Kinetics of the photoreduction of p-nitrobenzoic acid on Ag and Ag_xAu_{1-x} nanoparticle films

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Introduction

Surface-enhanced Raman spectroscopy (SERS) is a highly sensitive characterization technique discovered in the 1970's by Fleischman et al.[1] Early in SERS history Gersten, Nitzan, and Brus predicted photochemistry happened on certain surfaces. If those surfaces were altered, the SERS image would change as well.[2,3] Changes of the surfaces include size, shape, composition and/or roughness. This study focuses on the photoreduction of *para*-nitrobenzoic acid (PNBA).[4-7] This is a model reaction using SERS to study photochemistry at metal nanoparticle surfaces. We look to see how changing the composition and roughness of the metal nanoparticle surface will change the rate of the photoreduction reaction.
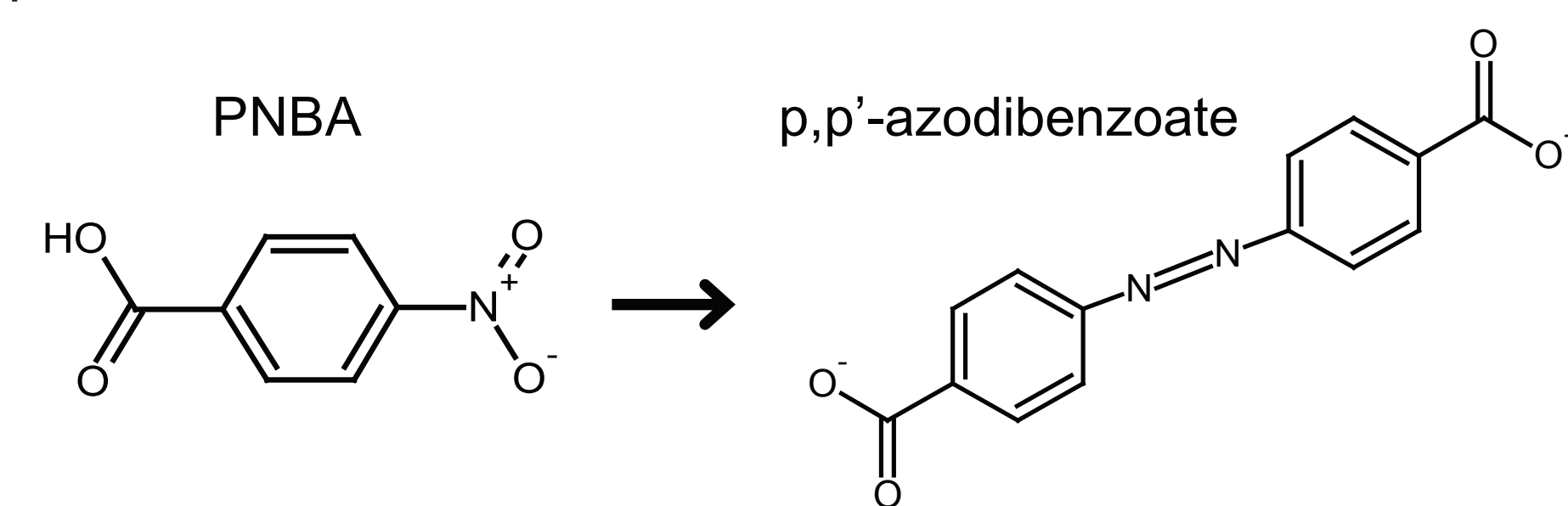

Figure 1. The photoreduction reaction of para-nitrobrnzoic acid into p,p'-azodibenzoate.

Materials and Methods

Materials. *Para*-nitrobenzoic acid was purchased from Lancaster Synthesis Inc. (Ward Hill, MA). Silver nitrate (99.8%) was purchased from Sigma-Aldrich (St. Louis, MO). Sodium citrate was purchased from VWR. All materials were used as received. Para-nitrobenzoic acid (5 mM) was prepared in ethanol (100%).

