L11-12
Single molecule spectroscopy

Why?

Analytical
Fundamental

What are those?

Absorption
Fluorescence
Infrared
Raman
NMR
Mass spectroscopy
Photoelectron spectroscopy
.....

Problems?

1.66×10^{-24} moles – yoctomole
1 in N or 10^{-23}, guacamole

Detection

Problems of single molecule spectroscopy

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Single Molecule Tip-Enhanced Raman Spectroscopy with Silver Tips

Weihua Zhang, Boon Siang Yeo, Thomas Schmid, and Renato Zenobi*

Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland

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We present single molecule tip-enhanced resonance Raman spectra from brilliant cresyl blue (BCB) submonolayers adsorbed on a planar Au surface with Ag tips. A gap of 1 nm between a Ag tip and the Au substrate was employed to create a highly enhanced electric field and to generate Raman scattering from an area of 100 nm2. Three lines of evidence are presented to prove the single molecule sensitivity of our experiments: (1) Extremely diluted samples were used. Estimations show that at most a few molecules were excited by the Ag tip. (2) Spectroscopic fluctuations, including intensity fluctuations, frequency shifts, and line shape changes were observed. A histogram analysis of the intensity fluctuations of two different BCB coverages was carried out. The results clearly show the features of single molecule behavior. (3) Discrete signal losses also were observed. This is because of photochemical processes involving single molecules. Besides BCB, which shows a strong resonant absorption at 633 nm (the wavelength of the excitation laser), a self-assembled monolayer of benzenethiol, which does not strongly absorb at 633 nm, was studied. Good quality spectra were recorded with a short exposure time (10 s) and time-dependent spectral changes were also observed.

Classical EM enhancement

Plasmons

No surface plasmon excitations on planar surfaces

$\varepsilon = \varepsilon' + i\varepsilon''$ wavelength dependent dielectric constant

Assume a particle is placed in an EM field.
Internal polarisation developed, **P(r)** will oscillate with the external field, $\mathbf{E_0}$

External EM field created by the internal polarisation can be represented by the field of a point dipole, p located at the sphere centre and scales with the sphere volume.

$$\mathbf{p} = 4\pi\varepsilon_0\varepsilon_m \{(\varepsilon - \varepsilon_m)/(\varepsilon + 2\varepsilon_m)\}R^3\mathbf{E_0}$$

ε_m is the ε of the medium, ε_0 is the permittivity of vacuum

In the electrostatic limit, P(r) is related to internal electric field strength $\mathbf{E_{in}(r)}$ and the incident field $\mathbf{E_0}$

$\mathbf{P(r)} = \varepsilon_0(\varepsilon - \varepsilon_m)\mathbf{E_{in}(r)} = 3\pi\varepsilon_0\varepsilon_m \{(\varepsilon - \varepsilon_m)/(\varepsilon + 2\varepsilon_m)\}\mathbf{E_0}$

p increases with the sphere size, but the distance from the surface also increases.

EM field outside the particle is a superposition of **p** and $\mathbf{E_0}$

This field is maximum at the surface.
$\mathbf{E_{surf}} = [3\varepsilon/(\varepsilon + 2\varepsilon_m)]\mathbf{E_0}$ and independent of R

At the dipolar plasmon resonance, the electric field inside and outside will be large.

$Q_{Ext} \sim Q_{Abs} = [4(2\pi R\varepsilon_o^{1/2})/\lambda]\mathrm{Im}[(\varepsilon-\varepsilon_m)/(\varepsilon+2\varepsilon_m)]$ Extinction and scattering efficiency

The position of the plasmon frequency depends on ε”, which is small for Ag, Au and Cu.

Generally, incident and scattered local fields lie in the plasmon enhancement region.
Thus apparent Raman cross section is enhanced by fourth power of the local field.

EM enhancement factor of 10^6 is seen due to this.

When particle size approaches wavelength, destructive interference occurs, reducing enhancement.

