INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

8409382

Bernard, Irene

EFFECT OF SOLUTION CONDITIONS AND ELECTRODE POTENTIAL ON THE SURFACE ENHANCED RAMAN SCATTERING OF NITROGEN HETEROCYCLES

City University of New York PH.D. 1984

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

EFFECT OF SOLUTION CONDITIONS AND ELECTRODE POTENTIAL ON THE SURFACE ENHANCED RAMAN SCATTERING OF NITROGEN HETEROCYCLES

by

Irene Bernard

A Dissertation Submitted to the Graduate Faculty in Chemistry
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy, The City University of New York.

1984

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

2-14-84
date

John R Lombardi
Chairman of Examining Committee

2-14-84
date

Executive Officer

Professor R.L.Birke

Professor D.M.Lindsay

Professor W.E.L.Grossman

Supervisory Committee

The City University of New York

ABSTRACT

EFFECT OF SOLUTION CONDITIONS AND ELECTRODE POTENTIAL ON THE SURFACE ENHANCED RAMAN SCATTERING OF NITROGEN HETEROCYCLES

by

Irene Bernard

Advisers: Ronald L. Birke
John R. Lombardi

pH and chloride effects on the spectrum of pyridine are reported. The concentration of the adsorbed pyridine and pyridinium molecules is heavily dependent on the pretreatment method and chloride concentrations employed. The surface line seen at 237 cm^{-1} is a pyridinium chloride-Ag vibration and not a chloride-Ag band since at a pH of 2, pure chloride does not display this band. Also, a chloride concentration study at a fixed pyridinium concentration indicates that at a low chloride concentration, the spectrum is hardly visible. As more of this electrolyte is added, the intensity increases up to a ratio of 1:1 chloride: pyridinium and then there is a decrease, due to desorption from the surface of the ion pair.

At pH = 8, the effects observed on pyridine are the following - the intensity ratio of the 1008 and 1035 cm^{-1} modes is nearly independent of the concentration ratio of chloride to pyridine, but highly dependent on the potential. Also, as more chloride is added, the voltage at which a spectrum can be seen becomes more negative, indicating that at a high bulk chloride concentration, the adsorbed

halide completely covers the surface, displacing pyridine.

A study of quiniclidine focuses on two degenerate peaks which show drastic changes in their relative intensities on the surface. In contrast with piperidine, the symmetric peaks shows a bigger halide dependence than the asymmetrical one.

Other reported results include SERS of acridine and isoquinoline. Acridine does not show significant changes in the spectrum upon protonation. Also the spectrum in the presence of Br^- was more intense than in the presence of Cl^-, differing in this from pyridine. Isoquinoline shows the same pH effects as pyridine in terms of the voltage dependence as a function of the halide employed and the behavior of the low lying vibration around 200 cm^{-1}.

Studies on Hg sols indicate that there is in fact a plasmon which absorbs at 210 nm. However, no SERS was observed, due to the dielectric properties of this metal.

IN MEMORIAM OF

DR. ALEX. BERNARD

" FELIX QUI POTUIT RERUM COGNOSCERE CAUSAS "

VIRGIL

TABLE OF CONTENTS

Table of Contents (Continued) Page

LIST OF FIGURES

List of Figures (Continued) Page

List of Figures (Continued) Page

LIST OF TABLES

CHAPTER 1

Introduction

The technique of Surface Enhanced Raman Spectroscopy (SERS) began with the work of Fleischmann et al in 1974 (1) and has developed considerably since then. The main reason for the growing interest in this technique is due to the enormous increase in the Raman scattering, which allows in-situ surface vibrational spectroscopy of a variety of molecules. This intensity can be as high as 10^6 times that of the intensity seen from the same number of molecules in the bulk solution. The desire to elucidate the causes of this effect has lead to numerous publications since then and several reviews (2,3,4,5,6,7); however, the mechanisms which give rise to this "Giant Raman Effect" are still controversial and not fully explained. A fascinating feature of the study of SERS is that it requires the mixing of a number of fields such as spectroscopy, electrochemistry, solid state, analytical and surface chemistry. This technique enables an in-situ diagnostic probe for detailed and unique vibrational patterns of the adsorbates. A high resolution can be obtained using the visible range (0.1 cm^{-1}) which is even better than that of EELS (electron energy loss spectroscopy) and also frequency modes as low as 5 cm^{-1} can be measured.

A. SERS in an Electrochemical Environment. SERS has been observed at a metal/gas interface, at metal/ultra high vacuum (UHV) interfaces, at solid/solid interfaces (tunnel junction configurations), at metal-island film/liquid interfaces, at metal grating/thin film interfaces, at silver and gold metal sol/liquid interfaces and on metal precipitates of silver in contact with aqueous solutions, and at a metal/solution interface.

The study reported here involves SERS in an electrochemical environment, where a metallic electrode is immersed in an electrolyte solution, thus establishing a solid-solution interface. This interface depends on the metal and the adsorbate, and also the ionic constituents of the solution. With an aqueous electrolyte, upon contact with the electrode, the water molecules adsorb to its surface. The distance of closest approach between the ions and the electrode is restricted by the hydration sheath of the electrode and also by the hydration spheres of the ions. Since the electrode is normally charged, there is a potential distance profile which depends on the nonhydrated ions, held tightly to the metal, and the nonrigidly held hydrated ions in the diffuse layer, which extends into the bulk solution.

One of the most striking differences between normal and surface Raman in the electrochemical environment is the potential dependence of the bands in the second case. This dependence can be interpreted as due to adsorption on the surface, i.e. accumulation of the species within the double layer. The point of zero charge (pzc) is the potential at which there is no surface charge on the electrode. This concept is of major importance, because it influences which species adsorb on the metal and the extent of adsorption at a given potential (8) which could be to the positive side of the pzc (the electrode is positively charged) or to the negative side of the pzc (the electrode is negatively charged).

When the applied potential is more negative than the pzc, the positive dipole of the water will point towards the metal. Positive ions will displace the water molecules, and will adsorb to the surface, thus establishing the IHP (inner Helmholtz Plane).

At the pzc, the ions in solution are completely solvated, and on the surface, the number of water molecules pointing with the hydrogen or oxygen towards the surface, is equal. Differential capacitance measurements show a peak in the capacity versus potential measurements (9), in the vicinity of the p.z.c.

At potentials more positive than the p.z.c. where anions adsorb specifically the adsorption of various ions is more complex. Close to the p.z.c. neutral molecules with a dipole, or water pointing with the oxygen to the metal adsorb on the surface. From differential capacitance measurements in a solution containing specifically adsorbing anions, it has been found that the surface coverage of anions can exceed that of the water, when the electrode is very positive of the p.z.c. (10-13). The water molecules, which are still adsorbed on the surface, are aligned with the oxygen pointing towards the electrode. The outer Helmholtz plane (OHP) consists of many anions and cations, solvated by the water molecules. When Na^+ is changed to K^+ and to Li^+ there are shifts in the stretching frequency of water bands, indicating an interaction of the water molecules solvating these cations in the OHP with the adsorbed H_2O in the IHP (14,15).

As the potential shifts very positive compared to the p.z.c., the coulombic interactions in the IHP increase, creating a partially covalent bond between the metal and the adsorbate. Interactions of this kind between the metal and halide or water molecules, can cause frequency shifts of the surface stretching band of adsorbed molecules to higher values, as the potential becomes more positive (16,17).

Different theories have been developed so far, in an attempt to explain the enhancement mechanism of SERS. None of the theories completely explains all the experimental evidence and it appears that the effect is a mixture of a few components, each one contributing in a different way to the total enhancement.

The term which identifies the enhancement is radiance per molecule, I. The total radiance, S, which is a function of I and N, the number of scattering centers, is in fact the parameter which is measured experimentally (4b).

I is defined according to Furtak (4b) as:

$$I = A(w)^4(\hat{e}\vec{\mu})^2 \qquad (1)$$

where $A = \mathrm{Sin}\ ^2\hat{e}/4\ R^2C^3$ where R is the distance to the detector, w is the scattered angular frequency, μ is the induced dipole representing the molecule-substrate combination and $\hat{e}$ is the unit vector along the polar angle e identifying polarization in the scattered beam. The induced dipole is related to the incident field through the effective polarizability, :

$$\vec{\mu} = \overleftrightarrow{\alpha} \cdot E^{in} \qquad (2)$$

where E^{in} is the incident field. Classically, $\overleftrightarrow{\alpha}$ is defined as

$$\overleftrightarrow{\alpha} = \frac{\partial \alpha}{\partial Q_i} dQ_i \tag{3}$$

where r is the equilibrium intermolecular distance and Q_i are the normal coordinates of the system. Quantum mechanically $\overleftrightarrow{\alpha}$ is

$$\overleftrightarrow{\alpha} = \sum_j \left| \frac{\vec{M}_{fj}\vec{M}_{ji}}{E_j - E_i - \hbar\omega^{in} - i\delta_j} + \frac{\vec{M}_{fj}\vec{M}_{ji}}{E_j - E_f + \hbar\omega^{in} - i\delta_j} \right| \tag{4}$$

where $M_{ab} = \int \Psi_b^* \vec{\mu} \Psi_a \, dt$ and the sum is over all the excited states, j, of the system. E_i and E_f are the energies of the initial and final states respectively and δ_j is inversely proportional to the lifetime of the excited states, j.

Most of the theories which attempt to explain SERS point to the fact that in order to achieve such a great enhancement as in SERS, the system must reach a state of resonance. All the resonance possibilities can be classified into two: 1) Optical. 2) Electronic.

B. Optical Resonance. In the proximity of the surface of a metal, the incident light field is modified due to the boundary conditions, resulting in a local field which depends on the optical properties of the substrate and the geometry of the surface. The effective polarizability

$$\vec{\mu} = \overleftrightarrow{\alpha}_{effective} E^{in} \tag{5}$$

becomes very large for specific molecule-metal separations and for specific conditions of excitation (18).

The detected field is defined:

$$E^{out} = E^{out}_{\substack{\text{boundary}\\\text{conditions}}} + B_w \alpha_{\text{classical}} E^{in} \qquad (6)$$

where B_w is an amplification factor due to the optical properties of the substrate. The coupling of the incident energy to the plasmon of the metal is reflected in the fact that geometries of 50 to 200 Å and also certain values of w, enhance B_w to large values. Thus the local field due to this optical resonance, can be much larger than the incident field.

Pettinger et al (19) tested the optical resonance by using a geometry which allows control of the coupling conditions. They used a thin Ag film on the back side of a glass internal reflection element to excite surface plasmon polaritons on the surface of the metal. Thus, when the photon vector parallel to the surface was equal to the surface plasmon polariton wavevector, there was coupling with the incident photon. This coupling could be increased or decreased by changing the incident angle. This study demonstrated directly the influence of the excited plasmon polariton on the electric field at the surface.

In order for a metal to have well defined collective electro excitations, and thus be suitable for optical resonance, the dielectric function has to have large and negative real components, and very small imaginary components.

Furtak and Kester (20,21) tested the change in the dielectric function by using alloy substrates. In the case of AgPd, the intensity decreased below the detection limit in the presence of only 4% Pd, while with AgAu, at small incident photon energies, the enhancement was observed over the entire concentration range. These effects correlate with the known optical properties of the alloys.

The optical resonance is expected to penetrate beyond the first layer, since the dynamic fields due to the surface plasmons extend beyond the metal-adsorbate interface. In order to test this, Murray et al. (22) performed experiments using a polymer spacer between the adsorbate (p-nitrobenzoic acid) and a roughened Ag overlayer. They found that the SERS signal decreased rapidly with increasing the separation between the molecule and the metal. There was still a signal, however, even when there was no direct contact between the surface and the adsorbate, which indicates a long range effect through coulomb coupling, enabled by the interaction of the optical field with the rough metal.

The optical resonance is independent of the chemical nature of the substrate as can be seen from the results of Trott and Furtak (23), who showed that the angular dependence of SERS on lightly roughened Ag films, was independent of the molecule. Creighton et al. (24) found that different substrates had the same excitation profile. Chen et al. (25) detected second harmonic generation which was strong on rough Ag and weak on smooth Ag. This detection of a nonlinear polarizability of the surface itself can be interpreted as a demonstration of optical effects and their independence of the nature of the molecule.

The optical resonance is well accepted among scientists, but not as the sole effect responsible for SERS. There are serious shortcomings with the optical resonance, since in many cases, where theoretically such a resonance should be expected, SERS is either weak or not detectable. Theoretical calculations put a limit to the surface roughness in order to avoid either retardation or damping effects; thus, the largest levels of enhancement are restricted to three orders of magnitude, which is not enough to explain all of the effect of SERS.

C. Electronic Resonance. Electronic Resonance arises when the denominator in the first term of eq. 4 becomes very small, i.e. when the incident photon energy is near to the energy separation between the ground state and one of the excited states j. The resonant state in SERS may be found by coulomb coupling between the metal and the adsorbate and the resulting shift and broadening of the molecular state. The interaction also involves charge transfer. Electronic resonance is restricted to the first layer of molecules, and is sensitive, in general, to the electronic structure of the molecule and the conditions which favor chemical bonds between the metal and the adsorbate, which stands in contrast with optical resonance.

One feature, which is needed for both types of resonance is the "active site", which necessitates an activation step prior to the detection of SERS. By studying the SERS of the adsorbate, it is possible to learn and make assumptions about the environment of the substrate.

Pettinger, Wenning and Kolb (26) and later Loo (27) came to the conclusion that the spectrum seen is characteristic of a chemical complex involving atoms of the substrate and the molecule. A few authors (28-31) studied the nature of the water-substrate complex, and found that it lead to SERS only under specific activation conditions and in the presence of certain electrolytes. The SERS of water is different than that of the bulk liquid and has only been observed in the presence of co-adsorbed halides and depends on the bulk solution pH and the type of cation in the supporting electrolyte. It has been proposed by Fleischmann et al. (28) that this form of water formed a complex with the halides and Ag atoms, and that in order to display SERS, water must be present in the active site.

The effect of the laser illumination on the SERS signal (due to the exposure of the electrode to the laser beam during the pretreatment step) is another factor which is related to the concept of active sites and surface roughness. Macomber et al. (32) found that the signal of pyridine, thiourea and water in halide solutions was further magnified when the silver electrode was illuminated by the laser beam during the pretreatment. Barz et al. (33) reported similar results with thiocyanate in KCl, and explain the findings in terms of a structural modification of the silver surface due to the creation of a large number of silver clusters created in the silver halide film by photodecomposition. It has been found by Chen et al. (34), who performed scanning electron microscopy studies that the structure of the Ag electrode was altered during the pretreatment step. Barz et al. (35) stepped the electrode potential to the region where hydrogen evolved prior to the pretreatment, and found that the SERS signal was further enhanced by one order of magnitude. They explain this additional enhancement as being due to the morphological changes caused by the presence of hydrogen bubbles during the reduction of the silver-chloride film.

Demuth et al. (36) studied the SERS of pyridine on single Ag crystal gratings in an UHV environment. The single crystallinity led to a predominance in the orientation of the crystal surface, in contrast with the randomly rough surfaces which are formed by the electrochemical pretreatment of the electrode. A plot of the relative SERS intensty as a function of the surface coverage of pyridine, shows an abrupt appearance of the enhancement at a coverage of 0.4 monolayers. The authors attribute this by correlation to photoemission data to a transition in which the pyridine molecules rotated from a flat configuration to an erect configuration. The latter position on the surface enabled a more effective interaction between the nitrogen lone pair and the surface, thus leading to a greater electronic resonance.

In order to test the importance of the active site, Wood and Klein (37) studied the SERS of pyridine on evaporated Ag under UHV condition. They prepared the substrates at low temperatures, where the surface migration of the Ag adatoms was minimal, leading to microscopic defects. Pyridine adsorbed on this surface did show SERS, however when the substrate was heated to room temperature, the signal was irreversibily quenched, due to thermal desorption and also due to annealing of the microscopic defects. The same effect of irreversibly destroying the enhancement has been observed in an electrochemical environment (38), where the surface complex was destabilized by the potential applied on the electrode. As the active sites were destroyed (by applying a potential negative to -1.1 volts), there was an irreversible loss of SERS. However when Ag was electrodeposited on the surface, the irreversibility disappeared, since the active sites were continually being created.

In the electronic resonance, an electronic transition is induced by the incident light on the active site. The association of the molecule with the surface through a chemical bond perturbs ground electronic states.

Charge transfer excitations between the adsorbed molecule and the metal surface which involve strong optical absorption have been found to be a plausible mechanism by various authors (39-49). Two distinct charge transfer mechansims have been proposed. The first suggests that the transferred charge affects the surface plasmon modes and modulation of this charge transfer by molecular vibrations yields a corresponding change in the surface plasmon contribution to light scattering by the metal surface (39,40,41). The resultant amplitude modulation of the scattered radiation is proposed to yield strongly enhanced Raman sidebands. The second proposed that virtual excitations to the charge transfer state, which can be partially resonant with the exciting radiation even at visible wavelengths, yield large contributions to the Raman scattering polarizability tensor of the combined metal-molecule system (42-45).

Demuth and Sanda studied the participation of charge transfer excitation (46) by performing low energy electron diffraction experiments. They observed a broad band corresponding to 2 ev which did not coincide with any known excitation in either Ag or pyridine. Later, Schmeisser, Demuth and Avouris (47) reported the observation of charge transfer excitations only when the surface was covered with atomic scale defects. Thus, this study has made a direct connection between electronic resonance through charge transfer and atomic defects.

The photon energy dependence of the coupling to the charge transfer excitation must influence the SERS excitation profile, and the efficiency of this coupling will be reflected by the intensity of Raman signal. Since charge transfer excitation involves spacially separated states, their relative energy difference can be modulated by applying a certain voltage to the system, as can be done in an electrochemical environment. The excitation profile should then be dependent on the applied voltage. In the case where the incident photon energy is fixed, the intensity of the signal should be a function of the applied potential (48,49). Furtak and Macomber (48) observed the shift in the electronic resonance changes in pyridine. A plot of the intensity vs. applied potential, shows a maximum of the intensity at -.5 V when the excitation light was 488 nm, and -.8 V when the laser light was 647.1 nm. They interpret the results in terms of a charge transfer excitation from a filled state in the bulk metal to an unoccupied state on the molecule, or from a state within the metal to an unoccupied surface state on the metal surface. Lombardi et al. (49) reported the Raman intensity vs. the electrode potential of a series of substituted pyridines and saturated nitrogen heterocyclic compounds, at two excitation energies (488 nm and 600 nm). The voltage maximum shifts to more positive potentials with increasing excitation energy for the substituted pyridines and to more negative potentials with increasing excitation energy for the saturated compounds. They correlated the voltage maxima with the Hammett sigma function for substituted pyridines and with pK_a for the saturated heterocycles. They interpret the results in terms of a charge transfer from the metal to the molecule in the case of the unsaturated molecules, and from the molecule to the metal in the case of the saturated heterocycles.

The role of charge transfer excitations as a manifestation of electronic resonance is established and generally accepted. However, the exact mechanism is still under debate.

D. The SERS Experiment and Characteristics. The SERS experiment for the electrochemical environment usually consists of a three electrode cell: the working, the counter and the reference electrodes. The cell is made of quartz, the bottom being optically flat see appendix. The laser beam is focused on a spot on the working electrode, which does not exceed the surface of the electrode. The laser power used at the electrode is usually less than 100 mW and the spectral bandpass is 2-5 cm^{-1}. The usual SERS electrochemical set-up includes the three electrode cell, connected to a wave form generator and a potentiostat. The laser beam is focused on the working electrode and then scattered and collected in a double monochromator. In our experimental set-up the signal is transferred to a photomultiplier, then to an amplifier-discriminator and then to a PDP-8/E computer. The most frequently used laser frequencies are 4880 Å, 5145 Å and 6470 Å. The dependence of the SERS signal on this parameter has been investigated by various groups (27,50-52) and an increase of twenty fold in the intensity of adsorbates on silver was found when the frequency was shifted from blue to red. On the other hand, copper and gold showed SERS only upon laser excitation in the red (51,53,54); when a 4680 Å line was used, no SERS was observed. When the logarithm of the experimental enhancement factor versus the excitation energy on Ag and Cu was plotted, it agreed with the theoretical plot.

Another characteristic of SERS is a background continuum, which extends from the Rayleigh tail to about 4200 cm^{-1} (55-57), and is found to be potential dependent. It has been attributed to luminescence caused by a radiative recombination, produced by photoionization (55). This interpretation was reinforced by picosecond Raman gain experiments at approximately 2000 cm^{-1}, which indicated that the background was not a Raman effect, but rather a result of luminescence (58). Pettinger and Wetzel (59) interpreted the continuum as being a superposition of numerous SERS weak bands, therefore its observed potential dependence.

Typically, SERS involves the use of a silver electrde, 0.05 M solution concentration of adsorbate and 0.1 M of the electrolyte. Numerous adsorbates have been investigated, such as pyridine and its derivatives, i.e. 2,3,4-cynaopyridines, pyridine d_5, aniline, 4-acetylpyridine, N-methyl imidazole, N,N-dimethylcyanamide(2), etc.

Recently, Busby and Creighton (60) have performed coulometric measurements and found a linear dependence between the charge applied during the pretreatment and the surface concentration. Based on that, they found that the enhancement was increased by a factor of 10 as a result of an increased concentration of the adsorbate on the surface. They have also studied (61) the Raman excitation profiles of of pyridine-2-azo-dimethylaniline and found that the strongly allowed electronic transition lies 400 Å away from the adsorption maximum of the molecule in the solution.

The only reports of SERS from radicals have been submitted by Regis and Corset (62), who investigated pyridine and by Melendres (63) who observed that methyl viologin (MV^+) radical cation was stabilized by electrode cycling and high halide concentrations.

Numerous anions have also been observed to show SERS, such as CN^- (64,65), SCN^- (66,67) and halide ions (66,68,69), N_3^- (70) cytrate (71), $RuCN_6^{-4}$ (72), MoO_4^- (73), etc. In the CN^- case, the results were interpreted in terms of different $AgCN^{-(n-1)}$ complexes. An assignment of three CN^- ions adsorbed to a Ag^+ adion was made (66) by comparison with the Normal Raman of $Ag(CN)_3^{2-}$. SCN^- showed a potential dependent weak band, which was assigned to be a AgSCN band.

Lately, researchers have become interested in SERS of molecules which exhibit resonance Raman, such as crystal violet, since the Raman cross section is large even without the surface enhancement and also because the metal-molecule interaction does not perturb the energy difference between electronic excited states and electronic ground states of the adsorbate. Since the fluorescence of the molecule under study can be quenched (74) all these effects make it possible to observe an enormous enhancement of selective modes of biological molecules having large molecular weights (75,76). Some of the biological systems are bile pigment biliverdine (77) on silver sols; cytochrome c and myoglobin (78) at a concentration below 10^{-6} M. Both cytochrome c and myoglobin seem to undergo reduction of the low spin iron(II) at the electrode; cobalt tetrasulfonate phthalocyanine was studied on a silver electrode at various laser excitation energies (79), using a rotating cell in order to avoid local heating effects; SERS of adenine, adenosine and adenosine 5'-monophosphate were studied as well by Koglin et al. (80,81). These molecules (80,81) do not show Resonance Raman and their intensity is solely due to SERS.

Itabashi et al. (82) have reported the surface enhanced resonance Raman of meso-tetrakis (4 sulfonatophenyl) porphine (TSPP) at a Ag electrode. The potential dependence of this system reveals two electrochemical processes at the Ag electrode: one which begins around -.3 V where the aggregated TSPP dissociates to monomers and the other one which occurs near -.4 V where the TSPP molecules become partially incorporated in the metal.

Lately, there has been a growing interest in the SERS of polymers. Metcalfe and Hester (83) studied the spectra of gold coated sinusoidal diffraction gratings overcoated with thin films of polystirene, using several excitation energies. They report the angular and polarization dependence of the intensity of the Raman bands and show that they correlate with the variations in the zero-order reflectivity of the grating. Heard et al. (84) report SERS of amphilic molecules at submonolayer coverages of Ag and Au colloidal metal surfaces. They have also found that polyvinylpyrrolidone shows SERS only when the sols aggregate. They conclude that aggregation of the colloidal substrate is an important factor for observing SERS. However, no other reports on sols mentioned so far, call for the need of aggregation for the enhancement to occur. Another interesting study was performed by Lee and Meisel (85) on polyvinyl alcohol (PVA), polyethylene glycol, carbowax and polyvinylpyridine (PVP) on Ag and Au sols. They conclude that PVA adsorbs on the metal through the unhydrolyzed acetate groups; carbowax adsorbs through the C-O-C groups, and PVP adsorbs through the pyridine system, which means that the molecule lies flat on the surface.

And finally, a nonaqueous SERS of pyridine in N-N'diemthylformamide solution at a silver electrode is reported by Hutchinson et al. (86). This is the first report of a nonaqueous solution and its is very important since it enables experimentalists to study the SERS of (nonpolar) molecules that do not dissolve in water or methanol. These authors used 0.1 M pyridine and 0.05 M tetrabutylammonium perchlorate. The fact that the spectrum of pyridine is similar to an aqueous one indicates the insensitivity of the surface-adsorbed species to the nature of the solvent.

E. Conclusion

A brief description of the electrochemical background, the theory and the characteristics, as well as various reports of SERS have been presented.

It seems that SERS is still a growing field which has expanded not only to new theories but also to new systems, such as biological and polymeric ones. Although the origin of the enhancement is not completely understood, it is a good and reliable technique for studying in-situ the interaction and the effects of a molecule adsorbed on a metal surface in different environments.

F. References

1) Fleischmann, M.; Hendra, P. J.; McQuillian, A. J. Chem. Phys. Lett. 1974, 26, 163.

2) Van Duyne, R. P. "Chemical and Biochemical Applictions of Lasers", C. B. Moore Editor, Academic Press, New York 1974, Vol. 4, Ch. 5.

