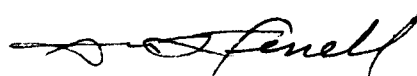


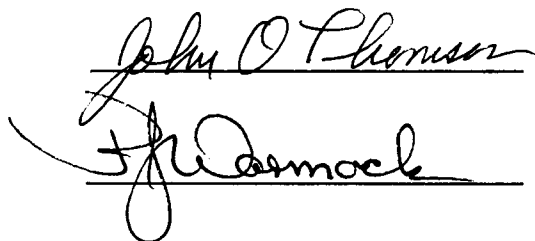
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SURFACE-ENHANCED RAMAN SPECTRA
OF SELECTED COMPOUNDS
IN THE PRESENCE OF OTHER COMPOUNDS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Makoto Namioka

August 1991

DEDICATION

Here, I would like to dedicate this thesis to my parents Takeshi and Sachiko Namioka who always love me dearly and give me a generous support.

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ABSTRACT

Pyridine is a well characterized standard for studying surface-enhanced Raman scattering (SERS), and its adsorption from solution onto silver metal has been thoroughly investigated. However, pyridine evaporates very quickly in air from the surface of silver metal at room temperature, so vapor-phase experiments have had to be performed at cryogenic temperatures. This thesis describes studies of the effects of materials which may assist adsorption of molecules such as pyridine on a silver metal surface at room temperature. Additionally, the reported work assesses the effects of contaminants on the SERS signal. Gold, carbon, and carbon monoxide were tested in order to determine if they assist adsorption on silver, or simply act as contaminants. Experiments were conducted in steady state vapor studies, surface deterioration, and open-system desorption using standard silver substrates and gold-coated silver substrates. An additional set of experiments was performed for toluene using similar silver substrates and gold-coated silver substrates.

The results of steady state vapor studies for pyridine show that there is no strong effect of laser power on adsorption/desorption at 70 mW for both the silver substrate and gold-coated silver substrate. It also appears that gold may tend to adsorb pyridine molecules slightly more strongly than does silver. The

results for toluene show irregular changes because of the relatively weak intensity of the signal. In some cases we observed substrate deterioration with time. There is a similarity of the deterioration curve (normalized SERS intensity) between the silver substrates and gold-coated substrates for both pyridine and toluene. The results of open-system desorption were expected to show the difference between the effects at ambient temperature and at 50° C. Contrary to expectation, no significant difference of this type was seen. The results for toluene were inconclusive because of high-noise levels and a weak SERS signal intensity. The results of carbon monoxide gas mixed with pyridine vapor showed a slightly faster drop of signal intensity than the results for pyridine vapor alone. However, both are fairly similar. The results for carbon-coated silver substrates mostly showed high background in the spectra. It was hard to see clearly any adsorbing effect because of the presence of a high noise background. The results do show that 6-nm carbon data is the most stable in terms of signal strength over a period of time.

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CHAPTER I

INTRODUCTION

In 1928, Raman scattering was discovered by C. V. Raman [1.1], [1.2], when he observed that a small fraction of light scattered by a liquid has an altered color. For his detailed observations, he was awarded the Nobel prize in 1930. Interestingly, the effect had been theoretically predicted by A. Smekal in 1923 [1.3]. It is an amazing fact that Raman discovered this extremely weak effect by using very simple equipment such as sunlight as a light source, a telescope to converge the sunlight, simple blue-violet and yellow-green filters, and his eyes as a detector. Raman spectra show that the colors vary with the chemical nature of the medium through which the light is passed. By using this characteristic it is possible to chemically identify unknown samples. It is also possible to observe Raman scattering from the surface of solids, as well as with light traversing liquids or gases.

The instruments and light sources have been significantly improved since Raman's discovery. Laser light sources and the use of photomultiplier tubes as detectors have had an enormous impact. It is very important to have an intense monochromatic light source for observing Raman spectroscopy. In 1952, Welsh

et al. introduced a low-pressure mercury discharge lamp (the Toronto arc mercury lamp) which emitted an intense blue line at 435.8 nm [1.4]; however, it restricted investigations because of several disadvantages as a light source for Raman scattering [1.5]:

1. The blue line at 435.8 nm cannot be used for some samples because it is absorbed by them;
2. This lamp emits other lines such as the line at 404.7 nm, necessitating the use of filters to eliminate them;
3. It is necessary to have a very large amount of pure or nearly pure material to get sufficiently strong spectra due to the weakness of the source;
4. With an arc source, it is very difficult to properly illuminate solids, and a weak spectral intensity is obtained.

In 1962 Porto and Wood [1.6] introduced the laser in this field. Their revolutionary light source, the pulsed ruby laser, provided highly monochromatic and intense lines, and revived broad interest in Raman spectroscopy. The following are the advantages of lasers for Raman spectroscopy:

1. They provide highly monochromatic and intense radiation;
2. It is easy to control the intensity and polarization;
3. The coherent beam can be easily focused to a small spot on a sample.

As already mentioned, Raman spectroscopy can be efficiently obtained from solids, liquids, gases, and solutions. Even with modern equipment, Raman spectroscopy, however, has disadvantages when dealing with thin layers or a monolayer of compounds on surfaces, since it generally takes a relatively large amount of material to provide a sufficient number of molecules for an adequate signal.

The discovery of surface-enhanced Raman scattering (SERS) was made by Fleischmann, Hendra, and McQuillan in 1974 [1.7], and later identified as a true surface-enhancement effect by Jeanmaire and Van Duyne [1.8]. Surface-enhancement of the signal makes it possible to study molecules and ions adsorbed on metal surfaces at submonolayer coverage, to observe adsorption processes, and to monitor reactions at solution-solid interfaces. Fleischmann, *et al.* observed the first SERS from pyridine adsorbed on a silver electrode which had been roughened by an oxidation-reduction cycle (ORC). Their conclusion was that the strong enhancement could be attributed to an increase in surface area of the solid metal electrode due to roughness. In 1977, two research groups, Jeanmaire and Van Duyne [1.8], and Albrecht and Creighton [1.9] independently reported that the SERS intensity could not be attributed to increased surface area of the roughened electrode alone, and that the recorded SERS cross section is approximately 10^5 to 10^6 times larger than that of a molecule in solution. A number of theories have subsequently been proposed

to explain this strong enhancement. These are discussed in greater detail in a later chapter.

Since the early work by Fleischmann and Van Duyne, various metals have been tested as SERS substrates, and it has been found that strong SERS occurs on rough noble metals (Ag, Au, and Cu) and alkali metals (Li, Na, and K) [1.8]-[1.15]. Indium also shows a strong SERS signal enhancement under certain conditions [1.16]. In addition to roughened electrodes, a number of other structures, such as metal island films [1.17], [1.18] and metal sols [1.19], [1.20] have been shown to be good SERS substrates. Of all materials, silver has been studied most extensively, and it provides the largest enhancement in the visible region of the spectrum.

It is difficult to adsorb many compounds on the surface of silver substrates at room temperature. The SERS signal from the most commonly studied compound, pyridine, was observed many times in the early history of SERS. However, these experiments were all done in a liquid environment or in ultra-high vacuum at low temperature (around 77K). At room temperature in the open air, the pyridine rapidly evaporates from silver. In this research, the main interest is in determining the effects of the presence of other materials on the SERS signal from a given compound. These materials may either assist adsorption of molecules on a rough silver surface at ambient temperature or simply act as contaminants. Substrates coated with gold, carbon, and carbon

monoxide (CO gas) were tested. SERS of carbon [1.21], [1.22] and carbon monoxide [1.23] have been previously reported. But compounds present on the substrate provide more complicated possibilities. In addition, experiments were conducted for this work using solid gold substrates instead of silver substrates. None of the tested surfaces showed more than a slight effect on the adsorption of pyridine. Additional research on steady state vapor, elevated temperature desorption, and surface deterioration was performed using silver and gold-coated silver substrates. As in the earlier study, there was no strong effect seen in most of the results. Slight differences were seen in the elevated temperature desorption, but normalized desorption curves showed similarities. Toluene was also tested for steady state vapor studies, elevated temperature desorption, and surface deterioration. Unfortunately, extremely high levels of noise are seen in the data because of the weak intensity of the toluene SERS signal, making quantitative conclusions impossible.

CHAPTER II

THEORY

A. INTRODUCTION

Since the discovery of SERS, several theories of the surface enhancement have been reported [2.1], [2.2]. However, the complete theoretical mechanism of SERS is still in doubt because several factors appear to work together in producing the maximum enhancement. Raman scattering results from an electric field-induced dipole moment $\vec{p}$:

$$\vec{p} = \alpha \cdot \vec{E}, \quad (1)$$

where α is a molecular polarizability, and $\vec{E}$ is the applied electromagnetic field experienced by the molecule. The intensity of the Raman signal is proportional to the square of $\vec{p}$. From this equation, it is logically correct to say that this significantly strong enhancement is from either or both the molecular polarizability and the electromagnetic field. The submitted theories are basically classified into two categories: the physical mechanism and the chemical mechanism. The physical mechanism is involved in both α and $\vec{E}$, while the chemical mechanism is only involved in α .

The following factors have been found to affect the SERS signal strength:

1. Laser flux on the sample. Nonlinear effects, such as stimulated Raman scattering, may occur with very high fluxes. At a given incident laser power, it is important to know exactly how much power reaches the sample for a given size and shape of the focal spot.
2. Polarization of the incident light.
3. Wavelength of the incident light.
4. Angle of incidence of the light.
5. Monochromaticity of the incident light.
6. Collection optics. Raman scattering is usually isotropic from randomly oriented molecules, but some alignment of molecules may occur on a surface, resulting in anisotropy. Also, stimulated Raman scattering occurs collinearly with the incident and reflected light. Thus, besides the dependence upon solid angle subtended by the collection optics, the signal may depend upon the angle at which the collection optics is set relative to the sample.
7. Spectrometer and detection system. A double monochromator or a single monochromator with a band-rejection (RB) filter is usually required in Raman scattering to eliminate the strong Rayleigh scattered light. However, in SERS, there are added complications

such as the unusual polarization dependence which leads to concern over the varying response of the grating as a function of polarization; this problem is easily addressed with a polarization scrambler, but is mentioned as only one of several things that require well-thought-out calibration of the system to eliminate potential sources of problems involved in SERS measurements. Other potential problems include the need to use a well-collimated beam at normal incidence on any interference filter utilized, elimination of stray light undergoing spurious reflections from the optics, and special problems associated with the high reflectivity of the substrate.

8. Raman activity of the target compound. Raman cross sections vary widely for various compounds. Furthermore, some compounds may exhibit secondary effects such as resonance Raman activity (referred to as SERRS), when adsorbed on the substrate.
9. Adsorption. The adsorption isotherm of the target compound on the substrate can greatly affect SERS response by controlling the amount of material on or near the surface.
10. Exposure. The amount of the target compound on the substrate and within the illuminated region of the sample.
11. Chemical interaction or chemisorption. Strength of interaction between the compound and substrate.

12. Charge transfer. For some molecules there may be empty molecular orbitals which can be partially occupied by electrons from the silver Fermi level. This results in an exchange of charge and a concomitant increase in the induced molecular dipole moment.
13. Surface plasmon resonance. Metal in the form of particles or continuous, but rough surfaces, sustains electrodynamic, induced-charge oscillations, the quanta of which are called "surface plasmons". There is typically a resonance or resonances in the optical absorption and reflection spectrum of the substrate. For different materials the surface plasmon lies at different wavelengths with different half-widths. The surface plasmon enhances greatly the electric field seen by the molecules at the surface.
14. Particle size. For separated metal particles on a transparent substrate the surface plasmon is a dipole oscillation resonance when the particles are small relative to the incident wavelength, but higher modes are induced for larger particles.
15. Particle shape. The shape of the metal particles controls the surface plasmon resonant frequency. For ellipsoids there are three different dipole surface plasmons (one for each axis) which may be induced depending upon the direction of the electric field of the incident light. All three may lie in the visible.

16. **Lightning-rod effect.** The shape of the metal particles, especially when sharp points or edges are involved, also affects how much stimulated Raman scattering may occur, and enhances the field much as in electrostatics.
17. **Particle spacing.** As the spacing of metal particles is reduced they begin to interact. This causes a broadening of the surface plasmon resonance and may act to reduce the SERS signal. However, the increased number of particles per area compensates to some degree for this effect.
18. **Base composition.** The material which supports the metal particles can affect the surface plasmon resonance position and the reflection coefficient.
19. **Sample-induced effects.** Some shift of the surface plasmon resonance frequency may be caused by the adsorbate.
20. **For continuous, but rough metal films,** propagating surface plasmons may be induced which enhance the signal but which are strongly dependent upon polarization, wavelength, and angle of incidence. The substrate roughness and thickness must be controlled if the parameters of the light are fixed.

B. LAPLACE EQUATION IN SPHERICAL COORDINATES

For purposes of general background, a basic theory of SERS physical mechanisms is developed below for substrates consisting of isolated silver spheres. We need an expression for the electrostatic potential for near a metal interface containing adsorbed molecules and being irradiated by a monochromatic light beam.

