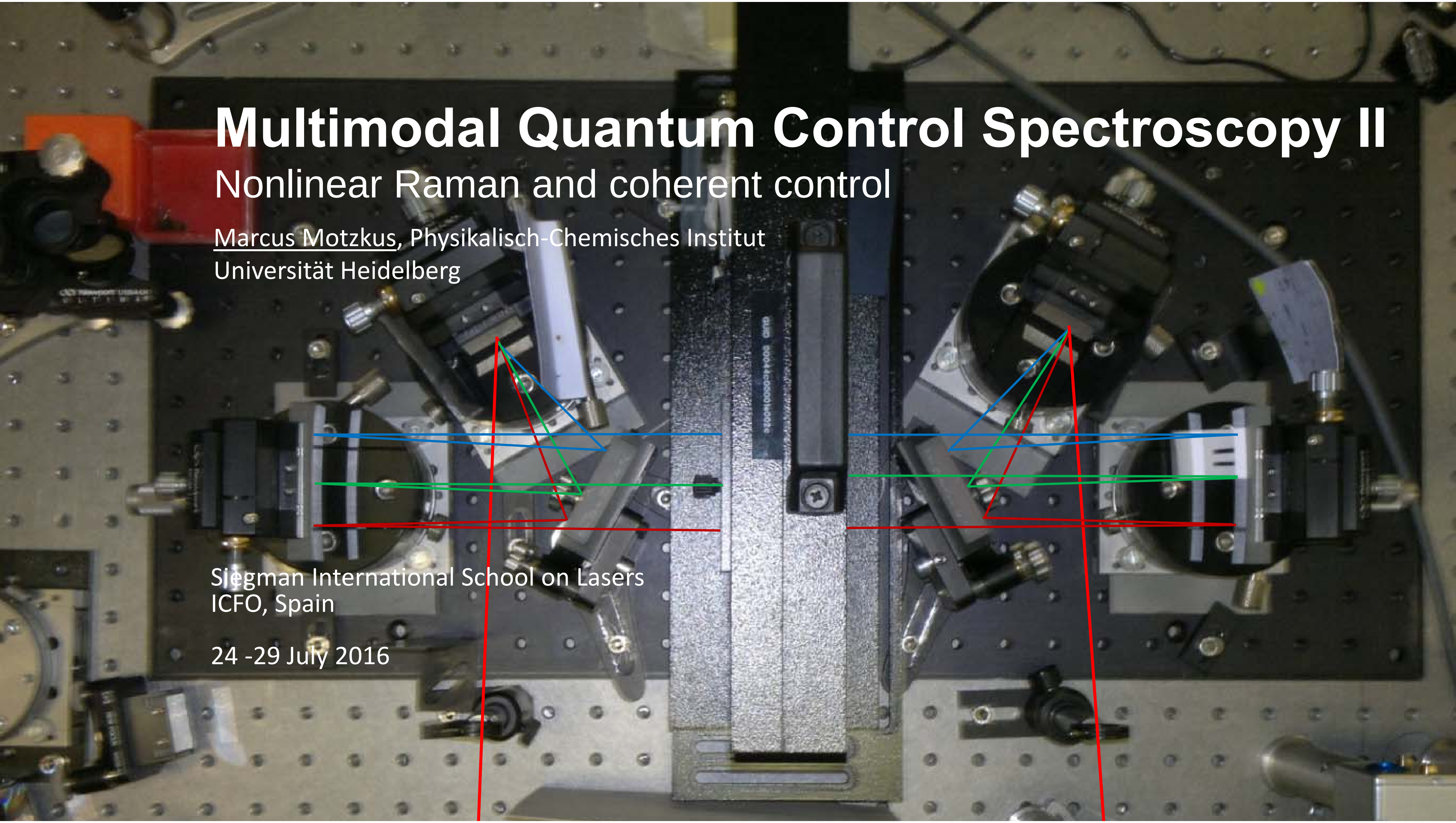


Multimodal Quantum Control Spectroscopy II

Nonlinear Raman and coherent control

Marcus Motzkus, Physikalisch-Chemisches Institut
Universität Heidelberg

Siegman International School on Lasers
ICFO, Spain

24 -29 July 2016

Outline

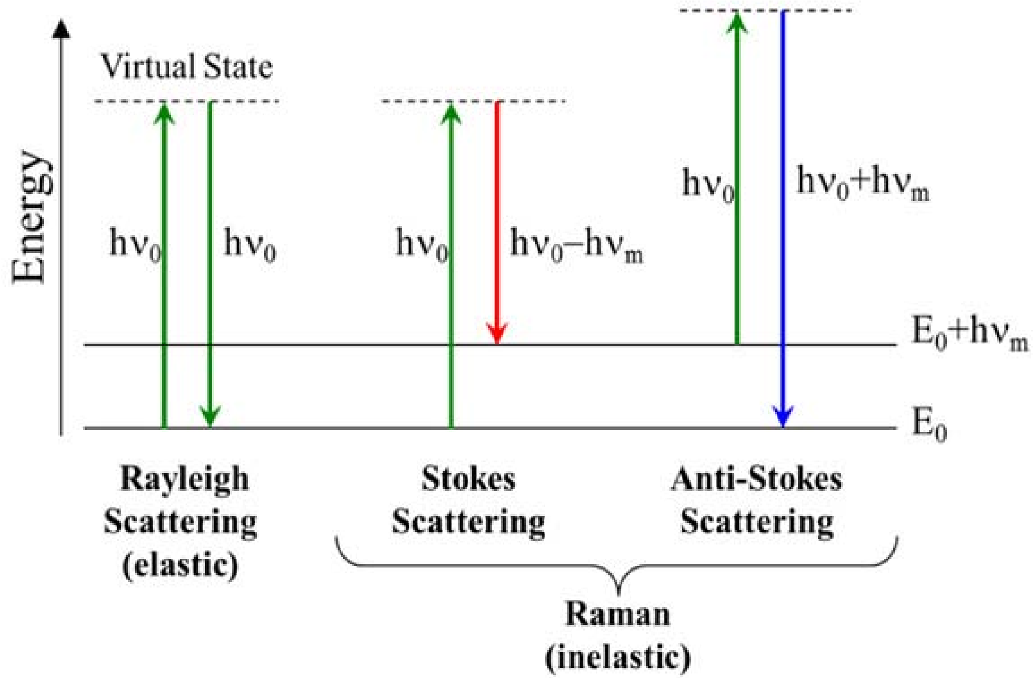
I. Coherent Control

- Concepts of Coherent Control
- Learning Loop: Pulse shaping, algorithms
- Applications:
  - Control of 2-Photon-Absorption
  - Control of energy transfer

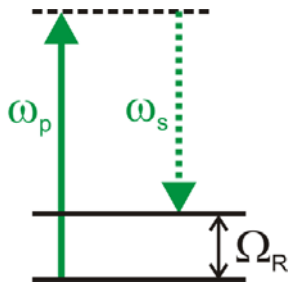
II. Single beam CARS

- Nonlinear Raman spectroscopy
- Shaped CARS
- Multimodal microscopy

Light Scattering: Rayleigh / Raman

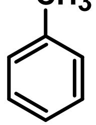


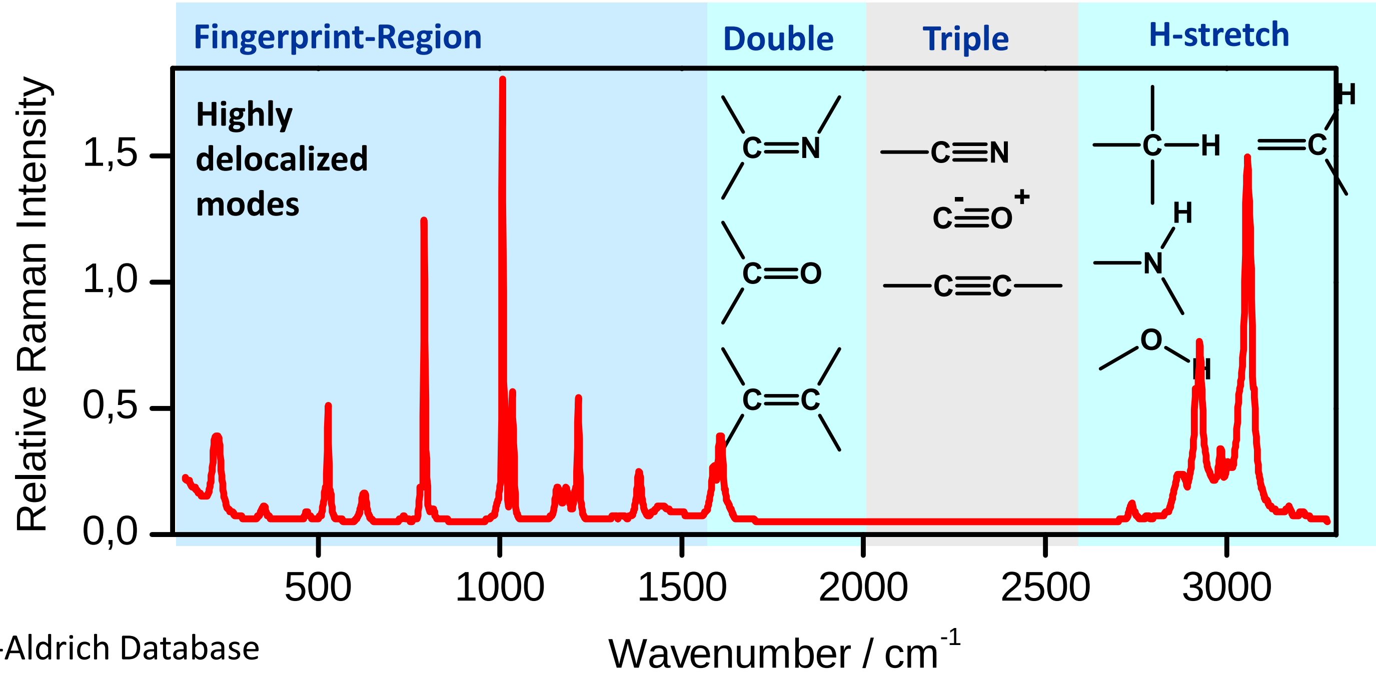
Raman spectroscopy



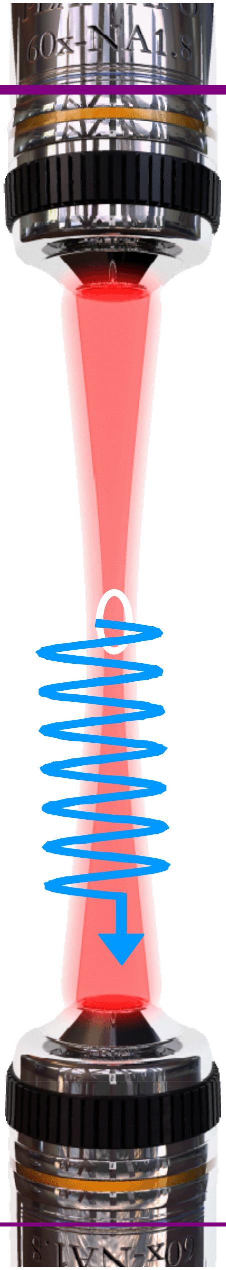
Spontaneous Raman

Important Raman spectral regions

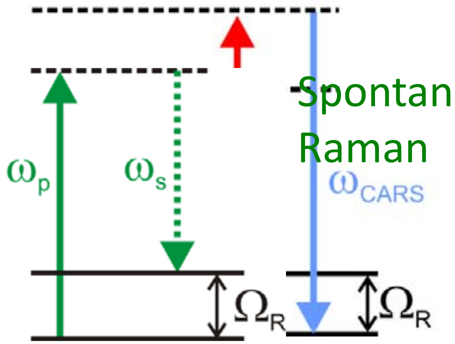




Sigma-Aldrich Database



Coherent Anti-Stokes Raman Scattering (CARS)



$$E_{CARS} = N \cdot \chi^{(3)}_{CARS} \cdot E_p \cdot E_s \cdot E_{p'}$$

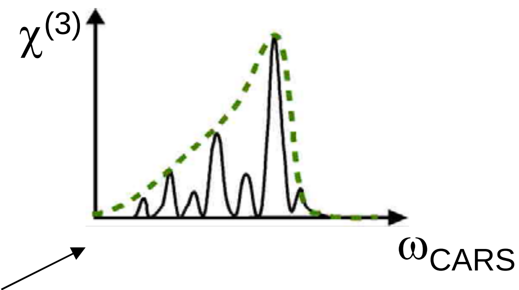
$$I_{CARS} \propto N^2 \cdot |\chi^{(3)}_{CARS}|^2 \cdot I_p \cdot I_s \cdot I_{p'}$$

- **Low scattering cross-section**
- **Fluorescence** background

- **Susceptibility $|\chi^{(3)}|^2$:** Chemical selectivity
- **Intensity I^3:** fs-pulses, Signal only from focus → 3D-imaging
- **Concentration N^2:** Detection of majority species

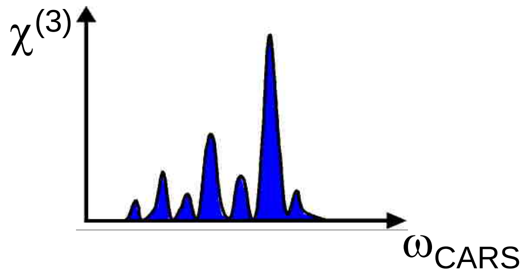
The nonlinear susceptibility $\chi^{(3)}$

envelope $\Rightarrow$ temperature

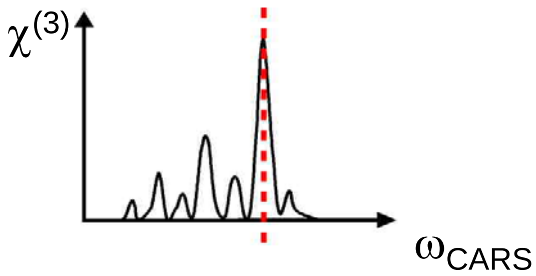


Example for $\chi^{(3)}$

$$\chi^{(3)} \sim N \cdot \sum_{a,b} \left(\frac{\partial \sigma}{\partial \Omega} \right)_{ab} \frac{\left(\rho_{aa}^{(0)} - \rho_{bb}^{(0)} \right)}{\left(\omega_{ba} - \omega_p + \omega_S - i\gamma_{ba} \right)}$$

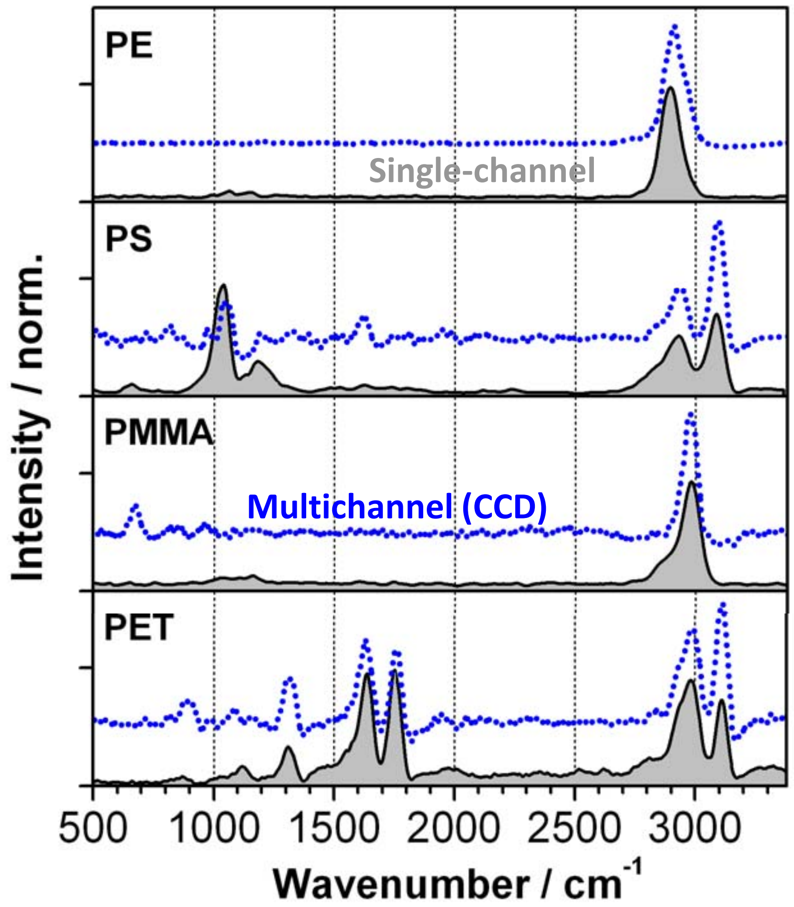


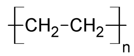
area $\Rightarrow$ concentration



position $\Rightarrow$ identification

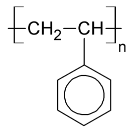
CARS-Spectra of neat Polymers





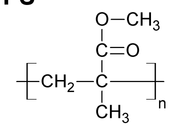
Poly(ethylen

PE



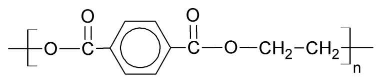
Poly(styrene

PS



Poly(methylmethacrylate)

PMMA



Poly(ethyleneterephthalate)

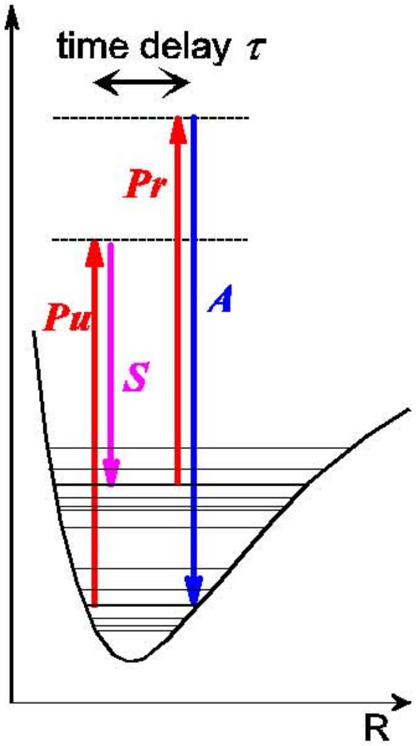
PET

CCD-Acquisition of >2000 cm^{-1} CARS spectrum in **~100 ms!**

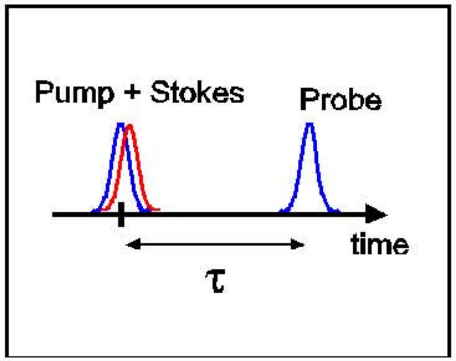
J. Raman Spectrosc., **38**, 916 (2007).

