Surface-Enhanced Raman Spectroscopy of Crystal Violet in the Presence of Halide and Halate Ions with Near-Infrared Wavelength Excitation

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The interaction of crystal violet (CV) with halide, halate ions, and pyridine and the interaction of CV with colloidal silver surface have been studied by surface-enhanced Raman spectroscopy (SERS) with near-infrared (NIR) excitation. Cl^-, Br^-, I^-, and BrO_3^- ions as well as pyridine give rise to a large enhancement of the Raman modes of CV, while no Raman bands of CV could be observed in the presence of ClO_3^- and IO_3^- ions. The adsorbability of the complexes CV/BrO_3^- and CV/pyridine is higher than that of ClO_3^- and IO_3^- ions, while the latter is higher than that of the complexes CV/ClO_3^- and CV/IO_3^-. CV interacts with the silver surface quite possibly through the lone pair electrons on the N atoms. Halide and halate ions account not only for part of the surface enhancement from the surface plasmon excitation resonance but also for the chemical enhancement in the NIR-SERS. The chemical enhancement factors caused by Cl^-, Br^-, I^-, and BrO_3^- ions are estimated to be about 49, 77, 15, and 36, respectively.

1. Introduction

Since the first report of surface-enhanced Raman spectroscopy by Fleischmann et al.,[1] much effort has been devoted to elucidate the enhancement mechanisms of this phenomenon and to establish it as a powerful potential for analytical purposes.[2−8] Several enhancement mechanisms such as electromagnetic enhancement due to the surface plasmon excitation resonance and chemical enhancement related to surface active sites or charge-transfer processes between the adsorbates and the metal substrates have been proposed to contribute to the overall surface enhancement.[2−5] However, a complete understanding of this effect has not been achieved and the relative importance of these mechanisms still remained a controversy. Extending the laser excitation wavelength and acquiring more experimental data are certainly necessary for both a better understanding of the enhancement mechanisms and practical applications of this effect as an useful analytical tool. In recent years, surface-enhanced Raman spectroscopy (SERS) has been demonstrated to be operative in the near-infrared wavelength region by several groups.[6−15] The experimental results showed that the enhancement factors in the near-infrared (NIR) wavelength region were found to be larger than or at least as large as those with visible light excitation. However, a proper explanation for the large enhancement in the NIR-SERS has not been reached. This results from the following reasons. (i) Electromagnetic theory predicts optimum enhancement in the visible region for silver. One does not expect a larger contribution of the surface plasmon to the surface enhancement excitation resonance with NIR wavelength excitation than with visible light excitations. (ii) Surface active sites or charge-transfer processes are also a resonance effect. It is generally accepted that the charge-transfer band contributes to the surface enhancement in the visible SERS, and it is too narrow to cover both the visible and NIR wavelength regions. (iii) Large enhancement was also found in surface-enhanced hyper-Raman scattering (SEHRS), which is also excited with NIR light but with the scattered light emitted in the visible region. Some authors[16,17] argued that the surface plasmon excitation resonance is too narrow to cover from the visible to the NIR wavelength region, and the charge-transfer band may contribute to the surface enhancement only if multiple charge-transfer bands exist to satisfy the resonance-like conditions. Although a chemical enhancement mechanism was suggested to contribute to the NIR-SERS,[13] direct evidence was still lacking. Accumulating more experimental results and finding out some evidence for the chemical effect in the NIR wavelength region are needed for a better understanding of the enhancement mechanisms of the NIR-SERS and SEHRS.

Recently, we have discovered the existence and contribution of the chemical effect to the surface enhancement in the NIR wavelength region for pyridine coadsorbed with halide and halate ions on colloidal silver surface. In this paper, as a continuation of our interest, we study the interaction of crystal violet (CV) with a colloidal silver surface in the presence of halide and halate ions as well as in the presence of pyridine with NIR wavelength excitation. Our attentions were payed to (i) the influence of these ions on the surface enhancement of crystal violet, (ii) the interaction of these ions with crystal violet, (iii) the interaction of the adsorbates with silver colloids, and (iv) the enhancement mechanisms, particularly the chemical enhancement effect in the NIR wavelength region.

