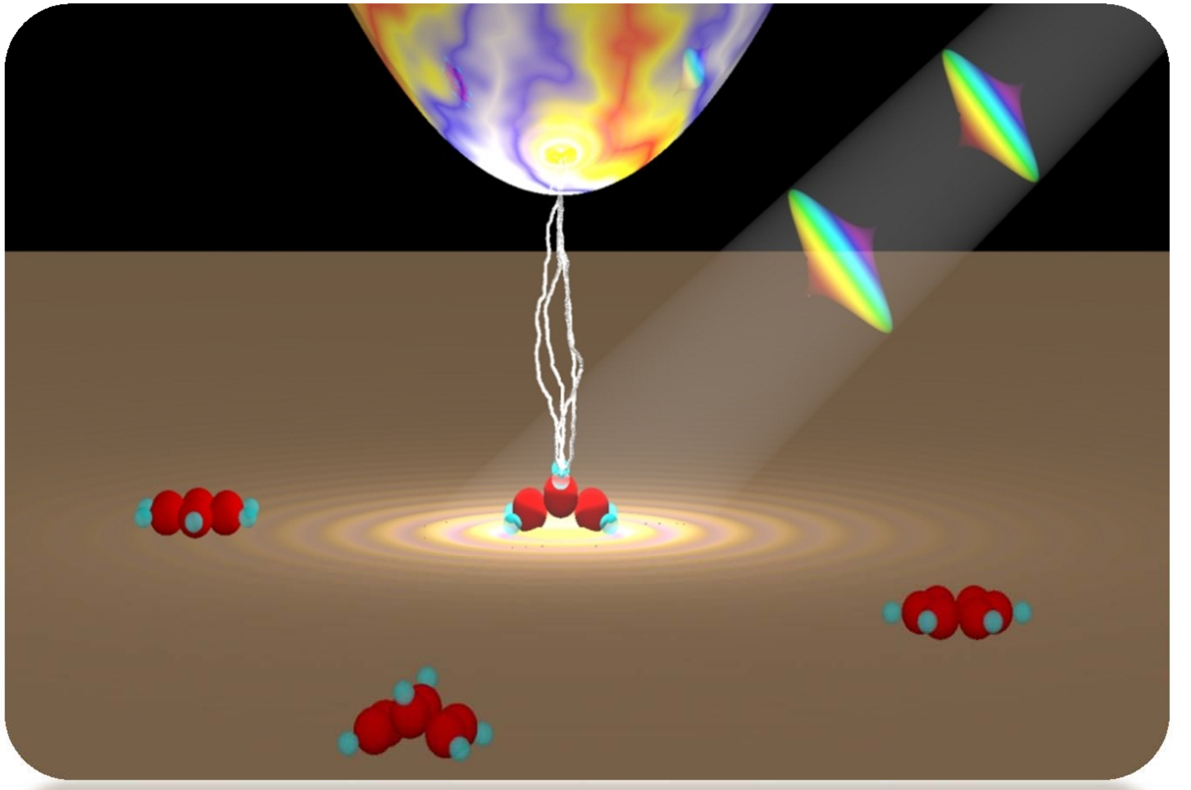
Photon Coupled STM



基于扫描探针显微镜的分析方法

What a photo-STM can do?

- **Tunneling Current Induced Photon Emission**
- **Photo induced molecule diffusion**
- **Photo induced molecular conformation change**
- **Surface photo voltage**
- **Local work function measurement**
- **Thermal Effect**
- **Tip enhanced Raman scattering**
- **Ultrafast Time Resolution**

Tunneling Current Induced Photon Emission

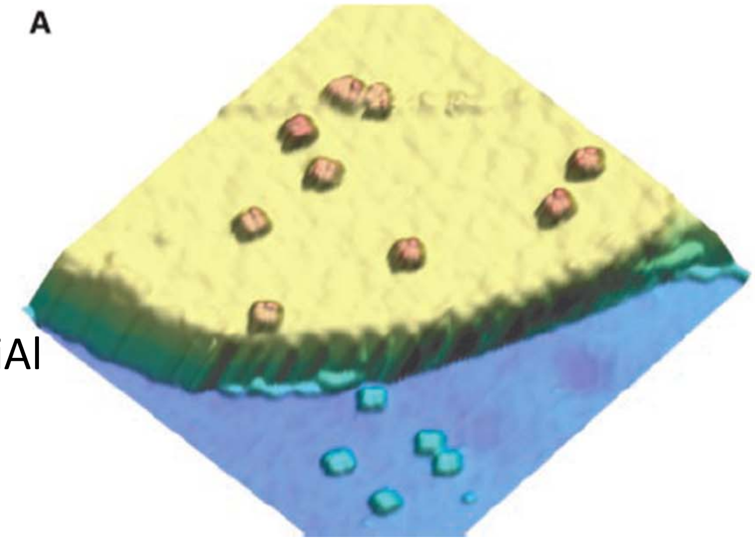
X. H. Qiu, *et al.*
Science **299**, 542 (2003);

Vibrationally Resolved Fluorescence Excited with Submolecular Precision

X. H. Qiu,* G. V. Nazin,* W. Ho†

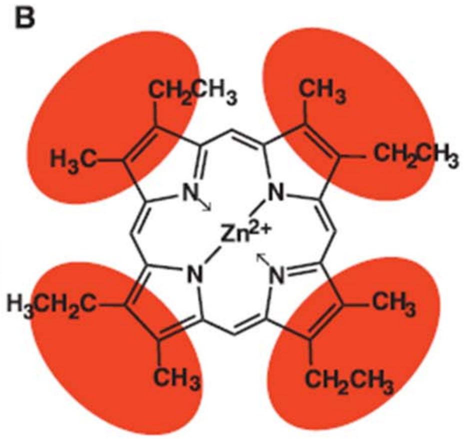
Tunneling electrons from a scanning tunneling microscope (STM) were used to excite photon emission from individual porphyrin molecules adsorbed on an ultrathin alumina film grown on a NiAl(110) surface. Vibrational features were observed in the light-emission spectra that depended sensitively on the different molecular conformations and corresponding electronic states obtained by scanning tunneling spectroscopy. The high spatial resolution of the STM enabled the demonstration of variations in light-emission spectra from different parts of the molecule. These experiments realize the feasibility of fluorescence spectroscopy with the STM and enable the integration of optical spectroscopy with a nanoprobe for the investigation of single molecules.

