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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*

*Corresponding author

Dr. Gediminas Niaura,
Department of Organic Chemistry,
Center for Physical Sciences and Technology,
A. Gostauto str. 9, LT-01108 Vilnius, Lithuania
Phone: +3705 2729642; Fax: +3705 2729373
E-mail: gniaura@ktl.mii.lt

† Electronic Supplementary Information (ESI) available: Comparison of solution Raman and SERS spectra at different concentrations (Fig. S1); SERS spectra of phosphate anions (Fig. S2); structures of Cu₆-ImMeOH-H₂O complexes (Fig. S3); calculated Mulliken atom charges (Table S1); calculated bond lengths of complexes Cu₆-ImMeOH-H₂O (Table S2). See DOI:

ABSTRACT

Adsorption of 4-imidazolemethanol (ImMeOH) on copper electrode has been investigated by *in situ* isotope-edited (H/D and $^{63}\text{Cu}/^{65}\text{Cu}$) surface enhanced Raman spectroscopy (SERS) in aqueous solutions with physiological pH (7.0) in potential window from -0.400 to -1.100 V. Theoretical modeling by DFT calculations at the B3LYP/6-311++G(d,p) level for light atoms and LANL2DZ with ECP for copper atoms has been employed for interpretation of experimental data. Copper surface was modeled by cluster of 6 atoms. It was found that imidazole ring adopts Tautomer-I form in adsorbed state and coordinates with Cu surface through the N3 atom. Linear potential-dependence of $\nu(\text{C4}=\text{C5})$ mode with the slope of $(15 \pm 1) \text{ cm}^{-1}/\text{V}$ was experimentally observed. The imidazole ring mode near 1492 cm^{-1} primarily due to $\nu(\text{C2}-\text{N3}) + \beta(\text{C2H})$ vibration also has showed considerable decrease in frequency at more negative electrode potentials with the slope of $(9 \pm 2) \text{ cm}^{-1}/\text{V}$. Both modes can be used as sensitive probes for analysis of interaction of imidazole ring with the metal surface. In agreement with experimental data theoretical modeling has predicted higher stability of surface bound Tautomer-I comparing with Tautomer-II. Formation of covalent bond between the metal and adsorbate was experimentally evidenced by metal isotopic ($^{63}\text{Cu}/^{65}\text{Cu}$) frequency shift of $\nu(\text{Cu}-\text{N})$ mode at 222 cm^{-1} , combined with theoretical modeling of the surface complex.

Keywords: imidazole ring; SERS; potential; theoretical modeling; DFT; copper isotopes

INTRODUCTION

Interaction of functional groups of amino acids with metals is an important issue in the fields of biocatalysis, biosensors, and biocompatibility. Imidazole ring plays an important role in coordination of metal ions in proteins and provides an active site for binding with metals in electrochemical interfaces.¹⁻⁴ In addition, participation of imidazole and its derivatives in corrosion prevention and modification of metal surfaces have been demonstrated.⁵⁻⁹ These compounds served as useful corrosion inhibitors in the case of copper electrode.⁸⁻¹¹ Relatively low toxicity of imidazole derivatives has been stressed as an important advantage for corrosion inhibition of Cu in hydrochloric and sulfuric acids.¹¹ To predict and control the formation of complexes at the interface, molecular-level understanding of the imidazole binding mode with the surface and adsorption geometry is required. Surface-enhanced Raman spectroscopy (SERS) is able to provide detailed information on adsorption of molecules and ions at certain metals (mainly Au, Ag, and Cu) because of submonolayer sensitivity and molecular specificity.¹²⁻¹⁴ Importantly, SERS spectra might be collected *in-situ* at potential control, because of low interference of water scattering to the surface spectrum.^{12,15-18} In addition, the low-frequency vibrational region (100–500 cm⁻¹) where important metal-adsorbate vibrational modes appear is easily accessible. These vibrational modes provide direct information on formation of surface complexes at the interface.¹⁹⁻²² Anionic and neutral forms of adsorbed imidazole ring on Ag surface depending on the electrode potential and solution pH were detected by SERS.²³ Previous studies of adsorption of histidine amino acid and histamine at metal surfaces have revealed the importance of carboxyl and amine functional groups in addition to ring nitrogen atoms on interaction with the surface.²⁴⁻²⁷ Reorientation of the imidazole ring of adsorbed histamine at Ag electrode from perpendicular to more parallel configuration was detected as the electrode potential was switched from -0.800 to -0.500 V (vs. Ag/AgCl).²⁶ The influence of electrode potential as well as the nature of solution anions (Cl⁻ and SO₄²⁻) and pH on the

coordination of histidine with copper electrode surface was demonstrated.²⁵ Dissimilar adsorption structures of histidine on Au and Ag nanoparticles have been revealed by SERS.²⁴ In the case of Au electrode flat ring orientation was suggested, while strong interaction of carboxylate group resulted in perpendicular ring orientation for Ag substrate. Recently, participation of imidazole ring of histidine amino acid residue in bonding with copper electrode of decapeptide neuromedin B was revealed by potential-difference SERS spectroscopy.²⁸

In this work we have chosen one of the simplest imidazole derivatives, 4-Imidazolemethanol (ImMeOH). It does not contain surface active or bulky functional groups, thus facilitating direct interaction of imidazole group with the metal. ImMeOH was used for synthesis of imidazole ring containing compounds.²⁹ A copper electrode was chosen because of biologically important metal known to interact with amino acids and peptides forming complexes in aqueous solutions.^{30,31} Furthermore, understanding of binding of imidazole ring containing derivatives to copper surface is important for corrosion inhibition development. In this work we have studied *in situ* the electrode potential effect on the adsorption behavior of 4-imidazolemethanol at copper electrode in buffered (pH 7.0) aqueous solution by using SERS technique. Isotopic-edited SERS based on labile hydrogen atoms substitution by deuterium and substrate ⁶³Cu exchange to ⁶⁵Cu was employed for reliable interpretation of the surface spectra.

EXPERIMENTAL

Materials

Millipore-purified water (18 MΩ cm) was used for preparation of solutions. Chemicals were of ACS reagent grade. ImMeOH and D₂O were purchased from Sigma-Aldrich GmbH (Germany). ⁶³CuO and ⁶⁵CuO were obtained from Cambridge Isotope Laboratories, Inc. (USA).

SERS and Raman measurements

Polarized Raman spectra of ImMeOH (0.5 M) in H₂O and D₂O solutions were recorded with Raman spectrometer inVia (Renishaw) equipped with a grating containing 1800 grooves/mm and CCD detector thermoelectrically cooled to -70 °C. The 532 nm radiation from a DPSS laser (Cobolt) was used as the excitation source. The laser power at the sample was 60 mW. Raman spectra were taken with using 5x/0.12 NA objective lens (Leica). The accuracy in measurement the depolarization ratios (ρ) was checked with CCl₄; the ρ values for 218, 315, and 459 cm⁻¹ bands were obtained to be 0.75, 0.75, and 0.008, respectively.

Near-infrared Raman and SERS spectra were recorded using Echelle type spectrometer RamanFlex 400 (PerkinElmer, Inc.) equipped with thermoelectrically cooled (-50 °C) CCD camera and fiber-optic cable for excitation and collection of the surface-enhanced Raman scattering. The 785 nm beam of the diode laser was used as the excitation source. The 180° scattering geometry was employed. The laser power at the sample was 30 mW, and the beam was focused to a 200 μ m diameter spot. The integration time was 10 s. Each spectrum was recorded by accumulation of 30 scans yielding overall integration time of 300 s. The Raman frequencies were calibrated using the polystyrene standard (ASTM E 1840) spectrum. Intensities were calibrated by a NIST intensity standard (SRM 2241). Experiments were conducted at 20 °C. Spectroelectrochemical measurements were carried out in a cylindrical three-electrode cell configured with a circular quartz window and a flat circular working Cu electrode of \sim 5 mm in diameter that was press-fitted into a Teflon rod. The working electrode was placed \sim 3 mm from the cell window. Pt wire and KCl-saturated Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. The potential values reported below refer to this reference electrode. To eliminate the laser-induced photo- and thermo-effects, the cell, together with the electrodes, was moved linearly with respect to the laser beam at a rate of 15–25 mm/s using custom-built equipment.^{20,32} Oxygen was eliminated from the solutions by continuously bubbling the ultra pure Ar gas. The solution concentration of ImMeOH in SERS studies was 10⁻⁴ M.

