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SURFACE RAMAN SPECTROSCOPIES OF THE THREE REDOX FORMS OF METHYLVIOLOGEN AND 4,4'-BIPYRIDINE

by

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Abstract

SURFACE RAMAN SPECTRA OF THE THREE REDOX FORMS OF METHYLVIOLOGEN AND 4,4'-BIPYRIDINE

by

Tianhong Lu

Adviser: Professor Ronald L. Birke and John R. Lombardi

The electrochemistry of methylviologen and 4,4'-bipyridine on polished and roughened Ag electrodes was studied. The electrochemical behavior of the two compounds on the polished Ag electrode is similar to that on the Hg electrode. However, on the roughened Ag electrode obvious differences were observed. Adsorption peaks for both compounds on the roughened Ag electrode were observed in cyclic voltammograms. Unstable reduction intermediates appear to be stablized by the roughened Ag electrode.

The surface Raman spectra of the three redox forms of methylviologen and 4,4'-bipyridine were studied. It was found that when the two compounds are electrochemically reduced on the roughened Ag electrode the surface Raman spectra are often a superposition of the surface enhanced Raman spectrum and resonance Raman spectrum and/or normal Raman spectrum of their reduction products. These Raman spectra can be clearly separated and shown to originate from different redox forms of the two compounds.

The intensity-potential profiles for surface enhanced Raman scattering of some molecules on the roughened Ag electrode were studied. The shape of the experimental profiles can be fit very well with the calculated curves from our charge transfer theory indicating that the intensity-potential profile is mainly related to the Raman polarizability of the molecule-metal system. However, sometimes the profile can be influenced by other factors such as electrode reaction, surface coverage and selfabsorption of adsorbed molecules. Therefore, when the calculated curve can not fit with the experimental profile there must be a factor which plays a more important role in the intensity-potential profile than that of Raman polarizability.

CONTENTS

1. BRIEF REVIEW

1-1. Introduction

1-1-1. Surface spectroscopy

When two or more substances are in contact, the boundary layer constitutes the interface. Although the mass of the interface is negligibly small compared with that of the bulk, the ability of surfaces at interfaces to influence on chemical reactions is far more significant than that of the bulk. Therefore, it is important to investigate fully the structure and properties of the surfaces of interfaces. However, only few methods of investigating interfacial systems are available at present. This is mainly because the surface is thought of as the top few atomic layers of a solid so that the mass on the surface is very small and the surface species are often so unstable that they are detected only in situ. Therefore, surface techniques must be very sensitive and should be used in situ.

The solid-gas (vacuum) interfaces are comparatively well understood This is partly because there are many sensitive surface techniques, such as Auger electron spectroscopy (AES) [1], ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) [2,3], secondary ion mass spectrometry (SIMS) [4,5], low energy electron diffraction (LEED) [6], and high resolution electron energy loss spectroscopy (EELS) [7]. However, such techniques require ultra high vacuum environments.

Electrochemists often deal with solid-liquid interfaces which are less well understood because the above surface spectroscopy cannot be used in situ to obtain the characteristics of solid-liquid interfaces. Electrochemists can use electrochemical methods to study solid-liquid interface processes. However, the electrochemically measurable parameters are often the result of a combination of surface processes. They can only yield information regarding the rate of reaction, the influence of diffusion, concentration, temperature etc. They cannot give information about the chemical identity, structure, configuration and orientation of surface species. Therefore, there is a great need for techniques which will permit both kinetic and structural characteristics of a surface reaction. Ideally, such a technique would be a combination of an electrochemical system with a spectroscopic method capable of being used in situ.

Some spectroscopic techniques can be used in the in situ study of species on surfaces, such as electroreflectance [8,9], ellipsometry [10,11], photoemission-into-electrolyte [12,13], photoacoustic spectroscopy and photothermal spectroscopy [14,15], infrared spectroscopy [16,17] and Raman spectroscopy [18,19]. Among them only infrared and Raman spectroscopies are capable of providing direct and detailed structure information. In situ infrared studies have been carried out using multiple internal reflection technique and infrared transparent electrode substrates. However, absorption and sensitivity are serious problems [20]. Raman spectroscopy has many advantages over infrared spectroscopy. For example, water, the most frequently used electrochemical solvent, is a weak Raman scatterer and therefore an excellent solvent for Raman work; glass and quartz can be used as Raman cells and salt windows are not required; Raman spectroscopy has excellent spectral range and resolution; only small samples are needed. However, Raman spectroscopy still suffers from low sensitivity.

About ten years ago, a phenomenon termed surface enhanced Raman (SER) scattering, was discovered. The SER scattering is a process in which the Raman scattering intensity of molecules adsorbed on rough metal surfaces is enhanced by factors of 10^4 - 10^6 compared to the intensity expected for nonadsorbed species at the same concentration. Such enormous enhancement overcomes the traditional low sensitivity problem associated with the normal Raman (NR) scattering process. Thus, it allows detailed in situ chemical analysis of monolayers of species adsorbed on metal surfaces and it may become a powerful in situ surface spectroscopy.

1-1-2. Surface enhanced Raman spectroscopy

In 1974, Fleischmann, Hendra and McQuillan [21] first reported the surface Raman spectra of pyridine adsorbed a silver electrode which has been electrochemically roughened, and gave a possible model of the structure of the double layer between silver and potassium chloride solution containing pyridine. The results were of great interest since they showed that Raman spectroscopy could be used to obtain molecular information for in situ studies at an electrode surface. However, the surface enhancement effect was not realized until 1977, in the work of Jeanmaire and Van Duyne [22], Albrecht and Creighton [23]. They independently found that the Raman signal per adsorbed pyridine molecule was roughly six orders of magnitude larger than that of a molecule in solution and that the signal from pyridine that Fleischmann et al. had observed, could not be attributed only to an increase in surface area of their roughened electrode. This surprising discovery touched off a flurry of experimental and theoretical activity. Since then, intense study on SER scattering has been and is being done. Hundreds of papers about SER scattering has been published. The SER effects have been observed in numerous different interfaces and environments. The SER scattering in the electrochemical system, i.e., electrode-electrolyte interface has been most widely investigated. Other interfacial systems in which SER scattering has been observed, are the metal-gas (vacuum) interface [24-33], the colloid-liquid interface [34-59], the solid-solid interface (tunnel-junction configuration) [60-63]. The SER phenomena are not substrate general since, at present, they have been convincingly shown to exist only on a few metals and semiconducts. Most SER scattering studies have been obtained on silver because silver shows the highest enhancement. More than 300 papers concerning SER scattering on silver have been published. Copper and gold also show high enhancement and have often been used as metal substrates. Many papers concerning SER scattering on copper [64-97] and gold [98-118] have also been published. In addition, the SER effect has been observed on platinum [119-126], nickel [127-133], aluminium [134-136], sodium [137-139] and semiconductors [140-148] etc. The SER phenomena are quite molecule general, for example, SER spectra of more than 200 different molecular species have been reported. The SER spectroscopy of pyridine have been most intensely studied. The SER spectroscopy of various kinds of compounds besides pyridine have also been investigated. Most of them are nitrogen heterocyclic compounds, such as methylpyridine [149,150], methylviologen [151-153], bipyridine [112, 154-157], piperidine [158], pyrazine [159-161], cyanopyridine [162], nitropyridine [163], dithizone [164,165], lutidine [166], mercaptobenzotriazole [167], etc. Some of the molecules are organic compounds containing no nitrogen, such as benzene [116, 120, 137, 141, 168-171], ethylene [39, 115, 172, 173], etc. The SER spectroscopy of other compounds, such as inorganic compounds [24, 122, 128, 129, 174-202], dyes [49, 53, 104, 203-206], metal complexes [83, 84, 207-212] and biochemical compounds [213-218], have also been widely studied. Many experimental characteristics of SER scattering which are different from that of NR and resonance Raman (RR) scattering, have been discovered. A large number of possible mechanisms for SER scattering have been proposed to explain the experimental characteristics, but no one mechanism can explain all the characteristics and there is some diversity among these mechanisms. It is now widely accepted that, broadly speaking, two separate mechanisms must be invoked to explain the phenomenon of SER scattering. One is the electromagnetic enhancement mechanism which results from the influence of the roughened surface on the local electric field of the incident radiation; another is the charge transfer mechanism which associated with electronic transitions between the adsorbate and metal surface. Recently, more and more applications of SER spectroscopy have been reported, but its application is still limited mainly due to the following reasons:

(a) Only Ag, Cu and Au show the high enhancement.

(b) The large enhancement is generated on a roughened metal surface which differs in its properties from the usual smooth surface.

From the above mentioned we know that although SER scattering has been intensely studied and seems to be a promising spectroscopic technique for in situ identification of adsorbates on metals, the phenomenon of SER scattering has been found to be complicated and confusing and is still not completely understood. Therefore, further investigation is indeed necessary.

1-2. Experimental characteristics

1-2-1. High enhancement

High enhancement factors are the most important characteristic of SER scattering. Since Jeanmaire and Van Duyne [22], and Albrecht and Creighton [23] pointed out that the Raman scattering from pyridine adsorbed on the silver surface was anomalously enhanced by at least five to six orders of magnitude over that of a molecule in solution, a new field of scientific inquiry, the study of enhanced optical scattering from a surface, was opened. However, quantitative evaluations of surface enhancement factor are very sparse. The original value of surface enhancement factor for pyridine at roughened silver electrode [18] is widely quoted. One factor responsible for the scarcity of surface enhancement factor determinations is the paucity of surface coverage data for SER-active adsorbates at substrates. Recently, in connection with kinetic and mechanistic studies at an electrode Weaver et al. [219] have developed methods for accurately evaluating surface concentrations for both electroactive and nonelectroactive species and have determined surface enhancement factors of 11 compounds on a silver electrode. All the surface enhancement factors are in the range between 1×10^5 - 8.5×10^7. The most interesting conclusion is that for adsorbates that do not display electronic resonance enhancement in the bulk phase for energies in the vicinity of the Raman excitation, the surface enhancement factors at silver electrode are insensitive to the adsorbate electronic structure and the adsorbate-surface interactions.

1-2-2. Frequency and relative intensity

The frequencies of the majority of bands in SER spectra are only slightly shifted from that in NR spectra of the same molecule. Therefore, the energies of the vibrational modes are not influenced very much by adsorption and one has to assume that weak bonds exist between adsorbed molecules and surface metal atoms. This assumption is confirmed by comparison of Raman spectra of pyridine adsorbed on silver with those from silver-ion-pyridine complexes which differ greatly in frequencies and intensities from pure pyridine spectrum [65]. However, the relative intensities are altered to a large extent because they are sensitive to the environment. In spite of change of the relative intensities, the SER and NR spectra are similar enough so that molecular identification is still easily facilitated.

1-2-3. Metal substrates

The degree of the enhancement for SER scattering is related to the substrates. Silver was widely used as a metal substrate for SER scattering because it shows the highest enhancement. Most of the earlier SER scattering work was accomplished with silver, but it is soon discovered that copper and gold surfaces show the SER effect. The first observation of SER scattering on copper with green laser exciting light was very weak [64]. It was found later that red laser excitation light allowed well-defined SER spectra for both the copper and gold electrodes. Pettinger and Wenning [65,100] reported that when the laser wavelength was tuned from 457 nm to 647 nm, a 200 fold increase of the enhancement factor for the breathing vibration in pyridine/Au and pyridine/Cu systems was observed;

whereas only a 20 fold increase was obtained for pyridine/Ag system. It was reported [65,66] that silver can show at least 10^6 times enhancement, copper can give 10^5 - 10^6 enhancement, for gold it is 10^4 - 10^5. However, more recently studies [220] in which roughness, frequency, coverage and electrode potential have all been optimized, indicated that the peak enhancements on all three metals are comparable to within a factor of 2. In addition, Weaver et al. [115,116] reported that the SER intensities for molecules, such as benzene, ethylene, carbon monoxide and oxyanione etc. at gold were much higher than that at silver.

The SER effect on other metal substrates, such as Pt, Ni, Al and Na etc., have also been reported by individual investigations. However, the enhancement on these metals is relatively low. For example, Bradley et al. reported [129] that the enhancement for carbon monoxide on Ni is only 70-100. In addition, SER spectra on these metals shows a remarkable intensity dependence on excitation wavelength, for example, Yamada and Yamamoto reported [119] that the SER spectra of pyridine on Ni and Pt can be observed with 514 nm excitation laser light, but it cannot with 600 nm light. It is likely that Hg and Cd do not support SER scattering even though there are published reports of the successful action of these metals [221-223]. Subsequent attempts to reproduce these experiments have not succeeded [224]. Attempts employing Pb, In, Sn have been unsuccessful [61].

1-2-4. Roughness of substrates

The most peculiar characteristic of SER scattering is that substrates must be roughened in order to observe SER spectra. For example, suitably roughened silver can provide an enhancement factor around six orders of magnitude, whereas a smooth silver substrate produces only an enhancement factor around 400 [225], for which the intensity of the SER scattering is below the sensitivity threshold of the Raman spectrometer [26].

There are different roughening methods for different systems. In the electrochemical system the electrode surface is generally roughened with the so-called oxidation-reduction cycle (ORC). During the ORC the electrode is subjected to a double potential step or triangular sweep between one potential limit at which the electrode can be oxidized, and another one at which the electrode can be reduced. Many factors can affect the SER intensity during the ORC. Firstly, the SER intensity is found to be related to the extent of charge passed in the anodization process in the ORC. The SER intensity increases with the charge up to 50 mc/cm^2 and then decreases beyond 50 mc/cm^2 [23,226]. Secondly, laser illumination of the electrode during the ORC increases the intensity by up to an order of magnitude over and above that produced by an ORC performed in the dark [227, 228]. Thirdly, the ORC is usually carried out in the presence of adsorbate in the solution. Although the presence of adsorbate in the solution during the ORC is not necessary, only weak Raman intensity is obtained when the adsorbate is added after the ORC [117,229]. In addition, it was reported [230] that stepping the potential of the electrode to the region of rapid hydrogen evolution prior to performing an ORC can result in the SER intensity that is more intense by almost an order of magnitude than that for an electrode subjected to the ORC alone.

It was indicated [164,227,231] that an electrochemical ORC is not necessary to observe the SER effect in an electrochemical system. Mechanically roughened electrodes also show the SER effect, but the enhancement factor for mechanically roughened electrodes is at least two orders of magnitude less than that of the electrochemically roughened electrode [174].

Other roughened substrate forms on which the SER effect has been observed so far, include colloidal metal particles [34], vacuum-deposited metal island films [232], matrix-isolated metal clusters [233], roughened surfaces of single crystals under ultra high vacuum (UHV) [234], tunnel junction structures [60], metal-capped polymer posts [235] and holographic gratings [236]. Recently, chemically prepared silver film on glass were found to exhibit a strong SER effect [237].

There apparently are three scales of roughness to be considered. One is 'macroroughness' which has particle sizes from 250-5000 angstrom, another scale, 'microroughness' has particle sizes from 50-250 angstrom, a third one is 'atomic scale microroughness' which is on the order of atomic dimensions. Although most of researchers active in the SER field agreed that some kind of roughness of the metal substrate surface is important, there is no agreement on the scale of this roughness. Some SER researchers have concluded that macroroughness is required to observe SER effect [26,82,160,231,238,239]. Roughness with the average particle size around 1000 angstrom for silver and 500 angstrom for copper can show the largest enhancement [82, 231]. Others concluded [240,241] that the microroughness is required in order to obtain the high enhancement. While still others think that the atomic scale roughness contributed by adatoms, clusters and surface defects is most important [177,180,242-245]. Roughness greater than wavelength of the exciting radiation has been excluded by most workers as being an essential component of SER scattering.

1-2-5. Angle of incidence of exciting light

There have been only few papers concerning the angular dependence of SER intensity on the angle of incidence of exciting light. Pettinger et al. [65,100,246] studied the angular-resolved Raman spectroscopy of pyridine on silver, copper and gold electrodes. They indicated that:

(a) The angular-resolved Raman spectra showed a sharp peak with a halfwidth of about 10°, the angle of incidence was around 60° for peak intensity.

(b) The angular dependence behavior for all the bands are identical.

(c)) The angular dependence behavior for Ag, Cu and Au are almost the same.

Mullins and Campion [247] measured the angular distribution of the Raman intensity of benzene adsorbed on Ag(111) at submonolayer coverage. The peak intensity was also located at about 60°, but the halfwidth was much larger than 10°.

1-2-6. Excitation profile

Since Creighton et al. [248] and Pettinger et al. [249] independently reported that the SER excitation profile did not obey the ω^4 dependence seen in the NR scattering case, various groups have investigated the dependence of the SER intensity on excitation frequency [18,27,30-32,34,53,65,66,100,204,246-255]. This dependence may contain some information on the SER mechanism and provide information about the intermediate electronic state in the SER process. Although the magnitude of the deviation from the ω^4 law differed from different studies a qualitatively similar trend was observed, i.e., the SER band intensities substantially increased with decrease in excitation frequency and the excitation profile maxima was located in yellow or red region. Some experimental results obtained for the SER excitation profile are:

(a) The SER excitation profile depends on the metal substrates. It was reported [65,100,246,248,249] that the SER signal of pyridine on silver electrode increased 20 fold when the laser excitation light shifted from blue to red, whereas 200 fold increase was observed for copper and gold electrode. Actually there was a wavelength threshold for observation of SER scattering from pyridine on copper or gold electrode [34,66]. In addition, the excitation profile maxima on silver was located in shorter wavelength region than that on copper or gold [30,34].

(b) The SER excitation profile also depends on nature of the interace system. The profile maxima for pyridine on silver electrode were in the 650-750 nm region [248-250], whereas they were located in 500-600 nm region for pyridine on silver colloid or silver film in UHV system [30-32,34].

(c) The SER excitation profile was sensitive to the surface states. It was reported that the profiles are different for different degrees of anodization of silver electrode [18,250,251]. In the pyridine/Ag colloid system the profile maximum moves to longer wavelengths as the particle size increases [34].

(d) The SER excitation profiles for different adsorbates vary. In order to compare the excitation profiles of different adsorbates without the effects of experimental conditions, Creighton et al. [251] took the excitation profiles of pyridine and triphenylphosphine which were coadsorbed on the same silver electrode and found that their excitation profiles are different.

(e) The different SER bands from the same molecule gave different excitation profiles [18,31,32,248]. Pockrand et al. [31,253] indicated that the position of the profile maximum was related to the energy of Raman bands. The profile maxima shifted to shorter wavelength with increasing energy of the Raman bands. For example, the profile maximum was observed at about 580 nm for the 622 cm^{-1} band and at about 500 nm for 3033 cm^{-1} band. They further indicated that the excitation profiles shifted roughly linearly with the energy of the Raman band.

(f) It was reported [34,249] that the excitation profile maximum coincided well with an electronic absorption band. The parallelism between the absorption band and SER excitation profile led these researchers to assign the SER mechanism as a RR effect.

(g) The effects of coverage on the SER excitation profile was studied by Pockrand [252]. It was found that the profile maximum from pyridine on coldly evaporated silver films exhibited a continuous red shift with increasing coverage. For example, the maximum is at 590 nm for 0.3 monolayer and at 645 nm for 1.0 monolayer.

(h) Recently, there have been several reports of very large Raman enhancements that can be attained from the vibrational modes of chromophoric molecules adsorbed on a silver electrode by the combination of RR and SER effects, i.e. surface enhanced resonance Raman (SERR) effects. The SERR excitation profiles have two maxima. The first one has been attributed to RR contribution and the longer wavelength maximum to the SER contribution [204,254,255].

1-2-7. Overtones and combination bands

Some experimental results showed that SER phenomenon involves a RR effect. For example, SER excitation profile maximum is located at the same position as that for an electronic absorption band [34,249,254,255]; the existence of a new electronic transition state has been shown by EELS of adsorbed pyridine on a silver film [256], which was assigned to be a charge transfer transition of the electron from the metal to the adsorbate. However, it is reasonable that if RR effect occurred overtones and combination bands whose intensities are comparable with that of fundamentals, should be observed. However, there have been a few reports of the observation of overtones and combination bands in SER spectra by Pettinger [257], Moskovits group [187] and Takahashi et al [258]. Pettinger [257] reported the overtones and combination bands of SER fundamentals for pyridine adsorbed on the silver electrode, but their intensities are less than 1% of fundamentals. Thus, the conclusion that simple RR scattering can explain SER phenomenon is questionable. Moskovits et al. [187] reported the observation of the overtone of the stretching fundamental of CO adsorbed on the silver film in UHV system. Its intensity is roughly 5% of the fundamentals. Takahashi et al. [258] more recently reported that unusually large intensity and well defined overtones and combination bands were observed exactly at the expected frequency for the SER spectrum of phenazine adsorbed on a silver electrode.

1-2-8. Depolarization ratio

One of the most interesting phenomena associated with SER scattering is the unusual depolarization effect. Several reports on SER spectroscopy [18,224,259-

261] have indicated that the majority of SER spectra are depolarized and the depolarization ratio, ρ, for all the SER bands is in the range of 0.60 to 0.75, whereas values of ρ are about zero for symmetric vibrations in NR spectrum. It was considered that the depolarization effect is mainly due to the roughness of the metal surface and the orientation of adsorbed molecules [261].

1-2-9. Lineshape

The bands in SER spectra are significantly broader than those in NR spectra. Furthermore, the shape of the bands in the NR spectra follows a single Lorentzian lineshape function, whereas for the SER spectra it does not. The broad non-Lorentzian lineshapes in SER spectra are probably the result of simultaneous existence of two or more surface environments for adsorbed molecules [18]. For example, Pettinger and Wenning [262] have found different linewidths for adsorbate pyridine on Ag(111) and Ag(100) and indicated that the linewidths were related to the electrode potential.

1-2-10. Background continuum

Otto [174] first mentioned that there was a strong background continuum in the SER spectrum and indicated that it is not due to Rayleigh scattering light. Several groups [175,176,263-267] later studied the SER background in details. Some features of the SER background continuum were indicated. First, it was observed that the entire SER spectrum was a series of SER bands superimposed on a continuum which extends from Rayleigh tail to about 4000 cm^{-1}. The continuum intensity decreases with wavenumber in 0-600 cm^{-1} region. Then, it is essentially flat in 600-4000 cm^{-1} region except for a hump between 1100-1700 cm^{-1}. Beyond 4000 cm^{-1} there is a gradual decrease to dark current [264]. Second, the continuum is similar in character to SER bands. For example,, the continuum intensity increases with anodization charge during an ORC pretreatment to a maximum at essentially the same charge at which the SER band intensity has a maximum [175,264]. The continuum has the same depolarization ratio as that for SER bands [175]. The same potential dependence of continuum and SER bands was observed [264,266]. Third, the continuum intensity was related to metal substrates. It was reported [267] that a Pd monolayer on a silver surface reduced the continuum intensity by a factor of five.

The continuum was considered to be due to luminescence [176] except in the 1100-1700 cm^{-1} region in which the continuum was attributed to surface carbon. The role of the surface carbon in SER scattering was studied by several groups [268-273]. Some groups considered that the SER scattering is mainly due to the surface carbon. However, the surface carbon continuum have not been observed from SER scattering on other metals, such as Au and Cu [264], and from SER scattering in organic electrolytes [264,275]. Therefore, it seems that surface carbon is not a prerequisite for SER scattering.

1-2-11. Coverage dependence

The determination of the coverage-dependence of SER scattering is fundamentally important in understanding the enhancement process. The dependence of the enhancement factor on the distance away from the metal surface can distinguish and estimate the contribution of "long range" and "short range" enhancement mechanisms. Also, in the submonolayer region, the study of coverage dependence of SER scattering can yield information on effects due to chemical bonding.

The coverage dependence of SER scattering is ideally studied in UHV system because the dosing of adsorbate can easily be controlled in UHV system. Several SER experiments [25-26,26,234,252,278-282] have been reported in which the coverage dependence of SER scattering of pyridine on silver surface was studied in a UHV system. However, the results vary and this may be due to the different pretreatment of silver surface and different methods for coverage measurement. For the distance dependence of SER scattering, there are two opposite conclusions. Some researchers [26,234,252,276-281] claimed that the SER signal from the adsorbate beyond the first monolayer is clearly enhanced and the enhancement factor is about two order of magnitude smaller than that for the first monolayer. On the other hand, some groups [24,25,28,282,283] concluded that the SER signal is enhanced only within the first monolayer. Studies of SER intensities as a function of coverage in the electrochemical system are difficult because the electrode surface has a pronounced effect on the intensities and cannot be reproduced from experiment to experiment. However, there are still some papers [261,284] in which it was reported that the enhancement from the molecules beyond the first monolayers is enhanced in the electrochemical systems. In the submonolayer region, it was reported that the SER intensity is nonlinear with coverage. Seki et al. [28] and Pockrand et al. [281] proposed that the enhancement only occurs for some fraction of the first monolayer and suggested that only molecules adsorbed on certain special sites, termed "active sites" produce the major portion of the SER signal. Afterwards, the concept of "active sites" was used in electrochemical systems [229, 285-290]. Some experiments for quenching the SER signal of pyridine on a silver electrode gave the best evidences for the "active sites". A very small underpotential coverage of deposited Tl, ca. 3%, or Pb leads to almost complete quenching of SER signal from pyridine on the silver electrode, and this quenching is irreversible since anodic stripping of Tl or Pb does not lead to restoration of SER signal [291-294]; The potential negative to -1.2 V vs SCE (saturated calomel electrode) can also quench the SER signal [18,264,295]; Cu deposition on Ag leads to a shift in the pyridine spectrum typical of a Ag surface to that of a Cu surface at only 0.1 monolayer [75]. All of these results can be interpreted as resulting from loss of of "active sites".

1-2-12. Potential dependence

One of the important features of SER scattering from an electrode surface is that both frequencies and intensities of SER bands are potential dependent. A few groups [18, 21, 126, 296, 297] have studied the potential dependence of frequency. They found that when the potential is shifted negative the frequency of the SER band moves to lower values. This is observed for different compounds, such as pyridine, pyrazine, p-nitrosodimethyl aniline and cyanide, etc., and for all the bands in SER spectrum, either internal or external surface bands, and for different electrolytes, such as KCl, NaOH, K_2SO_4 and H_2SO_4 etc. The shift is about few wavenumber per volt for internal bands and 20-30 wavenumber per volt for external bands. However, it was reported [158] that the potential dependence of frequency for piperidine is slightly different. The frequencies of some

SER bands for piperidine shift slightly to a higher value with more negative potential.

The potential dependence of the SER intensity has been more widely studied. The experimental features of the potential-intensity profile are as the following:

(a) The potential-intensity profile is usually bell-shaped and exhibits a maximum [22]. It was considered that because the shape of the intensity-potential profile is similar to that of the differential capacitance the potential dependence of intensity mainly reflects the change in coverage with the potential [298,299].

(b) The potentials, at which the maximum of the SER intensity occurred, are different for the different vibrational bands in the same spectrum [22, 158].

(c) Furtak and Macomber [300], and Billmann and Otto [301] found that the potential, at which the maximum of SER intensity occurred, changes with the energy of the incident photon. This phenomenon was explained by the shift of the energy of the charge transfer band with respect to the photon energy by a change in the electrode potential. Thus, the potential dependence of the SER intensity is mainly due to the change of the Raman polarizability of the molecule-metal system with the potential. Birke and Lombardi et al. [302] studied this phenomenon for a series of molecules and concluded that this phenomenon is also related to the structure of the adsorbed molecules.

(d) Weaver et al. [303,304] studied the intensity-potential profiles for some adsorbed molecules which can be reduced or oxidized on the electrode. It was found that there is a correspondence between the intensity-potential profile and the cyclic voltammogram in the potential range where the electrochemical reaction occurs.

