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ENHANCED SPECTROSCOPY AND PHOTOCHEMISTRY OF MOLECULES ADSORBED ON METAL SURFACES

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G.M. Goncher
(Ph.D. Thesis)

September 1984

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ENHANCED SPECTROSCOPY AND PHOTOCHEMISTRY OF MOLECULES ADSORBED ON METAL SURFACES

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Enhanced Spectroscopy and Photochemistry of Molecules Adsorbed on Metal Surfaces

Gary M. Goncher

Abstract

Our studies of Raman enhancement on silver single crystals roughened by ion bombardment in ultrahigh vacuum have shown that the enhancement is correlated with the appearance of particular types of surface topography on the crystals. The surfaces that produce maximum enhancement contain surface roughness features on two size scales, one of approximately 400 Å diameter and the other of approximately 2000 Å diameter. Raman enhancement is greatest for incident wavelengths near 500 nm, which is in good agreement with the resonance wavelength predictions of electrodynamic theory calculations for 400 Å silver spheroids coupled to the surface. The distance dependence of the enhancement indicates that enhancement of surface fields accounts for roughly a factor of 100 of the total observed enhancement of 1000 for an adsorbed monolayer; the remaining enhancement is due to a mechanism involving surface interactions that occur for only the first layer of molecules.

We have observed resonant photodecomposition of a variety of aromatic molecules on these rough surfaces. A continuous ion laser source at a number of different wavelengths in the region 350–410 nm was used to produce graphitic carbon on the surface, monitored by Raman spectroscopy at the 1580 cm⁻¹ band of surface carbon. Laser power
dependence studies of the fragmentation rate for several molecules at 406.7 nm indicate that the initial absorption step is a two-photon process, and energetic considerations imply that this is the case for other molecules observed to undergo photofragmentation. The only exception to this appears to be photodecomposition of benzaldehyde with 350.7 nm excitation, where the first singlet state is energetically accessible and the photodecomposition rate is linear in intensity.

Distance dependence studies of the fragmentation rate using an inert spacer layer of molecules show a maximum decomposition rate for pyridine 15-20 Å from the surface, indicating that energy transfer from molecules to the metal surface competes with enhanced excitation near the surface in determining the reaction rate. The reaction pathway for most of the molecules studied has not been established, but studies with pulsed lasers indicate that surface ionization at the low intensities we have used for photodecomposition is unlikely.
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Part I.

Surface Enhanced Raman Scattering
A. Introduction

Less than ten years ago the first reports of enhanced Raman cross-sections for molecules adsorbed on metal surfaces were published.\textsuperscript{1,2} Early experiments on surface enhancement effects were performed on electrochemically cycled silver electrode surfaces; since then the effect has been observed for a wide variety of different materials (Ag, Au, Cu, Pt, Ni, Na, Hg) in many configurations (mechanically and photochemically roughened crystals, evaporated films, island films, colloids, gratings, and tunnel junctions). There was initially much confusion, and many contradictory results were obtained regarding which factors were important in controlling enhancement. Early work in this laboratory was directed towards investigating enhancement effects on well-characterized surfaces in an ultrahigh vacuum (UHV) environment to remove ambiguities due to uncontrolled factors.\textsuperscript{3}

The early promise of surface enhanced Raman scattering (SERS) as a universal, high resolution probe of surface vibrational modes of adsorbed species has diminished somewhat as it has become evident from many experiments that large enhancement effects are restricted to a limited number of metals under certain specific conditions. The largest enhancement factors are observed for silver, copper, and gold; the effect is greatest when the surface is rough and when the excitation energy is below interband transitions in the substrate. These last observations, together with the existence of other enhanced effects such as second-harmonic generation and photochemistry, have led to a growing consensus that enhanced fields due to surface resonances are at least partially responsible for the enhancement mechanism in SERS.
For the adsorbate systems in which it can be usefully employed, enhanced Raman scattering provides detailed vibrational information with an energy resolution higher than that presently possible using other techniques such as electron energy loss spectroscopy (EELS). The technique is inherently surface-sensitive due to enhancement effects at the surface, and can provide useful information on surface species in systems where the surface is in contact with a large volume of material that would make the use of other probes such as infrared absorption impossible.

The unusual nature of the enhancement phenomenon has drawn great attention to the field of surface Raman scattering, and a correspondingly large body of theoretical work devoted to explaining the effect exists in the literature. This work has led to an improved understanding of a wide range of phenomena involving the interaction of photons with surfaces and adsorbed molecules. In the following pages our efforts to determine experimentally the factors controlling surface enhancement in the system we have worked with (roughened silver single crystals) will be detailed, together with the theoretical framework necessary to understand our observations.
B. Theory of Surface Enhancement

In order to predict Raman scattering intensity, one must be able to calculate the dipole moment induced by incident light in a molecule at the Stokes scattering frequency. This quantity depends on the molecular polarizability $\alpha$ and the local field experienced by the molecule:

$$\mu = \mathbf{\alpha}_{RS} \cdot \mathbf{E}_L(r) e^{-i(\omega - \omega_s) t}$$

For molecules adsorbed at a metal surface, several effects are immediately apparent. Firstly, the incident field at the molecule will contain a surface reflected component in addition to the primary field, resulting in an enhancement by up to a factor of 2. Secondly, since the polarizability is a tensor quantity, orientation of the molecules at the surface may provide some enhancement (up to an order of magnitude) in scattering intensity compared to randomly oriented molecules in the gas or liquid phase. In general, though, these effects are minor compared to the enhancements of $10^3 - 10^6$ observed for molecules adsorbed on some types of surfaces.

In attempting to determine the cause of this enhancement, one may consider two different sources: (1) an enhancement of the effective polarizability of the metal/molecule system, or (2) an increase in the local field experienced by the molecule adsorbed at the metal surface. This is a convenient distinction in that field effects can be considered as strictly electromagnetic interactions of the dipole and surface fields, while chemisorption and other interactive effects can be modeled as modifications of the molecular polarizability. The enhancement of
Raman scattering and other surface processes is a complex effect, and an extensive and diverse body of work has been developed during the last six years to explain the phenomenon (see for example references 4 and 5). Some of this work that is pertinent to our results will be reviewed and then applied to a description of our experimental system.

1. Molecule/Surface Polarizability Enhancement

**Image dipole effects** Considering the molecule/surface system, we can describe the electric field at the position of a particular molecule as the sum of a number of different terms:

\[
E_I(r,t) = E_i(r,t) + E_r(r,t) + E_{im}(r,t) + E_{int}(r,t)
\]

In this expression the first term \(E_i\) is the electric field of the incident laser beam in the absence of the metal or molecule, \(E_r\) is the reflected field caused by the polarization of the solid by the incident field, \(E_{im}\) is the field generated by polarization of an adsorbed molecule by the incident and reflected fields, and \(E_{int}\) is the field at the point of the molecule under consideration due to the combined effects of other surface-adsorbed molecules. The field that we are interested in here is the "image" field \(E_{im}\) caused by the response of metal electrons to the induced dipole generated in an adsorbed molecule.

If we consider the polarized molecule as a point dipole in the electrostatic approximation (which means there is infinitely fast response of electrons to the dipole fields), the image field can be easily calculated as
The induced dipole in the molecule is given by the equation

\[ \mu_{\text{ind}} = \frac{\varepsilon_\text{M} + \varepsilon_\text{A}}{4\varepsilon_\text{A} r^3 (\varepsilon_\text{M} + \varepsilon_\text{A})} \]

where the primary field \( E_p \) is the sum of the incident and reflected fields at the molecule. Assuming for simplicity that only the components of the polarizability perpendicular to the surface are non-zero, we can solve these two equations to obtain for the induced dipole

\[ \mu = \bar{\alpha} \cdot (E_p + E_{\text{im}}) \]

(5) \hspace{1cm} \mu = \bar{\alpha} \cdot (E_p + E_{\text{im}})

We can now define an apparent polarizability of the molecule in the presence of the surface as

\[ \alpha_{\text{app}} = \frac{\mu}{E_p} \]

(7) \hspace{1cm} \alpha_{\text{app}} = \mu/E_p

The scattered intensity actually depends on the derivative of the polarizability with respect to the vibrational normal coordinate \( Q \), which for the apparent polarizability is
The intensity enhancement factor is finally calculated to be
\[
\frac{d\alpha_{\text{app}}}{dQ} = \left(1 - \frac{(\epsilon_M - \epsilon_A)}{3\epsilon_A^2(\epsilon_M + \epsilon_A)}\right)^{-1} \frac{d\alpha}{dQ}
\]

where \( G \) is a geometrical factor dealing with molecule orientation and scattering angles which typically has a value of about 10 for a smooth surface.\(^7\)

Important features of this model are: (1) prediction of enhancement for molecules adsorbed at smooth surfaces, (2) extremely rapid increase in the enhancement factor at short molecule-surface separations, and (3) prediction of enhancement for metals only in wavelength regions where free electron behavior exists. There are several approximations made in this model which must be questioned, the most serious of which has to do with the image approximation at short distances from the surface. Experimentally, image field theories have been shown to describe successfully nonradiative decay of molecular electronic excitations for distances as close as 7 Å to the surface.\(^8\)

At shorter distances, however, the approximations are less valid; image calculations of frequency shifts of molecular excitations for molecules on the surface have been shown to be seriously in error.\(^9\)

There have been several attempts to eliminate approximations in the
image model as sources of error in calculations by including the effects of spatial dispersion in the metal dielectric response, modelling the metal surface with a continuous distribution of electron density rather than an abrupt interface, and replacing the point dipole with a charge distribution of finite size. The model of Ford and Weber\textsuperscript{10} incorporates the effect of finite dipole size by modelling the molecule as a uniform dielectric sphere of radius \( a \) which has multipole polarizabilities

\[
\alpha_l = \frac{\epsilon_1\epsilon_3 - \epsilon_1}{\epsilon_3 + (1+1)\epsilon_1} a^{2l+1}
\]

where \( \epsilon_1 \) is the dielectric constant of the medium outside the metal and \( \epsilon_3 \) is the dielectric constant of the sphere. Nonlocal effects are included by modelling the metal dielectric response with a modified Lindhard dielectric function:

\[
\epsilon_t(k,\omega) = \epsilon_b(\omega) - \frac{\omega^2 f_t(z,u)}{\omega(\omega+i\gamma)}
\]

\[
\epsilon_1(k,\omega) = \epsilon_b(\omega) + \frac{3a^2 u^2 f_1(z,u)}{(\omega+i\gamma)(\omega + i\gamma f_1(z,0))}
\]
where

\[ f_1(z,u) = \frac{1}{2} + \frac{1}{8z} \left[ \left( 1-(z-u)^2 \right) \log \frac{z-u+1}{z-u-1} \right. \]
\[ \left. + \left( 1-(z+u)^2 \right) \log \frac{z+u+1}{z+u-1} \right] \]

\[ f_t(z,u) = \left( z^2 + 3u^2 + 1 \right) - \frac{3}{32z} \left[ \left( 1-(z-u)^2 \right)^2 \log \frac{z-u+1}{z-u-1} \right. \]
\[ \left. + \left( 1-(z+u)^2 \right)^2 \log \frac{z+u+1}{z+u-1} \right] \]

In these equations \( \varepsilon_t \) and \( \varepsilon_l \) are the transverse and longitudinal response of the metal, \( \varepsilon_b(\omega) \) is the contribution of bound electrons, \( \omega_p \) is the plasma frequency, \( z = k/2k_F \) where \( k_F \) is the Fermi wavevector, and \( u = \omega + iy \)/\( kv_F \) where \( v_F \) is the Fermi velocity. These equations are a fairly simple approach to including nonlocal effects in the response of the metal and will be used again later. The main consequences of including these corrections in the image enhancement model are a decrease in the maximum enhancement predicted at small distances. A decrease by a factor of 100 occurs for inclusion of nonlocal effects, and a further decrease of \( 10^2 \) to \( 10^3 \) occurs for inclusion of the effects of finite dipole size, resulting in an enhancement factor of less than \( 10^3 \).

Calculations have been done by Korzeniewski, Maniv, and Metiu\(^{11,12}\) for a jellium model which allows for continuous variation of electron density across the molecule/surface interface. A wavevector-dependent dielectric response of the metal was included in the model, but the molecule was treated as a point dipole. Their calculated enhancement factor for a distance of 1.6 Å from the surface was reduced by a factor
of approximately 100 from that of the simple image model, a result which is consistent with that obtained by Weber and Ford.

In summary, the simple image model has serious shortcomings in attempting to describe the properties of an adsorbate very close to the surface. Although a complete microscopic description of the metal/molecule system does not exist, electron-gas models incorporating spatial dispersion\textsuperscript{10,11} and the gradual change in electron density at the surface\textsuperscript{11} indicate that the image model must be modified to give a smaller shift in dipole frequency, a much weaker dependence of enhancement on the incident light frequency, and an enhancement factor smaller by several orders of magnitude.

**Vibrational modulation of surface electrons** For molecules in close proximity to a metal surface where there is substantial overlap of adsorbate and metal wavefunctions, the vibrational motion of the adsorbate molecules may be coupled to electrons in the substrate. The metal electrons may then scatter incident photons at the Raman Stokes frequency, increasing the effective polarizability of the adsorbed molecule. Although only a small fraction of metal electrons may be involved in the scattering process, these electrons are highly polarizable and may contribute substantial Raman intensity. A number of different models have been proposed for the coupling mechanism whereby adsorbate vibrations modulate the metal electrons; although these models are difficult to evaluate quantitatively, they may provide substantial enhancement for molecules directly on the surface.

Perhaps the simplest model of this sort is that proposed by McCall and Platzman\textsuperscript{13} where the Raman cross-section is enhanced by motion of
charges from the metal into the molecule during nuclear vibrations. Motion of the adsorbate along the metal-adsorbate bond with an amplitude \( \Delta r \) produces a change in the metal susceptibility \( \Delta \chi \) in a volume of metal involved in the charge transfer that is given by

\[
\Delta \chi = \frac{\partial \chi}{\partial q} \frac{\partial q}{\partial r} \Delta r
\]

where \( q \) is the amount of charge transferred to the surface. The quantity \( \partial \chi / \partial q \) is estimated from a free electron model of the metal where

\[
\varepsilon_M = 1 - \frac{\omega^2}{\omega^2} = 4\pi \chi + 1
\]

Putting an extra electron per unit volume into the metal surface results in a change in the derivative of the susceptibility \( \partial \chi / \partial q \) by \( \frac{e^2}{m \omega^2} \). This results in a calculated Raman cross-section of

\[
\frac{\partial \sigma}{\partial \Omega} = \frac{1}{3} \left( -\frac{e^2}{2c} \right)^2 \left( \frac{\partial q}{\partial r} \right)^2 (\Delta r)^2
\]

Estimating \( \partial q / \partial r \) as 0.2 electrons/Å and \( \Delta r \) as 0.1 Å, an enhancement of approximately 20 is predicted for a molecule in a chemisorbed system where there is vibrational displacement of the atom bound to the surface.

A similar reflectivity-modulation model was proposed by Otto and developed by Maniv and Metiu. It is based on the microscopic theory of reflection by a metal surface: reflection occurs when the metal absorbs a photon to create an electron-hole pair, which then recombine and emit a reflected photon. When a molecule is present on the surface...
the electron (or hole) can interact with the molecular ion cores through Coulombic forces and excite them vibrationally. The photon emitted by subsequent electron-hole pair recombination has the frequency \( \omega_l - \omega_v \) and is detected as a Raman photon. The model calculation is very complex, and has used the jellium approximation with an infinite barrier 1.624 Å from the jellium edge to describe the metal surface. It was found that if the charge oscillating at the vibrational frequency is very close to the jellium edge (less than 0.5 Å) a polarizability enhancement as large as \( 10^4 \) can be obtained. This large an enhancement, however, can only occur when the oscillation of nuclear charges can effectively induce electrons near the jellium edge to follow their oscillation.

Another type of polarizability enhancement model postulates a transfer of charge from the metal to the molecule (or vice versa) as an initial resonant excitation step. This type of model was initially proposed\(^{16} \) before the existence of such charge-transfer excitations were actually observed for molecules at metal surfaces.\(^{17} \) The general features of this model are illustrated in figure 1, where the density of states of silver is shown together with an adsorbed molecule resonance located in the vicinity of the Fermi energy. An incident photon may scatter an electron in the metal/molecule system from below the Fermi energy to an unoccupied part of the molecule resonance above the Fermi energy. This charge-transfer excitation results in a change of the potential of the molecule which may result in the molecule ending up in a vibrationally excited state. Recombination of the excited electron will then result in an emitted photon with less energy than the incident photon - a Raman process. A Hamiltonian describing this scattering process formulated by Persson\(^{18} \) is
Figure 1. Model for Raman enhancement by charge transfer excitations. The left part of the diagram shows the density of states of silver for different energies relative to the Fermi energy, and the right part shows an unoccupied molecular level that has been broadened and shifted near the surface.
\[ H = (\epsilon_a(Q) - edE_z) n_a + \sum_{k} \epsilon_k a_k^\dagger a_k 
+ \sum_{k} (V_{ak} a_k^\dagger + V_{ak}^* a_k) + \hbar v b^\dagger b + H_{em} \]

In this description \( Q \) is the displacement associated with a vibrational mode of the molecule and \( \epsilon_a(Q) \) is an energy level of the molecule calculated for fixed \( Q \). The coupling of the molecule with the electric field occurs through the term \( -edE_z n_a \). The variables \( \epsilon_k \) are a set of energy levels for electrons in the solid, and \( V_{ak} \) is a tunneling integral for transfer of electrons between the molecule and the solid.\(^{19}\) Using parameters obtained by Demuth and Sanda\(^{17a}\) for charge-transfer excitations of pyridine adsorbed on Ag(111), Persson calculates an approximate Raman enhancement of 30.

Finally, a model proposed by Jha et al.\(^{20}\) also provides enhancement due to modulation of the surface polarizability by ion core modulation of the laser induced metal surface charge density. A light wave incident on a metal surface generates an oscillating surface charge density of the form

\[ n_s(r, \omega) = -\frac{1}{4\pi e} \mathbf{V} \cdot \mathbf{E}(r, \omega) \]

The authors calculate the electric field outside of a metal grating by perturbation theory, from which they obtain the surface charge density as a step function at the surface:

\[ n_s(r, \omega) = \sigma_s(r, \omega) \delta(z - \xi) \]
where \( z = \xi(x,y) \) is the departure of the grating surface from a flat plane. The step function in surface charge density is then replaced by a more realistic smooth, exponentially decaying function whose range is determined from the surface barrier potential \( \phi_B \). This decay function of the surface charge density, which is calculated to be

\[
F(r, R_m) = A \exp\left(2\frac{x^2}{\xi} \right) \left(\frac{2m}{\hbar^2} (\phi_B + \phi_{OUT}(r, R_m))\right)^{1/2}
\]

depends on the adsorbate position since there is a potential \( \phi_{OUT} \) outside the metal arising from the atomic charges \( Z_{je} \) in the molecule.

The surface dipole moment varying at the Stokes frequency \( \omega - \omega_v \) is then obtained as

\[
\mu(\omega - \omega_v) = -e\int d^3r \ (r - z_\xi) \ n_s(r, R_m, \omega)
\]

which then contributes to the scattered Stokes amplitude. Numerical results for this model show that there is strong enhancement of scattering for low surface barrier heights \( \phi_B < 1.0 \text{ eV} \) when the separation of the molecule from the image plane is small \( (d < 10 \text{ Å}) \).

The frequency dependence of enhancement determined by this model will follow the frequency dependence for excitation of surface plasmon resonances in the metal.

2. Surface Field Enhancement

An alternative to increasing the effective molecular polarizability to obtain a larger induced dipole for Raman scattering is to increase
the local field experienced at the surface by an adsorbed molecule. This "classical field enhancement" model has been proposed in many different variations by many different researchers (see references 4 and 5), and is generally acknowledged to be at least partially responsible for enhanced Raman scattering in most experimental geometries.

There are several ways of obtaining enhanced surface fields at the site of an adsorbed molecule. One method is to excite a delocalized surface resonance with the incoming laser. The appropriate excitation at optical frequencies for metals is the surface plasmon, a nonradiative mode that may be excited by phase-matching with an optically dense medium (prism) or with a grating profile at the surface. Localized surface resonances may also be excited in small metal particles of varying size and shape that have properties quite different from the modes that can be excited at a planar surface. In addition to the overall enhancement of surface fields due to resonances, there are geometrical effects due to concentration of fields at regions of maximum curvature (the so-called "lightning rod" effect). Each of these effects will be discussed in more detail in the following sections.

**Excitation of surface plasmons** Electrons in metals that are near the Fermi level are essentially free electrons in that they can be easily excited into other energy and momentum states with photons of very small energies. The optical response of a collection of free electrons is described by the Drude dielectric function
where $\omega_p^2 = 4\pi n e^2/m$ is the plasma frequency, a function of the density of free electrons $n$ and the effective mass of an electron $m$. The Drude dielectric function vanishes at $\omega = \omega_p$ if damping is neglected, corresponding to a longitudinal collective excitation of electrons. This effect, called a plasma oscillation or plasmon, is caused by long-range correlation of electrons through Coulomb forces. In the more general case of non-zero damping, the Drude dielectric function vanishes at the complex frequency $\omega_p - i\gamma/2$. Here one can refer to the excitation of a plasmon with energy $\hbar \omega_p$ and lifetime $\tau = 2/\gamma$. For the plasmon to be a well-defined entity, however, it must have a lifetime sufficiently long that $\omega_p \tau \gg 1$.

In describing the dielectric response of a real metal such as silver one must also consider interband transitions, which give rise to a substantial bound-electron component of the dielectric function and appreciably alter the free-electron optical properties. Since polarizabilities are additive, we can write the dielectric function as a sum of components due to free electron effects and bound electron effects:

$$
\varepsilon(\omega) = \varepsilon_b(\omega) + \varepsilon_f(\omega)
$$

$$
= \varepsilon_b + (1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega})
$$
For silver the calculated plasma frequency is found to be $\omega_p = 9.2 \text{ eV}$ using the appropriate electron density for silver. An appreciable contribution from bound charges, however, pulls up the dielectric function curve (figure 2) so that the real part of the dielectric function is zero at 3.8 eV rather than 9.2 eV as calculated for a free electron response. The measured silver plasmon resonance frequency is thus at 3.8 eV.

The modes of a free-electron plasma discussed to this point have been for an unbounded plasma which is characteristic of the bulk of a material, for which resonances are termed bulk or volume plasmons. For electrons near the boundary of a material, though, the presence of that boundary modifies the collective properties of the system. Modes termed surface plasmons exist with a resonance frequency of $\omega_p/(1+\varepsilon_A)^{1/2}$ at the interface with a medium of dielectric constant $\varepsilon_A$, which are confined to propagation along the interface. A solution of Maxwell's equations at the interface of a metal with dielectric function $\varepsilon_M(\omega)$ in contact with a medium of dielectric constant $\varepsilon_A > 0$ gives the following equations for the electric fields of a plane wave at the interface:

\begin{equation}
E = E_0 e^{ikx-i\omega t} x
\begin{cases}
(1, 0, i\omega/(k^2-\varepsilon_A\omega^2/c^2)^{1/2}) e^{-z(k^2-\varepsilon_A\omega^2/c^2)} \\
(1, 0, -i\omega/(k^2-\varepsilon_M\omega^2/c^2)^{1/2}) e^{+z(k^2-\varepsilon_M\omega^2/c^2)}
\end{cases}
\end{equation}

where the upper term is for the region above the metal ($z > 0$) and the lower term is for the region inside the metal ($z < 0$). The boundary
Figure 2. The free electron component $\varepsilon_f$ and bound electron component $\varepsilon_b$ of the silver dielectric function. The complete dielectric function of silver is indicated by the dashed line.
condition for continuity of the z-component of the electric field at the interface gives the following relation:

\[
\frac{\varepsilon_M}{(k^2 - \varepsilon_M \omega^2/c^2)^{1/2}} = -\frac{\varepsilon_A}{(k^2 - \varepsilon_A \omega^2/c^2)^{1/2}}
\]

or

\[
k^2 = \frac{\omega^2}{c^2} \frac{\varepsilon_A \varepsilon_M}{(\varepsilon_A + \varepsilon_M)}
\]

Such a surface wave is termed a surface plasmon polariton (sometimes called just a surface plasmon) and equation 24 gives an explicit expression for the magnitude of the wavevector of this mode as a function of frequency. If we substitute in this equation the dielectric function from equation 22 and neglect damping, we obtain for the dispersion relation at the interface of a nearly free electron metal such as silver and a medium of dielectric constant \(\varepsilon_A = 1\):

\[
\omega^2 = \frac{1}{2} \left( \frac{c^2 k^2}{\varepsilon_b} (1 + \varepsilon_b) + \frac{\omega_p^2}{\varepsilon_b} \right)
\]

\[
-\frac{1}{2} \left( \frac{c^2 k^2}{\varepsilon_b} (1 + \varepsilon_b) + \frac{\omega_p^2}{\varepsilon_b} \right)^2 - \frac{4c^2 k^2 \omega_p^2}{\varepsilon_b} \right)^{1/2}
\]

This equation is plotted in figure 3 for the optical constants of silver. In the limit \(k \rightarrow 0\) one obtains the relation \(\omega = c k\), which is just the dispersion relation of a free electromagnetic wave (light). In the limit \(k \rightarrow \infty\) one obtains the relation \(\omega = \omega_p/(\varepsilon_b + 1)^{1/2}\), which for the case of a free electron metal with \(\varepsilon_b = 1\) is the surface plasmon resonance frequency mentioned earlier.
This plot illustrates an interesting point: when light is incident on the metal surface it couples only to excitations whose surface wavevector \( k \) is equal to the component of the wavevector of the incident light \( k_L \) that is parallel to the surface. The parallel component of the light wavevector is given by \( k_L = (\omega/c)\sin \alpha \) where \( \alpha \) is the angle of incidence of the light wave. This quantity is always less than \( \omega/c \) and consequently the wave will couple only to modes to the left of the line labeled \( k = \omega/c \) in figure 3. Thus for all frequencies less than \( \omega_p \) there will be no coupling between an incident electromagnetic wave and surface plasmon polaritons.

There are several possible schemes, though, for coupling an incident light wave to surface plasmon modes. One is illustrated by the dash-dotted line in figure 3 which represents the parallel component of the wavevector of light propagating in a medium (prism) of refractive index \( n_A > 1 \). As the prism is brought close to the silver surface, there will be coupling between the light propagating in the prism and the metal surface modes at the point where this line crosses the solid line representing the dispersion relation for surface plasmons. This type of coupling, first proposed by Otto,\(^{22}\) was shown in a calculation by Chen et al.\(^{23}\) to be responsible for up to two orders of magnitude of enhancement in surface Raman scattering through enhanced surface fields. Experiments by Dornhaus et al.\(^{24}\) on evaporated silver films indicate an enhancement of \( 10 < \xi < 75 \) for adsorbed pyridine by excitation of surface plasmon polaritons with p-polarized light, incident at the appropriate angle on the silver layer through a hemicylindrical prism.

A second mechanism for coupling light waves to surface plasmons is
Figure 3. The surface plasmon polariton dispersion curve for a silver surface plotted using an ellipsometrically determined dielectric function. The dashed line shows the dispersionless relation between the frequency and wavevector of light in vacuum, and the dash-dotted line that of light in a medium of refractive index $n_A$. 
through the use of a grating superimposed on the metal surface. Coupling will occur for a surface profile consisting of a well-defined grating with a single surface wavevector $g = (k_x, k_y)$, or for a statistically rough surface which may be considered as a superposition of a number of different gratings of different wavevectors. This form of coupling will be discussed in the next section for surfaces with small surface roughness where perturbation theory may be applied ($\delta/\lambda << 1$ where $\delta$ is the root-mean-square roughness height and $\lambda$ is the incident wavelength).

