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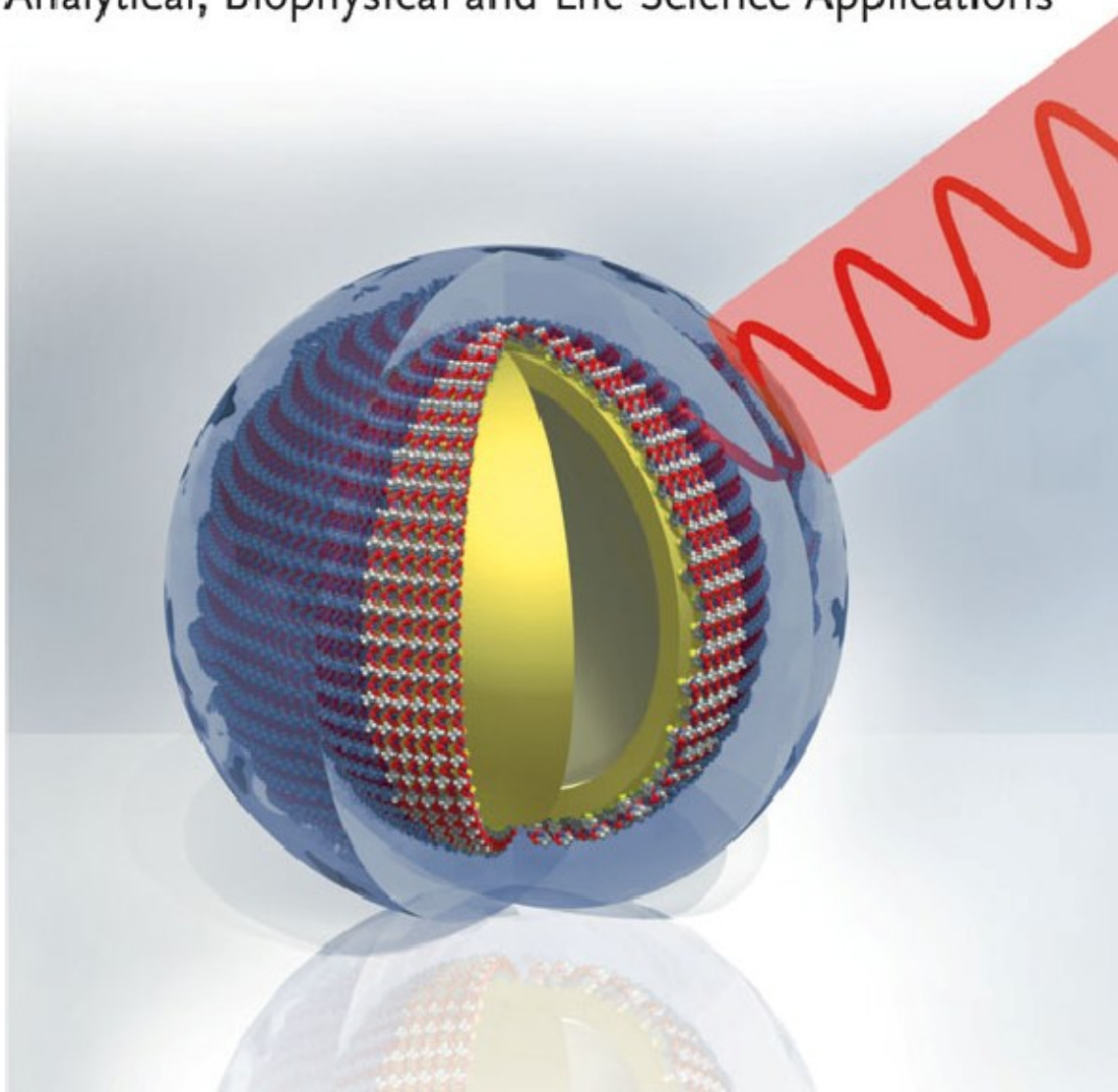
Surface Enhanced Raman Spectroscopy

