

Surface Raman spectroscopic investigation of pyridine adsorption at platinum electrodes—effects of potential and electrolyte

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Surface enhanced Raman spectra of pyridine (Py) at Pt electrodes have been investigated as a function of potential and supporting electrolyte. The results show a large difference from those reported for coinage metal electrodes of Ag, Au and Cu, emphasising the effective involvement of chemical enhancement on Pt surfaces. At very negative (or positive) potentials, Raman spectra show the competitive coadsorption of hydrogen (or oxygen-containing species) with Py, and in acidic solutions, PyH⁺ ions prefer to dissociate into Py adsorbed on Pt surfaces even in the presence of chloride ions. The differences in the surface bonding strength for Py on Pt and coinage metal electrodes are explained in terms of the different electronic configurations of the metals.

1 Introduction

Following the initial discovery of surface enhanced Raman scattering (SERS) from pyridine at electrochemically roughened Ag electrodes in the 1970s, the main SERS studies have concerned adsorption processes at molecular levels.^{1–10} Throughout, pyridine (Py) has been used most frequently as the indicator adsorbate, playing the role of a model system in an attempt to fully understand the SERS mechanism. In general, adsorption is controlled by the nature of the substrate, the electrode potential, the presence of a coadsorbate, concentration of the adsorbate and often by the electrolyte pH. Therefore, effects of these variables on the SERS of the adsorbates are of special interest in the SERS studies of electrochemical interfaces. However, for the past two decades, application of the SERS technique to the adsorption process has been overwhelmingly reported on the free-electron-like coinage metals of Ag, Au and Cu. With this serious limitation, SERS has not been regarded as a general tool for vibrational investigations of diverse metal surfaces.

Platinum is probably the most important and widely used electrode material in electrochemical research in view of its high electrocatalytic activity and much wider polarizable potential window. Accordingly, the utilisation of the SERS technique to probe the electrosorption process at the Pt electrode is, to some extent, more attractive than at any other electrode. However, very few surface Raman spectroscopic investigations of Py at Pt electrodes have been reported, indicative of the inherent difficulty in probing the SERS of this kind of electrode.^{11–13} Fleischmann *et al.*¹¹ presented one surface Raman spectrum of Py at a platinized Pt electrode with a low signal to noise ratio using near infrared FT-Raman spectroscopy, but no potential dependent spectra were reported; Bilmes *et al.*¹² gave the first spectra–potential profile for Py at electrodeposited Pt electrodes. Unfortunately, due to the limitation of their Raman instrumentation and the instability of their electrodes, most spectra were confined to the range from 950 to 1050 cm⁻¹ and the measurable potential window

was limited to between –0.43 and 0.65 V. Thus, some interfacial information could be overlooked. Moreover, the prolonged acquisition period they had to use (15 to 20 min for a spectrum) could result in a distortion of surface spectra to some extent, especially for their unstable, weak SERS-active Pt electrodes. As a consequence, little knowledge has ever been extracted from surface Raman spectroscopy concerning the adsorption of the SERS model species of Py at Pt electrodes.

Recently, with the latest combined advantage of the Raman instrumental sensitivity and surface roughening pre-treatment, stable and high quality surface Raman spectra of Py at Pt electrodes have been obtained over much wider spectral and potential ranges with a much shorter acquisition time in our laboratory.^{14–16} We have also been able to obtain, for the first time, high quality surface Raman spectra for Py, pyrazine and some inorganic species adsorbed on a series of bare transition metals including Ni, Co, Fe, Pd, Ru and Rh electrodes.^{14–20} Thus, a detailed surface Raman spectroscopic study is now practicable for the electrosorption processes occurring at non-traditional SERS active electrodes. In the present work, this is extended to a more detailed investigation of a series of variables on the SERS of Py adsorbed at roughened Pt electrodes. Firstly, we will report Raman spectroscopic evidence of the competitive coadsorption of Py and hydrogen (or oxygen-containing species) on the Pt surface over a very negative (or positive) potential range. Then, Py concentration, solution pH and the nature of supporting anions will be probed for their effect on Py adsorption behaviour.

