Coherent Control by Four-Wave Mixing

Hrvoje Skenderović
Institute of Physics, Zagreb

Graz, May 2008.

Four-wave Mixing

ß-Carotene

Experiment

Control of Vibrational Modes

Motivation for the fs FWM spectroscopy

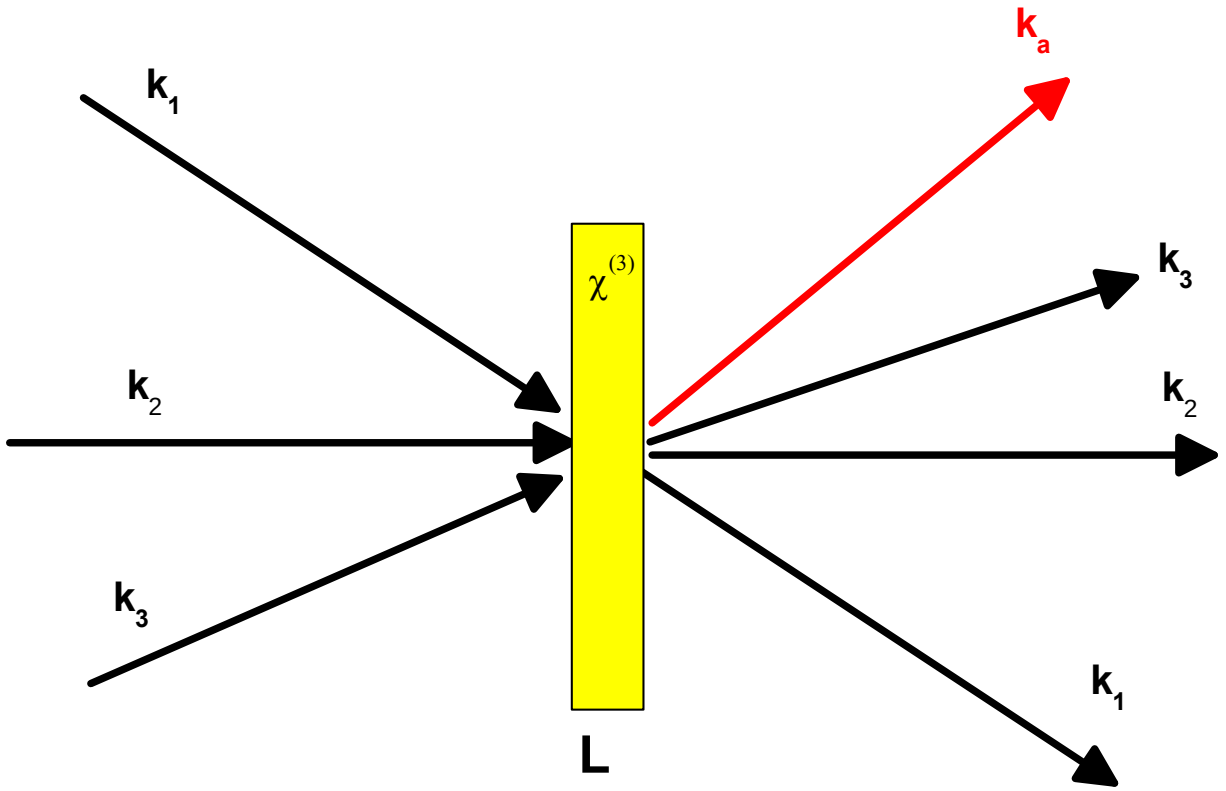
- **Fs FWM enables excitation and monitoring:**

In gas, liquid and solid state
Excited and ground states
Rotational, Vibrational and Electronic states

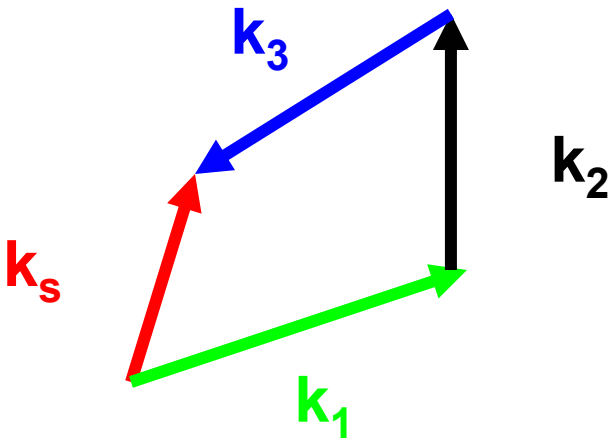
- **Determination od spectroscopic constants with high precision**
- **Ultrafast thermometry in extreme consitions (large pressure, large temperature)**
- **Real-time chemistry dynamics: Femtochemistry**
- **Control and monitoring of molecular dynamics with shaped pulses.**

K. Nelson, A. Weiner, Fleming, Kiefer, ..., Motzkus

The Four Wave Mixing (FWM) signal results from the polarization of the sample following three consecutive electric field interaction.

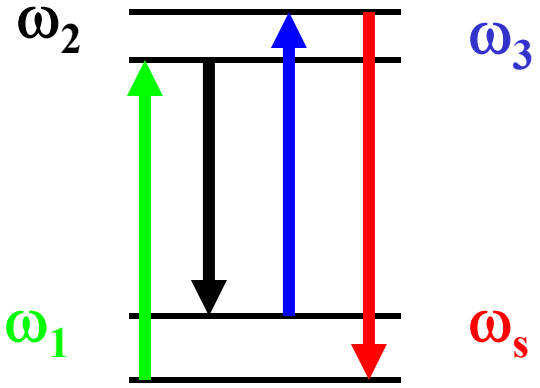


$$\vec{\mathbf{k}}_S = \pm\vec{\mathbf{k}}_1 \pm \vec{\mathbf{k}}_2 \pm \vec{\mathbf{k}}_3$$



Momentum and Energy conservation

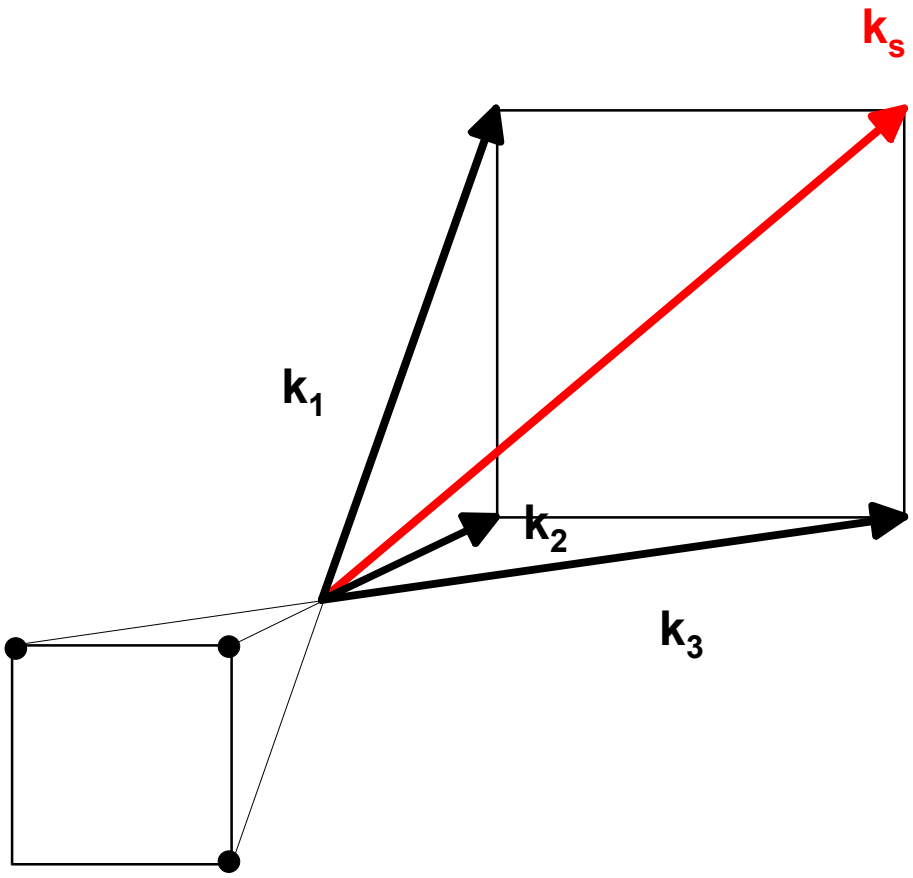
$$\omega_S = \pm\omega_1 \pm \omega_2 \pm \omega_3$$

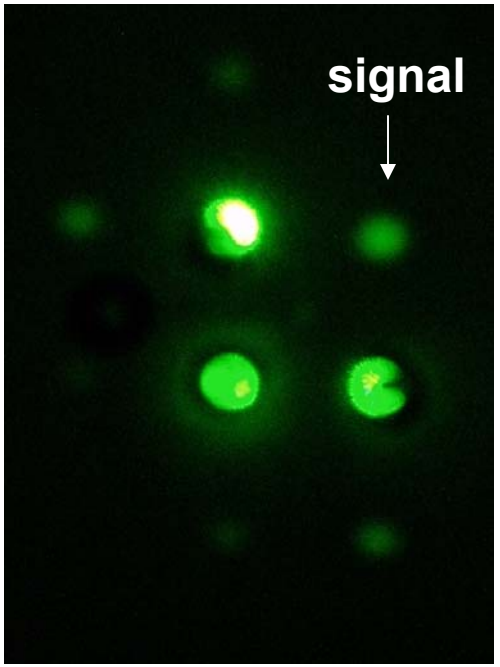


Time-resolved FWM experiments were done in the following configuration:

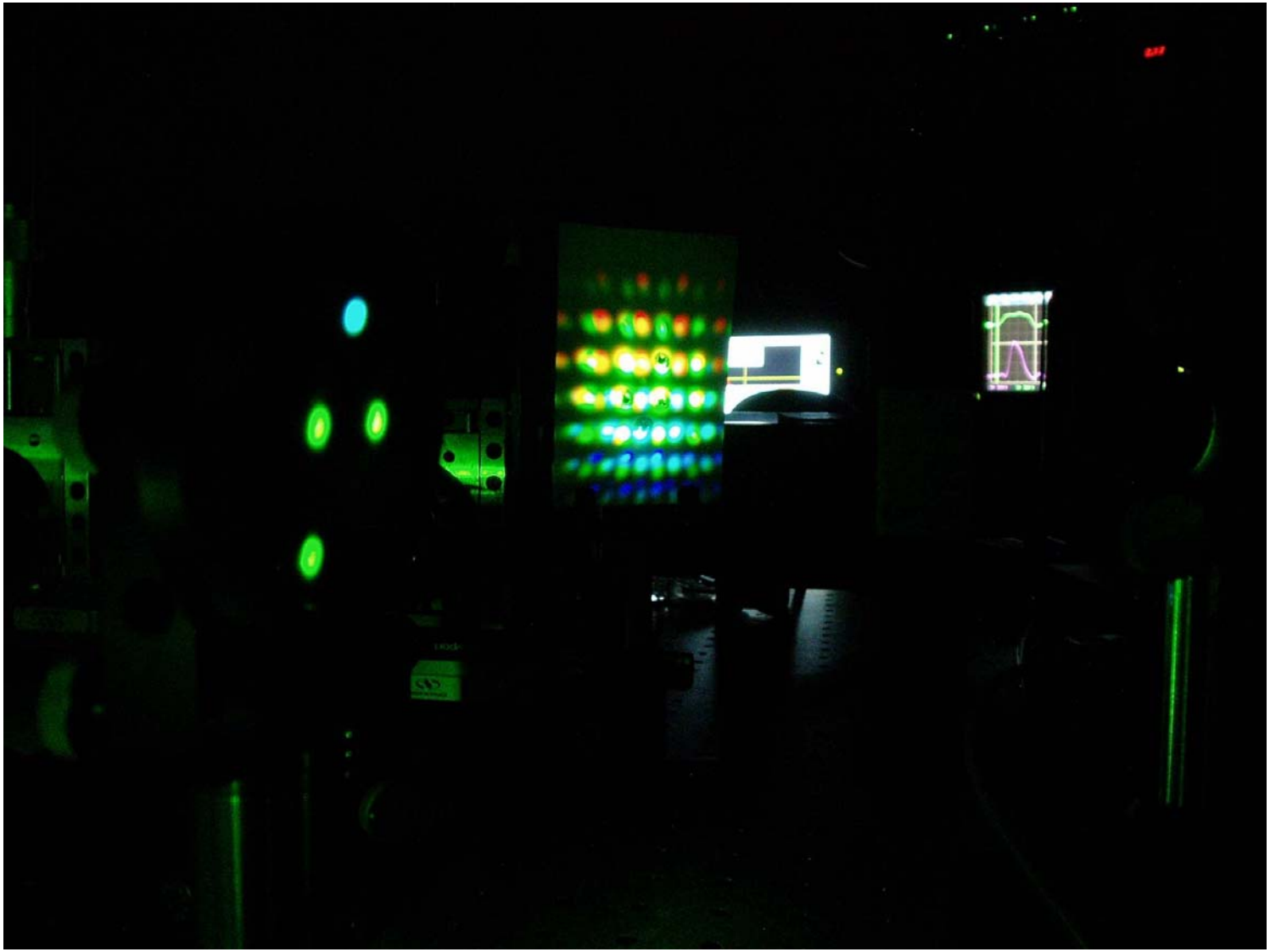
Temporal	→	**Transient Grating**
Geometrical	→	**Folded Box-Car**
Laser Frequencies	→	**Degenerate**

