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**Laser-induced thermal decay of pyridine and chloride
surface-enhanced Raman scattering as a probe of silver
surface-active sites**

Sobocinski, Raymond Louis, M.S.

The University of Arizona, 1987

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LASER-INDUCED THERMAL DECAY OF PYRIDINE AND CHLORIDE
SURFACE-ENHANCED RAMAN SCATTERING AS A PROBE
OF SILVER SURFACE-ACTIVE SITES

by

Raymond Louis Sobocinski

A Thesis Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

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26 October 1987
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DEDICATION

To my parents

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ABSTRACT

The activation parameters for the temperature dependent irreversible loss of surface-enhanced Raman scattered (SERS) intensity from pyridine and chloride adsorbed at silver surfaces in an electrochemical environment have been determined. Laser-induced heating is used to promote a first order surface reaction at these roughened silver electrodes, and is introduced as a probe of the chemical nature of SERS-active sites. Accurate laser-induced surface temperatures must be known for these experiments and are calculated from spectroscopic data. It is found that the kinetic data for both pyridine and chloride SERS deactivation follow Arrhenius behavior. The activation energies associated with the destruction of SERS-active sites at a surface roughened by an illuminated oxidation-reduction cycle (ORC) are 12.8 ± 3.2 kcal/mole and 27.7 ± 3.1 kcal/mole for pyridine at two different types of sites on the Ag surface. Similarly, values for coadsorbed chloride are found to be 11.1 ± 2.4 kcal/mole and 24.5 ± 3.8 kcal/mole. Experiments designed to elucidate the decay mechanism suggest that the laser-induced surface reaction involves desorption of pyridine and chloride from active sites allowing their incorporation into the Ag lattice. The observation of two activation energies in the same temperature region is interpreted in terms of SERS-active sites

which exist at a surface defect and on a terrace plane, respectively. This interpretation is based on the relative activation energies and pre-exponential factors. The activation parameters for pyridine and chloride desorption are also evaluated at a silver surface roughened by a nonilluminated ORC. An activation energy of 27.4 ± 1.9 kcal/mole is obtained for pyridine on these surfaces. This result suggests that a greater concentration of terrace plane SERS-active sites is present at a surface roughened by an illuminated ORC.

CHAPTER 1

INTRODUCTION:

ELECTROCHEMICAL AND SPECTROSCOPIC INVESTIGATIONS OF THE ELECTROCHEMICAL INTERFACE

A great deal of experimentation has been directed recently towards understanding the general nature and specific chemical reactivity of the electrochemical interface. It has been recognized that a better understanding of this complex region should provide greater predictive power in designing electrochemical systems. The development of many technologies are presently inhibited by the inability to probe the chemical nature of the electrochemical interface. These technologies include corrosion inhibition, electro-organic synthesis, fuel cells, and batteries, among others.

Electrochemical methods are useful for the quantitation of reactant amount and for obtaining thermodynamic information about adsorption and electron transfer reactions. However, it is difficult to obtain unambiguous molecularly-specific information about interfacial reactants using electrochemical techniques. A plethora of recent spectroscopic techniques have provided corroborative information for the molecular identification of

surface reactants and adsorbates, and for simple systems the identification is often unambiguous. Both in-situ and ex-situ surface sensitive spectroscopic techniques are being used to provide insight about molecular identity, orientation, and extent of surface-adsorbate interaction. Electrochemical and spectroscopic methods are reviewed here with respect to their ability to probe the electrochemical interface. This should provide a useful perspective for the evaluation of the work presented in this thesis.

Electrochemical Methods

An electrochemical interface is created when an electrode is brought into contact with an electrolyte solution. This interface has properties which are different from those in the bulk solution or bulk electrode material. This interface is said to be composed of an electrochemical "double layer", i.e. a layer that is highly oriented in the vicinity of the electrode surface and another that is significantly more diffuse. Electrochemists are interested in studying the molecular structure of these two layers and how they affect electrochemical reactions. The physical and electrochemical nature of the metal surface has also been shown to play an important role in controlling the interfacial structure (1). Presented here is a short synopsis of electrochemical methods that can provide information about the molecular nature of the metal/solution interface.

Electrochemical Methods for Characterization
of the Electrochemical Interface

Electrochemical techniques have facilitated the verification of many theoretical models for the double layer and have also provided a wealth of thermodynamic information regarding chemical reactions at the electrochemical interface. This section will describe methods which can provide quantitative information about reactions at metal electrodes. Electrochemical methods are useful for the measurement of many thermodynamic parameters such as bond strength between an adsorbate and the surface (ΔH_a°), the tendency of molecules or ions to adsorb (ΔG_a°), and the chemical reactivity at a given electrode surface ($\Delta G^\circ(\text{rxn})$) when electron transfer is involved. Electron transfer kinetics can also be readily evaluated using electrochemical techniques.

The energetics of adsorption play an important role in determining the failure or success of many electrochemical devices (2) such as fuel cells, batteries, and photoelectrochemical cells. An accurate evaluation of adsorption energetics can help optimize these reactions in a more systematic fashion.

ΔG_a° is the standard electrochemical free energy of adsorption which is a useful parameter for comparing the tendency of different molecules or ions to adsorb. This parameter is readily evaluated for the adsorption of organic species at a metal electrode

using a modified Langmuir isotherm (2):

$$\frac{\theta}{1-\theta} \cdot \frac{(\theta + (1-\theta))}{n^n} = \frac{C_{\text{org}}}{55.5} \exp(-\Delta G_a^0/RT) \quad (1.1)$$

where n is the number of solvent molecules that each organic molecule displaces, θ is the fractional adsorbate coverage, and C_{org} is the concentration of organic in solution. A value for n is often estimated, and θ may be determined using any number of electrochemical methods, including chronopotentiometry (3), chronocoulometry (4), potential step methods (5), AC voltammetry (6), and AC impedance techniques (7).

Standard free energy of adsorption for anions at metals may be evaluated from the Frumkin isotherm (8) shown below:

$$(C_b/C_o) \exp(-\Delta G_a^0/RT) = (\Gamma_s/\Gamma_o) (\theta/(1-\theta)) \exp(-g\theta) \quad (1.2)$$

where C_b is the bulk concentration of adsorbing species, Γ_s is the surface concentration at saturation, g is the interaction parameter and C_o and Γ_o are the standard states in bulk solution and at the interface. The standard states are usually 1 mole liter⁻¹ and 1 molecule cm⁻¹, respectively. Surface concentrations may be evaluated using electrochemistry as noted above. The standard enthalpy of an adsorption reaction, ΔH_a^0 , is a good measure of bond strength (i.e. bond dissociation energy). This parameter is evaluated from a plot of ΔG_a^0 vs. T as suggested by the familiar

thermodynamic equation $\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S_a^\circ$. The entropy of adsorption, ΔS_a° , is evaluated from the slope. ΔS_a° is near zero for a 1:1 displacement of adsorbed solvent molecules. An increase in entropy is observed when several molecules are released from the surface for each molecule adsorbed.

Chemical reactivity at a metal electrode can be evaluated quantitatively in terms of equation 1.3 where k is the rate constant for electron transfer, ΔG_a° is the free energy of activation, and A is the pre-exponential factor.

$$k = A \exp(-\Delta G_a^\circ / RT) \quad (1.3)$$

The rate constant is a direct measure of how rapidly a reaction occurs, while ΔG_a° is a measure of the energy required to form the "activated complex" (9). The pre-exponential factor is indicative of the rate of passage through the transition state, or the rate of collision in some cases. The determination of these activation parameters for simple homogeneous electron transfer reactions have frequently been made in addition to measurements of the rate constants themselves. However, measurements of activation parameters for heterogeneous electrochemical processes have remained extremely rare. In the past, there has been some doubt as to the experimental accessibility of these parameters for electrode reactions that can be interpreted on the same basis as chemical systems in solution (10). A good deal of theoretical and

experimental work by Marcus (11) and Weaver (12,13) has shown that expressions can be derived that are valid for the calculation of electrochemical activation parameters. However, electrochemistry is only useful for evaluating these activation parameters for reactions which involve electron transfer. Electrochemical methods may not be useful for the evaluation of activation parameters for a desorption reaction. However, activation parameters for surface-attached reactants involved in electron transfer can be evaluated using equation 1.3. An analogous equation is used for solution reactants at an electrode.

A "unique" redox potential can also help characterize the interfacial behavior and can determine, although often ambiguously, the identity of the interfacial species. Many other redox parameters, such as the number of electrons transferred per mole, can be determined to further characterize interfacial species. It is notable that these measurements do not provide much molecularly-specific information. However, recently, it has been shown that molecular orientation at a Pt surface could be evaluated using electrochemistry. An experiment by Hubbard (14) has demonstrated that the orientation of an organic adsorbate at a Pt electrode can be determined using thin layer electrochemical methods. This is a useful approach for many chemical systems, although the general applicability of this technique is not clear.

While electrochemical methods are useful for the evaluation of many thermodynamic and kinetic electrochemical parameters, they have a number of significant limitations. As already alluded to, the major problem is that electrochemistry is not molecularly-specific. For example, molecular identity is often difficult to determine by electrochemistry, alone. Also, the determination of activation parameters in electrochemical systems is somewhat rare in the literature, perhaps as a result of a lack of theoretical development of heterogeneous electron transfer theory. It is also noted that electrochemistry may not be useful for studying the kinetics of desorption reactions where there is little or no electron transfer.

Vibrational Spectroscopic Methods for Characterization of the Electrochemical Interface

Electrochemical methods are often combined with in-situ or ex-situ spectroscopic methods to further characterize the electrochemical interface. The most common ex-situ methods are x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), electron energy loss spectroscopy (EELS), and low energy electron diffraction (LEED); while the most common in-situ techniques include Raman, infrared (IR), and UV-Vis reflectance spectroscopy. A comprehensive review of ex-situ and in-situ methods has been compiled (15). Ex-situ techniques require that the electrode-solution interface remain intact upon emersion. These

techniques generally require transfer to an ultra-high vacuum (UHV) environment and strongly adsorbed surface species. Hubbard (16) has developed the necessary electrochemical-UHV transfer methodologies; however, the chemical and physical changes in the double layer during the transfer remain controversial (17-20). Until these changes are characterized, in-situ techniques will be the method of choice for studying interfacial species. Also, since most in-situ analytical methods are unobtrusive towards the double layer, they have been used more extensively than ex-situ methods.

Vibrational spectroscopies are extremely popular in-situ probes because they have the ability to unambiguously identify molecular species. A major obstacle for the development of in-situ vibrational methods is the problem of poor sensitivity and poor selectivity for interfacial studies. Good sensitivity is required due to the low surface concentration of analyte, which is on the order of 10^{-11} moles/cm² (monolayer or submonolayer amount). The method must also discriminate effectively against bulk solvent species, which are generally at a much higher concentration than surface species.

Raman and infrared spectroscopy have recently provided the best molecularly-specific in-situ information concerning interfacial molecular species. As a result, there has been intense interest in developing these techniques with the requisite surface selectivity and sensitivity. The development of IR methods must address several

problems. IR cell windows are generally not available for the transmission of low frequency photons ($<200\text{ cm}^{-1}$). An even greater problem is that of poor sensitivity for detecting low frequency IR radiation below 200 cm^{-1} . Another major obstacle is the problem of strong IR absorption from most polar solvents, particularly water, which limits the spectral region of study. However, a number of experimental designs have been used to circumvent the problem of bulk solvent interference. The most successful designs have been electrochemically modulated IR spectroscopy (EMIRS) and infrared reflectance absorption spectroscopy (IRRAS).

Electrochemically Modulated Infrared Spectroscopy (EMIRS)

EMIRS involves modulating the electrode potential at some frequency (usually about 10 Hz) between values where the species of interest is adsorbed and not adsorbed. Potential modulation allows discrimination of bulk solution from adsorbed species. The difference in IR reflectivity is measured at these two potentials, and peaks should only be related to adsorbed species. EMIRS has been applied to the study of CO adsorption onto Pt (21,22) and also methanol oxidation on Pt (23). Both reactions are technologically important in terms of the oxidation of C_1 hydrocarbons for use as fuels. Results from EMIRS experiments suggest that a bridging carbonyl species is the poisoning intermediate in the oxidation of methanol at Pt (23).

Polarization-Modulated Infrared Reflectance Absorption Spectroscopy (IRRAS)

This technique allows discrimination of surface species from bulk solvent through modulation of the incident IR polarization between parallel-polarized and perpendicular-polarized (usually at about 70 Hz). When the incident light is polarized perpendicular to the plane of incidence, the phase shift between the incident and reflected waves is 180° for all angles of incidence. Therefore, the sum of the electric field vectors at the surface is zero (24,25). Consequently, perpendicular-polarized radiation only samples the bulk solvent species. When the incident light is parallel-polarized, the incident angle can be adjusted such that the incident wave and reflected wave are 90° out of phase. This gives an elliptical standing wave which provides a significant electric field normal to the surface. Therefore, parallel-polarized light samples both the solution species and the surface bound species. An IR spectrum of the interfacial molecules can then be obtained by subtraction.

Polarization modulation methods offer a few advantages over EMIRS. The major advantage is that spectra are obtained at a constant potential. This allows the unambiguous interpretation of parameters such as peak frequency, or a shift in peak frequency, both of which are not unambiguously determinable using EMIRS (26,27). Since the resulting spectrum in EMIRS often has a

bisignate shape (resembling the differential of an absorption band), a large number of original spectra can account for the resulting spectrum. As a result, the actual peak frequency can be ambiguous using EMIRS. Most of the applications of IRRAS involve the study of adsorption and oxidation of CO on Pt as applied to fuel cell problems (28,29).

The greatest problem with IRRAS is that it is not very selective for surface species. Spectral interference is often a problem (30). Also IRRAS is less sensitive than EMIRS (31). Thus, the technique of choice depends on the type of information needed as well as the chemical nature of the system under study.

