

Surface-Enhanced Raman Spectroscopy Studies on the Interaction of Imidazole with a Silver Electrode in Acetonitrile Solution

Peigen Cao,[†] Renao Gu,^{*,†} and Zhongqun Tian^{*,‡}

Department of Chemistry, Suzhou University, Suzhou 215006, P. R. China, and State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry and Institute of Physical Chemistry, Xiamen University, Xiamen 361005, P. R. China

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Surface-enhanced Raman scattering (SERS) spectrum of imidazole adsorbed at a silver electrode in nonaqueous acetonitrile solution has been investigated as a function of applied potential. The electrolyte is 0.1 M LiClO₄. Results show that imidazole adsorbs on silver as a neutral molecule via the pyridine nitrogen atom. Coadsorption of perchlorate anion with imidazole, possibly by forming intermolecular hydrogen bonding, is also suggested by the enhancement of the ClO₄[−] band at 933 cm^{−1}. An edge-on orientation of imidazole at more positive potentials is proposed by the observation of the increase in frequency of the ring breathing modes, along with the enhancement of most of the in-plane modes of imidazole. When the potential is made more negative, particularly near −0.5 V, the imidazole ring may change from vertical to be slightly inclined to the silver surface at an intermediate angle from the surface normal. At the same time, a slight rotation of the imidazole ring plane may occur, evidenced by the observation of the changes in relative intensity of $\nu(\text{C}_2\text{H})$ to asymmetric $\nu(\text{HCCH})$ vibration. In addition, the decomposition reaction of the solvent acetonitrile at the silver surface is also assumed by the appearance of a characteristic band of cyanide ion at ca. 2110 cm^{−1}. Competitive adsorption of imidazole at more positive potentials inhibits significantly the decomposition of acetonitrile.

Introduction

The electrosorption and electrochemical behavior of imidazole on various metals have received extensive attention in the past, for its being a component of many biologically important molecules such as purine, histidine, nucleic acid, and related substances.¹ Some of its derivatives and imidazole itself have also been used as corrosion inhibitors and adhesion promoters, particularly for copper.²

Imidazole is regarded as a planar, five-membered heterocycle with nitrogen atoms in the one (N₁) and three (N₃) positions (Figure 1a). The N₁ nitrogen is saturated and referred to as the pyrrole nitrogen, whereas the N₃ nitrogen is unsaturated and referred to as the pyridine nitrogen. Imidazole behaves like a base in aqueous solutions and forms cations (ImH⁺, see Figure 1b), with N₃ being protonated (pK_{a1} = 6.99). The acidity of the hydrogen atom bonded to the pyrrole nitrogen is relatively weak (pK_{a2} = 14.4). The deprotonation occurs only in strongly basic solutions, with the Im[−] anion being formed (Figure 1c). There is another aromatic form of imidazole, called imidazolium ylide. It is formed by intramolecular hydrogen rearrangement and is, in fact, a neutral, dipolar tautomer of imidazole, possessing an unshared pair of σ electrons on C₂ (Figure 1d). Hence, the interaction of imidazole with metal surfaces is complicated by the existence of the above four structures of imidazole.

As a probe molecule being suitable for studies of the electrochemical double layer, imidazole has been studied repeatedly in the literature. A variety of techniques, including

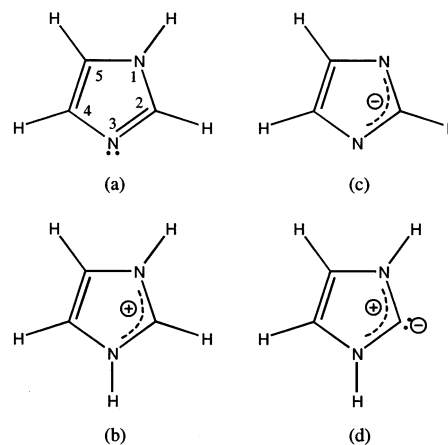


Figure 1. Structures of (a) neutral, (b) protonated, (c) deprotonated, and (d) ylide forms of imidazole.

cyclic voltammetry, tensammetry, and other electrochemical methods have been employed to probe the interaction between imidazole and metal surfaces.³ A great amount of macroscopic information concerning the metal–solution interface has been reported. Further information about the surface interaction at the molecular level was obtained by using X-ray photoelectron spectroscopy (XPS), second harmonic generation (SHG), and infrared (IR) techniques.^{2,4,5} For instance, Tompkins and co-workers⁵ concluded from XPS data that the copper atoms are etched from the surface and trapped into the imidazole coating. An ionic complex was claimed by them on the basis of the observation of the absence of NH bond in the infrared reflection–absorption spectra (IRRAS) upon adsorption. An *in situ* infrared spectroscopic study of imidazole films on copper electrodes was published recently by Faguy and colleagues.⁶

* To whom all the correspondence should be addressed. R.G.: tel, 86+512+65112813, 65112645; fax, 86+512+65231918; e-mail: ragu@suda.edu.cn. Z.T.: tel, 86+592+2181906; e-mail: zqtian@xmu.edu.cn.

[†] Suzhou University.

[‡] Xiamen University.

They found that the coating on the electrode consisted mainly of copper(I) imidazolate with either a random or perpendicular orientation to the polycrystalline surface. No change in orientation of the imidazole ring was observed with the variation in potential. On the other hand, Youshida and Ishida² observed the weakening of most of the in-plane bending modes of the imidazole ring in several analogues from IRRAS data and hence supposed a flat orientation of the ring upon adsorption onto copper and gold. Therefore, controversy still exists regarding the surface coordination modes and adsorbate orientational changes upon variations of the solution pH, applied potential, and other environmental factors.

Surface-enhanced Raman spectroscopy (SERS) has been proved to be a successful surface analytical technique with a high sensitivity and has also been applied to study the interactions of imidazole and its derivatives with various metallic surfaces.^{7–10} Most of the experiments were performed in aqueous solutions. The substrates used include copper, silver, gold electrodes, and silver sols for the great enhancement of Raman signals on these metal surfaces. Various adsorbed species (compare with Figure 1) and subsequent surface orientation have been identified and reported in the literature. For instance, Thierry and Leygraf⁷ studied the adsorption of imidazole on microlithographically prepared copper surfaces from NaCl solutions with SERS. The molecule was adsorbed nondissociatively on copper and a flat adsorption configuration was concluded on the basis of the measured spectra. On the other hand, Loo and co-workers^{8,9} recorded the SERS spectra of imidazole and imidazolium ions on copper and silver electrodes. A flat orientation was concluded for ImH^+ on both metals and the neutral imidazole molecule was supposed to adsorb via the N_3 nitrogen on a copper electrode and be flat on silver. Changes in orientation upon variation in concentration was reported by Siiman et al.¹⁰ They studied the adsorption of imidazole and its biologically important relatives (NAD, NADH) on silver colloids and found that the orientation of the imidazole ring changes from flat for the more dilute imidazole solutions (10^{-4} M) to perpendicular for more concentrated (10^{-3} M) solutions. Although the conclusions concerning the orientation of imidazole molecules with respect to the metal surface as well as the form of adsorbed species are various, the chemisorption of imidazole is believed to occur via the pyridine or pyrrole nitrogen atoms. Thus the metal–nitrogen bond is formed. The charge-transfer behavior of imidazole to the metal has been supported by Lombardi and Birke.¹¹