SERS of crystal violet have been studied by several groups. Jeanmaire and van Duyne[18] reported probably the first resonance surface Raman spectrum of CV. Watanabe and Pettinger[19] subsequently reported a comparative study of the resonance Raman and surface Raman spectra of CV on silver electrodes. Studies of CV on silver films,[20] silica gel[21] and gold electrodes,[22] and in silver colloids[23] have also been published. However, all of these studies have been carried out with visible light excitation. Besides, the interactions we aimed at were not or not well studied.

2. Experimental Section

To get the optimum enhancement in the NIR-SERS, 0.2 M halide (NaCl, NaBr, KI) and 0.2 M halate ($KClO_3$, $KBrO_3$,

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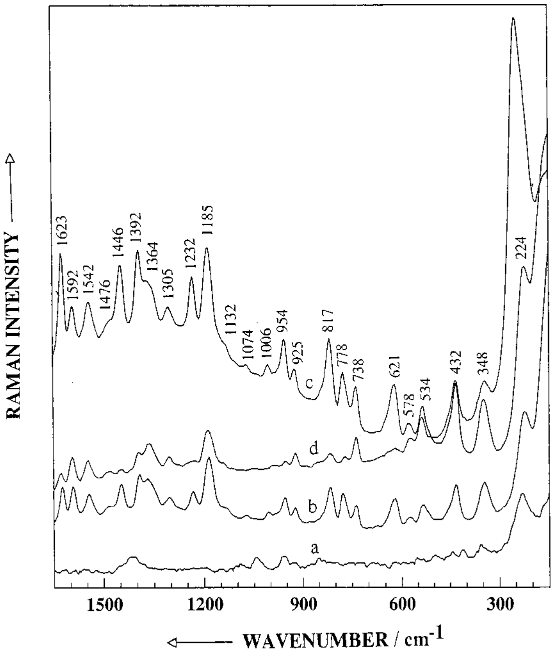

Figure 1. NIR-SER spectra of crystal violet (CV) in silver colloids: (a) CV; (b) CV + Cl^-; (c) CV + Br^-; (d) CV + I^- ions.

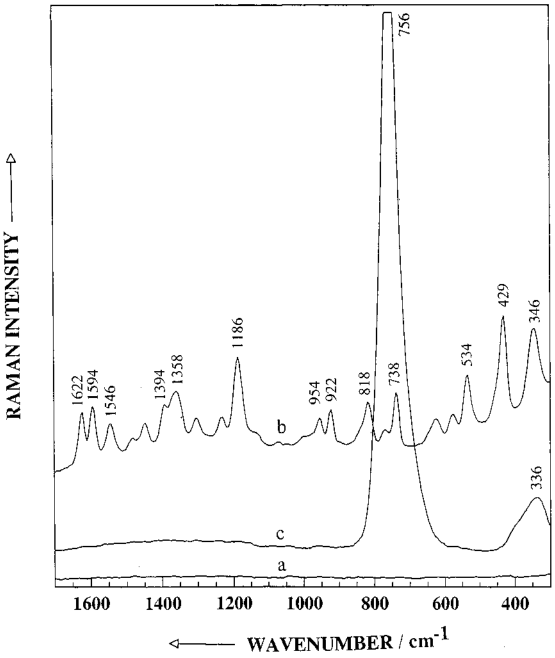

Figure 2. NIR-SER spectra of crystal violet in silver colloids in the presence of (a) ClO_3^-, (b) BrO_3^-, and (c) IO_3^- ions.

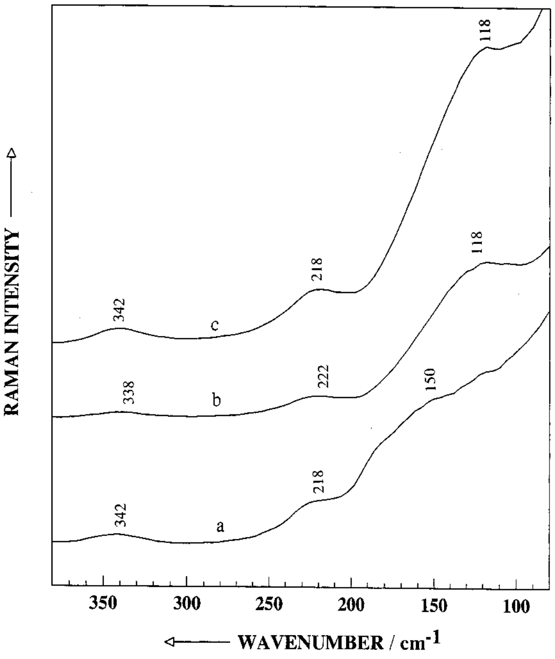

Figure 3. NIR-SER spectra of crystal violet in silver colloids in the presence of (a) Cl^- and Br^-, (b) Cl^- and I^-, and (c) Br^- and I^- ions.