**Surface plasmons on rough surfaces** The study of the effects of surface roughness on the optical properties of materials has a long history dating back to the classic papers of Rayleigh. If roughness can be considered a small perturbation on a plane metal surface (roughness parameter $\delta/\lambda << 1$) then standard perturbation theory techniques may be applied to the problem. In this regime, classical treatments of the effects of roughness on the scattering properties of metal surfaces have been done by a number of authors. When a surface polariton propagates over a rough surface, though, it has been found that the dispersion relation is altered compared to that observed at a flat surface. Perturbation theory treatments of this effect have also been done by several authors, as well as a quantum mechanical calculation and a non-perturbative classical treatment. In the following pages, the effects of surface roughness will be discussed in a general form based on the work of Toigo et al. Specific applications of the theory to Raman scattering on a grating surface and a randomly rough surface will then be considered.
The effects of surface roughness on the properties of a metal will be discussed on the basis of the model shown in figure 4. The height of the surface above the mean surface plane is given by the roughness function $\xi(x)$ where $x$ is a vector in the $x$-$y$ plane. It is useful to describe the surface in terms of the Fourier components of the roughness:

\begin{equation}
\xi_g = \int d^2r \, e^{-i\mathbf{g} \cdot \mathbf{x}} \xi(x)
\end{equation}

For a grating surface with a well-defined structure, one only needs to consider a single Fourier component $\xi_g$ where $g$ is the periodicity of the grating. Since we are using a linear theory, each Fourier component of the roughness of a randomly rough surface can be considered independently and the total effect determined by a superposition of the effects of each component.

For a randomly roughened surface, the roughness profile function $\xi$ is in general not known; the surface is described in terms of certain statistical properties of this function. The probability that $\xi(x)$ has a particular value at a point $x$ is given by a probability distribution function:

\begin{equation}
\langle \xi(x)\xi(x') \rangle = \delta^2 W(|x|)
\end{equation}

where $\delta = \langle \xi^2(x) \rangle^{1/2}$ is the root-mean-square height of the roughness above the mean surface plane and $W$ is a correlation function. To obtain quantitative results from the theory, one must use some explicit form for this correlation function such as the Gaussian form $W(|x|) =
Figure 4. A description of surface roughness at a vacuum interface using the roughness profile function $\xi(x,y)$.
\[ \exp(-x^2/\sigma^2). \] In this expression \( \sigma \) is the correlation length of the surface features. For a random surface such as this, the Fourier components \( \xi_g \) are also random quantities with the properties

\begin{align}
(28a) & \quad \langle \xi_g \rangle = 0. \\
(28b) & \quad \langle \xi_g (g) \xi_g (g') \rangle = (2\pi)^2 \delta^2 G(g) \delta(g-g')
\end{align}

where \( G(g) = \int d^2x \exp(-ig \cdot x) \mathcal{W}(|x|) \) is the "roughness power spectrum".

We can now consider the effects of such roughness on the properties of a metal surface when a light wave with electric field \( E_i(r,t) \) is incident upon it. The problem consists of solving Maxwell's equations

\begin{align}
(29) & \quad \nabla \times \nabla \times E(r,t) - \frac{\omega^2}{c^2} r(r,\omega) E(r,\omega) = 0 \\
(30) & \quad B(r,\omega) = \frac{c}{i\omega} \nabla \times E(r,\omega)
\end{align}

In these equations the dielectric function is given by a step function at the surface \( \epsilon(r,\omega) = \epsilon(\omega) \Theta(z-\xi) + \Theta(\xi-z) \). The boundary conditions are that the tangential components of the electric and magnetic fields must be continuous across the actual surface \( z = \xi(x) \). The solutions to Maxwell's equations will contain, in addition to the reflected and transmitted waves with tangential wavevectors \( k_t \), secondary waves induced by roughness with tangential wavevectors \( k_g = k_t + g \). The condition for the existence of a surface plasmon wave solution to these equations is to have \( k_g^2 > \omega^2/c^2 \). When this relationship is true the solutions to equation 29 can be written in the form
ik-z -ik-z

(3.1) \( E = (E_1 e^{-ik_z} + E_r e^{ik_z}) e^{-iK \cdot x} + E_g e^{-iK \cdot z} \) for \( z < \zeta \)

(3.2) \( E = E_t e^{-iK \cdot z} + E_g e^{iK \cdot z} \) for \( z > \zeta \)

where

\( \gamma_g = (k^2_g - \frac{\omega^2}{c^2})^{1/2} \)

\( \gamma^2 = k_t^2 - \frac{\omega^2}{c^2} \epsilon(\omega) \)

\( \gamma_g^2 = k_g^2 - \frac{\omega^2}{c^2} \epsilon(\omega) \)

and where \( k_t \) and \( k_z \) are the tangential and normal components of the wavevector, respectively. The notation used here is that of Jha et al.\(^\text{20}\) To solve for the fields, the equations must be expanded in the roughness \( \xi \) in the fashion \( e^{ik\xi} = 1 + i\xi + \ldots \) and the boundary conditions at the interface applied. Then by equating the Fourier components separately on both sides of the interface, the equation that is obtained for the p-polarized secondary field outside the metal surface is

\[
(3.2) \quad \frac{E_p}{g} = \frac{2(\xi \cdot K) k \gamma (1-\epsilon) \gamma_k \cdot K + \epsilon \gamma_k \cdot K/\gamma}{k_t (\epsilon \gamma_k + \gamma)} \left( \frac{\gamma_k \cdot K + \epsilon_k \cdot K/\gamma}{(\epsilon_k + i\gamma)} \right) \frac{E_p}{iz} + \frac{ik \cdot (k \times K) z}{(k + i\gamma)} \frac{E_s}{iz}
\]

where the incident field \( E_1 \) and the secondary field \( E_g \) have been split
up into s- and p-polarized components as follows:

\[(33a)\]
\[E_i = E_i^s(k \times \hat{z}) + E_i^{ll} k \times \hat{z} + E_i^p \hat{z}\]

\[(33b)\]
\[E_g = E_g^s(k \times \hat{z}) + E_g^{ll} k \times \hat{z} + E_g^p \hat{z}\]

Calculations of the electric field enhancement for Raman scattering based on equation 32 have been done by Jha et al.\(^{20}\) for the case of a silver grating. They calculate an enhancement factor proportional to 

\[|E_g^p \exp(-ra)/E_i^s|^2\]

where \(a\) is the effective distance of the molecule from the metal surface. Examining the equation for the secondary field \(E_g^p\) it can be seen that the field may become quite large at the surface plasmon frequency determined by the dispersion relation

\[\text{Re}(\epsilon r_g + \gamma_g) = 0.\]

Numerical results have been computed for a grating periodicity of 800 nm, \(\xi_g K_g = 0.2\), and 530 nm incident light; an enhancement of approximately \(10^4\) is calculated for light incident at the right angle for surface plasmon excitation.

A recent calculation by Weber and Ford, however, has indicated that the maximum enhancement that may be expected from coupling to surface plasmons is a factor of 200 based on energy conservation requirements.\(^{37}\) They believe the discrepancy by a factor of 50 from the calculation of Jha et al is due to the failure of first-order perturbation theory when the enhancement is large. Results by Sanda et al.\(^{38}\) for enhancement of pyridine adsorbed at a 1000 nm silver grating are consistent with a long-range enhancement of only 100 for coupling to plasmon modes.

The problem of calculating the fields and dispersion relation for a
surface polariton propagating over a randomly rough surface is more
difficult than solving the same problem for a grating. The difficulties
arise from the necessity of obtaining the electric field explicitly as a
function of the surface profile $\xi$ so that averaging over the ensemble of
possible rough surface profiles can be carried out. If we assume a
statistical form for the roughness features such as was discussed at the
beginning of this section, however, we can obtain the mean electric
field by averaging over the Fourier components of the roughness using
the statistical properties of the correlation function.

There are several important effects of random roughness on the
optical response of a metal surface. Firstly, there is an increase in
the electric field due to coupling to plasmons as was observed for a
grating. Secondly, the surface plasmon dispersion relation is modified
by the presence of the roughness. Toigo et al. have obtained the
dispersion relation for a surface with small random roughness by summing
the equations for surface fields over all wavevector components and
determining their resonance properties. In the same notation as used
earlier, this relationship is

\[
\epsilon \Gamma \gamma G = \delta^2 (1-e)^2 \int \frac{d^2k'}{(2\pi)^2} G(g-g') \frac{(K \cdot k' - \Gamma \gamma)(K \cdot k')}{(\epsilon_k + \gamma_k^2)}
\]

This expression may be contrasted with the simple expression described
earlier (equation 24) for the relation between $k$ and $\omega$ for a surface
plasmon polariton on a flat surface. In order to determine some of the
properties of a surface polariton propagating on a rough surface,
Maradudin\textsuperscript{34} makes the approximation that $\epsilon(\omega)$ appearing in equation 34 is purely real everywhere except in the denominator of the equation, where the small imaginary part of the dielectric function is retained. When this is done, he has shown that the equation can be rewritten in the form

$$\omega = \omega_0 + \Delta(k_t) - i\Gamma(k_t)$$

where $\omega_0$ is the frequency of a surface polariton at a flat surface, $\Delta$ is the shift in the frequency of the polariton due to surface roughness, and $\Gamma$ is related to the inverse lifetime of the mode due to attenuation by roughness. Using a Gaussian roughness power spectrum and the metal dielectric function of equation 21, Maradudin and Zierau\textsuperscript{31} have carried out numerical evaluations of $\Delta$ and $\Gamma$. For $\delta = \gamma = 250$ nm they find that surface roughness decreases the frequency of the excitation relative to that for a flat surface; for $k_t$ corresponding to visible frequencies the lifetime is also decreased by about 10 percent.

There have been very few attempts to calculate the surface enhancement factors for Raman scattering due to surface plasmons on statistically rough surfaces. Aravind and Metiu\textsuperscript{39} calculated the enhancement in emission intensity of a dipole near a surface with small Gaussian roughness based on the perturbation theory method of Maradudin and Mills.\textsuperscript{28} For a dipole spaced 2 Å from a silver surface with a mean roughness amplitude of 30 Å, they calculate an enhancement in emission intensity of 10 when the correlation length of the roughness is 20–50 Å. This small enhancement factor agrees with the qualitative discussion of Weber and Ford,\textsuperscript{37} who argue that coupling to surface
plasmons for statistically rough surfaces should be much lower than for grating surfaces where the plasmon resonance conditions can be matched by angle tuning.

Other recent calculations have addressed the question of enhancement at rough surfaces from a non-perturbation theory approach. An approximation method is used to obtain the two-photon Green's functions for a statistically rough surface, which are then used to solve the Bethe-Salpeter equation. Numerical results are presented for enhancement of electric field intensity near a surface with a Gaussian profile. Neglecting damping, an enhancement of 50-1000 is calculated over the visible frequency range for a silver surface with $\delta = 150 \text{ Å}$ and $\sigma = 400 \text{ Å}$. This enhancement is peaked at 3.2 eV, in contrast to first order perturbation theory results which have a very weak dependence on frequency.

The extent of enhancement by excitation of extended surface plasmon modes relative to field enhancement due to other effects has also been addressed in some recent experimental work. Coupling to surface plasmons was obtained using the prism coupling arrangement with light incident at the angle giving a surface reflectance minimum. The increase in the field enhancement for optimum coupling was determined to be approximately 20 for a flat surface. When the surface was roughened by electrochemical treatment, the field enhancement from this coupling dropped to a factor of 5 as determined from the change in surface reflectivity at the optimum coupling angle. The total Raman enhancement increased to $10^4$ for the roughened surface, so coupling to extended surface plasmon modes provided only a very small fraction of the total enhancement.
Resonance effects in small metal particles. As deviations from a planar surface become large ($\delta/\lambda > 0.02$) the effects of geometrical resonances in isolated protrusions of the surface become important. To a first approximation, these deviations from the surface can be modelled as half-spheres on top of a flat plane. If the planar surface is a perfect conductor (not too bad an approximation for silver in the visible region of the spectrum), the solution to the problem of the half-sphere/plane system is similar to that for an isolated sphere. For spheres that are small compared to the incident wavelength so that the electric field at one point of the sphere can be considered to act instantaneously on all other points in the sphere, the problem can be solved in the electrostatic limit. The problem of calculating the fields at the sphere for an incident light wave then reduces to solving Laplace's equation with the appropriate boundary conditions. Within the sphere the electric field intensity is uniform and is given by

\begin{equation}
E = \frac{3\varepsilon_A}{(\varepsilon_M + 2\varepsilon_A)} E_i
\end{equation}

The sphere has an induced dipole moment due to the incident light

\begin{equation}
\mu = 4\pi \varepsilon_A a^3 \frac{(\varepsilon_M - \varepsilon_A)}{(\varepsilon_M + 2\varepsilon_A)} E_i
\end{equation}

where $a$ is the sphere radius. The sphere now acts as an excited dipole which radiates a secondary field in all directions. This secondary field is given by the expression
at a distance \( r \) from the sphere in a direction \( \hat{r} \). Very close to the sphere the induction field given by the first term in equation 38 dominates; far from the sphere the only term that has appreciable magnitude is the third term which is the radiation field of the dipole.

It can be seen from these equations that the sphere has a resonance at the frequency where \( \varepsilon_M = -2\varepsilon_A \). Using the dielectric function for a free electron metal (equation 21) and neglecting damping, we find that this resonance frequency is

\[
\omega^2 = \frac{\omega_p^2}{1 + \frac{2\varepsilon_A}{\varepsilon}}
\]

This behavior is similar to that discussed previously for a flat surface, and the resonance frequency is termed the surface plasmon frequency of the sphere. The use of a bulk metal dielectric function in this equation is in general justified from experimental results, except in the case where the metal particle is smaller than the mean free path of conduction electrons. When this occurs, damping in the particle will be dominated by collisions with the particle boundary.\(^{43}\) This type of scattering modifies only the free-electron part of the metal dielectric function (equation 22) by adding an additional term to the damping constant \( \gamma \):

\[
\gamma = \gamma_{\text{bulk}} + \frac{v_F}{l}
\]
where $v_F$ is the velocity of conduction electrons at the Fermi surface and $l$ is the effective mean free path for collisions at the particle boundary. This mean free path is given approximately by $4a/3$ where $a$ is again the sphere diameter.\(^4\) The effect of this term is to increase the imaginary part of the dielectric function by about 10 percent for a 1000 Å radius sphere, and more than double it for a 100 Å sphere. This will both increase the width and lower the peak height of the surface plasmon absorption resonance.

In contrast to the plane surface results discussed previously, the surface plasmon modes of a sphere are radiative and can be excited by light incident on the sphere. Near the sphere surface plasmon resonance, defined as $\text{Re}(\varepsilon_M + 2\varepsilon_A) = 0$, the effective local field experienced by a molecule placed near the sphere will be enhanced relative to the applied field $E_i$. As discussed by McCall, Platzman, and Wolff\(^4\) the average Raman cross-section is expected to be enhanced by a factor proportional to $\left(\frac{\varepsilon_M - \varepsilon_A}{\text{Im} \varepsilon_M}\right)^4 \left(\frac{a}{r}\right)^{12}$ compared to the scattering from a free molecule. Assuming a distribution of resonant sphere frequencies, they calculate an enhancement of approximately $10^6$ in the resonance region. The enhancement is predicted to vary with distance from the sphere as $\left(\frac{a}{a + d}\right)^{12}$ where $a$ is the sphere radius and $d$ is the distance from the sphere surface, making it a fairly long-range effect.

When the spheres that we are considering are large enough that their diameter is an appreciable fraction of the wavelength of the light that is incident on them, the simple electrostatic picture used above is no longer adequate and the effects of phase retardation must be considered. The electrodynamic calculation for the interaction of light with metal spheres was first done by Mie,\(^4\) and has been discussed in
some detail by many modern authors (see references 46-48). The problem consists basically of solving the wave equations (equations 41a and b) describing the time-dependent electromagnetic field in a linear, isotropic, homogeneous medium while taking into account the boundary conditions appropriate for a spherical geometry.

\begin{align*}
(41a) & \quad \nabla^2 \mathbf{E} + k^2 \mathbf{E} = 0 \\
(41b) & \quad \nabla^2 \mathbf{H} + k^2 \mathbf{H} = 0
\end{align*}

The electric and magnetic fields in these equations are related to each other through the Maxwell relations

\begin{align*}
(42a) & \quad \mathbf{\nabla} \times \mathbf{H} = -k_1 \mathbf{E} \\
(42b) & \quad \mathbf{\nabla} \times \mathbf{E} = k_2 \mathbf{H}
\end{align*}

where

\begin{align*}
k_1 &= \frac{i\omega}{c} (\varepsilon + \frac{i\omega \sigma}{\omega}) \\
k_2 &= \frac{i\omega}{c} \\
k^2 &= -k_1 k_2
\end{align*}

and where the assumption has been made that the time dependence of the fields is a harmonic function \( e^{i\omega t} \).

From the work of Born and Wolf\(^4\) it can be shown that the solution to the vector wave equation (equation 41) can be related to the solution of the scalar wave equation
The quantities $\Theta$ and $\Psi$ that satisfy this equation corresponding to the vanishing of the electric or magnetic field in equation 41 are known as Debye potentials. The scalar wave equation written in spherical coordinates becomes

\[
\frac{1}{r^2} \frac{\partial^2 (r\Pi)}{\partial r^2} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \Pi}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Pi}{\partial \phi^2} + k^2 \Pi = 0
\]

The boundary conditions that must be satisfied are that the potentials $\Theta$ and $\Psi$ and their derivatives must be continuous at the sphere surface \( r = a \).

Solutions can be found for equation 44 by separation of the variables \( r, \theta, \) and \( \phi \), letting $\Pi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$. This gives the separated equations

\[
\begin{align*}
\frac{d^2 (rR)}{dr^2} + (\kappa^2 - \frac{\alpha^2}{r^2})rR &= 0 \\
\frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta}) + (\alpha - \frac{\beta}{\sin^2 \theta}) \Theta &= 0 \\
\frac{d^2 \Phi}{d\phi^2} + \beta \Phi &= 0
\end{align*}
\]

General solutions to these equations are well-known and have the forms

\[
\begin{align*}
(46a) \quad rR &= c_1 \psi_1(kr) + d_1 \chi_1(kr) \\
\end{align*}
\]
(46b) \[ \Theta = \mathcal{P}_{1}^{(m)}(\cos \theta) \]

(46c) \[ \phi = a_{m} \cos(m\phi) + b_{m} \sin(m\phi) \]

for \( m \) integer \( 1 > |m| \) integer

In these equations \( \psi_{1} \) and \( \chi_{1} \) are half-order Bessel and Neuman functions, respectively, and \( \mathcal{P}_{1} \) is an associated Legendre function. The general solution to the wave equation is obtained as the product of the equations:

\[
(47) \quad \Pi = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathcal{P}_{l}^{(2)}(\theta) \]

The scalar potentials that are obtained are then expanded in spherical harmonics and the appropriate boundary conditions at the surface are applied. This yields a series of linear equations in the expansion coefficients, which are solved to give the scattering coefficients \( a_{1} \) and \( b_{1} \) for the fields outside the sphere:

(48a) \[ a_{1} = \frac{\psi_{1}(\alpha)\psi'_{1}(\beta) - \omega_{1}(\beta)\psi'_{1}(\alpha)}{\zeta_{1}(\alpha)\psi'_{1}(\beta) - \omega_{1}(\beta)\zeta'_{1}(\alpha)} \]

(48b) \[ b_{1} = \frac{\omega_{1}(\alpha)\psi'_{1}(\beta) - \psi'_{1}(\beta)\psi'_{1}(\alpha)}{\omega_{1}(\alpha)\psi'_{1}(\beta) - \psi_{1}(\beta)\zeta'_{1}(\alpha)} \]
where \( \zeta_1 = \phi_1 - i \chi_1 \) is a Hankel function
\[ m = k_{\text{inside}}/k_{\text{outside}} \]
\[ \alpha = a k_{\text{outside}} \]
\[ \beta = a k_{\text{inside}} \]

The net energy flow in the sphere system can be calculated from the time average of the Poynting vector \( S = (E_i + E_s) \times (H_i + H_s) \) where the subscripts refer to the incident and scattered waves. In terms of the scattering coefficients in equation 48 the scattering efficiency \( Q_{\text{sca}} \) of the sphere (scattered power/incident power) is

\[
(49) \quad Q_{\text{sca}} = \frac{2}{(ka)^2} \sum_{l=1}^{\infty} (2l+1)(|a_l|^2 + |b_l|^2)
\]

As pointed out by Messinger et al\(^{49}\) \( Q_{\text{sca}} \) can be considerably greater than one for certain sphere parameters, indicating that the strength of the local fields around the sphere can be considerably greater than those of the incident wave that excited them. The scattering efficiency defined above is actually a measure of the far-field region \( R \gg a \):

\[
(50) \quad Q_{\text{sca}} = \lim_{R \to \infty} \frac{R^2}{\pi a^2} \int_0^{2\pi} \int_0^\pi E_s E_s^* \sin \theta \, d\theta \, d\phi
\]

In order to better describe the near-field effects of the sphere a new quantity can be defined as

\[
(51) \quad Q_{\text{nf}} = \frac{R^2}{\pi a^2} \int_0^{2\pi} \int_0^\pi E_s E_s^* \sin \theta \, d\theta \, d\phi \bigg|_{R=a}
\]

which is a near-field form of \( Q_{\text{sca}} \). In terms of the scattering
coefficients of equation 48 this efficiency is

\[ Q_{nf} = 2 \sum_{l=1}^\infty \left\{ |a_l|^2 [(l+1)|\xi_{l-1}^{(2)}|^2 + 1|\xi_{l+1}^{(2)}|^2] + (2l+1)|b_l|^2 |\xi_l^{(2)}|^2 \right\} \]

Numerical evaluations of this function have been done using the dielectric function of silver \(^4^9\), and give \( Q_{nf} = 1000 \) for a 220 \( \AA \) sphere at the resonance peak at 400 nm. For larger spheres retardation and multipole resonances give rise to additional peaks in the efficiency and shift the dipole resonance to longer wavelengths. A 1000 \( \AA \) sphere has a dipole resonance peak at 406 nm and a secondary peak at 500 nm, but the maximum efficiency has dropped to 80.

The calculations examined to this point for spheres consider only the increase in excitation of a molecule near a sphere due to increased local fields. The problem of calculating reradiation by the molecule in the presence of the sphere such as occurs in Raman scattering is considerably more complex. The theory has been worked out in detail, though, including both enhancement of the local field at the incident frequency and the reradiation efficiency at the Stokes scattered frequency. \(^5^0\) Numerical evaluations of the theory give results very similar to the features discussed above when only enhancement of molecular excitation was considered: maximum enhancement for small particles, decreasing as particle size increases and showing multipolar resonances at longer wavelengths. Raman enhancement may thus to a good approximation be considered as the square of the enhancement calculated for increased excitation due to local fields.

The model of surface roughness as hemispheres on a perfectly
conducting substrate which has been discussed so far may be improved by considering coupling between a hemispherical bump and an underlying surface with a real metal dielectric response. The geometry depicted in figure 5 has been analyzed by Ruppin,51 where the hemispherical bump and the surface from which it protrudes both have the same dielectric function. Calculated resonance modes will be surface plasmons of the entire plane-bump system. Using the method of Berreman,52 the potentials in the three regions of figure 5 are expanded in Legendre functions. Boundary conditions for the continuity of the tangential component of the electric field and the normal component of the electric displacement are applied at the interface regions, and equations for the expansion coefficients obtained. The calculation is done using the electrostatic approximation. Numerical results for the increase in Raman signal due to the increase in the electric field at the position of the molecule are an enhancement factor of $10^3$ at resonance conditions. The resonance extends over the energies 2.5-3.5 eV, but might be expected to extend to lower frequencies if less regular shapes are taken into account. The dependence of enhancement on separation of the molecule from the surface was calculated for a bump of 100 Å radius, where enhancement is predicted to drop by a factor of 10 at the third layer of molecules on the surface.

As a step toward considering more irregular surface geometries, several calculations have been done for the electromagnetic resonances of ellipsoidal particles.53-57 In the electrostatic approximation (for $a/\lambda \ll 1$) the problem reduces to finding the solution to Laplace's equation with the appropriate boundary conditions as was done for a sphere. The coordinate system for this geometry is that of a spheroid,
Figure 5. A model for surface roughness based on hemispherical bumps which consist of silver spheres half-buried in a surface with the same dielectric function.
related to cartesian coordinates as follows:

\[ x = f((\xi^2 - 1)(1 - \eta^2))^{1/2} \cos \phi \]
\[ y = f((\xi^2 - 1)(1 - \eta^2))^{1/2} \sin \phi \]
\[ z = f\xi \eta \]

where \( f = (a^2 - b^2)^{1/2} \) is a size parameter for a spheroid with a semi-major axis \( a \) and semi-minor axis \( b \). The surface of a spheroid is defined by \( \xi = \xi_0 \) where \( \xi_0 = a/f \). The dipole induced in a spheroid by an incident light wave is found after some calculation to be

\[ (53) \quad u = \frac{f^3 \xi_0 c_A (\varepsilon_M - \varepsilon_A)}{3Q_1(\xi_0)(\varepsilon_M + \chi \varepsilon_A)} E_1 \]

where \( Q_1 \) is a Legendre function of the second kind and \( \chi \) is given by the following expression:

\[ (54) \quad \chi = -1 + \left\{ (\xi_0^2 - 1)(-\frac{\xi_0}{2} \ln(-\frac{\xi_0 + 1}{\xi_0 - 1}) - 1) \right\}^{-1} \]

The factor \( \chi \) varies from 2 to \( \infty \) as the ratio \( a/b \) varies from 1 (a sphere) to \( \infty \) (an infinitely narrow ellipsoid). There is a surface plasmon resonance of the spheroid defined as the frequency at which the denominator of equation 53 vanishes; i.e., where \( \varepsilon_M = -\chi \varepsilon_A \). The plasmon resonance of the spheroid thus depends on its aspect ratio, since \( \chi \) is a function of the spheroid shape. The resonant frequency calculated from equations 53 and 54 using the dielectric function of silver is shown in figure 6 as a function of spheroid aspect ratio \( a/b \). As can be seen from this plot, the resonant frequency is in the visible region of the
Figure 6. Calculated resonance frequencies of spheroids with different aspect ratios from electrostatic theory (equation 53).
spectrum for aspect ratios between 2 and 4. Calculations of Raman enhancement for a molecule placed near such a particle\textsuperscript{53,54} indicate that at a resonant frequency of 2.5 eV for 2:1 spheroid, enhancement may be as large as $10^8$ for a molecule 5 Å from the tip of the particle.

There are several approximations made in this model, however, which can be treated in a more accurate fashion in more complex calculations. One of these approximations is that the calculation was done in the small particle limit using the electrostatic model. As the dimensions of a spheroid are increased, retardation effects become important and a full electrodynamic calculation must be done as was done for Mie scattering by a sphere. One approach is to solve the vector wave equations (equations 41a and b) as was done for the sphere, this time separating the scalar wave equation in the spheroidal coordinate system and applying boundary conditions for scattered waves at the surface of the spheroid.\textsuperscript{55} An alternative method is based on an integral equation formulation of the scattering problem, and involves obtaining a transition matrix (T-matrix) which linearly relates the expansion coefficients of the incident and scattered waves at an arbitrarily shaped particle.\textsuperscript{58} A numerical calculation has recently been done for silver spheroids using this latter method\textsuperscript{57} where the surface-averaged electric field intensity of the particle was calculated. The same general features were observed with increasing particle size in this calculation as were observed in the electrodynamic calculation for spheres: (1) the main (dipolar) resonance shifts to lower energies, (2) multipolar resonances become evident, and (3) the field intensity decreases rapidly as the particle becomes larger. Shown in figure 7 are calculated enhancements for silver spheroids with an
Figure 7. Calculated Raman intensity enhancements at the surface of a 2:1 aspect ratio spheroid as a function of spheroid size and incident wavelength (from reference 57).
aspect ratio of 2:1 as a function of particle size and incident wavelength from the calculation of Barber et al.\textsuperscript{57} The average enhancement at the plasmon resonance frequency is a factor of 100 for a spheroid with a semi-major axis of 500 Å and drops to a factor of 50 when the size increases to a semi-major axis dimension of 1000 Å.

Still not considered in any of the models discussed yet are the effects of interactions between particles that are spaced relatively close together. This effect was considered for a pair of spheres by Aravind et al.\textsuperscript{59}, who concluded that noticeable effects could be observed if the spheres were brought closer together than a distance equal to half a sphere radius. The interaction effect was to split the sphere resonance, with a second resonance peak appearing at longer wavelengths than the single sphere peak. A secondary effect observed was a redistribution of the electric field, with an increased local field observed between the spheres and a smaller field outside of this space.

