

Study of Stimulated Raman Spectroscopy for various molecules

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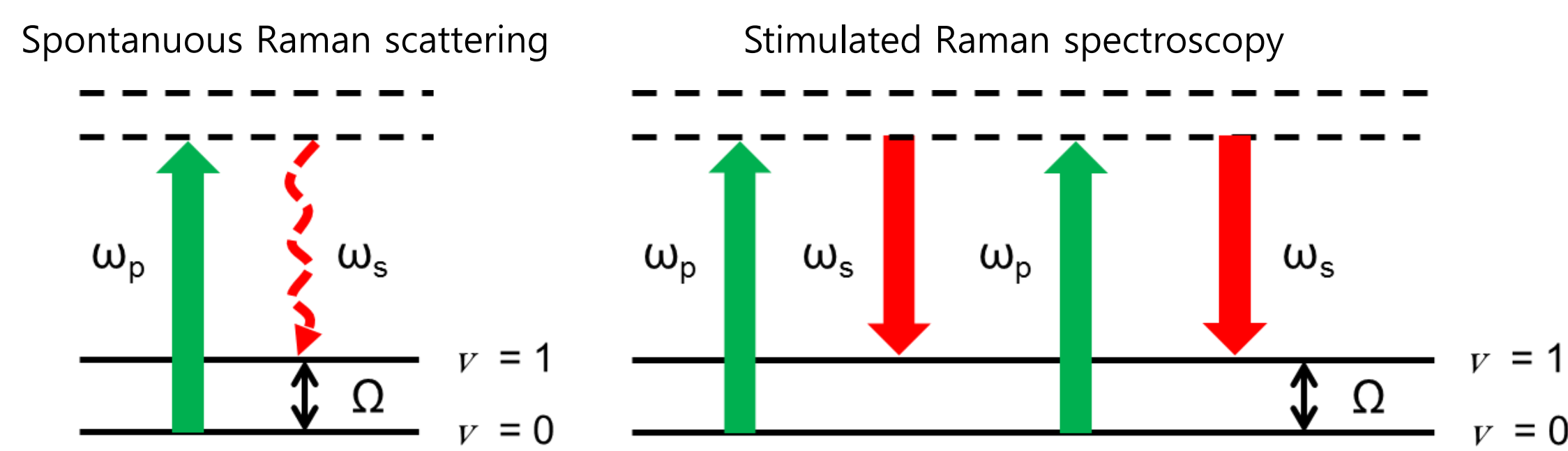
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Vibrational spectroscopy by Raman scattering process