KIO_3) aqueous solutions were prepared with deionized water and tested with 2×10^{-6} M aqueous solution of crystal violet and 0.2 M aqueous solution of pyridine in silver colloids. The volume proportion of silver sol:$X(O_3)^-$ solution:CV is 4:1:1. The final concentration of halide or halate ions used in the measurements is about 3.3×10^{-2} M. Silver colloids were prepared by a method similar to that reported by Lee and Meisel.[24] The detailed procedures for the preparation of this sol were reported in a previous paper.[14] The NIR-SERS spectra were recorded with a Jarrell-Ash Model 25-103 1 m *f*/8.7 double-grating monochromator, which is equipped with a Bruker Model D450 InGaAs detector and controlled by a computer. The 1064 nm output of a TEM_{00} mode linearly polarized continuous-wave Nd :YAG laser was used as excitation source. Absorption spectra and the time evolution of the absorption of silver colloids in the presence of halide and halate ions at the excitation wavelength were measured with a Perkin-Elmer UV−vis−NIR spectrometer (Lambda 19).

3. Results and Discussion

The NIR-SERS spectra of CV in the presence of halide and halate ions are shown in Figures 1 and 2, respectively. It is evident from Figures 1 and 2 that all three halide ions, Cl^-, Br^-, and I^-, enhance the Raman signal of CV considerably, whereas only BrO_3^- ions among the halate ions give rise to a large enhancement of the Raman modes of CV. In the presence of ClO_3^- and IO_3^- ions, the Raman bands from CV cannot be observed. The intense band at 756 and 336 cm^{-1} in spectrum c of Figure 2 was ascribed to the surface species of $AgIO_3$.[15] These results show that in the presence of ClO_3^- and IO_3^- ions, CV cannot adsorb onto the colloidal silver surface.

To understand the roles halide and halate ions played in the NIR-SERS of CV, a comparison with the NIR-SERS of pyridine in the presence of these ions may be useful. The Raman spectrum of pyridine is strikingly enhanced after addition of Cl^-, Br^-, ClO_3^-, BrO_3^-, and IO_3^- ions, while the enhancement could hardly be seen after addition of I^- ions.[15] Nevertheless, the Raman spectrum of CV can be considerably enhanced by Cl^-, Br^-, I^-, and BrO_3^- instead of ClO_3^- and IO_3^- ions. This means that pyridine can coadsorb with Cl^-, Br^-, ClO_3^-, BrO_3^-, and IO_3^- ions onto the silver surface and so does CV with Cl^-, Br^-, I^-, and BrO_3^- ions. The difference can only be understood by the fact that halide and halate ions interact not only with the silver colloids but also with the molecules. The two effects together give rise to the surface-enhanced Raman scattering of these molecules.

The interaction strength of halide and halate ions with silver increases in the order of $Cl^- < Br^- < I^-$, $ClO_3^- \approx IO_3^- < BrO_3^-$ ions.[15] This order stands also in the presence of pyridine.[15] To see what happens in the presence of CV, we measured the NIR-SER spectra of CV in the presence of mixtures of Cl^- and Br^-, Cl^- and I^-, and Br^- and I^- ions, respectively (see Figure 3). In the coexistence of CV, Cl^-, and I^- ions and of CV, Br^-, and I^- ions there appear only the Ag−I^- stretching mode (118 cm^{-1}) and the CV modes (218 and

