Atomic scale investigation of low-energy excitation at surface and interface by inelastic electron tunneling spectroscopy

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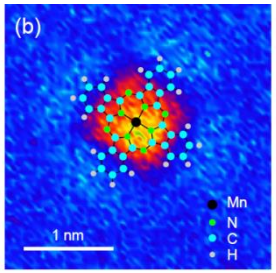
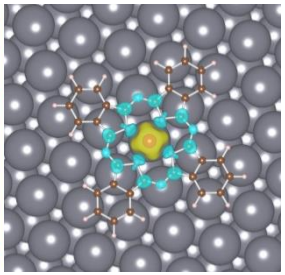
Research Interests

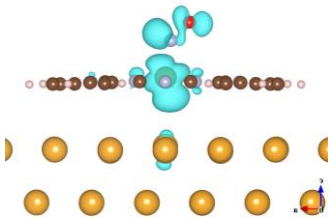
nano magnetism

Kondo effect, spin-orbit interaction, magnetic anisotropy

E. Minamitani, N. Tsukahara et al., Phys. Rev. Lett. 109, 086602 (2012)
E. Minamitani, Y. Fu et al., Phys. Rev. B 92, 075144(2015)
R. Hiraoka, E. Minamitani et al., Nat. Commun, 8, 16012(2017)



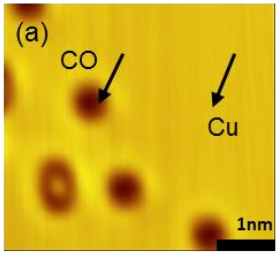


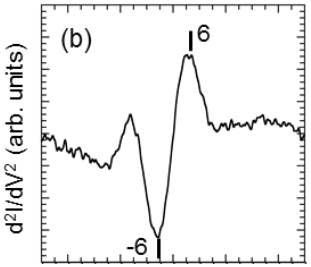


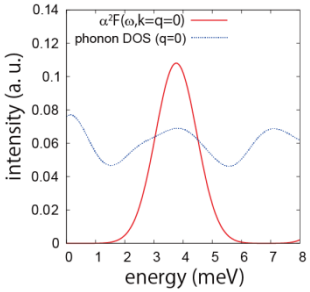
phonon

electron-phonon coupling

E. Minamitani, R. Arafune et al., Phys. Rev. B 88, 224301(2013)
E. Minamitani, R. Arafune et al., Phys. Rev. B 93, 085411(2016)



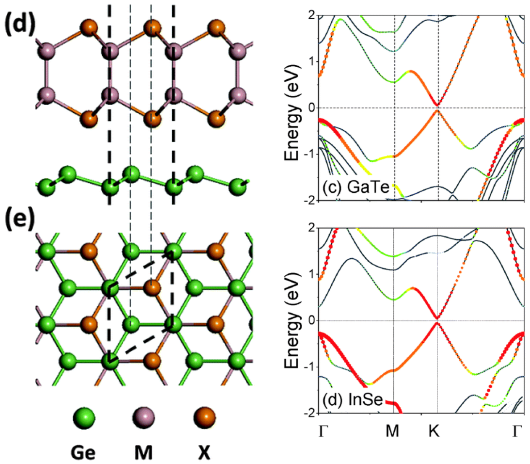




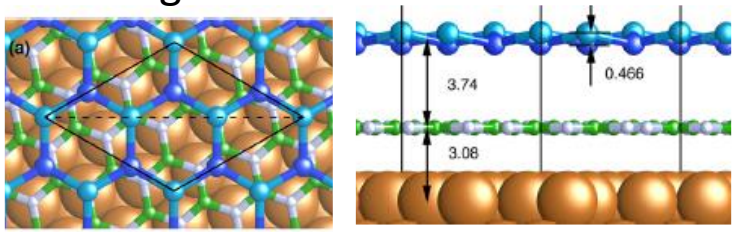
interactions at surface/interfaces

layered materials

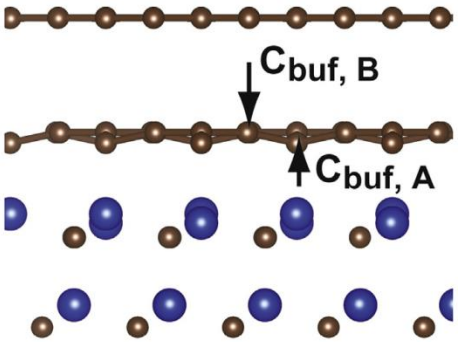
graphene, silicene, germanene etc…



Z. Ni, Phys. Chem. Chem. Phys, 17, 19039 (2015)



M. Kanno et al., New. J. Phys. 16 (2014) 105019



E. Minamitani, R. Arafune, T. Frederiksen, T. Komeda et al., Phys. Rev. B 96, 155431 (2017)

Collaborators

Experiment

Institute for Molecular Science

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Graduate School of Human and Environmental Studies, Kyoto University

Prof. Noriaki Takagi

National Institute for Materials Science

Dr. Ryuichi Arafune

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Prof. Tadahiro Komeda, Dr. Noriyuki Tsukahara

Theory

Department of Materials Engineering, the University of Tokyo

Prof. Satoshi Watanabe

Donostia International Physics Center

Prof. Thomas Frederiksen

Graduate School of Science and Engineering, the University of Toyama

Prof. Hiromu Ueba

Outline

Introduction

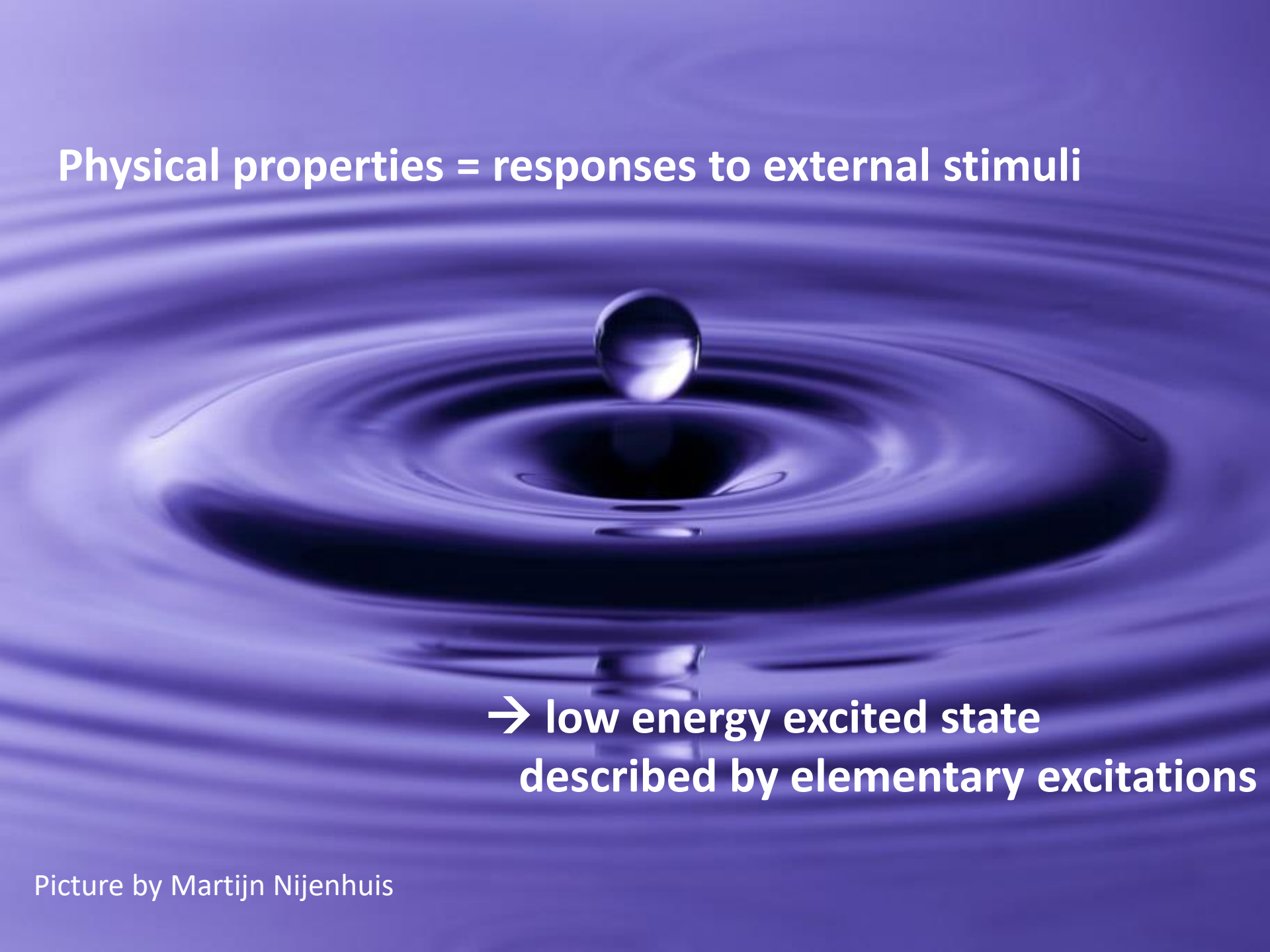
elementary excitation in solid and inelastic spectroscopy
→inelastic spectroscopy by scanning tunneling microscope (STM-IETS)

↓ phonon & spin at surfaces/interfaces

1. Application of STM-IETS to metallic solid surface
- Cu(110) surface

2. Application of STM-IETS to solid interface
- Graphene/SiC(0001)

3. Application of STM-IETS to spin excitation
- Fe-phthalocyanine/Au(111)

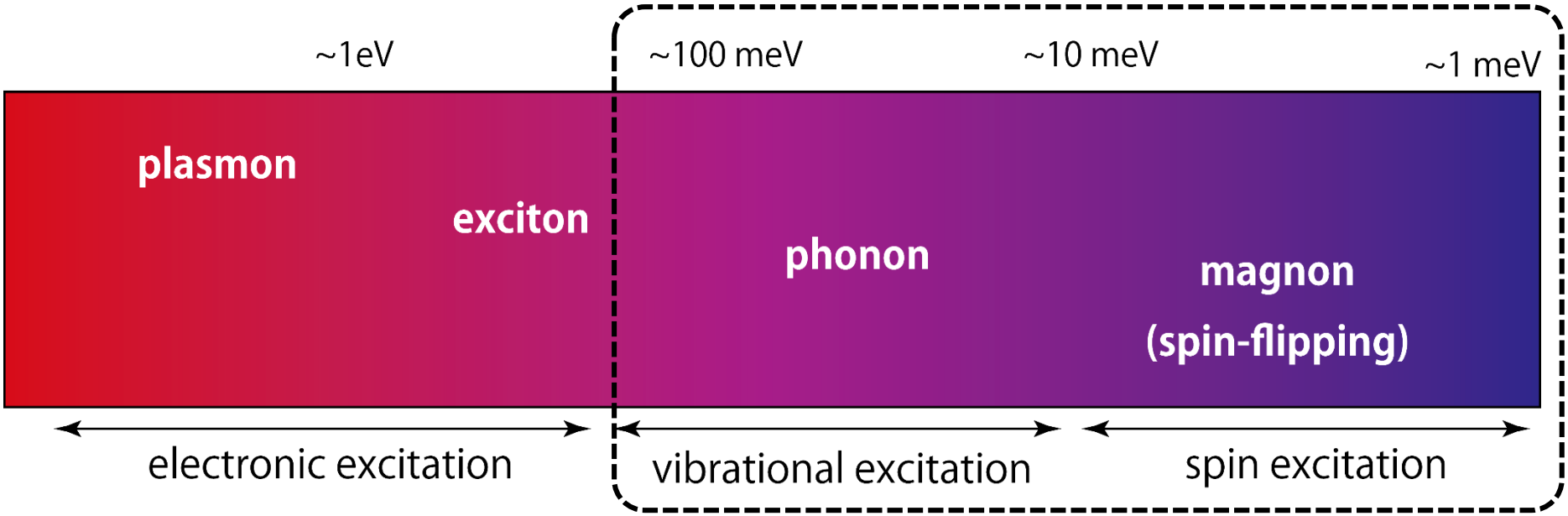


Physical properties = responses to external stimuli

→ low energy excited state described by elementary excitations

Picture by Martijn Nijenhuis

Energy scale of elementary excitations



targets of this research

How to observe these low-energy elementary excitations?

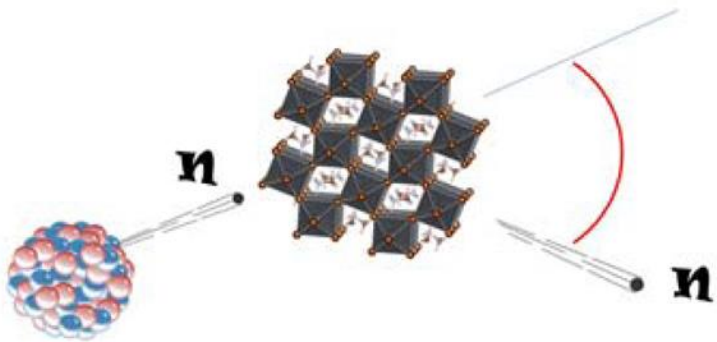
Energy conservation law + inelastic scattering process

→ inelastic scattering spectroscopy

Inelastic scattering spectroscopies

Inelastic neutron scattering

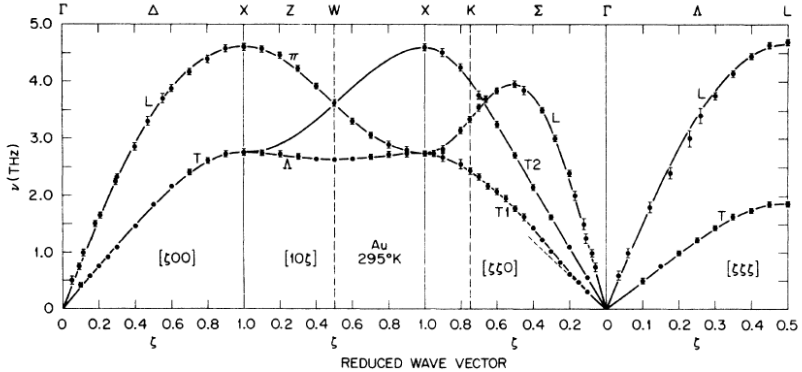
phonon
magnon



Energy loss
+ angle distribution

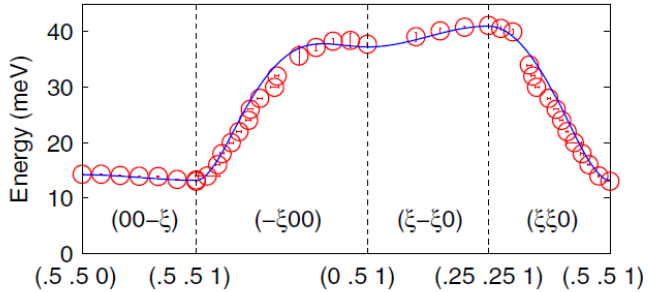
A. Létoublon et al., J. Phys. Chem. Lett. 7, 3776 (2016)

Phonon of Au bulk



J.W. Lynn et al., Phys. Rev. B, 8, 3493 (1973)

Magnon of Ca_2RuO_4



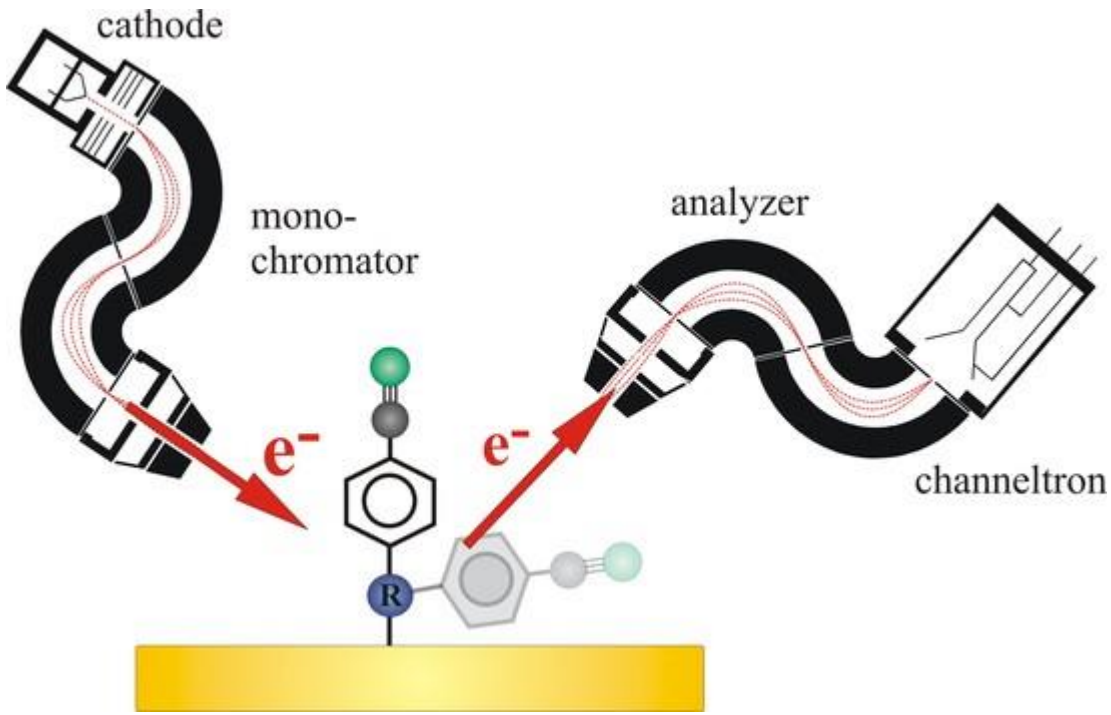
S. Kunkemöller et al., Phys. Rev. Lett. 115, 247201 (2015)

Very high accuracy for phonon & magnon dispersion in bulk.

