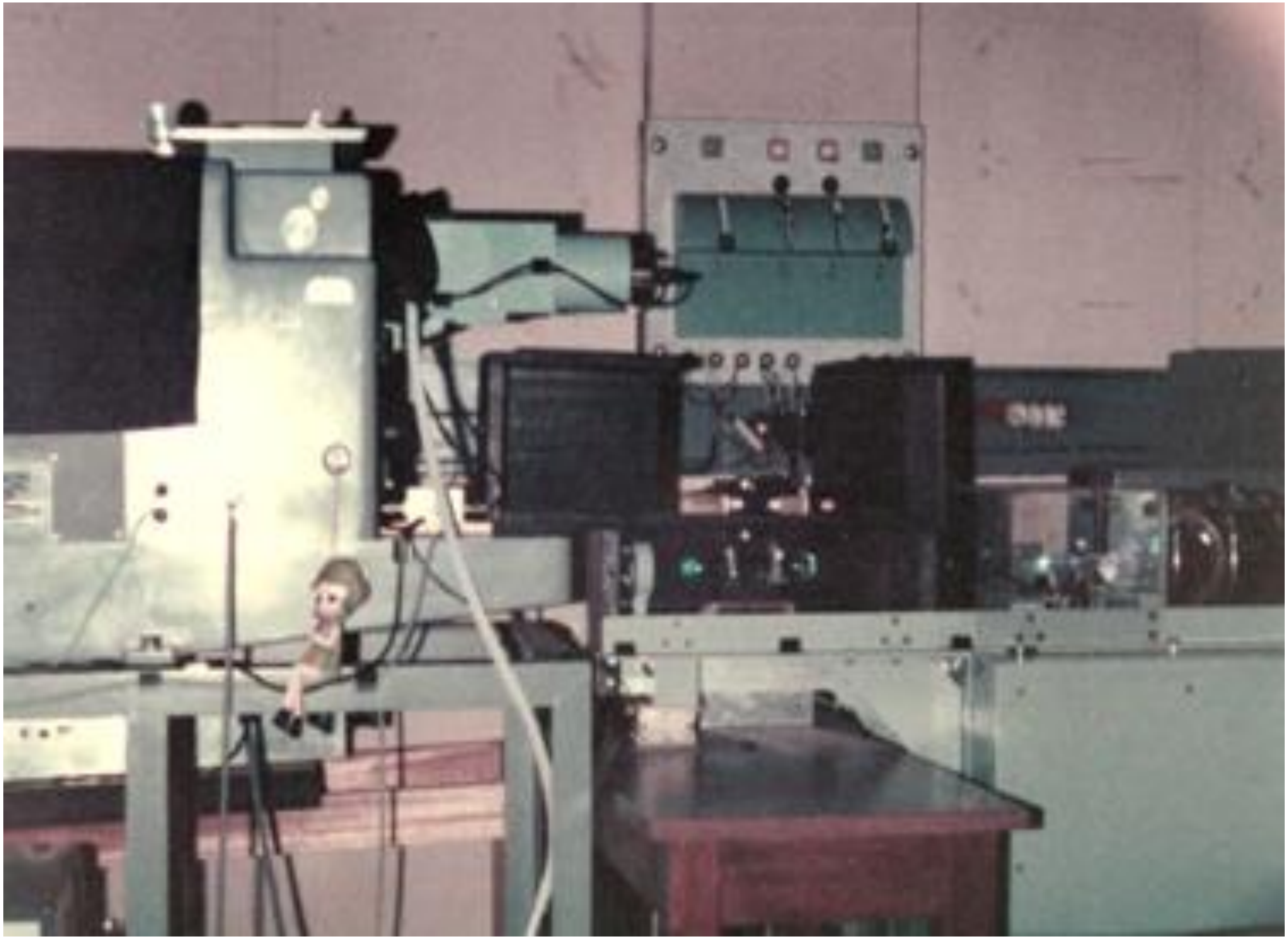
T. Shimanouchi, Tables of Molecular Vibrational Frequencies, NSRDS-NBS 39.

Molecule: 1,2-Dichloroethane CH_2ClCH_2Cl (trans form) **No. 160**

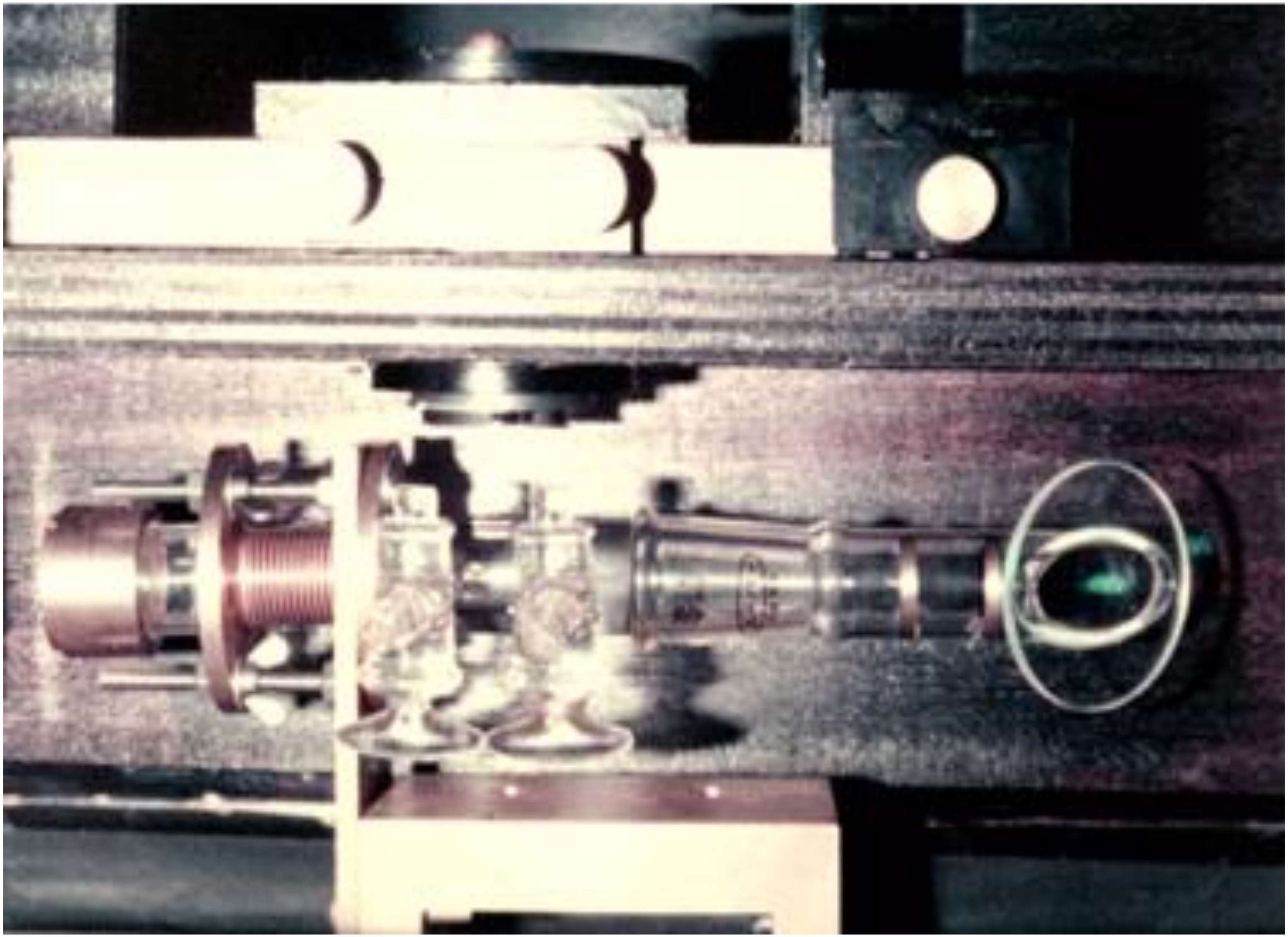
Symmetry C_{2h} Symmetry number σ = 2

Sym. species	No.	Approximate type of mode	Selected value of frequency	Infrared	Raman	Comments
				cm^{-1} (Gas)	cm^{-1} (Liquid)	
a_g	ν_1	CH_2 s-stretch	2957 D	ia	2957 (10) p	
	ν_2	CH_2 scis	1445 C	ia	1445 (4b) dp	
	ν_3	CH_2 wag	1304 C	ia	1304 (6) p	
	ν_4	CC stretch	1052 C	ia	1052 (4) p	
	ν_5	CCl stretch	754 C	ia	754 (10b) p	
	ν_6	CCCl deform	300 C	ia	300 (8) p	
a_u	ν_7	CH_2 a-stretch	3005 D	3005 W (liquid)	ia	SF (gauche ν_1, gauche ν_{11}).
	ν_8	CH_2 twist	1123 B	1122.5 W	ia	
	ν_9	CH_2 rock	773 B	772.5 M	ia	
	ν_{10}	Torsion	123 C	123 M	ia	
b_g	ν_{11}	CH_2 a-stretch	3005 D	ia	3005 (8b) dp	
	ν_{12}	CH_2 twist	1264 C	ia	1264 (3) dp	
	ν_{13}	CH_2 rock	989 C	ia	989 (2) p	
b_u	ν_{14}	CH_2 s-stretch	2983 C	2983.3 M	ia	
	ν_{15}	CH_2 scis	1461 A	1460.6 S	ia	
	ν_{16}	CH_2 wag	1232 B	1232.3 S	ia	
	ν_{17}	CCl stretch	728 C	728.3 VS	ia	
	ν_{18}	CCCl deform	222 C	222.3 W	ia	

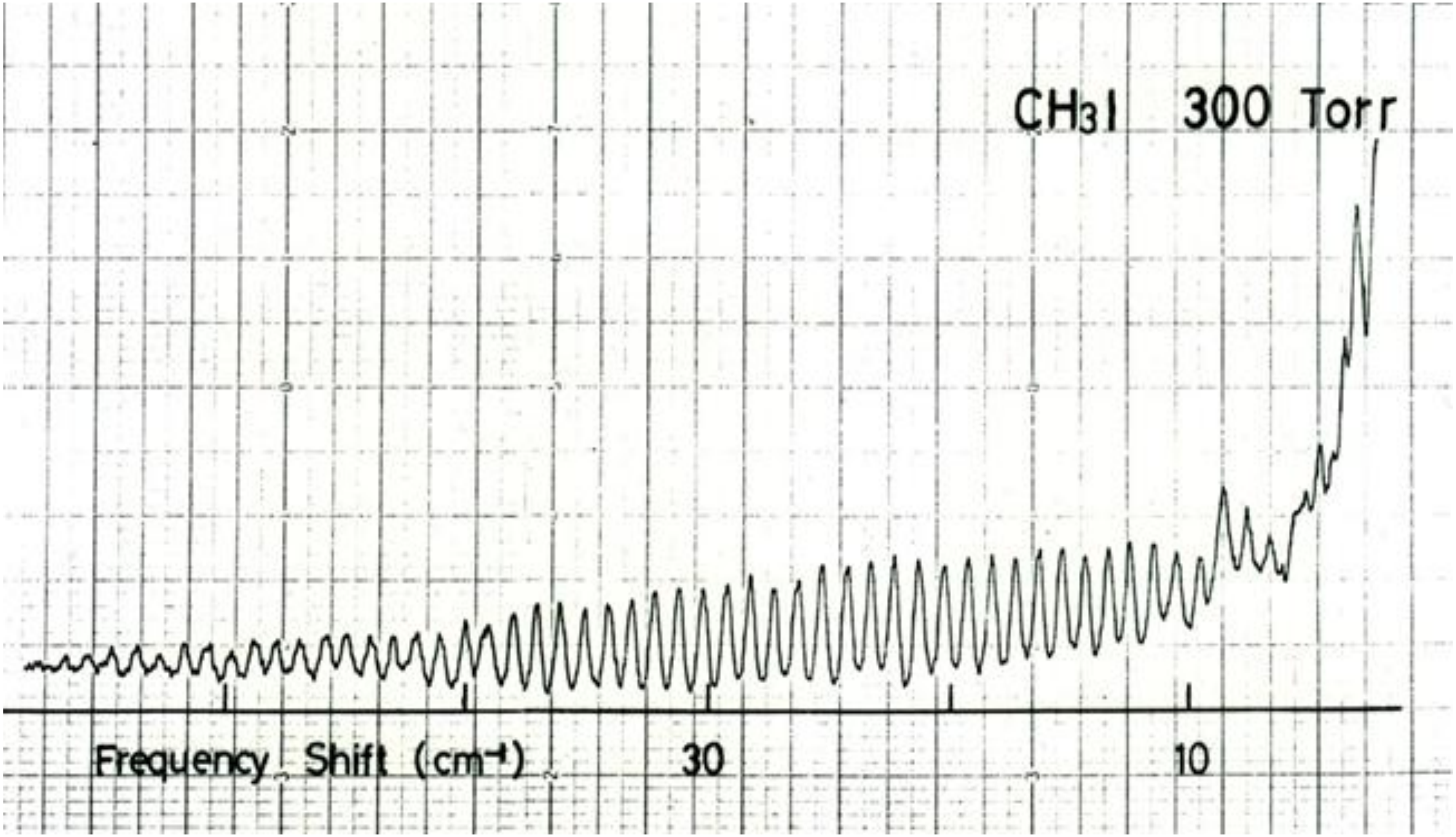
High Resolution Raman Spectrometer (1972)



Raman Gas Cell in Laser Cavity (1972)



Raman Spectrum of CH_3I (1972)



Resonance Raman scattering

RESONANCE RAMAN SPECTROSCOPIC STUDY ON IODINE IN VARIOUS ORGANIC SOLVENTS: SPECTROSCOPIC CONSTANTS AND HALFBAND WIDTHS OF THE I_2 VIBRATION* **

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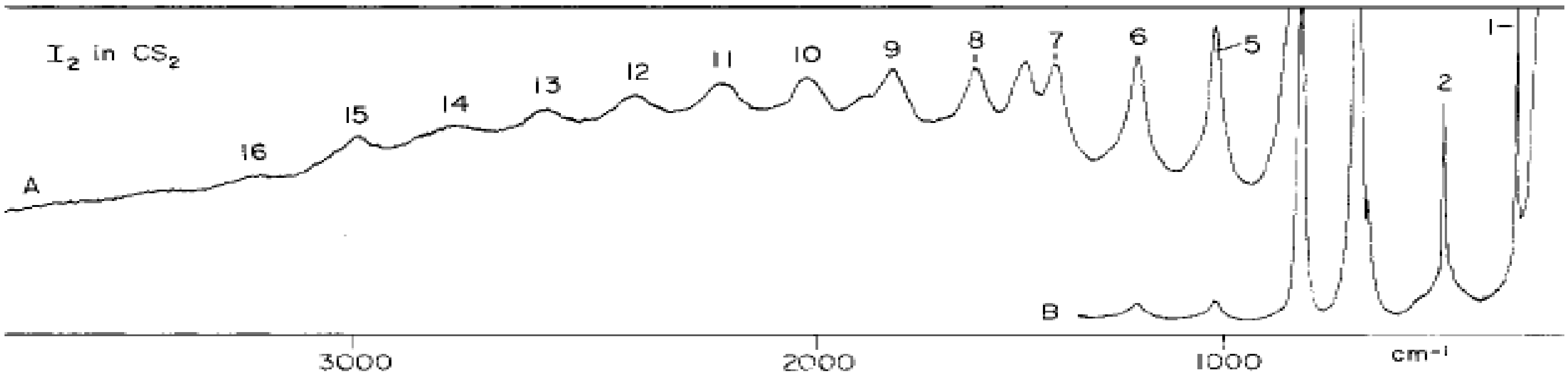
Sektion Physik der Universität München, Lehrstuhl J. Brandmüller, D-8 München 40, Germany

and

H. J. BERNSTEIN

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada

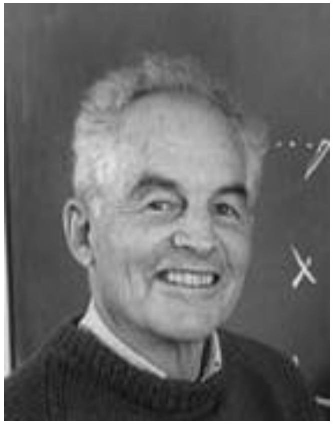


Theory of Resonance Raman Scattering

Albrecht's vibronic theory of resonance Raman Scattering

A. C. Albrecht, J. Chem. Phys. 34, 1476 (1961).

A. C. Albrecht
(1927-2002)

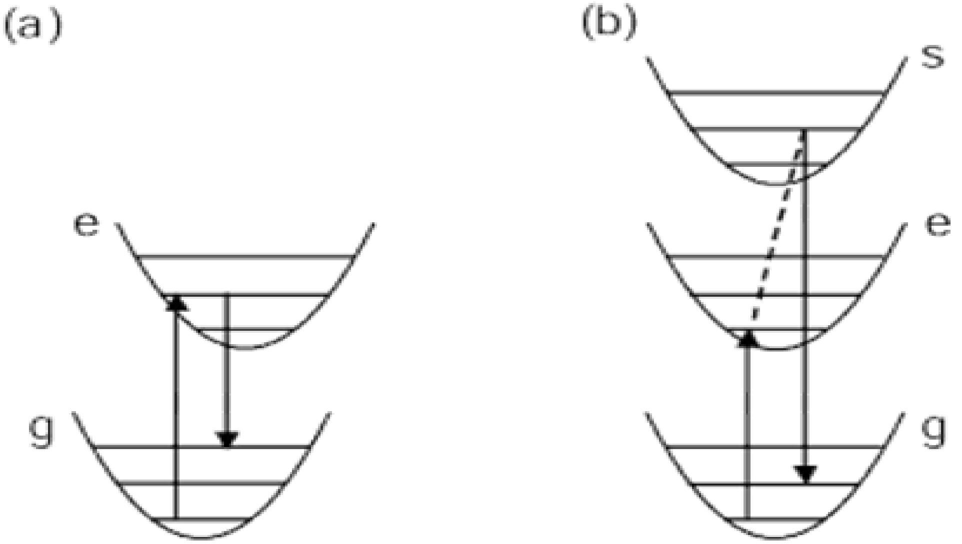


$a_{\rho\sigma}$ ~ A + B

A term: Franck-Condon term

Totally symmetric modes

High overtones

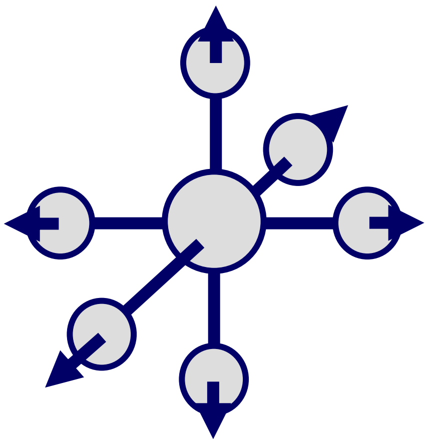


B term: Vibronic coupling

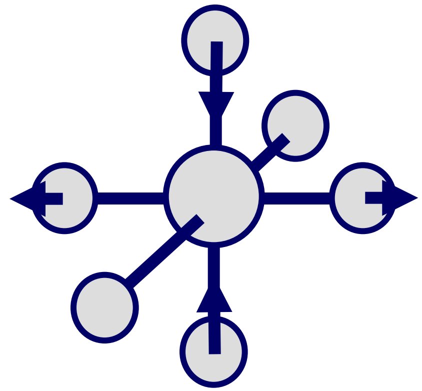
Non-totally symmetric modes

No high overtones

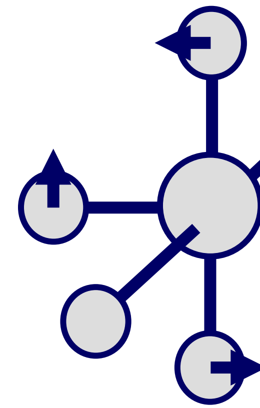
Raman Active Vibrations of MX_6 Octahedral Complexes



