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PHOTOLUMINESCENCE FROM THE NOBLE METALS

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G.T. Boyd
(Ph.D. Thesis)

December 1985

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The Enhancement of Optical Effects on Rough Metal Surfaces and Photoluminescence from the Noble Metals

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Ph.D. Thesis
December 1985

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The enhancement of optical effects on rough metal surfaces and photoluminescence from the noble metals

Gary Timothy Boyd

Abstract

Optical second-harmonic generation was used to study the local-field enhancement due to surface roughness on various materials ranging from the alkalis to a semiconductor. The roughness morphology was standardized by evaporating each material onto the same chemically etched glass slide, having microstructures hundreds to thousands of Å in size. With the laser excitation at 1.06 μm, the observed SH enhancements for different materials varied from 27 to $1 \times 10^{-3}$ times that of silver. They were in fair agreement with a simple model calculation assuming that the rough surface is composed of a distribution of noninteracting hemispheroids on a plane. The results are used to predict some rather substantial enhancements for surface Raman scattering for a number of substrate materials. In a separate experiment, single-photon and multi-photon induced luminescence spectra were obtained from clean samples of silver, copper, and gold with both smooth and rough surfaces. The spectra reveal new features, which are correlated with interband transitions at selected symmetry points in the Brillouin zone. The effects of roughness on the luminescence are
largely attributable to localized plasmon resonances in the rough surface protrusions. The results are used to evaluate photoluminescence as a band structure probe for metals.
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I. INTRODUCTION

The effective Raman cross-section of molecules can increase by many orders of magnitude when adsorbed onto roughened metal surfaces\textsuperscript{1}. The mechanism for this surface enhanced Raman scattering (SERS) effect, and its promise as a sensitive tool for surface spectroscopy, continue to attract considerable attention. In addition to Raman scattering, many other optical processes can be enhanced on roughened surfaces, including second-harmonic generation (SHG), photoabsorption, photoluminescence, and photochemical reactions\textsuperscript{2}. A major contribution to the enhancement of all these processes is the amplification of the optical fields at the rough surface protrusions by local plasmon resonances and corona effects. Although this amplification is expected to occur on many different substrates, most of the attention in the literature has been focused on the noble metals. The first portion of this thesis discusses a technique to measure the local field enhancement which is applied to a wide variety of materials. The results are used as a stringent test for the local field theory.

The second portion of this thesis deals with the intriguing broadband background observed in SERS spectra\textsuperscript{1}. One of the major contributions to this background is the photoluminescence from the substrate itself. While this luminescence constitutes the fundamental noise limit for SERS spectroscopy, it is probably the least explored aspect of the SERS phenomenon. Photoluminescence spectra from the noble metals were obtained which illucidate the underlying mechanism for the luminescence. The effect of roughness on the luminescence was also determined by obtaining spectra from both rough and smooth surfaces. Many of these effects are explained by the local field theory.
References:


II. STUDY OF LOCAL-FIELD ENHANCEMENT ON ROUGH SURFACES OF METALS, SEMI-METALS AND SEMICONDUCTORS USING OPTICAL SECOND-HARMONIC GENERATION

A. Introduction

It is generally accepted that there are two distinct contributions to the SERS enhancement. First, a chemical interaction between the adsorbed molecules and the substrate can lead to an intrinsic Raman cross-section different from that of the isolated molecules. Second, the incoming and outgoing optical fields can be enhanced because of local-field enhancement resulting from local plasmon resonances and corona (or lightening rod) effects in the rough surface protrusions. For noble metals, the second mechanism is believed to be dominating.\(^1\)

One expects from the local-field enhancement alone, that any roughened conductor could produce surface enhanced Raman scattering, although the magnitude of the enhancement may vary. However, very few materials have actually been examined.\(^1\)-\(^17\) Measuring the relative enhancement ability of various metals using Raman scattering is complicated by the fact that in many cases, even the SERS signal is too weak to detect, and that the surface coverage of adsorbates on different substrates varies widely and is very difficult to determine. If we are only interested in the local-field enhancement, then it is actually more appropriate to study surface enhancement of some other optical effects which occur on bare substrates, and require no adsorbates. Optical mixing on surfaces is an example. It should occur at a surface with or without adsorbates. Second-harmonic generation (SHG) is particularly attractive because the experimental arrangement is
simple and it provides easily detectable signals from both smooth and rough metal surfaces. In addition, SHG and Raman scattering have essentially identical dependences on the local-field enhancement at the surface.\(^{18}\) Four-wave mixing and higher-order processes generate hardly detectable signals from smooth surfaces. They are generally not useful as means to study surface enhancement.

Because SHG from both smooth and rough surfaces of any material is easily detectable, we can use it to measure the local-field enhancement at the surfaces of a variety of substances. In this chapter, we report our measurements on 16 different metals and one semiconductor. The surface local-field enhancement is defined as the ratio of the SH intensity from the rough surface to that from the smooth surface. Identical roughness was established for each material by evaporating the materials onto the same glass slide which had been roughened. Using this method, we could derive the relative surface enhancement of different materials, and find that several materials should have sufficiently high surface enhancement to be useful in surface Raman spectroscopy and other surface optical studies.

Our results also provide a quantitative test for the surface local-field theory.\(^{18}\) The local-field enhancement is expected to depend critically on the dielectric constant of the material. The wide range of materials with a wide range of dielectric constants used in our study can, therefore, subject the theory to a stringent test. The predictions were found to be in good agreement with our measurements. We can then use the theory to predict the local-field enhancement in surface Raman scattering for various materials.
As a side product, the SH measurements from smooth surfaces of various materials allowed us to estimate the second-order nonlinear optical coefficients for these materials. For many metals, they appeared to be within an order of magnitude of the predictions from a simple free electron model.

B. Experiment and Results

The rough and smooth surfaces were prepared by evaporating films of each material simultaneously onto smooth and roughened glass slides. The roughened slide had random, irregular surface protrusions, hundred to thousands of Å in size, produced by chemically etching a single face of a microscope slide with hydrofluoric acid vapor. The slide was pre-cleaned with soap and water, masked on one side, and then heated to approximately 100°C. It was then immersed into a sealed enclosure of warm (30°C) HF vapor, removed after about ten minutes, then rinsed thoroughly with distilled water. The heating was necessary to prevent large HF droplets from condensing onto the glass and dissolving the vapor-etched fine structures. Silver evaporated onto the etched slide gave somewhat less, but comparable, SH enhancements and showed similar surface features to that of electrolytically reformed silver, widely used to obtain large SERS enhancements.

The roughened slide was reused after each measurement by dissolving the evaporated film in aqua regia, and then cleaning the slide in distilled water, and drying it with nitrogen gas. A fresh smooth slide was used in each measurement, cleaned in a similar manner. Since both the rough and smooth surfaces were subject to the same cleaning conditions,
their intrinsic optical coefficients for SH generation were presumed the same. The measurements were fairly reproducible. It then suggested that the ratio of the SH intensities from roughened and smooth surfaces should be nearly independent of possible surface contamination.

The repeated cleaning and evaporation procedure did not significantly alter the etched surface. The SH intensity from the roughened surface of all the materials was reproducible to within a factor of two or better, after many cleanings and evaporations. The SH intensity from the smooth surfaces was reproducible to within 20%. Such variations were felt to be acceptable, compared to the many orders of magnitude over which the measured SH enhancements ranged.

The materials in this study had a wide range of dielectric constants: good conductors such as the alkali and noble metals, moderate conductors such as tin, lead, and nickel, as well as the semi-metal bismuth, and semi-conductor germanium. All materials were at least 99.9% pure.

The SH signals were obtained from the glass-film interfaces. High evaporation rates, typically 100 Å/sec, and low pressures, < 10^{-6} torr, in the evaporation chamber, were used to ensure the purity of the interface. Protection from oxidation for those measurements made in air was provided by evaporating films at least 3000 Å thick. The alkali metal films were kept under vacuum during the measurement in a specially constructed evaporation chamber equipped with a liquid nitrogen vapor trap. During the course of each measurement, the SH intensity from the samples never varied by more than 20%, and the smooth surfaces always maintained their shininess.

The apparatus for measuring the SH enhancement is shown in Fig. 1. A Q-switched Nd:YAG laser provided 6 ns excitation pulses at 1.06 μm. The
p-polarized beam, incident at 45° to the samples, was spectrally filtered to exclude any SH radiation generated before the sample. Input intensities at the samples were on the order of 1 MW/cm² with a beam diameter of 0.5 cm. The SH signals reflected from the glass-film interface were spectrally filtered to block the fundamental excitation. The signals were then collected by an f/2 lens, sent through an angularly tuned interference filter, and finally focused onto a photomultiplier tube (PMT). An additional spectral filter at the PMT served to block stray 1.06 µm light. Large SH signals were attenuated by calibrated neutral density filters. The electrical pulses from the PMT were processed by a gated integrator and averaged by a microcomputer over 800 laser shots. Standard deviations from the mean were less than 10% of the averages, primarily due to laser pulse fluctuations and photon counting statistics.

The SH radiation from the rough surfaces was diffused and unpolarized. The f/2 lens served to collect approximately 10% of the diffuse light. The smooth surfaces provided a collimated and p-polarized SH signal which was focused by the collection lens. An iris was placed at the focal point to pass the collimated light and block any diffuse light. Tests with spectral filters confirmed that the SH signals originated from the samples.

A similar experiment by Chen et al.¹⁹ on electrolytically roughened noble metal surfaces in air, revealed significant broad band luminescence, near the SH peak. We measured the signal spectrum near the SH for all the samples, using an angle-tuned interference filter (40 Å FWHM). Luminescence at 0.532 µm was then estimated and subtracted from the measured SH signal to obtain the true SH signal. We found that for our samples, the luminescence was comparable to the SH signal from the roughened
surfaces of only a few materials: Mn, Fe, Ni, and Ge. The ratio of the luminescence to the SH from copper and gold samples was much less than that reported by Chen et al.\textsuperscript{19}. It is possible that their luminescence background resulted from remnants of the electrolytic roughening process.

The SH signals from the smooth surfaces of each material were ratioed to that from gold. This comparison served to normalize all measurements against variations in the incident beam characteristics. The measured SH enhancements from rough surfaces of different materials were then ratioed to that of silver. Both the normalized SH surface enhancements and the normalized SH signals from different materials are listed in Table I. The absolute value of the SH enhancement for silver evaporated onto our roughened slide was $2.0 \times 10^3$. It is seen that several good conductors display local-field enhancements comparable to or larger than that of silver, while poorly conducting metals, semi-metals, and semiconductor Ge have much weaker enhancements. Overall, the enhancements range over four orders of magnitude. Since SH generation has essentially the same local-field dependence as Raman scattering (see Sec. III), the results in Table I give an immediate estimate of the local-field enhancements for SERS on the same materials. A more detailed discussion of these results will follow the theory section.

