

Surface-Enhanced Resonance Raman Spectra of Photochromic Crown Ether Styryl Dyes, Their Model Chromophores, and Their Complexes with Mg^{2+}

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The complexation of the derivatives of crown ether styryl dyes betaine 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium (**1a**) and perchlorate 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-ethylbenzothiazolium (**1b**) and their molecular fragment 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (**2**) with magnesium cations has been studied by the surface-enhanced Raman scattering (SERS) spectroscopy at very low (down to 10^{-8} M) concentrations. A detailed comparison of the Raman and SERS spectra of **1a,b** and their molecular fragments **2** and perchlorate 2-Me-3-ethyl benzothiazolium (**3**) enabled one to assign the vibrational modes and propose the model of dye interaction with the silver SERS-active surface. Benzo-15-crown-5 chromophore of **1a,b** was found to be adsorbed through its crown ether part so that the plane of benzene ring is nearly perpendicular to the surface of silver electrode. The C=C bond as well as the benzothiazolium chromophore being situated far from the electrode surface does not contribute noticeably to the SERS spectra. The sulfonate group of **1a** and alkyl group of **1b** do not affect the geometry of adsorption. The SERS spectra of *trans*-**1a,b** and their complexes with Mg^{2+} are observed selectively studying the photostationary mixtures of *cis* and *trans* isomers. The complexation of Mg^{2+} leads to the remarkable frequency shifts of several bands associated primarily with the benzo-15-crown-5 fragment of **1a,b**. The spectral effects which reflect the cation-induced intramolecular electron transfer were found to be very similar in both resonance Raman and SERS spectra of the dyes. Hence, the adsorption on the surface of silver electrode does not perturb the complexation of the dyes with Mg^{2+} . The results demonstrate that the SERS spectroscopy enables one to study the complexation of the photochromic crown ether styryl dyes with the metal cations, ensuring selective detection of *trans* isomers and high sensitivity to structural changes of the dyes in a wide range of concentrations.

Introduction

Styryl dyes containing crown-ether group and heteroaromatic residue with sulfoalkyl or alkyl N-substituent have been found to have strong electronic transition in the visible region and show significant hypsochromic shifts upon complexation with alkali- or alkaline-earth metal cations.¹ Changing a size of crown cycle and introducing O, N heteroatoms in different positions of crown cycle have yielded the high selectivity of binding for a number of cations.^{2–5} These chromoionophors exhibit high quantum yields of *trans*-to-*cis* and *cis*-to-*trans* photoisomerization. The *trans*-to-*cis* photoisomerization of the molecule complexed to metal cation results in the vanishing of absorption in the visible region. Sulfoalkyl N-substituent of the heteroatomic residue increases the stability of the *cis* isomer complex with metal due to the proximity of anionic sulfonate group to the crown ring and cooperative action of these two parts of the molecule. The photoresponsive styryl dyes can be used as ion-selective color indicators or structural elements for photosensitive molecular devices as well as for light-controlled

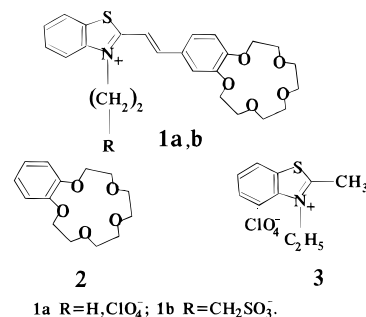


Figure 1. Structures of compounds **1a,b**, **2**, and **3**.

ion extraction.^{1–5} Being reconstructed into liposomes or lipid membrane, the dyes might serve as potential light-controlled selective regulators of transmembrane transport of metal ions.⁶

A 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium (**1a**, Figure 1) and perchlorate 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-ethylbenzothiazolium betaines (**1b**, Figure 1) are the particular representatives of the photoresponsive ionophors. UV-vis and fluorescence spectroscopy studies of their photoisomerization and complexation with alkaline-earth metal cations have revealed photo- and cation-dependent changes in the conformation, intermolecular interactions, and stoichiometry of metal–ligand complexes.⁷

