SURFACE RAMAN SPECTROELECTROCHEMISTRY

PART I. HETEROCYCLIC, AROMATIC, AND ALIPHATIC AMINES ADSORBED ON THE ANODIZED SILVER ELECTRODE

DAVID L. JEANMAIRE * and RICHARD P. VAN DUYNE **

Department of Chemistry, Northwestern University, Evanston, Ill. 60201 (U.S.A.)

(Received 7th October 1976; accepted 12th May 1977)

ABSTRACT

In this work we have verified the remarkable sensitivity of Raman spectroscopy for the study of adsorbed pyridine on a silver surface, and extended its applicability to other nitrogen heterocycles and amines. New bands in the scattering spectrum of adsorbed pyridine have been characterized, which were not previously reported, as well as the Raman intensity response of all the surface pyridine bands as a function of electrode potential. As a result of these experiments, we have proposed a model of the adsorbed species for pyridine in which the adsorption is anion induced, leading to an axial end-on attachment to the electrode surface. The ability to obtain resonance Raman spectra with good signal-to-noise with laser powers less than 1.0 mW, reported here for the first time, opens up possibilities of surface Raman studies with relatively inexpensive laser systems. As laser power requirements are relaxed, reliability is improved, and greater tuning ranges can be achieved for wavelength dependent studies. We previously demonstrated the potential of resonance Raman spectroscopy for monitoring solution kinetic behavior [2], and now have shown that NR as well as RR spectroscopy has sufficient sensitivity to extend the studies of kinetic processes to include those occurring at electrode surfaces.

INTRODUCTION

Interest in the mechanisms of electrochemical reactions has brought about the development of a number of new instrumental techniques for the investigation of the electrode/solution interface which possess high molecular specificity as well as the ability to monitor kinetic behavior [1,2]. Unfortunately, relatively few of these have sufficient sensitivity for the in situ study of electrode surfaces while still retaining the high resolution necessary for molecular specificity. Most of the progress that has been made thus far comes from such spectroscopic techniques as specular reflection [3], optical absorption [4], ellipsometry [5,6], and interferometry [7]. The greatest limitations in these techniques currently are: (1) there are few observables, or there is a difficulty

* 1975 ACS Analytical Chemistry Division Fellow; present address: Eastman Kodak Company, Rochester, N.Y. 14050.
** Alfred P. Sloan Foundation Fellow 1974–1978. To whom correspondence should be addressed.
in relating the observables to molecular parameters; (2) the selection of electrodes, potential range, or solvents is restricted; and (3) there is limited molecular specificity. Consequently, a definite need exists for the development of new spectroscopic methods.

The value of Raman spectroscopy for probing the solution/surface interface was first demonstrated by Hendra et al. for pyridine adsorbed on silver and copper electrodes [8–10]. The vibrational data thus obtained have inherently high resolution and are responsive to the detailed nature of the surface molecular environment and the orientation of Raman active molecules with respect to the electrode surface.

Our interest in the application of Raman spectroscopy to the study of pyridine adsorbed on the silver electrode was to verify the results of Hendra et al. in our laboratory, and to further the evaluation of Raman spectroscopy as a general tool for the study of adsorbed species on electrode surfaces. In view of the surprising intensity of the Raman scattering that we observed in our initial experiments, a systematic investigation was undertaken to determine the parameters influencing the Raman intensity using pyridine as a test molecule. The Raman intensity will be shown to be critically dependent upon: (1) electrode surface preparation; (2) bulk solution pyridine concentration; (3) nature and concentration of the supporting electrolyte anion; and (4) electrode potential. In addition, the time response of the surface Raman signal to a double potential step waveform is reported. It should be noted that, to our knowledge, this is the first example of a Raman intensity vs. time study of any surface process. A survey of a number of organic amines and nitrogen heterocycles indicates that a surface Raman scattering spectrum having a high S/N ratio can be obtained over a wide range of molecular structure variation, and that the sensitivity of the technique can be increased for molecules which absorb strongly at the laser excitation wavelength due to resonance enhancement of the cross section for Raman scattering.

EXPERIMENTAL

Cyclic voltammetry, double potential step chronoamperometry and double potential step chronocoulometry were performed in a “sandwich” type cell designed for semiinfinite diffusion resonance Raman spectrotelectrochemistry. This cell and the appropriate potentiostat have been described previously [1]. An integrator of conventional operational amplifier design along with a comparator and S-R flip-flop was adapted to permit control of the charge passed during electrode anodization experiments [11].

Two Hewlett-Packard Model 3300 function generators provided variable duty cycle, double potential step waveforms in addition to a triangular waveform for input to the potentiostat. A Hewlett-Packard Model 7004B XY recorder and Tektronix Model 564 storage oscilloscope were used for monitoring and recording the electrochemical responses.

Raman signal pulses from the photon counting discriminator were fed into the multichannel scaling input of a Nuclear Data Model 2400 Multichannel Analyzer (MCA). The MCA was pretriggered by a synchronizing pulse from the Hewlett-Packard generators. Double potential step Raman intensity versus time
transients were signal averaged in order to improve their S/N ratio. Raman intensity versus electrode potential curves were acquired in the multichannel scaling mode by applying a ramp potential to the electrochemical cell and acquiring the resulting Raman intensity versus potential profile in the MCA. A large spectrometer bandpass minimized the effects of band frequency shifts with electrode potential. Data stored in the MCA were transferred to a Raytheon 500 computer and plotted with a Complot Model DP-1 plotter.