Analytical, Biophysical and Life Science Applications



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Foreword

More than 80 years since the discovery of the Raman effect have passed and Raman spectroscopy has become one of the most important methods within the various methods of analysis and structural determinations. Certainly, the discovery of the laser in 1960 has opened up new horizons for Raman spectroscopy and brought several new useful techniques. One of the most interesting and significant findings in this field is undoubtedly surface-enhanced Raman scattering (SERS) which was discovered in 1977. Within this phenomenon, molecules adsorbed onto metal surfaces under certain conditions exhibit an anomalously large interaction cross section for the Raman effect. It might be thought that a subject originated more than three decades ago would be virtually exhausted by now, but nothing could be farther from truth. The recent developments in SERS have led to large increases in the sensitivity of SERS measurements and have enabled new phenomena to be observed and applied. SERS measurements are expected to become increasingly important in chemistry, biochemistry, and biophysics.

In the 14 chapters of this book, an authoritative, up-to-date account of the principles and fundamentals of SERS is given including many examples for its applications. The book includes the basic theory for SERS; summarizes the various SERS substrates; discusses quantitative SERS methods with emphasis on reproducibility, stability and sensitivity up to single molecule detection; and describes SERS microscopy, electrochemical SERS, surface enhanced resonance Raman scattering (SERRS), and surface-enhanced hyper Raman scattering (SEHRS), as well as surface- and tip-enhanced coherent anti-Stokes Raman scattering (SE-CARS, TE-CARS). Applications of SERS include the detection of organic pollutants and pharmaceuticals; studies of electron transfer of proteins at membrane models; investigations of microfluidics, quantitative DNA analysis, biomedical applications by means of SERS microscopy, SERS as an intracellular probe; and coupling of SERS with various separation methods (e.g. liquid or gas chromatography).

The abundant references provide ready access to the original research literature. As the field of SERS has sufficiently matured during the past decades, the danger of rapid obsolescence for this book is less. The subject matter, however, still offers plenty of opportunity for further exploration and exploitation. In my opinion this book, which clearly expresses the current excitement in this extremely active

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research area, will make a substantial contribution to the further growth of an increasingly important subfield of vibrational spectroscopy.

Professor Schlücker, editor of this volume, is one of the leading researchers working currently in the SERS field. As chemist at the University of Würzburg, Germany, and the National Institutes of Health, Bethesda, USA, and now as physicist at the University of Osnabrück, Germany, he has played a major role in introducing a few important new experimental techniques of SERS (e.g. the direct and label-free SERS detection of solid-phase bound compounds; immuno-SERS microscopy with nanoparticle probes). He is well qualified to present this book to the scientific community.

Wolfgang Kiefer
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Contents

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Preface

The field of surface-enhanced Raman scattering (SERS) is currently undergoing a very dynamic development and many novel directions are rapidly emerging. The aim of this book is to provide an overview of current exciting topics in SERS, focusing on analytical, biophysical and life science applications. International leaders in their respective research areas have contributed to this volume. Their original scientific background and training is quite diverse, ranging from bioorganic chemistry to physical chemistry and solid state physics – in my opinion, this directly reflects the highly multidisciplinary nature of SERS applications, a prerequisite for original and pioneering research between the boundaries of traditionally distinct disciplines. The selection of the scientific topics covered in the 14 chapters is naturally subjective and I must certainly apologize to those who have not received the opportunity to contribute to this edition.

This monograph is intended to be useful for both the newcomer with no or little background in Raman/SERS spectroscopy as well as for the experts in the field who are interested in achieving a quick overview as well as in-depth information on specific subjects.

