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XAS assignment

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Setup/physical principle

STM also known as Scanning Tunneling Microscopy is an experiment in which the microscope can image the surface of conductive materials. In the experiment, a sharp metal needle is used, which works as the tip of a microscope. The sample is brought close to the needle tip with a separation of about 1mm. As the tip is brought closer to the surface of the sample, a voltage applied between the two of them allows the electrons to tunnel through the vacuum without distributing them. That amount of distance is necessary because the tunneling current is sensitive. There is an exponential relationship between the tunneling current and the separation distance. Therefore, it is important to keep the tunneling current constant for the STM to be able to map the surface topography. A high-resolution image of the surface at the atomic level is recorded. The sketch of the setup:

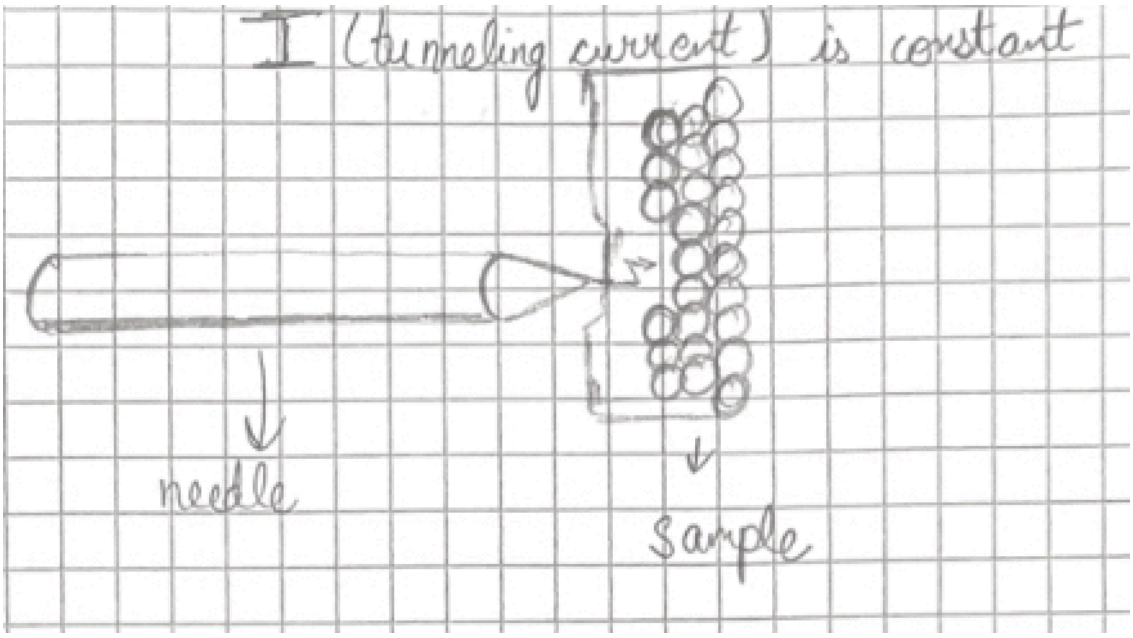


Fig 1: Sketch of the setup

2. Exercises to the experiment:

##2.1 In the STM, electrons tunnel from the tip to the sample (or reversed) but the scanning happens in air with ambient pressure. Is this a problem? How many molecules would be on average in the volume between the tip and the sample if the tip is 1 nm distance?

STM measures only on conductive surfaces. Working in the air with ambient pressure can affect image resolution and measurement due to gas molecules.
The atomic radius of platinum is = 0.139 nm , d = 0.278 nm, h = 1nm
The Area of the cylindrical gap is A = πr^2 = 0.0607nm^2

Volume = A × h = 0.0607 nm^3

Using ideal gas law, the number of molecules in a volume :
pV = nRT

$$n = \frac{1013250\times 6.07*\times10^{-29} m^3}{8.314\frac{J}{mol*K}\cdot 298K} \approx 2.48 \times 10^{-27} moles$$