Laser excitation sources consisting of an Ar⁺ and "jet stream" dye laser have been described previously [12]. Laser power measurements were made with a Coherent Radiation Model 210 broad band power meter. Raman scattered light was collected and analyzed via a 0.75 meter Spex Model 1400-II double monochromator equipped with a cooled (−20°C) RCA C31034 PMT and standard photon counting electronics. Raman spectra were recorded digitally on magnetic tape and processed and plotted by CDC 6400 computer and Calcomp plotter. Raman frequency shifts reported are accurate to ±2 cm⁻¹.

Epoxy resin (Varian Associates Torr-Seal) was used to mask a silver wire electrode to an active planar area of 1 × 4 mm. Before each experiment the electrode was mechanically polished to a mirror finish with 600 mesh Al₂O₃ and rinsed with de-ionized water. This procedure for electrode preparation is one which gives a relatively high surface area [13]. All chemicals were reagent grade, and solutions were deoxygenated by nitrogen bubbling.

RESULTS

Normal Raman spectroscopy of adsorbed pyridine

Prominent spectroscopic features of pyridine in bulk solution and adsorbed.

The normal Raman (NR) spectrum of a silver electrode in an aqueous 0.1 M KCl solution is shown in Fig. 1a. The spectrum consists of broad bands exclusively due to water, which is known to be a weak Raman scatterer, in the region 200 cm⁻¹ to 3500 cm⁻¹. Figure 1b is a NR spectrum of an aqueous solution of 50 mM pyridine and 0.1 M KCl. The most characteristic features of this spectrum are located at 1037 cm⁻¹ and 1005 cm⁻¹ and are due to the pyridine ring breathing modes. Hendra et al. centered their attention exclusively on these bands in their studies of adsorbed pyridine [8–10, 14–16]. A NR spectrum of pyridine adsorbed on an anodized silver electrode from a bulk aqueous solution of 50 mM pyridine and 0.1 M KCl is presented in Fig. 1c. The electrode surface was prepared by an anodization under our standard conditions, which were experimentally determined, and will be discussed in conjunction with the effect of electrode anodization on Raman signal intensity. It is immediately noted that the bands attributed to adsorbed pyridine in this spectrum are many times more intense than the bulk solution pyridine bands shown in Fig. 1b. In addition, one notes that the C–H stretch at 3076 cm⁻¹, almost obscured by water in Fig. 1b, now stands out clearly in Fig. 1c. This spectral feature was not reported by Hendra et al. since their studies were restricted to the region 990–1050 cm⁻¹. The wavenumber shifts for neat pyridine, aqueous pyridine, and adsorbed pyridine are tabulated for comparison purposes in Table 1, and a corresponding comparison of full range spectra is made in Fig. 2. In
Fig. 1. (a) Raman spectrum of a silver electrode immersed in 0.1 M KCl. (b) Raman spectrum of 50 mM aqueous pyridine and 0.1 M KCl. (c) Raman spectrum of pyridine adsorbed on a silver electrode from a bulk solution of 50 mM pyridine and 0.1 M KCl. Electrode potential = −0.2 V vs. SCE. The electrode was prepared by anodizing under our standard conditions as described in the text. All spectra were scanned at 0.3333 Å s⁻¹ with a 2 cm⁻¹ bandpass and a 1.0 s counting interval. Laser powers used were: (a) 200 mW, (b) 450 mW, and (c) 50 mW. An interference filter was used to eliminate plasma line contributions to the spectra.

order to obtain a S/N ratio sufficient to measure normal mode frequencies for aqueous pyridine, a 2.5 M solution was used in place of the 50 mM solution presented in Fig. 1b. Due to the large apparent enhancement in the surface pyridine signal strength, the contribution from the 50 mM bulk solution pyridine signal or the signal due to pyridine adsorbed on the cell window is negligible in Fig. 2c.

Preliminary experiments in our laboratory indicated that the Raman signal intensity due to adsorbed pyridine was strongly dependent on the method of electrode surface preparation. A Raman spectrum of adsorbed pyridine can be obtained from an electrode surface where pretreatment is restricted to mechanical polishing. The intensity of a surface Raman signal due to pyridine adsorbed from a 50 mM aqueous solution at a potential of −0.6 V vs. SCE under these pretreatment conditions is about 10 times stronger than that of the Raman signal from dissolved pyridine in solution. Anodization of the electrode in the presence of pyridine can further increase the surface signal strength
TABLE 1
Fundamental frequencies (cm^{-1}) for pyridine