Time-resolved CARS

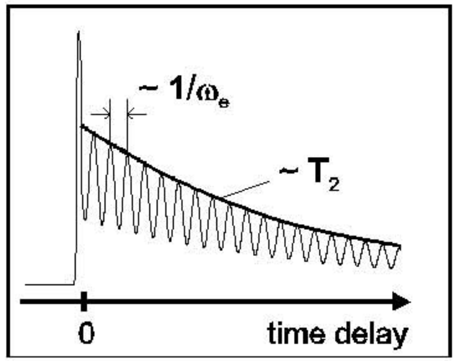
energy scheme



pulse sequence



FWM transient



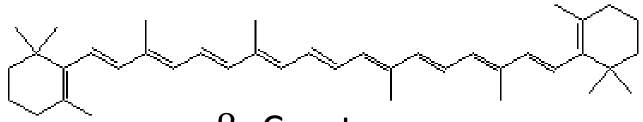
- four-wave-mixing signal

$$I_{\mathrm{FWM}} \sim \int dt \left| P^{(3)}(t) \right|^2$$

- third order nonlinear polarization

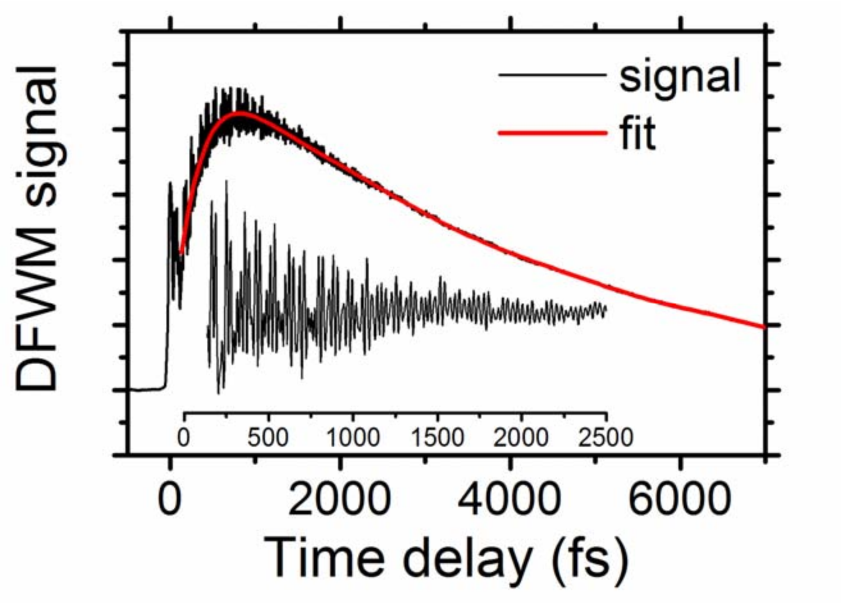
$$P_{\tau}^{(3)}(t) = E_P(t) \cdot \int_{-\infty}^{+\infty} E_L(t-\tau) E_S^*(t-\tau) \cdot R(t) dt$$

Time-resolved CARS

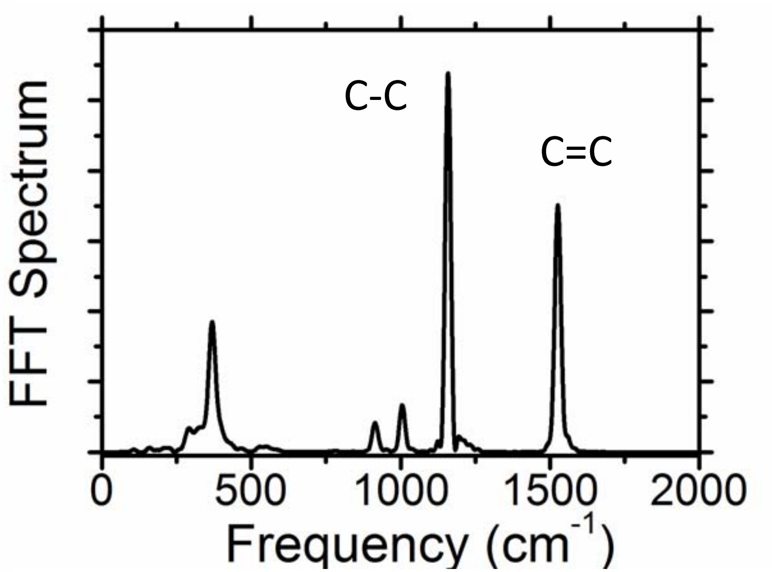


β–Carotene

Transient



FFT spectrum

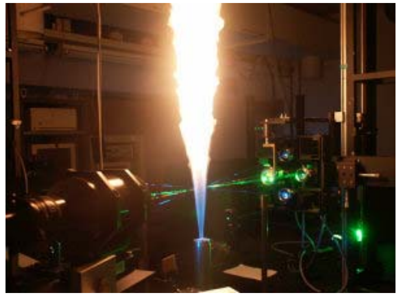


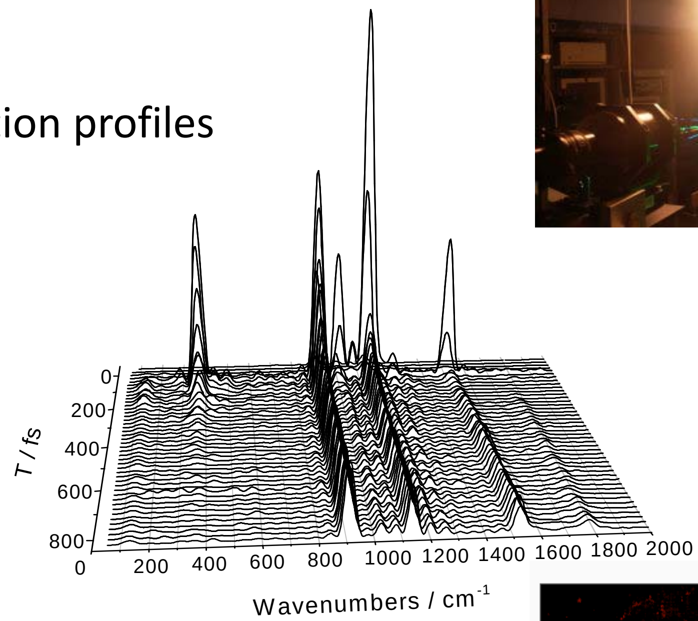
Annual. Rev. Phys. Chem. ***65*** *(2014) 39*

Major applications of CARS - today:

- **Combustion**

  → Temperature/concentration profiles in flames/engines



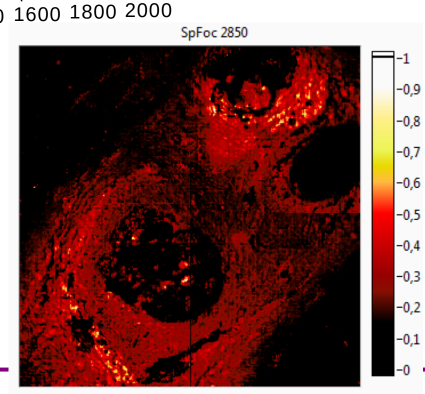


- **Ultrafast Spectroscopy**

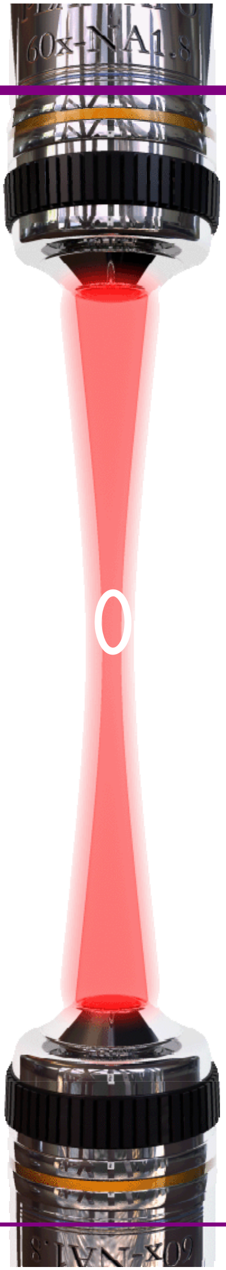
  → Time-resolved changes of molecular structures

- **Nonlinear Microscopy**

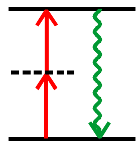
  → Fast chemical imaging of bio/medical samples

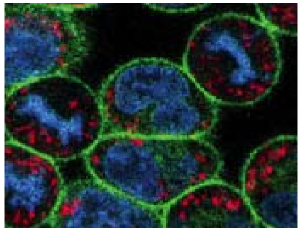


Multiphoton Microscopy



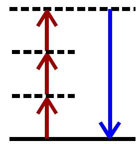
2PFE

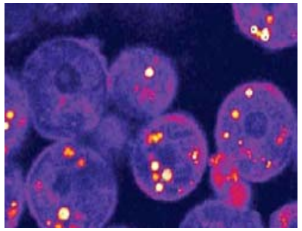




Zipfel et al., Nature Biotech. 21, 11, 1369 (2003).

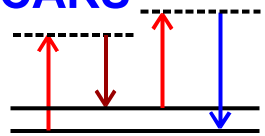
THG

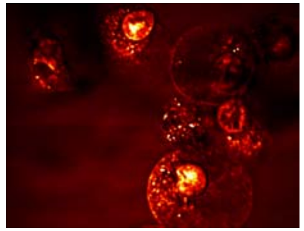




Débarre et al., Nature Methods 3, 47 (2006)

CARS





Cheng et al., Biophys. J. 83, 502 (2002).

$I_{Signal} \propto I_{Exc}^{n}$ → **3D resolution**

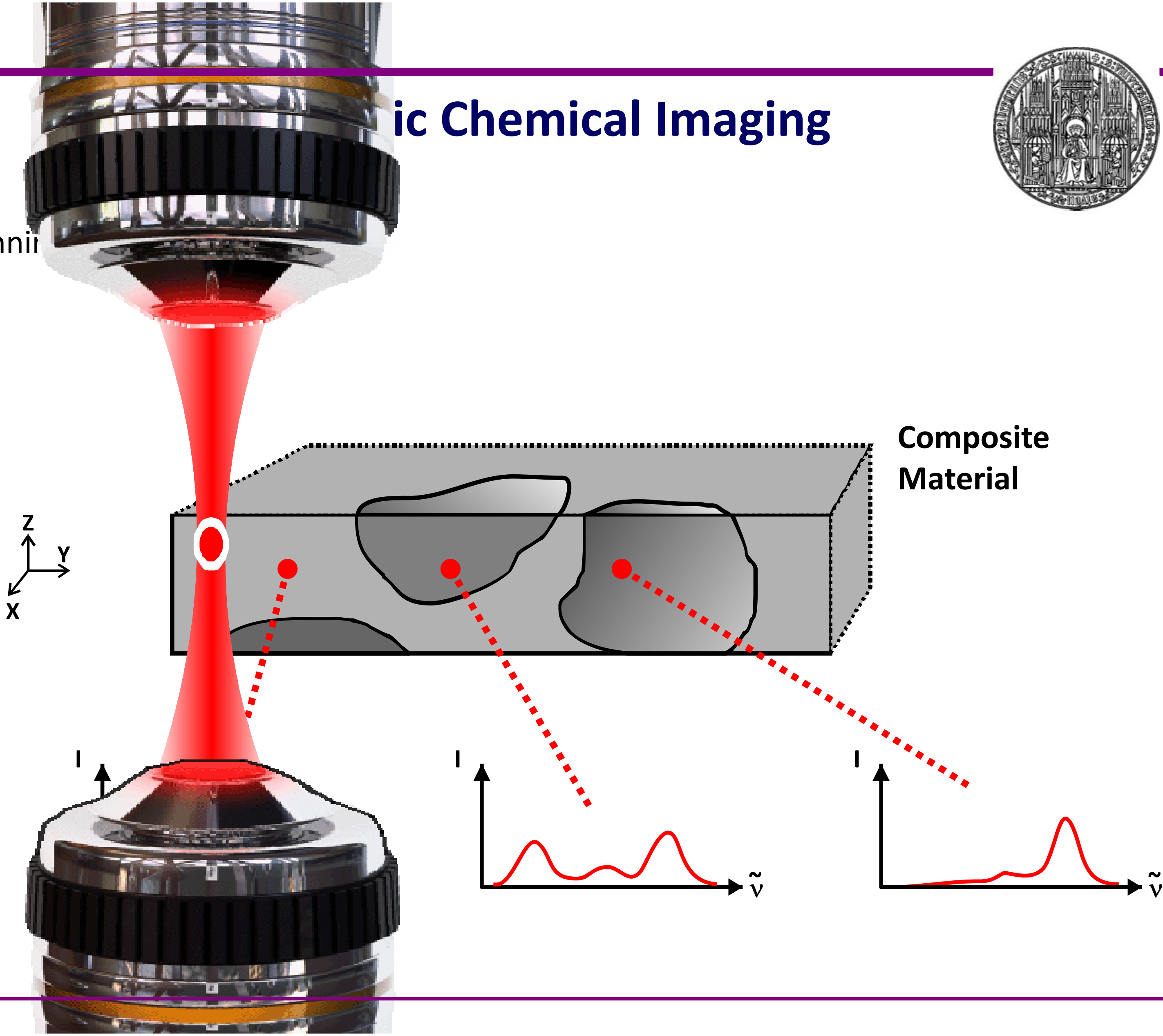
→ **Use ultrashort (fs) pulses:**

High peak intensity while low average power

Broad bandwidth for versatile excitation

ic Chemical Imaging

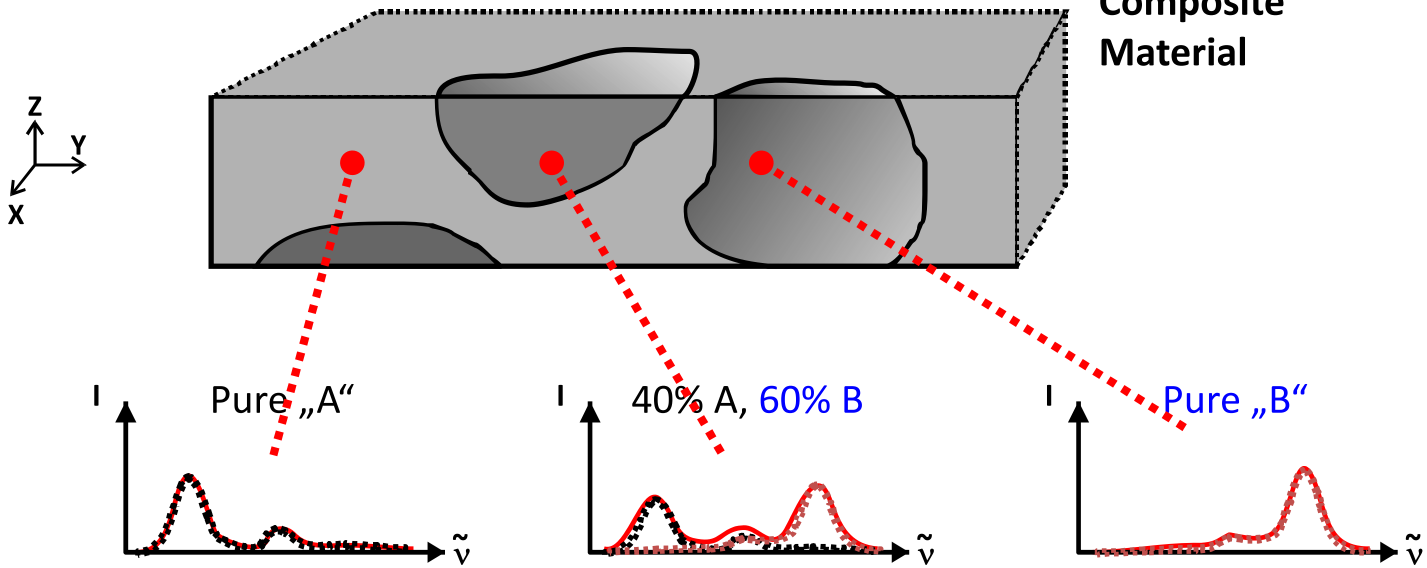
- Scanni



CARS Microscopic Chemical Imaging

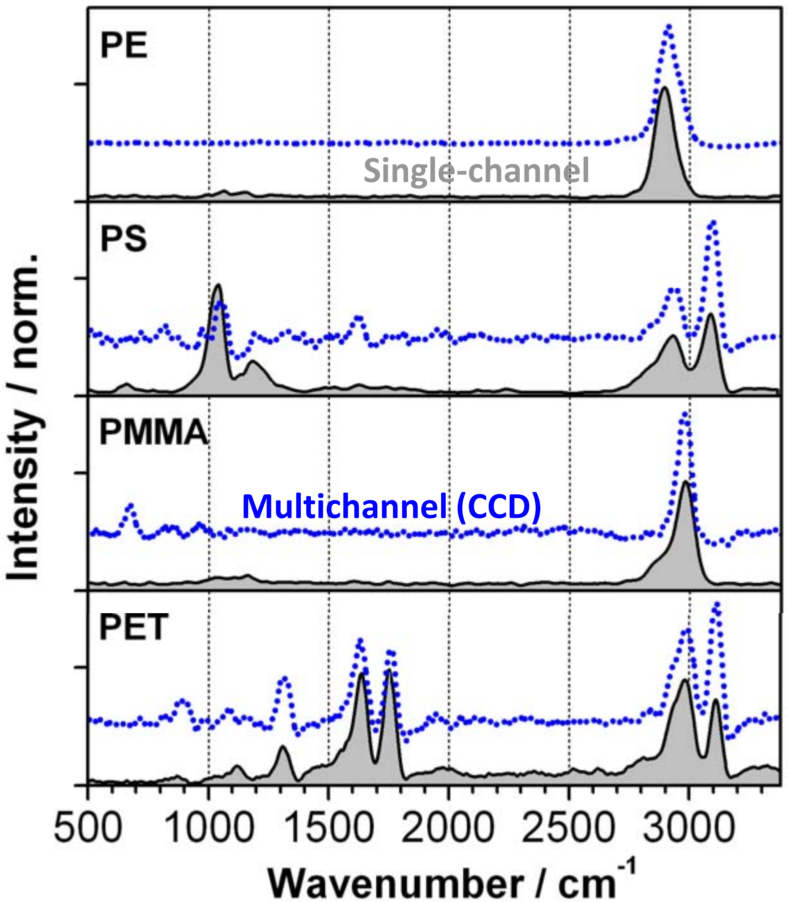
- Scanning the laser focus
- „Hyperspectral data“: Spectrum for each spatial position in the sample

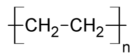
Decompose into chemical constituents



Composition from spectral fitting → Chemical maps

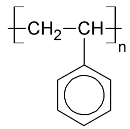
CARS-Spectra of neat Polymers





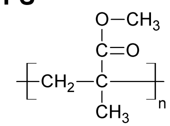
Poly(ethylen

PE



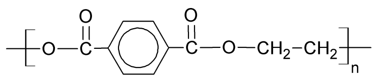
Poly(styrene

PS



Poly(methylmethacrylate)

PMMA



Poly(ethyleneterephthalate)

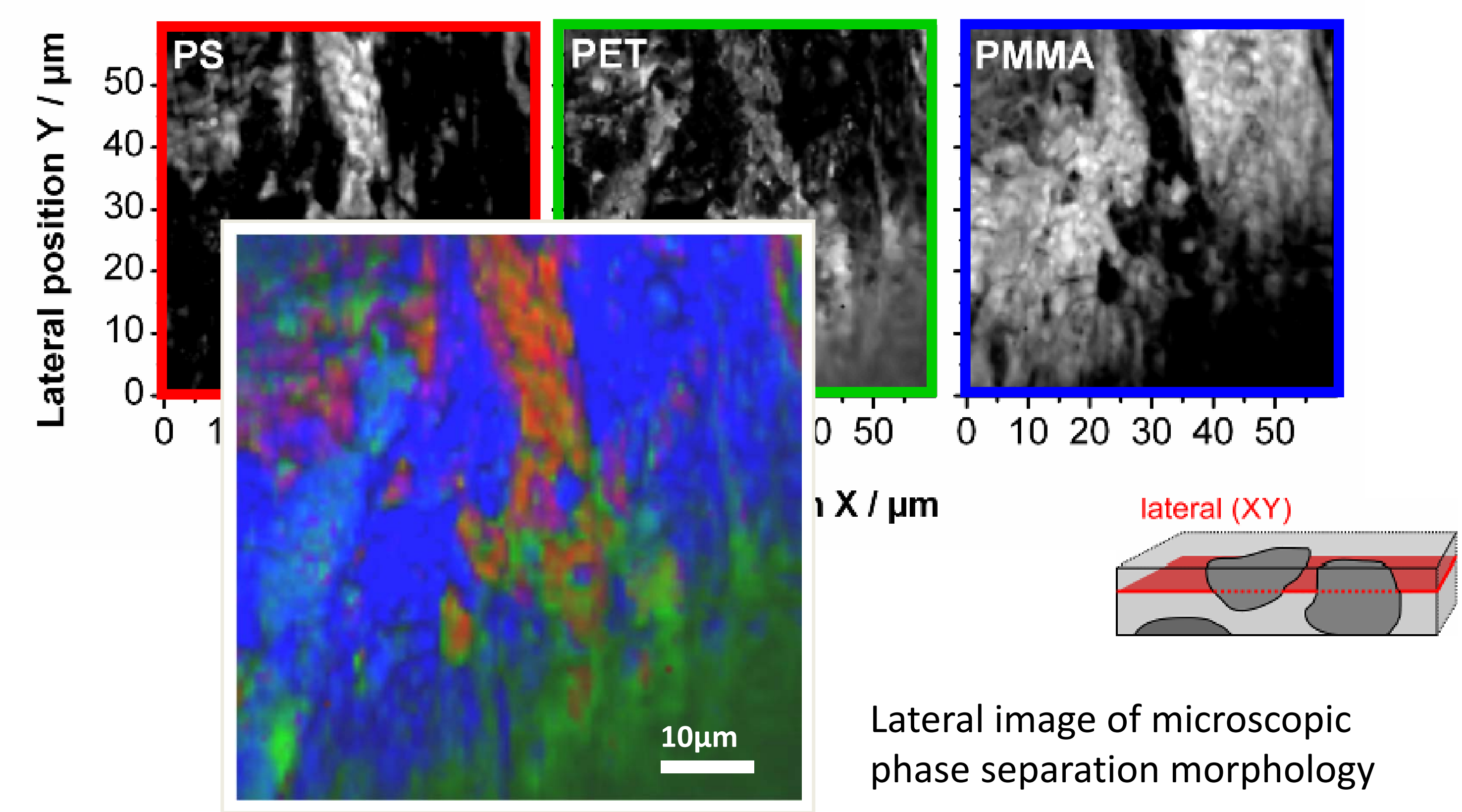
PET

CCD-Acquisition of >2000 cm^{-1} CARS spectrum in **~100 ms!**

J. Raman Spectrosc., **38**, 916 (2007).

CARS Microscopic Chemical Imaging

Ternary Polymer blend concentration map:

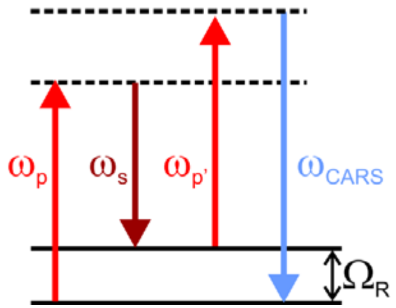


Lateral image of microscopic phase separation morphology

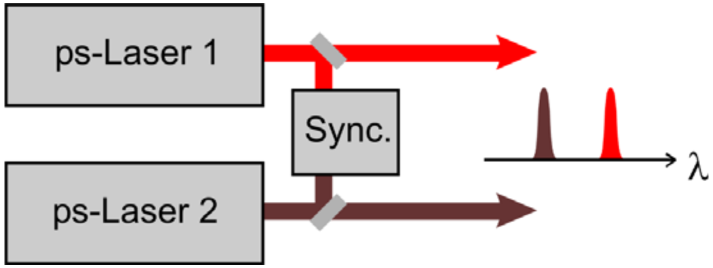
J. Raman Spectrosc., **38**, 916 (2007).

