Supporting information

Discrimination between hydrogen bonding and protonation in the spectra of a surface-enhanced Raman sensor

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1. Normalisation of spectra

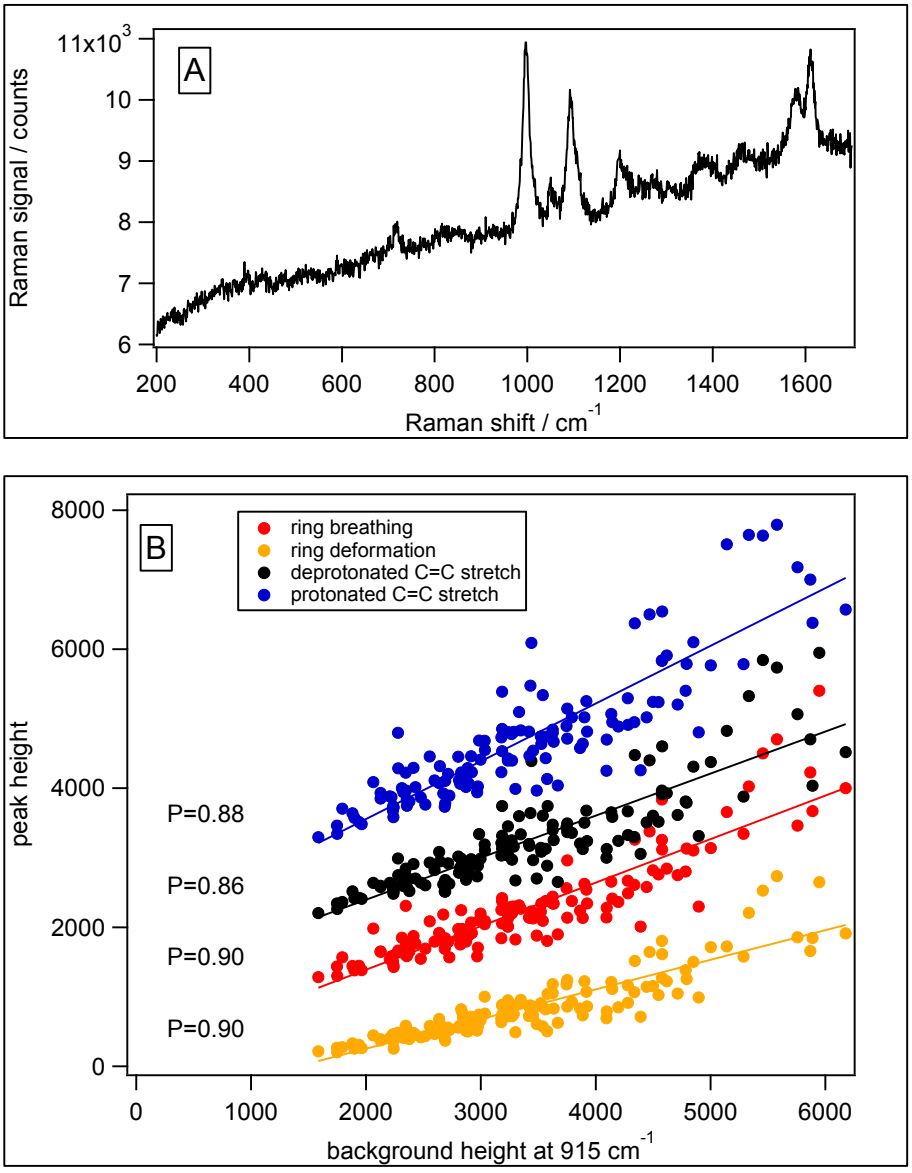

Figure S1. We used a Raman microscope (Renishaw inVia microscope with 50× objective and 785 nm diode laser) to record Raman spectra of pyS on rough gold in 0.1 M sulfuric acid every 5 µm (spot size about 10 µm diameter). Part A shows a representative spectrum and B shows the peak heights of ring breathing, trigonal deformation and ring stretching modes plotted versus background height at 915 cm^{-1}. SERS background intensity is caused by the creation of electron-hole pairs as the surface plasmon decays [1] and can thus be used as a measure for the Raman enhancement and as the basis for normalising spectra [4].