Coupling effects between metal spheroids have been calculated by Laor and Schatz.\textsuperscript{60} They considered dipolar coupling between a large number of hemispheroids, calculated by determining the induced dipole moment $\mu_i$ in the $i^{th}$ hemispheroid due to both the incident field and the fields of all the other dipoles. They obtain for the induced dipole

\begin{equation}
\mu_i = \frac{\sigma^2 \varepsilon_0 \varepsilon_A (\varepsilon - \varepsilon_A)}{3 \varepsilon_0 ( \varepsilon_0 + \chi \varepsilon_A)} (E_0 + \sum_{j \neq 1} \frac{\mu_j}{R_{ij}^3})
\end{equation}

where $R_{ij}$ is the separation between the centers of the $i^{th}$ and $j^{th}$ hemispheroids. Other variables are the same as defined for previous
equations. This equation can be rearranged to obtain in vector notation

\[ \mu = (\mathbf{D})^{-1} \alpha \mathbf{E}_0 \]

where \( D_{ij} = \delta_{ij} + (a_{ij}/R_{ij}^3)(1 - \delta_{ij}) \), and where \( \alpha_i \) is the factor outside the brackets in equation 55. When the determinant of \( \mathbf{D} \) vanishes, plasmon resonances of the coupled system exist. Calculation of the resonant frequencies for clusters of hemispheroids show that the number of resonance peaks depends on both the size and the symmetry of the cluster. A statistical calculation for a large number of hemispheroids with random dimensions between 0 and 200 Å was done. The particles were spread randomly on a square region 1000 Å across and periodic boundary conditions were used to extend the geometry to an infinite array. Raman intensity enhancements for silver were calculated to be \( 10^2-10^3 \) for all visible wavelengths.

Finally, coupling of hemispheroidal particles on a silver surface with the plasmon modes of the surface has been calculated by Das and Gersten. The same technique is used as in the calculation by Ruppin for coupling of hemispherical particles to a metal surface that has the same dielectric constant as the particle. Damping of local bump excitations is also accounted for in this calculation by including the classical decay rate of a dipole (in this case the induced dipole in the spheroid) near a metal surface. They find that the dipolar resonance frequency of an isolated spheroid is decreased by approximately 0.4 eV when the interaction with the surface is included.

A practical estimate of the importance of electromagnetic resonances of small particles for enhancement of Raman scattering of
adsorbed molecules has been obtained by Lyon and Worlock\textsuperscript{62} in a simple experiment using silver island films. Silver islands with diameters of 200–600 Å were deposited on a variable thickness SiO wedge on top of pyrolytic graphite, which is a lossy medium and strongly damps plasmon resonances in the silver particles. The Raman signal is shown to be decreased by a factor of 300 for molecules adsorbed on silver islands close enough to the graphite for damping of the island plasmon resonance to occur. Thus excitation of resonant plasmon modes in 200–600 Å particles in this geometry contributed a factor of 300 to Raman enhancement.

"Lightning rod" enhancement In the previous discussion it has been tacitly assumed that Raman scattering from molecules in each system is enhanced uniformly for all of the molecules involved. The electric field distribution at the metal surface in some of these systems, however, is highly non-uniform and the enhancement factors that have been discussed are averaged factors for a uniform coverage of Raman scatterers. The electric field at the surface of a metal shape is a maximum at the regions of greatest curvature, so Raman scattering will be most highly enhanced at the tip of a protrusion from the surface by a purely geometrical factor which is termed the "lightning rod" effect.

This effect has been discussed for Raman enhancement at silver ellipsoids by Liao and Wokaun.\textsuperscript{63} Rather than calculating the electric fields at the ellipsoid surface using Legendre polynomials as was discussed earlier, they express the fields in terms of depolarization factors. In their notation, the electric field at the tip of a spheroid in a laser field $E_1$ is given by
where \( \varepsilon \) is the dielectric function of the spheroid and \( A_a \) is a depolarization factor. At large distances from the spheroid, the electric field will simply be the radiation field due to the dipole induced in the spheroid given by equation 53. In the notation used here, the long range field is

\[
E_{\text{dipole}} = \frac{2\mu}{3a^2} = \frac{2b^2}{3a^2} \left( \frac{(\varepsilon - 1)}{1 + (\varepsilon - 1)A_a} \right) E_1
\]

At small distances from the spheroid surface, the shape concentrates the field at the tip by a factor which is the ratio of the fields in equations 57 and 58:

\[
\gamma = \frac{3}{2} \left( \frac{a}{b} \right)^2 (1 - A_a)
\]

For a sphere the factor \( A_a = 1/3 \) and \( \gamma \) is 1; for a 3:1 prolate spheroid \( A_a = 0.1087 \) and \( \gamma = 12 \). Thus for certain shapes of particles or surfaces, the electric field may be highly concentrated by geometric effects.
C. Experimental Section

Raman scattering was investigated for molecules adsorbed on the (110) and (111) faces of silver single crystals in an ultrahigh vacuum (UHV) environment. The crystals were cut by spark erosion from a silver rod (Aremco Products, 99.999+ % purity) and oriented to within ± 0.5° of the desired surface plane by Laue diffraction. The crystal surfaces were all initially prepared by mechanical polishing to a mirror finish by the following steps: abrasion on graded Al₂O₃ grit polishing paper, followed by polishing on a wheel with 6 μm and then 1 μm diamond paste, followed by polishing on a vibratory polisher using 0.05 μm Al₂O₃ slurry on a highly napped cloth. Additional polishing was performed on some surfaces by a combination of electropolishing and chemical polishing techniques to remove surface layers damaged by the mechanical polishing sequence. Electropolishing was done at a constant cell potential of 5 V by momentarily immersing the crystal in an electrolyte solution described by Tegart. This procedure was alternated with chemical polishing in an acidic chromate solution (100 ml saturated K₂Cr₂O₇, 2 ml saturated NaCl, 10 ml concentrated H₂SO₄; diluted to twice original volume with distilled water) until a mirror finish was obtained with no observable scratches under low power magnification. Electron microscopy of these surfaces shows that the submicron scratches produced by the mechanical polishing procedure are removed by this process, leaving a slightly wavy surface (figure 8).

Controlled roughness was introduced on these smooth surfaces by a variety of methods: mechanical erosion, ion sputtering, and electrochemical reforming of the surface. Roughening by mechanical
Figure 8. Electron micrographs at 2000X magnification of an Ag (110) surface after mechanical polishing to 0.05 μm (top) and after subsequent chemical and electrochemical polishing (bottom).
erosion was accomplished by bombarding the surface with 2μm polystyrene spheres in a sand-blasting apparatus. Ion sputtering was done in the UHV work chamber by flooding the chamber with 5 x 10^-5 Torr argon and bombarding the surface with 500-2000 V ions in a defocussed beam of 7 μA/cm² total ion current (Phi model 04-161 sputtering gun). Electrochemical roughening of the surface was done by subjecting the crystal to several positive and negative voltage cycles in a 0.1 M KCl electrolyte (0.5 mA/cm², 2 min duration) after mechanical polishing. A detailed description of the effects of these procedures on the surface structure and the scattering properties of the crystal will be given in the following sections.

The experiments were performed in a UHV chamber equipped with LEED and Auger optics for surface characterization and a quadrupole mass spectrometer for residual gas analysis and thermal desorption studies (figure 9). The base pressure in the chamber was 8 x 10^-11 Torr after bakeout at 200° C, and was in the range of 2-5 x 10^-10 Torr during the course of the experiments. The silver crystals were mounted inside the chamber on a manipulator equipped with liquid nitrogen cooling coils to cool the crystal to approximately 90 K for condensation of molecules on the surface. A resistive heater was mounted immediately behind the crystal and could be used in conjunction with the nitrogen cooling to maintain the crystal at any temperature between 90 K and 1200 K. The crystal surface was cleaned prior to adsorption of molecules by ion sputtering as described previously. When smooth surfaces were desired, the crystal was annealed at 620-670 K. Several 20 minute sputter/anneal cycles were sufficient in most cases to obtain a surface that was clean by Auger analysis. Mechanically polished crystals that received no
Figure 9. Schematic view of the vacuum chamber used for Raman scattering and photodecomposition experiments.
other treatment, though, retained some residual oxygen after this cleaning procedure which required extensive sputtering for removal.

Molecules were condensed on the crystal surface for study by cooling the crystal to 90 K and raising the pressure in the chamber to $5 \times 10^{-9}$ to $1 \times 10^{-6}$ Torr (uncorrected for ion gauge sensitivity) for the desired exposure time. No line-of-sight exposure system was used, except in the case of oxygen adsorption which required a high surface pressure to obtain monolayer coverage. In that case, a 3/8 inch stainless steel tube extending from the leak valve to approximately 1 cm from the crystal surface was used as a doser. The tube was capped with a ceramic microchannel plate to achieve a uniform dose of molecules at the crystal surface.

Calibration of surface molecule coverages was done by ellipsometry using a rotating analyzer ellipsometer. The optical arrangement for ellipsometry, shown in figure 9, consists of a collimated beam of light incident on the crystal surface through a linear polarizer whose angle can be varied under computer control. The polarization of the output beam reflected from the crystal is determined by sampling the output intensity through a rotating polarizer driven by a frequency-stabilized synchronous motor. The details of the construction and theory of operation of the rotating analyzer ellipsometer have been discussed elsewhere\textsuperscript{65–67} and will not be presented here. Ellipsometry allows non-destructive determination of adsorbate overlayer thicknesses from submonolayer coverages to thick multilayer coverages. Its disadvantage, though, is that changes in ellipsometric parameters are interpreted in terms of a model consisting of a flat, isotropic substrate and an overlayer separated by a sharp boundary. This description of the
surface region is obviously inappropriate for the roughened surfaces used in this study, so coverage calibrations were done on smooth, well-ordered crystal surfaces obtained after sputter/anneal cycles on electropolished single crystals. Results of this calibration indicate approximately monolayer coverage for a 5 Langmuir (1 L = 10⁻⁶ Torr·sec) exposure of pyridine.

Raman scattering from molecules adsorbed on the silver surfaces was investigated using the 514.5 nm output line of an argon ion laser (Coherent CR-8). Plasma lines of the laser were eliminated using an interference notch filter. The laser was focussed onto the crystal surface in a 150 μm wide line using a 300 mm focal length cylindrical lens. The laser was incident on the crystal at 70° from surface normal and was predominantly (>95%) p-polarized. Scattered light was collected in a 40° cone around the surface normal direction using a 50mm focal length f/1.4 camera lens mounted inside the vacuum chamber. The light was collimated and then focussed onto the slits of a 0.85 m double spectrometer (Spex 1400) with an f-matching lens. The spectrometer was equipped with 1200 g/mm gratings, and slits were adjusted to give a resolution of 5-12 cm⁻¹ depending on the particular experiment. Wavelength was scanned using a stepping motor under the control of an LSI-11 microprocessor (Digital Equipment Corp.), allowing long signal integration times to improve signal to noise ratio. The signal was detected with a photomultiplier (RCA C31034A-02) cooled to -20° C in a thermoelectric cooler and operated at -1500 V with photon counting electronics. The signal was routed to the microprocessor via a 32-bit binary counter (LSI Computer Systems LS7060) and a parallel interface board, and stored on a magnetic disk.
Raman scattered light from the crystal was also dispersed in some experiments with a Spex Tripplemate spectrometer equipped with two 600 g/mm filter stage gratings and interchangeable 600, 1200, and 1800 g/mm gratings in the spectrometer stage. The dispersed light was detected in this case with an OMA-2 multichannel detector using a 1254 SIT vidicon imaging tube (Princeton Applied Research Corp.) which was cooled to -50°C with a closed-cycle refrigeration system. Spectra were collected by allowing charge to accumulate on the detector surface for an extended period of time (500 sec) before readout with the electron beam of the vidicon. Due to the uneven sensitivity and background level of different elements in the detector array, a background signal with no light exposure had to be collected and subtracted from each spectrum. The multichannel capability of the OMA provided a substantial decrease in collection time for low-level spectra, but the high dark count rate and the relatively low sensitivity of the vidicon used in these experiments (approximately 1/10 of the quantum efficiency of the photomultiplier tube) gave the low-level detection edge to the scanned spectrometer/photon counting apparatus. Most of the Raman spectra in the experiments described in the following pages were thus collected using photon counting.

Calibration of the sensitivity of the collection optics/spectrometer/detector system for determining Raman cross-sections was done by flooding the vacuum chamber with an atmosphere of nitrogen and observing the intensity of the nitrogen 0-0 Raman band at 2331 cm⁻¹. The area under this peak was integrated and compared to the Raman intensity expected for perfect collection efficiency of scattered photons from nitrogen molecules in the interaction region of the laser.
beam. The Raman intensity expected for a collection efficiency of one is obtained from the equation

\[ I = I_0 \frac{nV}{A} \Omega_c \frac{d\sigma}{d\Omega} \]

where \( n \) is the density of scattering centers, \( V \) is the effective scattering volume, \( A \) is the cross-sectional area of the laser beam, \( \Omega_c \) is the solid angle of collection, and \( d\sigma/d\Omega \) is the total differential Raman scattering cross-section. A Raman cross-section of \( 2.7 \times 10^{-31} \) cm\(^2\)/sr·molecule was used for nitrogen.\(^5\) The collection efficiency of the system was determined to be \( 2.8 \times 10^{-3} \) for the photon counting detection apparatus with the spectrometer resolution set at 5 cm\(^{-1}\).

The properties of the silver surfaces used in these studies were investigated by a variety of methods. Some characterization of the degree of surface roughening of the crystals was possible inside the UHV chamber simply by observing the level of continuum background scattering from the surface under laser irradiation. Roughness could also be characterized in the chamber by observation of surface plasmon light emission during electron bombardment of the surface. Although surface plasmons are nonradiative at a smooth interface, there is coupling of plasmons with photons via surface irregularities as discussed earlier. Plasmon radiation was typically excited in our experiments with a 50 μA beam of 750 V electrons incident along the normal direction to the surface. The light was collected at 65° from normal through one of the ellipsometer ports, using a 350 mm focal length fused silica lens external to the vacuum chamber. The light was focussed into a Spex Doublemate spectrometer with a 150 mm concave aluminum mirror, and
detected with an EMI 6256S photomultiplier. The degree of surface roughness is proportional to the relative height of the surface plasmon emission peak near 340 nm compared to the transition radiation peak at the volume plasmon energy near 325 nm (figure 10).

Additional characterization of the crystal surface could be done in situ using scanning ellipsometry. Ellipsometric parameters are determined as a function of wavelength by scanning the source wavelength (in this case a continuous xenon arc lamp filtered through a double monochromator). Optical properties of the surface are then calculated assuming a sharp interface with the usual Fresnel reflection relations.69

After removal from the vacuum chamber the crystals used in these experiments were examined by scanning electron microscopy to determine the surface topography. The electron microscopy was done on an ISI DS-130 SEM using an accelerating potential of 25 kV. Under typical operating conditions the resolution of this instrument is approximately 100 Å. The crystals were tilted 45° to the electron beam to improve the contrast for the surface features. The results of the SEM surface studies and their relation to Raman enhancement will be presented in the following section.
Figure 10. Light emission spectra from electron bombarded silver surfaces using a 50 µA beam of 750 eV electrons. (a) Ag(110) annealed at 500°C. (b) Ag(110) sputtered 1 hour at 2000 eV with Ar+. The lower spectrum shows emission at energies below the surface plasmon energy due to roughness.
D. Correlation of Raman Enhancement with Surface Properties

Raman scattering was investigated for molecules adsorbed on silver crystals roughened by a variety of methods as were described in the previous section. The primary tool for investigation of the surface topography of these crystals was the scanning electron microscope. Electron micrographs were taken for representative samples of each of the types of rough surfaces prepared within several days of removal from the UHV chamber. This allowed direct observation of surface features down to the 100 Å limit of the microscope, but did not permit observation of sputtering features formed by ion sputtering at low temperature in UHV since silver anneals rapidly at room temperature. Small scale roughness induced by sputtering silver at liquid nitrogen temperature was studied by changes in LEED diffraction patterns. Other techniques, in particular electron stimulated light emission and ellipsometry, allowed characterization of larger scale roughness while the crystal was still mounted in the vacuum chamber.

1. Electron Microscopy

One of the initial aims of this work was to study molecules adsorbed on clean, well-ordered silver surfaces using Raman scattering. To this end, the surfaces were cleaned by sputter/anneal cycles in the vacuum chamber until they were free of impurities to the detection limit of Auger spectroscopy (a few percent of a monolayer, except for carbon where there is interference with the silver 266 V peak). Surprisingly, when single crystals which had been prepared by
mechanical polishing down to 0.05 μm were sputtered, they were observed to give strongly enhanced Raman signals for adsorbed molecules. Shown in figure 11 are two Raman spectra in the ring mode region for adsorbed pyridine: the lower spectrum was taken on an annealed surface, and the upper spectrum was taken after sputtering the surface for 30 minutes using 2 kV argon ions.

Electron micrographs of such sputtered surfaces show the reason for this strong enhancement. The low magnification micrograph in figure 12 shows conical sputtering features aligned along the direction of the ion flux with dimensions of 2000-5000 Å. At higher magnification, smaller feature in the size range 300-400 Å are visible superimposed on the larger scale roughness. Such sputtering-induced surface topography has been observed previously on mechanically polished metal surfaces, and can be understood by considering differential sputtering rates at the surface. Stewart and Thompson have shown based on calculations of energy loss rates for ions penetrating the surface that the surface sputtering yield varies with the ion incident angle in the following way:

\[ S(\theta) = \left( \frac{\pi}{4} \right) s a^2 n E_a R \sec\theta \]

where \( n \) is the density of surface atoms, \( R \) is the path length of the ions, and \( E_a \) is the value of ion kinetic energy that allows an ion and an atom to approach to a distance \( a = a_0/(z_1 z_2)^{1/2} \) in a head-on collision. In this latter expression \( z_1 \) and \( z_2 \) are the atomic masses of the ion and neutral atom and \( a_0 \) is the Bohr radius. This sputtering yield dependence holds true until the incident ion angle approaches 60°.
Figure 11. Raman spectra of 50 L pyridine adsorbed at an annealed Ag (110) surface (bottom curve) and at the same surface after sputtering for 30 minutes with 2 kV argon ions (top curve).
Figure 12. Electron micrographs of Ag(110) mechanically polished to 0.05 µm and sputtered at 2000 v in UHV. Top: 0.5 µm sized roughness features at 11800X magnification. Bottom: 400 Å roughness features at 46800X magnification.
from surface normal. At this angle, ion reflection from the surface becomes important for energies below 100 kV (figure 13). The angle \( \theta \) at which \( S(\theta) \) reaches its maximum value is determined by the point at which the potential barrier of the surface plane prevents ion penetration, and is given by the expression

\[
\frac{\pi}{2} - \theta = \left( \frac{\sigma \alpha^2 n^{2/3} z_1 z_2 E_R}{z_1^{2/3} + z_2^{2/3} E} \right)^{1/2}
\]

where \( E_R = 13.6 \text{ eV} \) is the Rydberg energy and the angle increases as the inverse square root of the incident ion energy \( E \).

The effect of this angular dependence of the sputtering yield is to cause regions of the surface which have a convex curvature to develop into conical features with a half-angle \( \theta \), a result of the different sputtering rates at different points on the protrusion due to the changing angle of the incident ion beam with the local surface normal.

The initial development of surface nonuniformities (bumps) on mechanically polished surfaces may be one of the following: (1) debris on the surface, (2) inclusion of grinding material in the surface, or (3) existence of non-crystalline defect regions with different sputtering rates than the surrounding material. There is also some evidence that hydrocarbon contamination of the surface may cause nucleation of these sputtering features.\(^72\) Contamination of this sort may exist on crystals during introduction into the vacuum system and lead to the sputtering features described.

In order to eliminate the surface topography described above, different methods of crystal surface preparation were used subsequent to the mechanical polishing procedure. As described earlier, a combination
Figure 13. A plot of sputtering yield $S(\theta)$ as a function of the incident angle of the ions relative to surface normal.
of chemical polishing in an acid dichromate solution and electrochemical polishing in a cyanide solution produced a good quality optical finish. Although initially rougher than the mechanically polished surface (figure 8), after sputtering in the vacuum chamber the crystal showed no Raman enhancement and an extremely low background count rate for 514.5 nm laser excitation. Electron micrographs of the surface after removal from the chamber showed a featureless plane with no evidence of cone formation. This result is typical of previous sputtering studies of metal single crystals\(^70\) where the absence of sputtering features was attributed to channeling of ions along preferred directions in the crystal.

The density and size of conical sputtering features formed on mechanically polished surfaces were sometimes difficult to reproduce, so during later experiments surface roughness was intentionally introduced by electrochemically cycling the surface in a KCl electrolyte prior to mounting the crystal in the vacuum chamber. Shown in figure 14a is a silver (110) single crystal surface which was subjected to several electrochemical roughening cycles during which 60 mC/cm\(^2\) of charge flowed. A high density of spherical and ellipsoidal particles ranging in size from 1000 to 5000 Å diameter can be observed. After light sputtering in the vacuum chamber, features such as those shown in figure 14b which are aligned along the sputtering direction could be observed. Further sputtering produces a surface close to that observed for sputtering on a mechanically polished but not electrochemically roughened surface (figure 11).

To determine whether other sizes of surface features could enhance Raman scattering on silver surfaces, other types of roughening
Figure 14. Electron micrographs of a polished Ag (110) surface after electrochemical roughening as described in the text (top), and after subsequent light sputtering with 2 kV argon ions (bottom).
procedures were used. In order to produce large scale roughness, a silver crystal was subjected to a sand-blasting procedure using 2 μm diameter polystyrene beads. This procedure resulted in surface pits 2 to 10 μm in diameter (figure 15). Although this roughening procedure produced a large amount of diffusely reflected light from the surface under laser irradiation, no enhancement of Raman signal from adsorbed pyridine could be observed.

Attempts were also made to produce surfaces with roughness on a much smaller size scale than the 400 Å features obtained by sputtering on mechanically polished surfaces. Such features could not be observed by scanning electron microscopy and will be discussed in the next section.

2. In Vacuo Surface Characterization

The existence of small scale roughness on an ordered single crystal surface can be determined through the use of low energy electron diffraction (LEED). A typical value for the coherence width of an electron beam used for LEED is 100 Å. 73 This limits the size of the surface regions for which information on deviations from two-dimensional periodicity can be obtained. Deviations on a larger, macroscopic scale will have little effect on the LEED pattern if regions of microscopic order of the dimensions 50-100 Å still exist.

Shown in figure 16a is the LEED pattern at 53 V electron energy of a smooth, annealed Ag(110) surface. The LEED pattern was taken after the crystal had been cooled to 90 K. The crystal was then sputtered with argon ions at 2 kV for 20 minutes, with the crystal at 90 K to
Figure 15. Electron micrographs at two magnifications (top: 1200X, bottom: 11800X) of a polished silver surface which was sand-blasted using 2 µm polystyrene spheres.
Figure 16. LEED patterns at 53 V electron energy for a smooth, annealed Ag (110) surface (top), and the same surface after sputtering for 20 minutes at 90 K using 2 kV argon ions (bottom).
prevent annealing of small surface damage. The second LEED pattern in figure 16b was then obtained. As can be observed the spots are considerably broadened and some changes in intensity have occurred, indicating that there has been a disruption of local order on a size scale smaller than 100 Å. Such a surface, however, produces no detectable enhancement of Raman signal for pyridine molecules that are condensed on it. The light emitted during electron bombardment of the surface shows only a peak at the bulk plasmon energy and no secondary peak near the surface plasmon energy, indicating that large scale roughness has not developed on the surface.

An investigation of the large scale roughness which is observed in the scanning electron micrographs was also done by looking at emission intensities during electron bombardment. Sputtering of a mechanically polished Ag (110) crystal with argon ions with energies of 1 kV or less produces no change in the emission spectrum shown in figure 10a. Sputtering for 40 minutes at 1.5 kV (approximately $10^{18}$ ions/cm$^2$ total ion dose) produces a barely perceptible increase in the emission intensity in the surface plasmon region near 340 nm. Sputtering for the same amount of time at the maximum ion energy available for our ion gun, 2 kV, produces a strong emission peak at 341 nm equal in intensity to the volume plasmon peak at 325 nm.

The theory of plasmon emission from rough surfaces under irradiation with normally incident electrons has been developed by Kretschmann et al. They model rough surfaces using a correlation function which has a monotonically decreasing low wavevector component and a high wavevector component which is treated as a delta function. They find that this model reproduces the double-peaked emission spectrum
that is observed experimentally. Both the intensity of the surface plasmon peak and the splitting between the two peaks is calculated to increase with $<s^2_h> k^2_h$, where $<s^2_h>$ is the mean square height of roughness features and $k_h$ is the dominant wavevector of the roughness. Shown in table 1 are experimental data on peak heights and splittings for sputtering of mechanically polished Ag (110) crystals with 2 kV argon ions. This information confirms the prediction that the peak splitting is expected to increase with increasing surface plasmon peak intensity, and indicates that the height of roughness features on our surfaces is increasing with extended sputtering time.

Table 1. Surface plasmon emission peak heights and positions as a function of sputtering duration

<table>
<thead>
<tr>
<th>Total ion dose per cm$^2$</th>
<th>Surface/volume plasmon peak ratio</th>
<th>Surface plasmon peak wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.66</td>
<td>(340 nm)</td>
</tr>
<tr>
<td>$5 \times 10^{17}$</td>
<td>0.77</td>
<td>340.3 nm</td>
</tr>
<tr>
<td>$1 \times 10^{18}$</td>
<td>0.96</td>
<td>341.0 nm</td>
</tr>
<tr>
<td>$2 \times 10^{18}$</td>
<td>1.07</td>
<td>342.6 nm</td>
</tr>
</tbody>
</table>

Looking at the plasmon emission spectrum for the sputtered surfaces in more detail (figure 17) one can see, in addition to the long tail in emission intensity which extends to lower energy from the surface plasmon peak, another broad peak between 500 and 550 nm. There is interference from electron gun filament emission in this region, so a
Figure 17. Electron stimulated light emission from a rough silver surface using 750 V electrons at normal incidence. The primary emission peak occurs at 346 nm near the surface plasmon resonance, and a secondary peak is observed around 500 nm which may be due particle plasmon excitation.
spectrum of filament emission under the same conditions was carefully subtracted from the data before plotting figure 17. A secondary surface plasmon peak such as observed in this plot may be due to an additional peak in the roughness correlation function at higher wavevector, or the existence of additional plasmon resonances in surface particles.

Some support for the existence of plasmon resonances at lower energies for the sputtered surfaces is obtained from the surface optical properties that were determined by scanning ellipsometry in the visible region of the spectrum (figure 18). The effective optical constants for these surfaces calculated using an abrupt interface model show a maximum in the absorption coefficient $k$ between 500 and 550 nm. Data obtained for rough surfaces in this manner by ellipsometry is of limited utility, however, since it is well known that surface roughness can substantially affect the calculated ellipsometric quantities. In order to determine surface properties accurately the surface would have to be described using an inhomogeneous film model for surface roughness and have its properties calculated accordingly.
Figure 18. Effective optical constants determined by ellipsometry for a smooth, annealed Ag(110) surface (top) and a rough, sputtered Ag (110) surface (bottom).
E. Enhanced Raman Scattering Results

Raman scattering studies were undertaken for molecules condensed on the rough, sputtered surfaces described above. The surfaces were cleaned before each spectrum by argon ion sputtering at room temperature until contaminants were not observable by Auger spectroscopy. As mentioned previously, however, interference with the silver 266 V Auger peak limits the detectability for carbon by Auger to approximately half a monolayer (4 x 10^{14} atoms/cm^2). Raman scattering from molecules adsorbed on these nominally clean, rough surfaces produces a spectrum such as that shown in figure 19. This spectrum of a 50 L exposure of pyridine condensed on the surface at 90 K shows molecular pyridine peaks superimposed on a continuum of approximately 1000 counts/sec that decays with increasing wavelength. This continuum is thought to arise from recombination fluorescence of electron-hole pairs generated by the laser at the rough surface.

