# Asymmetrical Spectral Continuum Background in Low-Frequency Surface-Enhanced Raman Spectroscopy

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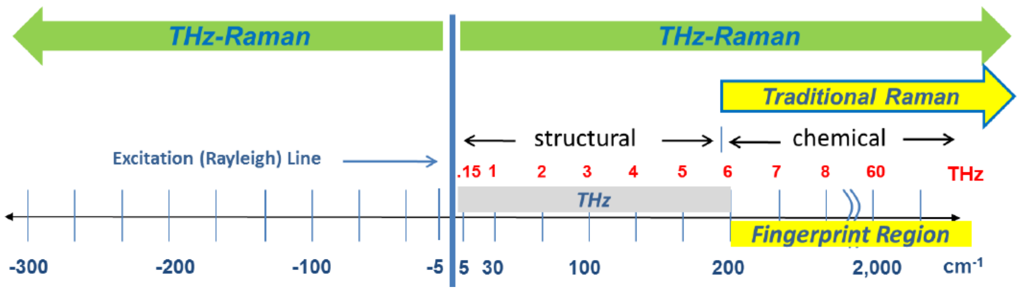
# Low frequency Raman scattering in the Terahertz range

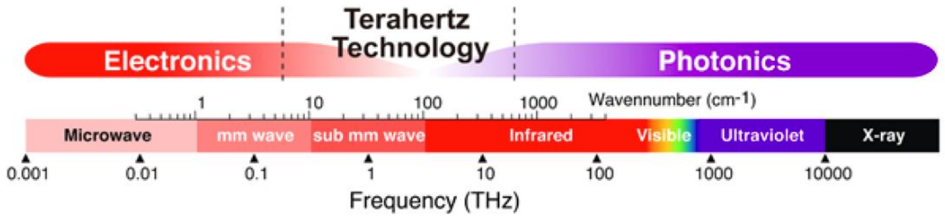
$$\omega_0 = \sqrt{\frac{k}{m}}$$

$k$ → soft bonds, collective modes, weak interactions

$m$ → heavy atoms, structural groups




*Proc. SPIE* **9073,** 90730K (2014).



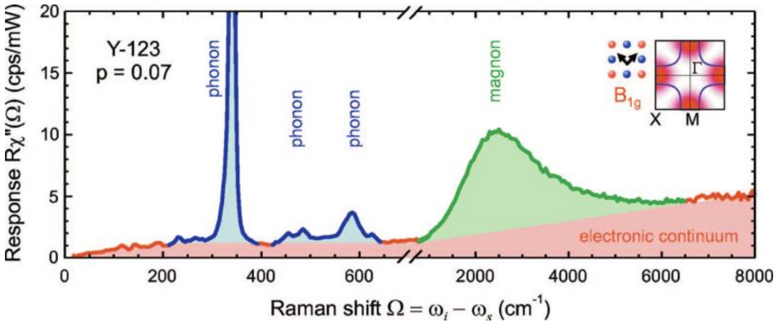

*Proc. SPIE* **7391,** 73910D (2009).

- Microwave and RF
  - E/M polarization, translation/rotation
- Optical and IR
  - electronic transitions, bond vibrations
- THz range
  - bridge between global and local dynamics

**<u>Example systems of interest</u>**

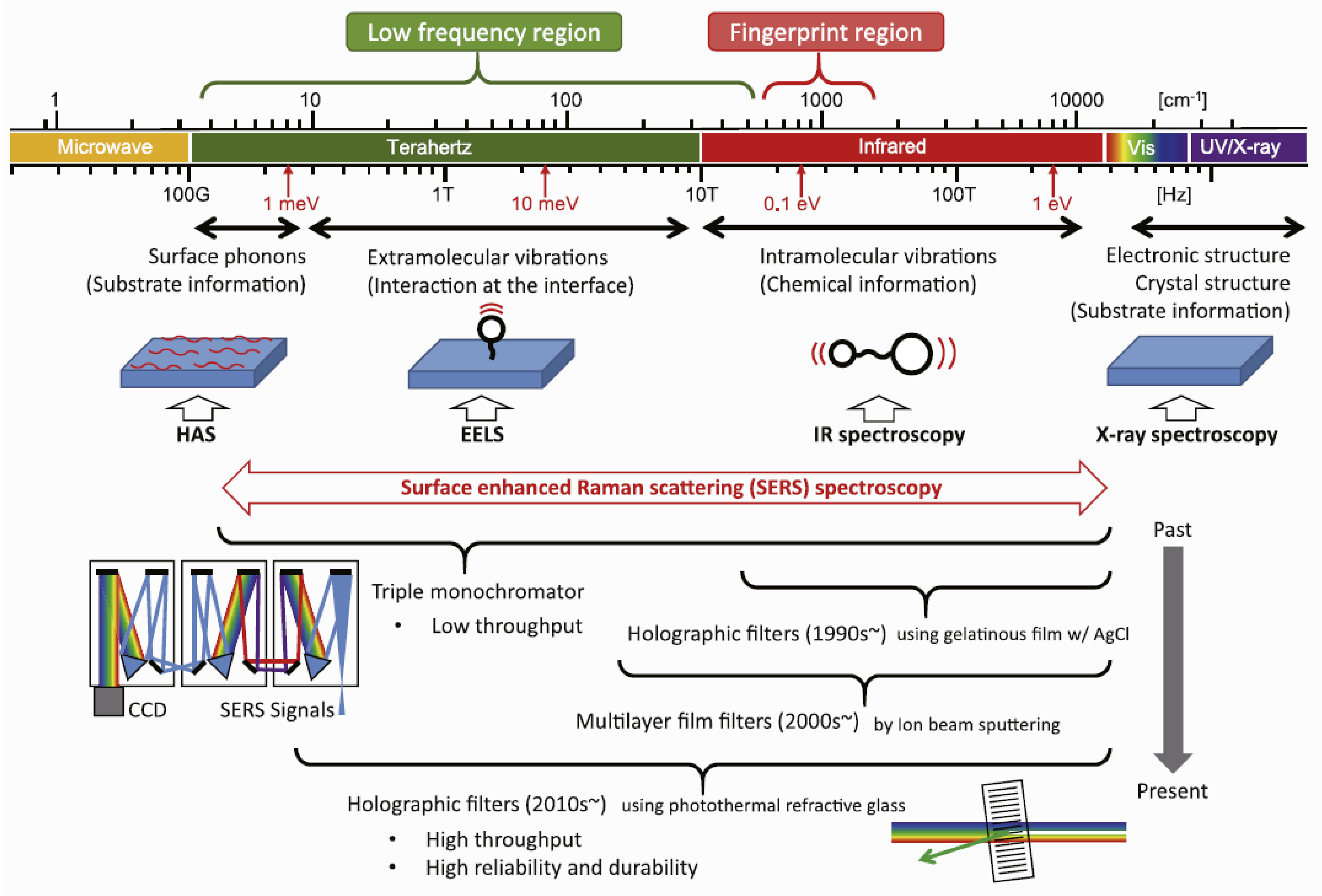
- Molecular crystals
- Clusters, clathrates
- Supramolecular complexes
- Halide perovskites
- MOFs, COFs, ZIFs
- Van der Waals materials
- Functional polymers

- Quantum materials
- Spin waves / magnons
- Intraband electronic transitions




*Rev. Mod. Phys.* **79,** 175 (2007).

