Surface-enhanced Raman spectroscopy of ethanethiol adsorbed at copper electrode

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Adsorption of ethanethiol at copper electrodes has been studied by surface-enhanced Raman spectroscopy (SERS). Interpretation of the spectra was based on the quantum chemical calculations. It was shown that the frequency of the stretching vibration of C–S bond decreased by 34 cm^{-1} in the adsorbed state as compared to ethanethiol in the liquid state, indicating the involvement of the sulphur atom in a direct covalent interaction with the Cu surface. The potential-induced frequency dependence of the symmetric stretching vibration of the methyl group was observed in the SER spectrum. It is suggested that a surface Stark effect is responsible for the observed frequency decrease at more negative potentials.

Key words: SERS, Raman, copper electrode, ethanethiol

INTRODUCTION

The surface properties of metals can be considerably modified by the spontaneous formation of densely packed films – self-assembled monolayers (SAMs) [1–5]. As the properties of the films can easily be altered by variation of the functional end-group and chain length, these structures have remarkable potential applications in the fields of biotechnology, corrosion, tribology, and photoelectronic industry [5].

While extensive studies were carried out on a SAM supported on Au [2, 5] and Ag [4] metals, less attention has been paid to Cu electrodes. The spontaneous self-assembly process is governed by two main forces [5]: (*i*) a strong bonding affinity of the sulphur atom to copper, and (*ii*) lateral interactions between the chains. The aim of our investigation was to probe preferentially the first part of this complex interaction.

We have chosen ethanethiol (SH-CH$_2$-CH$_3$, EtSH) as one of the simplest adsorbates containing a sulphur atom, which can serve as the useful model compound for the understanding of bonding with the copper surface.

EXPERIMENTAL

Aqueous solutions were made from Milli-Q (Millipore) water. Ethanethiol was purified by distillation.

Raman excitation was provided by a He–Ne laser at 632.8 nm. The laser power at the sample was approximately 15 mW. The laser beam was incident on the surface at an angle of approximately 60° with respect to the surface normal and was focused to a line with an area of about 1 mm^2. In order to reduce any photo/or thermo effects, the spectroelectrochemical cell, together with the working electrode, was moving with respect to the laser beam (~20 mm/s) [6]. The experiments were carried out in 90° geometry. The plasma lines were attenuated by means of an interference filter. The Raman scattered light was analysed with an f/5.3 double monochromator with 1200 lines/mm gratings and detected by a photomultiplier (water cooled to 10 °C) and a photon counting system. Elastic scattering was eliminated with a holographic laser line filter (Kaiser Optical Systems, Inc.). The spectral slit width was 6 cm^{-1} in the spectral region of 800 cm^{-1}. The overlapping bands were deconvoluted into a sum of Gaussian and Lorentzian shapes.

Electrochemical and SERS measurements were performed in a cylindrical closed three-electrode cell made from glass. The counter electrode was a Pt wire. Its compartment was separated from the working electrode compartment by glass frits. The potential of the working electrode was measured *versus* an Ag/AgCl, 3M KCl reference electrode supplied *via* a Luggin capillary, which was placed within ~1 mm of the working electrode surface. In order to minimize the influence of Cl$^-$ ions, the reference electrode was placed in a separate cell and connected to the main cell by a salt bridge filled with

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concentrated Na_2SO_4 solution. All potentials are given *versus* an Ag/AgCl, 3M electrode. Prior to use, the solutions were deoxygenated by bubbling Ar for about 40 min. A polycrystalline Pt disk (0.1 cm² geometrical area) inserted in a Teflon sheet was used as a working electrode. The preparation and activation of the Cu electrode was performed in three steps [7]. First, an approximately 20 μm Cu layer was electrodeposited on Pt from an acid copper plating bath (0.5 M H_2SO_4 + 0.5 M $CuSO_4$) at 20 °C. Secondly, an additional layer of Cu was electrodeposited from 0.02 M $CuSO_4$ solution (pH 4.5) at a constant potential, E = –0.50 V at 20 °C. The electrodeposition time was 120 s. Finally, the working electrode was kept in dearated 0.5 M H_2SO_4 + + 0.5 M Na_2SO_4 solution for 90 min at the open circuit potential at 20 °C. After such procedures, the electrode was rinsed with deoxygenated water and transferred to the spectroelectrochemical cell containing working solutions. The adsorption of EtSH was performed in a separate cell by immersing the SER-active electrode in ethanolic solution containing 10 mM EtSH for 10 min at ambient temperature.

