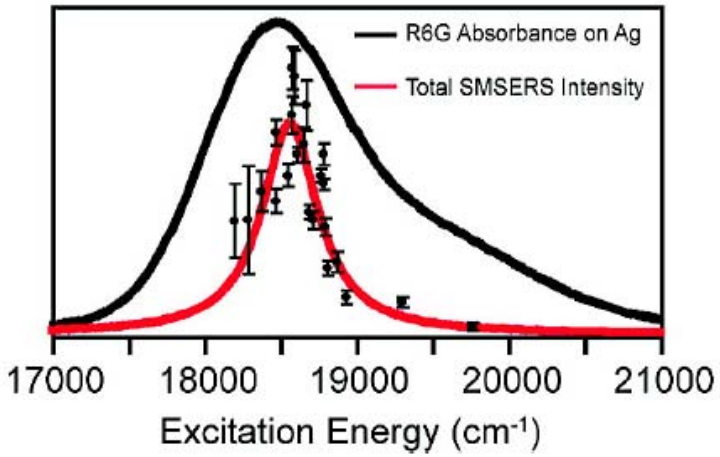
Surface-Enhanced Raman Excitation Spectroscopy of a Single Rhodamine-6G Molecule



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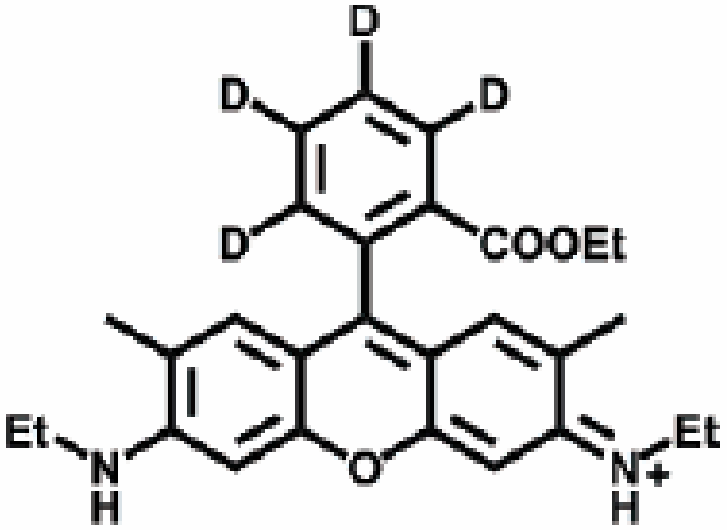
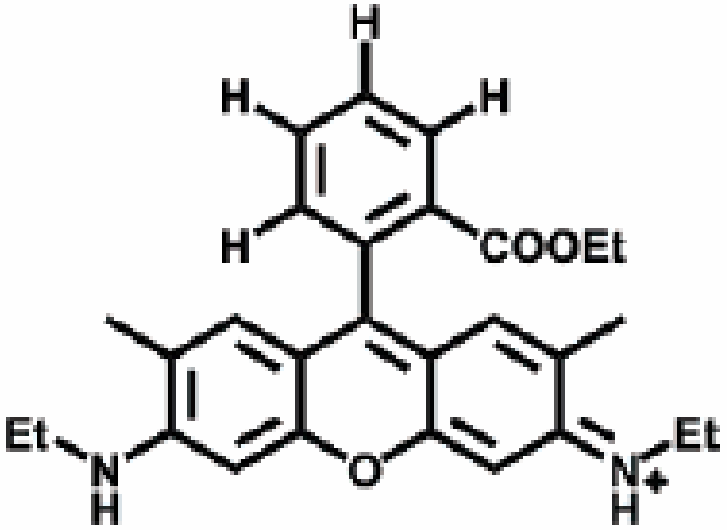


R6G-d_4



R6G-d_0

Overview:

- **The surface-enhanced Raman excitation profiles (REPs) of rhodamine 6G (R6G) on Ag surfaces are studied using a tunable optical parametric oscillator excitation source**

- **These experiments afford the ability to finely tune the excitation wavelength near the molecular resonance of R6G**

- **To perform wavelength-scanned surface-enhanced Raman excitation measurements of a single molecule**

- **The ensemble-averaged surface-enhanced REPs are measured for collections of molecules on Ag island films**

