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Surface-Enhanced Raman Scattering Spectroscopy of Organometallics in Systems with Aqueous Silver Colloids

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SERS (surface-enhanced Raman scattering) spectra of $[\text{Re}(\text{CO})_3\text{Br}]\text{L}$ ($\text{L} = \text{dpp} = 2,3\text{-bis}(2'\text{-pyridyl})\text{pyrazine}$, $\text{bpm} = 2,2'\text{-bipyrimidine}$, and $\text{bpy} = 2,2'\text{-bipyridine}$) complexes were investigated in systems with an aqueous Ag colloid. The organometallic species were added to the aqueous Ag colloid as solutions in dimethyl sulfoxide (DMSO). SERS spectra of DMSO and of the dpp and bpm ligands are also reported. Chemisorption of DMSO via the oxygen atom as well as co-adsorption of DMSO and of the complexes on the surface of Ag colloid was proved. The role of DMSO in formation of the SERS-active systems with the organometallics was elucidated. Good quality SERS spectra were obtained for the complexes with the tetradentate ligands $\text{L} = \text{dpp}$ and bpm , while, for the complex with bidentate ligand $\text{L} = \text{bpy}$, no SERS spectra were obtained. The difference is explained by chemisorption of the complexes with $\text{L} = \text{dpp}$ and bpm via the two uncoordinated N-atoms on the surface of Ag colloid in contrast to the absence of this interaction for the complex with $\text{L} = \text{bpy}$, in which the sites for chemisorption are absent. Formation of the $\text{Ag}_n^+ - \text{L} - \text{Re}(\text{CO})_3\text{Br}$ ($\text{L} = \text{dpp}$, bpm) heterobinuclear surface complexes is thus postulated.

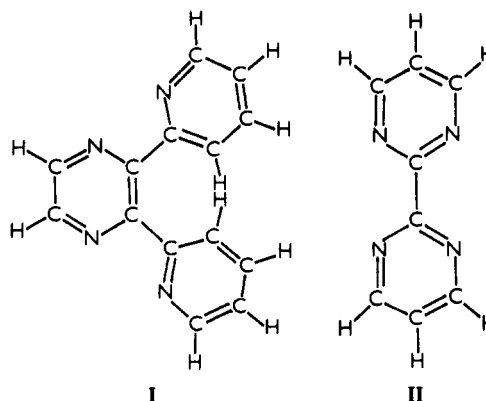
Introduction

The possibilities of SERS (surface-enhanced Raman scattering) spectral investigations of water-insoluble species are currently being explored. While silver electrodes are known to be the suitable surfaces for SERS experiments in the nonaqueous media,¹⁻³ applications of Ag colloids for this purpose are still rather limited. Two ways of preparation of Ag colloids in the nonaqueous media have been reported.^{4,5} However, the organosols are substantially less stable than the hydrosols and their utilization for SERS experiments usually requires addition of stabilizers.^{4,5} Investigation of the sparingly water-soluble species in MELLFs (metal liquidlike films) formed from the aqueous Ag colloid and the solution of the species in a water-immiscible solvent appears to be the more prospective alternative.⁶⁻⁹

In this paper, SERS spectra of sparingly water-soluble organometallics species measured directly in the system with an aqueous Ag colloid are reported. Tricarbonyl polypyridyl complexes of Re(I), which are currently the focus of interest for their photo- and electrocatalytic activity,^{10,11} were selected as model organometallics for this study. For these complexes, the prospect

of obtaining vibrational spectroscopic information from their SERS spectra is highly attractive, as resonance Raman (RR) spectral studies are hindered by the location of the lowest electronic transition around 400 nm,^{10,11} i.e. outside the range of the commonly used excitation wavelengths. Moreover, SERS spectroscopy provides a unique possibility of quenching the luminescence which seriously disturbs the RR spectra.

