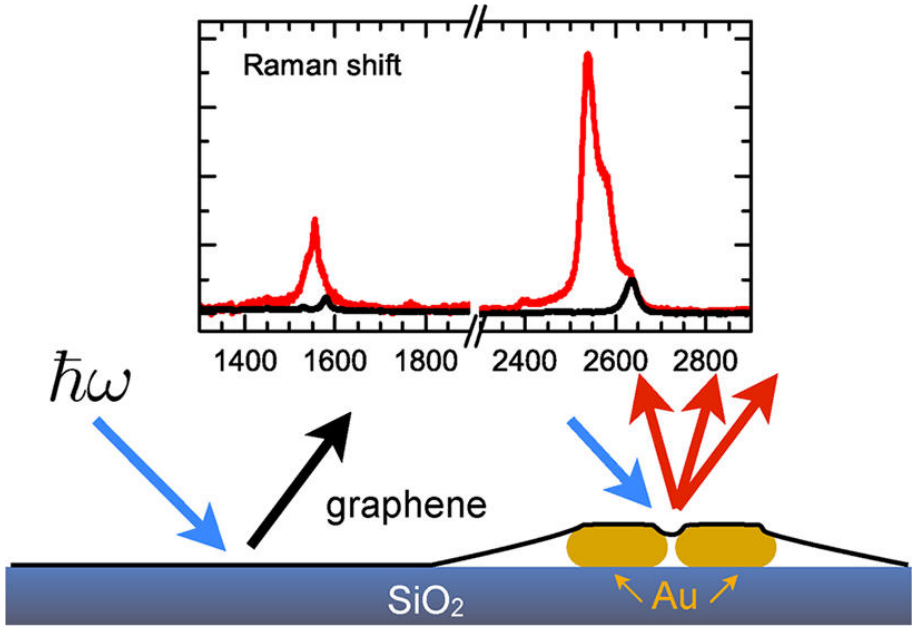
Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene



Talk by Niclas Müller

Pictures from: S. Heeg et al., Nano Letters 13, 2013

Structure of the talk

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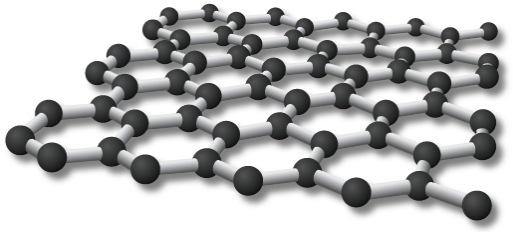
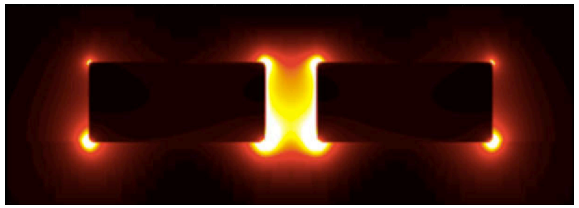
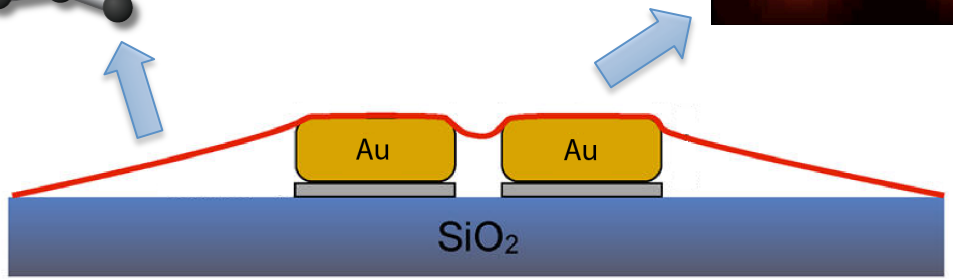
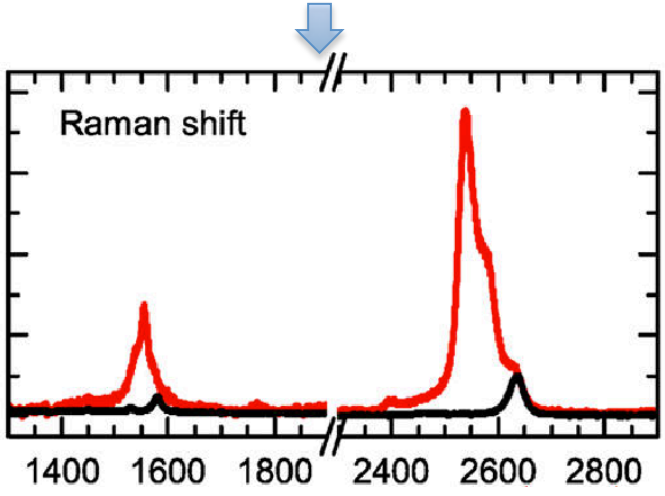
Graphene



Localized surface plasmons







Strain in graphene

Plasmonic enhancement

Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

1. Graphene

Fundamental properties

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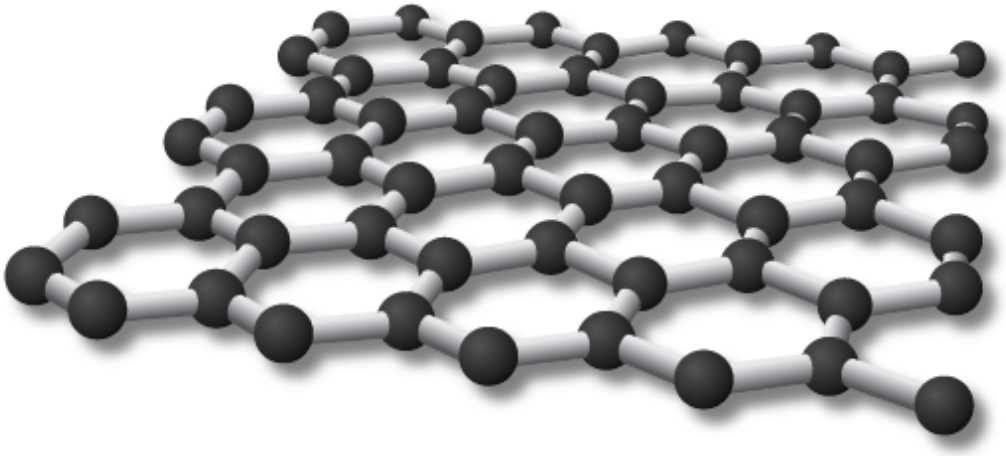
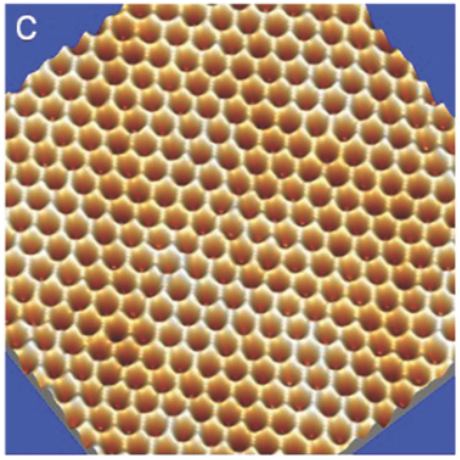
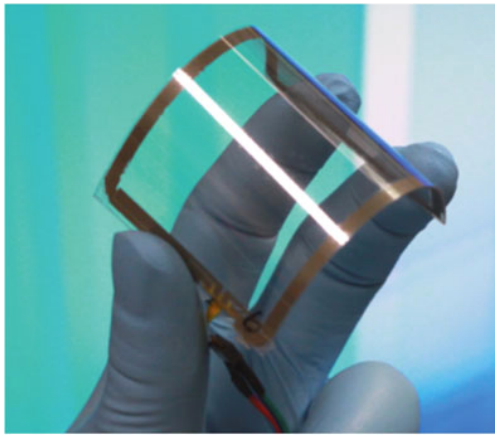
- Two-dimensional crystal of carbon atoms, stacked in a hexagonal lattice
- Extraordinary high charge carrier mobility, thermal conductivity, intrinsic strength
- Transparency of $\pi \cdot \alpha \approx 2.3\%$
- Complete impermeability to any gasses
- Can be chemically functionalized



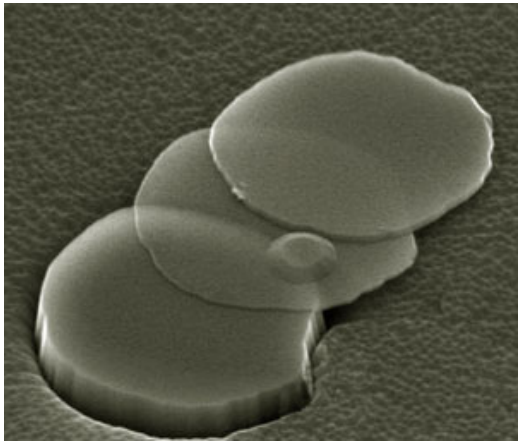


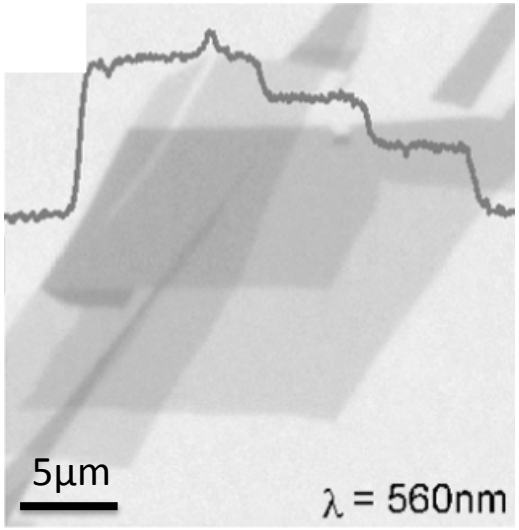


Pictures from: J. Mao et al., Appl. Phys. Lett. 100, 2012 and S. Bae et al., Nature Nanotechnology 5, 2010

