Planar Resonant Structures for Biosensing Applications

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract

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Doctor of Philosophy
Graduate Department of Physics
University of Toronto
2014

This thesis presents theoretical studies of spontaneous Raman scattering and coherent anti-Stokes Raman scattering (CARS) from molecules on resonant multilayer structures. A simple isotropic model is exploited to describe the Raman polarizability of molecules, and a Green function method is used to calculate the scattering fields from molecules. The response of the multilayer structures to incident fields is characterized through a transfer matrix method that allows derivation of semi-analytic expressions for Raman cross sections and CARS powers in terms of Fresnel coefficients of the structures.

The main focus in this thesis is on purely dielectric structures, especially truncated periodic multilayers that support Bloch surface waves (BSW). The dispersion relation of these resonances can be engineered to allow resonant coupling of all incoming and outgoing fields in spontaneous Raman scattering and CARS. As a result, the spontaneous Raman cross section is enhanced up to $10^6$ in particular directions and the CARS power from monolayers is significant for millimeter wide incident beams. I compare the spontaneous Raman and CARS powers from thin layers of molecules on multilayer structures supporting BSWs and show how these ratios scale when the molecules form lipid bilayers. I present experimental realizations of surface enhanced Raman scattering from acetone and sulphur molecules on BSW structures and show that the excitation of BSWs results in observation of Raman lines that are not observable on a bare prism.

I use a Fresnel coefficient pole analysis to develop a systematic strategy for designing
multilayer structures that support long range surface plasmons (LRSPs) and design a periodic multilayer structure that supports a LRSP with propagation length about 2 mm. With a view toward biosensing applications, I derive semi-analytic expressions for a standard surface sensing parameter in arbitrary planar resonant structures and compare the exact and approximate calculations for the designed LRSP structure.
Acknowledgements

I would like to express my sincere thanks to everyone who has contributed to this thesis, in particular, my PhD advisor Prof. John Sipe and supervisory committee, Prof. Henry van Driel, Prof. Sajeev John, Prof. Gilbert Walker, Prof. Mo Mojahedi, and external member Prof. Jayshri Sabarinathan, for their scientific advice and guidance on my PhD research work. It was an honor for me to work with such great scientists and learn from them. I especially would like to thank Prof. Henry van Driel for being so supportive and encouraging and for his many great comments and suggestions on the introductory chapters of this thesis.

Many thanks to Prof. Gilbert Walker for providing unique collaboration opportunities and funding resources through the BiopSys network, and thanks to Xiaoji Xu, Srinivasan Mysore, Marco Liscidini, Stefano Pirotta, Giacomo Dacarro, Maddalena Patrini, Matteo Galli, Giorgio Guizzetti, Daniele Bajoni, and Sudipta Maiti for their collaboration on parts of this thesis.

Thanks to Krystyna Biel, Teresa Baptista, Mandy Koroniak, and Joyce Guest for their supporting efforts.

Thanks to my friends and colleagues, especially Yasaman Soudagar, Ramy El-Ganainy, Parinaz Aleahmad, Marzieh Farhang, Ida Zadeh, Parisa Zarepour, Muhammad Zulfiker Alam, Parisa Khadem, Julien Rioux, Federico Duque Gomez, Sergei Zhukovsky, and Jin Luo Cheng for their friendship, help, and support through my PhD years.

I am deeply grateful to my family, my parents Asya and Vafaee and my sisters Sara, Hajar, and Vida for their love, support, and encouragement throughout my life and in the past few years. They have always reminded me of true values in life and I have been very fortunate to have them.

This thesis would not have been possible without the generous financial support of the Natural Sciences and Engineering Research Council of Canada Strategic Network for Bioplasmonic Systems (BiopSys) and University of Toronto graduate scholarships.
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c speed of light in vacuum
\( \lambda \) wavelength of light in vacuum
\( \omega \) angular frequency
\( \mu \) induced dipole moment
\( \mu_0 \) vacuum permeability
\( \epsilon_0 \) vacuum permittivity
\( \varepsilon_i \) dielectric constant of medium i
\( n_i \) index of refraction of medium i
\( E \) electric field
\( B \) magnetic field
\( D \) electric displacement
\( P \) polarization
\( k \) wavevector
\( \nu_{\pm} \) upward/downward wavevector
\( \kappa \) tangential (to the interface) component of the wavevector
\( w_i \) normal (to the interface) component of the wavevector in medium i
\( \tilde{\omega} \) wavenumber in vacuum \( (2\pi/\lambda) \)
\( r \) position vector
\( R \) tangential (to the interface) component of the position vector
\( \hat{s} \) \( s \)– polarization (TE) unit vector
\( \hat{p} \) \( p \)-polarization (TM) unit vector

\( M_{ij} \) transfer matrix between medium i and j

\( M_{ij} \) interface matrix between medium i and j separated by a single interface

\( M_i \) propagation matrix in medium i

\( t_{ij} \) transmission coefficient between medium i and j separated by a single interface

\( r_{ij} \) reflection coefficient between medium i and j separated by a single interface

\( T_{ij} \) transmission coefficient between medium i and j

\( R_{ij} \) reflection coefficient between medium i and j

\( R_{\text{per.}} \) reflection coefficient from a periodic structure

\( L \) lattice constant

\( n_{\text{eff}} \) effective index of a resonant mode

\( \kappa_{\text{res}} \) resonance wavenumber

\( \kappa_R \) real part of the resonance wavenumber

\( \kappa_I \) imaginary part of the resonance wavenumber

\( \delta(z) \) Dirac delta function

\( G \) Green function

\( \theta(z) \) step function

\( G \) surface sensing parameter

\( \alpha \) polarizability tensor

\( \alpha_1 \) Raman polarizability of an isotropic molecule

\( S \) Poynting vector

\( \delta \) Kronecker delta

\( \bar{n} \) average number of vibrational excitations

\( \ell_S \) characteristic oscillation length associated with Stokes radiation

\( \ell_A \) characteristic oscillation length associated with anti-Stokes radiation

\( \sigma_S \) Stokes cross section

\( \bar{\sigma}_S \) Stokes cross section normalized to Stokes cross section in free space
\( \Delta \quad \text{beam diameter (FWHM) divided by } 2\sqrt{\ln 2} \)

\( \omega_0 \quad \text{vibrational frequency} \)

\( \gamma \quad \text{homogeneous linewidth} \)

\( \rho \quad \text{areal density of scatterers} \)

\( I \quad \text{incident field intensity} \)

\( I_t \quad \text{molecular damage threshold intensity} \)
Chapter 1

Introduction

Detection and identification of specific biological species enable early diagnosis of diseases such as cancer. In the early stages of such diseases the number of abnormal cells or relevant proteins in a sample is small and the detection of specific molecules is challenging. Optical biosensing techniques and devices can significantly enhance the signal from low concentration samples by exploiting optical resonances. In the last few decades advances in integrated optics have paved the way for optical biosensors, which offer selectivity and specificity for molecular detection as well as the possibility of remote sensing, multiplexing, and compact design [1].

1.1 Surface plasmon resonance biosensors

Surface plasmon resonance (SPR) biosensors are among the most common optical biosensors and have been widely studied and commercialized. They employ excitation of surface plasmon polaritons (or SP for short) [2]. SPs are resonances associated with the collective oscillations of free electrons at metal-dielectric interfaces, and have recently attracted great interest for a wide range of applications including waveguiding and biosensing [3–5]. These resonances are nonradiative, meaning that their electromagnetic fields decay exponentially from the surface and they do not radiate energy away from the surface. In planar structures, the SPs are confined along the normal to the interface but propagate parallel to the interface and their energy dissipates by absorption in the metal. Therefore, the excitation of SPs at metal-dielectric interfaces appears as resonant decreases in reflectivity. In Fig. 1.1a a schematic diagram of a SPR experiment is shown where a laser beam is incident on a metal structure using a prism in the Kretschmann configuration [6] (discussed in more detail in chapter 2). For a laser beam with wavelength $\lambda=1064$ nm incident on a 40 nm gold film on a BK7 prism substrate with air cladding, the reflectivity
as a function of the angle of incidence ($\theta_{in}$) is plotted in Fig. 1.1b. The dip in the reflectivity at $\theta_{in} \approx 42^\circ$ corresponds to the resonant absorption due to the coupling of the incident field to a SP resonance. These resonances are usually sharp and sensitive to the changes in the refractive index of the cladding, thus they are very attractive for biosensing applications where the presence of biological species can be detected by monitoring the shift of the reflectivity dip. In order to detect a specific type of molecule it is necessary to functionalize the metal surface so that only the desired molecules bind to the metal surface. A typical implementation involves coating the metallic surface with antibodies that only bind to specific antigens [1,7] as shown in Fig. 1.1a. The antibody-antigen combination is sometimes considered as a lock (antibody) and key (antigen) combination since antibodies selectively bind with specific antigens because of their geometric compatibility [1].

![Figure 1.1: (a) A schematic diagram of a SPR experiment, where a laser beam incident at a prism in a Kretschmann geometry couples to a SP resonance at the metal surface. (b) The reflectivity as a function of angle of incidence $\theta_{in}$ for a 40 nm gold layer on a BK7 prism with air cladding at $\lambda$ =1064 nm.](image)

Noble metals such as gold and silver are among the most commonly used materials in SPR sensing and plasmonics. The loss in these materials typically restricts the SP’s propagation length (along the metal-dielectric interface) to only a few tens of microns. This limited propagation length of SPs is a limiting factor for integrated SPR biosensors. To reduce the losses, recently several non-metallic materials such as highly doped semiconductors including Si and Ge, transparent conducting oxides, and graphene have been studied for plasmonic applications [8–12]. The free carrier concentrations and the optical properties of these materials can be engineered to allow SP excitations [8]. These non-metallic plasmonic materials can offer flexibility in design, tunability, fabrication, and integration. Despite these potential advantages, optimization of optical properties
of these materials is still challenging and conventional SP structures are still preferred [8].

Another possibility to achieve a low loss SP structure is placing a thin metal layer between a cladding and a substrate with the same dielectric constant. In this symmetric structure the SPs at the two metal-dielectric interfaces can couple and form an excitation known as a long range surface plasmon (LRSP) [13,14], with much smaller electromagnetic fields in the metal and longer propagation length along the interface. In order for a metal film to support LRSP resonances, the dielectric constants of the cladding and substrate must be ideally identical, but the resonances survive if the difference between the dielectric constants of the cladding and substrate is not too large [15,16]. In many biosensing applications the cladding above the metal film is a gas or liquid, so it is challenging to find a solid substrate with a dielectric constant matching the cladding dielectric constant. Alternatively, a multilayer structure can be designed to support LRSP in an asymmetric configuration. LRSP excitations in a suspended waveguide structure [17] or in a 1D photonic crystal structure [18–20] have been studied. In this thesis a systematic method based on Fresnel coefficients pole analysis is presented for designing periodic multilayers that support LRSPs.

1.2 Surface enhanced spectroscopy

Detailed information about molecular structures can be obtained by spectroscopic methods. Fluorescence spectroscopy and microscopy are among the oldest and still most popular tools in biological studies [21]. The recent development of several fluorescence-based techniques such as confocal laser scanning [22] and two-photon fluorescence microscopy [23] have facilitated advances in molecular identification and imaging. Fluorescence is an optical process in which an electron initially in the ground state is excited by a photon with energy $\hbar \omega_F$ into an electronic excited state through a dipole-allowed transition (see Fig. 1.2). The electron quickly decays within the vibrational manifold of the electronic excited state through a nonradiative transition and finally decays into the ground state through spontaneous emission, emitting a photon with energy $\hbar \omega_F$ where $\hbar \omega_F < \hbar \omega_P$ [7]. The fluorescence spectrum reflects the electronic and vibrational structure of the molecule, but many molecular species are only weakly fluorescent or not fluorescent at all. Such molecules can be tagged with fluorescence dyes that have large electronic transition dipole moments, and therefore emit stronger fluorescence signals [7]. Labeling can perturb the target molecules’ emission (especially when the target molecules are smaller than the fluorescence dyes). Labeling is also not recommended for \textit{in vivo} medical ap-
applications on humans [24]. Another drawback of fluorescence is photobleaching, which occurs due to inter-system crossing between singlet and triplet states when the fluorescence dyes interact with Oxygen molecules [7]. The probability of the transition between the singlet and triplet states is small, however, if the dye molecules are exposed to high intensity light for a long period of time, the fluorescence signal decreases as the lifetime of the triplet states is much longer.

![Figure 1.2](image)

Figure 1.2: A schematic diagram of a fluorescence process. A photon with energy $h\omega_P$ is absorbed and after an intermediate non-radiative decay, a photon with a smaller energy $h\omega_F$ is emitted.

Vibrational spectroscopy techniques, such as Raman spectroscopy, provide more resolved vibrational information and better chemical selectivity with the possibility of obtaining structural information of complex analytes. In the last few decades Raman spectroscopy has been widely considered as a tool in optical sensing and molecular identification [7,25]. Raman scattering is an inelastic scattering process, and involves instantaneous absorption of an incident photon with energy $h\omega_P$ and emission of another photon with a different energy. Raman scattering on the quantum level is depicted in Fig. 1.3, where the dashed lines represent virtual states that are not stationary, but help visualize the process. If the molecule is excited from the ground state to a vibrational

![Figure 1.3](image)

Figure 1.3: (left) Stokes Raman scattering and (right) anti-Stokes Raman scattering. The dashed lines are virtual levels.
state (Fig. 1.3 left), the energy of the scattered field ($\hbar \omega_S$) is less than the energy of the incident field, and the process is called Stokes scattering. On the other hand, if the molecule relaxes from a vibrational state to the ground state (Fig. 1.3 right), the energy of the scattered field ($\hbar \omega_A$) is greater than the energy of the incident field, and the process is called anti-Stokes scattering. The anti-Stokes signal is much weaker than the Stokes signal since the anti-Stokes process occurs only if the molecule is initially in a vibrational state (due to thermal excitations). The energy difference between the incident and scattered photons is called the Raman shift, and is equal to the vibrational energy of the corresponding vibrational mode of the molecule.

Unlike fluorescence, Raman spectroscopy does not suffer from photobleaching, and the Raman spectrum provides a unique fingerprint of the molecules with the narrower Raman lines being more suitable for multiplexed detection. However, the Raman effect has the major limitation of being extremely inefficient [26,27] since typical Raman cross sections are only about $10^{-30} \text{ cm}^2$ per molecule, 14 orders of magnitude smaller than typical fluorescence cross sections of fluorescent dyes ($10^{-16} \text{ cm}^2$ per molecule) [28]. Nonetheless, Raman spectroscopy was revolutionized in 1974 when Fleischmann et al. observed intense Raman scattering from pyridine molecules adsorbed to a roughened silver electrode surface [29]. This phenomenon was later called surface enhanced Raman scattering (SERS). In the last thirty years SERS from molecules in proximity of metallic structures has been extensively studied. The structures studied for SERS include roughened metallic surfaces [7,30,31], nanoparticles on substrates [32–35], nanoparticles in colloidal solutions [7,25] with particles in the shapes of spheres, rods, and triangles, and mixed metallic-dielectric nanoparticles (nanoshells) [36]. In other applications, regular structures such as periodic arrays of metallic nanoparticles [3,37], holes in metallic films [3,38,39], as well as metallic gratings [40] have been studied. Solid and hollow core photonic crystal fibers with metal coated cladding and metallic nanoparticle filling, respectively, have also been considered as SERS substrates [41].

The large enhancement of the scattering signal in SERS is a result of coupling of incident and scattered fields to localized surface plasmon resonances in metallic structures [25,26]. To shed light on this, note that the Raman scattering can be viewed as a two step process where, in the first step, an incident pump field at the position of the molecule induces a dipole moment in the molecule and, in the next step, the scattered field is radiated by the induced dipole. To offer an example, consider the molecule is located in the vicinity of a small metal sphere (Fig 1.4a) with radius $a$ and dielectric constant $\varepsilon_m$ (a complex quantity in general), and is illuminated by an incident field with wavelength $\lambda$, where $\lambda \gg a$. Within the electrostatic approximation the problem is equivalent to
that of a sphere in a uniform external electric field. The induced dipole moment in the sphere, \( \boldsymbol{\mu} \), is found from the solution of electrostatic Maxwell equations as

\[
\boldsymbol{\mu} = 4\pi \varepsilon_0 \varepsilon (\frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon}) a^3 E_0
\]  

(1.1)

[42], where \( \varepsilon_0 \) is the electric permittivity of vacuum, \( \varepsilon \) is the dielectric constant of the surrounding medium and is taken to be real here, and \( E_0 \) is the incident electric field. Under the condition that \( \text{Re}(\varepsilon_m) \sim -2\varepsilon \), which is realizable for metals, the denominator of Eq. (1.1) becomes small and the optical response (here the polarizability) of the sphere becomes large, signaling excitation of a surface plasmon resonance. The large induced dipole moment of the sphere creates a large local field near the sphere, where the molecule is located. The large local field induces a large dipole moment (proportional to the amplitude of the local field) in the molecule and the molecule radiates a large scattering field. The presence of the metallic sphere also modifies the radiation from the molecule, and in particular, if the scattered field is coupled to another surface plasmon resonance, the Raman scattering signal benefits from a two-fold enhancement.

Figure 1.4: (a) A metal sphere with dielectric constant \( \varepsilon_m \) in a medium with dielectric constant \( \varepsilon \), subject to a uniform electric field with amplitude \( E_0 \). (b) A hot spot region, where the local electric field is maximized, occurs in the space between the two metal spheres.

The typical average SERS enhancement factor is about \( 10^4 - 10^6 \). However, the Raman scattering signal from molecules at certain locations in the metallic structure, known as hot spots, can be even more enhanced. For instance, in Fig 1.4b the electric field is maximized in the area between the two metal spheres, making that region serve as a hot spot for molecules. Enhancement factors up to \( 10^{14} \) for dye molecules at hot spots on aggregated gold and silver nanoparticles have been observed [28,43], enabling single molecule spectroscopy.

In a similar approach, resonant coupling of incident and scattered electromagnetic fields to guided modes in dielectric structures can also be exploited to enhance Raman
scattering. A dielectric waveguide structure supports resonant modes that are confined due to total internal reflection from cladding and substrate. Excitation of a waveguide mode results in large electric fields inside and at the surface of the waveguide structure, where the adsorbed molecules are located, and thus leads to SERS as well. In pioneer experiments by Levy et al., direct measurement of Raman spectra of a few micrometers thick polymer waveguide was reported [44]. Since then, slab waveguide structures have been widely considered for the study of Raman scattering from polymers and monolayers of biomolecules [45–52]. Coupled waveguides, consisting of identical planar waveguides, have also been used to study Raman scattering from a thin liquid film between them [53]. These experiments have demonstrated enhancement factors up to $10^3$ for the Raman scattering signal in slab waveguides. Although these purely dielectric structures do not seem to be able to compete with metallic structures in terms of the enhancement that can be achieved, the interest in the use of dielectric structures is still motivated by the wide range of experimental configurations that can be implemented as well as the possibility of working with transparent materials, which is particularly appealing for the realization of integrated on-chip Raman sensors.

Raman and fluorescence spectroscopy usually require assistance from SERS substrates or SERS tags (metal nanoparticles) and fluorescence labels (dyes) in order to generate a detectable signal. The Raman and fluorescence signals scale linearly with the number of emitters in a sample, since these optical processes are incoherent and therefore the emitters in a sample radiate independently with no certain phase relation among their radiated fields. In contrast, in coherent spectroscopy the radiation from different emitters interfere coherently and the overall signal scales quadratically with the number of emitters in the sample. Thus, for a large number of molecules in a sample the coherent spectroscopy techniques can offer label-free chemical detection or imaging. In nonlinear coherent processes the radiated signal also has a higher order dependence on incident laser powers, and therefore, coherent nonlinear spectroscopy employing high peak power ultrafast lasers can offer chemical sensing with better sensitivity. One example of such an approach involves coherent anti-Stokes Raman scattering (CARS), which was first observed in 1965 by Maker and Terhune at the Ford Motor Company [54]. Following advances in fast optical devices and laser sources, CARS has been extensively developed [55], and has especially attracted interests for imaging lipids [56–58] and proteins [59], and in vivo studies of tissues [60].

CARS is a third order nonlinear effect based on driving molecular vibrations at resonance. Since vibrational frequencies of molecules are far below optical frequencies, these vibrations can not be driven by a single laser field. However, the beat frequency of two
laser beams, often the pump and Stokes with frequencies $\omega_P$ and $\omega_S$, can match the molecular vibrational frequency and drive the vibrational oscillations. This driven vibration enlarges the scattering signal of a third probe field (often with the same frequency as the pump field) that is incident on the molecule. The driving force is increased by increasing the intensity of the pump and Stokes fields at the molecular position. This is achieved by tight focusing of the pump and Stokes beams containing short laser pulses [24,55,61]. The CARS process on the quantum level is schematically shown in Fig. 1.5, where the pump and Stokes photons create a coherence between the ground and vibrational states, and the scattering of a probe (with the same frequency as the pump) photon results in the emission of an anti-Stokes photon with frequency $\omega_A$. In an ensemble of molecules, all of the driven emitters oscillate with well defined phases and the scattered fields from all scatterers interfere coherently, resulting in a maximum anti-Stokes signal in particular directions due to constructive interference. In bulk samples, the CARS signal can be a few orders of magnitudes stronger than the spontaneous Raman scattering signal [62,63]. Moreover, the blue shifted CARS signal (with respect to the pump beam) makes the separation from the background fluorescence easier. The anti-Stokes signal is usually masked by a large nonresonant background signal at the same frequency, but the nonresonant signal can be removed using one of the several proposed techniques [64–66].

Even though the CARS signal from bulk samples is expected to be stronger than spontaneous Raman scattering, its sensitivity for monitoring molecules in very low concentrations is questionable. Similar to surface enhanced Raman scattering, CARS can also be enhanced by excitation of electromagnetic resonances in resonant structures. Surface enhanced CARS has been studied in thin film dielectric waveguides [67] and with colloidal metal nanoparticles [68–70]. In particular, a recent study reports an enhancement of $10^5$ over standard CARS when a nanovoid plasmonic structure is used as the substrate [71]. Ideally, coupling all the fields involved in CARS process to resonant
modes is desired to achieve a large enhancement. However, the phase matching condition in CARS, which will be discussed in detail in chapter 6, imposes a limitation on achieving this, so flexibility in tailoring the dispersion relation of the resonant modes is essential.

In this thesis, I report theoretical studies of surface enhanced spontaneous Raman scattering and CARS in dielectric structures supporting Bloch surface waves. Bloch surface waves (BSW) [72,73] are supported by periodic dielectric stacks (1D photonic crystals). These waves are confined to the surface of the structure due to the photonic bandgap from the photonic crystal and total internal reflection from cladding. Bloch surface waves can be seen as dielectric analogues of surface plasmons at planar metal-dielectric interfaces, but they do not suffer from absorption losses. These structures have attracted interest for sensing and biosensing applications [74–80]. The characteristic that makes these structures particularly appealing is the possibility of working over a wide spectral range [74,75] with several materials from oxides [81] to semiconductors [82], even when the refractive index contrast is very small. Bloch surface wave structures can be designed to have very narrow resonance peaks, and their dispersion relations can be widely tuned by changing the parameters of the multilayers. Thus, they offer more flexibility for sensing optimization than usual slab waveguides.

1.3 Outline of this thesis

The calculations of the electromagnetic fields in 1D multilayer structures are presented in chapter 2, where a transfer matrix method is used to describe fields in terms of the Fresnel coefficient of the multilayer structure. This formalism, as we see in the next chapters, also allows for the scattered fields in spontaneous Raman scattering and CARS to be expressed in terms of the Fresnel coefficients of the structures. I introduce the resonant structures studied in this thesis, including structures supporting surface plasmons, long range surface plasmons, waveguide modes, and Bloch surface waves, and in each case, show the calculations of the resonant modes. Experimental configurations for coupling incident or outgoing fields to resonant modes in multilayer structures, including Kretschmann and Otto configuration and grating coupling, are also briefly discussed. To address the problem of dipole radiation near planar structures, which arises in chapters 4 and 6, I introduce a Green function formalism and calculate the radiated fields by a point dipole near a planar interface.