2 Experimental

Raman spectra were obtained using a confocal microprobe Raman system (LabRam I). The microscope attachment was based on an Olympus BX40 system and used a 50 × long working-length (8 mm) objective. A holographic notch filter was equipped to filter the excitation line and an 1800 g mm⁻¹ holographic grating was employed to disperse the scattered light. A CCD, cooled thermoelectrically, was used as the detector. The excitation wavelength was either 632.8 nm with

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a power of 12 mW from an internal He–Ne laser or 514.5 nm with a power of 30 mW from an external Ar⁺ laser (Innova 200). The spot size focused on an electrode surface was ca. 5 μm . The slit and pinhole in experiments were 100 and 600 μm , respectively. With the 1800 g mm⁻¹ holographic grating, the spectral resolution was 1.5–3.0 cm⁻¹ varying with the spectral region. A Raman spectrum was recorded normally after keeping a Pt electrode at a potential for 2 min, and the potential profile of Raman spectra was acquired by moving the potential stepwise in either a positive or negative direction. The spectral acquisition time was 50 s for Pt electrodes and 1 s for Ag, Au and Cu electrodes.

A pure polycrystalline Pt rod ($\phi = 3.5$ mm) was embedded in a Teflon sheath and used as the working electrode. The unique surface roughening pre-treatment in H₂SO₄ has been described in detail elsewhere.^{14,15,20} Before Raman measurements, the roughened electrode was subjected to potential cycles between ca. -0.30 and +1.25 V at 0.2 V s⁻¹ until a typical and reproducible hydrogen adsorption/desorption peak was obtained in order to remove unstable atoms or clusters and ensure a clean surface. The charge quantities of hydrogen adsorption/desorption in the cyclic voltammogram can be used to estimate the surface roughness factor (R), assuming an equivalent charge quantity of about 0.21 mC cm⁻² for monolayer adsorption of H on an ideally smooth Pt surface.¹⁵ The roughened electrode was rinsed thoroughly and transferred immediately to a spectroelectrochemical cell containing 0.01 M Py and 0.1 M KCl (NaClO₄ or NaF) for measurement. The surface enhancement factor of the roughened electrode was evaluated to be one to two orders of magnitude, depending on the surface roughening procedure.¹⁵ A large Pt ring served as the counter electrode. All potentials are quoted *versus* a saturated calomel electrode (SCE). All chemicals used were of analytical-reagent grade and the solutions were prepared using triply distilled water.

3 Results and discussion

3.1 Competitive coadsorption of Py with H or O-containing species

Coadsorption of multiple species is a well-recognised phenomenon at electrochemical interfaces. In general, this can be divided into parallel coadsorption and induced coadsorption.^{21,22} Conventional electrochemical techniques, such as differential capacity measurements, cannot adequately characterise the complicated coadsorption process. In contrast, surface Raman spectroscopy may provide insight into such a process at the molecular level.^{21,22} Specifically, for Pt electrodes that display a wide inert potential window, the adsorption of H or O-containing species (*vide infra*) occurs as a result of the dissociation of water molecules at very negative or positive potentials. Below, we will investigate the

coadsorption behaviour of Py and H or O-containing species onto Pt electrodes from aqueous Py solutions, and show how the potential influences the adsorption behaviour of Py, using surface Raman spectroscopy.

Fig. 1 shows the potential dependent surface Raman spectra from a roughened Pt electrode ($R = 258$) over a negative potential range in 0.01 M Py and 0.1 M KCl solution. The broad band at about 1643 cm⁻¹ is due to the bending vibration of bulk water. At negative potentials in the range -0.2 to -0.8 V, the surface Raman spectrum is dominated by five characteristic bands of Py, *i.e.*, 641 (ν_{6b}), 1010 (ν_1), 1210 (ν_{9a}), 1565 (ν_{8b}) and 1595 cm⁻¹ (ν_{8a}). All these bands are assigned to in plane vibration modes (see Table 1). From -0.8 to -1.0 V, a broad band for the Pt–H vibration emerges at ca. 2046 cm⁻¹^{14,17} together with the bands of adsorbed Py. It seems to be the first surface Raman spectra obtained of the coadsorption of Py and H on a metallic electrode in electrochemical environments. As can be seen from Fig. 1, the surface H signal increases while the surface Py signal decreases with increasing negative potential. At -1.2 V, the Pt–H signal reaches a maximum, accompanied by the disappearance of the surface Py signal. Thus, the potential dependent spectra show clearly how the potential influences the competitive coadsorption of Py with H at Pt electrodes. It should be noted that the vibrational frequencies for both species do not shift appreciably for the condition of either sole adsorption or coadsorption. This means that the interaction between the two coadsorbates is much weaker in comparison with their respective interaction with the Pt electrode. Hence, the