The potential dependence of SER intensity was found to be complicated because it can be influenced by many factors. Further systematic study is necessary.

1-3. SER mechanisms

1-3-1. Electromagnetic mechanism

It is now widely accepted that two separate mechanisms, the electromagnetic and chemical mechanisms, must be involved to explain the phenomenon of SER scattering [224, 259, 305]. The relative contribution of the two effects depends on the individual adsorbate-adsorbent system [306]. The electromagnetic mechanism has been well studied both experimentally and theoretically. It involves small surface irregularities which allow optical frequency surface plasmon resonances resulting in strong local enhancement of the electric field both of incoming and scattered radiations [239]. This model does not require specific chemical bonds between adsorbate and metal, and explains the need for surface roughness, the observation of enhancement at some distance from the metal surface, as well as the angular dependence of the enhancement with respect to the direction of incoming radiation. Realistic electromagnetic enhancement factors of up to 10^4 can be explained by this mechanism [220]. However, early in the research into the SER phenomenon it was realized that the SER phenomenon is not only due to the electromagnetic effect. Many experimental results cannot be explained only by the electromagnetic mechanism. Among them are:

(1) The enhancement factors for many compounds, such as pyridine, pyrazine etc. [22, 219], which contain a lone pair of electrons available for bonding with

the metal surface, are about 10^6 which is greater than that due to the electromagnetic by factors of 10-1000.

(2) The electromagnetic mechanism focused the main attention on the role of the metal substrates. An adsorbed molecule is simply assumed as a dipole located near the substrate surface. There are no specificities for different molecules. Any molecule should exhibit SER effect on a rough metal surface. Actually, different molecules show very different enhancement factors. For example, N_2 and CO has the identical gas phase Raman cross section, but their SER enhancement factors are different. Ethylene showed the SER effect, but no SER spectrum could be observed for ethane. In addition, even in the same molecule different vibrations showed different enhancement. For example, for alkenes and alkynes the CH stretching vibrations are very weak in the SER spectra, although strong in the spectra of the bulk materials. The strongest bands in the SER spectra are those which involve significant amount of C=C or C≡C stretching motion regardless of the intensities of these modes in the corresponding spectra of the unadsorbed molecules [308].

(3) When several monolayers of molecules are successively adsorbed on a substrate surface the molecules in the first monolayer have a Raman cross section about 100 times large than that for molecules in the following monolayers [234].

(4) Many experiments showed the necessity of chemisorption or surface complex for the SER effect. For example, Chen et al. [19] reported that a SER signal is obtained for benzoic acid when it is chemisorbed on Ag island films, but not for benzene, when it is in close proximity but not chemisorbed on Ag. Furthermore, SER effect is sensitive to the adsorbate state. For example, using electron energy

loss spectroscopy and UV photoemission spectroscopy, Demuth et al. [256] successfully studied the chemisorption of pyridine on Ag. At low coverage pyridine is chemisorbed through the π-d interaction. Subsequent increase in coverage then leads to a compressional phase transition where pyridine bonds to the surface via the N lone pair electrons, where the SER scattering starts to be observed.

(5) As mentioned in section 1-2-11, not all the adsorbed molecules show the SER effect. Only molecules adsorbed on certain special sites, termed "active sites", produce the major portion of the SER signal [28, 229, 281, 285-290]. Many experiments demonstrated that only a small amount of "active sites" is on the substrate surface. For example, the SER signal in the electrochemical system can be irreversibly quenched by a very small underpotential coverage of deposited Tl, ca. 3% [291, 292]; Only 0.1 monolayer Cu deposition on Ag leads to a shift in the pyridine spectrum typical of a Ag surface to that of a Cu surface [75].

(6) When observed on an electrode surface a resonance shaped SER intensity profile as a function of applied potential can be obtained [22, 158, 298].

(7) According to the electromagnetic mechanism the SER excitation profiles of any molecules should be the same irrespective of geometries and properties of adsorption. Actually, excitation profiles of SER scattering change from molecule to molecule adsorbed on the same metal surface [27, 251]. In addition, as mentioned in section 1-2-6, The change of the SER intensity with the excitation wavelength does not obey the ω^4 law [248, 249].

(8) According to the electromagnetic mechanism no molecule should show SER scattering on metal surfaces whose plasmon resonances are damped due to the interband transitions of d electrons at optical frequencies. However, there

were some reports of SER scattering on Pt [120, 122] which is suggestive of some mechanism other than electrodynamic enhancement because the field enhancing plasmon resonances are strongly damped in Pt [309].

All these experimental results are suggestive of an additional chemical effect in SER scattering besides the electromagnetic effect. The chemical effects, which deal with the detailed interaction and bonding between the adsorbed molecules and the metal surface, have been relatively less elaborated than the electromagnetic effects. Among the various chemical effects, charge transfer interaction had attracted much attention.

1-3-2. Experimental evidences for a charge transfer effect

Since the observed Raman scattering cross sections were on the order of resonance Raman spectra, while no known molecular transition existed in that spectral region for free molecules, such as pyridine, pyrazine etc., it was speculated that when considering the molecule and metal system as a whole, adsorption induced charge transfer transitions from metal to adsorbed molecule or from molecule to metal were involved. This model was usually called the charge transfer model.

Evidence for the adsorbate-adsorbent interaction was given by Creighton et al. [34]. They compared the optical absorption spectra of Ag sols without and with pyridine. They found that there was a new absorption peak in the absorption spectrum of Ag sols with pyridine and the SER excitation profile of pyridine on Ag sols exhibited a maximum at approximately the same wavelength as that of the new absorption peak.

The significance of the adsorbate-adsorbent interaction can be inferred from the experiment by Hagen et al. [310]. They examined the Raman spectra of p-nitro-dimethylaniline (p-NDMA), which is known to exhibit a resonant Raman effect at 488 nm excitation in solution and the Raman intensity with 514.5 nm excitation was 10 times weaker than that with 488 nm. Upon its adsorption on a Ag electrode, p-NDMA showed approximately the same intensity for the Raman peak at both 488 and 514.5 nm excitations. This is possibly explained on the basis that the intrinsic electronic transition at 435 nm for free p-NDMA is shifted towards longer wavelengths as a result of the interaction of molecule with surface.

In addition to the observation of SER scattering itself, there has been considerable experimental work which reported the electronic or vibrational properties of adsorbed molecules giving rise to SER scattering. For the most extensively studied system of pyridine-Ag, the measurements of the X-ray photoelectron spectrum of the N 1s atom [311], of a change in the work function of Ag upon adsorption of pyridine [283], and also of the electron energy loss spectrum [256] clearly demonstrated that pyridine is chemisorbed on Ag, being accompanied by change transfer between them.

An important contribution to the charge transfer model aimed at a determination of the electronic states of pyridine adsorbed on Ag has been given by Demuth and Sanda [312]. Using electron energy loss spectroscopy they have observed an excitation band of pyridine chemisorbed on Ag (111) centered 1.9 eV above the Fermi level of Ag. This band is absent in pyridine in solution or the gas phase and was tentatively assigned to the adsorbate induced charge transfer excitation between pyridine and Ag. Such charge transfer excitation bands have also been observed in pyrazine [313], CO, O_2 and ethylene on Ag films [314].

Pettinger et al. [249] have measured the relative change of the reflection of pyridine-Ag electrode. They found an additional absorption band around 750 nm and explained their SER results as a resonant Raman effect due to the appearance of such an adsorbate induced level associated with a surface complex.

Another interesting experiment concerning charge transfer effect has been made by Marinyuk et al. [315] for the pyridine-Ag system. By measurement of the intensity ratio of Stokes and anti-Stokes bands, the electronic absorption band of pyridine was found at 1.92 eV, which was attributed to the electron transfer from the metal adatom that forms a complex with adsorbed molecules, to the Fermi level of the metal.

More directly convincing evidence for a metal-molecule charge transfer state is found in electrochemical cells. Not long ago, Otto et al. [301] measured a change in SER intensity for pyridine on a Ag electrode as a function of the electrode potential. They expected that when the electrode potential changes all of the factors which lead to optical resonance, remain constant, only the charge transfer excitation energy varies with the electrode potential. They observed that there is a maximum in the SER intensity versus electrode potential and the potential at which the SER intensity reached a maximum (V_{max}), varied linearly with the excitation frequency. They believed that the charge transfer excitation is involved as an intermediate state of the Raman scattering process. There arises the possibility that the SER intensity varies with the applied potential and shows a maximum when the energy of the charge transfer excitation controlled by the potential becomes resonant with the incident photon energy. They considered that the charge transfer for the pyridine-Ag system is from silver to pyridine. Later, they found that for the CN^--Ag system the charge transfer is from cyanide to silver [184]. A similar experimental results for pyridine-Ag and SCN^--Ag systems has also been presented by Furtak et al. [285,300]. They interpreted the change in SER intensity with the potential as a result of the charge transfer excitation which increases the effective polarizability of the pyridine-Ag system. However, the direction of the charge transfer for pyridine-Ag system is concluded to be from an occupied state on pyridine molecule to an empty state on Ag, which is in contrast to that of Otto. At about the same time Lombardi and Birke et al. [302] showed the above effect to exist for variety of molecules. They further showed that the molecules could be divided into two classes; those for which the V_{max} have a positive slope with the excitation frequency and those for which the slope is negative. They also showed that this effect could be correlated with the electron withdrawing ability of the ground or excited electronic states of the molecules involved. They indicated that two types of charge transfer could be envisioned. Molecule to metal surface, in which an electron is transferred from the highest occupied molecular orbital to the Fermi level of the metal was associated with the negative slope in V_{max} vs excitation frequency. Conversely positive slopes were associated with transition in which an electron is transferred from the Fermi level of the metal to the lowest unoccupied orbital in the molecule.

Some groups [108, 316] studied the SER scattering of molecules which can easily form charge transfer complexes with metals. It was indicated that adsorption induced shifts in the frequencies of the charge transfer related bands could be used to determine the extent of charge transfer between metal surface and adsorbed molecule. For example, It was determined that tetracyanoethylene-Ag system exhibits a 85% charge transfer from Ag to tetracyanoethylene [316]; tetrathiafulvalene-Ag (or Au) system shows a 100% charge transfer from tetrathiafulvalene to Ag (or Au) [108].

The experimental results mentioned above can be taken as strong evidences for the existence of the charge transfer effect.

1-3-3. Charge transfer theories

The charge transfer mechanism was first suggested by Gersten, Birke and Lombardi [317]. Based on the effective resonant model they evaluated the Rayleigh scattering intensity for adsorbed molecule and extended it to Raman scattering. They took a two level model for adsorbed molecule with one sharp level lying below and one broad level lying above the Fermi level. Virtual and real transition from lower level to the broad upper level just above the Fermi energy cause a large enhancement of the Raman cross section of the adsorbed molecule.

About the same time, Burstein et al. [108] gave a description of various types of resonant Raman process including a dynamical charge transfer mechanism for adsorbed molecules. They pointed out that the excitations of electron-hole pairs near the surface of metals interact with electronic and vibronic excitations of the adsorbed molecule. If the excited electrons or holes have energies equal to a virtual bound state of molecule they will make a resonant contribution to the Raman scattering.

Following Burstein et al. idea, Otto et al. [318] suggested a four step charge transfer model. Based on the active sites concept, they postulated an electronic (or hole) affinity level for an adsorbed molecule and a relatively narrow (0.5-1 eV) peak of the electronic density of states at active sites on metal surface near the Fermi energy in contrast to relatively wide distribution of the density of electronic states at atomically smooth parts of the surface. Then they proposed a four step charge transfer process (Fig.1a). In the first step, an electron on the metal side is excited by annihilation of the incident photon. In the second step, the excited electron tunnels into the electron (or hole) affinity level of the adsorbed molecule. Then the electron tunnels back to the metal (the third step), perhaps leaving the molecule in an excited vibrational state. In the fourth step the electronic excitation on the metal side is annihilated by emission of the Raman scattering photon. When the laser photon energy is about equal to the energy difference between the center of gravity of the filled (or unfilled) part of the density peak and the electron (or hole) affinity level a resonant charge transfer Raman scattering occurs. This model can explain some SER features, such as SER intensity-potential profiles. However, no mathematical expression was given for this model.

More complete theories of adsorbate induced resonant Raman scattering were presented by Ueba [319,320], Arya and Zeyher [321] and Persson [322]. Although their functional forms of the enhancement factor differ from each other, all theories claimed that there is a new adsorption induced charge transfer state near the Fermi level of metal for molecules adsorbed on metal surface and the Raman polarizability of the adsorbed molecules is enhanced when resonant charge transfer excitation is involved in Raman process. Arya and Zeyher [321] calculated the Raman scattering cross section of adsorbed molecules by taking into ac-

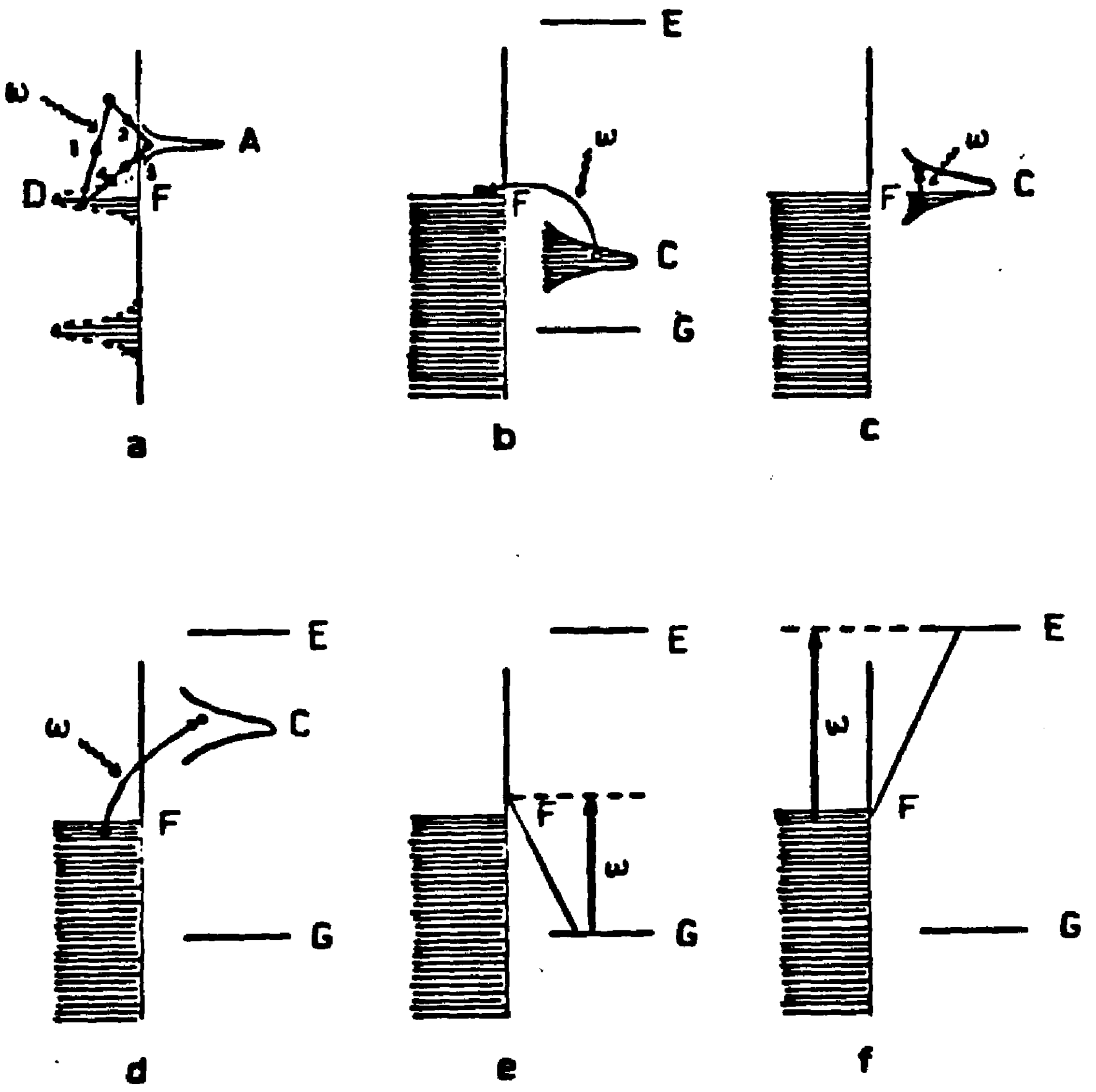


Fig.1. Schematic illustrations for possible charge transfer excitations between adsorbed molecule and metal. See the text for details.
A - electron (or hole) affinity level of
    adsorbed molecule,
D - Density states at active sites,
F - Fermi level, ω - Incident photon,
G - Ground state, E - Excited state,
C - Adsorption induced charge transfer state.

count both the electromagnetic and chemisorption effects. They showed that the charge transfer excitation from the upward shifted and broadened molecular ground state due to chemisorption to an vacant state of metal above the Fermi level (Fig.1b) gives rise to an onset structure of enhancement. Another model based on the charge transfer excitation was presented by Persson [322]. He assumed that an adsorbed molecule has a broadened level located in the vicinity of the Fermi energy and only partly filled and an electron in the partially filled molecular state located in the vicinity of the Fermi level can be excited by the incident photon to its unoccupied part above the Fermi level (Fig.1c). Using the data reported by Demuth and Sanda [312], he calculated an enhancement of about 100 for pyridine adsorbed on Ag. The result of his calculation agrees with the experimental finding [234]. Considering the energy diagram of pyridine on Ag, Ueba [320] indicated that the most probable path of the charge transfer excitation occurs from the highest occupied state of metal at the Fermi level to the unoccupied molecular state (Fig.1d). Using the Newns-Anderson model and assuming the coupling to the photon field to accompany the charge transfer excitation between the molecule and metal, they calculated the Raman polarizability with the perturbation expansion method with respect to the modified electron-phonon interaction caused by the electron hopping between the molecule and the metal. His theory can give the enhancement factor, explain the broadening of the SER bands and show necessity of the background continuum which agrees with experimental result reported by Udagawa et al [225]. Udagawa et al. have detected a SER signal of pyridine on a well characterized smooth Ag surface which cannot support the electromagnetic effect, and noted the presence of the background continuum, even though its intensity is weaker than is observed on rough Ag surface.

Another set of charge transfer theories was given by Adrian [323], Lippitsch [324] and Lombardi et al [325]. They assumed that the Fermi level of metal lay between the molecular ground state and one or more of the excited states, and transitions from the Fermi level of metal to the excited state (Fig.1e) or from the ground state to the Fermi level (Fig.1f) were involved. Their theories of Raman intensities based on the Franck-Condon and Herzberg-Teller vibrational coupling mechanisms follows Tang and Albrecht [326]. The Raman polarizability (α) derived is equal to the sum of three terms, i.e. $\alpha = A + B + C$. The A term comes from Franck-Condon coupling and the B and C terms from Herzberg-Teller coupling. The B term represents the transition from the ground state of the adsorbed molecule to metal and the C term represents the transition from metal to the excited state of molecule. Adrian [323] introduced vibronic coupling into the quantum mechanical expression for the polarizability limiting his consideration only to metal-to-molecule charge transfer. When this is done, two types of terms arise, one dependent only on Franck-Condon overlap integrals, and Herzberg-Teller term dependent on intensity borrowing from nearby allowed transitions. Adrian then claimed that the latter term should be overwhelmed by the former and thereby can be ignored. In considering the Franck-Condon term Adrian estimated a enhancement factor of 10-1000 and obtained the correct dependence of V_{max} on excitation frequency. However, his intensity vs potential profile does not fit experimental profiles for reasonable values of the damping constants. His theory fails to explain adequately why overtones are observed only weakly, if at all, in SER scattering. Furthermore, The Franck-Condon term indicates that totally symmetric modes should be enhanced considerably more than nontotally symmetric modes. This is contrary to observation. For example, Sanchez et al. [158] reported that a' and a" modes are equally enhanced for piperidine adsorbed on a Ag electrode.

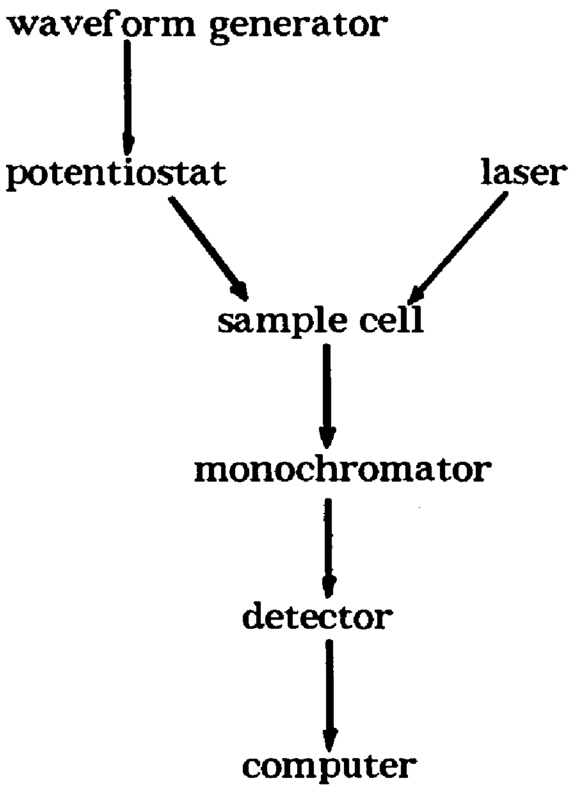
Metal-to-molecule transfer has also been considered by Lippitsch [324]. He considered that in usual SER systems there only exists charge transfer transition from the metal conduction band to unoccupied states of the adsorbed molecule, while a charge transfer transition from the ground state of the adsorbed molecule to the unoccupied states of metal has not been observed. Then, he assumed that the dipole moments from the ground state of molecules to the unoccupied states of metal is zero, then the A and B terms vanish and only the C term is responsible for SER scattering. Therefore, he emphasized that the enhancement in this model is attributed to the intensity borrowing mechanism. His theory can estimate a reasonable enhancement factor of 100-1000, explain the appearance of the Raman bands forbidden in the free molecule and show the orientation effect of the adsorbed molecule on the SER intensity. However, his theory fails to predict any dependence of V_{max} on excitation frequency. Lombardi and Birke et al. [325] indicated that both metal-to-molecule and molecule-to-metal charge transfer transitions are possible, which is consistent with the experimental observation [184,285,300-302]. Therefore, both Franck-Condon and Herzberg-Teller contributions to the SER intensity were considered. However, they noted that former contributes only to the intensity of totally symmetric vibrations, while the latter contributes to nontotally symmetric vibrations as well. Since the overtones observed in SER spectra are very weak, they considered that the Herzberg-Teller terms are most consistent with experimental finding and the SER scattering may be a resonance Raman effect in which intensity for charge transfer transitions is borrowed from an allowed molecular transition. The resulting formulas from this theory predicted that the SER scattering is a logarithmic resonance at the Fermi level of the metal which is consistent with the experimentally obtained intensity-potential profiles.

2. EXPERIMENTAL

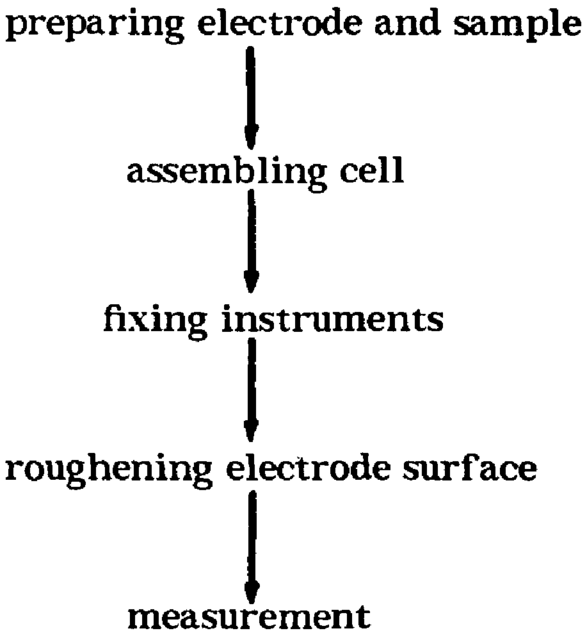
2-1. Introduction

In this section a brief account is given of the electrochemical and Raman instrumentation and experimental procedures employed in this work. The reagents and materials are also listed.

A line diagram of experimental instrumentation is given below:



A flow chart of experimental procedures is also given below:



2-2. Raman instrumentation

The basic elements of a SER experimental set-up are identical to those used in a normal Raman or resonance Raman instrument.

The monocromatic radiation sources were a Spectra Physics Model 164 Argon laser, a Spectra-Physics Series 2000 Krypton laser or a Spectra Physics Model 375 dye laser. The argon laser has strong output at 488.0 and 514.5 nm, the krypton laser has strong output at 647.1 nm, and the dye laser has a continuous output in the 560-620 nm range. The laser power on the cell was usually less than 50 mw in SER experiments. High power will cause photodecompositiom of species adsorbed on the electrode surface, especially when blue or green laser radiation is used. Higher power was used in normal Raman experiments. The laser power was measured using a Scientech 362 power energy meter. Laser plasma lines were filtered from main laser lines using a filter.

A 90^o geometry was used for the optical configuration as shown in Fig.2. A focusing lens was used to focus the laser beam at a spot on the SER working electrode. The incident light made an angle of 90^o with the optic axis of the monochromator.

The spectra were recorded with a Spex Model 1401 double monochromater with a resolution of about 2 cm^{-1}. The zero wavenumber position was carefully noted by scanning over the laser frequency.

After passing through the monochromator system the light was detected by a photomultiplier tube. Photomultiplier signals were amplified and processed by conventional photon-counting electronics. A digital output from this unit was fed to a PDP 8 computer. The spectrum can be recorded using a X-Y recorder or saved on a disc.

2-3. Electrochemical instrumentation

Fig.3 shows an electrochemical cell which was used in this work to study SER scattering on an electrode surface. This design is convenient for use with 90^o scattering geometry. This cell has an optically flat bottom and side with provisions for inert gas bubbling for deoxygenation, a port for adding solution, and a port with a stopcock for removing solution while the cell is still positioned in the spectrometer. The latter features are handy for flushing out the cell with blank electrolyte after adsorption has occurred from the test solution and can be accomplished under potential control of the working electrode without changing the

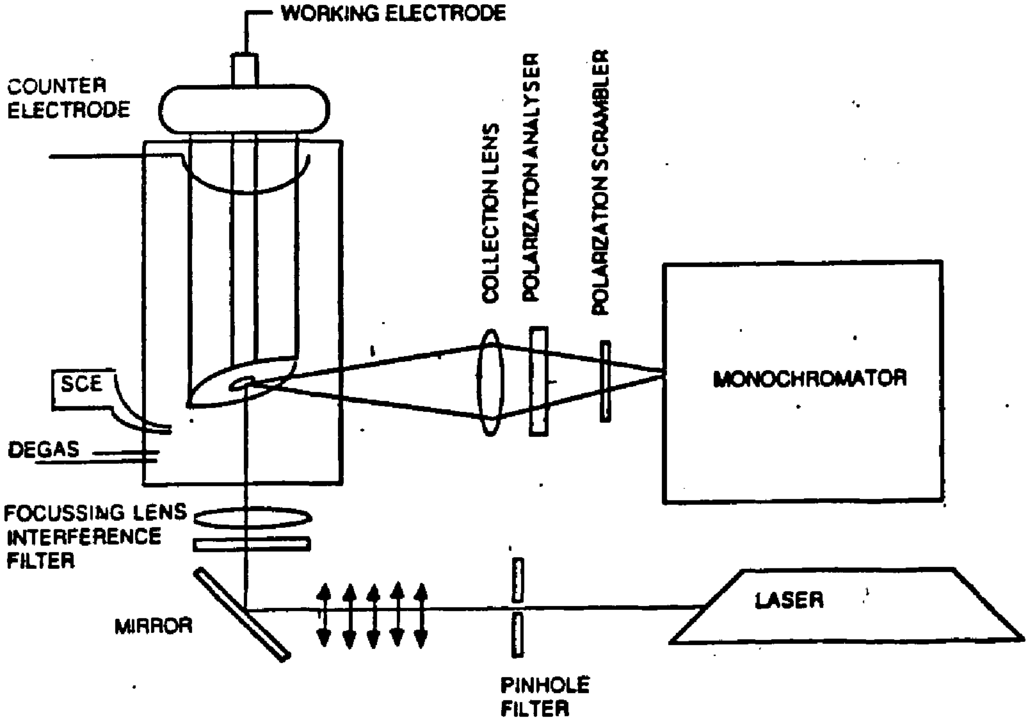


Fig.2. Optical set-up about the electrochemical cell in a 90 collection geometry.