3) Birke, R. L; Lombardi, J. R.; Sanchez, L. A. "Advances in Chemistry Series", No. 201, Karl M. Kadish, Editor, ACS 1982, Vol. 4, p. 69.

4) a) Furtak, T. E.; Reyes-Corona, J. Surf. Sci. 1980, 93, 382.
   b) Furtak, T. E. "Advances in Laser Spectroscopy," edited by B. R. Garetz, J. R. Lombardi (Heyden, London 1982).

5) Otto, A. Appl. Surf. Sci. 1980, 6, 309.

6) Pockrand, I. "Surface Enhanced Raman Vibrational Studies at Solid/Gas Interfaces", Springer Trcks in Modern Physics, March, 1983.

7) Chang , R. K.; Laube, B. L. CRC Critical Reviews in Solid State and Materials Science, submitted.

8) Bernard, I.; Birke, R. L.; Lombardi, J. R. to be published.

9) Bockris, J. O'M; Reddy, A. K. N. "Modern Electrochemistry", Vol. 2, Plenum Press, New York, 1970.

10) Parson, R. J. Electroanal. Chem., 1981 3, 118.

11) Valette, G. J. Electroanal. Chem. in press.

12) Valette, G. J. Electroanal. Chem. 1982 132, 311.

13) Valette, G. J. Electroanal. Chem. 1981, 122, 285.

14) Macomber, S. H.; Furtak, T. E.; Devine, T. M. Surf. Sci. in press.

15) Pettinger, B.; Moere, L. J. Electroanal. Chem. in press.

16) Kotz, R.; Yeager, E. J. Electroanal. Chem. 1981, 123, 335.

17) Anderson, A. B.; Kotz, R. ; Yeager, E. Chem. Phys. Lett. 1981, 82, 130.

18) King, F. W.; Van Duyne, R. P.; Schatz, G. C. J. Chem. Phys. 1978, 69, 4472.

19) Pettinger, B.; Tadjeddine, A.; Kolb, D. M. Chem. Phys. Lett. 1978, 66, 544.

20) Furtak, T. E.; and Kester, J. Phys. Rev. Lett. 1980, 45, 1652.

21) Kester, J. J.; Furtak, T. E. Solid State Commun. 1982, 41, 457.

22) Murray, C. A. in "Surface Enhanced Raman Scattering", R. K. Chang and T. E. Furtak editors, Plenum, New York 1982, p. 203.

23) Trott, G. R.; and Furtk, T. E. Solid State Comm. 1980, 36, 1011.

24) Creighton, J. E. in "Surface Enhanced Raman Scattering", R. K. Chang and T. E. Furtak editors, Plenum, New York, 1982, p. 315.

25) Chen, C. K.; de Castro, A. R. B.; Shen, Y. R. Phys. Rev. Lett. 1981, 46, 145.

26) Pettinger, B.; Wenning, U.; and Kolb, D. M. Ber. Bunsenges, Phys. Chem. 1978, 82, 1326.

27) Loo, B. H. J. Phys. Chem. 1982, 86, 433.

28) Flesichmann, M.; Hendra, P. J.; Hill, I. R.; and Pemble, M. E. J. Electroanal. Chem. 1981, 117, 243.

29) Pettinger, B.; Philpott, M.; Gordon, J. Surf. Sci. 1981, 105, 469.

30) Chen, T. T.; Owen, J. F.; and Chang, R. K. Chem. Phys. Lett. 1982, 89, 356.

31) Macomber, S. H. Furtak, T. E.; and Devine, T. M. Surf. Sci. in press.

32) Macomber, S. H.; Furtak, T. E.; and Devine, T. M. Chem. Phys. Lett. 1982, 90(6) 439.

33) Barz, F. G.; Gordon II, J. G.; Philpott, M. R.; and Weaver, M.J. Chem. Phys. Lett. 1982, 91(4) 291.

34) Chen, T. T. van Rabeu, K. U.; Owen, J. F.; Chang, R. K. and Laube, B. L. Chem. Phys. Lett. 1982, 91(6) 494.

35) Barz, F. T.; Gordon, II, J.G.; Philpott, M. R.; and Weaver, M. J. Chem. Phys. Lett. 1983, 94(2), 168.

36) Demuth, J. E.; Sanda, P. N.; Warlaumont, J. M.; Tsang, J. C. and Christman, K. in "Vibrations at Surfaces", editors R. Candano, J. M. Gilles, and A. A. Lueas, Plenum, New York, 1982, p. 391.

37) Wood, T. H.; and Klein, M. V. J. Vac. Sci. and Tech. 1979, 16, 459.

38) Furtak, T. E.; Trott G.; and Loo, B. H. Surf. Sci. 1980, 101, 374.

39) Kirtley, J. R.; Jha, S. S.; and Tsang, J. C. Solid State Commun. 1980, 35, 509.

40) McCall, S. C.; and Platzman, P. M. Phys. Rev. 1980, B22, 1660.

41) Abe, H.; Manzel, K.; Schutz, W.; Moskowitz, M.; and DiLella, D. P. J. Chem. Phys. 1981 74, 792.

42) Burstein, E.; Chen, Y. J.; Chen, C. Y.; Landquist, S.; and Tosatti, E. Solid State Commun. 1970, 29, 567.

43) Gersten, J. I.; Birke, R. L.; and Lombardi, J. R. Phys. Rev. Lett. 1979, 43, 147.

44) Persson, B. N. J. Chem. Phys. Lett. 1981, 82, 561.

45) Avouris, P. H.; and Demuth, J. E. J. Chem. Phys. 1981, 75, 4783.

46) Demuth, J. E.; Sanda, P. N. Phys. Rev. Lett. 1981, 47, 57.

47) Schmeisser, D.; Demuth, J. E.; and Avouris, P. H. Chem. Phys. Lett. 1982, 81, 324.

48) Furtak, T. E.; and Macomber, S. H. Chem. Phys. Lett. 1983, 95, 328.

49) Lombardi, J. R.; Birke, R. L.; Sanchez, L. A.; Bernard, I.; and Sun, S. C. J. Phys. Chem. in press.

50) Creighton, J. A.; Albrecht, H. G.; Hester, R. E.; Matthew, J. A. D. Chem. Phys. Lett. 1978, 55, 55.

51) Wood, T. H.; Klein, M. V. Solid State Commun. 1980, 35, 263.

52) Girlando, A.; Gordon II, J. G.; Heitman, D.; Philpott, M. R.; Seki, H.; Swalen, J. D. Surf. Sci., 1980 101, 417.

53) Wenning, U.; Pettinger, B.; Wetzel, H. Chem. Phys. Lett. 1980, 70, 49.

54) Allen, C. S.; Schatz, G. C.; Van Duyne, R. P. Chem. Phys. Lett. 1980, 75, 201.

55) Birke, R. L.; Lombardi, J. R.; Gersten, J. I. Phys. Rev. Lett. 1979, 43, 71.

56) Otto, A. Surf. Sci. 1978, 75, L392.

57) Furtak, T. E.; Reyes-Corna, J. Surf. Sci. 1980, 93, 351.

58) Heritage, J. P.; Bergman, J. G.; Pinczuk, A.; Worlock, J. M. Chem. Phy. Lett. 1979, 67, 229.

59) Pettinger, B.; Wetzel, H. Chem. Phys. Lett. 181, 78, 398.

60) Busby, C. C.; Creighton, J. A. J. Electroanal. Chem. 1982, 133, 183.

61) Campbell, J. R.; Creighton, J. A. J. Electronanal. Chem. 1983, 143, 359.

62) Regis, A.; Corset, J. J. Chim. Phys. 1981, 76, 687.

63) Melendres, C. A.; Lee, P. C.; and Meisel, D. J. Electrochem. Soc. 1983, 130(7), 1523.

64) Dornhaus, R.; Long, M. B.; Bennes, R. E.; Chang, R. K. Surf. Sci. 1980, 93, 240.

65) Billmann, J.; Kovacs, G.; Otto, A. Surf. Sci 1980, 92, 153.

66) Pemble, M E., Ph.D. Thesis, Univ. of Southampton, Southampton, England.

67) Gold, A. S.; Buck, R. P. J. Raman Spec. 1979, 8, 323.

68) Wetzel, H.; Gerischer, H. Chem. Phys. Lett. 1980, 76, 460.

69) Fleischmann, M.; Hendra, P. J.; Hill, I. R.; Pemble, M. E. J. Electroanal. Chem. 1981, 117, 243.

70) Kunz, R. E.; Gordon II, J. G./ Philpott, M. R.; Girlando, A. J. Electroanal. Chem. 1980, 112, 391.

71) Kerker, M.; Suman, O.; Bumm, L. A.; Wang, D-S. Appl. Opt. 1980, 19, 3253.

72) Allen, C. S. Van Duyne, R. P. J. Am. Chem. Soc. 1981, 103, 7497.

73) Allen, C. S. Van Duyne, R. P. Surf. Sci.

74) Kneipp, K.; Hinzmann, G.; Fassler, D. Chem. Phys. Lett. 1983, 99, 503.

75) Cotton, T. H. J. Am. Chem. Soc., 102, 7960, 1980.

76) McMahon, J. J. Proceedings of the VIIIth Raman International Conference on Raman Spectroscopy, 1982, 77.

77) Lippitsch, M. E. Chem. Phys. Lett. 1981, 79, 2.

78) Cotton, T. M.; Schultz, S. G.; Van Duyne, R. P. J. Am. Chem. Soc. 1981 102, 7960.

79) Kotz, R.; Yeager, E. J. Electroanal. Chem. 1980, 113, 113.

80) Koglin, E.; Seguaris, J. M.; Valenta, P. J. J. Mol. Struc. 1980, 60, 421.

81) Ervin, K. M.; Koglin, E.; Seguaris, J. M.; Valenta, P. J.; Nurenberg, H. W. J. Electroanal. Chem. 1980, 114, 179.

82) Itabashi, M.; Kato, K.; Itohi, K. Chem. Phys. Lett. 1983, 97, 528.

83) Metcalfe, K. and Hester, R. E. Chem. Phys. Lett. 1983, 94, 411.

84) Heard, S. M.; Grieser, F.; Barradough, C. G. Chem. Phys. Lett. 1983, 95, 154.

85) Lee, P. C. and Meisel, D. Chem. Phys. Lett. 1983, 99, 262.

86) Hutchinson, K.; McQuinllan, A. J.; Hester, R. E. Chem. Phys. Lett. 1983, 98, 27.

CHAPTER II

pH AND CHLORIDE CONCENTRATION EFFECTS ON THE SERS OF PYRIDINE

A. Introduction

The observation of a giant enhancement in the Raman spectra of molecules adsorbed on a silver substrate, has entailed considerable activity from various groups (1,2).

Most studies have been carried out so far with pyridine and pyridine derivatives, other nitrogen heterocycles and several anions. Less consideration has been given to the SERS of cationic species (3,4,5,6).

We have briefly discussed the SERS of pyridinium ion (7) and this report is a more detailed investigation of its SER spectra at a Ag electrode.

Van Duyne (1) decremented the pH of a solution of 0.05 M pyridine and 0.1 M KCl at -0.6 V vs SCE on Ag from pH = 13 to pH = 5, and found out that the SERS intensity was constant. But between pH = 5 and pH = 3, (pK_a = 5 for pyridine) the SERS intensity dropped to zero as the pH was further reduced. Since the potential in these experiments was on the positive side of the point of zero charge (p.z.c.), they concluded that the pyridinium ion was probably not strongly adsorbed.

Marinyuk et al. (4) studied the spectra of tetramethylammonium (TMA^+), tetraethylammonium (TEA^+) and tetrabutylammonium (TBA^+) cations and noticed that TMA^+ showed more noticeable frequency changes as a function of electrode voltage, than TEA^+ and TBA^+. The explanation given for this effect was that the increase in the length of the alkyl chain smeared out the charge over all atoms and therefore the vibrational frequencies of these cations were less sensitive to changes in the potential.

The fact that positively charged species have shown spectra at potentials positive to the p.z.c. raises questions pertaining to the adsorption of these species on the positively charged surface. Marinyuk et al. (4) studied the changes in the spectrum of pyridine adsorbed on silver in the presence of I^- and noticed that the spectrum was not affected by changing from H_2O to D_2O in neutral solutions while $C_5H_5ND^+$ is seen in addition to pyridinium in an acidic medium. They conclude that I^- adsorption gives rise to Lewis acid sites on the silver surface. This explanation for the appearance of the 1024 cm^{-1} band is similar to that given by Fleischmann (8), in the sense that a coordinated nitrogen displays a trigonal ring breathing mode which is shifted to a lower frequency compared to the 1036 cm^{-1} band. The 1024 cm^{-1} band was assigned by Fleischmann (8a) as pyridine chemisorbed to silver via Lewis acid coordination through the nitrogen, whereas the 1036 and 1008 cm^{-1} bands, being similar in frequency to those in aqueous solution were assigned as pyridine physisorbed at the electrode/electrolyte interface via water. The 1024 cm^{-1} has been discussed in detail in reference 8b, where the electrode was pretreated while the electrode was illuminated by an unfocussed laser beam. They noted a relative increase of the 1025 cm^{-1} line which they related to the atomic cluster known to form to varying extents upon photolysis of the different silver halides. However, prolonged radiation of the electrode caused a decrease in the intensity of the 1025 cm^{-1} band, leading to a corresponding increase in the 1007 cm^{-1} and 1037 cm^{-1} bands. They conclude that the chemisorbed species is formed at special sites on top of the geometrically defined surface, as a result of photolysis.

Earlier studies of Regis and Corset (3) on pyridinium (which agree with the data to be presented) lead them to introduce radical ions to explain the SERS of pyridine, but there is no proof for the existence of such species in the SERS phenomenon for pyridinium. These authors find that at a potential of -0.05 V there is a strong preferential adsorption of the pyH^+ ion at the electrode surface in the presence of specifically adsorbed Cl^- ions. Since the spectrum at pH = 8 showed three bands at 1008, 1025 and 1036 cm^{-1} at -0.05 V, they conclude that both the free and the protonated pyridine are responsible for these peaks. They point to the fact that the pyridinium ions are strongly bound at this conditions even though their concentration is very low. We doubt this conclusion, because the free pyridine is known to display three bands at 1008, 1025 and 1036 cm^{-1} at -0.05 V at pH = 8, and also because a solution of 0.05×10^{-3} M of pyridinium (which corresponds to the concentration of the protonated species at pH = 8) in 0.1 M KCl, did not lead to a detectable spectrum.

Atkinson et al. (6) studied the intensity of several Raman bands of pyridine in a chloride solution and their dependence on the applied potential and the pyridine concentration. They found that the intensity ratio of the 1038 and 1011 cm^{-1} bands of pyridine exhibited a similar potential dependence to the intensity of the 240 cm^{-1} band, indicating a surface complex involving both pyridine and chloride. They further elaborate that this complex, or pyH^+Cl^- ion pair is possibly in equilibrium with the pyridine radical and the Cl_2^- radical, as suggested by Regis and Corset (3).

All these studies indicate that positively charged molecules can in fact, show SERS, positive to the p.z.c. However, no study has carefully looked at the nature of the surface species involving these positively charged ions, and the influence of the halide on the behavior of the system.

In an attempt to elucidate this questions, we have investigated the SERS of pyridine at different pH values and as a function of chloride concentration, at various values of ionic strength, using different pretreatment methods.

B. Experimental

Raman spectra were obtained with a Coherent Radiation 52B Argon ion laser in conjunction with a Spex 1401 double spectrometer and PDP-8/E computer. The exciting line was 4880 Å. The electrochemical cell, scattering geometry and electrodes used for the measurement have been discussed elsewhere (2).

Electrode potentials of a 99.99% pure polycrystalline Ag electrode were controlled with a Princeton Applied Research (PAR) Model 173 Potentiostat, together with a PAR Model 175 Universal Programmer. All potentials are quoted versus a saturated calomel electrode.

The solutions were prepared with distilled pyridine and isoquinoline, obtained from Aldrich Chemical Company. The solutions were deaereated by bubbling nitrogen before use.

The time controlled pretreatment of the electrode included a step from -0.6 V to +0.2 V, holding it for 2 seconds at this voltage, and then stepping back to -0.6 V. All potentials are quoted vs. a saturated calomel electrode, SCE. The chloride was added to the solution without changing the alignment of the cell. After each chloride addition, the surface was cleaned and then pretreated in the manner indicated above.

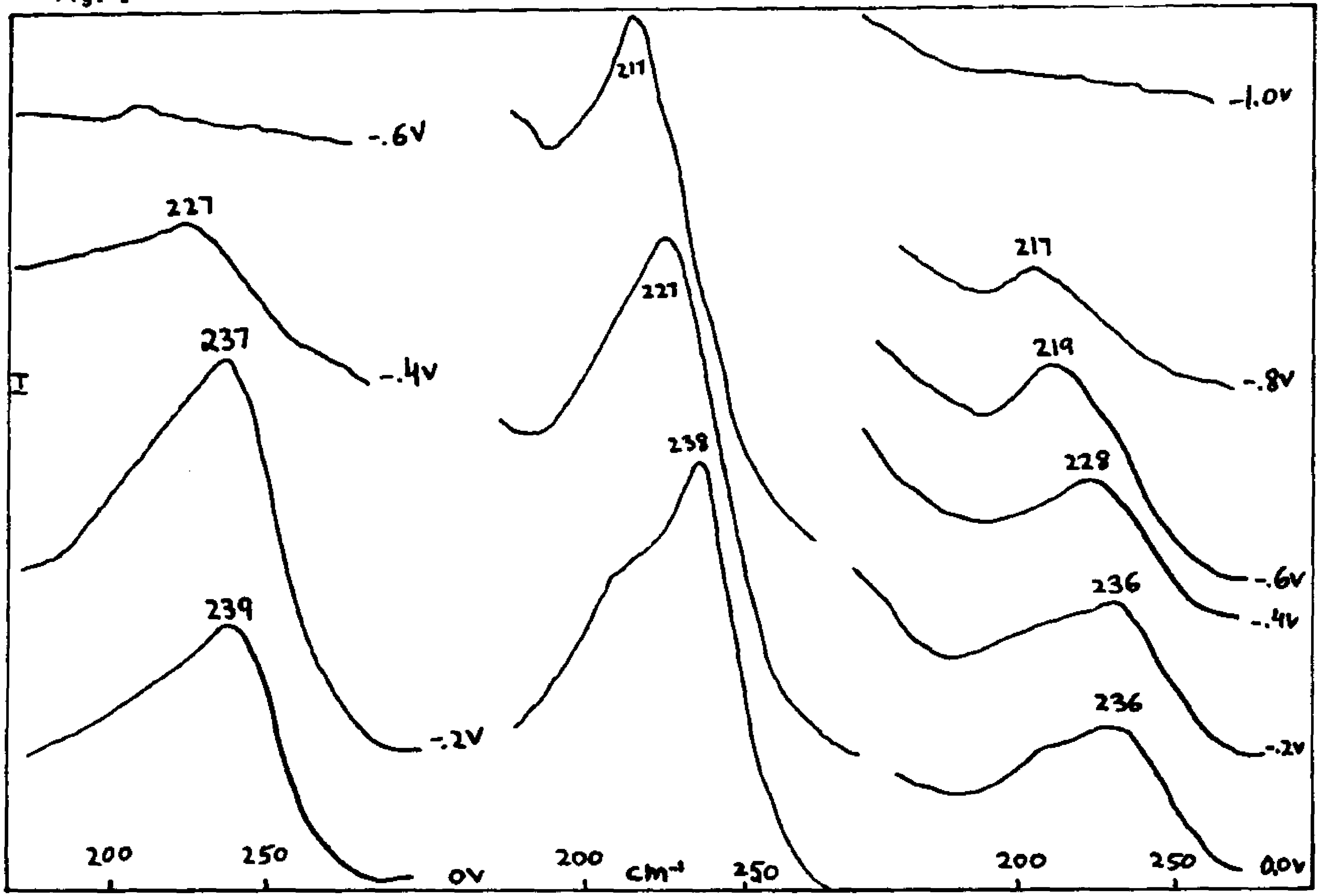
Also the charge controlled pretreatment was used in which 25 mC/cm^2 was passed in a solution of 0.005 M chloride and 0.05 M pyridinium. The electrode was then washed and inserted in the cell. All pretreatments were performed in the dark.

Since the alignment of the cell was changed after each pretreatment the relative intensities were calibrated by using a laser line (4964 Å), which was found to be time and voltage independent. Before the spectrum was taken the laser line was brought to the same intensity each time (keeping the laser power constant). The error in the reproducibility of the respective intensities was 8%.

C. Results and Discussion

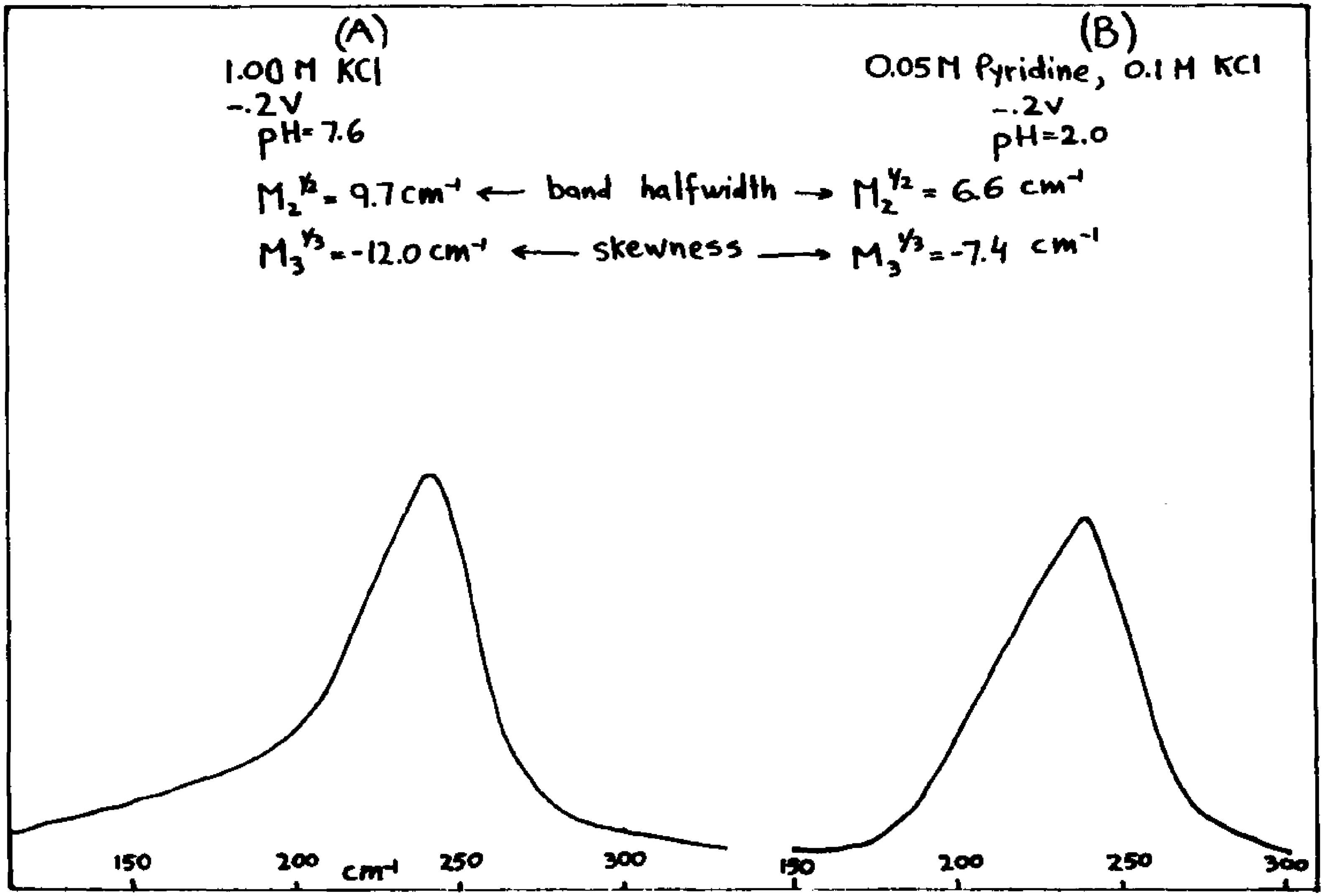
The low lying SERS vibration in the Ag/pyridine, KCl system typical of a surface band (not seen in solution) is shown as a function of pH and voltage in Fig. I. At pH = 2 the ratio of pyridinium to pyridine in solution is 1000:1, whereas at pH = 8 this ratio is inverted and becomes 1:1000. At pH = 5.2 = pK_a this ratio becomes 1:1.

