Wavepacket Dynamics of ß-Carotene Probed by Femtosecond Adaptive Four Wave Mixing Spectroscopy

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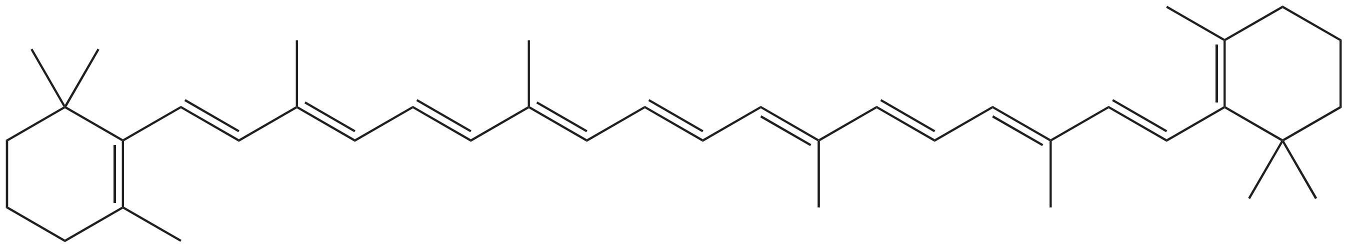
Time resolved resonant Degenerate Four Wave Mixing (DFWM) with sub-20 fs laser pulses is applied to probe the wavepacket dynamics in ground state of a large biologically important molecule.

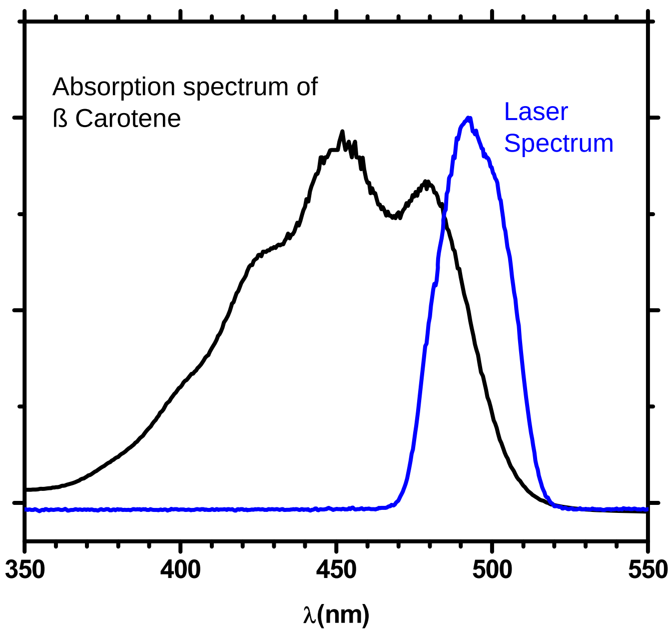
The electric fields of the pump and dump beam excite a coherent vibrational motion in the ground electronic state which is probed by the third beam. The generated FWM signal shows oscillatory pattern pertinent to the vibrational modes of the ground state.

The most prominent of these are: methyl rock at 1007 cm^{-1} ($C-CH_3$), the carbon single-bond stretch at 1159 cm^{-1} (C-C), and the carbon double-bond stretch at 1525 cm^{-1} (C=C).

Group velocity dispersion (GVD) introduced by the sample tends to decrease the efficiency of the mode excitation. In order to compensate the GVD the optimal phase is applied to the pump and dump beam by the shaper

All-*trans*-ß-Carotene (N=11)



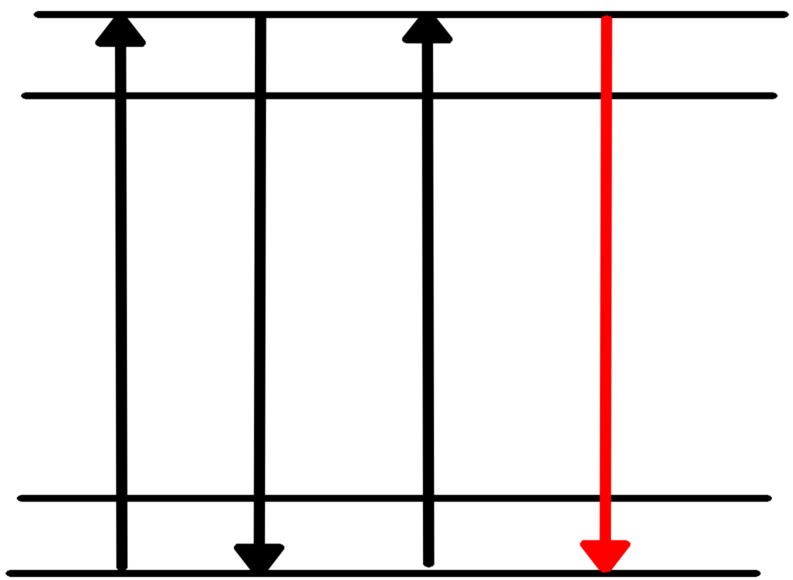


	S_0 modes (cm^{-1})
C=C, High frequency	
C=C Symmetric stretch	1524
C-H Plane bending	1269
C-C Symmetric stretch	1157
Methyl to chain rock	1004

