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Direct comparison of phase-sensitive vibrational sum frequency generation with maximum entropy method: Case study of water

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We present a direct comparison of phase sensitive sum-frequency generation experiments with phase reconstruction obtained by the maximum entropy method. We show that both methods lead to the same complex spectrum. Furthermore, we discuss the strengths and weaknesses of each of these methods, analyzing possible sources of experimental and analytical errors. A simulation program for maximum entropy phase reconstruction is available at: <http://lbp.epfl.ch/>. © 2011 American Institute of Physics. [doi:10.1063/1.3662469]

Introduction (SFG spectroscopy)

→ Second order polarization responses of material

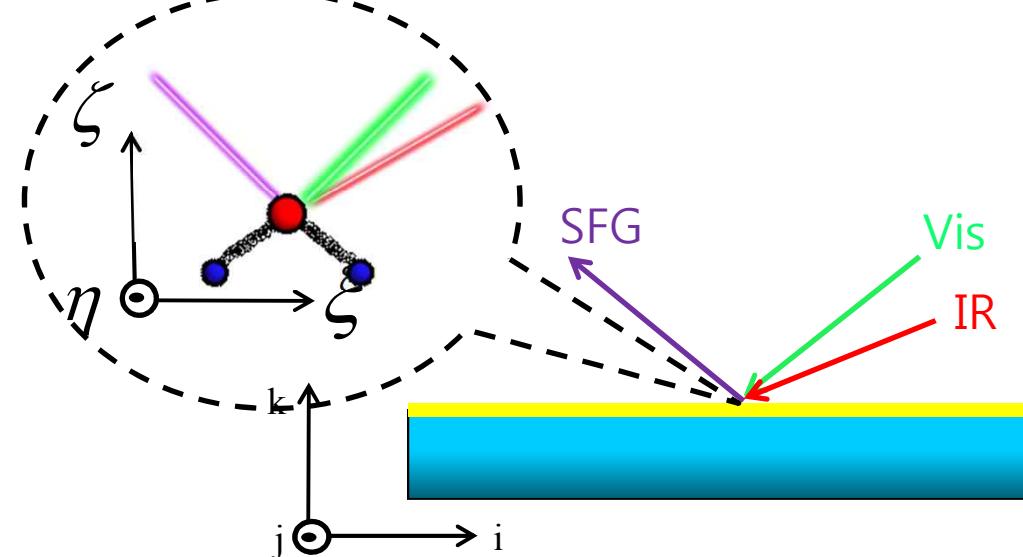
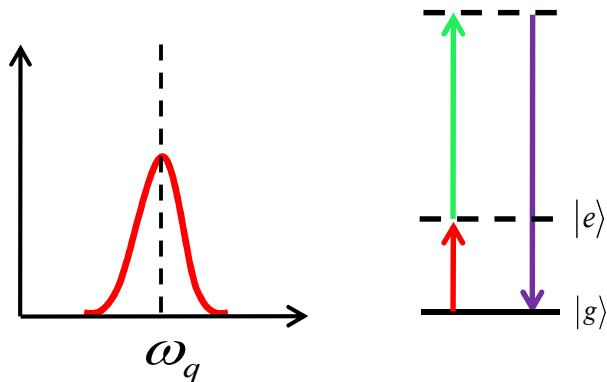
$$\vec{P} = \overleftrightarrow{\chi}^{(1)} \vec{E} + \overleftrightarrow{\chi}^{(2)} : \vec{E} \vec{E} + \overleftrightarrow{\chi}^{(3)} : \vec{E} \vec{E} \vec{E} + \dots$$
$$\vec{P}^{(2)}(\omega_{IR} + \omega_{VIS}) = \overleftrightarrow{\chi}^{(2)} : \vec{E}(\omega_{IR}) \vec{E}(\omega_{VIS})$$

→ Isotropic medium: inversion symmetry in **bulk**

$$-\vec{P}^{(2)} = \overleftrightarrow{\chi}^{(2)} : (-\vec{E})(-\vec{E}) = \overleftrightarrow{\chi}^{(2)} : \vec{E} \vec{E} = \vec{P}^{(2)} \quad \therefore \overleftrightarrow{\chi}^{(2)} = 0$$

→ Only responses from **surface** are detectable

Introduction (SFG spectroscopy)