But, need a huge equipment including nuclear reactor.

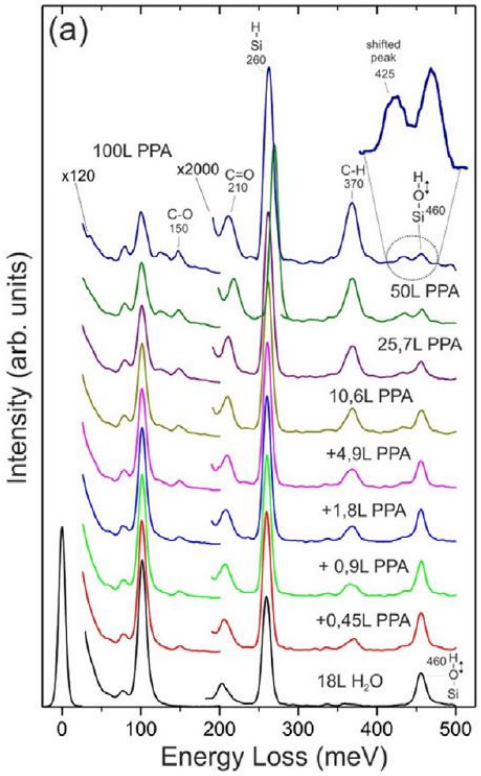
High-resolution electron energy loss spectroscopy (HREELS)

Detecting energy loss of electron during scattering at surface



http://www.uni-heidelberg.de/fakultaeten/chemgeo/pci/tegeder

Vibration of H, OH on Si(001)-2x1



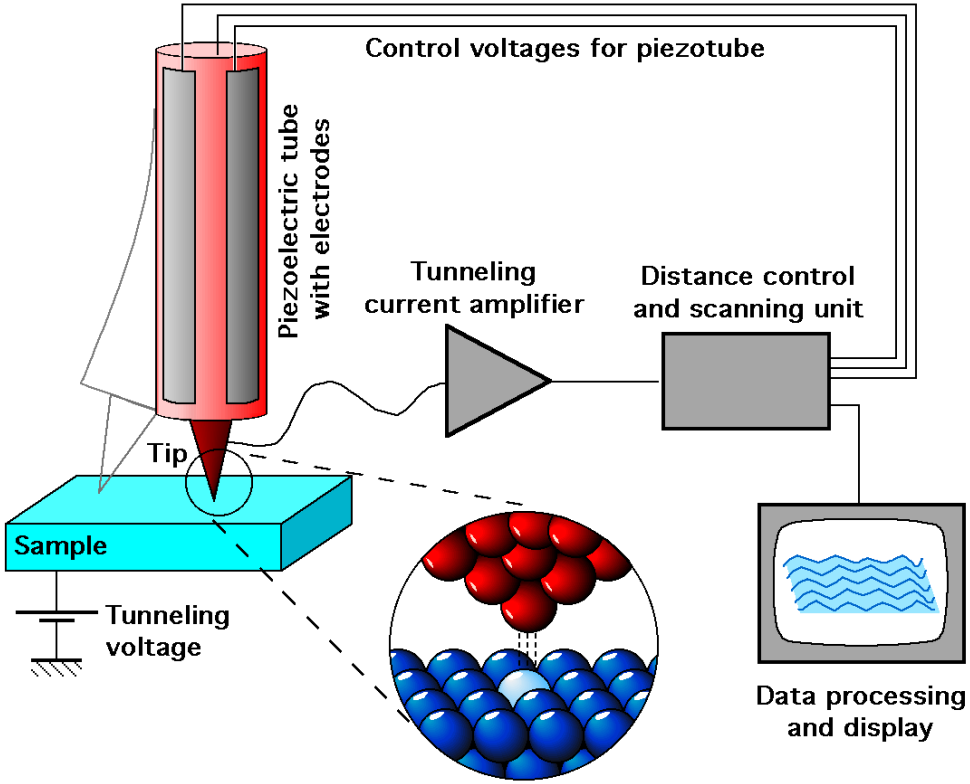
F. Bournel et al., JPCM, 27, 054005 (2015)

Surface sensitive, structure information

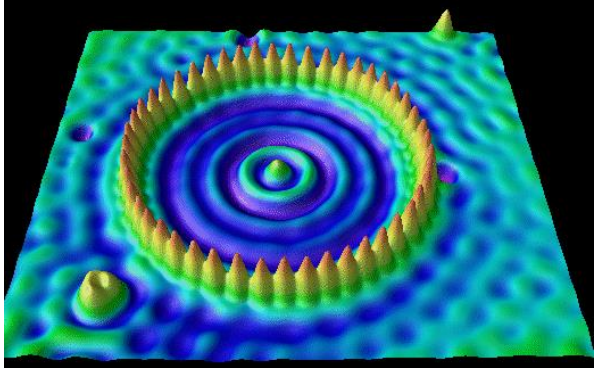
How to archive atomic scale spatial resolution by electron spectroscopy?
→ Combine scanning tunneling microscope + electron energy loss spectroscopy

Scanning tunneling Microscope (STM)

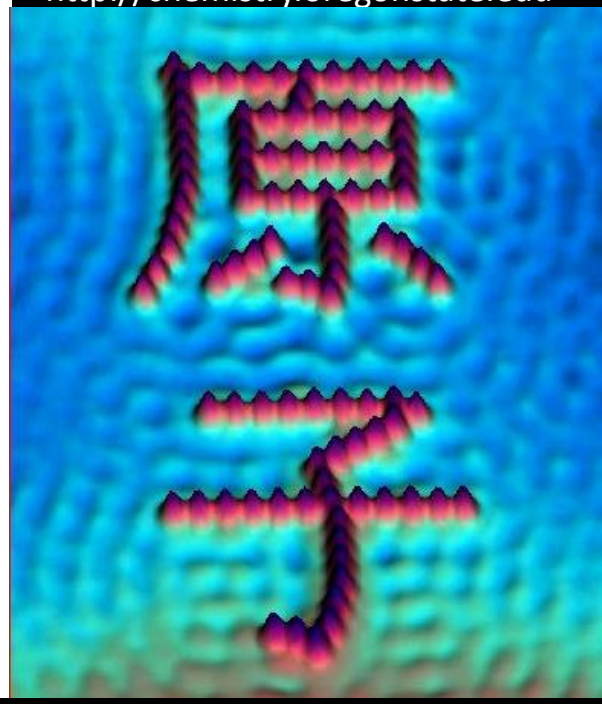
G. Binnig & H. Rohrer (in 1982)



Typical schematic image taken from Wikipedia



http://chemistry.oregonstate.edu

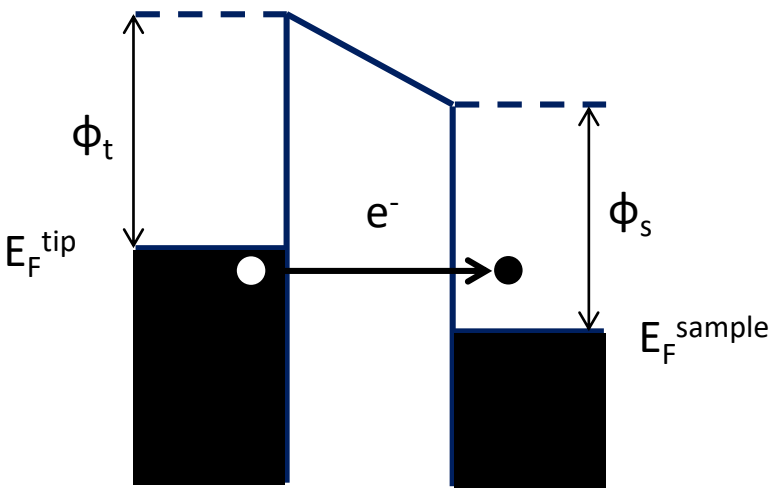


Image, manipulate & measure the electronic state at atomic scale

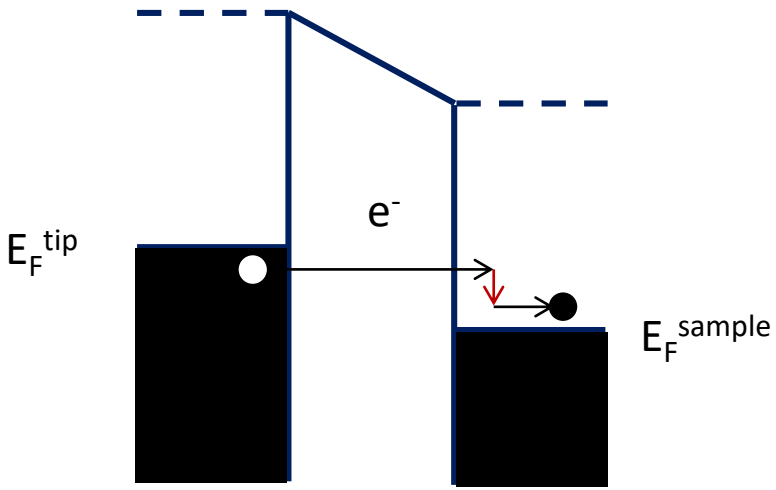
Inelastic electron tunneling spectroscopy by STM

Scanning tunneling spectroscopy with **energy loss**

STM/STS



STM-IETS



STS: scanning tunneling spectroscopy

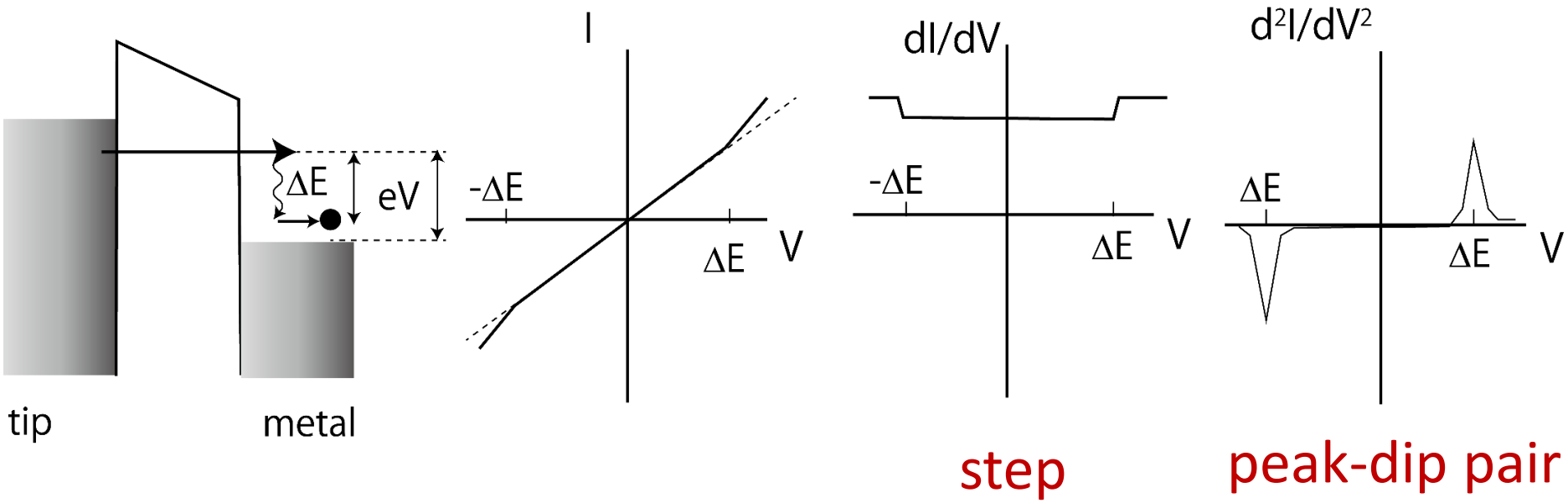
without energy loss
related to DOS

IETS: inelastic electron tunneling spectroscopy
include energy loss by **low energy excitation**
(spin, phonon)

IETS spectrum

The change of tunneling current induced by inelastic excitation is small

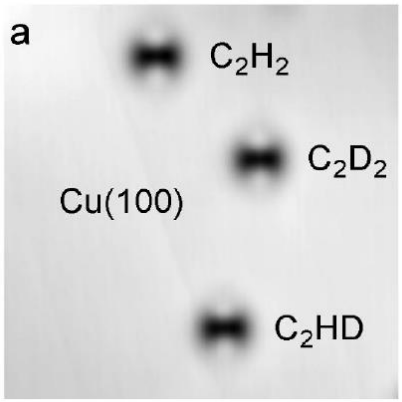
→ taking derivative as a function of bias voltage V

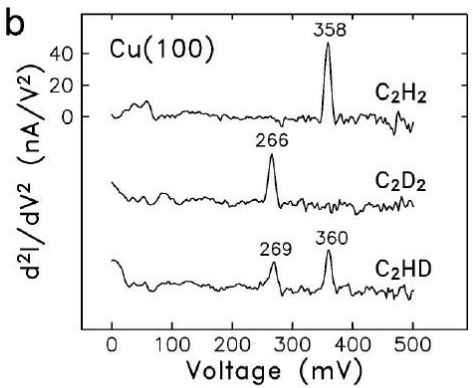


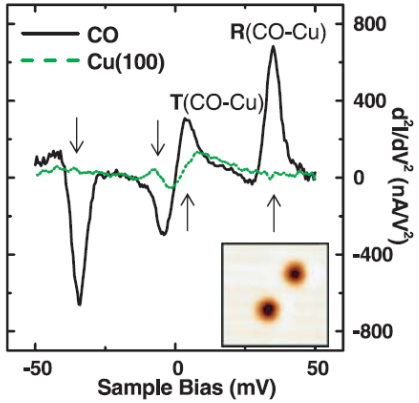
phonon spectroscopy at surface with meV energy and atomic spatial resolution

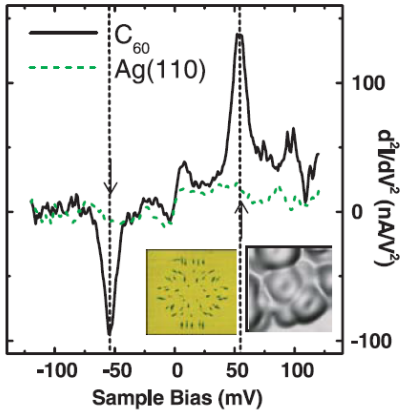
Applications of STM-IETS to single molecule

Molecular fingerprint







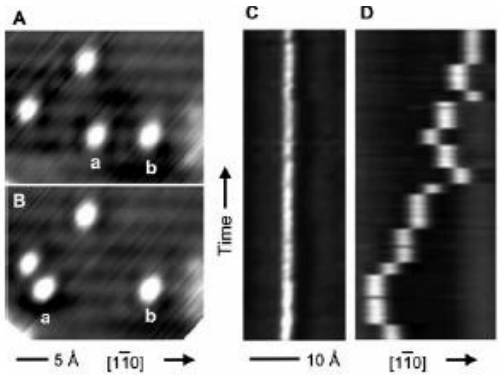


B. C. Stipe et al., Phys. Rev. Lett. **82**, 1724 (1999)

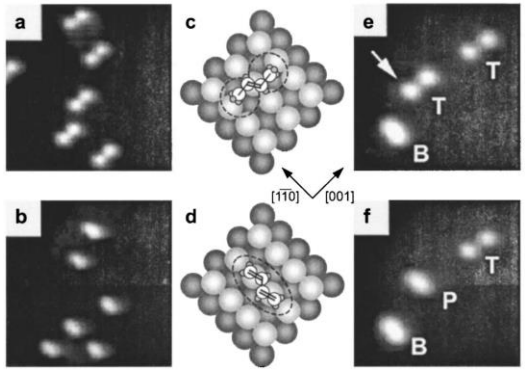
J. I. Pascual, Eur. Phys. J. D **35**, 327 (2005).