Superimposed also on the background are a broad peak at 1580 cm^{-1} with a shoulder at approximately 1350 cm^{-1}, and a much weaker peak near 700 cm^{-1}. These peaks have been identified by Tsang et al. as amorphous surface carbon using EELS and Raman spectroscopy of carbon-covered silver surfaces. SERS is extremely sensitive to small amounts of surface carbon due to its large Raman cross-section of 4.4 x 10^{-28} cm^2/sr·atom. The residual surface coverage of carbon on our "clean" surfaces can be estimated from this cross-section assuming that the Raman signal for atoms at the surface is enhanced by a factor of 1000 (see the following section). We calculate a residual coverage of 1.3 x 10^{13} atoms/cm^2, or 0.03 monolayers.
Figure 19. Raman spectrum of 50 L pyridine condensed on a rough, sputtered Ag (110) surface showing molecular pyridine peaks superimposed on broad peaks due to surface carbon.
The vibrational frequencies of the adsorbed molecules in figure 19 are typical of those observed for pyridine adsorbed at electrode surfaces, and may be shifted by up to 20 cm\(^{-1}\) from the values for liquid pyridine. Dornhaus et al\(^{79}\) have provided a useful compendium of vibrational mode frequencies for liquid pyridine, aqueous pyridine, and adsorbed pyridine together with the symmetries of these modes. Of the peaks observed in figure 19, all represent in-plane modes of the molecule except for two out-of-plane modes at 705 and 757 cm\(^{-1}\), using the normal mode analysis of Long, Murfin and Thomas.\(^{80}\) The observation of both types of modes is confirming evidence for the tilted-ring surface geometry proposed for pyridine adsorbed on silver.\(^{81}\)

1. Spectral Dependence

The dependence of surface enhanced Raman intensity on wavelength does not follow the \(v^4\) behavior of spontaneous Raman scattering for free molecules, but instead follows the resonance profile of the particular surface on which enhanced scattering is observed.\(^{82}\) The wavelength dependence of Raman scattering for molecules on the rough, sputtered surfaces used in these experiments was obtained using output lines of both argon and krypton ion lasers between 350.7 nm and 658 nm. Raman enhancement was very small at UV the wavelengths used, so the relative intensities of the surface carbon peaks with their large cross-sections for scattering were used to obtain information on enhancement. The data (table 2) show a maximum enhancement in the green region of the spectrum, at 514.5 nm. This agrees quite well with estimations of surface resonance frequencies made using data from ellipsometry and
electron beam stimulated light emission for this surface.

Table 2. Relative Raman enhancement as function of wavelength for rough, sputtered silver

<table>
<thead>
<tr>
<th>Laser wavelength</th>
<th>Raman enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.7 nm</td>
<td>0.014</td>
</tr>
<tr>
<td>363.8 nm</td>
<td>0.055</td>
</tr>
<tr>
<td>406.7 nm</td>
<td>0.13</td>
</tr>
<tr>
<td>457.9 nm</td>
<td>0.43</td>
</tr>
<tr>
<td>514.5 nm</td>
<td>1.00</td>
</tr>
<tr>
<td>647.1 nm</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The observed wavelength at which the maximum Raman enhancement occurs places constraints on which types of surface resonances can be responsible for the enhancement. Excitation of delocalized surface plasmon modes via surface roughness should produce a maximum enhancement where the density of surface plasmon states is greatest. As may be seen from figure 3 this occurs near the surface plasmon resonance frequency, which for silver is at 3.68 eV (340 nm). A full calculation for the rough surface resonance frequencies, including the effects of roughness on the surface plasmon dispersion relation, places the maximum Raman enhancement at 3.2 eV (390 nm). It is thus unlikely that excitation of delocalized plasmon modes of the surface provides a substantial amount of the enhancement observed.
Excitation of localized plasmon resonances on surface protrusions must also be considered as a source for the observed maximum in Raman enhancement. The surface topography discussed previously for the rough, sputtered silver surfaces used in these experiments is characterized by two types of roughness features: one has a width on the surface of approximately 400 Å and the other a width of approximately 2000 Å. If we consider a spherical particle of 400 Å diameter, a complete electrodynamic calculation of its scattering properties gives a resonance wavelength of 400 nm. As the sphere becomes larger (1000 Å) the primary resonance shifts to 410 nm and a secondary resonance, much weaker than the first, appears near 500 nm. If we consider now a 2:1 spheroid instead of a sphere, the resonance frequency for a full electrodynamic calculation with a minor axis diameter of 400 Å becomes 440 nm (figure 7). This frequency is calculated for an isolated particle, however, and if a red shift of 0.4 eV is included for interaction of the particles with the surface a resonance frequency of 510 nm is calculated. This frequency is quite close to the resonance wavelength observed experimentally in Raman enhancement. Full calculations for larger metal spheroids do not as yet exist, but resonances would be expected to shift slightly to longer wavelengths and decrease in magnitude.

2. Surface coverage dependence.

The coverage dependence of Raman enhancement was investigated for layers of pyridine condensed on the rough, sputtered surfaces used in these experiments. Pyridine has been the molecule used most frequently
in investigations of Raman scattering on surfaces, and results may be readily compared to other studies. Pyridine was condensed in timed exposures on the surface which were calibrated using ellipsometry as described earlier. Raman spectra were scanned over a 40 Å wavelength region in 0.5 Å increments, using a 30 second integration time per point for low coverages and a 15 second integration time for high coverages.

Briefly, we find the following results (figure 20): at low (submonolayer) coverages the $\nu_9$ symmetric ring breathing mode is shifted to 1005 cm$^{-1}$ from its liquid phase value of 992 cm$^{-1}$ and is selectively enhanced with respect to the asymmetric stretch at 1035 cm$^{-1}$, as has been observed in a number of other studies. We also see a peak at 1020 cm$^{-1}$ for very low coverages that is not observed at high coverages. We attribute this peak to pyridine adsorbed at surface carbon sites. At high coverages, the symmetric ring breathing mode appears to be a superposition of two peaks at 994 cm$^{-1}$ and 1005 cm$^{-1}$, with both types of molecules contributing to intensity at 1035 cm$^{-1}$ for coverages greater than half a monolayer (2.5 L). The splitting of the $\nu_9$ mode at different coverages was initially attributed to the difference between adsorption at different surface sites or the difference between physisorbed and chemisorbed pyridine, but now can be adequately explained by the occurrence of a phase transformation in the first layer of adsorbed pyridine between $\pi$-bonded and N-bonded species.

These results can be seen more clearly in a plot of the Raman intensity of the pyridine ring breathing modes as a function of surface coverage (figure 21). The peak at 1005 cm$^{-1}$ begins to increase at very low coverages, while the 994 cm$^{-1}$ peak does not begin to increase until
Figure 20. Raman spectra in the ring-breathing mode region for pyridine adsorbed on rough, sputtered Ag (110) as a function of surface coverage.
Figure 21. Coverage dependence of surface enhanced Raman signal for pyridine adsorbed on roughened Ag(110) at 90K for several ring-breathing modes.
approximately half monolayer coverage. The peak at 1035 cm\(^{-1}\) is intermediate between these two, corresponding to contributions from both types of molecule. Clearly observable in this plot is the sharp decrease in Raman intensity for additional molecules adsorbed beyond the first monolayer (5 L coverage). Raman enhancement factors calculated for each successive layer of pyridine (based on the system sensitivity calibration with N\(_2\)) show an enhancement of 1000 for the first layer of adsorbed pyridine and an enhancement of 60-80 for the next three layers. Some enhancement is thus observed for molecules spaced at least 20 Å from the surface, consistent with several other studies of Raman enhancement on rough silver.\(^{83,85,87}\)

A coverage-dependent study of Raman scattering for benzene condensed on rough, sputtered silver was also done, and also gave an enhancement factor of 1000 for the first adsorbed layer using the 987 cm\(^{-1}\) Raman peak. The distance dependence of enhancement was very similar to that found for pyridine.

We can now look at how the observed coverage dependence for these molecules compares with that predicted for various models of Raman enhancement. If we consider a sphere with a radius \(a\), the predicted Raman enhancement will decrease with increasing molecule-surface separation \(d\) as \(1/(a + d)^{12.44}\). For a sphere radius of 200 Å (corresponding to the 400 Å diameter surface particles observed by electron microscopy), a drop in Raman intensity of one order of magnitude is predicted to occur at the tenth layer of molecules as compared to the first monolayer. A calculation of the distance dependence of Raman enhancement from the tip of a 2:1 hemispheroid with a minor axis diameter of 500 Å shows a very similar dependence on
separation\textsuperscript{53} (neglecting the factor included by the authors for image dipole effects). This very weak dependence of enhancement on separation from the surface correctly reproduces the coverage dependence observed for multilayer coverages in this study, but does not account for the sharp increase in enhancement for the first monolayer.

Enhancement confined to the first adsorbed layer is predicted by a number of the theories discussed earlier. Enhancement due to image dipole effects, for example, depends on the distance from the surface as $1/d^{12}$ (equation 9), effectively limiting enhancement to the first layer. Large enhancements due to image effects are not possible in our experiments, since the image theory predicts enhancement for molecules adsorbed at a flat surface and our results indicate that there is no detectable enhancement without surface roughness. Enhancement of the first layer by a factor of 10 due to image effects is possible, however, since the sensitivity of our apparatus would make such a flat surface signal only marginally observable. Sophisticated models of electrodynamics in the near surface region reduce the large enhancements predicted by the simple electrostatic image model to this level or even lower, as has been discussed in section B-1.

Vibrational modulation of surface electrons is also a possible mechanism for enhancement of molecules in the first adsorbed monolayer. Charge oscillation along a metal-molecule chemisorption bond has been predicted as one such mechanism. This model requires substantial charge density in a chemisorption bond, however, and molecules studied here are not strongly bound to the silver surface. Shown in figure 22 are thermal desorption spectra for several coverages of pyridine on Ag (111). The surface adsorbed species at monolayer
Figure 22. Thermal desorption spectra for several coverages of pyridine on smooth, annealed Ag (111). The heating rate was approximately 2.5°/sec.
(5 L) coverage desorbs at approximately 180 K, indicative of very weak surface binding (physisorption). This peak is shifted only slightly for desorption from a roughened surface (figure 23). A stronger bond with the silver surface might be expected for a molecule such as benzaldehyde which contains a carbonyl group, since oxygen is known to interact strongly with the silver surface. The desorption peak for the surface-adsorbed species occurs at 210 K, though, which is still indicative of fairly weak binding (figure 24).

Other possibilities exist for vibrational modulation of metal surface electrons by adsorbates. The existence of a charge-transfer excitation for pyridine adsorbed on silver\textsuperscript{17} has led to the development of a theoretical framework where such excitations have been related to Raman enhancement, as has been discussed previously. Such a mechanism is probably not active for our experimental geometry, however, since a monolayer of benzene is enhanced by the same factor as a monolayer of pyridine; charge transfer excitations have not been observed to date in the electronic spectra of adsorbed benzene\textsuperscript{17}. The remaining models of Raman enhancement by modulation of surface electrons are difficult to compare quantitatively to our experimental data, but enhancement is predicted to be restricted to molecules on the surface and they may thus contribute the high enhancement observed for the first layer of molecules.

The absolute magnitude of the observed Raman enhancement is well within conservative estimates for each of the mechanisms discussed above. The predicted surface-averaged enhancement for an ellipsoid with a minor axis width of 400 Å and an aspect ratio of 2:1 is a factor of 500.\textsuperscript{57} Looking again at the electron micrograph of a roughened surface
Figure 23: Thermal desorption spectrum for 10 L pyridine adsorbed on a rough, sputtered silver surface. The heating rate was approximately $2^\circ$/sec.
Figure 24. Thermal desorption spectra for several coverages of benzaldehyde on smooth, annealed Ag (111). The heating rate was approximately 2.5°/sec.
(figure 12) we find a particle density of 110 particles/μm² in this size range, which corresponds to a fractional area of 11% of the total surface covered by these features. A hemispheroid with a 2:1 aspect ratio has a surface area 3.4 times greater than the area its base covers, so the number of molecules adsorbed at these features will be 37% of the total number of adsorbed molecules. Thus the predicted enhancement for our experimental geometry is a factor of 180, somewhat greater than the observed plasmon resonance enhancement factor of 100. As discussed earlier, though, the enhancement for a particular molecule adsorbed at the tip of a surface particle may be substantially greater than the average enhancement.

3. Polarization properties

The polarization properties for reflection spectroscopy of adsorbates on planar metal surfaces are well understood. For an adsorbed molecule whose principle axis of molecular polarizability lies along the surface normal and which has a vibrational mode which transforms as in 2, for example, there will be substantial excitation of the vibrational mode using p-polarized light at a high angle of incidence and very little excitation using s-polarized light. In our experiments, changing the incident radiation from p-polarized to s-polarized affected neither the relative nor absolute Raman intensities of the vibrational modes observed for pyridine on rough silver. This behavior is attributed to the random surface profile of the roughened surfaces used, and precluded the use of polarization properties in characterizing the metal/adsorbate system.
F. Conclusions

The enhancement of Raman scattering that we have observed on silver surfaces roughened by ion bombardment has been shown to be correlated with the appearance of particular types of topography on the crystal surfaces. SEM studies indicate that the surfaces that produce maximum enhancement contain surface features on two size scales, one of approximately 400 Å diameter and the other of approximately 2000 Å diameter. A study of the dependence of Raman enhancement on the wavelength of the incident light indicates that the maximum enhancement occurs near 500 nm for molecules adsorbed on these surfaces. Ellipsometric studies indicate that the surfaces have a peak in absorption in this region, which agrees well with the Raman results and with the resonance wavelength calculated by electrodynamic theory for 400 Å spheroids coupled to a silver surface.

Smooth silver surfaces prepared by chemical and electrochemical polishing of silver single crystals were shown to have an enhancement factor of less than 10 for Raman scattering by adsorbates. Small-scale roughness (<100 Å) produced by ion bombardment of these smooth surfaces at 90 K does not yield any increase in Raman for visible and near UV excitation. Large-scale roughness (>1 µm) produced by mechanical abrasion of the silver surface likewise did not produce any measurable Raman enhancement.

For the ion bombarded rough surfaces which were found to enhance Raman scattering, the enhancement factor was much larger for the first layer of adsorbed molecules than for subsequent layers. For pyridine and benzene, the observed enhancement was 1000 for the first layer and
60 to 80 for the next three layers. The long-range component of enhancement observed at the second layer and beyond agrees well with the predictions of Raman enhancement by large local fields at small metal particles, which decay as \(1/(a + d)^3\) with distance \(d\) from the surface for spheres of radius \(a\). This type of mechanism, however, predicts an enhancement of only 100 then for the first layer.

The increase in the enhancement observed for the first layer of molecules on a rough surface by a factor of 10 over that predicted by the field enhancement model has several possible origins. If the image enhancement model is still an appropriate description of the near surface region of a metal in the presence of roughness, then the additional enhancement could be considered to arise from image effects. Molecular vibrational modulation of metal surface electrons may also occur for the first adsorbed layer, and thus also provide additional enhancement for this layer.
Part II.

Photochemistry on Rough Metal Surfaces
A. Introduction

The possibility of using radiation to stimulate reactions of adsorbed species is an interesting one and has received much attention recently. It has long been known that certain chemical reactions will proceed rapidly on irradiated semiconductor surfaces where the semiconductor is excited with bandgap radiation and transfers energy to the adsorbates, or where electron transfer processes occur at the interface.\(^9\) Very little evidence has been accumulated, however, for true photoinduced reactions occurring at metal surfaces.\(^{91,92}\) Early reports of photodecomposition reactions of benzaldehyde on copper surfaces and acetone on nickel surfaces with light in the wavelength region 240-330 nm were very poorly documented.\(^9\) The only well-established evidence for photoreactions occurring at metal surfaces appears to be for the oxidation of CO at various transition metal surfaces\(^{94-97}\) or the reaction of CO with other molecules.\(^9\)

Recently, however, the possibility of enhancement of photoinduced reactions of adsorbates on metal surfaces has been hypothesized\(^9\) due to the existence of enhanced fields at certain surfaces as have been discussed here in relation to Raman scattering. In our investigations of Raman enhancement in the near UV region on roughened silver substrates, it quickly became apparent that some type of reaction was occurring for certain molecules under laser irradiation. We reported the first observation of enhanced photoreaction rates for the fragmentation of a number of molecules on rough silver using a laser at 363.8 nm.\(^1\) Other reports of enhanced decomposition rates have subsequently appeared for the decomposition of rhodamine-6G on silver
island films\textsuperscript{101} and for the photodissociation of dimethylcadmium on cadmium island films.\textsuperscript{102}

For weakly adsorbed species on metal surfaces (species for which discrete molecular electronic states, perturbed only slightly from gas phase values, still exist following adsorption) there are basically four mechanisms for the dispersal of energy following resonant absorption by the molecule: (1) radiative decay of the excitation (fluorescence or phosphorescence), (2) nonradiative decay of the excitation due to a transfer of energy to a continuum of states or to a particular resonance of the metal substrate, (3) nonradiative decay by an internal radiationless transition, perhaps involving desorption of the molecule by accumulation of energy in a molecule-surface vibrational mode, and (4) chemical reaction of the adsorbed species. We are relatively certain that nonresonant surface excitation (surface heating) does not play a significant role in the photoreactions we have observed for several reasons: a calculation of surface heating rates based on effective optical constants determined for our rough surfaces by ellipsometry show a negligible temperature rise (less than 1°C), and photodecomposition is observed experimentally for molecules separated from the surface by a spacer layer. In addition, the trend in calculated surface heating rates with wavelength (appendix A) does not match that observed for photochemistry (see section E-2).

In order to determine if photoinduced reactions of adsorbates can be generally observed, one must be able to predict whether or not energy dissipation through one of the other three pathways above will preclude reaction of the excited surface species. It is well known that energy transfer to a metal via the near field of an excited dipole becomes very
rapid as an excited molecule is brought close to a metal surface. In many cases this eliminates the emission of observable fluorescence or phosphorescence, since the lifetime of the molecular excited state becomes extremely short in close proximity to the surface. Because of this damping the initial photoreaction step must occur very rapidly to compete with de-excitation of the excited state by energy transfer to the surface. For some molecules, rapid intersystem crossing rates (perhaps enhanced by interaction of the adsorbates with the surface) may allow population of triplet states with intrinsically longer lifetimes than the initial photoexcited state, from which reactions may occur. If the initial excitation step is a two photon process, excitation of states not coupled to the ground state by strong dipole transition moments may occur. In this case de-excitation could proceed much more slowly, allowing time for chemical reaction.

Provided that the molecular excited state survives long enough on the surface for reaction to occur, an enhancement of reaction rate for surface adsorbed species relative to free molecules may be expected on the basis of enhancement of local surface fields. The existence of the surface fields is well established by the Raman work discussed in previous sections and the observation of efficient second harmonic generation on rough silver surfaces. Enhancement of local surface fields should yield enhanced absorption by molecules at the surface and hence an increase in photoreaction rate.

In the following sections the factors governing energy transfer from excited molecules to metal surfaces will first be discussed from the standpoint of recent theoretical developments. This will be followed by a discussion of linear vs. non-linear photoeffects at
surfaces where enhancement of local electric fields is known to occur. Finally, experimental results will be presented and their implications for photochemical pathways and the interplay between surface quenching and enhancement will be discussed.
B. Theory of Excited State Damping by Surfaces

The theory of excited state damping by energy transfer from excited molecules to metal surfaces was established following the experiments of Drexhage et al., who measured the fluorescent lifetime of an excited molecule which was spaced a known distance from a metal surface by Langmuir-Blodgett fatty acid layers. Two effects of the metal surface on molecular lifetimes were seen in these experiments. The first effect was a fluctuation in lifetime as a function of distance from the surface for large (>500 Å) separations, due to interference between light emitted from the dipole and reflected light from the surface. The second effect was a dramatic decrease in the lifetime (and consequently the quantum yield) as the separation from the surface decreased toward zero. This effect was shown to be due to nonradiative transfer of energy from the excited molecular dipole to the metal surface. The classical electrodynamic theory of this nonradiative coupling has been summarized by Chance et al., and will be discussed briefly in the following text.

1. Classical Dipole Theory of Energy Transfer

An oscillating dipole near a planar metal surface can be described by the following equation of motion:

\( \mu + \omega^2 \mu = \frac{e^2}{m} E_R - b_0 \mu \)  

In this equation \( \omega \) is the oscillator frequency in the absence of
damping, $m$ is the effective mass of the dipole, $E_R$ is the reflected field at the dipole position, and $b_0$ is the damping constant of the dipole without surface effects. We can assume the following time dependence for both the dipole moment and the reflected field, since both oscillate at the same frequency:

$$m = m_0 e^{-i(\omega+\Delta \omega)t - bt/2}$$  \hspace{1cm} \text{(64)}$$

$$E_R = E_0 e^{-i(\omega+\Delta \omega)t - bt/2}$$  \hspace{1cm} \text{(65)}$$

In these equations the perturbation of the surface on the motion of the dipole due to the reflected field $E_R$ is taken into account by a frequency shift $\Delta \omega$ and a damping factor $b$. By substituting these equations into the dipole equation of motion, we obtain for the frequency shift and damping constant:

$$\Delta \omega = b^2 2\mu \omega + \frac{e^2}{2\mu_0 m_0} \text{Re}(E_0)$$  \hspace{1cm} \text{(66)}$$

$$b = b_0 + \frac{e^2}{\mu_0 m_0} \text{Im}(E_0)$$  \hspace{1cm} \text{(67)}$$

Now the problem of calculating the damping rate has been reduced to a calculation of the electric field at the dipole position. The electric field around a free oscillating dipole has been obtained previously (equation 38). It consists of a long-range component varying as $1/r$ that determines the radiation field of the dipole, and other components varying as $1/r^2$ and $1/r^3$ that determine the near field of the dipole and are only important at short distances. At very short distances the
calculation of the electric field in the presence of the metal surface is the same problem as was encountered in the image dipole calculation of Raman enhancement, where only the $1/r^3$ component was considered to be of importance.

Chance et al.\textsuperscript{108} give a complete solution to the problem of calculating the electric field of the dipole in the presence of the surface, valid for all distances (except possibly very short distances where the assumptions of the model used begin to break down). They use the method of Sommerfeld\textsuperscript{109}, and consider all components of the dipole field with appropriate boundary conditions at the metal surface. For the cases of dipoles oriented parallel and perpendicular to the surface, the electric fields are calculated to be

\begin{align}
E_R'' &= \frac{k_1^3 u}{2\epsilon_1} \int_0^\infty \left( (1-u^2)R_p + R_s \right) e^{-2k_1 d} \frac{u}{1(u^2)} \, du \\
E_R^\perp &= -\frac{k_1^3 u}{2\epsilon_1} \int_0^\infty R_p e^{-2k_1 d} \frac{u^3}{1(u^2)} \, du
\end{align}

where $R$ is the reflection coefficient for light polarized parallel to the plane of incidence ($p$-polarized), and $R$ is the reflection coefficient for light polarized perpendicular to the plane of incidence ($s$-polarized), given by

\begin{align}
R_p &= \frac{\varepsilon_1^{1/2} - \varepsilon_2^{1/2}}{\varepsilon_1^{1/2} + \varepsilon_2^{1/2}} \\
R_s &= \frac{1^{1/2} - 2^{1/2}}{1^{1/2} + 2^{1/2}}
\end{align}

In these equations $k_1$ is the wavevector of light in the medium of
dielectric constant $\varepsilon_1$ containing the dipole, $\varepsilon_2$ is the frequency-dependent dielectric function of the metal, $\hat{d} = k_1 d$ is the normalized separation of the dipole from the surface, and $l_j = -i(\varepsilon_j/\varepsilon_1 - u^2)^{1/2}$. The decay rates for parallel and perpendicular dipoles in the presence of the surface are then given by the expressions

\begin{align}
(70a) \quad b_\parallel &= b_0 + \frac{3q b_0}{4} \text{Im}\left(\int_0^\infty (1-u^2) e^{21 u} e^{\frac{-21 u^2}{l_1}} du\right) \\
(70b) \quad b_\perp &= b_0 - \frac{3q b_0}{2} \text{Im}\left(\int_0^\infty e^{21 u} e^{\frac{-3 u^2}{l_1}} du\right)
\end{align}

where the equations have been simplified somewhat by introducing the quantum yield $q$ of the emitting state:

\begin{equation}
q = \frac{b_{\text{rad}}}{b_0} = \frac{2e^2 k_1^3}{n_1^2 b_0}
\end{equation}

and where $n_1$ in this new equation is the refractive index of medium 1 corresponding to the dielectric constant $\varepsilon_1$.

A physical picture of the processes contributing to energy transfer can be obtained by examining the integration range of the expression for the energy transfer rate given by equation 70. It has been shown\textsuperscript{110} that the integral over the region $0 < u < 1$ of the normalized surface wavevector $u$ corresponds to a radiative transfer of energy from the molecule due to the far field of the dipole. Near $u \approx 1$ (approximately $1 < u < 2u_{\text{sp}}^{-1}$, where $u_{\text{sp}}$ is the normalized surface plasmon wavevector) there is a pole in the integrand of equation 70 corresponding to excitation of surface plasmon modes of the metal surface. The integral range above this pole, $2u_{\text{sp}}^{-1} < u < \infty$, corresponds to excitation of
"lossy waves" in the surface (i.e., excitations of surface electrons which dissipate energy rapidly due to electron scattering). These last two terms make up the total nonradiative energy decay rate corresponding to the integral range \(1 < u < \infty\), which is due to transfer of energy by the near field components of the excited dipole.

The integrand of equation 70b is plotted as a function of the surface wavevector \(u\) in figure 25 for an excited dipole spaced varying distances from a silver surface. The free dipole emission wavelength is taken to be 350 nm. Clearly visible in this plot is a spike near \(u = 1\) due to energy transfer to surface plasmons. It can be seen that the contribution of this term to the total nonradiative energy transfer rate remains nearly unchanged over the range of molecule-surface separations plotted. The contribution to the nonradiative rate due to excitation of "lossy waves", however, changes dramatically as a function of distance from the surface. As the separation of the dipole from the surface becomes smaller, the magnitude of this term becomes larger and extends to higher wavevectors. This corresponds to an increasing interaction of the dipole near fields with the surface, which results in excitation of surface modes with higher wavevectors due to the spatial inhomogeneity of these fields. The divergence of the decay rate for a point dipole located directly on the surface is an unphysical artifact of this model, and must be corrected by using more sophisticated models.

Considering the case where the emitting dipole is close to the metal surface \((k_1d << 1)\), the equations presented for the electric fields (equations 68a and b) simplify to the image dipole expression (equation 4), and the energy transfer rate becomes:
Figure 25. A plot of the integrand of the energy transfer equation (equation 70b) as a function of the normalized surface wavevector $u$ for several different molecule-surface spacings.
Here $\theta$ is a numerical factor which is $3/2$ for a perpendicular dipole, $3/4$ for a parallel dipole, and $1$ for an isotropic mixture of the two types. It is evident from this equation that the nonradiative damping for an excited dipole increases as $1/d^3$ as the dipole is brought closer to the surface. For a molecule very near the surface, this effect can be substantial. The calculated lifetime from equation 72 has been plotted in figure 26 for a molecule located $1.6 \, \text{Å}$ from a silver surface as a function of oscillator strength (or transition dipole moment). The free molecule has been assumed to emit at $300 \, \text{nm}$ with a quantum yield of one. By way of comparison, the radiative lifetime for the free molecule with a transition of oscillator strength $f = 0.1$ is calculated to be $1.4 \times 10^{-8}$ from the relation 111:

$$\tau_{\text{rad}} = \frac{m c^2}{8 \pi^2 \epsilon_0^2 f^2}$$

The effects of the frequency dependence of the metal dielectric function on the energy transfer rate near the surface can be seen by substituting the Drude dielectric function (equation 21) into equation 72. When the damping term $\gamma$ is small, the nonradiative part of the energy transfer rate is proportional to 108:

$$b_{\text{nr}} \propto \frac{\omega_p^2 \omega \epsilon_1}{\omega_p^2 (1 + \epsilon_1) d^3 (\frac{\omega^2}{\omega_p^2} + \frac{\omega^2 \gamma}{\omega_0^2})}$$
Figure 26. Calculated image theory surface lifetimes for molecular excited states of different oscillator strengths. The molecules were taken to be perpendicular dipoles spaced 1.6 Å from a silver surface and were assumed to emit at 3000 Å. A silver dielectric constant of \( \varepsilon = 0.83 + 2.67i \) was used in the calculation.
MOLECULAR EXCITED STATE LIFETIMES AT A SILVER SURFACE

$\lambda = 3000 \text{ Å}$

d $= 1.6 \text{ Å}$
This expression has a resonance at \( \omega = \omega_p/(1+\varepsilon)_{1/2} \), which is just the condition for existence of a surface plasmon resonance (section B-2). Thus nonradiative energy transfer rates may be large near plasmon resonance frequencies of the metal substrate.