The general form of the Laplace equation can be written as

$$\nabla^2 \Phi = \frac{1}{\sqrt{g}} \frac{\partial}{\partial x^j} \left(\sqrt{g} g^{ji} \frac{\partial \Phi}{\partial x^i} \right), \quad (2)$$

where Φ is an electrostatic potential [2.3]. For spherical coordinates, we have

$$g_{ij} = \mathbf{e}_i \cdot \mathbf{e}_j = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2 \sin^2 \theta \end{pmatrix}, \quad (3)$$

where $\mathbf{e}_i$ and $\mathbf{e}_j$ are basis vectors ($i, j = 1, 2, 3$ or r, θ, ϕ). From Eq. (3),

$$g = \det g_{ij} = r^4 \sin^2 \theta, \quad (4)$$

$$\sqrt{g} = r^2 \sin \theta. \quad (5)$$

Hence, the Laplace equation in spherical coordinates can be written as

$$\nabla^2 \Phi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} = 0. \quad (6)$$

The solutions of Eq. (6) may be obtained from the method of separation of variables. If a product form for the potential is assumed, then it can be written as

$$\Phi(r, \theta, \phi) = R(r)P(\theta)Q(\phi). \quad (7)$$

Substitute Eq. (7) into Eq. (6), then we have

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{P} \frac{d}{d\theta} \left(\sin \theta \frac{dP}{d\theta} \right) + \frac{1}{Q} \frac{d^2 Q}{d\phi^2} = 0. \quad (8)$$

The ϕ dependence of the equation has now been isolated in the last term. Consequently, that term must be a constant. Let the constant be $-m^2$, then the last term becomes

$$\frac{1}{Q} \frac{d^2 Q}{d\phi^2} = -m^2. \quad (9)$$

This has solutions

$$Q = e^{\pm im\phi}. \quad (10)$$

In order that Q be single-valued, m must be an integer if the full azimuthal range is allowed. With Eq. (9), Eq. (8) can be written as

$$\left[\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right] + \left[\frac{1}{P \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dP}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} \right] = 0. \quad (11)$$

Each term in the brackets is dependent on r and θ so each term must separately equal a constant. Thus,

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dP}{d\theta} \right) + \left[l(l+1) - \frac{m^2}{\sin^2 \theta} \right] P = 0, \quad (12)$$

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - l(l+1)R = 0, \quad (13)$$

where $l(l+1)$ is a real constant. Eq. (13) has solutions

$$R(r) = A r^l + B r^{-(l+1)}. \quad (14)$$

By the substitution $x = \cos \theta$, Eq. (12) can be written as

$$\frac{d}{dx} \left[(1-x^2) \frac{dP}{dx} \right] + \left[l(l+1) - \frac{m^2}{1-x^2} \right] P = 0. \quad (15)$$

Eq. (15) is called the Legendre differential equation, and its solutions are the associated Legendre functions [2.4]. The latter have singularities at the poles $\theta=0, \pi$ and must be excluded if the polar axis is part of the region of interest [2.5]. For convenience' sake, only the principal results will be stated here. By the assumption of a power series solution of the ordinary Legendre differential equation for $m^2=0$, we have

$$\frac{d}{dx} \left[(1 - x^2) \frac{dP}{dx} \right] + l(l + 1)P = 0. \quad (16)$$

The assumption leads to the conclusion that, if l is an integer, $P(\theta)$ can be expressed as a polynomial which is continuous on the interval $-1 \leq x \leq 1$ and given by [2.6]

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l. \quad (17)$$

Eq. (17) is called Rodrigues' formula. The first few Legendre polynomials are

$$P_0(x) = 1, \quad (18)$$

$$P_1(x) = x, \quad (19)$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1), \quad (20)$$

$$P_3(x) = \frac{1}{2}(5x^3 - 3x), \quad (21)$$

$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3). \quad (22)$$

With all positive integral values of l , the Legendre polynomials generated by Eq. (17) constitute a complete orthogonal set in the interval $-1 \leq x \leq 1$, and hence non-integral values of l are not normally considered [2.7].

For $m \neq 0$, the associated Legendre function satisfies Eq. (15) and is given

by [2.8]

$$P_l^m(x) = (-1)^m (1 - x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x), \quad (23)$$

$$P_l^m(x) = (-1)^m \frac{(1 - x^2)^{\frac{m}{2}}}{2^l l!} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l. \quad (24)$$

In order to have finite solutions on the interval $-1 \leq x \leq 1$ the parameter l must be zero or a positive integer and the integer m can take on only the values $-l, -(l-1), \dots, 0, \dots, (l-1), l$. The associated Legendre functions are also orthogonal in the interval $-1 \leq x \leq 1$ so the orthogonarity relation can be obtained as [2.8]

$$\int_{-1}^1 P_l^m(x) P_l^m(x) dx = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} \delta_{l'l}. \quad (25)$$

When Eq. (7) is expanded in the terms of solutions which have been found for the constituent functions. The general solution for a boundary-value problem in spherical coordinates can be written in terms of spherical harmonics $Y_{lm}(\theta, \phi)$ and powers of r [2.9]. The general solution can be written as [2.10]

$$\Phi(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l [A_{lm} r^l + B_{lm} r^{-(l+1)}] Y_{lm}(\theta, \phi). \quad (26)$$

C. POLARIZABILITY

Consider a solid silver sphere of radius a_1 covered with molecules so that the total radius is a_2 . Let it be placed in a uniform electrostatic field directed along the z -axis of cartesian coordinates. The solid silver sphere with a radius a_1 is assumed to be much smaller than the wavelength of the incident light. The uniform electrostatic field is assumed to be formed by infinite or immovable sources. Then the resultant external potential field is the sum of the potential for the uniform electrostatic field Φ_0 and the potential Φ_1 produced by the induced charge distribution on and in the sphere [2.11]. The general solution of Laplace's equation in spherical coordinates is given by Eq. (26). Thus, the forms for the potential inside and outside of the sphere in spherical coordinates' (assuming axial symmetry) are given by

$$\Phi_{in}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta) \quad (27)$$

and

$$\Phi_{out}(r, \theta) = \sum_{l=0}^{\infty} [B_l r^l + C_l r^{-(l+1)}] P_l(\cos \theta). \quad (28)$$

We assumed that the uniform electrostatic field is directed along the z -axis so its electrostatic potential has the form

$$\Phi_i = -E_0 z = -E_0 r \cos \theta = -E_0 r P_1(\cos \theta). \quad (29)$$

Therefore, the total potential outside of the sphere $r \geq a_2$ can be written as

$$\Phi_1 = \left(A \frac{a_2}{r^2} - E_0 r \right) \cos \theta, \quad (30)$$

and the potential for the area $a_2 \geq r \geq a_1$ can be written as

$$\Phi_2 = \left(B \frac{a_1}{r^2} + C \frac{r}{a_2^2} \right) \cos \theta, \quad (31)$$

while the potential for the region $a_1 \geq r$ can be written as

$$\Phi_3 = D \frac{r}{a_1^2} \cos \theta, \quad (32)$$

where A , B , C , and D are constants.

The coefficients can be determined from the boundary conditions. We require the potential and the normal derivative of the displacement to be continuous so the boundary conditions at $r=a_1$ are

$$\Phi_2|_{r=a_1} = \Phi_3|_{r=a_1} \quad (33)$$

and

$$\epsilon_m \frac{\partial \Phi_2}{\partial r} \Big|_{r=a_1} = \epsilon_{Ag} \frac{\partial \Phi_3}{\partial r} \Big|_{r=a_1}, \quad (34)$$

where ϵ_m is the dielectric function of the adsorbed molecules and ϵ_{Ag} is the

dielectric function of silver. Application of the first boundary condition to Eqs. (31) and (32) gives

$$D = B + C \left(\frac{a_1}{a_2} \right)^2. \quad (35)$$

The second boundary condition applied to Eqs. (31) and (32) gives

$$D = \frac{\epsilon_m}{\epsilon_{Ag}} \left[-2B + C \left(\frac{a_1}{a_2} \right)^2 \right]. \quad (36)$$

From Eqs. (35) and (36),

$$B = C \left(\frac{a_1}{a_2} \right)^2 \frac{\epsilon_m - \epsilon_{Ag}}{\epsilon_{Ag} + 2\epsilon_m}. \quad (37)$$

We can substitute B and D using Eqs. (36) and (37), and rewrite the potentials Φ_1 and Φ_2 as

$$\Phi_1 = \left(A \frac{a_2}{r^2} - E_0 r \right) \cos \theta, \quad (38)$$

$$\Phi_2 = \frac{C}{a_2^2} \left(r - \frac{\alpha_{sp}}{r^2} \right) \cos \theta, \quad (39)$$

where

$$\alpha_{sp} = a_1^3 \left(\frac{\epsilon_{Ag} - \epsilon_m}{\epsilon_{Ag} + 2\epsilon_m} \right). \quad (40)$$

The boundary conditions at $r=a_2$ are

$$\Phi_1|_{r=a_2} = \Phi_2|_{r=a_2}, \quad (41)$$

$$\left. \frac{\partial \Phi_1}{\partial r} \right|_{r=a_2} = \epsilon_m \left. \frac{\partial \Phi_2}{\partial r} \right|_{r=a_2}. \quad (42)$$

Applying the first boundary condition to Eqs. (38) and (39) gives

$$A - E_0 a_2^2 = C \left(1 - \frac{\alpha_{sp}}{a_2^3} \right). \quad (43)$$

Applying the second boundary condition to Eqs. (38) and (39) gives

$$2A + E_0 a_2^2 = -\epsilon_m C \left(1 + 2 \frac{\alpha_{sp}}{a_2^3} \right). \quad (44)$$

From Eqs. (43) and (44), the constant A can be written as

$$A = \frac{a_2^2 E_0 \left[\epsilon_m \left(1 + 2 \frac{\alpha_{sp}}{a_2^3} \right) - \left(1 - \frac{\alpha_{sp}}{a_2^3} \right) \right]}{\epsilon_m \left(1 + 2 \frac{\alpha_{sp}}{a_2^3} \right) + 2 \left(1 - \frac{\alpha_{sp}}{a_2^3} \right)}. \quad (45)$$

Since the dipole moment can be written as $\mathbf{p} = \alpha \mathbf{E}$ the polarizability can be written as

$$\alpha = \frac{p}{E} = \frac{A a_2}{E_0} \quad (46)$$

or

$$\alpha = a_2^3 \left[\frac{\epsilon_m \left(1 + 2 \frac{\alpha_{sp}}{a_2^3} \right) - 1 + \frac{\alpha_{sp}}{a_2^3}}{\epsilon_m \left(1 + 2 \frac{\alpha_{sp}}{a_2^3} \right) + 2 \left(1 - \frac{\alpha_{sp}}{a_2^3} \right)} \right]. \quad (47)$$

With Eq. (47), the partial derivative of polarizability can be written as

$$\begin{aligned} \frac{\partial \alpha}{\partial y} = & \frac{a_2^3 \left[\frac{\partial \epsilon_m}{\partial y} (1 + 2W) + \epsilon_m (-2V - 4U) - V - 2U \right]}{\epsilon_m (1 + 2W) + 2 - 2W} \\ & - a_2^3 [\epsilon_m (1 + 2W) - 1 + W] \frac{\left[\frac{\partial \epsilon_m}{\partial y} (1 + 2W) + \epsilon_m (-2V - 4U) + 2V + 4U \right]}{[\epsilon_m (1 + 2W) + 2 - 2W]^2}, \end{aligned} \quad (48)$$

where

$$U = \frac{a_1^3 \frac{\partial \epsilon_m}{\partial y} (\epsilon_{Ag} - \epsilon_m)}{a_2^3 (\epsilon_{Ag} + 2\epsilon_m)^2}, \quad (49)$$

$$V = \frac{a_1^3 \frac{\partial \epsilon_m}{\partial y}}{a_2^3 (\epsilon_{Ag} + 2\epsilon_m)}, \quad (50)$$

$$W = \frac{a_1^3(\epsilon_{Ag} - \epsilon_m)}{a_2^3(\epsilon_{Ag} + 2\epsilon_m)}. \quad (51)$$

D. RAMAN SCATTERING CROSS SECTION

The cross section is obtained by using the polarizability. With the expression for the induced dipole moments, the scattered field at the area away from the sphere can be calculated using [2.12]

$$\vec{E}_{sca} = \frac{\omega^2 e^{i\vec{k} \cdot \vec{r}}}{c^2 r} [(\hat{n} \times \vec{p}) \times \hat{n}], \quad (52)$$

where $\hat{n}$ is a unit vector in the direction of observation and $\vec{r}$ is the distance from the scatterer. $\vec{p}$ is the induced dipole moment of the scatterer. Evaluation of the induced dipole moment of the small scatterer has been carried out previously [2.13] and the result is

$$\vec{p} = \alpha_o \vec{E}_o e^{-i\omega_o t} + \gamma_o \vec{E}_o e^{-i\omega_l t}, \quad (53)$$

where

$$\alpha_o = \alpha, \quad (54)$$

$$\gamma_o = \left. \frac{\partial \alpha_o}{\partial y} \right|_{y=0} \frac{y_o}{2}. \quad (55)$$

Eq. (52) may now be written as

$$\vec{E}_{sca} = \frac{\omega_o^2 e^{i\vec{k} \cdot \vec{r}}}{c^2 r} \left[(\hat{n} \times \vec{E}_o) \times \hat{n} \right] (\alpha_o e^{-i\omega_o t} + \gamma_o e^{-i\omega_1 t}). \quad (56)$$

Far away from the scatterer, the electromagnetic wave is transverse and its electric and magnetic fields in a vacuum are related by [2.14]

$$\vec{H} = \hat{n} \times \vec{E}. \quad (57)$$

From Eq. (56),

$$\vec{H}_{sca} = \frac{\omega_o e^{i\vec{k} \cdot \vec{r}}}{c^2 r} (\hat{n} \times \vec{E}_o) (\alpha_o e^{-i\omega_o t} + \gamma_o e^{-i\omega_1 t}). \quad (58)$$

To simplify, rewrite Eqs. (56) and (58) as

$$\vec{E}_{sca} = \vec{E}_{sca}^0 + \vec{E}_{sca}^1 \quad (59)$$

and

$$\vec{H}_{sca} = \vec{H}_{sca}^0 + \vec{H}_{sca}^1, \quad (60)$$

where

$$\vec{E}_{sca}^0 = \frac{\omega_o^2 e^{i\vec{k} \cdot \vec{r}}}{c^2 r} [(\hat{n} \times \vec{E}_o) \times \hat{n}] \alpha_o e^{-i\omega_o t}, \quad (61)$$

$$\vec{E}_{sca}^1 = \frac{\omega_o^2 e^{i\vec{k} \cdot \vec{r}}}{c^2 r} [(\hat{n} \times \vec{E}_o) \times \hat{n}] \gamma_o e^{-i\omega_o t}, \quad (62)$$

$$\vec{H}_{sca}^0 = \frac{\omega_o^2 e^{i\vec{k} \cdot \vec{r}}}{c^2 r} (\hat{n} \times \vec{E}_o) \alpha_o e^{-i\omega_o t}, \quad (63)$$

$$\vec{H}_{sca}^1 = \frac{\omega_o^2 e^{i\vec{k} \cdot \vec{r}}}{c^2 r} (\hat{n} \times \vec{E}_o) \gamma_o e^{-i\omega_o t}. \quad (64)$$

The time-averaged Poynting vector outside the sphere is given by [2.15]

$$\langle \vec{S} \rangle = \frac{1}{2} \frac{c}{4\pi} \text{Re}(\vec{E} \times \vec{H}^*). \quad (65)$$

Poynting vector represents the energy flux density which is the energy per unit area and time transported by the fields across a surface. With Eqs. (59) and (60), Eq. (65) can be written as

$$\langle \vec{S} \rangle = \frac{c}{8\pi} \left[\text{Re}(\vec{E}_{sca}^0 \times \vec{H}_{sca}^{0*}) + \text{Re}(\vec{E}_{sca}^1 \times \vec{H}_{sca}^{1*}) \right]. \quad (66)$$

From the definition [2.16], the differential scattering cross section is found to be

$$\frac{d\sigma}{d\Omega} = \frac{8\pi r^2 \langle \vec{S} \rangle}{c |\vec{E}_o|^2}. \quad (67)$$

With Eqs. (66) and (67), the total differential scattering cross section can be written as [2.17]

$$\frac{d\sigma}{d\Omega}_{total} = \frac{d\sigma}{d\Omega}_{Rayleigh} + \frac{d\sigma}{d\Omega}_{Raman}, \quad (68)$$

where

$$\frac{d\sigma}{d\Omega}_{Rayleigh} = \frac{\omega_o^4 |\alpha_o|^2}{c^4 |\vec{E}_o|^2} [|\vec{E}_o|^2 - (\hat{n} \cdot \vec{E}_o)(\hat{n} \cdot \vec{E}_o^*)], \quad (69)$$

$$\frac{d\sigma}{d\Omega}_{Raman} = \frac{\omega_o^4 |\gamma_o|^2}{c^4 |\vec{E}_o|^2} [|\vec{E}_o|^2 - (\hat{n} \cdot \vec{E}_o)(\hat{n} \cdot \vec{E}_o^*)], \quad (70)$$

The differential Raman scattering cross section can be rewritten as

$$\frac{d\sigma}{d\Omega}_{Raman} = \frac{\omega_o^4 |\gamma_o|^2}{c^4} (1 - \cos^2 \theta). \quad (71)$$

Here, the solid angle is written as

$$d\Omega = \sin \theta d\theta d\phi. \quad (72)$$

Hence, the Raman scattering cross section can be written as

$$\sigma_{Raman} = \int \frac{d\sigma}{d\Omega_{Raman}} d\Omega = \frac{\omega_o^4 \pi^2}{c^4} |\gamma_o|^2. \quad (73)$$

By Eq. (55), but with α of Eq. (47) replacing α_o , one then finds σ_{Raman} is proportional to ω_o^4 times the absolute square of the derivative of α with respect to the molecular coordinate y . Of the quantities in Eq. (47) only ϵ_m depends upon y and ϵ_m is related to the molecular polarizability α_m by the relation

$$\epsilon_m = 1 + 4\pi N\alpha_m, \quad (74)$$

where N is the number of molecule per volume. The above provides a simple basis for understanding the physical mechanisms in SERS. This theory is not tested in detail in the present work, but was used as a general guideline for assessing the choice of physical parameters.