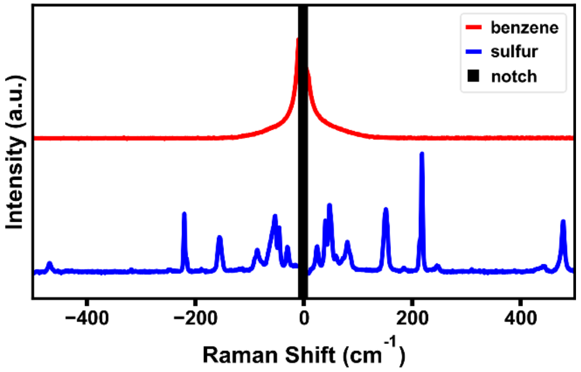
# Low frequency Raman scattering in the Terahertz range

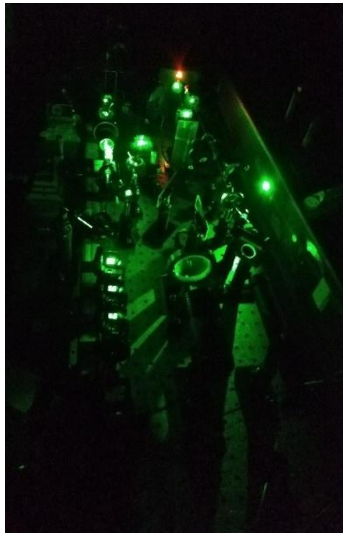


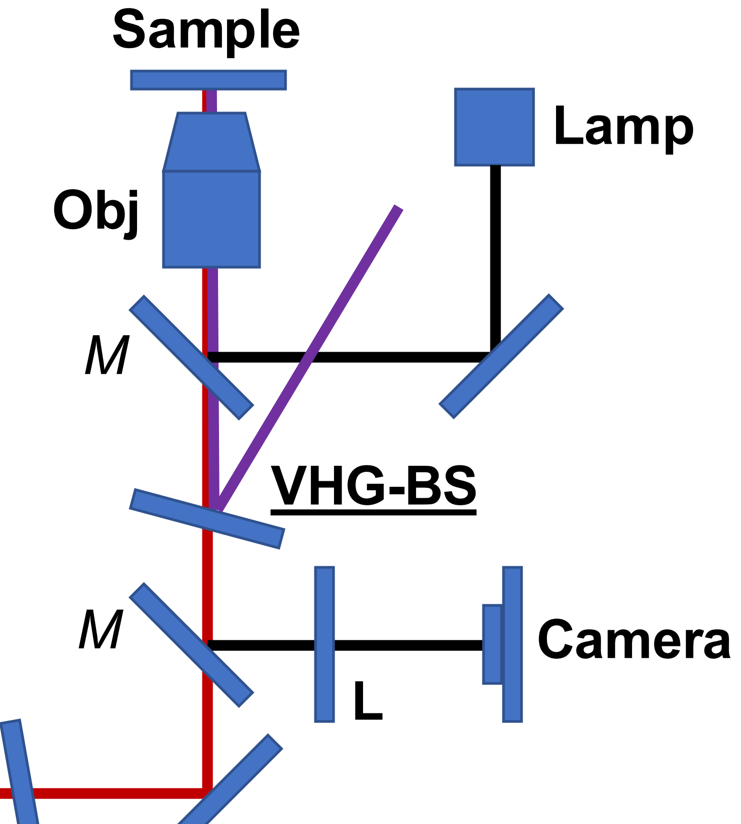

Inagaki, M. et al, *Curr Opin Electrochem* **2019**, *17*, 143–148.

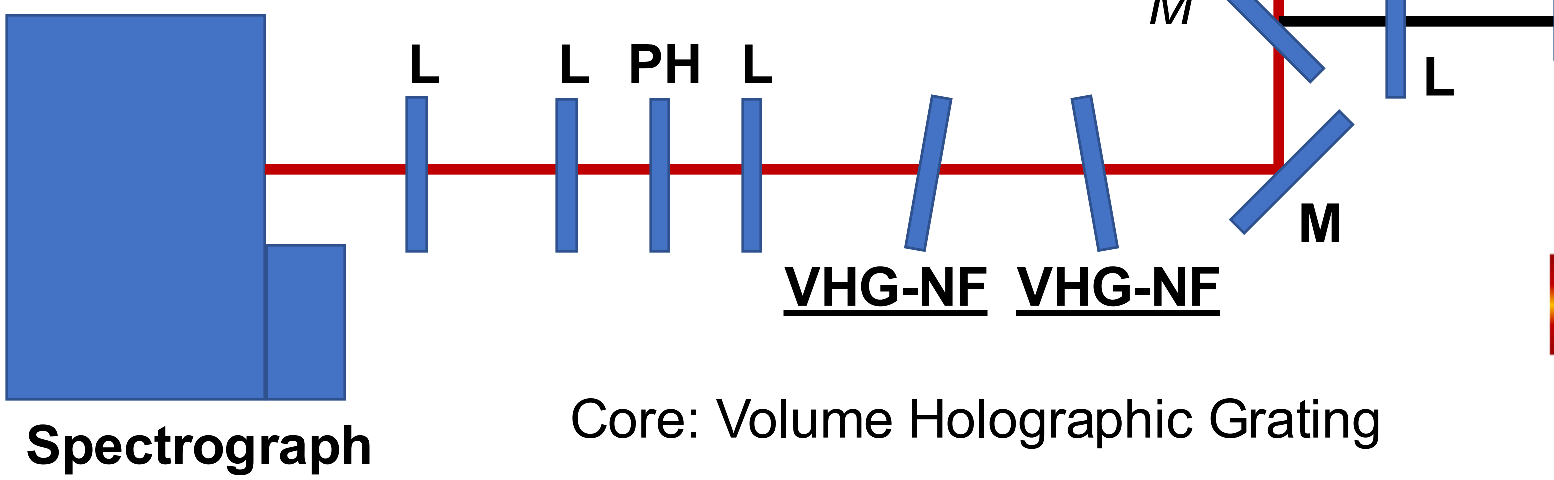
# Low frequency Raman scattering in the Terahertz range