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Pyridine</th>
<th>Aqueous pyridine (2.54 M)</th>
<th>Adsorbed pyridine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-0.2 V</td>
<td>-0.6 V</td>
</tr>
<tr>
<td>b_2</td>
<td>407 vw</td>
<td>409 vw</td>
<td>239 (broad)</td>
</tr>
<tr>
<td>b_2</td>
<td>601 w</td>
<td>618 vw</td>
<td>623 vw</td>
</tr>
<tr>
<td>a_1</td>
<td>650 w</td>
<td>655 vw</td>
<td>651 w</td>
</tr>
<tr>
<td>b_2</td>
<td>749 vw</td>
<td>751 vw</td>
<td>750 vw</td>
</tr>
<tr>
<td>a_2</td>
<td>886 vw</td>
<td>884 vw</td>
<td>883 vw</td>
</tr>
<tr>
<td>b_2</td>
<td>942 vw</td>
<td>946 vw</td>
<td>941 vw</td>
</tr>
<tr>
<td>a_1</td>
<td>991 vs</td>
<td>1005 vs (0.03)</td>
<td>1008 s</td>
</tr>
<tr>
<td>a_1</td>
<td>1030 vs</td>
<td>1037 vs (0.01)</td>
<td>1036 s</td>
</tr>
<tr>
<td>a_1</td>
<td>1069 vw</td>
<td>1070 vw</td>
<td>1068 w</td>
</tr>
<tr>
<td>b_1</td>
<td>1148 vw</td>
<td>1155 vw</td>
<td>1153 vw</td>
</tr>
<tr>
<td>a_1</td>
<td>1215 w</td>
<td>1221 w</td>
<td>1214 vw</td>
</tr>
<tr>
<td>b_1</td>
<td>1440 vw</td>
<td></td>
<td>1444 vw</td>
</tr>
<tr>
<td>a_1</td>
<td>1483 w</td>
<td>1491 vw</td>
<td>1489 vw</td>
</tr>
<tr>
<td>b_1</td>
<td>1574 w</td>
<td>1578 w</td>
<td>1571 w</td>
</tr>
<tr>
<td>*</td>
<td>1597 w</td>
<td>1598 w</td>
<td>1595 w</td>
</tr>
<tr>
<td>*</td>
<td>2366 vw</td>
<td></td>
<td>2212 vw</td>
</tr>
<tr>
<td>*</td>
<td>2454 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>2873 vw</td>
<td>2885 w</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>2906 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>2922 vw</td>
<td>2923 w</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>2858 w</td>
<td>2968 w</td>
<td>2960 w</td>
</tr>
<tr>
<td>a_1</td>
<td>3059 s</td>
<td>3076 s</td>
<td>3067 s</td>
</tr>
<tr>
<td>*</td>
<td>3146 w</td>
<td>3154 w</td>
<td>3142 w</td>
</tr>
<tr>
<td>*</td>
<td>3175 w</td>
<td>3189 w</td>
<td>3186 w</td>
</tr>
</tbody>
</table>

* = Combination band. Band symmetry assignments are from [17] and [18]. Numerical values in parentheses are depolarization ratios.

by factor as great as fifty. Addition of pyridine following the electrochemical anodization produces a signal increase equivalent to that produced when the anodization is carried out in the presence of pyridine.

The effect of electrode anodization on the surface Raman signal intensity.
While frequencies and relative intensities of adsorbed pyridine bands are unaffected by the anodization process, we have found that pyridine Raman intensity relative to a non-adsorbed internal standard is critically dependent upon the nature of the method of anodization, with key parameters being: (1) the extent of charge passed during anodization; (2) the bulk pyridine concentration; and (3) the nature of the supporting electrolyte anion and its concentration.

In the experiment of Hendra et al., the silver electrode was subjected to
cyclic linear sweeps between the potential limits of 200 mV and -300 mV (vs. SCE) for 15 min, during which the formation and reduction of silver chloride etched the silver surface. In contrast, our studies have shown such a time-consuming process of anodization to be unnecessary, in that comparable or superior signal intensities were obtained with an anodization time of only two seconds or less. To define more quantitatively the effect of the anodization process on the Raman intensity of adsorbed pyridine, a double potential step anodization procedure was devised. A single, double potential step was used, having an initial potential step from -0.6 V (vs. SCE) to +0.2 V until the passage of a predetermined amount of charge occurred, whereupon the potential was automatically returned to its initial value of -0.6 V. The Raman signals appeared only after the potential step causing reduction of the silver chloride was complete. Efficiencies of charge recovery in the reverse step were better than 0.2% for forward step transfers of 25.0 mC cm\(^{-2}\) or less with KCl as the supporting electrolyte. For charge transfers above 50 mC cm\(^{-2}\) the AgCl layer becomes thick enough so that the efficiencies of charge recovery in the reverse...
step decrease appreciably. In general, the Raman signal due to adsorbed pyridine increases with the extent of charge passed in the forward step up to 50 mC cm$^{-2}$. Beyond 50 mC cm$^{-2}$ the intensity measurements become erratic due to the decreased efficiency of charge recovery. The effect of extent of charge transferred will be discussed more quantitatively below. To enable the study of Raman intensity as a function of other parameters, a standard amount of charge to be passed in the forward step of anodization was chosen. A value of 25.0 mC cm$^{-2}$ provided a near maximum in the intensity of adsorbed pyridine and allowed good reproducibility between separate experiments.

A cyclic voltammetric investigation of the anodization process is shown in Fig. 3. The solid trace is a first scan voltammogram on a polished silver electrode with 0.1 M KCl as a supporting electrolyte. The dashed curve represents the change caused by the addition of 50 mM pyridine to the cell. At a sweep rate of 1.0 V s$^{-1}$ two waves are observed now on the reverse scan. At slower sweep rates the two waves merge and approach the solid trace. The form of the cyclic voltammogram is not a strong function of the limits of the potential scan, and for the anodization process a positive limit of +0.2 V was chosen to provide a rapid anodization without driving the potentiostat into current saturation for a significant fraction of the forward step time. The activity of pyridine in the cyclic voltammogram can be explained as being due to the formation of the complex Ag(PY)$^+$ in aqueous solution. The second wave at a more positive potential in the reverse sweep of the cyclic voltammogram then corresponds to reduction of this species.

An examination of the Raman signal intensity of the 1006 cm$^{-1}$ band due to adsorbed pyridine as a function of pyridine bulk concentration was carried out using our standard anodization procedure for electrode preparation. A plot

![Graph](image1)

**Fig. 3.** First-scan cyclic voltammogram of the anodization process. The solid trace is on a polished silver electrode with 0.1 M KCl as the supporting electrolyte. The dashed curve represents the deviation caused by the addition of pyridine to the cell. The cell potential was swept at a rate of 1.0 V s$^{-1}$.