Infrared Spectroscopy versus Raman Spectroscopy

Infrared and Raman spectroscopy are often considered complementary techniques with respect to their different selection rules. For example, Raman spectroscopy is more sensitive to totally symmetric vibrations, while IR is more sensitive to antisymmetric modes where a change in dipole moment occurs. However, in many cases, Raman spectroscopy offers several advantages over IR spectroscopy for interfacial analysis. Raman spectroscopy is usually more useful for studying aqueous systems since water is a weak Raman scatterer; this results in little or no spectral interference from the bulk solvent. Low frequency metal-ligand vibrations down to about 5 cm^{-1} are also accessible using Raman, because photomultiplier tubes are used for photon detection and cell

windows are transparent to the scattered visible radiation. Moreover, Raman is useful for the study of fast chemical events, and is only limited by the width of the laser pulse (femtosecond time scale). IR methods have a much slower time response due to the high electrical resistance in the current path. In an ATR (attenuated total reflectance) cell, the high resistance is in the working electrode itself; in the external reflectance technique, the thin layer of solution between the electrode and the cell window has the high resistance. Reaction rates down to milliseconds have been studied using IR (32). Another advantage of Raman is that it permits a more precise two-dimensional mapping of surface composition because the visible light in Raman can be readily focused down to about $1\text{ }\mu\text{m}$ (33).

Although the detection schemes are fairly sensitive in Raman spectroscopy, the inherent scattering efficiency is poor. The stray light and detection noise can easily swamp the small number of inelastically scattered photons from the monolayer or submonolayer coverage of adsorbate (about 10^{14} - 10^{15} molecules/cm²). A number of workers have circumvented this problem, in part, by using a triple monochromator for better discrimination against stray light and have also used multichannel detection schemes for decreasing noise and allowing faster acquisition of spectra (34). This approach has only been applied ex-situ due to the poor selectivity when used in-situ. Since this technology was developed after the advent of surface-

enhanced Raman scattering (SERS), it is often termed surface-unenhanced Raman spectroscopy or SUERS. Essentially, SUERS is the Raman scattering from molecules adsorbed to "smooth" metal surfaces. Two methods for enhancing the Raman signal (up to 10^5 - 10^6), for a given surface concentration of adsorbate, are resonance Raman spectroscopy (RRS) and surface-enhanced Raman spectroscopy (SERS).

Normal Raman Scattering from Surface-Adsorbed Molecules

In 1982, Campion and coworkers (34) demonstrated that observation of normal Raman scattering from adsorbates in an ultra-high vacuum (UHV) environment was possible. The detection of a submonolayer (about 0.75) amount of nitrobenzene on Ni (111) was made possible by the use of a multichannel detection scheme. This approach offers the advantage of general applicability in terms of adsorbate as well as substrate. In addition to the observation of many adsorbates with large scattering cross-sections (which include nitrobenzene (35), pyridine (36), p-aminobenzoic acid (37), and p-nitrobenzoic acid (37)), ethylene (38) has been observed on a Ag (110) surface at a submonolayer coverage (0.5) at 100 °K. Ethylene is a significantly weaker Raman scatterer than these others; for example, it has a scattering cross-section which is more than a factor of ten smaller than nitrobenzene. The spectra in these studies were obtained with the use of a colored glass filter to eliminate detection of the laser line. As a result, only spectra greater than 600 cm^{-1} are obtained. A triple monochromator might be

used to circumvent this problem; however, the detection of low frequency metal-ligand vibrations using this technique has not been demonstrated. It should also be pointed out that the applicability of SUERS for the study of the electrochemical interface has not been demonstrated. Additional background, particularly from solution scattering, may be a problem.

The technique of normal or unenhanced Raman spectroscopy at metals will be useful for studying a wide variety of catalytic surfaces in the UHV environment and emersed electrode systems. As a result of its low S/N ratio and small spectral range, however, it is presently of limited use for studying the electrochemical interface. This technique is certainly in its infancy and will, undoubtedly, be an area to watch as detection schemes become more sensitive and more discriminating.

Resonance Raman Spectroelectrochemistry (RRSE)

The most useful characteristic of resonance Raman spectroscopy for electrochemical studies is that laser excitation within an electronic absorption band results in enhancements of the Raman signal by factors as large as 10^5 - 10^6 for certain vibrational modes of adsorbates or electrogenerated species. This technique has been used extensively for the study of reaction kinetics at electrodes, because usually the concentration of intermediates is low making increased sensitivity highly desirable. Van Duyne and

coworkers (39) have used RRSE to study the one-electron oxidation of tetramethyl-p-phenylene di-amine (TMPD) to its cation radical, $\text{TMPD}^{+\bullet}$, at Pt. It was found that the maximum amount of $\text{TMPD}^{+\bullet}$ in the diffuse double layer is at a reaction time of 50 milliseconds. Simic-Glavaski and coworkers (40-42) have made extensive use of RRSE to study the adsorption of phthalocyanines at Ag, Au and other electrodes.

In some cases, selectivity can be enhanced by the appropriate choice of laser excitation frequency. The incident laser frequency can often be set to a value close to the frequency for electronic absorption in the molecule. This will help discriminate against bulk solvent, solution species, or reaction species.

Of course the major problem with RRSE is that it is extremely molecule dependent, i.e. only those molecules with accessible electronic absorption frequencies can be studied with this technique. Therefore, unless the molecule of interest happens to be highly colored and have an extinction coefficient greater than $1000 \text{ M}^{-1}\text{cm}^{-1}$, RRSE is of limited use.

Surface-Enhanced Raman Scattering (SERS)

A second enhancement approach which allows for the study of submonolayer amounts of surface species in electrochemical systems is surface-enhanced Raman scattering (SERS). The advantage of SERS over resonance Raman scattering is that, for the most part, SERS is

not adsorbate specific. Seki (43) has recently compiled a list of adsorbates which have been detected using SERS. These include such species as halides, metals and organics. The major disadvantage of the approach, at this time, is that it has only been documented for a limited number of metal surfaces: Ag (44-47), Cu (48-50), Au (51-53), Li (54,55), K (56,57), Na (58-61), Ni (62-72) and Pt (73,74). Clearly, a better understanding of the fundamental nature of SERS will be required in order to extend this enhancement phenomenon to other metal surfaces.

SERS was first discovered in 1974 by Fleischman, Hendra and McQuillan (75), who employed Raman spectroscopy, for the first time, to directly study the adsorption of molecules at electrodes. These authors observed high quality Raman spectra from pyridine adsorbed on an electrochemically roughened silver electrode surface, and attributed the large signals to the increased surface area resulting from the electrochemical pretreatment and the possibility that multilayers are formed. It was soon realized by Jeanmarie and Van Duyne (76), and independently by Albrecht and Creighton (77), that the Raman scattering cross-section itself must have undergone an increase of 10^5 - 10^6 for the adsorbed molecule. Since Raman scattering is an inherently weak process, this generated a great deal of excitement in the scientific community and resulted in a tremendous outpouring of theoretical and experimental work.

SERS Mechanisms. Although there have been many conflicting and irreproducible experimental results, there is now general agreement about the following observations, which motivate the mechanistic discussion below.

1. SERS occurs for a variety of molecules (43) adsorbed on the surfaces of relatively few metals. The effect has been confirmed for Ag, Cu, and Au, metals that are highly reflective in the visible (78)
2. Surface roughness appears to be required. The major contribution can be submicroscopic (10-100 nm) roughness or atomic scale roughness (steps, kinks, or adatoms, for example), depending on the system (78)
3. The excitation profile (intensity versus incident wavelength) deviates markedly from ν^4 for many vibrational bands, displaying broad resonances (79)
4. The enhancement may be long-ranged, depending on the surface topography. Appreciable enhancement has been observed for molecules that are tens of nanometers from the surface (80,84)
5. Selection rules for Raman scattering are relaxed, resulting in the appearance of modes that are normally Raman inactive and even infrared inactive in the gas phase (81)
6. Vibrational frequencies and excitation profiles are both functions of applied potential in electrochemical experiments. The excitation profiles of different vibrational modes are different (79)
7. Surfaces that support SERS invariably display a weak continuum inelastic scattering, even in the absence of an adsorbed species (82).

Two mechanisms, which may not be exclusive, appear to contribute to the observed enhancement: an electromagnetic (EM) mechanism and a chemical mechanism. The EM model involves the excitation of conduction electron resonances (i.e. localized surface plasmons) in the metal by both the incident laser and the Raman oscillator. This results in an enhanced electric field at the molecule such that all molecules should show the same enhancement factors at similar vibrational frequencies. The molecular mechanism, on the other hand, is somewhat adsorbate-specific. This idea draws an analogy to resonance Raman scattering, involving adsorption-induced charge transfer states as resonant intermediate states.

Electromagnetic Enhancement. Electromagnetic enhancement models are based on the fact that localized surface plasmons in some metals can be excited by incident photons. Enormous electric fields can result at the metal particle surface, essentially increasing the laser power at the molecule. It is proposed that this electric field also interacts with the Raman scattered radiation, thus increasing the intensity further. These surface plasmons are generally defined as oscillations of valence electrons at the metal surface. The excitation of surface plasmons and, consequently, the extent of enhancement depends on the frequency dependent dielectric constant of the metal, $\epsilon(\omega) = \epsilon' + i\epsilon''$, the dielectric constant of

the surrounding medium, ϵ , and metal particle geometry and size (78).

EM models provide a qualitative understanding of many of the experimental results. For example, EM models predict the dependence of enhancement on incident frequency, the qualitative behavior of the decrease of the SERS intensity as the separation between the surface and molecule are increased, and the large enhancement factors for Ag, Cu, Au and the alkali metals. For free electron metals, the condition for the excitation of localized plasmons occurs at frequencies where the refractive index, n , approaches zero (83), i.e. where the imaginary part of the dielectric constant ($\epsilon'' = 2nk$) is small. At these frequencies, the electric field is reradiated and not absorbed. Another apparent requirement for resonance is that the real part of the metal dielectric constant ($\epsilon' = n^2 - k^2$) has a large negative value. This explains the frequency dependence and the large enhancement factor for the free electron metals. The nonlocal nature of SERS is predicted by EM models and demonstrated by polymer spacer experiments (80), and also by multilayers of deuterated pyridine on Ag (84).

Surface particle size and geometry also play a role in the EM enhancement (78). On flat planar surfaces, the excited plasmon cannot emit the incident photons, due to momentum and energy considerations. Surface roughness (i.e. curvature) allows the radiation of these photons which produce enhanced electric fields.

The role of particle size has not been well characterized either in theory or empirically. Recent evidence (85) suggests that most of the enhancement may be supported by submicroscopic size particles. These particles are difficult to measure experimentally and there is often a wide distribution of particle sizes which must be considered. Furthermore, the extent of interparticle interaction is difficult to determine in real systems.

Although EM models explain many of the experimental observations, they fail to explain others. These models explain the SERS-active metals, requirement of surface roughness, long-ranged enhancement, and the deviation from normal ν^4 intensity dependence (86). EM models do not account for the excitation profiles of different vibrational modes as a function of applied electrode voltage. The continuum of inelastic scattering at all frequencies is also difficult to reconcile using EM models alone.

Chemical Enhancement. Potential-dependent excitation profiles provide the best evidence to support a chemical mechanism involving an intermediate resonant state. EM enhancement is still operative, but the overall enhancement may be controlled by another factor: the availability of an intermediate electronic state. The applied electrode potential can alter the enhancement factor (EF) by a factor of 10 - 30 (87) , excluding the effect of surface concentration changes.

Most of the adsorbates studied with SERS do not have electronic transitions in the visible portion of the spectrum. Proponents of the chemical mechanism suggest a new resonant intermediate state is created upon adsorption. These resonant intermediate states are often called charge transfer states and are proposed to exist at or above the Fermi level in the metal, which is known to be potential dependent. Charge transfer excitation can take place either from the Fermi level to an unoccupied energy level in the adsorbate, or the optically excited electron can originate in an occupied portion of the adsorbate orbitals and terminate in empty metal states above the Fermi level. Strong evidence for this theory has been obtained in the form of potential dependent excitation profiles (87-93). For example, more negative potentials increase the energy of the Fermi level; for a metal-to-adsorbate charge transfer, this change in energy would result in a red-shifted frequency for maximum enhancement. It has been proposed that these localized electronic states are primarily operative only at sites of atomic scale roughness (91,92), such as adatoms or small clusters of atoms. Although the role of atomic scale features is often associated with the chemical mechanism, it could also be taken as support for an EM mechanism. It is possible that these atomic features exist on submicroscopic "bumps" which have enormous enhancement factors controlled by EM mechanisms alone. The requirement of chemisorption for enhancement (81) is also associated

with the chemical mechanism and these atomic scale features.

Clearly, the role of atom clusters or singular atomic sites in supporting SERS is not well understood.

Recently, there has been much interest in elucidating the nature of the SERS-active site. However, due to the small particle size and distribution of particle sizes in real systems, this has proven to be an arduous task. It has been suggested (89) through Tl underpotential deposition experiments on Ag that the active sites for SERS are associated with surface defects that cover only about 3% of the surface. Potential excursion experiments in electrochemical systems have also provided evidence that atomic scale roughness plays a large role in supporting SERS (81,94-98). These experiments have shown that a large portion of the initial SERS intensity is irreversibly lost when potential excursions are performed where the probe molecule or ion is no longer adsorbed. It has been shown that "macroscopic" (i.e. particles with a diameter >100-200 nm) roughness is insensitive to the destruction of atomic scale features. Presumably, these active sites are destabilized upon potential excursion, and therefore, migrate along the surface where they become incorporated into the metal lattice at a defect site.