**Energy range probed in LFR**
**<10 $cm^{-1}$ – 200 $cm^{-1}$**
**0.3 THz – 6 THz**
**1.24 meV - 24.8 meV**

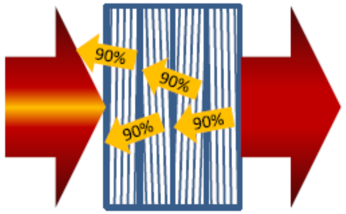




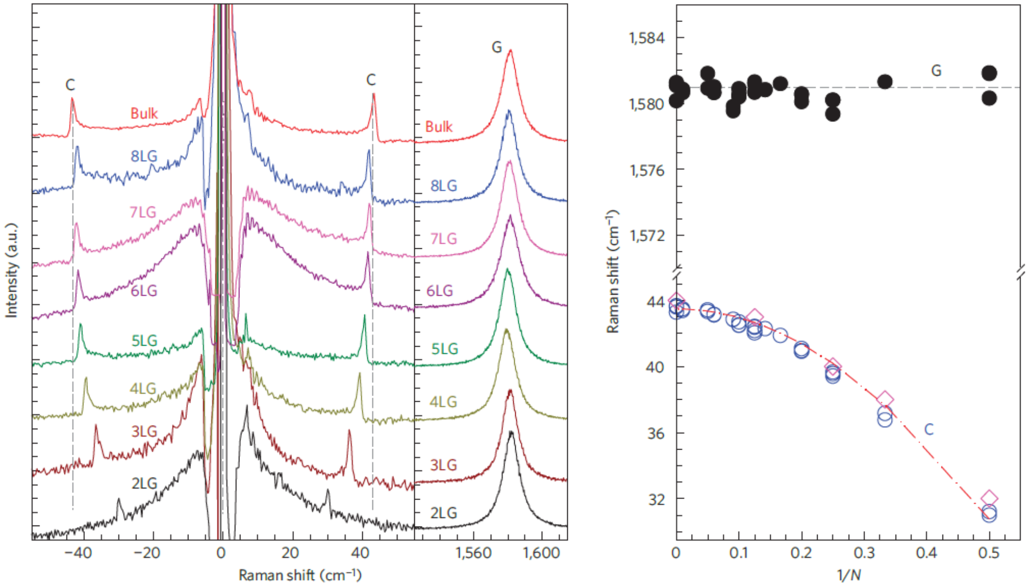

Core: Volume Holographic Grating



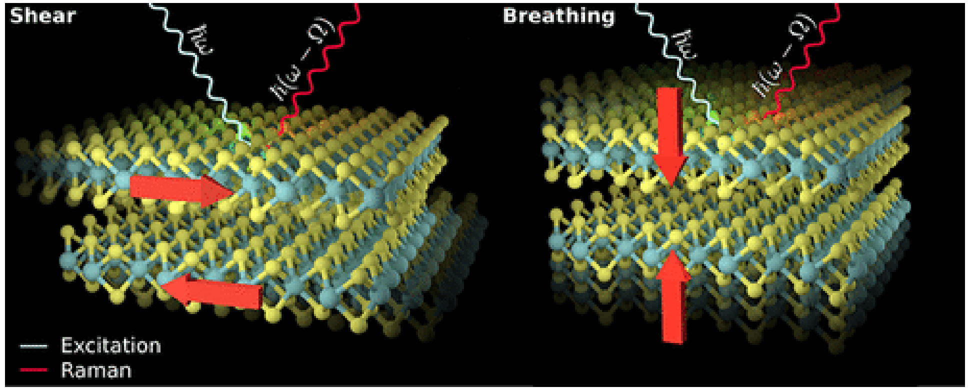

VHG filters

# Low frequency Raman scattering in the Terahertz range

**Interlayer modes of vdW materials**

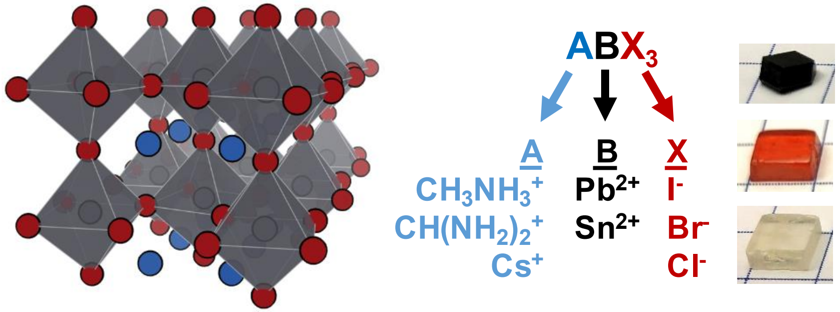



*Nat. Mater.* **2012**, *11* (4), 294–300.

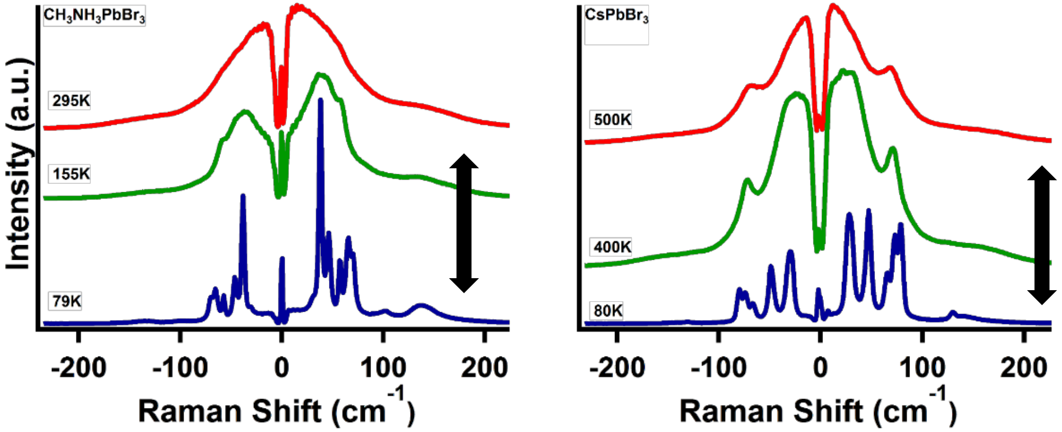



*ACS Nano* **11,** 11777 (2017).

