Spectroscopy and Control *with* Ultra-Short Laser Pulses

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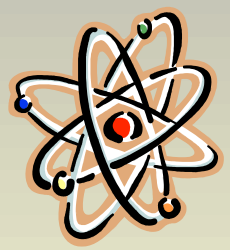
Controlled coherent excitation

- The large bandwidth and high coherence of femtosecond pulses can be exploited for controlled excitation of quantum systems.
- The subsequent evolution of those systems results from the combination of the mixture of states coherently excited and the phase and amplitude pattern of the exciting field.
- This can be used to control system behaviour, or probe the system spectrum.
- Two examples:
  - Femtosecond adiabatic passage
  - Coherent Raman spectroscopy

Outline

1. Main tools

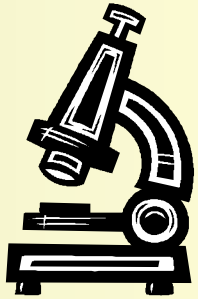
Spectral Shaping of Ultra-short Pulses



2. Quantum Control

Control of adiabatic dynamics with non-adiabatic pulses

3. Spectroscopy



Coherent spectroscopy with incoherent pulses

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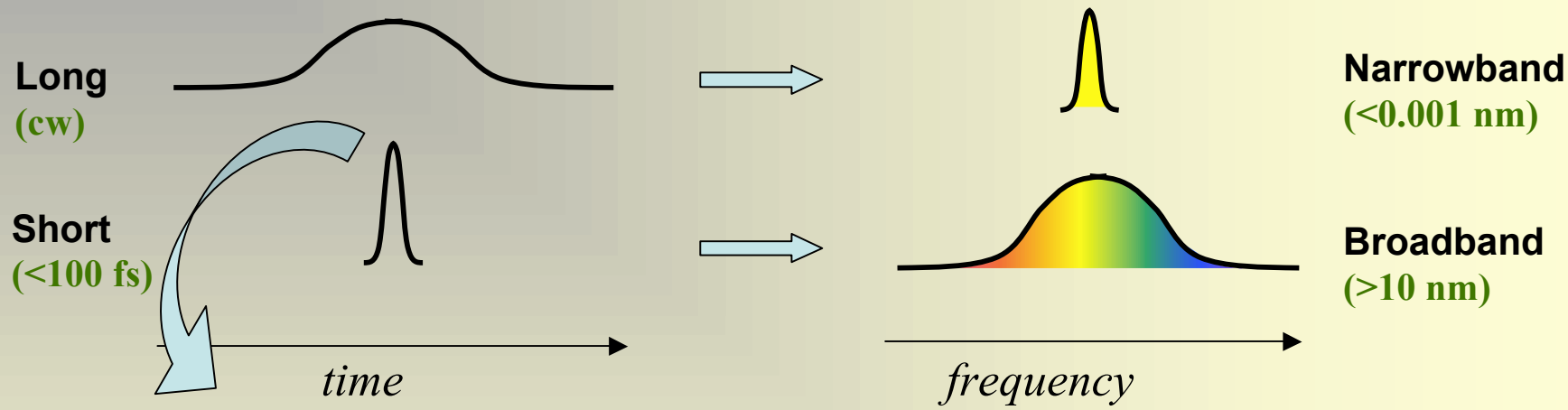
Broadband pulses



We would like to modulate field on a *femtosecond time scale*

$$E_{out}(t) = E_{in}(t) \times H(t)$$

Electro-optics too slow!

Spectral Pulse Shaping. *Principle*

Amplitude & Phase mask for individual spectral components

IN

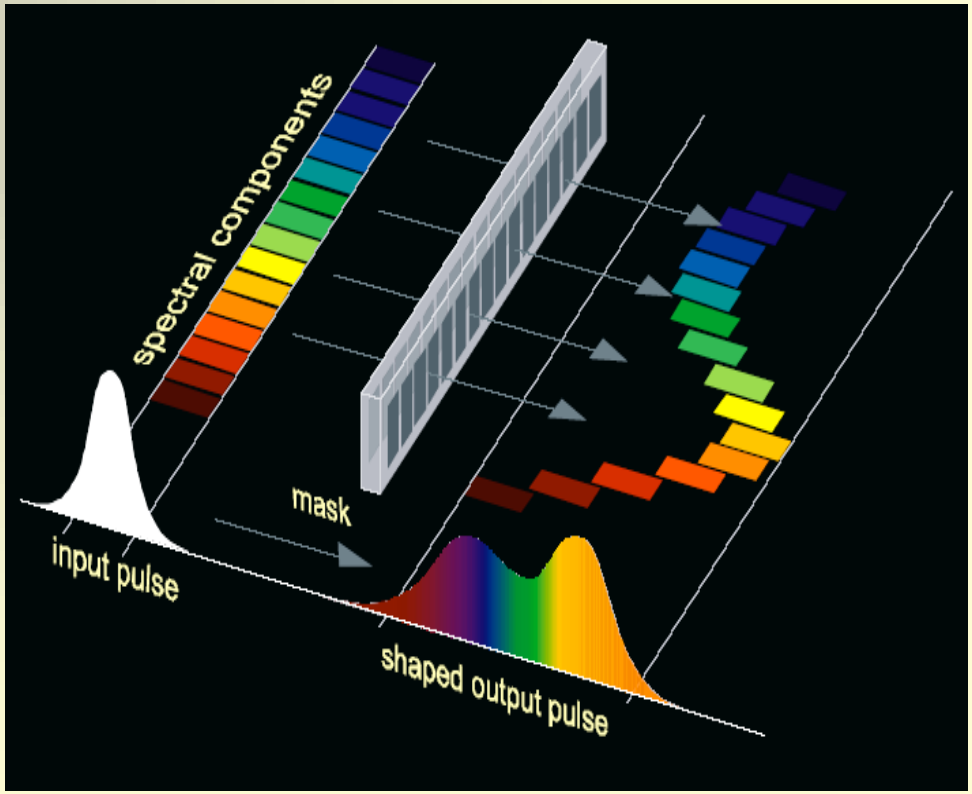
$$E_{in}(t) \xrightarrow{\text{Fourier Transform}} E_{in}(\omega)$$

$$E_{out}(\omega) = E_{in}(\omega) \times H(\omega)$$

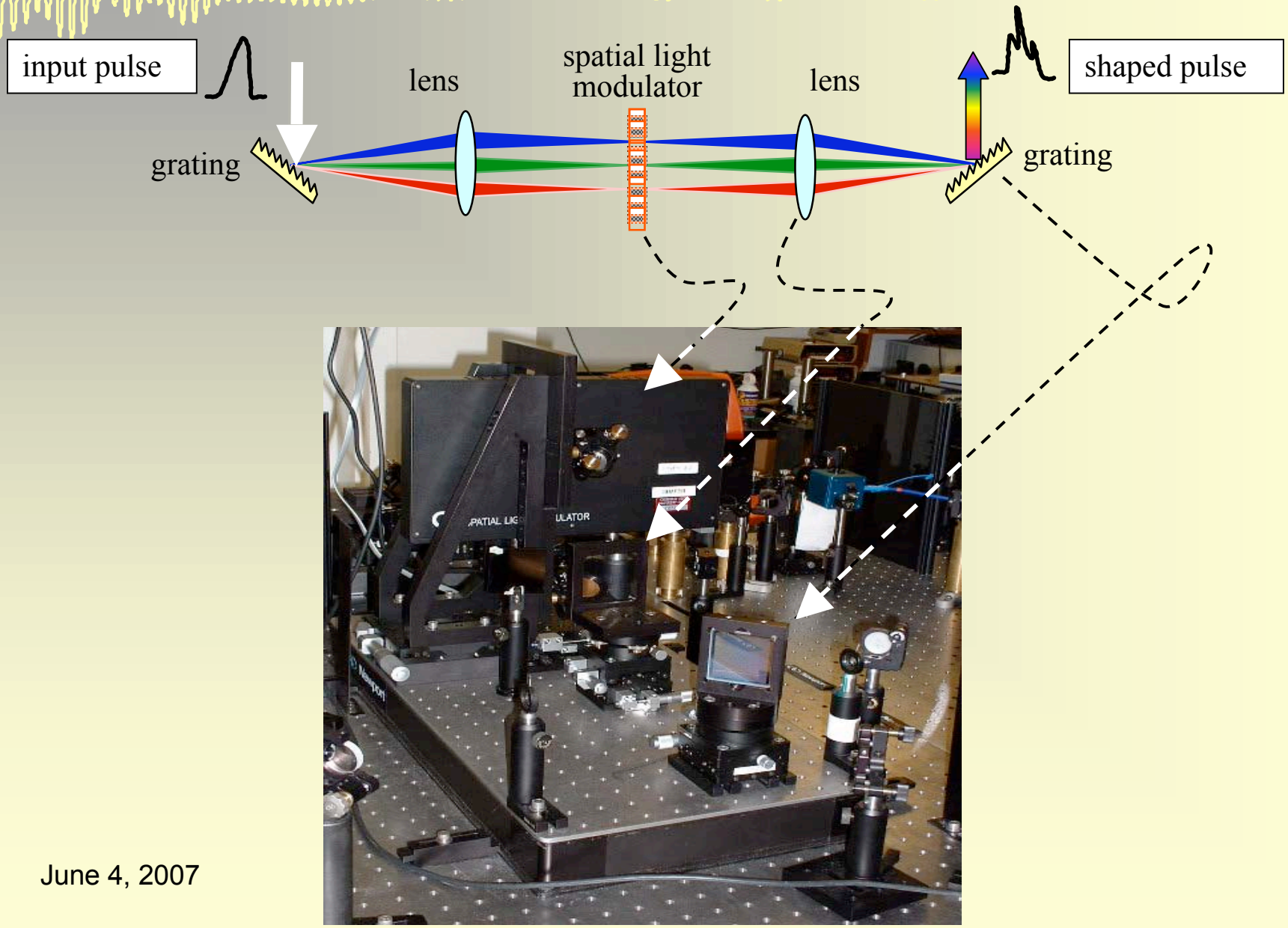
$$H(\omega) = T(\omega) \mathrm{e}^{i\varphi(\omega)}$$

$$E_{out}(\omega) \xrightarrow{\text{Fourier Transform}} E_{out}(t)$$

OUT



Spectral Pulse Shaping. *Implementation*



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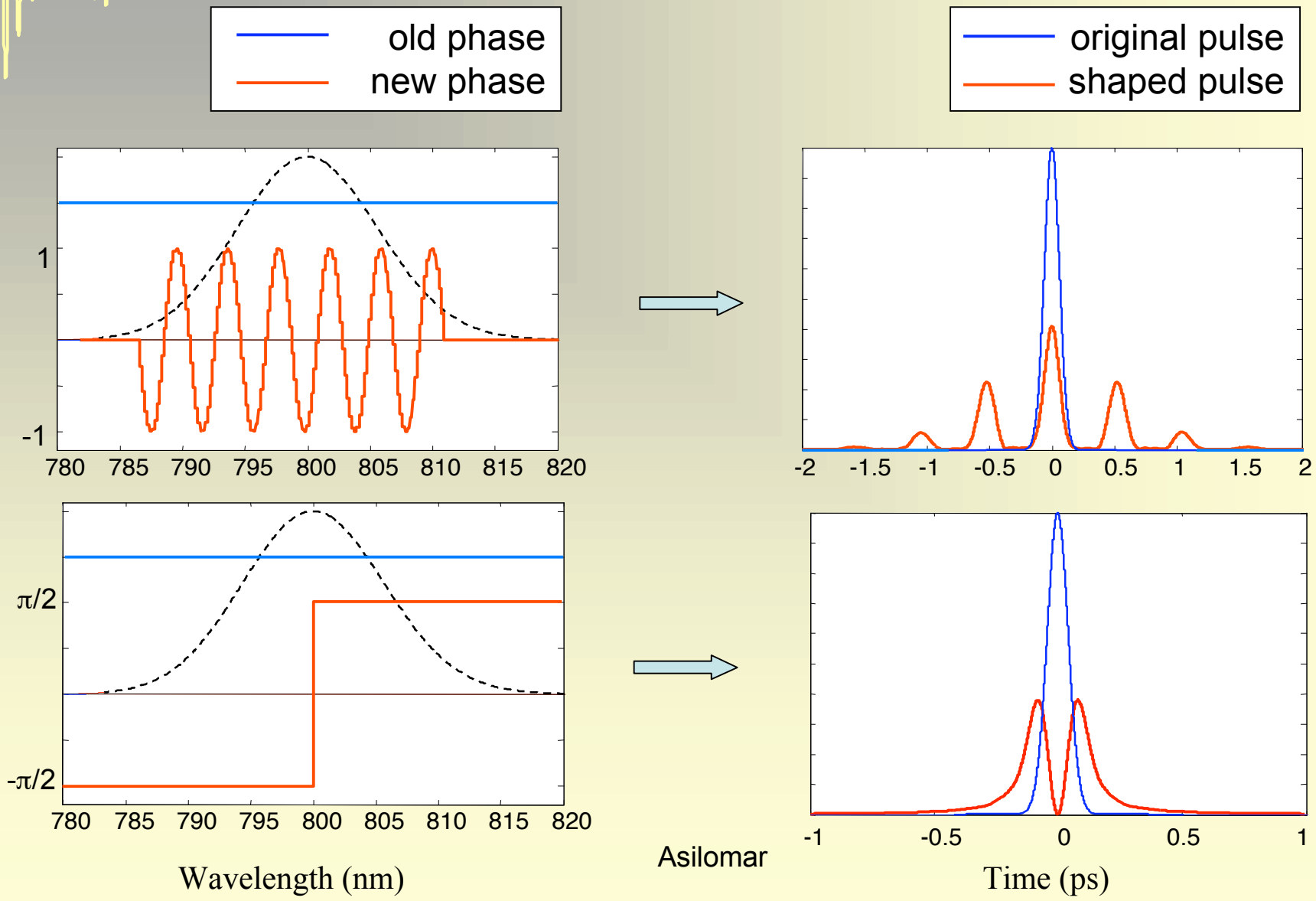
Shaped pulses. *Examples*



