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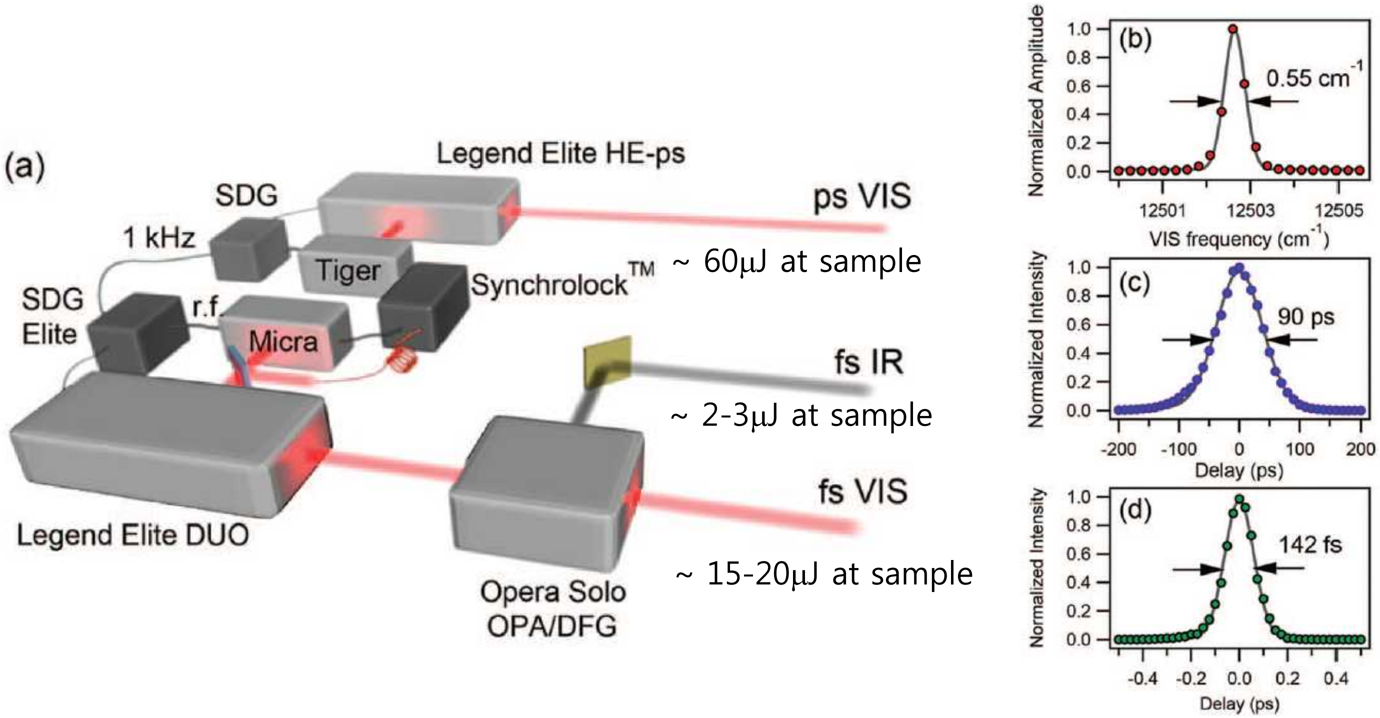
Unified treatment and measurement of the spectral resolution and temporal effects in frequency-resolved sum-frequency generation vibrational spectroscopy (SFG-VS)