There is relatively little work reported on the SERS spectra of imidazole in nonaqueous systems. In an early paper by Gu et al.,¹² the adsorption of imidazole on a silver electrode from a nonaqueous solution of methanol/0.1 M LiCl was investigated with SERS. The spectra were compared with those recorded from aqueous solutions without further conclusions related to the orientation of the adsorbate. The reason for the appearance of few SERS spectra in nonaqueous systems in the literature is mainly due to the rather low detection sensitivity. With the development of the Raman instrumentation, particularly the advent of the CCD cameras, the signal-to-noise (S/N) is improved greatly. The equipment of the confocal lens makes it possible to eliminate mostly the interference from the bulk electrolytes. This enables us to study in our last work the decomposition of acetonitrile as a solvent even on the transitive platinum electrode surface.¹³ Adsorption and electro-oxidation of carbon monoxide at the platinum–acetonitrile interface was also reported recently.¹⁴ Our aim of these related works is to help in the clarification of the surface chemistry (structure,

orientation, and configuration of surface species) at the nonaqueous interface and also to complement our understandings of the basic mechanisms for SERS.

In the present study, we report here the SERS spectra of imidazole on a silver electrode in acetonitrile solutions. The potential dependence of the surface species, orientation, and surface bond will be analyzed in detail. The motivation for the choice of this system is based on the following facts. First, most of the related SERS studies were performed in aqueous solutions. SERS data from nonaqueous solutions should provide a better understanding of the general surface interaction between imidazole and metals. Second, although the adsorption of imidazole on metal surfaces has been studied extensively and imidazole and its derivatives have been used as corrosion inhibitors for over 30 years, inconsistent results appeared in the literature and the mechanisms of the surface interaction still remain uncertain. The aim of this work is to elucidate the nature of this interaction in nonaqueous systems. In addition, the extension of SERS studies to nonaqueous solutions is of importance for the application of nonaqueous solvents in electrochemistry, particularly as a component of the electrolyte in battery research.¹⁵ The competitive adsorption of imidazole and the solvent acetonitrile is also discussed in this work.

Experimental Section

Imidazole (99.5%) was of analytical reagent and used as received. The SERS measurements were made in 0.1 M Imidazole and 0.1 M LiClO_4 acetonitrile solutions at room temperature. The anhydrous salt used in this work, lithium perchlorate (analytical reagent grade), was dried by heating under vacuum up to 60 °C for 6 h before use. Acetonitrile (HPLC grade, 0.003% water) was distilled twice from calcium hydride and stored before use in sealed containers over Woelm alumina.

The spectroelectrochemical cell used was of a previously published design¹³ except that the working electrode was a polycrystalline silver (99.999%) rod embedded in a Teflon sheath, with a geometric surface area of ca. 0.05 cm². A large Pt ring served as the counter electrode. Prior to the SERS measurements, the cell was dried in a vacuum oven at 120 °C for 2 h. All the potentials, unless specified, are reported versus a Ag/Ag^+ reference electrode in CH_3CN containing 0.1 M LiClO_4 and 0.01 M AgNO_3 (0.268 V versus a saturated calomel electrode, SCE; see ref 16). An EG&G model 173 potentiostat was employed to control the applied potentials.

Roughening of the silver electrode to obtain a SERS-active surface for the Raman measurements was accomplished by a single oxidation–reduction cycle (ORC). Because of the possibility of the inducement of the surface species caused by the in situ ORC treatment, the roughening of silver was performed ex situ in a solution without imidazole. Briefly, the Ag electrode was first mechanically polished successively with 0.5 μm aluminum powder down to 0.05 μm to a mirror finish followed by ultrasonic cleaning with Milli-Q water. Then, the electrode was transferred to a separate electrochemical cell with 1 M KCl solution. The electrode was first polarized at -0.25 V (SCE) and then stepped up to $+0.17$ V (SCE) where the potential was held for 10 s. Then the potential was scanned back to -0.25 V at 5 mV/s to complete a thorough reduction of the electrode surface. The roughened silver electrode was then immersed in acetonitrile and rinsed by the solvent several times before use to eliminate the contamination of water.

Normal Raman spectra of bulk imidazole and related compounds were recorded with a Fourier Transform Raman 960

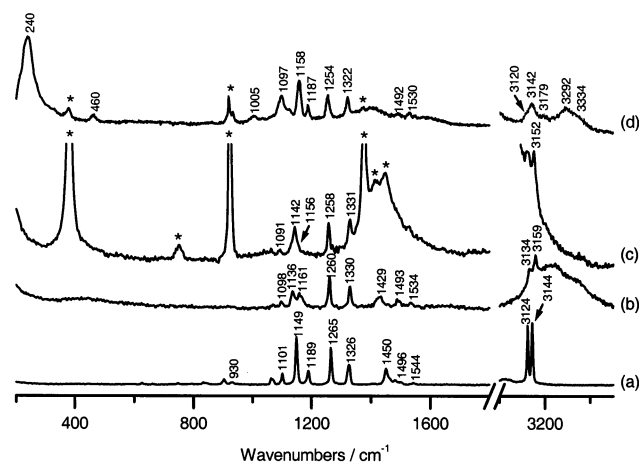


Figure 2. Normal Raman spectra of (a) solid imidazole, (b) imidazole in 0.1 M ImH/water, (c) imidazole in 0.1 M ImH/CH₃CN, and (d) SERS spectrum of imidazole adsorbed on a silver electrode in 0.1 M ImH + 0.1 M LiClO₄/CH₃CN.

spectrometer (Nicolet Inc.). The excitation wavelength was 1064 nm pumped by an air-cooled Nd:VO₄ laser. A highly sensitive liquid nitrogen cooled germanium detector was utilized. The incident laser power was maintained at 100 mW.

SERS data were obtained using a confocal microprobe Raman system (LabRam I from Dilor, France). The equipment of the confocal microprobe lens makes it possible to eliminate most of the interference from bulk solutions upon recording the surface Raman spectra. The excitation wavelength was 632.8 nm from an inner air-cooled He–Ne laser with a power of 10 mW and a spot of size 3 μ m at the sample surface. The slit and pinhole used were 200 and 800 μ m, respectively. The acquisition time was 100 s with four accumulations for each spectrum. With a holographic notch filter and a CCD detector, it has an extremely high detecting sensitivity. A 50 \times long working-length objective (8 mm) was used so that it was not necessary for the objective to be immersed in the solution. A detailed description of this spectrometer can be found elsewhere.¹⁷ All the SERS experiments were performed at the room temperature.