CARS Technological Challenges

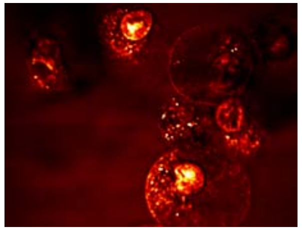
Picosecond CARS



Two syncronized ps-lasers:



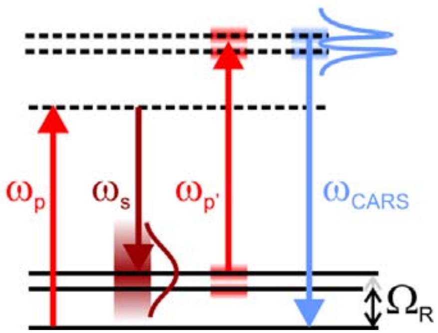
- **+** Benchmark setup in literature
- **-** Detection of a single resonance: slow, problems with contrast in complex samples
- **-** Synchronization difficult



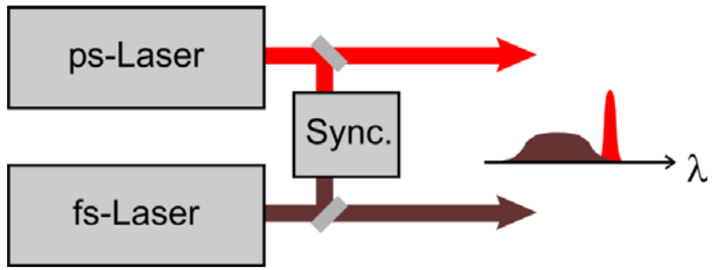
Cheng et al.,
Biophys. J. ***83*** *(2002) 502*

CARS Technological Challenges

Multiplex CARS (MCARS)



Syncronized ps- and fs-laser:



- ps-Laser (ω_p, $\omega_{p'}$) determines spectral resolution
- Broadband fs-Laser (ω_s) for spectral coverage

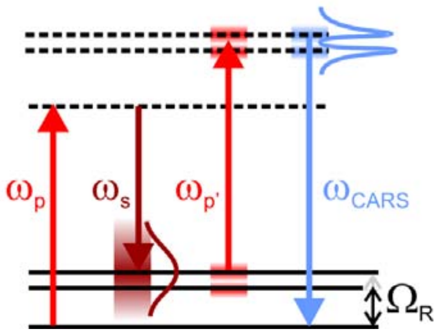
\+ Rapid spectral acquisition

\+ Complex samples

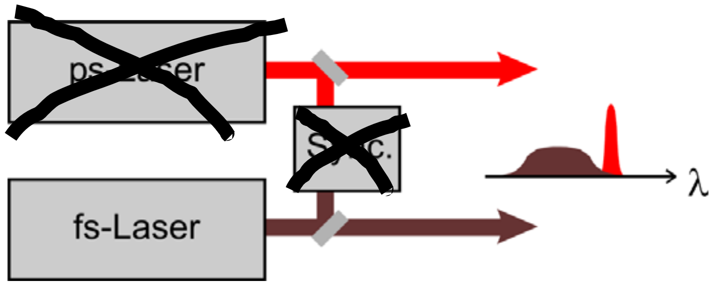
\- Synchronization

MCARS with only One Laser

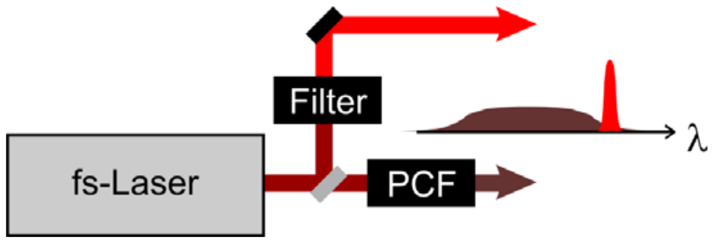
Multiplex CARS (MCARS)



Syncronized ps- and fs-laser:

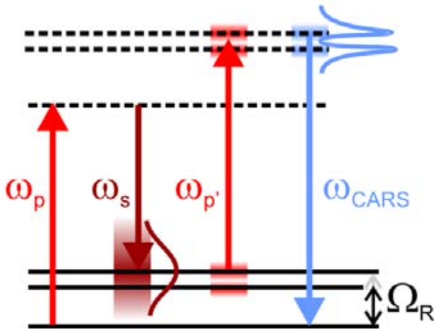


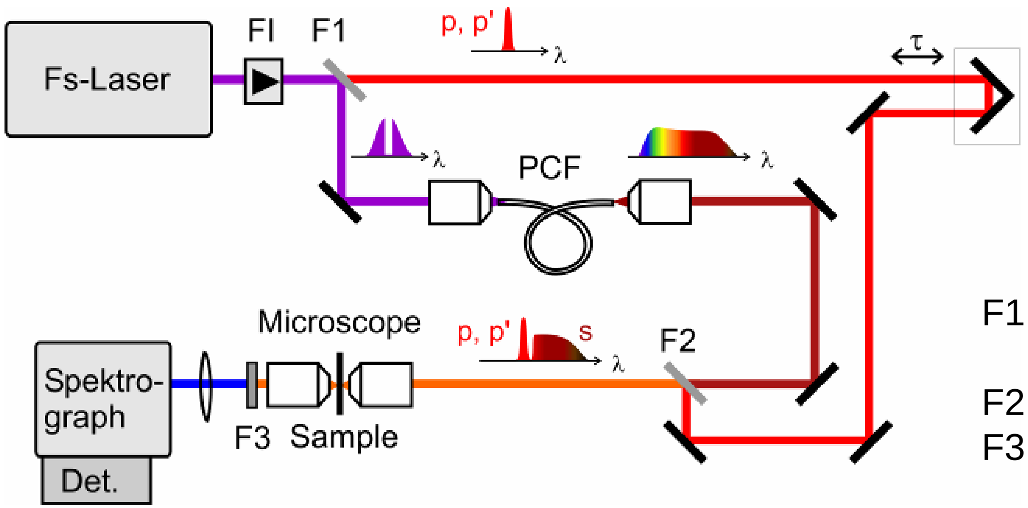
One laser broadband MCARS[1-3]:



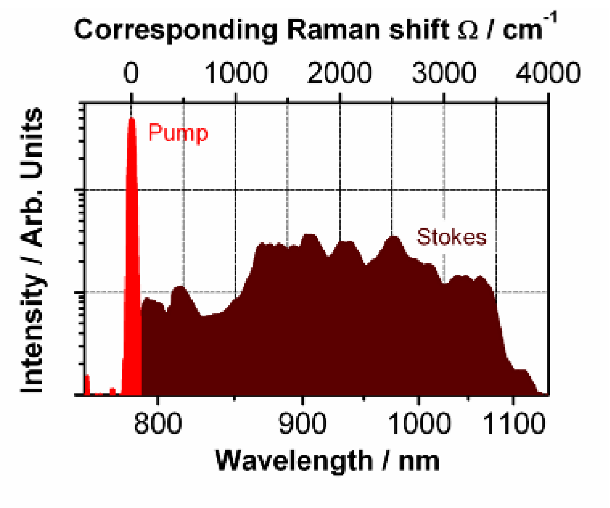
[1] T. W. Kee and M. T. Cicerone, *Opt. Lett.* **29**, 2701 (2004)
[2] H. Kano and H. Hamaguchi, *Appl. Phys. Lett.* **85**, 4298 (2004)
[3] E. R. Andresen et al., *J. Opt. Soc. B* **22**, 1935 (2005)

Multiplex CARS





F1: Narrow Bandpass filter
F2: Longpass filter
F3: Shortpass filter



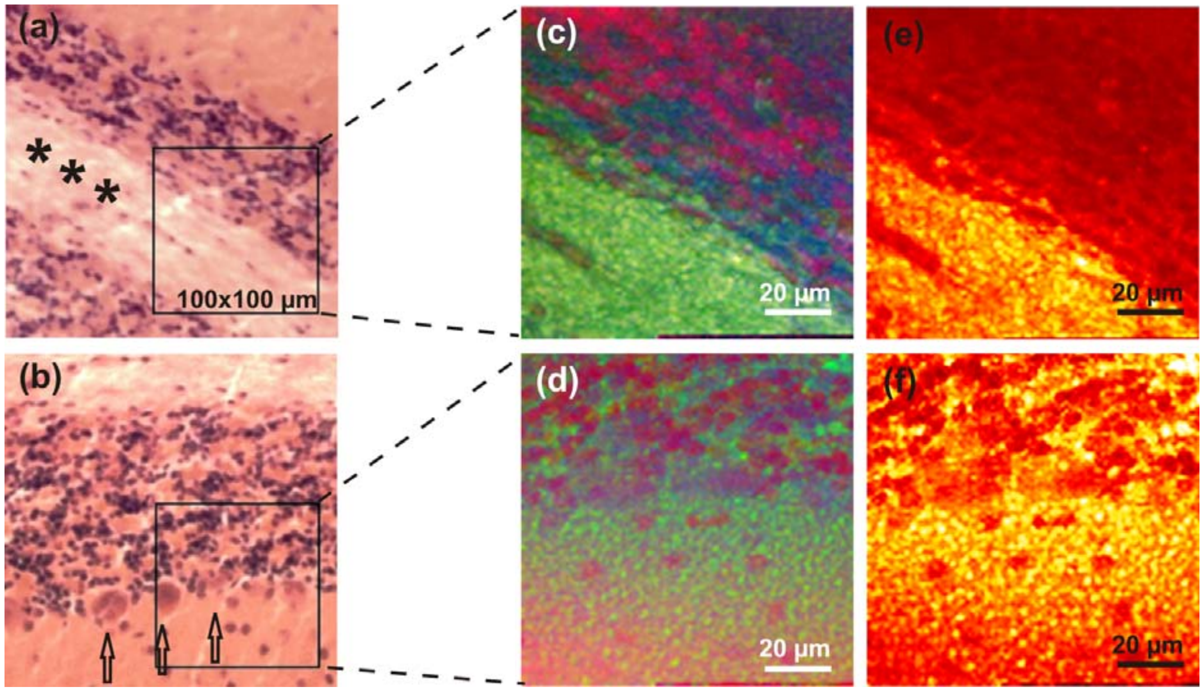
- **Narrowband Pump** (< 3 nm, better than 60 cm^{-1} spectral resolution)
- **Broadband Stokes** (> 300 nm, coverage up to 3500 cm^{-1})

J. Raman Spectrosc., **38**, 916 (2007).

Mouse brain tissue

HE stained samples | CARS microscopy

PCA | intensity at 2845 cm^{-1}

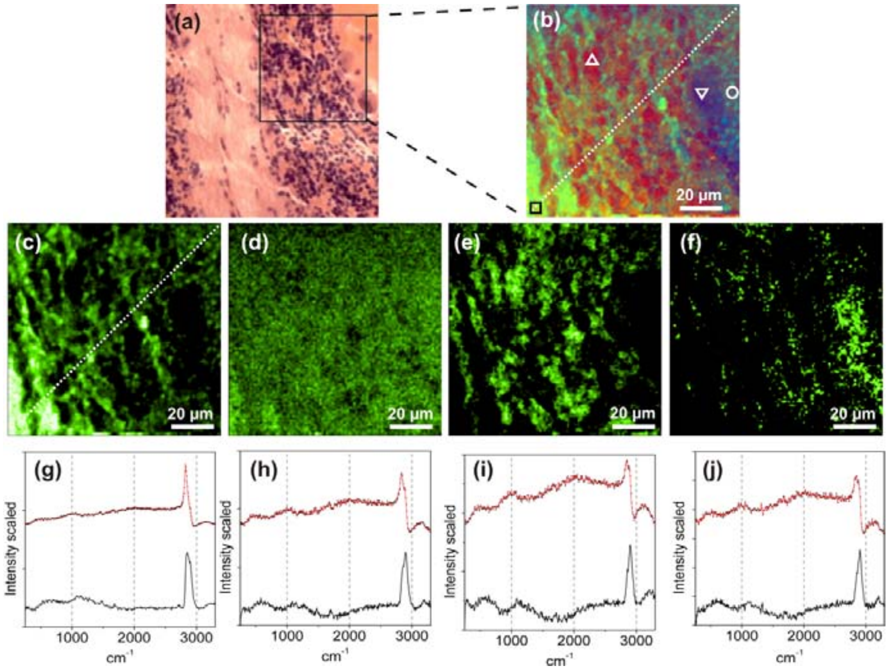


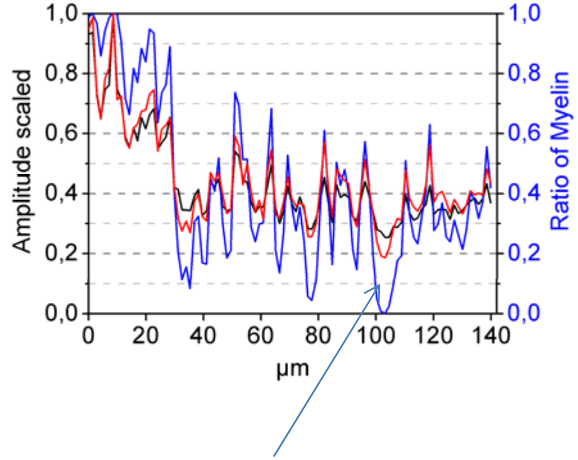
Purkinje cells (red)
grey matter (orange)
nuclei of granule cells (dark blue)
white matter (myelin, pink fiber bundles)

Samples: A. Pagenstecher, Marburg

Fast tissue imaging with CARS: Mouse brain

Quantitative backward calculation of the sample components





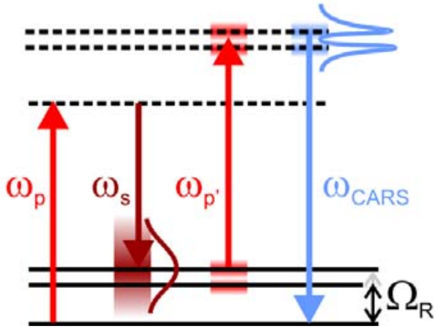
Quantitative fitting → Improved contrast ➔

CARS provides same information as HE stained reference !!

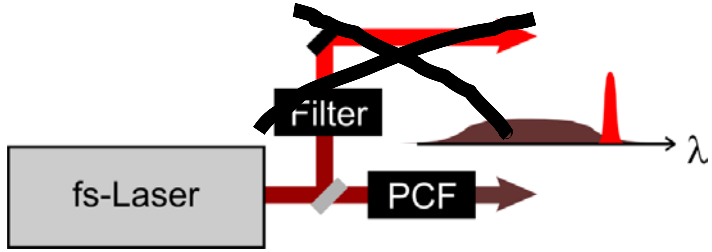
Samples: A. Pagenstecher Marburg

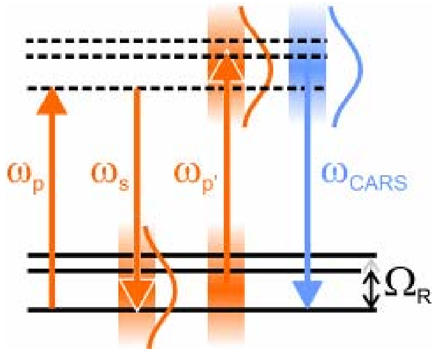
Biomedical Opt. Exp. ***2*** *(2011) 2110*

Simplify CARS even further…



One laser broadband MCARS:

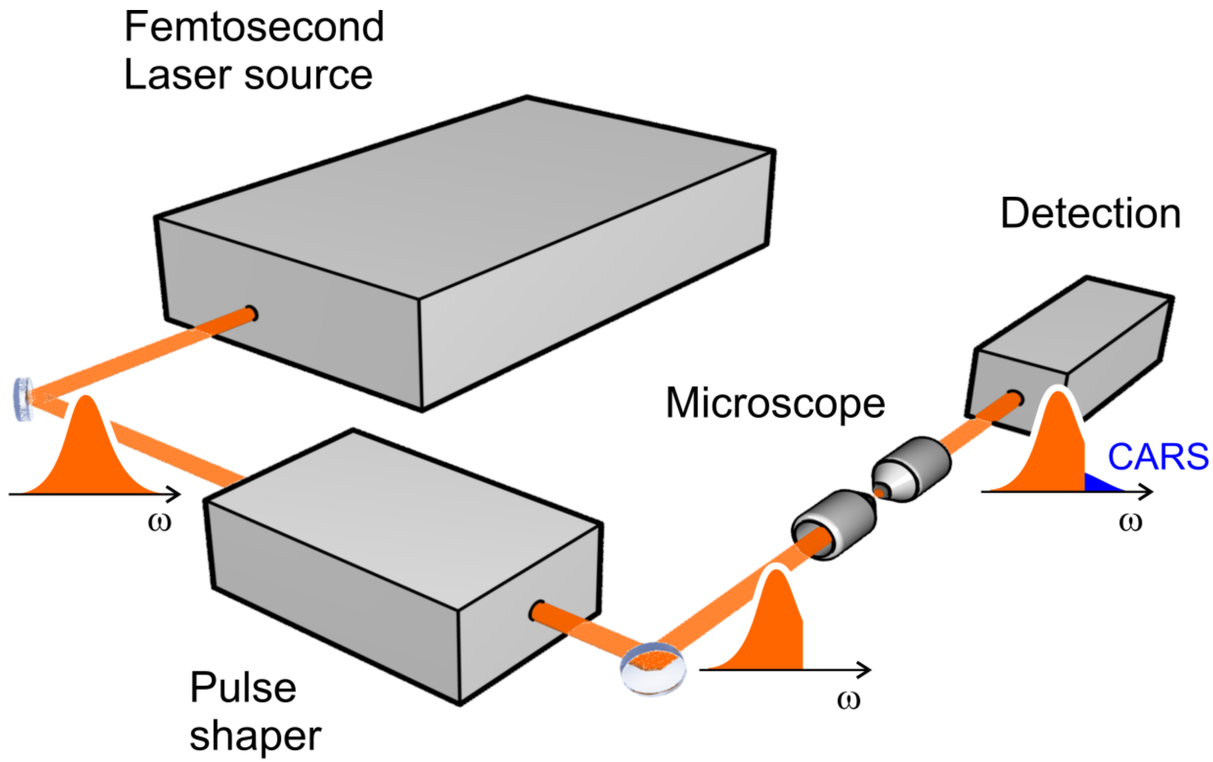




Single-beam CARS[1-3]:

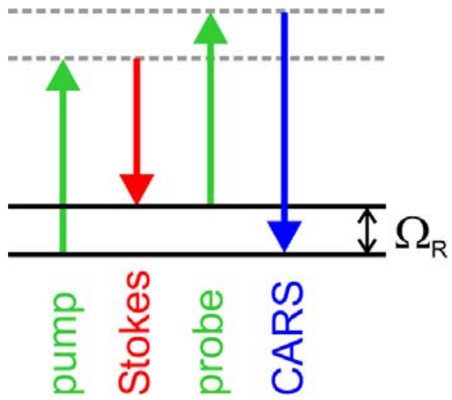
[1] N. Dudovich, D. Oron, Y. Silberberg, *Nature* **418**, 512 (2002)
[2] S.-H. Lim, A. Caster, S. R. Leone, *Phys. Rev. A.* **72**, 041803 (2005)
[3] B. von Vacano, W. Wohlleben, M. Motzkus, *J. Raman Spectrosc.* **37**, 404 (2006)

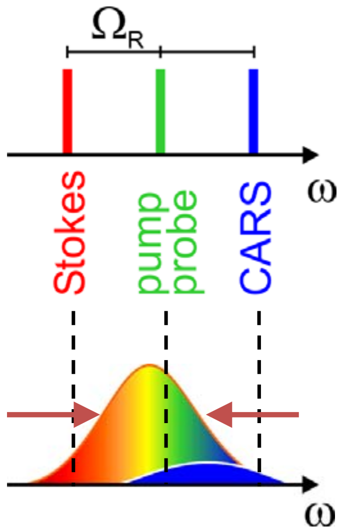
Nonlinear microscopy with shaped pulses



Phys. Chem. Chem. Phys. ***10*** *(2008) 681*

Single-beam CARS



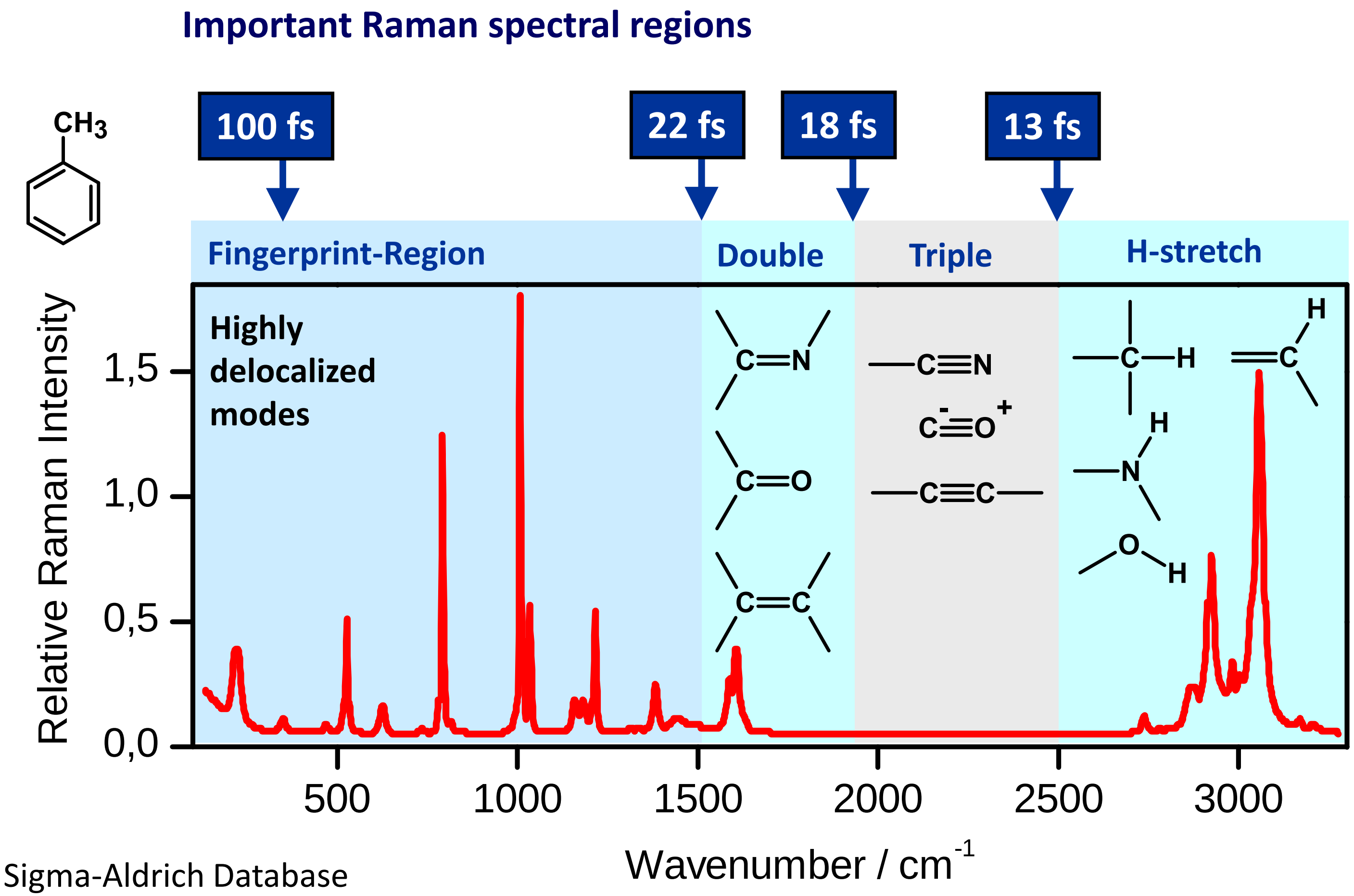


- CARS with a single beam of fs-pulses
- Spectral width $\Delta\omega > \Omega_R$