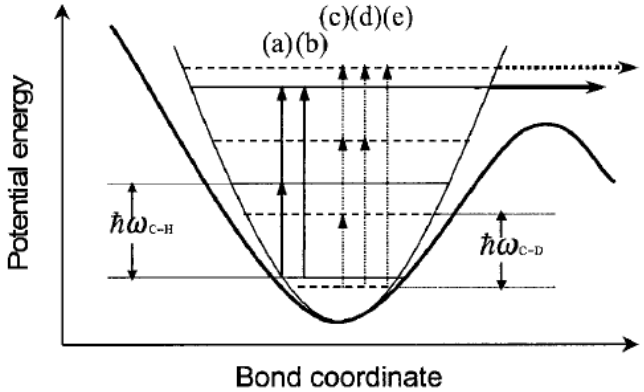
Dynamics & chemical reaction

CO on Pd(110)



trans-2-butene to 1,3-butadiene on Pd(110)





T. Komeda, Y. Kim, M. Kawai, B. N. J. Persson, H. Ueba, Science **295**, 2055 (2002).

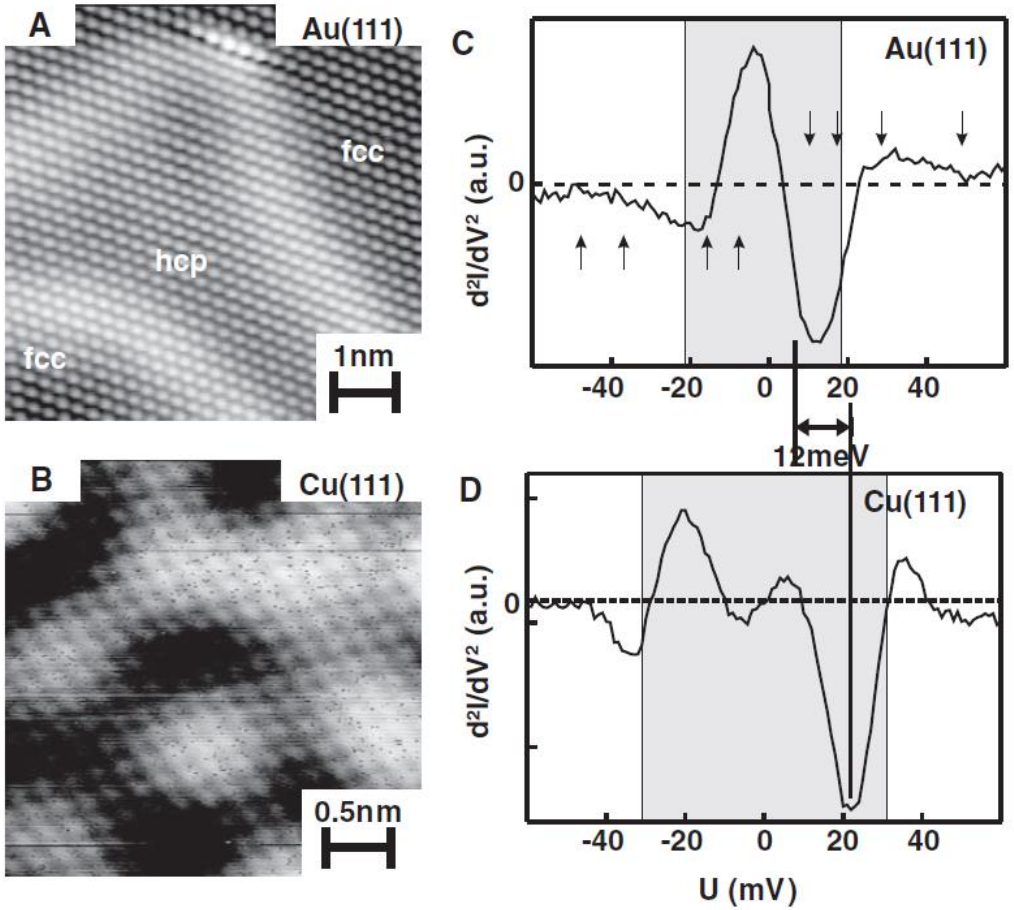
Y. Kim, T. Komeda, and M. Kawai, Phys. Rev. Lett. **89**, 126104 (2002).

Is it possible to apply STM-IETS to more various targets?

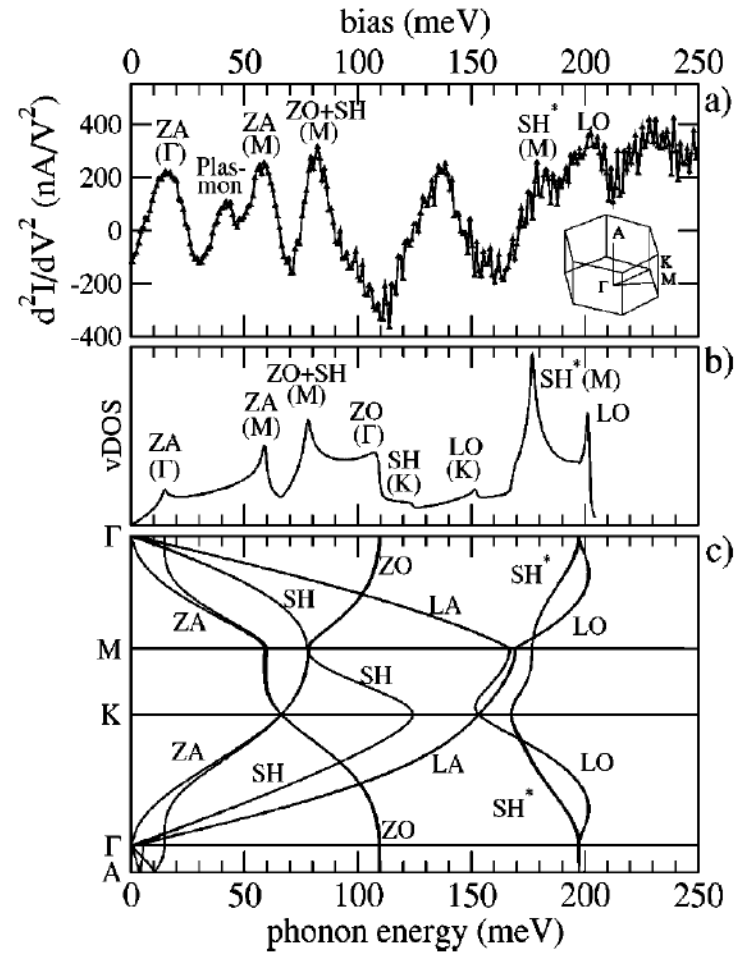
Applications of IETS to solid surface & interface

Example of IETS at solid surface

Au(111) & Cu(111)



Graphite

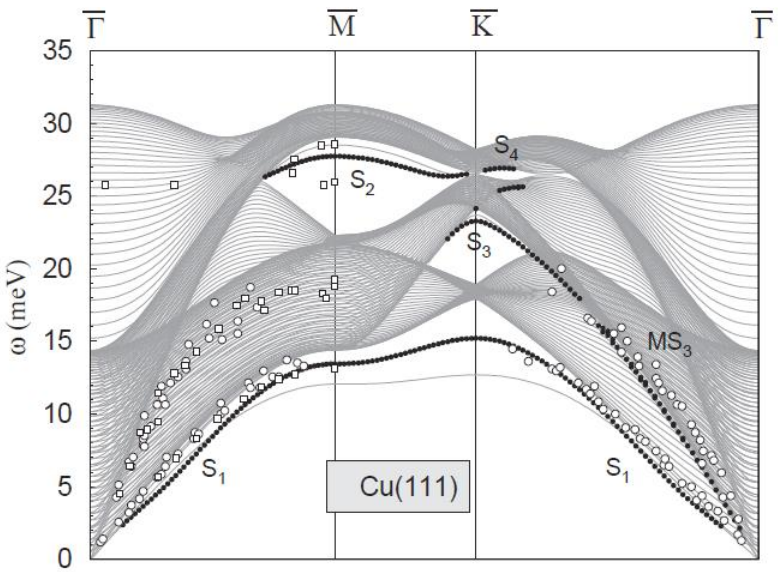


H. Gawronski et al., Science, 319 (2008) 930

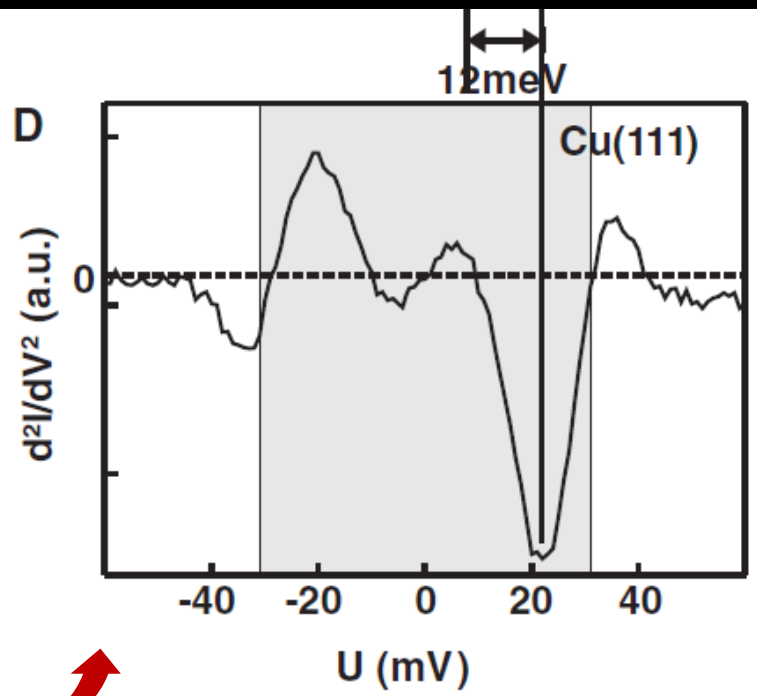
L. Vitali et al., Phys. Rev. B, 69, 121414 (2014)

Puzzles in IETS spectrum at solid surface

The phonon dispersion and density of states are **continuous**.
A lot of phonon modes can be excited by tunneling electron.
But **only some specific modes** appear in IETS spectrum.



R. Heid & K. –P. Bohnen
Phys. Rep. **387** (2003) 151



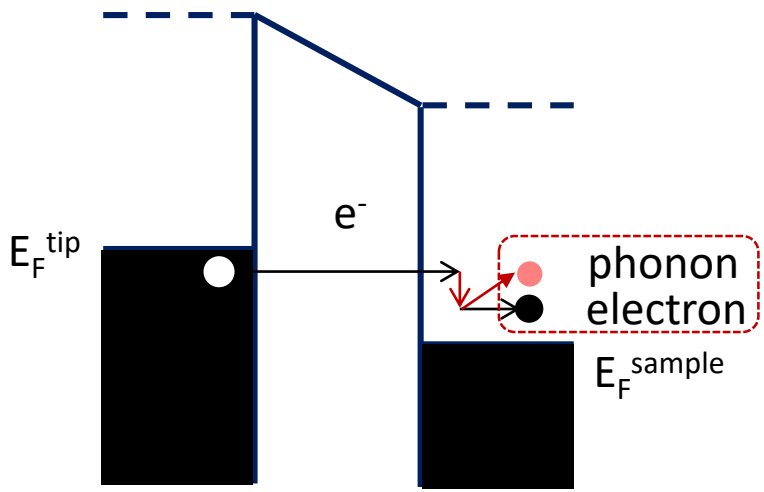
H. Gawronski et al., Science, **319** (2008) 930

Why??

E. Minamitani, R. Arafune et al, Phys. Rev. B, 93, 085411 (2016)

Mechanism of IETS at metal surface

Go back to the original physical process in IETS



Inelastic current
∝ generation of dressed electron
induced by electron-phonon coupling

Information of electron-phonon coupling would be an important key

model Hamiltonian

tip — electron; substrate — electron, phonon; tip-substrate — tunneling

$$H = \sum_p \varepsilon_p c_p^\dagger c_p + \sum_{k,\eta} \varepsilon_k^\eta c_{k\eta}^\dagger c_{k\eta} + \sum_{q\lambda} \hbar\omega_q^\lambda a_{q\lambda}^\dagger a_{q\lambda} + \sum_{p,k,\eta} W_{pk}^\eta \left(c_p^\dagger c_{k\eta} + h.c.\right)$$

$$+ \sum_{k,p,\lambda,\eta,\eta'} M_{kq}^{\eta'\eta\lambda} c_{k+q\eta'}^\dagger c_{k\eta} \left(a_{q\lambda} + a_{-q\lambda}^\dagger\right)$$

electron-phonon

Derivation of IETS spectrum

$$I = 2 \times \frac{\partial}{\partial t} e \sum_p c_p^\dagger(t) c_p(t) = \frac{-2e}{i\hbar} \sum_p \left[c_p^\dagger(t) c_p(t), H \right]$$

$$= \frac{8\pi e}{\hbar} \int d\omega \sum_{pk\eta} W_{kp}^\eta W_{pk}^\eta \left(f(\omega) - f(\omega - eV) \right) \rho_p \boxed{\Im G_{k\eta k\eta}^r(\omega)}$$

imaginary part of surface Green's function

$$\frac{\mathrm{d}^2 I}{dV^2} = -\frac{8\pi e^3}{\hbar} \sum_{pk\eta} \left| W_{pk}^\eta \right|^2 \rho_p \left| \frac{\partial}{\partial \omega} \boxed{\Im G_{k\eta k\eta}^r(\omega)} \right|_{\omega = eV}$$

Electron phonon coupling is encoded in this Green's function

Within the second order in the electron-phonon coupling,

$$G_{k\eta k\eta}^r(\omega) \sim G_{k\eta k\eta}^{0r}(\omega) + G_{k\eta k\eta}^{0r}(\omega) \boxed{\Sigma^r\ (k, \eta, \omega)} G_{k\eta k\eta}^{0r}(\omega)$$

Electron-phonon self-energy

via emission or absorption of a single phonon

$$\Sigma^r\ (k, \eta, \omega) = \sum_{\eta', q, \lambda} \left| M_{k-q\ q}^{\eta' \eta \lambda} \right|^2 \left(\frac{N_{q\lambda} - f\left(\varepsilon_{k-q}^{\eta'}\right) + 1}{\omega - \omega_q^\lambda - \varepsilon_{k-q}^{\eta'} + i\delta} + \frac{N_{q\lambda} + f\left(\varepsilon_{k-q}^{\eta'}\right)}{\omega + \omega_q^\lambda - \varepsilon_{k-q}^{\eta'} + i\delta} \right)$$

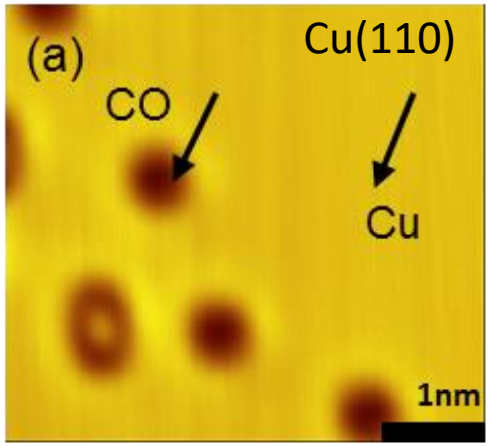
Further approximation : tunneling event mostly taken at k=0 and q=0 point

(reasonable approximation for metal surface)

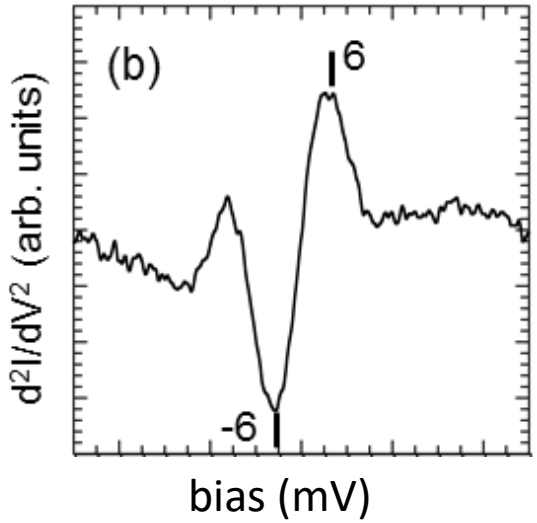
$$\frac{\mathrm{d}^2 I}{dV^2} \propto \sum_{\lambda\eta\eta'} \left|M_{\Gamma\Gamma}^{\eta'\eta\lambda}\right|^2 \delta\left(\mathrm{E}_F - \varepsilon_\Gamma^{\eta}\right)^2 \delta\left(\mathrm{E}_F - \varepsilon_\Gamma^{\eta'}\right) \left\{\delta\left(eV - \omega_\Gamma^{\lambda}\right) - \delta\left(-eV - \omega_\Gamma^{\lambda}\right)\right\}$$

$\propto$ Eliashberg function $\alpha^2 F(\omega)$ limited to k=q=0

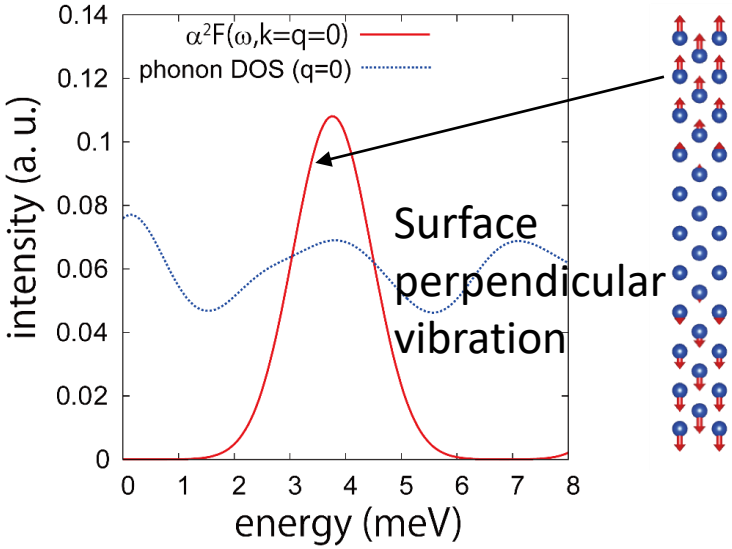
topographic image



on clean area



Ab-initio calculation of $\alpha^2 F(\omega)$



STM-IETS spectrum $\propto$

e-p coupling, Eliashberg function well known in solid state physics

E. Minamitani, R. Arafune et al, Phys. Rev. B, 93, 085411 (2016)

code: Quantum-Espresso pseudo: ultrasoft xc: GGA

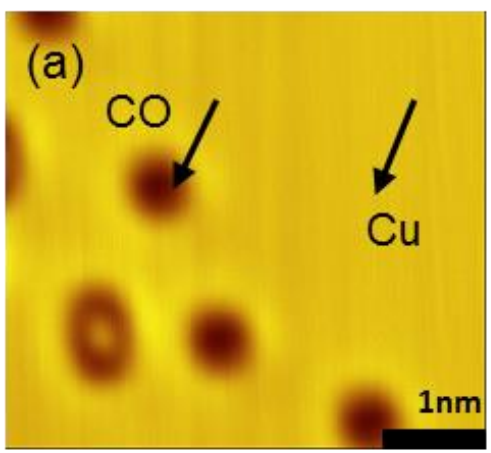
Summary of the 1st part

STM-IETS can utilize to the phonons at metal surface.