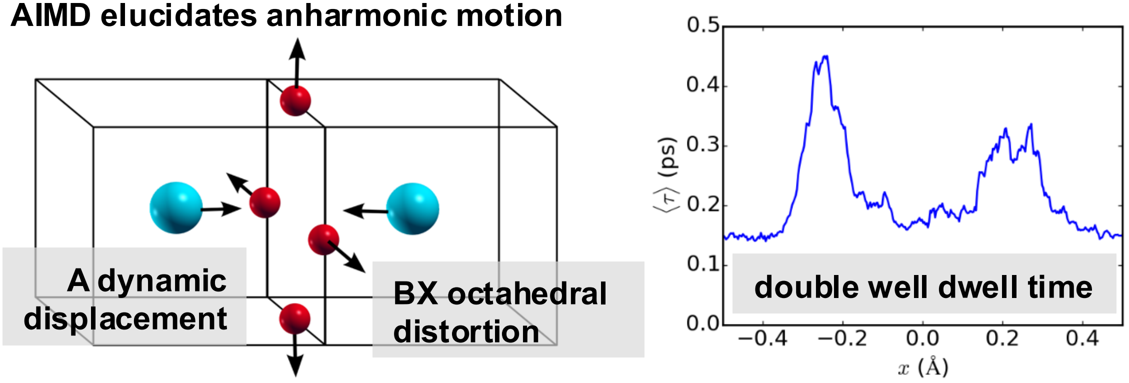
**Lattice dynamics of lead halide perovskites**




**LFR reveals extreme anharmoncity**



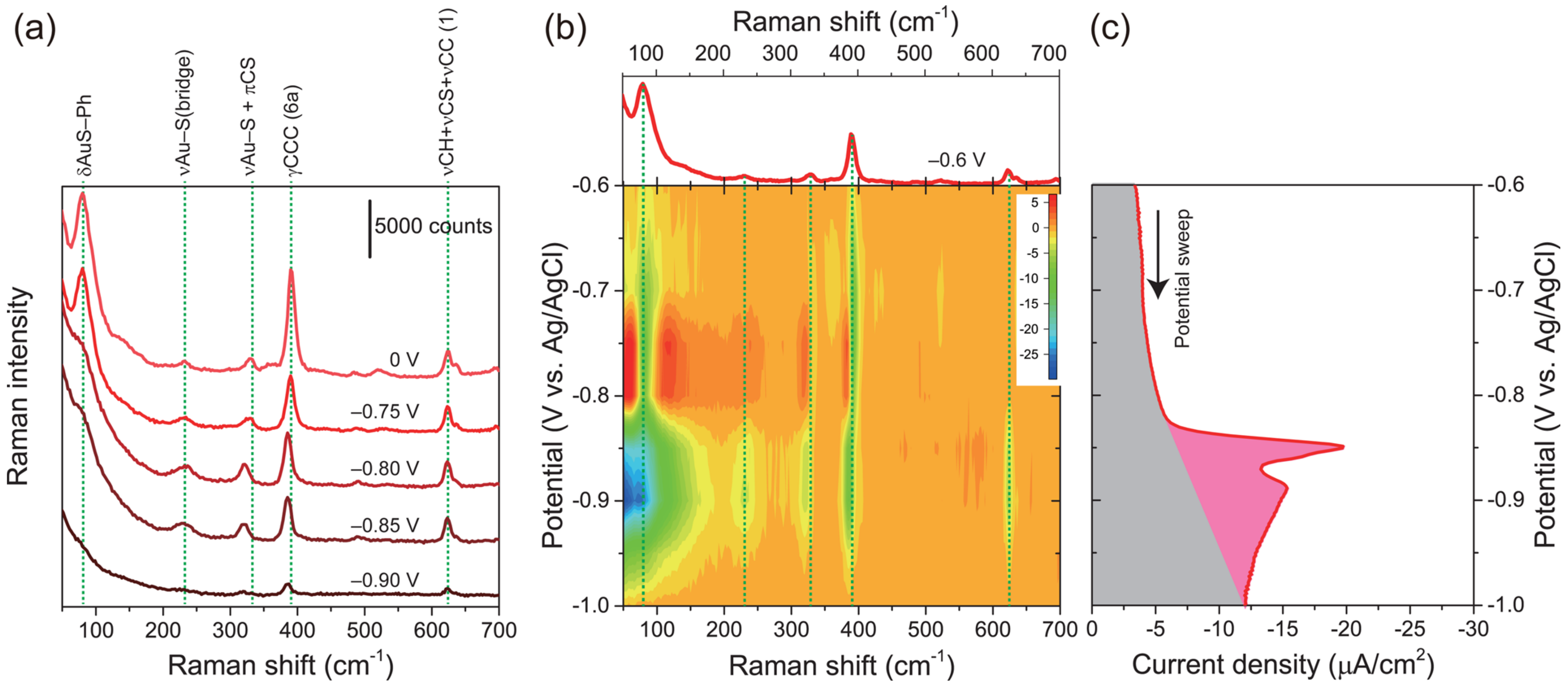

**AIMD elucidates anharmonic motion**




*Yaffe, O.,† Guo, Y.,† et al. Phys. Rev. Lett.* **2017**, *118* (13), 136001.

# Low-frequency SERS and TERS in the Terahertz range

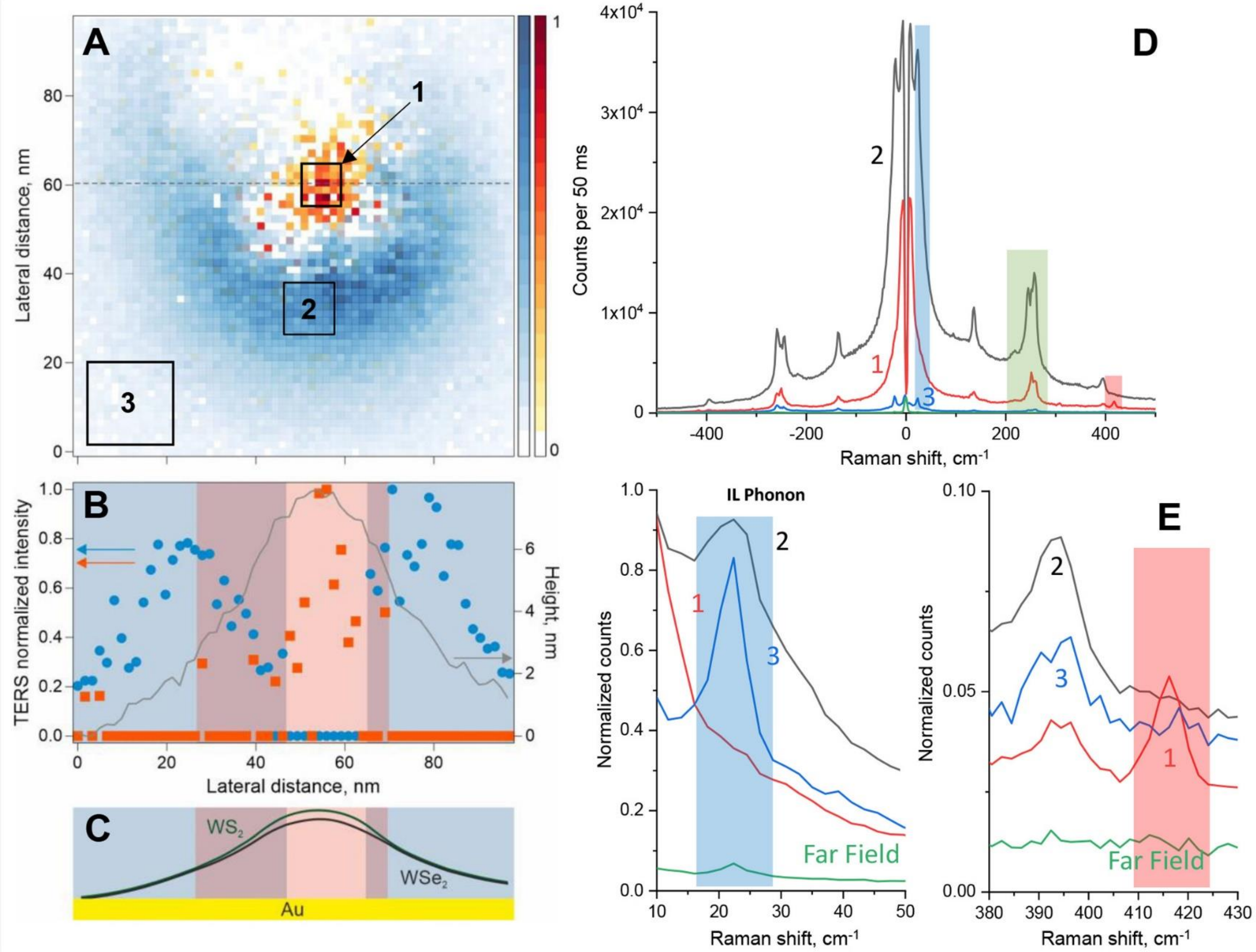
Electrochemical THz-SERS Observation of Thiol Monolayers on Au(100) Using Nanoparticle-Assisted Gap-Mode Plasmon Excitation.




