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Interaction of halide and halate ions with colloidal silver and their influence on surface-enhanced Raman scattering of pyridine with near-infrared excitation

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Abstract

The interactions between halide and halate ions and colloidal silver surfaces are studied by surface-enhanced Raman spectroscopy (SERS) with excitation in the near-infrared (NIR) wavelength region. The interaction strength of halide ions with silver surface decreases in the order $I^- > Br^- > Cl^-$ while the enhancements of the Raman modes of pyridine caused by addition of these ions range in the order of $Cl^- \approx Br^- > I^-$. ClO_3^- and BrO_3^- ions in silver colloids give rise to SERS bands at about 226 and 158 cm^{-1}, respectively, while IO_3^- ions on colloidal silver surface result in two Raman bands at about 750 and 334 cm^{-1}. These results indicate that the interactions of ClO_3^- and BrO_3^- ions with silver surface are through their lone pair electrons of Cl and Br. Nevertheless, IO_3^- ions bond to silver surface through their negatively charged O^-. The interaction strength of halate ions with silver are measured to be $BrO_3^- > ClO_3^- \approx IO_3^-$. The enhancements of the Raman modes of pyridine caused by addition of halate ions increase in the order $ClO_3^- < IO_3^- < BrO_3^-$. These ions contribute not only to the electromagnetic enhancement but also to the chemical enhancement in the NIR-SERS. BrO_3^- ions are able to create about 2.2 and 3.7 times more surface active sites on colloidal silver surface than ClO_3^- and IO_3^- ions do. © 1997 Elsevier Science B.V.

1. Introduction

Halide ions were frequently used in SERS studies both in silver colloids and on silver electrodes in electrochemical cells [1–15]. It was found that these ions play an important role in the enhancement of the Raman signals of the adsorbed molecules on silver surface. Their functions in SERS are many-fold. Among those, the most important ones are

probably (i) to shift the surface plasmon resonance of the silver colloids to a longer wavelength at which the molecules are excited and large enhancements are observed and (ii) to create surface active sites on which the probe molecules are adsorbed or surface complexes are formed. The charge transfer process between the adsorbed molecules and metal substrate may take place through such surface active sites. In previous papers [13,15], we studied the interaction of halide ions with colloidal silver surface in the presence of pyridine and crystal violet with NIR-excita-

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tion. The interaction between the halide ions and silver surface and the interaction between the adsorbed molecules and the metal substrate were discriminated. The importance of point (i) for the NIR-SERS was demonstrated and the role of point (ii) was also suggested [13–15]. Several authors [13–18] claimed that the enhancement factors are larger in the NIR-SERS than in the SERS with visible light excitation. However, direct evidences of the chemical enhancement in NIR-SERS are still lacking.

Although halide ions have been extensively studied by SERS, few studies on halate ions could be found in SERS literature. The interaction of such ions with metal surface has not been well defined. This makes it difficult or impossible to assign some of the SERS bands, particularly in the low wavenumber region. Pagannone et al. [19] prepared a SERS substrate by etching methods and found that intense SERS spectra of sulphate were obtained on addition of ClO_3^- ions to the etching solution. However, they encountered the difficulty in identifying the low wavenumber bands. In our opinion, it results from the lack of the vibrational data of the halate–metal interactions. Besides, Cl^- ions were frequently used to enhance the Raman signal of molecules in silver colloids. Whether halate ions are also suitable for this purpose is not yet clear. Detailed investigations on the interactions of halate ions with silver surface by SERS and on the roles they may play in the NIR-SERS is certainly necessary and interesting.

In the present paper, we study the interactions of halide and halate ions with silver in silver colloids by SERS with NIR wavelength excitation. Our motivations of this work are (i) to study the interaction strength order of these ions with silver surface and (ii) to gain some more insight into the mechanisms of the influence of these ions on the surface enhancement in the NIR-SERS. Both pure solutions of each type of these ions and different mixtures of them in silver colloids are studied. Pyridine is used as a probe molecule and halate ions are investigated in more detail.

2. Experimental

In order to determine the optimum concentration of halide and halate ions for the best enhancement in

the NIR-SERS, 0.05, 0.1, 0.2, 0.3 and 0.5 M halide (NaCl, NaBr, KI), and halate ($KClO_3$, $KBrO_3$, KIO_3) aqueous solutions were prepared with deionized water and tested with 0.2 M aqueous solution of pyridine in silver colloids. The optimum concentration of these ions is measured to be about 0.2 M. Therefore, 0.2 M solutions of these ions are used in the following experiments. The volume ratio of silver sol:$X(O_3)^-$ solution:pyridine 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 [20]. The detailed procedures for the preparation of this sol were reported in a previous paper [15]. In order to exclude the possibility of chemical reactions between the halide ions and the reductive reagent sodium citrate in silver colloids, another type of silver colloids were also prepared for comparison. During the preparation of this sol, a silver plate was polished with sand paper and was thoroughly rinsed with deionized water. Afterwards, the silver plate was put into a clean flask filled with deionized water. The 532 nm output of a Spectra-Physis pulsed Nd:YAG laser was focused on the silver plate for about 10 min. The silver colloids were produced by the laser ablation of the silver particles from the silver plate to the water. 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 recorded with a Perkin Elmer UV/VIS/NIR spectrometer (Lambda 19).

