Surface-Enhanced Raman Scattering of P- aminobenzoic acid on Nobel Metal Nanoparticle Surfaces

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Introduction

- Surface-enhanced Raman spectroscopy (SERS) is a surface sensitive technique which enhances the Raman scattering of adsorbed molecules on rough metal surfaces. SERS is a good way to test how adsorbed molecules interact with nanoparticle surfaces including their orientation reactivity on the surfaces. In this study, SERS spectra of *para* aminobenzoic acid (PABA) were obtained on both silver and gold nanoparticles in solutions at varied concentrations of PABA.

Methods and Materials

- *Preparation of Ag Nanoparticles*

  To prepare silver colloids, 0.05-0.06 grams $AgNO_3$ were dissolved in 250 mL of deionized water and brought to a boil in. 5 mL of sodium citrate (1%) was added in 1 mL increments 1minute apart. After adding the final addition of sodium citrate boiled for 10-15 minutes, the solution was then placed in an ice bath and poured in a storage container.

Adapted from Lee, P.C and Meisel, D. *J. Phys. Chem A.* 1982,86,3391-3395

Methods and Materials

- *Colloidal metal film preparation*

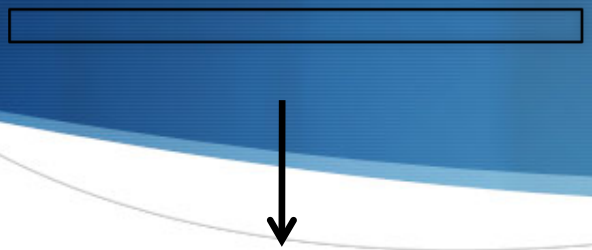
  Submerge precut slides (microscope slides, cut to fit a cuvette) in piranha solution, for 10 minutes (1 part H_2SO_4, 4 parts H_2O_2 (35%)). After rinsing the slides thoroughly with methanol, soak in solution with 1 part 3-aminopropyl trimethyloxysilane (APTMS), 4 part methanol for 48 hours. Rinsed with methanol again, individually placed in vials with silver colloid for 24 h, and then rinsed with deionized water. The slides were kept in deionized water prior to use.

  Adapted from Keating C.D., Kovaleski K.M., Natan M.J.*J Phys Chem B.* 1988,102, 9404-9413

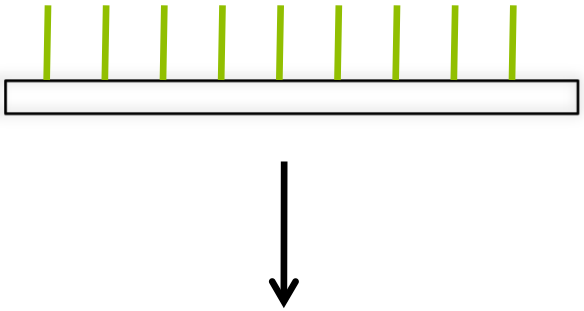
Methods and Materials

- *UV/Vis*

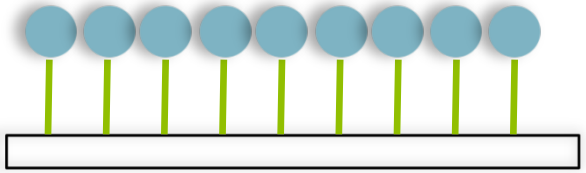
  Uv-Vis absorbance spectra were obtained for each colloid and each colloidal metal film. SERS spectra were also obtained by using Raman spectrometer (532 nm, 150 mW, 30 μ m slits, auto-background subtraction, acquisition times vary). Two processes were used: invertase was mixed with silver colloid in a glass micro-well plate, or, invertase was placed directly on the colloidal film slide. All spectra were analyzed with Origin (OriginLab, Northampton, MA).



Glass microscope slide, cleaned in piranha.



Slides functionalized with APTMS.



Ag nanoparticles bind to slides through NH_2 group on APTMS.

Raman Spectrum

The normal Raman spectrum of solid PABA is shown in Figure 1. This spectrum was obtained by focusing the laser on solid PABA powder, and acquiring for 1 second, a total of five times. The PABA Raman spectrum is dominated by ν_{8a}, an in-plane ring torsion at 1605 cm^{-1}.

