

ORIENTATIONAL SPECIFICITY OF RAMAN SCATTERING FROM MOLECULES ADSORBED ON SILVER ELECTRODES

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Surface enhanced Raman (SER) spectra of 2-, 3-, and 4-cyanopyridine (2-, 3-, and 4-CP) adsorbed on silver electrodes suggest that the surface enhancement cross section of the CN stretching vibration is strongly dependent upon the orientation of the CN group with respect to the electrode surface.

1. Introduction

Recent reports of anomalously intense Raman scattering from pyridine adsorbed on silver electrode surfaces have stimulated interest in the application of Raman spectroscopy to the study of metal/adsorbate systems in solution as well as in vacuum. The Raman technique is well suited to the study of the solid/liquid interface in situ since UV or visible photons are employed as both exciters and as information carriers and these are transmitted by a variety of materials. Raman spectroscopy, in providing vibrational information, also possesses the molecular specificity required to study adsorbate/surface interactions (bonding) in detail. Until recently, however, the low cross section for normal Raman scattering, combined with the low number of surface scatterers (ca. 2×10^{-14} mole cm^{-2}) had apparently precluded its application as a surface probe. Fleischmann et al. [1] were the first to obtain high quality surface Raman spectra using the Ag/pyridine/KCl system and these results have subsequently been verified by van Duyne and Jeanmaire [2], Albrecht and Creighton [3], and Marinyuk and Lazorenko-Manevich [4]. After refinements of the experimental procedure, van Duyne and Jeanmaire [2] recognized the enormous enhancement (ca. 10^6) of the Raman scattering, extended the study to include other adsorbates, and began a systematic investigation of the enhancement process. Experimental and theoretical endeavors to date have been recently reviewed [5-7].

In an effort to help elucidate the enhancement mechanism, we have examined the surface enhanced Raman (SER) spectra of the isomeric monocyanopyridines. The results indicate that there exists a strong dependence of the enhanced Raman cross section upon the position of CN substitution and hence upon the orientation of the CN group with respect to the electrode surface. These results are analyzed in terms of current models for the enhancement mechanism.

2. Experimental

Cyanopyridines were obtained from Aldrich Chemical Co., Milwaukee, WI, and were purified as follows: 2-cyanopyridine (2CP) was distilled in vacuum, 3- and 4-cyanopyridine (3CP and 4CP) were recrystallized twice from hexane/xylene mixtures and vacuum sublimed immediately before use. Normal Raman spectra of the purified compounds exhibited minimal background fluorescence and correlated well with previously published spectra [8].

In all electrochemical experiments, the concentration of surface active component (cyanopyridine) in the bulk phase was 0.05 M with 0.1 M KCl added as supporting electrolyte. Solutions were prepared with distilled, deionized water (Milli-Q, Millipore Corp., Bedford, MA) and were deaerated by bubbling with prepurified nitrogen.

The Ag(I) complexes of the cyanopyridines were

prepared by adding dropwise a *n*-propanol solution of the corresponding cyanopyridine to an aqueous solution of silver nitrate in a mole ratio (CP/Ag) of 2 to 1. The normal Raman spectra obtained agree well with the previously reported infrared spectra [9]. The Raman spectroelectrochemical cell and Raman spectrometer system have been described in detail elsewhere [6]. All Raman spectra were excited with the 514.5 nm line of an argon ion laser (Coherent Radiation model CR-3). Preliminary electrode surface preparation was accomplished by mechanical polishing with 600 grit alumina and rinsing with distilled water. The electrode was placed in the electrochemical cell and potentiostatted at -0.6 V versus SCE. A single double potential step ($E_1 = -0.6$ V, $E_2 = +0.15$ V) pulse was applied in the presence of the adsorbate. Current passed in the forward step was integrated and the working electrode potential was returned to E_1 after 20 mCoul/cm² of charge had passed. Electrode surfaces prepared in this fashion gave rise to intense, reproducible SER spectra.

3. Results

The SER spectra of 2CP, 3CP, and 4CP are shown in fig. 1. The most striking feature is the intensity of

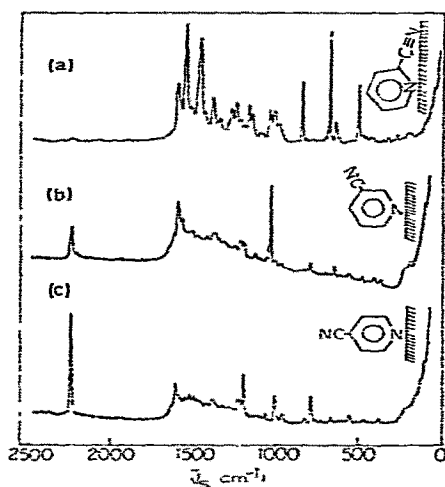


Fig. 1. SER spectrum of (a) 2-cyanopyridine, (b) 3-cyanopyridine, (c) 4-cyanopyridine; all adsorbed on polycrystalline Ag wire electrodes. Excitation: 514.5 nm, power 100 mW, slits 2 cm^{-1} , -0.6 V.