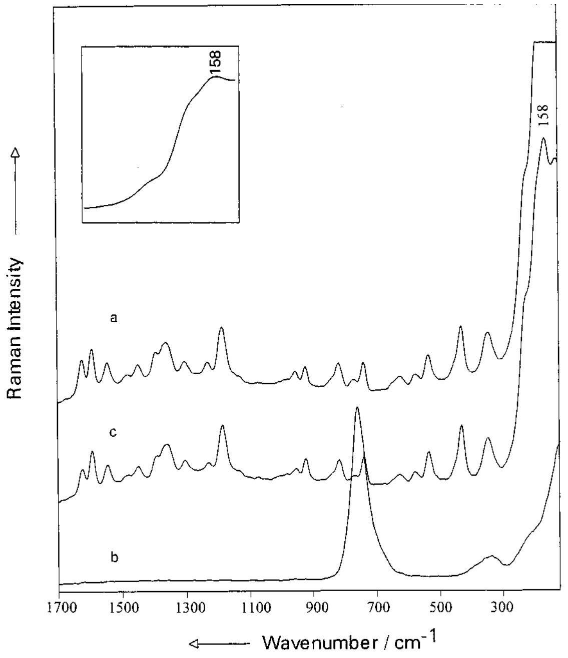

Figure 4. NIR-SER spectra of crystal violet in silver colloids in the presence of (a) ClO_3^- and BrO_3^-, (b) ClO_3^- and IO_3^-, and (c) BrO_3^- and IO_3^- ions. Insert shows the low wavenumber bands of spectrum a.

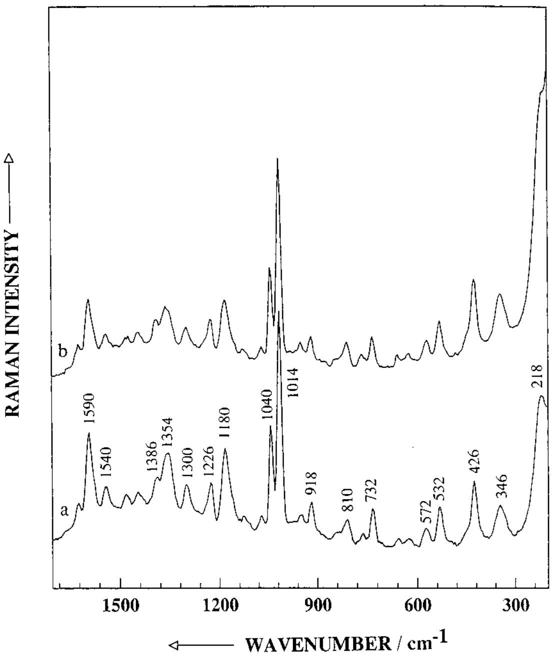

Figure 5. NIR-SER spectra of crystal violet in silver colloids in the presence of (a) pyridine and (b) pyridine and IO_3^- ions.

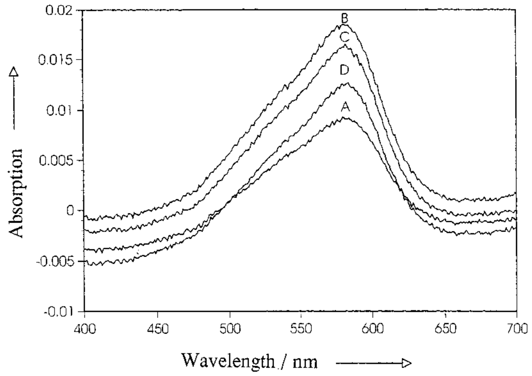

Figure 6. Absorption spectra of crystal violet in the presence of (A) H_2O, (B) Cl^-, (C) Br^-, and (D) I^- ions.

