Moving Nanoparticles with Raman Scattering

M. Ringler,[†] T. A. Klar,[*,†] A. Schwemer,[†] A. S. Susha,[†] J. Stehr,[†] G. Raschke,[†] S. Funk,[†] M. Borowski,[†] A. Nichtl,[‡] K. Ku1rzinger,[‡] R. T. Phillips,[§] and J. Feldmann[†]

[†]Ludwig-Maximilians-Universitat Munchen,

[‡]Roche Diagnostics GmbH,

[§]University of Cambridge.

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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.

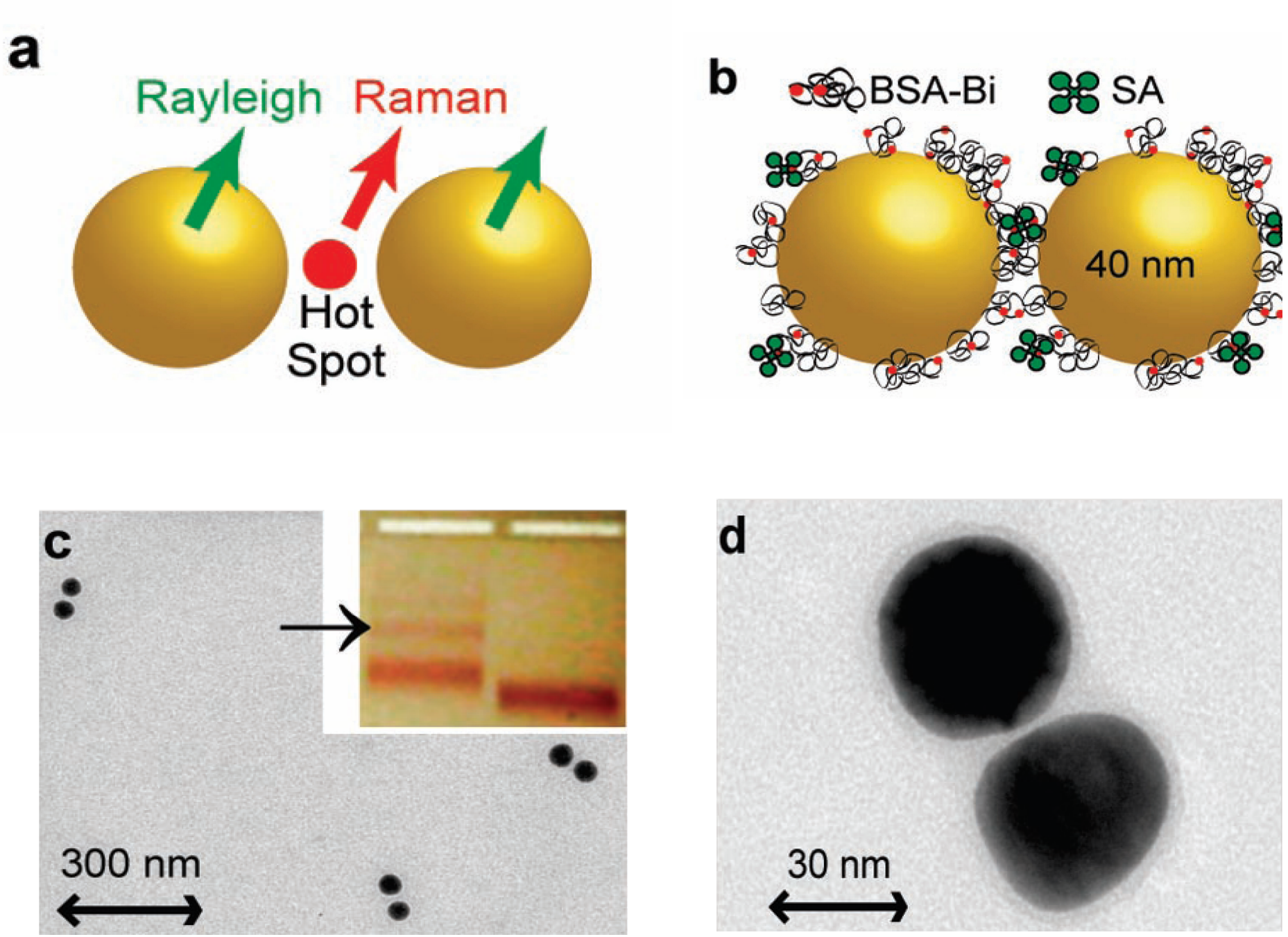
Introduction

- 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
d
30 nm

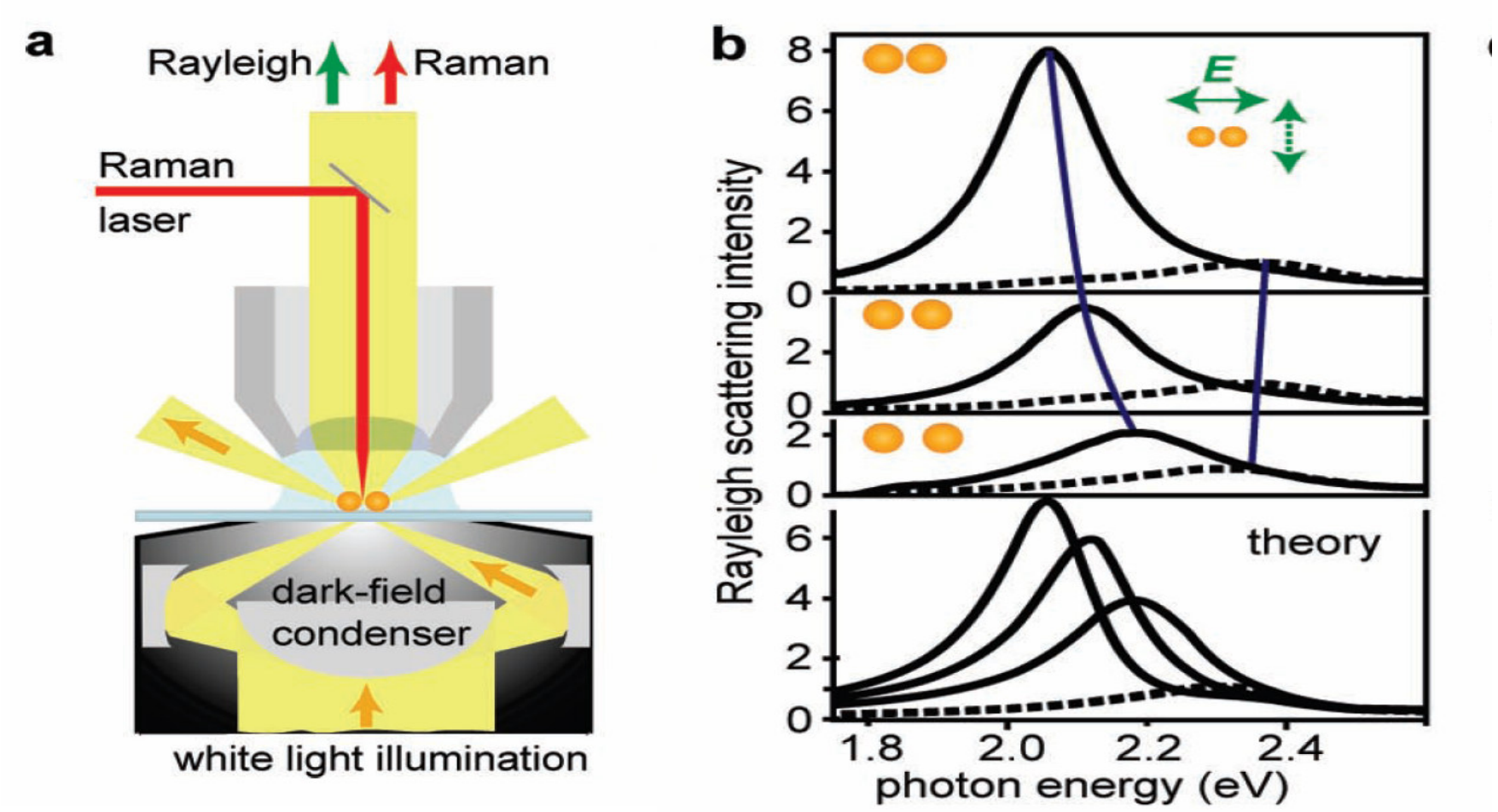


Figure 2. (a) Experimental setup. (b) Rayleigh scattering spectra.

