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

(7 - 18 February 2005)

"Surface-Enhanced Raman Scattering"-III

presented by:

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Lecture 3: Loose ends and applications

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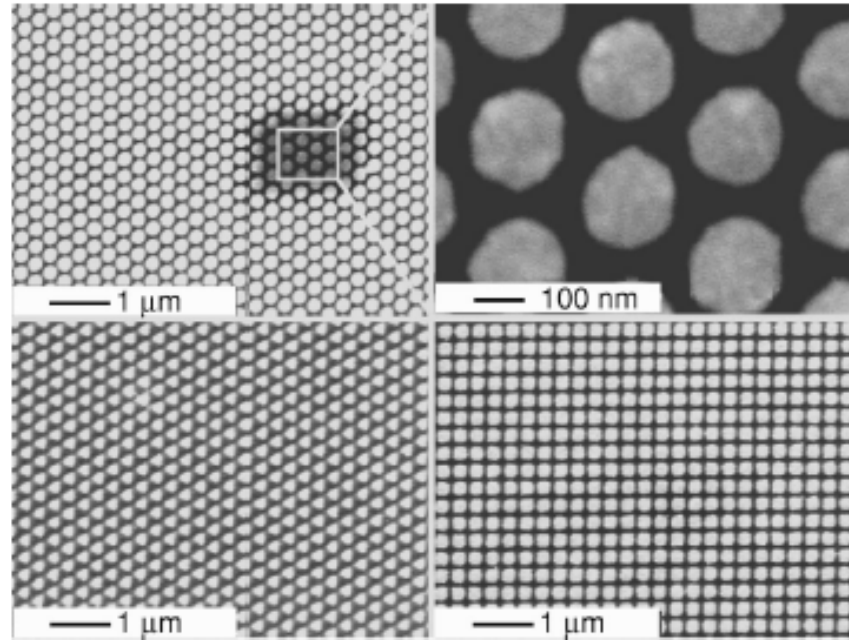
*Seoul National University

ICTP Winter Workshop

FIG. 1. Scanning electron micrographs of SERS substrates. Examples consists of circular (top left and right), triangular (bottom left), and square (bottom right) 30-nm-thin Ag particles on Si. The predefined particle length scale, defined as the diameter in the case of circular particles and the edge length in the case of triangles or squares, was $D=200$ nm and the predefined interparticle separation distance, defined as the minimum edge-to-edge distance, was $d=100$ nm.
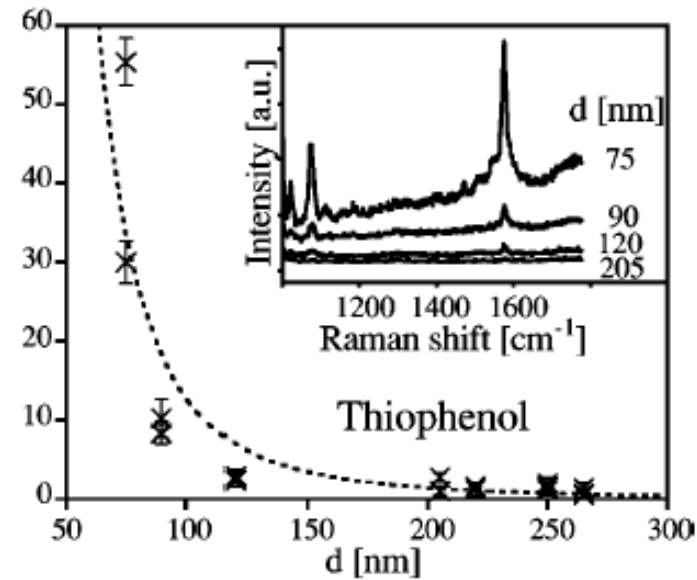
FIG. 3. Relative SERS-substrate efficiency vs d, quantified as $I^{SERS}(d)/I^{SERS}(d^{max})$, for two different adsorbates: R6G (circular particles, $D=200$ nm) and thiophenol (square particles, $D=200$ nm). Insets show examples of Raman spectra for different d values. Dashed lines are fits using the electrostatic model $I^{SERS} \propto (d+D)^{-2}[A(D/d+1)^4+B]$, where A and B are fitting constants.

L. Gunnarsson, E. J. Bjerneld, H. Xu, S. Petronis, B. Kasemo, and M. Kall, APL **78, *802*** 2001

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 ~10-100-fold additional increase in SERS enhancement. Also the SERS enhancement observed by Nie, Kneipp, Käll and Brus in single-molecule SERS is ~ 10^{14} while em calculations top out at ~ 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.

Bloch bands due to 2-D monolayer of adsorbate
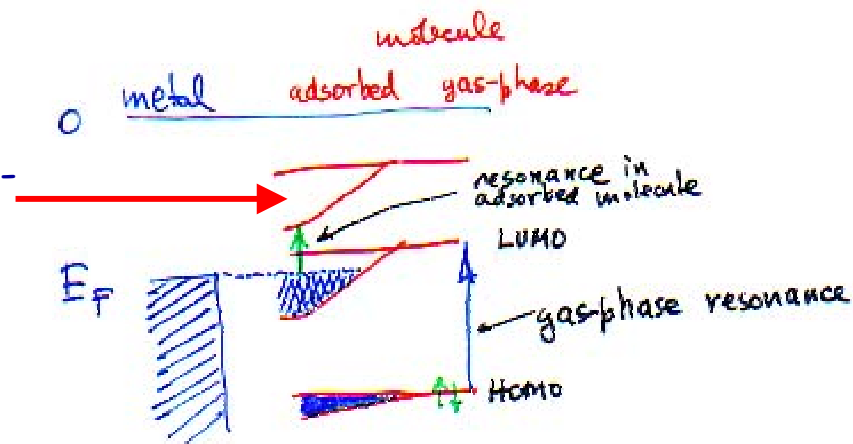
Also, there's the enhanced continuum: This is successfully accounted for in terms of intraband transitions of the conductance electrons in nanostructured metal. (A great deal of new interest in this background.)
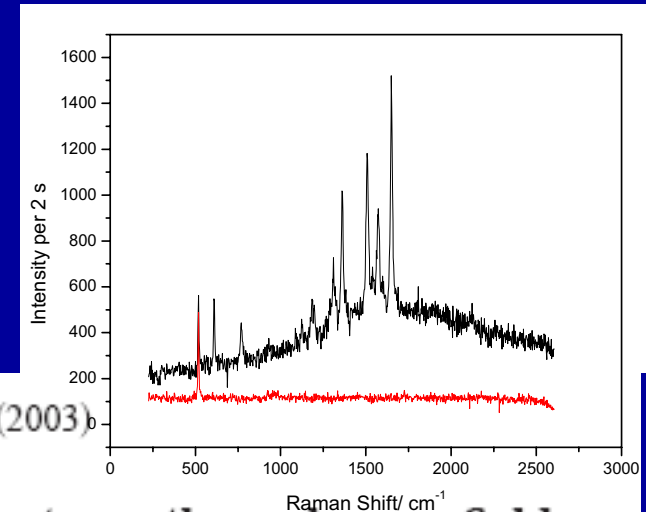
Continuum generation from single gold nanostructures through near-field mediated intraband transitions

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A broad visible and infrared photoluminescence continuum is detected from surface-plasmon-enhanced transitions in gold nanostructures. We find that the ratio of generated infrared to visible emission is much stronger for gold nanostructures than for smooth gold films. While visible emission is well explained by interband transitions of d-band electrons into the conduction band and subsequent radiative recombination, the

numbers of electrons in the metal, and the associated field gradients give rise to higher-order multipolar transitions. We compare photoluminescence spectra for single gold spheres, smooth and rough gold films, and sharp gold tips and demonstrate that the infrared signal is only present for surfaces with nanometer-scale roughness.