Ab initio (*AI*) calculations were performed with the GAUSSIAN 98W program [8]. All the calculations were carried out using a hybrid density functional theory (DFT: the B3LYP/6-311++G** level). An excellent review on the DFT method is available [9]. A complication is that the EtSH molecules occur in two conformations where the torsional CCSH angle (τ) can have two values: $\tau \sim 60°$ (*gauche*) and where $\tau \sim 180°$ (*trans*). Work carried out [10] has established that *gauche* is the global minimum energy structure. From the internal coordinates of the structures, normal coordinates [11, 12] have been derived and will be used to analyse the potential energy distributions [13] (PEDs, Table) of the normal coordinates in the calculated Raman spectra (for the molecules in the gas phase at 298 K and 1 atm using the most abundant atomic isotopes). To confirm the PED analysis, the Raman spectrum of deuterated *gauche* EtSH (EtSD) was calculated and analysed (using identical normal coordinates). The peak positions of the calculated spectra (Table) show an excellent peak position agreement with the experimental Raman spectrum.

RESULTS AND DISCUSSION

Figure 1 compares the Raman spectra obtained from EtSH in different states and SER spectrum observed from Cu electrode at –0.400 V in the frequency range from 150 cm⁻¹ to 1750 cm⁻¹. The Raman spectra in the high frequency range from 2700 cm⁻¹ to 3050 cm⁻¹ are presented in Fig. 2. Assignments of the bands based on the previous investigations [14–17] and our own preliminary *ab initio* calculations of the EtSH molecule in the gas phase are provided in Table.

Table. Experimental and calculated Raman frequencies (cm⁻¹) and potential energy distribution (%) of the vibrational modes of ethanethiol

Experimental			Calculated[a]		Assignments[b]
Liquid EtSH	Ethanethiolate[c]	SERS[d]	EtSH	EtSD	
2962 m dp	–	2951 w	3114	3114	$\nu_{as}(CH_2)$ 78 + $\nu_s(CH_3)$ 12
			3092	3092	$\nu_{as}(CH_2)$ 78
			3081	3081	$\nu_{as}(CH_3)$ 83 + $\nu_{as}(CH_2)$ 11
2928 vs p	2927 m	2914 m	3022	3022	$\nu_s(CH_3)$
2872 m p	2865 m	2859 m	3056	3056	$\nu_s(CH_2)$
2569 vs p	–	–	2661	1911	$\nu(SH)/\nu(SD)$
1447 w dp	1446 w	1444 w	1480	1480	$\delta(CH_2)$
1271 w p	1259 w	1234 w	1282	1288	$\rho_r(CH_2)$ 41 + $\delta_{as}(CH_3)$ 37
1090 w p	–	–	1123	1090	$\delta_{as}(CH_3)$ 49 + $\rho_t(CH_2)$ 29
1050 w p	1050 w	1041 w	1066	1063	$\delta_{as}(CH_3)$ 60 + $\rho_w(CH_2)$ 13
974 w dp	–	977 m	982	981	$\delta_{as}(CH_3)$ 59 + $\nu(CC)$ 20 + $\rho_w(CH_2)$ 11
870 w p	–	–	875	793	$\delta_{as}(CH_3)$ 45 + $\delta(CSH)$ 27 + $\rho_r (CH_2)$ 10
736 w p	–	–	741	660	$\rho_t(CH_2)$ 72 + $\rho_{as}(CH_3)$ 19
659 vs p	656 vs	625 vs	645	612	$\nu(CS)$ 44 + $\rho_t(CH_2)$ 17 $\delta_{as}(CH_3)$ 10
333 m p	341 w	–	327	322	$\delta(CCS)$ 63 + $\delta_{as}(CH_3)$ 26
–	–	274 w	–	–	$\nu(Cu–S)$?