3. Results and discussion

The NIR-SERS of halide ions were published in Ref. [15]. We will not present them here. In Fig. 1a–c we show the NIR-SERS of pyridine in the presence of Cl^-, Br^-, and I^- ions, respectively. The intense Raman bands in the low wavenumber region at about 246, 154 and 118 cm^{-1} are depending on

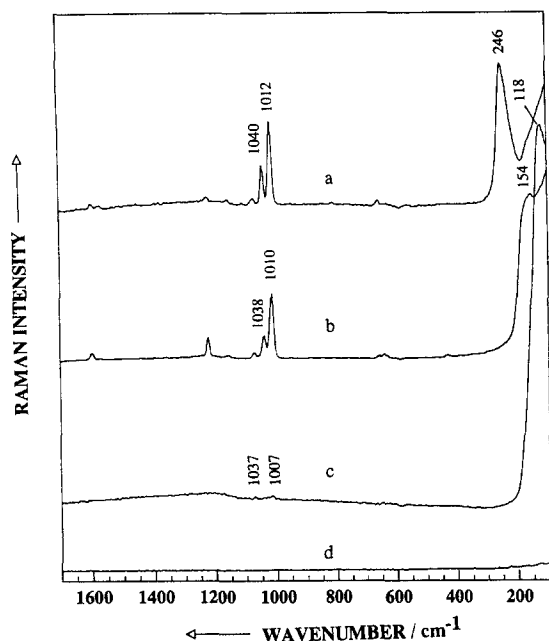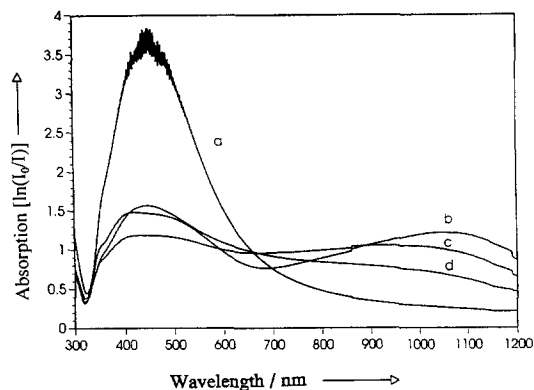Fig. 1. NIR-SER spectra of pyridine in silver colloids: (a–c) in the presence of Cl⁻, Br⁻ and I⁻ ions, respectively; (d) in the absence of halide ions.

Fig. 2. Absorption spectra of pyridine in silver colloids: (a) in the absence of halide ions; (b–d) in the presence of Cl⁻, Br⁻ and I⁻ ions, respectively.

the nature, particularly of the mass of the halide ions. They were assigned to the Ag–Cl⁻, Ag–Br⁻, and Ag–I⁻, stretching vibrations, respectively [7,15]. It is obvious that Cl⁻ and Br⁻ ions cause large enhancement not only for the ring breathing modes of pyridine but also for the Ag–X (X = Cl⁻, Br⁻) stretching modes. In the presence of I⁻ ions, the Ag–I⁻ stretching mode is intense while the ring breathing modes of pyridine are much less enhanced. From these results, one may expect that Cl⁻ and Br⁻ ions may have a larger capacity than I⁻ ions to cause the silver sol to aggregate and move the surface plasmon resonance to the NIR wavelength region. In other words, the surface plasmon resonance in the NIR wavelength region is stronger in the presence of Cl⁻ and Br⁻ ions than in the presence of I⁻ ions. The red shift of the surface plasmon resonance accounts mainly for the large enhancement in the NIR wavelength region. This point may be confirmed by the absorption spectra of the systems of interest. As shown in Fig. 2, in the NIR wavelength region Cl⁻ and Br⁻ ions cause indeed stronger surface plasmon resonances than I⁻ ions do. However, a comparison of Fig. 1 and Fig. 2

shows that other factors must be also in operation in the NIR-SERS because (i) the Ag–I⁻ stretching vibration at 118 cm⁻¹ is very intense and (ii) the surface plasmon resonance in the presence of Br⁻ lies in the middle of those in the presence of Cl⁻ and I⁻ ions while the enhancement of the ring breathing modes of pyridine caused by addition of Br⁻ ions is almost the same as that caused by Cl⁻ ions and much stronger than that caused by I⁻ ions.