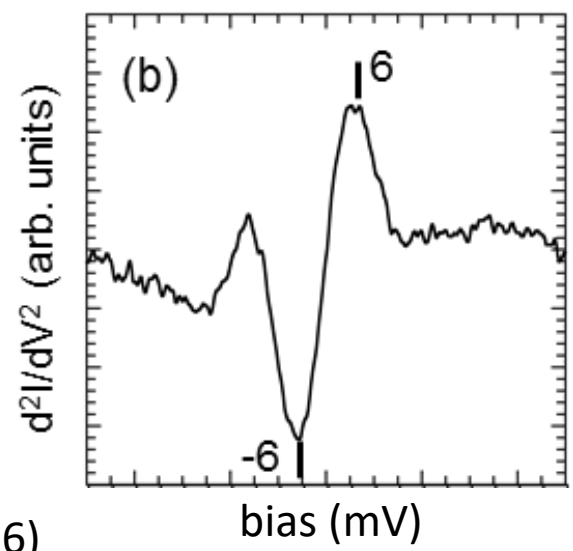
In this case, IETS spectrum proportional to the **electron-phonon coupling in the substrate**.
(similar conclusion: J. Jandle et al., PRB, 93, 060505 (2016))

For metal surface with simple electron and phonon dispersion, IETS spectrum proportional to the **Eliashberg function** which can be estimated from ab-initio calculation.

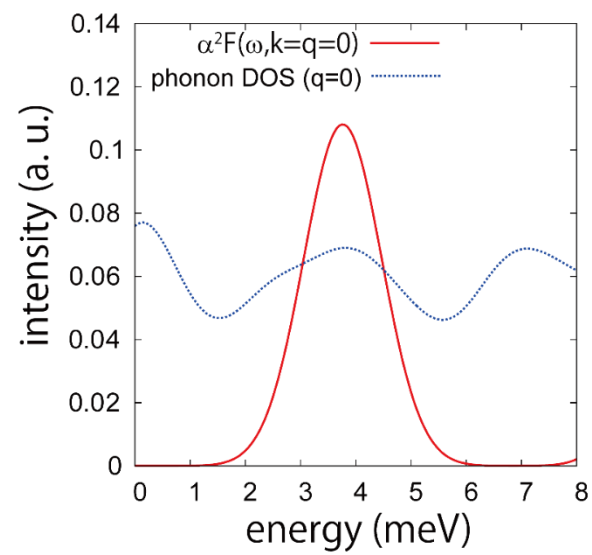
topographic image



on clean area



Ab-initio calculation of $\alpha^2 F(\omega)$



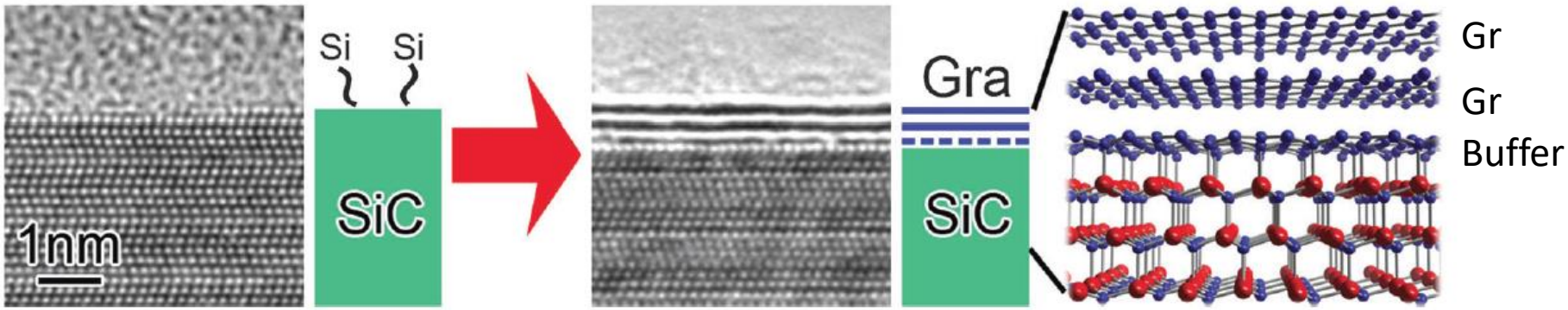
Phys. Rev. B, 93, 085411 (2016)

2. Application of IETS to solid interface
- Graphene/SiC(0001)

E. Minamitani, R. Arafune, T. Frederiksen, T. Suzuki, S. M. F. Shahed, T. Kobayashi, N. Endo, H. Fukidome, S. Watanabe, T. Komeda, Phys. Rev. B 96, 155431 (2017)

Epitaxial graphene on SiC(0001)

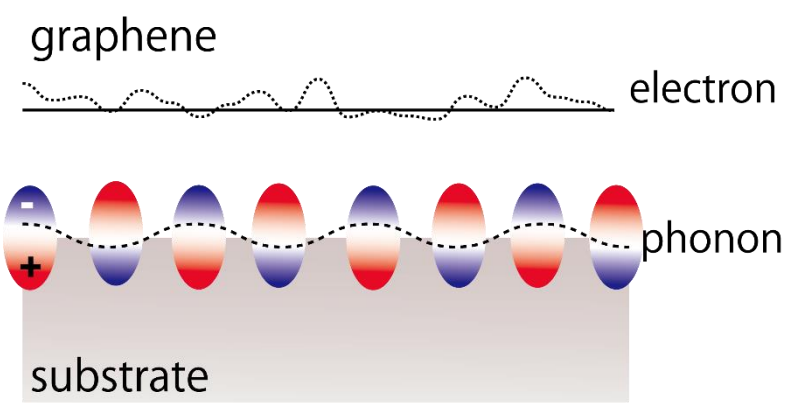
layer by layer epitaxy by thermal decomposition of SiC



W. Norimatsu and M. Kusunoki, Phys. Chem. Chem. Phys. 16, 3501 (2014)

Pros & Cons in epitaxial graphene on SiC

- ○ Direct formation of large area and high quality graphene on semiconducting substrate
- ✕ Mobility of electron is limited by the <u>effect from interface</u>



Remote phonon scattering
(scattering of electron by local electric field induced by interfacial phonon)

Interfacial phonon is an important key!

Quest for hidden interfacial phonon

Directly detecting the **interfacial phonon** hidden beneath the layered material is a challenge like to find out a pea under comforters.

Very sensitive probe is necessary.

⇩

tunneling electrons

The tunneling electrons can

1. uncover characteristic structure at interface hidden beneath the surface.

2. catch the interfacial phonon.

IETS spectrum on Graphene/SiC

Sample preparation

n-type 4H-SiC(0001)
Si-terminated surface
Annealing at 1650℃ for 1 min under Ar atmosphere
+ cleaned at 573K in UHV chamber

➡ Graphene/buffer/SiC interface

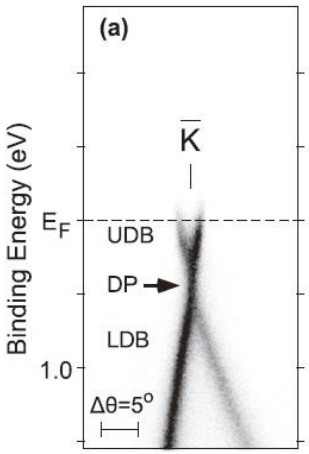
ARPES: T. Someya et al.,
Appl. Phys. Lett. 104, 161103(2014)

STM topographic image shows dark/bright contrast with

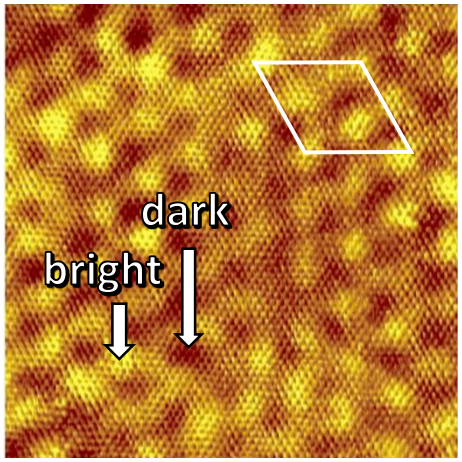
$6\sqrt{3} \times 6\sqrt{3}\ R30^\circ$ periodicity

dI/dV and d^2I/dV^2 spectra are different at dark and bright areas

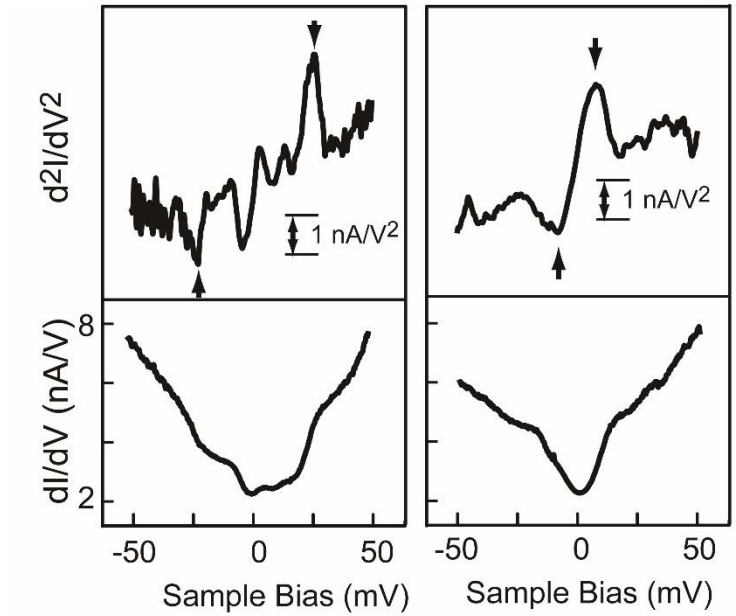
ARPES



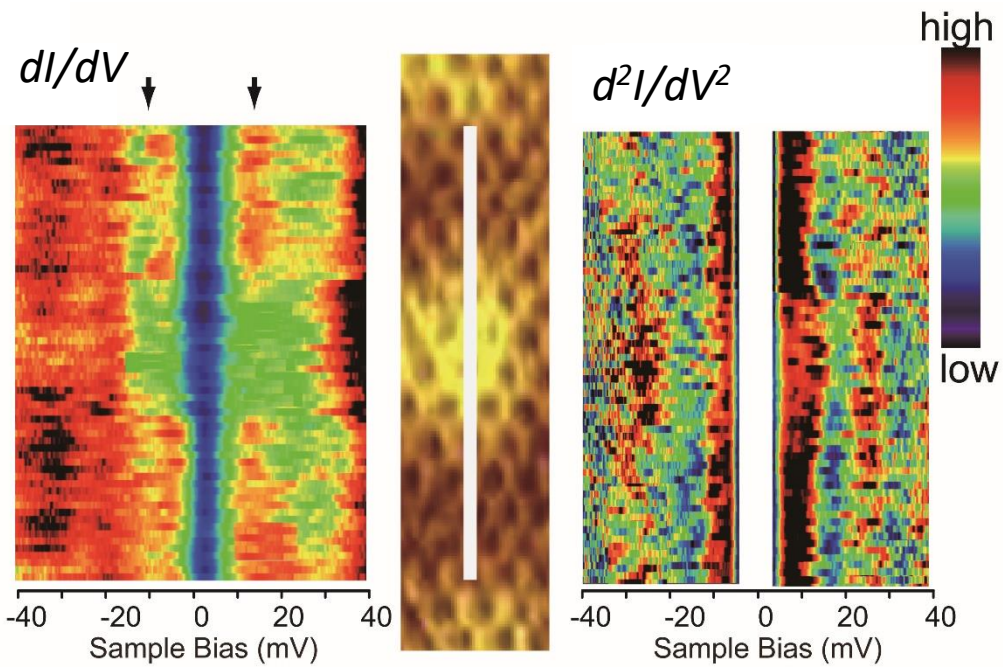
STM topographic image



bright dark



Correlation between topographic and IETS mapping image



periodicity of *dI/dV* and d^2I/dV^2 matches with that in topographic images

spatial dependence in these IETS spectra originates from interface?

Puzzles to solve

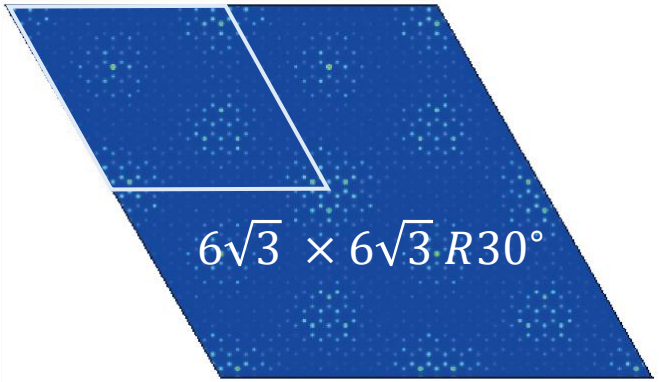
What is the origin of bright and dark contrast?
What kind of phonons are related to inelastic process?

→ab-initio analysis

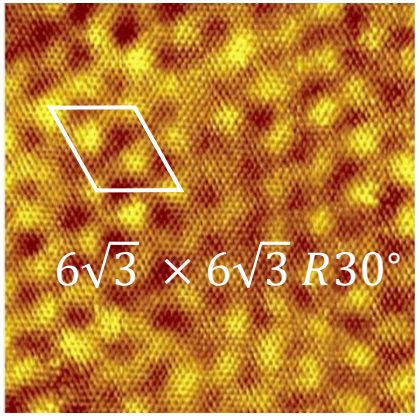
What brings dark/bright contrast?

direct STM simulation for $6\sqrt{3} \times 6\sqrt{3}\,R30°$ structure

simulation results

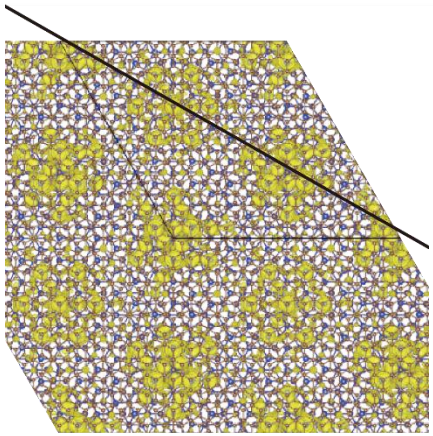


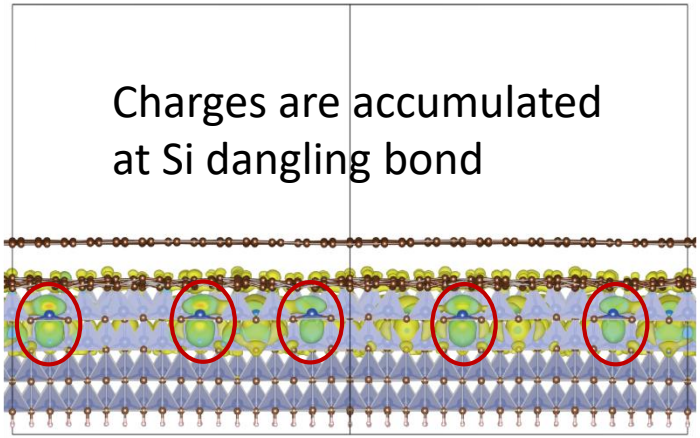
STM topographic image



dark/bright contrast matches with experiment

cut





Bright spots in topographic image originate from interfacial Si dangling bonds

code: VASP pseudo: PAW xc: LDA

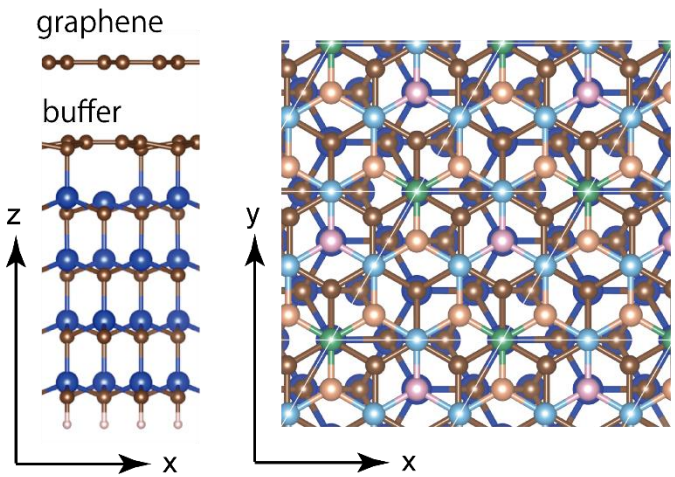
Hints from phonon calculations

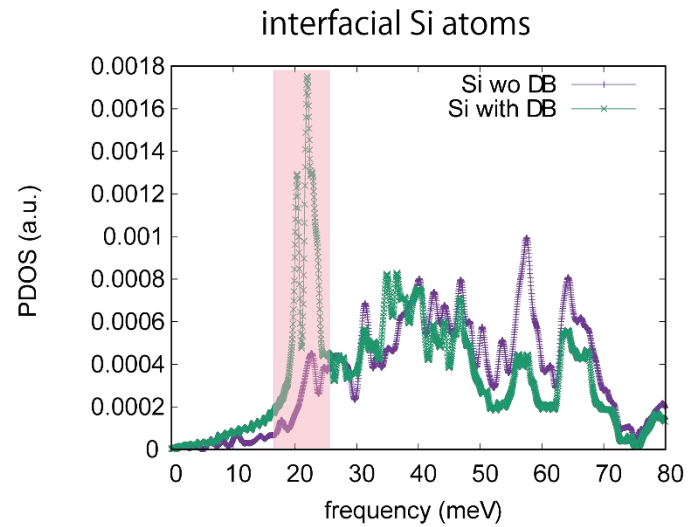
Ab-initio phonon calculation with smaller $\sqrt{3}R30^\circ$ model with typical atomic environments