ν_1
(a_{1g})



ν_2
(e_g)

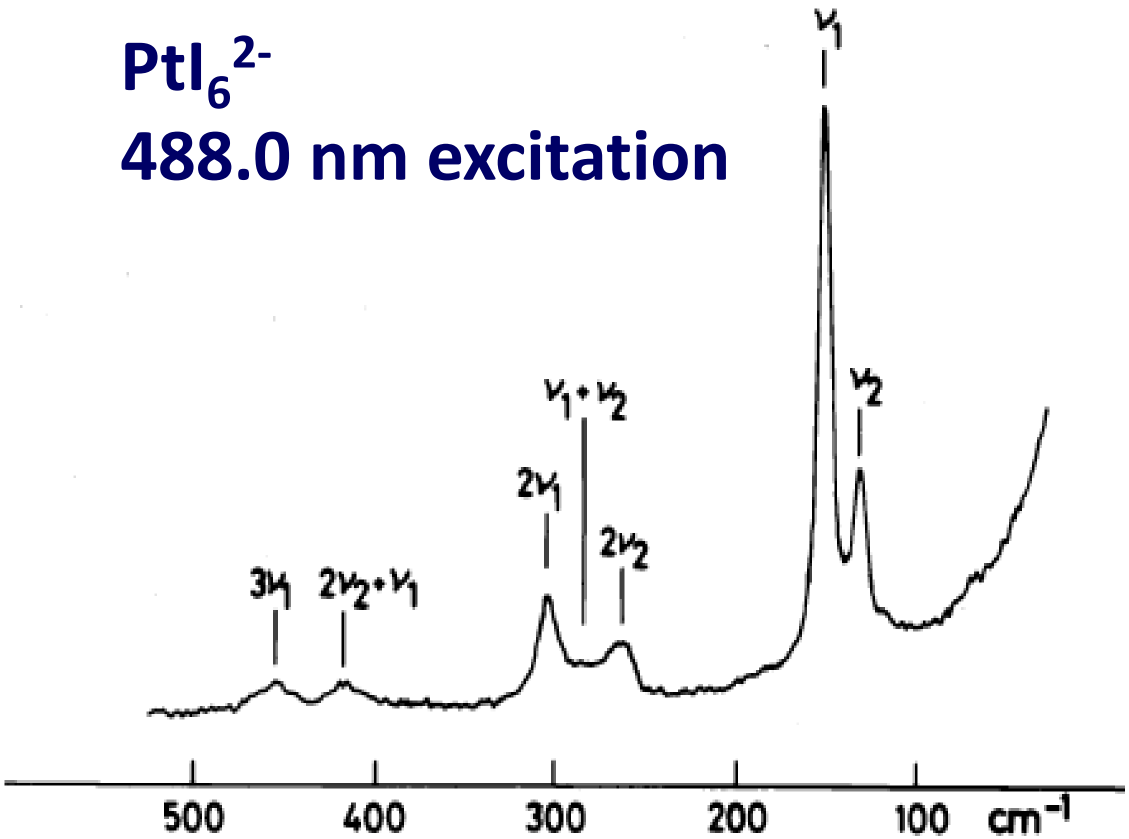


ν_5
(t_{2g})

$$a_{1g} \sim \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad e_g \sim \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad t_{2g} \sim \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$\rho=0$ $\qquad$ $\rho=0.75$ $\qquad$ $\rho=0.75$

Resonance Raman spectrum of PtI_6^{2-}

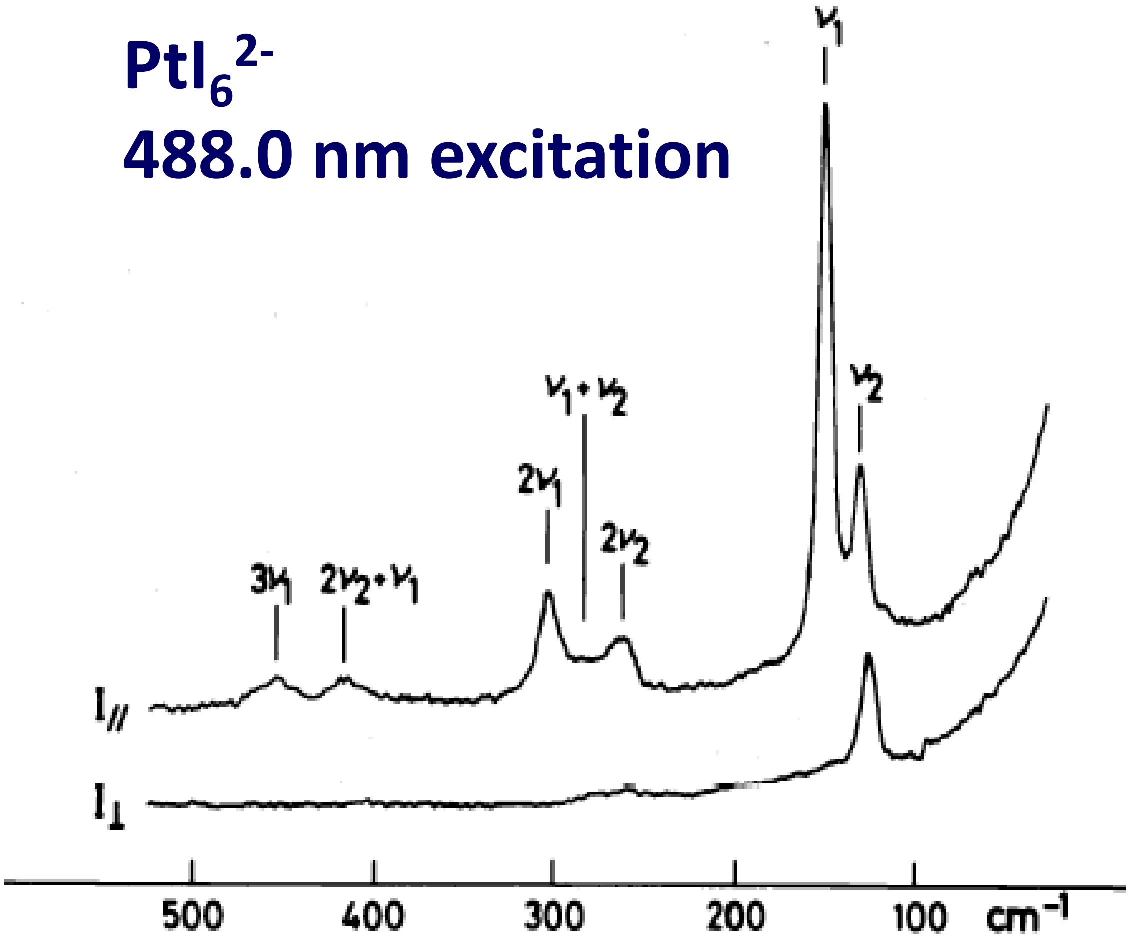


Totally symmetric mode (ν_1, $2\nu_1$, $3\nu_1$) → **A term**

Non-totally symmetric mode (ν_2, $2\nu_2$, $\nu_1+\nu_2$, $2\nu_1+\nu_2$) → **B term**

H. Hamaguchi, I. Harada, T. Shimanouch, *J. Raman Spectrosc.*, **2**, 517-528 (1974).

Polarized Resonance Raman Spectra of PtI_6^{2-}

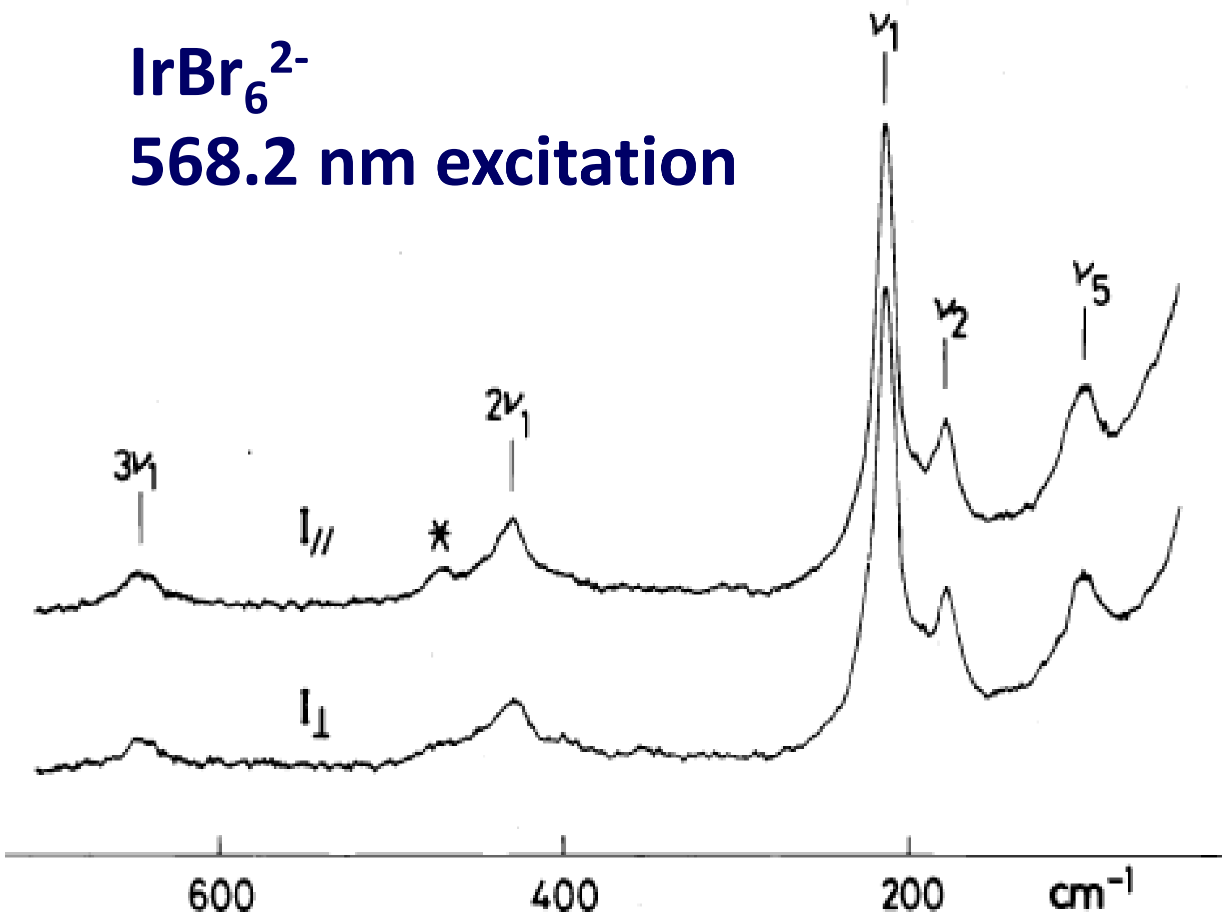


ν_1, $2\nu_1$, $3\nu_1$ bands ρ=0 ; ν_2 band ρ=0.75

H. Hamaguchi, *J. Chem. Phys.*, **69**, 569-578 (1978).

Polarized Resonance Raman Spectra of $IrBr_6^{2-}$

$IrBr_6^{2-}$
568.2 nm excitation



ρ=1 for all bands; **forgot to rotate the analyzer?**

H. Hamaguchi, *J. Chem. Phys.*, **66**, 5757-5768 (1977) ; **69**, 569-578 (1978).

Raman Scattering Tensors and Depolarization ratio of the Totally Symmetric Mode of the $IrBr_6^{2-}$ Ion

$|g(\alpha)\rangle \longrightarrow |g(\alpha)\rangle$ $\begin{pmatrix} 1 & i & 0 \\ -i & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $G_0=3, G_a=2, G_s=0$

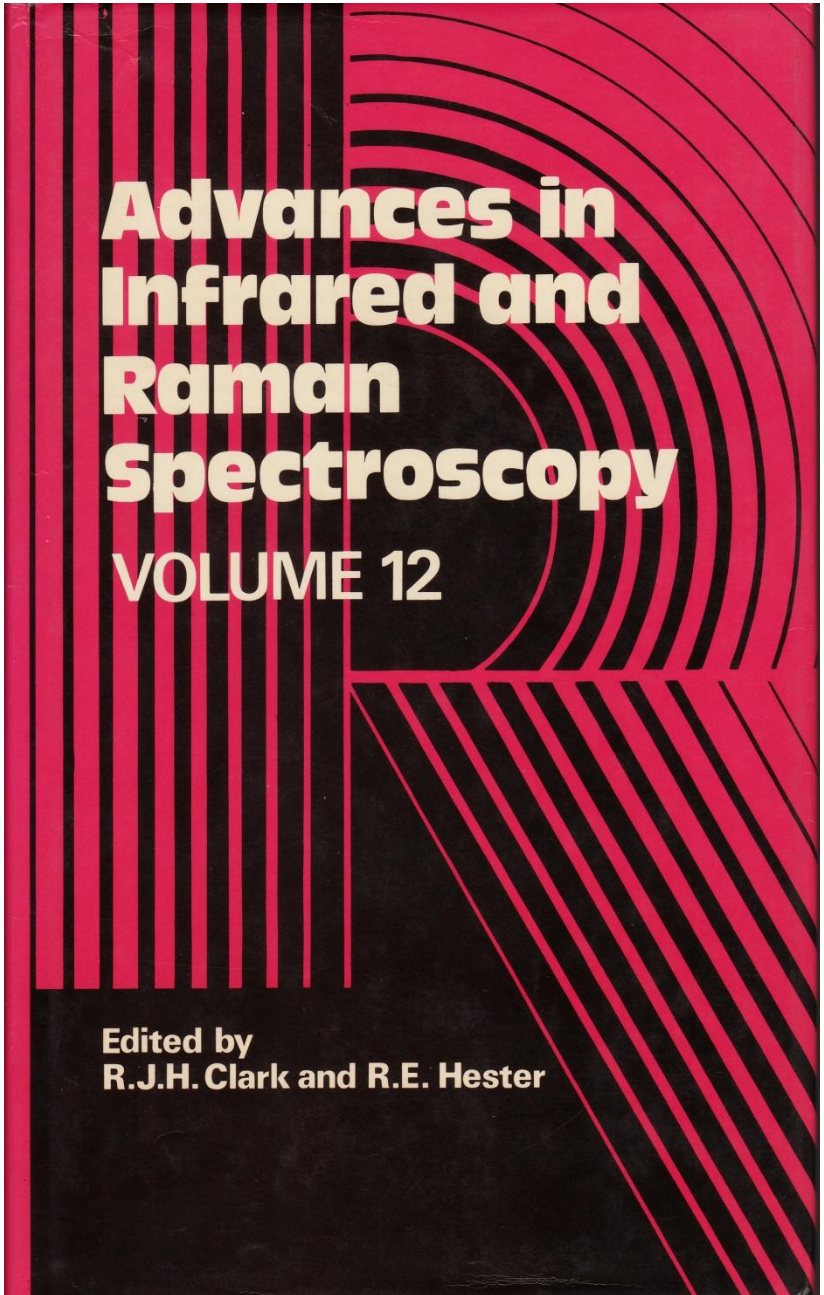
$|g(\alpha)\rangle \longrightarrow |g(\beta)\rangle$ $\begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & -1 \\ i & 1 & 0 \end{pmatrix}$ $G_0=0, G_a=4, G_s=0$

$|g(\beta)\rangle \longrightarrow |g(\alpha)\rangle$ $\begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 1 \\ i & -1 & 0 \end{pmatrix}$ $G_0=0, G_a=4, G_s=0$

$|g(\beta)\rangle \longrightarrow |g(\beta)\rangle$ $\begin{pmatrix} 1 & -i & 0 \\ i & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $G_0=3, G_a=2, G_s=0$

$G_0=6, G_a=12, G_s=0$ $\rho=(3G_s+5G_a)/(10G_0+4G_s)=1$

H. Hamaguchi, *J. Chem. Phys.*, **66**, 5757-5768 (1977).



(1985)

Chapter 6

THE RESONANCE EFFECT AND DEPOLARIZATION IN VIBRATIONAL RAMAN SCATTERING

Hiro-o Hamaguchi

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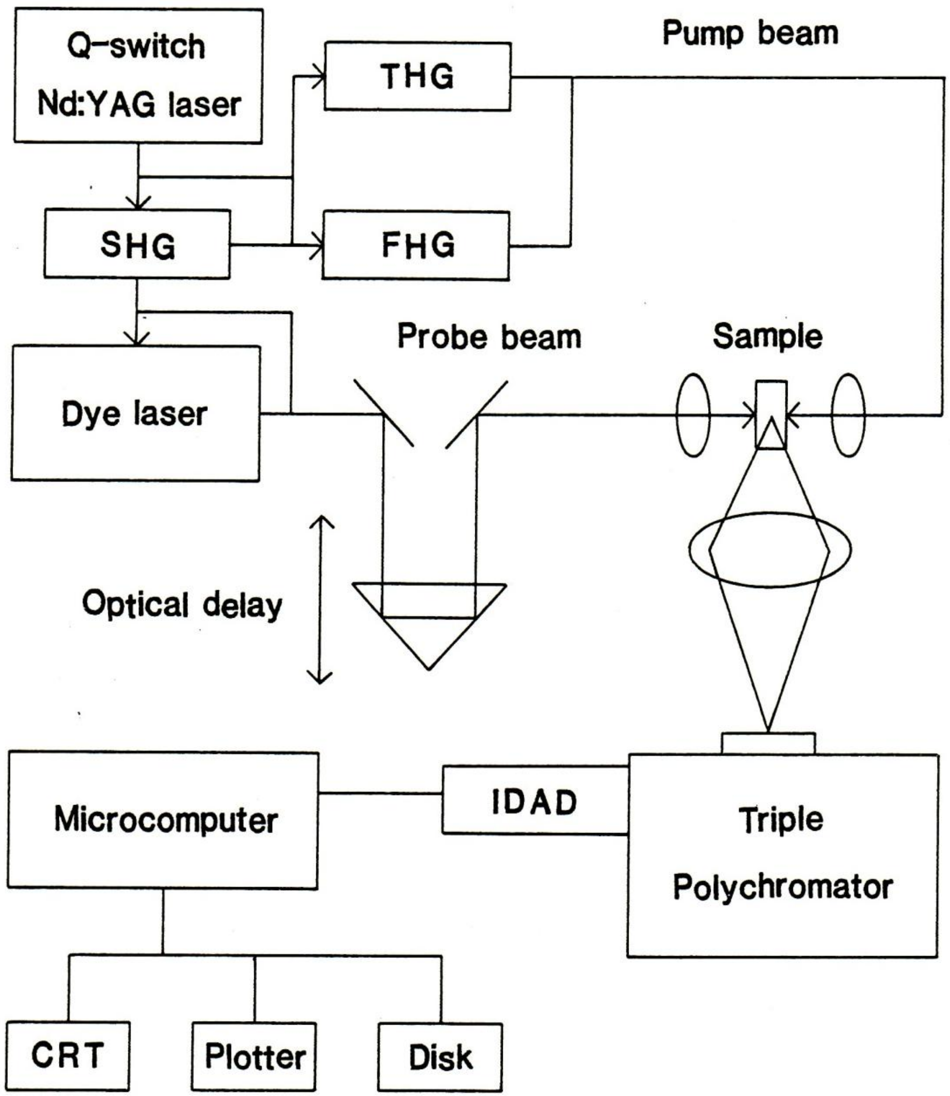
1 INTRODUCTION

Vibrational Raman scattering is essentially a vibronic process which involves the initial, intermediate, and final vibronic states. Under certain conditions, however, it can be regarded as a purely vibrational process similar to infrared absorption. This was first shown by Placzek,[1] who proved that if (i) the ground electronic state is nondegenerate and (ii) the excitation is off-resonant, the vibrational Raman intensities are approximately given by the vibrational matrix elements at the electronic polarizability (the Placzek polarizability theory). Conditions (i) and (ii) are well satisfied for off-resonant vibrational Raman scattering from molecules in their nondegenerate ground electronic states and the polarizability theory has been extensively used by vibrational spectroscopists, who found it convenient to treat vibrational Raman scattering with an exact parallelism to infrared absorption; the intensity of infrared absorption is related to the vibrational-coordinate dependence of the dipole moment, while the vibrational Raman intensity is correlated with that of the polarizability. The Placzek polarizability theory has another advantage in that it is in harmony with the classical picture of vibrational Raman scattering, in which the oscillating dipole moment induced by the electric field of the incident light is modulated by the vibrational motions, resulting in scattering with shifted frequencies.

