

Supplemental Information

Optimization of Silver Nanoparticles for Surface Enhanced Raman Spectroscopy of Structurally Diverse Analytes using Visible and Near-Infrared Excitation

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Figure S1. Transmission electron microscopy images of silver nanoparticles synthesized with (a) 1.5 mL; (b) 1.0 mL; (c) 0.8 mL; (d) 0.5 mL; (e) 0.2 mL 1% w/v citrate. See Experimental section for additional details.

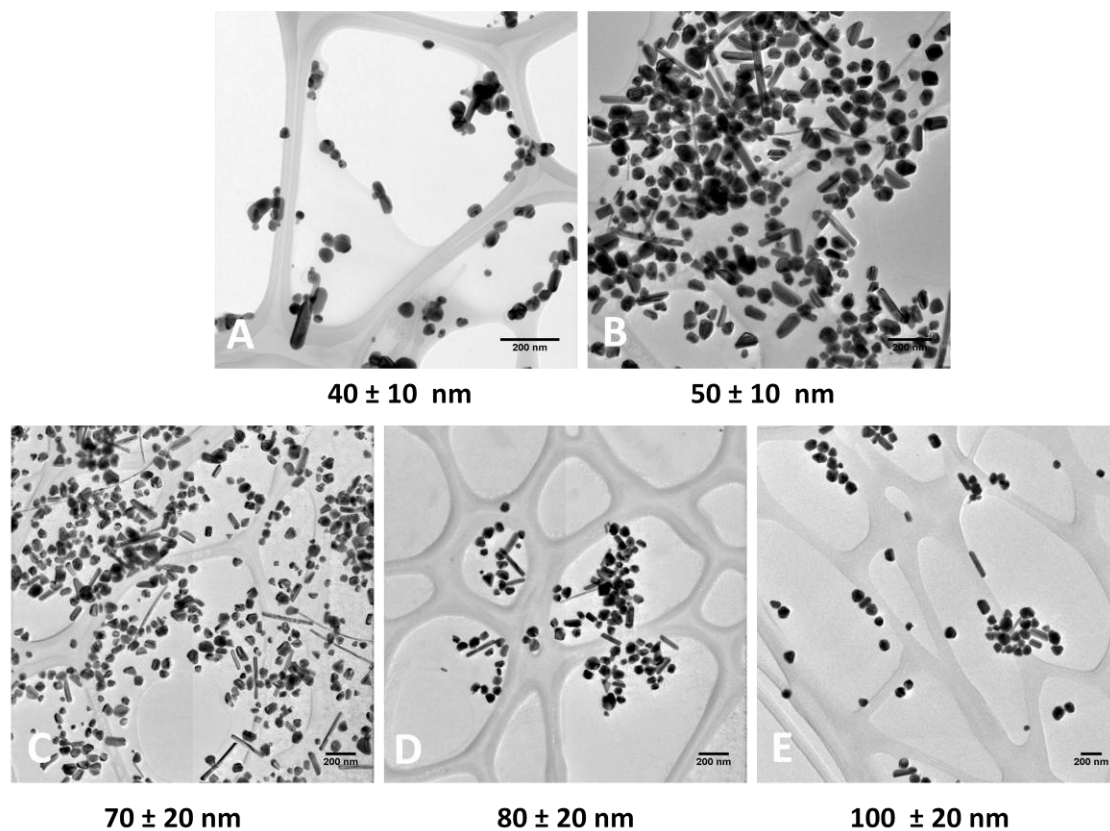


Figure S2. Extinction curves for the silver nanoparticles with the indicated average diameter (top) before and (bottom) after adding 50 μL 2 mM pyridine mixed with 450 μL 70 nm silver nanoparticles and 5 μL 0.5 M MgCl_2 (final concentration 0.99% v/v). The color scheme is the same in both graphs.

