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# Surface-enhanced Raman scattering of halide ions, pyridine and crystal violet on colloidal silver with near-infrared excitation: low-wavenumber vibrational modes

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## Abstract

Surface-enhanced Raman scattering from halide ions, pyridine and crystal violet with and without coexistence of halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) in the low-wavenumber region is studied by using a conventional scanning Raman spectrometer and near-infrared excitation. It is found that there exist at least two active Raman modes in the wavenumber region between 200 and  $300\text{ cm}^{-1}$  for pyridine adsorbed on colloidal silver in the presence of chloride ions as well as that the halide ions affect also the ring breathing modes of adsorbed pyridine. Enhancement and shift in band positions of the ring breathing modes decrease in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . The observed band at about  $240\text{ cm}^{-1}$  is assigned to the Ag–Cl stretching vibration whereas a band at about  $221\text{ cm}^{-1}$  is due to the surface complex of the adsorbed pyridine. We also found that more than one Raman mode in the low-wavenumber region are simultaneously active for adsorbed crystal violet on colloidal silver in the presence of chloride ions. The experimental results indicate that the Ag–Cl stretching vibration accounts for the Raman band at about  $240\text{ cm}^{-1}$  and that the Raman mode at about  $210\text{ cm}^{-1}$  is specific for crystal violet.

**Keywords:** Crystal violet; Halide ions; Pyridine; Raman spectrometry; Silver sols; Surface enhanced Raman spectrometry

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## 1. Introduction

The discovery of the surface-enhanced Raman scattering (SERS) effect of pyridine adsorbed on an electrochemically roughened silver electrode has opened a wide research field in both physics and chemistry of interfaces and Raman spectroscopy [1–6]. SERS has been extensively studied with visible light excitation and pyridine is one of the most extensively studied molecules. However, a complete

understanding of this phenomenon has not been established. Some basic problems in SERS remain still unclear.

Halide ions play an important role in the surface enhancement in both electrochemical environments and metal colloids. Although many articles [7–22] deal with the SERS of halide ions and adsorbed molecules coexisting on a silver electrode or on colloidal silver, the basic mechanisms of the influence of halide ions on the surface enhancement are still not understood. Furthermore, the SERS spectra of pyridine and crystal violet revealed some new lines particularly in the wavenumber region between

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200 and 300  $\text{cm}^{-1}$  but no corresponding Raman modes appear in their solution spectra. This has attracted particular attention because the vibrational frequencies for surface–adsorbate bonds involving heavy atoms are generally below 300  $\text{cm}^{-1}$  and one may gain insight into the nature of the metal–adsorbate bonding from the low-wavenumber Raman studies. However, the dispute about the correct assignment of these new Raman modes in the low-wavenumber region continues. The difficulty for the correct assignment of these lines may arise from the following. (i) The low wavenumber modes usually appear when chloride ions and adsorbed molecules such as pyridine coexist. It is difficult to distinguish the interactions between the surface and chloride ions and the interactions between the surface and pyridine. (ii) These modes do not always appear with visible light excitation in the absence of either pyridine or chloride ions and sometimes even not in the presence of both. (iii) Visible light excitation may induce photo-dissociation of the silver salts formed on the surface.

Recently SERS was shown to be operative in the near-infrared (NIR) wavelength region by Fourier transform (FT) Raman [23–28] and conventional scanning Raman [29,30] techniques. Our earlier studies showed that the Raman modes in the low-wavenumber region are much more sensitive to NIR excitation than to visible light excitation [29,30]. In this paper, we take this advantage to study the SERS of halide ions, pyridine and crystal violet with and without coexistence of halide ions in silver colloids. Particular attention is drawn to the low-wavenumber Raman modes with the motivation to give a better understanding of the nature of these bands.

## 2. Experimental

Two types of silver colloids were used in the experiments. Yellow silver colloids were prepared by a method similar to that reported by Creighton et al. [31]. A typical procedure is as follows. 100 ml of  $1.0 \times 10^{-3}$  M  $\text{AgNO}_3$  and 300 ml of  $2.0 \times 10^{-3}$  M  $\text{NaBH}_4$  were prepared with deionized water at room temperature. The  $\text{AgNO}_3$  solution was rapidly added to the  $\text{NaBH}_4$  solution. During and a few minutes after mixing the mixture was stirred vigorously. The

