



The Abdus Salam
International Centre for Theoretical Physics



SMR: 1643/12

*WINTER COLLEGE ON OPTICS ON OPTICS AND PHOTONICS
IN NANOSCIENCE AND NANOTECHNOLOGY*

(7 - 18 February 2005)

"Surface-Enhanced Raman Scattering"-II

presented by:

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University of California
Santa Barbara
U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.



Lecture 2: Engineered Nanostructures for Giant Optical Fields

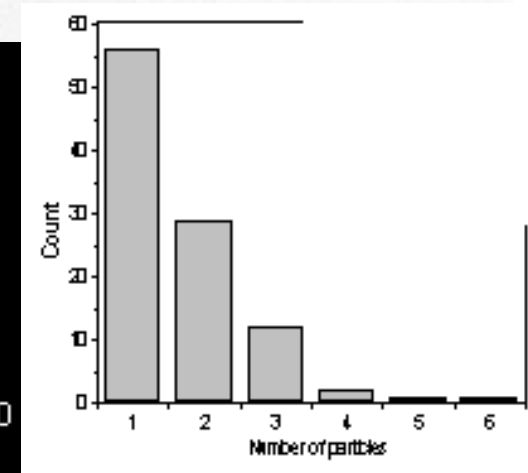
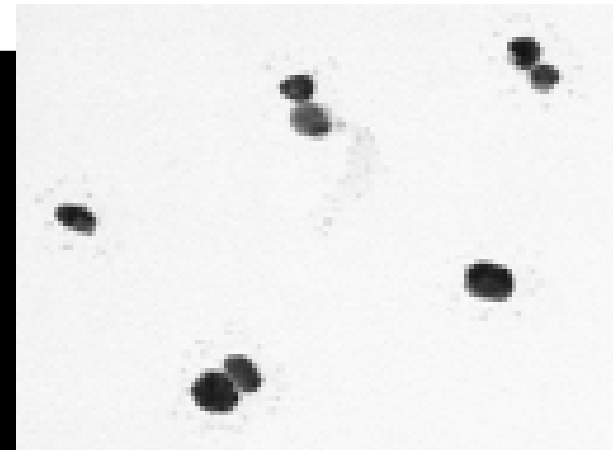
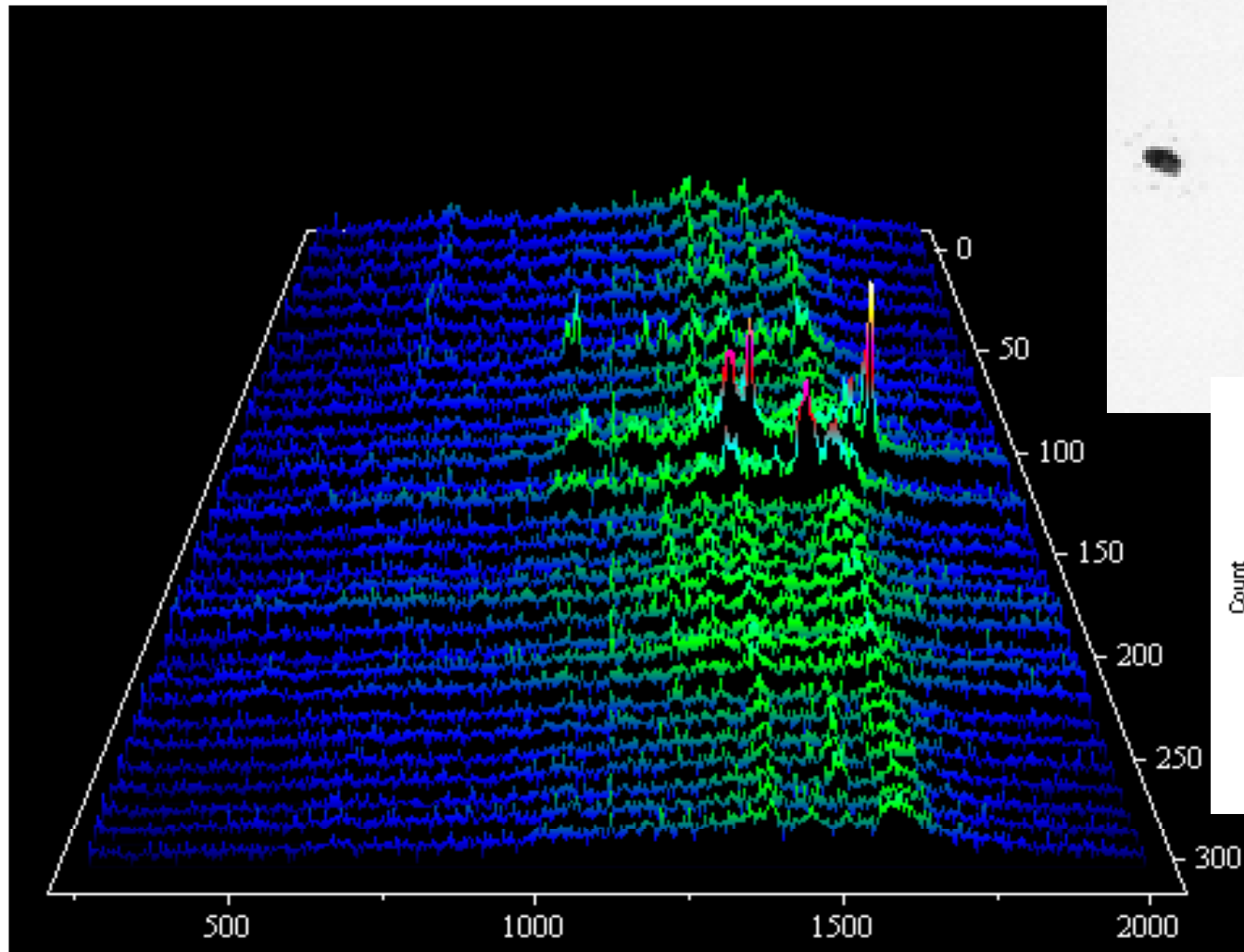
Martin Moskovits, Dr. Ioana Pavel

Dae Hong Jeong, Tsachi Livneh, Andrew Morrill, Professor Kevin Plaxco, Dr. Blanka Vlčkova*

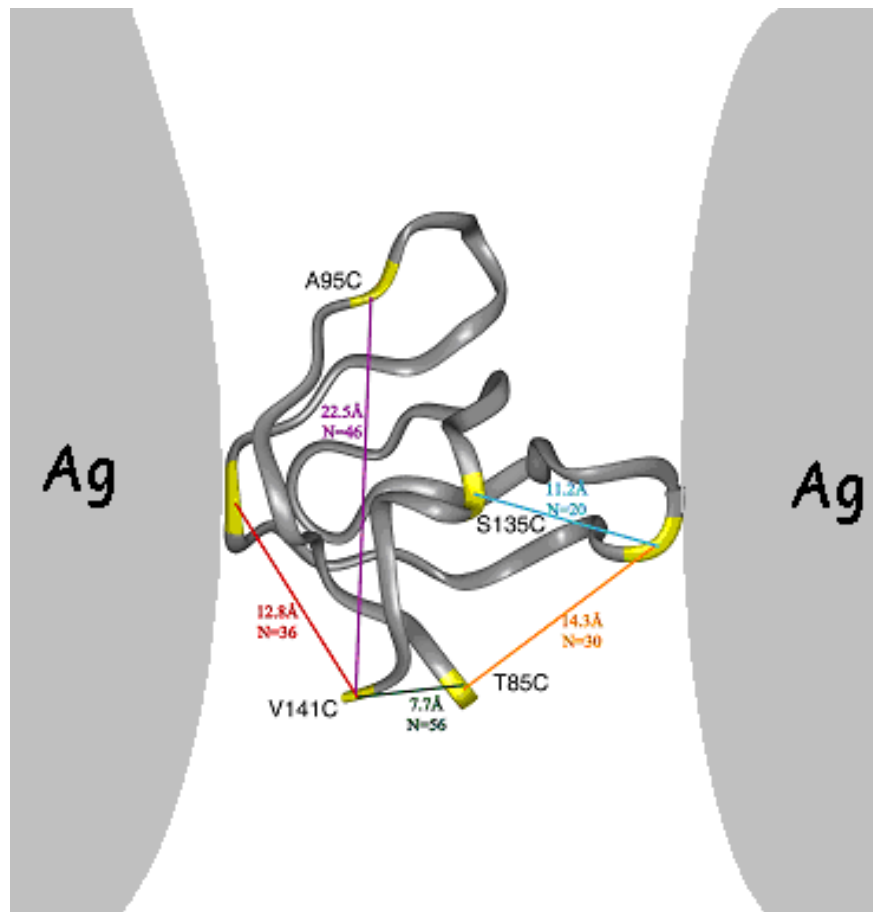
Department of Chem/Biochem, CNSI and the Canadian Institute for Advanced Research Nanoelectronics Program