Fig. I



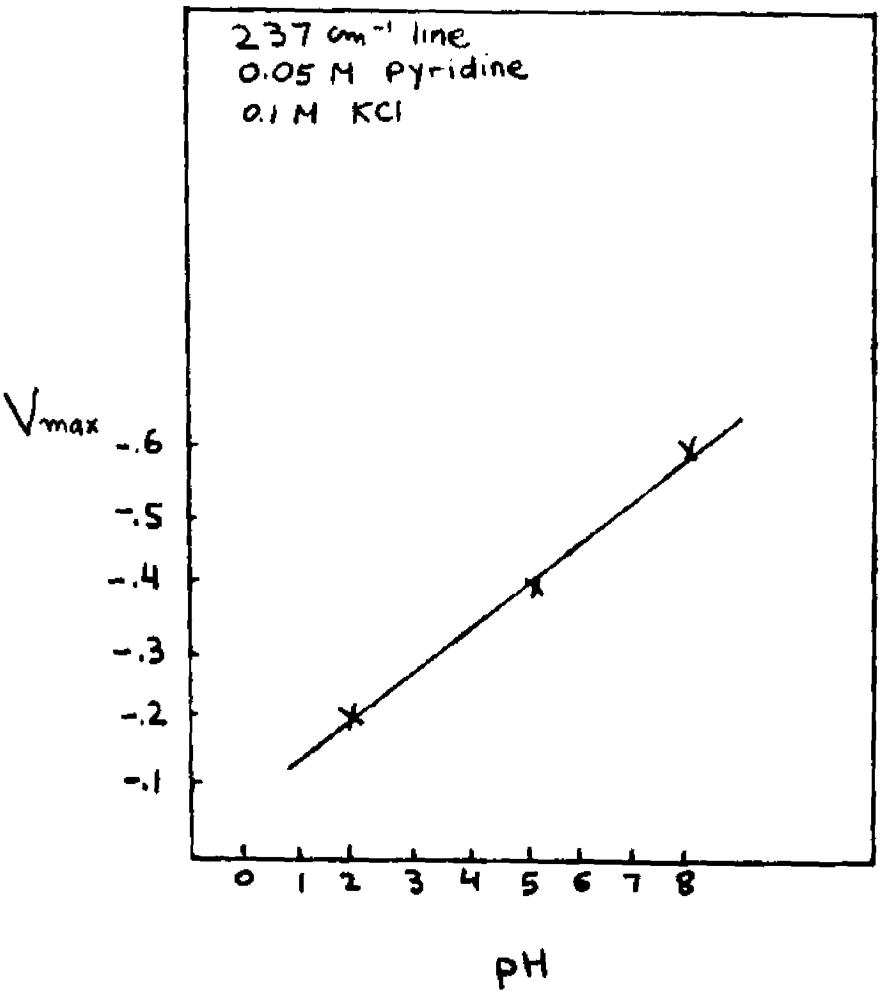
SERS of Pyridine at pH=2, 5.2 and 7.8 in the region I50-300 cm^{-I}

Fig. 2



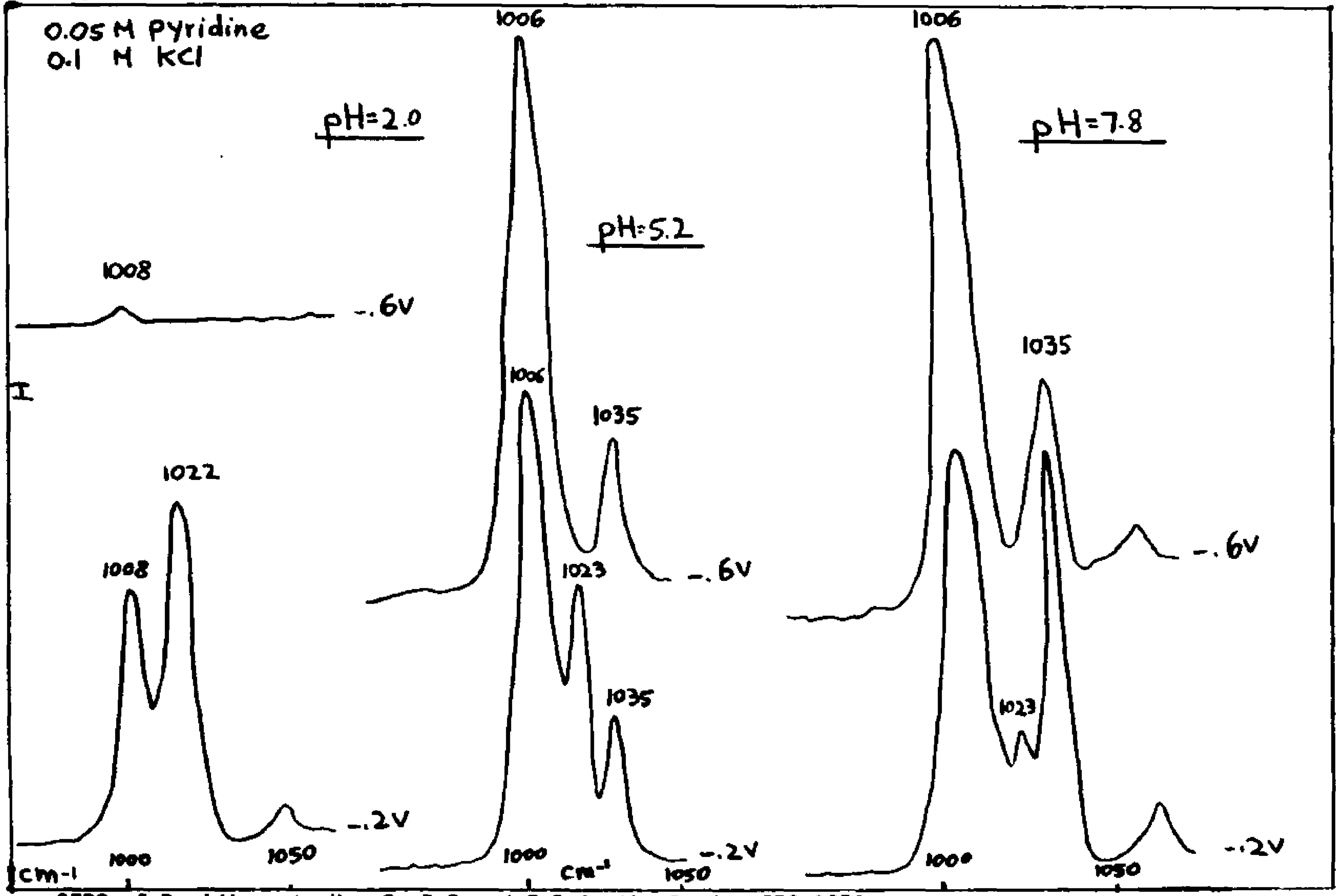
The 237 cm^{-I} band in various solution conditions

Fig. 3



The Potential of Peak in Intensity Versus pH for 0.05 M Pyridine

Fig. 4



SERS of Pyridine at pH = 2, 5.2 and 7.8 in the Region 950-1050.

The SERS spectrum of the molecular lines at pH = 2 and -.2 V is typical of pyridinium; at pH = 8 and -.6 V it is typical of pyridine; and at pH 5.2 it is a mixture of both. The surface line at 237 cm^{-1} (±3 cm^{-1}, depending on the voltage) and pH = 2 peaks at the same voltage as the 1006 cm^{-1} and 1022 cm^{-1} bands of pyridinium (-.2 V). Since at -.2 V the surface is positively charged and so is the protonated pyridine, the formation of a chloride-pyridinium ion pair, which adsorbs to the surface through the halide has been suggested (7). The 237 cm^{-1} band seen in the presence of 0.05 M pyridinium at pH = 2 and -.2 V differs in line shape from the one seen in a solution containing only 1.0 M KCl at pH = 7.6, as can be seen by the moment analysis of the two lines shown in Fig. 2. The square root of the second moment gives the half width of the spectral line, and the cube root of the third moment gives a measure of the skewness of the line. Band A (Fig. 2) has a linewidth of 9.7 cm^{-1} and is more skewed than line B which has a linewidth of 6.6 cm^{-1}. Previously the low lying surface band at 237 cm^{-1} was assigned to Ag-Cl stretch; however, the difference in line shapes between band A and B strongly suggests that the 237 cm^{-1} line in presence of pyridinium is not a pure Ag-Cl band.

At pH = 7.8 (Fig. 1), the low lying band is very broad between 0 and -.2 V, and shifts to a lower frequency (217 cm^{-1}) as the voltage becomes more negative. The behavior is probably due to the fact that this band is a mixture of Ag-N and Ag-Cl vibrations between 0.0 and -.2 V, and becomes only the second type of line at -.6 V. It may be that these two types of surface lines are a result of the fact that there is a complex between pyridine and the chloride (7), and depending on the voltage, a different site of the complex adsorbs to the surface.

At pH = 5.2 the band peaks at -.4 V, which is a potential half-way between that of the other two pH systems. A plot of the potential of maximum intensity V_{max} vs. pH shows a straight line, see Fig. 3.

Fig. 4 shows a different portion of the spectrum in the region 950-1050 cm^{-1}, as a function of pH and applied voltage. The typical spectrum of pyridinium at pH = 2 shows two lines, one at 1006 cm^{-1} and the other at 1022 cm^{-1}, which peak at -.2 V. The accepted assignments in the Wilson vibrations are ν_1 and ν_{18} (or ν_{12}) respectively (9,10,11) see Appendix for a diagram. Both lines are of a_1 symmetry. At -.6 V the lines disappear almost completely. At pH = 7.8 at -.2 V, the typical spectrum of pyridine at this portion of the spectrum shows a line at 1008 cm^{-1} and two lines at 1025 cm^{-1} and 1035 cm^{-1}. The 1025 cm^{-1} band is typical of pyridine adsorbed to the surface and disappears at voltages more cathodic than -.2 V (8). At -.6 V the spectrum of pyridine peaks in intensity, in contrast with that of pyridinium.

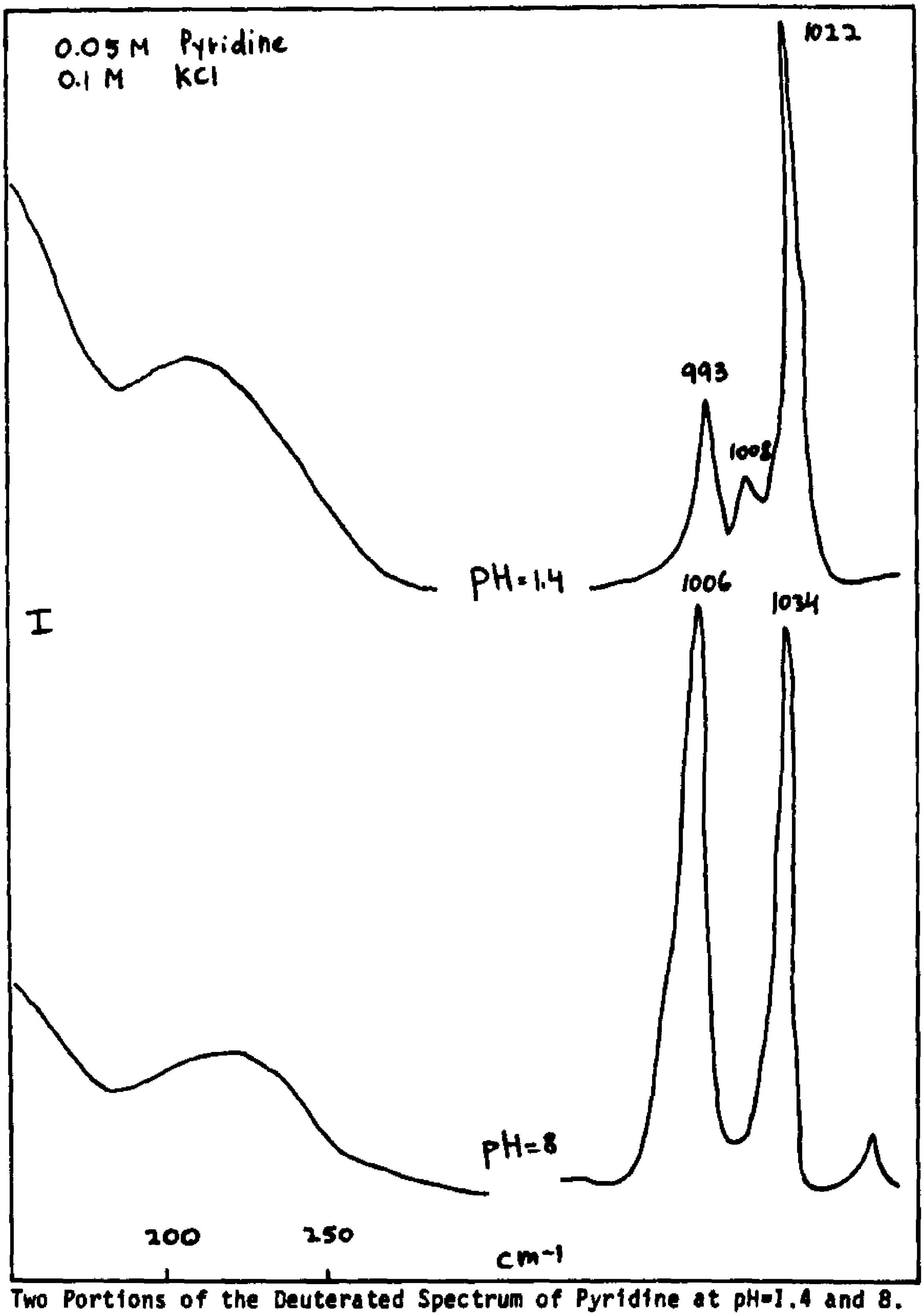
It is characteristic of the SERS of pyridine at pH = 7.8 to peak at -.6 V; to show three lines at 1008 cm^{-1}, 1025 cm^{-1} and 1035 cm^{-1} at -.2 V and only two lines at -.6 V (the 1025 cm^{-1} band disappears), and for pyridinium at pH = 2 to peak in intensity at -.2 V, to show two lines at 1006 cm^{-1} and 1022 cm^{-1} and for all lines to disappear at -.6 V.

Since a chloride-pyridinium ion-pair was invoked, and since the pyridinium molecule lines showed the same voltage dependence as the 237 cm^{-1} band the nature of this low lying band was examined, in order to better understand the nature of the surface-halide-pyridinium interaction.

In order to verify whether the 237 cm^{-1} band was due to pure chloride or due to the ion-pair, SERS of a solution of 1.0 M KCl pH = 2 was taken, however, there was no surface band at 237 cm^{-1}, although a line can be seen in Fig. 2 at pH 7.6 for pure 1.0 M KCl. This indicates that the appearance of the 237 cm^{-1} at pH = 2 necessitates the presence of the pyridinium cation, which means that this band is due to a surface-ion pair vibration. This conclusion is reinforced by the fact that when H_2O is replaced by D_2O at pH = 1.4, the surface line shifts from 237 cm^{-1} to 215 cm^{-1}, see Fig. 5, which would not have happened if this band were a pure Ag-Cl vibration.

In order to further investigate the nature of the 237 cm^{-1} band, I performed two types of titrations in-situ: 1) starting at pH = 7, adding HNO_3 until pH 2.4; 2) starting at pH 2.3 and adding NaOH until pH = 7. In the first case, there was a surface line at 237 cm^{-1} which was indifferent to the change in the pH, see Fig. 6. In the second case, no line was observed, even when the pH became basic. The pretreatments were carried out in both cases in-situ. In order to verify whether the surface line did not show as a result of the pretreatment in an acidic medium, I pretreated the electrode ex-situ, (pH = 8) then I inserted it into the cell, where the pH was 2.3. A surface line appeared at 237 cm^{-1}, and again, as in Fig. 6 it was indifferent to the changes in the pH, when the solution was titrated to pH 7, 9, and 12. Fig. 7 is a plot of $I_{237\ cm^{-1}}$ vs. the ratio [pyridinium]/[Cl^-]. The concentration of the chloride was constant (0.1 M) and pyridinium was added, 0.05 M each time. In the absence of pyridinium, there was no line around 237 cm^{-1}, but as pyridinium was added, it showed up and peaked in intensity at [pyridinium]:[Cl^-]

Fig. 5



Two Portions of the Deuterated Spectrum of Pyridine at pH=1.4 and 8.

= 1:1.

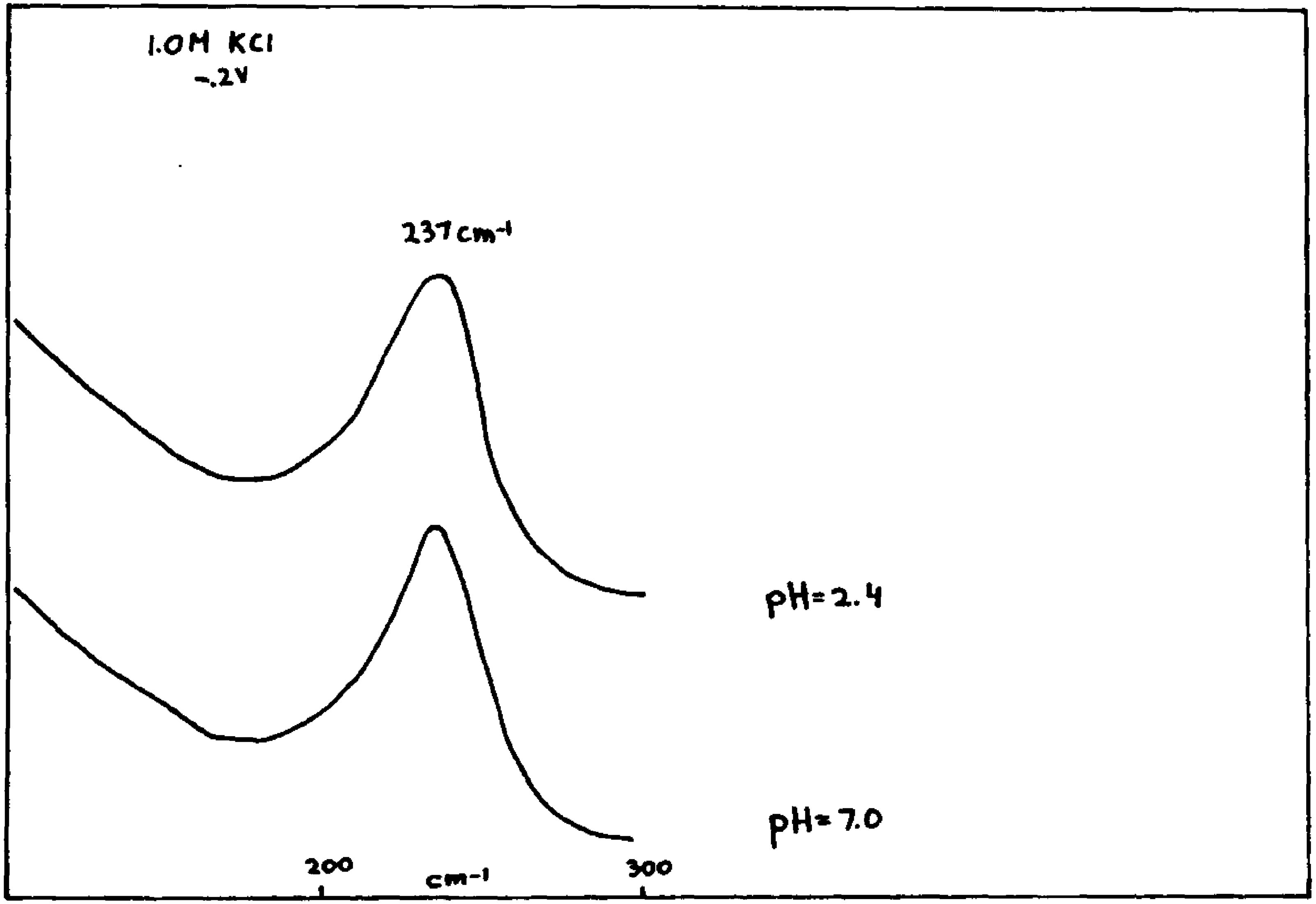
I conclude, therefore, that the 237 cm^{-1} band in the presence of pyridinium is a chloride-pyridinium-surface band, and its onset or disappearance is diagnostic of the adsorption of the ion-pair to the surface. The fact that this band did not seem to have a detectable intensity upon pretreatment in and acidic medium, indicates that this system is extremely sensitive to the topography of the surface; and it may be that the number and/ or the shape of the surface sites created during the pretreatment, are pH dependent.

Incidentally, isoquinoline shows the same voltage dependence and pH effects as pyridine. In this case, the Ag-N line at pH = 8 shows up at 200 cm^{-1}, which is expected since the mass of isoquinoline is larger than that of pyridine. The participation of the halide in the adsorption of pyridinium is also indicated by the fact that in a KBr solution the most intense SERS spectrum is shifted to -.4 V, typical of the bromide ion adsorption.

Fig. 4 shows that the spectrum of pyridinium is different from that of pyridine in the region between 950-1050 cm^{-1}. A new line at 1022 cm^{-1} appears at pH = 2. In order to ascertain that it is indeed the pyridinium species which is responsible for the appearance of this line, a spectrum was taken in D_2O, as shown in Fig. 5. The pretreatment was carried out in the absence of laser light to avoid the onset of the 1025 cm^{-1} band as a result of photolysis, as suggested by Fleischmann (8).

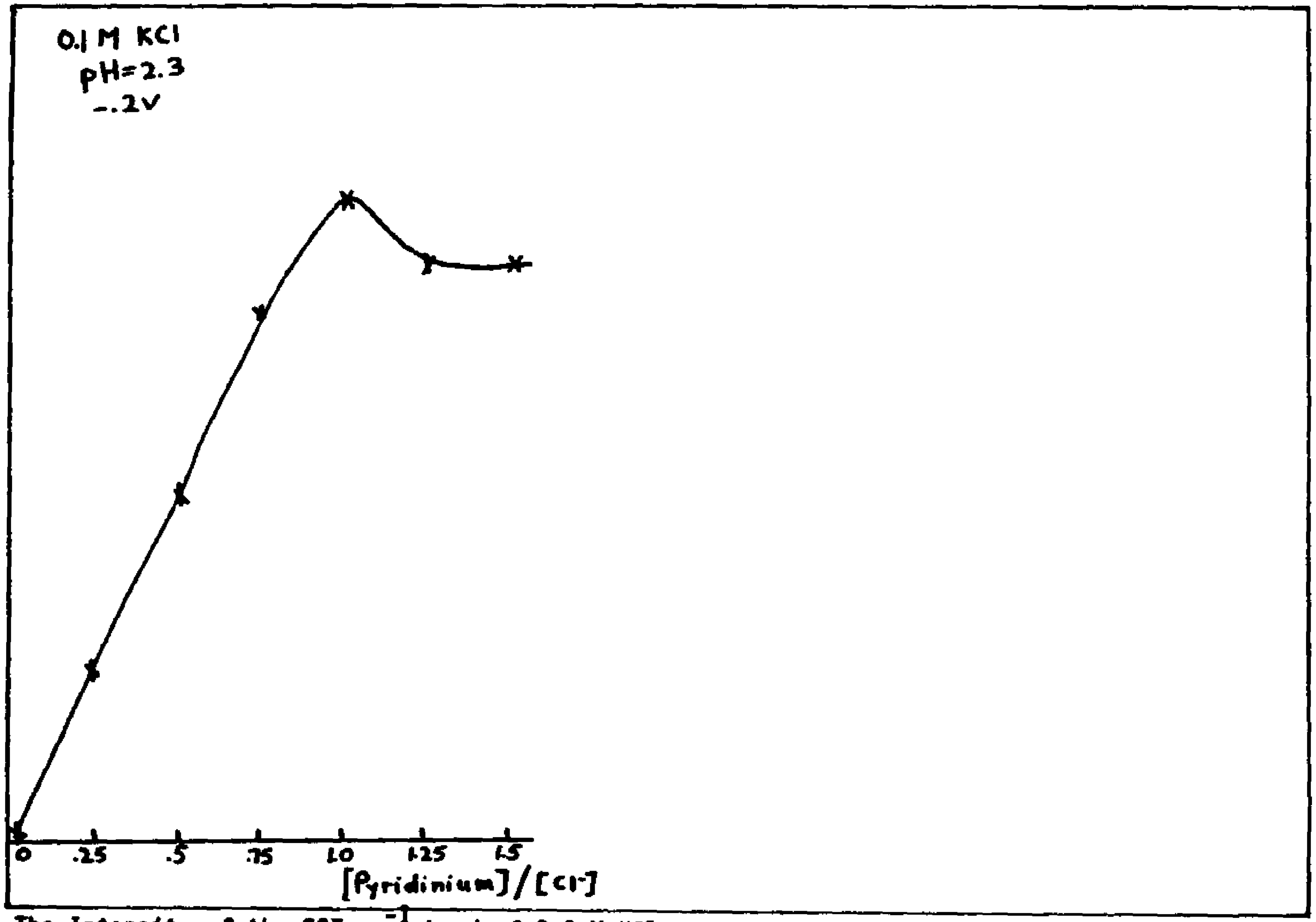
Upon deuteration, the ring breathing mode at 1022 cm^{-1} shifts little or not at all (10,11,12), whereas the totally symmetric

Fig. 6



The Intensity of the Ag-Cl Surface Band as a Function of pH

Fig. 7



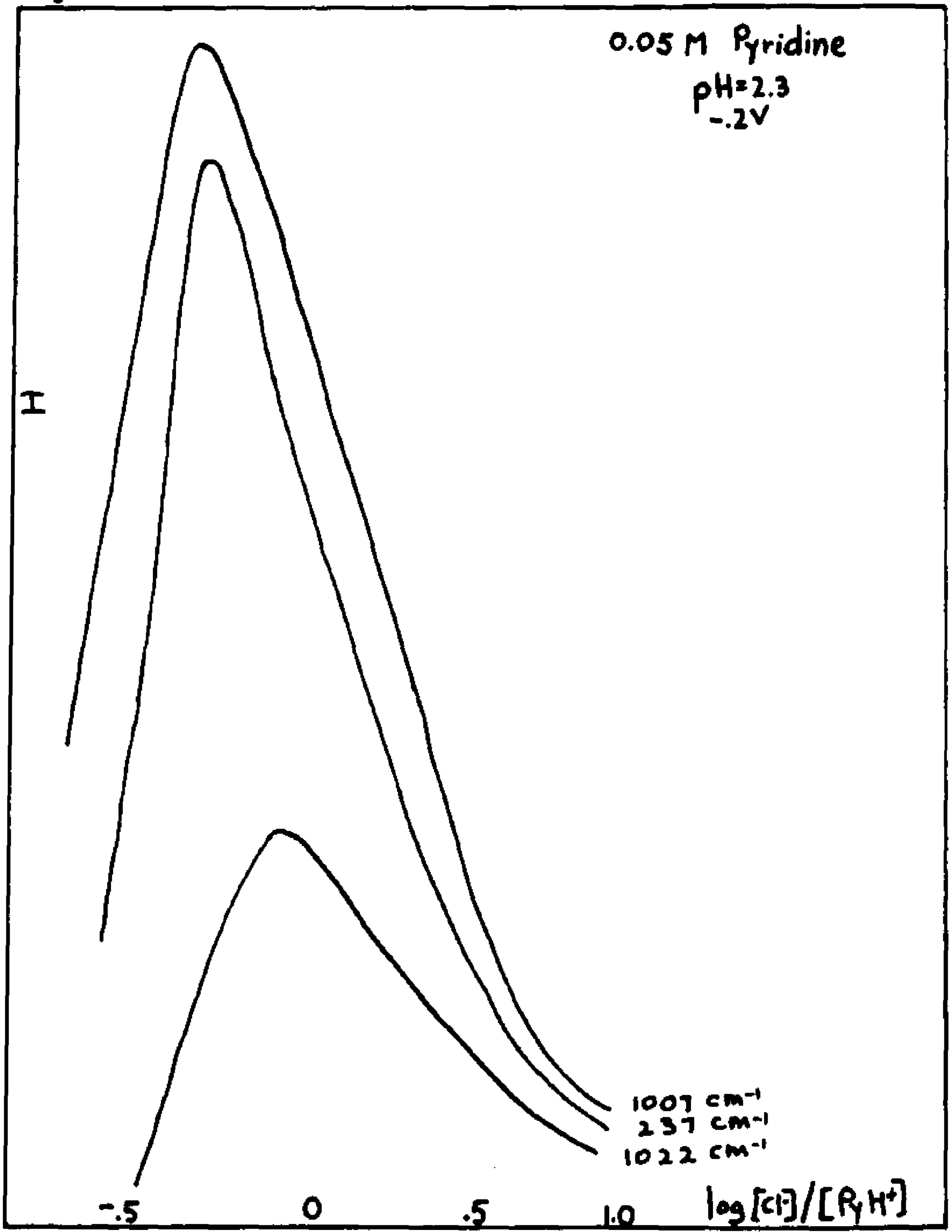
The Intensity of the 237 cm^{-1} band of 0.1 M KCl at Various Pyridine Concentrations vibration at 1008 cm^{-1} shifts to lower frequencies by about 10 cm^{-1}. I therefore assign the 993 cm^{-1} band as being due to $C_5H_5ND^+$, the band at 1008 cm^{-1} being due to $C_5H_5NH^+$ (even in D_2O the solution contains H^+ since the pH was controlled by adding HNO_3) and the band at 1022 cm^{-1} as coming from both species. This spectrum shows a broad shoulder around 2400 cm^{-1}, indicative of a deuterated medium. Note the low intensity of the 1008 cm^{-1} band, which points to the low concentration of $C_5H_5NH^+$. The 993 cm^{-1} band has been assigned in the literature as being a ν_1 Wilson vibration; however, there is a controversy with respect to the 1022 cm^{-1} band (9-12). Since this band did not shift to a lower frequency upon deuteration it can not be ν_{12}, which includes a vibration of the N-H part of the molecule. I therefor accept the assignment of Cook (11) which is ν_{18} for the 1022 cm^{-1} line and does not include a vibration of the N-H part of the molecule. Note that in Fig. 5 at pH = 8 there are two bands between 950-1050 cm^{-1}, at 1006 cm^{-1} and 1035 cm^{-1}, typical of the spectrum of pyridine which are not affected by deuteration.