C. Theory and Comparison with Experiment

The enhancement of optical signals from adsorbates on roughened surfaces is due to both chemical and electromagnetic interactions.\textsuperscript{18,20,21} By chemical interactions, we mean the significant modification of the eigenenergies and eigenfunctions of a molecule, in the absence of any applied
field, when adsorbed onto a substrate. With the presence of an applied field, induced dipole-induced dipole interaction between molecules and induced dipole-image dipole interaction between the molecules and substrate also occur. This we refer to as the microscopic local-field effect.\textsuperscript{22} A second type of electromagnetic effect is the change in the incoming and outgoing fields at the surface of a substrate according to the macroscopic Maxwell equations and the surface boundary conditions. This is the macroscopic local-field effect which can lead to another local-field enhancement. On a bare substrate surface without adsorbates, the enhancement of optical signals from the rough surface can only come from the electromagnetic interaction. The microscopic local field is expected to be the same for smooth and rough surfaces. Therefore, the surface enhancement should be the result of only the macroscopic local-field enhancement.

The macroscopic local-field enhancement can be very large on rough surfaces which have protrusions on the order of hundreds to thousands of Å. Fields tend to concentrate at the tips of these protrusions in an effort to be nearly perpendicular to a metal or semiconductor surface. This is known as the lightning rod effect.\textsuperscript{23,24} In addition, collective oscillation of the electrons in these protrusions can be induced by the optical fields. The resonance produces a large local-field enhancement, which is referred to as the local plasmon effect.\textsuperscript{23,24} These are the dominant field enhancement mechanisms at rough surfaces.

Chen et al.\textsuperscript{18} have used the local-field correction factor to describe the macroscopic local-field enhancement. For the rough surface, the following simple model was assumed: The surface is represented by a collec-
tion of noninteracting hemispheroids sitting upward on a plane (Fig. 2). In the presence of an infinite plane wave \( \hat{E}(w) \), the local fields just outside and inside a hemispheroid are, respectively,\(^{23,25}\)

\[
\begin{align*}
\hat{E}^\text{out}_\parallel(w) & = [L^\text{out}_\parallel(w)\sin\alpha \hat{n} + L^\text{out}_\perp(w)\cos\alpha \hat{e}]E_\parallel(w) \\
\hat{E}^\text{in}_\perp(w) & = [L^\text{in}_\parallel(w)\sin\alpha \hat{n} + L^\text{in}_\perp(w)\cos\alpha \hat{e}]E_\parallel(w),
\end{align*}
\]

(1)

where \( E_\parallel(w) \) is the plane wave component perpendicular to the plane, and the angle \( \alpha \) and unit vectors \( \hat{n} \) and \( \hat{e} \) are defined in Fig. 2. The local-field correction factor \( L \)'s satisfy the relations

\[
\begin{align*}
L^\text{in}_\parallel(w) = L^\text{in}_\perp(w) = L^\text{out}_\parallel(w) = [\varepsilon(w)/\varepsilon_m(w)]L^\text{out}_\perp(w), \\
L^\text{out}_\parallel(w) = L_{LR}L_p(w),
\end{align*}
\]

(2)

with

\[
L_{LR} = 1/A \\
L_p = (\varepsilon_m/\varepsilon)/[\varepsilon_m/\varepsilon - 1 + (1/A)[1 + \frac{4\pi^2}{3} \frac{V}{\lambda^3} (1 - \varepsilon_m)\varepsilon^{1/2}]]
\]

where \( A = [1 - \varepsilon Q_1'(\xi)/Q_1(\xi)]^{-1}, \xi = [1 - (b/a)^2]^{-1/2}, Q_1(\xi) = (\xi/2)\ln[(\xi + 1)/(\xi - 1)]^{-1}, \) is the Legendre function of the second kind,\(^{26}\) \( Q_1' = dQ_1/d\xi, \varepsilon_m \) and \( \varepsilon \) are the dielectric constants of the hemispheroid and the surrounding medium, respectively, \( V = 4/3 \pi ab^2 \) is the full spheroid volume, and \( \lambda \) is the wavelength of the driving field. We shall use this model to discuss the surface enhancement of SHG from various materials.
The lightning rod and local plasmon resonance contributions to the local field are explicitly exhibited in the factors $L_{LR}$ and $L_p$, respectively. $L_{LR}$ is a function only of the hemispheroid shape, given by the aspect ratio, $a/b$. For a hemisphere, $a/b = 1$, we have $L_{LR} = 3$. For elongated hemispheroids, $a/b >> 1$, we have $L_{LR} = (a/b)^2/\ln(a/b) >> 1$. A plot of $L_{LR}$ versus $a/b$ is given in Fig. 3a.

The local plasmon factor $L_p$ may also be much larger than unity. Its resonance occurs when the frequency $\omega = \omega_0$ satisfies the relation

$$\text{Re}[\epsilon_m(\omega_0)/\epsilon(\omega_0)] = 1 - 1/(A(a/b)). \quad (3)$$

We have, on resonance

$$|L_p(\omega_0)| = \frac{\epsilon_m(\omega_0)/\epsilon(\omega_0)}{\text{Im}[\epsilon_m(\omega_0)/\epsilon(\omega_0)] + \frac{1}{A(a/b)} \frac{4\pi^3}{3} \frac{V}{\lambda^3} [1 - \epsilon_m(\omega_0)][\epsilon(\omega_0)]^{1/2}}. \quad (4)$$

The resonant enhancement is limited by the damping factors in the denominator. The first term, $\text{Im}(\epsilon_m/\epsilon)$, is determined by the characteristic loss in the hemispheroid. If $l$ is the mean free path of electrons in the bulk and $b$ is the smaller hemispheroid dimension, then $\text{Im}(\epsilon_m)$ is that of the bulk multiplied by $1 + l/b$, often known as the wall collisional effect. The other damping term in Eq. (3) is caused by radiation loss. The field, enhanced by $L_{LR} = 1/A(a/b)$, induces a dipole moment in the hemispheroid which radiates with a dipole-like $1/\lambda^3$ dependence and a power proportional to the number of oscillating electrons. In a free electron metal, the number of electrons is proportional to $[1 - \epsilon_m(\omega)]V$. Expanding the hemispheroid volume increases the radiative
damping, but decreases the wall collisional damping. An optimum value of \( V \) therefore exists.

The local-field correction factor \( L_{\text{out}} = L_{\text{LR}}L_p \) is plotted against \( a/b \) in Fig. 3b for a metal hemispheroid with an electron density \( N_e = 10^{23} \text{ cm}^{-3} \) and a bulk mean free path of 500 Å, close to that of silver. The wavelength is fixed at \( \lambda = 1.06 \mu\text{m} \). The dashed curve shows the sharp plasmon resonance when only the bulk \( \text{Im}(\varepsilon_{\text{m}}) \) damping is considered. A near optimum value of \( V = 5 \times 10^{-4} \lambda^3 \) was chosen to include the wall collisional damping contribution in curve 2, and the additional radiative damping contribution in curve 3. The resonant peak is shifted to smaller value of \( a/b \) for curve 4 when \( N_e \) is reduced to \( 10^{22} \text{ cm}^{-3} \), since from Eq. (3), we have \( \text{Re}[\varepsilon_{\text{m}}/\varepsilon] = -\omega_p^2/\omega_0^2 = A \) which decreases with \( a/b \). The value of \( |L_{\text{out}}| \) also decreases with \( a/b \) because of the smaller lightning rod factor, \( L_{\text{LR}} \).

The above discussion is for a single hemispheroid. The rough surfaces used in surface enhancement experiments actually contain protrusions of a wide variety of shapes and sizes. Our model then assumes that the rough surface can be approximated by a set of noninteracting hemispheroids of randomly distributed sizes and shapes, that is, a random distribution of \( a \) and \( b \) values. In this model, any optical frequency can find some resonant protrusions on the surface. According to the local plasmon resonance condition of Eq. (3), lower frequencies should find plasmon resonances in the more elongated protrusions, which will yield a large lightning rod effect. Thus, the local-field enhancement for the rough metal surface should increase monotonically with the wavelength. At a given frequency, \( \omega \), a range of different protrusions can be near resonance. A broader
resonant peak in the plot of $L$ versus $a/b$ in Fig. 3b indicates that more near-resonant protrusions contribute to the local-field enhancement. Although increased damping reduces the amplitude of the plasmon resonance, the additional broadening, on the contrary, can help the enhancement. The local-field correction factors can be used to calculate the enhancement of an optical signal from a rough surface. In the calculation, we clearly need to sum over the random distribution of the hemispheroidal shapes and sizes.

We now consider the local-field enhancement of SHG from a rough surface relative to that from a smooth surface. For p-polarized excitation, the SH power from a smooth surface, characterized by a second order polarizability $\alpha(2)$, is given by,

$$P_{SH}(2\omega) = \frac{2\pi c}{\sqrt{\epsilon}} \left(\frac{2\omega}{c}\right)^2 N^2 \mathcal{A} \left|\hat{n} \times \hat{a}^{(2)}\right|^2 \hat{L}(2\omega)\hat{L}(\omega)\hat{L}(\omega)\hat{E}(\omega)\hat{E}(\omega) \text{ plane sec} \theta,$$

where the input at $\omega$ is incident on the plane at an angle $\theta$ and illuminates an area $\mathcal{A}$ containing $N$ atoms per unit area. The output at $2\omega$ propagates in the direction $\hat{n}$. The local-field tensor, $\hat{L}$, for the plane follows directly from the Fresnel equations. Just inside the substrate, we find

$$L_{\perp} = \frac{\epsilon}{\epsilon_m}(1 + r)$$

$$L_{\parallel} = 1 - r,$$

in which $r$ is the reflection coefficient of a p-polarized field.

We shall assume that $\alpha^{(2)}$ dominates in $\hat{a}^{(2)}$ for simplicity, as sug-
gested in Ref. 18. The SH output from the smooth surface then becomes

\[ P_{\text{plane}}(2\omega) \equiv \frac{8\pi c}{\sqrt{\varepsilon}} \left( \frac{2\omega}{c} \right)^2 N^2 \alpha_{L} |a_{L}(2\omega)L_{\parallel}(\omega)L_{\perp}(\omega)|^2_{\text{plane}} \times E^4(\omega)\cos^3\theta \sin^2\theta. \] (7)

The SH power from a highly elongated hemispheroid, \( a/b \gg 1 \), has been calculated by Chen et al.\(^1\) A modification of their result gives,

\[ P_{\text{hemisphere}}(2\omega) = \frac{27}{3} \pi^2 c \sqrt{\varepsilon} \left( \frac{2\omega}{c} \right)^4 N^2 b^4 x^2 |a_{L}(2\omega)L_{\parallel}(\omega)L_{\perp}(\omega)|^2_{\text{hemisphere}} \times E^4(\omega)\sin^4\theta, \] (8)

where \( x(a/b) = [(a/b)^2 / [(a/b)^2 - 1]] - [1 - \ln(a/b)^2] / [(a/b)^2 - 1] \) is a geometric function which generalizes the result of Chen et al. to include all hemispheroids with aspect ratio \( a/b > 1 \). The ratio of \( P_{\text{hemisphere}}(2\omega) \) to \( P_{\text{plane}}(2\omega) \) with \( \alpha = \pi b^2 \) yields the enhancement factor

\[ n_{\text{SH}}(a,b) = \frac{4\pi}{3} \left[ \frac{\pi(bx)^2}{\lambda^2} \right] \sin^2\theta \sec^3\theta \times 2^6 \frac{|L_{\parallel}(2\omega)L_{\parallel}(\omega)L_{\perp}(\omega)|^2_{\text{hemisphere}}}{|L_{\parallel}(2\omega)L_{\parallel}(\omega)L_{\perp}(\omega)|^2_{\text{plane}}} \] (9)

which is primarily dependent on the ratio of the local-field correction factors for the hemispheroid and plane. The factor of \( 2^6 \) comes from the image of the hemispheroid fields in the conducting plane. The factor in brackets is a ratio of the area of the hemispheroid and plane which radiate the fundamental fields in phase to generate the SH.