In particular, the $[\text{Re}(\text{CO})_3\text{Br}]\text{L}$ complexes (**C1**, **C2**, **C3**) where $\text{L} = \text{dpp} = 2,3\text{-bis}(2'\text{-pyridyl})\text{pyrazine}$ (**I**), $\text{bpm} = 2,2'\text{-bipyri-$



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midine (**II**), and $\text{bpy} = 2,2'\text{-bipyridine}$ were investigated. While the dpp and bpm ligands in the **C1** and **C2** complexes, respectively, are bidentately coordinated tetradentate ligands, bpy (in **C3**) is a bidentately coordinated α -diimine (i.e. bidentate) ligand. The special characteristic of the **C1** and **C2** complexes is thus the presence of two uncoordinated nitrogen atoms which represent the possible sites for chemisorption of **C1** and **C2** on the surface of Ag colloid. By contrast, no such sites are available in **C3**, as the coordination ability of the bpy ligand is already saturated by coordination to Re(I).

Preparations of the SERS-active systems are based on addition of the solution of the organometallic species (**C1**, **C2**, and/or **C3**)

in a particular, water-miscible solvent to aqueous Ag colloid. The choice of the solvent is the crucial point of the study, as the solvent can play an important role in formation of the SERS-active system. On the basis of the preliminary experiments, we have selected DMSO (dimethyl sulfoxide), which meets two elementary criteria: miscibility with water and a sufficient solubility of the complexes C1, C2, and C3 (10^{-3} M solutions). Furthermore, the experiments with the Ag sol prepared in DMSO⁵ give credit for the expectation that addition of DMSO will not seriously destabilize the aqueous Ag colloid. Finally, solvation of the complexes by DMSO can protect the complexes against a slow hydrolysis undergone in aqueous media.

Particularly, our effort is concentrated on answering the following questions: (1) Can the organometallic species added to Ag colloid as a solution in DMSO be adsorbed on the surface of Ag colloid and yield a SERS spectrum? (2) Is DMSO co-adsorbed with the complex on the surface of Ag colloid? (3) Does the presence of the uncoordinated N-atoms in the structure of C1 and C2 in contrast to their absence in C3 seriously influence the adsorption of the complexes on the surface of Ag colloid and, consequently, their SERS spectra?

To accomplish this task, we have investigated the SERS spectra of the Ag colloid/(complex + DMSO) systems (complex = C1, C2, C3) at two excitation wavelengths, together with the SERS spectra of the dpp and bpm ligands and of DMSO. The SERS spectra of bpm are compared with the data previously published,^{12,13} while the SERS spectra of DMSO and dpp are newly reported.

Experimental Section

Ag colloid was prepared by reduction of silver nitrate by sodium borohydride using the procedure described in ref 14. C1, C2, and C3, were synthesized according to the procedures described in ref 15–19. Ag colloid/(complex + DMSO) SERS-active systems were prepared by adding 30 μ L of the 10^{-3} M solution of C1, C2, or C3 in DMSO to 3 mL of the aqueous Ag colloid (aged for 1 day in the dark). The final concentrations of C1 and C2 (system II) and/or C3 in the systems were 10^{-5} M. In addition, preparation of the Ag colloid/(C2 + DMSO) system (system I) with a lower concentration of C2 ($c_{C2} = 3.3 \times 10^{-6}$ M) was accomplished by adding 10 μ L of the 10^{-3} M solution of C2 to 3 mL of Ag colloid. The Ag colloid/DMSO system was prepared by adding 30 μ L of DMSO to 3 mL of the aqueous Ag colloid. All the above systems were SERS-active within 2 h after preparation. Ag colloid/dpp and Ag colloid/bpm systems: 10 μ L of a 10^{-2} M aqueous solution of the ligand was added to 3 mL of the aqueous Ag colloid, and the SERS spectra of the resulting systems were investigated immediately after preparation.

SERS spectra were measured on a multichannel Raman spectrometer Dilor XY using a Spectra Physics 2016 argon ion laser as the source of the exciting radiation, both directly ($\lambda_{exc} = 514.5$ nm) and indirectly in conjunction with a Coherent Radiation Model CR 590 dye laser, using Rhodamine 6G as a dye ($\lambda_{exc} = 569$ nm). Laser power at the sample was 30 mW. The SERS spectra presented are the results of 20 spectral accumulations (accumulation time 10 s). UV/vis absorption spectra were measured with a Perkin-Elmer Lambda 5 spectrometer. For both types of measurements, the samples were placed in quartz cells (10-mm optical path).

