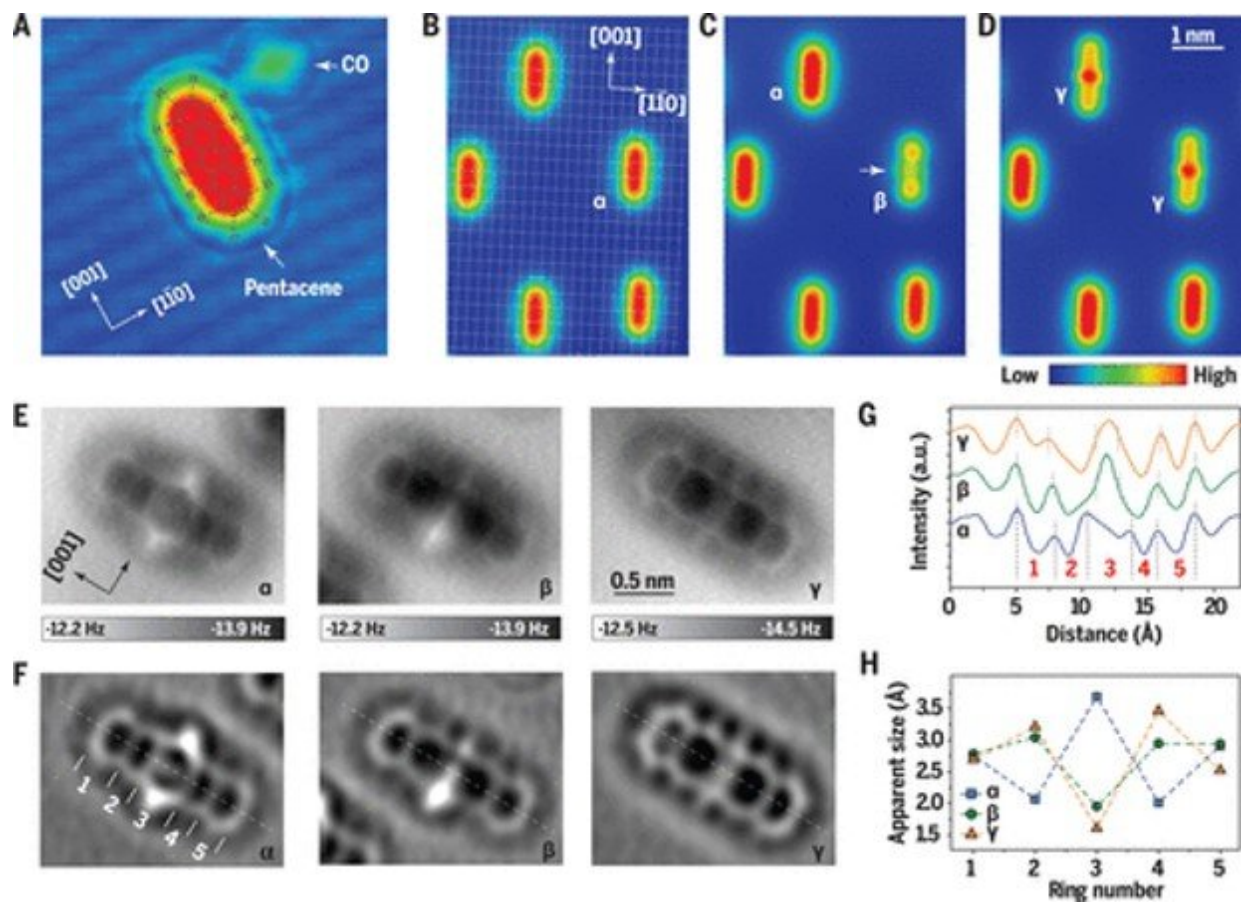# Understanding the structural and chemical heterogeneities of surface species at the single-bond limit