A number of other experimental observations have suggested that the extent of specific chemical interaction may play a role in supporting SERS. These observations also support the chemical enhancement mechanism. For example, although water is normally

present at or near the electrode surface, the SERS of water is only observed in the presence of high electrolyte concentrations (99-101). The importance of "chemical effects" is also demonstrated by the degree of enhancement observed for ethane and ethylene adsorption on Ag (102). While ethylene displays significant enhancement, the adsorbed ethane does not. These observations suggest that the chemical nature of the adsorbate plays a role in the chemical enhancement mechanism. On the other hand, the availability of electronic levels in different molecules may affect the charge transfer resonance (90). Some work by Campion (103) has suggested that chemisorption alone is not sufficient to produce SERS. In conclusion, it appears that the effects of electromagnetic resonance, charge transfer, and chemisorption at defect sites are somewhat entangled, and it would be useful to do a little more unraveling.

Research Problem

The overall objective of this research was to provide insight into the chemical enhancement mechanism in an electrochemical SERS experiment. More specifically, the goal was to obtain quantitative information regarding the energetics associated with the SERS-active site where pyridine and chloride are coadsorbed at a roughened Ag electrode. There has been very little quantitative information reported in the literature concerning the energetics of SERS-active complexes. The heterogeneous nature of the roughened

surface, and perhaps experimental protocol, has made these determinations somewhat difficult in the past. Although the chemical nature of the metal-adsorbate interaction appears to control SERS intensities, little is known about its mechanism for enhancement. A quantitative determination of the stability of surface species should provide more detailed information about the active site.

A primary focus of the research presented in this thesis was to demonstrate the viability of a new technique for determining the activation energy for the destruction of metal-adsorbate complexes at these roughened surfaces. The method involves the use of SERS for detecting the rate of complex destruction as the surface is heated using laser radiation. Application of the Arrhenius expression then allows the calculation of activation parameters associated with these laser-induced surface processes.

Evidence for the role of atomic scale roughness in SERS has been demonstrated in both UHV and electrochemical environments through the application of perturbations which cause irreversible quenching of SERS intensities (104,105). Cold Ag island films evaporated at 120 °K in vacuum exhibit irreversible quenching of both background and adsorbate SERS signals upon annealing of the atomic scale roughness features (106). Macomber and Furtak have observed the irreversible quenching of the SERS intensity of the $\nu(\text{Ag-Cl})$ vibration from specifically adsorbed chloride at a silver

electrode upon heating the electrochemical system (107). These workers attributed the quenching to thermal dissociation of Ag adatom - chloride complexes at the surface. The continuum background signal generally associated with SERS was also observed to decrease in intensity with the irreversible loss of intensity of the $\nu(\text{Ag-Cl})$ mode in these studies.

Several reports of irreversible quenching of SERS intensity with the application of negative potentials for adsorbates at Ag electrodes also exist in the literature. This has been reported for many adsorbates by Wetzal, Gerischer and Pettinger (108,109), Chang and coworkers (110), Weaver and coworkers (96), and Baltruschat and Heitbaum (111). Weaver and coworkers found that the intensity-time decay profile for SCN^- , upon application of a negative potential step, did not fit a simple kinetic model. However, Baltruschat and Heitbaum measured both the potential and temperature dependence of the quenching rate for CN^- at silver electrodes.

It has been shown (112-118) that laser illumination during the ORC in the presence of halide solutions has the effect of increasing the SERS intensities substantially. At a Ag electrode, the SERS intensities are enhanced by a factor of 3-10 (115), depending on the adsorbate and the halide electrolyte. This additional enhancement appears to be the result of a greater number of "small" particles formed during the ORC (114). Although the macroscopic features (i.e. those down to 100 nm detectable with a

scanning electron microscope) are smaller at an illuminated ORC surface, it is not clear what size particles are responsible for the enhancement. It is surmised that a greater concentration of surface active sites are produced with an illuminated ORC as a result of photodecomposition of the AgCl film during reduction. Another possibility is that more optimum particle sizes are created for the enhancement process. The feasibility of silver halide photodecomposition is demonstrated by the well-known photographic effect (119). There has been no mention of the effect of an illuminated ORC for Cu or Au in the literature. In any case, the active sites produced by an illuminated ORC are still a point of controversy.

Despite the indirect evidence implicating the importance of atomic scale roughness in SERS, very little quantitative information is available regarding the energetics of these atomic scale roughness features and their interactions with adsorbates. This thesis details a sensitive method for probing the energetics of Ag atomic scale roughness - adsorbate interactions in an electrochemical environment. The method is based on the thermally-induced irreversible decay of SERS signals for pyridine and chloride adsorbed at roughened silver electrodes. The decay of SERS intensities at a constant electrode potential, after an oxidation-reduction cycle (ORC) roughening procedure, has been observed previously in electrochemical systems (96,107,111,120). However, the kinetics of this decay are often complex and have remained

somewhat elusive (96,107). Using the technique reported here, a first order decay of the SERS intensities is observed at a constant surface temperature. This result allows the determination of activation parameters associated with these laser-induced surface processes.

On the Calculation of Thermodynamic Parameters
From Kinetic Information

Chemical kinetics is useful for providing values of important thermochemical quantities that are difficult or impossible to obtain by other means. It will be useful to demonstrate the type of information that can be extracted from kinetic data and the significance of this information to the system at hand.

The idea that many reactions show inverse exponential temperature dependence was first proposed by S. Arrhenius in 1889 (121). He also proposed that the rate constant is also related to the difference in heat content between the activated and inert molecules. This equation is expressed in the following form:

$$k = Ae^{-E_a/RT} \quad (1.5)$$

where A is called the pre-exponential or frequency factor. Strictly speaking, the quantity E_a is most correctly defined as the "experimental activation energy", because it is obtained in practice from the plot of $\ln(k)$ versus T^{-1} . The heat, or enthalpy, of activation is reserved for the quantity ΔH° .

It was first suggested in 1911 (122) that it is more reasonable to write:

$$k = A \exp(-\Delta G_{\ddagger}^{\circ}/RT) \quad (1.6)$$

$$= A \exp(-\Delta H_{\ddagger}^{\circ}/RT) \exp(\Delta S_{\ddagger}^{\circ}/R) \quad (1.7)$$

where $\Delta G_{\ddagger}^{\circ}$ and $\Delta S_{\ddagger}^{\circ}$ are the free energy and entropy of activation, respectively. The factor that determines reaction rates is not necessarily E_a , but rather $\Delta G_{\ddagger}^{\circ}$. Consider the energy diagram in Figure 1.1 which illustrates the relationships between activation parameters and thermodynamic quantities for an adsorption/desorption reaction of a chemisorbed species, which is the type considered in this research. $E_a(f)$ and $E_a(r)$ denote the activation energies of the forward and reverse reactions. E_a is defined as the change in internal energy in going from one of the minima to the maximum, which is called the transition state or activated complex. The enthalpy of activation, $\Delta H_{\ddagger}^{\circ}$, would then be $E_a + \Delta(PV) - RT$, but $\Delta(PV)$ is usually negligible in condensed phase reactions; thus, $E_a = \Delta H_{\ddagger}^{\circ} + RT$ for the system at hand. The Arrhenius equation can be recast as

$$k = A \exp(-E_a + RT) \exp(-\Delta S_{\ddagger}^{\circ}/R) \quad (1.8)$$

or as

$$k = eA \exp(\Delta S_{\ddagger}^{\circ}/R) \exp(-E_a/RT) \quad (1.9)$$

The pre-exponential factor, A , was first derived in 1936 by Wynne-Jones and Eyring (123). The first derivation was based on the

Figure 1.1 Enthalpy versus reaction coordinate for an adsorption/desorption reaction of a chemisorbed species.

translational partition function and the result of this treatment is the following:

$$A = kT/h \quad (1.10)$$

The quantity kT/h is of great importance here, because it allows the a priori determination of A , assuming that the rate of passage through the transition state is near the vibrational frequency. However, it is possible that every oscillation does not take the molecule through the transition state; this is because the critical conformation of the molecule has a complicated dependence on the arrangement of all the atoms in the complex. In certain cases, the overall conformation might not be appropriate for the formation of products. Rotations may also play a role in forming the activated complex. In order to take these factors into account, it is written:

$$k = \kappa \cdot \frac{kT}{h} \cdot \exp(\Delta S_{\ddagger}^{\circ}/R) \exp(-E_a/RT) \quad (1.11)$$

where the reaction rate is proportional to the vibrational frequency and κ is called the transmission coefficient. As the reactions become more adiabatic, κ approaches unity. It is often implicitly assumed that chemical reactions are adiabatic (i.e. $\kappa \approx 1$). However, it is believed that nonadiabatic pathways ($\kappa \ll 1$) are commonly encountered at electrode surfaces (124,125) and in homogeneous solution (126). The value of kT/h is about 6×10^{12}

sec^{-1} at 298 °K, therefore when $A < kT/h$, $\kappa < 1$. This treatment suggests that large differences in the pre-exponential factor (i.e. many orders of magnitude) between different Arrhenius plots may be due to large differences in κ . While the physical interpretation is somewhat ambiguous (i.e. what is causing the reaction to be more or less nonadiabatic), such results would suggest that significant differences exist between the reaction pathways giving rise to different Arrhenius plots.

Research Objectives

Specific objectives of the research are as follows:

1. To determine the local laser-induced surface temperatures from spectroscopic data (i.e. the Stokes and anti-Stokes intensities of adsorbed molecules).
2. To induce and observe an n^{th} order decay of the Raman intensity associated with the destruction or migration of the SERS-active surface complex.
3. To demonstrate the viability of the laser-induced decay method for determining activation energies.
4. To compare the energetics of SERS-active surface complexes formed after different roughening procedures and at selected electrode potentials.

Local laser-induced surface temperatures are calculated from an extended Boltzmann equation described in chapter 3. The kinetics associated with the laser-induced process is studied by monitoring the SERS intensities of adsorbed pyridine and chloride. The loss of SERS intensity is related to the surface concentration of SERS-active sites. In order to demonstrate the viability of laser-induced decay for determining activation energies, the effect of electrode potential is studied. Also, the effect of an illuminated and a nonilluminated oxidation-reduction cycle (ORC) roughening procedure on activation parameters is studied. Increased SERS intensities are obtained at a surface roughened by an illuminated ORC and the origin of this increase is of interest.

CHAPTER 2

EXPERIMENTAL

Spectroscopic Instrumentation

The complete spectroelectrochemical system, including excitation source, electrochemical set-up and detection scheme, is shown in Figure 2.1. Excitation was provided exclusively by the 514.5 nm line of a Coherent Radiation Innova 90-5 Ar⁺ laser. Plasma lines are removed with appropriate filters (50% transmission, bandpass about 3 nm). The laser was focused to a beam diameter of ca. 50 microns at the electrode surface as confirmed by SEM measurements on electrode surfaces, and also by experiments performed using a micrometer positioned at the most narrow focus of the actual laser beam. The incoming radiation is specularly reflected at 60° normal to the electrode surface. SERS intensities are a function of incident angle as demonstrated by Pettinger and coworkers (127). After an excessive charge transfer on the order of 20-100 monolayers (about 125 monolayers are dissolved and redeposited in these experiments), a broad unstructured curve of intensity versus angle of incidence is seen which extends over the entire range of incidence angle (0-90°); this is the result of the superposition of many narrow peaks. This specific angular

Figure 2.1 Schematic diagram of the Raman spectroelectrochemical instrumentation. (M) flat mirror; (A) polarization analyzer; (C) collection optics; (S) polarization scrambler.

Figure 2.1 Schematic diagram of the Raman spectroelectrochemical system

dependence of the Raman intensities may be the result of excitation of surface plasmons (128) which require a relatively unique type of roughness. This roughness is proposed (127) to have a large correlation length (e.g. grain boundaries, well separated nuclei, etc.), because only a discrete set of surface momentum vectors can lead to such discrete excitation (or emission) angles.

Scattered radiation is collected about π steradians using a concave mirror, is reflected with a planar mirror, passed through a polarization scrambler (this is used as a result of the polarization dependence of grating efficiency), and is then focused onto rectangular slits at the entrance to the double monochromator. The wavelengths of the scattered radiation are separated by a Spex 1403 Ramalog double monochromator (see Figure 2.2) with 1800 grooves/mm holographically ruled gratings. Detection is accomplished with a high sensitivity, GaAs photocathode, RCA C31034 photomultiplier tube which is thermoelectrically cooled to ca. -25°C to reduce the dark current. Typical dark count values were 50-100 counts/second. The amount of scattered radiation and the resolution, or spectral bandwidth, is controlled by adjustment of the entrance slit, two middle slits and an exit slit. Spectral bandpasses used were generally between 2.0 and 5.0 cm^{-1} depending on the laser power used.

The spectrometer system is interfaced to a Spex Datamate dedicated microcomputer system for spectrometer control, data

Figure 2.2 Schematic diagram of the Ramalog double monochromator. (S1) entrance slit, (S2,S3) middle slits, (S4) exit slit, (M) mirror, (G) holographic grating.

Figure 2.2 Schematic diagram of the Ramalog double monochromator

acquisition, and data analysis. Dual disk drives are employed for data storage.

Electrochemical Instrumentation

A specially designed spectroelectrochemical cell was used for several reasons. It was constructed to be compatible with an X-Y-Z- θ translator used to maintain maximum reproducibility in electrode surface positioning (which is important due to the high sensitivity of the experiment). The cell is a sandwich-type design as shown in Figure 2.3. This allows for quick and thorough clean-up of the cell. The cell is connected to an L-frame (shown in Figure 2.3) which stabilizes the working electrode and also facilitates the mounting of the cell to the X-Y-Z- θ translator. The translator allows control of the laser beam angle of incidence to within 1 degree and the x, y, and z distances to within 1 mm.

Paraffin-wrapped teflon O-rings sealed the cell at the glass window and PVC backplate. Another small O-ring was used to seal the working electrode at the cell body. The cell body was constructed of Kel-F which is chemically resistant to most acids, bases, and organic compounds. Approximately 5 mL of solution fills the cell.