Results

Surface Plasmon Absorption (SPA) Curves of SERS-Active Systems. The SPA curves of the Ag colloid/DMSO, Ag colloid/

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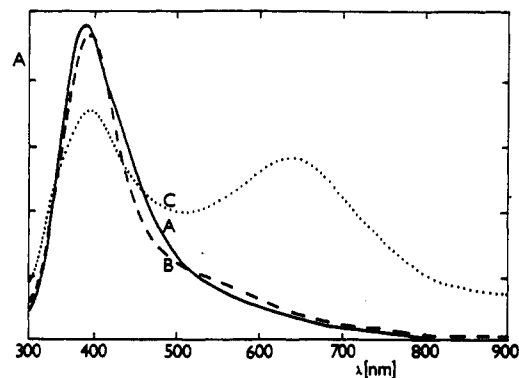


Figure 1. Surface plasmon absorption (SPA) of SERS-active systems: (A) Ag colloid/DMSO; (B) Ag colloid/[Re(CO)₃Br]bpm in DMSO; (C) Ag colloid/bpm.

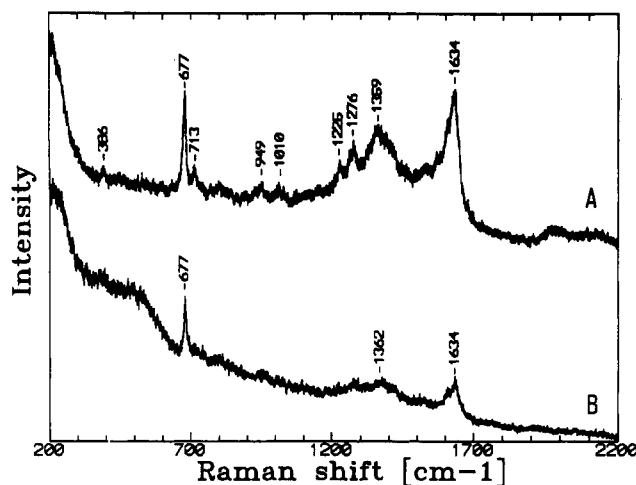


Figure 2. SERS spectra of Ag colloid/DMSO system excited at (A) 514.5 nm and (B) 569 nm.

Table 1. Comparison of SERS and Raman Spectra of DMSO in the 350–1700-cm⁻¹ Region ($\lambda_{exc} = 514.5$ nm)

SERS	Raman	assgnt
1634		$\delta(\text{H-O-H})$
1359	1418	$\delta(\text{CH}_3)$
1276, 1225	1315	$\delta(\text{CH}_3)$
1010	1047	$\nu(\text{S=O})$
949	959	$\rho(\text{CH}_3)$
713	697	$\nu(\text{C-S})$
677	666	$\nu(\text{C-S})$
386	384	$\delta(\text{C-S-C})$

C2 in DMSO, and Ag colloid/bpm systems are compared in Figure 1. While the SPA curves of the Ag colloid/DMSO (curve A) and Ag colloid/C2 in DMSO (curve B) are strikingly similar, they both differ substantially from the SPA curve of the Ag colloid/bpm system (curve C). Differences in the SPA curves are usually interpreted in terms of differences in the internal structure of the aggregates. The comparison of the SPA curves (Figure 1) thus indicates that the aggregation pattern of the Ag colloid/C2 in DMSO system is similar to that of the Ag colloid/DMSO system, which, in turn, demonstrates that adsorption of DMSO plays an important role in the formation of the Ag colloid/complex + DMSO systems.