We noticed that the surface plasmon resonance in the NIR wavelength region changes with time. In order to avoid errors caused by chance in the experiments and to get more reliable insight into the relationship between the surface plasmon resonance and the SERS in the NIR wavelength region, it is necessary to monitor the two processes at the same
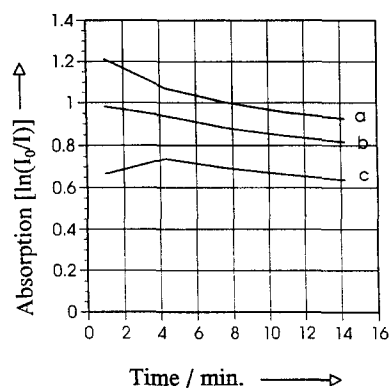

Fig. 3. Time evolution of the absorption of pyridine in silver colloids at the excitation wavelength (1064 nm) after addition of (a) Cl⁻, (b) Br⁻ and (d) I⁻ ions.
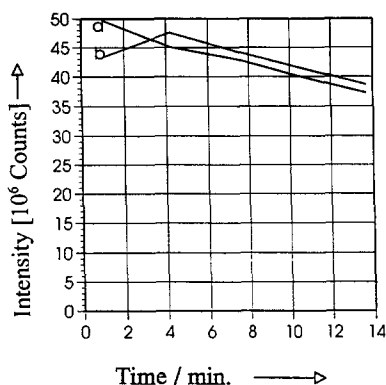
Fig. 4. Time dependence of the NIR-SERS intensity of the 1010 cm^{-1} mode of pyridine in silver colloids after addition of (a) Cl$^-$ and (b) Br$^-$ ions.

time. For this purpose, we carried out parallel experiments, in which the surface plasmon resonance at the excitation wavelength and the NIR SERS of pyridine in the presence of halide ions were measured at the same time. The results are shown in Figs. 3 and 4, respectively. Because the SERS intensity of pyridine in silver colloids in the presence of I$^-$ ions is too weak, only Cl$^-$ and Br$^-$ ions are studied by this method. The curves depicted in Fig. 4 represent the NIR-SERS intensities after substraction of the backgrounds. From Figs. 3 and 4, we see that the changes of the SERS intensity with time agree well with those of the surface plasmon resonance. This indicates that the electromagnetic enhancement mechanism plays an important role in the NIR-SERS. It is interesting to notice that the SERS intensity of pyridine in the presence of Br$^-$ ions increases while the surface plasmon resonance decreases during the first several minutes. Throughout the experiments, the surface plasmon resonance in the presence of Cl$^-$ ions is always stronger than in the presence of Br$^-$ ions while the SERS intensity of pyridine does not behave in the same way. These results reveal that other effects besides surface plasmon resonance operate in the NIR-SERS as well. One possible contribution arises from the surface active sites which are created by the halide ions. Pyridine or the surface complexes of pyridine/halide adsorbed on the special sites results in an additional enhancement through charge transfer resonances between the surface complexes and the silver colloids. A comparison of Fig.

3 with Fig. 4 shows that Br$^-$ ions may create surface active sites in a more moderate but effective way than Cl$^-$ ions. More detailed investigations on the chemical effect has been carried out. The results will be published separately [21].

In Fig. 5a–c are shown the NIR-SERS of Cl$^-$/Br$^-$, Cl$^-$/I$^-$ and Br$^-$/I$^-$ mixtures, respectively. In each of the spectra, only one Raman band appears. If Cl$^-$ and Br$^-$ ions are mixed, the Ag–Br$^-$ stretching mode at about 158 cm^{-1} appears. No Raman band at the Ag–Cl$^-$ stretching region could be observed. This implies that Br$^-$ ions instead of Cl$^-$ ions interact directly with the silver surface. Cl$^-$ ions cannot be adsorbed on or will be removed from the silver surface when Cl$^-$ and Br$^-$ ions coexist in the solution. In both the mixture of Cl$^-$/I$^-$ and the mixture of Br$^-$/I$^-$, only the Raman band indicating Ag–I$^-$ stretching vibrations appears. It means that the interaction of I$^-$ ions with colloidal silver is stronger than the interaction of Cl$^-$ and Br$^-$ ions with silver. Cl$^-$ and Br$^-$ ions could be removed from the silver surface by I$^-$ ions. These results indicate that the interaction strength of the halide
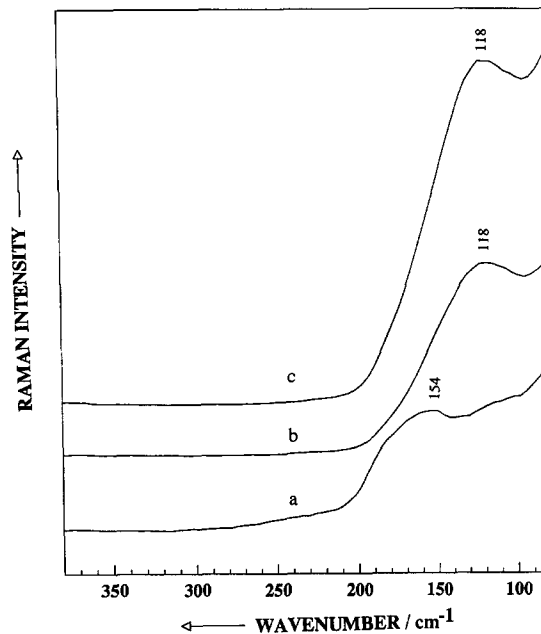

Fig. 5. NIR-SER spectra of (a) Cl$^-$ and Br$^-$, (b) Cl$^-$ and I$^-$ and (c) Br$^-$ and I$^-$ mixtures in silver colloids.

ions with colloidal silver surface increases in the order $Cl^- < Br^- < I^-$.