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The vibrational spectroscopy has proven to provide an important information about the structure of these molecules and complexes. Resonance Raman spectroscopy was applied to the study of **1a,b** and their complexes with Mg^{2+} in acetonitrile solution.⁸ Preliminary assignment of the Raman bands were made, and the frequency shifts on the complexation with Mg^{2+} were described. Unfortunately, the resonance Raman spectroscopy of these dyes appeared to be strongly restricted by the concentration (not less than 10^{-4} M) as well as by the intense interference from fluorescence. From the other hand, time-resolved fluorescence experiments⁷ suggest the critical role of dyes aggregation in dilute solutions in course of the divalent alkaline-earth cations complexation and geometric photoisomerization. Hence, the molecular background of the dye-ion complexation processes and photoisomerization should be investigated in the range of concentrations 10^{-5} – 10^{-8} M if the overall pattern of dye structure–function relationships in terms of their applications needs to be clarified.

SERS spectroscopy turned out to have the enhancement of Raman cross section by several orders of magnitude and revealed significant quenching of the chromophore fluorescence.^{9–11} The method was adjusted to investigate the photoresponsive molecules^{12,13} and ligand–metal cation complexes at different levels of structural organization.^{14–16} Nowadays SERS spectroscopy is well developed to probe molecules in water solutions and hardly works in nonaqueous medium where some methodological restrictions appear.^{17,18}

In this paper, we present the SERS spectra of *trans*-**1a,b** (Figure 1), and their molecular fragments benzo-15-crown-5 (**2**) and 2-Me-3-ethylbenzothiazolium (**3**), recorded in the electrochemical cell at the very low (down to 10^{-8} M) concentrations. Vibrational assignments of the SERS active modes and their comparison with the Raman spectra enabled one to find the preferable orientation of the molecules when adsorbed on a silver surface. Complexation of *trans*-**1a,b** and **2** with magnesium cations was studied at the concentrations of ionophors *ca.* 10^2 lower than those of the same compounds used for resonance Raman spectra recording in acetonitrile solutions.

Experimental Section

Photochromic crown ether styryl dyes betaine 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium (**1a**), perchlorate 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-ethylbenzothiazolium (**1b**), and their molecular fragment perchlorate 2-Me-3-ethylbenzothiazolium (**3**) were synthesized and purified as described previously.¹ 2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (**2**) was purchased from Merck. Acetonitrile was doubly distilled from P_2O_5 and CaH_2 to remove traces of water which disturb complexation of the ionophors with metal cations and promote dark *cis*–*trans*- isomerization of **1a,b**. Magnesium perchlorate was dried under vacuum at 180 °C. The preparation of dye solutions in acetonitrile and all experiments were carried out under red light. All measurements were performed in acetonitrile at room temperature.

Raman and SERS spectra were recorded with a single-channel Ramanor HG-2S spectrometer (Jobin Yvon, France) using an Ar^+ laser (Spectra-Physics, Model 164-03) and a Kr^+ laser (Karl Zeiss, Model ILK-120). The laser power was 50 mW ($\lambda_{\text{exc}} = 647.1$ nm), 5 mW ($\lambda_{\text{exc}} = 457.9$ nm), 15 mW ($\lambda_{\text{exc}} = 488$ nm), or 25 mW ($\lambda_{\text{exc}} = 514.5$ nm). Typically, spectra were recorded in 150–1700 cm^{-1} range at 1 cm^{-1} increments with 1 s integration time as the average of 1–4 accumulations.

SERS spectra were obtained for the molecules adsorbed on electrochemically roughened silver electrode. Oxidation–

reduction cycle was performed in the standard electrochemical cell in the aqueous electrolytic solution. The electrode was treated following the standard procedure described previously.¹² The roughened electrode was washed with triply distilled water, dried, and washed again with acetonitrile to remove electrolyte and water traces. For SERS measurements the roughened electrode was immersed in the quartz cell with the analyt acetonitrile solution. The SERS signal detected in this experimental system was found to be very stable and reproducible during several hours. All spectra were reproduced at least three times for various sample preparations. The spectral differences were reproducible from one preparation to the next and over multiple experiments. It is worth mentioning that other SERS-active systems, namely, silver island films, citrate, and borohydrate silver colloids, were shown to be unstable in acetonitrile solution especially with Mg^{2+} cations added. SERS spectra of *trans*-**1a,b** were recorded also with the gold island films at 647.1 nm excitation but the surface-induced enhancement observed in these experiments was at least 10 times lower as compared to the electrochemically roughened silver electrode.

