of radiationless decay by the micellar environment which immobilize the cyanine dyes to some extent. The polarity present in the local environment of the dyes was not related to the fluorescence yield.[12] The microviscosity of SDS micelle measured near room temperature is reported to be about 15-30 cp,[17] which is significantly higher than in methanol. Although the exact location of the dye within the micellar region is not known we may assume that TX-100 micelle has similar microenvironment as SDS micelles based on the experimental results that in both micellar media, Rh6G$^+$ showed nearly the same fluorescence spectral behavior.

On the other hand, the most effective deaggregation by CTAB is apparently achived in a different way. Rh6G$^+$ is effectively repelled from like-charged CTA$^+$ or its micelle electrostatically due to the relatively high concentration of surface charge and exists predominantly as monomeric species as evidenced by essentially no spectral shift. Instead it is quite possible that TPB$^-$ may be incorporated into the micellar media,[18] which inhibits the ion-pairing and aggregation.

Attractive electrostatic interaction occuring between surfactant and Rh6G$^+$ may be not strong enough to differentiate significantly the spectral behaviors in the presence of SDS from those in TX-100. However, the minimum concentration of TX-100 required to dissociate completely Rh6G$^+$-TPB$^-$ aggregates was larger than its cmc in pure water while that of SDS was found to be less than its cmc in pure water possibily due to the weaker electrostatic interaction with TX-100.

In summary, the hydrophobic interaction led to the formation of Rh6G$^+$-TPB$^-$ aggregates is overwhelmed by a stronger micellar interaction with the dye or the ion pairs. The cationic dye predominantly exists as a monomeric species while it may incorporate into nonionic or anionic micellar environment.

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Surface Enhanced Raman Scattering of Methoxybenzonitriles in Silver Sol

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The surface-enhanced Raman scattering(SERS) of methoxybenzonitrile in a silver sol was investigated. All of ortho-, meta-, and para-substituted benzonitriles were found to adsorb on the silver surface via the nitrogen lone pair electrons. The benzene ring of meta derivative seemed likely to stand perpendicular to the silver surface, while the benzene rings of both ortho and para derivatives assumed tilted stances with respect to the surface. The SERS technique appeared to be a useful means to study the substituent electronic effects.

Introduction

The surface-enhanced Raman scattering(SERS) technique has been demonstrated to be a powerful tool in the study

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of interfacial structures at the molecular level[1]. Specifically, information regarding the chemical identity, structure and orientation of the species at the interfaces can be readily inferred from the SER spectra.

The benzonitrile molecule has a very interesting char-
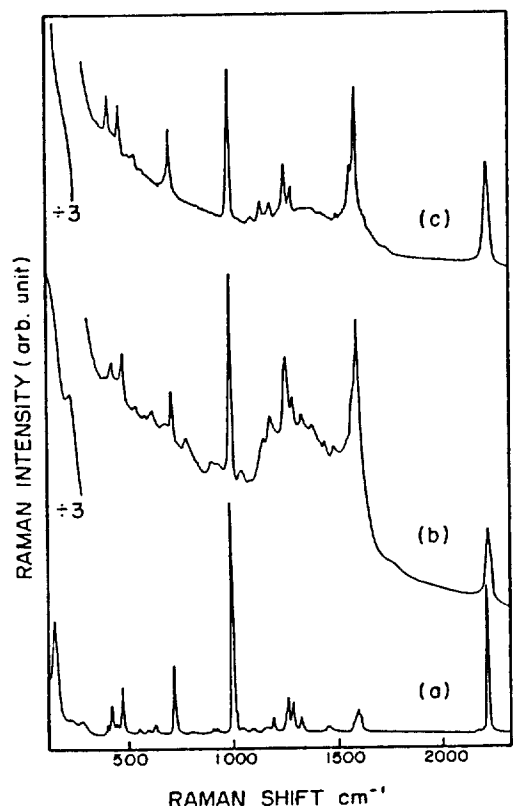
Figure 1. Ordinary Raman spectrum of m-methoxybenzonitrile(a), and its SER spectra in silver sol at neutral pH(b) and at pH 4(c).

acter in that three different binding sites(aromatic ring, π-bond of CN group, and lone pair electrons of nitrogen atom) are available for the adsorption of the molecule on the metal surface[2]. In the SERS study of benzonitrile in Ag sol[3] the molecule appeared to adsorb on the silver surface via the nitrogen lone pair electrons. Although the orientation of the benzene ring with respect to the silver surface plane could not be determined conclusively from the surface selection rule, it seemed likely that the molecule stands perpendicular to the silver surface.