If pyridine is added to the above three mixtures, the strength order of the interactions between the halide ions and the silver surface does not change as shown in Fig. 6. The enhancement of the Raman bands of pyridine are weak whenever I^- ions are present in the mixture. It is similar to the case of the SERS of pyridine in the presence of pure I^- ions. This indicates that the enhancement of the Raman signal results from the I^- rather than Cl^- and Br^- ions. The Raman bands of pyridine gain much larger enhancement in the mixture of Cl^- and Br^- ions. The enhancement is caused by Br^- instead of Cl^- ions. This could be understood by the facts that (i) the SERS spectrum of pyridine resembles that obtained with Br^- ions (spectrum b in Fig. 1) but not that with Cl^- ions (spectrum a in Fig. 1); (ii) the $Ag-Br^-$ stretching mode appears while the $Ag-Cl^-$ stretching mode is not observed in the spectrum of the mixture. If we suppose that the surface complex of Ag/pyridine/halide ions as a whole adsorbed on a special active site, the halide ions in the surface complex can be replaced by other halide ions. Cl^-
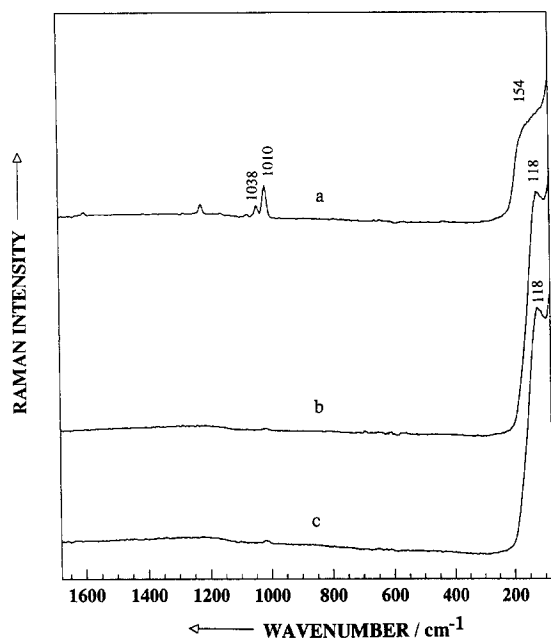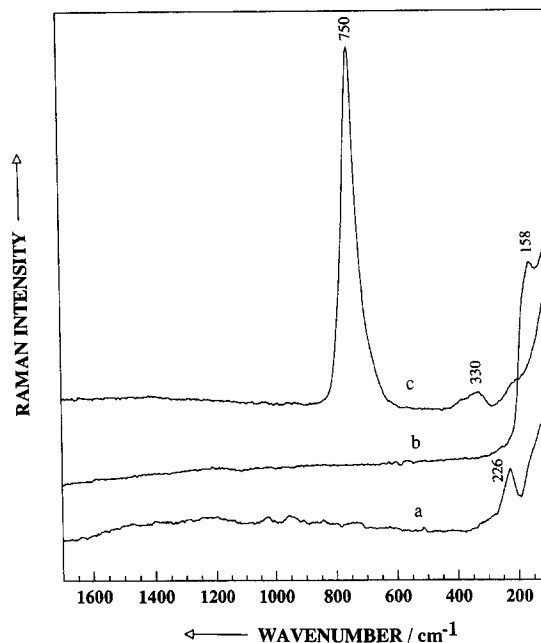

Fig. 7. NIR-SER spectra of (a) ClO_3^-, (b) BrO_3^- and (c) IO_3^- ions in silver colloids.

ions could be replaced by Br^- or I^- ions and Br^- ions could be replaced by I^- ions. As can be seen below, this role stands for halate ions with pyridine on colloidal silver surface as well. However, a much different behavior is found for crystal violet with these ions on colloidal silver surface [22].

In Fig. 7a–c we show the NIR-SERS of ClO_3^-, BrO_3^- and IO_3^- ions in silver colloids, respectively. It is interesting to notice that the NIR-SERS of these three ions are very different from those of halide ions on colloidal silver surface which depend on the mass of the halide ions. ClO_3^- and BrO_3^- ions on colloidal silver surfaces give rise to Raman bands at about 226 and 158 cm^{-1}, respectively. They are very similar to the cases of Cl^- and Br^- ions on colloidal silver surfaces. We tried to record the normal Raman spectra of these anions in pure solution, but no Raman bands could be observed even with a higher concentration (0.5 M). Normal Raman spectra of the powders of potassium halates were recorded and the most intense Raman bands for $KClO_3$, $KBrO_3$ and KIO_3 are located at about 944, 797 and 755 cm^{-1}, respectively. All these results suggest that the Raman bands observed on the colloidal silver surface can be ascribed to the adsorbed species and are enhanced by

Fig. 6. NIR-SER spectra of pyridine in silver colloids after addition of (a) Cl^- and Br^-, (b) Cl^- and I^- and (c) Br^- and I^- mixtures.