Before experiments Cu electrode was polished with soft sandpaper (P2500) and a 0.3 μm alumina slurry (Stuers, Denmark) for refreshing the surface and sonicated in water-ethanol mixture (1:1, v/v) for 10 min. Then, the electrode was transferred into the cell containing 0.02 M CuSO_4 with pH adjusted to 4.5 and SERS active fresh Cu layer was electrodeposited at -0.500 V potential for 3 min.¹⁹ The morphology of roughened Cu electrode surface was characterized previously.³³ Isotopic experiments $^{63}\text{Cu}/^{65}\text{Cu}$ were performed by dissolving the required amount of ^{63}CuO and ^{65}CuO in dilute H_2SO_4 solution while heating to obtain 0.02 M CuSO_4 (pH 4.5) electrolytes. Subsequently, SERS active ^{63}Cu and ^{65}Cu electrodes were obtained by electrodeposition.

Frequencies and intensities of the SERS bands were determined by fitting the experimental contour with Gaussian-Lorentzian form components. Background spectrum of 0.1 M Na_2SO_4 containing 0.01 M phosphate buffer ($\text{H}_2\text{O}/\text{D}_2\text{O}$) was subtracted from SERS spectra. Spectral analysis was performed by using GRAMS/A1 8.0 (Thermo Scientific) software.

Theoretical modeling

All calculations were performed using Gaussian for Windows package version G03W D.01.³⁴ Geometry optimization and harmonic vibrational frequency calculations were accomplished with density functional theory (DFT) method, using B3LYP functional. Calculations were done using 6-311++G(d, p) basis set for C, H, N, and O atoms, and LANL2DZ with ECP for Cu atoms. The cluster model used to represent the metal surface was built with fully optimized 6 copper atoms. Calculated frequencies were scaled by the relation: $\nu' = \alpha(\nu) \cdot \nu$, where ν' and $\alpha(\nu)$ is the scaled frequency and scaling factor, respectively. The scaling factor was defined by the following equation:³⁵

$$\alpha(\nu) = 1 - (1 - \alpha^F) \frac{\nu - \nu^0}{\nu^F - \nu^0}, \quad (1)$$

using the parameters: $\alpha^F=0.97$, $\nu^F=4000$, and $\nu^0=600$. Calculated Raman scattering activities (S_j) were scaled by converting them to the Raman cross sections ($\partial\sigma/\Omega$) which are proportional to the Raman intensities and can be compared with the experimental data. The Raman scattering cross sections were calculated by using the following equation:^{36,37}

$$\frac{\partial\sigma_j}{\partial\Omega} = \left(\frac{2^4\pi^4}{45}\right) \left(\frac{(\nu_0 - \nu_j)^4}{1 - \exp\left[\frac{-hc\nu_j}{kT}\right]}\right) \left(\frac{h}{8\pi^2c\nu_j}\right) S_j, \quad (2)$$

where ν_0 is the laser excitation frequency, ν_j is the vibrational frequency of the j th normal mode, and h , c and k are the universal constants. Predicted vibrational spectra were generated by using Lorentzian function for broadening of Raman lines with 4 cm^{-1} full width at half-maximum (FWHM) values.

RESULTS AND DISCUSSION

Solution Raman spectra of ImMeOH

In neutral aqueous solutions ImMeOH may exist in two tautomeric forms (Fig. 1) depending on which of nitrogen atoms (N1 or N3) is protonated. These tautomers can be easily discriminated by Raman spectroscopy.^{38,39} Fig. 2 compares parallel (\parallel) and perpendicularly (\perp) polarized solution Raman spectra of ImMeOH in H_2O and D_2O . The depolarization ratios ($\rho = I_{\perp}/I_{\parallel}$) of Raman bands provide information on the symmetry of the vibrations and are very useful in making the assignments of the bands. Peak positions and depolarization ratios as well as assignment of the bands are listed in Table 1. The intense polarized band observed at 1575 and 1568 cm^{-1} in H_2O and D_2O solutions, respectively, belongs to $\nu(\text{C4}=\text{C5})$ stretching vibrations and its position indicates that Tautomer-I dominates in aqueous solutions of ImMeOH. The low intensity shoulder detected at 1591 cm^{-1} near the 1575 cm^{-1} peak is assigned to $\nu(\text{C4}=\text{C5})$ mode from Tautomer-II.^{38,39} Based on

integrated intensity ratio, A_{1575}/A_{1591} , the concentration ratio of Tautomer-I to Tautomer-II is found to be 6.1. This is considerably higher prevalence of Tautomer-I comparing with aqueous solution of histidine amino acid (4 times).⁴⁰ The calculated spectra of Tautomer-I of Im-CH₂-OH and deuterated for labile hydrogens form ImD-CH₂-OD are also displayed in Fig. 2. In excellent agreement with experimental spectra the $\nu(\text{C4}=\text{C5})$ bands were predicted at 1574 and 1567 cm⁻¹ for natural and deuterated structures. Calculated spectra, ρ values determined from experimental data, and previously published studies on vibrational analysis of imidazole ring derivatives³⁸⁻⁴¹ were used for assignment of the bands presented in Table 1. In C-H stretching frequency region two pair of bands associated with stretching vibrations of methylene group (2888–2954 cm⁻¹) and imidazole ring (3133–3157 cm⁻¹) is clearly visible (Fig. 2). Calculated spectra allowed secure assignment of $\nu(\text{C5-H})$ and $\nu(\text{C2-H})$ modes of imidazole ring to 3157 and 3133 cm⁻¹ components of experimental spectrum (Table 1).

Overview of the SERS spectra of ImMeOH on Cu electrode

Fig. 3 compares 785-nm excited solution Raman and SERS spectra of ImMeOH at 0.5 M and 10⁻⁴ M concentrations, respectively. No bands associated with solution ImMeOH were possible to observe at 10⁻⁴ M concentration (Fig. S1 in ESI[†]), indicating that roughened Cu electrode used in this work support SERS effect. Numerous changes in the peak positions, relative intensities, and widths of the bands are visible in the SERS spectrum. The intense feature visible near 937 cm⁻¹ belongs to adsorbed phosphate anions.⁴²⁻⁴⁴ This band usually appears in neutral or slightly alkaline phosphate buffer solution providing the Cu surface is sufficiently clean without amorphous carbon impurities or strongly chemisorbed organic species.⁴⁴ The peak frequency of the phosphate band downshifts and full width at half maximum (FWHM) decreases at more negative electrode potentials. SERS bands of adsorbed phosphate anions are clearly visible in the blank solution spectrum before the introduction of ImMeOH (Fig. S2, ESI[†]). The well-defined bands in the

fingerprint spectral region (Fig. 3A) near 1107, 1279, 1345, 1491, and 1579 cm^{-1} belong to imidazole ring vibrations of adsorbed ImMeOH. Observation of SERS bands from both phosphate species and imidazole ring modes indicates that phosphate anions and ImMeOH coadsorb at Cu electrode surface. The relative intensities of the bands near 982, 1325, 1464, and 1575 cm^{-1} considerably decrease in surface spectrum. Particularly substantial is decrease in relative intensity of 982 cm^{-1} mode associated mainly with rocking vibration of C_6H_2 side chain group, $\text{rock}(\text{C}_6\text{H}_2)$; this band is also coupled with in-plane deformation vibration of imidazole ring, $\delta(\text{C}_2\text{N}_3\text{C}_4)$ and stretching vibration of carbon–oxygen bond, $\nu(\text{C}_6\text{--O}_7)$ (Table 1). The other band associated with deformation vibration of C_6H_2 group appears as an intense band in the solution spectrum near 1464 cm^{-1} . Assignment of this band is confirmed by the high value of depolarization ratio ($\rho=0.55$) (Fig. 2, Table 1). However, this band is barely visible in the SERS spectrum (Fig. 3A). It seems that intensity of deformation and rocking modes of the side chain C_6H_2 group is considerably attenuated in the SERS spectrum. In the C–H stretch spectral region (Fig. 3B) SERS bands broaden and shift to lower wavenumber range. In particular, downshift of stretching vibrational modes of methylene group near 2889/2953 cm^{-1} is considerably higher (27/45 cm^{-1}) comparing with 3133- cm^{-1} imidazole ring =C–H vibration (4 cm^{-1}).

