

VILNIUS UNIVERSITY
INSTITUTE OF CHEMISTRY

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VIBRATIONAL SPECTROSCOPIC STUDIES ON THE STRUCTURE AND
INTERACTION WITH SOLUTION COMPONENTS OF BIFUNCTIONAL
ORGANIC COMPOUNDS ADSORBED AT METAL ELECTRODES

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VILNIAUS UNIVERSITETAS
CHEMIJOS INSTITUTAS

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BIFUNKCINIŲ ORGANINIŲ JUNGINIŲ, ADSORBUOTŲ ANT METALINIŲ
ELEKTRODŲ, STRUKTŪROS IR SAŲVEIKOS SU TIRPALO KOMPONENTAIS
TYRIMAS VIRPESIŲ SPEKTROSKOPIJOS METODAIS

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INTRODUCTION

Interaction of tryptophan and tyrosine side chains with other amino acid residues in proteins and enzymes plays an important role in controlling the folding process. The indole ring of tryptophan is able to stabilize the tertiary structure by hydrogen bonding interaction through the NH group, π - π interaction with other aromatic residues, and cation- π interaction between a positively charged metal cation (Na^+ , K^+) and delocalized π -electron cloud of the ring. The phenol ring of tyrosine among the interactions through the π -electron system is able to participate in hydrogen bonding interaction through the OH group. These complex interactions are difficult to study in real systems, therefore, construction of well-defined model systems with properties variable in controllable manner is highly needful. Self-assembled monolayers (SAMs) constructed by adsorption of thiols at metal (Au, Ag, Cu) surfaces offer possibility to create stable molecular structures suitable for application in fundamental studies of electron transfer processes, ion-pairing at interfaces, interaction between the terminal functional group of the monolayer and solution species, electrocatalytical reactions, in the fields of biotechnology, corrosion, tribology, and photoelectronic industry. In order to control such structures and design surfaces with particular properties relevant to technological processes, molecular level understanding of monolayer structure and interactions between the functional groups of adsorbed molecules and with the surface are required.

For structural studies of the surface confined functional groups the technique able to characterize monolayer at the molecular level must be applied. Among the methods suitable for structural characterization of the monolayer, surface-enhanced Raman spectroscopy (SERS) seems particularly attractive because of possibility to record *in-situ* vibrational spectrum of less than monolayer of surface-confined species in the wide frequency region ($100\text{-}3700\text{ cm}^{-1}$), in aqueous solution, and at controlled electrode potential. SERS provides molecular level information on bonding, orientation and conformation of chemisorbed molecules and ions at electrode/electrolyte interfaces. Indole and phenol rings are exclusively suitable for Raman spectroscopic analysis because of intense and characteristic spectral features sensitive to the ring structure, hydrophobicity of the environment, and hydrogen bonding interaction. On the other hand, infrared spectroscopy provides information on hydrogen bonding interaction of amide, ring NH and OH groups. Non-linear vibrational spectroscopic technique, sum frequency generation (SFG) spectroscopy provides exclusive information on order and orientation of polar molecular groups at interface. Thus, progress in understanding of monolayer structure at molecular level, orientation and interaction of functional groups in the monolayer is expected from application of several surface vibrational spectroscopic techniques. Identification of spectroscopic markers characteristic for functional indole and phenol rings which are extremely useful in the analysis of interactions between biomolecules in biochemical and biotechnological processes are expected from such studies.

The aim of this work was to get better insight into the structure and interactions of bifunctional molecules containing thiol and indole or phenol ring terminal functional groups with metal surface, neighboring molecules, and solution components.

The main objectives of the work were as follows:

1. To evaluate the structure and adsorption peculiarities of bifunctional organothiol molecules at metal electrodes at the initial stage of monolayers formation by means of vibrational spectroscopy.
2. To evaluate the state of amide bond in the bifunctional self-assembled monolayers by means of reflection-absorption infrared spectroscopy.
3. To determine the orientation and structure of amide and terminal ring functional groups in the monolayer by means of non-linear vibrational spectroscopy technique, sum-frequency generation spectroscopy.
4. To access the structural features of self-assembled monoalyers formed from bifunctional organothiol molecules on gold, silver, and copper electrodes by surface-enhanced Raman spectroscopy.
5. To evaluate the electrode potential impact on the properties of the terminal functional groups (indole and phenole rings) of the monolayer by means of surface-enhanced Raman spectroscopy.

The novelty and significance of the work

The indole and phenole rings comprise the main part of tryptophan and tyrosine side chains in proteins and play an important role in the stabilization of tertiary structure, interaction with active centers in biomolecules, and electron transfer phenomena. To get better insight into the interactions of these functional groups, the artificial monomolecular structures have been constructed from the synthesized bifunctional compounds with thiol and indole or phenole ring functional groups able to form self-assembled monolayers on gold, silver and copper electrodes. Properties of these monolayers were studied by Raman, infrared, and sum-frequency generation spectroscopies. It was demonstrated for the first time that at the initial stage of monolayer formation the methylene groups interact with the metal surface. Evidence for the metal-induced lowering of the C–H stretching mode frequency down to 2820 cm^{-1} was provided. It was demonstrated that indole ring interacts with the Ag electrode surface at sufficiently negative potentials and this interaction can be recognized from the downshift of the W16 mode from $\sim 1010\text{ cm}^{-1}$ to $\sim 1001\text{ cm}^{-1}$. Investigations of indole ring terminated and mixed with octadecanethiol monolayers have revealed new spectroscopic marker for the mutual interactions of indole rings (decrease of W16 mode frequency by $\sim 4\text{ cm}^{-1}$), which might be used for interaction studies in biomolecules by Raman spectroscopy.

The defense statements of the work:

1. At the initial stage of self-assembled monolayers formation from alkanethiol molecules the lower frequency “soft” C–H vibrational mode associated with interaction of methylene groups with the surface appears in the surface-enhanced Raman spectra at $\sim 2820\text{ cm}^{-1}$.
2. Indole ring interacts with the silver electrode surface at sufficiently negative electrode potentials and such interaction can be recognized from the shift of W16 mode frequency from $\sim 1010\text{ cm}^{-1}$ down to $\sim 1001\text{ cm}^{-1}$.
3. At the initial stage of monolayers formation the ratio of *gauche/trans* conformers of C–C–S moiety depends on the electrode potential and increases at more negative potential values, while the frequency of C–S *gauche* and *trans* modes increases as potential becomes more negative.
4. It was established the spectroscopic marker indicating on the interaction between the indole rings.
5. Accessibility of indole ring NH group by water molecules depends on the electrode potential and increases at more negative potential values. Also, strength of hydrogen bonding interaction of NH group increases as potential becomes more negative.
6. The strength of hydrogen bonding interaction of OH groups of phenol ring terminated self-assembled monolayers might be controlled by the electrode potential.
7. Molecules in investigated bifunctional monolayers are connected by strong hydrogen bonds of amide groups and amide N–H bond is oriented near parallel with respect to the electrode surface.

MATERIALS AND METHODS

Materials

8-bromooctanoic acid (97%) and tryptamine (98%) was obtained from Aldrich and was used without additional purification. Sodium phosphate monobasic and sodium phosphate dibasic were ACS reagent grade (ACROS ORGANICS). Deuterium oxide was purchased from Sigma-Aldrich Chemie GmnH and used without further purification. Deionized and subsequently double distilled water was used throughout the experiments. Some experiments were conducted by using the Millipore purified ($18.2\text{ M}\Omega\text{ cm}$) water. Studied bifunctional compounds N-[2-(1H-indol-3-yl) ethyl]-8-mercaptooctanamide (MOTRP) and N-(4-(hydroxyphenethyl)-8-mercaptooctanamide (MOTYR) (Fig. 1) were synthesized by dr. Zenonas Kuodis (Department of Organic Chemistry, Institute of Chemistry).

