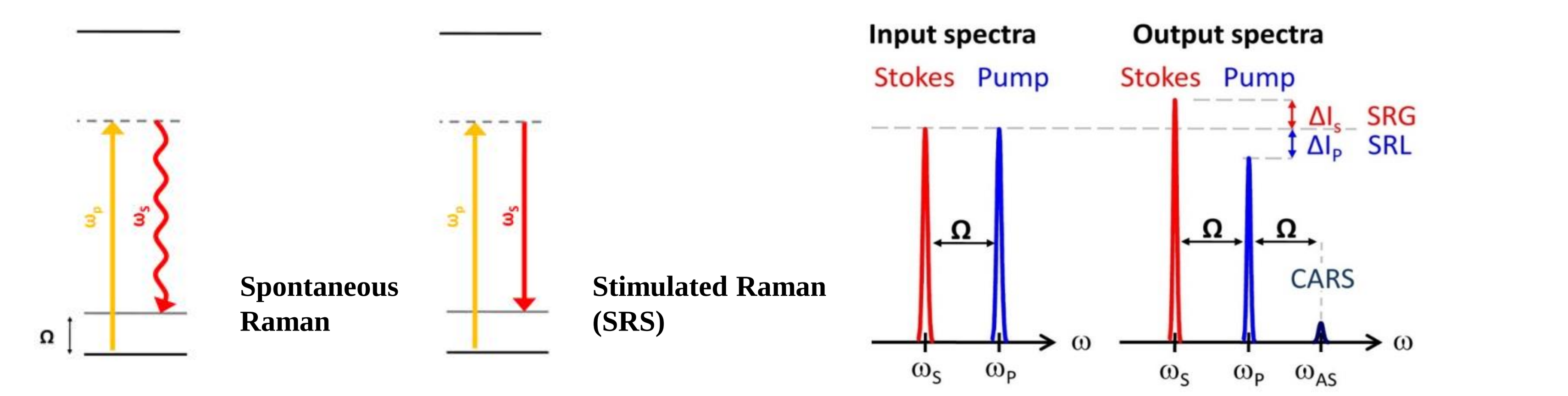
Vibrational mode competition in three-color stimulated Raman scattering (SRS) spectroscopy

Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 136-701, Republic of Korea
Department of Chemistry, Korea University, Seoul 136-701, Republic of Korea

Doyeon Kim, Dae sik Choi, Jiwoong Kwon, Hanju Rhee, Minhaeng Cho and Sang-Hee Shim