Labile hydrogens H/D isotope-edited SERS spectra

To ensure accurate assignments of the bands, isotope-edited SERS experiments for labile hydrogen atoms at imidazole ring and OH group were performed in solutions prepared with H_2O and D_2O at -1.100 V electrode potential (Fig. 4). Two well-defined bands located at 1579 and 1491 cm^{-1} clearly shift in D_2O solution to 1574 and 1486 cm^{-1} , respectively. Comparison with solution and calculated spectra allowed assignment of these bands to $\nu(\text{C}_4=\text{C}_5)$ and mixed $\nu(\text{C}_2\text{--N}_3) + \beta(\text{C}_2\text{H})$ modes, respectively. Observed shifts immediately confirm that in the adsorbed state one of the imidazole ring nitrogen atoms is protonated. The peak at 1279 cm^{-1} shows only slight shift and was

assigned to imidazole ring breathing mode coupled with C2–H in-plane bending vibration. It was demonstrated that position of this band is extremely useful for discrimination of different tautomeric forms of imidazole ring appearing near 1282 and 1260 cm^{-1} for Tautomer-I and Tautomer-II, respectively.³⁸ Thus, experimental SERS data evidence that in the adsorbed state the Tautomer-I dominates. In such structure the interaction with surface must take place through the N3 atom of imidazole ring (Fig. 1).^{40,41} Analysis of Raman spectra of metal complexes of histidine revealed upshift of C4=C5 mode upon binding with metal cations.⁴¹ As seen from Fig. 3 the frequency of C4=C5 band increases in SERS spectra by 4 cm^{-1} . Such frequency upshift value is characteristic for N3–Metal coordinated complexes⁴¹ and provides evidence that direct interaction with copper electrode surface takes place through the N3 site. The intensification of the band near 1328 cm^{-1} was clearly observed in D₂O solution Raman spectrum (Fig. 2). Because, Tautomer-I prevails in aqueous solution, observation the similar band in SERS spectrum of Cu electrode immersed in solution prepared with D₂O solvent (1333 cm^{-1}) confirms the dominating Tautomer-I form in adsorbed state of ImMeOH. Finally, the intense peak in D₂O SERS spectrum near 1103 cm^{-1} corresponds to mixed $\nu(\text{N1–C2}) + \beta(\text{N1H}) + \beta(\text{C2H})$ mode (Table 1). Position of this band is blue-shifted by 5 cm^{-1} comparing with solution D₂O Raman spectrum. Because of involvement of N1H bending mode this shift might be associated with changes in hydrogen bonding interaction strength for adsorbed molecule.

Potential dependence

Figure 5 compares SERS spectra of ImMeOH at selected Cu electrode potentials. It should be noted that adsorbed species are visible in the broad potential window (from –0.500 to –1.100 V). The positions of two bands located near 1579 and 1491 cm^{-1} ($E = -1.100$ V) are highly sensitive to the electrode potential. More quantitative analysis of potential dependence of these bands is provided in Figure 6. Linear dependence is observed for the $\nu(\text{C4=C5})$ mode with the slope of $(15 \pm 1) \text{cm}^{-1}/\text{V}$.

Analysis of crystalline compounds of metal complexes with imidazole ring have revealed correlation between the $\nu(\text{C4}=\text{C5})$ band frequency and $\text{C4}=\text{C5}$ bond length,⁴¹ higher frequency corresponds to shorter bond. In the case of N1-H/N3-metal complexes (Tautomers-I) the 1573, 1580, and 1588 cm^{-1} wavenumbers correspond to 137.9, 136.9, and 135.4 pm bond lengths.⁴¹ Thus, observed decrease in peak frequency at more negative electrode potential reveal lengthening of $\text{C4}=\text{C5}$ bond because of decrease in interaction strength with the metal surface.

The peak position of second lower frequency band also shifts to lower wavenumbers at more negative electrode potentials (Fig. 6b). However, the slope was found to be considerably smaller ($9 \pm 2 \text{ cm}^{-1}/\text{V}$). This mode involves large contribution from C2-N3 stretching and C2-H in-plane bending vibrations. Because for Tautomer-I the N3 atom of imidazole ring is involved in bonding with the metal, potential-induced changes in interaction with surface might modulate this mode frequency. Importantly, in the case of Tautomer-II the main contributions for the experimentally observed band near 1493 cm^{-1} in the solution spectrum consists from $\nu(\text{N1-C2}) + \beta(\text{C2H})$.³⁸ Thus, this mode must be coordination sensitive band, because involves the bonded with the metal atom N1 . Indeed, appearance of the new band at higher frequencies (1503 cm^{-1}) was clearly visible in the experimental Raman spectra of $\text{Cu(II)-}(\beta\text{Ala-His})$ or $\text{Zn(II)-}(\text{zinc finger})$ complexes with N3-H/N1-Metal coordination state.⁴¹

The positions of the high frequency C-H stretching bands of methylene group are considerably downshifted in SERS spectra (2878–2925 cm^{-1}) (Fig. 4) comparing with solution Raman spectrum (2889 and 2953 cm^{-1}) (Fig. 3 and Table 1). The effect is even better pronounced at more negative electrode potentials (Fig. 7A). This indicates surface induced restriction to vibrations because of contact the imidazole ring and methylene group with Cu atoms. For more detailed analysis of C-H stretching bands the potential-difference spectrum was constructed (Fig. 7A). Broad positively-going feature with maximum near 2844 cm^{-1} is visible in the difference spectrum.

Previously, we have identified an unusually low frequency C–H stretching band of methylene groups from bifunctional thiols adsorbed at Ag and Au electrodes associated from the direct interaction of methylene groups with the metal surface.⁴⁵ Similar soft methylene stretching bands were observed by infrared reflection absorption spectroscopy studies of adsorption of alkyl chain containing molecules on metal surfaces.^{46,47} Importantly, such low frequency band was also observed in the SERS spectra of adsorbed peptides at Ag electrode at sufficiently negative potential values.⁴⁸ Thus, presented data indicate that methylene group contacts the electrode surface upon adsorption of ImMeOH at copper electrode at more negative electrode potentials. Such contact with surface might be responsible for the attenuation of relative intensities of deformation scissoring and rocking modes of C₆H₂ group in SERS spectra. The soft mode intensity dependence on electrode potential (Fig. 7B) indicates that reorientation of molecule so that CH₂ groups approach the Cu electrode surface takes place in the potential region from –0.60 to –0.90 V. It should be noted that C–H stretching bands considerably broaden upon adsorption of ImMeOH on Cu electrode. Thus, width of the methylene group C–H stretching bands determined as FWHM increases from 32 (2889 cm⁻¹ band) and 41 cm⁻¹ (2953 cm⁻¹ band) to 109 (2878 cm⁻¹ band) and 57 cm⁻¹ (2925 cm⁻¹ band) for adsorbed species at –0.5 V potential, respectively. Considering the imidazole ring =C–H stretching modes, only one broad feature near 3130 cm⁻¹ was visible in the surface spectrum, while two clear bands at 3133 and 3157 cm⁻¹ exhibits solution Raman spectrum. It should be noted that deuteration of imidazole ring induces slight shift of 3157 cm⁻¹ component to 3154 cm⁻¹ for ImMeOH in D₂O solvent (Fig. 2). FWHM of the imidazole ring =C–H stretching mode broadens from 26 cm⁻¹ (3133 cm⁻¹ band) to 111 cm⁻¹ for adsorbed species. Such considerable broadening of =C–H band confirms the involvement of imidazole ring in bonding with electrode surface.

Important information on orientation of imidazole ring with respect to the copper electrode surface might be derived from the analysis of relative intensities in solution Raman and SERS spectra. SERS surface selection rule suggests that the most intense bands are associated with the

vibrational modes with polarizability tensor components oriented perpendicular to the metal surface.^{49,50} In the case of compounds with planar structure, particularly useful is analysis of relative magnitude of =C–H stretching band.^{51,52} Since for aromatic molecules polarizability tensor lies predominantly along the =C–H axis, observation of intense band indicates predominant vertical orientation of molecule at the metal surface.⁵² We have estimated relative surface enhancement factor (SEF) by comparing the integrated intensity ratio for =C–H stretching vibrational mode of imidazole ring in SERS and solution spectra [$SEF_{(=C-H)} = (A_{SERS}/A_{solution})_{=C-H}$]. Intensities were normalized to breathing vibrational mode of imidazole ring observed at 1284 and 1279 cm^{-1} in solution and surface spectra, respectively (Fig. 3). At electrode potential -1.100 V the $SEF_{(=C-H)}$ value was found to be 1.75, indicating tilted orientation of imidazole ring plane. Shift electrode potential to -0.500 V results in decrease of $SEF_{(=C-H)}$ to 1.35. Thus, it can be suggested that angle between the ring plane and surface normal increases as potential becomes less negative.