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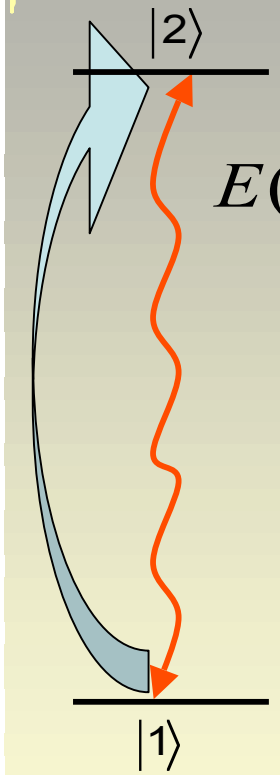
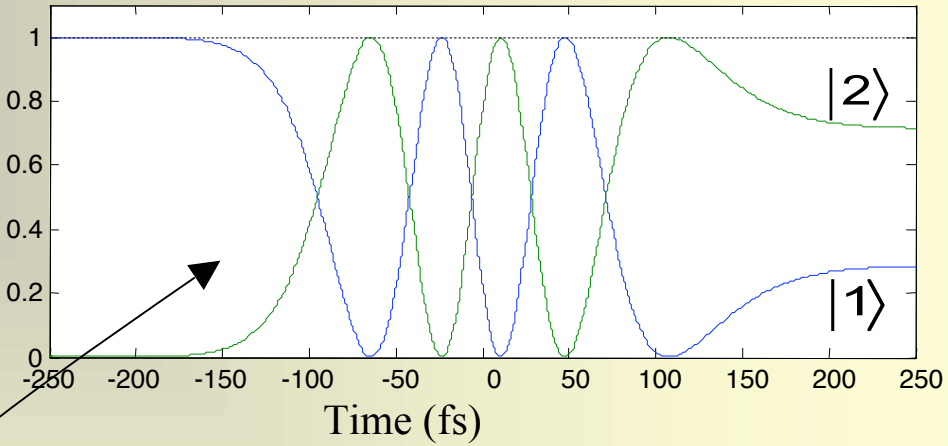
Application I. *Quantum control*

Non-adiabatic population transfer between two quantum states



$$E(t)e^{i\omega_0 t+\varphi(t)}$$



$$|\psi_2|^2 = \cos^2(\Omega t)$$

$$\Omega = \mu_{12}E(t)/\hbar$$

$$\varphi(t) \equiv 0$$

Constant phase

Rabi oscillations:

+ Fast
- Sensitive to precise timing
- Sensitive to exact frequency
- Sensitive to phase coherence

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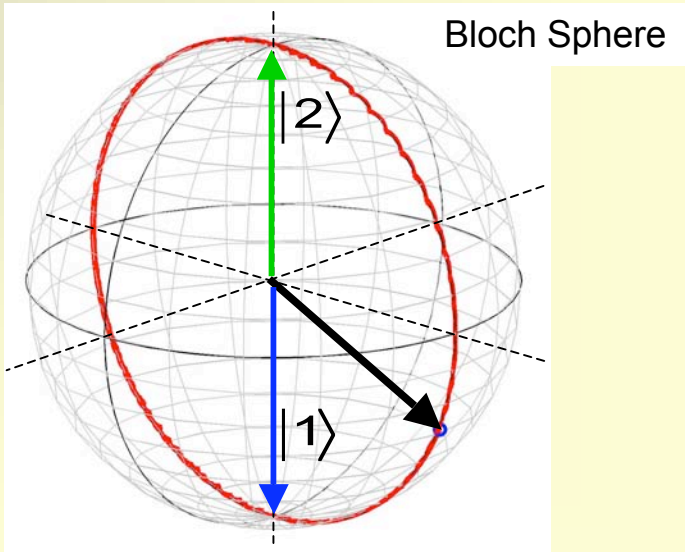
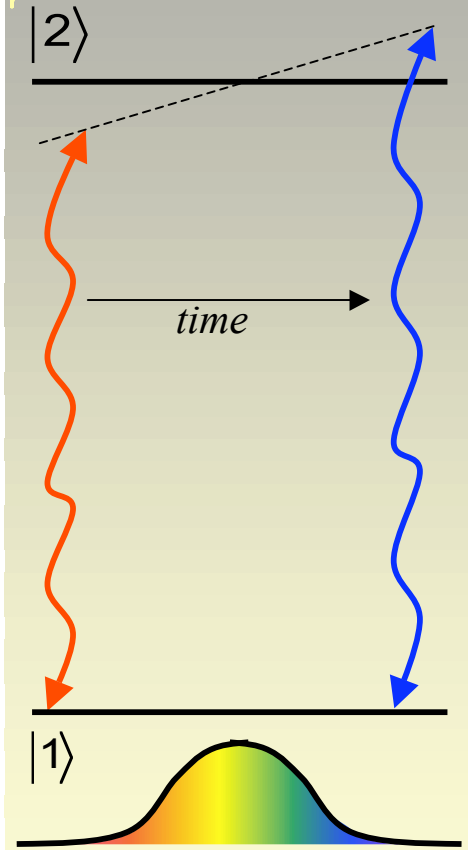


Application I. *Quantum control*

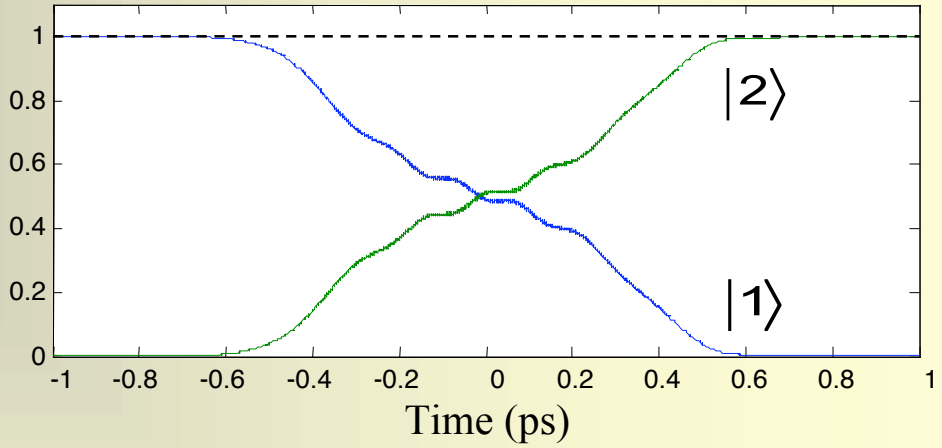
Adiabatic population transfer between two quantum states



$$E(t)e^{i\omega_0 t+\varphi(t)}$$

$$\omega \equiv \omega(t)$$

$$= \omega_0 + \frac{d}{dt}\varphi(t)$$



Adiabaticity: pulses are long on the time scale of system's evolution

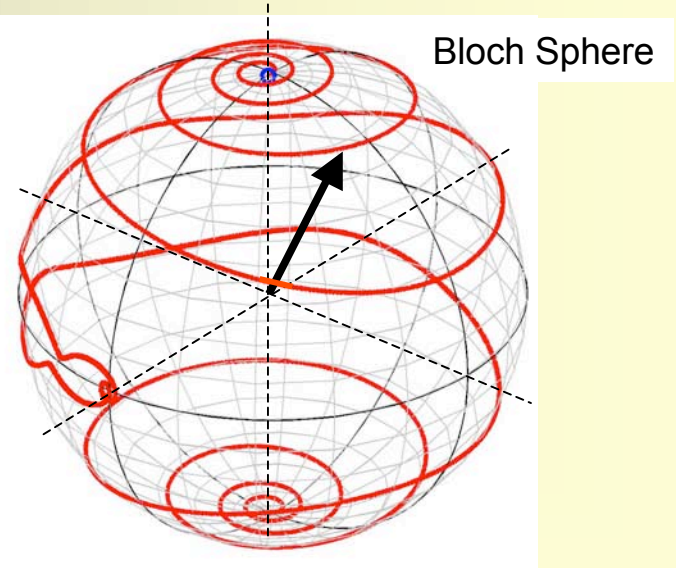
$$\frac{d}{dt}\Delta(t) << \left(\Omega(t)\right)^2$$

Adiabatic passage:

+ Slower but still fast
+ Much more robust

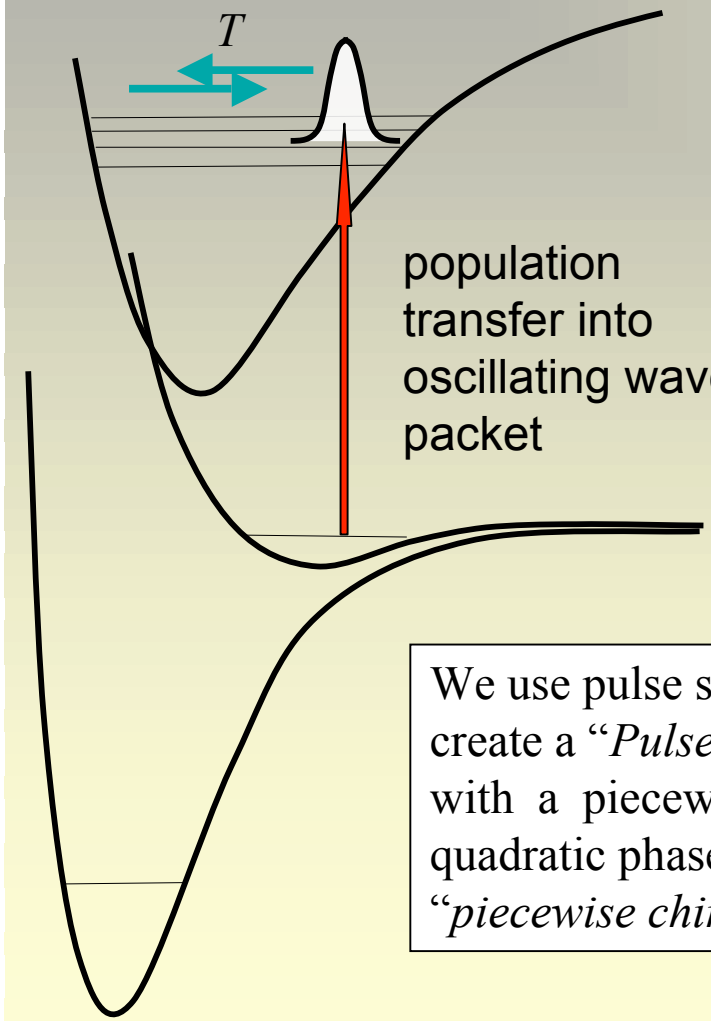
$$\varphi(t) \propto t^2 \rightarrow \omega(t) \propto t$$