$\Delta\omega = f / \Delta\tau_{pulse}$

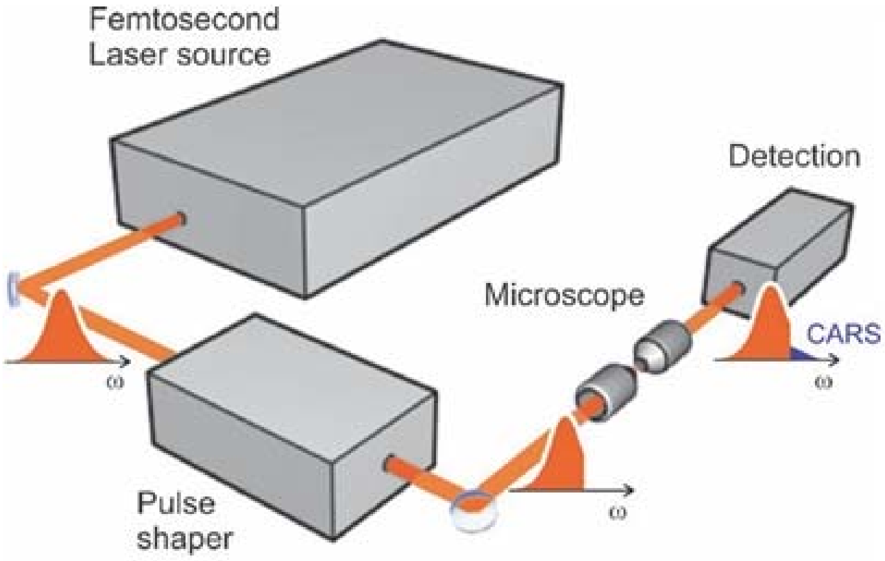
Spectral width and pulse duration are directly related

Single-beam CARS: Need for short pulses

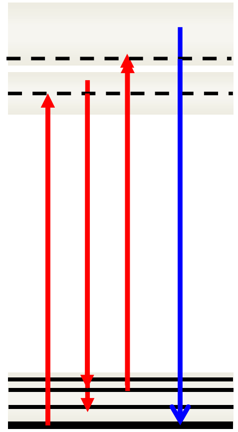


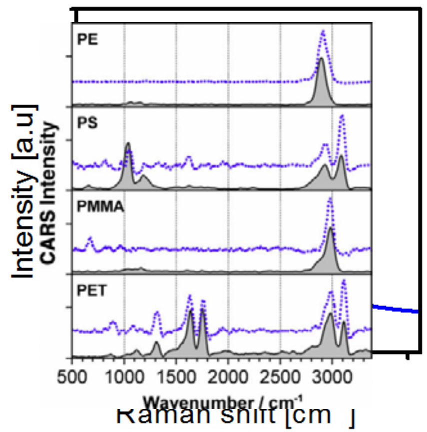
Sigma-Aldrich Database

Single-beam-CARS



All spectral components are provided by a single laser pulse

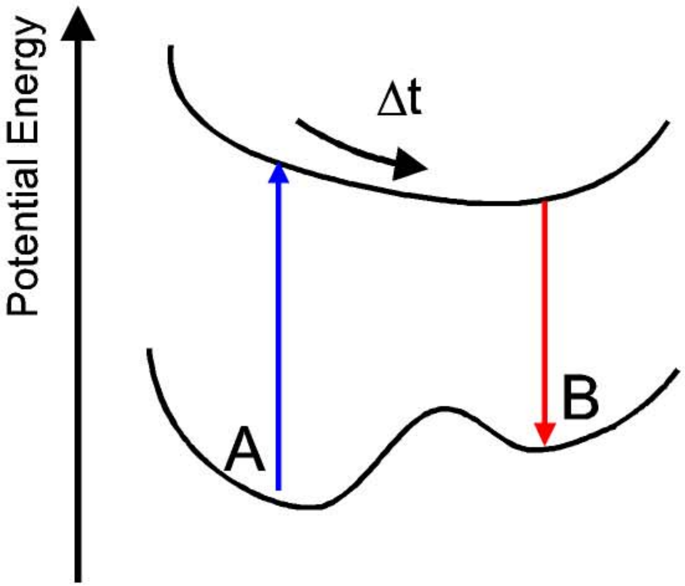




Von Vacano et al. J. Raman Spec. ***38*** *(2007) 916*

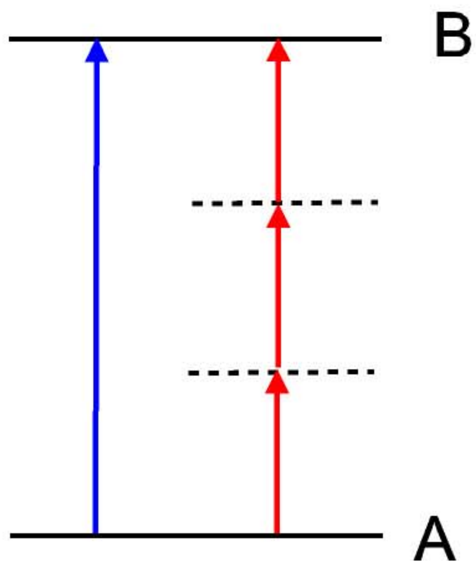
Control strategies

Tannor-Kosloff-Rice
JCP 85, 5805 (1986)



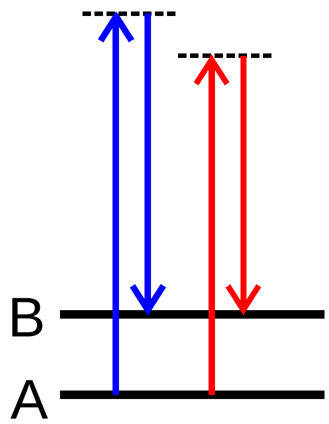
time delay: Δt

Brumer-Shapiro
CPL 126, 54 (1986)



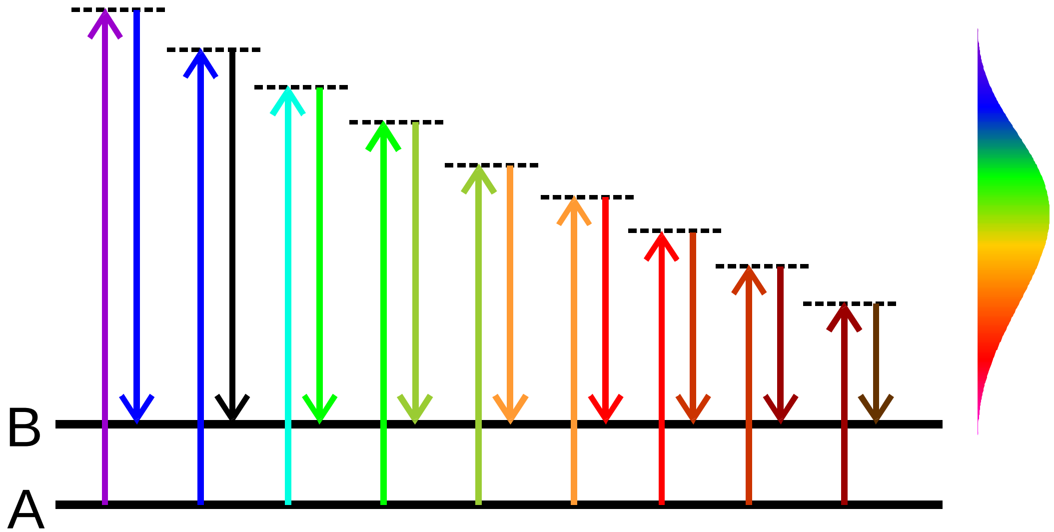
phase difference: $\Delta\phi=\phi_{\omega}-\phi_{3\omega}$

Control of Raman transitions



Two coherent Raman excitations
→ **interfering pathways** (like double slit)

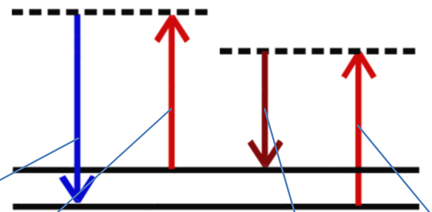
Control of Raman transitions



Broadband spectrum, many colors

→ **Many interfering pathways**

Effect of phase shaping on CARS



CARS Signal:

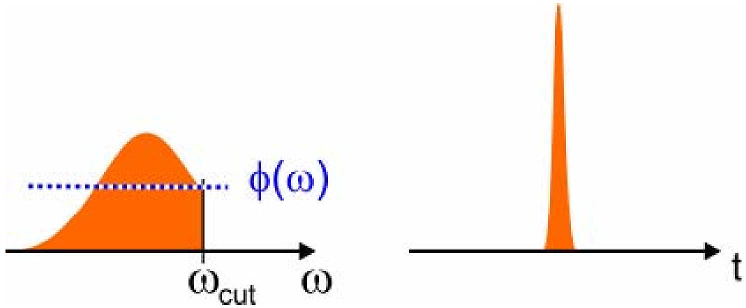
$$E_{CARS}(\omega) \propto \int E_{pr}(\omega-\Omega)\chi^{(3)}(\Omega)\int E_S^{*}(\omega'-\Omega)E_p(\omega')d\omega' d\Omega$$

$$E_{CARS}(\omega) \propto \iint \left|E_{pr}(\omega-\Omega)\right|\left|E_S(\omega'-\Omega)\right|\left|E_p(\omega')\right|\chi^{(3)}(\Omega).$$

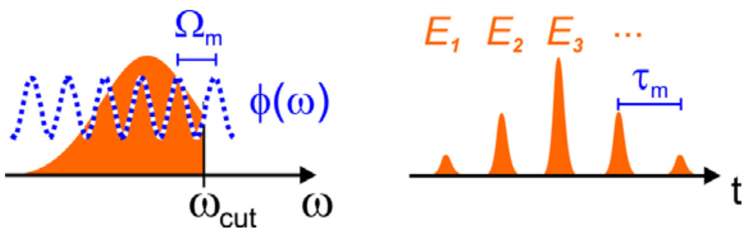
$$\times \exp\left(i\boxed{\left(\varphi(\omega')-\varphi(\omega'-\Omega)+\varphi(\omega-\Omega)\right)}\right)d\omega' d\Omega$$

Dependence on the phase

Modulation of phase:
time vs. frequency domain

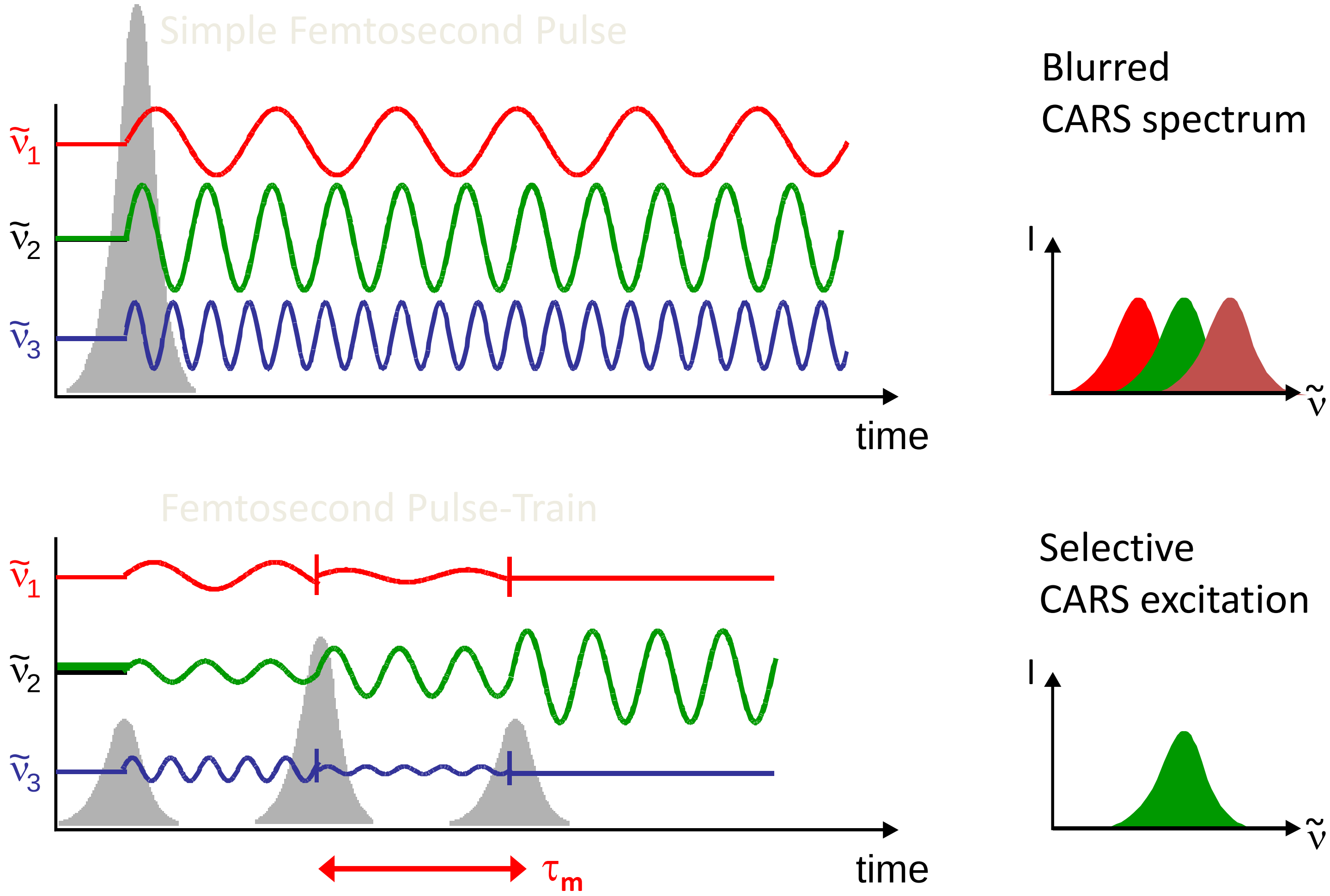


- Transform limited pulse, no spectral discrimination

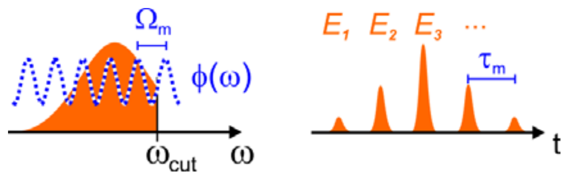


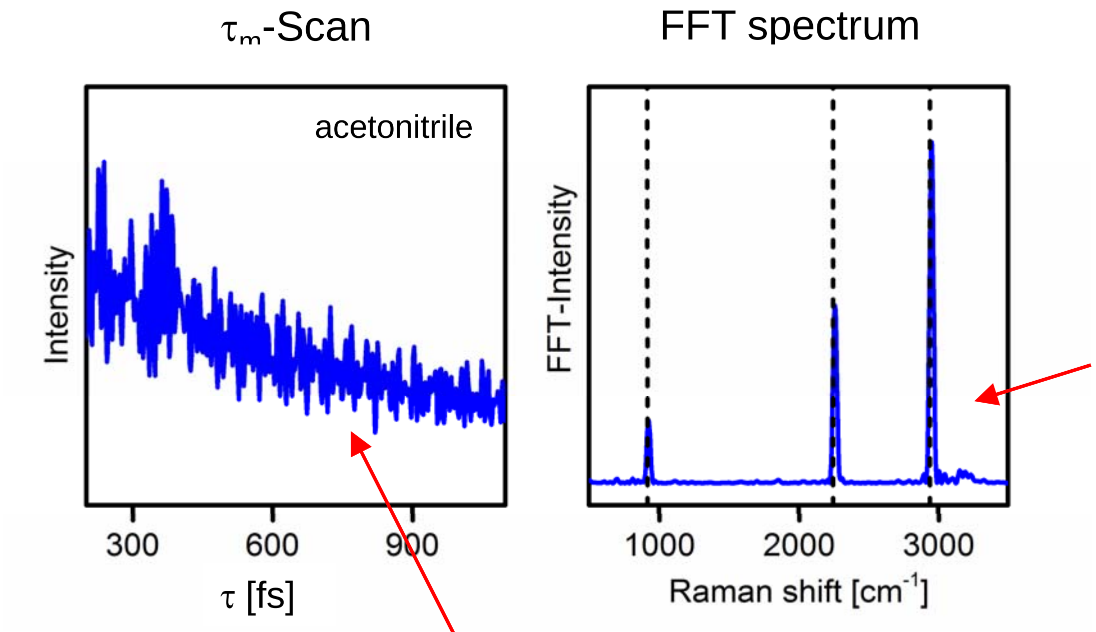
- Sine phase with period Ω_m creates subpulses spaced in time $\tau_m = 2\pi / \Omega_m$