⁶³Cu/⁶⁵Cu metal isotope-edited SERS spectra in the low frequency region

Direct information on bonding of adsorbates with metal surface might be extracted by SERS technique from the analysis of low-frequency spectral region.^{21,22} Fig. 8 shows SERS spectra in the range from 120 to 800 cm^{-1} at selected electrode potentials. Three bands located near 149, 222, and 313 cm^{-1} (-1.100 V) might be associated with deformation and stretching vibration of Cu–N bond.⁵³ The position of the former two bands slightly varies (within 4 cm^{-1}) with electrode potential, while frequency of the latter band more clearly decreases at more negative electrode potential. The $\nu(\text{Cu–N})$ band was detected near 310 cm^{-1} by Raman spectroscopic analysis of Cu(II)-histamine complex.⁵⁴ For precise assignment of metal-adsorbate vibrational modes we have performed metal isotope-edited SERS experiments (Fig. 9). The blue shift for band located near 219 cm^{-1} was clearly visible when ⁶⁵Cu layer was changed to ⁶³Cu. Exact isotope-induced frequency shift [$k = \nu(^{63}\text{Cu–N}) - \nu(^{65}\text{Cu–N})$] was determined from the analysis of second derivatives of the

corresponding SERS spectra and it was found to be $2.6 \pm 0.5 \text{ cm}^{-1}$. The shoulder near 258 cm^{-1} observable in the SERS spectrum became clearly visible in the second derivative spectrum. No frequency shift was detected for this mode in the wavenumber limit of $\pm 0.5 \text{ cm}^{-1}$. Thus, this vibrational mode does not involve motion of Cu atom and probably is associated with deformation vibration of adsorbate. It was not possible to determine precisely the shift of the broad low frequency feature near 149 cm^{-1} . However, we can conclude that this band remains unshifted in frequency limit of $\pm 2 \text{ cm}^{-1}$.

Theoretical modeling of surface complex

In order to confirm the assignments of the bands and get insight into the bonding of imidazole ring with copper surface theoretical modeling of Cu_6 -ImMeOH complexes for Tautomer-I and Tautomer-II was performed. Structures with fully optimized metal clusters ($^{65}\text{Cu}/^{63}\text{Cu}$) were considered. Fig. 10 shows the optimized geometries of Cu_6 -ImMeOH complexes. The calculated energies revealed that the Tautomer-I complex structure is more stable (by 7.7 kcal/mol) than the Tautomer-II. This theoretical prediction is in accord with experimental SERS observation of prevalence of Tautomer-I in adsorbed state. The main difference between these complexes is that weak interaction of OH group takes place in the Tautomer-I case with one of the Cu atom. Such interaction is clearly visible by the downshifted $\nu(\text{O-H})$ mode frequency from 3689 cm^{-1} (Tautomer-II) to 3515 cm^{-1} (Tautomer-I). The bond lengths for different conformers are compared in Table 2. The O7-H bond length increases by 0.90 pm upon bonding of Tautomer-I with Cu_6 cluster, while the length of this bond slightly decreases (0.12 pm) in the case of Tautomer-II. Other bonds of imidazole ring are affected at higher extent for this structure as well. To account the bonding with metal cluster induced perturbations in the structure of adsorbate, we have introduced the average bond change:

$$\delta = n^{-1} \sum_n |\Delta_i|, \quad (3)$$

where Δ_i is the lengthening (shortening) of the particular i bond because of bonding of molecule with the metal cluster and n is the number of considered bonds in the adsorbate. For bonded Tautomer-I and Tautomer-II the δ value was found to be 0.84 and 0.42 pm, respectively. Thus, interaction of Tautomer-I with copper cluster results in considerably higher structural perturbations of molecule. The lengths of the bonds adjusted to the N atom, which is involved in the bonding with copper cluster (C2–N3 and C4–N3 for Tautomer-I and C5–N1 and C2–N1 for Tautomer-II) increases upon chemisorption. However, the length of C4=C5 bond decreases by 0.48 pm upon formation of surface complex in the case of Tautomer-I (Table 2). Correspondingly, the frequency of $\nu(\text{C4}=\text{C5})$ mode increases. Such adsorption induced blue shift is consistent with experimentally observed SERS spectra (Table 1). It should be noted that calculations suggest smaller decrease in bond length (less frequency shift) upon formation of surface complex with Tautomer-II (Table 2). The calculated Cu–N bond length (203.3 pm) for surface bound imidazole ring of Tautomer-I is slightly higher comparing with crystalline metal ion complexes of histidine and histidine-containing peptides observed experimentally (196.2–201.9 pm).⁴¹ Calculations predict Cu–N stretching vibrational mode at 242.3 and 239.9 cm^{-1} for $^{63}\text{Cu}_6\text{-ImMeOH}$ and $^{65}\text{Cu}_6\text{-ImMeOH}$ complexes, respectively (Fig. 9). Metal isotopic frequency shift for model surface complexes ($k=2.4 \text{ cm}^{-1}$) coincides very well with experimentally observed value ($k=2.6 \text{ cm}^{-1}$), confirming assignment of this band to the Cu–N stretching vibrational mode. Calculations suggest that the experimentally observed band near 313 cm^{-1} is associated mainly with rocking vibration of C6H₂ group with some contribution from $\delta(\text{C6C4})$ in-plane and $\delta(\text{CuN})$ vibrations; no isotopic frequency shift was detected for this mode. Other lower frequency bands exhibiting clear downshift (199.9 cm^{-1} /197.4 cm^{-1} and 168.2 cm^{-1} /166.9 cm^{-1}) upon $^{63}\text{Cu}/^{65}\text{Cu}$ exchange are associated mainly with stretching

and deformation vibrations of metal cluster. Thus, experimentally observed band near 149 cm^{-1} might be tentatively assigned to stretching vibration of electrode copper atoms.

To investigate the changes in electronic structure of ImMeOH, the Mulliken charges on atoms of adsorbate before and after the surface complex formation was analyzed (Table S1, ESI†). Before bonding the N3/N1 (Tautomer-I/Tautomer-II) atoms had the largest excess electronic population ($\sim 0.3\text{--}0.4\text{ e}$) of imidazole ring, indicating nucleophilic nature of these centers in their interaction with a metal surface. As can be seen from the charge difference of atoms, $\Delta q_j = q_j(\text{complex}) - q_j(\text{free})$ (for particular j atom), bonding of molecule with Cu_6 cluster results in pronounced charge redistribution. First of all, the negative charge on bonded N3/N1 (Tautomer-I/Tautomer-II) atoms considerably decreases (by $\sim 0.31\text{--}0.45\text{ e}$), while the relative negative charge on C4/C5 atoms, which are close to the bonded nitrogen atom significantly increases (by $\sim 0.43\text{--}0.47\text{ e}$). Secondly, in the case of Tautomer-I the noticeable electron density decrease was characteristic for the H13 atom of C6–O7H13 moiety indicating the participation of the hydroxyl group in the interaction with the surface. Such charge redistribution results in lengthening of O7–H bond and downshift of corresponding calculated stretching frequency (Table 1). Comparison of net charges for adsorbed different conformers revealed 0.111 electron charge transfer from molecule to the metal cluster in the case of Tautomer-I, while only 0.007 electron charge transfer was obtained for Tautomer-II (Table S1, ESI†).