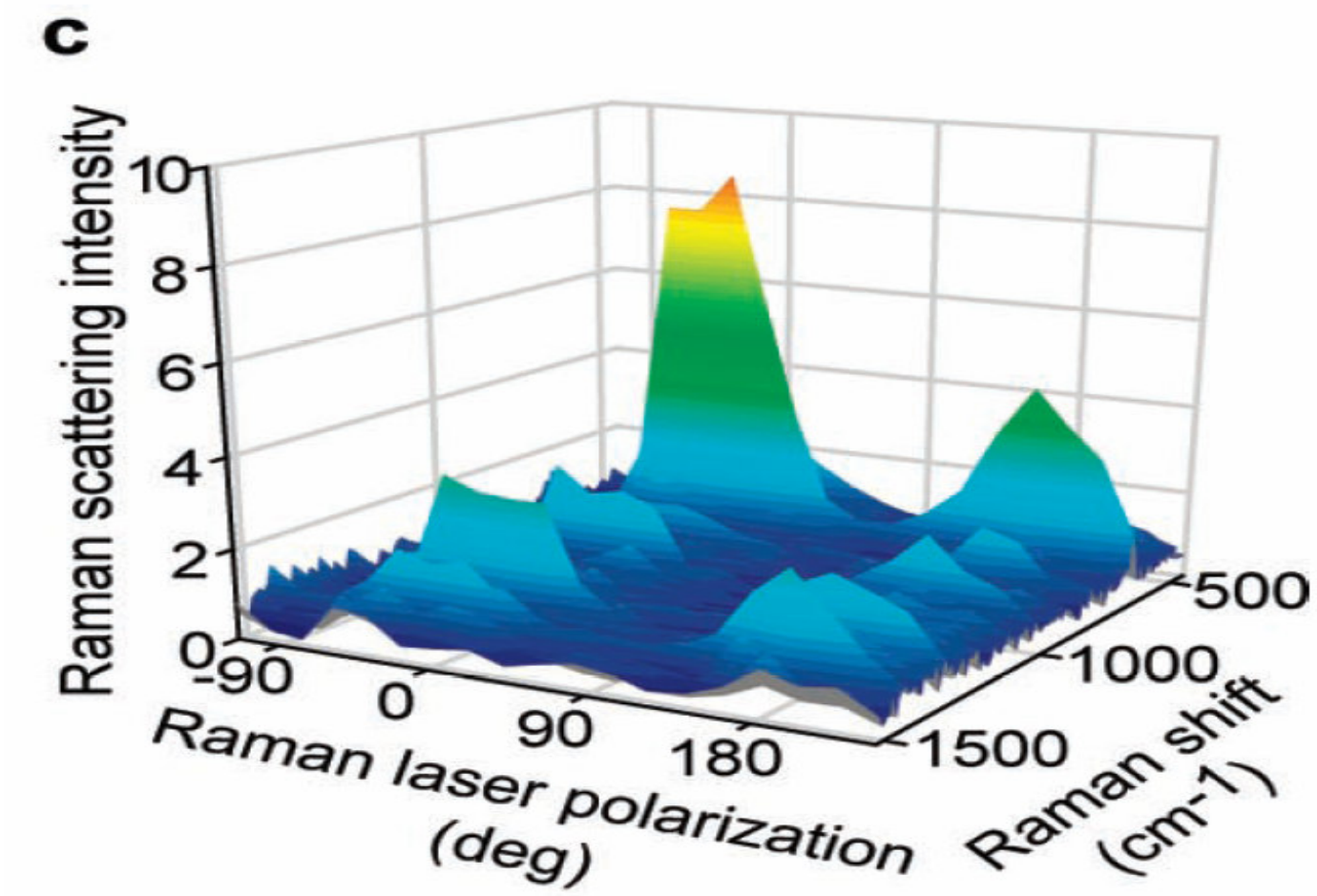


Figure 2: (c**)** Typical polarization-dependent Raman spectra.