342 cm^{-1}), whereas in the coexistence of CV, Cl^-, and Br^- ions, only the Ag$-$Br$^-$ (150 cm^{-1}) stretching mode and the CV modes are observed. These results indicate that the interaction strength order of halide ions with silver does not change even when CV is present. In parts a$-$c of Figure 4 we show the NIR-SERS of CV in the coexistence of ClO_3^- and BrO_3^-, of IO_3^- and BrO_3^-, and of ClO_3^- and IO_3^- ions, respectively. Following the measurement of Figure 4b, we added BrO_3^- ions to the mixture and measured the Raman spectrum again (not shown here). The result is the same as parts a and c of Figure 4. In the coexistence of ClO_3^- and IO_3^- ions, no Raman modes from CV can be seen while the Raman modes from $AgIO_3$ (750 and 336 cm^{-1}) and Ag$-ClO_3^-$ (226 cm^{-1}) appear clearly. As long as BrO_3^- ions are present in the mixture, the Raman bands from CV and the Ag$-BrO_3^-$ stretching vibration (158 cm^{-1}) appear, accompanied by the disappearance of the Raman bands from $AgIO_3^-$ and Ag$-ClO_3^-$ ions. Based on the results of Figure 4, it can be concluded that (i) the interaction strength order of halate ions with silver does not change in the presence of CV and (ii) once BrO_3^- ions are present, IO_3^- and ClO_3^- ions cannot remove CV molecules from the silver surface. Instead, ClO_3^- and IO_3^- ions will be removed from silver surface.

ClO_3^- and IO_3^- are not able to be coadsorbed with BrO_3^- ions, but they can be coadsorbed with pyridine on a colloidal silver surface. If the depletion of ClO_3^- and IO_3^- on the silver surface is due only to the competitive adsorption of BrO_3^- ions, we should observe the Raman signal of ClO_3^- or IO_3^- ions if we add pyridine instead of BrO_3^- ions to the mixture of CV and ClO_3^- ions or to the mixture of CV and IO_3^- ions. Otherwise, some other effects have to be considered. In parts a and b of Figure 5 the NIR-SERS of CV in the presence of pyridine are shown without and with addition of IO_3^- ions, respectively. As can be seen, in the presence of pyridine, not only are the Raman modes from CV enhanced considerably but also those from pyridine (1014 and 1040 cm^{-1}). No Raman bands from IO_3^- ions can be observed. This indicates that pyridine also causes CV to be adsorbed onto and IO_3^- ions to be desorbed from the colloidal silver surface. However, the disappearance of IO_3^- ions from the silver surface is not a pure effect of competitive adsorption of pyridine with IO_3^- ions. This confirms that the interaction of pyridine and BrO_3^- ions with CV plays an important role in the desorption of ClO_3^- and IO_3^- ions and in the adsorption of CV. We may call the interaction between CV and pyridine or BrO_3^- ions a coordination effect.

ClO_3^-, BrO_3^-, and IO_3^- ions have identical structure and charge property. Therefore, they should interact with CV in a similar manner. To understand the SERS behavior of CV in Figure 2 and to confirm the interaction of CV with these ions, we measured the absorption spectra of CV before and after addition of Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, and IO_3^- ions, respectively (see Figures 6 and 7). Corresponding absorption spectra in silver colloids (Figures 8 and 9) are also measured. The absorption bands around 560 and 500 nm from CV in Figures 6 and 7 are obviously increased after addition of each of the six anions. However, these bands cannot be observed in Figures 8 and 9 because of the strong absorption of silver colloids. Figures 6 and 7 indicate that the interaction of halide and halate ions with CV increases the transition probability from the electronic ground state to the two corresponding excited electronic levels of CV. This may imply a higher population of electrons in the ground state, which is caused by the interaction of the anions and CV. After addition of halide and halate ions, the central C^+ in CV will be embedded by the halide ions owing to the attraction property of the oppositely charged

TABLE 1: Observed Wavenumbers (cm^{-1}) in Crystal Violet and Their Assignment[a]