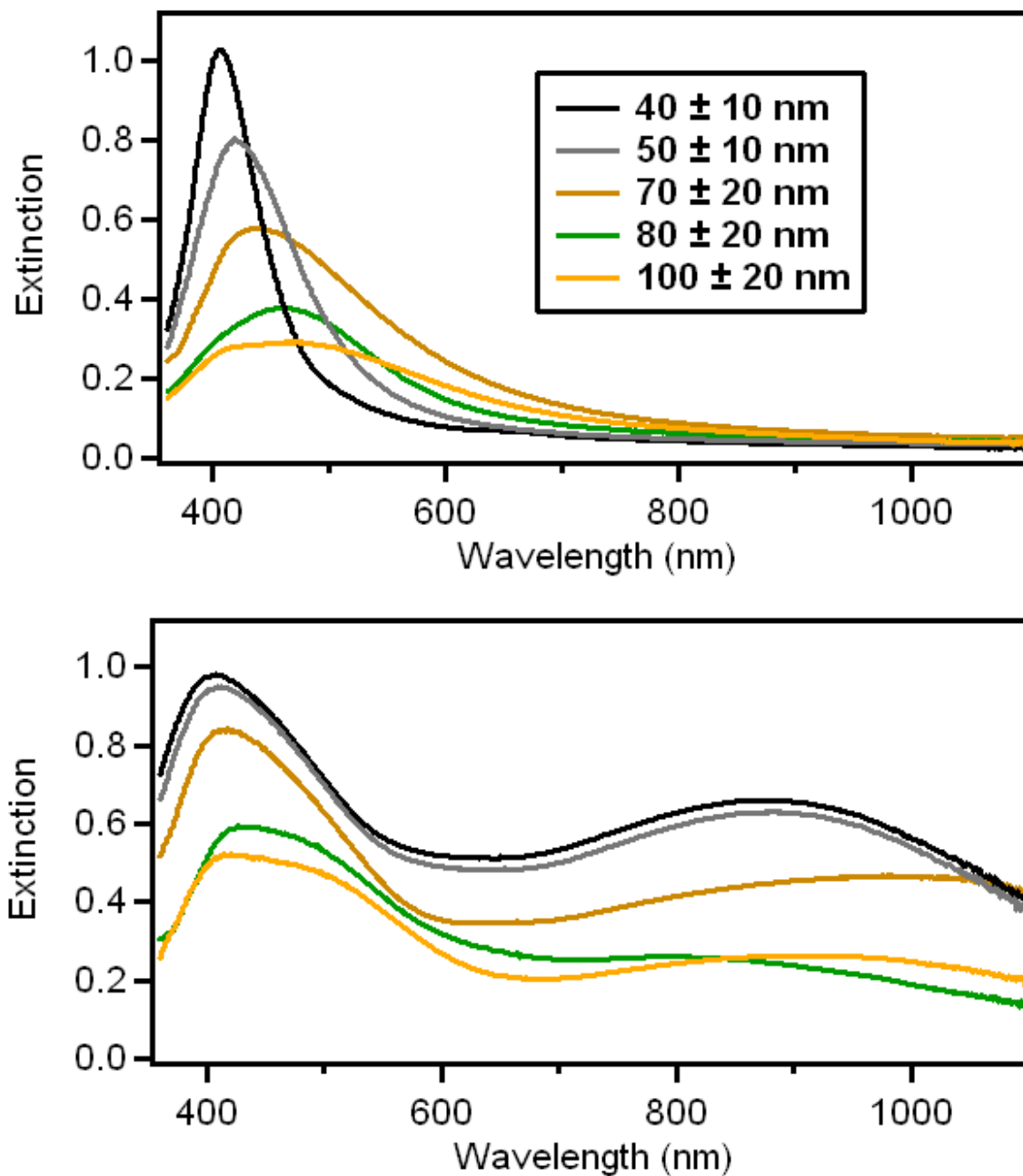


Figure S3. Surface enhanced Raman spectra of 50 μL 2 mM pyridine mixed with 450 μL 70 nm silver nanoparticles and 5 μL 0.5 M (final concentration 0.99% v/v) of the indicated salt.