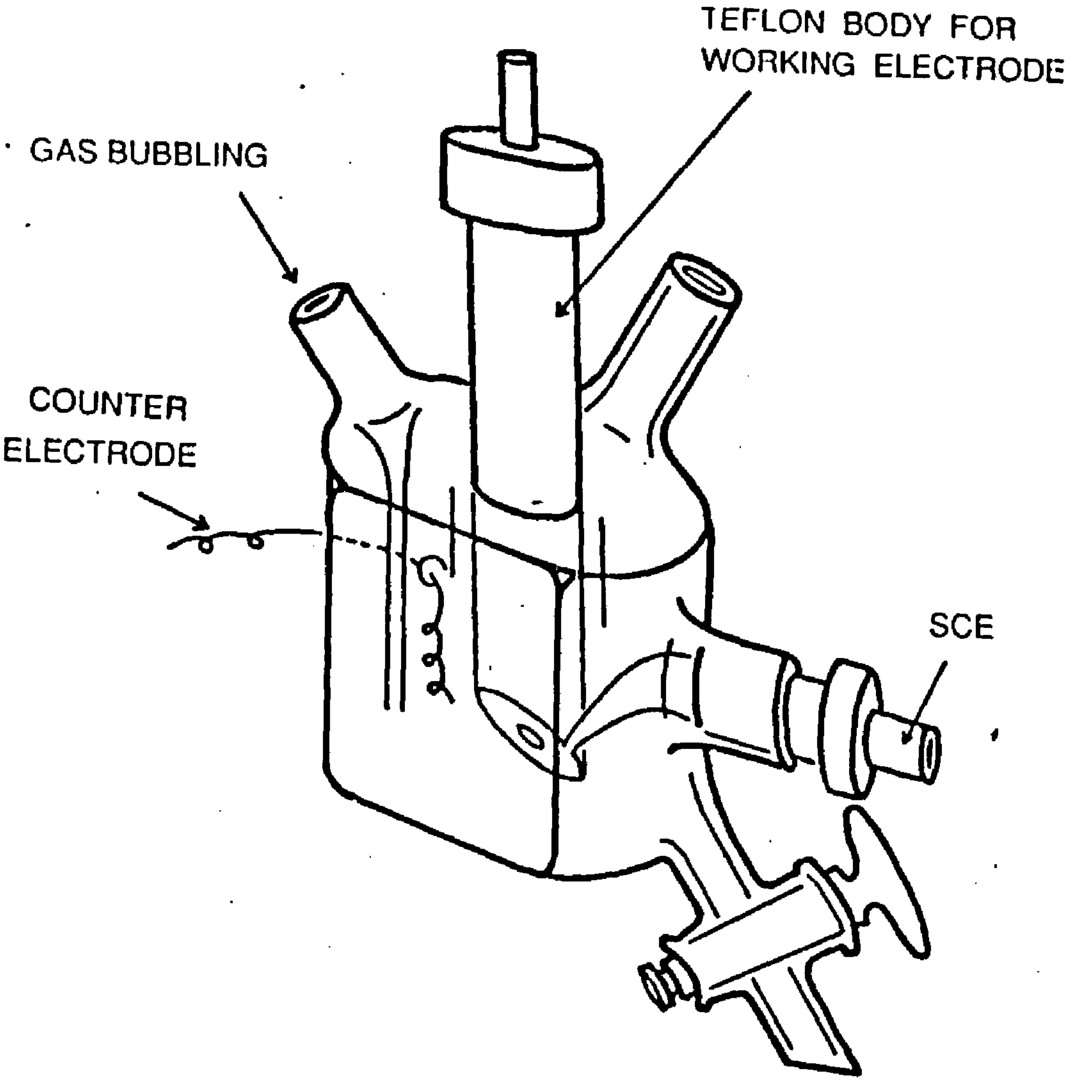


Fig.3. Electrochemical cell for SER scattering with 90° collection geometry.

optical alignment. This technique was used to separate the Raman scattering of an irreversibly adsorbed species from that of an intense RRS in solution.

As usual, this electrochemical set-up is a three electrode cell consisting of a working electrode, an inert counter electrode and a reference electrode. In this work the working electrode was constructed from a Ag wire which is embedded in a Teflon cylinder to reduce edge effects. The electrode is cut at 45^o angle to facilitate the 90^o scattering angle with the laser beam entering from the bottom of the cell. The surface area of the working electrode is about 1.4 mm^2. The counter electrode is a Pt wire. It was separated from the working and reference electrodes by a separate compartment with a ground glass frit separator in order to avoid some deleterious species produced at the counter electrode diffusing to the working electrode. The reference electrode is a saturated calomel electrode (SCE). All potentials are quoted relative to the SCE. A Luggin capillary from the reference electrode was positioned very near to the surface of the working electrode to minimize the effects of solution resistance.

The fundamental electrochemical instrumentation consists of a potentiostat and a waveform generator. The potentiostat controls the potential of working electrode and waveform generator can apply a potential pulse or a triangle waveform to the potentiostat input. A Model 173 potentiostat and a Model 175 Universal Programmer waveform generator were used in SER experiments. A RD3 Pine Instrument Company Potentiostat was used for cyclic or linear sweep voltammographic experiments. A Tacusel type PRG 5 polarographic instrument was used for polarographic experiments.

2-4. Reagents and materials

Methylviologen chloride ($MVCl_2$) was obtained from Sigma Chemical Co. Pyridine, piperidine and 4,4'-bipyridine (4,4'-BP) from Aldrich Chemical Co. They were all used as received. Reagent grade KCl was supplied by Fisher Scientific Co., KBr by Mallinckrodt Inc., $KClO_4$ by J. T. Baker Chemical Co. The working electrode was 99.99% pure polycrystalline Ag wire.

2-5. Experimental procedures

The sample solutions were prepared with deionized, distilled water and deaerated before use by nitrogen bubbling. Generally, the concentration of $MVCl_2$ or 4,4'-BP was 10^{-3} M and the concentration of pyridine or piperidine was 0.05 M. Generally, 0.1 M KCl was used as the supporting electrolyte. Sometimes, 0.1 M KBr or $KClO_4$ was used.

The pretreatment of the Ag working electrode was the following: The working electrode was polished with alumina (particle size: 0.3 micron), then immersed in a solution of H_2O_2 and NH_3 (1:1) for about 10 s and washed with deionized distilled water. Finally, the electrode was mounted in the cell, and an oxidation-reduction cycle (ORC) applied to the Ag electrode with a double potential step: -0.2V to +0.3 V to -0.2 V. The pulse duration was 5 s. The charge passed during oxidation was about 2mC. Here we will refer to a Ag electrode without an ORC as a "polished Ag electrode" and one with an ORC as a "roughened Ag electrode".

Raman spectra were generally taken after an ORC. Generally, when a Raman spectrum was taken the potential of the working electrode was hold at certain value. In the measurement of an intensity-potential profile the SER intensity can be measured while the potential was scanned. The potential scan rate used was 5 mV/s. At the same time the current can be recorded, thus the CV or LSV can also be obtained. During the measurement of intensity-potential profiles a large bandpass of 6-10 cm^{-1} should be used to minimize the effect on the observed intensity response of band-maxima shifts with changes in electrode potential.

In order to carry out electrochemical and spectral measurements of surface species without interference from solution species, in some experiments, after an ORC, the cell was washed in situ under potential control with 0.1 M KCl solution, i.e., the bulk solution in the cell was replaced with 0.1 M KCl solution, and then measurements were carried out.

3. RESULTS AND DISCUSSION

3-1. Introduction

In this work methylviologen ($MVCl_2$) and 4,4'-bipyridine (4,4'-BP) were chosen as the model molecules for studying SER phenomena and mechanisms.

Both $MVCl_2$ and 4,4'-BP are very interesting and useful molecules. They can be used as herbicides [326], electrochemical display devices [327,328], complex reagents [329-331], electron mediators in biological systems [332] and in photoelectrolysis [333]. They are especially important as materials to chemically modified electrodes [334-338] in order to promote the electron transfer reactions of some biochemical compounds. The electrode meanism of such promotion is not well understood. In order to get more information about such electrode processes the SER spectra of $MVCl_2$ and 4,4'-BP should be studied at electrode surfaces because SER spectroscopy is a powerful in situ technique for the study of surface and interfacial phenomena.

Both $MVCl_2$ and 4,4'-BP can be electrochemically reduced and the effect of the electrochemical reaction on SER scattering can be studied. In addition, their radicals which are reduction products or intermediates, have a blue color and show the RR effect. Comparing the RR scattering with the SER effect may lead to better understanding of the SER mechanism.

Both $MVCl_2$ and 4,4'-BP can be adsorbed on roughened Ag electrodes more strongly than pyridine. Comparing the SER intensity-potential profile for $MVCl_2$ and 4,4'-BP with that for pyridine whose SER scattering has been intensely studied, should give some insight into the potential dependence of the SER intensity.

Recently, SER and RR techniques have been used to characterize the viologens such as methylviologen and heptylviologen [151-153,340,341]. These investigations were mainly devoted to the Raman spectra of the monoradical viologen cation which shows a RR effect because it displays a wide absorption band in the 450-650 nm region [335]. Lee et al. [340] have reported the RR spectrum of the monoradical cation of methylviologen (MV^+) in aqueous solution. When one studies the Surface Raman spectrum of MV^+, the question arises as to whether it is a SER spectrum, a surface enhanced resonance Raman (SERR) spectrum , or a mixture of a SER and RR process. Some investigations [153,339] have discussed this question in order to understand the mechanism of the SER effect, but their conclusions are different and not entirely clear.

The study of SER scattering of 4,4'-BP has so far been limited. Cotton et al. [154,155] first reported the SER spectra of 4,4'-BP on Ag electrodes. Taniguchi et al. [112] reported the SER spectra of 4,4'-BP on gold electrodes. The assignment of vibration modes in SER spectra of 4,4'-BP was given by Farquharson et al. [341]. These studies were only preliminary and further studies are necessary.

3-2. Electrochemistry

3-2-1. Electrochemistry of methylviologen

It is now well known that $MVCl_2$, i.e. 1,1'-dimethyl-4,4'-bipyridyl cation, can be generated in three redox forms, as a result of the following equilibria:

$$MV^{2+} + e^- = MV^+$$

$$MV^+ + e^- = MV^0$$

The first reduction step is highly reversible. The further reduction to the fully reduced state is less reversible. Fig.4 is the differential pulse voltammogram (DPV) of $MVCl_2$ on a polished Ag electrode. We can see that for the first reduc-

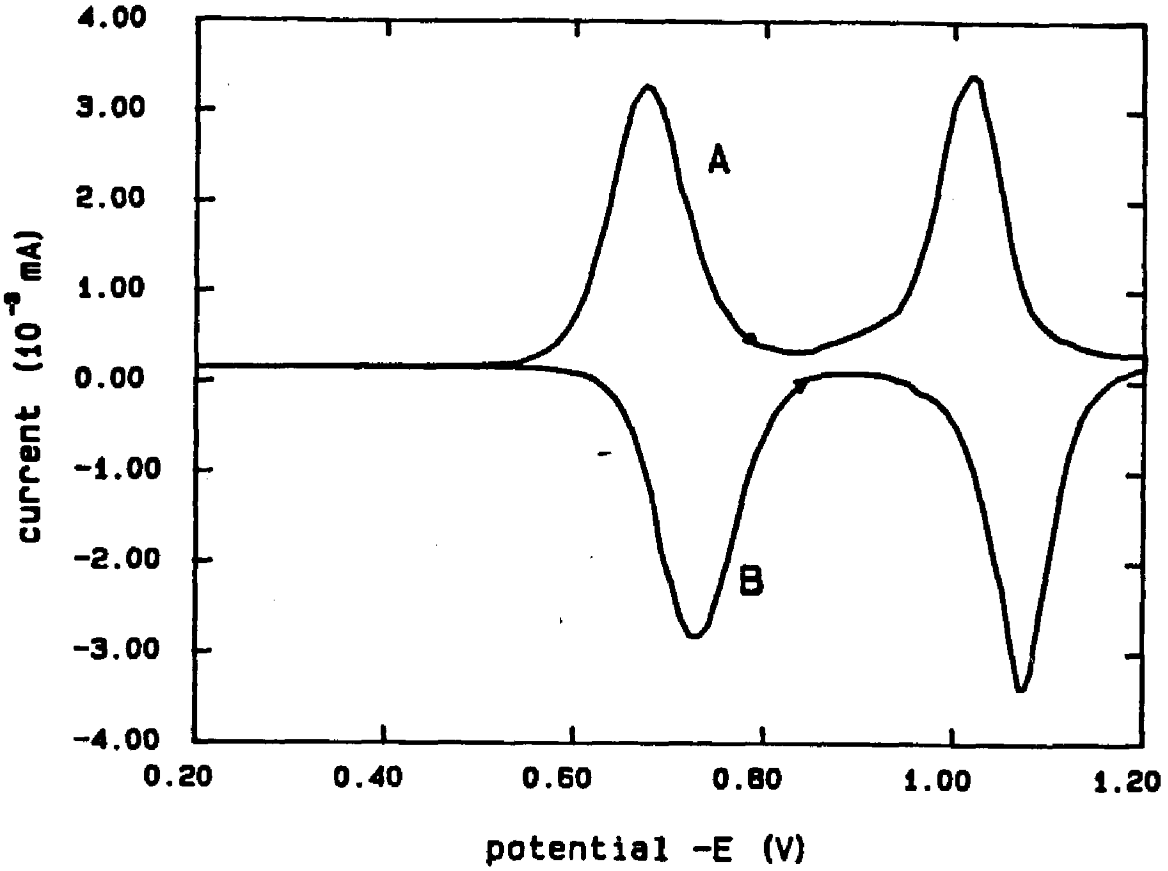


Fig.4. Differential pulse voltammogram of 10^{-3} M $MVCl_2$ in 0.1 M KCl on a polished Ag electrode: scan rate, 4 mV/s; pulse height, $|\Delta E| = 50$ mV; (A) cathodic pulse curve; (B) anodic pulse curve.

tion step the peak potential difference is equal to the pulse magnitude, $|\Delta E|$, and the peak current ratio is unity, i.e.,

$$E_p^c - E_p^a = |\Delta E|$$

$$|I_p^a / I_p^c| = 1$$

Thus, this step is reversible on polished Ag according to the DPV criteria of Birke et al. [342]. The second reduction step does not satisfy the above equations and is not reversible.

Generally, there are two reduction peaks in the cyclic voltammogram (CV) or DPV of MV^{2+}, however, after an ORC at the Ag electrode three peaks appear. Fig.5 is a cyclic voltammogram on the roughened Ag electrode. We can clearly see that there are three reduction peaks with a new reduction peak located at about -0.57 V. This prepeak was mentioned by Melendres [153] and attributed to the reduction of MV^{2+} with strong adsorption of the product of the cathodic reduction, i.e. MV^+ or a related species. The cyclic voltammogram (Fig.5) shows the prepeak discussed by Wopschall and Shain [343] indicating the reduction of dissolved MV^{2+} to adsorbed MV^+. However, after an ORC and thorough washing of the cell with 0.1 M KCl solution at -0.2 V, the CV curve shows that the two normal reduction peaks disappear, but the prepeak still exist with a peak potential at ca. -0.57 V. In addition, the SER spectrum of MV^{2+} at -0.2 V is still observed after washing. Thus MV^{2+} is irreversibly adsorbed on the roughened Ag electrode. It is apparent that the ORC stablizes the adsorption since without it the prepeak can not be seen. For the latter conditions the prepeak is due to the reduction of MV^{2+} adsorbed on sites which are produced by the ORC process. The reduction product, MV^+ or a related species, is adsorbed on the electrode more strongly than MV^{2+} because the potential of the prepeak is more positive than

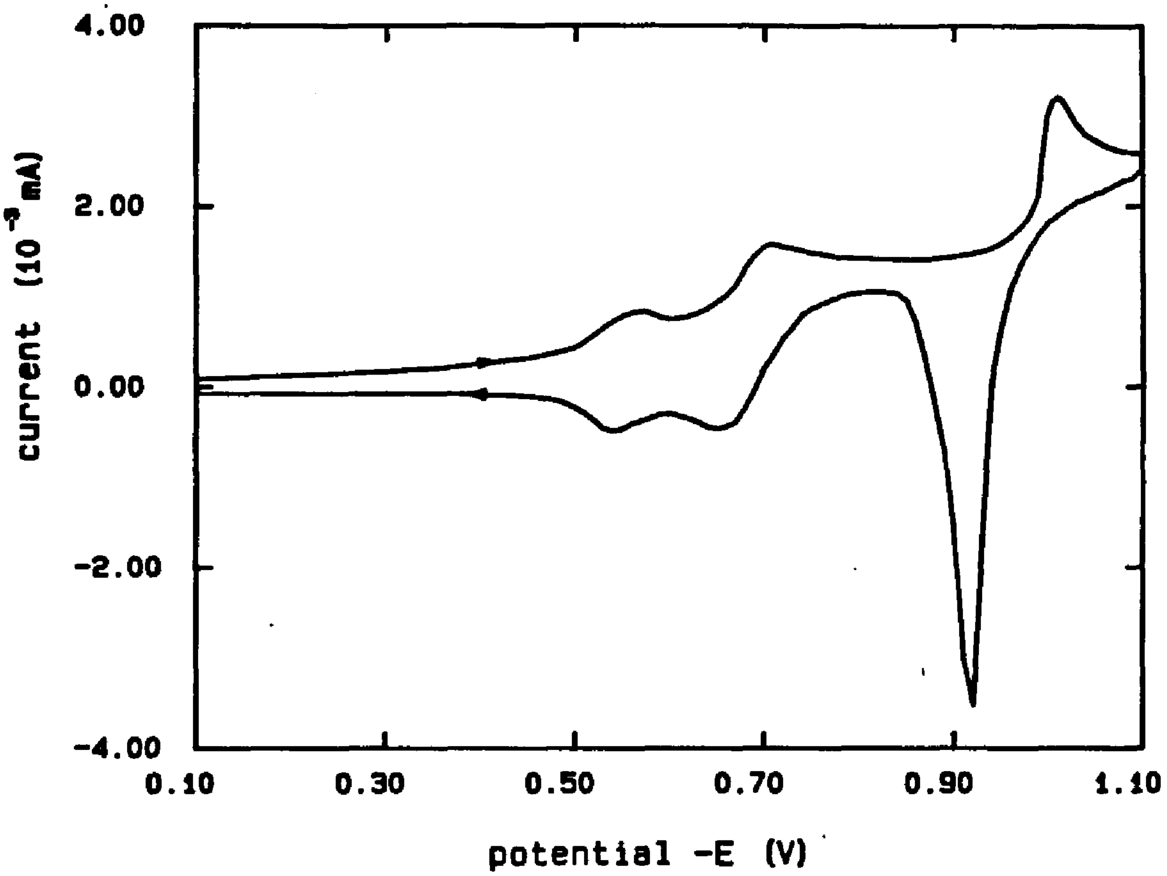


Fig.5. Cyclic voltammogram of 10^{-3} M MV^{2+} in 0.1 M KCl solution on the rough Ag electrode: scan rate, 4 mV/s.

that of the normal reduction peak of MV^{2+}. In addition, we can see that the third anodic peak is quite sharp suggesting that the fully reduced product is deposited on the electrode.

When a halide such as Cl^- or Br^- was used as supporting electrolyte some unusual electrochemical phenomena can be observed. Firstly, the prepeak in CV of $MVCl_2$ after an ORC is small comparing with bulk peaks (Fig.5), but it is much higher than bulk peaks in the DPV (Fig.6). When other supporting electrolytes not containing halide were used the prepeak was always smaller than bulk peaks in the CV or DPV after an ORC. Secondly, the prepeak in CV or DPV after an ORC actually consists of two small peaks when a halide was used as the supporting electrolyte (Fig.7). Fig.8A is the DPV after an ORC in 0.1 M KCl solution without $MVCl_2$. A small peak at about -0.57 V can be observed. If $MVCl_2$ is added into the solution after the ORC in 0.1 M KCl solution, two prepeak can be clearly observed in DPV and the second prepeak is at about -0.57 V (Fig.8B). If other electrolytes were used as the supporting electrolyte only one prepeak can be observed. These unusual electrochemical phenomena may be related to the specific adsorption of the halide. However, the mechanism of such unusual phenomena are not understood.

The electrochemical measurement at a roughened electrode is more difficult that that at a polished electrode because the electrochemical behavior on a roughened electrode is not stable. Fig.9 shows the DPV of $MVCl_2$ for potential scans of different times after the ORC. We can see that the peak current decreases with potential scan times very quickly.

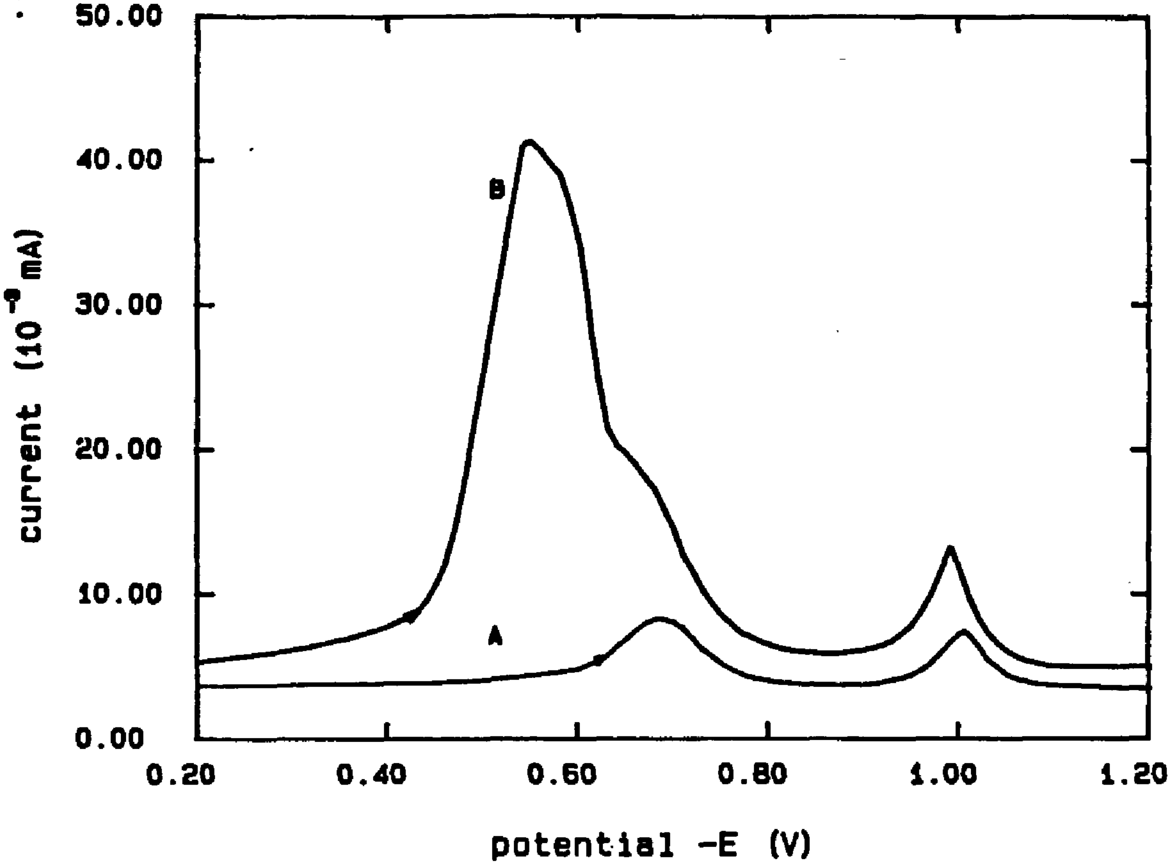


Fig.6. Differential pulse voltammogram of 10^{-3} M $MVCl_2$ in 0.1 M KCl on Ag electrodes: scan rate, 4 mV/s; pulse height, $|\Delta E| = 50$ mV; (A) on a polished Ag electrode; (B) on a roughened Ag electrode.

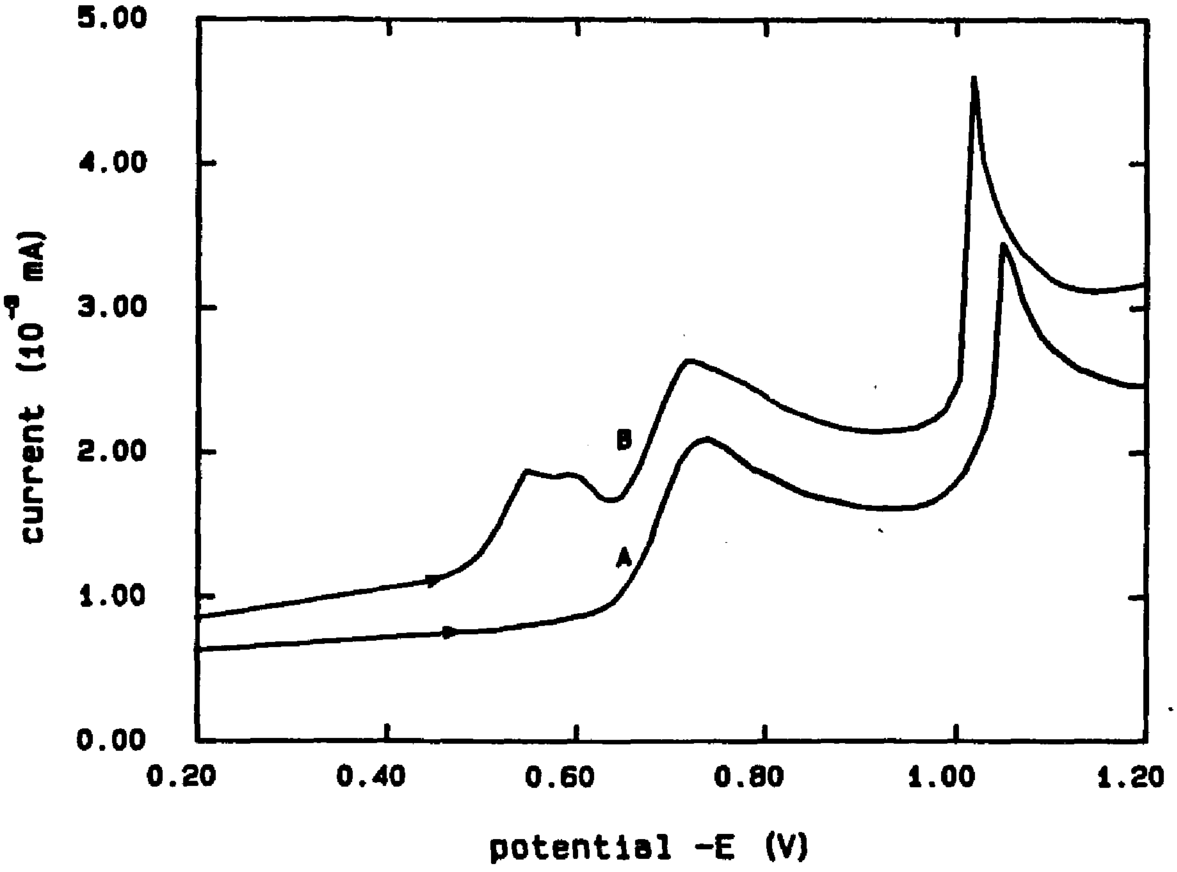


Fig.7. Linear sweep voltammogram of 10^{-3} M MV^{2+} in 0.1 M KCl solution on Ag electrodes : scan rate, 4 mV/s; (A) on a polished Ag electrode; (B) on a roughened Ag electrode.