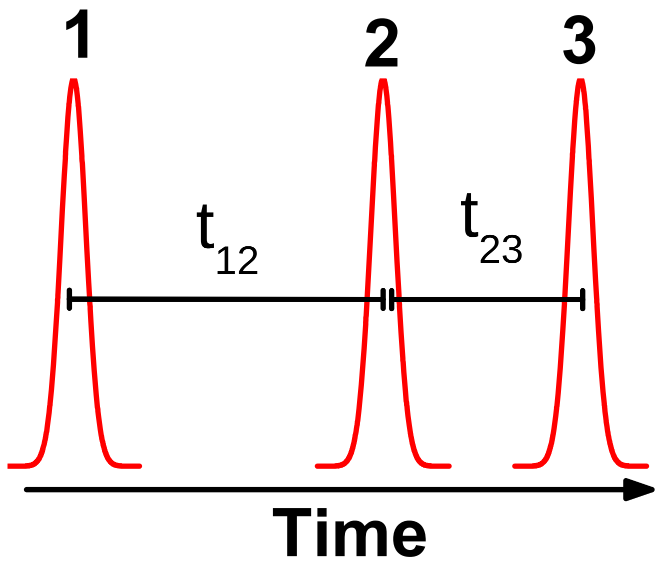
→D. McCamant, P. Kukura, and R. A. Mathies, “”, J. Phys. Chem. A, **107**, 8208 (2003)

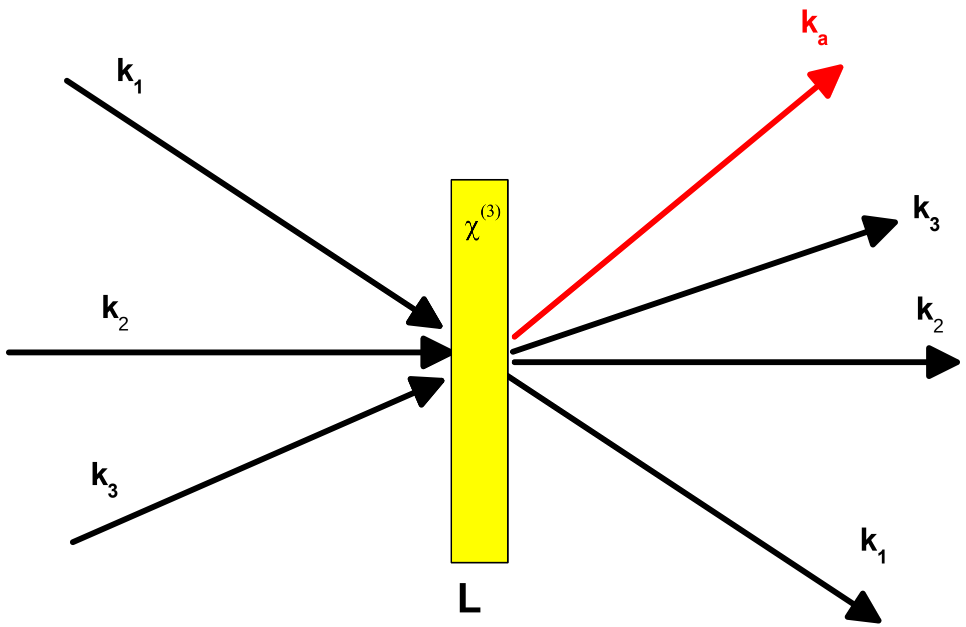
What is Four Wave Mixing ?

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

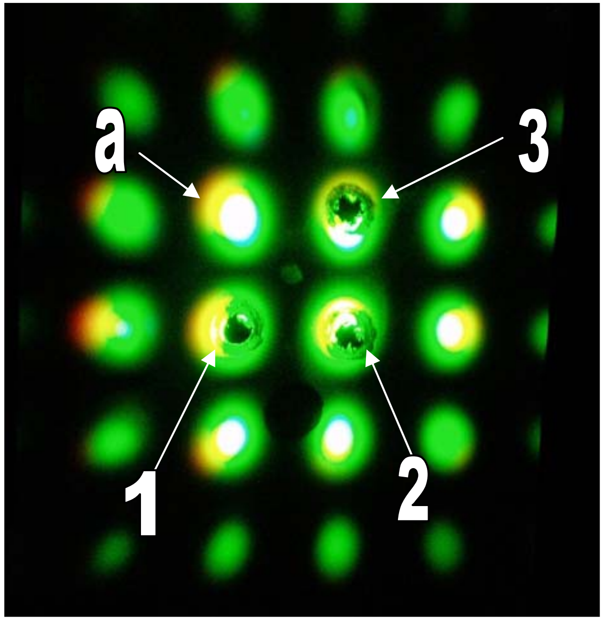


Time resolved FWM:



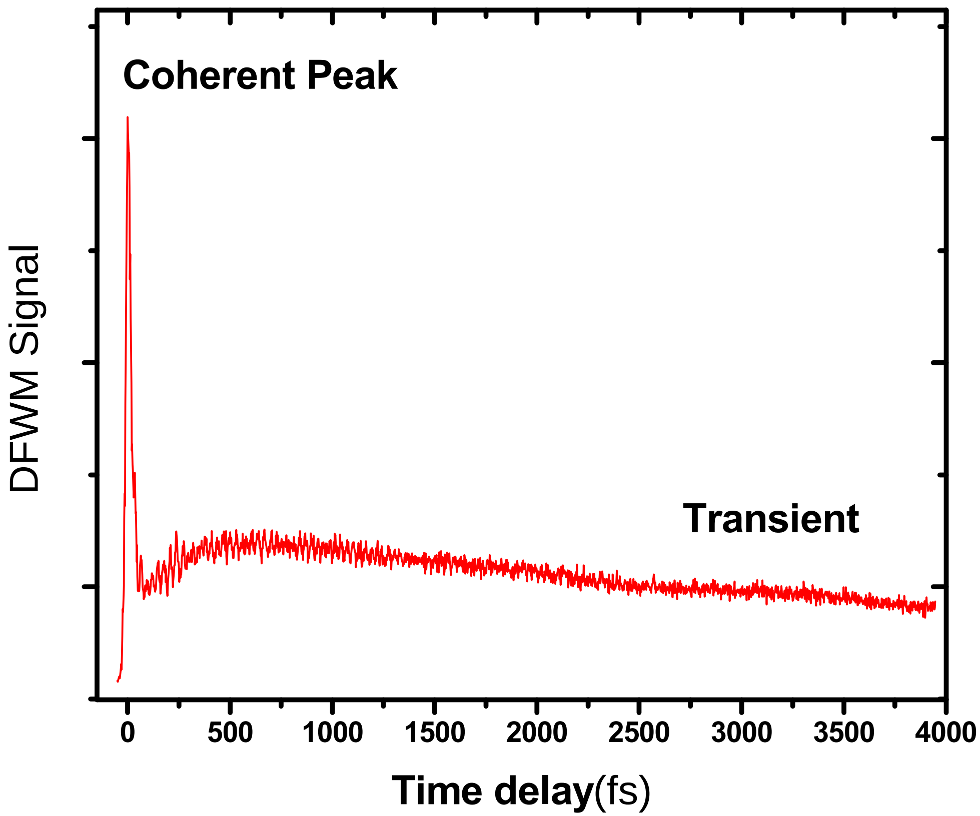


Phase matching: $k_a = k_1 - k_2 + k_3$



Degenerate Four Wave Mixing in glass with fs pulses at 560 nm

A typical DFWM signal in ß-Carotene (t_{12}=0, t_{23} scanned)



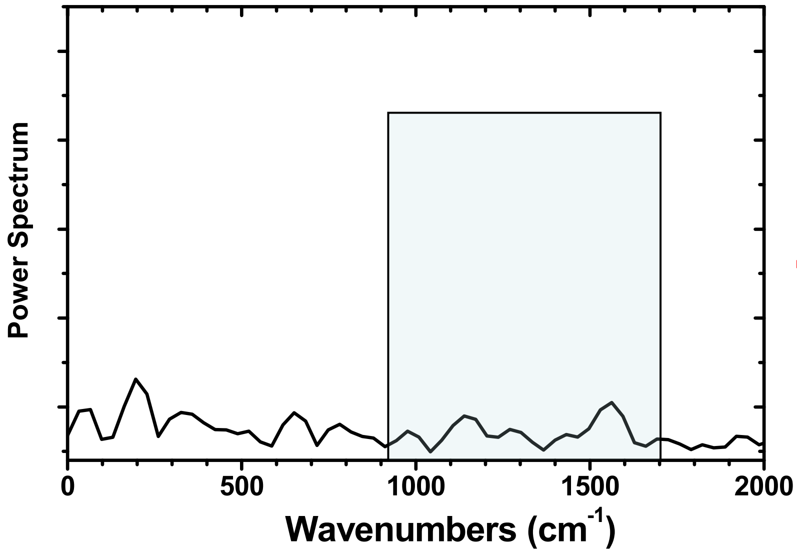
A pulse travelling through a resonant medium exhibits a phase change. To compensate this change (i.e. to keep the pulse short inside the sample) the phase of the pulse was shaped by Liquid Crystal Mask.