Isomerization state, metal ion complexation, and the influence of laser irradiation on the compounds **1a,b** at the concentrations above 2×10^{-6} M were monitored by comparing the absorption spectra before and after recording of the SERS spectra. A Cary-209 spectrophotometer (Varian, USA) was used for absorption measurements. Concentrations of sample solutions were determined on the basis of the molar absorption coefficients of *trans*-**1a,b** 39 000 $\text{M}^{-1}\text{cm}^{-1}$ (at 435 nm) and of (*trans*-**1a,b**)- Mg^{2+} 36 000 $\text{M}^{-1}\text{cm}^{-1}$ (at 393 nm) published elsewhere.⁷ The sampled solutions of the dyes (10^{-6} – 10^{-8} M) were prepared diluting 5×10^{-6} M stock acetonitrile solution just before the experiments. Defocused laser beam with 457.9 nm wavelength was utilized for photoisomerization. All spectroscopic measurements were performed in the quartz cuvettes pretreated by trimethylchlorosilane to minimize dye adsorption on the cuvette walls.

Results and Discussion

Raman and Preresonance Raman Spectra of Dyes and Vibrational Assignments. Preliminary assignment of the preresonance and resonance Raman bands of **1a** and **1b** (Figure 1) both free and complexed with Mg^{2+} in acetonitrile solution has been proposed by Lednev *et al.*⁸ To improve the resolution due to the elimination of the solvent-induced broadening of the Raman bands, the Raman spectra of **1a,b** as well as their fragments **2** and **3** (all in the solid state) were recorded (Figure 2) at out-of-resonance excitation (647.1 nm, Figure 3).

Following the conclusion of Wilbrandt *et al.*¹⁹ that the preresonance Raman spectrum of *all-trans*-diphenylbutadiene can be analyzed as a superposition of vibrational bands of both substituted benzene rings and butadiene, we considered the spectra of **1a,b** as a sum of fragments **2**, **3** (Figure 1), and ethylene bands. Hence, analyzing the Raman spectra of **2** and **3** we could evaluate the relative contribution of their chromophores to the spectra of **1a,b**. The assignment of the $\text{C}=\text{C}$ stretching vibration (*ca.* 1610 cm^{-1}) in **1a,b** was made before⁸ and used by us without revision (Table 1).

A detailed assignment of the bands of compound **3** (2,3-substituted benzothiazolium fragment of **1a,b**, Figure 1) can be drawn on the basis of the normal mode analysis of structurally similar compounds *o*-aminothiophenol and 1-chloro-2-methylbenzene.²⁰ The normal-modes frequencies of the model compounds correlate well with the spectral features of **3** providing direct assignment of bands related to substituted benzene (Table 1). $\text{N}^+=\text{C}$ stretching mode and $\text{C}-\text{S}-\text{C}$ vibrational modes have been assigned before.⁸ We used these assignments without

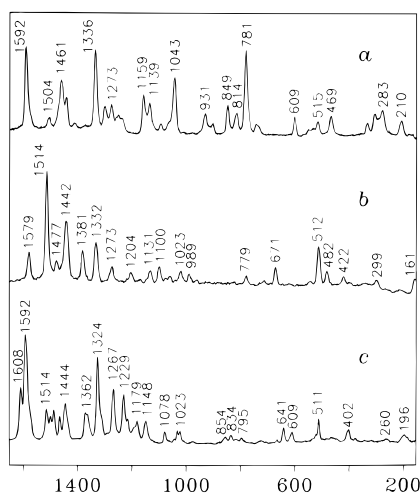


Figure 2. Raman spectra of compounds **2** (a), **3** (b) and **1a,b** (c) in the solid state. Excitation wavelength 647.1 nm. See text for details.