Results

Comparison of the Normal Raman and SERS Spectra of Imidazole. Figure 2a–d compares the normal Raman (NR) spectrum of solid and solution imidazole (in aqueous and nonaqueous acetonitrile solutions, respectively) and the typical SERS spectrum acquired at -0.4 V at an electrochemically activated silver electrode in 0.1 M ImH and 0.1 M LiClO₄/acetonitrile. The spectrum was given in two frequency regions: 200–1800 and 3000–3500 cm^{-1} . Several problems should be discussed before the interpretation of the spectra. The first was the possible existence of a low level impurity in commercial imidazole. Misinterpretation of the SERS spectra can be made for this coexistence. Loo et al.⁹ once assumed π -bound imidazole on silver and π -bound imidazolium ions on copper in acidic solutions on the basis of the observance of two strong bands at 1027 and 1349 cm^{-1} . However, the evidence presented by Pemberton and Carter¹⁸ in a later published paper concluded that this was not due to adsorbed imidazole but was in fact an impurity in the commercial imidazole. They recorded several samples from different chemical manufacturers, and results supported their conclusions. In this work, the NR spectrum of solid imidazole shows good agreement with that of imidazole purified and used by Pemberton and Carter¹⁸ in their studies.

Therefore, the misinterpretation caused by the impurities can be avoided.

The second was the photolysis of imidazole adsorbed on silver under the irradiation of laser with high power values. This phenomenon was also discovered by Pemberton and Carter.¹⁸ As a result, the laser power used in their studies was reduced from 200 mW to less than 50 mW. In this study, particularly regarding the acquisition of the SERS spectra, the laser power was adjusted to less than 10 mW at the sample surface. Thus, the photoinduced effect on imidazole would be minimal.

The Raman spectra of imidazole in the vapor, solid, and aqueous solution phases have been described several times in the literature,^{18–20} and normal modes have been derived from ab initio calculations.^{21–24} Much attention was given to the assignments of the vibrational bands of imidazole. However, inconsistent results always appeared in the literature,^{18–24} particularly on the ring stretching and NH and CH in-plane deformation modes. Assignment of the bands of imidazole in the present paper is performed by combining the information from our experimental data and from the literature.^{7,18–25}

The Raman spectrum of solid imidazole exhibits four strong bands in the frequency region 200–1800 cm^{-1} (see Figure 2a). Specifically, the main Raman bands are observed at 1149, 1265, 1326, and 1450 cm^{-1} . The former two bands are assigned to ring breathing and CH in-plane deformation ($\delta(\text{CH})$) modes; the later two are both from ring stretching modes. Assignment of the 1101 cm^{-1} band is somewhat difficult. According to the literature, it mainly corresponds to the CH in-plane deformation. However, we will show in the Discussion that it may also contain a component of ring mode. The band at 1189 cm^{-1} attributed to NH in-plane deformation is of great interest. It is very sensitive to changes in the environmental factors. In addition, some minor bands are also evident at 627 cm^{-1} (γ_{ring}), 902 cm^{-1} (δ_{ring}), 930 cm^{-1} ($\gamma(\text{NH}) + \delta_{\text{ring}}$), and 1066 cm^{-1} ($\delta(\text{CH})$). Although theoretical calculations^{21–24} showed that three $\nu(\text{CH})$ vibrations should be observed, the $\nu(\text{C}_2\text{H})$ vibration and the symmetric and asymmetric $\nu(\text{HCCH})$ vibrations of C₄ and C₅, only two bands are well-resolved at ca. 3124 and 3144 cm^{-1} in the 3000–3500 cm^{-1} frequency region. The third CH stretching mode may be overlapped with the strong 3124 cm^{-1} band according to the literature.^{20,25}

After dissolving imidazole in an aqueous solution, changes in the spectral features indicative of the solvation effect are obvious (see Figure 2b). The most striking differences are the large red shifts for the ring breathing mode (from 1149 to 1136 cm^{-1}) and the ring stretching mode (from 1450 to 1429 cm^{-1}). The NH in-plane deformation band is also observed at 1161 cm^{-1} with a red shift value of 28 cm^{-1} . This is likely caused by the partial breaking of the strong intermolecular hydrogen bonding in the solid state instead of the interaction of imidazole with water molecules.

The NR spectrum of imidazole in acetonitrile is also presented in Figure 2c. The bands characterized by the asterisk correspond to the vibronic transition of the solvent. Due to the appearance of the strong broad bands from ca. 1350 to 1600 cm^{-1} , associated to acetonitrile, the accuracy of comparisons in this region is limited. As can be seen from the figure, some band frequency shifts are also observed in comparison with the NR spectra of the solid and aqueous solution imidazole. By contrast, the 1091 cm^{-1} band is observed to red shift from 1098 cm^{-1} in aqueous solution with 6 cm^{-1} . A significant change is evident for the NH in-plane deformation. It seems absent from the spectrum. However, the basicity of imidazole is known to be stronger than acetonitrile. The latter is not active enough to

capture the N_1 -bonded hydrogen in the imidazole ring. Imidazole is hence mainly in its neutral molecule form in solution studied in this work. It seems in conflict with the disappearance of the $\delta(NH)$ band. Considering the high value of the full width at half-maximum (fwhm) for the 1142 cm^{-1} band in contrast to that in aqueous solution, we believe that $\delta(NH)$ may be overlapped with the 1142 cm^{-1} band. Further red shift of $\delta(NH)$ is then derived by comparison with that in aqueous solution (see Figure 2b,c), suggestive of a weaker intermolecular hydrogen bond in acetonitrile. In the $3000\text{--}3500\text{ cm}^{-1}$ region, three CH stretching modes can be well resolved at ca. 3119 , 3129 , and 3152 cm^{-1} .

Figure 2d presents a typical in situ SERS spectrum of a roughened silver electrode immersed in $0.1\text{ M ImH} + 0.1\text{ M LiClO}_4/\text{acetonitrile}$ at an electrode potential of -0.4 V . As can be seen from the figure, the interferential Raman bands from the organic solvent (marked by asterisk) are suppressed significantly by using the confocal microprobe Raman system. The broad background features between 1300 and 1600 cm^{-1} were also observed and called "cathedral peaks" in the previous studies and have been attributed to the presence of surface carbon impurities.²⁶ The SERS spectrum in Figure 2d presents new bands and some frequency shifts of vibrational modes in relation to the normal Raman spectrum of imidazole in acetonitrile. For instance, the ring stretching mode is shifted from 1331 to 1322 cm^{-1} , indicating some structural changes upon adsorption of imidazole molecule onto the silver surface. Interesting features were observed for the ring breathing and NH in-plane deformation modes. Both of them blue shift 16 and 31 cm^{-1} , respectively, approaching the band frequencies for the solid spectrum. That is to say, the influence of the adsorption is just contrary to the solvation effect, indicating some similarities of the structural arrangements of imidazole adlayers to that in the solid phase. Additionally, a shift of the 1254 cm^{-1} band frequency is slight and within 5 cm^{-1} . Changes of the relative band intensity have also been observed. For instance, the ratio of the integrated intensity of the 1097 cm^{-1} band to that of the 1254 cm^{-1} band changes from ca. 0.18 to 0.95 . It can also be found from the figure that most of the enhanced Raman bands are within the in-plane modes. The out-of-plane modes mainly below 900 cm^{-1} were hardly detectable in the SERS spectrum. This may indicate some preference of imidazole orientation on the silver surface.

