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Temporal effects on spectroscopic line shapes, resolution, and sensitivity of the broad-band sum frequency generation

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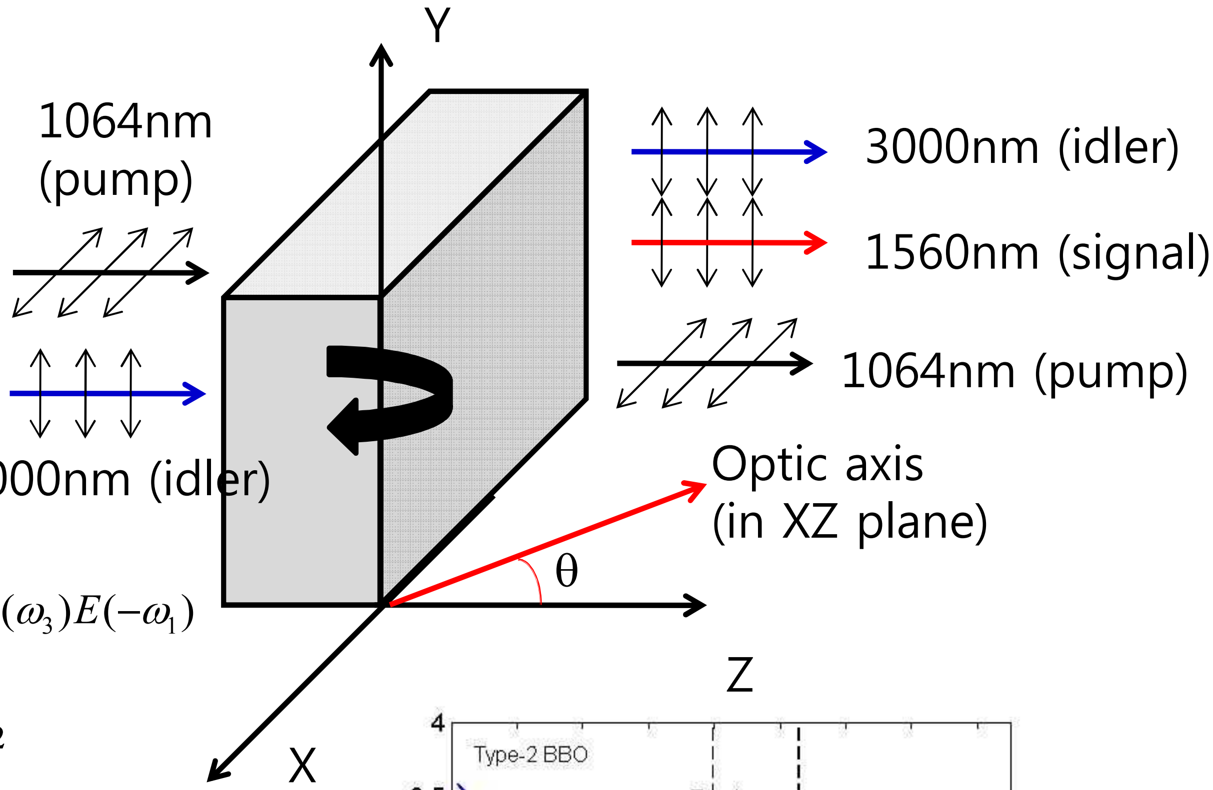
Conventional SFG system