Number of molecules (N) = n × Avogadro's number
= 2.48×10^{-27} mol ×6.022×10^{23} molecules/mole

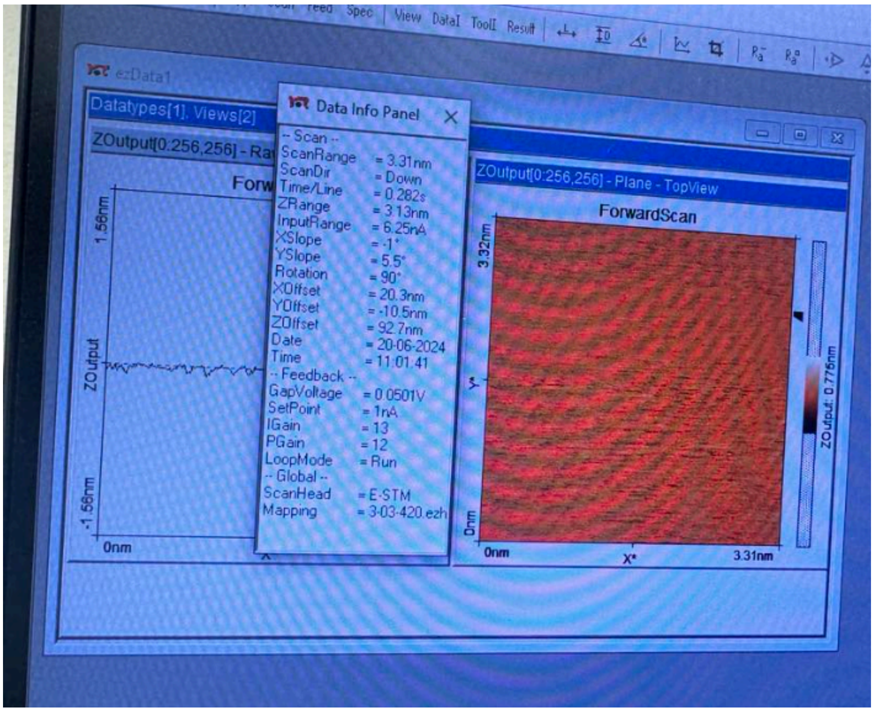
≈ 1.49×10^{-3} molecules

This is the very small number of molecules that would be on average in the volume between the tip and the sample if the tip is 1 nm away.

2. The area of the surface is 5mm × 5mm ($25 \times 10^{12} nm^{2}$.). The resolution 3.32 nm ×3.32 nm(11.022)nm^2. The sample size that we used in the lab is 25 mm^2.

We performed the experiment and our image was scanned by 256 lines and each line took 0.282 ms. so the total time would be 256 × 0.282 = 72.192 s.

The total time would be $\frac{25 \times 10^{12}\ nm^{2}}{11.022\ nm^{2}}$ × 72.192 s = 1.63×10^{14} s.



3. Atomic distance measurement, according to our figure (reference fig) all measurements are done in exercise 3.2 below

4. The spot has a diameter of 0.1 mm. Assuming the number of atoms and time to scan the whole spot with atomic resolution.

To find the atom converting the scale of diameter mm to nm, that is 0.1mm is equal to 100,000 nm.

Distance between atom from our fig 0.217 nm

Numbers of atoms in 1 row = $\frac{100,000}{0.217}$ = 460829.4931

So, the number of atom present is spot (0.1mm× 0.1 mm) =($460829.4931)^2$ = 2.12×10^{11}

We have calculated the time for area 5mm×5mm that was 1.63×10^{14} seconds

Now for 0.1mm ×0.1mm that would be $\frac{0.1^2}{25} * 1.63 * 10^{14} = 6.52 * 10^{10}$s.