Several extant theoretical problems among them: a good description of the excitation of single-electron events by collective electron excitations.

E_{in} creates a coherently oscillating dipole **P** that scales in magnitude with a^3 where a is the radius of the particle (note that we use cgs units). The local field of **P**(ω) creates the enhanced E_s. In a dielectric material, **P** represents polarization of bound electrons. In a metal at the dipolar plasmon resonance, **P** is a coherent sum of electron-hole pairs oscillating along the direction of **E**, and size quantized in the sphere.[24] Individual electron-hole pairs in the superposition have an energy difference that corresponds to the photon energy. These pairs cannot be characterized by a temperature; they are ballistic electron-hole pairs that have not dephased. **P** can re-radiate without energy loss at the frequency of the driving **E** field, or dephase by scattering and relaxation down to the Fermi level on a femtosecond time scale. The latter process corresponds to irreversible photon absorption yielding heat. To quote Kawabata and Kubo, "Thus, the plasma resonance can be considered as the free carrier absorption which is enhanced by a sort of anti-shielding at the frequency of the plasma mode." Both local field enhancement and coherent, ballistic electron-hole pair oscillation are simply different aspects of the EM response of small metallic particles. If **P** is large, then E_s is enhanced.

Lou Brus, JACS 1999

Otto and co-workers have systematically explored the strong SERS that occurs for a number of chemisorbed molecules with low lying LUMOs on rough surfaces. They qualitatively suggest that hot electrons generated in the metal transiently localize on the chemisorbed molecules, then tunnel back into the metal and subsequently emit. They also note that the strong inelastic continuum is associated with SERS. For R6G on Ag colloidal particles, Pettinger has quantitatively modeled a related idea; the entire plasmon (both electron and hole) transiently localizes on the molecule. This later process is exchange coupled resonant energy transfer. Pettinger has also stressed the importance of a large Rayleigh cross section in enabling strong SERS.

Brus et al. JACS 1999

In the large crystalline 100-200 nm particles in our [I.e. Brus et al.] study, the dominant $P(\omega)$ decay mode must be radiative Rayleigh scattering. Yet, the prior literature teaches us that plasmons in crystalline Ag particles are also quite sensitive to dephasing by transient negative ion formation on chemisorbed molecules. We suggest that, most remarkably, in these large particles, the plasmon can dephase by electron localization on just one chemisorbed R6G. When the electron tunnels back into the metal, it has some probability of inelastically exciting one real quantum of some lower energy plasmon of the complex particle, as suggested by the STM experiments and Persson's calculation. This lower energy plasmon emits with its full femtosecond radiative width. This broad emission may contribute to the broad underlying continuum in SERS.

Brus et al. JACS 1999

This is what was written when it was still believed that SM-SERS was a "single" Ag particle phenomenon.

Michaels et al. Showed that enhanced Rayleigh and the SERS response of small clusters were uncorrelated (JACS **121**, 9932, 1999). This is a really strong challenge to the em picture IF SM-SERS is a single-particle effect. Once, it was realized that small clusters were responsible the picture was corrected (JPC, 2000). However, this fact is still being quoted by some workers believing themselves on track to a fundamental theory of SERS.

SERS spectra
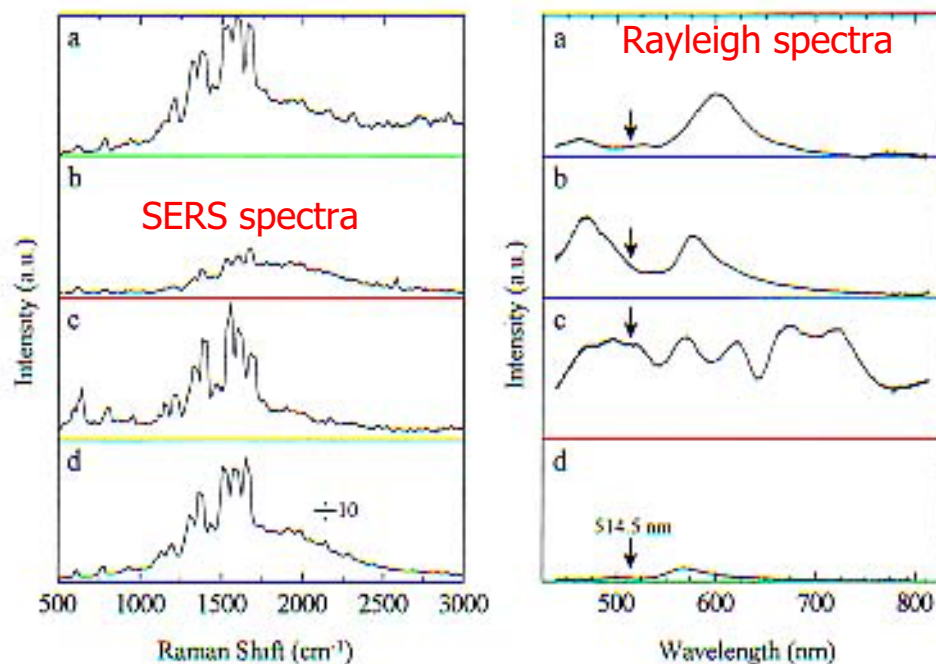
Rayleigh spectra

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

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
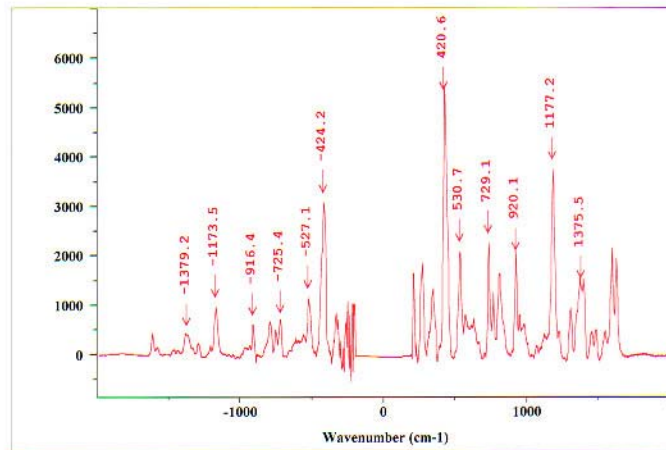
Often people forget that SERS is scattering by the metal and NOT by the molecule. Thus, while SERS benefits from the enhancement of both the incident and the Raman-scattered field, Raman pumping occurs only due to the enhanced *incident* field. Hence, when the SERS enhancement 10^{14} the incident field intensity is enhanced only by 10^{7} which is insufficient enhancement to account for intense antistokes Raman
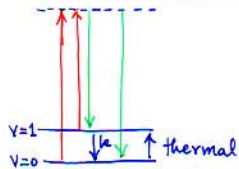
$$\frac{I_{antistokes}}{I_{stokes}} \simeq e^{-\Delta E/k_B T} + \sigma I_L \tau_{vib}$$