Conventional SFG system - controlling IR wavelength by <u>Angle tuning</u>

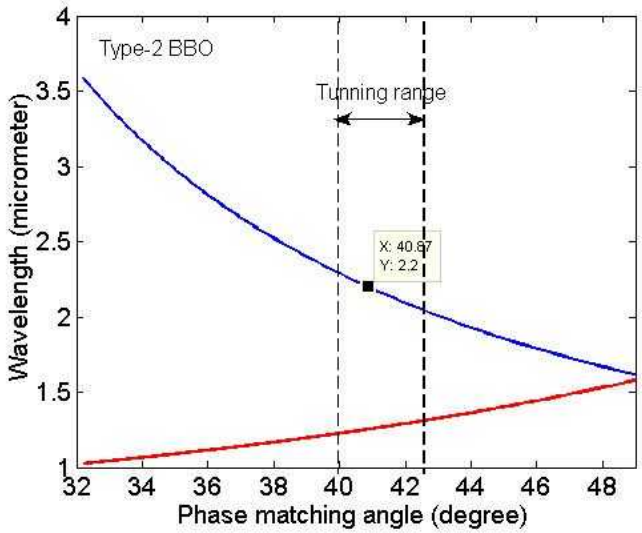


Second order process: $P(\omega_2) = \vec{\chi} E(\omega_3) E(-\omega_1)$

Energy conservation : $\omega_3 = \omega_1 + \omega_2$

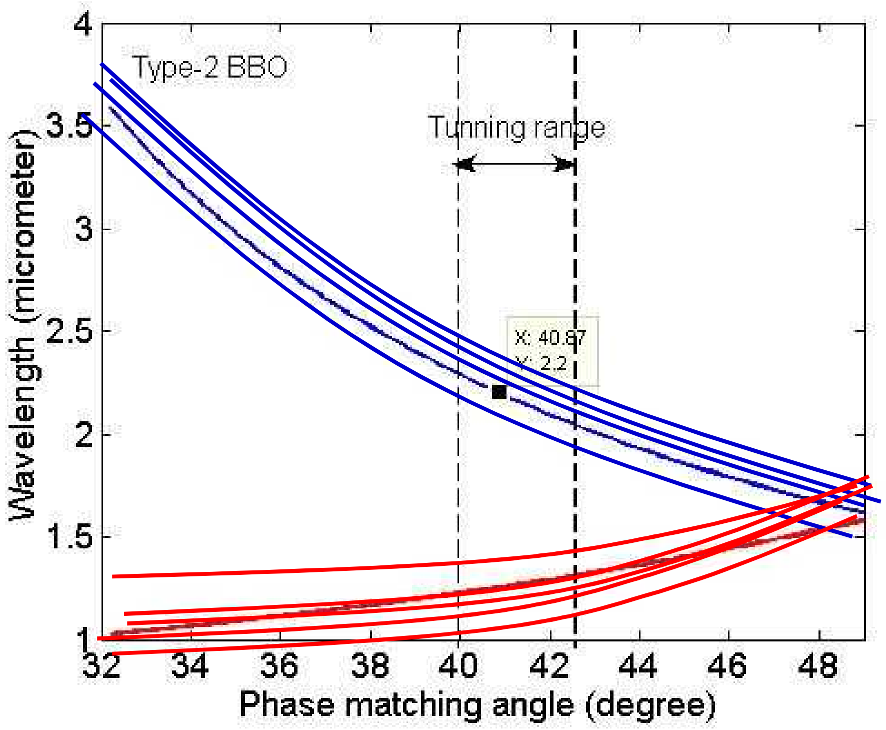
Momentum conservation :
$\mathbf{n_{3,e}\, k_3 = n_{1,o}\, k_1 + n_{2,o}\, k_2}$

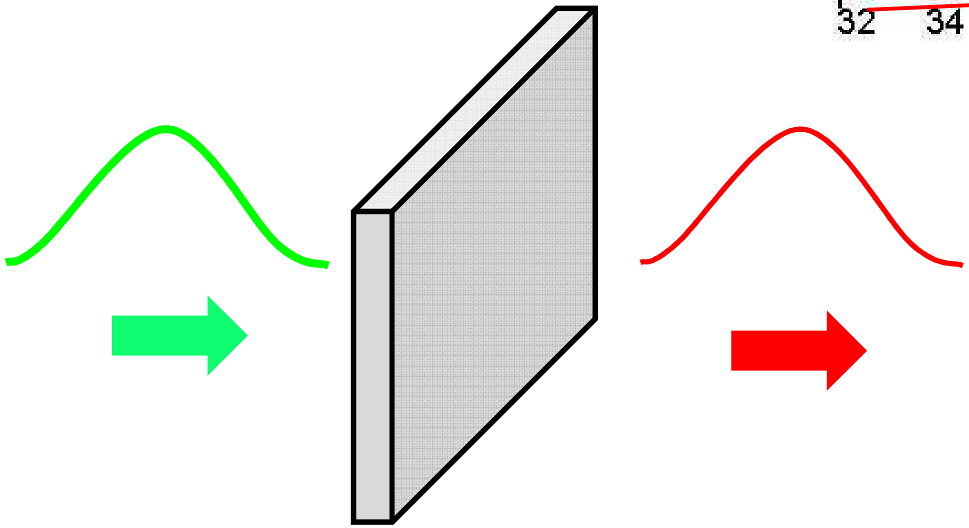
$$\frac{1}{n_e^{\,2}(\omega_3)} = \frac{\cos^2\theta}{n_o(\omega_3)^2} + \frac{\sin^2\theta}{n'_e(\omega_3)^2}$$