![Graph](image2)

**Fig. 4.** Raman intensity of the 1006 cm$^{-1}$ band due to adsorbed pyridine as a function of bulk pyridine concentration. The intensity is arbitrarily normalized to 10 for a 50 mM solution concentration. The electrode surface was prepared according to our standard anodization procedure in which the electrode rest potential is −0.6 V vs. SCE. The supporting electrolyte concentration was 0.1 M KCl, and each data point represents a new experiment.
of surface Raman intensity as a function of pyridine bulk concentration is
given in Fig. 4. The intensity rises rapidly with increasing solution concentr-
tion and then reaches a plateau. Simultaneous variation of the amount of
charge passed in the forward step of anodization and of the pyridine solution
concentration produced the empirical relation that charge transferred in the
forward step of anodization multiplied by pyridine solution concentration
equals a constant Raman intensity at a fixed supporting electrolyte concen-
tration and for charge transfers less than 50 mC cm\(^{-2}\).

In a related series of experiments the electrode surface was prepared with
our standard anodization procedure and the pyridine solution concentration
was held constant while the supporting electrolyte concentration was varied.
The results are shown in Fig. 5. Curve (a) is that due to a 50 mM bulk concen-
tration of pyridine as a function of the KCl supporting electrolyte concen-
tration, and curve (b) for a 5.0 mM bulk pyridine solution. Both curves exhibit
maxima near a 2:1 concentration ratio of KCl to pyridine. Substitution of
other anions for chloride, or the use of different solvent systems has a large
effect on the Raman intensity of adsorbed pyridine. Br\(^-\) behaves in a nearly
identical manner to Cl\(^-\); whereas, substitution of I\(^-\) for Cl\(^-\) results in a mar-
kedly different surface spectrum. Other anions (0.1 M ClO\(_4\)^-, C\(_2\)O\(_4\)^2-, SCN^-,
SO\(_4\)^2-, and HPO\(_4\)^-) produced adsorbed pyridine spectra identical to that
generated by chloride but of lower intensity. The exceptional behavior of I\(^-\)
may indicate a surface reaction leading to new surface species. Further discus-
sion of the I\(^-\) case is reserved for a future publication. No surface Raman signal
could be observed for pyridine dissolved in organic solvents such as methanol,
dichloromethane, or acetonitrile.

**Dependence of surface Raman signal intensity on applied electrode potential.**
Variation of the electrode potential produces dramatic changes in the NR

![Raman intensity as a function of supporting electrolyte concentration](image)

Fig. 5. Raman intensity as a function of supporting electrolyte concentration for the 1006
\(\text{cm}^{-1}\) band due to adsorbed pyridine. The intensity for each curve is arbitrarily normalized
to 10 for the point of maximum intensity. Curve (a) is for a solution 50 mM in pyridine, and
curve (b) for a 5.0 mM solution. The intensity was recorded after the electrode surface was
anodized under our standard conditions in which the electrode rest potential is \(-0.6\) V vs.
SCE. The supporting electrolyte concentration was 0.1 M KCl, and each data point represents
a new experiment.
Fig. 6. Raman spectra of pyridine adsorbed on a silver electrode from a solution of 50 mM pyridine and 0.1 M KCl. Electrode potentials are: (a) −0.2 V, (b) −0.4 V, (c) −0.6 V, and (d) −0.8 V vs. SCE. The electrode surface was prepared according to our standard anodization procedure. The laser power was 80 mW at 5145 Å. The spectra were recorded with a 2 cm⁻¹ bandpass with a 0.3333 Å s⁻¹ scan speed and a 1.0 s counting interval.

Fig. 7. Raman intensity dependence due to adsorbed pyridine as a function of electrode potential. (a) 1006 cm⁻¹, (b) 1035 cm⁻¹, (c) 3056 cm⁻¹, (d) 1215 cm⁻¹, (e) 1594 cm⁻¹, (f) 623 cm⁻¹. The electrode surface was anodized under our standard conditions. A relatively large spectrometer bandpass (20 cm⁻¹) was used to minimize the error in intensity measurement due to the effect of band frequency changes with electrode potential. Laser excitation wavelength = 5145 Å. The electrode potential was scanned at a rate of 1.024 V s⁻¹ beginning at 0.0 V vs. SCE. Each curve was signal averaged over ten potential scans.

spectrum of adsorbed pyridine. Figure 6 shows these changes as the potential is made increasingly more negative. New Raman bands appear at 623, 1215, and 1594 cm⁻¹, accompanied by an increase in the intensity of the bands already manifested at more positive potentials. The strong band at 1025 cm⁻¹ observed by Hendra et al. and ascribed by them to pyridine coordinated to Lewis acid sites is, for unknown reasons, very weak or absent in our spectra. In their work the bands at 523, 1215, and 1594 cm⁻¹ were not observed. Band frequency shifts of several wavenumbers accompany the potential variation in the range of 0.0 to −1.0 V vs. SCE. The intensities of the major Raman modes as a function of potential are given in Fig. 7. Several intensity reversals occur, and maxima in the intensity vs. potential plot are not observed to be coincident.
Time dependence of the surface Raman signal intensity in response to a double potential step waveform. The Raman time response to a double potential step has been investigated in order to verify that the pyridine Raman signal was indeed of surface origin, rather than a diffusional or bulk solution effect. A repetitive potential step waveform consisting of a forward step from $-0.1$ V to $-0.6$ V vs. SCE and subsequent return after 10 ms, with a 20% duty cycle was applied to a silver electrode subjected to a standard anodization cycle. The signal averaged (10,000 repetitions) double potential step Raman intensity vs. time behavior of the 1006/1008 cm$^{-1}$ band at a pyridine solution concentration of 0.5 mM pictured in Fig. 8a. As expected for a surface phenomenon, the

Fig. 8. (a) Raman time response of the intensity due to the 1006/1008 cm$^{-1}$ band of adsorbed pyridine on a silver electrode where the initial potential is $-0.1$ V (SCE) and the step is to $-0.6$ V for a duration of 10 ms with a 20% duty cycle. The electrode was prepared under our standard anodization conditions in the presence of a 0.5 mM bulk concentration of pyridine and a 0.1 M KCl supporting electrolyte concentration. (b) Double potential step voltage waveform input to the potentiostat. (c) Electrochemical cell current for the above potential step.