Colloid preparation. Silver colloid was prepared using the method of Lee and Meisel[8] with slight alterations; silver nitrate (0.05-0.06 g) was dissolved in deionized water (500 mL) and sodium citrate (5.0 mL, 1.0 mL/min) was added once the solution was boiling. The resulting colloids were yellow-brown with an extinction maximum near 420 nm. Alloy colloids were prepared using the method of Link et al.[9] with slight alterations; chloroauric acid (1.0 mM) and silver nitrate (1.0 mM) were used (total of 0.025 mmoles metal). The total volume was brought to 75 mL and the solution was heated. Once boiling, sodium citrate (5.0 mL) was added and boiled (30 min).

Colloidal metal film preparation. Silver nanoparticle slide preparation was adapted from Natan.[10] Quartz, ITO and glass slides were cut and immersed in piranha (1 part H_2O_2 (35%): 4 parts conc. H_2SO_4) for cleaning (10-15 min). The slides were rinsed well with methanol and soaked in silane solution (4 parts 3-aminopropyl tri-methyloxysilane: 1 part methanol) for 48 h. After rinsing with methanol again, the slides were individually placed in vials with colloid for 24 h and were rinsed with deionized water.

Instrumentation. Absorbance spectra were acquired for colloids and metal films. Raman spectra were obtained with a custom-built Raman spectrometer (532 nm, 150 mW, 50 µm slits). Spectra were analyzed using Origin (OriginLab, Northampton, MA).
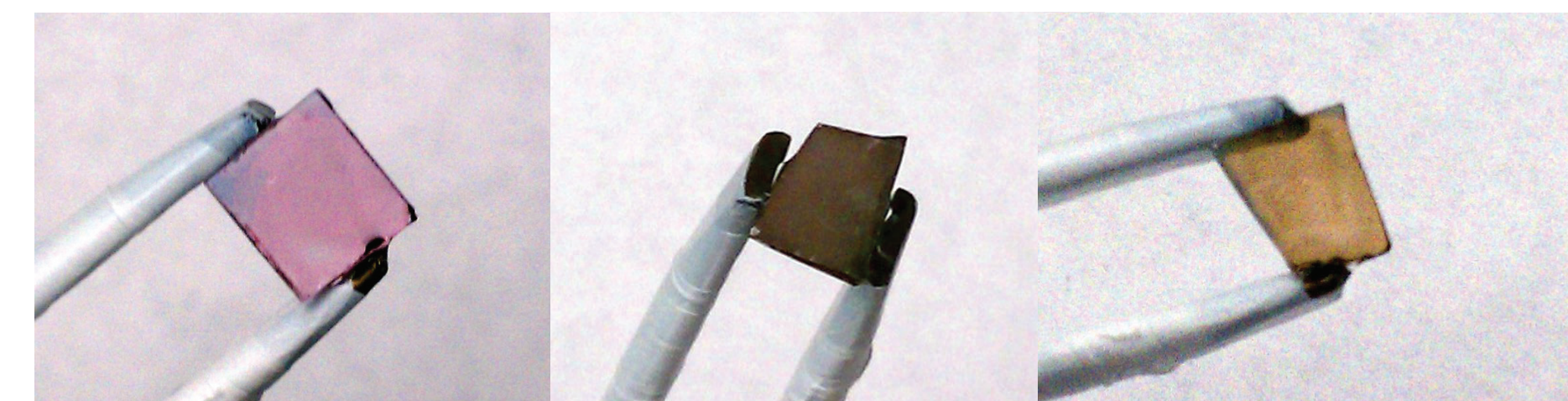
Experimental