The breakdown of the polarizability theory manifests itself most clearly in the polarization properties of vibrational Raman scattering. As predicted by Placzek,[1] the removal of either or both of conditions (i) and (ii) may lead

Nanosecond Transient Raman Spectrometer (1983)



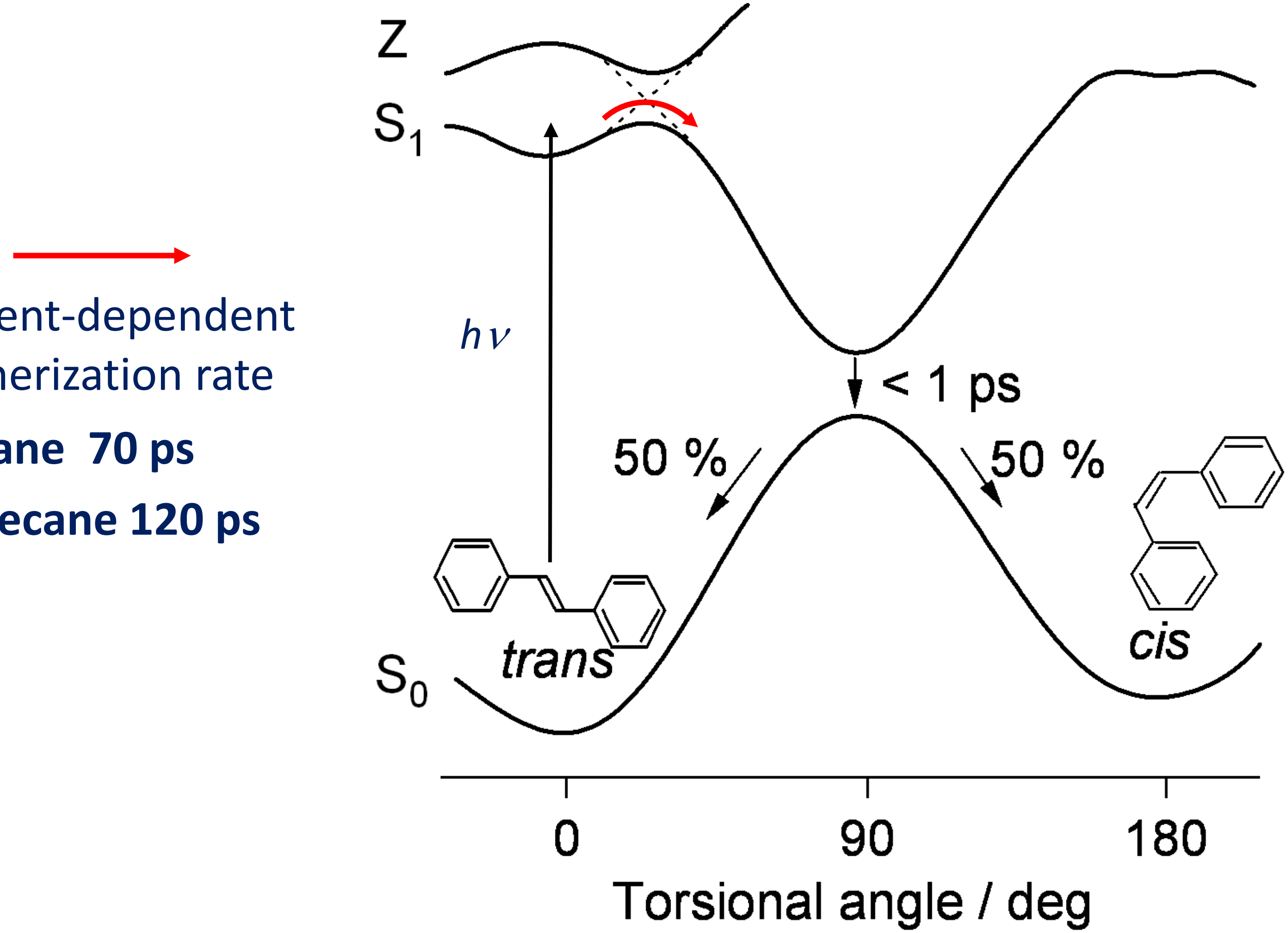
Photoisomerization of *Trans*-Stilbene

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

Solvent-dependent isomerization rate

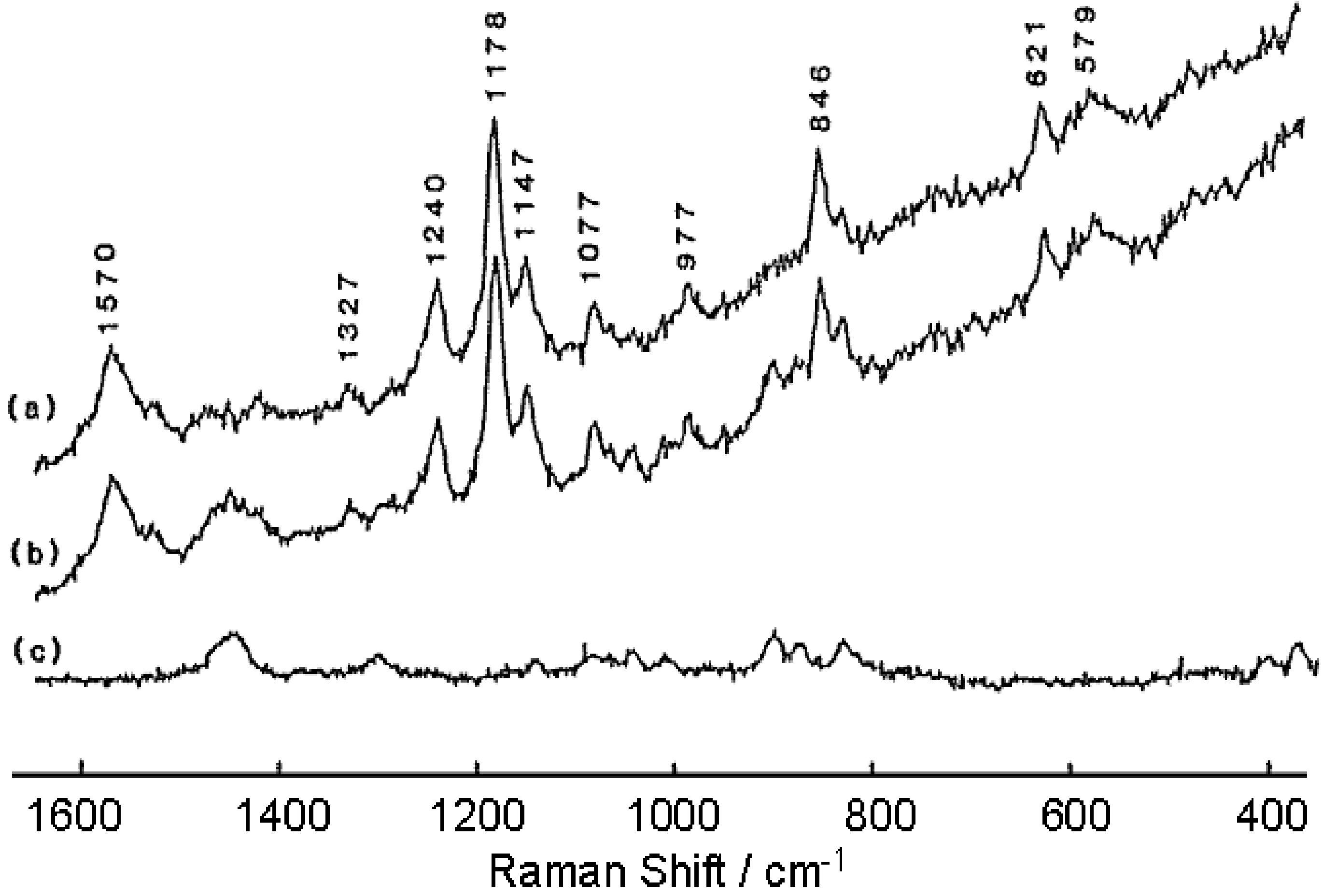
Hexane 70 ps

Dodecane 120 ps



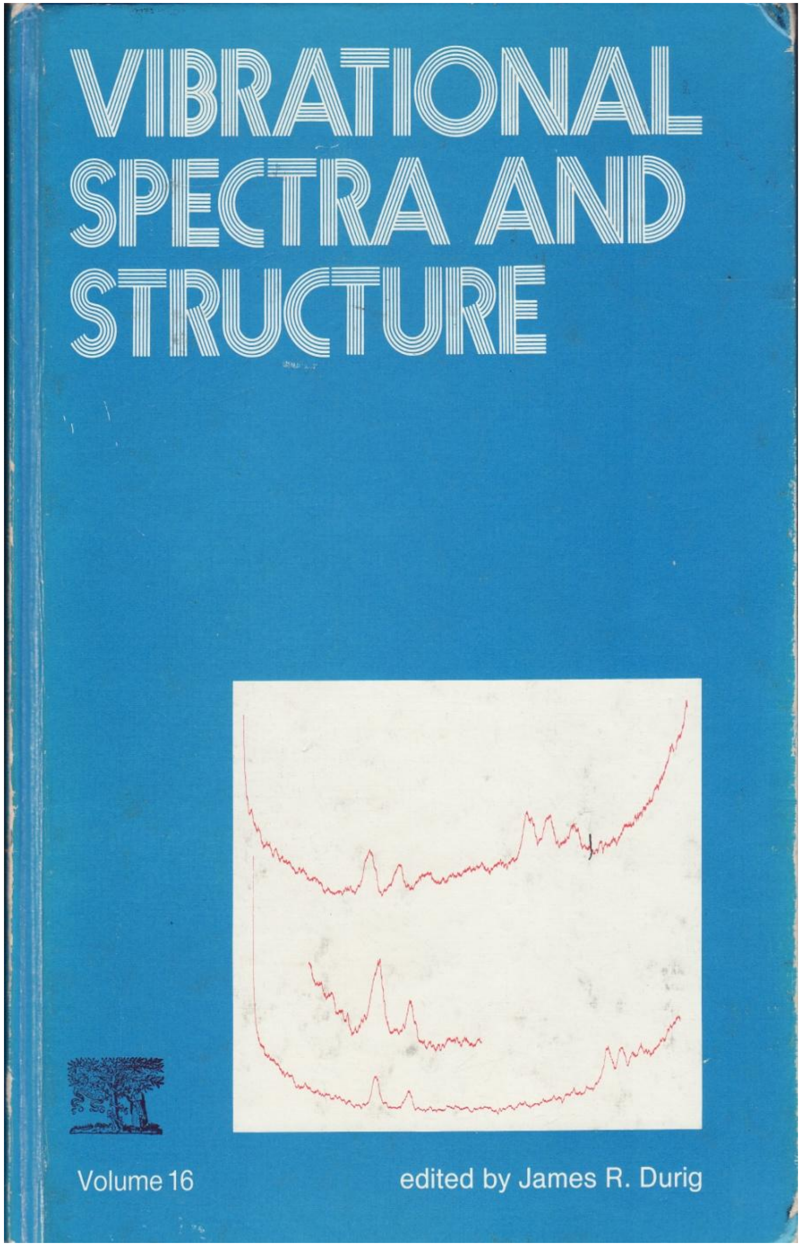
Probe solvent dependent structure and dynamics of S_1 trans-stilbene by time-resolved Raman spectroscopy

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



T. L. Gustafson, D. M. Roberts, and D. A. Chernoff, J. Chem. Phys. 79, 1559 (1983).
H. Hamaguchi, C. Kato, M. Tasumi, Chem. Phys. Lett., **100**, 3-7 (1983).

Three Raman Stilbenists on a Bridge near the Noishvanstein Castle (1985)



(1987)

Chapter 4

TRANSIENT AND TIME-RESOLVED RAMAN SPECTROSCOPY OF SHORT-LIVED INTERMEDIATE SPECIES

Hiro-o Hamaguchi

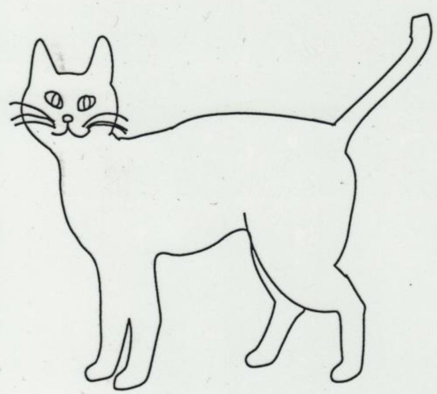
Department of Chemistry
Faculty of Science
The University of Tokyo
Tokyo, Japan

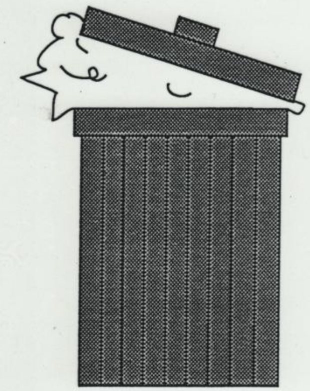
KAST

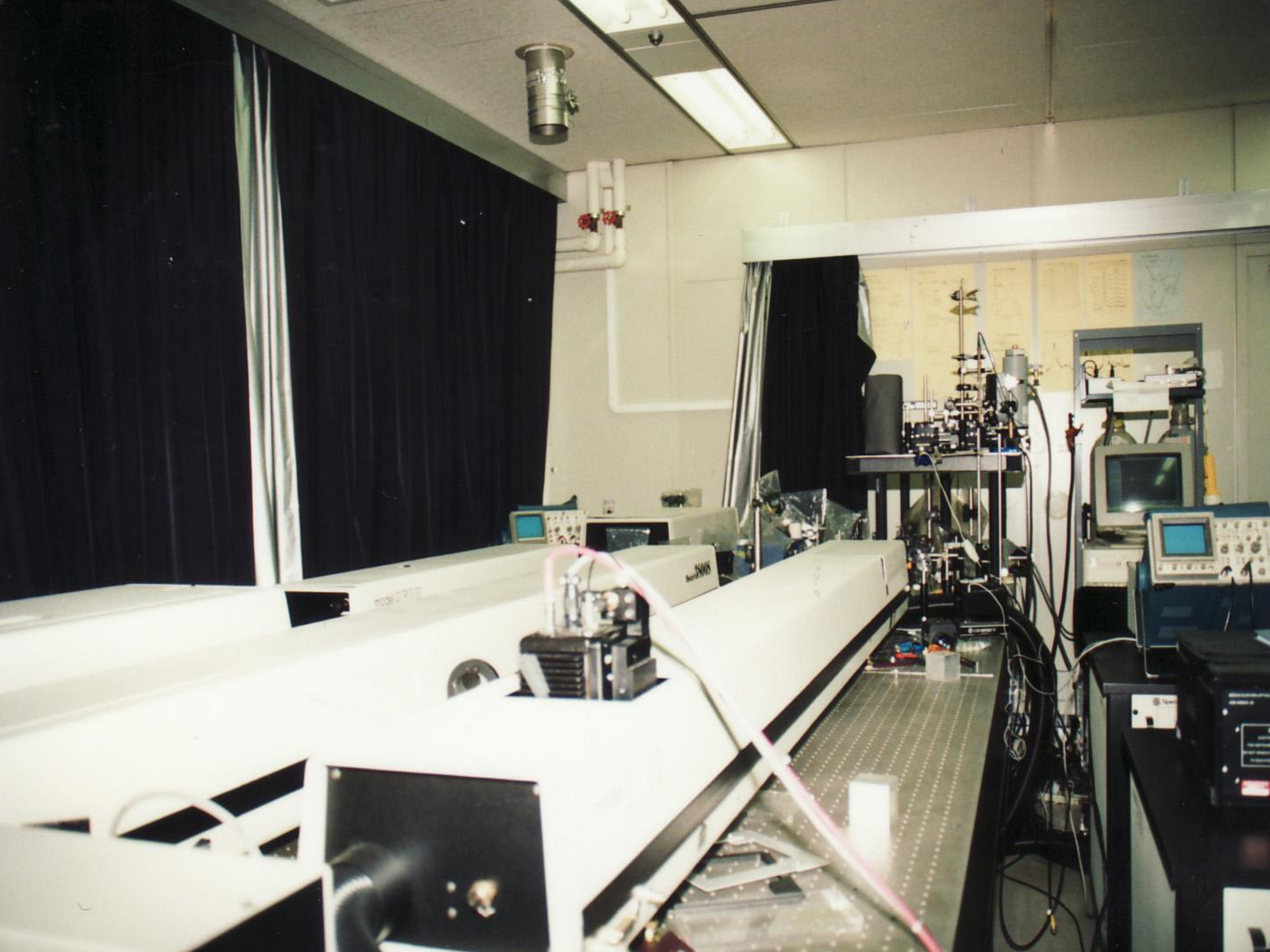
(Kanagawa Academy of Science and Technology)