Fig. 9. (a) Raman time response of the intensity due to the 1006/1008 cm$^{-1}$ band of adsorbed pyridine on a silver electrode. The conditions are identical to those for Fig. 8a, except the solution pyridine concentration is 50 mM. (b) Same as above for a solution pyridine concentration of 5.0 mM. (c) Double potential step voltage waveform input to the potentiostat.
time profile tracks the excitation potential signal with only a small amount of time lag, attributed to double layer charging time, in contrast with a bulk solution diffusional response [2]. Figure 8c displays the current vs. time trace due to charging the double layer and demonstrates that shorter duration potential steps with our present potentiostat would be distorted due to a non-negligible double layer charging time. Substitution of a higher speed potentiostat should permit shorter time measurements to be made. At higher bulk solution concentrations of pyridine the time response of the Raman signal exhibits significantly more time lag as seen in Fig. 9 for solution concentrations of (a) 50 mM and (b) 5.0 mM. The fall time of the Raman signal is substantially longer than the rise time, and this effect is most pronounced for the 50 mM pyridine solution concentration. We interpret the rise and fall time in this experiment to correspond to the times for adsorption and desorption. This is the first reported application of Raman spectroscopy for the investigation of a time dependent surface process.

Normal Raman spectroscopy of other adsorbed amines

In addition to pyridine, we have found that many other amines, both aliphatic and aromatic, produce intense Raman scattering when adsorbed on a silver electrode. Nearly all amines containing an aromatic heterocyclic ring system, having a solubility in water greater than 1.0 mM, will have an observable Raman signal. Table 2 lists a selection of the amines we have examined, their primary structural feature, and whether or not a spectrum of the adsorbed material could be obtained.

Resonance Raman spectroscopy of adsorbed amines

The adsorption experiments that have been described here require that the electrode be immersed in an aqueous bulk solution of the amine during the Raman experiment. A volume element in front of the electrode, in addition to the electrode surface is inevitably sampled, which produces no difficulties in the case where the bulk species does not have an electronic transition in the region of the laser excitation wavelength. However, an optically absorbing sample attenuates both the laser beam before it strikes the electrode, and the Raman scattered light radiating from the electrode. There is also a strong possibility that the scattering spectrum of the bulk amine will be resonance enhanced, becoming either competitive with, or obscuring a surface signal. In an attempt to circumvent this difficulty for the resonance Raman active compounds, methyl orange and crystal violet, which both have intense absorption in the visible, an alternative procedure was used. Initially, the electrode was anodized in the presence of a 0.5 mM solution of the amine according to our standard procedure for pyridine and then the working electrode was open circuit. 0.1 M aqueous KCl was employed to displace the amine solution in the cell, followed by potentiostating the working electrode at −0.2 V vs. SCE. The resulting intense resonance enhanced Raman scattering from the electrode surface for both methyl orange and crystal violet is shown in Fig. 10. The laser power used to excite the crystal violet spectrum was only 1.0 mW at 5145 Å.
<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SURVEY OF SOME STRUCTURAL CRITERIA FOR OBSERVING</td>
</tr>
<tr>
<td>SURFACE RAMAN SPECTRA</td>
</tr>
<tr>
<td>OF NITROGEN HETEROCYCLES AND AMINES</td>
</tr>
<tr>
<td>HETEROCYCLIC AROMATIC AMINES - 1N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>( \text{NH}_3 )</td>
</tr>
<tr>
<td>( \text{N} )</td>
<td>( \text{NH}_2 )</td>
</tr>
<tr>
<td>( \text{C} )</td>
<td>( \text{CH}_3 )</td>
</tr>
<tr>
<td>(yes)</td>
<td>(yes)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HETEROCYCLIC AROMATIC AMINES - 2N</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>( \text{N} )</td>
</tr>
<tr>
<td>(weak)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AROMATIC AMINES - 1N</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>( \text{C} )</td>
</tr>
<tr>
<td>( \text{NH}_2 )</td>
</tr>
<tr>
<td>(yes)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AROMATIC AMINE - 2N</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{N} )</td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
</tr>
<tr>
<td>(no)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ALIPHATIC AMINES - 1N</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>( \text{NH} )</td>
</tr>
<tr>
<td>(no)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ALIPHATIC AMINES - 2N</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_2\text{CH}_2\text{-CH}_2\text{-NH}_2 )</td>
</tr>
<tr>
<td>(no sharp features)</td>
</tr>
</tbody>
</table>
and a spectrum of equal intensity was obtained with only 0.5 mW at 6328 Å from a small He–Ne alignment laser. The surface RR spectrum of methyl orange differs extensively from a resonance Raman spectrum reported for an aqueous solution, while the surface RR spectrum of crystal violet corresponds closely to its solution spectrum [19]. A preparation of the electrode with pyridine, identical to that for crystal violet, produced a Raman signal that decayed in several minutes, however, the intensity responded rapidly and reversibly to variations in potential in the range −0.2 V to −0.8 V (vs. SCE).