Intensity of SFG signal

$$\rightarrow I(\omega_{SFG} = \omega_{IR} + \omega_{VIS}) \propto |\chi_{eff}^{(2)}|^2$$

$$\chi_{ijk}^{(2)} = N_s \sum_{\xi, \eta, \zeta} \alpha_{\xi \eta \zeta}^{(2)} \langle (\xi \cdot i)(\eta \cdot j)(\zeta \cdot k) \rangle$$

Information about molecular orientation

$$\alpha_{\xi \eta \zeta}^{(2)} = \alpha_{NR}^{(2)} + \sum_q \frac{\alpha_q}{\omega_{IR} - \omega_q + i\Gamma_q}$$

Intrinsic property of molecule

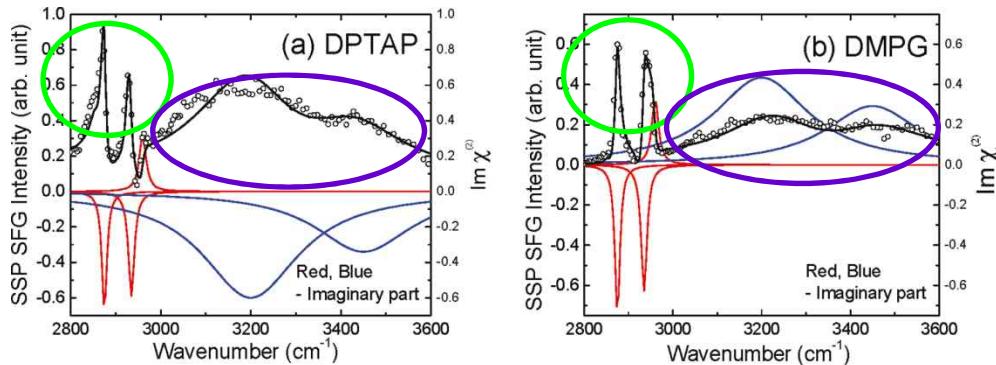
Introduction (SFG spectroscopy)

What is the problem?

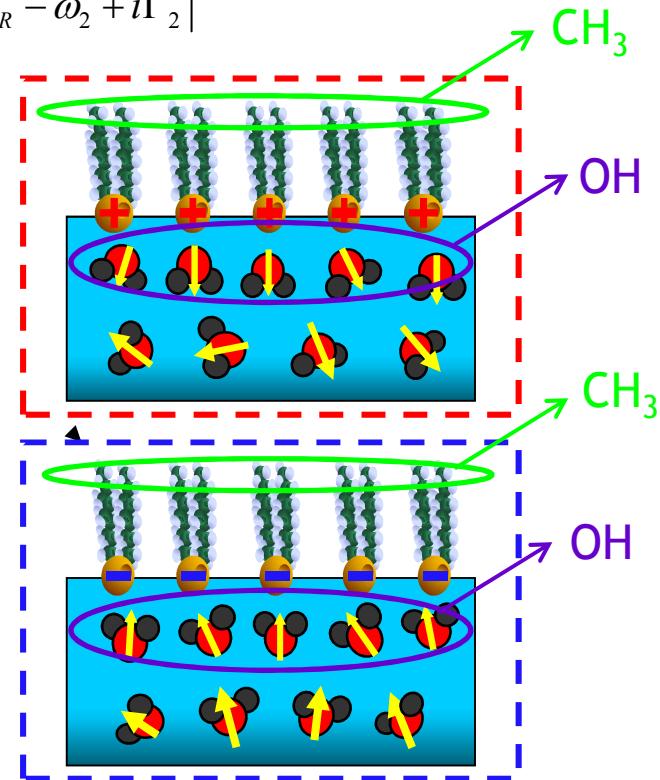
$$I(\omega_{SFG} = \omega_{IR} + \omega_{VIS}) \propto |\chi_{eff}^{(2)}|^2$$