1. Graphene

Micromechanical cleavage of graphene





- Method for research and prototyping
- Repeatedly peeling off thin layer from highly ordered pyrolitic graphite (HOPG)
- Single layer on Si+300nm SiO_2 is visible through optical microscope

Pictures from: A. K. Geim, Phys. Scr. T146, 2012 and P.Blake et al., Appl. Phys. Lett. 91, 2007

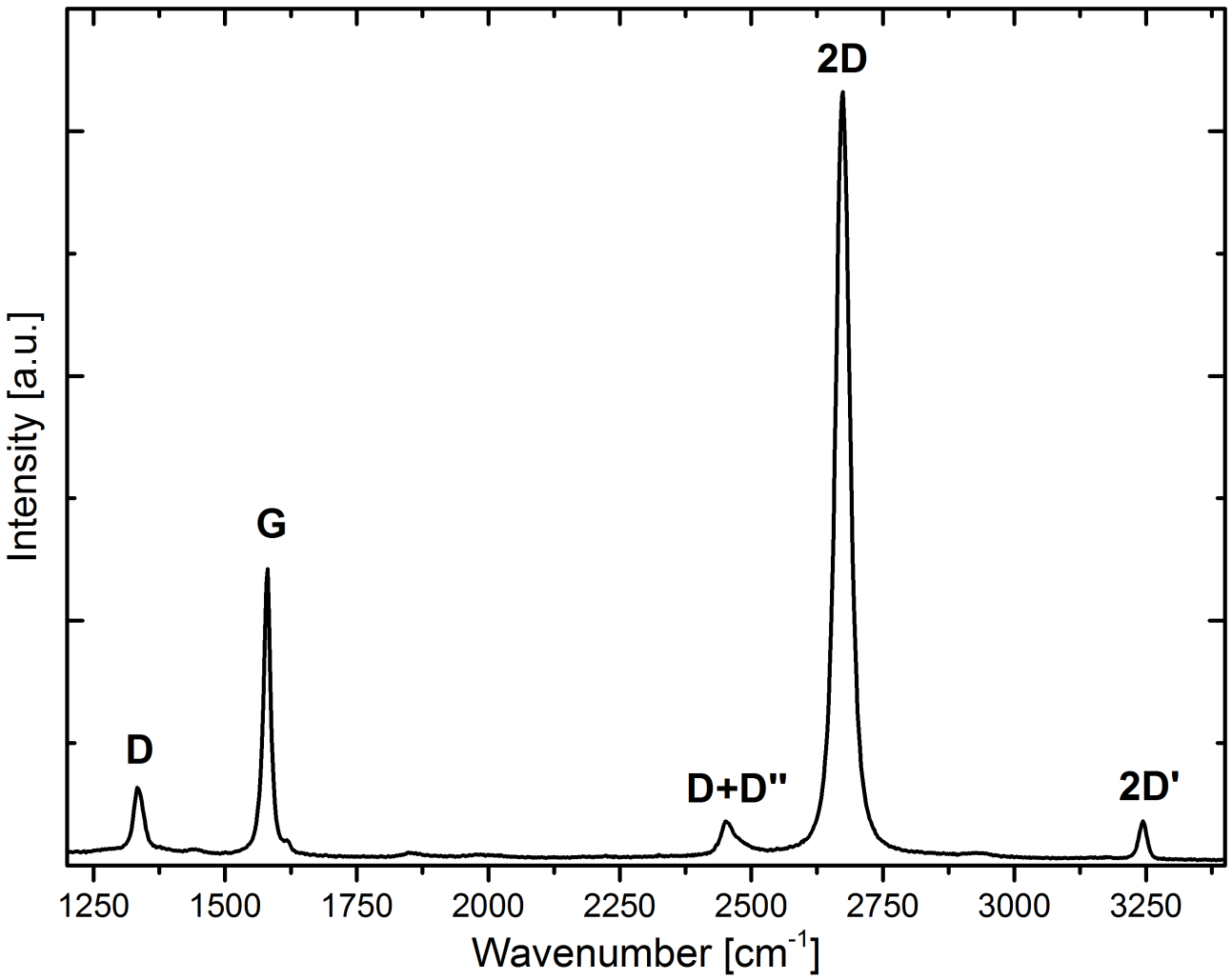
1. Graphene

Micromechanical cleavage of graphene

Pictures from: S. Heeg et al., Nano Letters 13, 2013

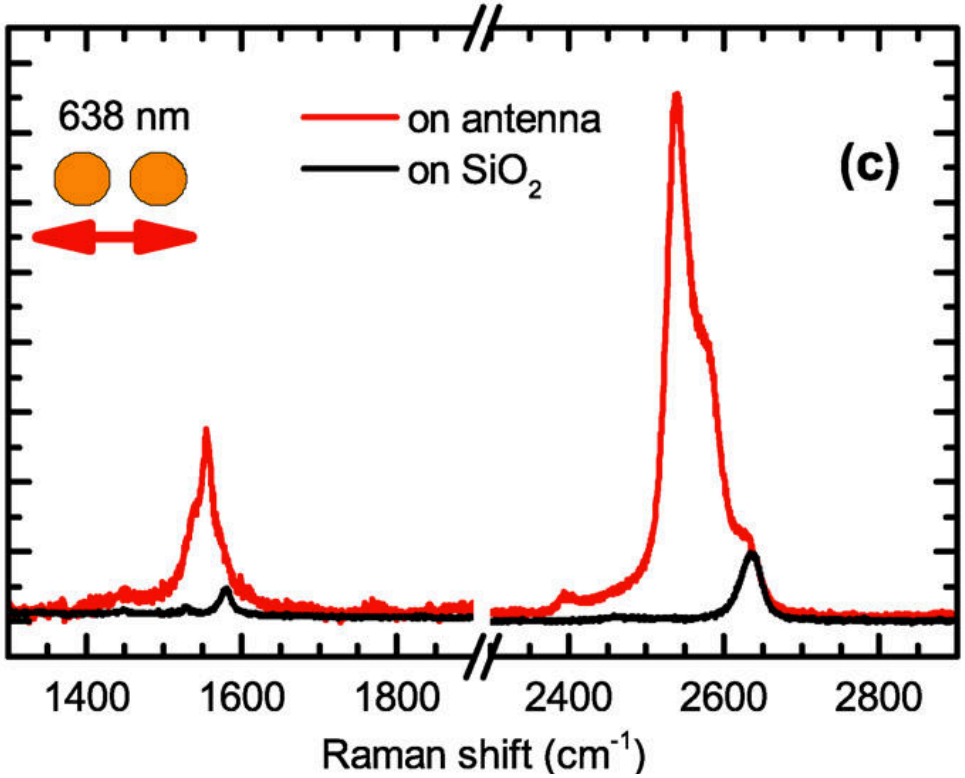
2. Raman spectroscopy of graphene

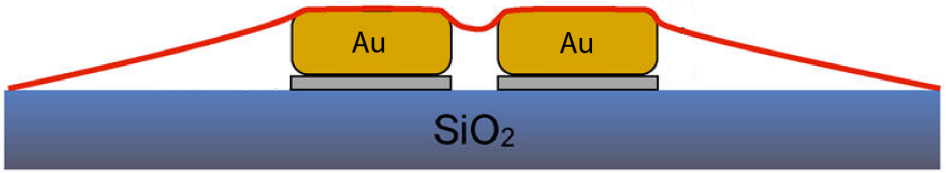
Typical spectrum



2. Raman spectroscopy of graphene

Spectrum of seminar paper

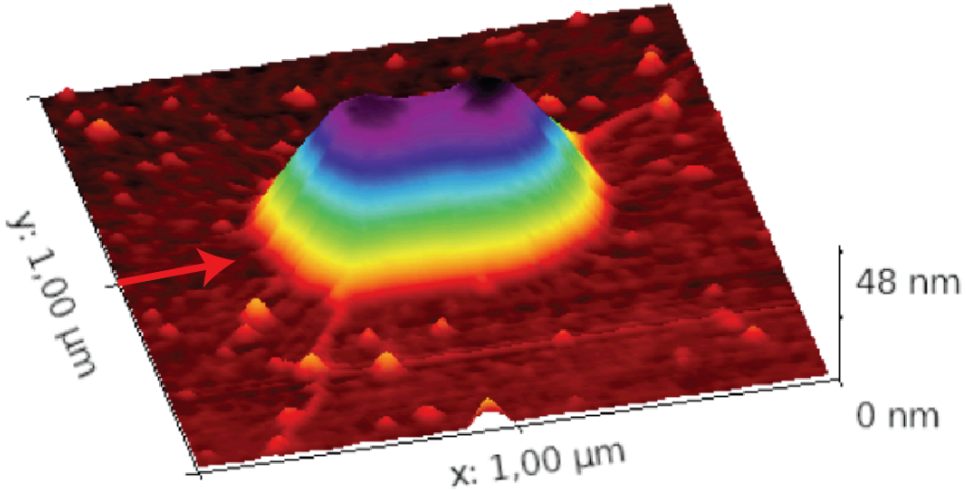


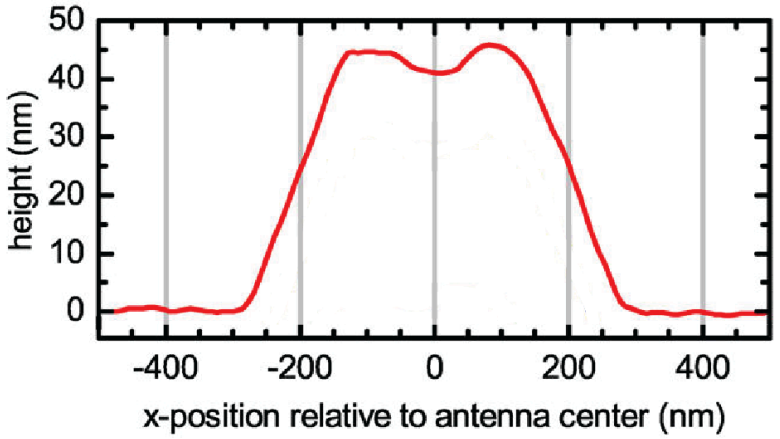


Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

2. Raman spectroscopy of graphene

Effect of strain



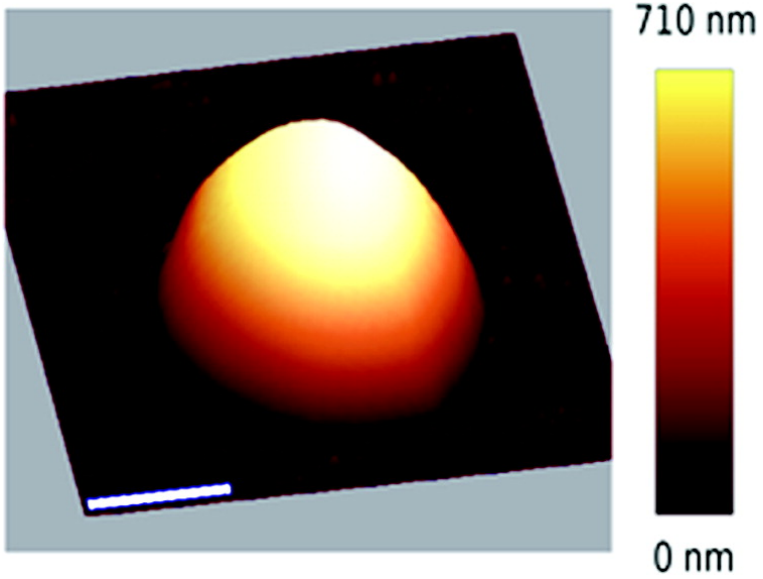


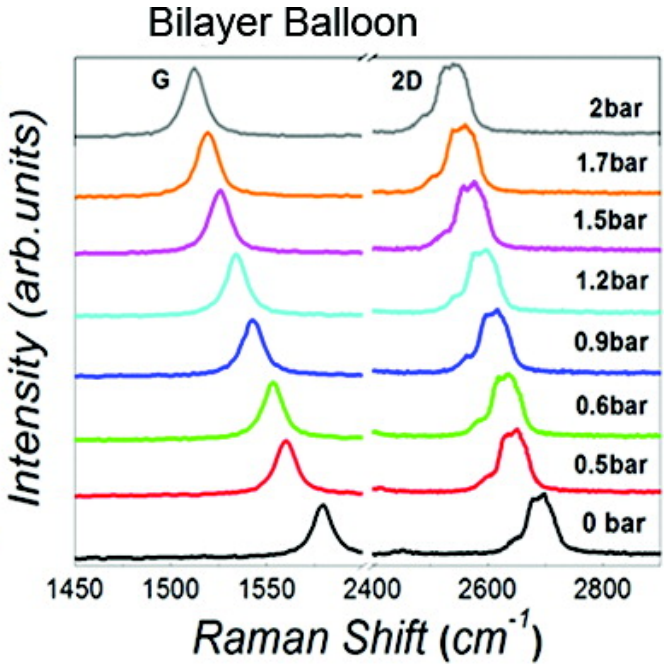