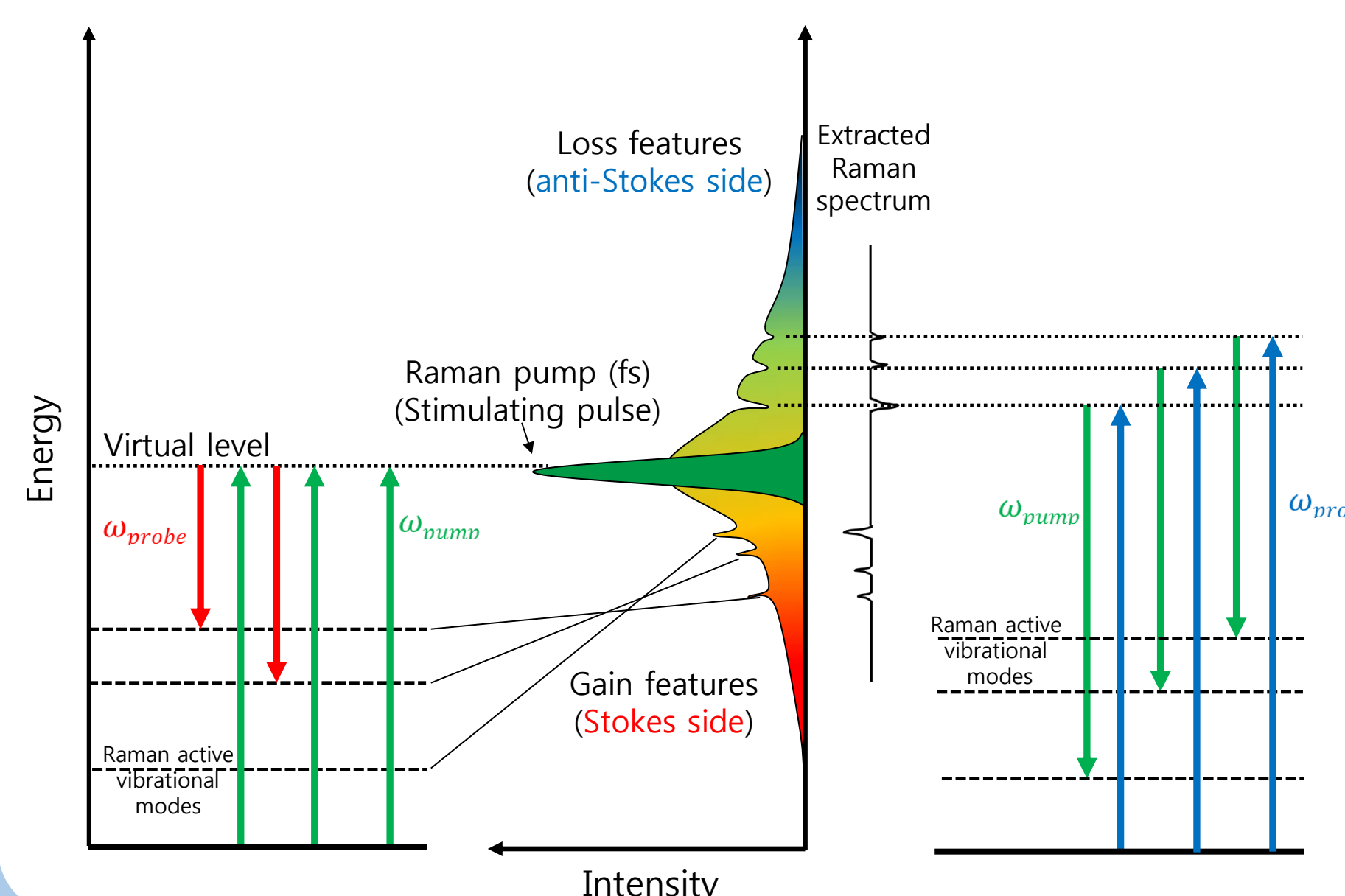
Phase matching condition

$$\vec{k}_s = \vec{k}_s - \vec{k}_p + \vec{k}_p$$

$$\omega_s = \omega_s - \omega_p + \omega_p$$

- ✓ In the spontaneous Raman spectroscopy a coherent pump beam at ω_p is incident on a sample, and Stokes ω_s or anti-Stokes ω_{AS} photons are generated.
- ✓ However, 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