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

V=1 ——— thermal
V=0 ———

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

CV/Ag Power dependence
Square: stokes intensity
Star: antistokes intensity
(1181 cm^{-1} band)

Crystal violet decomposes to surface carbon at this point

Haslett et al J. Chem. Phys. 113, 1641 (2000).
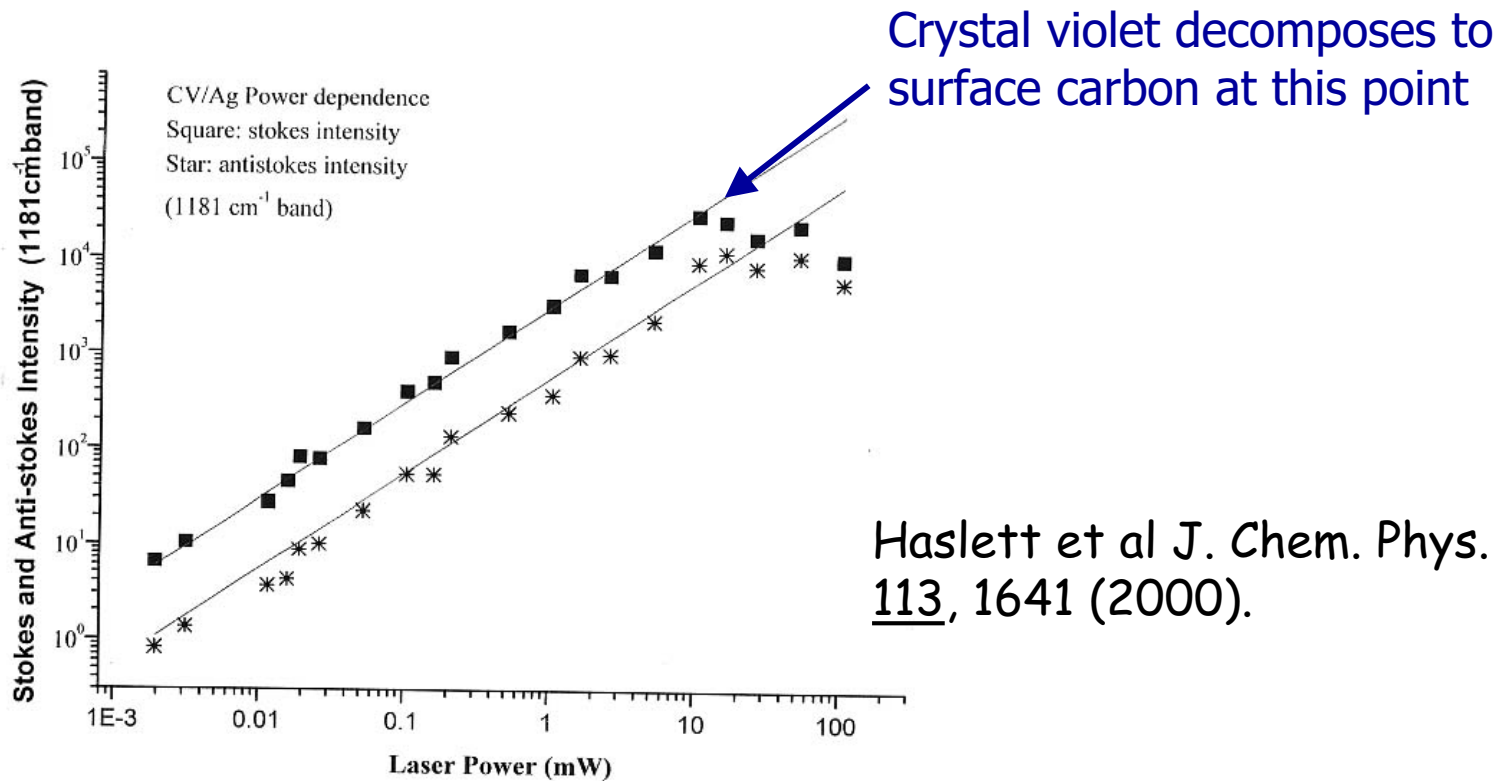
Indeed, strictly linear (as opposed to quadratic) power dependence is observed for both the Stokes and anti stokes components over many order of power until decomposition takes place. And while intense antistokes emissions are observed with a few dye molecules, no intense antistokes lines are observed with the vast majority of small molecules studied (which, nevertheless showed intense SERS activity).

kinetics of the photodecomposition of 2-pyrazinecarboxylic acid
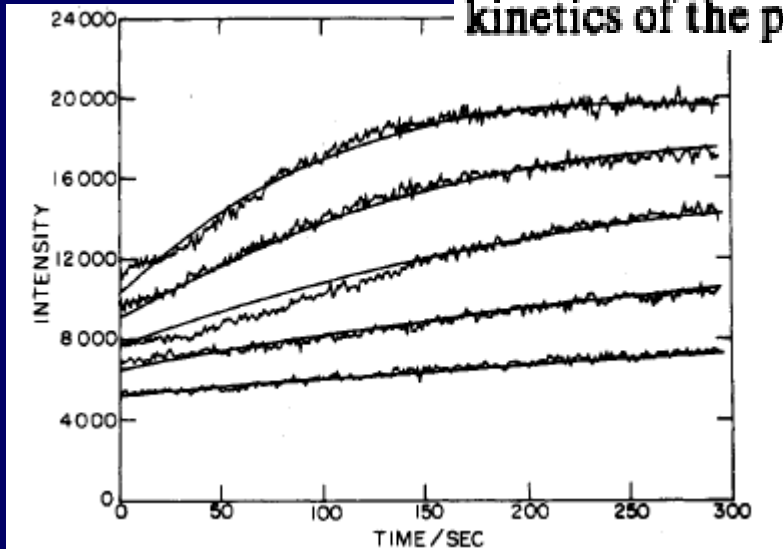
The eventual product is carbon.