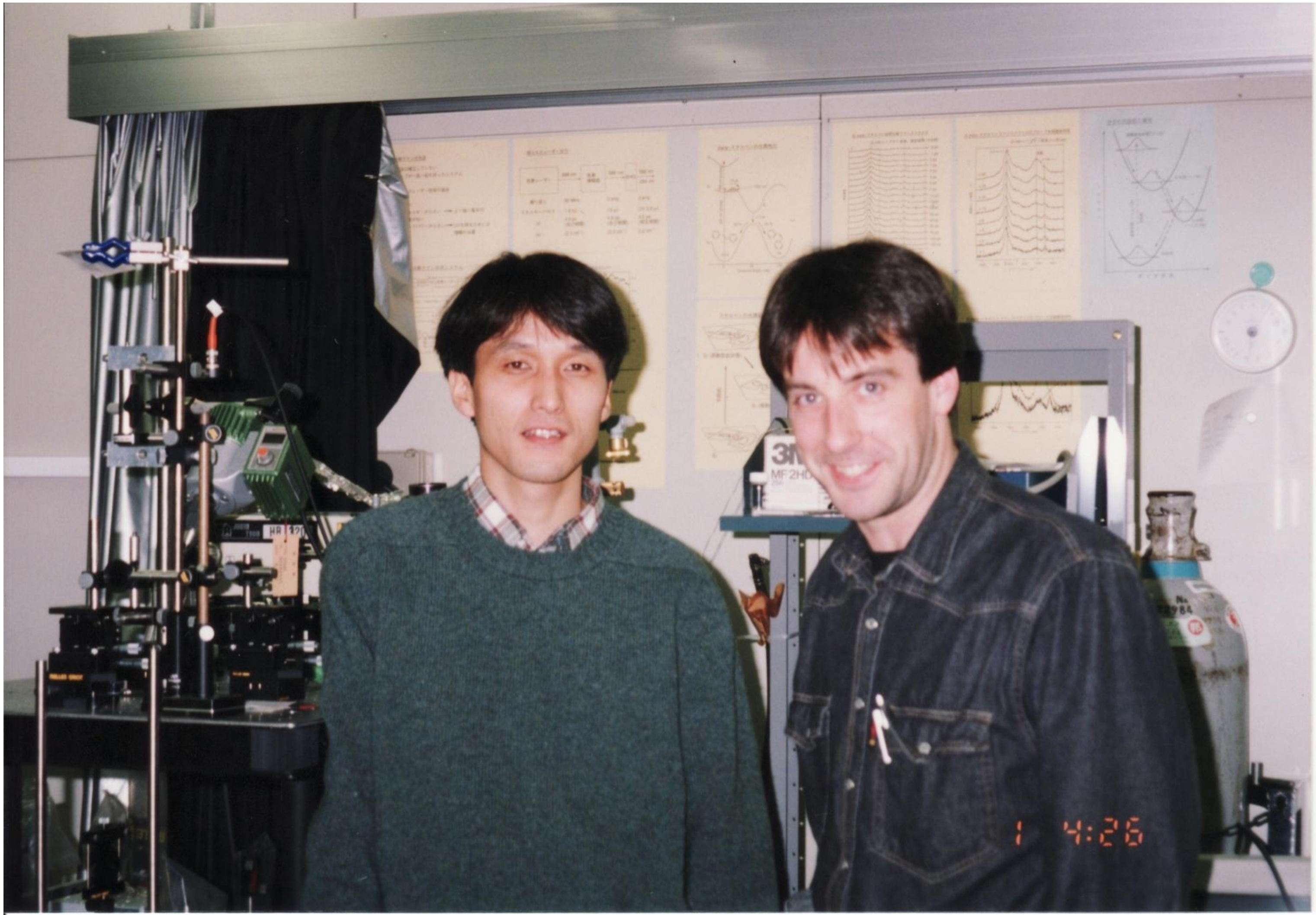
KAT

KAS



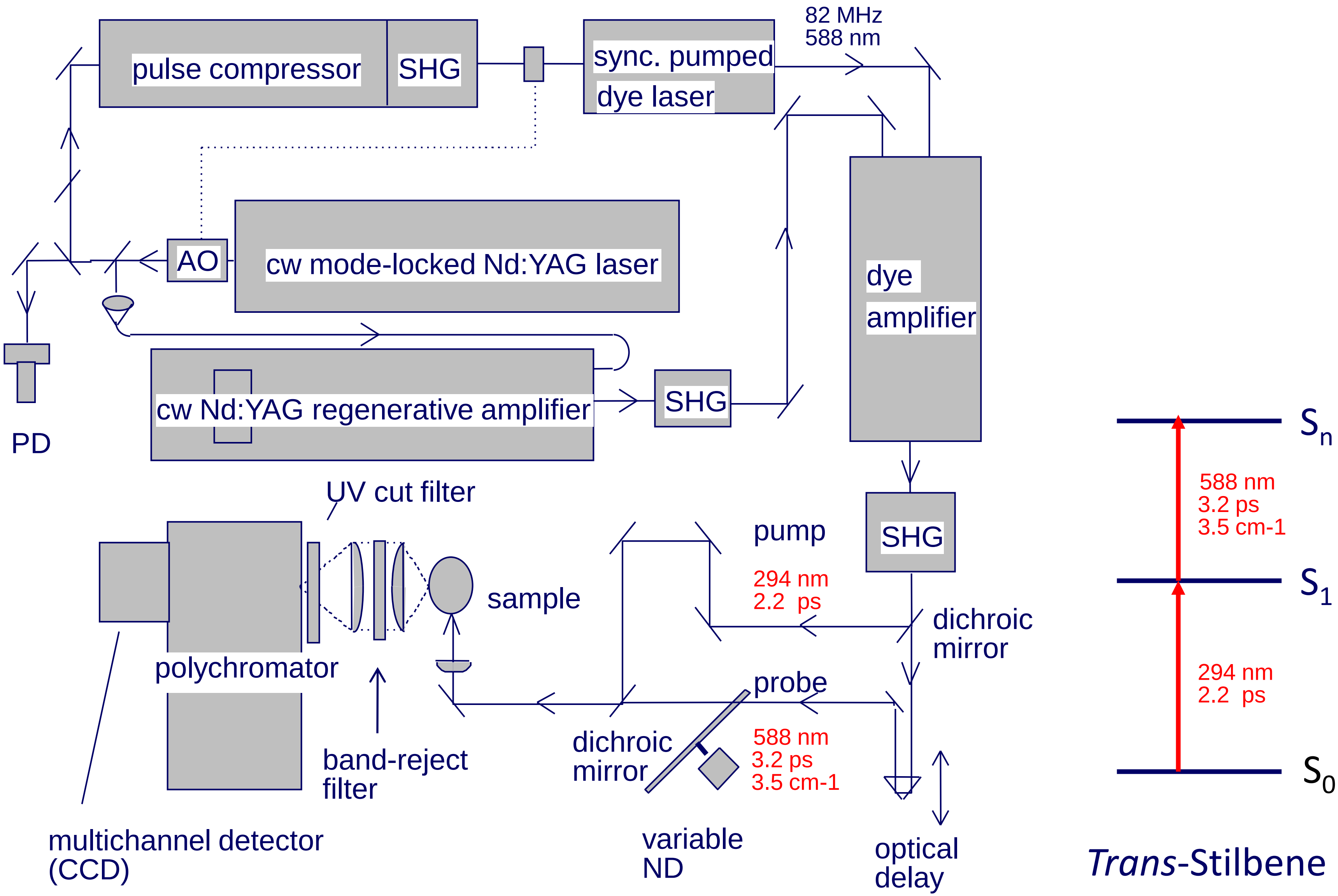




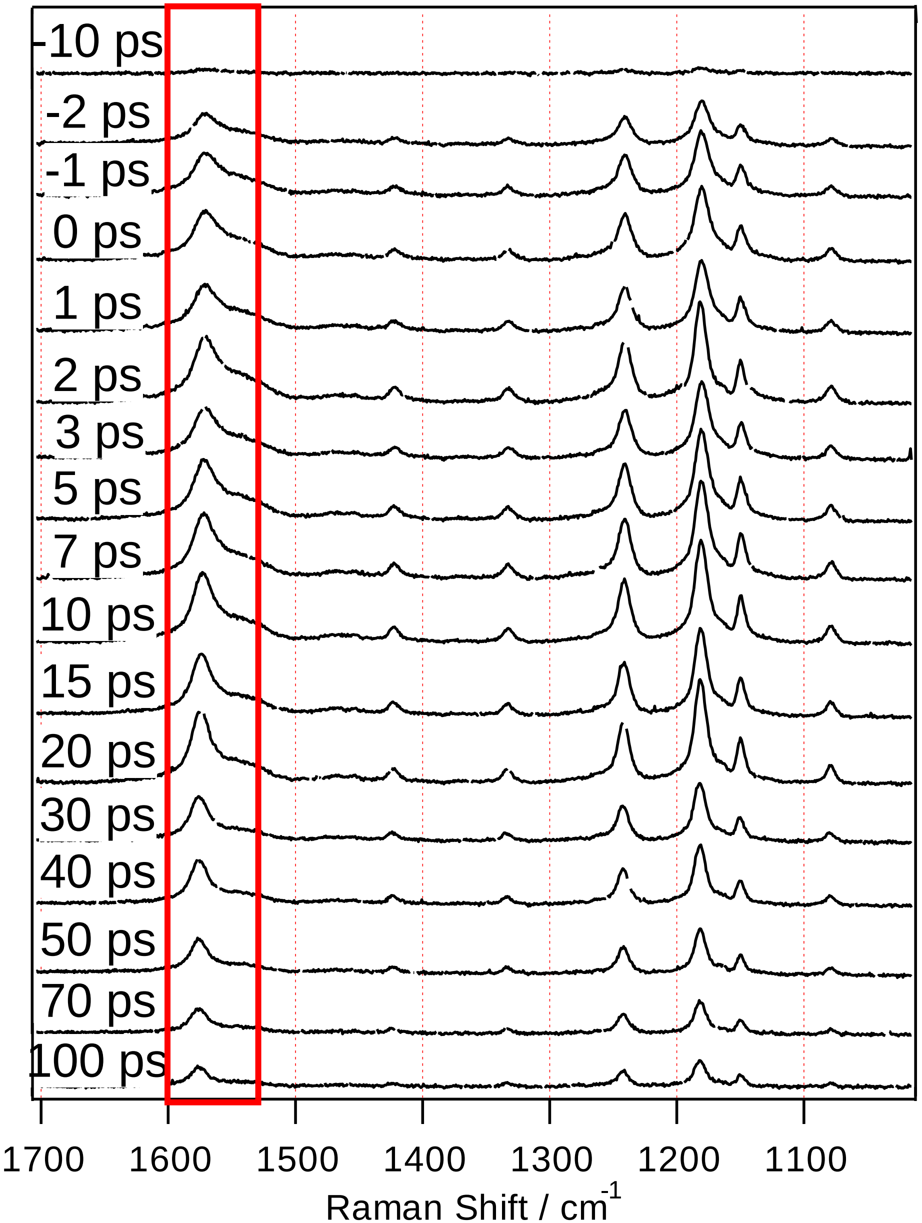


Koichi Iwata Volker Deckert

Picosecond Time-resolved Raman Spectrometer



S_1 *trans*-Stilbene in $CHCl_3$



Pump 294 nm
Probe 588 nm (0.1 mW)

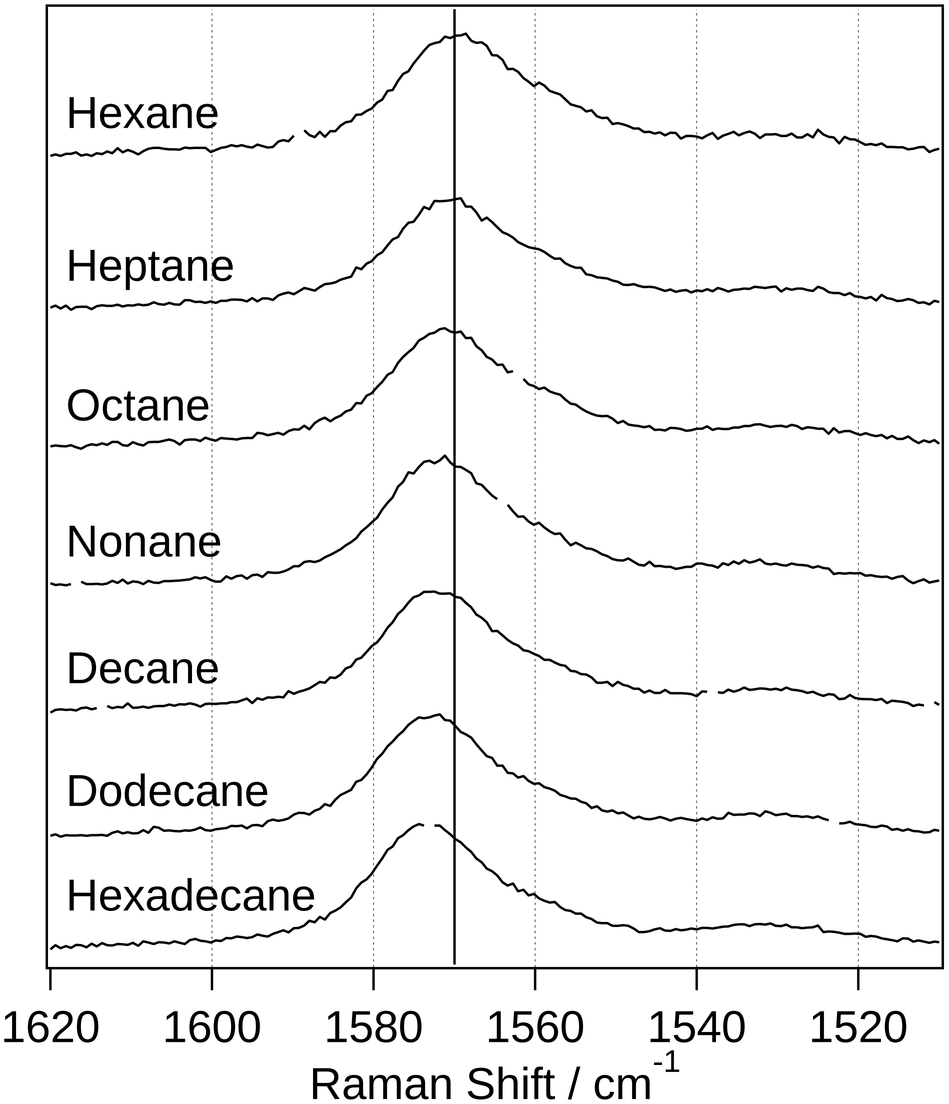
C=C stretch vibration

1560 cm^{-1}: double bond

Why rotation occurs

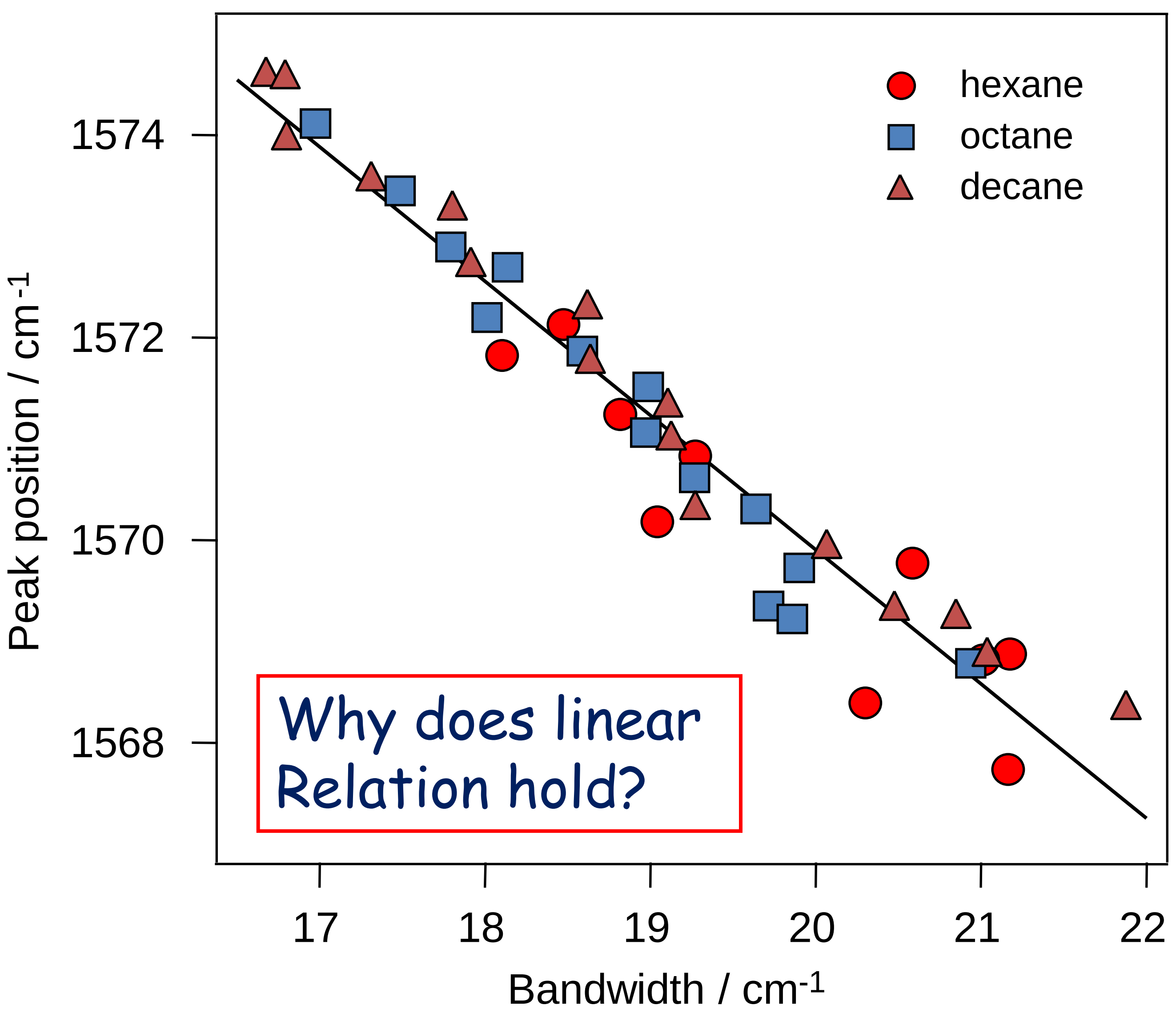
around a double bond ?

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?

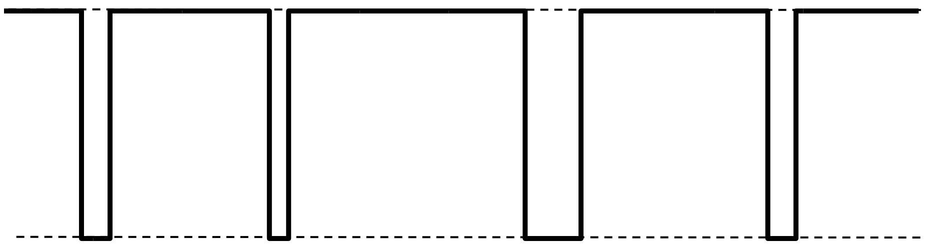
Peak Position vs Band Width in Alakne Solvents at Different Temperatures