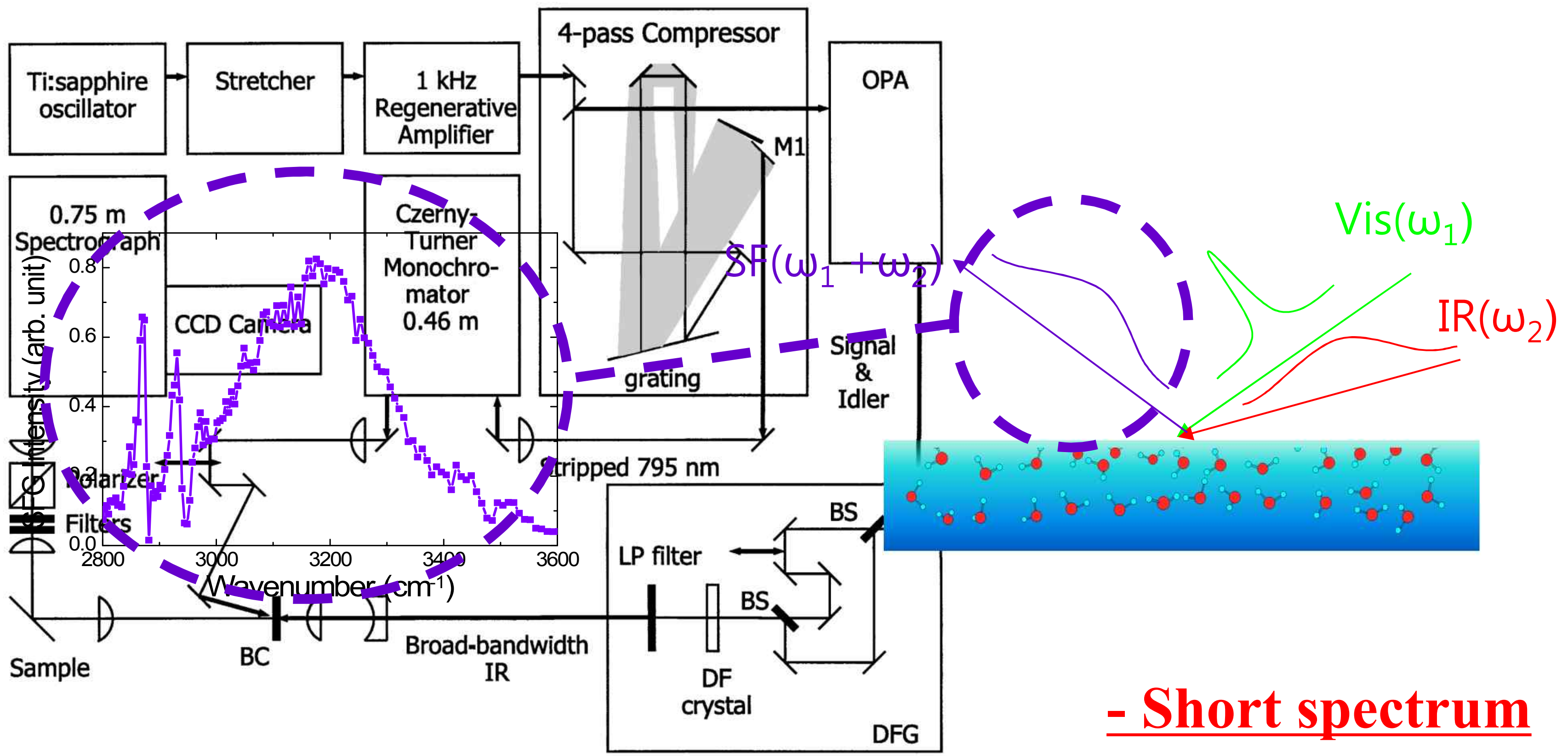
Broadband SFG system

Broadband SFG system -
<u>no angle tuning</u>





Broadband SFG system



- Short spectrum acquisition time

- Sub picosecond time resolving

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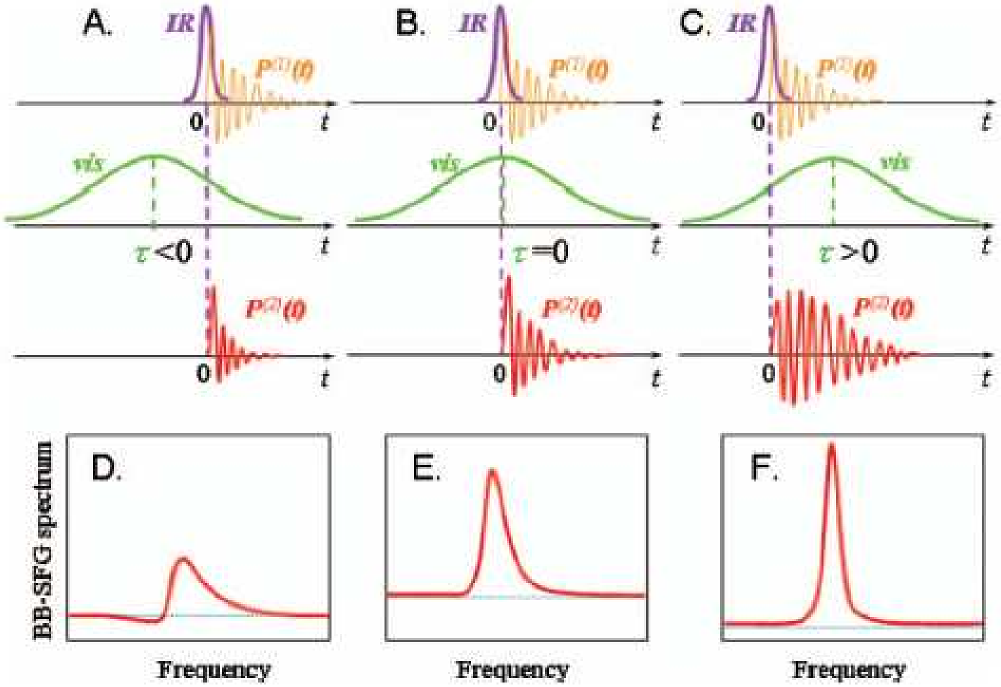
Spectral resolution of BBSFG



$$P^{(2)}(t) = \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dt_2 