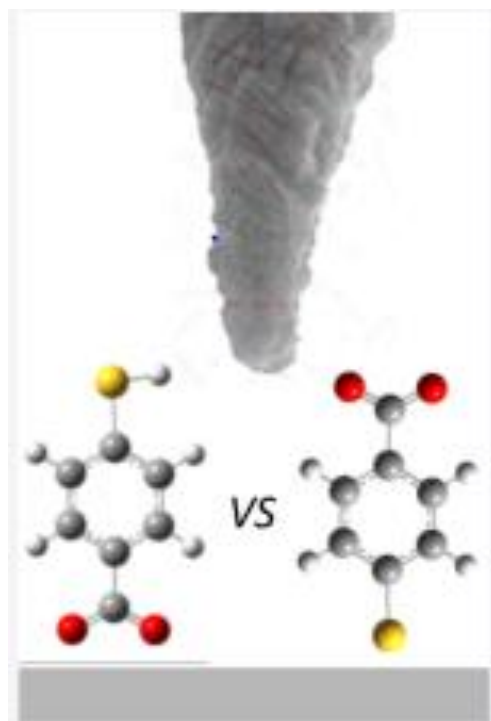
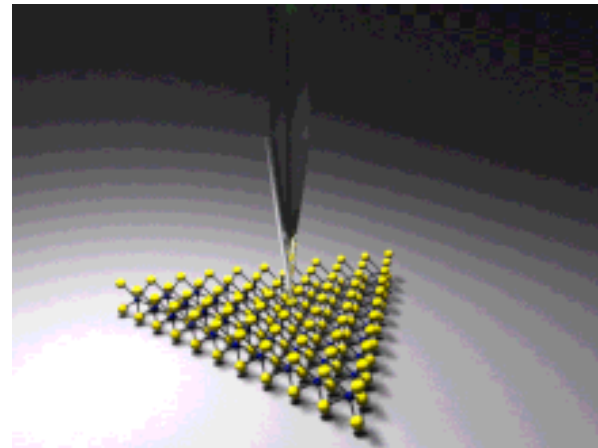
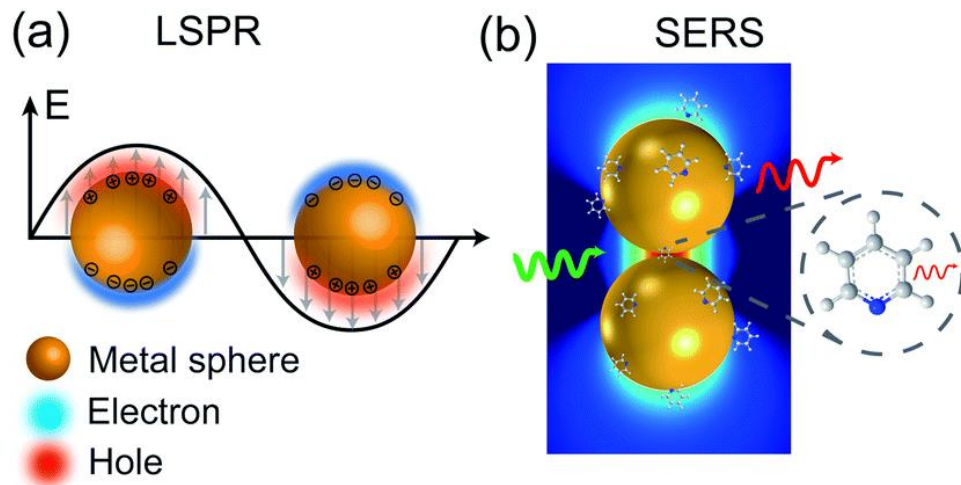


Mapping Molecular Adsorption Configurations with <5 nm Spatial Resolution through Ambient Tip-Enhanced Raman Imaging

