# Study of Stimulated Raman Spectroscopy for chiral molecules


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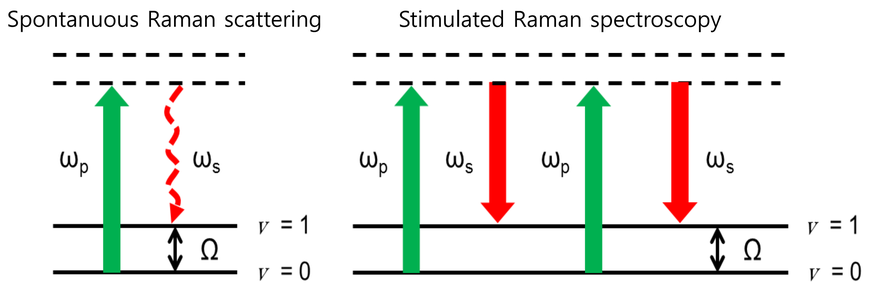
## ❖ Vibrational spectroscopy by Raman scattering process



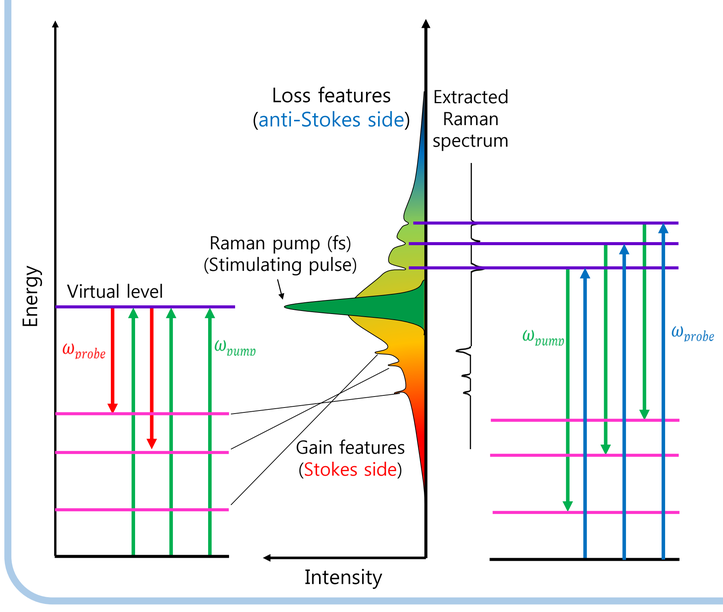

**Phase matching condition**

$$\vec{k_s} = \vec{k_s} - \vec{k_p} + \vec{k_p}$$
$$\omega_s = \omega_s - \omega_p + \omega_p$$

✓ In the spontaneous Raman spectroscopy, a coherent pump beam at $\omega_p$ is incident on a sample, and Stokes $\omega_S$ or anti-Stokes $\omega_{AS}$ photons are generated.

✓ The stimulated Raman scattering (SRS) is a four-wave interaction. The Stimulated Raman Scattering (SRS) represents one of the third-order nonlinear optical processes.