Frequency chirping



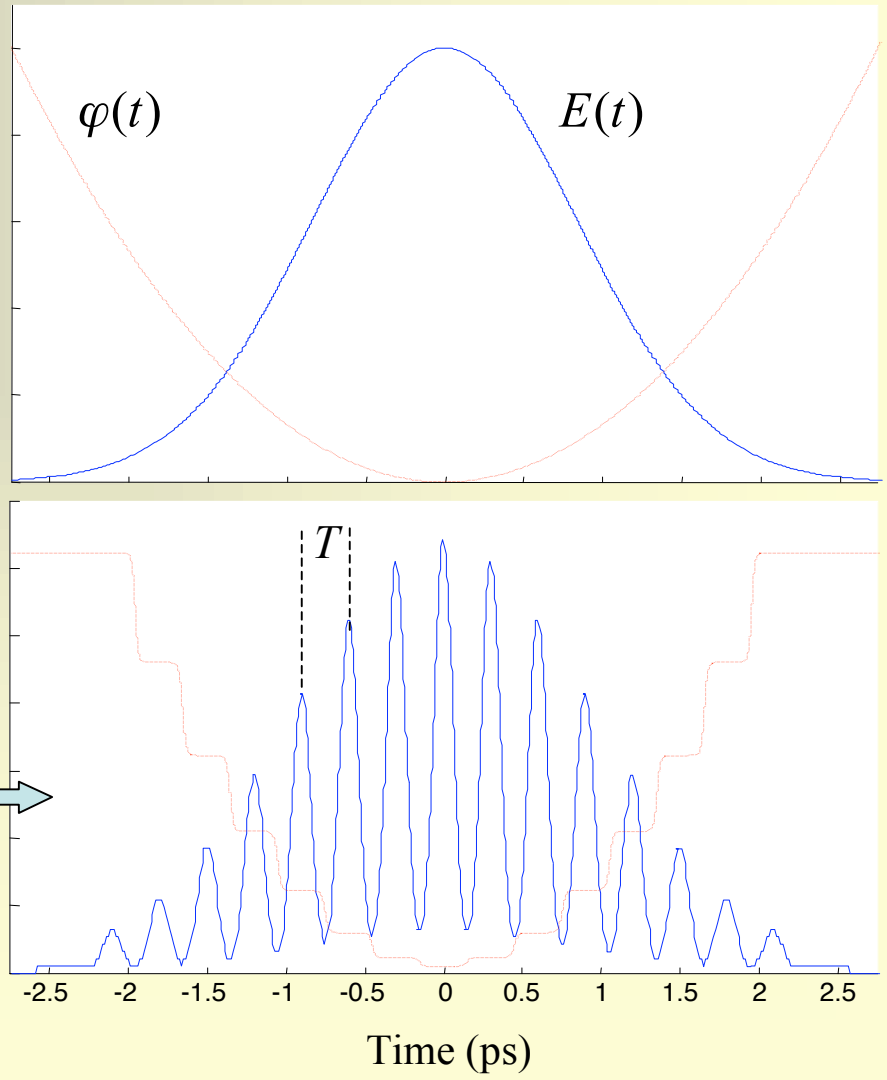
Piecewise Adiabatic Passage

What if the dynamics is fast even on a picosecond scale ?

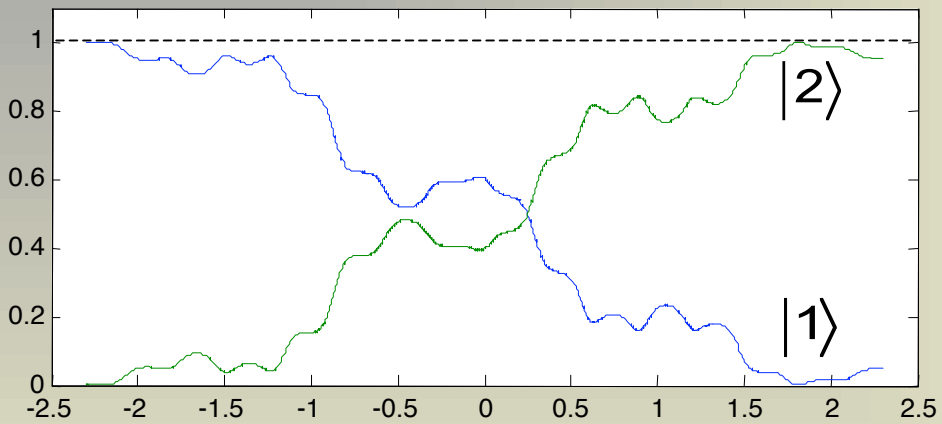


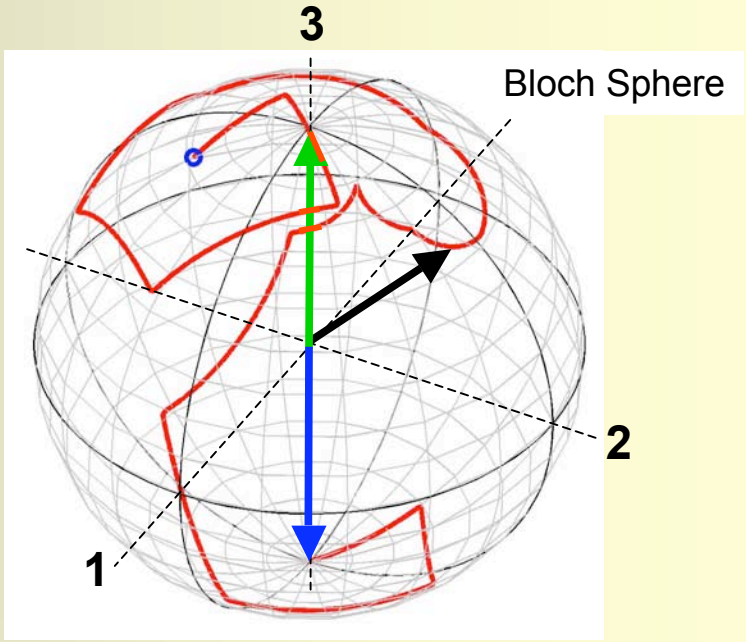
population transfer into oscillating wave packet

We use pulse shaping to create a "*Pulse train*" with a piecewise quadratic phase or a "*piecewise chirp*"



Piecewise Adiabatic Passage





Dynamics of the state vector is a series of rotations:

State vector adiabatically follows the axis of rotation !

$$\hat{R} = \prod \hat{R}_{Rabi} \times \hat{R}_{\varphi}$$

$$\left.\begin{aligned} \hat{R}_{Rabi} &= \hat{R}_1(\Omega\tau) \\ \hat{R}_{\varphi} &= \hat{R}_3(\Delta\varphi) \\ \hat{R}_{Rabi} \times \hat{R}_{\varphi} &= \hat{R}_{(\theta,\phi)}(\alpha) \end{aligned}\right\}$$

$$\left.\begin{aligned} \alpha &= \sqrt{(\Omega\tau)^2/2 + (\Delta\varphi)^2/2} \\ \phi &= \pm\pi/2 - \Delta\varphi/2 \\ \tan(\theta) &= \pm\frac{\Omega\tau}{\Delta\varphi} \end{aligned}\right\}$$

1. Start : $\Omega\tau << \Delta\varphi \rightarrow \theta = 0$
2. Middle : $\Omega\tau >> \Delta\varphi \rightarrow \theta = \pi/2$
3. End : $\Omega\tau << \Delta\varphi \rightarrow \theta = \pi$

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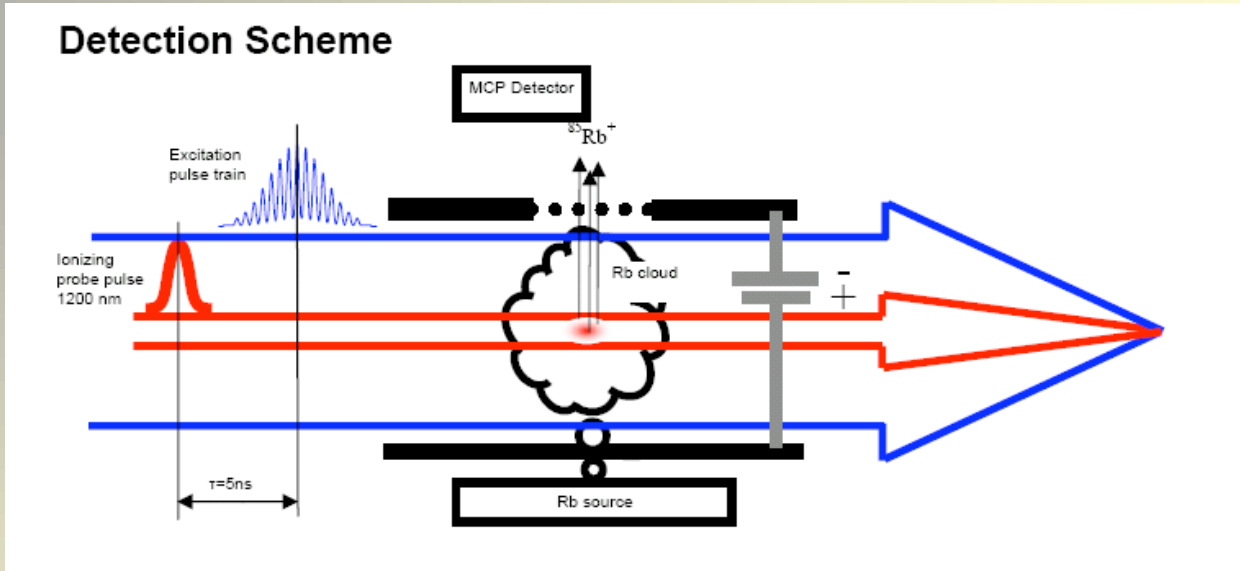
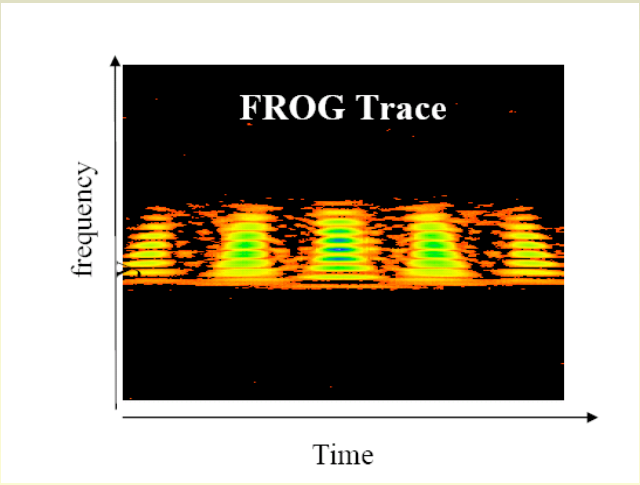
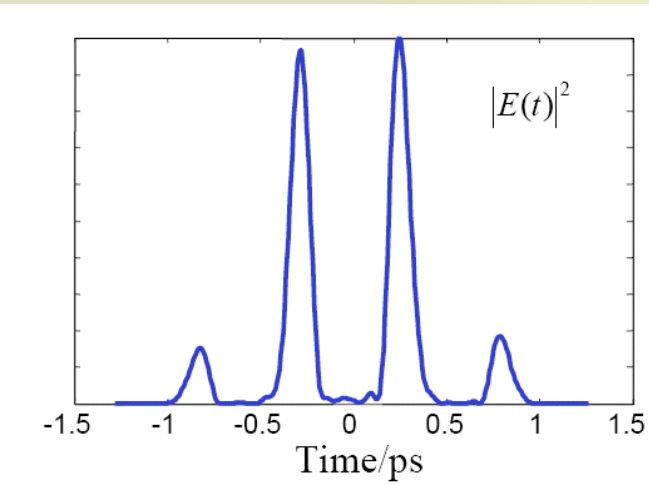
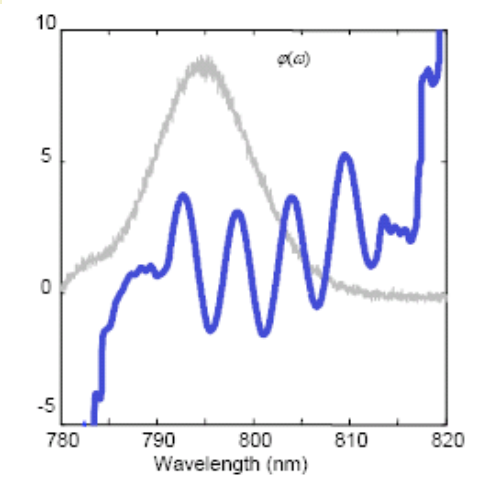
Preliminary results: ^{85}Rb 5s→5p Piecewise Adiabatic Passage