Figure 2. Nanoparticle surfaces; Au on the left, Ag coated Au in the middle and $Ag_{0.5}Au_{0.5}$ on the right.
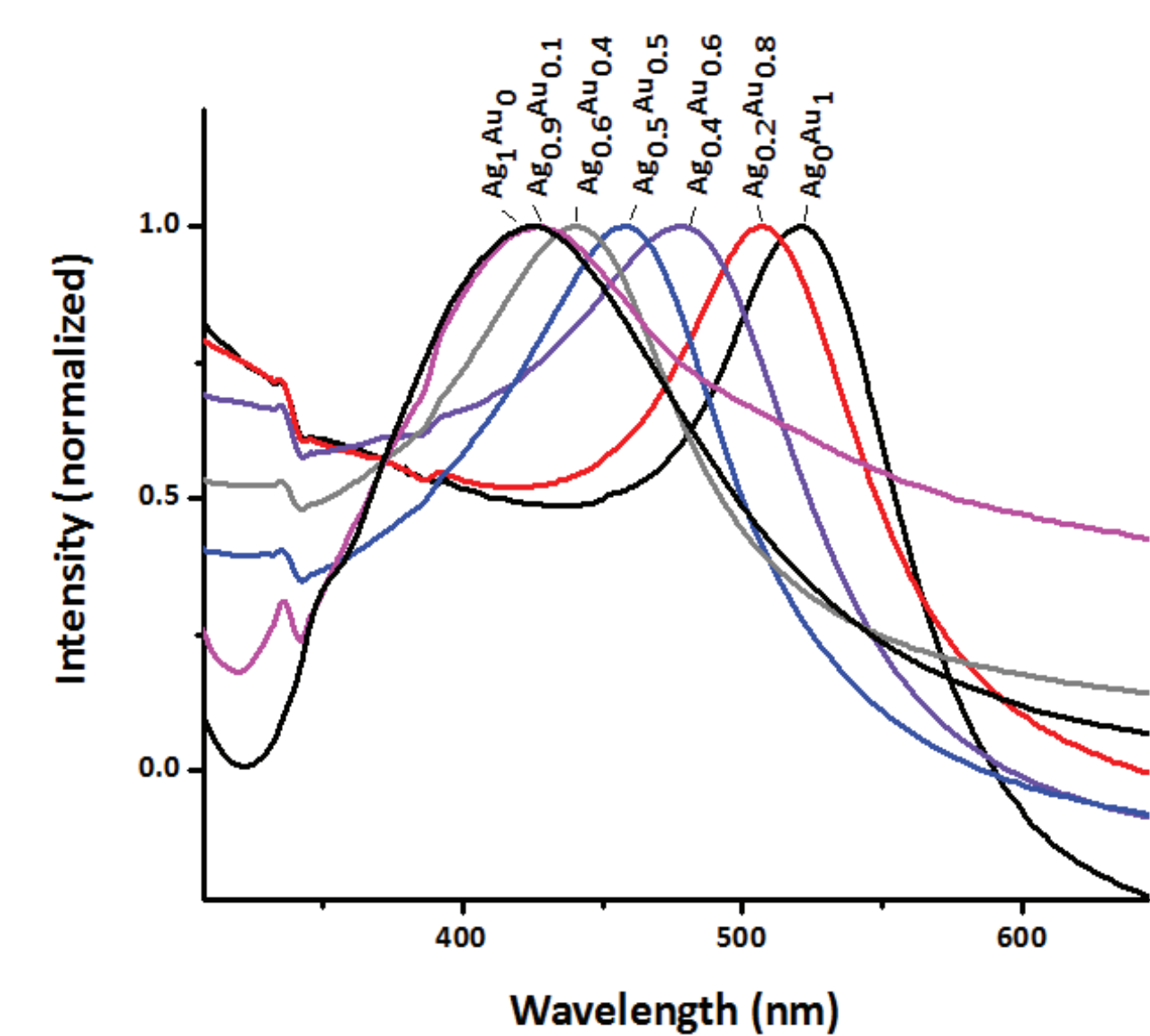