Luis Velarde and Hong-Fei Wang*

Setup: HR-BB-SFG / BB-SFG system

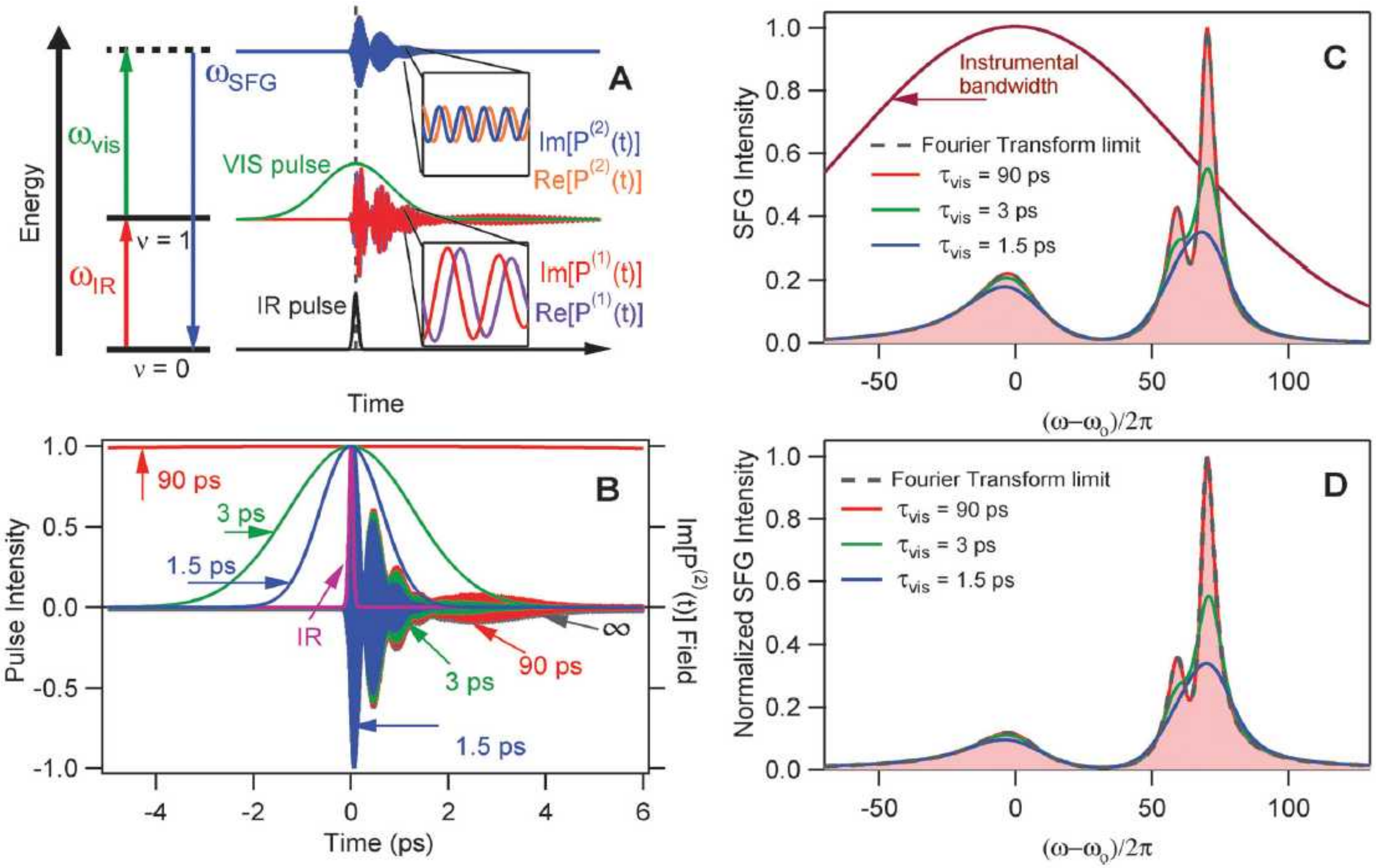


J. Chem. Phys. **139**, 084204 (2013).

Beam spot: IR ~ 200μm
VIS ~ 500μm

Electron-Multiplied CCD camera (Andor Newton 971P, back-illuminated) containing a 1600×400, 16 μm2, pixel array
/ Shamrock Andor spectrometer, Grating : 1200/mm