- Au nanoparticles cause tensile strain in graphene
- Strain also present in gap between particles

Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

2. Raman spectroscopy of graphene

Effect of hydrostatic strain



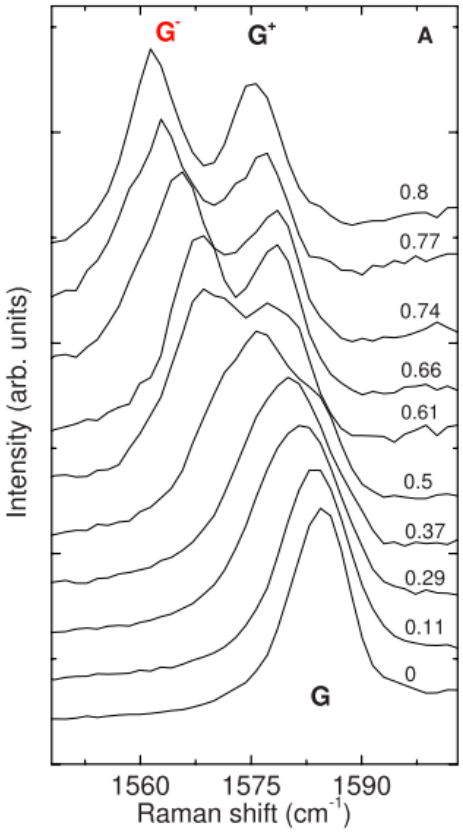


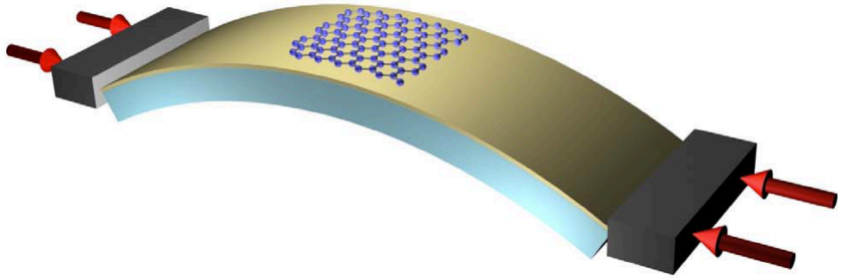
- Hydrostatic strain observed in pressurized graphene balloon
- Downshift of G and 2D mode with increasing strain

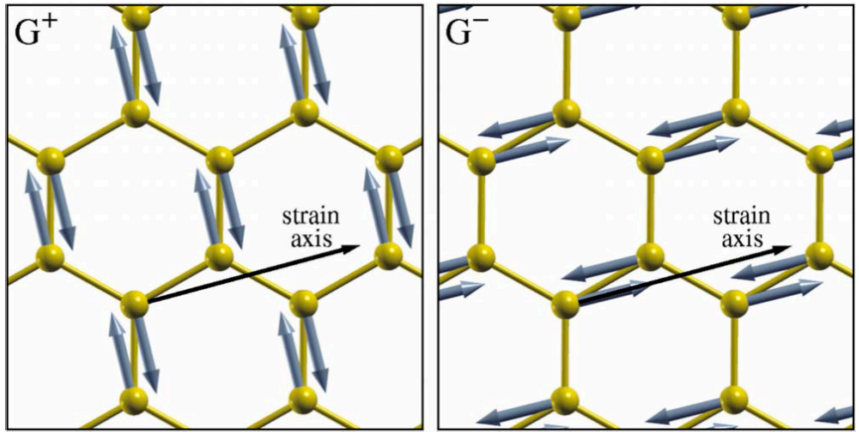
Pictures from: J. Zabel et al., Nano Letters 12, 2012

2. Raman spectroscopy of graphene

Effect of shear strain







- Shear strain induced by uniaxial strain on flexible substrate
- Splitting of G peak into G^+ and G^- peak

Pictures from: T. M. G. Mohiuddin et al., Physical Review B 79, 2009

2. Raman spectroscopy of graphene

Convolution effects

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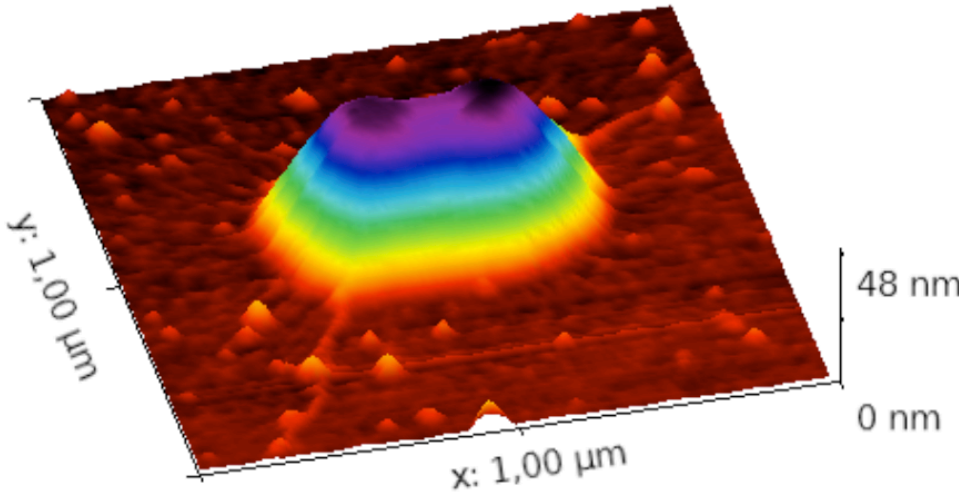
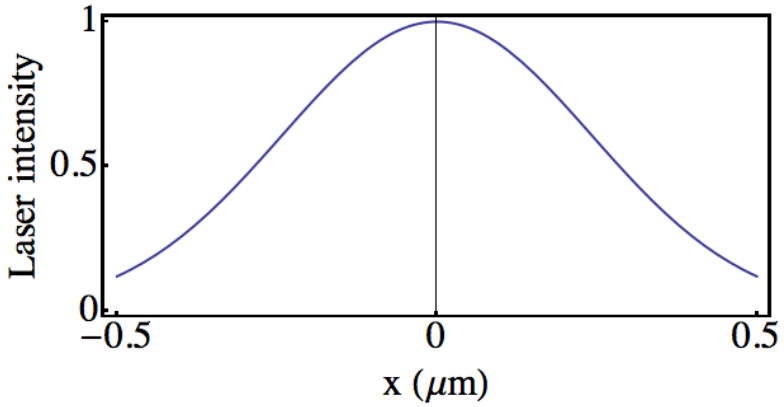
- Laser spot larger than Au nanoparticles (FWHM=570nm)