The working electrode consisted of a polycrystalline Ag disk (99.9%, Johnson Matthey) of geometrical area 0.38 cm^2 which was mechanically polished to a mirror finish using successively finer grades of alumina (Buehler) down to 0.05 microns, rinsed with triply distilled water, and then sonicated for exactly 2 minutes to remove

Figure 2.3 Schematic diagram of the spectroelectrochemical cell. (a) micrometer shaft, (b) electrical connection, (c) pin attachment (d) threaded teflon shroud, (e) lucite back plate, (f) viton o-ring, (g) Kel-F backplate, (h) teflon coated o-ring, (i) fill port, (j) Kel-F cell body, (k) reference electrode connection and fill port, (l) AUX electrical connection, (m) coarse frit, (n) glass AUX compartment, (o) teflon-coated o-ring, (p) front glass plate, (q) lucite front plate, (r) L-frame cell mount, (s) micrometer entrance opening, (t) X-Y-Z- θ translator mounting holes, (u) cell mounting holes.

Figure 2.3 Schematic diagram of the spectroelectrochemical cell

any trapped alumina. Paraffin was used to wrap the rest of the electrode in the cell. The distance between the electrode surface and the glass window is reproducibly controlled by the micrometer shaft depicted in Figure 2.3. The silver disk is connected to a brass mount which screws into the teflon shroud until it comes into electrical contact with the micrometer. A platinum wire which enters through the stopcock wall served as the auxiliary electrode. A saturated calomel electrode (SCE) served as the reference electrode.

Electrode potentials were controlled with an IBM model EC/225 voltammetric analyzer and were measured and reported versus an SCE reference electrode. Linear potential ramps were performed using a triangle wave format for the oxidation-reduction cycles. Total charge passed was monitored with a digital coulometer (Princeton Applied Research Model 379).

Materials

Solutions were prepared as 0.10 M KCl supporting electrolyte and 0.05 M pyridine with no pH adjustment. The natural pH is approximately 8.3 for this solution. All solutions were prepared daily from triply distilled, deionized water, the second distillation being from a NaOH/KMnO₄ solution. Solutions were deaerated with nitrogen for 10 minutes prior to use.

KCl (Fisher, reagent grade) was used as received. High

purity pyridine (Burdick and Jackson) was used with no further purification.

Procedures

The Oxidation-Reduction Cycle. Perhaps the most popular roughening procedure is the electrochemical oxidation-reduction cycle (ORC). This popularity is due, in part, to the superior enhancement obtained from this procedure compared to other types of pretreatment, such as mechanical roughening or chromic acid treatments. The ORC procedure used here involves a triangular linear potential sweep in a potential region where Ag is oxidized and reduced such that a total of 20-50 mC/cm^2 anodic charge is passed. A potential step ORC has also been used successfully to produce surface features which are even more uniform (129,130) than the sweep method. Only potential sweep ORCs were used in the research reported here.

A typical cyclic voltammogram for a linear potential sweep ORC carried out in a solution containing 0.1 M KCl and 0.05 M pyridine is shown in Figure 2.4. The initial potential is normally around -0.20 V vs SCE and is ramped in a positive direction at 5 mV/sec. The silver surface begins to oxidize at ca. +0.050 V and current due to Ag oxidation to AgCl is observed. A AgCl precipitate quickly forms at the surface which is relatively insoluble in water. At a predetermined charge value, the scan direction is reversed such that the total anodic charge passed is 20-30 mC/cm^2 .

Figure 2.4 Cyclic voltammogram of an ORC at a silver electrode in 0.1 M KCl/0.05 M pyridine, scan rate = 5 mV/sec, $S = 0.80 \text{ mA/cm}^2$.

Figure 2.4 Cyclic voltammogram of an ORC at a silver electrode

The reduction of the silver chloride proceeds until about -0.150 V, resulting in a rough Ag surface. Charge recovery is about 99% suggesting that nearly all of the oxidized silver is still at the surface, except now it has a large number of the desired roughness features.

All ORCs performed for the research presented here were in the presence of 0.1 M KCl and 0.050 M pyridine with no pH adjustment. Following the ORC, the laser beam is blocked until the experiment is completely set-up (about 1 minute). The electrode potential is then moved manually to the potential of choice. The surface is then exposed to the laser beam and the vibrational intensities are monitored for ca. 90 - 120 minutes.

Illuminated ORC vs. Nonilluminated ORC. It is well documented (112-118) that SERS intensities can be enhanced by a factor of 3-10 when an illuminated ORC pretreatment is used instead of a nonilluminated ORC. It is proposed that illumination affects the reduction process of AgCl to Ag metal. The end result is the production of more particles with the optimum size (or geometry) for electromagnetic enhancement. This conclusion is based on the observation of a larger number of "small" macroscopic particles (i.e. greater than 200 nm in diameter). It is proposed that these particles contain even smaller "bumps" of the optimum size for enhancement which is calculated to be about 50 nm at an incident wavelength of 514.5 nm (114).

The research performed here involves, in part, the comparison of the effects of these two roughening methods in terms of surface complex activation energies and their kinetic behavior. To the author's knowledge, this type of kinetic analysis has never been performed on illuminated ORC surfaces; in fact, very few studies have been performed on illuminated surfaces. The illuminated ORC pretreatment in these studies used 200 mW laser power at an incident wavelength of 514.5 nm.

Determination of Intensities. Vibrational intensities are determined from the area under the peak of interest. Due to the very large intensities produced, peak areas were accurately determined by digital integration above a straight baseline formed between appropriate baseline points. In fact, comparable precision in the decay plots was obtained by this method versus a background subtraction technique.

Reproducibility. The success of this quantitative method depends to a large degree on the reproducibility of the ORC roughening procedure. In fact, it is the roughened nature of these surfaces that has made quantitation so difficult in the past. Reproducibility in polishing the silver surface was evaluated by measuring the actual surface area from the underpotential deposition (UPD) of Pb using a value of 300 microcoulombs/cm² for one Pb monolayer as reported by Dickertmann, Koppitz and Schultze (131).

The reproducibility of the surface area was found to be $\pm 8\%$. The reproducibility in the ORC roughening procedure is $\pm 7\%$.

CHAPTER 3

DETERMINATION OF SURFACE TEMPERATURES

In order to apply the Arrhenius equation for the determination of activation energies in these systems, it is necessary to know the electrode surface temperature. From a plot of $\ln(k)$ versus T^{-1} , the activation energy may be calculated from the slope, $-E_a/R$. Due to the local nature of the laser-induced surface heating, it is necessary to obtain the local temperature. A common device for measuring surface temperature is the thermocouple. However, this device provides a value for the average surface temperature which is expected to be much different than at the illuminated portion of the surface, which is a very small fraction of the total surface area. It is possible to calculate the local surface temperature, however, from the Stokes and anti-Stokes intensities of adsorbed molecules. The surface temperature is related to these Raman intensities through the Boltzmann distribution function when the system is at equilibrium. These calculations are discussed below.

Normal Raman Scattering

It is well known (132,133) that solution temperatures can be readily calculated from the ratio of Stokes intensities to anti-Stokes intensities for vibrational bands. For normal Raman scattering, this ratio is related to the temperature through equation 3.1 below.

$$\frac{I_s}{I_{as}} = \frac{(\nu_0 - \nu_K)^4}{(\nu_0 + \nu_K)^4} \exp(hc\nu_K/kT) \quad (3.1)$$

Here, ν_K is the frequency of the K^{th} vibrational mode of pyridine in wavenumbers, ν_0 is the frequency of exciting laser radiation, and all other terms have their usual meaning.

While the use of equation 3.1 is commonly used to determine solution temperatures, there have not been many reports concerning its application to the determination of surface temperatures. It is demonstrated here that surface temperatures may be successfully determined using this relationship and the Raman intensities of adsorbed molecules.

Initial attempts to determine these laser-induced surface temperatures involved the application of equation 3.1. However, the temperatures calculated from equation 3.1 for the 1010 cm^{-1} ring breathing vibration of adsorbed pyridine were found to be low by ca. 20°K . This led to the use of a different model to describe the Stokes and anti-Stokes intensities.

Resonance Raman Scattering

The SERS phenomenon is a resonance-type process in two ways. Electromagnetic models suggest that the incident laser frequency is often, to some extent, in resonance with a localized surface plasmon such that the induced electric field is enhanced to varying degrees. This appears to be the controlling resonance factor in determining enhancement. Proponents of chemical enhancement mechanisms claim another resonance mechanism is operative which controls the enhancement up to a factor of 100. It is also noted that a deviation from the normal ν^4 intensity dependence has been observed experimentally by Van Duyne (79) and Creighton (134).

Recently, it has been shown that SERS is more enhancing for the totally symmetric a_1 modes (135), a behavior also exhibited by resonance Raman scattering. Moskovits (136) has demonstrated that SERS is a resonance phenomenon which can be successfully related, experimentally, to the excitation frequency, ν_0 , the absolute frequency of the scattered light, ν , and the electronic resonance frequencies, ν_e and ν_s , by a Lorentzian-type function. The Raman scattering cross-section from solution or molecules at a surface, can be related to the above resonance parameters through an equation outlined by Albrecht and Hutley (137). According to this equation, the scattering cross-section is directly related to the frequency dependent terms F_A and F_B as defined here.

$$F_A = \nu^2(\nu_e^2 + \nu_o^2)/(\nu_e^2 - \nu_o^2)^2 \quad (3.2)$$

$$F_B = 2\nu^2(\nu_e\nu_s + \nu_o^2)/(\nu_e^2 - \nu_o^2)(\nu_s^2 - \nu_o^2) \quad (3.3)$$

F_A and F_B are dimensionless frequency terms derived from a quantum-mechanical treatment of the polarizability tensor, ν_o is the excitation frequency, ν is the absolute frequency of the scattered light, and ν_e and ν_s are the frequencies for electronic resonance. Experimentally, it was found that F_B alone provided the best intensity versus ν_o fit for p-nitroaniline between 488.0 and 632.8 nm excitation wavelength. It was noted that p-nitroaniline has a resonance in the ultraviolet region and that F_A is expected to have a significant contribution to the intensity at higher energies, i.e. with blue excitation. A plot of F_A/ν^2 versus ν_o was calculated from the above equation using $\nu_e = 10755 \text{ cm}^{-1}$ (929 nm) for pyridine adsorbed to a roughened Ag surface (136). The value for ν_e was calculated from an equation which is strongly dependent on the plasma frequency of the metal and the density of metal clusters on the surface. Several values for ν_e were used to try and fit the theoretical F_A/ν^2 versus ν_o plot to the experimental result. A value of $\nu_e = 929 \text{ nm}$ provided the best results. The F_A/ν^2 versus ν_o plot was determined experimentally by Creighton and coworkers (134) for the 1008 cm^{-1} vibration of adsorbed pyridine at a Ag electrode, and was found to be relatively close to the calculated plot obtained by Moskovits (136). The work presented in this thesis was performed at $\nu_o = 19436 \text{ cm}^{-1}$ which falls in the frequency range studied by

Moskovits and Creighton. The same pyridine band was also used in the temperature calculations determined here. Consequently, these results suggest that a Lorentzian-type function may be used to describe the frequency dependence of the 1008 cm^{-1} pyridine SERS intensities.

Application of an extended frequency expression for resonance Raman scattering to SERS from adsorbed pyridine has been reported by Marinyuk and coworkers (138). This equation is given below.

$$\frac{I_s}{I_{as}} = \frac{(\nu_o - \nu_K)^4}{(\nu_o + \nu_K)^4} \cdot \frac{(\nu_o - \nu_e + \nu_K)^2 + \Gamma^2}{(\nu_o - \nu_e - \nu_K)^2 + \Gamma^2} \exp(hc\nu_K/kT) \quad (3.4)$$

In this expression, ν_e represents the frequency of the absorption maximum in wavenumbers for resonance and Γ represents the full-width-at-half-maximum (FWHM) in wavenumbers for the resonance. The resonance term used to calculate surface temperatures in equation 3.4 differs slightly from the resonance term in equation 3.2 used by Moskovits. While both are Lorentzian functions, the resonance term used in equation 3.4 is a quantum-field theoretical extension (139) of the calculations used to obtain equations 3.2 and 3.3. A damping term, Γ , is introduced so the intensity does not go to infinity at resonance, but stays at some experimentally observed level. These results are believed to be more accurate than those obtained from equations 3.2 and 3.3 because the authors have treated the Raman

process with a second, third, and fourth-order time-dependent perturbation theory (139). The equations are alleged to be more accurate, because they consider the vibrational quantum as a separate step in a series of time-ordered processes involving both light and vibrational quantum. Marinyuk and coworkers used the known temperature and equation 3.4 to estimate values for ν_e and Γ . Their results are similar to the experimental results from the excitation profile of adsorbed pyridine. While this suggests that the equation may be reasonably valid, it does not experimentally demonstrate the validity of the method for determining surface temperatures.

Previous excitation studies on the SERS of adsorbed pyridine at Ag electrodes clearly demonstrate that the 1010 cm^{-1} and 1038 cm^{-1} bands do not follow the intensity dependence of normal Raman scattering (79,134). Instead, as mentioned previously, the excitation profiles resemble a resonance Raman process. The most complete excitation profile for the 1010 cm^{-1} band of adsorbed pyridine has been published by Creighton (140). It shows a maximum at ca. 650 nm (15385 cm^{-1}) and a FWHM of ca. 200 nm (5000 cm^{-1}). Use of these values for ν_e and Γ , respectively, in equation 3.4 yields much more realistic values of surface temperature as a function of laser power.

Figure 3.1 shows a plot of surface temperature as a function of laser power calculated from the SERS Stokes and anti-Stokes

Figure 3.1 Calculated surface temperature of a roughened silver electrode versus laser power.

intensities of the 1010 cm^{-1} vibrational band of adsorbed pyridine. The surface temperatures calculated from these data and equation 3.4 range from $296.4\text{ }^{\circ}\text{K}$ for 50 mW of laser power to $312.5\text{ }^{\circ}\text{K}$ for 1 W of power.