Longer Vis duration – more precise information of FID

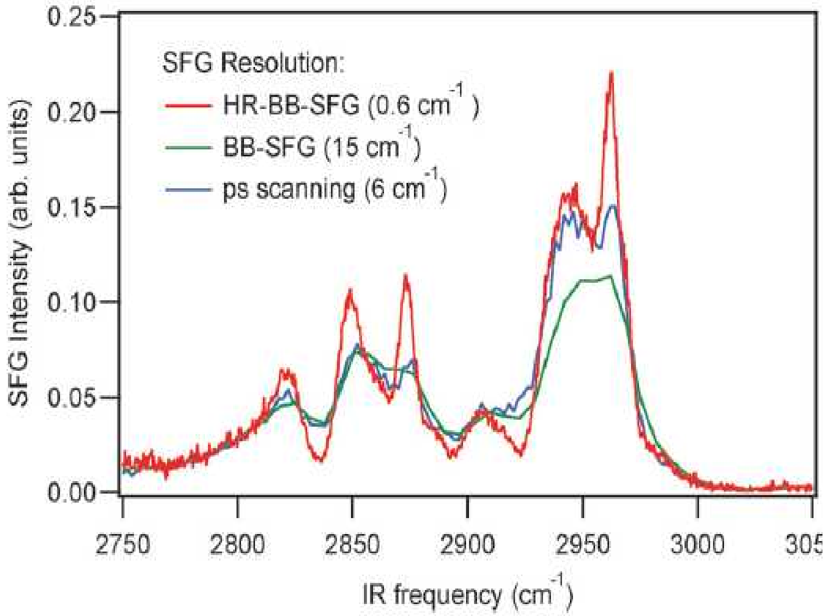


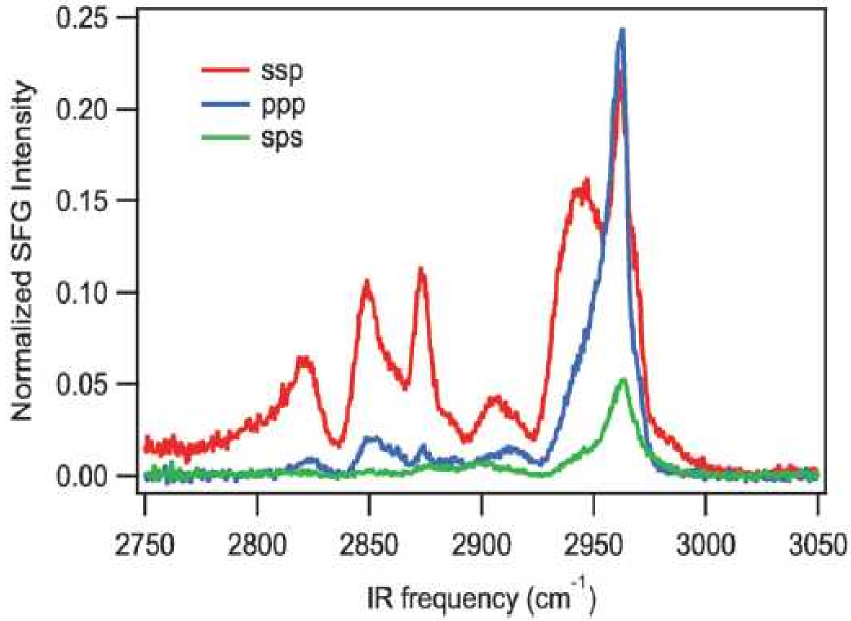
$$R^{(2)}(t_1) = |A_{\mathrm{NR}}|\mathrm{e}^{i\psi_{\mathrm{NR}}}\delta(t_1) - i\theta(t_1)\sum_q A_q \mathrm{e}^{-i\omega_q t_1}\mathrm{e}^{-\frac{t_1}{T_{2q}}}\mathrm{e}^{-\frac{\Delta\omega_q^2 t_1^2}{2}}. \qquad (11)$$

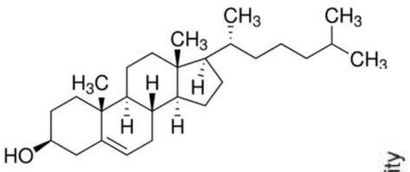
$$\tilde{R}^{(2)}(\omega_{\mathrm{IR}}) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{i\omega_{\mathrm{IR}}t} R^{(2)}(t)\mathrm{d}t. \qquad (12)$$

$$\begin{aligned}\hat{R}^{(2)}(\omega_{\mathrm{IR}}) &= |A_{\mathrm{NR}}|\mathrm{e}^{i\psi_{\mathrm{NR}}} + \sum_q \frac{A_q}{(\omega_q - \omega_{\mathrm{IR}}) - i\Gamma_q} \otimes \mathrm{e}^{-\frac{\omega_{\mathrm{IR}}^2}{2\Delta\omega_q^2}} \\ &= |A_{\mathrm{NR}}|\mathrm{e}^{i\psi_{\mathrm{NR}}} + \sum_q \int_0^{\infty} \frac{A_q}{(\omega_q - \omega') - i\Gamma_q} \mathrm{e}^{-\frac{(\omega_{\mathrm{IR}}-\omega')^2}{2\Delta\omega_q^2}} \mathrm{d}\omega'\end{aligned} \qquad (13)$$