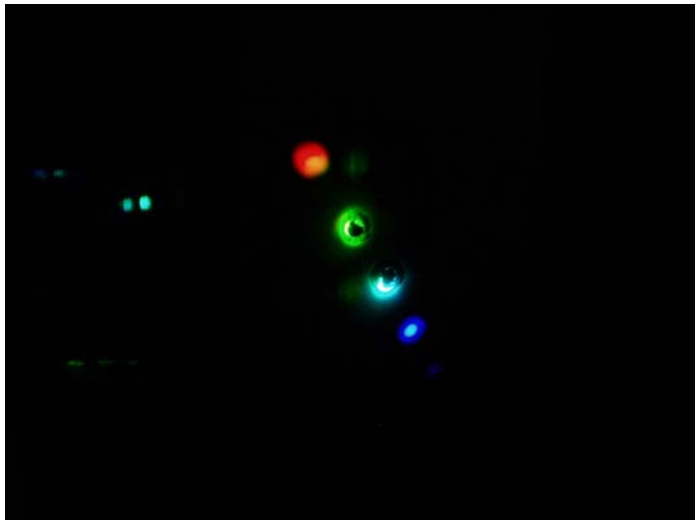
Boxcar configuration

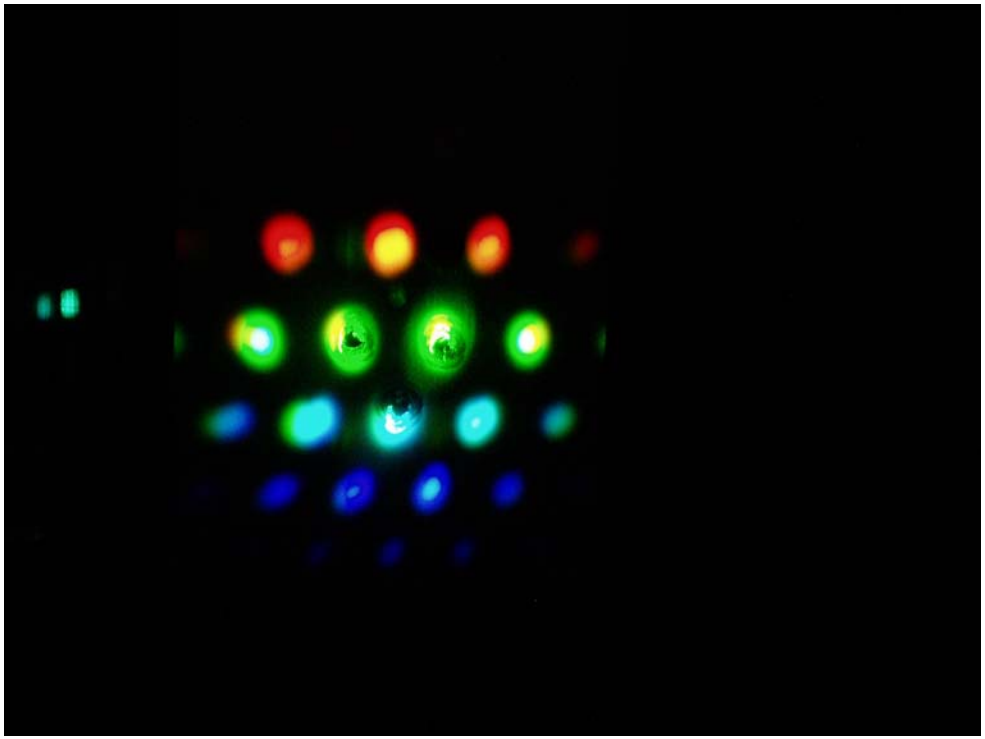




We look for the signal in the direction: $k_s = k_1 - k_2 + k_3$

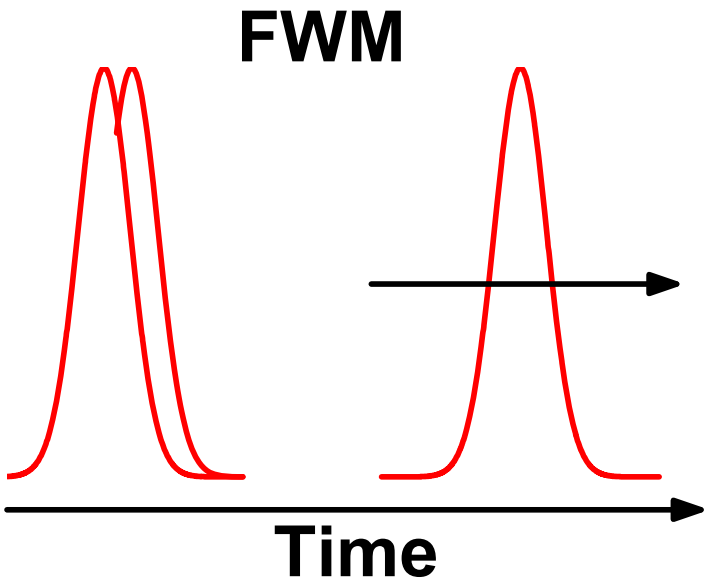


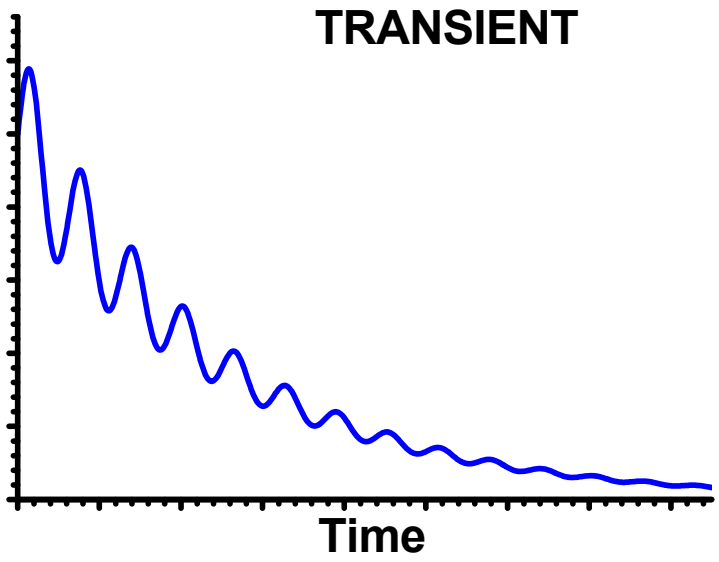


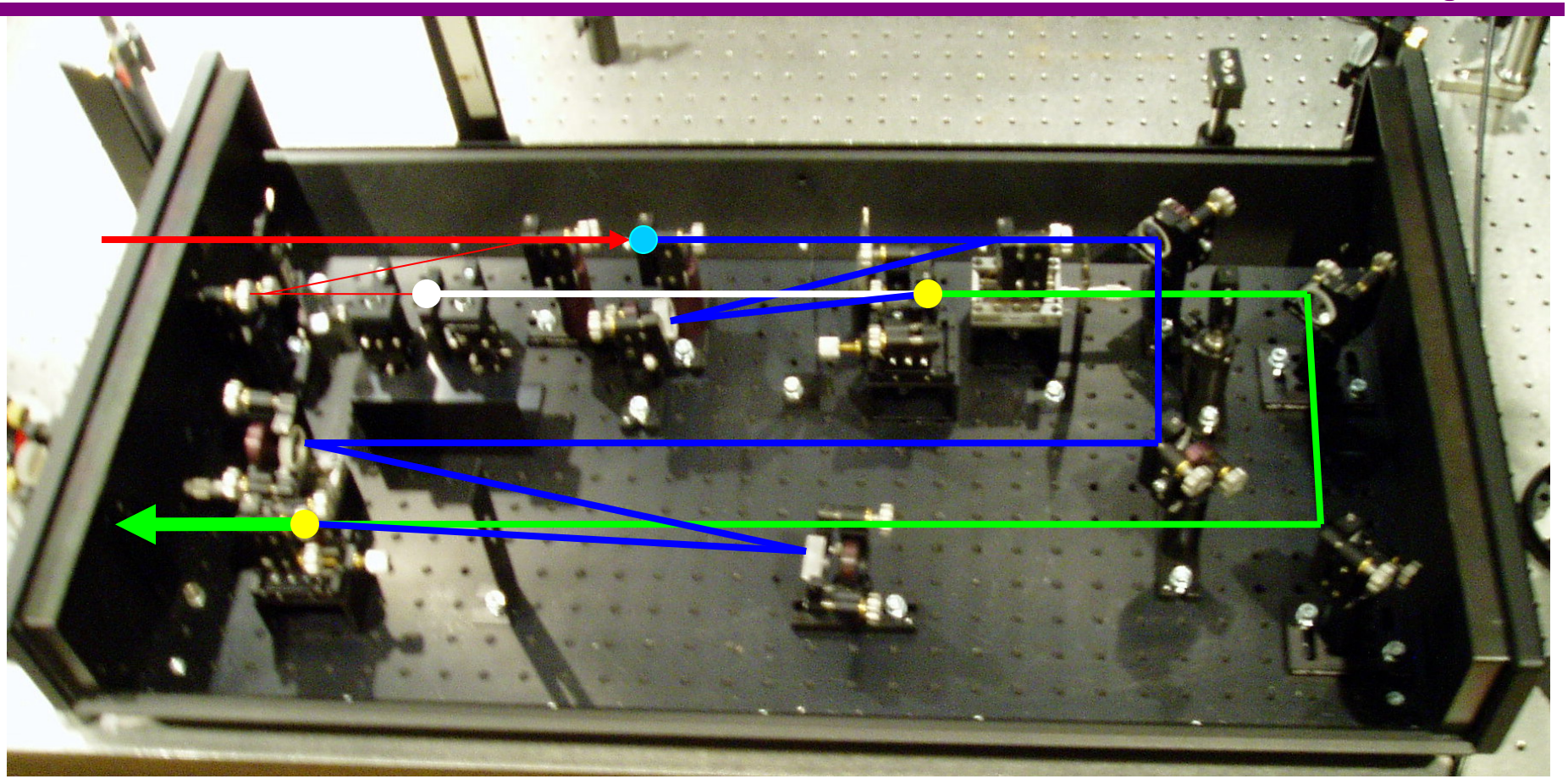


Transient grating: Two pulses come simultaneosly

The third is scanned in time





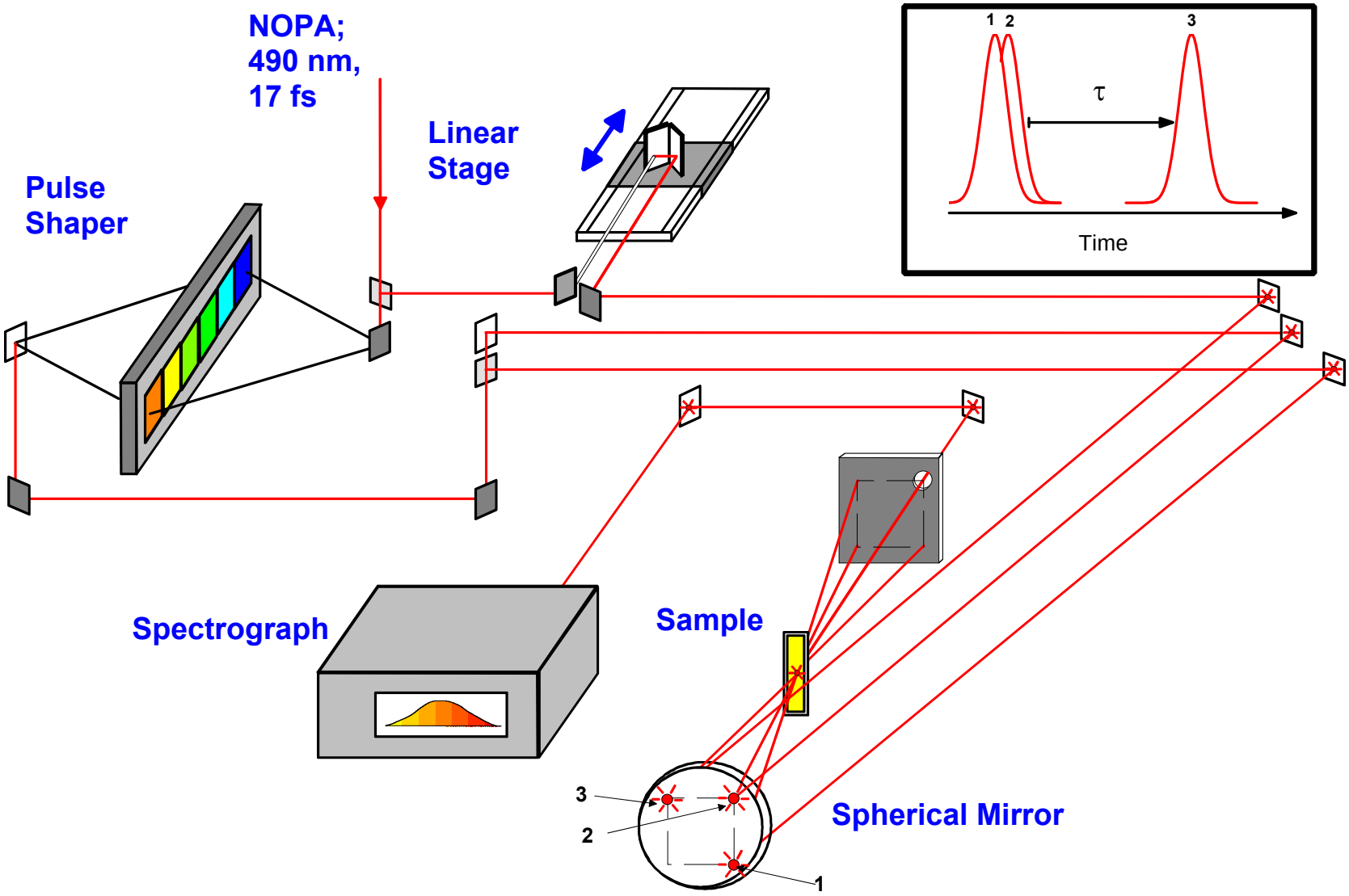


- Optical Parametric Generation
- White Light Generation
- Second Harmonic Generation