The first part of this book (Chapters 1–3) lays the foundation for the entire book by providing important theoretical and practical background. Topics are the basic electromagnetic theory of SERS, various aspects of metal colloids as plasmonic nanostructures and practical considerations for quantitative SERS. The second part (Chapters 4–14) covers various analytical, biophysical and life science applications of SERS. Chapters 4 through 8 describe analytical applications of SERS, including single-molecule and trace detection, sensors for detecting organic pollutants based on host–guest systems as well as the detection of pharmaceuticals. Two chapters describe the promising combination of SERS with other analytical techniques such as separation methods and microfluidic platforms for lab-on-a chip detection. Chapters 9 and 10 cover spectroelectrochemistry as a classical and important topic in SERS. After an introduction into the theory and experimental setups for combining SERS with electrochemistry, applications to several biological molecules are summarized. Biophysical applications of spectroelectrochemistry with SERS are focused on the electron transfer in membrane models, in particular cytochrome c on coated electrodes. Chapters 11 through 14 report on recent life science applications of SERS. Quantitative DNA analysis with immense multiplexing and ultrasensitive

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detection capabilities is demonstrated by surface-enhanced resonance Raman scattering (SERRS). Selective protein localization in cells and tissue specimens via SERS microscopy requires the design and fabrication of functionalized metal colloids for labeling target-specific ligands such as antibodies. Information on intracellular biochemical composition and physiological conditions is accessible via one- or two-photon excited SERS in a label-free approach in conjunction with microscopy. Surface- and tip-enhanced coherent anti-Stokes Raman scattering (CARS) as advanced microspectroscopic techniques with sub-diffraction limited spatial resolution together with first applications to DNA are discussed in the last chapter.

I would like to thank all authors for their hard work and commitment to contribute their chapters. This international and multidisciplinary book project would not have been possible without their dedication. The support from Lesley Belfit (Wiley-VCH) and Manfred Köhl (now Thieme) is greatly appreciated. Thanks to Wolfgang Kiefer for his foreword – many of his former students including the editor have contributed to this book. Finally, I would like to thank my wife Uta-Maria, our sons Jan and Henrik, my parents Marianne and Eberhard as well as my group members for their continuous support.

Osnabrück, August 2010 *Sebastian Schlücker*

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1
Basic Electromagnetic Theory of SERS

Pablo G. Etchegoin and Eric C. Le Ru

1.1
Introduction

This chapter is aimed at introducing the newcomer to the field of surface-enhanced Raman spectroscopy (SERS), and is not intended to supplant the already available exhaustive literature in the field either in the form of review articles [1, 2] or books [3, 4]. As a technique, SERS is relatively exposed to the dangers of specialization due to its (intrinsic) multidisciplinary nature. The technique is becoming widespread and is finding new and exciting horizons in analytical chemistry [5–7], biology and biotechnology [8–12], forensic science [13, 14] and in the study of artistic objects [15–17]. While this is in many ways an advantage, it is also a handicap in the sense that scientists approaching the technique from a more 'biological' or 'applied' aspect might not have the appropriate background (or predisposition) to venture into the depths of electromagnetic theory and to understand the basic concepts of the theory of plasmon resonances in metallic nanostructures. This could be particularly true for students in the biotechnology field, who might find it desirable to have access to the elementary concepts (with a bare minimum of mathematics) but with enough insight to understand what they are actually doing in the lab. We believe that the success and use of the technique – in an environment which is by nature multidisciplinary – will be more effective if accessible presentations of the basic principles aimed at broader audiences are available at all times (and reviewed over prudent periods of time). This chapter (hopefully) fulfils part of that requirement.

This chapter is organized as follows: in Section 1.2, we introduce the basic principles of plasmon resonances and their associated field enhancements. Section 1.3, on the other hand, looks at the field enhancement distribution and localization produced by these plasmon resonances, while Sections 1.4 and 1.5 study the origin of the enhancement factor (EF) and its characteristic magnitude. Finally, Section 1.6 presents some conclusions and summarizes several main concepts.