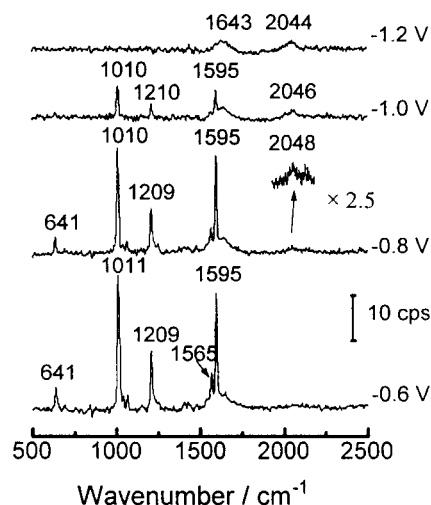


Fig. 1 Surface Raman spectra from a roughened Pt electrode ($R = 258$) in 0.01 M Py + 0.1 M KCl, showing the potential dependent competitive coadsorption of Py and H over a negative potential range. The excitation line is 514.5 nm, the integration time is 50 s.

Table 1 Wavenumbers and Raman intensities of some ring vibrations of Py at Pt electrodes and in aqueous solution, and the corresponding ring vibration modes of benzene

Adsorbed Py on Pt			Aqueous Py		Py		Benzene liquid	
ν/cm^{-1}	I^a		ν/cm^{-1}	I^a	Symmetry class (C_{2v})	Wilson labeling	ν/cm^{-1}	Symmetry class (D_{6h}) ^b
	-0.6 V	0.2 V						
1595	(67)	(30)	1593	(8)	a_1	ν_{8a}	1596	e_{2g}
1565	(18)	(15)	1575	(6)	b_2	ν_{8b}	1596	e_{2g}
1209	(40)	(10)	1220	(7)	a_1	ν_{9a}	1178	e_{2g}
1037	(3)	—	1036	(58)	a_1	ν_{12}	1008	e_{1u}
1010	(100)	(100)	1003	(100)	a_1	ν_1	992	a_{1g}
641	(18)	<2)	654	(6)	b_2	ν_{6b}	604	e_{2g}

^a Intensities relative to the most intense band for each potential ^b Ref. 30.

coadsorption of the two species can be regarded as the parallel type of coadsorption. Otherwise, a reverse situation could be expected in the case of induced coadsorption.^{21,22} This phenomenon can be mainly assigned to the strong interaction between H and Pt as well as the large number of adsorption sites for H on a highly roughened Pt electrode. It may be necessary to point out that although far more intense surface Raman signals of adsorbed Py can be detected on roughened Au, Ag and Cu electrodes than on a Pt electrode, no such spectra of coadsorbed H species have been reported, mainly due to a much weaker interaction of H with those coinage metals at negative potentials.

Over the positive potential range ($\geq ca. 0.5$ V) Pt atoms, PtO_{ads} and PtO species coexist on a Pt electrode surface. For example, at 1.0 V in H₂SO₄, the surface composition of Pt anodes consists of 39% Pt, 37% PtO_{ads} and 24% PtO, whereas at 0.5 V it consists of 56% Pt, 39% PtO_{ads} and 5% PtO.^{23,24} In neutral solution, PtOH_{ads} is also possibly present on the surface. In this paper, 'O-containing species' is tentatively used to represent various oxygen species (O_{ads}, OH_{ads} and O) on Pt surfaces as a whole, and for convenience, PtO is regarded as a special adsorption form although in fact the interaction between Pt and O is much stronger for PtO than for PtO_{ads}. The wavenumbers of PtO, PtO_{ads} and PtOH_{ads} have not yet been determined unambiguously under electrochemical conditions due to the fact that these bands are generally overlapped and are exhibited as a broad peak ranging from 480 to 600 cm⁻¹. The band position depends on the crystal facets and surface species as hinted from spectroscopic measurements in UHV.²⁵ In the present study, NaF was chosen as the supporting electrolyte in order to eliminate the influence of specifically adsorbed anions that may exhibit the Pt-anion vibration in the same frequency region. Fig. 2 shows that a broad peak at *ca.* 570 cm⁻¹ emerges at +0.6 V and increases in intensity with the positively moving potential, which results from O-containing species formed at the Pt electrode. In addition, the surface Py signal can still be seen at this potential. According to ref. 26, Py may be adsorbed either on Pt atoms or platinum oxides. The former configuration corresponds to the parallel coadsorption of Py with O-containing species on the Pt surface. In order to determine the adsorption configuration of Py at such a positive potential, we further measured the time-resolved surface Raman spectra of Py upon a potential step from the open circuit potential to +0.6 V (see Fig. 3). The time-dependent spectra show that the