In the $3000\text{--}3500\text{ cm}^{-1}$ frequency region, three CH stretching modes are observed at 3142 , 3120 , and 3179 cm^{-1} . The latter two exist as shoulders of the former. A broad band centered at 3292 cm^{-1} is also clearly observed with a shoulder at 3334 cm^{-1} . A detailed analysis of this broad band is given in the Discussion. One of the most striking features is the observation of a new band located at ca. 240 cm^{-1} in the low-frequency region. It does not correlate with any intramolecular vibrational bands of imidazole but relates to the metal-adsorbate vibration, which is indicative of the strong interaction of imidazole with silver surface.

Another surprising phenomenon is the observation of two new bands located at ca. 460 and 1005 cm^{-1} . Attempts to give a proper assignment of these two bands failed, because they do not correspond to any of the normal modes of either imidazole or acetonitrile. However, the appearance of the 460 cm^{-1} band is accompanied by the appearance of the broad background features of the surface carbon. Subsequently, this band may be caused by the surface carbonization. We cannot give a proper explanation of the 1005 cm^{-1} band now. The SERS spectrum in Figure 2d also shows a very intense band at 933 cm^{-1} , arising

from the totally symmetric stretching mode of the electrolyte anion ClO_4^- . Despite no changes of the frequency of this band compared to the free anion, the enhanced band intensity is also indicative of coadsorption of this species with imidazole. Similar observations have been obtained in previous coadsorption studies of thiourea with ClO_4^- on copper and silver.²⁷ A summary of the normal Raman and SERS vibrational frequencies for imidazole together with ClO_4^- is presented in Table 1.^{18–20, 28–30}

Potential-Dependent SERS Spectra of Imidazole. For a better understanding of the interaction of imidazole with the silver surface and also the coadsorption with perchlorate anions, the potential dependency of the SERS spectra of imidazole was investigated. Figure 3 shows a series of SERS spectra of imidazole at a variety of potentials in three frequency regions: $300\text{--}1700$, $1800\text{--}2200$, and $3000\text{--}3500\text{ cm}^{-1}$. The electrolyte solution was the same with that used in Figure 2d. The open circuit potential measured for this system was approximately -0.2 V , where the first spectrum was acquired. For convenient discussion purpose, the potentials investigated have been divided into three regions: (i) -0.2 to -0.5 V , (ii) -0.5 to -0.9 V , and (iii) -0.9 to -1.3 V (see Figure 3). In the first potential region, the band intensity of imidazole changes greatly with variations of potential, whereas the frequency remains almost constant. Most of the bands reach their maximum intensities at -0.4 V . The only exception is that the 1187 cm^{-1} band decreases in intensity upon negative going potentials in potential region (i). When the silver electrode is polarized at -0.5 V , this band is hardly resolved. Instead, a new band appears at ca. 947 cm^{-1} , albeit with rather weak intensity. The new band was also observed in the aqueous SERS studies of imidazole and has been attributed to the combination of the in-plane ring deformation and out-of-plane NH deformation modes according to the literature.^{18,20} This may indicate an orientational change occurring at the surface. In addition, the CH stretching modes and the broad band at ca. 3292 cm^{-1} also decrease in intensity when the potential is made more negative.

In the second potential region, the S/N of the spectrum decreases significantly. Upon scanning potential to more negative values, most of the imidazole bands decrease in intensity with an exception of increasing of intensity for the 947 cm^{-1} band. A large red shift of frequency upon variations of potential was also observed for the 1096 and 1157 cm^{-1} bands in this potential region. Note that the ring stretching mode at 1322 cm^{-1} remains almost constant in frequency in the whole potential region (i and ii). Another interesting feature is observed for the 933 cm^{-1} band. Its intensity rises and decreases simultaneously with those characteristic of imidazole with variations of the applied potential, suggestive of coadsorption of ClO_4^- with imidazole. However, the frequency for this band remains constant, indicating a weak or no direct interaction of ClO_4^- with silver. In the high-frequency region, the broad band at 3292 cm^{-1} decreases in intensity and disappears at approximately -0.7 V . Interesting changes were also observed for the CH stretching modes. The shoulder at 3120 cm^{-1} rises in relative intensity to that of the 3142 cm^{-1} band with negative going potentials and becomes well-resolved at -0.7 V . On the other hand, the CH mode at 3179 cm^{-1} cannot be observed in the whole potential region (ii).

When the potential moves into the third potential region, particularly negative to -1.0 V , all the bands from imidazole disappear, along with the disappearance of the 933 cm^{-1} band. This may be interpreted by desorption of both imidazole and ClO_4^- . Instead, a new band centered at ca. 2110 cm^{-1} was detected at -0.9 V and reaches its maximum at ca. -1.1 V .

TABLE 1: Assignment of Vibrational Bands in the normal Raman Spectrum of Imidazole and the SERS Spectra for Adsorption of Imidazole at a Silver Electrode^{7,18–20, 28–30}

assignments	normal Raman			SERS on Ag	
	solid	aq ^a	nonaq ^b	Ag(Im) ₂	
$\nu(\text{Ag}-\text{N})$				196 ^c (m)	240 (vs)
$\text{A}_2^d \gamma_{\text{ring}}$	627 (w)	624 (w)		628 (w)	
$\text{A}_2 \gamma_{\text{ring}}$	662 (w)	671 (w)		656 (w)	
$\text{A}_2 \gamma(\text{CH})$	747 (w)	761 (w)		770 (w)	
	831 (w)			826 (w)	
$\text{A}_2 \gamma(\text{CH})$	839 (w)	845 (w)			
$\text{A}_2 \gamma_{\text{ring}}$	849 (w)	865 (w)		869 (w)	
$\text{A}_1 \delta_{\text{ring}}$	902 (m)				
$\nu(\text{ClO}_4^-)$					933 (m)
$\text{A}_2 \gamma(\text{NH}) + \text{A}_1 \delta_{\text{ring}}$	930 (w)	930 (w)		969 (s)	933 (w)
$\text{A}_1 \delta(\text{CH})$	1066 (m)	1070 (w)	1061 (w)	1068 (w)	947 (m)
$\text{A}_1 \delta(\text{CH}) + \text{A}_1 \nu_{\text{ring}}$	1101 (s)	1098 (m)	1091 (w)	1096 (m)	1097 (s)
$\text{A}_1 \nu_{\text{ring}}$	1149 (vs)	1136 (s)	1142 (s)	1172 (s)	1158 (vs)
$\text{A}_1 \delta(\text{NH})$	1189 (s)	1161 (s)	1156 (m)		1187 (m)
$\text{A}_1 \delta(\text{CH})$	1265 (vs)	1260 (vs)	1258 (s)	1278 (vs)	1254 (s)
				1306 (m)	
$\text{A}_1 \nu_{\text{ring}}$	1326 (s)	1330 (vs)	1331 (s)	1330 (m)	1322 (s)
$\text{A}_1 \nu_{\text{ring}}$	1450 (s)	1429 (m)		1477 (m)	1321 (m)
$\text{A}_1 \nu_{\text{ring}}$	1482 (w)	1493 (w)		1489 (s)	1492 (w)
$\text{A}_1 \nu_{\text{ring}}$	1501 (w)				1530 (w)
$\text{A}_1 \nu_{\text{ring}}$	1543 (w)	1534 (w)			
$\nu(\text{CN}^-)$					2110 (w)
$\text{A}_1 \nu(\text{NH})$	2836 (w)				3334 (m)
$\text{A}_1 \nu(\text{NH})$	2929 (w)				
$\text{A}_1 \nu(\text{CH})$	3028 (w)		3119 (w)	3111 (s)	3120 (m)
$\text{A}_1 \nu(\text{CH})$	3124 (vs)	3134 (w)	3129 (w)	3121 (vs)	3142 (s)
$\text{A}_1 \nu(\text{CH})$	3144 (vs)	3159 (m)	3152 (m)	3130 (m)	3179 (w)