We report here the SERS of ortho, meta, and para methoxybenzonitriles in aqueous silver sol. The primary objective of this work is to investigate whether the observations found for benzonitrile are similarly extendible to substituted benzonitriles. We obtain information on the nature of the chemical bonding between the adsorbate and substrate as well as the orientation of the adsorbed species with respect to the metal surface. In addition, the frequencies of the ν_{CN} mode in adsorbed substituted benzonitriles were briefly discussed in terms of the substituent electronic effects.

Experimental

Preparation and spectral properties of silver sol solution have been reported previously[4]. Raman spectra were obtained with a Japan Spectroscopic Company model R-300 laser Raman spectrophotometer using the 514.5 nm line of an Ar^+ laser(Spectra Physics model 164-06) as an exciting source. Glass capillary tube was used as sampling device and Raman scattering was observed with 90° geometry. Raman signals were detected using a commercial photon counting system.

Methoxybenzonitrile was somewhat unfavorable as an ag-

gregation agent of the silver sol for giving large SERS enhancement. Relatively large amount of methoxybenzonitrile was needed for the silver sol aggregation. The SER spectra were thus obtained by sampling the neat methoxybenzonitriles directly into the silver sols to the final concentration of 10^{-3}M.

The ordinary Raman spectra were obtained for the CCl_4 and CH_3OH solutions containing methoxybenzonitriles by 1%. The solvent peaks were manually substracted to get the sole spectra of methoxybenzonitriles.

All the chemicals used in this work were reagent grade, and triply distilled water was used for preparation of solutions.

Results and Discussion

The ordinary Raman spectrum of m-methoxybenzonitrile and its SER spectrum in silver sol are shown in Figure 1(a) and 1(b), respectively. The latter spectrum has a broad background in the frequency region of 1100-1600 cm^{-1}. The broad band has diminished significantly as the pH of the sol solution was adjusted to 3-4(Figure 1(c)). However, the peak positions of the major vibrational bands were not changed upon the pH adjustment. Above observation was independent of the acid species used. In the case of the SERS of adenine nucleotides reported previously[5], pH of the solution did not affect the sol property or SERS directly. Rather, the effect was indirect through the change in the charged form of the adsorbates. The broad band in the region of 1100-1600 cm^{-1}, which is commonly called 'cathedral peaks', is often attributed to the adsorbed carbonaceous species[6]. Then, the pH decrease in the bulk solution may desorb some of the carbonaceous impurities from the sol surface.

As can be seen from Figure 1, the SER spectrum of m-methoxybenzonitrile is similar to its ordinary Raman spectrum. Hence, it is rather straightforward to correlate the vibrational lines between the two spectra. For example, the major bands associated with the benzene ring vibrational modes[7-9] appeared at 464 (ν_{16b}), 710(ν_4), 993(ν_{12}), 1197 (ν_{15}), 1272(ν_{13}), 1295(ν_3), and 1604(ν_{8a}, ν_{8b}) cm^{-1} in the ordinary Raman spectrum, and the corresponding peaks appeared in the SER spectrum at 477, 714, 994, 1203, 1261, 1294, and 1603 cm^{-1}, respectively.

Even though the SER spectrum and the ordinary Raman spectrum of m-methoxybenzonitrile are quite similar to each other, it is also noticeable that some spectral changes occur following the adsorption of the molecule on the silver sol surface. A few SER bands show significant shifts in frequencies from the ordinary Raman bands. In addition, the widths of some SER bands are quite different from those of the corresponding bands in the ordinary Raman spectrum. Such phenomena may indicate that the electronic structure of m-methoxybenzonitrile is more or less perturbed when the molecule adsorbs on Ag. Details of the spectral differences will be discussed later.

In the vibrational studies of benzene and alkylbenzenes[10-12], the bands due to the ring breathing modes were observed to red shift by ~10 cm^{-1} with the increase in their widths when the molecules adsorb to metal surfaces via the π system of the benzene ring. Such a red shift arises from the bond weakening of the benzene ring system caused by the back donation of the metal d electrons to the benzene ring antibonding π^* orbital. Metal surface is also supposed

to provide an extra vibrational relaxation channel resulting in the increase of the bandwidth of the ring breathing mode.

No appreciable peak shift was observed for the ring breathing mode of m-methoxybenzonitrile as the molecule adsorbed on silver. For instance, the ν_{12} ring breathing mode appeared at 993 and 994 cm^{-1}, respectively, in the ordinary and the SER spectra. The bandwidths were also hardly different from each other. These observations may indicate that the benzene ring is not directly bound to the silver surface via the π system.