DISCUSSION

Intensity of the surface Raman signals

Perhaps the most interesting feature of this study is the realization that the Raman signal intensities we have measured here for the adsorbed amines greatly exceed that which was a priori expected on the basis of the following detection limit calculation. Barradas and Conway [20] have calculated that a pyridine molecule adsorbed in a flat configuration on an electrode surface occupies a 38 Å² site. One can estimate a corresponding site area of 25 Å² from a model in which a pyridine molecule is attached axially to the electrode and is capable of rotating to create a cylindrical volume element. Utilization of the latter model gives a larger value of molecular surface coverage, and therefore yields
the most optimistic monolayer detection limits. For a line focus of the 5145 Å laser beam 50 μm wide and 3 mm high, a coverage of ten close-packed, axial monolayers, and a real to apparent area factor of 5 to account for surface roughness, $3 \times 10^{13}$ molecules are sampled. A 0.5 mM solution of pyridine in methylene chloride, contained in a 1.0 mm thick cell in order to define a scattering volume, represents a practical lower limit of detection on our apparatus. This volume contains $4.5 \times 10^{14}$ molecules. Thus, a conservative estimate for the discrepancy between the expected pyridine surface signal intensity over the available sensitivity is an order of magnitude. Greenler and Slager [21] have reported the successful acquisition of the Raman spectrum of a 50 Å thick film of benzoic acid on a silver surface with a S/N ratio of approximately 3. This sensitivity approaches that needed to observe adsorbed pyridine according to the above limit of detection calculation. Given that the experimentally observed intensities of NR scattering from adsorbed pyridine in our laboratory are 5–6 orders of magnitude greater than expected, we felt that some property of the electrode surface or the electrode/solution interface is acting to enhance the effective Raman scattering cross section for these adsorbed amines. The mechanism for this signal enhancement has not been conclusively determined in the present work; however, a plausible hypothesis will be presented below. A study of the wavelength dependence of the surface pyridine signal showed, within experimental error, a fourth power wavelength dependence over the range 4600 Å to 6300 Å. This immediately ruled out the possibility that the observed signal enhancement was caused by coupling of the laser field with an electronic transition in the adsorbed species on the electrode surface. In the case of methyl orange and crystal violet, both of which absorb strongly at the exciting wavelength, a wavelength dependent resonance enhancement quite different from that for pyridine was observed. For these molecules, and especially for the case of crystal violet, two enhancement processes contribute to the Raman intensity, the first being a surface enhancement effect identical to that for pyridine, and the second a resonance enhancement effect due to the coupling of the scattering process with an electronic transition in the adsorbed molecule.

The anodization process

Hendra et al. reported [8] that the formation and reduction of silver chloride “resulted in considerable etching of the silver surface”, and that the surface area was increased by a factor greater than ten. Although these authors subjected the electrode to 15 min of anodization, we have found that a single cycle can be equally effective for the production of Raman signal strength. A fifty fold increase in signal strength due to anodization is large enough that it cannot be accounted for only in terms of an increase in surface area, but rather is due to the formation of active sites as well as an increase in surface area. The anodization is not thought to produce any thick surface film of a silver compound due to a faradaic process since: (1) greater than 99.8% of the charge is recovered in the double potential step anodization; (2) the anodization is equally effective in increasing the Raman intensity whether it is carried out in the presence or absence of pyridine; and (3) no measurable faradaic current
corresponds with the Raman intensity changes in the potential region 0.0 to
-0.9 V.

An analysis of the Raman intensity of the 1006 cm⁻¹ band due to adsorbed
pyridine as a function of bulk solution pyridine concentration (Fig. 4) allows
an estimate to be made of the degree of surface coverage. Hendra et al. did not
deal with the topic of surface coverage, although an adsorption isotherm had
been measured for the adsorption of pyridine on silver from aqueous solution
by Barradas and Conway [20]. In their latter work the adsorption isotherm
reached a plateau value at solution concentrations of pyridine around 1 ×
10⁻⁵ M; several orders of magnitude less than in our work. Also, it was
postulated by them that pyridine had a tendency to lie flat upon the electrode
surface. We have determined that at the higher pyridine solution concentrations
used in our experiments, for reasons to be discussed as part of the section
dealing with the nature of the adsorbed species, that an anion induced adsorp-
tion leads to an axial, end-on adsorption of pyridine rather than a flat orienta-
tion. We further suppose that this axial packing of surface molecules has a ΔG
of adsorption which is a strong function of surface coverage, and does not
reach a surface coverage near 1 until the pyridine bulk solution concentration
exceeds 50 mM. As a result of the surface enhancement effect to be discussed
in conjunction with the potential and time dependence of the Raman signal,
we further postulate that a molecule which is in a flat configuration is not
observable in our Raman experiments. This implies that the Raman intensity in
Fig. 4 is due solely to axially bound pyridine, which accounts for the drop-off
and inflection in the curve at lower pyridine solution concentrations. This
interpretation is consistent with our conclusion that we are indeed observing a
monolayer of adsorbed pyridine.

Experiments involving anodization in organic solvents showed no adsorption
signal of pyridine. This has also been observed by other workers [20] and is
attributed to a higher energy of solvation for pyridine in the organics than in
water, pyridine favoring the bulk solution over the interfacial region.

