

## In-situ ultra-low frequency SERS spectroscopy at electrified interfaces

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Surface-specific vibrational spectroscopy is recognized as a powerful tool for in-situ observation of electrode/electrolyte interfaces. However, terahertz (THz) or far-infrared (FIR) absorption spectroscopy is hardly applicable to in-situ observation of such “buried” interfaces, especially for detecting low frequency extramolecular vibrations including rich information on electrode/molecule interactions. On the other hand, surface enhanced Raman scattering (SERS) spectroscopy has a potential advantage in detecting such low frequency vibration modes even under electrochemical conditions. Based on recent technological advancements in fabrication of optical notch filters, we have extended the detectable frequency range of SERS into the ultra-low frequency region [1]. Moreover, this ultra-low frequency SERS was combined with sphere-plane type gap-mode SERS method, which enabled us to conduct SERS spectroscopy even at atomically defined single crystalline surfaces of various metals [2-4].

Figure 1 shows SERS spectra of 4-methylbenzenethiol measured on Au(111) and Au(100) as well as on a conventional SERS-active rough Au surface. Here, the measured SERS spectra were converted to  $\chi''$  spectra to reduce thermal factor, scattering efficiency factor, and SERS enhancement factor, which significantly affect apparent spectral features especially in the ultra-low frequency region [5]. Extramolecular vibrations such as  $\nu_{\text{Au-S}}$  or  $\delta_{\text{AuS-Ph}}$  clearly exhibited the crystal orientation dependence.

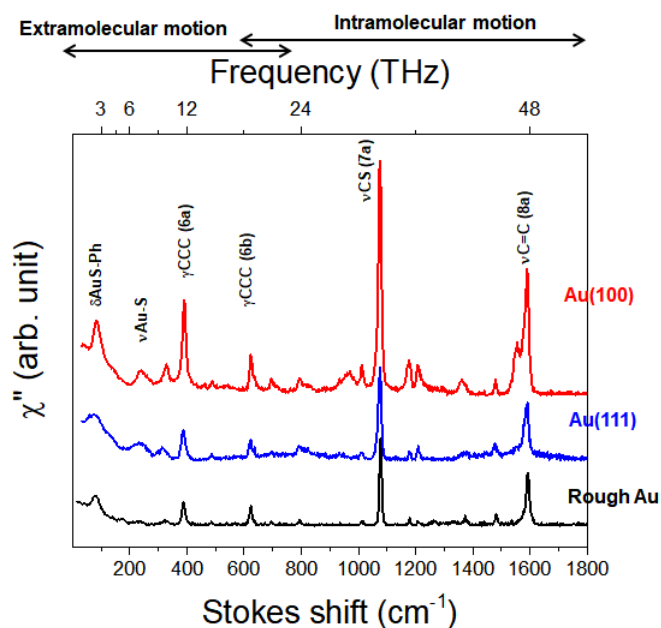


Figure 1. SERS spectra of 4-methylbenzenethiol on rough Au, Au(111), and Au(100).

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