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.

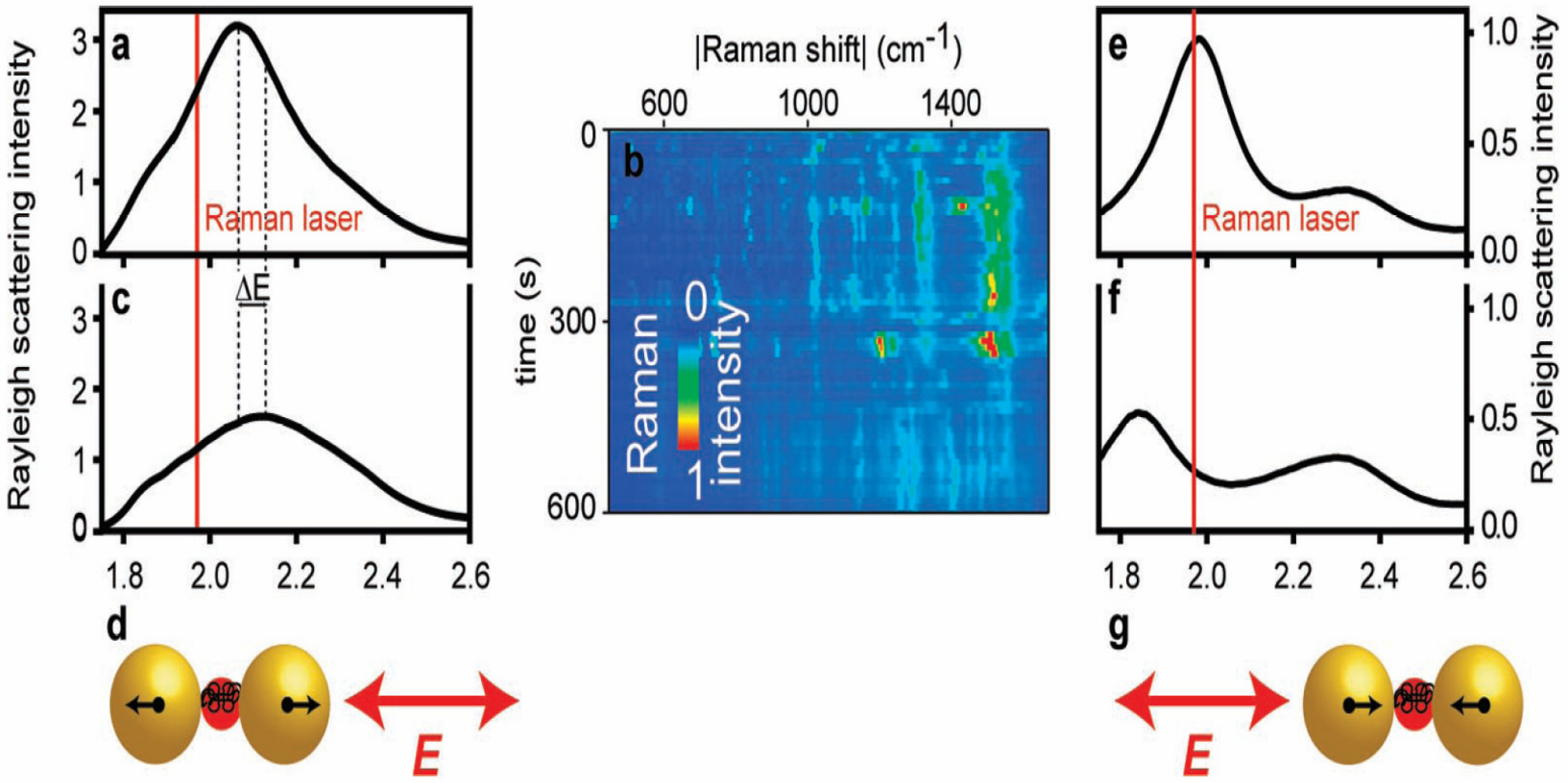


Figure 3. Moving nanoparticles with Raman scattering.