S^{(2)}(t_1, t_2) E(t - t_2) E(t - t_2 - t_1). \quad (1)$$

Molecular vibraitional damping time 1-10ps (except strong damping)

Second order interaction can be truncated by visible pulse

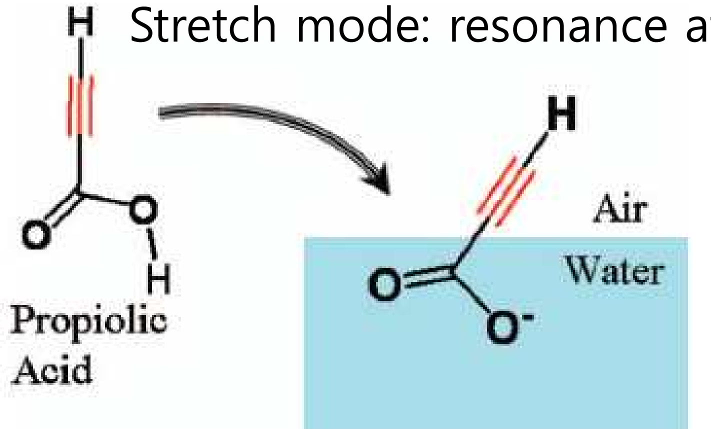
↓

Lorenztian line shape is broken

Spectral resolution of BBSFG

Q: 1) What time delay makes SFG spectra better??
2) How about visible pulse shape??