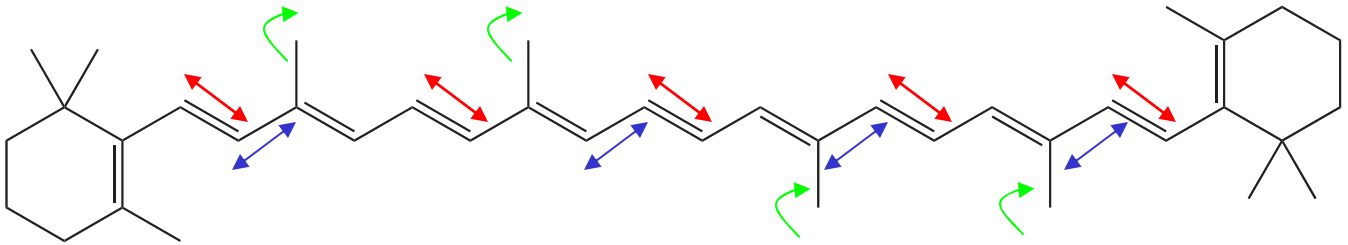
Noncollinear optical Amplifier NOPA (J. Yvon, A.G. Riedle)

17 – 20 fs

Experimental Setup



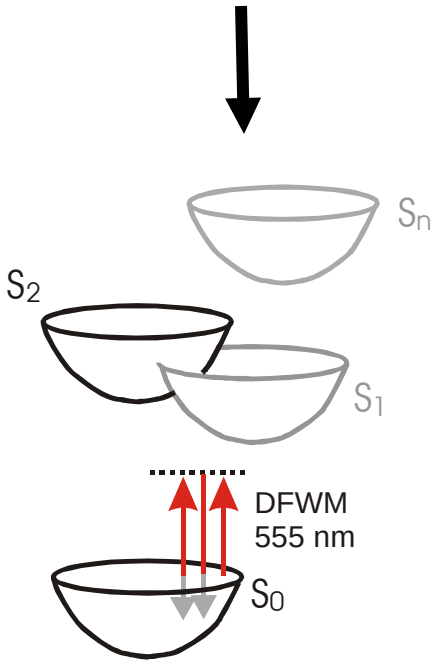
All-*trans*-ß-Carotene (N=11)



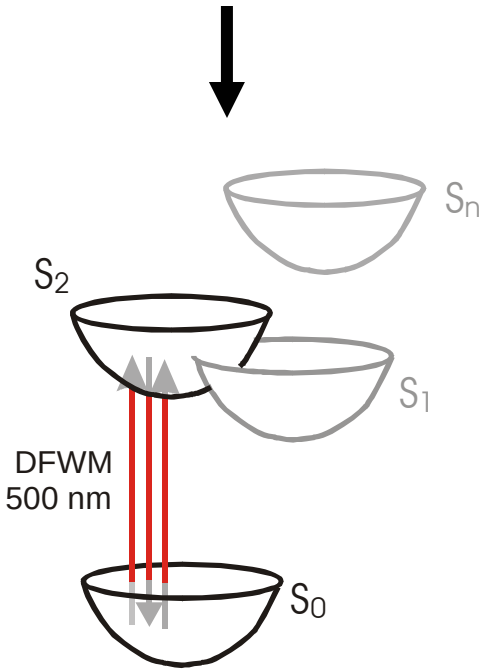
Ground State Vibrations	Freq.(cm^{-1})
C=C Symmetric stretch	1524
C-H Plane bending	1269
C-C Symmetric stretch	1157
Methyl to chain rock	1004

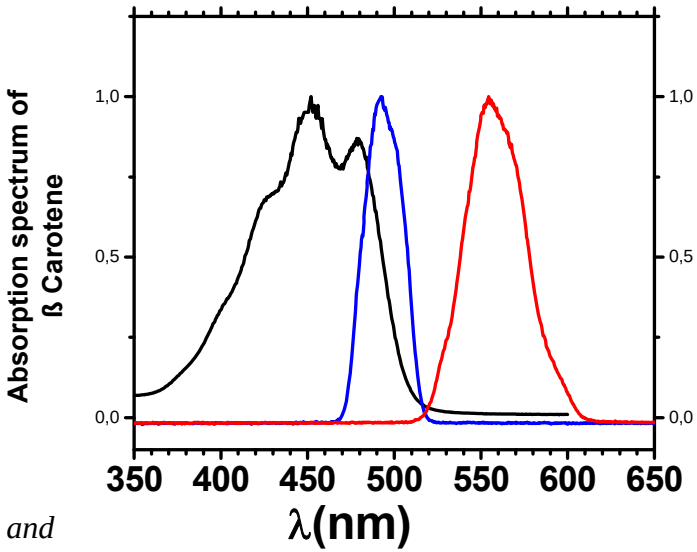
FWM in ß-Carotene

Non-resonant

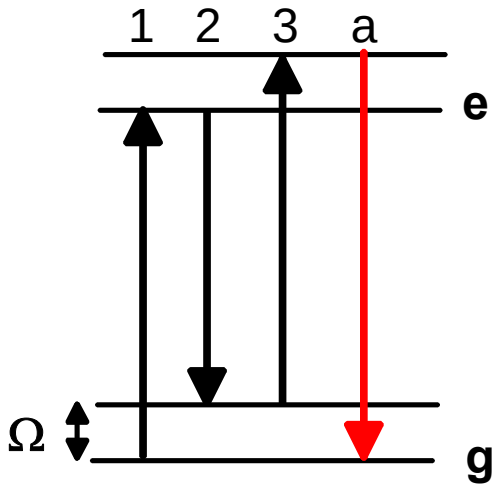


Resonant





Hornung T. Skenderović H. Motzkus M.
Observation of all-trans-beta-carotene wavepacket motion on the electronic ground and excited dark state using degenerate four-wave mixing (DFWM) and pump-DFWM,
Chemical Physics Letters. 402(4-6):283-288, 2005 Feb 4.



The first two pulses generate wave packets in the ground and excited state via Impulsive Raman scattering.

Propagation of the packets is monitored by the third pulse.

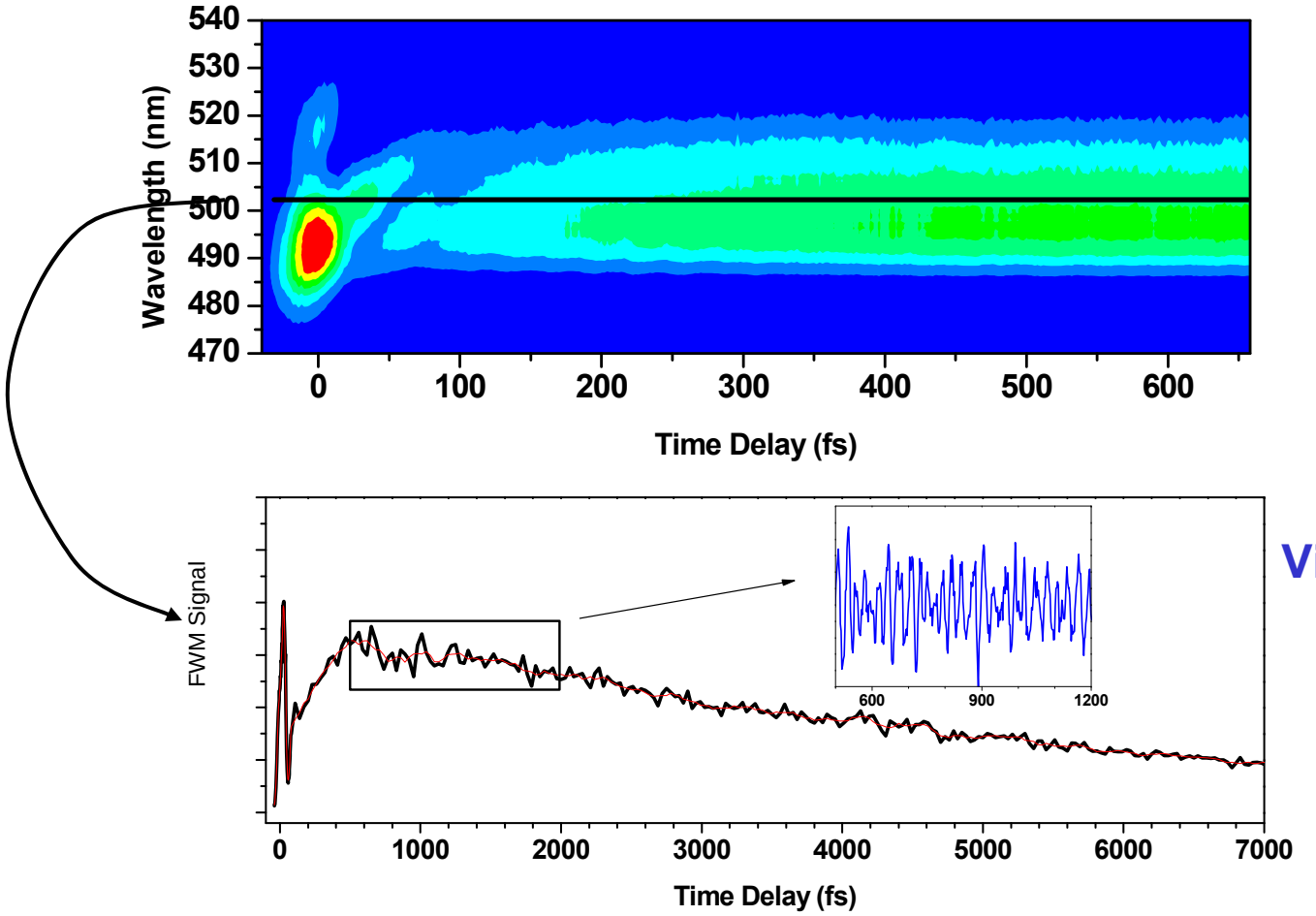
Observation of real-time vibrations requires that the frequency bandwidth of the laser pulses overlap two or more vibrational levels.