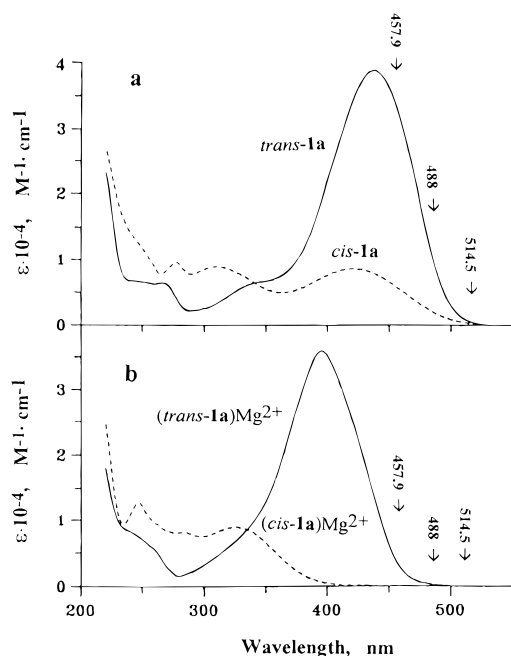


Figure 3. Absorption spectra of (a) free **1a** and (b) complexes **(1a)**- Mg^{2+} in the *trans* and *cis* conformations. The spectra were recorded in acetonitrile solution. Arrows indicate the excitation wavelengths being used to record the SERS spectra. $[\mathbf{1a}] = 2 \times 10^{-5}$ M; $[\text{Mg}^{2+}] = 10^{-4}$ M. Adapted from Gromov *et al.*^{2,5}

revision with the exception of the band at 1023 cm^{-1} which should be reassigned as prevalently due to the ν_{18b} mode (in Wilson notation) according to the normal-mode analysis of *o*-di-“light”-“heavy”-substituted benzene.²⁰

The spectrum of **2** can be considered by means of the normal-mode analysis published for *o*-di-“light”-substituted benzenes: veratrole, pyrocatechol, and 3-(3',4'-dimethoxyphenyl)propanoic acid.²⁰ Besides the vibrational modes of substituted benzene, some modes of the crown ether part of the molecule were found to make a significant contribution to the spectrum of **2** (Table 1). Assignments of these modes could be based on the Raman spectra of aliphatic alcohols and ethers. Doing that, the Raman bands at 814 and 1139 cm^{-1} must be assigned to C—O—C symmetric and asymmetric stretching motions, respectively.²¹ H—C—H and C—C—H deformational motions were concluded to contribute to Raman bands at 1461 and 1336 cm^{-1} , respectively. Very strong band at 1043 cm^{-1} is attributed to C—C—O asymmetric stretching motion.

The contribution of the benzo-15-crown-5 fragment into the Raman spectra of **1a,b** could be considered in terms of the normal-mode analysis of 1,2,4-tri-“light”-substituted benzenes.²⁰ Positions of vibrational modes of *o*-di-“light”-substituted benzene and 1,2,4-tri-“light”-substituted benzene were found to be very similar (with the exception of the modes ν_{7b} , ν_{9a} , and ν_{17a}), thus permitting the assignments of **2** to be used for benzo-15-crown-5 part of **1a,b** analysis (Table 1). The crown ether modes in the spectra of **1a,b** were less prominent, as compared with **2**. The modes of substituted benzenes are relatively more enhanced in the spectra of **1a,b** due to the preresonance with the electronic transition localized on the $\text{Ph}-\text{N}^+=\text{C}=\text{C}-\text{Ph}$ fragment of the molecule.⁸

The Raman band positions of the compounds **1a** and **1b** in the solid state (Table 1) were proved to be very similar to those in acetonitrile solution (our spectra, not shown, and data from ref 8). In this way, we compared the assignments made for the solid samples with the corresponding SERS spectra and proposed the geometrical model of dye interaction with the silver surface.

General Characteristics of the SERS Spectra of the Dyes.

Nowadays, SERS spectroscopy is a well-developed technique for investigation of water-soluble molecules and rarely applied for nonaqueous solutions.¹⁸ Hence, the first goal of our SERS research was to find and optimize an experimental system suitable for recording stable and reproducible spectra of dyes in acetonitrile solutions. All traditional SERS-active systems (e.g., silver island films, citrate and borohydrate aqueous silver colloids) used by us before^{12,18} were found to be dramatically unstable in acetonitrile solutions, especially in the presence of Mg^{2+} cations. Since the surface of the electrochemically roughened silver electrode turned out to be much more stable in the presence of organic solvents,¹² we tried to use it as a SERS-active substrate in our studies of the styryl dyes. Finally, silver electrode roughened in the electrochemical cell in the aqueous buffer solution and washed in acetonitrile afterwards was shown to be an optimum system for nonaqueous solutions of the dyes featuring the superior stability, mass sensitivity, and *in situ* applicability.