resulting solution was kept at room temperature for several hours without stirring. Afterwards it was kept in a sealed flask in a refrigerator. The silver colloids prepared in this way color yellowish brown and are stable for at least several months. Grey silver colloids were prepared as described by Lee and Meisel [32]: 90 mg  $\text{AgNO}_3$  were dissolved in 500 ml deionized water and the solution was heated till boiling. To the boiling solution 10 ml aqueous solution of 1% sodium citrate were slowly added. The solution was kept boiling for about 40 min. The final volume was adjusted to 500 ml with deionized water. The main differences between these two kinds of sols are their particle size and the peak positions of their surface plasmon resonances. The former has a small particle size (ca. 10 nm in diameter) with an absorption maximum at about 390 nm while the latter has a larger particle size (ca. 40–50 nm in diameter) and its surface plasmon resonance peaks at about 440 nm. A 0.2 M pyridine solution was prepared with deionized water. The final concentration of pyridine throughout the experiments was about  $1.67 \times 10^{-2}$  M. Crystal violet and halide salts ( $\text{NaCl}$ ,  $\text{NaBr}$  and  $\text{KI}$ ) were dissolved in deionized water. The concentration used is indicated in each figure caption. The NIR-SERS spectra were recorded with a Jarrell-Ash Model 25-103 1 m  $f/8.7$  double-grating monochromator, which was equipped with a Bruker Model D450 InGaAs detector and controlled by a computer. The spectral resolution is about 6  $\text{cm}^{-1}$ . The 1064 nm output of a TEM<sub>00</sub>-mode linearly polarized continuous-wave Nd:YAG laser was used as excitation source. More details about the experimental set-up have been reported elsewhere [33].

## 3. Results and discussion

Fig. 1 shows the NIR-SERS spectra of (a) aqueous  $\text{NaCl}$ , (b)  $\text{NaBr}$  and (c)  $\text{KI}$  on grey colloidal silver. It is obvious that these spectra depend on the nature of the halide ions.  $\text{Cl}^-$  ions alone on colloidal silver give rise to a broad band between 200 and 300  $\text{cm}^{-1}$  which peaks at about 242  $\text{cm}^{-1}$  (243  $\text{cm}^{-1}$  in yellow silver colloids for the same concentration). By replacing  $\text{Cl}^-$  with  $\text{Br}^-$  and  $\text{I}^-$  ions, the Raman band shifts down to 158  $\text{cm}^{-1}$  and 117  $\text{cm}^{-1}$ , respectively. These observations are in agreement

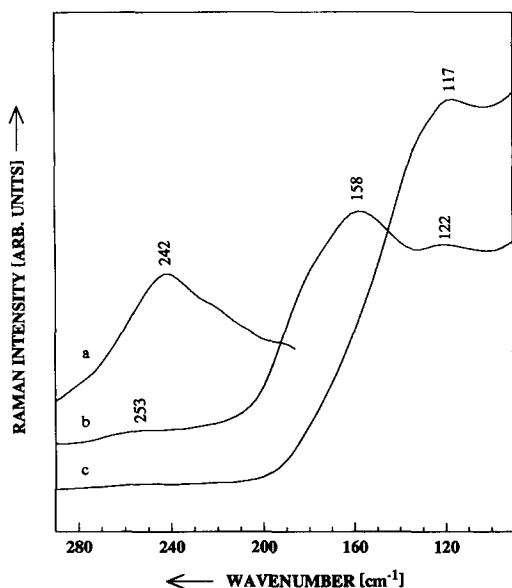


Fig. 1. SERS spectra of (a) 0.2 M aqueous NaCl, (b) 0.2 M aqueous NaBr and (c) 0.2 M aqueous KI in grey silver sol with a volume ratio of 1:10.

with those for a silver electrode with 676 nm excitation reported by Wetzel et al. [17] and are also in agreement with theoretical calculations of the symmetric stretching mode perpendicular to the silver metal surface for adsorbed  $\text{Cl}^-$  ( $240\text{ cm}^{-1}$ ),  $\text{Br}^-$  ( $150\text{ cm}^{-1}$ ) and  $\text{I}^-$  ( $113\text{ cm}^{-1}$ ) at full coverage [34]. Since the experiments are carried out in a pyridine-free environment, these bands may well be ascribed to the Ag–Cl ( $242\text{ cm}^{-1}$ ), Ag–Br ( $158\text{ cm}^{-1}$ ) and Ag–I ( $117\text{ cm}^{-1}$ ) stretching vibrations. Besides the prominent bands there exist some weaker features at about 122 and  $253\text{ cm}^{-1}$ . The additional bands were considered as skeletal vibrations of surface complexes [35], as an indication of surface complex formation involving more than one halide ion [17] or as internal vibrations of  $\text{Ag}_n$  clusters [16]. Definite assignments and unquestionable evidences for these assignments are still lacking. Though these bands appear after addition of halide ions, they are independent of the nature of the halide ions. Therefore, they must be related to the silver sol itself. Other