SERS Spectra of the Ag Colloid/DMSO System. SERS spectra of the Ag colloid/DMSO system measured with the 514.5- and 569-nm excitations are shown in Figure 2. Several bands at 1634, 1359, 1276, 1225, 1010, 949, 713, 677, and 386 cm^{-1} are observed in the SERS spectrum measured at 514.5-nm excitation (Figure 2A), while only the two most intense of the bands at 1634 and 677 cm^{-1} appear in the SERS spectrum excited at 569 nm (Figure 2B). The observed bands have their counterparts in the normal

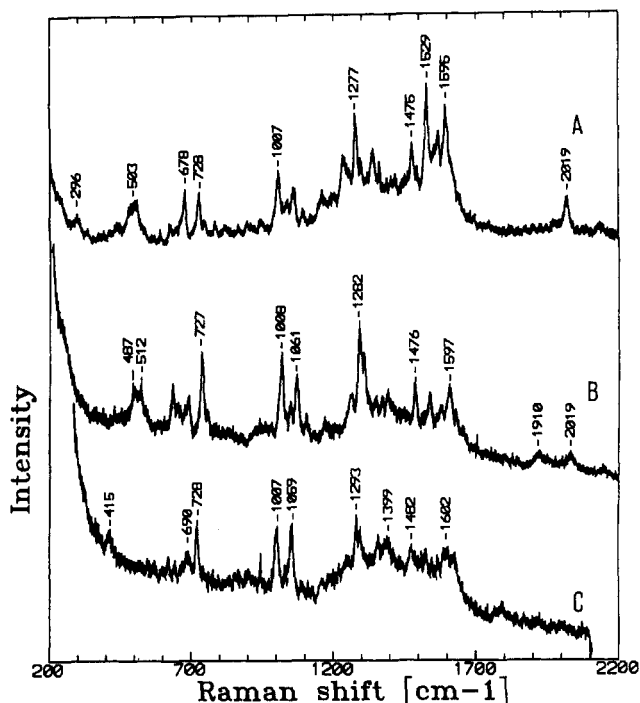


Figure 3. SERS spectra of (A) Ag colloid/[Re(CO)₃Br]dpp in DMSO; 514.5-nm excitation, (B) the same as (A), 569-nm excitation, and (C) Ag colloid/dpp; 569-nm excitation.

Raman spectrum of DMSO (Table 1), the only exception being the band at 1634 cm⁻¹ attributed here to the δ (H–O–H) mode of water molecules associated with DMSO. Analogous bands were observed in SERS spectra of Triton X-100,²⁰ Polyethylenglycol 400,²⁰ and bovine serum albumin.²¹

The most significant differences between the SERS and the normal Raman spectra of DMSO are (1) the apparent (–37 cm⁻¹) shift of δ (S=O), which indicates coordination of DMSO to Ag_n⁺ active sites²² via the lone electron pair located on the oxygen atom,^{23,24} and (2) low-frequency shifts of the bands of the methyl deformation modes accompanied with the splitting of the δ_d (CH₃) band into a doublet. The latter changes can be explained in the following manner: Upon chemisorption of DMSO to the silver surface via oxygen, the methyl groups are located very close to the surface, as the C₂–S–O skeleton of the DMSO molecule is bent (C_s symmetry). The close proximity of CH₃ groups to the surface can account for the observed splitting and shifts of their SERS spectral bands. The above spectral analysis thus provides the basis necessary for inspection of SERS spectra of the Ag colloid/complex + DMSO systems for the presence of the bands of DMSO.

SERS of ReBr(CO)₃dpp–C1. SERS spectra of C1 measured at 514.5 and 569 nm are shown in Figure 3A,B. The frequencies of the SERS-active modes are listed in Table 2. These modes can be categorized into several groups:

(1) The majority of the spectral bands have their counterparts in the SERS spectrum of the dpp ligand measured in the Ag colloid/dpp system (Figure 3C). The comparison of the wavenumbers of bands in SERS of dpp and of C1 (Table 2) indicates either the coincidence or small frequency shifts (up to 13 cm⁻¹) of the corresponding bands.