[a] Calculated frequencies for *gauche* rotomer; [b] Potential energy distribution for *gauche* EtSH, %, only contributions higher than 10%; [c] From solution, 1 M EtHS + 3.2 M NaOH; [d] adsorbed on Cu electrode at E = –0.400 V, solution, 0.1 M Na_2SO_4 + 0.01 M H_2SO_4. Abbreviations: dp, depolarized; p, polarized; m, middle; vs, very strong; s, strong; w, weak; ν, stretching; ν_s, symmetric stretching; ν_{as}, asymmetric stretching; δ, deformation; δ_{as}, asymmetric deformation; ρ_r, rocking; ρ_w, wagging; ρ_t, twisting; ?, provisional assignment.
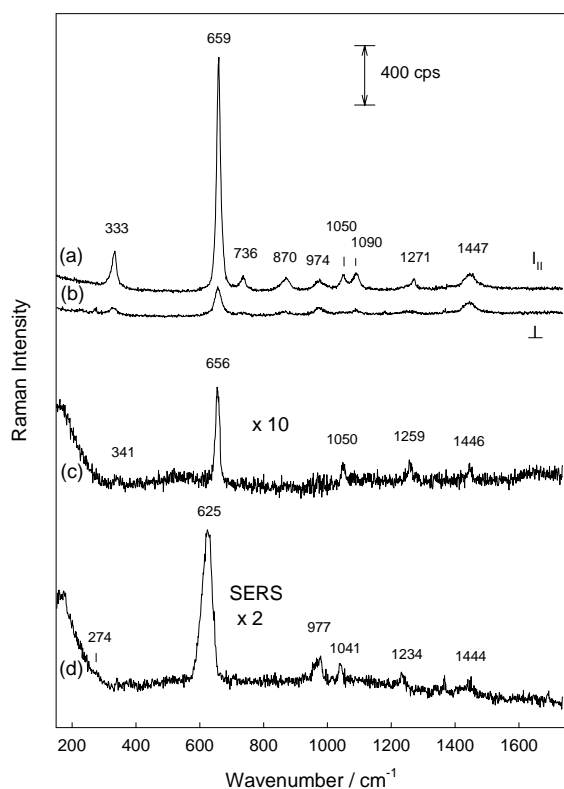
Fig. 1. Raman spectra of ethanethiol in different states in the frequency range from 150 cm^{-1} to 1700 cm^{-1}: (*a*) solution Raman spectrum of liquid ethanethiol taken with parallel polarization; (*b*) solution Raman spectrum of liquid ethanethiol taken with perpendicular polarization; (*c*) Raman spectrum ethanethiolate anion obtained in 1M ethanethiol + 3.2 M NaOH solution. Parallel polarization; (*d*) SER spectrum of ethanethiol adsorbed at Cu electrode at –0.400 V. Solution: 0.1 M Na$_2$SO$_4$ + 0.01 M H$_2$SO$_4$

A strong and relatively narrow feature at 659 cm^{-1} dominates in the parallel-polarized Raman spectrum of liquid EtSH (Fig. 1a). This band can be easily assigned to the stretching motion of C–S bond (Table). It should be noted that calculations indicate mixing of this mode with the twisting vibration of CH$_2$ group and asymmetric deformation motion of CH$_3$ group (Table). For assignments of other modes, a comparison of differently polarized spectra is necessary [Fig. 1(a) and (b)]. First of all, the depolarized band at 1447 cm^{-1} can be immediately assigned to the deformation vibration of methylene group (Table). The other depolarized mode at 974 cm^{-1} should be primarily assigned to the asymmetric vibration of C–C bond (with a quantity from the methyl deformation). It should be noted that *ab initio* calculations have indicated that the stretching vibration of C–C bond and deformation motion of CH$_3$ group are heavily mixed in EtSH making the assignments of these bands rather soft. The mode at 1050 cm^{-1} was assigned to the deformation vib-