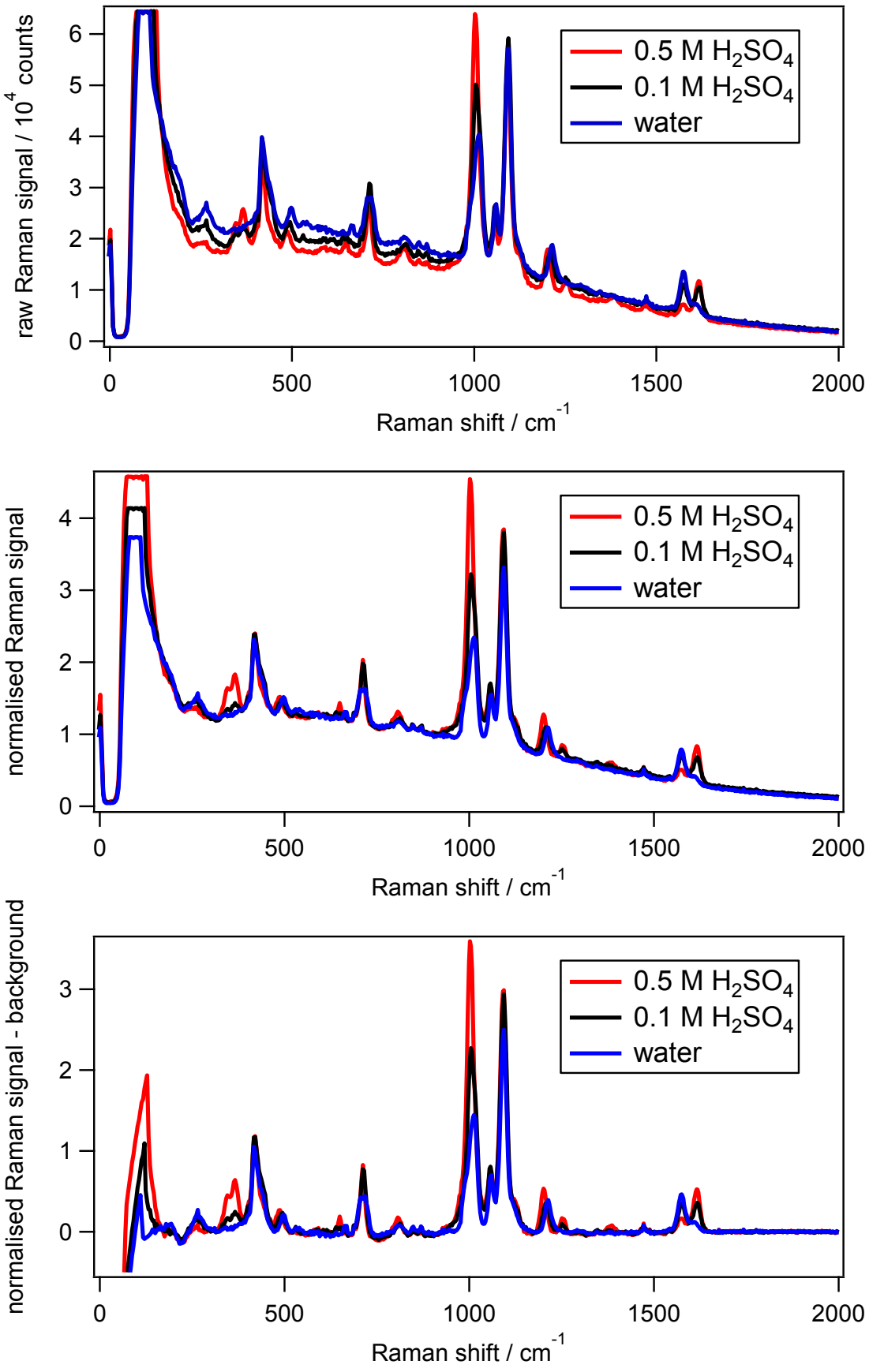

Figure S2. Raw, normalised and background-subtracted spectra for Figure 1 in the main text.

