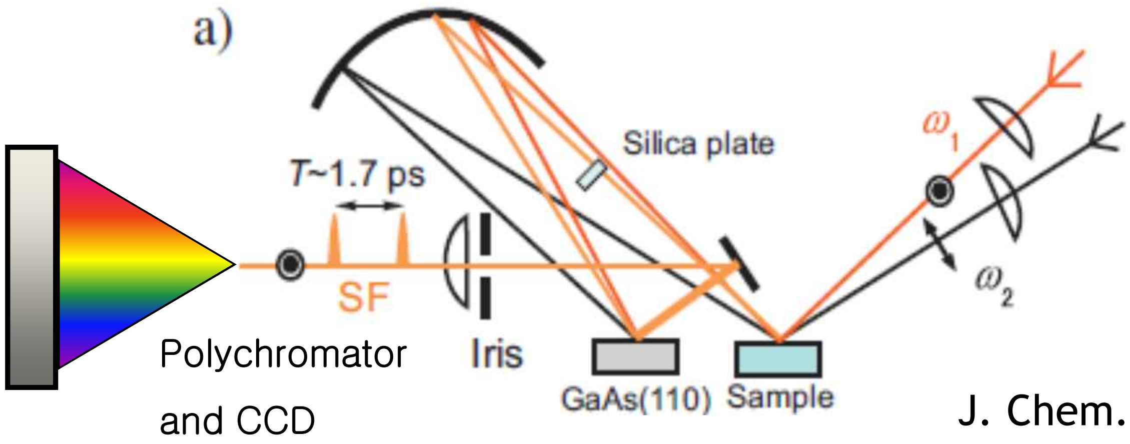
Phase sensitive SFVS



J. Chem. Phys. **130,** 204704 **(2009)**

1) w_1 (visible) and w_2 (infrared) are spatially and timely overlapped at the sample surface.

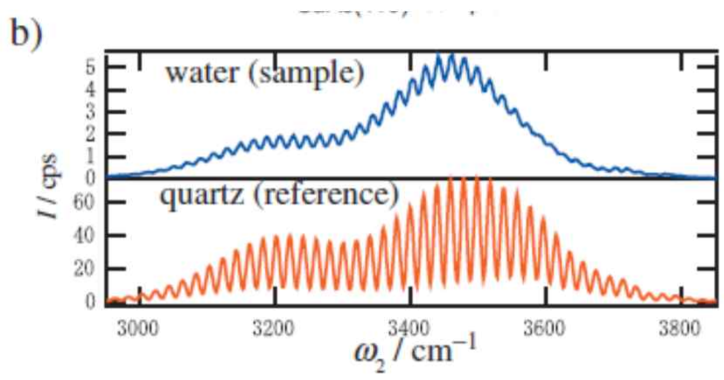
2) At the sample, SF light comes out and propagates through silica plate. (relative phase can be adjusted)

3) SF signal and two light sources are overlapped again at LO surface. SF signal from LO collinearly propagates with retarded SF signal from the sample.

4) In polychromator pulses are stretched in time domain and generate interference pattern in frequency domain.

$$E_{tot}(w) = E_s(w)e^{iw(t-T)} + E_{LO}(w)e^{iwt}$$

$$E_{LO}(w) > E_s(w)$$



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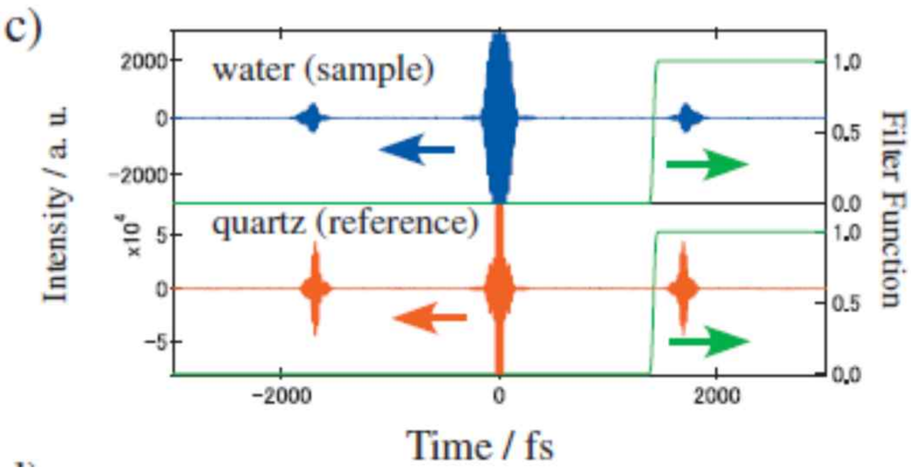
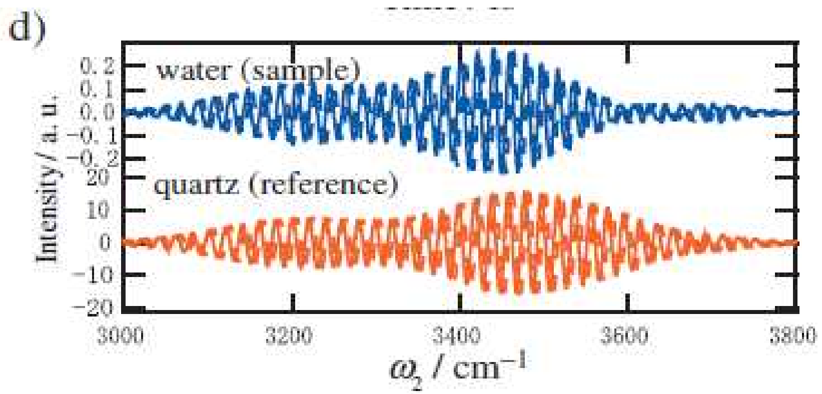