Stretch mode: resonance at ~2135 cm^{-1} , damping~10 cm^{-1}

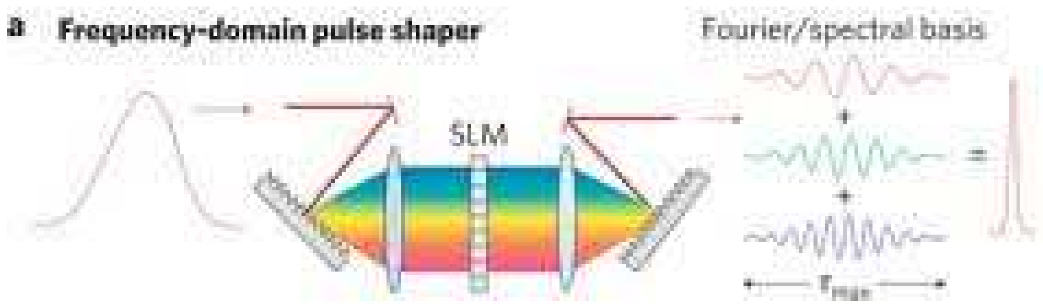


SCHEME 1.

Take SFG spectra of Air / water interface with varying time delay (-1000fs ~ +1000fs)

Preparation for experiment

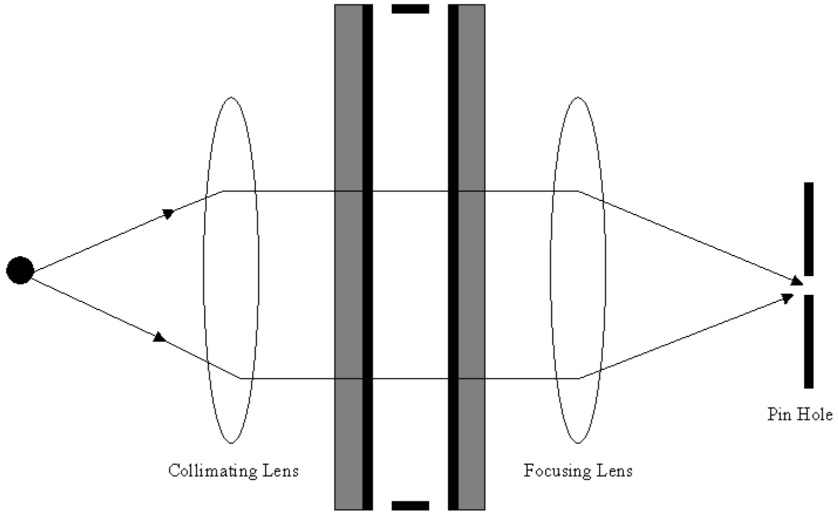
1) 4f pulse shaper

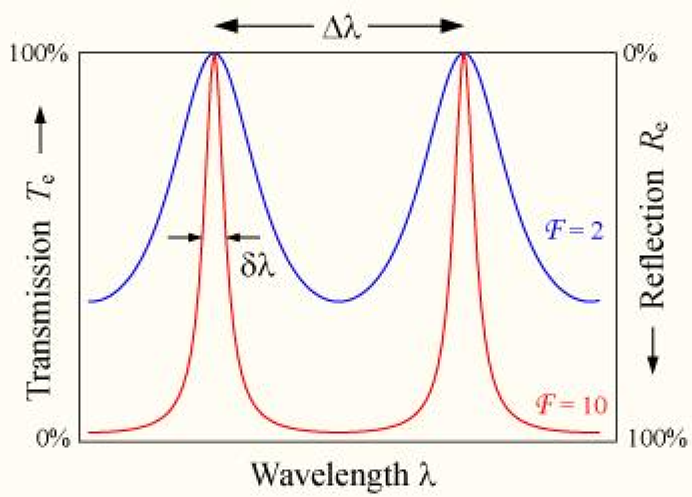


$$E_{\text{vis}}^{\text{stretcher}}(t) = \frac{1}{2}E_{\text{vis}}^{0}\int_{\omega_{\text{vis}}-\sigma}^{\omega_{\text{vis}}+\sigma}\exp(-i\omega t)d\omega$$
$$= E_{\text{vis}}^{0}\frac{\sin(\sigma t)}{t}\exp(-i\omega_{\text{vis}}t),$$