→ Convolution of spectra beside and on Au nanoparticles

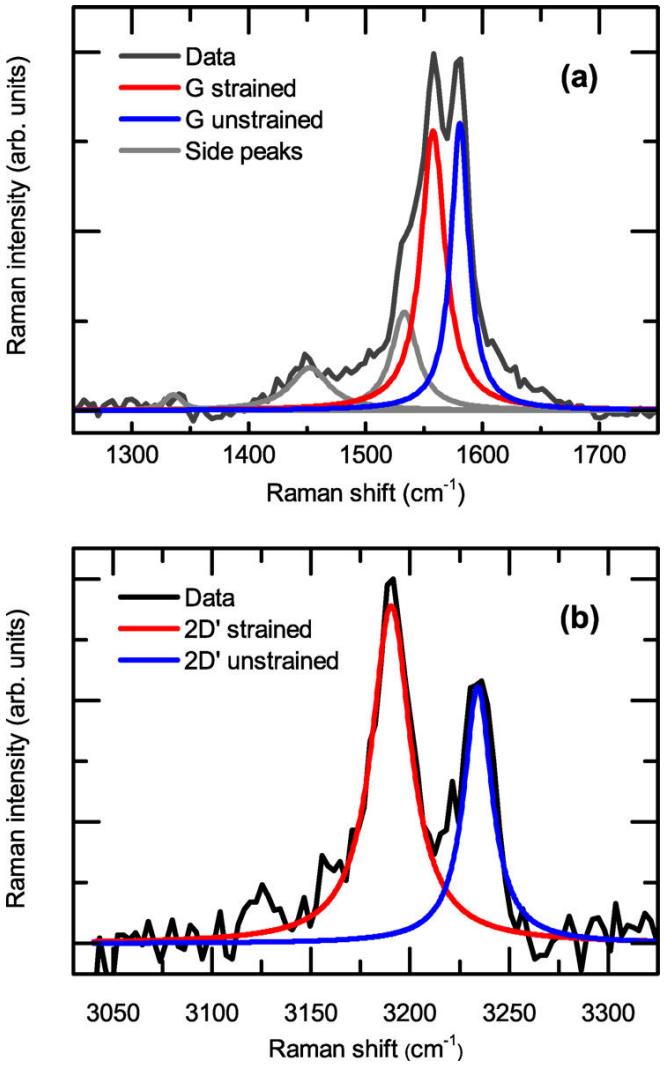




Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

2. Raman spectroscopy of graphene

Effect of strain – Seminar paper

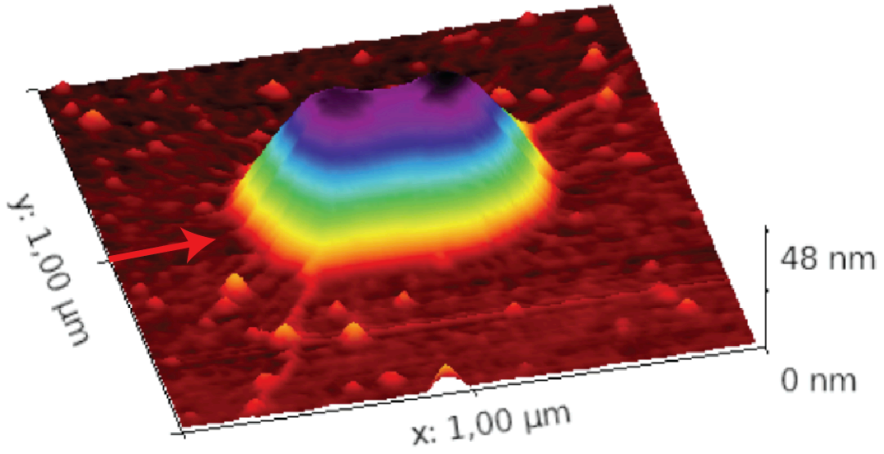


- Evaluation for G and 2D‘ peak (frequency depends only on strain and not on electronic structure)
- Observation of strained (red) and unstrained (blue) peaks
- Shift of peaks attributed to hydrostatic strain of 0,8%
- Broadening of peaks attributed to shear strain of <0,4%
- Peaks of strained graphene come from graphene in cavity (explanation later)

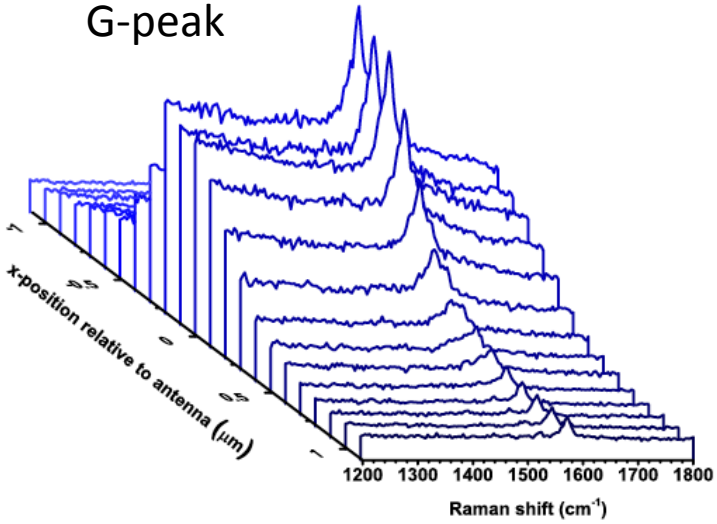
Pictures from: S. Heeg et al., Nano Letters 13, 2013