We finally sum the contributions from hemispheroids of various shapes
and sizes, assuming equal probability distribution with reasonable cutoff points, to obtain the total SH enhancement:

\[ \eta_{\text{SH}}^T = C[\Delta(a/b), \Delta V] \sum_{V, a/b} \eta_{\text{SH}}(a, b), \]  

(10)

where \( C[\Delta(a/b), \Delta V] \) is the fraction of the illuminated area occupied by hemispheroids with volume \( V = 4/3 \pi ab^2 \pm \Delta V \), and aspect ratio \( a/b \pm \Delta(a/b) \).

The local-field enhancement of Raman scattering can be similarly calculated.\(^{18}\) It is usually defined as the ratio of the Raman signal from molecules adsorbed uniformly on a rough surface to that of the same number of molecules in space. Assuming that the \( q_R \) component of the Raman polarizability tensor dominates, we find the total surface enhancement as

\[ \eta_{\text{R}}^T = C[\Delta(a/b), \Delta V] \sum_{V, a/b} \eta_{\text{R}}(a, b), \]  

(11)

where

\[ \eta_{\text{R}}(a, b) = \frac{2}{\pi} \sin^2 \theta \frac{b}{a}^3 \sqrt{\epsilon} 2^4 |L_{\text{out}}(\omega) L_{\text{out}}(\omega) |^2_{\text{hemisph}} \]

with \( \omega \) and \( \omega_3 \) being the incoming and Raman scattering frequencies, respectively.

Both the SH and Raman enhancements have essentially the same dependence on the local-field factors because \( \omega - \omega_3 \) in the Raman case, while the SH radiation is predominantly from hemispheroids resonant at the funda-
mental frequency $\omega$ and far off-resonant at $2\omega$ with $L(2\omega) - 1$. Relating the inside and outside local-field factors using Eq. (2) allows us to conclude that both $n_{SH}$ and $n_R$ are proportional to $|L^\perp_{\text{out}}(\omega)|^4$.

In the SHG experiment, if we assume that the second order polarizabilities of the smooth and rough surfaces in our experiment were the same, due to their similar preparation conditions, we can then compare our measurements with the predictions of Eq. (9) or (10). Since all the materials were evaporated on the same roughened slide, the rough surface morphology was identical for all of them. We can then eliminate $C$ in Eq. (10) by always referring the SH enhancement to that of a chosen standard material. The relative $\frac{n_{SH}}{\text{SH}}$ should therefore be calculated to compare with the measured relative SH enhancement. To calculate $n_{SH}(a,b)$, we have used the dielectric constants listed in Table II, which were taken from the most recent literature values, or for Ga and Mg, calculated from the Drude model. Because of the local plasmon resonance function $L_p$, $n_{SH}(a,b)$ peaks at particular values of $a$ and $b$ for each material. It then allows us to limit the summation in Eq. (10) to $a/b = 1$ to 20 and $V/\lambda^3 = 10^{-5}$ to $10^{-4}$, for all the materials. At $\lambda = 1.06 \mu m$, this range roughly describes shapes and sizes of the protrusions seen in electron-photomicrographs of the actual roughened surfaces.

The measured and calculated values of the SH enhancements relative to silver are compared in Fig. 4. For perfect agreement, the experimental data would lie on the dashed line. It is seen that overall, the local-field theory is accurate to better than an order of magnitude, for measurements which ranged over four orders of magnitude. The experimental error bars indicate the reproducibility of each measurement. The theoreti-
cal error bars were derived either from the published accuracy of the dielectric constants or the parameters needed to calculate them.

The fractional coverage factor, $C$, in Eq. (10) may be deduced from the ratio of the measured $n_{SH}$ to the calculated summations of $n_{SH}(a,b)$. For all the materials it was found $C \approx 3 \times 10^{-4}$, for summations carried out at a fixed optimum $V$, and $\Delta(a/b) = .1$. Thus, an average of $0.03\%$ of the surface is occupied by protrusions with an effective $a/b$ lying between $a/b - .1$ and $a/b + .1$. An examination of photomicrographs of the rough surface shows this to be a reasonable result.

D. Discussion

The success of the simple model of the rough surface is somewhat surprising, since the actual surfaces hardly resemble a distribution of isolated hemispheroids on a conducting plane. This is presumably because the model emphasizes the local-field contributions of the lightning rod and local plasmon resonance effects, which occur predominantly at the tips of the surface protrusions. At a given excitation frequency, only those tips with the proper shape are resonantly excited. They are rare enough to be considered as non-interacting. Even if a cluster of protrusions resonate collectively,\textsuperscript{20} the resonance may be approximated by that of a properly shaped single hemispheroid.

The observed wide range of the SH enhancements on different materials can be understood from the local-field model. The largest enhancements came from good conductors with relatively high electron densities. In Fig. 2b, we notice that at the same excitation frequency, the plasmon resonance should occur in more elongated protrusions for metals with higher
electron densities, giving rise to a larger lightning rod effect. This explains why Al and Ga, having calculated plasmon resonances at $a/b = 13.3$ and 12.0, respectively, have a larger SH enhancement than Na, whose lower electron density shifts the resonant shape to $a/b = 3.3$. The poorer conductors such as Pb, Sn, and Ni, have still lower enhancements due to their higher intrinsic $\text{Im}(\varepsilon_m)$ which damps the plasmon resonance. This effect is partially offset, however, by the broader width of $L_p$, as a function of $a/b$, which means more protrusions can contribute near-resonantly to the enhancement. The enhancement on rough Ge should be due to the lightning rod effect alone, since the positive dielectric constant of Ge precludes any plasmon resonance. A local-field model more suited to insulators and semiconductors should presumably include oblate as well as prolate hemispheroids on a dielectric plane.

The above considerations also apply to the local-field enhancement for Raman scattering, due to the common $|L_{\text{out}}^\perp(\omega)|^4$ dependence. We have used Eqs. (10) and (11) to calculate the enhancements for various materials relative to silver. The sum in Eq. (11) is taken over the same range as in the calculation of the SH enhancement and the approximation $\varepsilon_m(\omega) = \varepsilon_m(\omega_R)$ is used. The ambient is chosen to be vacuum with $\varepsilon = 1$. Two excitation wavelengths of 0.53 $\mu$m and 0.65 $\mu$m are considered to illustrate the marked dispersion of some materials in the visible. The results of the calculations are shown in Fig. 5. The values of $n_R^T/n_R^A (\text{Ag}, .53 \mu m)$ are listed in decreasing order and extended horizontally for clarity only. Using $C = 3 \times 10^{-4}$ from the SH measurements, we estimate the absolute value of $n_R^T (\text{Ag}, .53 \mu m) = 2 \times 10^4$. From Fig. 5, it is seen that the surface local-field enhancement for surface Raman scattering can be
significant for many roughened materials not yet explored in SERS studies. Several of them can have enhancements exceeding that of silver.

The Raman calculations appear to be reasonable. For a SERS enhancement of $10^6$ for pyridine on roughened silver, $n_A^T (.53 \text{ } \mu m) = 2 \times 10^4$ implies an additional enhancement of 50 due to chemical interactions. The dramatic drop in SERS for Cu and Au, when the excitation wavelength is decreased (Fig. 5), has been confirmed by many experiments.\textsuperscript{1, 28-30} The calculated dispersion of SERS is shown for the three noble metals in Fig. 6, assuming a Raman shift $\omega - \omega_R = 1000 \text{ } \text{cm}^{-1}$. The general trend of decreasing $n_A^T$ with decreasing wavelength for most of the metals can be qualitatively understood from the free electron model. The plasmon resonance condition, $A = (\omega_0/\omega_p)^2\varepsilon$, tells us that decreasing the excitation wavelength increases $A(a/b)$, and shifts the resonance to less elongated protrusions. This results in a smaller lightning rod enhancement, which diminishes $n_A^T$.

As a by-product of our experiment, we can estimate the second order nonlinear optical coefficients for various materials from the SH measurements on smooth surfaces. We again take $\alpha^{(2)}_{||}$ as the dominant component of $\alpha^{(2)}$, neglecting contributions from possible surface contaminants. The coefficient $\alpha^{(2)}_{||}$ is proportional to the coefficient $\beta$ often used in the literature:\textsuperscript{31-35} $N\alpha^{(2)}_{||} = [\epsilon_m^{(\omega)} - \epsilon^{(\omega)}]\beta$, where $N$ is the molecular density.\textsuperscript{18} According to Eq. (7), the value of $\beta$ for a given material relative to a standard material can be deduced from the ratio of the SH powers:

$$\frac{P_{SH}^{(2\omega)}}{P_{SH,S}^{(2\omega)}} = \frac{|\beta|^2}{|\beta_S|^2} \frac{|\epsilon_m^{(\omega)} - \epsilon^{(\omega)}|^2 |L_{||}^{in(2\omega)L_{||}^{in(\omega)L_{||}^{in(\omega)}}|^2_{plane}}}{|\epsilon_m^{(\omega)} - \epsilon^{(\omega)}|^2 |L_{||}^{in(2\omega)L_{||}^{in(\omega)L_{||}^{in(\omega)}}|^2_{plane}}}. $$
Using the data in Table I and the dielectric constants in the literature, the ratios of $\beta/\beta(\text{Ag})$ can be computed and are listed in Table III. For most of the metals, the values of $\beta$ are within a factor of two of one another. This tends to confirm the prediction of the free electron model of metals that leads to $\beta = e/8\pi m^* \omega^2$,\textsuperscript{31,32} which is independent of the free electron density, assuming that the effective electron mass $m^*$ is close to $m$. Notable exceptions to this in Table III are Ga, Pb, and Ni, in which interband contributions to $\beta$ may play a significant role. A truly accurate measurement of all the nonlinear optical coefficients would require a systematic study of the intensity and phase of the SH, using a variety of input angles and polarizations, on clean surface in an ultrahigh vacuum environment.
References

1. For a recent review, see Surface Enhanced Raman Scattering, eds. R. K. Chang and T. E. Furtak (Plenum, New York, 1982).