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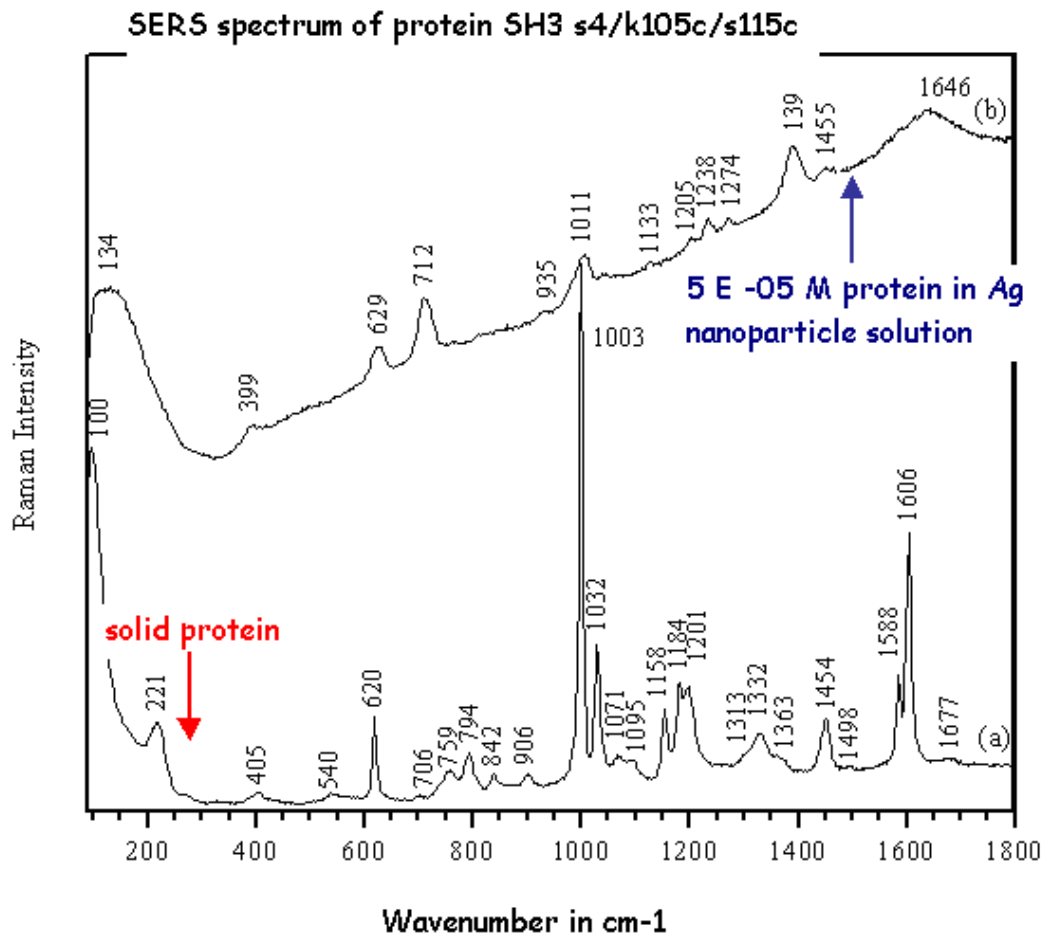
ICTP Winter
Workshop



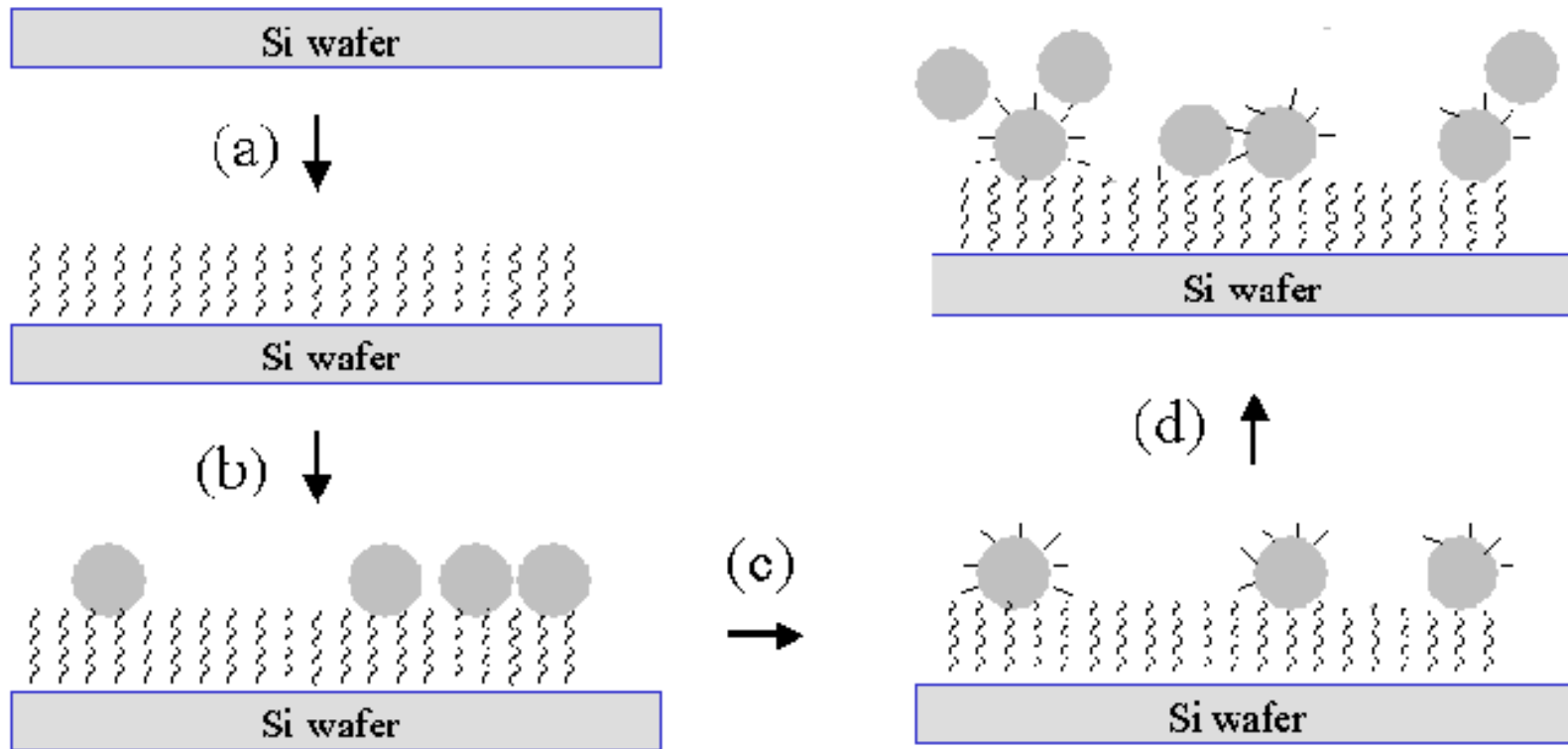
Time evolution of the SERS signal from a 4,4'-diaminoazobenzene-bridged dimer or small aggregate



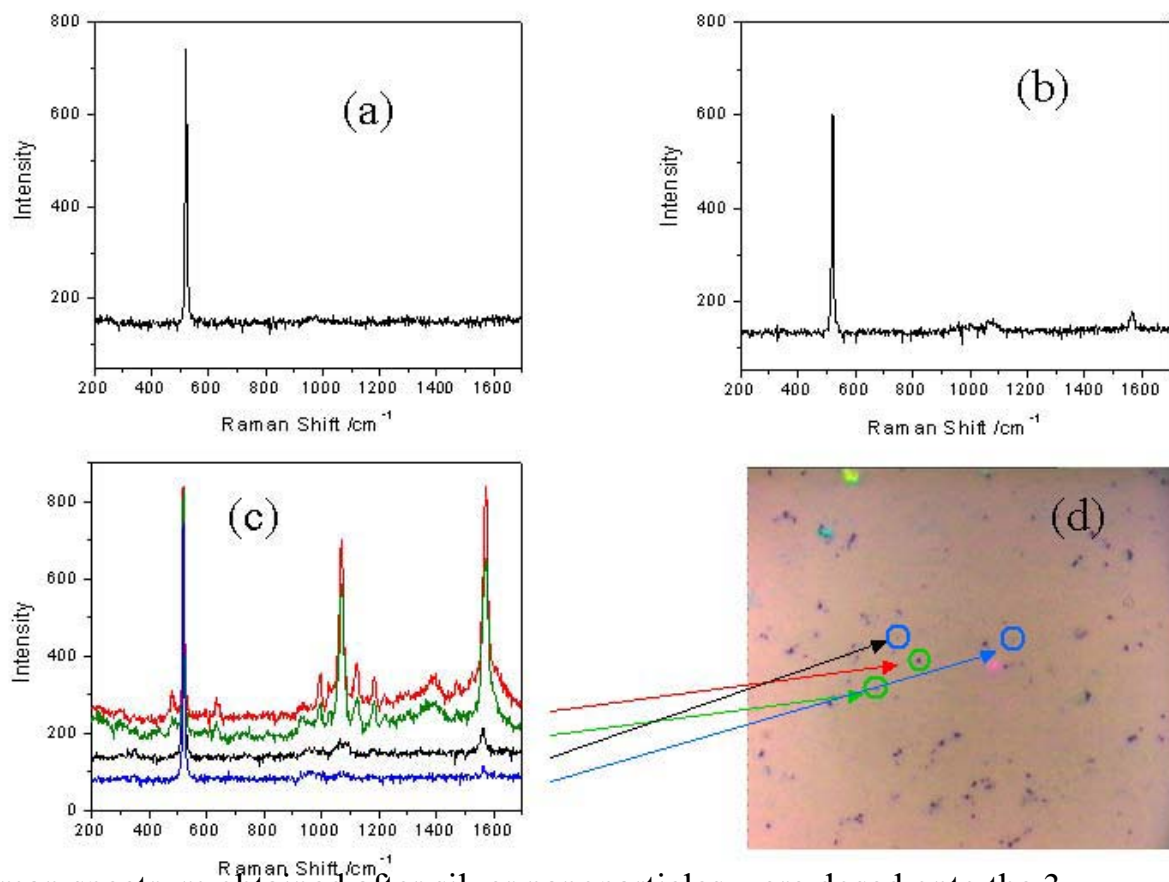
Using well-established site-specific mutagenesis techniques one is able to place, for example, cysteine in a protein converting it to a silver-nanoparticle linker through the thiol groups. For example the fynSH3 domain of the protein SH3 s4/k105c/s115c (left) can bind a target potentially diagnostic of HIV. The protein is found to efficiently link silver nanoparticles.