Measurement: cholesterol monolayer on water







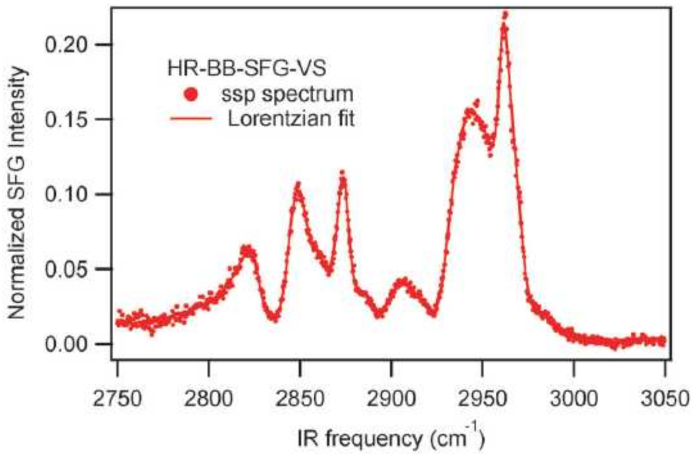
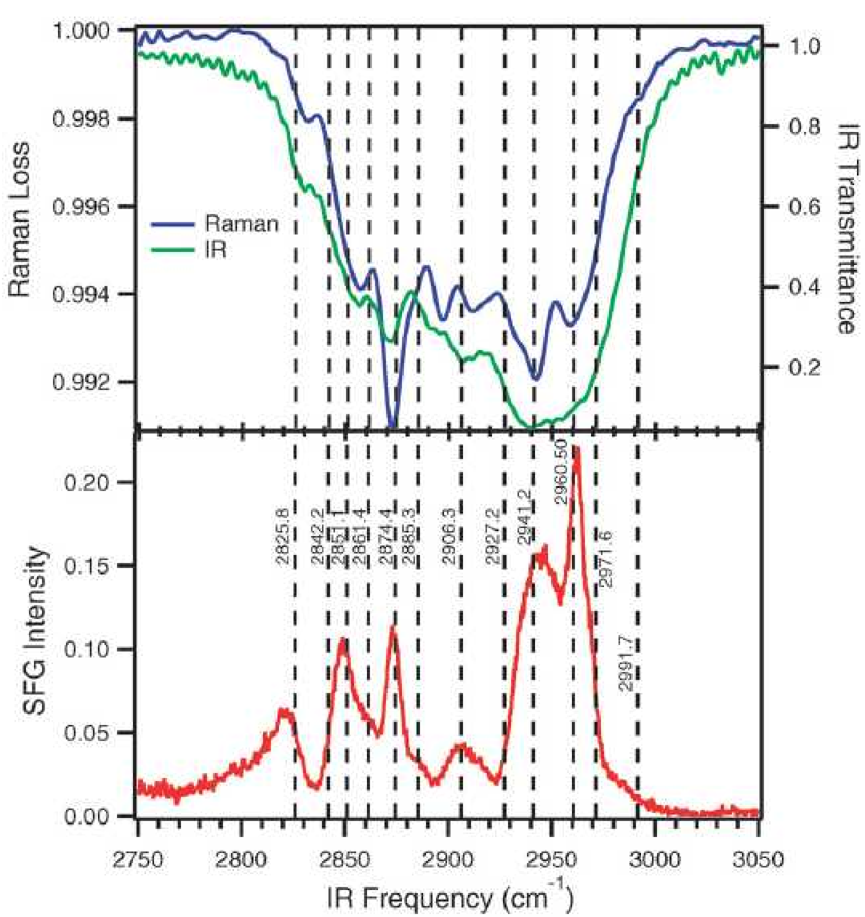
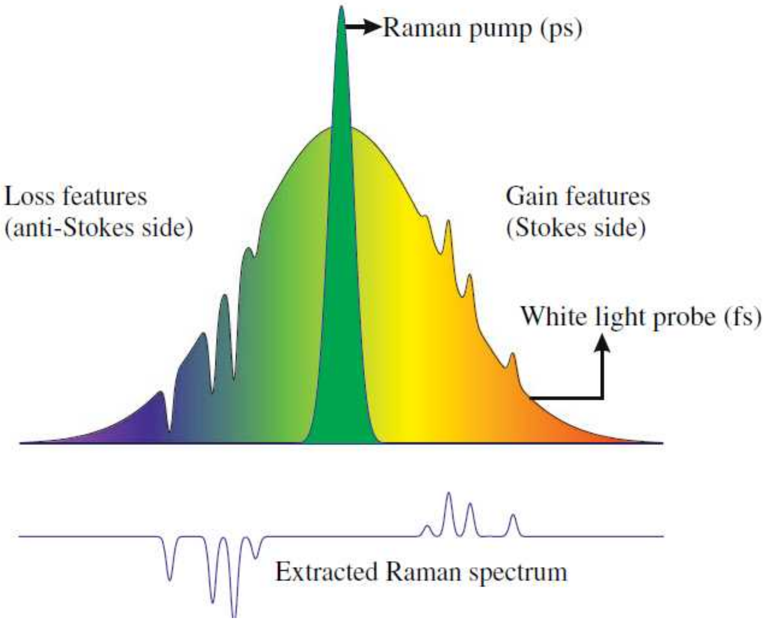


