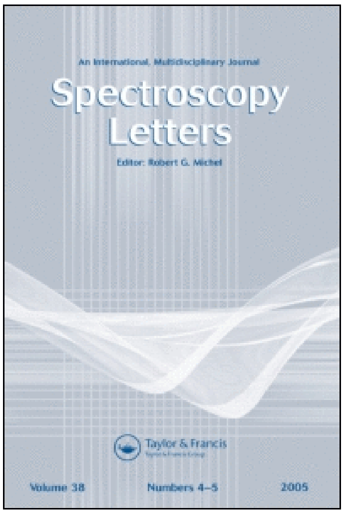

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STUDY ON ADSORPTION STATES BY SURFACE-ENHANCED RAMAN SPECTROSCOPY

Key Words: Pyridine, Methylene Blue, Adsorption state, Surface-enhanced Raman Spectroscopy

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ABSTRACT

SERS has been used as a state-resolving probe to study the adsorption states. In the case of pyridine (Py) adsorbed on the Ag electrode surface, the equilibrium and transition between two adsorbed states, i.e., the perpendicular mode adsorbed through the nitrogen lone-pair electrons and the flat mode through the π electrons of the aromatic ring, were studied. It was found that in the low pyridine concentration or the initial stage of adsorption, the flat mode was favored. While the concentration became higher and the adsorption tended to equilibrium, the adsorbed molecules would transit to the perpendicular mode. The similar phenomenon was also observed when changing the applied electric potential and the pH value of the solution. In the case of the adsorption of Methylene Blue (MB) on the HNO_3-etched silver surface, the influence of Cl^- ions on the adsorption states of MB was investigated. It showed that MB molecules adsorbed on the silver surface tended to transform from the "lying-down" state to the "end-on" state while adding Cl^- ions.

INTRODUCTION

Many special features such as high sensitivity, mode resolution, non-destructive detection, feasible for *in situ* measurement make Surface-enhanced Raman Spectroscopy (SERS) an attractive analyses technique and having a great potential in the application of surface studies. SERS is extremely sensitive in probing monolayerly-adsorbed molecules on several special kinds of metals. It is remarkable that the different orientation and adsorption states of adsorbed molecules can make a great difference to the enhancement factor of the same vibration mode in SERS spectra. Thus, it is possible using SERS to discriminate the adsorption states of adsorbed molecules, and makes SERS a very powerful tool for studying surface adsorption and surface reaction.

There are many research papers on the SERS spectra of pyridine adsorbed on a silver surface[1-3]. As is generally supposed, the stable adsorption state is that the pyridine molecule is adsorbed on the silver surface perpendicularly through its nitrogen lone-pair electrons coordinated with silver surface atoms. But some evidences were proposed that the pyridine molecule can also be adsorbed parallel to the silver surface through the π electrons of its aromatic ring interacting with silver surface atoms. However, there exists no detailed exploration on the relationship of those two kinds of adsorption states and the conditions of the equilibrium and transition between these states until now.

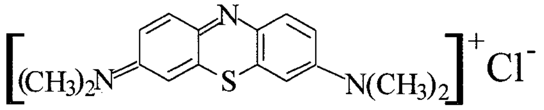
Recent studies suggested that dye molecules containing nitrogen or sulfur atoms could produce sufficiently strong and stable signals on an HNO_3-etched silver surface[4,5]. It was proven that the adsorption of dye molecules, like that of pyridine, consisted of the interaction of either nitrogen lone-pair electrons or aromatic ring π electrons with silver surface atoms.

In this paper, we applied SERS to study the adsorption states of pyridine (Py) molecules adsorbed on the electrochemically-disposed silver surface and Methylene Blue (MB) dye molecules on an HNO_3-etched silver surface according to the relative intensity changes of spectral lines in SERS. The change of adsorption states was observed on different adsorptive conditions, which brought forth the exact evidences of the transition between different adsorption states.