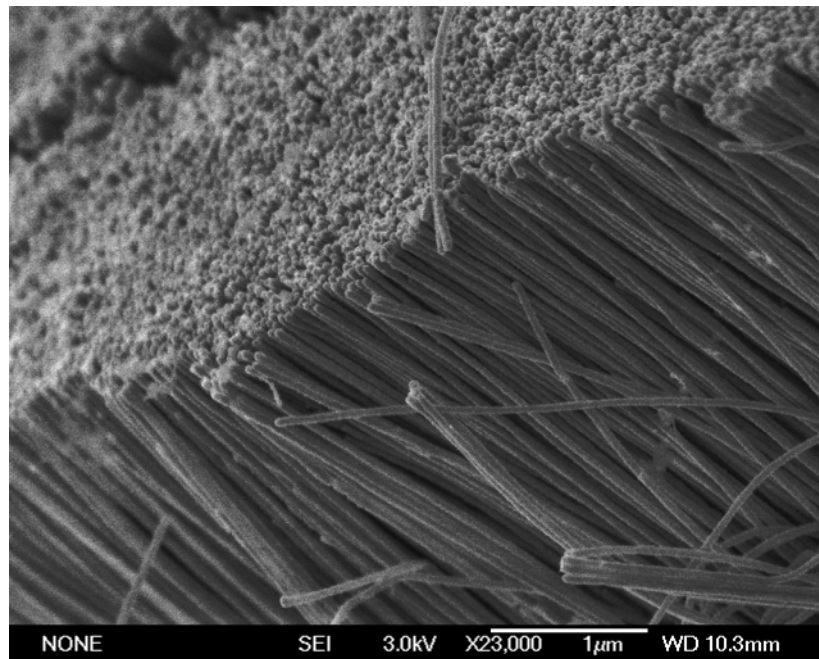
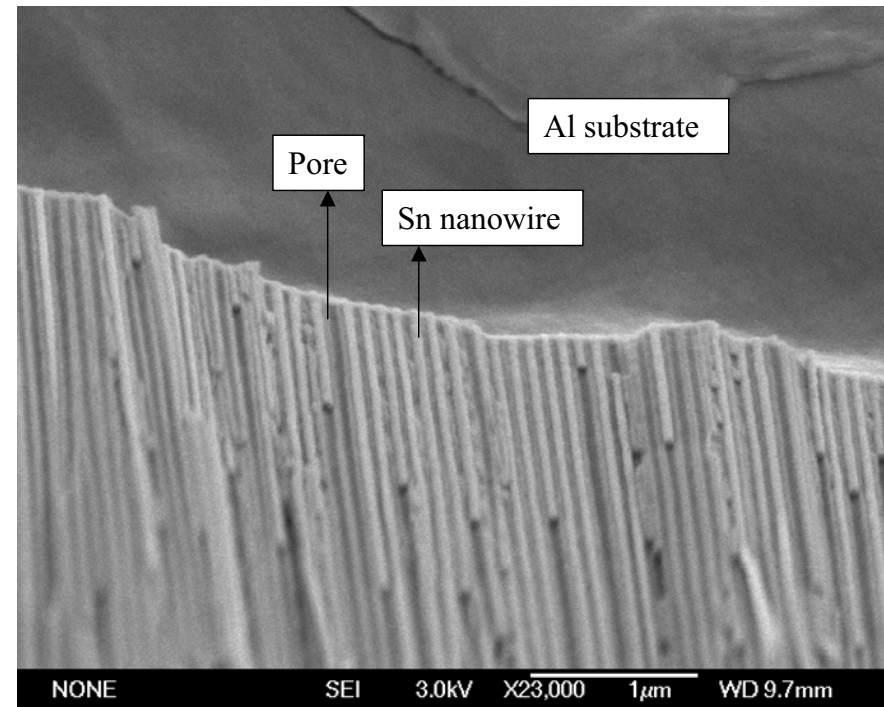
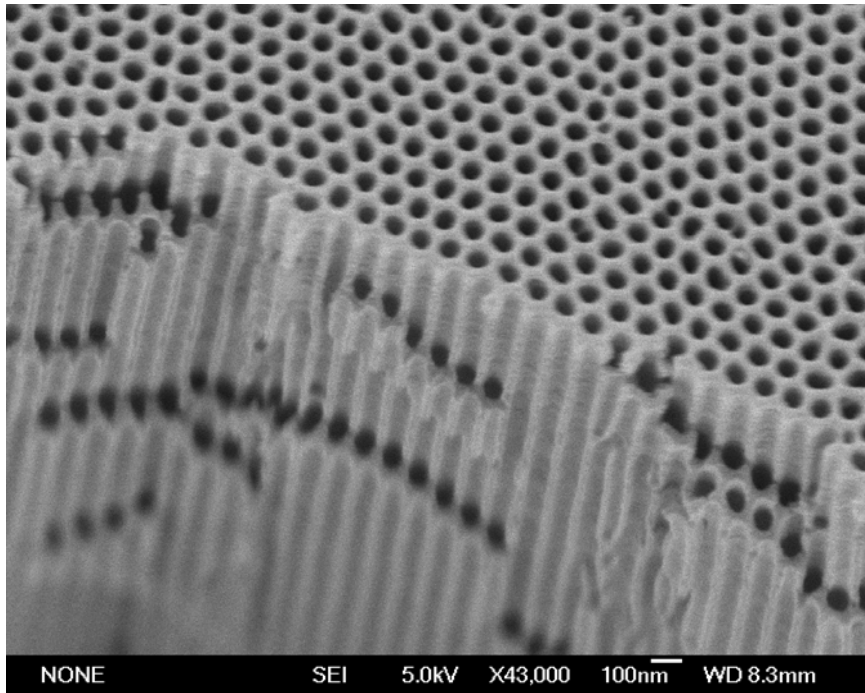
The Raman spectrum of 5-10 molecules of protein **SH3 s4/k105c/s115c** linking silver particles illustrating the ability to detect this protein down to near single-molecule levels.



The fabrication of linked silver nanospheres (a) A silicon-oxide-covered silicon wafer is derivatized with 3-aminopropyltrimethoxysilane. The silyl group links to the oxide leaving the amino group as a weak ligand for silver. (b) Silver nanoparticles (~20 nm di) produced by reducing silver nitrate with sodium borohydride is sparingly dosed on the derivatized surface. (c) The dithiol linker, 1,4-benzenedithiol, is allowed to bind to the silver nanoparticles. (d) The surface is once again exposed to a dilute silver nanoparticle solution. Some of the nanoparticles will occupy positions on the derivatized Si surface. Many, however, will bind to the dithiolated silver nanoparticles forming linked nanoparticle dimers and clusters.



(a) Raman spectrum obtained after silver nanoparticles were dosed onto the 3-aminopropyltrimethoxysilane-derivatized silicon oxide surface (i.e. after step b in Fig. 1.). Only a single Si peak is visible in the spectrum. Specifically no trace of the aminosilane surface derivative is visible. (b) Raman spectrum obtained after the 1,4-benzenedithiol linker is dosed on the surface. Most locations on the surface showed no trace of Raman belonging to the dithiol. Occasionally a weak peak belonging to the dithiol is observed (as shown). (c) After dosing the surface with a second layer of silver nanoparticles many spots on the surface show strong SERS signals belonging to the dithiol. (d) An optical microscope image of the sample from which the SERS spectra shown in c were obtained showing that the surface was only sparingly covered with silver nanoparticles. Hence, most of the hot particles consist of very small silver nanoparticle clusters.



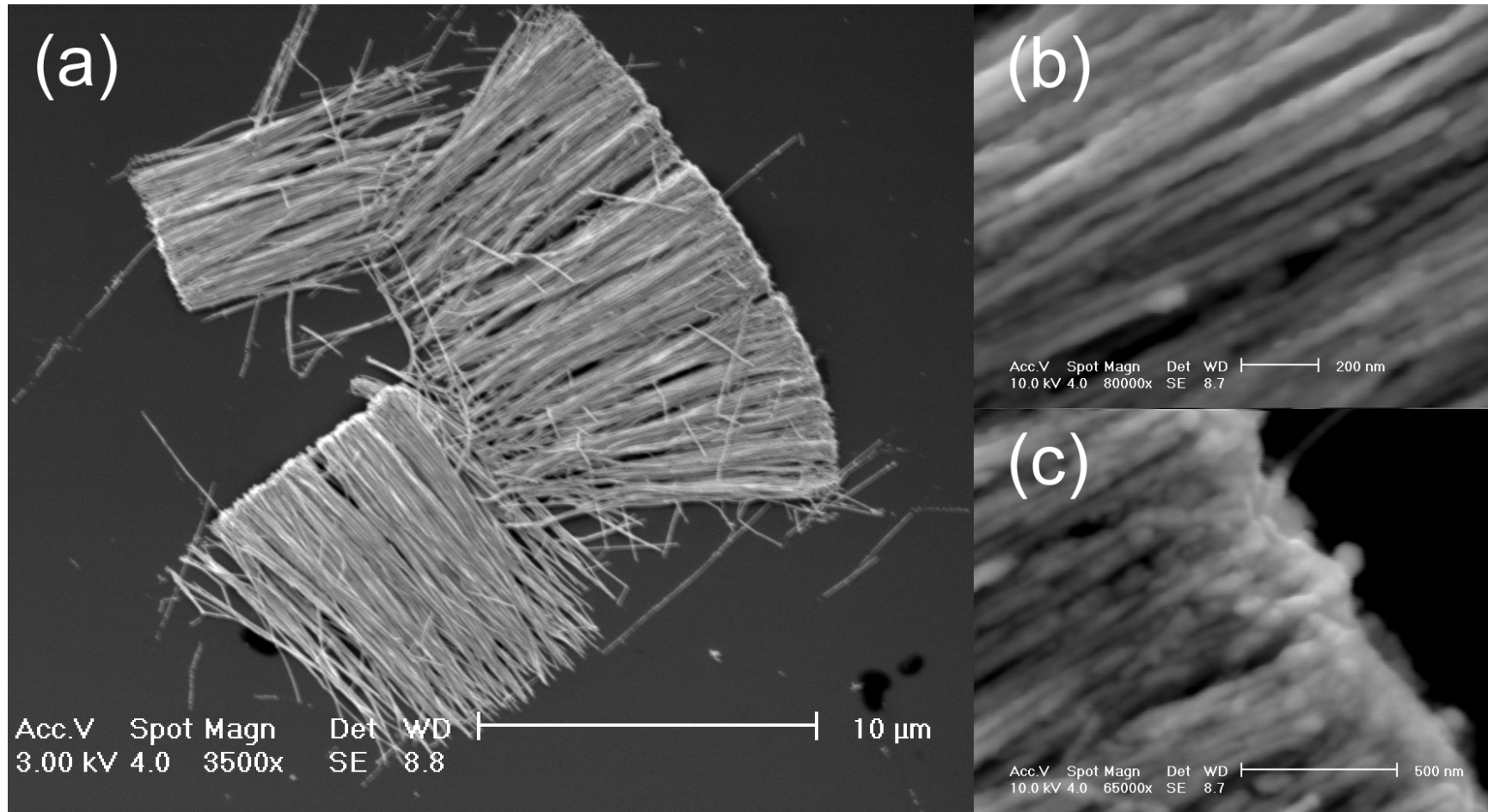


Figure 1. (a) Arrays of silver nanowires with parallel alignment. Closer views in the middle (b) and roots (c) of nanowires.