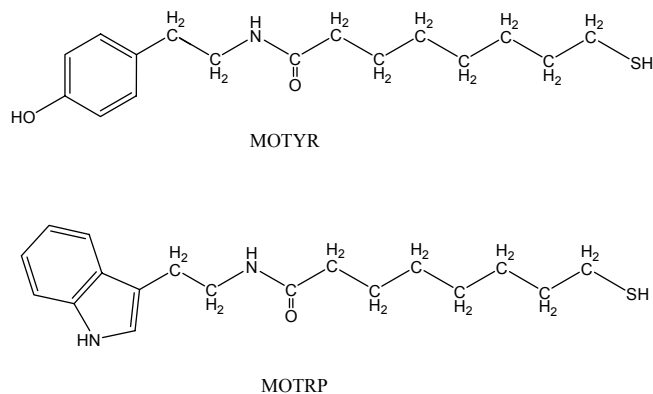


Figure 1. Structures of studied compounds: ω -mercaptooctyltyramide (MOTYR) and ω -mercaptooctyltryptamide (MOTRP).

Electrode preparations

SERS measurements were performed in a cylindrical closed three-electrode cell made from glass. A polycrystalline rod of Ag (99.99 % grade), Au (99.99 % grade) and Cu (99.99%) pressed into a Teflon sleeve served as the working electrodes. The counter electrode was a Pt wire. The potential of the working electrodes was measured vs. Ag/AgCl, 3M KCl reference electrode.

The working Au electrode was polished by polishing paper, 0.2, and 0.05 μm alumina (Struers, Denmark) slurry, then sonicated for 3 min in a 1:1 mixture of water and ethanol, washed with water, and electrochemically cleaned by keeping the electrode potential at -1.0 V for 1 min in 0.1 M NaCl solution. After these procedures, the electrode was electrochemically roughened by 50-fold scanning the electrode potential from -0.30 to 1.30 V (sweep rate 500 mV/s) with holds of 90 s at the negative potential and 2 s at the positive potential. In some experiments the roughened Au electrode was transferred to 0.1 M Na_2SO_4 solution and kept at -1.00 V potential for 3 min to remove adsorbed Cl^- ions.

The working Ag electrode was polished, sonicated for 1 min in a water, washed with water and acetone, and transferred in the separate cell containing 1M NaClO_4 solution, then electrochemically roughened by cycling three times from -0.50 to 0.60 V (sweep rate 100 mV/s), with holds of 30 s at the negative potential and 10 s at the positive potential.

The working Cu electrode was polished, washed with water and ethanol, and electrochemically roughened by deposition of Cu from diluted CuSO_4 solution (0.02 M CuSO_4 ; pH=4.5, $E=-0.50$ V vs Ag/AgCl; $t=180$ s).

After roughening, the Au and Ag electrodes were immersed into the ethanolic 1 mM MOTYR or MOTRP solutions for 16-24 hours for complete monolayers formation. Special care was taken to avoid oxidation of Cu electrode surface. Adsorption solution was prepared from ethanol:water (1:1) mixture containing 1mM H_2SO_4 and 1 mM

MOTYR or MOTRP. Prior the electrode immersion, the solution was degassed by bubbling ultrapure Ar. After formation of monolayers, the electrodes were rinsed with ethanol, kept in ethanol for 3 min, rinsed with water and dried. Finally, electrodes were transferred into the spectroelectrochemical cell containing the working solutions. Electrochemical control was accomplished by using PI-50-1 model potentiostat, arranged with PR-8 model programmer.

Raman spectroscopy measurements

Raman and surface-enhanced Raman scattering measurements were conducted with 647.1, 676.6, 785, and 1064 nm excitation wavelengths by using several Raman instruments. The main experiments were performed with dispersive Echelle type spectrometer providing near-IR (785 nm) excitation. In order to reduce photo- and thermo-effects, the cell together with the electrodes was moved linearly with respect to the laser beam with the rate of about 20 mm/s in all surface enhanced Raman spectroscopy experiments. To determine parameters of the bands, experimental spectra were fitted by mixed Gaussian-Lorentzian components by using vibrational spectra analysis software (Grams).

647.1 nm excited spectra were recorded using a 400 mm focal length, f/2.5 spectrograph equipped with 600 lines/mm grating and a thermoelectrically cooled (203 K) CCD camera (Princeton Instruments, Model: Spec-10:256E). An edge filter (Omega Optical, Inc., Model: 659AELP) was placed in front of the entrance slit of the spectrograph to eliminate Rayleigh scattering from the sample. Raman measurements were carried out in 90° geometry. The 647.1 nm beam of the Kr-ion laser (Coherent, Model: Innova 90-K) was used as the excitation source. The incidence angle of the laser beam was 60° and the laser power at the sample was typically 50-100 mW. The Raman frequencies were calibrated using the toluene spectrum. The integration time was 1 s. Each spectrum was recorded by accumulation of 100 scans.

676.4 nm excited spectra were recorded using a 500 mm focal length, f/6.4 aperture ratio spectrograph (Acton Research Co., Model: SpectraPro-2500i) equipped with 600 lines/mm grating and a thermoelectrically cooled (-60 °C) CCD camera (Princeton Instruments, Model: Spec-10:256E). The cut-off filter (Semrock Inc.) was placed in front of the entrance slit of the spectrograph to eliminate Rayleigh scattering from the sample. The 676.4 nm beam of the Kr-ion laser (Coherent, Model: Innova 90-K) was used as the excitation source. The incidence angle of the laser beam was 60° and the laser power at the sample was typically 10-30 mW. Each spectrum was recorded by accumulation of 30 scans. To increase signal-to-noise ratio 5 spectra were averaged.

785 nm excited Raman 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 Raman spectra. The 785-nm beam of the diode laser was used as an excitation source. The 180° scattering geometry was employed. The laser power at the sample was restricted to 20-30 mW and the beam was focused to a 200 μm diameter spot on the electrode. The integration time was 10 s. Each spectrum was recorded by accumulation of 10-50 scans. In some studies 5-10 spectra were co added to increase signal to noise ratio.

1064 nm excited Raman measurements were carried out in 180° geometry with the FT-Raman spectrometer (Perkin-Elmer, Model Spectrum GX) equipped with an InGaAS

detector operating at the room temperature. The excitation was provided by an air-cooled diode-pumped Nd-YAG laser with an emission wavelength of 1064 nm. The laser beam was focused to a spot of area $\sim 1 \text{ mm}^2$, and the laser power at the sample was set to 50 mW or 300 mW. The experiments were carried out in 180° geometry. The spectral resolution was set at 4 cm^{-1} and the wavenumber increment per data point was 1 cm^{-1} . All of the spectra were acquired by 300 scans.

Infrared spectroscopy measurements

Infrared spectra were recorded with Spectrum GX model FTIR spectrometer (Perkin-Elmer) equipped with DTGS (deuterated triglycine sulfate) detector. The spectral resolution was set to 4 cm^{-1} , and spectra were acquired by accumulation of 50-200 scans. Reflection-absorption infrared spectroscopy measurements were conducted by means of variable angle reflectance accessory (PIKE) at 80° incidence angle. Glass slide with evaporated Au (200 nm) served as a reference sample. Prior the measurements the reference sample was cleaned in 5:1:1 mixture of water, 25% hydrogen peroxide, and 30% ammonia for 5 min at 80°C temperature to remove organic impurities.

Sum frequency generation (SFG) spectroscopy measurements

SFG spectra were recorded by using EKSPLA (Vilnius, Lithuania) picosecond SFG spectrometer. The spectrometer is build around a mode-locked EKSPLA PL2143A/20 Nd:YAG laser generating 28 ps pulses at 1064 nm with 20 Hz repetition rate. The second harmonic radiation from this laser (532 nm) was used as a visible beam (ω_{VIS}). The tunable infrared pulses (ω_{IR}) in the 2600-3700 cm^{-1} frequency region were produced in parametric generator EKSPLA PG401VIR/DFG pumped by third harmonic (355 nm) and fundamental radiation of the laser. The bandwidth of the infrared beam was less than 6 cm^{-1} . To produce SFG spectra, the visible and infrared beams were incident at angles of 60 and 53° , respectively, and overlapped at the sample within an area of $\sim 5 \text{ mm}^2$. The sum frequency radiation (ω_{SFG}) was filtered by the holographic notch filter and monochromator and detected by a photomultiplier tube and gated registration system. The signal was averaged over 100 pulses. Sum frequency generation spectra were normalized according to the intensity of infrared beam to take into account the changes in infrared beam energy with wavelength. The frequencies were calibrated by the infrared spectrum of polystyrene film placed in the path of the infrared beam. To extract the parameters of SFG resonances, the experimental spectra have been fitted using eq 1:

$$I(\omega_{\text{SFG}}) \approx \left| \chi_{\text{NR}}^{(2)} + \sum_n \frac{A_n e^{i\psi_n}}{\omega_{\text{IR}} - \omega_n + i\gamma_n} \right|^2 I(\omega_{\text{VIS}}) I(\omega_{\text{IR}}), \quad (1)$$

where $I(\omega_{\text{SFG}})$ is the sum frequency intensity, $\chi_{\text{NR}}^{(2)}$ is the nonresonant contribution to the nonlinear susceptibility, and A_n , ψ_n , ω_n , γ_n are the strength, relative phase, resonant frequency, and line width of the n th vibration, respectively.