At low laser fluences the product rate of appearance is consistent with a two-photon initial step.
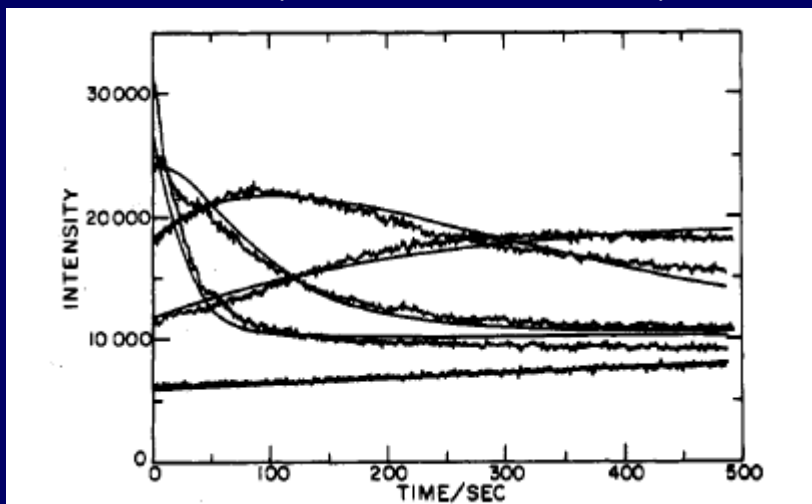
At higher laser fluences, the silver nanoparticle aggregates begin to fragment. By assuming the local temperature to be linear in laser fluence a good fit to the data is obtained and a barrier to fragmentation ~0.7 eV and a local temperature at the highest fluences used ~1000K
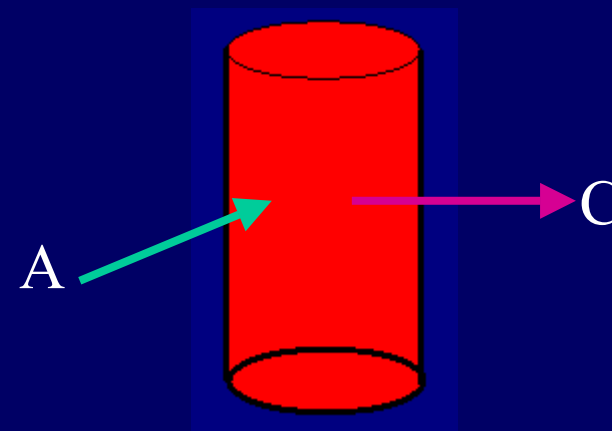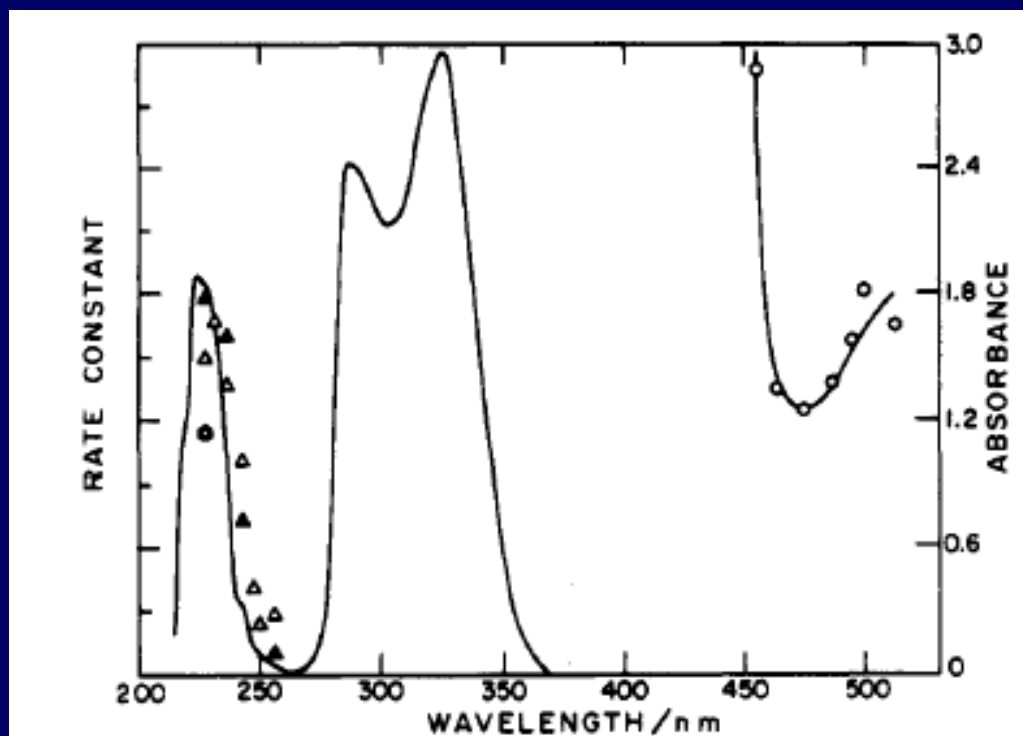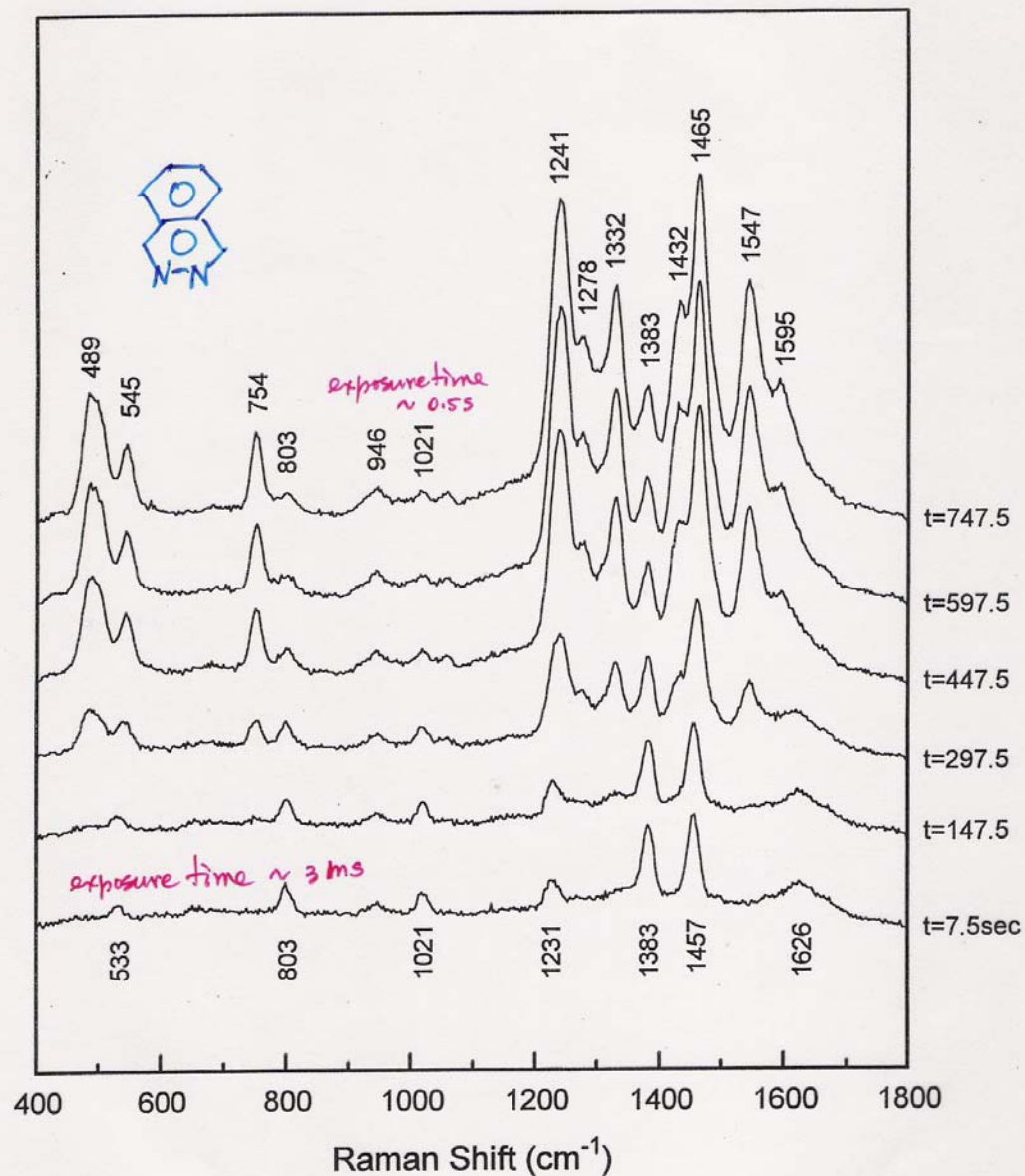
Experiments as a function of wavelength convinces us that the (2-photon) π to π^* transition of the arene is the first step. The "spectrum" of the enhancement is also extractable from the calculation
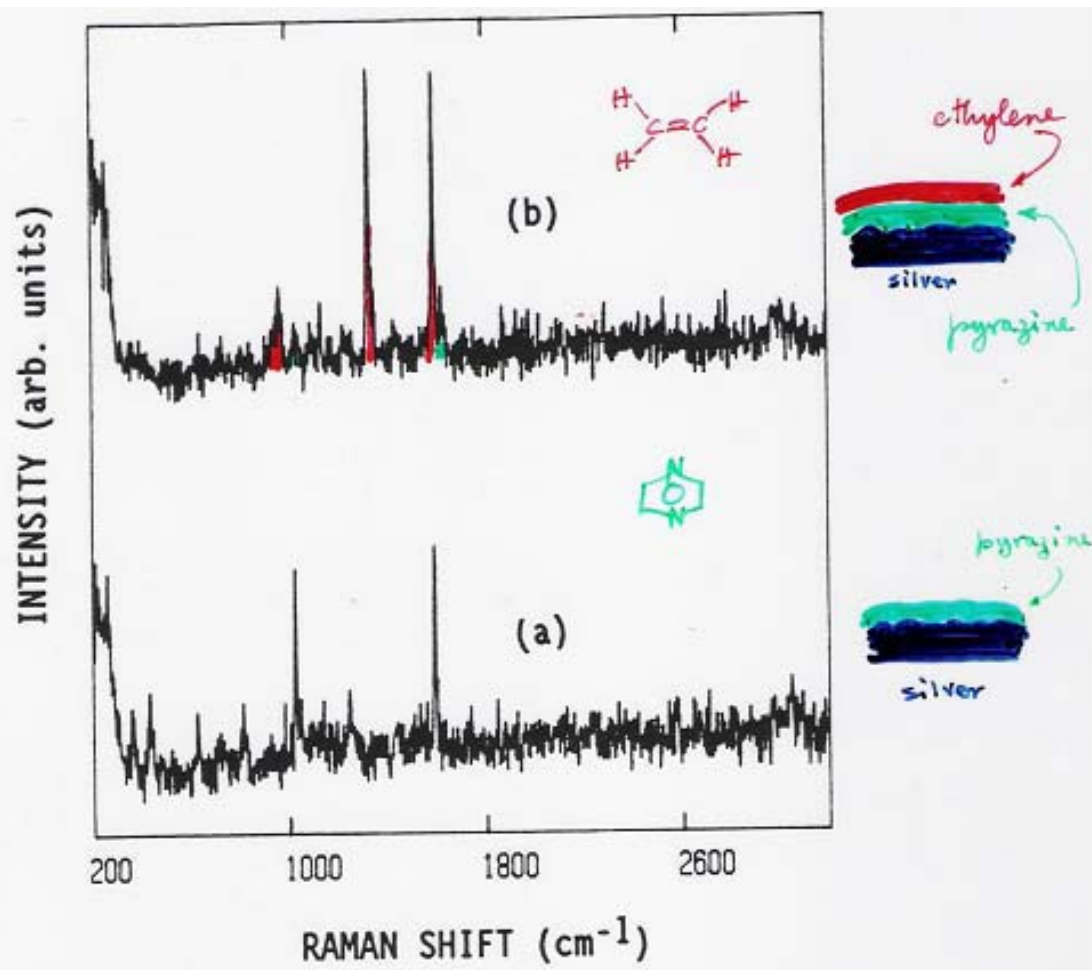
Blue et al J. Phys. Chem. 93, 8080 (1989)