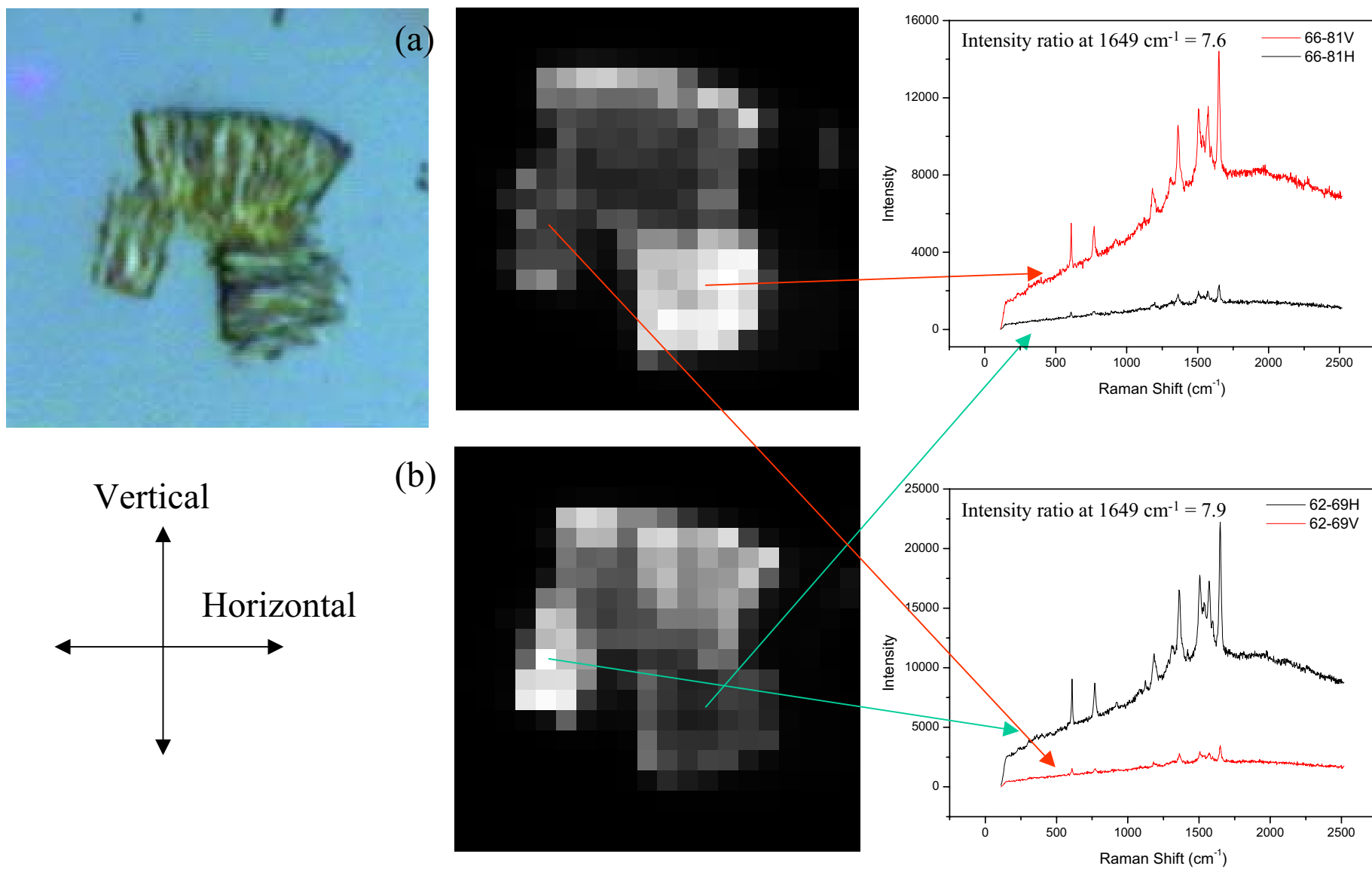
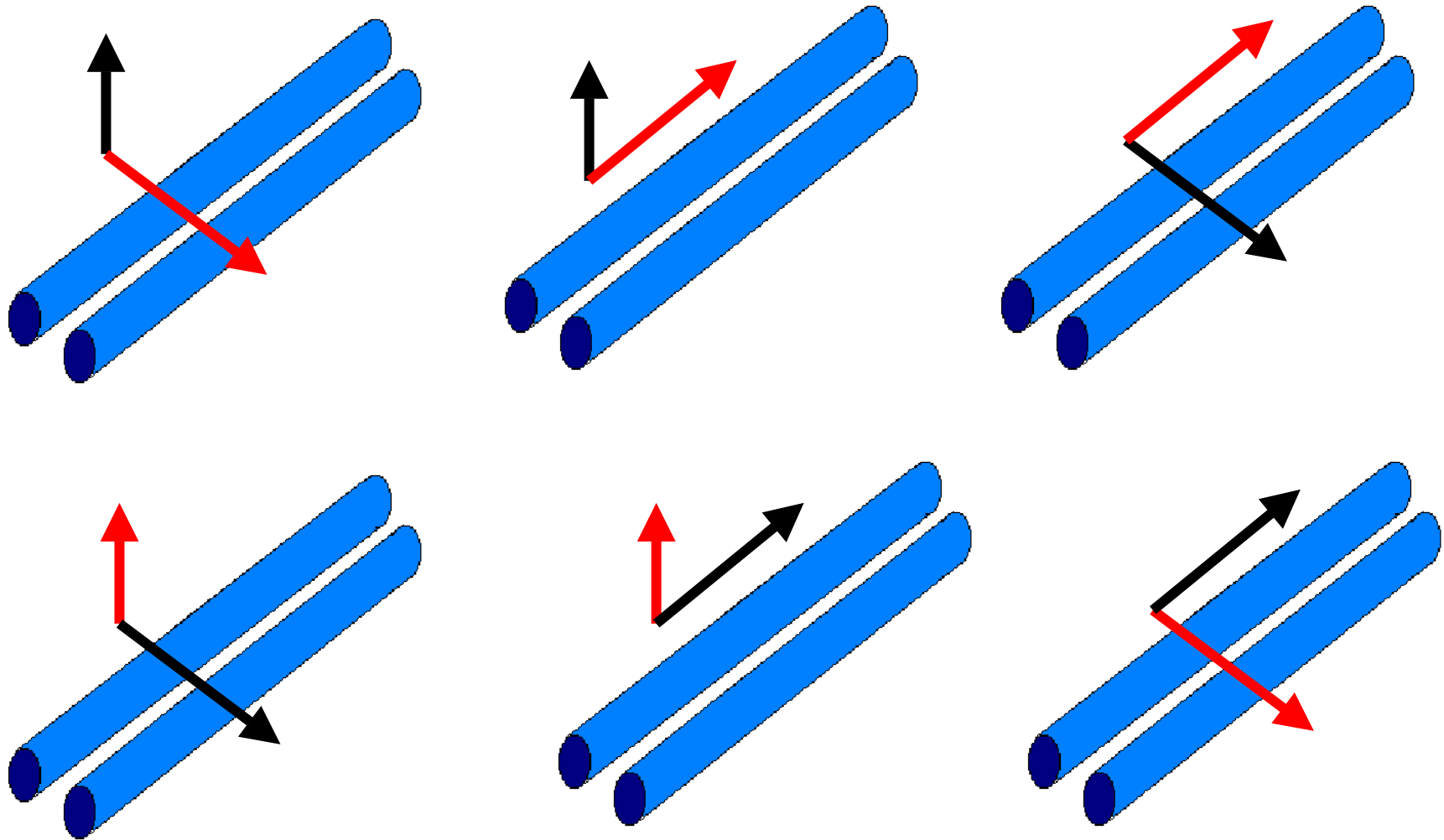


Figure 2. Maps of SERS intensity with incident light normal to the surface and vertical (a) and horizontal (b) polarizations.



The six canonical light propagation and polarization directions possible with a pair of nanowires