The sum frequency generation experiments were carried out in collaboration with dr. Zenonas Kuprionis (“EKSPLA UAB”, Vilnius).

Theoretical modeling of the vibrational spectra

All calculations were performed using Gaussian for Windows package version G03W. Geometry optimization and frequency calculations were accomplished with density functional theory (DFT) method, using B3LYP functional. Calculations were done using 6-311++G(2d, p) basis set. Presented frequencies are not scaled. Calculations were performed in collaboration with dr. Olegas Eicher-Lorka (Institute of Chemistry, Vilnius).

RESULTS AND DISCUSSION

Surface-enhanced Raman spectroscopic observation of “soft” C–H stretching mode

Fig. 2 shows the SERS spectra of bifunctional alkanethiol molecules (MOTYR) adsorbed on Au surface in C–H bond stretching vibration region. Two distinct bands at 2853 and 2907 cm^{-1} belong to methylene groups C–H symmetric stretching and asymmetric stretching vibrations, respectively. The broad 2907 cm^{-1} feature might contain contribution from Fermi resonance (FR) interaction between the CH_2 deformation and stretching modes. Presence of the aromatic head group at the interface is visible from the 3062 cm^{-1} band associated with =C–H stretching vibration. SERS spectra depend on the electrode immersion time in ethanolic 2×10^{-3} M MOTYR solution (Fig. 2A). For samples prepared with relatively short immersion times the unusual low frequency shoulder is visible near 2820 cm^{-1} . This feature disappeared completely for surfaces prepared with sufficiently long immersion time where ordered self-assembled monolayer is expected to be formed. The low frequency component is clearly visible in the difference spectra constructed by subtraction the complete monolayer spectrum (94 h immersion time) from those recorded at shorter immersion times (Fig. 2B). The width of this band (full width at half maximum, fwhm) was found to be 54 cm^{-1} ; relatively high value as compared with fwhm of 2853 cm^{-1} band (28 cm^{-1}) obtained after decomposition of the experimental spectral contour (30 s immersion time) into the mixed Gaussian-Lorentzian components.

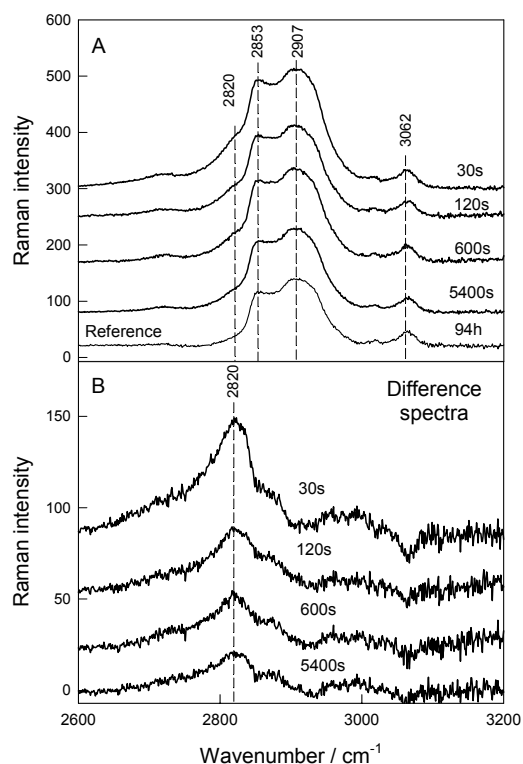


Figure 2. SERS spectra of MOTYR adsorbed at Au surface at different adsorption times (A) and difference spectra (B) obtained by subtraction of complete monolayer spectrum (reference) which was produced by immersion of Au electrode in 2×10^{-3} M MOTYR solution for 94 h. Spectra are normalized according to intensity of phenol ring band at 644 cm^{-1} . Spectra are recorded for dry Au/MOTYR sample in air. Excitation wavelength is 785 nm (20 mW), integration time is 500 s.

To get better insight into the origin of lowered frequency 2820 cm^{-1} mode we have conducted potential- and temperature-dependent SERS studies. Potential-dependent experiments revealed several tendencies, which more clearly are visible in the difference spectra (Fig. 3):

- (i) Nature of the electrode controls the potential at which intensity of the 2820 cm^{-1} mode reaches its maximal value; for Au electrode intensity of the peak decreases, while for Ag electrode, increases as potential becomes more negative.
- (ii) Frequency of the lowered frequency mode slightly depends on the electrode potential.

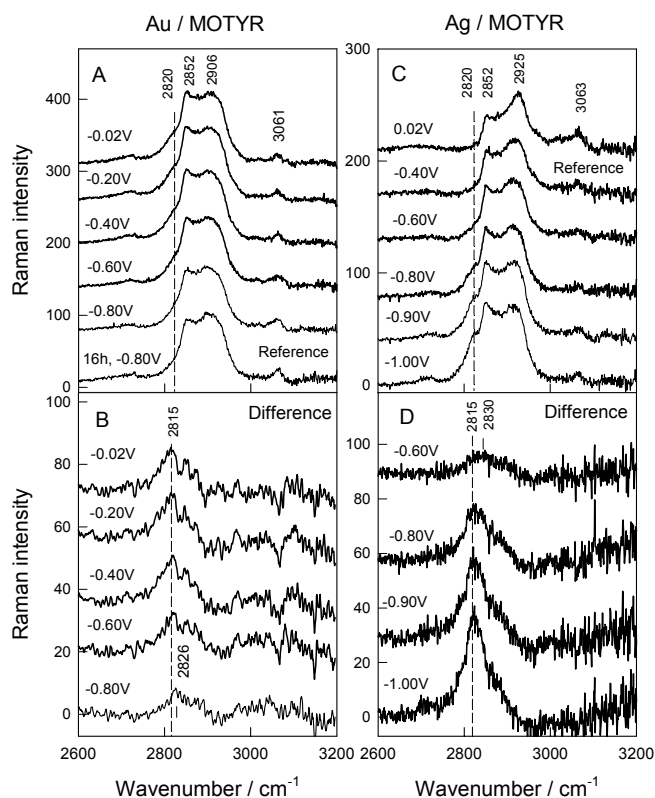


Figure 3. SERS spectra of MOTYR adsorbed at Au (A, B) and Ag (C, D) electrodes at different potentials. Difference spectra (B, D) constructed by subtraction the reference spectrum normalized to the intensity of the peak near 2905 cm^{-1} are also shown. Au and Ag electrodes were immersed in ethanolic 10^{-3} M MOTYR solution for 10 and 30 s, respectively. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 . Excitation wavelength is 785 nm (30 mW), integration time is 300 s.

Temperature-dependent SERS spectra for Au/MOTYR system in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 are displayed in Fig. 4. As can be seen lowered frequency mode is clearly visible in the spectra recorded at 10 and 40 $^{\circ}\text{C}$ temperatures, indicating that the terminal group of the studied compounds does not control the appearance of the 2820 cm^{-1} feature. Difference spectra (Fig. 4B) clearly show that intensity of the peak decreases at higher temperatures. In addition, peak position shifts slightly to lower wavenumbers at higher temperatures.