It should also be mentioned that some ring modes are blue-shifted by 10-15 cm^{-1} as the m-methoxybenzonitrile adsorbs to silver surface. For instance, the bands due to the ν_{16a}, ν_{16b}, ν_{18a}, ν_2 modes appeared at 418, 464, 1046, and 1159 cm^{-1}, respectively, in the ordinary Raman spectrum whereas the corresponding bands in the SER spectrum appeared at 428, 477, 1055, and 1172 cm^{-1}, respectively. Above blue-shift is supposed to be related with the substituent mass effect rather than with the direct interaction between the benzene ring π system and the metal d orbitals. It is a well-known experimental fact[8,22] that for benzene derivatives with two substituents in meta position the ring modes such as ν_2, ν_{16a}, ν_{16b}, and ν_{18a} are more sensitive to the mass of the substituent than other ring modes. On the other hand, the ring modes such as ν_3, ν_{12}, and ν_{14} are known to be rather insensitive to the substituent. In fact, smaller shifts (< 2 cm^{-1}) were seen for these modes in the SER spectrum of m-methoxybenzonitrile. As mentioned previously, the ν_{12} band appeared at 993 and 994 cm^{-1}, respectively, in the ordinary and the SER spectra. The ν_3 and ν_{14} bands appeared at 1295 and 1334 cm^{-1}, respectively, in the ordinary Raman spectrum and at 1294 and 1336 cm^{-1}, respectively, in the SER spectrum. Regardless of the substituent sensitivity of the peak positions, no distinguishable changes in the bandwidths were observed for the benzene ring modes in the SER spectrum. Hence, it seems that the m-methoxybenzonitrile molecule is bound to the silver surface via the cyano group rather than via the benzene ring itself. In this respect, we now consider the spectral changes associated with the ν_{CN} mode.

In the SER spectrum, the ν_{CN} mode appeared at 2238 cm^{-1}. The bandwidth was measured to be 29 cm^{-1}. The corresponding band occurred at 2231 cm^{-1} in the ordinary Raman spectrum with the 9 cm^{-1} bandwidth. Hence, the ν_{CN} band blue-shifted by 7 cm^{-1} and its bandwidth increased by 20 cm^{-1}. This observation reflects the direct interaction of the ν_{CN} group with the silver surface. As mentioned in the introductory part, however, the CN group can bind to the metal surface through either its π system or the nitrogen lone pair electrons. It is to be determined which of the two sites is actually involved in the adsorption of m-methoxybenzonitrile onto the silver surface.

From the studies of the metal-nitrile complexes and the nitriles adsorbed on the metal surfaces using EELS, XPS, UPS, and other techniques[13-17], it has generally been accepted that the linear coordination(σ-bonding) through the nitrogen lone pair electrons results in an increase in the C $\equiv$ N stretching frequency from that of the free molecule. On the other hand, coordination through the C $\equiv$ N π system is known to result in a decrease in the C $\equiv$ N stretching frequency. Hence, the experimental fact that the ν_{CN} mode blue-shifts by 7 cm^{-1} in the SER spectrum may indicate that the m-methoxybenzonitrile molecule is adsorbed to the silver

Table 1. Frequencies and Relative Raman Intensities of the Ring Modes in the SER and Ordinary Raman Spectra of m-Methoxybenzonitrile, and the Relative Enhancement Factors for the SER Bands

Class	Frequencies(cm^{-1})[a]		Vibrational assignment[b]	Relative enhancement factors[c] I_{SERS}/I_{ORD}
	Ordinary	SERS		
in-plane modes	623(10)	623(10)	6a	1.0
	993(100)	995(100)	12	1.0
	1046(11)	1055(11)	18a	1.0
	1159(11)	1172(16)	2	1.5
	1197(15)	1203(26)	15	1.7
	1272(59)	1261(76)	13	1.3
	1295(31)	1294(17)	3	0.5
	1334(14)	1336(10)	14	0.7
	1604(60)	1603(220)	8a,b	3.7
out-of-plane modes	418(27)	428(15)	16a	0.6
	464(38)	477(28)	16b	0.7
	710(31)	714(24)	4	0.8
	796(62)	777(16)	17b	0.3

[a]Values in parentheses are the normalized peak intensities. [b]Taken from refs. [7,8,9]. [c]Normalized to 1.0 at 993 cm^{-1}.

surface via the nitrogen lone pair electrons. Then, the band near 215 cm^{-1} in the SER spectrum which has no obvious counterpart in the ordinary Raman spectrum of m-methoxybenzonitrile would be attributable to a Ag-N stretching vibration.