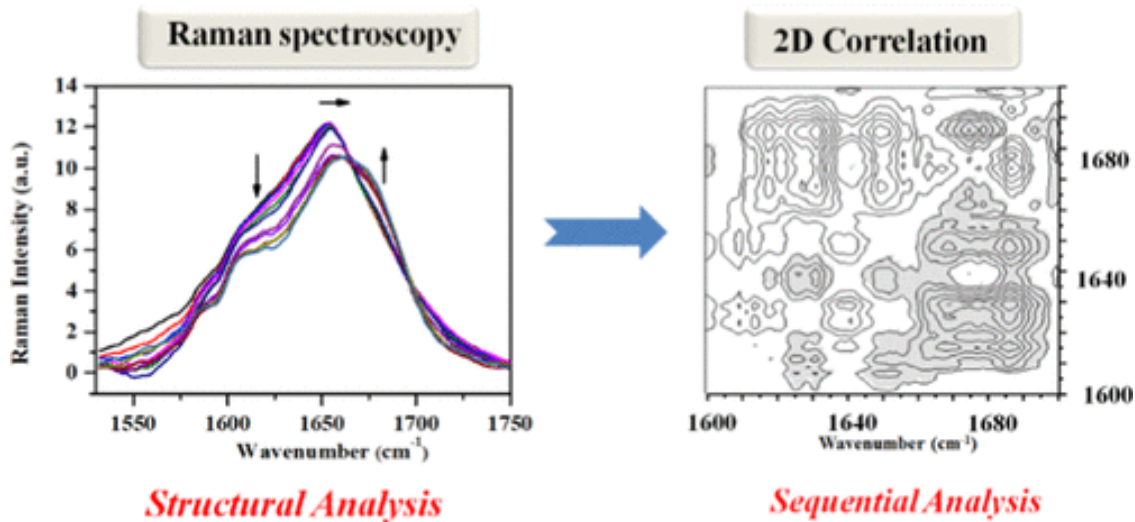
Matthew Gabel, Brian T. O'Callahan, Chloe Groome, Chih-Feng Wang, Regina Ragan, Yi Gu, and Patrick Z. El-Khoury*



i) Surface enhanced Raman spectroscopy (SERS) ii) Tip enhanced Raman spectroscopy (TERS)



iii) 2D correlation spectroscopy



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Article

Spatially Resolved Mapping of Three-Dimensional Molecular Orientations with ~ 2 nm Spatial Resolution through Tip-Enhanced Raman Scattering

Patrick Z. El-Khoury* and Edoardo Aprà

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Letters

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Letter

The Prevalence of Anions at Plasmonic Nanojunctions: A Closer Look at *p*-Nitrothiophenol

Chih-Feng Wang, Brian T. O'Callahan, Dmitry Kurouski, Andrey Krayev, and Patrick Z. El-Khoury*

Three Distinct Geometries of Surface-Adsorbed Carboxylate Groups

Jung Sang Suh* and Jurae Kim

Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea

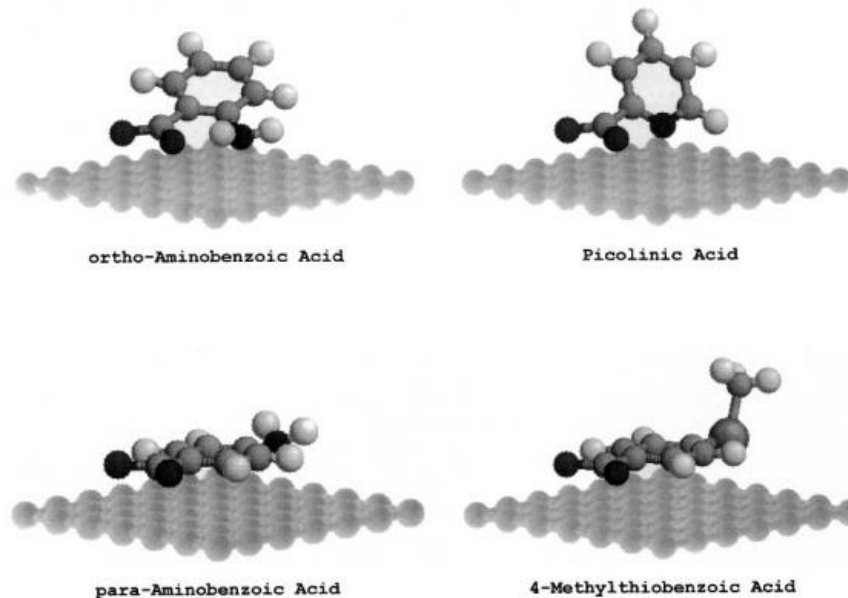


Figure : The proposed surface geometries of p-aminobenzoic, 4-methylthiobenzoic, o-aminobenzoic and picolinic acid

Motivation

- Combination of TER spectroscopy and microscopy and 2D correlation spectroscopic studies to understand various motifs of binding of a molecular reporter.

Why this paper?

- First report of the different binding motifs of p-MBA on a Silver surface with <5 nm spatial resolution.