The expressions for energy transfer rates discussed in this section are valid when the molecular excited state can be considered as an excited dipole and dipolar coupling terms between the excited state and the surface are the dominant ones. For the case where a molecular transition is not dipole-allowed (for example, where there is a multiphoton excitation of a state that is forbidden for a one photon transition), these equations are not adequate and multipolar coupling terms must be considered. Coupling due to magnetic dipole and electric quadrupole terms has been calculated by Chance, Prock, and Silbey\textsuperscript{108,112} and is expected to be much weaker than electric dipole coupling.

Elaborations of the image model for energy transfer to metal surfaces with multiple overlayers and anisotropic overlayers have also been done by these authors.\textsuperscript{108} When molecules are situated in the very near surface region (first or second adsorbed monolayer), though, some of the assumptions of the image model are no longer valid and more complex models must be considered.

2. Nonlocal Corrections to Dipole Theory

The image model described above is a very useful tool for describing quantitatively the behavior of an excited molecule near a metal surface for separations greater than approximately 10 Å. At distances shorter than this, however, several approximations in the model are no longer
very good and a more accurate description is needed. The approximations that are questionable are the following: (1) the use of a local (wavevector independent) dielectric function for the metal, (2) use of a step-function change in the electron density at the metal surface, and (3) the use of a point dipole to describe the excited molecule.

Addressing the first of these points, the image model assumes that the polarization induced in the metal surface at a given frequency at some particular point is a function only of the incident field at that point, and is independent of the incident field at an adjacent point on the surface. This approximation is valid if the spatial scale of the field variation is much larger than the electron correlation length; this is certainly true if the external field is a light source with slowly varying fields on atomic dimensions. When the polarization in the metal is caused by oscillating charges near the surface, however, the external field varies rapidly in space and a description of the surface based on Maxwell's equations will no longer work.

A number of authors have recently proposed improved descriptions of a metal surface in the presence of an excited dipole which include the effects of a nonlocal response in the metal. The approach of Ford and Weber is to use a wavevector-dependent Lindhard dielectric function (equation 11) to describe the metal response, terminating the metal at an infinite barrier at the surface. A set of reflection coefficients for the metal which include the nonlocal response are calculated and used in equation 70 to determine the rate of energy transfer from the molecule to the metal. From plots of the integrand of this equation as a function of wavevector, they find that the rates for radiative energy transfer and for nonradiative energy transfer to
Surface plasmons are unchanged from the local model, but that the response to high wavevector excitations is qualitatively different. The power dissipated at high wavevectors in the nonlocal model is due to electron-hole pair excitations, which will only occur over the wavevector range \( 0 < \mathbf{u} < \frac{c}{\omega} \left( \frac{2m\omega}{h+k_F^2} + k_F \right) \) due to momentum conservation restrictions. The result is that the unphysical divergence of the decay rate at the surface is removed, while the rate of energy transfer due to high wavevector excitations in close proximity to the surface is increased.

Korzeniewski, Maniv, and Metiu\textsuperscript{114} use a somewhat different approach to calculate the field due to a nearby oscillating dipole at a nonlocal metal surface. They use a jellium model (electrons moving in a positive background obtained by smearing out the positive ion cores) in which the dielectric response is allowed to vary continuously across the surface region. An infinite barrier is placed 1.624 Å from the jellium edge. A point dipole near the surface is used in their calculation which causes an induced charged density in the metal, from which the metal polarization can be computed. The metal polarization is then renormalized within the random phase approximation (RPA) due to screening effects in the metal. Numerical estimates of the electric fields at the surface are made, and it is found that the use of a smoothly varying dielectric response produces a smoothly varying electric field at the surface, rather than a cusp at the barrier position as is calculated using the model of Ford and Weber. Unfortunately, no estimates of energy transfer rates were made by the authors.

Another calculation of nonlocal metal surface response has been
done by Persson and Lang,\textsuperscript{115} who again use a jellium model with a continuous surface electron density distribution. Rather than an infinite surface barrier, however, a realistic surface potential derived by Lang and Kohn\textsuperscript{117} is used. The damping rate for a molecule in an excited state is calculated from the golden-rule formula:

\begin{equation}
\frac{1}{\tau} = \frac{2\pi}{\hbar} \int d^3k d^3k' n_k (1-n_{k'}) x \left| \langle k', n=0 | \tilde{\phi}_{\text{dipole}}(x) | k, n=1 \rangle \right|^2 \delta (\epsilon_k - \epsilon_{k'} - \hbar \omega)
\end{equation}

where

\begin{align*}
n_k &= 1 \text{ if } k < k_F \\
n_k &= 0 \text{ if } k > k_F
\end{align*}

and where $\epsilon_k$ and $\epsilon_{k'}$ are the energies of electrons in states $k$ below the Fermi surface and states $k'$ above the Fermi surface. In the above equation $\tilde{\phi}_{\text{dipole}}(x)$ is the screened dipole potential derived from the work of Lang and Kohn. After some calculation the surface damping rate is found to be approximately

\begin{equation}
\frac{1}{\tau} \approx 0.3 \frac{\omega}{\omega_F} \frac{\mu^2}{k_F d^4}
\end{equation}

for a material with an electron gas parameter $r_s = 3$, where $k_F$ and $\omega_F$ are the Fermi wavevector and frequency and $\mu$ is the transition dipole moment of the molecule. This model appears to provide an improved description of the energy transfer rate at short distances for molecules near free electron metals.\textsuperscript{118-120}

For excited molecules adsorbed at a metal surface where there is substantial metal–molecule wavefunction overlap, the possibility of
energy decay via electron exchange between the surface and the molecule must also be considered. Mechanisms of this type, first summarized by Hagstrum\(^{121}\) are depicted schematically in figure 27. Persson and Avouris\(^{122}\) have recently attempted to evaluate the contribution of mechanism b in figure 27 to the energy decay rate for molecules adsorbed on metals. Using a Hamiltonian for the metal-molecule system that includes a term which allows electrons to jump between the upper molecular orbital \(\left| 2 \right>\) and the metal orbital \(\left| k \right>\), they calculate an energy transfer rate using the golden rule formula of

\[
\frac{1}{\tau_{\text{electron transfer}}} = \frac{2\pi}{h} \sum_k \left| V_k \right|^2 \delta (\varepsilon_2 + u_{12} + u - \varepsilon_k)
\]

where \(u\) is the Coulomb repulsion energy for electrons in molecular orbitals \(\left| 1 \right>\) and \(\left| 2 \right>\) and \(u_{12}\) is the repulsion energy between an electron in orbital \(\left| 1 \right>\) and another in orbital \(\left| 2 \right>\). \(V_k\) is a tunneling integral that allows transfer of electrons between the molecule and the metal, as in equation 16. Qualitative agreement between the predictions of this model and the frequency shift and width of electronically excited Xe on Au was reported.\(^{122}\)

### 3. Effects of Surface Roughness

The theory that has been discussed so far regarding the decay of molecular excited states near metal surfaces has considered the surface to be a perfectly flat plane. Judging from the effects of surface roughness on the surface electric fields discussed in conjunction with Raman scattering, roughness effects may be expected to have an effect on
Figure 27. Energy decay mechanisms for an excited molecule near a metal surface. On the left of each part is shown the metal conduction band filled to the Fermi level $\varepsilon_F$, and on the right are two levels of an adsorbed molecule (the lower level X being the highest occupied level in the ground state). (a) Energy transfer by dipole coupling between the molecule and the metal, causing excitation of a metal electron-hole pair. (b) Resonant transfer (process 1) of an excited electron into an unfilled level of the metal conduction band. The resulting ion usually relaxes via Auger neutralization (process 2) where a metal electron fills the lower molecular level with ejection of a metal Auger electron. (c) For an excited state below the Fermi level, resonant transfer is inhibited and one step Auger deexcitation (Penning ionization) may take place.
the excited state decay rates that are observed near these surfaces. Although only a few calculations have been performed to date on the effects of roughness on the decay rate, these effects will be discussed briefly in two limits: the limit of large-scale roughness which can be considered as isolated spheres and spheroids on the surface, and the limit of small-scale random roughness.

The case of energy transfer near a sphere has been treated by Ruppin,\textsuperscript{123} who has done a full electrodynamic calculation based on the results of Kerker et al.\textsuperscript{50} for the electric fields of a dipole near sphere. The transmitted field $E_{tr}$ inside the sphere is obtained by applying boundary conditions at the sphere surface with the dipolar fields $E_{dip}$ and scattered fields $E_{sc}$ outside the sphere. The rate of energy loss from the molecule is then calculated as the sum of two terms: the radiative loss due to the fields outside the sphere, and the nonradiative loss due to energy absorbed inside the sphere. The radiative decay rate is calculated by evaluating the Poynting vector and integrating the energy flux obtained from it over the surface of a large sphere, as was done in calculating the scattering efficiency from a sphere in Mie theory. The rate at which energy is absorbed in the sphere is calculated from Joule heating losses inside the sphere:

\begin{equation}
 b_{nr} = \frac{1}{2\omega} \int \sigma(\omega) \left| E_{tr}(r,\omega) \right|^2 dr
\end{equation}

where $\sigma(\omega)$ is the conductivity of the sphere which is proportional to the imaginary part of the dielectric function. The lifetimes that are calculated using this equation indicate that at small separations ($d < 50 \text{ Å}$ for an emission wavelength of 300 nm) from the surface of a 100 Å
radius sphere, the energy transfer rates away from resonances are identical to those observed near a flat surface. Thus for small separations from the sphere, the local geometry looks like a planar metal surface to the molecule. The frequency dependence of the nonradiative decay rate, however, is changed significantly and shows peaks near the surface plasmon resonance conditions for the sphere.

A somewhat different result is obtained when the energy transfer rates from a molecule to a spheroid are considered. Gersten and Nitzan have calculated the total dipole moment of a system consisting of a spheroid with a molecule located on a line extending along the major axis in the electrostatic limit. Considering only excitations of dipolar modes parallel to the major axis of the spheroid, they calculate a radiative decay rate as the emission from this fluctuating dipole moment and a nonradiative decay rate as the Joule heating in the spheroid (equation 78) caused by the fluctuating fields of the dipole. Results obtained using this model for the nonradiative decay rate are depicted in figure 28 as a function of the separation of the molecule from the tip of the spheroid. For the case of a sphere (aspect ratio = 1) the same results are obtained as in the previous calculation: the nonradiative decay rate is nearly the same as that for a planar surface out to a distance of over 100 Å. For spheroids with aspect ratios of 1.75 (resonant with the emission energy) and 3.0 (nonresonant), however, the nonradiative rate increases above that expected for a planar surface for separations greater than 5-10 Å. This effect is due to the concentration of the electric field at the tip of the spheroid ("lightning rod" effect), which increases the loss due to Joule heating.

The only theoretical treatment to date of the lifetime of a
Figure 28. Calculated nonradiative decay rates for a molecule near spheroids of several different aspect ratios as a function of molecule-surface separation. The molecule is taken to be a perpendicular dipole emitting at 3.17 eV with a quantum yield of one and a free radiative decay rate of $4.3 \times 10^8$ sec$^{-1}$ (from reference 124).
molecule near a surface with small, random roughness is that of Arias et al.\textsuperscript{125} The surface profile used in this calculation is that depicted in figure 4, with a Gaussian roughness correlation function and root-mean-square roughness heights $\delta$ in the range of 20-150 Å. Using the results of Rahman and Maradudin\textsuperscript{126} for the image potential of a point charge above a rough surface (calculated electrostatically by solving Poisson's equation above and below the surface and applying boundary conditions), they calculate the image field of a point dipole near a rough surface. The energy transfer rate is then calculated by using this modified image field in equation 67 to determine lifetimes at a rough surface:

\begin{equation}
\begin{aligned}
b = b_0 + \frac{\varepsilon}{\varepsilon_\infty} \operatorname{Im} \left( \frac{8}{3} \frac{(\varepsilon-1)^2}{\varepsilon+1} \right) \int_0^\infty f(\varepsilon, \xi) e^{-2\xi d/a} d\xi
\end{aligned}
\end{equation}

In this equation $d$ is the distance between the molecule and the mean surface plane, $a$ is the correlation length of surface roughness, $\varepsilon(\omega)$ is the dielectric function of the metal, and $f(\varepsilon, \xi)$ is a complex function which is given in detail in reference 125.

Numerical computations using equation 79 indicate that the energy transfer rate near a rough surface can be much larger than that near a flat surface. The effect is most pronounced for small separations from the surface ($d < 30 \, \text{Å}$), and increases with increasing roughness height $\delta$ and decreasing correlation length $a$. The largest effects are seen near the surface plasmon resonance frequency, on the low energy side of the resonance. The largest increase in energy transfer rate calculated by Arias et al.\textsuperscript{125} was a factor of 20 over that calculated for a flat surface for a dipole emission energy of 3.5 eV and a surface roughness amplitude $\delta = 150 \, \text{Å}$. 
C. Theory of Nonlinear Photoeffects at Metal Surfaces

The nonlinear optical properties of a material can be expressed as a power series in the electric field of the polarization $P$ induced in the material by the fields:

$P = \vec{\chi} \cdot \vec{E} + \chi^{(2)} \vec{E} \vec{E} + \chi^{(3)} \vec{E} \vec{E} \vec{E} + \ldots$  \hspace{1cm} (80)

Having established from the Raman experiments that there are enhanced local fields at the surfaces of the rough, sputtered silver crystals used in these studies, we can expect from the above equation that enhancement effects will be observed for nonlinear phenomena as well as linear phenomena such as Raman scattering. Since nonlinear effects are proportional to a higher power of the electric field than linear phenomena, they are expected to be more sensitive to local field factors.

The lowest order nonlinear effects are due to the second-order susceptibility $\chi^{(2)}$ in equation 80. Second order polarization effects include sum and difference frequency generation, second harmonic generation, and optical rectification (d.c. voltage generation). The polarization due to the nonlinear term $\chi^{(2)}$ is a quadratic function of the field:

$P_i(\omega_3, \vec{r}) = \frac{1}{2} \chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)$

$\propto \frac{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{r} - i(\omega_1 + \omega_2) \xi_1}{\omega_2 + c.c.}$  \hspace{1cm} (81)

$E_j(\omega_1) = E_j(\omega_1) \text{ and } E_k(\omega_2) = E_k(\omega_2)$

$\xi_1 = \xi_1(\vec{k}_1, \vec{k}_2, \vec{r})$
In an isotropic medium such as a metal single crystal, symmetry conditions indicate that second harmonic generation (SHG) from the second-order susceptibility \( \chi^{(2)} \) is zero in the dipole approximation. If the symmetry is broken at the surface by the presence of roughness or adsorbates that are noncentrosymmetric, however, there may be large dipolar contributions to SHG from the surface region.

At a surface where enhancement of the electric field exists, the intensity in the beam at the harmonic frequency is proportional to \(^{127}\)

\[
I_{\text{SHG}} \propto \left| \chi^{(2)} L(2\omega) L^2(\omega) E^2(\omega) \right|^2
\]

where \( L(2\omega) \) and \( L(\omega) \) are quantities describing the enhancement of the electric field at the second harmonic and incident frequencies, respectively. Enhancement of SHG will thus be proportional to the fourth power of the local field enhancement factor at the incident frequency and the square of the field enhancement factor at the harmonic frequency. Unfortunately, for the case of silver surfaces when the incident field is in the visible region of the spectrum where enhancements are very high, the harmonic frequency is in the deep UV where absorption in the metal is very high. For incident frequencies in the near IR, however, the incident field is unenhanced but the second harmonic field is enhanced by the factor \( L(2\omega) \). The intensity enhancement factor \( L^2(2\omega) \) has been shown to be as large as 1000 for a second harmonic wavelength of 532 nm. \(^{103}\)

Higher order nonlinear effects which are due to the third-order susceptibility \( \chi^{(3)} \) include third harmonic generation, various three-wave mixing processes, and two photon absorption. The third-order
nonlinear susceptibility is nonvanishing even in media with inversion symmetry, and induces a dipole moment in the material which is cubic in the electric field:

\[ P_1(\omega_4, \mathbf{r}) = \frac{1}{2} \chi^{(3)}_{ijk1}(\omega_4, \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_1(\omega_3) \]

\[ \times e^{i(k_1 + k_2 + k_3) \cdot \mathbf{r} - i\omega_4 t} + \text{c.c.} \]

Third harmonic generation will occur for \( \omega_1 = \omega_2 = \omega_3 = \omega \) and \( \omega_4 = 3\omega \). The intensity in the third harmonic beam at a surface where enhancement occurs will be given by

\[ I_{THG} \propto \left| \chi^{(3)}_{L(3\omega)} L^3(\omega) L^3(\omega) \right|^2 \]

It can be seen from this equation that enhancement at the fundamental frequency is expected to be enhanced by the field enhancement factor \( L(\omega) \) to the sixth power. Again, however, for frequencies in the visible (or near IR) the third harmonic frequency will be in the UV and will be severely attenuated for silver. If the incident beam is in the IR, the third harmonic beam will be in the visible region and can be enhanced by a factor of \( L^2(3\omega) \) in the right wavelength region. Enhanced third harmonic generation is expected to be much smaller than enhanced SHG since third-order susceptibilities are in general much smaller than second-order; third harmonic generation has not yet been observed at rough silver surfaces.

When the frequencies in equation 83 are taken to be \( \omega_3 = -\omega_1 \) so that \( \omega_4 = \omega_2 \), the polarization in the nonlinear medium becomes

\[ \chi^{(3)}_{L(3\omega)} L^3(\omega) L^3(\omega) \]
This polarization, which is proportional to the intensity at $\omega_1$ and the imaginary part of the susceptibility $\chi^{(3)}$, describes two-photon absorption by the material. The absorption will then be proportional to the product of the intensities in the two beams at $\omega_1$ and $\omega_2$. If two-photon absorption occurs from a single beam, $\omega_1 = \omega_2 = \omega$ and the power absorbed in the two-photon process is

\begin{equation}
\mathcal{P}(\omega) = \chi^{(3)} | E(\omega_1) |^2 \, E(\omega_2) \, e^{i(k_2 \cdot r - \omega_2 t)}
\end{equation}

Two-photon absorption is thus expected to be proportional to the fourth power of the field enhancement factor $L(\omega)$ at whatever incident frequency is used; for rough silver in the visible region of the spectrum, this enhancement may be quite large. Two-photon absorption may thus be more sensitive to surface field enhancement on silver than the other nonlinear processes that have been discussed.

Two-photon absorption by molecules at the metal surface may be observed in two ways: luminescence at the two-photon frequency or photochemical reaction of the molecule. For molecules very near a rough silver surface, the excited state lifetime is expected to be severely shortened by energy transfer to the surface, and the luminescence quantum yield will become very low. Enhanced two-photon luminescence has, however, been observed for molecules on silver island films, presumably due to molecules on the substrate between silver islands where the energy transfer rate is lower and luminescence can be
observed. If a rapid photochemical step occurs for the adsorbed molecule before de-excitation by energy transfer takes place, then strongly enhanced two-photon photochemistry may occur at a rough silver surface.
D. Experimental Section

Photodecomposition of a large number of different molecules on rough silver substrates in UHV was investigated using the visible and near UV output of argon and krypton ion lasers. Decomposition was observed by monitoring the Raman spectrum of the molecule under irradiation in the graphitic carbon C-C stretch region of the spectrum near 1580 cm\(^{-1}\), using the same laser light for Raman scattering that was used to cause fragmentation of the molecule. Laser intensities used were in the range of 20-1000 W/cm\(^2\), obtained by focussing the output of the ion lasers to a 50x130 \(\mu\)m ellipse on the silver surface with a 350 mm focal length lens.

Spectroscopy and photochemistry were done using p-polarized light incident at 70° from surface normal. Scattered light was collected normal to the silver crystal surface using an f/1.0 fused silica collimator inside the vacuum chamber (Figure 9). The collimated light was brought out of the chamber through a quartz viewport and focussed onto the slits of a Spex 1400 double monochromator with an f–matching lens. The spectrometer was scanned using a stepping motor under the control of an LSI-11 microprocessor, and signal was detected using a photomultiplier with photon counting electronics. For UV spectra an EMI 6256S phototube was used, cooled to -50°C with dry ice and operated at -1300 v. The signal was routed to the microprocessor via a 32-bit binary counter and stored on a magnetic disk.

The experiments were performed in the same UHV work chamber as was used for the Raman scattering studies. The surfaces used in this study were rough silver single crystals prepared by sputtering on mechanically
polished surfaces as described earlier. Molecules were condensed on the surface by cooling the crystal to 90 K using liquid nitrogen. Between experiments the crystal was warmed to room temperature and sputtered with argon ions to remove fragmentation products and surface carbon. Residual surface carbon was detected using surface enhanced Raman scattering.

Pulsed laser studies of photochemistry on the surface were done using several types of lasers and experimental configurations, with peak laser intensities in the range of \(10^5 - 10^8\) W/cm\(^2\). Studies of the effects of pulsed laser excitation on the rate of surface carbon formation obtained using ion laser excitation at 363.8 nm were done by simultaneously irradiating the surface with both lasers. An unfocussed pulsed beam was brought into the chamber through a second quartz viewport and directed to cover most of the approximately 1 cm\(^2\) area of the crystal surface. Pulses of 5 nsec duration with pulse energies in the range of 0.5 - 3.5 mJ at 400 nm were obtained by frequency doubling the output of an Nd:YAG laser (Quanta-Ray DCR-1) and pumping a dye laser (Quanta-Ray PDL-1). The dye laser output (DCM dye) was mixed with the 1.06 \(\mu\)m output of the YAG laser in a KDP crystal to obtain pulses at 400 nm.

Studies were also done of ionization of surface adsorbed molecules using pulsed lasers. In this experiment, an XeCl excimer laser (Lumenics 861-II) was used to pump a dye laser (Lambda Physics 2002E) with an output at 364 nm using BPBD dye. To extend the frequency range of these studies, the output of the dye laser using Coumarin 540A dye was doubled to obtain pulses in the 270-290 nm region. The laser output (approximately 0.5 mJ/pulse) was weakly focussed on the silver surface.
using a 250 mm focal length fused silica lens to obtain peak intensities in the $10^6 - 10^8 \text{ W/cm}^2$ range for surface photoionization.

Ions desorbed from the silver surface were detected in a modified quadrupole mass spectrometer (UTI 100C) in which the electron multiplier was replaced with a high gain channeltron version (Galileo 4817G). The ionizer was removed from the mass spectrometer, and a one inch diameter nickel grid was mounted three inches from the focus plate at the entrance to the quadrupole. In operation, the silver crystal was biased at +300 V with a battery, the collection grid was biased at -50 V, and the focus plate was biased at -70 V. These modifications provided a large increase (over two orders of magnitude) in ion sensitivity compared to operation of the quadrupole with the ionizer turned off.
E. Photodecomposition

1. Decomposition using 406.7 nm excitation

All of the molecules investigated for photodecomposition on rough silver (with the exception of benzaldehyde) showed a maximum decomposition rate at 406.7 nm compared to the other ion laser lines used in the study (Ar 363.8 nm, 457.9 nm, and 514.5 nm; Kr 350.7 nm). One of the few things that all of the molecules exhibiting photodecomposition at this wavelength have in common is the lack of any electronic states at or below this energy. Recent studies of the electronic states of aromatic molecules adsorbed on silver indicate that the low lying electronic states of benzene, pyridine, and pyrazine are perturbed by only a few tenths of an eV from gas phase values by interaction with the metal surface. It is thus highly unlikely that the low lying electronic states of any of the aromatic molecules studied are shifted sufficiently by interaction with the surface to be in resonance with the laser excitation energy.

The only possibilities energetically allowed for absorption by the molecule are the simultaneous absorption of two or more photons, or frequency up-conversion at the metal surface followed by molecular absorption. To differentiate between these two absorption processes we compare two photon absorption (using a typical cross section of $10^{-50}$ cm$^4$ sec molecule$^{-1}$ photon$^{-1}$) to that of surface second harmonic generation (SHG) followed by an allowed one photon absorption (cross section $10^{-15}$ cm$^2$ molecule$^{-1}$). Using the highest values for surface SHG reported for silver surfaces (for 1.06 μm incident on electrochemically roughened surfaces) we find that excitation via two photon absorption
is several orders of magnitude larger than that of SHG followed by a one-photon absorption. Studies of SHG on rough silver at shorter wavelengths (683 nm) where Raman enhancement is $10^6$ show a drop in SHG intensity by a factor of 100 from that observed at 1.06 μm. Although data is lacking for the wavelengths and exact surface structures employed in our experiments, the available evidence implies that two-photon absorption is by far a more efficient process than SHG followed by absorption. A similar conclusion was reached in two-photon fluorescence experiments on silver island films where SHG was found to be too small to account for the observed fluorescence signal.

A two-photon initial absorption step in our photofragmentation experiments is supported by studies of the initial decomposition rate as a function of incident laser power for pyridine and benzaldehyde. As shown in figure 29 the photodecomposition rate for pyridine with 406.7 nm excitation varies approximately as the square of the incident light intensity for laser power between 5 and 50 mW. Some saturation of initial decomposition rate is observed for higher incident power. This is apparently due to depletion of molecules on the surface, since although appreciable surface carbon increase is still observed several minutes after irradiation is begun, it occurs at a much lower rate than that observed initially. Possible mechanisms for energy redistribution and fragmentation following multiphoton absorption will be discussed in the next sections.

Pyridine and pyrazine The electronic states of the azabenzenes have been quite thoroughly studied. The presence of lone pair electrons on the nitrogen heteroatoms of these molecules give rise to
Figure 29. Photodecomposition rate as a function of incident laser power for 10L pyridine adsorbed on roughened Ag(110). Decomposition rate is measured as a change in the Raman signal per unit time (counts/sec^2), corrected for the difference in Raman intensity at different incident laser intensities.
PYRIDINE PHOTODECOMPOSITION RATE ON A ROUGHENED Ag(I1O) SURFACE

\[ \lambda = 4067 \text{ Å} \]

Initial Surface Photodecomposition Rate

Slope = 1.8

Incident Laser Power (mW)
strong $n\pi^*$ transitions not observed in benzene. Shown in figures 30 and 31 are the energy levels of known electronic excitations labeled with excited state symmetries for gas phase molecules. Electron energy loss studies of these molecules adsorbed on Ag(111)\textsuperscript{9} show energy levels of the adsorbed phase molecules 0.1-0.2 eV higher than values observed in the gas phase.

The three most prominent transitions observed in both gas phase and condensed phase one-photon absorption spectra of pyrazine ($^1B_3u$, $^1B_2u$, and $^1B_1u$) are not allowed for two photon transitions due to their odd parity. For molecules adsorbed on a surface, though, these symmetry rules may be broken by interaction with the surface. In any case these states can have vibronically allowed two photon transitions, and the $B_3u$ state has been studied by two photon absorption with fluorescence and phosphorescence detection.\textsuperscript{133,134} Studies of gas phase pyrazine in the energy region for two photon absorption at 406.7 nm (6.10 eV) produced no evidence for vibronically allowed absorption to the $B_1u$ state, though, but instead showed a two photon allowed $n\rightarrow 3s$ ($A_1$) transition to a Rydberg state.\textsuperscript{135,136} This transition may not be observed in condensed phases, however, since Rydberg states are generally weakened substantially as well as broadened compared to the gas phase.\textsuperscript{137}

A study by Esherick et al\textsuperscript{133} of two photon absorption in pyrazine crystals indicates that the observed two photon transition intensities to the $B_2u$ ($\pi\pi^*$) state were much larger than their calculations of vibronic interactions indicated that they should be. Their hypothesis was that the majority of intensity in this region was due to the presence of a $B_2g$ state at an energy slightly higher than that of the $B_2u$ state. Recent calculations of pyrazine energy levels by SCF-CI\textsuperscript{138}
Figure 30. Energy levels of pyridine and appearance potentials of possible fragmentation products. The arrows along the left side correspond to the energies of photons at 350.7 nm and at 406.7 nm.
Figure 31. Energy levels of pyrazine and appearance potentials of possible fragmentation products.
and valence bond methods also place the \( ^1B_{2g} (\pi\pi^*) \) transition in this energy region rather than near the \( B_{3u} \) state as has been assumed by many others. Thus we can tentatively assign the initial absorption step in our pyrazine photodecomposition experiments to a two photon allowed transition to the \( ^1B_{2g} \) state.