Single-beam CARS with multipulses



Single-beam CARS with Multipulses

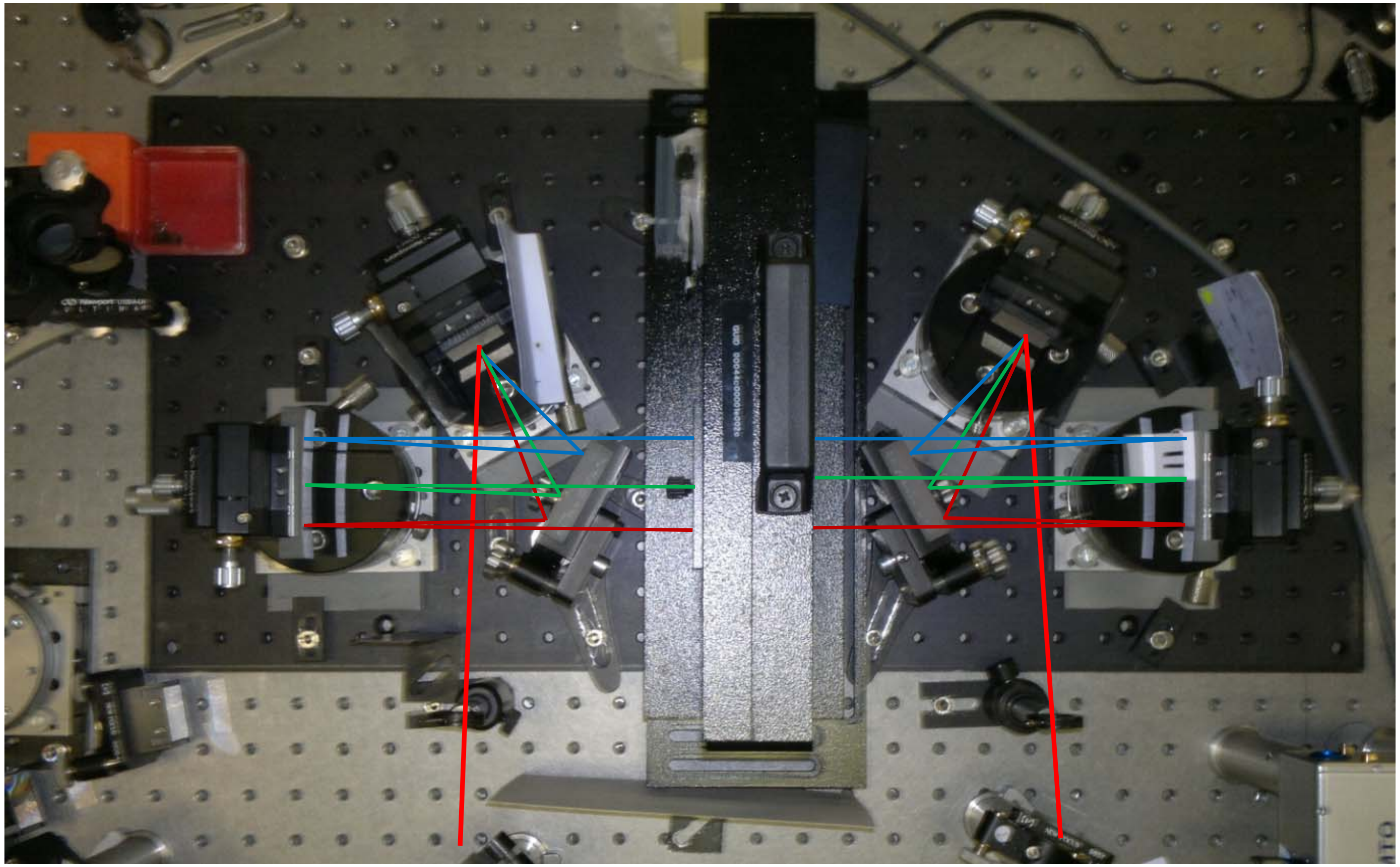




Acetonitrile vibrational spectrum with < 30 cm-^{1} resolution

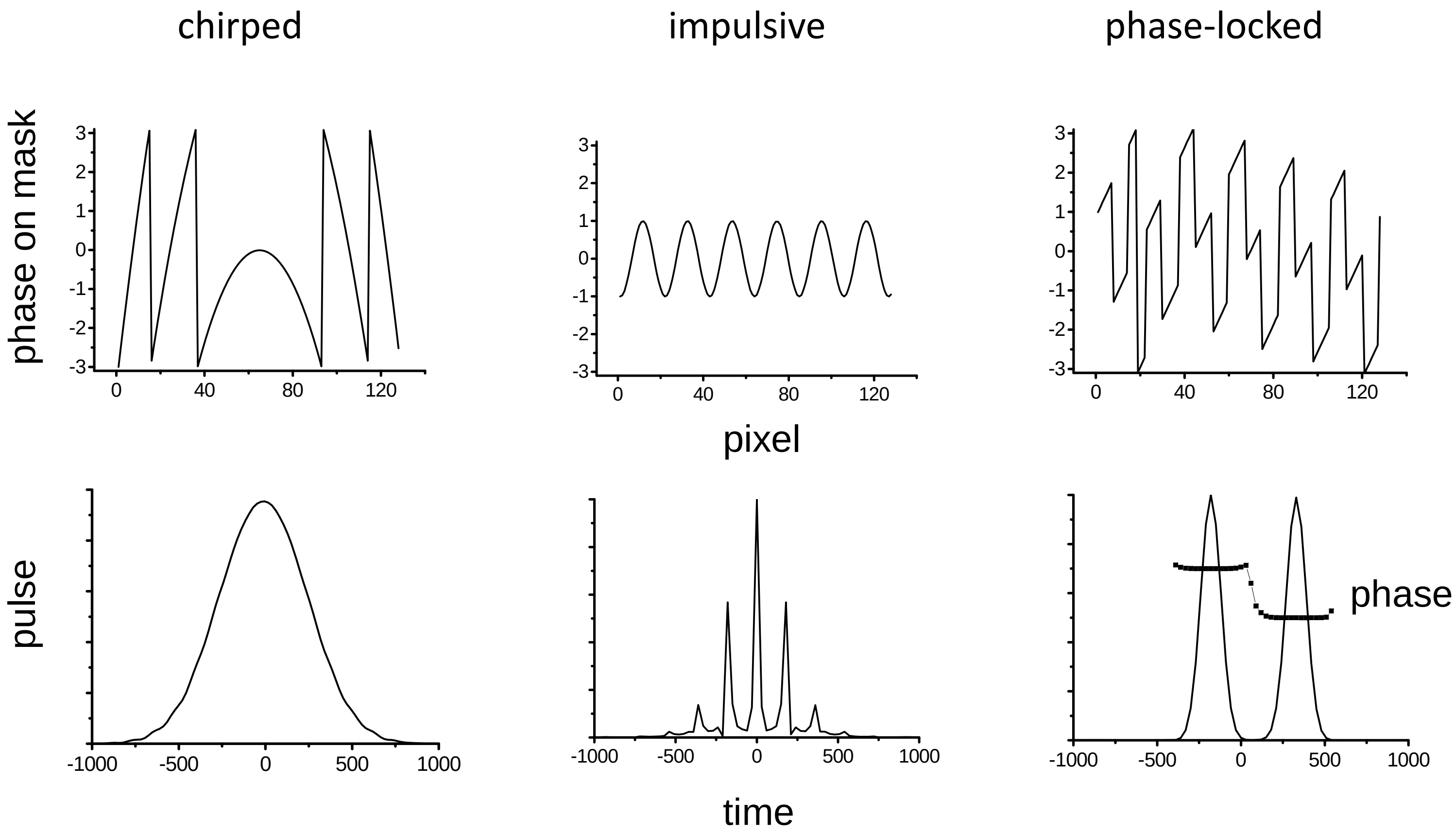
Oscillations encode molecular vibrations

Principles of pulse shaping



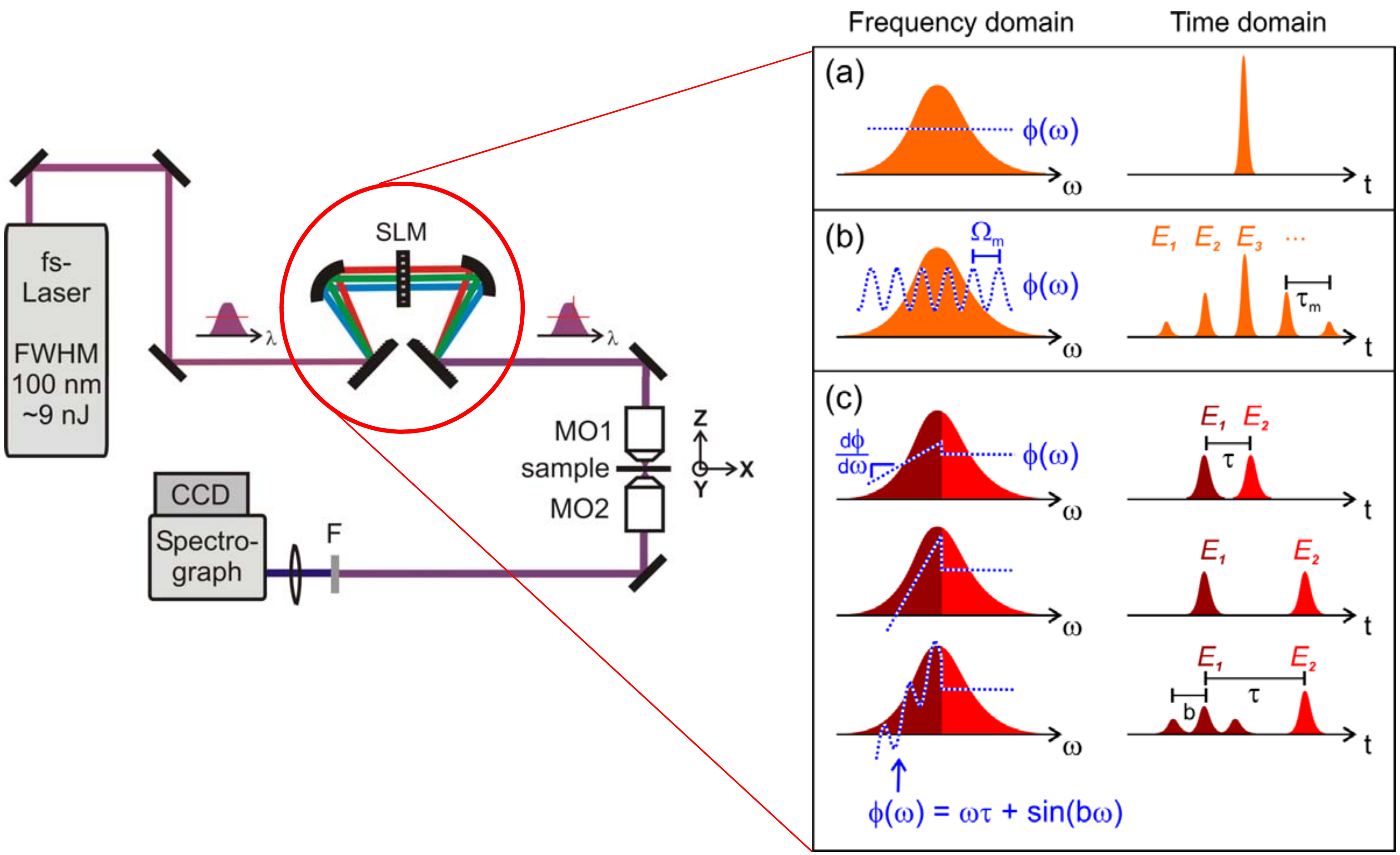
Appl. Phys. B ***72*** *(2001) 627*

Parameterization of excitation mechanism



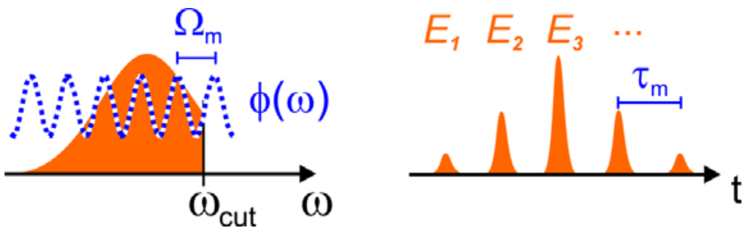
Chem. Phys. Lett. **326** (2000) 445, Phys. Rev. A **64** (2001) 023420

Single-beam-CARS schemes



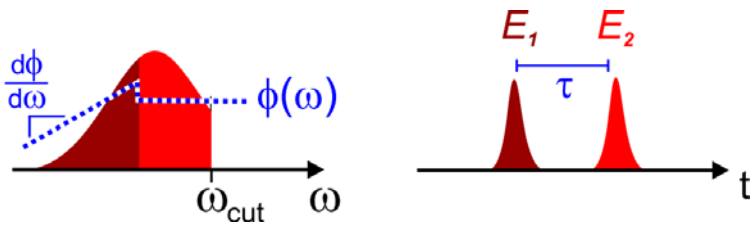
Truly time-resolved Single-beam CARS

Multipulses



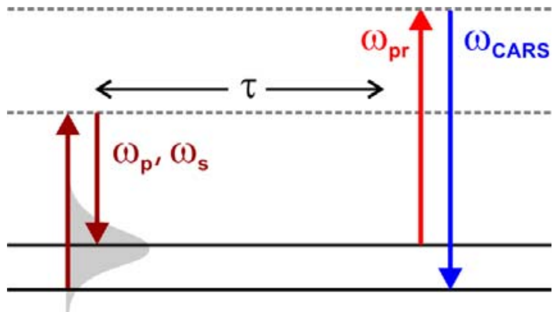
- E_1, E_2 , E_3, … with indistinguishable roles: Pump, Stokes, probe
- Only one octave of wavenumbers

Two-color double pulses

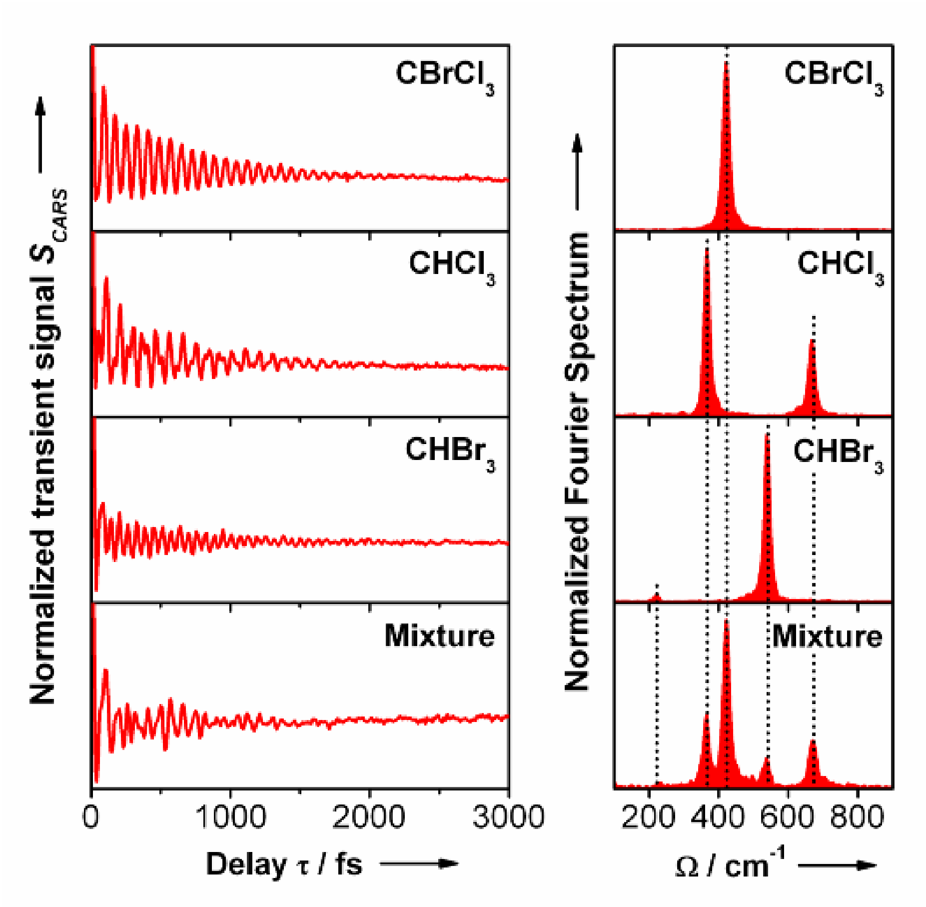


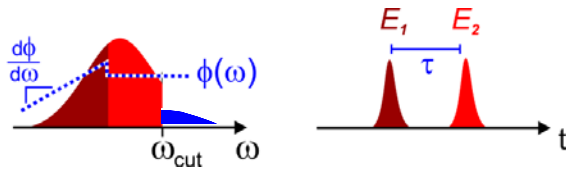
→ „Pump/Probe“-scheme with shaping from a single beam

- Defined roles: **Pump + Stokes (E_1)** and **probe (E_2)**



Truly time-resolved Single-beam CARS

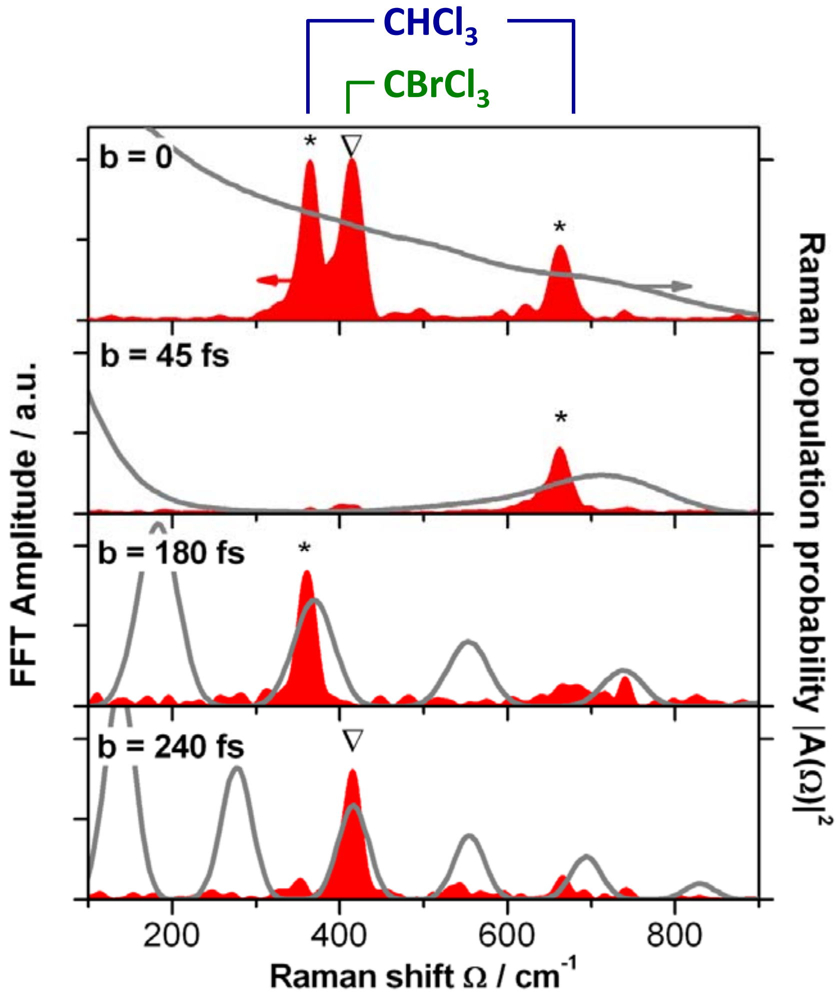


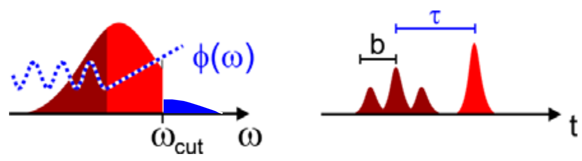


Phys. Chem. Chem. Phys. ***10*** *(2008) 681*
Opt. Comm. ***264*** *(2006) 488*

- **Unambiguous data analysis**, arbitrary wavenumber range

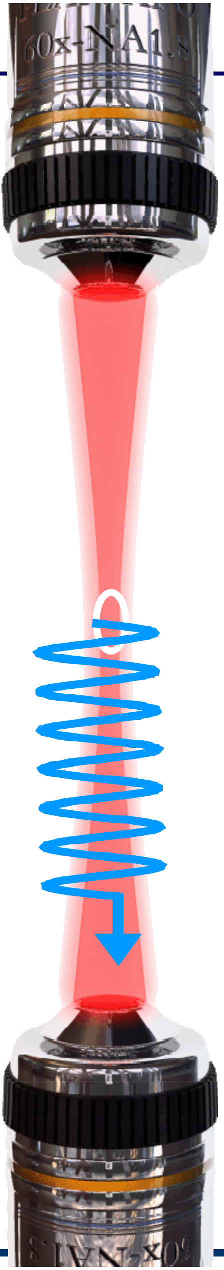
Raman Control of a Binary Mixture



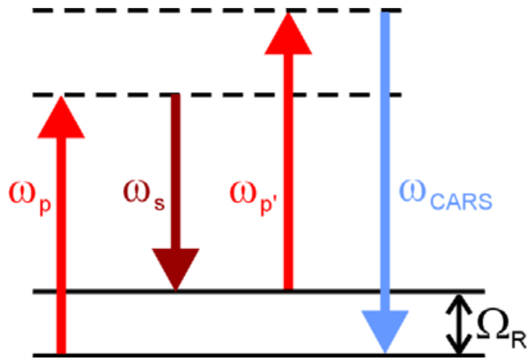


- Combine **multipulse** sequence for selective excitation with **time-delayed probe pulse**
- Raman quantum control of molecular vibration!

J. Chem. Phys. **127**, 144514 (2007).



Coherent Anti-Stokes Raman Scattering (CARS)



$$E_{CARS} = N \cdot \chi^{(3)}_{CARS} \cdot E_p \cdot E_s \cdot E_{p'}$$

$$I_{CARS} \propto N^2 \cdot |\chi^{(3)}_{CARS}|^2 \cdot I_p \cdot I_s \cdot I_{p'}$$

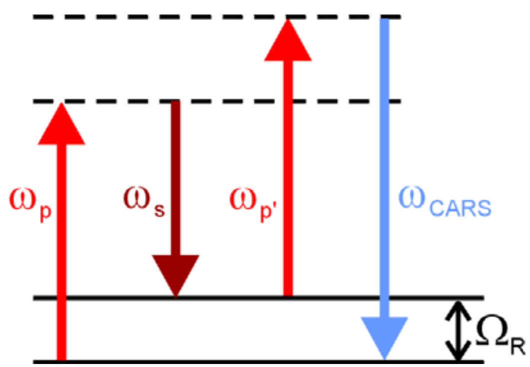
Dependencies of the signal at square law detection:

- **Susceptibility $|\chi^{(3)}|^2$:** Chemical selectivity
- **Intensity I^3:** Signal only from the focus, 3D-imaging
- **Concentration N^2:** Detection of majority species

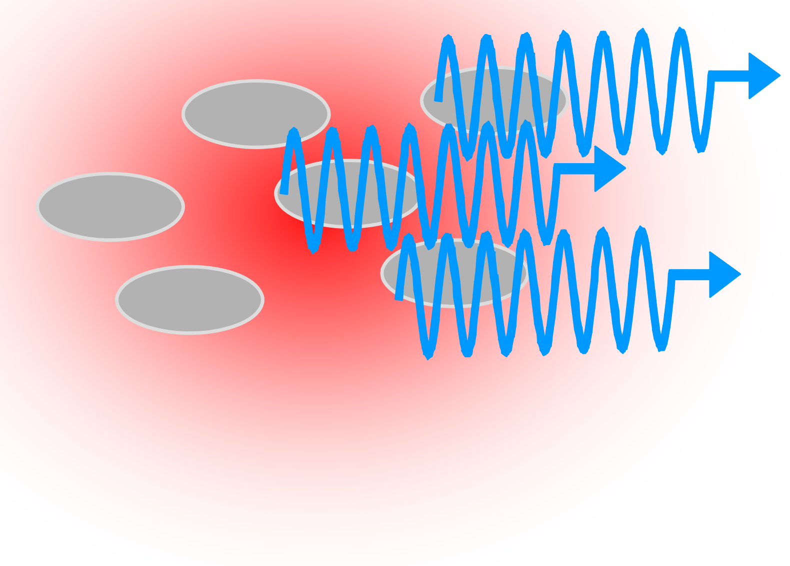
Sensitivity?