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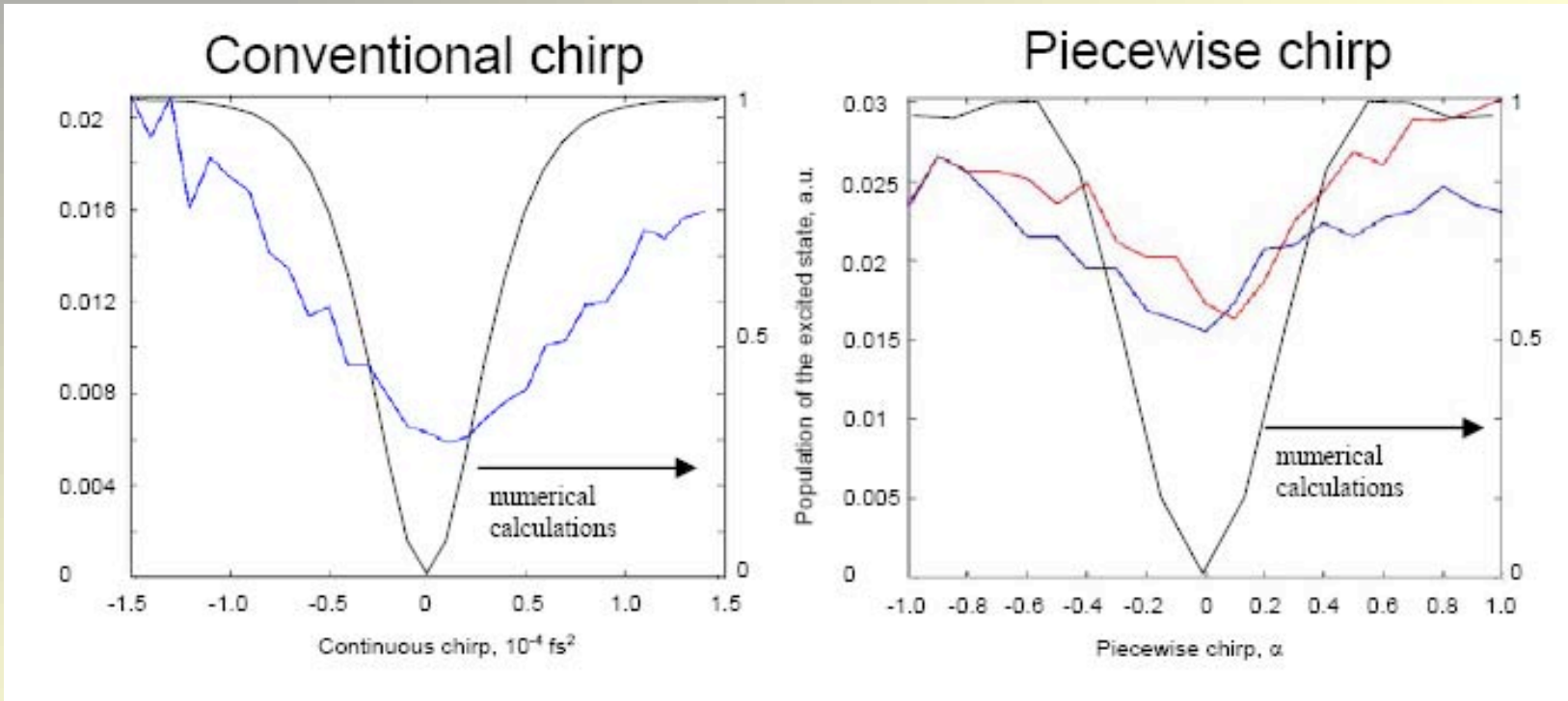
Very preliminary results



Rb 5p population as a function of chirp

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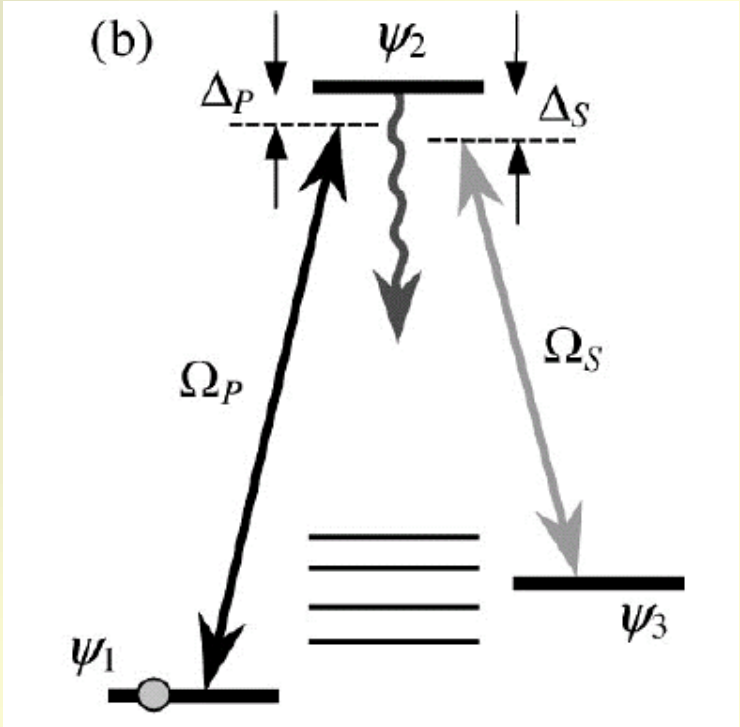
Stimulated Raman population transfer

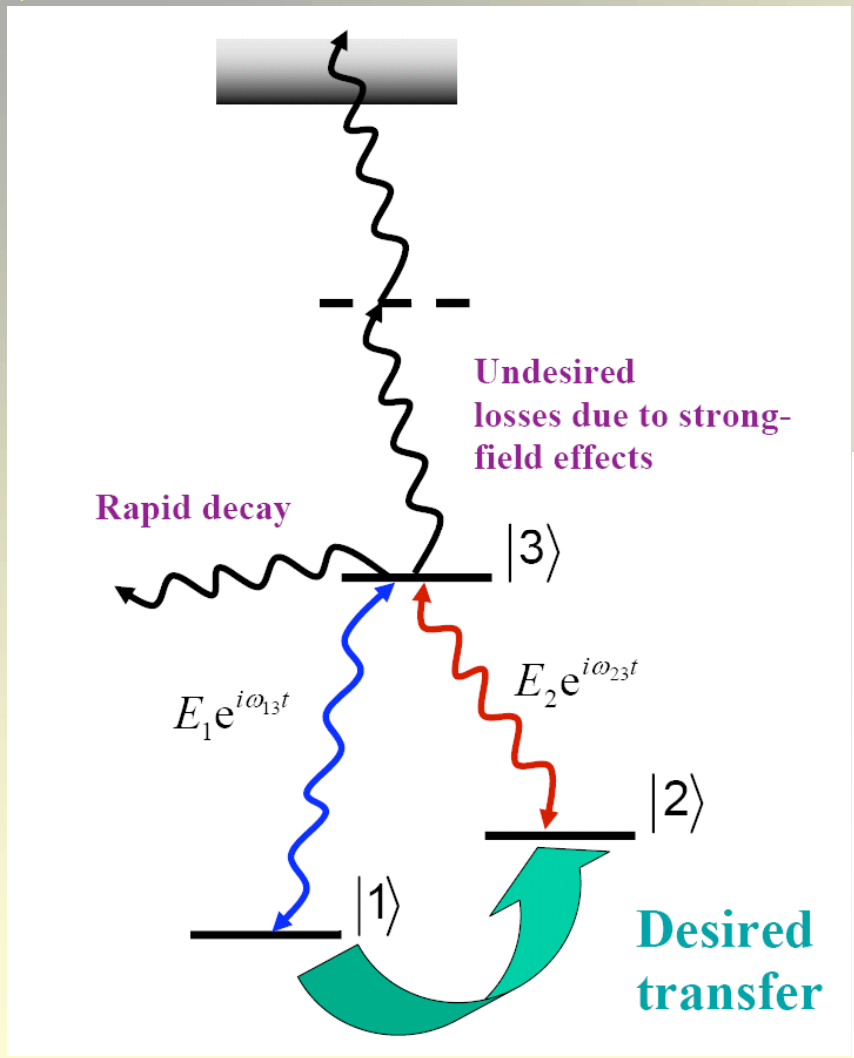
- To reach optically inaccessible states, or to cool highly vibrationally excited molecules
  - Example: cooling ultracold molecules formed by photo-association
- Need to use Raman type transitions:

  Ω_P connects Ψ_1 and Ψ_2 (pump)

  Ω_S connects Ψ_2 and Ψ_3 (Stokes)



Stimulated Raman Adiabatic Passage: STIRAP



- Create a state that evolves from |1> to |2> without developing amplitude in |3>
- Do this by starting with ω_{23}, then applying ω_{13}: counter-intuitive ordering

$$\psi(t) = a_1 e^{i\omega_1 t}|1\rangle + a_2 e^{i\omega_2 t}|2\rangle + a_3 e^{i\omega_3 t}|3\rangle$$

$$\frac{\hbar}{i}\frac{d}{dt}\bar{a}(t) = \hat{H}\bar{a}(t), \quad \bar{a} \equiv (a_1, a_2, a_3)$$

$$\hat{H} = \begin{pmatrix} 0 & \mu_{13}E_1 & 0 \\ \mu_{31}E_1^* & 0 & \mu_{32}E_2 \\ 0 & \mu_{23}E_2^* & 0 \end{pmatrix}$$

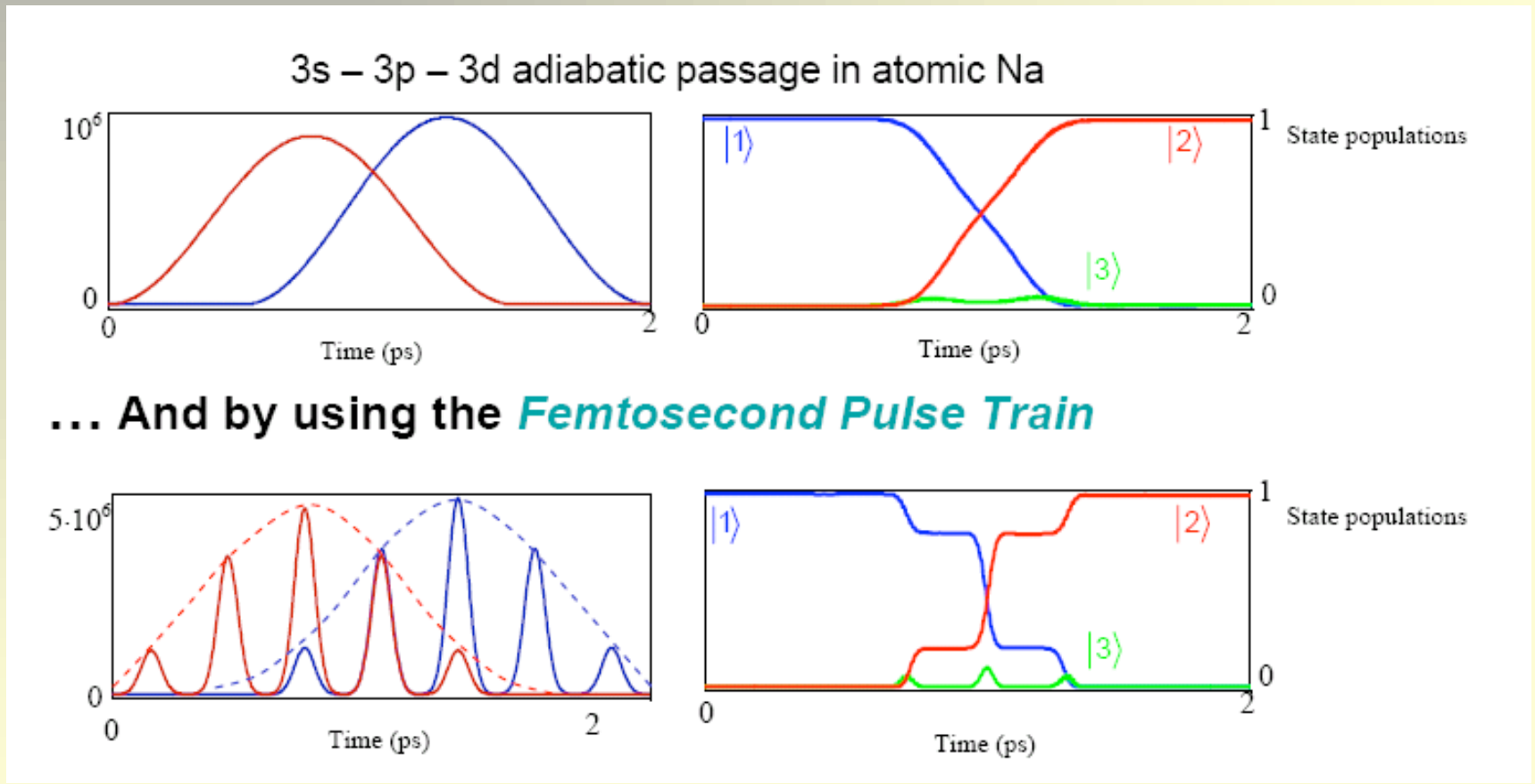
… By creating the *Dark State* with counter-intuitive pulse sequence…

$$\psi_0(t) \propto \mu_{23}E_2|1\rangle - \mu_{31}E_1^*|2\rangle$$

$$\hat{H}\psi_0(t) \equiv 0$$

Simulations for Na

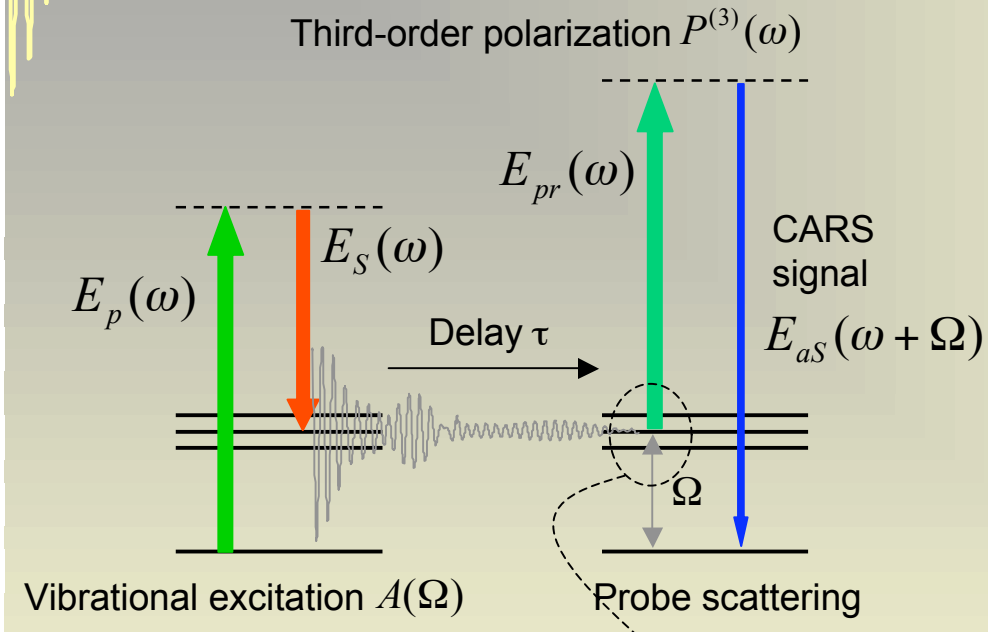
Again, to avoid problems caused by longer pulses, can use a pulse sequences.



