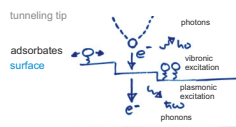


Motivation

Bottom up understanding of the electronic transport processes within organic molecules

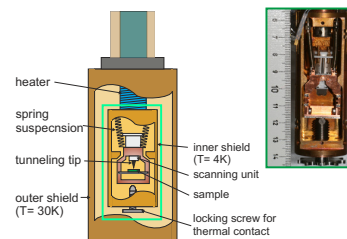
- beside the elastic tunneling processes in a scanning tunneling microscopy (STM) experiment, also a fraction of inelastic processes take place
- e.g. plasmonic or vibronic excitation of the sample may be induced by the injection of electrons
→ relaxation via light emission
- characterisation of individual molecules with submolecular spatial resolution



Low Temperature-STM

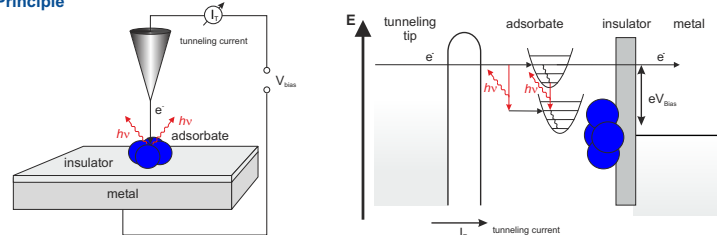
Compact design homebuilt system

- entire scanning unit cooled to 7K (80K) with liquid He (N_2) using a continuous flow cryostat
- temperature stability is maintained for several days (N_2) / weeks (N_2)
- tips can easily be exchanged during the experiment
- transferable molecular evaporators allow for an evaporation of molecules onto the cooled sample within the STM (30K)



STM Induced Light Emission (STM-LE)

Principle

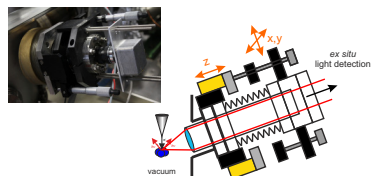


- hot electrons are injected into the adsorbate by the tunneling tip
- most electrons tunnel elastically, i.e. without losing energy
- a small part of the electrons (approx. 10^{-7} - 10^{-8}) tunnels inelastically

- inelastic tunneling processes may excite plasmonic or vibronic states at the surface
- the relaxation may follow different pathways, e.g. a radiative decay
→ emission of photons

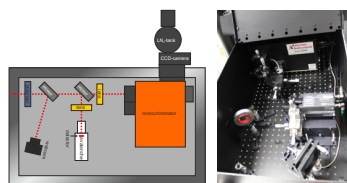
X.H. Qui, G. V. Nazin, W. Ho, Science **299**, 542 (2003)
R. Berndt et al., Science **252**, 1425 (1993)

In situ light collection



- the light is collected by a lens inside the vacuum system
- position of the lens can be adjusted in x,y- (commercial gimbal) and z- (homebuilt adjustment unit) direction
- detection table is parallel to the light path
→ no additional mirrors needed

Ex situ light detection



- light is detected outside the vacuum system
- the photons can be focused on either a webcam, an avalanche diode or a monochromator with an attached CCD-camera
- optionally, a polarising filter, etc. can be placed into the optical path

Latest Changes of the STM-LE

Scanning Unit

- to increase the photon count rate the aperture in the sample stage is enlarged
- three point support of sample holder on stainless steel balls
- springs are pushing onto the sample carrier from above to ensure a safe fixation of the sample holder

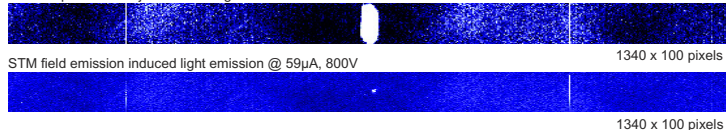
Shields

- additional window was added to detect the photons when the shields are closed
- to reduce heating by thermal radiation during the experiment, an ITO coated glass sheet is placed in front of the window