Van Duyne has reported that the 1215 cm^{-1} band of adsorbed pyridine does follow the ν^4 intensity dependence expected for normal Raman scattering with 514.5 nm excitation (79). Thus, the surface temperature can also be calculated from the Stokes and anti-Stokes intensities of this band using equation 3.1. This band therefore provides a check for the temperatures calculated from equation 3.3 for the 1010 cm^{-1} band. Using the intensities for the 1215 cm^{-1} band, the surface temperatures calculated for 200 mW and 1 W of incident laser power are $303.6\text{ }^{\circ}\text{K}$ and $311.8\text{ }^{\circ}\text{K}$, respectively. These values are comparable to the values shown in Figure 3.1 for the 1010 cm^{-1} band. However, the larger intensities of the 1010 cm^{-1} band provide greater precision than the weaker 1215 cm^{-1} band. Recall that the change in temperature is actually more important than the actual temperature because the activation energies are determined from the change in $\ln(k)$ over a given change in surface temperature. Therefore, the surface temperatures used in this study were those determined using the Stokes and anti-Stokes intensities of the 1010 cm^{-1} pyridine band.

The question of equilibrium is important when applying the Boltzmann distribution function, as mentioned earlier. In order to

Table 3.1 Calculated surface temperatures at selected decay times and laser powers.

Laser Power (mW)	Surface Temperature (°K)	Time (min)
200	298.2	5
200	300.8	20
200	300.1	30
600	305.5	15
600	304.8	40
600	305.3	60
800	308.1	5
800	307.4	25
800	307.7	60

verify that the system is at thermal equilibrium, surface temperatures were calculated as a function of time during the experiment. The results for 200 mW, 600 mW and 800 mW are shown in Table 3.1. The calculated temperatures do not appear to change significantly during the decay period. Therefore, the system appears to be fairly close to thermal equilibrium and the application of equations 3.1 and 3.4 is valid.

While the accurate determination of surface temperature is important, the precision of these calculations is even more important for the determination of activation parameters. The ability to know the change in surface temperature determines, in part, the accuracy of the activation energy determination. The precision of surface temperature determinations is probably limited by the much lower intensities of the anti-Stokes bands relative to the Stokes bands. However, due to the surface enhancement at Ag, even the anti-Stokes intensities are extremely large. A sample set of Stokes and anti-Stokes bands for adsorbed pyridine are given in Figure 3.2. These are original spectra with no spectral smoothing. The ratio of anti-Stokes to Stokes intensity for the 1010 cm^{-1} band is on the order of 1.0% at ambient temperatures. These data demonstrate that precise surface temperatures are easily determined by this approach.

Figure 3.2 Stokes and anti-Stokes bands of adsorbed pyridine used to calculate surface temperature.

- a) Stokes bands at $T=300.7\text{ }^{\circ}\text{K}$ (200 mW)
 $S_1=1.1\times 10^5$ counts/sec
- b) Anti-Stokes bands at $T=300.7\text{ }^{\circ}\text{K}$ (200 mW)
 $S_2=8.5\times 10^2$ counts/sec
- c) Stokes bands at $T=305.6\text{ }^{\circ}\text{K}$ (600 mW)
 $S_3=2.0\times 10^5$ counts/sec
- d) Anti-Stokes bands at $T=305.6\text{ }^{\circ}\text{K}$ (600 mW)
 $S_4=1.8\times 10^3$ counts/sec

CHAPTER 4

DETERMINATION OF KINETIC PARAMETERS ASSOCIATED WITH LASER-INDUCED SURFACE REACTIONS AT A SILVER ELECTRODE

This chapter is a summary and analysis of the laser-induced decay profiles of pyridine and chloride SERS at roughened Ag electrodes. The chapter further serves to demonstrate the valid application of the Arrhenius equation for determining activation parameters using the laser-induced heating method.

Decay Profiles

The experiments for obtaining decay profiles, and subsequently rate constants, involve acquiring spectra of the adsorbate every 5-10 minutes for a period of ca. 90 minutes. This decay is then analyzed for kinetic information. Figure 4.1 shows a series of SERS spectra of pyridine adsorbed at Ag at selected decay periods and at a series of representative surface temperatures. Figure 4.2 shows a similar series of spectra in the region between 175 and 275 cm^{-1} where the $\nu(\text{Ag-Cl})$ band is observed. All of these spectra were obtained at -0.60 V on a silver electrode which had been subjected to an ORC under laser illumination as described

Figure 4.1 SERS spectra of the 1010 cm^{-1} pyridine band at decay times up to 90 minutes and at surface temperatures of a) $300.7\text{ }^{\circ}\text{K}$ (200 mW), b) $305.6\text{ }^{\circ}\text{K}$ (600 mW) and c) $308.1\text{ }^{\circ}\text{K}$ (800 mW).

Figure 4.2 · SERS spectra of the 222 cm^{-1} $\nu(\text{Ag-Cl})$ band at decay times up to 90 minutes and at surface temperatures of a) $300.7\text{ }^{\circ}\text{K}$ (200 mW), b) $305.6\text{ }^{\circ}\text{K}$ (600 mW) and c) $308.1\text{ }^{\circ}\text{K}$ (800 mW).

previously. This potential was chosen for convenience as it provides large intensities for both chloride and pyridine.

Decay Profiles at -0.60 V After an Illuminated ORC

The work presented here made extensive use of the illuminated ORC pretreatment for various reasons. There have been relatively few studies on surfaces treated in this fashion despite the enormous enhancement (a factor of 3 -10 depending on the vibrational band and electrolyte) in observed intensities relative to the signals from a nonilluminated ORC. Previous work suggests that the greater intensities are the result of a greater concentration of surface active sites produced by photodecomposition of AgCl during the ORC. The illuminated ORC also provides a useful and convenient means for changing the surface in a systematic fashion which is desirable for mechanistic SERS investigations. The enhanced sensitivity is particularly useful for detecting the weak signals of adsorbed chloride. Without this added enhancement, there is much less precision in determining the laser-induced decay rates, and subsequently less precision in the activation parameters. Additional evidence for the importance of atomic scale roughness in SERS may be obtained from a study of surfaces prepared by an illuminated ORC.

At an electrode potential of -0.60 V, two types of laser-induced SERS decay profiles are observed from an illuminated ORC surface. These have been designated type A and type B. Examples of

both kinds of decay behavior at selected surface temperatures are shown in Figures 4.3 - 4.6. Both types indicate a first order surface reaction, as demonstrated by the linear behavior in the $\ln(I_t/I_i)$ versus time plots. Here, I_t and I_i represent the digitally integrated Raman intensities at time t and at time zero, respectively. Although the decay profiles cannot be fit to an n^{th} order equation for the entire profile, a significant portion of the decay can be fit to first order kinetics.

At -0.60 V, type A behavior is characterized by the absence of a "large" increase in intensity during the first 10-20 minutes of the experiment, and also by the magnitude of the rate constant. At an electrode potential of -0.60 V, the first order rate constants for type A decay range from ca. 0.012 min^{-1} at 300.7°K to ca. 0.025 min^{-1} at 308.1°K . For the $\nu(\text{Ag-Cl})$ band, the rate constants for type A decay range from ca. 0.019 min^{-1} at 303.8°K to ca. 0.025 min^{-1} at 308.1°K . A summary of the type A rate behavior at -0.60 V after an illuminated ORC is given in Table 4.1.

At -0.60 V, type B decay behavior is characterized by the presence of a "large" increase in intensity during the first 10-20 minutes of the experiment, and also by the magnitude of the rate constants which are significantly less than those for type A behavior. For the pyridine band, the rate constants range from ca. 0.0024 min^{-1} at 300.7°K to ca. 0.0055 min^{-1} at 308.1°K . The rate constants for type B behavior for the $\nu(\text{Ag-Cl})$ band range from ca.

Figure 4.3 Type A first-order decay profiles for the 1010 cm^{-1} pyridine band at -0.60 V after an illuminated ORC, and at surface temperatures of a) $300.7\text{ }^{\circ}\text{K}$ (200 mW), b) $305.6\text{ }^{\circ}\text{K}$ (600 mW) and c) $308.1\text{ }^{\circ}\text{K}$ (800 mW).

Figure 4.3 Type A first order decay profiles for the 1010 cm^{-1} pyridine band at -0.60 V after an illuminated ORC

Figure 4.4 Type A first-order decay profiles for the 222 cm^{-1} $\nu(\text{Ag-Cl})$ band at -0.60 V after an illuminated ORC, and at surface temperatures of a) $300.7\text{ }^{\circ}\text{K}$ (200 mW), b) $305.6\text{ }^{\circ}\text{K}$ (600 mW) and c) $308.1\text{ }^{\circ}\text{K}$ (800 mW).

Figure 4.4 Type A first order decay profiles for the 222 cm^{-1} $\nu(\text{Ag-Cl})$ band at -0.60 V after an illuminated ORC

Figure 4.5 Type B first-order decay profiles for the 1010 cm^{-1} pyridine band at -0.60 V after an illuminated ORC, and at surface temperatures of a) $300.7\text{ }^{\circ}\text{K}$ (200 mW), b) $305.6\text{ }^{\circ}\text{K}$ (600 mW) and c) $308.1\text{ }^{\circ}\text{K}$ (800 mW).

Figure 4.5 Type B first order decay profiles for the 1010 cm^{-1} pyridine band at -0.60 V after an illuminated ORC

Figure 4.6 Type B first-order decay profiles for the 222 cm^{-1} $\nu(\text{Ag-Cl})$ band at -0.60 V after an illuminated ORC, and at surface temperatures of a) $300.7\text{ }^{\circ}\text{K}$ (200 mW), b) $305.6\text{ }^{\circ}\text{K}$ (600 mW) and c) $308.1\text{ }^{\circ}\text{K}$ (800 mW).

Figure 4.6 Type B first order decay profiles for the $222 \text{ cm}^{-1} \nu(\text{Ag-Cl})$ band at -0.60 V after an illuminated ORC

0.0020 min^{-1} at $300.7 \text{ }^{\circ}\text{K}$ to 0.0060 min^{-1} at $312.5 \text{ }^{\circ}\text{K}$. These results are summarized in Table 4.1 along with the type A results.

It appears that both type A and type B profiles may be accessible on the same electrode surface. Sample preparation is exactly the same prior to the observation of type A or type B decay behavior. The statistical observations concerning these two behaviors are the following. For 30 experiments, about 30% gave type A profiles for both pyridine and chloride, 10% gave type A profiles for chloride and type B for pyridine, and the remaining 60% gave type B profiles for both species. Type A behavior for pyridine is never observed along with type B for chloride. The three different events described above are distributed fairly evenly during several days of experiments. It would not be uncommon to see the two high percentage behaviors on the same day of experimentation. This suggests that observations are a result of the complex nature of the surface, rather than some systematic experimental error.

The specific criteria for determining type A and type B profiles at -0.60 V after an illuminated ORC are outlined here. Type A profiles are characterized by (1) no significant increase in the SERS intensity during the experiment, and (2) $k(\text{pyr})$ and $k(\text{Ag-Cl})$ which are greater than 0.010 min^{-1} at the temperatures studied (above $300 \text{ }^{\circ}\text{K}$). Type B profiles are characterized by (1) a significant increase in the SERS intensity during the experiment,

Table 4.1 Summary of rate constants at -0.60 V after an illuminated ORC.

<u>Type A</u>				
Surface Temperature (°K)	$\bar{k}(\text{Ag-Cl})$ (min ⁻¹)	σ_{n-1}	$\bar{k}(\text{pyr})$ (min ⁻¹)	σ_{n-1}
298.2	0.0114	---	---	---
300.7	---	---	0.0117	0.0012
301.0	---	---	0.0150	---
303.8	0.0190	0.0021	0.0197	0.0051
305.6	0.0172	0.0012	0.0187	---
306.5	0.0190	0.0050	0.0213	0.0050
308.1	0.0260	0.0085	0.0222	0.0007

<u>Type B</u>				
Surface Temperature (°K)	$\bar{k}(\text{Ag-Cl})$ (min ⁻¹)	σ_{n-1}	$\bar{k}(\text{pyr})$ (min ⁻¹)	σ_{n-1}
296.6	---	---	0.000763	0.000024
298.2	0.00157	---	0.00107	---
300.7	0.00200	0.00036	0.00208	0.00074
303.8	0.00255	0.00047	0.00203	0.00053
305.6	0.00476	0.00043	0.00364	0.00119
308.1	0.00549	0.00150	0.00515	0.00078

and (2) $k(\text{pyr})$ and $k(\text{Ag-Cl})$ which are less than 0.010 min^{-1} at the temperatures studied. While these criteria appear arbitrary, they have in fact been dictated by experimental results which indicate that two, statistically different, distributions of decay rates are observed at any given surface temperature. This is clearly shown by the decay rates tabulated in Table 4.1.

Another parameter for characterizing type A and type B kinetics is the $k(\text{Ag-Cl})/k(\text{pyr})$ ratio. The bar graph in Figure 4.7 shows the distribution of $k(\text{Ag-Cl})/k(\text{pyr})$ ratios for type B profiles at -0.60 V after an illuminated ORC. About 83% of these ratios are less than 2.0 and 62% are less than 1.5. One of the criteria for type B kinetics was that $k(\text{Ag-Cl})/k(\text{pyr}) \leq 2.0$. This is a reasonable value as the bar graph illustrates. A ratio above 2.0 is observed infrequently and is not reproducible. For type A profiles, and less often type B profiles, the chloride occasionally appears to act independently of the pyridine (i.e. $k(\text{Ag-Cl})/k(\text{pyr}) > 1.0$ as shown in Table 4.2). Consequently, no restriction on the rate ratios can be made for type A profiles at this time. It is not clear why chloride can act independently of the pyridine, nor is it clear why these rates are occasionally higher than the pyridine rates. It is known that chloride adsorption is stabilized by surface-bound pyridine, and if the chloride is blocked from interacting with the pyridine, for example by impurities or SERS-inactive clusters, then the chloride may become destabilized.