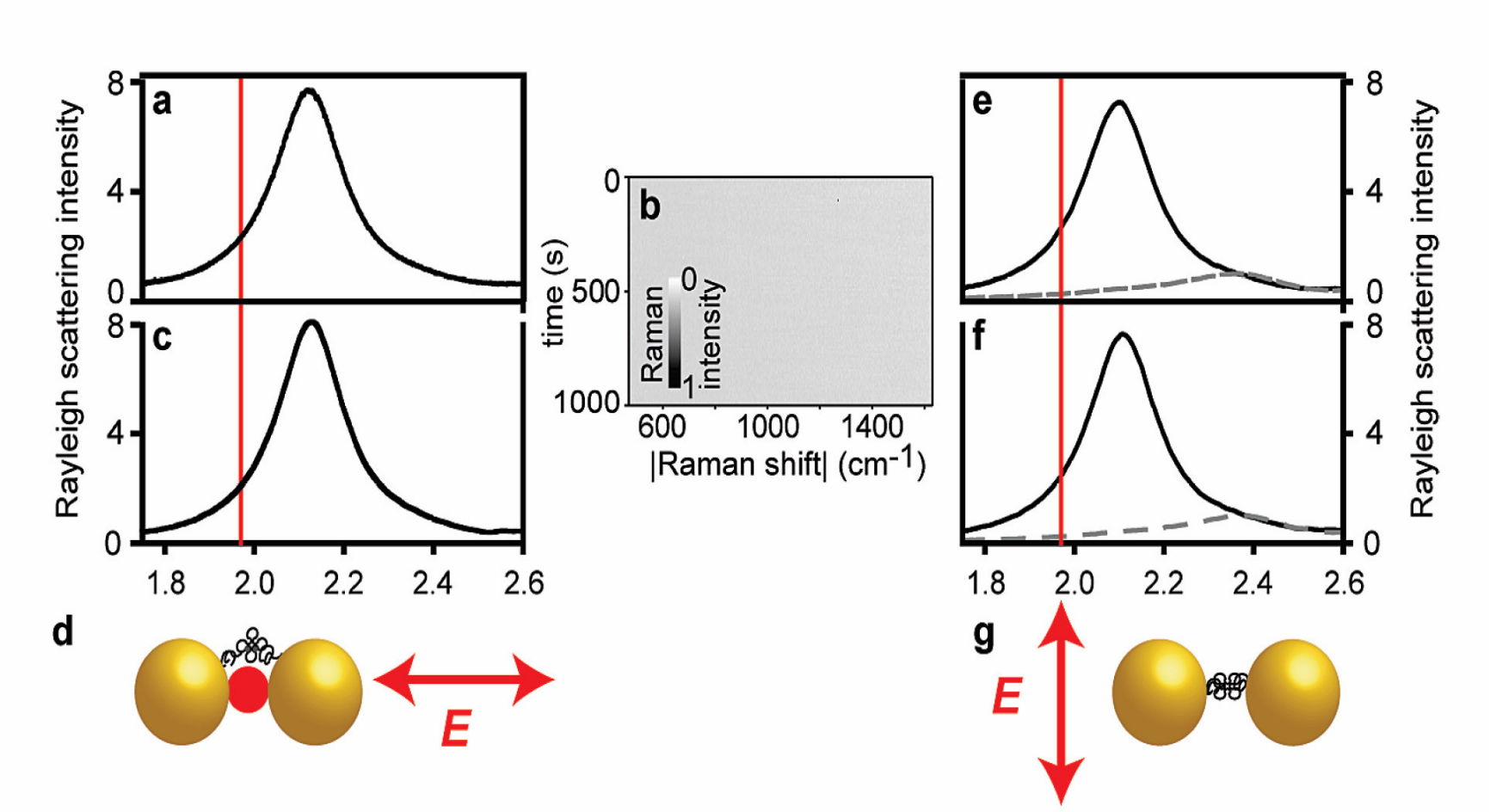


Figure 4. The inter-nanoparticle distance remains constant when no Raman emission is observed.