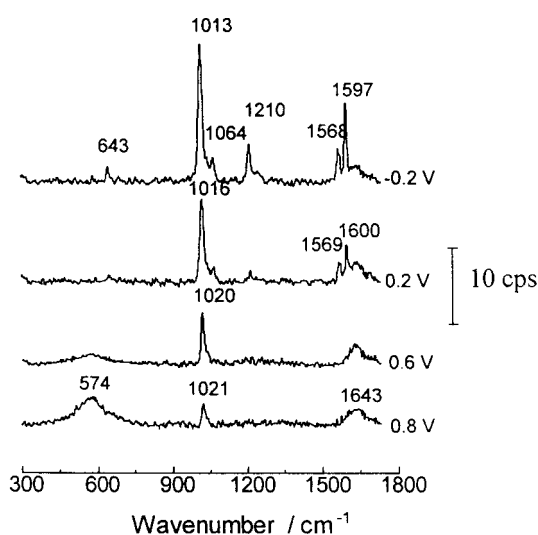


Fig. 2 Surface Raman spectra from a roughened Pt electrode ($R = 258$) in 0.01 M Py + 0.1 M NaF, showing the potential dependent competitive coadsorption of Py and O-containing species over a positive potential range. The excitation line is 514.5 nm, the integration time is 50 s.

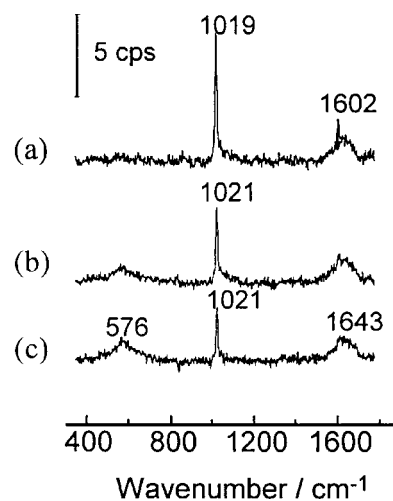


Fig. 3 Time-dependent Raman spectra showing the competitive coadsorption of O-containing species and Py at a roughened Pt electrode ($R = 150$) in 0.01 M Py + 0.1 M NaF as the potential steps from +0.385 (open circuit) to +0.6 V: (a) +0.385 V; (b) +0.6 V, 1st acquisition; (c) +0.6 V, 2nd acquisition following (b). The excitation line is 514.5 nm, the integration time is 50 s.

surface signal of adsorbed Py decreases with increasing O-containing species, indicating that the adsorbed Py is replaced by the O-containing species gradually formed at +0.6 V. As can be seen in Fig. 3, the characteristic frequency of the ν_1 band for Py has a slight blue-shift of 2 cm⁻¹ and is not markedly influenced in the presence of the O-containing species. Therefore, the competitively parallel coadsorption configuration is assumed to be preferable. The assumption agrees well with the finding that the ratio of Pt atoms to O-containing species on the Pt surface decreases with increasing potential.²³ Furthermore, it is notable that in the negative potential region as shown in Fig. 1 the frequencies and relative intensities of the bands of Py remain almost constant although the absolute intensities change significantly with potential. By contrast, in the positive potential region, both the frequencies and relative intensities change considerably with increasing positive potential (see Fig. 2). This infers that Py bonds more strongly to the substrate when the surface is positively charged and the adsorption orientation may change when the potential crosses the potential of zero charge (p.z.c.) of about +0.1 V, which will be discussed in more detail in the next section.

The roughened Pt electrode was surprisingly found to be significantly better than roughened Ag and Cu electrodes and reasonably better than the roughened Au electrode in terms of stability and reversibility for potential- and time-dependent SERS measurements. In general, after three coinage metal electrodes are used for SERS measurements, they have to be re-polished and re-roughened in the KCl solution for the next experiment. By contrast, the Pt electrode can be reused many times without a significant loss of surface Raman signals for a week or more. Before each Raman measurement, the roughened Pt electrode needs only to be electrochemically cleaned in an H₂SO₄ solution to attain a stable and reproducible cyclic voltammogram exhibiting a typical adsorption/desorption peak relating to the electroadsorption and electrodesorption of the hydrogen monolayer. The electrochemical cleaning procedure ensures that the Pt surface property is the same for each experiment. Fig. 4 demonstrates that the Pt electrode has a very good potential reversibility in terms of the SERS intensity in an NaClO₄ solution. When the potential was moved from -0.4 to -1.1 V, the SERS signal of adsorbed Py vanished completely, indicating desorption of Py from the surface. Only a weak band at 934 cm⁻¹ of ClO₄⁻ from the solution phase can be detected at that potential. As the potential was moved back to the potential region