3. Plasmonics

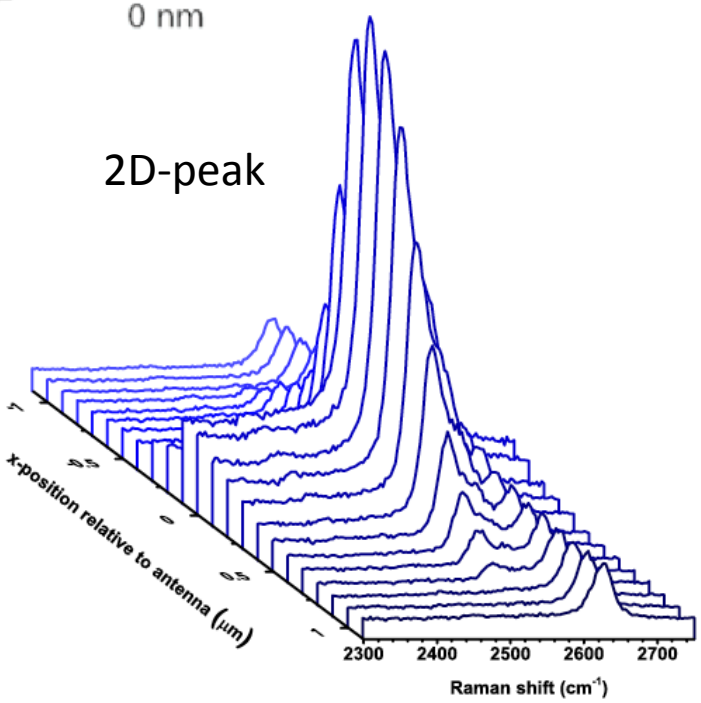
Enhanced Raman signal on cavity



G-peak



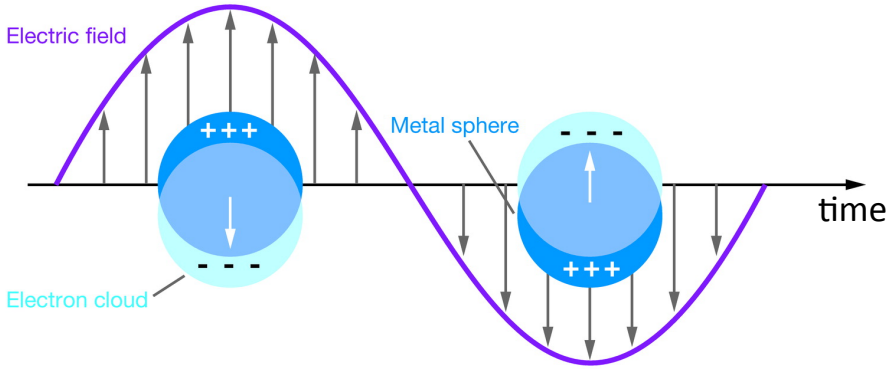
2D-peak

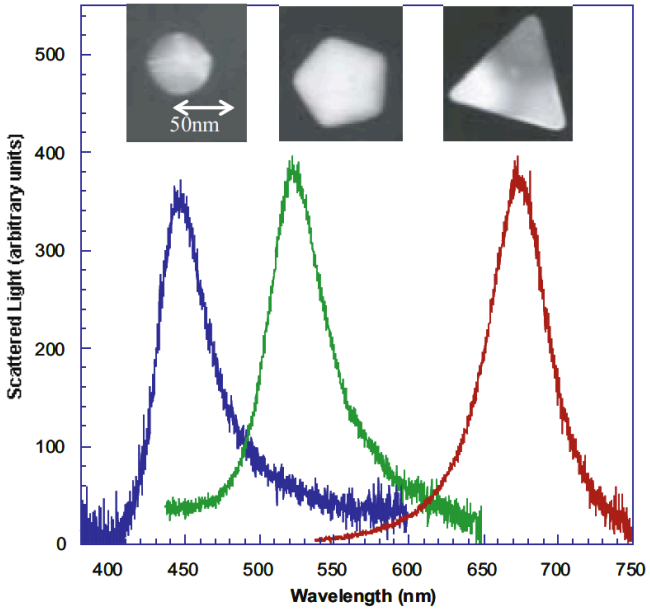


Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

3. Plasmonics

Localized surface plasmons



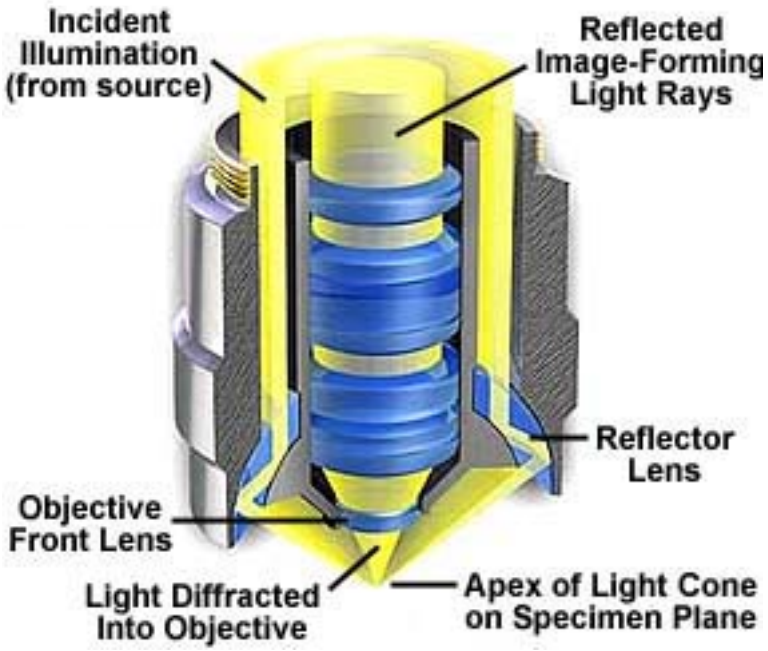


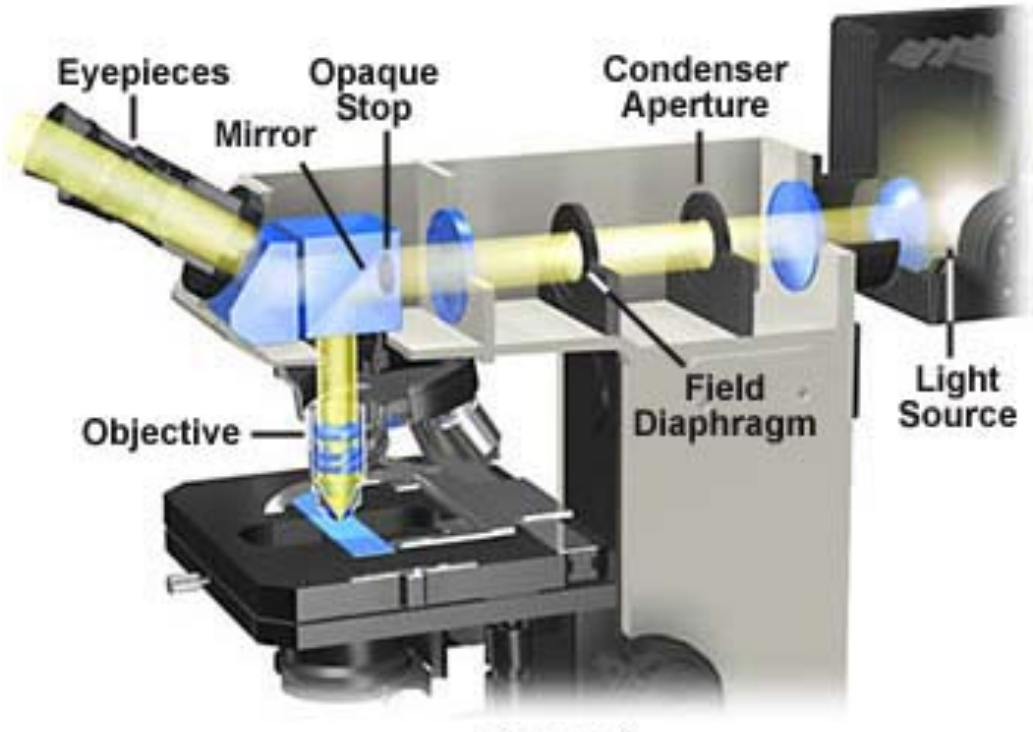
- Non-propagating excitation of conduction electrons in metallic nanostructures coupled to EM field
- Resonance leading to enhancement of EM field inside and in the near field zone
- Excitation possible by direct light illumination
- For Au and Ag resonance in the visible regime
- Resonance influenced by shape, size and environment

Pictures from: O. Bernson, Nature 480, 2011 and J. J. Mock et al. J. Chem. Phys. 15, 2002

3. Plasmonics

Dark field microscopy



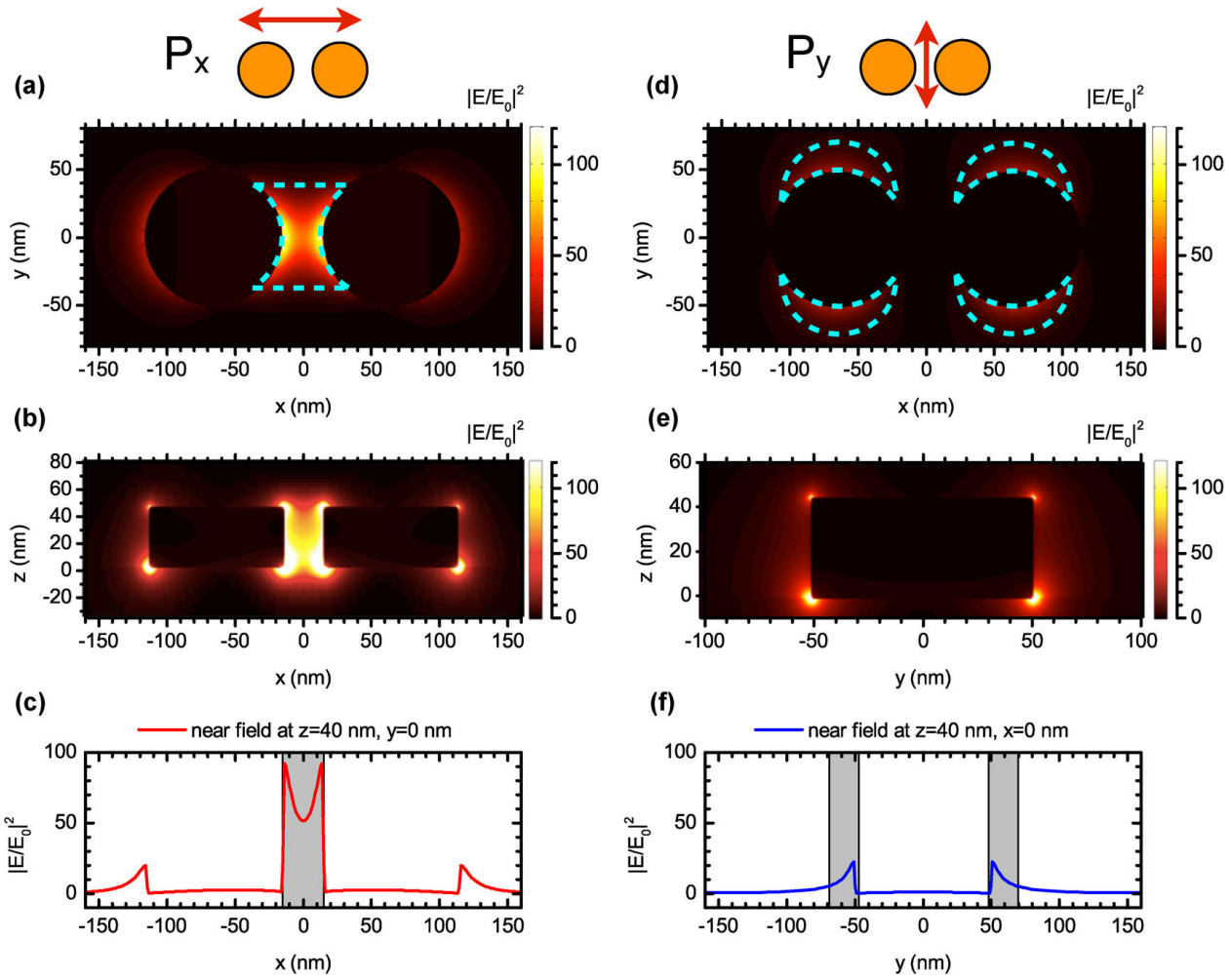


Pictures from: Olympus America Inc. 2012

3. Plasmonics

Coupling of localized surface plasmons

- Point dipoles interacting via their near-field
- Hot spot in cavity between particles with strong near-field enhancement
- Finite-difference time-domain (FDTD) code for simulation