SERS spectra of **1a,b**, **2**, and **3** adsorbed on the surface of the roughened silver electrode were recorded at the 457.9, 488, and 514.5 nm excitations. The excitation wavelengths used were in resonance with longer wavelength electronic transition of the *trans* isomers of **1a,b** ($\lambda_{\text{max}} = 435\text{ nm}$, Figure 3). The *cis* isomers of **1a,b** also have electronic transitions in the visible region ($\lambda_{\text{max}} = 421\text{ nm}$), although *ca.* 4.6 times less intensive (Figure 3). The SERS spectra of free *cis*-**1a,b** were expected to be observed in the photostationary state with a large relative amount of the *cis* isomer. Nevertheless, we failed to find any spectral features attributable to the *cis* isomer in the SERS spectra of *cis/trans* photostationary mixtures recorded at different excitation wavelengths providing various relative concentrations of *cis/trans* conformers. The dominance of the *trans* isomer in the resonance Raman spectra was reported before and explained in terms of prominent differences between Raman cross sections of vibrational modes of *trans* and *cis* isomers in the visible region.⁸ The selectivity of the resonance SERS spectroscopy in respect to the *trans* isomer could be accounted for in the same manner.

An enhancement of the photochemical processes of the adsorbate (in terms of the electromagnetic theory of the SERS effect) can induce changes in the isomerisation state of the molecule. But this seems to be not the case when the SERS spectra of the photochromic crown ether dyes are recorded with 457.9, 488, and 514.5 nm excitations. Illumination of the sample at these wavelengths (Figure 3a) induces effective

enhancement (resonance SERS effect) for the *trans* isomer adsorbed on the silver electrode. The coupling of both effects results in an increase in signal intensity by factor *ca.* 10^4 over that achieved in resonance Raman measurements of these compounds⁸ or observed in our SERS spectra of noncolored compounds **2** and **3**. The compounds **2** and **3** possess no absorption in the visible region, and the SERS spectra of these molecules cannot be recorded at concentrations below 10^{-4} M (Figure 4).

Severe adsorption of the *trans*-**1a,b** on the cuvette walls cannot be eliminated at the concentrations less than 10^{-8} M and causes a large error in the concentration-dependent measurements of SERS spectra. A strong fluorescence emission interferes with the SERS measurements at concentration larger than 10^{-4} M.

Vibrational Assignments of SERS-Active Modes and Effects of Interaction of Ionophores with Silver Surface. The SERS spectrum of **3** (Figure 4a) reveals the prominent differences from corresponding Raman spectrum. The modes of δ -(CH₃), ν_{13} , ν_5 , and ν_1 are not enhanced in the SERS. Instead, the new bands appear at 1608, 1231, 846, and 626 cm^{-1} assigned to ν_{8b} , ν_{7a} , ν_{12} and C—S—C symmetrical stretching, and ν_4 vibrational mode, respectively (Table 1). Moreover, the frequencies of the δ (C—C—H) and CH₂ wagging, ν_3 , ν (C—N), and some other modes are strongly (up to 17 cm^{-1}) shifted in the SERS spectrum of **3** as compared with its normal Raman spectrum (Table 1). These facts show that both the benzene ring and five-membered cycle of the 2-Me-3-ethylbenzothiazolium chromophore may participate in the direct interaction with the silver surface. Besides, the SERS spectrum of **3** is characterized by the dramatic relative decrease of the low-frequency (usually related to out-of-plane) vibrations. Only a few in-plane vibrations are enhanced in this (<1000 cm^{-1}) region (Table 1). This finding could be explained in terms of changes in Raman selection rules of the SERS spectra when the molecule is adsorbed on the surface in a tilted rather than flat manner.²²