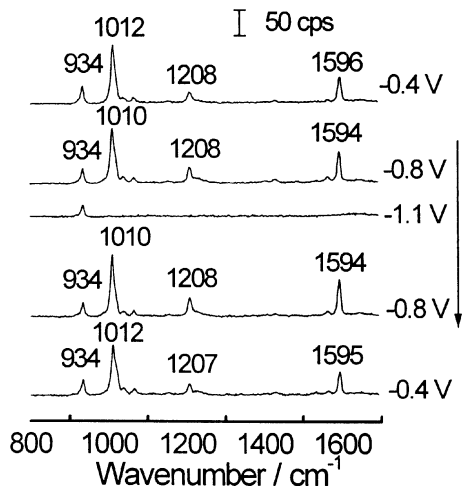


Fig. 4 Surface Raman spectra from a roughened Pt electrode ($R = 258$) in 0.01 M Py + 0.1 M NaClO₄. The excitation line is 632.8 nm, the integration time is 50 s.

of Py adsorption, the SERS signal would be fully recovered. As is known, after such a negative potential excursion to the potential of Py desorption, SERS signals are almost irreversibly lost for Ag and Cu electrodes and the signal can only be regained to some extent, *e.g.*, less 50%, in intensity for Au electrodes. This could be mainly due to the fact that the Pt atom is considerably less mobile at the surface and the roughening procedure is carried out in H₂SO₄ rather than in KCl solutions. The electrochemical cleaning procedure is certainly a help to the better potential reversibility. This electrode property for Pt is vitally important for the SERS study as it ensures that the experimental results are reasonably representative of those for the entire surface rather than for some unstable SERS active sites. Therefore, the SERS data can correlate well with the electrochemical results.

3.2 Different effects of surface enhanced mechanism(s)

In addition to the spectral features mentioned above for Py adsorbed at Pt electrodes, some distinctive differences such as the frequency–potential profiles for Pt and the coinage metals (Ag, Au and Cu) should be noted (see Fig. 5). For Pt, the frequency of the ν_1 mode increases almost linearly from *ca.* 1010 cm⁻¹ at -0.8 V to about 1023 cm⁻¹ at 1.0 V where some platinum oxides are formed. The large tuning rate of

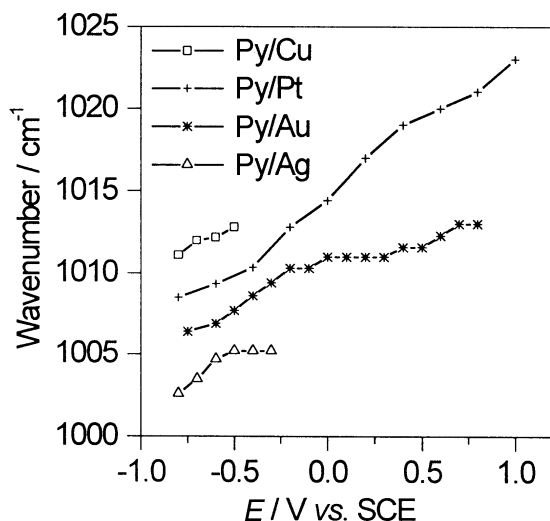


Fig. 5 Frequency–potential profiles for the ν_1 mode of Py adsorbed at roughened Cu, Au, Ag and Pt electrodes in 0.01 M Py + 0.1 M KCl. The excitation line is 632.8 nm.

frequency with potential is found to be $dv/dE \approx 7 \text{ cm}^{-1} \text{ V}^{-1}$ while for the coinage metal systems the frequency shift upon potential is considerably less in the whole potential region studied. These results illustrate that the interaction of Py with coinage metals is relatively weak, and Py can bond more strongly to both Pt and its partially oxidised surfaces, probably involving an orientation change. It may also reveal the different roles played by the surface enhancement mechanism(s) for the transition and coinage metals.

Most researchers now agree that the surface Raman enhancement (EM) mechanism and a chemical [*i.e.*, charge transfer (CT)] mechanism.^{4–8} However, for different systems, these two very different mechanisms act together in varying proportions which are extremely difficult to be verified and distinguished. The detection threshold for conventional Raman instruments only allows us to detect surface signals with an enhancement factor larger than 10² or 10³. SERS appears to be an all-or-nothing effect as the Raman intensity disappears below the threshold for detection. The present results obtained with a highly sensitive Raman instrument indicate the possibility of studying the diverse metals only having substantially weak enhancement. However, it is very hard at present to explicate thoroughly the above observations, since the possible SERS mechanism(s) for Pt has received far less attention^{27,28} and the systematic study on this aspect has not yet been carried out. Nevertheless, it may be helpful to present a very brief discussion based on the EM and CT models and the adsorption orientation.