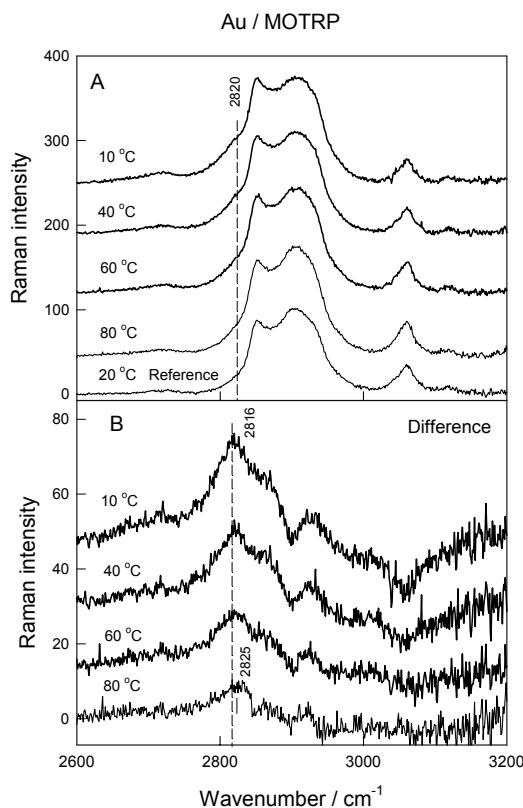


Figure 4. SERS spectra of MOTRP adsorbed at Au electrode at different temperatures (A) and difference spectra (B) constructed by subtraction the reference spectrum normalized to the intensity of the peak near 2905 cm^{-1} . Reference spectrum was recorded after several temperature cycles between 10 and $80\text{ }^{\circ}\text{C}$. Electrode was immersed in ethanolic 10^{-3} M MOTYR solution for 30 s . Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 . Excitation wavelength is 785 nm (30 mW), integration time is 500 s .

Let us now discuss the origin of the 2820 cm^{-1} band. Because studied compounds do not contain CH_3 group, this feature must belong to vibration of methylene group. Frequency of the band under investigation lies below the “normal” methylene symmetric stretching band usually observed at 2850 cm^{-1} . Thus 2820 cm^{-1} band is associated with perturbed C–H stretching mode. Several reasons may cause this perturbation. One of them is presence of *gauche* defects in the alkane chains. We have calculated vibrational modes of octanethiol (model compound of our studied alkanethiols) in all-*trans* conformation and four types of molecules with *gauche* defects in various chain places by using the density functional theory (DFT) method at the B3LYP/6-311++G(2d,p) level of theory. The lowest frequency symmetric stretching mode of CH_2 groups was found at 2992 cm^{-1} (unscaled frequency) for all-*trans* conformer. No clear detectable shift of this

band (within 2 cm^{-1}) to lower wavenumbers was found for *gauche* conformers. Thus, appearance of *gauche* conformers alone cannot explain observed experimental findings in this work.

The second frequency lowering reason might be related with interaction of methylene groups with the metal surface. The lowered C–H stretching bands (called soft modes) were found earlier (Demuth et al., 1978; Hoffman and Upton, 1984) in the reflection-absorption infrared spectroscopy (RAIRS) and high resolution electron energy loss (HREEL) spectroscopy studies of cyclic hydrocarbons adsorbed at catalytically active metals (Pt, Ru, and Ni). Considerable frequency lowering (more than 400 cm^{-1} for Ru) has been explained by dipole – image dipole interaction. Hydrogen bonding type interaction between the C–H group and metal was also used as an explanation for mode softening for cyclohexane adsorbed at Ni, Pt, and Cu (Raval and Chesters, 1989; Lamont et al., 1997). IRRAS studies of long-chain n-alkane (tetratetracontane, $n\text{-C}_{44}\text{H}_{90}$) adsorbed at Ag(111) and Au(111) surfaces revealed softened modes at 2814 and 2817 cm^{-1} , respectively (Yamamoto et al., 2000). The softening of the modes was explained by the electromagnetic interaction between the induced dipole of the C–H group and image dipole in the metal. Importance of small degree of charge transfer from the metal into the alkane molecule in softening of C–H modes has recently been pointed out (Fosser et al., 2003). It should be noted that range of soft mode frequencies ($2814\text{-}2817\text{ cm}^{-1}$) observed in the IRRAS spectra of long-chain n-alkane ($n\text{-C}_{44}\text{H}_{90}$) adsorbed at Ag and Au surfaces is rather close to peak position ($2815\text{-}2830\text{ cm}^{-1}$) of unusual bands observed in our SERS spectra of bifunctional alkanethiols anchored to Au and Ag electrodes. Experimental findings provided in this work strongly support interpretation of 2820 cm^{-1} band as soft C–H stretching mode perturbed by contact of CH_2 groups with the surface:

- 1) Intensity of the lowered frequency band depends on both the nature of the electrode and its potential; for Ag electrode intensity of the band always increases at more negative potentials;

- 2) Frequency of the band depends on the potential, indicating changes in interaction of CH_2 groups with the metal;

- 3) Band intensity decreases and frequency increases at higher temperatures for Au/MOTRP system in buffered aqueous solution; Frequency upshift indicates weakening of CH_2 groups interaction with the surface. Interestingly, similar soft modes located near 2820 cm^{-1} we observed recently in the SERS spectra of adsorbed peptides (phenylalanine-substituted bombesin fragments) at Ag electrode at sufficiently negative electrode potentials (Podstawka and Niaura, submitted).

Thus, observed softening of C–H bands is rather general phenomenon and might be important in analysis of interaction of alkanethiols, alkanes, and biomolecules with surfaces.

In conclusion, we have provided experimental evidence of the direct alkane chain contact with surface importance in lowering of the C–H stretching frequency in SERS spectra of bifunctional alkanethiols adsorbed at Au and Ag electrodes at short immersion times in monolayer formation solution. These results open the way for further SERS investigation of interaction of organic molecules possessing methylene groups with the metal surface.

Interaction of indole ring with silver electrode surface at the initial stage of monolayer formation

Interaction of indole ring with metal surface is important issue in interdisciplinary area of surface science and biochemistry, because such interactions are critical in adsorption studies of proteins and peptides. Studies of tryptophan amino acid revealed adsorption through the carboxylate and amino groups, no direct interaction of indole ring with surface was observed (Aliaga et al., 2008). However, different situation was observed in spectroscopic analysis of adsorption of MOTRP compound at the initial stage of monolayer formation on Ag electrode surface.

Potential-dependent SERS spectra of MOTRP at Ag electrode surface are displayed on

Figure 5. At 0.00 V potential the W16 band due to out-of-phase breathing vibrations of benzene and pyrrole rings is clearly visible near 1010 cm^{-1} . The second intense feature is located near 757 cm^{-1} (W18). This band belongs to in-phase breathing vibrations of benzene and pyrrole rings (indole ring breathing vibration). The broad bands at 623 and 694 cm^{-1} are associated with MOTRP compound (Fig. 1) C–S bond stretching vibration. Frequency of this mode is sensitive to *gauche/trans* isomerization around the C–C–S moiety. The higher frequency is characteristic to *trans* conformer.

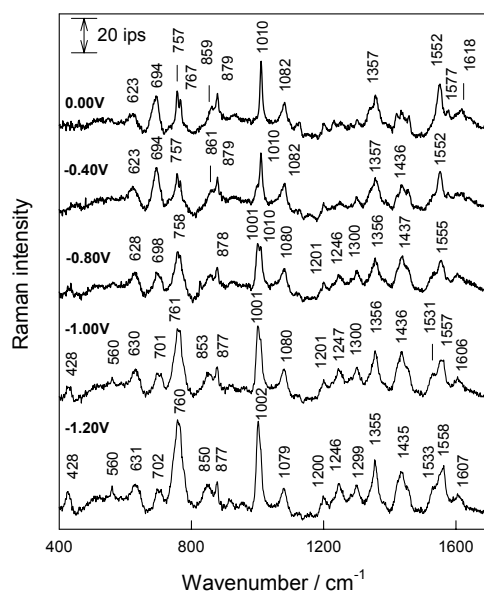


Figure 5. SERS spectra of MOTRP adsorbed at Ag electrode at different potentials in $400\text{--}1700\text{ cm}^{-1}$ spectral range. Electrode was immersed in ethanolic 10^{-3} M MOTRP solution for 10 s. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing $0.1\text{ M Na}_2\text{SO}_4$. Excitation wavelength is 785 nm (30 mW), integration time is 500 s .