Piecewise Adiabatic Passage. *Summary*

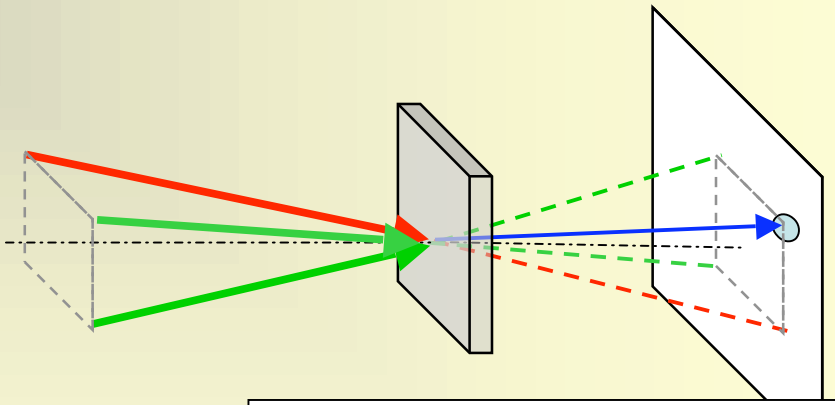
- Spectral pulse shaping enables creation of femtosecond pulse trains with predefined temporal amplitude and phase
- Tailoring the amplitude and phase of the pulses in the train allows to mimic traditional (continuous) adiabatic passage in a piecewise manner
- Piecewise adiabatic passage is as robust (vs intensity and timing) as the traditional adiabatic passage
- Piecewise adiabatic passage offers new possibilities of controlling quantum dynamics of complex systems on a femtosecond time scale
- Theory: accepted to *PRL*
- Experiment: underway

Application II. *Ultrafast Spectroscopy*



Coherent anti-Stokes Raman Scattering

- Coherent (directional): easy to detect
- Non-resonant (electronic): low fluorescence background
- High efficiency: low average power, non-invasive imaging in bio-applications
- Low non-resonant background

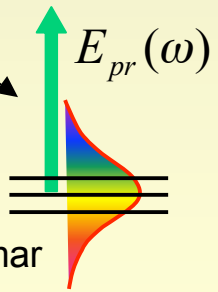


Ultrafast CARS

- High time resolution (< 10^{-12} s) !

  BUT

- Poor spectral resolution (>100 cm^{-1})



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Improve spectral resolution?

- Scan time delay, then do Fourier transform (too long…)
- Reduce bandwidth (waste of energy or too many lasers)
- **PULSE SHAPING !**

CARS with shaped pulses

In time

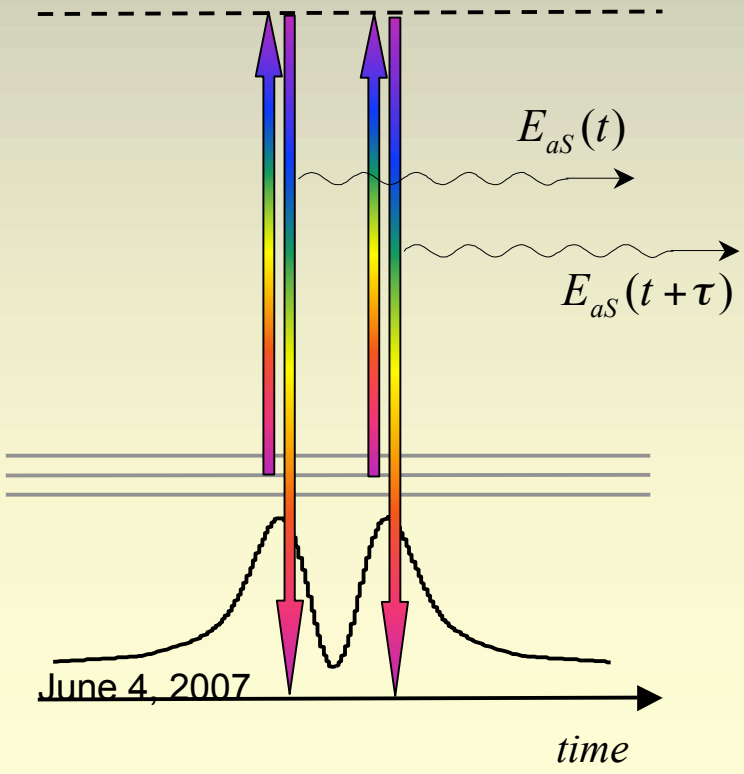
$$A(t) = C_{NR} + \sum C_n \exp(i\Omega_n t - \Gamma_n t)$$

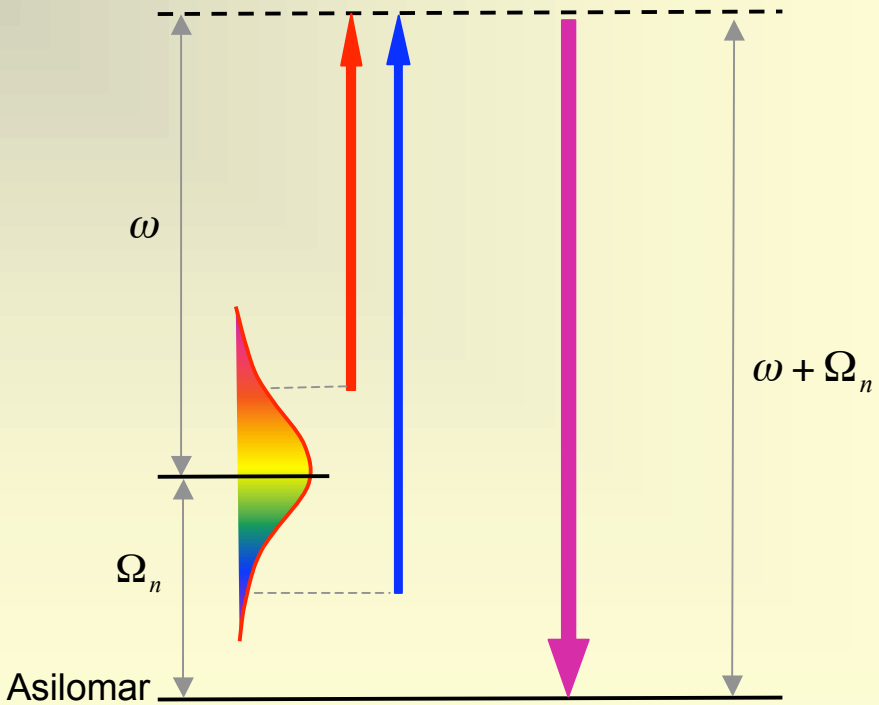
$$E_{aS}(t) \propto P^{(3)}(t) \propto A(t)E_{pr}(t)$$

In frequency

$$A(\Omega) = C_{NR} + \sum \frac{C_n}{\Omega - \Omega_n + i\Gamma_n}$$

$$E_{aS}(\omega) \propto P^{(3)}(\omega) \propto \int A(\Omega)E_{pr}(\omega - \Omega)d\Omega$$

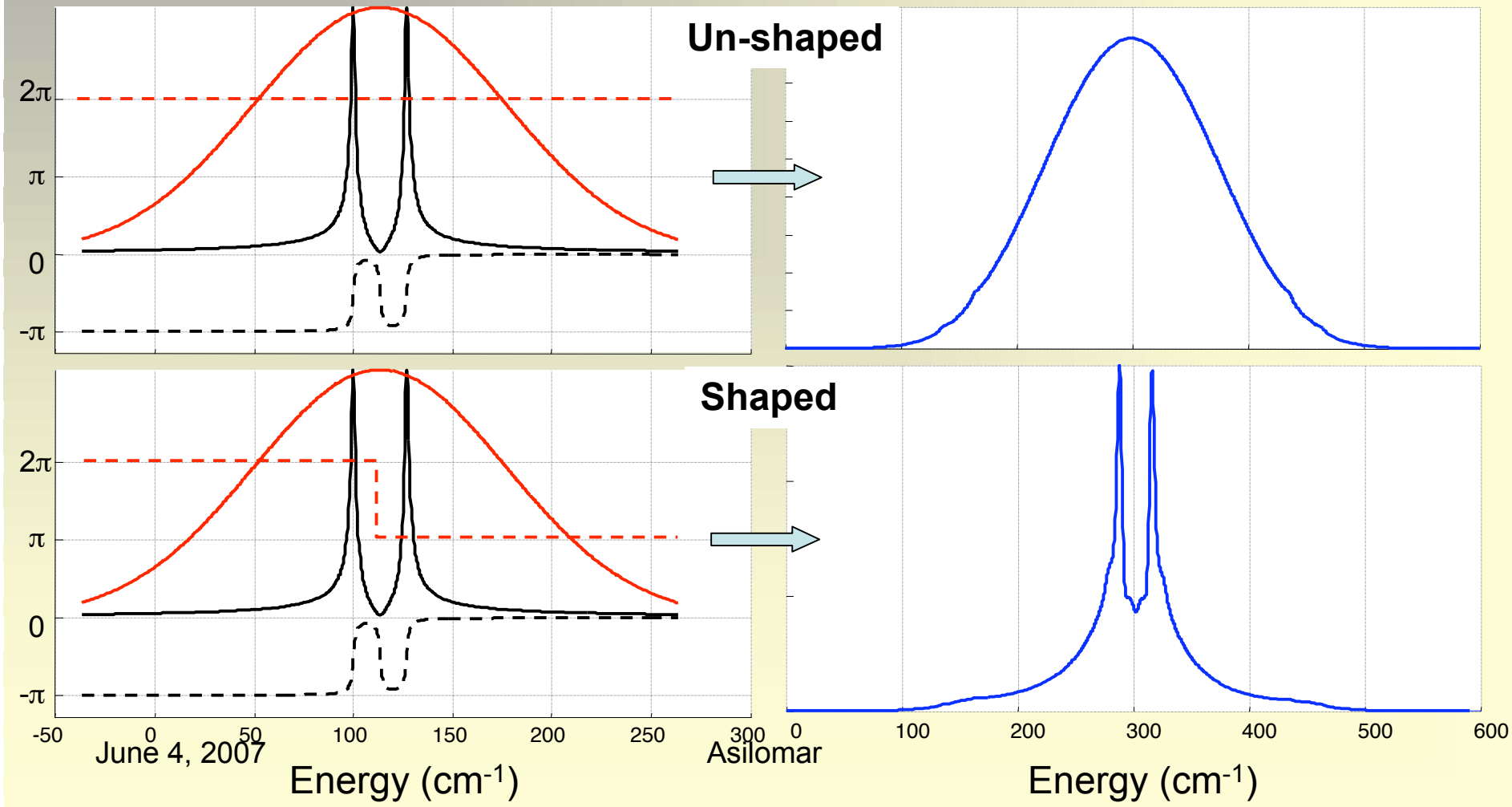




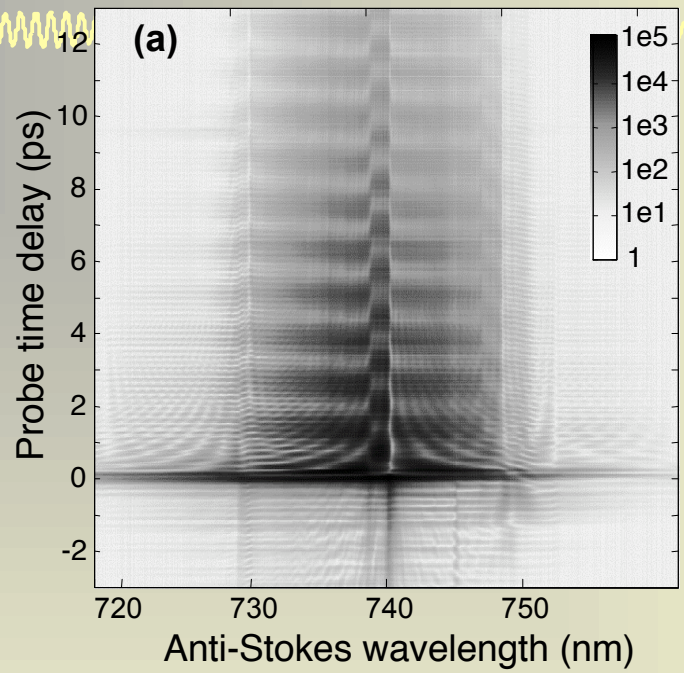
CARS with shaped pulses

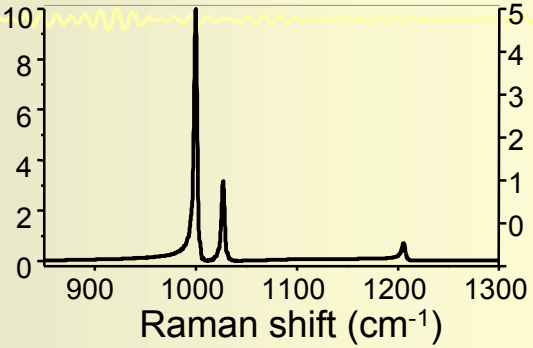
Vibration: — *amplitude;* - - - *phase*
Probe field: — *amplitude;* - - - *phase*