Lost information of E-field

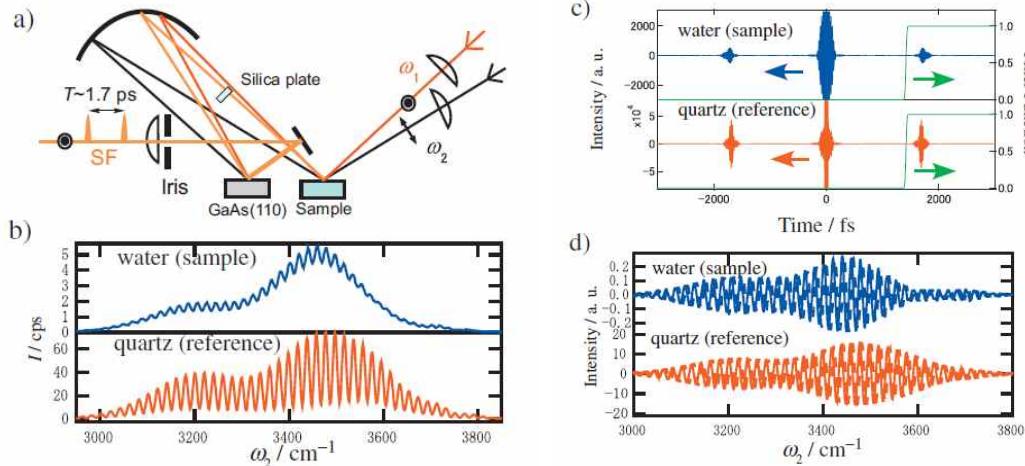
$$|\chi_{ijk}^{(2)}|^2 = (\chi_{NR}^{(2)} + \frac{A_1}{\omega_{IR} - \omega_1 + i\Gamma_1} + \frac{A_2}{\omega_{IR} - \omega_2 + i\Gamma_2})^2 = \left| \frac{A_1}{\omega_{IR} - \omega_1 + i\Gamma_1} \right|^2 + \left| \frac{A_2}{\omega_{IR} - \omega_2 + i\Gamma_2} \right|^2 + \text{crossterm}$$



Langmuir, 26 ,18266 (2010)

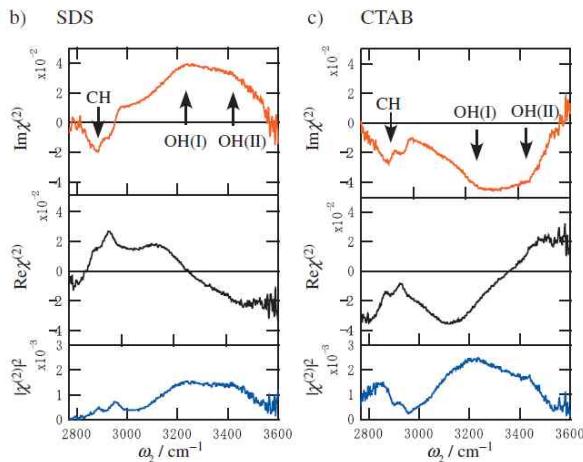


Phase sensitive SFVS



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

4) Plot Im and Re of $\chi_{\text{sample}}^{(2)}$



1) Mix SF signal from sample and LO (GaAs)

2) Take one of crossterms in time domain

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

3) FT and divide signal by reference (quartz)