In chapter 3 a new approach for designing a periodic multilayer structure supporting LRSPs is presented, exploiting a Fresnel coefficient pole analysis. In particular, an ap-
proximate linear relation between the thicknesses of the alternating layers in such periodic multilayer structures is provided. The field intensity profile of the LRSP supported by a multilayer structure is compared to the LRSP in a symmetric structure, and absorption and coupling losses for finite symmetric and asymmetric structures are calculated as a function of the thickness of the structure. For biosensing applications and in order to characterize the effect of thin molecular layers on the optical properties of arbitrary planar resonant structures, I derive a semi-analytic expression for a standard surface sensing parameter and compare the exact and approximate calculations for the symmetric and asymmetric structures.

The calculations for surface enhanced Raman scattering on planar multilayer structures are presented in chapter 4. The Raman cross section is calculated for a molecule embedded in a uniform medium and on an arbitrary multilayer structure. In the multilayer structure case, the expressions for the Raman cross section in the cladding and substrate are expressed in terms of the Fresnel coefficients of the structure. This allows for identification of any guided modes, and the construction of approximate semi-analytic expressions, as well as implementation of numerical calculations. I show the numerical calculations for particular multilayer structures supporting surface plasmons, waveguide modes, and Bloch surface waves, and discuss the extension of the results to excitation with finite beams and the relevance of finite beam corrections.

The experimental realization of surface enhanced Raman scattering in the presence of multilayer structures supporting Bloch surface waves is presented in chapter 5. The Bloch surface wave assisted Raman scattering is observed in two different multilayer structures that have been designed to work with pump wavelengths in visible and infrared and with claddings of water and air, respectively. The surface enhanced Raman spectra of acetone and sulfur with visible and infrared pumps, respectively, are shown. The enhancement factors are compared with photoluminescence measurements as well as theoretical calculations.

In chapter 6 calculations of coherent anti-Stokes Raman scattering for thin layers of molecules in a uniform medium and on an arbitrary planar structure are presented. I derive expressions for the CARS power in terms of the Fresnel coefficients of the planar structures. These expressions are simplified using a pole expansion approach for the case that the multilayer structure supports resonant modes for the pump, Stokes and anti-Stokes fields. The dispersion relation of Bloch surface waves in a multilayer structure is engineered such that all the fields involved in the CARS process couple to resonant modes. I compare the CARS power in the presence of the resonant multilayer structure with CARS power obtained by tight focusing, and also compare CARS and spontaneous
Chapter 1. Introduction

Raman scattering powers in a uniform medium and on the resonant multilayer structure.

Chapter 7 ends the thesis with the conclusions and final remarks.

Chapters 4 and 5 have been published in J. Opt. Soc. Am. B 29, 1863-1874 (2012), and J. Phys. Chem. C 117, 6821-6825 (2013). Two manuscripts based on the contents of chapter 3 and chapter 6 have been prepared.
Chapter 2

Background

In this chapter I review the previously developed treatments [42,72,83–85] of some of the underlying electromagnetic problems in this thesis. Sec. 2.1 introduces a transfer matrix formalism for calculating electromagnetic fields in 1D layered structures in the absence of free charges or currents [72,83]. The transfer matrix algorithm simplifies numerical calculations significantly and the resulting Fresnel coefficients are useful for analyzing the behavior of the multilayer structures near resonance [85]. As examples for applications of this method, in Sec. 2.2, I derive resonance conditions for surface plasmons, long range surface plasmons, waveguide modes, and Bloch surface waves, and show the intensity distribution of the above resonances in the corresponding multilayer structures. The experimental configurations for coupling incident fields to these resonant modes are also discussed. Sec. 2.3 discusses the problem of dipole radiation near planar structures, which arises in chapter 4 and 6 where spontaneous Raman scattering and CARS on multilayer structures are studied. I introduce a Green function formalism [83,84], which is used to calculate electromagnetic fields radiated by a point dipole source near a planar interface.

2.1 Electromagnetic fields in multilayer structures

Consider a uniform medium with dielectric constant \( \varepsilon = \epsilon/\epsilon_0 \), where \( \epsilon \) and \( \epsilon_0 \) are the electric permittivities of the medium and vacuum, respectively. The index of refraction is \( n = \sqrt{\varepsilon} \), and \( n \) and \( \varepsilon \) are in general frequency and position dependent complex quantities. The electromagnetic fields in this medium satisfy Maxwell equations

\[
\nabla \cdot D = \varrho, \quad \nabla \cdot B = 0
\]

12
and
\[ \dot{B} + \nabla \times E = 0, \quad \nabla \times H = \dot{D} + J \] (2.1)

[42], where the dot indicates \( \partial / \partial t \) and \( \rho \) and \( J \) are the charge and current densities. The electric displacement is \( D = \varepsilon_0 \varepsilon E \) and, ignoring magnetizations, \( H = B / \mu_0 \) with \( \mu_0 \) the vacuum permeability. In the absence of free charges
\[ \nabla \cdot D = 0, \quad \nabla \cdot B = 0, \] (2.2)

and the dynamical equations are
\[ \dot{B} = -\nabla \times E, \quad \dot{E} = \frac{1}{\varepsilon_0 \mu_0 \varepsilon} \nabla \times B. \] (2.3)

These equations have plane wave solutions of the form
\[ E(r, t) = E e^{i \mathbf{k} \cdot \mathbf{r} - i \omega t} + c.c. \] (2.4)

where \( \mathbf{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z} \) is the wavevector and the \( \hat{x}, \hat{y}, \) and \( \hat{z} \) are the unit vectors in the indicated directions. The Maxwell equations enforce \( k_x^2 + k_y^2 + k_z^2 = (\tilde{\omega} n)^2 \), where \( \tilde{\omega} = \omega / c \) and \( c \) is the speed of light [42,83]. Following the notation in [83], I define \( \mathbf{\kappa} = k_x \hat{x} + k_y \hat{y} \) and \( w = \sqrt{(\tilde{\omega} n)^2 - \kappa^2} \) and for a complex quantity \( Z \) use the square root convention that \( \text{Im}(Z) \geq 0 \), and if \( \text{Im}(Z) = 0 \), then \( \text{Re}(Z) \geq 0 \). The possible \( \mathbf{k} \) for a given \( \mathbf{\kappa} \) are
\[ \mathbf{\nu}_\pm = \mathbf{\kappa} \pm w \hat{z}. \] (2.5)

The spatial part of the plane wave solution in (2.4), \( E e^{i \mathbf{k} \cdot \mathbf{r}} \), can be written as
\[ E_+ e^{i \mathbf{\nu}_+ \cdot \mathbf{r}} = E_+ e^{i \mathbf{k} \cdot \mathbf{R} e^{i w z}}, \]
\[ E_- e^{i \mathbf{\nu}_- \cdot \mathbf{r}} = E_- e^{i \mathbf{k} \cdot \mathbf{R} e^{-i w z}}, \] (2.6)

where \( \mathbf{R} = x \hat{x} + y \hat{y} \) is the projection of the position vector onto the \( xy \) plane. The \( E_+ \) and \( E_- \) are identified as the upward and downward waves, respectively. As a result of the Maxwell equations the \( E_+ \) (\( E_- \)) must be perpendicular to \( \mathbf{\nu}_+ \) (\( \mathbf{\nu}_- \)). The \( E_+ \) (\( E_- \)) can be split into two perpendicular components \( s- \) and \( p- \) representing the TE and TM polarizations, respectively, with unit polarization vectors
\[ \hat{s} = \hat{\kappa} \times \hat{z}, \]
\[ \hat{p}_\pm = \frac{\kappa \hat{z} \mp w \hat{\kappa}}{\tilde{\omega} n}, \] (2.7)
such that $\mathbf{E}_\pm = E_\pm^s \hat{s} + E_\pm^p \hat{p}_\pm$. The spatial parts of the electric and magnetic fields associated with the upward and downward waves are

$$
\mathbf{E}_\pm(r) = \mathbf{E}_\pm(z) e^{i\kappa R},
$$

$$
\mathbf{B}_\pm(r) = \mathbf{B}_\pm(z) e^{i\kappa R},
$$

(2.8)

with

$$
\mathbf{E}_\pm(z) = (E_\pm^s \hat{s} + E_\pm^p \hat{p}_\pm) e^{\pm i w z},
$$

$$
\mathbf{B}_\pm(z) = \frac{n}{c} (E_\pm^p \hat{s} - E_\pm^s \hat{p}_\pm) e^{\pm i w z}
$$

(2.9)

These equations describe the electromagnetic fields in any uniform medium. Consider an arbitrary layered structure and label the layers by $i = 1, 2, \ldots, N$ and indicate the thickness of layer $i$ by $d_i$. Take the $z$ axis to be normal to the structure such that the dielectric constant varies from one layer to another along the $z$ axis but is constant in the $xy$ plane. The electromagnetic fields in each layer are given by the above equations, with the proper $E_\pm^s$ and $E_\pm^p$ that satisfy the boundary conditions; at any interface the tangential components of $\mathbf{E}$ and $\mathbf{H}$ and the normal components of $\mathbf{D}$ and $\mathbf{B}$ must be continuous. Each polarization component of $\mathbf{E}_\pm(z)$ at $r_a = \mathbf{R}_a + z_a \hat{z}$ in layer $i$ can be specified using a vector notation

$$
e_i(z_a) = \begin{pmatrix} E_{i+} e^{i w_i z_a} \\ E_{i-} e^{-i w_i z_a} \end{pmatrix}.
$$

(2.10)

The fields at each two points can be related using a transfer matrix (see Sec. A.1 in Appendix A). In particular, for a multilayer structure extending from $z = 0$ (layer 1) to $z = -D$ (layer $N$) $e_1(0) = \mathcal{M}_{1N} e_N(-D)$, where $\mathcal{M}_{1N}$ is the transfer matrix between medium 1 and medium $N$:

$$
\mathcal{M}_{1N} = M_{12} M_{23} M_3(d_3) \cdots M_{N-1,N} M_{N-1,N},
$$

(2.11)

with $M_{ij}$ the interface transfer matrix between medium $i$ and $j$, and $M_i(d_i)$ the propagation transfer matrix in medium $i$ [83]. The Fresnel reflection coefficients $R_{1N}$ and $R_{N1}$ are defined as

$$
R_{1N} = \frac{E_{1+}}{E_{1-}} \quad \text{and} \quad R_{N1} = \frac{E_{N-} e^{i w_N D}}{E_{N+} e^{-i w_N D}},
$$

(2.12)
and the Fresnel transmission coefficients \(T_{1N}\) and \(T_{N1}\) are defined as

\[
T_{1N} = \frac{E_{N-}e^{i\nu ND}}{E_{1-}} \quad \text{and} \quad T_{N1} = \frac{E_{1+} + E_{N+}e^{-i\nu ND}}{E_{N+}e^{-i\nu ND}}.
\]

These coefficients can be expressed in terms of the elements of the transfer matrix \(M_{1N}\), for instance

\[
T_{1N} = \frac{1}{M_{1N}(2,2)} \quad \text{and} \quad R_{1N} = \frac{M_{1N}(1,2)}{M_{1N}(2,2)}.
\]

The transfer matrices can be calculated numerically and in this thesis the numerical calculations are done using a Fortran code.

### 2.2 Electromagnetic resonances in multilayer structures

So far I have introduced a formalism for calculating the electromagnetic fields in arbitrary layered structures. In this thesis, 1D layered structures that support resonant modes at certain frequencies (\(\omega\)) and wavenumbers (\(\kappa\)) are considered. In general the resonances of a system are signalled by the poles of the response function of the system. In the context of the multilayer structures the Fresnel coefficients characterize the response of the structures to incident fields (reflection or transmission), and therefore, the resonant modes are signalled by the poles of the Fresnel coefficients \([85]\). This implies that at resonance the Fresnel coefficients diverge, however, note that the energy conservation laws are not violated, since the electromagnetic fields, as we see later, are evanescent and do not carry energy away from the interface.

In this section I show examples of electromagnetic resonances that are studied in this thesis and present a Fresnel coefficient pole analysis approach for calculating the resonance conditions. I also calculate the intensity distribution of the corresponding resonant modes and, following \([86]\), normalize the fields in the generally dispersive and absorptive media \([87,88]\) such that

\[
\int_V \epsilon_0 \left( \bar{\varepsilon}(\mathbf{r}, \omega) + \frac{\omega}{2} \frac{\partial}{\partial \omega} \bar{\varepsilon}(\mathbf{r}, \omega) \right) |\mathbf{E}(\mathbf{r})|^2 d^3 r = \frac{\hbar \omega}{2},
\]

where \(V\) is the normalization volume and \(\bar{\varepsilon}(\mathbf{r}, \omega)\) is an approximate effective real dielectric constant with

\[
\frac{1}{\bar{\varepsilon}(\mathbf{r}, \omega)} \equiv Re\left( \frac{1}{\varepsilon(\mathbf{r}, \omega)} \right).
\]
which has been defined to approximate the lossy modes of the metallic structures as real excitations [86].

Surface plasmons

A plasmon is a quasi-particle associated with the elementary modes of charge density oscillation in a plasma such as the free electron plasma of a metal. If the excitation is bound to a surface, the new mode is called surface plasmon or simply SP [7]. Surface plasmons are supported by metal-dielectric interfaces. Consider a structure consisting of a semi-infinite metal layer (medium $m$) with dielectric constant $\varepsilon_m$ for $z < 0$, and a semi-infinite cladding (medium 1) with dielectric constant $\varepsilon_1$ for $z > 0$ (Fig. 2.1a). The

![Figure 2.1: (a) A surface plasmon structure consisting of a semi-infinite metal layer with dielectric constant $\varepsilon_m$ for $z < 0$ and a semi-infinite cladding with dielectric constant $\varepsilon_1$ for $z > 0$. (b) The intensity distribution (in logarithmic scale) along the $z$ axis for $p-$ polarized SP at the gold-air interface.](image)

SPs are signalled by the poles of the Fresnel coefficients between the cladding and metal. The reflection coefficient for $p-$ polarization $r_{m1}^p$ is

$$r_{m1}^p = \frac{w_m\varepsilon_1 - w_1\varepsilon_m}{w_m\varepsilon_1 + w_1\varepsilon_m}$$  \hspace{1cm} (2.16)$$

and has a pole when

$$w_m\varepsilon_1 + w_1\varepsilon_m = 0.$$  \hspace{1cm} (2.17)$$

Recall that $w_i = \sqrt{\omega^2\varepsilon_i - \kappa^2}$ and square the above equation

$$(\omega^2\varepsilon_m - \kappa^2)\varepsilon_1^2 = (\omega^2\varepsilon_1 - \kappa^2)\varepsilon_m^2,$$  \hspace{1cm} (2.18)$$
which gives the surface plasmon resonance wavenumber

$$
\kappa_{SP} = \tilde{\omega} \sqrt{\frac{\varepsilon_1 \varepsilon_m}{\varepsilon_1 + \varepsilon_m}}
$$

(2.19)

[85, 89]. The dielectric constant of the metal, \( \varepsilon_m \), is complex, so \( \kappa_{SP} \) is complex. The imaginary part of \( \kappa_{SP} \) determines the surface plasmon wave decaying along the metal-dielectric interface as a result of absorption losses in the metal. It can be shown that for \( s- \) polarization, the reflection coefficient does not have a pole, and therefore the surface plasmons are only \( p- \) polarized.

Consider an air-gold interface with the dielectric constant of gold \( \varepsilon_m = -48.47 + 3.60i \) [90] at \( \lambda = 1064 \text{ nm} \). From (2.19) \( \kappa_{SP} = (5.97 + i4.65 \times 10^{-3}) \mu \text{m}^{-1} \). The intensity propagation length of the SP along the interface is given by \( 1/(2 \text{Im}(\kappa_{SP})) \) and is about 110 \( \mu \text{m} \). In Fig. 2.1b the intensity distribution (in logarithmic scale) along the \( z \) axis for the \( p- \) polarized SP is plotted. The field is evanescent in air and in gold, and the intensity decay length in gold (10 \( nm \)) is much smaller than the intensity decay length in air (0.6 \( \mu \text{m} \)). Note that since the energy flux of an evanescent wave is zero, there is no energy dissipation along the \( z \) axis.

### Long range surface plasmons

The main drawback of the SP structure is the large absorption losses in the metal that limit the propagation length of the SP along the interface. The losses can be minimized if the metal layer is embedded between two media with the same dielectric constant. The SPs supported by the two metal-dielectric interfaces couple and form an excitation with a smaller electromagnetic field in the metal. The coupled SP mode can propagate a larger distance along the interface and is called long range surface plasmon (LRSP) [13, 14]. Consider a LRSP structure consisting of a metal layer with dielectric constant \( \varepsilon_m \) between a cladding and substrate with dielectric constant \( \varepsilon_1 \) (see Fig. 2.2a). The resonances are signalled by the poles of the Fresnel coefficients between the cladding and substrate. The Fresnel reflection coefficient between the cladding and substrate is

$$
R_{11} = r_{1m} + \frac{t_{1m}r_{m1}t_{m1}e^{2i\omega_m d}}{1 - r_{m1}t_{m1}e^{2i\omega_m d}}, \quad (2.20)
$$

similar to Eq. (A.9), and has a pole when

$$
1 - r_{m1}^2 e^{2i\omega_m d} = 0, \quad (2.21)
$$
which is

\[ r_{m1} = +e^{-iw_md}, \]

or

\[ r_{m1} = -e^{-iw_md}. \]  \( (2.22) \)

For \( p^- \) polarization, the first line of \( (2.22) \) corresponds to the solutions with symmetric magnetic fields (with respect to the center of the metal film), while the second line of \( (2.22) \) corresponds to the solutions with antisymmetric magnetic fields \([91,92]\). The symmetric modes generally have much smaller attenuations and much longer propagation lengths than the antisymmetric modes, and thus the term long range is usually reserved for the symmetric modes \([93]\). The imaginary part of the complex LRSP resonance wavenumber \( \kappa_{LRSP} \) gives the mode losses and, for the symmetric mode, decreases as the thickness of the metal film decreases \([93]\).

![Figure 2.2: (a) A LRSP structure consisting of a metal layer with dielectric constant \( \varepsilon_m \) and thickness \( d \) between two dielectric media with the same dielectric constant \( \varepsilon_1 \). (b) The intensity distribution (in logarithmic scale) along the \( z \) axis for a symmetric \( p^- \) polarized LRSP in a structure consisted of a gold layer with \( d=20 \) nm between an air cladding and substrate.](image-url)

As an example, consider a 20 nm gold film with dielectric constant \( \varepsilon_m=-48.47+3.60i \) \([90]\) at \( \lambda=1064 \) nm, between a cladding and substrate of air. From \( (2.22), \kappa_{LRSP}=(5.91+i1.03\times10^{-4}) \mu\text{m}^{-1} \) for the symmetric \( p^- \) polarized mode. Compared to the \( \kappa_{SP} \) of the single interface, \( \kappa_{LRSP} \) has a smaller real part meaning that the LRSP mode is less confined, and has a smaller imaginary part meaning that the LRSP mode is less attenuated. The LRSP intensity propagation length along the interface is \( 1/(2\text{Im}(\kappa_{LRSP}))=4.9 \) mm and is about 45 times larger than the corresponding length of the ordinary SP. In Fig. 2.2b the intensity distribution (in logarithmic scale) along the \( z \) axis for the symmetric
p− polarized LRSP mode is plotted. The field is evanescent in the air cladding and substrate with an intensity decay length of 1.5 μm. The intensity in the metal film and away from the interfaces is very small.

**Waveguide modes**

Consider a dielectric film with thickness $d$ and dielectric constant $\varepsilon_2$ for $0 < z < -d$, between a cladding with dielectric constant $\varepsilon_1$ for $z > 0$ and a substrate with dielectric constant $\varepsilon_3$ for $z < -d$ (see Fig. 2.3a). If $n_2 > n_1, n_3$, the structure supports waveguide resonances that are electromagnetic waves that propagate in the guiding film (medium 2), but are evanescent in the cladding and substrate due to total internal reflection. The waveguide modes are signalled by the poles of the Fresnel coefficients between the cladding and substrate. The Fresnel reflection coefficient between the cladding and substrate, $R_{13}$, is

$$R_{13} = r_{12} + \frac{t_{12} r_{23} t_{21} e^{2 i w_2 d}}{1 - r_{21} r_{23} e^{2 i w_2 d}},$$

similar to Eq. (A.9). The $R_{13}$ has a pole when

$$1 - r_{21} r_{23} e^{2 i w_2 d} = 0. \quad (2.24)$$

Since $w_2$ is real, and $w_1$ and $w_3$ are imaginary, $r_{21}$ and $r_{23}$ are complex quantities with norm of unity (see (3.17) and (3.20)), and

$$R_{13} = \frac{-r_{21} + r_{23} e^{2 i w_2 d}}{1 - r_{21} r_{23} e^{2 i w_2 d}},$$

$$= 2 \text{Re}\left((r_{23} e^{2 i w_2 d} - r_{21}^*)^{-1}\right), \quad (2.25)$$

so $R_{13}$ is real in the region of interest. The waveguide wavenumbers can be calculated from the roots of the inverse of the reflection coefficient. Since $R_{13}$ is real, the resonance wavenumbers can be calculated numerically using a bisection method.

Consider a Ta$_2$O$_5$ layer with $d$=200 nm and dielectric constant $\varepsilon_2$=4.17 [94] on a substrate of SiO$_2$ with dielectric constant $\varepsilon_3$=2.1 [94] at $\lambda$=1064 nm, and with air cladding. From (2.25), $\kappa_{WG}$=9.76 μm$^{-1}$ for the lowest order s− polarized WG mode. The imaginary part of $\kappa_{WG}$ is zero, meaning that the field propagates along the surface without dissipation, as expected for the lossless structure considered here. In Fig. 2.3b the intensity distribution along the $z$ axis for the s− polarized WG mode is plotted. The field is evanescent in the cladding and substrate with an intensity decay length of 60 nm and 110 nm in air and SiO$_2$, respectively.
Figure 2.3: (a) A waveguide structure consisting of a guiding layer with thickness $d$ and dielectric constant $\varepsilon_2$, with a semi-infinite cladding and substrate with dielectric constants $\varepsilon_1$ and $\varepsilon_3$, respectively. (b) The intensity distribution along the $z$ axis for the lowest order $s$- polarized WG mode in a waveguide structure of $\text{Ta}_2\text{O}_5$ with $d=200$ nm, with a cladding of air and a substrate of $\text{SiO}_2$.

**Bloch surface waves**

Bloch Surface Waves (BSWs) are analogous to SPs, since they are also electromagnetic modes confined to the interface of two semi-infinite media. However, here one of the media is a 1D photonic crystal [95,96] consisting of a stack of layers with periodic dielectric constants. The Bloch Surface waves can neither propagate in the cladding due to the total internal reflection, nor in the photonic crystal due to the photonic band gap, but they can propagate along the interface [72]. In this section I show an approach for calculating the bandgap structure and BSW resonance wavenumbers in periodic multilayer structures.

**Photonic bandgap**

Photonic bandgaps in photonic crystals are similar to electronic bandgaps in semiconductors. In the same way that periodic modulation of the electric potential in semiconductors results in electronic bandgaps, the periodic modulation of the the dielectric constant in photonic crystals results in photonic bandgaps, where propagation of electromagnetic fields with certain frequencies lying in some regions (gaps) in the band structure is forbidden. This can be understood as a result of the destructive interference of the fields transmitted or reflected from different interfaces in the structure. A periodic multilayer structure is a 1D photonic crystal, and the propagation of electromagnetic fields along the axis of periodicity of the structure is prevented for certain frequencies.