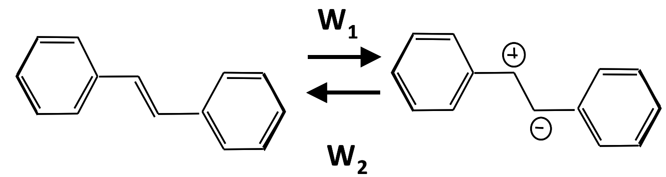


Dynamic Frequency Exchange Model and Vibrational Bandshapes

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

(a) Two Frequency Exchange Model

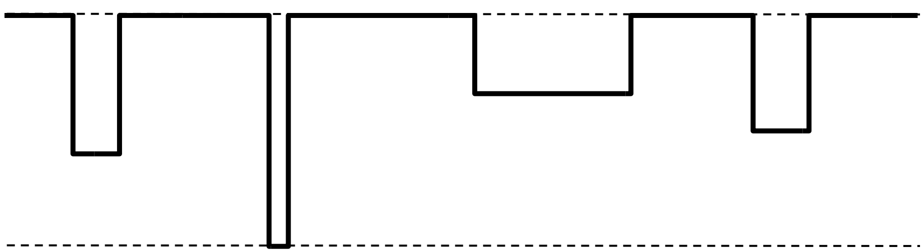




$$\Delta\Omega = W_1\tau/(1+\tau^2) \quad \Delta\Gamma = W_1\tau^2/(1+\tau^2)$$

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

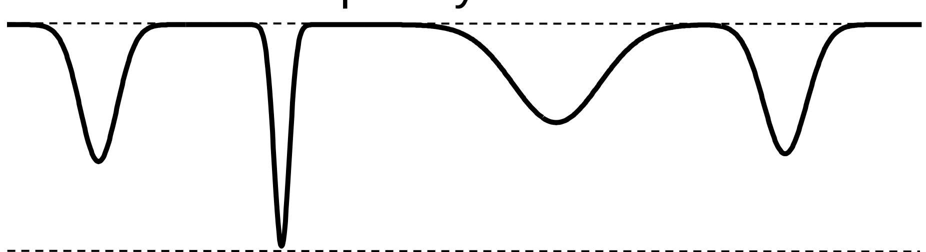
(b) Many Frequency Exchange Model



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

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

(c) Continuous Frequency Modulation Model

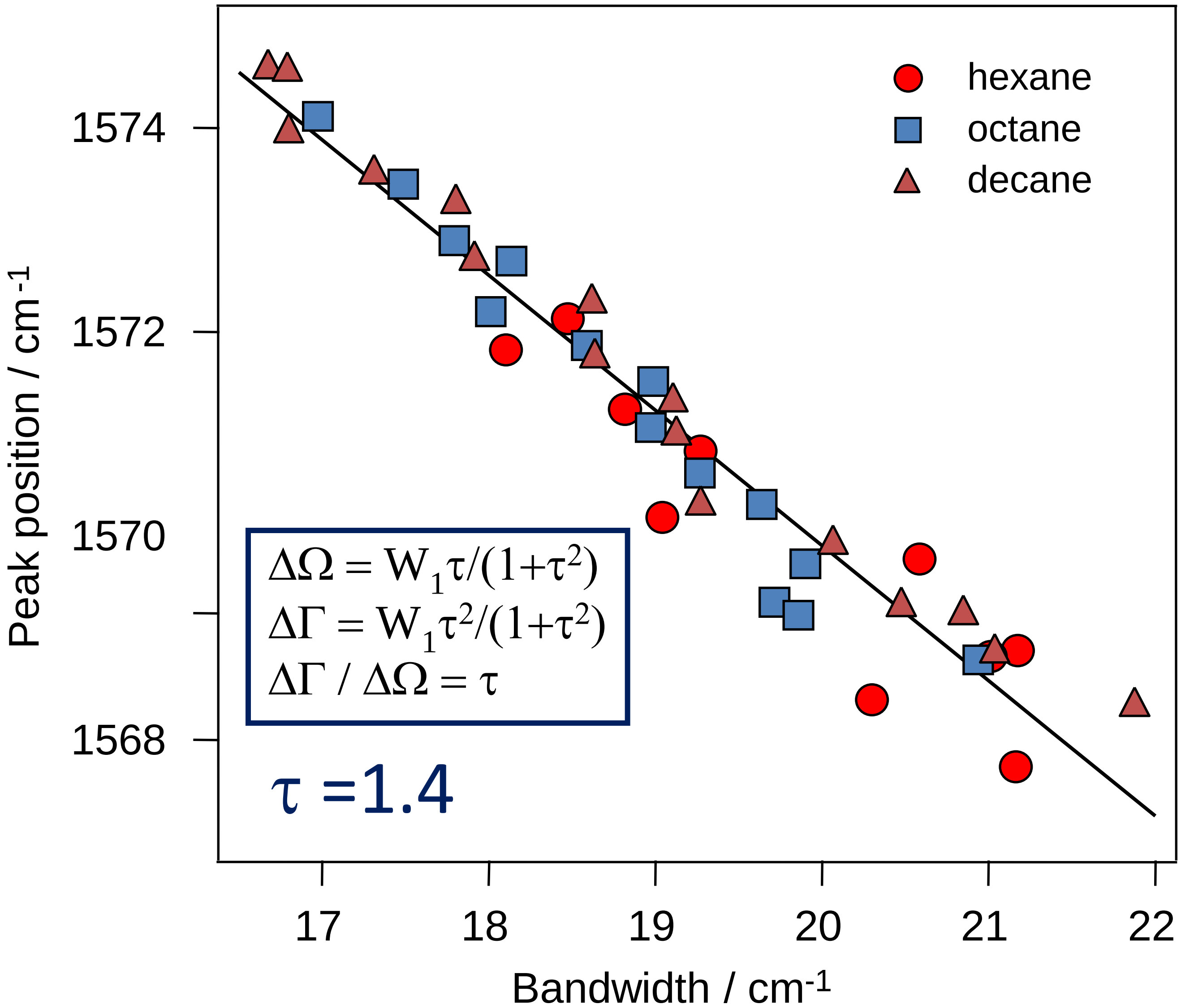


$$\Delta\Omega = \frac{W_1 \int_{-\infty}^{0} G(\tau)\tau/(1+\tau^2)d\tau}{\int_{-\infty}^{0} G(\tau)d\tau}$$

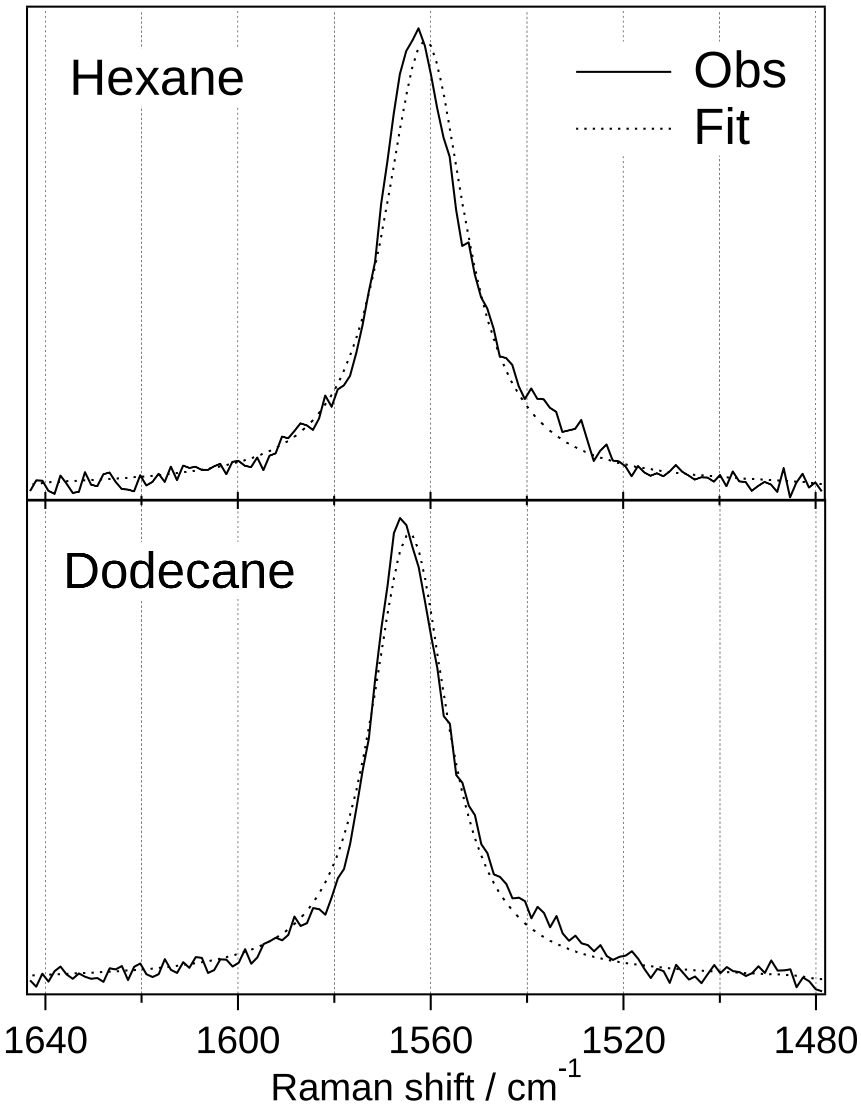
$$\Delta\Gamma = \frac{W_1 \int_{-\infty}^{0} G(\tau)\tau^2/(1+\tau^2)d\tau}{\int_{-\infty}^{0} G(\tau)d\tau}$$

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

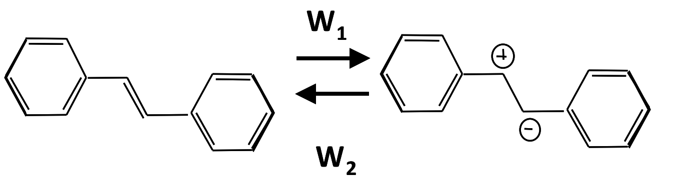
Peak Position vs Band Width in Alakne Solvents at Different Temperatures



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

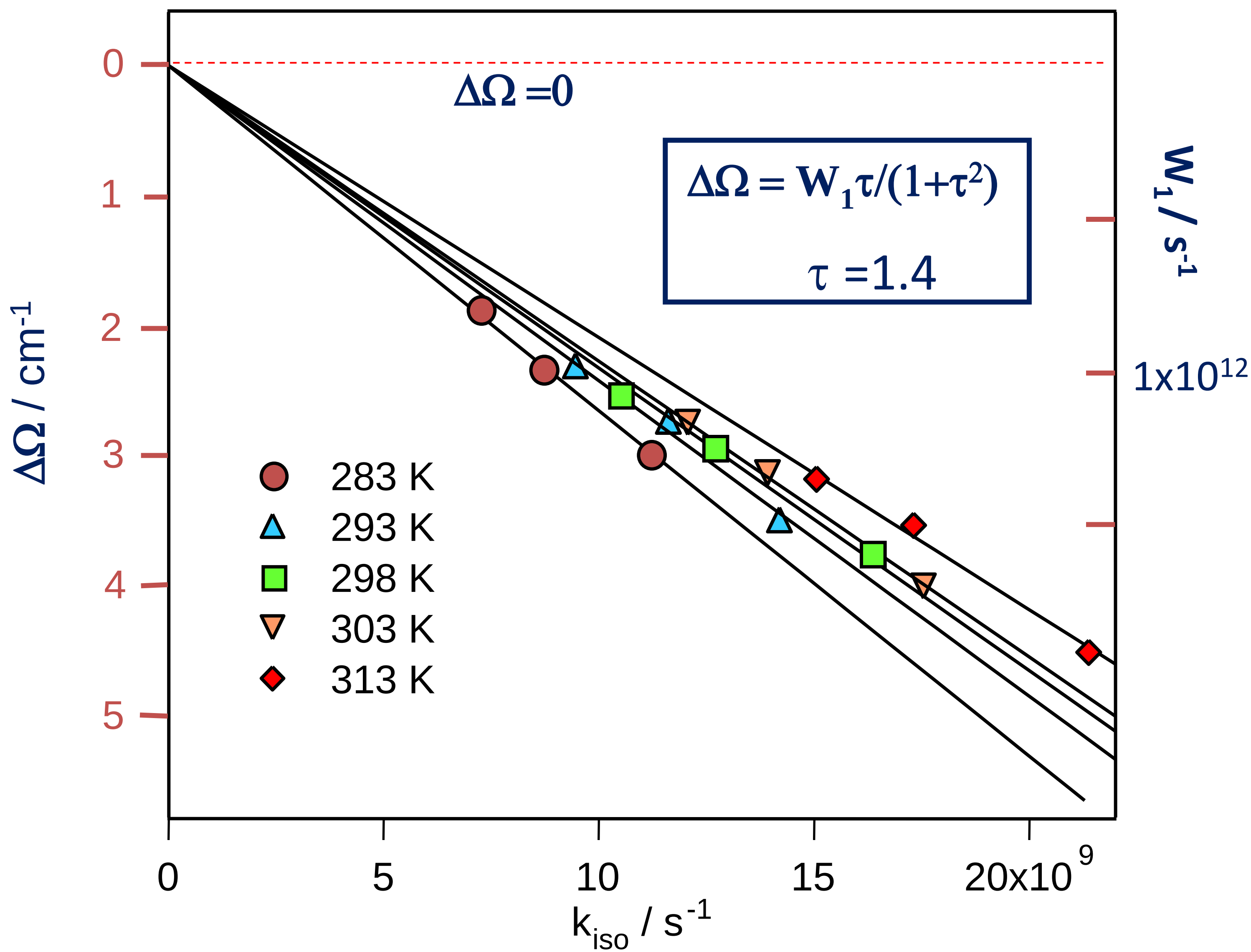


W_1=2.7x10^{12} sec^{-1} (370 (fs)$^{-1}$)

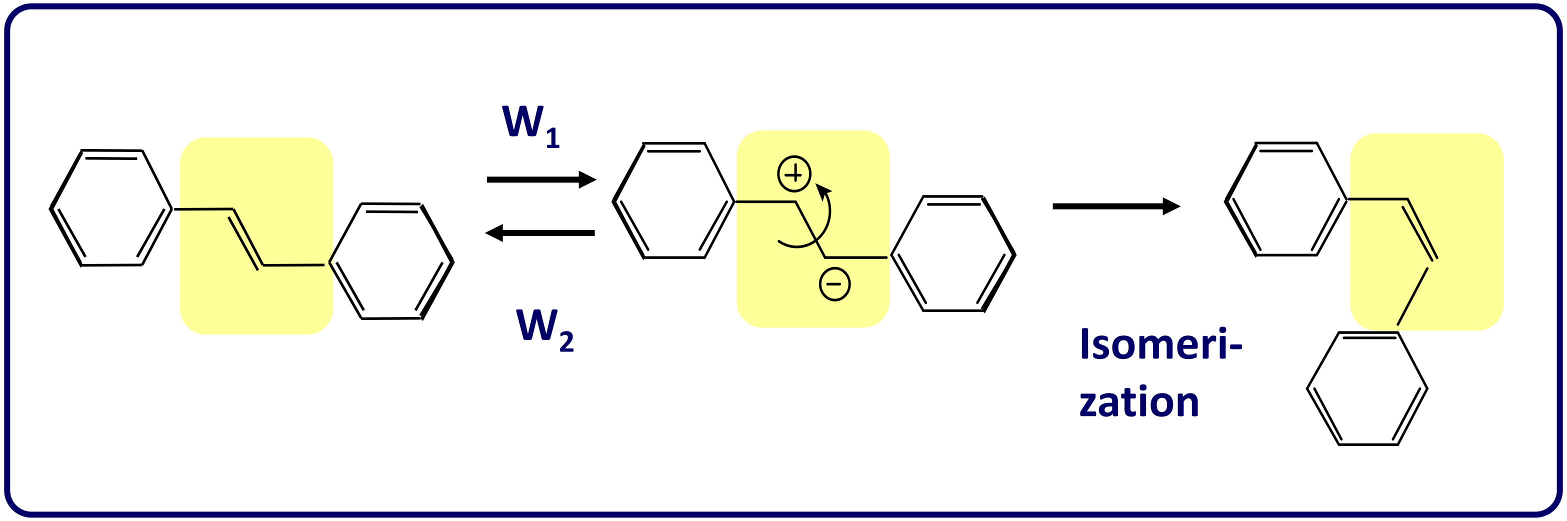


W_1=1.5x10^{12} sec^{-1} (670 (fs)$^{-1}$)

Isomerization Rate k_{iso} is Proportional to W_1



Dynamic Polarization Model of Isomerization

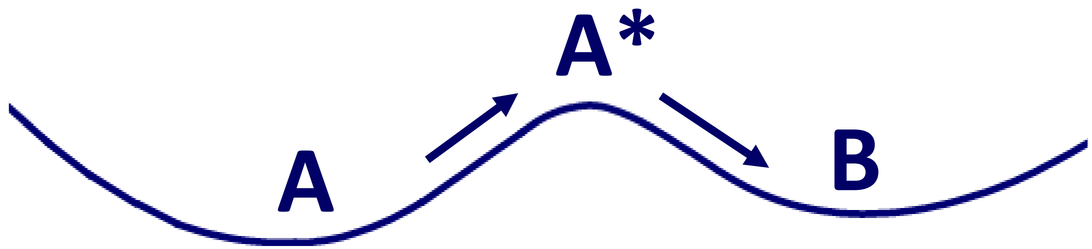


Hamaguchi, Iwata, *CPL* **208**, 465 (1993).

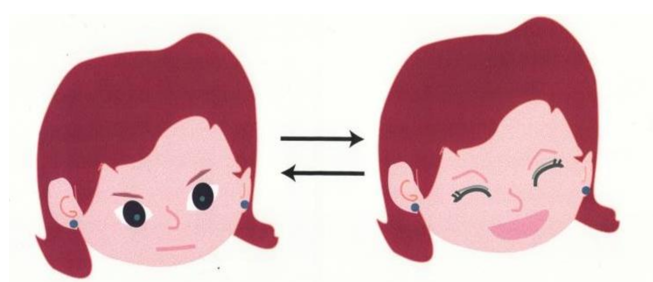
Deckert, Iwata, Hamaguchi, *J. Photochem. Photobiol*. **102**, 35 (1996).

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

How Do Chemical Reactions Proceed?



$$A \rightleftharpoons A^* \longrightarrow B$$



Cf. Michaelis-Menten kinetics

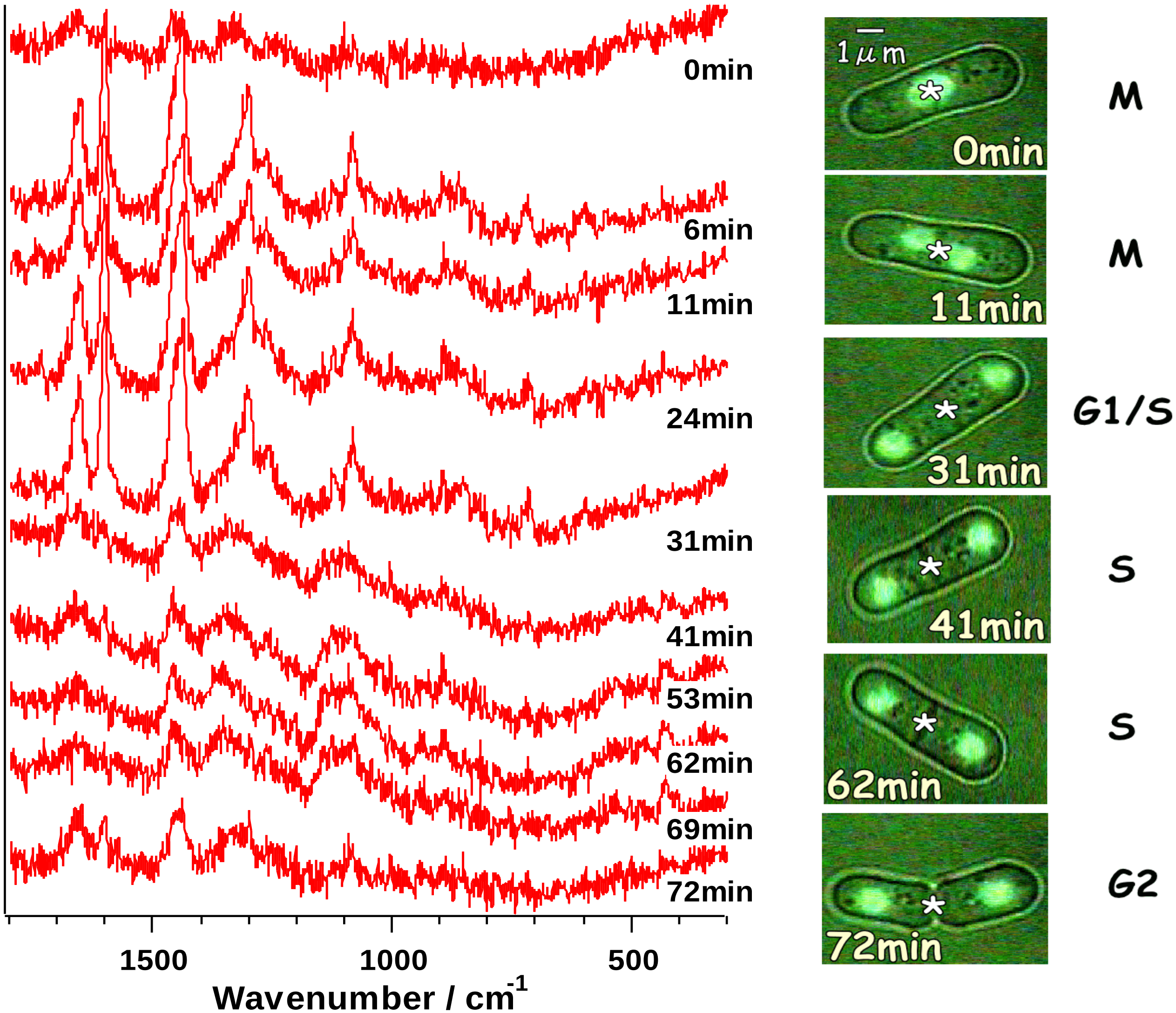
"How can the events in space and time which take place within the spatial boundary of a living organism be accounted for by physics and chemistry ?"