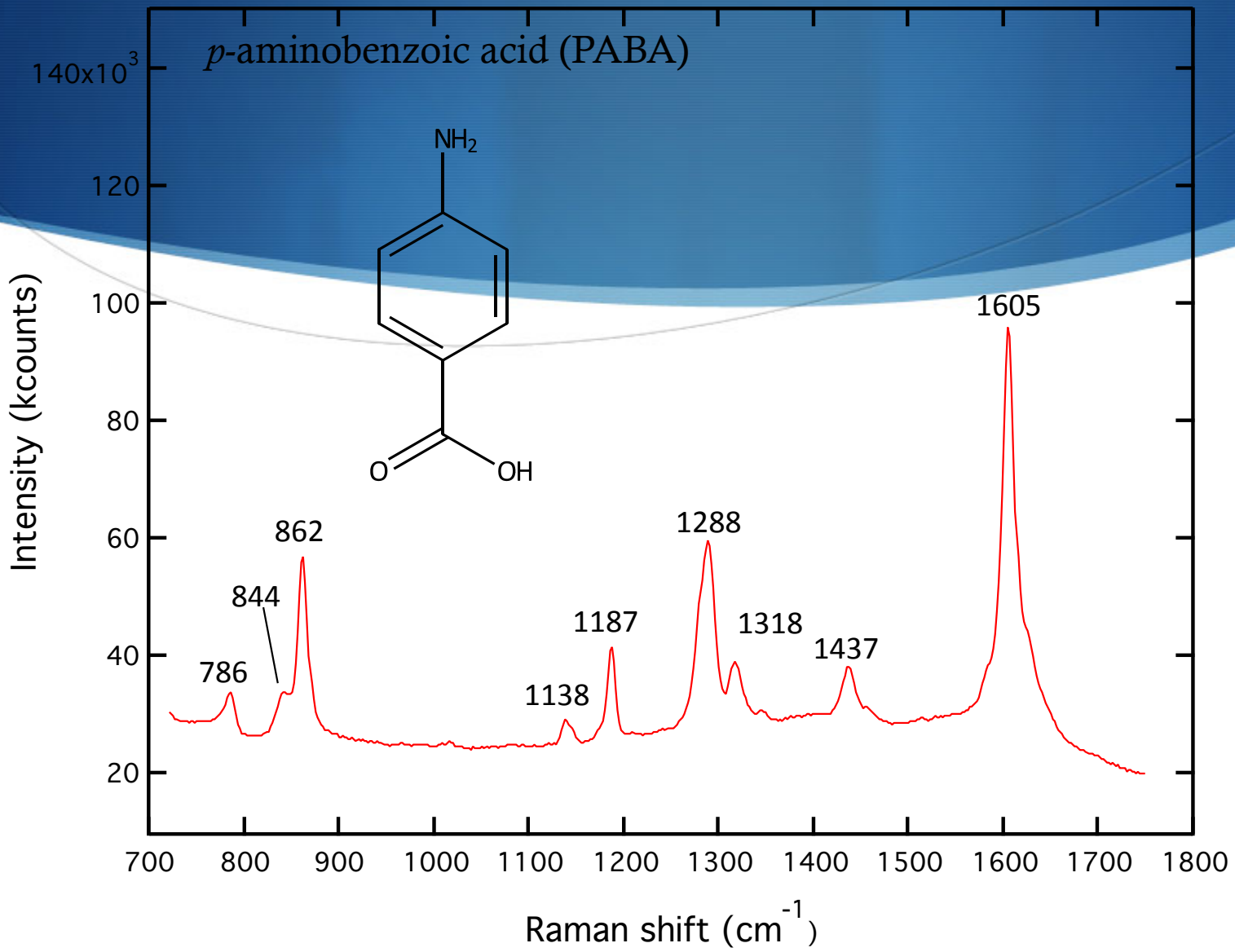


Figure 1. The Raman spectrum of solid PABA powder.

PABA SERS on Ag Colloids

The SERS spectrum of PABA is shown in Figure 2. This spectrum was obtained by focusing the laser in a solution that contained approximately 15 mg PABA/mL. This solution was made by mixing 30 mg/mL PABA in ethanol with aqueous silver colloids. The PABA SERS spectrum is dominated by ν_{8a}, and the carboxyl stretch (ν_s COO^-) at 1376 cm^{-1}.