Classification of C atoms in graphene layer

	C in B	Si
C1	○	○
C2	○	X
C3	X	○
C4	X	X

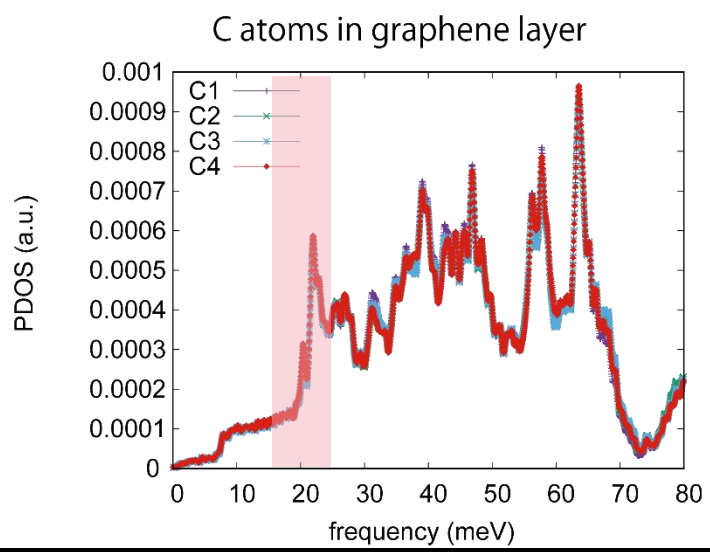
(B: Buffer)

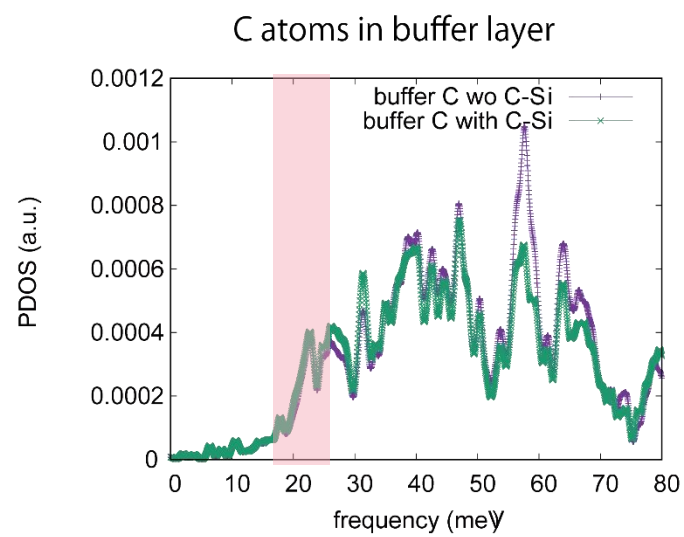




Phonons in top Gr layer show no spatial dependence.

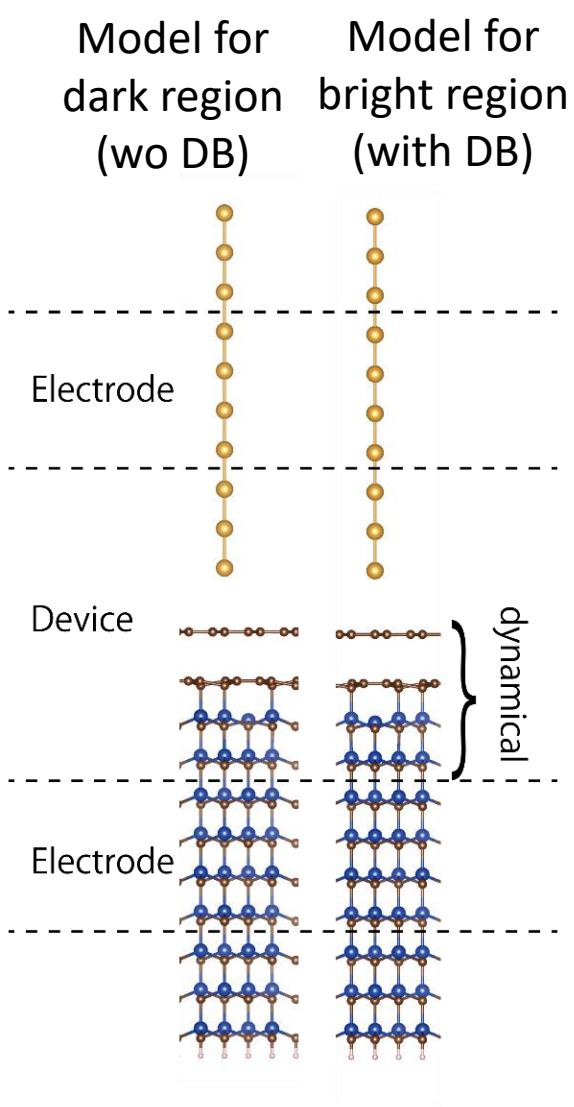
Phonon at interfacial Si shows strong spatial dependence.





code: Quantum-Espresso pseudo: ultrasoft xc: LDA

Atomistic Models for the IETS calculation



Transiesta two-terminal setup calculation
+ Inelastica
→ Tunneling current including inelastic contribution from interfacial phonon

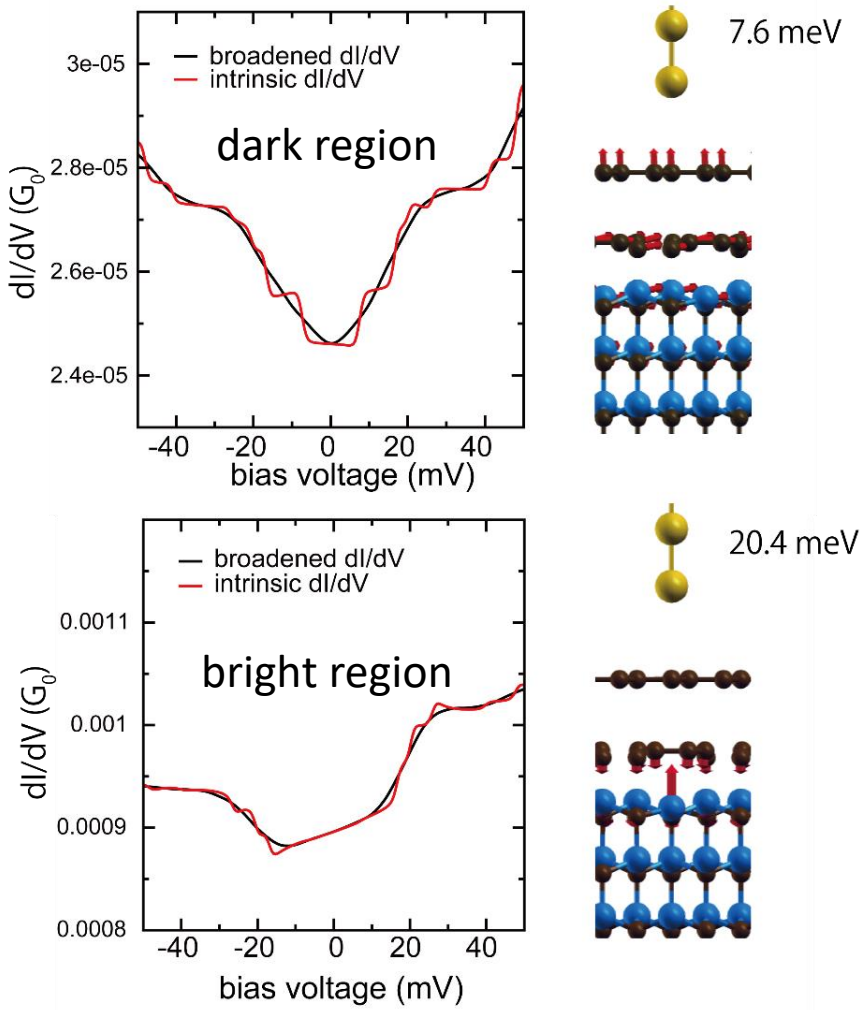
STM tip is approximated by a gold chain

Phonons at graphene, buffer layer and four atomic layer of SiC surface are considered

n-type properties of SiC substrate are treated by the virtual crystal approximation

code: siesta/transiesta/inelastica pseudo: norm-conserving xc: LDA

dI/dV calculation results



Conductance in dark region << bright region

→ Reproduce the contrast

dark region → narrow dip
bright region → wider gap

→ Reproduce dI/dV spectrum

Related phonon mode is different!
Bright region → vertical vibration of Si at interface with dangling bond

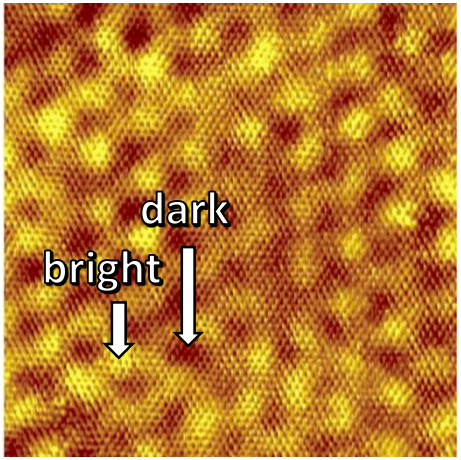
code: siesta/transiesta/inelastica pseudo: norm-conserving xc: LDA

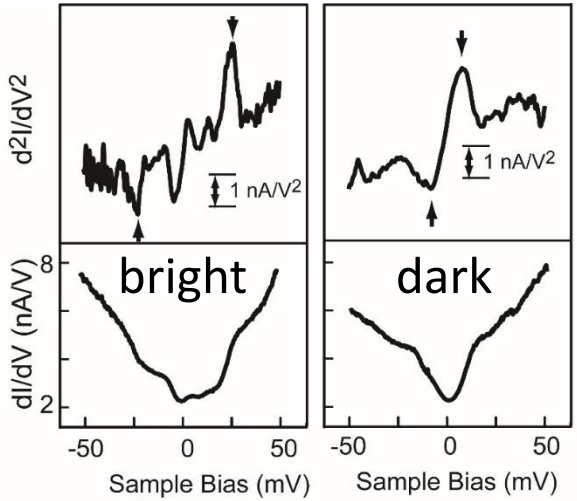
Summary of the 2nd part

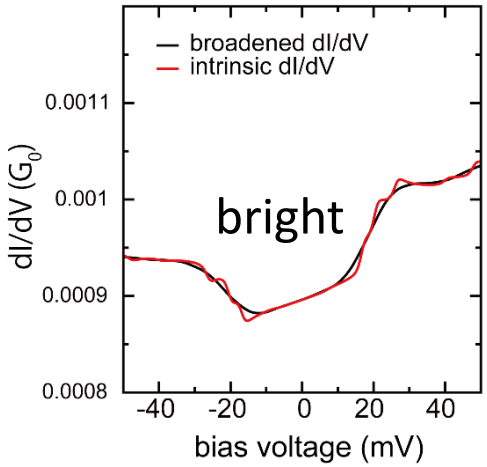
In epitaxial graphene on SiC(0001), IETS spectrum shows strong spatial dependence.

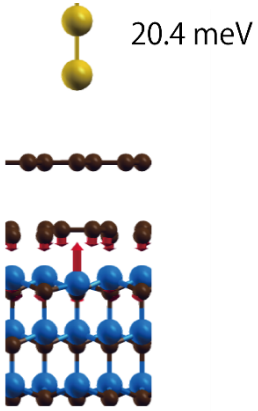
The variation in the IETS spectrum originates from a localized low-energy vibration of the interfacial Si atom with a dangling bond.

Optical phonon → source of the remote-interfacial phonon scattering @ room temperature









Phys. Rev. B 96, 155431 (2017)

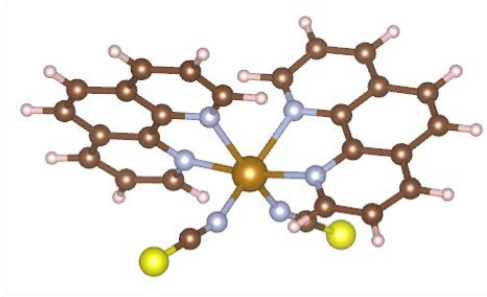
3. Application of STM-IETS to spin excitation - Fe-phthalocyanine/Au(111)

R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai, N. Takagi, *Nat. Commun* 8 16012 (2017).

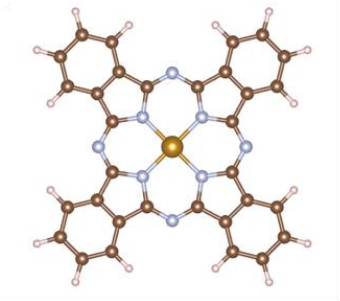
Magnetism in molecules

Transition metal complex

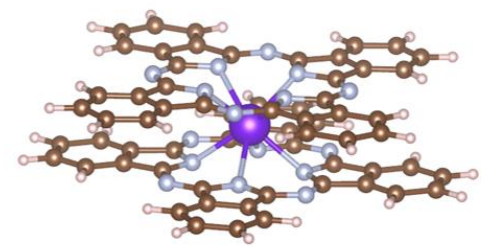
$Fe(Phen)_2(NCS)_2$



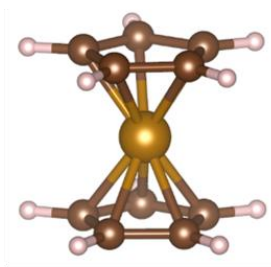
phthalocyanine



double decker

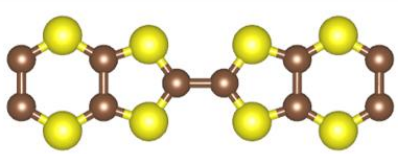


ferrocene

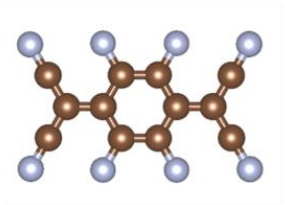


Charge transfer complex

BEDT-TTF

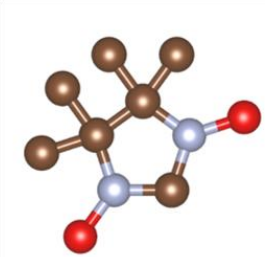


TCNQ

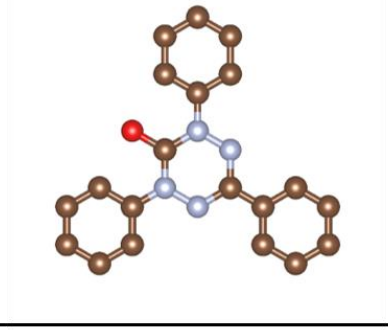


Organic radical

nitronyl nitroxide



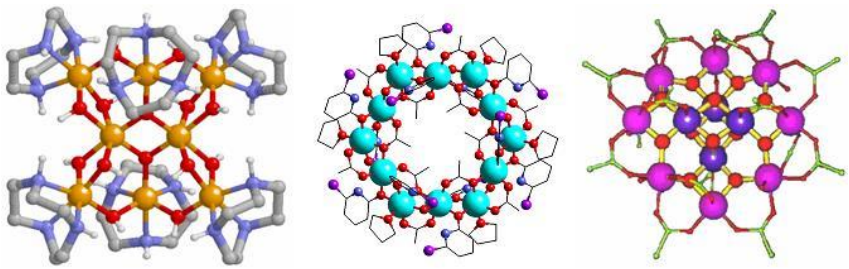
TOV



→ Single molecular magnet, spin-dependent transport

Application of molecular magnetism

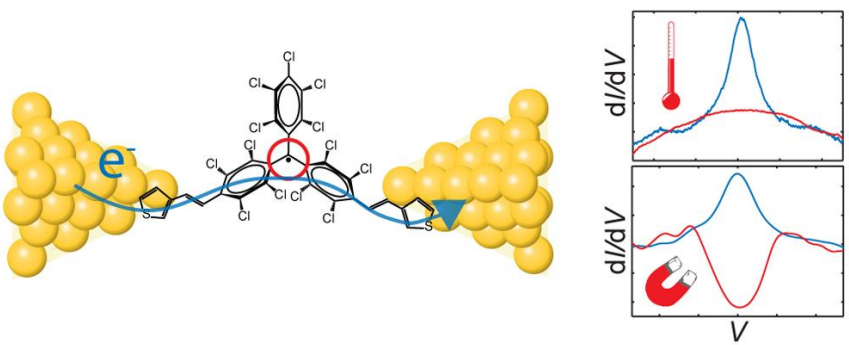
1. molecular magnet



http://qsd.magnet.fsu.edu/research.html

large magnetic anisotropy induced by spin-orbit interaction

2. spin dependent transport (magnetoresistance etc…)