silver colloids. A question is raised by these spectra that ClO_3^- and BrO_3^- ions bond to the silver surface through the negatively charged O^- or the lone pair electrons of the Cl and Br. One may expect the interaction of these ions with colloidal silver surfaces through the negatively charged O^-. If this is the case, the Ag–O stretching mode should have little dependence on the mass of halides for different halate ions and should appear at about the same position. However, the observed SERS band positions depend obviously on the mass of the halides. This suggests that ClO_3^- and BrO_3^- ions interact with the silver surface quite probably through their lone pair electrons in Cl and Br instead of through the negatively charged O^-. In the halate structure, the valance of Cl, Br and I is +5. Lone pair electrons may have the affinity to bond to silver. In this case, the Cl and Br act as the electron donor and Ag acts as electron acceptor. The observed band at about 226 cm^{-1} in Fig. 7a may be assigned to the stretching vibrations of $Ag-ClO_3^-$ while the band at about 158 cm^{-1} in Fig. 7b may be attributed to the $Ag-BrO_3^-$ stretching mode. In contrast to the spectra of ClO_3^- and BrO_3^- ions, the NIR-SERS of IO_3^- ions is much different from the spectrum of I^- ions on colloidal silver surfaces. No Raman band in the $Ag-I^-$ stretching vibration region could be seen. The SERS spectrum of IO_3^- ions is dominated by a broad and very intense Raman band at about 750 cm^{-1} and a broad band at about 330 cm^{-1}. This result indicates that the adsorption of IO_3^- ions on the colloidal silver surface is different from those of ClO_3^- and BrO_3^- ions. The surface reaction of IO_3^- ions with silver surfaces occurred quite possibly through their negatively charged O^-. The reaction product is expected to be $AgIO_3$. This assumption is supported by the Raman spectrum of solid KIO_3 as shown in Fig. 8. The NIR-SERS of IO_3^- on silver surfaces is very similar to the normal Raman spectrum of solid KIO_3 both in band position and relative intensity. A comparison of Fig. 7 and Fig. 8 shows that the observed SERS bands at about 750 and 334 cm^{-1} have multi-components which are not resolved.

The different adsorption manner of halate ions on colloidal silver surfaces may be explained by the surface potential of the silver colloids. It was found that the relative intensity of the two ring breathing
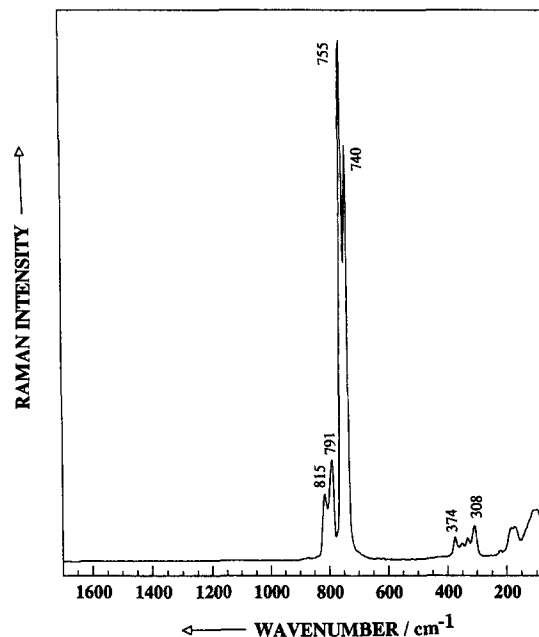

Fig. 8. Raman spectrum of solid KIO_3.

modes of pyridine changes with the applied potentials of the silver electrode. The ratios of I_{1038}/I_{1010} under different electrode potentials with 488.0 and 514.5 nm excitation were determined by Atkinson et al. [5]. We measured the intensity ratio of I_{1308}/I_{1010} of pyridine in silver colloids by using the same excitation wavelengths and compared it with that in [5]. The surface potential of silver colloids we used is estimated to be about −0.3 V. This potential is very approximate to the potential −0.3551 V under which the reaction

$$Ag + IO_3^- \rightarrow AgIO_3 + e$$
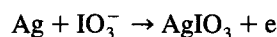
occurs [23]. However, this potential seems not favorable for the formation of $AgBrO_3$ (−0.680 V) and $AgClO_3$ (no available data) on colloidal silver surfaces.

The interaction strength order between halate ions and silver is studied with the mixtures of these ions. The results are shown in Fig. 9. In both the mixture of ClO_3^- and BrO_3^- ions and the mixture of BrO_3^- and IO_3^- ions, there appears only one Raman band at about 158 cm^{-1}. As discussed above, this band is characteristic of the $Ag-BrO_3^-$ interactions. These results indicate that in the two mixtures, BrO_3^- ions

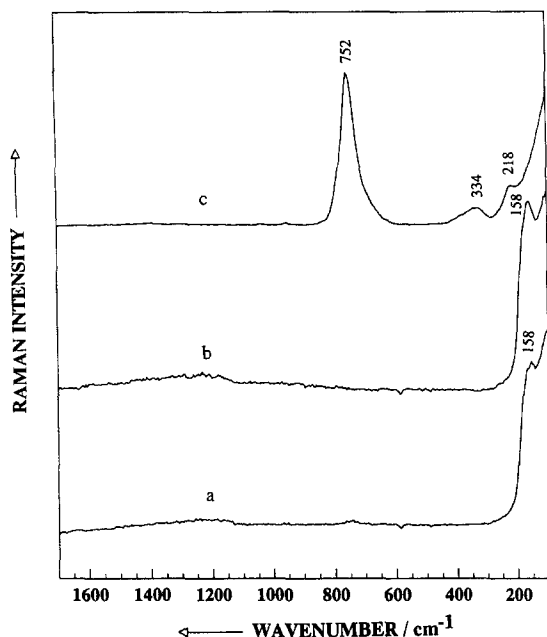Fig. 9. NIR-SER spectra of (a) BrO_3^- and IO_3^-, (b) ClO_3^- and BrO_3^- and (c) ClO_3^- and IO_3^- mixtures in silver colloids.