CARS spectrum $I_{aS}(\omega) \propto \left|E_{aS}(\omega)\right|^2$

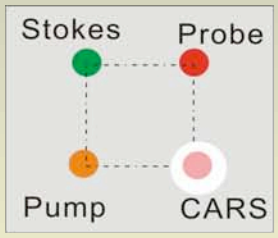


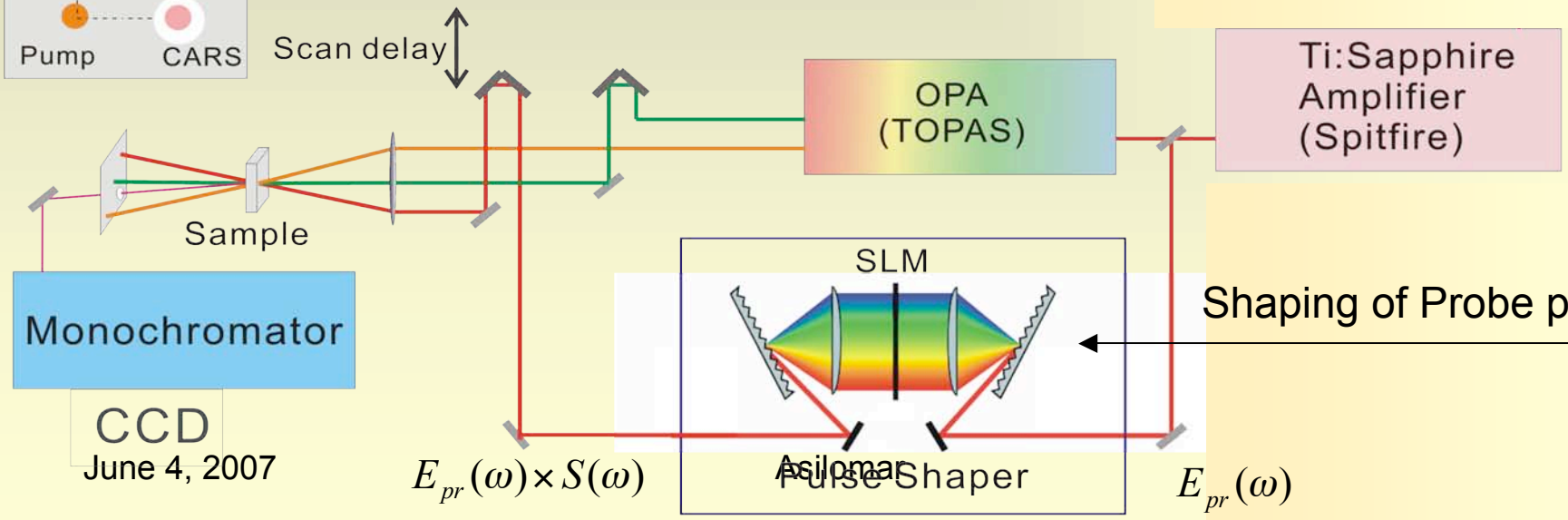
CARS with shaped pulses. *Experiment*





Raman spectrum of Toluene





Shaping of Probe pulse

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Good news and bad news

- Recovery technique analogous to cross-correlation frequency resolved optical gating (XFROG), standard technique used to measure femtosecond pulses.
- We recover full phase and amplitude information about the system – locations and decoherence times of all resonances
- However, this technique requires knowledge of the probe field, and controlled phase coherence of that field
- Also, requires a scan of the time delay, resolution determined by the maximum time delay
- A “scan-less” method would be better
- Complex media (i.e. cells) introduce incoherence in the probe that cannot be corrected for

Correlations in CARS spectrum

Assuming two infinitely narrow resonances :

$$E_{aS}(t) = E_{pr}(t) \times (e^{i\Omega_1 t} + e^{i\Omega_2 t})$$

Intensity spectrum is the Fourier transform of the field correlation function :

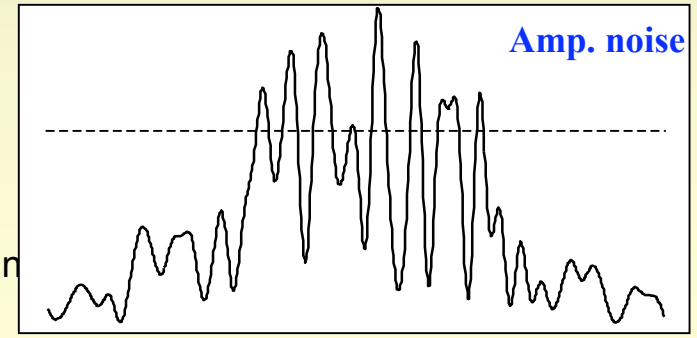
$$G_{E_{aS}}(\tau) = \int E_{aS}(t) E_{aS}^{*}(t-\tau) dt = G_{E_{pr}}(\tau) \times \left(e^{i\Omega_1 \tau} + e^{i\Omega_2 \tau}\right)$$

Applying Fourier transform :

$$I_{aS}(\omega) = I_{pr}(\omega + \Omega_1) + I_{pr}(\omega + \Omega_2)$$

Thus, resonances introduce new correlations in the spectrum :

$$G_{I_{aS}}(\Delta\omega) = 2G_{I_{pr}}(\Delta\omega) + G_{I_{pr}}(\Delta\omega + \delta\Omega) + G_{I_{pr}}(\Delta\omega - \delta\Omega)$$



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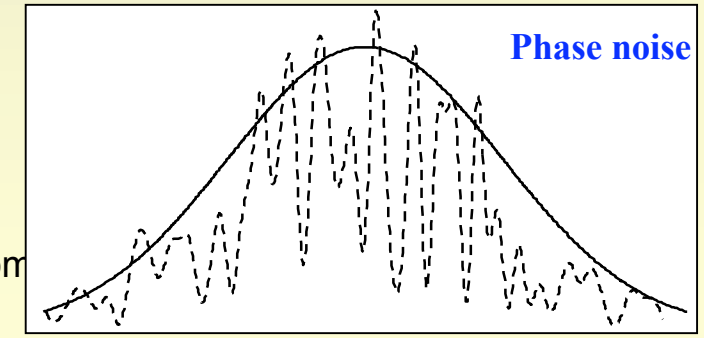

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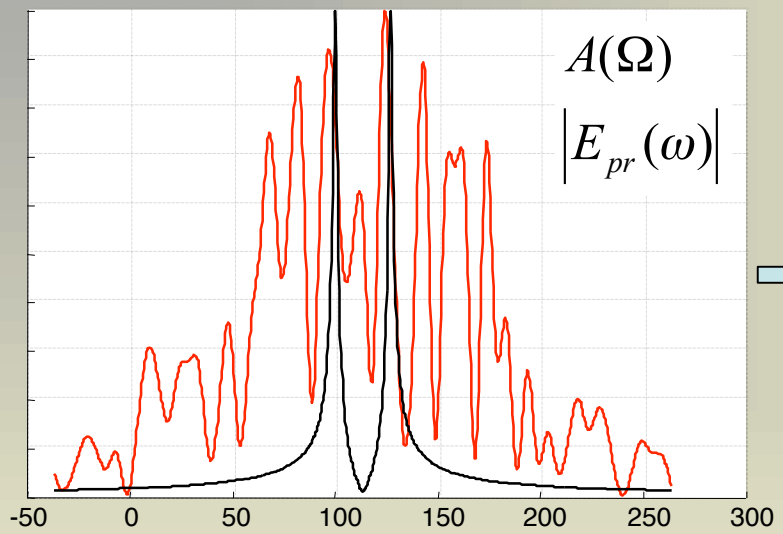
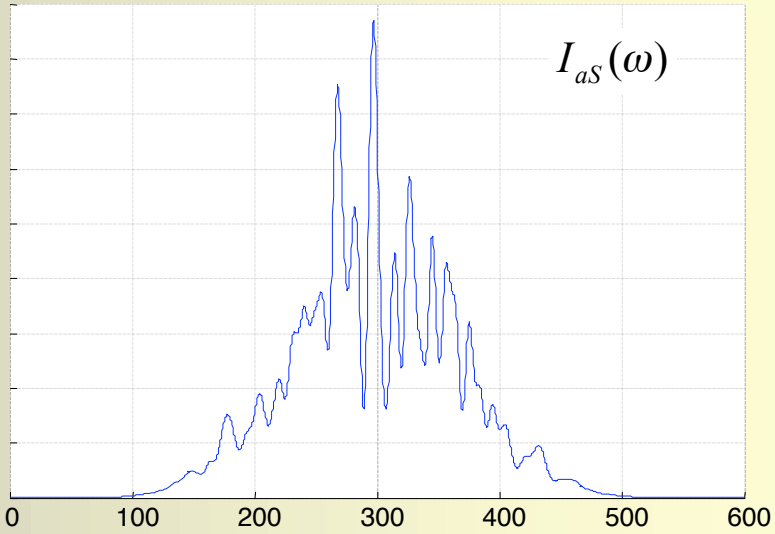
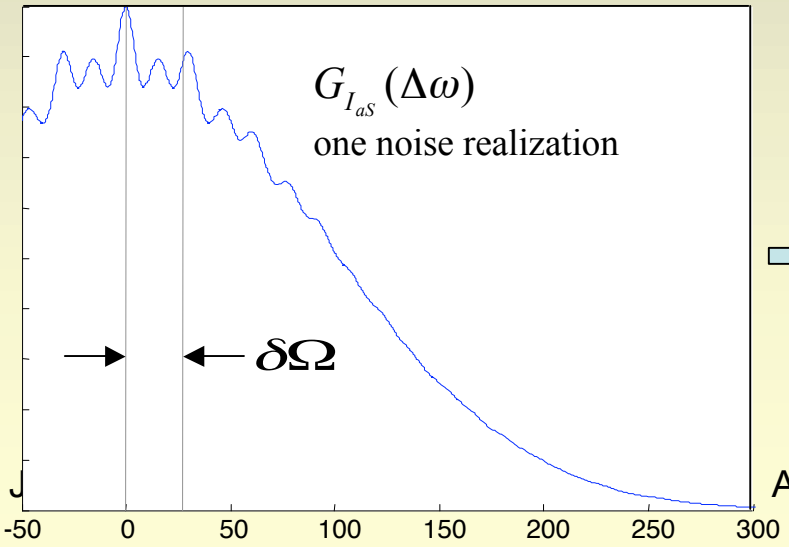
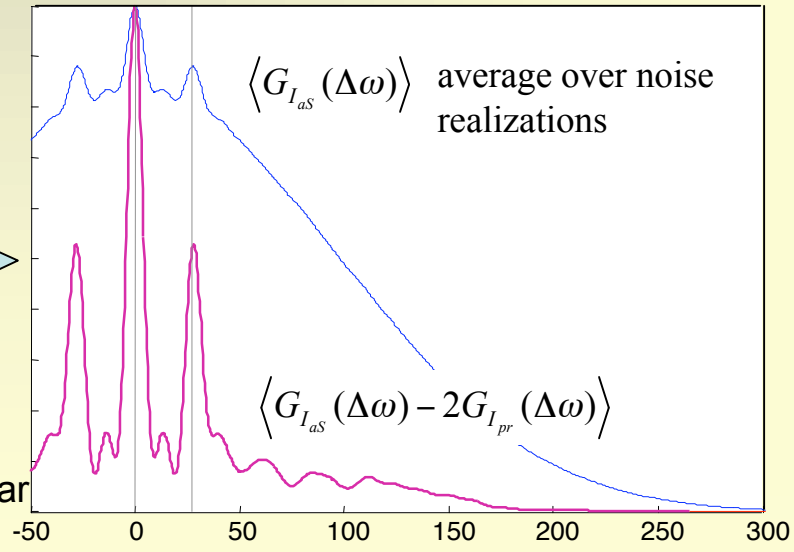
CARS with *noisy* pulses. *Calculations*