There are two ideal configurations for adsorbed Py molecules, *i.e.*, the vertical (or end-on) adsorption and the flat (or face-on) adsorption for Py at Pt electrodes. In the first case, Py molecules are bonded to the Pt surface through the lone pair of electrons localised on the nitrogen atoms, whereas in the second case, the Py ring plane orients parallel to the surface. Using a radioactive-labelling technique, Wieckowski and co-workers²⁹ have concluded that the vertical adsorption is formed at a relatively high concentration of Py in the bulk solution, such as $1.0 \times 10^{-2} \text{ M}$. It can also be inferred from a previous *in situ* UV/VIS spectroscopic study³⁰ that Py molecules are preferably adsorbed with this configuration. Creighton²⁸ has derived the expression for the surface EM enhancement factors for a molecule with a general polarizability tensor adsorbed on the surface of a small sphere, that simulates the roughened surface, in the dipole approximation. He deduced that the b_2 vibration modes of Py are mostly enhanced with the vertical adsorption and the least enhanced for the flat-on adsorption. From the viewpoint of the EM model, the appearance of 641 and 1568 cm⁻¹ bands (b_2 mode) favours the vertical adsorption geometry of Py. The variation of relative Raman band intensities for adsorbed Py with potential may reflect the re-orientation of Py to some extent, such as a degree of inclination of the Py ring plane with respect to the surface. This would result in re-allocation of Raman tensor components and thus a change of relative enhancement factors for different symmetry classes (a_1 , b_2 , a_2 and b_1) and even for different vibrations in the a_1 symmetry class. It is generally accepted that both EM and CT enhancements are involved for the coinage metals with the former being a predominant effect. By contrast, Pt cannot effectively yield EM enhancement due to its complex dielectric constant. The surface plasmon polariton excited by visible laser irradiation is strongly damped by the intrinsic absorption of the bulk metal itself. The surface enhancement factor for Py on the roughened Pt in the present study is only about one to two orders in magnitude.¹⁵ Therefore, it seems reasonable to assume that the CT enhancement mechanism may make a more important contribution to this weak surface enhancement for Py on Pt in comparison with that on the coinage metals.

We have initially found that with lowering the excitation energy, the Raman intensity–potential profile for Py adsorbed at a roughened Pt electrode moves negatively,¹⁵ suggesting the effective involvement of the CT enhancement related to the symmetries of the lowest unoccupied orbitals of Py. It indicates a resonance-like Raman process associated with a photon-driven charge transfer from the Pt metal to the unoccupied π^* orbitals of Py at negative potentials.³¹ On group theoretical grounds, Creighton³² concluded that the vibrational modes of adsorbed Py, which would be expected to be strongly enhanced due to the above CT mechanism, are those which correlate with a_{1g} and e_{2g} modes of benzene.³³ This is in reasonable agreement with our experimental observations for Pt electrodes at negative potentials, as shown in Table 1, where the correlation of some interesting modes with the vibrational modes of benzene is given. Clearly, the abnormal reduction of the ν_{12} band corresponds to the *ungerade* b_{1u} modes of benzene, which from the Jahn–Teller theorem in D_{6h} symmetry, can not participate in excited state relaxation and is one of the Raman-inactive fundamentals. Future systematic investigation is required on the SERS mechanism(s) in order to draw a definite conclusion.

3.3 Effects of the electrolyte anions, pH and the concentration of Py

A large amount of investigation has been conducted to determine the solution effect on the SERS of Py at roughened silver electrodes.^{34–40} It has been claimed that specifically adsorbed anions, for example, chloride ions, are closely linked to the enhancement and stability of SERS signals at Ag electrodes. When the anions desorb, the SERS signals diminish irreversibly.³⁴ Furthermore, Cl^- ions are considered to be essential to obtain the SERS signals of acidified Py species, *i.e.*, PyH^+ .^{35,36} It is of interest to study the effect of electrolyte anion on the SERS of Py at roughened Pt electrodes.