- ✓ It addresses that MBA chemisorbs onto the plasmonic particles with at least two distinct configurations: S- and CO₂- bound.
- ✓ A combination of tip enhanced Raman spectroscopy and microscopy, 2D correlation analysis and density functional theoretical calculations is used to establish the result.
- ✓ The distinct adsorption geometries with a pixel-limited (<5 nm) spatial resolution is obtained.

Results and discussion

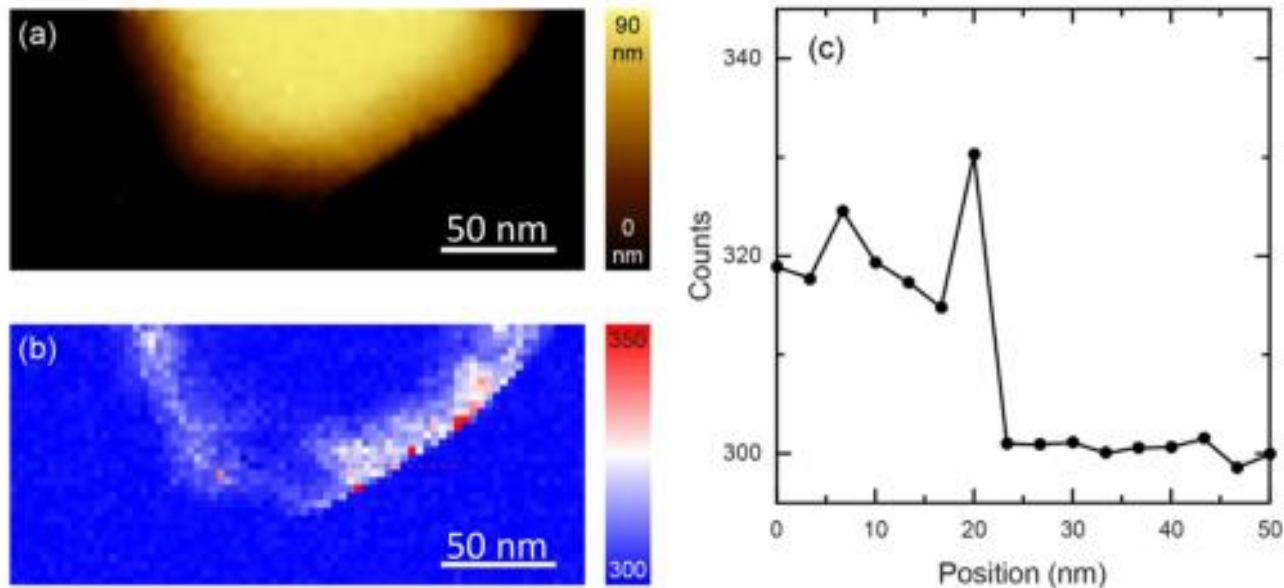


Figure 1. Concurrent AFM (a) and TERS (b) mapping of an MBA-coated silver nanocube. The TERS image is integrated in the 1557–1587 cm^{-1} spectral range. The dashed red line in (b) marks the positions at which the cross-sectional line profile in (c) was taken. The scale bars in (a) and (b) indicate 50 nm. Conditions used for TERS mapping: integration time = 0.5 s; power = 150 μW , focused using a 100 \times /NA = 0.7 objective; lateral step size \approx 3.3 nm.