CHAPTER III

EXPERIMENTAL

A. SUBSTRATE PREPARATION

Metal coated polystyrene microspheres [3.1] on glass microscope slides [3.2] were used as the SERS substrate. As mentioned previously, there are many different substrates available for SERS measurements. Compared to other SERS substrates, the microsphere substrate is reproducible, easy to prepare, and provides an excellent enhancement.

Before microspheres were deposited on the surface, the glass microscope slides were carefully cleaned with a liquid laboratory detergent [3.3] mixed with distilled water, then well rinsed in hot flowing water, and finally were rinsed again in flowing distilled water. Each rinsing lasted more than 10 min to assure that all detergent was removed from the slides. After rinsing, the slides were placed in clean acetone and agitated in an ultrasonic bath for 10 min. Lastly, the slides were placed into methyl alcohol and cleaned in the ultrasonic bath for 10 min. After this cleaning process, the slides were thoroughly dried with nitrogen gas.

The 340-nm-diameter polystyrene microspheres were deposited on the cleaned slides by spin coating. The microsphere solution was well mixed in the ultrasonic bath prior to deposition on the slides. The solution was made from the commercial stock solution, which was diluted from 10 % solids to 5 % solids with distilled water. Then, a 130 μL aliquot of the diluted microsphere solution was placed on a slide using a microliter pipette. The slide was spun at 1800 rpm for 40 sec or until dry. The rate of rotation was carefully selected in order to obtain a uniform microsphere layer on each slide. Microsphere surfaces were examined with a scanning electron microscope [3.4] to establish the surface topography and surface composition. An electron micrograph of a portion of a representative sample is shown in Figures 3-1 and 3-2.

The slides were mounted in a thermal evaporator system for deposition of the silver. The slides were placed in a sample holder which was set at a 45 degree angle relative to the silver source, and turned slowly by a motor during evaporation to ensure uniform coating. The mean distance between sample and source was approximately 13 cm. The evaporation system was evacuated to 5.0×10^{-2} Torr by a mechanical pump, and the system was further evacuated to 3.0×10^{-6} Torr by an oil diffusion pump with a liquid nitrogen cooled trap. A 82.5-nm layer of silver was deposited on the slides at an evaporation rate of about 0.2 nm/sec. The average thickness of the film and the rate of deposition were monitored by a quartz crystal thickness monitor at normal incident to the

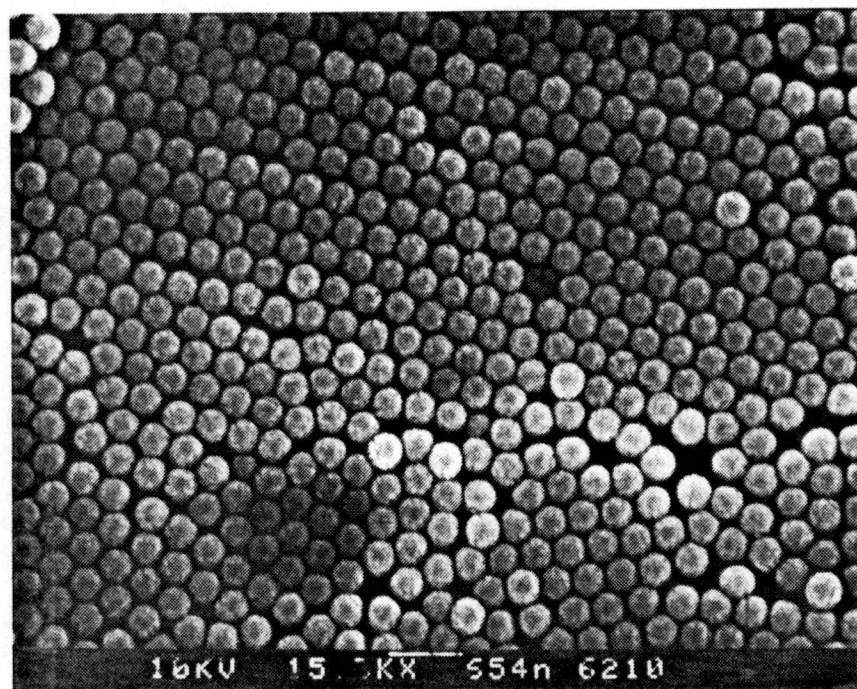


Figure 3-1. Scanning electron micrograph of 340-nm-diameter polystyrene microspheres on a substrate. The angle of observation is along the substrate normal. The length of bar is equal to 654 nm.

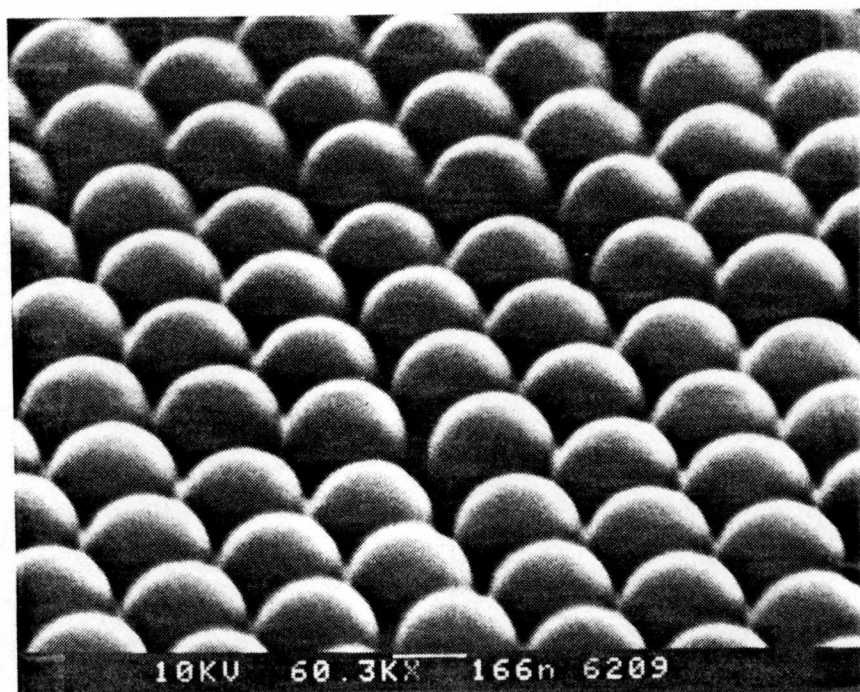


Figure 3-2. Scanning electron micrograph of 340-nm-diameter polystyrene microspheres on a substrate at 60 degrees. The angle of observation is 60 degrees from the substrate normal. The length of bar is equal to 166 nm.

evaporation beam.

Gold and carbon were deposited on the silver coated microsphere slides in the same way. The base pressure was controlled to 2.0×10^{-6} Torr for gold and $1.0\text{-}3.0 \times 10^{-6}$ Torr for carbon. The thickness of gold tested was 15 nm, and the thicknesses of carbon tested were 0, 1, 2, 3, 6, and 18.5 nm. The evaporation rate for gold was about 0.1 nm/sec. The carbon was deposited at a constant rate that was much less than 0.1 nm/sec because of the desire to obtain very thin layers and due to the extremely high evaporating temperature of carbon. The high temperature also caused difficulty in measuring the thickness because the quartz oscillator was very sensitive to temperature.

After evaporative coating, the substrates were removed from the evaporator and used for SERS experiments. Most experiments were done within several hours after evaporation. In the time between the evaporation and SERS experiments, the substrates were kept in an evacuated desiccator. The gold (99.999%) and silver (99.999%) were obtained from CERAC, Incorporated [3.5].

B. APPARATUS

Briefly, the Raman spectrometer consists of a band-pass (BP) filter, a band-rejection (RB) filter, several lenses, laser, spectrograph, and detector.

The BP filter and RB filter were placed at the laser head and at the spectrometer entrance port, respectively, and were selected for the laser wavelength to be used. A schematic view of the Raman spectrometer is shown in Figure 3-3.

The laser used for excitation was a Coherent Innova Model 90K krypton ion laser which provides a number of lines in the 350.7-799.3 nm band with 800 mW maximum overall total power [3.6].

The laser wavelength can be selected by changing the internal optics. The 647.1 nm red line of krypton is commonly used for gold and copper substrates, while the 514.5 nm green line of an argon ion laser is the most commonly used line for silver substrates. Here, all experiments were done at 647.1 nm.

The spectrograph was an Instruments SA HR-640 single-grating spectrograph with a 600 grooves/mm, 500 nm blaze mechanically ruled grating, with a focal length of 640 mm [3.7]. The detector was a Princeton Instruments IRY-700 optical multichannel analyzer (OMA) [3.8]. This intensified silicon photodiode array detector was purged with nitrogen gas and cooled thermoelectrically. Operation of the spectrograph and OMA were controlled by a personal computer using Enhanced Prism software [3.7]. Data was acquired and saved on hard disk or floppy disk.

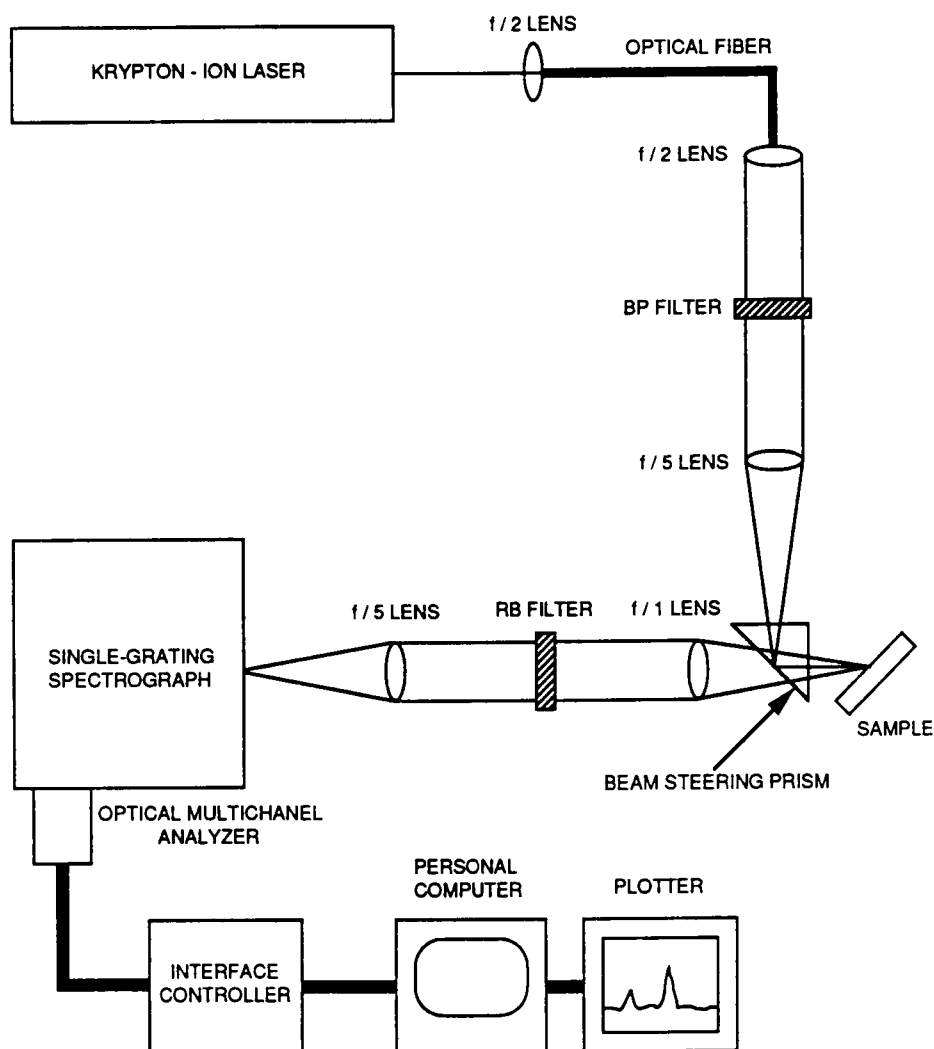


Figure 3-3. A schematic view of the Raman spectrometer.