Consider a multilayer structure consisting of layers $a$ and $b$ with thicknesses $d_a$ and
\(d_a\) and \(d_a + d_b = L\). The fields at point \(z\) in layer \(a\) and just below the interface with layer \(b\) are related to the fields at \(z = z + L\) in the next layer \(a\) with

\[
e_a(z) = \mathcal{M}_{\text{unit}} e_a(z + L), \tag{2.26}
\]

where \(\mathcal{M}_{\text{unit}}\) is the unit cell transfer matrix given by \(\mathcal{M}_{\text{unit}} = M_a(d_a)M_{ab}M_b(d_b)M_{ba}\). As a consequence of the Bloch theorem

\[
e_a(z + L) = e^{-iKL} e_a(z), \tag{2.27}
\]

where \(K\) is the complex Bloch wavenumber \([72]\). From (2.27) and (2.26) it is clear that \(e^{iKL}\) are the eigenvalues of the unit cell transfer matrix. Identifying the unit cell matrix elements by \(A, B, C,\) and \(D\),

\[
\mathcal{M}_{\text{unit}} = \begin{pmatrix} A & B \\ C & D \end{pmatrix}, \tag{2.28}
\]

and it can be shown that the determinant of \(\mathcal{M}_{\text{unit}}\) is unity. The eigenvalues of \(\mathcal{M}_{\text{unit}}\) are

\[
e^{iKL} = \frac{A + D}{2} \pm \sqrt{\left(\frac{A + D}{2}\right)^2 - 1}, \tag{2.29}
\]

and the product of the eigenvalues is unity. If \(|A + D|/2 < 1\), then \(K\) is real and the fields propagate in the multilayer structure. If \(|A + D|/2 > 1\), then \(K\) has an imaginary part and the fields have evanescent envelope functions in the multilayer structure and are in the bandgap \([72]\). The multilayer structure acts as a mirror in the bandgap region and the incident fields are totally reflected. Thus, in the bandgap \(|R_{\text{per.}}| = 1\) with \(R_{\text{per.}}\) the reflection coefficient from the periodic structure. In chapters 4, 5, and 6 examples of bandgap structures in periodic multilayers are presented.

**BSW resonance**

The periodic multilayer structure supports defect modes, such as Bloch surface waves (BSW), when defects are introduced in the periodicity of the structure \([72]\). As mentioned earlier, BSWs are confined to the surface of the structure because of the total internal reflection from the cladding and also the photonic bandgap of the periodic structure. Consider a semi-infinite multilayer structure for \(z < 0\), and a cladding with dielectric constant \(\varepsilon_1\) for \(z > 0\). The multilayer structure consists of \(n\) non-periodic overlayers (defects) including media 1, 2, 3, \(\ldots\), \(n\) for \(0 > z > z_0\), and a periodic part for \(z < z_0\) with
layer $a$ the first layer of the periodic part just under the overlayers (see Fig. 2.4a). The

Figure 2.4: (a) A Bloch surface wave structure, consisting of a periodic multilayer for $z < z_0$, with $n$ non-periodic overlayers between $z = 0$ and $z = z_0$, and a cladding with dielectric constant $\varepsilon_1$ for $z > 0$. (b) The intensity distribution along the $z$ axis for the $s-$ polarized BSW in a multilayer structure of SiO$_2$ and Ta$_2$O$_5$ (the details of the structure are in the text), and air cladding.

Bloch surface waves are signalled by the poles of the Fresnel coefficients between the cladding and the semi-infinite multilayer structure. The Fresnel reflection coefficient can be expressed as

$$ R_{1s} = R_{1a} + \frac{T_{1a}R_{per}T_{a1}}{1 - R_{per}R_{a1}}, $$

where $R_{1a}$, $T_{1a}$, $R_{a1}$, and $T_{a1}$ are the Fresnel coefficients resulted from

$$ M_{1a} = M_{12}M_{23}(d_2)M_{34}(d_3)M_{45}...M_{na} $$

[89]. The elements of $M_{1a}$ and $R_{per.}$ are in general complex, however as discussed in Sec. A.2 of Appendix A, the $R_{1s}$ is real in the region where the fields are evanescent in the cladding and are in the the bandgap of the multilayer structure. This simplifies the numerical calculations for finding the poles of $R_{1s}$. In this thesis, the resonance wavenumbers and dispersion relation of BSWs are calculated from the roots of $1/R_{1s}$ using a bisection method.

As an example, consider an air cladding and a multilayer structure consisting of alternating layers of Ta$_2$O$_5$ with dielectric constant $\varepsilon_{Ta_2O_5}=4.17$ [94], and SiO$_2$ with dielectric constant $\varepsilon_{SiO_2}=2.10$ [94] at $\lambda=1064$ nm. The thicknesses of the Ta$_2$O$_5$ and SiO$_2$ layers in the periodic part are $d_{Ta_2O_5}=200$ nm and $d_{SiO_2}=250$ nm, respectively, with two overlayers with thicknesses $d_{Ta_2O_5}=80$ nm and $d_{SiO_2}=10$ nm. From Eq. (2.30), $\kappa_{BSW}=7.69$
μm⁻¹ for the s– polarized BSW. The imaginary part of \( \kappa_{BSW} \) is zero indicating that the field propagates along the interface without any dissipation, similar to the waveguide structure. In Fig. 2.4b the intensity distribution along the z axis for the s– polarized BSW is plotted. Fig. 2.4b shows that at BSW resonance, the field is evanescent in the cladding with an intensity decay length of 100 nm in air. In the multilayer structure, the field intensity has an evanescent envelope function. There is also an oscillation in the intensity in different layers, which is due to the multiple reflections and interferences in the multilayer structure.

### 2.2.1 Resonant mode excitation

In the last section examples of electromagnetic resonances supported by infinite multilayer structures were discussed. At resonance the fields are confined close to the surface of the structures and drop evanescently away from the surface. The resonance wavenumber \( \kappa_{res} \) is larger than \( \kappa = \tilde{\omega}n_1 \), meaning that the momentum (along the \( xy \) plane) of a propagating electromagnetic field in the cladding is always smaller than the momentum of the resonant mode, and because of this momentum mismatch a propagating electromagnetic field in the cladding cannot directly excite the resonant mode.

There are several approaches for providing the missing momentum, including prism coupling (Fig. 2.5a and 2.5b) as well as surface roughness or grating coupling (Fig. 2.5c) [7]. The prism coupling schemes are based on total internal reflection (ATR). For an angle of incidence \( \theta_{in} \) greater than the critical angle \( \theta_c = \sin^{-1}(n_1/n_{pr}) \) (with \( n_{pr} \) the refractive index of the prism), the wavenumber of the propagating field in the prism becomes greater than \( \tilde{\omega}n_1 \), so the momentum of the incident field can match the momentum of the resonant mode at a specific \( \theta_{in} \). The Otto configuration [97], shown in Fig. 2.5a, suggests using a prism on top of the resonant structure with a small gap in between and exciting the resonant mode from the cladding. The Kretschmann configuration [6], shown in Fig. 2.5b, suggests depositing the multilayer structure on a prism and exciting the resonant mode from the substrate.

Another approach for coupling the incident field to the resonant mode makes use of a grating, as shown in Fig. 2.5c. This approach is based on relaxing the momentum conservation in \( xy \) plane by breaking the translational invariance of the structure in the \( xy \) plane. A grating with period \( \Lambda \) provides additional momentums of \( m(2\pi/\Lambda) \) with \( m = ..., -1, 0, 1, ... \), and therefore coupling to the resonant mode is possible at certain frequencies or angles of incidence. A random surface roughness, however, completely breaks the translational invariance of the structure and propagating electromagnetic fields
in the cladding can always couple into the resonant modes [7]. This is usually not desired, since it also allows the resonant modes to couple out to the propagating fields and radiate. In this thesis, the Kretschmann configuration is considered for coupling propagating fields to resonant modes, because of the easier fabrication techniques and simpler theoretical analysis.

In the infinite structures, at $\kappa_{res}$ the Fresnel coefficients have a pole and diverge. In the finite structures, the resonant modes are leaky, and the Fresnel coefficients do not diverge at $\kappa_{res}$ but become large. The large Fresnel transmission coefficient between the substrate and the cladding means that an incident field from the prism substrate creates a large field at the surface of the resonant structure. In the next chapters, I will show that this field enhancement can enhance the linear or nonlinear optical processes such as spontaneous Raman scattering or coherent anti-Stokes Raman scattering.

### 2.3 Dipole radiation near multilayer structures

In chapters 4 and 6, spontaneous Raman scattering and coherent anti-Stokes Raman scattering near resonant multilayer structures are studied. As mentioned in chapter 1, in Raman scattering, a dipole moment is induced in the molecule by the pump field and the scattering signal is the radiation emitted by the oscillating dipole. The dipole radiation is modified near an interface, due to the change in the boundary conditions of the electromagnetic fields, which affects the radiative decay rate and the spatial distribution of the emitted radiation [98,99]. In this section, following the Green function approach in [83,84], I discuss the modification of electromagnetic fields radiated by a dipole source near a planar structure.
2.3.1 A Green function formalism

Consider a polarization source oscillating at frequency $\omega$ embedded in a uniform medium with dielectric constant $\varepsilon$. The dynamical Maxwell equations (the third and fourth of Eq. (2.1)) are

$$
\begin{align*}
  i\omega B(r) &= \nabla \times E(r), \\
  -\frac{i\omega\varepsilon}{c^2} E(r) &= \nabla \times B(r) + i\omega \mu_0 P(r),
\end{align*}
$$

(2.31)

where $P(r)$ is the polarization and $J = \partial P/\partial t$ has been used. A general polarization distribution, $P(r)$, can be Fourier decomposed in the $xy$ plane as

$$
P(r) = \int \frac{d\kappa}{(2\pi)^2} P(\kappa, z) e^{i\kappa \cdot R},
$$

(2.32)

which then can be written as

$$
P(r) = \int \frac{d\kappa}{(2\pi)^2} dz_0 \bar{P}(r, \kappa, z_0) \quad \text{with} \quad \bar{P}(r, \kappa, z_0) = \delta(z - z_0) P(\kappa, z) e^{i\kappa \cdot R}.
$$

(2.33)

If $\bar{E}(r, \kappa, z_0)$ and $\bar{B}(r, \kappa, z_0)$, defined in a similar same way, satisfy

$$
\begin{align*}
  i\omega \bar{B}(r, \kappa, z_0) &= \nabla \times \bar{E}(r, \kappa, z_0), \\
  -\frac{i\omega\varepsilon}{c^2} \bar{E}(r, \kappa, z_0) &= \nabla \times \bar{B}(r, \kappa, z_0) + i\omega \mu_0 \bar{P}(r, \kappa, z_0),
\end{align*}
$$

(2.34)

then because of the linearity of these equations and by superposition,

$$
\begin{align*}
  E(r) &= \int \frac{d\kappa}{(2\pi)^2} dz_0 \bar{E}(r, \kappa, z_0), \\
  B(r) &= \int \frac{d\kappa}{(2\pi)^2} dz_0 \bar{B}(r, \kappa, z_0)
\end{align*}
$$

(2.35)

satisfy (2.31). Eq. (2.34) can be solved essentially by guessing the form of solution [83]. For $z \neq z_0$, $\delta(z - z_0) = 0$, and equations in (2.34) are simply the Maxwell equations in the uniform medium in the absence of free charges. A reasonable guess solution is

$$
\begin{align*}
  \bar{E}(r, \kappa, z_0) &= \theta(z - z_0) e^{-i\omega z_0} \bar{E}_+(r, \kappa, z_0) + \theta(z_0 - z) e^{i\omega z_0} \bar{E}_-(r, \kappa, z_0) \\
  &\quad + \mathcal{E} \delta(z - z_0) e^{i\kappa \cdot R}, \\
  \bar{B}(r, \kappa, z_0) &= \theta(z - z_0) e^{-i\omega z_0} \bar{B}_+(r, \kappa, z_0) + \theta(z_0 - z) e^{i\omega z_0} \bar{B}_-(r, \kappa, z_0),
\end{align*}
$$

(2.36)
[83], where \( \theta(z - z_0) \) is a step function with value 1 for \( z > z_0 \) and 0 otherwise. The constant phase factors \( e^{\pm iw_0} \) are introduced only to make some of the intermediate steps simpler. The above guess implies that for \( z > z_0 \) (\( z < z_0 \)), the \( \vec{E}_+(r, \kappa, z_0) \) and \( \vec{B}_+(r, \kappa, z_0) \) (\( \vec{E}_-(r, \kappa, z_0) \) and \( \vec{B}_-(r, \kappa, z_0) \)) are the solutions of Maxwell equations in the absence of free charges. A Dirac delta function is added to the guess solution for \( \vec{E}(r, \kappa, z_0) \), since there is a Dirac delta function in \( \vec{P}(r, \kappa, z_0) \). When (2.36) is substituted to (2.34) and after some simplification steps (see [83]), \( \vec{E}(r, \kappa, z_0) \) is found as

\[
\vec{E}(r, \kappa, z_0) = \frac{i\omega^2}{2\epsilon_0 w} e^{iw(z-z_0)} \theta(z-z_0) \left[ \hat{s}(\hat{s} \cdot \vec{P}(\kappa, z_0)) + \hat{p}_+(\hat{p}_+ \cdot \vec{P}(\kappa, z_0)) \right] e^{i\kappa \cdot R} + \frac{i\omega^2}{2\epsilon_0 w} e^{-iw(z-z_0)} \theta(z_0-z) \left[ \hat{s}(\hat{s} \cdot \vec{P}(\kappa, z_0)) + \hat{p}_-(\hat{p}_- \cdot \vec{P}(\kappa, z_0)) \right] e^{i\kappa \cdot R} - \frac{1}{\epsilon_0 \varepsilon} \delta(z-z_0) \vec{z} \cdot \vec{P}(\kappa, z_0) e^{i\kappa \cdot R},
\]  

(2.37)

and \( \vec{B}(r, \kappa, z_0) \) is found as

\[
\vec{B}(r, \kappa, z_0) = \frac{i\omega^2 n}{2\epsilon_0 wc} e^{iw(z-z_0)} \theta(z-z_0) \left[ \hat{s}(\hat{p}_+ \cdot \vec{P}(\kappa, z_0)) - \hat{p}_+(\hat{s} \cdot \vec{P}(\kappa, z_0)) \right] e^{i\kappa \cdot R} + \frac{i\omega^2 n}{2\epsilon_0 wc} e^{-iw(z-z_0)} \theta(z_0-z) \left[ \hat{s}(\hat{p}_- \cdot \vec{P}(\kappa, z_0)) + \hat{p}_-(\hat{s} \cdot \vec{P}(\kappa, z_0)) \right] e^{i\kappa \cdot R}
\]  

(2.38)

[83]. In \( \vec{E}(r, \kappa, z_0) \) the first term corresponds to an upward field with the \( s- \) component proportional to \( \hat{s} \cdot \vec{P}(\kappa, z_0) \) and the \( p- \) component proportional to \( \hat{p}_+ \cdot \vec{P}(\kappa, z_0) \). The second term corresponds to a downward field with the \( s- \) component proportional to \( \hat{s} \cdot \vec{P}(\kappa, z_0) \) and the \( p- \) component proportional to \( \hat{p}_- \cdot \vec{P}(\kappa, z_0) \). The third term indicates a local field with a \( z \) component proportional to \( \hat{z} \cdot \vec{P}(\kappa, z_0) \), which is associated with the electrostatic field of the polarization source. The fields can be written as

\[
\vec{E}(r, \kappa, z_0) = \vec{G}_E(\kappa, z-z_0) \cdot \vec{P}(\kappa, z_0) e^{i\kappa \cdot R},
\]

\[
\vec{B}(r, \kappa, z_0) = \vec{G}_B(\kappa, z-z_0) \cdot \vec{P}(\kappa, z_0) e^{i\kappa \cdot R},
\]  

(2.39)

where \( \vec{G}_E \) and \( \vec{G}_B \) are Green functions, defined as
\[ G_E(\kappa, z - z_0) = \frac{i\omega^2}{2\epsilon_0w} e^{i\omega(z-z_0)} \theta(z - z_0)(\hat{s}\hat{s} + \hat{\mathbf{p}}_+\hat{\mathbf{p}}_+) \]
\[ + \frac{i\omega^2}{2\epsilon_0w} e^{-i\omega(z-z_0)} \theta(z_0 - z)(\hat{s}\hat{s} + \hat{\mathbf{p}}_+\hat{\mathbf{p}}_-) \]
\[ - \frac{1}{\epsilon_0\varepsilon} \delta(z - z_0) \hat{z}\hat{z}, \tag{2.40} \]

and
\[ G_B(\kappa, z - z_0) = \frac{i\omega^2 n}{2\epsilon_0wc} e^{i\omega(z-z_0)} \theta(z - z_0)(\hat{\mathbf{p}}_+ - \hat{\mathbf{p}}_-\hat{s}) \]
\[ + \frac{i\omega^2 n}{2\epsilon_0wc} e^{-i\omega(z-z_0)} \theta(z_0 - z)(\hat{\mathbf{p}}_- + \hat{\mathbf{p}}_-\hat{s}) \tag{2.41} \]

[83]. When (2.39) is inserted into (2.35), the electric and magnetic fields are
\[ E(r) = \int \frac{d\kappa}{(2\pi)^2} E(\kappa, z) e^{i\kappa \cdot R}, \]
\[ B(r) = \int \frac{d\kappa}{(2\pi)^2} B(\kappa, z) e^{i\kappa \cdot R}, \tag{2.42} \]

with
\[ E(\kappa, z) = \int G_E(\kappa, z - z_0) \cdot P(\kappa, z_0) dz_0, \]
\[ B(\kappa, z) = \int G_B(\kappa, z - z_0) \cdot P(\kappa, z_0) dz_0 \tag{2.43} \]

[83].

### 2.3.2 A point dipole near a planar interface

The Green function obtained for a source in a uniform medium is the starting point for calculations of dipole radiation in nonuniform media. Following the discussion in [84], we can calculate the fields of a point dipole near a planar structure. Consider a planar interface at \( z = 0 \), between medium 1 with dielectric constant \( \varepsilon_1 \) for \( z > 0 \), and medium 2 with dielectric constant \( \varepsilon_2 \) for \( z < 0 \). Assume a point dipole source with dipole moment \( \textbf{\mu} \) embedded in medium 1 a distance \( d \) above the interface (at \( z = d \), and \( x = y = 0 \), as in Fig. 2.6, so the polarization is
\[ P(r) = \textbf{\mu} \delta(R) \delta(z - d), \tag{2.44} \]
and can be written as
\[
P(r) = \int \frac{d\kappa}{(2\pi)^2} e^{i\kappa \cdot R} \mu \delta(z - d),
\]
thus \( P(\kappa, z) = \mu \delta(z - d) \). If the dipole were embedded in a uniform medium with dielectric constant \( \varepsilon_1 \), Eqs. (2.42) and (2.42) could be used to construct the electric field from

\[
E(\kappa, z) = G_E(\kappa, z - d) \cdot \mu
= \frac{i\tilde{\omega}^2}{2\epsilon_0 w_1} e^{iu_1(z - d)} \hat{\theta}(z - d) (\hat{s} \hat{s} + \hat{p}_{1+} \hat{p}_{1+}) \cdot \mu
\]

\[
+ \frac{i\tilde{\omega}^2}{2\epsilon_0 w_1} e^{-iu_1(z - d)} \hat{\theta}(d - z) (\hat{s} \hat{s} + \hat{p}_{1-} \hat{p}_{1-}) \cdot \mu.
\]

Here the local field contribution is ignored since we are interested in far field radiation,

\[
\begin{array}{c}
\mathcal{E}_1 \\
\downarrow \\
\mathcal{E}_2 \\
\downarrow \\
z = 0 \\
\end{array}
\]

Figure 2.6: A point dipole at \( z = d \) in medium 1, above a planar interface at \( z = 0 \).

where the effect of local field is not significant. To take into account the effect of the interface, note that in medium 1 the downward waves are reflected to upward waves by the interface. If the Fresnel reflection coefficients between medium 1 and medium 2, \( r_{12}^s/r_{12}^p \), are considered and the change of the polarization vectors is taken into account appropriately, in medium 1 and in the presence of the interface

\[
E(\kappa, z) = \frac{i\tilde{\omega}^2}{2\epsilon_0 w_1} e^{iu_1z} (e^{-iu_1d} \hat{s} \hat{s} + e^{-iu_1d} \hat{p}_{1+} \hat{p}_{1+}) \cdot \mu
\]

\[
+ \frac{i\tilde{\omega}^2}{2\epsilon_0 w_1} e^{iu_1z} (e^{iu_1d} r_{12}^s \hat{s} \hat{s} + e^{iu_1d} r_{12}^p \hat{p}_{1+} \hat{p}_{1-}) \cdot \mu.
\]

When a vector

\[
e(\kappa) = \frac{\tilde{\omega}^2}{4\pi\epsilon_0} \left( \hat{s} (e^{-iu_1d} \hat{s} + e^{iu_1d} r_{12}^s \hat{s}) + \hat{p}_{1+} (e^{-iu_1d} \hat{p}_{1+} + e^{iu_1d} r_{12}^p \hat{p}_{1-}) \right) \cdot \mu,
\]
is introduced, the electric field above the interface and in medium 1 is

$$E(r) = \int \frac{id\kappa}{2\pi w_1} e_1(\kappa)e^{i\nu_1 r}.$$  \hfill (2.49)

In the far field ($r \rightarrow \infty$) and at a fixed $\hat{r}$, the contribution associated with the wave vector that is exactly in the direction of $\hat{r}$ is expected to be most dominant in the above integral. The asymptotic calculations in [84] confirm this with

$$\int \frac{id\kappa}{2\pi w_1} e_1(\kappa)e^{i\nu_1 r} \sim e_1(\kappa) e^{i\omega n_1 r},$$  \hfill (2.50)

where $\kappa = \omega n_1 \hat{r} \cdot (\hat{x}\hat{x} + \hat{y}\hat{y})$ is the component of the wave vector $\omega n_1 \hat{r}$ in the plane of the interface. Thus, the electric field in medium 1 becomes

$$E(r) = \frac{\omega^2}{4\pi \epsilon_0} e^{-i\omega z} \left( s(e^{-i\omega d_s s} + e^{i\omega d_s s}) + \hat{p}_1(e^{-i\omega d_s p} + e^{i\omega d_s p}) \right) \cdot \mu.$$  \hfill (2.51)

The electric field in medium 2 can be calculated in a similar way. Here, there are no upward waves and the presence of the interface affects the transmission of the downward waves to medium 2. Using the appropriate Fresnel transmission coefficients between medium 1 and medium 2, $t_s^{12}/t_p^{12}$, and the relevant polarization vectors,

$$E(\kappa, z) = \frac{i\omega^2}{2\epsilon_0 w_1} e^{-i\omega z} \left( s(e^{i\omega d_s s} + e^{-i\omega d_s s}) + \hat{p}_2(e^{i\omega d_p p} + e^{-i\omega d_p p}) \right) \cdot \mu.$$  \hfill (2.52)

For

$$e_2(\kappa) = \frac{\omega^2}{4\pi \epsilon_0} \left( s\left( \frac{w_2}{w_1} e^{i\omega d_s s} \right) + \hat{p}_2 \left( \frac{w_2}{w_1} e^{i\omega d_p p} \right) \right) \cdot \mu,$$  \hfill (2.53)

the electric field below the interface in medium 2 is

$$E(r) = \int \frac{id\kappa}{2\pi w_2} e_2(\kappa)e^{i\nu_2 r}.$$  \hfill (2.54)

With an asymptotic expression similar to (2.50) the electric field in medium 2 becomes

$$E(r) = \frac{\omega^2}{4\pi \epsilon_0} e^{i\omega n_2 r} \left( s\left( \frac{w_2}{w_1} e^{i\omega d_s s} \right) + \hat{p}_2 \left( \frac{w_2}{w_1} e^{i\omega d_p p} \right) \right) \cdot \mu,$$  \hfill (2.55)

where $n_2 = \sqrt{\varepsilon_2}$, and the $\kappa$ dependent quantities are evaluated at $\kappa = \omega n_2 \hat{r} \cdot (\hat{x}\hat{x} + \hat{y}\hat{y})$ [84].

