Supplementary Information

Interaction of 4-imidazolemethanol with copper electrode revealed by isotope-edited SERS and theoretical modeling

Ieva Matulaitienė,[a] Eglė Pociūtė,[b] Zenonas Kuodis,[a] Olegas Eicher-Lorka,[a] and Gediminas Niaura*[a]

[a]*Department of Organic Chemistry, Center for Physical Sciences and Technology, A. Gostauto 9, LT-01108, Vilnius, Lithuania*
[b]*Faculty of Chemistry, Vilnius University, Naugarduko 24, LT-03225, Vilnius, Lithuania*

* To whom correspondence should be addressed. E-mail: (G.N.) gniaura@ktl.mii.lt.

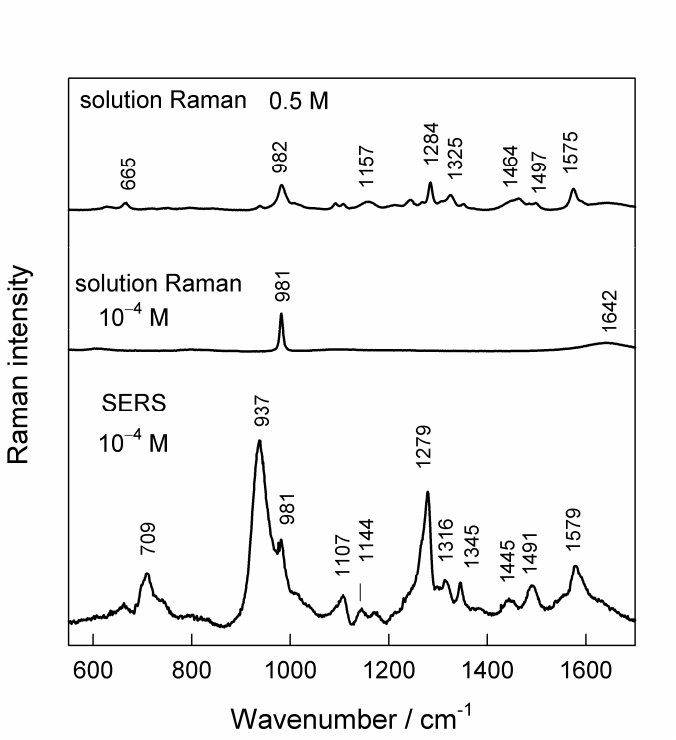

Fig. S1 Raman spectra of (a) 0.5 M ImMeOH solution, (b) 10^{-4} M ImMeOH solution containing 0.1 M Na_2SO_4 and 0.01 M phosphate buffer (pH 7.0), and (c) SERS spectrum from roughened Cu electrode in 10^{-4} M ImMeOH solution containing 0.1 M Na_2SO_4 and 0.01 M phosphate buffer (pH 7.0) at –1.100 V potential. Excitation wavelength is 785 nm (30 mW).

Fig. S1 compares solution Raman and SERS spectra of ImMeOH. At 0.5 M concentration of ImMeOH Raman spectrum exhibits characteristic peaks associated with imidazole ring vibrations. However, only totally symmetric stretching vibrational mode of SO_4^{2-} anions at 981 cm^{-1} and broad band due to scissoring deformation vibration of water molecules near 1642 cm^{-1} are visible in the Raman spectrum of solution containing 10^{-4} M ImMeOH, 0.1 M Na_2SO_4 and 0.01 M phosphate buffer (pH 7.0). Nevertheless, intense SERS spectrum is visible from roughened Cu electrode immersed in this solution. Presented figure clearly demonstrates operation of SERS effect in the studied system.

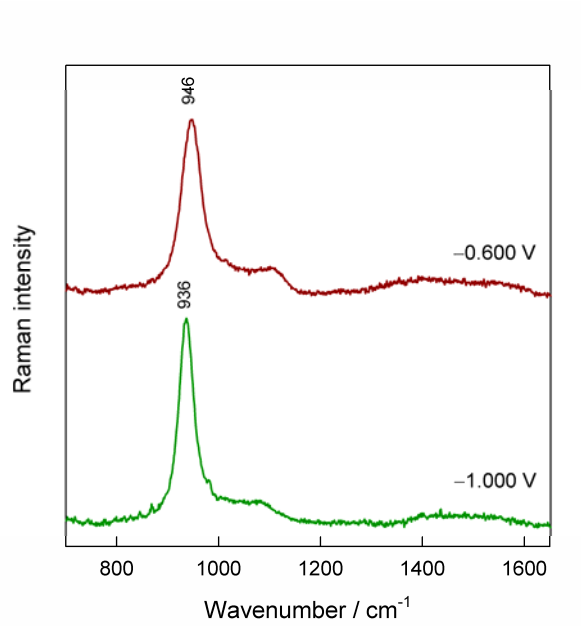

Fig. S2 SERS spectra of phosphate anions adsorbed on Cu electrode at –0.600 and –1.000 V electrode potentials in 0.01 M phosphate buffer (pH 7.0) containing 0.1 M Na_2SO_4. Solution spectrum is subtracted. Measurement conditions: excitation wavelength, 785 nm; laser power at the sample, 30 mW; integration time, 300 s.