- **The relative contributions of the 0-0 and 0-1 vibronic transitions to the surface-enhanced REPs vary with vibrational frequency**

Introduction:

- **In the original single molecule surface enhanced raman spectroscopy (SMSERS) reports, the enhancement factor (EF) was estimated to be 10^{14}-10^{15} by comparing the measured SER cross-section of rhodamine 6G (R6G) on Ag nanoaggregates (~10^{-15} cm^2) to a typical Raman scattering cross-section (~10^{-30} cm^2)**

- **But now the resonance Raman contribution accounts for as much as 10^7 of the previously predicted ~10^{15} enhancement in the R6G/Ag system and rest 10^8 comes from surface effects**

- **Prior studies were not performed on the *same* nanoparticle aggregate nor the *same* molecule and have been limited to fixed-frequency laser sources and hence this work seek to characterize the resonance Raman contributions to SMSERS intensity about the molecular resonance**

Experimental section:

~35 nm size Ag nanoparticle were prepared by usual citrate reduction method

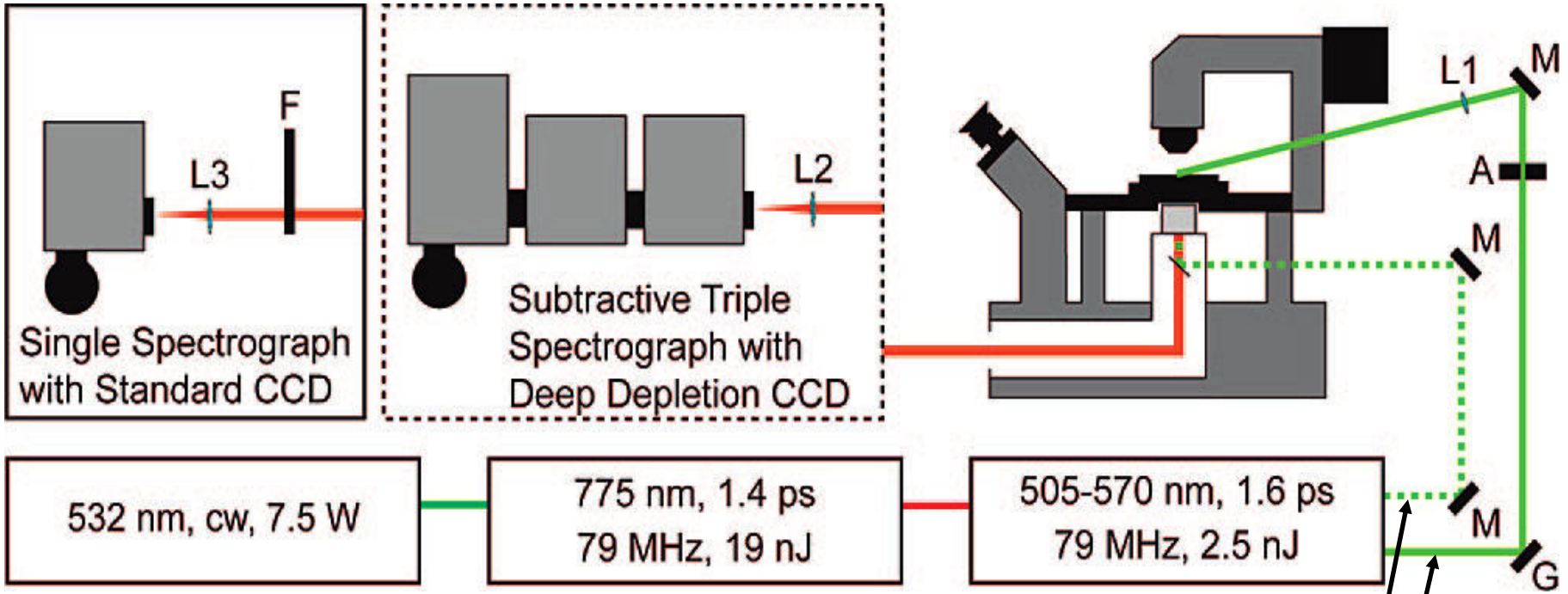
SERS Sample Preparation

Silver island films (AgIF) were prepared by electron beam evaporation of 6 nm Ag onto piranha-cleaned, base-treated glass cover-slips at a rate of 2.0 Å· s^{-1} The island films were incubated in ethanolic solution containing either 10^{-4} M R6G

SMSERS Sample Preparation

A 10 mL solution of chemically prepared Ag nanoparticles was treated with 1 mL of a 50:50 mixture containing R6G (5 x10^{-10} M) and R6G-d_4 (5 x 10^{-10} M) such that ~0.5 R6G and 0.5 R6G-d_4 were adsorbed per nanoparticle. Then 20 mM NaCl solution added to cause aggregation only.