C. EXPERIMENTAL PROCEDURE

1. STEADY STATE VAPOR DATA

For these experiments, the silver substrate and gold-coated silver substrate were used. The silver substrate is composed of 340 nm microspheres on a glass slide covered with 82.5 nm of silver. This coating thickness produced consistently high signals. For some of these samples, an additional 15 nm layer of gold was deposited on the slides. Each substrate was exposed to pyridine (or toluene) vapor for 10 min inside a sealed vial containing a saturated piece of filter paper. From the vapor pressure formula, the concentration of pyridine and toluene at room temperature are approximately 65 ppm and 110 ppm respectively. Then, SERS spectra were taken under this equilibrium. To obtain a SERS spectrum, first, the substrate was aligned to get a minimum size of focused laser spot, then the laser beam was blocked; then the substrate was moved slightly to get a fresh surface for data acquisition; finally the laser beam was unblocked and data acquisition was begun. After obtaining 10 spectra over a period of 10 min, the laser beam was again blocked for 10 min to allow the surface to re-equilibrate. After that, the beam was cleared, and 10 more SERS spectra were obtained from the same spot as before.

Figure 3-4 is a simple diagram of the experimental process. Here, the

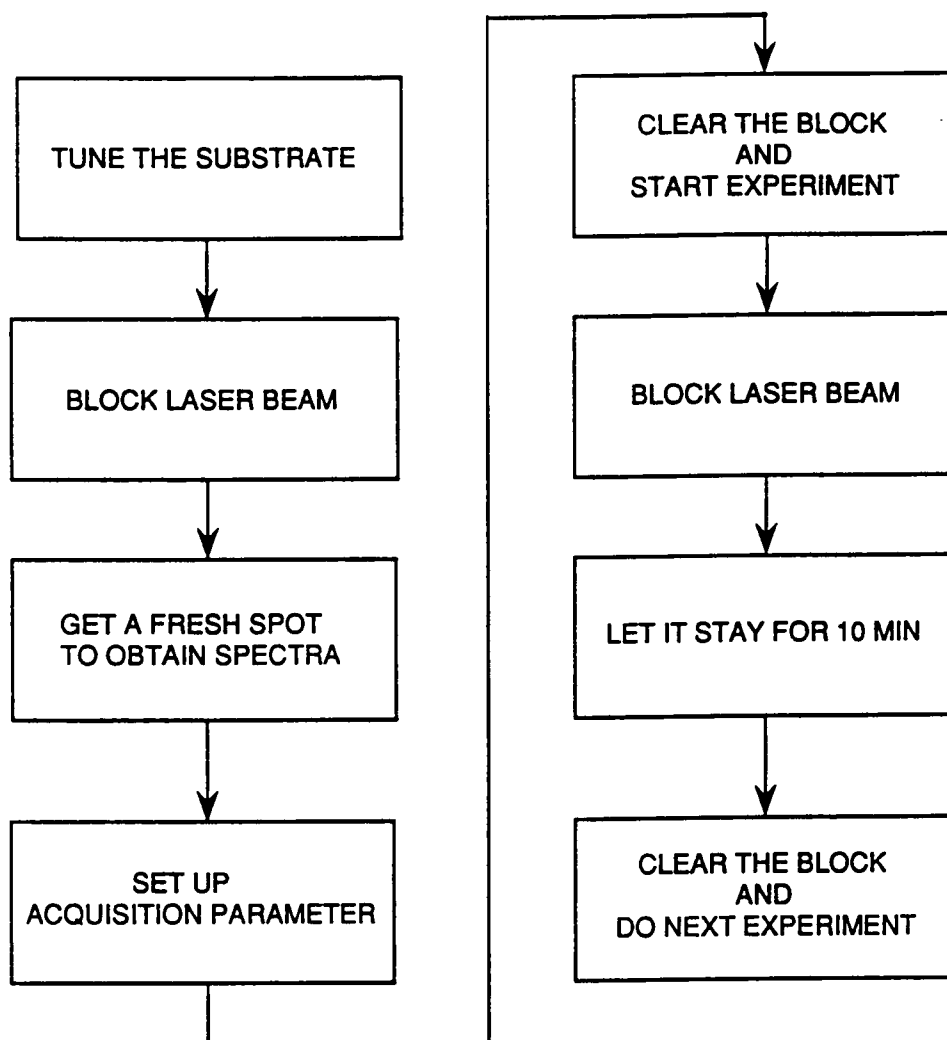


Figure 3-4. A flow chart of the SERS measurement process for the steady state vapor studies.

Chrono-burst mode is a data collection routine which performs a number of measurements with a set time delay between collections. One set of measurements involves a sequential acquisition of 10 spectra with a constant 10 sec integration period; the delay between acquisitions was set to be 60 sec, so there is a 50 sec delay from the end of the last read to the start of the next measurement. A spectrum of silver substrates does not show any peaks in the region used for these experiments. Substrate background subtraction was not performed. These experiments were performed under the following conditions:

Room temperature	19.0°C
Laser wavelength	647.1 nm
Laser power, at the sample	70 mW
Integration time	10 sec
Number of integrations	10
Delay between integrations	60 sec

The focused laser spot size at the sample was adjusted to be a minimum. This spot size was calculated to be 125 μm in diameter based upon the final optical configuration. A power density of 570 W/cm^2 was calculated by using this calculated diameter.

2. OPEN-SYSTEM DESORPTION

Silver substrates and gold-coated silver substrates like those described in the previous section were used. The substrates were exposed in a sealed vial to pyridine (or toluene) vapor for 10 min. From the vapor pressure formula, the concentration of pyridine and toluene are approximately 65 ppm and 110 ppm respectively. Following exposure, the substrates were removed from the vial, and a SERS spectrum was immediately acquired. The substrates were then placed in an oven at 50°C for 10 min. Then, SERS spectra were taken again. The samples were replaced in the oven for an additional 20 min. Then the SERS spectra were obtained in the same way. Because of irreproducibility in positioning samples after placing in the oven, the exact location examined on the surface of the substrate in each experiment was different. This experiment was done at ambient temperature in the same way. Because of the non-equilibrium nature of the experiment, the signal had to be optimized by finding a best spot and angle in a very limited time. Substrate background subtraction was not performed. These experiments were performed under the following conditions:

Room temperature	19.3 °C
Oven temperature	50 °C
Laser wavelength	647.1 nm
Laser power, at the sample	35 mW
Integration time	2 sec
Number of acquisitions	10

3. SUBSTRATE DETERIORATION

Silver substrates and gold-coated silver substrates as described in the previous section were used. The substrates were exposed to pyridine (or toluene) vapor for 10 min, then a SERS spectrum was obtained *in situ*. From the vapor pressure formula, the concentration of pyridine and toluene are approximately 65 ppm and 110 ppm respectively. After each experiment, the substrates were removed from the vial and placed in an evacuated desiccator. This experiment was repeated daily for one week. Substrate background subtraction was not performed. These experiments were performed under the following conditions:

Room temperature	Varied daily between 19°C and 20°C
Laser wavelength	647.1 nm
Laser power, at the sample	70 mW
Integration time	1 sec
Number of acquisitions	10

4. CARBON MONOXIDE EFFECTS

The silver substrates described previously were used. The substrates were placed for 10 min into a vial which was filled with a mixture of pyridine vapor and CO gas. Then SERS spectra were collected in the closed-system. The substrates were then taken out from the vial, and a SERS spectrum was immediately collected. Later, the same SERS measurements were repeated after 10, 20, 30 min following exposure. From the vapor pressure formula, the concentration of pyridine is approximately 74 ppm. Substrate background subtraction was not performed. These experiments were performed under the following conditions:

Room temperature	21.2°C
Laser wavelength	647.1 nm
Laser power, at the sample	35 mW
Integration time	2 sec
Number of integrations	10

5. EFFECTS OF CARBON-COATING

Silver substrates and carbon-coated silver substrates were used. The silver substrates were prepared as stated in the previous section. Carbon was deposited on the Ag substrates at a thickness of 0, 1, 2, 3, 6, and 18.5 nm. The substrates were placed in the pyridine vapor chamber and exposed for 10 min. From the vapor pressure formula, the concentration of pyridine is approximately 79 ppm. Then SERS spectra were taken under the closed-system conditions. After the measurement, the substrates were removed from the vial, and a SERS measurement was immediately performed. The same experiments were subsequently repeated under open-system conditions 10, 20, and 30 min later. Substrate background subtraction was not performed. These experiments were performed under the following conditions:

Room temperature	Different for each thickness, in range from 20 °C to 24 °C
Laser wavelength	647.1 nm
Laser power, at the sample	35 mW
Integration time	2 sec
Number of integrations	10

CHAPTER IV

RESULTS AND DISCUSSION

A. INTRODUCTION

In SERS experiments with dry samples, the best signals are obtained when the target molecules are deposited upon a textured silver substrate with the texture scale being at least as small as 500 nm [4.1]. Polystyrene spheres of 340 nm diameter when spin coated from a liquid suspension form a monolayer on a microscope slide and this yields an excellent base upon which silver may be deposited by vacuum evaporation. The resulting substrate gives a consistently strong SERS signal for several types of compounds adsorbed on the surface. The typical variation of SERS signal intensity due to a spot change of substrate is 10-40% over most of sample. These substrates were used as a standard in all of the work. Research on equilibrium vapor desorption, open-system desorption, and one-week substrate deterioration was carried out using the above mentioned silver substrate and gold-coated, but otherwise similar, silver substrates. Pyridine and toluene were used for comparative measurements in these experiments. The effects of carbon monoxide and a

variety of thicknesses of carbon were also tested using pyridine adsorbed on the substrates. Figures 4-1 and 4-2 show the spectra of pyridine and toluene respectively.

Tested surfaces showed only slight effects on the signal obtained from pyridine. Fortunately, there were no unexpectedly strong decaying effects as a result of illumination of the substrates with 70 mW of laser power. This permitted lengthy testing. Substrate deterioration curves did show steady decreases in SERS activity following a rapid drop the first day, but these effects did not quench the signal past the point at which useful measurements could be made until a complete set of data could be obtained. In addition, similar normalized deterioration curves were seen between silver substrates and gold-coated silver substrates suggesting comparable surface chemistries for the two materials. Open-system desorption showed slight differences in desorbing effects for different surfaces and temperatures. While toluene data is included in this discussion, relatively high levels of noise make it very difficult to discuss its characteristics quantitatively.

B. CONSIDERATIONS

Both single monochromators and double monochromators are commonly used for SERS experiments. Each monochromator has distinct merits so that

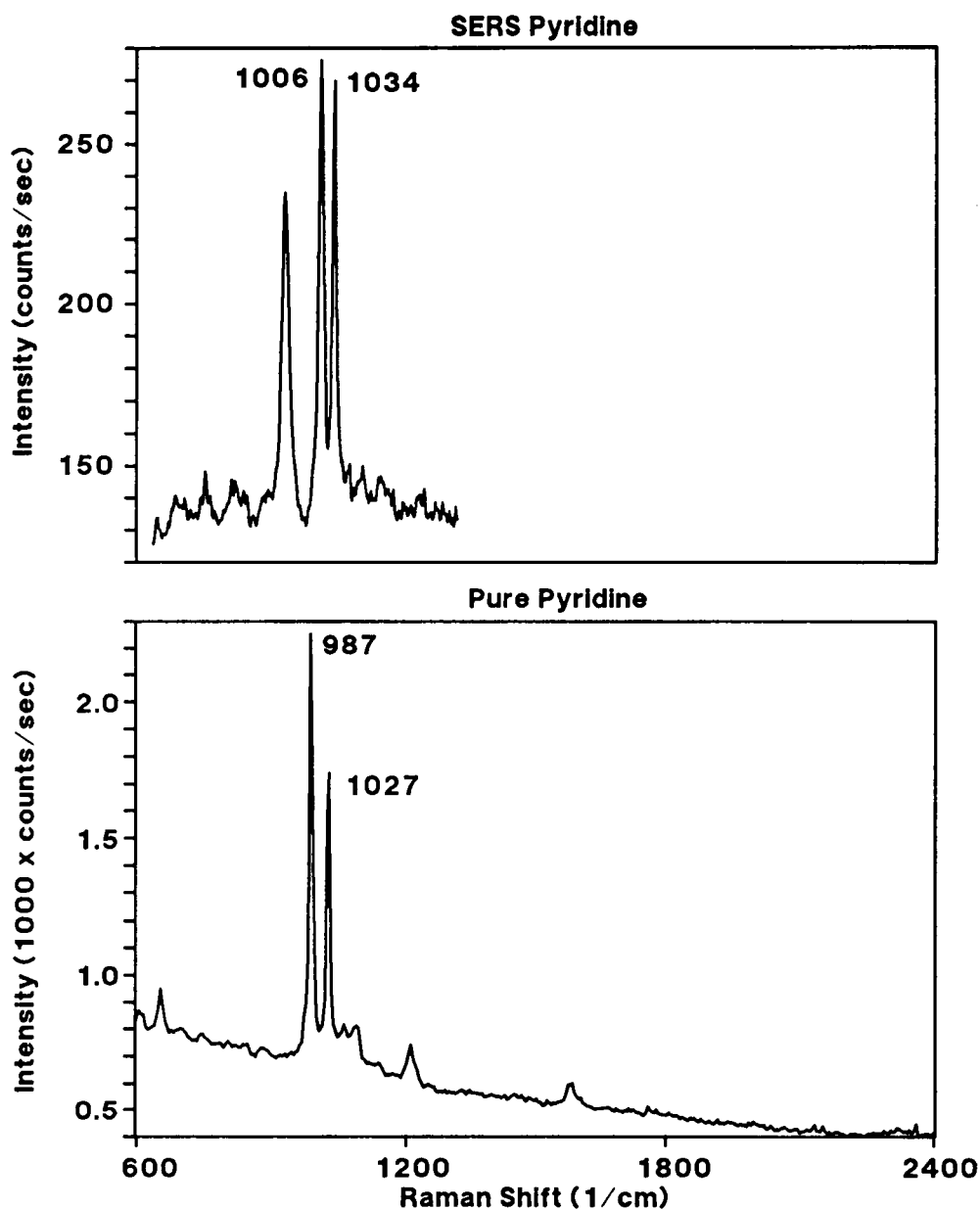


Figure 4-1. Comparison of SERS pyridine and pure pyridine. SERS spectrum was taken from pyridine adsorbed on a silver-coated microsphere substrate in the closed-system. Pure pyridine spectrum was obtained from bulk pyridine liquid.