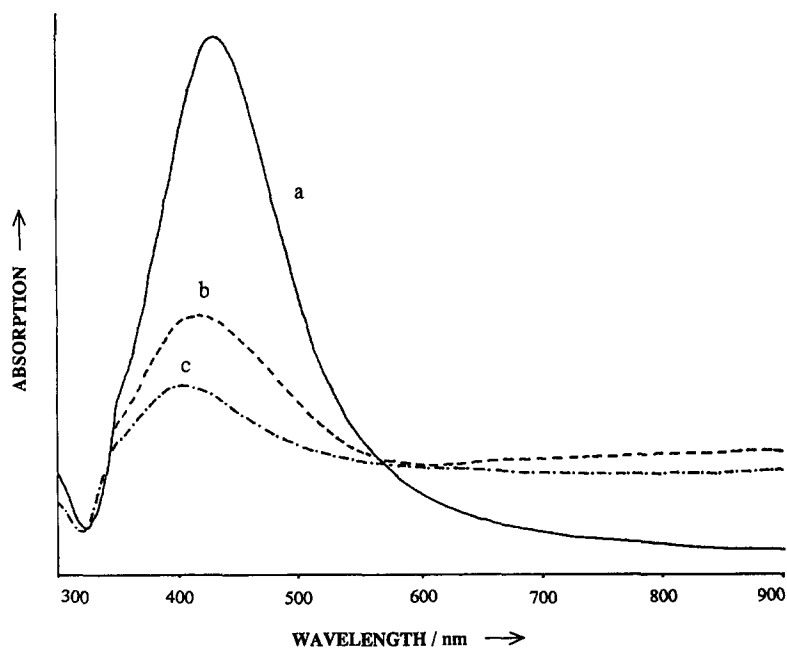


Fig. 2. Absorption spectra of (a) grey silver sol, (b) immediately after addition of 0.2 M aqueous NaCl to the sample of (a) with a volume ratio of 1:10 and (c) 4 min after addition of 0.2 M NaCl to the sample of (a).

possible origins of these modes are disorder-induced Raman scattering from silver metal phonons [36] and resonance Raman localized modes of small silver aggregates formed at defects in the AgX (X = Cl, Br, I) lattice [37]. Ag<sub>3</sub> clusters that are known to give rise to a Raman band at about 120.5 cm<sup>-1</sup> [38] may contribute to the 122 cm<sup>-1</sup> band. The inter-particle and intra-particle correlation effects may also contribute to these bands. More detailed studies on these modes are needed.

Pettinger et al. [16] stated that the Ag–X (X = Cl, Br, I) vibrations were only observed in the presence of pyridine. Wetzel et al. [17] failed to observe an SERS signal from 0.1 M NaCl electrolyte on a silver electrode with 514.5 nm excitation, but they observed an SERS band for the same sample with 647 and 676 nm excitation. These authors attributed the failure to observe SERS for the Ag–halide vibrations with 514.5 nm excitation to the low number of Raman scatterers. In contrast, with NIR excitation we can always observe SERS for the Ag–halide vibrations on colloidal silver in the absence of pyridine, even if the electrolyte concentration is as low as 5 mM. No attempt was made to detect the lowest concentration limit in our study. To explain the higher sensitivity of the Ag–halide modes to NIR excitation, we argue that if one changes solely the excitation wavelengths while the concentration of the sample does not change, the number of Raman scatterers should be the same. Of course, photo-induced dissociation may occur when the sample is excited with higher energy photons. An alternative explanation for the response of the Ag–halide vibration modes to different excitation wavelengths may be as follows. The adsorption of halide ions causes the surface plasmon resonance to shift to a longer wavelength, which is favorable for red or NIR excitation. This assumption is verified by an absorption spectral study from the silver sol–halide systems as shown in Fig. 2. The halide ions shift the surface plasmon resonance to the red/NIR spectral region, which is caused by multipolar interactions among the particles due to the aggregation of the sol and is induced by the chemisorption of the halide ions. Generally, the aggregation of the sol is of importance for the observation of SERS.

The SERS spectra of pyridine in grey silver sol before and after addition of NaCl are shown in Fig.

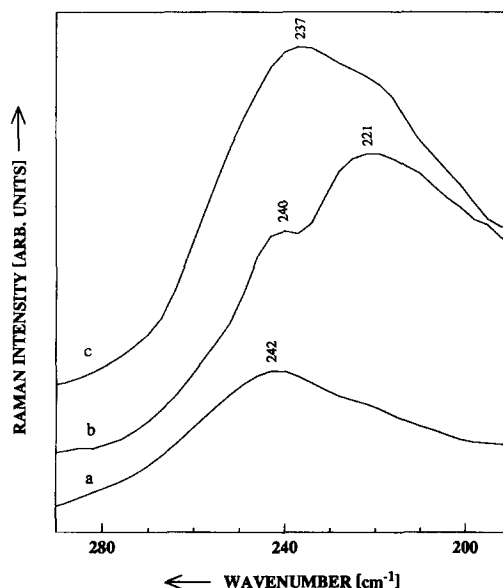


Fig. 3. SERS spectra of (a) 0.05 ml of 0.2 M NaCl in 0.5 ml grey silver sol, (b) pyridine in grey silver sol immediately after addition of 0.2 M NaCl and (c) the same as (b) except for 10 min after addition of NaCl. The final concentration of NaCl is ca.  $1.67 \times 10^{-2}$  M.