The SERS spectrum of **2** (Figure 5c) differs from corresponding Raman spectrum as well (Figure 2a, Table 1). Adsorption on the silver electrode induces considerable shifts of frequencies of the δ (C—C—H) and CH₂ wagging, ν_{9a} , ν (C—C), and ν_3 vibrational modes. CH₂ deformational mode seems to be split and appears as the 1461 cm^{-1} (as in normal Raman spectrum) and 1488 cm^{-1} bands. Strong and medium bands at 1589, 1361, and 1225 cm^{-1} in the SERS spectra were assigned to ν_{8a} , ν_{14} , and ν_{7a} vibrational modes, respectively (Table 1). The single band at 1592 cm^{-1} in the Raman spectrum of the solid **2** (Figure 2a) was assigned to the degenerated ν_{8b} and ν_{8a} modes of benzene (Table 1). The degeneracy disappears upon adsorption of **2** on the silver surface, and two separate SERS bands are enhanced at 1608 and 1589 cm^{-1} (Figure 4c). They could be assigned to the ν_{8b} and ν_{8a} modes, respectively, on the basis of normal mode analysis for the *o*-di-“light”-substituted benzenes.²⁰ The normal-mode analysis has proved that the ν_{8b} vibration has a larger wavenumber than the ν_{8a} mode in these compounds. Finally, both benzene and crown ether vibrations were enhanced upon the adsorption of **2** on the silver surface. Relative intensities of the out-of-plane vibrations in the SERS spectrum of **2** are much lower as compared with the corresponding Raman signals (Figures 2a and 4c). Hence, the tilted rather than flat geometry of adsorption of **2** on the surface occurs.²²

The general features of the SERS spectra of *trans*-**1a** and *trans*-**1b**, in particular positions and relative intensities of the bands, were found to be practically identical at all the excitations

used. Hence, we conclude that vibrational modes of the sulfonate or alkyl radicals (Figure 1) are not enhanced in the SERS spectra of *trans*-**1a,b**.

The SERS spectra of *trans*-**1a** were almost coincident with **2** (Figure 4b,c and Table 1). The characteristic spectral bands of **3**, namely, enhanced ν_{18a} benzene mode (1134 cm^{-1}), and δ (H—C—H) mode (1463 cm^{-1}), are barely observable in the spectra of *trans*-**1a**. Attempting to calculate the spectrum of *trans*-**1a** as a superposition of the spectra of **2** and **3** revealed the probable contribution of **3** could not exceed 10%. Then the contribution of the benzothiazolium chromophore to the SERS spectrum of *trans*-**1a** proved to be negligible. Hence, adsorption of **1a** through its benzo-15-crown-5 fragment as well as the remote position of the benzothiazolium moiety in respect to the SERS-active surface is suggested.

Assuming the dominance of chemisorption in the adsorption of **1a,b** on the electrode, the clusters of silver atoms (Ag_4^+ or similar clusters²⁴) on the surface as well as other surface defects of atomic lattice can be considered as possible centers of adsorption. So, it is probable that the high affinity of the benzo-15-crown-5 part of the molecule to metal ions favors the interaction of **1a,b** with ionized and/or polarized states of silver atoms on the roughened metal surface and determines the mode of adsorption via the benzo-15-crown-5 chromophore. Interaction of **1a,b** with the adsorption centers can not be described in terms of formation of “classic” (**1a,b**) Ag^+ complexes and, as will be shown below, it does not inhibit the complexation of dissolved Mg^{2+} cations.

The resonance SERS spectrum should predominantly include the modes originating from the Ph—N=C—C=C—Ph fragment of *trans*-**1a** in which the electronic transition is localized.⁸ On adsorption of **1a** the C—Ph part of this fragment is in the close proximity to the SERS-active surface. That is why the spectrum of **1a** includes strongly enhanced benzene modes of benzo-15-crown-5 part of the molecule. The remoteness of the benzothiazolium moiety from the electrode surface is confirmed by the fact that the SERS spectra of *trans*-**1a** and *trans*-**1b** are almost identical even though the molecules carry different charges in the vicinity of benzothiazolium chromophore. An orientation of the tail part of **1a** to the electrode surface seems to be defined by the chemical structure of benzothiazolium chromophore. When the benzothiazolium chromophore of **1a** is substituted for the quinoline chromophore (unpublished results), the quinoline chromophore of such molecule participates in adsorption on the electrode and makes strong contribution to the SERS spectrum. An absence of adsorption of the charged molecule via the positively charged nitrogen is not surprising if the difference in the affinity of the diverse chromophores of **1a** to the silver surface is taken into account. Assuming the short-range (chemical) nature of Raman enhancement²³ readily clarifies the preferential enhancement of the benzo-15-crown-5 vibrations for the proposed adsorption model.