With the electric fields derived above and below the interface, it is straightforward
to find the magnetic fields from the first of (2.31), if desired. For a dipole near a more complicated planar interface such as a multilayer structure the fields can be calculated in a similar way, if the appropriate Fresnel coefficients are taken into account. This is discussed in more details in chapters 4 and 6, where spontaneous Raman scattering and CARS from molecules near multilayer structures are studied.
Chapter 3

LRSP in Asymmetric Multilayer Structures

LRSP with small propagation losses have attracted interest for a wide range of applications. In biosensing applications, when the cladding above the metal film is a gas or liquid, it is challenging to find a solid substrate that comes close to matching the cladding dielectric constant. If the cladding is an aqueous solution, Teflon and Cytop are two of the few candidate materials that can provide such a match [15,16]. An alternate approach is to design an asymmetric layered structure that can support LRSP; examples include a suspended waveguide structure [17] and 1D photonic crystal structures [18,19]. In particular, Konopsky has proposed a method based on impedance analysis [100,101] for designing 1D photonic crystal structures supporting LRSP [20]. In this chapter a new approach for designing asymmetric structures for LRSPs is presented by using a Fresnel coefficient pole analysis. Motivated by biosensing applications, a water cladding is considered and the focus is on minimizing the electric field in the metal in order to reduce the losses. In a scenario where the structure is used for sensing molecules adsorbed onto the metal film from the water, I calculate the value of a standard surface sensing parameter [5,17] that results and show that in the limit of thin molecular layers it can be derived from a semi-analytic expression that also follows from the pole analysis.

The organization of this chapter is as follows: In Sec. 3.1 a new strategy for designing a periodic multilayer structure supporting LRSPs is presented. In Sec. 3.2 I compare the intensity profile of the LRSP supported by the multilayer structure to the LRSP in a symmetric structure, and calculate absorption and coupling losses for finite symmetric and asymmetric structures. In Sec. 3.3 I derive a semi-analytic expression for a standard sensing parameter used to characterize the effect of thin molecular layers on the optical properties of arbitrary planar resonant structures, and compare exact and approximate
calculations for the structures studied in Sec. 3.2. The chapter ends with the conclusions and a comparison with related works.

### 3.1 Asymmetric multilayer structures for LRSPs

As a reference, consider a symmetric structure consisting of a thin layer of metal of thickness $d_m$ with a dielectric constant $\varepsilon_m$, sandwiched between a cladding and substrate of the same dielectric constant $\varepsilon_1$ (Fig. 3.1a). From Eq. (2.20) the Fresnel reflection coefficient for light incident on the metal from the cladding and with wavevector component $\kappa$ parallel to the interfaces is

$$R_{cs} = r_{1m} + \frac{t_{1m}r_{m1}t_{m1}e^{2i\omega_m d_m}}{1 - r_{m1}r_{m1}e^{2i\omega_m d_m}}, \quad (3.1)$$

where $w_i = \sqrt{\omega^2 \varepsilon_i - \kappa^2}$ and $\tilde{\omega} = \omega/c$. From the definition of $w_i$, it is clear that the Fresnel coefficients are functions of the wavenumber $\kappa$ or equivalently the angle of incidence $\theta$. It is straightforward to describe any Fresnel coefficient in terms of $\kappa$ or $\theta$ using Eqs. (A.5) and (A.6). In this chapter in order to reduce the complexity of the equations involving Fresnel coefficients of rather complicated structures, the $\kappa$ or $\theta$ dependence of the Fresnel coefficients are kept implicit.

As mentioned in chapter 2, the surface resonances of the structure in Fig. 3.1a satisfy

$$1 - r_{m1}^2e^{2i\omega_m d_m} = 0, \quad (3.2)$$

Eq. (3.2) can be satisfied at a resonance wavenumber $\kappa_{res}^{sym}$, which is complex due to absorption in the metal. The real part of $\kappa_{res}^{sym}$ is greater than $\tilde{\omega}n_1$, indicating a field bound to the region of the metal film. For a symmetric structure consider a gold metal layer with a thickness $d_m=20$ nm and water as the cladding and substrate. At a wavelength of $\lambda=1310$ nm with dielectric constants of water and gold taken as $\varepsilon_{water}=(1.3159+i1.639\times10^{-5})^2$ [17] and $\varepsilon_{gold} = -86.08 + i8.322$ [17], a numerical search of $\kappa$ in the complex plane identifies the symmetric LRSP mode by finding the complex value $\kappa_{res}^{sym}$ where the first of (2.22) is satisfied. I find an effective index of $n_{eff}^{sym}=1.31829+i5.3\times10^{-5}$ for the LRSP, where $n_{eff}^{sym} = \kappa_{res}^{sym}/\tilde{\omega}$. The very small imaginary part leads to a mode loss of about 2.23 dB/mm (also considered by Min et al. [17]) or equivalently an energy propagation length of about 1.95 mm. The resonance wavenumber of the antisymmetric mode, which satisfies the second of (2.22), has a larger real part and therefore the mode is more confined. However, the attenuation of the antisymmetric mode is much larger and its propagation
length is only about 8 μm. For calculations in this chapter the symmetric \( p- \) polarized mode, which is the long range excitation of the structure, is considered.

For a typical LRSP symmetric structure such as the one above, suppose that \( \kappa_{res}^{sym} \) has been found. I now want to design an asymmetric structure (Fig. 3.1b) where the substrate has been replaced by a multilayer structure to support LRSPs that mimic those of Fig. 3.1a. Any surface electromagnetic resonances in this new structure are

![Figure 3.1: (a) A symmetric structure for LRSP with a metal layer between two media with the same dielectric constant, (b) An asymmetric structure with a multilayer substrate beneath the metal layer, (c) an infinitesimally thin layer of medium with dielectric constant \( \varepsilon_1 \) inserted under the metal layer, and (d) an asymmetric structure with a metal film supported by an infinite periodic structure consisting of layers of dielectric constant \( \varepsilon_a \) and \( \varepsilon_b \).](image)

signalled by poles in the Fresnel coefficients, for example in the reflection coefficient for light incident from the cladding \( \bar{R}_{1s} \),

\[
\bar{R}_{1s} = r_{1m} + \frac{t_{1m} \bar{R}_{ms} t_{m1} e^{2i\omega_m d_m}}{1 - r_{m1} \bar{R}_{ms} e^{2i\omega_m d_m}},
\]

(3.3)

where \( \bar{R}_{ms} \) is the Fresnel reflection coefficient for light incident from a semi-infinite metal placed above the multilayer structure of interest in Fig. 3.1b. The reflection coefficient \( \bar{R}_{1s} \) has a pole when

\[
1 - r_{m1} \bar{R}_{ms} e^{2i\omega_m d_m} = 0.
\]

(3.4)

This will clearly lead to a \( \kappa_{res} \) equal to \( \kappa_{res}^{sym} \) (recall Eq. (3.2)), if

\[
\bar{R}_{ms} = r_{m1},
\]

(3.5)

where the Fresnel coefficients are evaluated at \( \kappa_{res}^{sym} \); I take this as the design target. Eq. (3.5) can be simplified so that it only involves the properties of the metal layer through a dependence on \( \kappa_{res}^{sym} \) by the following strategy: Insert an infinitesimally thin layer with a thickness of \( d_i \to 0 \) and dielectric constant \( \varepsilon_1 \) between the metal layer and the multilayer
(Fig. 3.1c). Then $\bar{R}_{ms}$ is easily found to be

$$\bar{R}_{ms} = r_{m1} + \frac{t_{m1}R_{1s}t_{1m}}{1 - r_{1m}R_{1s}},$$

(3.6)

where $R_{1s}$ is the Fresnel reflection coefficient for light incident from the cladding to the multilayer structure when there is no metal layer present. From Eq. (3.6) it is clear that (3.5) is satisfied if $R_{1s} = 0$ at $\kappa_{res}^{sym}$.

I now specialize to a periodic multilayer structure consisting of layers $a$ and $b$ with thicknesses $d_a$ and $d_b$ and real dielectric constants $\varepsilon_a$ and $\varepsilon_b$ and with $\varepsilon_a, \varepsilon_b > \varepsilon_1$. For an infinite periodic structure the Fresnel coefficient $R_{1s}$ is given by

$$R_{1s} = r_{1a} + \frac{t_{1a}R_{per}t_{a1}}{1 - r_{a1}R_{per}},$$

(3.7)

where the top layer is taken to be of type $a$ and $R_{per}$ is the reflection coefficient for light incident on the periodic structure from a semi-infinite medium of dielectric constant $\varepsilon_a$ (see Fig. 3.1d). In the second line of Eq. (3.7) the Fresnel coefficient identities $t_{ij}t_{ji} - r_{ij}r_{ji} = 1$ and $r_{ij} = -r_{ji}$ [83] have been used, and from that line it is clear that the condition $R_{1s} = 0$ is satisfied if

$$R_{per} = r_{a1},$$

(3.8)

which I refer to as the matching condition. When considering propagation of the LRSP, if the multilayer is to simulate a uniform substrate with dielectric constant equal to that of the cladding or at least nearly so, this condition must be satisfied or nearly satisfied, when the Fresnel coefficients are evaluated at $\kappa_{res}^{sym}$.

To establish a protocol for designing such a multilayer it is useful to begin by neglecting all loss in the cladding and the metal and any that might be present in the multilayer. In this approximation $\varepsilon_1, \kappa_{res}^{sym}$, and $n_{eff}^{sym}$ are replaced by their real parts. This lossless approximation will allow us to winnow down the parameter space easily to the point that the design can be completed; thus, until the last four paragraphs of this section I assume $\kappa_{res}^{sym} = \tilde{\omega}n_{eff}^{sym}$ and $\varepsilon_1$ to be real in our analyses and use the real parts of the actual quantities in our calculations.

The $\kappa_{res}^{sym}$ is to the right of the light line of the cladding and very close to the light line for the wavelength range of our interest. Thus, the field is evanescent in the cladding and $w_1$ is purely imaginary. I assume the dielectric constants of the layer materials are
large enough so that the fields are propagating within the layers themselves (\(w_a\) and \(w_b\) real), so \(|r_{a1}| = 1\) and from (3.8) we must have \(|R_{\text{per.}}| = 1\). This requires that at \(\kappa_{\text{res}}^{\text{sym}}\) we are within one of the photonic bandgaps of the multilayer structure, so that the overall field structure is evanescent in the multilayer and the reflectivity \(R_{\text{per.}}\) is of unit norm.

To identify the condition for this to be so, note that the unit cell transfer matrix of the periodic multilayer structure is 

\[
M_{\text{unit}} = M_a(d_a)M_{ab}M_b(d_b)M_{ba},
\]

and \(R_{\text{per.}}\) is calculated from the eigenvector of \(M_{\text{unit}}\),

\[
M_{\text{unit}} \left( \begin{array}{c} R_{\text{per.}} \\ 1 \end{array} \right) = e^{iKL} \left( \begin{array}{c} R_{\text{per.}} \\ 1 \end{array} \right)
\]

with eigenvalue \(e^{iKL}\), where \(L = d_a + d_b\) and \(K\) is the complex Bloch wavenumber. For an overall field structure that is evanescent in the multilayer structure, signalling that we are in a photonic bandgap, we must have \(|e^{iKL}| > 1\) \cite{72}. Writing the unit cell matrix elements by \(A, B, C,\) and \(D\),

\[
M_{\text{unit}} = \begin{pmatrix} A & B \\ C & D \end{pmatrix},
\]

we have

\[
R_{\text{per.}} = \frac{B}{e^{iKL} - A}
\]

with

\[
e^{iKL} = \frac{A + D}{2} \pm \sqrt{\left(\frac{A + D}{2}\right)^2 - 1}.
\]

\cite{72}. The \(M_{\text{unit}}\) is found by multiplying the appropriate transfer matrices; in particular,

\[
\frac{A + D}{2} = \frac{1}{1 - r_{ba}^2} \left( \cos(w_a d_a + w_b d_b) - r_{b a}^2 \cos(w_a d_a - w_b d_b) \right).
\]

Location within a bandgap (\(K\) purely imaginary, \(e^{iKL}\) real) is thus signalled by \(|A + D|/2 > 1\). At the band edges \(e^{iKL} = \pm 1\) and \(|A + D|/2 = 1\) \cite{72}. It is within the bandgaps that we have \(|R_{\text{per.}}| = 1\) and it is there we must seek to satisfy Eq. (3.8). This task can be addressed once a choice of multilayer materials (with fixed \(\varepsilon_a\) and \(\varepsilon_b\)) has been made. If we then consider letting \(d_a \to 0\), any existing bandgap will necessarily vanish since the medium will become uniform and at best we can have \(|A + D| = 2\) in the limit. From (3.13) we see that as \(d_a \to 0\) there are only discrete \(d_b\) (satisfying \(\cos(w_b d_b) = \pm 1\)) where this will hold. Similarly as \(d_b \to 0\) there are only discrete \(d_a\) (satisfying \(\cos(w_a d_a) = \pm 1\))
for which $|A + D| = 2$. Connecting the corresponding discrete points $(0, d_b)$ and $(d_a, 0)$ in the $(d_a, d_b)$ plane by straight lines should then give a rough indication of the location of the bandgaps as $d_a$ and $d_b$ are varied. Those straight lines are easily identified by

$$w_a d_a + w_b d_b = m\pi \quad \text{with} \quad m = 1, 2, 3, \ldots$$

(3.14)

Figure 3.2: (a) The $d_{SiO_2}$ and $d_{TiO_2}$ (solid black lines) for which $\kappa_{\text{res}}^{\text{sym}}$ is on a band edge of the periodic multilayer structure in the lossless case, and the straight lines of $w_{SiO_2} d_{SiO_2} + w_{TiO_2} d_{TiO_2} = m\pi$ (black dotted lines) with $m = 1, 2$. (b) The $d_{SiO_2}$ and $d_{TiO_2}$ for which $\kappa_{\text{res}}^{\text{sym}}$ is on a band edge of the periodic multilayer structure in the lossless case, and the straight lines of $w_{SiO_2} d_{SiO_2} + w_{TiO_2} d_{TiO_2} = m\pi$ (black dotted lines) with $m = 1, 2$.

Now consider periodic multilayers of SiO$_2$ and TiO$_2$, with the dielectric constants of SiO$_2$ and TiO$_2$ as $\varepsilon_{SiO_2} = \varepsilon_a = 2.0932$ [17] and $\varepsilon_{TiO_2} = \varepsilon_b = 7.421$ [94]. In Fig. 3.2a the solutions of Eq. (3.14) are plotted as dotted lines. The solid lines indicate the solutions for the band edges ($|A + D| = 2$ for $d_a$ and $d_b$ in general both nonzero) with the region in between each pair of lines indicating the values of $(d_a, d_b)$ for which $\kappa_{\text{res}}^{\text{sym}}$ is in the photonic bandgap. We see that the dotted lines do indeed give a good indication of where in the $(d_a, d_b)$ plane the bandgaps lie; I refer to the lines identified by Eq. (3.14) as guide lines. Note that the canonical “quarter-wave stack” with $w_a d_a = w_b d_b = \pi/2$ lies within the first bandgap and in fact is precisely on the line (3.14) with $m = 1$.

To satisfy the matching condition (3.8) at $\kappa_{\text{res}}^{\text{sym}}$ we must be in the bandgap region ($|R_{\text{per.}}| = |r_{a1}|$) and have $\arg (R_{\text{per.}}) = \arg (r_{a1})$. It is easy to determine where the latter condition is satisfied in the bandgap region, and I plot that as the blue dash dotted line in Fig. 3.2b, together with the solutions of Eq. (3.14) again as dotted lines, focusing on a
region of the \((d_a, d_b)\) plane where the \(m = 1\) guide line is close to the center of the bandgap region. Thus in the lossless limit it is possible to choose a multilayer structure so that (3.8) is exactly satisfied and the LRSPs in the symmetric and antisymmetric structures share the same \(\kappa_{sym}^{res}\). Note that while the structures that do this are characterized by values \((d_a, d_b)\) that lie close to the guide lines, the solutions of \(\arg(R_{per}) = \arg(r_{a1})\) do not run all the way to \(d_a = 0\) and \(d_b = 0\) as do the guide lines, since the solutions encounter the band edges before those limits are reached.

Now reinstate loss in \(\kappa_{sym}^{res}\) and in the water cladding. We no longer have \(|R_{per}| = |r_{a1}|\) holding automatically and to achieve (3.8) we would have to satisfy two nontrivial conditions, \(|R_{per}| = |r_{a1}|\) and \(\arg(R_{per}) = \arg(r_{a1})\). We can find curves in the \((d_a, d_b)\) plane where each of these conditions is satisfied, but for our choice of materials these curves do not intersect. So at least for some choices of dielectric materials it is impossible to satisfy (3.8) at \(\kappa_{sym}^{res}\) in the presence of losses; we cannot simply replace a uniform substrate with a periodic multilayer structure and maintain the same LRSP. Nonetheless, we can find \((d_a, d_b)\) for which (3.8) is satisfied at a complex wavenumber close to \(\kappa_{sym}^{res}\), denoted by \(\kappa_{asym}^{res}\). In fact this is possible for a wide range of values \((d_a, d_b)\) indicated by the red line in Fig. 3.2b. The \((d_a, d_b)\) points that satisfy (3.8) in the presence of losses (red line) are very close to the \((d_a, d_b)\) points that satisfy (3.8) in the absence of losses (the blue line). While the guide lines provide a rough estimation of where the \((d_a, d_b)\) of interest should be sought, the solutions of (3.8) in the lossless case give a better indication of the layer thicknesses satisfying (3.8) at a complex wavenumber close to \(\kappa_{sym}^{res}\). Note that in general the different points on the red line in Fig. 3.2b correspond to different values of \(\kappa_{asym}^{res}\), unlike the different points on the blue line which all correspond to Re(\(\kappa_{sym}^{res}\)).

A reasonable design strategy is to adopt thicknesses \((d_a, d_b)\) associated with the center of the bandgap region resulting in an LRSP with a field in the multilayer well-confined near the metal, and for which we can expect a better tolerance for any fabrication errors. In line with this but still somewhat arbitrarily, I take \(d_{SiO_2} = d_a = 453.5\) nm and \(d_{TiO_2} = d_b = 161\) nm for the rest of this chapter. This yields an \(n_{asym}^{res} = \kappa_{asym}^{res}/\tilde{\omega} = 1.31824 + i 5.17 \times 10^{-5}\) corresponding to a loss of 2.15 dB/mm and an energy propagation length of about 2 mm. The real part of \(n_{asym}^{res}\) is very close to the real part of \(n_{sym}^{res}\) and the loss for the asymmetric structure is actually slightly less than the loss for the LRSP of the original symmetric structure. Thus, while our original goal was to match \(\kappa_{sym}^{res}\) and achieve the low loss of a LRSP in a symmetric structure, we find that using a multilayer structure it is possible to achieve even lower loss than in a symmetric structure.

To verify that the resonance mode supported by the multilayer structure is indeed a
LRSP, the intensity distribution of the mode is shown in Sec. 3.2.

3.2 LRSP intensity distribution

Some insight into the nature of the LRSPs in the infinite symmetric and asymmetric structures (see Fig. 3.3) can be gained by comparing the LRSP field profiles in the two structures. A fair comparison involves field profiles that are associated with the different structures and have the same field energy. Scaling the intensity profiles of the resonances in the two structures in the same way (see Eq. (2.15) and [86]) yields the results shown in Fig. 3.4. The intensity in the cladding ($z > 0$) is evanescent and very similar in the two structures. In the metal layer (inset) the intensity in the multilayer structure overlaps with the intensity in the symmetric structure and both reach zero at the center of the metal layer. While $|E|^2$ is symmetric about the center of the gold film in the symmetric structure, it exhibits an evanescent envelope function in the multilayer in the asymmetric structure. Compared to an earlier proposed multilayer structure for the LRSP [19], in this structure the field is less confined but the attenuation is smaller in the metal layer. The minimum intensity in the metal film is the signature of LRSP mode excitation, and the resonant mode in Fig. 3.4 is clearly distinguishable from Fabry-Perot resonances that are not in the photonic bandgap.

In realistic structures the behavior of the fields is modified by the presence of substrates. While I continue to treat the cladding as infinite assuming that in sensing applications the thickness of the water above the gold will be greater than the evanescent decay length of the field, I now consider the gold to be deposited on a finite multilayer structure with an SiO$_2$ substrate (see Fig. 3.5b). For comparison I also consider a struc-
Figure 3.4: The normalized intensity profile (see text below) of the resonant mode of the asymmetric structure (solid blue line) and the LRSP mode of the symmetric structure (dash dot red line). Inset: the zoomed intensity profile in gold. The \( z \) axis is normal to the plane of the structure, and the (top) gold-water interface is at \( z = 0 \).

Figure 3.5: (a) A finite symmetric (b) finite asymmetric multilayer structure, supporting LRSP.

ture with an SiO\(_2\) substrate placed a finite distance below the gold film in an otherwise symmetric structure (see Fig. 3.5a). The properties of the LRSP that result in these structures can be studied by considering coupling into them with an incident field from the substrate, which is the usual Kretschmann configuration [6] mentioned in chapter 2. In such an excitation the reflected field to the substrate is minimized when the rate of energy incident from the substrate equals the rate of energy absorption in the metal layer [102], and thus this usually identifies an optimum structure for sensing applications. For the symmetric structure this critical coupling occurs when the thickness of the water layer below the gold film is about 4.59 \( \mu \)m, and for the asymmetric structure it occurs when the number of periods is 25 corresponding to a multilayer thickness of 15.36 \( \mu \)m.
Fig. 3.6a shows the reflectivity $|R|^2$ of the two structures, each at its critical coupling thickness, as a function of angle of incidence; $R$ is the Fresnel coefficient for $p$-polarized light incident from the substrate. The enhancement of the fields at the surface of each structure is determined by the Fresnel transmission coefficient from the substrate to the cladding for $p$-polarized light, $T$, and we see from Fig. 3.6b that an enhancement in the square of the field of the order of 400 is expected. The narrow resonances shown in these plots indicate poles in the Fresnel coefficients $R$ and $T$. With respect to the poles in the corresponding infinite structures (see Fig. 3.3), the real parts of the poles are shifted slightly and the imaginary parts (and thus the losses) are increased due to radiative coupling into the substrate. A search in the complex plane finds the pole for the symmetric structure at $\kappa = \bar{\omega} n_{\text{eff}}^{\text{sym}}$, where $n_{\text{eff}}^{\text{sym}} = 1.31814 + i 1.11 \times 10^{-4}$, with the imaginary part corresponding to a loss of about 4.6 dB/mm, or equivalently an energy propagation length of about 0.94 mm, and the pole for the asymmetric structure at $\kappa = \bar{\omega} n_{\text{eff}}^{\text{asym}}$, where $n_{\text{eff}}^{\text{asym}} = 1.31825 + i 1.05 \times 10^{-4}$ with the imaginary part corresponding to a loss of about 4.39 dB/mm or equivalently an energy propagation length of 1 mm.