Diffusion of ethylene through a thin organic layer (pyrazine) and its displacement from the Ag surface

476.5 nm

Suh et al *J. Phys. Chem.* **1996,** *100,* 805-813
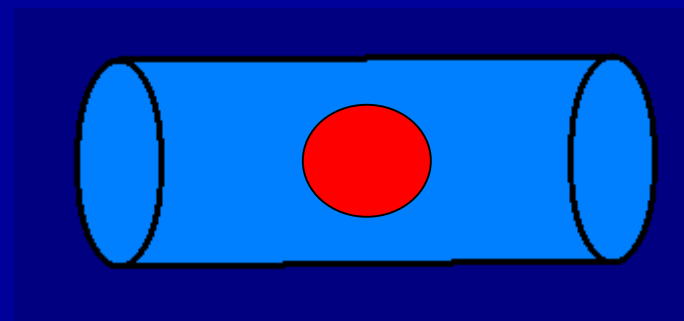
Photochemical exposure is determined by the rate of flow of the Ag colloid solution through a capillary.

A side-message: many SERS reports are actually of photochemical products.

The photoproduct appearance curves were fit simultaneously to the rate equation convolved with the equation expressing the solution flow-rate decrease with time, which was measured independently as a check.
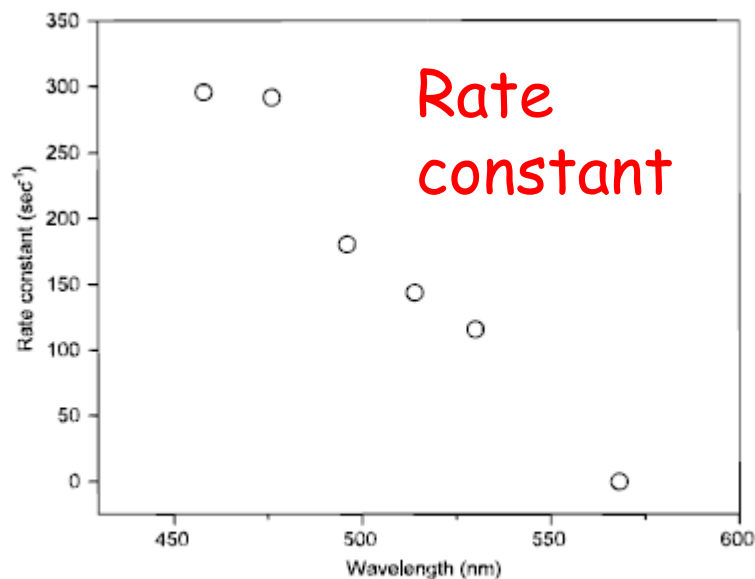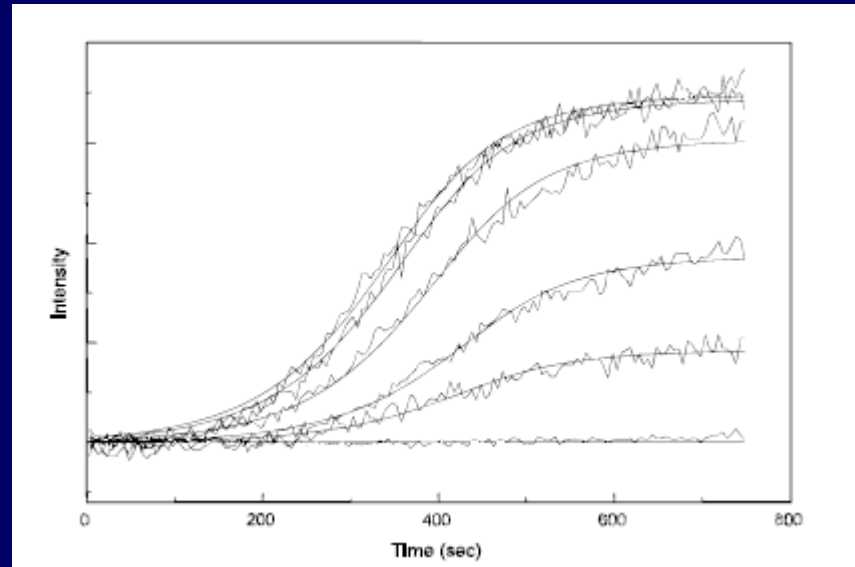
Rate constant