EXPERIMENTAL METHODS

1. Chemicals and Reagents

Methylene Blue (Shanghai Chemical Reagent Co.) was recrystallized twice s before use. The IR spectrum of the resultant was consistent with the standard. The structure formula of the Methylene Blue (MB) molecule is as follows:



The water used in experiments was deionized and distilled. All other chemical reagents were of analytical grade and used directly without further purification.

Silver foils (99.99%) purchased from Aldrich Company were 0.0025 cm thick. HNO_3-etched silver surface technique referred to literature [4].

2. Sample Preparation

The SERS measurement of pyridine (Py) was performed in a cell consisting of a working electrode, a counter electrode and a saturated calomel reference electrode. The working electrode used was 99.99% purity of Ag, inserted at the end of a PMMA protecting hood. The surface was polished with emery paper and then rinsed with distilled and deionized water. Its distance to the optical window can be ranged from 0.5 mm to 5 mm. The electrolyte was 0.1 mol/L KCl solution, purged with nitrogen gas before used.

The oxidation-reduction cycle (ORC) procedure was carried out in KCl electrolyte solution without pyridine. The ORC was performed with the electric potential increasing from -0.48 V (vs SEC) to +0.60 V then returning back to -0.48V, and the voltage scanning rate was 15 mV/sec. Pyridine was added carefully to the experimental concentration after ORC. The desired concentration was obtained by diluting the solution *in situ* with KCl solution.

In the case of Methylene Blue adsorption, the area of each silver foil was 0.5 cm^2. After dipping in the MB solution for a certain while, the silver foils which had been etched under the same experimental conditions were taken out and the remaining liquid on the surface was removed by absorbing and drying in the air. Then the observation of SERS signals was undertaken.

3. Raman Spectroscopy

SERS experiment of pyridine was carried out on the LRZ-1 Raman Spectrometer with a double monochrometer. All spectra were excited with the 488.0 nm line of an Ar^+ laser with a power of about 25 mW measured at the electrochemical cell.

Raman scattering of MB was carried out on a Brucker-RSF100 Laser Raman Spectra Instrument. The wavelength of the laser was 1064 nm and the power in our experiment was 30~100 mW.

RESULTS AND DISCUSSION

1. Adsorption state of pyridine on the electrochemical-disposed silver surface

Figure 1 is the SERS spectra of 0.05 mol/L pyridine adsorbed on a Ag

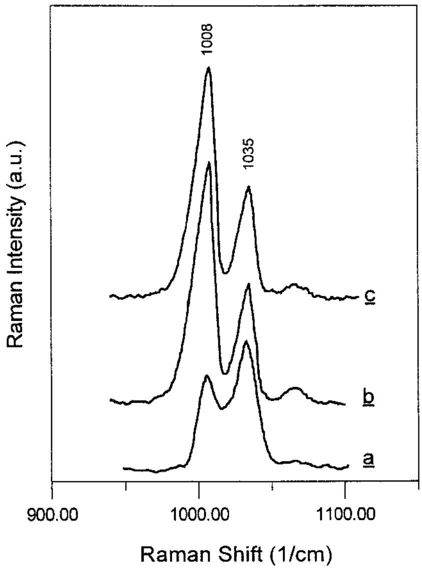


FIG.1 Relationship of SERS signal intensity of Pyridine adsorbed on Ag electrode surface with adsorption time ([Py] = 0.05 mol/L)
(a) 1 min. (b) 5 min. (c) 15 min.

electrode surface. From Fig.1, we can see that SERS signals of samples first attained the maximum, and then kept unchanged after pyridine was adsorbed for 5 min., and adsorption equilibrium could be justified at this moment. Two spectral peaks at 1008 cm^{-1} and 1035 cm^{-1} can be observed clearly from Fig.1, among which the intensity of 1008 cm^{-1} peak was stronger than that of 1035 cm^{-1}. But at the beginning of adsorption, i.e., within about 1 min. after the ORC procedure finished, an inversion of intensity could be observed between the two spectral peaks, though their absolute intensity was much weaker in comparison with that at equilibrium.