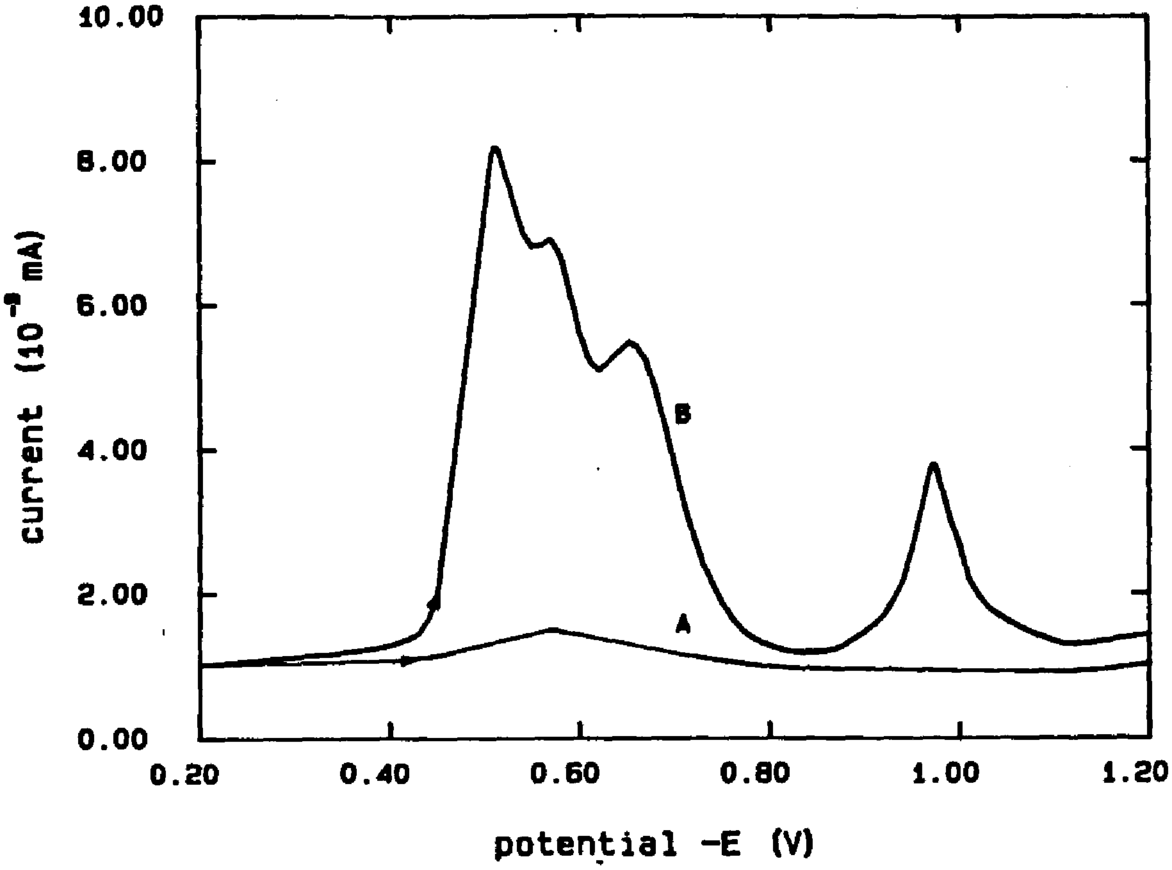


Fig.8. Differential pulse voltammogram of 0.1 M KCl solution with and without $MVCl_2$ on the roughened Ag electrodes: scan rate, 4 mV/s; pulse height, $|\Delta E| = 50$ mV; (A) without $MVCl_2$; (B) with $MVCl_2$ which was added after ORC in 0.1 M KCl.

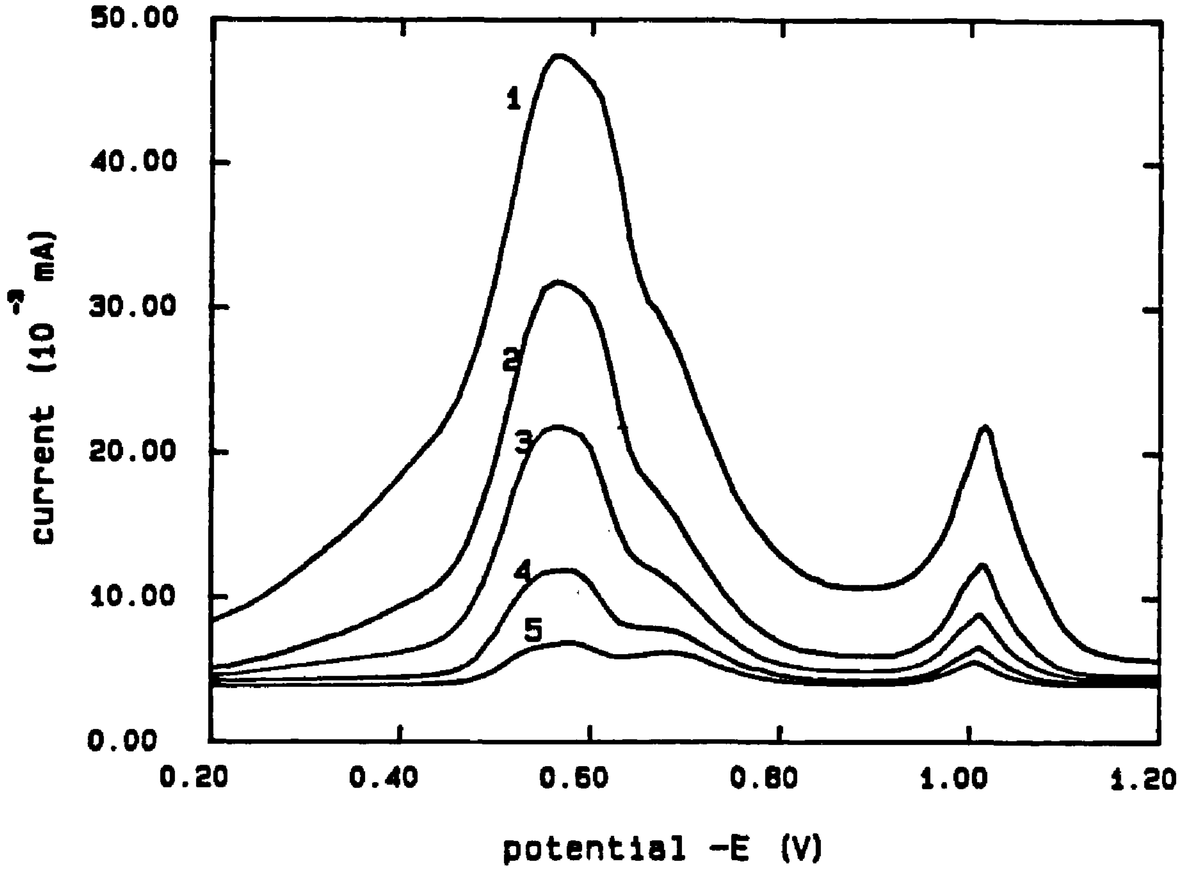


Fig.9. Differential pulse voltammograms of 10 M MVCl in 0.1 M KCl on a roughened Ag electrode: scan rate, 4 mV/s; pulse height, | E| = 50 mV; (1) the first scan, 6 minutes after ORC; (2) the second scan, 12 minutes after ORC; (3) the fourth scan, 24 minutes after ORC; (4) the sixth scan, 36 minutes after ORC; (5) the eighth scan, 48 minutes after ORC.

3-2-2. Electrochemistry of 4,4'-bipyridine

The electrochemistry of 4,4'-BP at a Hg electrode has been well studied [344-348]. These studies indicated that the electrochemical reduction of 4,4'-BP in the aqueous solution is pH-dependent, because 4,4'-BP can be protonated:

$4,4'\text{-BP} + H^+ = 4,4'\text{-BPH}^+$

$4,4'\text{-BPH}^+ + H^+ = 4,4'\text{-BPH}_2{}^{2+}$

Musgrave and Mattson [331] gave the acid dissociation constants of the protonated 4,4'-BP:

$pK_1 = 3.5$

$pK_2 = 4.9$

In the acidic solution (pH <2) 4,4'-BP is reduced in two one-electronic steps:

$4,4'\text{-BPH}_2{}^{2+} + e^- = 4,4'\text{-BPH}_2{}^{+\cdot}$

$4,4'\text{-BPH}_2{}^{+\cdot} + e^e = 4,4'\text{-BPH}_2$

Therefore, two reduction peaks in CV can be observed. The cation radical dissolves in solution and has intense blue color. However, in the basic solution (pH > 11) only one reduction peak was observed. Thus, Musgrave and Mattson [331] considered that 4,4'-BP reduction in the basic solution takes place in another manner: a single two-electronic step. Volke and Volkova [348] suggested a possible mechanism:

$4,4'\text{-BP} + 2e^- = 4,4\text{-BP}^{2-}$

$4,4'\text{-BP}^{2-} + 2H_2O = 4,4'\text{-BPH}_2 + 2OH^-$

We studied the electrochemistry of 4,4'-BP at polished and roughened Ag electrodes. The behavior of 4,4'-BP at a polished Ag electrode is similar to that at a Hg electrode. When the solution is acidic (pH = 1.8), the first one-electronic reduction peak is at about -0.68 V in CV. The blue color of the radicals in the solution can be observed, when the electrode potential was hold at about -0.7 V. The second reduction peak can not be observed because of the reduction of hydrogen. When the solution is basic (pH = 12), only a two-electronic reduction peak at about -1.40 V appeared and no color in the solution can be observed.

When the roughened Ag electrode was used the situation is somewhat different. If the solution was acidic (pH = 1.8), the first one-electron reduction peak in the CV was at about -0.48 V which is -0.2 V more positive than that on the polished Ag electrode. The second one-electron reduction peak can not be observed also due to the reduction of hydrogen. If the solution is basic (pH = 12), two reduction peaks in the CV can be observed (Fig.10). The first reduction peak is at about -1.23 V and the second at about -1.42 V.

For the first reduction peak the peak current was found to be proportional to the scan rate and the anodic and cathodic peak currents in the CV were equal. Although there was a difference between anodization and reduction peak potentials in the CV (Fig.10), it was due to the solution resistance because the difference became very small when the scan rate was slow. In addition, according to [349]

$$i_{pr} = n\upsilon QF/4RT$$

and we found n = 2.02,

where

n is electron number per molecule reduced

i_{pr} is reduction peak current,

υ is the scan rate of potential,

Q is the charge associated with the reduction of adsorbed molecules and represented by the area under the reduction peak.

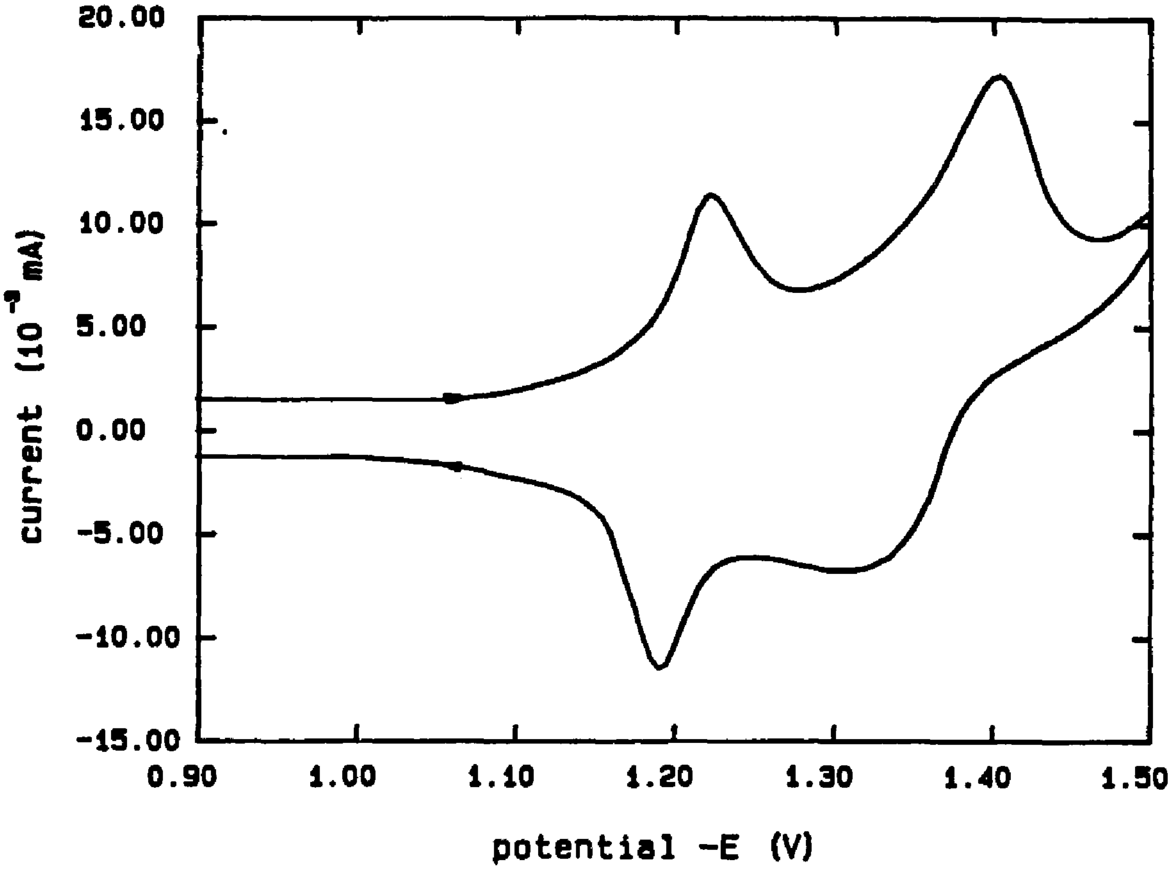


Fig.10. Cyclic voltammogram of 10^{-3} M 4,4'-bipyridine in 0.1 M KCl solution on the roughened Ag electrode: scan rate, 50 mV/s.

(The area must be corrected for the current due to the second reduction peak because the two peaks are partially superimposed.)

For the second reduction peak the peak current was proportional to the square root of the scan rate of potential. If the cell was washed with 0.1 M KCl solution, the second peak disappeared and only the first peak was still observed. Therefore, we consider that the first reduction peak was due to the two-electron, reversible reduction of adsorbed 4,4'-BP molecules and the second reduction peak was due to the reduction of diffusing bulk molecules.

Usually, a pH 6.5 solution was used for SER study. The CV of 4,4'-BP at a roughened Ag electrode in pH 6.5 solution was similar to that in pH 12 solution because most of 4,4'-BP molecules were still not protonated at pH 6.5 ($pK_2 = 4.9$).

Volke and Volkova [348] suggested a single two-electronic mechanism for the reduction of 4,4'-BP in the basic solution on Hg. However, the Raman bands due to the 4,4'-BP radical were still observed on the roughened Ag electrode at potentials more negative than -1.2 V in the basic solution (This will be discussed in detail in the later section). Therefore, we suggest that the electrochemical reduction of 4,4'-BP in the basic solution on Ag still passes through the radical step. Generally, the radicals are so unstable that they are immediately reduced to the fully reduced 4,4'-BP and they can not be detected. However, on the roughened Ag electrode they can be detected by the SER technique.

3-2-3. Conclusion

The electrochemistry of $MVCl_2$ and 4,4'-BP was studied on both a polished and roughened Ag electrode. The electrochemical behavior of the two compounds on the polished Ag electrode is similar to that on the Hg electrode. However, the electrochemistry of these compounds on the roughened Ag electrode differs from that on the polished Ag electrode in the following ways:

(a) The reduction potentials of bulk molecules on the roughened Ag electrode are slightly different from those on the polished Ag electrode. For example, the two reduction peaks of bulk $MVCl_2$ on the polished Ag electrode in the CV are -0.73 and -1.04 V respectively, they are -0.71 and -1.01 V on the roughened Ag electrode.

(b) Reduction peaks for adsorbed $MVCl_2$ and 4,4'-BP on the roughened Ag electrode were observed in the CV or DPV. It is apparent that the ORC can stablize the adsorption since the adsorption peak can not be seen on the polished Ag electrode.

(c) The unstable intermediate can be detected on the roughened Ag electrode. It was considered previously that the 4,4'-BP in the basic solution can be electrochemically reduced in a single two-electronic step because the 4,4'-BP radical can not be detected on smooth electrodes. However, it was detected on the roughened Ag electrode because SER scattering is very sensitive on a roughened Ag electrode. Thus, a two one-electron step mechanism for the electrochemical reduction of 4,4'-BP on Ag in the basic solution can be suggested.

(d) The electrochemical measurement on a roughened Ag electrode is difficult because the electrochemical behavior on a roughened Ag electrode is not stable.

3-3. SER spectra of the three redox forms of methylviologen

3-3-1. SER spectrum of MV^{2+}

After an ORC of the Ag electrode the Raman spectrum of 1.0×10^{-3} M

$MVCl_2$ in 0.1 M KCl was taken on the roughened Ag electrode at -0.2 V. The results are similar to those reported by Regis and Corset [151]. For comparison with MV^+ and MV^0, the bands observed for MV^{2+} are listed in Table 1. Fig.11 shows the NR spectra of solid and solution of $MVCl_2$ and the surface Raman spectrum of $MVCl_2$ on the roughened Ag electrode at -0.2 V. Typical of most SER spectra of colorless molecules, these bands do not show large changes from the normal Raman spectrum of MV^{2+} in solution except for slight wavenumber shifts in band positions and changes in the relative intensities of some bands. From the electrochemistry we know that MV^{2+} is not reduced at -0.2 V. In addition, after the cell was washed in situ with 0.1 M KCl solution the spectrum did not change. These experiments illustrated that the Raman spectrum of $MVCl_2$ on the roughened Ag electrode at -0.2 V is the SER spectrum due to the MV^{2+} irreversibly adsorbed on the electrode surface.

3-3-2. Nature of surface Raman spectra of MV^+

When the solution of $MVCl_2$ is reduced at -0.8 V, the MV^+ radical is obtained and a blue color is produced at the electrode surface. Fig.12A is the RR spectrum of MV^+ obtained at a polished Pt electrode. The bands observed and their assignments are listed in Table 1. The vibrational modes are described by Wilson for the parent benzene ring [350] and by Kohlrausch for substituted benzenes [351]. These bands are nearly identical to those seen in the solution RR spectrum of MV^+ prepared by chemical reduction with $Na_2S_2O_4$ [340]. Normally it is difficult to obtain the RR spectrum of a colored species at a nonenhancing electrode surface if other RR active species are in the bulk. In the present case, the only RR active species is MV^+ which is produced at the electrode surface by the reduction reac-

Table 1

Raman lines of methylviologen and their assignment

SER lines of MV^{+2} (cm^{-1})	SER lines of MV^{+} (cm^{-1})	RR lines of MV^{+} (cm^{-1})	SER lines of MV^{0} (cm^{-1})	normal Raman lines of MV^{0} (cm^{-1})	assignment
240(vs)					Ag-Cl
280(m)	280(w)		282(w)		c
410(w)	360(w)		340(w)		16a
560(w)	550(w)		546(w)		16b
653(w)	618(w)		612(w)		6b
674(w)	678(w)		676(w)		d^{*}
			742(s)		
	790(s)	818(w)	794(w)		11
840(s)					d
1034(w)	1008(s)	1026(s)	996(s)	992(s)	17a
1054(w)					18b
1188(s)	1190(m)		1208(w)		9a
1238(m)	1236(s)	1212(w)	1240(s)		1/12
1292(s)	1352(m)	1350(m)	1380(w)		w_1
1480(w)	1506(m)		1512(s)		19b
1520(w)		1530(s)		1538(s)	19a
1573(w)	1592(s)		1612(s)		8b
1638(s)		1656(m)		1656(m)	8a
				1668(w)	

Table 2

The overtone and combination lines of RR lines of MV^{+}

frequencies of lines in Fig.6-A (cm^{-1})	frequencies of possible overtone or combination lines of RR lines (cm^{-1})
2050	2052 (1026 + 1026)
2376	2376 (1026 + 1350)
2532	2556 (1026 + 1530)
2556	2562 (1212 + 1350)
2682	2682 (1026 + 1656)
	2700 (1350 + 1350)
2870	2868 (1212 + 1656)
	2880 (1350 + 1530)
3014	3006 (1350 + 1656)
3060	3060 (1530 + 1530)

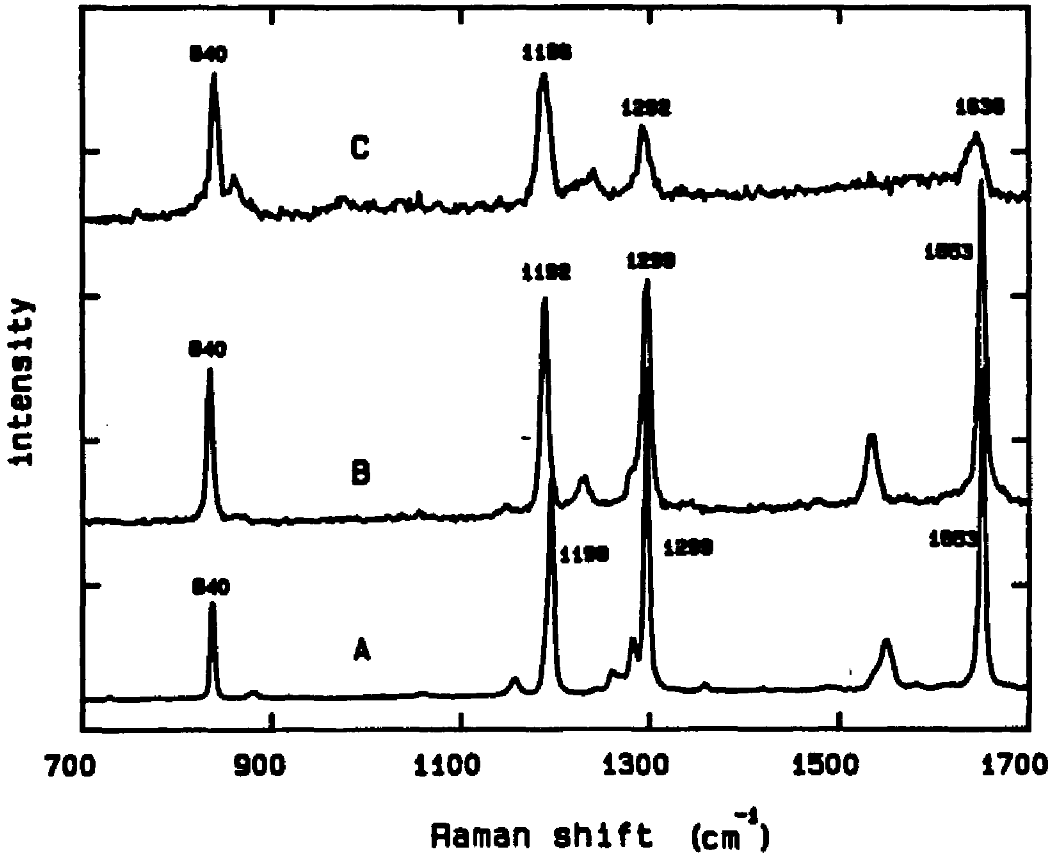


Fig.11. Raman spectra of MVCl : 488-nm argon laser light, 200 mw for A and B, 20 mw for C; (A) NR spectrum of $MVCl_2$ solid; (B) NR spectrum of $MVCl_2$ solution; (C) SER spectrum of 10^{-3} M $MVCl_2$ in 0.1 M KCl on the roughened Ag electrode.

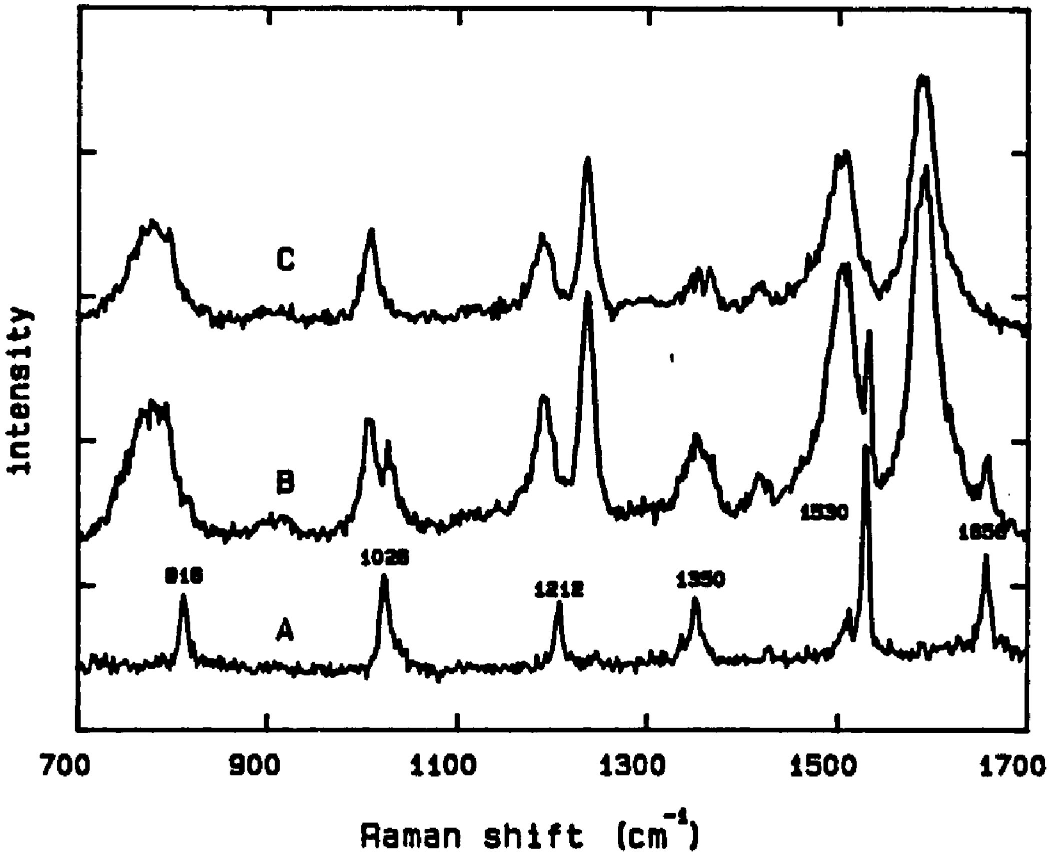


Fig.12. Raman spectra of MV^{+}: 488-nm argon laser light, 100 mw for A, 10 mw for B and C; (A) RR spectrum of MV^{+} on a polished Pt electrode at -0.8 V; (B) surface Raman spectrum of MV^{+} on a roughened Ag electrode at -0.8 V before washing the cell with 0.1 M KCl; (C) after washing.

tion, and the RR spectrum of MV^+ in the diffusion layer is easily obtained.