Pyridine (\( C_2v \) symmetry) is a molecule of low symmetry compared to pyrazine (\( D_{2h} \)). Consequently, the electric dipole selection rules are much less restrictive for pyridine transitions and all of the symmetry species can give rise to an allowed two photon transition from the ground state. The initial absorption step in our studies of pyridine is most likely two photon absorption into the \( ^1A_1 (\pi\pi^*) \) state at 6.2 eV.

Pyridine and pyrazine both readily photodecompose on rough silver surfaces with 406.7 nm irradiation (table 3). There have been few other studies of the photodecomposition of these molecules — most attempts to photolyze pyridine and pyrazine have shown that they do not photodecompose under normal spectroscopic conditions.\(^{140}\) Mathias and Heiklen,\(^{141}\) however, have done a careful study of the gas phase photolysis of pyridine using intense light at 213.9 nm and 228.8 nm. They report that pyridine photodecomposes at a rate dependent on the total energy content of the excited state (whether thermal or photolytic) by molecular elimination into one molecule of acetylene and one molecule of acrylonitrile. At room temperature in their experiments the acrylonitrile leads predominantly to a polymer, while at high temperature (260°C) the acrylonitrile is photolized to form \( C_2H_2 \) and \( HCN \) and/or \( C_2N_2 \) and \( H_2 \).
Table 3. Relative photodecomposition rates at 350.7 nm and 406.7 nm for 20 mW incident laser power

<table>
<thead>
<tr>
<th></th>
<th>406.7 nm</th>
<th>350.7 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Pyridine</td>
<td>35</td>
<td>14</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>490</td>
<td>10</td>
</tr>
<tr>
<td>Aniline</td>
<td>97</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>140</td>
<td>2050</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>&lt; 0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

The initial step in the surface photodecomposition of pyridine may be direct fragmentation to neutral molecule fragments as has been observed for the gas phase, or may involve other surface intermediate species such as radicals or ions. We have looked for intermediate species in surface photodecomposition reactions using Raman spectroscopy. The only evidence we have of intermediates in the decomposition of pyridine or pyrazine is the appearance of a CN stretching mode near 2200 cm⁻¹ (figure 32). This frequency is substantially shifted from the 2113 cm⁻¹ vibration observed for CN adsorbed on a silver electrode surface¹⁴² and may indicate the presence of larger fragments such as CH₂=CHCN (vCN = 2222 cm⁻¹) on the surface.

Shown in figures 30 and 31 are the formation energies of a number of possible intermediate and product species in the photolysis of pyridine and pyrazine. Fragmentation may occur through multiphoton
Figure 32. Raman spectra of (a) pyrazine and (b) pyridine photodecomposed using 406.7 nm excitation.
absorption into the ion continuum of states, followed by subsequent additional absorption steps and fragmentation. The formation of ionic fragments of pyridine has been studied by electron impact mass spectrometry\textsuperscript{143} and by multiphoton ionization using 193 nm excitation.\textsuperscript{144} The observation of charge-transfer excitations for pyridine and pyrazine adsorbed on silver\textsuperscript{9} raises the possibility of fragmentation by excitation of a bonding electron into the silver continuum above the Fermi level for a molecule adsorbed directly at the surface. Jonsson et al\textsuperscript{145} indicate that excitation of a pyridine 1b\textsubscript{1} electron (IP = 12.2 eV) from a strongly C–C bonding π orbital will break the ring.

Published reports of pyrazine photolysis are almost nonexistent. One of the few recent reports is the observation by Webb et al\textsuperscript{134} of fluorescence emission by cyanyl radicals following two photon absorption by pyrazine at 4.0 eV. The large number of relatively low energy radical fragments of pyrazine (figure 31) indicates that radical formation is a likely fragmentation pathway for this molecule.

**Benzaldehyde and acetophenone** Both benzaldehyde and acetophenone have also been well studied spectroscopically.\textsuperscript{146} Although the molecules are very similar structurally and electronically, they exhibit strikingly different behavior photochemically in our experiments. Excitation for both molecules with 406.7 nm irradiation is probably two photon absorption into a 1A\textsuperscript{-} (ππ\textsuperscript{*}) state near 6 eV (figure 33). This assignment is consistent with intensity dependence measurements for the photodecomposition of benzaldehyde which show an approximately quadratic dependence of rate on incident laser power. Acetophenone, however,
Figure 33. Energy levels of benzaldehyde and appearance potentials of possible fragmentation products.
shows no photofragmentation under our conditions.

The photochemistry of benzaldehyde has been investigated extensively by Berger et al.\textsuperscript{147} They examined the photochemistry and phosphorescence emission of benzaldehyde for excitation into the first and second excited states (365 nm and 276 nm, respectively). For excitation into $S_2$, they found rapid population of two vibrationally excited triplet states which both dissociate at low pressure to form molecular benzene and CO. Collisional deactivation of these states yielded the lower vibrational levels of the lowest triplet state from which no photochemistry was observed. For excitation into $S_1$ no benzene or carbon monoxide formation was observed but benzaldehyde was consumed, leading apparently to polymer formation by a radical mechanism. The general features of this photochemical behavior were confirmed by Robin and Kuebler\textsuperscript{148} who additionally found radical formation from excitation into $S_3$.

The photochemistry of acetophenone was found by Berger and Steel\textsuperscript{149} to be qualitatively different than that of benzaldehyde as a function of excitation wavelength. For excitation into the $S_1$ ($n\pi^*$) state of acetophenone no photochemistry was observed. For excitation into $S_2$ ($\pi\pi^*$) rapid intersystem crossing was observed into a vibrationally excited triplet, which could then undergo decomposition to radicals at low pressure. At high pressures the excited state underwent collisional deactivation and photochemistry did not occur. The same type of collisional deactivation was observed for excitation into $S_3$ of acetophenone.

Thus for excitation into highly excited singlet states, benzaldehyde and acetophenone both undergo decomposition to yield
radicals. The difference between the two molecules appears to be that benzaldehyde undergoes a primary photochemical step at a far faster rate than the collision frequency to give radicals, while for acetophenone a second gas can quench free radical photochemistry by collisional deactivation. These gas phase photochemical results are consistent with the surface photochemistry we have observed for benzaldehyde and acetophenone. The faster fragmentation timescale of benzaldehyde may allow this pathway to continue to be important even in the presence of strong surface damping of the excited state where acetophenone is rapidly quenched, thus explaining the observed difference in fragmentation rates for these two molecules with two photon 406.7 nm excitation in our experiments.

The Raman spectra of benzaldehyde during photodecomposition at 406.7 nm and 350.7 nm show several interesting features (figure 34). The peaks near 1000 cm\(^{-1}\) and 1180 cm\(^{-1}\) can be assigned to vibrational modes of adsorbed benzaldehyde. Although no new modes appear that can be assigned to surface intermediate species, the carbon mode that normally appears at 1350 cm\(^{-1}\) in other spectra of photofragmented molecules with 406.7 nm excitation is shifted. It appears at 1320 cm\(^{-1}\) in the 406.7 nm spectrum and at 1295 cm\(^{-1}\) in the 350.7 nm spectrum. This carbon peak in the 1300 cm\(^{-1}\) region is attributable to an in-plane \(A_g\) mode of graphite which is silent for an infinite carbon layer but becomes active for small or imperfect layers due to relaxation of wavevector selection rules.\textsuperscript{150} The shifts observed in the benzaldehyde spectra are most probably due to differing surface carbon morphology.

Other molecules Benzene, as mentioned in the preceding
Figure 34. Raman spectra of photodecomposed benzaldehyde using (a) 350.7 nm excitation and (b) 406.7 nm excitation.
discussion, was one of the few aromatic molecules examined which did not decompose to any extent at 406.7 nm. The photochemistry of benzene has been examined extensively\textsuperscript{151}, and while many isomers of benzene have been found to form upon excitation into lower singlet states, fragmentation has not been observed. Multiphoton ionization of benzene has also been studied extensively in both the gas\textsuperscript{152-156} and liquid\textsuperscript{157} phases. For excitation wavelengths near 400 nm, the ionization has been shown to be a three photon process with a two photon resonance at the $^{1}B_{1u}$ state of benzene. Mass spectroscopy studies in the gas phase indicate that primarily the benzene ion is formed at low intensities, while substantial fragmentation is observed at higher intensities (approx. $10^{10}$ W/cm\textsuperscript{2}) resulting from absorption of up to nine photons.\textsuperscript{154} Fragmentation of benzene thus appears to occur readily for sequential photon absorption by benzene ions, but not through neutral intermediates. Photochemistry under our conditions would depend on the generation and lifetime of benzene and fragment ions. If ionic intermediates are not sufficiently long-lived on the surface for further absorption of photons to occur, fragmentation to carbon would not be observed.

Aniline was found to decompose readily under the conditions of our study at 406.7 nm (table 3). A survey of the energy levels of aniline (figure 35) indicates that the lowest excited states of aniline are above the laser energy at 406.7 nm, but that there is a two photon resonant state at 6.1 eV. Aniline dissociation has been studied by flash photolysis in solution\textsuperscript{158} where anilino radical formation has been observed. Aniline cation radicals were found under the same conditions in higher dielectric constant solvents. Multiphoton ionization and
Figure 35. Energy levels of aniline and appearance potentials of possible fragmentation products.
fragmentation of aniline in the gas phase has also been observed\textsuperscript{159,160} with an order of magnitude higher cross-section than that of benzene.\textsuperscript{160} Photofragmentation under our conditions may occur by either of these mechanisms following resonant two photon absorption.

2. Decomposition at other wavelengths

As indicated in table 3, photodecomposition rates were investigated for a number of molecules for excitation with both 406.7 nm and 350.7 nm light from a krypton laser. In general, with the exception of benzaldehyde and possibly benzene, the measured decomposition rate after correction for Raman detection efficiency (table 2) was higher at 406.7 nm than at 350.7 nm. For one of the molecules studied, pyridine, decomposition rates were measured at several intermediate wavelengths (356.4 and 363.8 nm) and were found to be smoothly decreasing toward shorter wavelengths. Pyridine photodecomposition was also looked for at 457.9 nm and 514.5 nm - no decomposition was observed at these wavelengths for the same incident power as used in the UV experiments (20 mW). The photodecomposition rate is peaked near 400 nm, then, with a gradual decrease in rate at shorter wavelengths and a sharp falloff at longer wavelengths.

As mentioned earlier, the wavelength dependence of Raman enhancement on the surfaces used in this study were determined by measuring carbon 1580 cm\textsuperscript{-1} peak height at constant energy resolution for the various excitation wavelengths available. Raman enhancement at 350.7 nm is a factor of 9 smaller than that observed at 406.7 nm, while the enhancement at 457.9 nm is a factor of 3 larger than that observed
at 406.7 nm. If photodecomposition rate and Raman enhancement are controlled by the same mechanism then one should observe a decreasing photodecomposition rate as the exciting wavelength is changed from 406.7 nm to 350.7 nm and the Raman enhancement drops, provided that there are no dramatic changes in the cross-section for electronic excitation at these wavelengths. This appears to hold true for pyridine, pyrazine, and aniline - broad absorption peaks near 6 eV are observed for all these molecules. A sharp drop in decomposition rate at longer wavelengths is expected as there will no longer be a resonant two photon absorption.

An entirely different trend is seen, however, with benzaldehyde. The photodecomposition rate at 350.7 nm is $1.5 \times 10^2$ times faster than at 406.7 nm. Looking at the energy levels of benzaldehyde it can be seen that the energy of a single laser photon at 350.7 nm is now above the lowest singlet $n^* \rightarrow \pi^*$ transition. Berger, Goldblatt, and Steel report that gas phase benzaldehyde undergoes polymerization via a radical mechanism upon excitation into $S_1$. We propose that in our surface experiments benzaldehyde undergoes decomposition also directly from the lowest excited singlet. This hypothesis is supported by laser power dependence studies of photodecomposition rates at 350.7 nm and 406.7 nm. At 406 nm the fragmentation rate depends on the square of the incident power for low laser powers, while at 350 nm the dependence becomes linear in laser power. Thus in this case fragmentation to carbon atoms begins as a result of single photon absorption with a higher absorption probability at the intensities used in these experiments than that for two photon processes.
3. Temperature dependence

Preliminary experiments were done to investigate the temperature dependence of pyridine photodecomposition on rough silver. Photodecomposition of pyridine on a surface maintained at 125 K showed an initial decomposition rate a factor of 15 larger than that observed when the surface was at 90 K. When the surface temperature was raised to 180 K no fragment carbon signal increase was observed, corresponding to desorption of molecules from the surface. Thermal desorption spectra for a monolayer coverage of pyridine adsorbed on the surface show a desorption temperature of 173 K (this corresponds to a physisorbed pyridine desorption peak reported by others\textsuperscript{161}).

This preliminary data indicates that the reactions leading to surface carbon are thermally activated, possibly by activation of surface migration of intermediate species. A more detailed study of the temperature dependence of surface photofragmentation is necessary before any more definitive conclusions can be drawn.

4. Distance dependence

In order to determine whether or not the photofragmentation process observed on our silver surfaces depends on distance from the surface in the same way as Raman enhancement, molecules of a substance which showed surface photodecomposition (pyridine) were spaced varying distances from the silver surface with a layer of a substance which did not show any appreciable decomposition (benzene). The thickness of the spacer layers was determined by exposing the surface at 90 K to a timed exposure of
the spacer molecule. The exposures were calibrated on a smooth silver surface by ellipsometry, which indicated a 10 ± 2 Å coverage of both benzene and pyridine for a 10L exposure.

Photodecomposition rate was measured for a 20L exposure of pyridine on rough silver with varying thicknesses of an intervening spacer layer. The results are depicted in figure 36, where it is seen that the initial decomposition rate increases for 10L and 20L spacer layers but decreases again for thicker spacer layers. It is evident from these results that the mechanism responsible for enhancement of photofragmentation shows a component with a much more extended range from the surface than excited state damping by dipolar coupling to surface modes. This topic will be discussed further in the following section.

5. Decomposition using pulsed excitation

Photodecomposition of a number of molecules (pyridine, pyrazine, and aniline) adsorbed on rough silver was investigated using pulsed excitation to determine what effect the high peak powers obtainable using pulsed lasers would have on surface photodecomposition rates. Evidence of photodecomposition induced by the pulses was looked for by observing the amorphous surface carbon region (1580 cm⁻¹ Raman shift) with 514.5 nm ion laser excitation, and hitting the surface with 400 nm pulses at 10 Hz with peak intensities in the range of 3 x 10⁵ - 3 x 10⁶. No evidence of any change in the surface carbon Raman peak height could be observed.

In another experiment pyridine was fragmented on the surface using
Figure 36. Photodecomposition rate for 20L pyridine deposited on a benzene spacer layer of varying thickness with 406.7 nm excitation. The different symbols correspond to experiments on different areas of the same crystal.
argon excitation at 363.8 nm, with the rate being determined by monitoring the carbon peak height at 1580 cm\(^{-1}\) shift from the laser line. Laser pulses at 400 nm were then superimposed on this excitation to determine their effect on the fragmentation rate. For intensities below \(2 \times 10^6\) W/cm\(^2\) no effect was observed on the rate; for intensities slightly above this level the decomposition rate was observed to drop to zero. Increasing the incident intensity still further by focussing the pulsed laser using a 30 cm focal length lens to obtain an intensity at the surface of \(6 \times 10^7\) W/cm\(^2\), the carbon peak height was observed to drop suddenly to a very low level when the pulsed laser was turned on.

These effects are interpreted as follows: for pulsed laser intensities below \(2 \times 10^6\) no fragmentation occurs due to the pulsed laser, as determined by observing the amount of carbon on the surface. This pulsed laser intensity corresponds to an energy density in the laser pulse of approximately 10 mJ/cm\(^2\), which for the 10 Hz repetition rate used yields an average power density to the surface of 0.1 W/cm\(^2\). If the surface photofragmentation rate is postulated to be limited by some rate-limiting step other than the excitation rate at intensities slightly above those used in continuous laser experiments, then excitation with pulses at the above power density should give results similar to continuous excitation at that power density. The assumption of a rate limiting step at intensities greater than approximately 1000 W/cm\(^2\) is not unreasonable given the saturation effects observed near this intensity in figure 27. Continuous laser excitation will not produce any observable signal at that low of a power density in our experiments; pulsed laser excitation would thus not be predicted to produce measurable decomposition.
Pulsed laser intensities in the range of $2-3 \times 10^6 \text{ W/cm}^2$ cause a decrease in the rate of surface carbon formation induced by continuous UV ion laser excitation. This is interpreted as desorption of the reactant molecules from the surface due to thermal effects. The temperature rise needed to desorb pyridine from the surface is on the order of $\Delta T = 80^\circ$ (figure 23), which may easily be obtained at the high peak intensities of the pulsed laser (see appendix A). As the pulsed laser intensity is raised still further to $6 \times 10^7 \text{ W/cm}^2$, desorption of surface carbon occurs (due also presumably to thermal effects) which results in a decrease in the carbon peak. It thus does not appear likely that the photofragmentation effects that we have observed using low power ion laser excitation can be observed using short pulse length, high peak power lasers due to desorption from the surface.
F. Energy damping vs. photofragmentation

As discussed by Nitzan and Brus,\(^3\) the observation of enhancement in photochemical reactions near a metal surface will depend on the interaction of two competing factors: enhanced accumulation of energy by the molecule due to interaction with the surface versus very effective transfer of energy from the molecule to the metal at short distances. Considering first the process of energy damping by the metal surface, it has been shown that the simple classical image formula for the nonradiative decay rate via dipole coupling predicts quantitatively the rate of energy damping for a molecule as close as 10 Å to a silver flat surface.\(^162\) As discussed previously, however, at distances shorter than this the assumptions of the image model are no longer very good and the theory cannot be expected to accurately predict the energy damping rates or frequency shifts without certain corrections to the model.

An estimate of the consequences of ignoring these corrections to the image theory for calculating energy transfer rates for the type of system we are working with, however, can be obtained from the work of Avouris and Demuth,\(^9\) who have determined the lifetime of pyrazine adsorbed on Ag(111) from electron energy loss linewidths. They estimate the surface lifetime of the pyrazine \(^1\)B\(_{2u}\) state to be \(5 \times 10^{-15}\) sec for the first monolayer and \(3 \times 10^{-14}\) sec for the second layer, assuming their measured linewidths to be homogeneous. An image calculation of the lifetime gives a prediction of \(1.1 \times 10^{-15}\) sec for the first monolayer and \(1.2 \times 10^{-13}\) sec for the second layer. Comparing these values they find that the image formula overestimates the damping rate for the first layer by a factor of four and underestimates the damping
of the second layer by a factor of four. Image dipole coupling thus appears to give a fairly good prediction of the surface lifetime, a perhaps fortuitous result of the infinity at $d = 0$ cancelling an underestimate of the decay rate very close to the surface due to non-inclusion of other decay channels. Image theory can thus be used to provide at least a first order estimate of molecule excited state lifetimes on the metal surface.

Since the surfaces employed in our experiments are not flat, however, we must account for the deviation of these surfaces from a planar geometry in order to predict energy transfer rates with any accuracy. As discussed earlier, the frequency dependence of the energy transfer rate is expected to be considerably different from that of a flat surface since there will be resonant modes at different frequencies for surfaces which have roughness features. An estimate of the difference in damping rates can be obtained by calculating nonradiative rates from the classical dipole theory (equation 70b) using effective optical constants determined for the rough surface ellipsometrically. Shown in figure 37 are relative nonradiative energy transfer rates for a perpendicular excited dipole spaced 5 Å from smooth and rough silver surfaces calculated from the optical constants of figure 38. As can be seen, the rough surface has a much higher rate of nonradiative damping at longer wavelengths due to excitation of localized plasmon modes, while at shorter wavelengths the large peak in the nonradiative energy transfer rate near the flat surface plasmon energy has been almost completely attenuated in the case of the rough surface.

The dynamics of benzaldehyde photodecomposition from its lowest excited singlet state can now be examined in a calculation based on gas
Figure 37. Relative nonradiative energy transfer rates calculated for a molecule spaced 5 Å from a smooth, annealed Ag (110) surface (top) and a rough, sputtered Ag (110) surface (bottom) as a function of emission wavelength. The silver optical constants used in the calculation were taken from figure 38.
Figure 38. Effective optical constants in the near UV region determined by ellipsometry for a smooth, annealed Ag (110) surface (top) and a rough, sputtered Ag (110) surface (bottom).
phase molecular properties and energy damping by classical dipole coupling to the surface. Radical formation occurs with a quantum yield of 0.4 in the gas phase, probably directly from the excited singlet since addition of a triplet quencher does not affect the reaction.\textsuperscript{158} The process must occur with a rate constant of at least $10^{12}$ sec\textsuperscript{-1}, the estimated intersystem crossing rate of benzaldehyde $S_1$.\textsuperscript{163} The nonradiative relaxation of the excited state near a silver surface can be calculated using the image formula and the oscillator strength $f = 0.00055$\textsuperscript{164} of the benzaldehyde $S_1$ excitation. The dielectric constant used for silver is $\varepsilon_{\text{Ag}} = -0.59 + 0.90i$ determined ellipsometrically at 350 nm. The results, shown in Table 4, indicate that there may be substantial deactivation of the excited state on the timescale of the reaction for the first and possibly the second molecular layer. At distances of 10 Å or greater from the surface, though, the energy transfer rate appears to be much smaller than the reaction rate.

**Table 4. Calculated surface lifetimes for benzaldehyde above a rough silver surface**

<table>
<thead>
<tr>
<th>Distance from surface</th>
<th>$\tau_{\text{NR}}$ (energy transfer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6 Å (1\textsuperscript{st} monolayer)</td>
<td>$1.7 \times 10^{-13}$ sec</td>
</tr>
<tr>
<td>5 Å</td>
<td>$5.2 \times 10^{-12}$ sec</td>
</tr>
<tr>
<td>10 Å</td>
<td>$4.1 \times 10^{-11}$ sec</td>
</tr>
<tr>
<td>20 Å</td>
<td>$3.3 \times 10^{-10}$ sec</td>
</tr>
<tr>
<td>30 Å</td>
<td>$1.1 \times 10^{-9}$ sec</td>
</tr>
</tbody>
</table>
From the observed surface-molecule distance dependence of photodecomposition rate, it is clear that the distance dependence of enhanced photochemistry is quite different from that of surface Raman enhancement. Nitzan and Brus\textsuperscript{99} indicate that for the simple model of surface roughness as silver spheres the surface damping rate would be expected to decrease as $d^{-3}$ (image dipole model) while the resonance induced local field enhancement would decrease as $(d + a)^{-3}$ where $a$ is the sphere radius. Since the field enhancement will then decay more slowly as a function of separation than the surface damping, this model predicts a maximum in the photochemistry rate at some intermediate molecule-surface separation. Such an effect is seen in our studies where the pyridine photodecomposition rate is a maximum at a separation of 15–20 Å from the surface, as shown in figure 36.
G. Decomposition mechanism: neutral or ionic pathway?

Most recent studies of molecule fragmentation in the gas phase have come from the rapidly expanding field of multiphoton ionization mass spectrometry. The general fragmentation process is usually interpreted in terms of three separate steps: (1) multiphoton excitation of the molecule to a resonant intermediate state, (2) ionization of the excited neutral molecule to the parent ion by absorption of another photon, and (3) fragmentation of the parent ion by absorption of one or more photons to yield a distribution of daughter ions. The work of Boesl, Neusser, and Schlag confirmed this for benzene by studying ionization and fragmentation patterns for light of different frequencies separated by time delays. This is also the case for the multiphoton fragmentation of acetaldehyde where identical resonances in excitation wavelength were observed by monitoring parent and fragment ions. It is not clear whether this scheme of ionization followed by fragmentation can be expected to occur for surface adsorbed molecules.

Recent gas phase multiphoton ionization-fragmentation studies of benzaldehyde indicate that there is competition between two fragmentation pathways depending on the excited state manifold to which the molecule is excited. For excitation into $S_2$ with 266 nm light, competition is found to occur between multiphoton ionization of the parent molecule and dissociation into $C_6H_6$ and CO followed by multiphoton ionization of $C_6H_6$ which then fragments. Excitation into $S_1$ with 355 nm photons yields decomposition only by the first channel - ionization of the parent molecule followed by fragmentation. Thus from these experiments one must conclude that benzaldehyde apparently follows
the same trend observed for many other molecules of parent molecule ionization with subsequent fragmentation.

Whetten et al. have also recently studied multiphoton fragmentation of benzaldehyde. Their experiments consisted of measurements of total and fragment ion signal from a number of molecules as the wavelength was varied in the range of 275 - 295 nm. Results for benzaldehyde were a spectrum consisting largely of carbon atom two photon resonance ionization peaks. Analysis of the C+/total ion signal for benzaldehyde showed that more than eight times the background total ion signal is found at the carbon atom resonance lines. Thus at least part of the carbon atoms formed in this study must be produced by entirely neutral pathways. This surprising result is not inconsistent with the previously discussed data on multiphoton ionization-fragmentation of benzaldehyde, since carbon neutrals may have been present in those experiments which were not ionized at the particular laser frequencies used and thus were not detected.

It appears from these results and the previously cited gas phase photochemical studies of benzaldehyde that neutral decomposition from higher excited singlet states of benzaldehyde is a fairly efficient process, and that subsequent photon absorption to produce ionized molecules and fragments is not necessary to explain the observed fragmentation. Indeed, Antonov et al. report that the benzaldehyde photoionization cross section is approximately two orders of magnitude lower than that observed for benzene at the wavelengths they have studied. In our experiments benzene does not decompose to any extent while benzaldehyde fragments readily. Based on this evidence, and the aforementioned gas phase data on neutral decomposition to atomic carbon,
we believe that neutral fragmentation may be an important mechanism in benzaldehyde photodecomposition on silver surfaces.

For other molecules, however, the choice of fragmentation pathway is not as clear. For surface experiments, the resonant state in multiphoton absorption will have a greatly decreased lifetime due to energy transfer to the surface, except possibly in those cases where a two photon resonant state is not strongly dipole-coupled to the ground state. In view of this, it becomes attractive to postulate excitation into an ionic continuum from which fragmentation or further absorption could occur. There is some recent evidence that ion formation by multiphoton absorption on metal surfaces may be a more favorable process than ionization in the gas phase. Ion formation on the surface might be aided by direct excitation of molecular valence electrons into unoccupied metal orbitals above the Fermi level as suggested by the observation of charge-transfer excitations for some molecules on silver. At present, however, we have no evidence for the presence of ionic intermediates in the fragmentation of aromatic molecules on silver.
H. Surface Ionization Using Pulsed Lasers

We have attempted to examine photoionization processes occurring at silver surfaces with the objective of determining whether these processes are enhanced relative to the gas phase, and whether ionization is important in photochemistry at the surface. Experiments were done at 364 nm (where surface photochemistry is observed using ion laser excitation) and at 280 nm (where substantial fragmentation of benzaldehyde to atomic carbon is observed to occur\textsuperscript{169}). Pulses with peak intensities in the range of $7 \times 10^5 - 6 \times 10^7 \text{ W/cm}^2$ and a duration of 8 nsec were generated using an excimer pumped dye laser as described earlier.

Results for an adsorbed monolayer of benzaldehyde on rough silver are that the molecules can be desorbed with a peak surface power density of approximately 5 mJ/cm$^2$ at 280 nm ($7 \times 10^5 \text{ W/cm}^2$ intensity), although no ionization occurs at this power level. Ionization is detected at a threshold power density of $30 \text{ mJ/cm}^2$ ($4 \times 10^6 \text{ W/cm}^2$ intensity) for adsorbed benzaldehyde; this is also approximately the threshold where ionization is observed from the rough surface with no adsorbate present. There is no visible damage to the rough silver surface until an order of magnitude higher power density is used.