R. Frisenda et al., Nano Lett., 15, 3109 (2015)

Kondo effect induced by hybridization between the molecular spin and conduction electron

Spectroscopy of spin-orbit interaction & Kondo effect
→ Molecules adsorbed on surface + STM

Spectroscopy of spin-orbit interaction

Spin-orbit interaction (SOI)

→ Zero field splitting (ZFS)

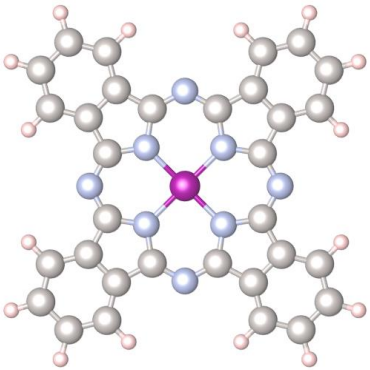
$$H_{SOI} = \xi L \cdot S$$

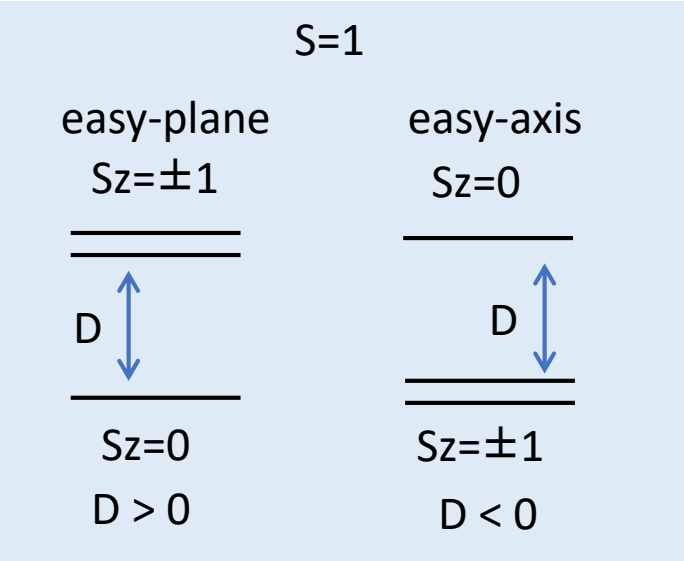
Second order perturbation of SOI

$$H_{ZFS} \sim D S_z^2 + E(S_x^2 - S_y^2)$$

Hamiltonian of ZFS depends on the symmetry

4-fold symmetric case $H_{ZFS} \sim D S_z^2$

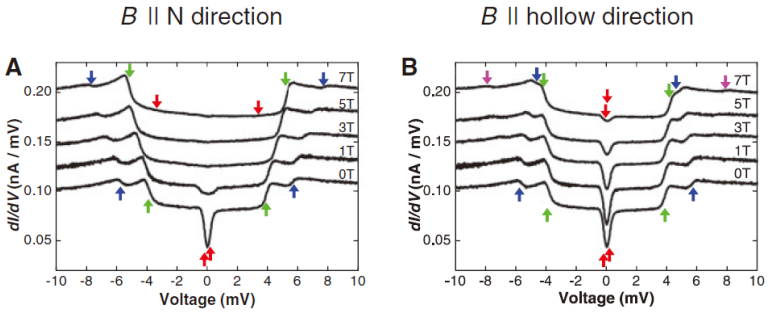




Appears as step in dI/dV spectrum in scanning tunneling microscope (STM)

→ Inelastic spin-flipping

Fe atom on CuN/Cu(001)



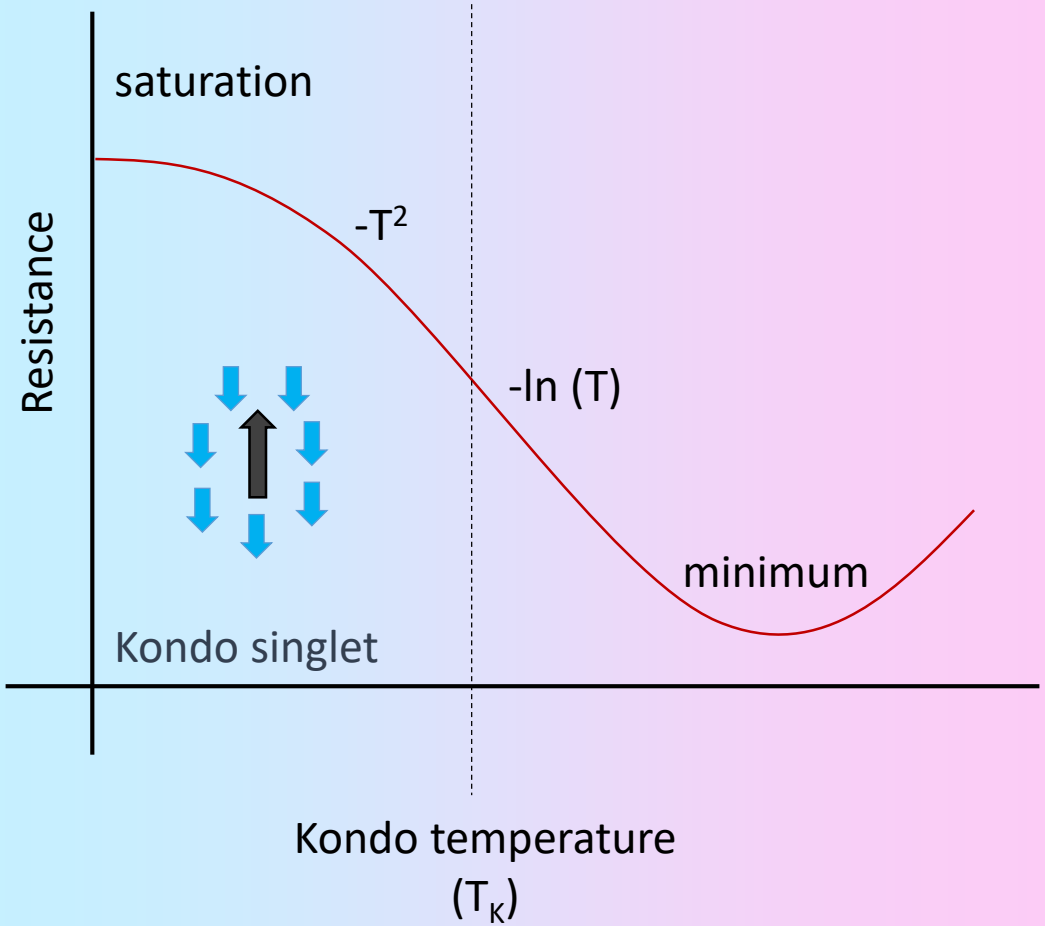
C. F. Hirjibehedin et al., Science 317, 1199 (2007)

Spectroscopy of Kondo effect

interaction with conduction electron

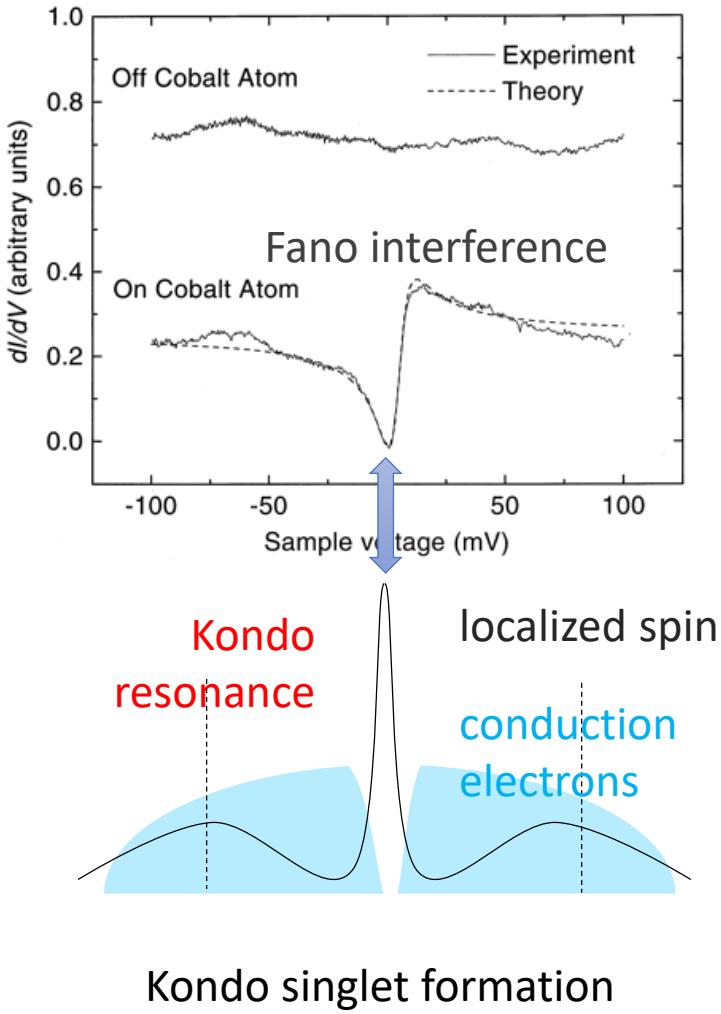
→Kondo effect

Resistance minimum in dilute magnetic alloy



Appears as peak/dip in dI/dV

Co atom on Au(111)

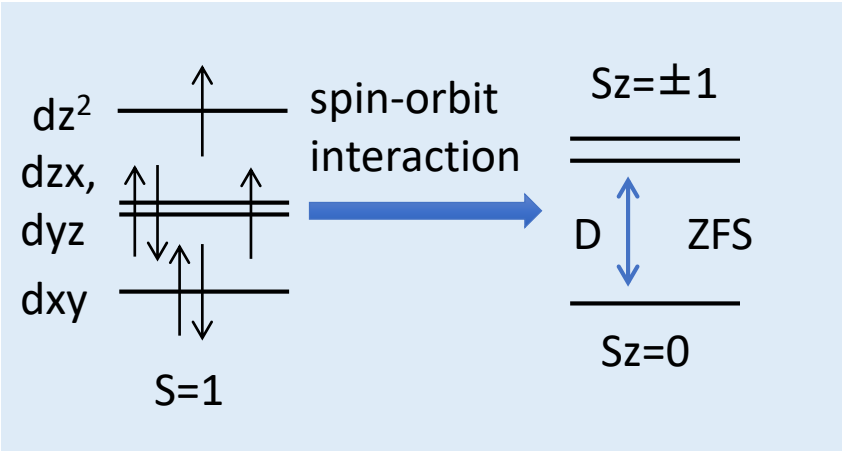


Kondo singlet formation

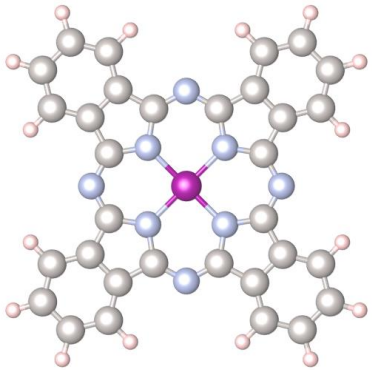
ZFS in Fe-phtalocyanine (FePc)

Fe-phtalocyanine molecule: both the ZFS & Kondo effect

gas-phase FePc → S=1 spin state



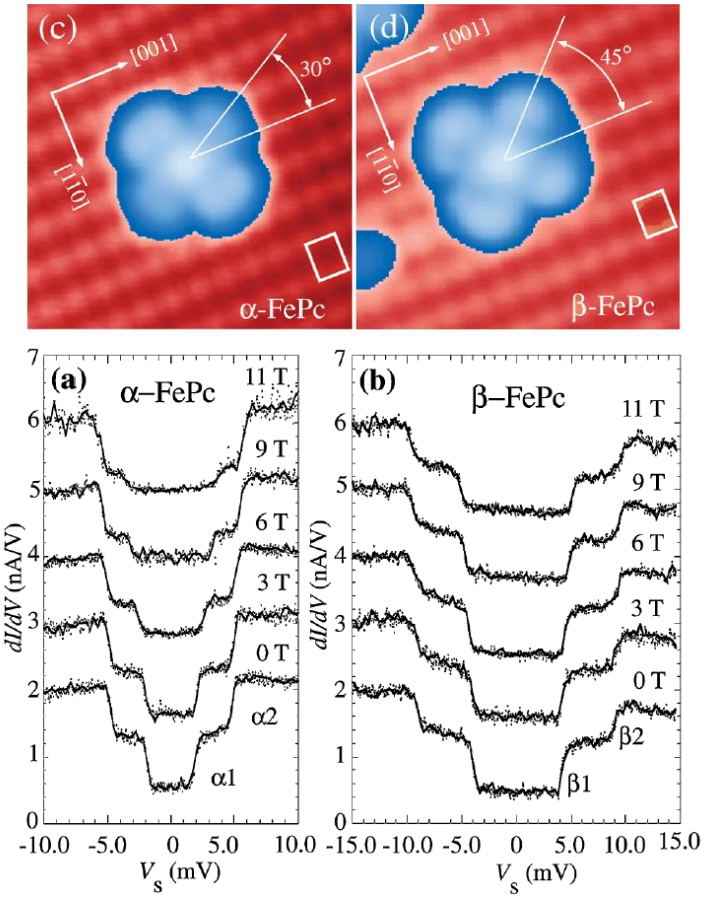
B. W. Dale et al., J. Chem. Phys. 49, 3441 (1968)



$$H_{ZFS} \sim D S_z^2$$

D>0:
Magnetic moment prefers in-plane direction

FePc on insulating surface
Cu(110)(2x1)-O

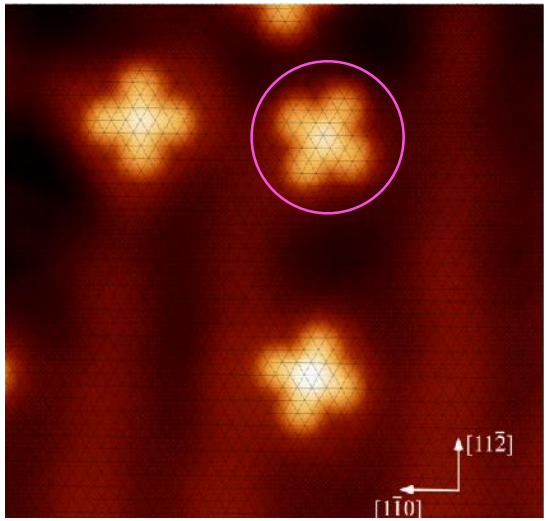


N. Tsukahara et al., PRL, 102, 167203 (2009)

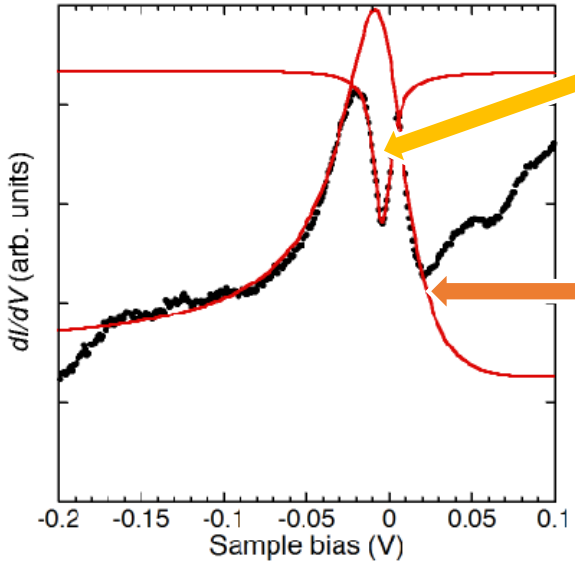
Kondo effect in Fe-phtalocyanine (FePc)

on Au(111)→Multi-orbital 2-stage Kondo effect

scanning tunneling microscope (STM) image



scanning tunneling spectroscopy (STS) spectrum



low Kondo temperature (inner dip structure) → d_{zx}/d_{yz} orbital

high Kondo temperature (broad peak) → dz^2 orbital

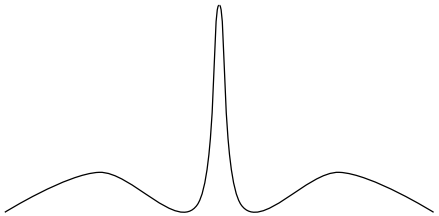
S=1 spin in FePc is fully screened by 2-stage Kondo effect on Au(111)