Because of the studied compound is able to form hydrogen bonds, the surface complexes with added explicit water molecule were calculated (Fig. S3, ESI†). In the case of Tautomer-I formation of chemical bond between water molecule and copper atom was observed, while for Tautomer-II water molecule was found to be in the solution phase. Optimized structures revealed formation of hydrogen bond between the oxygen atom O7 of adsorbed Tautomer-I and the hydrogen atom of water molecule ($\text{O7}\cdots\text{HOH}$). For Tautomer-II formation of $(\text{O7})\text{H}\cdots\text{OH}_2$ hydrogen bond was estimated. Surprisingly, addition of water molecule induced minor changes in

the geometry of surface complexes. Comparison of calculated energies revealed that surface complex $\text{Cu}_6\text{-Tautomer-I-H}_2\text{O}$ (N3-Cu bonded) with explicit water molecule is more stable by 7.78 kcal/mol comparing with $\text{Cu}_6\text{-Tautomer-II-H}_2\text{O}$ (N1-Cu bonded) surface complex. Analysis of water-induced changes in structure of adsorbed $\text{Cu}_6\text{-Tautomer-I-H}_2\text{O}$ indicates slight lengthening of chemical bonds except of N3–Cu bond (Table S2, ESI†). The average perturbation of chemical bonds (δ) was found to be 0.50 pm. In the case of $\text{Cu}_6\text{-Tautomer-II-H}_2\text{O}$ structure, the water-induced changes in the structure of ImMeOH is less pronounced ($\delta=0.36$ pm). Importantly, in both cases interaction of water with adsorbed ImMeOH slightly decreases the nitrogen-copper bond length (increases interaction strength). Experimentally adsorbed water molecules have not been detected by SERS method in this work. It is well-known that special conditions are required for SERS observation of interfacial water.^{55,56}

CONCLUSIONS

Imidazole ring is a key functional group in metal-coordinating proteins and peptides. The present study provides detailed insight into the vibrational properties of one of the simplest imidazole derivatives, 4-imidazolemethanol (ImMeOH), adsorbed on copper electrode surface in neutral aqueous solution. Stable isotope-edited (ImMeOH/ImDMeOD and $^{63}\text{Cu}/^{65}\text{Cu}$) SERS and theoretical modeling at DFT-B3LYP/6-311++G(d,p) level for light atoms and LANL2DZ with ECP for copper atoms were employed to probe the potential-dependent adsorption behavior of imidazole derivative. The adsorption complex was modeled by 6 copper atoms, $\text{Cu}_6\text{-ImMeOH}$. Co-adsorption of phosphate anions and ImMeOH in a wide potential region has been evidenced from SERS spectra. Two imidazole ring high frequency stretching bands located near 1580 [$\nu(\text{C4}=\text{C5})$] and 1492 cm^{-1} [$\nu(\text{C2}-\text{N3}) + \beta(\text{C2H})$] have demonstrated considerable downward frequency shift at more negative electrode potentials indicating sensitivity of these modes to binding of imidazole ring with copper surface. Appearance of “soft” C–H stretching feature near 2805 cm^{-1} has indicated contact of

methylene group with metal surface upon adsorption of ImMeOH on Cu electrode at more negative electrode potentials. Experimental spectra and theoretical modeling both suggested that the most stable form of adsorbed molecule is Tautomer-I and the imidazole ring N3 atom is a primary binding site to copper. The metal-adsorbate vibrational mode has been clearly identified in metal isotope-edited ($^{63}\text{Cu}/^{65}\text{Cu}$) SERS spectrum near 222 cm^{-1} . This assignment was confirmed by theoretical modeling of $^{63}\text{Cu}_6\text{-ImMeOH}$ and $^{65}\text{Cu}_6\text{-ImMeOH}$ complexes. The results presented in this work demonstrate the utility of metal ($^{63}\text{Cu}/^{65}\text{Cu}$) isotope-edited SERS as a probe of metal-adsorbate interactions.

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Table 1 Experimental and calculated wavenumbers (in cm^{-1}), depolarization ratios (ρ), and assignments of ImMeOH in solution and in adsorbed state on Cu electrode

Raman			Calculated ^a	SERS ^b		Calc. complex ^c	Assignment
H ₂ O	D ₂ O	ρ^d		H ₂ O	D ₂ O		
3157 m	3154 s	0.22	3156			3164	$\nu(\text{C5-H})$
3133 vs	3133 s	0.19	3134	3129 m	3129 m	3155	$\nu(\text{C2-H})$
2953 s	2954 s	0.16	2952	2908 s	2910 s	2991	$\nu_{\text{as}}(\text{C6H}_2)$
2889 s	2888 s	0.05	2907	2862 s	2864 s	2916	$\nu_{\text{s}}(\text{C6H}_2)$
1575 vs	1568 vs	0.04	1574	1579 s	1574 s	1584	$\nu(\text{C4=C5}) +$ $\nu(\text{C4-C6}) + \beta(\text{C5H})$
1497 m	1482 m	0.14	1506	1491 m	1486 m	1508	$\nu(\text{C2-N3}) + \beta(\text{C2H})$ $+ \nu(\text{C2-N1}) +$ $\nu(\text{C5-N1})$
1464 m	1466 w	0.55	1435			1472	$\delta(\text{C6H}_2)$
1444 sh		~ 0.1	1419	1445 m		1453	$\beta(\text{N1H}) + \nu(\text{N1-C2})$
1325 s	1328 vs	0.14	1345	1345 m	1333 s	1331	$\nu(\text{C2-N3}) +$ $\nu(\text{N3-C4}) + \beta(\text{C5H})$
1284 vs	1283 vs	0.10	1296	1279 vs	1276 s	1287	$\nu(\text{Im})$ breathing + $\beta(\text{C2H}) + \nu(\text{C4-C6})$
1243 m	1218 m	0.62	1249		1210 w	1244	$\beta(\text{C5H}) + \beta(\text{C2H}) +$ $\nu(\text{C5-N1})$
1157 s	1098 s	0.06	1114	1144 w	1103 s	1143	$\nu(\text{N1-C2}) + \beta(\text{N1H})$ $+ \beta(\text{C2H})$
1108 m		0.15	1081	1107 m		1083	$\nu(\text{C5-N1}) + \beta(\text{C5H})$
1093 m		0.28	1012		1038 m	1041	$\nu(\text{C6-O}) + \nu(\text{C6-C4})$ $+ \nu(\text{C4-N3})$
982 vs	982 s	0.10	982	987 w		1007	rock(C6H_2) + $\delta(\text{C2N3C4}) +$ $\nu(\text{C6-O7})$
937 w	925 w	0.68	948			942	$\delta(\text{C5N1C2}) +$ $\delta(\text{C2N3C4})$

665 m	667 m	0.12	674	709 s		667	$\gamma(\text{Im})$
629 w	629 m	0.40	648	663 w		648	$\gamma(\text{Im})$
435 m	433 m	0.21	422	444 m		432	$\gamma(\text{C4C6O})$
322 w	322 w	0.73		313 m	311 m	332	rock(C6H ₂) + $\delta(\text{C6C4}) + \delta(\text{CuN})$
				222 s	222 s	242	$\nu(\text{Cu-N})$
				148 s	152 s	167	$\nu_s(\text{Cu}_6)$

^aCalculated for Tautomer-I of ImMeOH in vacuum; ^bAt electrode potential -1.100 V; ^cCalculated for Tautomer-I of complex Cu₆-ImMeOH; ^dEstimated for ImMeOH in H₂O. Abbreviations: ν , stretching; δ , deformation; β , in-plane bending; γ , out-of-plane deformation; ν_s , very strong; s, strong; m, middle; w, weak; wag, wagging; Im, imidazole ring.

Table 2.

Calculated bond lengths (pm) of Tautomer-I and -II of ImMeOH (Fig. 1) and model complexes Cu₆-ImMeOH of surface bound Tautomer-I and -II (Fig. 10).

Bond	Tautomer-I			Tautomer-II		
	Free	Surface-bound complex	difference	Free	Surface-bound complex	Difference
C4=C5	137.03	136.55	0.48	137.01	136.84	0.17
C5-N1	137.49	137.85	-0.36	137.61	138.07	-0.46
C2-N1	136.48	135.23	1.25	131.10	131.87	-0.77
C2-N3	130.88	131.65	-0.77	136.33	135.59	0.74
C4-N3	137.98	138.52	-0.54	137.82	137.98	-0.16
C4-C6	148.85	149.66	-0.81	148.50	149.08	-0.58
C6-O7	143.70	142.11	1.59	143.55	143.19	0.36
O7-H	96.35	97.25	-0.90	96.34	96.22	0.12
Cu-N		203.32			203.54	

Figure Captions

Fig. 1 Structures and atom numbering of 4-Imidazolemethanol (ImMeOH) tautomers optimized at DFT-B3LYP/6-311++G(d,p) level.