Although the molecule adsorbs onto the silver surface via the nitrogen lone pair electrons, the orientation of the benzene ring with respect to the surface plane is still undetermined. The orientation of an adsorbed molecule on the silver surface may be investigated by SERS once its selection rule is known. The surface selection rules proposed by Nichols[18], Moskovits[19], Creighton[20], and Hallmark[21] have one common feature that the vibrational mode having a fairly large normal mode component perpendicular to the surface should be significantly enhanced. On the other hand, the mode having the normal mode component wholly parallel to the surface is negligibly enhanced. In this respect, we have classified the ring modes of m-methoxybenzonitrile into two groups, i.e. out-of-plane modes and in-plane modes. Then, if the benzene ring of m-methoxybenzonitrile stands perpendicular to the surface, the in-plane modes will be more enhanced than the out-of-plane modes. The latter modes will be more enhanced than the former modes when the benzene ring lies flat on the surface.

Table 1 lists the normalized peak intensities and the intensity ratios of the benzene ring modes in the SER spectrum with respect to the corresponding modes in the ordinary Raman spectrum. Vibrational assignments made in Table 1 are based on the works by Varsanyi[8], Green et al.[7], and Goel et al.[9]. Peak intensities were normalized to the intensity of the ν_{12} mode in each spectrum. The SERS-to-ordinary Raman intensity ratios for each Raman peak were then evaluated. It is seen from Table 1 that the surface enhancements for the in-plane modes are, in general, larger than those for the out-of-plane modes. This may indicate that the benzene ring of the m-methoxybenzonitrile molecule stands perpendicular to the silver surface. This would support also
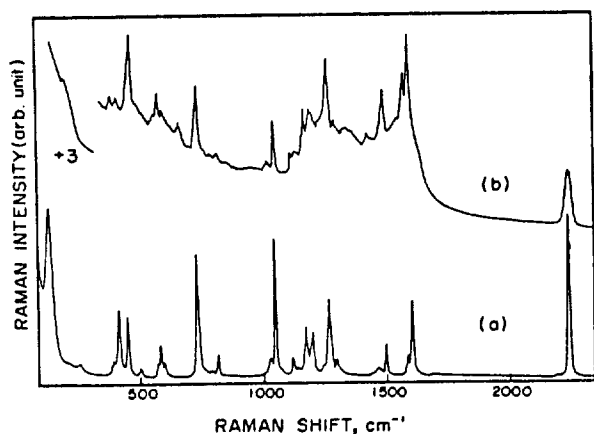
Figure 2. (a) Ordinary Raman spectrum of o-methoxybenzonitrile. (b) SER spectrum of o-methoxybenzonitrile in a silver sol.

Table 2. Frequencies and relative Raman intensities of the ring modes in the SER and ordinary Raman spectra of o-methoxybenzonitrile, and the relative enhancement factors for the SER bands

Class	Frequencies(cm⁻¹)[a]		Vibrational assignment[b]	Relative enhancement factors[c] I_{SERS}/I_{ORD}
	Ordinary	SERS		
in-plane modes	500(6)	495(broad)	6b	—
	596(11)	598(26)	6a	4.1
	730(100)	737(100)	1	1.8
	813(14)	816(8)	12	1.0
	1024(19)	1017(15)	18b	1.4
	1114(7)	1113(16)	18a	4.0
	1166(37)	1166(30)	9a	1.4
	1261(79)	1263(102)	13	2.3
	1459(11)	1423(20)	19a	3.2
	1496(16)	1491(50)	19b	5.5
	1583(13)	1574(72)	8a	9.7
	1599(44)	1595(123)	8b	4.9
out-of-plane modes	452(45)	468(142)	16b	5.4
	571(11)	565(16)	16a	2.5
	789(7)	789(3)	11	0.8

[a]Values in parentheses are the normalized peak intensities. [b]Taken from refs. [7,8]. [c]Normalized to 1.0 at 813 cm⁻¹.

the previous conclusion that the molecule adsorbs to the silver surface via neither benzene ring nor the $C \equiv N$ π system.

Binding through the nitrogen lone pair electrons seemed applicable to other methoxybenzonitriles as well. The ordinary Raman spectrum of o-methoxybenzonitrile and its SER spectrum in silver sol are shown in Figure 2(a) and 2(b), respectively. As was seen in the SER spectrum of m-methoxybenzonitrile, the latter spectrum has a broad background in the frequency region of 1100-1600 cm⁻¹. The broad band has diminished here again as the pH of the sol solution was adjusted to 3-4. The vibrational peak positions as well as the relative intensities of each peak changed negligibly upon the pH adjustment. It was also rather straightforward to correlate the vibrational lines between the ordinary Raman and the SER spectra.

For o-methoxybenzonitrile, there are two kinds of ring breathing modes[8], namely ν_1 and ν_{12}. The bandwidths of these two modes in the SER spectrum are observed to be hardly different from those in the ordinary Raman spectrum. On the other hand, the two modes, ν_1 and ν_{12}, were blue-shifted by 7 and 3 cm⁻¹, respectively, in the SER spectrum from those in the ordinary Raman spectrum. That is, the ν_1 and ν_{12} bands appeared at 737 and 816 cm⁻¹, respectively, in the former spectrum and at 730 and 813 cm⁻¹, respectively, in the latter spectrum.