In "What is Life"

Erwin Schrödinger

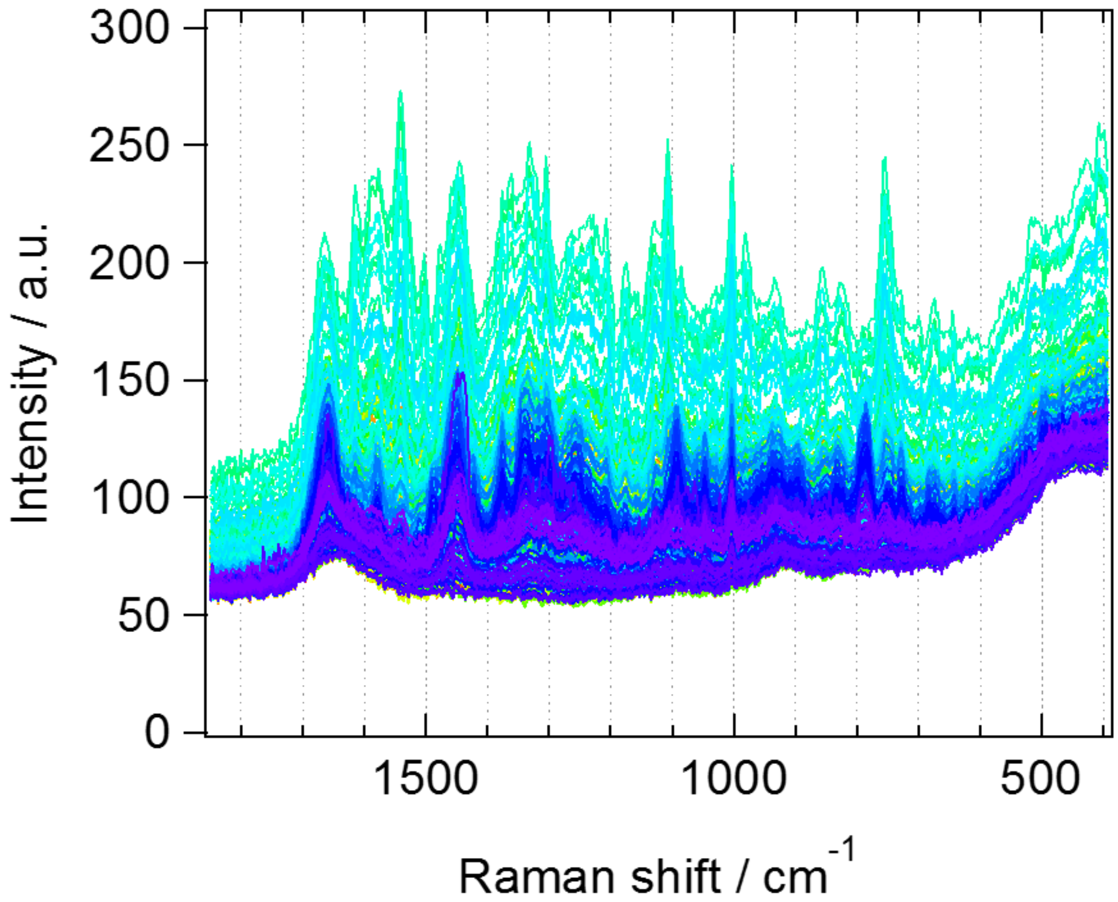
E. Schrödinger
(1887-1961)

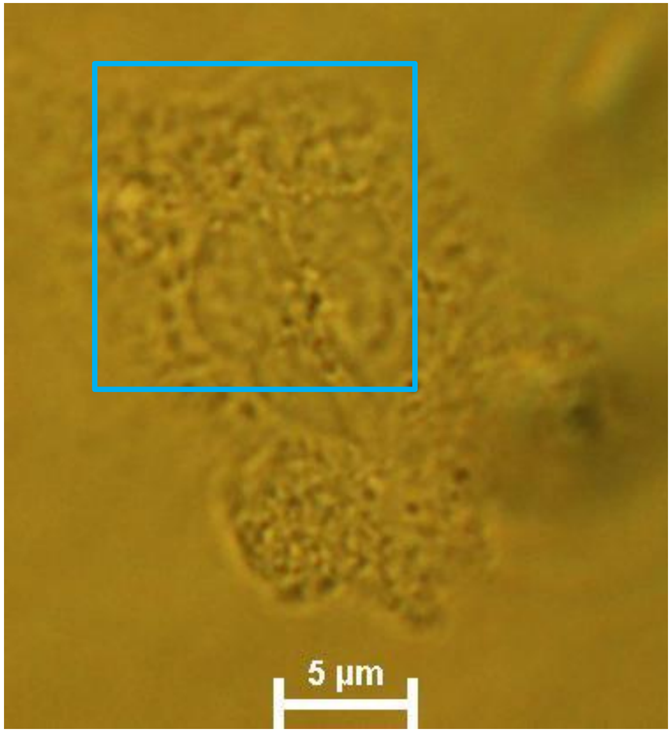
Raman Spectroscopy of Really Living Cell



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

Molecular Component Distribution Imaging (MCDI) of Living Cells with Multivariate Curve Resolution Analysis





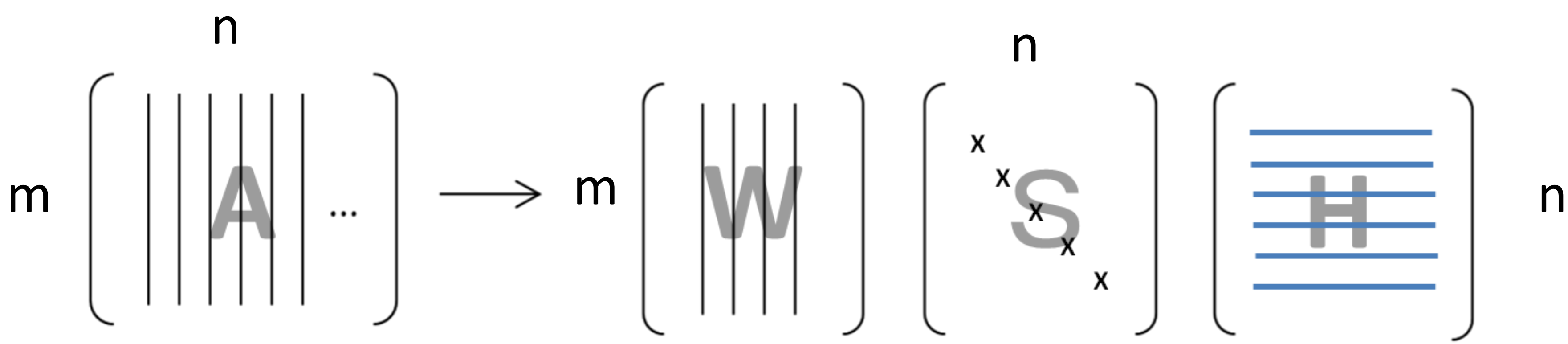
white blood cell

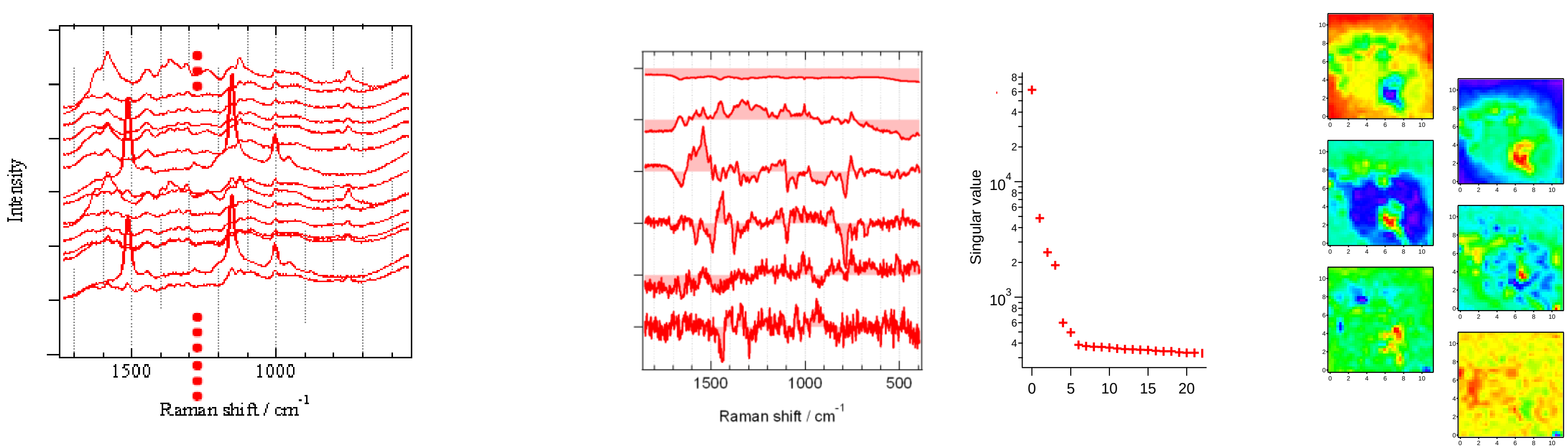
Thorough interpretation of complicated spectra is very difficult.

Multivariate Analysis

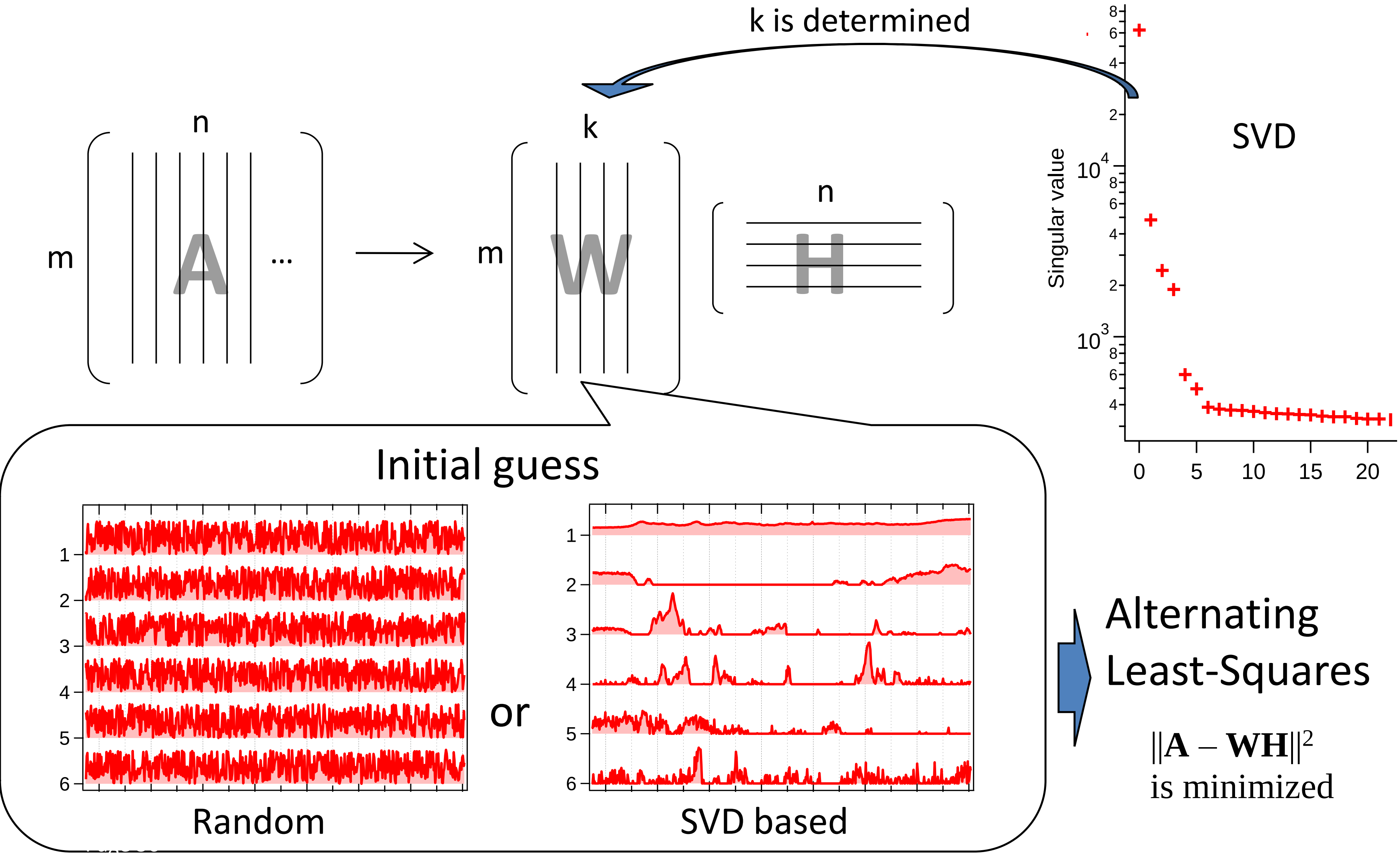
Matrix factorization by Singular Value Decomposition (SVD)

$$\mathbf{A} \approx \mathbf{WSH}$$



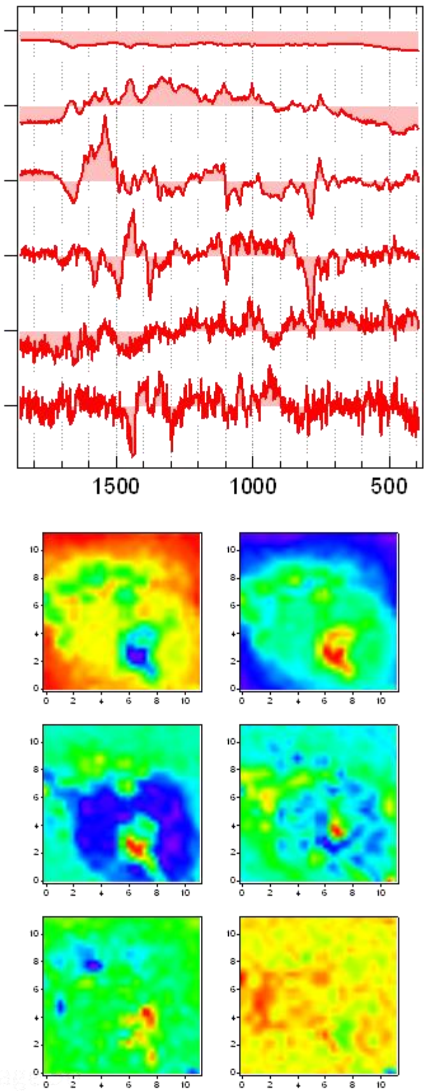


Multivariate Curve Resolution (MCR)