Figure 3. Extinction spectra of nanopartilces with varying composition.
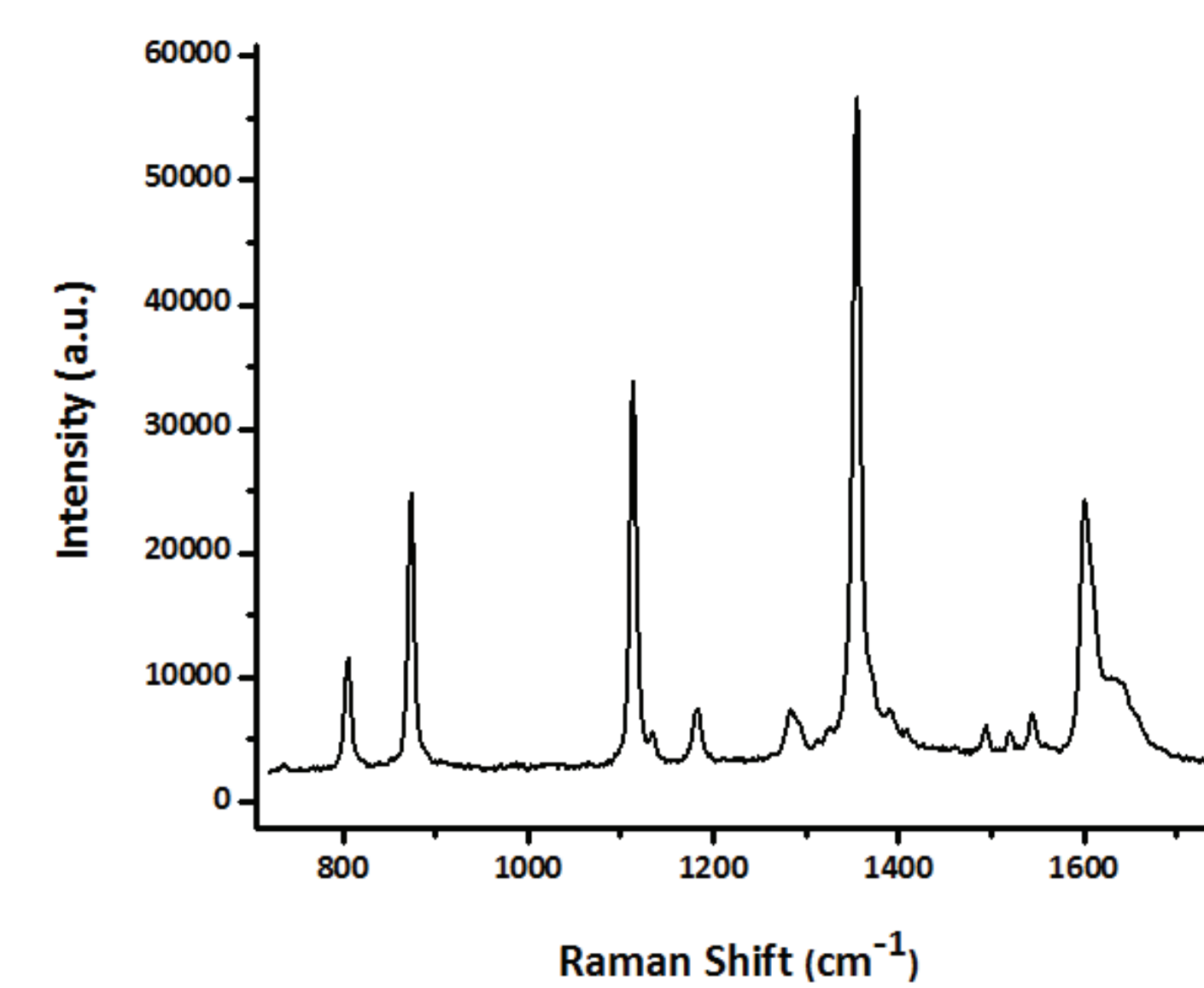
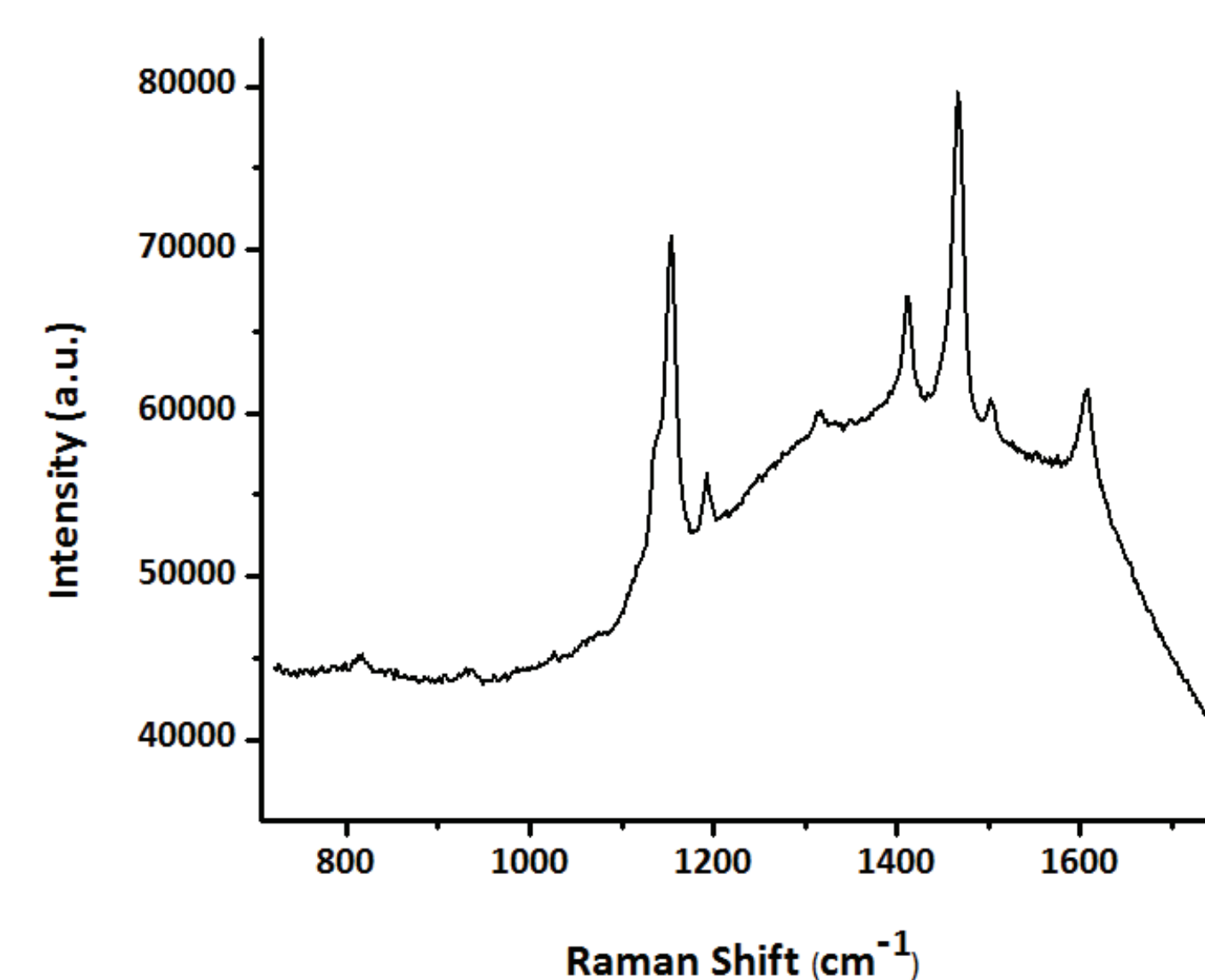