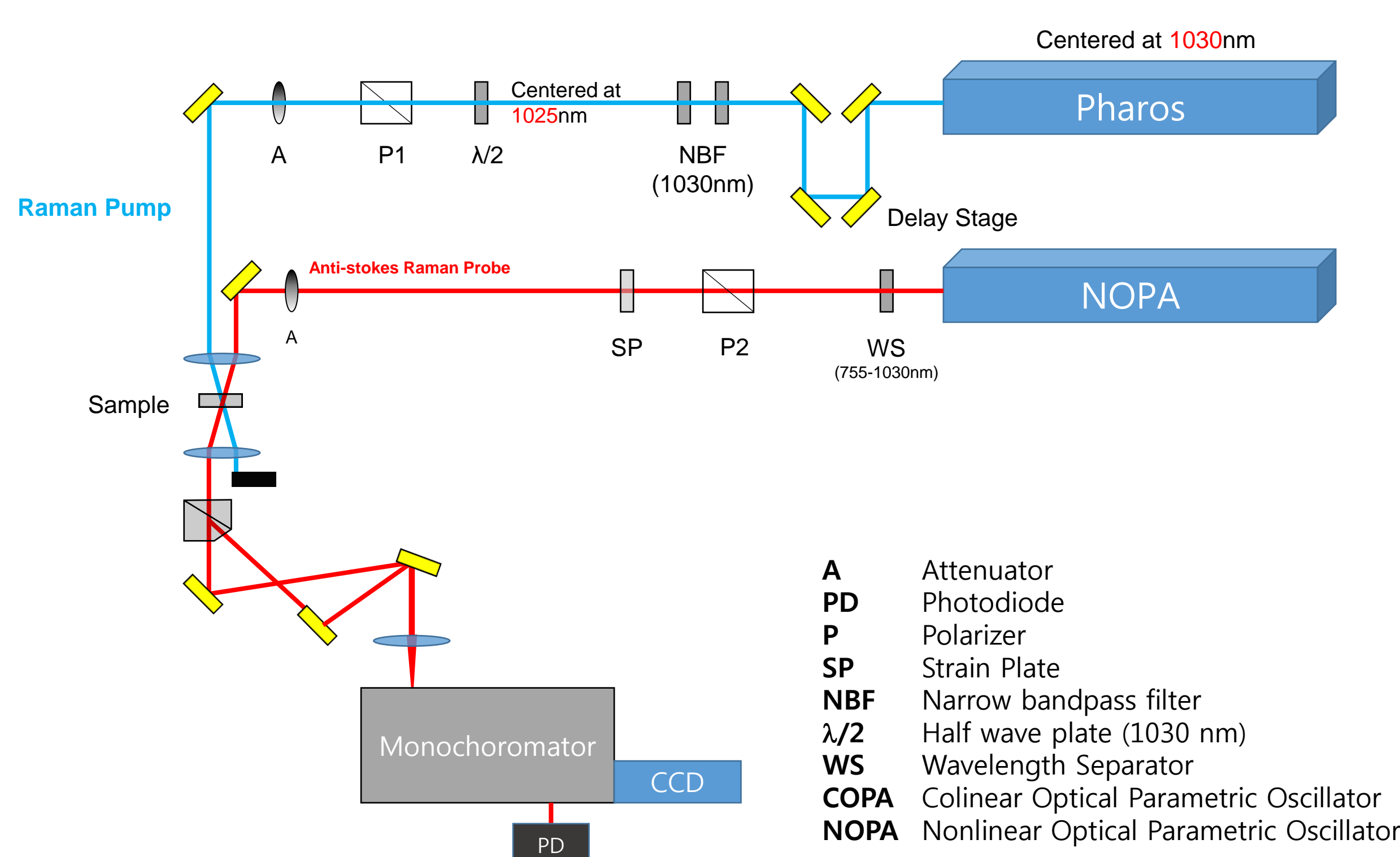


$$\text{Gain or Loss} = \frac{\text{Raman probe with Raman pump on}}{\text{Raman probe with Raman pump off}}$$