Fig.12B is the Raman spectrum of $MVCl_2$ on a roughened Ag electrode at -0.8 V, at which MV^{2+} is reduced to the MV^+ radical. After taking this spectrum the cell was carefully washed in situ with 0.1 M KCl solution. During the washing the potential was kept at -0.8 V. Then the spectrum was taken again (Fig.12C). It is seen that the spectrum before washing is different from that after washing with some bands being lost after washing. The lost bands are exactly the same as those found in the RR spectrum of the MV^+ radical (Fig.12A). Thus, it is clear that the spectrum of $MVCl_2$ on the roughened Ag electrode is the superposition of the RR spectrum of MV^+ in the solution near the electrode surface and the surface Raman spectrum of MV^+ on the electrode surface. Melendres et al.[153] reported both sets of bands in the same spectrum, indicating the likelihood that they were observing an overlap of both spectra.

The observed surface Raman spectrum of the irreversibly adsorbed species is quite different from the solution RR spectrum showing strong to medium strength bands at 790(s), 1008(s), 1190(m), 1236(s), 1352(m), 1506(m) and 1592(s) cm^{-1} while major bands of the RR spectrum of the solution species appear at 1026(s), 1350(m), 1530(s) and 1656(m) cm^{-1} (Table 1). Only the 1350 cm^{-1} band is common to the two spectra. These large changes in bands position make it obvious that the surface Raman spectrum is not a SERR scattering of an adsorbed MV^+ radical monomer. The SERR scattering is a RR process additionally enhanced by an electromagnetic effect. In this case one would expect more of a correspondence in the observed band positions of SERR and solution RR spectra. Other possibilities are that the surface spectrum is the SER scattering of a chemisorbed monomer MV^+ species exhibiting a combined charge transfer and electromagnetic enhancement or either SER scattering or SERR scattering originating from a chemisorbed dimer MV^+ [352] or a polymer MV^+ species [335]. For the reasons indicated below, we believe that the surface spectrum originates from the SER scattering of the monomer.

Landrum et al. [335] indicated that the polymer film of MV^+ radical can be formed by electrochemical means under conditions which, however, are different from the present case. The prominent characteristic of this polymer film is its stability with respect to the application of an electrode potential between +0.50 and -0.95 V vs. Ag|AgCl. Our experiments show that the MV^+ species on the surface of a roughened Ag electrode is not stable in the above potential range. For example, after taking the spectrum at -0.8 V, if the potential is returned to -0.2 V, the SER spectrum of MV^{2+} can be observed again. This procedure can be repeated many times and the same spectra appear (only the intensity is lowered). In addition, the reduction peak at about -0.57 V in the CV can be still observed. Thus the polymer film of Landrum et al. is not formed on the surface of the roughened Ag electrode under the our experimental condition and the surface Raman spectrum is not due to the polymer of the MV^+ radical. On the basis of the CV curves for this system, Melendres et al. reached a similar conclusion [153].

Ohsawa et al.[339] reported the RR spectrum of MV^+ and its dimer and indicated that only two weak bands at 1513 and 1340 cm^{-1} can be assigned to the dimer. Since these dimer bands are not observed in the surface Raman spectrum mentioned above, it is not due to the RR effect of the dimer of the MV^+ radical.

Additional experiments support the conclusion that the surface Raman spectrum is due to the typical SER effect. For example, if a polished Ag electrode or Pt electrode is used, only the RR spectrum can be observed, and the surface Raman spectrum only develops after an ORC pretreatment on Ag which is typical SER scattering behavior.

Further evidence that the surface Raman spectrum is due to the SER effect is obtained by observing the overtone or combination bands. We observe bands in the 2040-3064 cm^{-1} region on the roughened Ag electrode at -0.8 V before washing the cell with 0.1 M KCl solution, but most of the bands disappear after washing. The frequencies of those bands which disappear correspond to overtone or combination bands of the RR spectrum (Table 2). They are around 5% bands of the intensity of the fundamentals. The question arises as to whether or not overtones are observed in a SER spectrum. The only specific report of the observation of overtones in a SER spectrum is that by Pettinger[257]. However as far as we can tell their intensities are less than 1% of the fundamentals. Since in the theory of RR spectroscopy relative intensities depend only on relative Franck-Condon factors, there is no particular restriction on the intensities of overtones. In principal an overtone could even be more intense than a fundamental. However in NR spectroscopy, as well as the charge transfer theories of SER spectroscopy based on Herzberg-Teller scatting [325] the relative intensities come from terms involving the normal IR matrix elements. In the harmonic oscillator approximation, one predicts zero intensity for overtones and combinations. However, if anharmonic corrections are included one expects some intensity in overtones and combination bands for NR and SER spectroscopy. The larger the anharmonic correction, the greater would be the overtone intensity. Note for MV^+ the overtones are almost exactly twice the fundamental frequencies (Table 2) which indicates only slight anharmonicity. Thus, we would expect almost no intensity of overtone or combination bands in the SER spectrum, and these bands can be considered as the overtone or combination bands of RR bands. This is consistent with the theoretical prediction given by Adrian [323], and more recently by Lombardi et al. [325].

The SER scattering may, in fact, be due to the MV^+ radical monomer or a dimer which is in equilibrium with the monomer. However, when the surface Raman spectra were taken for different concentrations of $MVCl_2$ in solution, it was noted that the relative intensities of the bands in the surface Raman spectra did not change with respect to each other as the $MVCl_2$ solution concentration was varied from 5×10^{-7} M to 10^{-2} M. One would expect some change with concentration if a dimer species was the source of SER scattering.

The question arises as to why the surface Raman spectrum is very different from the RR spectrum. Efrima [206] indicated that the interaction between adsorbed molecule and the metal can lead to a shift in molecular states, i.e. a nonchromophric molecules can be "pushed" into resonance and exhibit SER scattering, and a chromophoric molecules can, on the other hand, be "pushed" out of resonance. The MV^+ radical may be a good example of the later situation. Therefore, the surface Raman spectrum is very different from the RR spectrum. In fact, the SER spectrum may be similar to the solution NR of MV^+, however, the strong absorption of the colored MV^+ throughout the visible region prevents the observation of an off resonance spectrum.

The surface Raman band assignments of MV^+ are listed in Table 1. The following observations should be mentioned:

(a) We observed the characteristic shift of the 1292 cm^{-1} band of MV^{2+} to 1350 cm^{-1} for MV^+. This band is attributed to the C4-C4' stretch. As shown by Dewar and Trinajstic [353] the lowest unoccupied molecular orbital in biphenyl,

ϕ_7, contains considerable electron density in this bridging carbon-carbon bond, thus accounting for the sizeable upward shift in frequency. These results have also been observed by Takahashi and Maeda [354] in biphenyl.

(b) The assignment of other bands is of some dispute. Lee et al. [340] give their 818 cm^{-1} band the same assignment as the 840 cm^{-1} band in MV^{2+} (d mode, principally C-C-C bend [355]). On other hand Regis and Corset [151] assign their 1027 cm^{-1} band to the same vibrational mode as the 840 cm^{-1} band in MV^{2+}. This latter assignment is unlikely for such a large shift (about 180 cm^{-1}) in a C-C-C bending motion could not be so strongly affected by addition of an electron to the ϕ_7 orbital where most of the additional electron density is added perpendicular to the molecular plane. On this basis we tend to agree with the assignment of Lee et al. [340].

(c) Regis and Corset [151] did not observe some bands, such as the strong SER bands at 790, 1008, 1506 and 1592 cm^{-1}. By means of the assignment of bands from $MVCl_2$ solution by Regis and Corset [151] and the assignment of SER bands of pyridine by Fleischmann and Hill [356], the 790 cm^{-1} SER band is assigned to υ_{11}, the 1008 cm^{-1} SER band is given the same assignment as the 1026 cm^{-1} RR band, (υ_{17a}), the 1506 cm^{-1} SER band is assigned to υ_{19b} and the 1592 cm^{-1} SER band to υ_{8b}.

In addition, the following phenomena are worth mentioning. Generally, an ORC at the Ag electrode was applied by a double potential step: -0.2 V to +0.3 V to -0.2 V. When the potential was adjusted to -0.8 V and the Raman spectrum of MV^+ was taken, we found that the relative intensity of the SER and RR bands in the spectrum of MV^+ changed with the duration time, $t_{-0.2}$ for which the electrode is held at -0.2 V after ORC. The shorter $t_{-0.2}$ is, the weaker the surface Raman bands are. This phenomenon is caused by two factors. First, the development of the intensity of SER bands of MV^{2+} after ORC is a slow process. The intensity quickly reaches about 50% of the maximum in about 10 s after ORC, and then, it slowly rises to a maximum in approximately 10 minutes. Secondly, after the electrode potential is adjusted to -0.8 V, the intensity of SER bands do not increase any more. This means that the Raman-active adsorbed MV^{+} can be obtained only by reduction of adsorbed MV^{2+} and are not formed directly from MV^{+} in the solution.

3-3-3. Raman spectrum of MV^{0}

In Fig.13A we show the Raman spectrum of $MVCl_2$ on a polished Ag electrode at -1.2 V. We believe this spectrum to be the NR spectrum of an MV^{0} polymer film formed on the polished Ag electrode, because under these conditions a barely visible transparent layer of material is observed to be coated on the surface of the Ag electrode. This observation is consistent with the electrochemical results (Fig.5).

Fig.13B is the Raman spectrum of MV^{0} on a roughened Ag electrode at -1.2 V. Similar to the situation of MV^{+}, this spectrum consists of two kinds of bands: SER bands of MV^{0} adsorbed on the electrode surface and NR bands of the MV^{0} polymer. If we wash the cell with 0.1 M KCl solution at -0.8 V, only the adsorbed MV^{+} species is left on the surface of the roughened Ag electrode. On adjusting the potential to -1.2 V, the SER spectrum of MV^{0} (Fig.13C) is obtained. There are no NR bands of the MV^{0} polymer in this spectrum, and the SER bands of MV^{0} are not very stable. Their intensities decrease with time and they almost disappear in about one hour.

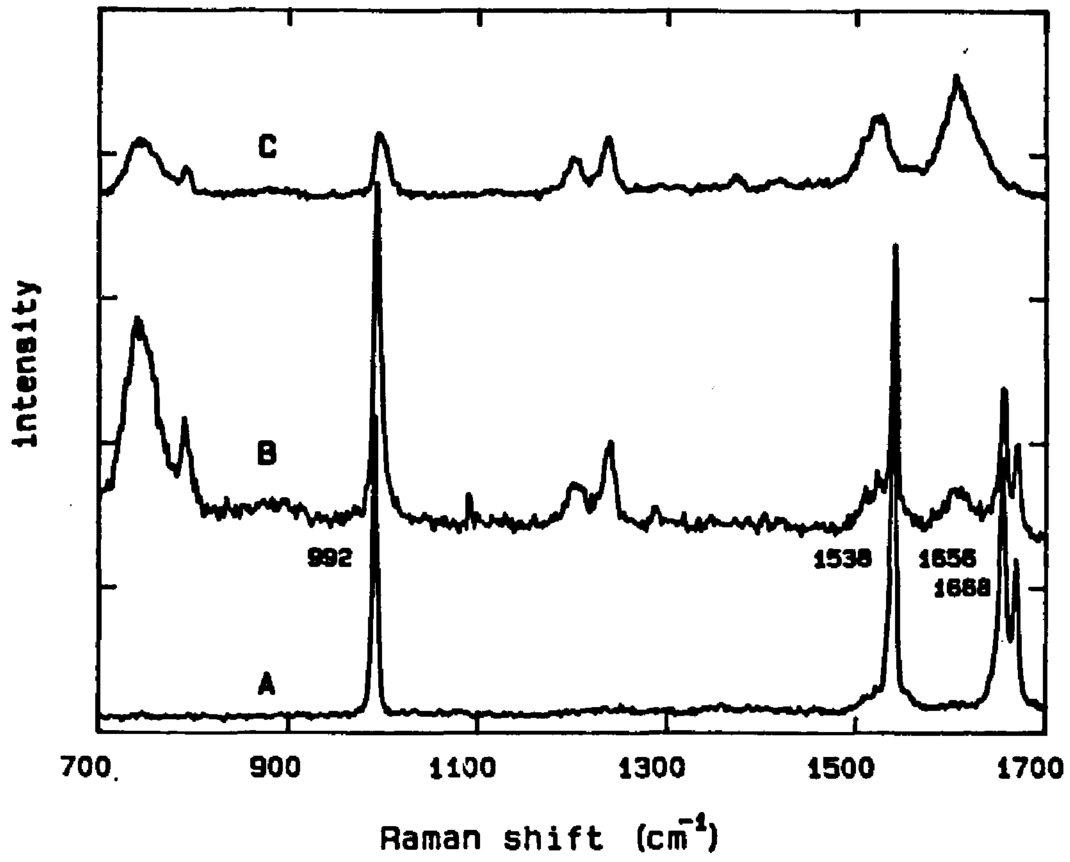


Fig.13. Raman spectra of MV^0 on Ag electrodes at −1.2 V: 488-nm argon laser light, 100 mw for A, 10 mw for B and C; (A) NR spectrum of MV^0 on a polished Ag electrode; (B) surface Raman spectrum of MV^0 on a roughened Ag electrode before washing the cell with 0.1 M KCl; (C) after washing the cell with 0.1 M KCl at −0.8 V, then adjusting the potential to −1.2 V.

The SER and NR bands of MV^0 observed are listed in Table 1 (P.58). In the SER spectrum of MV^0 no band is seen at 1292 or 1350 cm^{-1} but instead a band is observed at 1380 cm^{-1}. Most likely the bridge carbon-carbon stretch at 1352 cm^{-1} for MV^+ has been shifted to still higher frequency when a second electron is added to the ϕ_7 orbital. The second electron will not have as large an effect as the first (1292 cm^{-1} for MV^{2+} shifts to 1352 cm^{-1} for MV^+) due to electron-electron repulsions which will tend not to allow a simple doubling of the electron density buildup in this bond.

There is a band at 996 cm^{-1} in the SER spectrum of MV^0 which is analogous to the band 1008 cm^{-1} for MV^+ and the 1034 cm^{-1} band for MV^{2+}. The decrease in frequency on adding an electron is consistent since this vibration does not involve a stretching motion of the bridge carbons. Instead it arises from the out-of-plane bending motion of the ring carbon atoms. The lowest unoccupied molecular orbital ϕ_7 has a number of nodes which cross several carbon-carbon bonds. Thus addition of an electron to this orbital would result in a slight weakening of those bonds and consequently a slight decrease in frequency.

A strong band at 744 cm^{-1} in the SER spectrum of MV^0 is also seen. This corresponds to the 741 cm^{-1} band in biphenyl. However, the assignment is not certain. In addition, we are not certain of the assignment of the 1668 cm^{-1} band.

Similar to the situation of MV^+, when we use the double potential step: -0.2 V to +0.3 V to -1.2 V in an ORC without pausing at -0.2 V, the intensities of the SER bands of MV^0 are weaker. This means that the SER spectrum of MV^0 is only due to the adsorbed MV^0 species which can be obtained only by reduction of adsorbed MV^{2+} or MV^+.

From the above analysis we obtained the real SER spectra of three redox

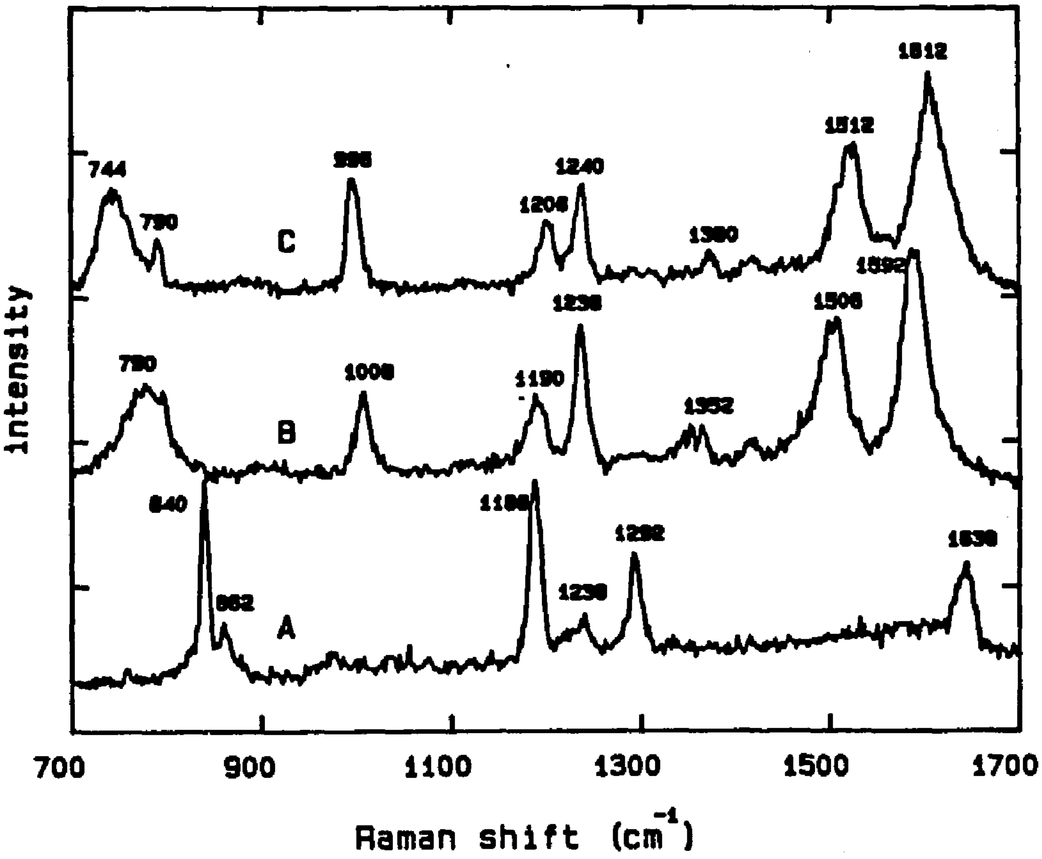


Fig.14. SER spectra of three redox forms of $MVCl_2$ on the roughened Ag electrodes: 488-nm argon laser light, 10 mw; (A) MV^{2+}, at -0.2 V; (B) MV^{+}, at -0.8 V; (C) MV^{0}, at -1.2 V.

forms of $MVCl_2$: MV^{2+}, MV^{+} and MV^{0} (Fig.14).

3-3-4. Photoelectrolysis of methylviologen

On comparing the SER spectrum of MV^{+} (Fig.15C) for which a 488 nm argon laser light (20 mW) is used as an excitation source with the spectrum (Fig.15B) for which a yellow or red dye laser light (20 mW) or low power (less than 10 mW) 488 nm excitation is used, some differences are observed between the two spectra. For example;

(a) There is no 1292 cm^{-1} band in Fig.15B, instead the 1350 cm^{-1} band appears as mentioned above. A strong 1292 cm^{-1} band is observed in Fig.15C.

(b) A 768 cm^{-1} band is observed in Fig.15C.

(c) The 1592 cm^{-1} band in Fig.15B shifts to 1604 cm^{-1} in Fig.15C.

We find that the 768, 1292 and 1604 cm^{-1} are characteristic bands for the SER spectrum of 4,4'-BP (Fig.15A). These phenomena seem to indicate that a demethylation reaction has taken place on the surface when the 488 nm laser light at higher power is used, and that there is an apparent threshhold for the process. These observations of surface photochemistry are of sufficient interest to warrant further study.

3-3-5. Conclusion

The surface Raman spectroscopy of the three redox forms of $MVCl_2$ was studied on a roughened Ag electrode. The surface Raman spectrum of the monoradical cation of methylviologen on the roughened Ag electrode at -0.8 V was found to be a superposition of the SER spectrum of the adsorbed radical and the RR spectrum of the dissolved radical. These two kinds of Raman spectra can be clear-

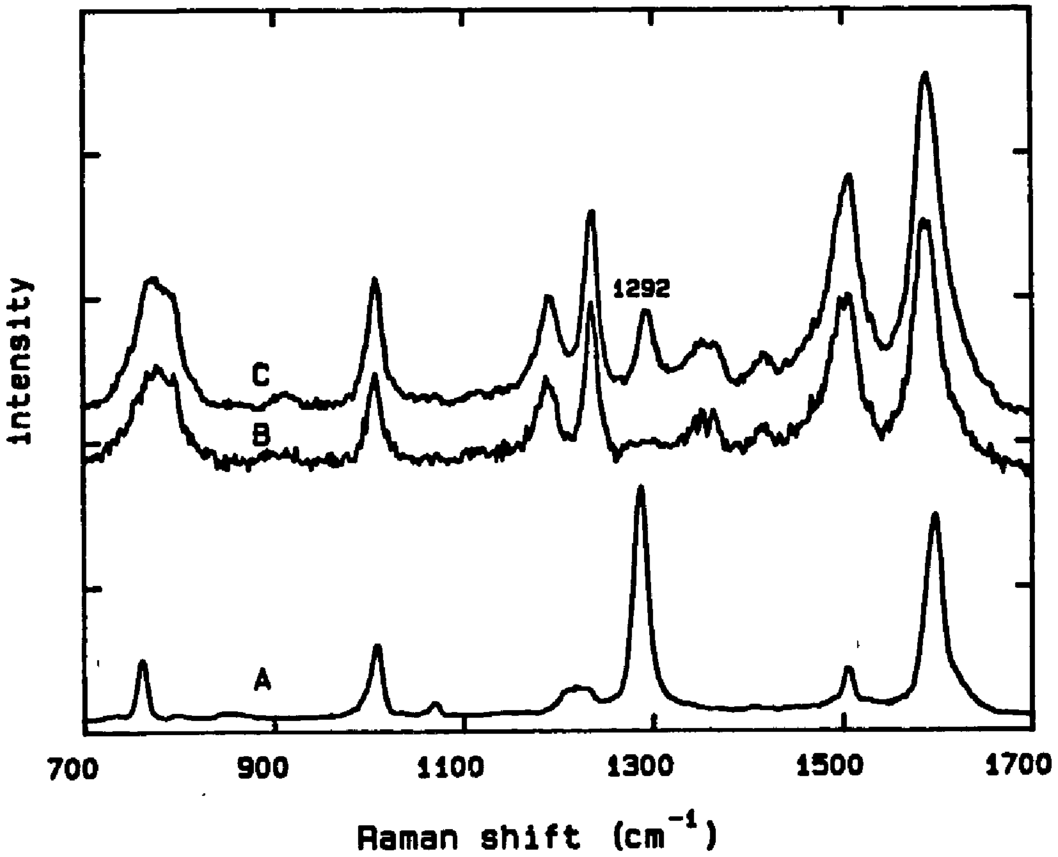


Fig.15. SER spectra of MV$^+$ and 4,4'-bipyridine on the roughened Ag electrodes at -0.8 V: (A) 4,4'-bipyridine, 488-nm argon laser light, 20 mw; (B) MV$^+$, 585-nm dye laser light, 20 mw; (C) MV$^+$, 488-nm argon laser light, 20 mw.

ly separated. The SER spectrum of the adsorbed radical is totally different from the RR spectrum of the dissolved radical. This is because the interaction between adsorbed molecules and the metal lead to a shift in molecular states, i.e. the chromophoric methylviologen radical is pushed out of resonance when it is adsorbed on the roughened Ag electrode. This is the good evidence for the charge transfer mechanism of SER scattering. Similarly, the surface Raman spectrum of the fully reduced methylviologen on the roughened Ag electrode at -1.2 V is the superposition of the SER spectrum of adsorbed MV^0 and the NR spectrum of the coated MV^0. In addition, a demethylation reaction on the roughened Ag electrode was found when the 488 nm laser light with higher power is used.

3-4. SER spectra of three redox forms of 4,4'-BP

3-4-1. SER spectra of 4,4'-BP molecule

After an ORC of the Ag electrode the surface Raman spectrum of 10^{-3} M 4,4'-BP in 0.1 M KCl was taken on the roughened Ag electrode at -0.2 V (Fig.16C). Typical of most SER spectra of colorless molecules, the surface Raman spectrum is similar to the NR spectra of solid and solution of 4,4'-BP (Fig.16A and 16B) except for slight wavenumber shifts in band position and changes in the relative intensities of some bands. From the electrochemistry we know that 4,4'-BP is not reduced at -0.2 V. In addition, after the cell was washed in situ with 0.1 M KCl solution the spectrum did not change. The intensity after washing was comparable to that before washing. These experiments illustrate that the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at -0.2 V is the SER spectrum due to the irreversibly adsorbed species on the electrode surface.

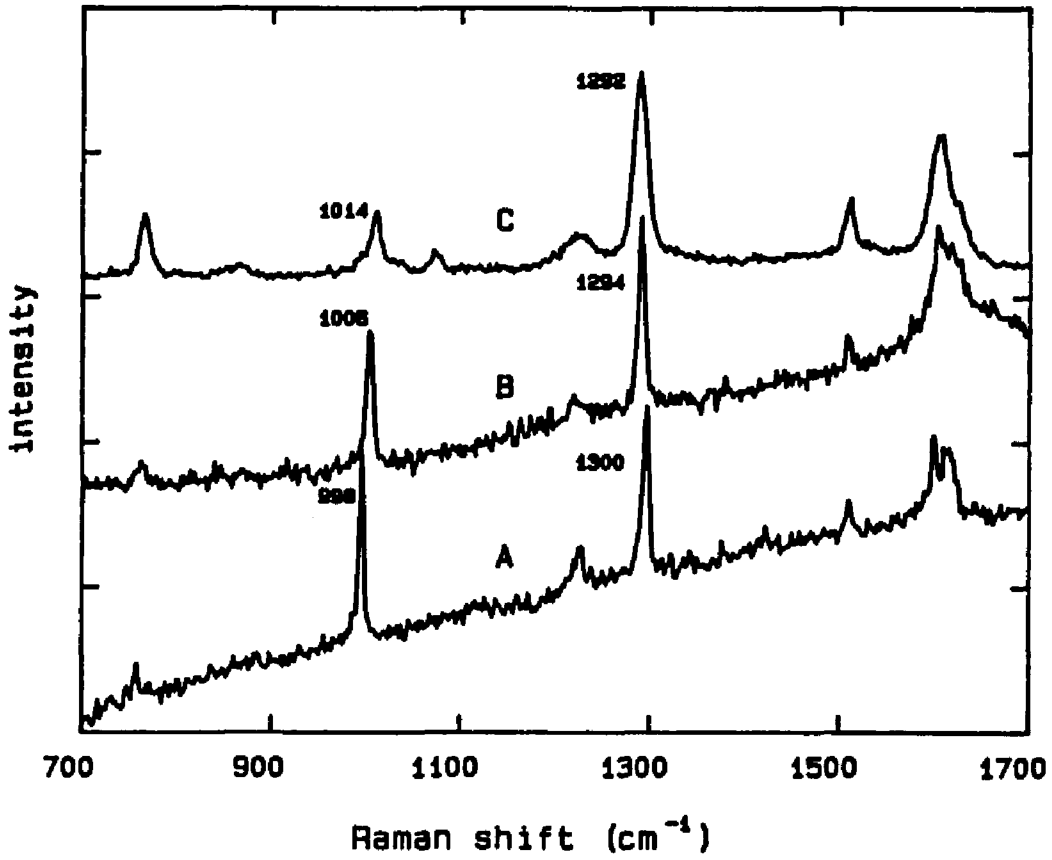


Fig.16. Raman spectra of 4,4'-BP: 488 nm argon laser light, 200 mw for A and B, 20 mw for C; (A) NR spectrum of 4,4'-BP solid; (B) NR spectrum of 4,4'-BP solution; (C) SER spectrum of 10^{-3} M 4,4'-BP in 0.1 M KCl on the roughened Ag electrode.