Fig. 7 shows a plot of the intensity of the 237 cm^{-1} line vs the concentration ratio of pyridine to chloride at pH = 2.3, -.2 V and 0.1 M KCl. The pretreatment was carried out in-situ. Each point belongs to a different concentration of pyridine. In the absence of pyridinium, the intensity of this line is zero. As more pyridinium is added, the band increases in intensity up to a ratio of 1:1, then decreases and levels off. The fact that the intensity of the 237 cm^{-1} band is directly related to the pyridinium concentration indicates that this cation is not only needed during the pretreatment for this band to appear, but furthermore - this surface band is a result of the chloride-pyridinium-surface vibration. The results of Fig. 7 reinforce the ones drawn from Fig. 5 and 6 about the nature of the 237 cm^{-1} line.

In order to further elucidate the nature of the halide-pyridinium species, I carried out chloride to pyridinium concentration-ratio studies, where the pyridinium ion concentration was kept constant at 0.05 M (pH = 2.3, -.2 V) and the chloride concentration was varied, see Fig. 8. The halide additions were performed in-situ at the same alignment, and the pretreatment was time controlled (the voltage step was two seconds long). There is a peak in the intensity for all the three lines at a ratio of 1:1 chloride to pyridinium and then a decrease in the intensity. This behavior is typical of all three lines, which are nearly parallel in the rise and fall of their intensity. A time study of the system indicated that there was a decrease of the intensity (within ten minutes the intensity of the spectrum diminished by more than 25%).

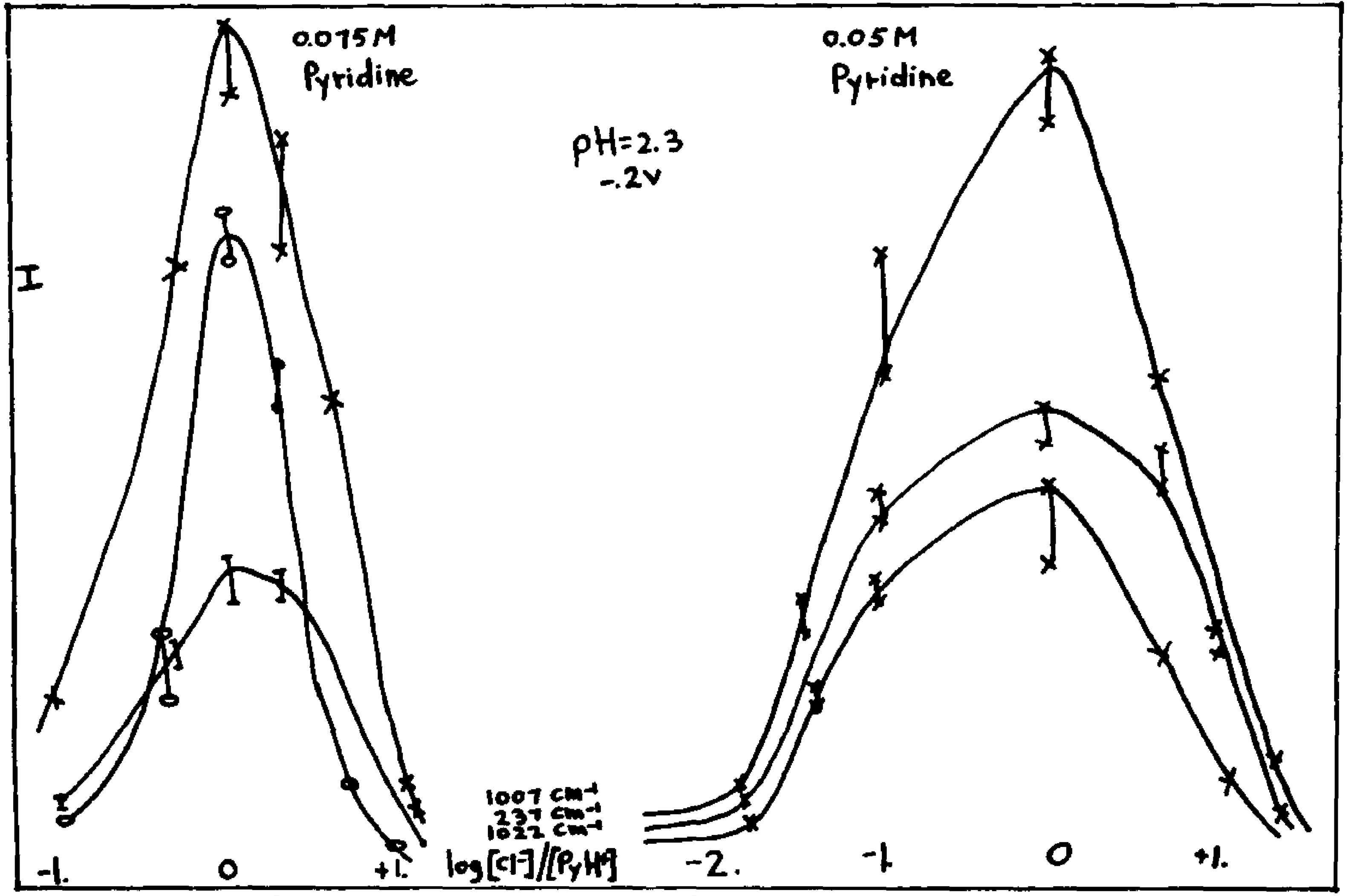
In order to determine whether this decrease in the ratio was due to the time dependence of the system, I repeated the plot by taking a spectrum at each chloride concentration, directly after pretreating the electrode outside the cell (see Fig. 9). The pH was 2.3, the voltage -.2 V and the pretreatment was charge controlled (25 mC/cm^2 were applied). It is evident from Fig. 9 that the intensity peaks for all the lines at both pyridinium concentrations (0.05 M and 0.075 M) at a solution ratio of 1:1 halide-pyridinium. This indicates that there is a complex formation of 1:1, in fact an ion-pair, and it

Fig. 8



Intensity Versus Chloride Concentration of Three Bands in the Pyridinium spectrum. Time Controlled Pretreatment.0.05M Pyridinium.

Fig. 9



Intensity versus Chloride Concentration of Three Bands in the Pyridinium Spectrum, After a Charge Controlled Pretreatment. 0.05M and 0.075 M Pyridinium.

is this species which adsorbs to the surface. The formation of such complexes in solution has been previously reported by other authors (13). Mierzecki et al. studied the Raman spectra of various concentrations of pyridine in formic, acetic and butyric acids. Variation of the intensity of the 1003 cm^{-1} with concentration indicates the formation of a complex of one molecule of pyridine with one molecule of the acids.

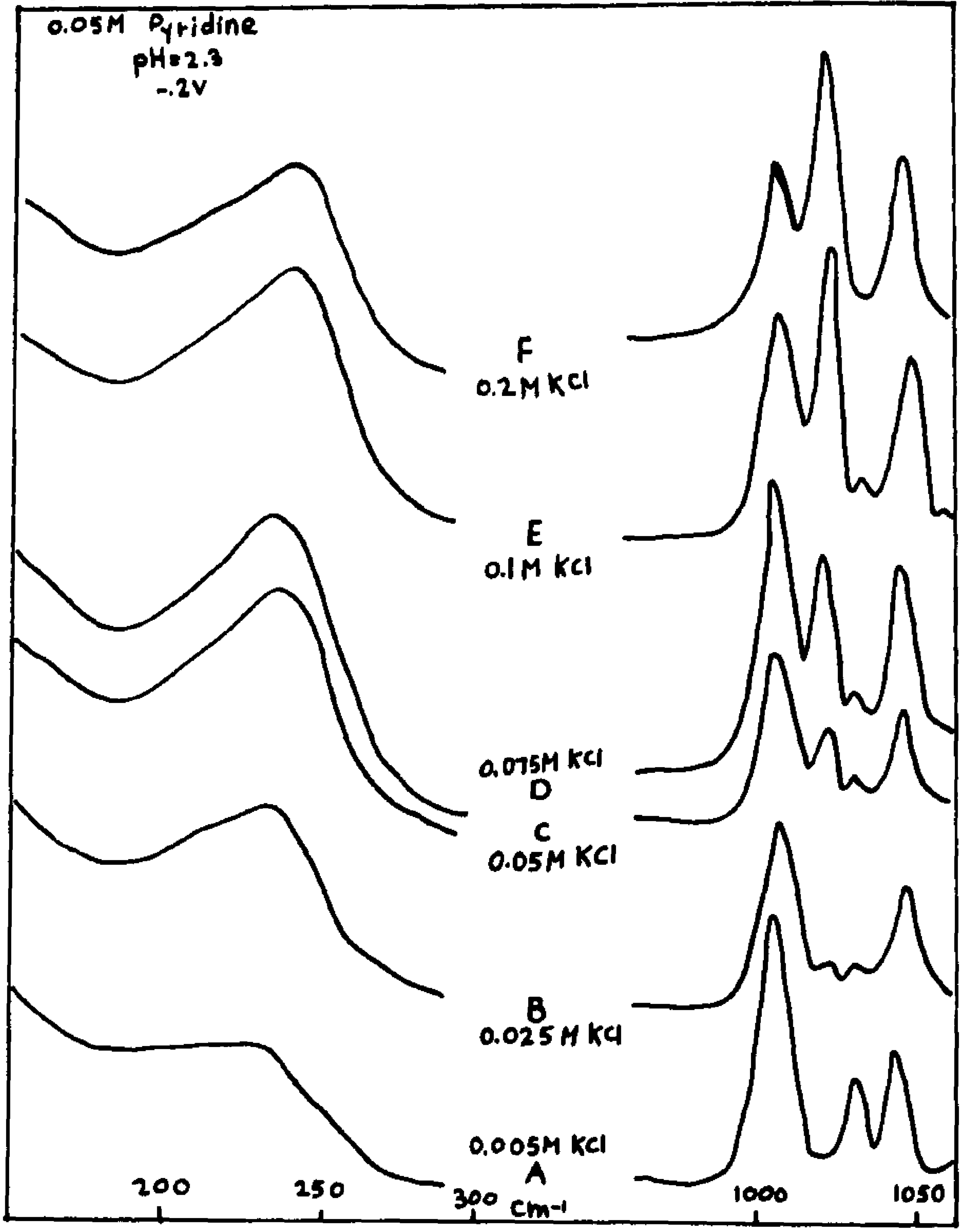
At a ratio of chloride:pyridinium greater than one, there is a decrease in the intensity of all the lines, including the 237 cm^{-1} band, which indicates desorption of the complex from the surface. The fact that I could not detect this line (237 cm^{-1}) at pH = 2.3 in 1.0 M KCl and that its behavior upon chloride addition in Fig. 8, 9 is similar to that of the molecular bands of pyridinium is further evidence for the conclusion that the 237 cm^{-1} is a complex band. The decrease in the intensity of all the bands upon addition of chloride (at a chloride: pyridinium ratio larger than one) is possibly related to a competition between the incoming chloride and the ion pair. At low bulk chloride concentrations, the spectral intensity is low, and as more chloride is added, the intensity builds up. As the chloride concentration is increased and exceeds the 1:1 ratio to pyridinium, the incoming chloride could cause desorption of the ion pair, following Le-Chatelier's principle, according to the following equilibrium:

$$Cl^-_{(aq)} + (Cl^-PyH^+)ad \rightleftharpoons Cl^-_{ad} + (PyH^+Cl^-)_{aq}$$

It may also be that this equilibrium is responsible for the time dependence of the adsorbed ion pair on the surface. Also, note that at the voltage V_{max} at which this study was carried out, the silver surface is positively charged. Since the ion pair is neutral and the chloride ion is negatively charged, it may be that from pure electrostatic grounds, the adsorption of the halide is preferred over that of the ion-pair on a positively charged electrode. This could also explain the decrease in the intensity of the bands at high chloride concentrations. However, since there is no detectable Ag-Cl surface line at this pH, it is hard to determine the amount of chloride on the surface under these conditions.

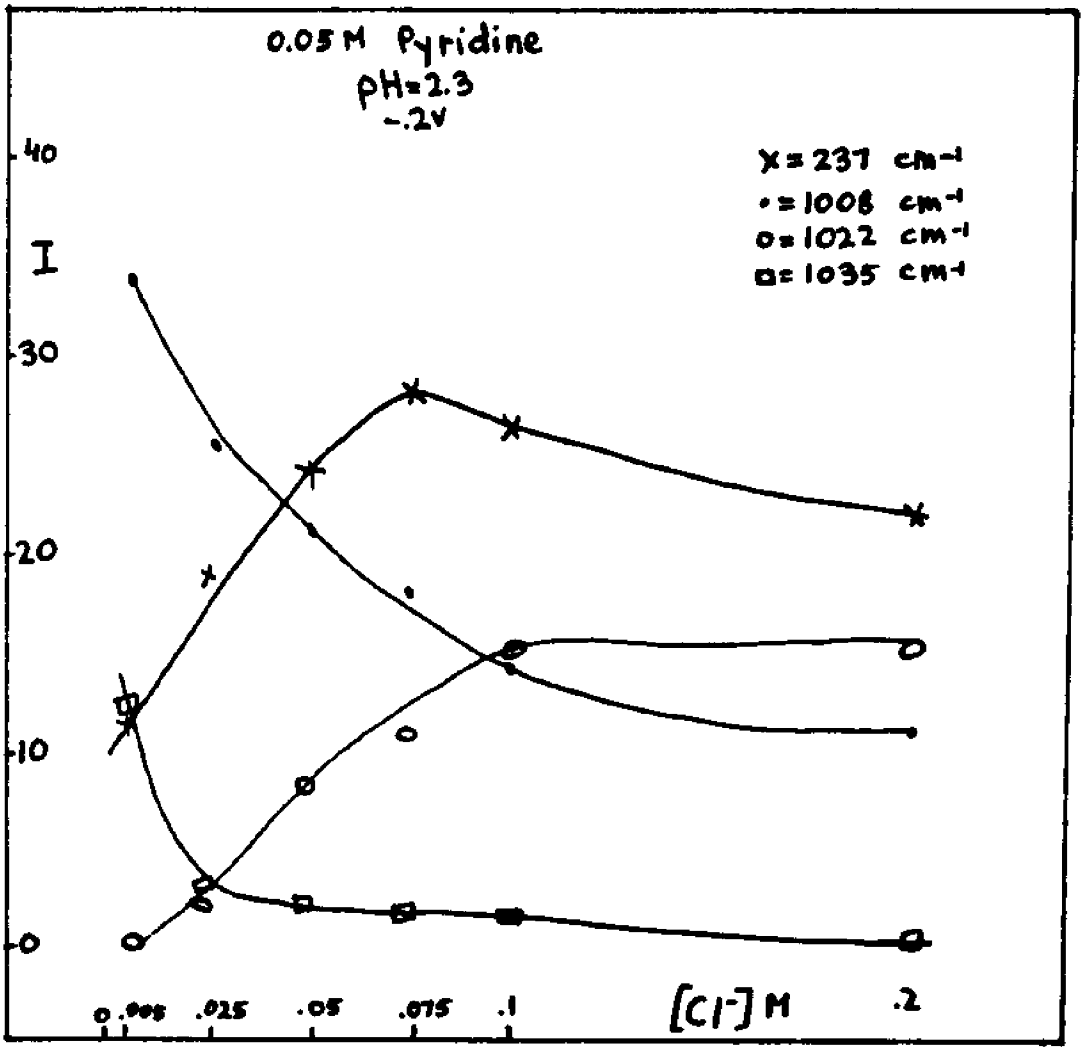
Fig. 10 shows two portions of the spectrum of pyridine at pH = 2.3 at -.2 V and at different chloride concentrations. The line at 1045 cm^{-1} comes from the nitrate ion, which was kept constant at 1 M, in order to maintain a constant ionic strength and thus avoid complications as a result of the change in this parameter. Note that this is a spectrum following a time controlled pretreatment step. At $[Cl^-]$ = 0.005 M, there are two lines in the region 950-1050 cm^{-1}, one at 1006 cm^{-1} and the other one at 1035 cm^{-1}, which is typical of pyridine at pH = 8. As the chloride concentration is increased, this line diminishes in intensity and another line at 1022 cm^{-1} builds up. At (Cl^-) = 0.1 M, the 1035 cm^{-1} band is hardly seen, and at $[Cl^-]$ = 0.2 M it disappears completely, leading to a spectrum typical of pyridinium. The intensity of the 1022 cm^{-1} line follows that of the 237 cm^{-1} band, (shown on the left side on Fig. 10 and Fig. 11) since they both increase in intensity as more chloride is added to the bulk. The 1022 cm^{-1} line becomes well defined at a ratio of 1:1 pyridinium

Fig. 10



Two Portions of the Spectrum of 0.05 M Pyridinium at Various Chloride Concentration at a Fixed Ionic Strength of 1 M.

Fig. 11



The Intensity of the 237 cm^{-1} 1005 cm^{-1}; 1022 cm^{-1} and 1035 cm^{-1} Bands at Various Chloride Concentrations in 0.05 M Pyridine at pH 2.3 and -.2 V.

to chloride. Also, at this ratio of 1:1, the surface line shifts to 237 cm^{-1}, whereas at $[Cl^-] = 0.005$ it peaks around 220 cm^{-1}. At $[Cl^-] = 0.025$ M the surface band peaks between these two frequencies and also the 1022 cm^{-1} and 1035 cm^{-1} lines are equal in intensity; this indicates that there is a mixture of pyridine and pyridinium on the surface. This behavior which is plotted in Fig. 11 indicates that at a fast pretreatment and/or at small chloride concentrations in the bulk, the effective amount of chloride on the surface is negligible and the formation of ion pairs is not possible. In this case, the first equilibrium (1) is most probably dominant, whereas at larger chloride concentrations it may be that the second possibility, equilibrium (2), is preferred:

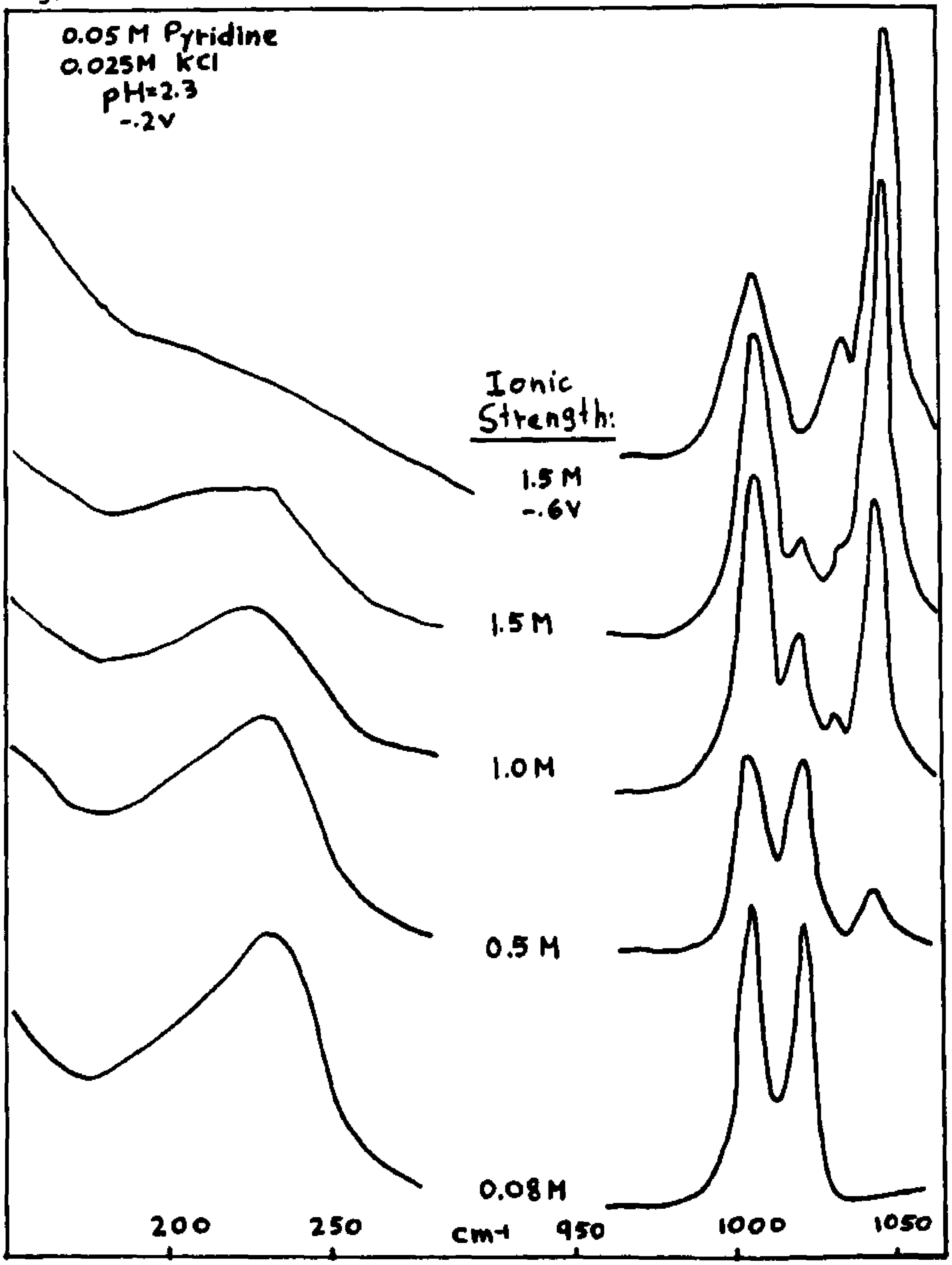
$$PyH^+_{(aq)} \rightleftharpoons Py_{(aq)} + H^+_{(aq)} \rightleftharpoons Py_{(ad)} + H^+_{(aq)} \qquad (1)$$

$$PyH^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons (PyH^+Cl^-)_{(aq)} \rightleftharpoons (PyH^+Cl^-)_{(ad)} \qquad (2)$$

Since this effect was not observed in Fig. 8 and 9, where the ionic strength was low, I studied the behavior of pyridinium in the presence of a low chloride concentration (0.025 M), as a function of the ionic strength. I performed this study twice, using either the nitrate or the perchlorate ions, in order to verify whether this was specifically a nitrate effect or an ionic strength effect.