Table 2 Fitting parameter of HR-BB-SFG-VS ssp spectra using $|\tilde{R}^{(2)}(\omega_{IR})|^2$ with a Lorentzian lineshape. The first row shows the value of $|A_{NR}|e^{i\psi_{NR}}$. Here $T_{2q} = 1/(2\pi c\Gamma_q)$ is calculated from the Γ_q values. It is going to be used in the simulation using the time-domain eqn (11)

A_q	ω_q (cm^{-1})	Γ_q (cm^{-1})	T_{2q} (ps)
0.035 ± 0.002			
1.05 ± 0.07	2825.8 ± 0.2	7.5 ± 0.3	0.71 ± 0.03
−0.7 ± 0.3	2842.2 ± 0.6	6.6 ± 1.2	0.80 ± 0.15
1.6 ± 0.5	2851.1 ± 0.4	8.1 ± 1.3	0.65 ± 0.10
0.38 ± 0.15	2861.4 ± 0.4	5.2 ± 1.0	1.02 ± 0.20
1.07 ± 0.05	2874.4 ± 0.08	4.7 ± 0.2	1.12 ± 0.05
0.42 ± 0.08	2885.3 ± 0.4	6.2 ± 0.9	0.84 ± 0.12
0.69 ± 0.17	2906.3 ± 0.4	8.6 ± 1.1	0.62 ± 0.08
−1.5 ± 0.4	2927.2 ± 0.2	8.5 ± 0.9	0.62 ± 0.07
9.9 ± 1.1	2941.2 ± 1.0	22.6 ± 1.4	0.23 ± 0.01
0.60 ± 0.04	2960.50 ± 0.07	3.67 ± 0.15	1.44 ± 0.06
−1.32 ± 0.14	2971.6 ± 0.2	7.8 ± 0.5	0.68 ± 0.04
−0.9 ± 0.2	2991.7 ± 1.0	13.4 ± 2.2	0.40 ± 0.06

Comparison to bulk IR and Raman measurement





Ultrafast Raman Loss spectroscopy (URLS)

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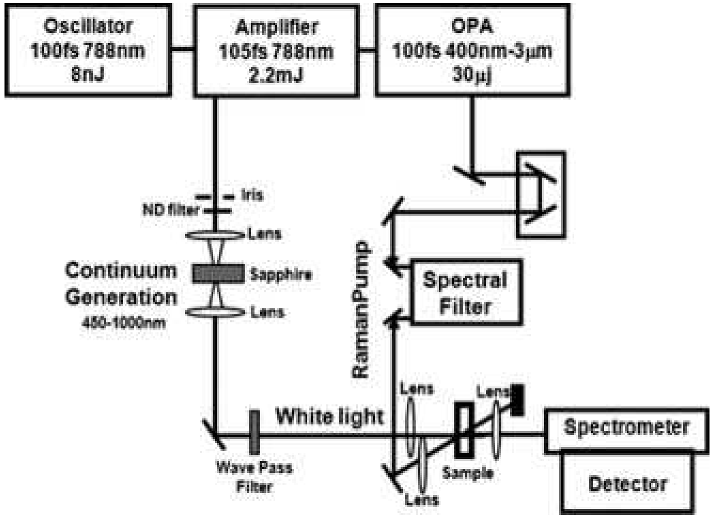