Table I. SH Data

<table>
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<tr>
<th>Material</th>
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<th>SH intensity from smooth films relative to Ag</th>
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Table II. Dielectric Constants

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Table III. Second order optical coefficients relative to Ag.

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Figure Captions

Fig. 1. Experimental setup. CF: spectral filter; IF: interference filter; PMT: photomultiplier tube.

Fig. 2. A rough surface model.

Fig. 3. Plot, versus a/b, of (a) the lightning rod factor $L_{LR}$ and (b) the local-field factor $L_{\text{out}}$ with 1) bulk $\text{Im}(\varepsilon_m)$ damping only, 2) wall collisional damping included, and 3) further addition of radiative damping. Curve 4) is for a metal with a lower electron density, including all damping effects.

Fig. 4. Experimental versus theoretical SH enhancements, relative to silver.

Fig. 5. Theoretical local-field Raman enhancements relative to Ag at .53 µm, for excitation at $\lambda = .65$ µm (filled in circles) and .53 µm (open circles). Points are displayed horizontally for clarity only.

Fig. 6. Theoretical dispersion of local-field enhancements for the noble metals, for $\omega - \omega_R = 1000$ cm$^{-1}$ and $\varepsilon = 1$. 
LASER INPUT
1.06 μm

Sample

CF

IF

CF

PMT

Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 6
III. PHOTO-INDUCED LUMINESCENCE FROM THE NOBLE METALS AND ITS ENHANCEMENT ON ROUGHENED SURFACES

A. Introduction

Photo-luminescence has been used extensively in the study of inelastic scattering processes in semiconductors. Its use in characterizing carrier relaxation and the band structure of metals was first suggested by the discovery of photoluminescence from copper and gold by Mooradian\(^1\). In the original experiment, monochromatic light at 4880 Å was used to excite a luminescence spectrum which displayed a broad peak centered near the interband absorption edge of the metals. The peak was attributed to direct radiative recombination of electrons near the fermi level with holes in the first d-band. Many of the essential details of this mechanism, such as the excited electron and hole population distributions, the specific regions in the Brillouin zone where the recombination takes place, and the reabsorption of the emitted luminescence, have not been discussed. By Mooradian's hypothesis, additional peaks in the luminescence spectra should result if higher energy excitations are used to create holes in lower lying d-bands. The peak energies would correspond to the energy difference between the fermi-level and the various d-bands at certain symmetry points. Despite the possible usefulness of this technique as a band structure probe, luminescence from metals has remained relatively unexplored since Mooradian's original experiment\(^2,\,3\).

Renewed interest in luminescence from metals came with a number of discoveries related to noble metals with roughened surfaces. Much excitement was generated by the observation of an enormous enhancement
in the Raman cross-section of molecules adsorbed to a roughened noble metal surface\(^4\). In addition to the sharp Raman peaks from the adsorbed molecules, a broadband luminescence background was observed\(^5\). Experiments in ultra-high vacuum showed that at least part of the luminescence must originate from the substrates\(^6-8\). This background currently constitutes the fundamental noise limit for surface enhanced Raman scattering (SERS). It is now widely accepted that for optical processes, the primary role of the roughness in metals is to enhance the local optical fields via localized plasmon resonances, and thus improve the efficiency of light absorption and emission. This so-called local field effect is responsible for a major part of the Raman enhancement\(^3\), and for a variety of other effects including the enhancement of luminescence of dyes adsorbed to roughened metals\(^9,10\), and the increase in photochemical activity of adsorbates on roughened metals\(^11\). Local field effects are also used to explain the enhancement of light emission from tunnel junctions with roughened noble metal electrodes\(^12-14\). The broadband spectra from these junctions are strongly influenced by the dispersion of the localized plasmon resonances. It is expected that the same resonances will affect the photo-induced luminescence spectra as well. A comparison of such spectra from rough and smooth metal samples would provide a probe of the plasmon dispersion and a test for the local field models.

Luminescence may also be excited by multi-photon absorption. Multi-photon induced luminescence was first observed as a broadband background in SHG measurements on roughened noble metals\(^15\). Preliminary studies revealed significant differences between the broadband emission excited by single-photon and multi-photon absorption\(^16\). In the former
case, the luminescence intensity rises with increasing emission energy towards the pronounced interband peak, for both rough and smooth surfaces. However, the multi-photon induced luminescence from the roughened surfaces dramatically decreases with increasing emission energy, and displays no detectable peak. Some authors have speculated that the missing peak is the result of two-photon selection rules\textsuperscript{17}. The mixed parity of the d and sp bands for these metals, however, weakens this argument. On the other hand, because the multi-photon luminescence was observed from a roughened metal, the effects of the localized plasmon resonances must be included in the interpretation of the spectra. In particular, the multi-photon luminescence is more sensitive to the local fields than the single-photon luminescence. Since the local fields are strongest just outside the metal surface, multi-photon induced emission from the surface atoms may dominate over that from the bulk, yielding different luminescence spectra from the bulk.

In addition to the many unexplored theoretical questions regarding metal luminescence, much of the previous experimental data may have been complicated by emission from surface contaminants, since many of the spectra were obtained from samples exposed to the air or immersed in an electrochemical cell. Unless precautions against contamination are taken, it is possible that the photo-induced luminescence from a roughened sample may include enhanced luminescence from adsorbates. Another complexity in the existing experimental results is the dispersion of the various detection systems. Since the emission energies may range over many electron volts, a correction for this dispersion is essential to obtain the true luminescence spectra.
This paper presents spectra of single and multi-photon induced luminescence obtained from clean films of silver, copper, and gold, prepared and maintained in high vacuum (10^{-9} \text{ torr}). All spectra were corrected for the dispersion of the detection system. Furthermore, in order to probe the lower lying d-bands, higher excitation energies than those of previous experiments were used. New features appear in the single-photon induced luminescence spectra as a result. When possible, spectra were obtained from both smooth and rough surfaces, with the same surface morphology for all metals. The multi-photon induced spectra could be detected only from the roughened samples.

The details of the sample preparation, the excitation source, and the detection system are given in the next section. Following this, we present the single-photon induced luminescence spectra from smooth samples of silver, copper, and gold, and include a brief physical interpretation of the results. The effects of roughness on these spectra are then described and discussed. The multi-photon induced luminescence spectra from the rough samples are then presented, and contrasted with the single-photon induced luminescence. A more detailed interpretation of all the spectra is given in the Discussion section. There we present a simple calculation which correlates the spectral peaks with interband recombination at selected symmetry points in the Brillouin zone. The excited electron and hole energy distributions are deduced from the data to provide insight into the carrier relaxation process. The effects of roughness on the luminescence are estimated with a simple local field model and compared with the data. We then examine the multi-photon induced luminescence spectra, stressing the effects of local plasmon resonances in interpreting the spectra. We
conclude with a summary of the results and an evaluation of photoluminescence as a band structure probe for metals.

B. Experiment

1. Sample Preparation

In an effort to eliminate possible contributions to the luminescence from surface adsorbates, the samples were prepared and maintained in high vacuum \((10^{-9} \text{ torr})\). The samples were made by evaporating approximately 1000 Å of high purity metals (99.998%) onto roughened and smooth substrates. The pressure during the evaporation did not exceed \(10^{-7} \text{ torr}\). Before each evaporation, the chamber and the source filament were outgassed at high temperature (200°C for the chamber, 800°C for the filament), for 24 hours. Several measurements were performed to establish that these films were sufficiently clean: 1) No surface enhanced Raman peaks were detected from these samples, indicating that they were free from organic adsorbates. 2) Rough samples in air produced as much as 100 times the two-photon induced luminescence as these samples in vacuum. 3) Gold films prepared under similar conditions have been shown to be free of surface adsorbates\(^\text{18}\). On the other hand, the luminescence intensity from our Au films exceeded that from Ag and Cu, which under these conditions could still be contaminated by surface oxide\(^\text{19}\). This indicates that the minor surface contamination on Ag and Cu contributed negligibly to the luminescence, if at all.

The substrate used was a glass slide, half of which was roughened by a chemical etching technique\(^\text{20}\). The evaporated films conformed to
the substrate morphology to produce a metal surface half of which was rough and half of which was smooth (Fig. 1). Electron photomicrographs of the rough samples revealed a surface covered with structures 100 – 1000 Å in size. The same roughness morphology was guaranteed for each metal by chemically removing the metal films and reusing the same substrate.

2. Optical Arrangement and Detection System

A Q-switched Nd:YAG laser and a harmonic generator were used to provide excitation energies of 1.17 eV, 2.34 eV, 3.50 eV, and 4.67 eV. The incoming beam was p-polarized, having a nearly Gaussian spatial profile, and was incident at 45° to the sample surface. The intensities used were typically 1–10 MW/cm², with pulse durations of 8 ns. The luminescence was collected at 90° to the incident beam by an f/1.5 fused quartz lens, and focused either onto a triple monochromator (80 Å FWHM) in the case of the one-photon induced luminescence, or, for the weaker multi-photon induced spectra, onto a single monochromator (100 Å FWHM) equipped with spectral filters. The monochromators were scanned in 10 nm intervals. Any incident light which was specularly reflected was removed by a non-luminescing absorber. Tests using the monochromators and spectral filters were routinely performed to insure that the signals included no elastically scattered light. Additional spectral filters were used in some cases to avoid higher order diffraction from the monochromator gratings. A photo-multiplier which had a broad spectral response (Hamamatsu H955), was used as the detector. The electrical signal was processed by a gated integrator, interfaced to a micro-computer which averaged each spectral point over at least 1500 laser pulses.
Absolute spectra were obtained by compensating the data for the
dispersion of the detection system, measured with a calibrated
tungsten-halogen lamp. All final spectra were repeatable typically to
within 20%.

C. Results

1. Single-Photon Excited Spectra from Copper

(a) Smooth Sample

The spectra of single-photon induced luminescence, from the
smooth sample of Cu, are shown as solid curves in Figs. 2a-c, at
increasing excitation energies. At the lowest excitation energy (Fig.
2a), the spectrum consists of a single peak at 2.15 eV, in good
agreement with the spectra obtained by others1-3. The quantum
efficiency of the luminescence was approximately $10^{-10}$, which is also
in agreement with earlier measurements1. The peak has been attributed
by Mooradian to recombination radiation between electrons near the fermi
level and photo-excited holes in the first d-band.

At a higher excitation energy of 3.50 eV, we observe an
additional peak in the luminescence at 2.90 eV (Fig. 2b). Since 3.50
eV photons have enough energy to excite electrons from the second d-band
of Cu21, we will attribute the second peak to recombination radiation
between electrons near the fermi level and holes in the second d-band.
The spectrum also displays a slight rise in intensity toward the
excitation energy. Various tests were made to assure that this is
definitely from luminescence instead of elastic scattering. Because
there are no further d-band transitions which can be reached by 3.50 eV
photons21, we have to attribute it to recombination radiation between
photo-excited electrons above the fermi level, and holes in the first and second d-bands.