Results and discussion

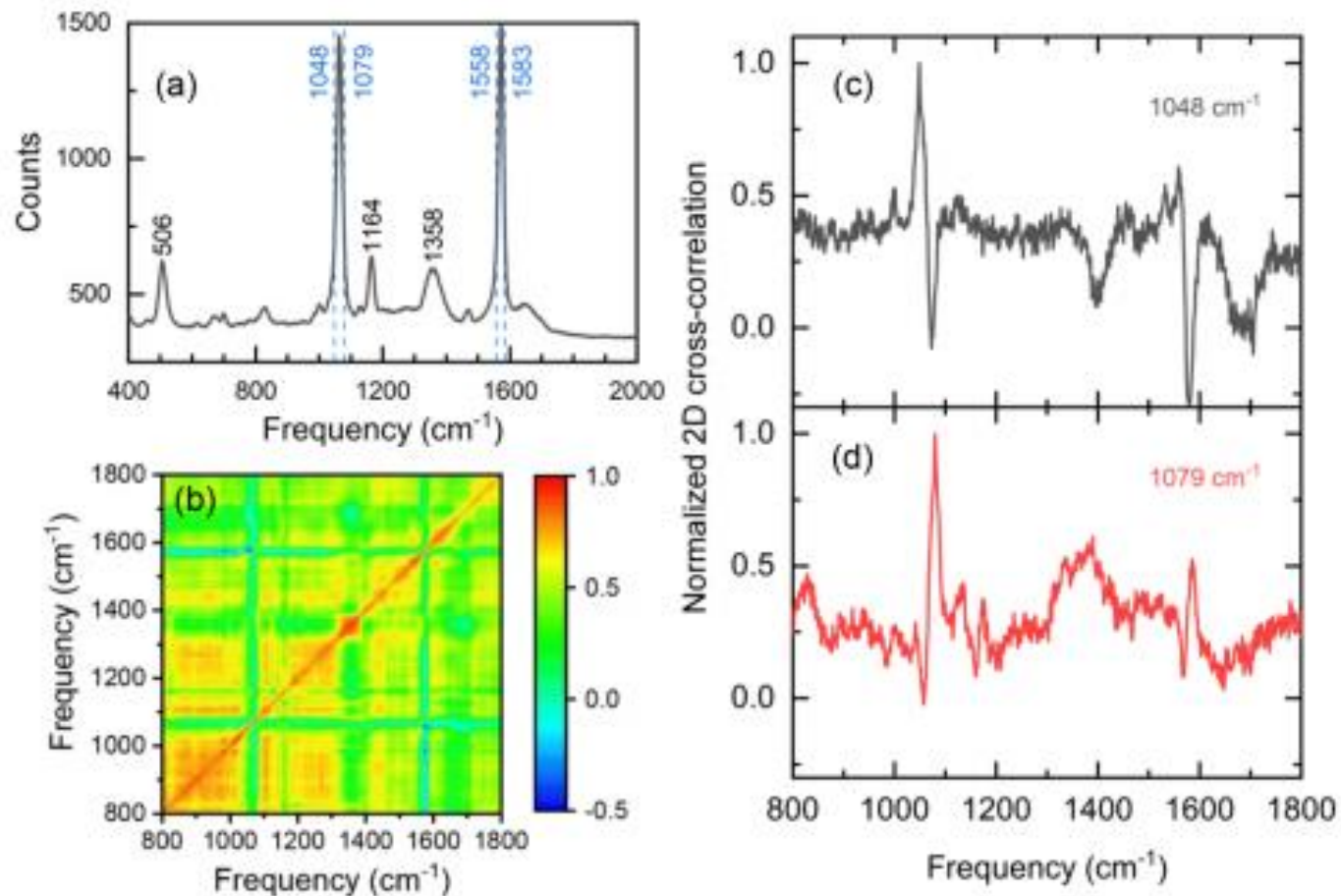


Figure 2. (a) Spatiotemporally averaged TERS response, taken from the data set shown in Figure 1b. A cross-correlation map ($\rho_{j,k} = \sigma_{jk}^2 / \sigma_{jj} \cdot \sigma_{kk}$) of the spatially varying TERS spectra is shown in (b). Cross-correlation slices ($\nu_j \neq \nu_k$) are taken at two frequencies and shown in (c) and (d)

