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Direct Wiring of Photons Into Molecules: TERS in the ANF

The atomic limit in optical microscopy was attained through Tip-enhanced Raman scattering (TERS) in the atomistic near-field (ANF). [1,2] By replacing the compound optical microscope with an atomically terminated Ag needle that functions at once as plasmonic antenna, waveguide and focusing lens, an image resolution of 1.6 Å, equaling the radius of the Ag atom, is attained.[1,2] While the images make it clear that light is atomically confined, it is possible to further establish experimentally and theoretically that the photon is atomically confined at the tip apex. Atomically confined photons acquire mass, charge and momentum of an electron, which is measured in tunneling TERS microscopy. In this limit, photon and electron become indistinguishable, optical and electron microscopy merge, and TERS functions as a network analyzer of molecular electronic circuits that can probe atom-resolved point contacts. This is illustrated in Fig. 1a for a pyridine molecule chemisorbed on copper, probed through its meta-CH bond terminal. The equivalent circuit in Fig. 1b is illustrative of a network analyzer. The far field photon impinging on the tip antenna (green wave) is focused into the apex mode and injected into the σ-network of the molecular circuit (yellow arrows), which is interconnected to the π-network (red arrows) through the π-backbond at the copper atom. As in a supply line terminated at an impedance, Z, the reactive optical current is radiated back into the far field. Vibrational line intensities now measure conductivity of the molecule along paths traced by the normal modes and governed by quantum interference among the open channels. The fundamental processes of electron transport and bond selective intramolecular conduction is for the first time accessible through TERS in the ANF.

References

[1] J. Lee, K. Crampton, N. Tallarida, V. A. Apkarian, Nature, 568 (2019), p. 78.
[2] Y. Zhang et al., Nat. Sci. Rev, 6 (2019), p. 1169.

Figures

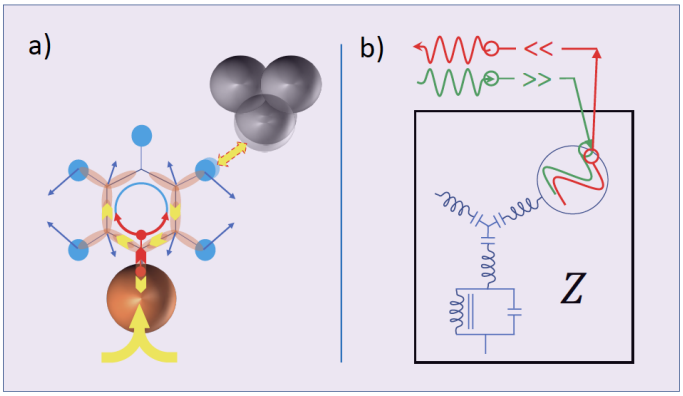

Figure 1: a) A pyridine molecule chemisorbed on copper, probed with an atomically terminated Ag tip at its meta-CH bond terminal. The photon is injected into the molecule as optical current that connects the Ag tip to the Cu substrate through the intramolecular circuit traced by the normal modes. b) TERS as a network analyzer operating at optical frequency, with the tip acting as transimpedance wire connecting the radiation in the far field to the intramolecular current in the atomistic near-field (ANF).