J. E. Demuth[6] and H. Yamada[7] ever pointed out that there were two different adsorbed states of pyridine on a Ag surface, i.e., the perpendicular mode adsorbed through the nitrogen lone-pair electrons coordinated with the unoccupied orbits of silver surface atoms and the flat mode through the π-electrons of the aromatic ring respectively. But the perpendicular mode is more stable and has a greater surface adsorption density than the flat mode, as a result of which, its signal intensity is stronger also.

As discussed by D.H. Ling[8], the intensity of the 1008 cm^{-1} peak of pyridine was stronger than that of the 1035 cm^{-1} peak for the perpendicular adsorbed pyridine molecule while the strength of the bands inversed in the case of flat mode. According to the "surface selection rule" of SERS[9,10], the normal modes of adsorbed molecules involving changes in molecular polarizability with a component perpendicular to the surface are subject to the greatest enhancement. As the 1008 cm^{-1} peak was corresponding to the in-plane stretch mode of the pyridine ring and the 1035 cm^{-1} to the out-of-plane bend mode, it was obvious that the enhancement ratio of the two spectral peaks at a perpendicular adsorption mode would be different from that at the flat mode. So changes of the relative intensity of two SERS lines at 1008 cm^{-1} and 1035 cm^{-1} could serve as an indicator of the adsorption states of pyridine.

Our observations showed that the perpendicular and flat adsorption states of the pyridine molecule co-existed and could transfer mutually to reach the equilibrium under certain conditions. At the beginning stage of adsorption, the coverage of a Ag electrode surface was very low, more area of the surface could be covered by means of flat adsorption. So the flat mode became the favorable adsorptive state. But at a certain high concentration of pyridine (e.g. 0.05 mol/L), as the adsorption time went, the surface coverage increased. Then the flat mode tended to convert to a perpendicular mode in order that more molecules could be adsorbed to decrease the free energy of system. When the equilibrium was attained we could get the relative intensity of the two peaks of 1008 cm^{-1} and 1035 cm^{-1}.

Above deductions could also be supported by observing SERS spectra at the saturated adsorption under different pyridine concentrations. As shown in Fig.2,

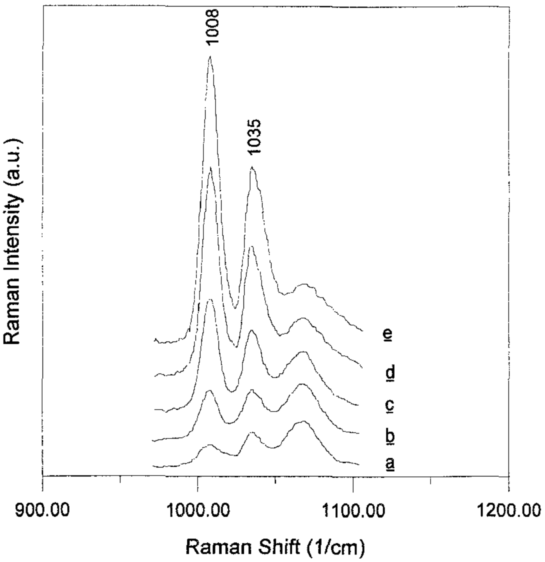


FIG.2 Relationship of SERS signal intensity of Pyridine with the concentration while adsorption equilibrium is reached on the Ag electrode surface
(a) 0.105×10^{-3} mol/L (b) 0.178×10^{-3} mol/L (c) 0.404×10^{-3} mol/L
(d) 1.110×10^{-3} mol/L (e) 3.180×10^{-3} mol/L

when pyridine concentration varied from about 0.1×10^{-3} mol/L to about 3.0×10^{-3} mol/L, the relative intensity changes of 1008 cm^{-1} and 1035 cm^{-1} spectral peaks could be observed easily. At a rather low concentration of pyridine, the 1035 cm^{-1} peak was stronger which indicated that the surface coverage was low at equilibrium and the pyridine molecule was favored to adsorb flatly. While pyridine concentration stepped up, all peaks in SERS spectra gradually increased, in which the 1008 cm^{-1} peak increased more quickly. This told that the surface coverage went up and the adsorption states changed from flat mode to perpendicular mode at a rather high concentration of pyridine. Of course, further study should be achieved on the quantitative relation between the two adsorption states.