The dips in the reflectivities in Fig. 3.6a occur at angles $\theta^{\text{sym, asym}}$ associated with the real part of effective indices $\text{Re}(n_{\text{eff}}^{\text{sym}}) = n_{\text{SiO}_2} \sin \theta^{\text{sym}}$ and $\text{Re}(n_{\text{eff}}^{\text{asym}}) = n_{\text{SiO}_2} \sin \theta^{\text{asym}}$ respectively, where $n_{\text{SiO}_2} = 1.447$ is the index of refraction of the substrate at $\lambda=1310$ nm, and the widths of the dips are associated with the imaginary parts of the effective indices. Note that in extracting the poles of the Fresnel coefficients, we should choose a definition of the square roots of $w_i(\kappa)$ such that the calculated values of the Fresnel coefficients in

![Figure 3.6](image)
the upper half of the complex $\kappa$ plane join continuously to those calculated on the real $\kappa$ axis. This can be guaranteed by choosing a branch cut that lies along the negative imaginary $\kappa$ axis. This ensures that the positions and widths of the resonances in Fig. 3.6, which are calculated by evaluating the Fresnel coefficients at real $\kappa$, agree with the real and imaginary parts of the complex resonance wavenumbers given by poles of the Fresnel coefficients in the complex $\kappa$ plane.

![Figure 3.7: The loss of the LRSP in the symmetric (dash dot red line) and asymmetric (solid blue line) structures as the thickness of the structures changes.](image)

If we turn from Kretschmann configurations to applications involving end-fire coupling into LRSPs [93], optimization for sensing applications typically involves the minimization of propagation loss. That loss decreases as the thickness of the structure between the metal film and the substrate increases, since for larger thicknesses the radiative loss of light into the substrate decreases. In Fig. 3.7 the calculated losses of the LRSPs in the symmetric and asymmetric structures are shown as a function of the thickness of the structure, as extracted from the poles of the Fresnel coefficients. In the symmetric structure for a water layer thickness larger than about 15 $\mu$m the mode loss approaches a limiting value of 2.23 dB/mm corresponding to the mode loss of the infinite structure; in the asymmetric structure for a multilayer thickness larger than about 30 $\mu$m (49 periods) the mode loss approaches a limiting value of 2.15 dB/mm corresponding to the mode loss of the infinite structure.

### 3.3 Sensing with planar resonant structures

Optical properties of resonant structures supporting guided modes, such as those considered above, are modified by the presence of new species on the surface of the structure...
where the fields are largest. Thus, these devices can be used as sensors detecting changes near the surface. In this section I derive a semi-analytic expression for a standard surface sensing parameter that characterizes the effectiveness of such a sensor, and apply it to the structures introduced in the last section.

Consider an arbitrary planar resonant structure (Fig. 3.8a) supporting a resonant mode at a complex wavenumber $\kappa_{res}^0 = \kappa_R + i\kappa_I$. If a thin molecular layer with effective dielectric constant $\varepsilon_2$ is placed on the structure (Fig. 3.8b), the complex wavenumber of the mode shifts and a surface sensing parameter can be defined as

$$G = \frac{1}{\kappa_I} \frac{\partial}{\partial d} \text{Re}(\Delta \kappa_{res})$$  \hspace{1cm} (3.15)$$

where $\Delta \kappa_{res} = \kappa_{res}^m - \kappa_{res}^0$ and $\kappa_{res}^m$ is the complex wavenumber of the mode in the presence of the molecular layer. For $\kappa$ close to $\kappa_{res}^0$ we can use a pole expansion \cite{81,85}

Figure 3.8: (a) A bare resonant structure with a cladding of dielectric constant $\varepsilon_1$, (b) with a thin layer of molecules with dielectric constant $\varepsilon_2$ on top, (c) an infinitesimally thin layer of medium 1 under the molecular layer, and (d) the molecular layer between to medium with dielectric constant $\varepsilon_1$.

for the reflection coefficient from the cladding to the bare resonant structure, denoted by $\bar{R}_{1s}$, such that

$$\bar{R}_{1s} \sim \frac{\rho_{1s}}{\kappa - \kappa_{res}^0},$$  \hspace{1cm} (3.16)$$

where $\rho_{1s}$ characterizes the pole strength and is in general complex. For the resonant structure with the molecular layer on top modelled as a thin dielectric film, we can construct an expression for the Fresnel reflection coefficient $\bar{R}'_{1s}$ in terms of $\bar{R}_{1s}$ by adding an infinitesimally thin layer with a thickness $d_i \to 0$ and a dielectric constant $\varepsilon_1$ just below the molecular layer (Fig. 3.8c). Then

$$\bar{R}'_{1s} = R + \frac{TR_{1s}T}{1 - RR_{1s}},$$  \hspace{1cm} (3.17)$$

where $R$ and $T$ are the Fresnel reflection and transmission coefficients for the molecular
layer sandwiched between two media with dielectric constant $\varepsilon_1$ (Fig. 3.8 d). When (3.16) is inserted into Eq. (3.17),

$$\bar{R}'_{1s} = R + \frac{T\rho_{1s}T}{\kappa - (\kappa_{res}^0 + R\rho_{1s})}$$

(3.18)

implying that the complex wavenumber of the mode in the presence of molecules is $\kappa_{res}^m = \kappa_{res}^0 + R\rho_{1s}$ and the shift in the complex wavenumber is

$$\Delta\kappa_{res} = R\rho_{1s}.$$  

(3.19)

The pole strength $\rho_{1s}$ is a parameter of the bare resonant structure and does not depend on the properties of the molecular layer; in general it must be determined numerically. The reflection coefficient $R$ (see Fig. 3.8d), however, is

$$R = r_{12} + \frac{t_{12}r_{21}t_{21}e^{2iw_2d}}{1 - r_{21}r_{21}e^{2iw_2d}}$$

(3.20)

where $d$ is the thickness of the molecular layer and $r_{12}$, $t_{12}$, $r_{21}$, and $t_{21}$ are the Fresnel reflection and transmission coefficients between the cladding and the molecular layer (recall (A.5) and (A.6)). When (A.5) or (A.6) are inserted into Eq. (3.20) and for thin molecular layers with

$$(w_1 \pm w_2)d \ll 1,$$

(3.21)

for $s$-polarization

$$R \approx \frac{n_{os}}{1 - n_{os}}$$

(3.22)

with

$$n_{os} = \frac{i\bar{\omega}^2}{2w_1}(\varepsilon_2 - \varepsilon_1)d,$$

while for $p$-polarization

$$R \approx \frac{n_-}{1 - n_+}$$

(3.23)

with

$$n_\pm = \frac{i\kappa^2}{2w_1} \frac{(\varepsilon_2 - \varepsilon_1)d}{\varepsilon_2} \pm \frac{i w_1}{2} \frac{(\varepsilon_2 - \varepsilon_1)d}{\varepsilon_1}.$$

These calculations agree with the similar calculations presented earlier by Cheng et al. [103]; using (3.22) or (3.23), and (3.19) in Eq. (3.15), I find a semi-analytic expression for the surface sensing parameter in terms of the thickness of the molecular layer, the dielectric constants of the molecular layer and the cladding, and the pole strength. I assume a molecular layer with an effective index of refraction of 1.5 and thickness up to 10
nm, and calculate the sensing parameters for the symmetric and asymmetric structures discussed in the previous section, both exactly by numerically determining the shift $\Delta \kappa_{\text{res}}$ in the position of the pole of the full structures and approximately from the semi-analytic expressions presented in this section; here the $p$-polarized expressions are the relevant ones. In Fig. 3.9 the results for $\text{Re}(\Delta \kappa_{\text{res}})/\kappa_I$ of the infinite symmetric and asymmetric structures are shown. The semi-analytic calculations match with the exact calculations for $d < 5$ nm, but as the thickness of the molecular layer increases the assumption (3.21) loses its validity and the approximated calculations deviate more from the exact calculations; nonetheless, they remain accurate to about 10% for thicknesses as large as 10 nm. The slope of the curves in Fig. 3.9 around $d=0$ gives $G$, and $G=1.09$ nm$^{-1}$ and $G=1.28$ nm$^{-1}$ are obtained for the infinite symmetric and asymmetric structure, respectively; the larger $G$ for the asymmetric structure is due to the slightly smaller resonance width ($\kappa_I$) in the asymmetric structure. From Fig. 3.7 it is clear that if the thickness of the finite symmetric (or asymmetric) structure is larger than about 15 $\mu$m (or 30 $\mu$m), the loss in the structure is about the same as the loss in the corresponding infinite structure. As expected, the results for $\text{Re}(\Delta \kappa_{\text{res}})/\kappa_I$ for a 15 $\mu$m symmetric structure and a 30 $\mu$m asymmetric structure are indistinguishable from the corresponding infinite structures, as shown in Fig. 3.9. I have done similar calculations for the finite symmetric and asymmetric structures at thicknesses corresponding to the critical coupling thickness ($4.59$ $\mu$m for the symmetric structure and 15.36 $\mu$m for the asymmetric structure), and the result is
shown in Fig. 3.10. These would be relevant for sensing in a Kretschmann configuration rather than an end-fire coupling configuration. I find $G=0.55$ nm$^{-1}$ and $G=0.63$ nm$^{-1}$ for the finite symmetric and asymmetric structures, respectively, which are smaller than the corresponding values shown in Fig. 3.10 as the coupling losses are larger here.

### 3.4 Conclusion

In this chapter I have presented a new strategy for designing asymmetric multilayer structures that support LRSPs. I have shown that if the Fresnel reflection coefficient from the cladding to the multilayer structure below the metal film vanishes at the complex wavenumber of the LRSP in a symmetric structure, the LRSP resonance condition for the symmetric and asymmetric multilayer structures become the same and the asymmetric structure supports a LRSP equivalent to that supported in the symmetric structure. For an arbitrary choice of materials for the multilayer structure, it is impossible to satisfy this condition exactly but at a complex wavenumber close to that of the LRSP in the symmetric structure, and a LRSP is found with even less loss than that of the LRSP in the symmetric structure. In these calculations the radiation and scattering losses due to surface roughness in the layered structures have not been considered. In particular, the multilayer structure that consists of a larger number of layers is expected to be more significantly affected by these losses.

I have provided a protocol for determining this resonance condition based on first describing a model system without loss, and then including the loss in the final design.
I have also studied how the losses depend on the thickness of the multilayer structure, taking into account radiative contributions to the substrate. For the multilayer of SiO$_2$ and TiO$_2$ the radiative losses are minimum if the multilayer structure thickness is about or greater than 30 $\mu$m.

For biosensing applications involving an arbitrary planar resonant structure, I have derived a semi-analytic expression for a standard surface sensing parameter identifying the dependence of the sensing parameter on the dielectric constant of the molecular layer, its thickness, and the original pole strength of the resonance on the bare structure; for typical parameters there is a good match between these semi-analytic expressions and the exact results if the thickness of the molecular layer is less than about 5 nm, with corrections only on the order of about 10% for molecular layer thicknesses up to 10 nm. For a 20 nm gold film the surface sensing parameter for the 30 $\mu$m thick multilayer structure is $G = 1.28$ nm$^{-1}$, and is larger than the value of $G = 1.09$ nm$^{-1}$ for a 15 $\mu$m thick symmetric structure.

The design strategy presented here can be applied to a range of structures involving other metals and other multilayers to systematically explore the parameter space and optimize the predicted behavior. Designing LRSP structure can be done using impedance matching strategies [100,101], where the existence of surface waves between medium 1 and 2 with impedances $Z_1$ and $Z_2$, respectively, requires the condition $Z_1 + Z_2 = 0$ to be satisfied. Konopsky has proposed an impedance matching protocol for designing asymmetric multilayer structures supporting LRSPs [20]. In Konopsky’s approach, the thickness parameters of the periodic multilayer structure are determined by maximizing the bandgap and the thickness of the metal layer is calculated by solving an impedance matching condition at a particular wavenumber. Further adjustments of the thickness of the metal film and other layers of the multilayer structure might be necessary for fabrication purposes [20]. The approach presented in this chapter is based on Fresnel coefficient pole analysis and provides a simple linear expression as a rough estimation for the thickness parameters of a multilayer structure that is completely periodic. Compared to the structure studied by Konopsky et al. [19], the multilayer structure presented here does not require an additional layer between the metal and the periodic multilayer. However, a direct comparison of the losses and the surface sensing parameters of these two structures is not possible, as the metal layer in the work of Konopsky et al. [19] is palladium, which is lossier than gold. Nevertheless, if the number of the periods in that multilayer structure is increased from 14 periods, the mode losses can be decreased by a factor of two. Compared to the 20nm gold structure of Min et al. [17], which has an intensity attenuation of 3.26 dB/mm and a surface sensing parameter $G = 1.29$ nm$^{-1}$,
the asymmetric multilayer structure presented here has a smaller loss (minimum of 2.15 dB/mm) and a similar sensing parameter \((G=1.28 \text{ nm}^{-1})\). However, the structure of Min et al. [17] is a thin film suspended in air and compared to the multilayer structure discusses here is expected to be less stable and harder to fabricate.

In chapter 4 I calculate Raman scattering from molecules on planar resonant dielectric structures and show that the Raman signal is enhanced when the pump field couples to a resonant mode. The asymmetric multilayer structure studied in this chapter can also be used as a substrate for surface enhanced Raman scattering (SERS) [7] when the pump field is coupled to the LRSP excitation. In particular, the good surface functionalization of gold films make these structures more promising SERS substrates than fully dielectric multilayer structures [104].
Chapter 4

SERS in Multilayer Structures

In this chapter a theoretical study of SERS from molecules adsorbed on planar multilayer structures and probed in the Kretschmann configuration [6] is presented. The Kretschmann configuration has been widely employed in biosensing based on changes in the refractive index [7,105]. In this configuration the scattered signal is detected through a prism substrate, reducing the interaction of the scattered field with the solution containing the analyte; as well, microfluidic systems for the delivery of the analytes are easily envisioned. Moreover, this configuration allows for the coupling of the scattered field into guided modes of the planar structure, which as we see in this chapter, further enhances radiation in specific directions; this may be important for extensions to multiplexing.

This chapter is organized as follows: As a benchmark I begin in Sec. 4.1.1 by calculating the Raman cross section for a molecule embedded in a uniform background medium, adopting a simple isotropic model for the Raman polarizability. Although in a design study for a particular sensing application this would have to be replaced by a more realistic model, the simple isotropic model allows us to focus on the enhancement of the Raman scattering in the different planar geometries. In Sec. 4.1.2 I describe the Raman scattering from a molecule over a very general multilayer structure, identifying expressions for the Raman scattering into the cladding and substrate. The results are expressed in terms involving the Fresnel coefficients of the structure. This allows for identification of any guided modes and construction of approximate semi-analytic expressions characterizing their effects as well as the implementation of numerical calculations. In Sec. 4.2 I turn to example calculations involving particular multilayer structures. Besides waveguide and Bloch surface wave structures, planar surface plasmon structures are also considered. While these are not the best metallic structures for SERS, they provide an

Chapter 4. SERS in Multilayer Structures

indication of what Raman signal enhancement could be achieved with the kind of planar
surface plasmon structures commonly used in biosensing [7,105]. All these calculations
employ a plane wave analysis, which can be suspect with resonant structures. In Sec. 4.3
the results are generalized to excitation with finite beams and corrections to the plane
wave analysis are considered. In Sec. 4.4 I present the conclusions.

4.1 Raman cross section

I calculate spontaneous Raman scattering within a semi-classical approximation: The
incident field is taken as classical but the vibrations in the molecule are treated quantum
mechanically. All optical fields are taken to be at frequencies far below any electronic
resonances. The response of the molecule to incident radiation is described by a polar-
izability tensor $\alpha(t)$, which is modulated by molecular vibration. The dipole moment is
$\mathbf{\mu}(t) = \alpha(t)E(t)$, where $E(t)$ is the field at the position of the molecule resulting from
the incident beam. In this approach $\mathbf{\mu}(t)$ is an operator by virtue of its dependence on
the molecular vibration through $\alpha(t)$. Thus the radiated fields are operators too, and
the scattered light is calculated by taking the expectation value of the resulting Poynting
vector operator. This allows for capturing the correct intensities of Stokes and anti-Stokes
radiation.

I take the polarizability tensor to be of the form

$$\alpha(t) = \alpha_0 + \sum_{\xi} \alpha_{1\xi} q_\xi(t), \quad (4.1)$$

where $\alpha_0$ and $\alpha_{1\xi}$ are respectively the Rayleigh polarizability tensor and the Raman
polarizability tensor associated with the vibrational degree of freedom $\xi$; $q_\xi(t)$ is the
canonical coordinate associated with this degree of freedom. Since our main concern
here is the enhancement of Raman scattering that can result from the use of multilayer
structures and not the detailed description of the Raman scattering from a particular
molecule, I consider only one degree of freedom and model the vibration as a harmonic
oscillator at frequency $\omega_0$. I consider only spontaneous processes and, ignoring the de-
tails of the frequency width of the Raman lines due to coupling of the molecule with
environmental degrees of freedom, take

$$q(t) = \left( \frac{\hbar}{2m\omega_0} \right)^{1/2} (ae^{-i\omega_0 t} + a^\dagger e^{i\omega_0 t}), \quad (4.2)$$

where $a$ and $a^\dagger$ are the lowering and raising operators of the harmonic oscillator, re-
spectively. I now denote the Raman polarizability tensor simply by $\alpha_1$; to simplify the calculations the Raman polarizability is treated as isotropic with $\alpha_1$ proportional to the unit tensor, and the proportionality constant is denoted by $\alpha_1$. Generalization to treat more realistic polarizability tensors is straightforward.

### 4.1.1 A molecule in free space

Consider a molecule embedded in a uniform medium with real refractive index $n_1(\omega)$, and subject to a continuous wave (CW) incident pump field at frequency $\omega_P$; I make calculations by assuming an incident pump pulse with duration $T$,

$$E_{\text{inc}}(t) = \begin{cases} \mathcal{E}e^{-i\omega_P t} + \text{c.c.} & -T/2 < t < T/2, \\ 0 & \text{otherwise}, \end{cases}$$

(4.3)

where $E_{\text{inc}}(t)$ is the electric field at the position of the molecule, and finally take the limit $T \to \infty$. For all fields $f(t)$ positive and negative frequency parts are introduced as

$$f^{\pm}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f^{\pm}(\omega)e^{-i\omega t},$$

(4.4)

where $f^{\pm}(\omega) = \theta(\pm\omega)f(\omega)$ with $\theta(s) = 1, 0$ as $s > 0, s < 0$, and

$$f(\omega) = \int_{-\infty}^{\infty} f(t)e^{i\omega t}dt.$$

(4.5)

Then, for $\omega_P \gg \omega_0$ to good approximation the positive frequency component $\mu^+(\omega)$ of the dipole moment operator is related to the positive frequency components of the incident field,

$$\mu^+(\omega) = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \alpha_1 (\alpha E_{\text{inc}}^+(\omega - \omega_0) + a^\dagger E_{\text{inc}}^+(\omega + \omega_0)),$$

(4.6)

where Rayleigh scattering has been neglected. The fields radiated by this resulting dipole moment can be found from the usual solutions [42] of the Maxwell equations,

$$E^+(\mathbf{r}, \omega) = \frac{\tilde{\omega}^2}{4\pi \epsilon_0} \frac{e^{i\tilde{\omega} n_1 r}}{r} (\hat{\mathbf{r}} \times \mu^+(\omega)) \times \hat{\mathbf{r}},$$

$$H^+(\mathbf{r}, \omega) = \frac{\tilde{\omega}^2 n_1 c e^{i\tilde{\omega} n_1 r}}{4\pi} \frac{\mathbf{r} \times (\hat{\mathbf{r}} \times \mu^+(\omega))}{r},$$

(4.7)

where $c$ is the speed of light, and $\tilde{\omega} = \omega/c = 2\pi/\lambda$ is the (circular) wavenumber. The quantities $E^+(\mathbf{r}, \omega)$ and $H^+(\mathbf{r}, \omega)$ are operators by virtue of the fact that $\mu^+(\omega)$ is an
operator. The radiated energy per area per unit time at position \( r \) with respect to the molecule is
\[
S(r, t) = E(r, t) \times H(r, t).
\]

Integration over time gives
\[
\int_{-\infty}^{\infty} S(r, t) dt = \int_{0}^{\infty} S(r, \omega) d\omega,
\]

where
\[
S(r, \omega) = \frac{1}{2\pi} \left( (E^+(r, \omega))^\dagger \times H^+(r, \omega) - (H^+(r, \omega))^\dagger \times E^+(r, \omega) \right)
\]

is the radiated energy per area per unit frequency interval at position \( r \). From (4.7) and (4.10),
\[
S(r, \omega) = \frac{\tilde{\omega}^4 n_1 c}{16\pi^3 \epsilon_0 r^2} \Gamma_{\text{free}}(\hat{r}) : (\hat{\mu}^+(\omega))^\dagger \hat{\mu}^+(\omega),
\]

where \( \Gamma_{\text{free}}(\hat{r}) = \delta^{ij} - r^i r^j / r^2 \) and the colon product of tensor \( T \) and vectors \( A \) and \( B \) is defined as \( T : AB = T^{ij} A^i B^j \). The expectation value of \( S(r, \omega) \) is
\[
\langle S(r, \omega) \rangle = \frac{\tilde{\omega}^4 n_1 c}{16\pi^3 \epsilon_0 r^2} \Gamma_{\text{free}}(\hat{r}) : \langle (\hat{\mu}^+(\omega))^\dagger \hat{\mu}^+(\omega) \rangle.
\]

From (4.6) and (4.3), in the limit \( \omega_P T \gg 1 \),
\[
\frac{\langle (\hat{\mu}^+(\omega))^\dagger \hat{\mu}^+(\omega) \rangle}{T} = \frac{\pi(\alpha_1 \ell_A)^2}{2} E^* E \delta(\omega - \omega_P - \omega_0)
+ \frac{\pi(\alpha_1 \ell_S)^2}{2} E^* E \delta(\omega - \omega_P + \omega_0),
\]

where
\[
\ell_S = \sqrt{\left(\frac{h}{2m\omega_0}\right)(\bar{n} + 1)} \quad \text{and} \quad \ell_A = \sqrt{\left(\frac{h}{2m\omega_0}\right)\bar{n}}
\]
are characteristic lengths associated with Stokes and anti-Stokes radiation respectively, and \( \bar{n} = (e^{h\omega_0/k_B T} - 1)^{-1} \) is the average number of the vibrational excitations. When the temperature approaches zero, \( \ell_A \) vanishes and \( \ell_S \) characterizes the zero-point motion of the oscillator. On the contrary, when \( k_B T \gg h\omega \), \( \ell_A \) and \( \ell_S \) become equal and characterize the thermal motion of the oscillator.
The radiated energy per unit area per time at position \( \mathbf{r} \) is

\[
\frac{1}{T} \int_0^\infty \langle \mathbf{S}(\mathbf{r}, \omega) \rangle d\omega = \frac{\tilde{\omega}_S^4 n_1(\omega_S) c}{32\pi^2 \varepsilon_0} (\alpha_1 \ell_S)^2 \hat{\mathbf{r}} \cdot \hat{\mathbf{r}} \Gamma_{\text{free}}(\hat{\mathbf{r}}, \omega_S) : (\mathbf{E}^* \cdot \mathbf{E})
\]
\[
+ \frac{\tilde{\omega}_A^4 n_1(\omega_A) c}{32\pi^2 \varepsilon_0} (\alpha_1 \ell_A)^2 \hat{\mathbf{r}} \cdot \hat{\mathbf{r}} \Gamma_{\text{free}}(\hat{\mathbf{r}}, \omega_A) : (\mathbf{E}^* \cdot \mathbf{E}),
\]

where \( \omega_S = \omega_P - \omega_0 \) and \( \omega_A = \omega_P + \omega_0 \) are the Stokes and anti-Stokes frequencies, and the first and second term correspond to the Stokes \( \mathbf{h}_S \) and anti-Stokes \( \mathbf{h}_A \) radiation, respectively. If we consider only the Stokes field, the total power radiated at \( \omega_S \) is given by

\[
P_S = \int \langle \mathbf{S}_S(\mathbf{r}) \rangle \cdot \hat{\mathbf{r}} r^2 d\Omega = \frac{\tilde{\omega}_S^4 n_1(\omega_S) c}{12\pi \varepsilon_0} (\alpha_1 \ell_S)^2 \mathbf{E}^* \cdot \mathbf{E},
\]

where \( \langle \mathbf{S}_S(\mathbf{r}) \rangle \) has been integrated over the solid angle \( \Omega \). We can define the Stokes Raman differential cross section in a uniform medium as

\[
\sigma_S^o(\hat{\mathbf{r}}) = \frac{\langle \mathbf{S}_S(\mathbf{r}) \rangle \cdot \hat{\mathbf{r}} r^2}{S_P},
\]

where

\[
S_P = \frac{2n_1(\omega_P)}{c \mu_0} (\mathbf{E}^* \cdot \mathbf{E})
\]

is the magnitude of the Poynting vector of the pump field. I obtain

\[
\sigma_S^o(\hat{\mathbf{r}}) \equiv \frac{\tilde{\omega}_S^4 n_1(\omega_S)}{4n_1(\omega_P)} \left( \frac{\alpha_1 \ell_S}{4\pi \varepsilon_0} \right)^2 \Gamma_{\text{free}}(\hat{\mathbf{r}}, \omega_S) : (\hat{\mathbf{e}}_{inc} \cdot \hat{\mathbf{e}}_{inc}),
\]

where the incident field is taken to be polarized along \( \hat{\mathbf{e}}_{inc} \). Finally, the total Raman cross section is found by integrating \( \sigma_S^o(\hat{\mathbf{r}}) \) over the solid angle

\[
\sigma_S^o = \int \sigma_S^o(\hat{\mathbf{r}}) d\Omega = \frac{2\pi \tilde{\omega}_S^4 n_1(\omega_S)}{3n_1(\omega_P)} \left( \frac{\alpha_1 \ell_S}{4\pi \varepsilon_0} \right)^2.
\]

Similar results for the radiated power and the differential cross-section are obtained for the anti-Stokes radiation.