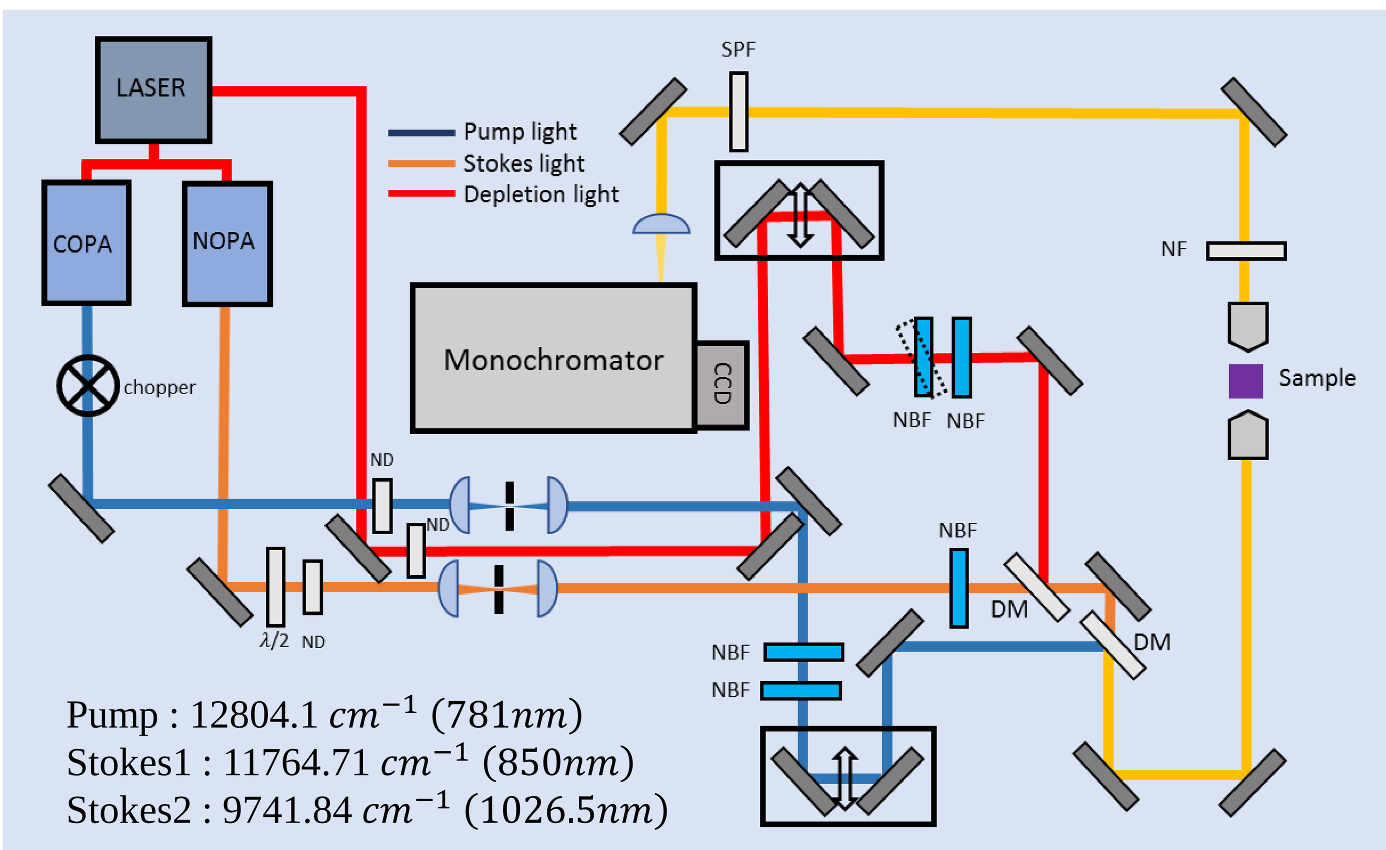
❖ Raman Spectroscopy



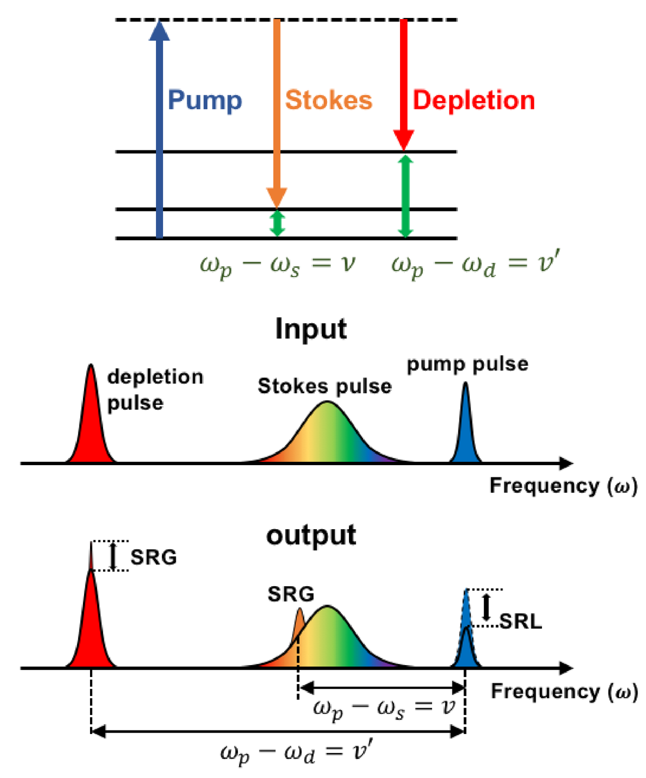
- Raman microscopy offers a contrast mechanism probing the intrinsic vibrational frequencies of chemical bonds or groups.
- SRS gives identical spectral profile as spontaneous Raman scattering and it provides several orders of magnitude stronger signal through stimulated scattering.