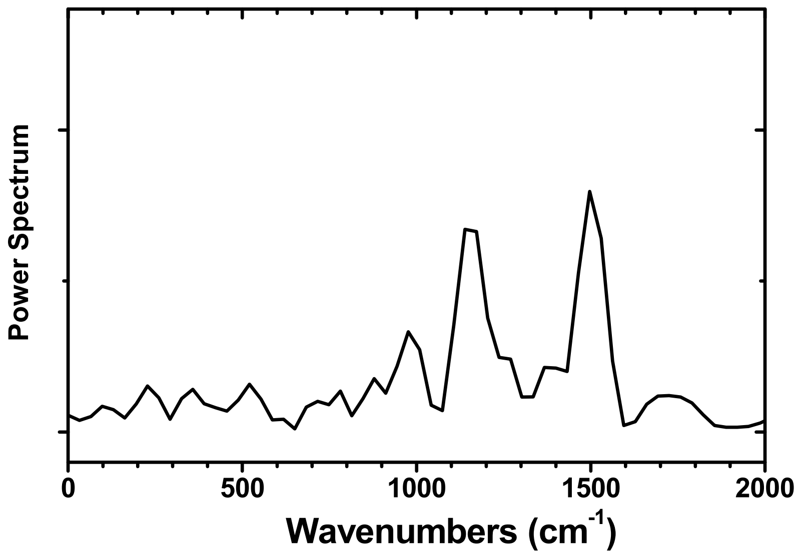
An efficient compensation leads to the change in the shape of DFWM signal: the Coherent Peak becomes narrower, and the Transient shows deeper modulation.

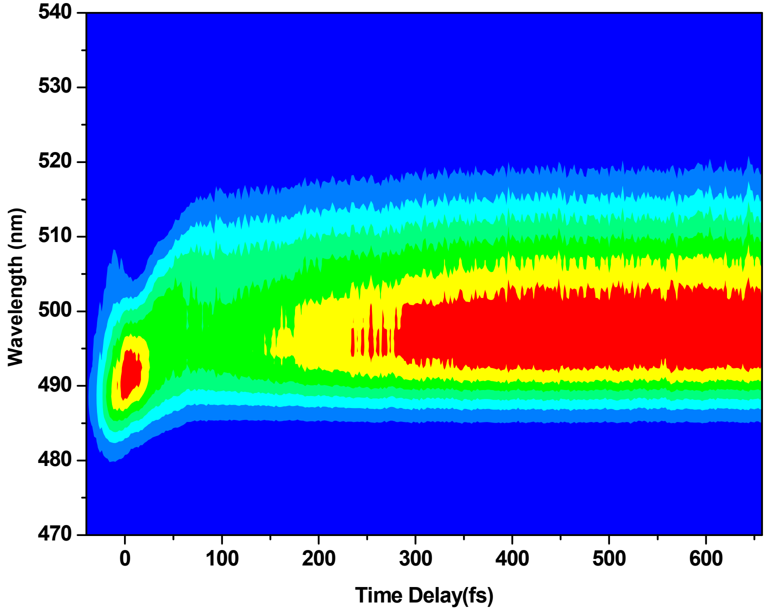
The optimal phase is found in a closed loop optimization employing evolutionary algorithm

Optimization:

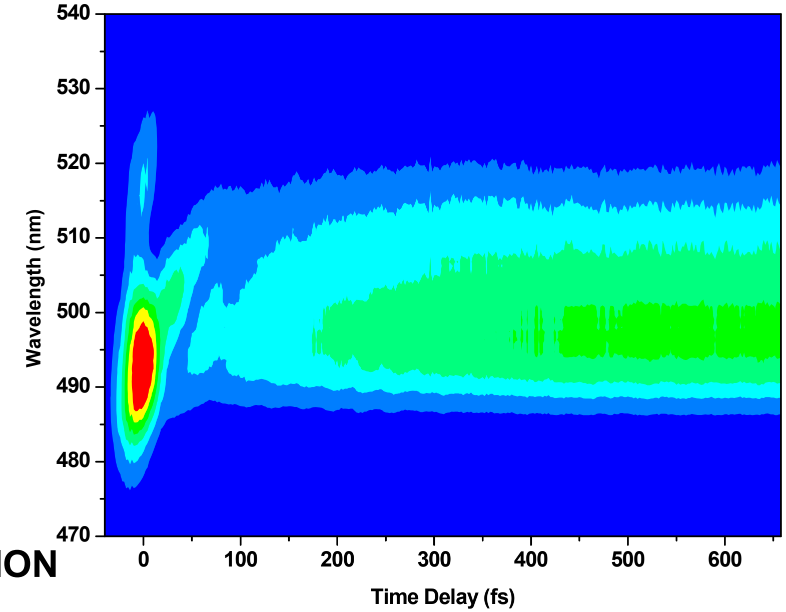
- **A short 1D transient was taken (200-300 fs)**
- **FFT spectrum of the transient was caculated**
- **The target for the algorithm was to maximize the spectrum in the range of the ß-Carotene modes**