rather than IO_3^- and ClO_3^- ions interact directly with the silver surface. In the mixture of ClO_3^- and IO_3^- ions, besides the two Raman bands at about 752 and 334 cm^{-1}, a Raman band at about 218 cm^{-1} appears. The former two bands result from the IO_3^- ions on the silver surface while the latter is due to the $Ag-ClO_3^-$ stretching vibrations. It suggests that in the mixture of IO_3^- and ClO_3^-, both ions interact simultaneously with the silver surface. From these results we conclude that among the halate ions, BrO_3^- ions interact most strongly with the silver surface. The interaction between ClO_3^- ions and the silver surface and the interaction between IO_3^- ions and the silver surface rank in about the same order.

Halide ions are frequently used to enhance the Raman spectra of molecules in silver colloids and at silver electrodes. We tested the possibility to use halate ions to enhance the Raman spectra of pyridine and crystal violet with NIR excitation. In Fig. 10a–c we show the NIR-SERS spectra of pyridine in the presence of ClO_3^-, BrO_3^- and IO_3^- ions, respectively. It is obvious that all of these three halate ions can enhance the Raman scattering of pyridine in silver colloids considerably. The Raman signal of both

pyridine and halate ions are enhanced simultaneously. Best enhancement of the ring breathing modes of pyridine is observed in the presence of BrO_3^- ions. IO_3^- and ClO_3^- ions enhance the ring breathing modes of pyridine to a lesser extent.

In Fig. 11a–c we show the NIR-SERS spectra of pyridine in the presence of the mixtures of ClO_3^-/IO_3^-, BrO_3^-/IO_3^- and ClO_3^-/BrO_3^-, respectively. It is obvious that large enhancements of the Raman signal of pyridine are obtained in the presence of the mixture of ClO_3^-/BrO_3^- and of the mixture of BrO_3^-/IO_3^-. At the same time, the Raman band indicating $Ag-BrO_3^-$ vibrations at about 158 cm^{-1} are also observed. These results indicate that the Raman signal of pyridine is enhanced by the BrO_3^- ions rather than ClO_3^- and IO_3^- ions. This conclusion is further supported by NIR-SERS of pyridine with isolated halate ions (Fig. 10). In the presence of the mixture of the ClO_3^- and IO_3^- ions, the Raman signal of pyridine is less enhanced. The appearance of the Raman bands at about 750 and 220 cm^{-1} suggests that both of the halate ions contribute to the enhancement of Raman modes of pyridine. Fig. 11 shows also that the interaction
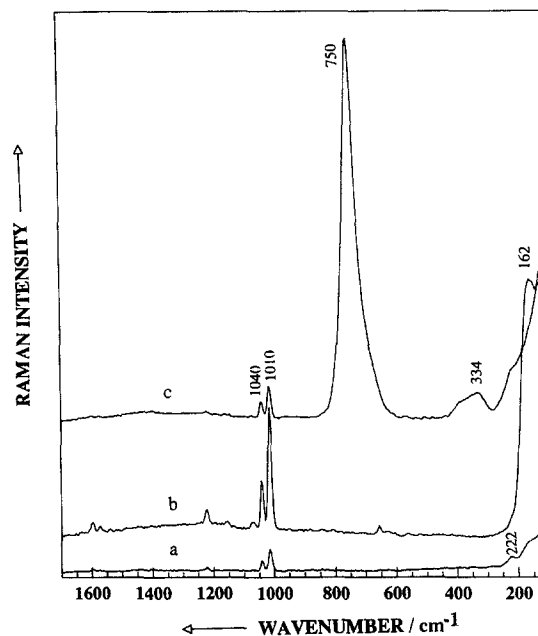

Fig. 10. NIR-SER spectra of pyridine in silver colloids in the presence of (a) ClO_3^-, (b) BrO_3^- and (c) IO_3^- ions.