Fig. 2 Polarized (||) and depolarized (\perp) Raman spectra in 400–1800 cm^{-1} (left panel) and 2800–3250 cm^{-1} (right panel) spectral regions of 0.5 M ImMeOH in H_2O and D_2O solutions and calculated Raman spectrum of Im- CH_2 -OH and ImD- CH_2 -OD. Measurement conditions: excitation wavelength, 532 nm; laser power at the sample, 60 mW; integration time, 200 s.

Fig. 3 Raman spectrum of (a) 0.5 M ImMeOH aqueous solution and (b) SERS spectrum from Cu electrode in 10^{-4} M ImMeOH aqueous solution containing 0.1 M Na_2SO_4 and 0.01 M phosphate buffer (pH 7.0) at -1.100 V potential. Background spectrum of water and buffer was subtracted from solution and SERS spectra, respectively. Measurement conditions: excitation wavelength, 785 nm; laser power at the sample, 30 mW; integration time, 300 s.

Fig. 4 SERS spectra of ImMeOH adsorbed on Cu electrode at -1.100 V potential in solutions prepared from H_2O and D_2O . Raman spectrum of buffer was subtracted. Measurement conditions: 0.1 M Na_2SO_4 solution containing 0.01 M phosphate buffer (pH 7.0) and 10^{-4} M of ImMeOH; excitation wavelength, 785 nm; laser power at the sample, 30 mW; integration time, 300 s.

Fig. 5 SERS spectra of ImMeOH adsorbed on Cu electrode at -0.500 (a), -0.700 (b), -0.900 (c), and -1.100 V (d) electrode potentials in the fingerprint (A) and C–H stretching frequency (B) spectral regions. Raman spectrum of buffer was subtracted. Measurement conditions: 0.1 M Na_2SO_4

solution containing 0.01 M phosphate buffer (pH 7.0) and 10^{-4} M of ImMeOH; excitation wavelength, 785 nm; laser power at the sample, 30 mW; integration time, 300 s.

Fig. 6 Potential dependence of SERS peak wavenumbers for (a) $\nu(\text{C4}=\text{C5})$ and (b) $\nu(\text{C2}-\text{N3}) + \beta(\text{C2H})$ vibrational modes.

Fig. 7 SERS spectra in C–H stretching spectral region of ImMeOH adsorbed on Cu electrode at (a) -1.100 V and (b) -0.500 V. Difference spectrum (c) is also shown. Measurement conditions: 0.1 M Na_2SO_4 solution containing 0.01 M phosphate buffer (pH 7.0) and 10^{-4} M of ImMeOH; excitation wavelength, 785 nm; laser power at the sample, 30 mW; integration time, 300 s.

Fig. 8 Potential dependence of SERS spectra of ImMeOH adsorbed on Cu electrode in the low frequency spectral region. Measurement conditions: 0.1 M Na_2SO_4 solution containing 0.01 M phosphate buffer (pH 7.0) and 10^{-4} M of ImMeOH; excitation wavelength, 785 nm; laser power at the sample, 30 mW; integration time, 300 s.

Fig. 9 Isotopic $^{63}\text{Cu}/^{65}\text{Cu}$ edited SERS spectra of ImMeOH adsorbed on Cu electrode at -1.100 V in the metal-adsorbate spectral region with corresponding second derivative SERS spectra (multiplied by -1) (upper panel), and calculated low-frequency Raman spectra of $^{65}\text{Cu}_6$ -ImMeOH and $^{63}\text{Cu}_6$ -ImMeOH complexes (bottom panel).

Fig. 10 Structures of Cu_6 -ImMeOH 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.

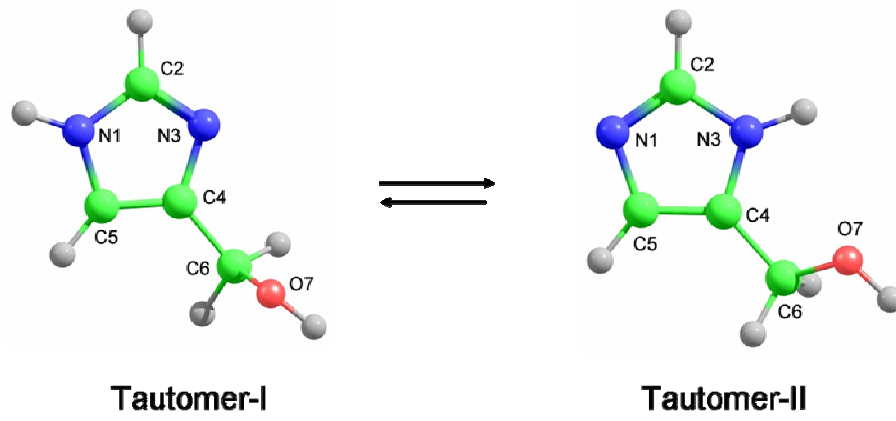


Figure 1.

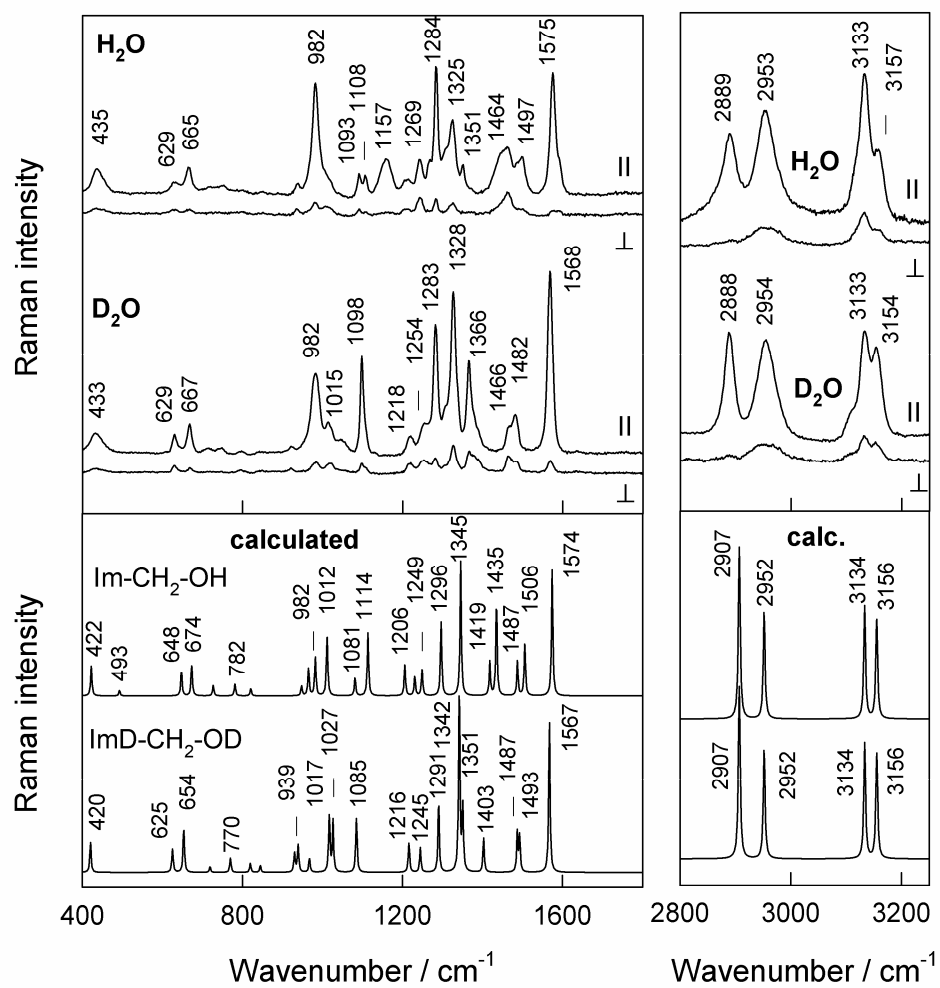


Figure 2.