ration of the methyl group coupled with the twisting motion of methylene group. There are several noticeable changes in the Raman spectrum of ethanethiolate anion (EtS$^-$), after proton dissociation in alkaline aqueous solution (Fig. 1c). First of all, the frequency of the rocking deformation vibration of methylene group mixed with the deformation motion of methyl group at 1271 cm^{-1} in EtSH decreases by 12 cm^{-1} and appears at 1259 cm^{-1} in the spectrum of EtS$^-$. Secondly, the relative intensities of δ(CCS) at 333 cm^{-1}, twisting δ(CH$_2$) 736 cm^{-1}, and deformation motion of δ(CH$_3$) at 1090 cm^{-1} decrease considerably. The frequency of the most intense ν(C–S) mode decreases only by 3 cm^{-1}. Adsorption of EtSH on copper electrode induces remarkable perturbations in the vibrational spectrum [Fig. 1(d)]. It should be noted that adsorption of EtSH was performed in ethanolic 10 mM solution, and the presented spectrum was recorded in EtSH-free solution of 0.1 M Na$_2$SO$_4$ + 0.01 M H$_2$SO$_4$ at E = –0.400 V. The most intense ν(C–S) band shifts to a wavenumber lower by as much as 34 cm^{-1} compared with the liquid state and considerably broadens. Such a high shift indicates direct involvement of the sulphur atom in the bonding with copper; as the result the strength of the C–S bond and the corresponding stretching vibrational frequency decreases. The high width of the band indicates inhomogeneous energy of the different adsorption sites on Cu surface. The frequency of the rocking motion of methylene group is also extremely sensitive to the adsorption and decreases from 1271 cm^{-1} in the liquid state to 1234 cm^{-1} in the adsorbed state. Finally, in the SER spectrum we observed a shoulder in the low frequency range at 274 cm^{-1}. This band was assigned temporally to the direct stretching motion of the Cu–S bond, although the intensity of this mode is too low for a more conclusive statement and experiments are in progress to clarify the presence of metal-adsorbate vibration in this system.

In the high frequency range the stretching vibrations of methylene and methyl groups dominate (Fig. 2). The two most intense peaks at 2872 cm^{-1} and 2928 cm^{-1} in the parallel polarized Raman spectrum of liquid EtSH can be immediately assigned to the symmetric stretching motion of methylene and methyl groups, respectively. The asymmetric stretching motion of CH$_3$ group is observed at 2962 cm^{-1}. The position of the ν_s(CH$_3$) was in general insensitive to the deprotonation effect, while the frequency of the ν_s(CH$_2$) decreased by several cm^{-1}. It should be noted that the symmetric vibration of CH$_2$ group in solution phase is rather broad (Fig. 2c) and the uncertainty in the frequency determination for this
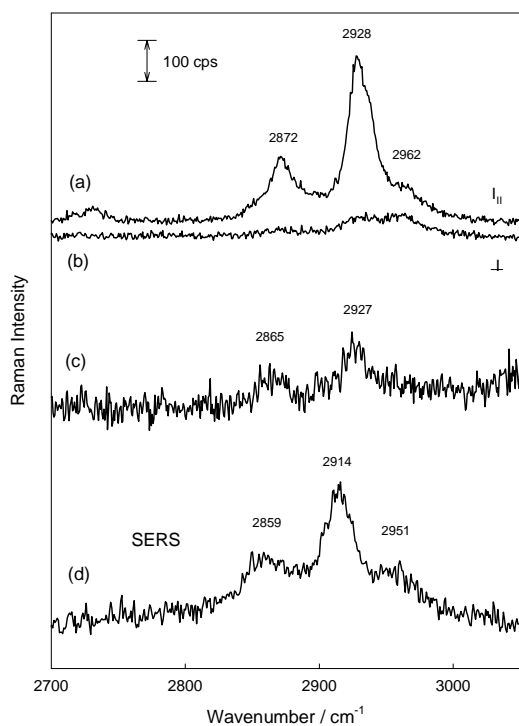
Fig. 2. Raman spectra of ethanethiol in different states in the frequency range from 2700 cm⁻¹ to 3050 cm⁻¹: (*a*) solution Raman spectrum of liquid ethanethiol taken with parallel polarization; (*b*) solution Raman spectrum of liquid ethanethiol taken with perpendicular polarization; (*c*) Raman spectrum ethanethiolate anion obtained in 1M ethanethiol + 3.2 M NaOH solution. Parallel polarization; (*d*) SER spectrum of ethanethiol adsorbed at Cu electrode at –0.400 V. Solution: 0.1 M Na$_2$SO$_4$ + 0.01 M H$_2$SO$_4$