In ortho-disubstituted benzene, the frequencies of ν_1, ν_{10a}, ν_{10b}, ν_{12}, and ν_{16b} modes are known to be more sensitive to the masses of the substituents than other ring modes[8,22]. The 7 and 3 cm⁻¹ blue-shifts of the ν_1 and ν_{12} modes, respectively, in the SER spectrum of o-methoxybenzonitrile are thus supposed to be caused by the substituent mass effect rather than by the direct interaction between benzene ring π system and the metal d orbitals. In the latter case, both modes should show red shifts, instead of the blue shifts described above, as the molecule adsorbs on the silver surface. Although the ν_{10a} and ν_{10b} modes were hardly observable in the SER spectrum, the remaining substituent sensitive mode, ν_{16b}, was observed to be blue-shifted by 16 cm⁻¹. Specifically, the band appeared at 452 and 468 cm⁻¹, respectively, in the ordinary Raman spectrum and the SER spectra. On the other hand, negligible shifts were seen for the substituent insensitive modes such as ν_3, ν_{9a}, and ν_{18a}.

These bands appeared at 1291, 1166, and 1114 cm⁻¹, respectively, in the ordinary Raman spectrum and at 1291, 1166, and 1113 cm⁻¹, respectively, in the SER spectrum. It should also be mentioned that no appreciable changes in the bandwidths were observed for the benzene ring modes regardless of the substituent sensitivity. Hence, it appears now that the o-methoxybenzonitrile molecule is also bound to the silver surface via its cyano group rather than via the benzene ring itself.

In the SER spectrum of o-methoxybenzonitrile, the ν_{CN} mode appeared at 2234 cm⁻¹ with the bandwidth of 31 cm⁻¹. The corresponding band occurred at 2230 cm⁻¹ with the 10 cm⁻¹ bandwidth. Accordingly, the ν_{CN} band blue-shifted by 4 cm⁻¹ and its bandwidth increased by 21 cm⁻¹ upon the adsorption of the molecule on silver surface. Such a band broadening suggests that the molecule adsorbs to the silver surface via the cyano group. Although the frequency shift is somewhat less than that observed in the case of m-methoxybenzonitrile, the 4 cm⁻¹ blue-shift would be indicative of binding of the molecule to the silver surface via its nitrogen lone pair electrons. Appearance of a band at 215 cm⁻¹ in the SER spectrum of o-methoxybenzonitrile is very likely to support above argument. No obvious analogous band was observed in the ordinary Raman spectrum of the molecule. Moreover, the position of that band is found to be the same as that observed in the SER spectrum of m-methoxybenzonitrile. It is to be recalled that for the latter spectrum, we have already assigned the band at 215 cm⁻¹ to the Ag-N stretching vibration. Hence, it is concluded that both molecules, ortho and meta methoxybenzonitriles, adsorb to the silver surface via their nitrogen lone pair electrons.

To investigate the orientation of the adsorbed o-methoxybenzonitrile, we have classified the benzene ring modes of the molecule into two groups, in-plane modes and out-of-plane modes, as was done for m-methoxybenzonitrile. Table 2 lists the vibrational assignments, normalized peak inten-
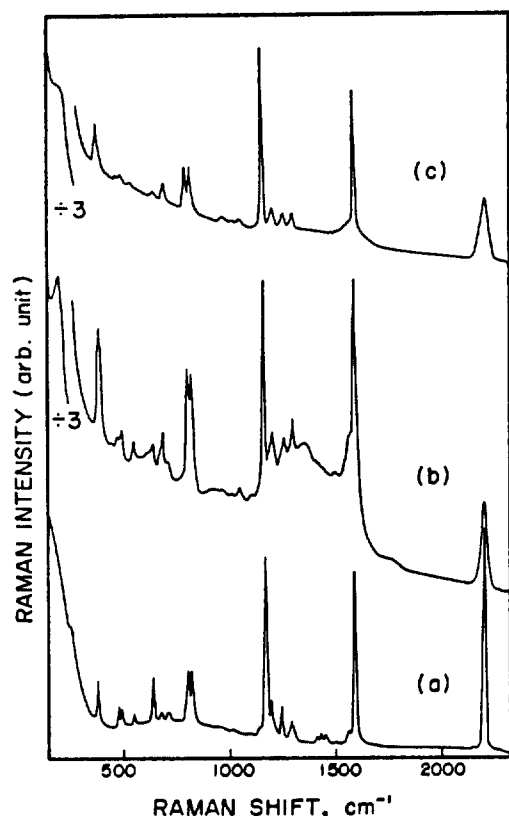
Figure 3. Ordinary Raman spectrum of p-methoxybenzonitrile(a), and its SER spectra in silver sol at neutral pH(b) and at pH 4(c).