March 24 2021, by Thamarasee Jeewandara

Transformations of pentacene on the Ag(110) surface. (A) Atomically resolved Ag(110) surface with adsorbed pentacene and CO molecules. STM imaging conditions: 60 mV and 1000 pA with a CO-decorated tip. (B to D) STM topographic images of individually intact pentacene molecules (a) and the transformed species (b and g) classified according to shape. The middleright

molecule was transformed by two consecutive voltage pulses of 2.0 V, and the upper molecule was transformed by a 2.6-V voltage pulse. The superposed grids in (B) indicate the Ag(110) surface lattice. STM imaging conditions: 0.1 V and 200 pA. (E and F) Constant-height AFM images and the corresponding Laplacefiltered images of species a, b, and g. Quality factor Q ≈ 12,000. (G) Line profiles obtained along the white dashed lines in (F), with numbers labeling the benzene rings. (H) Relative apparent size changes of the five benzene rings in α, β, γ. Credit: Science, doi:10.1126/science.abd1827

Advances in tip-based microscopy in materials science have allowed imaging at angstrom-scale resolution, although the technique does not provide clear characterization of the structural and chemical heterogeneities of surface species. In a new report now published on *Science*, Jiayu Xu and a research team in quantum information and quantum physics at the University of Science and Technology of China used a model system of [pentacene](#) derivatives on a silver surface. The researchers then combined a range of materials characterization techniques including [scanning-tunneling microscopy](#), [atomic force microscopy](#) and tip-enhanced Raman scattering to provide electronic, structural and chemical information to characterize diverse, yet structurally similar chemical species relative to their interaction with the metal surface at single-bond resolution. The proposed multi-technique approach has wide applications across fundamental studies for heterogenous catalysis of surface chemistry.

Joint strategy for surface chemistry

Molecules that are [adsorbed on a surface](#) can undergo marked changes to form different surface [species](#) as a result of structural defects, [chemical](#) bond breaking and/or chemical bond formation. Materials scientists are keen to identify the structure or heterogeneity of surface species to