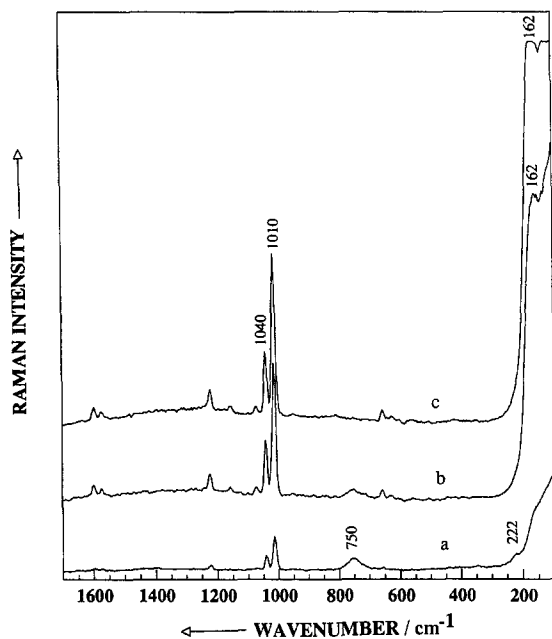Fig. 11. NIR-SER spectra of pyridine in silver colloids in the presence of (a) ClO_3^- and IO_3^-, (b) BrO_3^- and IO_3^- and (c) ClO_3^- and BrO_3^- mixtures.

Fig. 13. Absorption spectra of pyridine in silver colloids: (a) in the absence of halate ions; (b–d) in the presence of ClO_3^-, BrO_3^- and IO_3^- ions, respectively.

strength order of the halate ions with the silver surface is not altered in the presence of pyridine.

As in the case of halide ions, surface plasmon resonance is probably one of the major contributions to the observation of the NIR-SERS of halate ions and pyridine in the presence of halate ions. In order to confirm this point, we measured the absorption
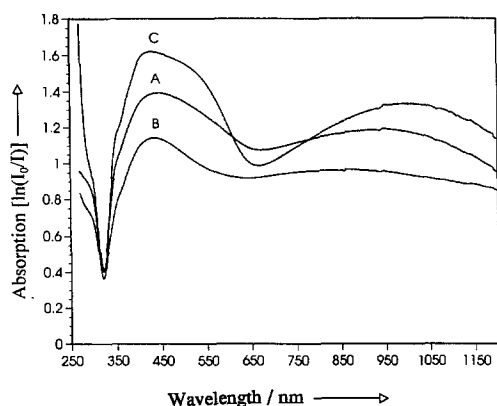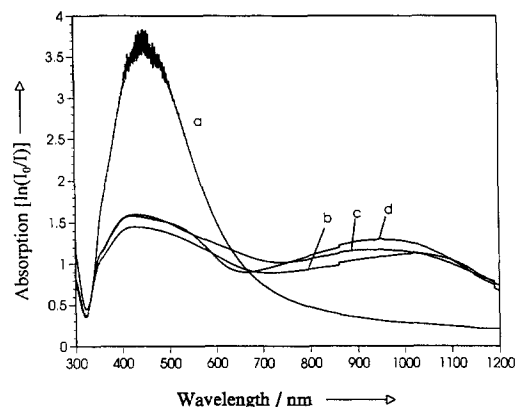
spectra in the two cases as shown in Figs. 12 and 13, respectively. As can be seen from Fig. 13a, no absorption band appears in the NIR wavelength region if only pyridine is added to the silver sol. After addition of halate ions, a broad absorption band in the NIR wavelength region appears, no matter whether pyridine is absent or present. These absorption spectra indicate that halate ions cause the silver particles to aggregate and move the surface plasmon resonances to the NIR-wavelength region. The maximum position of the surface plasmon resonances appears at about the same wavelength as the excitation line. These results confirm that the surface plasmon resonance is a major contribution to the NIR-SERS.
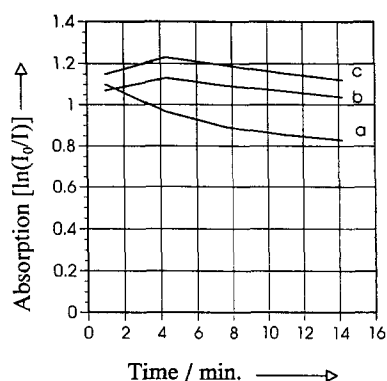

Fig. 12. Absorption spectra of (a) ClO_3^-, (b) BrO_3^- and (c) IO_3^- ions in silver colloids.

Fig. 14. Time evolution of the absorption of pyridine in silver colloids at the excitation wavelength in the presence of (a) ClO_3^-, (b) BrO_3^- and (c) IO_3^- ions.
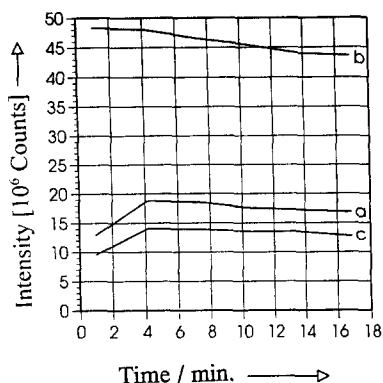
Fig. 15. Time dependence of the NIR-SERS intensity of the 1010 cm^{-1} band of pyridine in silver colloids in the presence of (a) ClO_3^-, (b) BrO_3^- and (c) IO_3^- ions.