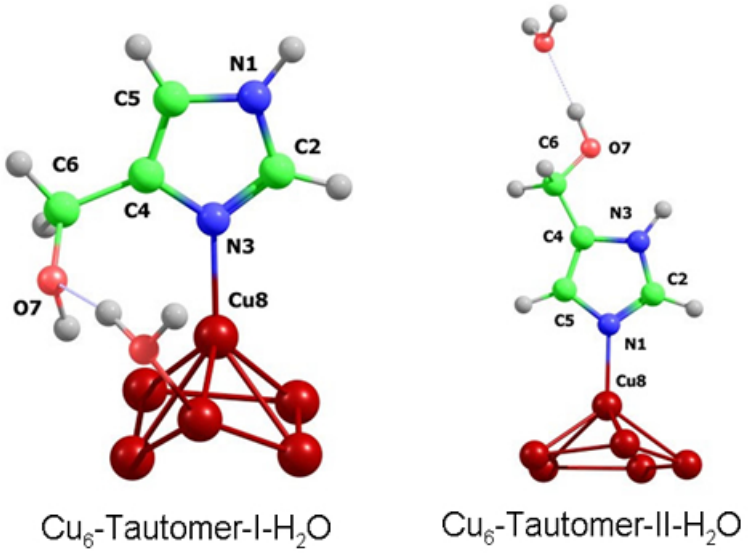

Fig. S3 Structures of Cu_6-ImMeOH-H_2O complexes optimized at DFT-B3LYP/6-311++G(d,p) level for C, H, N, and O atoms, and LANL2DZ with ECP for Cu atoms.

Table S1 Calculated Mulliken atom charges of Tautomer-I and –II of ImMeOH (Fig. 1) and model complexes Cu_6–ImMeOH of surface bound Tautomer-I and –II (Fig. 10)

Atom	Tautomer-I			Tautomer-II		
	Surface-bound complex	Free	Difference (Δq_j)[a]	Surface-bound complex	Free	Difference (Δq_j)
N1	–0.209	–0.246	0.037	0.111	–0.335	0.446
C2	–0.098	0.190	–0.288	–0.171	0.112	–0.283
N3	–0.055	–0.366	0.311	–0.105	–0.279	0.174
C4	0.061	0.492	–0.431	0.479	0.498	–0.019
C5	–0.261	–0.135	–0.126	–0.658	–0.186	–0.472
C6	–0.176	–0.644	0.468	–0.632	–0.510	–0.122
O7	–0.394	–0.373	–0.021	–0.300	–0.389	0.089
H8[a]	0.184	0.167	0.017	0.161	0.155	0.006
H9	0.277	0.254	0.023	0.333	0.261	0.072
H10	0.165	0.156	0.009	0.178	0.140	0.038
H11	0.140	0.120	0.020	0.169	0.147	0.022
H12	0.111	0.134	–0.023	0.183	0.124	0.059
H13	0.366	0.251	0.115	0.259	0.262	–0.003
Total charge of ImMeOH	0.111	0.000	0.111	0.007	0.000	0.007

[a] Defined as: $\Delta q_j = q_j(\text{complex}) - q_j(\text{free})$, for particular j atom; [b]Labeling of H atoms: C2–H8; N1–H9/N3–H9; C5–H10; C6–H11,H12; O7–H13.

Table S2 Calculated bond lengths (pm) of Cu_6-Tautomer-I and Cu_6-Tautomer-II structures (Fig. 10) and corresponding surfaces complexes with added explicit water molecule (Cu_6-Tautomer-I-H_2O and Cu_6-Tautomer-II-H_2O) (Fig. S3)

Bond	Tautomer-I			Tautomer-II		
	Surface-bound complex	Surface-bound complex with water	difference	Surface-bound complex	Surface-bound complex with water	Difference
C4=C5	136.55	136.93	–0.38	136.84	136.90	–0.06
C5–N1	137.85	138.07	–0.22	138.07	138.17	–0.10
C2–N1	135.23	135.63	–0.40	131.87	131.94	–0.07
C2–N3	131.65	131.80	–0.15	135.59	135.56	0.03
C4–N3	138.52	138.59	–0.07	137.98	137.75	0.23
C4–C6	149.66	149.85	–0.19	149.08	149.57	–0.49
C6–O7	142.11	143.23	–1.12	143.19	142.37	0.82
O7–H	97.25	98.09	–0.84	96.22	97.18	–0.96
Cu–N	203.32	202.18	1.14	203.54	203.07	0.47
Cu–O(water)	216.05					
O7–H(water)	184.68					
O7H–O(water)					187.63	