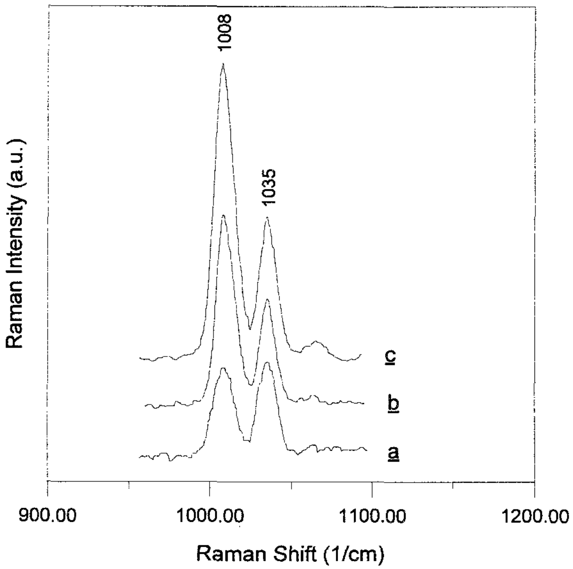


FIG.3 Influence of electric potential on the SERS signal intensity of Pyridine adsorbed on the Ag electrode surface after ORC ([Py] = 0.05 mol/L)
(a) -0.20 V (b) -0.40 V (c) -0.51 V

In addition, similar phenomenon of intensity inversion of SERS spectral lines could be observed while changing other experimental conditions such as the pH value of the solution and the applied electric potential. In Fig.3, we showed SERS signals obtained while keeping the silver electrode at different ending potential after ORC procedure. When the potential was at -0.20 V, the intensity of the 1035 cm^{-1} peak was stronger than that of the 1008 cm^{-1} peak, whereas at -0.51 V, the 1008 cm^{-1} peak increased greatly. It is more difficult to explain the effect of the external potential, for besides the influence of potential to the adsorption state, there also existed the change of the Fermi energy level of the Ag atom as a result of the external potential which influenced the charge-transfer resonance. More likely it was a multi-factor effect[2].

When the pH value of KCl electrolyte solution varied, the relative intensity of spectral lines also changed accordingly. Moreover, a new peak at 1026 cm^{-1} appeared which may be due to PyH^+ ions[11]. Naturally, the very cause of these phenomena needs further exploration.

2. Adsorption state of MB molecules on the surface of HNO_3-etched silver

From the experiment of MB adsorbed on the HNO_3-etched Ag surface, we found that at a rather low concentration of 3×10^{-6} mol/L, MB was adsorbed homogeneously on the silver surface and no changes of adsorption states happened during the adsorption process. But when the concentration went up to 3×10^{-5} mol/L, the adsorption behavior of MB changed greatly which proved that MB was no longer adsorbed homogeneously and different adsorption states occurred on the silver surface[12]. In this case, Cl^- ion of certain concentration existed in the bulk solution due to the fact that MB is a sort of salt containing Cl^- ion. As reported in the literatures[13,14], the Cl^- ion of proper concentration could influence adsorption behavior of some type of molecules adsorbed on a silver surface. So we ascribed the anomalous behavior of adsorbed MB molecules to the influence of Cl^- already contained in MB solution.

The MB spectra of normal Raman spectrum (NRS), SERS and SERS in the presence of Cl^- ions were recorded respectively and shown in Fig.4. The relative intensity of some main spectral peaks and their vibration mode assignment were presented in Table 1.