“The Ag tips used in our experiment were fabricated by electrochemical etching.27 A mixture of perchloric acid (70%, Riedel-de Hae¨n) and ethanol with a volume ratio of 1:4 was used as etchant. A gold ring with a diameter of 1 cm was employed as the negative electrode and the Ag wire (99.99+%, Aldrich) with a diameter of 0.25 mm was used as the positive electrode. During etching, a constant voltage of 1.6 V was applied; the part of the Ag wire close to the etchant surface was etched the fastest. When the lower part of the Ag wire dropped off, a sharp tip was formed (Figure 1a). The tips were rinsed with methanol after etching. We found that the tip shape was sensitive to the etching geometry. In our case, a 10 mm length of Ag wire was immersed in the solution, and the Au electrode was positioned just below the surface of the etchant. It also has been reported that the shut-off time of the etching voltage after the lower part of the metal wire drops off determines the sharpness of the tip .28 Our method was to use short pulses instead of a constant voltage just before the drop off, so that only a small amount of charge passed the tip end after the drop off.”

“Our TERS setup, as illustrated in Figure 1b, was composed of a homemade micro-Raman system and a commercial STM system (EasyScan, NanoSurf) which was mounted on a translation stage. The excitation laser (633 nm, He-Ne laser, Thorlabs) was guided in by a single mode optical fiber. P polarized light (parallel to the tip axis) was chosen using a polarizer; half of the laser power was reflected by a beam splitter (BS) and focused onto the tip-sample gap by a long working distance microscopic objective (N.A.) 0.35, Olympus) with an angle of 45° with respect to the tip axis. The scattered light was collected by the same objective and coupled into a Raman spectrograph (Holospec VPT, Kaiser) by a multimode fiber. Spectra were recorded by a liquid nitrogen cooled chargecoupled device (CCD) camera (LN/CCD-2500, Princeton Instruments). We would like to point out that this system is not fully optimized. The two 50-50% BSs decreased the signal by a factor of 4 times and the laser power reaching the sample was only about 0.5 mW. Nevertheless, it will be shown below that the enhancement reached by our gap TERS system was so large that clean spectra could be observed with short exposure times even with this unoptimized system.”

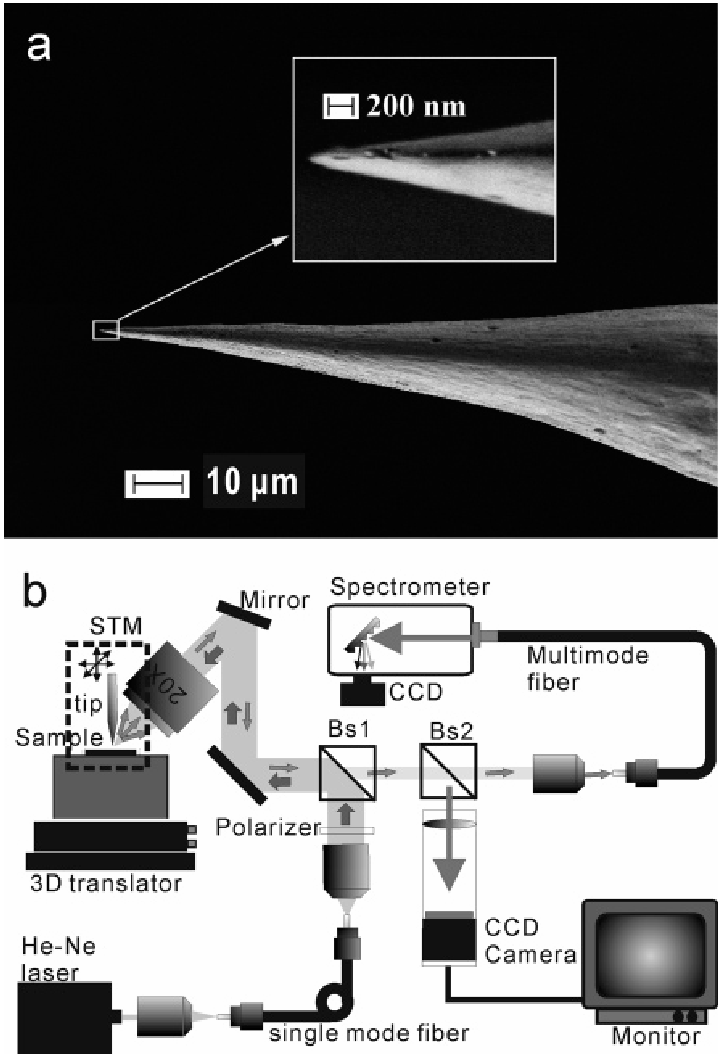

Figure 1. SEM images of a typical Ag tip (a). The inset of (a) shows a zoom of the tip apex, which is sharper than 50 nm. The lower part (b) is the schematic diagram of our setup, which is composed of a home-built micro-Raman system and a commercial STM.