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1.2
Plasmon Resonances and Field Enhancements

1.2.1
Optical Properties of Simple Metals

None of the modern optical techniques such as surface-enhanced fluorescence (SEF) [18–20], surface plasmon resonance spectroscopy [21–23] or SERS itself [1, 4] would exist without the particular optical properties of *coinage metals* (with silver (Ag) and gold (Au) standing out as the most useful ones). The first obvious question is then what is it that makes the optical properties of metals so interesting? Hence, it is worth spending a few paragraphs on the topic of the optical properties of *bulk metals* such as Ag and Au to understand why they are so interesting, and why we use them in the aforementioned techniques.

The optical properties of bulk materials are characterized by their *dielectric function* $\epsilon(\omega)$. Most students from scientific disciplines would have come across the related *index of refraction* $n(\omega)$, which is linked to the former by $n(\omega) = \sqrt{\epsilon(\omega)}$. Both $n(\omega)$ and $\epsilon(\omega)$ depend on the frequency (ω) of the light (with $\omega = 2\pi c/\lambda$, where c is the speed of light and λ the wavelength), due to the fact that most materials respond differently to electromagnetic waves at different frequencies (wavelengths). The dielectric function can therefore be considered indistinctly as either a function of ω ($\epsilon(\omega)$) or λ ($\epsilon(\lambda)$). We shall use one or the other according to convenience. In the most elementary treatments of the optics of material objects (lenses, prisms, etc.) [24], both the dielectric function and the index of refraction are *positive real numbers* (more precisely $\epsilon,\ n \geq 1$). More often than not, however, the dielectric function of materials at a given wavelength will be a *complex* (rather than real) number, and the material will not be transparent. In fact, this is more the rule than the exception, since the list of transparent materials constitutes a really small fraction of the materials we see around us. Metals are amongst the list of materials in which $\epsilon(\omega)$ is complex. The ultimate reason for the optical properties of materials is their *electronic structure*, and this is a canonical topic in solid-state theory [25, 26]. We shall not dwell too much on the details of the connection between the dielectric function of metals and their electronic structure (see Appendix D of Ref. [4] for a slightly more in-depth discussion), but rather take the properties of $\epsilon(\omega)$ of metals as given.

Figure 1.1 shows the dielectric functions of Ag and Au with their real and imaginary parts spanning from the near-UV (∼300 nm) to the near-IR (NIR) range (∼900 nm). These are analytical representations that interpolate rather well a collection of experimental results for $\epsilon(\lambda)$ obtained with different techniques. The accuracy and limitations of these fits are discussed in more detail in Refs. [4, 27]; here, we shall take these results as the starting point of our discussion on why the optical properties of metals are interesting. The main characteristics of the real and imaginary parts of the bulk $\epsilon(\lambda)$ for both metals can be summarized as follows:

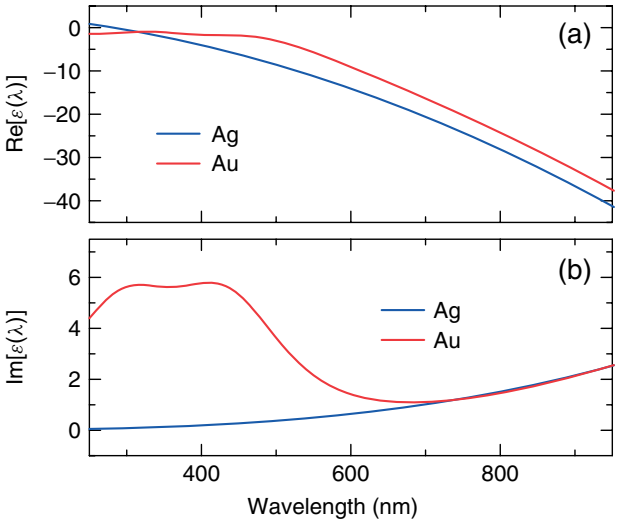

Figure 1.1 The real (a) and imaginary (b) parts of $\epsilon(\lambda)$ for the two most useful metals in SERS; that is, Ag and Au. Note the different vertical scales in (a) and (b); the imaginary parts of $\epsilon(\lambda)$ span over a smaller range and they are always *positive*. The real parts are *negative* across the visible range (∼400–750 nm) and show the overall (expected) characteristic of the simplest description of the dielectric function of metals (the lossless Drude model [25]), which predicts a $\sim -\lambda^2$ dependence for real part of $\epsilon(\lambda)$ at long wavelengths. See the text and Ref. [4] for further details.

- The real part of the dielectric function of both metals, for most of the visible range, is both *large* (in magnitude) and *negative*. *Later, this will turn out to be one of the most important properties of these metals* as far as their optical properties are concerned, and one of the main reasons for their usefulness as plasmonic materials. Furthermore, ignoring the imaginary parts of $\epsilon(\lambda)$ momentarily, we can claim that the real parts follow at long wavelengths one of the simplest models for the dielectric function of a (lossless) metal, which is the *lossless Drude model*. The latter predicts a dielectric function of the form [4, 25, 26]:

$$\epsilon = \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2}\right) = \epsilon_\infty \left(1 - \frac{\lambda^2}{\lambda_p^2}\right) \tag{1.1}$$

where $\omega_p = 2\pi c/\lambda_p$ is the so-called *plasma frequency*[1)] of the metal (proportional to the square root of the density of free electrons in it). The first expression on the right-hand side in Equation (1.1) holds if we want to express the dielectric function ϵ as a function of ω, while the last expression holds if ϵ is expressed as a function of $\lambda(= 2\pi c/\omega)$. Figure 1.1a reveals that both Ag and Au have actually very similar electronic densities, since the real parts of their dielectric functions are not too far away from each other. This is the approximate quadratic

1) For both Au and Ag, $\lambda_p = 2\pi c/\omega_p$ is around ∼280 nm; that is, in the UV range.

downturn of the real part of $\epsilon(\lambda)$ seen in Figure 1.1a for longer wavelengths. We can see that, to a good approximation, the simplest lossless Drude model describes already a good fraction of the experimental results for the real parts seen in Figure 1.1a.

- Real bulk metals are *not* lossless, and this is where the imaginary part of $\epsilon(\lambda)$ comes into play. Even though when the $\mathrm{Im}[\epsilon(\lambda)]$ for both metals are smaller than their real counterparts for most of the visible range, their effects are important and – in some cases – crucial. The imaginary part is always related to the *absorption* of the material (a material with $\mathrm{Im}[\epsilon(\lambda)] = 0$ does not absorb light, and has a real index of refraction $n(\lambda) = \sqrt{\mathrm{Re}[\epsilon(\lambda)]}$). It turns out that the imaginary part of $\epsilon(\lambda)$ for Ag can be obtained by a relatively easy generalization of the lossless Drude model (Equation 1.1). For Au, the situation is slightly more complicated; $\epsilon(\lambda)$ has additional contributions (in addition to that from the free electrons) from other electronic transitions in its electronic band structure [27]. This is the reason for the relatively higher absorption of Au (with respect to Ag) for $\lambda \leq 600$ nm, with a 'double hump' structure in the imaginary part ($\sim$400 nm), which comes from the so-called interband electronic transitions. Note, however, that for $\lambda \geq 600$ nm, the imaginary parts of $\epsilon(\lambda)$ for both Ag and Au become completely comparable (Figure 1.1b) and – with their real parts being comparable too in this range – both materials are similar (from the viewpoint of their electromagnetic response). Their surface chemistries are of course different, and one material might be preferred over the other for specific chemical reasons. But, as far as the electromagnetic response is concerned, Au is comparable to Ag in the near- and far-IR range.