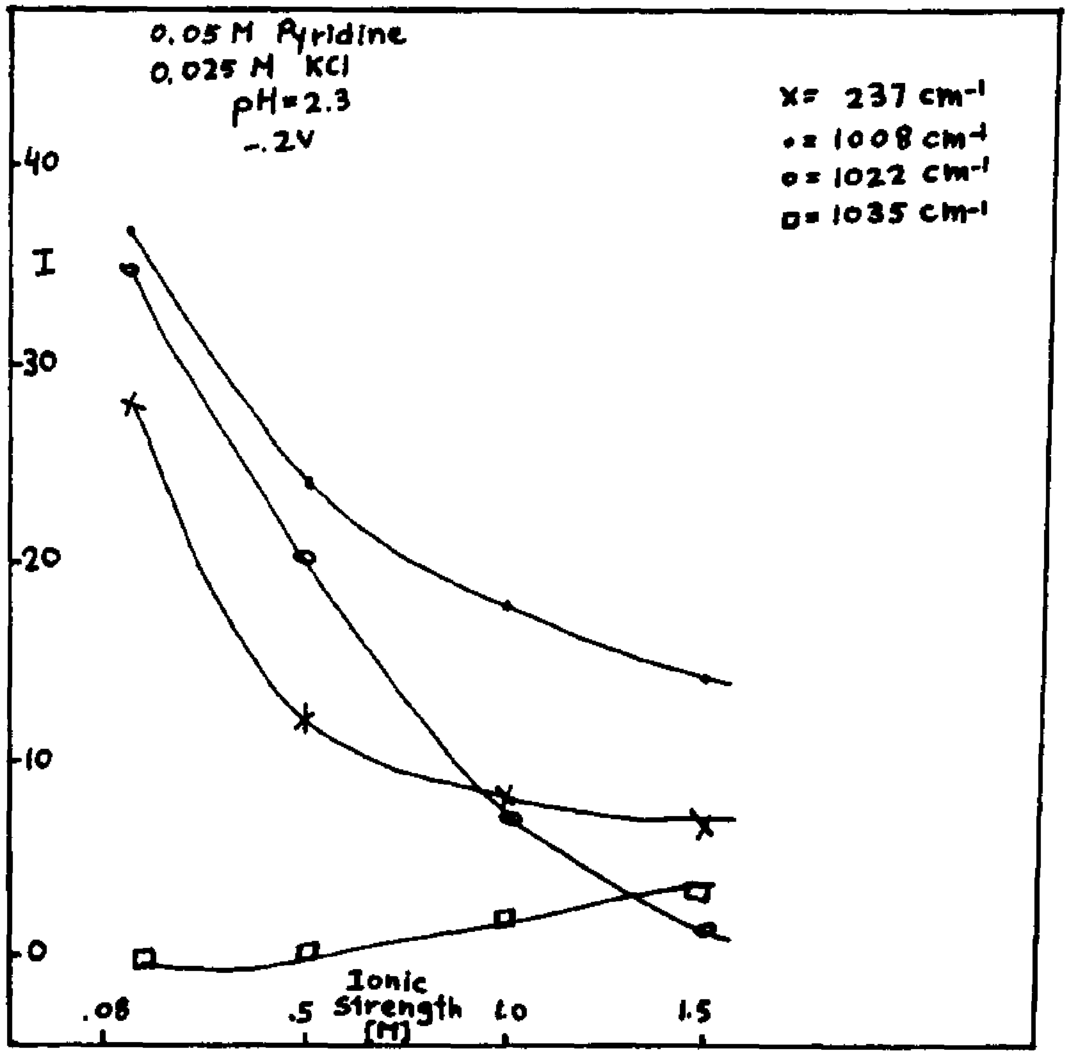
Fig. 12 and 13 show the effect of the ionic strength on the spectrum of pyridinium at pH 2.3, -.2 V. As the ionic strength is increased (by adding KNO_3 pH = 2.3) the 237 cm^{-1} band becomes wider

Fig. 12



Two Portions of th Spectrum of 0.05 M Pyridinium at Various Values of Ionic Strength

Fig. 13



The Intensity of the 237 cm^{-1}, 1006 cm^{-1}, 1022 cm^{-1} and 1035 cm^{-1} Bands at Various Values of Ionic Strength. 0.05M Pyridine, 0.025 M KCl pH = 2.3, and -.2 V and shifts to a lower frequency, whereas the 1022 cm^{-1} line disappears and instead another line builds up at 1035 cm^{-1}. Also, the surface line at 237 cm^{-1} becomes wider and shifts to lower frequencies as the nitrate ion becomes more concentrated, indicative of a change from pyridinium to pyridine. Since the same effect was observed when perchlorate was used, that means that the ionic strength, in addition to the chloride concentration, can determine the extent of pyridine and pyridinium adsorption on the surface. There are three cases to consider: first, at low (Cl^-) and low ionic strength. In this case, either no spectrum or a very low intensity spectrum is detected, since there are no or few ion pairs on the surface. Secondly, as the ionic strength is increased, (without changing any other parameters) the behavior of the system becomes typical of pyridine. It may be that at a high ionic strength, where the hydrogen bonds in the solution are broken, the water close to the pyridinium on the surface creates hydrogen bonds with the proton of the pyridinium, stripping it off the molecule. There are no electrochemical effects related to this effect, since cyclic voltammograms of pyridinium taken at various chloride and/or various ionic strength values, are similar to the same cv taken with pure chloride. We conclude that the change in the behavior of pyridinium to pyridine is not a result of an electrochemical reduction of this molecule. The third possibility at high (Cl^-) and high ionic strength, where the anion is specifically adsorbed, has been discussed previously.

In all cases, when the behavior of the system is typical of pyridine (although the bulk pH is 2.3), upon changing the voltage from -.2 V to - .6 V, the intensity of the bands increased which confirmed that it was indeed the unprotonated species which showed those lines.

The fact that in the absence of chloride the 1022 cm^{-1} band is not observed points to the dependence of this line on the halide. As the voltage was changed from -.2 V to -.6 V, the intensity increased - again a behavior typical of pyridine, which is similar either to the case where the chloride concentration was low, or to the case where the halide employed was KF (which is known to adsorb in negligible amount.)

The 1022 cm^{-1} band also shows a dependence on the amount of charge applied to the electrode during the pretreatment step, see Table I. When the amount of charge was increased, a higher intensity of the 237 cm^{-1} band was observed, followed by an increase in the ratio of the intensity of the 1022 cm^{-1} line to that of 1006 cm^{-1}.

The protonation state of pyridine at pH = 2.3 and -.2 V at different chloride concentrations present in the pretreatment step in the bulk solutions is depicted in Table II (the pretreatment was time controlled in all three cases). In case I and II, the spectra were taken at the same bulk conditions, i.e. 0.005 M KCl and 0.05 M pyridinium. However, the pretreatment was carried out in 0.2 M KCl in case I and 0.1 M KCl in case II. Case II and III underwent identical pretreatments, but the bulk chloride concentrations are different (0.005 M in I and II, and 0.01 M in III; the pyridinium concentration in all solution was 0.05 M). The behavior of I and III around 950-1050 cm^{-1} is similar, resembling that of pyridinium, while

TABLE I

The intensity of three lines in the pyridinium spectrum as a function of the charge applied during the pretreatment step. The concentrations were 0.05 M pyridinium and 0.1 M KCl, taken at -.2 V.

Pretreatment Step mC/cm^2	$I_{237\ cm^{-1}}$	$I_{1023\ cm^{-1}}/I_{1006\ cm^{-1}}$
25.0	6.0	1.0
37.5	13.0	1.4
50.0	20.0	3.9

TABLE II

The protonation state of adsorbed pyridine as a function of the chloride concentration during the ex-situ pretreatment step and the bulk solution.

Case	Ex-situ Pretreatment Conditions $[Cl^-]$	Bulk $[Cl^-]$ M	Bulk $[PyH^+]$ M	ν cm^{-1}
I	0.2	0.005	0.05	1007, 1022
II	0.1	0.005	0.05	1005, 1035
III	0.1	0.01	0.05	1007, 1022

II shows a spectrum typical of pyridine. In both I and III the pyridinium molecules were exposed to a greater concentration of chloride compared to II, either in the pretreatment step, or in the bulk solution.

This indicates that the pretreatment methods, as well as the bulk chloride concentration, can change the state of protonation of the adsorbed pyridine, which is related to the pH of the system. Whether this parameter can be exactly estimated as a function of the intensity ratio of spectral lines, as well as frequency shifts, remains to further be investigated.

D. Conclusion

The spectrum of pyridine has been reported as a function of pH, electrode pretreatment, halide concentration and ionic strength. The protonated pyridine is different than the free species in the voltage dependence and interaction with the surface. While pyridine adsorbs directly to the surface, pyridinium communicates with the surface via the halide with which it forms an ion-pair. Thus, pyridinium does not interact directly with the surface and this long range effect is probably responsible for the fact that the SERS enhancement for pyridinium is about ten times less than that of pyridine.

Under certain conditions, such as low ionic strength, low chloride concentration and fast pretreatment, the spectrum of pyridinium at a bulk pH 2.3 seemed to resemble that of pyridine. The explanation given to the effect was related to the fact that at small chloride concentrations, the formation of ion pairs was not possible. At high ionic strength values, where there are no hydrogen bonds in the solution, it is possible that the water molecules in the vicinity of the surface create hydrogen bonds with the proton of the pyridinium, thus changing the protonation state of the latter. However I do not exclude other possibilities which can explain the protonation effects such as adsorption to impurity sites or defect sites which have a dipole moment. Further studies are needed in order to conclude unequivocally the cause to the protonation effects of pyridine.

D. References

1) Van Duyne, R. P. in "Chemical and Biochemical Applications of Lasers", Vol. 4, ch. 5, edited by C. B. Moore, 1978.

2) Birke, R. L.; Lombardi, J. R. and Sanchez, L. A. in "Advances in Chemistry Series" No. 201, p. 69.

3) Regis, A. and Corset, J. Chem. Phys. Lett. 1980, 70, 305.

4) a) Marinyuk, V. V.; Lazarenko-Manevich, R. M. Soviet Electrochem. 1978, 14, 1522.
   b) Marinyuk, V. V.; Lazarenko-Manevich, R. M. Dokl. Akad. Nauk. S.S.S.R. 1978, 242, 1382.

5) Bunding, K. A. and Durst, R. Chem. Phys. Lett. 1982, 89(1), 54.

6) a) Atkinson, G. F.; Guzonas, D.A.; Irish, D. E. Chem. Phys. Lett. 1980, 75, 557.

7) Birke, R. L.; Bernard, I.; Sanchez, L. A.; and Lombardi, J. R. J. Electroanal. Chem. 1983, 150, 447.

8) a) Fleischmann, M.; and Hill, I. R. in "Surface Enhanced Raman Scattering", edited by Chang, R. K. and Furtak, T. E., Plenum Press, New York 1982.
   b) Fleischmann, M.; and Hill, I.R. J. Electroanal. Chem.1983, 146, 353.

9) Dollish, F. R.; Fateley, W. G.; and F. F. Bentley in "Characteristic Raman Frequencies of Organic Compounds", Wiley Interscience 1974, p. 264-265.

10) Foglizzo, R.; and Novak, A. Chim. Phys. 1969, 66, 1539.

11) Cook, D. Canad. J. Chem. 1961, 39, 2009.

12) Spinner, E. J. Chem. Soc. 1963, p. 3870.

13) Mierzecki, R. Acta. Phys. Polon. 1960, 19(1), 41, in French.

CHAPTER III

THE EFFECT OF HALIDE ION ON THE SERS SPECTRA OF PYRIDINE

A. Introduction

Surface enhanced Raman scattering (SERS) spectra of nitrogen heterocyclic compounds on a polycrystalline silver electrode have been widely studied (1) since the seminal paper on pyridine SERS by Flesichmann et al. in 1974 (2). One goal of many of these studies have been the elucidation of the detailed molecular structure of the chemical entity or entities at the surface which give rise to the scattering. This study is a further effort toward that goal.

Two new features of the SERS pyridine spectrum, which relate to the surface species and which are absent from the normal Raman spectrum of pyridine in aqueous KCl, are the bands at ca. 240 cm^{-1} and 1025 cm^{-1} (2,3). The band at 240 cm^{-1} has now been assigned to a surface Ag-halide (Ag-Cl) stretch (4) and the one at 1025 cm^{-1} to chemisorbed pyridine bound to a Lewis acid site. Although no definite experimental proof of the geometry of a surface complex has yet been presented, various structures involving surface silver, halide and pyridine have been postulated (1,3-6,8).

The influence of surface Cl^- on the SERS spectrum of neutral pyridine has been studied by Atkinson et al. (9). They found that the intensity ratio of the 1038 cm^{-1} (ν_{12}, trigonal ring breathing) to the 1010 cm^{-1} band (ν_1, symmetrical ring breathing) as a function of potential has the same slope as the intensity of the 233 cm^{-1} band vs. potential between 0.0 V and -0.60 V vs. SCE. They were led from Regis and Corset's results (7) to conclude that the ion pair $PyH^{+}Cl^{-}$ is a possible surface species which desorbs near the p.z.c. being replaced by pyridine or a pyridine radical hydrogen bonded to water (9). However, experiments with D_2O solutions by Marinyuk et al. (10) with pyridine and I^{-} as the halide show no shift of the 1006 cm^{-1} and 1025 cm^{-} bands indicating the absence of hydrogen bonded pyridine in neutral solutions. Fleischmann and Hill now believe that neutral pyridine is in direct contact with silver, that the chemisorbed pyridine has a Ag^{+} species and the physisorbed pyridine a Ag^{0} species (8).

Several research groups have noted the effect of the potential and chloride concentration on the intensity ratio of the 1035 cm^{-1} to 1010 cm^{-1} bands (6,8,9,11,12). The 1035 cm^{-1} band is more intense that the 1010 cm^{-1} at potentials very positive to the p.z.c., and there is an intensity reversal at around -0.4 V vs. SCE which continues to change as the potential is moved negative to the p.z.c. Van Duyne (3) studied the dependence of the 1006 cm^{-1} (which we observed at 1008 cm^{-1}) line intensity on the bulk chloride concentration and found that the maximum SERS intensity occurred when the ratio of the chloride to pyridine concentrations was 2:1. However, since the electrode was pretreated ex-situ in 0.1 M KCl (a higher halide concentration than the in-situ solution) the electrode was covered with an amount of chloride typical of the ex-situ halide concentration and not the in-situ one. Therefore, the above mentioned ratio of 2:1

can not be taken to reflect the ratio of bulk chloride to pyridine concentration. I report in the following sections the same study as the one carried out by Van Duyne (3), but under different ex-situ solution conditions.

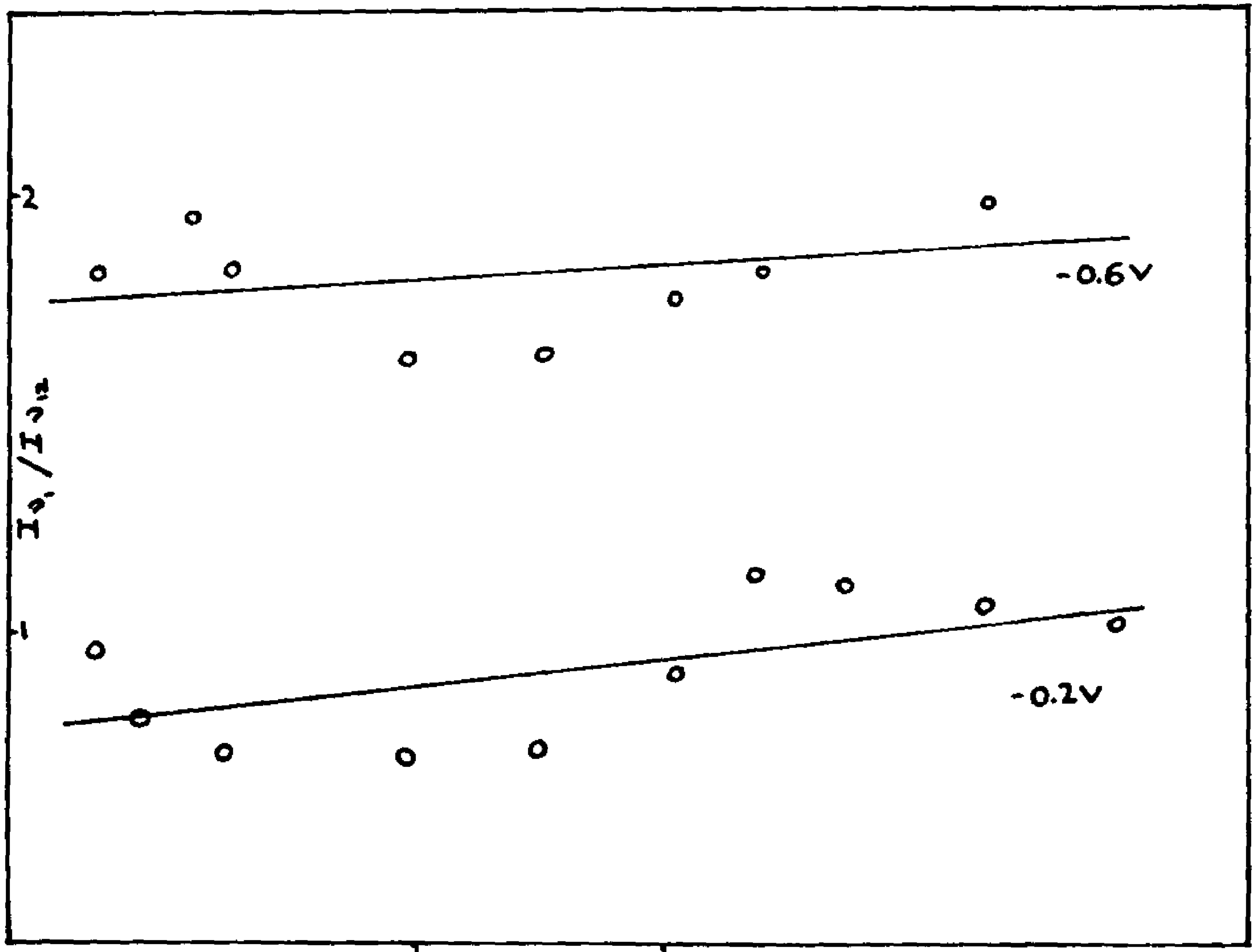
B. Experimental

The experimental set-up is similar to that described elsewhere (12). Raman spectra of pyridine were taken at various potassium halide concentrations and pH in aqueous solutions on the surface of an electrochemically roughened Ag electrode at various constant potentials in a three-electrode cell. Some solutions were acidified to pH 2 with H_2SO_4. An Ar^+ laser at 488 nm at approximately 50 mW (on the surface) was the excitation source, and spectra were recorded with a Spex model 1401 double monochromator. A double-potential step oxidation reduction electrochemical pretreatment was run with both the halide electrolyte and the nitrogen heterocycle in the cell under laser illumination for most experiments. The pretreatment potential variation was -0.06 V 0.25V 0.60 V. The 2.0-s time duration at 0.25 V was used. All chemicals were reagent grade and all potentials quoted are vs. the saturated calomel electrode, SCE.

C. Results and Discussion

I have examined the effect of bulk Cl^- ion concentration on the intensity ratio of 1008 cm^{-1}, ν_1, to the 1035 cm^{-1}, ν_{12}, of free pyridine (pH 7.8). This plot (Fig. 14) has been made for a ratio of

Fig. 14

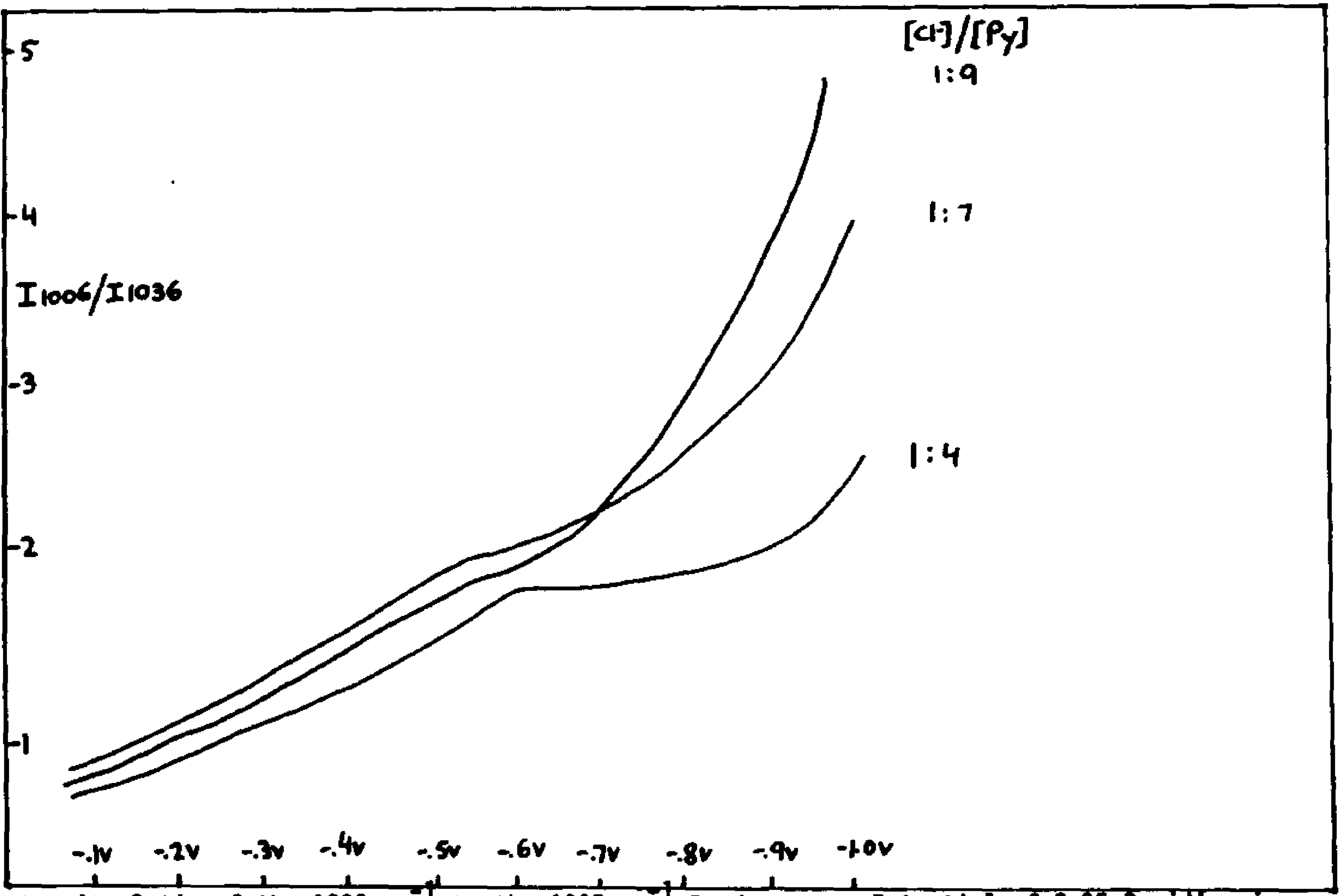


Intensity Ratio of the 1008 cm^{-1} to the 1035 cm^{-1} Band at -.2 V and -.6 V versus the Logarithm of Chloride to Pyridine Concentration Ratios. 0.05 M Pyridine, the Chloride Concentration is Varied.

Cl^- to pyridine concentrations of 0.01:1 to 20:1 at -0.2 and -0.6 V. Points below a 1:1 ratio are adjusted to a constant total ionic strength of 0.1 M with KNO_3. The NO_3^- ion is assumed to be indifferent since comparison of the intensity ratios for a system with 0.05 M pyridine, 0.05 M KCl to that of 0.05 M pyridine, 0.05 M KCl + 0.05 M KNO_3 showed little difference in the intensity ratio. Although there is considerable scatter in the data, there seems to be no pronounced effect of bulk chloride ion concentration on the intensity ratio at either potential. This result differs from the piperidine case where at -0.6 V the intensity ratio changes from ca. 0.6 to 1.1 over the concentration ratio range showing a reversal in the intensities of the bands at very low ratios (13). The fact that bulk chloride ion concentration changes have relatively little effect on the intensity ratio at these voltages, I_{v1}/I_{v12}, is consistent with the previously given symmetry argument where bands of the same symmetry representation (1008 and 1036 cm^{-1} are both a_1 modes) should be affected by a Cl^- point source in the same way. On the other hand, the pronounced dependence of the intensity ratio on electrode potential indicates that the electric field perpendicular to the electrode surface has more of an effect on this ratio than the variation of bulk Cl^- ion concentration and in turn surface Cl^- ion.