	NIR-SERS					NR[b]	RR[b,25]
bands in solution	Cl^-	Br^-	I^-		BrO_3^-	Py	powder
breathing of central bonds	224	224	224	224	218	206	
Ph−C$^+$−Ph bend (∥)	344	348	344	346	346	341	334
Ph−C$^+$−Ph bend (⊥)	432	432	432	429	426	422	426
ring skeletal vib of radical orientation	536	534	532	534	532	528	532
same as above	572	578	574	578	572	563	570
same as above	621	621	620	626	626	608	616
ring C−H bend (⊥)	738	738	736	738	732	728	729
ring C−H bend (⊥)	773	778	776	770	762	770	770
ring C−H bend (⊥)	817	817	814	818	810	826	810
ring skeletal vib of radical orientation	922	925	924	922	918	920	918
same as above	953	954	954	954	950	944	942
same as above	986	1006	1004	990		1000	982
ring C−H bend (∥)	1142	1132	1136	1138	1125	1139	1142
ring C−H bend (∥)	1188	1185	1184	1186	1180	1175	1182
ring C−H bend (∥)						1190	1192
ring C−H bend (∥)	1230	1232	1232	1230	1226	1229	
ring C−C stretching	1305	1305	1304	1302	1300	1302	1306
N−phenyl stretching	1364	1364	1369	1358	1354	1360	1377
N−phenyl stretching	1395	1392	1394	1394	1386	1391	1390
ring C−C stretching	1446	1446	1446	1451	1446	1451	1454
+ ring deformation	1480	1476	1480	1482	1482	1481	1489
ring C−C stretching	1547	1542	1544	1546	1540	1539	1542
ring C−C stretching							1550
ring C−C stretching	1592	1592	1592	1594	1590	1583	1594
ring C−C stretching	1629	1623	1624	1622	1622	1616	1624

[a] ∥ and ⊥ indicate in-plane and out-of-plane vibrations. [b] NR and RR denote normal and resonance Raman, respectively.

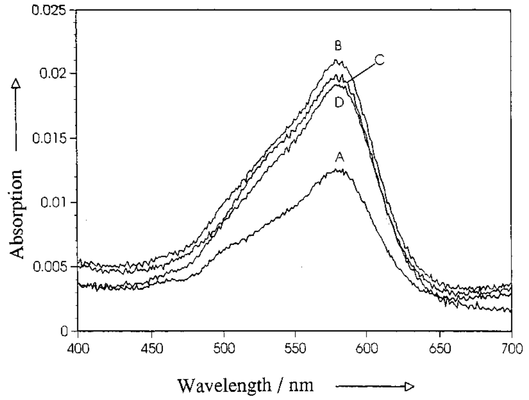

Figure 7. Absorption spectra of crystal violet in the presence of (A) H_2O, (B) ClO_3^-, (C) BrO_3^-, and (D) IO_3^- ions.

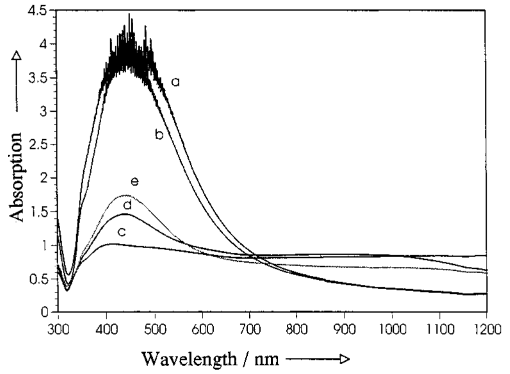

Figure 8. Absorption spectra of silver colloids in the presence of (a) H_2O, (b) CV, (C) CV + Cl^-, (d) CV + Br^-, and (e) CV + I^- ions.

ions. This will cause the positive charge to move toward the center C$^+$−phenyl bonds and result in a relatively higher electron density in the phenyl ring and the N−Ph bond. From Figures 6 and 7 we see that CV is complexed with halide and halate ions. Considering the results from Figures 2, 4, and 5, we conclude that the adsorbability of the complexes CV/BrO_3^- and CV/pyridine is larger than that of ClO_3^- and IO_3^- ions while

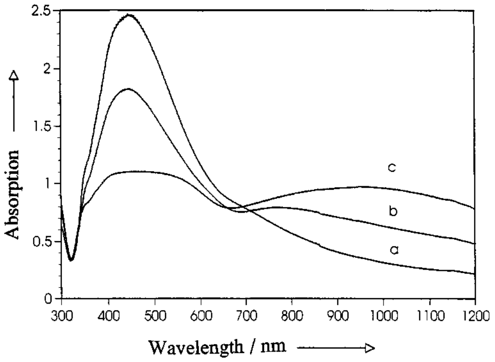

Figure 9. Absorption spectra of silver colloids in the presence of (a) ClO_3^-, (b) BrO_3^-, and (c) IO_3^- ions.

the latter is larger than that of the complexes CV/ClO_3^- and CV/IO_3^- ions.