1.2.2 Planar Surfaces

Once the complex dielectric function $\epsilon(\lambda)$ is known, all the electromagnetic properties of the material can be calculated in different geometries. The normal reflectance R (in the direction perpendicular to the surface) arises as a natural consequence of matching the boundary conditions of the fields at the interface.[2)] The reflectance is plotted for Ag and Au in Figure 1.2b using the complex dielectric functions shown in Figure 1.1a and b. Silver has a very high reflectivity $\sim$100% across the entire visible range. Gold, on the contrary, has $\sim$50% for $\lambda \leq 600$ nm (from the yellow-green region towards shorter wavelengths in the UV). This is the reason for the 'yellowish/reddish' colour of flat gold when compared to silver. The overall high reflectivity of Ag does not come as a surprise; this is the reason why Ag

2) The standard boundary conditions for all electromagnetic problems require that the components of the electric field *parallel* to the surface (on both sides of the interface) are equal, as well as the *perpendicular* components of the displacement vector $\mathbf{D} = \epsilon(\lambda)\mathbf{E}$. In standard notation [4, 28, 29] for an interface between medium 1 and 2: $E_1^{\parallel} = E_2^{\parallel}$, and $\epsilon_1(\lambda)E_1^{\perp} = \epsilon_2(\lambda)E_2^{\perp}$. The normal reflectance at a planar surface between the two media is given by $R = |(n_2 - n_1)/(n_2 + n_1)|^2$, with $n_1 = \sqrt{\epsilon_1}$ and $n_2 = \sqrt{\epsilon_2}$.

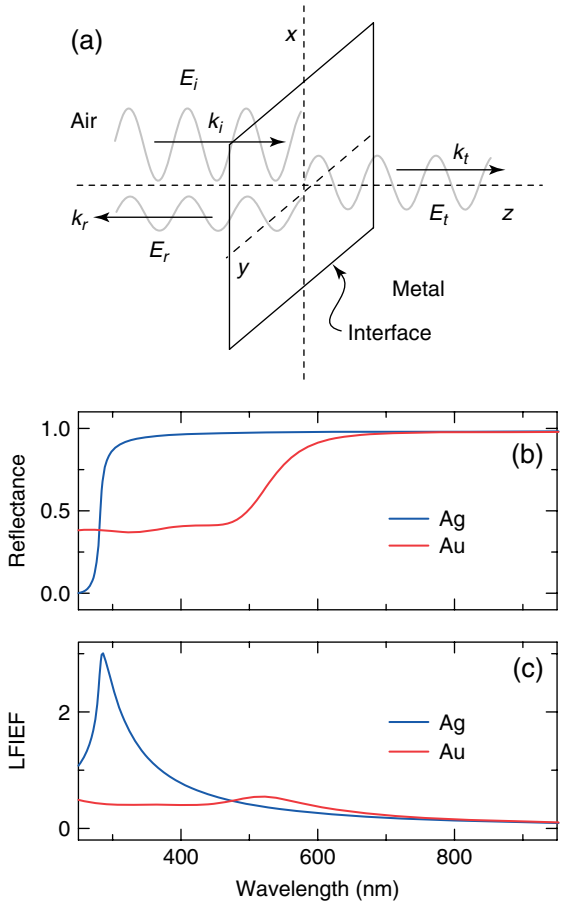

Figure 1.2 (a) An incident electromagnetic wave (with electric field E_i and wavevector k_i) impinges from the left (along z) onto a sharp interface with a (bulk) metal lying in the x–y plane, and transmitted and reflected waves result. The amplitude of the reflected (E_r) and transmitted (E_t) waves result from the matching of boundary conditions for the field at the interface, and depend only on the (complex) index of refraction of the metal ($n = \sqrt{\epsilon(\lambda)}$) [4, 28, 29]. (b) Reflectance at normal incidence for Au and Ag, using the dielectric functions shown in Figure 1.1. Note that Ag has a reflectance close to ∼100% across the entire visible range, while for Au the reflectivity decreases from ∼500 nm towards the UV range. (c) Local field intensity enhancement factor (LFIEF) at the surface of the metal [(x–y) plane] for Au and Ag (at normal incidence). Note that, in general, the LFIEF is <1 across the visible, meaning that the intensity is typically 'quenched' at the (flat) surface of the metal.

is used as a mirror in the visible. Gold mirrors, on the other hand, are preferred for NIR applications where it reflects as much as Ag, but it is more stable with respect to effects caused by long-term exposure to ambient conditions.