Fig. 3. Potential-dependent SER spectra of ethanethiol adsorbed at Cu electrode in the frequency range from 500 cm⁻¹ to 1200 cm⁻¹. Potentials: (*a*) –0.200 V; (*b*) –0.400 V; (*c*) –0.600 V. Solution: 0.1 M Na$_2$SO$_4$ + 0.01 M H$_2$SO$_4$

mode is rather high (±4 cm⁻¹). Surprisingly, stretching vibrations of methylene and methyl groups are extremely sensitive to the adsorption of EtSH (Fig. 2d). All the modes in this spectral region shift to lower wavenumbers upon adsorption. The intense ν_s(CH$_3$) band in this spectral region is most appropriate for a detailed analysis. The frequency of this vibration decreases by 14 cm⁻¹ upon adsorption of EtSH, although, contrary to the vibration of C–S bond, no broadening in SER spectrum was observed for the ν_s(CH$_3$) mode. We will see later that this mode is also sensitive to the electrode potential.

The potential-dependent SER spectra from adsorbed EtSH at Cu electrode in 0.1 M Na$_2$SO$_4$ + + 0.01 M H$_2$SO$_4$ solution is presented in Fig. 3. There are three clear potential-induced effects on the parameters of ν(C–S) band. First of all, the intensity of this band considerably increases going from –0.200V to –0.400 V. Secondly, the frequency of this mode increases at more negative potentials. This is an indication that the Cu–S bond weakens at more negative potential values. Finally, the width of the band decreases at more negative potentials. No es-
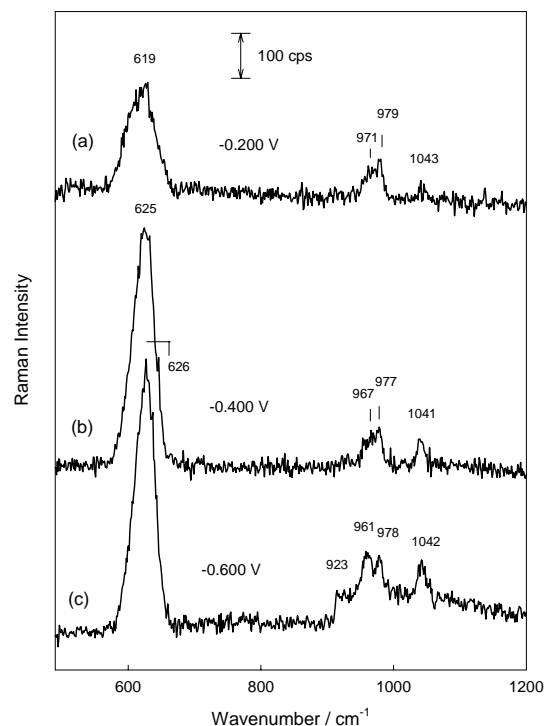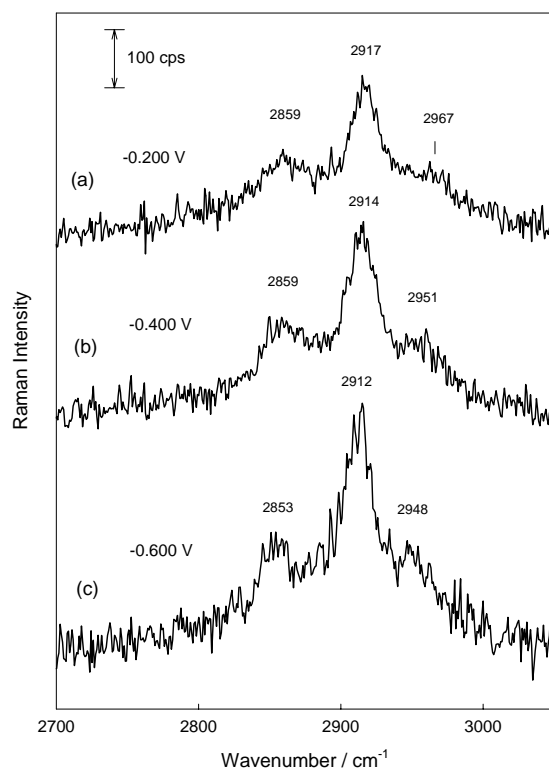