(2) The characteristic bands of ν (CO) are observed at 2019 cm⁻¹ (both at 514.5- and 569-nm excitation, Figure 3A,B) and

Table 2. Wavenumbers (cm⁻¹) of Bands Observed in the SERS Spectra of the dpp Ligand and the ReBr(CO)₃dpp Complex

dpp (514.5, 580 nm)	ReBr(CO) ₃ dpp	
	514.5 nm	568 nm
1628		
1602	1595	1597
	1569	1568
1535	1529	1529
1482	1475	1476
1400	1415	
1370	1362	1362
	1338	1338
1302	1297	1297
1293	1277	1282
		1253
1231	1235	
	1161	1159
	1092	1094
1059	1060	1061
	1039	1039
1007	1007	1008
904	946, 916	941
862	862, 819	
	783, 748	
728	728	727
690		
	678 ^a	681 ^a
618	628	625
	503, 487	512, 487
415		
219	296	

^a Bands of DMSO.

1910 cm⁻¹ ($\lambda_{exc} = 568$ nm, Figure 3B). The band at 2019 cm⁻¹ most probably belongs to the in-phase symmetric ν (C–O) vibrational mode of all three carbonyls. An analogous band is observed in the RR spectra of the complexes containing the [Re(CO)₃Br]L unit.^{25,26} The band at 1910 cm⁻¹ has its counterpart in a doublet at 1922 and 1902 cm⁻¹ observed in the IR spectrum of [Re(CO)₃Br]L^{11,25} and assigned to the out-of-phase asymmetric ν (C–O) modes.

(3) The doublet 512, 487 cm⁻¹ and/or the broad band at 503 cm⁻¹ is attributed to Re–C stretching vibrations. The assignment is confirmed by observation of their counterparts in SERS of C2.

The simultaneous observation of the Re–C and the carbonyl stretching modes together with the vibrational modes of dpp (not fully identical with those of the adsorbed dpp ligand) in the SERS spectra of C1 indicates that the complex has been adsorbed on the surface of Ag colloid without decomposition into the individual components.

Furthermore, the presence of the characteristic marker band of DMSO at 678 (681) cm⁻¹ in the SERS spectra of the Ag colloid/C1 + DMSO system (Figure 3A,B) indicates that DMSO is co-adsorbed with the complex on the Ag colloidal surface.

Besides the bands discussed above, several additional bands are observed in SERS at C1, in particular those at 1569, 1338, 1161, and 1092 cm⁻¹ and a group of bands in the 700–1000-cm⁻¹ spectral region (Table 2). Their origin is discussed below.

SERS of ReBr(CO)₃bpm–C2. SERS spectra of C2 were investigated in two types of Ag colloid/C2 + DMSO systems: system I (Figure 4) and system II (Figure 5). The concentrations of both C2 and DMSO are three times higher in system II than in system I while the C2:DMSO ratio is identical in both systems.

Several common spectral characteristics have been found in the SERS spectra of both systems I and II (Table 3):

(1) Spectral bands which exactly correspond to those of bpm adsorbed on Ag colloid are observed at both 514.5- and 569-nm

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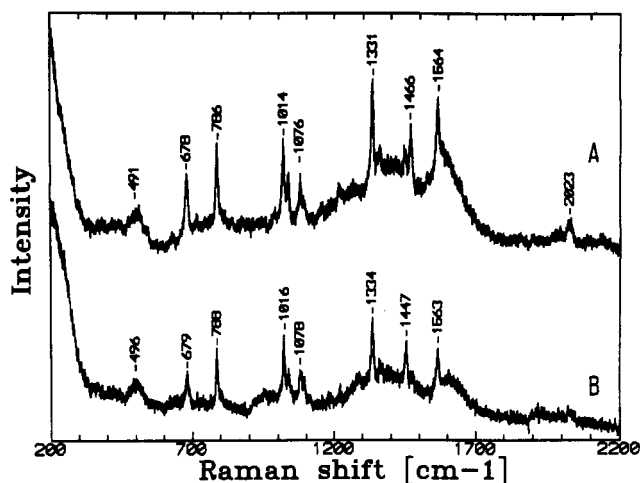


Figure 4. SERS spectra of Ag colloid/[Re(CO)₃Br]bpm in DMSO-system I: (A) 514.5 nm; (B) 569 nm.