^a 1.0 M imidazole/water. ^b 1.0 M imidazole/acetonitrile. ^c Wavenumbers (in cm^{-1}) followed by relative intensities (vs, very strong; s, strong; m, medium; w, weak). ^d A_1 denotes in-plane modes. A_2 denotes out-of-plane modes.

This band was also obtained in our previous studies^{13,14} and has been associated with the adsorption of cyanide ion (CN^-). Detailed analysis of this band is given in the Discussion.

Discussion

Identification of Adsorbed Species. The adsorption of imidazole on metal surfaces is complicated by the existence of four different forms, as mentioned in the Introduction. A detailed analysis of the published papers shows that the relative amount of these forms at the surface depend on the electrode potential, solution pH, electrolyte composition, metallic substrate, and possibly the laser power.^{18,28–30} Briefly, the adsorption of neutral imidazole molecule is observed mainly in the neutral or slightly alkaline solutions. Adsorption of imidazolate anion occurs in the alkaline solution, or in the neutral solution at more positive potentials. A preferential edge-on adsorption of imidazolate with respect to the silver colloidal surface was also observed by addition of a small quantity of halide anions into the neutral imidazole solution.³⁰ The SERS spectrum of Im^- was even observed in acidic solutions, particularly at the gold electrode surface.²⁸ The adsorption of protonated imidazolium cation is detected only in acidic solution. Reports on the adsorption of the ylide form are scarce. Bukowska and co-workers²⁹ detected the coexistence of the ylide form and ImH^+ at the silver surface in acidic media. Characteristic bands of the ylide form were found at 1025, 1285, and 1350 cm^{-1} .

Careful examination of the literature shows that the laser power may have some effects on the surface adsorbed forms of imidazole, particularly on the formation of surface complex. For instance, Bukowska and co-workers²⁹ suggested a change from imidazole neutral form to imidazolate anion, mainly trapped in the surface complex, when the applied potential was made more positive than -0.6 V (SCE) by using a 514.5 nm laser of 150 mW . However, no such change was observed by

Pemberton and Carter¹⁸ under the same conditions except for the use of laser powers less than 50 mW . Hence, the formation of the ionic complex on silver observed by Bukowska et al. should be attributed at least in part to the illumination of the laser with high power values. Studies on the gold electrode supported this assumption.²⁸ Therefore, in this work the laser power was lowered to less than 10 mW for the SERS measurements, to eliminate the effect of the laser illumination.

In Figure 3, the appearance of the $\delta(\text{NH})$ mode in the SERS spectrum in the potential region (i) indicates that two forms with a N–H bond of imidazole, neutral and ylide forms, may be adsorbed onto the surface. However, no characteristic bands of ylide tautomer were observed. In addition, ylide is known to be an acid-catalyzed proton-exchange process and its formation is facilitated in acidic media.³¹ Hence, we assume that imidazole may adsorb onto the silver surface mainly as its neutral form. Observation of three CH stretching modes at more positive potentials (see Figure 3 and Table 1) supports this assumption, because theoretical calculations showed that in the $3000\text{--}3500 \text{ cm}^{-1}$ region imidazole exhibits three CH stretching vibrations of the A_1 mode, whereas the ylide tautomer shows only two CH vibrations of A_1 and B_2 modes.²³ Surface-adsorbed forms of imidazole in the potential region (ii) will be discussed in a later part of this paper.

The potential dependence of the normalized relative intensity for the 933 cm^{-1} band and those characteristic bands of imidazole at 1098, 1159, 1254, and 1322 cm^{-1} determined from Figure 3 is shown in Figure 4. The relative intensity was first divided by the solvent peak at 918 cm^{-1} and then normalized to the 1159 cm^{-1} at -0.4 V . A striking feature is found for the simultaneous increase in intensity of the 933 cm^{-1} band with those related to imidazole, as is described in the Results. Most of the bands including ClO_4^- reach the maximum intensity at approximately the same potential -0.4 V , indicating coadsorp-

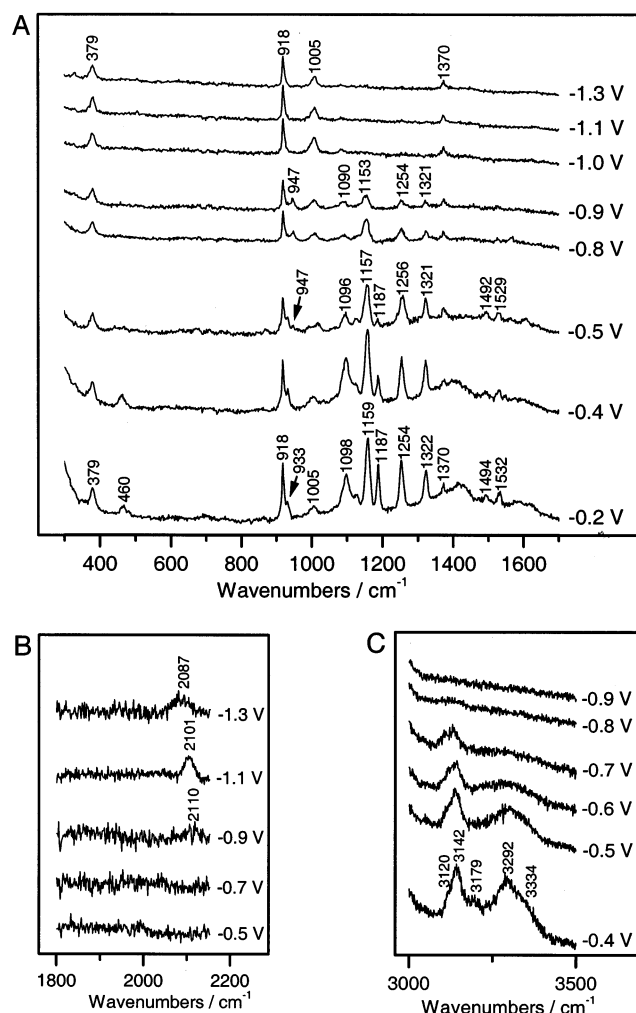


Figure 3. Representative potential-dependent SERS spectra for imidazole adsorbed onto a silver electrode in three frequency regions: 300–1700, 1800–2200, and 3000–3500 cm⁻¹ (A–C respectively).