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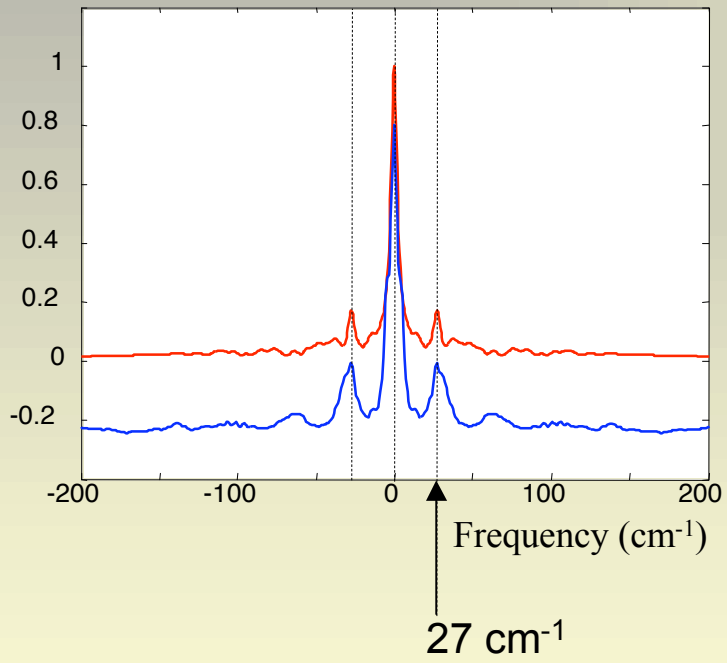
CARS with *noisy* pulses. *Experiment*

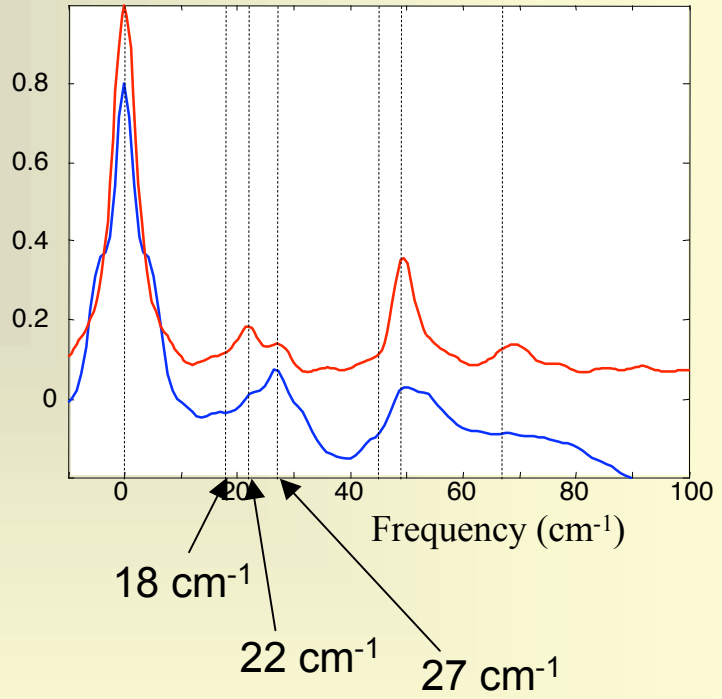
Toluene

$\Omega_n = (1000,\ 1027)\ \mathrm{cm}^{-1}$



Toluene + Ortho-xylene

$\Omega_n = (982,\ 1000,\ 1027,\ 1049)\ \mathrm{cm}^{-1}$



Resolution is determined by the granularity of noise (not by the pulse bandwidth)

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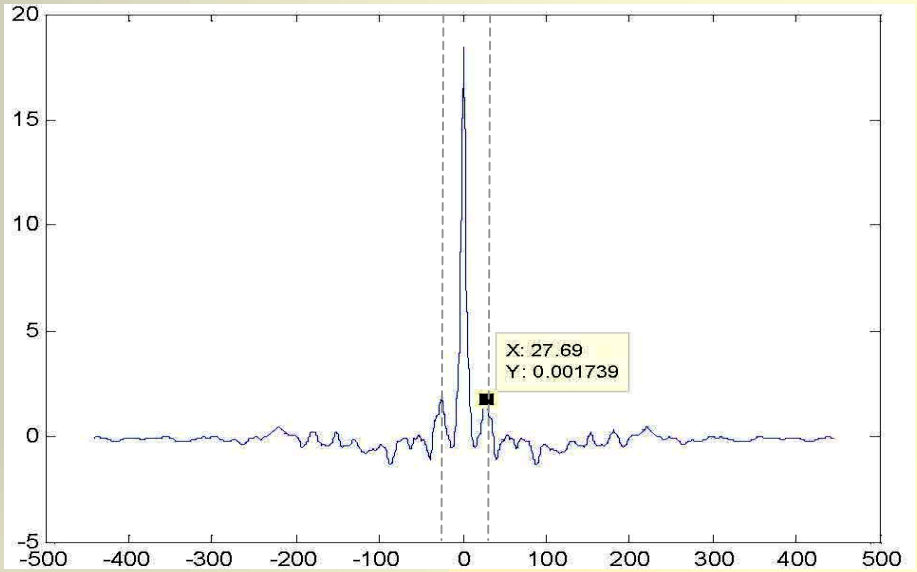
What can we call this new method?

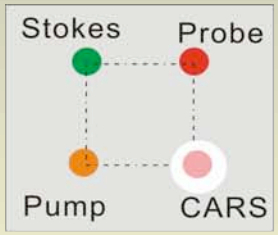
- Relies on **N**oise **A**utocorrelation
- It is a **S**pectroscopy
- Although general for non-linear spectroscopies, this realization is based on **C**oherent **A**nti-Stokes **R**aman **S**cattering

NASCARS

“Cheap” shaping for NASCARS

Toluene
Preliminary results





Scan delay

OPA (TOPAS)

Ti:Sapphire Amplifier (Spitfire)

Sample

Monochromator

CCD

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multi-mode fiber

Temporal randomization (noise) by means of fiber mode dispersion

Spectroscopy with Shaped Pulses. *Summary*

- Broad spectral bandwidth of ultra-short pulses offers new ways of “interference spectroscopy”
- Pulse shaping technology enables design of “spectrally incohererent” pulses with no correlation between separate spectral components of the pulse
- Interference of noise, coherently produced via CARS, results in the appearance of correlations in the Raman spectrum
- Identifying Raman resonances by the spectral correlations of interference noise offers quick and easy way of doing Raman spectroscopy with femtosecond pulses.

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Experiment

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Theory

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Alternate formulation of dark state (1)

Hamiltonian for 3 states:

$$\mathbf{C}(t) = [C_1(t), C_2(t), C_3(t)]^T$$

$$\mathrm{H}(t) = \hbar \begin{bmatrix} 0 & \frac{1}{2}\Omega_P(t) & 0 \\ \frac{1}{2}\Omega_P(t) & \Delta_P & \frac{1}{2}\Omega_S(t) \\ 0 & \frac{1}{2}\Omega_S(t) & \Delta_P - \Delta_S \end{bmatrix}.$$

Here $\Omega_P(t)$ and $\Omega_S(t)$ are the Rabi frequencies of the pump and Stokes pulses, respectively, and Δ_P and Δ_S are the single-photon detunings of the pump and Stokes lasers from their respective transitions, $\hbar\Delta_P = E_2 - E_1 - \hbar\omega_P$, $\hbar\Delta_S = E_2 - E_3 - \hbar\omega_S$. An essential condition for STIRAP is the two-photon resonance between states ψ_1 and ψ_3, $\Delta_P = \Delta_S = \Delta$. Then the three instantaneous eigenstates of $\mathrm{H}(t)$ (the adiabatic states) are given by

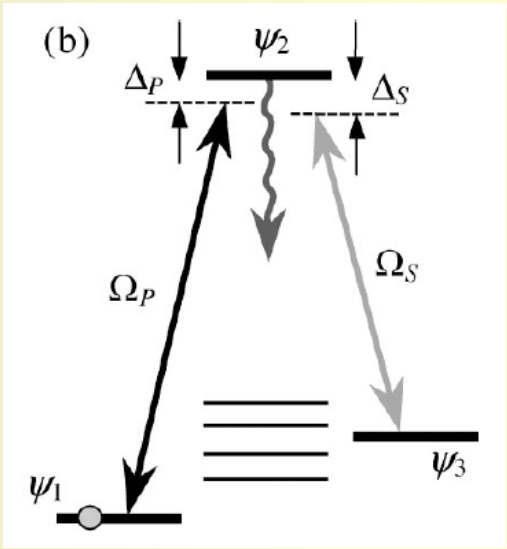
$$\Phi_+(t) = \psi_1 \sin\vartheta(t) \sin\varphi(t) + \psi_2 \cos\varphi(t) + \psi_3 \cos\vartheta(t) \sin\varphi(t), \qquad 20.$$

$$\Phi_0(t) = \psi_1 \cos\vartheta(t) - \psi_3 \sin\vartheta(t), \qquad 21.$$

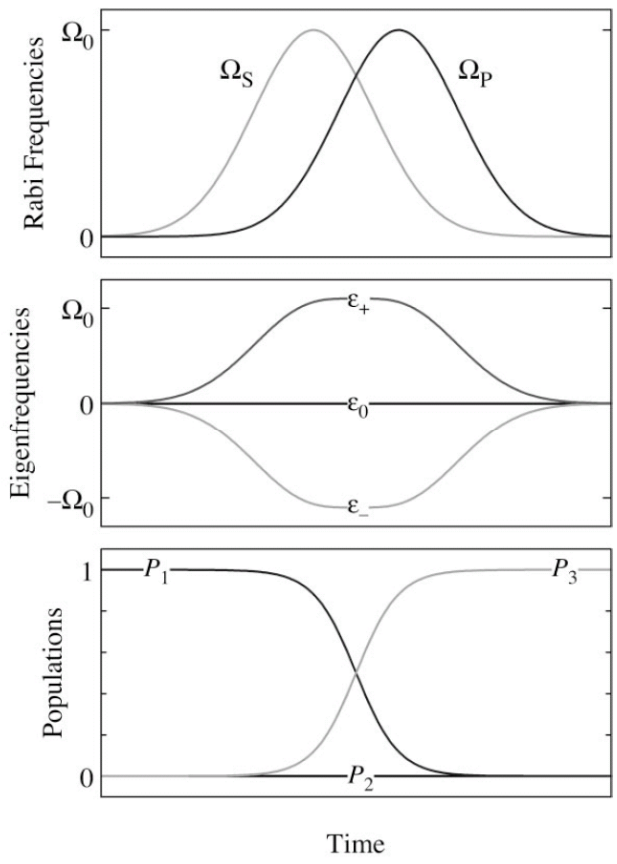
$$\Phi_-(t) = \psi_1 \sin\vartheta(t) \cos\varphi(t) - \psi_2 \sin\varphi(t) + \psi_3 \cos\vartheta(t) \cos\varphi(t), \qquad 22.$$

where the mixing angles $\vartheta(t)$ and $\varphi(t)$ are defined (modulo π) as $\vartheta(t) = \arctan[\Omega_P(t)/\Omega_S(t)]$, $\varphi(t) = \frac{1}{2}\arctan[\sqrt{\Omega_P^2(t) + \Omega_S^2(t)}/\Delta]$. These eigen states have the following eigen frequencies:

$$\varepsilon_0(t) = 0, \quad \varepsilon_\pm(t) = \tfrac{1}{2}\Delta \pm \tfrac{1}{2}\sqrt{\Delta^2 + \Omega_P^2(t) + \Omega_S^2(t)}. \qquad 23.$$



Alternate formulation (2)