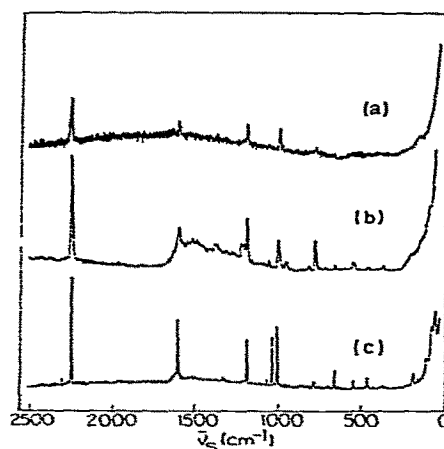


Fig. 2. 4-cyanopyridine. (a) NR spectrum, 0.25 M aqueous solution, 150 mW, 514.5 nm, 2 cm^{-1} slits; (b) SER spectrum -0.6 V, 100 mW, 514.5 nm, 2 cm^{-1} slits; (c) $\text{Ag}(4\text{CP})_2\text{NO}_3$ solid, 50 mW, 514.5 nm, 2 cm^{-1} slits.

the CN stretching vibration ($\approx 2240\text{ cm}^{-1}$) compared with the intensity of the ring breathing modes near 1000 cm^{-1} . The rapid fall-off in intensity for the series 4 to 3 to 2 is indicative of an orientation dependence of the enhancement mechanism.

In fig. 2, the NR spectra of aqueous 4CP and solid $\text{Ag}(4\text{CP})_2\text{NO}_3$ are reproduced along with the SER spectrum at -0.6 V. As was the case for pyridine [2],

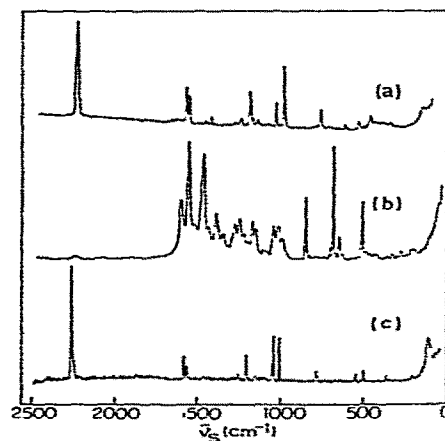


Fig. 3. 2-cyanopyridine. (a) NR spectrum, 0.25 M aqueous solution, 350 mW, 514.5 nm, 2 cm^{-1} slits; (b) SER spectrum -0.6 V, 100 mW, 514.5 nm, 2 cm^{-1} slits; (c) NR spectrum of $\text{Ag}(2\text{CP})_2\text{NO}_3$ solid, 15 mW, 514.5 nm, 2 cm^{-1} slits.

the bands in the SER spectrum correlate well with those in the NR spectra of bulk phases and one can estimate an enhancement factor of 10^5 to 10^6 for the CN stretch. 3CP exhibits much the same behavior as 4CP.

Bulk phase and surface enhanced Raman spectra of 2CP are shown in fig. 3. It can readily be seen that the SER spectrum is quite different from either bulk phase spectrum. The strong CN vibration in the solid complex and aqueous solution is barely visible in the surface spectrum (i.e., is enhanced by a factor less than 10^4) and there is no one-to-one correlation between bands in the bulk phases and on the surface. This is especially noticeable in the 500 to 1000 cm^{-1} region.

To examine the CN intensity more quantitatively, one can compare the intensity ratios (CN/ring breathing) for cyanopyridines in all environments. These ratios are given in table 1. While the CN intensities are approximately the same for 3CP and 4CP in the bulk phases, the CN intensities on the surface show an eightfold decrease on going from substitution in the four position to the three position and a further fivefold decrease on going from three to two. The complexity of the 2CP SER spectrum makes such comparisons difficult on an absolute scale but the trend is unmistakable.

Care must be taken in interpreting these intensity ratios in terms of orientation. The assumption implicit here is that the mode of bonding is the same for all three isomers. For purposes of discussion we have assumed that the cyanopyridines are bound to the surface via the pyridine nitrogen as opposed to the nitrile nitrogen. This assumption seems reasonable, at least for the 3CP and 4CP, but the 2CP requires closer examination. Table 2 lists the CN stretching frequencies

Table 1
Raman intensity of the CN stretching vibration relative to the ring breathing mode for cyanopyridines in various environments

Compound	$I_{\text{CN}}/I_{\text{ring}}$		
	aqueous soln	SERS -0.6 V	$\text{Ag}(\text{r-CP})_2\text{NO}_3$ solid
4CP	2.24	3.96	1.79
3CP	2.26	0.46	1.65
2CP	1.55	0.1	2.56

Table 2
CN stretching frequencies in cyanopyridines measured versus Ne lamp frequency standard ($\pm 2\text{ cm}^{-1}$)

Compound	$\tilde{\nu}_{\text{CN}} (\text{cm}^{-1})$		
	aqueous soln	SERS -0.6 V	$\text{Ag}(\text{r-CP})_2\text{NO}_3$ solid
4CP	2249	2238	2245
3CP	2242	2237	2238
2CP	2245	2246 (broad)	2262

for the cyanopyridines in all three environments.