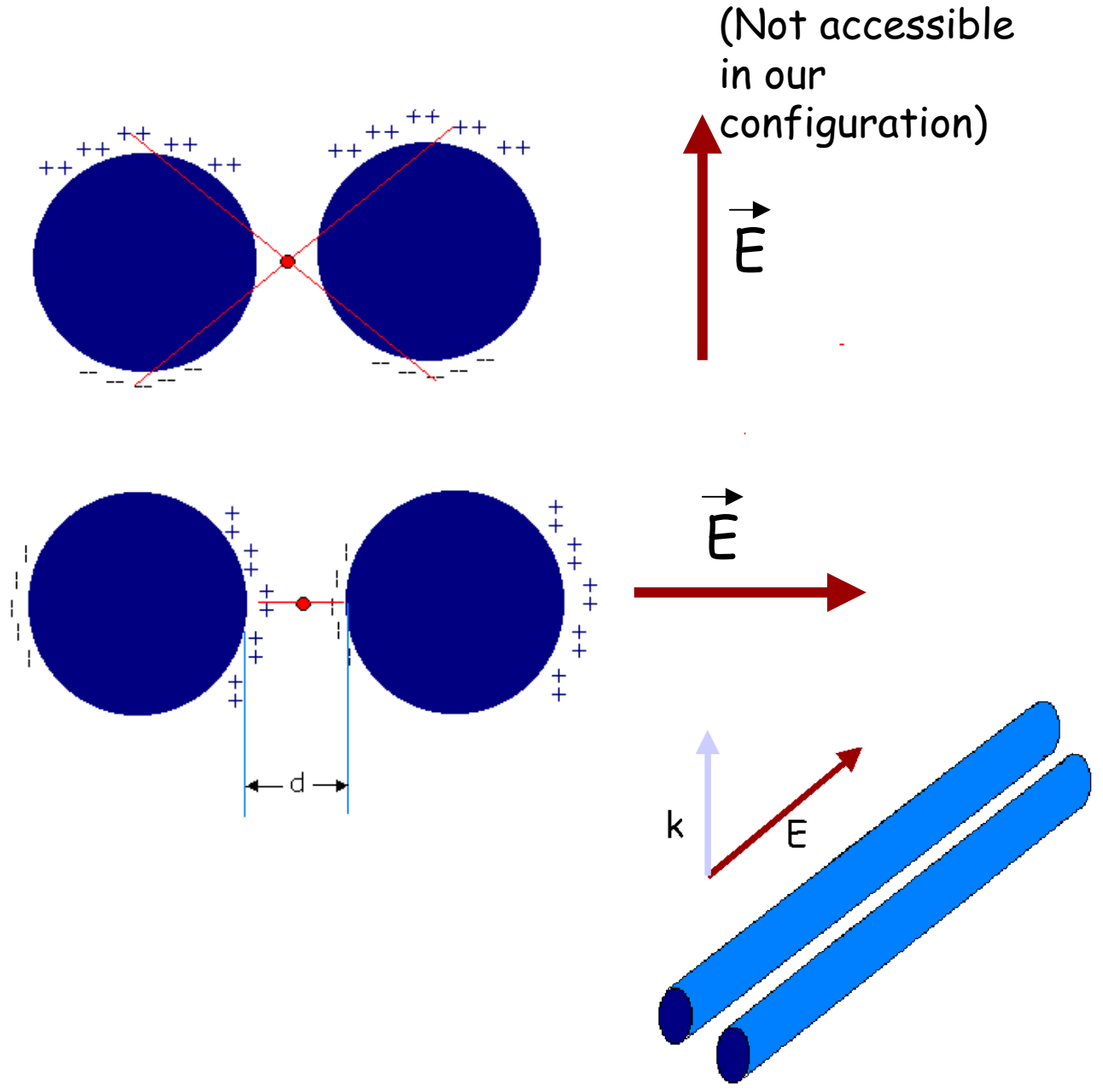


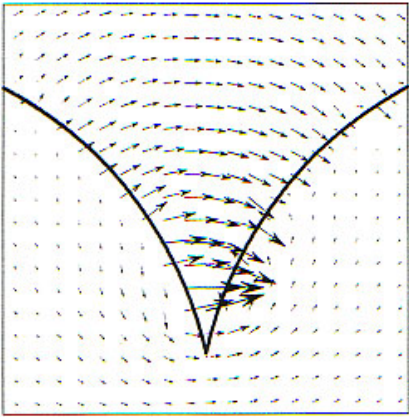
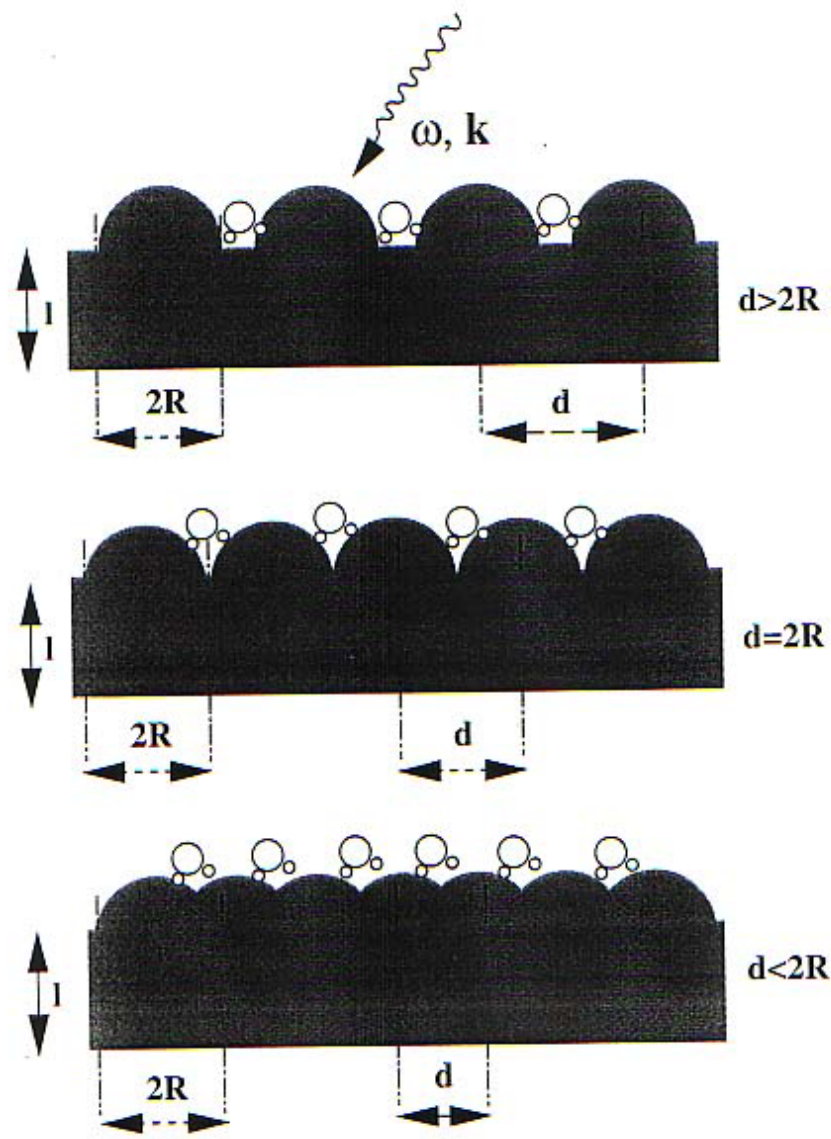
k-vector



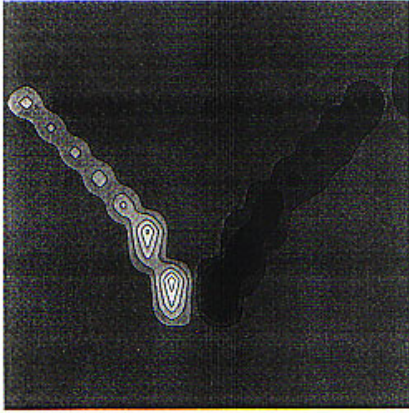
E-vector

Simple graphical illustration of the reason that light polarized with the E-vector along the inter-particle axis can result in huge enhancements at the point indicated with the red dot, while the orthogonal polarization cannot.

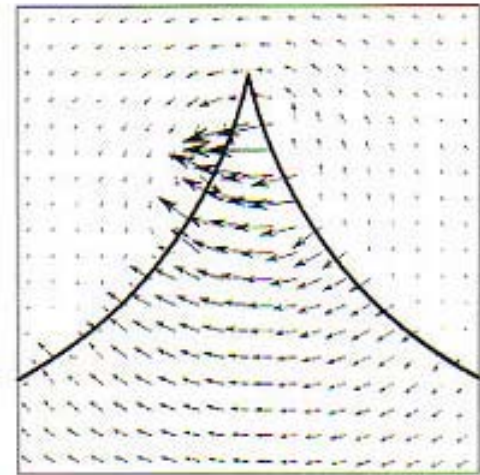
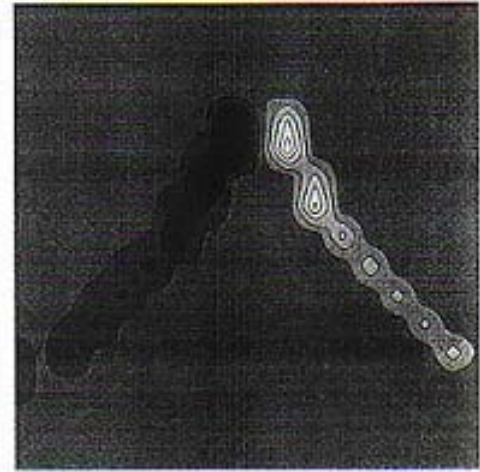
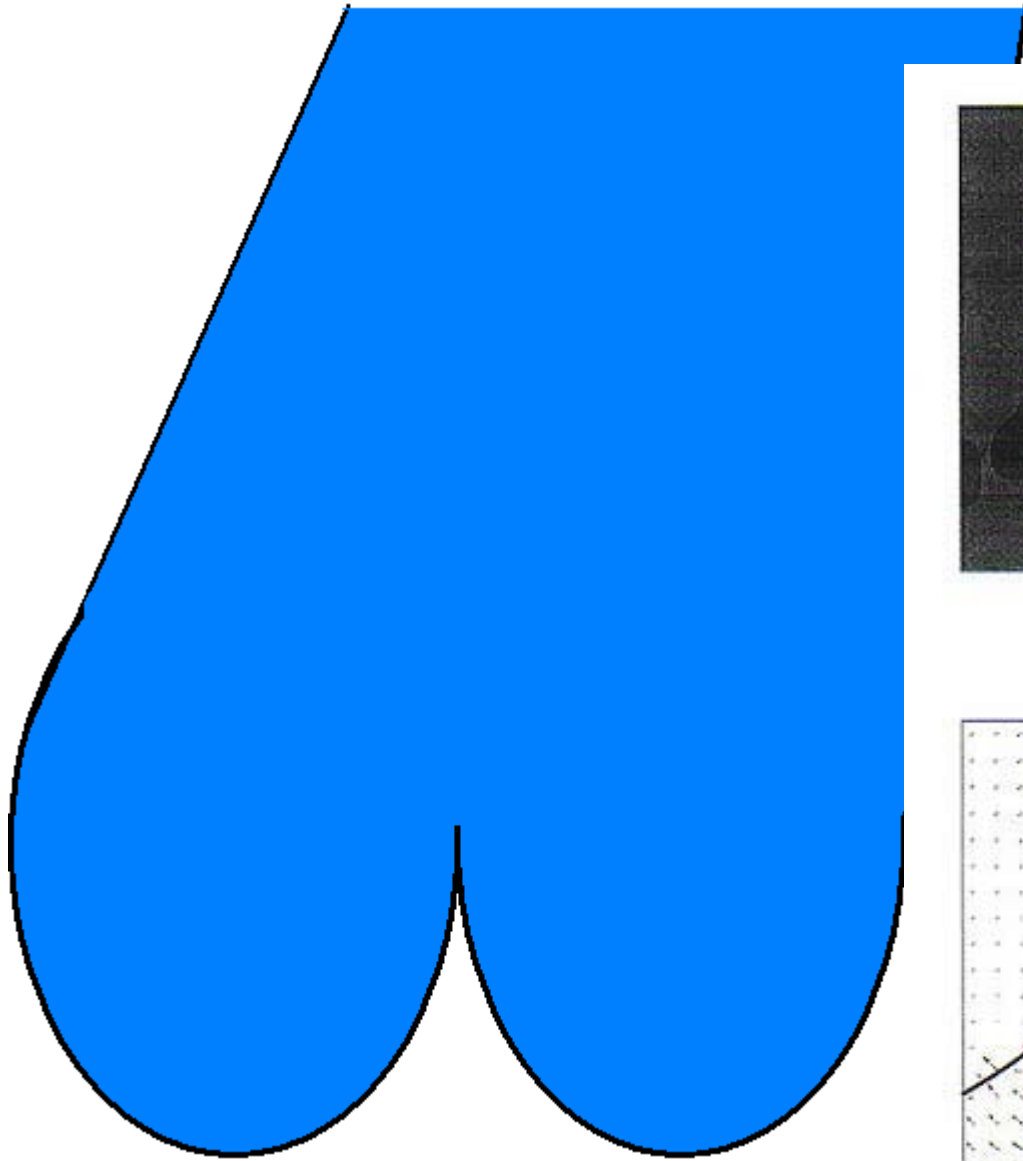