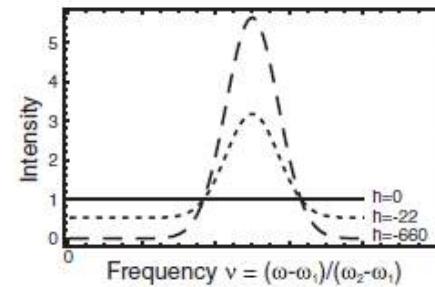
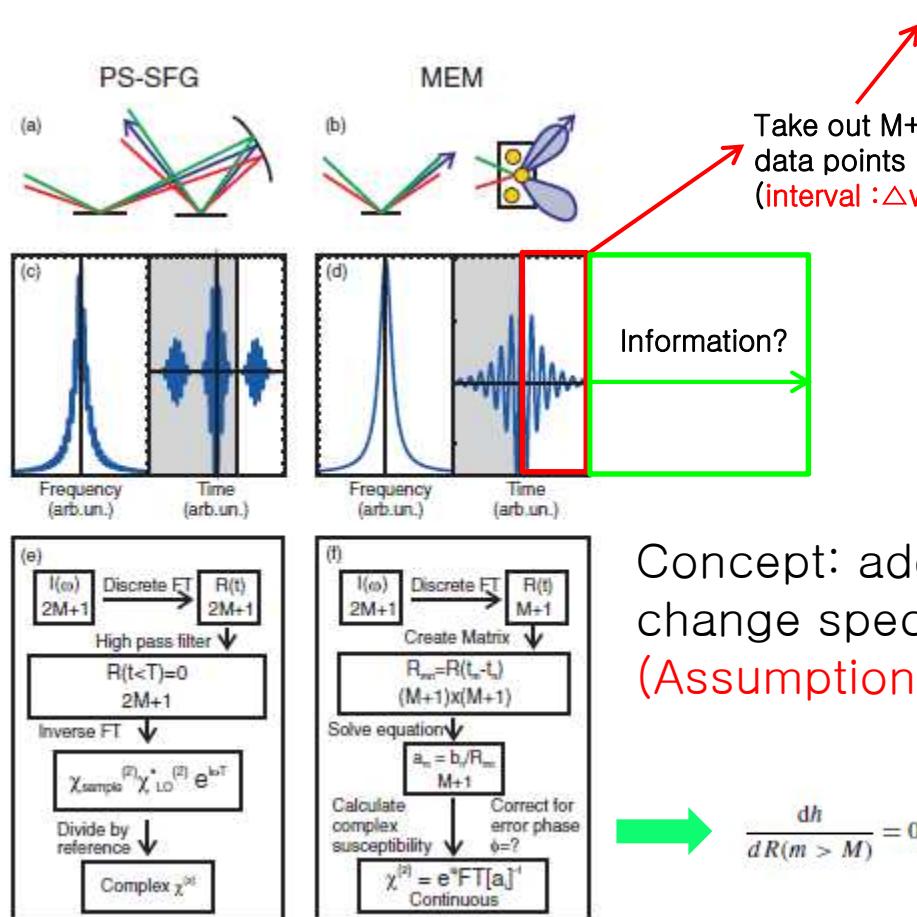
$$\frac{\chi_{\text{sample}}^{(2)}}{\chi_{\text{ref}}^{(2)}} = \frac{C_{\text{sample}}}{C_{\text{ref}}} \frac{E_{\text{sample}}(\omega) E_{\text{LO}}^* e^{i\omega T}}{E_{\text{ref}}(\omega) E_{\text{LO}}^* e^{i\omega T}} + \frac{C_{\text{sample}}}{C_{\text{ref}}} \frac{E_{\text{sample}}(\omega)}{E_{\text{ref}}(\omega)},$$

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

Clear Information about molecular orientation

Maximum entropy method

“The MEM describes a method of finding auto correlation values of $t > T_{\max}$ by quantifying the information content of spectrum by means of the spectral entropy h .”



$$h = \int_0^1 \log[I(v)] dv$$

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

Concept: adding information of $t > T_{\max}$ should not change spectral entropy!
 (Assumption: all of information is in spectrum!)

$$\frac{dh}{dR(m > M)} = 0 = \int_0^1 \frac{1}{I(v)} \frac{dI(v)}{dR(m > M)} dv.$$

Maximum entropy method

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

$$P(f) = \frac{1}{2W} \sum_{n=-\infty}^{+\infty} R(n) e^{-2\pi ifn\Delta t} \quad h = \int_{-W}^W \ln \left[\frac{1}{2W} \sum_{n=-\infty}^{+\infty} R(n) e^{-2\pi ifn\Delta t} \right] df$$
$$\frac{\partial h}{\partial R(s)} = \int_{-W}^W P^{-1}(f) e^{-2\pi ifs\Delta t} df = 0, \text{ for } (s > |N|)$$

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

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

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

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

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

Maximum entropy method

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

By taking summation of R(n),



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

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

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



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

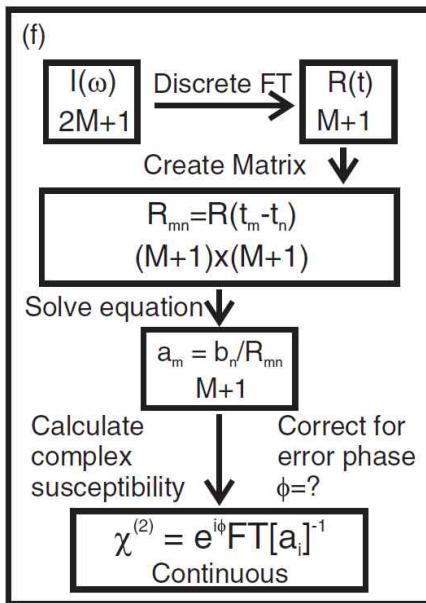
$$\sum_{n=0}^N a_n^* \square R(n-r) = 0 \text{ for } r>0$$