Beside vibrational, other dynamics are present. Rotational, restoration of solvent configuration, etc...

$$I_{FWM}(\tau) = \int \left| P^{(3)}(t,\tau) \right|^2 dt$$

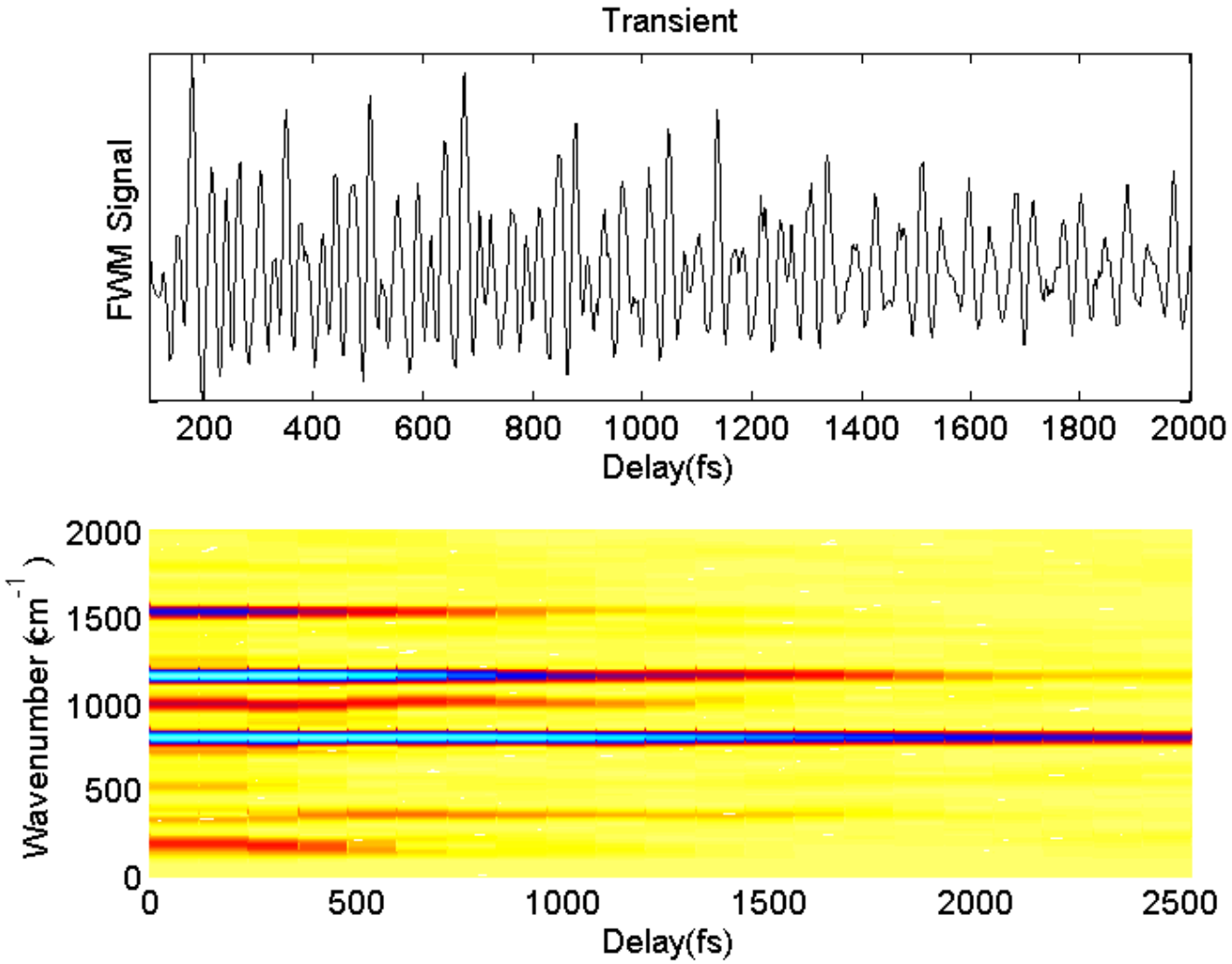
Calculation of the induced Polarization requires knowledge of the third order density operator $\rho^{(3)}(t)$. The form of $\rho^{(3)}(t)$ follows from a perurbative solution of the Liouville equation that describes evolution of the system under the influence of the incident laser fields and intrisic relaxation.

2D Transient → 1D Transient

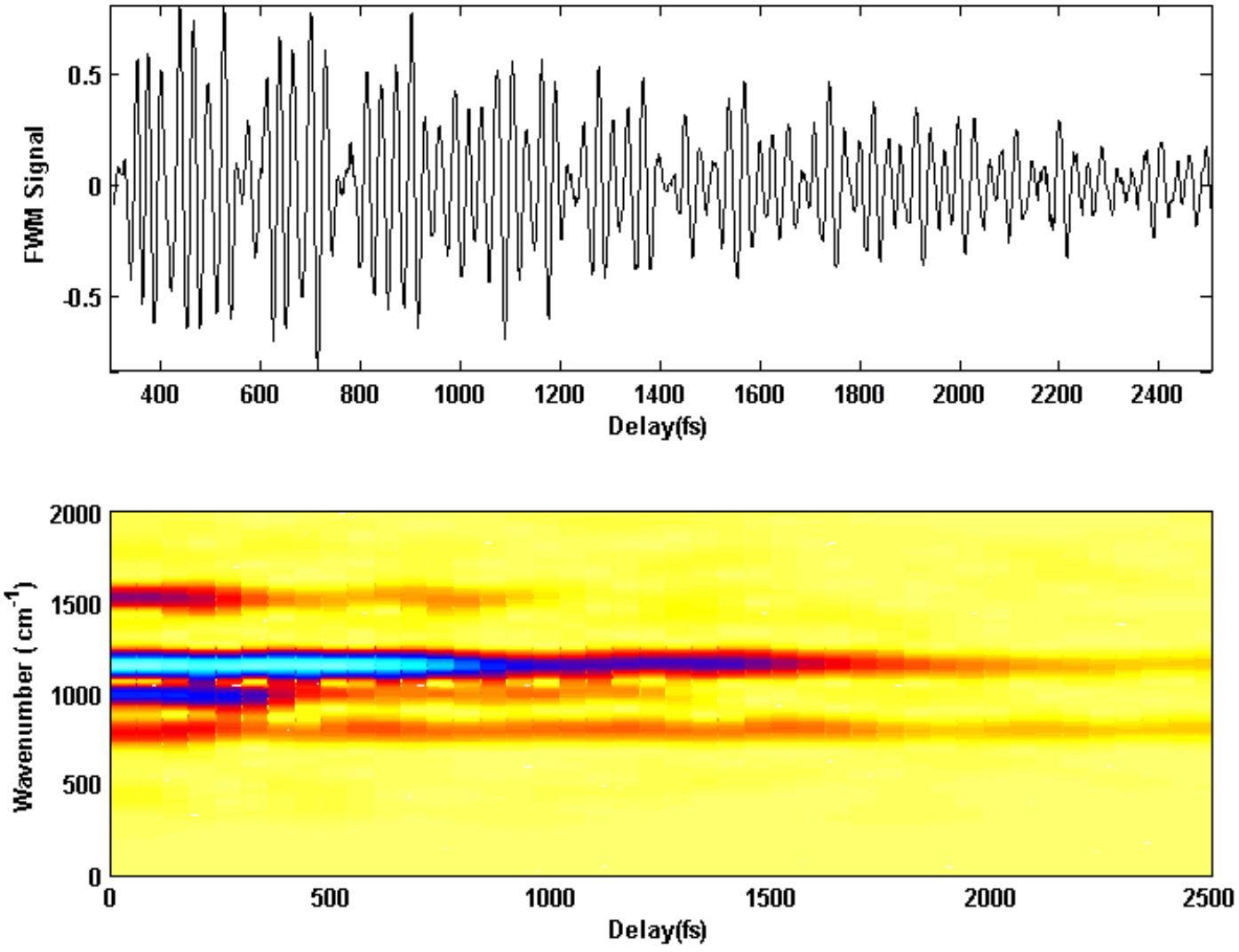


Vibrational dynamics

Transient, nonresonant excitation, and sliding window spectrogram

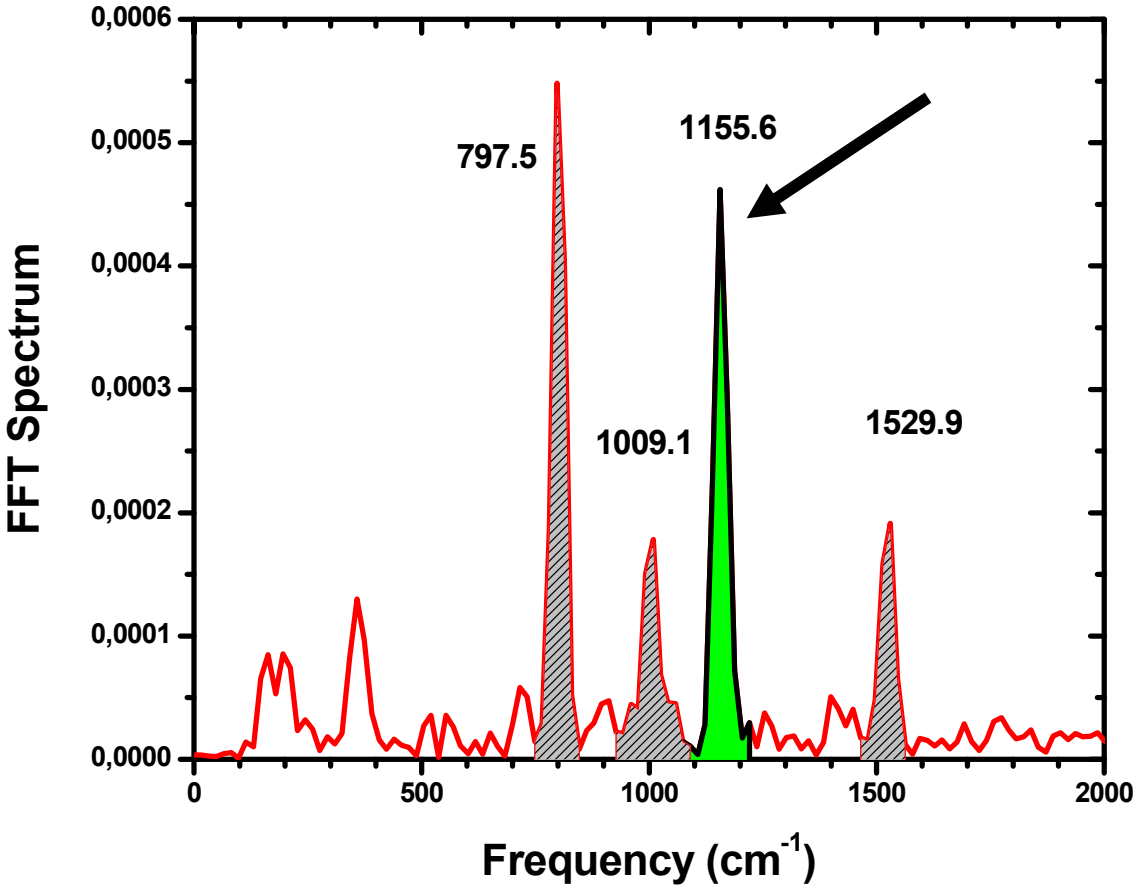


Transient, resonant excitation, and sliding window spectrogram



Coherent Control

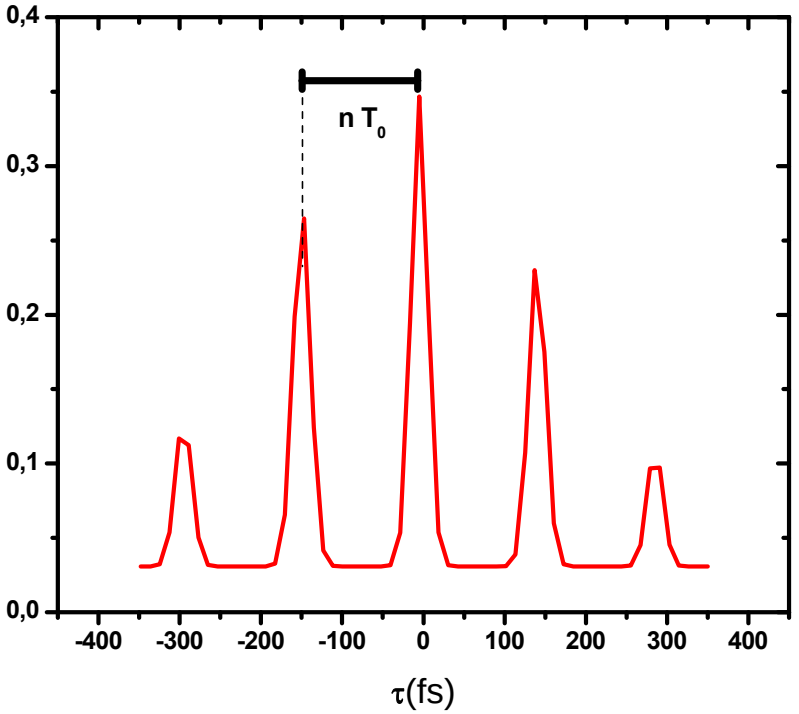
Can we selectively excite just one mode employing pulse shaping?