2. Verification of calculations

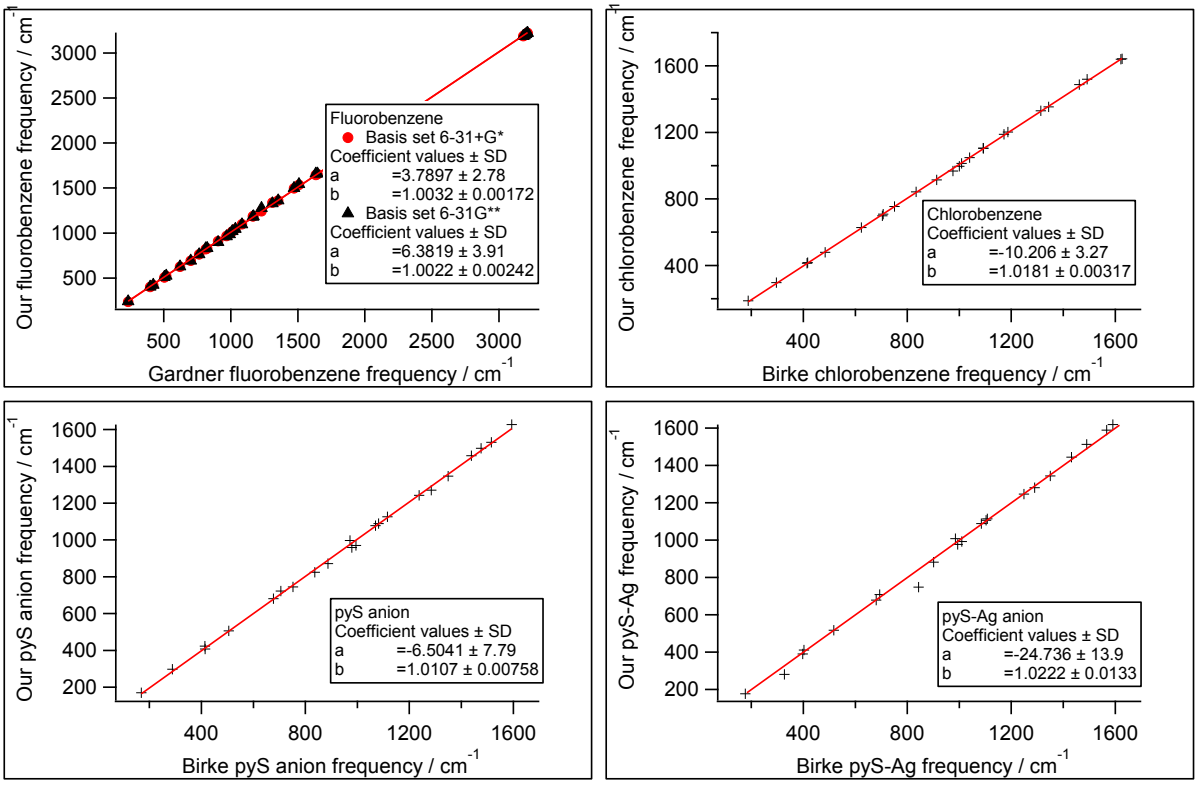

Figure S3. Comparison of our Spartan 16 calculations against fluorobenzene by Gardner *et al.* [2] and pyS-Ag, pyS anion and chlorobenzene as calculated by Birke et al. [3].