$$I_{\text{vis}}^{\text{etalon}}(\omega) = E_{\text{vis}}^{0\ 2}\frac{1}{1+\frac{4F^2}{\pi^2}\sin^2\left(\frac{\tau_{\text{RT}}\omega}{2}\right)},$$

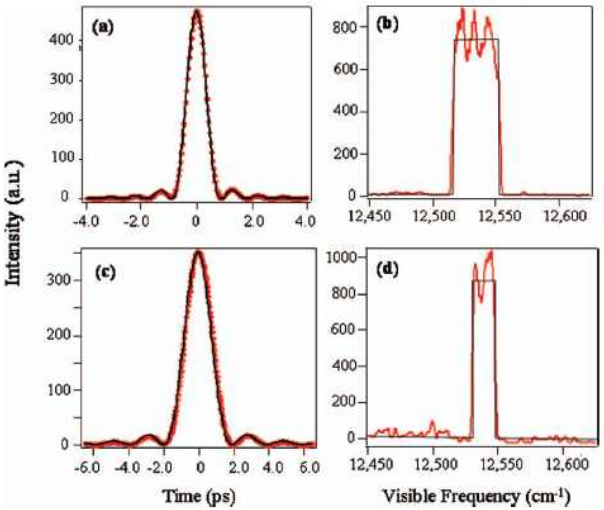
2) Fabry–Perot etalon





Preparation for experiment

1) 4f pulse shaper



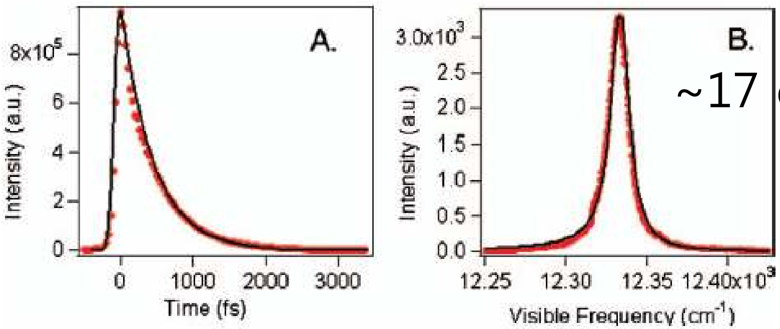
~37 cm^{-1}

~17 cm^{-1}

$$E_{\mathrm{vis}}^{\mathrm{stretcher}}(t) = \frac{1}{2}E_{\mathrm{vis}}^{0}\int_{\omega_{\mathrm{vis}}-\sigma}^{\omega_{\mathrm{vis}}+\sigma} \exp(-i\omega t)\,d\omega$$

$$= E_{\mathrm{vis}}^{0}\frac{\sin(\sigma t)}{t}\exp(-i\omega_{\mathrm{vis}}t),$$