Recipe

Shape the Pulse into several replicas. Make the separation between replicas equal to $n\ T_0$ (T_0 is vibrational period of the mode to be excited)

[M. M. Wefers, K. A. Nelson, J. Opt. Soc. Am. B 12, 1342 (1995)]



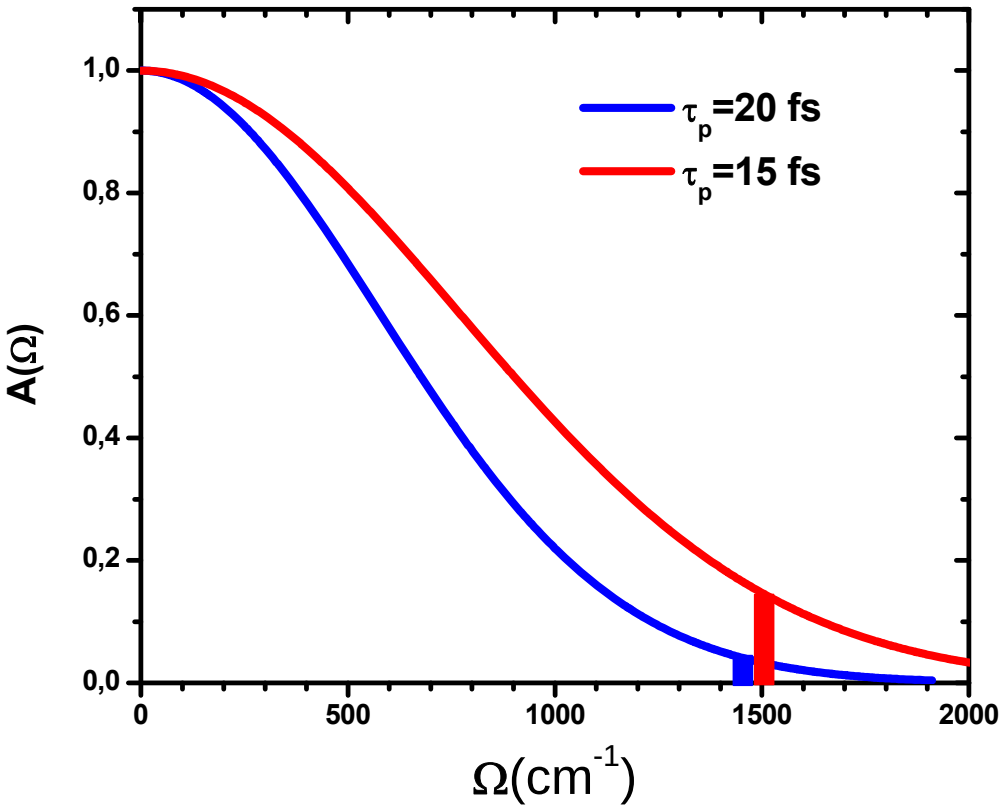
Energy (cm^{-1})	T(fs)	2 T(fs)	3 T(fs)	4 T(fs)	5 T(fs)
1524	21.9	43.8	65.7	87.6	109.5
1157	28.8	57.6	86.4	115.2	144
1004	33.2	66.4	99.6		

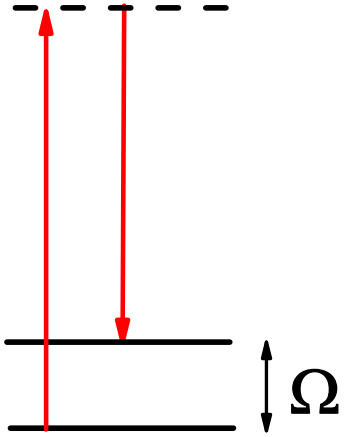
Third order polarisation, [Silberger et al, J.Chem. Phys. **118** 9208 (2003)]

$$P^{(3)}(\omega) = C \int d\Omega \frac{1}{\Omega - \Omega_R - i\Gamma_R} E_3(\omega - \Omega) A(\Omega)$$

Two Photon Absorption:

$$A(\Omega) = \int d\omega' E_2^*(\omega') E_1(\Omega + \omega')$$





How to select Ω_R : Frequency domain approach

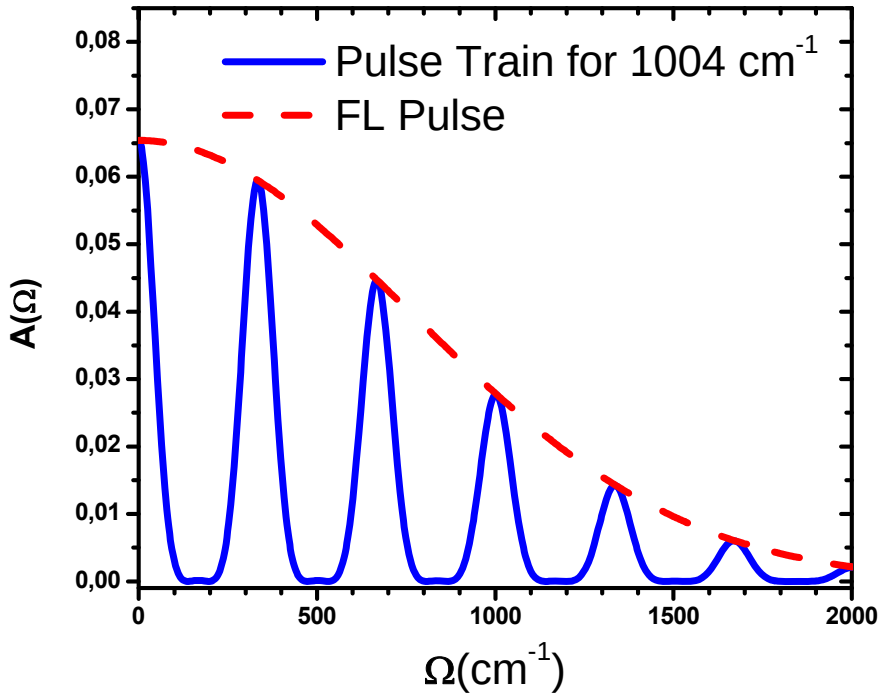
$$A(\Omega_R) = \int d\omega' E_2^*(\omega') E_1(\Omega_R + \omega')$$

$$E(\omega) = |E(\omega)| e^{i\Phi(\omega)}$$

$$\Phi(\omega) - \Phi(\Omega_R + \omega) \approx 0$$

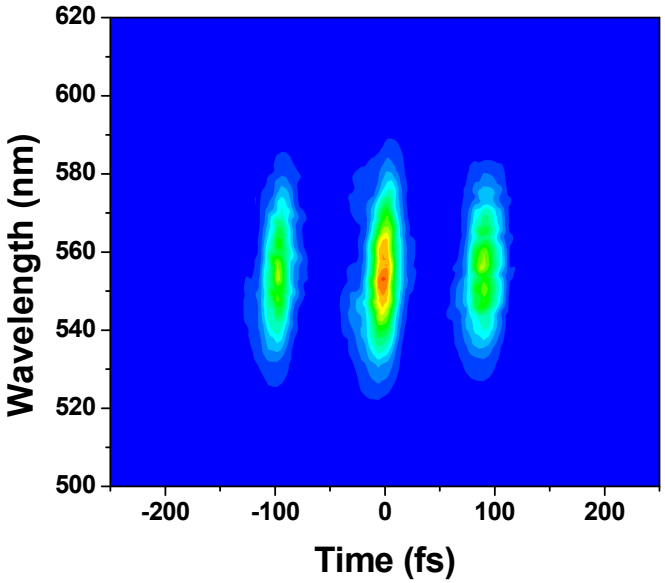
Konstructive Interference at Ω_R for every ω

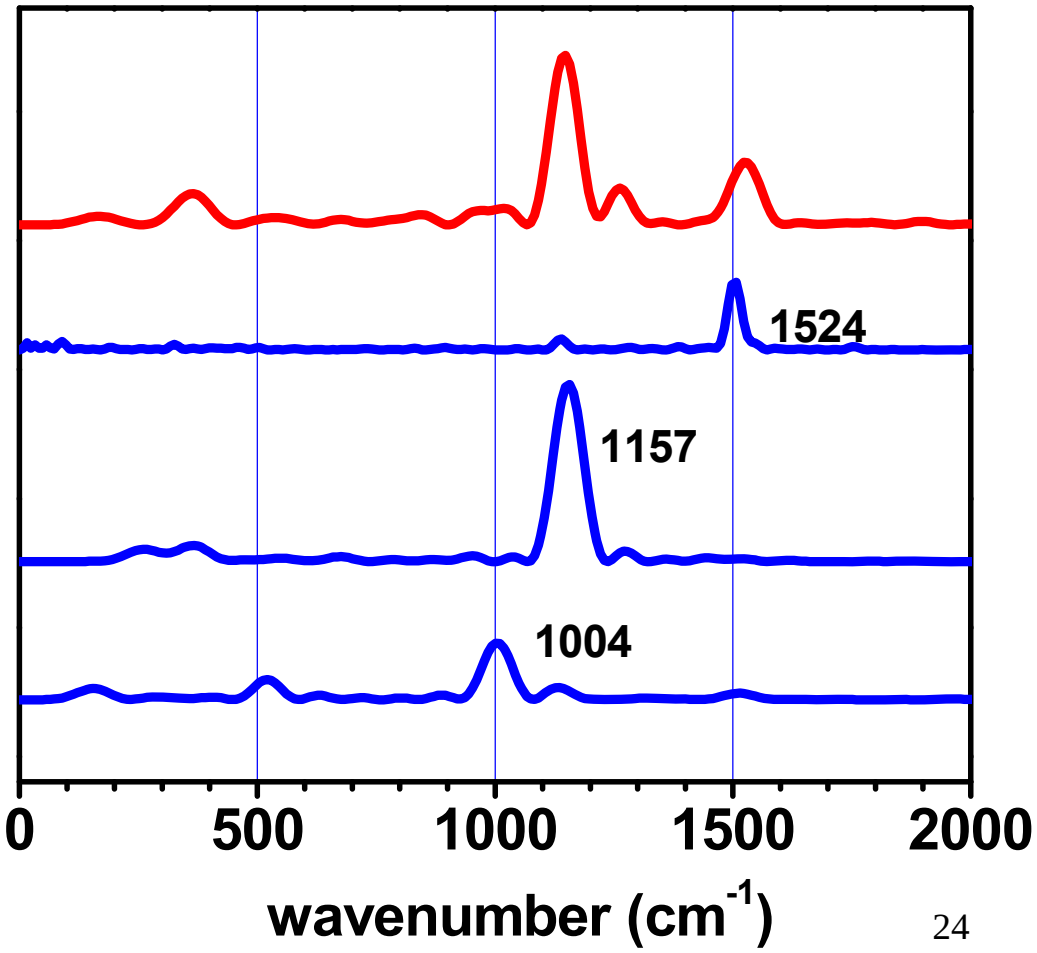
Destructive Interference for other ω



→ Phase should be periodic with Ω_R

$$\Phi(\omega) = a \sin\left(2\pi N \frac{\omega}{\Omega_R} + c\right)$$

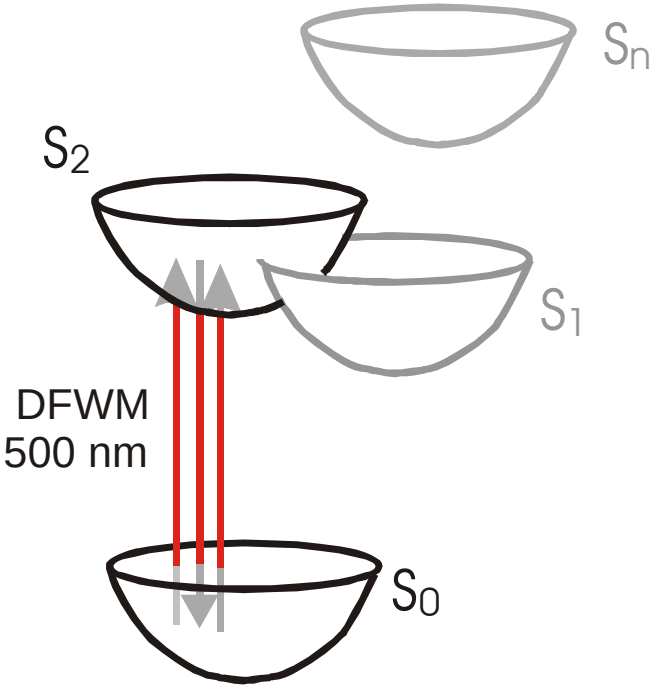

620
600
580
560
540
520
500
Wavelength (nm)
-200
-100
0
100
200
Time (fs)


1524
1157
1004
0
500
1000
1500
2000
wavenumber (cm-1)

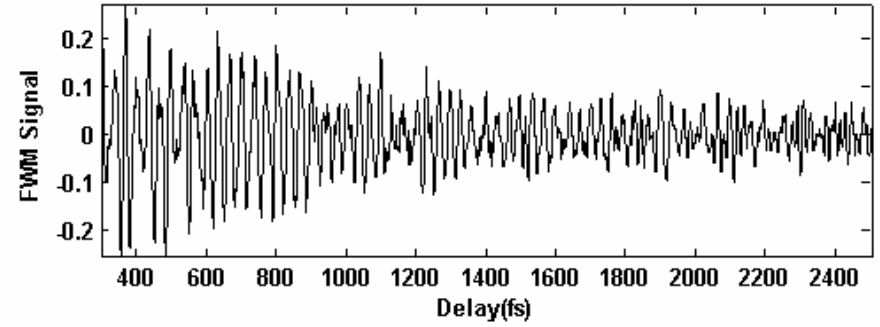
Non-resonant case, conclusions

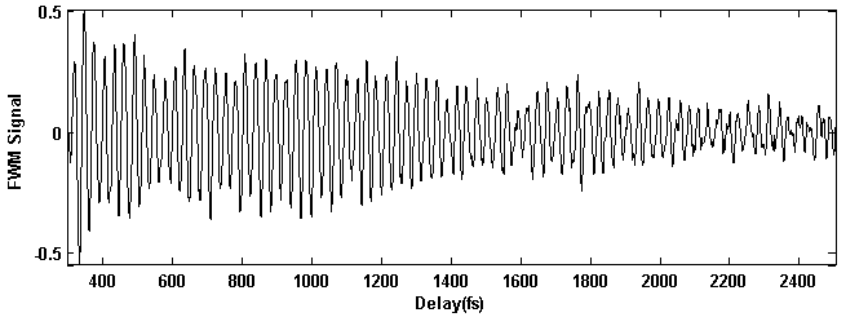
- Non resonant DFWM with ultrashort pulses efficiently excites high-frequency vibrational modes in ground state with pulse replicas set at N * T
- Selective excitation with shaped pulses is achieved
- Can we increase the selective excitation efficiency with resonant DFWM?