At the highest excitation energy of 4.67 eV, only a weak signal could be detected from smooth Cu, and no spectral structure could be clearly discerned.

(b) Rough Sample

The effects of roughness on the one-photon luminescence were also investigated. The spectra from the rough Cu film are shown as dashed curves in Figs. 2a-c. At the lowest excitation energy (Fig. 2a), the spectral peak is eight times larger than that from the smooth sample, and is shifted to a lower energy. This shift of the emission peak is a natural consequence of localized plasmon resonances which produce an increasingly large surface enhancement as the emission energy decreases.

At the excitation of 3.50 eV (Fig. 2b), again because of the localized plasmon resonances, only the low energy peak appears to have shifted to lower energies from that of the smooth sample, in addition to being more intense. The rise in intensity near the excitation energy, which is evident from the smooth sample, is absent in the rough sample spectrum. This could be due to roughness quenching of the photo-excited electrons above the fermi level. At the excitation energy of 4.67 eV, however, roughness quenching is apparently insufficient to remove the tail in the spectrum of the rough sample, seen in Fig. 2c. We also observe in this spectrum a broad feature from 1.9 eV to 3.3 eV containing several weak peaks, which are shifted from those of Fig. 2b.

2. Single-Photon Excited Spectra from Gold

(a) Smooth Sample
The one-photon luminescence spectra from the smooth sample of Au are shown as solid curves in Figs. 3a-c. The peak which has been observed by other investigators at 2.4 eV\(^1,22\), is just above our first excitation energy of 2.34 eV. The spectrum shown in Fig. 3a is evidently the tail of this peak, which monotonically decreases with decreasing emission energy. At the higher excitation energy of 3.50 eV a peak appears at 2.50 eV in addition to one at 2.95 eV. As with Cu, we will attribute these peaks, as well as the weak structure near 1.8 eV, to recombination between electrons near the fermi level and holes in the top two d-bands. The sharp rise toward the excitation energy is also evident as in the case of Cu.

At the highest excitation of 4.67 eV, many new features appear in the spectrum (Fig. 3c). Pronounced peaks at 2.2 eV and 3.2 eV are evident, with additional features at 1.9 eV, 2.55 eV, and 3.0 eV. The rise towards the excitation energy is also very strong. Most of the new features will be assigned to transitions involving holes created in the three d-bands.

(b) Rough Sample

The one-photon induced luminescence spectra from the rough sample of Au are shown as dashed curves in Figs. 3a-c. For the excitation energies of 2.34 eV, as with Cu, the roughness broadens the luminescence, especially at energies below the interband absorption edge. For the excitation energy of 4.67 eV (Fig. 3c), the major spectral feature near 3.2 eV is strongly suppressed. In all cases, the sharp increase of luminescence towards the excitation energy observed from smooth samples is strongly suppressed, presumably due to roughness quenching.
3. Single-Photon Excited Spectra of Silver

(a) Smooth Sample

No luminescent peak can be expected from excitation below 3.5 eV for Ag. With the excitation at 4.67 eV, the spectrum, shown as a solid curve in Fig. 4, consists of a single peak, extending from 3.6 eV to 3.9 eV, and a shoulder above 4 eV. An examination of the band structure calculations for Ag\textsuperscript{21}, and the photo-absorption\textsuperscript{23} and photothermal data\textsuperscript{24,25} from the literature, reveals that the peak position is far from any direct fermi level to d-band transition. However, the volume and surface plasmon energies for Ag are in close correspondence with the observed peak\textsuperscript{23}.

(b) Rough Sample

The one-photon induced luminescence from rough Ag is shown in Fig. 4 (dashed curve). The essential effect of the roughness is to broaden the luminescence peak to energies as low as \approx 3 eV. We will attribute the broadening to surface plasmons. It is well documented that surface plasmon emission for Ag may be extended to these energies by roughening the surface\textsuperscript{26}.

4. Multi-Photon Excited Spectra

Photo-luminescence was also induced by multi-photon absorption. The resulting spectra from the rough samples of Cu, Au, and Ag, are shown as solid curves in Fig. 5. No multi-photon induced luminescence could be detected from any of the smooth samples.

All the spectra exhibit a second-harmonic, and in some cases, a third harmonic peak resulting from surface harmonic generation. The broadband luminescence in each spectrum rises monotonically with decreasing emission energy.
The number of photons involved in the multi-photon excitation can be inferred from the high energy cutoff of the luminescence spectrum. For Cu and Au, at an excitation energy of 1.17 eV, the cutoff is at the two-photon energy, implying that the luminescence was initiated by two-photon absorption. To confirm this, the power dependence of the luminescence (as well as the second harmonic) was obtained, and found to be quadratic to within experimental error. For Ag, at an excitation of 1.17 eV, the luminescence extends continuously to the three-photon energy, implying its initiation by three-photon absorption. For an incident energy of 2.34 eV, the luminescence from Ag cuts off at an energy which implies two-photon absorption.

The one-photon induced luminescence spectra from the smooth samples are reproduced as dashed curves in Fig. 5, for comparison. The peaks in the one-photon spectra of Cu and Ag are not apparent from the two-photon excited spectra (Fig. 5a and 5d). In addition, for all three metals, the one-photon luminescence decreases towards the low emission energies, while for the two-photon luminescence it increases. This can be attributed to the dispersion of the localized plasmon resonances on the rough surface.

D. Discussion

Our discussion of the photoluminescence spectra proceeds in several steps. We begin in section 1 by developing an expression for the luminescence resulting from direct transitions. A detailed comparison between the predictions and the data is then given in section 2. The luminescence from the rough samples is treated in section 3 by replacing the local fields of the smooth surface with those of the rough
surface, derived from a simple model. The results are compared with the observed spectra in section 4 for both the single-photon and multi-photon induced luminescence.

1. General Theory

Photoluminescence in solids is a three-step process involving photoexcitation of an electron-hole pair, the relaxation of the excited electrons and holes, and finally emission from the electron-hole recombination. The process is diagrammed in Fig. 6a between two representative bands for Au. We shall consider only direct transitions in the absorption and emission processes.

We may express the single-photon induced luminescence from a slab of width \( dz \) at a depth \( z \) into the metal as

\[
I_L(\omega_2)dz = I(\omega_1, z)Y_{\text{abs}}Y_RY_{\text{em}}dz,
\]

where \( \omega_2 \) and \( \omega_1 \) are the luminescence and incident frequencies, respectively, \( I(\omega_1, z) \) is the excitation intensity at \( \omega_1 \) at a depth \( z \), \( Y_{\text{abs}} \) is the probability for a single-photon absorption at \( \omega_1 \), \( Y_R \) is the probability of relaxation of the electrons and holes from the excited states to the emitting states, and \( Y_{\text{em}} \) is the emission probability of radiative recombination at \( \omega_2 \). The excitation intensity is given by

\[
I(\omega_1, z) = I_0(\omega_1) |L(\omega_1)|^2 \exp[-\alpha(\omega_1)z],
\]

where \( I_0(\omega_1) \) is the source intensity, \( |L(\omega_1)|^2 \) is the Fresnel transmission coefficient at \( \omega_1 \), and \( \alpha \) is the absorption coefficient.
For two-photon induced luminescence, \( I(\omega_1, z)Y_{1abs} \) becomes \( I^2(\omega_1, z)Y_{2abs} \), where \( Y_{2abs} \) is the two-photon absorption probability at \( 2\omega_1 \).

The direct absorption of photons at \( \omega_1 \) will promote electrons from bands below the fermi level into bands above the fermi level at all points in the Brillouin zone where the band energy separation is \( \hbar\omega_1 \).

The theory for direct photo-absorption in the noble metals is treated in Refs. 21 and 24, and need not be reproduced here. After the absorption, the electrons and holes will relax from their initial excited states to new energy states, via the many scattering processes in the noble metals\(^\text{27} \). The luminescence results from the radiative recombination of these relaxed carriers. We will account for the relaxation by assuming a simple energy distribution of the relaxed electrons and holes in the calculation for the emission probability.

The probability of emission at \( \omega_2 \) will be proportional to the total radiative recombination rate between all electrons and holes with an energy difference of \( \hbar\omega_2 \). If we designate the energy and wave vector of the Bloch state to which the electrons relax as \( E \) and \( k \), respectively, then from Fermi's golden rule for spontaneous emission from direct recombination (into a solid angle \( d\Omega \) and bandwidth \( d\omega_2 \)), we have

\[
Y_{em} \propto \omega_2 d\omega_2 d\Omega |L(\omega_2)|^2 \exp[-\alpha(\omega_2)z]
\]

\[
\times \iint |p_2|^2 \delta(E - E_U(k)) \delta(E - \hbar\omega_2 - E_L(k))
\]

\[
f_e(E) f_h(E - \hbar\omega_2) dE d^3k
\]
where $E_U$ and $E_L$ are the energies of the upper electron and lower hole bands, respectively. $P_2$ is the momentum matrix element between the bands, and $|L(\omega_2)|^2$ is the Fresnel transmission coefficient at $\omega_2$.

The factor $\exp[-\alpha(\omega_1)z]$ accounts for the absorption of the outgoing light within the metal. The functions $f_e$ and $f_h$ are the electron and hole population distributions, respectively, which result from the excitation and relaxation processes. These distribution functions are difficult to calculate from first principles, because they depend on the complex scattering processes in the metal. However, we expect the electron and hole populations to diminish continuously away from their initially excited states. For simplicity, we assume that these populations decay exponentially as the electrons sink down the upper band and the holes float up the lower band. If we designate the initial excited state energy of the electrons as $E_0$, then

\begin{equation}
    f_e(E) = F_D(E) + \theta(E - E_0)\exp[(E - E_0)/\delta_e],
\end{equation}

where $F_D(E) = [1 + \exp(E/kT)]^{-1}$ is the Fermi-Dirac distribution, the step-function $\theta(x)$ is zero for $x<0$ and constant for $x>0$, and $\delta_e$ is an adjustable parameter representing the exponential width. The hole distribution is similarly written as

\begin{equation}
    f_h(E_h) = 1 - F_D(E_h) + \theta(E_{oh} - E_h)\exp[(E_{oh} - E_h)/\delta_h],
\end{equation}

where the hole energy is $E_h = E - h\omega_2$, $E_{oh} = E_0 - h\omega_1$, and $\delta_h$ is also an adjustable exponential width. These functions are plotted in Fig. 6b. The exponential terms in $f_e$ and $f_h$ are used to fit the observed
rise in the luminescence intensity near the excitation energy. The rise
is attributed to radiative recombination of excited electrons above the
fermi level with the excited holes in the lower band.

Further simplifications in the calculation of $Y_{em}$ can be made.
The integration over the Brillouin zone may be approximated by
considering only those regions close to the symmetry points, since they
will contribute the largest joint density of states for emission. We
also need only consider the regions where the band pairs have an energy
difference no greater than the excitation energy. In addition, we will
ignore those regions in which the excited electrons and holes would
scatter in different $k$ directions such that direct recombination would
not be possible. After an examination of the calculated band structures
of the noble metals\textsuperscript{21} it is apparent that, for the excitations used in
this experiment, these restrictions limit us to regions near the X and
L symmetry points for all the noble metals. We will further assume that
the momentum matrix elements are independent of $k$ over such regions.
This latter approximation has been used successfully in the calculation
of the dielectric constants of the noble metals\textsuperscript{21,24}.