STIRAP is based on the zero-eigenvalue adiabatic state $\Phi_0(t)$, which is a coherent superposition of the initial state ψ_1 and the final state ψ_3 only. This adiabatic state has no component of the excited state ψ_2, and hence it has no possibility of radiatively decaying; it is a trapped state (of population) or a radiatively dark state (85–89). For the counterintuitive pulse ordering the relations $\Omega_P(t)/\Omega_S(t) \overset{t\to-\infty}{\longrightarrow} 0$ and $\Omega_P(t)/\Omega_S(t) \overset{t\to+\infty}{\longrightarrow} \infty$ apply; hence, as time progresses from $-\infty$ to $+\infty$, the mixing angle $\vartheta(t)$ rises from 0 to $\pi/2$. Consequently, the adiabatic state $\Phi_0(t)$ evolves from the bare state ψ_1 to a superposition of states ψ_1 and ψ_2 at intermediate times and finally to the target state ψ_3 at the end of the interaction; thus, state $\Phi_0(t)$ links adiabatically the initial state ψ_1 to the target state ψ_3. Because the Hamiltonian is explicitly time dependent, diabatic transitions between the adiabatic states will occur. The goal is to reduce the diabatic transition rates to negligibly small values. When the system can be forced to stay in the dark state at all times, a complete population transfer from ψ_1 to ψ_3 will be achieved, as shown in Figure 9. This can be realized by ensuring adiabatic evolution; then no transitions between the adiabatic states can take place. The adiabatic condition requires that the coupling between each pair of adiabatic states is negligible compared with the difference between the energies of these states. With respect to the dark state $\Phi_0(t)$, the adiabatic condition reads (5, 6)

$$\left|\varepsilon_0 - \varepsilon_\pm\right| \gg \left|\left\langle \dot{\Phi}_0 \middle| \Phi_\pm \right\rangle\right|. \qquad 24.$$

On one-photon resonance ($\Delta = 0$) the adiabaticity condition simplifies and becomes (81)

$$\sqrt{\Omega_P^2 + \Omega_S^2} \gg \left|\dot{\vartheta}\right| \propto T^{-1}, \qquad 25.$$

where T is the pulse width. Assuming that the pump and Stokes pulses have the same peak Rabi frequency Ω_0, this condition can be written as $\Omega_0 T \gg 1$. Hence,

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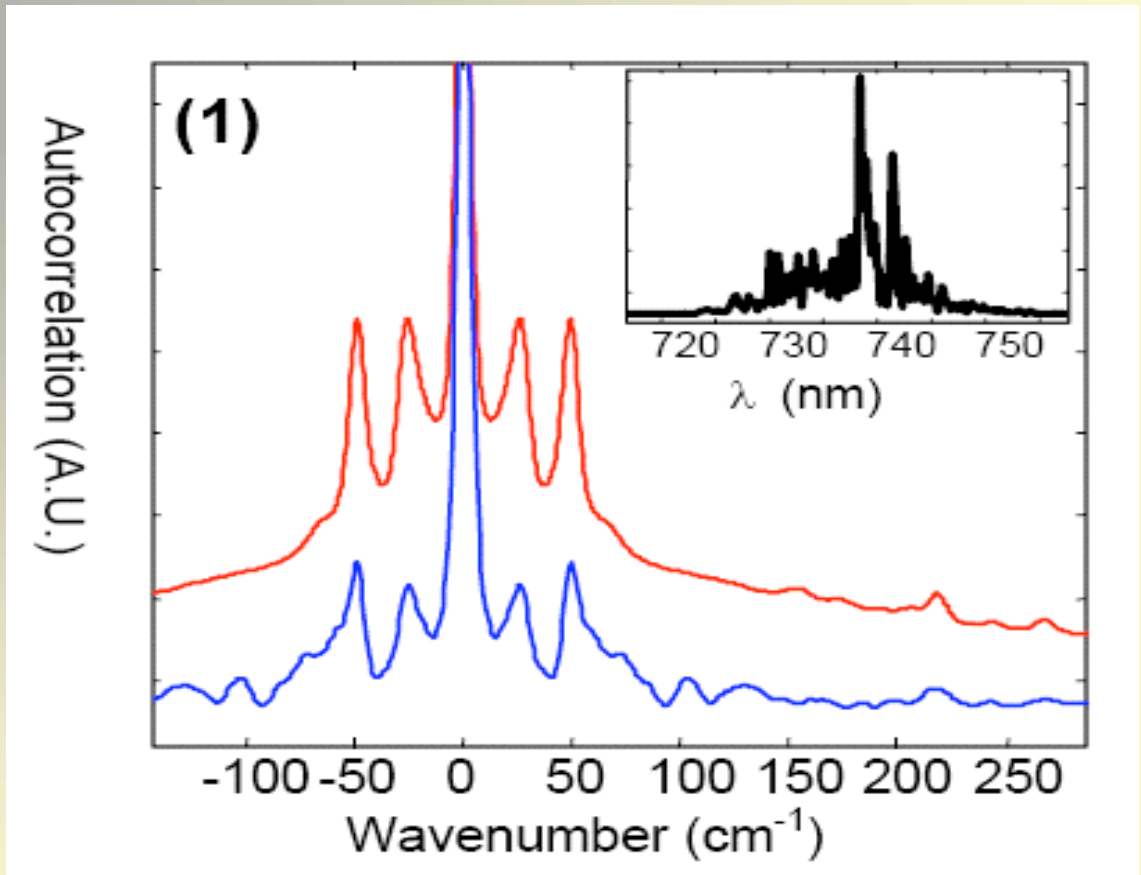

Experimental NASCARS spectrum of a mixture of toluene ($782cm^{-1}$, $1000cm^{-1}$, $1027cm^{-1}$) with ortho-xylene ($982cm^{-1}$, $1049cm^{-1}$) mixture. Noise is introduced using spectral pulse shaper. Result is averaged over 100 noise realizations. Red curve is autocorrelation of Raman spectrum as reference

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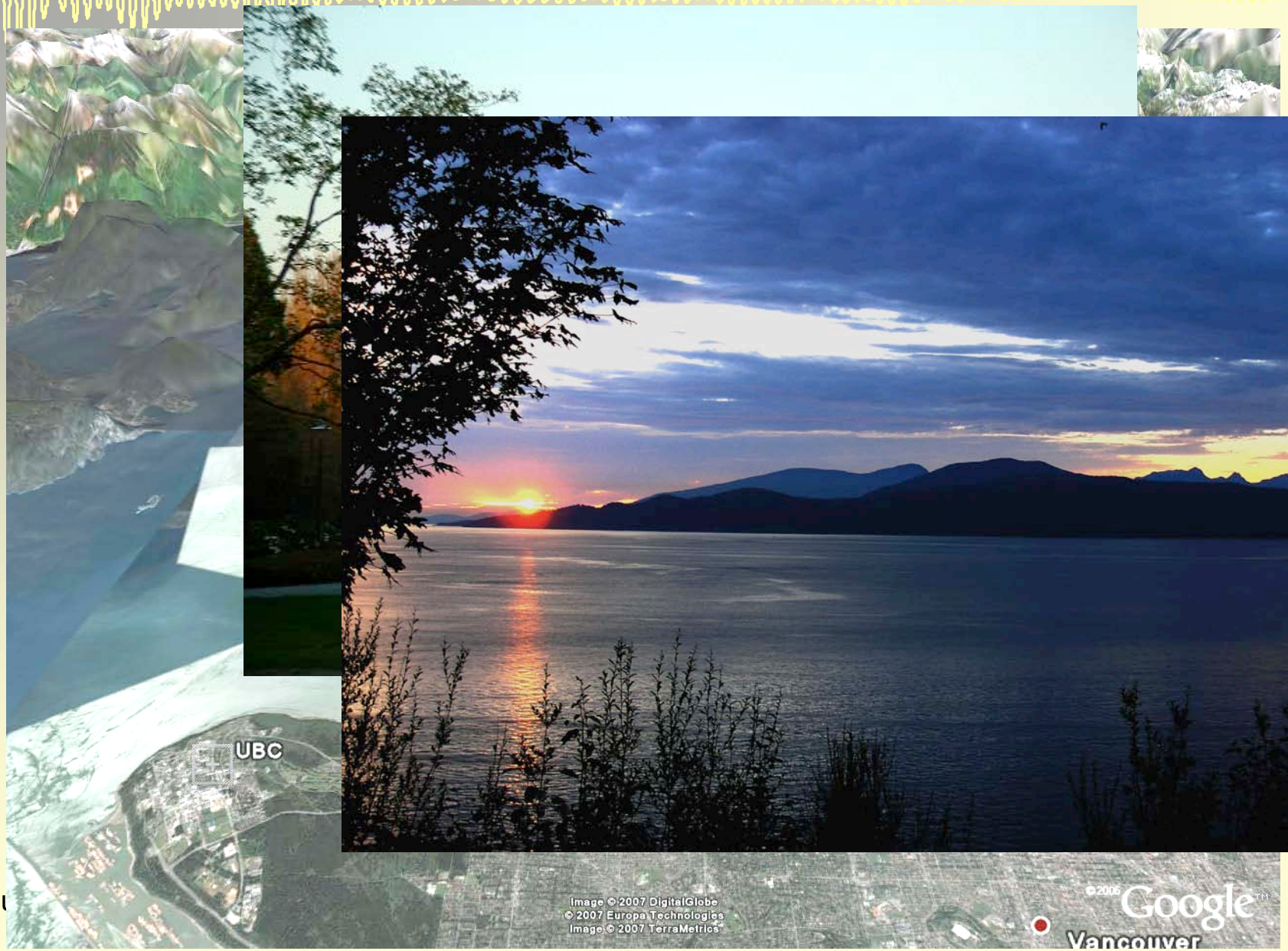

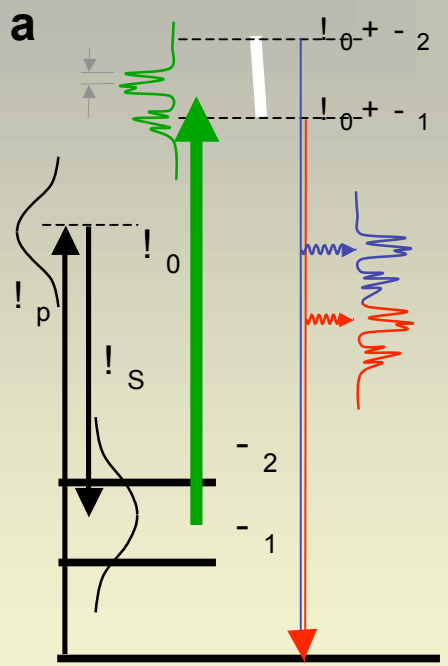

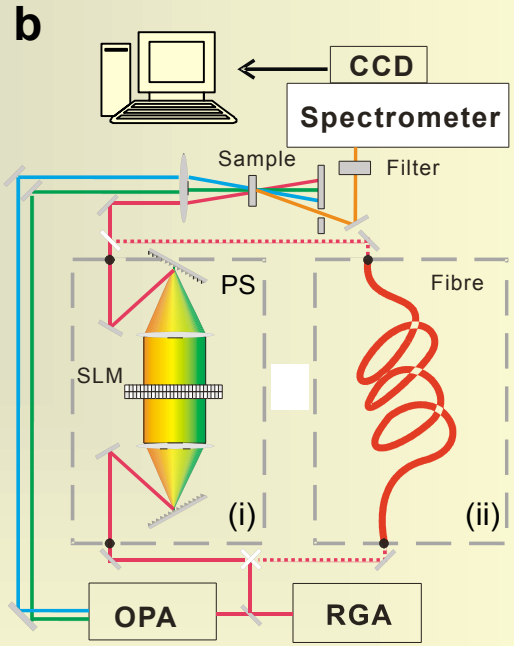

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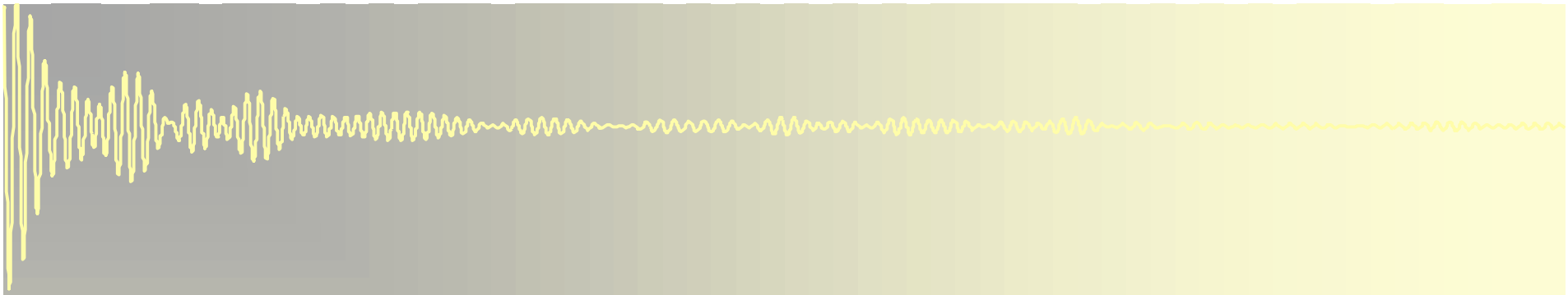

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