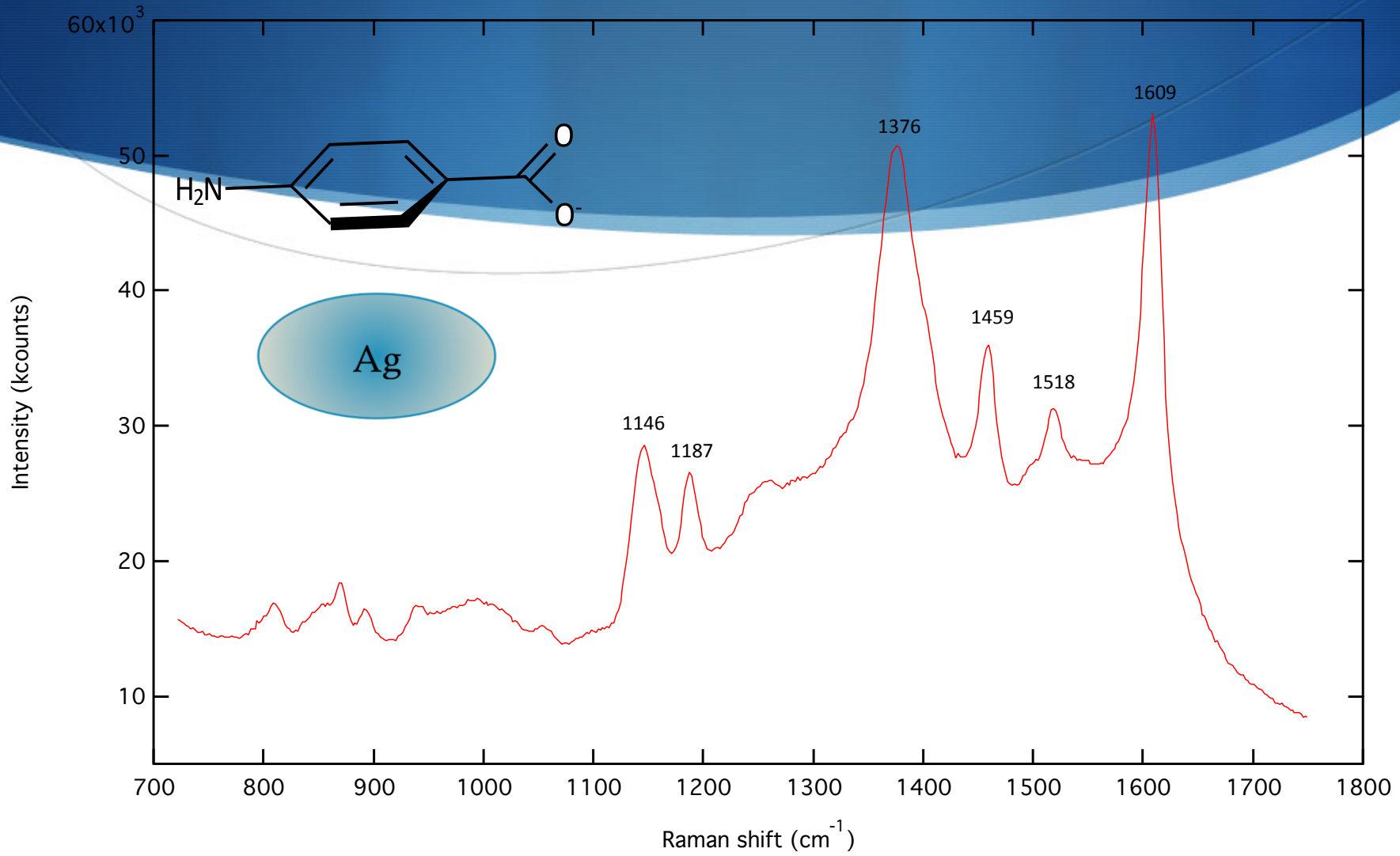


Figure 2. Solution SERS of PABA on silver colloids with 5 second exposure at 30 μ m silts demonstrates peaks corresponding to p-aminobenzoic acid vibrational model.

PABA SERS on Ag Nanoparticle Films

The SERS spectrum of PABA on Ag nanoparticle films is shown in Figure 3. The spectrum was obtained by coating the film with a solution of PABA (30 mg/mL in ethanol), acquiring for 5 seconds, 5 times. Like the PABA SERS spectrum on Ag colloids, this spectrum is dominated by ν_{8a}, and the carboxyl stretch (ν_s COO^-) at 1376 cm^{-1}.