Table 3. Frequencies and relative Raman intensities of the ring modes in the SER and ordinary Raman spectra of p-methoxybenzonitrile, and the relative enhancement factors for the SER bands

Class[a]	Frequencies(cm^{-1})[b]		Vibrational assignment[c]	Relative enhancement factors[d] I_{SERS}/I_{ORD}
	Ordinary	SERS		
in-plane modes along z-axis	499(5.1)	504(11)	6a	1.9
	827(36)	826(40)	1	1.0
	1175(97)	1173(100)	2	0.9
	1258(10)	1270(19)	13	1.7
	1609(100)	1602(143)	8a	1.3
in-plane modes along y-axis	384(34)	400(65)	9b	1.7
	646(12)	646(10)	6b	0.8
	1208(21)	1213(54)	15	2.3
	1306(19)	1316(12)	14	0.6
out-of-plane modes	481(7)	486(7)	16b	0.9
	683(5.5)	692(28)	4	4.5
	814(65)	813(42)	17b	0.6

[a]See text. [b]Values in parentheses are the normalized peak intensities. [c]Taken from ref. [9]. [d]Normalized to 1.0 at 829 cm^{-1}.

sities, and relative enhancements for each peak of ortho-methoxybenzonitrile. Here, the intensity of each peak was normalized with respect to that of ν_{12} band. Unlike the case of m-methoxybenzonitrile, the surface enhancements of both the in-plane and out-of-plane modes are rather comparable to each other. Hence, it seems likely that the benzene ring neither lies flat on nor stands perpendicular to the surface but assumes a tilted stance with respect to the surface. Such an orientation may arise, in part, from the steric interaction between the methoxy group and the silver surface.

The ordinary Raman spectrum of p-methoxybenzonitrile and its SER spectrum are shown in Figure 3(a) and 3(b), respectively. As were the cases of ortho and meta derivatives, the broad background in the latter spectrum diminished substantially in the acidic condition without any noticeable change in both the peak positions and the relative intensities. The SER spectrum taken at pH 4 is shown in Figure 3(c).

For p-methoxybenzonitrile, the benzene ring modes such as ν_1, ν_4, ν_{6a}, ν_{9b}, and ν_{13} are substituent sensitive while the modes such as ν_{6b}, ν_{10a}, and ν_{17b} are less sensitive[8,9,22]. The former modes were observed at 827, 683, 499, 384, and 1258 cm^{-1}, respectively, in the ordinary Raman spectrum, whereas at 826, 692, 504, 400, and 1270 cm^{-1}, respectively, in the SER spectrum. Except for the ν_1 mode, the substituent sensitive modes are substantially blue-shifted. On the other hand, the substituent insensitive modes appeared nearly at the same positions for both the ordinary Raman and SER spectra. For instance, the bands due to the ν_{6b}, ν_{10a}, and ν_{17b} modes appeared at 646, 717, and 814 cm^{-1}, respectively, in the ordinary Raman spectrum and at 646, 717, and 813 cm^{-1}, respectively, in the SER spectrum. Regardless of

the substituent sensitivity, the bandwidths of the ring modes were, however, comparable in the two spectra as were the cases of ortho and meta derivatives. These observation would suggest that the p-methoxybenzonitrile is also bound to the silver surface via its cyano group.

In the SER spectrum of p-methoxybenzonitrile, the ν_{CN} mode appeared at 2230 cm^{-1}. The bandwidth was measured to be 33 cm^{-1}. The corresponding band occurred at 2228 cm^{-1} in the ordinary Raman spectrum with the 10 cm^{-1} bandwidth. Hence, the ν_{CN} band blue-shifted by 2 cm^{-1} and its bandwidth increased by 23 cm^{-1}. Such a large increase in bandwidth is, in fact, indicative of the direct interaction of the cyano group with the metal surface. Although the frequency shift in the ν_{CN} mode is not large, the blue-shift itself is supposed to reflect the binding of the molecule to silver surface via the nitrogen lone pair electrons. This is further supported by the following evidence. In the SER spectrum of o- and m-methoxybenzonitriles, we have already assigned the 215 cm^{-1} band to the Ag-N stretching vibration. Similarly, a distinct band appeared at 215 cm^{-1} in the SER spectrum of p-methoxybenzonitrile, having no obvious counterpart in its ordinary Raman spectrum. This could be one supporting evidence for the binding through the nitrogen lone pair electrons. The observation that the ν_{9b} mode is considerably blue-shifted (16 cm^{-1}) as the p-methoxybenzonitrile molecule adsorbs to the silver surface is also very informative. The ν_{9b} mode is, in fact, strongly coupled with the C-CN bending mode. In the coordination chemistry of acetonitrile[23], it is a well-known fact that the C-CN bending mode blue-shifts as the molecule forms a coordination complex through the nitrogen lone pair electrons. Similarly, the large blue-shift in the ν_{9b} mode of p-methoxybenzonitrile may indicate that the molecule adsorbs to the silver surface, indeed, via its nitrogen lone pair electrons.