Instrumentation

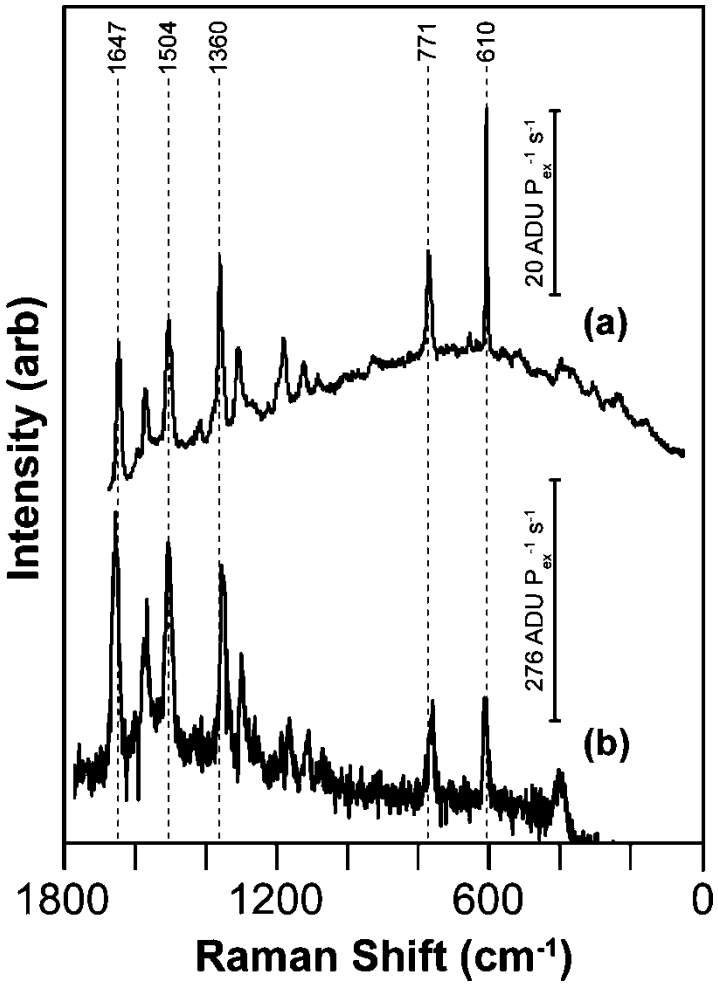


An optical microscope coupled to a tunable excitation source and detection system for ensemble-averaged studies