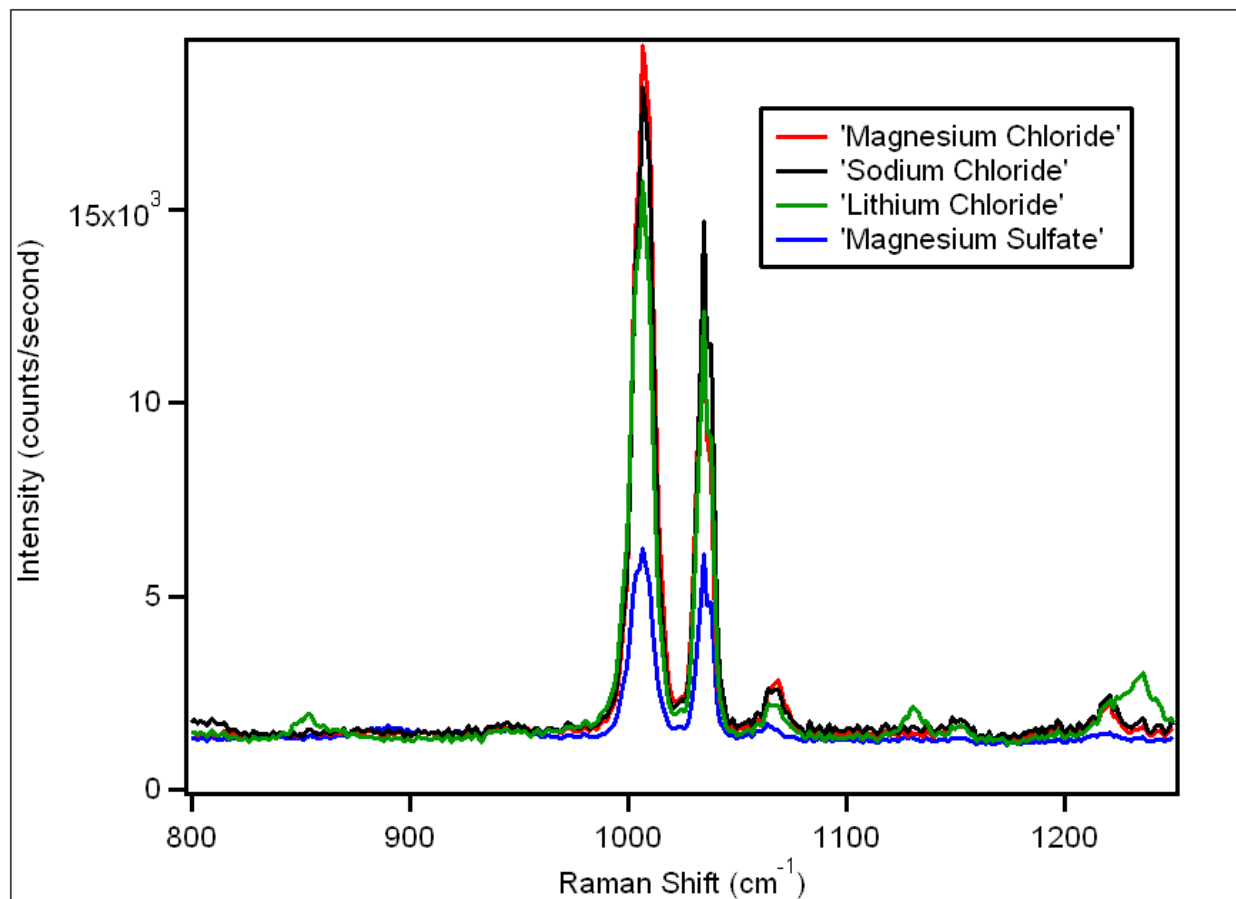


Figure S4. Histograms showing nanoparticle and aggregate hydrodynamic diameter as measured by dynamic light scattering for particles before (solid markers) and after (dashed markers) adding 0.99% v/v 0.5 M MgCl₂. The amount of 1% w/v citrate added during nanoparticle synthesis was (blue) 1.5 mL; (black) 1.0 mL; (yellow) 0.8 mL; (green) 0.5 mL; (red) 0.2 mL. The corresponding aggregates follow the same color scheme.