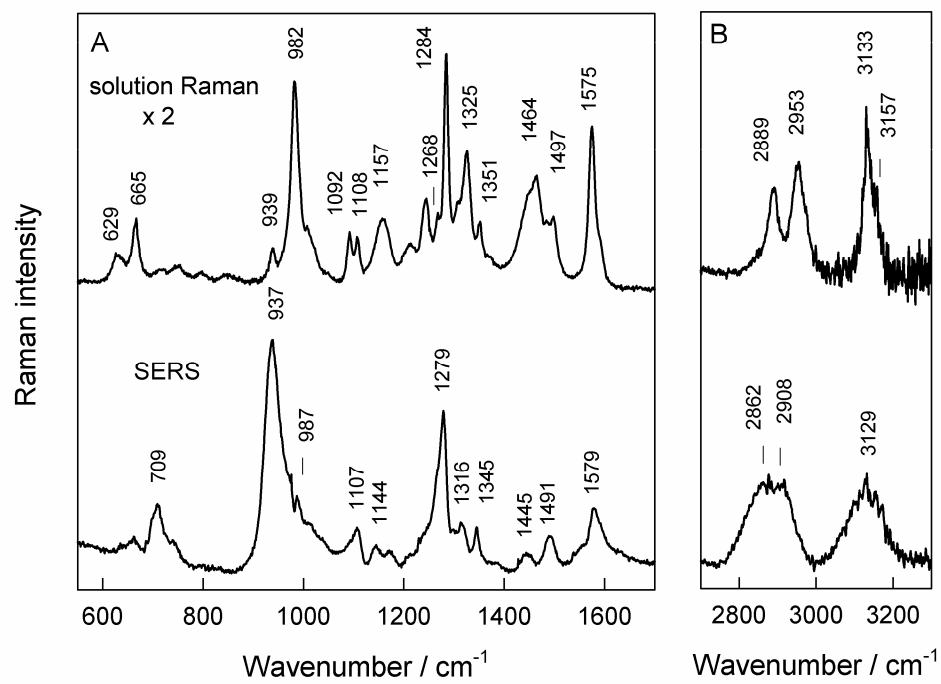


Figure 3.

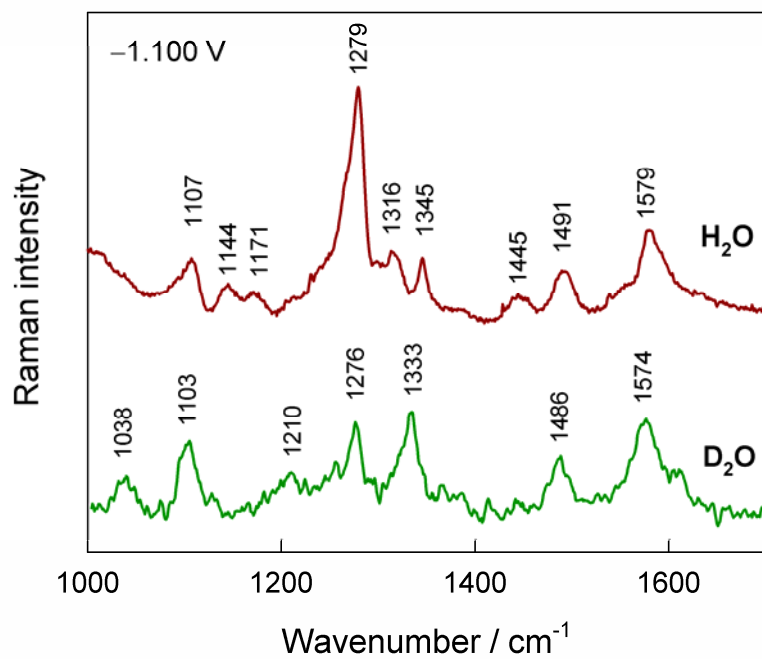


Figure 4.

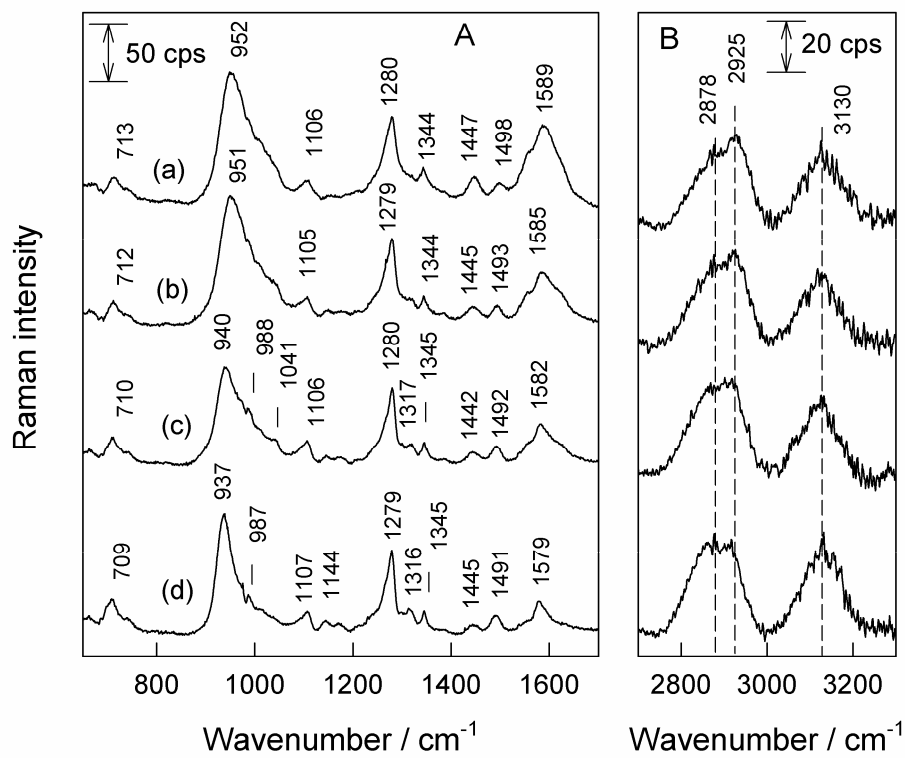
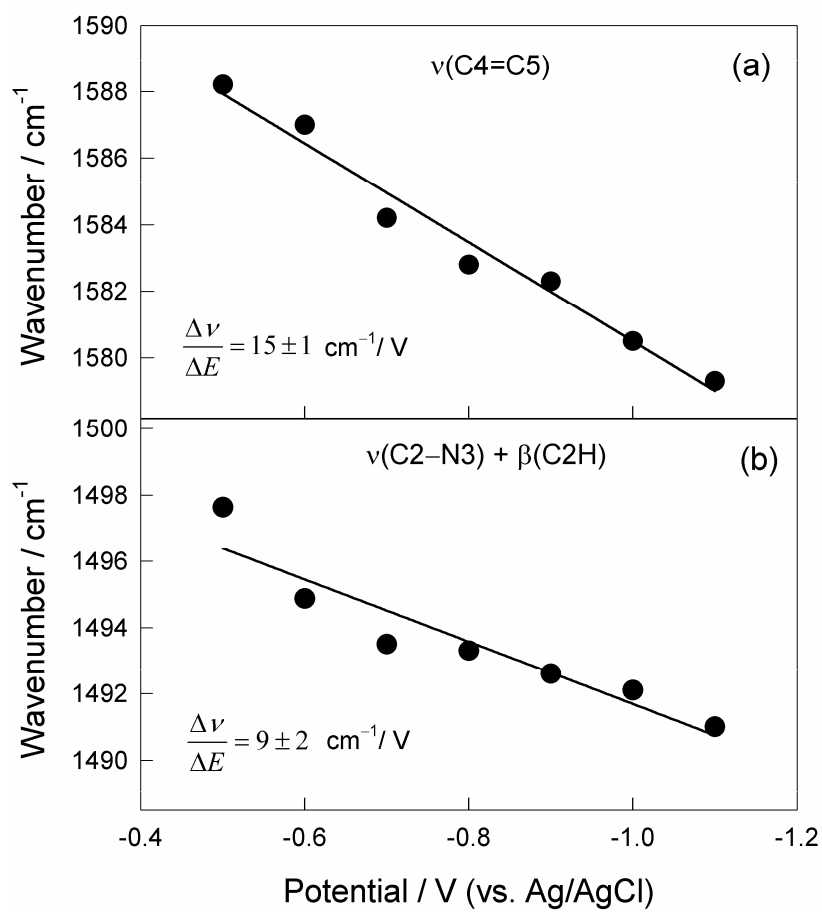
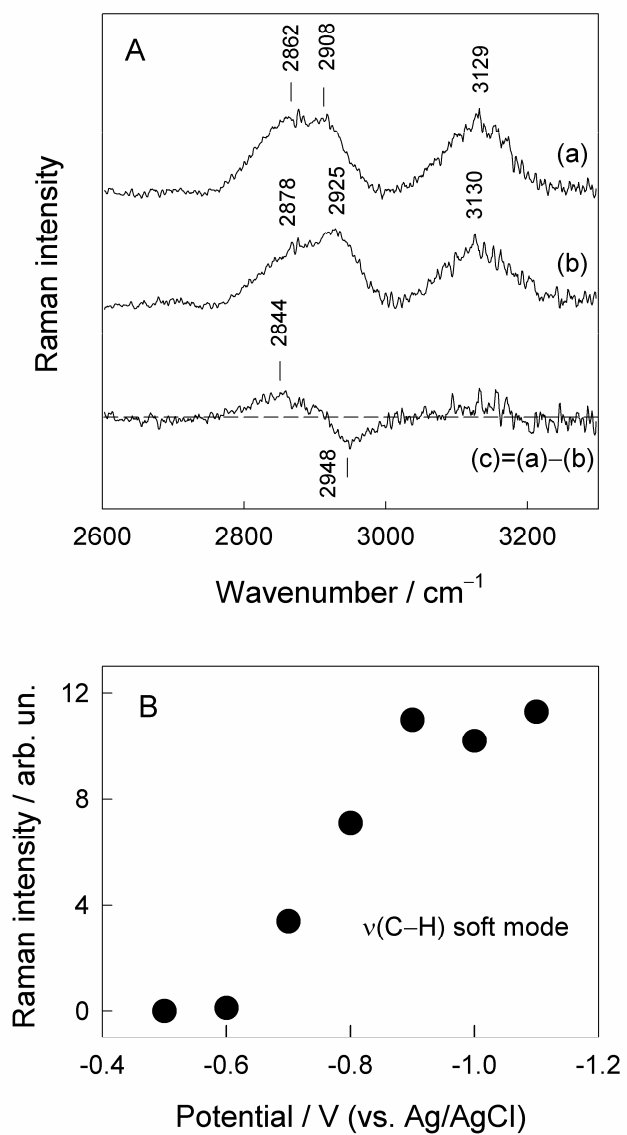