As electrode potential becomes more negative, several clear changes take place in the SERS spectra: (i) W16 mode broadens and splits into the doublet, (ii) W18 mode broadens and relative intensity of this band increases, (iii) frequency of W3 mode increases from 1552 cm^{-1} at 0.00 V to 1558 cm^{-1} at 1.20 V , (iv) relative intensity of C–S bands near 623 and 694 cm^{-1} changes. Figure 6 shows more detailed analysis of potential-dependent transformation of W16 band. Experimental spectral contours were fitted by Gaussian-Lorentzian components. Such fitting enables more precise determination of parameters of the bands. At -0.60 V potential, the intensity of initial peak at 1011 cm^{-1} decreases nearly twice, while simultaneously new lower frequency band appears at 999 cm^{-1} , intensity of which increases at more negative potential value (-1.200 V), and frequency shifts to 1001 cm^{-1} . In the high frequency spectral region the lower frequency “soft” C–H mode was observed near 2823 cm^{-1} at more negative electrode potentials, indicating that some of the studied MOTRP molecules lie down on the surface and methylene groups interact with Ag. *Gauche/trans* isomerization analysis in $580\text{-}735\text{ cm}^{-1}$ region (Figure 7) also showed increase in relative population of *gauche* conformers around the C–C–S moiety, as electrode potential became more negative, providing possibility for contact interaction of MOTRP ring with the surface. Taking together all discussed experimental evidence it was concluded that the lower frequency 1001 cm^{-1} component (Fig. 6) belongs to W16 mode of indole rings directly interacting with Ag electrode surface at sufficiently negative electrode potentials.

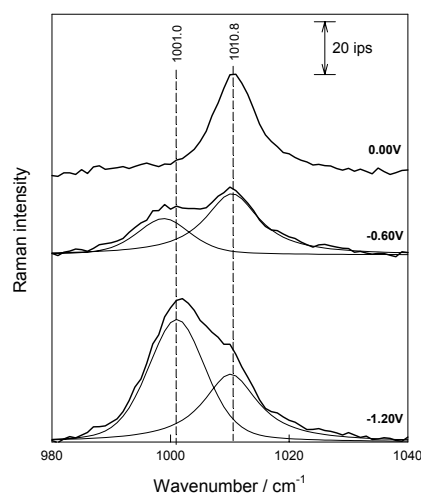


Figure 6. SERS spectra of MOTRP adsorbed at Ag electrode at different potentials in W16 mode frequency region ($980\text{-}1040\text{ cm}^{-1}$). Fitted Gaussian-Lorentzian components are also shown. Electrode was immersed in ethanolic 10^{-3} M MOTRP solution for 10s. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 . Excitation wavelength is 785 nm (30 mW), integration time is 500 s .

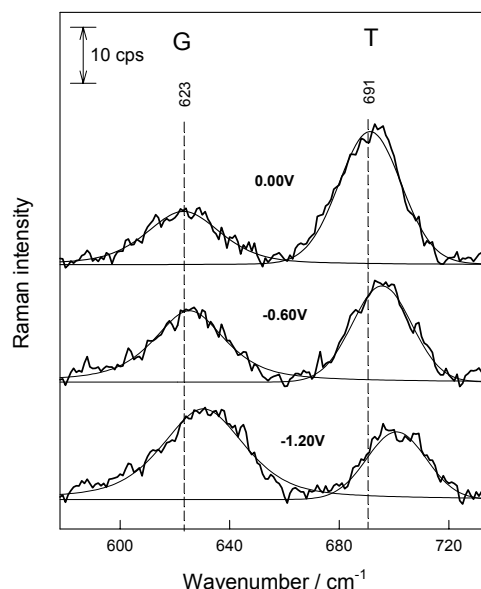


Figure 7. SERS spectra of MOTRP adsorbed at Ag electrode at different potentials in C–S bond stretching vibration frequency region ($580\text{--}735\text{ cm}^{-1}$). Fitted Gaussian-Lorentzian components are also shown. Bands associated with *gauche* and *trans* conformers labeled as **G** and **T**, respectively. Electrode was immersed in ethanolic 10^{-3} M MOTRP solution for 10 s. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 . Excitation wavelength is 785 nm (30 mW), integration time is 500 s.

Influence of the nature of the metal substrate on the structure of monolayer formed from bifunctional compound with terminal indole ring group

Nature of the metal substrate might control the structure, function, and stability of the self-assembled monolayers, because of the difference in metal atoms radiuses and interaction strength of S atom with the metal. To gain better insight into the molecular changes within the monolayer induced by different metal substrates, SERS studies of MOTRP self-assembled monolayers on Au, Ag, and Cu electrodes have been accomplished.

Figure 8 compares the SERS spectra in the low frequency region of MOTRP adsorbed at Au, Ag, and Cu electrodes and Raman spectrum of MOTRP compound in the solid state. Interestingly, the metal-sulphur stretching vibrational modes $\nu(\text{Me-S})$ are clearly visible at 276 , 227 , and 287 cm^{-1} for Au, Ag, and Cu substrates, respectively. In the calculated spectrum of MOTRP model compound and Cu_3 cluster, the corresponding $\nu(\text{Cu-S})$ mode was detected at slightly higher frequency (366 cm^{-1}). Calculations show that the lower frequency modes at 177 , 157 , and 157 cm^{-1} for Au, Ag, and Cu electrodes

are associated with vibration of metal cluster. Observation of $\nu(\text{Me-S})$ modes immediately indicates that S atom forms covalent bonds with studied metals, and because $\nu(\text{Ag-S})$ frequency is the lowest one, the Ag-S bond is more ionic as compared with Au-S and Cu-S bonds.

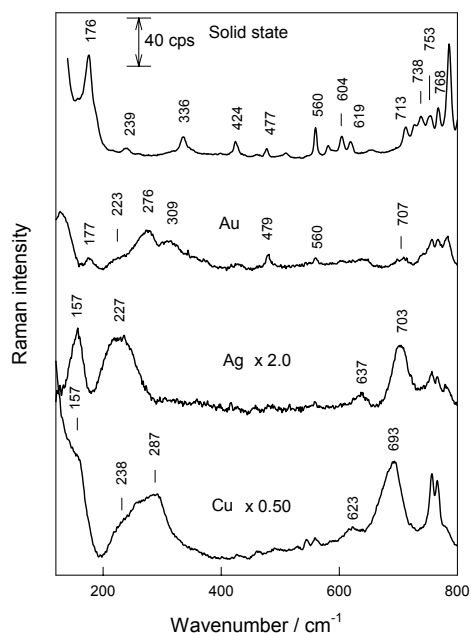


Figure 8. Raman spectrum of MOTRP in the solid state and SERS spectra of MOTRP adsorbed at Au, Ag, and Cu electrodes in the low frequency spectral range (110-800 cm^{-1}). Electrodes were immersed in ethanolic 10^{-3} M MOTRP solution more than 16 h. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 at -0.80 V potential. Excitation wavelength is 785 nm (30 mW).

The C-S stretching vibration modes of *trans* conformers were detected at 707, 703, and 693 cm^{-1} for Au, Ag, and Cu substrates, respectively (Fig. 8). Frequency of $\nu(\text{C-S})$ mode for Cu electrode was very well reproduced in the calculated spectrum (687 cm^{-1}), indicating that calculations reproduce C-S bonding and $\sim 50 \text{ cm}^{-1}$ downward shift of $\nu(\text{C-S})$ frequency and increase in C-S bond length due to formation of Cu-S bond. Experimental spectra show the lowest $\nu(\text{C-S})$ frequency for Cu electrode, suggesting the highest interaction strength of S atom with copper as compared with Au and Ag metals.