Fa-Ke Lu et al. *PNAS* 112 11624 (2015)

❖ SRS Spectroscopy Set up



❖ Three-color stimulated Raman scattering (SRS)



- Here we carried out three-beam double SRS measurements, where ps Raman pump, fs Stokes, and ps depletion beams are overlapped in time and space to induce two SRS processes.
- The frequency difference ($\Delta\omega_\nu$) between the pump and Stokes beams is matched to ν=992 cm^{-1}, whereas that ($\Delta\omega_{\nu'}$) between the pump and depletion beams is to ν'=3056 cm^{-1}, leading to two different SRS processes.
- Since they both require annihilations of the common Raman pump photons, a strong competition between the two SRS processes arises. As the intensity of the depletion (the second Stokes) beam increases, the SRS signal generated by the pump and Stokes beams is shown to be suppressed.

❖ Theoretical description

$$n_d(0) > n_p(0) > n_s(0)$$

$$\frac{d\Delta I_s(z)}{dz} = G_s I_s(0)\left(\frac{\mu_p V}{\hbar\omega_p c} I_p(0) - \frac{\mu_d V}{\hbar\omega_d c}\Delta I_d(z)\right)$$

$$\frac{d\Delta I_d(z)}{dz} = G_d\left(\frac{\mu_p V}{\hbar\omega_p c} I_p(0) - \frac{\mu_d V}{\hbar\omega_d c}\Delta I_d(z)\right)\left(I_d(0)+\Delta I_d(z)\right)$$

Stokes gain signal

$$\Delta I_s(z) = G_s I_s(0)\left(\frac{\mu_p V}{\hbar\omega_p c} I_p(0) + \frac{\mu_d V}{\hbar\omega_d c} I_d(0)\right) z + \frac{G_s}{G_d} I_s(0)\left\{\ln\left(\frac{\mu_p\omega_d I_p(0)}{\mu_d\omega_p I_d(0)}+1\right) - \ln\left(\frac{\mu_p\omega_d I_p(0)}{\mu_d\omega_p I_d(0)} + e^{G_d\left[\frac{\mu_p V}{\hbar\omega_p c} I_p(0) + \frac{\mu_d V}{\hbar\omega_d c} I_d(0)\right] z}\right)\right\}$$

Depletion efficiency

$$\eta \equiv \frac{\Delta I_s(z, I_d(0)=0) - \Delta I_s(z, I_d(0))}{\Delta I_s(z, I_d(0)=0)}$$

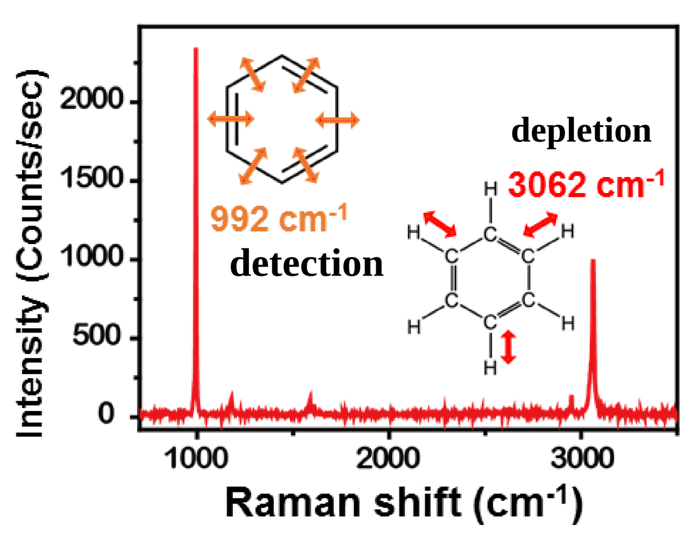
$$\eta = 1 - \left\{(1+x) + \frac{1}{\xi}\ln\left(\frac{x+1}{x e^{\xi(1+x)}+1}\right)\right\}$$