Figure 4.7 Bar graph of number of experiments versus $k(\text{Ag-Cl})/k(\text{pyr})$ for type B profiles after an illuminated ORC.

Table 4.2 Examples of $\nu(\text{Ag-Cl})$ SERS deactivation which occur at rates independent of pyridine SERS deactivation rates. These examples are indicated by an asterisk (*); other results are more typical and are shown for comparison. Decay rates were obtained at -0.60 V after an illuminated ORC.

<u>Type A</u>			
$k(\text{Ag-Cl})$ (min^{-1})	$k(\text{pyr})$ (min^{-1})	$k(\text{Ag-Cl})/k(\text{pyr})$	Surface Temperature ($^{\circ}\text{K}$)
0.020	0.022	0.93	308.1
0.032	0.023	1.40 *	308.1
0.021	0.024	0.88	303.8
0.043	0.021	2.05 *	303.8

<u>Type B</u>			
$k(\text{Ag-Cl})$ (min^{-1})	$k(\text{pyr})$ (min^{-1})	$k(\text{Ag-Cl})/k(\text{pyr})$	Surface Temperature ($^{\circ}\text{K}$)
0.0023	0.0026	0.87	300.7
0.0062	0.0025	2.48 *	300.7

For type A decay behavior, $k(\text{Ag-Cl})/k(\text{pyr}) = 0.8 - 2.0$ occurs 55% of the time while $k(\text{Ag-Cl})/k(\text{pyr}) > 2.0$ occurs 45% of the time. In general, there are no rate constants between 0.007 and 0.010 min^{-1} for either type A and type B profiles at the powers studied. Also, about 90% of the type A profiles have a rate constant greater than 0.015 min^{-1} . Therefore, these rate constants are statistically different than those less than 0.007 min^{-1} at the same surface temperatures. This observation is shown graphically by the error bars on the corresponding Arrhenius plot discussed later.

These criteria and statistical observations are important, because they allow one to determine if two types of sites are truly being studied or if there is some problem with impurities, inability to make the "same" surface, or simply operator error. The statistics suggest that assignment of the data in terms of discrete decay profiles is valid.

The observation of two discrete types of decay behavior is somewhat surprising. The absence of intermediate decay rates suggests that discrete adsorption sites are involved. These discrete sites may even coexist at the sampled portion of the surface. Since the absolute Raman intensity from a type B profile is larger than that of a type A profile, the intensity from type B "sites" may swamp the signal from type A "sites". Preliminary results suggest that the SERS intensity from a type B profile is about twice that from a type A profile.

Decay Profiles at -0.60 V After a Nonilluminated ORC

SERS investigations more commonly employ a nonilluminated, or "dark" ORC. The lower intensities from the nonilluminated ORC surface are a source of greater error in the rate constant determinations. Representative decay profiles after a nonilluminated ORC are shown in Figure 4.8. It is clear from these plots that the precision in determining peak areas is much less for the nonilluminated ORC surface.

It is of interest to compare the kinetic behavior at surfaces roughened by these two procedures. These results should provide some insight into the effect of illumination during the ORC and also about the active sites that SERS investigators more commonly study at a nonilluminated ORC surface. At -0.60 V it is found that the nonilluminated ORC only provides the type B decay behavior. Type A behavior is not observed. There is generally a large increase in both the $\nu(\text{Ag-Cl})$ and pyridine SERS during the first 30-60 minutes. After an illuminated ORC, only 10-20 minutes are required for the SERS intensities to maximize. These shorter times may be related to the formation of a greater number of more stable complexes formed during the illuminated ORC. The increased number of sites is consistent with the greater number of smaller particles formed during the illuminated ORC (114). The nonilluminated ORC may produce larger particles which undergo dispersion to form SERS-active sites. If so, once the large

Figure 4.8 First order decay profiles of pyridine after a nonmilluminated ORC and at surface temperatures of a) 300.7 °K, b) 303.8 °K, and c) 305.6 °K.

Figure 4.8 First order decay profiles of pyridine after a nonilluminated ORC at selected surface temperatures.

particles are dispersed, the "new" active sites give rise to slower decay rates than the sites formed by an illuminated ORC.

A summary of the rate constants and associated standard deviations for pyridine and chloride SERS decay is shown in Table 4.3. Apparently, the longer "rise" time at the nonilluminated ORC surface provides more stable surface complexes. The origin of this increased stability is not clear. While this is preliminary data, it suggests that the laser-induced method can be used successfully to evaluate the kinetics at these surfaces.

Decay Profiles at -0.80 V After an Illuminated ORC

One of the primary goals of this work is to demonstrate the utility of the laser-induced heating method for determining decay rates, and ultimately activation parameters. The effect of electrode potential on decay rates is discussed here to demonstrate the validity as well as the advantages and limitations of the technique. A practical limitation for the evaluation of kinetic parameters is the ability to detect the Raman scattering from the adsorbate. Since the SERS intensities are a function of electrode potential, this behavior was considered before the effect of electrode potential on decay rate was studied. The potential dependence of the SERS intensity and peak frequency of pyridine and chloride is given in Figure 4.9. The SERS intensities of both species are only useful for kinetic studies in the potential region between -0.20 V and -0.90 V. Chloride SERS is nearly undetectable

Table 4.3 Summary of rate constants at -0.60 V after a nonilluminated ORC.

<u>Type A</u>				
none				
<u>Type B</u>				
Surface Temperature (°K)	$\bar{k}(\text{Ag-Cl})$ (min ⁻¹)	σ_{n-1}	$\bar{k}(\text{pyr})$ (min ⁻¹)	σ_{n-1}
296.6	---	---	0.000266	---
300.7	---	---	0.000651	---
303.8	0.0010	---	0.00104	---
305.6	0.0017	0.0001	0.00121	0.00002
308.1	0.0020	---	0.00164	---

Figure 4.9 a) Pyridine SERS intensity and peak frequency
versus electrode potential

b) $\nu(\text{Ag-Cl})$ SERS intensity and peak frequency
versus electrode potential

beyond -0.90 V, and there may be oxidation of Ag to AgCl at potentials more positive than -0.20 V (141). The intensity-potential behavior may be related to a number of factors, including: (1) adsorbate coverage, (2) particle sizes at the surface, (3) dielectric constant of the medium, (4) electrode potential, and (5) nature of adsorbate (i.e. the "accessibility" of electronic levels by incident radiation). When pyridine and chloride become coadsorbed at a Ag surface, it appears that there is "extensive electronic communication" which has the effect of increasing the SERS intensities of both adsorbates (142). The "electronic communication" may have the effect of altering the electronic levels of the adsorbate so they are "tuned" into resonance. Additionally, a change in adsorbate coverage may also occur as a result of this electronic communication. This is supported by the observation that, in the absence of pyridine, the $\nu(\text{Ag-Cl})$ intensity decays smoothly with potential and does not exhibit a peak at -0.60 V. At electrode potentials more negative than -0.60 V, the Fermi level is moved out of resonance resulting in the decrease of pyridine and chloride SERS. The individual surface coverage of chloride and pyridine is difficult to evaluate since these species are coadsorbed. The expected surface coverage of pyridine as a function of potential (143), in the absence of chloride, is shown graphically in Figure 4.10a. The surface coverage of chloride in the absence of pyridine has been determined by Hupp (8) and the results are shown

Figure 4.10 a) Surface coverage of neutral organic adsorbates versus electrode potential referenced to the potential of zero charge.

b) Surface concentration of specifically adsorbed chloride at electropolished (solid curves) and roughened silver (dashed curves) versus electrode potential for bulk chloride concentrations of 0.015 M and 0.10 M (8).
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in Figure 4.10b. It is not clear how these isotherms are altered as a result of coadsorption. However, when adsorbed separately, the chloride is most strongly adsorbed at more positive potentials, and pyridine is most strongly adsorbed at potentials just positive of the pzc = -0.80 V (where the neutral pyridine can effectively compete with water molecules for adsorption sites). It is expected that when these species are coadsorbed, the electronic communication will, to some extent, alter the adsorption behavior.

Ultimately, one would like to compare the activation energies obtained at different potentials to determine the extent of the method's application. According to Fleischmann and coworkers (144), pyridine exhibits specific reorientations at -0.30 V and -0.45 V versus SCE. However, this conclusion has not been confirmed by other workers. The effect of potential on kinetic parameters may be interpreted more accurately in a potential region where the pyridine orientation does not change significantly. This is because activation energies can depend on molecular orientation. Therefore, potentials positive of -0.50 V were not studied. An electrode potential of -0.80 V was chosen for study, because it is reasonably far from -0.60 V while still providing good intensities for kinetic analysis. Also, the pyridine orientation is not expected to change significantly. This should allow a more accurate interpretation of the effect of potential on kinetic parameters.

A summary of the decay behavior at -0.80 V is given here. Both type A and type B profiles are observed at -0.80 V when the surface is roughened with an illuminated ORC. This behavior is analogous to the behavior at -0.60 V; however, at -0.80 V a decay rate of ca. 10^{-5} min^{-1} is often (75% of the time) observed from a type A profile (i.e. no large increase in intensity). Recall that a decay rate magnitude of ca. 10^{-5} min^{-1} at -0.60 V is associated with a type B profile. Therefore, the morphology of the decay profile is not always a good criterion for separating the types of sites studied. At -0.80 V, a better criterion for separating types A and B is the magnitude of the rate constant. Type A profiles are observed 90% of the time compared to 50% of the time at -0.60 V. However, type A magnitudes (10^{-4} min^{-1}) of the decay rates are only observed 25% of the time. Type B profiles may be rare as a result of some rearrangement that occurs on a much faster time scale (i.e. less than 5 minutes). Therefore, the large increase in SERS intensity is not observed at -0.80 V for type B magnitudes of the decay rate. In any case, two types of sites appear to exist at -0.80 V as well as -0.60 V. Examples of type B profiles obtained at -0.80 V are shown in Figure 4.11 and the rate behavior at selected temperatures are summarized in Table 4.4.

Peak Frequency Analysis of Decay Profiles

Peak frequencies are often sensitive to the extent of adsorbate-metal interaction, adsorbate orientation at the surface,

Figure 4.11 Type B decay behavior of a) 1010 cm⁻¹ pyridine band and $\nu(\text{Ag-Cl})$ at -0.80 V after an illuminated ORC

Table 4.4 Summary of Type B rate constants at -0.80 V
after an illuminated ORC.

Surface Temperature (°K)	$\bar{k}(\text{Ag-Cl})$ (min^{-1})	σ_{n-1}	$\bar{k}(\text{pyr})$ (min^{-1})	σ_{n-1}
300.7	0.00401	0.00040	0.00412	0.00017
303.8	0.00522	0.00031	0.00488	0.00011
305.6	0.00960	0.00269	0.00188	0.00035
308.1	0.00834	0.00041	0.00924	0.00074

and intermolecular interactions. Figure 4.12 shows plots of peak frequency for the pyridine and $\nu(\text{Ag-Cl})$ bands as a function of time during the intensity decay. These plots are superimposed on the corresponding first order decay profiles. Figure 4.12a shows that during the initial stages of the type A decay profile for pyridine, the peak frequency increases. This mode increases a total of ca. 4 cm^{-1} after two hours of laser illumination at all of the surface temperatures studied. For type B decay profiles the increase is usually somewhat less, and is near 3 cm^{-1} . However, the majority of the frequency increase, in both cases, occurs before first order kinetics are followed. During the first order decay, the peak frequency remains relatively constant.

Figure 4.12b shows the peak frequency of the $\nu(\text{Ag-Cl})$ vibration as a function of time. The peak frequency increase of this band is greater than that of the pyridine band, increasing from 221 cm^{-1} to between 230 and 237 cm^{-1} depending on the surface temperature. The higher peak frequencies for this band are only reached at the higher surface temperatures for a two hour analysis. Although these data reflect only the peak frequency, closer inspection of the spectra in Figure 4.2 reveals a highly asymmetric envelope that has previously been fit with two $\nu(\text{Ag-Cl})$ bands (142,145). In fact, as the spectra in Figure 4.2 show, the 221 cm^{-1} band disappears leaving the 237 cm^{-1} band to predominate as the decay proceeds.

Figure 4.12 First order decay profile from an illuminated ORC superimposed on the plot of peak frequency versus time for a) adsorbed pyridine at $T = 300.7\text{ }^{\circ}\text{K}$ and b) adsorbed chloride at $T = 306.5\text{ }^{\circ}\text{K}$.

Figure 4.12 First order decay profiles superimposed on plots of peak frequency versus time

These two bands have been interpreted as two different types of active sites (142). The site contributing to the 237 cm^{-1} $\nu(\text{Ag-Cl})$ band clearly provides a stronger Ag-Cl bond, because this site is less susceptible to thermally-induced destruction. Thus, these results are analogous to the negative potential quenching experiments of Furtak who found that the band at 208 cm^{-1} disappeared upon application of negative potentials, but the band at 240 cm^{-1} remained of measurable intensity (142).

The peak frequency increase for both adsorbates during the intensity decay suggests that the stability of the active sites may be intimately related to the strength of the adsorbate-active site bond. The increase in peak frequency of the totally symmetric ring breathing mode of pyridine is more complex than for the $\nu(\text{Ag-Cl})$ and probably has contributions related to Ag-pyridine bond strength. It has been suggested that the peak frequency for the ring breathing vibration may also be related to the orientation of pyridine (144). For example, the higher peak frequencies at more positive potentials are probably related to a flat π -bonded configuration which increases the vibrational frequency, perhaps as a result of increasing the electron density in the π -ring. At more negative potentials, it is thought that the pyridine molecule "stands up" and becomes less π -bonded which would have the effect of decreasing the vibrational frequency. Thus, the observed increase in peak frequency may be related to both a change in pyridine orientation

and an increase in the Ag-N interaction. Interpretation of the $\nu(\text{Ag-Cl})$ increase is less ambiguous, and is most likely related to the predominance of more strongly adsorbed chloride. It is concluded, therefore, that the more strongly bound chloride is also the most stable, since it predominates over the low frequency species during the first order decay profiles.