4. Plasmon enhanced Raman scattering

Scattering cross section of Au nanostructure

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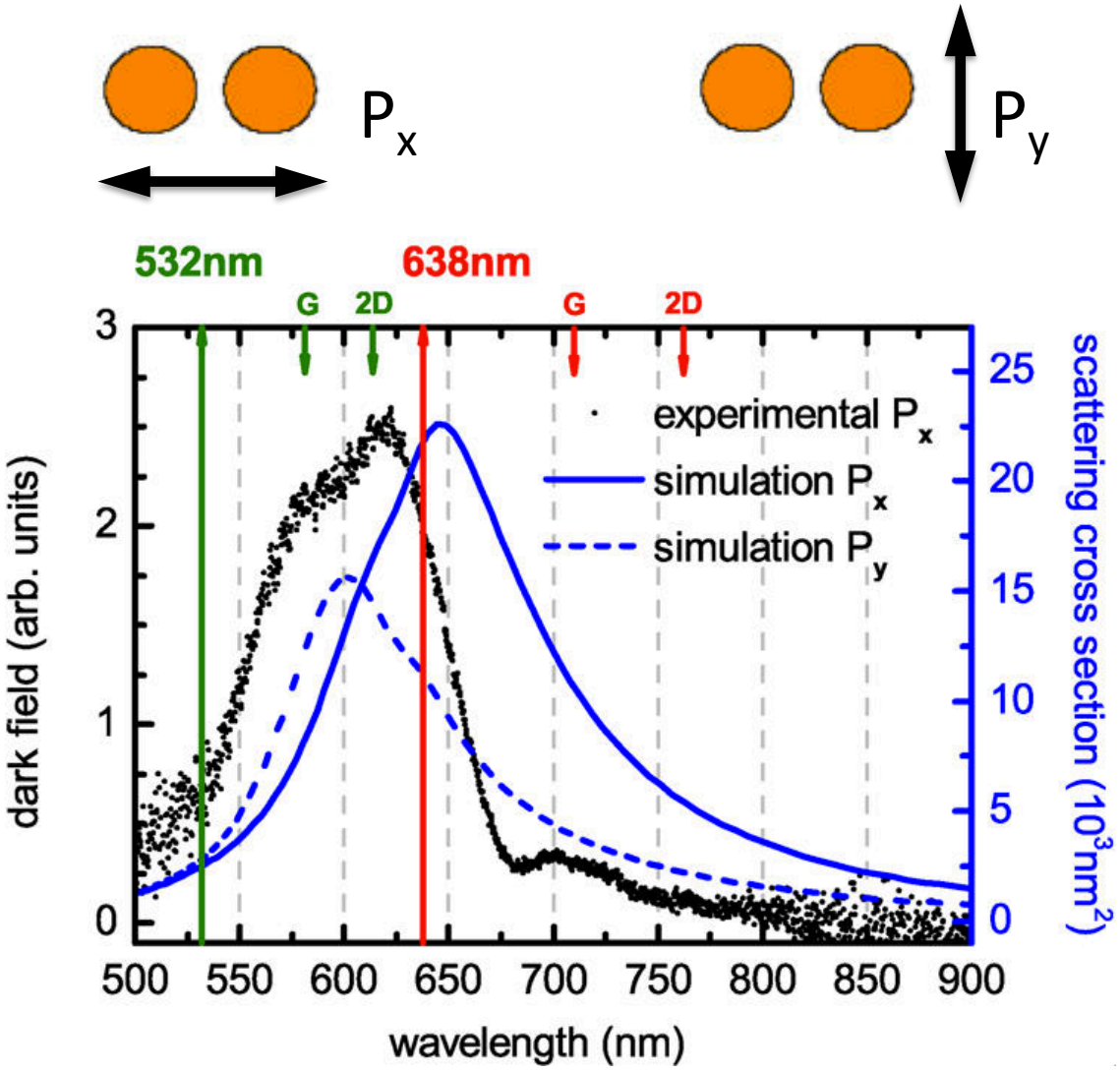
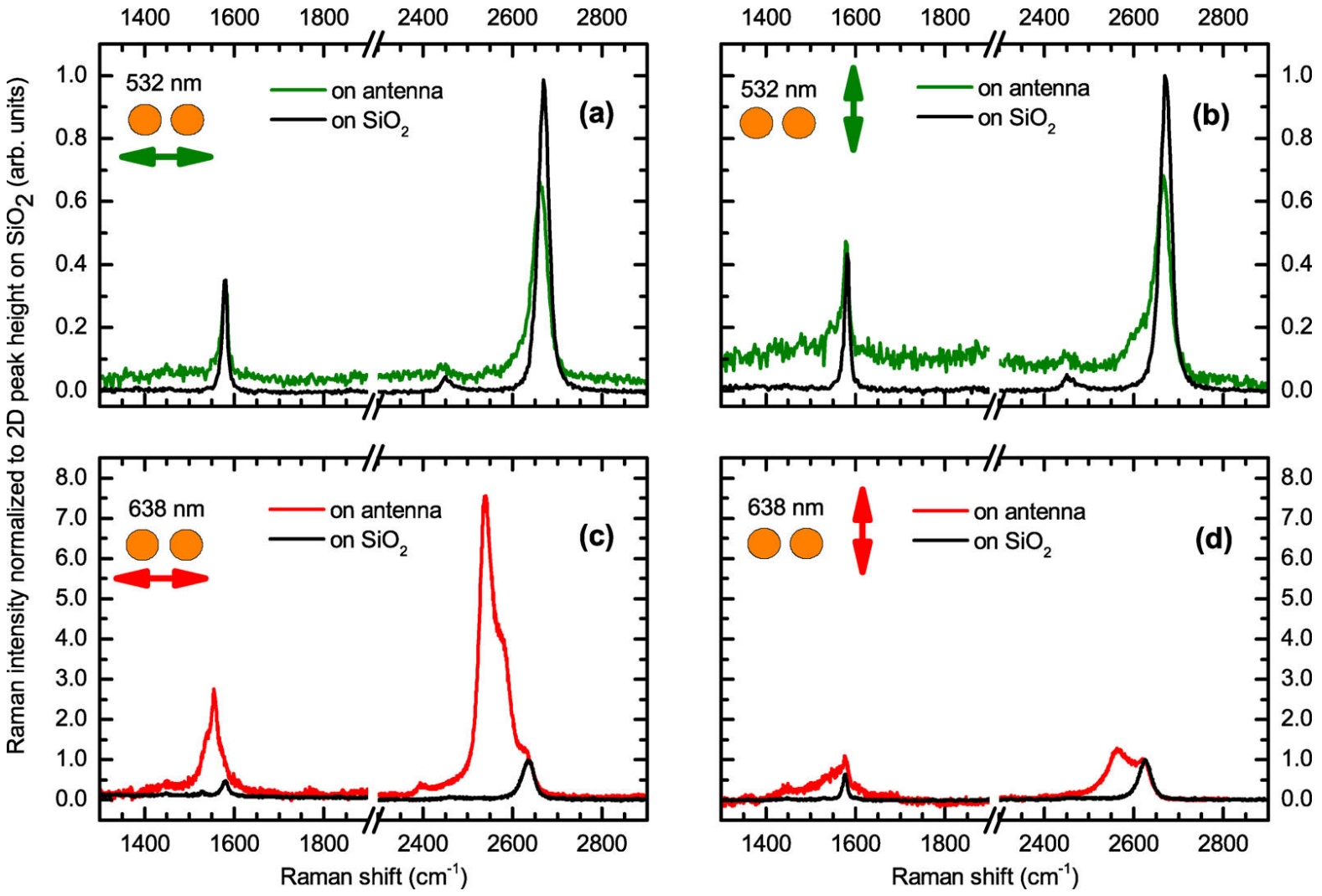
- Geometry of plasmonic particles such that resonance matches 638nm excitation laser (enhanced absorption)
- Enhanced emission expected for 532nm excitation
- Shift for different polarizations because of near-field coupling
- Blue shift of experimental data due to geometrical deviations



Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

4. Plasmon enhanced Raman scattering

Raman spectra on plasmonic structure



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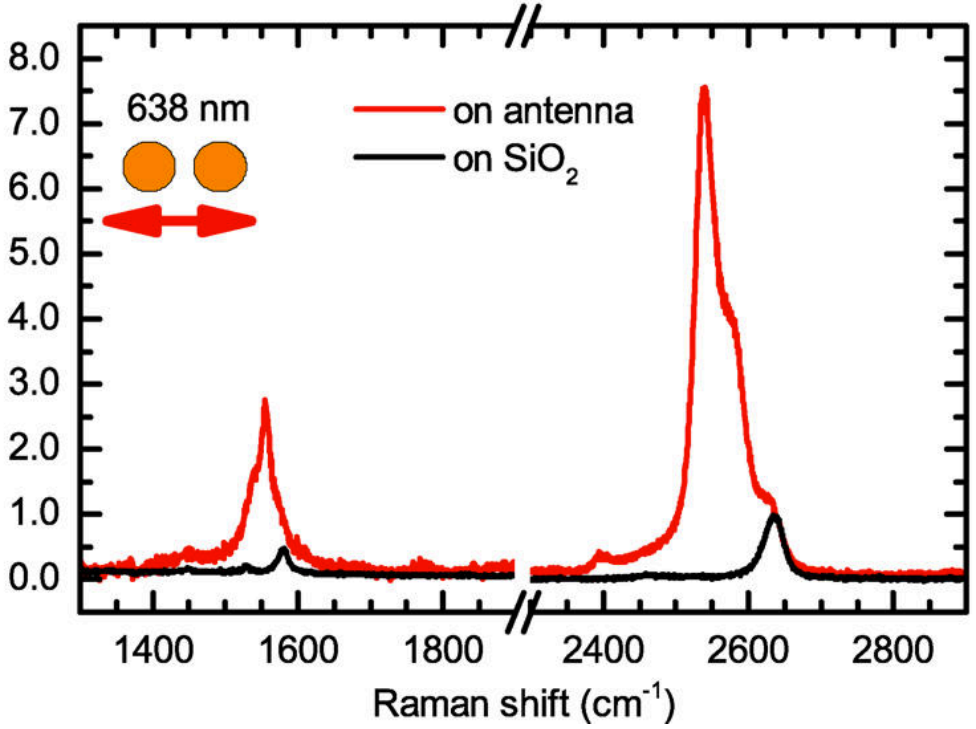