The emission spectrum is estimated by evaluating $Y_{em}$, using the
assumed electron and hole distribution functions in Eqs. (4) and (5).
After combining Eqs. (1) - (5) and integrating over $z$ we have, with the
above approximations,

\begin{equation}
I_L(\omega_2) = \int dE \left( D(E, \hbar \omega_2) f_e(E) f_h(E - \hbar \omega_2) \right),
\end{equation}

where $F(\omega_1, \omega_2) = \omega_2 |L(\omega_1)|^2 |L(\omega_2)|^2 z_0 (\omega_1, \omega_2)$, $z_0 (\omega_1, \omega_2) = 1/[\alpha(\omega_1) + \alpha(\omega_2)]$, and
Rosei evaluates \( D(E, \hbar \omega_2) \) by writing the energy of the Bloch state near the L and X symmetry points as

\[
E_i(k) = \Delta_i + \frac{h^2 k_1^2}{2m_1} + \frac{h^2 k_2^2}{2m_2}.
\]

where \( \Delta_i \) is the energy of the \( i \)th band at the symmetry point, measured from the fermi level, \( \vec{k}_1 \) is the electron wave vector pointing from the L or X symmetry point to \( \Gamma \), \( \vec{k}_2 \) is perpendicular to \( \vec{k}_1 \), and \( m_1 \) and \( m_2 \) are the band masses. Equation (7) then becomes

\[
D(E, \hbar \omega_2) \propto |E - E_i(\hbar \omega_2)|^{1/2},
\]

where

\[
E_i(\hbar \omega) = \Delta_U + \frac{m_{2L}(\Delta_U - \Delta_L - \hbar \omega)}{(m_{2U} - m_{2L})}.
\]

The limits of integration in Eq. (6) are given by \( E_{\text{min}} = E_1(\hbar \omega_1) - \hbar \omega_1 + \hbar \omega_2 \), and \( E_{\text{max}} = E_1(\hbar \omega_1) \) for \( \hbar \omega_2 \geq \Delta_U - \Delta_L \), while for \( \hbar \omega_2 < \Delta_U - \Delta_L \), \( E_{\text{max}} = \Delta_U + (\Delta_U - \Delta_L - \hbar \omega_2)m_{1L}/(m_{1U} - m_{1L}) \).

2. Calculated Single-Photon Excitation Spectra and Comparison with Experiment

We evaluate the single-photon excitation spectra from Eq. (6) by first evaluating the factor \( F(\omega_1, \omega_2) \), containing the Fresnel
transmission coefficients at $\omega_2$, and the effective absorption depth, $z_0$. For the smooth surface, with p-polarized incident light, the dominant fields inside the metal will be parallel to the surface. The relevant Fresnel coefficient is then\(^{28}\)

\[
L(\omega) = \frac{2\cos\theta_m}{[\varepsilon_m^{1/2}(\omega) \cos \theta + \cos \theta_m]},
\]

where $\varepsilon_m$ is the metal dielectric constant, $\theta$ is the angle of incidence, and $\theta_m$ is the angle of refraction in the metal. Figure 7 shows a plot of $F = \omega_2 |L(\omega_1)|^2 |L(\omega_2)|^2 z_0 (\omega_1, \omega_2)$ versus $\omega_2$, for $\theta = 45^\circ$ and $\hbar\omega_1 = 3.50$ eV. The necessary dielectric constants were obtained from reference 23. We see from the figure that for Cu and Au, $F$ shows a peak around the onset of the interband transitions. The peak for Ag which appears at 3.78 eV corresponds to the excitation of a volume plasmon, where $\text{Re} \varepsilon_m = 0$. Such a peak is expected to strongly affect the spectrum from Ag.

The integral in Eq. (6) was evaluated using band parameters obtained from the calculations of Lasser and Smith\(^{21}\), listed in Table I. The bands are numbered beginning with the lowest d-band as band 1. The resulting spectra are shown in Figs. 8-10. The notation in the figures, e.g. 6-5L, refers to radiative recombination of electrons in band 6 (sp conduction band) with holes in band 5 (top d-band), near the L symmetry point. In the spectral range we have studied, we only need to calculate luminescence from the radiative recombination of electrons in band 6 with the scattered holes in the d-bands. The decrease in the luminescence at low energies results from a diminishing hole population (the exponential term in Eq. (5)), and the dispersion
of the factor F (Fig. 7). Because of the many approximations used in this calculation, we should not take the calculated spectrum too seriously, but simply focus our attention on the peak positions.

(a) Copper

The calculated luminescence peak, at ≈2.0 eV shown in Fig. 8a for Cu for the excitation energy of 2.34 eV, results from transitions from band 6 to band 5 near the L symmetry point. The position of the peak is within 0.1 eV of that measured from the smooth sample (Fig. 2a), and is well within the accuracy of the band structure parameters from Table I. At the excitation of 3.50 eV, holes are also created in the second highest d-band (4), giving rise to the second major peak at 2.7 eV in Fig. 8b, also in good agreement with observation from the smooth sample (Fig. 2b). The calculated rise in intensity near the excitation energy results from recombination of holes and electrons near their initial excitation energies. This is also evident in the measured spectrum in Fig. 2b.

The calculated spectrum with 4.67 eV excitation is shown in Fig. 8c. There is a transition from a lower d-band (3) near the X symmetry point which contributes a peak near that of the 6-5L transition. Because an experimental spectrum is not available in this case, no comparison between theory and experiment can be made.

(b) Gold

The calculated luminescence spectrum for smooth Au, excited at 2.34 eV, is shown in Fig. 9a. This energy is just sufficient to promote electrons from the top d-band to the fermi-level near L. Consequently, the spectrum shows only part of a peak. The calculation is in reasonable agreement with the data in Fig. 3a. For the excitation
energy of 3.50 eV, the full peak of the 6-5L transition at 2.4 eV is evident in Fig. 9b, along with peaks at 3.1 and 1.9 eV from the 6-4L and 6-5X transitions, respectively. The shoulder at 2.4 eV in the 6-4L contribution is due to dispersion of the Fresnel factor (Fig. 7b). The observed peaks in the luminescence spectrum from the smooth sample of Au (Fig. 3b), differ from the 2.4 and 3.1 eV peaks in the calculation by less than 0.1 eV and 0.3 eV, respectively, which is within the accuracy of the band parameters used. The weak structure in the data near 1.9 eV correlates with the calculated peak position of the 6-5X transition.

At the excitation energy of 4.67 eV, many more transitions become possible in Au, as is evident in Fig. 9c. A comparison of this figure with the measured spectrum in Fig. 3c leads to the following assignments: The main peak at 3.1 eV in the experiment appears to be a composite of the 6-4L and 6-3X transitions. The smaller peak at 2.2 eV is a combination of the 6-5L and 6-4X transitions, while the weaker structure near 1.9 eV may correspond to the 6-5X transition. The rise in the luminescence near the excitation energy is again attributed to recombination of electrons and holes near their initial excitation energies.

(c) Silver

For the excitation of 4.67 eV, Eq. (6) predicts luminescence peaks for Ag at 4.0 and 4.3 eV, resulting from the 6-5L and 6-4L transitions, respectively. Unlike Cu and Au, however, the Fresnel factor shows a pronounced peak (Fig. 7c) at the volume plasmon resonance energy, which masks over these interband peaks. The calculated spectrum is shown in Fig. 10. The positions of the interband
transition peaks are indicated by the vertical arrows in the figure. The calculation is in reasonable agreement with the measured spectrum from the smooth sample (Fig. 4). The step in the data above 4 eV corresponds with the calculated step due to the 6-4L transition at 4.3 eV.

The measured peak actually appears to be shifted by ~0.1 eV below the volume plasmon energy of 3.8 eV. This lower energy cutoff of the peak is likely due to the surface plasmon resonance at the Ag-vacuum interface ($\text{Re}(\varepsilon_m) = -1$). There is ample evidence in the literature suggesting that coupling between radiative fields and surface plasmons can occur on evaporated Ag films via grain boundary scattering. The peak we observe from Ag at ~3.7 eV may therefore result from luminescence via combined volume and surface plasmon emission. To our knowledge, such a photo-induced plasmon emission from a vacuum-metal interface has never been reported.

Whittle and Burstein have suggested that this peak results from electron-hole recombination between two conduction bands, namely 7-6L. However, photo-absorption from band 6 to band 7 is relatively weak in Ag. An examination of the calculated band structures for Ag further shows that electrons photo-excited into the upper conduction band should relax to a minimum at L, after which direct recombination would yield a peak near 4.3 rather than 3.7 eV.

3. Effects of Roughness on the Surface Local Fields.

From SERS and surface enhanced SHG studies, it is known that an important effect of surface roughness is the enhancement of the incoming and outgoing fields via local plasmon resonances. For the smooth surfaces, the Fresnel factors $L(\omega_1)$ and $L(\omega_2)$ were used to
account for the changes in the incoming and outgoing fields after
crossing the metal surface. These factors may be thought of as
macroscopic local field correction factors, which can also be derived
for a rough surface. A simple model can be used to approximate a
rough surface, and has been successfully applied to the analysis of
surface enhanced Raman scattering, absorption, and SHG results. The
rough surface is assumed to be a random collection of non-
interacting hemi-spheroids of dielectric constant \( \varepsilon_m \), sitting
perpendicularly on an infinitely conducting plane. The local field
factors for each hemi-spheroid, \( L_{\text{SPH}} \), will be a function of \( \varepsilon_m \), their
height, \( a \), and radius \( b \). From Ref. 28, we have for the local field
factor within the spheroid,

\[
(12) \quad L_{\text{SPH}}(\omega) = A^{-1}[\varepsilon_m(\omega) - 1 + A^{-1}[1 + i4\pi^2V(1-\varepsilon_m(\omega))/3\lambda^3]]^{-1}
\]

where the depolarization factor \( A = 1 - \xi Q_1'(\xi)/Q_1(\xi) \), \( \xi = [1 - (b/a)^2]^{1/2} \),
\( Q_1(\xi) = (\xi/2) \ln[(\xi + 1)/(\xi - 1)] - 1 \), \( Q_1'(\xi) = dQ_1(\xi)/d\xi \), \( \lambda \) is the
optical wavelength, and \( V = 4\pi ab^2/3 \) is the spheroid volume. The
emitted single-photon luminescence power from the volume of the hemi-
spheroid is then

\[
(13) \quad P_{1\text{SPH}}(\omega_2, a/b, V) = \beta_1 \frac{4}{\lambda^2} |\vec{E}_0|^2 V[L^2(\omega_1) L^2(\omega_2)]_{\text{SPH}}
\]

where \( \beta_1 \) is a proportional constant which includes the intrinsic
luminescence spectrum, and \( \vec{E}_0 \) is the incident electric field. The
effects of spheroid shape on the dispersion of \( P_1 \) may be seen in a plot
of \( P_1/\beta_1 \) versus \( h\omega_2 \) and \( a/b \). Figure 11 shows such a plot for Cu
spheroids with $\hbar \omega_1 = 3.50$ eV. We see from the figure that each emission energy is resonantly enhanced within a specifically shaped spheroid. At progressively lower emission energies, the resonance shifts to more prolate spheroids, where the so-called lightening rod effect increases the local field enhancement\(^{20}\). At emission energies above the interband absorption edge, the plasmon resonance is significantly damped (near 2 eV for Cu), resulting in a sharp drop in $P_1$.