For single molecule studies

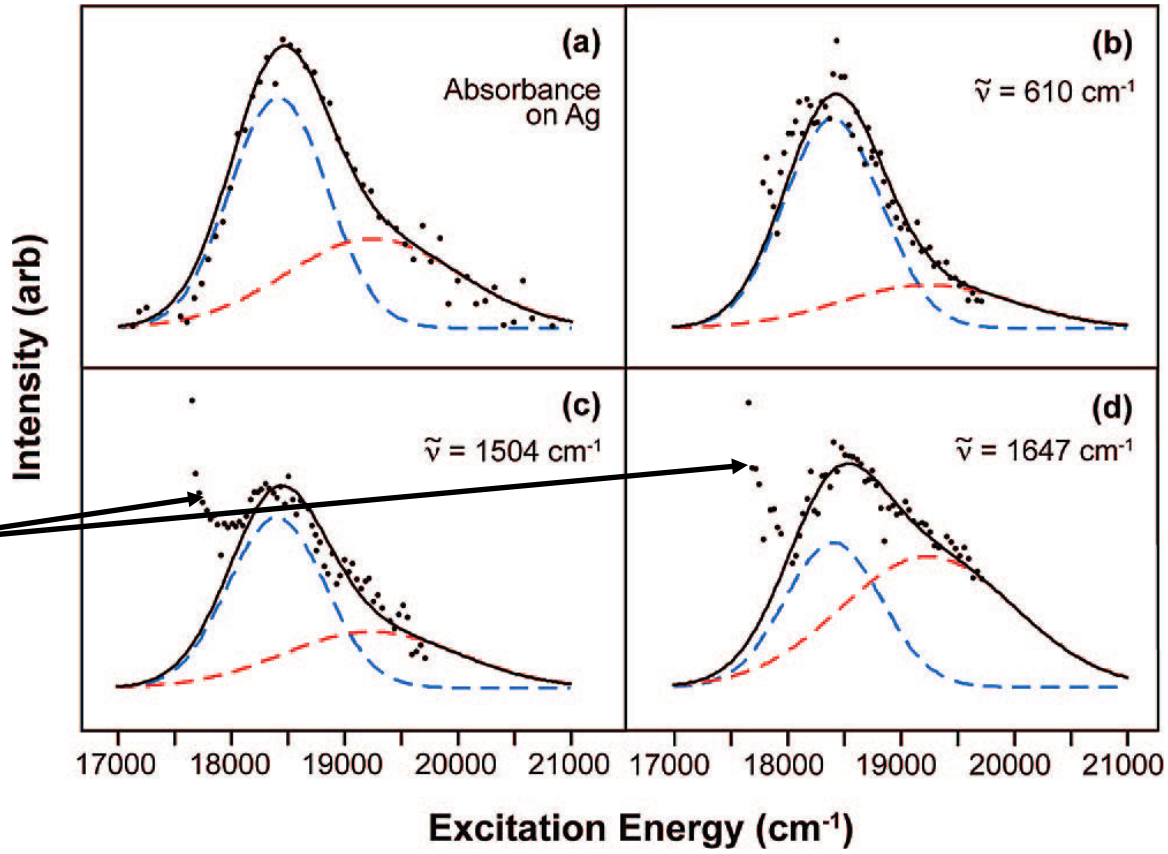
Results and discussion:

a) SERS of R6G



In ethanolic solution, R6G exhibits an absorbance maximum (E_{max}) at 18986 cm^{-1} (526.7 nm) with a vibronic shoulder at 19960 cm^{-1} (501.0 nm). The FWHM of each peak is 974 and 1997 cm^{-1}, respectively.