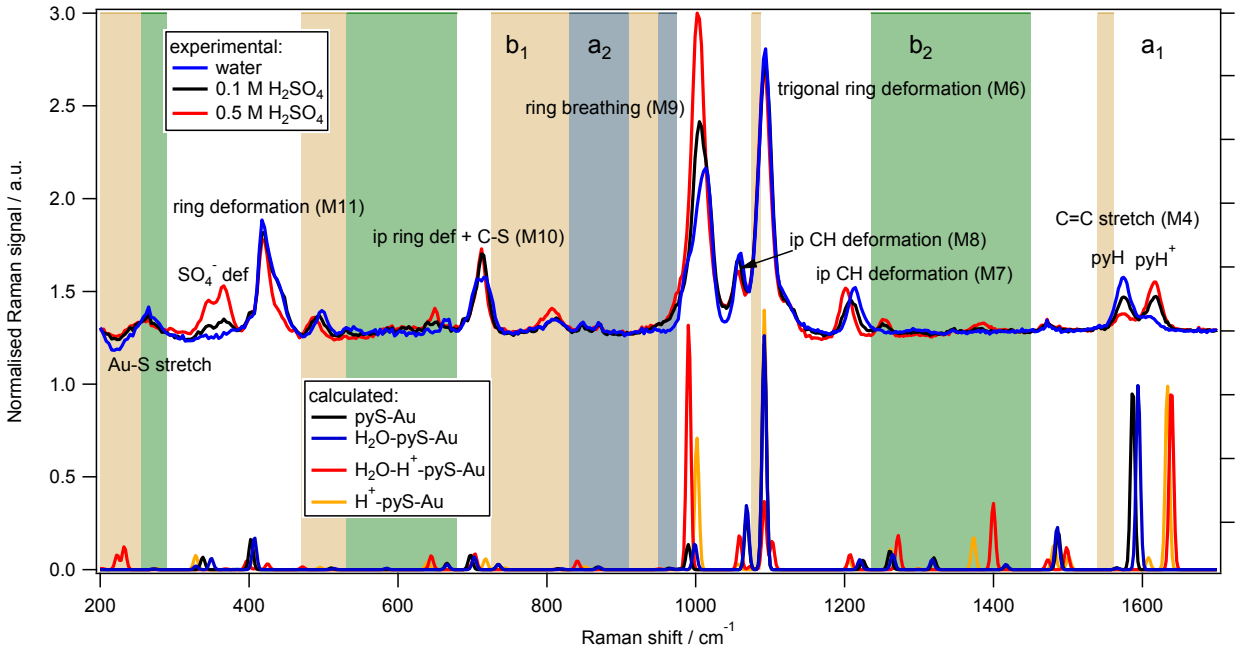

Figure S4 – Comparison between spectra from Figure 1 (main text) and the DFT calculation of various mercaptopyridine species bound to a single Au atom. The background is coloured according to the symmetry of the mode (with reference to the C_{2v} symmetry of the pyridine ring).

3. Additional spectra

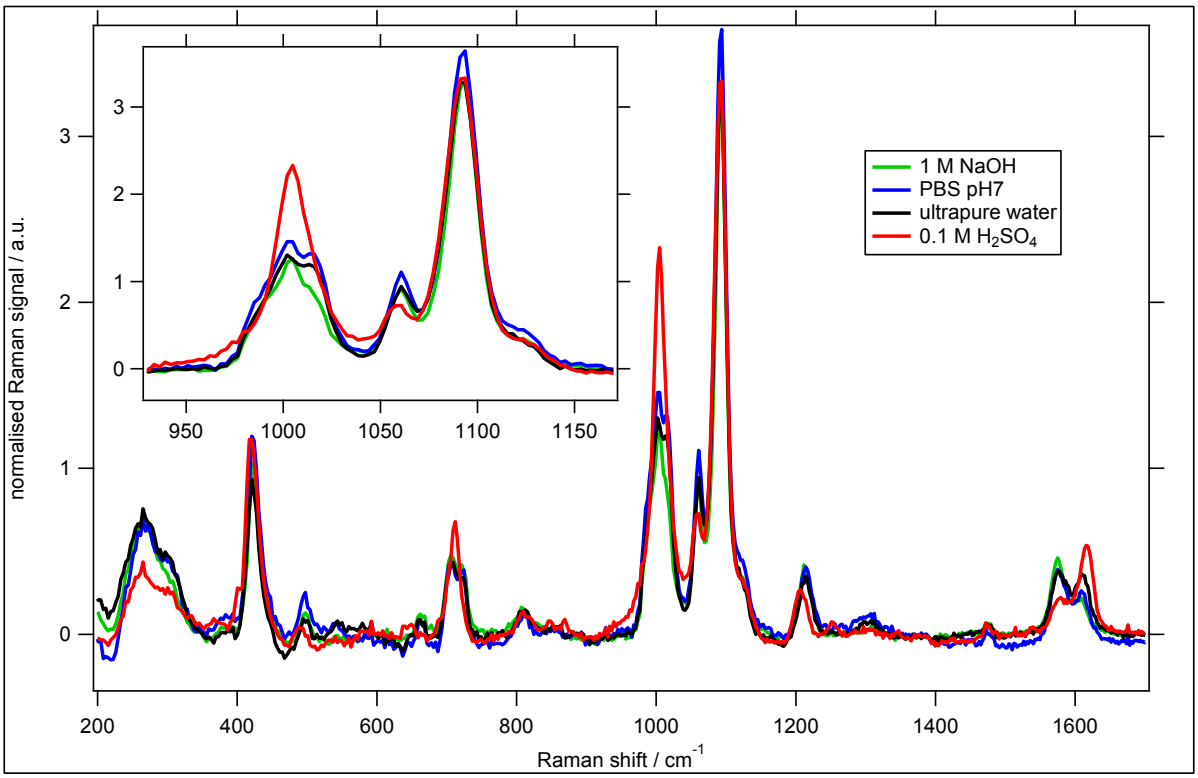

Figure S5 – Additional SER spectra of 4-mercaptopyridine adsorbed on roughened gold in acidic and basic solutions.