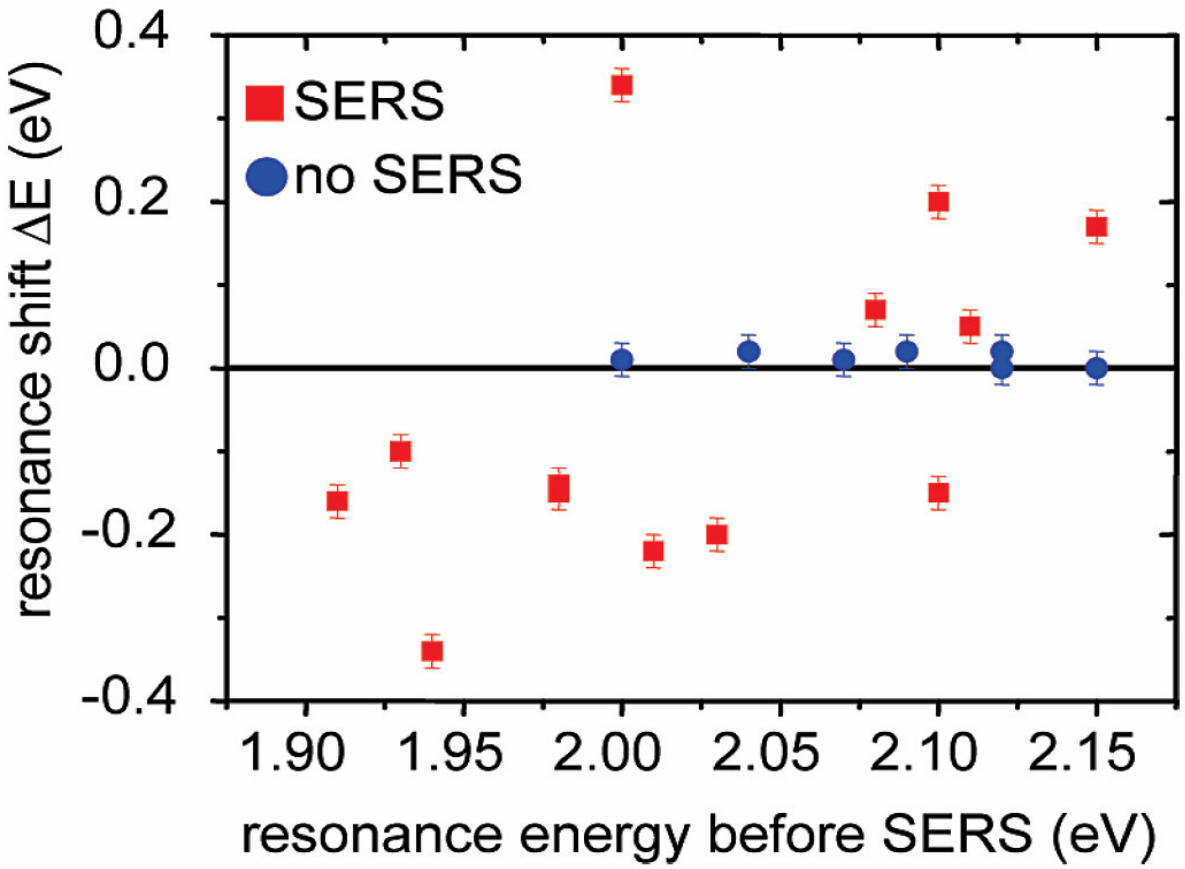


Figure 5. Shift of the longitudinal-mode Rayleigh scattering resonance energy ΔE vs initial resonance energy.

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.