## ❖ Stimulated Raman Scattering (SRS) energy diagram

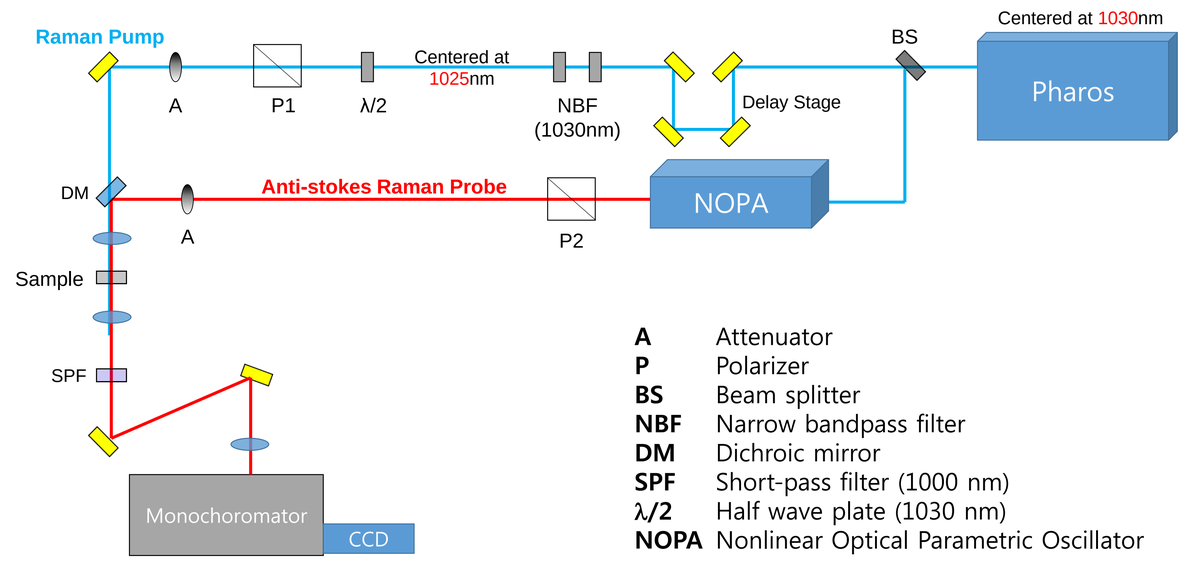



$$Gain\ or\ Loss = \frac{Raman\ probe\ with\ Raman\ pump\ on}{Raman\ probe\ with\ Raman\ pump\ off}$$

Pink lines represent Raman active vibrational modes. Purple lines stand for virtual levels.

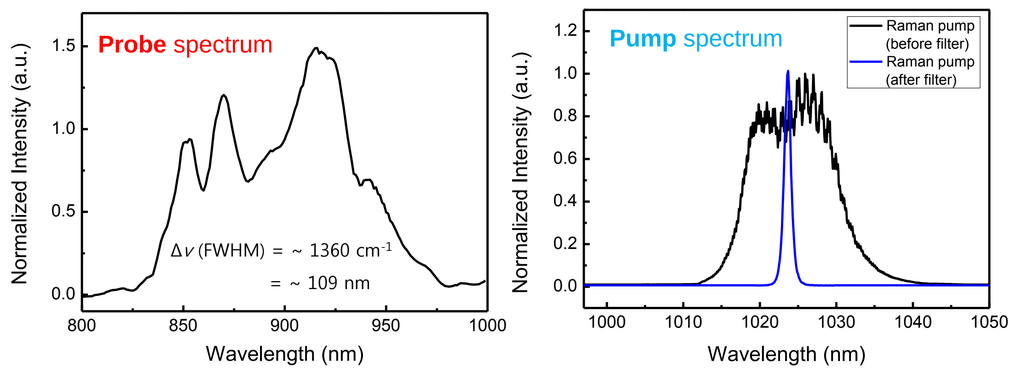
Stimulated Raman interactions between a white light probe pulse (frequency components, $\omega_{probe}$) and an intense Raman pump pulse ($\omega_{pump}$) cause amplifications (stokes side) and signal reductions (anti-Stokes side) of the white light.

## ❖ Layout of the stimulated Raman spectrum measurement system




**A** Attenuator
**P** Polarizer
**BS** Beam splitter
**NBF** Narrow bandpass filter
**DM** Dichroic mirror
**SPF** Short-pass filter (1000 nm)
**λ/2** Half wave plate (1030 nm)
**NOPA** Nonlinear Optical Parametric Oscillator