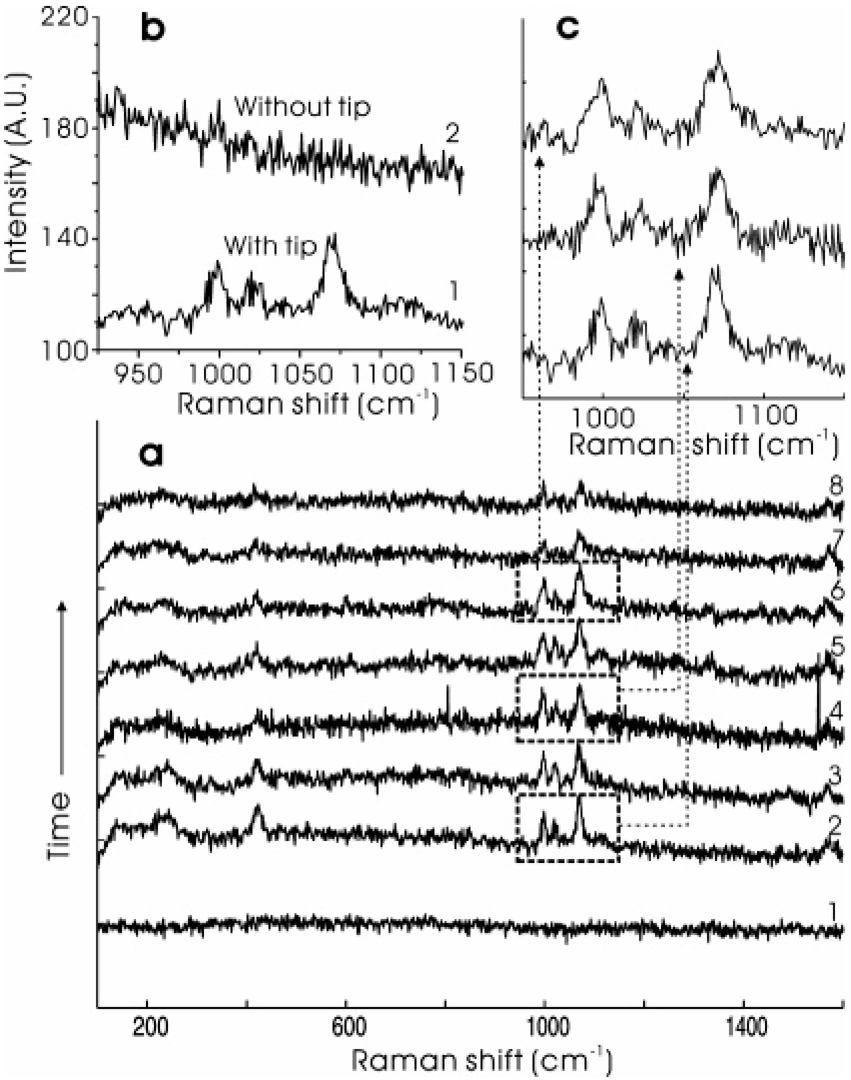

Figure 2. Tip-enhanced Raman spectra from a BT SAM on a planar Au surface. Spectra were collected continuously before and after the tip approaching with an exposure time of 10 s per frame (a). Line 1 was collected before the tip was brought onto the sample and lines 2-8 were collected with the tip in tunneling feedback. After the tip approached to the sample, peaks from BT were observed with a 10 s exposure time (line 1 in (b)). Without the tip, no distinguishable pea was observed even with a 10 min exposure time (line 2 of (b)). The intensity of the signal decreased and the line shape also changed with time. Figure (c) shows the details of the modes at ~1000 cm-1 corresponding to the parts boxed in (a).

TABLE 1: Assignment of Benzenethiol Vibrational Modes

vibrational assignment	frequency (cm^{-1})	
	TERS	SERS29
7a(a1), νCS+βCCC	424	417
12(a1), β CCC	998	999
18a(a1), ν CH	1020	1022
1(a1), βCCC + ν CS	1069	1073
8a(a1), ν CC	1568	1573

* T. H. Joo, M. S. Kim, K. Kim, *J. Raman Spectrosc*. **1987**, *18*, 57.