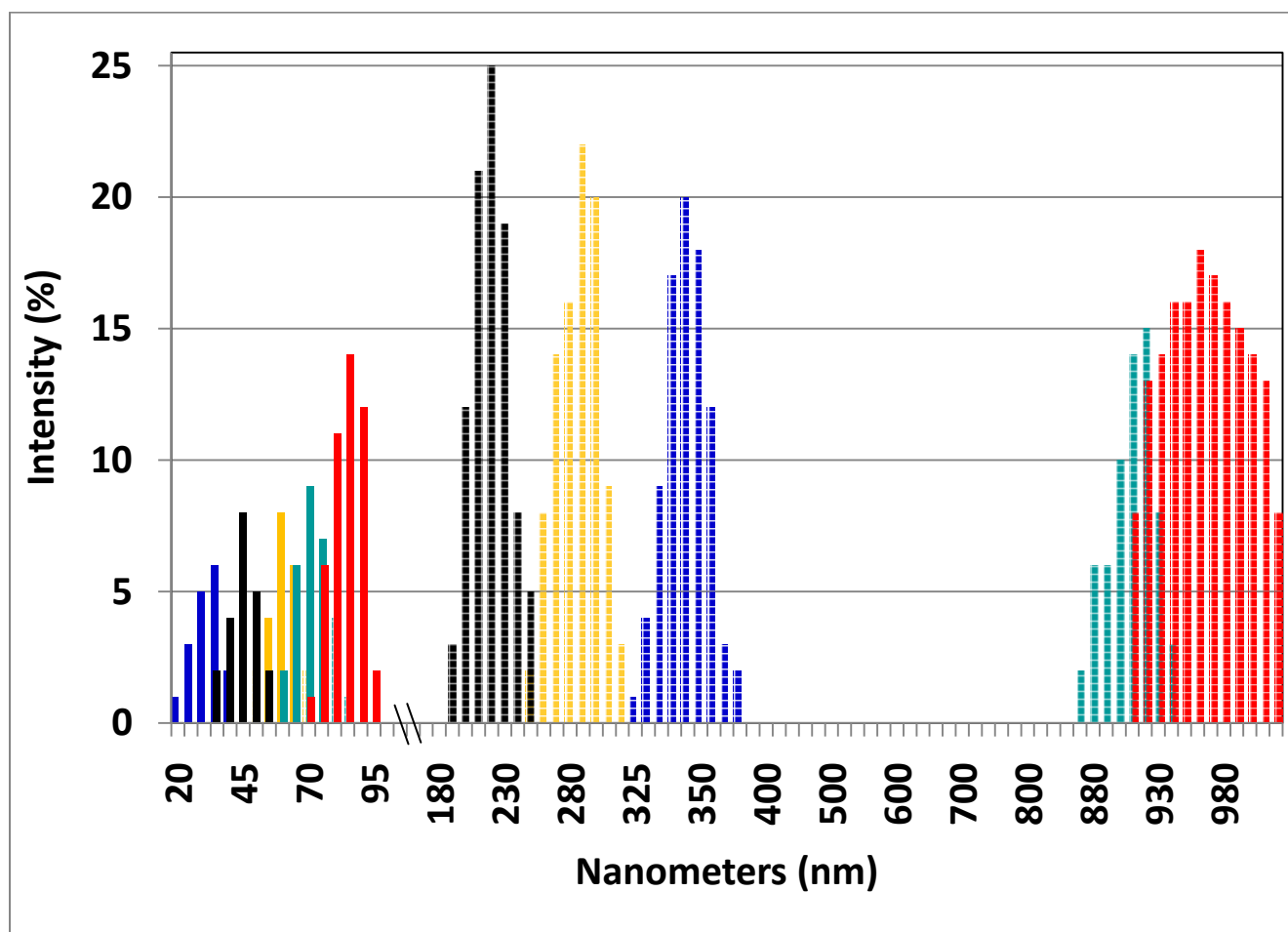


Figure S5. Average aggregate hydrodynamic diameter for 70 ± 20 nm silver nanoparticles (grey) and 80 ± 20 nm silver nanoparticles (black), as measured by dynamic light scattering, for the solution containing $50 \mu\text{L}$ 2 mM pyridine, $450 \mu\text{L}$ silver nanoparticles and $5 \mu\text{L}$ 0.5 M MgCl_2 between 1 minute to 90 minutes after adding the salt aggregating agent. Stable aggregates are measured between 30 and 90 minutes after mixing.