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

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

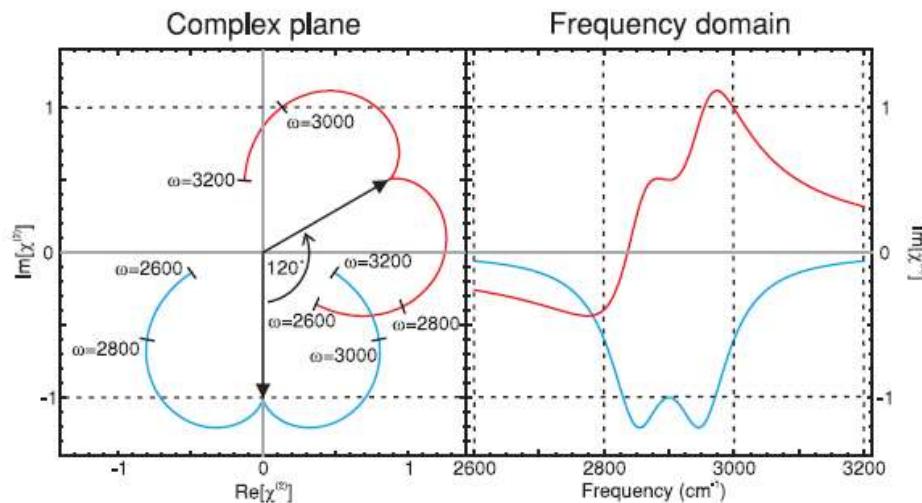
$$\chi^{(2)}(v) = \frac{be^{i\phi}}{g(v)} = \frac{be^{i\phi}}{\sum_{m=0}^M a_m e^{imv}}$$

Effect of error phase



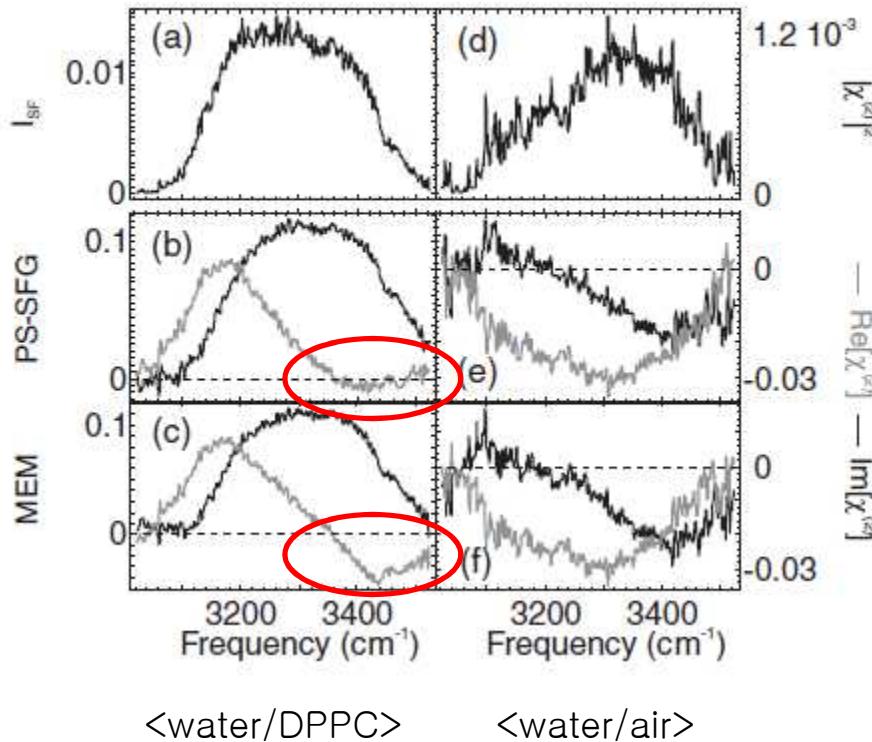
$$\chi^{(2)}(\nu) = \frac{be^{i\phi}}{g(\nu)} = \frac{be^{i\phi}}{\sum_{m=0}^M a_m e^{im\nu}}$$

Overall phase change give erroneous Imaginary spectra.