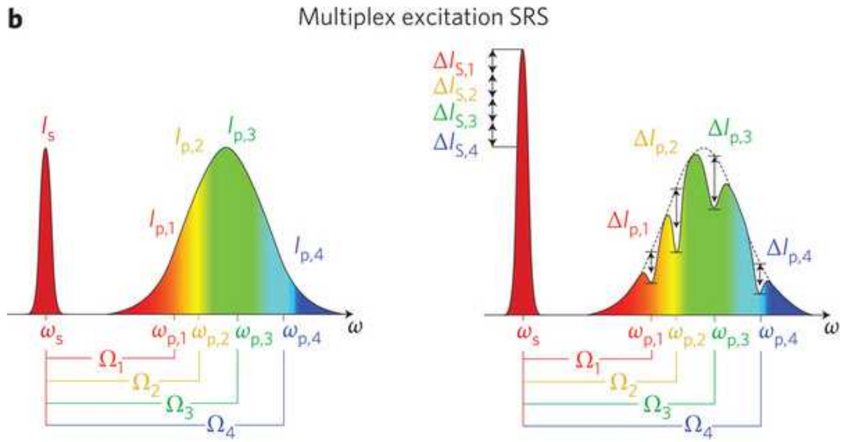

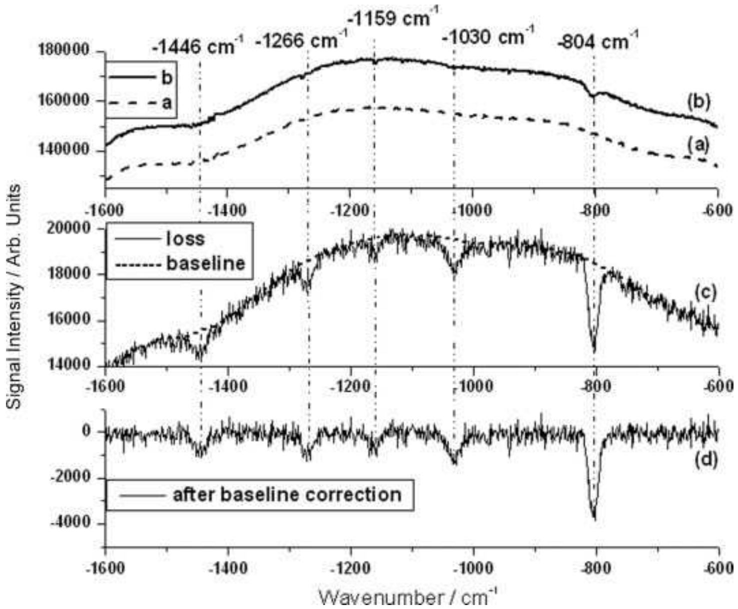

Mallick et al. J. Raman Spectrosc. **2011**, *42*, 1883–1890.

THE JOURNAL OF CHEMICAL PHYSICS **135**, 241102 (2011)

Communication: Spectroscopic phase and lineshapes in high-resolution broadband sum frequency vibrational spectroscopy: Resolving interfacial inhomogeneities of "identical" molecular groups