$$I = |\tilde{E}_{\mathrm{tot}}(\omega)|^2 = |\tilde{E}_{\mathrm{sample}}|^2 + |\tilde{E}_{\mathrm{LO}}|^2 + \tilde{E}_{\mathrm{sample}}\tilde{E}^*_{\mathrm{LO}} \exp(i\omega T) + \tilde{E}^*_{\mathrm{sample}}\tilde{E}_{\mathrm{LO}} \exp(-i\omega T). \quad (1)$$

5) By Fourier transformation, SF Intensity is represented in time domain. And only right side is obtained.

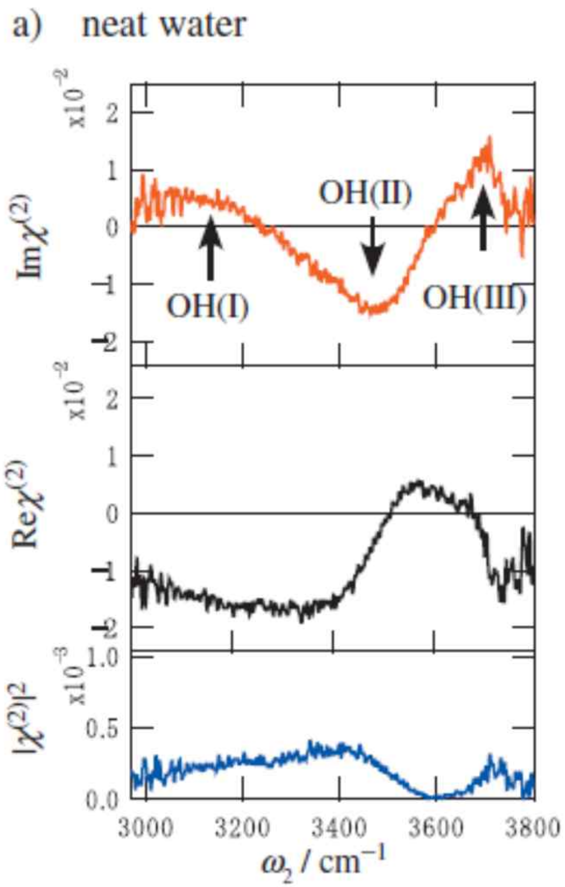


6) Again, take inverse Fourier transformation of the interference part.

$$E_s(w)\,\tilde{E}_{LO}(w)e^{iwT} = |E_s(w)||E_{LO}(w)|e^{iwT+\phi_{LO}+\phi_s}$$

$$= |E_s(w)||E_{LO}(w)|\{\cos(wt+\phi_{LO}+\phi_s) + i\sin(wt+\phi_{LO}+\phi_s)\}$$

Phase sensitive SFVS

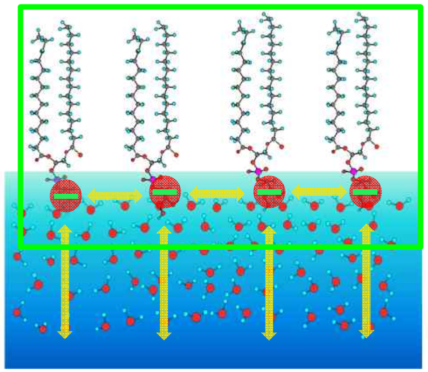


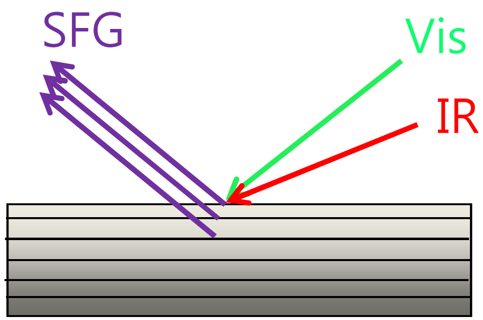
7) Divide sample/LO interference signal by reference / LO interference signal.