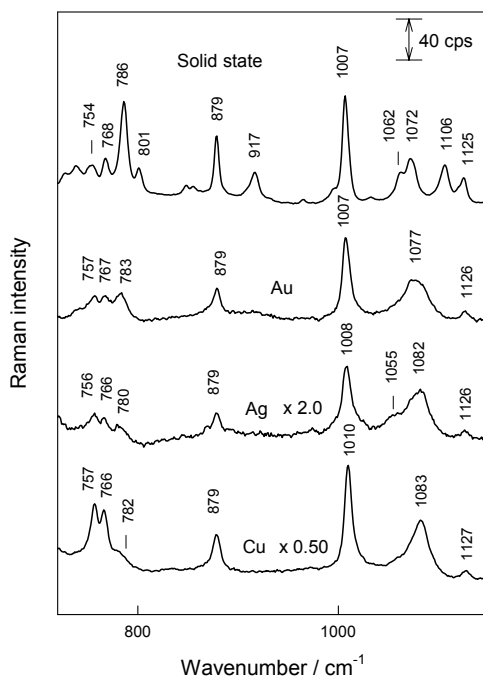


Figure 9. Raman spectrum of MOTRP in the solid state and SERS spectra of MOTRP adsorbed at Au, Ag, and Cu electrodes in the spectral range 700-1200 cm^{-1} . Electrodes were immersed in ethanolic 10^{-3} M MOTRP solution more than 16 h. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 at -0.800 V potential. Excitation wavelength is 785 nm (30 mW).

Figure 9 compares the SERS spectra from different electrodes in the spectral region where intense W18, W17, and W16 indole ring modes are expected to be observed. The most interesting changes are associated with W16 mode near 1010 cm^{-1} . In the case of Au electrode frequency of this mode is close to the corresponding band of MOTRP in the solid state, and increases in the order $\text{Au} > \text{Ag} > \text{Cu}$. To gain better insight if this frequency shift is associated with difference in the interaction between indole rings in the monolayers, the SERS experiments with mixed monolayers have been conducted.

Figure 10 shows SERS spectra of mixed ODT (octadecanethiol): MOTRP monolayer and ODT monolayer self-assembled on Au surface. The most intense bands (1296 and 1130 cm^{-1}) in the spectra correspond to C-C stretching vibration of alkane chains in all-*trans* conformation, indicating that the mixed monolayer is well ordered with low number of *gauche* defects. To observe bands of indole rings in the mixed monolayer, the difference spectrum was constructed. The W16 band is clearly visible in the difference spectrum at 1011 cm^{-1} . Because interaction between the neighboring indole rings is reduced in the mixed monolayer, the 1011 cm^{-1} frequency value must represent frequency of W16 mode of isolated indole rings.

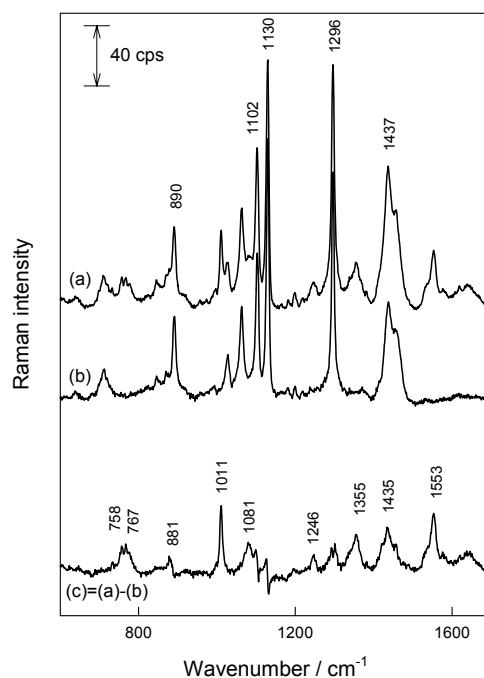


Figure 10. SERS spectra: (a) mixed self-assembled monolayer ODT:MOTRP at Au electrode formed from ethanolic solution containing ODT and MOTRP at 0.25 and 0.75 μM concentrations, respectively; (b) ODT self-assembled monolayer at Au electrode formed from ethanolic solution containing 1 mM ODT; (c) difference spectrum obtained by normalization of (a) and (b) spectra according to the intensity of C–C stretching band at 1130 cm^{-1} . Electrodes were immersed in adsorption solutions more than 16 h. Spectra were recorded in aqueous 0.01 M phosphate buffer solution containing 0.1 M Na_2SO_4 at 0.20 V potential. Excitation wavelength is 785 nm (30 mW), integration time is 500 s.

Presented analysis of experimental data in this section proves that interaction between indole rings in the monolayer depends on the nature of metal substrate and decreases in the order $\text{Au} > \text{Ag} > \text{Cu}$. Interaction between the indole rings can be recognized from the downward shift of the W16 mode frequency. This spectral marker can be used in analysis of biomolecules by Raman spectroscopy.

In-situ surface-enhanced Raman spectroscopic investigation of NH site of indole ring-terminated self-assembled monolayer on gold electrode

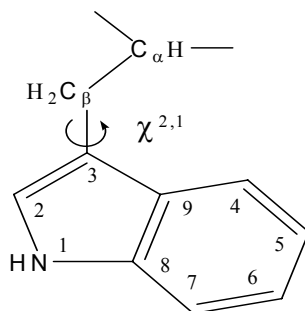


Figure 11. Structure and atom numbering scheme for tryptophan derivatives.

Indole ring contains hydrophilic center, NH group (Figure 11), able to participate in hydrogen bonding interaction. For indole ring-terminated SAM the accessibility of NH group to water molecules might be restricted because of compact arrangement of bulky aromatic groups. Figure 12 shows SERS spectra of SAM of MOTRP compound on gold electrode in aqueous solutions prepared with H_2O or D_2O solvent. The dominant bands in the spectra are associated with vibrations of the indole ring. It should be noted that MOTRP monolayer spectrum on Au electrode differs slightly as compared with Ag at the same electrode potential. Interestingly, the W3 peak position for monolayer on Au surface shifts slightly to lower wavenumbers ($2-3\text{ cm}^{-1}$) as compared with Ag electrode (676.4 nm excitation), indicating subtle changes in the torsion angle about the $C_\beta-C_3$ bond. Two bands located at 1078 and near 1445 cm^{-1} were attributed to C-C stretching and CH_2 scissoring bending vibrations of alkyl chain, respectively.

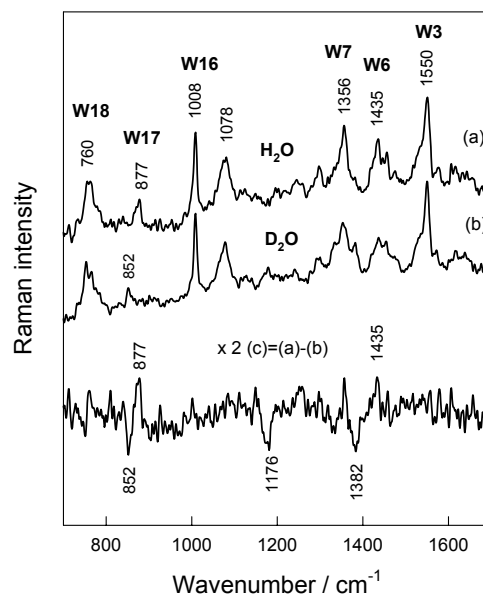


Figure 12. SERS spectra of indole-ring terminated SAM on gold electrode at 0.30 V (vs Ag/AgCl, 3 M KCl) observed in 0.1 Na₂SO₄ solution containing 0.01 M sodium phosphate buffer (pH 7.0) prepared with H₂O (a) or D₂O (b) solvent. Difference spectrum (c) is also shown. Excitation wavelength is 1064 nm. Spectra were obtained after excursion to -0.70 V for 20 min.

Several changes in band positions due to solvent H₂O exchange to D₂O are clearly visible in the difference spectrum (Figure 12c). The derivative-like feature in the vicinity of W17 mode shows decrease in peak frequency from 877 cm⁻¹ in H₂O solution to 852 cm⁻¹ in D₂O. This is because W17 mode involves deformation vibration of N1H group, and therefore is one of the hydrogen bonding interaction marker of indole ring. The second feature clearly sensitive to H/D exchange at nitrogen atom of indole ring is the peak located at 1435 cm⁻¹ (W6), which shifts in D₂O solution to 1382 cm⁻¹. It should be noted that isotopic changes for W6 mode is not obvious in original spectra of the monolayers, because of overlap with vibrations of alkyl chains of MOTRP compound. However, isotopic shift is clearly visible in the difference spectrum, which selectively probes spectral changes associated only with H/D exchange at nitrogen atom of indole ring. The W6 mode involves stretching vibration of pyrrole ring N1-C2=C3 moiety and N1H deformation motion coupled with CH deformation of benzene ring. It should be noted that origin of the negative feature in the difference spectrum at 1170 cm⁻¹ remains unclear.