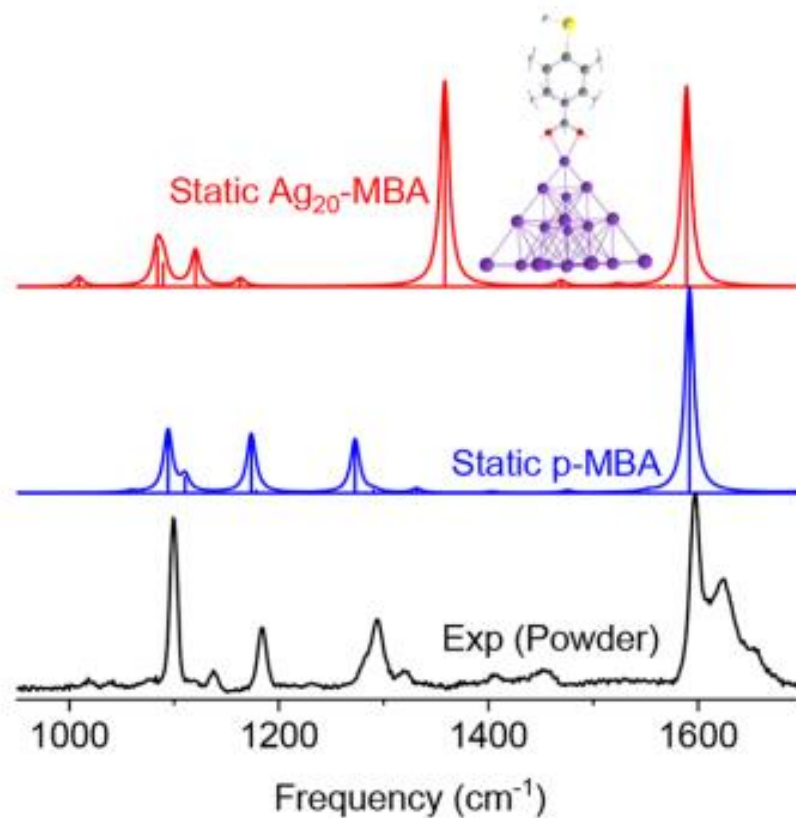


Figure 3. Experimental powder spectrum (black, 633 nm, 50 $\mu\text{W}/\mu\text{m}^2$) is shown along with the simulated spectra of the isolated (blue) and Ag₂₀-bound (red) MBA complex. The inset shows the structure of the CO₂-Ag bound complex

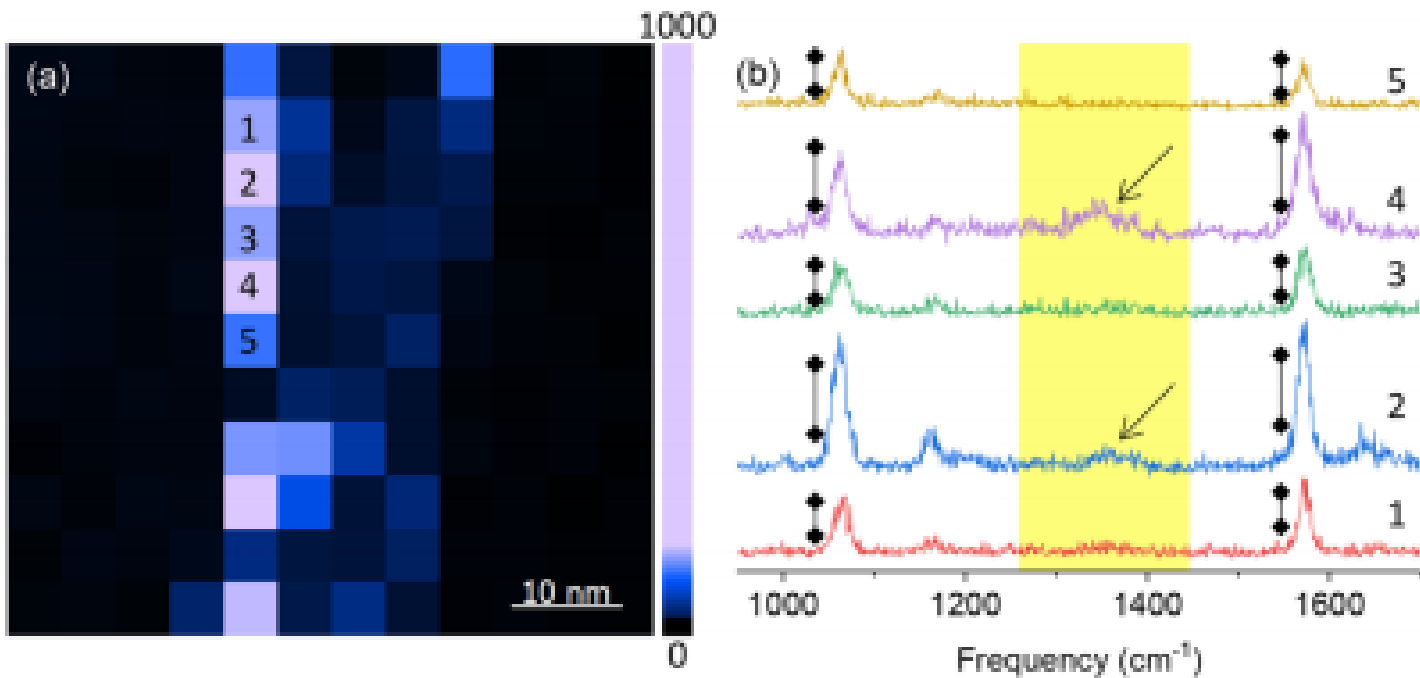


Figure 4 : Zoomed in TERS image, tracing the edge of a silver nanocube (centered to the left of the image shown in panel a) Several pixels are enumerated in (a) and plotted in (b). They show the prevalence of the CO₂-bound vs S-bound MBA.