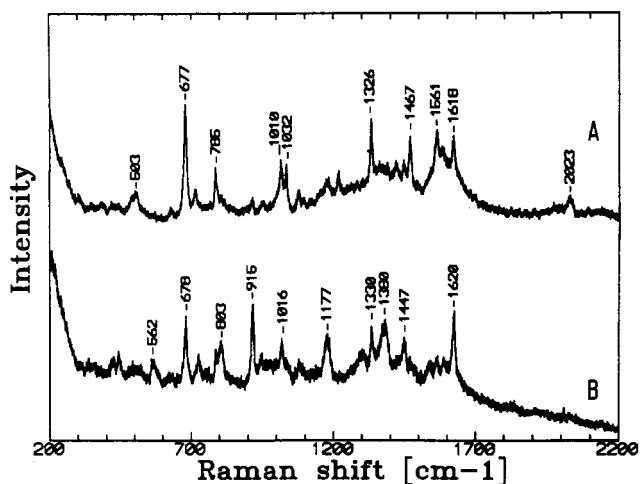


Figure 5. SERS spectra of Ag colloid/[Re(CO)₃Br]bpm in DMSO-system II: (A) 514.5 nm; (B) 569 nm.

excitation (Table 3). The vibrational frequencies of adsorbed bpm as listed in Table 3 are in a good agreement with those reported in ref 12.

(2) The band at 2023 cm⁻¹ attributed to $\nu(\text{CO})$ is observed in the SERS spectra excited at 514.5 nm (Figures 4A and 5A), while, in the spectra measured at 569-nm excitation, this band is almost missing.

(3) The broad band observed at 491 (Figure 4A), 496 (Figure 4B), and 503 cm⁻¹ (Figure 5), respectively, is assigned to the Re-C stretching mode. This assignment is corroborated by observation of the analogous bands (doublet 487 and 512 cm⁻¹ and/or the broad band at 503 cm⁻¹) in the SERS spectra of C1, in which the arrangement of donor atoms in the coordination sphere of the Re(I) central atom is analogous to that in C2.

(4) Two additional bands which do not coincide with the SERS-active bands of adsorbed bpm are observed at 1466 cm⁻¹ (upon 514.5-nm excitation) and at 1035 cm⁻¹ (at both 514.5- and 569-nm excitation) (Table 3).

(5) The characteristic marker band of DMSO at 678 cm⁻¹ is observed in all the SERS spectra in Figures 4 and 5 indicating thus the co-adsorption of DMSO and C2 on the surface of Ag colloid.

On the other hand, there are also remarkable difference between SERS spectra of system I and system II. Most importantly, SERS spectra of system II (Figure 5) show a series of bands which do not have any counterparts in SERS of system I (Figure 4). The wavenumbers of these additional bands are listed in Table 3. The relative intensities of the additional bands with

Table 3. Wavenumbers of Bands (cm⁻¹) Observed in SERS Spectra of the bpm Ligand and of the ReBr(CO)₃bpm Complex

bpm ($\lambda_{\text{exc}} = 569 \text{ nm}$)	ReBr(CO) ₃ bpm			
	c for $\lambda_{\text{exc}} = 514.5 \text{ nm}$		c for $\lambda_{\text{exc}} = 569 \text{ nm}$	
	$3.3 \times 10^{-6} \text{ M}$	10^{-5} M	$3.3 \times 10^{-6} \text{ M}$	10^{-5} M
			1618	1620
			1581	1585
1564	1564	1561	1563	1560
				1537
1466	1466	1467		
	1446	1442	1447	1447
		1418		
1326	1356			
	1331	1326	1334	1330
				1301
	1215	1212		
	1154			
		1173		1177
1076	1076	1075	1078	1083
	1035	1032	1035	
1076	1014	1010	1016	1016
		953		949
		910		915
				803
786	786	785	788	783
	705 ^a	713 ^a		724 ^a
	678 ^a	677 ^a	679 ^a	678 ^a
	622	622		
	491	503	496	562
				503
				440
				424

^a Bands of DMSO.