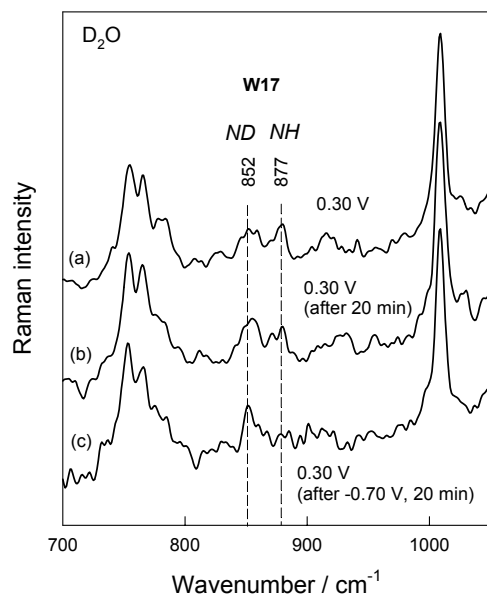


Figure 13. SERS monitoring of H/D exchange process at N1H site of indole ring-terminated SAM on Au electrode. Spectra were obtained (a) immediately after immersion of electrode in 0.1 M Na₂SO₄ solution containing 0.01 M sodium phosphate buffer (pH 7.0) prepared with D₂O solvent at 0.30 V, (b) after 20 min at 0.30 V, and (c) after excursion of electrode potential to -0.70 V for 20 min and return back to 0.30 V. Excitation wavelength is 1064 nm.

Figure 13 demonstrates the influence of electrode potential on the H/D exchange process at ring nitrogen atom site. We have monitored spectral changes in the parameters of hydrogen bonding marker mode W17, which shifts from 876 cm⁻¹ to 852 cm⁻¹ upon transformation of N1H to N1D. After immersion of Au electrode modified by SAM into D₂O-based electrolyte at 0.30 V (Figure 13a) only part of N1H sites transforms to N1D as evident by near equal intensities of 852 and 877 cm⁻¹ components of W17 mode. Little decrease in intensity of 877 cm⁻¹ component was detected after 20 min at 0.30 V (Figure 13b), indicating that the majority of the labile hydrogens of N1H site have already exchanged by deuterons. The remaining indole rings seems to be buried at the interface, and D₂O molecules hardly approach the N1H sites at 0.30 V. It was found that H/D exchange rate considerably depends on the electrode potential. The spectrum (c) of Figure 13 clearly shows complete disappearance of the W17 mode component due to N1H groups at 877 cm⁻¹ after holding the electrode potential at -0.70 V for 20 min.

The indole ring forms hydrogen bond at the N1H moiety as a proton donor. Thus vibrational modes coupled with N1H vibrations may serve as hydrogen bonding marker bands. Figure 14 shows dependence of the W17 mode frequency on the electrode potential. Given the sensitivity of the W17 mode frequency to hydrogen bonding (lower

frequency reflects stronger bonding); presented data suggest an increase in hydrogen bonding interaction strength at N1H indole site at sufficiently negative electrode potentials.

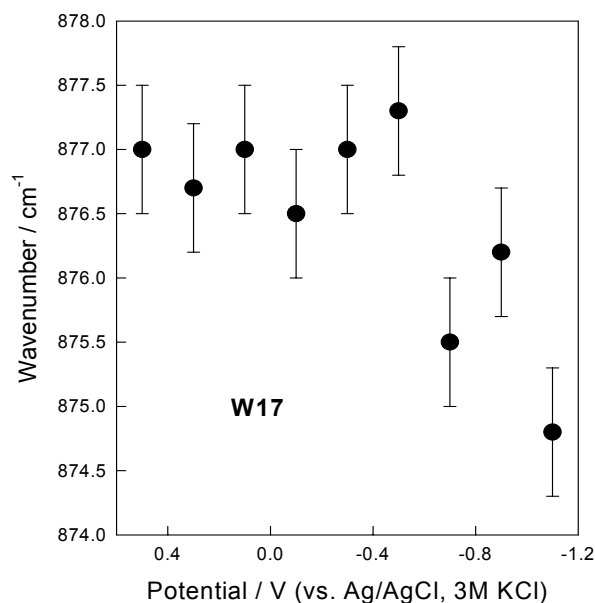


Figure 14. Potential dependence of W17 peak position in SERS spectra of indole-ring terminated SAM on Au in 0.1 M Na₂SO₄ solution containing 0.01 M sodium phosphate buffer (pH 7.0). Excitation wavelength is 1064 nm.

Sum frequency generation spectroscopy studies of order and orientation of functional groups in the monolayer

Sum frequency generation (SFG) spectroscopy offers possibility to record vibrational spectrum of various molecules at interfaces without the spectral interference from the compounds in the bulk, and determine the order and orientation of functional groups with respect to the surface. Surface sensitivity of the technique arises from the fact that within the electric dipole approximation the nonlinear generation of the sum frequency signal from the overlapped visible and infrared beams is forbidden in the media of randomly oriented molecules or in the centrosymmetric media but is allowed at

the interface where inversion symmetry is broken. Molecular specificity emerges from the ability to record vibrational spectrum.

SFG spectrum of MOTYR monolayer on Au substrate and infrared spectrum of studied compound in the solid state are compared in Figure 15. Because of the interference between the nonresonant background from the Au surface and resonant signal from the adsorbate (equation 1), the resulting resonances are pointed downward. Intense resonances due to methylene groups C–H stretching symmetric and asymmetric vibrations are clearly visible in the ppp-polarized spectrum at 2860 and 2921 cm^{-1} , respectively. The corresponding bands in the infrared spectrum are located at 2854 and 2927 cm^{-1} . Observation of these resonances in SFG spectrum indicates presence of *gauche* defects in the MOTYR monolayer as in all-*trans* configuration of alkyl chains with even number of CH_2 groups the signal should not be detected due to the centrosymmetrical local arrangement. For alkyl chains with odd number of CH_2 groups (as in our case) the CH_2 resonances in all-*trans* configuration might be observed, but should be of very low intensity. Resonances at 3066 and 3118 cm^{-1} belong to aromatic ring $\nu(\text{C}=\text{H})$ vibrations. Corresponding bands in the infrared spectrum is very weak. Observation of $\nu(\text{C}=\text{H})$ resonances in SFG spectrum indicates that phenol rings in the monolayer are ordered. Finally, the high frequency resonance at 3288 cm^{-1} belongs to N–H stretching vibration of amide groups. In the infrared spectrum this band is seen at slightly higher frequency 3306 cm^{-1} . Analysis of N–H stretching band results in two conclusions:

1. Lowered frequency in SFG spectrum as compared with solid sample infrared spectrum indicates strong hydrogen bonding interaction of amide groups in the MOTYR monolayer;

2. N–H dipoles are ordered in the monolayer.

Comparison of SFG spectra obtained with different polarization combinations allows drawing conclusions regarding the orientation of particular groups with respect to the surface. According to SFG selection rules, ppp-polarized beams probe surface vibrational modes with a projection dipole moment both perpendicular and parallel with respect to the surface, while ssp-polarized beams probe only vibrational modes with a projection dipole moment perpendicular to the surface. Comparison of experimental SFG spectra observed with ppp- and ssp-polarization combinations shows that N–H groups are oriented near parallel with respect to the surface, because N–H resonance is not visible in the ssp-polarized spectrum.