CARS Microscopy

Coherent Anti-Stokes Raman Scattering



CARS-Field: Coherent sum



$$E_{CARS} = N \cdot \chi^{(3)}_{CARS} \cdot E_p \cdot E_s \cdot E_{p'}$$

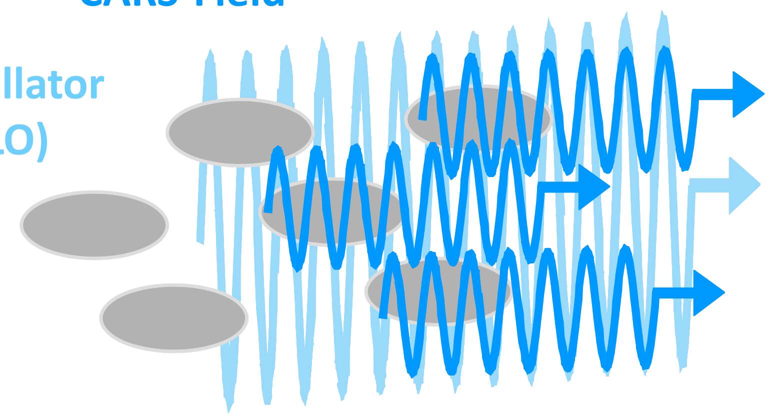
$$I_{CARS} \propto N^2 \cdot |\chi^{(3)}_{CARS}|^2 \cdot I_p \cdot I_s \cdot I_{p'}$$

$$E_{CARS} = \sum_N E_{Mol,\,N} \rightarrow$$

Detect Field: Linear in N!

$$I_{CARS} \propto \left| \sum_N E_{Mol,\,N} \right|^2$$

Interferometric / Heterodyne CARS

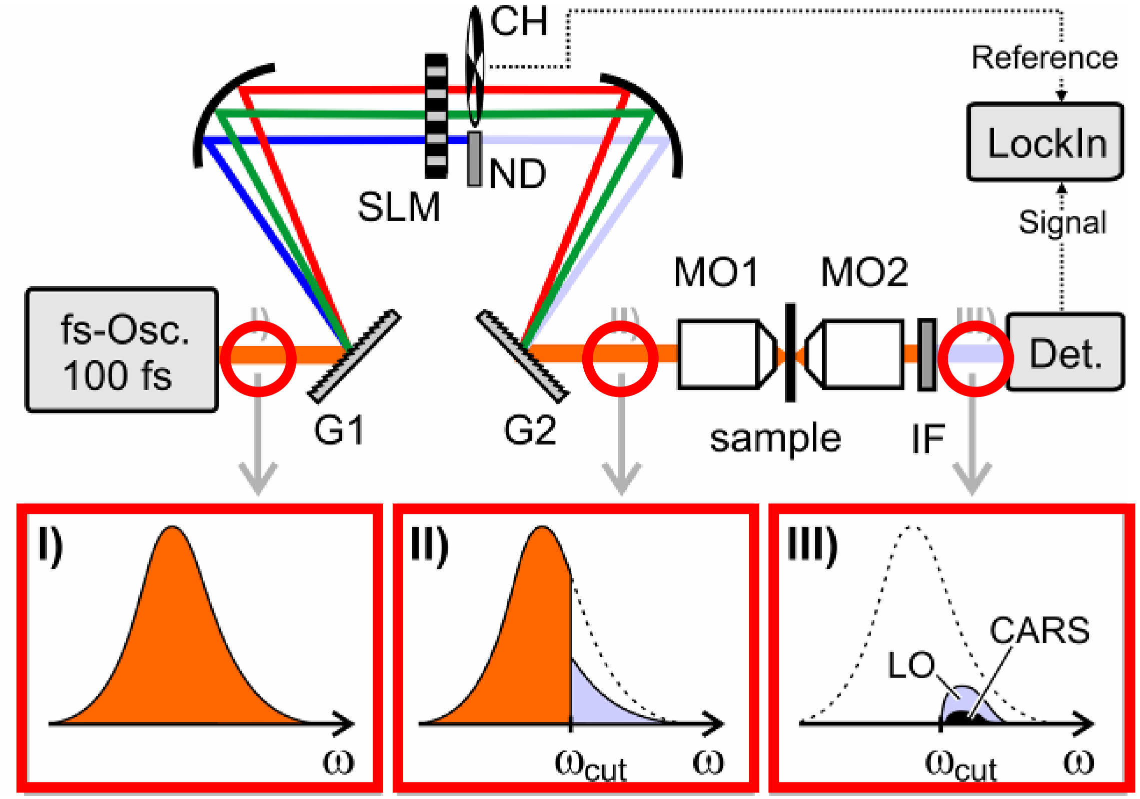


Interferometric Field detection - Mix CARS-Signal with Local oscillator:

$$I_{Det} \propto \left| E_{CARS} + E_{LO} \right|^2 \propto I_{CARS} + I_{LO} + \underbrace{2\sqrt{I_{LO}\, I_{CARS}} \cdot \cos \Delta\phi_{LO}}_{S^{(Het)}}$$

- $S^{(Het)}$ scales linearly with N: **Linearization**
- $S^{(Het)}$ is proportional to the square root of I_{LO}: **Amplification**
- $S^{(Het)}$ is sensitive to $\Delta\varphi_{LO}$

Experimental Setup

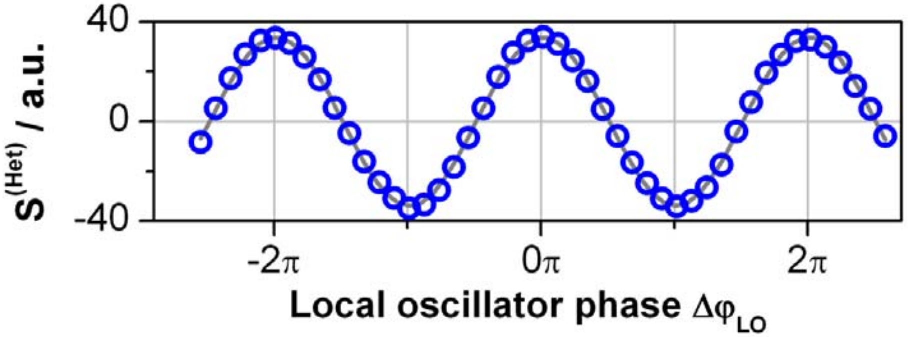


- The **LO** is created from the blue spectral part (ND)
- The **excitation part** of the spectrum is chopped for Lock-In detection

Optics Letters **31**, 2495 (2006)

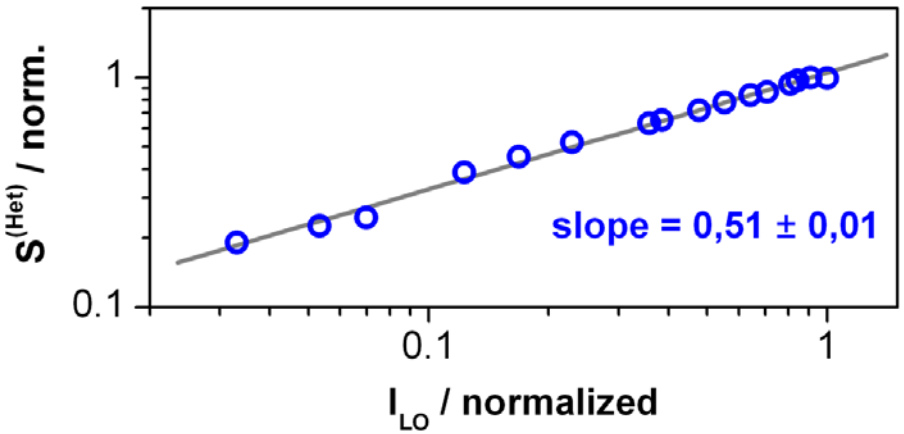
Results: Proof of Heterodyne Detection

Theory: $S^{(Het)} = 2\boxed{\sqrt{I_{LO}\, I_{CARS}}} \cdot \boxed{\cos \Delta\varphi_{LO}}$



Phase dependence:
$\Delta\varphi_{LO}$ controlled by SLM

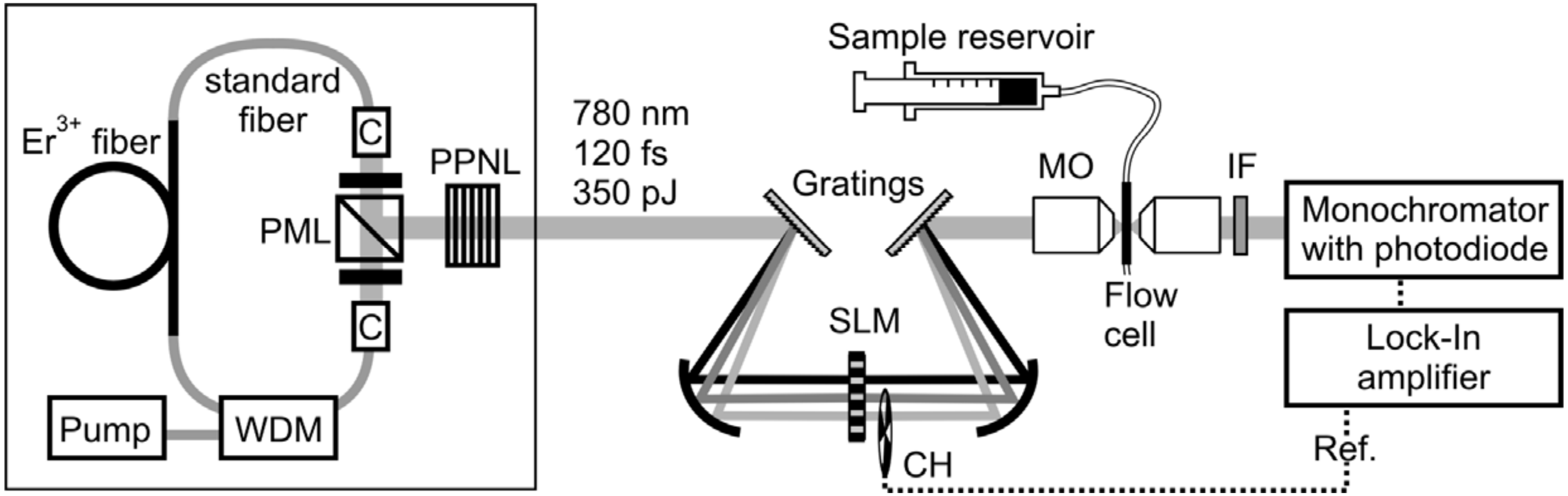
✓



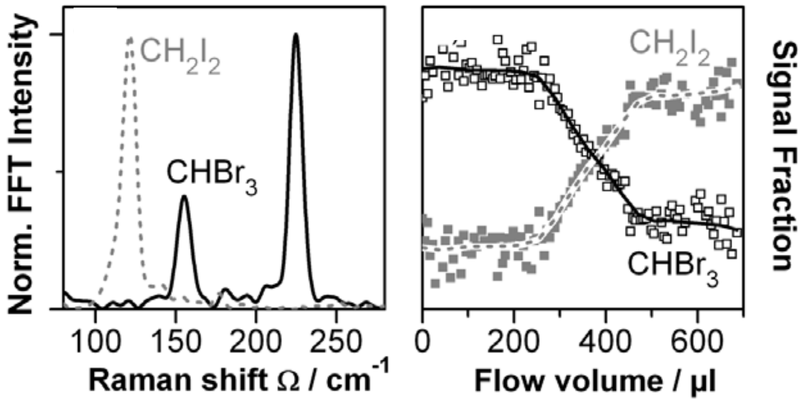
Intensity
dependence

✓

Application to Microfluidic Detection

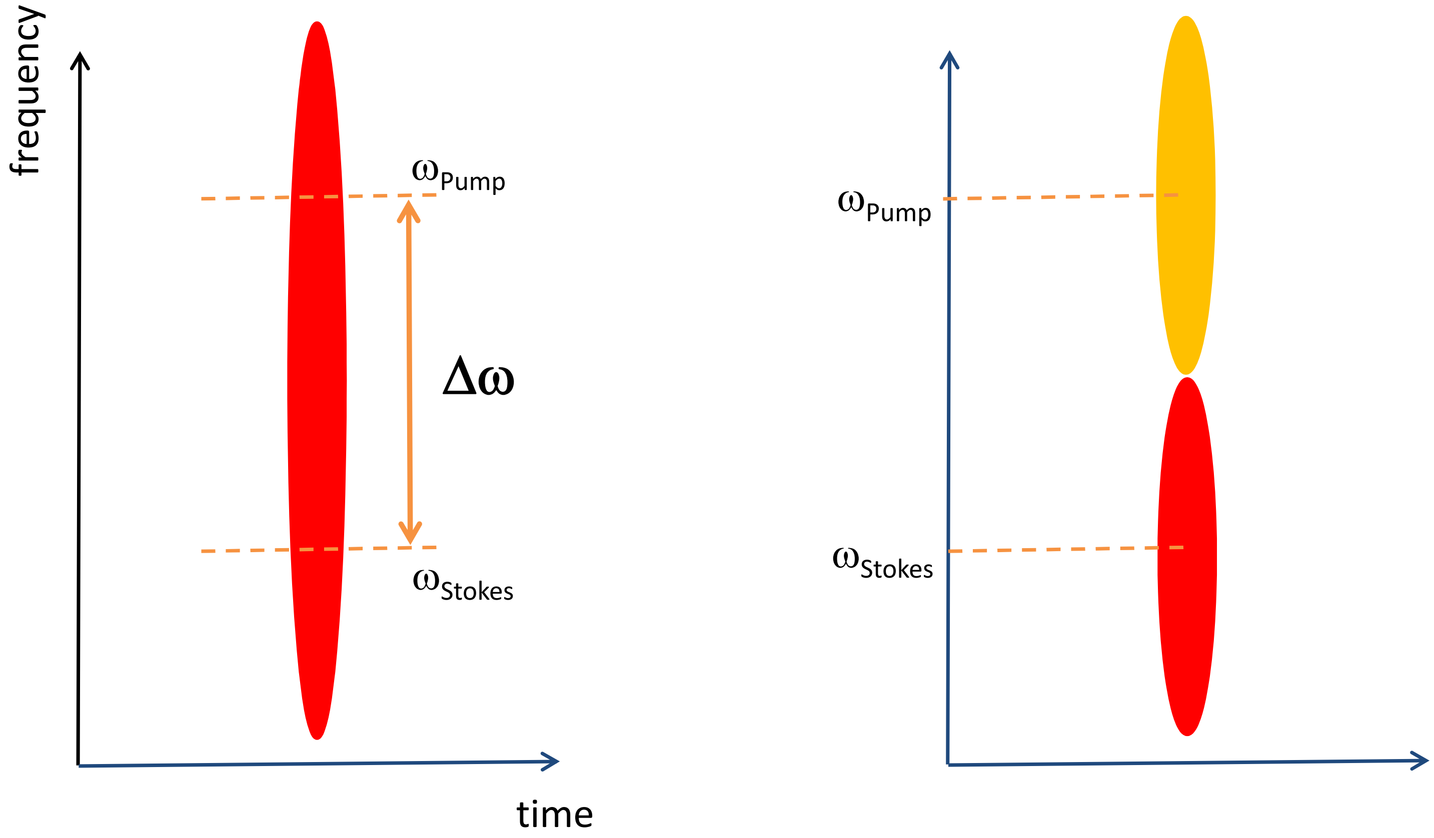


- Use CARS as detection scheme in a 100 µm capillary
- Further simplification: compact fiber laser

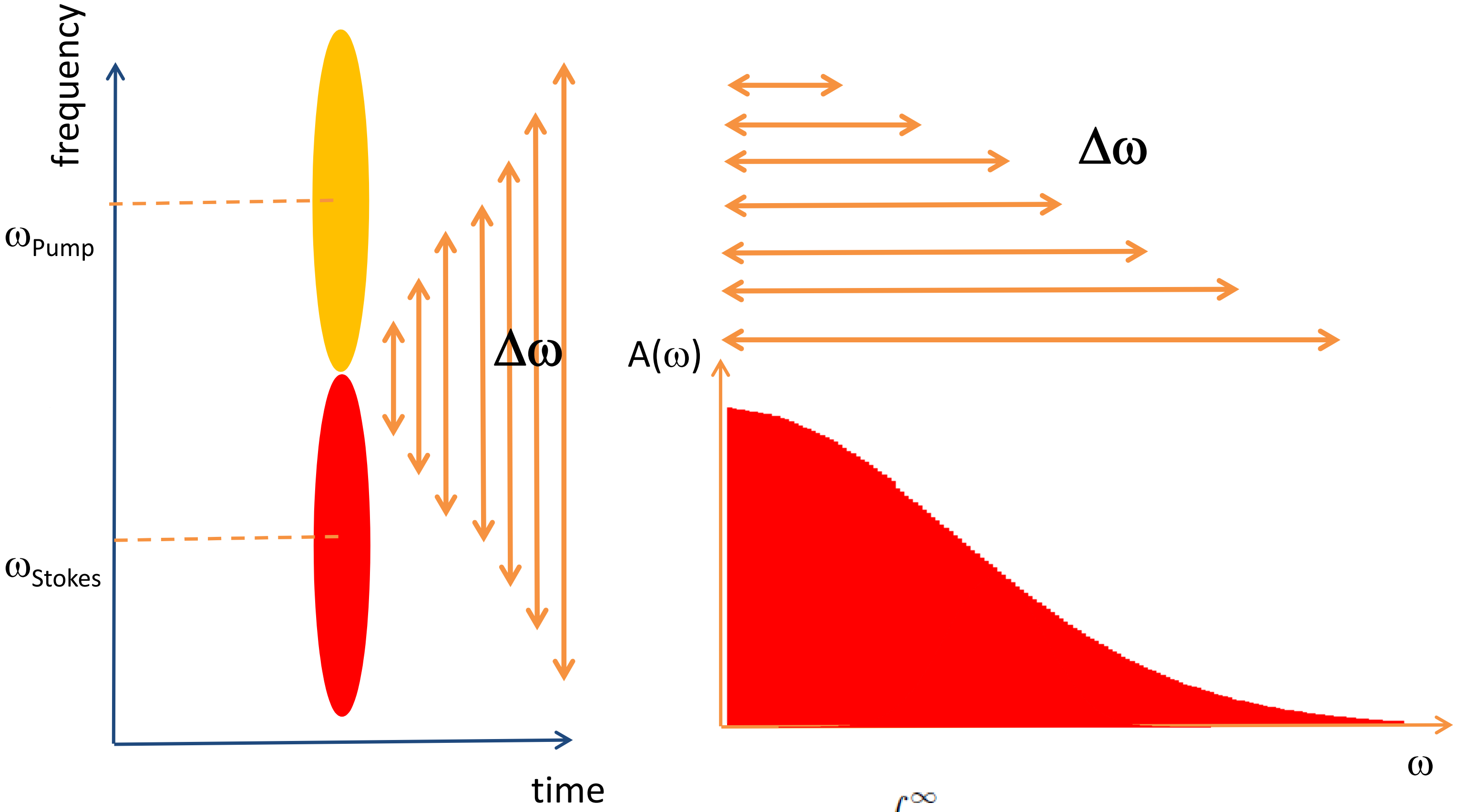


Appl. Phys. B ***91*** *(2008) 213*

Pulse shaping for CARS control: Spectral focussing



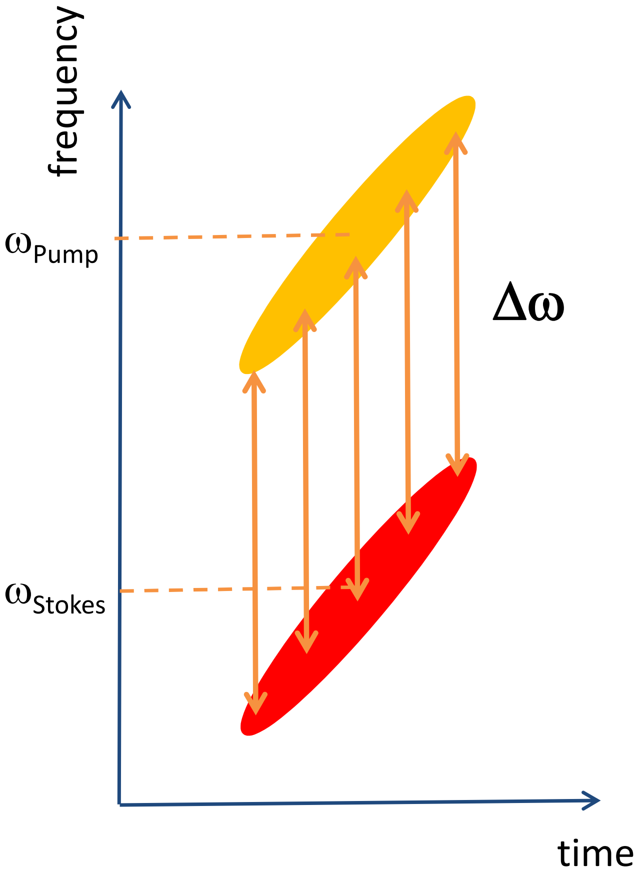
Single-beam spectral focusing: time picture



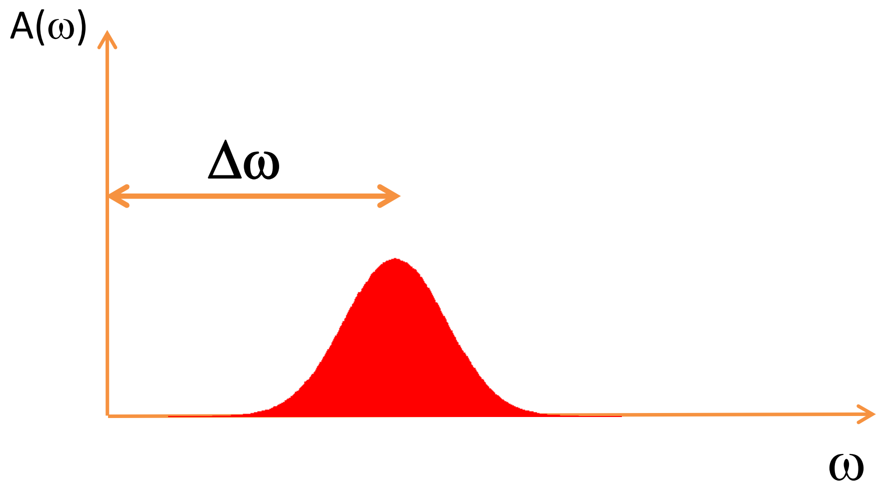
→ **unspecific excitation !**

$$A(\Omega) = \int_0^{\infty} |E^*(\omega')| \, |E(\Omega + \omega') \exp(i \, \Delta\phi) \, d\omega'$$

Single-beam spectral focusing: time picture



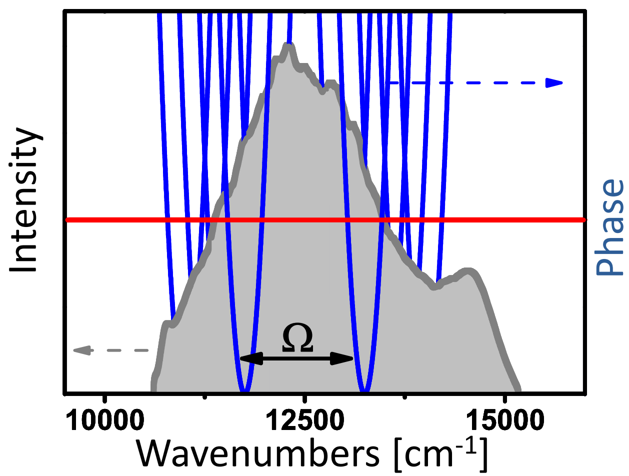
Shaped pulse:
- From fs to ps pulse duration
- Efficient excitation of one resonance

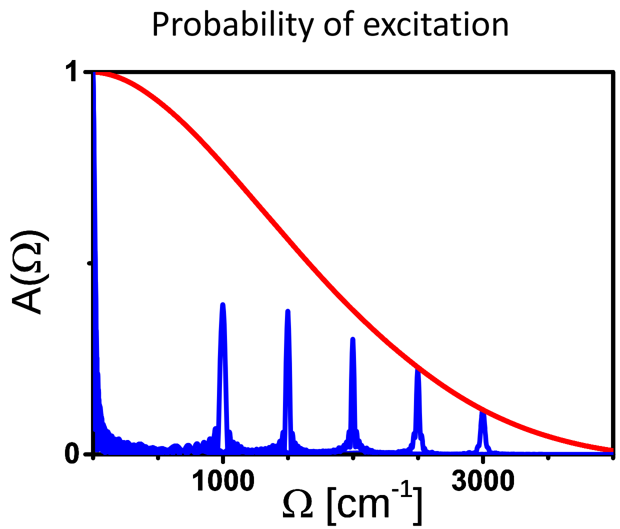


→ increased specificity for imaging
→ decreased multiphoton photodamage

Naumov et al. Appl. Phys. B ***77*** *(2003) 369*
Hellerer et al. Appl. Phys. Lett. ***85*** *(2004) 25*

Single-Beam fs-pulse shaping: Spectral Focusing





Focusing on transitions by controlling the excitation!