$$(\xi \equiv G_d n_p(0) z,\ \ x = n_d(0)/n_p(0))$$

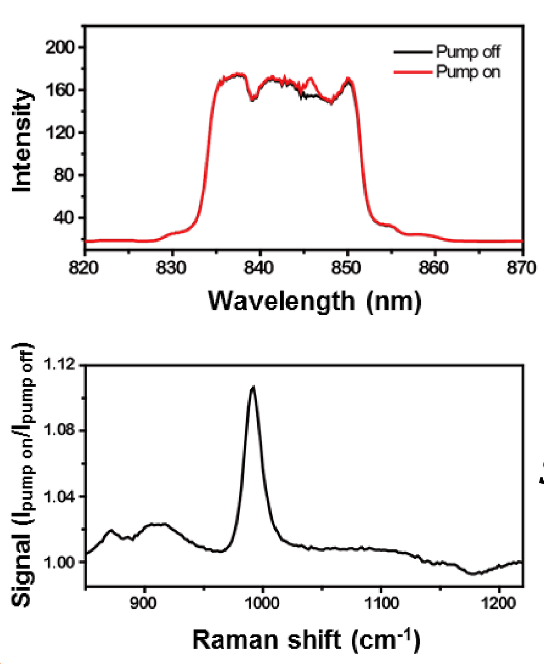
M. Cho *J. Chem. Phys. Submitted* (2017)