Fig. 6 shows the potential dependence of SERS intensities of the ν_1 band of surface Py obtained from a roughened Pt electrode in 0.01 M Py + 0.1 M KCl and 0.01 M Py + 0.1 M NaClO_4 respectively. There is no substantial difference between the two intensity–potential profiles in Fig. 6. It can be concluded that the SERS of Py at Pt electrodes is essentially independent of the supporting electrolyte anions. Moreover, the stability and reversibility with potential for the SERS signal are much better for Pt than Ag and Cu electrodes in solutions containing specifically adsorbed species such as Cl^- . We have not found a significant reduction of SERS signal even after the Pt electrode undergoes a cathodic excursion as negative as -1.2 V, where all the Py and Cl^- species are desorbed. When the same experiment is performed on Ag or

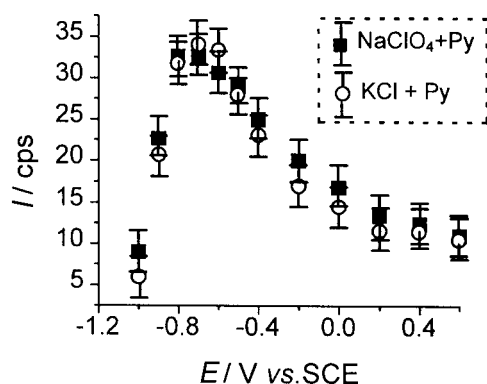


Fig. 6 Intensity–potential profiles for the ν_1 mode of Py adsorbed at a roughened Pt electrode ($R = 150$) in 0.01 M Py + 0.1 M KCl and 0.01 M Py + 0.1 M NaClO_4 respectively. The excitation line is 514.5 nm, the integration time is 50 s.

Cu electrodes, however, the SERS signal is almost quenched irreversibly. As has been mentioned above, the Pt surface structure is much more stable in a wide potential range than that of the coinage metals in electrochemical environments. Furthermore, the electrolyte for the roughening procedure of Pt is free of Cl^- ions, and the additional surface treatment of repetitive cycling the as-roughened Pt electrode in 0.5 M H_2SO_4 before the Raman measurement ensures that nearly all the metastable Pt clusters and atoms are removed. For the coinage metals, Cl^- ions are generally involved in the roughened procedure by oxidation–reduction cycle to get the suitable surface morphology for optimising the SERS signal. As the specifically adsorbed anion to the coinage metals, Cl^- ions are often used as one of the electrolyte components in the SERS studies in order to stabilise the metastable SERS-active sites, particularly at relatively positive potentials. As a consequence, it causes the problem of instability and irreversibility of the SERS effect with respect to the potential change.

The different role of Cl^- on the surfaces of Pt and Ag electrodes can be further seen from the SERS at the Pt electrode immersed in an acidified Py solution. The 0.01 M Py + 0.1 M KCl and the 0.01 M Py + 0.1 M NaClO_4 are adjusted, respectively, by chloric acid and perchloric acid, attaining an acidity of *ca.* pH 2.88. The ratio of PyH^+ to Py in the acidified solution is approximately 303 : 1, calculated from the following equation, *i.e.*,

$$\frac{a_{\text{PyH}^+}}{a_{\text{Py}}} = \frac{k_b a_{\text{H}^+}}{k_w} \quad (1)$$

where $k_b = 2.3 \times 10^{-9}$ and $k_w = 1.0 \times 10^{-14}$ are the base dissociation constant of Py and the dissociation constant of H_2O , respectively. Fig. 7 presents a set of spectra in the selected frequency range for the Pt electrode immersed in acidified 0.01 M Py + 0.1 M KCl solution. Surprisingly, the potential dependent spectra are similar to those measured for a neutral solution, no obvious reduction of SERS intensity and no substantial shift of vibration frequencies at a positive potential can be found, irrespective of the nature of supporting anions. The three bands at *ca.* 1016, 1040 and 1070 cm^{-1} can be assigned to ν_1 , ν_{12} and ν_{18a} vibration modes of adsorbed Py, respectively. These bands can also be found in the SERS from the Pt electrode immersed in neutral Py solution. In contrast, if an Ag electrode is used in the acidified Py solution, the band at 1036 cm^{-1} diminishes almost completely while a new intense band characteristic of PyH^+ at ≈ 1026 cm^{-1} emerges at relatively positive potentials.³⁵ Since the electronic lone pair of nitrogen in pyridinium ion is screened by the complexing proton, it is most likely that PyH^+ is induced by the

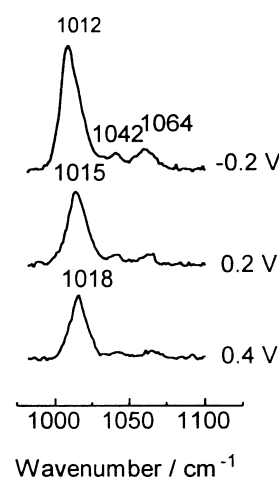


Fig. 7 Surface Raman spectra from a roughened Pt electrode ($R = 90$) in acidified 0.01 M Py + 0.1 M KCl (pH 2.88). The excitation line is 514.5 nm, the integration time is 50 s.