However, at very negative potentials, starting at -.8 V, the intensity ratio of the 1008 cm^{-1} to the 1036 cm^{-1} band is no longer indifferent to the bulk chloride ion concentrations, see Fig. 15. At potentials equal or negative to -.8 V where the chloride does not adsorb specifically, the geometric electrostatic effect of the halide

Fig. 15



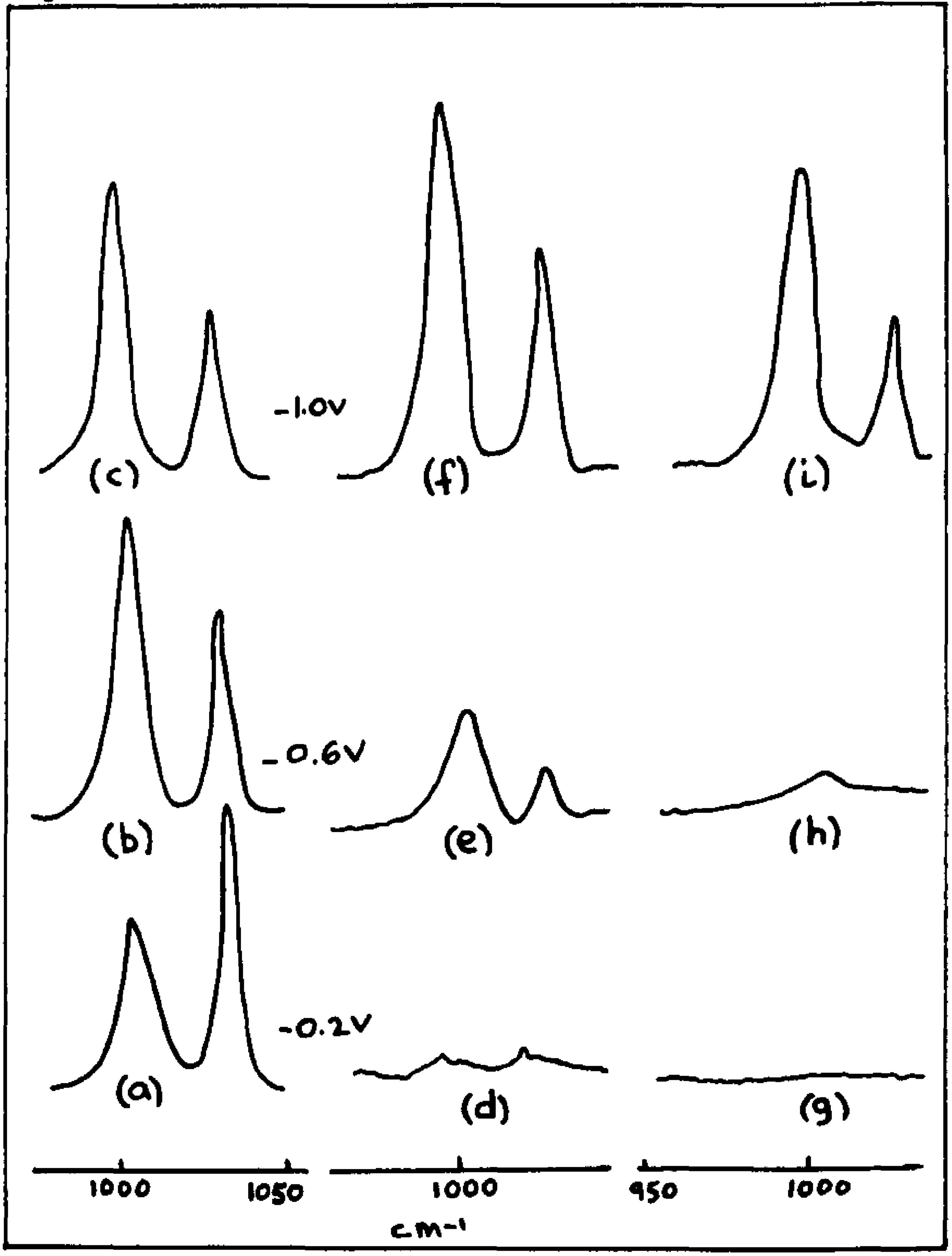
Intensity Ratio of the 1008 cm^{-1} to the 1035 cm^{-1} Bands versus Potential of 0.05 Pyridine in Various Chloride Concentrations.

cannot be invoked anymore. Therefore it is reasonable to assume a field effect which splits the energy difference between these two a_1 vibrations, as a result of the applied potential. The role of the chloride in this instances is rather to modulate the potential felt by the molecule on the surface.

At very high ratios of Cl^- ion to pyridine a new phenomenon is apparent as seen in Fig. 16. At a 4:1 Cl^- to pyridine ratio strong 1008 cm^{-1} and 1035 cm^{-1} bands are observed at -0.2, -0.4, and -1.0 V and similar sets of spectra are observed up to 20:1 ratio, but at 50:1 the spectrum disappears at -0.2 V and is much weaker at -0.6 and -1.0 V. At a 100:1 ratio corresponding to 4.0 M $[Cl^-]$ the spectrum is only observable at -1.0 V, although at lower intensity. This set of data strongly suggests that at a high enough bulk Cl^- concentration, the adsorbed Cl^- completely covers the surface displacing pyridine. This is another indication that for neutral pyridine the SERS species is bound directly to the silver electrode surface.

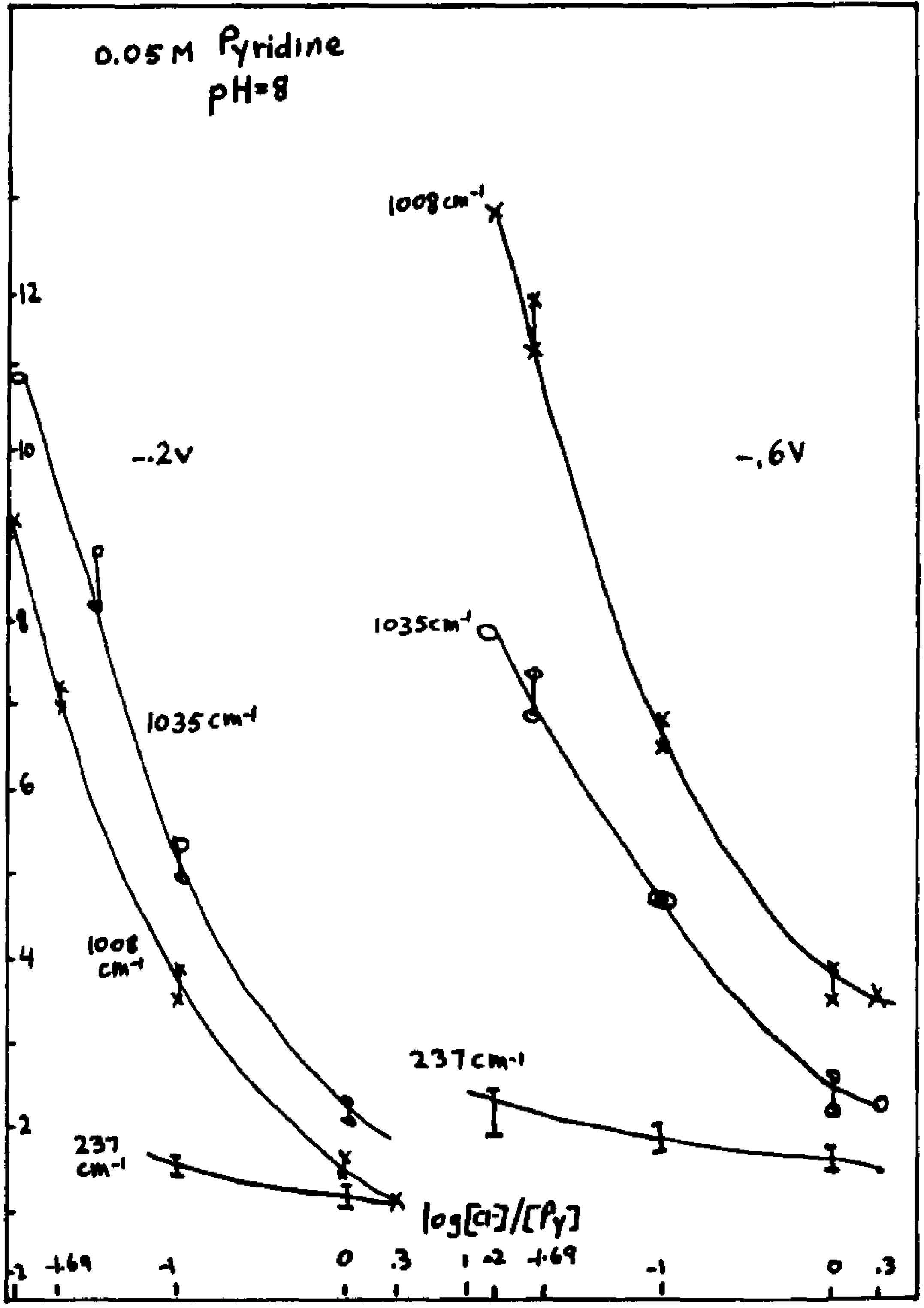
Fig. 17 shows the effect of the concentration of chloride on the intensity of the 237 cm^{-1}, 1008 cm^{-1} and 1035 cm^{-1} bands of pyridine, at -.2 V and -.6 V. A charge controlled pretreatment was employed, where 25 mC/cm^2 were applied to the silver electrode. The results indicate that as the chloride concentration was increased, the intensity of the molecular lines decreased. This can be attributed to the competition for surface sites between the halide and the pyridine. At low bulk chloride concentrations, there is still enough halide necessary for the formation of active sites during the electrode pretreatment, but not enough halide to compete with the

Fig. 16



Pyridine SERS Breathing Modes as a Function of Potential and Chloride Concentration.

Fig. 17



Intensity of Three Bands of 0.05 M Pyridine at Various Chloride Concentrations pyridine for adsorption to the surface. As more chloride is added, the molecular lines drop in intensity since the competition for adsorption increases, while the number of active sites remains constant. This behavior is the same at both -.2 V and -.6 V.

The low lying vibration around 200 cm^{-1} is also shown in Fig. 17 and seems to also decrease when the halide concentration is increased. At -.2 V it shows up at 237 cm^{-1} and at -.6 V it appears at 217 cm^{-1}. If this were a pure chloride-Ag vibration, it would have grown in intensity as more chloride had been added. Since this is not the case, and since it decreases in a similar fashion as the other lines, (1008 cm^{-1} and 1036 cm^{-1}) I interpret the 237 cm^{-1} line at -.2 V to be due to a pyridine-chloride-complex which adsorbs through the chloride. The fact that the line shifts to 217 cm^{-1} at -.6 V and that it also behaves as the 1008 cm^{-1} and 1036 cm^{-1} bands, is indicative of the fact that at this potential there is still a chloride-pyridine complex which adsorbs through the nitrogen lone pair.

These results stand in contrast with those of Van Duyne (3), who found that the maximum SERS intensity occurred when the ratio of the chloride to pyridine concentrations in the bulk was 2:1. However, their pretreatment method, which was performed in 0.1 M KCl ex-situ, exposed the electrode to a higher halide concentration that the one in-situ. They stopped the pretreatment step at -.6 V, a voltage at which they assume complete desorption of the chloride from the surface. Therefore, when they inserted the electrode in the cell they related the adsorption of the halide on the surface to the adsorption isotherm. However, it is not clear whether there is indeed complete desorption of the chloride from the surface at -.6 V.

The only difference between Van Duyne's and my experiment lies in the fact that pretreated the electrode ex-situ in a solution of 5×10^{-4} M KCl (which corresponds to the lowest halide concentration shown in Fig. 17) I therefore relate the difference between our results and those of Van Duyne to the concentration of the chloride during the pretreatment of the electrode.

D. References

1) Birke, R. L.; Lombardi, J. R.; and Sanchez, L. A. in "Symposium on Electrochemistry and Spectrochemistry of Biological Redox Components", Kadish, K. Ed., ACS Books, 1982, 201, 69.

2) Fleischmann, M.; Hendra, P. J.; and McQuillan, A. J. Chem Phys. Lett. 1974, 26, 163.

3) Jeanmaire, D. L.; and Van Duyne, R. P. J. Electroanal. Chem. 1977, 84, 1.

4) Dornhaus, R.; Chang, R. K. Solid State Commun. 1980, 34, 811.

5) Pettinger, B.; and Wetzel H. Chem. Phys. Lett. 1981, 78, 398.

6) Pemble, M. E. Ph.D. Dissertation, University, Southampton, 1980.

7) Regis, A.; and Corset, J. Chem. Phys. Lett. 1980, 70, 305.

8) Fleischmann, M.; and Hill, I. R. in "Surface Enhanced Raman Scattering", Chang, R. K. and Furtak, T. E. Editors, Plenum Press, New York, p. 281.

9) Atkinson, G. F.; Guzonas, D. A.; and Irish, D. E. Chem. Phys. Lett. 1980, 75, 557.

10) Marinyuk, V. V.; Lazareuko-Manevich, K. M.; and Kolotyrkin, Y. A. Sov. Electrochem. 1978, 14, 1522.

11) Wetzel, H. A.; Gerischer, H.; and Pettinger, B. Chem. Phys. Lett. 1982 85, 187.

12) Bunding, K. A.; Birke, R. L.; and Lombardi, J. R. Chem. Phys. Lett. 1980, 54, 115.

13) Sanchez, L. A.; Lombardi, J.R.; and Birke, R. L. J. Phys. Chem. in press.

CHAPTER IV

THE SERS OF QUINUCLIDINE AS A FUNCTION OF pH AND CHLORIDE CONCENTRATION

A. Introduction

The area of SERS has developed considerably since Fleischmann's (1) seminal work and the recognition of Albrecht et al. (2) and Van Duyne (3) of the "Surface Enhancement". The most widely investigated molecule since then has been pyridine, which is an aromatic molecule. The fact that this molecule has a π system had lead to different postulates regarding the interaction between the aromatic ring and the metal, in order to explain the structure of the adsorbed species (4,5,6). The two possible ways for interaction of pyridine with the surface are through the nitrogen lone pair, or through the π-system. There is a big controversy with respect to this interaction since there is a surface line around 200 cm^{-1} which has been assigned by some authors to be a Ag-N line, which indicates a silver-lone pair interaction, and by others as a Ag-Cl band, (4,7,8). The existence of a Ag-Pyridine mode of interaction is not yet clearly established. Therefore, it is of interest to study nonaromatic heterocycles, which can communicate with the metal only through the lone pair of the nitrogen.

Piperidine, which is the saturated analog of pyridine, has been studied by Van Duyne (4) who briefly reported SERS of this molecule, and later Pemble (9) reported that there was no potential dependence between -.2 V and -.6 V of the bands in the region 980-1090 cm^{-1}. Sanchez et al. (10,11) performed a detailed analysis of the potential dependence of pyridine and concluded that it adsorbed end-on, i.e. the molecule communicated with the surface via the lone pair of the nitrogen. While there were no noticeable frequency shifts, the relative intensities of the bands changed considerably (and in a parallel fashion) with the variation of either the potential, or the chloride concentration. Two pairs of degenerate bands were studied in particular (10), 434 cm^{-1} (A') and 459 cm^{-1} (A") and 1157 cm^{-1} (A') and 1177 cm^{-1} (A"). The A" vibrations peaked at -.4 V and the A' bands peaked at -.8 V. Also, the $A''/_{A'}$ intensity ratios peaked at high chloride concentrations, which indicates that the intensities of the A" band were dependent on the chloride, while the A' bands were indifferent to the halide. Piperidine belongs to the C_s point group and the components of the polarizability tensor of A" are α_{xy} and α_{zy}; therefore, taking into account the chloride dependence of the A" bands, the authors of reference (10) conclude that the halide ions must be positioned on the xy and zy plane, i.e. on the y axis (xz is the plane of symmetry of piperidine). Thus, an electro-geometrical effect has been established for piperidine.

Sanchez et al. (11) used a quantum mechanical model to study the potential dependence of the A', A" bands, and conclude that in the presence of an electric field at the interface, there is a mixing of the energy levels of these vibrational states.

Quinuclidine is a rigid derivative of piperidine, which cannot flip and belongs to the C_{3v} point group. The only allowed vibrations in Raman are A_1 and E. pH Studies of this system indicate that quinuclidinium does show SERS, while piperidinium does not. Also, chloride concentration variations, show a different behavior of symmetric vs. asymmetric modes in quinuclidine, in comparison with piperidine.

B. Experimental

The laser-Raman spectrometer and electrochemical set-up were reported previously (7). The solutions were prepared using deionized, distilled water. Quinuclidine, KBr and KCl were reagent grade and supplied by Fisher Scientific Company.

The preparation of the electrode before the electrochemical pretreatment was as follows. First the electrode was polished with emery paper until bright, then it was subjected to a chemical cleaning process by submersion in a (50/50) solution of H_2O_2 and concentrated NH_4OH for about 20 seconds and washed with distilled water.

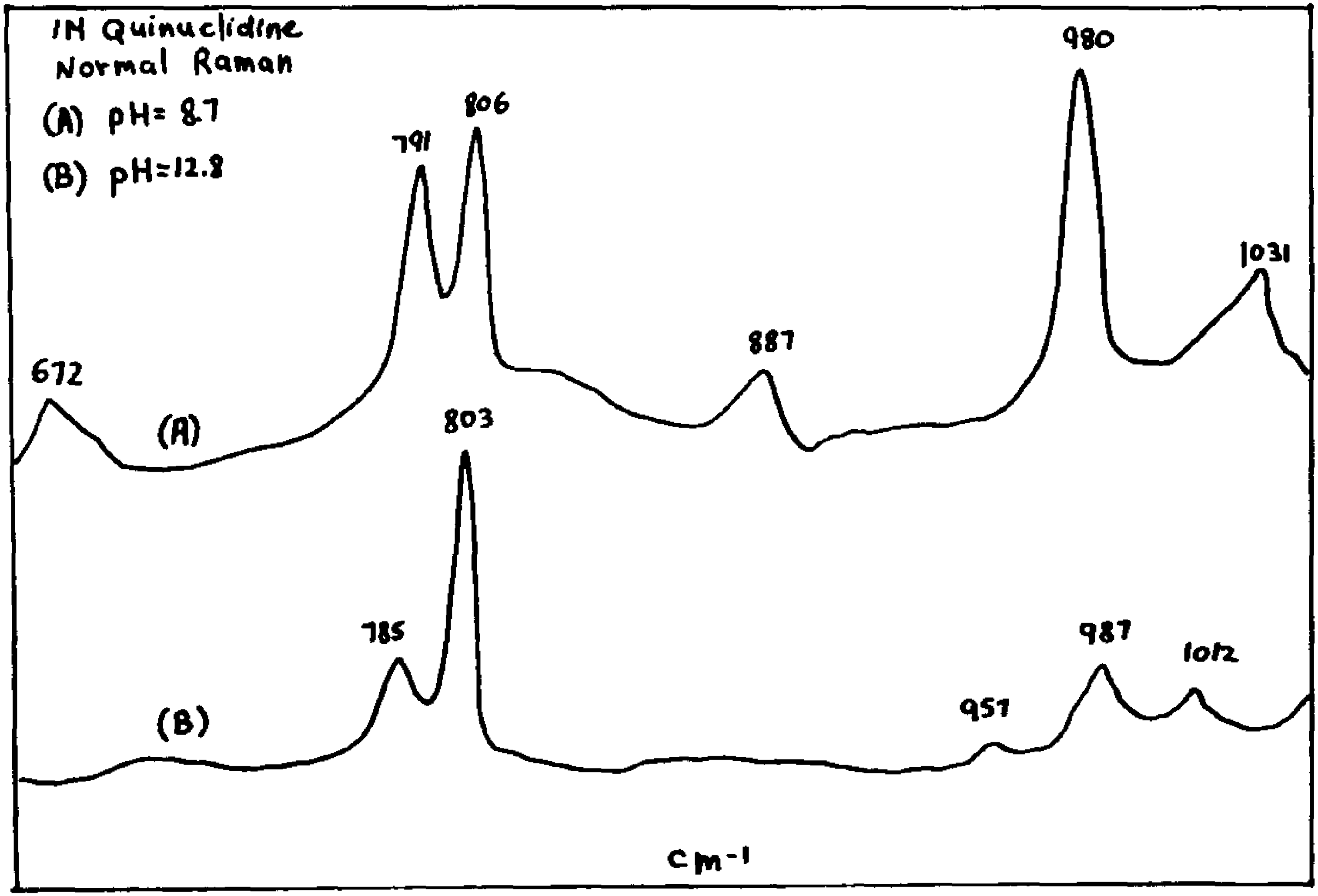
The electrochemical pretreatment was carried out by setting the applied potential at -0.6 V and then applying a potential step of 1 second duration at 0.20 V and back to the working potential. All the potentials were measured versus a saturated calomel electrode (SCE).

C. Results and Discussion

Fig. 18 shows a portion of the solution spectrum of 1 M quinuclidine at pH 12.8 and 8.7 (Fig. 18a) between 612-1112 cm^{-1}. Since $pK_a = 11$, these spectra correspond to quinuclidine and quinuclidinium, respectively. The assignments are made for the unprotonated species (12). The spectrum at the various pH is different not only in the frequency of the bands, but also in the relative frequencies, see Table III. Fig. 19a shows a SERS spectrum in the same spectral region as in Fig. 18a, of 0.05 M quinuclidine in 0.1 M KCl at -.6 V. As can be seen from Table III the spectrum resembles the one in solution. The major difference lies in the two bands at 786 cm^{-1} and 805 cm^{-1}. These two vibrations are degenerate in bicyclo (2.2.2) octane and belong to the E type of symmetry. Upon lowering the symmetry by introducing the nitrogen, these two bands are assigned as a_1 vibrations (12). The relative intensity of the 786 cm^{-1} to the 805 cm^{-1} band is 1:4 in solution and changes to 1:1 on the surface at -.6 V and at a chloride concentration of 0.1 M. It is not the case with quinclidinium, where the intensity ratio of these lines is close to one, both on the surface and in solution, see Fig. 19b. It is interesting that piperidinium does not seem to show SERS on the surface under the same conditions, however the reasons for this effect are not clear.

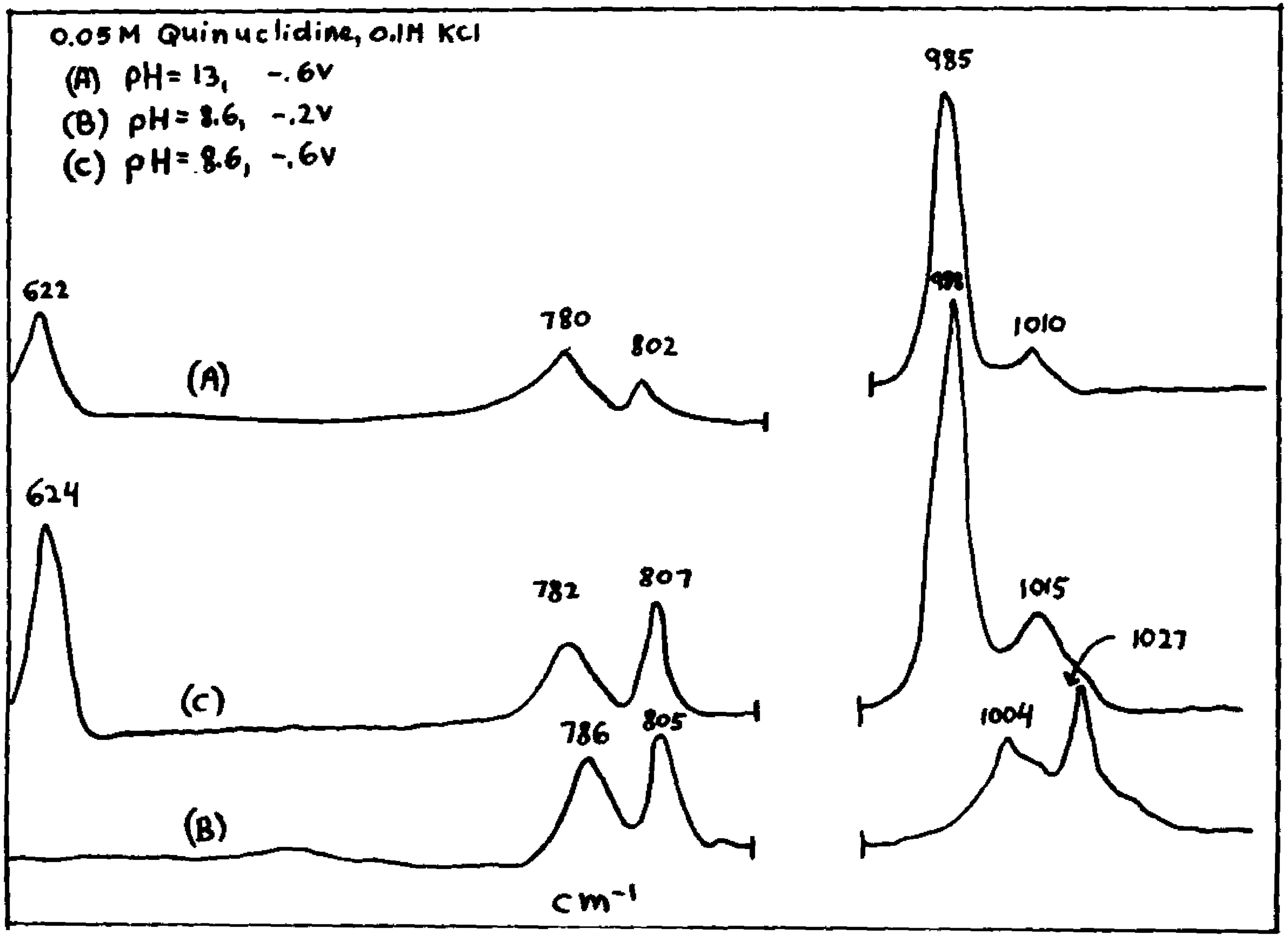
It has been found by Sanchez et al. (11) that in the presence of an electric field at the interface, there is a mixing of the vibrational energy levels of the A' and A" bands in piperidine. It is not the case here, i.e. the change in the relative intensity of the 786 cm^{-1} and 805 cm^{-1} bands can not be due to the same kind of mixing, since they are both a_1 vibrations. This case is similar to the effects seen on the 1008 cm^{-1} and 1035 cm^{-1} bands in pyridine (10) which are both of a_1 symmetry. Since the mixing of these two vibrations is not possible, it may be that each one mixes separately with

Fig. 18



Portion of the Solution Spectrum of Quinuclidine at pH = 8.7 and 12.8 in the Region Between 612-1124 cm^{-1}.

Fig. 19



Portion of SERS of Quinuclidine at pH = 13 and 8.6.