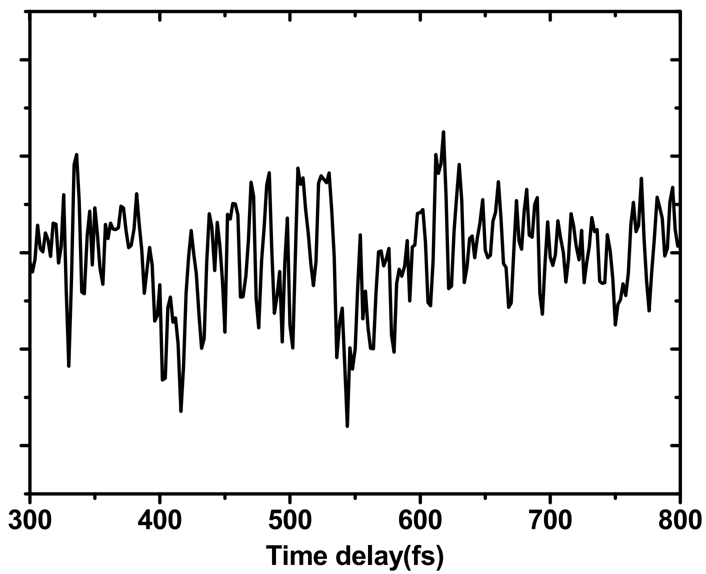


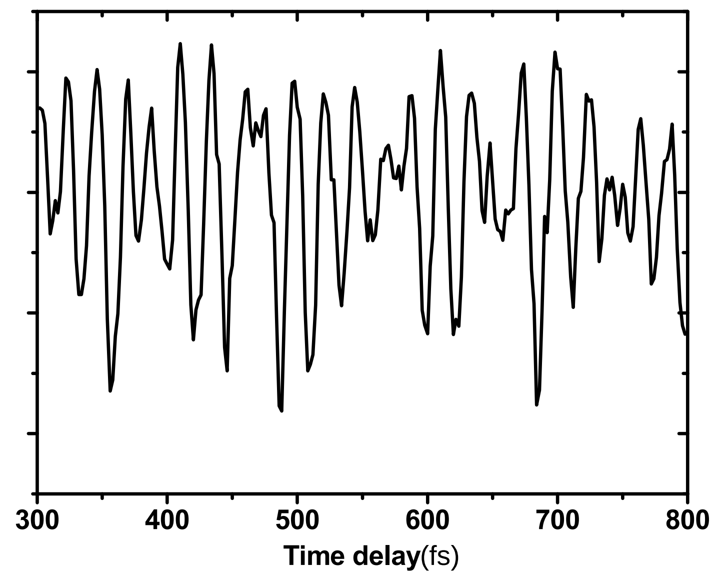




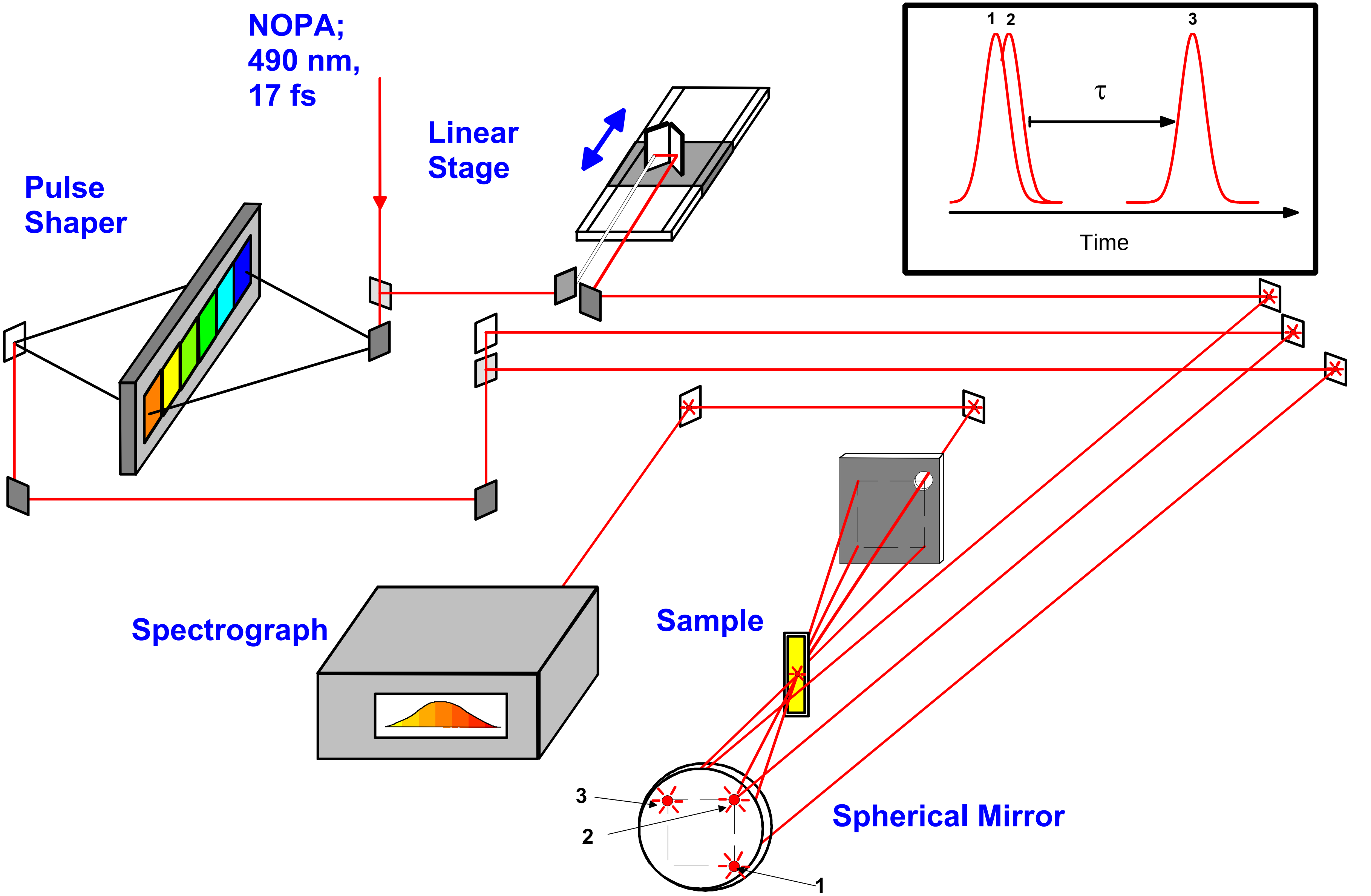
OPTIMIZATION



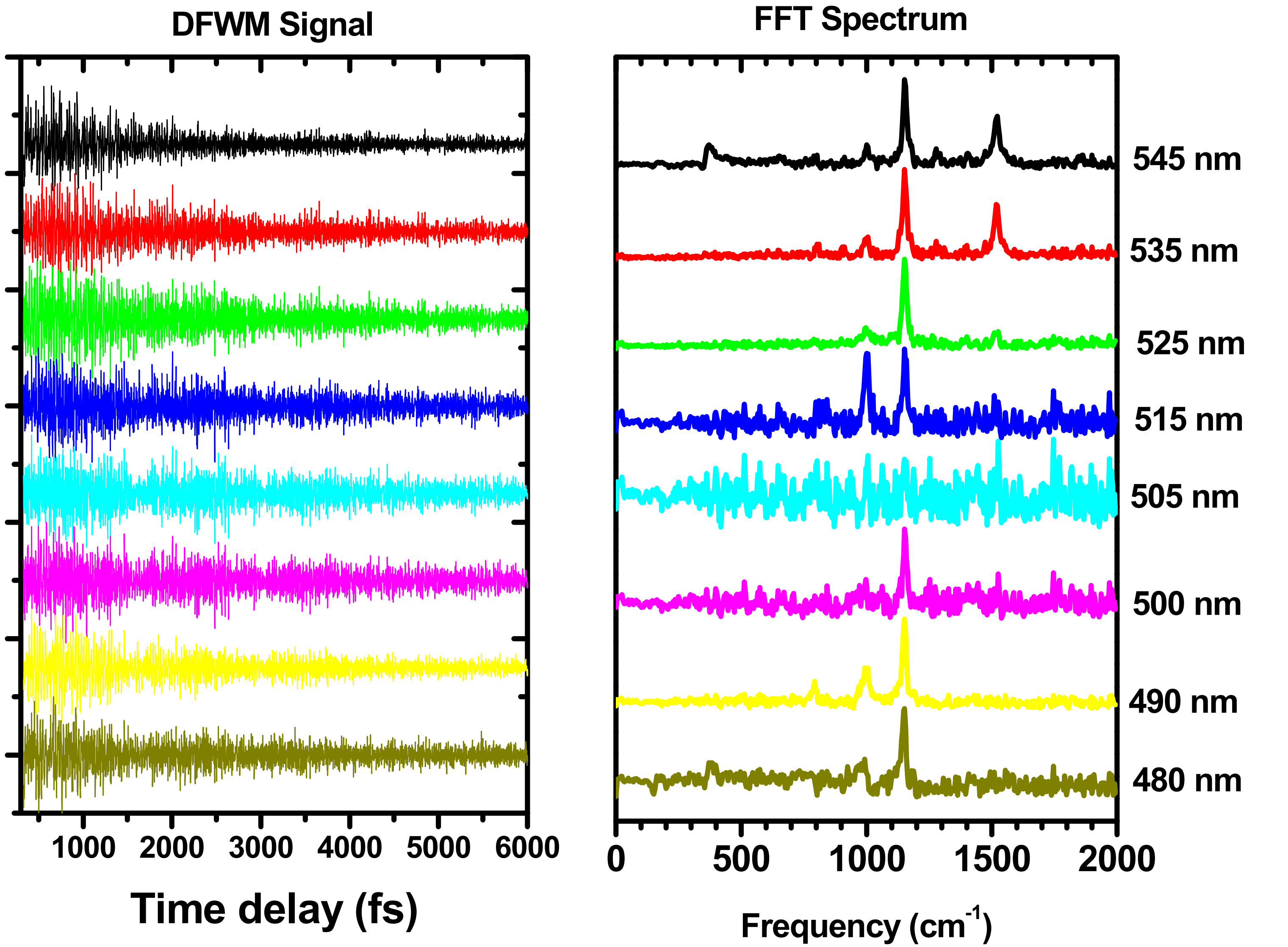




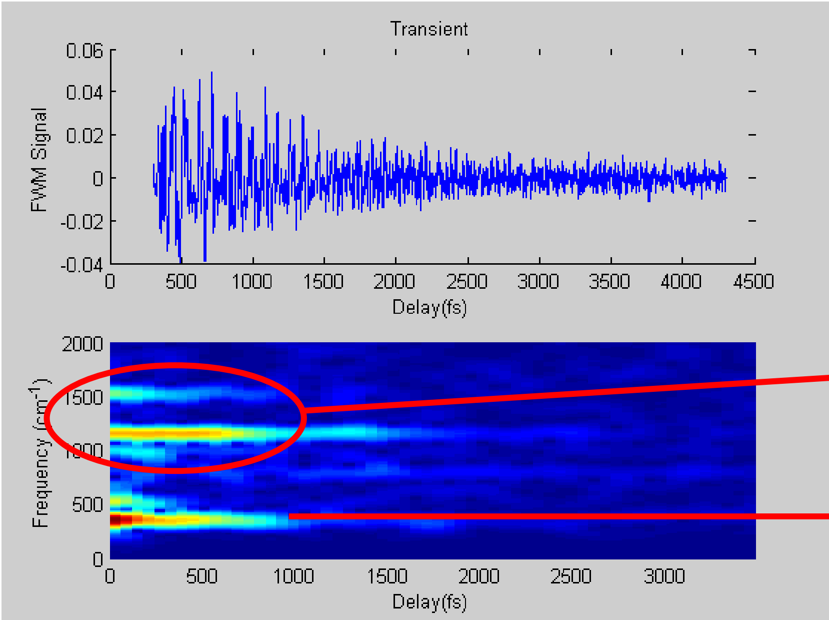
Experimental Setup



Transients taken at different detection wavelength show different patterns

