Moving Nanoparticles with Raman Scattering

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SERS

- Metallic nanostructures increase Raman signals by a factor of up to $10^{14}$, making surface-enhanced Raman scattering (SERS) a highly sensitive and selective detection method even for single molecules.

- While chemical enhancement also contributes, the main cause of the SERS effect is the enhancement of the local electric field at hot spots of a nanostructured substrate.

Hot spot

- Hot spots arise where localized nanoparticle plasmons couple to each other.
Introduction

• Raman active molecules can act back on the hot spot, pushing the nanoparticles apart or pulling them together.

• Such a change of the inter-nanoparticle distance can be accurately measured by Rayleigh-scattering spectroscopy.
Production of protein-linked nanoparticle dimers

- Gold nanoparticles with a diameter of 40 nm are coated with biotinylated bovine serum albumin (BSA-Bi).
- Add 150 streptavidin molecules per nanoparticle and allow clusters of nanoparticles to form over several hours.
- Submarine agarose gel electrophoresis is used to analyze and purify the sample.
- After electrophoresis, the dimer band is excised and the nanostructures are retrieved from the gel by electroelution.
a) Rayleigh Raman
   Hot Spot

b) BSA-Bi SA
   40 nm

c) 300 nm
   Image 1
   Image 2

(d) 30 nm
   Image 3
Figure 2. (a) Experimental setup. (b) Rayleigh scattering spectra.
Figure 2: (c) Typical polarization-dependent Raman spectra.
Experimental

• First, Rayleigh spectra are measured to obtain the initial distance and orientation of the dimer.
• Then, the dimer is exposed to laser light of moderate intensity (<100 $\mu$W/m$^2$), which is polarized along the interparticle axis $d$, and Raman spectra are collected.
• Finally, another Rayleigh spectrum is recorded.
Figure 3. Moving nanoparticles with Raman scattering.
Figure 4. The inter-nanoparticle distance remains constant when no Raman emission is observed.
Figure 5. Shift of the longitudinal-mode Rayleigh scattering resonance energy $\Delta E$ vs initial resonance energy.
Significance

• For the design and understanding of SERS sensors.
• Additional source for the explanation of blinking, spectral jumping, and bleaching in SERS experiments and applications.
• It is also important for the dynamics of self-adaptive metal-nanoparticle SERS substrates.
Conclusion

• Raman-excited protein linkers between two nanoparticles change the inter-nanoparticle distance.

• When the linker protein is exposed to the strongly enhanced electric field in the interparticle hot spot, the protein actively alters this hot spot.

• Results can be explained by vibrational excitation of the protein, which leads to a change of its conformation that pushes the nanoparticles apart or pulls them together, until where the coupled plasmon is no longer in resonance with the Raman laser.