❖ Spectroscopic Results

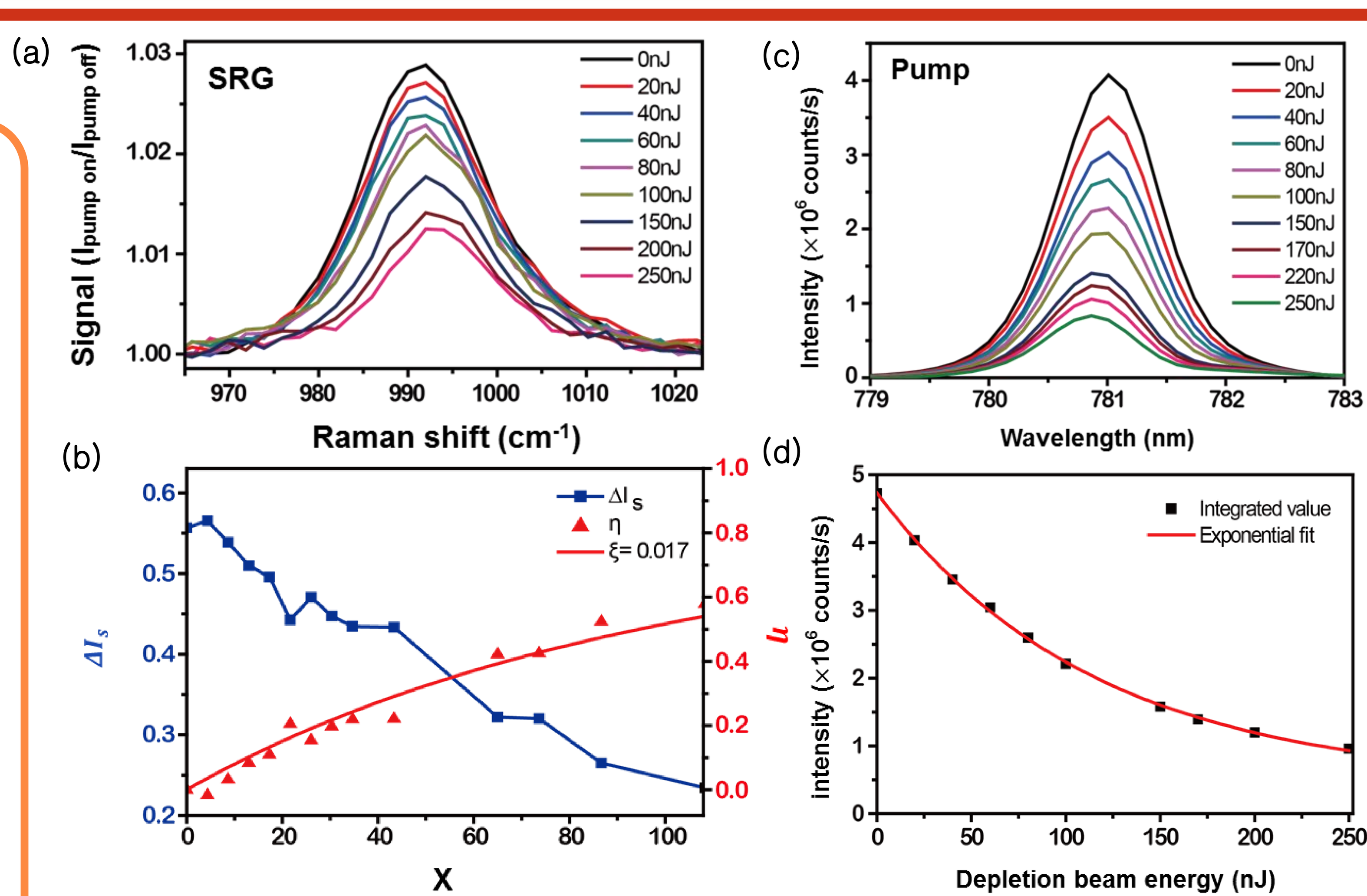
Target mode



SRG spectrum

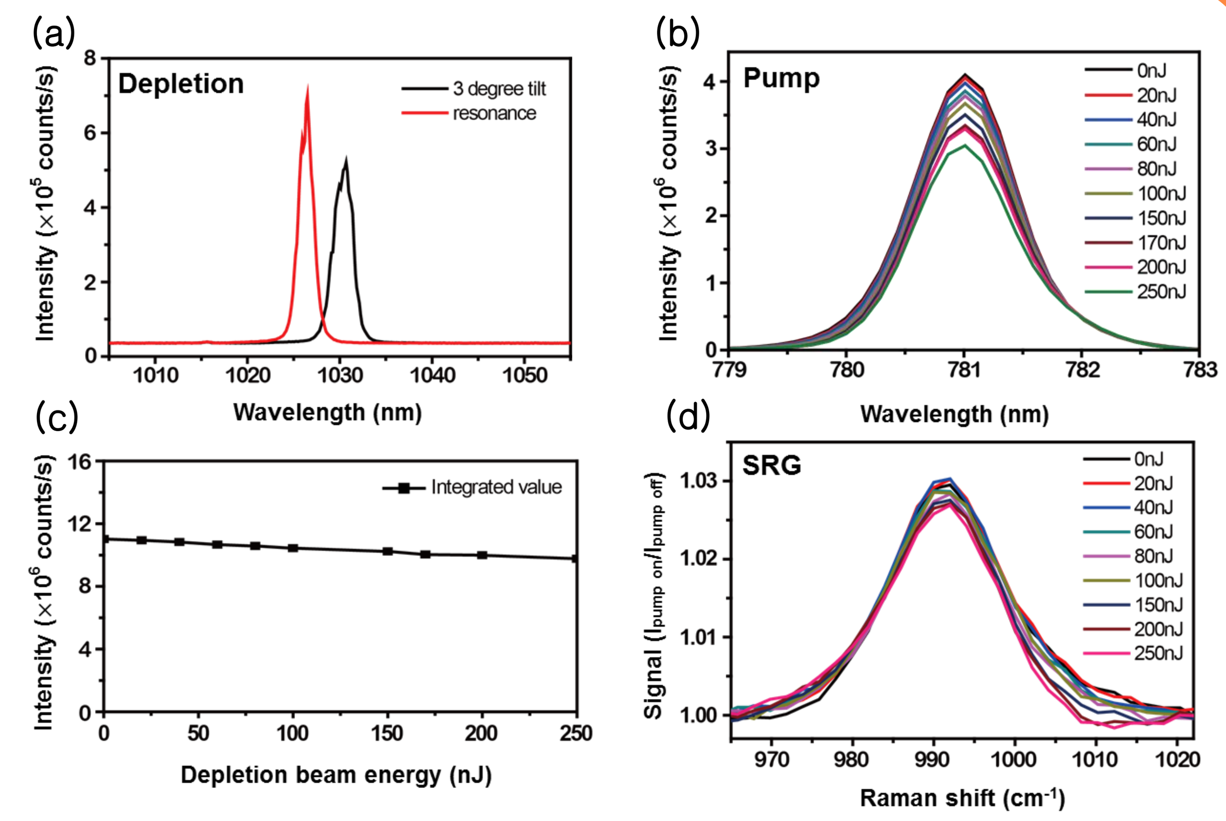


$$SRG = \frac{I_{pump_{on}}}{I_{pump_{off}}}$$



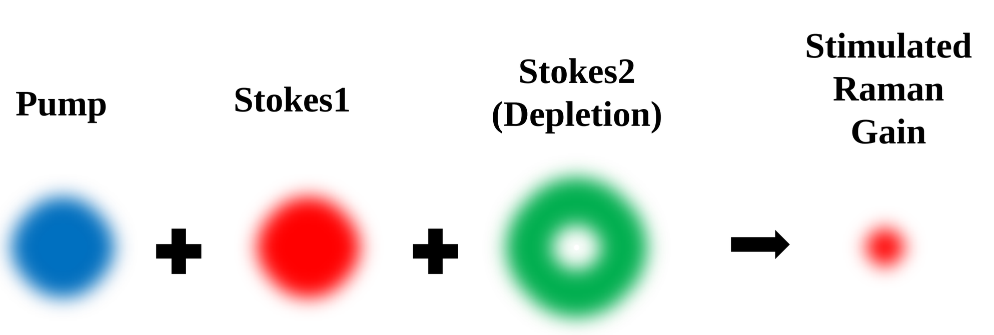
- We measured SRS spectra of the ring breathing mode at various intensities of the depletion beam, which acts as a stimulating Stokes beam for another SRS process of C-H stretch modes. While the Raman pump energy per pulse was fixed at 3 nJ and the pulse energy of the depletion beam (λ = 1026.5 nm) was increased from 0 to 250 nJ (corresponding to a peak intensity of ~2.1 TW/cm2), we measured the pump-Stokes SRG spectra associated with the ring breathing mode at 992 cm^{-1} (a). SRG intensity of the ring breathing mode is strongly suppressed by the competing SRS process of C-H stretch induced by the pair of pump and depletion beams. In the case that the depletion beam energy is 250 nJ, which is approximately 100 times stronger than the pump energy, the suppression efficiency is about 58 % (b).
- To further investigate the underlying mechanism of our three-beam double SRS process, we measured the pump spectra with increasing energy of the depletion beam (c). The maximum value of the pump intensity decays exponentially (with decay constant 114.5 nJ) as the energy of depletion beam increases (d).

Non-resonant condition



- To experimentally confirm that the suppression of the Stokes gain signal is induced by the depletion of the pump beam due to the competing SRS process, we changed the wavelength of the depletion beam. Tilting the corresponding bandpass filter by 3 degrees makes the center wavelength of the depletion beam shifted by about 4 nm (38 cm^{-1}) (a).