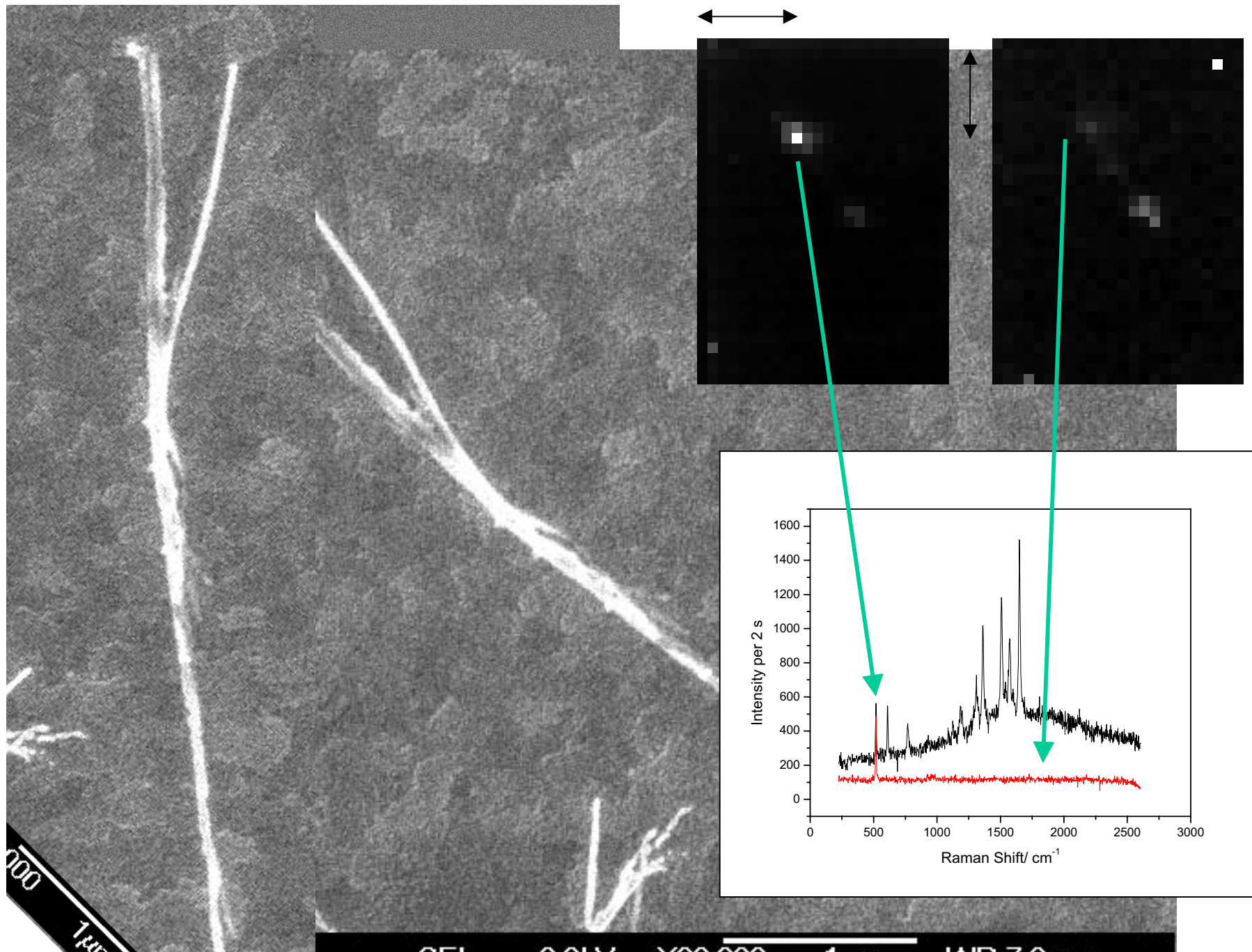
Calculated field in a cleft of a periodic metal grating



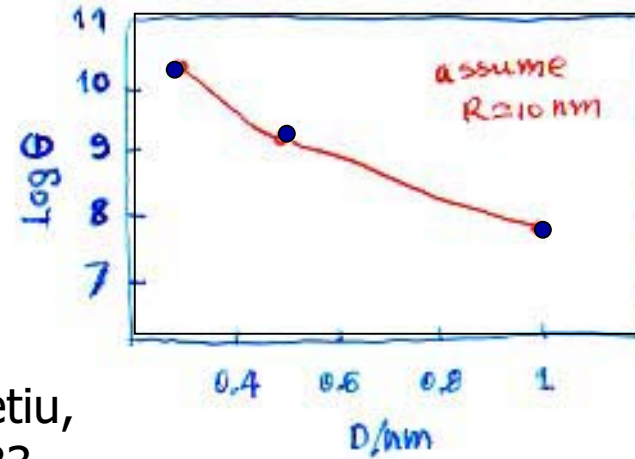
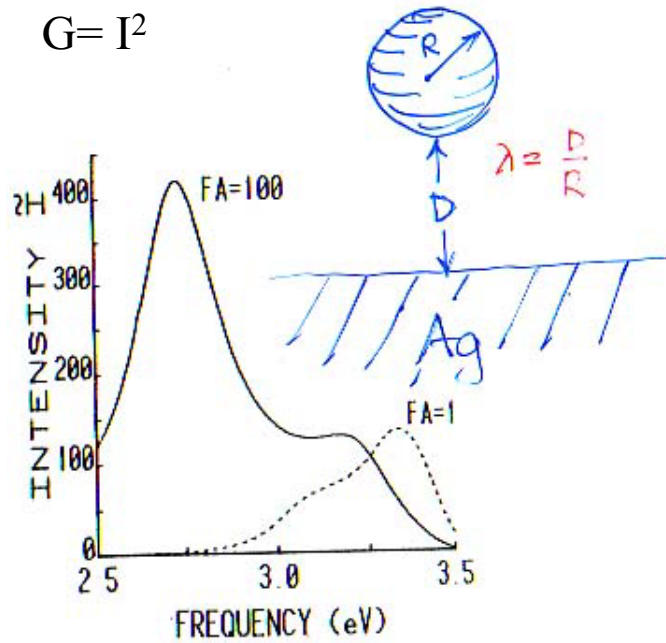
Garcia-Vidal and Pendry, PRL



Garcia-Vidal and Pendry, PRL

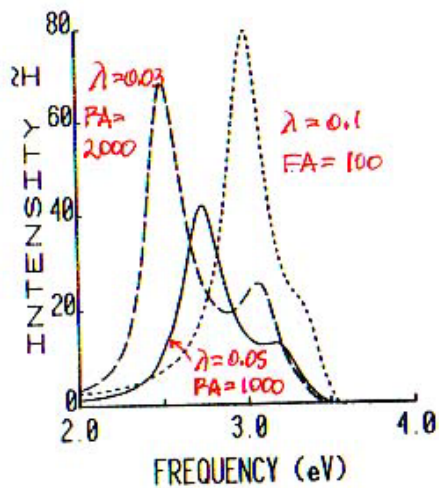


$$G = I^2$$

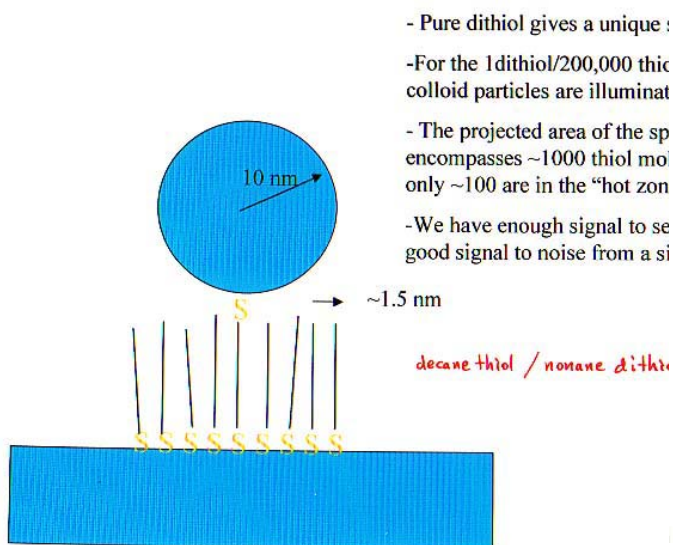


Aravind & Metiu,
Surf. Sci. 1983

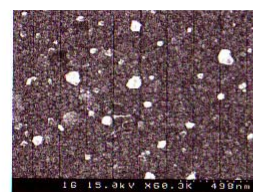
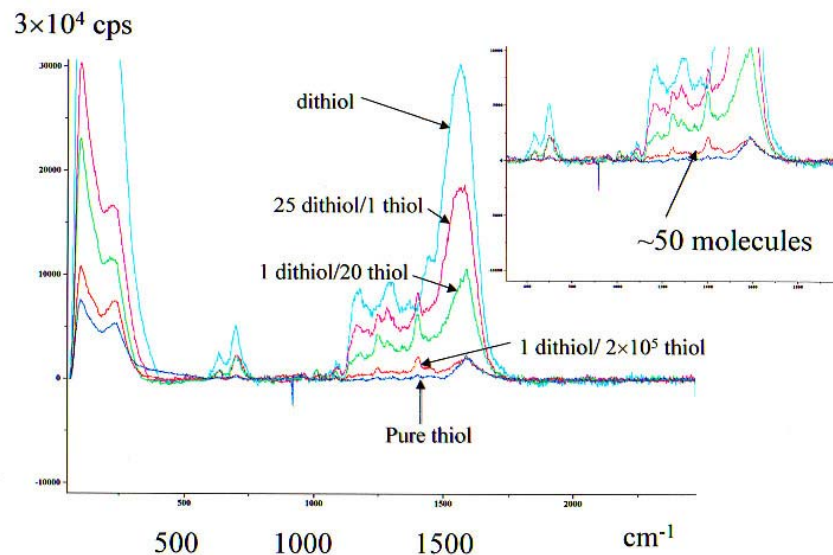
A small metal sphere in close proximity to a highly conductive metal surface is similar to a two-sphere model because of the image-charge effect. The spot immediately underneath the sphere is also capable of producing SERS enhancements $\sim 10^{11}$.



