MERIT Report of Long-term oversea dispatch

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**The study of the joint STM-AFM-TERS method**

## Background

Molecules have multidimensional endogenous parameters such as electronic states, spin states, and vibrational states, and these different endogenous parameters determine the specific properties and rich functions of molecules. In the real environment, the interfacial interactions between molecules or molecular substrate materials, as well as the action of external fields can also lead to the variation of these parameters. The global and high-precision characterization of molecular multidimensional endowment parameters is of great scientific importance and application value for the understanding of primitive chemical reactions, materials synthesis, molecular electronics, quantum information and other fields. How to realize the global characterization of molecular multiple endowment parameters and understand the dynamic evolution of endowment parameters under the action of environment and external field is a major challenge for quantum precision measurement technology and a frontier scientific problem that needs to be tackled urgently.

The nanoscience research group at the University of Science and Technology of China has developed a scanning tunneling microscopy (STM)-atomic force microscopy (AFM) tip-enhanced Raman spectroscopy (TERS) coupling technique, i.e., STM-AFM-TERS coupling technique, to address this problem. Using this coupling technique, they achieved precision measurements of single chemical bonding limits for multiple endogenous parameters such as electronic states, molecular structure and vibrational dynamics, and chemical reactions, using a silver [Ag(110)] surface of a pentacene molecule and its derivatives as a model system, and demonstrated the feasibility of tracking and measuring chemical reactions on a time scale of ~ 25 ms. The related results were published in Science 2021. The author contacted the leader of the group, Prof. Tan, and received permission to enter the group for an in-depth study of the principles and experimental procedures of TERS.

## Research Content

During this MERIT long-term overseas dispatch, I spent three months in China on an exchange program at the Nanoscience Research Laboratory of the University of Science and Technology of China (USTC). The Nanoscience Research Laboratory at the University of Science and Technology of China was founded by Prof. J. G. Hou in 1997, which introduced the first scanning tunneling microscope in China. After 25 years of development, the Hou Lab has grown into a large research group with several smaller subgroups working in different research areas. Prof. J. G. Hou has been the president of the Chinese Academy of Sciences since 2020.

Figure 1 The first set of scanning tunneling microscope in China

Around 2000, a research group proposed to combine Raman spectroscopy and SPM imaging techniques to produce a technique with real-space chemical recognition capability, namely Tip-enhanced Raman spectroscopy (TERS).TERS is based on the scanning function of the SPM probe, which makes the highly locally enhanced equipartition excitations formed between the probe and the substrate movable, thus obtaining real-space chemical recognition of surface substances. Raman spectroscopy imaging, further using the mature and perfect fingerprint library of Raman technology to achieve the chemical identification of surface materials.

Figure 2 Instruments used to prepare TERS's tips

In 2013, Zhenchao Dong's group developed an ultra-high vacuum, 78 K TERS technique to achieve the first sub-nanometer chemical identification of single molecules (less than 1 nm). In 2019, their group advanced the spatial resolution of this technique to 1.5 Å, obtained the Raman spatial distribution of different vibrational modes of single molecules of magnesium porphine (MgP), and proposed the use of TERS to determine the chemical structure of molecules. In the same year, Apkarian's group developed a new method for determining the chemical structure of MgP molecules. In the same year, Apkarian's group obtained TERS images of single molecules of CoTPP on Cu(111) surface with a spatial resolution of 1.67 Å at ultra-high vacuum liquid helium temperature, and clearly characterized the spatial distribution of different vibrational modes of CoTPP. Following year, Kim's group measured the TERS images of CuNc single molecules adsorbed on the surface of NaCl at an angstrom resolution and illustrated the Raman enhancement effect under the absorption resonance condition by comparing the Raman scattering spectra produced by the incident laser at different wavelengths.

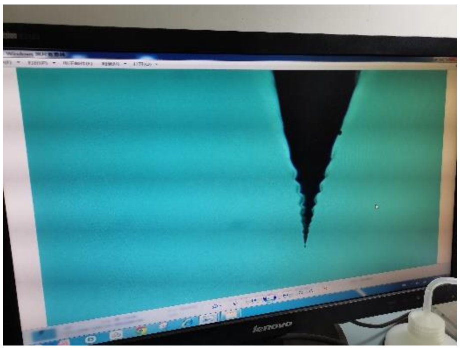

Figure 3 The tip of the optical microscope

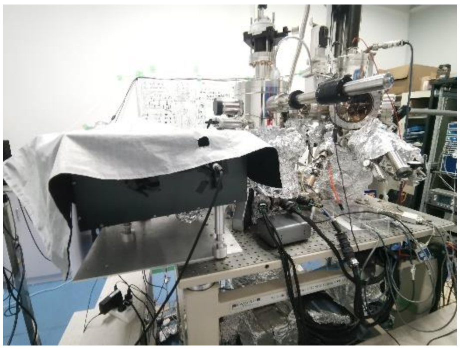

Figure 4 TERS Instruments

In order to successfully initiate equipartition excitations between the tip and the atoms on the sample surface, TERS has special requirements for the tip used. In the group, the junior students are responsible for preparing the tip, using chemical etching, and then observing the tip shape using an optical microscope. The tip is then passed to a senior student who passes the tip into an ultra-high vacuum to test the tip's TERS properties.

The key point of the TERS system is the measurement of Raman. Raman spectroscopy is a method of analyzing matter based on the Raman scattering effect discovered by the Indian scientist C. V. Raman in 1928. When light strikes a substance, the vast majority of photons undergo elastic scattering in which the scattered photons have the same frequency as the incident photons, also known as Rayleigh scattering; a very small number of photons undergo inelastic scattering in which the frequency of the scattered photons changes, also known as Raman scattering. The Raman spectrum contains information about the vibrations and rotations inside molecules, and has a "fingerprint" effect. The group designed their own optical path to achieve this, and used linearly polarized incident light at 532 nm to obtain TERS spatial imaging of fixed vibrational modes with a time resolution of less than 0.1 s. During the time of the author's study, the experimental group used TERS on pentacene. The author studied its experimental procedure and operation carefully.

**Research Life**

Hefei, China, is located in the middle of Anhui Province, between Jiangsu and Huaihua, in the western wing of the Yangtze River Delta, and is one of the important birthplaces of Chinese civilization. Hefei is one of the "Four Great Bases of Science and Education" in China, the second comprehensive national science center approved for construction, and one of the member cities of the WTA (World Technopolis Alliance). Hefei is the hometown of Nobel Laureate Professor Chen Ning Yang. Hefei boasts 3 national laboratories, including the Hefei National Laboratory for Microscale Matter Science, to which the author belongs this time. In addition to the 3 national laboratories, Hefei has 7 large scientific devices, the first in the country in the number of large scientific devices, including a total of 7 such as HT-6M controlled thermonuclear reactor, HT-7 and EAST tokamak.

**Acknowledgements**

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