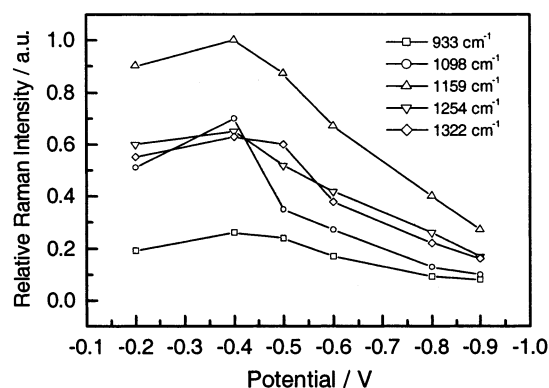


Figure 4. Dependence of the normalized Raman intensity upon applied potential for the major bands of imidazole together with the ClO₄⁻ band as indicated (see text).

tion of ClO₄⁻ with imidazole. Usually, this behavior was observed between ClO₄⁻ and the protonated forms of organic adsorbates, as in the case of thiourea adsorption from acidified perchlorate solutions.³² The protonation of the NH₂ group of thiourea was assumed to facilitate the electrostatic attraction of anions such as ClO₄⁻. However, in the present nonaqueous system, no protonation of imidazole occurred. The interaction between imidazole and ClO₄⁻ would be expected to be rather weak compared with the ion pairs reported in the literature.³²

Another interesting feature in Figure 3 is the appearance of the broad band centered at ca. 3292 cm⁻¹ at more positive potentials. The assignment of this band is not easy and unequivocal. A similar SERS band near 3220 cm⁻¹ was also observed from a silver electrode in 1 M LiI/CH₃CN containing 4 × 10⁻⁴ M H₂O by Irish and co-workers.³³ They suggested a surface species similar to LiOH·H₂O. In our previous studies,³⁴ we also detected a SERS feature at 3258 cm⁻¹ on silver in acetonitrile without imidazole, suggesting no correlation of this band with imidazole. Combining the literature and our experimental results, we ascribed the broad band at 3292 cm⁻¹ to the existence of trace interfacial water. Note that the nonaqueous system used in the present study is not an “absolute” media without water. The above assignment is hence reasonable. Thus, the coadsorption of imidazole, perchlorate anion, and water molecules may occur at the silver surface. Additionally, there is a shoulder at 3334 cm⁻¹ coexisting with the above broad band. Assignment of this band to the NH stretching mode was tentatively made. Calculations predicted that NH stretching will appear above 3500 cm⁻¹.^{21–24} Experimental data from vapor,²⁵ matrix,³⁵ and solid state²⁵ appear at 3518, 3504, and 2800 cm⁻¹, respectively. The rather low frequency value for solid imidazole is mainly due to the strong intermolecular hydrogen bonds. However, such a strong hydrogen bonding network would be expected to be destroyed in the double-layer region due to the interaction of imidazole with the surface, resulting in a frequency of ν(NH) higher than that in the solid state. On the other hand, a lower frequency of ν(NH) should be expected in comparison with that in the vapor state due to the possible existence of hydrogen bonding among the adsorbed imidazole molecules and probably with the coadsorbed ClO₄⁻ and water at the Ag/ acetonitrile interface. The observation of the NH stretch at ca. 3334 cm⁻¹ is consistent with these considerations. Additionally, the appearance of the NH stretching band further supports the adsorption of neutral imidazole molecules.

Imidazole Orientation. A summary of the studies on the adsorption of some related N-containing heterocycles should be helpful to the present discussion on imidazole orientation. Pemberton and Carter¹⁸ have summarized the adsorption behavior of a number of N-containing heterocycles and related benzene and its derivatives on metal surfaces. Two conceptual adsorption modes were predicted for these molecules, edge-on and flat-on through nitrogen atom and the ring π system, respectively. A number of SERS features have been cited as evidence for the two surface bonding modes. In brief, for the edge-on mode, vibrational modes that are out-of-plane are either not present or weak compared to in-plane modes of the adsorbate due to SERS surface selection rules.^{36,37} Second, a ν(metal–N) band can often be observed in the low-frequency region for the adsorbed N-containing heterocycles.^{38–40} In addition, the ring breathing vibrations of the adsorbate usually increase upon adsorption, particularly at more positive potentials. Another interesting feature for the edge-on adsorption mode is the observation of a decrease in frequency for most bands as the potential is made more negative.

For the flat-on adsorption mode via the π orbital, the frequency shifts of the adsorbate are completely different. Briefly, the frequencies of modes associated with the π bond decrease upon adsorption at more positive potentials.⁴¹ The frequencies of the ring breathing mode generally increase as the potential is made more negative. However, reports on the π-bound molecules are fewer than N-bound adsorbates, indicating the relatively weak nature of the flat-on adsorption mode.

In the case of neutral imidazole, three conceptual adsorption modes would be expected: N_3 -, N_1 -, and conjugated π -bound configurations. Hence, the imidazole ring will be oriented vertically, at an angle of approximately 60° from the surface normal, and parallel to the surface, respectively. The mode of interaction of imidazole and orientation will be compared to the SERS data. By comparison of the NR spectrum of imidazole in acetonitrile and the SERS data (Figure 2), most of the enhanced bands are from the in-plane modes, suggestive of an edge-on orientation. This assignment is also supported by the following observations: the increase in frequency of the ring breathing mode at 1158 cm^{-1} upon adsorption and its decrease upon negative going potentials.

If the imidazole is oriented vertically on the surface in the potential region (i), it is probably adsorbed through the pyridine nitrogen. The low-frequency mode observed at ca. 240 cm^{-1} (Figure 2d) could then be assigned to Ag–N stretching, consistent with the edge-on adsorption via the N_3 atom. A similar $\nu(\text{metal}-\text{N})$ mode was also observed in the SERS spectra of other N-containing heterocycles.^{38–40} In the present study, the interaction of the solvent acetonitrile with the surface can be eliminated because no SERS spectrum of acetonitrile was observed. Additionally, if the imidazole adsorbs through the pyrrole nitrogen lone pair, the N–H bond would be nearly parallel with respect to the surface. According to the surface selection rules, no SERS signal of the in-plane NH modes will be observed. This is in conflict with the experimental results. Hence the interaction of Ag– N_1 should also be ruled out.