One observes negative shifts on going from aqueous solution to SER for both 3CP and 4CP but 2CP shows a small positive shift. If one compares CN frequencies in the Ag complexes, one observes a large positive shift to 2262 cm^{-1} for the 2CP case which has been interpreted as being indicative of nitrile bonding in this complex [9]. The complexity of the 2CP SER spectrum combined with the observed upshifting of the CN stretching frequency would seem to indicate that the bonding of 2CP to the electrode surface may involve coordination via both the pyridine and the nitrile nitrogens.

As in the case of pyridine SER, the cyanopyridine surface spectra are potential dependent and preliminary studies indicate that 2CP is adsorbed strongly even at quite negative potentials (-1.0 V). This is in contrast to pyridine or 3CP where SER intensity falls off significantly as the potential is moved cathodically from the potential of zero charge ($\text{pzc} = -0.7\text{ V}$ for Ag). This too seems to indicate a stronger chemisorption bond to the silver surface in the case of 2CP.

It should also be noted that over the anodization potential range there was no oxidation or reduction of any of the cyanopyridines [10]. Electrochemical experiments carried out using silver working electrodes demonstrate that 4CP can be reduced at -1.1 V versus SCE on a silver electrode while monitoring the SER spectrum [11].

4. Discussion

The observed orientational dependence of the enhanced Raman intensity of the CN stretching vibrations in cyanopyridines can be interpreted in the light of the

image field model proposed by King et al. [12]. In a classical picture of Raman scattering one can consider the Raman scattered light as having originated from an oscillating dipole induced by the incident electromagnetic radiation. For the special case of Raman scattering by a molecule adsorbed on a metal surface, the incident light contains both direct and reflected components and the Raman scattering arises from both the dipole induced in the molecule and from the image dipole of that molecule in the metal surface. For components of the radiating dipoles parallel to the metal surface, the induced molecular and image dipoles are exactly out of phase and cancel at large distances, whereas the perpendicular components are in phase and constructively contribute to the scattered intensity. Hence one expects intensity enhancements via an image field mechanism to be stronger for those modes which have a large projection onto the perpendicular.

If one assumes all other factors equal in comparing the CN intensities of the cyanopyridines, one might expect the relative magnitudes to be related by:

$$I_{\text{CN}}^{\text{SERS}} = EF \cos^2 \theta I_{\text{CN}}^{\text{soln}}, \quad (1)$$

where θ is the angle between the CN bond axis and the z axis perpendicular to the metal surface and EF is the SERS enhancement factor which has been determined experimentally as 10^6 for pyridine [13]. In order to apply this model and calculate relative CN intensities one needs to assume:

$$I_{\text{ring}}^{\text{SERS}} = EF I_{\text{ring}}^{\text{soln}}, \quad (2)$$

then one can easily calculate CN/ring intensity ratios to compare with the experimental values of table 1, using

$$I_{\text{CN}}^{\text{SERS}} / I_{\text{ring}}^{\text{SERS}} = \cos^2 \theta I_{\text{CN}}^{\text{soln}} / I_{\text{ring}}^{\text{soln}}. \quad (3)$$

Estimated angles between the CN bond and the surface normal θ and the calculated intensity ratios are given in table 3.

The experimentally observed orientational dependence is stronger than predicted on the basis of this crude model but is otherwise the same direction (order of CN intensities 4 to 3 to 2), and illustrates the strong orientational selectivity of SERS. Bonding interactions of the nitrile group in 2CP, as mentioned above, may be responsible for a different bonding geometry for that molecule. Preliminary experiments also show [13] that the CN intensity in 2CP is dependent upon surface

Table 3

Raman intensity of the CN stretching vibrations in SER spectra of cyanopyridines calculated by eq. (3)

Compound	θ (deg)	$\cos^2 \theta I_{\text{CN}}^{\text{soln}} / I_{\text{ring}}^{\text{soln}}$
4CP	0	2.24
3CP	60	0.57
2CP	111 a)	0.20

a) Using space filling models, one can predict that steric interaction of the CN group in 2CP with the metal surface would result in a slight tilting of the molecule in the plane of the ring. Assuming no strong electronic interaction of the nitrile group with the surface, a 9° tilt from the "normal" orientation assumed by pyridine, 3CP and 4CP is expected (see inset fig. 1a).

roughness induced by repetitive anodization; the more roughened the surface, the greater the CN intensity (up to about $0.29 I_{\text{ring}}^{\text{soln}}$). It might also be imagined that the relative enhancements might be a function of the distance of the CN from the electrode surface, although if there is a strong electronic "communication" between the CN and the pyridine ring, one would expect that the distance of the CN group from the surface would not affect the SERS intensity. Since any distance dependence would reduce the intensity of 4CP relative to 2CP, it appears that any distance effects are much weaker than the orientation effects.

A more complete theoretical interpretation of these results requires a SERS theoretical model which goes beyond the point dipole approximation as well as quantitative knowledge about the polarizability tensor and its modulation by CN vibrations. More experimental work is in progress to determine the generality and origin of orientational and symmetry properties of SERS.

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