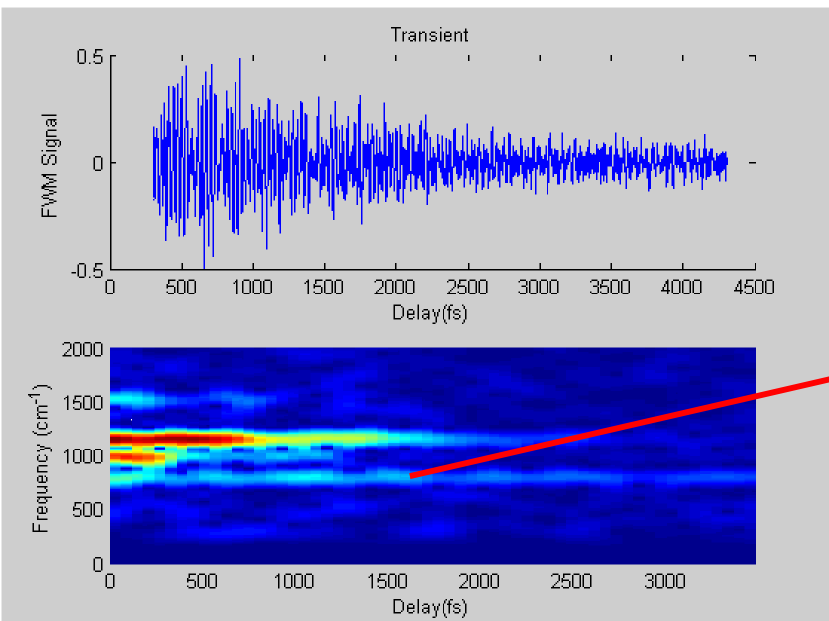


Real-time dynamics of the vibrational modes



ß-Carotene modes

Beatings between the modes



A vibrational mode of the solvent

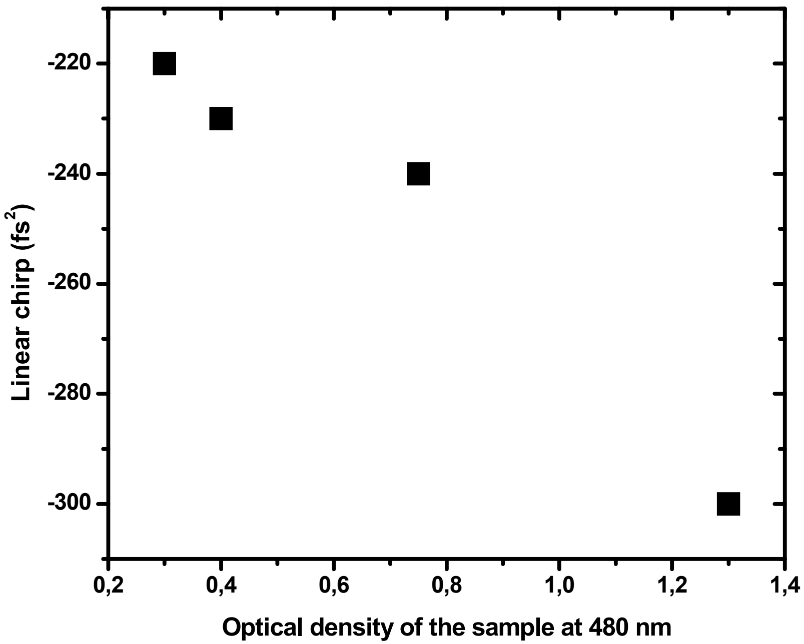
Electric field in frequency domain:

$$E(\omega)=E_0 \exp\left[-\left(\frac{\omega-\omega_0}{\Delta\omega}\right)^2\right]\exp\left[i\,\varphi(\omega)\right]$$

$$\varphi(t)=b_0+b_1(\omega-\omega_0)+b_2(\omega-\omega_0)^2+b_3(\omega-\omega_0)^3+\ldots$$

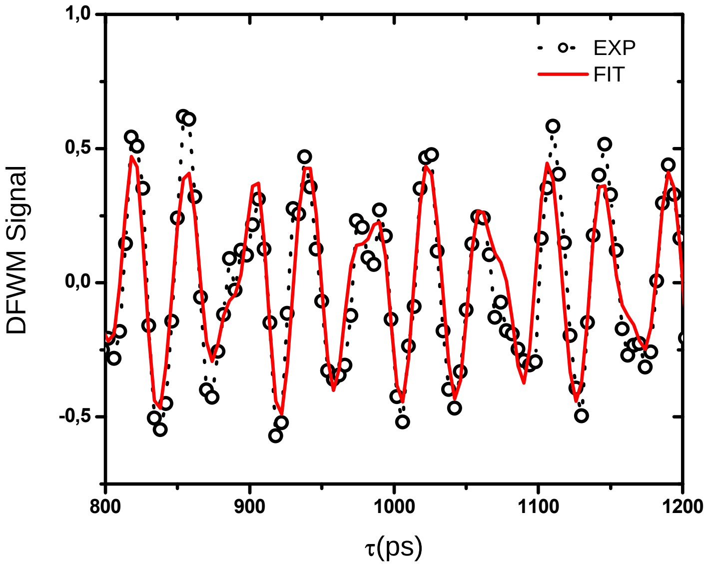
Linear Chirp

It was found that the just a linear chirp contributes to the optimal phase. The value of the chirp depends on optical density of the sample.



Time development of the vibrational modes was modeled with decaying oscillating function:

$$I(t) = \sum a_i \exp\left[-\frac{t}{\tau_i}\right] \sin(\omega_i t + \phi_i)$$



Mode	τ / ps
800	4.7 (.4)
1001	0.7 (.3)
1159	1.3 (.1)
1530	0.9 (.1)