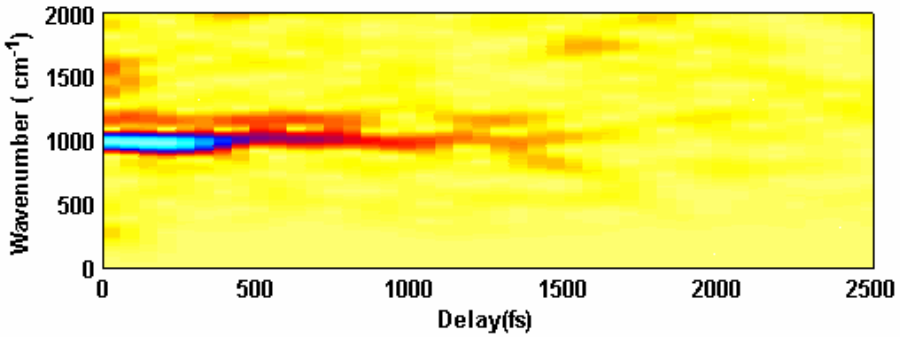
DFWM - Resonant case

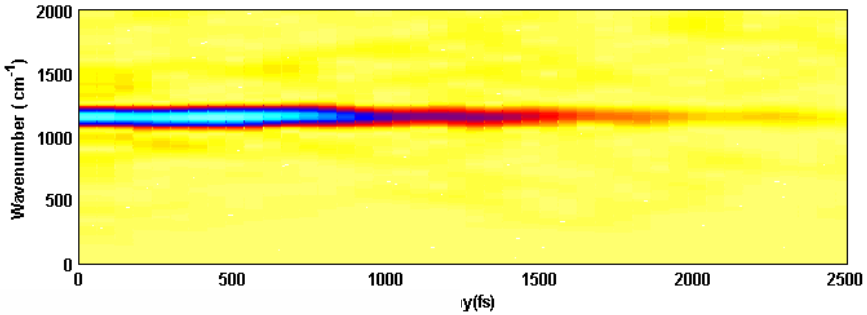


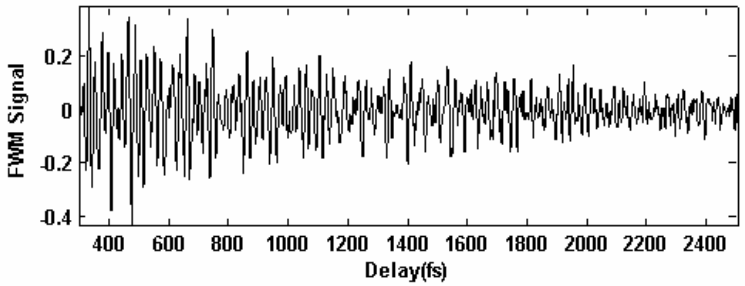
Hauer J. Skenderović H. Kompa K-L. Motzkus M.
Enhancement of Raman Modes by Coherent Control in ß-Carotene.
Chem. Phys. Lett. **421 523-528 (2006).**
Hauer J. Buckup T. Skenderović H. Kompa K.-L. Motzkus, M. Selective preparation of vibrational states in complex molecules by quantum control //
Quantum Computing: Back Action, Kanpur, India 2006..

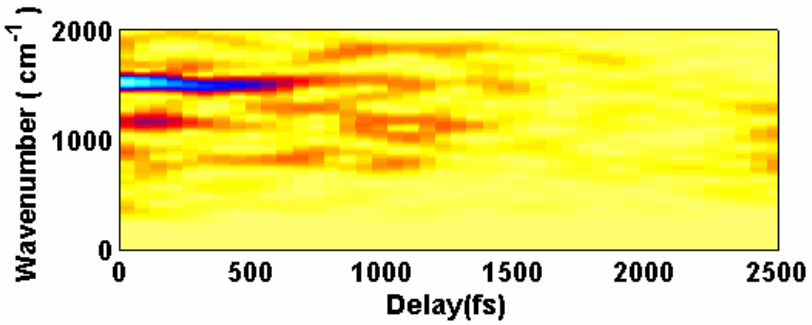

FWM Signal
0.2
0.1
0
-0.1
-0.2
400 600 800 1000 1200 1400 1600 1800 2000 2200 2400
Delay(fs)


FWM Signal
0.5
0
-0.5
400 600 800 1000 1200 1400 1600 1800 2000 2200 2400
Delay(fs)

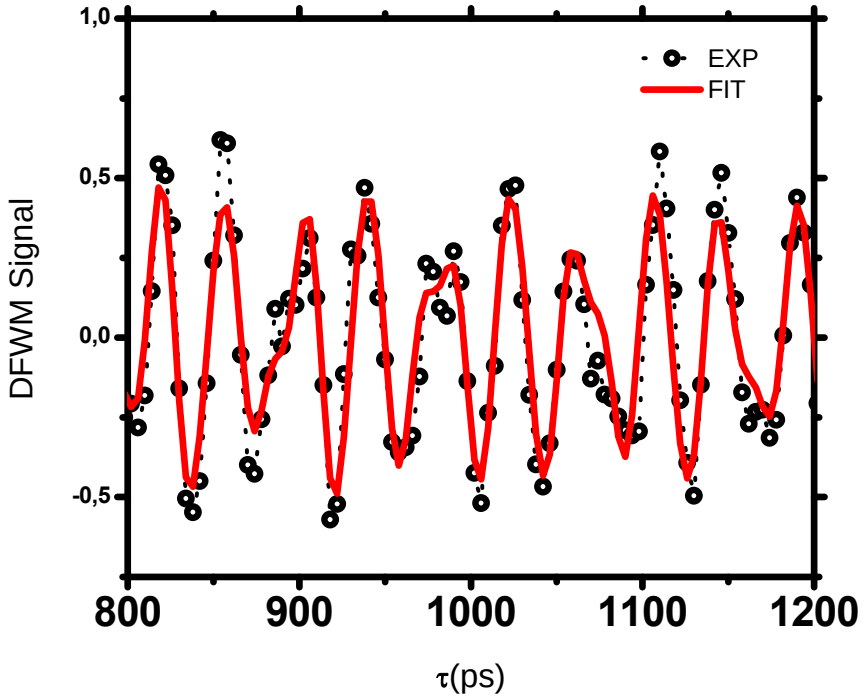

Wavenumber (cm-1)
2000
1500
1000
500
0
0 500 1000 1500 2000 2500
Delay(fs)


Wavenumber (cm-1)
2000
1500
1000
500
0
0 500 1000 1500 2000 2500
y(fs)


FWM Signal
0.2
0
-0.2
-0.4
400 600 800 1000 1200 1400 1600 1800 2000 2200 2400
Delay(fs)


Wavenumber (cm-1)
2000
1000
0
0 500 1000 1500 2000 2500
Delay(fs)

$$S(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i} \sin(\omega_i t + \phi_i)$$

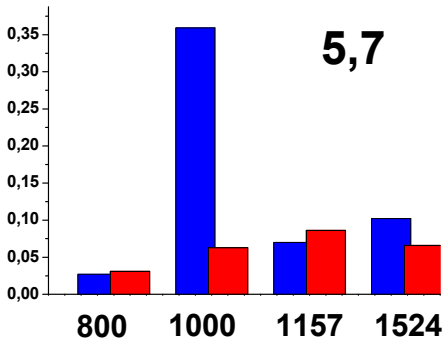


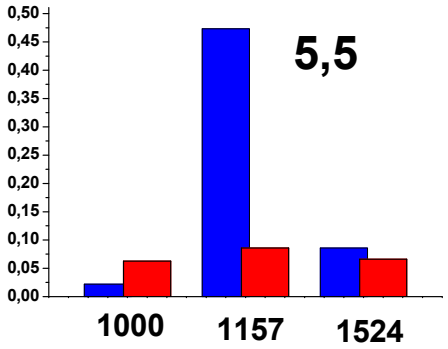
ω	τ / fs
1004	1200
1156	1350
1532	650
1390	144

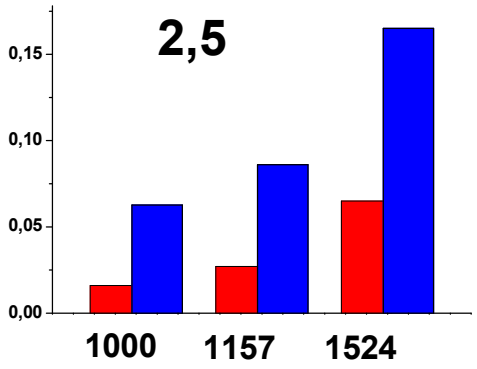
Applying multipulse sequences matching the periodicity of single vibrations, the modes of b-carotene solvated in cylcohexane were not only specifically excited, but under resonant conditions also enhanced compared to the Fourier-limited case.

This effect is attributed to an increased population transfer to the excited state and stronger coherences created and demonstrates the feasibility to selectively amplify ground state Raman modes by coherent control.

At 484 nm



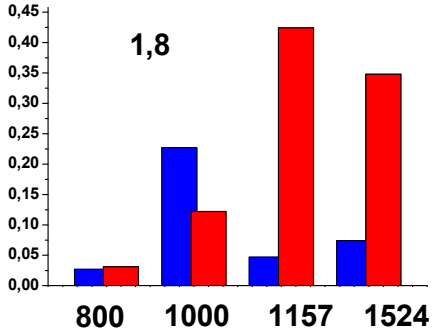


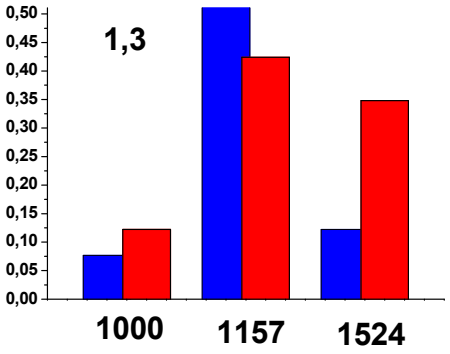


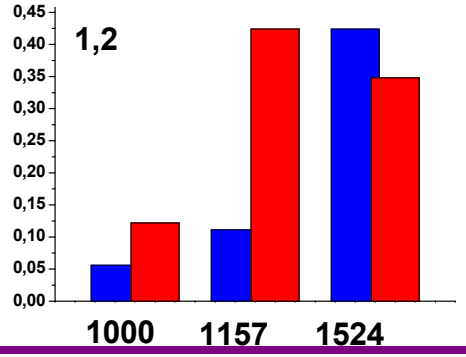
Shaped

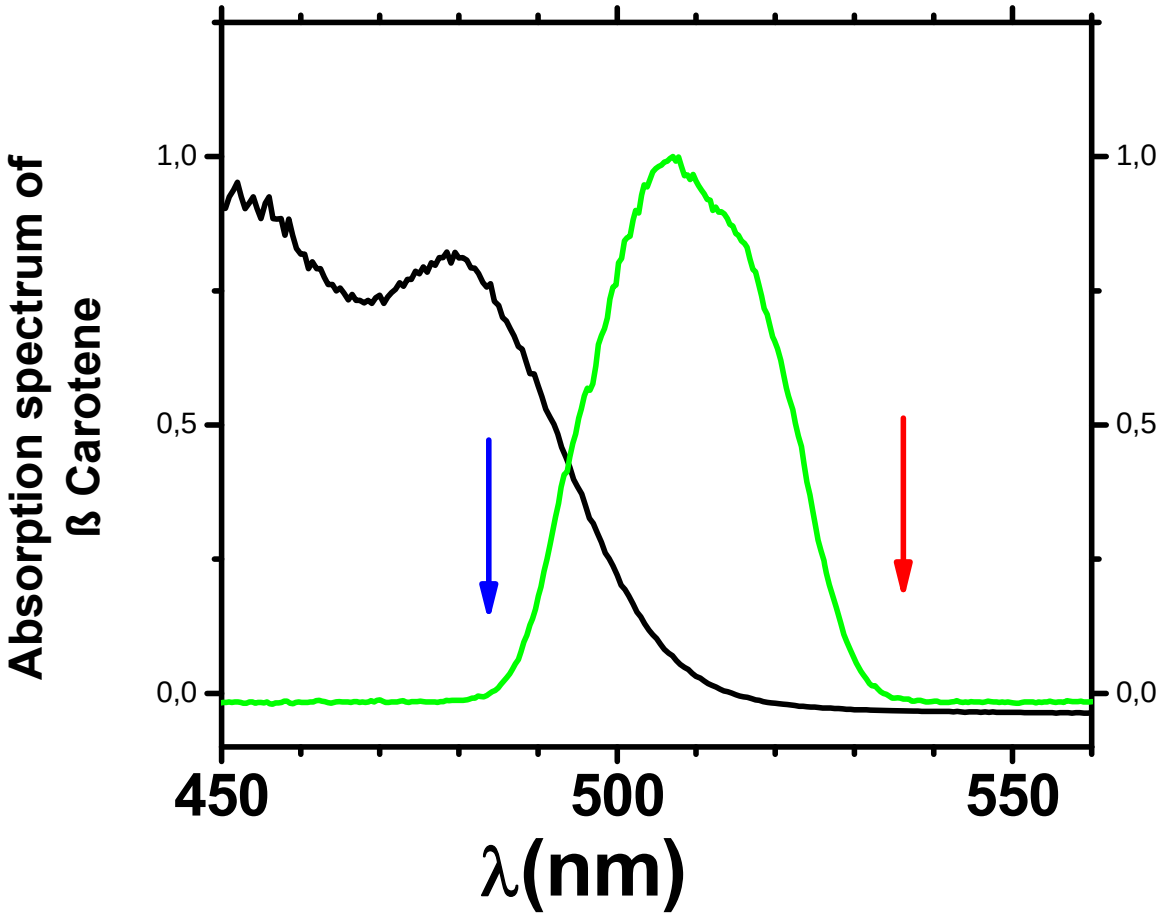
Unshaped

At 538 nm








Absorption spectrum of
ß Carotene
1,0
0,5
0,0
1,0
0,5
0,0
450
500
550
λ(nm)