More detailed measurements about the time evolution of the surface plasmon resonance of the silver colloids at the excitation wavelength and the NIR-SERS of the 1010 cm^{-1} band of pyridine are shown in Figs. 14 and 15, respectively. As can be seen from Figs. 14 and 15, in stable state the surface plasmon resonance of silver colloids caused by addition of halate ions decreases in the order $IO_3^- > BrO_3^- > ClO_3^-$. However, the enhancement of the ring breathing modes of pyridine caused by addition of halate ions ranges in the order $BrO_3^- \gg ClO_3^- > IO_3^-$. These results suggest that another enhancement mechanism in addition to the electromagnetic enhancement must exist in the NIR-SERS. The additional enhancement mechanism is a chemical effect and is related to the nature of the halate ions. As in the case of halide ions, surface active sites may be created on colloidal silver surfaces by the halate ions. The additional enhancement may result from the surface complexes of pyridine/halate ions which are adsorbed on the special active sites. BrO_3^- ions are possibly to create surface active sites on colloidal silver surfaces much more effectively than ClO_3^- and IO_3^- ions. Based on the experimental data in Figs. 14 and 15, about 2.2 and 3.7 times more surface active sites are estimated to be produced by BrO_3^- ions than by ClO_3^- and IO_3^- ions.

4. Conclusion

We have studied the interaction of halide and halate ions with colloidal silver surfaces and the influence of these ions on the enhancement of the Raman bands from pyridine. The experimental results reveal that the interaction strength between halide ions and the silver surface decreases in the order $I^- > Br^- > Cl^-$, with or without pyridine. The enhancements of the Raman bands of pyridine caused by addition of these ions range in the order $Cl^- \approx Br^- \gg I^-$. The SERS spectra of ClO_3^-, BrO_3^- and IO_3^- reveal that the adsorption manners of these ions on colloidal silver are different. ClO_3^- and BrO_3^- ions interact with silver surface through their lone pair electrons of Cl and Br while IO_3^- ions bind to the silver surface through their negatively charged O^-. The characteristic Raman bands indicating these interactions are located at about 226 $(Ag–ClO_3^-)$, 158 $(Ag–BrO_3^-)$, 750 and 334 $(AgIO_3)$ cm^{-1}, respectively. BrO_3^- ions cause the largest enhancement of the ring breathing modes of pyridine in silver colloids while ClO_3^- and IO_3^- ions follow in order. Absorption spectroscopic studies of these ions in silver colloids indicate that halide and halate ions contribute not only to the electromagnetic enhancement but also to the chemical enhancement of the NIR-SERS of these ions and pyridine. Br^- ions have a higher ability than Cl^- and I^- ions in creating surface active sites. In the case of halate ions, more surface active sites are produced by BrO_3^- ions than by ClO_3^- and IO_3^- ions.

Acknowledgements

References

[1] R.L. Garrel, K.D. Shaw, S. Krimm, J. Chem. Phys. 75 (1981) 4155.

[2] A. Regis, J. Corset, Chem. Phys. Lett. 70 (1980) 305.

[3] J.F. Evan, M.G. Albrecht, D.M. Ullevig, R.M. Hexter, J. Electroanal. Chem. 106 (1980) 209.

[4] J.R. Lombardi, E.A. Shields Knight, R.L. Birke, Chem. Phys. Lett. 79 (1981) 214.

[5] G.F. Atkinson, D.A. Guzonas, D.E. Irish, Chem. Phys. Lett. 75 (1980) 557.

[6] R. Dornhaus, R.E. Beuner, R.K. Chang, H. Chabae, Surface Sci. 101 (1980) 367.

[7] B. Pettinger, M.R. Philpott, J.G. Gordon II, J. Phys. Chem. 85 (1981) 2746.

[8] B. Pettinger, K. Krischer, G. Ertl, Chem. Phys. Lett. 151 (1988) 151.

[9] M. Kim, K. Itoh, J. Phys. Chem. 91 (1987) 126.

[10] S.Y. Fu, P.X. Zhang, J. Raman Spectrosc. 23 (1992) 93.

[11] H. Saito, J. Raman Spectrosc. 24 (1993) 191.

[12] S.S. Park, K. Kim, M.S. Kim, Chem. Phys. Lett. 230 (1994) 171.

[13] E.J. Liang, C. Engert, W. Kiefer, J. Raman Spectrosc. 24 (1993) 775.

[14] E.J. Liang, C. Engert, W. Kiefer, Vib. Spectrosc. 6 (1993) 79.

[15] E.J. Liang, C. Engert, W. Kiefer, Vib. Spectrosc. 8 (1995) 435.

[16] S.M. Angel, D.D. Archibald, Appl. Spectrosc. 43 (1989) 1097.

[17] D.B. Chase, B.A. Parkinson, Appl. Spectrosc. 42 (1988) 1186.

[18] P.X. Zhang, X. Wang, Z.G. Guo, Chin. Phys. Lett. 7 (1990) 465.

[19] M. Pagannone, L.G. Quagliano, L. Mattioli, J. Mattei, J. Raman Spectrosc. 22 (1991) 825.

[20] P.C. Lee, D.P. Meisel, J. Phys. Chem. 86 (1982) 3391.

[21] E.J. Liang, W. Kiefer, to be published.

[22] E.J. Liang, X.L. Ye, W. Kiefer, to be published.

[23] R.C. Weast, G.L. Tuve (Eds.), Handbook of Chemistry and Physics, 53rd ed., CRC press, Boca Raton, FL, 1972–1973, D-111.