3, spectra a–c. No Raman bands can be observed between 200 and 300 cm<sup>-1</sup> for pure pyridine in silver sols. After addition of NaCl, intense Raman bands in this region appear. It is obvious from spectrum b of Fig. 3 that at least two Raman modes are simultaneously active. One peaks at about 240 cm<sup>-1</sup> and another at about 221 cm<sup>-1</sup>. Both are broad and they overlap. They appear in some cases as one broad asymmetric band which peaks between 220 and 242 cm<sup>-1</sup> as shown in Fig. 3, spectrum c. In this case, it is difficult to distinguish one from another. This may be the main cause of the debate and misinterpretation about the low-wavenumber modes of pyridine in the presence of chloride ions. As mentioned in the introduction section, the low-wavenumber modes do not always appear in the same environment with visible light excitation. With NIR excitation, these modes always appear with high intensities. Similar results with yellow silver colloids are obtained as shown in Fig. 4. The similarity of the spectra in both sols indicates that the two bands are independent of the procedures and the chemicals used in preparing the sols. This suggests that the

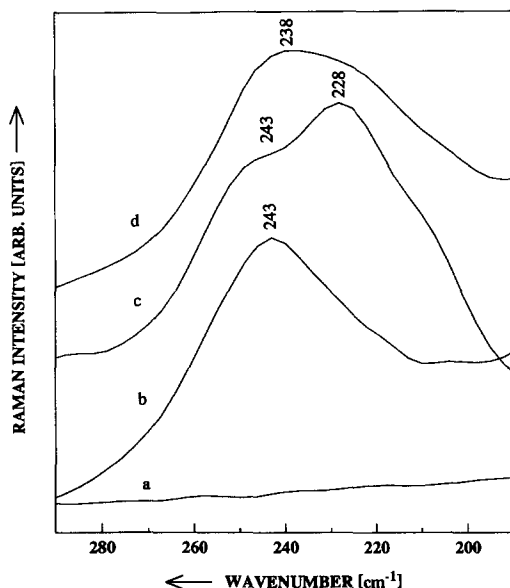


Fig. 4. SERS spectra of (a) pyridine in yellow silver sol, (b) 0.05 ml of 0.2 M NaCl in 0.5 ml yellow silver sol, (c) pyridine in yellow silver sol immediately after addition of 0.2 M NaCl and (d) the same as (c) except for 10 min after addition of NaCl. The final concentration of NaCl is the same as in Fig. 3.

origins of the two bands are related to the surface complex of chloride and pyridine.

A Raman band at  $239\text{ cm}^{-1}$  for pyridine on a silver electrode was first observed by Creighton et al. [7]. They assigned the band to Ag–N stretching vibrations of the adsorbed pyridine on the basis that the corresponding infrared line for Ag–pyridine complex  $[\text{Ag}(\text{C}_5\text{H}_5\text{N})_2]^+$  is measured at  $245\text{ cm}^{-1}$ . Van Duyne has attributed a line at  $239\text{ cm}^{-1}$  to a surface layer of AgCl for potentials more positive than  $-0.4\text{ V}$  and a line at  $216\text{ cm}^{-1}$  to an Ag–N surface bond for more negative potentials [8]. Evans et al. [11] carried out studies on well-characterized very clean silver surfaces and concluded that the  $240\text{ cm}^{-1}$  band could be attributed to an Ag–Cl stretching mode due to the residual  $\text{Cl}^-$  remaining on the surface. Also, Dornhaus et al. [15] and Pettinger et al. [16] have attributed this band to the Ag–Cl stretching mode. A Raman line at  $227\text{ cm}^{-1}$  in the presence of pyridine and chloride ions on a silver electrode was observed by Regis and coworkers [9,10]. They assigned it to the formation of  $\text{Cl}_2^-$  ions stabilized in the AgCl solid layer. They argued that

the band cannot be due to an Ag–pyridine stretching vibration since (i) the band is still observed at pH 1.2 and (ii) the band disappears when the  $\text{Cl}^-$  ions are replaced by  $\text{Br}^-$  ions in the solution. Lombardi et al. [13] observed a line in the same region of the SERS spectra of several molecules under  $\text{Cl}^-$ -free conditions and supported the assignment by Creighton et al. [7]. Hildebrandt and Stockburger [18] observed an SERS band at about  $232\text{ cm}^{-1}$  from R6G/ $\text{Cl}^-$ /silver sol system and assigned it to Ag–N stretching vibrations based on the result that the band did not vanish by replacing  $\text{Cl}^-$  with  $\text{Br}^-$ . However, they failed to record this band by replacing  $\text{Cl}^-$  with  $\text{I}^-$ . More recently, Kim and Itoh [19] studied the SERS from 2,2'-bipyridine adsorbed on silver colloids and observed a band at about  $240\text{ cm}^{-1}$ . They assigned it to the Ag– $\text{Cl}^-$  stretching vibration based on the results that this band disappears when HCl is replaced by HBr or HI. Saito [20] observed a band at  $227\text{ cm}^{-1}$  from pyridine on a silver electrode in aqueous KCl media and attributed it to a Ag–pyridine stretching mode in the adsorbed complex which gives rise to the  $1025\text{ cm}^{-1}$  band. By replacing the  $\text{Cl}^-$  ions with  $\text{Br}^-$  ions, this band did not disappear. The low-wavenumber band was assigned by these authors only to one surface species, mostly either solely to Ag–Cl or solely to Ag–N. Even in the case where only one band appears, the asymmetry and width of the band may raise one's doubt that the band is due only to Ag–Cl or Ag–N stretching vibrations.