The above power density for surface ionization of benzaldehyde may be contrasted with that used by Whetten et al.\textsuperscript{169} for gas phase ionization of benzaldehyde in the same wavelength region. They use a minimum pulse power of 30 nJ from an Nd:YAG-pumped dye laser with a 5 nsec duration, focussed into the gas with a 20 cm focal length lens. Assuming a Gaussian beam profile, the peak power density at the beam
waist for these conditions is approximately 50 J/cm². Thus ionization occurs on the rough surface at a power level smaller by a factor of approximately 2000 than that for gas phase ionization of benzaldehyde at 280 nm.

The number of different species formed during surface ionization is very large; a complete characterization of different charge/mass peaks was not done in our studies because a separate experiment is required for each peak using quadrupole detection. Time-of-flight detection of ions formed at silver island films indicates that a substantial number of ions including silver and silver-adsorbate fragment complex ions are formed during surface ionization due to plasma formation from thermal effects. An attempt was made to determine whether the efficient neutral carbon atom formation by photolysis of benzaldehyde observed in the gas phase occurs at the surface by looking for carbon atom ionization resonances near 280 nm. This proved impractical due to fluctuations in laser power from shot to shot, since the experiment must be done essentially with a single shot.

Ionization was also observed for benzaldehyde on rough silver using 364 nm excitation. The threshold power density for ionization of a monolayer of benzaldehyde is 55 mJ/cm² (7 x 10⁶ W/cm² intensity), slightly higher than that observed at 280 nm. Again the power density threshold for ion formation from the clean surface is very close to that for ionization of an adsorbed monolayer. The difference in the ionization threshold between 280 nm and 364 nm appears to be due principally to thermal effects from differences in absorption by the silver surface, since the thresholds for covered surfaces and clean surfaces are both affected.
In summary, although the efficiency for ionization of molecules is dramatically increased by adsorption at a rough silver surface, this appears to be due to high absorption by the surface with thermal plasma formation producing ionization of the adsorbate. Desorption of intact adsorbates from the surface is possible with laser powers that are a factor of about 5 smaller than those that produce ionization. There does not appear to be any ion formation due to enhanced surface fields at these lower powers within the sensitivity of our apparatus. Although this evidence is not conclusive, it suggests that surface ionization at the low powers used in photofragmentation with ion lasers is unlikely.
I. Conclusions

During this investigation we have established that a variety of aromatic molecules undergo resonant absorption and decomposition on a rough silver surface. For two molecules studied (pyridine and benzaldehyde) laser power dependence studies with 406.7 nm light indicate that the absorption step is a two photon process. Energetic considerations make it likely that absorption by the other molecules studied is also a multiphoton process, except for benzaldehyde with 350.7 nm irradiation where photochemistry apparently occurs directly from the first excited singlet state following a one photon absorption.

The decomposition reaction pathway to surface carbon most likely occurs by a neutral pathway for benzaldehyde, since gas phase photochemistry takes place via radical formation and neutral fragmentation all the way to carbon atoms has been observed in multiphoton absorption experiments. Further study is necessary to determine whether rapid ionization preceeding fragmentation as observed in most multiphoton fragmentation experiments in gases is a possible pathway for surface reactions of other molecules, although pulsed laser experiments suggest it is not.

We have observed the presence of intermediate species in surface photofragmentation reactions using Raman spectroscopy. A CN stretching mode is seen in the Raman spectrum of pyridine and pyrazine during decomposition. The frequency of this mode is shifted substantially from that usually observed for CN adsorbed on silver, however, indicating that a larger fragment such as C_2H_3N (observed in gas phase multiphoton fragmentation of these molecules) may be the actual surface species.
observed. No additional Raman bands that could be assigned to surface intermediates were seen in the photofragmentation of benzaldehyde, but different Raman shifts for the surface carbon formed were observed for decomposition at different wavelengths. Hence different carbon structures may be formed by decomposition following absorption by a one or a two photon process.

Finally, studies of the distance dependence of decomposition rate by the use of spacer molecules shows a maximum decomposition rate at a separation of 15-20 Å from the surface. The surface distance dependence of Raman enhancement is markedly different, exhibiting a sharply peaked enhancement for the first adsorbed layer and a much smaller enhancement for several subsequent layers. This behavior is consistent with that predicted for an enhanced surface photochemical process where the different distance dependences of damping by energy transfer to surface modes competes with enhanced energy absorption, resulting in a peak photochemical rate at some distance from the metal surface.
Appendix A: Surface Heating Calculations

The temperature rise induced at a metal surface by laser irradiation can be determined using the heat equation\textsuperscript{172} if the optical and thermal properties of the surface are known:

\begin{equation}
\nabla^2 T - \frac{\rho C}{K} \frac{\partial T}{\partial t} = -\frac{G(r,t)}{K}
\end{equation}

In this equation $K$ is the thermal conductivity, $C$ is the heat capacity, $\rho$ is the density, and $G(r,t)$ is the net energy generated per unit volume per unit time inside the solid. For a Gaussian laser beam the heat source term $G$ has the form

\begin{equation}
G(r,t) = (1-R) \alpha I_0 e^{-\alpha z} e^{-r^2/w^2} f(t)
\end{equation}

where a cylindrical coordinate system $r = (r,\theta,z)$ aligned along the incident laser beam has been used. Here $R$ is the surface reflectivity, $\alpha$ is the absorption coefficient, $I_0$ is the incident laser intensity, and $w$ is the beam width of the Gaussian intensity distribution in the laser beam.

For continuous laser excitation, we can consider the time-independent case (steady-state temperature). For this case the heat equation becomes:

\begin{equation}
\nabla^2 T = -\frac{(1-R)\alpha I_0}{K} e^{-\alpha z} e^{-r^2/w^2}
\end{equation}

This problem has been solved by Lax\textsuperscript{173} where the surface is considered
to be a semi-infinite slab. Using the dimensionless variables \( R = r/w \), \( Z = z/w \), and \( W = \alpha w \), he finds that the temperature rise is given by

\[
T(R, Z, W) = B \int_0^\infty J_0(\lambda R) F(\lambda) \frac{W e^{-\lambda Z} - \lambda e^{-WZ}}{W^2 - \lambda^2} \, d\lambda
\]

Here \( J_0 \) is a Bessel function, \( F(\lambda) \) is the Bessel transform of the laser spatial distribution \( f(R) = e^{-R^2} \), and \( B = \alpha P/2\pi K F(0) \) where \( P \) is the total incident laser power. Lax has shown that the spatial distribution of the temperature rise on the surface can be expressed in the form

\[
T(R, Z, W) = T_{\text{max}} N(R, Z, W)
\]

where \( T_{\text{max}} \) is the temperature rise in the center of the beam in the limiting condition \( W \to \infty \) (i.e., infinite absorption at the surface), and where \( N(R, Z, W) \) describes the reduction in the temperature rise caused by finite penetration of the beam into the surface. For a Gaussian laser beam \( T_{\text{max}} \) is given by

\[
T_{\text{max}} = \frac{P}{2\pi^{1/2} kwk}
\]

The factor \( N(0,0,W) \) has been evaluated by Lax, and it is found that \( N > 0.9 \) for \( W = \alpha w > 10 \). For a 50 \( \mu \text{m} \) wide laser beam incident on a silver surface in the near UV where \( \alpha = 4\pi k/\lambda = 5 \times 10^5 \text{ cm}^{-1} \), we find that \( W = 2.5 \times 10^3 \). Thus \( N \approx 1 \) in this case (the light is absorbed very near the surface) and \( T = T_{\text{max}} \). Using a thermal conductivity of 4.81 \( \text{W/cm K} \) for bulk silver at 77 K, an incident laser power of 20 mW (p-polarized), and a beam width of 50 \( \mu \text{m} \), we calculate a temperature rise...
of $0.16^\circ$ for a rough silver surface at 363.8 nm using the optical constants of figure 38. The relative heating rates calculated for the different wavelengths used in our experiments from the experimentally determined optical constants for our rough surfaces (figures 18 and 38) are tabulated below.

Table 5. Relative surface heating rates as a function of wavelength

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Surface heating rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.7</td>
<td>0.8</td>
</tr>
<tr>
<td>363.8</td>
<td>1.0</td>
</tr>
<tr>
<td>406.7</td>
<td>1.1</td>
</tr>
<tr>
<td>457.9</td>
<td>1.2</td>
</tr>
<tr>
<td>514.5</td>
<td>1.3</td>
</tr>
<tr>
<td>647.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

For short laser pulses the above analysis is not valid, since the time dependence of the heat generation term in the heat equation must be included. This has been done by Bechtel$^{174}$ for a semi-infinite slab occupying the region $z > 0$ using the heat generation term

\[ G(r,t) = (1-R) \alpha I_0 e^{-\alpha z} e^{-r^2/\omega^2} e^{-t^2/\tau^2} \]

with the boundary conditions of no heat flow across the
This heat generation term corresponds to a Gaussian laser pulse both in space and in time. The following solution is obtained for the temperature change:

\[
\Delta T = \int_{-\infty}^{t} \frac{(1-R)I_0 \alpha \omega^2}{2 \kappa (4\kappa (t-t') + \omega^2)} e^{-\left(\frac{t-t'}{\tau}\right)^2} e^{-\frac{\tau^2}{4\kappa (t-t')} + \omega^2} 
\]

\[
x \left[ e^{-\alpha z + \kappa \alpha^2 (t-t')} \text{erfc} \left( \frac{-z + 2\kappa \alpha (t-t')}{2(\kappa (t-t'))^{1/2}} \right) 
\]

\[
+ e^{\alpha z + \kappa \alpha^2 (t-t')} \text{erfc} \left( \frac{z + 2\kappa \alpha (t-t')}{2(\kappa (t-t'))^{1/2}} \right) \right] \, dt'
\]

where \( \kappa = K/C \) and the other variables have been defined previously.

This equation has been numerically integrated using dimensionless variables, and results presented graphically for various values of the parameters. 174

Fortunately, if certain assumptions are made the solution to the heat equation with time-dependent heat generation becomes much simpler. The first assumption that can be made is that the heating is due strictly to surface absorption. This is not a bad approximation for rough silver in the near UV, since as mentioned before \( \alpha \) is approximately \( 5 \times 10^5 \) cm\(^{-1} \) in this region. Secondly, instead of using a Gaussian time dependence for the laser pulse, a square pulse can be used. These approximations considerably simplify the mathematics, and the temperature change becomes

\[
\Delta T(0,t) = \frac{2(1-R)I_0}{K} \left( \frac{\kappa t}{\pi} \right)^{1/2} \quad 0 < t < \tau
\]
\( \Delta T(0,t) = \frac{2(1-R)I_0}{K} \left( \frac{\kappa t}{\pi} \right)^{1/2} x \left( \left( \frac{t}{\tau} \right)^{1/2} - \left( \frac{t}{\tau} - 1 \right)^{1/2} \right) \quad t > \tau \)

where \( \tau \) is the length of the square laser pulse. Using \( K = 4.81 \text{ W/cm K} \) and \( \kappa = K/\rho C = 2.9 \text{ cm}^2/\text{sec} \, (C = 1.63 \times 10^2 \text{ J/kg K at 80 K}) \), we obtain a 27° temperature rise for a 10 nsec laser pulse with a peak intensity of \( 10^6 \text{ W/cm}^2 \) incident on rough silver at 360 nm where the reflectivity \( R = 0.33 \). At shorter wavelengths the reflectivity of silver drops further and the temperature increase will correspondingly be greater.
Appendix B: Computer Programs

An LSI-11 microcomputer (Digital Equipment Corp.) was used in these experiments both for data collection and storage, and for data retrieval and graphic display. Most of the programs used were written in FORTRAN IV, with data collection routines that were executed many times written in MACRO-11 assembly language for speed of execution and ease of accessing I/O device status registers. Collected data was normally stored on a floppy disk as an unformatted series of REAL*4 numbers, preceded by the following quantities: (1) an INTEGER*2 number indicating the total number of records in the file, (2) a REAL*4 number indicating the starting x-axis value, (3) a REAL*4 number indicating the ending x-axis value, and (4) a REAL*4 number indicating the x-axis increment for each data point. The following text briefly describes each of the programs used for collection and display of Raman spectra, thermal desorption spectra, surface ionization spectra, etc.

ROLL  This program was written to collect photon counting spectra. Photon pulses from a photomultiplier were amplified and put through a pulse-height discriminator (EG&G model TD101/N differential discriminator), then were lengthened slightly with a Lawrence Berkeley Laboratories 14X2991 P-1 fast/slow logic interface and accumulated in a binary counter (LSI Computer Systems LS7060). The count total was read from the binary counter into the computer via a DRV-11 parallel interface board with the subroutine COUNT. The 32-bit count total appears 8 bits at a time on the output lines of the counter chip, and must be stepped four times using the data trans pulse from the DRV-11 to
obtain the entire number. The stepping motor controlling the wavelength scan of the monochromator is then stepped by momentarily increasing the y-DAC output from 0 to 10 V, and the process is repeated. At the end of a scan, the stepping motor is reset using the subroutine REWIND.

**PLOTW** This program plots the output of the program ROLL on a Tektronix 4010-series compatible terminal using PLOT-10 commands (the latest version is stored on disk as PT2.FOR). The program calls the subroutines GRAPH, HICK, and WINADJ from the plotting library PACLIB, and calls PLOT-10 subroutines from the library TCSLIB. Since the data were quite often Raman spectra with the x-axis in Angstroms, the program gives the user the option of converting to a scale showing wavenumber shift from the laser line. The option of plotting a smoothed curve is available in the subroutine SMOOTH using a 5-point Savitsky-Golay smoothing procedure. Hardcopies of the plots are possible if a plotter is available at an address specified by the terminal-interchange program SWAPM.

**VT PLOT** This program also plots the output of the program ROLL, this time on a Tektronix 4027-series compatible terminal (such as the DEC VT-100 terminal with retrographics). The MACRO-11 subroutines PLOT and VECPLT plot the data using 4027 mode commands and draw a movable screen cursor through the data. The x value and y value of the data point at the location of the cursor are printed on the screen to aid in determining peak positions.

**TDS** This program was designed to collect sequential data from one of
the input lines of a multiplexed A/D converter (Adac Corp. model 600-LSI-11). Timing for the program is done by looping through A/D conversion cycles in the subroutine INPUT for a specified number of times. The timing is calibrated for an LSI-11 cpu with the extended instruction set (EIS). Programs were also written with more accurate timing using the line time clock in the computer, but the number of A/D conversions was significantly reduced by the amount of time it took the computer to check the time, and signal/noise was adversely affected.

The program was typically used to collect a thermal desorption spectrum or a surface ionization spectrum using a UTI model 100C quadrupole mass analyzer set at a single mass/charge peak. The data is written on disk in a form compatible with the plotting routines PLOTW and VT PLOT.

**TDS5** This program is an expanded version of the program TDS which will collect multiplexed thermal desorption spectra at 5 mass/charge peaks using the UTI 100C mass analyzer. The quadrupole is sequentially stepped to different peaks using the y-DAC output in the subroutine SWEEP. Timing is again done by looping through program instructions. The data is stored on disk as sequences of different mass peaks (up to 5), repeated for the number of points in each spectrum (up to 1000). These numbers are preceded in the disk file by several INTEGER*2 values: (1) the total number of records in the file, (2) the number of loops in a single data averaging cycle, (3) the number of data points in each spectrum, (4) the number of different mass peaks sampled, and (5) a series of up to 5 numbers indicating which masses were sampled.

**TDS5PL** A plotting program for Tektronix 4010-series compatible
terminals that sequentially plots the thermal desorption spectra stored by the program TDS5. The subroutines used in this program are the same as those used in the plotting program PLOTW.
PROGRAM ROLL
DIMENSION VAL(1000)
DO 1 I=1,1000
1 VAL(I)=0.0
INTEGER*4 POINT
WRITE(5,100)
100 FORMAT(' THIS PROGRAM WILL COLLECT A SPECTRUM BY '/
1 ' /' COUNTING PULSES WITH THE 32 BIT COUNTER'/
1 ' /' VIA THE DRV-11 PARALLEL INTERFACE'/
1 ' /' THE SPECTRUMETER IS STEPPED WITH THE'/
1 ' /' Y DAC FROM THE ADAC BOARD, AND RESET'/
1 ' /' WITH THE X DAC')
WRITE(5,110)
110 FORMAT(' ENTER THE INITIAL AND FINAL SCAN WAVELENGTHS...')
READ(5,115)SWL,FWL
115 FORMAT(2F10.3)
WRITE(5,116)
116 FORMAT(' INPUT THE NUMBER OF STEPS PER ANGSTROM (I5)'/
1 ' $S AND THE NUMER OF ANGSTROMS BETWEEN POINTS (F5.2)...')
READ(5,117)ISTEP,ANG
117 FORMAT(I4,F5.2)
WRITE(5,118)
118 FORMAT(' ENTER THE SAMPLE TIME PER POINT WITH A MAX'/
1 ' $OF TEN MINUTES AS MIN,SEC,SEIXTIETHS OF SEC (3I5)...')
READ(5,119)IMIN,ISCNDS,I60THS
119 FORMAT(3I5)
WRITE(5,120)
120 FORMAT(' ENTER THE NUMBER OF SCANS (I5)...')
READ(5,121)ISCAN
121 FORMAT(IS)
INUM=I60THS+60*ISCNDS+3600*IMIN
SCNDS=FLOAT(INUM)/60.
NPNTS=INT((FWL-SWL)/ANG)+1
NRCDS=NPNTS+4
WRITE(5,275)NPNTS,NRCDS
275 FORMAT(2I10)
WRITE(1,1)
1 WRITE(NRCDS,2,3) SWL
WRITE(4) ANG
IPOP=INT(ISTEP*ANG)
NPOP=(NRCDS-5)*IPOP
DO 20 J=1,ISCAN
DO 10 I=1,NPNTS
CALL COUNT(POINT,INUM,IPOP)
VAL(I)=VAL(I)+AJFLT(POINT)/(SCNDS*FLOAT(ISCAN))
INDEX=NPNTS-I+1
WRITE(5,140)INDEX,VAL(I)
10 CONTINUE
CALL REWIND(NPOP+IPOP)

CONTINUE

DO 30 I=1,NPNTS
    J=I+4
    WRITE(1,'(J) VAL(I)')
30 CONTINUE

STOP

END

.TITLE COUNT
.GLOBL COUNT
.MCALL .GTIM
DATIN=167774
BITOUT=167772

COUNT: BIC #40,#167770 ;DISABLE THE INTERRUPTS
       BIC #100,#167770 ;IN THE STATUS CONTROL WORD
       CLR R1
       MOV 2(R5),R2 ;R2 POINTS TO THE DATA LOCATION
       MOV @4(R5),R4 ;FETCH THE NUMBER OF CLOCK TICKS
       MOV @6(R5),PULSE ;FETCH NUMBER OF MOTOR PULSES
       CLR (R2)
       CLR 2(R2)

.GTIM #LIST,#START ;CHECK THE STARTING TIME
MOV #3,#BITOUT ;PREPARE TO COUNT
BIC #1,#BITOUT ;RESET THE COUNTERS
BIS #1,#BITOUT ;START THE COUNT
1$: .GTIM #LIST,#STOP ;MEASURE NEW TIME
MOV @#START+2,R1 ;CALCULATE THE ELAPSED TIME
SUB @#START+2,R1 ;OF COUNTING PHOTONS
CMP R1,R4
BLT 1$ ;TIME NOT UP, KEEP WAITING
BIC #2,#BITOUT ;LATCH DATA ONTO MULTIPLEXER
BIS #2,#BITOUT ;LOAD THE OUTPUT
MOV #70,R3 ;LOOP TO ALLOW
2$: DEC R3 ;DATA TO SETTLE
       CMP #1,R3
       BLOS 2$
       MOV @#DATIN,R3 ;GET FIRST BYTE
       MOV R3,BUFF ;
       MOVB @#BUFF,(R2) ;PUT IN DATA WORD
       INC R2
       MOV @#DATIN,R3 ;GET SECOND BYTE
       MOV R3,BUFF ;
       MOVB @#BUFF,(R2) ;PUT IN DATA WORD
       INC R2
       MOV @#DATIN,R3 ;GET THIRD BYTE
       MOV R3,BUFF ;
       MOVB @#BUFF,(R2) ;PUT IN DATA WORD
       INC R2
MOV @#DATIN,R3  ;GET FOURTH BYTE
MOV R3,BUFF
MOV  @#BUFF,(R2)  ;PUT IN DATA WORD
MOV  #4000,@#176762
MOV  #0,@#176762
MOV  #3000,R3    ;DELAY BETWEEN STEPS
3$: MOV  #1,PULSE
BLX  4$    ;COUNT DOWN PULSES
CMP  #1,PULSE
BLOS  3$
RTS PC
START: .WORD 0,0
STOP: .WORD 0,0
BUFF: .WORD 0
PULSE: .WORD 0
LIST: .BLKW 2
.END

.TITLE REWIND
.GLOBL REWIND
REWIND: MOV  @2(R5),R2  ;GET NUMBER OF STEPS
MOV  #10,R1
ADD  R1,R2    ;ADD OVERSHOOT
1$: MOV  #4000,@#176760
MOV  #0,@#176760
MOV  #3000,R3    ;DELAY
2$: DEC  R3
BNE  2$    ;CHECK FOR POINTS REMAINING
DEC  R2
BNE  1$
3$: MOV  #4000,@#176762
MOV  #0,@#176762
MOV  #30000,R3    ;TO ELIMINATE BACKLASH
4$: DEC  R3
BNE  4$
DEC  R1
BNE  3$
RTS PC
.END
PROGRAM PLOTW
CALL INITT(480)
DIMENSION X(1001),Y(1001),YB(1001)
LOGICAL*1 FARRAY(11),GARRAY(11),ANS,YES
DATA YES/'Y'/
CALL SCOPY('(F7.0)',GARRAY)
CALL SCOPY('(F6.0)',FARRAY)
WRITE(5,100)
100 FORMAT('ENTER THE NAME OF THE FILE TO BE PLOTTED...')
CALL ASSIGN(1,8020,-1)
DEFINE FILE 1 (5005,2,U,IBUM)
READ(1,'1,ERR=90)NRCD
READ(1,'2)SWL
READ(1,'3)FWL
READ(1,'4)ANG
NPNTS=NRCD-4
WRITE(5,110)NPNTS,SWL,FWL
110 FORMAT('THERE ARE ',I7,' DATA POINTS IN THE FILE'
1' ', ', 'ANGSTROMS AND GOES TO'
1' ', ', 'ANGSTROMS')
WRITE(5,120)
120 FORMAT('THE LARGEST NUMBER OF POINTS TO BE PLOTTED AT ONCE IS'
1' 1001. YOU MAY PLOT FEWER.')
WRITE(5,121)
121 FORMAT('STO PLOT IN WAVENUMBERS ENTER A 1 ...')
READ(5,122)IPLT
122 FORMAT(I1)
IF(IPLT.NE.1) GO TO 99
WRITE(5,123)
123 FORMAT('ENTER THE LASER WAVELENGTH...')
READ(5,124)WLASER
124 FORMAT(F6.0)
WNLAS= 1.E8/WLASER
SWN= WNLAS-(1.E8/SWL)
FWN= WNLAS-(1.E8/FWL)
WRITE(5,125) SWN,FWN
125 FORMAT('THE SCAN STARTS AT ',F6.0,' WAVENUMBERS AND GOES TO'
1' ', ', 'WAVENUMBERS')
WRITE(5,126)
126 FORMAT('ENTER THE INITIAL AND FINAL PLOTTING WAVENUMBERS...')
READ(5,127)SPWN,FPWN
127 FORMAT(2F6.0)
SPWL= 1.E8/(WNLASR-SPWN)
FPWL= 1.E8/(WNLASR-FPWN)
GO TO 136
99 WRITE(5,130)
130 FORMAT('ENTER THE INITIAL AND FINAL PLOTTING WAVELENGTHS.')
READ(5,135)SPWL,FPWL
135 FORMAT(2F10.2)
136 NUM=INT((FPWL-SPWL)/ANG)+1
IF(NUM.LE.1001)GOTO 700
WRITE(5,600)
600 FORMAT('YOU WILL EXCEED 1001 POINTS WITH THIS RANGE!!!')
GOTO 99
LOW=5+INT((SPWL-SWL)/ANG)
DO 10 I=1,NUM
READ(I'LOW)Y(I)
X(I)=SPWL+FLOAT(I-1)*ANG
IF(I.PLOT.EQ.1) X(I)=WNLASR-1.E8/X(I)
10 LOW=LOW+1
CLOSE(UNIT=1)
WRITE(5,140)
FORMAT('DO YOU WANT TO SUBTRACT BACKGROUND...')
READ(5,145)ANS
145 FORMAT(A1)
IF(ANS.NE.YES) GO TO 88
WRITE(5,150)
FORMAT('ENTER THE BACKGROUND FILE NAME...')
CALL ASSIGN(1,BOZU,-1)
DEFINE FILE 1 (5005,2,U,INUM)
READ(I'1)NRCDSB
READ(I'2)BSWL
READ(I'3)BFWL
READ(I'4)BANG
NPTSB=NRCDSB-4
IF(CHARACTER(LEN=2,BOZU,FLOAT(LEN=1,BOZU,BOZU))=5005,2,U)
READ(1•1)BSWL
READ(1•2)BSWL
READ(1•3)BFWL
READ(1•4)BANG
NPTSB=NRCDSB-4
IF(BSWL.LE.SPW) GO TO 161
IF(FPWL.LE.BFWL) GO TO 161
WRITE(5,160)
160 FORMAT('THE BACKGROUND FILE DOES NOT COVER THE PLOTTING RANGE',/ 
1' FILE STARTS AT',F5.0,' ANGSTROMS AND GOES TO',F5.0,' ANGSTROMS')
GO TO 99
161 WRITE(5,170)
FORMAT('ENTER THE BACKGROUND MULTIPLIER...')
READ(5,175)FACTOR
175 FORMAT(F10.8)
LOW=5+INT((SPWL-BSWL)/BANG)
DO 20 I=1,NUM
READ(I'LOW)YB(I)
Y(I)=Y(I)-FACTOR*YB(I)
20 LOW=LOW+1
CLOSE(UNIT=1)
88 CALL PREP(6,7)
CALL GRAPH(NUM,X,Y,-1,2)
CALL WINADJ(X1,X2,Y1,Y2)
77 CALL NEWPAG
CALL GRAPH(NUM,X,Y,-1,0)
CALL HICK(11,11,FARRAY,GARRAY,6,7)
CALL HOME
WRITE(5,176)
176 FORMAT('DO YOU WANT A HARDCOPY? ') 
READ(5,145)ANS
IF(ANS.NE.YES) GO TO 177
CALL SWAPM
CALL GRAPH(NUM,X,Y,-1,0)
IF(NUM.GE.500) CALL WAIT(10.)
CALL HICK(11,11,FARRAY,GARRAY,6,7)
CALL HOME
CALL SWAPB
CALL NEWPAG
WRITE(5,180)
180 FORMAT('DO YOU WANT TO CHANGE ANY POINTS? ')
READ(5,145)ANS
IF(ANS.NE.YES) GO TO 211
MIN=0
MAX=0
YMIN=0.0
YMAX=0.0
DO 30 I=1,NUM
IF(Y(I).LT.YMAX) GO TO 66
YMAX=Y(I)
MAX=I
66 IF(Y(I).GT.YMIN) GO TO 30
YMIN=Y(I)
MIN=I
30 CONTINUE
WRITE(5,190)MIN,Y(MIN-2),Y(MIN-1),Y(MIN),Y(MIN+1),Y(MIN+2)
190 FORMAT(' THE Y-VALUES AROUND THE MINIMUM AT X=',I4,' ARE',/ 1 5F10.2)
WRITE(5,200)MAX,Y(MAX-2),Y(MAX-1),Y(MAX),Y(MAX+1),Y(MAX+2)
200 FORMAT(' THE Y-VALUES AROUND THE MAXIMUM AT X=',I4,' ARE',/ 1 5F10.2)
WRITE(5,210)
210 FORMAT('$INPUT NUMBER AND NEW VALUE OF POINT TO BE CHANGED...')
READ(5,215)N,VALUE
215 FORMAT(I4,F10.2)
Y(N)=VALUE
GO TO 88
211 WRITE(5,300)
300 FORMAT('DO YOU WANT TO SMOOTH DATA? ') 
READ(5,145)ANS
IF(ANS.NE.YES) GO TO 212
CALL SMOOTH(NUM,Y)
GO TO 88
212 WRITE(5,220)
220 FORMAT('DO YOU WANT TO PLOT A NEW FILE? ') 
READ(5,145)ANS
IF(ANS.EQ.YES) GO TO 90
GO TO 88
CONTINUE
STOP
END
C