respect to the "common" bands (e.g. those of coordinated bpm) increase with the excitation wavelength shifting from 514.5 to 569 nm. Furthermore, there is a difference between the systems I and II in the relative intensity changes of the $\nu(\text{Re}-\text{C})$ band at 491/496 cm⁻¹ (Figure 4, system I) and 503 cm⁻¹ (Figure 5, system II) upon shifting the excitation wavelength from 514.5 to 569 nm. In SERS of system I (Figure 4), this band is observed with about the same relative intensity (with respect to the bands of coordinated bpm ligand) at both the 569 and 514.5 nm. By contrast, in SERS of system II, the band active at 514.5 nm (Figure 5A) is almost missing at 569-nm excitation (Figure 5B). Finally, comparing the intensity of the DMSO marker band (678 cm⁻¹) to that of the most intense band of C2 (1331 cm⁻¹ in Figure 4A, 1326 cm⁻¹ in Figure 5A; $\lambda_{\text{exc}} = 514.5 \text{ nm}$), we find out that the intensity ratio in SERS of system I (0.7) is markedly different from that in SERS of system II (1.7) despite the fact that the concentration ratios of DMSO:C2 are identical for both systems. The fact that co-adsorption of DMSO and C2 is not governed simply by the ratios of the adsorbate concentrations points to some kind of interaction between C2 and DMSO occurring prior to the adsorption, such as solvation of C2 by DMSO.

SERS of ReBr(CO)₃bpy-C3. The SERS spectra of C3 in the Ag colloid/C3 + DMSO system were investigated at the 514.5- and 569-nm excitation. The spectra obtained are very similar to those of Ag colloid/dmsol system shown in Figure 1A,B. This fact indicates that C3 does not experience the surface enhancement of Raman scattering and is thus most probably not adsorbed on the surface of Ag colloid.

SERS of C1 and C2 in the Absence of DMSO. SERS spectra of samples prepared by adding saturated (approximately 10⁻⁴ M) aqueous solutions of C1 and C2, respectively, to aqueous Ag colloid were measured. Poor quality SERS spectra (not shown here) consisting of only weak and broad bands were obtained. This experiment proves an important role of DMSO in obtaining good quality SERS spectra of organometallic species C1 and C2 in systems with aqueous Ag colloids.

Discussion and Conclusion

The above results show that of the three organometallic species investigated in the Ag colloid/complex + DMSO system, C1 and C2 yielded good quality SERS spectra, while the SERS spectra of C3 could not be obtained. The presence of two uncoordinated N-atoms in the structure of C1 and C2 is thus proved to be essential for adsorption of the species on the surface of Ag colloid under the conditions of their administration to the aqueous Ag colloid in the form of a solution in DMSO.

Co-adsorption of DMSO with C1 and C2, respectively, is demonstrated by the presence of the typical marker band at 678 cm^{-1} (belonging to the $\nu_s(\text{C-S})$ mode of adsorbed DMSO) in the SERS spectra of both C1 and C2. Analysis of the SERS spectrum of the Ag colloid/DMSO system shows that DMSO is chemisorbed on the surface of Ag colloid. The fact that the C1 and C2 complexes are adsorbed on the surface together with the chemisorbed DMSO indicates that C1 and C2 compete successfully with the chemisorbed DMSO for the active sites (most probably Ag_n^+ clusters²²) and thus have to be chemisorbed, too. By contrast, due to the absence of the N-donor atoms suitable for chemisorption, the C3 complex can only be physisorbed. The substantially lower ΔG of adsorption thus disables the C3 in the competition with DMSO. This is the reason why only the spectral features of DMSO are observed in SERS of C3.

The importance of the presence of DMSO in the SERS-active systems with C1 and/or C2 and the aqueous Ag colloid is demonstrated by the contrast between the SERS spectra in Figures 3–5 and the poor quality spectra obtained in absence of DMSO. A dual role of DMSO in the SERS-active system with the organometallics can be envisaged: (1) solvation of the complexes by DMSO and their protection from a slow hydrolysis undergone in aqueous media (witnessed by the nonregularity of the concentration dependence of the SERS signal of the complexes in comparison to that of DMSO); (2) rapid chemisorption of DMSO on the surface of Ag colloid promoting aggregation of the colloid and, consequently, formation of the SERS-active system (corroborated by the similarity of the SPA curves of the Ag colloid/DMSO and the Ag colloid/complex + DMSO systems).