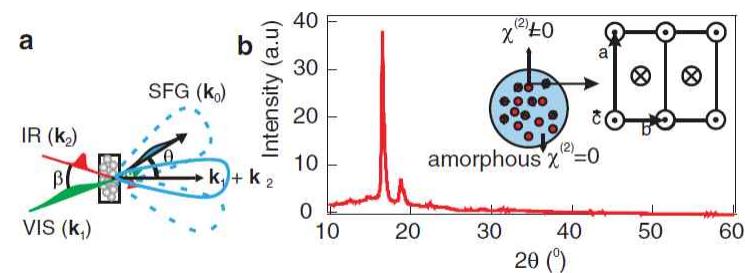
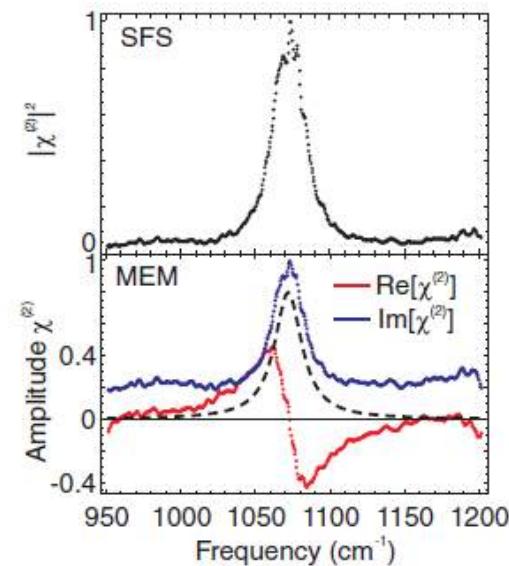
By checking Lorentzian line shape of Im spectra, correct Im spectra can be recovered.

Comparison of PS-SFVS and MEM



Data from – J. Am. Chem. Soc. 132, 11336 (2010).

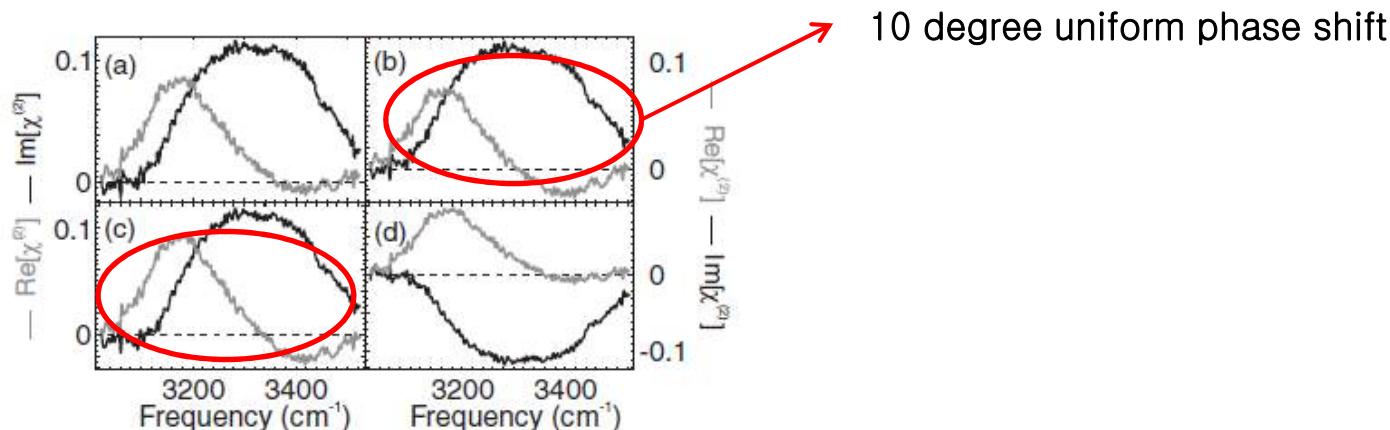
MEM could reproduce Im and Re spectra similar with result from PS-SFVS.



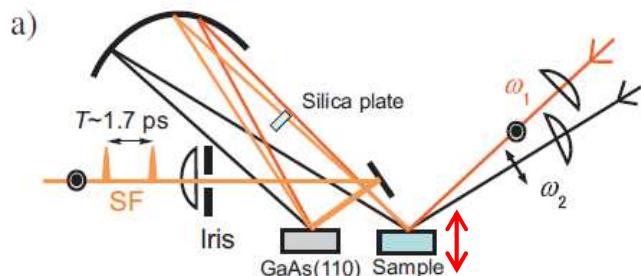
Phys. Rev. Lett. 095502 (2009)

Possible source of error

- 1) Phase shift - reference (quartz) has resonant component
(second order susceptibility is not purely real...??...)