The 4,4'-BP molecules were adsorbed on the roughened Ag electrode so strongly that even though the roughened Ag electrode was taken out of the 4,4'-BP solution and washed with distilled water, then put into the 0.1 N KCl solution, the spectrum obtained was still comparable to that before removal.

Fig.17 shows the NR spectra of 4,4'-BP solutions with different pH. The differences are mainly in the 1500-1650 cm^{-1} region. For the pH 1.8 solution in which most of 4,4'-BP molecules are protonated, there is a strong band at 1648 cm^{-1}. For the pH 6.5 solution where most of 4,4'-BP molecules are not protonated, there is no 1648 cm^{-1} band. Instead the 1606 cm^{-1} band appears. Therefore, the 1648 cm^{-1} band must relate to the vibration of N-H. Fig.18 shows the SER spectra of 4,4'-BP on the roughened Ag electrode at -0.2 V for solutions with different pH. We can see that even though the pH of the solution is 1.8, the 1648 cm^{-1} band does not appear (Fig.18A). This may mean that when the protonated 4,4'-BP molecules are adsorbed on the Ag surface the molecules are deprotonated. It was reported that since pyridinium (protonated pyridine) is positively charged and does not have a lone pair of electrons at the nitrogen, it is unlikely to be adsorbed directly on the Ag surface. Thus, an ion pair interaction of pyridinium with specifically adsorbed chloride has been suggested by several groups [357-361] as a model of the surface species. The principal evidence for this model is that in the absence of chloride there is no detectable intensity of SER signal of pyridinium at low pH [359,360,362]. However, the situation for protonated 4,4'-BP is different. Even though there is no chloride in the solution the SER spectrum can still be observed at low pH and it is the same as that in the presence of chloride ions. Therefore, it is likely that the protonated 4,4'-BP molecules are adsorbed on the Ag surface not through the ion pair interaction, but through deprotonation

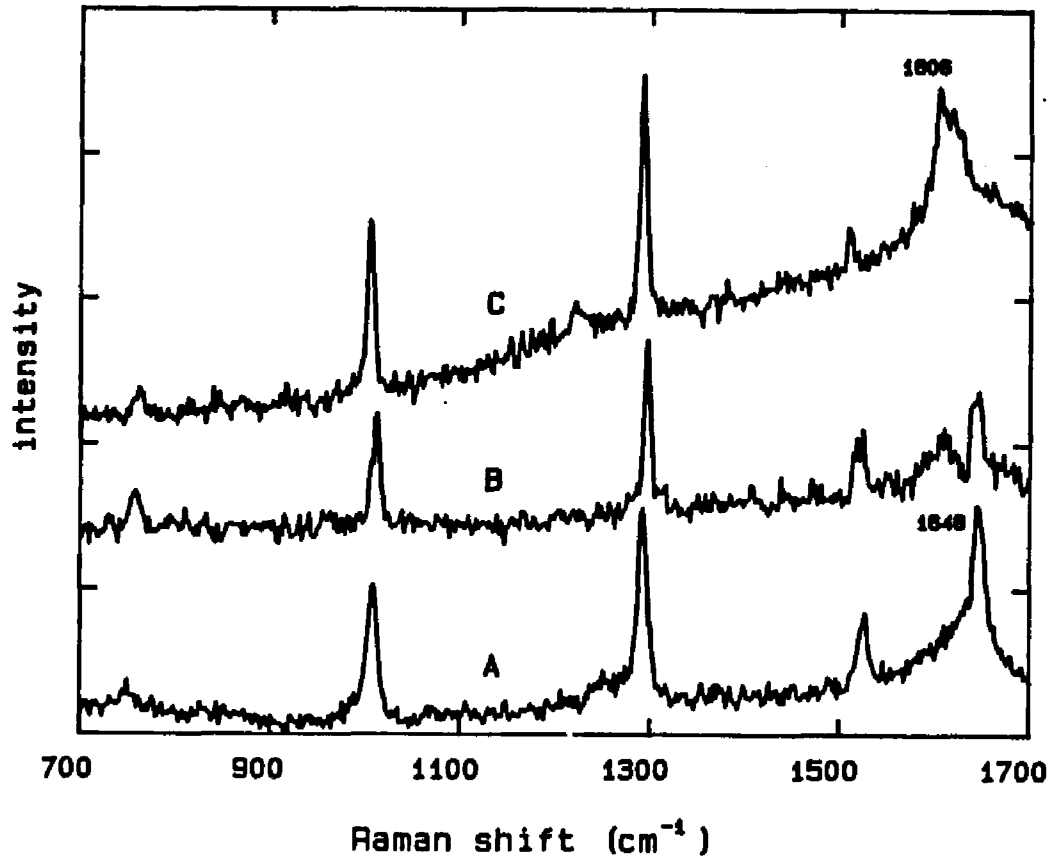


Fig. 17. NR spectra of 4, 4'-BP solution at different pH: 488 nm argon laser light, 200 mw; (A) pH 1.8; (B) pH 3.5; (C) pH 6.5.

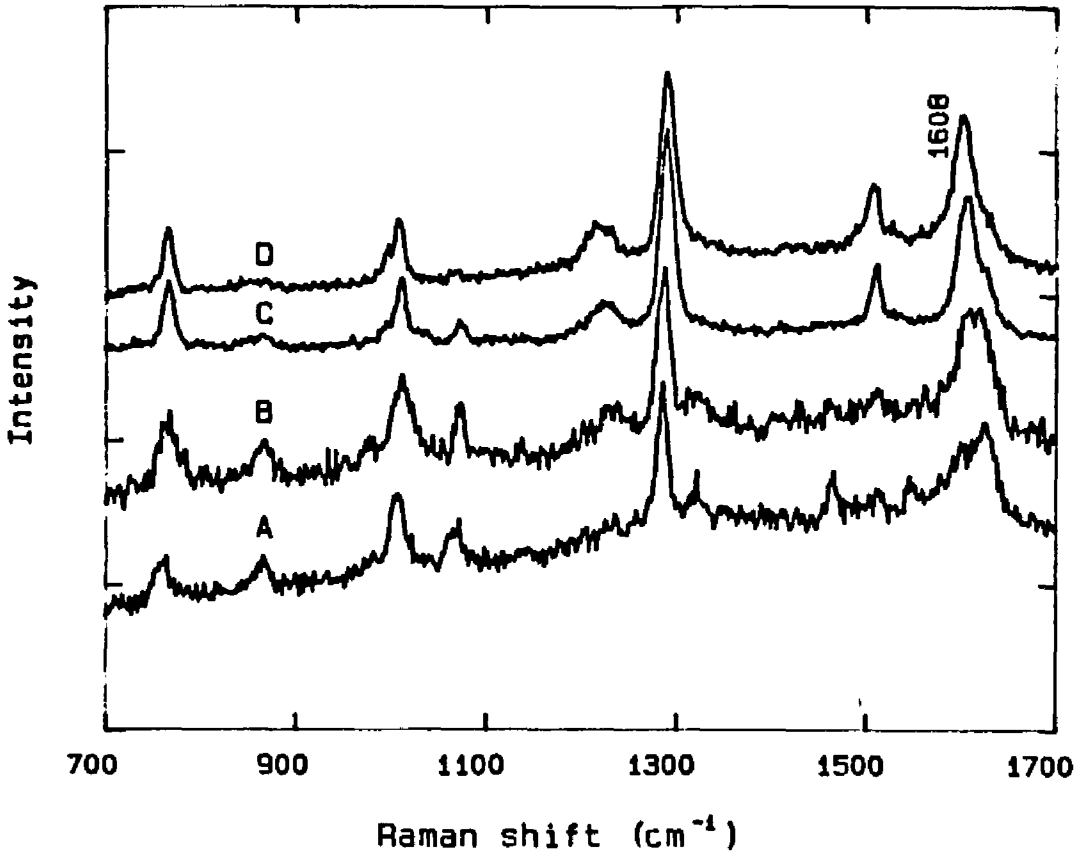


Fig.18. SER spectra of 4,4'-BP on the roughened Ag electrode at -0.2 V in the solutions at different pH: 488 nm argon laser light, 20 mw; (A) pH 1.8; (B) pH 3.5; (C) pH 6.5; (D) pH 12.

mechanism. This may be due to the strong affinity of 4,4'-BP for adsorption on the Ag surface.

3-4-2. The Surface Raman spectra of 4,4'-BP radical in acidic solution

From the electrochemistry of 4,4'-BP we know that 4,4'-BP molecules can be protonated at low pH, such as pH 1.8, and reduced at -0.7 V producing a cation radical which has blue color and dissolves in the aqueous solution. Thus, if the pH 1.8 solution of 4,4'-BP is electrolyzed at -0.7 V using a Ag electrode with large surface area, the blue protonated radical solution of 4,4'-BP is obtained. Then a RR spectrum for this radical can easily be observed (Fig.19A).

As mentioned above, Fig.18A is a SER spectrum of 4,4'-BP on the roughened Ag electrode at -0.2 V in the pH 1.8 solution. If the potential is adjusted to -0.7 V. the surface Raman spectrum obtained (Fig.19B) is different from that at -0.2 V. Some bands shift slightly and four new bands (1040, 1352, 1520 and 1654 cm^{-1}) appear. These new bands are coincident with the bands in the RR spectrum of protonated 4,4'-BP radical. If the cell is carefully washed in situ with pH 1.8, 0.1 M KCl solution, then we may take the spectrum again (Fig.19C). The spectrum before washing is different from that after washing with some bands lost after washing. The lost bands are exactly the same as those found in the RR spectrum of protonated 4,4'-BP radical in the pH 1.8 solution. From the above we can conclude that the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at -0.7 V in the pH 1.8 solution is the superposition of the SER spectrum of adsorbed radicals of 4,4'-BP and the RR spectrum of 4,4-BP radical dis-

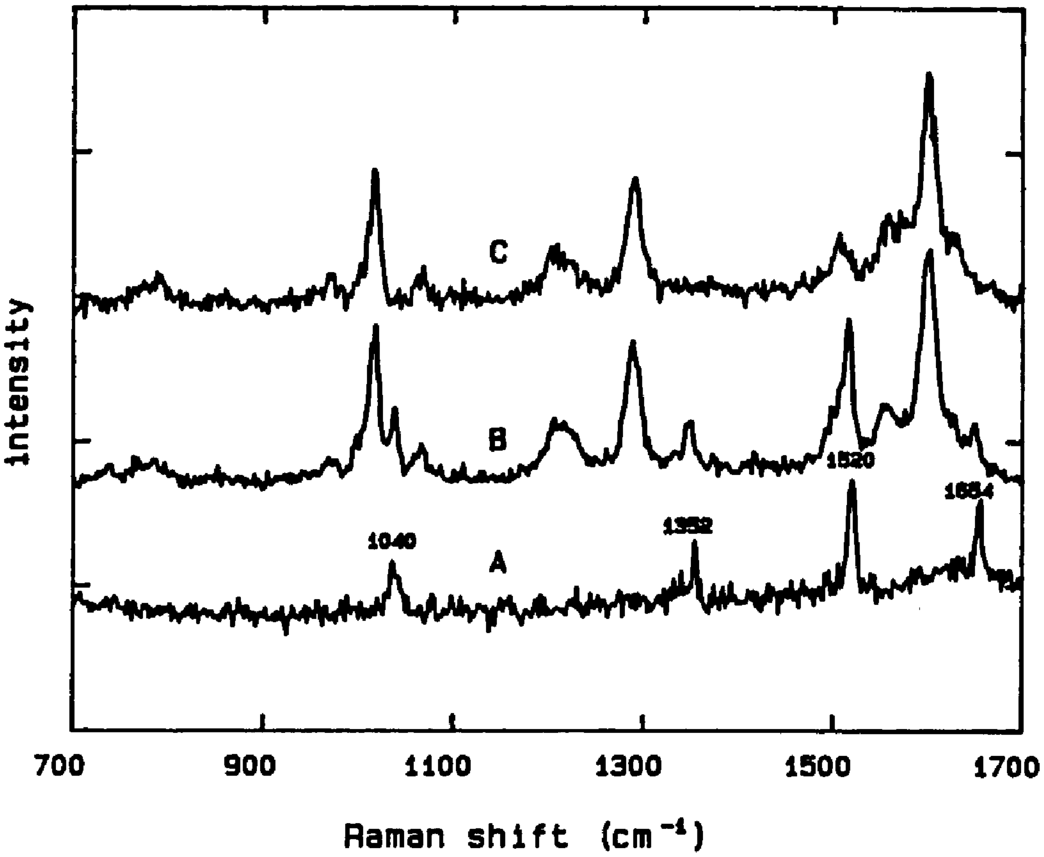


Fig.19. Raman spectra of 4,4'-BP radical in pH 1.8 solution: 488 nm argon laser light. 100 mw for A, 20 mw for B and C; (A) RR spectrum of 4,4'-BP radical in solution; (B) surface Raman spectrum of 4,4'-BP radical on a roughened Ag electrode at -0.7 V before washing the cell with 0.1 M KCl; (C) after washing.

solved in the solution. This situation is similar to that for MV^+, i.e. the SER spectrum of the adsorbed 4,4'-BP radical is totally different from the RR spectrum of the dissolved radical and this is because the interaction between adsorbed molecules and the metal leads to a shift in molecular state.

3-4-3. surface Raman spectra of reduction product and intermediate of 4,4'-BP in pH 6.5 solution

Fig.20 shows the surface Raman spectra of 4,4'-BP on a roughened Ag electrode at -0.2, -0.8 and -1.2 in pH 6.5 solution. The spectra at -0.2 and -0.8 V are very similar. Only the intensity at -0.8 V is higher than that at -0.2 V. However, the spectrum at -1.2 V is very different from those at -0.2 and -0.8 V. Many new bands appear. From the electrochemistry of 4,4'-BP we know that 4,4'-BP can be reduced at the potential more negative than -1.1 V on the roughened Ag electrode. Therefore, these new bands must relate to the reduction of 4,4'-BP. We found that the bands in the spectrum at -1.2 V (Fig.20C) can be divided into three types:

type "a": 992, 1532 and 1650 cm^{-1}
type "b": 1040, 1334 and 1498 cm^{-1}
type "c": 1006, 1220, 1288 and 1592 cm^{-1}

The different types of bands have different behaviors. For example, the intensities of different types of bands changes with frequencies of the excitation sources in different ways. Fig.21 shows the spectra of 4,4'-BP on the roughened Ag electrode at -1.2 V for the different frequencies of excitation sources. We can see that the

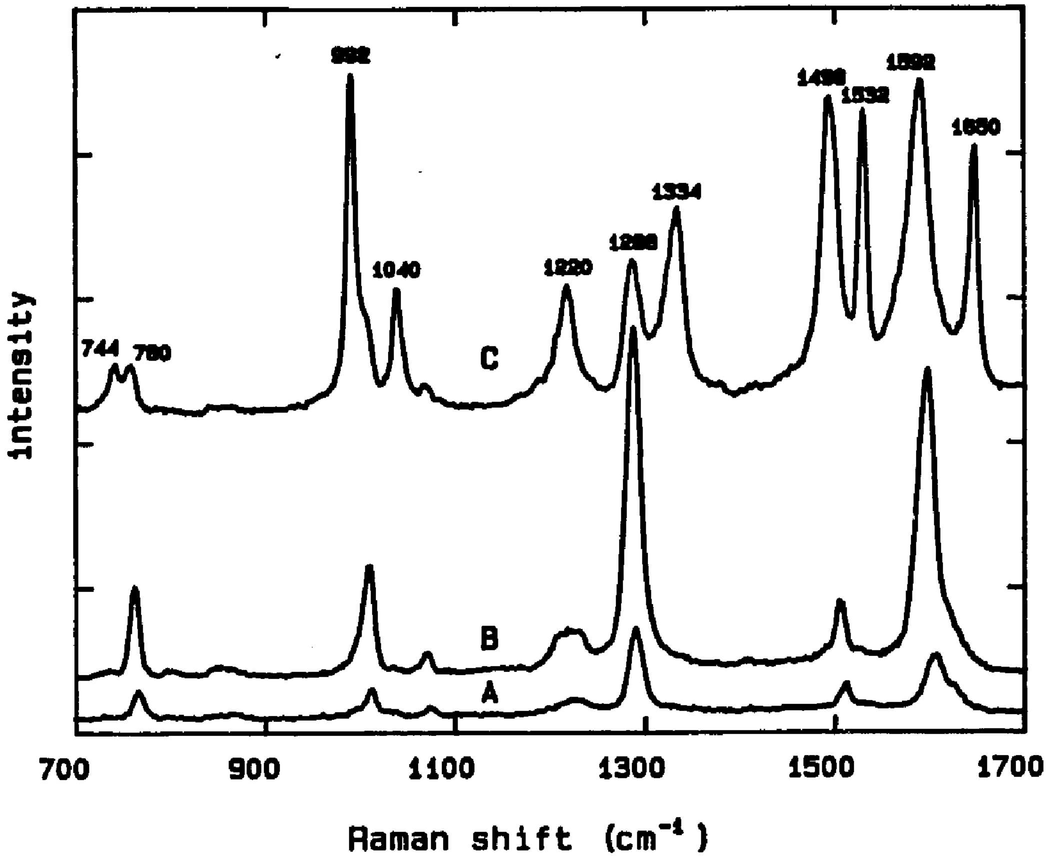


Fig.20. Surface Raman spectra of 4,4'-BP on a roughened Ag electrode at different potentials in pH 6.5 solution: 488 nm argon laser light, 20 mw; (A) −0.2 V; (B) −0.8 V; (C) −1.2 V.

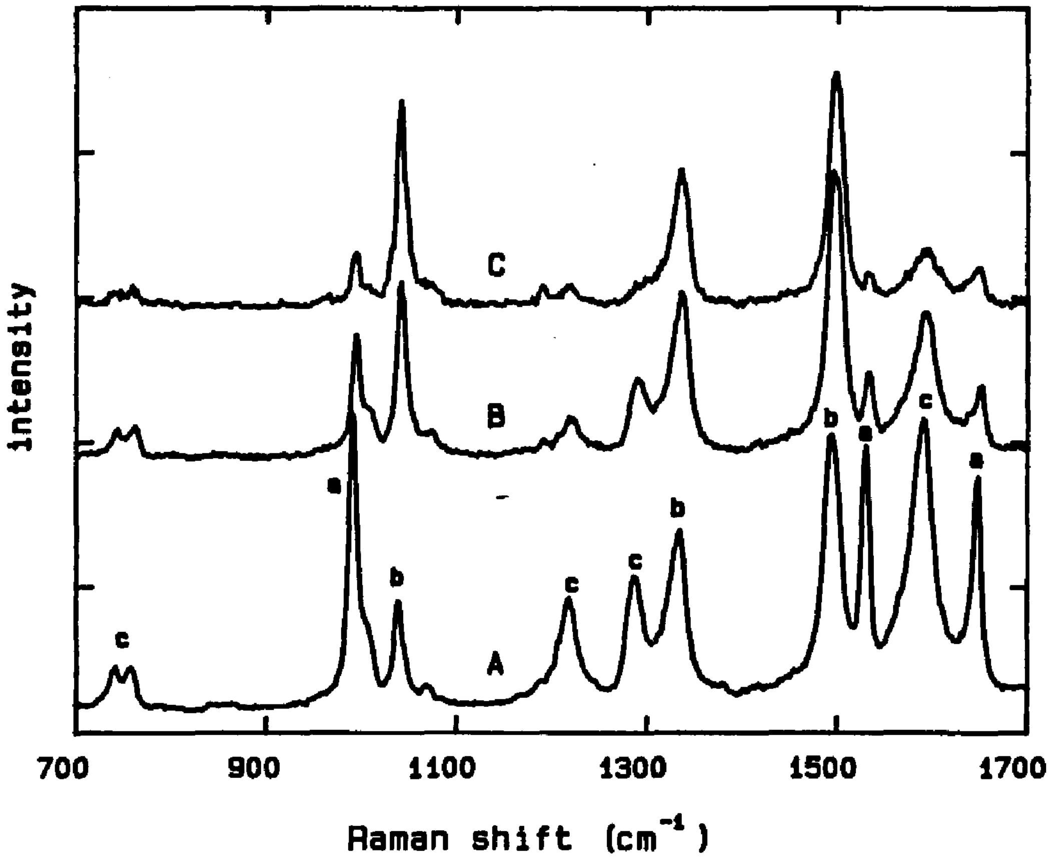


Fig.21. Surface Raman spectra of 4,4'-BP on a roughened Ag electrode at -1.2 V in pH 6.5 solution using different excitation sources: (A) 488 nm; (B) 514.5 nm; (C) 610 nm.

behavior of the type "b" bands are like RR bands having the maximum intensity for red excitation source. The type "a" and "c" bands have the maximum intensity for blue excitation source, but the intensities of type "a" bands dramatically decrease with decreasing frequency of excitation source and obey the ω^4 law. Thus, the type "a" bands may represent NR scattering. If the cell is carefully washed with 0.1 M KCl solution at -1.2 V, the spectrum of 4,4'-BP on the roughened Ag electrode at -1.2 V before washing (Fig.22B) is different from that after washing (Fig.22C) with some bands being lost after washing. The lost bands are found to be exactly the same as the type "a" bands. This means that the type "a" bands are due to a different species from that for type "b" and "c" bands.

When surface Raman spectra are studied on a polished Ag electrode, no Raman bands can be observed if the potential is made more positive than -1.1 V. However, if the potential is adjusted to more negative than -1.1 V, a film forms on the electrode surface and a Raman spectrum (Fig.22A) can be obtained. The bands in the spectrum are exactly the same as the type "a" bands in the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at -0.12 V. From the electrochemistry of 4,4'-BP we know that a two-electron reduction of 4,4'-BP takes place on a polished Ag electrode at potentials more negative than -1.1 V in pH $>$ 6.5 solution giving the protonated, fully reduced 4,4-BP. Therefore the Raman spectrum on the polished Ag electrode at more negative than -1.1 V (Fig.22A) is the NR of the film of the protonated, fully reduced 4,4'-BP. From the above experimental results we conclude that the type "a" bands in the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at -1.2 V are the NR bands of protonated, fully reduced 4,4'-BP covered on the electrode surface.

From Fig.21A we can see that when the 488 nm excitation laser light is used

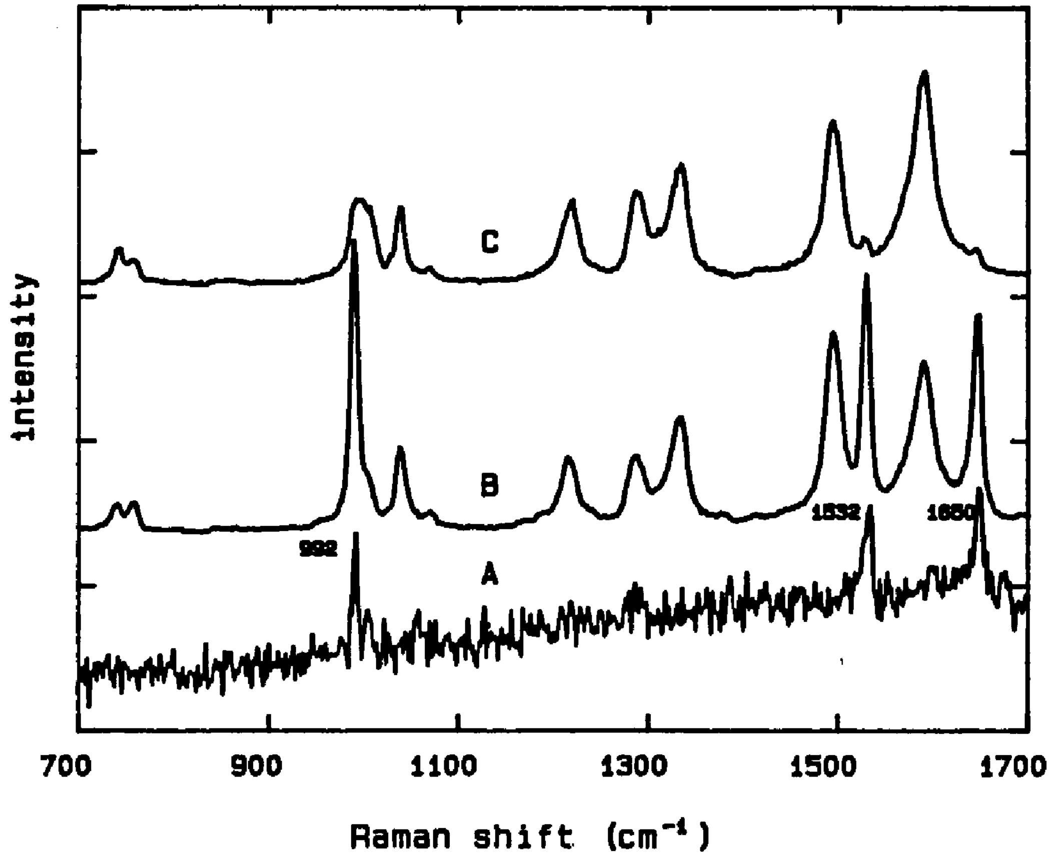


Fig.22. Surface Raman spectra of 4,4'-BP on Ag electrodes at -1.2 V in pH 6.5 solution: 488 nm argon laser light, 100 mw for A, 20 mw for B and C; (A) NR spectrum, polished Ag electrode; (B) surface Raman spectrum, roughened Ag electrode, before washing the cell with 0.1 M KCl solution at -1.2 V; (C) after washing.

the intensities of the type "b" bands are comparable to those of the type c bands. However, if the cell is washed with 0.1 M KCl solution at -0.2 V after an ORC of the Ag electrode, then the potential is adjusted to -1.2 V and the spectrum is taken again, the type "b" bands almost disappear and only the type "c" bands are observed. Therefore, the type "b" and "c" bands are also due to different surface species. As indicated by Cotton [155], after washing only a monolayer of adsorbed 4,4'-BP exists on the surface of the roughened Ag electrode and 4,4'-BP molecules are not protonated on reduction. Thus, it was considered that the type "c" bands are the SER bands of the non-protonated, fully reduced 4,4'-BP molecules strongly adsorbed on the Ag surface.

For type "b" bands we found that they are similar to the bands in the RR spectrum of the protonated 4,4'-BP radicals in the pH 1.8 solution (Fig.19A) except in the type "b" bands there is no 1654 cm^{-1} band which is related to the protonation of the ring nitrogens (see section 3-4-1 and [155]). As mentioned above, the type "b" bands show strong intensities when the red excitation source is used. This is characteristic of RR scattering. Therefore, it was considered that the type "b" bands are the RR bands of the non-protonated, 4,4'-BP radical adsorbed on the surface of the roughened Ag electrode.

We can conclude that the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at more negative than -1.1 V is the superposition of the three different spectra:

(a) the NR spectrum (the type "a" bands) which is due to the protonated, fully reduced 4,4'-BP film covered on the surface of the roughened Ag electrode.

(b) the RR spectrum (the type "b" bands) which is due to the non-protonated 4,4'-BP radical adsorbed on the surface of the roughened Ag electrode,

(c) the SER spectrum (the type "c" bands) which is due to the non-protonated, fully reduced 4,4'-BP strongly adsorbed on the surface of the Ag electrode.