SUBROUTINE WAIT(SEC)
TIME=SECNDOS(0.0)
999 IF(SECNDOS(TIME).GE.SEC) RETURN
END
SUBROUTINE SMOOTH(NUM,Y)  
DIMENSION Y(NUM)  
DIMENSION YWINDO(S)  
SUB1 = Y(1)  
SUB2 = Y(2)  
DO 10 I=2,5  
     J = I+4  
10 YWINDO(I) = Y(J)  
DO 20 I=1,NUM-4  
     J = I+4  
20 CONTINUE  
  DO 30 I=2,NUM-3  
     K = NUM-I  
30 Y(K) = Y(L)  
Y(2) = SUB2  
Y(1) = SUB1  
RETURN  
END
PROGRAM VTPlot
LOGICAL*1 ANS, YES
DIMENSION X(1001), Y(1001)
COMMON /X/ X
COMMON /Y/ Y
DATA YES /'Y'/
WRITE(5, 100)
100 FORMAT('ENTER THE NAME OF THE FILE TO BE PLOTTED: ') CALL ASSIGN(1, BOZO, -1) DEFINE FILE 1 (1005, 2, U, IBUM) READ(1'1, ERR=10) NRCDS READ(1'2) SWL READ(1'3) FWL READ(1'4) ANG NPNTS = NRCDS - 4 WRITE(5, 110) NPNTS, SWL, FWL 110 FORMAT('THERE ARE ', I4, ' DATA POINTS IN THE FILE'/ 'THE SCAN STARTS AT ', F5.0, ' ANGSTROMS AND GOES TO '/ 'F5.0, ' ANGSTROMS') WRITE(5, 120)
120 FORMAT('TO PLOT IN WAVENUMBERS ENTER A ONE: ') READ(5, 130) IPLOT
130 FORMAT(I1) IF(IPLOT.LT.1) GO TO 99 WRITE(5, 140)
140 FORMAT('ENTER THE LASER WAVELENGTH F6.0 : ') READ(5, 150) WLASER
150 FORMAT(F6.0)
WLASER = 1.E8 / WLASER SWN = WNLASR - (1.E8 / SWL) FWN = WNLASR - (1.E8 / FWL) WRITE(5, 160) SWN, FWN
160 FORMAT('THE SCAN STARTS AT ', F6.0, ' WAVENUMBERS AND '/ ' GOES TO ', F6.0, ' WAVENUMBERS') WRITE(5, 170)
170 FORMAT('ENTER THE INITIAL AND FINAL PLOTTING'/ 'WAVENUMBERS 2F6.0 : ') READ(5, 180) SPWN, FPWN
180 FORMAT(2F6.0) SPWL = 1.E8 / (WNLASR - SPWN) FPWL = 1.E8 / (WNLASR - FPWN) GO TO 88
99 WRITE(5, 190)
190 FORMAT('ENTER THE INITIAL AND FINAL PLOTTING'/ 'WAVELENGTHS 2F10.2 : ') READ(5, 200) SPWL, FPWL
200 FORMAT(2F10.2)
88 NUM = INT((FPWL - SPWL) / ANG) + 1 IF(NUM .LT. 1001) GO TO 77 WRITE(5, 210)
210 FORMAT('YOU WILL EXCEED THE MAXIMUM OF 1001 POINTS WITH '/ 'THIS RANGE') GO TO 99
77 LOW = 5 + INT((SPWL - SWL) / ANG)
DO 10 I=1,NUM
READ(1,'LOW')Y(I)
X(I)=SPWL+FLOAT(I-1)*ANG
IF(IPLOT.EQ.1) X(I)=WNLASR-1.E8/X(I)
10 LOW=LOW+1
CALL CLOSE(1)
YMIN=0.0
YMAX=0.0
DO 30 I=1,NUM
IF(Y(I).LT.YMAX) GO TO 20
YMAX=Y(I)
20 IF(Y(I).GT.YMIN) GO TO 30
YMIN=Y(I)
30 CONTINUE
CALL PLOT(NUM,SPWL,FPWL,YMIN,YMAX,X,Y)
WRITE(5,220)
220 FORMAT(' DO YOU WANT TO PLOT A NEW FILE? ')
READ(5,230)ANS
230 FORMAT(A1)
IF(ANS.EQ.YES) GO TO 999
CONTINUE
STOP
END

.TITLE PLOT
.GLOBL PLOT,VEC,CNVRT,ASCII,NOUT
.GLOBL JAFIX,XVAL,YVAL,X,Y,COORD
.MCALL .PRINT

RCSR=177560
RBUF=177562
PLOT: .PRINT #SETUP ;SET GRAPHICS AREA
.PINT #BOX ;DRAW BOX
JSR PC,WAIT
.PINT #TICKH ;DRAW X-AXIS TICKS
JSR PC,WAIT
.PINT #TICKV ;DRAW Y-AXIS TICKS
JSR PC,WAIT
MOV @2(R5),NUM ;GET NUMBER OF POINTS
MOV 4(R5),R3 ;GET SPWL ADDRESS
MOV 6(R5),R4 ;GET FPWL ADDRESS
MOV #XMM,RO ;SAVE SPWL,FPWL AT #XMM
MOV (R3)+,(RO) ;
MOV (R3),2(RO) ;
MOV (R4)+,4(RO) ;
MOV (R4),8(RO) ;
MOV 10(R5),R3 ;GET YMIN ADDRESS
MOV 12(R5),R4 ;GET YMAX ADDRESS
MOV #YMM,R1 ;SAVE YMIN,YMAX AT #YMM
MOV (R3)+,(R1) ;
MOV (R3),2(R1)
MOV (R4)+,4(R1)
MOV (R4)+,6(R1)
MOV NUM,RO ;GET # OF DATA POINTS
ADD NUM,RO
MOV 14(R5),R2 ;GET X ARRAY ADDRESS
MOV 16(R5),R3 ;GET Y ARRAY ADDRESS
MOV #X,R4
MOV #Y,R5
DATA: MOV (R2)+,(R4)+ ;PUT X VALUES IN X
MOV (R3)+,(R5)+ ;PUT Y VALUES IN Y
SOB RO,DATA
MOV #BLOCK1,R2
MOV (R1)+,(R2)
MOV (R1)+,2(R2)
MOV (R1)+,4(R2)
MOV (R1)+,6(R2)
FSUB R2 ;CALCULATE RANGE OF Y
SUB #4,R2
MOV YSCALR,(R2)
MOV YSCALR+2,2(R2)
FDIV R2 ;CALCULATE Y SCALE FACTOR
CLR COUNT
MOV #BLOCK2,R3
MOV (R2)+,(R3)+
MOV (R2),(R3)
MOV #Y,R2
PLL: MOV #BLOCK2,R3
MOV (R2)+,4(R3)
MOV (R2)+,6(R3)
FDIV R3 ;DIVIDE Y VALUE BY SCALE FACTOR
MOV (R3)+,YVALR
MOV (R3),YVALR+2
MOV #YVALR,ARGBLK+2
MOV #YVALI,ARGBLK+4
JSR PC,CNVRT ;CONVERT Y VALUE TO INTEGER
MOV YVALI,YVAL
MOV COUNT,R4
MUL #709,R4
DIV NUM,R4 ;CALCULATE X VALUE
MOV R4,XVAL
JSR PC,VEC ;PLOT VECTOR
INC COUNT
CMP NUM,COUNT ;LOOP TO PLOT ALL VECTORS
BNE PLL

;THIS PART OF PROGRAM CONTROLS SCREEN CURSOR

CURSOR: .PRINT #COMPL ;TURN ON COMPL MODE
.PPRINT #PROMPT ;CURSOR SCREEN PROMPT
.BIS #1,FLAG
.BIC #100,RCSR ;DISABLE INTERRUPTS
CHECK: BIT #200,RCSR ;CHECK FOR TTY INPUT
.BEQ CHECK
GETC: MOV RBUF,RO ;GET CHARACTER
CMPB #103,RO ;CHECK IF EXIT REQUEST
BNE CHAR ;ENABLE INTERRUPTS
BIS #100,RCSR
JMP OUT
CHAR: CMPB #60,RO ;CURSOR RIGHT REQUEST
BEQ CURS1
CMPB #61,RO ;CURSOR LEFT REQUEST
BEQ CURS2
BR CHECK ;BRANCH IF INVALID CHAR
CURS1: INC XO ;CURSOR RIGHT ONE STEP
CMP #709,XO ;CHECK FOR EDGE
BNE FAST1
CLR R1
FAST1: MOV #5000.,RO ;DELAY TO ALLOW CRT TO
DLY1: SOB R0,DLY1 ; FINISH LAST CURSOR DRAW
BIT #200,RCSR ;CHECK IF INPUT PENDING
BEQ CURSP1 ;BR TO DRAW CURSOR IF NOT
MOV RBUF,RO
ADD #10.,XO ;CURSOR RIGHT TEN STEPS
CMP #709,XO ;CHECK FOR EDGE
BGE FAST1
CLR XO
BR FAST1
CURS2: DEC XO ;CURSOR LEFT ONE STEP
BPL FAST2 ;CHECK FOR EDGE
MOV #708,XO
FAST2: MOV #5000.,RO ;DELAY TO ALLOW CRT TO
DLY2: SOB R0,DLY2 ; FINISH LAST CURSOR DRAW
BIT #200,RCSR ;CHECK IF INPUT PENDING
BEQ CURSP1 ;BR TO DRAW CURSOR IF NOT
MOV RBUF,RO
ADD #10.,XO ;CURSOR LEFT TEN STEPS
BPL FAST2 ;CHECK FOR EDGE
MOV #708,XO
BR FAST2
CURSP1: BIT #1,FLAG
BNE CURSP2
.BPRINT #CVEC ;BLANK CURRENT CURSOR
CURSP2: BIC #1,FLAG
MOV #CVEC+5,R4 ;GET CURSOR ADDRESS
MOV #COORD,R1
MOV XO,RO ;GET NEW CURSOR POSITION
JSR PC,ASCII ;FILL OUTPUT LINE
JSR PC,NOUT ;
MOV #61,(R4)+ ;
MOV #54,(R4)+ ;
JSR PC,ASCII ;
JSR PC,NOUT ;
MOV #63,(R4)+ ;
MOV #66,(R4)+ ;
MOV #62,(R4)+ ;
MOV #15,(R4)+ ;
MOV #12,(R4)+ ;
; THIS PART OF PROGRAM PRINTS X AND Y VALUES FOR CURSOR POSITION

; GET CURSOR POSITION
MOV XO,RO

; CALCULATE X VALUE FOR CURRENT CURSOR POSITION
MUL NUM,RO
DIV #709,RO
MUL #4,RO
MOV R1,N
MOV #X,RO
ADD N,RO

; CONVERT TO INTEGER
MOV (RO)+,XVALR
MOV (RO),XVALR+2
MOV #XVALR,ARGBLK+2
MOV #XVALI,ARGBLK+4
JSR PC,CNVRT
MOV XVALI,RO

; FILL OUTPUT LINE
MOV #XNUM+20,R4
MOV #COORD,R1
JSR PC,ASCII

; PRINT X=VALUE
XPR: MOVB -(R1),(R4)+
CMP #COORD,R1
BNE XPR
MOV #XNUM ; PRINT X=VALUE
MOV #WORK1

; GET Y VALUE FOR CURRENT CURSOR POSITION
MOV #Y,RO
ADD N,RO

; CONVERT TO INTEGER
MOV (RO)+,YVALR
MOV (RO),YVALR+2
MOV #YVALR,ARGBLK+2
MOV #YVALI,ARGBLK+4
JSR PC,CNVRT
MOV YVALI,RO

; FILL OUTPUT LINE
MOV #YNUM+20,R4
MOV #COORD,R1
JSR PC,ASCII

; PRINT Y=VALUE
YPR: MOVB -(R1),(R4)+
CMP #COORD,R1
BNE YPR
MOV #YNUM ; PRINT Y=VALUE
MOV #COMPL ; TURN ON COMPL MODE
JMP CHECK ; CHECK FOR MORE INPUT

OUT: .PRINT #WORK2
RTS PC

CNVRT: MOV R1,-(SP) ; SUBROUTINE TO CONVERT
MOV R2,-(SP) ; REAL*4 TO INTEGER
MOV R3,-(SP)
MOV R4,-(SP)
MOV  #2, ARGBLK
MOV  #ARGBLK, R5
JSR  PC, JAFIX
MOV  (SP)+, R4
MOV  (SP)+, R3
MOV  (SP)+, R2
MOV  (SP)+, R1
RTS  PC

WAIT: MOV  #65535, R0
BR:  SOB  R0, BR
RTS  PC

ARGBLK:  .BLKW  3
XVALI:  .BLKW  2
XVALR:  .BLKW  2
YVALI:  .BLKW  2
YVALR:  .BLKW  2
COUNT:  .BLKW  1
XMM:   .BLKW  10
YMM:   .BLKW  10
BLOCK1: .BLKW  10
BLOCK2: .BLKW  10
NUM:   .BLKW  1
YSCALR: .FLT2  363.
YSCALE: .BLKW  2
N:      .WORD  0
XVAL:  .WORD  0
YVAL:  .WORD  0
FLAG:  .WORD  0
XO:    .WORD  0

SETUP:  .ASCIIZ  /SHR D!WOR 33!GRA 1,26,8,78/ (15)(12)
BOX:   .ASCIIZ  /VEC 0,0,709,0,709,363,0,363,0,0/ (15)(12)

TICKH:  .ASCIIZ  /VEC 70,0,70,5!VEC 141,0,141,10!VEC 212,0,212,5/
        /ASCIIZ /VEC 283,0,283,10!VEC 354,0,354,5/
        /ASCIIZ /VEC 425,0,425,10!VEC 496,0,496,5/
        /ASCIIZ /VEC 567,0,567,10!VEC 638,0,638,5/ (15)(12)

TICKV:  .ASCIIZ  /VEC 0,72,0,72!VEC 0,145,0,145/!
        /ASCIIZ /VEC 0,218,0,218!VEC 0,291,0,291/ (15)(12)

PROMPT:  .ASCIIZ  /CURSOR ENABLED: (0)= +,(1)= -,(C)= EXIT/ (200)
COMPL:  .ASCIIZ  /!CMO Y/
NCOMPL: .ASCIIZ  /!CMO N/

.TITLE VECPLT
.GLOBL VEC, ASCII, NOUT, XVAL, YVAL, LINE, COORD
.MCALL .PRINT

VEC:   MOV  R0, -(SP)  ;SAVE REGISTERS
MOV  R1, -(SP)
MOV  R2, -(SP)
MOV R3,-(SP)
MOV R4,-(SP)
MOV R5,-(SP)
MOV #2,R3
MOV #LINE+15,R4 ;GET VECTOR ENDPOINT
MOV #LINE+5,R5 ;GET VECTOR START
SHIFT:
MOVVR (R4)+,(R5)+ ;SHIFT ENDPOINT TO START
CMPB #44.,(R4)
BNE SHIFT
SOB R3,SHIFT
MOVB #44.,(R5)+
MOV #LINE+15,R4 ;GET VECTOR ENDPOINT
FILL:
CMP R4,R5
BHI SPACE
BR CONT
SPACE: MOVB #40, (R5)+
BR FILL
CONT: MOV #COORD,R1 ;GET ASCII LIST ADDRESS
MOV XVAL,RO ;GET X VALUE
JSR PC,ASCII ;CONVERT TO ASCII FORMAT
JSR PC,NOUT ;PUT IN OUTPUT LINE
MOV YVAL,RO ;GET Y VALUE
JSR PC,ASCII ;CONVERT TO ASCII FORMAT
JSR PC,NOUT ;PUT IN OUTPUT LINE
MOVB #15,(R4)+ ;TERMINATE OUTPUT LINE
MOVB #12,(R4)+
MOVB #200,(R4)+
.PRT #LINE ;PLOT VECTOR
MOV (SP)+,R5 ;RESTORE REGISTERS
MOV (SP)+,R4
MOV (SP)+,R3
MOV (SP)+,R2
MOV (SP)+,R1
MOV (SP)+,R0
RTS PC
ASCII: MOV R0,R3 ;GET INTEGER NUMBER
ASC2: CLR R2 ;DIVIDE NUMBER BY TEN
DIV #10,R2 ;CONVERT TO ASCII
ADD #60,R3 ;CHECK IF QUOTIENT ZERO
MOVB R3,(R1)+
MOV R2,R3
TST R2
BNE ASC2
RTS PC
NOUT: MOVB -(R1),(R4)+ ;REPACK ASCII CHARACTERS IN
CMP #COORD,R1 ;PROPER ORDER IN OUTPUT LINE
BNE NOUT
MOVB #44.,(R4)+ ;INSERT COMMA
RTS PC
COORD: .BLKW 10
LINE: .ASCIIZ /!VEC
.END VEC
PROGRAM TDS
DIMENSION VAL(8000)
INTEGER*4 DATA
WRITE(5,100)
100 FORMAT(' THIS PROGRAM COLLECTS A SPECIFIED NUMBER OF DATA'//
 1' POINTS THROUGH A/D #0 ; EACH POINT IS AVERAGED'//
 1' FOR A SPECIFIED NUMBER OF LOOPS OF APPROXIMATE'//'//
 1' DURATION 1/1000 SEC'//)
WRITE(5,110)
110 FORMAT(' ENTER THE NUMBER OF POINTS (MAX 8000) : ') READ(5,120) NPNTS
120 FORMAT(I5) PNTS=FLOAT(NPNTS) WRITE(5,130)
130 FORMAT(' ENTER THE NUMBER OF AVERAGING LOOPS : ') READ(5,140) NLOOPS
140 FORMAT(I5)
TLOOPS=8.
IF(NLOOPS.GT.64) TLOOPS=TLOOPS+1. START=0.0
ANG=1.0
NRCDS=NPNTS+4 WRITE(5,150)
150 FORMAT(' ENTER THE COMPLETE STORAGE FILE NAME ') CALL ASSIGN(1,BOZO,-1)
DEFINE FILE 1 (NRCDS,2,U,IBUM)
DO 10 I=1,NPNTS
  CALL INPUT(NLOOPS,DATA) VAL(I)=AJFLT(DATA)/(FLOAT(NLOOPS)*TLOOPS)
10 CONTINUE
WRITE(1,'(1X,N5)') NRCDS WRITE(1,'(1X,F10.6)') START WRITE(1,'(1X,F5.1)') PNTS
WRITE(1,'(1X,F8.4)') ANG DO 20 I=1,NPNTS J=I+4
WRITE(1,'(1X,F10.6)') VAL(I)
20 CONTINUE
STOP
END
.TITLE INPUT
.GLOBL INPUT
STATUS=176770
DATA=176772

INPUT:  MOV @2(R5),R1 ;NUMBER OF LOOPS
MOV 4(R5),R2 ;DATA POINTER
CLR (R2) ;CLEAR DATA LOCATION
CLR 2(R2)
MOV #10,LTIME
CMP #100,R1
BPL 1$
INC LTIME
1$:  MOV LTIME,R3 ;SET LOOP DURATION
2$:  MOV #31,@#STATUS ;START CONVERSION
3$:  BIT #200,@#STATUS ;CHECK IF FINISHED
BEQ 3$ ;BRANCH IF NOT DONE
MOV @#DATA,R4
BPL 4$ ;CHECK IF DATA NEGATIVE
COM R4
SUB R4,(R2) ;SUBTRACT NEGATIVE DATA
SBC 2(R2)
BR 5$
4$:  ADD R4,(R2) ;ADD IN POSITIVE DATA
ADC 2(R2)
5$:  DEC R3
BNE 2$ ;FINISH LOOP
DEC R1
BNE 1$ ;FINISH ALL LOOPS
RTS PC
LTIME: .WORD 0
.END
PROGRAM TOS5
DIMENSION MASS(5),NUM(5)
INTEGER*4 DATA(5000)
INTEGER OFFSET
WRITE(5,100)
100 FORMAT(' THIS PROGRAM WILL COLLECT DESORPTION SPECTRA FOR'//
1' UP TO 5 MASS PEAKS FROM THE UTI 100C, INPUT THROUGH'//
1' ADC 0. MASSES ARE SAMPLED SEQUENTIALLY FOR AN INTERVAL'//
1' SPECIFIED BY THE NUMBER OF AVERAGING LOOPS FOR EACH'//
1' POINT (100 MICROSEC PER LOOP, 11 MSEC BETWEEN POINTS).'//
1' MASS POSITIONS ARE CALIBRATED FOR UTI CONTROLLER #02-944'//
1' AND ADAC BOARD IN SURFACE COMPUTER.'//)
WRITE(5,110)
110 FORMAT(' ENTER THE NUMBER OF AVERAGING LOOPS: ') READ(5,120) NLOOPS
120 FORMAT(I5)
WRITE(5,130)
130 FORMAT(' ENTER THE NUMBER OF DATA POINTS IN SPECTRA: ') READ(5,120) NPOINT
WRITE(5,140)
140 FORMAT(' ENTER THE NUMBER OF MASS PEAKS: ') READ(5,120) NMASS
WRITE(5,150)
150 FORMAT(' ENTER THE MASS NUMBERS TO BE COLLECTED, '/'
1' ONE AT A TIME: ') READ(5,120) (MASS(I), I=1,NMASS)
ITIME=INT((FLOAT(NLOOPS)*0.10+11.)*FLOAT(NPOINT)/10**3)*NMASS
WRITE(5,160) ITIME
160 FORMAT(/' THE PARAMETERS ENTERED WILL COLLECT SPECTRA THAT'//
1' ARE',I4,' SECONDS IN DURATION'//)
DO 10 I=1,NMASS OFFSET=11
IF(MASS(I).LT.12) OFFSET=10
10 NUM(I)=INT(FLOAT(MASS(I))*2048./300.)-OFFSET NRCDS=(NPOINT+1)*NMASS
WRITE(5,170) NRCDS
170 FORMAT(' ENTER THE STORAGE FILE NAME: ') CALL ASSIGN (1,BOZO,-1)
DEFINE FILE 1 (NRCDS,2,U,IBM)
WRITE(1,'(I)') NRCDS
WRITE(1,'(I)') NLOOPS
WRITE(1,'(I)') NPOINT
WRITE(1,'(I)') NMASS
DO 20 I=1,NMASS J=I+4
20 WRITE(1,'(I)') MASS(I)
CALL SWEEP (NLOOPS,NPOINT,NMASS,NUM,DATA)
DO 30 I=1,NMASS K=I + NMASS*(NPOINT-1)
DO 29 J=I,K,NMASS L=(J-I)/NMASS + (I-1)*NPOINT + NMASS + 5
29 WRITE(I,'(I)') DATA(J)
30 CONTINUE
STOP
END
.TITLE SWEEP
.GLOBL SWEEP
STATUS=176770
DATA=176772
DAC=176762

Sweep: MOV @4(R5),POINT   ;GET NPOINT
       MOV 12(R5),R3      ;GET DATA POINTER
1$:  MOV @6(R5),MASS    ;GET NMASS
       MOV 10(R5),R2     ;GET MASS POINTER
2$:  MOV @2(R5),LOOP   ;GET NLOOPS
       CLR (R3)          ;CLEAR DATA LOCATION
       CLR 2(R3)
       MOV (R2)+,@#DAC   ;MOVE TO MASS LOCATION
       MOV #2420,R4      ;DELAY TO ALLOW
11$: DEC R4             ;MASS SPEC TO SETTLE
       BNE 11$.
3$:  MOV #31,@#STATUS   ;START CONVERSION
       BIT #200,@#STATUS ;CHECK IF FINISHED
       BEQ 4$
       MOV @#DATA,R4     ;CHECK SIGN OF DATA
       BPL 5$
       COM R4
       SUB R4,(R3)        ;SUBTRACT IF NEGATIVE
       SBC 2(R3)
       BR 6$
5$:  ADD R4,(R3)        ;ADD IN DATA
       ADC 2(R3)
6$:  DEC LOOP           ;GO TO NEXT MASS
       BNE 3$
       ADD #4,R3          ;LOOP FOR SPECIFIED
       DEC MASS           ;NUMBER OF POINTS
       BNE 2$
       DEC POINT
       BNE 1$             ;LOOP FOR SPECIFIED
       RTS PC

Point: .WORD 0
Mass:  .WORD 0
Loop:  .WORD 0
.END
PROGRAM TDS5PL
DIMENSION X(1000), Y(1000), MASS(5)
INTEGER*4 IDATA
LOGICAL*1 FARRAY(10), GARRAY(10), ANS, YES
DATA YES/'Y'/
CALL SCOPY('F6.0'), GARRAY
CALL SCOPY('F6.0'), FARRAY
CALL INITI(480)
WRITE(5,100)
100 FORMAT(' THIS PROGRAM PLOTS THE OUTPUT OF THE TDS5 PROGRAM'://
1' BY SUCCESSIVELY READING TDS SCANS FOR DIFFERENT MASSES'://
1' FROM THE SPECIFIED DATA FILE.':///)
WRITE(5,110)
110 FORMAT('ENTER THE DATA FILE NAME: ')
CALL ASSIGN(1,BOZO,-1)
DEFINE FILE 1 (1010,2,1,IBUM)
READ(1') NRCDS
READ(1') NLOOPS
READ(1') NPOINT
READ(1') NMASS
DO 10 I=1,NMASS
J=I+4
10 READ(1') MASS(I)
ITIME=INT((FLOAT(NLOOPS)*100./10**3+11.)*NPOINT/10**3)*NMASS
WRITE(5,120) NMASS, ITIME
120 FORMAT(' THE FILE CONTAINS',13,' SPECTRA OF',14,/
1' SECONDS DURATION.'://)
WRITE(5,130)
130 FORMAT(' THE SPECTRA CORRESPOND TO THE FOLLOWING MASSES:')
WRITE(5,140) (MASS(I), I=1,NMASS)
140 FORMAT(110)
PAUSE
IPL0T=0
15 DO 20 I=1,NPOINT
J=IPL0T*NPOINT + I + NMASS + 4
READ(1') IDATA
Y(I)=AJFTL(IDATA)/FLOAT(NLOOPS)
20 X(I)=((FLOAT(NLOOPS)*100./10**3+11.)*FLOAT(I)/10**3)*FLOAT(NMASS)
CALL PREP(6,6)
30 CALL NEWPAG
CALL GRAPH(NPOINT, X, Y, -1)
CALL HICK(11,11,FARRAY,GARRAY,6,6)
CALL HOME
35 WRITE(5,500)
500 FORMAT(' DO YOU WANT A HARDCOPY? ')
READ(5,510) ANS
510 FORMAT(A1)
IF(ANS.NE.YES) GO TO 40
CALL SWAPM
CALL GRAPH(NPOINT, X, Y, -1)
CALL HICK(11,11,FARRAY,GARRAY,6,6)
CALL SWAPS
40 WRITE(5,600)
600 FORMAT(' DO YOU WANT TO CHANGE PLOTTING VALUES? ')
READ(5,510) ANS
IF(ANS.NE.YES) GO TO 50
CALL NEWPAG
CALL WINADJ(X1,X2,Y1,Y2)
CALL GRAPH(NPOINT,X,Y,-1,0)
CALL HICK(11,11,FARRAY,GARRAY,6,6)
CALL HOME
GO TO 35
50    IPLOT=IPLOT+1
      IF(IPLOT.LT.NMASS) GO TO 15
      STOP
END
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References

75. R. M. A. Azzam and N. M. Bashara, op. cit., p. 361.


151. N. J. Turro, Modern Molecular Photochemistry (Benjamin/Cummings, Menlo Park, 1978), ch. 11,12.


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