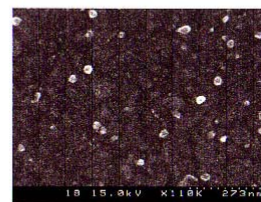
Darren Anderson



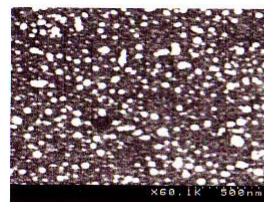
This prediction is verified by experiment. Mixtures of thiol and dithiol molecules are used to produce progressively lower surface coverages of anchored silver nanoparticles.



1/2000

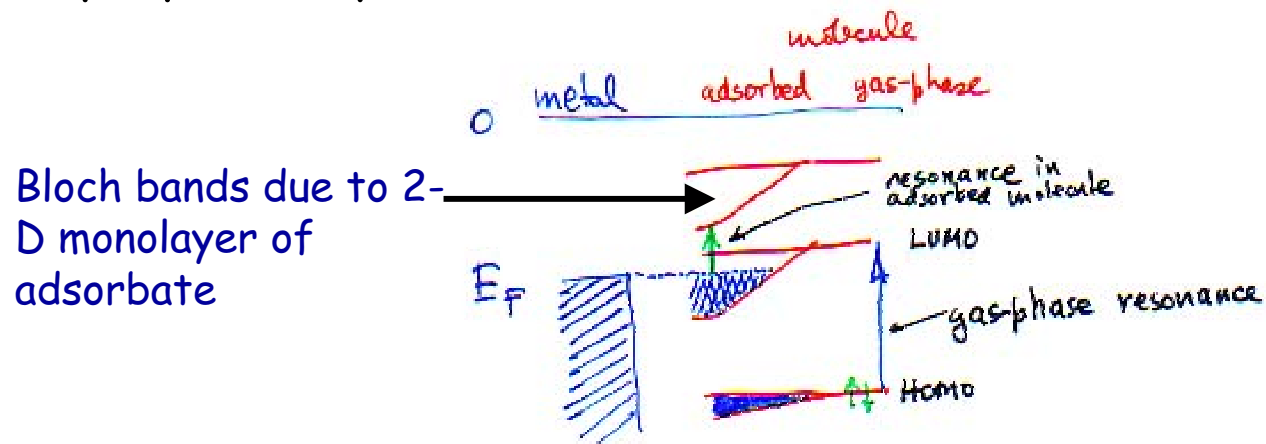


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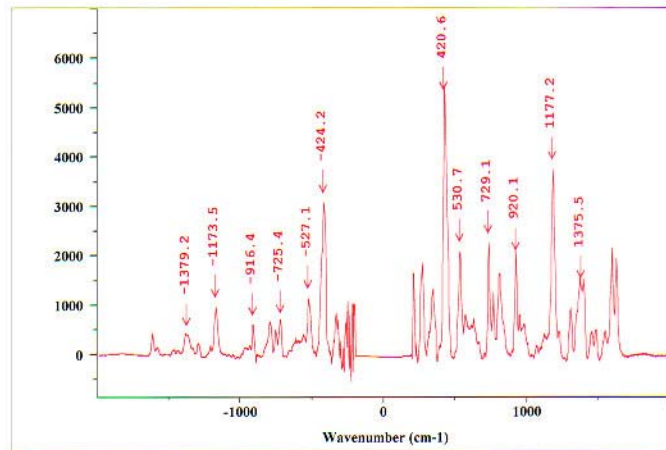
Pure dithiol

Although the em effect accounts for the major portion of the SERS story it is not the whole story. E.g. molecules adsorbed directly on the metal show ~ 10 -fold increase in SERS. Also the SERS enhancement observed by Nie, Kneipp, Käll and Brus in single-molecule SERS is $\sim 10^{14}$ while em calculations top out at $\sim 10^{12}$. The additional enhancement is probably due to resonances, which could result from new channels that open upon adsorption. Such effects, called chemical enhancement by A. Otto, were also proposed by Persson and by Burstein.

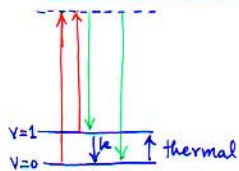


But the proposal (Kneipp 1998) that the very large (10^{14}) enhancement observed in single-molecule SERS also implies Raman-pumped excited vibrational states leading to intense antistokes is still wrong. The observation is due to slightly differing levels of enhancement resulting from resonance when some but not all molecules are adsorbed on silver.

Crystal Violet on Au Colloid
782 nm laser / 1 mW / 10 s



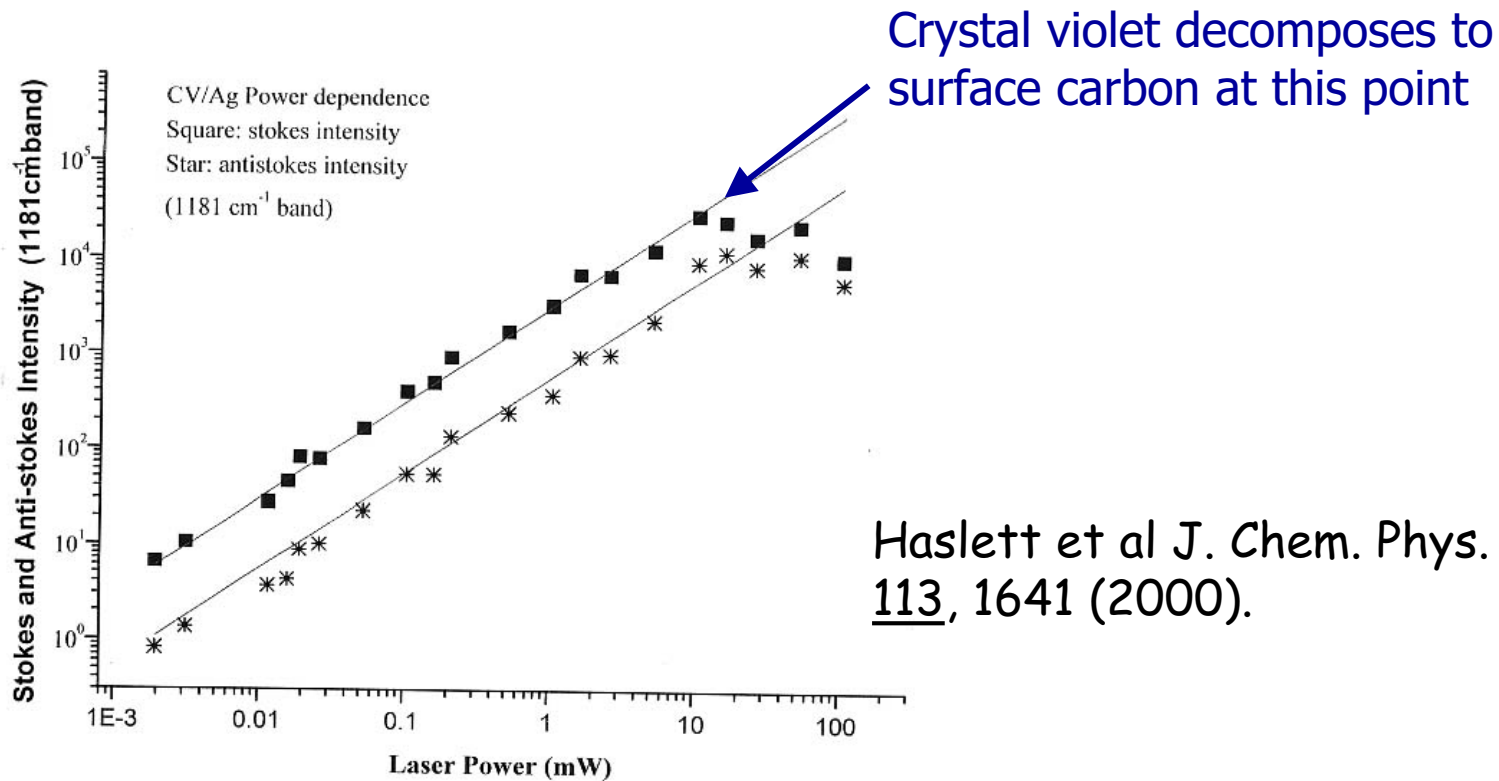
Often people forget that SERS is scattering by the metal and NOT by the molecule. Thus, while SERS benefits from the enhancement of both the incident and the Raman-scattered field, Raman pumping occurs only due to the enhanced *incident* field. Hence, when the SERS enhancement 10^{14} the incident field intensity is enhanced only by 10^7 which is insufficient enhancement to account for intense antistokes Raman



$$\frac{I_{\text{antistokes}}}{I_{\text{stokes}}} \cong e^{-\frac{4E}{k_B T}} + \sigma I_L \tau_{\text{vib}}$$

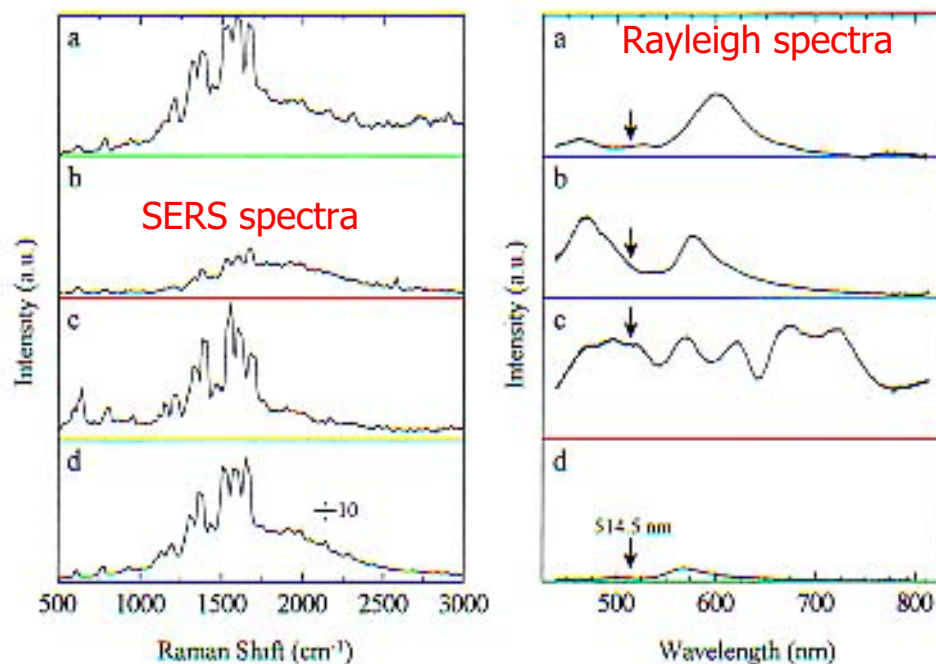
$\tau_{\text{vib}} = k^{-1}$

simple calculation proposed by Kneipp et al
imply $\sim 10^{14}$ increase in Raman cross-section or 10^{14} increase in the value of the local field intensity i.e. local powers
 $\sim 10^{20}$ watts cm^{-2} .