better understand surface science. Such efforts require precise characterization of chemical bonds within molecules and substrates. Researchers have used a variety of tip-based microscopic and spectroscopic methods to achieve the task including scanning-tunneling microscopy (STM), scanning-tunneling spectroscopy (STS) and noncontact atomic force microscopy (AFM), to resolve static electronic structures and intramolecular geometric surface species maintaining high energy and resolution. The techniques are limited due to a lack of chemical sensitivity, which can hinder its ability to determine the heterogeneity (diversity) of surfaces. To overcome the weakness, researchers have used tip-enhanced Raman spectroscopy (TERS). Based on the method, scanning Raman picoscopy (SRP) provided an optical method with single-bond resolution to fully map individual vibrational modes and visually develop chemical structures of single molecules. All three methods can reach an angstrom-level resolution in real space, a combination of these methods can provide comprehensive detail to interrogate the heterogeneity of surface species. Xu et al. first selected pentacene ($C_{22}H_{14}$) on the silver surface as the model system. Pentacene is a benchmark system often used to characterize the resolution and performance of STM and AFM techniques.
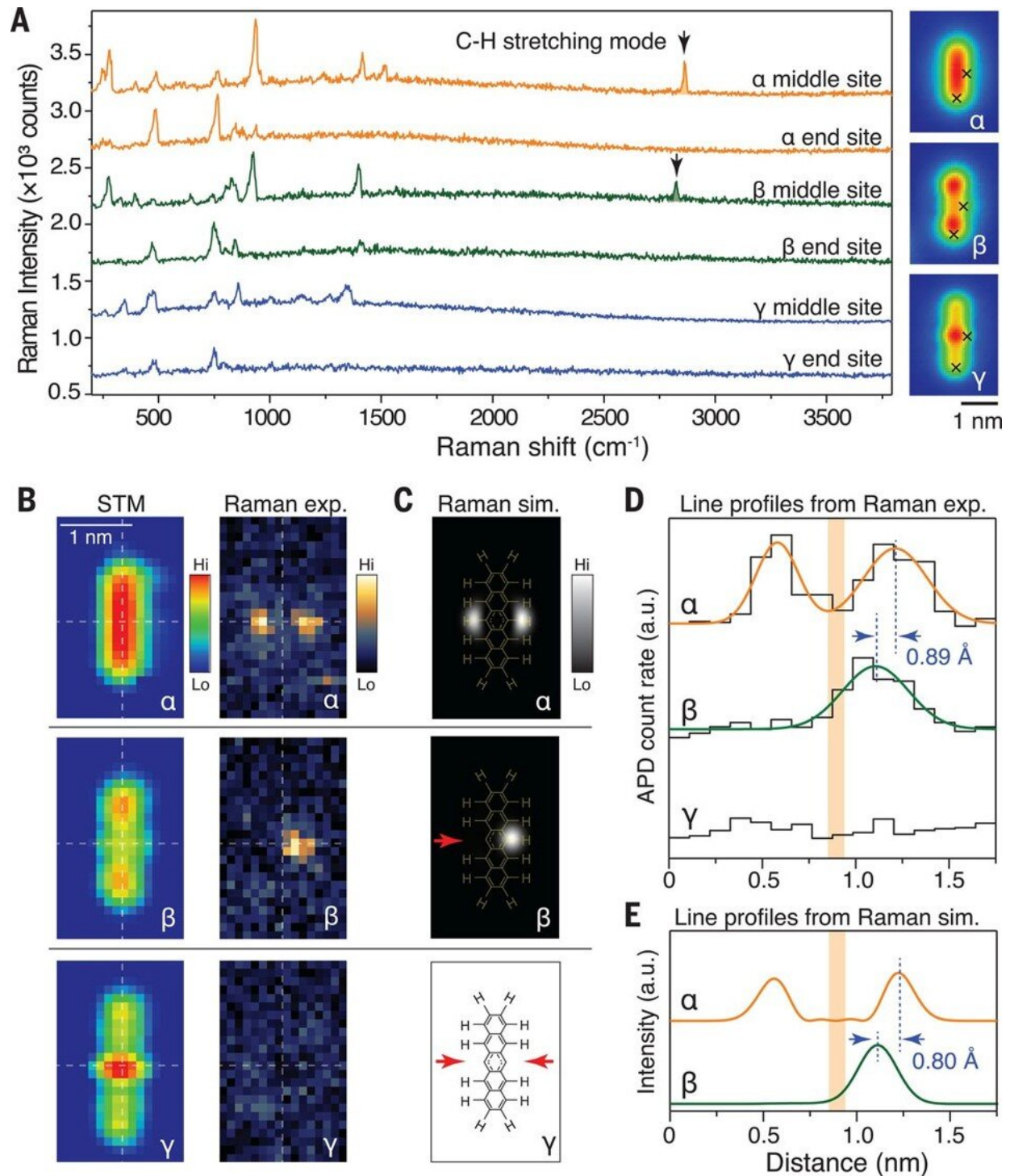
Determining C–H breaking by Raman spectra and maps. (A) Typical Raman spectra obtained at the middle and end sites marked by the crosses over the species of a, b, and g in the right panel. Parameters for tip-sample nanocavity: 0.1 V and 8 nA. Excitation light: 532 nm and 0.2 mW. CCD spectrometer

integration time: 5 s. The spectra are shifted by a separation of 500 counts for clarity. (B) Simultaneously obtained STM topographic images and Raman maps for the C–H stretching mode of the pentacene species a, b, and g. Vertical and horizontal lines indicate the long and short molecular axes, respectively. STM imaging conditions: 0.05 V and 8 nA. Raman maps were collected by introducing the photons in the ~2800 to 2900 cm−1 wave-number window to the APD detector, with a duration time of 25 ms per pixel (see fig. S9). (C) Simulated Raman maps of the C–H stretching mode for the three pentacene species. Red arrows indicate C–H bond breaking at the central benzene ring in b and g. (D and E) Line profiles obtained along the short molecular axis in the experimental and simulated Raman maps, respectively, vertically shifted for clarity. The orange and green curves in (D) are the Gaussian fitting of the peaks. Credit: Science, doi:10.1126/science.abd1827