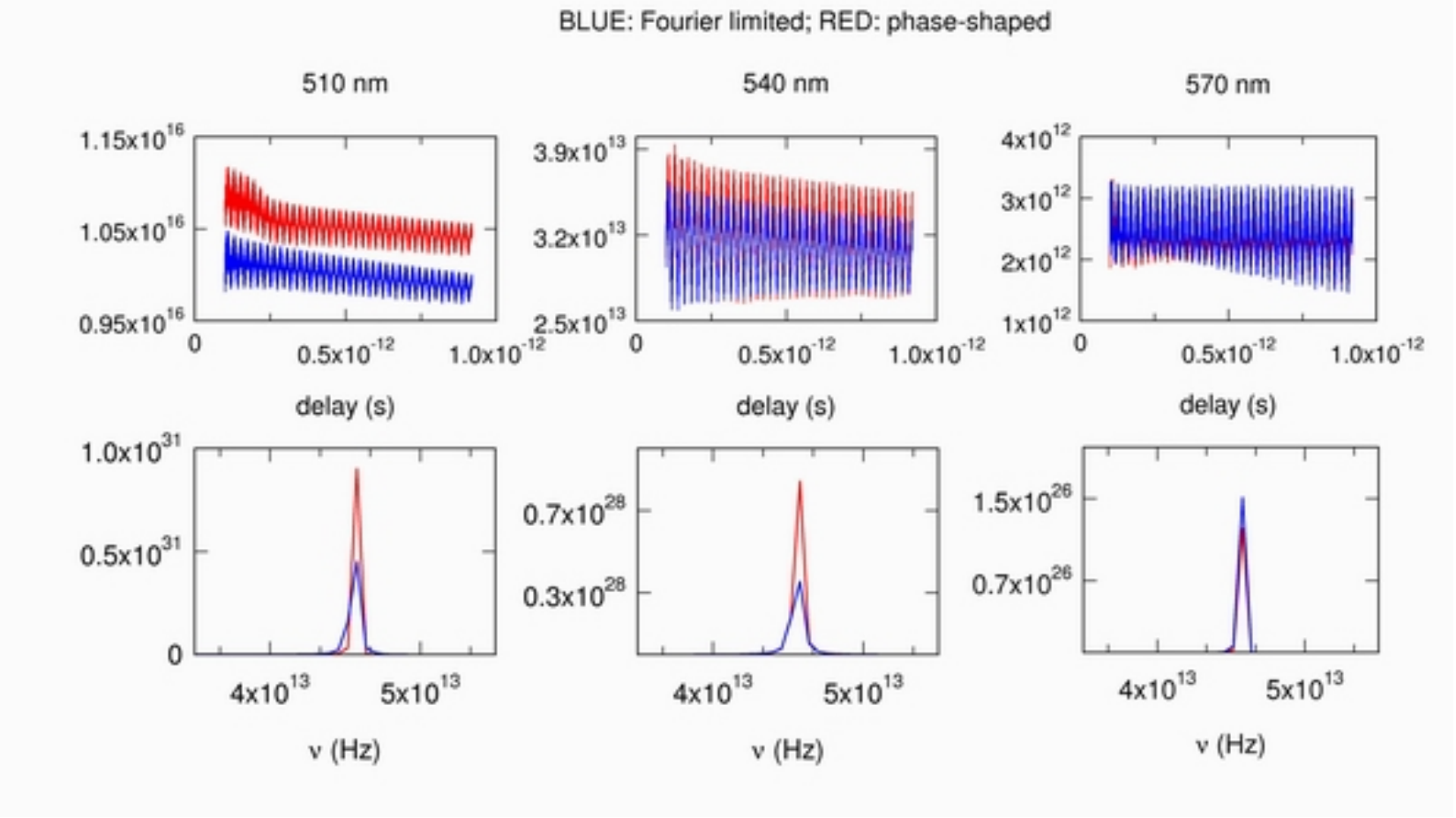
„[…] we conclude that the physical mechanism responsible for increasing/suppressing of the *S*0 *S*1 population transfer is resonant excitation of

the underlying vibrational states

by keeping them in a coherent superposition during the excitation.“

[N. A. Prokhorenko Vl, Miller RJD, *JOURNAL OF CHEMICAL PHYSICS* 122, Art. No. 184502 (MAY 8 2005, 2005)]

•Theory of resonant DFWM



Buckup T. Hauer J. Serrat C. Motzkus M. Control of excited-state population and vibrational coherence with shaped-resonant and near-resonant excitation *Journal of Physics B-Atomic Molecular & Optical Physics. 41(7):74024, 2008 Apr 14.*

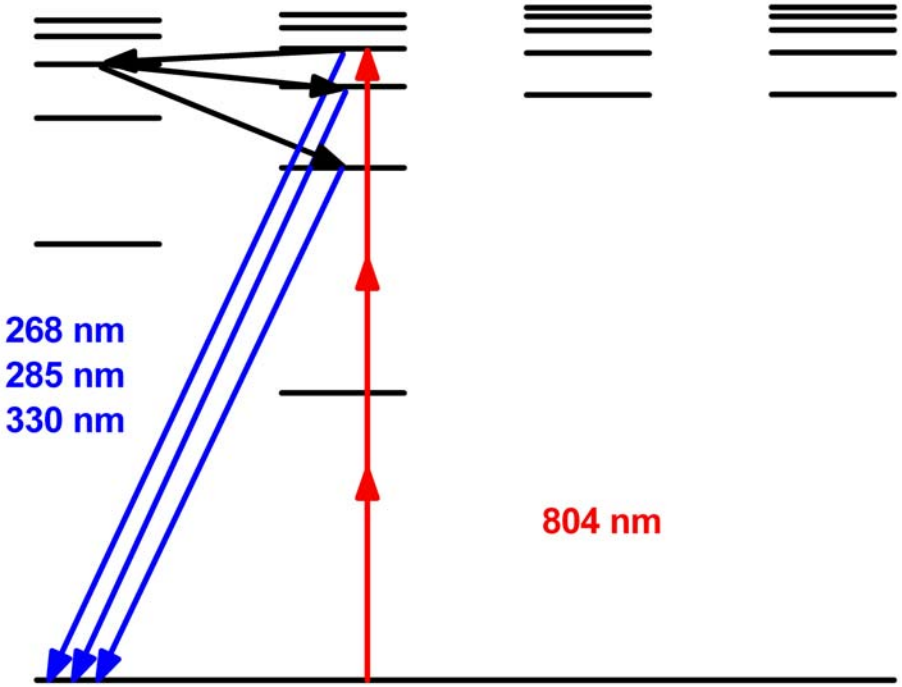
Acknowledgment

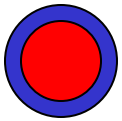
Max-Planck-Institut für Quantenoptik, D-85748 Garching
Institute of Physics, HR-10001, Zagreb

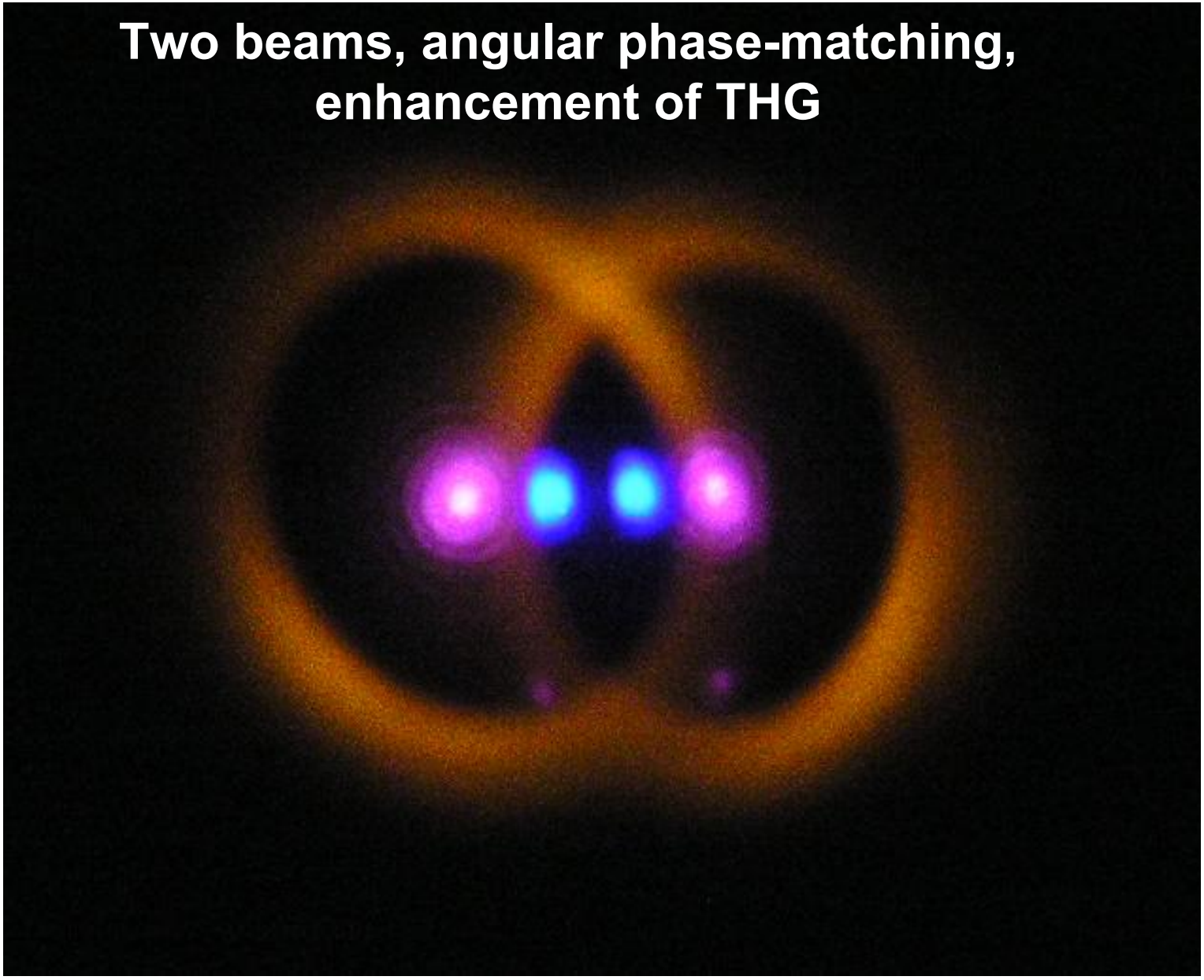
J. Hauer
T. Hornung
M. Motzkus

K. L. Kompa
G. Pichler

Third harmonic generation in sodium by Parametric Wave Mixing PWM






Two beams, angular phase-matching,
enhancement of THG

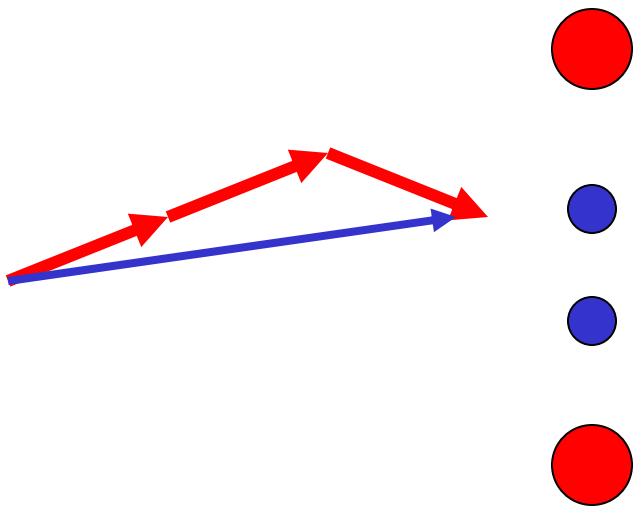
$$\chi^{(3)}(3\omega) = \frac{N}{\hbar^3}\sum_{mn\nu}\mu_{g\nu}\mu_{\nu n}\mu_{nm}\mu_{mg}$$