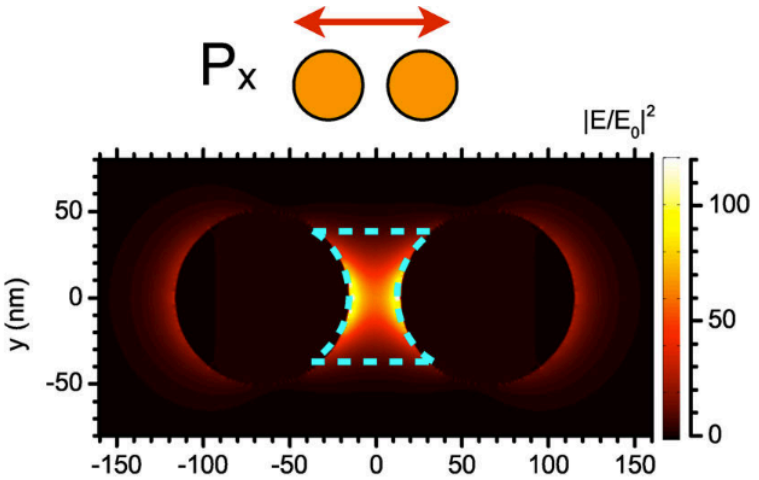

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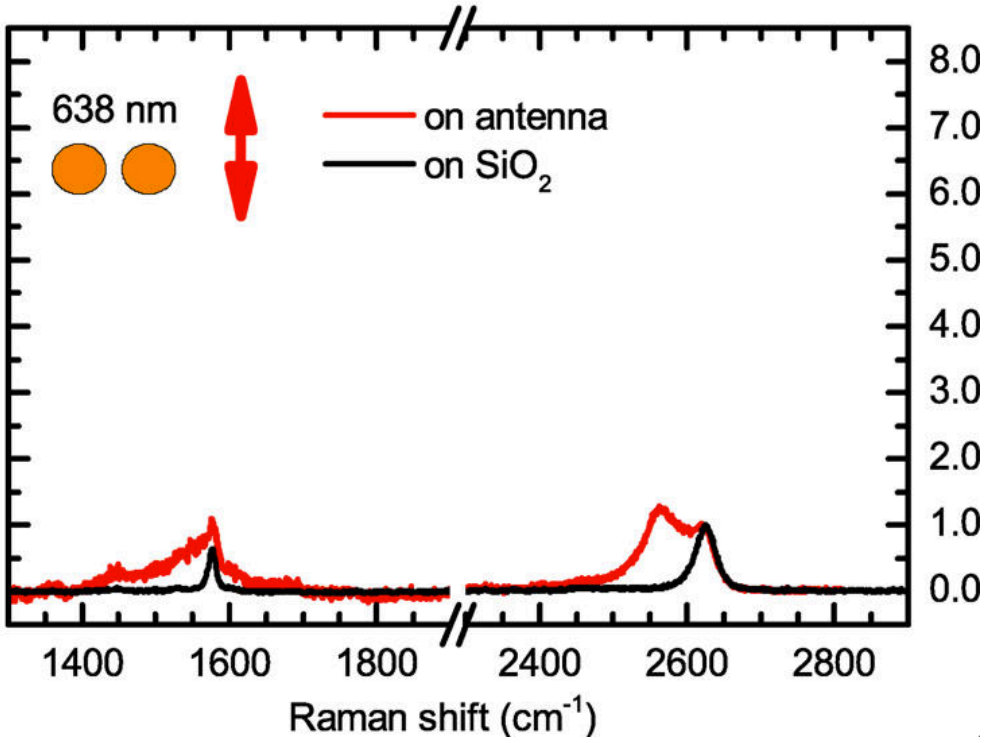
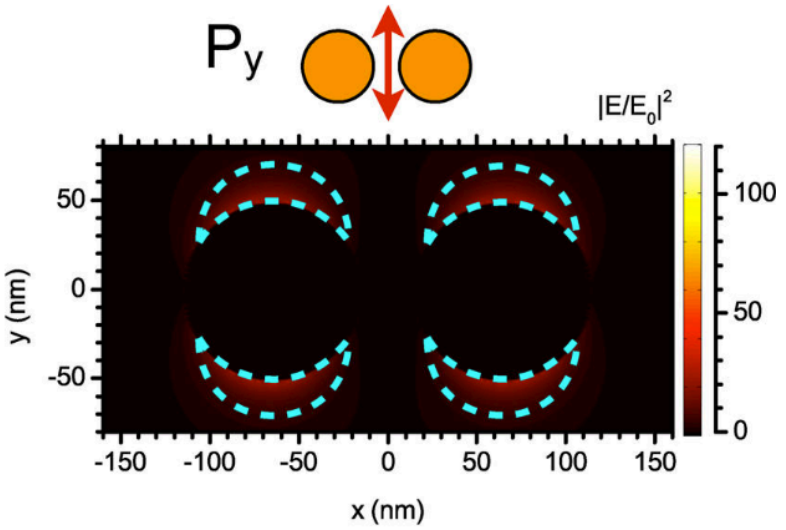
4. Plasmon enhanced Raman scattering

Raman spectra on plasmonic structure





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4. Plasmon enhanced Raman scattering

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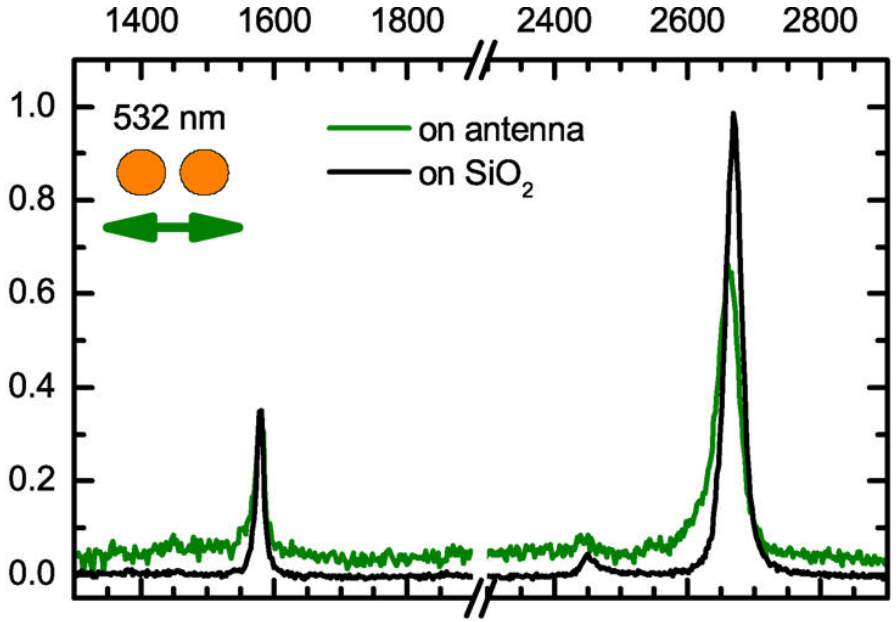
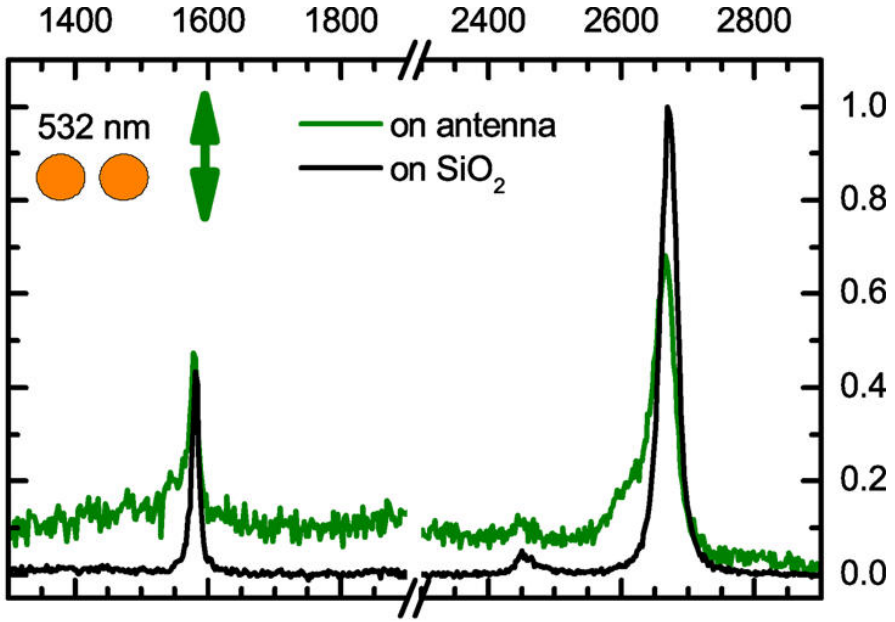


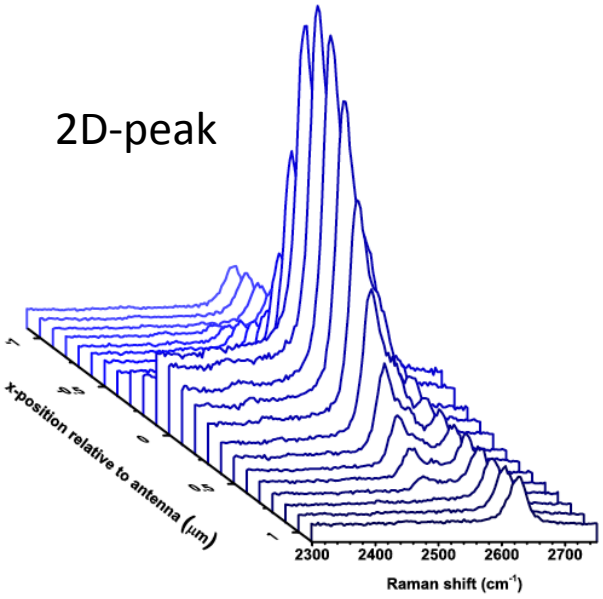


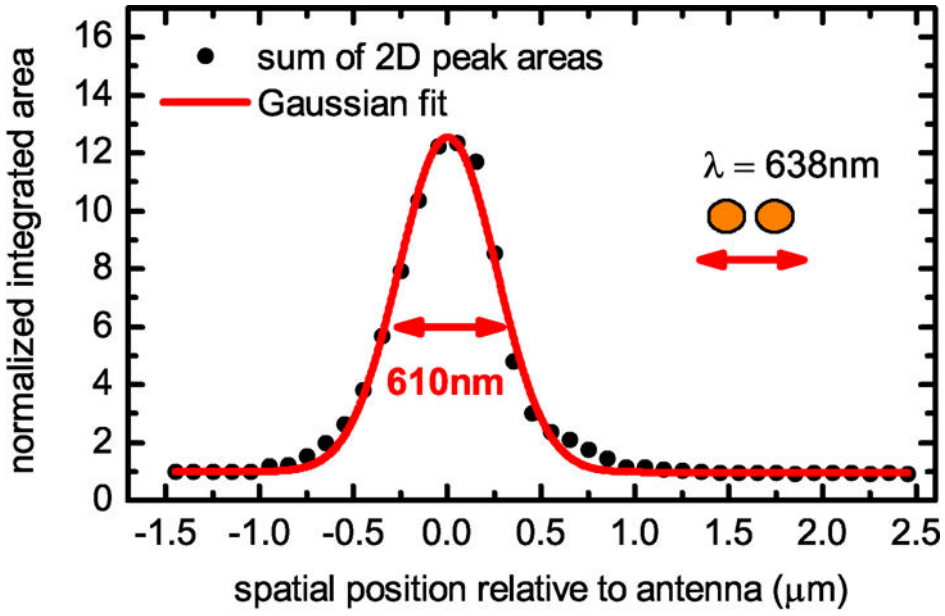
Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