$$\frac{|E_s(w)||E_{LO}(w)|e^{iwT+\phi_{LO}+\phi_s}}{|E_{ref}(w)||E_{LO}(w)|e^{iwT+\phi_{LO}+\phi_{ref}}} = \frac{|E_s(w)|e^{i\phi_s}}{|E_{ref}(w)|e^{i\phi_{ref}}}$$

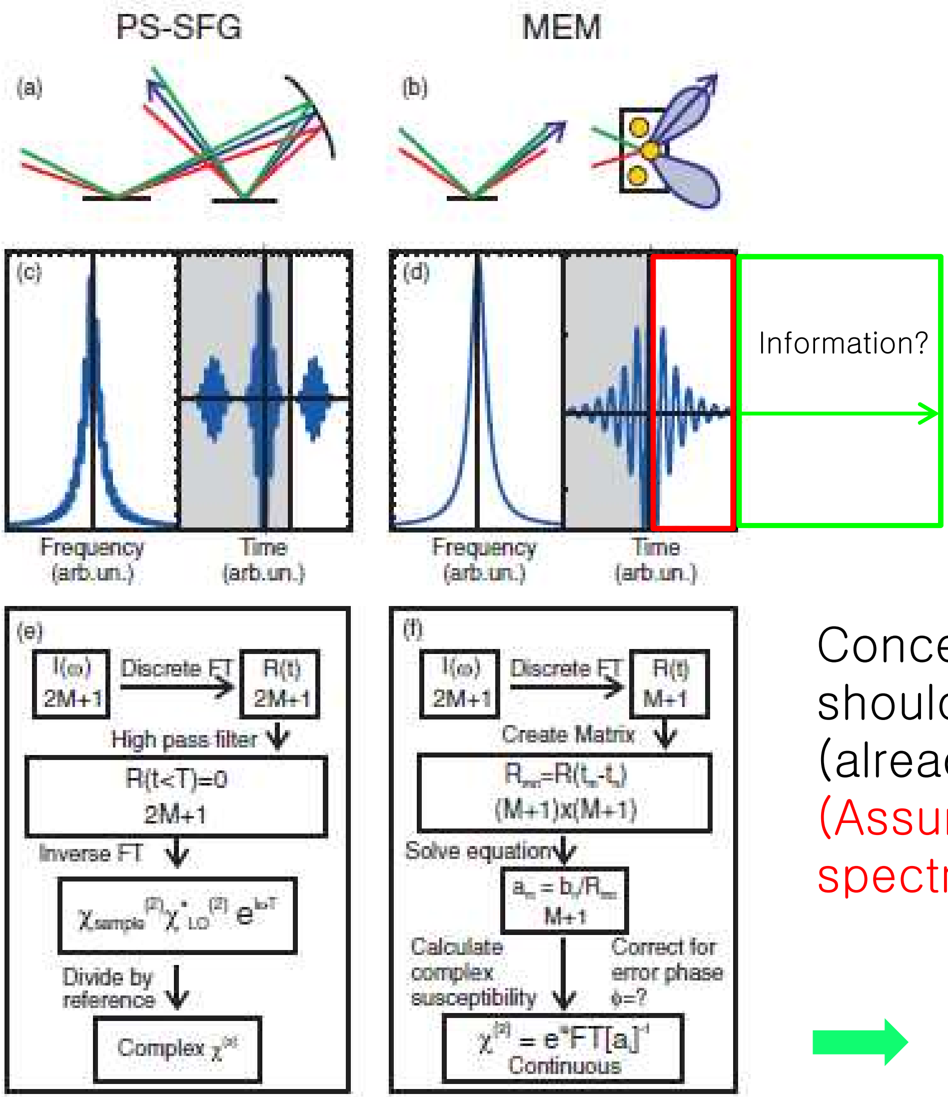
8) Because SF from z-cut quartz is non-resonant, phase of reference is constant. So, phase of sample can be obtained.