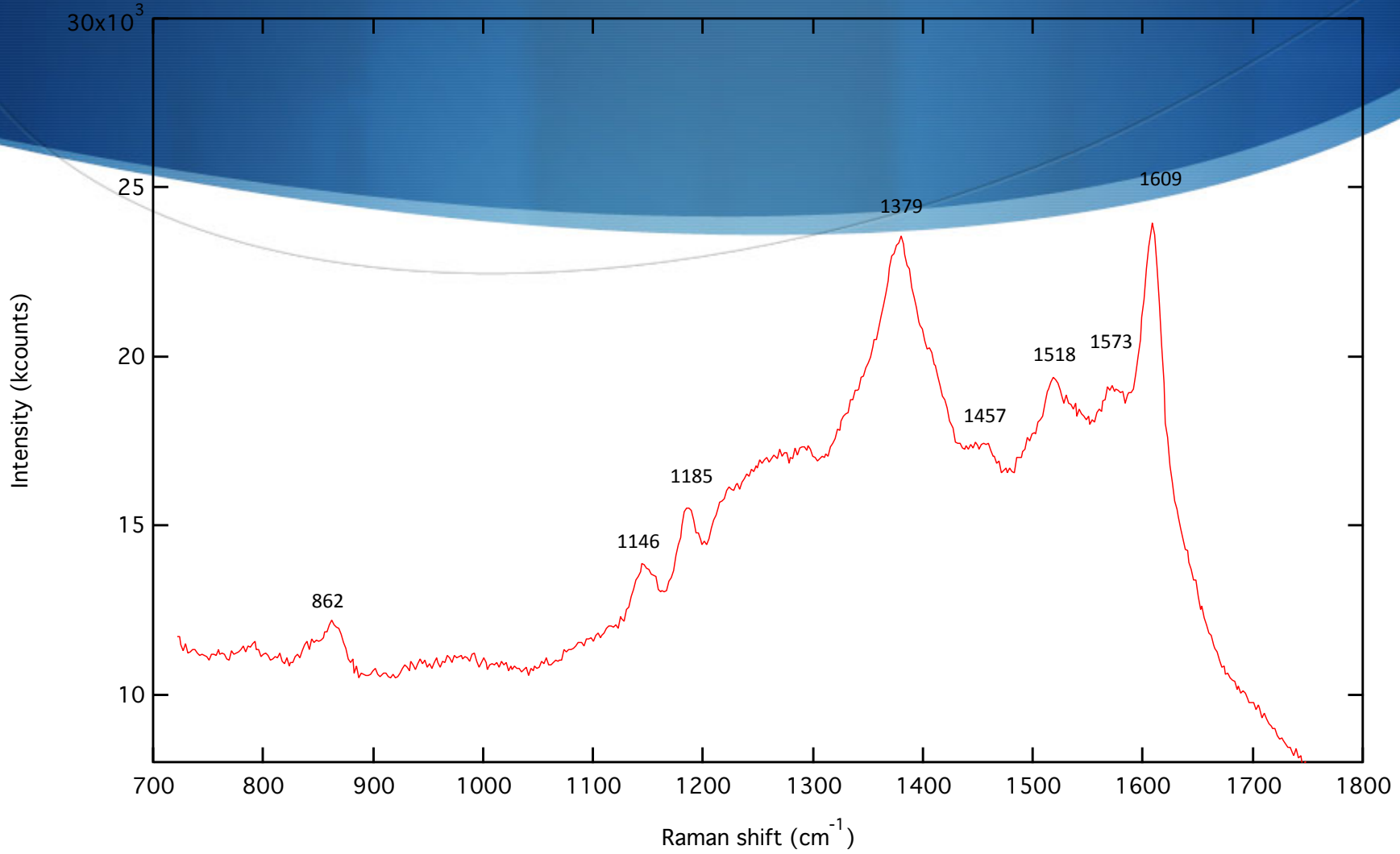


Figure 3. SERS spectrum of PABA absorbed on Ag nanoparticles with 5 second exposure at 50 μ m slits demonstrates peaks primarily corresponding to the carboxyl group.

Conclusions

Two conclusions may be drawn from this SERS spectrum:

1. PABA occurs as the anion (presence of ν_s COO^- and the NH_2 torsion, τ_{NH} at 1146 cm^{-1}).
2. PABA is likely oriented on the Ag nanoparticles as pictured on the inset (due to enhancement of benzene ring modes).

These results agree with Suh, J.Phys. Chem. 87, 1540 (1983)

Acknowledgments

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