Supporting Information: SERS Speciation of the Electrochemical Oxidation-Reduction of Riboflavin

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Abstract:

This supplement contains additional details including Tables S-1 and S-2, and Figures S-1, S-2, S-3, and S-4. Figure S-1 shows a comparison of the solid Raman spectrum of riboflavin to the theoretical frequency calculation of oxidized riboflavin to determine how to the calculations were scaled. Table S-1 highlights the observed SERS frequencies and their assignments of the pH 7.15 riboflavin solution during the potential sweep from Figure 3. Table S-2 highlights the frequencies and their assignments for the pH 12.55 riboflavin solution during the voltammogram from Figure 4. Figure S-2 shows the voltammetry, SERS heatmap, representative spectra, and chemometric analysis from the pH 4.11 riboflavin solution. Figure S-3 compares the calculated neutral semi-quinone to spectra from Figure 3. Figure S-4 compares the calculated anionic semi-quinone to spectra from Figure 4.

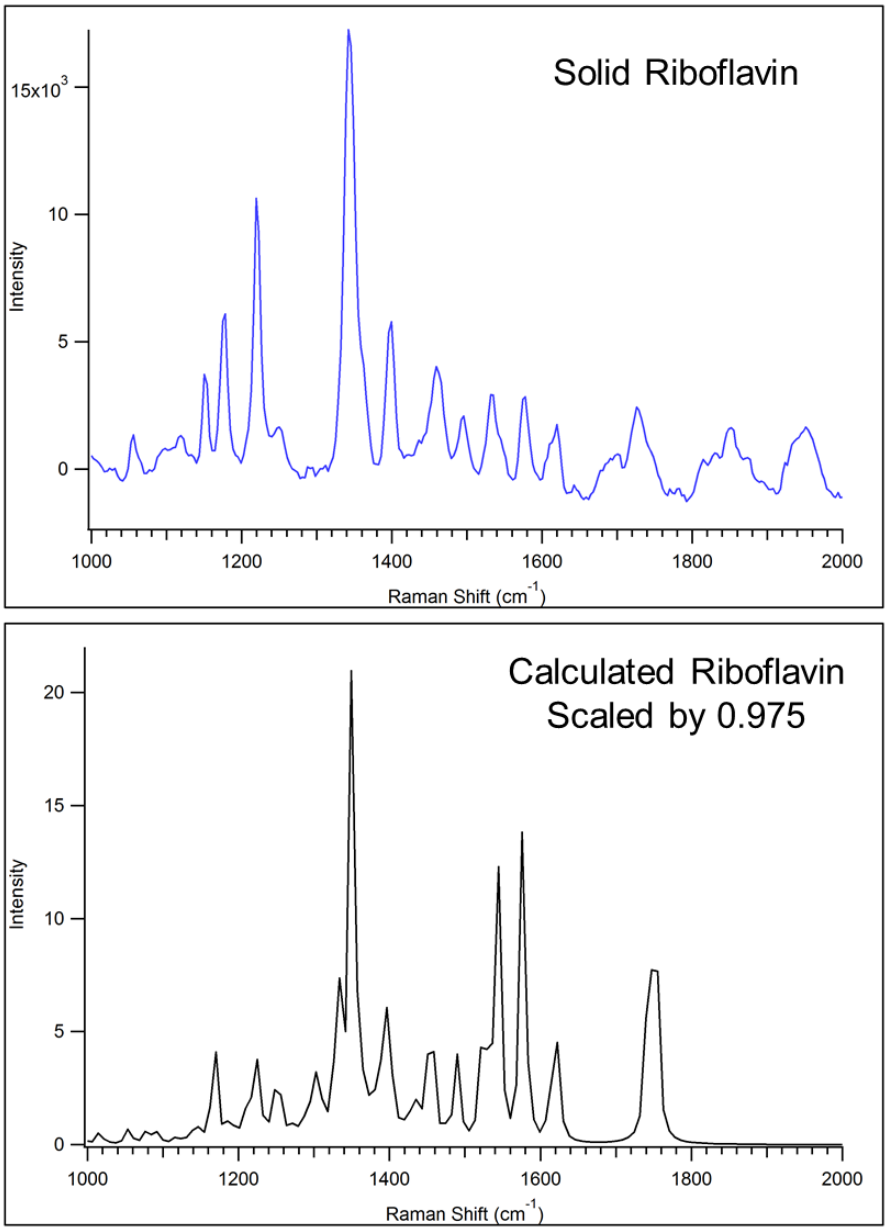

Figure S-1: Comparison of (top) the solid Raman spectrum of Riboflavin and the (bottom) calculated spectrum of oxidized riboflavin. The theoretical frequency calculations were scaled by a factor of 0.975.