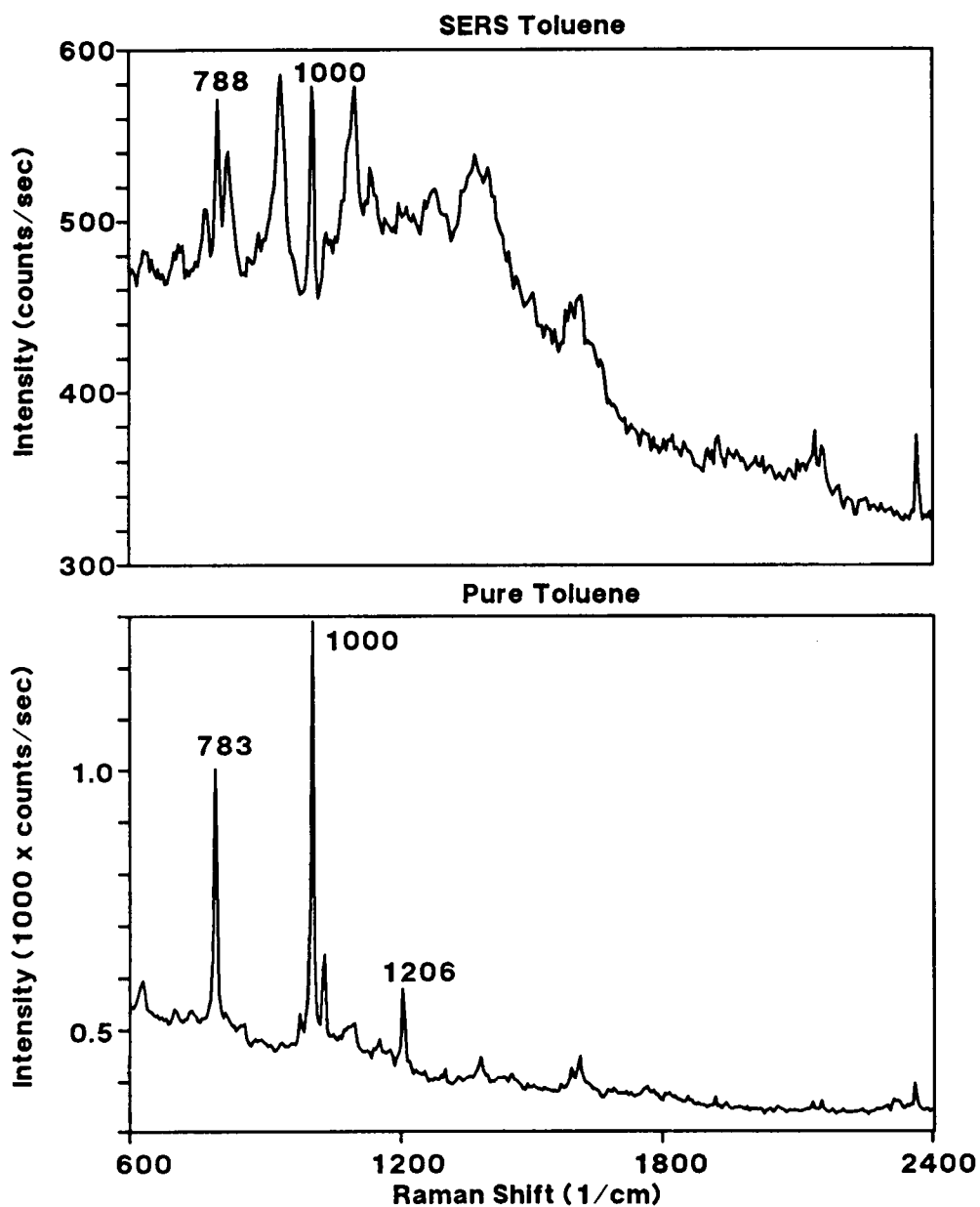


Figure 4-2. Comparison of SERS toluene and pure toluene. SERS spectrum was taken from toluene adsorbed on a silver-coated microsphere substrate in the closed-system. Pure toluene spectrum was obtained from bulk toluene liquid.

the choice of monochromator is very much dependent on use. Figure 4-3 shows a schematic of a single grating monochromator.

Double monochromators are composed of two separate monochromators so that the spectrum is well purified, so that Rayleigh scattered light and potential grating ghost effects are eliminated. While the second stage of a double monochromator works to eliminate the Rayleigh scattered light, one half to one fourth of spectral intensity is lost at the same time. This efficiency problem can be circumvented by the use of a single monochromator. Instead of using the second stage, band-rejection (RB) filters are used to eliminate Rayleigh scattered light prior to input into the monochromator. However, if excitation is performed at several wavelengths, then a good RB filter for each laser wavelength is necessary. It can be said that the single monochromator is not always practical for using a variety of laser lines. In addition, it is not possible to use the single monochromator for tunable lasers such as a dye laser because of the continuum of potential lines. Good RB filters usually cost \$100-\$500 each. It should be noticed that the RB filter has bad transmission near the wavelength of laser line; as a result, the spectra close to the laser line will not be shown. This problem can be overcome by using better filters, which cost \$1000-\$5000; however, from consideration of cost vs. performance, it is generally too expensive to buy more than one filter. It is clear that double or triple monochromators are superior in getting spectra near the laser line, or

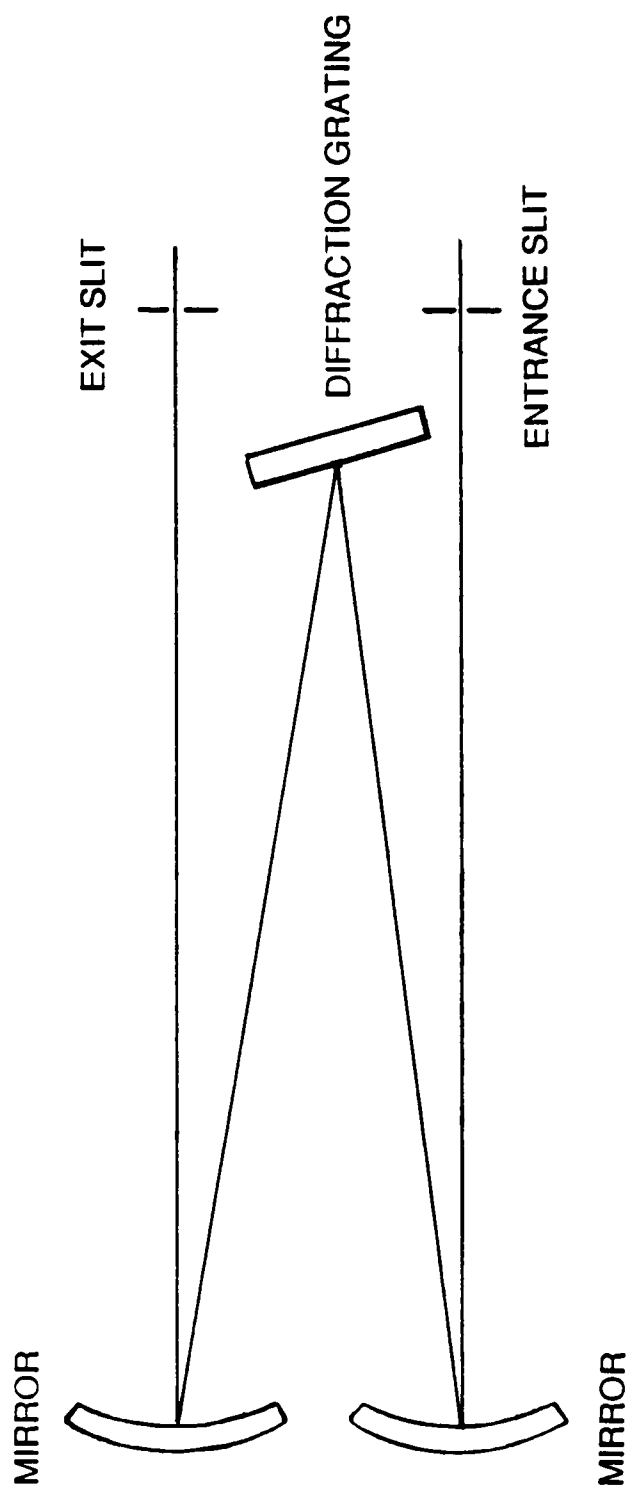


Figure 4-3. A schematic of the single monochromator.

when using a tunable laser. It is also obvious that the higher-efficiency single monochromator has advantages when research interest is not in the region close to the laser wavelength, and when a variety of laser lines are not to be used. The single monochromator was used in this research for these reasons.

C. STEADY STATE VAPOR DATA

The results of the steady state vapor experiment are shown in Figure 4-4 and Table 4-1. The peak area data is obtained from the peak area integrated between the base of each peak. The lines in the figure are determined by the least square method, where the peak area of the 1006-cm^{-1} line of pyridine and the 1000-cm^{-1} line of toluene were used to obtain the peak area data for this experiment. The purpose of this experiment is to show how laser power affects desorption of the sample from the substrates. A blank time (laser power off) was used in the middle of the run to allow molecules to re-equilibrate with the substrate. Figure 4-4 shows that for the silver substrate in pyridine vapor, a gradual decrease in intensity occurs during the first 10 min; however, after 10 min of laser power off, no significant change in SERS intensity was observed. The curve for the gold-coated silver substrate shows stable response. This indicates that there is no significant effect of laser power on adsorption/desorption at 70 mW. It also indicates that the gold might be

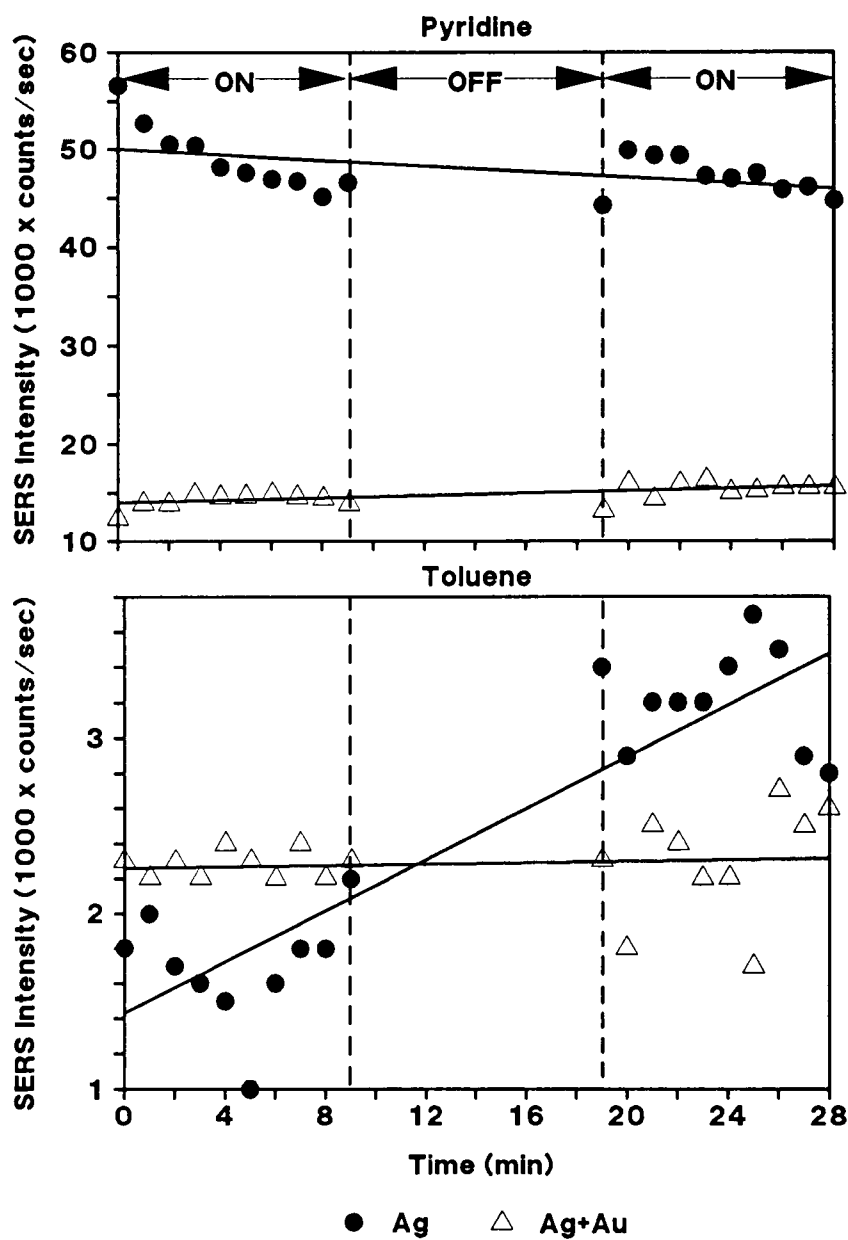


Figure 4-4. Steady state vapor data. Time dependence of SERS intensity in the closed-system with continuous laser radiation. ON/OFF represents ON/OFF of laser radiation. Ag represents silver substrate. Ag+Au represents gold-coated silver substrate.

Table 4-1. Peak area data of steady state vapor studies.

Time(min)	Ag/Pyr	Ag+Au/Pyr	Ag/Tol	Ag+Au/Tol
————— counts/sec —————				
0	56600	12400	1800	2300
1	52700	13900	2000	2200
2	50500	13800	1700	2300
3	50400	14800	1600	2200
4	48200	14500	1500	2400
5	47600	14700	1000	2300
6	47000	14900	1600	2200
7	46700	14500	1800	2400
8	45200	14400	1800	2200
9	46600	13800	2200	2300
19	44300	13200	3400	2300
20	49900	16000	2900	1800
21	49400	14300	3200	2500
22	49400	15900	3200	2400
23	47300	16300	3200	2200
24	47000	15000	3400	2200
25	47500	15200	3700	1700
26	45900	15500	3500	2700
27	46200	15500	2900	2500
28	44800	15600	2800	2600

helping to adsorb molecules of pyridine slightly better than that of silver because of the apparent stability of the response, but there is no clear experimental evidence to prove this. The graph of the toluene data shows irregular changes, primarily due to high relative noise levels in the data because of the weak SERS intensity of toluene.