Inagaki, M. et al. *J. Phys. Chem. Lett.* **2017**, *8* (17), 4236–4240.

# Low-frequency SERS and TERS in the Terahertz range

Nano-Optical Visualization of Interlayer Interactions in WSe2/WS2 Heterostructures

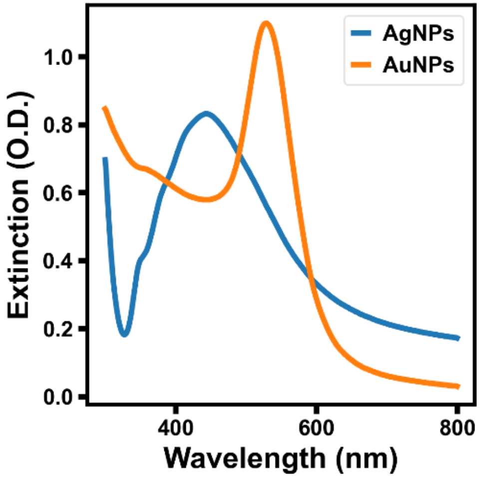



Rodriguez, A. et al. *J. Phys. Chem. Lett.* **2022**, *13* (25), 5854–5859.

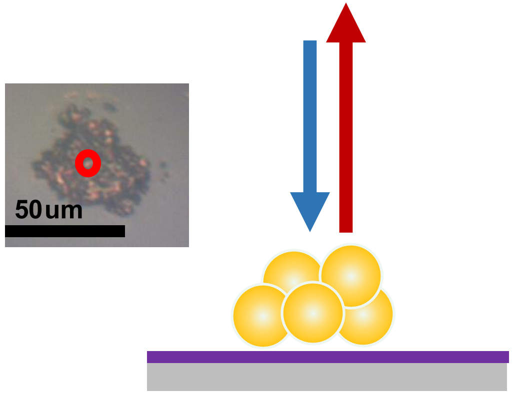
# Asymmetrical spectral background continuum in LF-SERS

**Colloidal plasmonic nanoparticles**

AuNPs and AgNPs

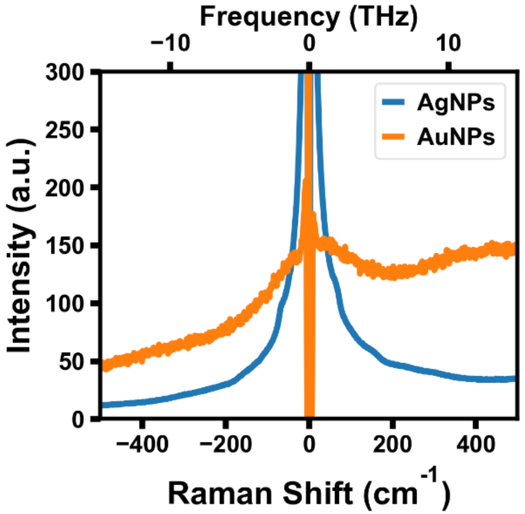



NP aggregates dropcast on Si wafer




**Asymmetric background continuum in LF-SERS**

- central peak (around the Rayleigh line)
- merging into a finite flat baseline (Stokes side)
- sloping down toward zero (anti-Stokes side)




AgNPs intensity scaled down by 10 fold and vertically offset

# The Bose Einstein factor is inherently asymmetrical

**Asymmetric Bose-Einstein scaling**

$$I \propto f_{BE}\chi''$$

$$f_{BE} = \begin{cases} n_{BE} + 1 & \text{(Stokes scattering)} \\ n_{BE} & \text{(anti-Stokes scattering)} \end{cases}$$

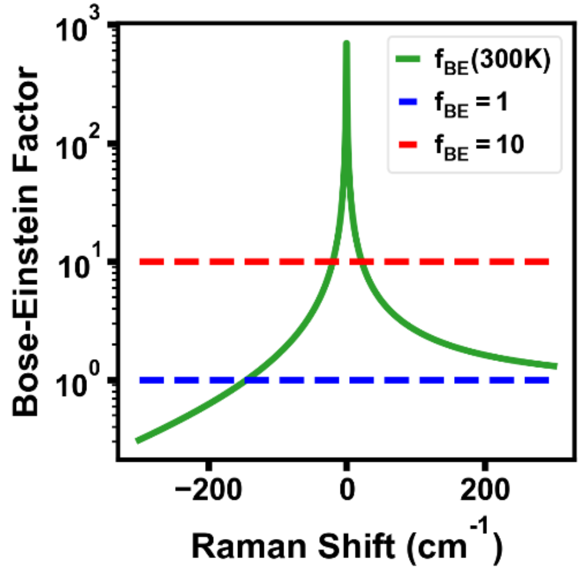
$$n_{BE}(\omega, T) = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