Table S-1: Observed Raman shifts (cm^{-1}) and vibrational band assignments of SERS of the pH 7.15 riboflavin solution during the potential sweep from Figure 3.

Assignments	Spectrum A & D	Spectra B	Spectra C
$\delta(C_1\text{-}C_{14}\text{-}C_{13}, C_4\text{-}C_3\text{-}C_2), \nu(C_2\text{-}C_1)$	738	738	738
Ribose Group, $\delta(C_{13}\text{-}N_{12}\text{-}C_{11})$	N/A	871	871
$\nu(C_9\text{–}N_8, C_6\text{–}C_7, C_6\text{–}C_{11}, N_5\text{-}C_6)$,	1158	N/A	N/A
$\nu(C_{11}\text{-}C_6\text{-}C_7, N_{10}\text{-}C_9\text{-}N_8\text{-}C_7)$	1215	N/A	N/A
$\nu(C_{11}\text{-}N_{10}\text{-}C_9\text{-}N_8\text{-}C_7)$	N/A	1239	1239
$\nu(N_{10}\text{-}C_9\text{-}N_8\text{-}C_7, N_{10}\text{-}C_{11})$	1255	N/A	N/A
$\nu(C_{11}\text{-}C_6\text{-}C_7)$	N/A	1289	1289
$\nu(C_4\text{-}N_5\text{-}C_6)$	1313	N/A	N/A
$\nu(N_{12}\text{-}C_{11}, C_4\text{-}C_{13})$ involves $N_5\text{-}C_6\text{-}C_{11}\text{-}N_{10}\text{-}C_9$ system	1355	1344	N/A
$\nu(C_{11}\text{-}C_6\text{-}C_7, C_6\text{-}N_5, N_{10}\text{-}C_9\text{-}N_8)$	1381	1381	1381
$\nu(N_{12}\text{-}C_{13}\text{-}C_{14}, C_{11}\text{-}N_{10}, C_6\text{-}N_5, C_7\text{-}N_8, C_4\text{-}C_3)$	1462	1452	1452
$\nu(C_4\text{-}N_5\text{-}C_6, C_{11}\text{-}N_{10}, C_{11}\text{-}N_{12}, C_{11}\text{-}C_6$, Ring 1	1490	N/A	N/A
$\nu(N_{10}\text{-}C_{11}$, Ring I)	1526	1526	1510
$\nu(N_{12}\text{-}C_{11}\text{-}C_6, C_{11}\text{-}N_{10})$	1550	1558	1558
$\nu(C_7\text{-}C_6\text{-}C_{11}\text{-}N_{10}, C_7\text{-}N_8$, Ring I	N/A	1590/1610	1610
$\nu(N_5\text{-}C_6)$ and $\nu(C_{11}\text{-}N_{10})$.	1620	N/A	N/A

Table S-2: Observed Raman shifts (cm^{-1}) and vibrational band assignments of SERS of the pH 12.55 riboflavin solution during the potential sweep from Figure 4.