Figure 7. Plot of the photochemical rate constant derived from the data shown in Figure 6 as a function of excitation wavelength.
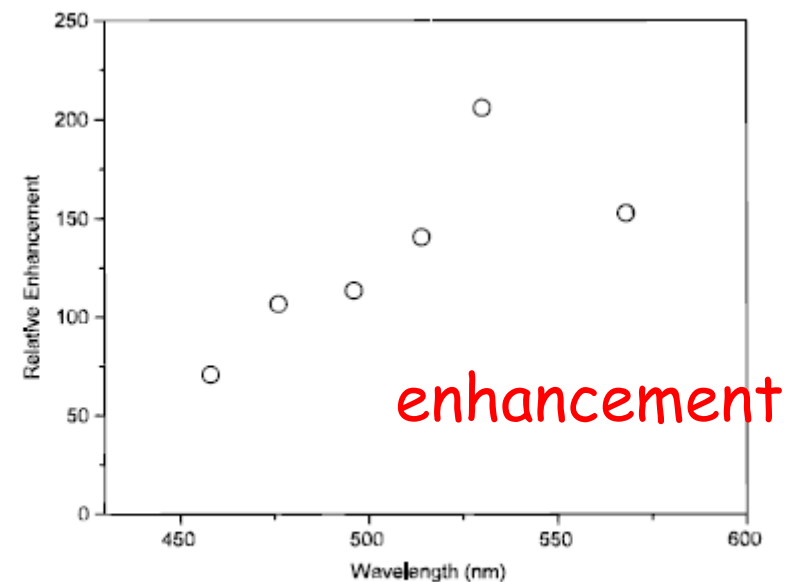
enhancement

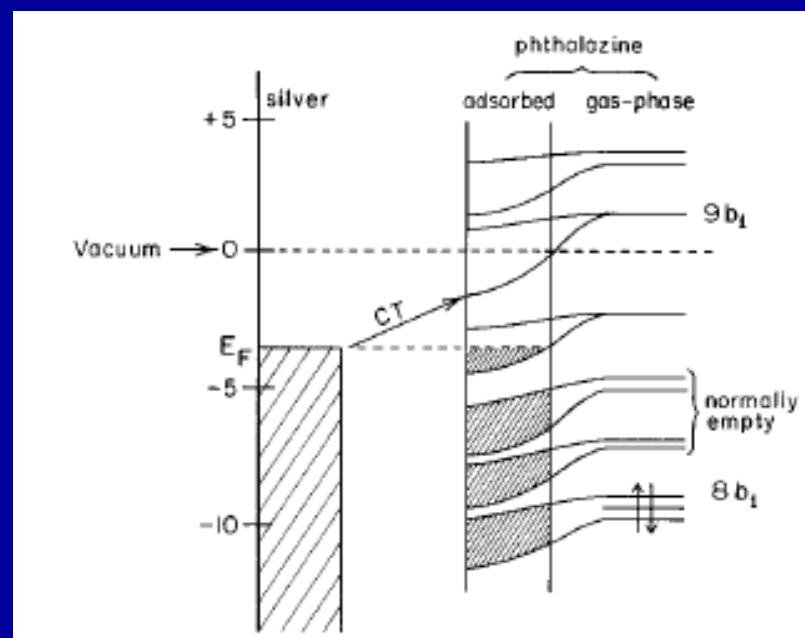
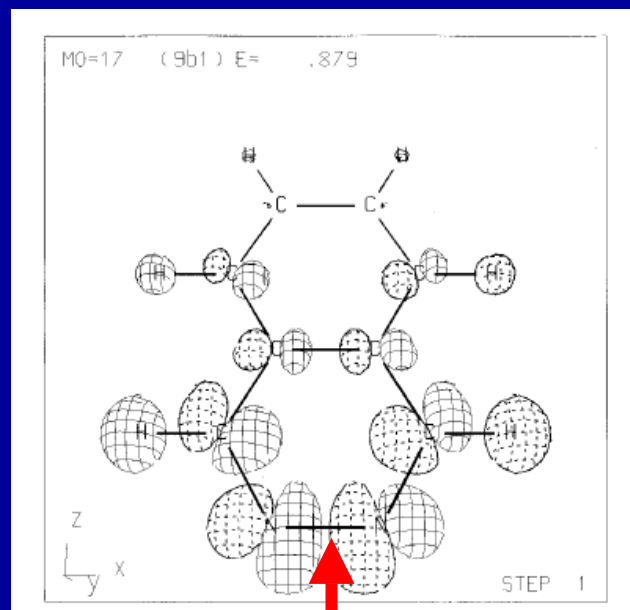
Figure 10. Measured wavelength dependence of the SERS enhancement of phthalazine adsorbed on colloidal silver.