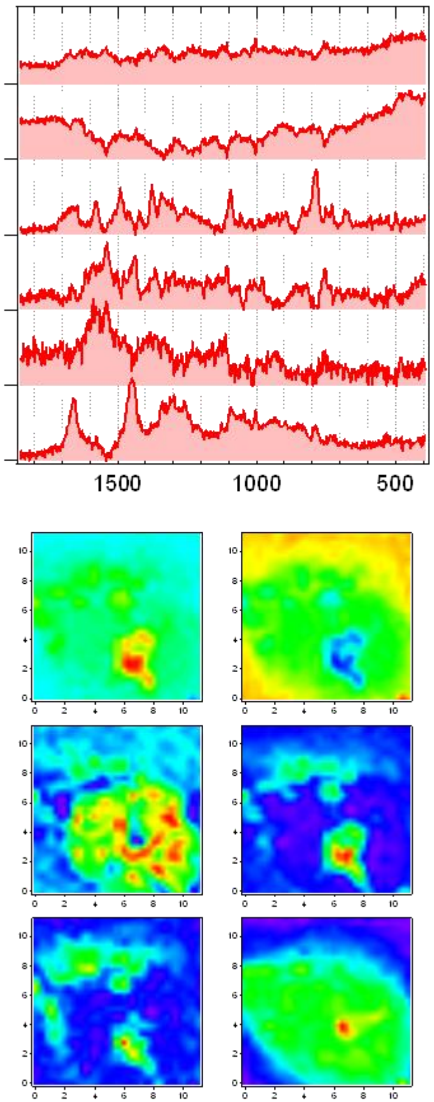
Multivariate Analyses: Comparison

SVD



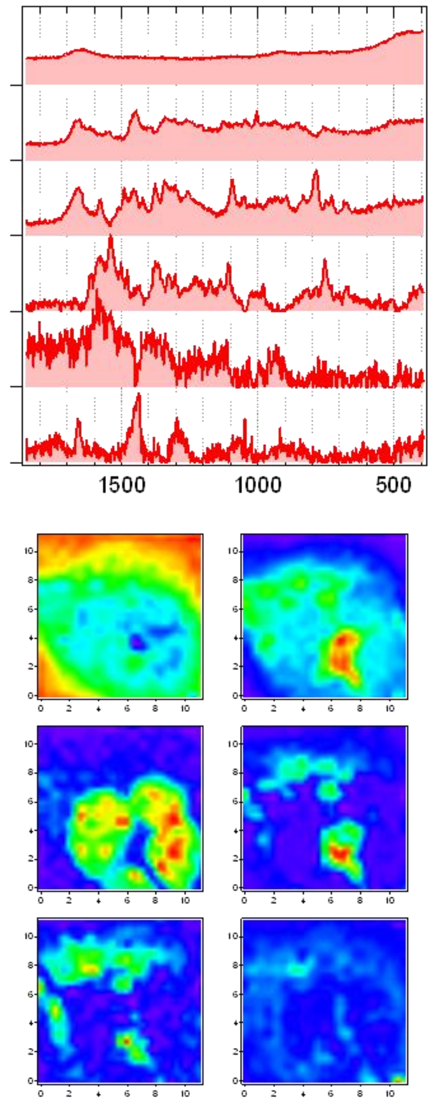
MCR

W, **H** ≥ 0 , $L_1 = 0$

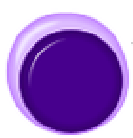


MCR

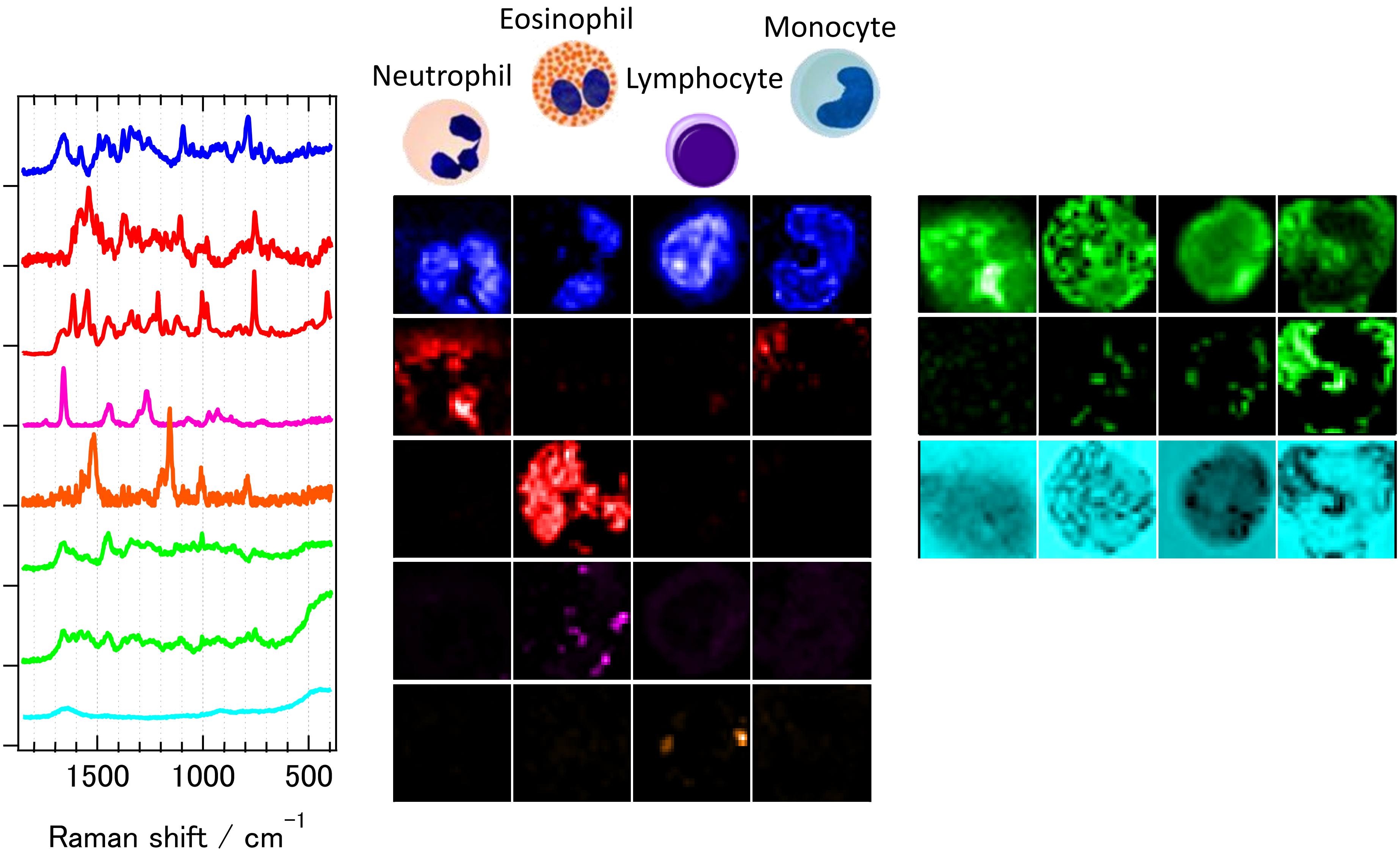
W, **H** ≥ 0 , $L_1 = 0.001$



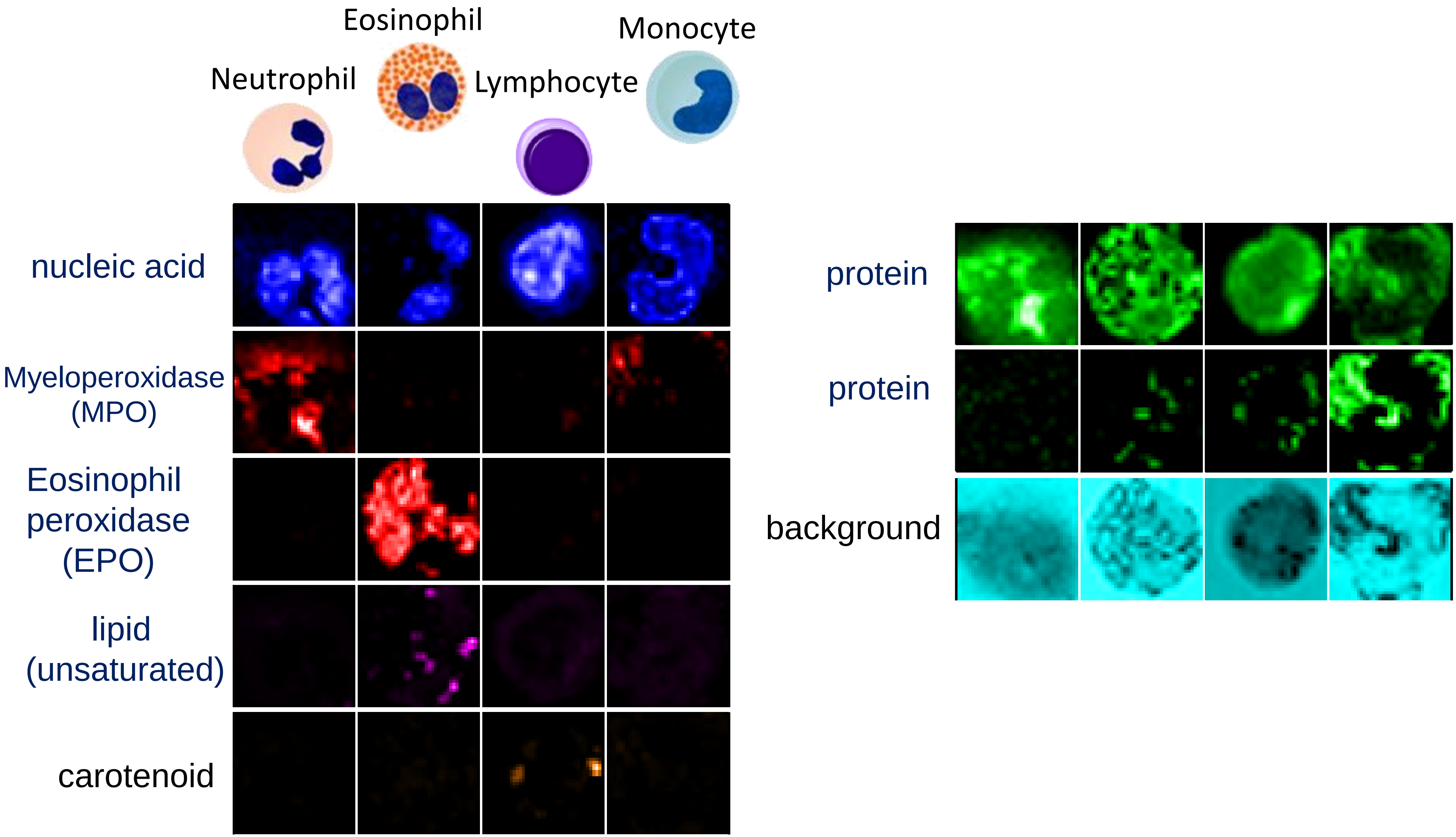
White Blood Cells

Neutrophil 	50-70 %	10-12 μm	Phagocytosis - bacteria, fungi
Eosinophil 	2-5 %	10-12 μm	Combating parasites Modulate allergic inflammatory responses
Basophil 	< 1 %	12-15 μm	release histamine for inflammatory responses
Lymphocyte 	20-40 %	7-8 μm	B cells T cells NK cells
Monocyte 	3-6 %	14-17 μm	Differentiate into tissue resident macrophages

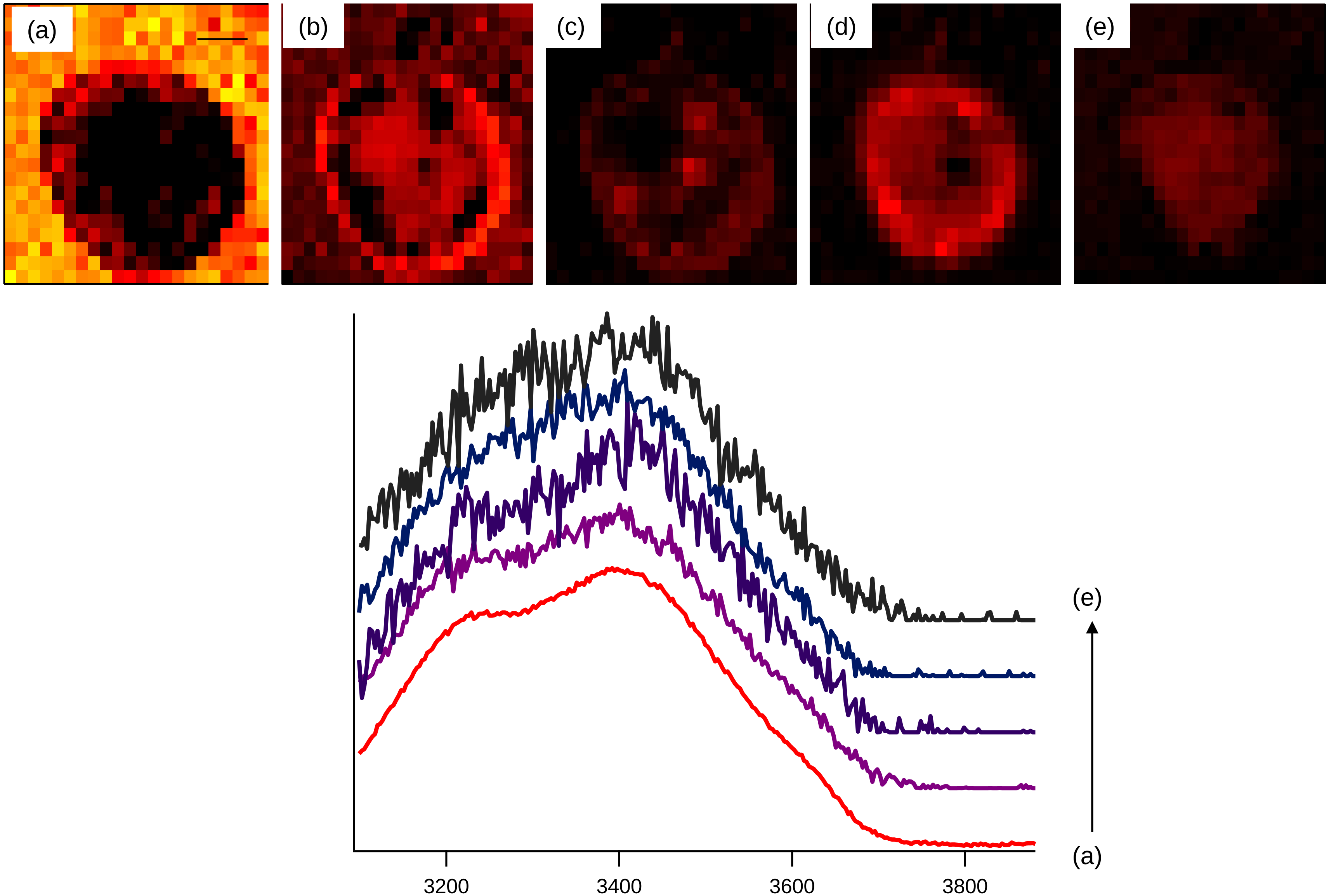
MCR Analysis of White Blood Cells



MCDI of White Blood Cells

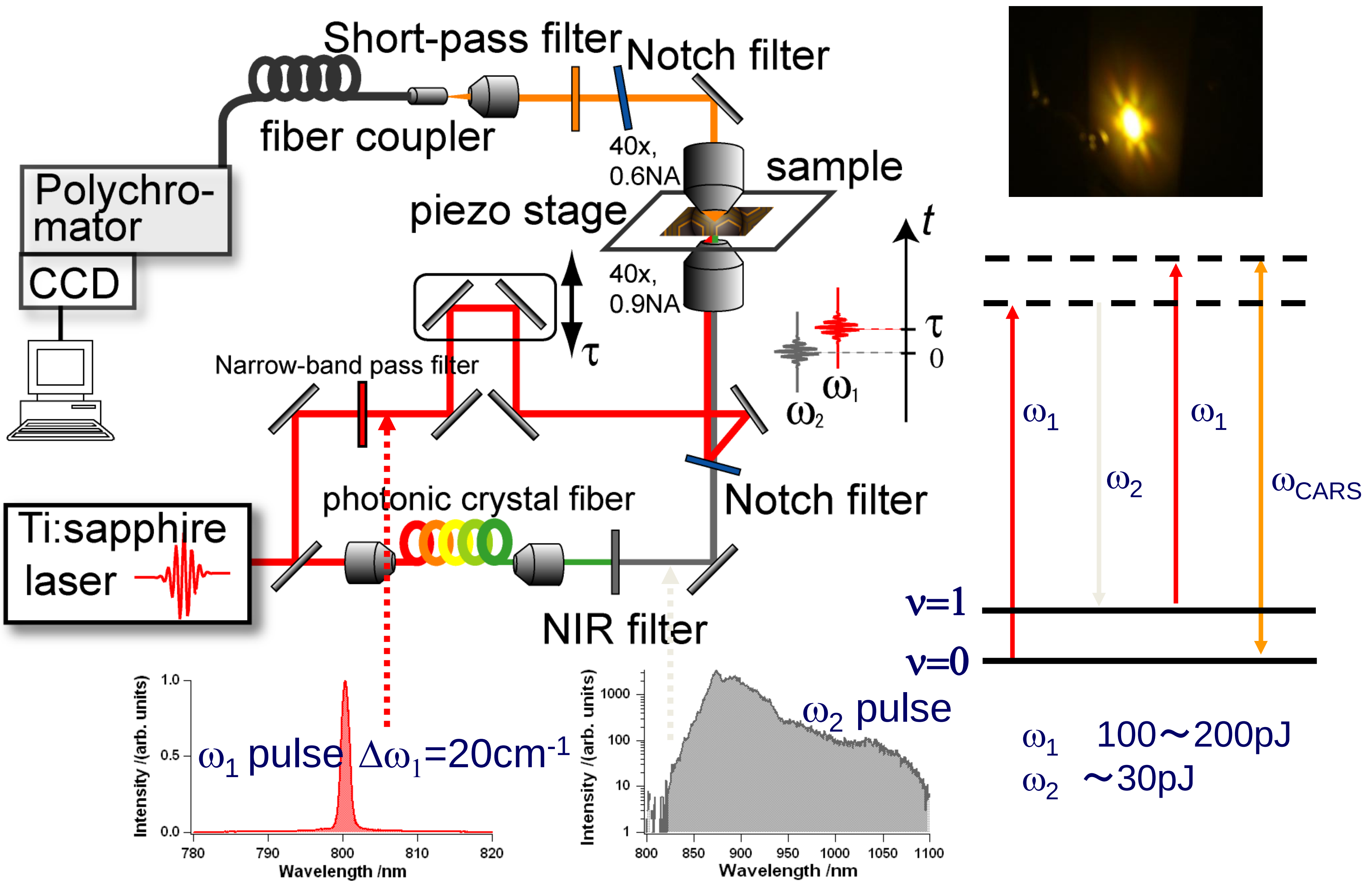


Organelle Specific Waters in a Living Cell



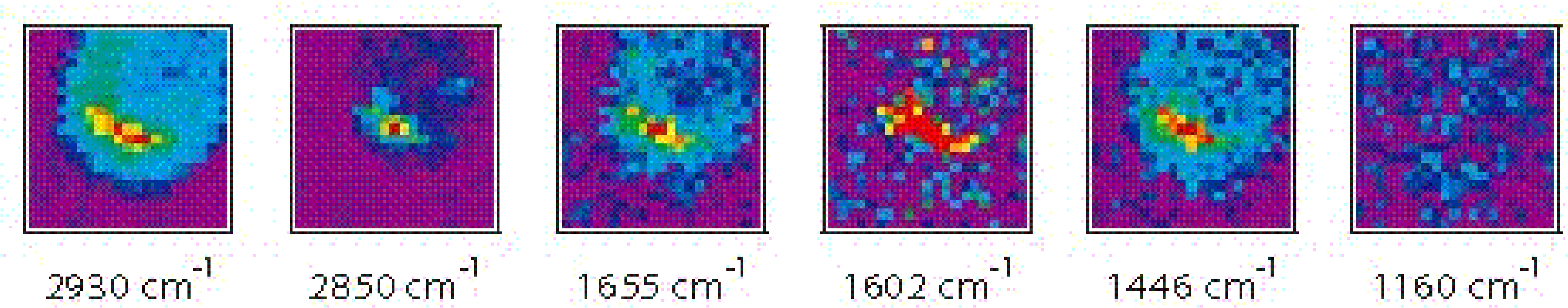
S. Tiwari, M. Ando*a* and H. Hamaguchi, in preparation