D. OPEN-SYSTEM DESORPTION

Figures 4-5, 4-6, and 4-7 show the results of open-system desorption; the 1006-cm^{-1} line of pyridine and the 1000-cm^{-1} line of toluene were used to obtain the peak area data for this experiment. Figure 4-8 shows the spectra of pyridine adsorbed on a silver-coated substrate at ambient temperature to clarify the peak existence at each minute. Tables 4-2, 4-3, and 4-4 show the numerical data. For all substrates studied, once substrates were transferred to open-system conditions, the SERS signal dropped very rapidly. The major interest of these experiments is how the surrounding temperature (ambient or 50°C) affects adsorption/desorption of the test molecules. Contrary to expectation, there is no clear difference between the ambient temperature and 50°C results, apparently because of the weakness of adsorption. Furthermore, only minor changes in desorption due to gold overcoating are evident. It was impossible to detect line shifts from these spectra because of severe interferences from

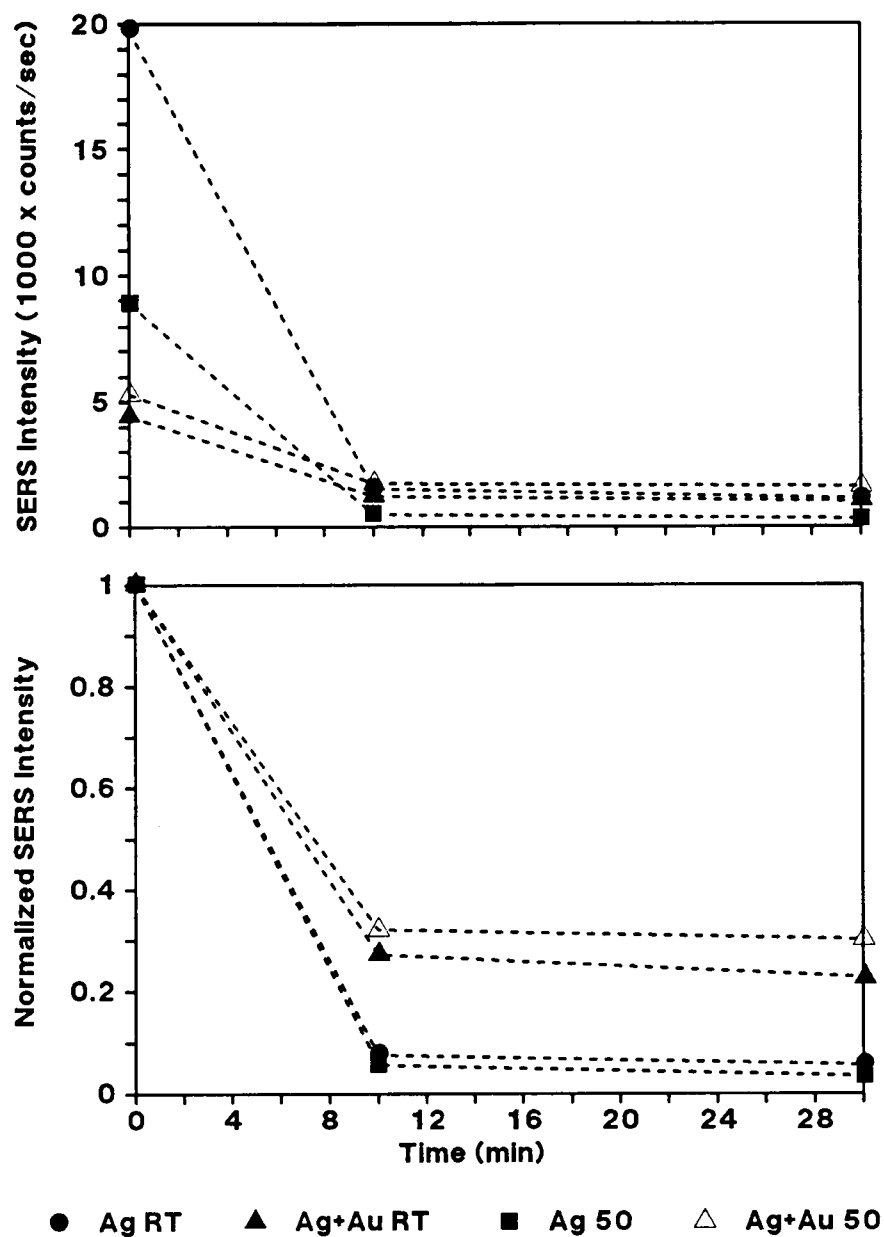


Figure 4-5. Peak area and normalized data of open-system desorption for pyridine. The upper figure is based on the peak area data of SERS intensity. The lower figure is based on the data of SERS intensity normalized by the data at 0 min. Ag represents silver substrate. Ag+Au represents gold-coated silver substrate. RT and 50 represent room temperature and 50°C respectively.

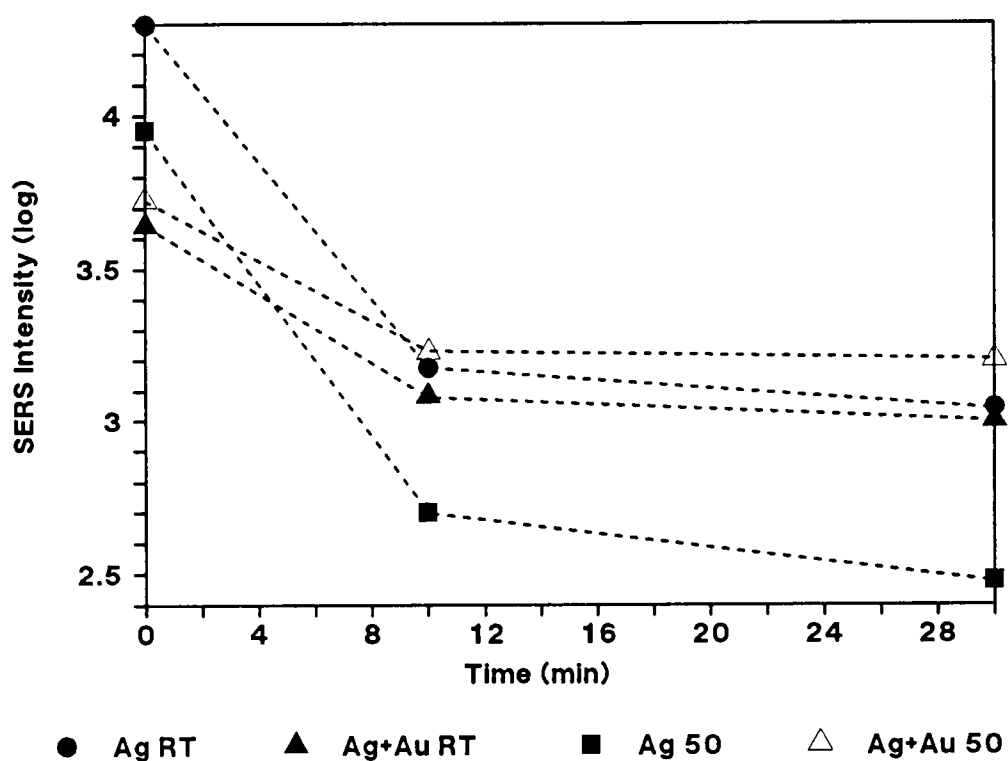


Figure 4-6. Logarithmic data of open-system desorption for pyridine. The figure is based on the logarithmic data of SERS intensity. Ag represents silver substrate. Ag+Au represents gold-coated silver substrate. RT and 50 represent room temperature and 50°C respectively.

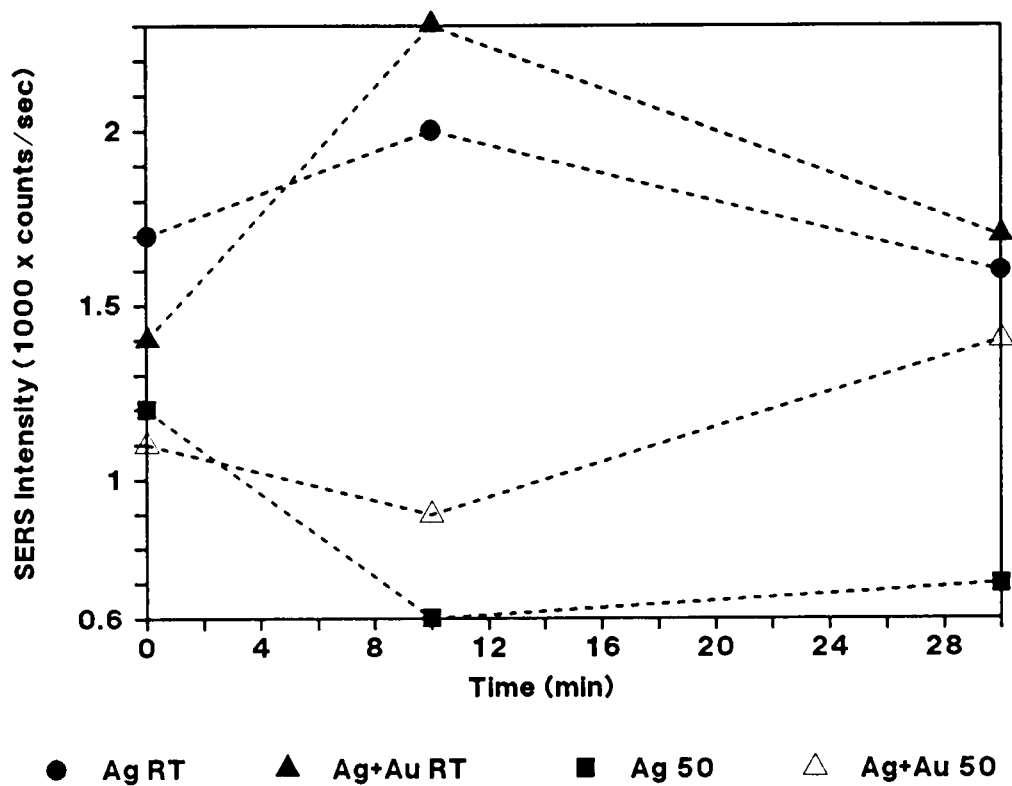


Figure 4-7. Open-system desorption for toluene. The figure is based on the peak area data of SERS intensity. Ag represents silver substrate. Ag+Au represents gold-coated silver substrate. RT and 50 represent room temperature and 50°C respectively.

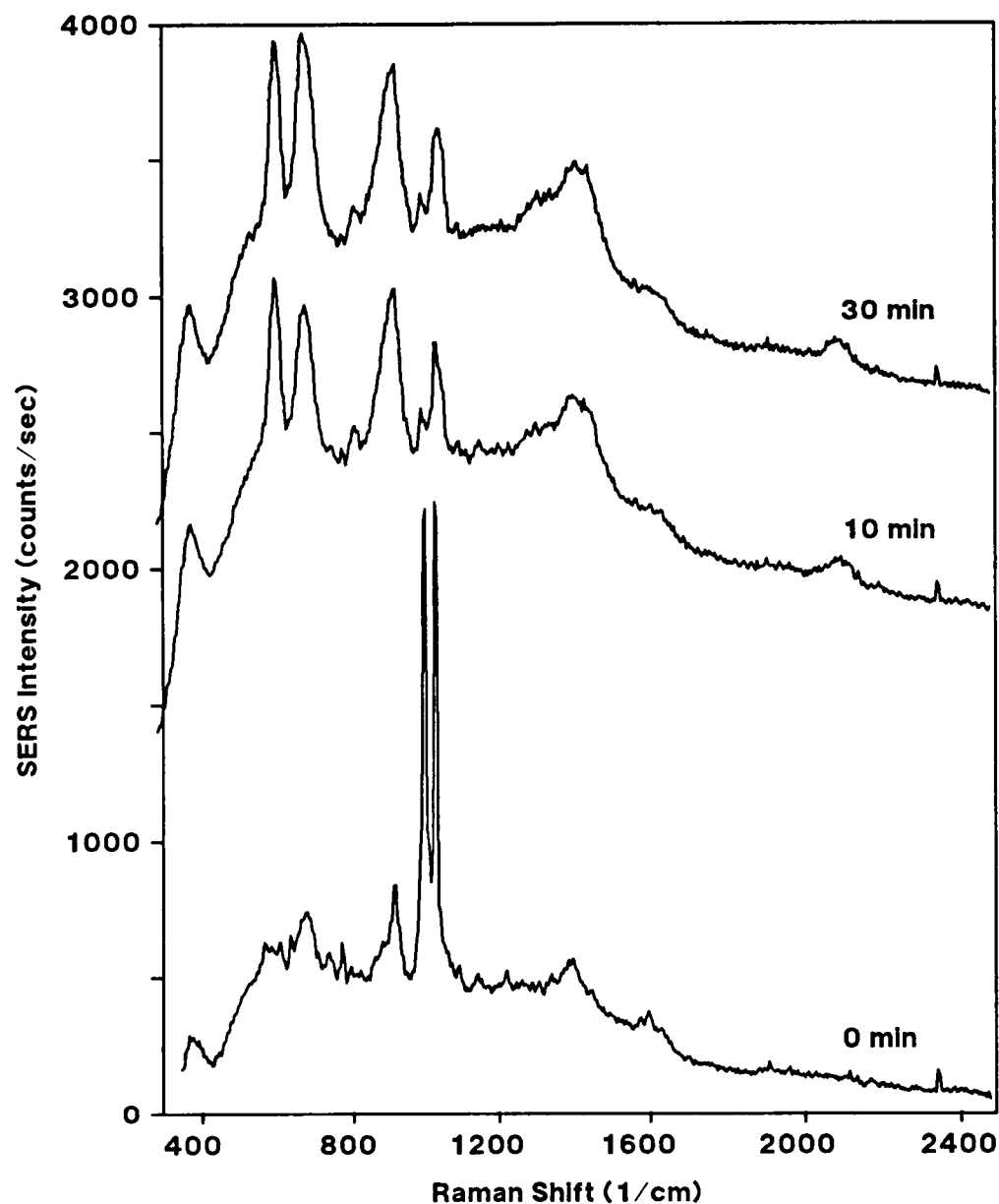


Figure 4-8. SERS spectra of pyridine for open-system desorption. All spectra were taken from pyridine adsorbed on a silver-coated substrate in the open-system. 0, 10, 30 min represent a time after the substrate removal from the vial. Vertical scale is arbitrary shifted for clarify.

Table 4-2. Peak area data of open-system desorption.

Time(min)	Ag/Pyr	Ag+Au/Pyr	Ag/Tol	Ag+Au/Tol
————— counts/sec —————				
AMBIENT TEMPERATURE				
0	19800	4400	1700	1400
10	1500	1200	2000	2300
30	1100	1000	1600	1700
50°C				
0	8900	5300	1200	1100
10	500	1700	600	900
30	300	1600	700	1400

Table 4-3. Normalized data of open-system desorption.

Time(min)	Ag/Pyr	Ag+Au/Pyr	Ag/Tol	Ag+Au/Tol
AMBIENT TEMPERATURE				
0	1.000	1.000	1.000	1.000
10	0.076	0.273	1.176	1.643
30	0.056	0.227	0.941	1.214
50°C				
0	1.000	1.000	1.000	1.000
10	0.056	0.321	0.500	0.818
30	0.034	0.302	0.583	1.273

Table 4-4. Logarithmic data of open-system desorption.

Time(min)	Ag/Pyr	Ag+Au/Pyr	Ag/Tol	Ag+Au/Tol
AMBIENT TEMPERATURE				
0	4.297	3.643	3.230	3.146
10	3.176	3.079	3.301	3.362
30	3.041	3.000	3.204	3.230
50°C				
0	3.949	3.724	3.079	3.041
10	2.699	3.230	2.778	2.954
30	2.477	3.204	2.845	3.146

grating ghosts compared with the weak SERS signals; furthermore, quantitative area measurements at low intensities are suspect due to these effects.