- Due to the non-resonance of the pump-depletion difference frequency field component with the C-H stretch mode of benzene, the amount of pump energy loss becomes much less (11 % efficiency) than the case before shifting the wavelength of the depletion beam (80 %) (b,c).
- When the wavelength of the depletion beam is tuned to be slightly non-resonant with the C-H stretch mode. Then, the maximum suppression efficiency is about 21 %, which is much smaller than the maximum suppression efficiency of 58 % when the pump-depletion beam pair was tuned to be fully resonant with the C-H stretch mode.

❖ Conclusion and Future work



- Our work provides a theoretically and experimentally new concept of three-color double resonance femtosecond SRS spectroscopy that is capable of effectively suppressing the SRS signal of interest by means of another SRS process. We here experimentally demonstrate this scheme and described the results with theoretical expressions obtained by solving the coupled differential equations for the Stokes and depletion beam intensities.
- We are planning to implement our scheme to a new method for sub-diffraction-limit Raman imaging. This technique is based on the depletion principle of STED, combined with a stimulated Raman technique. A typical SRS imaging setup uses tightly focused Raman pump and Stokes beams and the SRS signals are detected by using lock-in amplification method while modulating pump or Stokes intensities. If we add a doughnut-shaped depletion beam to selectively suppress the imaging target SRS signal in the peripheral region at the focal spot of both the pump and Stokes beams, it will be possible to break the diffraction limit of SRS microscopy. The three-beam double SRS technique with Gaussian pump, Gaussian Stokes, and doughnut-shape depletion beams can be a novel approach to super-resolution label-free vibrational imaging tool.