Tunneling Current Induced Photon Emission



Al_2O_3/NiAl

Topograph



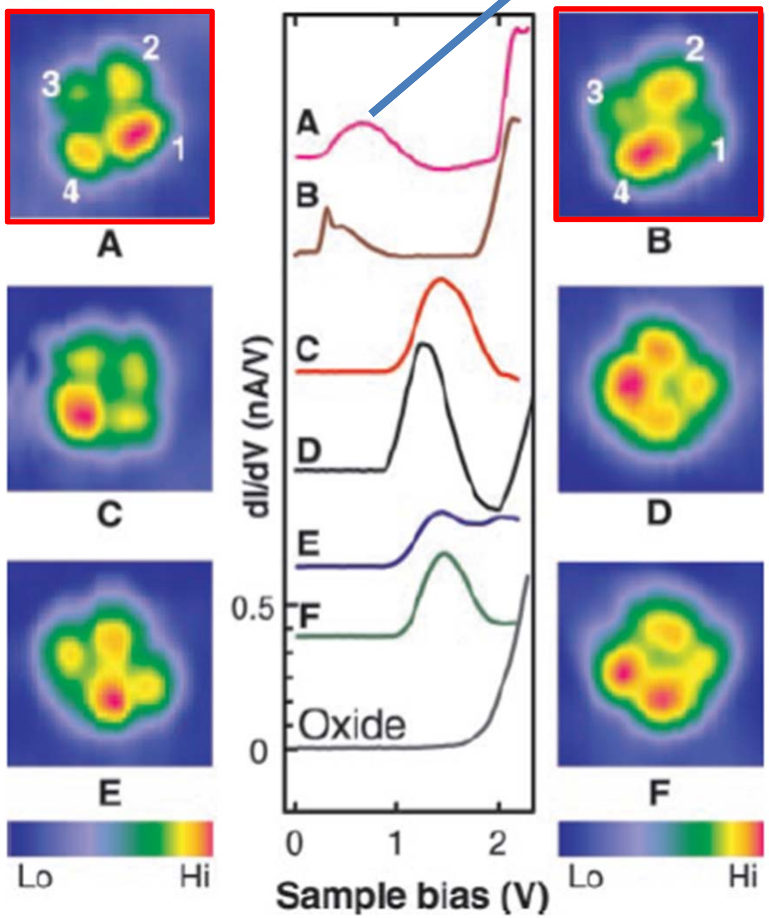
ZnEtiol

Tunneling Current Induced Photon Emission

Topograph of different conformations on oxide

Necessary for Luminesce

dI/dV spectra



Saddle: 30%

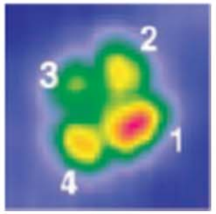
A, B illuminates

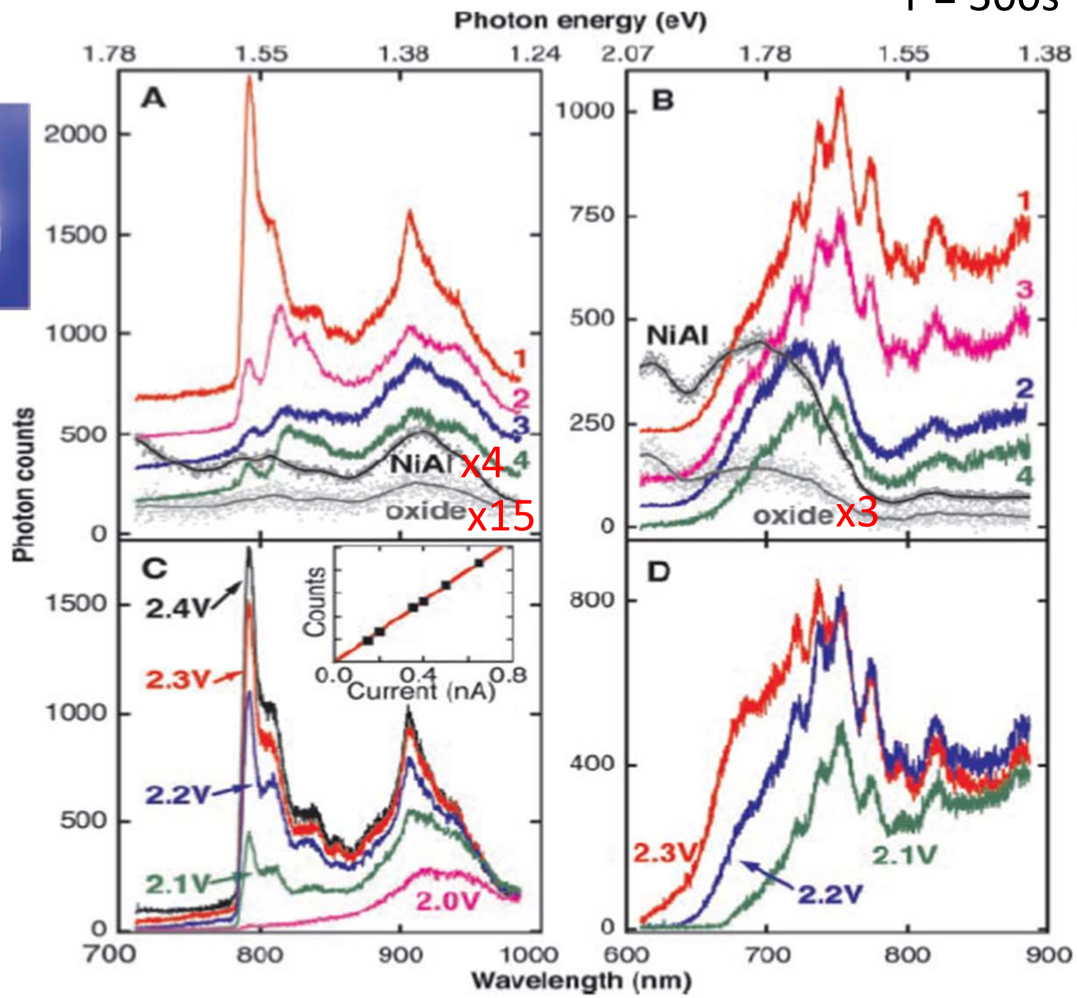
Size: 32x32 A
V = 2.35V, I = 0.1A

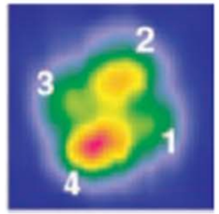
Tunneling Current Induced Photon Emission

B: V = 2.2V, I = 0.5nA
T = 300s

A: V = 2.35V, I = 0.5nA
T = 100s







Position dependence

Bias dependence

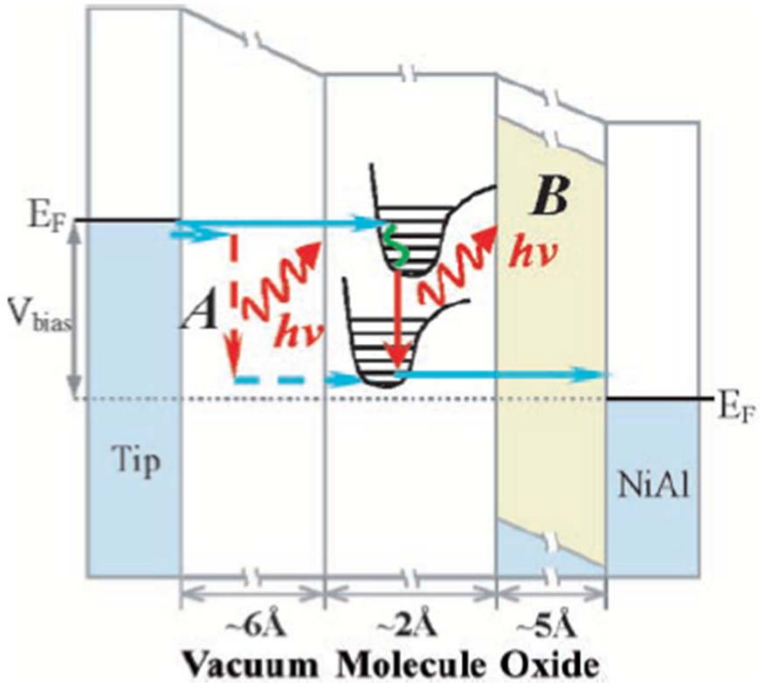
Current dependence
800nm, 2.35V

Tunneling Current Induced Photon Emission

Two major processes:

A: Inelastic tunneling

B: fluorescence channel
charged molecule

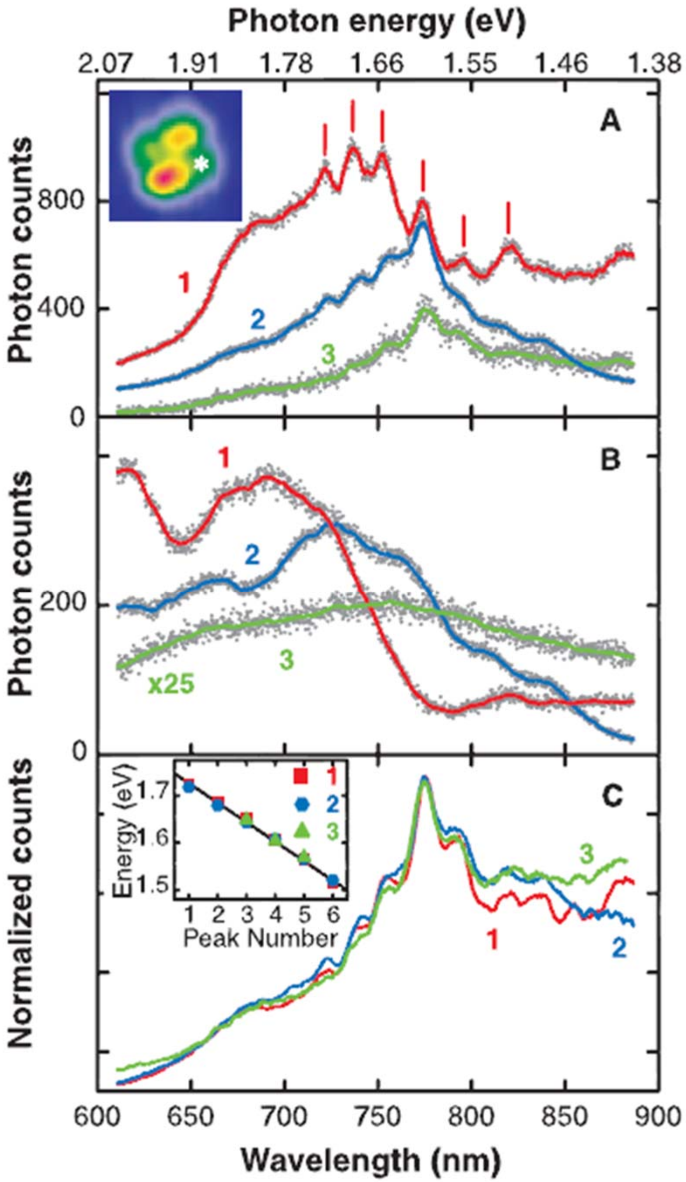


Tunneling Current Induced Photon Emission

Tip effect (tip plasma)

1: 2.35V, 0.5nA, Ag tip
300s
2: 2.35V, 0.6nA, Ag tip
200s
3: 2.3V, 1nA, W tip
600s

Vibrational features:
Equaldistant



On molecule

On NiAl surface

Normalized

Tunneling Current Induced Photon Emission

Applied Physics Express **3** (2010) 015201

Anomalous Light Emission from Metal Phthalocyanine Films on Au(111) Activated by Tunneling-Current-Induced Surface Plasmon

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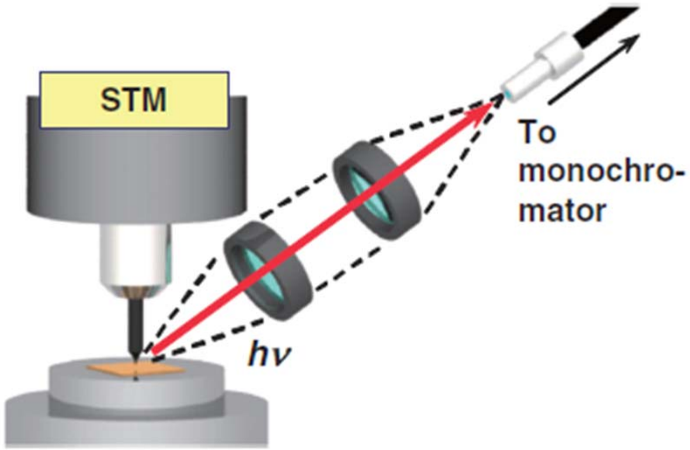
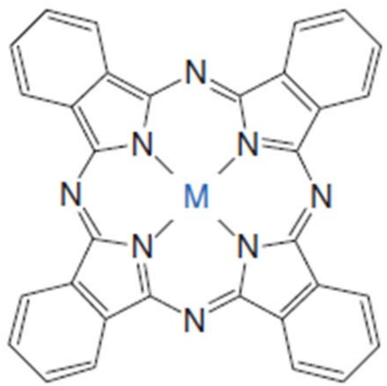
Received November 30, 2009; accepted December 16, 2009; published online January 15, 2010