Table S1 – Conditions and fitting results for the data points shown in Figure 3.

Roughened gold (spectra acquired on same sample in sequence shown)		
Condition	**Ring ratio**	**C=C ratio**
Ultrapure water	0.709	0.875
Buffer	0.703	0.720
0.1 M H_2SO_4	1.530	1.470
+ conc. H_2SO_4	1.720	1.740
++ conc. H_2SO_4	1.850	1.950
+++ conc. H_2SO_4	1.960	1.990
Ultrapure water	1.360	1.010
Buffer	0.856	0.945
Buffer	0.820	1.040
NaOH	0.887	0.605
+ conc. NaOH	0.903	0.482
++ conc. NaOH	0.960	0.346
Ultrapure Water	0.693	0.492
Buffer	0.743	0.407
0.1 M H_2SO_4	1.280	1.140
Ultrapure Water	0.825	0.603
SHINs		
Condition	**Ring ratio**	**C=C ratio**
Sample 1, 1 M $HClO_4$	1.250	0.548
Sample 1, 2 M $HClO_4$	1.170	0.337
Sample 1, 1 M $HClO_4$	1.250	0.507
Sample 1, 0.5 M $HClO_4$	0.937	0.469
Sample 2, spot 1, Ultrapure water	0.375	0.277
Sample 2, spot 2, Ultrapure water	2.440	1.870
Sample 3, Ultrapure water	1.910	2.040
Sample 2, spot 3, 0.1 M Acetic acid	1.590	1.170
Sample 2, spot 3, 0.1 M HCl	1.010	0.595
Sample 2, spot 4, Ultrapure water	1.540	1.520

4. Detailed DFT results

Table S2: Frequencies and geometric parameters of all species calculated. *Constrained to ring plane at right angle to the Au-S bond.

Species	Trigonal frequency / cm^{-1}	Scaled (f*0.99) C=C stretch / cm^{-1}	Scaled (f) ring breathing / cm^{-1}	N-H bond distance / Å	Scaling factor f	Colour symbol
pyS-Au	1112	1571.04	989.871	2.4	0.982014	black square
H_2O-pyS-Au	1114	1578.11	994.955	1.978	0.980251	light blue
$(H_2O)_2$-pyS-Au	1118	1578.27	997.256	1.86	0.976744	light blue
C_2H_5OH-pyS-Au	1114	1578.11	998.876	1.967	0.980251	light blue
H^+OH^--pyS-Au	1113	1578.56	998.792	1.986	0.981132	light blue
CH_3NO-pyS-Au	1114	1580.05	997.896	1.997	0.980251	light blue
H^+-pyS-Au	1111	1617.41	1001.57	1.016	0.982898	red
H_2O-H^+-pyS-Au (constrained*)	1110	1622.59	1005.43	1.043	0.983784	red
C_6H_6-H^+-pyS-Au	1127	1608.67	983.478	1.025	0.968944	yellow
H_2O-H^+-pyS-Au	1118	1622.75	990.419	1.039	0.976744	yellow
H_3O^+-pyS-Au	1123	1615.53	986.009	1.04	0.972395	yellow
H_2O-H_3O^+-pyS-Au	1120	1617.76	987.675	1.06	0.975	yellow
py	1050	1577.71	991.743	2.4	0.980952	black triangle
H_2O-py	1049	1584.99	1003.49	1.976	0.981888	light blue
$(H_2O)_2$-py	1049	1590.76	1006.43	1.85	0.981888	light blue
C_2H_5OH-py	1050	1585.40	1002.53	1.942	0.980952	light blue
CH_3NO-py	1050	1584.44	1001.55	2.024	0.980952	light blue
H^+-py	1048	1615.4	1005.43	1.085	0.982824	red
C_6H_6-H^+-py	1048	1633.66	1011.33	1.024	0.982824	yellow
H_3O^+-py	1046	1621.38	1010.31	1.046	0.984704	yellow
H_2O-H^+-py	1046	1621.38	1010.31	1.047	0.984704	yellow