TABLE III

List of observed frequencies of quinclidine

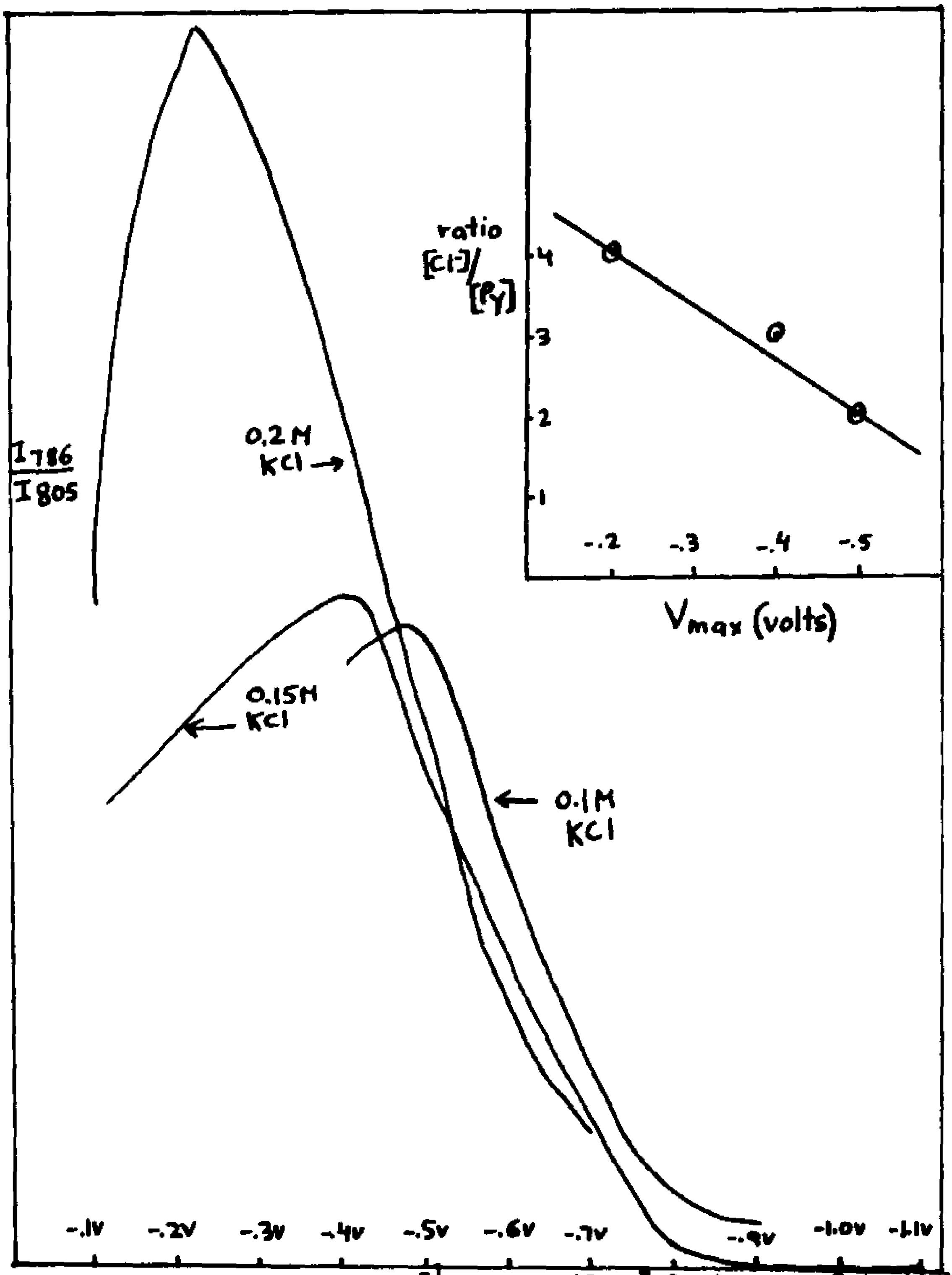
ν cm^{-1} Normal	ν cm^{-1} SERS		ν cm^{-1} SERS	
pH = 13.5			pH = 8.6	
	-.2	-.6	-.2 V	-.6 V
305 w	no SERS	217 w	235 s	217 m
405 w (a_1)		622 m		624 m
545 w (e)				
632 vw (a_1)				
790 m (a_1)		780 w	786 m	782 w
806 vs (a_1)		802 w	805 m	807 w
988 m		985 s		
1015 (combination band)		1010 w	1004 m	1015 w
1057 m (a_1)				
1120 mw (e)				
1208 mw (e)				
1450 m (a_1)		1324 w	1395 s	
1463 m				
			1600 (broadband)	

other E vibrations of this molecule. Or it may be that the field applied on the system through the electrode potential mixes the levels of the 786 cm^{-1} and 805 cm^{-1} bands. In order to determine the causes to the changes in the relative intensity of these two bands further studies have to be carried out; other bands of E symmetry have to be examined as well as the changes in their intensity with respect to the 786 cm^{-1} and 805 cm^{-1} bands.

The ratio of these two bands is also dependent on the chloride concentration, see Fig. 20. As the chloride concentration is increased from 0.1 M to 0.15 and then to 0.2, two effects can be seen: I sym/I asym peaks at more positive voltages and also its numerical value increases. This indicates that the symmetrical band is more chloride dependent then the asymmetrical one, unlike piperidine. However, no electrogeometrical effects can be considered as in piperidine (10), since both bands belong to the same symmetry type.

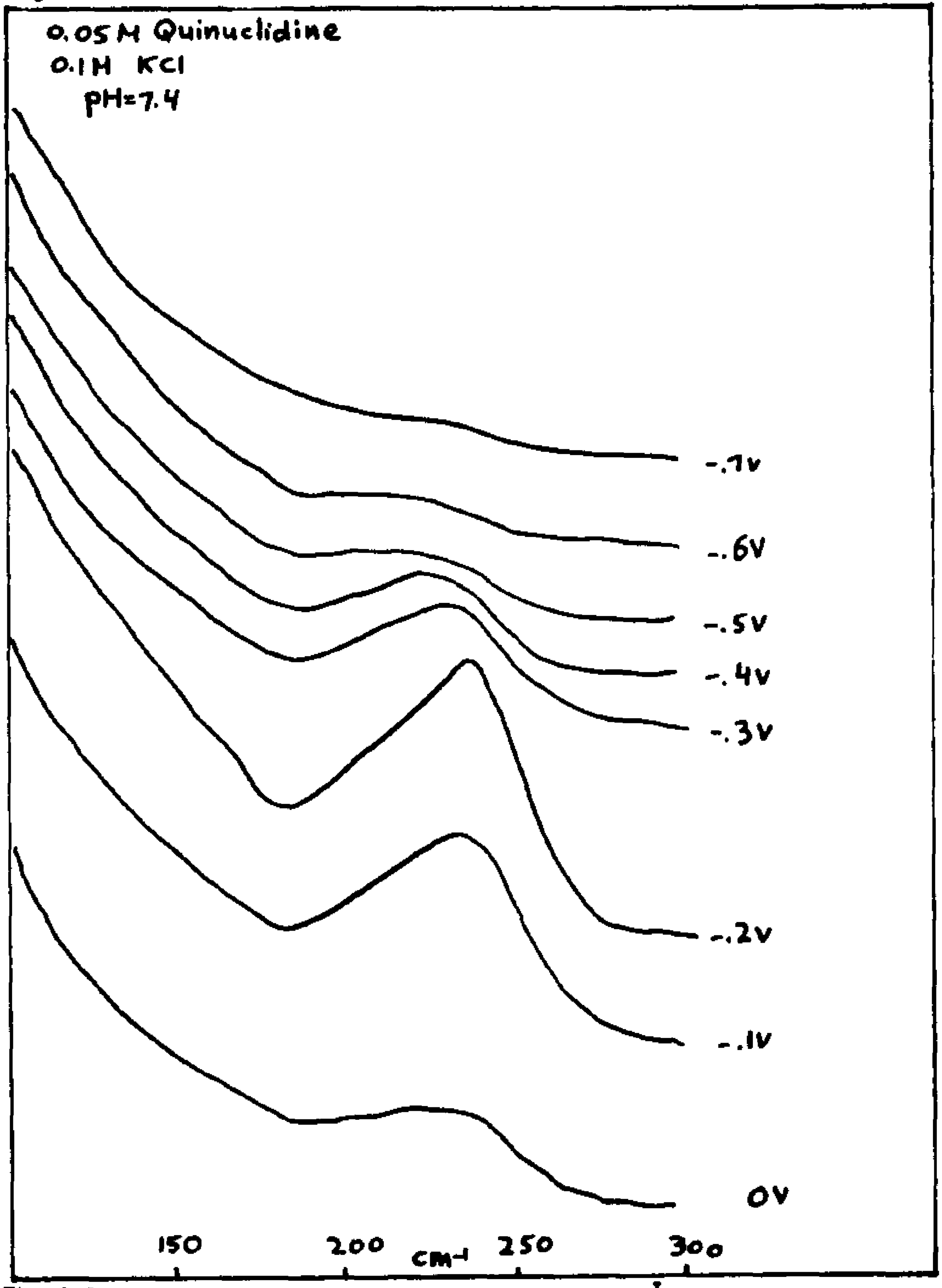
Fig. 21 shows the spectrum of quinuclidinium between 100-300 cm^{-1}. The surface line is similar in the line shape and potential dependence to the one seen from pyridinium and also from pure chloride on the surface (13). This fact reinforces the concept that a positively charged molecule, which adsorbs positive to the point of zero change (p.z.c.), communicates with the surface via the halide. In other words, an ion pair is formed and it adsorbs to the metal, the halide pointing to the silver electrode. The two configurations of this ion pair on the surface are either end-on, or the ion pair lying flat on the surface. Since quinuclidinium does not have a π system, a flat configuration is not acceptable, since it

Fig. 20



Intensity Ratio of the 786 cm^{-1} to the 805 cm^{-} Band versus Potential of 0.05 M Quinuclidine in Various Chloride Concentrations, at pH = 13.

Fig. 2I



The SERS of Quinuclidinium Between 100-300 cm^{-1}, Various Potentials would create steric hindrance and would not be stabilized by an interaction with the metal.

A very interesting effect can be seen by comparing Fig. 19a, 19b and 19c. Both 19b and 19c were taken at pH = 8.6 where most of the molecules are protonated. Fig. 19b, which was taken at -.2 V, shows a spectrum of quiniclidinium, whereas Fig. 19c, where only the applied voltage was changed to -.6 V, shows a typical spectrum of quiniclidine, see Table III, although the bulk pH is 8.6. This effect has been studied in detail elsewhere (13), as a functon of electrode pretreatment, chloride conentration and ionis strength. The pH effect observed in quinuclidine is probably a result of the electrode pretreatment, which was a double-potential step (applied from -.4 V to +.2 V, where it remained from 1 second, and then back to -.2 V) where the charge was not controlled. This means that the effective chloride concentration on the surface during and after the pretreatment was low compared to a charge controlled pretreatment. As a result the active sites favorable to the quinuclidinium-chloride ion-pair are limited. The desorption to the solution of this ion-pair at -.6 V can shift the following equilibrium to the right, thus leading to a spectrum of free quinuclidine:

$$\mathrm{QH^{+}\cdots Cl^{-}_{(ad)}\text{-}\,Ag \rightleftharpoons QH^{+}_{(aq)} + Cl^{-}_{(aq)} + Ag \rightleftharpoons Q_{ad}\text{-}\,Ag + H^{+}_{(aq)} + Cl^{-}_{(aq)}}$$

D. Conclusion

In conclusion, pH effects have been shown on a non-aromatic molecule. This indicates that a π system is not necessarily required for a protonated heterocycle to show SERS. This reinforces the model of an ion-pair, which adsorbs to the surface through the halogen, at potentials positive to the p.z.c.

E. References

1) Fleischmann, M.; Hendra, P. J.; and McQuillan, A. J. Chem. Phys. Lett. 1974, 26, 163.

2) Albrecht, M. G.; Creighton, J. A. J. Am. Chem. Soc. 1977, 99, 5215.

3) Jeanmaire, D. L.; Van Duyne, R. P. J. Electroanal. Chem. 1977, 84, 1.

4) Van Duyne, R. P. "Chemical and Biochemical Applications of Laser, Moore, C. B. Ed.; Academic Press, New York 1979; Vol. 4, Ch. 5.

5) R. L. Birke et al. SERS, Advances in Chemistry Series No. 201, Ch. 4 ed. M. Kadish, 1982.

6) Lee, P. C. and Meisel, D. Chem. Phys. Lett. 1983, 99, 262.

7) Lombardi, J. R.; Shield-Knight, E. A.; Birke, R. L. Chem. Phys. Lett. 1981, 79, 214.

8) Creighton, J. A.; Albrecht, M. G.; Hester, R. E.; Mathew, J. A. D. Chem. Phys. Lett. 1978, 55, 55.

9) Pemble, M. E., Ph.D. Thesis, University of Southampton, Southampton, England, 1980.

10) Birke, R. L.; Bernard, I.; Sanchez, L. A.; and Lombardi, J. R. J. Electroanal. Chem. 1983, 150, 447.

11) Sanchez, L. A.; Lombardi, J. R.; and Birke, R. L. J. Phys. Chem. in press.

12) Bruesh, P. Spectrochim. Acta 1966, 22, 867.

13) Bernard, I.; Birke, R. L.; and Lombardi, J. R. to be published.

CHAPTER V

VARIOUS OTHER RESULTS

Other studies which are repored here are on: 1) acridine, 2) isoquinoline, 3) Hg sols.

A. Acridine. Acridine is an aromatic three membered ring and shows SERS, however anthracene, which has the same conformation and mass (the difference lies in the presence of a nitrogen in acridine), does not seem to display a SERS under the same conditions, i.e. 0.05 M in 0.1 M KCl. This fact confirms the importance of the nitrogen for binding through the lone pair when the molecule is neutral in its charge, and the need for the basic site in order to complex to the halide at an acidic pH, similar to pyridine (see Chapter II). Table IV shows the normal and surface lines of acridine vs. the assigned Raman bands of anthracene.

The force constant of a few molecules has been calculated, using the reduced mass of the respective molecule and one silver atom, see Table I, using the formula

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

where ν is the frequency of the band, k is the force constant and μ is the reduced mass. The force constant increases with the increase in the number of aromatic rings. There may be some back bonding from the d orbitals of the silver atoms to the antibonding orbitals of the molecule. Since the lowest antibonding energy levels are those

TABLE IV

ACRIDINE Normal Raman cm^{-1}	SERS cm^{-1}	Solution Anthracene
	220 m	
	245 m	244 (b_{1g})
400 w	405 s	396 (a_g, b_{3g})
	618 s	615 (b_3)
	1000 w	999 (b_3)
	1015 w	
1028 vs (methanol)		
1165 vw	1175 m	1163 (a_g)
1285 vw	1280 w	1259 (a_g)
1417 m	1407 vs	1401 (a_g)
1475 m	1485 vw	1482 (a_g, b_{3g})
	1588 m	1557 (a_g)
	1620 s	1632 (b_{3g})
	1805 vw	
	2018 vw	
	2570 vw	
	2800 vw	
2858 s (methanol)		
2965 s (methanol)		
	3049 vw	3049 (b_2)

of acridine, π back bonding is more likely in this molecule than in the other ones mentioned in Table V. Also, this extended aromatic system enables a better resonance as compared with pyridine and explains therefore the difference in the force constants between these molecules. 4-Cyano-pyridine, which has an electron withdrawing group, favors this π back bonding and indeed, its force constant is higher than that of pyridine. These results are in accord with the basicity of these molecules, which is the highest for acridine.

The effect of protonation of acridine has also been studied. Since $pK_a = 5.5$ for this molecule, at pH 2.5 all the molecules are protonated and at pH = 7.5 the spectrum is that of the free species. As can be seen from Table VI there is no effect on the spectrum upon protonation. However, when the excitation frequency was changed, the spectrum was different. This behavior is diagnostic of a Resonance Raman, which I suspect is the case here. In order to check whether there was a resonance responsible for this effect, I took the absorption spectrum of acridine at pH = 2.8 and 7.7. There was a sharp peak around 455 nm at pH = 2.8 and one around 405 nm at pH = 7.7. These peaks indicate that Resonance Raman of acridine using a 488 nm laser light is a plausible assumption. Also, a cyclic voltammogram of acridine did not show any electrochemistry at the potential where the spectra were taken. Therefore, the difference in the spectra upon changing the excitation frequency must be due to Resonance Raman, or due to photolysis.

Another effect observed in acridine is the fact that the intensity obtained in the presence of bromide was higher than with

TABLE V

Molecule	K 10^5 dyne/cm	w	$1/\mu$	pK_b
pyridine	1.29	219	45.6	8.75
4-cyano-pyridine	1.48	218	53	?
isoquinoline	1.7	222	58.8	8.58
acridine	2.29	240	67.4	8.42

TABLE VI*

4880 Å pH = 2.8 νcm^{-1}	4880 Å pH = 7.7	6700 Å pH = 7.7
		235 m
400 m	400 w	250 m
		410 m
614 ms	614 w	475 w
998 vw		746 w
1014 w	1014 w	768 s
1169 m	1169 wm	1172 w
1224 w	1224 w	1275 w
1274 m	1270 w	1275 w
1290 w	1290 w	1415 s
1400 s	1400 s	1430 shoulder
1581 ms	1581 m	1597 m
1614 w		

*0.025 M Acridine, 0.1 M KCl at -.28 V.

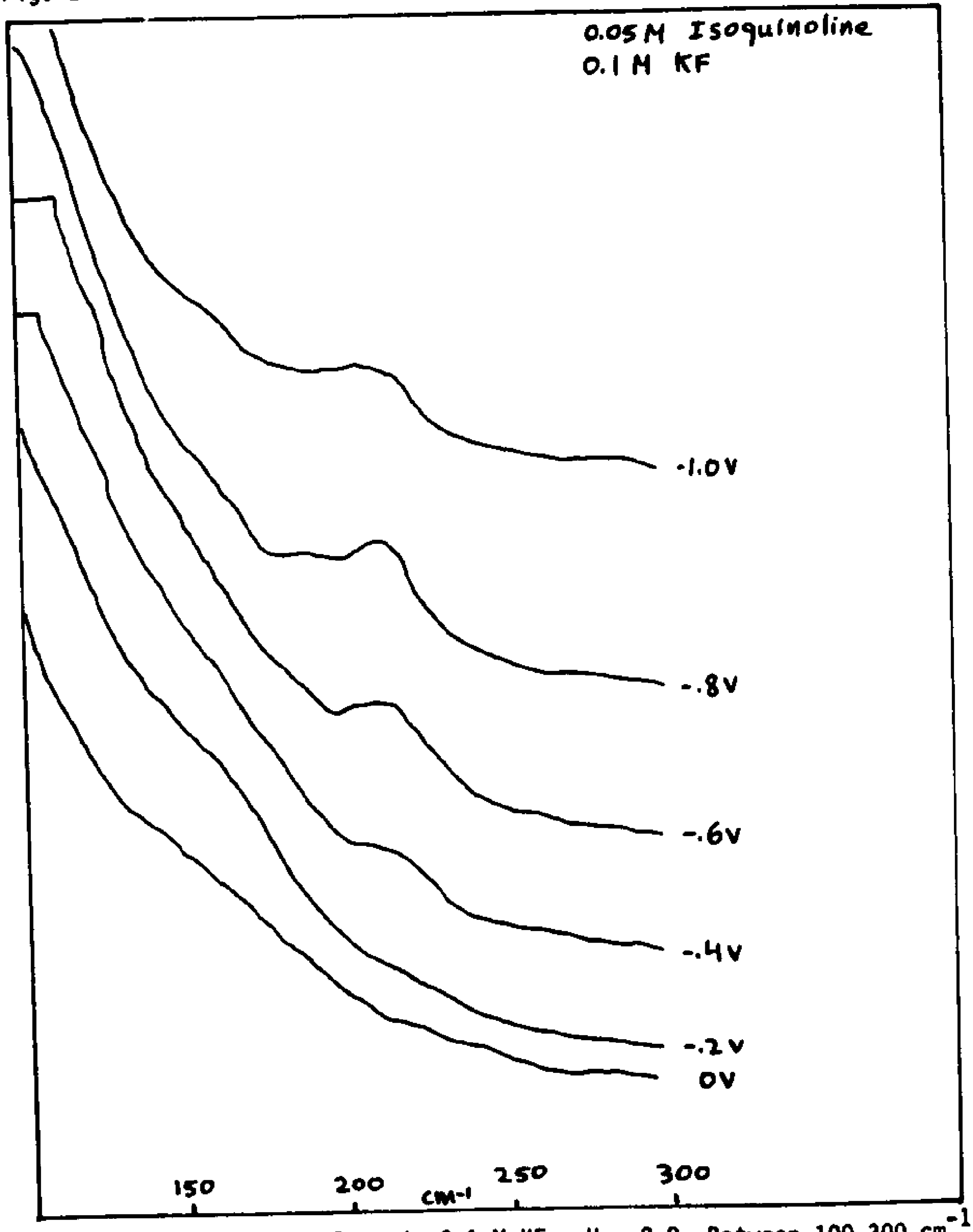
chloride, at pH = 2.5. Since acridine has an extended aromatic ring, and since bromide is more polarizable than chloride, the acridinium-bromide ion pair is more polarizable than acridinium chloride and shows a bigger enhancement, in spite of the larger distance from the surface. It may be that for ion pairs, the Ag-complex distance is not as crucial as for neutral molecules.

B. Isoquinoline. Isoquinoline is another aromatic molecule, a derivative of pyridine, which has two rings. Its surface line around 200 cm^{-1} has been studied as a function of pH and halide, see Fig. 22-27. The surface line studied here does not change when the halide is changed from F^- to Cl^- to Br^-, around pH = 8. However, at an acidic pH (around 2), this band seems to be specific of the halide used. At pH = 2.8 in KF, (F^- is known to adsorb specifically in negligible amounts), the spectrum seen is specific of the unprotonated isoquinoline, therefore I conclude that the formation and consequently adsorption of ion pairs on the surface is impossible under these conditions. To summarize: at pH = 8, isoquinoline adsorbs, and the band seen at 205 cm^{-1} is a Ag-N stretch. At pH = 2, the isoquinoline forms an ion pair with the halide, therefore the band observed shifts when the halide is changed. This reinforces the adsorption mechanism proposed for pyridine in Chapter II.

The protonation of isoquinoline does not change the spectrum except for a band seen at 1582 cm^{-1} at pH = 2 and 1626 cm^{-1} at pH = 7.7. Also, the molecular spectra of isoquinoline were identical under the same conditions for either chloride or bromide, at an acidic pH, except for the Ag-halide stretch, as can be seen in Fig. 22-27.

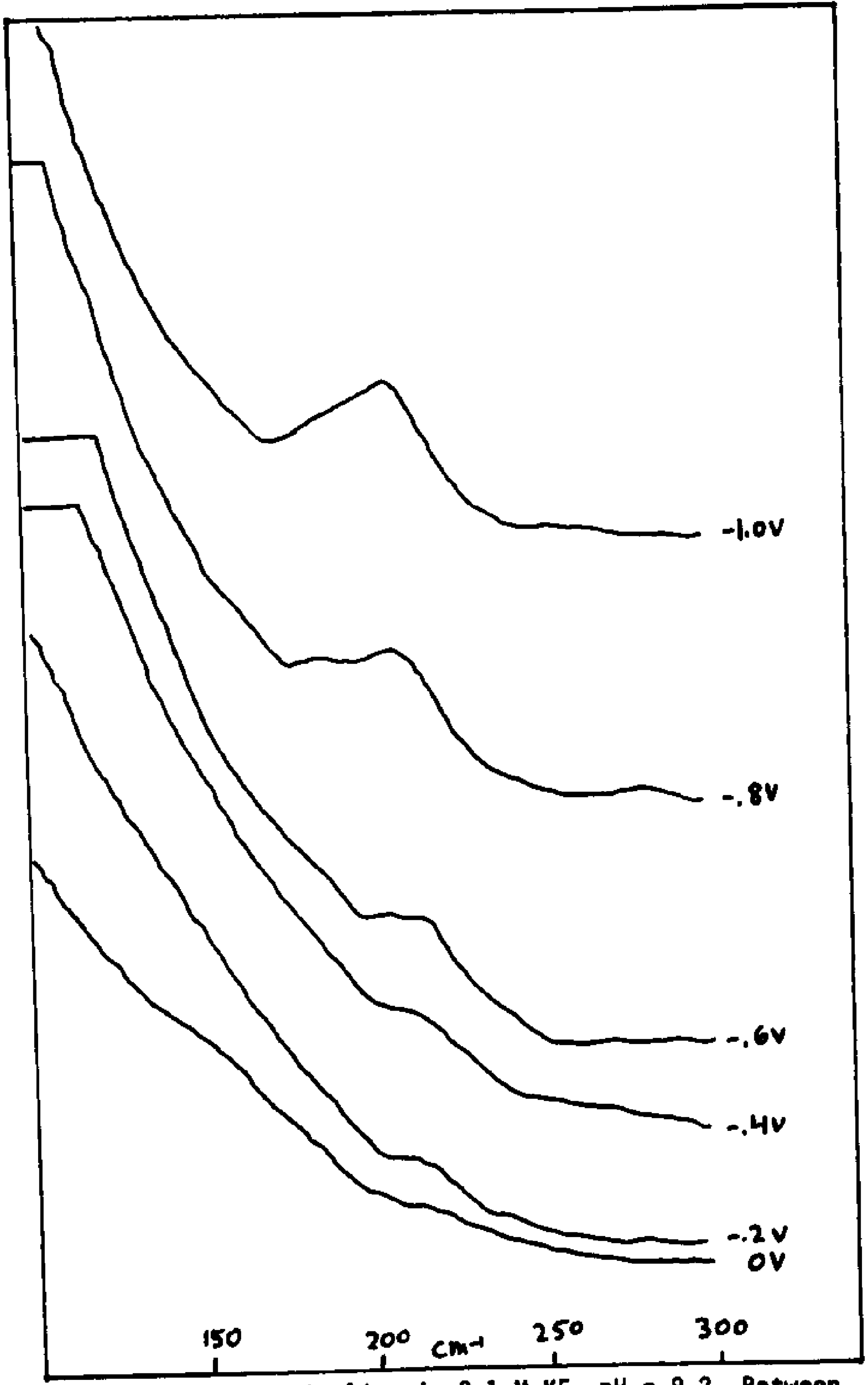
C. <u>Hg Sols</u>. Hg sols have been studied in an attempt to see whether pyridine would show SERS under these conditions. The sols were prepared by cooling a solution of 0.67 x 10^{-3} M $NaBH_4$ and another one of 10^{-3} M $AgNO_3$. 50 mls of the silver Solution were added to 150 ml of the $NaBH_4$ solution, while stirring constantly at a uniform speed. The solution changed color upon formation of the sols and turned grey. An absorption spectrum showed a peak at 210 nm, see Fig. 28 which is expected for the plasmon of mercury. However, no SERS was obtained from Hg sols and this can be attributed to the high damping effects of this metal. In order to be suitable for an electrostatic enhancement the real part of the dielectric function ($Re\epsilon$) has to be negative and large and the imaginary part has to be small ($Im\epsilon$). However, for Hg, $Re\epsilon = -1.65$ and $Im\epsilon = 1.035$; compared to silver, these numbers cause high damping effects, and this is probably the reason we could not detect a SER spectrum of pyridine on Hg sols.