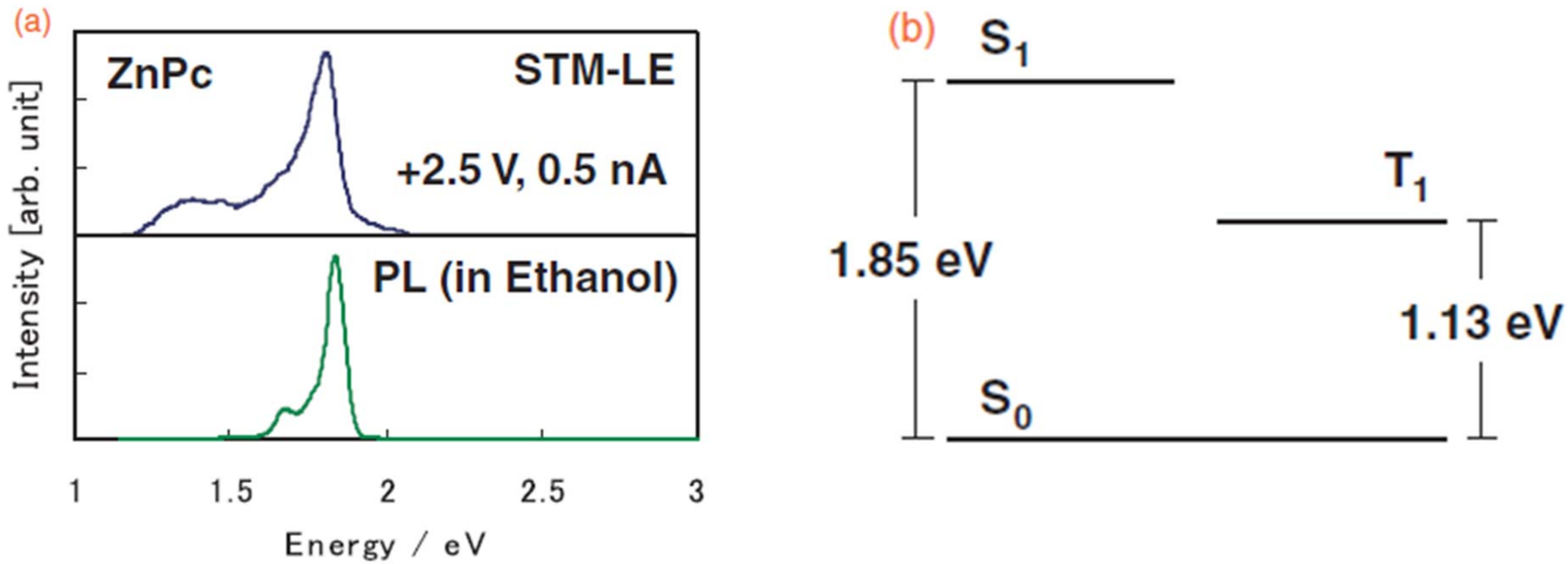
We performed a scanning-tunneling-microscopy-induced light emission (STM-LE) study on Cu- and Zn-phthalocyanine films formed on a Au(111) surface. Optical emission with transition between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) was observed at bias voltages lower than the energy corresponding to the molecular HOMO–LUMO gap. The voltage and current dependences of STM-LE intensities show an inconsistency for both samples, i.e., although the former shows the existence of onsets below the HOMO–LUMO gap energies, suggesting excitations by a two-electron process via an intermediate state, the latter shows a linear relationship expected from one-electron excitation processes.





In air, Pt/Ir tip

Tunneling Current Induced Photon Emission



Tunneling Current Induced Photon Emission

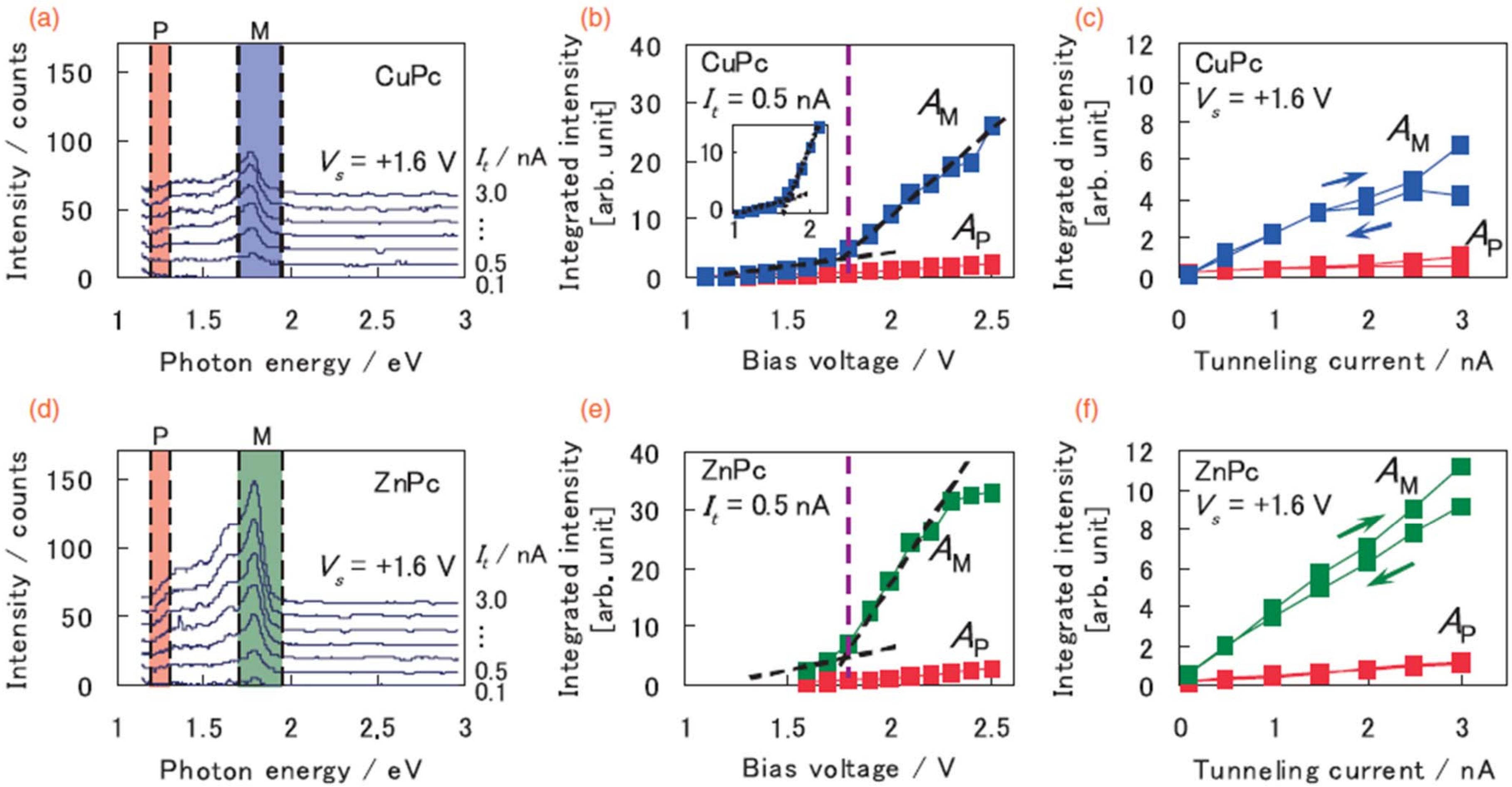


Photo induced molecule diffusion

Science AAAS

Real-Space Observation of Molecular Motion Induced by Femtosecond Laser Pulses
Ludwig Bartels, *et al.*
Science **305**, 648 (2004);
DOI: 10.1126/science.1099770

Ludwig Bartels,[1] Feng Wang,[2] Dietmar Möller,[2] Ernst Knoesel,[3] Tony F. Heinz[2]*

Femtosecond laser irradiation is used to excite adsorbed CO molecules on a Cu(110) surface; the ensuing motion of individual molecules across the surface is characterized on a site-to-site basis by in situ scanning tunneling microscopy. Adsorbate motion both along and perpendicular to the rows of the Cu(110) surface occurs readily, in marked contrast to the behavior seen for equilibrium diffusion processes. The experimental findings for the probability and direction of the molecular motion can be understood as a manifestation of strong coupling between the adsorbates' lateral degrees of freedom and the substrate electronic excitation produced by the femtosecond laser radiation.