We compare the luminescence from the rough surface to that from a smooth surface. The one-photon induced luminescence power emitted from the bulk of a smooth metal can be rewritten from Eq. (6) as

\[(14) \quad P_{1PLANE}(\omega_1, \omega_2) = P_{0} \left| E_0 \right|^2 A_0 \omega_2 \left| L_{1}^{(\omega_1)} L_{2}^{(\omega_2)} \right|\]

in which $A$ is the illuminated area. Assuming that the smooth and rough surfaces differ only in their $L$ factors, the one-photon luminescence enhancement from a single type of spheroids will be $\eta_1 = N(a/b, V) P_{1SPH}/P_{1PLANE}$, where $N(a/b, V)$ is the number of spheroids of volume $V$ and aspect ratio $a/b$ within a specified interval $\pm \Delta V$ and $\pm \Delta (a/b)$. To obtain the total luminescence enhancement, we sum $\eta_1$ over a distribution of $a/b$ and $V$ which simulates our rough surfaces. From Eqs. (13) and (14) the total enhancement becomes

\[(15) \quad \eta_1(\omega_1, \omega_2) = \sum_{a/b, V} \left( \frac{N(a/b, V)}{A} \right)^2 \frac{V}{z_0} \frac{L_{2}^{(\omega_1)} L_{2}^{(\omega_2)}}{L_{1}^{(\omega_1)} L_{2}^{(\omega_2)}} \right)\]
We make the approximation that all shapes are equally probable so that the factor N/A in Eq. (15) can be taken out of the sum. The factor N/A represents an effective shape density, and may be used to characterize the rough samples. It may be determined by comparing the calculated sum \( \eta_{1T}/(N/A) \) with the luminescence enhancement, defined as the ratio of the single-photon luminescence from the rough samples to that from the smooth.

The effects of local field enhancement is expected to be more pronounced for the multi-photon induced luminescence, because of the higher power dependence in the incident field. The largest fields on the rough samples will be at the surface of the metal protrusions, being roughly \( \varepsilon_m/2 \) times the fields in the metal bulk. If we consider for example, the two-photon induced luminescence from the surface atoms, over a thickness t on a metal spheroid, and compare it to that from the spheroid volume, we have

\[
P_{2\text{SURF}}/P_{2\text{VOL}} = \frac{[L^4_{\text{Sph}}(\omega_1)L^2_{\text{Sph}}(\omega_2)ab]}{[L^4_{\text{Sph}}(\omega_1)L^2_{\text{Sph}}(\omega_2)ab]}_{\text{VOL}} = 2^{6}\varepsilon_m(\omega_1)\varepsilon_m(\omega_2)t/b.
\]

For \( \hbar\omega_1 = 1.17 \text{ eV} \), \( \hbar\omega_2 = 2 \text{ eV} \), and \( t/b = .05 \), \( P_{2\text{SURF}}/P_{2\text{VOL}} = 300 \) for Au and Cu, and \( 1.4 \times 10^3 \) for Ag. Thus, although the volume contains more atoms, the local field enhancement is sufficient to make the contribution from the surface atoms dominate. A similar estimate for one photon-induced luminescence yields \( P_{1\text{SURF}}/P_{1\text{VOL}} = 0.2, 0.3, 1.6 \) for Au, Cu, and Ag, respectively \( (\hbar\omega_1 = 2.34 \text{ eV}, \hbar\omega_2 = 2.0 \text{ eV}) \), indicating that the surface contribution is less important.
The complete expression for the two-photon excited luminescence power from a single hemi-spheroid comes after integrating the fields over its surface:

\[
P_2 = \beta_2 \left| E_0 \right|^4 b^2 t \left( L_{\text{SPH}}(\omega_1) \right) L_{\text{SPH}}(\omega_2)
\]

where \( \beta_2 \) incorporates the intrinsic luminescence spectrum, and \( L_{\text{SPH}}(\omega) = \varepsilon_m L_{\text{SPH}}(\omega) \). The geometric factor \( f(a/b) \) is

\[
f(a/b) = \xi^5 \left( \frac{c\omega}{1.17 \text{ eV}} \right) \cos^{-1}\left( \frac{b}{a} \right) + \left( \frac{a}{b} \right)^3 \left[ \frac{10}{3} - \frac{1}{2} \xi^2 - \frac{5\xi}{2} \right]
\]

\[
- \frac{(b/a)^2}{3} \quad (a \gg b).
\]

The effects of the spheroid shape on the dispersion of \( P_2 \) may be seen in the plot of \( P_2/\beta_2 \) in Fig. 12 for Cu, using \( h\omega_1 = 1.17 \text{ eV} \). Since \( P_2 \) is dependent on \( L_{\text{SPH}}(\omega_1) \), the luminescence predominantly emanates from spheroids resonant at \( \omega_1 \), here at \( a/b = 10.0 \). The plasmon resonance at \( \omega_1 \) will significantly modify the intrinsic multi-photon luminescence spectrum, causing the intensity to rise near \( \omega_1 \), and drop above the interband absorption edge (\( \approx 2 \text{ eV for Cu} \)) where the plasmon resonance is damped.

We sum \( P_2 \) over all values of \( a/b \) and \( V \), as was done for the single-photon excitation. We designate the total two-photon induced luminescence power as

\[
P_{2T} = \sum_{a/b, V} N(a/b, V) P_2(a/b, V).
\]
In addition, we obtain for the two-photon luminescence enhancement,

\[ \eta_{2T} = \sum \pi 2^7(N/A)f(a/b)b^2[L'^4(\omega)L'^2(\omega)]_{\text{SPH}}/[L'^4(\omega)L'^2(\omega)]_{\text{PLANE}} \]

where\(^{28}\)

\[ L'_{\text{PLANE}}(\omega) = 2 \varepsilon_m^{1/2}(\omega)\cos\theta/(\varepsilon_m^{1/2}(\omega)\cos\theta + \cos\theta_m) \]

4. Comparisons with the Luminescence from the Rough Surfaces

In this section, the local field calculations of section 3 are compared with the measured one-photon luminescence enhancement, and with the multi-photon luminescence spectra of the rough surfaces of noble metals.

(a) Single-Photon Excitation

Copper

The measured surface enhancement of the luminescence spectrum, which is the ratio of the one-photon excited spectra from the rough and smooth samples, is compared with the predictions of Eq. (15) for Cu in Figs. 13a and 13b. For the excitations of 2.34 and 3.50 eV, we deduce a value for \(N/A = 0.2/\mu m^2\), using the optimum spheroid volume in the calculation, and \(\Delta(a/b) = 1\). From electron photomicrographs of our rough surfaces, this value for \(N/A\) is quite reasonable. The dispersion of the enhancement is in good agreement with the predictions of the spheroid model of the rough surface. Little or no enhancement is predicted for \(\hbar\omega > 2.2\) eV, due to the damping of the localized plasmon
resonances. Below this energy, the rise in $\eta_{1T}$ is due to a shift of the resonances to more prolate structures which show stronger enhancement due to the lightning rod effect.

A similar dispersion in the enhancement is expected for the excitation at 4.67 eV (Fig. 14a). However, because an experimental spectrum from the smooth surface is not available, we cannot make a comparison between the theoretical and experimental enhancements. We see from Fig. 14a that the local field enhancement should only affect the luminescence spectrum below 2.2 eV. The spectrum from the rough surface (Fig. 2c) shows peaks at 2 eV, 2.4 eV, and 3 eV, in addition to a rise in intensity near the excitation. With the exception of the 2.4 eV peak, the agreement with the peak positions from the analysis for the smooth surface (Fig. 8c) is satisfactory. The origin of the 2.4 eV peak is unknown.

Gold

The measured and calculated single-photon luminescence enhancements for Au are compared in Figs. 13c and 13d. We deduce a value for $N/A$ from the comparison, for both the 2.34 and 3.50 eV excitations, which is approximately one fourth the value obtained for Cu. This discrepancy is in spite of the fact that the same roughened substrate was used for both metals, implying similar morphologies, and that the calculated resonant values for $a/b$ were also approximately the same. Because of the crudity of the rough surface model, however, close agreement for the absolute value of $N/A$ is not expected. The dispersion of the luminescence enhancement is in reasonable agreement with the local field calculation. The predicted leveling off above 2.2 eV results from the damping of the plasmon resonances. Essentially the
same dispersion is predicted for the surface enhancement with the 4.67 eV excitation, but is different from what we observed (Fig. 14b). The order of magnitude decrease in the rise in the luminescence near the excitation can be modeled by a decrease in $\delta_e$ and $\delta_h$ in the electron and hole distributions in Eqs. (4) and (5). This implies a more rapid energy decay of the carriers, perhaps induced by more frequent collisions with the rough surface. A decrease in these exponential widths, however, does not explain the suppression of the luminescence peak near 3.2 eV. It is unknown why this peak, assigned to the 6-4L and 6-3X transitions, is suppressed by roughness.

**Silver**

For $\hbar \omega_1 = 4.67$ eV, Eq. (15) predicts a single-photon luminescence enhancement for Ag which rises monotonically with decreasing emission energy (Fig. 14c). However, the actual ratio of the spectra from the rough and smooth samples of Ag shows an enhancement which levels off below 3.3 eV. It seems that surface roughness on Ag is more effective in enhancing and extending the surface plasmon emission to lower energies via increased momentum scattering than enhancing luminescence via local plasmon resonances. This effect has already been observed for Ag in surface plasmon emission induced by electron bombardment. The low energy cutoff we observed in the rough sample spectrum is then related to the limit in scattering momentum available from our roughened surface.

**Multiple-Photon Excitation**

Unlike the single-photon induced luminescence, multi-photon luminescence could not be detected from the smooth surfaces with our detection system. This sets a lower limit for the enhancement of
approximately $10^2$ for all the metals. On the other hand, we may estimate the two-photon luminescence enhancement from Eq. (19). Using $\hbar \omega_1 = 1.17$ eV, and the values already deduced for N/A, we find $\eta_{2T} = 10^8$ for Ag, and $\eta_{2T} = 10^6$ for Cu and Au. Thus, the multi-photon induced luminescence is not likely to be detected without the local field enhancement. The effect of the rough surface on the dispersion of the multi-photon luminescence may be estimated from Eqs. (16) - (18). The results of the calculation are compared with the measured spectra in Figs. 15 and 16.