All these results show that imidazole may be oriented vertically via N_3 to the surface. However, a decrease in frequency of the ring stretching mode at 1322 cm^{-1} upon adsorption was also observed and seems inconsistent with the above assignment. This decrease in frequency suggests occurrence of adsorption through π interactions according to the literature.⁴¹ Pemberton and Carter reconciled this inconsistency by assuming a tilted orientation for imidazole.¹⁸ Considering the observation of a nearly constant frequency of the 1322 cm^{-1} band upon potential variations, we present here another explanation. As can be seen from Figure 2d, the rather strong metal–imidazole bond (240 cm^{-1}) probably arises from lone pair electron donation from N_3 atom of the ligand to empty metal orbitals, along with back-donation from filled metal d-orbitals to antibonding ligand orbitals.⁴² Thus a weakened CN double bond (close to N_3 ; see Figure 1a) and then a decrease in frequency of this bond would be expected. As the potential is made more negative, the silver–imidazole σ bond is weakened and hence the CN bond strengthened; at the same time there is increased back-donation from the filled metal d-orbitals to the ligand antibonding orbital, resulting in a weakened CN bond. Subsequently, overall a little shift for the CN double bond stretch would be expected. This is exactly consistent with the experimental results if we assign the 1322 cm^{-1} band mainly to the CN double bond stretching. By careful comparison of the frequency of this band in the NR and SERS spectra (Figure 2), we find that the 1322 cm^{-1} band is very sensitive to the coordination of the pyridine nitrogen. Upon formation of a strong intermolecular hydrogen bond, a decrease in frequency of 4 cm^{-1} can be observed; in the case of formation of the silver– N_3 bond, a decrease with 9 cm^{-1} is found. This may further indicate the interaction between imidazole and the silver surface is stronger than the hydrogen bonds among the imidazole molecules.

Another interesting feature found in Figure 3 is the similar frequency changes of the 1098 cm^{-1} band to the ring breathing

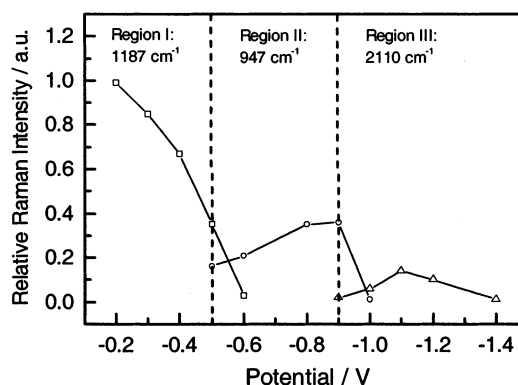


Figure 5. Normalized Raman intensity–potential profiles for three typical SERS bands at 1187 , 947 , and 2110 cm^{-1} (see text). The three potential regions correlate well with the adsorption behavior of imidazole on Ag: region I for the nearly vertical orientation of imidazole, region II for the tilted orientation, and region III for desorption of imidazole and the occurrence of acetonitrile decomposition.

mode at 1159 cm^{-1} . This may indicate some similar components in these two vibrational modes. Previous theoretical and experimental studies have assigned this band to CH in-plane deformation.^{7,21,22} However, another band at 1254 cm^{-1} assigned clearly to $\delta(\text{CH})$ by Hodgson²⁰ exhibits little shift in frequency upon potential variations. This seems in contrast to the behavior of the 1098 cm^{-1} band. Considering the effect of the outer electric field, the frequency shift upon applied potential for the bands that have no direct electronic interaction with the metal surface, like the CH in-plane mode from edge-on adsorbate, was often observed within $5\text{ cm}^{-1}/\text{V}$.^{38–40,43} The large Stark tuning rate of $11\text{ cm}^{-1}/\text{V}$ observed for the 1098 cm^{-1} band suggests that there is at least another component existing, such as the ring breathing vibration. A recent theoretical calculation for imidazole using the 6-311G basis set concluded that three components, ring stretching and CH and NH in-plane deformation, contribute altogether to the 1098 cm^{-1} band.²⁴ This is in good agreement with our experimental data.

When the potential is made more negative, the disappearance and appearance of the 1187 and 947 cm^{-1} band occur consecutively. The potential dependence of the integrated band intensity for the two bands determined from Figure 3 is shown in Figure 5. At first we suggested a deprotonation process of imidazole for the disappearance of the 1187 cm^{-1} as well as the NH stretching at 3334 cm^{-1} (Figure 3). However, this process should occur easily at more positive potentials, as was found in the literature.^{29,43} In addition, characteristic intense bands for imidazolate anion at ca. 1490 , 1300 , and 920 cm^{-1} found by Bukowska et al.²⁹ was not observed in the present SERS spectra. For comparison purposes, the silver(I) imidazolate complex was synthesized in our Lab according to the literature.⁴⁴ The NR spectrum of this anionic complex is given in Figure 6. By contrast, the complex spectrum correlates well with that observed by Bukowska²⁹ but not well with the present SERS of imidazole in the potential region (ii). Therefore, the formation of surface ionic complex by deprotonation of imidazole can be ruled out. Considering the appearance of the rather intense out-of-plane mode at 947 cm^{-1} to other in-plane modes, an orientational change to more flat with respect to the surface is proposed. The decrease of the surface adsorption quantity of imidazole at more negative potentials may facilitate this change. However, the in-plane modes still existing in the potential region (ii) suggest that the imidazole ring plane may be inclined to the surface normal at an intermediate angle. The degree of the angle depends on the applied potential.

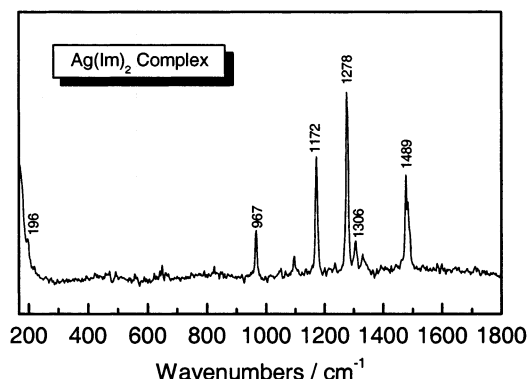


Figure 6. Normal Raman spectrum of the complex $\text{Ag}(\text{Im})_2$.

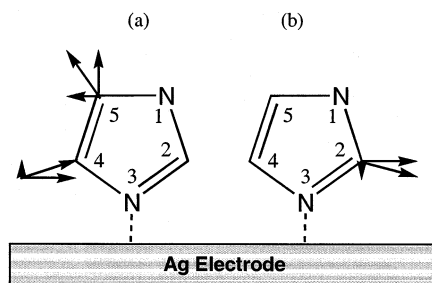


Figure 7. Components of the $\nu(\text{CH})$ mode that are normal and parallel to the surface for N_3 -bound imidazole: (a) asymmetric $\nu(\text{HCCH})$; (b) $\nu(\text{C}_2\text{H})$.