2) Fabry–Perot etalon

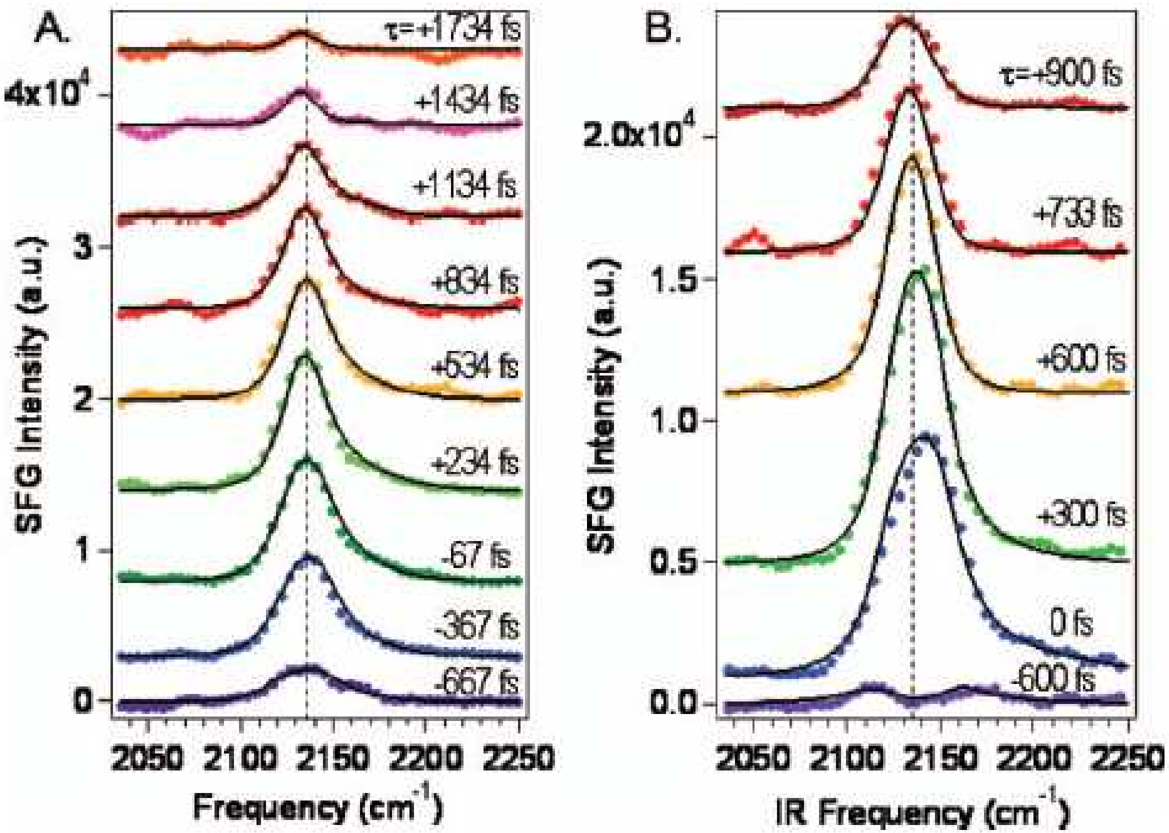


~17 cm^{-1}

$$E_{\mathrm{vis}}^{\mathrm{etalon}}(t) = E_{\mathrm{vis}}^{0}(1-R)\sum_{n=0}^{\infty} R^{n} \exp\left\{-\frac{(t-n\tau_{\mathrm{RT}})^{2}}{\tau_{\mathrm{vis}}^{2}}\right\}$$

$$\times\exp\{-i\omega_{\mathrm{vis}}(t-n\tau_{\mathrm{RT}})\}.$$

SFG spectra with 4f pulse shaper



At positive time delay ($t_2 > t_1$) spectrum looks more similar to Lorenztian line shape

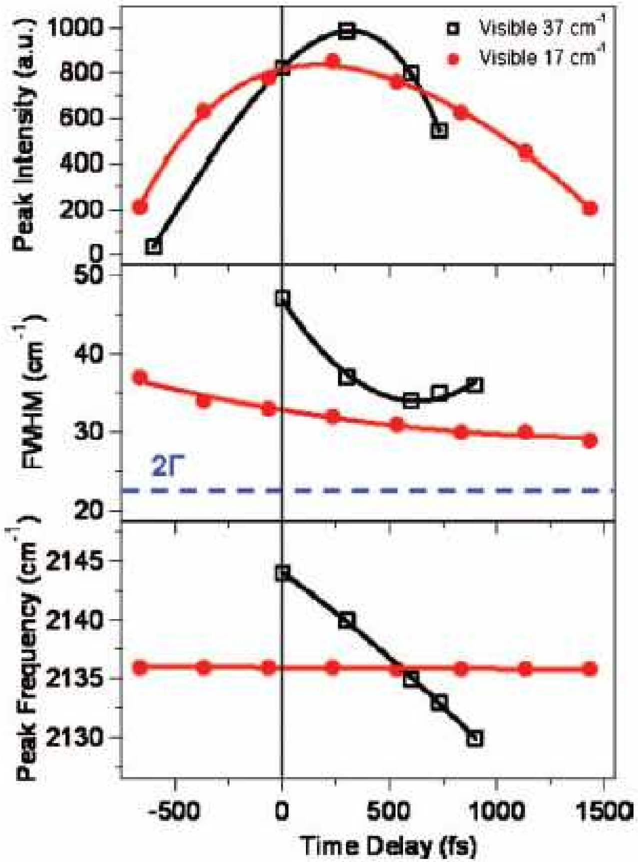
SFG spectra with 4f pulse shaper - fitting