E. Minamitani, N. Tsukahara et al., Phys. Rev. Lett. 109, 086602 (2012)

Two different limits governed by hybridization

On metal substrate

Strong hybridization with conduction electrons



Kondo effect

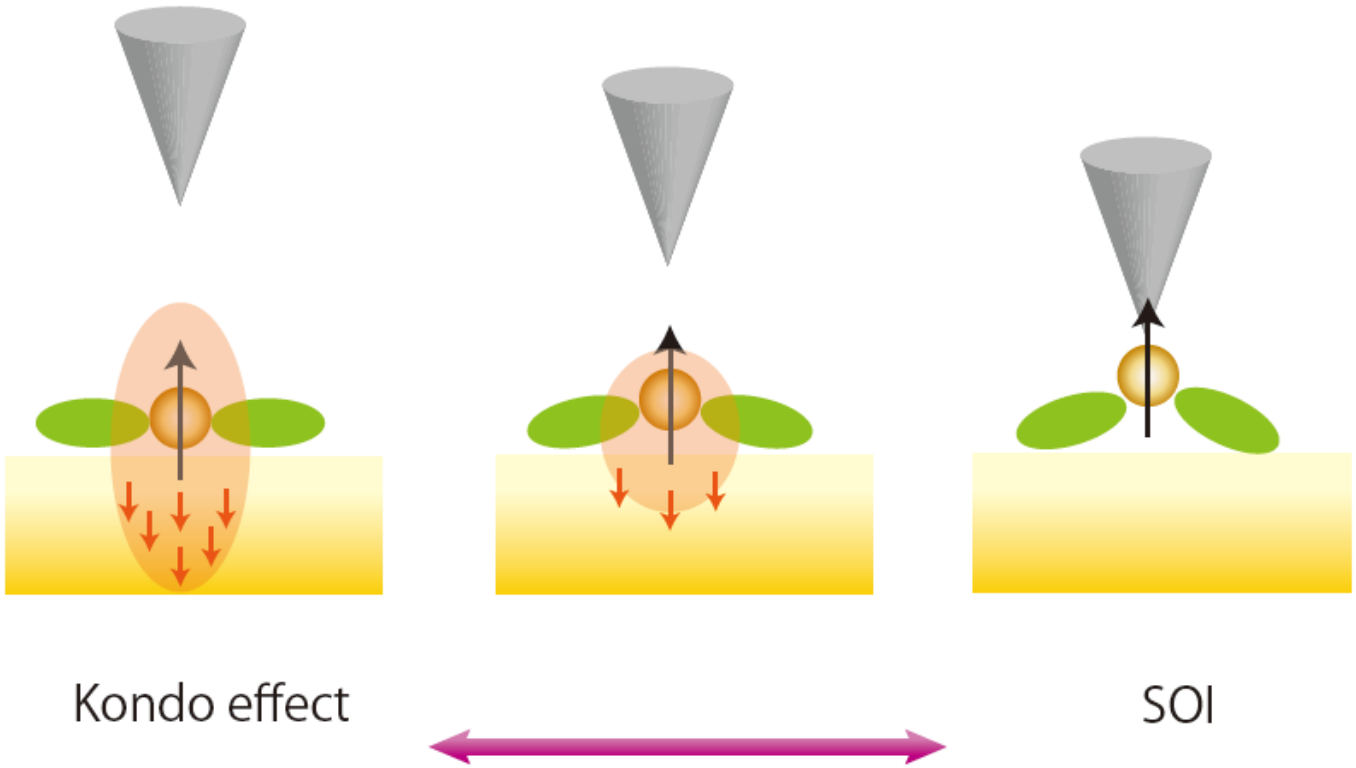
On insulator substrate

Weak hybridization with conduction electron

Zero field splitting

Mechanical control of transition between two limits

Instead of changing the substrate…



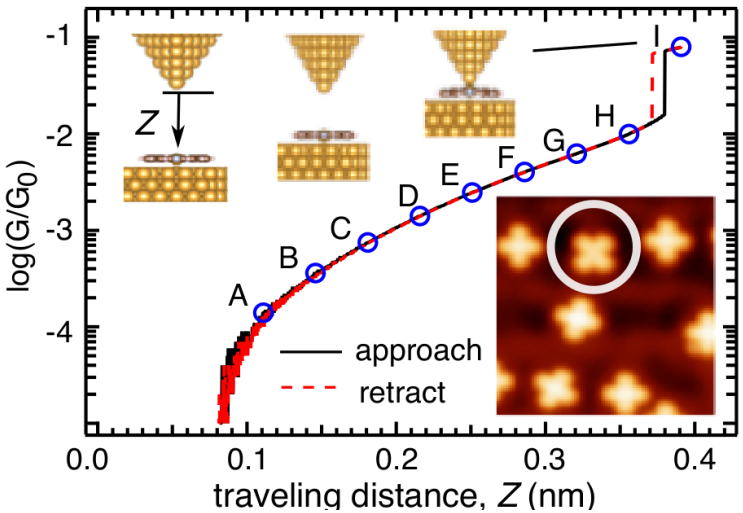
full screening
Kondo effect

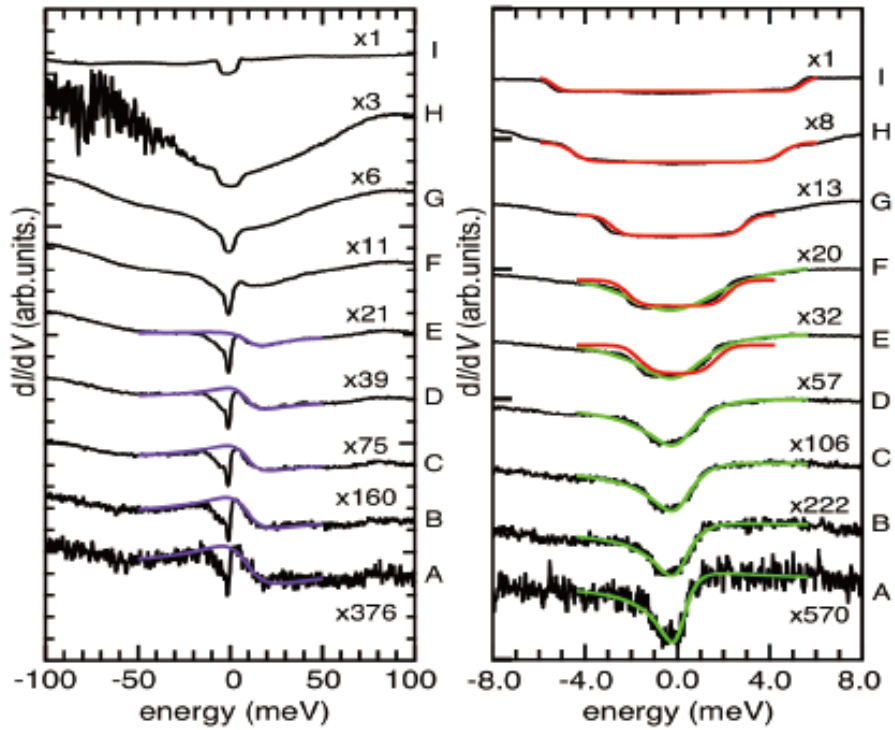
Reversible
Keeping the number of
the unpaired electron

S=1 + ZFS

Spectral evolution with tip approaching

dI/dV with STM tip approach

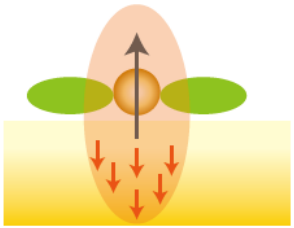




STM tip far from the Fe ion (A, B)

→asymmetric broad peak + inner dip structure

→Kondo + Fano effect

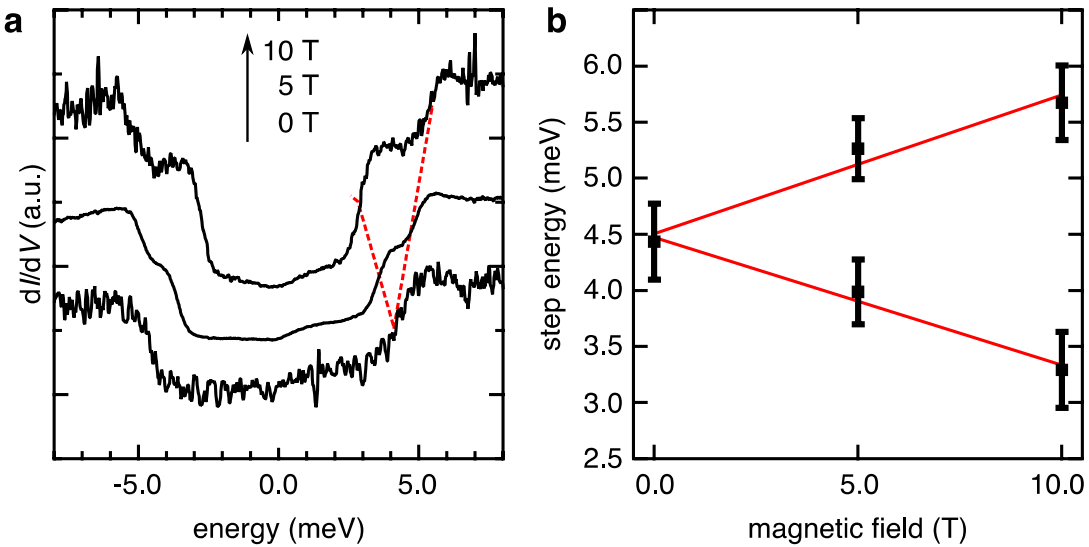


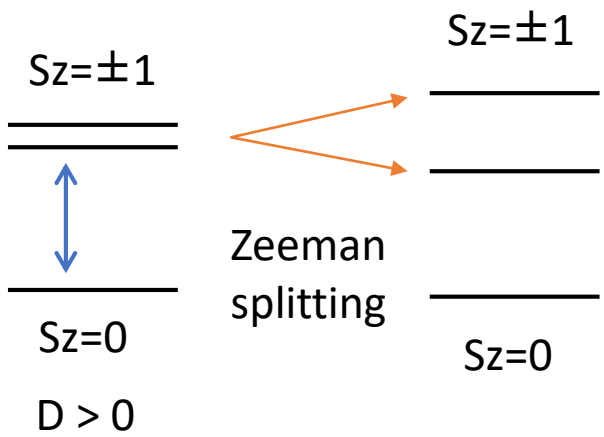
Inelastic spin-flipping signal with tip contact

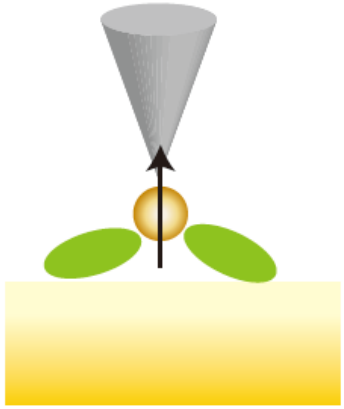
STM tip contact case (I)

Magnetic field → Zeeman splitting

Lande g-factor of 2.0±0.4







STM tip contact case

→ S=1 with D~5 meV

→ SOI >> Kondo effect

What happens during the spectral evolution?

Theoretical method

Molecular characteristics + electron correlation

To treat both effects, combining two different method

Density Functional Theory(DFT)

Effect of tip approaching, local density of states…

simulation code : VASP (PAW pseudo potential) LDA+*U* method

Extract effective model Hamiltonian

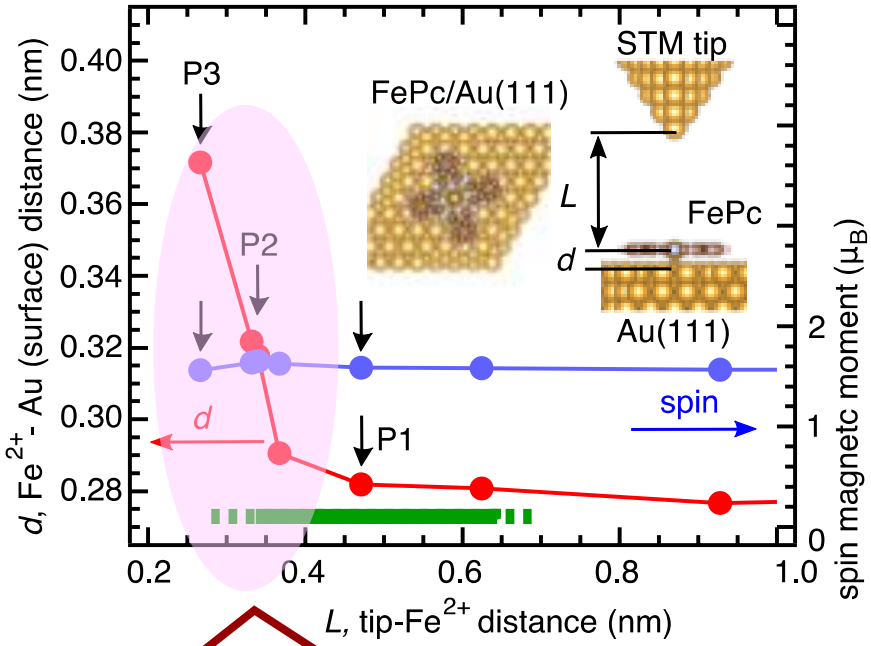
Numerical Renormalization Group(NRG)

My own build code (Fortran 90 core solver with MPI+openMP parallelization, with support program by Java to generate the inputs for various model Hamiltonians)

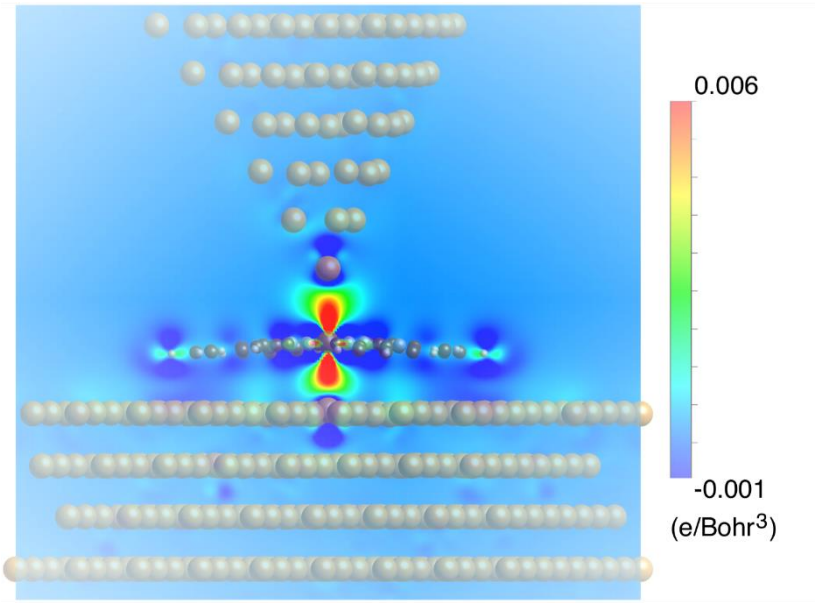
spectrum calculation method : complete Fock space method
(F. B. Anders, and A. Schiller, *Phys. Rev. B* **74**, 245113 (2006))

Effect of tip approaching

Fe position and magnetic moment



differential charge distribution



Fe ion moves upward

Spin state does not change

Interaction between tip apex & Fe ion

Model Hamiltonian

S=1 spin state consisting of two-orbital

two screening conduction electron channel

$$H = \sum_{k\sigma i=1,2} \varepsilon_{ki\sigma} c^{\dagger}_{ki\sigma} c_{ki\sigma} + \sum_{kk'\sigma\sigma' i=1,2} J_i\, c^{\dagger}_{ik\sigma}(\sigma)_{\sigma\sigma'} c_{ik\sigma} \cdot S_i + J_H S_1 \cdot S_2 + D\left(\sum_{i=1,2} S_{iz}\right)^2 .$$

conduction electron of two channel

S-d coupling in respective channels

Hund's coupling

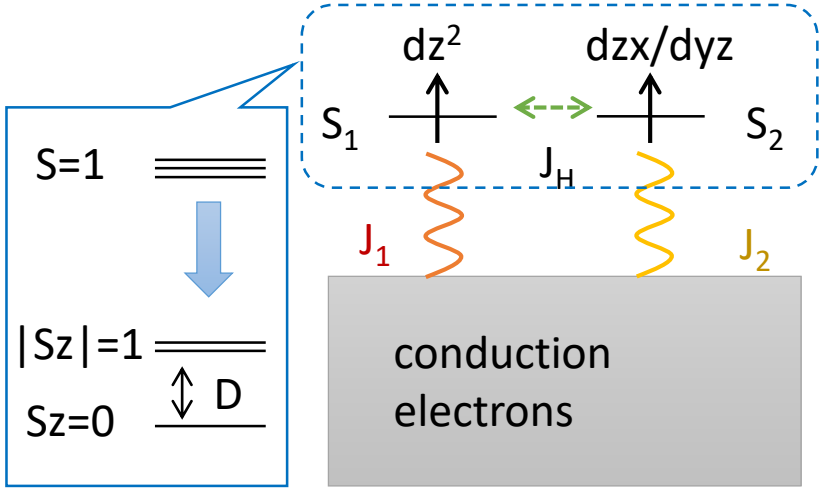
ZFS

$J_H < 0$ Ferromagnetic

$D > 0$, D=5 meV

$J_1 > J_2$ J_1: high T_K channel (dz^2)
J_2: low T_K channel (dzx/dyz)

Upward movement of the Fe ion
→ reduce J_1 and J_2

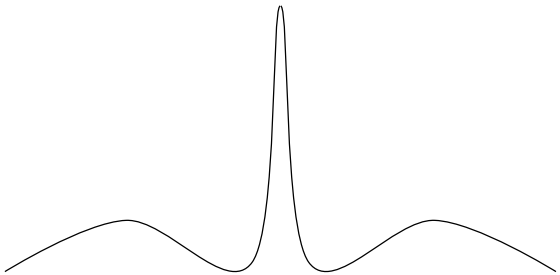


Simulation of *dI/dV* based on model Hamiltonian

total dI/dV =

elastic

∝ density of states
+ Fano interference



$\sim Im\ G^r(\omega)$

retarded Green's function

+

inelastic

from spin excitation

∝ ? ?