Photo induced molecule diffusion

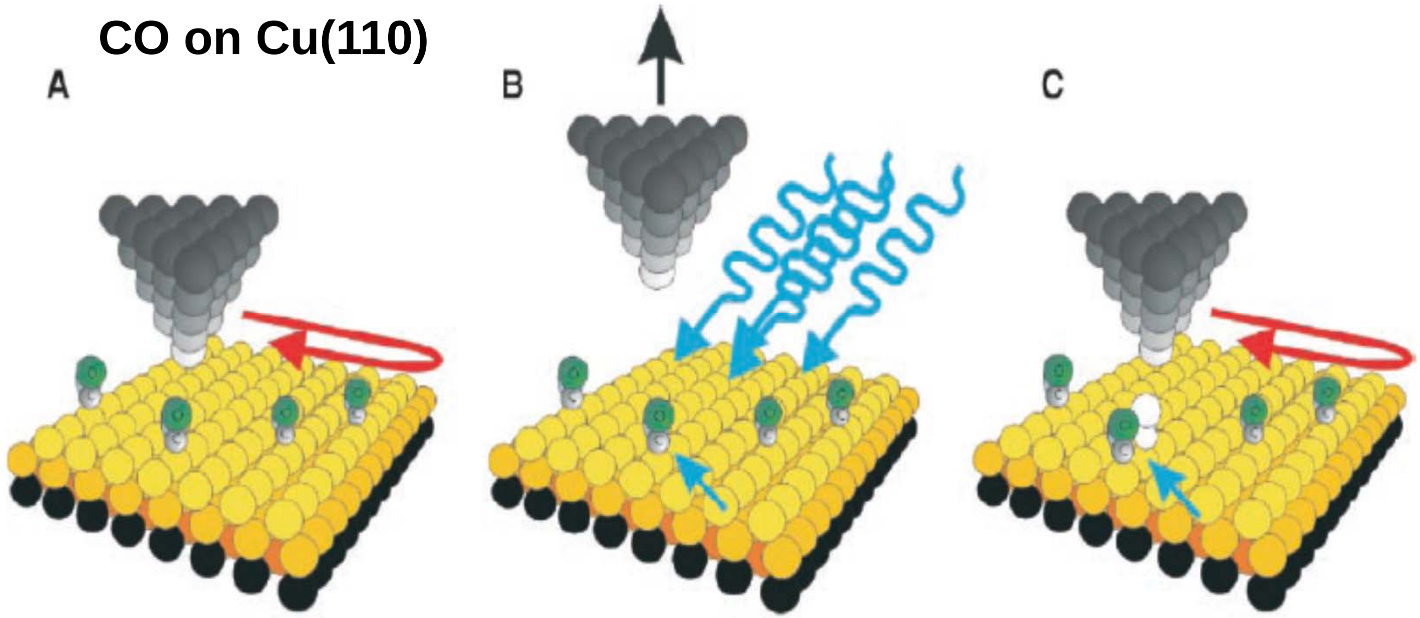
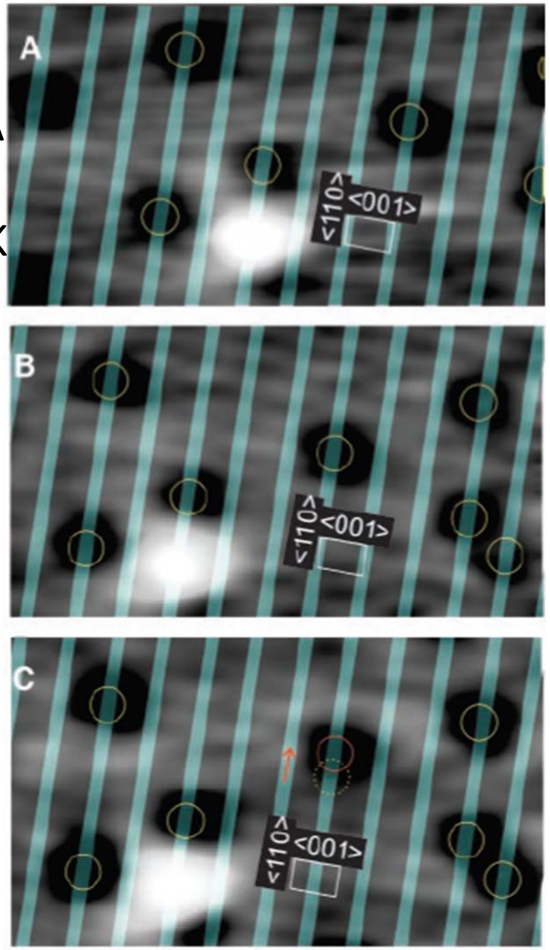


Photo induced molecule diffusion

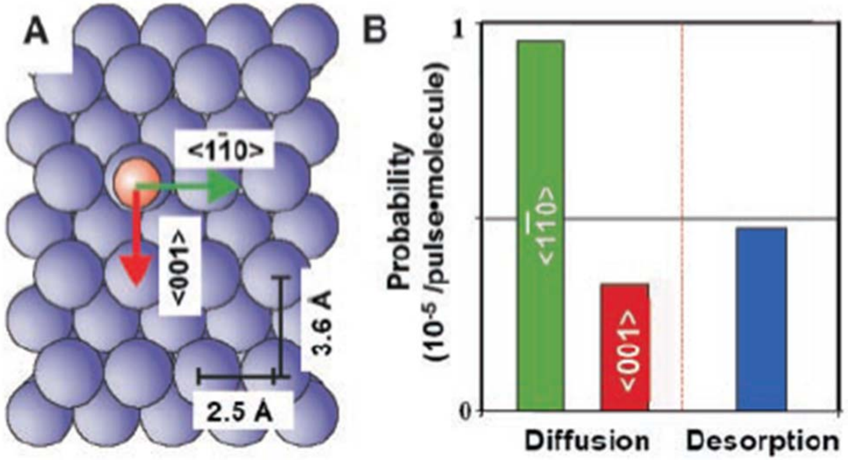
V = 1V, I = 0.2nA
Size: 50x25A
Cu(110), T = 22K

A: before laser
B: after laser
C: comparison

Laser:
200fs, 1kHz
1000 pulses



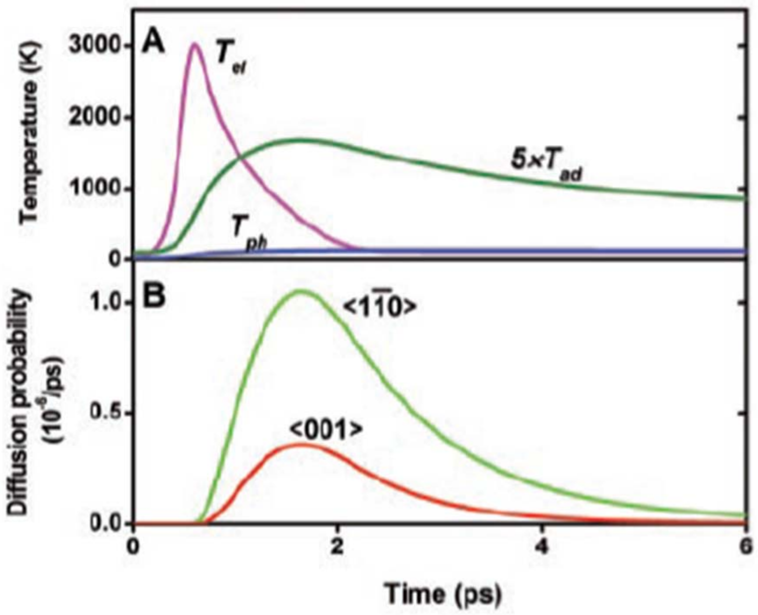
Total: 3000



Hopping along 001: never observed before

Photo induced molecule diffusion

Calculated temperature profile
T_el: Substrate electrons
T_ph: Phonons
T_ad: adsorbate



Electronic driven process

Hopping probability per laser pulse: 10^(-6)

Coupling Photons to Single Molecule

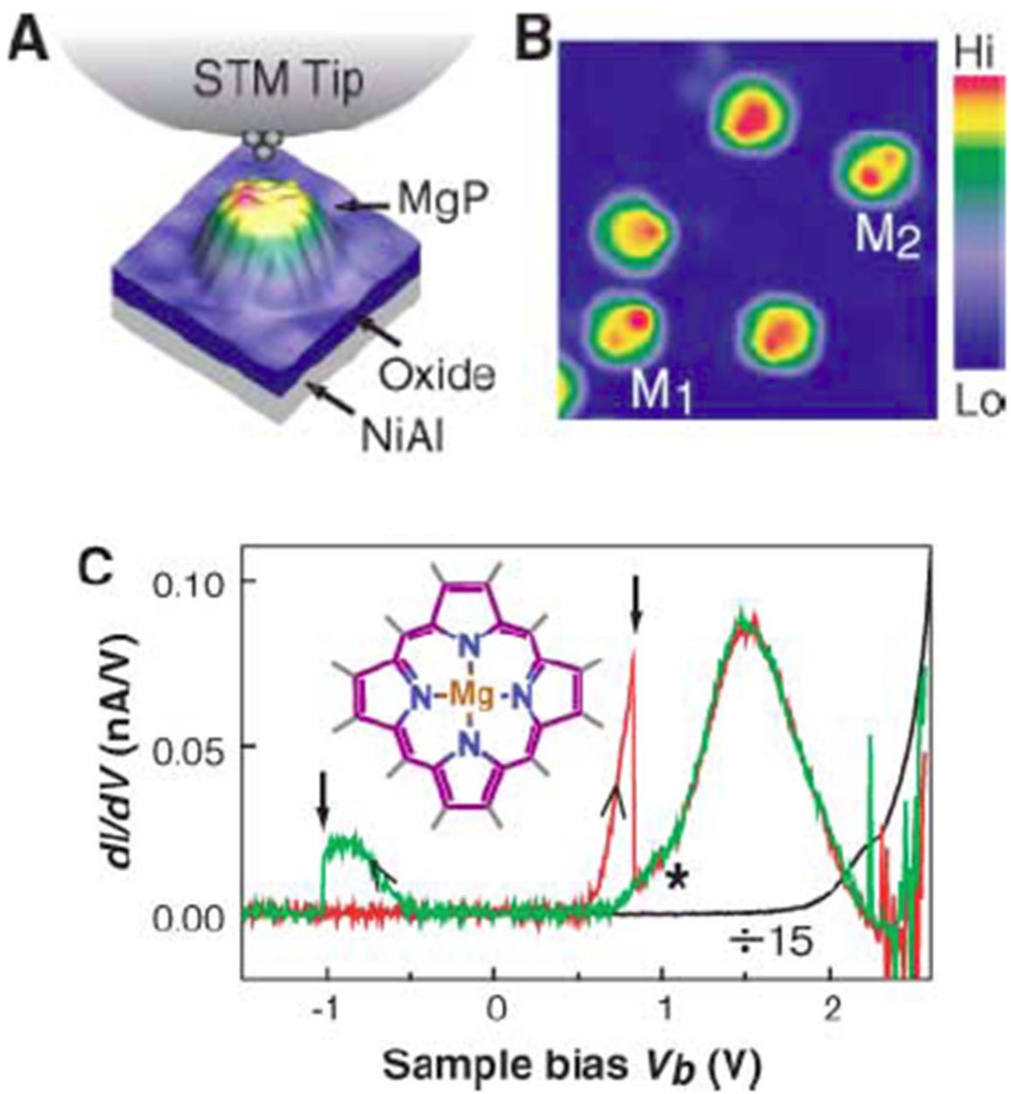
Science
AAAS

Atomic-Scale Coupling of Photons to Single-Molecule Junctions
S. W. Wu, *et al.*
Science **312**, 1362 (2006);
DOI: 10.1126/science.1124881