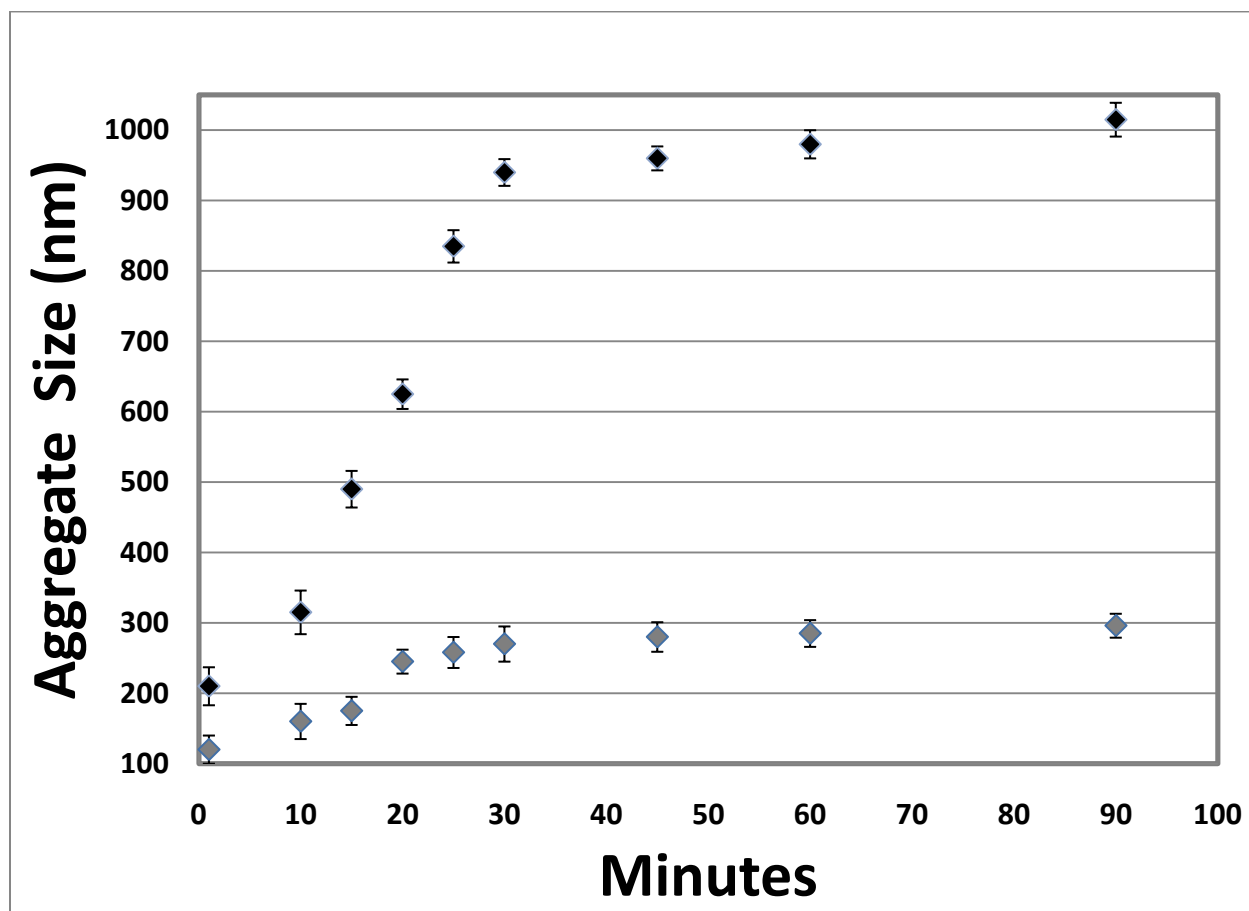


Figure S6. Adsorption isotherms measured by Raman spectroscopy for the adsorbates: (a) pyridine; (b) benzoic acid; (c) 4-mercaptopyridine; (d) 4-methylthiobenzoic acid. Isotherms were analyzed with the 1006 cm^{-1} (pyridine), 1004 cm^{-1} (benzoic acid), 1008 cm^{-1} (4-mercaptopyridine), and 1074 cm^{-1} (4-methylthiobenzoic acid) Raman peak areas. The spectral contribution of molecules in solution represent no more than 0.9% (pyridine); 3.3% (4-mercaptopyridine); 4.6% (4-methylthiobenzoic acid); or 3.6% (benzoic acid) of the total signal at the highest analyte concentration. Data were collected using 247 mW 1064 nm excitation with 10 second acquisition times. The concentration of nanoparticles and salt were held constant using the concentrations described in the Experimental section: SERS measurements, while varying the concentration of analyte. The data fit well to a