How to calculate including the Kondo effect??

Elastic component: Kondo resonance + Fano interference

$$\frac{dI_{el}(\omega)}{dV} = C_{\mathrm{ch1}} \sum_{\sigma} \{(q_1^2 - 1)\underbrace{\Im G^r_{11\sigma}(\omega)}_{\text{Kondo resonance}} - 2q_1 \underbrace{\Re G^r_{11\sigma}(\omega)}_{\text{Fano interference}}\}$$
$$+ C_{\mathrm{ch2}} \sum_{\sigma} \{(q_2^2 - 1)\Im G^r_{22\sigma}(\omega) - 2q_2 \Re G^r_{22\sigma}(\omega)\}.$$

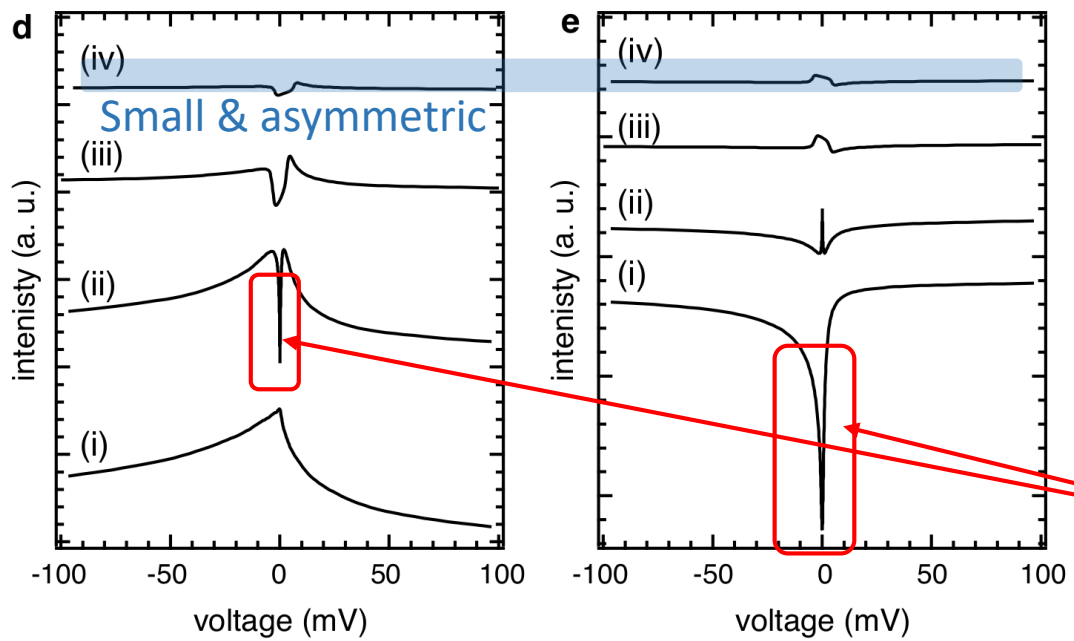
q_1=3.0, q_2=0.3

tip position close

far

high T_K channel (dz^2)

low T_K channel (dzx/dyz)



J_1=0.25 eV, J_2=0.2 eV

J_1=0.4 eV, J_2=0.25 eV

J_1=0.6 eV, J_2=0.3 eV

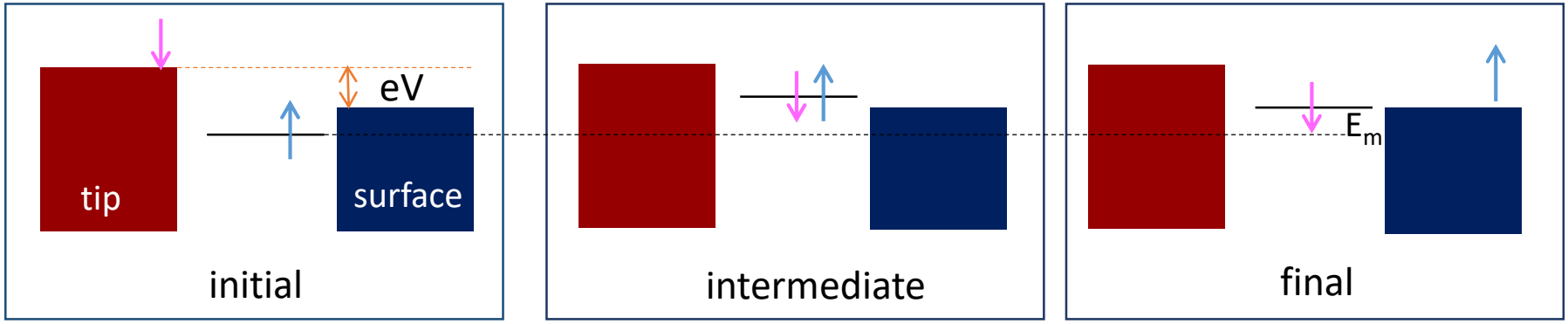
J_1=0.75 eV, J_2=0.4 eV

Similar dip but different origin

Dip width becomes wider with tip approach ○

Symmetric step & finite intensity when tip close to the Fe ion ×

Inelastic spin-flipping



S_{z0} $S_{z0} \pm 1$

If the bias voltage >> energy difference between initial and final spin states

→ energy transfer from tunneling electron can flip the spin

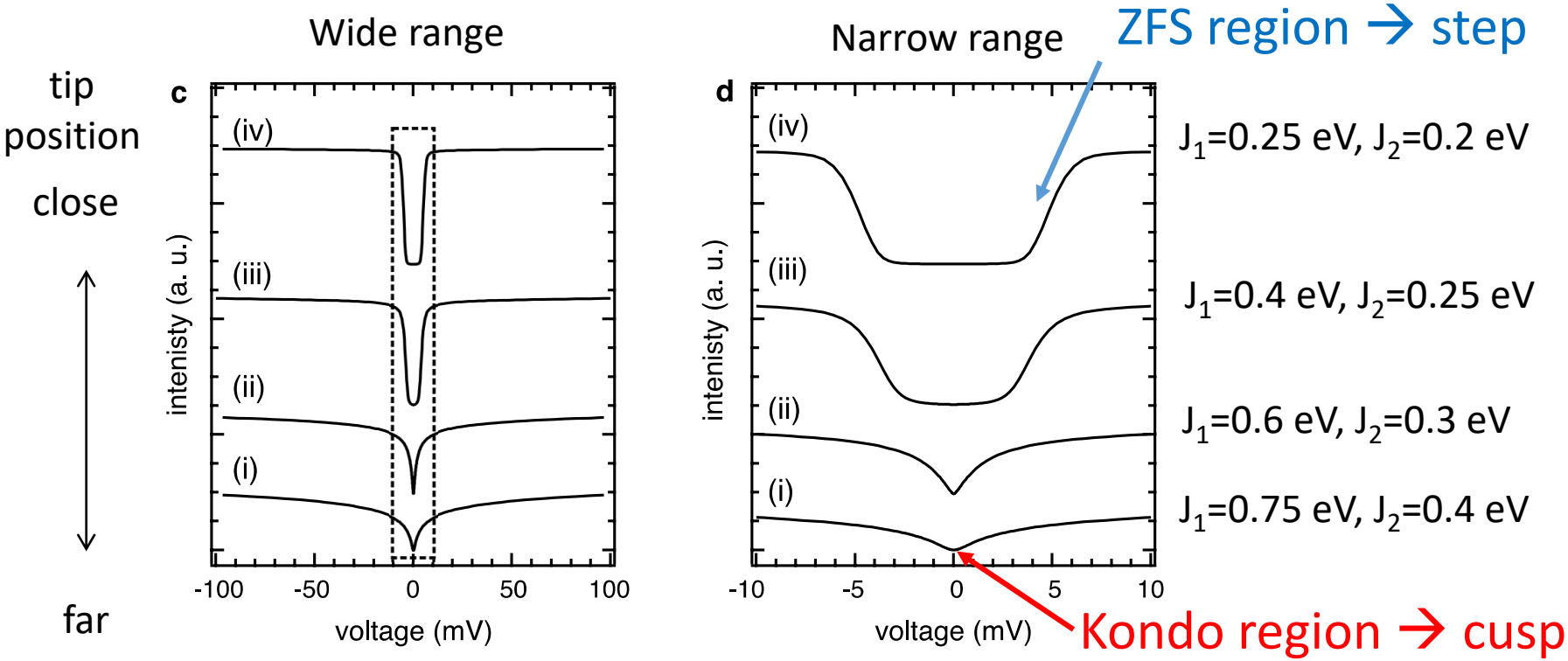
N. Lorente et al., PRL, 103, 176601, J. Fernández-Rossier PRL, 102, 256802
F. Delgado and J. Fernández-Rossier PRB, 82, 134414

Probability of spin-flipping

$$I_{\text{inel}} \propto \sum_m \{\underbrace{< g|S_-|m >< m|S_+|g > + < g|S_+|m >< m|S_-|g >}\}\theta(eV - E_m)\,.$$

Estimate by NRG→ include both Kondo effect & SOI

Inelastic spin-flipping spectrum

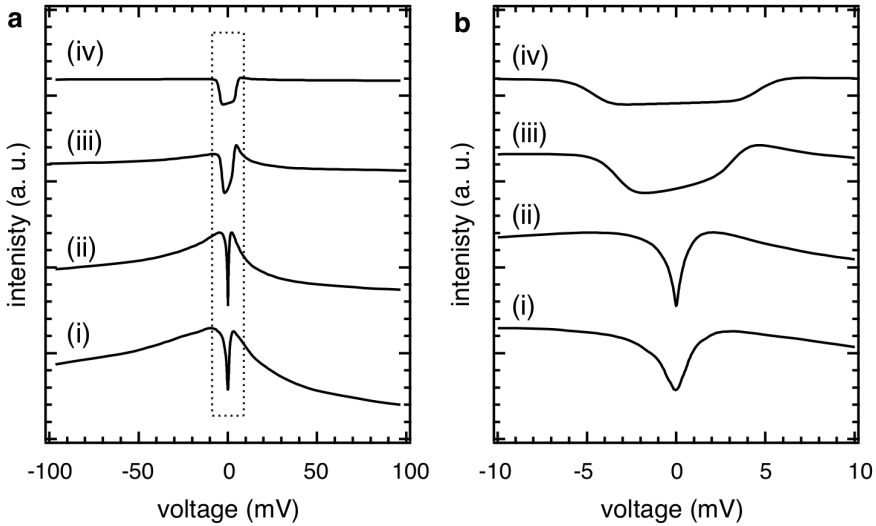


Symmetric step & finite intensity when tip close to the Fe ion

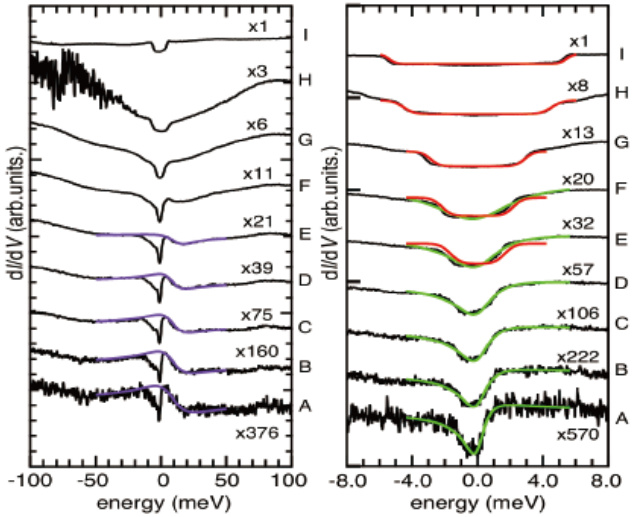
Inelastic channel becomes dominant instead of elastic one

Kondo resonance + Fano effect + inelastic spin-flipping

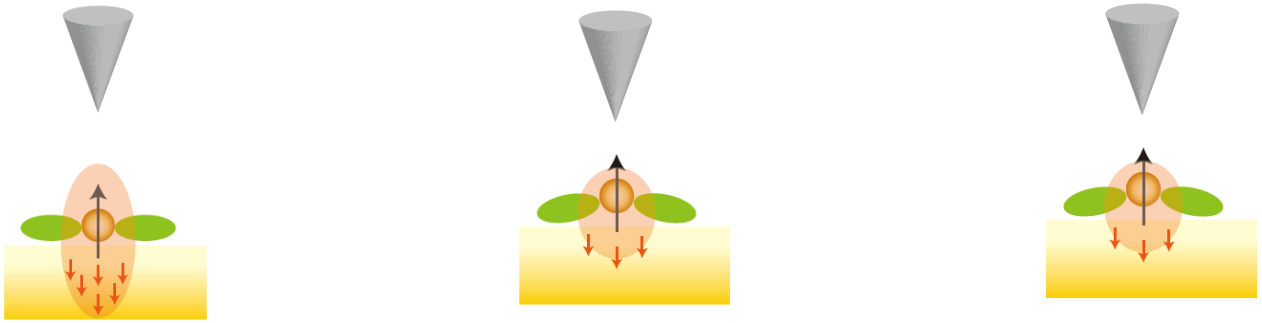
Theory



Experiment



→ Well reproduces the experimental results



Kondo effect
Nonmagnetic, conducting

SOI dominant
Magnetic, gapped

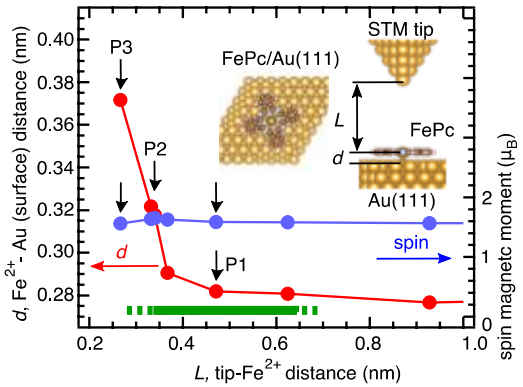
Summary of the 3rd part

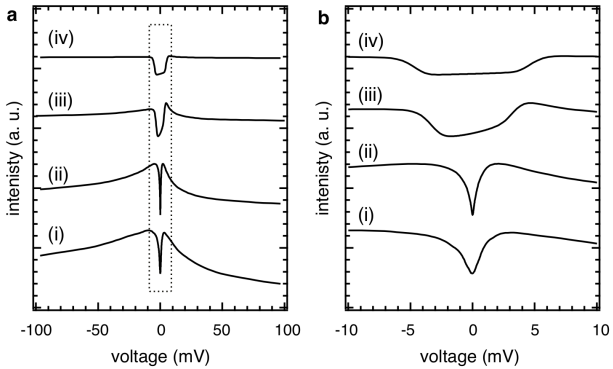
Spin-orbit interaction and Kondo effect can be observed by STM at atomic scale in a single molecules at surface.

Whether the spin-orbit interaction or the Kondo effect becomes dominant can be controlled by molecular manipulation through changing the interaction between molecule and substrate.
→ Control over the quantum critical transition @ single molecule

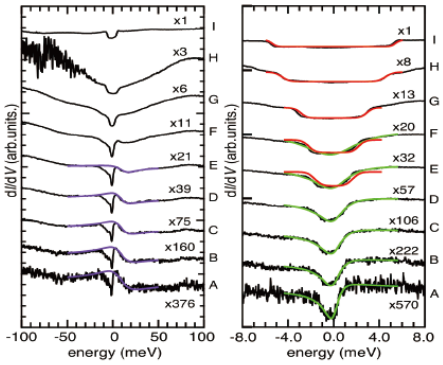
Experimentally observed dI/dV spectrum is well explained by the simulation of elastic and inelastic current including many-body effect

Theory





Experiment



Summary

Theory

DFT calculation

Non-equilibrium Green's function

Techniques for many-body problem (NRG etc…)

Experiment

Atomic resolution
+ meV energy resolution STM

Low-energy phonon & spin excitation becomes visible, accessible, and controllable @ surface

New testing field of novel solid state physics