Exercise 3.2

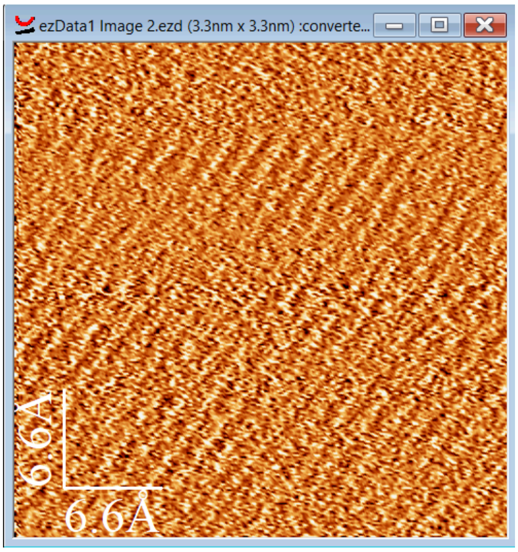
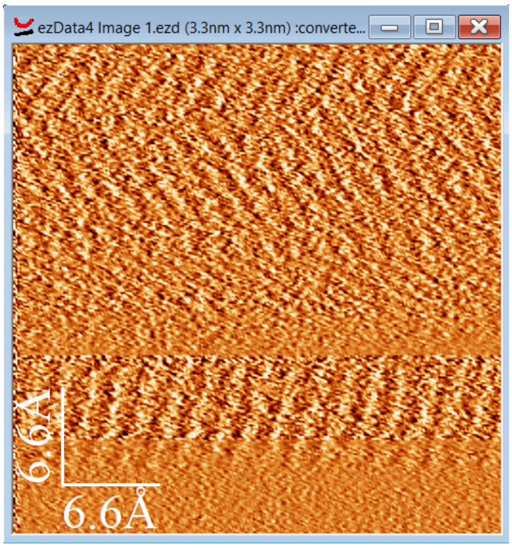
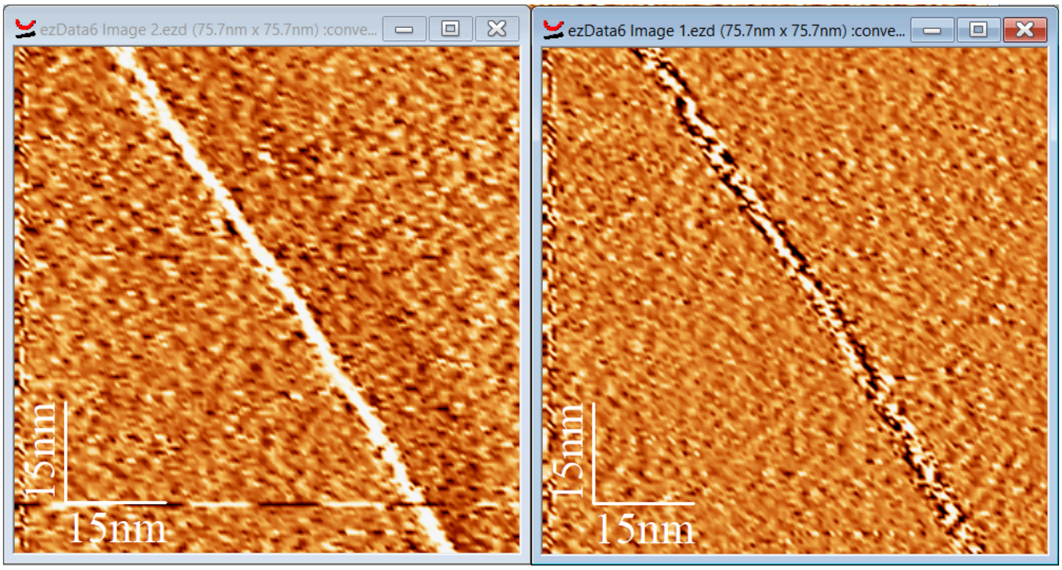
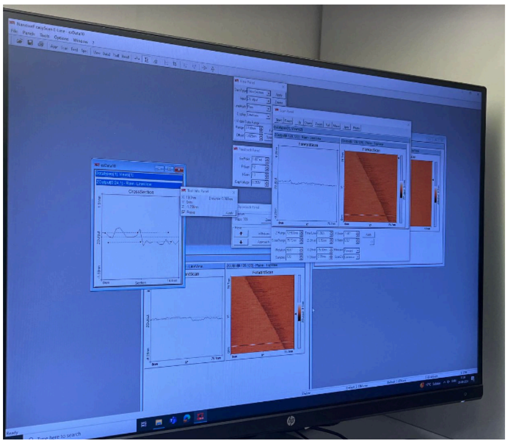
Constant current image	Constant height image
	