Broadband Multiplex CARS Microspectroscopy



H. Kano and H. Hamaguchi, *Anal. Chem.*, **79**, 8967-8973 (2007).

Vibrational CARS Movies of a Single Budding Yeast Cell

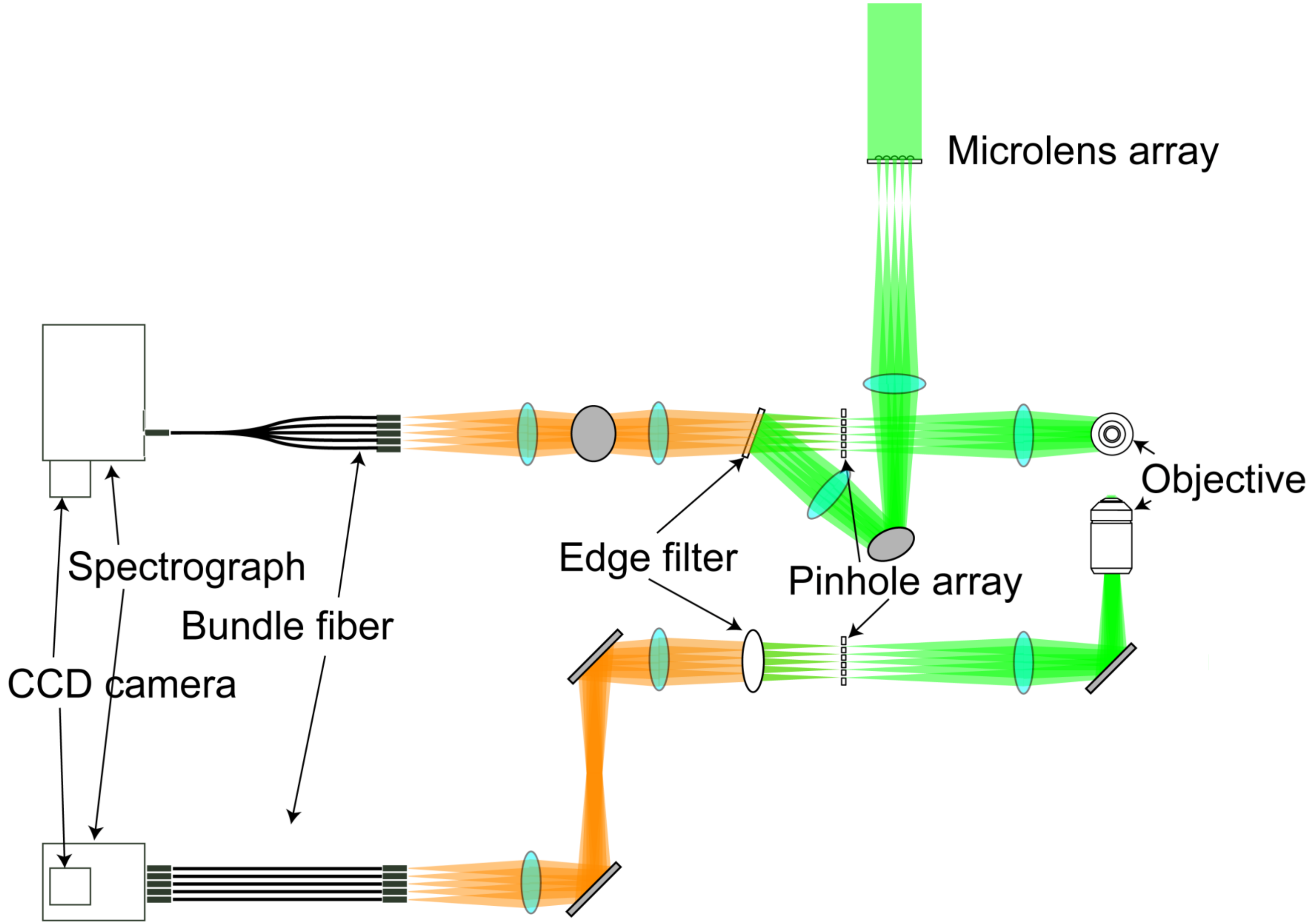


ω_1: 10 mW, ω_2: 10 mW

Expo. time/pixel: 30 msec

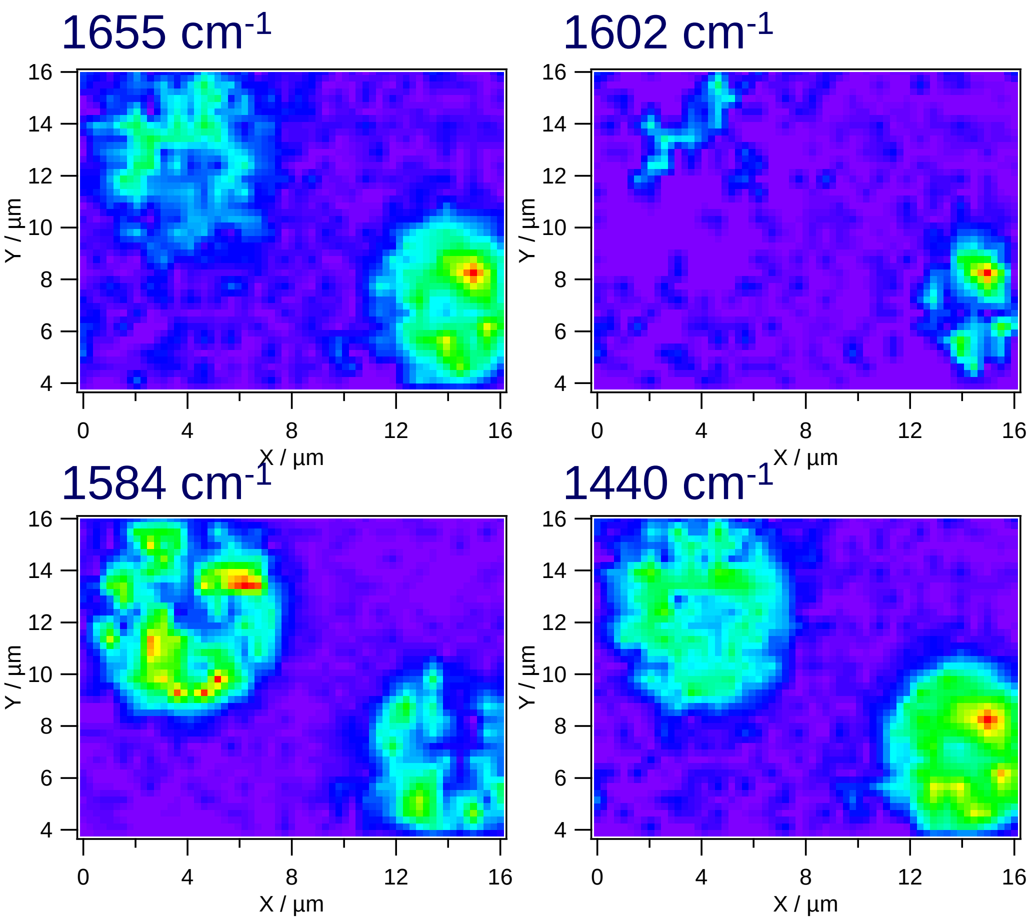
Image acquisition time: ~ 12 sec

Multi-focus Confocal Raman Microspectroscopy



M. Okuno and H. Hamaguchi, *Opt. Lett.*, **35**, 4096-4098 (2010).

Budding yeast cells



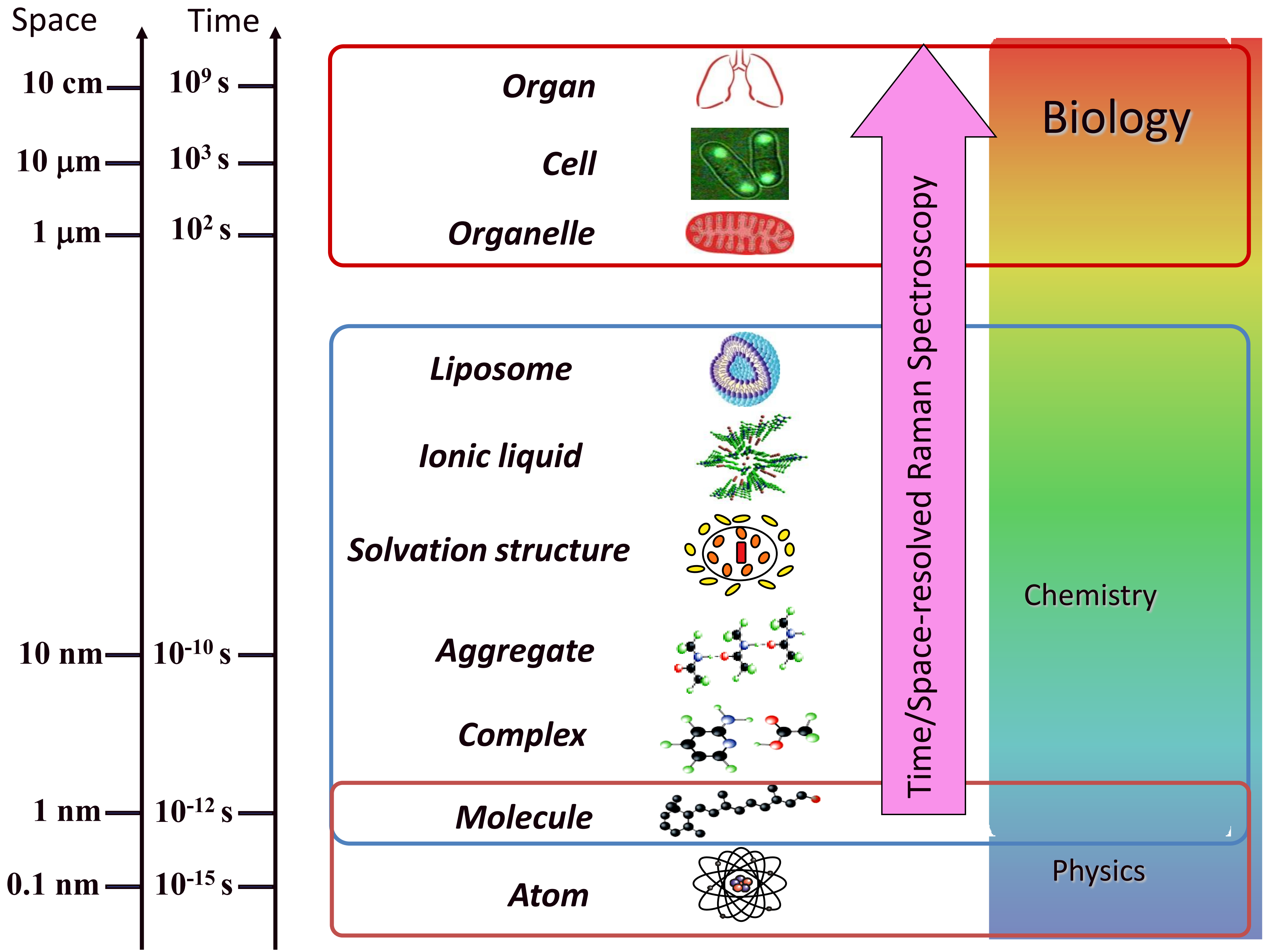
- Laser power : 1 mW
- Exposure time: 1 sec
- Readout time: ~150 msec
- PZT scan 4 x 4 points

  2 x 2 µm

  Total area: 16 x 12 µm
- Total image acquisition time

  (1 sec+ 0.2 sec) x 4 x 4

~20 sec / image !!



Space
Time
10 cm
10⁹ s
10 μm
10³ s
1 μm
10² s
10 nm
10⁻¹⁰ s
1 nm
10⁻¹² s
0.1 nm
10⁻¹⁵ s
Organ
Cell
Organelle
Liposome
Ionic liquid
Solvation structure
Aggregate
Complex
Molecule
Atom
Time/Space-resolved Raman Spectroscopy
Biology
Chemistry
Physics

Raman Measurement of Food *in situ*

Raman Application to Food Science

Natural or cultured food resources

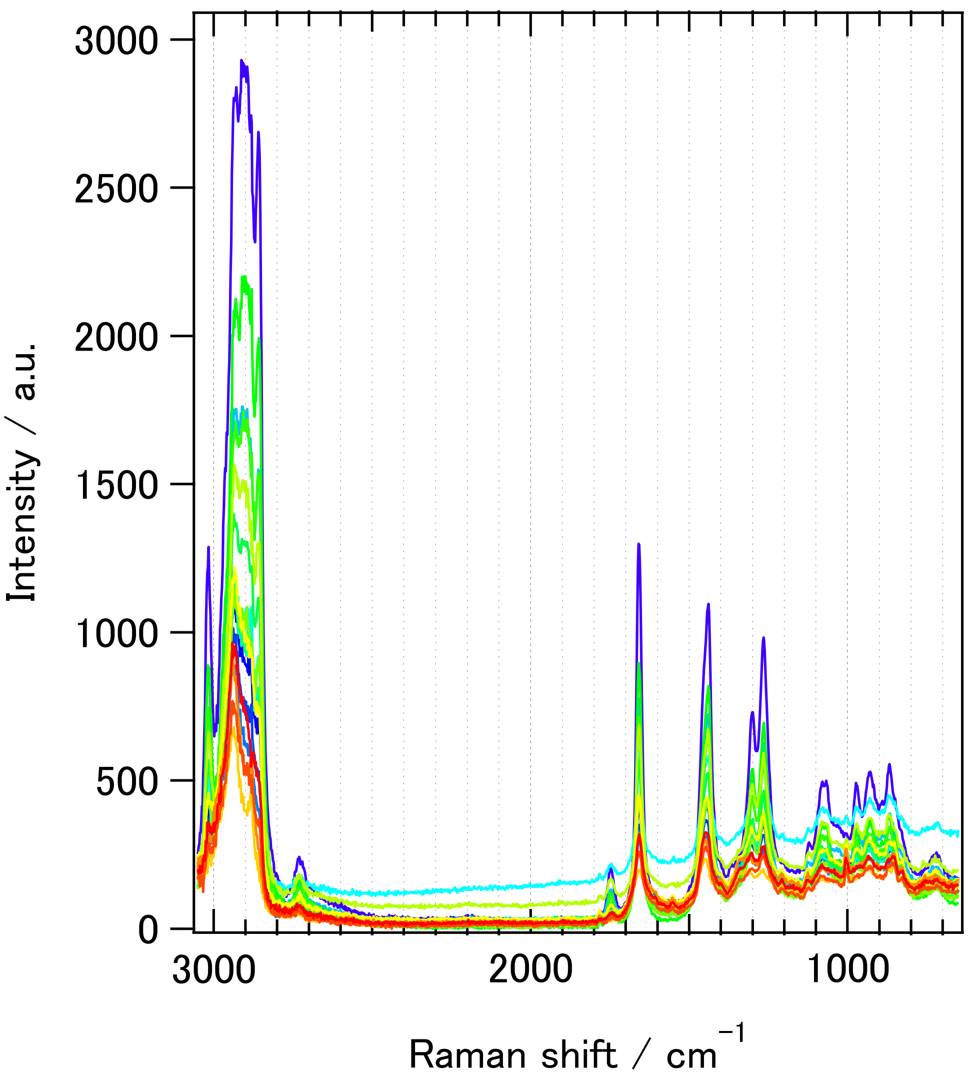
Food processing

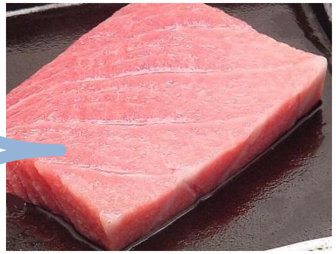
<u>Food safety & quality control</u>:

- Food constituent
- Functional ingredient
- Contamination of pathogens or residual pesticides

Label-free, less invasive and rapid analysis by using Raman spectroscopy

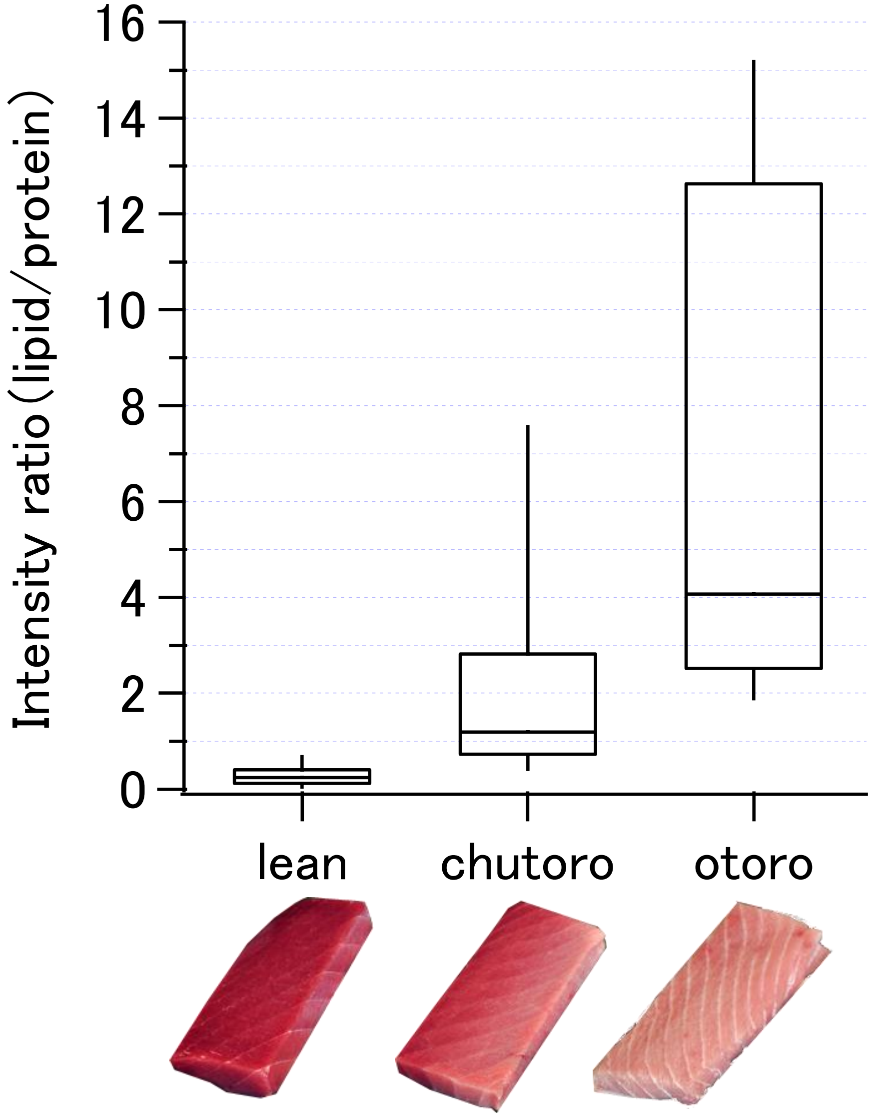
Raman Spectra of Tuna

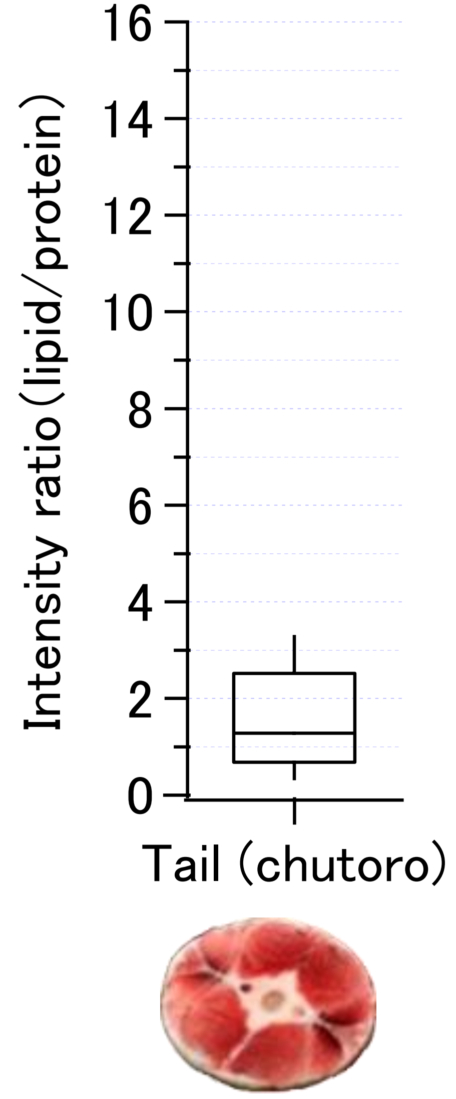




Quantification of lipids / proteins
⇒ evaluation of food quality and taste

Lipid Content Analysis of Tuna





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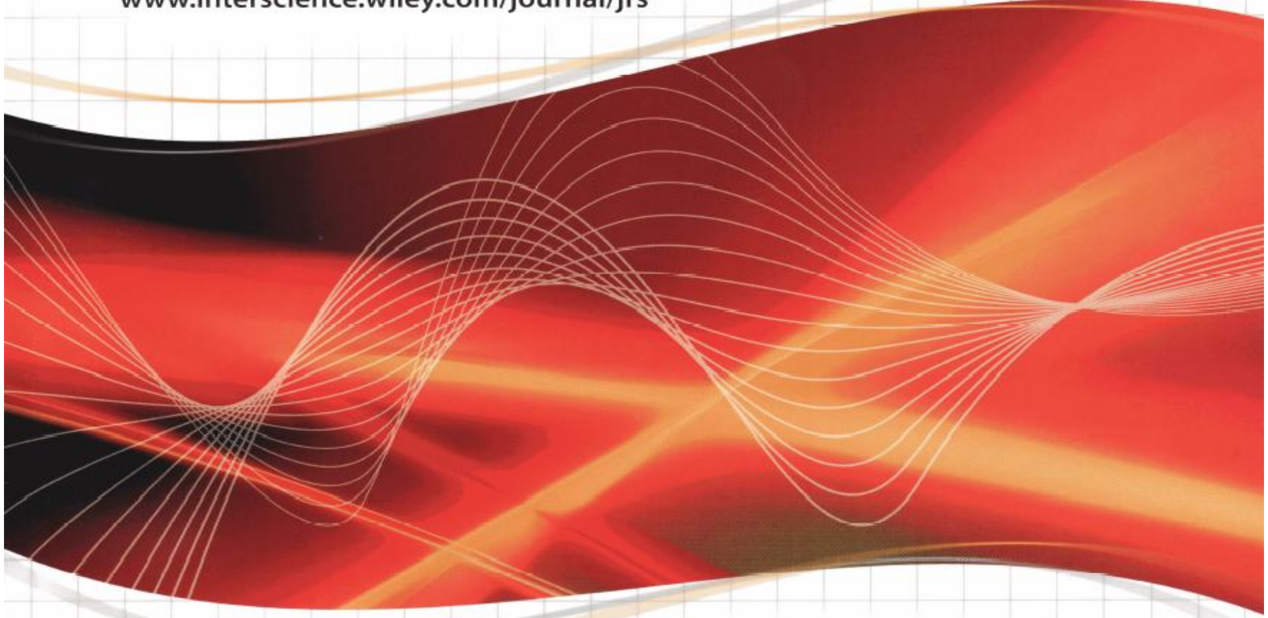

Commemorative Issue:
For Hiro-o Hamaguchi on the Occasion of his 60th Birthday

Guest Editors: V. Deckert, M. W. George and S. Umapathy

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First Student Summer Camp of Taiwan Association of Raman Spectroscopy (2013.7.6 at Jianshi)