Figure 4. Normal Raman spectrum of PNBA.

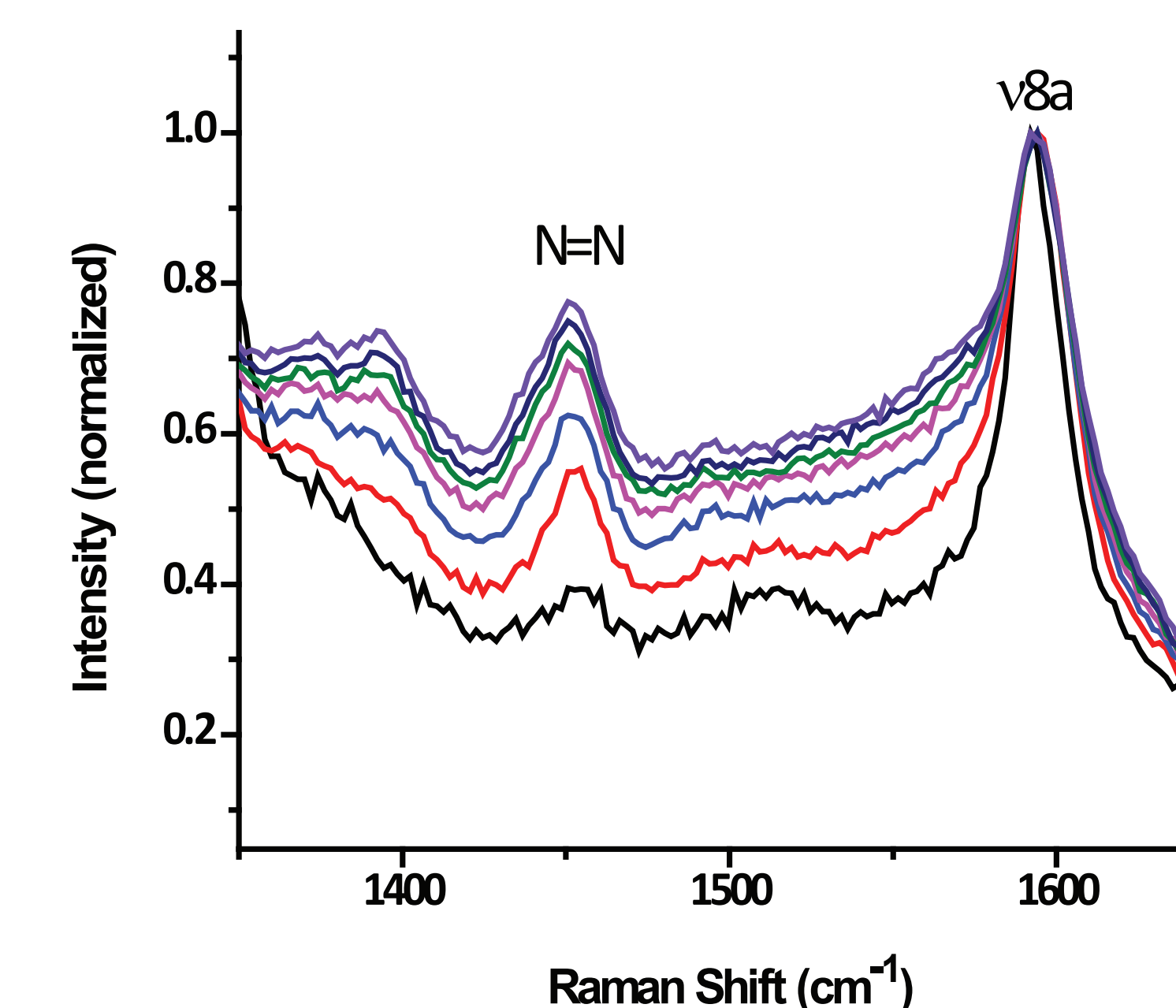Figure 5. Normal Raman spectrum of p,p'-azodibenzoate.