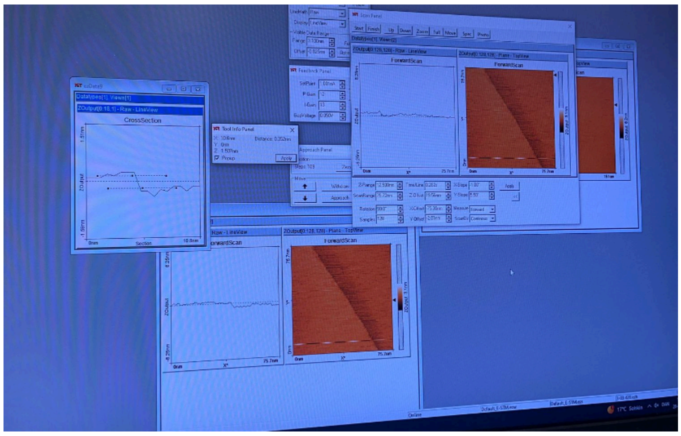
Fig 2 :

Images of step between layers

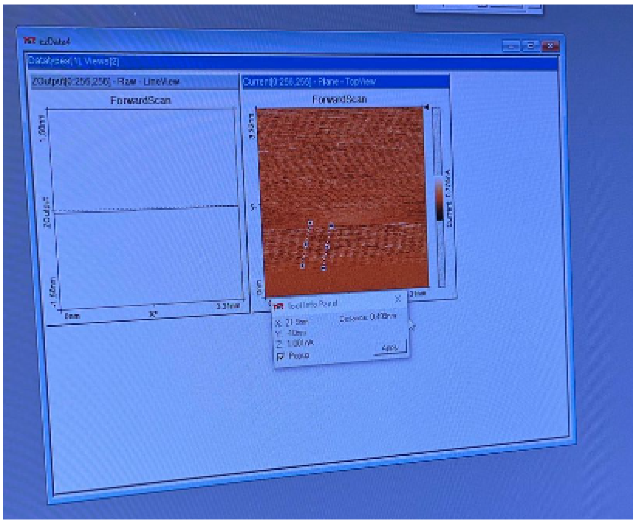


Measurements of the height between the layers in EasyScan software





Measurement of the distance between rows of atoms



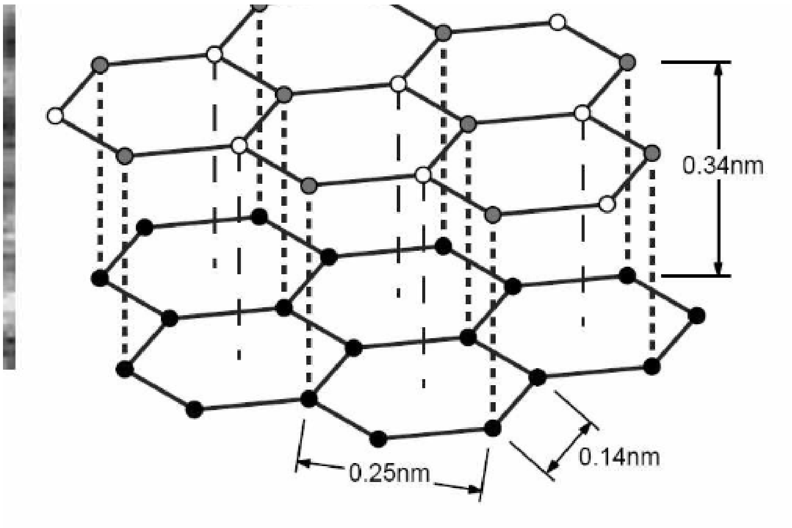
Atomic distance measurements

$$h^2 + \left(\frac{x}{2}\right)^2 = x^2$$

$$h^2 = \frac{3}{4}x^2$$

$$x = h * \frac{2*\sqrt{3}}{3}$$

	Distance between 2 rows of atoms, (2h) nm	Distance between 1 row of atoms, (h) nm	Distance between atoms, (x) nm
1	0.355	0.178	0.205
2	0.409	0.205	0.237
3	0.363	0.182	0.210
Average			0.217



The measured distance of 0.217 nm is 13% less than the given distance of 0.25 nm. This discrepancy can be attributed to the low number of measurements and noisy images.

The height difference between a step between two graphite layers

	Drop, nm
1	0.365
2	0.352
Average	0.359

Based on the average drop height, we can conclude that the height difference of the graphene layers observed in the images corresponds to one atomic layer, with a measurement discrepancy of 5.44%. The discrepancy can again be attributed to the low number of measurements and noisy images, and the fact that while measuring the drop height we didn't account quantitatively for the average height before and after the drop, which could highly affect the measurements.

STM for catalysis: Scanning tunneling microscopy is used to characterise catalytic surfaces. The HOPG graphite you used as a sample in the STM experiment may be used as a substrate to carry catalytic nanoparticles. Catalysis is quite often a surface science and nanoparticles are used in order to increase the surface area for a given amount of material. By reducing the size of each individual particle the ratio of surface to volume increases. As an example calculate the surface area of a 12 nm nanocube. Imagine now to cut the particle into a number of 3 nanometer cubes. What will be the new total surface area? (Platinum particles of the order of 3 nanometers are common in electrolysers for water splitting and in fuel cells for electricity production).