### ● Raman pump and Raman probe spectra




**Fundamental Raman pump**
Δν (FWHM) = ~ 156 cm$^{-1}$
= ~ 12 nm

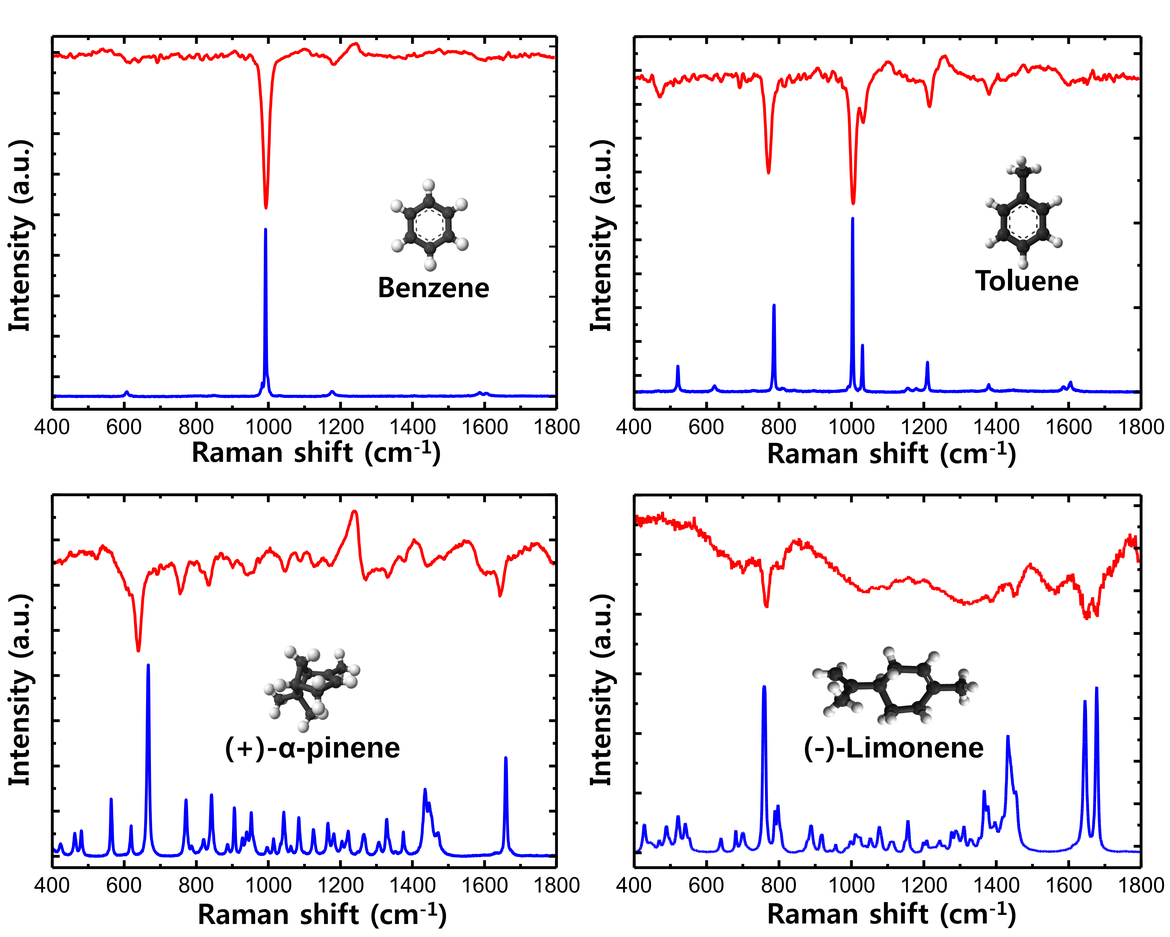
**Raman pump after NBP filter**
Δν (FWHM) = ~ 12 cm$^{-1}$
= ~ 1 nm

✓ The fundamental pump beam is centered at 1030nm, after filter pair, the pump pulse is centered at 1024 nm with a bandwidth of 12 cm$^{-1}$. Because we can control the center of pump pulse by tilting angle of narrow band-pass filters.

✓ A broadband Raman probe pulse (800–980 nm) providing the Anti-stokes field (the spectral window from 400 cm$^{-1}$ to 1800 cm$^{-1}$) with a 130 fs NOPA (Nonlinear Optical Parametric Oscillator).