The chemical identity of the Raman active surface species

An initial examination of the dependence of the surface Raman intensity
on the bulk pyridine concentration and the chloride ion concentration
prompted a series of further experiments in which the pH of the bulk solution
was varied from pH 1–13. The identity of the Raman active surface species,
whether ionic or neutral, can be inferred from these experiments in which pH
adjustment of the bulk solution ensures a predominance of either the neutral or
protonated forms of pyridine. As the buffered pH of a series of 50 mM aqueous
pyridine solutions was decremented, the signal from adsorbed pyridine
decreased to zero abruptly between pH 4 and pH 3. The corresponding concen-
tration fractions of unprotonated pyridine molecules are 4.3% and 0.43%,
respectively. Good quality spectra are easily obtained from unbuffered solu-
tions of bases with moderately high basicity constants such as benzylamine
(K_b = 0.23) where only 2% of a 5.0 mM solution is unprotonated. Thus, the
Raman active surface species is likely to involve the neutral form even though it
may be present at rather low bulk concentration. It has been generally con-
cluded that for an adsorbed aromatic or heterocyclic system at surface coverages less than 0.75 the strong interaction of the \( \pi \) electrons with the metal forces the molecule to assume a flat orientation on the electrode; whereas, aliphatics are attached to the metal through the non-bonding lone pair electrons, and are directed away from the surface [20,22]. If the neutral pyridine molecule is involved in the adsorbed species responsible for the Raman surface signal, adsorption is most probably via the lone-pair on nitrogen rather than through the \( \pi \) electron cloud. The facts which argue in favor of this interpretation are: (1) an end on attachment is more likely to result in a high surface number density than a flat orientation consequently being easier to detect, and (2) amines without a \( \pi \) electron cloud, such as piperidine, which can only adsorb via the nitrogen lone-pair give rise to intense surface Raman spectra (Table 2.).

Further analysis of surface orientation comes from the measurement of Raman depolarization ratios. For pyridine in solution, the 1006 cm\(^{-1}\) and 1037 cm\(^{-1}\) modes exhibit depolarization ratios near zero; whereas, adsorption of the molecule produces a dramatic increase in the depolarization ratio to 0.64 and 0.62, respectively (Table 1). Surface roughness prohibits a rigorous comparison of experimental and theoretical depolarization ratios, but qualitative conclusions can still be drawn. In the first case to be considered, pyridine lies flat on a planar surface with incident light normal to the surface. Since the elements of the scattering tensor for a totally symmetric mode are diagonal, input radiation which is polarized along a molecular axis will result in the scattered light having its polarization vector along the same axis. For this reason, pyridine in a flat configuration will have a depolarization ratio of zero for a totally symmetric mode. Even for an arbitrarily rough surface, the ratio will be near zero. A simple calculation, reproduced below, indicates the direction of the change in the depolarization ratio expected in going to a second case in which the molecule is attached axially and perpendicularly to a planar electrode. Figure 11 shows a molecular plane MP perpendicular to the electrode surface. \( \mathbf{R} \) is the electric field vector of the exciting radiation and \( \mu \) is the induced dipole moment which must be in the plane MP. The magnitude of the

![Diagram](image-url)

Fig. 11. Diagram for the derivation of the depolarization ratio for a thin planar molecule attached axially (end-on) to an electrode surface. MP is the molecular plane, \( \mathbf{R} \) the electric field vector of the incident radiation, \( \mathbf{I} \) the electric field vector of the scattered Raman radiation, \( I_p \) and \( I_{l} \) are the parallel and perpendicular components of \( I \) relative to \( \mathbf{R} \). \( \theta \) is the angle of the incident radiation from a normal to the molecular plane MP.
induced dipole moment is:

$$|\mu| = |R| \rho \sin \theta$$  \hspace{1cm} (1)

where $\rho$ is the appropriate component of the polarizability tensor for the normal mode, and the intensity of the scattered radiation is given by:

$$I = \mu \cdot R = |R|^2 \sin^2 \theta$$  \hspace{1cm} (2)

The parallel component of the scattered radiation is,

$$I_\parallel = |R|^2 \sin^2 \theta \sin \theta$$  \hspace{1cm} (3)

and the perpendicular component,

$$I_\perp = |R|^2 \sin^2 \theta \cos \theta$$  \hspace{1cm} (4)

Averaging over $\theta$, corresponding to random orientations of the molecular plane for $I_\perp$ and $I_\parallel$, and taking the ratio $I_\parallel / I_\perp$ we get:

$$\frac{I_\parallel}{I_\perp} = \frac{\int_0^\pi |R|^2 \sin^2 \theta \cos \theta \, d\theta}{\int_0^\pi |R|^2 \sin^3 \theta \, d\theta} = \frac{1}{2}$$  \hspace{1cm} (5)

thus supporting the interpretation of an end-on adsorption configuration for pyridine. A more detailed analysis of the depolarization ratio will be the subject of a future communication in which other molecular orientation possibilities and the effect of finite molecular thickness will be taken into account. Experiments will be carried out on vapor deposited silver films to determine the effect of surface roughness on the depolarization ratio and the Raman intensity.

Further insight into the nature of the adsorbed species can be obtained from the curves of Raman intensity due to adsorbed pyridine as a function of supporting electrolyte concentration. These curves (Fig. 5) had maxima at a 2:1 solution concentration ratio of KCl to pyridine. This ratio leads to a model of the Raman active surface species consisting of two specifically adsorbed chloride ions and one adsorbed pyridine molecule. We further postulate that the chloride ions cause a positive polarization of the local surface Ag atom, permitting delocalized bonding between the pyridine lone-pair and the Ag d-orbitals. For anions which are specifically adsorbed to a lesser degree than chloride, such as ClO$_4^-$, the surface complex is less stable, which results in lower observed Raman intensity.

\textit{Dependence of surface Raman signal intensity on potential and time}

In order to explain the shape of the Raman intensity vs. electrode potential curves (Fig. 7) and the appearance of new bands in the Raman spectrum of adsorbed pyridine as the electrode potential is made increasingly more negative (Fig. 6), we propose that there are two main effects which give rise to the potential dependence of the Raman signal: (1) an adsorption/desorption pro-
cess; and (2) electric field enhancement of the Raman scattering cross section.