Results

Figure 6. SERS of PNBA on a LI silver coated surface showing the growth of the peak at 1452 cm^{-1}.
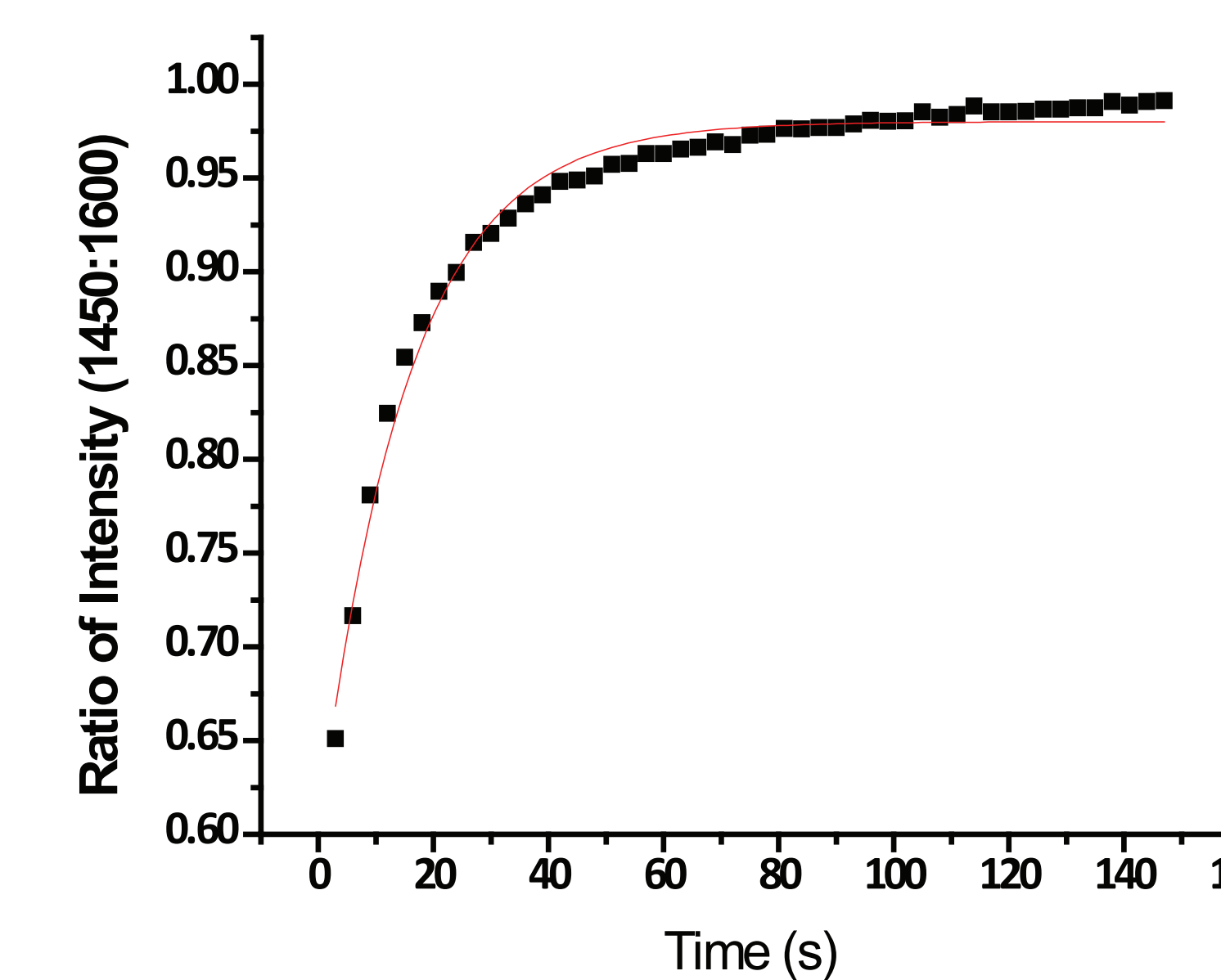

Figure 7. The relationship between the ratio of the intensities of the peaks and time. The curve is formatted as $y=A_1-A_2e^{-kx}$. A_1 is the background, A_2 is the amplitude of the exponential, and k is the rate constant. In this case, the slide was soaked in LI silver for 11 min and the rate constant is 0.065 M/s.

Slide type	Rate Constant, k
Pure silver nanoparticles	0.2546
Silver coated: 5 min	0.0927
Silver coated: 10 min	0.0672
Silver coated: 15 min	0.0425
Silver coated: 25 min	0.0376
Alloy: Ag_4Au_6	0.0556
Alloy: Ag_5Au_5	0.0791
Alloy: Ag_6Au_4	0.0833

Table 1. The comparison of the slide type and the corresponding rate constant.

Conclusions

We have observed the photoreduction on the alloy surfaces as well as the LI silver surfaces. All data thus far has fit to a first order rate law and from which a rate constant can be determined. A problem arises when two data sets are compared: two surfaces prepared in seemingly identical ways may give different rate constants. The lack of consistency between surfaces has made it difficult to determine the pattern in which rate constants vary depending on the morphology and composition of the surface. Future work on this project includes a substantial amount of work making the surfaces more consistent. In addition, we are working with Portland State University who is allowing us to use their scanning electron microscope to help determine how the surfaces look on a nanoscale level and compare that to our current information on rate constants.

References

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Acknowledgments

For Further Information

Please contact kcorp@linfield.edu or bgilber@linfield.edu for questions. More information on this and related projects can be obtained at www.linfield.edu/chem.

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