### 4.1.2 A molecule above a planar structure

Now I turn to the problem of interest (see Fig. 4.1). A molecule is embedded in a medium of real refractive index \( n_1(\omega) \) at a distance \( d \) above a planar structure oriented with a normal vector \( \hat{\mathbf{z}} \) and extending from \( z = 0 \) to \( z = D \) with a uniform substrate medium
with real refractive index \(n_N(\omega)\) for \(z < 0\). I take the position of the molecule to be 
\[ r_0 = (d + D) \hat{z} + R_0, \]
where \(R_0 = (x_0, y_0)\). Consider a configuration in which the pump beam is incident from the substrate such that the field at the position of the molecule, \(E_L(t)\), is

\[
E_L(t) = \begin{cases} 
E_L e^{-i \omega_0 t} + c.c & -T/2 < t < T/2, \\
0 & \text{otherwise}.
\end{cases}
\]

In analogy to (4.6) the expression for the induced dipole moment of the molecule can be written

\[
\mu^+(\omega) = \left( \frac{\hbar}{2m\omega_0} \right)^{1/2} \alpha_1 (a E_L^+ (\omega - \omega_0) + a^\dagger E_L^+ (\omega + \omega_0)).
\]

As discussed in chapter 2, the fields radiated by the dipole are modified in the presence of the structure [84]. In particular, in the cladding

\[
E^+(r, \omega) = \int \frac{id\kappa}{2\pi w_1} e_1(\kappa, \omega) e^{i\mu_{1+}r},
\]

where

\[
e_1(\kappa, \omega) = \frac{\bar{\omega}^2}{4\pi\epsilon_0} (\hat{s} \gamma_{s1}(\kappa, \omega) + \hat{p}_1 + \gamma_{p1}(\kappa, \omega)) \cdot \mu^+(\omega),
\]

with

\[
\gamma_{s1}(\kappa, \omega) = (e^{-i\mu_{1d}} + e^{i\mu_{1d}} R_{1N}^s) \hat{s},
\]

\[
\gamma_{p1}(\kappa, \omega) = (e^{-i\mu_{1d}} \hat{p}_1 + e^{i\mu_{1d}} R_{1N}^p \hat{p}_1).\]

The unit polarization vectors of the radiated field are defined according to (2.7), and \(R_{1N}^s\) and \(R_{1N}^p\) are the Fresnel reflection coefficients (from the cladding to the substrate) for \(s\) and \(p\) polarizations, respectively. As we are interested in the far field radiation, I consider the asymptotic limit \(r \to \infty\) for a fixed \(\hat{r}\). The far field radiation is expected to
be dominated by the contribution associated with the wavevector that is exactly in the
direction of $\hat{r}$. This is indeed the case \[84\] and the field (4.23) in the cladding and far
from the dipole source is given by

$$E^+(r, \omega) \sim \frac{\tilde{\omega}^2}{4\pi \epsilon_0} (\hat{\mathbf{s}} \gamma_{s1}(\kappa, \omega) + \hat{\mathbf{p}}_{1+} \gamma_{p1}(\kappa, \omega)) \cdot \mu^+(\omega) \frac{e^{i\omega_1 r}}{r},$$  \hspace{1cm} (4.26)

and

$$H^+(r, \omega) \sim \frac{n_1 \tilde{\omega}^2}{4\pi} (\hat{\mathbf{s}} \gamma_{p1}(\kappa, \omega) - \hat{\mathbf{p}}_{1+} \gamma_{s1}(\kappa, \omega)) \cdot \mu^+(\omega) \frac{e^{i\omega_1 r}}{r},$$  \hspace{1cm} (4.27)

where $\kappa = \tilde{\omega} n_1 (\hat{x} \hat{x} + \hat{y} \hat{y}) \cdot \hat{r}$ and the bars on each quantity indicate its evaluation at $\kappa$.

When Eq. (4.26) and (4.27) are inserted into (4.10), the Stokes radiation per time per
unit area in the cladding at $r$ is found as

$$\langle S_S(r) \rangle = \frac{\tilde{\omega}_S^2 n_1(\omega_S)c}{32\pi^2 \epsilon_0} (\alpha_1 \ell_S)^2 \frac{\hat{r}}{r^2} \Gamma_{clad}(\hat{r}, \omega_S) : (E_L^* E_L),$$  \hspace{1cm} (4.28)

with

$$\Gamma_{clad}(\hat{r}, \omega_S) = \gamma_{s1}^* (\kappa, \omega_S) \gamma_{s1}(\kappa, \omega_S) + \gamma_{p1}^* (\kappa, \omega_S) \gamma_{p1}(\kappa, \omega_S).$$  \hspace{1cm} (4.29)

Now we can relate $\langle S_S(r) \rangle$ to the field incident from the substrate. I take that field to be

$$E_{inc}(r, t) = E e^{i k^p \cdot R} e^{i \omega t} e^{-i \omega pt} + c.c.,$$  \hspace{1cm} (4.30)

within the time window $T$ (4.21). The superscript $P$ on a quantity indicates evaluation
for the pump beam. Here $E = E e_{inc} = (F_s \hat{\mathbf{s}}^P + F_p \hat{\mathbf{p}}_{N+}^P) E$, where $F_s$ and $F_p$ indicate the $s-$ and $p-$ polarized components of the incident beam, $|F_s|^2 + |F_p|^2 = 1$. Then the field
at the position of the molecule is specified by

$$E_L = e_L(\kappa^p, \omega_P) E e^{i k^p \cdot R},$$  \hspace{1cm} (4.31)

with

$$e_L(\kappa^p, \omega_P) = (T_{N1}^s(\kappa^p, \omega_P) F_s \hat{\mathbf{s}}^P + T_{N1}^p(\kappa^p, \omega_P) F_p \hat{\mathbf{p}}_{N+}^P) e^{i \omega t}.\hspace{1cm} (4.32)$$

where $T_{N1}^s$ and $T_{N1}^p$ are the Fresnel transmission coefficients for $s$ and $p$ polarizations, respectively. From (4.31) and (4.28),
\[ \langle S_S(r) \rangle = \frac{\tilde{\omega}_S^4 n_1(\omega_S) c |\mathcal{E}|^2}{32\pi^2 \epsilon_0} (\alpha_1 \ell_S)^2 \frac{\hat{r}}{r^2} \Gamma_{clad}(\hat{r}, \omega_S) : (e_L^* e_L). \quad (4.33) \]

Analogous to (4.17) we can define the Stokes cross section for the molecules on planar structures as
\[ \sigma_S(\hat{r}) = \frac{\langle S_S(r) \rangle \cdot \hat{r} r^2}{S_P}, \quad (4.34) \]
where
\[ S_P = \frac{2n_N(\omega_P)}{c\mu_0} (\mathcal{E}^* \cdot \mathcal{E}). \quad (4.35) \]
Thus, the differential Stokes cross section for the radiation into the cladding becomes
\[ \sigma_S(\hat{r}) = \frac{\tilde{\omega}_S^4 n_1(\omega_S)}{4n_N(\omega_P)} \left( \frac{\alpha_1 \ell_S}{4\pi \epsilon_0} \right)^2 \Gamma_{clad}(\hat{r}, \omega_S) : (e_L^* e_L). \quad (4.36) \]

It is convenient to introduce a normalized differential cross section, \( \bar{\sigma}_S(\hat{r}) \), by dividing \( \sigma_S(\hat{r}) \) by the total cross section calculated assuming the molecule is embedded in a uniform medium of index \( n_1(\omega) \),
\[ \bar{\sigma}_S(\hat{r}) = \frac{\sigma_S(\hat{r})}{\sigma_S^*} = \frac{3n_1(\omega_P)}{8\pi n_N(\omega_P)} \Gamma_{clad}(\hat{r}, \omega_S) : (e_L^* e_L). \quad (4.37) \]
From (4.29), (4.32), and (4.37) we have
\[ \bar{\sigma}_S(\hat{r}) = \frac{3}{8\pi n_N(\omega_P)} \left( |\gamma_{s1}(\vec{k}, \omega_S) \cdot e_L|^2 + |\gamma_{p1}(\vec{k}, \omega_S) \cdot e_L|^2 \right). \quad (4.38) \]
For an arbitrary \( \vec{k} \) I take \( \phi \) to be the angle \( \vec{k} \) makes with \( \vec{k}^P \) such that
\[ \tilde{s} = \hat{s}^P \cos \phi + \hat{k}^P \sin \phi, \]
\[ \tilde{\vec{k}} = -\hat{s}^P \sin \phi + \hat{k}^P \cos \phi. \quad (4.39) \]
Then the normalized differential cross section (4.37), which contains several inner products, will be a function of \( \phi \) and \( \theta \) with \( \theta \) the angle between \( \hat{r} \) and \( \hat{z} \) (See Fig. 4.1). In a typical experimental set-up a detector will average only over a small range of \( \theta \) and \( \phi \). In planar structures the dependence on \( \phi \) arises largely from the nature of the Raman tensor. For an isotropic Raman polarizability the resulting \( \phi \) dependence of the Raman signal is weak and unrealistically small, because of the choice of our simple model, chosen to focus on the effect of the resonances of a planar structure, which have their main dependence on \( \theta \). To concentrate on this latter dependence in a simple way, I focus on
the integral of the differential cross section over $\phi$,

$$\bar{\sigma}_{\text{clad}}(\theta) = \int_0^{2\pi} \bar{\sigma}_S(\hat{r})d\phi, \quad (4.40)$$

which gives

$$\bar{\sigma}_{\text{clad}}(\theta) = \frac{3}{8} \frac{n_P}{n_N} \left( \left| (1 + e^{2i\omega_1 d} R_{1N}^s) T_{N1}^P F_s e^{i(w_P^f - w_1)d} \right|^2 
+ \left| (1 + e^{2i\omega_1 d} R_{1N}^s) \frac{w_1^P}{\omega P N_1^P} T_{N1}^P F_p e^{i(w_P^f - w_1)d} \right|^2 
+ 2 \left| \frac{\kappa}{\omega n_1} (1 + e^{2i\omega_1 d} R_{1N}^p) \frac{\kappa P}{\omega P N_1^P} T_{N1}^P F_p e^{i(w_P^f - w_1)d} \right|^2 
+ \left| \frac{w_1}{\omega n_1} (1 - e^{2i\omega_1 d} R_{1N}^p) \frac{w_1^P}{\omega P N_1^P} T_{N1}^P F_p e^{i(w_P^f - w_1)d} \right|^2 
+ \left| \frac{w_1}{\omega n_1} (1 - e^{2i\omega_1 d} R_{1N}^p) T_{N1}^P F_s e^{i(w_P^f - w_1)d} \right|^2 \right). \quad (4.41)$$

Other than the quantities evaluated at $\kappa^P$ and $\omega_P$, as indicated by the superscript $P$, all quantities are evaluated at $\bar{\kappa}$ and $\omega_S$. Equation (4.41) describes the azimuthally integrated differential Stokes cross section for radiation into the cladding in terms of the Fresnel coefficients of the structure, which can be numerically calculated using the transfer matrix method [106]. The result is a sum of several terms, which depend on the fraction of the incident intensity that is transmitted through the structure multiplied by that fraction scattered into the cladding, which includes the direct scattered amplitude as well as the reflected scattered amplitude from the structure. The total normalized Stokes cross section for the radiation into the cladding is found by integrating $\bar{\sigma}_{\text{clad}}(\theta)$ over the angle $\theta$,

$$\bar{\sigma}^\text{tot}_{\text{clad}} = \int_0^{\pi/2} \bar{\sigma}_{\text{clad}}(\theta) \sin(\theta)d\theta. \quad (4.42)$$

The Stokes cross section for the radiation into the substrate can be found following the same approach. Analogous to the expressions (4.26) and (4.27), the radiated electromagnetic fields into the substrate are [84]

$$\mathbf{E}^+(r, \omega) \sim \frac{\tilde{\omega}^2}{4\pi \varepsilon_0} \left( \tilde{s}_\gamma_{SN}(\bar{\kappa}, \omega) + \tilde{p}_{N-\gamma_{pN}}(\bar{\kappa}, \omega) \right) \cdot \mathbf{\mu}^+(\omega) \frac{e^{i\tilde{\kappa}m_{NR}}}{r}, \quad (4.43)$$
and

\[ H^+(r, \omega) \sim \frac{n_N C \bar{\omega}^2}{4\pi} (\bar{s} \gamma_{pN}(\bar{\kappa}, \omega) - \bar{p}_N - \gamma_{sN}(\bar{\kappa}, \omega)) \cdot \mu^+(\omega) \frac{e^{\bar{\omega} \omega_N r}}{r}, \]  

(4.44)

with

\[ \gamma_{sN}(\bar{\kappa}, \omega) = \left( \frac{w_N T_{1N}^s e^{i w_1 d}}{w_1} \right) \bar{s}, \]
\[ \gamma_{pN}(\bar{\kappa}, \omega) = \left( \frac{w_N T_{1N}^p e^{i w_1 d}}{w_1} \right) \bar{p}_N. \]  

(4.45)

Here \( \bar{\kappa} = \bar{\omega} n_N (\hat{x} \hat{x} + \hat{y} \hat{y}) \cdot \hat{r} \) and the overbars again denote evaluation at \( \bar{\kappa} \). Similar to the calculations for the Stokes radiation in the cladding, the Stokes radiation per unit time per unit area in the substrate is

\[ \langle S_S(r) \rangle = \frac{\bar{\omega}^4 n_N(\omega_S)}{32\pi^2 \varepsilon_0} (\alpha_1 \ell_S)^2 \frac{r^2}{r^2} \Gamma_{sub}(\hat{r}, \omega_S) : (e^*_L e_L), \]  

(4.46)

with

\[ \Gamma_{sub}(\hat{r}, \omega_S) = \gamma_{sN}^*(\hat{\kappa}, \omega_S) \gamma_{sN}(\hat{\kappa}, \omega_S) + \gamma_{pN}^*(\hat{\kappa}, \omega_S) \gamma_{pN}(\hat{\kappa}, \omega_S). \]  

(4.47)

The normalized differential cross section in the substrate is then found as

\[ \bar{\sigma}_S(\hat{r}) = \frac{3 n_1(\omega_P) n_N(\omega_S)}{8\pi n_1(\omega_S) n_N(\omega_P)} \Gamma_{sub}(\hat{r}, \omega_S) : (e^*_L e_L). \]  

(4.48)

We can then find the azimuthally integrated differential cross section for the radiation into the substrate

\[ \bar{\sigma}_{sub}(\theta) = \frac{3 n_1^P n_N}{8 \bar{\omega} n_1 n_N^P} \left| \frac{w_N T_{1N}^s}{w_1} T_{N1}^s F_s e^{i(w_P^1 + w_1) d} \right|^2 + \left| \frac{w_N T_{1N}^p}{w_1} T_{N1}^p F_p e^{i(w_P^1 + w_1) d} \right|^2 \]  

+ \left| \frac{w_N T_{1N}^p}{\bar{\omega} n_1} T_{N1}^p F_p e^{i(w_P^1 + w_1) d} \right|^2 + \left| \frac{w_N T_{1N}^p}{\bar{\omega} n_1} T_{N1}^p F_p e^{i(w_P^1 + w_1) d} \right|^2 \]  

+ \left| \frac{w_N T_{1N}^p}{\bar{\omega} n_1} T_{N1}^p F_p e^{i(w_P^1 + w) d} \right|^2. \]  

(4.49)
where $T_{s1}^N$ and $T_{p1}^N$ are the Fresnel transmission coefficients from the cladding to the substrate. As it is expected, (4.49) shows that the cross section in the substrate depends on the fraction of the incident intensity transmitted through the structure from substrate to the cladding multiplied by that fraction scattered through the structure from cladding to the substrate. The total Stokes cross section for radiation into the substrate is then

$$\bar{\sigma}_{\text{tot}}^{\text{sub}} = \int \frac{\bar{\sigma}_{\text{sub}}(\theta) \sin(\theta)}{\pi/2} d\theta,$$

where

$$(4.50)$$

analogous to (4.42).

We are interested in structures that have poles in their Fresnel coefficients. For example, if the structure has a resonance at the Stokes frequency for s-polarization, the transmission coefficient $T_{s1}^N$ will have a pole at a complex wavenumber $\kappa_{res}^S$,

$$T_{1N}^s \sim \frac{\tau_{1N}^S}{\kappa - \kappa_{res}^S},$$

for $\kappa$ close to $\kappa_R^S \equiv Re(\kappa_{res}^S)$, where $\kappa_{res}^S = \kappa_R^S + i\kappa_I^S$, and $\tau_{1N}^S$ is also in general a complex number. Thus, for an incident s- polarized pump field (4.49) simplifies to

$$\bar{\sigma}_{\text{sub}}(\theta) \sim \frac{3 n_1^P n_N^P}{8 n_1 n_N} \frac{w_N}{w_1} \left| T_{1N}^P e^{(w_P^r + w_1)} d \right|^2 \frac{|\tau_{1N}^S|^2}{(\kappa - \kappa_R^S)^2 + (\kappa_I^S)^2};$$

near the resonance. To calculate the contribution of the pole to $\bar{\sigma}_{\text{sub}}^{\text{tot}}$, I evaluate the slowly varying terms in (4.52) at $\theta_R = \sin^{-1}\left(\frac{\kappa_R^S}{\kappa_I^S}\right)$, where the Lorentzian is centered and integrate over the Lorentzian. The resonance contribution to the total Stokes cross section in the substrate becomes

$$\bar{\sigma}_{\text{pole}}^{\text{sub}} \simeq \frac{|\tan \theta_R|}{2n_N} \lambda \kappa_I^S \bar{\sigma}_{\text{max}}^{\text{pole}},$$

where $\bar{\sigma}_{\text{max}}^{\text{pole}}$ comes from evaluating (4.52) at $\theta_R$. Equation (4.52) and (4.53) show that the resonance contribution $\bar{\sigma}_{\text{pole}}^{\text{sub}}$ scales with the inverse of $\kappa_I^S$ and thus is maximized by maximizing the propagation length $((\kappa_I^S)^{-1})$ of the excitation signaled by the resonance (4.51). I will show examples of this below.

### 4.2 SERS in multilayered structures

The approach presented in the previous section can be used to describe Raman scattering in an arbitrary planar structure. Here we are interested in the enhancement of the
Raman scattering due to the resonant coupling of both pump and Stokes radiations into the guided modes of layered structures. In particular, I consider three types of guided modes: a Bloch surface wave (BSW) supported by a periodic multilayer, a waveguide mode (WG) supported by a slab waveguide, and a surface plasmon (SP) supported by a metal/dielectric interface. While my focus here is on dielectric structures, and it is well-known that the Raman scattering from molecules at smooth metal surface can be significantly enhanced by introducing roughness, I include the planar SP structure because such structures are of interest in sensing applications[7] and from the fundamental optics point of view.

I present example calculations for pumps at 532 nm and 1064 nm and consider a Raman shift of $3000 \text{ cm}^{-1}$ [107]. For the metal I choose gold. For the dielectric materials I choose SiO$_2$ and Ta$_2$O$_5$. Commonly used in Raman filters, these dielectrics are expected to exhibit a weak photoluminescence when pumped in the energy ranges of interest. I first consider semi-infinite versions of these structures, shown in Fig. 4.2, taking the cladding in all structures to be air.

The multilayer structure shown in Fig. 4.2a is a truncated 1D photonic crystal with a unit cell composed of two layers of thicknesses $d_{\text{SiO}_2}=153 \text{ nm}$ and $d_{\text{Ta}_2\text{O}_5}=87 \text{ nm}$ and two additional top layers of thickness $d_{\text{top, Ta}_2\text{O}_5}=10 \text{ nm}$ and $d_{\text{top, SiO}_2}=10 \text{ nm}$. It supports an $s-$ polarized BSW over a wide range of wavelengths that includes $\lambda=532 \text{ nm}$; the BSW dispersion relation and the band regions are shown in the figure, where the dependence of the refractive indices on the photon energy is taken into account [108]. While the position of the photonic bandgap is determined by the choice of the unit cell, the dispersion relation of the BSW depends mainly on the truncation of the photonic crystal and it is very sensitive to the thickness of the two layers closest to the cladding. As expected, the BSW is found within the bandgap region and below the cladding (air) light-line. Indeed, the mode is confined at the multilayer side by the photonic bandgap and at the cladding side by total internal reflection. I also consider a second structure, with a unit cell composed of two layers of thicknesses $d_{\text{SiO}_2}=401 \text{ nm}$ and $d_{\text{Ta}_2\text{O}_5}=223 \text{ nm}$ and two top layers of $d_{\text{top, Ta}_2\text{O}_5}=65 \text{ nm}$ and $d_{\text{top, SiO}_2}=10 \text{ nm}$; it supports an $s-$ polarized BSW over a wide range of wavelengths that includes $\lambda=1064 \text{ nm}$.

The slab waveguide structures consist of SiO$_2$ covered with a single layer of Ta$_2$O$_5$; I choose a thickness of 100 nm for Ta$_2$O$_5$ for a pump at $\lambda=532 \text{ nm}$, and 200 nm for a pump at $\lambda=1064 \text{ nm}$. Waveguide modes (WG) are confined by total internal reflection from the cladding as well as from the underlying SiO$_2$; Fig. 4.2b shows the dispersion relation of the $s-$ polarized fundamental WG mode for the first of these two structures. As expected, it lies below the light-lines of air and SiO$_2$. 
Figure 4.2: (a) Bloch surface waves dispersion curve (red solid) and cladding light-line (LL) (black dash) (b) Waveguide dispersion curve (red solid), cladding light-line (black dash), and substrate light-line (dash-dot) (c) surface plasmon dispersion curve (red solid) and cladding light-line (black dash).
The third system under investigation supports surface plasmons that exist at a metal/dielectric interface. In this case, the surface plasmon dispersion relation is for the gold/air interface, and is shown in Fig. 4.2c, where I have used Johnson and Christy’s gold dielectric function [90] and plotted the real part of the surface plasmon wavenumber \( \kappa_{SP} = \tilde{\omega} \sqrt{\varepsilon_m / (\varepsilon_m + 1)} \) (see Eq. (2.19)), where \( \varepsilon_m \) is the dielectric constant of the metal. Here the confinement is due to total internal reflection from the cladding and the evanescent behavior in the metal resulting from the negative real part of the dielectric function.

