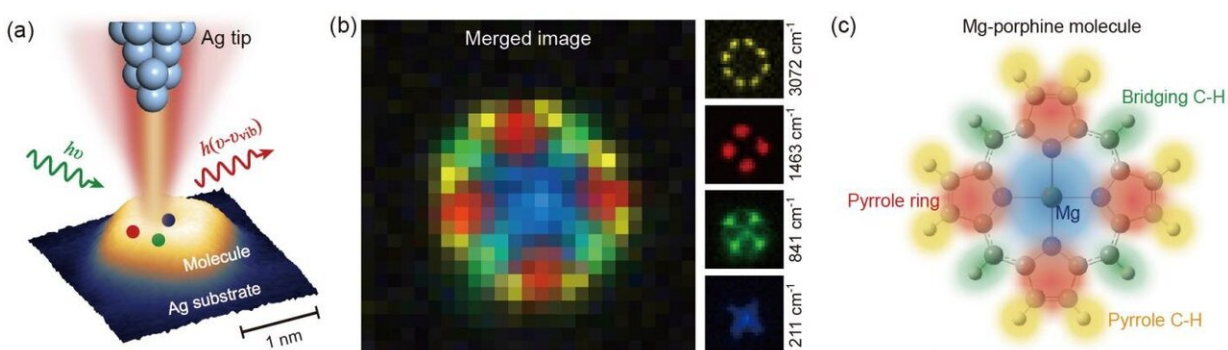


Scanning Raman picoscopy: A new methodology for determining molecular chemical structure

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(a) Schematic of scanning Raman picoscopy (SRP). When a laser beam is focused into the nanocavity between the atomistically sharp tip and substrate, a very strong and highly localized plasmonic field will be generated, dramatically enhancing the Raman scattering signals from the local chemical groups in a single molecule right underneath the tip. (b) Merged SRP image by overlaying four typical Raman imaging patterns shown on the right insets for four different vibrational modes. (c) Artistic view of the Mg-porphine molecule showing how four kinds of chemical groups (colored "Legos") are assembled into a complete molecular structure. Credit: Science China Press

Precise determination of the chemical structure of a molecule is of vital importance to any molecular related field and is the key to a deep understanding of its chemical, physical, and biological functions.

Scanning tunneling microscopy and atomic force microscopy have outstanding abilities to image molecular skeletons in real space, but these techniques usually lack chemical information necessary to accurately determine molecular structures.

Raman scattering spectra contain abundant structural information about molecular vibrations. Different [molecules](#) and chemical groups exhibit distinct spectral features in Raman spectra, which can be used as the "fingerprints" of molecules and chemical groups. Therefore, the above mentioned deficiency can in principle be overcome by a combination of scanning probe microscopy with Raman spectroscopy, as demonstrated by tip enhanced Raman spectroscopy (TERS), which opens up opportunities to determine the chemical [structure](#) of a single molecule.

In 2013, a research group led by Zhenchao Dong and Jianguo Hou at University of Science and Technology of China (USTC) demonstrated sub-nanometer resolved single-molecule Raman mapping for the first time [*Nature* 498, 82 (2013)], driving spatial resolution with chemical identification capability down to ~ 5 Å. Since then, researchers around the world have been progressing on developing such single-molecule Raman imaging techniques to explore what is the ultimate limit of spatial resolution and how this technique can be best utilized.

Recently, the USTC group published a research paper in *National Science Review* (NSR) entitled "Visually Constructing the Chemical Structure of a Single Molecule by Scanning Raman Picoscopy," pushing the spatial resolution to a new limit and proposing an important new application for the state-of-art technique. In this work, by developing a cryogenic ultrahigh-vacuum TERS system at liquid-helium temperatures and fine-tuning the highly localized plasmon field at the sharp tip apex, they further drive the spatial resolution down to 1.5 Å on the single-chemical-bond level, which enables them to achieve full spatial mapping of various intrinsic vibrational modes of a molecule and discover

distinctive interference effects in symmetric and antisymmetric vibrational modes. More importantly, based on the Ångström-level resolution achieved and the new physical effect discovered, and by combining with a Raman fingerprint database of chemical groups, the researchers further propose a [new methodology](#). Coined as Scanning Raman Picoscopy (SRP), the technique will visually construct the chemical structure of a single molecule. This methodology highlights the remarkable ability of Raman-based scanning technology via an atomically sharp tip to reveal the molecular chemical structure in real space, just by "looking" at a single molecule optically, as schematically shown in Figure (a).

By applying the SRP methodology to a single magnesium porphyrin model molecule, the researchers at USTC obtained a set of real-space imaging patterns for different Raman peaks, and found that these patterns show different spatial distributions for different vibrational modes. Taking the typical C-H bond stretching vibration on the pyrrole ring as an example, for the antisymmetric vibration (3072 cm^{-1}) of two C-H bonds, the phase relation of their local polarization responses is opposite. When the tip is located right above the center between two bonds, the contributions from both bonds to the Raman signals cancel out, giving rise to the "eight-spot" feature in the Raman map for the whole molecule, with the best spatial resolution down to 1.5 Å . These "eight spots" have good spatial correspondence with the eight C-H bonds on the four pyrrole rings of a magnesium porphyrin molecule, indicating that the detection sensitivity and [spatial resolution](#) have reached the single-chemical-bond level.

Raman imaging patterns of other vibrational peaks also show good correspondence to relevant chemical groups in terms of characteristic peak positions and spatial distributions [as shown in Figures (b) and (c)]. The correspondence provided by the simultaneous spatially and energy-resolved Raman imaging allows them to correlate local vibrations with

constituent chemical groups and to visually assemble various chemical groups in a "Lego-like" manner into a whole molecule, thus realizing the construction of the chemical structure of a molecule.

Scanning Raman picoscopy (SRP) is the first optical microscopy technique that has the ability to visualize the vibrational modes of a molecule and to directly construct the structure of a molecule in [real space](#). The protocol established in this proof-of-principle demonstration can be generalized to identify other molecular systems, and can become a more powerful tool with the aid of imaging recognition and machine learning techniques. The ability of such Ångström-resolved scanning Raman picoscopy techniques to determine the [chemical](#) structure of unknown molecules will undoubtedly arouse extensive interest of researchers in the fields of chemistry, physics, materials, biology and so on, and is expected to stimulate active research in the fields, as SRP develops into a mature and universal technology.

More information: Yao Zhang et al, Visually Constructing the Chemical Structure of a Single Molecule by Scanning Raman Picoscopy, *National Science Review* (2019). [DOI: 10.1093/nsr/nwz180](https://doi.org/10.1093/nsr/nwz180)

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