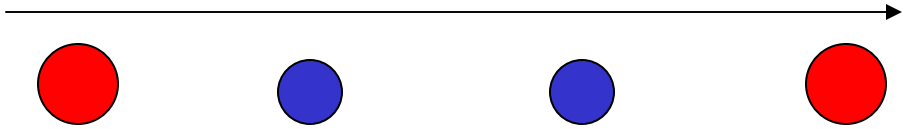
$$\times\left[\frac{1}{(\omega_{\nu g}-3\omega)(\omega_{ng}-2\omega)(\omega_{mg}-\omega)}\right.$$

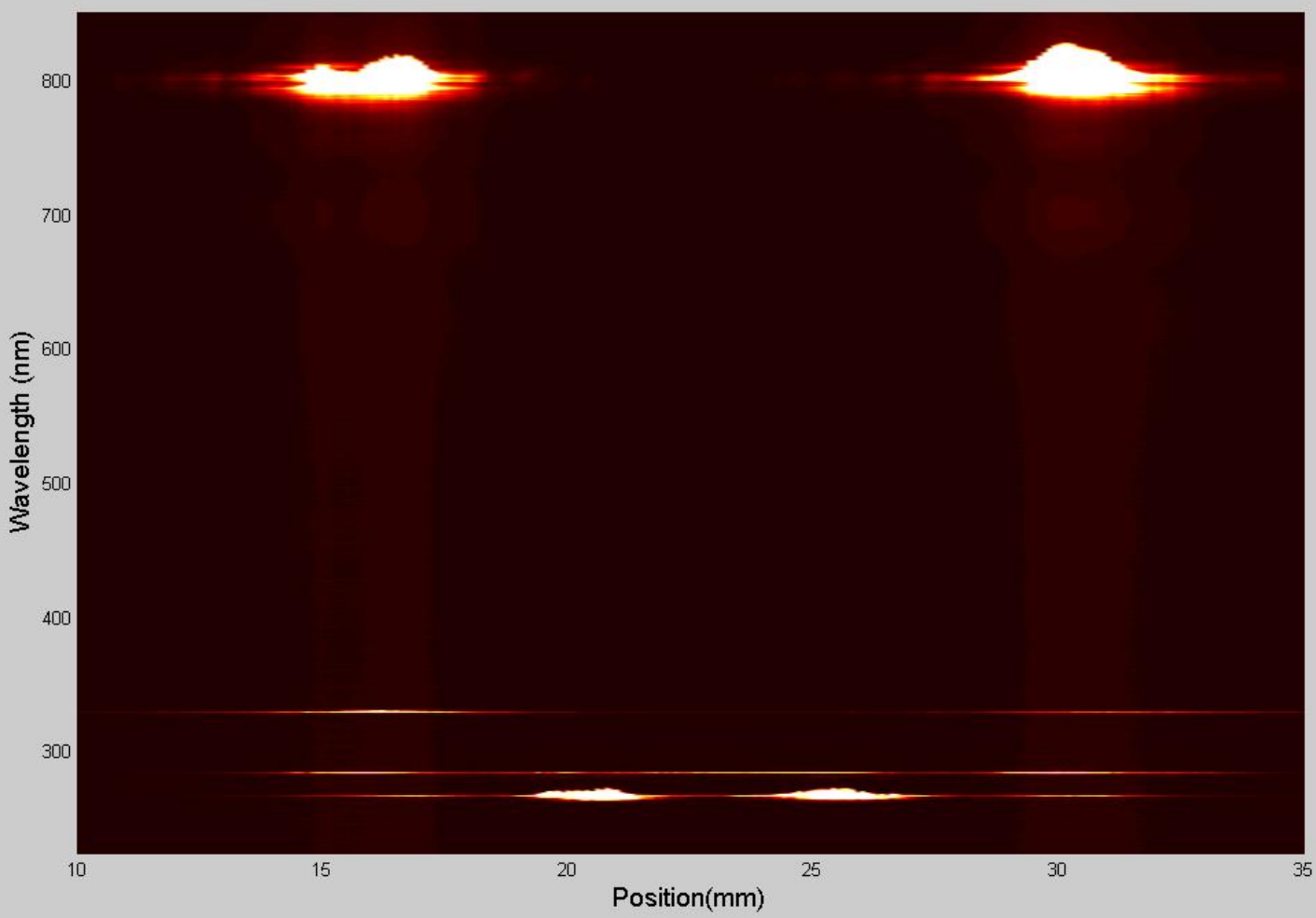
$$+\frac{1}{(\omega_{\nu g}+\omega)(\omega_{ng}-2\omega)(\omega_{mg}-\omega)}$$

$$+\frac{1}{(\omega_{\nu g}+\omega)(\omega_{ng}+2\omega)(\omega_{mg}-\omega)}$$

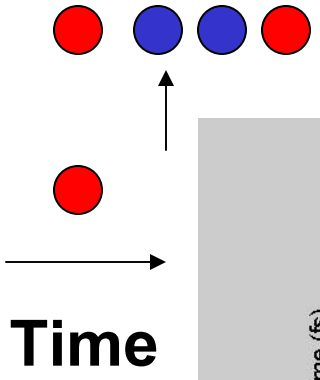
$$\left.+\frac{1}{(\omega_{\nu g}+\omega)(\omega_{ng}+2\omega)(\omega_{mg}+3\omega)}\right]$$

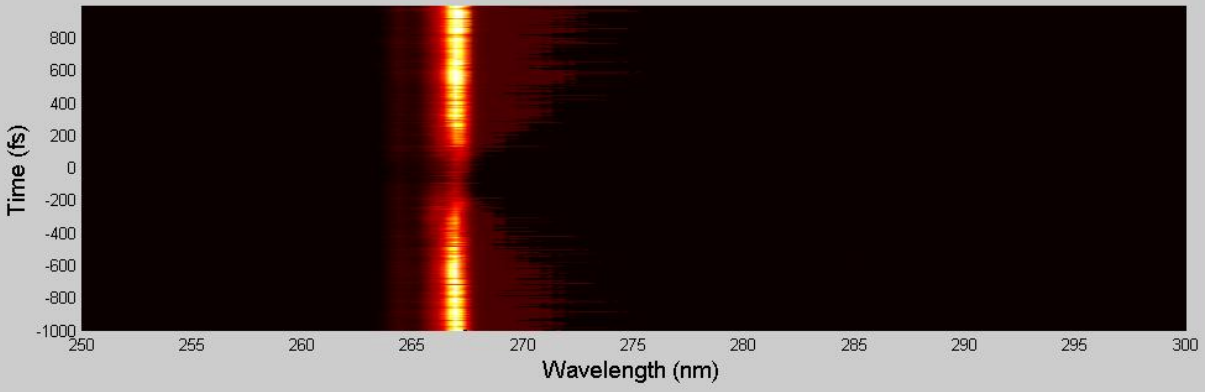


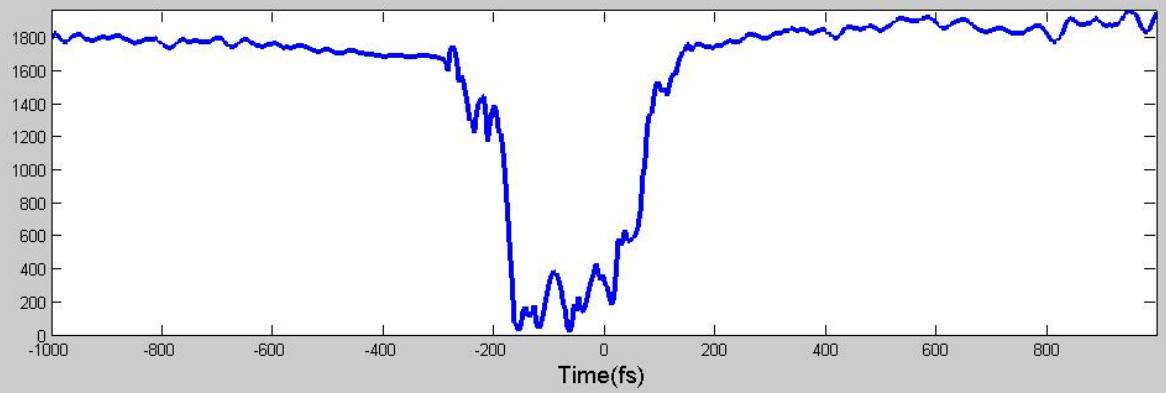


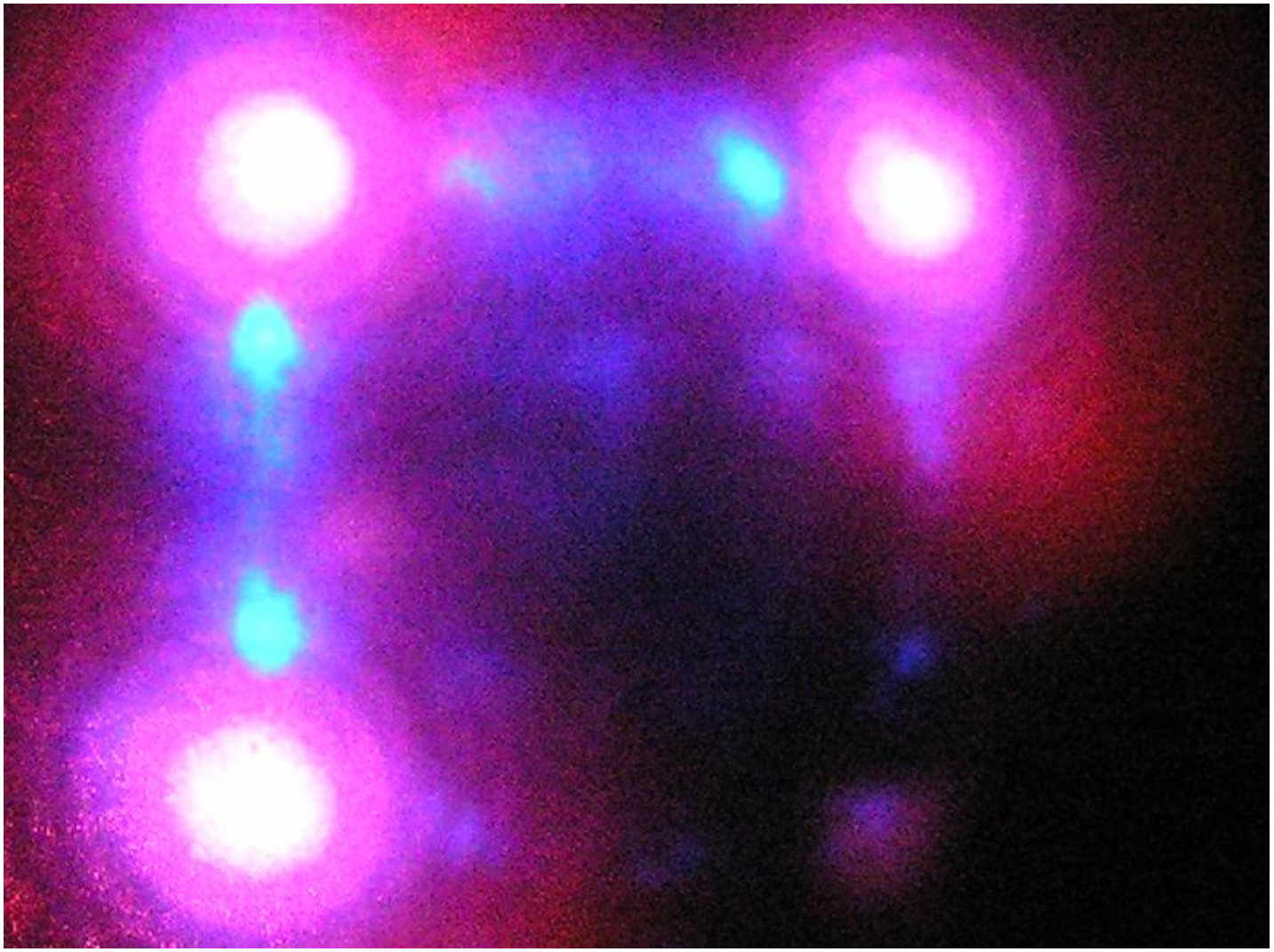

800
700
600
500
400
300
Wavelength (nm)
10
15
20
25
30
35
Position(mm)

Third beam - Mode competition









Dr. Goran Pichler
Dr. Ticijana Ban
Dr. Damir Aumiler
Silvije Vdovic
Natasa Vujicic
H.S.

Thank you