The peak frequency increases in a similar fashion for pyridine and chloride which are adsorbed at -0.80 V after an illuminated ORC. During the initial increase in intensity, both the pyridine and $\nu(\text{Ag-Cl})$ peak frequency increases 2 - 3 cm^{-1} . The larger increase of ca. 3 cm^{-1} is observed for type A profiles, which is similar to the result at -0.60 V. These results suggest that similar SERS-active sites are studied at -0.60 V and -0.80 V.

At a nonilluminated ORC surface the pyridine and $\nu(\text{Ag-Cl})$ peak frequency only increases 0.5 - 1.0 cm^{-1} during the initial increase in SERS intensity. This observation is consistent with the formation of more stable sites during the nonilluminated ORC. The slower decay rates after a nonilluminated ORC also support the idea that more stable sites are produced from a nonilluminated ORC.

FWHM Analysis of Decay Profiles

The full-width-at-half-maximum (FWHM) of the 1010 cm^{-1} pyridine band was studied during the decay process to provide some insight about the heterogeneity of surface sites. During the first 10-20 minutes of the type A behavior, the FWHM increases about 1.0

cm^{-1} and remains constant during the first order kinetics. For type B behavior, the 1.0 cm^{-1} increase in FWHM required about 30 minutes but also remained constant during the first order decay. These observations are consistent with the increase in peak frequency during the initial portion of the decay profile. The FWHM results support the conclusion that there is a change in the heterogeneity of surface sites during the initial period of both type A and type B decay profiles.

Determination of Activation Energies

In order to apply the Arrhenius expression for the determination of activation energies at these SERS-active surfaces, the system must be at thermal equilibrium and the decay of the SERS signals must be thermally-induced. The system was shown to be near thermal equilibrium in Table 3.1; however, the possibility of a photo-induced decay must also be considered.

The intensity decay is shown to be thermally-induced by control experiments where the surface is probed with 50 mW of laser light for 15-20 seconds every ten minutes while the surface is maintained at room temperature, $296 \text{ }^{\circ}\text{K}$. The resulting intensity versus time decay profile is first order and similar to all of the others observed with constant illumination (see Figure 4.13). An average rate constant of $0.000763 \text{ min}^{-1}$ is observed for this decay at $296 \text{ }^{\circ}\text{K}$ after an illuminated ORC pretreatment. A decay rate of $0.000169 \text{ min}^{-1}$ is obtained after a nonilluminated ORC. As shown

Figure 4.13 Typical decay profile at room temperature ($T = 23^\circ\text{C}$) after an illuminated ORC pretreatment. Spectra were obtained at 100 mW laser power once every ten minutes; spectral acquisition required 30 seconds.

later on, these values fit the Arrhenius plots associated with the type B kinetics. Therefore, the decay of SERS intensities appears to be strictly thermally-induced, rather than photo-induced.

The possibility of a photo-effect was further investigated by probing the nonilluminated surface at selected distances from the illuminated portion of the surface. If the decay is photo-induced, little or no decay should be observed beyond the illuminated spot. These experiments were performed for both the illuminated and nonilluminated ORC pretreatment. The more controlled experiment involves the nonilluminated ORC pretreatment since the effect of laser light during the ORC changes the nature of the original surface. These experiments involve illumination of the roughened Ag electrode for ca. 1.5 hours at 200 mW (300.7 °K) after which the laser beam is repositioned ca. 1 mm from the original spot and the intensity monitored for 20 minutes. For the nonilluminated ORC pretreatment, the intensity at the new spot is much greater than the original spot at time zero (see Figure 4.14). This supports the idea that a thermal effect may be present which extends beyond the laser beam and which causes the rearrangement of surface particles. These results support the possibility of a thermally-induced decay of SERS intensities which extends beyond the laser beam diameter. For the illuminated ORC, the intensity at the repositioned spot is always significantly less than the original intensity at time zero and no increase is observed as with the original spot (see Figure

Figure 4.14 First-order decay profile for a) pyridine SERS and b) $\nu(\text{Ag-Cl})$ SERS at a roughened silver electrode for 70 minutes. Electrode was then repositioned ca. 1 mm from the original spot and SERS decay was monitored. Note: ORC was performed in the absence of laser illumination.

Figure 4.15 First order decay profile for the 1010 cm^{-1} pyridine band at -0.60 V after an illuminated ORC. After 90 minutes the electrode was repositioned ca. 1 mm from the original illuminated area.

4.15). Since the nonilluminated portion of the surface did not undergo the same roughening procedure as the illuminated portion, any conclusions from these experiments must be made with a fair amount of speculation.

Activation Parameters at -0.60 V After an Illuminated ORC

It was found that both type A and type B kinetics at -0.60 V follow Arrhenius-type behavior over the temperature range studied (296 - 310 °K). This behavior is demonstrated by the corresponding pyridine and chloride Arrhenius plots in Figures 4.16 and 4.17, respectively. The activation energies associated with type A kinetics for pyridine and chloride are 12.8 ± 3.2 kcal/mole and 11.1 ± 2.4 kcal/mole, respectively. The activation energies associated with type B kinetics are significantly greater, and are found to be 27.7 ± 3.1 kcal/mole and 24.5 ± 3.8 kcal/mole for adsorbed pyridine and chloride, respectively. The similarity in energies for these two species is probably related to the fact that the pyridine and chloride are coadsorbed. The error associated these activation energies is simply the standard deviation evaluated from a linear least squares analysis outlined by Bevington (146). These calculations assume that the error in evaluating surface temperature is negligible compared to the error associated with the rate constant determination. This is a good assumption since the average relative standard deviation (rsd) is only 0.41% for the temperature

Figure 4.16 Arrhenius plots for adsorbed pyridine at -0.60 V after an illuminated ORC.

Figure 4.17 Arrhenius plots for adsorbed chloride at -0.60 V after an illuminated ORC.

determinations and is 27.4% for the type B rate constant determinations. The large error in rate constant determinations is probably related to the inability to produce the same roughened surface for each experiment. Recall that the error in producing the same surface area is at least 7% and may be as high as 15% (see chapter 2). Notice that the kinetics at room temperature ($T=296\text{ }^{\circ}\text{K}$) are plotted on the Arrhenius plot for pyridine in Figure 4.16. These data support the conclusion that the observed decay behavior is thermally-induced, as previously described.

Pre-exponential factors are evaluated from the y-intercept and provide information about the activation pathway. The frequency factor for type B kinetics is ca. 10^{14} s^{-1} , and is about 10^5 s^{-1} for type A kinetics. The error in these frequency factors is $\pm 10^2\text{ s}^{-1}$ for both type A and type B kinetics. The physical meaning of these values for the frequency factors can only be evaluated in light of the decay mechanism discussed later.

Activation Parameters at -0.60 V After a Nonilluminated ORC

The preliminary results show that decay behavior at a nonilluminated ORC also follows Arrhenius behavior. The corresponding Arrhenius plot for type B pyridine kinetics is shown in Figure 4.18. Recall that type A kinetics are not observed after a nonilluminated ORC. Activation energies for type B pyridine kinetics were found to be $27.4 \pm 1.9\text{ kcal/mole}$, which is within the

Figure 4.18 Type B Arrhenius plot for adsorbed pyridine at -0.60 V after a nonilluminated ORC.

experimental error of the 27.7 ± 3.1 kcal/mole observed at the illuminated ORC. The chloride kinetics also appear to follow Arrhenius-type behavior. The pre-exponential factor from the pyridine Arrhenius plot is $10^{14} \pm 10^1$ s⁻¹, again, similar to the result from the illuminated ORC. These activation energies and pre-exponential factors suggest there is little or no difference in the chemical behavior of the active sites produced by these two roughening procedures. This supports the conclusion that the illuminated ORC produces a greater surface concentration of SERS-active sites, rather than sites with better enhancing properties.

Activation Parameters at -0.80 V After an Illuminated ORC

The effect of electrode potential on decay rate is studied here to demonstrate the validity as well as the advantages and limitations of the laser-induced heating technique. This electrode potential was chosen for reasons outlined earlier in this chapter. Since very few type A decay rates were observed at -0.80 V, only type B decay rates are evaluated here. While type A rates are observed at all powers, very few experiments were performed and sufficient data were not obtained for an Arrhenius plot. There is also a fair amount of scatter in this data.

An Arrhenius plot for type B pyridine and chloride kinetics is given in Figure 4.19. The type B activation energies at -0.80 V are 22.2 ± 4.6 and 19.8 ± 8.1 kcal/mole for adsorbed pyridine and

Figure 4.19 Type B Arrhenius plots for a) adsorbed pyridine and b) adsorbed chloride at -0.80 V after an illuminated ORC.

Table 4.5 Comparison of activation parameters for adsorbed pyridine at -0.60 V and -0.80 V following an illuminated ORC.

E = -0.60 V

$E_a = 27.7 \pm 3.1$ kcal/mole

$A = 10^{14} \pm 10^2$ sec⁻¹

$k = 10^{-5}$ min⁻¹

E = -0.80 V

$E_a = 22.2 \pm 4.6$ kcal/mole

$A = 10^{11} \pm 10^3$ sec⁻¹

$k = 10^{-5}$ min⁻¹

chloride, respectively. The frequency factors are ca. $10^{11} \pm 10^3$ s^{-1} and $10^{10} \pm 10^3$ s^{-1} , for pyridine and chloride, respectively. Given the nature of the experiments and the error associated with these activation parameters, these results are not significantly different from those at -0.60 V after an illuminated ORC. These activation parameters, and the associated errors, at -0.60 V and -0.80 V are compared in Table 5. While the data suggest that the activation energies are about 7 kcal/mole less at -0.80 V, such a conclusion must be tentative due to the large error associated with the calculation.

Decay Mechanism

In order to interpret the activation parameters evaluated here, the surface reaction involved in the decay of SERS signals must be understood. There are a number of possible surface reactions which might occur as a result of heating the electrode surface; the most likely of these reactions are migration, electron transfer, or desorption. Migration of the surface complex would involve the activation of Ag-Ag bonds allowing the complex to diffuse or migrate along the surface. Electron transfer would involve reduction of the silver cluster, assuming the site has an overall positive charge. This is a reasonable assumption based on the molecular orbital calculations of Baetzold (147). Desorption of pyridine and chloride would result in the destabilization of the

active site allowing it to diffuse along the surface and become irreversibly incorporated into the Ag lattice.

The rate constant as a function of electrode potential was studied to elucidate the decay mechanism. Figure 4.20 shows the plot of rate versus potential for pyridine and chloride at 300.7 °K for type B kinetics obtained from an illuminated ORC. A minimum in this plot was observed for both adsorbates at about -0.60 V. Only desorption can account for a minimum in this plot. For desorption as the decay mechanism, a minimum would be expected to occur where these adsorbates are most strongly adsorbed. In fact, pyridine is expected to be most strongly adsorbed near the potential of zero charge which is ca. -0.80 V (144). This is relatively close to -0.60 V where the minimum is observed. At more negative potentials than -0.60 V, the rate constant increases for both adsorbates. This increase is explained by the weaker adsorption of chloride at more negative potentials. At more positive potentials than -0.60 V, the decay rates increase significantly. This increase may be due to the fact that pyridine is less strongly adsorbed at more positive electrode potentials. The extensive electronic communication between pyridine and chloride (142) from -0.40 V to -0.60 V may be responsible for the somewhat anomalous decrease in the chloride decay rate from -0.45 V to -0.60 V.

Electron transfer and migration cannot account for the dependence of rate on electrode potential, as observed here. An

Figure 4.20 Rate constant versus electrode potential for (●) pyridine and (■) chloride adsorbed at a roughened Ag electrode. ($T = 300.7^\circ\text{K}$).

electron transfer reaction involving the reduction of Ag_w^+ (where w = number of Ag atoms in cluster participating in the active site) should have a rate constant which increases as more negative potentials are induced. Therefore, a minimum in the plot of rate versus potential is not predicted by electron transfer. If migration is the decay mechanism, then the activation energy describes the energy to activate a Ag-Ag bond. Therefore, migration of the surface complex should have a rate constant which decreases as more positive potentials are induced. This conclusion assumes that electrostatics control the stability of the surface complex. Thus, a minimum in the rate versus potential plot is not predicted by migration.

An additional experiment was performed to confirm that desorption is the decay mechanism. This experiment involved the comparison of the rate constant and peak frequency as a function of potential for chloride in the absence of pyridine. The surface was roughened by an illuminated ORC in the presence of 0.5 M KCl. The resulting plots are given in Figure 4.21. Notice the peak frequency increases up until -0.20 V; this is due to the fact that chloride becomes more strongly adsorbed as the potential is made more positive. At more positive potentials, the chloride coverage levels off (see Figure 4.10) and the peak frequency decreases as a result of significant anion-anion repulsion which may destabilize the surface complex. Notice that the rate constant is the slowest where

Figure 4.21 a) Rate constant versus electrode potential for adsorbed chloride in the absence of pyridine (Note: ORC was performed in 0.50 M KCl).

b) Peak frequency of $\nu(\text{Ag-Cl})$ versus electrode potential. (Note: ORC was performed in 0.50 M KCl).

the peak frequency is the largest. Since the peak frequency is directly related to the Ag-Cl force constant (or bond strength) through Hooke's law, the minimum in rate constant appears to be correlated with the maximum in bond strength. This is consistent with a surface reaction involving desorption. The experimental evidence presented here suggests the laser-induced decay of pyridine and chloride SERS is the result of thermal desorption.