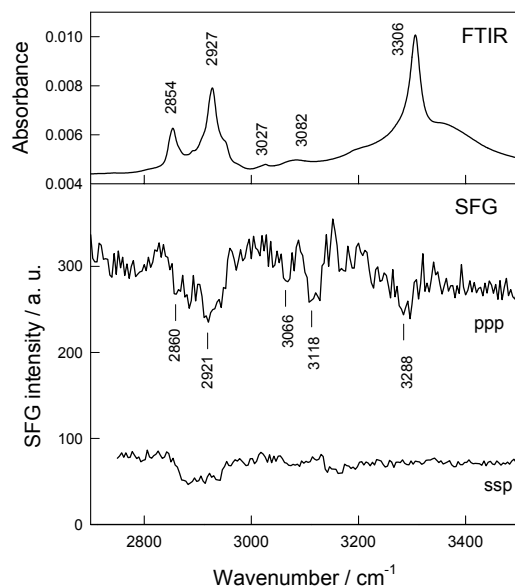


Figure 15. Infrared spectrum of MOTYR compound in the solid state and SFG spectra of MOTYR self-assembled monolayer on Au electrode at ppp (p-SFG, p-532 nm, p-IR) and ssp polarization combinations.

CONCLUSIONS

1. It was demonstrated for the first time by using surface-enhanced Raman spectroscopy that at the initial stage of the monolayer formation (at 10-30s immersion times) on Au and Ag electrodes the new lower frequency C–H vibrational mode appears in the vicinity of 2820 cm^{-1} due to the interaction of methylene groups with the metal surface. Appearance of such band indicates that at the initial stage of the monolayer formation alkyl chains contact with the metal.
2. Based on spectroscopic measurements of bifunctional alkanethiols at the initial stage of the monolayer formation (at 10 s immersion time) it was found that the indole ring interacts with the Ag electrode surface at sufficiently negative electrode potentials. This interaction might be recognized from the shift of the W16 mode frequency from 1010 cm^{-1} downward to $\sim 1001\text{ cm}^{-1}$. In addition, interaction results in increased W18 band (near 757 cm^{-1}) relative intensity and W3 mode frequency.
3. Potential-dependent spectroscopic studies of bifunctional alkanethiols with indole ring terminal group at initial monolayer formation stage (at 10s immersion

time) revealed increase in population of C–C–S fragment *gauche* conformers and increase of both *gauche* and *trans* C–S modes frequency at more negative electrode potentials. For *trans* conformer linear frequency dependence on potential was observed.

4. Surface-enhanced Raman spectroscopic study of indole ring terminated and mixed monolayers with octadecanethiol revealed interaction between the indole rings in the monolayer, which depends on the nature of the electrode and decreases in the order Au > Ag > Cu. In the same order increases the W16 mode frequency. For mixed monolayer the W16 mode frequency of non-interacting indole rings was found at 4 cm⁻¹ higher value (1011 cm⁻¹) as compared with Au electrode. Determined spectral marker for interaction of indole rings might be used in analysis of biomolecules by Raman spectroscopy.
5. Spectroscopic studies of H/D exchange and hydrogen bonding interaction at N1H site of indole ring terminated self-assembled monolayers revealed potential dependent accessibility of N1H site, access of water molecules increases at more negative potentials. It was demonstrated that frequency of W17 band decreases and hydrogen bonding interaction strength at N1H site increases as potential becomes more negative.
6. Surface-enhanced Raman spectroscopic studies of bifunctional monolayers with phenol ring terminal group have shown that hydrogen bonding strength of OH group can be controlled by the electrode potential.
7. Based on sum-frequency generation and reflectance-absorption infrared spectroscopies data it was found that bifunctional molecules are bound by strong hydrogen bonds of amide groups in the monolayer and the N–H bonds are oriented near parallel with respect to the metal surface.

LIST OF PUBLICATIONS

Articles on the subject of dissertation

1. Inga Razmutė, Zenonas Kuodis, Olegas Eicher-Lorka, Gediminas Niaura. Surface-enhanced Raman spectroscopy of indole ring-terminated self-assembled monolayer on silver electrode. *Chemija*, **17**, 2006, Nr.1, 25-30.
2. Inga Razmutė-Razmė, Zenonas Kuodis, Olegas Eicher-Lorka, Gediminas Niaura. In-situ surface-enhanced Raman spectroscopic investigation of NH site of indole ring-terminated self-assembled monolayers on gold electrode. *Chemija*, **18**, 2007, No.4, 16-20.

Conference materials on the subject of dissertation

1. I. Razmutė, Z. Kuodis, O. Eicher-Lorka, G. Niaura, "Surface-enhanced Raman spectroscopy of indole ring-terminated self-assembled monolayer on silver and gold

- electrode“, “Chemistry and chemical technology dedicated to 100th anniversary of born professor J. Janickis”, Kaunas 2006, Abstracts, p. 30.
2. I. Razmutė-Razmė, Z. Kuodis, O. Eicher-Lorka ir G. Niaura, “Temperature dependence of the structure of indole ring-terminated self-assembled monolayer on gold electrode“, “Chemistry 2007” 8th National Lithuanian Conference dedicated to 210th anniversary of Chemistry department at Vilnius University, Vilnius 2007, Abstracts, p. 35.
 3. I. Razmutė-Razmė, Z. Kuodis, O. Eicher-Lorka ir G. Niaura, „Indole ring-terminated self-assembled monolayers at gold electrode as studied by SERS“, “The 9-th International Conference-School. “Advanced Materials and Technologies“, Palanga 2007, Abstracts, p. 63.

Submitted articles on the subject of dissertation

1. Inga Razmutė-Razmė, Zenonas Kuodis, Olegas Eicher-Lorka, Gediminas Niaura. SERS observation of soft C-H vibrational mode of bifunctional alkanethiol molecules adsorbed at Au and Ag electrodes. *Physical Chemistry Chemical Physics*, 2009 (under review).
2. Inga Razmutė-Razmė, Zenonas Kuodis, Olegas Eicher-Lorka, Gediminas Niaura. Surface enhanced Raman spectroscopic observation of indole ring interaction with silver electrode surface. *Journal of Raman Spectroscopy*, 2009 (under review).

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BIFUNKCINIŲ ORGANINIŲ JUNGINIŲ, ADSORBUOTŲ ANT METALINIŲ ELEKTRODŲ, STRUKTŪROS IR SĄVEIKOS SU TIRPALO KOMPONENTAIS TYRIMAS VIRPESIŲ SPEKTROSKOPIJOS METODAIS

ANOTACIJA

Triptofano ir tirozino aminorūgščių funkcinės grupės – indolo ir fenolio žiedai, stabilizuoja baltymų tretinę struktūrą, sąveikauja su aktyviais centrais biomolekulėse, dalyvauja elektronų pernašos procesuose. Siekiant giliau suprasti kaip šios grupės sąveikauja, buvo sukonstruotos dirbtinės monosluoksninės struktūros, sudarytos iš susintetintų bifunkcinių junginių, turinčių galines tiolio ir indolo žiedo arba fenolio žiedo grupes ir gebančių formuoti savitvarkius monosluoksnius ant aukso, sidabro ir vario elektrodų. Jų savybės iširtos Ramano, infraraudonosios ir suminio dažnio generacijos spektroskopijų metodais.

Pagrindiniai darbo tikslai buvo nustatyti bifunkcinių alkantiolių struktūrą ir adsorbcijos ypatumus pradinėje monosluoksnio formavimosi stadijoje, elektrodo prigimties įtaką monosluoksnių struktūrai ir potencialo įtaką galinių funkcinų grupių savybėms.

Paviršiaus sustiprintos Ramano spektroskopijos metodu pirmą kartą parodyta, kad pradinėse monosluoksnių formavimo stadijose metileno grupės sąveikauja su metalo paviršiumi. Darbe įrodyta, kad dėl sąveikos su metalu spektruose atsiranda žemesnio dažnio („minkšta“) C–H juosta ties 2820 cm^{-1} . Pirmą kartą parodyta, kad indolo žiedas sąveikauja su Ag paviršiumi, esant pakankamai neigiamiems potencialams ir tą sąveiką galima spektriškai atpažinti pagal W16 modos ties $\sim 1010\text{ cm}^{-1}$ dažnio sumažėjimu iki $\sim 1001\text{ cm}^{-1}$. Tiriant indolo žiedu terminuotus ir mišrius monosluoksnius su įterptomis oktadekantolio molekulėmis nustatytas naujas indolo žiedų tarpusavio sąveikos spektrinis žymeklis – W16 juostos dažnio sumažėjimas $\sim 4\text{ cm}^{-1}$, kuris gali būti plačiai naudojamas, tiriant sąveikas biomolekulėse Ramano spektroskopijos metodu.

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