Charge-transfer into normally-empty states of the phthalazine means that the molecule is largely anionic on the surface. The $9b_1$ state has a node in the its wf in the NN bond. (I.e. is is antibonding at the NN bond). The photoprocess is likely an NN bond scission resulting in an adsorbed ortho-disubstituted benzene.
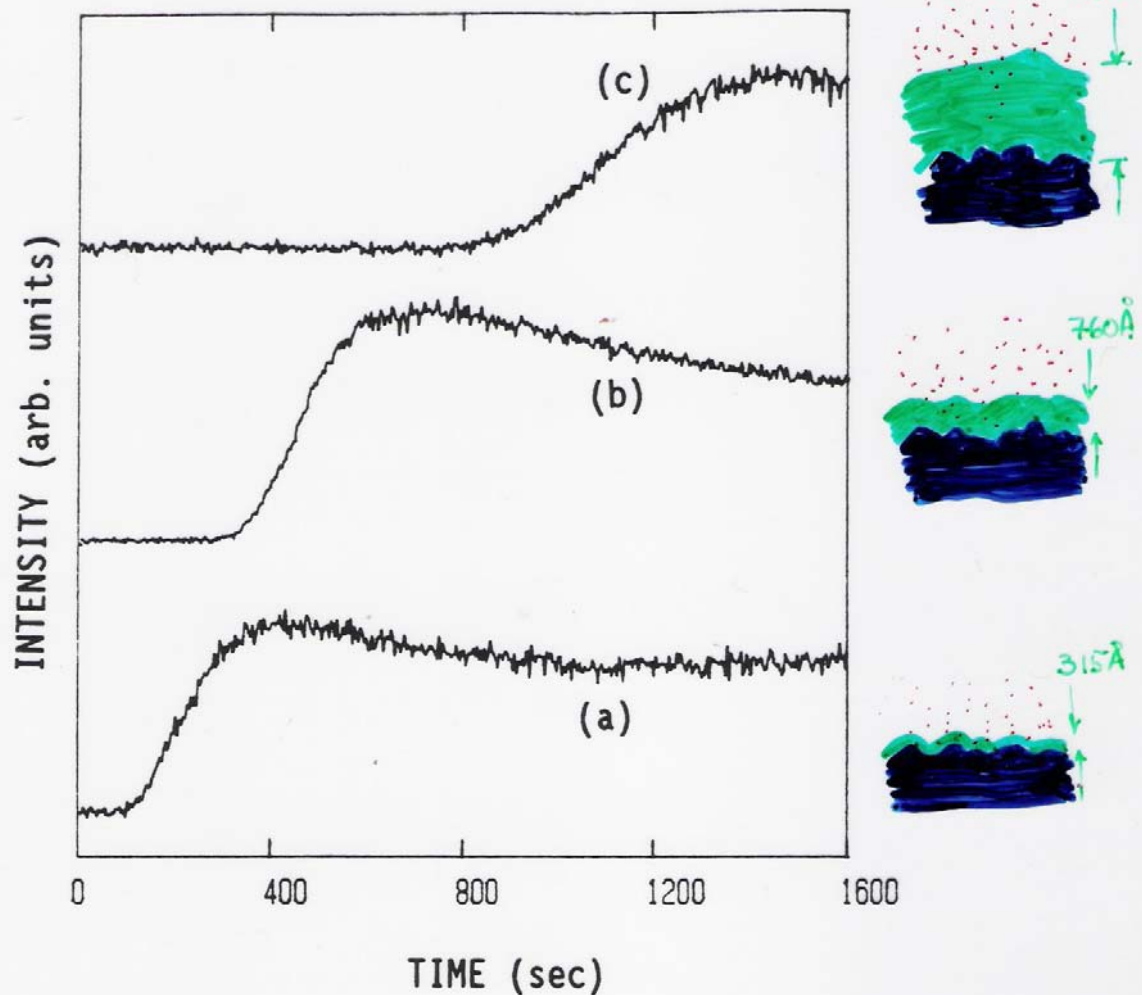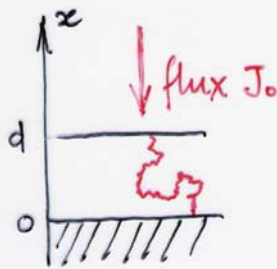
Figure 2-16 : Time evolution of the ν_3 SERS signal of C_2H_4 for 5×10^{-8} torr C_2H_4 being added to a Ag surface ($T_S=42°K$) covered by pyrazine overlayers of a)315Å; b)760Å; and c)1460Å.

Diffusion measurements of ethylene through an organic layer.

Blue et al J. Phys. Chem. 93, 8080 (1989)

a concentration at $x=0$ as a function of time for constant flux J_0 is

$$C(0,t) = \frac{J_0 t}{d} + \frac{J_0 d}{D}\left\{ \frac{-1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-Dn^2\pi^2 t/d^2}\right\}$$
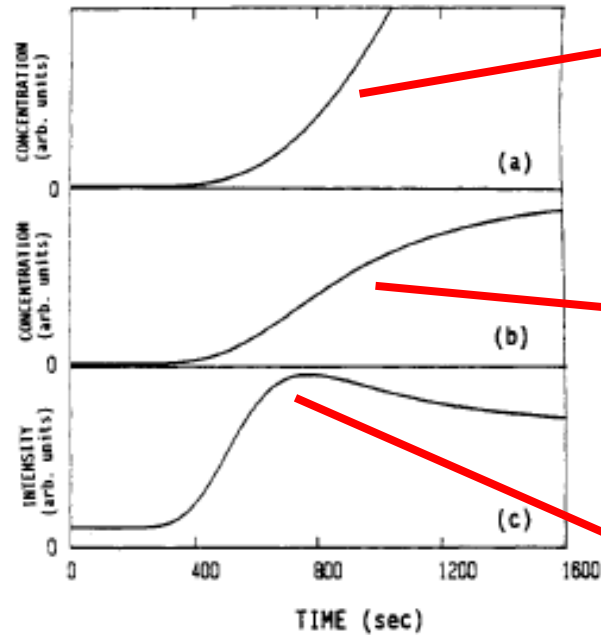
we wish to determine D.

b we must include a term to express the fact that the first layer saturates: simple-mindedly we chose a Langmuir isotherm:

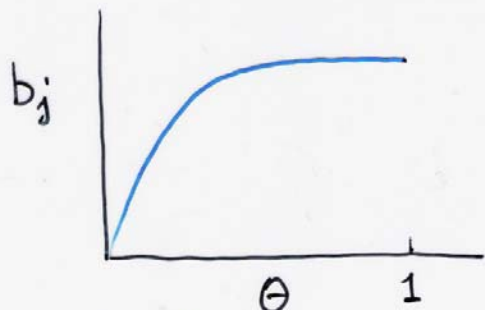$$\theta = \frac{b\,C(0,t)}{1 + b\,C(0,t)}$$

c we must include the effect of dipole coupling
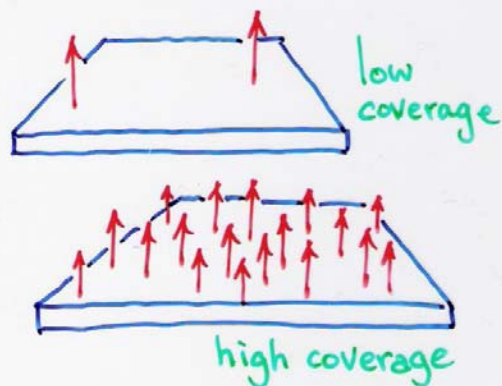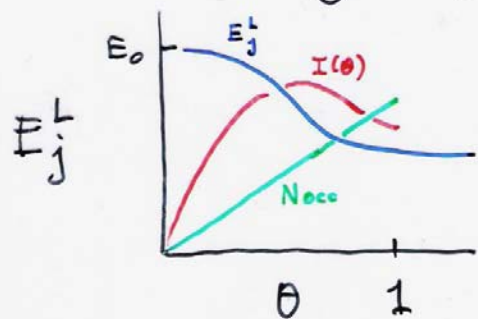
$$I(t) \propto \frac{\theta}{(1+\beta\theta)^4}$$