Attempts at measuring SERS from toluene were not successful. Considerably higher relative noise levels are observed because of its weak SERS intensity. There was no line shift for toluene, so it can be concluded that the toluene molecules are only undergoing weak ring interaction to the surface. Unlike the pyridine, toluene does not have heteroatomic moieties or other functional groups capable of charge-transfer interactions with the surface, so it is not expected that the toluene molecules assume a standing position on the surface. Compared with pyridine, the toluene showed much weaker intensity in the closed-system; this is expected, since toluene molecules have only weak ring interaction with the surface, resulting in weak SERS signals.

E. SUBSTRATE DETERIORATION

Figures 4-9 and 4-10 show the data from the study of substrate deterioration using pyridine and toluene. Table 4-5 shows the numerical data for this experiment. The 1006-cm^{-1} line of pyridine and the 1000-cm^{-1} line of toluene were used to obtain the peak area data. Figure 4-9 indicates that there is a significant drop in SERS activity between the first day and the second day for both pyridine and toluene. The rate of deterioration then decreased

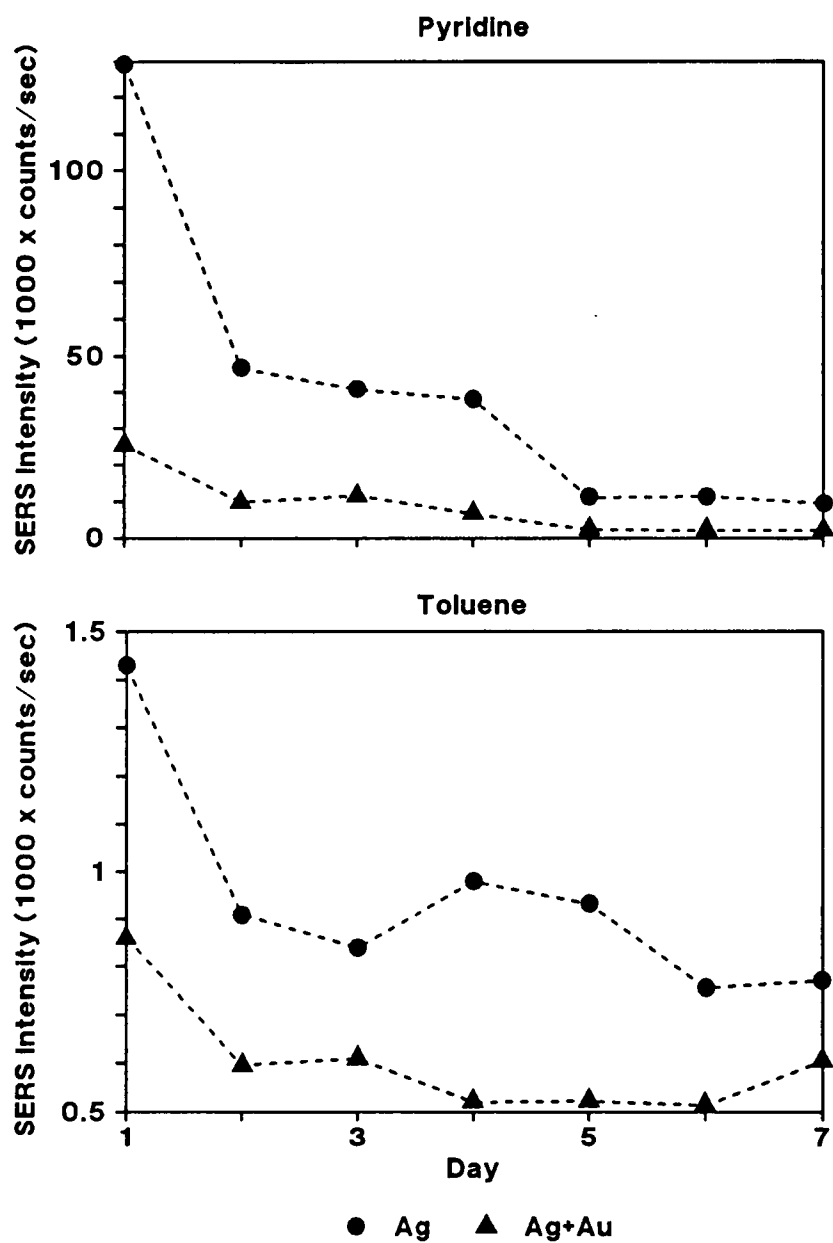


Figure 4-9. Peak area data of substrate deterioration. Both figures are based on the peak area data of SERS intensity. The solid circle represents the use of silver substrate, and the solid triangle represents the use of gold-coated silver substrate.

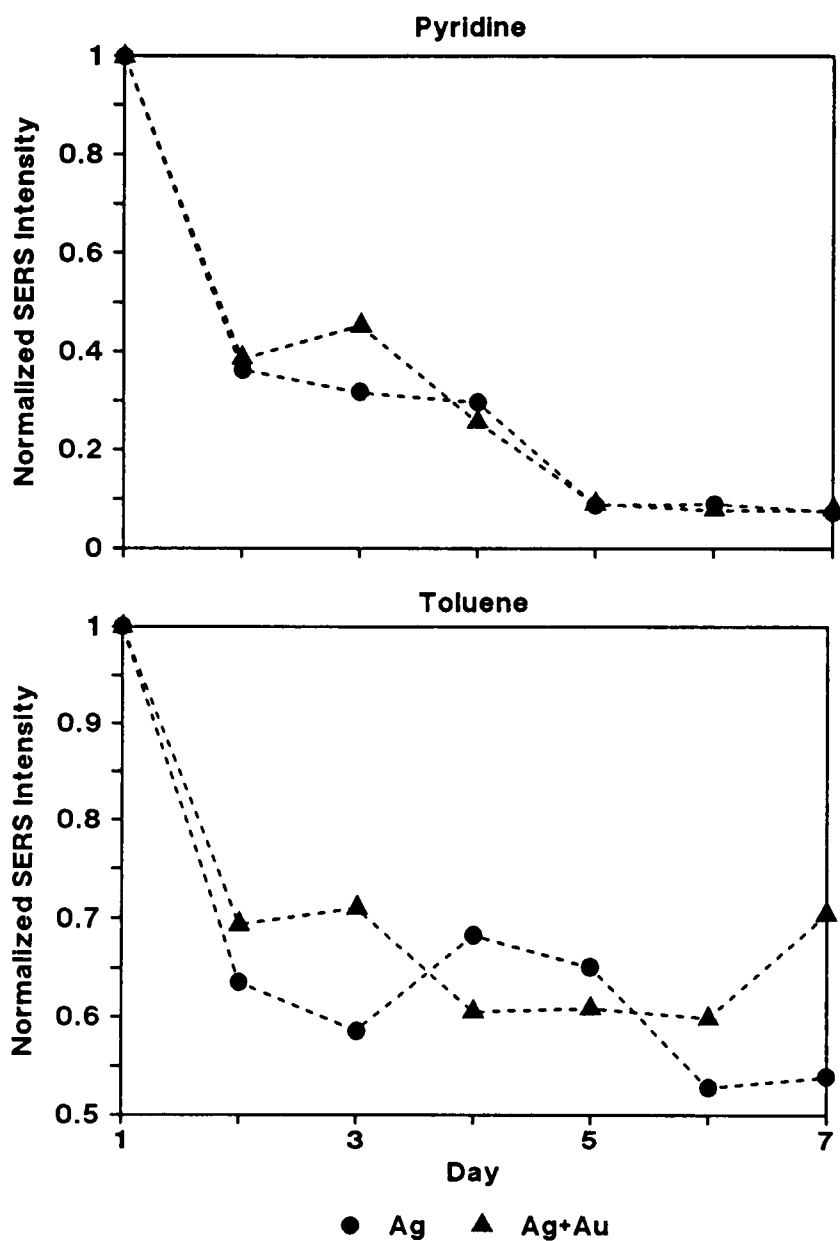


Figure 4-10. Normalized data of substrate deterioration. Both figures are based on the data of SERS intensity normalized by the data of the first day. The solid circle represents the use of silver substrate, and the solid triangle represents the use of gold-coated silver substrate.

Table 4-5. Peak area and normalized data of substrate deterioration.

Day	Ag/Pyr	Ag+Au/Pyr	Ag/Tol	Ag+Au/Tol
PEAK AREA DATA (counts/sec)				
1	128919	25493	1430 $\pm$ 120	859 $\pm$ 40
2	46711	9775	908 $\pm$ 105	596 $\pm$ 69
3	40770	11522	838 $\pm$ 20	610 $\pm$ 37
4	38186	6518	977 $\pm$ 210	520 $\pm$ 35
5	11192	2295	930 $\pm$ 57	523 $\pm$ 110
6	11411	1956	755 $\pm$ 21	514 $\pm$ 113
7	9412	1958	771 $\pm$ 35	605 $\pm$ 88
NORMALIZED DATA				
1	1.000	1.000	1.000	1.000
2	0.362	0.383	0.635	0.694
3	0.316	0.452	0.586	0.710
4	0.296	0.256	0.683	0.605
5	0.087	0.090	0.650	0.609
6	0.089	0.077	0.528	0.598
7	0.073	0.077	0.539	0.704

gradually during the remainder of the experiment.

Surface deterioration may be caused by two possible mechanisms of degradation; a chemical degradation and an atomic-scale degradation. Chemical degradation is caused by reaction of the surface with components in the atmosphere; changes in surface chemistry can reduce sample adsorption or change surface dielectric properties, interrupting the function of the SERS substrate as a result. Atomic-scale changes are the result of gradual annealing of the surface at room temperature. When the metal was originally evaporated onto the surface, individual atoms were deposited with numerous surface-defects; later these atoms tend to take a stable energy state and try to move to the lower energy state. This makes the surface smoother, and it has been suggested that this reduces SERS activity of the substrate¹.

Figure 4-10 shows very similar curves for both pyridine and toluene. It also suggests that for gold-coated silver surfaces, the surface might in fact consist of a mixture of silver and gold. It was expected that there would be substantial differences between the silver substrate and the gold-coated silver substrate because of the substantially greater oxidizability of the silver. A 15 nm layer of gold was deposited over the silver so that the silver was expected to have a complete coverage of gold. However, during or subsequent to

¹Personal conversation with Dr. E. A. Wachter, Oak Ridge National Laboratory, Fall 1990.

deposition on the surface, gold might have alloyed with the silver and formed an alloyed surface. This is a plausible explanation for the observed similarity between silver substrates and gold-coated silver substrates in the deterioration process.

F. CARBON MONOXIDE EFFECTS

Figures 4-11 and 4-12 show the time dependence intensity curves of pyridine adsorbed on a silver substrate with and without prior exposure to carbon monoxide gas. Table 4-6 shows the numerical data for this experiment. The 1006-cm^{-1} line of pyridine was used to obtain the peak area data. It was confirmed that the SERS signal from carbon monoxide does not show any strong line between 980 cm^{-1} and 1190 cm^{-1} [1.23]. Both pyridine vapor and carbon monoxide gas mixed with pyridine vapor show very similar results. Carbon monoxide does not appear to affect adsorption of pyridine except in a competitive way by decreasing the surface density of pyridine molecules and lowering its SERS intensity. Changes in line shift were not observed because of the heavy interferences from grating ghosts, but they may be present.

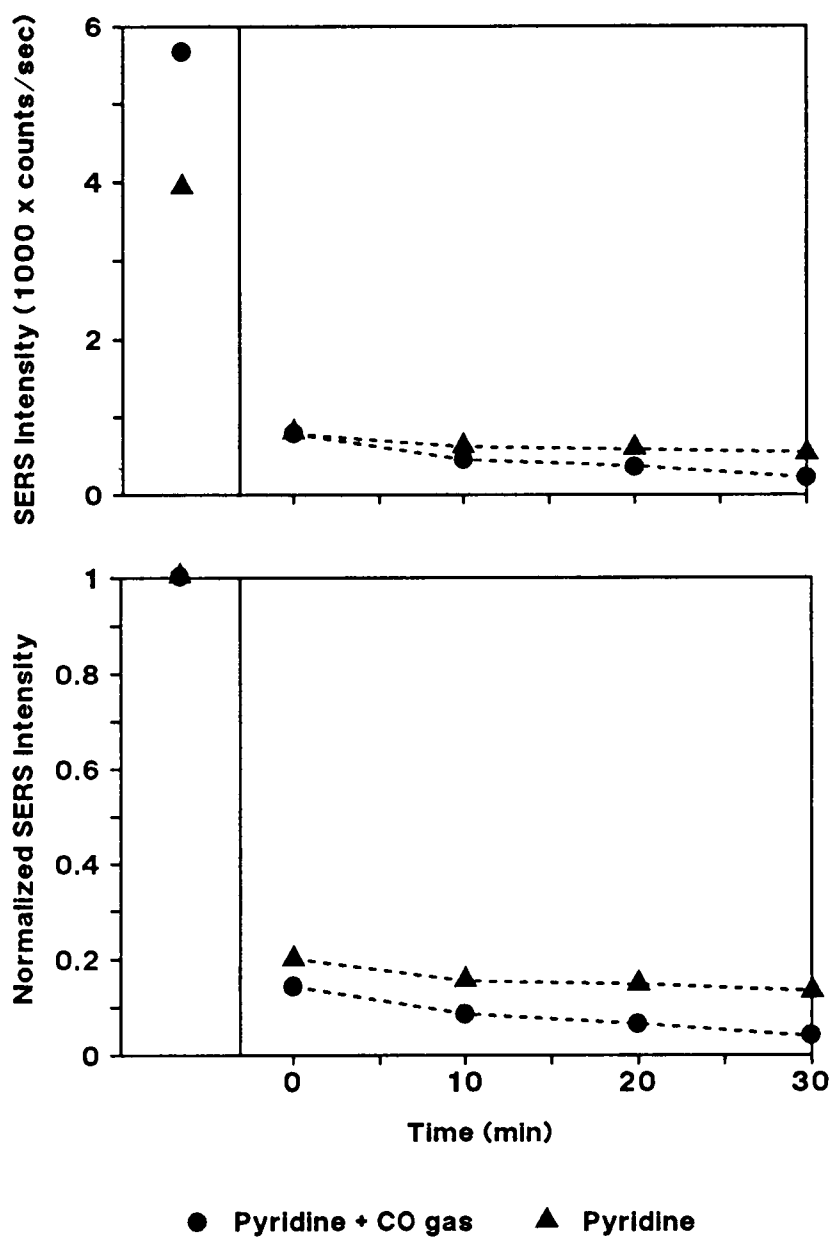


Figure 4-11. Peak area and normalized data of carbon monoxide effects. The upper figure is based on the peak area data of SERS intensity. The lower figure is based on the data of SERS intensity normalized by the data taken in the closed-system. The dots located on the left side of the line were taken in the closed-system. The time parameter is used for the open-system.