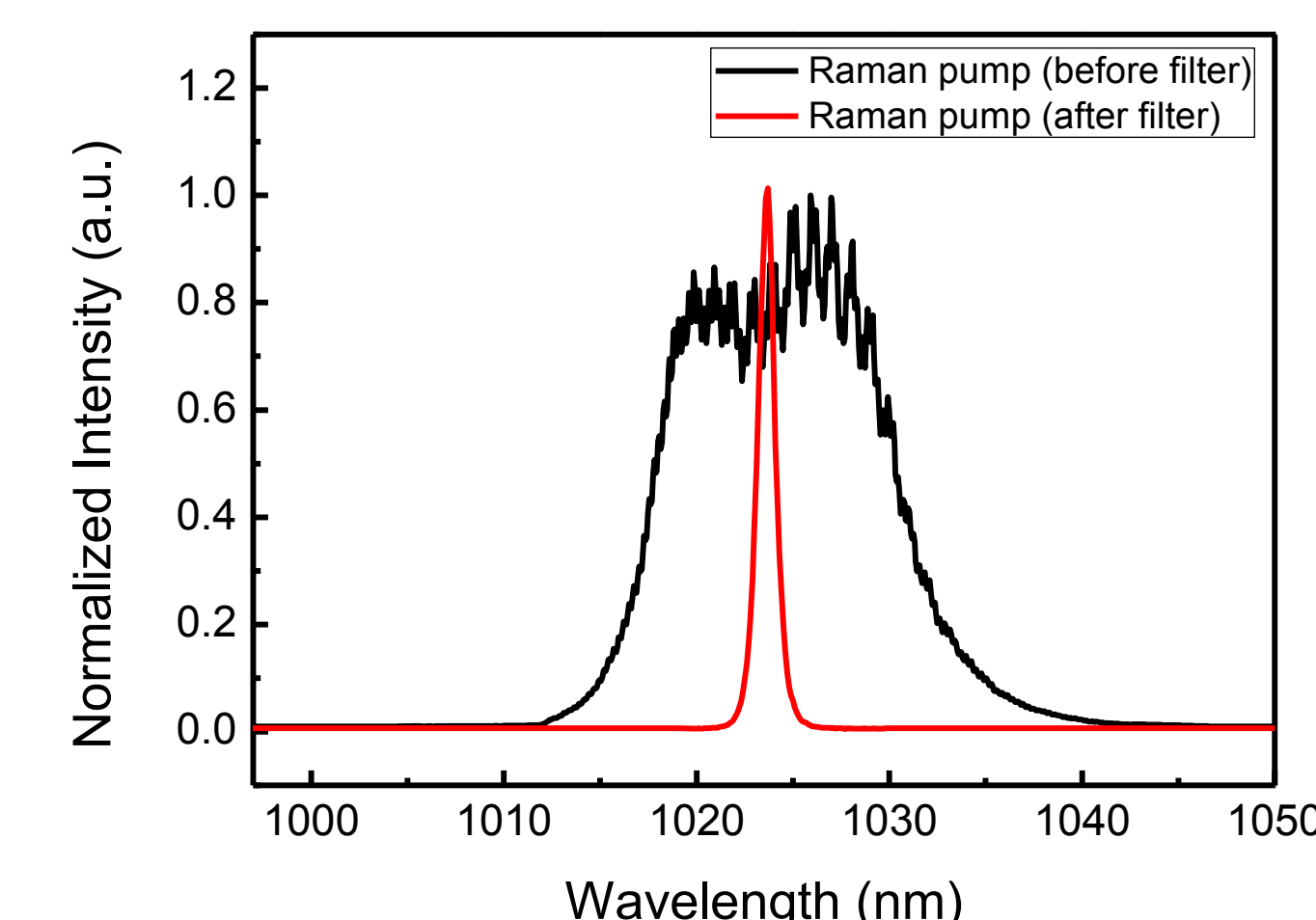
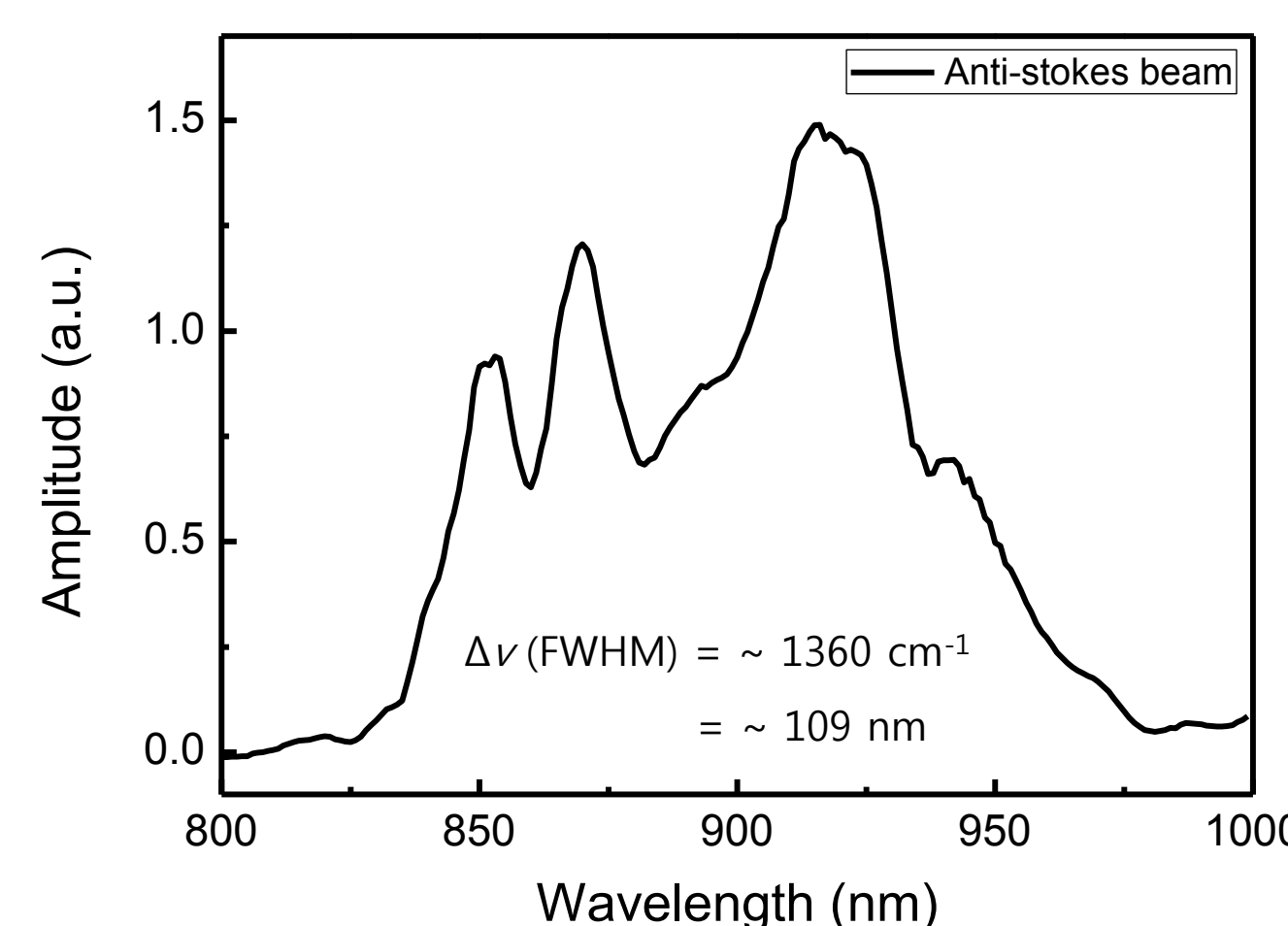
Thick dashed lines represent Raman active vibrational modes. Thin dashed lines stand for virtual levels.