S. W. Wu,* N. Ogawa,* W. Ho†

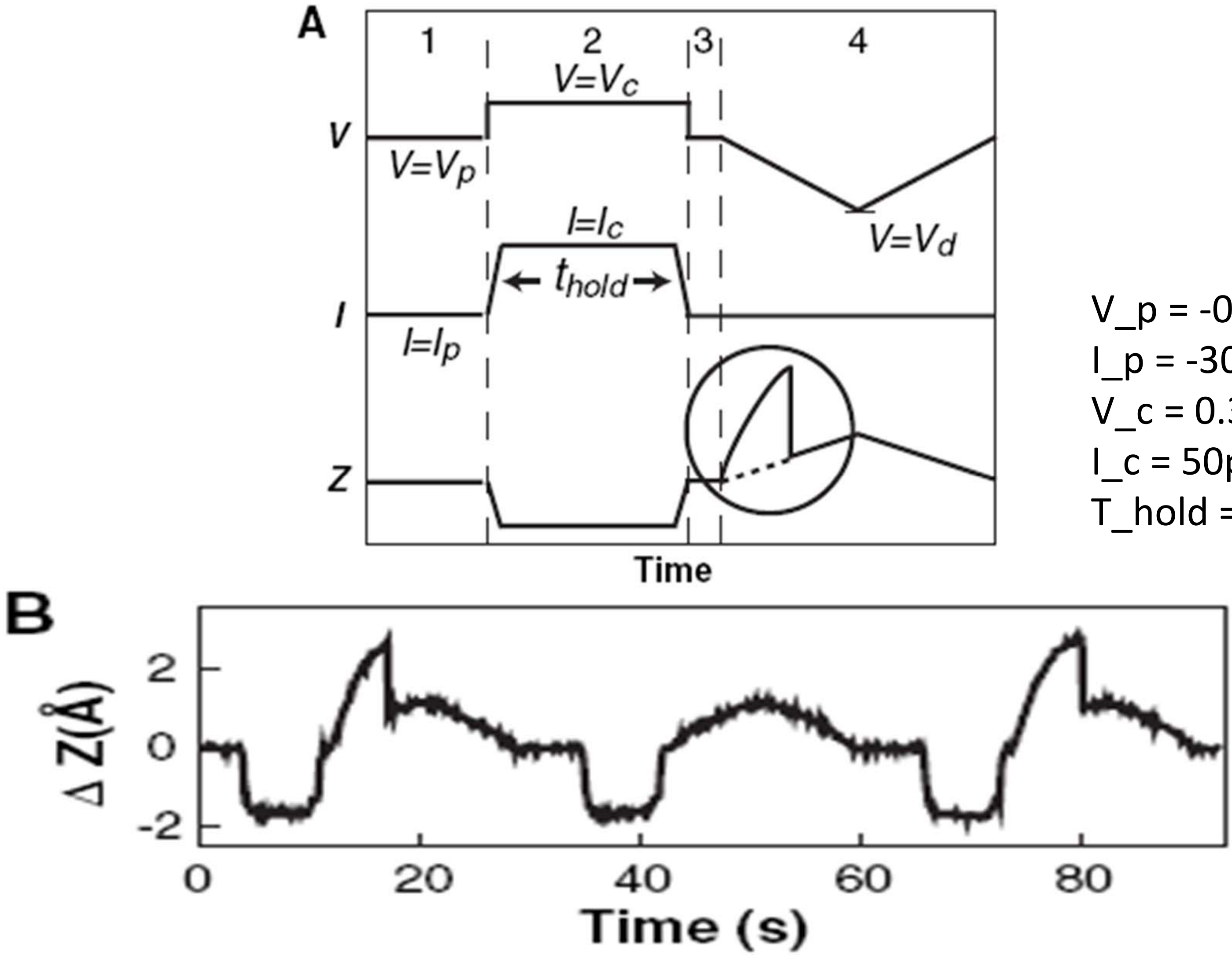
Spatial resolution at the atomic scale has been achieved in the coupling of light to single molecules adsorbed on a surface. Electron transfer to a single molecule induced by green to near-infrared light in the junction of a scanning tunneling microscope (STM) exhibited spatially varying probability that is confined within the molecule. The mechanism involves photo-induced resonant tunneling in which a photoexcited electron in the STM tip is transferred to the molecule. The coupling of photons to the tunneling process provides a pathway to explore molecular dynamics with the combined capabilities of lasers and the STM.