Cotton et al. [155] also indicated that the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at potentials more negative than -0.9 V consists of different types of bands. However, their assignments fro bands were different form ours. They considered that the bands at about 1334, 1532 and 1650 cm^{-1} are due to the protonated 4,4'-BP radical and the bands at about 1040 and 1498 cm^{-1} are attributed to the two-electron reduced 4,4'-BP.

3-4-4. Conclusion

The surface Raman spectroscopy of 4,4'-BP and its reduction products on a roughened Ag electrode was studied. When the pH of 4,4'-BP solution is less than 2, the 4,4'-BP molecules can be electrochemically reduced to a protonated cation radical at -0.7 V. The surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at -0.7 V in the solution of pH less than 2 is the superposition of the SER spectrum of the adsorbed, non-protonated cation radicals of 4,4'-BP and the RR spectrum of protonated 4,4'-BP cation radical dissolved in solution. The two kinds of Raman spectra can be clearly separated. When the pH of t e 4,4'-BP solution is higher than 6.5, the surface Raman spectrum of 4,4'-BP on the roughened Ag electrode at potentials more negative than -1.1 V is a superposition of three kinds of Raman spectra: NR spectrum of the diprotonated, fully reduced 4,4'-BP film covered on the surface of the roughened Ag electrode; RR spectrum of the non-protonated, adsorbed 4,4'-BP radical, and SER spectrum of the non-protonated, fully reduced 4,4'-BP molecule strongly adsorbed on the Ag surface.

3-5. Intensity-potential profiles

3-5-1. Raman polarizability factor

It is now widely accepted that both electromagnetic and chemical effects must be involved in the phenomenon of SER scattering. However, a less well resolved problem is the relative importance of the two effects, since it is difficult to separate them. A possible way to separate the chemical effect from the electromagnetic effect is observation of a change of SER intensity with electrode potential in the electrochemical system, because when the electrode potential changes, all of the factors which lead to optical resonance, remain constant, only the chemical effect varies with the potential. In addition, the study of the SER intensity-potential profile has given directly convincing evidence for a metal-molecule charge transfer theory [184,285,300-302]. Therefore, the SER intensity-potential profiles for various electrochemical systems were widely studied. However, it was found that the potential dependence of the SER intensities are complicated because it can be influenced by many factors, such as Raman polarizability, surface coverage, electrochemical reaction on the electrode surface, etc. The experimental results and conclusions were controversial. For example, some groups [22,298,299] claimed that the potential dependence of intensity mainly reflects the change in surface coverage with the potential, while several groups [184,285,300-302,325] concluded that the potential dependence of intensity is mainly related to the Raman polarizability of molecule-metal system. Thus, further and systematic study is necessary. we have presented a charge transfer theory beginning from the following equation [325].

$$I = [8\pi(\omega \pm \omega_{FI})^4 I_L / 9c^4] \sum |\alpha_{\rho\sigma}|^2$$

where I is the Raman intensity, I_L is the incident laser intensity at frequency ω, while ω_{FI} is a molecular transition frequency between states I and F, α is the Raman polarizability, ρ and σ each represent the three spatial directions x, y, z involved in the tensor, c is the light speed. Using second-order perturbation theory and applying the Herzberg-Teller conditions to a molecule-metal system, we obtained

$$\alpha_{\rho\sigma} = A + B + C$$

After a series of steps and simplification we finally obtain

$$A_f = \kappa_A \rho_0 \left[\ln \left| \frac{\omega_{FI} + \omega_f - \omega}{\omega_{BI} + \omega_f - \omega} \right| + \ln \left| \frac{\omega_{FI} + \omega_f + \omega}{\omega_{BI} + \omega_f + \omega} \right| \right]$$

$$A_k = \kappa_A \rho_0 \left[\ln \left| \frac{\omega_{KF} + \omega_k - \omega}{\omega_{KA} + \omega_k - \omega} \right| + \ln \left| \frac{\omega_{KF} + \omega_k + \omega}{\omega_{KA} + \omega_k + \omega} \right| \right]$$

$$B = \frac{\kappa_B \rho_0}{2} \left| \frac{1}{\omega_{KI} - \omega} \ln \frac{|\omega_{FI} - \omega|}{|\omega_{BI} - \omega|} + \frac{1}{\omega_{KI} + \omega} \ln |\omega_{FI} + \omega| \, |\omega_{BI} + \omega| \right|$$

$$C = \frac{\kappa_C \rho_0}{2} \left| \frac{1}{\omega_{KI} - \omega} \ln \frac{|\omega_{KA} - \omega|}{|\omega_{KF} - \omega|} + \frac{1}{\omega_{KI} + \omega} \ln \frac{|\omega_{KF} + \omega|}{|\omega_{KA} + \omega|} \right|.$$

where the term A_f represents resonant molecule-to-metal charge transfer from the molecular ground state I to one of the unfilled metal levels M, while A_k represents resonant metal-to-molecule charge transfer from a filled metal state M to an molecular excited state K, the term B represents molecule-to-metal charge transfer from the molecular ground state I to one of the unfilled metal levels M, while term C represents metal-to-molecule charge transfer from one of the filled metal levels M to the molecular excited state K, κ_A, κ_B, κ_C are the coefficients of the integrals in A, B and C terms, respectively, ρ_0 is the density of the metal states, ω_{FI}, ω_{BI}, ω_{KI}, ω_{KF}, ω_{KA} are transition frequencies between states I and F, I and B, I and K, F and K, A and K, respectively, while ω_k and ω_f are the frequencies of a particular excited or ground state vibration, respectively (Fig.23).

Notice that all these terms have logarithmic singularities. When the excitation frequency is near a singularity we should include a phenomenological damping factor $i\Gamma$ where Γ is the inverse of some characteristic damping time in the conduction band. Considering only the dominant term, we then expect the SER line shape in each case to be

$I \;\alpha\, [\ln|\omega_{FI} + \omega_k - \omega + i\Gamma|]^2,$

$I \;\alpha\, [\ln|\omega_{KF} + \omega_k - \omega + i\Gamma|]^2,$

$I \;\alpha\, [\ln|\omega_{FI} - \omega + i\Gamma|]^2,$

$I \;\alpha\, [\ln|\omega_{KF} - \omega + i\Gamma|]^2.$

These terms give the correct dependence of V_{MAX} since $h\,\omega_F{}' = E_F(0) + eV$ where $E_F(0)$ is the Fermi level at an arbitrary zero applied potential with respect to a reference electrode. As a test of the line shapes we have fit these equations to a variety of experimental data, using Γ as an adjustable parameter and choosing ω_{KI} to be the lowest lying allowed molecular transition frequency. The resonance frequency is selected so that the V_{MAX} of the observed profile matches the calculated curve. In Fig.24 we show a fit of the predicted intensity-potential profile for the case of molecule-to-metal transfer. The example chosen is the 1020 cm^{-1} band in piperidine on a roughened Ag electrode. For the optimum fit we use a linewidth Γ of 0.3 eV and $\omega_{KI} = 9$ eV. Similarly in Fig.25 we show a fit for the case of metal-to-molecule transfer in the 1008 cm^{-1} band in pyridine. We choose Γ of 0.3 eV and $\omega_{KI} = 4$ eV. In both cases the fit may be termed excellent. The value for Γ is consistent with typical metal damping times and is not

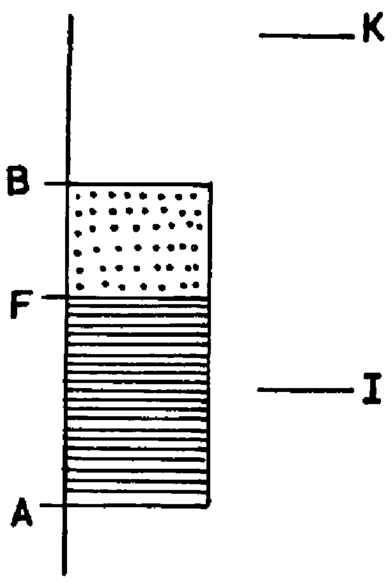


Fig.23. Energy level scheme for molecule metal system. The molecular levels are I and K. The metal levels of the conduction band of the metal are shown on the left. The conduction band ranges between A and B. The filled levels range up to F, the Fermi level, and are depicted by lines, while the unfilled levels are depicted by dots.

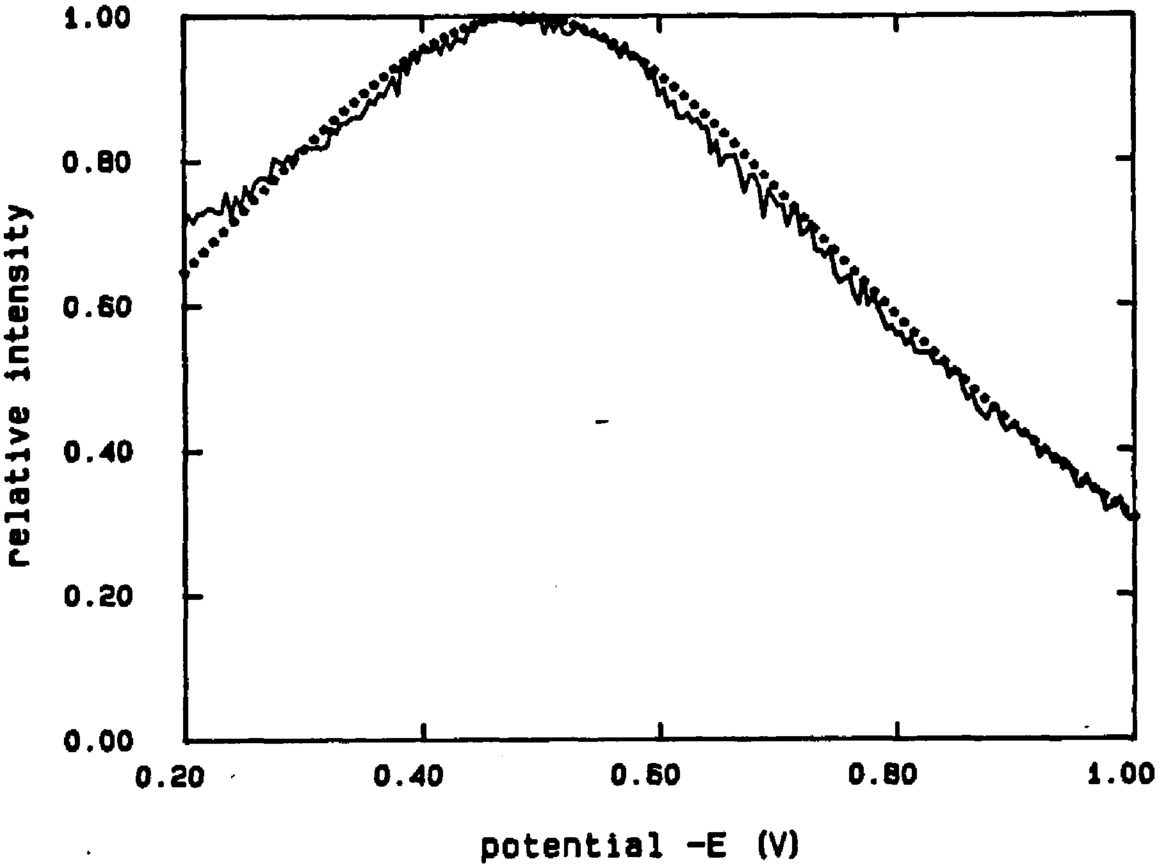


Fig.24. Intensity-potential profile for the 1020 cm^{-1} band of piperidine on a Ag electrode. Dots show the best fit of the calculated curve using a linewidth parameter Γ = 0.3 eV.

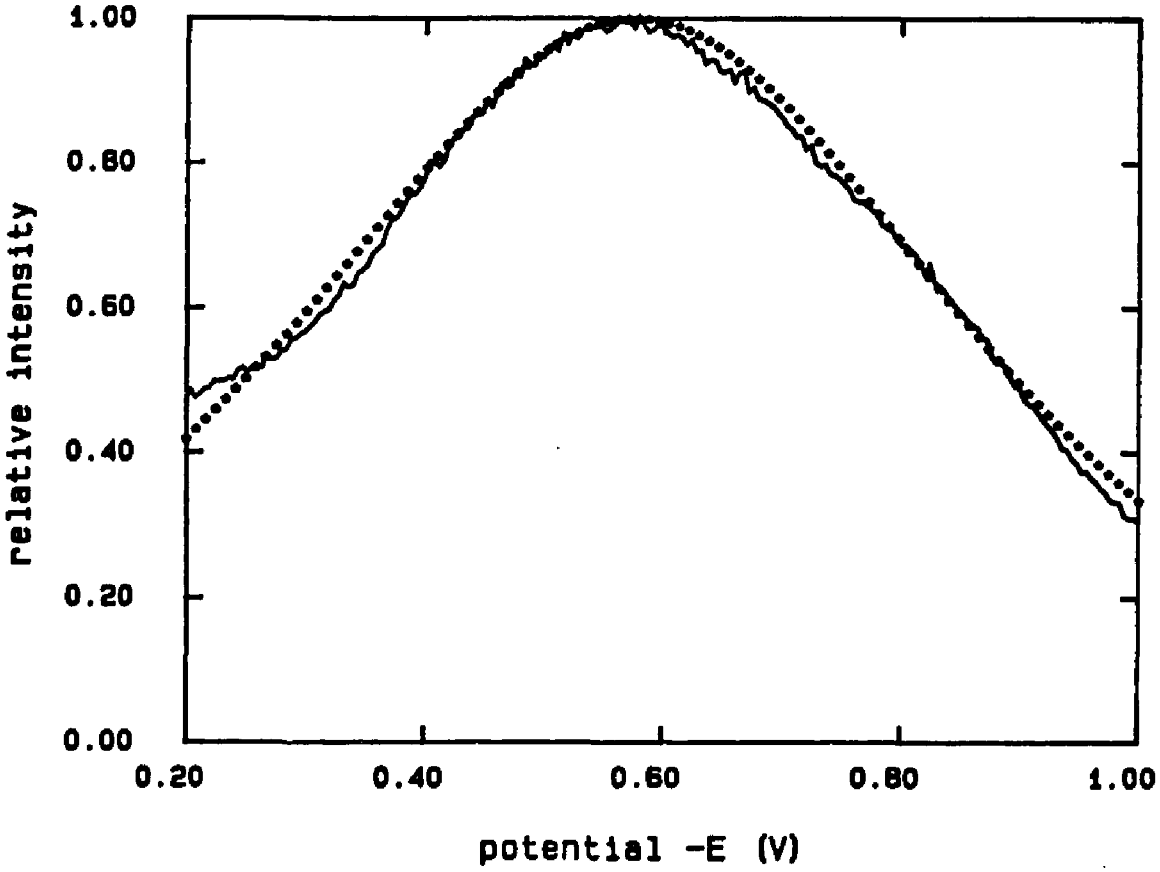


Fig.25. Intensity-potential profile for the 1008 cm^{-1} band of pyridine on a Ag electrode. Dots show the best fit of the calculated curve using a linewidth parameter $\Gamma = 0.3$ eV.

too sensitive to the choice of ω_{KI} . For some other molecules such as 4,4'-BP, the excellent fit can also be obtained(Fig.26).

In addition to the excellent fit of the predicted intensity-potential profile with the experimental result, our theory can explain several other pertinent experimental observations, such as weak overtones for SER scattering, 0.60-0.75 depolarization ratios for all the SER bands and why V_{MAX} are different for the totally and nontotally symmetric vibration modes [325]. Therefore, our theory is consistant with experimental characteristics of SER scattering, and it suggests that the potential dependence of the SER intensity is indeed mainly related to the Raman polarizability of the molecule-metal system if no other important factors exist.

3-5-2. Electrode reaction factor

Although the predicted intensity-potential profiles can fit the experimental curves for quite a few molecules it fails for methylviologen. Fig.27 shows the profile of the 840 cm^{-1} band of the methylviologen dication. The fit is good until the potential reaches -0.55 V at which point the experimental curve drops rapidly. From the electrochemistry we found that the adsorbed methylviologen dications begin to be reduced to the monocation radicals on a roughened Ag electrode at -0.55 V. Fig.28 compares the SER intensity-potential profile of the 840 cm^{-1} of MV^{2+} with the cathodic part of the CV which was taken simultaneously with the intensity-potential profile. We can see that the potential region where the intensity rapidly decreases, matches the potential region where the adsorption reduction peak is located. Therefore, we consider that the SER intensity-potential profile mainly depends on the electrode reaction in the potential region where the

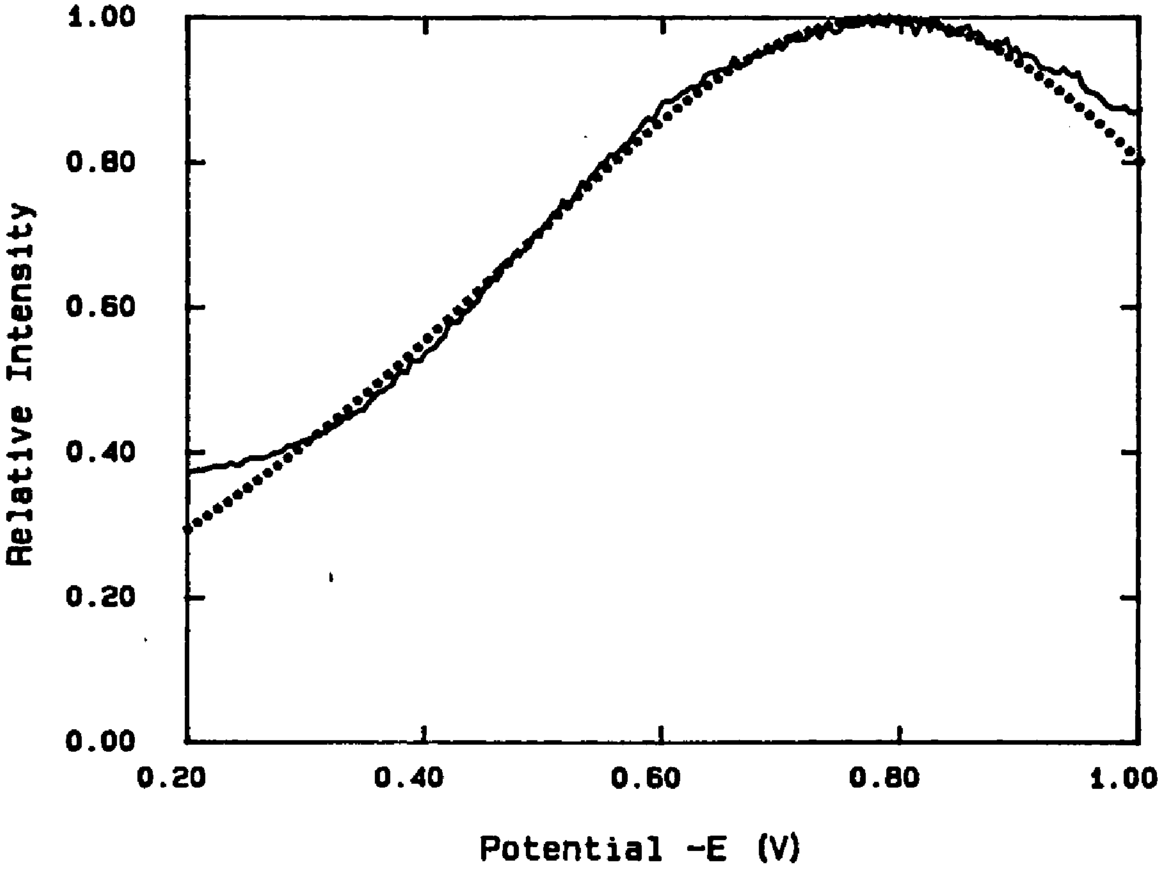


Fig.26. Intensity-potential profile for the 1292 cm^{-1} band of 4,4'-BP on a Ag electrode. Dots show the best fit of the calculated curve using a linewidth parameter $\Gamma = 0.3$ eV.

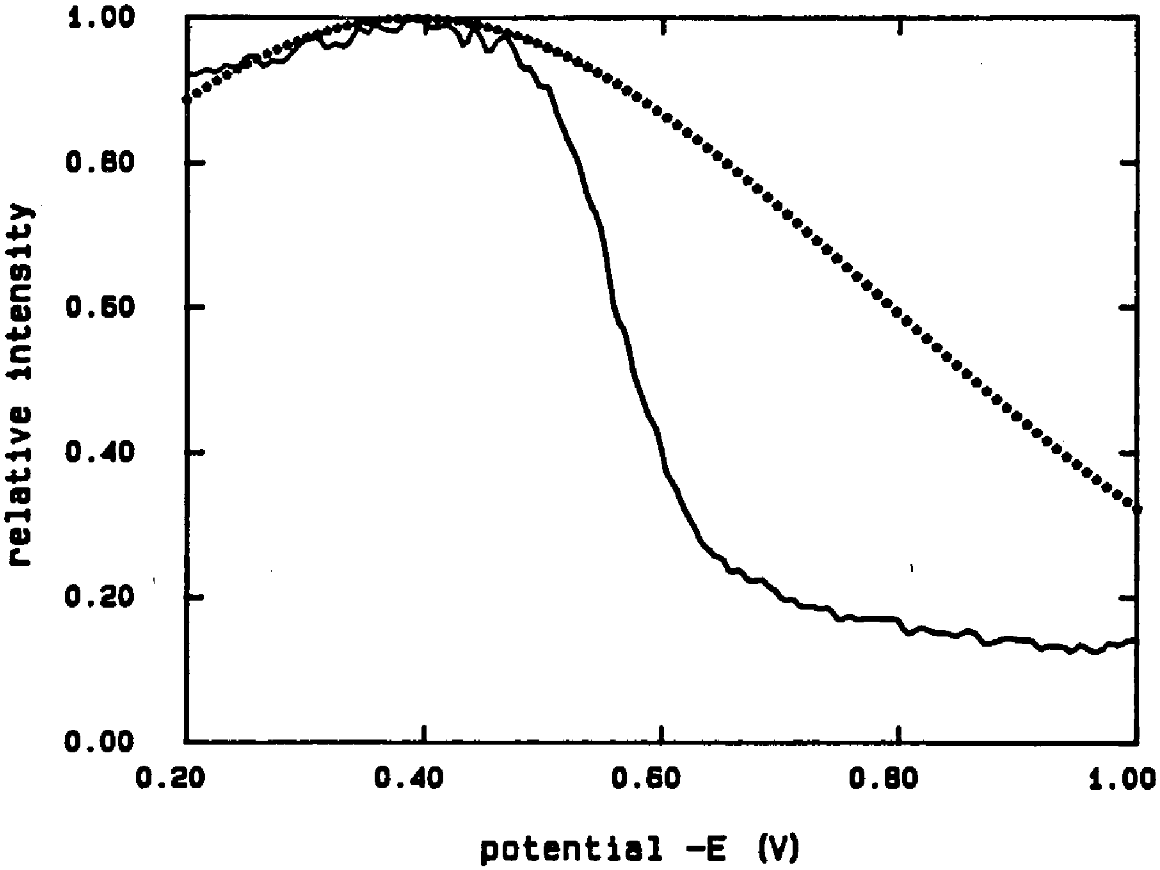


Fig.27. Intensity-potential profile for the 840 cm^{-1} band of methylviologen on a Ag electrode. Note that at -0.55 V a reduction takes place so a fit to the calculated curve is only good for the region before the onset of the reaction.This illustrates the effect of electrode reaction on the derived profiles.

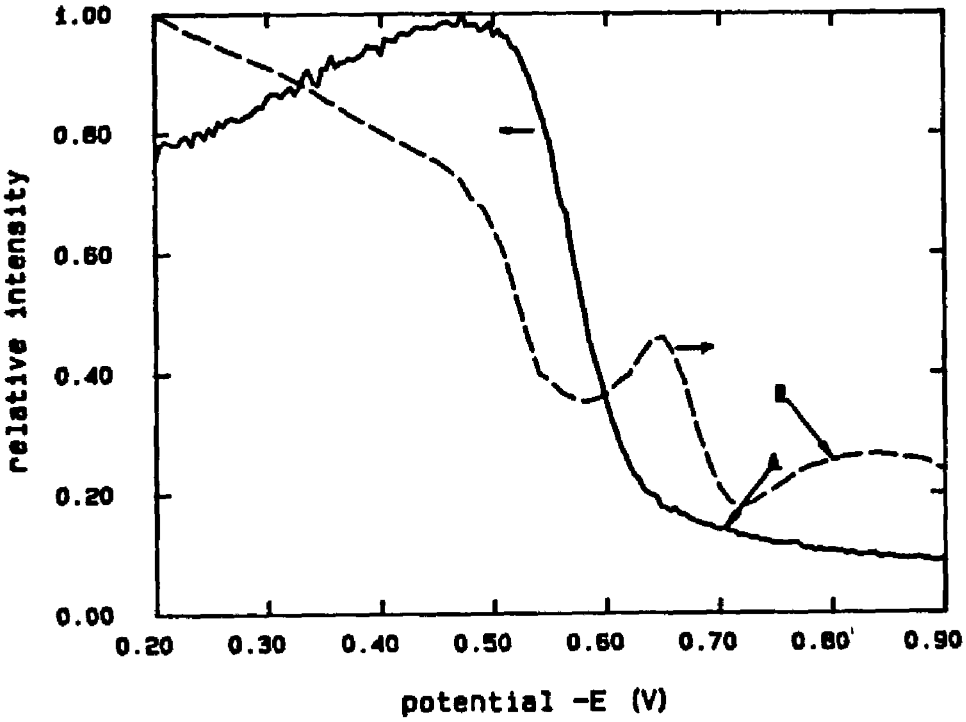


Fig.28. Intensity-potential profile for the 840 cm^{-1} band (solid line) and the cathodic part of the CV of methylviologen (dashed line) in 0.1 M KCl solution.

electrode reaction takes place. Further evidence for such agreement can be obtained. When KBr is used as a supporting electrolyte instead of KCl the adsorption reduction peak shifts to the more negative potential. The intensity-potential profile has a corresponding shift (Fig.29).

Similarly, such correspondence between the intensity-potential profile and the cathodic part of the CV can also be observed for a band, such as the 790 cm^{-1} band which is due to the adsorbed monocation radical of methylviologen. The only difference is that when the adsorbed MV^{2+} species are reduced to the MV^{+} the intensity of the 790 cm^{-1} band increases (Fig.30B). There are two intensity-potential profiles in Fig.30. Profile A (Fig.30A) is for 840 cm^{-1} band which is due to the adsorbed MV^{2+}. The profile B (Fig.30B) is for 790 cm^{-1} band which is observed only in the SER spectrum of the adsorbed MV^{+}. The crossing point of the two profiles is at -0.57 V. This potential is exactly equal to the potential of the adsorption reduction peak measured with the electrochemical method (Fig.5). This result is not surprising because of the correspondence between the intensity-potential profile and the cathodic part of the CV.