The confusion about the origin of the low-wavenumber bands arose from the following facts: (i) The Ag–Cl and Ag–N stretching vibrations are located in the same spectral region. (ii) The band do not always appear in a chloride-free medium upon visible light excitation. This band is missing in Raman spectra of pyridine adsorbed on silver island films under UHV conditions [39]. With 514.5 nm and NIR excitations we did not observe any Raman modes between 200 and  $300\text{ cm}^{-1}$  for pure pyridine in silver colloids [29]. Nevertheless, a Raman band around  $230\text{ cm}^{-1}$  appears from pyridine on a silver nitrate treated metal surface [40]. Since this experiment was carried out in a halide-free environment, this band should be assigned to the Ag–N (or Ag–pyridine) stretching mode. (iii) In some cases, the Raman band for chloride ions on silver cannot be observed without

addition of pyridine as pointed out by Pettinger et al. [16]. Nevertheless, the low-wavenumber bands do not always appear upon visible light excitation even if both chloride ions and pyridine are present. With NIR excitation, the low-wavenumber bands can always be observed and are very intense when both halide ions and pyridine are present. Taking this advantage, we demonstrated that there exist at least two Raman active modes in the wavenumber region between 200 and 300  $\text{cm}^{-1}$ . On the basis of the previous assignments by others mentioned above and our experimental results in Figs. 1, 3 and 4 together with the result of Fig. 1 in Ref. [40], we tentatively assign the band around 240  $\text{cm}^{-1}$  to an Ag–Cl stretching mode and the band at 221  $\text{cm}^{-1}$  (228  $\text{cm}^{-1}$  in yellow silver colloids) to an Ag–N (Ag–pyridine in the adsorbed complex, in which chloride ions are probably involved) stretching mode. The relative intensity of the two bands in Figs. 3 and 4 behaves differently with time. This may be taken as a further evidence that the two bands are from different origins. If only one asymmetric broad band (or with a shoulder) such as in spectra c (Fig. 3) and d (Fig. 4) is observed and both pyridine and chloride ions are present, it should be a contribution from both.

In Fig. 5 we show the SERS spectra of pyridine on colloidal silver in different halide media. It is obvious that if the  $\text{Cl}^-$  ions are replaced by  $\text{Br}^-$  ions, a weak broad Raman band appears around 247  $\text{cm}^{-1}$ . Since spectrum b in Fig. 5 is measured in a  $\text{Cl}^-$ -free medium, this band cannot be attributed to an Ag–Cl stretching vibration. Considering the result in Fig. 1, spectrum b, the band around 247  $\text{cm}^{-1}$  in spectrum b of Fig. 5 may have the same origin as the band around 253  $\text{cm}^{-1}$  in spectrum b of Fig. 1. However, they differ both in intensity and position from each other. This is probably due to the fact that a surface complex of silver–pyridine, in which  $\text{Br}^-$  is also involved [20], contributes also to the band around 247  $\text{cm}^{-1}$ . However, if the  $\text{Cl}^-$  ions are replaced by  $\text{I}^-$  ions, the weak feature in the same wavenumber region can hardly be recognized.

As mentioned above, the low-wavenumber modes for pyridine on colloidal silver in the presence of halide ions depend on the nature of the halide ions. This feature may affect the ring breathing modes of pyridine. If the halide ions are involved in the sur-

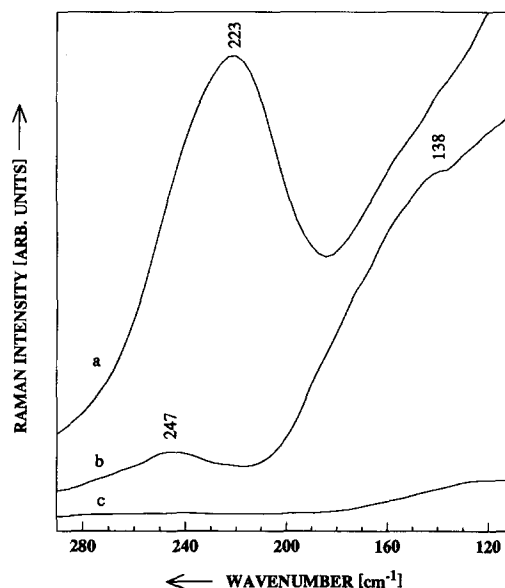


Fig. 5. SERS spectra of pyridine in the presence of (a) 0.2 M NaCl, (b) 0.2 M NaBr and (c) 0.2 M KI. The final concentration of the halides is ca.  $1.67 \times 10^{-2}$  M.