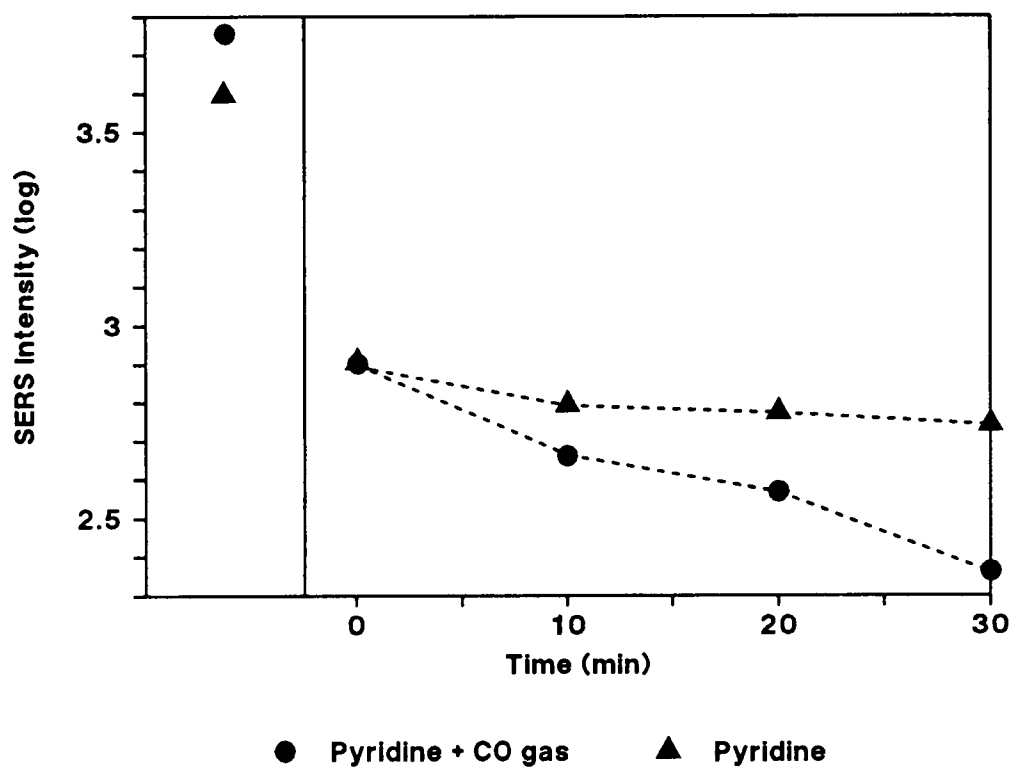


Figure 4-12. Logarithmic data of carbon monoxide effects. The figure is based on the logarithmic data of SERS intensity. The dots located on the left side of the line were taken in the closed-system. The time parameter is used for the open-system.

Table 4-6. Carbon monoxide effects.

Time(min)	Substrate			Average ^a	No CO gas
	#1	#2	#3		
PEAK AREA DATA (counts/sec)					
CLOSE ^b	7182	4550	5320	5684 ±1353	3940 ±593
0	581	388	1410	793 ±542	785 ±91
10	266	400	714	460 ±230	619 ±180
20	416	344	350	370 ±40	592 ±177
30	199	166	324	230 ±83	550 ±237
NORMALIZED DATA					
CLOSE ^b	1.000	1.000	1.000	1.000	1.000
0	0.080	0.085	0.265	0.144 ±0.105	0.201 ±0.024
10	0.037	0.088	0.134	0.086 ±0.048	0.155 ±0.027
20	0.058	0.076	0.066	0.066 ±0.009	0.148 ±0.024
30	0.027	0.036	0.061	0.042 ±0.017	0.135 ±0.042
LOGARITHMIC DATA					
CLOSE ^b				3.755	3.595
0				2.899	2.895
10				2.663	2.792
20				2.568	2.772
30				2.362	2.740

^aAverage of three substrates.^bData were taken under the closed-system.

G. EFFECTS OF CARBON-COATING

Figures 4-13 and 4-14 show the time dependence intensity curve of pyridine adsorbed on carbon-coated silver substrates with a variety of carbon thicknesses. Tables 4-7, 4-8, and 4-9 show the numerical data for this experiment. The 1006-cm^{-1} line of pyridine was used to obtain the peak area data. Unexpectedly, the figure shows that the 2-nm carbon data has considerably greater intensity than the others; there does not seem to be any prior theoretical or other experimental support for this fact. None of the carbon-coated silver substrates show the 924-cm^{-1} line which is usually present in the pyridine SERS signal taken from silver substrates. The graph shows that 6-nm carbon data is the most stable, suggesting an optimal coating thickness in this range. Note that due to the extreme difficulty in deposition of carbon films, the actual thickness is probably somewhat less than this nominal value. No line shifts were confirmed because of the severe interferences from grating ghosts relative to the weak SERS signals.

H. SUMMARY

To sum up, slight effects on adsorption and desorption of pyridine were seen for gold, carbon, and carbon monoxide. However, as mentioned

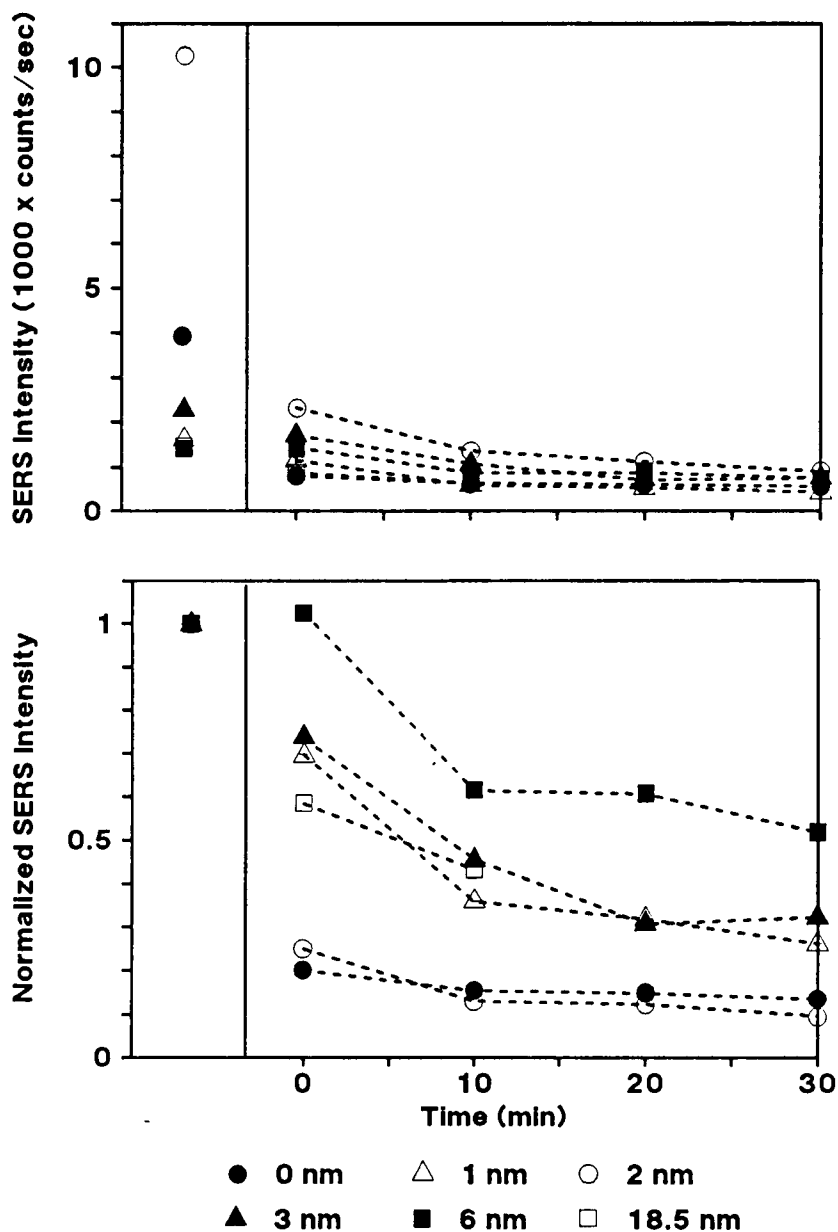


Figure 4-13. Peak area and normalized data of carbon-coating effects. The upper figure is based on the peak area data of SERS intensity. The lower figure is based on the data of SERS intensity normalized by the data taken in the closed-system. The dots located on the left side of the line were taken in the closed-system. The time parameter is used for the open-system.

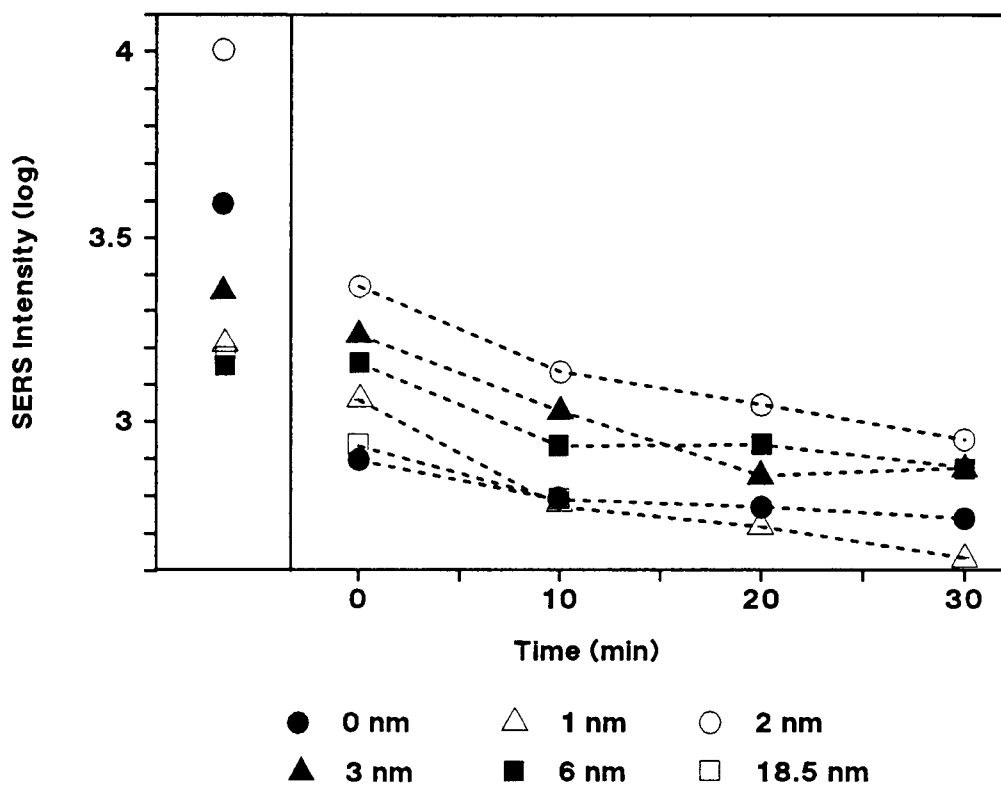


Figure 4-14. Logarithmic data of carbon-coating effects. The figure is based on the logarithmic data of SERS intensity. The dots located on the left side of the line were taken in the closed-system. The time parameter is used for the open-system.

Table 4-7. Peak area data of carbon-coating effects.

Time(min)	0 nm	1 nm	2 nm	counts/sec		
				3 nm	6 nm	18.5 nm
CLOSE*	3940 ±593	1641	10302 ±3511	2329	1424 ±230	1482 ±146
0	785 ±91	1141	2338 ±497	1712	1440 ±5	858 ±194
10	619 ±180	590	1361 ±595	1064	860 ±43	616 ±84
20	592 ±177	523	1110 ±507	715	864 ±128	N/A
30	550 ±237	430	894 ±193	752	754 ±310	N/A

*Data were taken under the closed-system.

Table 4-8. Normalized data of carbon-coating effects.

Time(min)	0 nm	1 nm	2 nm	3 nm	6 nm	18.5 nm
CLOSE ^a	1.000	1.000	1.000	1.000	1.000	1.000
0	0.201 ±0.024	0.695	0.250 ±0.133	0.735	1.026 ±0.169	0.584 ±0.149
10	0.155 ±0.027	0.360	0.130 ±0.013	0.457	0.614 ±0.130	0.434 ±0.112
20	0.148 ±0.024	0.319	0.123 ±0.091	0.307	0.607 ±0.008	N/A
30	0.135 ±0.042	0.262	0.096 ±0.052	0.323	0.519 ±0.134	N/A

^aData were taken under the closed-system.

Table 4-9. Logarithmic data of carbon-coating effects.

Time(min)	0 nm	1 nm	2 nm	3 nm	6 nm	18.5 nm
CLOSE ^a	3.595	3.215	4.013	3.367	3.154	3.171
0	2.895	3.057	3.369	3.234	3.158	2.933
10	2.792	2.771	3.134	3.027	2.934	2.790
20	2.772	2.719	3.045	2.854	2.937	N/A
30	2.740	2.633	2.951	2.876	2.877	N/A

^aData were taken under the closed-system.

previously, it would be very beneficial to find materials which adsorb particular chemicals well at room temperature; for pyridine and toluene, these coatings do not appear efficacious.

SERS is a very sensitive technique. However, to have optimal SERS using silver substrates, there are a few points which need to be mentioned. It is very difficult to produce a homogeneous submonolayer of microspheres consistently using the spin-coating technique. Thus, substrates must be carefully assayed for homogeneity, and the spot examined on the substrate surface should not be changed if it is not necessary. Furthermore, it might be advantageous to use the 514.5-nm line of the argon ion laser instead of the 647.1-nm line of krypton ion laser; it is possible to get approximately three times stronger SERS intensity from the 514.5-nm line compared to the 647.1-nm line, due to the ν^4 relationship for Raman cross sections. Especially for this kind of adsorption research, it would be very beneficial to get a stronger spectrum.

Further experimental investigations with better spectrometer configurations are required to certify the desorption data and the adsorption line shifts. The measurements reported here show relatively crude measurements of the desorbing effects and the slight adsorbing effects. However, severe interferences from grating ghosts make interpretation at low signal levels extremely hard. To solve the problem of grating ghosts, it is recommended that a holographically ruled grating be used; holographically

ruled gratings have no grating ghosts so it is expected that significantly less background would be observed. The purified spectrum will be useful to confirm the desorbing effects and the adsorbing effects. The existence of line shift might confirm conformation of pyridine ring and the possible existence of supramonolayer coverages.

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