Assignments	Spectra A & D	Spectrum B	Spectrum C
$\delta(C_1\text{-}C_{14}\text{-}C_{13}, C_4\text{-}C_3\text{-}C_2), \nu(C_2\text{-}C_1)$	738	738	738
Ribose Group, $\delta(C_{13}\text{-}N_{12}\text{-}C_{11})$	N/A	871	871
$\nu(C_9\text{–}N_8, C_6\text{–}C_7, C_6\text{–}C_{11}, N_5\text{-}C_6)$,	1152	1152	N/A
$\nu(C_{11}\text{-}C_6\text{-}C_7, N_{10}\text{-}C_9\text{-}N_8\text{-}C_7)$	1210	1210	1210
$\nu(C_{11}\text{-}N_{10}\text{-}C_9\text{-}N_8\text{-}C_7)$	N/A	1244	1244
$\nu(N_{10}\text{-}C_9\text{-}N_8\text{-}C_7, N_{10}\text{-}C_{11})$	1264	1264	N/A
$\nu(C_{11}\text{-}C_6\text{-}C_7)$	N/A	1295	1295
$\nu(C_4\text{-}N_5\text{-}C_6)$	1313	N/A	N/A
$\nu(N_{12}\text{-}C_{11}, C_4\text{-}C_{13})$ involves $N_5\text{-}C_6\text{-}C_{11}\text{-}N_{10}\text{-}C_9$ system	1346	1346	1330
$\nu(C_{11}\text{-}C_6\text{-}C_7, C_6\text{-}N_5, N_{10}\text{-}C_9\text{-}N_8)$	1367	1381	1381
Ring 1	1404	1394	N/A
$\nu(N_{12}\text{-}C_{13}\text{-}C_{14}, C_{11}\text{-}N_{10}, C_6\text{-}N_5, C_7\text{-}N_8, C_4\text{-}C_3)$	1462	1462	N/A
$\nu(C_4\text{-}N_5\text{-}C_6, C_{11}\text{-}N_{10}, C_{11}\text{-}N_{12}, C_{11}\text{-}C_6$, Ring 1	1490	N/A	N/A
$\nu(N_{10}\text{-}C_{11}$, Ring I)	1510	1510	1510
$\nu(N_{12}\text{-}C_{11}\text{-}C_6, C_{11}\text{-}N_{10})$	1550	1554	1558
$\nu(C_7\text{-}C_6\text{-}C_{11}\text{-}N_{10}, C_7\text{-}N_8$, Ring I	N/A	1595/1615	1610
$\nu(N_5\text{-}C_6)$ and $\nu(C_{11}\text{-}N_{10})$.	1630	N/A	N/A