The experiments

During this work, the team obtained STM (scanning-tunneling microscopy) images of an anatomically resolved metal surface with adsorbed pentacene and carbon monoxide (CO) molecules at a low voltage bias. When the team applied voltage pulses of 2.0 V on to a molecule, they formed two kinds of new species with different shapes. These included species β with a dumbbell-like shape and species γ with a spindle-like shape. Pentacene and its derivatives also strongly showed voltage-dependent contrast in the STM topographies alongside different electronic states in the STS spectra. The plasmonic excitation of the system appeared to be strongly responsible for the transformation of pentacene. The use of STM and STS (scanning-tunneling microscopy and scanning-tunneling spectroscopy) alone could not directly determine the actual chemistry of the transformed species. As a result, Xu et al. used AFM (atomic force microscopy) with a CO-decorated tip to further understand the three species, which include the intact pentacene molecule (α). They noted the appearance of dark halos, arising from van

der Waals attraction at the periphery of all three species (α, β, γ) where the inner molecular structures maintained atomic resolution, which originated from short range Pauli repulsion. The AFM method provided more structural detail compared to STM. The work showed how the center of carbon atoms of pentacene could interact with the silver surface. Xu et al. noted interactions between two possible sources of transformation from α to γ, allowing the central benzene ring to open with atom rearrangements; to confirm either hypothesis, they needed to know more about local chemical bonds.
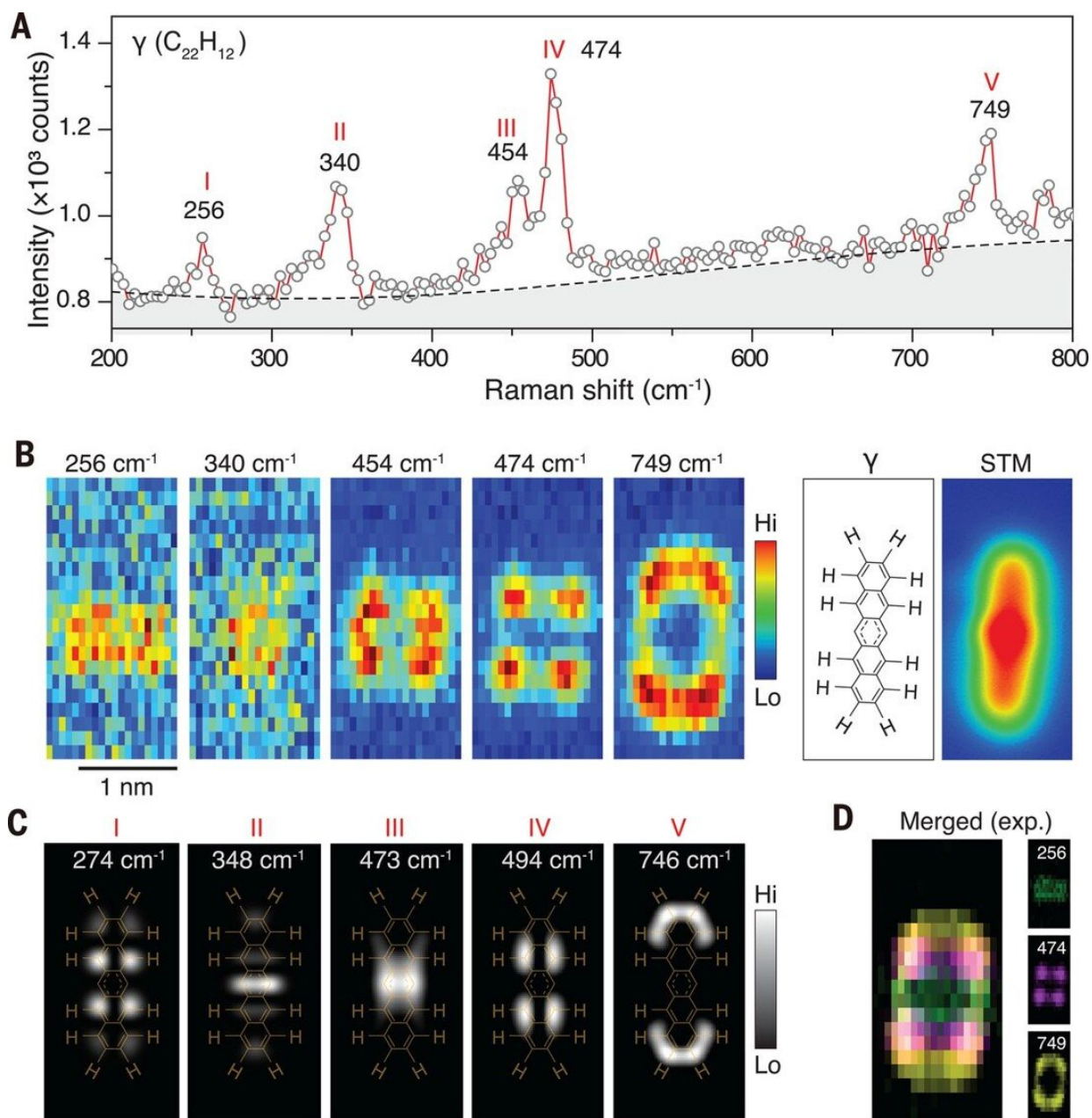
Raman spectra and maps of the characteristic vibrations in the molecular skeleton. (A) Typical Raman spectra recorded around the central benzene ring of species g (C22H12). The five peaks are denoted as the vibrations "I" to "V" in the low-wave-number range. The dashed line indicates the background counts extracted from the baseline correction method. (B) Raman maps of γ recorded by integrating the signals at the corresponding peaks in (A) with background subtracted. The corresponding STM topographic images and the structure are shown in the right panels. (C) Simulated Raman maps of the corresponding