3-5-3. Surface coverage factor

Fleischmann et al. [298,299] indicated that the SER intensity-potential profile mainly reflects the change in surface coverage with the potential because the shape of the intensity-potential profile for pyridine-Ag electrode system is similar to that of the differential capacitance curve. However, when we studied the SER intensity-potential profile of 4,4'-BP which can be strongly adsorbed on the roughened Ag electrode, we found that the intensity-potential profiles for different concentration of bulk 4,4'-BP in 10^{-2} - 10^{-7} M range are almost the

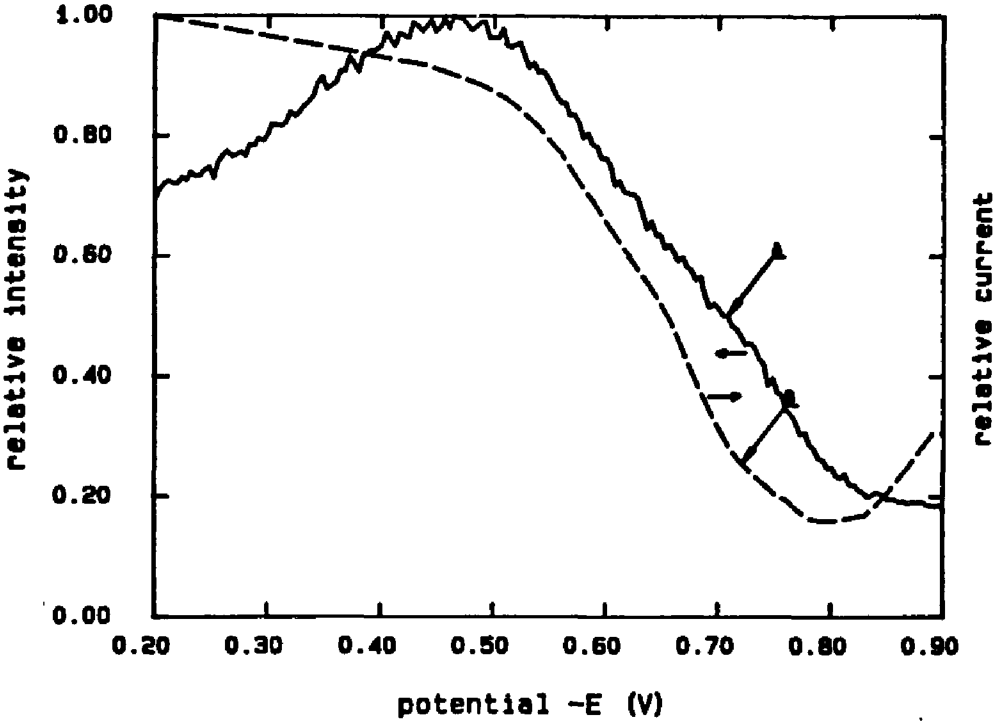


Fig.29. Intensity-potential profile for the 840 cm^{-1} band (solid line) and the cathodic part of the CV of methylviologen (dashed line) in 0.1 M KBr solution.

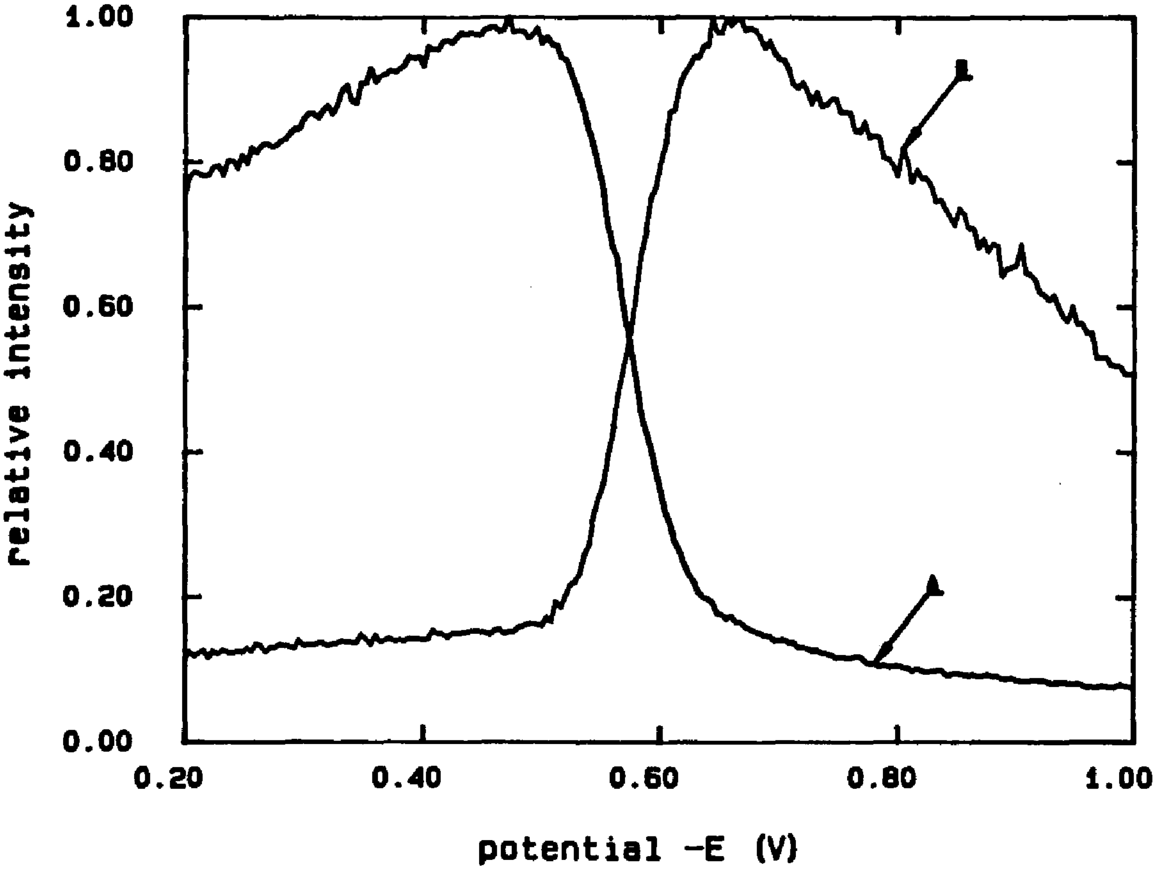


Fig.30. Intensity-potential profiles for 790 and 840 cm^{-1} bands of methylviologen. The crossing point of two profiles is at about -0.57 V.

same. If the surface coverage is the main factor the intensity-potential profiles should show some differences for different concentrations of bulk 4,4'-BP. Furthermore, Fig.31 shows the intensity-potential profiles for the 1292 cm^{-1} band before (curve B) and after (curve A) washing the cell with 0.1 M KCl solution at -0.2 V. We can see that they are almost the same. Since no 4,4'-BP molecules are in the solution after washing no more 4,4'-BP molecules can be adsorbed on the surface of the roughened Ag electrode from the 0.1 M KCl solution when the potential scans to the more negative direction. Thus, the increase of the intensity with change of the potential can not be attributed to increased adsorption of 4,4'-BP molecules from the solution and it becomes clear that the intensity-potential profiles is not mainly due to the coverage change with the potential.

Although pyridine is adsorbed on the roughened Ag electrode less strongly than 4,4'-BP, the effect of the surface coverage on the intensity-potential profile is small. For example, the intensity-potential profiles for different concentrations of bulk pyridine have almost the same shapes, only the V_{MAX} are slightly different. The V_{MAX} for 1008 cm^{-1} band of pyridine on the roughened Ag electrode is -0.56 V for 0.5 M pyridine solution, -0.59 V for 0.05 M pyridine solution, -0.62 V for 0.005 M and 0.00005 M pyridine solutions. Fig.32 shows the intensity-potential profiles for 1008 cm^{-1} band for 0.05 M pyridine solution pyridine on the roughened Ag electrode before (curve A) and after (curve B) washing the cell with 0.1 KCl solution at -0.2 V. The shapes of the profiles before and after washing are similar, only the V_{MAX} after washing slightly shifts to the more negative potential and the decrease of the intensity in the potential region more negative than V_{MAX} is more rapidly than that before washing. These differences are due to the effect of the surface coverage. Therefore we can conclude that for

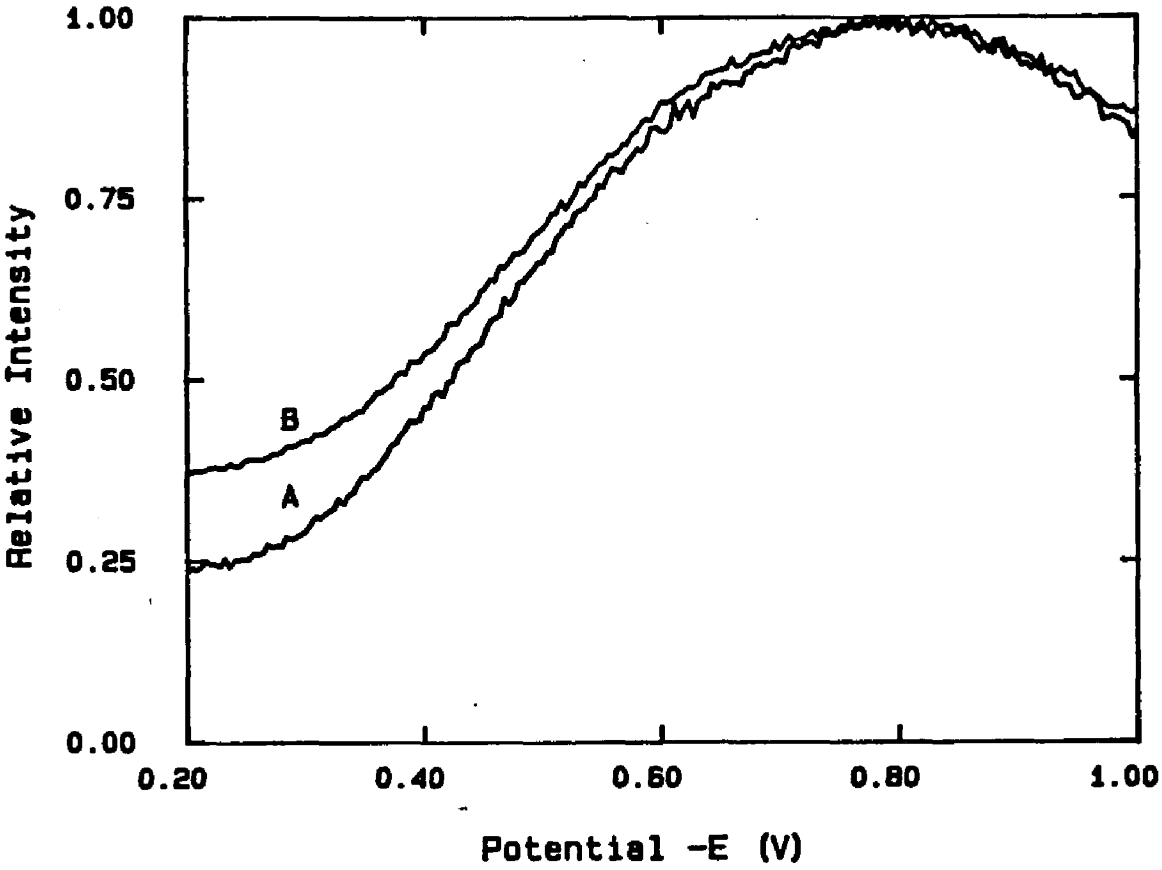


Fig.31. Intensity-potential profiles for 1292 cm^{-1} band of 4,4'-BP before and after washing the cell with 0.1 M KCl solution at -0.2 V.488 nm argon laser light, 20 mw; (A) after washing; (B) before washing.

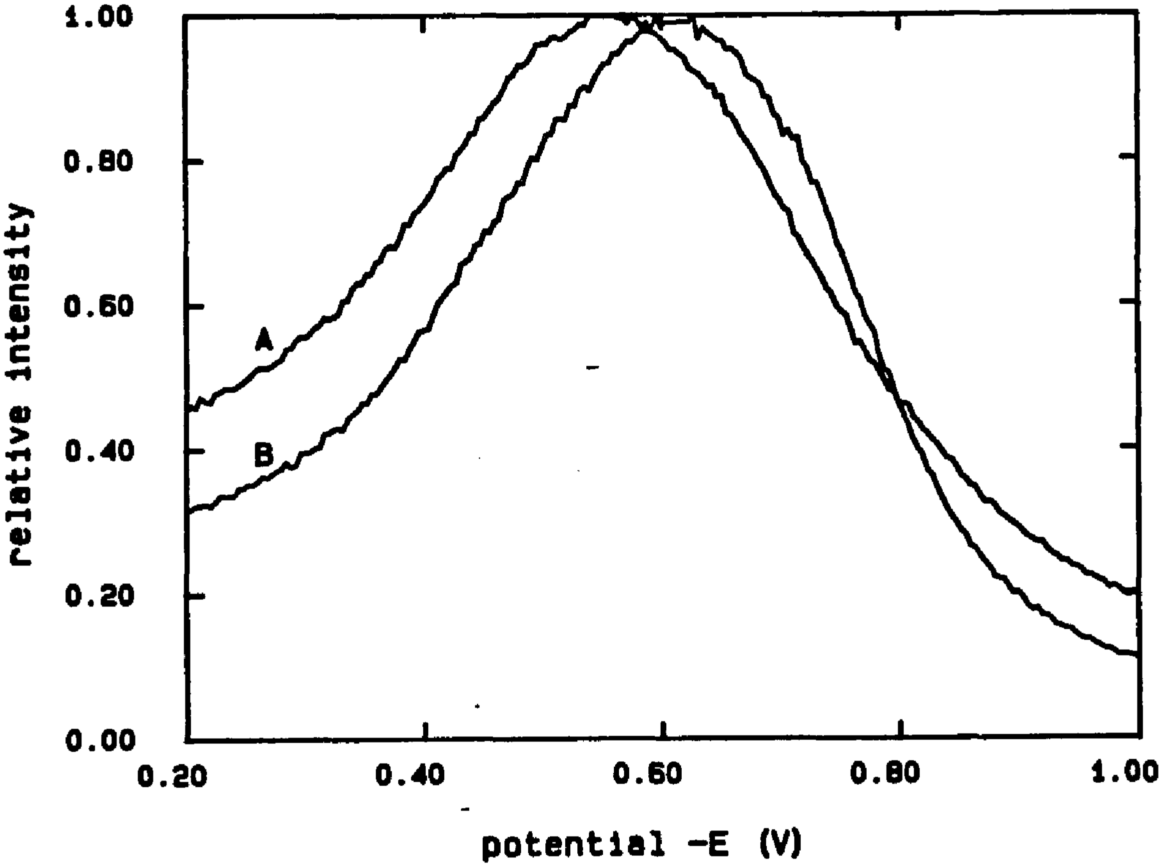


Fig.32. Intensity-potential profiles for 1008 cm^{-1} band of pyridine before and after washing the cell with 0.1 M KCl solution at -0.2 V. 488 nm argon laser light, 20 mw; (A) before washing; (B) after washing.

4,4'-BP-Ag electrode and pyridine-Ag electrode systems the surface coverage has much less effect on the intensity-potential profiles than that of the Raman polarizability.

3-5-4. Selfabsorption factor

According to the charge transfer theory [325], the SER intensity-potential profile can be fit with the calculated curve and the V_{MAX} should shift with the wavelength of the excitation sources. However, for the 4,4'-BP-Ag electrode system these features can not be observed. Fig.33 shows the intensity-potential profiles of the 1292 cm^{-1} band of 4,4'-BP adsorbed on the roughened Ag electrode for different wavelengths of excitation sources. We can see that the V_{MAX} does not change with the wavelength of the excitation sources in the 488-605 nm region and the differences between relative intensities at -0.2 V and at V_{MAX} become small (Fig.34). When the 647 nm excitation source is used the V_{MAX} can not be observed and the experimental profile can not be fit with the calculated curve. This unusual phenomenon may mean that there is a unknown factor influencing the SER intensity-potential profiles of 4,4'-BP-Ag electrode system.

One possible factor is absorption of the adsorbed 4,4'-BP molecules. After a ORC of the Ag electrode, multilayer of 4,4'-BP molecules can be adsorbed on the surface of the roughened Ag electrode. They may have a strong absorption peak in the 700-800 nm region, which is similar to that for pyridine-Ag system [249]. Then, the SER scattering light from the first layer of 4,4'-BP molecules can be adsorbed by succeeding layers of 4,4'-BP molecules. When the blue laser light is used such absorption is weak and the intensity-potential profile is less affected by such absorption so that the profile can still be fit with the calculated curve

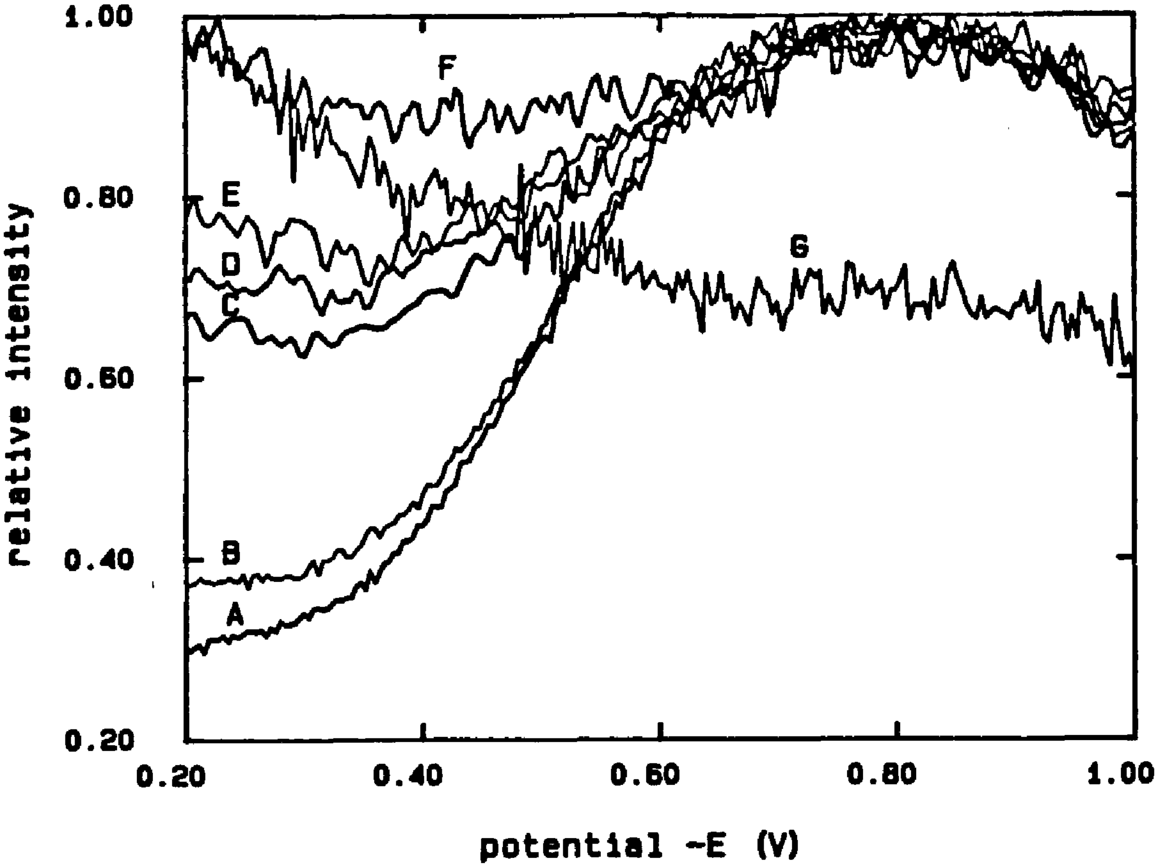


Fig.33. Intensity-potential profiles for 1292 cm^{-1} band of 4,4'-BP using different excitation laser lights. (A) 488 nm; (B) 514 nm; (C) 572 nm; (D) 581 nm; (E) 593 nm; (F) 605 nm; (G) 647 nm.

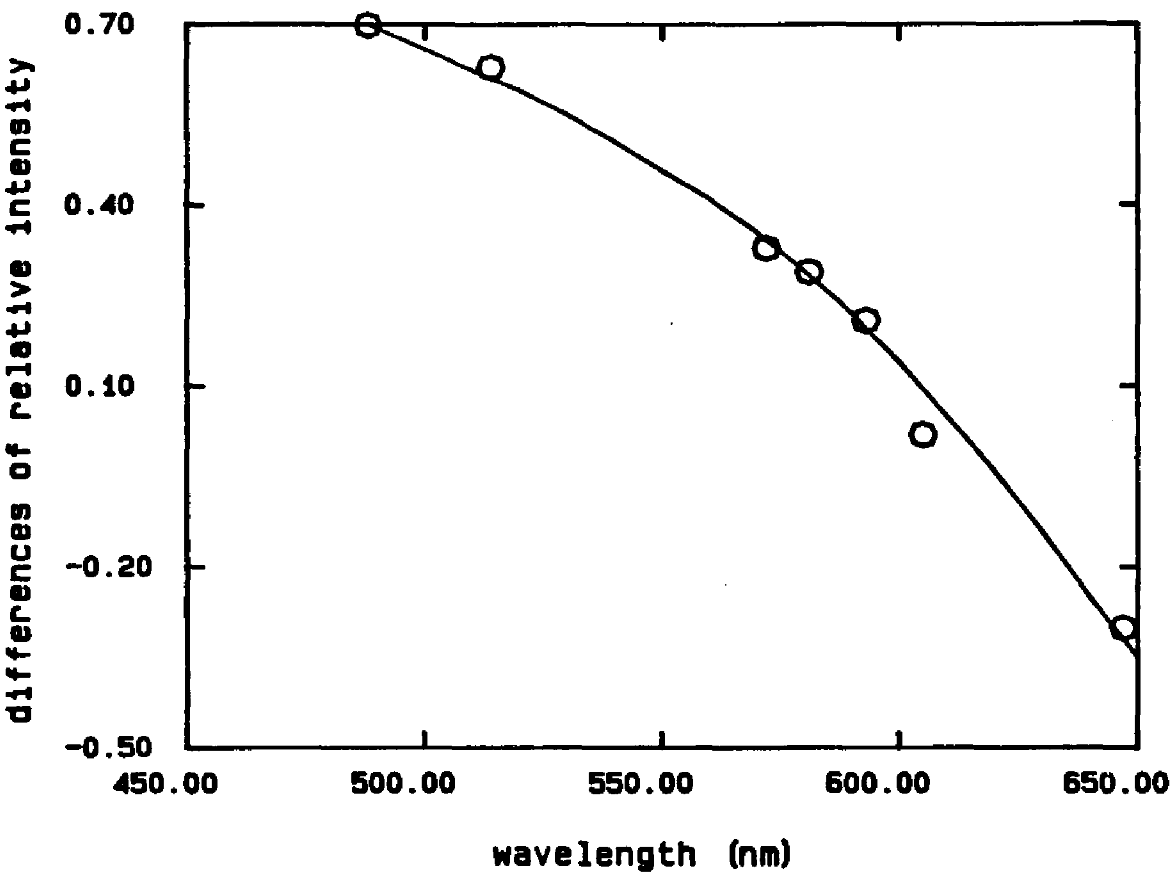


Fig.34. Differences between relative intensities at -0.2 V and V_{MAX} in the intensity-potential profiles of 1292 cm^{-1} band of 4,4'-BP vs wavelength of excitation laser light.

(Fig.26). However, when the red laser light is used the absorption is so strong that the usual V_{MAX} can not be observed and the profile can not be fit with the calculated curve.

Evidence for such absorption can be obtained. When the concentration of the 4,4'-BP solution is large than 10^{-4} M the SER intensity decreases with increasing the concentration of 4,4'-BP. When we compare the SER spectrum of 4,4'-BP on the roughened Ag electrode at -0.2 V after washing the cell with 0.1 M KCl solution with that before washing, we found that the intensity after washing is higher than that before washing by a factor of 5-10. In addition, when we compare the intensity-potential profile for the 1292 cm^{-1} band for 10^{-5} M 4,4'-BP solution with that for 10^{-3} M 4,4'-BP solution using the red laser light, we find that the profile for dilute solution is similar to that using the blue laser light (Fig.35).

The above consideration is only tentative and further study is necessary.

3-5-5. Conclusion

The SER intensity-potential profiles for some molecules on the roughened Ag electrode were studied. The shape of the experimental profiles can be fit very well with the calculated curve from the charge transfer theory presented by Lombardi et al. [325]. Thus, we can conclude that, usually, the SER intensity-potential profile is determined by the Raman polarizability of the molecule-metal system. However, sometimes the profile can be influenced by other factors such as electrode reaction, surface coverage, or selfabsorption of adsorbed molecules. We found that when the calculated curve can not fit the the experimental

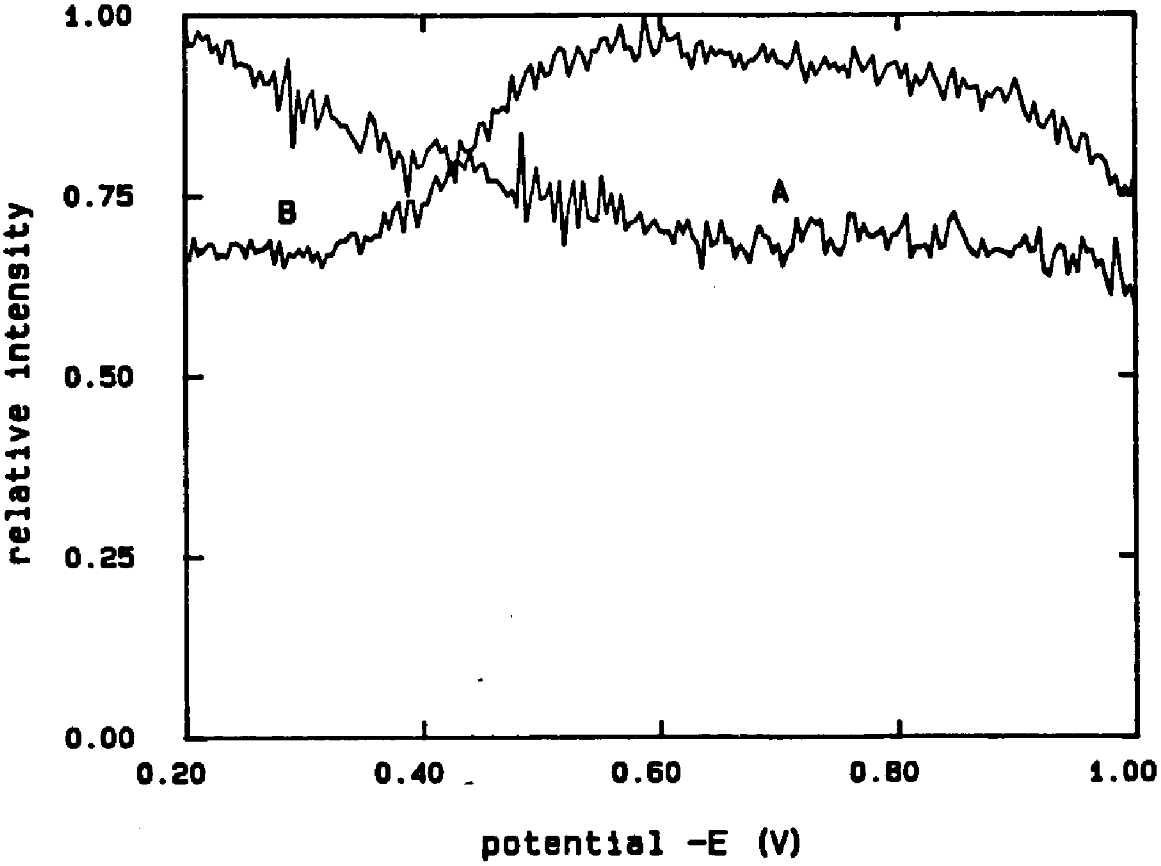


Fig.35. Intensity-potential profiles for 1292 cm^{-1} band of 4,4'-BP for diffrent bulk concentrations. 647 nm kripton laser light, 20 mw; (A) 10^{-3} M 4,4'-BP solution; (B) 10^{-5} M 4,4'-BP solution.

profile, there must be a factor which must also be considered in the SER intensity-potential profile in addition to that of Raman polarizability.

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