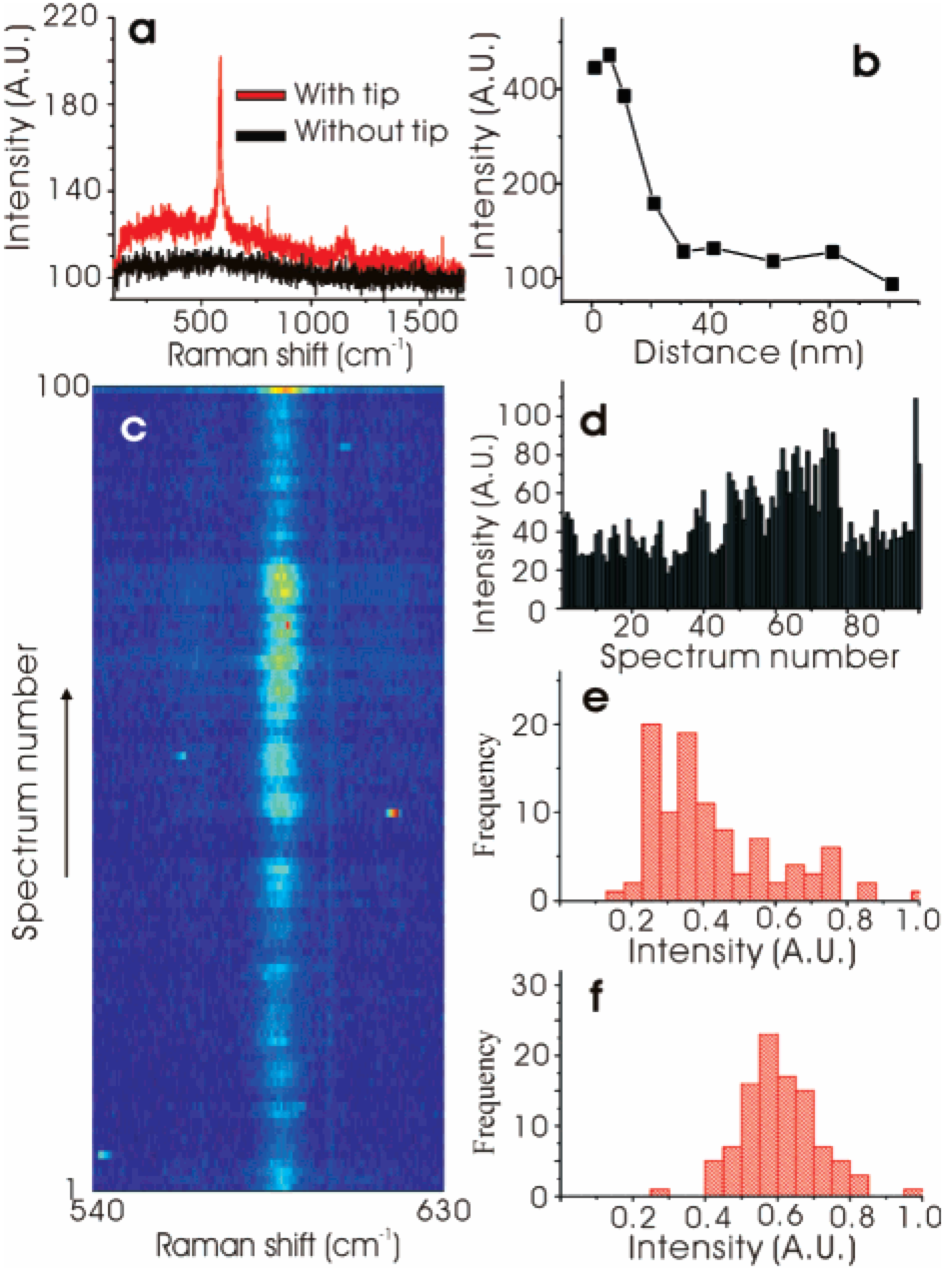

Figure 3. Tip-enhanced Raman spectra from BCB submonolayers. The peak at 585 cm-1 was greatly enhanced after the tip approached the sample surface (a). The collection time was 10 s. To make sure that it is a pure near-field effect, Raman intensity as a function of tip -sample distance was measured (b). The signal is enhanced only if the tip-sample distance is smaller than 30 nm. Time-resolved TERS measurements also have been done. A tip-enhanced spectral series of one hundred exposures from a BCB submonolayer made by spin coating a 10-5 M solution on an Au substrate (c) were collected continuously with an exposure time of 5 s per spectrum. The peak intensity 585 cm^{-1} shows a random fluctuation (d). Panel (e) is the histogram of (d). It shows a broad distribution of the intensity. The same experiment was done with a sample made by spin coating a 10-4 M BCB solution on an Au substrate, and its histogram of the peak intensity (f) shows a completely different pattern from (e).