vibrations of the γ species. (D) Merged image of the experimental Raman maps of 256, 474, and 749 cm−1 with different colors. Credit: Science, doi:10.1126/science.abd1827

Understanding chemical bonds

The researchers used TERS (tip-enhanced Raman spectroscopy) measurements to characterize chemical bond information—since the Raman signals were directly related to the vibrational motion of the bonds. The team obtained Raman spectra from species α, β and γ by locating the tip across the sites of the sample. The carbon-hydrogen (C-H) stretching mode of pentacene appeared alone in the high-wave number region to provide a clear energy window to monitor the structure of change relative to C-H bonds. The team obtained the most convincing evidence of C-H bond breaking from Raman maps relative to specific vibrational modes. Alternatively, they could also use a high-speed, single-photon avalanche photodiode (APD) with an edge-tunable band-pass filter to record the TERS maps. They characterized the major difference among the three pentacene species based on the number of C-H bonds in the central ring and during structural transformation. The simulated Raman maps were in good agreement with the experimental outcomes and showed how all vibrational modes maintained highly localized features. For example, the TERS signals were located at the central ring or the outer rings of the species implying highly conjugated pentacene to be partially conjugated. The experimental Raman modes could also be further described by theoretical simulations for the suggested molecular structure. By combining the chemical components obtained using TERS and AFM techniques, the team also verified the possible chemical structures of the γ species.
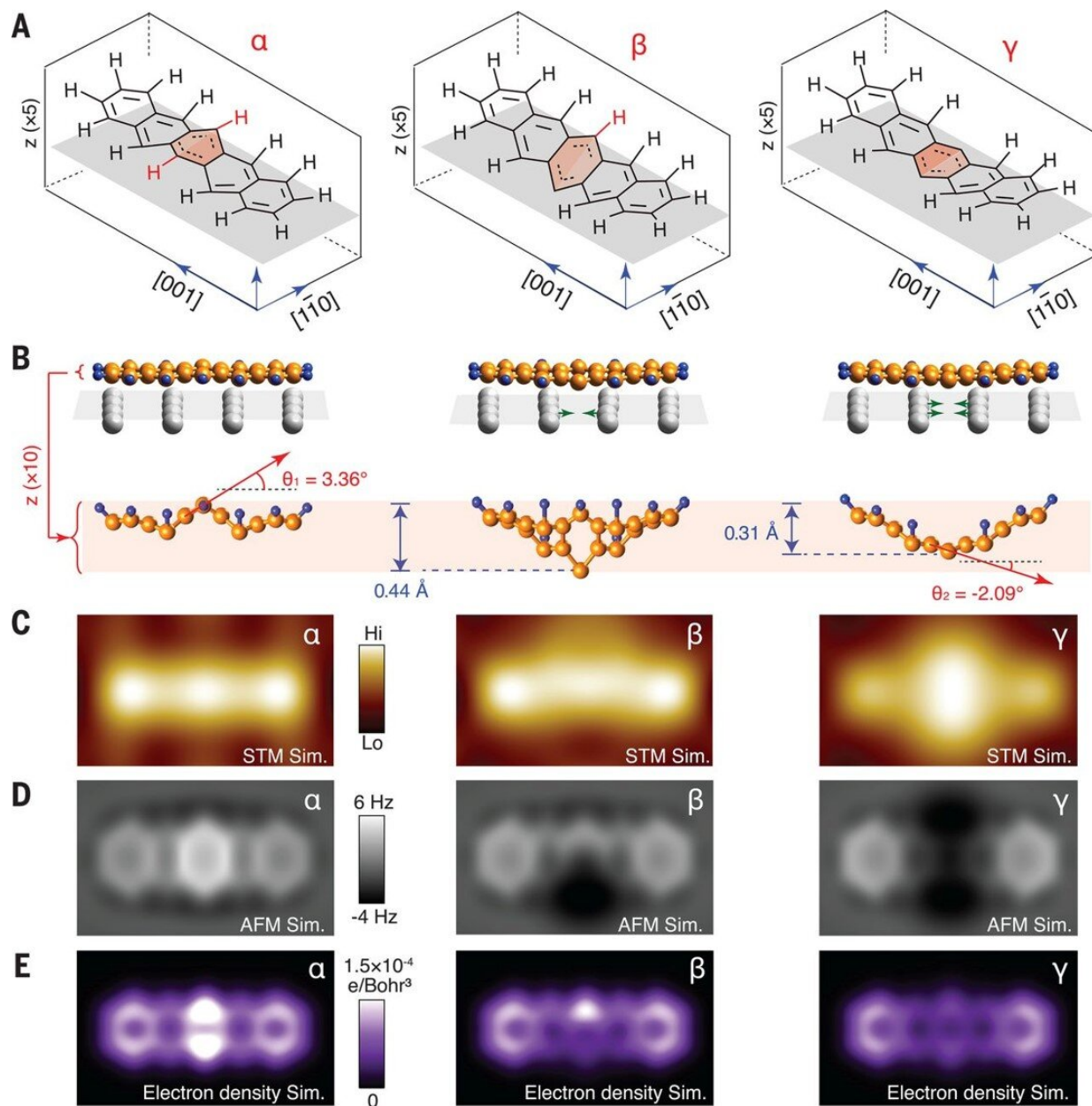
Optimized structures and simulated images. (A) Optimized 3D geometries of the pentacene species a,b, and g, with enlarged scale (×5) along the surface normal. (B) Top panel is a side view of the optimized geometries. The slight displacement of Ag atoms along the [001] direction is indicated by the green arrows under b and g. Bottom panel is a side view of the distorted skeletons with enlarged scale (×10) in the surface normal. q1 and q2 denote the distortion of the central benzene ring in a and g, respectively, with respect to the surface plane. d = 0.44 Å, and 0.31 Å labels the displacement of central C atom along the surface