face complex of Ag–pyridine, a spectral change for the ring breathing modes should be observed. To confirm this point, we measured the spectra of pyridine in the ring breathing vibration region as shown in Fig. 6. As expected, the SERS spectra of the ring breathing modes depend on the nature of halide ions as well. The enhancement for these modes increases in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . The band positions are also slightly affected by the halide ions. As already pointed out in our earlier study [29],  $\text{Cl}^-$  ions cause the ring breathing modes to shift to higher wavenumbers relative to those of pure pyridine on colloidal silver. Chloride ions result in the largest shift to the higher wavenumbers of the ring breathing modes.  $\text{Br}^-$  and  $\text{I}^-$  ions follow in order. These observations for the ring breathing modes together with those for the low-wavenumber modes may be explained as follows.  $\text{Cl}^-$  and  $\text{Br}^-$  ions have a higher ability than  $\text{I}^-$  ions to form a surface complex with pyridine on colloidal silver. The surface complex contributes to the shift of the ring breathing modes to higher wavenumbers and to the appearance of one of the Raman modes between 200 and 300  $\text{cm}^{-1}$ . Besides,  $\text{Cl}^-$  and  $\text{Br}^-$  ions may have a larger capacity than  $\text{I}^-$  ions to cause the silver sol to aggregate and move

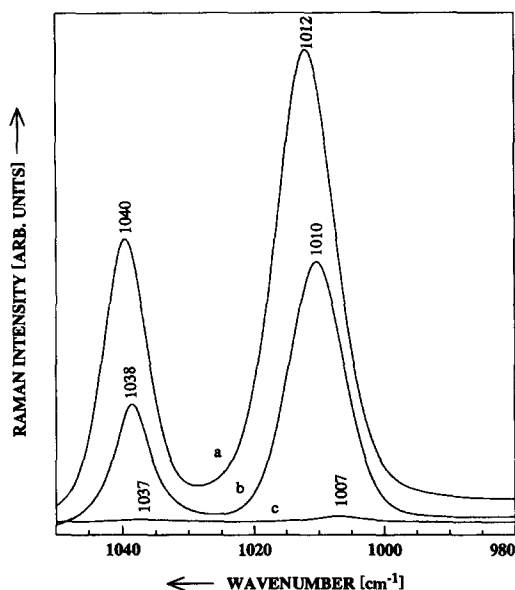


Fig. 6. SERS spectra of the ring breathing modes of pyridine in the presence of (a) 0.2 M NaCl, (b) 0.2 M NaBr and (c) 0.2 M KI. The final concentration of the halides is the same as in Fig. 5.

the surface plasmon resonance to the NIR wavelength region. The red shift of the surface plasmon resonance accounts mainly for the large enhancement in the NIR spectral region. This is confirmed by the absorption spectra of the corresponding systems which are shown in Fig. 7.

The same difficulty in the assignment of the low-wavenumber bands exists for crystal violet on silver. In Fig. 8 we show our experimental results of the low-wavenumber bands of crystal violet on colloidal silver. No Raman bands between 200 and 300  $\text{cm}^{-1}$  could be observed for crystal violet on colloidal silver before addition of NaCl. After addition of NaCl, the low-wavenumber bands appear and increase with time. From Fig. 8 (spectra a–c) we clearly see that in this wavenumber region more than one Raman modes are active. In spectrum a of Fig. 8 the Raman mode at about 246  $\text{cm}^{-1}$  is the most intense while in spectrum b (Fig. 8) the Raman mode at about 210  $\text{cm}^{-1}$  surpasses the one at about 240  $\text{cm}^{-1}$  in intensity. At a stable state the spectrum