Langmuir isotherm model (solid line) within experimental uncertainty. Error bars represent one standard deviation from at least three replicate experiments.

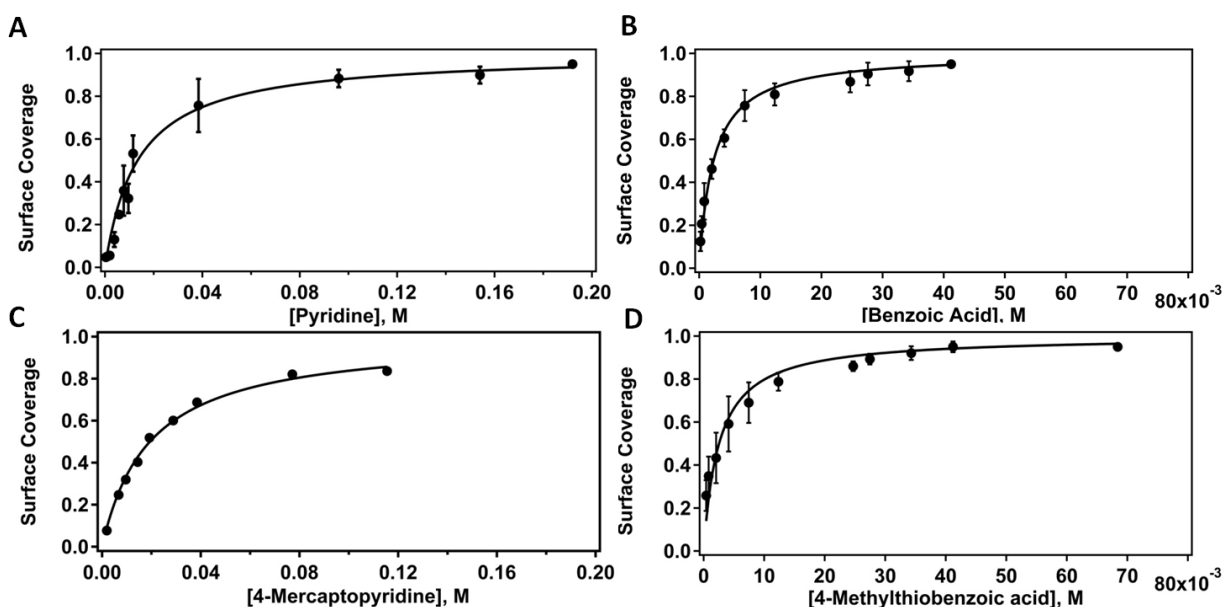


Table S1. Raman peaks used to compare intensities and surface enhancements with the indicated analytes.

| Molecule | Aqueous Solution (cm⁻¹) | SERS (cm⁻¹) | Assignment |
|----------------------------------|---|-------------------------------|--|
| Pyridine | 1002 | 1006 | Ring Breathing Mode |
| 4-Mercaptopyridine | 1002 | 1008 | Ring Breathing Mode |
| Benzoic Acid | 1004 | 1004 | Ring Breathing Mode |
| 4-Methylthio Benzoic Acid | 1092 | 1074 | Ring CCH bending |
| Phenylalanine | 1004 | 1004 | Ring Breathing Mode |
| Phenylalanine-Cysteine | 1002 | 1002 | Ring Breathing Mode |
| Angiotensin I | 1004 | 1004 | Phenylalanine Ring Breathing Mode |
| Hemoglobin | N/A | 1125 | C_mH Out of Plane Deformation Stretching Mode |