Changes in the SERS features upon potential in the 3000–3500 cm^{-1} region may bring about further information regarding the surface orientation of imidazole. As described in the Results, three CH stretching modes can be resolved. By comparison with the studies by Pemberton and Carter,¹⁸ including the papers cited by them,⁴⁵ the highest frequency $\nu(\text{CH})$ observed at 3179 cm^{-1} is assigned to the symmetric $\nu(\text{HCCH})$ vibration. This band was also observed at 3171 cm^{-1} in the SERS spectra of imidazole on iron.⁴⁶ According to the deuteration experiment, the bands at 3120 and 3142 cm^{-1} are assigned to $\nu(\text{C}_2\text{H})$ and asymmetric $\nu(\text{HCCH})$ vibrations, respectively.²⁴ The 3179 cm^{-1} band is rather weak and the following discussion is limited to the other two CH modes.

Surface selection rules are applied again to ascertain the orientational changes of imidazole. On the basis of the assumption that the major change in polarizability ellipsoid of the C–H bond is predominantly along the bond axis, Figure 7 represents the polarizability of $\nu(\text{C}_2\text{H})$ and asymmetric $\nu(\text{HCCH})$ for N_3 -bound imidazole on silver. If the imidazole ring rotates slightly clockwise (see Figure 7), the component normal to the surface for the asymmetric $\nu(\text{HCCH})$ would be expected to decrease, and that for the $\nu(\text{C}_2\text{H})$ to increase. Then, the relative SERS intensity of $\nu(\text{C}_2\text{H})$ to asymmetric $\nu(\text{HCCH})$ should be observed to increase based on the selection rules. This is supported by the experimental observations. In this case, the N–H bond would be nearly parallel to the surface and the in-plane $\nu(\text{NH})$ would not be observed. This is also consistent with the disappearance of the shoulder peak at 3334 cm^{-1} in the potential region (ii). Therefore, a rotation of the imidazole ring along with the inclination of the ring plane to the surface normal is suggested when the potential is made more negative, particularly near -0.5 V.

Competitive Adsorption of Imidazole and Acetonitrile. In the potential region (iii), SERS features change greatly (see Figure 3). A new broad band at 2110 cm^{-1} at -0.9 V appears along with the significant decrease in intensity of most imidazole

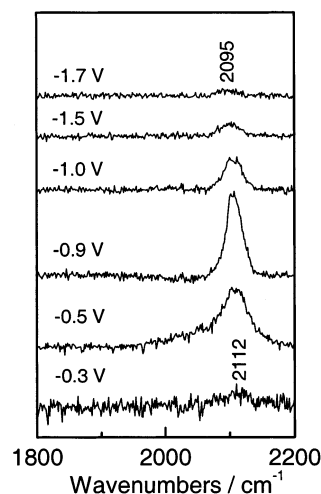


Figure 8. Potential-dependent surface Raman spectra at a silver electrode in acetonitrile with 0.1 M LiClO_4 .

bands. Potential dependence of the normalized intensity of this band is also plotted in Figure 5. Its existence even at more negative potentials, where imidazole desorbs from the surface, reminds us of the possibility of the chemisorbed reaction of the solvent acetonitrile on such a roughened silver electrode. We then recorded the surface Raman spectra of a silver electrode in a similar acetonitrile solution without imidazole, as depicted in Figure 8. A new band at ca. 2112 cm^{-1} at -0.3 V was observed, which is not a component of the Raman spectrum of free or coordinated acetonitrile.⁴⁷ On the basis of the observation of the characteristic frequency value and its behavior upon potential variation, we have assigned this band in our previous work to CN stretching of cyanide ion (CN^-) and a decomposition reaction of acetonitrile was proposed.^{13,14} This decomposition reaction was also reported on copper, silver, and gold.^{13,48}

The apparent difference between Figures 3B and 8 is the observation of different initial potential, at which CN^- band is observed. The initial potential for the imidazole-containing solution is far more negative than that for the system without imidazole. This may be suggestive of the competitive adsorption occurring at more positive potentials in the $\text{ImH}/\text{CH}_3\text{CN}$ solution. Interaction of imidazole with the silver surface would be expected to be stronger than that of the solvent. Decomposition of acetonitrile can only occur at more negative potentials where imidazole desorbs, as is indicated by the appearance of CN^- SERS band. Similar competitive adsorption has been reported for CO and acetonitrile,¹⁴ iodide, and acetonitrile.⁴⁹

Summary

SERS spectra of imidazole adsorbed on silver in a nonaqueous acetonitrile solution have been presented. The use of a confocal microprobe Raman system eliminated most of the interference from the bulk solution, facilitating the present study. The interactions between anions, imidazole, and silver surfaces were established on the basis of the analyses of the potential dependence of the SERS spectral features. The main observations and conclusions in this work are as follows.

1. Potential-dependent SERS spectra of imidazole adsorbed on a silver electrode in 0.1 M ImH + 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ have been observed. The main Raman bands are observed at 1097, 1158, 1187, 1254, and 1322 cm^{-1} and compared with the normal Raman spectra of imidazole in solid, aqueous solution, and nonaqueous acetonitrile solution.

2. The appearance of $\delta(\text{NH})$ at 1187 cm^{-1} and $\nu(\text{NH})$ at ca. 3334 cm^{-1} at -0.4 V indicates the existence of neutral imidazole

molecule on silver. Coadsorption of perchlorate anion with imidazole, possibly by forming intermolecular hydrogen bonding, is suggested also by the enhancement of the 933 cm^{-1} band assigned to the symmetric stretching mode of ClO_4^- . Existence of the water molecule in the double-layer region is assumed.

3. The increase in frequency of the ring breathing modes upon adsorption of imidazole, along with the decrease in frequency of these modes when the potential is made more negative is clearly observed and interpreted by an edge-on orientation of imidazole with respect to the silver surface. This is also evidenced by the enhancement of most of the in-plane modes of imidazole.

4. The appearance of the low-frequency mode at ca. 240 cm^{-1} assigned to $\nu(\text{Ag}-\text{N})$ suggests N-coordination of imidazole with silver. Combining the vertical orientation of imidazole, the molecule is adsorbed via the pyridine nitrogen lone pair. The decrease of the ring stretching mode at 1322 cm^{-1} is then interpreted on the basis of this coordination mode. The surface interaction between imidazole and the silver surface should be stronger than that of the intermolecular hydrogen bonds in solid imidazole.

5. When the potential is made more negative, particularly near -0.5 V , an orientational change is observed. The imidazole ring may be inclined to the silver surface at an intermediate angle from the surface normal. This is supported by the decrease in intensity of most in-plane modes and the appearance of a new intense band at 947 cm^{-1} . At the same time, a rotation of the imidazole ring plane may occur, as evidenced by the observation of the changes in relative intensity of $\nu(\text{C}_2\text{H})$ to asymmetric $\nu(\text{HCCH})$ vibration.

6. The decomposition reaction of the solvent acetonitrile at the silver surface was also assumed by the appearance of a characteristic band of cyanide ion at ca. 2110 cm^{-1} . This decomposition reaction is inhibited significantly by adsorption of imidazole. The interaction of the latter with silver is then assumed to be stronger than that of the solvent.

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