In Table 1, we list the band positions and relative intensities of the NIR-SERS of CV in the presence of Cl^-, Br^-, I^-, BrO_3^-, and pyridine as well as the resonance Raman spectra from literature. The assignments of the Raman modes are also given in Table 1. A comparison of the NIR-SERS with the resonance Raman spectrum shows that (i) the band at 344 cm^{-1} due to C $^+$−Ph in-plane bending vibrations and the band at about 432 cm^{-1} due to C $^+$−Ph and ring skeletal out-of-plane vibrations shift by 7−14 and 3−6 cm^{-1} to higher wavenumbers in the NIR-SERS spectra, respectively. (ii) Similar band shifts are also observed for the ring skeletal vibrations of radical orientation at about 572, 621, 922, 953, and 986 cm^{-1} and for the C−H out-of-plane bendings at about 738, 773, and 817 cm^{-1}. (iii) The bands at about 1364 and 1395 cm^{-1}, which can be assigned to the N−Ph stretching vibrations, shift 8−19 cm^{-1} to the lower wavenumbers for the former and 2−5 cm^{-1} to higher wavenumbers for the latter, and (iv) Br^- ions result in the largest band shifts for the C$^+$−Ph in-plane bending vibrations at 348 cm^{-1} and the ring skeletal vibrations at about 578 cm^{-1}.

In summary, halide and BrO_3^- and pyridine cause the N−phenyl ring and the ring C−C stretching mode (19b) to shift obviously to lower wavenumbers while they cause the C$^+$−

phenyl ring in-plane bending mode and the ring skeletal vibrations to shift to higher wavenumbers. The breathing mode of the entire molecule at about 202 cm^{-1} also shifts considerably to higher wavenumbers in the NIR-SER spectra. The upshift in wavenumbers indicates strengthening of the corresponding bond. However, the shifts for most of these bands are smaller in the presence of pyridine, particularly the bands at about 426, 532, 572, 918, and 950 cm^{-1}, which are attributed to the ring skeletal vibration of the radical orientations and the modes at 732 and 810 cm^{-1}, indicating the out-of-plane ring C−H bending vibrations. This indicates that these vibrations of CV are less affected by pyridine but more affected by halide and halate ions.

After the discussion of the vibrational features of the NIR-SERS of CV, it is possible for us to discuss the interaction of CV with the colloidal silver surface. As mentioned above, the halide and halate ions interact with CV through its central C$^+$ ion. This may explain at least partially the large shifts of the band positions for the C$^+$−phenyl center in-plane bending, the ring C−C stretching, the breathing mode, and the ring skeletal vibrations. If we suppose the molecule is adsorbed through the central C$^+$ ion on the silver surface, it may also result in the changes in the above modes. In this case, the N−phenyl stretching vibrations should be less affected because they are located far from the interaction center. However, the largest changes of the N−phenyl stretching vibrations are observed. This may indicate that the interaction of CV with the silver surface are through lone pair electrons on the N atoms. The interaction of CV with halide or halate ions increases the electron density of the phenyl ring and the N−phenyl end. The increment of the electron density of the lone pairs will in turn strengthen the interaction between CV and the silver surface.

As can be seen from Figures 8 and 9, no absorption band appears in the NIR wavelength region for pure CV in the silver colloids while after addition of halide and halate ions a broad absorption band appears in this region. This band is a characteristic of the absorption of surface plasmon excitation resonance. A large enhancement of NIR-SERS occurs with the appearance of this band. This indicates that resonance excitation of surface plasmons contributes mainly to the surface enhancement observed in the NIR wavelength region. However, we should notice the different enhancement factors caused by different ions. This may indicate that different ions may create surface active sites differently. Generally, the chemical enhancement factor was estimated by the ratio of the SERS intensities with and without addition of chloride ions.[26] This is not valid because (i) the anions contribute not only to the chemical but also to the electromagnetic enhancement and (ii) both the SERS intensity and absorption at the excitation wavelength change with time. The anions affect the electromagnetic enhancement through two ways: by causing the silver particles to aggregate and by causing the particle size to grow. Both effects have been demonstrated by transmission electron microscopy.[28] The particle size growth results from the breakdown of the surface potential equilibrium of silver particles upon adsorption of the anions. This causes the surface atoms and also the adsorbates to mobilize and makes the particles slightly soluble. Because the particle size differs one from another, the mobilizing of the surface atoms should be toward reducing the total surface area of the particle system. Therefore, the solubility of a smaller particle is greater than that of a larger one. As a consequence, the surface atoms and adsorbates will dissolve from smaller particles and precipitate on the surface of larger ones. The aggregation stage of silver colloids can also be changed by adsorption of anions because the stability of silver colloids is governed by the balance between van der Waals attraction and Coulombic repulsion forces of the charged particles. Any increase of the van der Waals attraction force or decrease of the Coulombic repulsion force will cause the colloids to aggregate if they have not been initially aggregated or to be more aggregated if they have been aggregated before the addition of the anions. The adsorption of anions weakens the Coulombic repulsion force and therefore results in the aggregation to a larger extent. Increases in particle size and/or in the aggregation stage shifts the surface plasmon resonance to longer wavelength. Both of the processes are time dependent.