## ❖ Experimental results

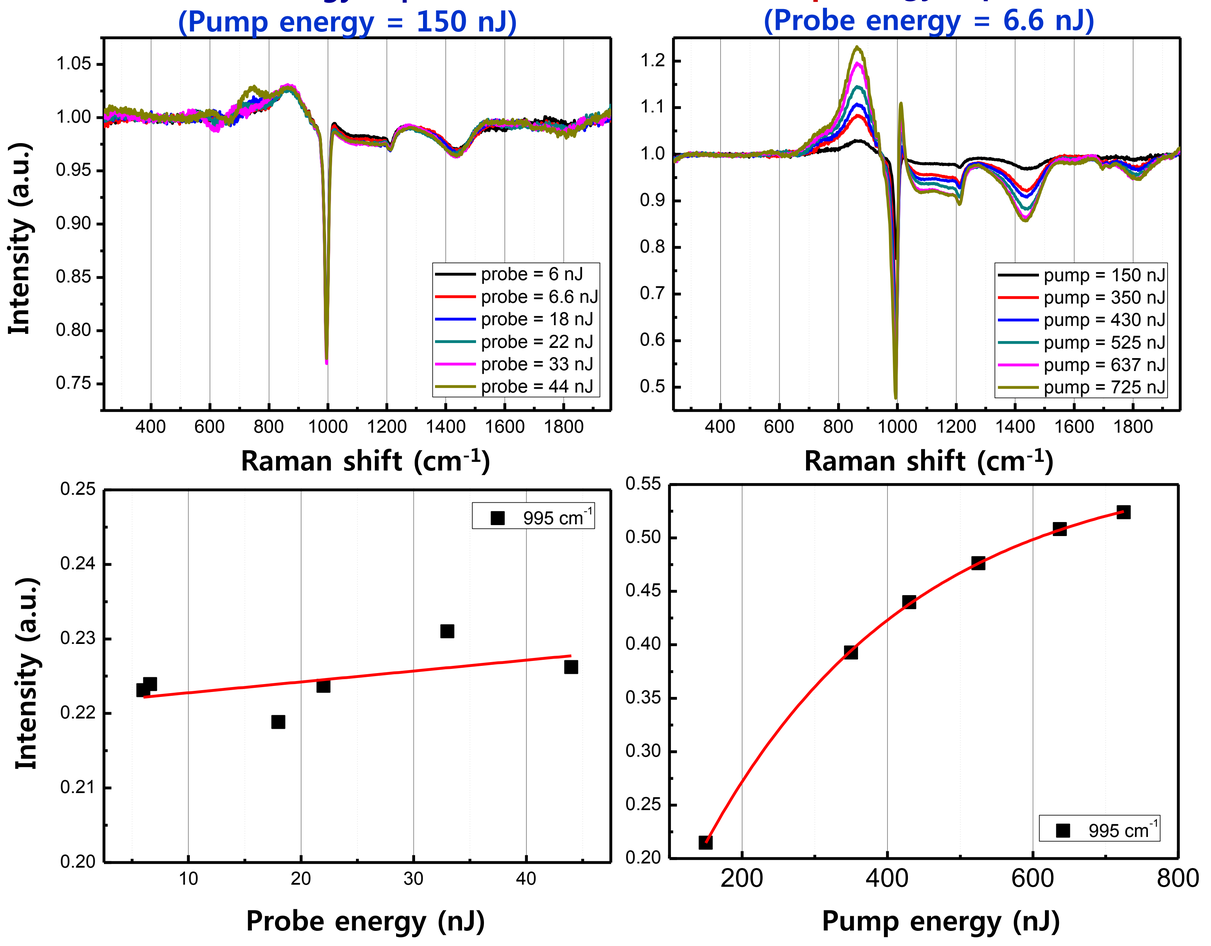
### ● Stimulated Raman spectra




✓ The probe spectrum for the Raman pump on and off, gives the loss spectrum (**stimulated Raman spectra**). The peak positions are well correlated with them of the **spontaneous Raman spectra**.

✓ Benzene and Toluene which has ring structure are used for a reference in Raman spectroscopy, because these molecules have the strong Raman active mode around ~1000 cm$^{-1}$ (the ring vibration mode).

### ● Power dependent SRS spectra of benzene




### ● Equation of Raman loss signal on experimental parameter

$$Raman\ loss = \frac{I}{I_0} \propto exp(\sigma_R \cdot c \cdot I_{pu} \cdot z)$$

$\sigma_R$ = *Raman scattering cross section*
$c$ = *Sample concentration*
$z$ = *Sample pathlength*
$I_{pu}$ = *Intensity* ($\frac{photons}{cm^2}/s$) *of the Raman pump pulse*

David W. McCamant, Rev. Sci. Inst, 75, **2004**, 4971-4980.

## ❖ Conclusion

✓ We performed the stimulated Raman spectroscopy for various molecules such as benzene, toluene, (+)-α–pinene, and (-)-limonene as reference and chiral molecules. We successfully have been observed the Raman active modes in our SRS loss measurement. Our results indicate that the peak positions and overall spectral shapes obtained from the stimulated Raman spectra are well matched with them of the spontaneous Raman spectra.

✓ We showed that the SRS intensity exponentially increases with the pump energy, whereas it doesn't depend on the probe energy from the pump and probe energy dependent measurement.

✓ We are currently extending this approach to ROA measurement and combining it with coherent Raman process such as stimulated Raman spectroscopy (SRS) to achieve an effective ROA measurement. We anticipate that this new approach will be applicable to femtosecond ROA spectroscopy and chiral microscopy for stereo-chemical imaging of chiral drugs and biomolecules.

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