## Supplemental Information

## Near IR Scanning Angle Total Internal Reflection Raman Spectroscopy at Smooth Gold Films

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**Figure S1.** Schematic of the scanning angle total internal reflection Raman microscope. The excitation beam for collecting bulk Raman spectra travels path "a", for TIR and SPR Raman spectra the excitation beam travels path "b". Optics in the dashed boxed are oriented perpendicular to the optical table, and have been offset for clarity.



Figure S2. Contact mode AFM image  $(5x5 \ \mu m)$  of the smooth gold film. The z-scale is 0 to 25 nm and the RMS roughness was measured as 0.639 nm.



**Figure S3.** SPR Raman spectra of a washed benzenethiol monolayer (black, benzenthiol monolayer/water interface) and neat benzenethiol (grey) at the SPR angle for each interface, 51.25 and 69.85 degrees, respectively.



Pyridine		4-Mercaptopyridine (Gold)		Benzenethiol (Gold)		Nitrobenzene	
Assignment	Raman Shift (cm⁻¹)	Assignment	Raman Shift (cm⁻¹)	Assignment	Raman Shift (cm⁻¹)	Assignment	Raman Shift (cm⁻¹)
						6b	611
6a	617					6a	681
						ONO s bend	852
12	1035			12	1002	12	1003
						10b	1021
1	1003	1	998	1	1091	1	1106
18a	1070	18a	1049	18a	1025		
		18b	1093				
				15	1159		
						9b	1162
9a	1218					9a	1172
						NO <sub>2</sub> s stretch	1346
8b	1577	8b	1580			8b	1525
8a	1595	8a	1607	8a	1584	8a	1589

**Table S1.** Raman peak assignments using Wilson notation.