$$E_j^L = E_0 - p_j b_j / a^3 = E_0 \, a^3 / (a^3 + \alpha b_j)$$
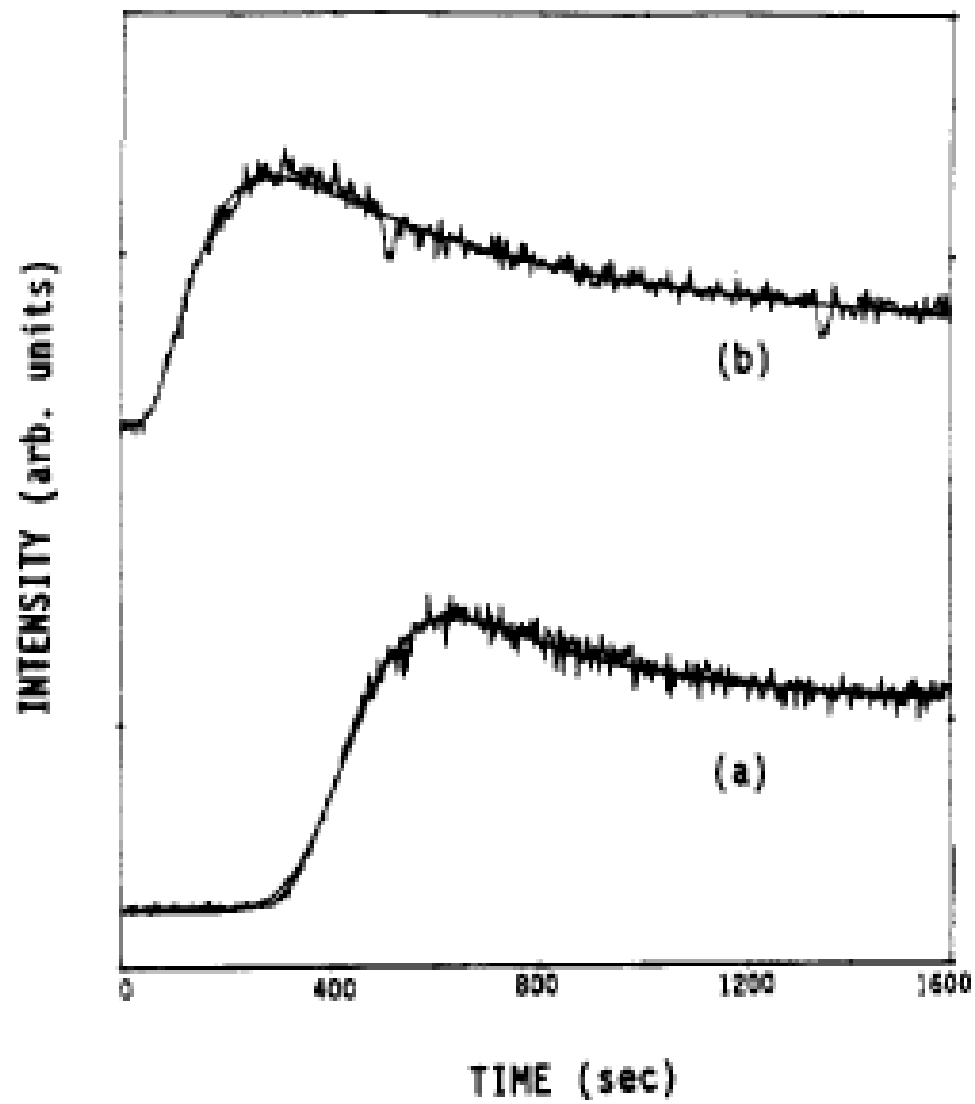
$$E_j^L / E_0 = a^3 / (a^3 + \alpha b_j)$$

b_j vs θ (0 to 1)

$$\theta = \frac{\text{number of occupied sites}}{\text{Total number of site}}$$

E_j^L vs θ (0 to 1): E_0, E_j^L, $I(\theta)$, N_{occ}

low coverage

high coverage

$$I(\theta) \propto \sum_{j=1}^{N_{occ}} \left[a^3 / (a^3 + \alpha b_j) \right]^4$$

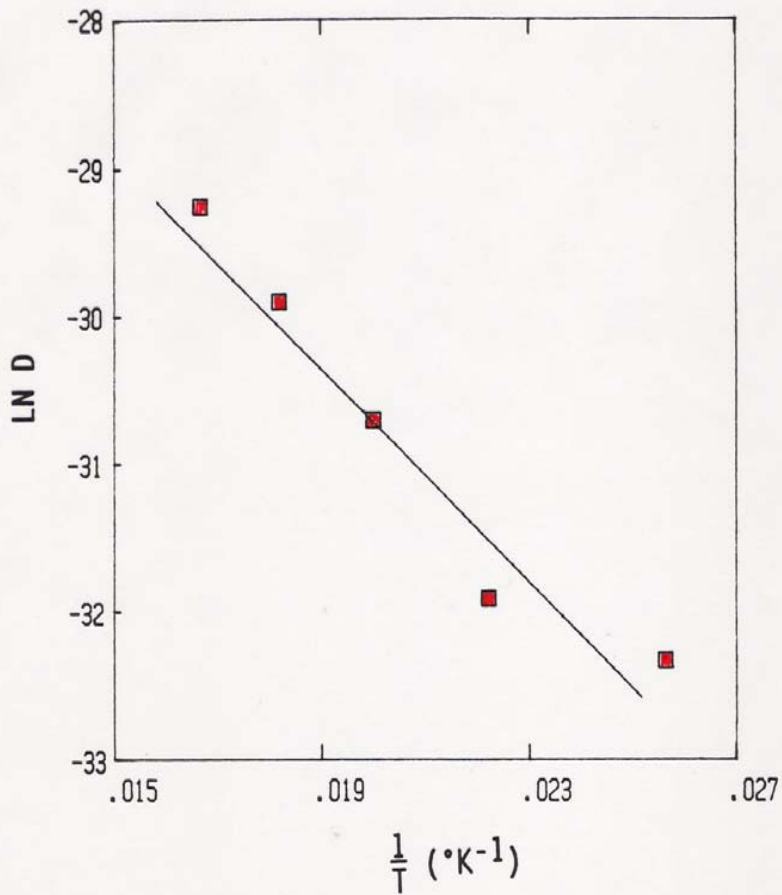enhanced Raman intensity

A very good fit

Figure 2-27 : Arrhenius plot of the average values of the fitted diffusion coefficients versus (1/T) for data given in table 2-8. The fitted activation parameters are $E_D = 0.7$ kcal/mole and a preexponential factor of $D_0 = 6 \times 10^{-11}$ cm^2/s, with a correlation constant of r = 0.971 .

$$\nu \sim 7 \times 10^4 \, \text{sec}^{-1}$$

$$D(T) = D_0 \, e^{-E_D/kT}$$

Careful temperature studies were carried out by producing the metal surface and the films at the highest temperature used in the experiment then working up and down. The pre-exponential factor is unusually small implying a snow-like structure for the organic layer.

Conclusions:

There's fire in SERS yet, both in recasting the phenomenon into better quantum language

and

in application