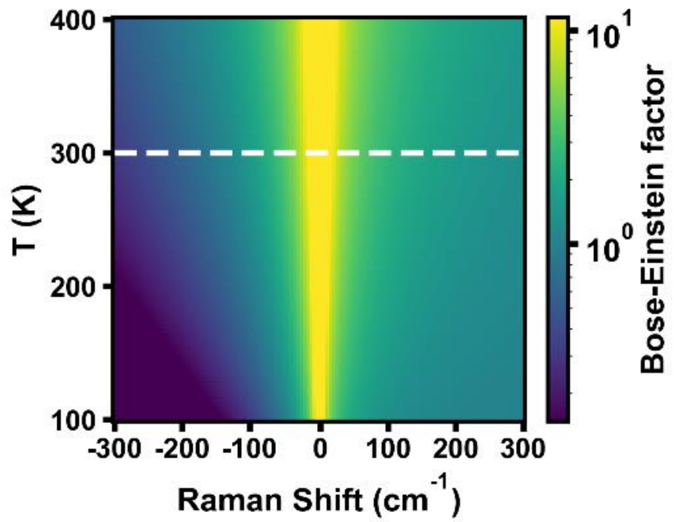
**Origin of asymmetry:**
**Stokes (Anti-Stokes) scattering creates (annihilates) one excitation**

$$I_{ij} \propto \left|R_{ij}^{(m)}\right|^2 |\langle n+1|Q_m|n\rangle|^2$$

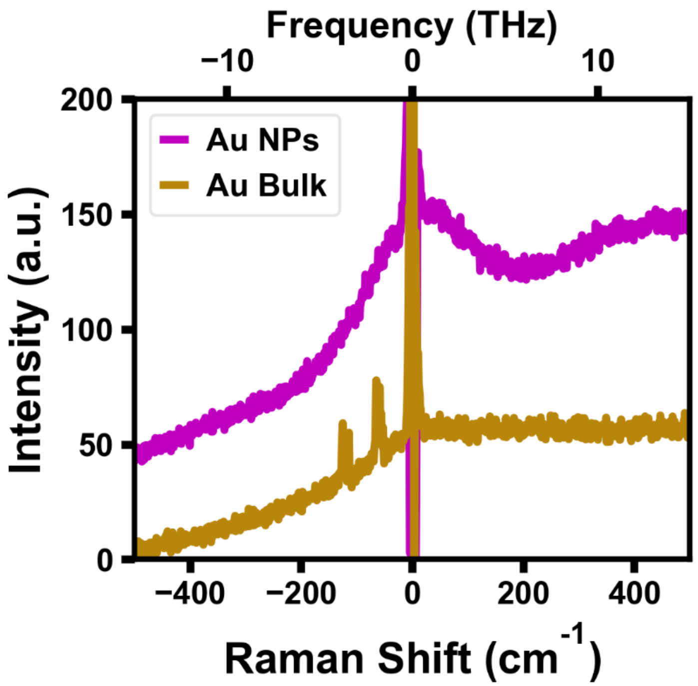
$$\langle n+1|Q_m|n\rangle \sim \sqrt{(n_{BE}+1)}$$

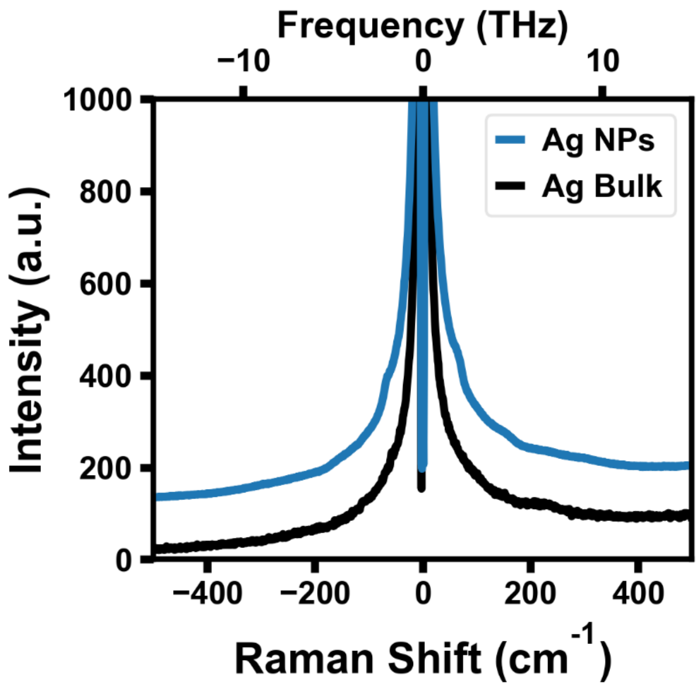
$$\langle n-1|Q_m|n\rangle \sim \sqrt{n_{BE}}$$



# Variety of LF-SERS background continuum lineshapes




AgNPs intensity scaled down by 10 fold and vertically offset

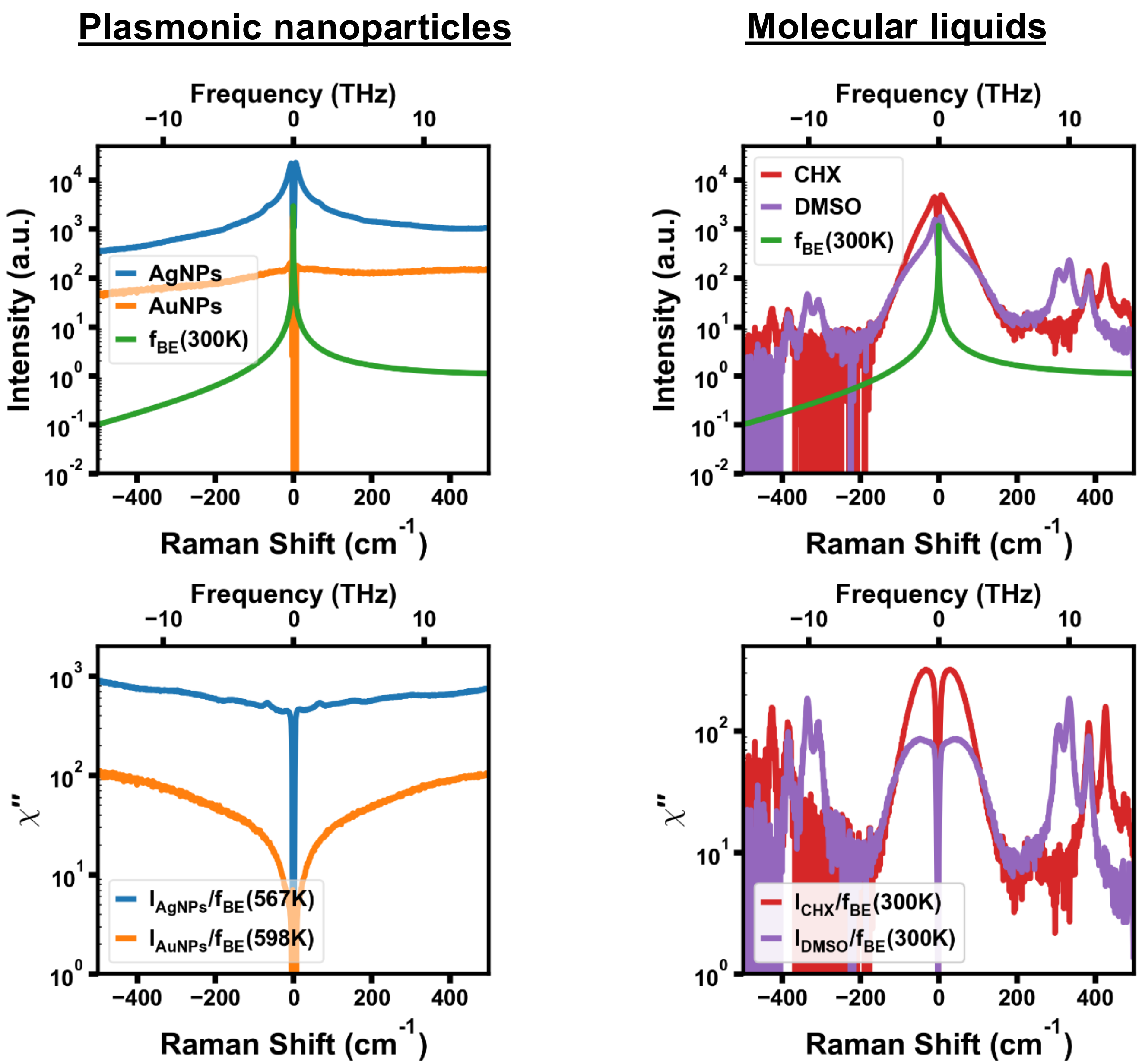
- $n_{BE} = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$ $\quad$ $\omega \to 0 \Rightarrow n_{BE} \to \frac{kT}{\hbar}\frac{1}{\omega}$
- As frequency approaches 0, the Bose-Einstein factor diverges as $\frac{1}{\omega}$
- Much weaker divergence (or flat lines) were observed in various cases
- The shape of the background continuum is morphology/material dependent