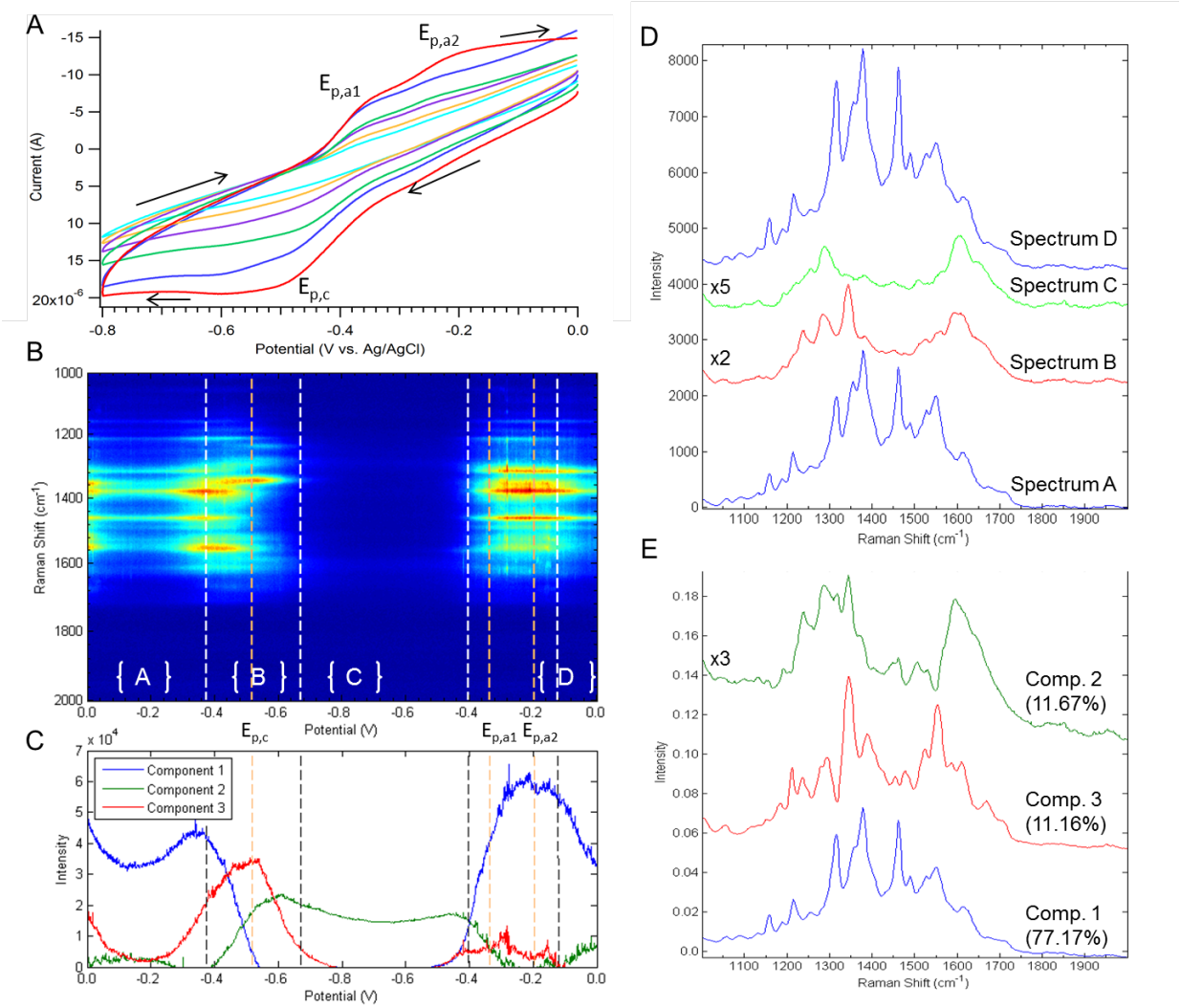

Figure S-2: (A) Cyclic voltammogram of the pH 4.11 riboflavin solution, (B) Heatmap showing the SERS intensity with respect to potential and Raman shift where Epc, Epa1, and Epa2 are highlighted, (C) Plot showing the intensity of each component calculated using MCR versus the applied potential, and (D) Shows the spectrum corresponding to the highlighted regions in the heatmap. (E) MCR calculated pure components from SERS data are shown.

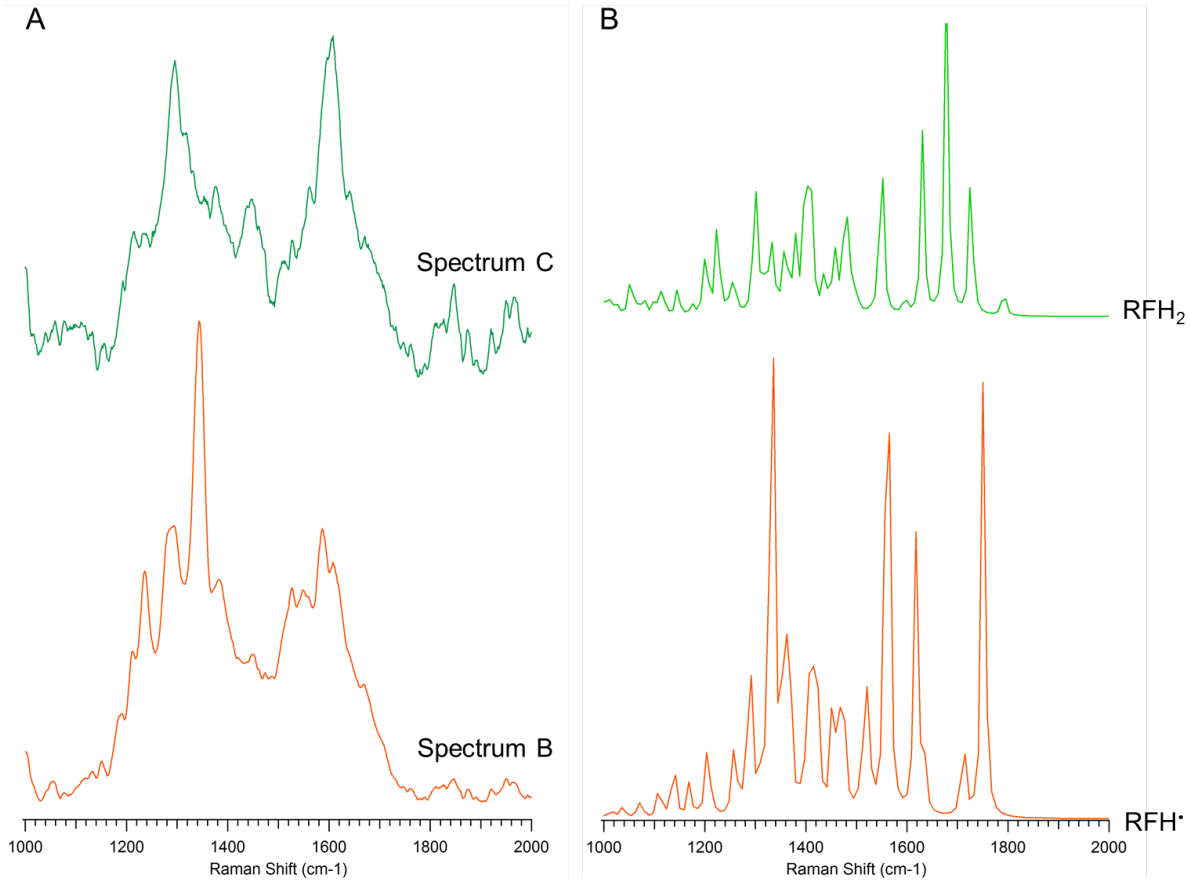

Figure S-3: Comparison of the (A) experimental data from pH 7.15 and (B) the calculated neutral semi-quinone and reduced forms of riboflavin.