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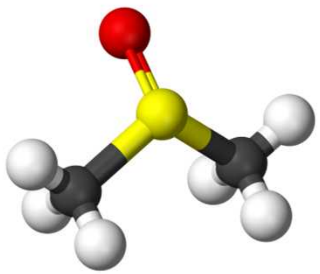
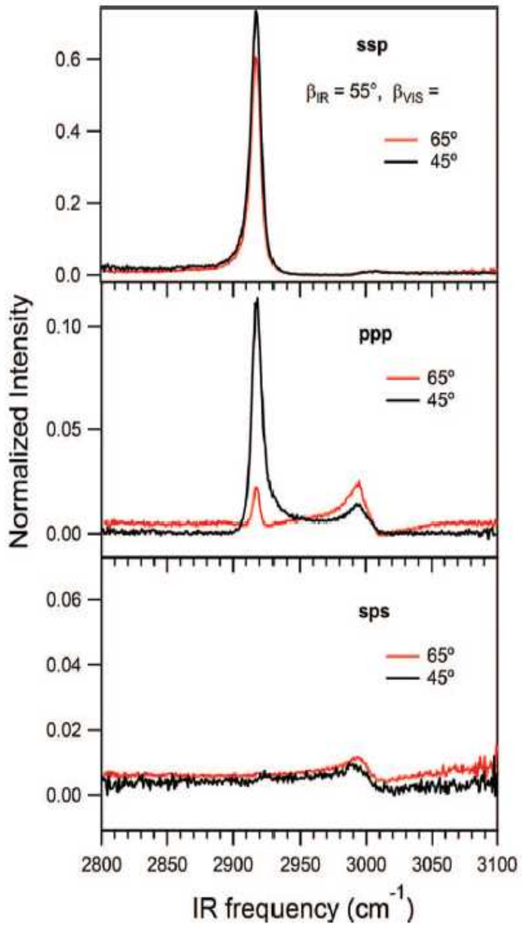
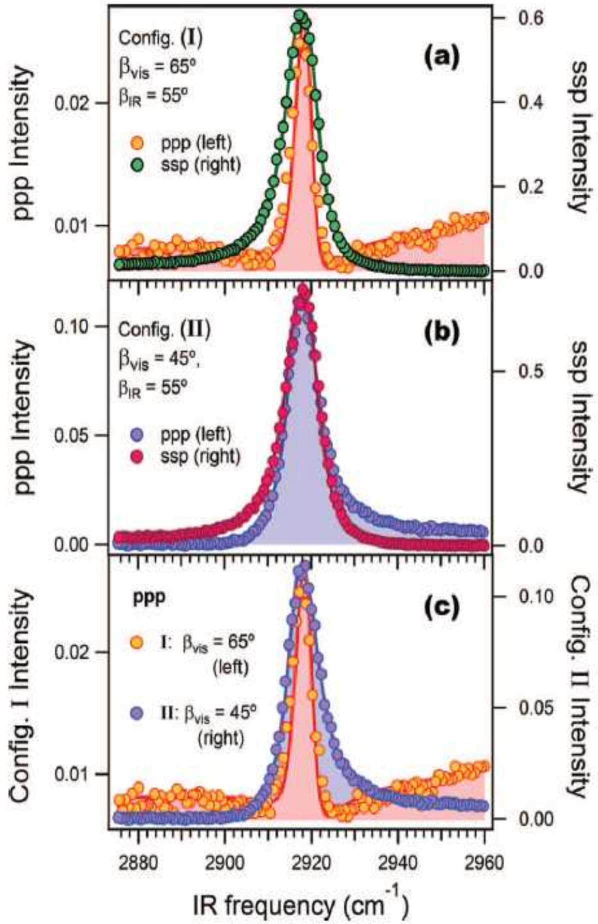
The ability to achieve sub-wavenumber resolution (0.6 cm^{-1}) and a large signal-to-noise ratio in high-resolution broadband sum-frequency generation vibrational spectroscopy (HR-BB-SFG-VS) allows for the detailed SFG spectral lineshapes to be used in the unambiguous determination of fine spectral features. Changes in the structural spectroscopic phase in SFG-VS as a function of beam polarization and experimental geometry proved to be instrumental in the identification of an unexpected 2.78 ± 0.07 cm^{-1} spectral splitting for the two methyl groups at the vapor/dimethyl sulfoxide (DMSO, $(CH_3)_2SO$) liquid interface as well as in the determination of their orientational angles.
 [doi:10.1063/1.3675629]