4. Plasmon enhanced Raman scattering

Quantifying the enhancement

- Superposition of Raman spectra on and around plasmonic nanostructre
- Field localized in very small area compared to laser spot
- Actual enhancement significantly higher than 12.8 for P_x



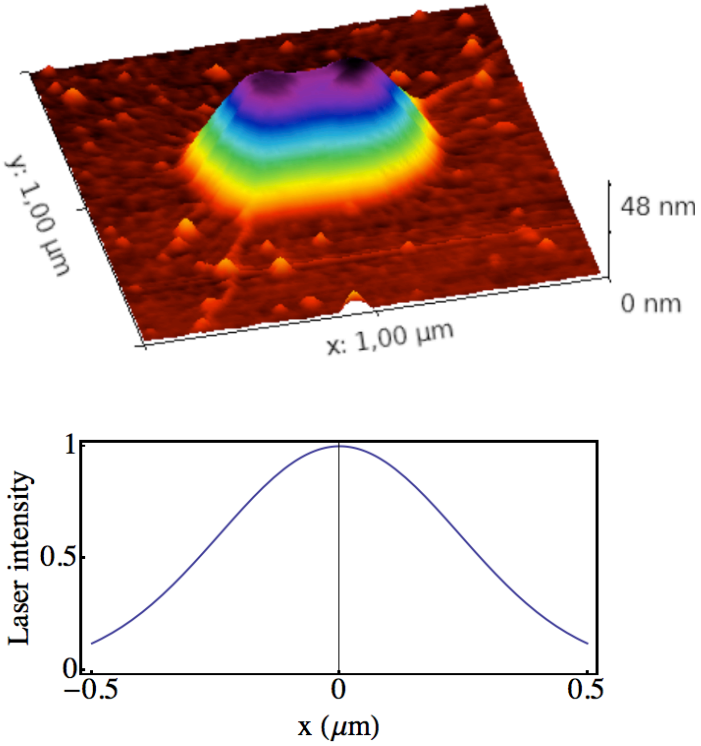


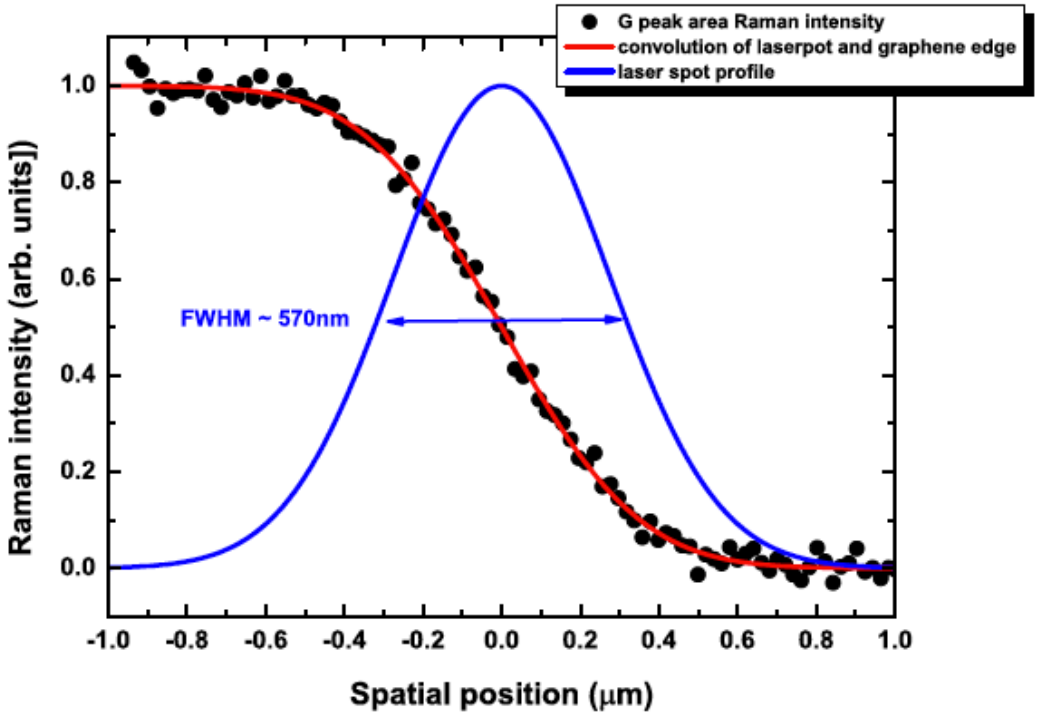
Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

4. Plasmon enhanced Raman scattering

Quantifying the enhancement

- Deconvolution technique to determine size of laser spot → FWHM = 570nm





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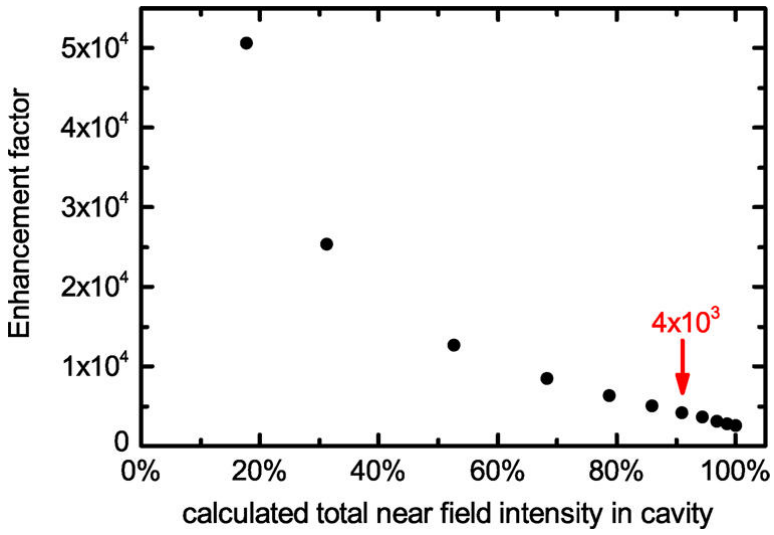
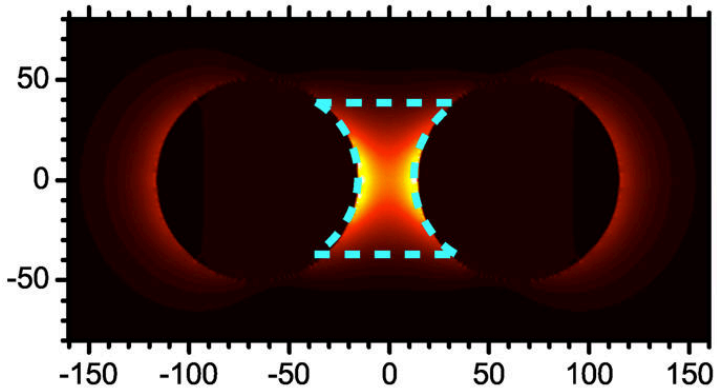
4. Plasmon enhanced Raman scattering

Quantifying the enhancement



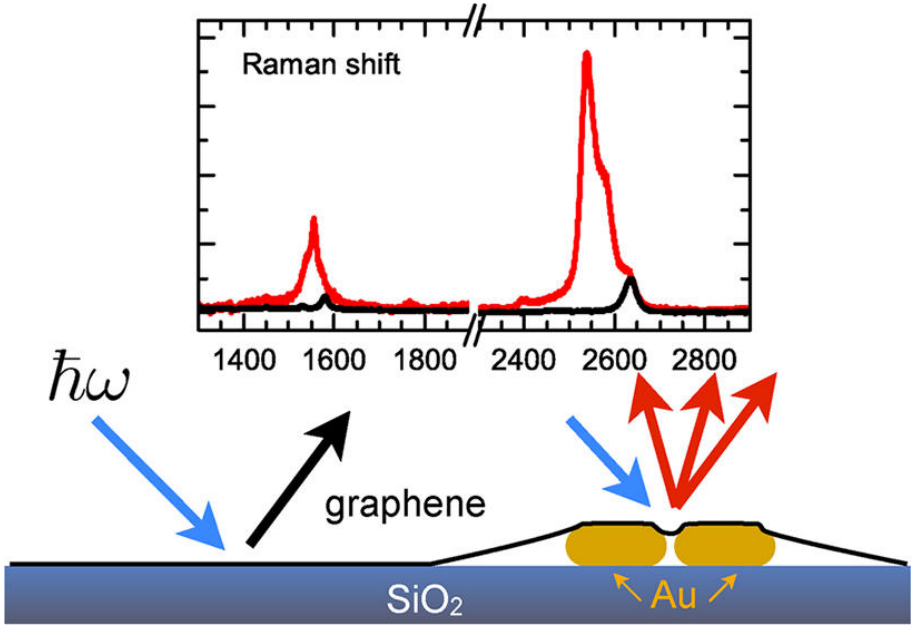


- Determine area of plasmonic enhancement from FDTD simulation
- For 90% of integrated near-field intensity → Enhancement of 4000
- Enhancement of 220 for P_y polarization (no cavity effect)
- Enhancement slightly smaller because of interference effect with SiO_2 layer

Pictures adapted from: S. Heeg et al., Nano Letters 13, 2013

5. Conclusion

- Enhancement of graphene Raman spectrum on Au dimer cavity
- Localize position of enhancement through effect of strain on Raman spectrum
- Enhanced absorption, but no enhanced emission



Pictures from: S. Heeg et al., Nano Letters 13, 2013