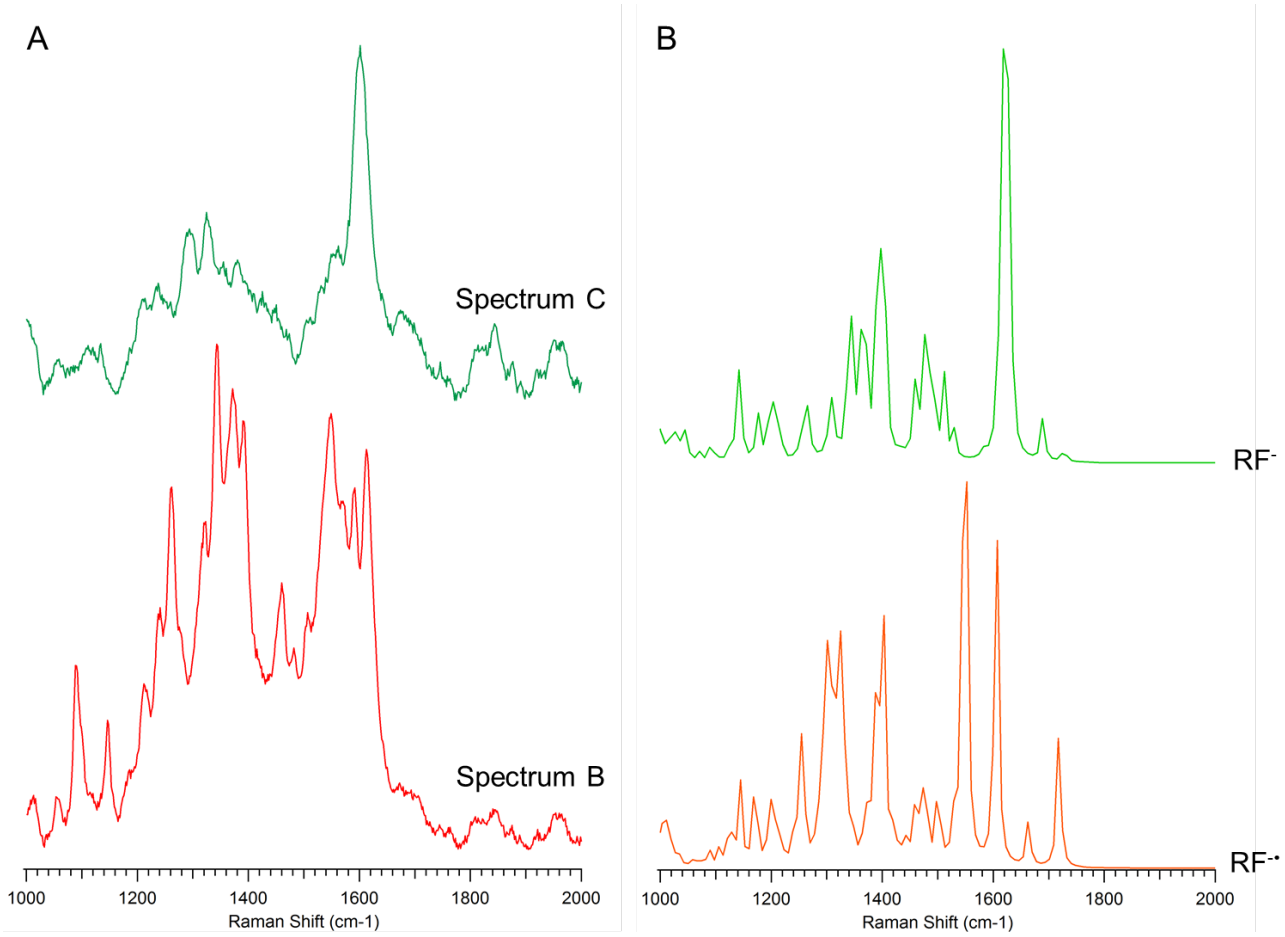

Figure S-4: Comparison of the (A) experimental data from pH 12.55 and (B) the calculated anionic semi-quinone and reduced forms of riboflavin.