Another aspect of interest, while we dwell on the simplest of examples, is the Local Field Intensity Enhancement Factor (LFIEF) at the surface (i.e. by how much

the intensity of the electromagnetic field is changed with respect to the intensity we would have had at the place without the metal). The local field intensity at a specific point is proportional to the square of the electric field amplitude at that point: $|E(r)|^2$.[3] The LFIEF at a specific point is then the normalized value of $|E(r)|^2$ with respect to the intensity of the incoming field at that point: $|E_0(r)|^2$. Explicitly,

$$\mathrm{LFIEF}(r) = |E(r)|^2/|E_0(r)|^2 \tag{1.2}$$

The LFIEF is, therefore, an adimensional magnitude expressing the (normalized) change in local intensity at a specific point produced by the presence of objects (which perturb the electric field of the light). Any optical technique that depends on the intensity of the light at a specific point will hence be linked to the LFIEF and, in general, depending on whether the LFIEF is >1 or <1 the optical process involved will be enhanced or quenched. The LFIEF will also depend on ω (or, equivalently, on λ), simply because the local field at a specific point depends on ω. We can formally write

$$\mathrm{LFIEF}(r,\omega) = |E(r,\omega)|^2/|E_0(r,\omega)|^2 \tag{1.3}$$

In general, however, we will simplify the notation and emphasize only the most important dependence for the explanation of a specific aspect. We will refer, for example, to the LFIEF at a well-specified point in a geometry and at given frequency ω simply as LFIEF(ω).

The LFIEF at a flat surface for normal incidence (which results from the interference between E_i and E_r on the surface, see Figure 1.2) is another aspect of the classical problems in basic electromagnetic theory (and optics) [4, 28, 29], and (like R) is solely determined by ϵ_1 and ϵ_2.

The LFIEF on the surface – for both an interface of Ag and Au with air – are plotted in Figure 1.2c.[4] As can be appreciated, the LFIEF is in general for normal incidence <1 at the surface of a planar interface separating a bulk metal (like Au or Ag) from air; that is, the intensity is 'quenched' at the surface compared to what we would have had in its absence. An ideal (100%-reflective) lossless metal will create a field on the surface, which cancels exactly the incoming one ($(E_i + E_r) = 0$), thus cancelling exactly the transmitted field too ($E_t = 0$) and sending the impinging electromagnetic wave back in the opposite direction from where it came. Therefore, a low LFIEF at the surface (achieved by the condition $E_i \sim -E_r$) is a natural consequence of having a very high reflectivity. In reality, the cancellation is not complete, but it is efficient enough to guarantee a low LFIEF on the surface and a concomitant high reflectance. The LFIEF is only >1 for Ag when $\lambda \leq 400$ nm, but this is the region where it actually stops being a good reflector. Larger (but, nevertheless moderate) LFIEFs may also be obtained at other angles of incidence (different from normal incidence shown here) and it is then also dependent on the incident polarization [4]. The reflection process for an arbitrary angle of incidence

3) We shall avoid vector notations throughout for simplicity.

4) The LFIEF immediately above the flat surface for normal incidence is given by $\mathrm{LFIEF} = \left|\frac{4n_1}{n_1+n_2}\right|^2$ [4, 28, 29], where (as before) $n_1 = \sqrt{\epsilon_1}$ and $n_2 = \sqrt{\epsilon_2}$.