It is well known that neutral organic compounds are preferentially adsorbed near the point of zero charge (p.z.c.) [22]. As the electrode potential is varied anodically or cathodically from the p.z.c., desorption is expected to occur. Evidence for an adsorption/desorption effect comes from the experiments which measured the time response of the surface Raman signal (Figs. 8 and 9). As the bulk concentration of pyridine is increased in these experiments, the Raman intensity response begins to lag behind the input waveform with noticeable rise and fall times. This lengthening of the rise and fall times of the Raman response with increasing solution concentration of pyridine can be explained as being due to the longer times required for the adsorption and desorption of greater amounts of pyridine. From an examination of the curves of the surface Raman intensity as a function of electrode potential, it is clear that none of the maxima coincide. If the adsorption/desorption process was the only effect contributing to the potential dependence, the existence of multiple surface species would have to be postulated; specifically, a different molecular species or surface site for each new band observed in the Raman spectrum of adsorbed pyridine at negative potentials. In view of the fact that all of the bands due to adsorbed pyridine have identical time responses within experimental error, such a large number of different surface species is unlikely. An alternative explanation, which proposes a single surface species, relies on the concept of an electric field modulation of the Raman scattering tensor of the adsorbed molecule.

Electric field enhanced Raman scattering has been observed experimentally in semiconductors and crystals for electric field gradients ranging from $10^4$–$10^5$ V cm$^{-1}$, and a theoretical treatment presented [23–25]. Electric field gradients in the vicinity of the electrode can attain values of $10^6$ V cm$^{-1}$ [25] which are well within the range needed to observe electric field enhanced scattering. The Raman intensity vs. potential curves could, therefore, represent a composite of two effects: (1) the adsorption/desorption process and (2) electric field enhancement. Although the p.z.c. is reported to be approximately $-0.71$ V vs. SCE for a silver electrode in $10^{-2}$ M Cl$^-$ [26], there can be a substantial electric field gradient near the outer Helmholtz plane at the p.z.c. due to the fact that the chloride ion is specifically adsorbed [27]. It is reasonable to postulate that the electric field gradient increases toward more negative potentials in the region $-0.2$ V to $-1.0$ V. Because amines tend to be most strongly adsorbed at the p.z.c., those normal modes which have the greatest electric field enhancement would be expected to exhibit the most negative maxima in the Raman intensity vs. potential curves (Fig. 7) in that the electric field effect is increasing more rapidly than the desorption of the amine. A rapid inspection of Fig. 7 indicates that the curves fall largely into two groups according to the general location of their intensity maxima. The first group with intensity maxima at more positive potentials due to the bands at 1006 cm$^{-1}$, 1035 cm$^{-1}$, and 3056 cm$^{-1}$, is composed of the modes that are present in the Raman scattering spectrum at all potentials in the range of $0.0$ V to $-1.0$ V vs. SCE. The second group, due to bands at 623 cm$^{-1}$, 1215 cm$^{-1}$, and 1594 cm$^{-1}$, is one which consists of bands that increase in intensity from very weak features at $0.0$ V into strong bands at $-0.8$ V, and hence tend to appear as new bands in the Raman spectrum. This appearance with increasingly negative
potential could be due to a large relative enhancement of those modes whose vibrational coordinate has a significant component of motion within the electric field gradient. This large enhancement shifts their maxima in the intensity vs. electrode potential curves toward substantially more negative potentials as compared with the location of the maxima for the first group of bands.

Further evidence for an electric field enhancement comes from an experiment similar to that used to study crystal violet and methyl orange. The electrode surface was prepared by anodization in the presence of pyridine, followed by displacing the bulk pyridine solution with one containing only supporting electrolyte, in a procedure identical to that used for obtaining the surface Raman spectrum of crystal violet. A Raman signal due to adsorbed pyridine was observed upon potentiostating the electrode to $-0.2 \text{ V vs. SCE}$. As the electrode potential was made more negative (i.e., toward the p.z.c. where pyridine is more strongly adsorbed), the Raman signal intensity increased until at $-0.6 \text{ V}$ the signal intensity was more than a factor of 2 greater than at $-0.2 \text{ V}$. This intensity increase was, therefore, seen for a surface in contact with bulk solution which contained only a trace amount of pyridine. Here the probability of a reversible adsorption/desorption process contributing entirely to the intensity change with potential is greatly reduced, and this experiment indicates that there must be a process which produces intensity changes at a constant surface coverage, which would be accounted for by an electric field enhancement effect.

The postulation of an electric field enhancement permits further comment on surface orientation and Raman signal strength. In the cases of pyrazine and $p$-phenylenediamine, molecules which are constrained to a flat orientation if both nitrogens are bonded to the surface, only a weak Raman spectrum is obtained. This might be rationalized as a lack of interaction between the electric field and the totally symmetric modes of the molecule due to the orthogonality imposed by a flat configuration. Although the Raman active form of pyridine was determined to be the neutral form rather than the protonated, this does not imply that neutral molecules are adsorbed while the protonated are not. In fact, there is evidence that both can be adsorbed to a similar degree if the solution pH and electrode potential are adjusted accordingly [20]. The critical difference may be in the molecular orientation of the molecule. Neutral pyridine has been discussed as having an end-on attachment; whereas, protonated pyridine may be bonded through the $\pi$ orbitals, thus constraining it to be flat on the electrode.

ACKNOWLEDGMENTS

The support of this research by the National Science Foundation (MPS74-12573 A01 and CHE75-15480) is gratefully acknowledged. In addition D.L.J. acknowledges a fellowship from the ACS Analytical Chemistry Division sponsored by the Perkin-Elmer Corporation for the academic year 1975—1976 and R.P.V.D. acknowledges support from the Alfred P. Sloan Foundation 1974—1978.
REFERENCES