Due to surface effect

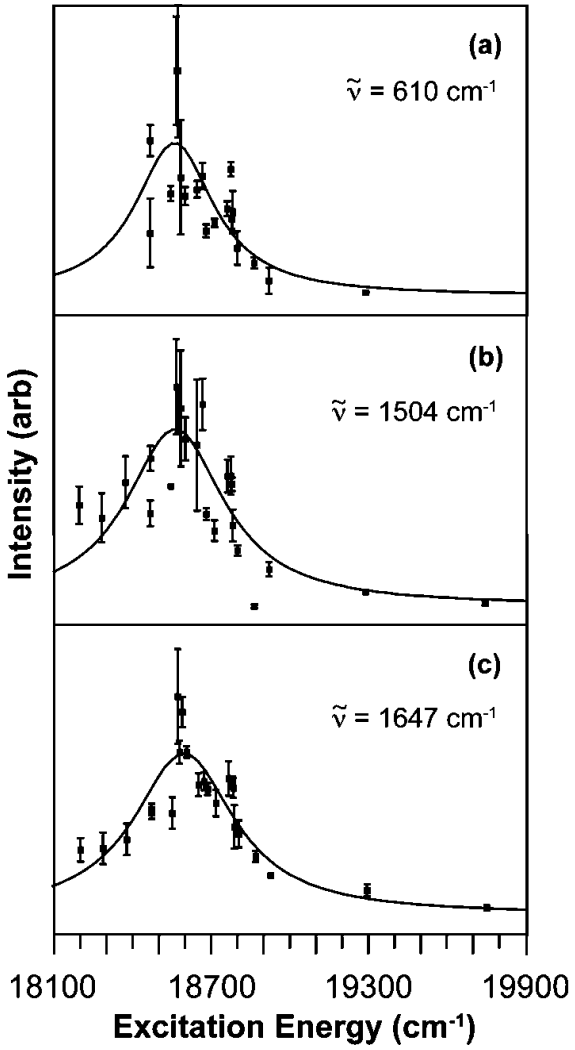


(a) Surface absorbance of R6G on Ag

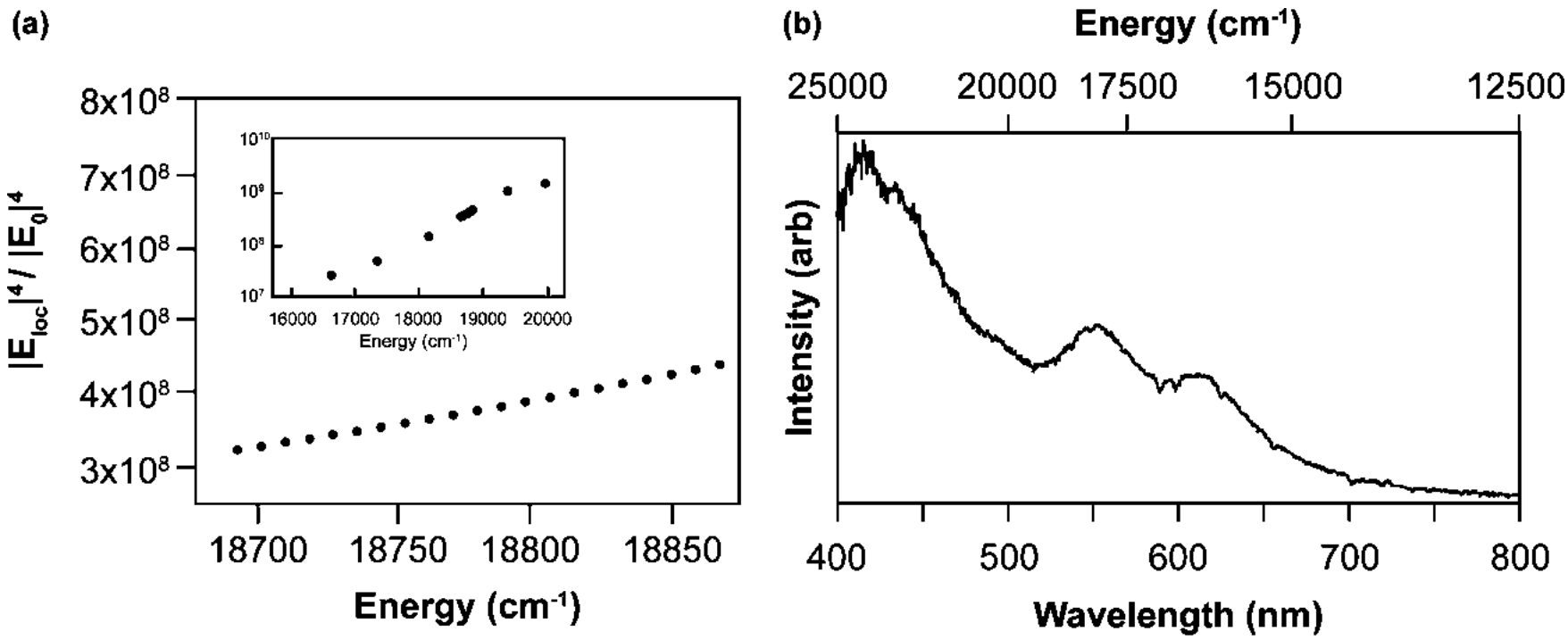
Ensemble-averaged surface enhanced Raman excitation profiles of different Raman modes of R6G on AgIF. (b) ν = 610, (c) 1504 and (d) 1647 cm^{-1}

The best fit corresponds to maxima and FWHM of E_{max} = 18409 cm^{-1} (543.2 nm), FWHM = 1004 cm^{-1} (0-0 transition) and E_{max}= 19246 cm^{-1} (519.6 nm), FWHM = 1822 cm^{-1} (0-1 transition)