Fig. 22



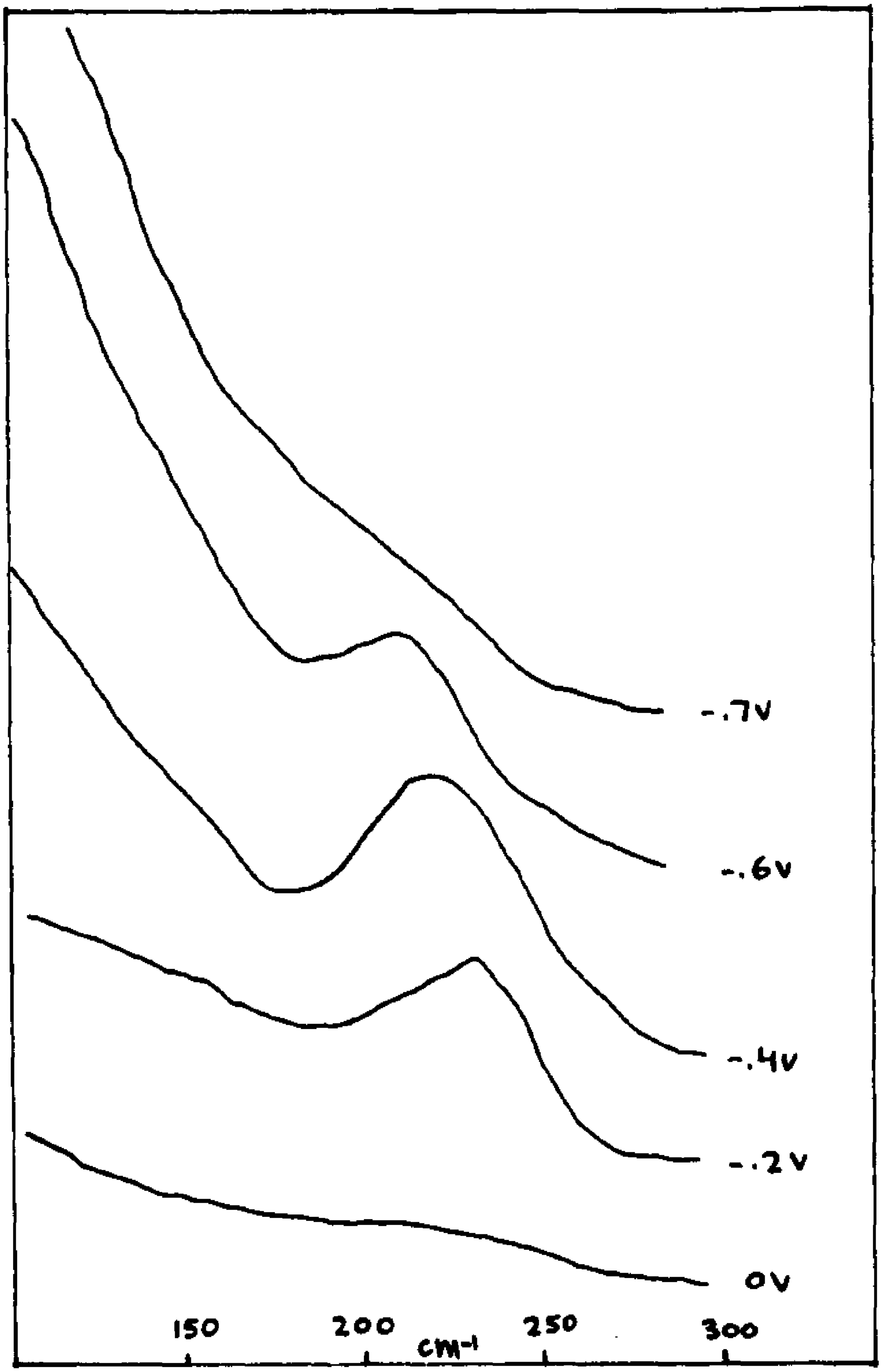
SERS of 0.05 M Isoquinoline in 0.1 M KF, pH = 2.8, Between 100-300 cm^{-1}.

Fig. 23



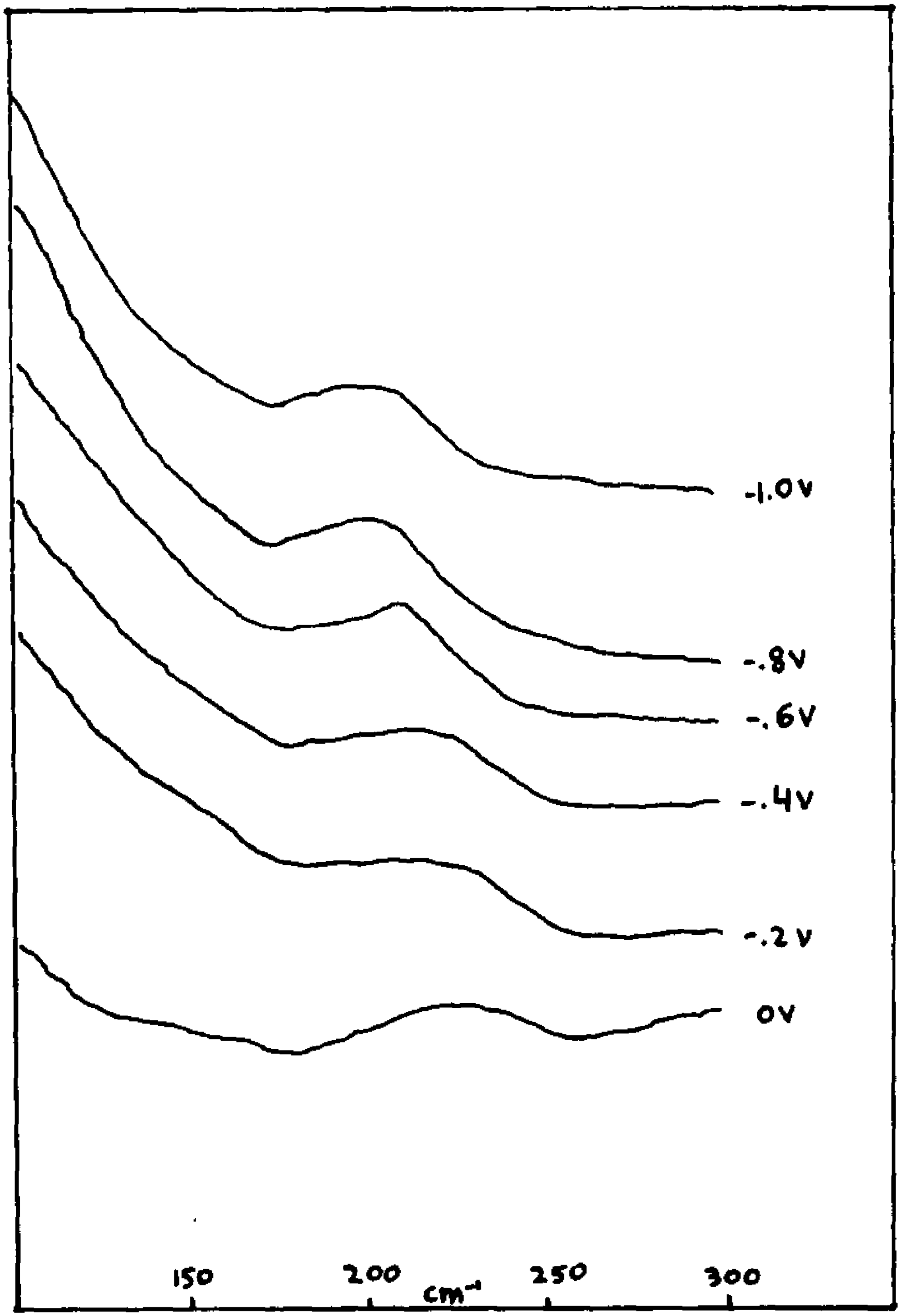
SERS of 0.05 M Isoquinoline in 0.1 M KF_1 pH = 8.2, Between 100-300 cm^{-1}.

Fig. 24



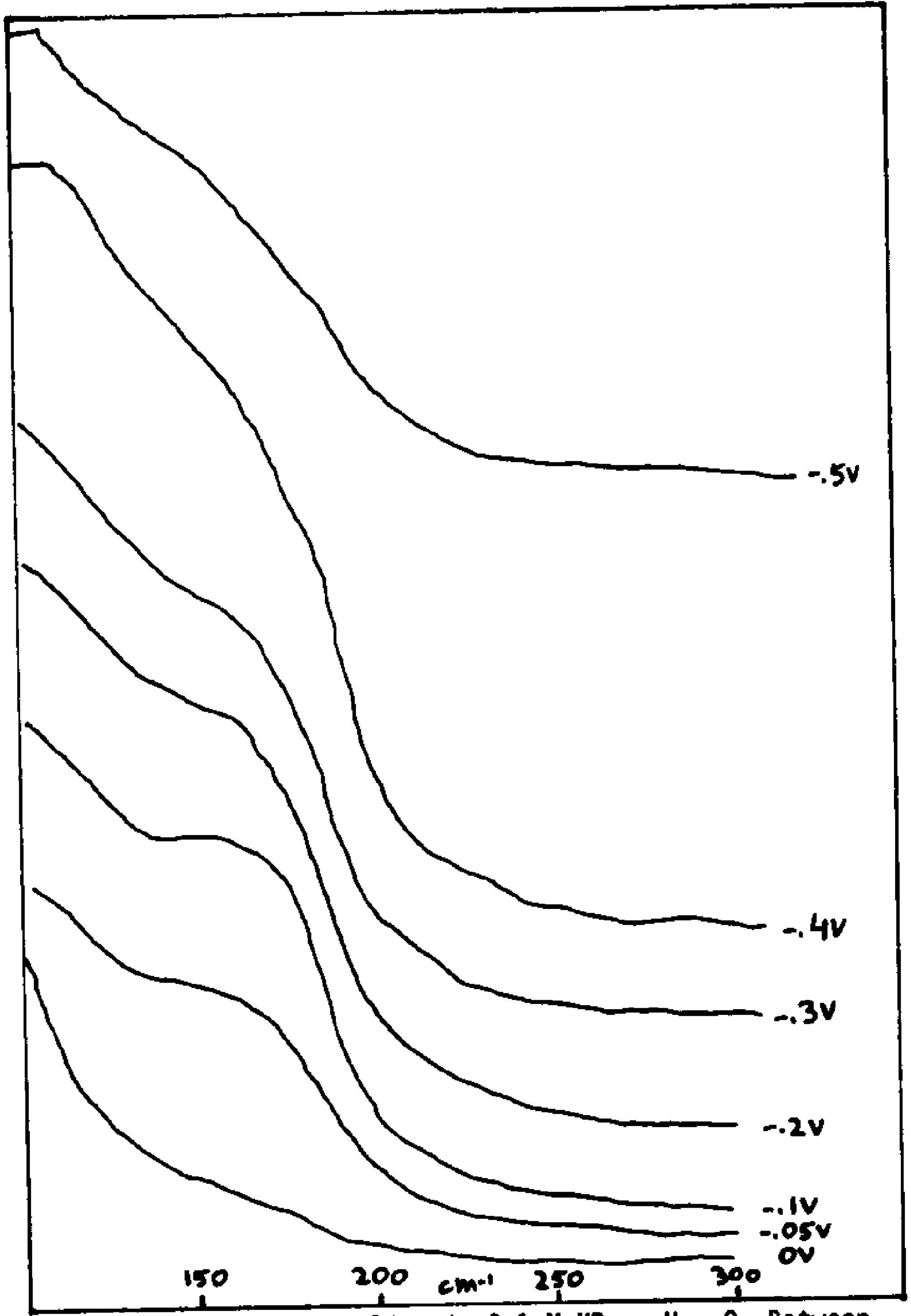
SERS of 0.05 M Isoquinoline in 0.1 M KCl pH = 1.2. Between 100-300 cm^{-1}.

Fig. 25



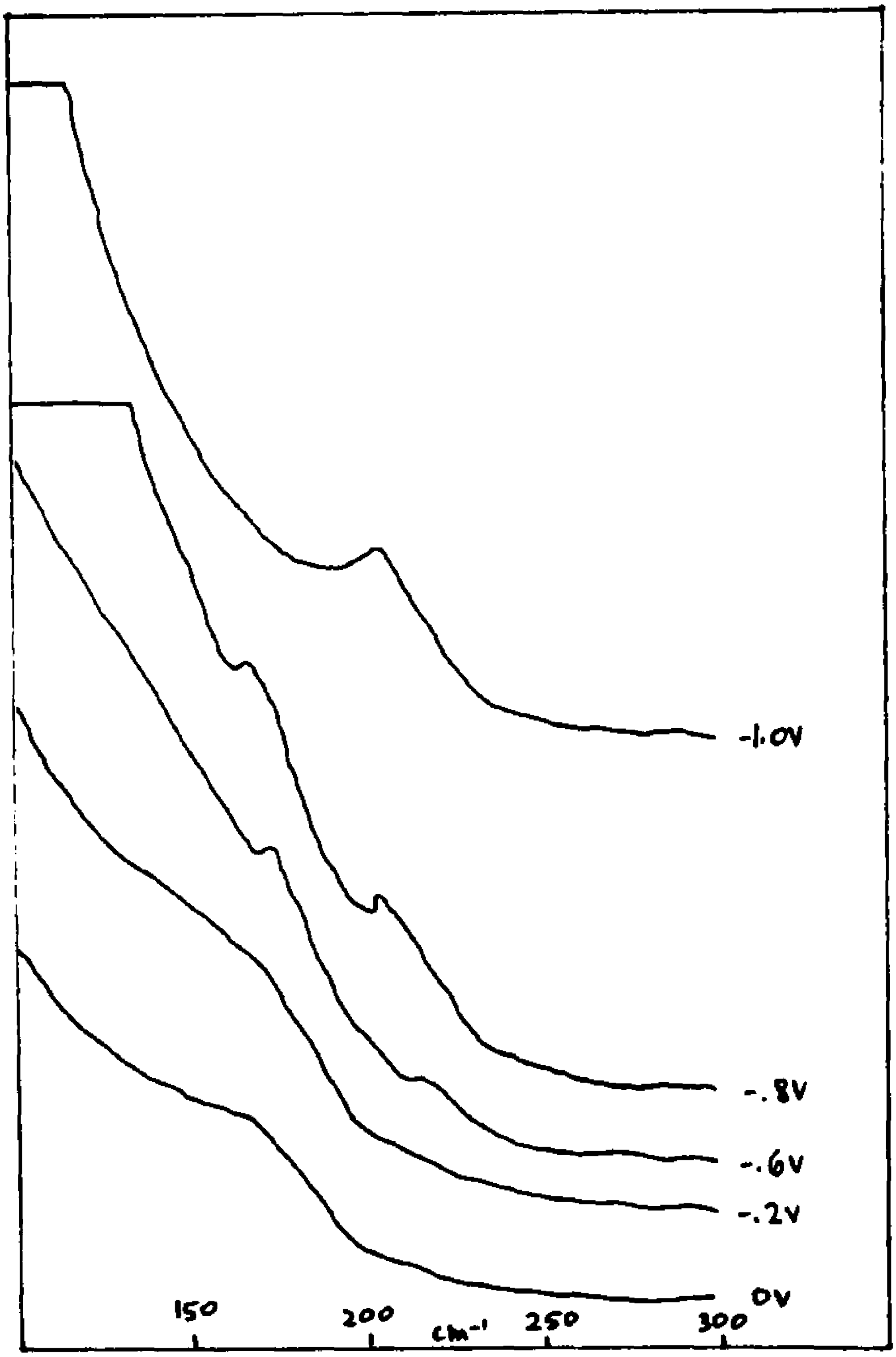
SERS of 0.05 M Isoquinoline in 0.1 M KCl, pH = 8.3, Between 100-300 cm^{-1}.

Fig. 26



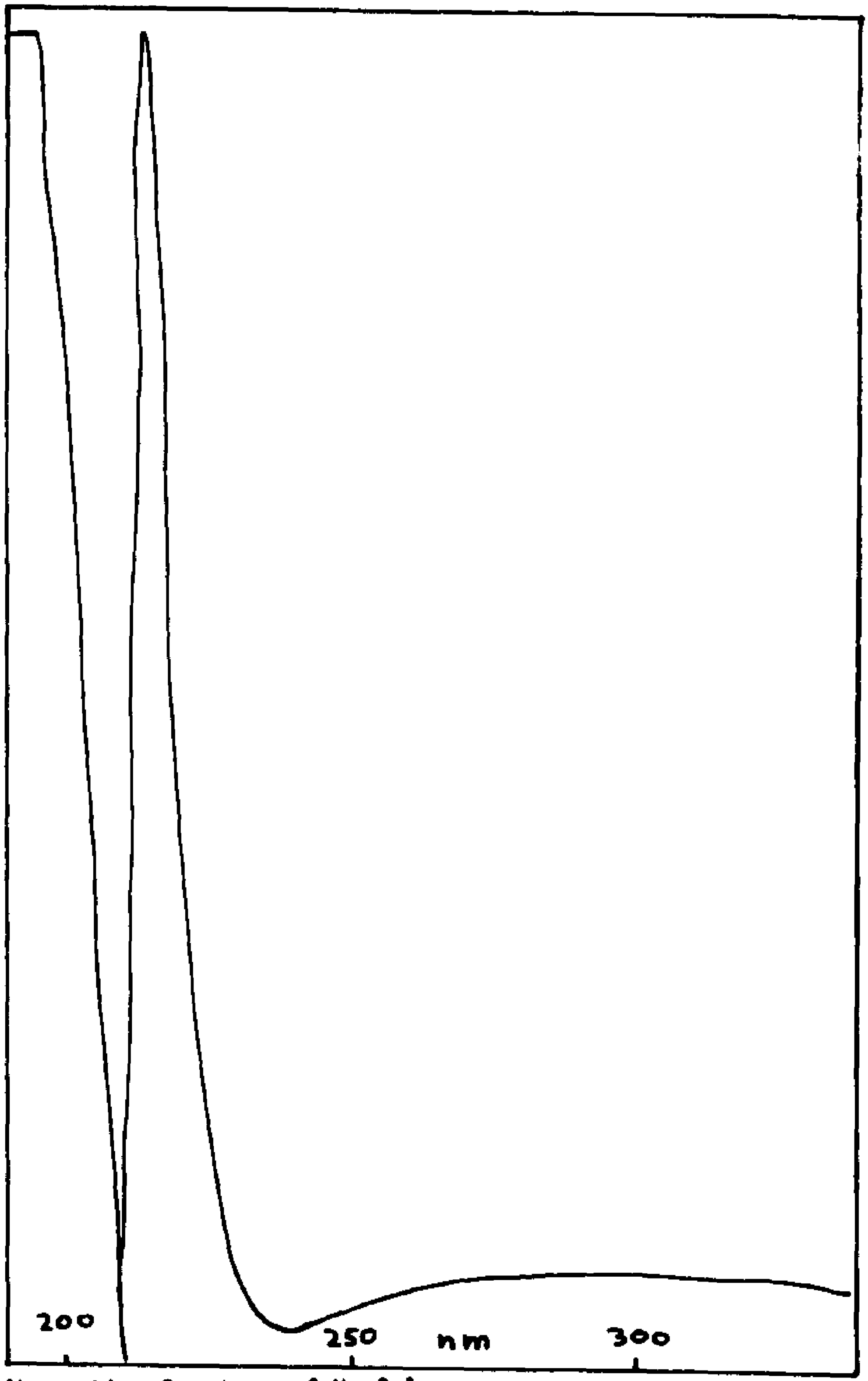
SERS of 0.05 M Isoquinoline in 0.1 M KBr, pH = 2, Between 100-300 cm^{-1}.

Fig. 27

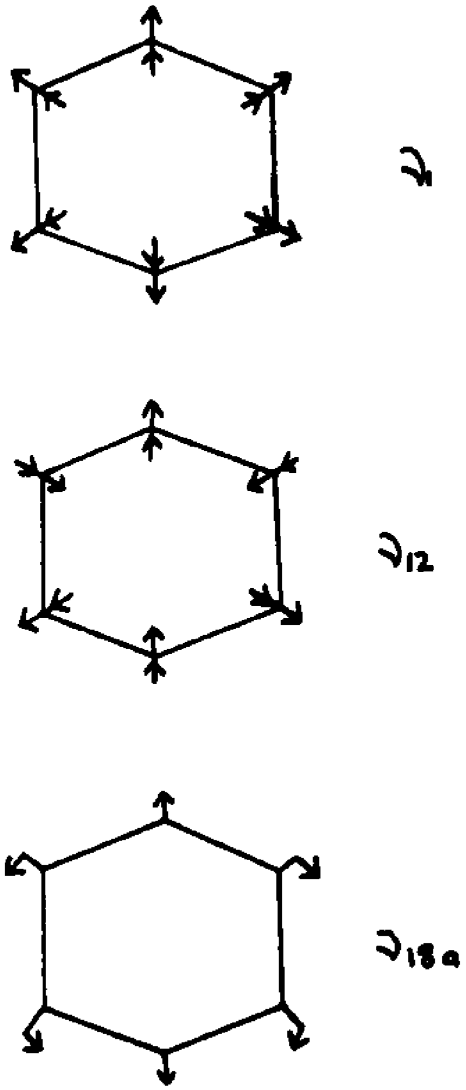


SERS of 0.05 M Isoquinoline in 0.1 M KBr, pH = 7.7, Between 100-300 cm^{-1}.

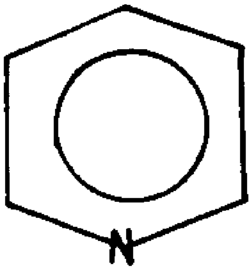
Fig. 28



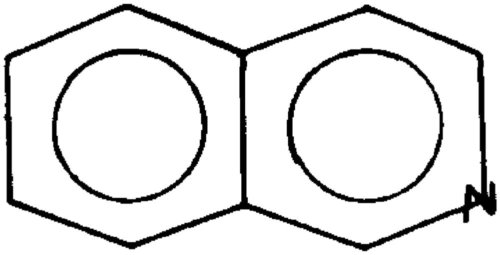
Absorption Spectrum of Hg Sols.



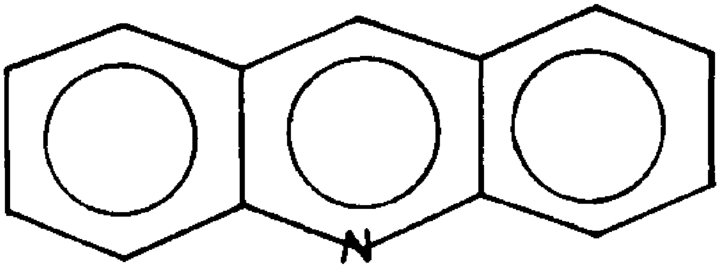
THE WILSON VIBRATIONS (1, 12, 18a)



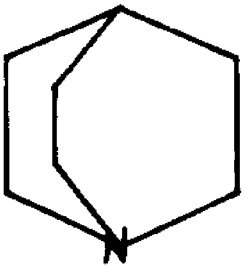
PYRIDINE



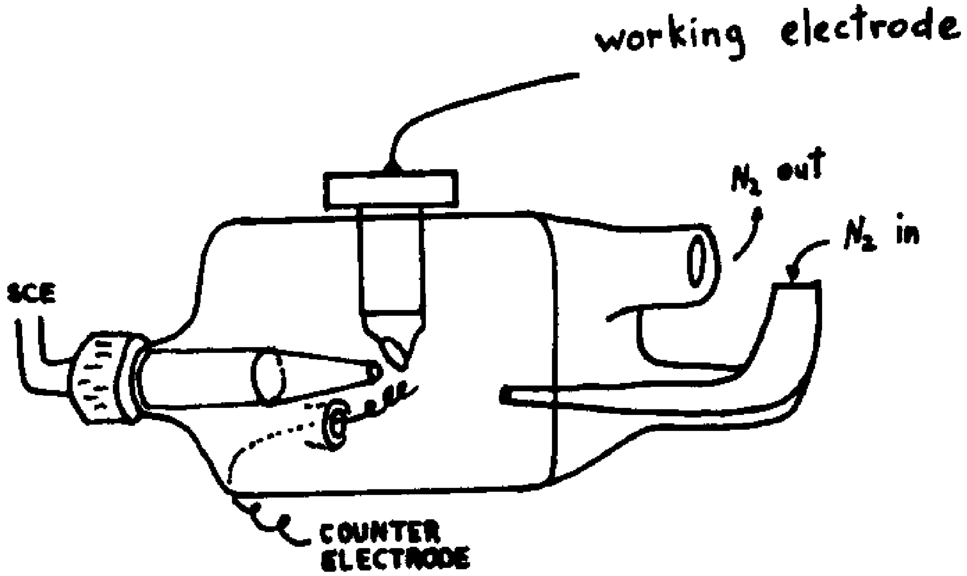
ISOQUINOLINE



ACRIDINE



QUINUCLIDINE



THE SERS EXPERIMENTAL CELL