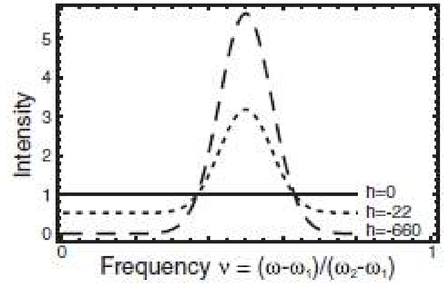
$$\chi^{(2)}_{ref} = \chi^{(2)}_{ref,bulk} / i(\Delta k) : \frac{\pi}{2}\ phase\ (known)$$





Maximum entropy method





$$h = \int_0^1 \log[I(\nu)]\mathrm{d}\nu$$

$$\nu = \frac{\omega - \omega_1}{\omega_2 - \omega_1},$$

Take out M+1
data points
(interval : △w)

$T_{max} = 2\pi$ / △w

Concept: adding information of t > T_{max} should not change spectral entropy! (already maximum)

(Assumption: all of information is in spectrum!)

$$\frac{\mathrm{d}h}{dR(m > M)} = 0 = \int_0^1 \frac{1}{I(\nu)} \frac{\mathrm{d}I(\nu)}{\mathrm{d}R(m > M)} \mathrm{d}\nu.$$

Constraint

Maximum entropy method

From J.P.Burg ph.D, dissertation, Stanford university *(1975).*

$$P(f) = \frac{1}{2W}\sum_{n=-\infty}^{+\infty} R(n)e^{-2\pi ifn\Delta t} \qquad h = \int_{-W}^{W} \ln[\frac{1}{2W}\sum_{n=-\infty}^{+\infty} R(n)e^{-2\pi ifn\Delta t}]df$$

$$\frac{\partial h}{\partial R(s)} = \int_{-W}^{W} P^{-1}(f)e^{-2\pi ifs\Delta t}df = 0, for(s > |N|)$$

Here, inverse of power spectrum $P^{-1}(f)$ can be expanded in Fourier series of λ_n.

$$P^{-1}(f) = \sum_{n=-\infty}^{+\infty} \lambda_n e^{-2\pi ifs\Delta t} \Rightarrow R(n) = \int_{-W}^{W} \frac{e^{+2\pi ifn\Delta t}}{\sum_{s=-N}^{+N} \lambda_n e^{-2\pi ifs\Delta t}} df\,(n \le |N|), z = e^{+2\pi if\Delta t}$$

$$\Rightarrow R(n) = \frac{1}{2\pi i\Delta t}\oint \frac{z^{-n-1}}{\sum_{s=-N}^{+N} \lambda_s z^s} dz, (n \le |N|)$$

$$\sum_{s=-N}^{+N} \lambda_s z^s = P^{-1}(f) = [P_N \Delta t]^{-1}[1 + a_1 z + \dots a_N z^N][1 + a_1^* z^{-1} + \dots a_N^* z^{-N}]$$

$$= [P_N \Delta t]^{-1} \sum_{s=0}^{+N} a_s z^s \sum_{s=0}^{+N} a_s^* z^{-s}$$

Maximum entropy method

$$R(n)=\frac{P_N}{2\pi i}\oint\frac{z^{-n-1}}{\sum_{s=0}^{+N}a_s z^s\sum_{s=0}^{+N}a_s^{\,*}z^{-s}}dz,(n\le|N|)$$

By taking summation of R(n),

$$\Rightarrow \sum_{n=0}^{N}a^*{}_n R(n-r)=\frac{P_N}{2\pi i}\oint\frac{z^{-r-1}\sum_{n=0}^{+N}a_s^{\,*}z^{-n}}{\sum_{s=0}^{+N}a_s z^s\sum_{s=0}^{+N}a_s^{\,*}z^{-s}}dz=\frac{P_N}{2\pi i}\oint\frac{z^{-r-1}}{\sum_{s=0}^{+N}a_s z^s}dz$$

Since function in denominator is analytic, this contour integration can be calculated by Cauchy integral formula.

$$\frac{1}{2\pi i}\oint\frac{f(z)}{z}dz=f(0)$$

$$\Rightarrow \sum_{n=0}^{N}a^*{}_n R(n-r)=P_N \text{ for r=0,}$$

$$\sum_{n=0}^{N}a^*{}_n R(n-r)=0 \text{ for r>0}$$

$$\begin{pmatrix} R(0) & R^*(1) & \cdots & R^*(M) \\ R(1) & R(0) & \cdots & R^*(M-1) \\ \vdots & \vdots & \ddots & \vdots \\ R(M) & R(M-1) & \cdots & R(0) \end{pmatrix}\begin{pmatrix}1\\ a_1\\ a_2\\ \vdots\\ a_M\end{pmatrix}=\begin{pmatrix}b\\0\\0\\ \vdots\\0\end{pmatrix} \quad (11)$$

M+1 by M+1 matrix (M+1 variables).

$$\chi^{(2)}(v)=\frac{be^{i\phi}}{g(v)}=\frac{be^{i\phi}}{\sum_{m=0}^{M}a_m e^{imv}}$$