It is worth noticing that BSW and WG dispersion relations can be adjusted on demand by modifying the geometrical parameters of the structures. In contrast, the SP dispersion relation of the simple structure considered here is essentially determined by the dielectric function of the chosen materials.

### 4.2.1 Pump intensity enhancement

I now turn to the finite versions of these structures, which can be employed in sensing devices based on the Kretschmann geometry [6], as shown in Fig. 4.3. The prism material is chosen so that its light-line lies to the right of the dispersion relation of the guided mode of interest. Thus the truly guided modes of the corresponding infinite systems become leaky, allowing coupling of pump radiation into and out of the modes through the prism.

![Figure 4.3: Structures](image)

From (4.31) and (4.32) we see that for a molecule at a distance \( d \) above a multilayer the pump field amplitude depends on the \( s- \) and/or \( p- \) polarized Fresnel coefficients \( T_{N1} \). In particular, when the structure supports a guided mode, such a transmission coefficient has a pole in the complex plane and an enhancement \( |E_L/E|^2 \) occurs as light incident from the prism is coupled into the mode through prism. Fig. 4.4 shows this *pump enhancement factor* associated with the modes under investigation as a function...
of the detuning of the pump incident angle, $\theta_p$, from $\theta_0$, which is the coupling angle that corresponds to the maximum enhancement and it is different in the three cases. Here I take $d=1$ nm, a BK7 prism with index $n_{\text{prism}}=1.5$ for the BSW and SP structures, and a gadolinium gallium garnet prism with $n=1.98$ for the WG structures; note that the BK7 prism could not be used for the latter, since the effective indices of the guided modes are greater than 1.5. As a reference I also indicate the pump enhancement factor in the cladding at $d=1$ nm above a bare prism (Fig. 4.3d), where there is no mode. In all but the surface plasmon structure $s-$ polarized light is considered.

![Figure 4.4](image)

Figure 4.4: Pump enhancement factor for multilayer (red solid), waveguide (green dash), surface plasmon (purple dash dot), and bare prism (brown dash dot dot) at (a) 532 nm and (b) 1064 nm. In (a) the very small rise in $|\mathcal{E}_L/\mathcal{E}|^2$ as $\theta \to \theta_0$ for the surface plasmon and bare prism structures can not be seen.

The pump enhancement factor increases as the mode losses decrease. For the dielectric structures (Fig. 4.3a,b), where there is no absorption and scattering losses due to fabrication imperfections are neglected, it diverges as the number of periods (thickness of the buffer layer) of the BSW structure (WG structure) increases, and the angular width of the peak tends to zero. In plotting Fig. 4.4 I have chosen 5(3) periods for the multilayer designed for 532 nm (1064 nm), and a buffer thickness of 340 nm (640 nm) for the waveguide designed for 532 nm (1064 nm). These parameters give $\Delta \kappa_{\text{res}} \simeq 20(\Delta \kappa_{2\text{mm}})$, where $\Delta \kappa_{\text{res}}$ is the width of the resonance at the pump frequency and $\Delta \kappa_{2\text{mm}}$ is the spread in $\kappa$ corresponding to an incident beam of width 2 mm. I confirm in Sec. 4.3 that the plane wave analysis we are pursuing here will be accurate for such a beam. For the surface plasmon structure, if the thickness of the metal layer is too small, the SP will be strongly damped due to radiation leaking to the substrate. If the thickness of the metal layer is too large, the SP can not be excited efficiently due to absorption losses
in the metal. I have chosen a metal thickness of 50 nm, as it gives the maximum pump enhancement factor (at $\theta_0$). Compared to the dielectric structures, the SP resonance is broader and its width is determined both by absorption losses and coupling losses into the prism with the two contributions roughly equal. The surface plasmon structure shows a particularly poor enhancement at $\lambda=532$ nm, due to large losses in the metal. These are reduced by working at longer wavelengths, but even at $\lambda=1064$ nm the enhancement for the surface plasmon structure is smaller than that shown by the dielectric structures.

4.2.2 Stokes radiation

As discussed in Sec. 4.1, the Raman scattering process can be treated as a two step process: (i) the pump field at the position of the molecule induces a dipole moment proportional to the amplitude of the local field, and (ii) the Stokes field is radiated by the induced dipole. In the previous section I showed that the incident field at the position of the molecule can be enhanced when a leaky mode is excited through the prism, and the appropriate $T_{N1}$ at the pump frequency becomes large. To optimize the Raman signal, for each structure I choose a fixed incident angle at which the pump enhancement factor $|E_L/E|^2$ is maximized; here the induced dipole oscillates at its largest amplitude and the dipole radiates everywhere into the cladding and substrate. From (4.49) we see that the Stokes radiation in particular directions in the substrate can be further enhanced if $T_{1N}$ is large at the Stokes frequency, for example in the presence of a leaky mode at that frequency. In this case the Stokes radiation can resonantly couple through that mode before exiting through the prism. The designed structures and the choice of the proper prism allow this “double resonance” condition for Stokes shifts up to 3000 cm$^{-1}$. In contrast, since there is no channel for the coupling of light from the modes into the cladding, there is no additional enhancement in Stokes or anti-Stokes radiation in that direction.

Calculation for the azimuthally integrated differential cross-section for Stokes radiation into the substrate are shown in Fig. 4.5; note the logarithmic scale. For each structure there is a strong peak corresponding to the coupling of the Stokes field to leaky modes. In addition, for the WG and BSW structures other small peaks appear. These correspond to Fabry-Perot interferences, typical of a multilayered structure. The strong suppression of Stokes signal around the BSW peak is due to the photonic bandgap, which attenuates the transmission of the Stokes radiation through the multilayer. The calculations show a maximum enhancement of about $10^6$ and $10^5$ for the BSW and WG structures at 532 nm (Fig. 4.5a), and more than $10^4$ for the SP structures at 1064 nm.
Figure 4.5: Normalized differential cross section for the scattered field in the substrate (a) $\lambda=532$ nm (b) $\lambda=1064$ nm for multilayer (red solid), waveguide (green dash), surface plasmon (purple dash dot), and bare prism (brown dash dot dot) structures.

(Fig. 4.5b).

Figure 4.6: Integrated Raman cross section versus the distance of the molecule from the surface of the structure (a) $\lambda=532$ nm (b) $\lambda=1064$ nm for multilayer (red solid), waveguide (green dash), surface plasmon (purple dash dot), and bare prism (brown dash dot dot) structures. The $\bar{\sigma}_{\text{sub}}^{\text{tot}}$ of SP and bare prism structures have been multiplied by 20.

It is interesting to consider $\bar{\sigma}_{\text{sub}}^{\text{tot}}$ (see (4.50)), the total normalized cross-section for Raman radiation in the substrate. In a scenario where additional optical elements are used to collect the scattered light over a wide range of angles in the substrate, this would be the relevant parameter to characterize the overall enhancement of the collected Raman scattered light. Fig. 4.6 shows $\bar{\sigma}_{\text{sub}}^{\text{tot}}$ as a function of the distance $d$ of the molecule from
the surface of the structure; \( \sigma_{\text{tot}}^{\text{sub}} \) decreases as \( d \) increases, since at the significant \( \kappa \) all the fields in the cladding are evanescent. Note that the \( \sigma_{\text{tot}}^{\text{sub}} \) calculations for the SP and bare prism structures are multiplied by 20. The total Raman cross section in the substrate and cladding add up to a value that is within a factor of two of the pump field intensity enhancement. Roughly speaking, this indicates that although resonance coupling of the Stokes field results in large Stokes cross section in specific directions, the total Stokes cross section only benefits from the pump field resonance coupling and light is only redistributed in space due to the Stokes resonance coupling.

We can also find the contribution of the resonance coupling of the Stokes field to the total Stokes cross section using (4.53). While \( \sigma_{\text{pole}}^{\text{sub}} / \sigma_{\text{sub}}^{\text{tot}} \) is only about 0.25 for the WG structures and about 0.60 for the BSW structures, it reaches to 1 for the SP structures. Unlike the dielectric structures, the metallic structure leads to an increase in the radiation only when the scattered field is coupled through the SP modes. Indeed, the light that is scattered by the molecule above the metal layer is transmitted into the substrate only through the excitation of the SP, since the metal/air interface reflectivity is very high.

### 4.3 Finite beam corrections

![Figure 4.7: A finite beam of light incident on the multilayer structure, and its reflected beam.](image)

In Sec. 4.1.2 we assumed the incident beam to be a plane wave (4.30) within our time window \( T \). Taking \( \kappa_P \) to lie in the \( x \) direction and choosing a new set of direction identified by \( (x'y'z') \), where \( z' \) indicates the direction in which the plane wave is propagating,

\[
\begin{align*}
x' &= -z \sin \theta_P + x \cos \theta_P, \\
y' &= y, \\
z' &= z \cos \theta_P + x \sin \theta_P
\end{align*}
\] (4.54)

(see Fig. 4.7), the field (Eq. (4.30)) can be written as \( \mathbf{E}_{\text{inc}}(x', y', z') \exp(-i\omega_P t) + c.c.\),
where \( \mathbf{E}_{\text{inc}}(x', y', z') = \hat{s}^p \mathbf{E}_{\text{inc}}(x', y', z') \) if the incident plane wave is \( s \)-polarized and \( \mathbf{E}_{\text{inc}}(x', y', z') = \hat{p}^p \mathbf{E}_{\text{inc}}(x', y', z') \) if it is \( p \)-polarized, with

\[
\mathbf{E}_{\text{inc}}(x', y', z') = \mathcal{E} e^{i \nu_N^p z'}
\]  

(4.55) actually depending only on \( z' \) and \( \nu_N^p = \tilde{\omega}_P n_N \). In a more realistic treatment we should consider a finite incident beam, which is a superposition of many plane waves with slightly different propagation directions and therefore slightly different wavevectors. This is particularly important for our dielectric structures, as they support very narrow resonant modes, and thus coupling is possible in a very small angular range.

For the finite incident beam I use \( \theta_P \) to indicate only the angle of incidence of the central wavevector in the superposition, which I now take to define the \( z' \) direction. Indeed, in moving from the field of an incident plane wave to the field of an incident finite beam resulting from such a superposition, (4.55) is replaced by an expression for the incident field that will depend on \( x' \) and \( y' \) as well as \( z' \). I neglect the small differences between the polarization vectors of each component in the superposition, which I take to yield a finite beam that is approximately linearly polarized, and assume that the polarization direction of the full field can be approximated by either \( \hat{s}^p \) or \( \hat{p}^p \) for the central component. For simplicity I take the amplitude \( \mathbf{E}_{\text{inc}}(x', y', z') \) of the incident finite beam to be a Gaussian, given by

\[
\mathbf{E}_{\text{inc}}(x', y', z') = \mathcal{E} e^{i \nu_N^p z'} e^{-\left(\frac{x'^2 + y'^2}{2\Delta^2}\right)}
\]  

(4.56)

where \( \Delta \) determines the width of the beam; this replaces the plane wave limit (4.55), and we have

\[
\int |\mathbf{E}_{\text{inc}}(x', y', z')|^2 \, dx' \, dy' = |\mathcal{E}|^2 A,
\]  

(4.57)

where \( A = \pi \Delta^2 \).

Using our original coordinate system, taking \( E_{\text{inc}}(x, y, z) = \mathcal{E}_{\text{inc}}(x', y', z') \), we can write (4.56) as

\[
E_{\text{inc}}(x, y, 0) = e^{i \nu_N^p x \sin \theta_P} \mathcal{E} f_{\text{inc}}(x, y)
\]  

(4.58)

along the plane \( z = 0 \), where

\[
f_{\text{inc}}(x, y) = e^{-\frac{x^2 \cos^2 \theta_P}{2\Delta^2}} e^{-\frac{y^2}{2\Delta^2}}.
\]  

(4.59)

The pump field driving the molecules is the field that results at \( z = D + d \), but I first determine the field at \( z = D^+ \), denoted by \( E_{\text{clad}}(x, y, D) \); as for \( E_{\text{inc}}(x, y, 0) \), we can
approximately characterize its polarization by that of the central component, which will be either $\hat{s}^P$ or $\hat{p}^P_{1\pm}$ depending on whether the field is $s$– or $p$– polarized.

For the structures studied here, where a surface excitation exists in the limit of a semi-infinite structure, the Fresnel coefficient $T^P_{N1}$ at the pump frequency has a pole at a complex wavenumber $\kappa_{res}$,

$$T^P_{N1} \sim \frac{\tau^P_{N1}}{\kappa - \kappa^P_{res}},$$ \hspace{1cm} (4.60)

when $\kappa$ is close to $\kappa^P_R \equiv Re(\kappa^P_{res})$ and $\tau^P_{N1}$ is also in general a complex number. I write $\kappa^P_{res} = \kappa^P_R + i\kappa^P_I$ with $\kappa^P_I$ describing the mode propagation losses due to absorption, if there is any, and the coupling to the substrate. The values of $\kappa^P_{res}$ and $\tau^P_{N1}$ can be extracted numerically from the full expression for $T^P_{N1}$, as well, semi-analytic expressions can be constructed for them. To maximize the field enhancement in the cladding above the structure, assume that $\theta_P$ is chosen such that $\nu^P_N \sin \theta_P = \kappa^P_R$. Then the field in the cladding just above the structure will be of the form

$$E_{\text{clad}}(x, y, D) = e^{i\nu^P_N x} \tilde{E}_{\text{clad}}(x, y, D),$$

where, within the approximation (4.60), $\tilde{E}_{\text{clad}}(x, y, D)$ satisfies

$$\frac{\partial}{\partial x} \tilde{E}_{\text{clad}}(x, y, D) + \kappa^P_I \tilde{E}_{\text{clad}}(x, y, D) = i\tau^P_{N1} \mathcal{E} f_{\text{inc}}(x, y)$$ \hspace{1cm} (4.61)

for the incident field $E_{\text{inc}}(x, y, 0)$ of the form (4.58) \[85\]. The solution of this equation can be written as

$$\tilde{E}_{\text{clad}}(x, y, D) = -\frac{\tau^P_{N1}}{i\kappa^P_I} \mathcal{E} f(x, y),$$ \hspace{1cm} (4.62)

where

$$f(x, y) = \kappa^P_I \int_{-\infty}^{x} e^{-\kappa^P_I(x-x')} f_{\text{inc}}(x', y) dx'.$$ \hspace{1cm} (4.63)

In the limit of a very broad beam ($\kappa^P_I \Delta \gg 1$), $f_{\text{inc}}(x', y)$ varies little over the integration range and we can write $f_{\text{inc}}(x', y) \approx f_{\text{inc}}(x, y) + (x' - x)(\frac{\partial f_{\text{inc}}(x, y)}{\partial x}) + \ldots$ in (4.63), giving

$$f(x, y) \approx f_{\text{inc}}(x, y) - (\kappa^P_I)^{-1} \frac{\partial f_{\text{inc}}(x, y)}{\partial x} + \ldots \approx f_{\text{inc}}(x - (\kappa^P_I)^{-1}, y).$$ \hspace{1cm} (4.64)

The result is clearly more general than the particular form (4.59) and holds whenever the propagation length $(\kappa^P_I)^{-1}$ is negligible compared to the beam width. Except for this
small shift, we can obtain (4.62) and (4.64) simply by assuming that locally the incident field can be treated as a plane wave, and putting \( \hat{E}_{\text{clad}}(x, y, D) = T_{N1}^P \mathcal{E}_\text{inc}(x, y) \) with \( T_{N1}^P \) given by (4.60) with \( P = \kappa_R^P \).

On the other hand, if the propagation length \( (\kappa_I^P)^{-1} \) is much larger than the width \( \Delta \) of the incident beam \( (\kappa_I^P \Delta \ll 1) \), in the integral in (4.63) we can expand the exponential about \( x_0 = 0 \), \( \exp \left( -\kappa_I^P (x - x') \right) \approx \exp (-\kappa_I^P x)(1 + \kappa_I^P x' + \ldots) \) and thus \( (\kappa_I^P)^{-1} \) sets the size of \( f(x, y) \) in the \( x \)- direction: we have \( f(x, y) \approx 0 \) for \( x \ll \Delta \), and for \( x \gg \Delta \)

\[
f(x, y) \rightarrow \frac{\sqrt{2\pi \kappa_I^P \Delta \cos \theta_P}}{\cos \theta_P} e^{-\frac{y^2}{2\Delta^2}} e^{-\kappa_I^P x}. \tag{4.65}
\]

Using this in (4.62), we see that in the \( x \) direction \( \hat{E}_{\text{clad}}(x, y, D) \) extends over a range that is much larger than the distance characterizing the intersection of the beam with the plane \( z = 0 \).

![Figure 4.8](image)

Figure 4.8: Normalized intensity distribution of incident beams at 532 nm with (a) 2 mm and (c) 50 \( \mu \)m FWHM, and the corresponding intensity in the cladding for the BSW structure (b) and (d) respectively.

Fig. 4.8(a) and (c) show the normalized intensity distribution, \( |E_{\text{inc}}(x, y, 0)/\mathcal{E}|^2 \), of an incident beam with a Gaussian intensity distribution in the \( xy \) plane and characterized by a FWHM of 2 mm and 50 \( \mu \)m, respectively. The light is incident from the substrate at an angle \( \theta_P = 50.6^\circ \) such that \( \nu_K^P \sin \theta_P = \kappa_R^P \) for the BSW structure designed for use at \( \lambda = 532 \) nm. Fig. 4.8(b) and (d) show the corresponding normalized intensity distribution just above the structure in the cladding, \( |E_{\text{clad}}(x, y, D)/\mathcal{E}|^2 \). For the 2 mm beam, the shape of the beam is not much distorted, suffering mainly a shift as discussed above.
For this structure $\kappa^P_I \sim 6 \text{ mm}^{-1}$ and the full range of wavevectors in the incident beam, characterized by $\Delta \kappa \approx (1/2 \text{ mm})=0.5 \text{ mm}^{-1}$, can couple into the BSW resonance; the field at the interface of the multilayer and the cladding is greatly enhanced. On the other hand, the 50$\mu$m beam has a wider range of wavenumbers $\Delta \kappa \approx 20 \text{ mm}^{-1}$ and not all can couple into the BSW resonance. The distance over $x$ that $|f(x, y)|^2$ is substantial is now limited not by the width of the incident beam, but by the propagation length $(\kappa^P_I)^{-1} \gg \Delta$, as indicated by (4.65), and the enhancement is smaller.

As the field at the interface of the cladding and multilayer is modified compared to the limit of plane wave excitation, so will the prediction of the Raman signal change. For a molecule at position $r_0 = (d + D)\hat{z} + R_0$, we can immediately calculate this, since the total Stokes Raman light scattered by a molecule into the substrate depends on the pump field at the position of the molecule. For a finite incident beam, the Stokes radiation per unit time per unit area in the substrate is

$$\langle S_S(r) \rangle = \frac{\tilde{\omega}_S^4 n_N(\omega_S)c}{32\pi^2\epsilon_0} (\alpha_1 \ell_S)^2 \frac{\hat{r}}{r^2} \Gamma_{nsub}(\hat{r}, \omega_S) : (e'_L(x_0, y_0) e_L(x_0, y_0))$$

(replacing (4.46)), where

$$e'_L(x_0, y_0) = f(x_0, y_0) e_L. \quad (4.67)$$

I neglect the small differences in the wavevector components of the incident beam and evaluate $e_L$ (4.32) at $\kappa^P = \kappa^P_R$. For an ensemble of $N$ molecules uniformly distributed with an areal density $\rho$ in a plane at $z = d + D$, the total Stokes radiation, $\langle S^\text{all}_S(r) \rangle$, is the sum of the radiation from all the individual molecules, since the spontaneous Raman scattering is an incoherent process. For a large number of molecules, we can convert the sum into an integral

$$\langle S^\text{all}_S(r) \rangle = \rho \frac{\tilde{\omega}_S^4 n_N(\omega_S)c}{32\pi^2\epsilon_0} (\alpha_1 \ell_S)^2 \frac{\hat{r}}{r^2} \Gamma_{nsub}(\hat{r}, \omega_S) : (e'_L e_L)$$

$$\times \int |f(x_0, y_0)|^2 dx_0 dy_0. \quad (4.68)$$

To characterize the signal, consider the ratio of the total power of the Stokes Raman light radiated into the substrate,

$$P_S = \int \langle S^\text{all}_S(r) \rangle \cdot \hat{r} r^2 d\Omega,$$

(4.69)

to the incident pump power $P_{\text{pump}} = S_p A$ normalized to the Raman cross section in free
space. This ratio can be written as

\[
\frac{1}{\sigma^o_S} \frac{P_S}{P_{pump}} = \rho \bar{\sigma}_{sub}^{tot} \int \left| f(x, y) \right|^2 \frac{dxdy}{A},
\]

(4.70)

with \( \bar{\sigma}_{sub}^{tot} \) given by (4.50). In the limit of very broad beam (\( \kappa^p \Delta \gg 1 \)),

\[
\frac{1}{\sigma^o_S} \frac{P_S}{P_{pump}} \to \frac{\rho \bar{\sigma}_{sub}^{tot}}{\cos \theta_P}
\]

and becomes constant and independent of the beam size. On the other hand, for a very small spot size (\( \kappa^p \Delta \ll 1 \)),

\[
\frac{1}{\sigma^o_S} \frac{P_S}{P_{pump}} \to \frac{\sqrt{\pi} \rho \bar{\sigma}_{sub}^{tot}}{\cos^2 \theta_P} \kappa^p \Delta,
\]

exhibiting a linear dependence on the beam size with a slope inversely proportional to the propagation length.

Fig. 4.9 shows the quantity in (4.70) (divided by \( \rho \)) for the bare prism, SP, WG, and BSW structures at 532 nm and 1064 nm (multiplied by 40 for the prism and SP structure) as the spot size varies. The bare prism does not have a resonant mode and we can not use the above pole expansion calculation. In this case, the beam undergoes a Goos-Hänchen shift [109], which is very small compared to the size of the beam. The other
three structures support resonant modes, and therefore we can use the pole analysis. For small spot sizes, as mentioned earlier, the coupling of the incident beam to the resonance mode is poor, and therefore molecules on the surface feel a smaller field. In addition, a small spot size can illuminate only a small surface area of the structure, and therefore the field scatters off only a small number of molecules, making the scattering signal small. On the contrary, as the spot size increases both the number of illuminated molecules and the pump field coupling efficiency are larger, and therefore the Raman signal increases.

At 532 nm, the WG structure seems to enhance the Raman signal even more than the BSW structure. The reason is that while the value of $\bar{\sigma}_{sub}^{tot}$ for the WG and BSW structures are very close (see Fig. 4.6), the integral in (4.70) depends on $1/\cos \theta_P$. The resonance angle of WG structure is smaller than the one of BSW structure such that $1/\cos \theta_P$ when multiplied by $\bar{\sigma}_{sub}^{tot}$ becomes larger for the WG structure. At 1064 nm, $\bar{\sigma}_{sub}^{tot}$ of the WG structure is about half of the one of the BSW structure, and thus it can not be compensated by the slightly smaller resonance angle of the WG structure.

4.4 Conclusion

I have presented a systematic study of spontaneous Raman scattering for molecules on an arbitrary planar structure. The Raman cross sections for scattering into the cladding and substrate are expressed in terms of the Fresnel coefficients of the structure. This is particularly useful in studying Raman scattering in structures supporting guided modes, where the modes are signalled by poles in the Fresnel coefficients, and semi-analytic expressions for the radiation through the guided modes to the substrate can be derived.