Coupling Photons to Single Molecule



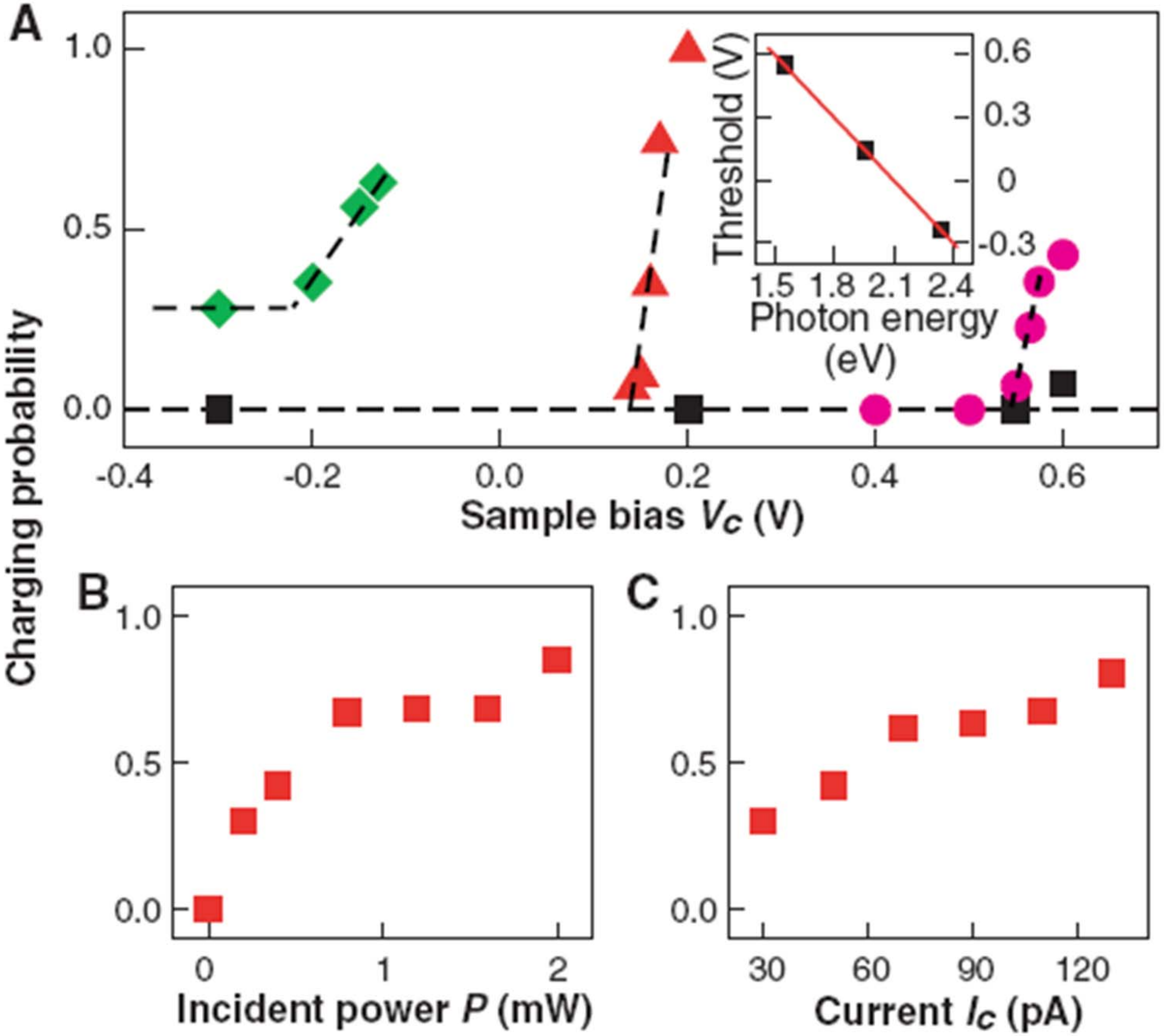
V = 1.5V, I = 30pA
Size: 11nm

Coupling Photons to Single Molecule



V_p = -0.3V,
I_p = -30pA
V_c = 0.3V
I_c = 50pA
T_hold = 5s

Coupling Photons to Single Molecule



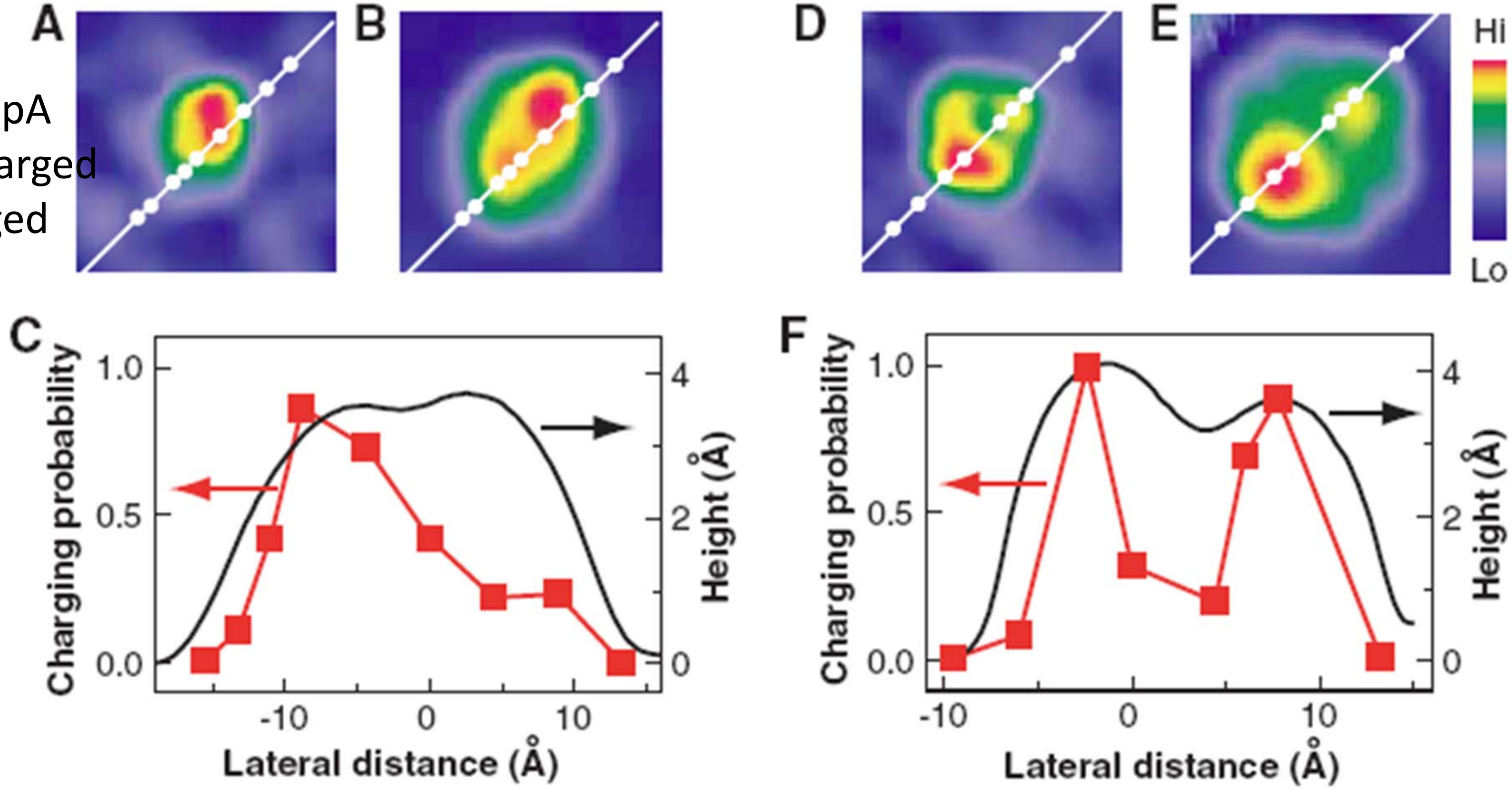
532nm
633nm
800nm
P = 0.2mW

Coupling Photons to Single Molecule

Spatial dependence of photon coupling

0.25V, 50pA
23x23A

0.3V, 50pA
A: uncharged
B: charged
34x34A

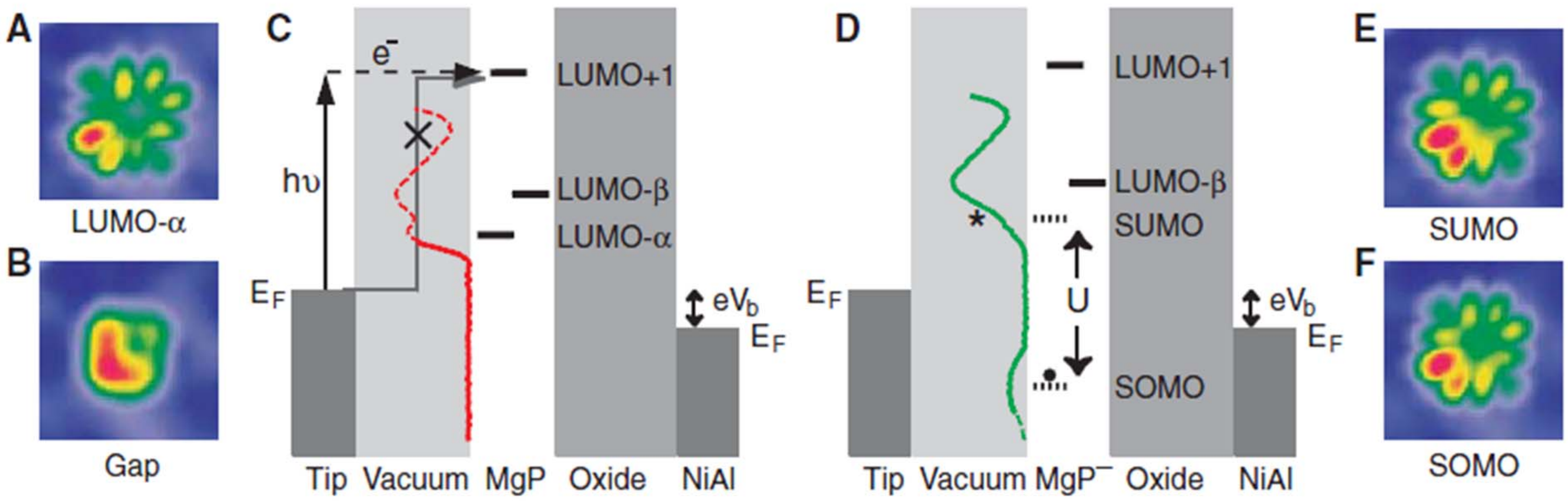


Ag Tip, 10 time better
P = 0.4mW
633nm

W Tip
P = 1.2mW
633nm

Coupling Photons to Single Molecule

Photo-induced resonant tunneling



Neutral Molecule
A: 0.57V, B: -0.4V

Charged Molecule
E: 0.75V, F: -0.4V

Surface photo voltage

SPV: the change in surface potential of a semiconductor material caused by superband gap illumination.

Usage: polarity and magnitude of surface band bending,
the recombination rate of photocarriers,
surface conductivity

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 18 3 MAY 2004

Light-modulated scanning tunneling spectroscopy for nanoscale imaging of surface photovoltage

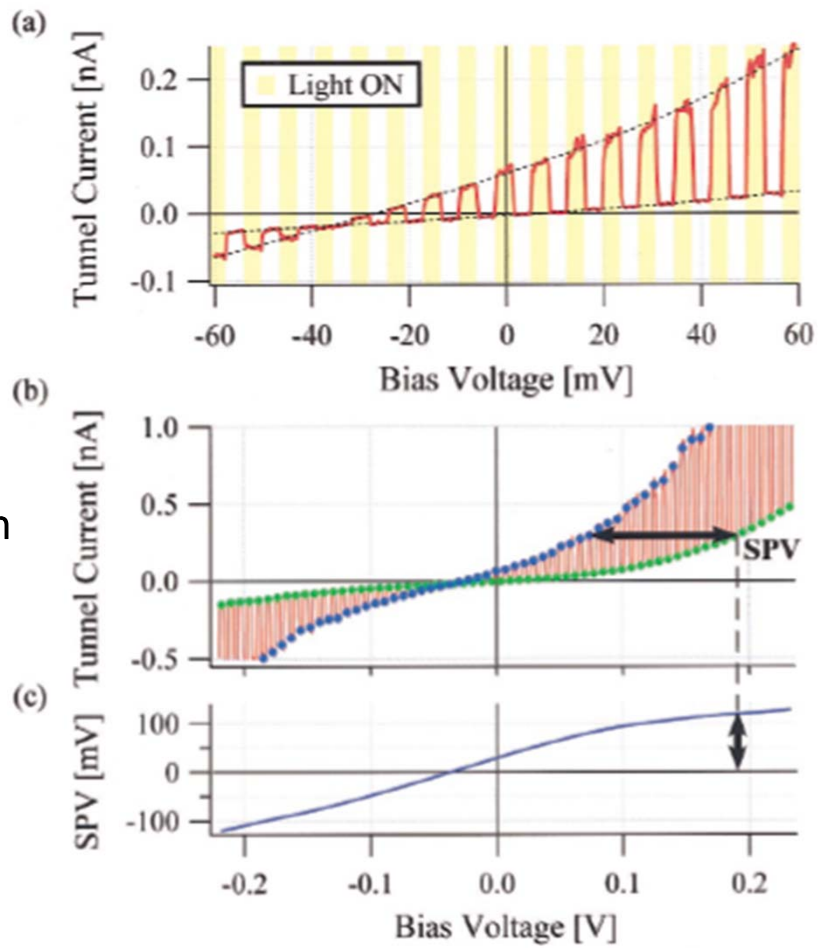
Osamu Takeuchi, Shoji Yoshida, and Hidemi Shigekawa[a)]
Institute of Applied Physics, 21st century COE, University of Tsukuba 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

(Received 16 May 2003; accepted 12 March 2004; published online 20 April 2004)