The plot of the calculated spectrum $P_{2T}(\omega_2)$ from Eq. (18) for Cu is shown as a solid curve in Fig. 15a. The rise in intensity with decreasing emission energy results from the resonance at $\omega_1$ discussed in section 3. The leveling off of $P_{2T}$ near the interband absorption edge is due to the damping of the plasmon oscillations. The same behavior is observed in the measured spectrum shown as a dashed curve in the same figure. In a similar calculation of the two-photon luminescence originating from the bulk of the spheroids, only a very gradual rise in intensity with decreasing $\omega_2$ is predicted. This is consistent with an earlier conclusion in section 3 that the enhanced multi-photon luminescence predominately emanates from the surface atoms of the rough structures. The one-photon luminescence, on the other hand, is more likely to originate from the bulk. This could explain the lack of a luminescence peak in the two-photon excited spectrum from Cu, since the dispersion of the surface enhancement strongly dominates and since the spectra from the surface and bulk atoms may be very different. It has also been suggested that the peak is missing because of two-photon selection rules$^{17}$. However, we do not expect the band parities to be
so well defined as to forbid direct two-photon absorption at transitions allowed for one-photon excitation.

A plot of the calculated $P_{2T}(\omega_2)$ for Au, using $\hbar\omega_1 = 1.17$ eV, is shown as a solid curve in Fig. 15b. As with Cu, the local field dispersion for the surface atoms of the spheroid corresponds with the observed luminescence spectrum (dashed curve). The same calculation for emission from the spheroid bulk gives a much more gradual rise. We conclude, as with Cu, that the two-photon induced luminescence emanates predominately from the surface atoms of the roughness protrusions.

The solid curve in Fig. 16a is a plot of the calculated $P_{2T}(\omega_2)$ for Ag, for the $\hbar\omega_1 = 2.34$ eV. As with Cu and Au, the observed rise in intensity with decreasing emission energy is predicted by the local field model, assuming emission is predominantly from the surface atoms. The dip in $P_{2T}(\omega_2)$ near the volume plasmon energy of 3.8 eV results from a decrease in the fields at the surface as $\text{Re}(\varepsilon_m) = 0$. This reduction in the local field enhancement may be the reason why no peak exists at this energy in the measured two-photon luminescence spectrum (Fig. 5d).

For $\hbar\omega_1 = 1.17$ eV, the observed multi-photon excited spectrum from rough Ag extends out to the three-photon energy (Fig. 5c). Assuming that the luminescence was induced by three-photon excitation, we computed the emitted luminescence power, as in section 3, from the surface of a distribution of spheroids. The result, designated as $P_{3T}(\omega_2)$, is plotted as a solid curve in Fig. 16b. The rise in the luminescence with decreasing emission energy is again predicted. We note that because the dispersion of this curve results from the
 localized plasmon resonance at $\omega_1$, we obtain qualitatively the same result as for $P_{2\gamma}(\omega_2)$.

We have estimated that the enhancement of the three-photon luminescence exceeds that of the two-photon luminescence by $\sim 10^5$ for Ag, but only $\sim 10^4$ for Au and Cu, for $h\omega_1 = 1.17$ eV. This may help to explain why the luminescence is very weak at energies above $2\omega_1$ for Au and Cu.

E. Conclusions

The luminescence spectra induced by single-photon absorption from the smooth noble metals, display pronounced structures. A detailed calculation qualitatively reproducing most of the observed structures suggests that the peaks in Cu and Au result from direct radiative recombination of electrons below the fermi level with holes in the d-bands around the X and L symmetry points. The decrease in the luminescence on the low energy side of the peaks results from a diminishing hole population in the d-bands, and a decrease in the transmission coefficient of the outgoing light. The rise in the luminescence intensity near the excitation energy is believed to originate from radiative recombination of electrons and holes near their initially excited energies. In contrast to Cu and Au, the single-photon excited luminescence spectrum from Ag appears to be dominated by radiative emission of the surface and volume plasmons.

Many of the effects of roughness on the single-photon excited spectra may be attributed to the effects of localized plasmon resonances. In particular, the enhancement of the luminescence by such resonances begins only at emission energies below the interband
absorption edge of the metal, where the plasmon oscillations are less damped. However, the observed suppression of certain spectral features when the surfaces are roughened cannot be explained by a simple local field theory for the rough surface. We suggest that the roughness may somehow quench the luminescence, for example by increasing the non-radiative recombination rate, perhaps via collisions with the rough surface.

For the multi-photon excited spectra from the rough samples, we observe a monotonic rise in the luminescence intensity with decreasing emission energy, and an absence of the peaks which characterize the single-photon spectra. An analysis of the effects of local-field enhancement shows that the multi-photon luminescence is emitted predominantly from the surface atoms of protrusions on the rough surface with localized plasmon resonances at $\omega_1$. The rise in the luminescence intensity towards lower energies is attributed to this resonance. The peak near 2 eV in the one-photon luminescence spectrum from Cu is believed to be missing from the two-photon spectrum, because of an intrinsic difference in the luminescence of the surface atoms from that of the bulk. For Ag, the peak at 3.7 eV is believed to be missing from the two-photon spectrum because of a drop in the local field enhancement at this energy, at the surface of the protrusions, as $\text{Re}(\varepsilon_m) = 0$.

As we see, the uncertainties in the population distribution of the electrons and holes, and the various local field effects, complicate the interpretation of the spectra. This limits the use of photoluminescence as a band structure probe. One could, however, obtain far more complete band structure information if the excitation frequency $\omega_1$ could be scanned continuously to yield a series of
luminescence spectra. Despite the limitations of the present photoluminescence technique, it may still prove useful in complementing the data from other techniques, such as photo-absorption and photo-emission, for studying the electronic properties of metals.
References


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Band parameters used in the calculation derived from Ref. 22. Masses are in units of the electron mass. The energy Δ is in eV.
Figure Captions

Fig. 1: Diagram of the experimental apparatus. Noble metal films were evaporated from source (S) onto smooth and roughened substrates in a high vacuum chamber. The excitation beam was p-polarized by prism (P) and passed through a spectral filter (F). The luminescence was focused onto a monochromator (M) and detected with a photomultiplier (D).

Fig. 2: Luminescence spectra from smooth (-----) and rough (-----) samples of copper induced by incident energies of a) 2.34 eV, b) 3.50 eV, and c) 4.67 eV.

Fig. 3: Luminescence spectra from smooth (-----) and rough (-----) samples of gold induced by incident energies of a) 2.34 eV, b) 3.50 eV, and c) 4.67 eV.

Fig. 4: Luminescence spectra from smooth (-----) and rough (-----) samples of silver induced by an incident energy of 4.67 eV.

Fig. 5: Multi-photon induced luminescence spectra from rough samples of Cu, Au, and Ag (-----). Dashed curves show corresponding one-photon induced spectra from smooth samples, taken from Figs. 2 and 4.

Fig. 6: (a) Partial band structure of Au at the L symmetry point showing excitation and emission paths. The band energies are relative to the fermi level. (b) Electron and hole distribution functions used in the calculation. E₀ is the electron energy after excitation by the incident photons.

Fig. 7: The effects of the Fresnel coefficients and the absorption of the outgoing light on the one-photon induced luminescence from
the smooth surface are seen in a plot of $F = \omega_2 |L(\omega_1)|^2$ $|L(\omega_2)|^2 z_0 (\omega_1, \omega_2)$ versus $\omega_2$, for $\hbar \omega_1 = 3.50$ eV.

Fig. 8: Calculated one-photon induced luminescence spectra for smooth Cu for excitation energies of a) 2.34 eV, b) 3.50 eV and c) 4.67 eV. (---) 6-5L transitions, (----) 6-4L transitions, (--.--.) 6-3X transitions.

Fig. 9: Calculated one-photon induced luminescence spectra for smooth Au for excitation energies of a) 2.34 eV, b) 3.50 eV and c) 4.67 eV. (---) 6-5 transitions, (----) 6-4 transitions, (--.--.) 6-3 transitions.

Fig. 10: Calculated one-photon induced luminescence spectrum for smooth Ag for the excitation energy of 4.67 eV. Vertical arrows indicate the position of two peaks resulting from the 6-5L transition (---), and the 6-4L transition (----).

Fig. 11: Calculated single-photon induced luminescence power, $P_{1SPH}/\beta_1$ from Cu hemi-spheroids of height $a$ and radius $b$, versus $a/b$ and the emission energy, $\hbar \omega_2$, with $\hbar \omega_1 = 3.50$ eV.

Fig. 12: Calculated single-photon induced luminescence power, $P_2/\beta_2$ from Cu hemi-spheroids of height $a$ and radius $b$, versus $a/b$ and the emission energy, $\hbar \omega_2$, with $\hbar \omega_1 = 1.17$ eV.

Fig. 13: Ratio of the measured one-photon induced luminescence from the rough samples to that from the smooth (dots), compared with the prediction (solid curves).

Fig. 14: Ratio of the measured one-photon induced luminescence from the rough samples to that from the smooth (dots), compared with the prediction (solid curves), for $\hbar \omega_1 = 4.67$ eV. The ratio could not be obtained for Cu.
Fig. 15: Solid curves indicate the calculated two-photon induced luminescence power from a distribution of spheroids, $P_{2T}$, versus the emission energy $\hbar \omega_2$, using $\hbar \omega_1 = 1.17$ eV. The dashed curves are the measured spectra from Fig. 5.

Fig. 16: Solid curves indicate a) the calculated two-photon induced luminescence power from a distribution of spheroids, $P_{2T}$, versus the emission energy, $\hbar \omega_2$, for Ag with $\hbar \omega_1 = 2.34$ eV, and b) the three-photon induced luminescence power, $P_{3T}$, for $\hbar \omega_1 = 1.17$ eV. The dashed curves are the measured spectra from Fig. 5.
Fig. 1
Fig. 2
Fig. 3
Ag

$\hbar\omega_1 = 4.67 \text{ eV}$

![Graph showing the relationship between $I_L$, the intensity of light, and $\hbar\omega_2$, the energy of the second photon, with a peak at $\hbar\omega_1 = 4.67 \text{ eV}$.](image)

Fig. 4
Fig. 5
Fig. 6
\[ \hbar \omega_1 = 2.34 \text{eV} \]

\[ \hbar \omega_1 = 3.50 \text{eV} \]

\[ \hbar \omega_1 = 4.67 \text{eV} \]

Fig. 8
Fig. 9

\[ \hbar \omega_1 = 2.34 \text{ eV} \]

\[ \hbar \omega_1 = 3.50 \text{ eV} \]

\[ \hbar \omega_1 = 4.67 \text{ eV} \]
Fig. 10
Fig. 11
Fig. 14
Fig. 15

P_{2T}

Cu

(b)

Au

\( \hbar \omega (eV) \)

1.75

2.00

2.25

2.50

Fig. 15
Fig. 16
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