Some information is available concerning the activation energy for the diffusion of metal adatoms on metal surfaces in a UHV environment (148,149); however, there is no information regarding diffusion of Ag adatoms in either the vacuum or electrochemical environments. Ehrlich and coworkers (148) have shown that the activation energy for migration of a single Re atom along the (111) channels of W(211) is 19.8 ± 0.7 kcal/mole at $T = 286-351$ °K. These authors comment on the unavailability of desorption energies. Attempts have been made to obtain the desorption energy from field desorption measurements (150,151); however, their interpretation depends on assumptions made about the mechanism of field desorption that remain to be validated. The results must also be corrected for the polarizability of the adatom, for which data are scarce (152). It should be noted, that while the activation energy for migration is probably small compared to that for desorption (148), it is difficult to estimate these energies for Ag complexes on polycrystalline Ag in an electrochemical environment.

The residence time of the adsorbates (over two hours) is not inconsistent with the relatively long residence time for desorption. Equation 4.1 has been used to estimate the residence time for a surface species in UHV (153).

$$\tau = \tau_0 \exp(E_a/RT) \quad (4.1)$$

where $\tau_0 = 1/A$. An E_a of 24 kcal/mole (and guessing that $\tau_0 = 10^{-14}$ s (154)) gives a residence time, τ , of 3×10^3 s (about an hour) at room temperature. This is similar to the first order decay period of one hour observed for a type A profile at 308.1 °K (Figure 4.3c). The decay period is not known for lower temperatures and slower decay rates; however, they are expected to be longer but of similar magnitude.

The magnitude of the rate constants (10^{-5} min^{-1}) observed here are also inconsistent with electron transfer. Electron transfer rates are, in general, much faster than the rates observed here. These rates are often on the order of 60 - 200,000 min^{-1} for surface-attached organic, or inorganic complexes (125); a rate of 6 - 6,000 min^{-1} (depending on the electrode potential) has also been reported for the electron transfer rate involving surface-attached silver cyanide complexes at a roughened silver surface (111). If the reaction mechanism strictly involves electron transfer, the rate constants are expected to be considerably greater than 10^{-5} min^{-1} , and closer to 10^{+5} min^{-1} (i.e. the electron transfer rate for

surface-attached organic or inorganic complexes). Admittedly, there is a scarcity of data concerning electron transfer rates for surface-attached reactants; however, the observed rate constants ($k=10^{-5} \text{ min}^{-1}$) are more consistent with desorption reactions (149).

While a conclusion is still somewhat speculative, the experimental evidence presented here suggests the laser-induced decay of pyridine and chloride SERS is the result of thermal desorption.

Reversibility

The decay process was found to be irreversible between the temperatures of 300.7 and 308.1 °K. The 1010 cm^{-1} pyridine band was monitored at -0.60 V after an illuminated ORC for 60 minutes at each of the laser powers. Following the decay period of 60 minutes at a given surface temperature, the electrode was placed in the dark for 15 minutes where it presumably was allowed to return to room temperature. Spectra acquired after this cooling period showed no change in the shape of the spectra, while the intensities were somewhat lower (see Figures 4.22 and 4.23). These results suggest that "simple" thermal desorption of these adsorbates is not responsible for the SERS decay upon illumination. As a result of chloride desorption, the active site is destabilized and can migrate along the surface, eventually becoming incorporated into the metal lattice. Readsorption of the desorbed species may occur at SERS-inactive sites, thereby avoiding detection. An irreversible decay

Figure 4.22 Irreversibility of a) pyridine and b) $\nu(\text{Ag-Cl})$ SERS after 60 minutes of 400 mW laser illumination at -0.60 V, plus 15 minutes in the dark.

Figure 4.23 Irreversibility of a) pyridine and b) $\nu(\text{Ag-Cl})$ SERS after 60 minutes of 800 mW laser illumination at -0.60 V, plus 15 minutes in the dark.

of the $\nu(\text{Ag-Cl})$ intensity was also reported by Macomber and Furtak (107) in quenching experiments in which the surface temperature was raised from 296 °K to about 365 °K.

Summary and Conclusions

The results presented in this chapter have demonstrated that it is possible to evaluate the chemical energetics of pyridine and chloride at these complex, roughened Ag surfaces in an electrochemical environment. The laser-induced heating method described in this thesis has been successfully employed for inducing a first order surface reaction, from which desorption activation energies can be determined. This technique is also significant in its good sensitivity for the detection of surface complexes, which is manifest by the detection of what appears to be two distinct surface sites.

It was found that desorption from these two SERS-active sites (type A and type B) can only be detected at -0.60 V and -0.80 V after an illuminated ORC roughening pretreatment. Only the type B SERS-active site is detected at -0.60 V after a nonilluminated ORC. The activation energies associated with type B desorption kinetics for pyridine are 27.7 ± 3.1 kcal/mole and 27.4 ± 1.9 kcal/mole for an illuminated and nonilluminated ORC surface, respectively. These results suggest that a greater concentration of the same active site is present at a surface roughened by an illuminated ORC. This result is consistent with the observation low-frequency bands at 110

and 160 cm^{-1} for both illuminated (113) and nonilluminated (155) ORC surfaces. These bands are due to the vibrational modes of Ag_4^+ pyramidal clusters (82), and if these are the proposed SERS-active sites, then it supports the conclusion that the enhanced signals are due to a greater concentration of these sites rather than a more optimum cluster size.

The activation energy associated with the type B kinetics for pyridine desorption at -0.80 V after an illuminated ORC is 22.2 kcal/mole . Given the large error associated with this value ($\pm 4.6\text{ kcal/mole}$), it is not significantly different from the activation energy of 27.7 kcal/mole at -0.60 V after an illuminated ORC. The large error is probably associated with the ability to produce the same roughened surface for each decay profile.

While activation energies provide a useful means for comparing the chemical behavior at different surfaces, the rate constants can provide additional insight. These rates may be particularly useful for SERS investigators studying desorption from type A or type B sites. The decay rates suggest that the sites responsible for type B kinetics are slightly more stable following a nonilluminated ORC compared to an illuminated ORC. While an illuminated ORC provides larger SERS intensities, the active sites exhibit less thermal stability. The increased stability at a nonilluminated ORC surface may be related to a lower concentration of surface sites.

Type B decay rates at -0.80 V are generally faster than rates at -0.60 V, after the same illuminated ORC roughening procedure (see Tables 4.4 and 4.3, respectively). The faster decay rates at -0.80 V are consistent with the destabilization of chloride at more negative potentials. The relatively small differences in the magnitudes of the decay rates at -0.60 V and -0.80 V may indicate that similar types of sites are present at these two potentials.

The morphology of the decay profiles also provides some insight about the laser-induced surface reaction. For example, the longer time for SERS intensities to maximize suggests that rearrangement of surface complexes is slower at a nonilluminated ORC surface. The absence of an increase in intensity during the profile at -0.80 V may be related to the poor stability of these complexes at such negative potentials. This would allow the complexes to rearrange on a much faster time scale, thus giving rise to a type B decay rate from a type A profile.

The increase in Ag-Cl vibrational frequency during the type A and type B profiles suggests that only the most strongly bound chloride species predominate during the first order decay process. It was concluded that the increase in the symmetric ring breathing vibrational frequency of pyridine may be due to a change in orientation or an increase in Ag-N interaction. The increase in peak frequency and FWHM during the initial period of the decay

profiles is probably indicative of the "rearrangement" of surface complexes, which may involve, for example, the dispersion of Ag clusters. After this initial period, the peak frequency and FWHM are relatively constant and a first order decay proceeds, suggesting that the distribution of surface complexes is no longer changing.

While the rate constants and activation energies suggest that the type B site stabilizes the surface complex to a greater extent than the type A site, it is not obvious what surface features are responsible for this selective stabilization. In order to determine the physical difference in the active sites giving rise to these two kinetic behaviors, the chemical process being activated must be understood. For example, it would be helpful to know which adsorbate is controlling the rate of desorption. Consider the observation that chloride decay rates can be significantly faster than the coadsorbed pyridine, where $k(\text{Ag-Cl})/k(\text{pyr}) = 1 - 3$. See Table 4.2. This result suggests that pyridine desorption can occur somewhat independent of chloride. Pyridine decay rates are never significantly faster than chloride as indicated by the minimum $k(\text{Ag-Cl})/k(\text{pyr})$ ratio of 0.8. In the latter case where the ratio is near 1.0, it might be assumed that pyridine desorption controls the rate of chloride desorption. Additional evidence for this is the rate versus potential behavior shown in Figure 4.22. The large increase in decay rate from -0.60 V to -0.45 V is explained by pyridine desorption controlling the decay rate of $\nu(\text{Ag-Cl})$ intensities. If

chloride controlled the rate versus potential behavior, the rates should decrease from -0.60 V to -0.45 V, based on electrostatic theory. These observations support the conclusion that, while the rates may be a convolution of effects (e.g. where $k(\text{Ag-Cl}) > k(\text{pyr})$), they are controlled by pyridine desorption at -0.60 V. At -0.80 V, where pyridine is expected to be most strongly adsorbed, it appears that chloride controls the rate of pyridine desorption to some extent. This conclusion is based on the increasing decay rates from -0.60 V to -0.80 V, consistent with the weaker adsorption of chloride at more negative electrode potentials. Further evidence is the fact that $k(\text{Ag-Cl})/k(\text{pyr}) < 1.0$ occurs about 78% of the time at -0.80 V and only 35% of the time at -0.60 V.

Based on the above arguments, the active site which gives rise to type B kinetics is envisioned to exist on a terrace plane where the accessibility to the Ag lattice is low. On the other hand, the type A site may exist at a surface defect (such as a step or kink site) where the accessibility to the Ag lattice is considerably higher. This concept is illustrated in Figure 4.24. The effect of a type A site on pyridine adsorption is not obvious because of the large number of possible orientation effects. At -0.60 V, the type A kinetics may be related to the greater Ag - π interaction afforded by the type A active site. This increased Ag - π interaction is analogous to the behavior of pyridine at more positive potentials where pyridine is less strongly adsorbed. The

Figure 4.24 SERS-active sites envisioned to give rise to type A and type B decay profiles.

result is that pyridine desorption should be more easily activated at a type A site.

At -0.80 V, chloride is less strongly bound and, based on the previous arguments, controls the rate of pyridine desorption. While there are orientation effects on pyridine between type A and type B sites, they are not expected to play as large a role on the rate of desorption as chloride effects. The chloride is also expected to be destabilized at a type A site as a result of the greater accessibility of electrons from the surface. This creates greater repulsion of the chloride, thereby destabilizing the anion. There is no a priori reason to believe chloride or pyridine will be preferentially destabilized between -0.60 V and -0.80 V. However, these conclusions about the physical nature of the active sites are based on the rate versus potential behavior and the known adsorption behavior of pyridine and chloride.

The calculated pre-exponential factors are consistent with the proposed physical models for type A and type B SERS-active sites. Recall, the pre-exponential factor can provide information about activation pathways. The conclusions proposed here are based on desorption as the decay mechanism. The low pre-exponential factors of 10^4 - 10^5 s⁻¹ for type A kinetics suggest that molecular motion besides vibrations may be involved in forming the activated complex. Rotational motion at a type A site would likely create a variety of Ag - π interactions, some which may form a more optimum

conformation for desorption compared to any conformation at a type B site. This would explain the lower activation energies at a type A site. The pre-exponential value of $\approx 10^{14} \text{ s}^{-1}$ for type B kinetics suggests that only vibrational motion is important in forming the activated complex. Rotational motion of pyridine at a type B site should not change the extent of Ag-N interaction, assuming pyridine is mostly N-bound (which is probably true between -0.60 V and -0.80 V). This may explain the larger activation energies at a type B site.

Future Work

The material presented in this thesis has established much of the groundwork for the exploitation of a technique for studying SERS-active metal surfaces in the electrochemical environment. There are a number of areas that would benefit from further study and these are outlined here.

It would be useful to study a variety of adsorbates to determine the applicability of the technique and perhaps better characterize the chemical nature of the active site. For example, it may be insightful to evaluate the activation parameters for organics which are more strongly adsorbed than pyridine, such as dihydroxypyridazine (156). A study of simple chemical systems, where no coadsorption is present, would allow more direct data interpretation. Such systems might involve nonspecifically adsorbed anions. The behavior of simple inorganic adsorbates such as SCN^-

and CN^- should provide additional detailed information about the chemical nature of the SERS-active sites.

A more comprehensive investigation of the decay rates as a function of electrode potential should further demonstrate the utility of this technique, and should also provide some insight into the mechanistic details concerning the decay at type A and type B sites. The latter may be accomplished from careful rate versus potential studies between -0.60 V and -0.80 V . In this thesis, the kinetics were only studied over a limited potential region (-0.45 V to -0.80 V). It may be useful to study the potential region near -0.20 V where chloride is known to be most strongly adsorbed and the pyridine is weakly adsorbed. The change in decay rate from -0.45 V to -0.10 V should provide some indication of what process is being activated, and should also provide some insight into the feasibility of obtaining Arrhenius plots in this potential region.

Methods for improving the reproducibility may help determine subtle differences (if there are any) in the activation energies at an illuminated ORC surface versus a nonilluminated ORC surface. Greater precision would also help distinguish the effects at different electrode potentials. As alluded to earlier, the poor precision in the activation energy determinations (ca. $\pm 5 \text{ kcal/mole}$) is probably related to the inability to produce the same roughened surface. This may be improved by using a potential step ORC procedure as shown by recent work in our laboratory (129,130).

Two experiments are proposed here which should determine what properties of the Ag surface are responsible for the observation of two kinds of decay profiles from an illuminated ORC surface. It is proposed that type A and type B profiles are the result of nucleation at different crystal faces. It is known that the energetics for adsorption are quite different at the three different faces as indicated by the different potentials of zero charge for these surfaces. It would be interesting to determine if an illuminated ORC at one single crystal surface will give rise to one type of decay profile.

Also, it may be that both types of profiles are accessible on the same electrode surface. Insight to this question may be obtained from an illuminated ORC which involves illumination of the entire electrode surface during the ORC. A more focussed laser may then be used to probe different portions of the electrode surface. Based on the random nature of the type A and type B profiles reported in this thesis, it is predicted that both kinds of profiles are accessible at a given electrode surface.

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