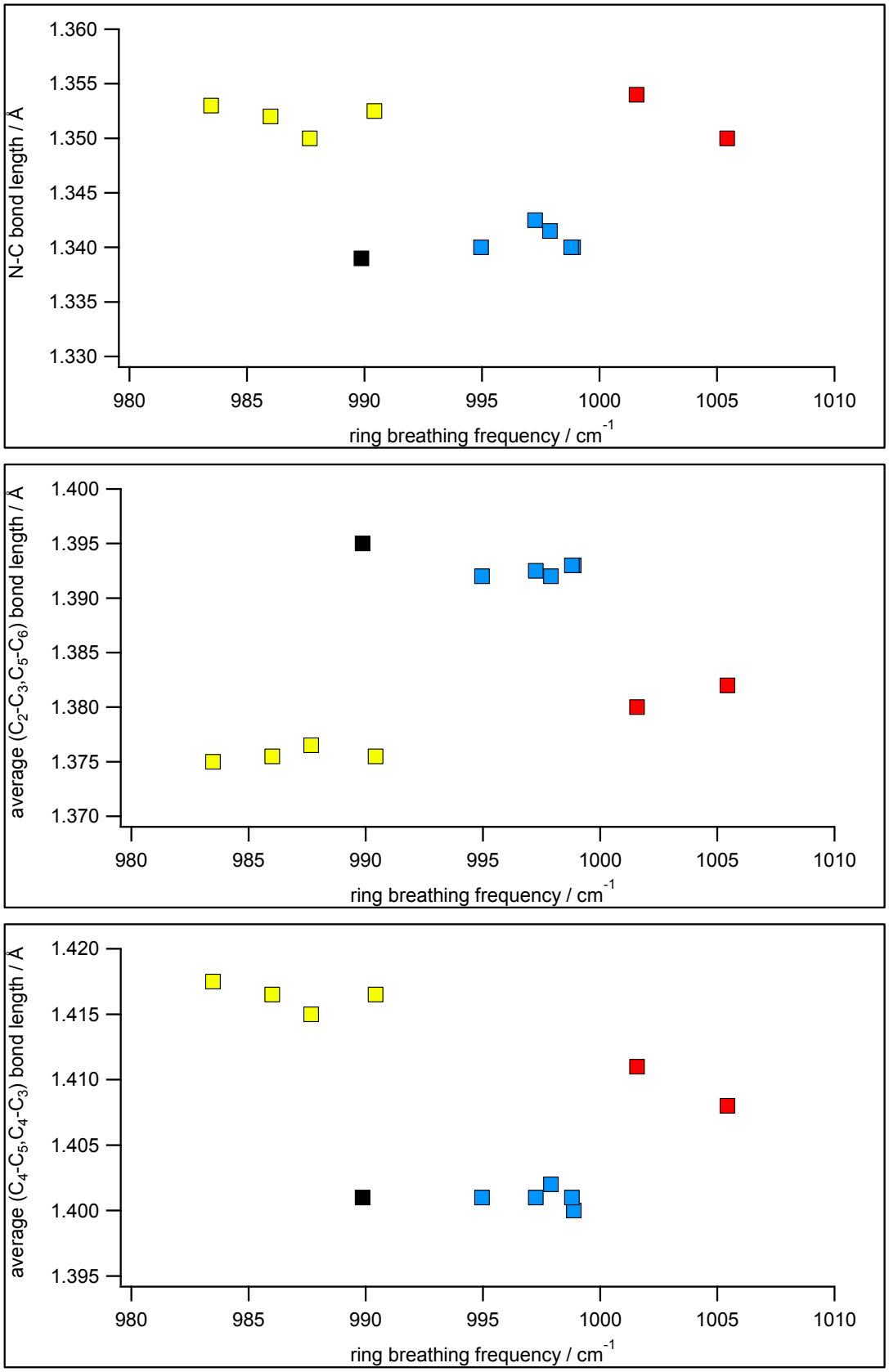

Figure S6 – Relationship between N-C and C-C bond lengths in adsorbed pyS-Au and the ring breathing frequency. Black: free pyS-Au. Blue: hydrogen-bonded species. Red: protonated species with ring plane nearly perpendicular to Au-S bond. Yellow: protonated species with ring plane nearly parallel to Au-S bond.

References

[1] Mahajan, S.; Cole, R. M.; Speed, J. D.; Pelfrey, S. H.; Russell, A. E.; Bartlett, P. N.; Barnett, S. M.;

Baumberg, J. J., The Journal of Physical Chemistry C 2010, 114(16), 7242.

[2] Gardner, A. M.; Wright, T. G., J Chem Phys 2011, 135(11), 114305.

[3] Birke, R. L.; Lombardi, J. R., Journal of Optics 2015, 17(11), 114004.

[4] Faraday Discussions 2017, Surface Enhanced Raman Scattering, Discussion Session 4: Analytical SERS.