Comparison to bulk IR and Raman measurement



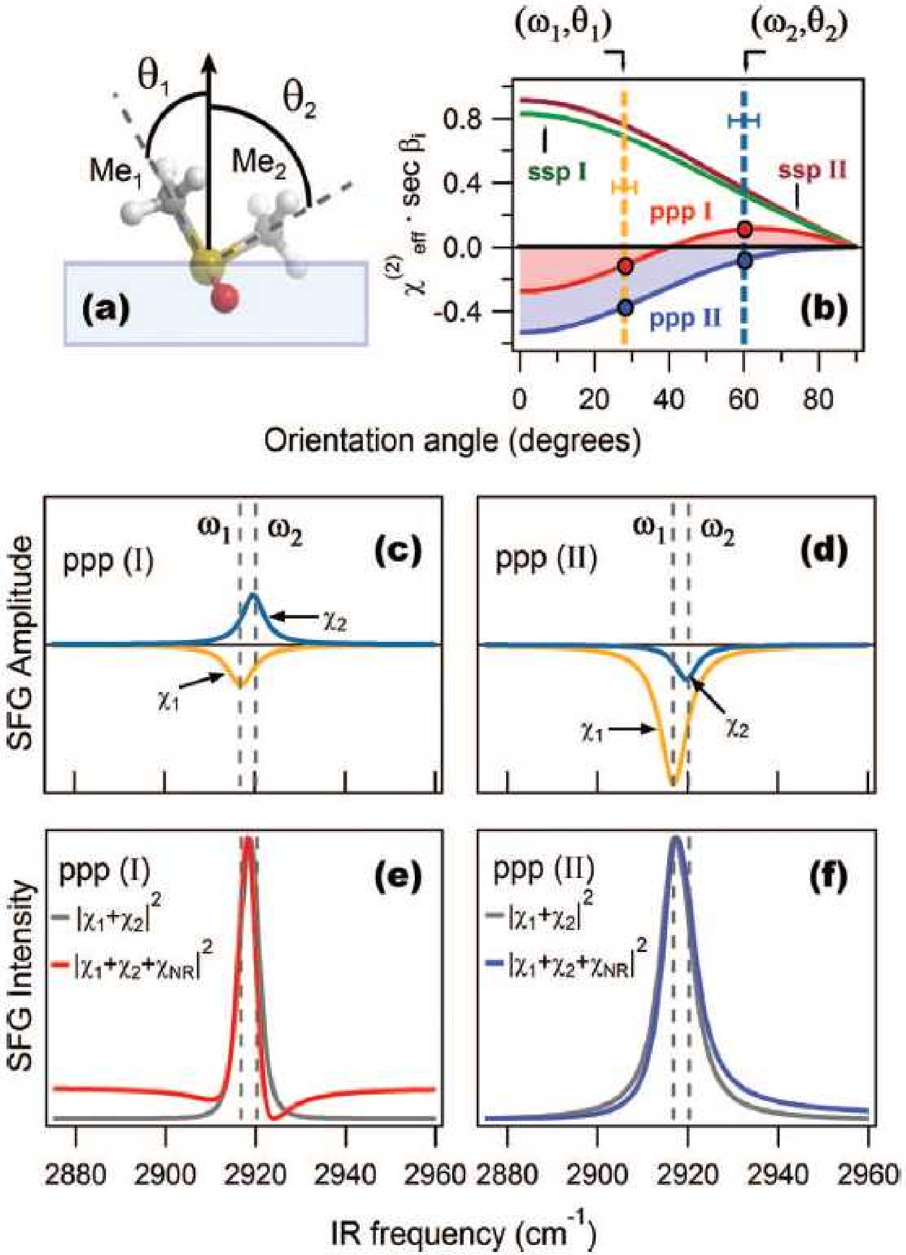
DMSO





$$
\begin{aligned}
\chi^{(2)}_{\mathrm{eff,SSP}} &= L_{yy}(\omega_{\mathrm{SF}})L_{yy}(\omega_{\mathrm{Vis}})L_{zz}(\omega_{\mathrm{IR}})\sin\beta_2\cdot\chi^{(2)}_{yyz},\\
\chi^{(2)}_{\mathrm{eff,PPP}} &= -L_{xx}(\omega_{\mathrm{SF}})L_{xx}(\omega_{\mathrm{Vis}})L_{zz}(\omega_{\mathrm{IR}})\cos\beta\cos\beta_1\sin\beta_2\cdot\chi^{(2)}_{xxz}\\
&\quad -L_{xx}(\omega_{\mathrm{SF}})L_{zz}(\omega_{\mathrm{Vis}})L_{xx}(\omega_{\mathrm{IR}})\cos\beta\sin\beta_1\cos\beta_2\cdot\chi^{(2)}_{xzx}\\
&\quad +L_{zz}(\omega_{\mathrm{SF}})L_{xx}(\omega_{\mathrm{Vis}})L_{xx}(\omega_{\mathrm{IR}})\sin\beta\cos\beta_1\cos\beta_2\cdot\chi^{(2)}_{zxx}\\
&\quad +L_{zz}(\omega_{\mathrm{SF}})L_{zz}(\omega_{\mathrm{Vis}})L_{zz}(\omega_{\mathrm{IR}})\sin\beta\sin\beta_1\sin\beta_2\cdot\chi^{(2)}_{zzz}, \qquad (5)\\
\chi^{(2)}_{\mathrm{eff,SPS}} &= L_{yy}(\omega_{\mathrm{SF}})L_{zz}(\omega_{\mathrm{Vis}})L_{yy}(\omega_{\mathrm{IR}})\sin\beta_1\cdot\chi^{(2)}_{yzy},
\end{aligned}
$$

Assignment of modes : from Me_1 and Me_2



Summary

1) HR-BB-SFG setup consist of ps and fs amplifier system which are internally syncronized.

2) Longer duration (~90ps) of visible pulse gives high resolution (~$0.6 cm^{-1}$) of SF spectra.

3) For simple DMSO molecules at air / water interface, observed SF spectra of CH3 modes shows assymetric peak shape presumably due to different local environment of Me_1 and Me_2. And analysis on $CH_{3,ss}$ fits well with two different frequencies.