→ well suited for imaging

→ usually CH-stretching vibration $\Delta\omega=2845\ cm^{-1}$

→ chemical map of lipid distribution

*Naumov et al. Appl. Phys. B **77** (2003) 369*
*Hellerer et al. Appl. Phys. Lett. **85** (2004) 25*
*Langbein et al. Appl. Phys. Lett. **95** (2009) 081109*
*Chen et al. J. Phys. Chem. B **114** (2010) 16871*

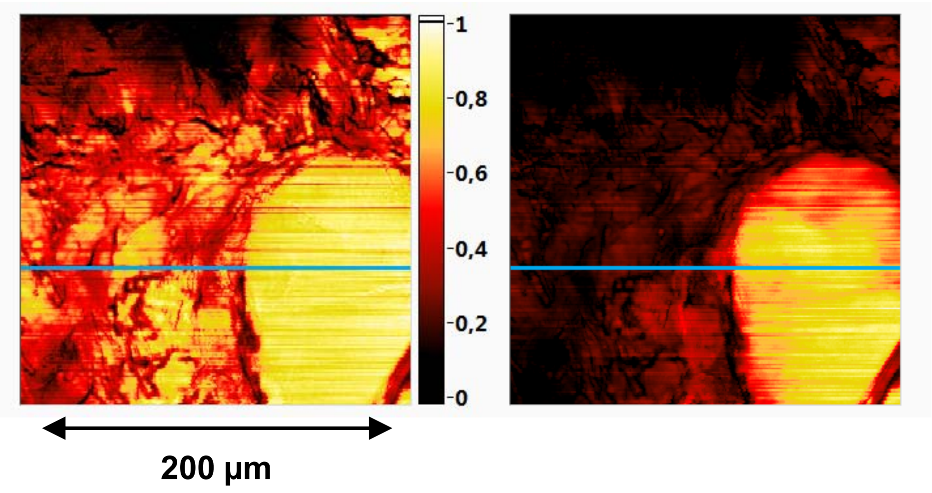
Contrast & increased signal

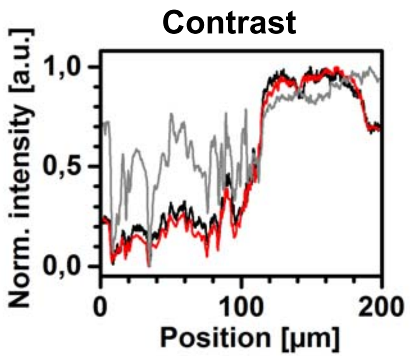
Transform-limited

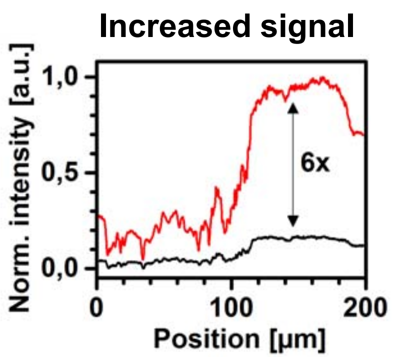
- Concentration differences determine signal

Spectral Focusing

- Vibrational contrast achieved





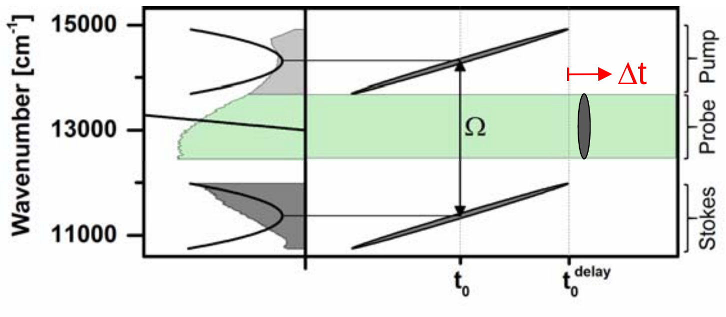


Skin samples kindly provided by Prof. Schäkel from the department of dermatology at the Heidelberg University hospital

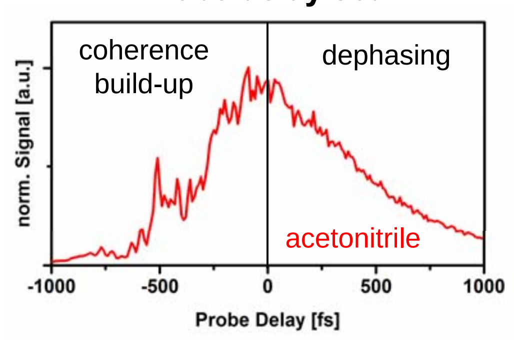
Opt. Lett. ***40*** *(2016) 5204*

Time-delay Scan

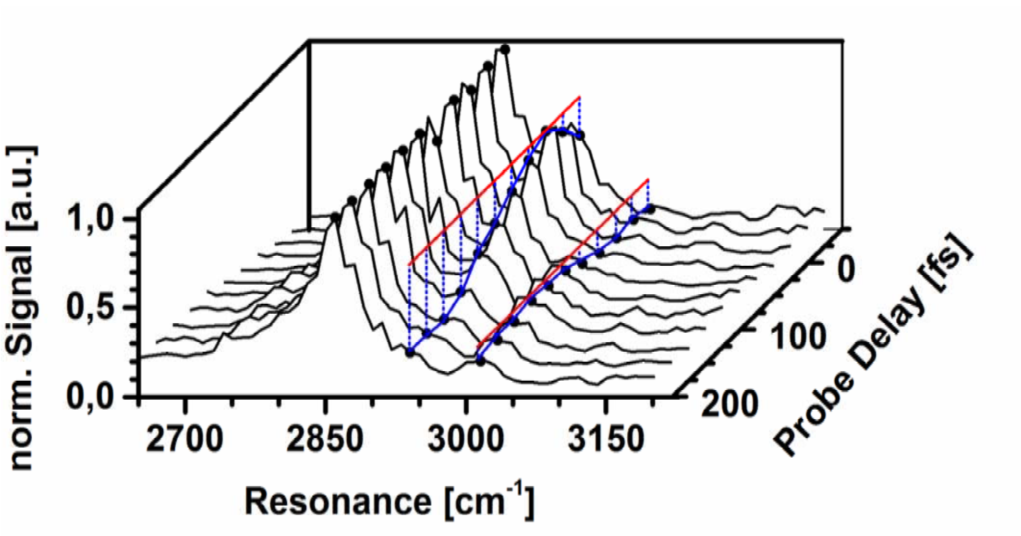
concept



Probe delay scan



time-dependent spectra

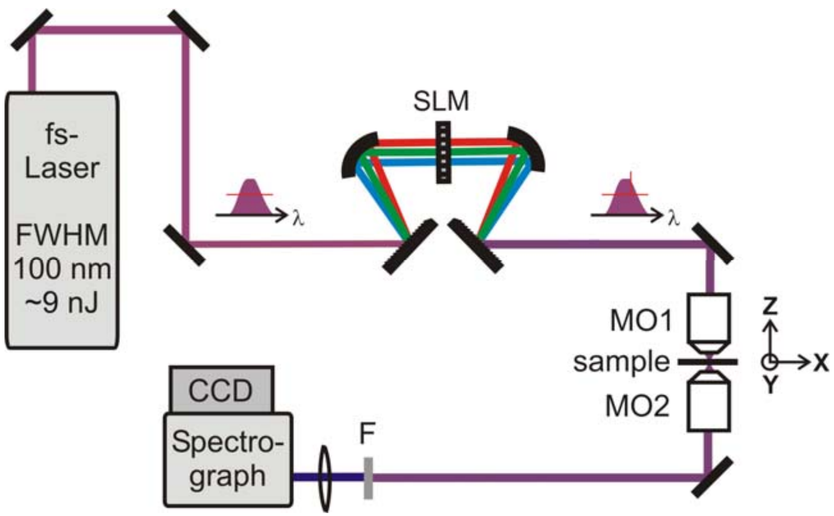


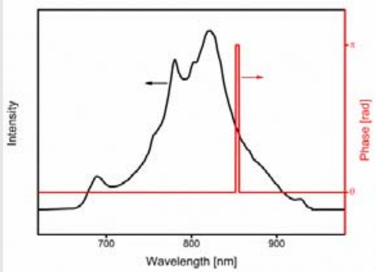
→ Suppression of fast decaying NRB

→ Contrast based on coherence times

JOSA B ***33*** *(2016) 1482*

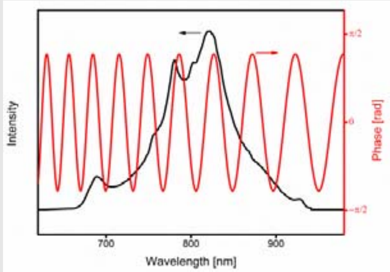
Single-beam-CARS schemes





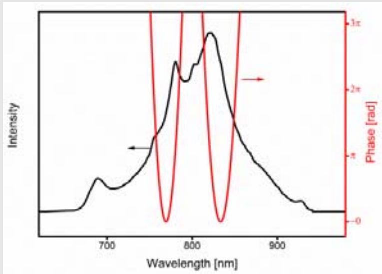
Multiplexing

Appl. Phys. Lett. ***100*** *(2012) 071102*



b-scan

PCCP
10 *(2008) 681*

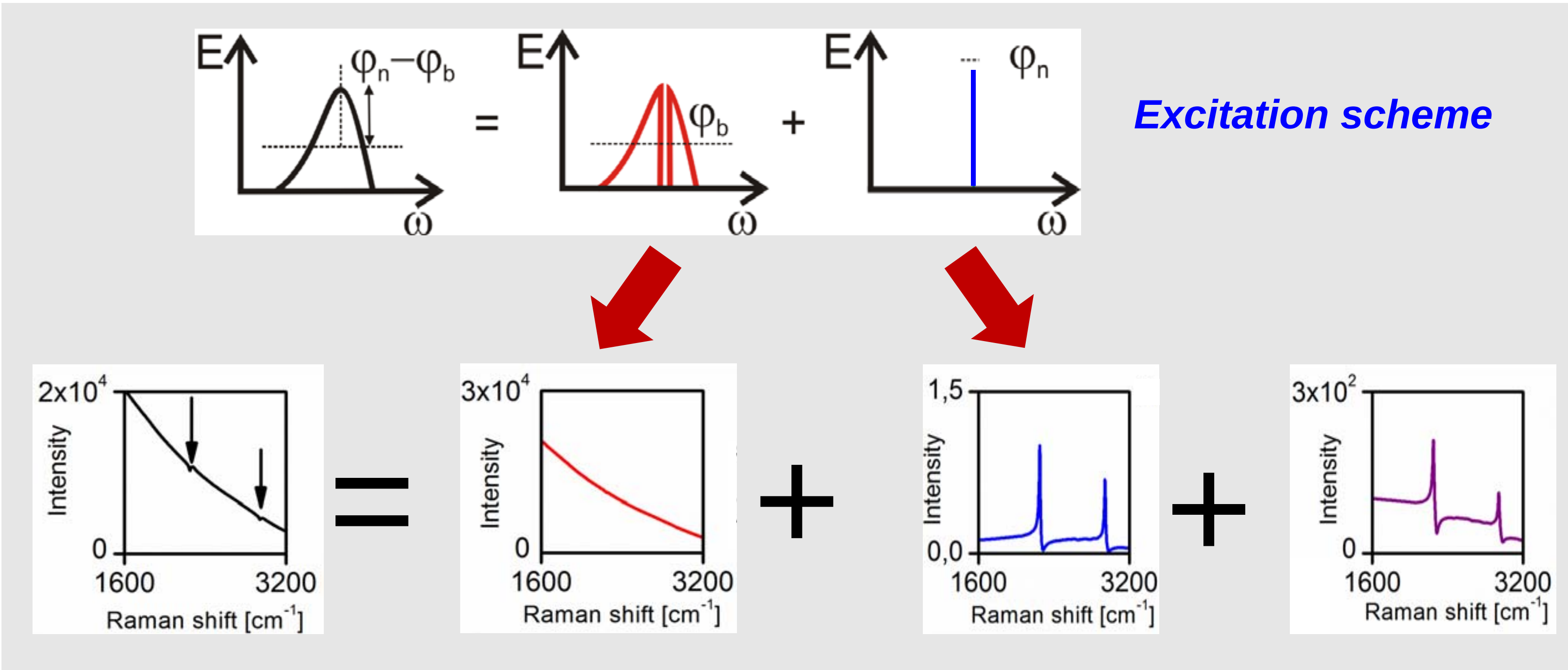


Spectral focusing

Lim Group.

Review:
Silberberg Annu. Rev. Phys. Chem. ***79*** *(2009) 2009.60*

Multiplex CARS: Narrowband probing



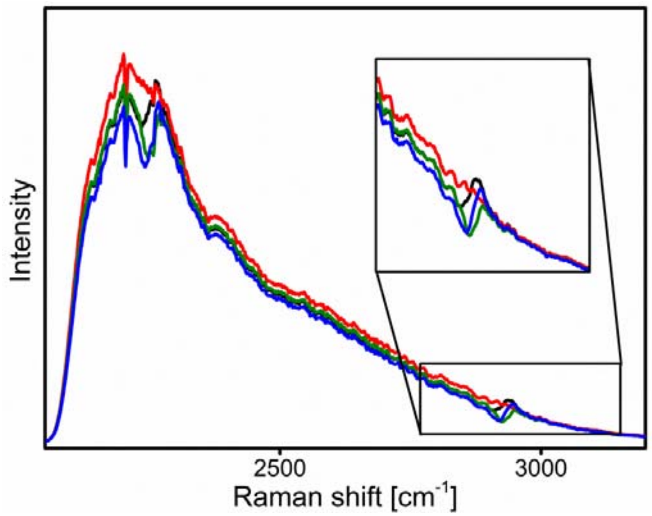
$$S(\omega) \propto \left|E_{CARS,b}(\omega)+E_{CARS,n}(\omega)\right|^2 = \boxed{\left|E_{CARS,b}(\omega)\right|^2} + \boxed{\left|E_{CARS,n}(\omega)\right|^2} + \boxed{2\left|E_{CARS,b}(\omega)E_{CARS,n}(\omega)\right|\cos\varphi}$$

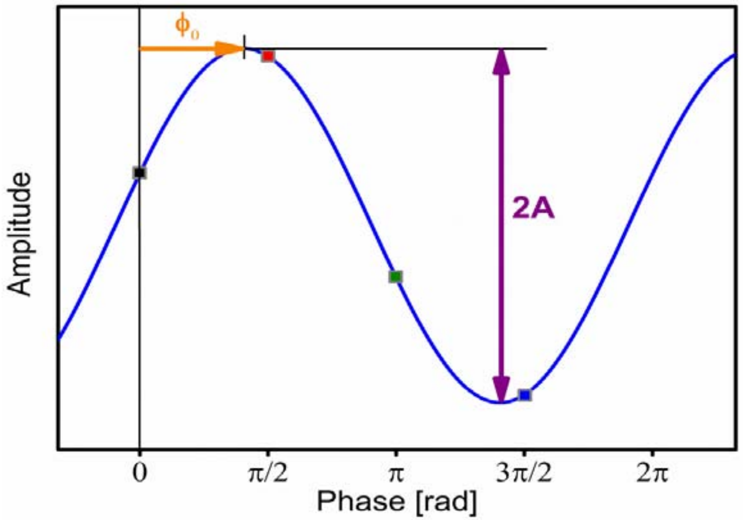
→Broadband probe provides a *Local oscillator*

Oron et al. Phys. Rev. Lett. ***89*** *(2002) 273001*
Lim et al. Phys. Rev. A ***72*** *(2005) 041803*
Appl. Phys. Lett. ***100*** *(2012) 071102*

Multiplexing single-beam-CARS

$$S(\omega) \propto \left|E_{CARS,b}(\omega) + E_{CARS,n}(\omega)\right|^2 = \left|E_{CARS,b}(\omega)\right|^2 + \left|E_{CARS,n}(\omega)\right|^2 + 2\left|E_{CARS,b}(\omega)E_{CARS,n}(\omega)\right|\cos\varphi$$





$$\left|E_{CARS,n}(\omega)\right| = \frac{1}{4\left|E_{CARS,b}(\omega)\right|}\sqrt{[S(\omega)|_{\varphi_n=0} - S(\omega)|_{\varphi_n=\pi}]^2 + [S(\omega)|_{\varphi_n=\pi/2} - S(\omega)|_{\varphi_n=-\pi/2}]^2}$$

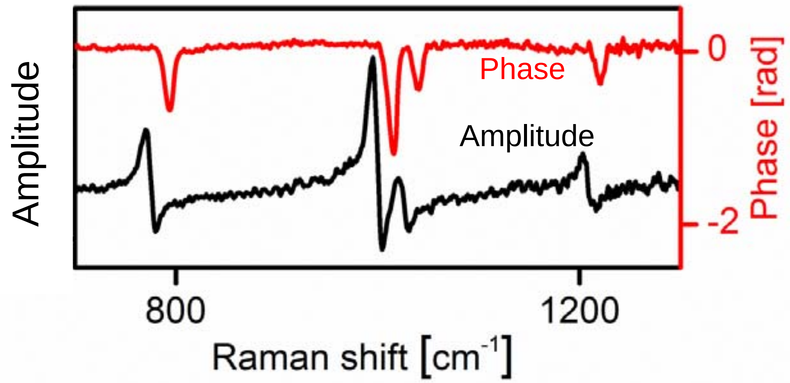
DQSI:
Double quadrature spectral interferometry

*Lepetit et al J. Opt. Soc. Am. B **12** (1995) 2467*

$$\phi_0 = \arctan\left[\frac{S(\omega)_{\varphi_n=\pi/2} - S(\omega)_{\varphi_n=-\pi/2}}{S(\omega)_{\varphi_n=0} - S(\omega)_{\varphi_n=\pi}}\right]$$

*Opt. Lett. **37** (2012) 4239*

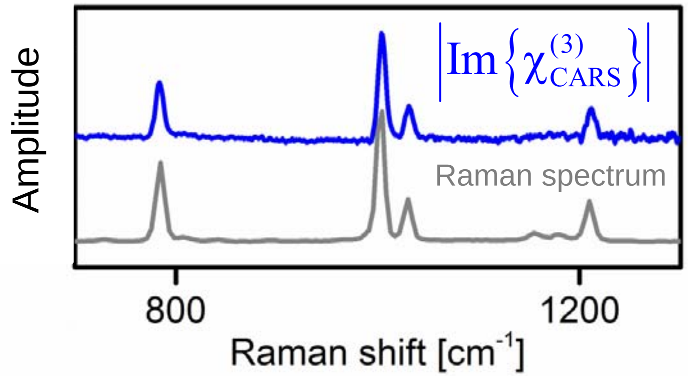
Further modalities:
Heterodyne Multiplex CARS using phase gate