- 2) Phase drift - possibility of sample and reference placing

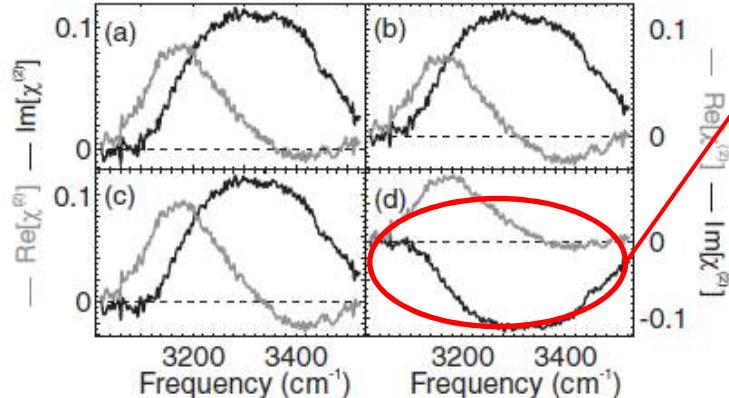


2. Phase drift

PS-SFG requires a stable experimental configuration. Care should be taken that the time delay T between the signals of the local oscillator and the sample or reference does not change between measurements. A difference in time delay would lead to a phase modulation $\exp[i\omega\Delta T]$, where ΔT is the time delay difference. For typical bandwidths of broadband systems, ω varies over a range of $250\text{--}400\text{ cm}^{-1}$, so that a difference in time delay of 40 fs leads to a phase drift of $17^\circ\text{--}27^\circ$ over the range of the spectrum. The effect of such a phase drift can be seen in Fig. 5(c): in this case, the peak in

Possible source of error

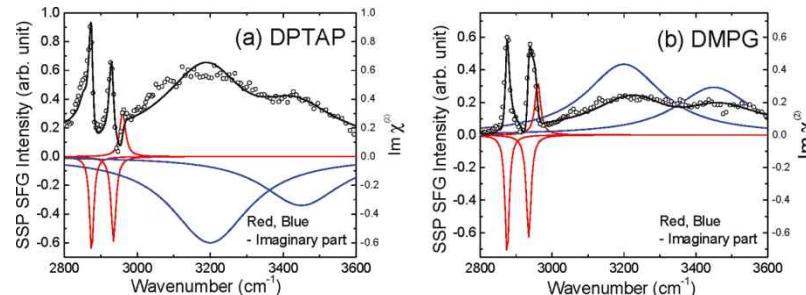
3) Complex conjugation



180degree inversion

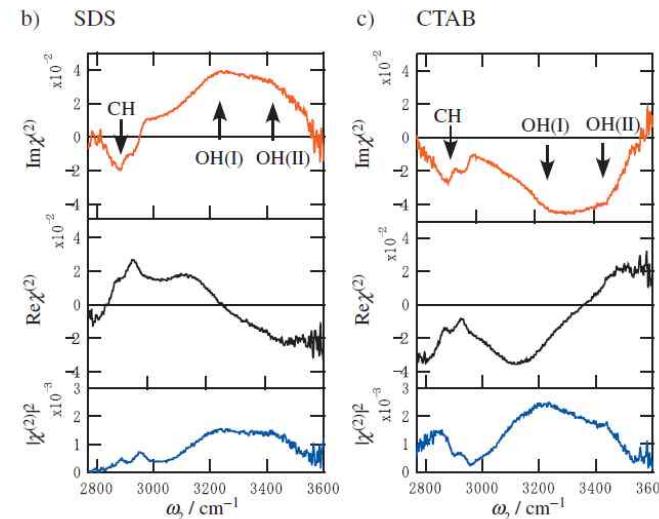
$$\sum_q B_q e^{iw_q t} e^{-\Gamma_q t} \rightarrow \chi_{\text{eff}}^{(2)}(w) \propto \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q}$$

$$\sum_q B_q e^{-iw_q t} e^{-\Gamma_q t} \rightarrow \chi_{\text{eff}}^{(2)}(w) \propto \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q - i\Gamma_q}$$



Langmuir, 26 ,18266 (2010)

the autocorrelation is used. The resulting spectrum is again complex conjugated with respect to the regular result. Since complex conjugation cannot be corrected for by applying a phase factor, such as in the error phase correction procedure, care must be taken that the same conventions are used when comparing spectra.



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