STM for catalysis:

The scanning tunneling microscope (STM) is a unique tool for resolving the atomic-scale structure of surfaces and nanoclusters. In recent years, STM studies of model systems have made it possible to address many important, fundamental questions related to catalytic processes by imaging the atomic-scale structure of relevant systems, such as nanoclusters dispersed on surfaces.
For STM experiments, Highly Oriented Pyrolytic Graphite (HOPG) is frequently utilized as a substrate because of its good electrical conductivity and smooth, flat surface. HOPG provides a great platform for catalytic nanoparticle support in catalysis studies.
To calculate the total surface area of a single 12 nm nanocube, for instance, we first calculate its surface area. This allows us to divide the nanocube into smaller 3 nm cubes.

Calculating the surface area of a 12 nm nanocube:

Surface Area = 6 × side $length^2$ [formula]

Surface Area = 6 $\times (12nm)^2$

Surface Area = 144 nm^2

Surface Area = 864 nm^2

now cutting the particle into a number of 3 nanometer cubes:

Volume calculation:

volume = side $length^3$

volume = $(12nm)^3$

volume = $1728\, nm^3$

The volume of a single 3 nm cube is:

Volume = $(3nm)^3$

volume = $27nm^3$

The number of 3 nm cubes that can fit into the volume of the 12 nm cube is:

$\frac{1728\, nm^3}{27\, nm^3}$

Number of cubes = 64

Surface area calculation:

The surface area of a single 3 nm cube is:

Surface Area = 6 × $(3\ nm)^2$

Area = 6 × $(9\ nm)^2$

Surface Area = 54 mn^2

<u>Total surface area of 64 smaller nanocubes:</u>

Total Surface Area = 64 × 54 nm^2

Total Surface Area = 3456 nm^2

Surface area of the original 12 nm nanocube: 864 nm^2

Total surface area after dividing into 3 nm nanocubes: 3456 nm^2

Subdividing the 12 nm nanocube into smaller 3 nm nanocubes results in a notable increase in the surface area. This idea is especially crucial in applications where 3 nm-sized platinum nanoparticles are frequently used, like electrolysis for water splitting and fuel cells for electricity generation.