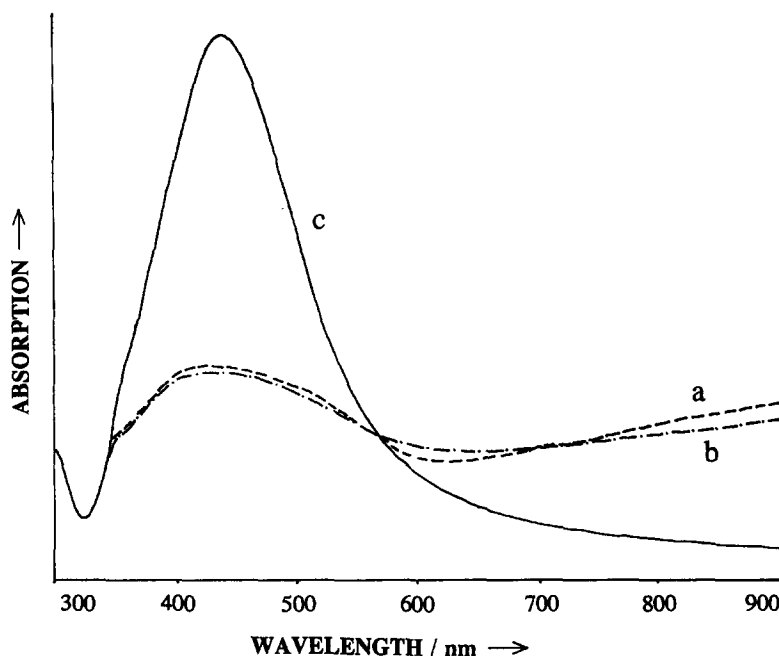


Fig. 7. Absorption spectra of 0.2 ml of 0.2 M pyridine in 2.0 ml grey silver sol in the presence of 0.2 ml of (a) 0.2 M NaCl, (b) 0.2 M NaBr and (c) 0.2 M KI.



appears as shown in spectrum c. The Raman band at about  $222\text{ cm}^{-1}$  is the most intense and the band at about  $240\text{ cm}^{-1}$  appears as a shoulder. These results indicate that there exist more than one surface species which account for the different vibrational modes. At the initial state, different surface species compete in occupying the surface sites and result in the spectral changes. This competitive adsorption is caused by the addition of chloride ions. The band near  $240\text{ cm}^{-1}$  may well be assigned to the Ag–Cl stretching vibrations according to Figs. 1 and 8. The other Raman bands are quite possibly silver–crystal violet relevant.

In order to get a better understanding of the nature of these Raman modes, we carried out an experiment in which  $\text{Cl}^-$  ions were replaced by  $\text{Br}^-$  and  $\text{I}^-$  ions. The results for crystal violet in grey silver sol are shown in Fig. 9. The same results are obtained in yellow sols. Fig. 9 shows that though no Raman bands could be observed for pure crystal violet on colloidal silver between 200 and  $300\text{ cm}^{-1}$ , after addition of the halide ions Raman bands appear in this region. It is apparent that the Raman band in a  $\text{Br}^-$  or  $\text{I}^-$  medium differs from that in the presence of  $\text{Cl}^-$  ions. The band at about  $240\text{ cm}^{-1}$  vanishes

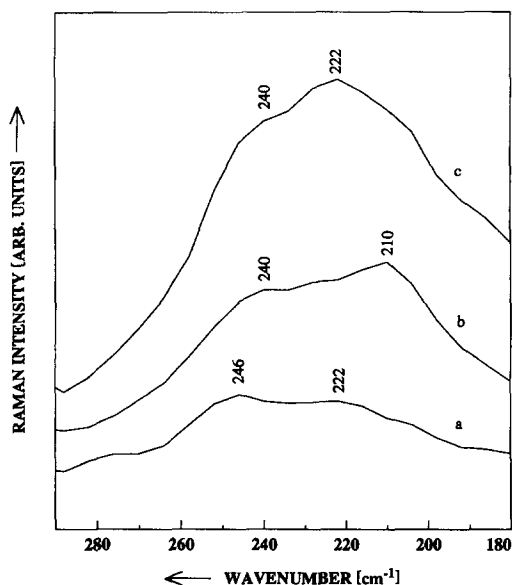


Fig. 8. SERS spectra of  $0.05\text{ ml}$  of  $1.0 \times 10^{-6}\text{ M}$  crystal violet in  $0.5\text{ ml}$  grey silver sol (a) immediately after mixing, (b) 3 min and (c) 20 min after addition of  $0.05\text{ ml}$  of  $0.2\text{ M}$  NaCl.

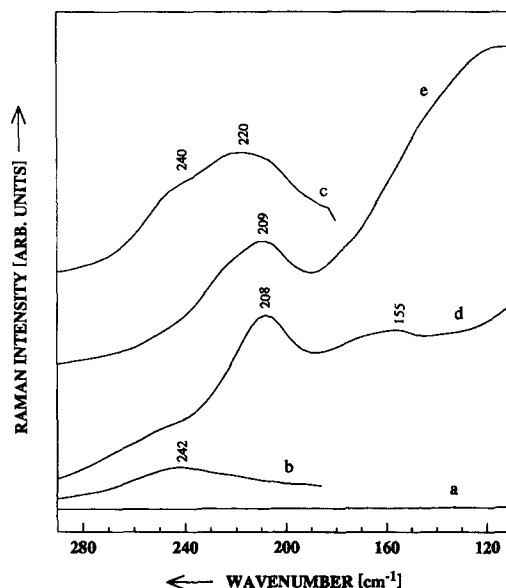


Fig. 9. SERS spectra of (a)  $0.05\text{ ml}$  of  $1.0 \times 10^{-6}\text{ M}$  crystal violet in  $0.5\text{ ml}$  grey silver sol, (b)  $0.05\text{ ml}$  of  $0.2\text{ M}$  NaCl in  $0.5\text{ ml}$  grey silver sol, (c)–(e)  $0.05\text{ ml}$  of  $1.0 \times 10^{-6}\text{ M}$  crystal violet in  $0.5\text{ ml}$  grey silver sol after addition of  $0.05\text{ ml}$   $0.2\text{ M}$  NaCl, NaBr and KI, respectively.