For a correct interpretation of the SERS spectra of C1 and C2, the effect of their chemisorption on the Ag surface onto their molecular structure had to be considered in detail. The difference in the adsorption abilities of C1 and C2 and of C3 indicates that C1 and C2 are chemisorbed via the bidentate coordination of two N-atoms of the dpp and/or bpm ligands to a silver active site Ag_n^+ in a manner similar to chemisorption of the free ligands dpp and bpm. Formation of the $\text{Ag}_n^+ - \text{dpp} - \text{Re}(\text{CO})_3\text{Br}$ and the $\text{Ag}_n^+ - \text{bpm} - \text{Re}(\text{CO})_3\text{Br}$ heterobinuclear surface complexes is thus postulated.

Furthermore, formation of the heterobinuclear surface complexes appears to be the most probable reason for observation of the "additional" bands (i.e. those which do not correspond to the bidentately coordinated ligand) in the SERS spectra of C1 and C2 complexes: The SERS-active bands show pronounced and diverse changes of their intensity with only a moderate shift (55 nm) of the excitation wavelength which is not typical for SERS excitation profiles. On the other hand, it is well-known that the synthetically prepared heterobinuclear complexes involving the $\text{Re}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}$) fragment and dpp and/or bpm as bridging ligands bound to another metal-containing fragment, e.g. $[\text{Ru}(\text{bpy})_2]^{2+}$, show a distinct shift of the absorption band of the MLCT transition of higher wavelengths^{15,16} (e.g. for $[(\text{bpy})_2\text{Ru}-\text{bpm}-\text{Re}(\text{CO})_3\text{X}]$, the shift is from 384 to 558 nm¹⁵). It can well be expected that such a shift of the MLCT band will occur also in the case of the $\text{Ag}_n^+ - \text{L} - \text{Re}(\text{CO})_3\text{X}$ ($\text{L} = \text{dpp}, \text{bpm}$) surface complexes. Interestingly, for the $(\text{CO})_5\text{Mn}-\text{Re}(\text{CO})_3-\text{bpm}-\text{Re}(\text{CO})_3\text{X}$ complex, the absorption bands belonging to two different MLCT transitions were observed.²⁶ The low-energy transition is localized on the binuclear $\text{Re}-\text{Mn}$ fragment, while the high-energy transition is attributed to the MLCT transition of the mononuclear $[\text{Re}(\text{CO})_3\text{Br}]$ fragment. Different sets of bands, both attributed to the bpm ligand, were observed in the RR spectra of the complex when the excitation wavelength was brought to resonance with one or the other electronic transition. Similarly, the comparison of the RR spectra of $[(\text{bpy})_2\text{Ru}-\text{dpp}-(\text{bpy})_2\text{Ru}]^{4+}$ with those of its monomeric analogue showed a wavelength-dependent activation of two different sets of spectral bands for the bidentately and the tetradentately coordinated dpp.²⁷ The most probable explanation of the wavelength-dependent presence and/or absence of the "additional" bands in the SERS spectra of C1 and C2 complexes is thus a wavelength-selective activation of vibrational modes of the tetradentately coordinated bpm and/or dpp ligand via the additional contribution of the resonance enhancement of Raman scattering upon excitation into the absorption band of the MLCT transition of the $\text{Ag}_n^+ - \text{dpp} - \text{Re}(\text{CO})_3\text{Br}$ and/or the $\text{Ag}_n^+ - \text{bpm} - \text{Re}(\text{CO})_3\text{Br}$ heterobinuclear surface complexes. This explanation should be verified by a more detailed investigation of the excitation wavelength dependence of the SERS (and/or SERRS) spectra of the surface complexes formed from C1 and C2. This work is currently in progress in our laboratories and will be the subject of our forthcoming paper.

In conclusion, this paper proves that SERS spectroscopy in systems with Ag colloids not only is able to provide vibrational spectroscopic information on organometallics species but offers a unique possibility to follow the surface chemistry of organometallics.

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