In order to examine the orientation of an adsorbed p-methoxybenzonitrile, we have classified the ring modes into three groups, *i.e.*, out-of-plane modes and two kinds of in-plane modes. The in-plane modes are divided into two

Table 4. Frequency shifts and SER bandwidths of the ring breathing mode and the ν_{CN} mode in benzonitrile and its methoxy derivatives

	Molecule	ν_{SERS}(cm^{-1})	$\Delta\nu$(cm^{-1})[c]	SER bandwidth (cm^{-1})[d]
Ring-breath-ing mode[a]	benzonitrile[b]	1001	+1	7(5)
	o-methoxy-benzonitrile	816	+3	6(5)
	m-methoxy-benzonitrile	994	+1	7(5)
	p-methoxy-benzonitrile	826	−1	11(8)
C≡N stretch-ing mode	benzonitrile[b]	2244	+14	25(10)
	o-methoxy-benzonitrile	2234	+4	31(10)
	m-methoxy-benzonitrile	2238	+7	29(9)
	p-methoxy-benzonitrile	2230	+2	33(10)

[a]Ring breathing mode is ν_{12} mode for benzonitrile, ortho-, and para-methoxybenzonitrile, but ν_1 mode for p-methoxybenzonitrile. [b]Taken from ref. [3]. [c] $\Delta\nu = \nu_{SERS} - \nu_{ORD}$. [d]Values in parentheses are the bandwidths in the ordinary Raman spectra.

groups, depending on the vibrational axes. The bands such as ν_4, ν_{16b}, and ν_{17b} belong to the out-of-plane modes. The bands such as ν_1, ν_2, ν_{6a}, ν_{8a}, and ν_{13} belong to the in-plane modes which have the normal mode components along the molecular principal z-axis. The modes such as ν_{6b}, ν_{9b}, ν_{14}, and ν_{15} belong to the in-plane vibrations along the molecular y-axis. If the benzene ring plane is parallel to the silver surface, the out-of-plane modes should be more enhanced than the in-plane modes. On the other hand, if the benzene ring is perpendicular to the silver surface, the in-plane vibrations along the z-axis should be more enhanced than other groups.

Table 3 lists the vibrational assignments, peak intensities normalized with respect to the ν_{12} mode, and SERS-to-ordinary Raman intensity ratios. The relative enhancements of these groups are seen to be rather comparable to one another. Hence, the p-methoxybenzonitrile molecule seems to be adsorbed to the silver surface via the nitrogen lone pair electrons with the benzene ring inclined to the surface.

Spectral data on the ring breathing mode and the ν_{CN} mode are collectively summarized in Table 4. For comparison, the spectral data on benzonitrile are also included in Table 4. As far as the ring breathing mode is concerned, no appreciable spectral change occurs following the adsorption of nitrile molecule to silver as mentioned previously. On the other hand, significant spectral change occurs for the ν_{CN} mode. In specific, its bandwidth changes considerably upon the adsorption of nitriles to silver. It is very interesting to notice that the frequency shift in the ν_{CN} mode is quite different for o-, m-, and p-methoxybenzonitriles while the increase in bandwidth is nearly same for these molecules

Various correlations have been reported between substituent constants and infrared absorption frequencies[24-26]. For substituted benzonitriles, the frequency of the ν_{CN} mode was observed to decrease as the resonance donor character of the substituent increases. The methoxy group is a strong

resonance donor and the cyano group is a weak resonance acceptor. The inductive character of the methoxy group in m-methoxybenzonitrile is rather similar to that in p-methoxybenzonitrile. However, the resonance character is very different for the two molecules. It is generally known that the resonance donor power of the methoxy group is much weaker in meta-substituted benzonitrile than in ortho-and para-substituted benzonitriles.

In the ordinary Raman spectra, the ν_{CN} bands of methoxybenzonitriles appeared nearly at the same position as that of the benzonitrile molecule. However, the positions of the ν_{CN} modes in the SER spectra of methoxybenzonitriles are significantly different from that in the SER spectrum of benzonitrile. Specifically, the frequency differences are measured to be 14, 10, and 6 cm^{-1}, respectively, for p-, o-, and m-methoxybenzonitriles. Hence, it appears that the resonance effect of the methoxy group is to become more evident as the methoxybenzonitrile molecules adsorb to the metal surfaces. The observation made here that the substituent effect is in the order of para- > ortho- > meta-isomers is also consistent with the previous infrared studies on various compounds.