when  $\text{Cl}^-$  ions are replaced by  $\text{Br}^-$  or  $\text{I}^-$  ions. This implies that the band near  $240\text{ cm}^{-1}$  is  $\text{Cl}^-$  specific. The band at about  $210\text{ cm}^{-1}$  always appears no matter what kind of halide ion is used. This indicates that this band must be related to the adsorbed crystal violet. Two possible events may be responsible for the observation of the Raman band at about  $222\text{ cm}^{-1}$ : (i) the overlap of the band at about  $240\text{ cm}^{-1}$  and the band at about  $210\text{ cm}^{-1}$  causes a band peaking in between; (ii) a third surface species may be induced by the interaction of chloride ions and crystal violet. The SERS spectral profile from yellow silver sol (see Fig. 10, spectrum d) implies that the second assumption cannot be excluded. More experiments are certainly necessary for further clarification of these points.

Finally, we like to point out that the band profile and the maximum position of the low-wavenumber bands of crystal violet in the presence of chloride ions depend on the concentration of  $\text{Cl}^-$  as shown in Fig. 10 (spectra a–c). With a higher concentration ( $1.0\text{ M}$ ), the low-wavenumber modes in grey silver sol appear as one broad band peaking at about  $240$

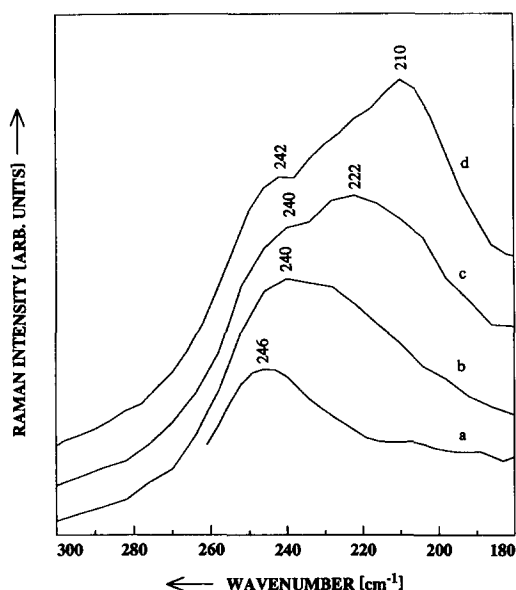


Fig. 10. SERS spectra of (a) 0.05 ml of 1.0 M NaCl in 0.5 ml grey silver sol, (b) and (c) 0.05 ml of  $1.0 \times 10^{-6}$  M crystal violet in 0.5 ml grey silver sol after addition of respectively 1.0 M and 0.2 M NaCl (0.05 ml); (d) is the SERS spectrum of 0.05 ml of  $1.0 \times 10^{-6}$  M crystal violet in 0.5 ml yellow silver sol after addition of 0.05 ml of 1.0 M NaCl.

$\text{cm}^{-1}$ , which is approaching the position of the Raman mode on the higher-wavenumber side. This may be taken as a further evidence for our assignment of the Raman mode at about  $240 \text{ cm}^{-1}$  to an Ag–Cl stretching vibration. However, in this case one cannot discriminate different Raman modes from different surface species. This result indicates also that care must be taken in assigning the low-wavenumber modes in SERS spectra.

#### 4. Conclusion

We have studied the SERS spectra of halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), pyridine and crystal violet with and without halide ions in the low-wavenumber region with the help of a conventional scanning Raman spectrometer and NIR excitation.  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions adsorbed on colloidal silver give rise to Raman bands at about  $242 \text{ cm}^{-1}$ ,  $158 \text{ cm}^{-1}$  and  $117 \text{ cm}^{-1}$ , respectively. These bands are attributed to the silver–halide stretching vibrations. The easy observability of these bands with NIR excitation is ex-

plained in terms of the red shift of the surface plasmon resonance caused by the aggregation of the sols due to the chemisorption of the halide ions. The adsorbed pyridine on silver surface in the presence of chloride ions gives rise to at least two active Raman modes in the low-wavenumber region. One is ascribed to the Ag–Cl stretching vibration and another is possibly due to the surface complex of the adsorbed pyridine. The halide ions affect not only the low-wavenumber modes but also the ring breathing modes. The capacity to cause the enhancement and shift of the ring breathing modes of pyridine on colloidal silver ranges in the order of  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . We demonstrated that multi-Raman modes in the low-wavenumber region are active for crystal violet on colloidal silver in the presence of chloride ions. We attributed the mode at about  $240 \text{ cm}^{-1}$  to the Ag–Cl stretching vibrations and the mode at about  $210 \text{ cm}^{-1}$  to the surface complex of the adsorbed crystal violet. Two possibilities are presented for the appearance of the Raman band at about  $222 \text{ cm}^{-1}$ .

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