The absence of a positive band in the *ca.* 1610 cm^{-1} region of difference SERS spectrum of *trans*-**1a** minus **2** (Figure 4d) shows that the C=C stretching vibration (1610 cm^{-1} in the resonance Raman spectrum of **1a**)⁸ provides no contribution in the SERS spectrum of **1a**. The difference SERS spectrum of *trans*-**1a** minus **2** reveals two quite pronounced positive bands at 1598 and 1324 cm^{-1} , demonstrating higher relative intensities of the ν_{8a} and δ (C—C—H) and CH₂ wagging modes in the SERS spectrum of *trans*-**1a** as compared with **2** (Figure 4d). These effects seem to be opposite to those found on going from the normal Raman to the SERS spectrum of **2** and could indicate the separation of some part of the benzo-15-crown-5 chromophore from the silver surface (*i.e.*, elimination or decrease

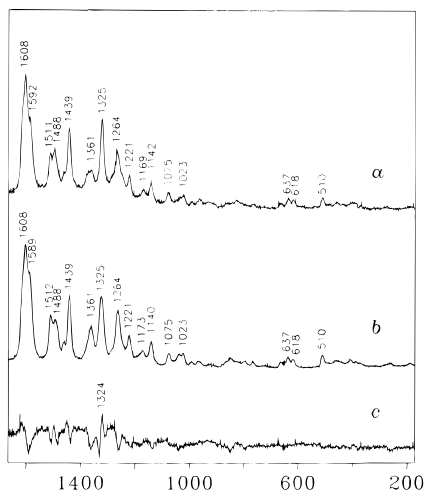


Figure 5. SERS spectra of complexes (*trans*-**1a**)Mg²⁺ (a) and (**2**)Mg²⁺ (b) in acetonitrile solution and their difference spectrum (c). Excitation wavelength 457.9 nm. Spectrum of solvent was subtracted. (*trans*-**1a**)Mg²⁺: [**1a**] = 10⁻⁵ M; [Mg²⁺] = 10⁻³ M. (**2**)Mg²⁺: [**2**] = 5 × 10⁻⁴ M; [Mg²⁺] = 10⁻² M.

of the surface-induced effects on the frequencies and intensities of vibrations arising from this part of the molecular fragment). A tilted geometry of adsorption of the **1a** through the crown ether part of the molecule is confirmed by hardly observable out-of-plane benzene modes of the benzo-15-crown-5 fragment of the molecule (Figure 4b).

The spectral features of **1a,b** mentioned in this section can be summarized and used to model the dye orientation relative to the silver surface:

- (i) The dyes are adsorbed through the crown ether part of the molecule so that the plane of benzene ring is nearly perpendicular to the surface of the electrode.
- (ii) The C=C bond as well as benzothiazolium chromophore is located relatively far from the electrode surface.
- (iii) The sulfonate group of **1a** and alkyl radical of **1b** are positioned aside the electrode surface.

Effect of Ionophores Interaction with Mg²⁺. Formation of the complexes of **1a,b** with Mg²⁺ was performed for the 10⁻⁵–10⁻⁸ M solutions of the dyes and at the Mg²⁺/dye ratios from 0.5 to 100. UV-vis spectroscopy was applied to detect the complex formation as described⁷ when the concentrations of dyes higher than 2 × 10⁻⁶ were used. Formation of complexes was accompanied by the characteristic changes in the corresponding SERS spectra (Figure 5a) and these spectral features (namely, shifts of the frequencies, Table 1) were found to be very similar to those described before for the resonance Raman spectra of the dyes/cation complexes.⁸