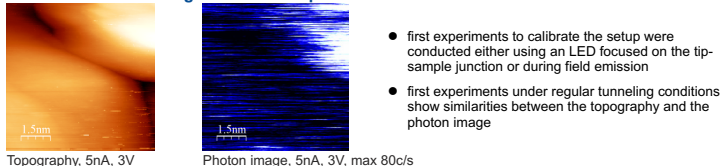
First Measurements

Photon detection using a CCD detector @ RT

LED coupled to STM junction for alignment



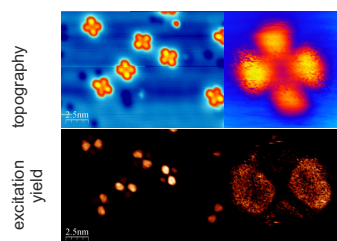
Photon detection using an Avalanche photo diode



- first experiments to calibrate the setup were conducted either using an LED focused on the tip-sample junction or during field emission
- first experiments under regular tunneling conditions show similarities between the topography and the photon image

Tunneling Current Induced Excitation of Individual Phthalocyanine and Porphyrin Molecules

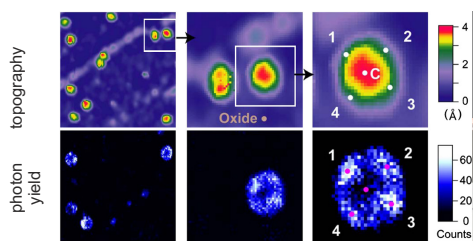
Möller Group: molecular switching



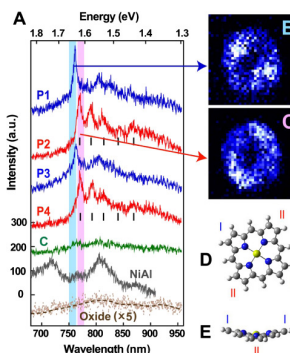
Individual copper phthalocyanine (CuPc) molecules on Cu(111). $V_{bias} = 2V$, $I = 100pA$. The individually adsorbed CuPc molecules show a tunneling current induced molecular switching.

J. Schaffert et al., Nature Materials **12**, 223 (2013)

Ho Group: STM-LE



Individual magnesium porphyrine (MgP) molecules on $Al_2O_3/NiAl(110)$. $V_{bias} = 2.2V$, $I = 200pA$. Scan size from left to right: $24nm \times 24nm$, $6.8nm \times 6.8nm$, $3.5nm \times 3.5nm$. The individually adsorbed MgP molecules show a tunneling current induced photoemission.



(A) Vibrionically resolved emission spectra taken at five positions inside the MgP molecule, on the oxidized substrate (Al_2O_3), and the metal substrate (NiAl). (B), (C) Photon images of individual vibronic peaks. $V_{bias} = 2.3V$, $I = 400pA$. Scan size for both images: $3.5nm \times 3.5nm$. (D), (E) Top and side view of the molecular structure of MgP.

Chi Chen, ..., C.A. Bobisch, W. Ho et al., PRL **105**, 217402 (2010)

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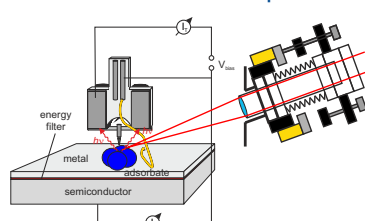
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Outlook

Combined BEEM and STM-LE experiments at low temperatures

- ballistic electron emission microscopy (BEEM) experiments at low temperatures down to 7K
- combination of two complementary techniques
→ comprehensive characterization of individually adsorbed molecules and thin organic layers
- measurements with ultimate stability and spatial resolution
- bottom up approach to future electronic devices



Bell, L. D. and Kaiser, W. J., Physical Review Letters **61** (20), 2368 (1988)

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