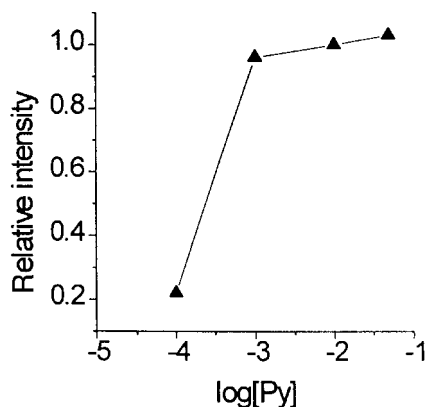


Fig. 8 Dependence of the relative intensity of the ν_1 band for adsorbed Py at a roughened Pt electrode ($R = 90$) on the Py concentration in 0.1 M NaClO₄ + x M Py solutions. The excitation line is 514.5 nm, the integration time is 50 s.

strongly adsorbed Cl⁻ ions through electrostatic force, then coadsorbed at the Ag surface. The coadsorption process could take place for pyridinium ion on top of the specifically adsorbed Cl⁻ ion layer. In contrast to this, the ν_{12} band cannot be detected from the Pt electrode in the same electrolyte. This suggests that Py preferably interacts with Pt atoms instead of with H⁺ through its lone pair of electrons localised on the nitrogen atoms. Therefore, PyH⁺ is unstable on Pt surfaces and may dissociate into H⁺ and Py that is competitively coadsorbed with Cl⁻ on the Pt surface. Two such contrasting cases in surface bonding for Pt and Ag are mainly due to two different electronic configurations of the metal, *i.e.*, d⁹ for Pt and d¹⁰ for Ag. Because of the d-band formation in the solid creating the d-orbital vacancies, Pt can accept Py electron density in a strong donating mode of bonding while the Ag electrode can only have a weak electron-donating type of surface configuration.^{41,42} Monitoring the SERS response to varying bulk Py concentrations can further prove this assumption. Fig. 8 shows the Py concentration dependence of the ν_1 band intensity. It turns out that there is a steep reduction of the band intensity as the Py concentration is decreased to as low as 10⁻⁴ M. Considering that only 3.3 × 10⁻⁵ M of Py are present in the acidified Py solution, we can reasonably assign the nearly unchanged SERS intensity and frequency to the dissociation of PyH⁺ into Py at the Pt electrode, *i.e.*, PyH_{aq}⁺ + (Pt) → Py(Pt) + H_{aq}⁺.

4 Conclusions and remarks

The Pt electrode is one of the most technologically important electrodes for electrochemical applications, and Py is the model adsorbate most frequently used in SERS studies. In this paper, we report the surface Raman spectroscopic investigation on the adsorption behaviour of Py at Pt electrodes over a wide potential range of 2 V, in terms of the effects of potential and solution composition. At very negative (or positive) potentials, the surface Raman spectra can be detected showing the competitive coadsorption of H (or O-containing species) with Py. In an acidified solution (pH 2.8), pyridinium ions tend to dissociate into Py to adsorb on the Pt surface even in the presence of chloride ions, which is different from reported coadsorption of Cl⁻ and pyridinium ions on the Ag surface. The differences in the bonding strength for Py on Pt and Ag electrodes are briefly explained based on their differences in the distribution of d-electrons of two metals, that may change the nature of the surface coordination significantly. The present results indicate that the CT enhancement mechanism seems to make a more important contribution to the weak surface enhancement for Py on Pt in comparison with that on

the coinage metals where the EM enhancement is predominant. It is assumed that the incident photon may drive the charge transfer from the Pt electrode to the unoccupied π^* orbital of Py. Recently, we have also obtained high quality surface Raman spectra for Py adsorbed on many transition metals including Ni, Co, Fe, Pd, Ru and Rh electrodes.^{18,43} The systematic study of a series of transition metal systems will certainly be of great help in gaining deep insights into both the electroadsorption behaviour of Py and the SERS mechanism(s).

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