Fig. 4. Potential-dependent SER spectra of ethanethiol adsorbed at Cu electrode in the frequency range from 2700 cm⁻¹ to 3050 cm⁻¹. Potentials: (*a*) –0.200 V; (*b*) –0.400 V; (*c*) –0.600 V. Solution: 0.1 M Na$_2$SO$_4$ + 0.01 M H$_2$SO$_4$

sential potential-dependent changes in the width of the $\nu_s(CH_3)$ were observed in the high-frequency SER spectra (Fig. 4), while the frequency of this mode was potential-sensitive and decreased at more negative potential values. As the CH_3 group cannot directly interact with the surface (this statement is also supported by the absence of broadening of this mode upon adsorption, see Fig. 2), such a frequency alteration with potential can be explained as associated with a surface Stark effect.

References

1. H. Hagenström, M. A. Schneeweiss, and D. M. Kolb, *Electrochim. Acta*, **45**, 1141 (1999).

2. H. Hagenström, M. A. Schneeweiss, and D. M. Kolb, *Langmuir*, **15**, 2435 (1999).

3. H. Hagenström, M. A. Schneeweiss, and D. M. Kolb, *Langmuir*, **15**, 7802 (1999).

4. D. W. Hatchett, K. J. Stevenson, W. B. Lacy, J. M. Harris, and H. S. White, *J. Am. Chem. Soc.*, **119**, 6596 (1997).

5. H. O. Finklea, in *Electroanalytical Chemistry*, (Eds. A. J. Bard and I. Rubinstein.), Vol. **9**, Marcel Dekker, New York, p. 109 (1996).

6. G. Niaura, A. K. Gaigalas, and V. L. Vilker, *J. Raman Spectrosc.*, **28**, 1009 (1997).

7. G. Niaura and A. Malinauskas, *Chem. Phys. Lett.*, **207**, 455 (1993).

8. GAUSSIAN 98W program: M. J. Frisch, G. W. Trucks, H. B. Schleger, G. E. Scuseria, M. A. Robb, J. R. Cheesman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, (1998).

9. *Chem. Rev*. **100** (2) (2000).

10. Unpublished data.

11. P. Pulay, G. Fogarsi, Pang, and J. E. Boggs, *J. Am Chem. Soc.*, **101**, 2550 (1979).

12. P. Pulay, G. Fogarsi, G. Pongor, J. E. Boggs, and A. Vargha, *J. Am. Chem. Soc.*, **105**, 7037 (1983).

13. E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations,* Dover, NY. (1980).

14. T. H. Joo, K. Kim, and M. S. Kim, *J. Phys. Chem.*, **90**, 5816 (1986).

15. N. L. Allinger, M. Quinn, M. Rahman, and K. Chen, *J. Phys. Organ. Chem.*, **4**, 647 (1991).

16. C. H. Kwon, D. W. Boo, H. J. Hwang, and M. S. Kim, *J. Phys. Chem.*, **103**, 9610 (1999).

17 W. Qian, and S. Krimm, *Biopolymers*, **32**, 1503 (1992).

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ETANTIOLIO, ADSORBUOTO ANT VARIO ELEKTRODO, SUSTIPRINTA PAVIRŠIUMI RAMANO SPEKTROSKOPIJA

S a n t r a u k a

Etantiolio adsorbcija ant vario elektrodo tirta sustiprintos paviršiumi Ramano spektroskopijos (SPRS) metodu. Spektro interpretacija atlikta pasinaudojus molekulės kvantinės chemijos skaičiavimais. Parodyta, kad C–S jungties valentinio virpesio dažnis adsorbcinėje būsenoje sumažėja 34 cm^{-1}, palyginti su skystos būsenos etantiolio spektru. Tai rodo, kad sieros atomas tiesiogiai dalyvauja susidarant kovalentinei jungčiai su vario paviršiumi. Pastebėta, kad metilo grupės valentinio simetrinio virpesio dažnis priklauso nuo elektrodo potencialo. Padaryta prielaida, kad paviršinis Štarko efektas lemia virpesio dažnio sumažėjimą, neigiamėjant elektrodo potencialui.