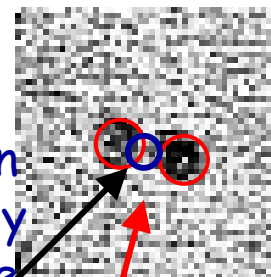
Indeed, strictly linear (as opposed to quadratic) power dependence is observed for both the Stokes and anti Stokes components over many order of power until decomposition takes place. And while intense anti-stokes emissions are observed with a few dye molecules, no intense anti-stokes lines are observed with the vast majority of small molecules studied (which, nevertheless showed intense SERS activity).

The em theory was challenged on the basis of the fact that the enhanced Rayleigh and the SERS response of small clusters were uncorrelated (JACS **121**, 9932, 1999). However this was corrected almost immediately (JPC, 2000). However, this fact is still being quoted by some workers believing themselves on track to a fundamental theory of SERS

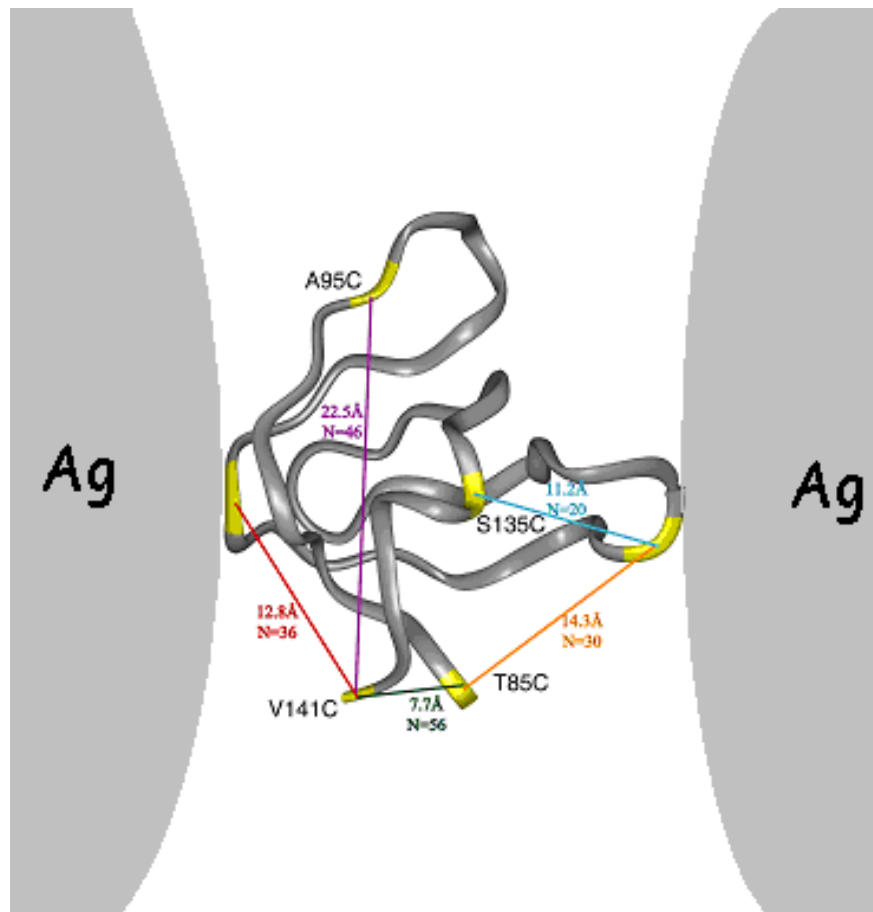


SERS excitation is determined by the em response of this region

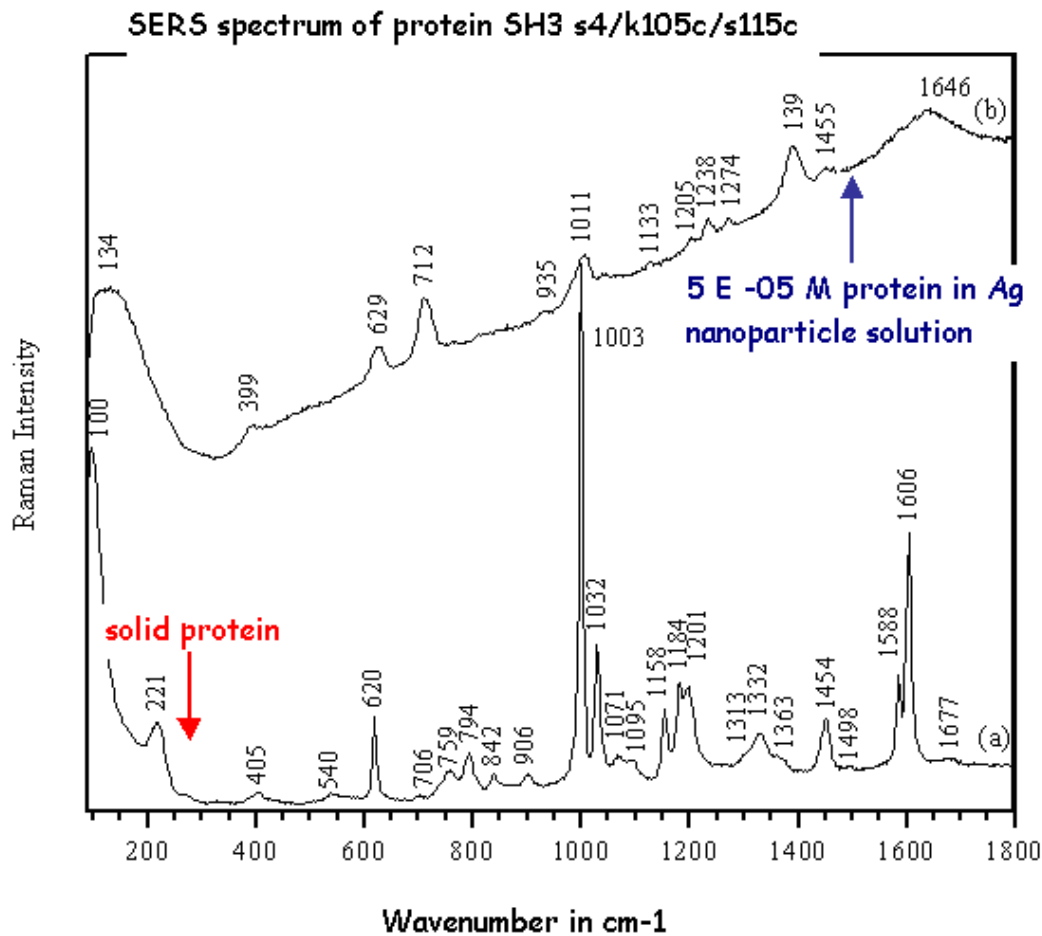
Rayleigh spectrum is governed by the em response of the entire particle cluster.



Michaels, Nirmal and Brus, JACS, 1999



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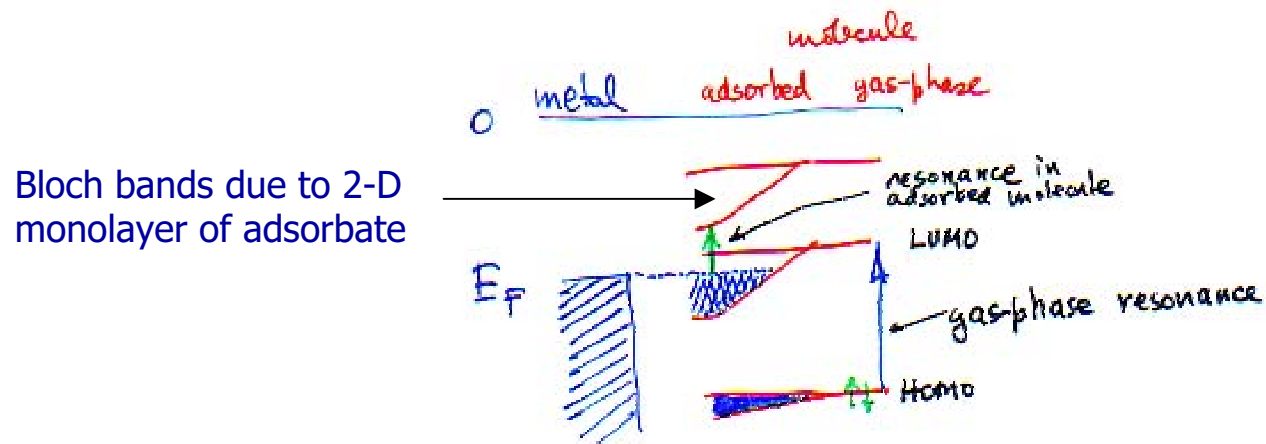


The Raman spectrum of 5-10 molecules of protein **SH3 s4/k105c/s115c** linking silver particles illustrating the ability to detect this protein down to near single-molecule levels.

Conclusions and perspective:

Combining simple concepts derived from the theory of SERS together with simple nanoparticle synthesis and assembly strategies, one can fabricate appropriate nanostructures that yield single - (or few -) molecule SERS sensitivity on demand; automatically binding target molecules at the sites where the electromagnetic enhancement is highest. Using a few rudimentary chemical principles one can create systems with the chemical flexibility and specificity required to analyze a broad range of biomolecules.

These high fields at "hot spots" in small colloid clusters or in fractal aggregates explains most of the SERS enhancement observed by Nie, Kneipp, Käll and Brus in single-molecule SERS. An enhancement $\sim 10^{14}$ is reported by them for most studies. This is $>$ the 10^{11} predicted by em calculations. The additional enhancement is probably due to some form of resonance, which could result from new channels that open upon adsorption. Such effects, called chemical enhancement by A. Otto, were also proposed by Persson and by Burstein.



Actually very large local enhancements were observed and reported by Pettinger and by Hildebrand and Stockberger in the 1980s.