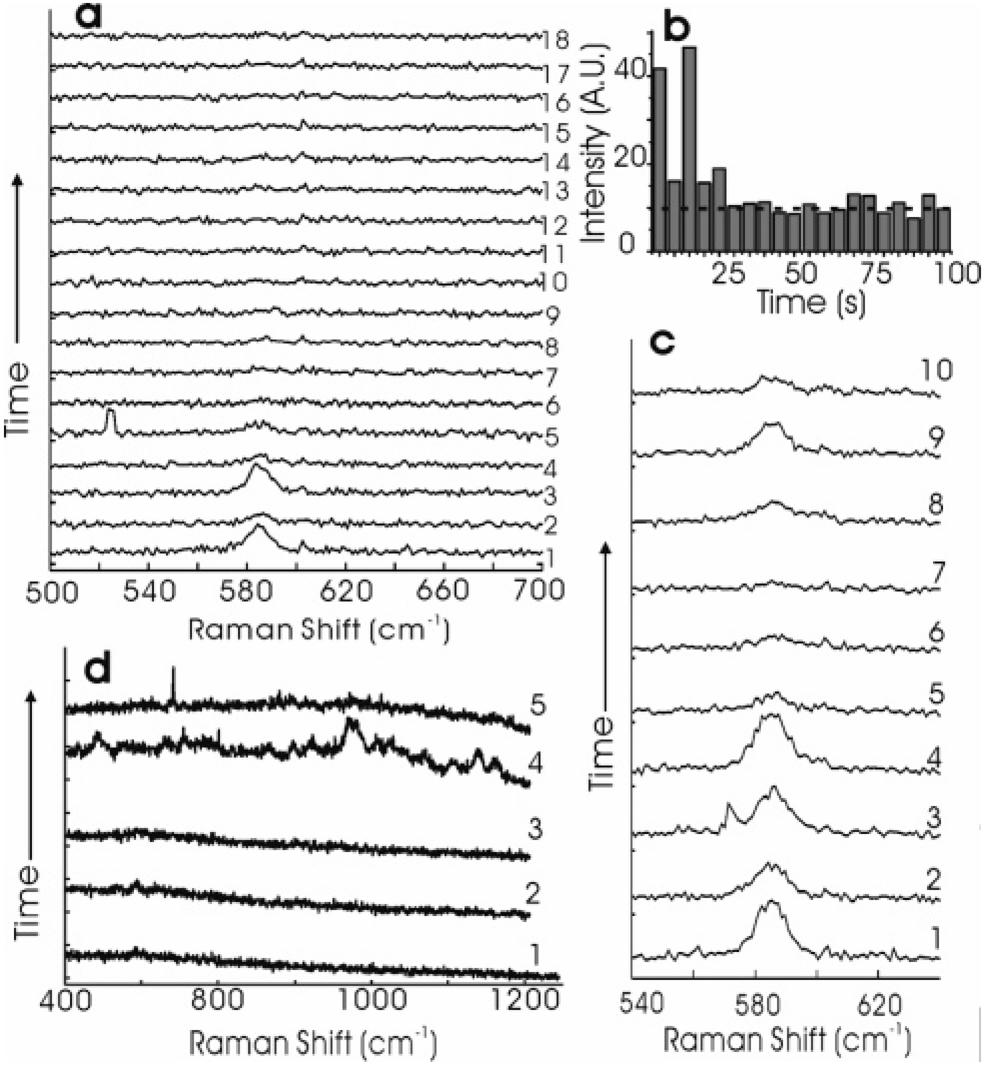

Figure 4. (a) and (b) are examples for single-step bleaching of the tip-enhanced Raman scattering. The spectral series was collected with 5 s per exposure (a) and the peak intensity sequence (b) shows an obvious discrete decrease after the first 5 frames. The dashed line denotes the background level. Panel (c) shows the fluctuation of the line shape of BCB. Sometimes the tip-enhanced signal even shows random fluctuation (d) irrelevant to the sample molecule BCB. The collection time used in (c) and (d) was 10 s per exposure.