# Survey and comparison of low frequency spectral continua

**A different central peak**

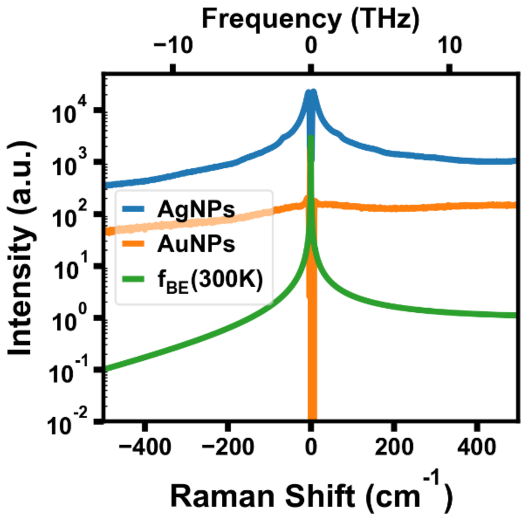
Key differences:
- Baseline Intensity
- Frequency dependence
- Optimal temperature

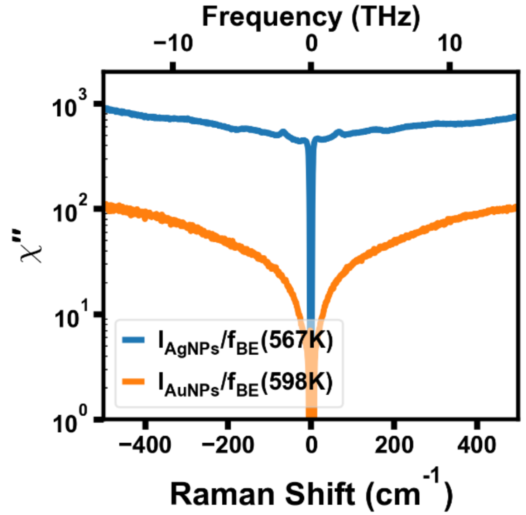
Physical origins
- Anharmonic / relaxational *structural* dynamics
- Intraband *electronic* Raman scattering



# Distinctions in signal origins: AuNPs vs. AgNPs

Plasmonic nanoparticles




**Key differences after B-E normalization**

- AgNPs: flat baseline with vibrational features
- AuNPs: negative divergence near Rayleigh line

**Signals of Bosonic origins**

- Molecular vibrations
- Optical / acoustical phonons
- Relaxational motions in liquids
- Elementary excitation of an electron gas

❖ Anything described as a harmonic oscillator
❖ Scaled by the B-E factor

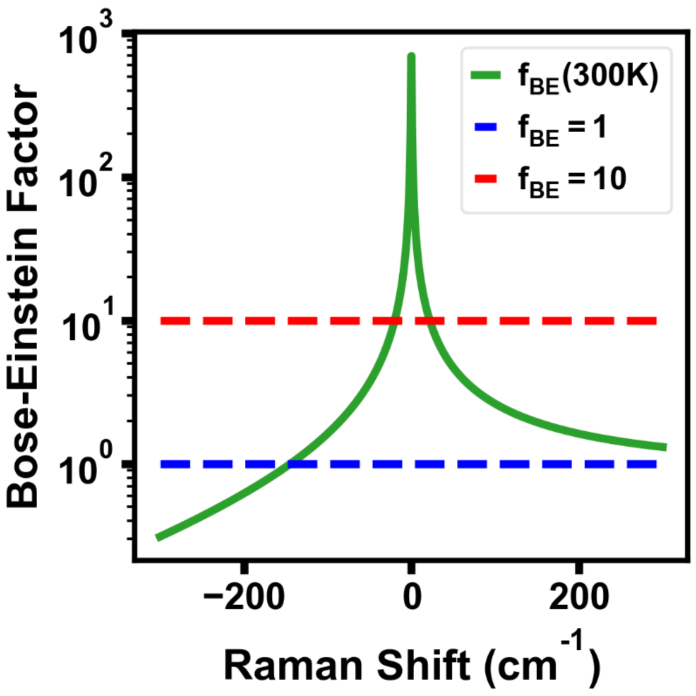
**Signals of non-Bosonic origins**

- Photoluminescence

❖ Not scaled by the B-E factor

Bose-Einstein scaling behaviors reveal the nature of signal origins

# The Bose-Einstein factor as a signal enhancement mechanism




Viewing the Bose-Einstein factor as a signal enhancement mechanism

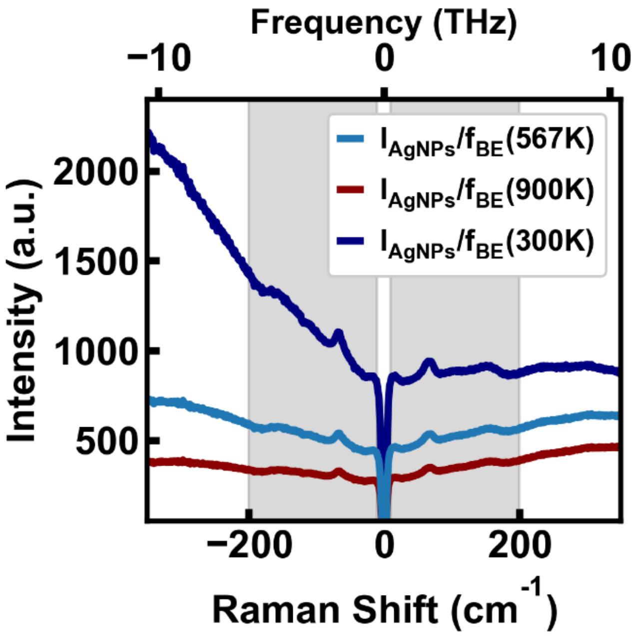
- ❖ Significant for the low frequency THz region
- ❖ Universal and inherent
  - resonance enhancement
  - plasmonic enhancement
  - independent of materials properties and substrate structures
- ❖ Depends only on $T$ and $\nu$