The shifts of the SERS bands upon Mg²⁺ complexation appear along with the changes of the intensity of the ν_3 , δ -(HCH), ν_{19b} , ν_{8a} , and ν_{8b} modes relative to the intensity of the (C–C–H) and CH₂ wagging and ν_{19a} vibrations. The ratio of intensities of the 1608 and 1592 cm⁻¹ bands ($I(\nu_{8b})/I(\nu_{8a})$) was found to be very sensitive to the dye/Mg²⁺ complexation and could serve as SERS detection of the complex formation. The $I(\nu_{8b})/I(\nu_{8a})$ ratio being equal to 0.54 for free **1a,b** increases up to the ca. 1.5–1.7 upon titration of dye solution with Mg²⁺ cations. Hence, the characteristic changes in the SERS spectra of **1a,b** induced by addition of Mg(ClO₄)₂ (Figure 5a) demonstrates that interaction of crown ether with silver in our SERS-active system is relatively weak and no disturbance of the complexation of **1a,b** to Mg²⁺ happens.

The SERS spectra of complexes of **2** with Mg²⁺ were recorded at the same ionophore/Mg²⁺ ratios as for **1a,b** but at

the much higher (ca. 5 × 10⁻⁴ M) concentration of ionophore (Figure 5b). As mentioned in the previous section, SERS spectra of **2** and **1a,b** are very similar showing a preferential adsorption of **1a,b** through its benzo-15-crown-5 fragment on the silver surface. Moreover, the SERS spectrum of **2** was found to be affected upon Mg²⁺ complexation in the same way as for **1a,b**: nearly the same difference spectra of (**1a,b**)/Mg²⁺ minus (**2**)Mg²⁺ (Figure 5c) and **1a,b** minus **2** (Figure 4d) were obtained. A close similarity of the changes in the SERS spectra of **1a,b** and **2** induced by the complex formation as well as the absence of the new bands and remarkable distortion of the relative intensities of the SERS spectra of (**1a,b**)Mg²⁺ compared to (**2**)Mg²⁺ suggest the geometry of adsorption of (**1a,b**)Mg²⁺ on the silver surface is nearly the same as for the free dyes.

The SERS spectra of complexes of *trans* isomers of **1a** or **1b** with Mg²⁺ could be detected selectively in the photostationary mixture of *cis* and *trans* conformers due to the strong resonance with electronic transitions (λ_{\max} = 393 nm) of (*trans*-**1a,b**)Mg²⁺ (Figure 3). The complexes of *cis*-**1a,b** with Mg²⁺ do not absorb light in the 457–514 nm region and cannot be detected by the SERS spectroscopy at concentrations less than 10⁻⁴ M. The SERS spectra of (**1a,b**)Mg²⁺ measured in the photostationary state at different (10⁻⁵–10⁻⁸ M) concentrations of the dyes were found to be identical and well corresponding to the resonance Raman spectra of *trans* isomer's complexes. Moreover, even if the photostationary states with more than 99% of the *cis* complex were prepared by long irradiation of the dye solution with the 457.9, 488, or 514.5 nm laser light, no bands corresponding to the complexes of the *cis* isomers with Mg²⁺ were detected in the SERS spectra. Hence, the contribution of the (*cis*-**1a,b**)Mg²⁺ to the SERS spectra of the dyes was said to be negligible.

Conclusion

The results demonstrate the potency of the SERS spectroscopy in the studies of non-aqueous solutions of photochromic crown ether dyes in the wide range (10⁻⁴–10⁻⁸ M) of dye concentrations and cation/dye ratios. The high sensitivity and selectivity of the SERS spectroscopy relative to *trans* isomers of **1a,b** and their complexes with Mg²⁺ are explained by the coupling of the resonance Raman effect with the surface-induced enhancement. An interaction of the molecules with the surface of the silver electrode does not disturb the complexation of the ionophores to Mg²⁺. Consequently, the structure and self-association of the photochromic crown ether dyes both in free and complexed form can be studied by SERS *in situ* at concentrations unachievable with other spectroscopic techniques. The SERS study of Mg²⁺-dependent dimeric aggregation of the dyes in dilute solutions, as well as the structure of dimers as a function of the state of molecular isomerization, is a subject of our current research.

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Registry No. **2**, 3, 5, 6, 8, 9, 11, 12-octahydro-1, 4, 7, 10, 13-benzopentaoxacyclopentadecin, 69271-98-3; Ag, 7440-22-4.

References and Notes

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