Figure 5.

**Figure 6.**

**Figure 7.**

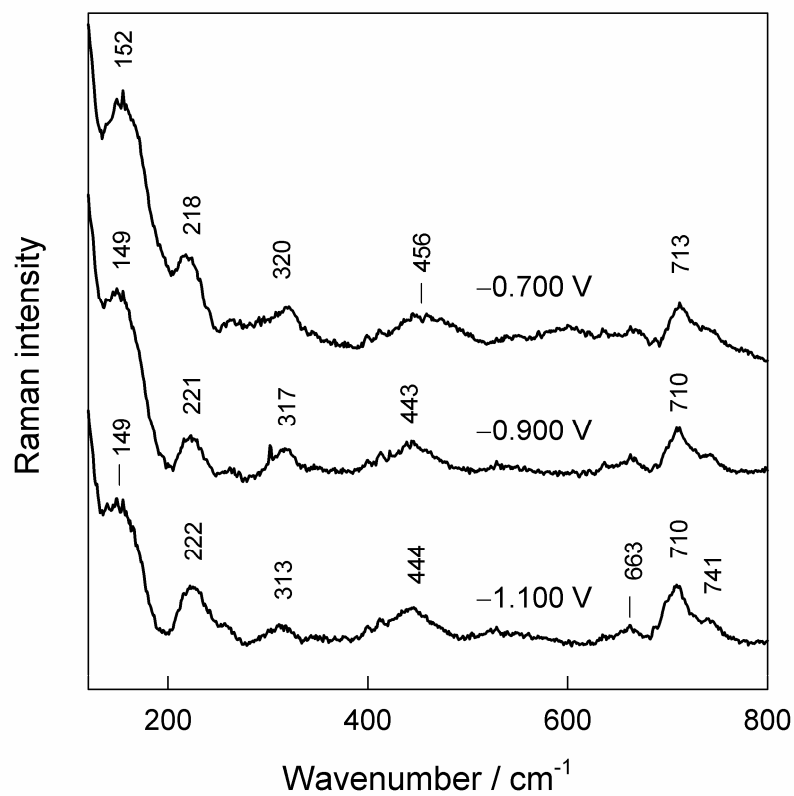


Figure 8.

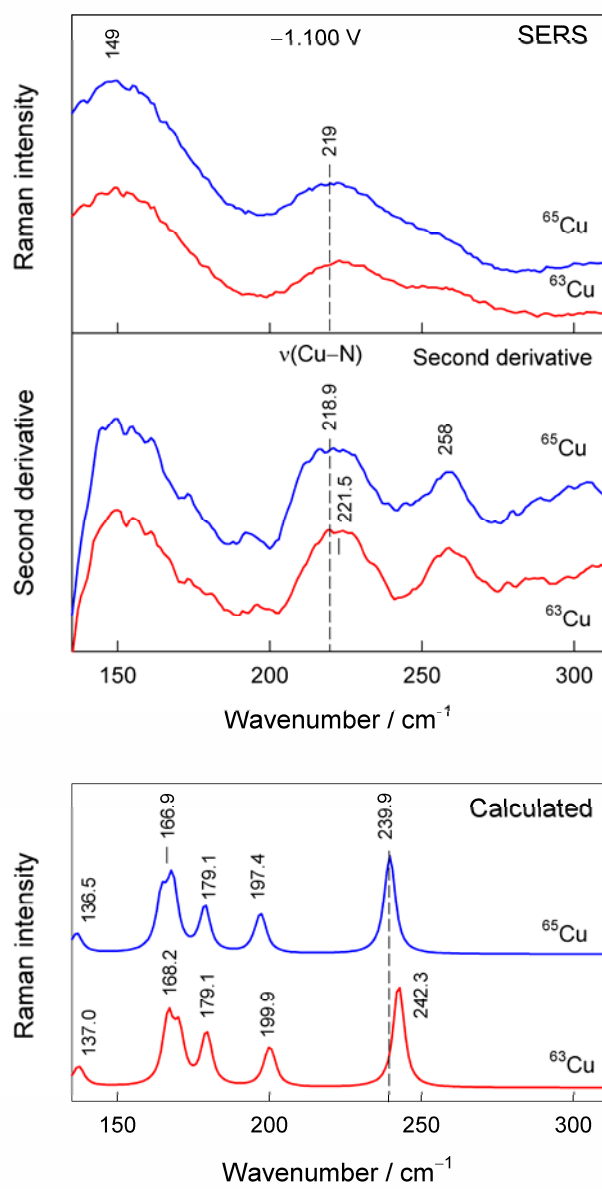


Figure 9.

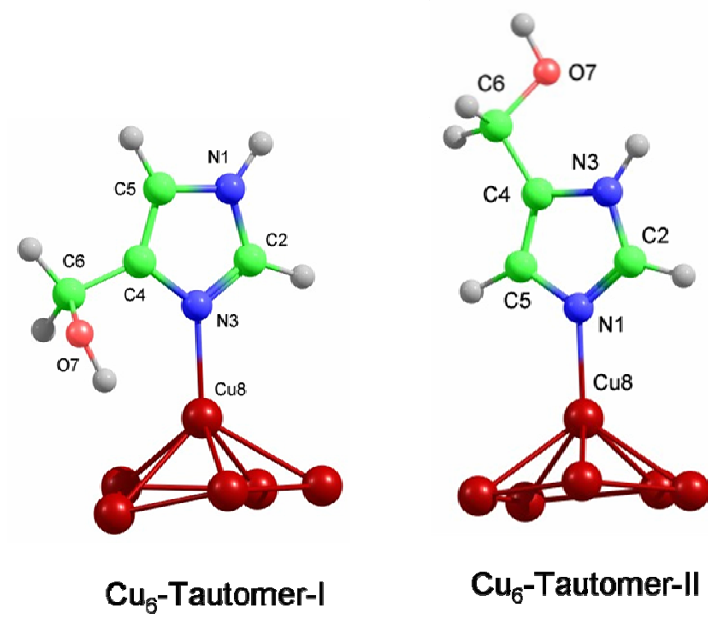


Figure 10.