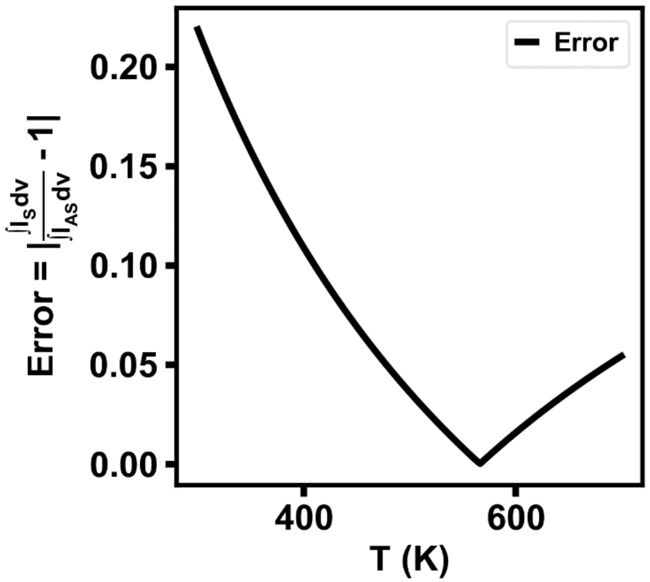
# Bose-Einstein normalization thermometry

## Thermometry via the Boltzmann factor

$$\frac{I_{anti-Stokes}}{I_{Stokes}} = C\frac{n}{n+1} = C\exp\left(-\frac{\hbar\omega}{k_B T}\right)$$

- Peak pair intensity ratio
  - start with well defined peaks
  - model peak lineshape
  - calculate intensity ratio and T



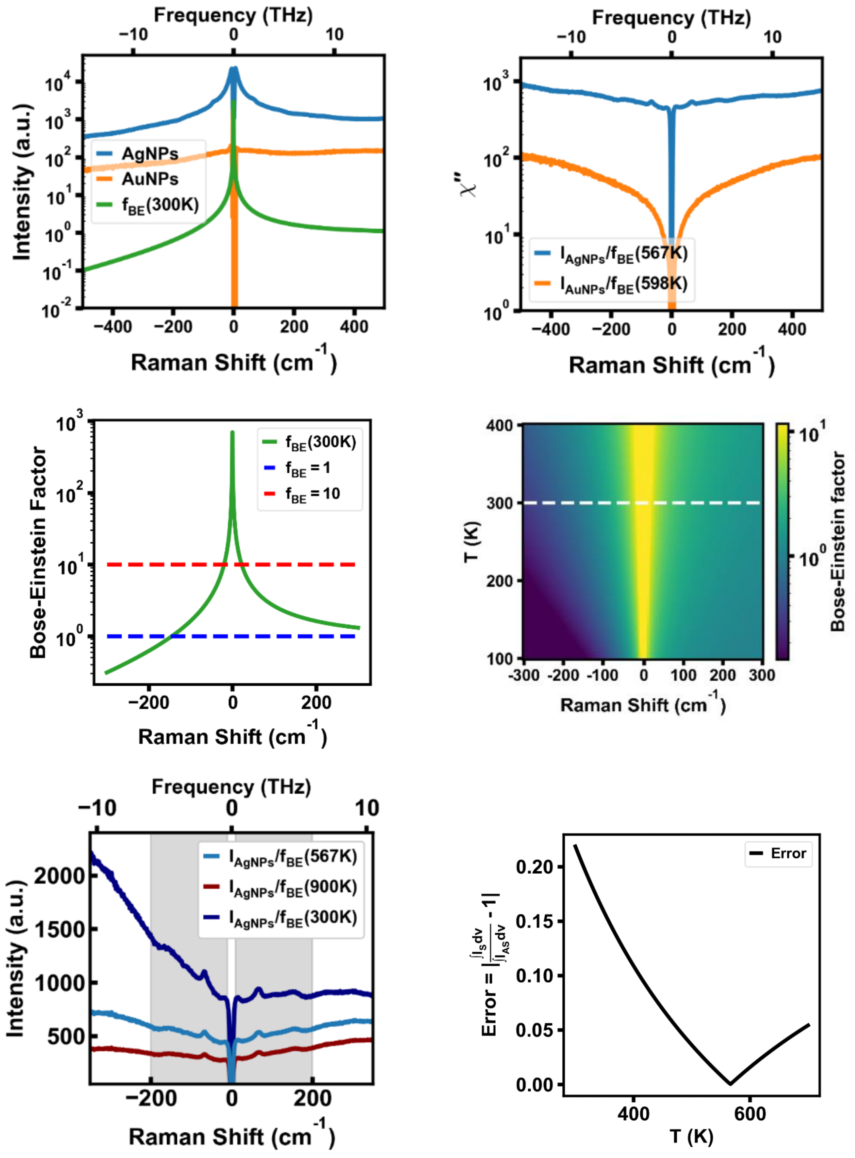




## Thermometry via the Bose-Einstein factor

$$\underset{T>0}{\arg\min}\ Error(T;\ \omega_1, \omega_2) = \left| \frac{\int_{\omega_1}^{\omega_2} \frac{I_S(\omega)}{n_{BE}(\omega;T)+1} d\omega}{\int_{\omega_1}^{\omega_2} \frac{I_{AS}(\omega)}{n_{BE}(\omega;T)} d\omega} - 1 \right|$$

- Numerically robust
  - single variable, single minimum
  - Well-behaved optimization routine
- Model independent, lineshape free
  - spectral continuum
  - broad peaks or groups
  - reduces to peak-pair intensity ratio when integrating over a sharp peak

# Summary




- ❖ Asymmetrical spectral continuum background observed in LF-SERS

- ❖ The Bose-Einstein factor
  - symmetrizes the spectra
  - reveals underlying responses
  - distinguishes signal origins
  - enhances signal strength
  - measures sample temperature

Sun, S.; Rathnayake, D. T. N.; Guo, Y.
*J. Phys. Chem. C* **2022**, *126* (27), 11193–11200.

# Acknowledgements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