From Fig.4 and Table 1, it was found that the relative intensity of the C-N stretch mode in SERS was weaker than that in NRS. According to the above-mentioned "surface selection rule" [9,10], it implied that MB molecules were adsorbed "lying-down" on the silver surface. While in the presence of Cl^- ion, the intensity of this mode increased. It might be due to the adsorbed MB molecules transformed from "lying-down" to "end-on" molecular state under the influence

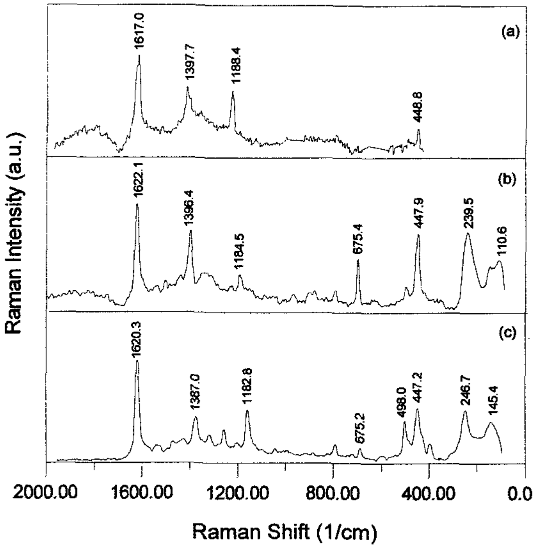


FIG.4 Raman spectra of Methylene Blue (MB)

(a) Normal Raman spectrum (NRS) of MB

(b) SERS of MB on HNO_3-etched silver surface ([MB] = 3.5×10^{-5} mol/L)

(c) SERS of MB (3.5×10^{-5} mol/L) in the presence of Cl^- ions (0.01 mol/L)

TABLE 1: SERS modes assignment and signal intensity for MB adsorption

	NRS	SERS	SERS in presence of Cl^-
ring stretch (cm^{-1})	1617.0 (s)	1622.1 (s)	1620.3 (s)
CH_3 deformation (cm^{-1})	1397.7 (s)	1396.4 (s)	1387.0 (m)
C-N stretch (cm^{-1})	1188.4 (m)	1184.5 (w)	1182.8 (m)
Ring out-of-plane bend (cm^{-1})		675.4 (s)	675.2 (w)
Ag substrate (cm^{-1})		239.5 (wide, m) 110.6 (wide, m)	246.7 (wide, m) 145.4 (wide, m)

Note: s – strong; m - medium; w - weak.

of Cl^- ions. In addition, the change of the 675.2 cm^{-1} peak which was attributed to the out-of-plane bending of the aromatic ring also confirmed this state transformation. The intensity of this mode was stronger in SERS indicating the molecular plane was parallel to the surface. While adding Cl^-, the peak grew smaller showed that more MB molecules flipped to "end-on" positions with the molecular plane perpendicular to the surface.

Additionally, the peak of Ag substrate in SERS shifted obviously after Cl^- was added, which told that an interaction between Cl^- ion and Ag surface existed. In reference to the study of pyridine, the lone-pair electrons of the nitrogen atom contained in the heterocycle of MB, might well be coordinated with the unoccupied orbit of silver surface atoms to form a complex adsorbed perpendicularly to the surface. The existence of the Cl^- ion may stabilize the complex, which caused the adsorption states of MB to convert from the flat mode to the perpendicular mode. This may also be the possible cause for the change of SERS signal in the presence of the Cl^- ion.

CONCLUSIONS

SERS is a powerful tool for probing surface adsorption states. It can be used to discriminate different adsorption states in surface adsorption or surface reaction.

With analysis of SERS spectral lines, we found that at a rather low concentration or at the beginning of adsorption, pyridine molecules tended to adsorb flatly on electrochemically-disposed silver surfaces. While at a sufficiently high concentration, the flat mode was inclined to convert to the perpendicular mode which was more stable.

The flat adsorption states were favored for MB molecules adsorbed on HNO_3-etched silver surfaces at a low concentration. But as the concentration of

Cl⁻ ion increased, the interaction between the Cl⁻ ion and the silver surface precipitated the adsorption of MB to convert from a "lying-down" state to an "end-on" state.

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