normal direction from a to g. (C) Simulated constant current STM images with integrated DOSs in the range from 0.2 to 0.3 V. The images have been processed with Gaussian smoothing with an SD of 1.33 Å. (D and E) Simulated AFM images and electron density maps of a, b, and g. AFM images are simulated with the effective lateral stiffness k = 0.5 N·m−1 and q = 0.2e. Credit: Science, doi:10.1126/science.abd1827

Outlook

The combined experiments using STM, AFM, and TERS (scanning-tunneling microscopy, atomic force microscopy and tip-enhanced Raman spectroscopy) additionally provided a better reference parameter for selection during density functional theory (DFT) simulations. For example, the STM image simulations reproduced the characteristic rod-like, dumbbell-like and spindle-like features for α, β and γ respectively, albeit with marginal error, which Xu et al. clarified relative to reliable structural information. In this way, Jiayu Xu and colleagues showed how modern tip-based techniques could be used to characterize surface chemistry in materials science. Using a joint strategy of STM-AFM-TERS, they experimentally determined the interrelated structure and chemical heterogeneities of surface species relative to these pentacene species on a metallic surface. The experimental protocol detailed in this work can be widely applied to study the surface chemistry and catalysis at the single-bond limit in materials science.

More information: Xu J. et al. Determining structural and chemical heterogeneities of surface species at the single-bond limit, *Science*, 10.1126/science.abd1827

Zhang R. et al. Chemical mapping of a single molecule by plasmon-enhanced Raman scattering, *Nature*, doi.org/10.1038/nature12151