Light-modulated scanning tunneling spectroscopy (LM–STS) is proposed as a useful method for investigating spatially resolved surface photovoltage (SR–SPV). LM–STS provides the dependences of SR–SPV on bias voltage under constant tip-sample distance simultaneously with the entire dark/illuminated $I-V$ curves. With this method, it is shown that SPV of a metallic Si(111) surface can be bias-dependent and SPV at zero bias voltage for Si(001) can be tip-sample-distance-dependent under conditions of small tip-sample distance and high illumination intensity. The importance of the experimental condition for interpreting experimentally obtained SR–SPV was suggested. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1737063]

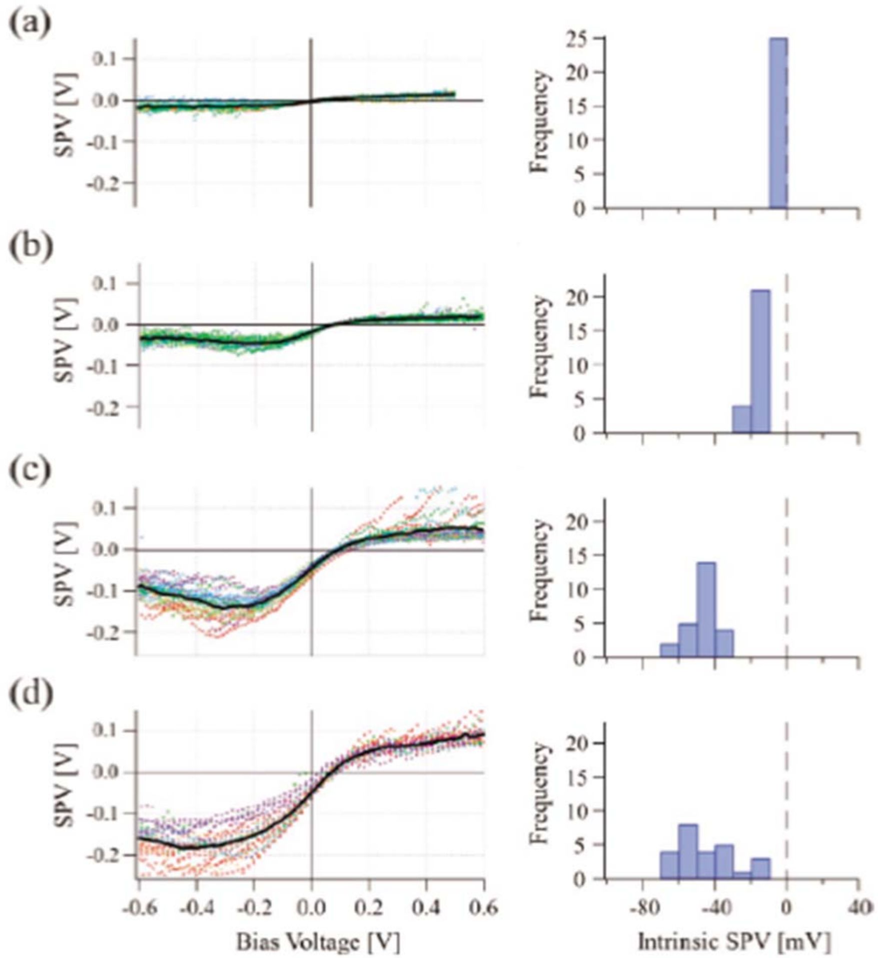
Surface photo voltage

W tip
Laser: 325nm, 441nm
Power < 1mW