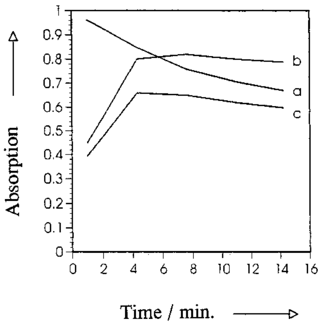

Figure 10. Time dependence of the absorption of silver colloids at the excitation wavelength in the presence of (a) Cl$^-$, (b) Br$^-$, and (c) I$^-$ ions.

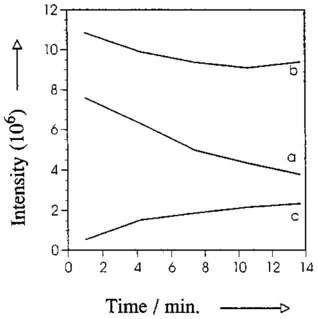

Figure 11. Time dependence of the NIR-SERS of the 432 cm^{-1} band of crystal violet in the presence of (a) Cl$^-$, (b) Br$^-$, and (c) I$^-$ ions.

To get more reliable information on whether the chemical enhancement mechanism exists in the NIR wavelength region, it is necessary to observe the absorption at the excitation wavelength and the NIR-SERS simultaneously. We carried out such measurements, the results of which are shown in Figures 10 and 11. At a given time, the typical value of the absorption in the absence and presence of Cl$^-$, Br$^-$, I$^-$, and BrO$_3^-$ ions are 0.3266, 0.8479, 0.8010, 0.6603, and 0.8845, respectively. The corresponding NIR-SERS intensity are $\leq 5 \times 10^4$, $6.32 \times 10,^6$ 9.39×10^6, 1.52×10^6, and 4.9×10^6, respectively. From these measurements we are able to estimate roughly the contributions from surface plasmon resonance and from the chemical effect. The enhancement factors caused by addition of Cl$^-$, Br$^-$, I$^-$, and BrO$_3^-$ ions are about 126, 188, 30.4, and 98, respectively. In a separate paper,[27] we presented an expression for the estimation of the chemical enhancement factor. With this expression the chemical enhancement factor is estimated after correction with the absorption at the excitation wavelength. Based on this expression, we estimated the enhancement factors from the chemical contribution to be about 49, 77, 15, and 36 in the presence of Cl$^-$, Br$^-$, I$^-$, and BrO$_3^-$ ions, respectively. These data present at least an approximate magnitude of chemical enhancement in NIR-SERS.

4. Summary

We have studied the SERS of CV in the presence of halide and halate ions with a conventional scanning Raman spectrometer and NIR wavelength excitation. The interaction of CV with halide and halate ions as well as pyridine and also the interaction of CV with silver surface are investigated. CV interacts with the anions through its central C^+ ion, while it interacts with silver surface quite possibly through the lone pair electrons on the N atoms. The anions and pyridine are able to complex with CV and enhance its adsorbability. The coordination of CV with BrO_3^- and pyridine is greater than that of CV with ClO_3^- and IO_3^-. Surface active sites created upon addition of halide and halate ions in silver colloids and complexation of them with CV are the origins of the chemical enhancement mechanism. Halide and halate ions account not only for the chemical enhancement factor but also for part of the electromagnetic enhancement factor.

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