Amplitude and phase of the susceptibility can be extracted

→ **MCARS spectrum**

Appl. Phys. Lett. ***100*** *(2012) 071102*



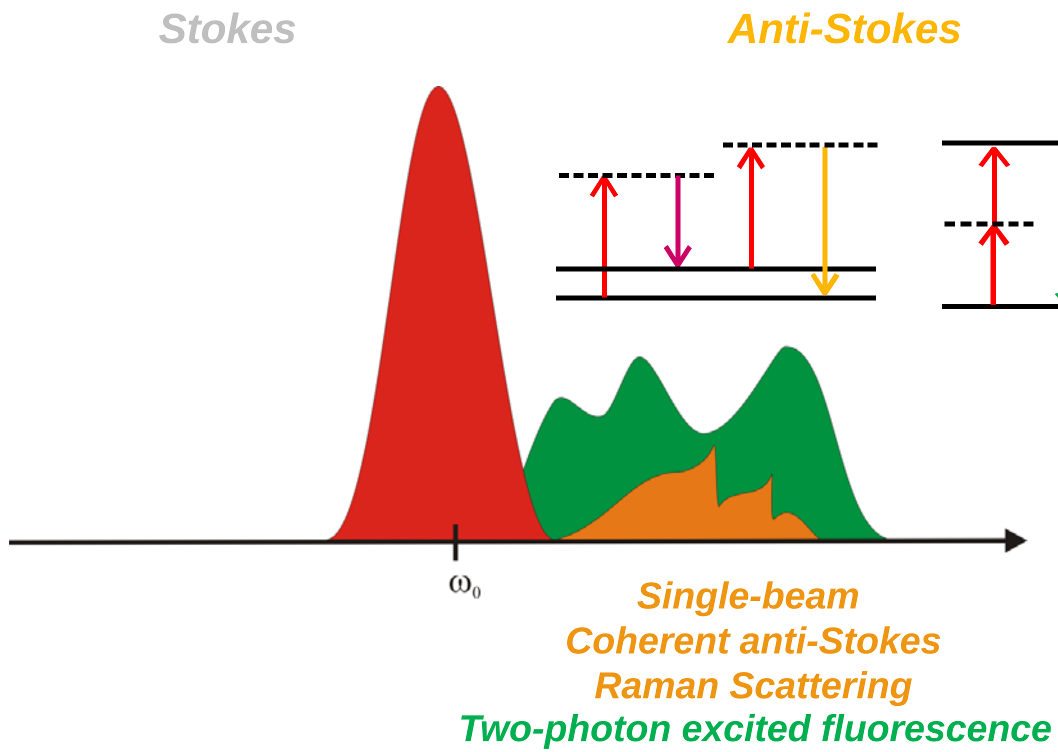
Imaginary part can easily be obtained

→ **Spontaneous Raman spectrum**

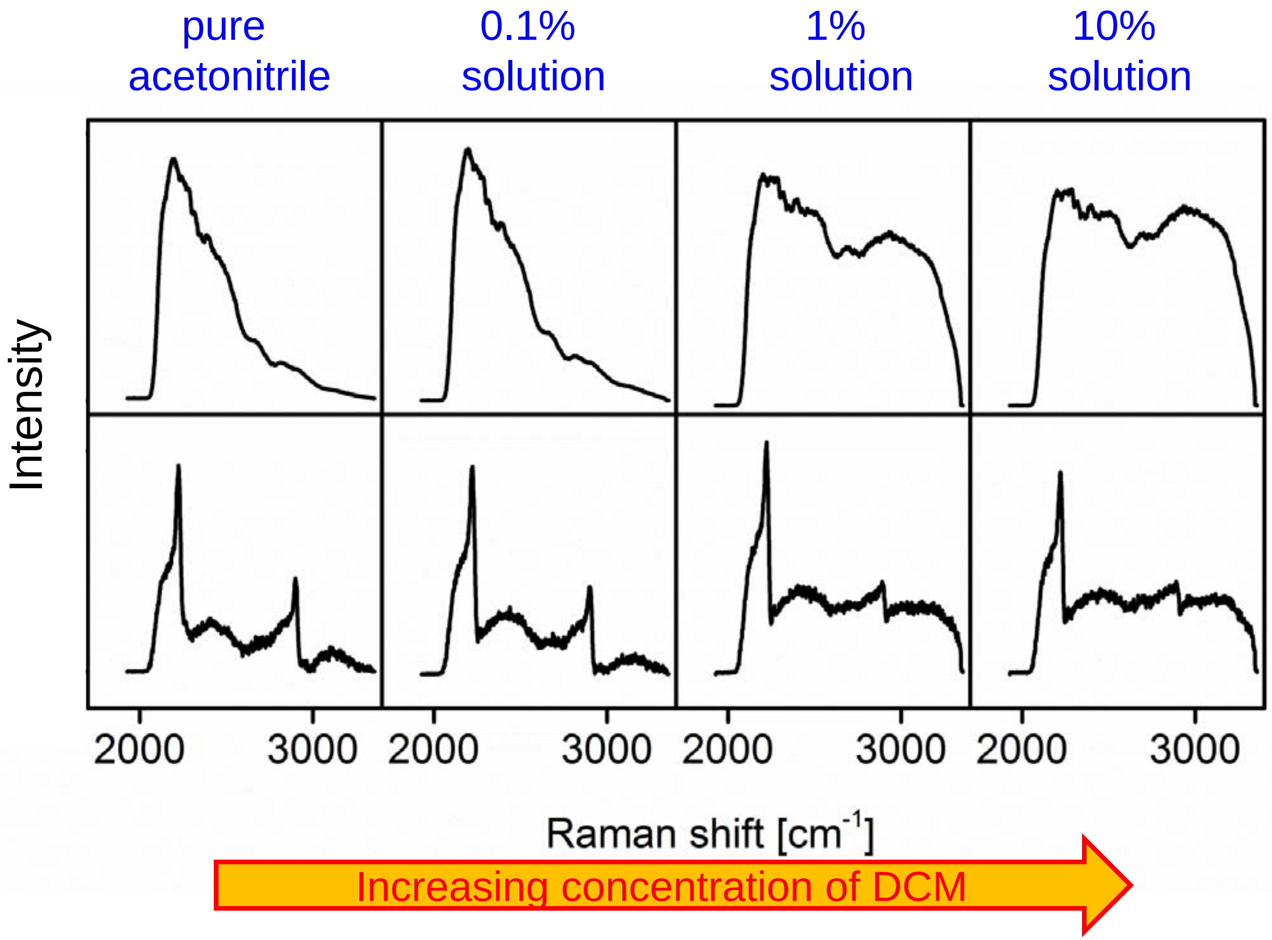
Opt. Lett. ***37*** *(2012) 4239*

→ Single-beam-CARS and phase shaping gives spontaneous Raman spectrum!

Single-beam-CARS and two-photon fluorescence

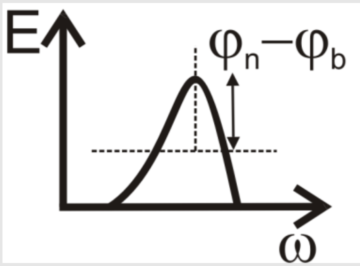


Measurements on acetonitrile and DCM

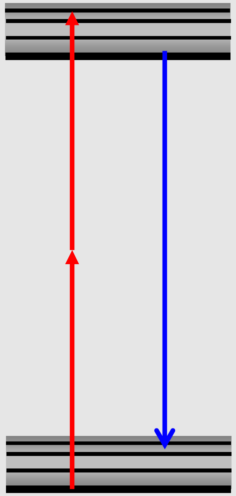


Strong 2PEF decreases effectiveness of the DQSI operation

Phase-dependence of the 2PEF

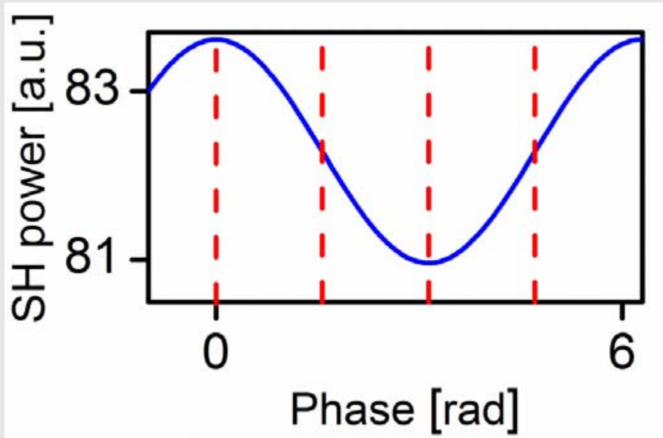


Excitation spectrum



TPA

$$S^{(2)}_{\mathrm{tot}} \propto \int \left| \int E(\omega)E(\Omega-\omega)\,d\omega \right|^2 d\Omega$$



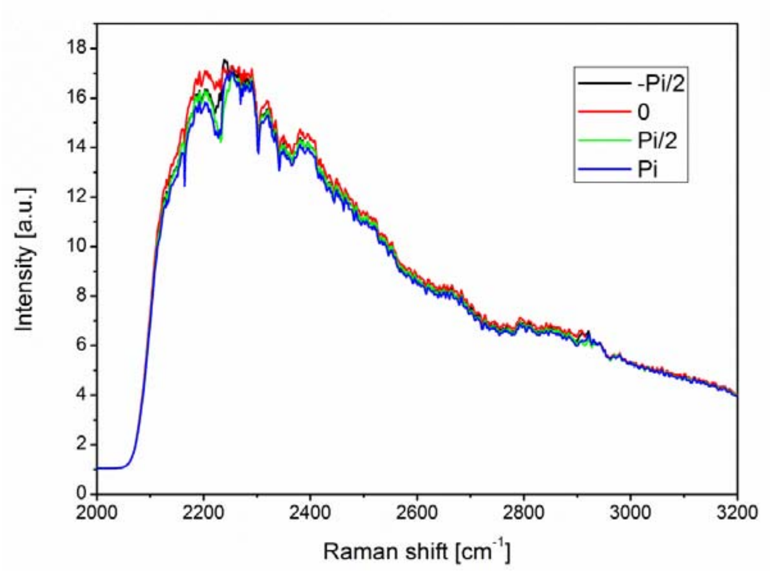
Integrated SH power spectrum

→ DQSI signal is overlaid by 2PEF

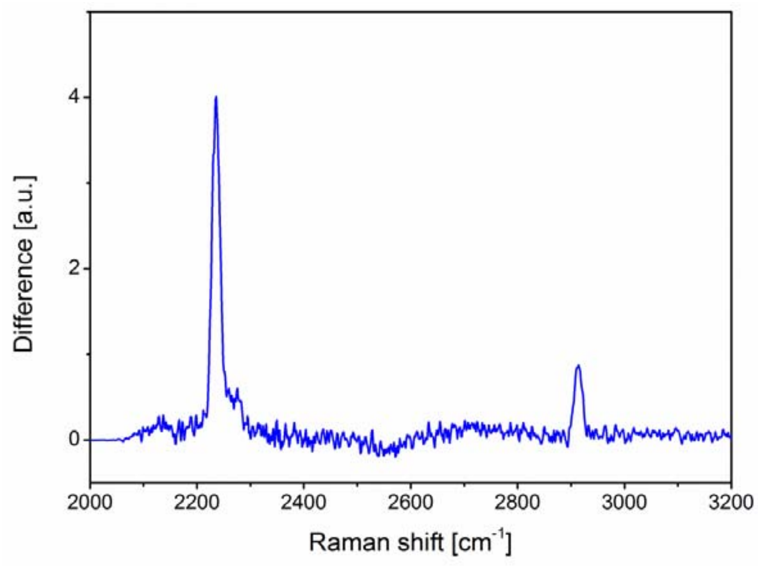
J. Raman Spec. ***44*** *(2013) 1379*

CARS and 2PEF

CARS spectra of acetonitrile and DCM for four different phases of the gate.



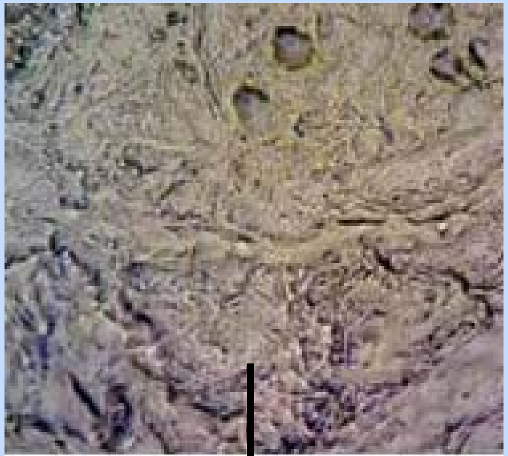
Difference of spectra for $\pi/2$ and - $\pi/2$ → Raman spectrum!



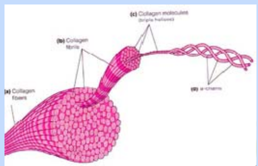
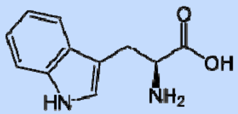
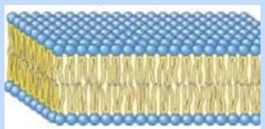
J. Raman Spec. ***44*** *(2013) 1379*

Outlook: Multimodal microscopy with shaped pulses

Brightfield microscope image

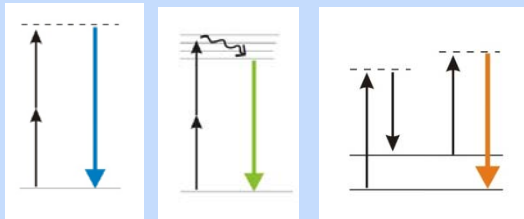


?

Collagen	Fluorophores	Lipids
		

Contrast mechanisms:
Nonlinear microscopy

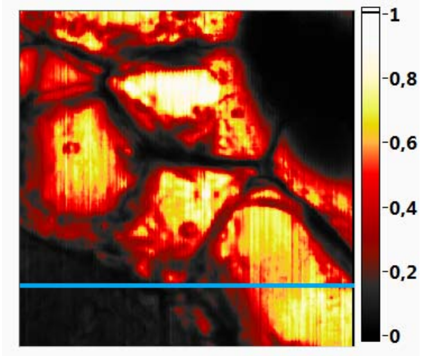
SHG TPEF CARS



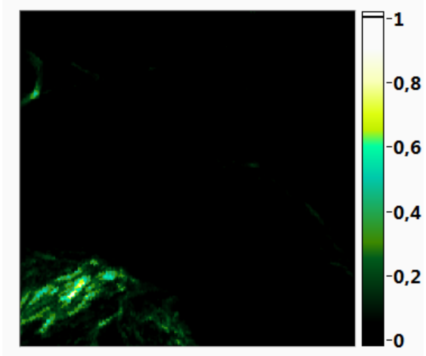
Opt. Express. ***22*** *(2014) 28790*

Simultaneous multimodal imaging

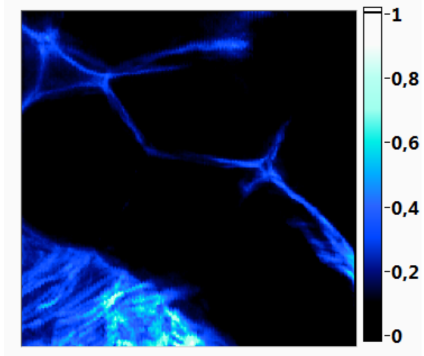
CH-resonance (lipids)



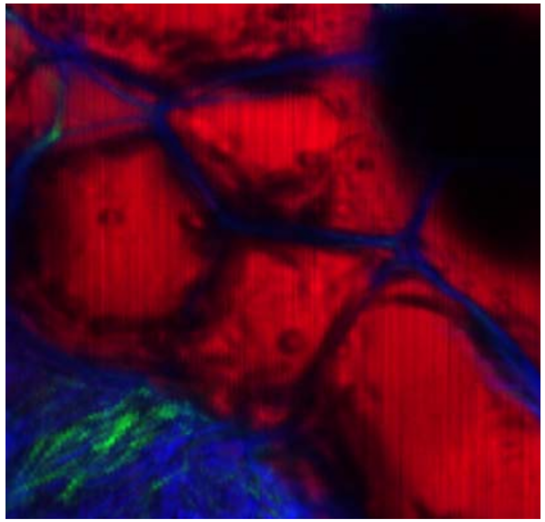
TPEF



SHG



Multimodal RGB image



Transform-limited probing region

- Highly increased multimodal signal
- Simultaneous acquisition together with resonant CARS

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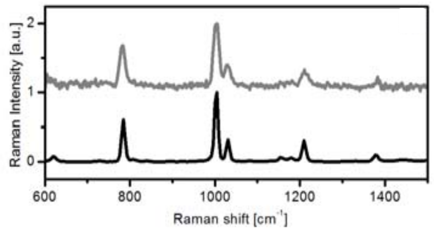
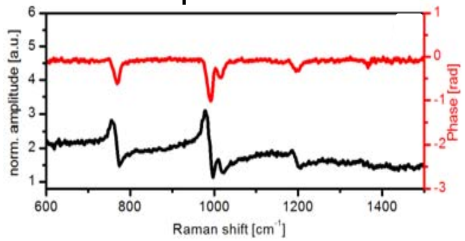
Opt. Lett. ***40*** *(2015) 5204*
JOSA B ***33*** *(2016) 1482*

Multimodal Quantum Control Spectroscopy

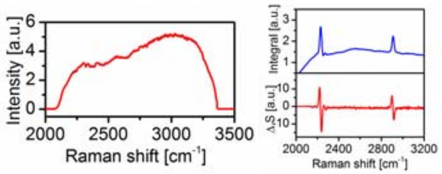
Spontaneous Raman

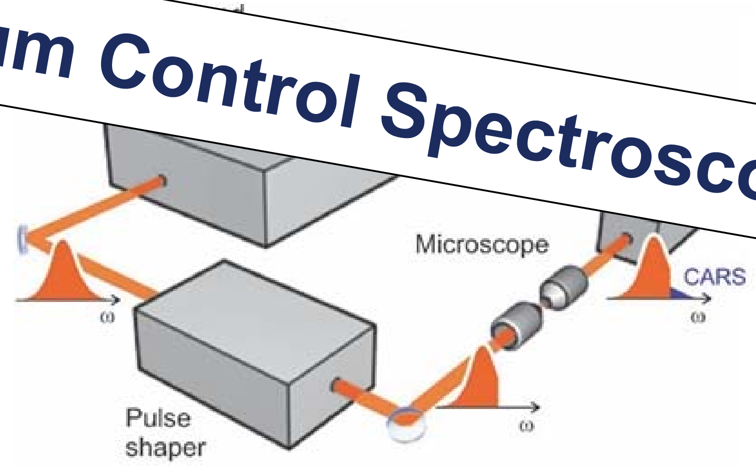


Multiplex-CARS

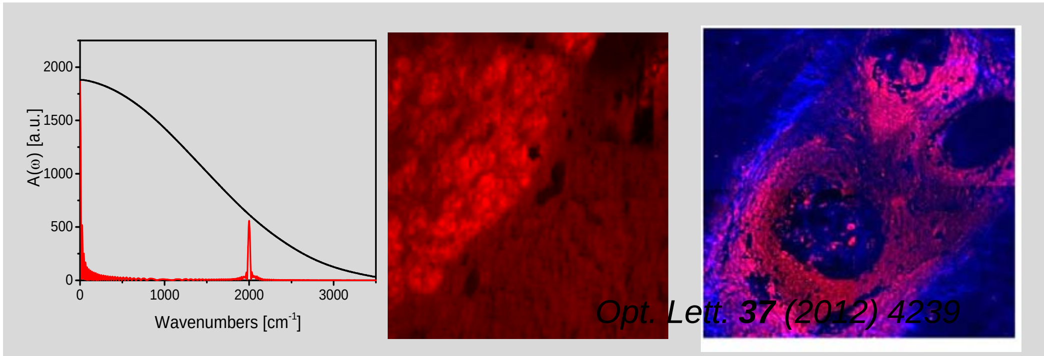


Compensation of 2PEF





Selective multimodal imaging



Opt. Lett. 37 (2012) 4239

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EU: CROSSTRAP

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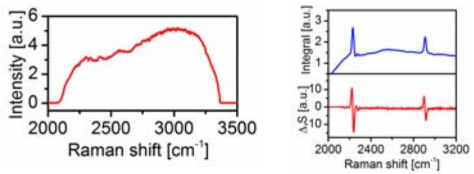
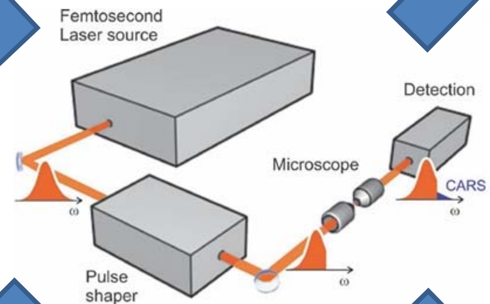
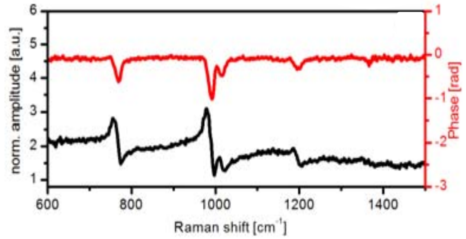
Single-beam CARS + Shaper



Compensation of 2PEF

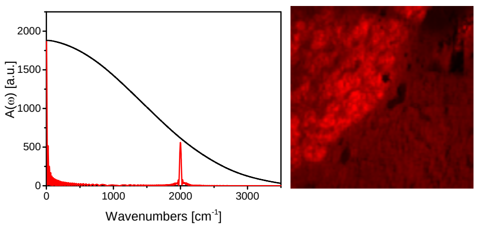
J. Raman Spec. ***44*** *(2013) 1379*





Multiplex-CARS

Appl. Phys. Lett.
100 *(2012) 071102*

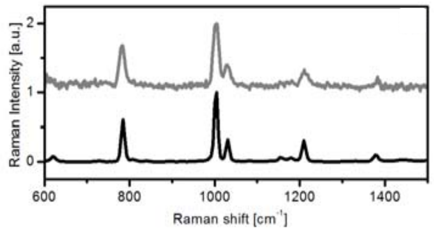


Selective imaging with CARS

Opt. Express. ***22*** *(2014) 28790*
Opt. Lett. ***40*** *(2015) 5204*
JOSA B ***33*** *(2016) 1482*

In addition:

- 2P Fluorescence
- SHG
- THG



Spontaneous Raman

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