When a methoxybenzonitrile molecule adsorbs to metal surface via the nitrogen lone pair electrons, the ν_{CN} band should blue-shift from that of free molecule. However, considering the resonance donor effect of the methoxy group, the amount of blue-shift is not expected to be large. For p-methoxybenzonitrile, the ν_{CN} mode blue-shifted only by 2 cm^{-1} upon the adsorption of the molecule on silver surface. Supposedly, this is due to a rather strong resonance donor power of methoxy group in the para-isomer. In order to justify the above argument, we need, of course, more extensive SERS studies on various benzonitrile derivatives in addition to those reported here.

In summary, we have performed a detailed SERS study on the methoxybenzonitrile molecules in the aqueous silver sol. In view of the changes in the frequencies and the bandwidths of both the C ≡ N stretching and the benzene ring modes, it was concluded that all of ortho-, meta-, and para-methoxybenzonitrile molecules adsorbed on the silver surface via their nitrogen lone pair electrons. Although we could not present concrete evidence, it seemed more likely that the benzene ring of the m-methoxybenzonitrile molecule stands perpendicular to the silver surface, whereas the benzene rings of both the ortho- and the para-derivatives assume tilted stances with respect to the silver surface. Moreover, the frequency of the ν_{CN} mode in the adsorbed species appeared to be affected more strongly by the substituent electronic effect than that in the solution state.

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Precipitation, Resolubilization and Luminescent Properties of Tris(2,2'-diimine)Ruthenium(II) Complexes in Premicellar Anionic Surfactant Solutions

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Premicellar precipitation, resolubilization and luminescing behaviors of RuL$_3^{2+}$ (L = bpy, phen, Me$_2$bpy) in aqueous alkylsulfate and sulfonate solutions were studied. Addition of the anionic surfactants to RuL$_3^{2+}$ solutions caused initial precipitation which was redissolved by further addition of the surfactants. The apparent solubility products K$_{sp}$'s of the precipitates were evalulated assuming 1:2 salt formation. The values were smaller as the ligand is more hydrophobic and the length of hydrocarbon chain of the surfactant is longer. The K$_{sp}$ values for L = bpy were constant over wide surfactant concentration range. However, those for L = Me$_2$bpy and also for phen, but to less extent, increased with the surfactant concentration. The resolubilization of 1:2 salts was followed by red-shift of emission band and extensive emission quenching above critical concentration of the surfactants. The critical concentration was lower for more hydrophobic surfactant. For L = Me$_2$bpy, the blue-shifted emission band with enhanced emission intensity was observed in intermediate surfactant concentration region. The high ionic strength of media prevented the precipitate formation, but facilitated the red-shift of the emission bands. The results support that the precipitate is dissolved by accretion of surfactant anions to the salts to form water-soluble surfactant-rich RuL$_3$-surfactant anionic species. These species appeared to aggregate cooperatively to produce large clusters which exhibited the red-shifted emission.

Introduction

In recent years, the photochemical and photophysical behaviors of tris(2,2'-bipyridine)ruthenium(II), Ru(bpy)$_3^{2+}$, and related complex cations have been a subject of intense study.[1] This is primarily due to the promise of a convenient solar energy conversion using the complex cations as a photosensitizer. To increase the energy conversion efficiency, anionic surfactant systems, especially sodium dodecylsulfate (SDS), were extensively employed.[2-16] The large changes in the luminescent and photochemical properties of the photosensitizers in the SDS solutions were mainly attributed to the binding of the cations on the anionic micelle. Meanwhile it was noticed that the properties of Ru(bpy)$_3^{2+}$ in the sub-

micellar concentration of SDS are considerably different from those observed in the absence of SDS and in SDS micellar solutions.[3,6,9,10] When SDS is added to Ru(bpy)$_3^{2+}$ solutions, precipitate is formed at initial stage and the emission band shifts to shorter wavelength region. Further addition of SDS redissolves the precipitate and the red-shift of the emission band is observed. The decay kinetics of the excited Ru (bpy)$_3^{2+}$ in premicellar SDS solutions is much faster than that obtained in the absence of SDS or at higher SDS concentration. This was attributed to the triplet-triplet annihilation due to the formation of the Ru(bpy)$_3^{2+}$-rich clusters.[2,6,10] The emission quenching of Ru(bpy)$_3^{2+}$ by methylviologen[9] and by cationic dyes[8] was reported to be more efficient in premicellar region of SDS. Similarly, the enhanced energy transfer