Chopping: 40Hz

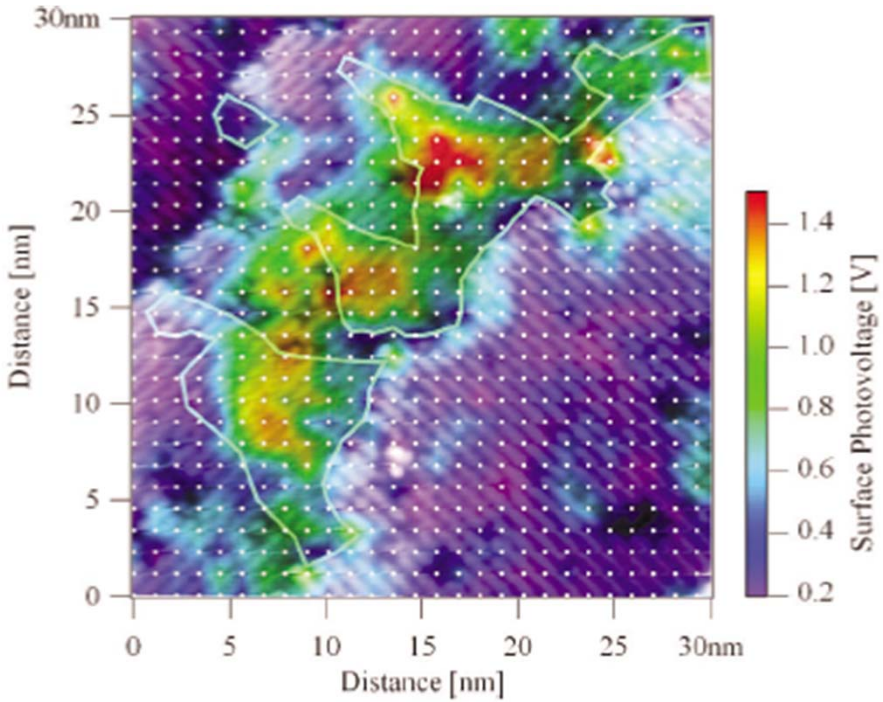


Surface photo voltage

Setpoint: 1nA
V:
0.3V
0.4V
0.5V
0.6V



Surface photo voltage



Ag island on Si(001), V = 2.4V

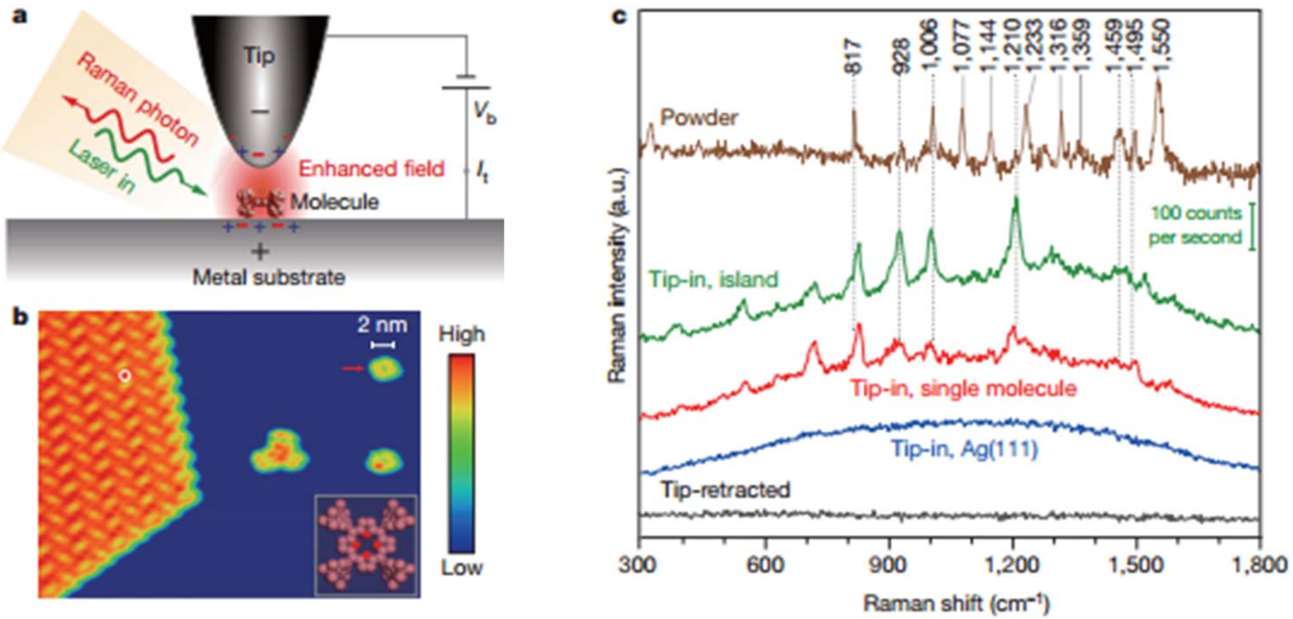
Tip enhanced Raman scattering

LETTER

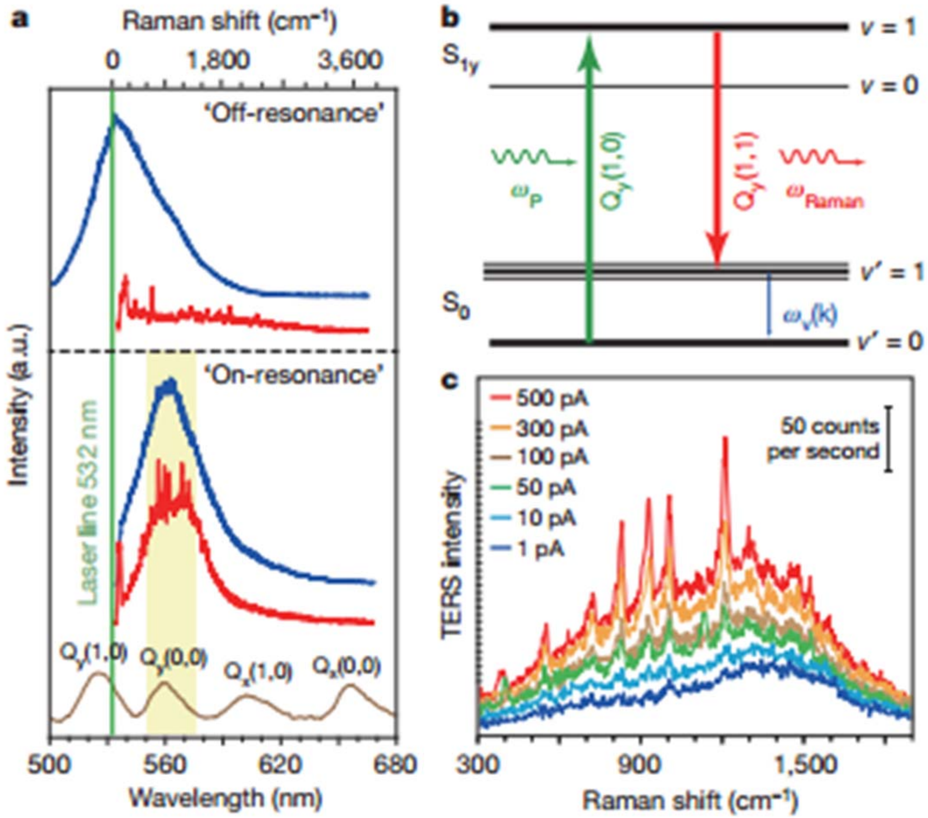
doi:10.1038/nature12151

Chemical mapping of a single molecule by plasmon-enhanced Raman scattering

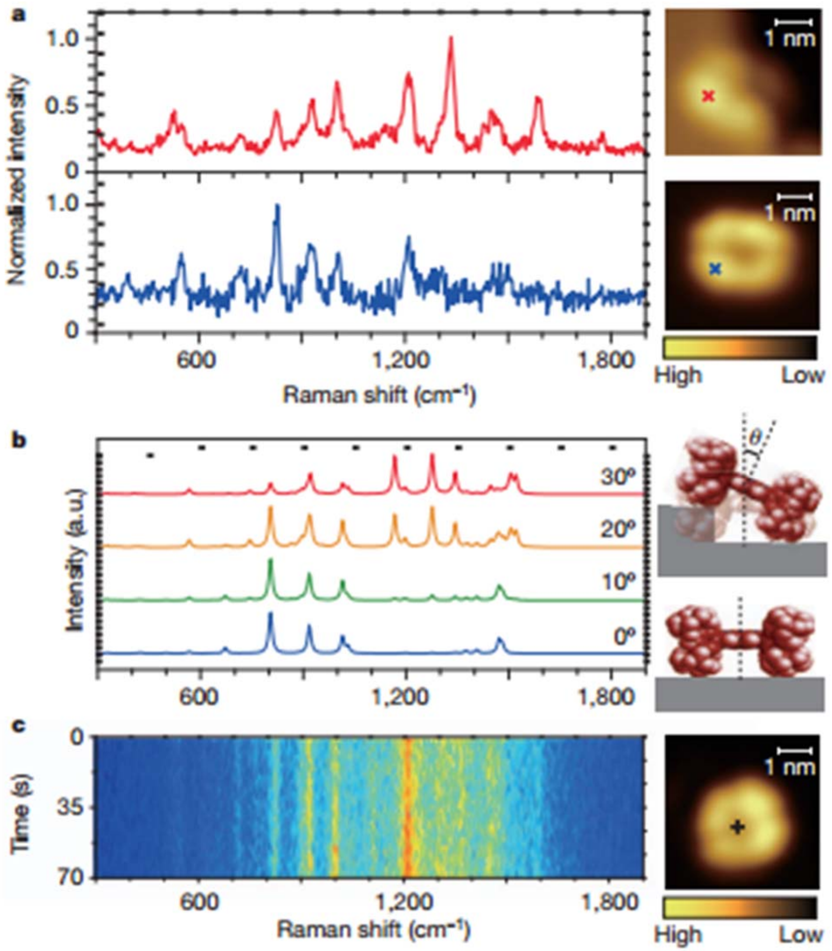
R. Zhang[1]*, Y. Zhang[1]*, Z. C. Dong[1], S. Jiang[1], C. Zhang[1], L. G. Chen[1], L. Zhang[1], Y. Liao[1], J. Aizpurua[2], Y. Luo[1,3], J. L. Yang[1] & J. G. Hou[1]



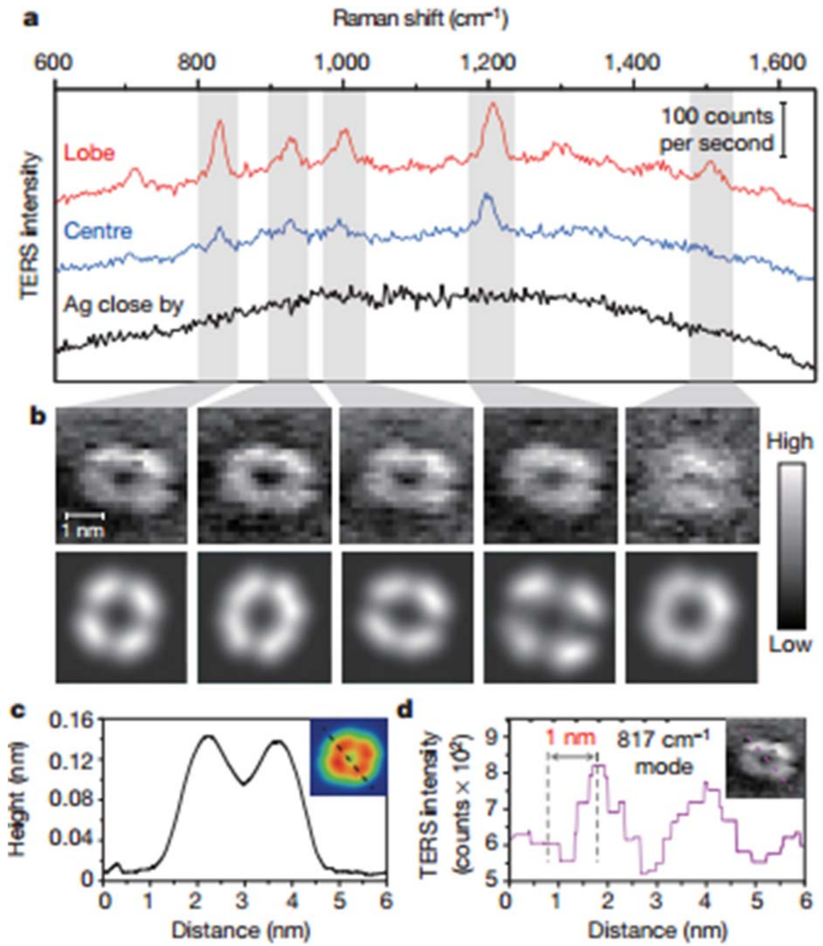
Tip enhanced Raman scattering



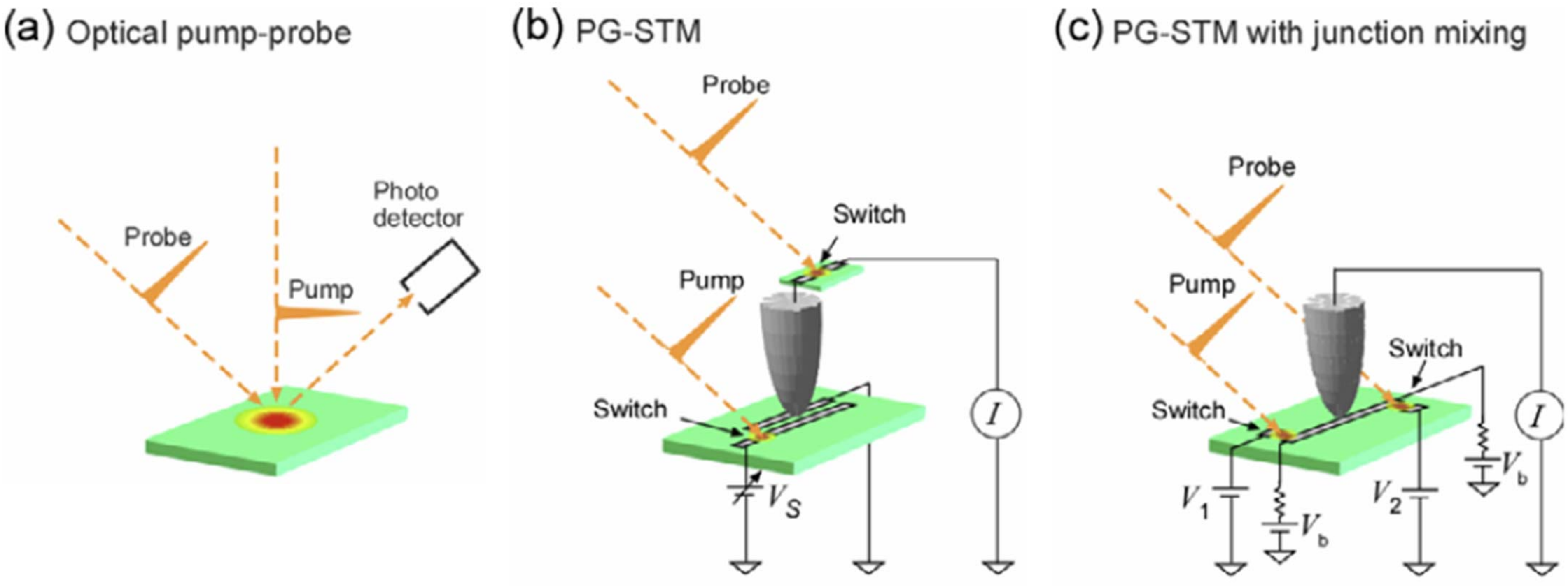
Tip enhanced Raman scattering



Tip enhanced Raman scattering



Ultrafast Time Resolution



Ultrafast Time Resolution