$$P^{(2)}(t) = \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dt_2 S^{(2)}(t_1,t_2)E(t-t_2)E(t-t_2-t_1).$$

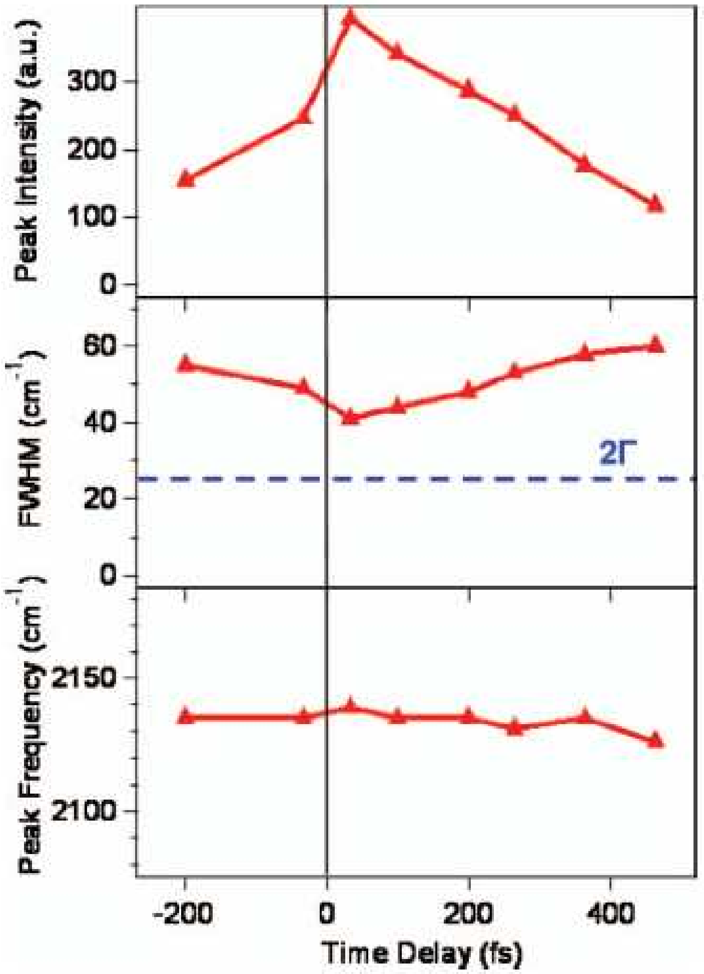
$$S(t_1) = A_{\mathrm{NR}} \exp(i\varphi_{\mathrm{NR}})\delta(t_1) - i\theta(t_1)B\Gamma \exp(-i\omega_0 t_1 - \Gamma t_1).$$

$$E_{\mathrm{IR}}(t) = \sum_j E^0_{\mathrm{IR}j} \exp\left\{-\frac{(t-t_j)^2}{\tau^2_{\mathrm{IR}j}}\right\}\exp(-i\omega_{\mathrm{IR}j}t).$$

$$E^{\mathrm{stretcher}}_{\mathrm{vis}}(t) = \frac{1}{2}E^0_{\mathrm{vis}}\int_{\omega_{\mathrm{vis}}-\sigma}^{\omega_{\mathrm{vis}}+\sigma} \exp(-i\omega t)d\omega$$
$$= E^0_{\mathrm{vis}}\frac{\sin(\sigma t)}{t}\exp(-i\omega_{\mathrm{vis}}t),$$



SFG spectra with etalon- fitting



Sharp change near zero delay
: due to steep edge of visible pulse