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

Layout of the stimulated Raman spectrometer (Raman loss measurement)

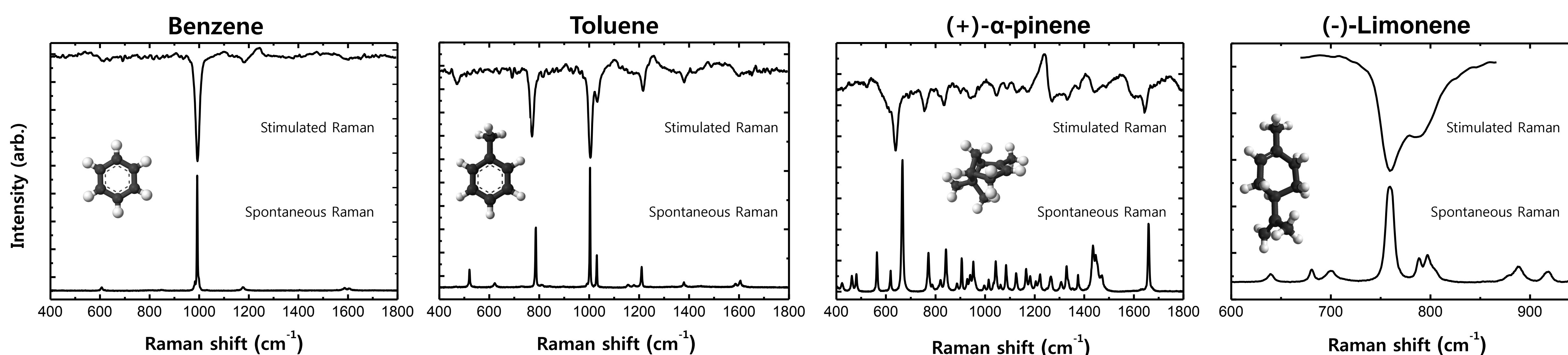


Raman pump and Raman probe spectra



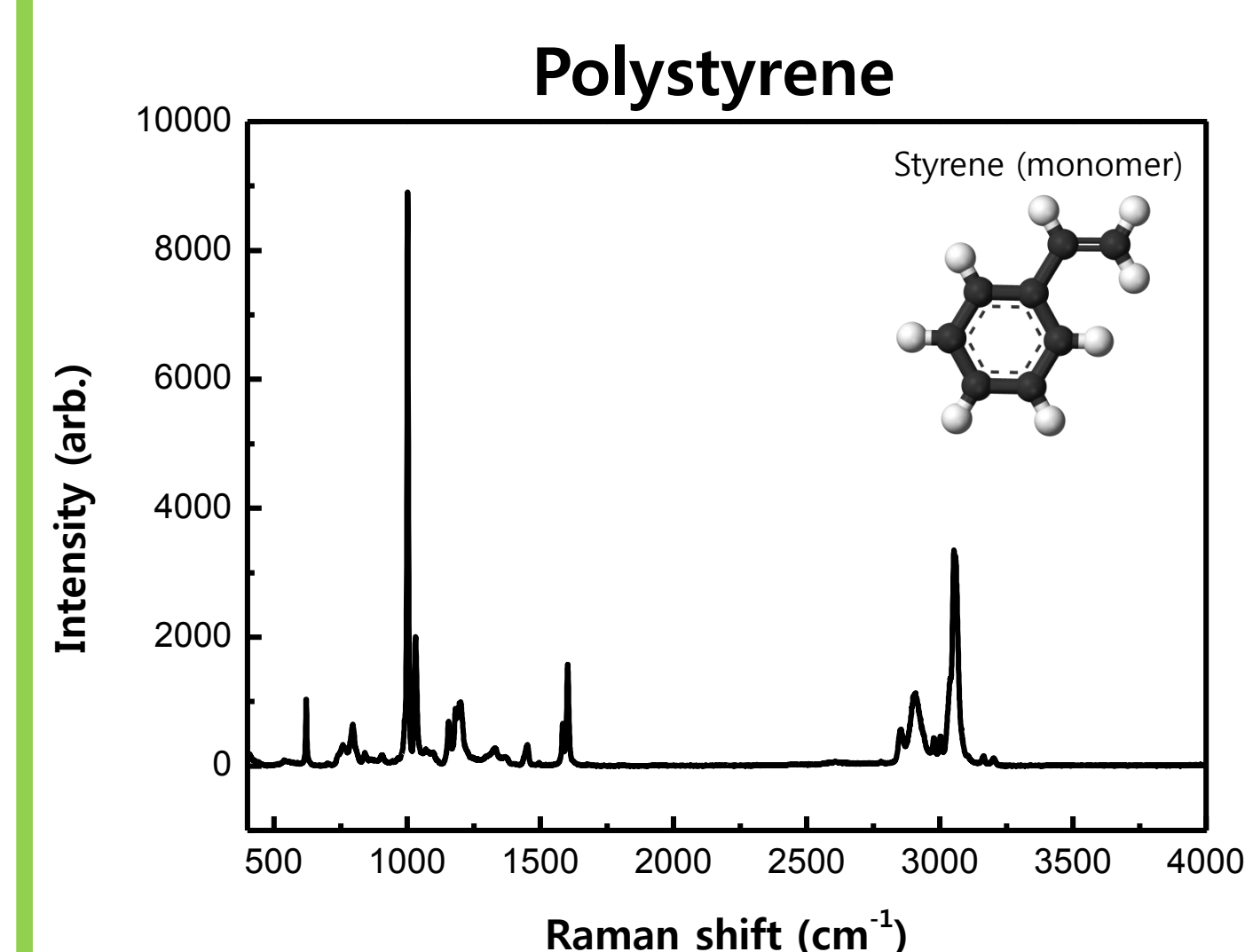
- ✓ Two narrow band-pass filters (1030 nm) are used for generating the spectrally narrow pulse. The fundamental pump beam is centered at 1030nm, after filter pair, the pump pulse is centered at 1024 nm with a bandwidth of 12 cm^{-1} . Because we can control the center of pump pulse by tilting angle of 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). When the two fields overlap spatially and temporally on the sample, we can observe loss features on the probe beam.

Stimulated Raman spectra



- ✓ The probe spectrum for the Raman pump on and off, gives the loss spectrum (upper). The peak positions are well correlated with them of the spontaneous Raman spectra (lower).
- ✓ 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 $\sim 1000 \text{ cm}^{-1}$ (the ring vibration mode).

Spontaneous Raman spectrum



- ✓ Raman spectra were collected on a confocal micro-Raman spectrometer equipped with a grating with a 600 grooves per mm, a CCD detector with a Pelletier cooling, and a 100 × objective.
- ✓ Raman spectra were excited by 532 nm beam with 50 mW power.

Future work

Chiroptical spectroscopy offers decisive information on stereochemical structures of chiral molecules in condensed phase. In particular, Raman optical activity (ROA) as a vibrational chiroptical probe has been proven to be of critical use in distinguishing different structural chiralities *induced by molecular vibration* by measuring a difference between vibrational Raman scatterings for left- and right-circularly polarized (LCP and RCP) radiation. However, the conventional ROA measurement method suffers from the intrinsic weakness of the corresponding signal ($10^{-5} \sim 10^{-3}$ of Raman intensity), which has restricted its wide range of applications including time-resolved and space-resolved microscopic studies.

We are currently extending this approach to ROA measurement and combining it with coherent Raman process such as stimulated Raman scattering (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.

References

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- [2] Seung Min Jin, Young Jong Lee, Jongwan Yu, and Seong Keun Kim, "Development of femtosecond stimulated Raman spectroscopy: stimulated Raman gain via elimination of cross phase modulation", *Bull. Korean. Chem. Soc.* 25, 1829 (2004)