b) SMSERS of R6G

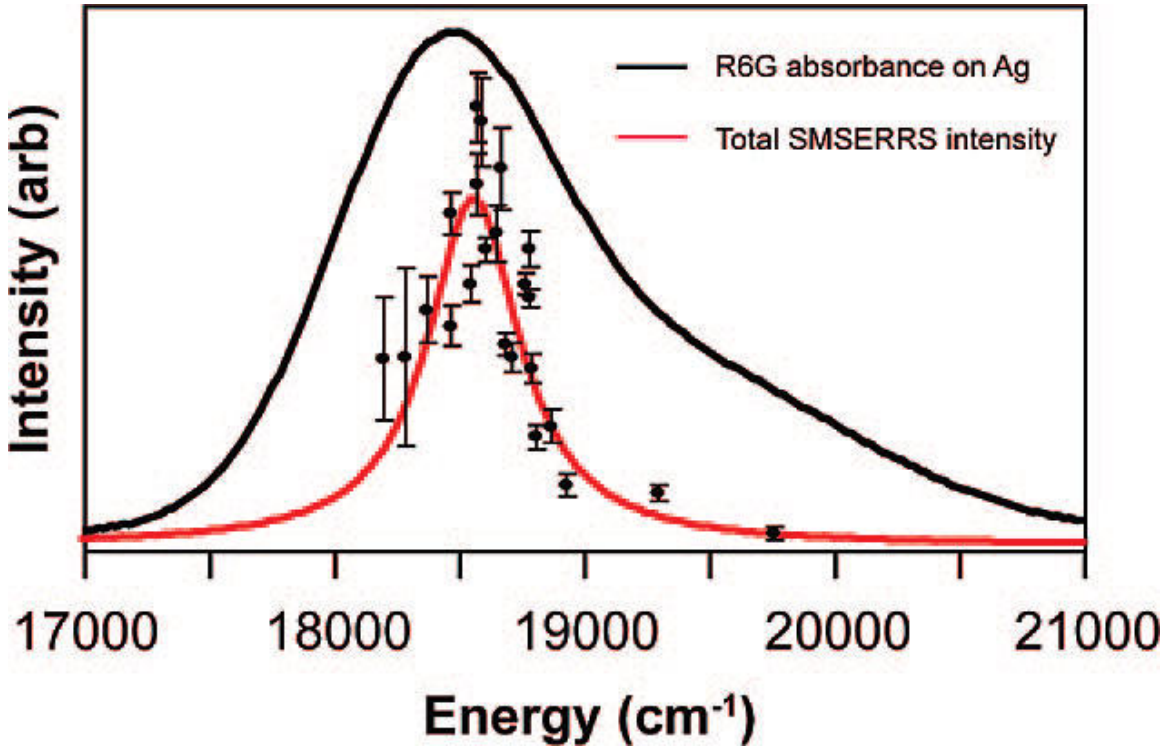


Best fit to the data for the 610 cm^{-1} mode (4a) corresponds to E_{max} = 18562 cm^{-1} (538.7 nm) and FWHM = 365 cm^{-1}. For the 1504 cm^{-1} mode (4b) E_{max} = 18561 cm^{-1} (538.7 nm) and FWHM = 451 cm^{-1}. The 1647 cm^{-1} mode (4c) was fit to a single Lorentzian function with E_{max} = 18598 cm^{-1} (537.7 nm) and FWHM = 463 cm^{-1}



a) **Discrete-dipole approx. (DDA) calculations on a model T-shaped SMSERS aggregate demonstrate that EM enhancement in the hot spot does not fluctuate on sub-nanometer (~9 cm^{-1}) increments over a 200 cm^{-1} range (centered at ~18 775 cm^{-1}) and exhibit a gradual downward slope**

b) **Resonant Rayleigh scattering spectrum of the nanoparticle aggregate used in the SMSERS study**



Comparison of the single-molecule surface-enhanced resonance REP of R6G to the ensemble-averaged surface absorbance spectrum on Ag

Conclusion:

• The structure of the single-molecule surface-enhanced REPs is dominated by the resonance Raman enhancement while the magnitude is dominated by electromagnetic enhancement

• The ensemble-averaged surface-enhanced REPs are well described by a sum of two gaussians, corresponding to the 0-0 and 0-1 vibronic transitions

• The relative ratios of the 0-0 and 0-1 transitions varies with vibrational frequency

We can study similarly with our nanostructures/mesostructures e.g., rod, flower, cube etc

the effect of anisotropy on a molecule

• The line-widths of the single-molecule surface-enhanced REPs are narrower than the analogous ensemble-averaged line-widths


Thank you