In comparing the Raman scattering of molecules on a planar structure supporting a guided mode to those in free space, I find that in general there is a two-fold enhancement, with the Stokes cross section proportional to both pump and Stokes intensity enhancements. As long as there is a guided mode at the Stokes frequency, the differential cross section for scattering into the substrate exhibits a Lorentzian peak around a resonance polar angle with an angular width depending on the propagation losses in the structure. For simplicity I have assumed that the Raman polarizability tensor is isotropic; therefore the dependence on the azimuthal angle is weak and the Stokes intensity is peaked at the cross section of a cone defined by the Stokes resonance angle.

I have numerically calculated the differential Raman Stokes cross sections for a set of multilayer structures, some supporting surface plasmons, some waveguide modes, and some Bloch surface waves, with guided modes present in all cases at both pump and Stokes frequencies. For the surface plasmon structures, essentially all of the light radiated
into the substrate is coupled through the surface plasmon resonance, where a maximum enhancement of more than $10^4$ was found for excitation at 1064 nm. For the dielectric structures there is non-negligible radiation into the substrate outside the resonance cone of the guided modes, but even so a maximum enhancement of about $10^6$ was found for excitation of a Bloch surface wave structure at 532 nm. The Stokes cross section integrated over all angles, however, is enhanced by a smaller factor, up to 10 for the surface plasmon structures and up to $10^3$ for the Bloch surface wave structures. This is a result of the enhancement of the pump field, with the excitation of the guided modes at the Stokes frequency leading mainly to a redistribution in angle of the radiated power.

I have also confirmed that these results, initially derived from a plane wave analysis, survive the extension of the theory to treat the more realistic scenario of excitation by a finite pump beam, as long as that beam is on the order of millimetres in diameter. For smaller beam sizes, the coupling of the incident field to the guided mode is decreased, as is the number of molecules illuminated by the incident beam, and therefore the power of the Stokes radiation is decreased.

The enhancements predicted for the dielectric structures are still less than those reported in traditional SERS substrates of rough metal surfaces, or metal surfaces decorated with metallic nanoparticles. However, the dielectric structures do not suffer from absorption losses, and they offer the possibility of decoration with metallic nanoparticles to achieve larger cross sections despite the induced losses. The Bloch surface wave structures also offer more freedom for design, and the possibility of tailoring the dispersion relation. The latter would be extremely important in an extension to treat coherent anti-Stokes Raman scattering (CARS), which would benefit from phase matching; I will return to this in chapter 6. Further, the confinement of Bloch surface waves into 1D channels is possible when additional guiding structures are fabricated on a BSW structure [82,110–112]. This would lead to possibilities for multiplexed sensors above and beyond the multiplexing that may be possible with the use of the Kretschmann configuration considered here.
Chapter 5

Experimental Realization of SERS in BSW Structures

In this chapter experimental realizations of SERS in Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> truncated periodic multilayers are presented. The Raman results are analyzed with the aid of angle-resolved attenuated total reflectance (ATR) and photoluminescence measurements. I compare the experimental measurements with theoretical predictions from the semi-classical calculations presented in chapter 4. SERS is observed in two different samples that have been designed to work with different pump wavelengths, demonstrating the applicability of this approach from the infrared to the visible spectral region.

This chapter is organized as follows: in Sec. 5.1 the multilayer structures and their linear characterization by means of angle-resolved ATR measurements are discussed. In Sec. 5.2 the Raman spectra for visible and infrared pumps are presented, and the origin and the value of the enhancement are discussed by comparing these results with photoluminescence measurements and our theoretical model. Finally, in Sec. 5.3 I present the conclusions.

5.1 Multilayer structure and characterization

A sketch of the typical structure of the samples investigated in this chapter is shown in Fig. 5.1(a). Each sample consists of a Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> multilayer grown by magnetron sputtering [113] on the hypotenuse of a 45-90-45 N-BK7 prism. The nominal parameters

---

of infrared and visible structures are reported in Table 5.1. Each multilayer stack is composed of 5 periods of a bilayer unit cell (thicknesses $d_1$ and $d_2$ of the Ta$_2$O$_5$ and SiO$_2$ layers respectively) with two additional layers on the top of the structure (thicknesses $s_1$ and $s_2$ of the Ta$_2$O$_5$ and SiO$_2$ layers respectively, with the SiO$_2$ layer closest to the cladding) to obtain the desired BSW dispersion following the procedure suggested in [74]. Two different samples are designed, one to support a BSW in the visible and one in the infrared spectral regions, with the upper cladding being water and air, respectively. In both cases $s$-polarized BSWs are considered (see Fig. 5.1), but note that multilayers can be designed to support BSWs in either $s$- or $p$- polarization [74]. The two samples were characterized by means of angle-resolved ATR measurements in the Kretschman configuration [114] to verify the presence of BSWs and to map their dispersion relations. In this configuration (see Fig. 5.1b), the excitation of a BSW is indicated by a dip in the reflectance due to the unavoidable scattering losses at the surface of the sample [115]. Similar but larger dips can be observed in structures involving surface plasmons, where the losses are much larger and primarily due to absorption (see Fig. 1.1).

Fig. 5.2a shows the ATR spectra obtained for the visible sample when the upper cladding is water ($n \approx 1.33$) at different external angles of incidence $\theta_{\text{ext}}$ from 27.5$^\circ$ to 60$^\circ$, with steps of 2.5$^\circ$. These curves are obtained using a FTIR spectrometer (Bruker IFS 66/S) coupled to an external home-made micro-reflectometer equipped with a Si photodiode detector. The BSW dispersion curve calculated using the nominal parameters of Table 1 is shown in Fig. 5.2b. As expected, the curve is within the photonic bandgap determined by the multilayer and below the water light line, which describes the photon
visible sample
\( (\lambda_{\text{pump}}=780 \text{ nm}) \)

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Spectrum Thin Films [116]</th>
<th>Iridian Spectral Technologies [117]</th>
</tr>
</thead>
<tbody>
<tr>
<td>s(_1) (Ta(_2)O(_5))</td>
<td>50 nm</td>
<td>80 nm</td>
</tr>
<tr>
<td>s(_2) (SiO(_2))</td>
<td>10 nm</td>
<td>10 nm</td>
</tr>
<tr>
<td>d(_1) (Ta(_2)O(_5))</td>
<td>150 nm</td>
<td>200 nm</td>
</tr>
<tr>
<td>d(_2) (SiO(_2))</td>
<td>150 nm</td>
<td>250 nm</td>
</tr>
<tr>
<td>Periods</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5.1: Nominal parameters of visible and infrared samples.

Figure 5.2: (a) TE angle-resolved attenuated total reflectance spectra of the visible sample, curves are vertically shifted for clarity. (b) Calculated dispersion of the BSW (black solid) and BSW energies data obtained from the ATR measurements (red square) for the visible sample. Water (blue dashed) and Ta\(_2\)O\(_5\) (green dotted) light lines are also shown. The photonic band gap region between the two light lines is highlighted in yellow.

dispersion relation in water. There is good agreement between the theoretical curve and the experimental points extracted from the dips in the ATR spectra of Fig. 5.2a. A similar optical characterization has been performed on the infrared sample.

Fig. 5.3 shows an optical image and the calculated intensity profile (discussed in chapter 4) of the spot arising when the BSW is excited at the surface of the visible sample with a s- polarized pump at wavelength \( \lambda=780 \text{ nm} \) and external angle of incidence \( \theta_{\text{ext}} \approx 31^\circ \). Along the y direction the spot has a full width at half-maximum FWHM\(_y\)=479 \( \mu\text{m} \), which is the same as the spot impinging the prism facet. Along the x direction the spot in the focus of the lens has FWHM\(_x\) of 265 \( \mu\text{m} \), but on the multilayer surface it is elongated due to the finite angle of incidence on prism and with a comet-like shape.
corresponding to the excitation of the BSW.

![Image of optical image and calculated intensity profile](image)

Figure 5.3: (a) Optical image on the surface of the visible sample when the BSW is excited at $\lambda=780$ nm and $\theta_{\text{ext}} \simeq 31^\circ$, and (b) Calculated intensity profile using the sample nominal parameters, considering a spot with FWHM$_y=479$ $\mu$m and FWHM$_x=265$ $\mu$m.

### 5.2 Raman scattering results and discussion

![Experimental configuration sketch](image)

Figure 5.4: Sketch of the experimental configuration used in Raman and photoluminescence measurements.

We have investigated Raman scattering from a substance nearby the sample surface in the experimental configuration depicted in Fig. 5.4, where the pump beam is impinging
from the prism facet and Raman scattering is detected from the top of the sample through a microscope objective. In this configuration it is possible to observe SERS given by the excitation of BSWs by the pump beam. We consider $s$− polarized pump at wavelengths 780 nm and 1064 nm for the visible and infrared samples, respectively, and collect the total Raman scattering from the cladding side independently of the polarization.

5.2.1 a. The visible sample

Pirotta et al. have considered the use of the visible sample to detect Raman scattering arising from a solution in a slide-cell realized on the sample surface. When the cell is filled with a solution of acetone in distilled water (4:1 v/v), having refractive index $n \approx 1.33$, the visible sample supports a BSW that can be excited at $\lambda_{pump} \approx 780$ nm at the external angle $\theta_{ext} \approx 31^\circ$. A continuous-wave (CW) laser-diode (Thorlabs L785P090) has been used as the source; the beam is focused on the sample by means of a 25 cm focal-length lens with about 50 mW power on the sample. The Stokes Raman signal is collected from the top of the sample through a microscope objective (Mitutoyo 5X, NA=0.14), and a Semrock 785 nm RazorEdge ultra steep long-pass edge filter is used to remove the Rayleigh scattering contribution coming from the pump. Finally, the signal is sent to a monochromator (Acton SP-2300, Princeton Instruments) coupled to a liquid nitrogen-cooled Silicon CCD (Spec-10 System, Princeton Instruments). To evaluate the enhancement value of the Raman signal, Pirotta et al. have considered a bare (without the multilayer structure) N-BK7 prism with an identical slide-cell filled with the same solution as our reference. Raman spectra are also collected when the cells of visible sample and bare prism are filled with pure water to measure the background Raman scattering contribution coming from the prism and the multilayer (see the inset of Fig. 5.5a).

The main panel of Fig. 5.5a shows the Raman spectrum of the acetone solution for the visible sample after background subtraction. Fig. 5.5b shows a zoom of the spectrum around the acetone Raman peak at about 800 cm$^{-1}$ along with the signal detected from the bare prism structure. The absence of the acetone peak in the case of the bare prism does not allow us to estimate the corresponding enhancement due to the excitation of the BSW. Yet it is still possible to give a lower bound of the Raman enhancement by taking the ratio between the intensity of the strongest acetone Raman peak and the noise amplitude of the bare prism measurement: the ratio is $\sim 50$.

I use the theoretical calculations in chapter 4 to analyze the performance of the visible structure, considering the bulk Raman contribution given by the entire solution...
subjected to the evanescent field associated with the excitation of the BSW. Our expected enhancement curve as a function of the pump external angle of incidence is presented in Fig. 5.6, where the maximum enhancement at resonance is about 400 and occurs when a BSW is excited. The calculation predicts an expected enhancement eight times larger than the lower bound of the enhancement set by the Raman experiment. Because there is no acetone Raman signal detectable from the bare prism structure, Raman results alone will not allow a more exact comparison of theory with experiment.

As discussed in chapter 4, Raman scattering can be modeled as resulting from the spontaneous emission of light at the Stokes frequency, where the molecules are driven by the pump field, with the frequency and intensity of the Raman response described...
by the Raman susceptibility tensor. Thus we can use another spontaneous process, photoluminescence, to estimate the actual Raman enhancement. Pirotta et al. have employed a specific fluorophore (S0456 fluorophore from FEW Chemicals [118] that is optimized for absorbing at about 780 nm has been used: 2 \mu g in 1 ml of distilled water) in water solution that can be excited at 780 nm and emits in the range of the investigated Stokes Raman signal. The advantage of considering the corresponding photoluminescence experiment is that this process has a much larger cross section than Raman scattering; thus a detectable signal is expected for the bare prism. Although photoluminescence and Raman scattering are two different processes, the enhancement associated with the excitation of the BSW depends only on the optical properties of the samples at the pump and emitted light wavelengths. Thus, when working in the experimental configuration of Fig. 5.4, the ratio between the photoluminescence signals measured from the multilayer and the bare prism should be a good estimate of the Raman enhancement.

The measured photoluminescence spectra for visible and bare prism samples are shown in Fig. 5.7. They are collected by means of the same apparatus utilized in the Raman measurements (that is, exciting the BSW with a s–polarized pump beam and collecting the unpolarized light emitted in the cladding), but using a Mitutoyo 10X, NA=0.26 microscope objective and working with a lower pump power, about 100 \mu W, to avoid dye photobleaching. The photoluminescence of the visible sample is about 210 larger than that of the bare prism sample. This value is within a factor of two of what is expected from the theoretical analysis. The discrepancy can be ascribed to scattering and absorption losses, which are neglected in the calculations.
5.2.2 b. The infrared sample

It is possible to obtain SERS working with pump wavelengths from visible to infrared using the same materials for the construction of the multilayer structures. For example, this allows one to work at longer pump wavelengths to significantly reduce fluorescence background. A wide range of target materials can also be studied. To demonstrate this flexibility, I now turn to the infrared sample that has been designed to work with a pump at 1064 nm, and present the results of spontaneous Raman scattering from sulphur powder deposited on the multilayer surface.

Pirotta et al. have pumped the infrared sample with a Nd:YAG laser (1064 nm Teem Photonics) at an external excitation angle $\theta_{\text{ext}} \simeq 32^\circ$, which corresponds to the excitation of the BSW. The value of the resonance angle agrees with the calculated BSW angle if the measured thickness parameters of the multilayer structure (obtained from scanning electron microscopy images) and the change in the index of refraction of the cladding due to the presence of the thick sample are considered. The experimental configuration is conceptually the same as in Fig. 5.4. Here the pump laser is focused on the prism facet by a long focus lens (f=100 cm), with a spot on the multilayer surface with FWHM of 1-2 mm. The incident power on the sample is about 220 mW. The scattered light is collected from the surface through a microscope objective (Olympus 10X, NA =0.25 ), the Rayleigh component is filtered out by a long wave pass dichroic filter (Semrock LPD01-1064RU), and the signal is coupled into a multimode optical fiber and sent to a monochromator (SP-2500, Princeton Instruments) coupled with a silicon CCD (PIXIS-400, Princeton Instruments). Given the silicon CCD sensitivity, an integration time of 30 min has been used to obtain the Raman spectra shown in Fig. 5.8. Note that
this configuration allows probing the sample response at different external angles while maintaining the same light collection conditions.

As before, a bare N-BK7 prism has been considered as a reference to evaluate the Raman scattering enhancement. The Stokes Raman spectrum collected between 100 and 300 cm$^{-1}$ and without background subtraction is shown in the main panel of Fig. 5.8, where the two sulphur peaks at $\sim 150$ cm$^{-1}$ and $\sim 210$ cm$^{-1}$ are clearly visible. In the inset I show the stronger Raman peak for the infrared sample along with the Raman signal detected from the bare prism, where no peaks are visible. As in the previous case, we can only estimate a lower bound for the enhancement by dividing the intensity of the peak of the infrared sample by the noise amplitude in the bare prism spectrum: this ratio is $\sim 50$.

### 5.3 Conclusions

In this chapter I presented the experimental realization of SERS in fully dielectric structures supporting BSWs. This has been done by studying the Raman response of an aqueous solution as well as sulphur powder. This approach allows working over a wide spectral region, from visible to infrared, where the optical properties of the structure can be designed without changing the constituent materials. The theoretical model of Raman scattering suggests that the actual enhancement is indeed much larger: about
400 times. I showed that a similar enhancement is indeed observed in a photoluminescence experiment where a dye solution is excited by the same pump used in the Raman experiment and the light is collected in the same frequency range given by the Stokes shift in the Raman experiment. These results demonstrate that dielectric multilayers supporting BSWs are a promising alternative to metallic structures for the realization of optical sensors based on Raman spectroscopy.
Chapter 6

Surface Enhanced CARS in Multilayer Structures

In this chapter I study coherent anti-Stokes Raman scattering (CARS) from thin layers of molecules on planar structures. For bulk samples the strength of the CARS signal can be several orders of magnitudes larger than the spontaneous Raman signal [62,63], however, this may not be true if monolayers of molecules containing smaller numbers of scatterers are probed. The CARS signal can be enhanced when the incident or scattered fields are coupled to surface waves in resonant structures [67–70]. Coupling all the fields involved in CARS process to resonant modes requires flexibility in tailoring the dispersion relation of the resonant modes. In this chapter I consider dielectric multilayer structures supporting Bloch surface waves (BSW) [73,76], as they offer more degrees of freedom for design.

The rest of this chapter is organized as follows: In Sec. 6.1 I adopt a simple isotropic Raman polarizability for molecules and model molecular vibrations as classical harmonic oscillators. In Sec. 6.2 and Sec. 6.3 I show CARS calculations for sheets of molecules in a uniform medium and on an arbitrary planar structure, and derive expressions for the CARS power in terms of the Fresnel coefficients of the structure. In Sec. 6.4 I present a resonant multilayer structure that has been designed to support BSWs for all the fields involved in the CARS process. The comparisons of CARS and spontaneous Raman scattering in the uniform medium and on the resonant planar structure are given in Sec. 6.5, and Sec. 6.6 ends the chapter with the conclusions.
Chapter 6. Surface Enhanced CARS in Multilayer Structures

6.1 A simple model

I use a standard classical approach to calculate the coherent anti-Stokes Raman scattering (CARS) [119]. The incident fields are assumed to have frequencies far below the electronic resonance frequencies of the molecules, so no electronic transitions are excited. As in chapter 4, I characterize the response of the molecules to the incident fields through a polarizability tensor, $\alpha(t)$,

$$\alpha(t) = \alpha_0 + \sum_{\xi} \alpha_{\xi} q^\xi(t). \quad (6.1)$$

I neglect the Rayleigh scattering and for simplicity consider only one degree of freedom with coordinate $q$. To simplify the calculations even further, I treat the Raman polarizability tensor, $\alpha_1$, as isotropic such that $\alpha_1$ is equal to a constant $\alpha_1$ multiplied by the unit tensor.

Consider a molecule at position $r_0$ embedded in a medium with refractive index $n_1(\omega)$. An incident field of $E(r_0, t)$ induces a dipole moment $\mu(r_0, t) = \alpha(t)E(r_0, t)$ in the molecule, with the Raman dipole moment

$$\mu^R(r_0, t) = \alpha_1 q(t)E(r_0, t). \quad (6.2)$$

In CARS the incident fields drive the molecular vibrations, so consider a damped driven harmonic oscillator model to describe the molecular vibrations,

$$\frac{d^2q(t)}{dt^2} + \frac{dq(t)}{dt} + \omega_0^2 q(t) = \frac{F(t)}{m}, \quad (6.3)$$

where $\omega_0$, $m$, and $\gamma$ are the vibrational frequency, mass of the oscillator, and damping constant respectively. The driving force $F$ is given by $F = -\partial U/\partial q$, where $U$ is the energy associated with the Raman polarizability of the molecule $U = -\frac{1}{2}\mu^R \cdot E$, and therefore $F(t) = \frac{1}{2}\alpha_1 E(t) \cdot E(t)$. The vibrational frequencies of the molecules are far below the optical frequencies and the oscillations can not be driven by a single laser field. However, the beat frequency of a pump field with frequency $\omega_P$ and a Stokes field with frequency $\omega_S$ can match the molecular vibrational frequency. The driving force is increased by increasing the amplitude of the incident electric field; however in order to avoid damaging molecules subject to large field intensities, the interaction time must be decreased by employing short laser pulses. Yet, the duration of the pulses should be long enough that their frequency bandwidth is smaller than the width of the vibrational resonance of the molecules. The recommended pulse lengths for CARS are a few picoseconds [55] containing about 1000 periods of an electromagnetic wave in the
near infrared region, and therefore we can treat them as continuous waves. The field at
the position of the molecule is

$$E(r_0, t) = E_P(r_0)e^{i(k_P \cdot r_0 - \omega_P t)} + E_S(r_0)e^{i(k_S \cdot r_0 - \omega_S t)} + c.c. \quad (6.4)$$

where $E_P(r_0)$ and $E_S(r_0)$ are the pump and Stokes field amplitudes, assumed to vary
slowly with $r_0$, and $k_P$ and $k_S$ are the central wavevectors of the pump and Stokes fields,
respectively. The driving terms in $F(r_0, t)$ are

$$F(r_0, t) = \alpha_1 E_P(r_0) \cdot E^*_S(r_0)e^{i(k_P - k_S) \cdot r_0 - i(\omega_P - \omega_S) t} + c.c. \quad (6.5)$$

Equations (6.3) and (6.5) give

$$q(t) = \frac{\alpha_1}{m} \frac{E_P(r_0) \cdot E^*_S(r_0)}{\omega_0^2 - (\omega_P - \omega_S)^2 - i\gamma(\omega_P - \omega_S)}e^{i(k_P - k_S) \cdot r_0 - i(\omega_P - \omega_S) t} + c.c. \quad (6.6)$$

The vibrational amplitude given in Eq. (6.6) depends on the frequency difference of the
pump and Stokes fields, with the maximum at $\omega_P - \omega_S = \omega_0$. The frequency width is set
by the damping constant, $\gamma$, which identifies the homogeneous linewidth of the Raman
line.

The anti-Stokes (and Stokes) field is radiated when a third probe field with frequency
$\omega_{pr}$ and wavevector $k_{pr}$,

$$E_{pr}(r_0, t) = E_{pr}(r_0)e^{i(k_{pr} \cdot r_0 - \omega_{pr} t)} + c.c. \quad (6.7)$$

scatters off the molecule. The probe field induces a Raman dipole moment $\mu^R(r_0, t) = \alpha_1 q(t)E_{pr}(r_0, t)$ in the molecule. If $E_{pr} = E_P$, the component of the dipole moment responsible for the anti-Stokes radiation is

$$\mu^A(r_0, t) = \frac{i\alpha_1^2}{\gamma \omega_0} \frac{E_P(r_0) \cdot E^*_S(r_0)}{E_P(r_0)e^{i(2k_P - k_S) \cdot r_0 - i\omega_A t} + c.c.} \quad (6.8)$$

where $\omega_A = 2\omega_P - \omega_S$ is the anti-Stokes frequency, and I have assumed the resonance
condition, $\omega_0 = \omega_P - \omega_S$, holds.

### 6.2 Molecules in a uniform medium

Consider a sheet of $N$ molecules distributed uniformly with an areal density $\rho$ and em-
bedded in a uniform medium of refractive index $n_1(\omega) = n_1^i$, where $i$ is P for pump, S
for Stokes, or \( A \) for anti-Stokes. We can take a coordinate system in which the molecules are located at \( z = 0 \) plane with molecule \( a \) at \( \mathbf{R}_a = x_a \hat{x} + y_a \hat{y} \). The molecular vibrations are driven by the incident pump and Stokes fields and the probe field induces a dipole moment of the form
\[
\mathbf{\mu}^A(\mathbf{R}_a, t) = \mathbf{\mu}^A(\mathbf{R}_a) e^{-i\omega_At} + c.c
\]
in molecule \( a \), with
\[
\mathbf{\mu}^A(\mathbf{R}_a) = \frac{i\alpha^2}{m} \mathbf{E}_P(\mathbf{R}_a) \cdot \mathbf{E}_S^*(\mathbf{R}_a) \mathbf{E}_P(\mathbf{R}_a) e^{i(2\kappa_P - \kappa_S)\mathbf{R}_a},
\]
where \( \kappa = \mathbf{k} \cdot (\hat{x}\hat{x} + \hat{y}\hat{y}) \). The radiated electric and magnetic fields from molecule \( a \) at a point \( \mathbf{r} \) in the far field, where \( r/r_a \gg 1 \), are
\[
\mathbf{E}_a(\mathbf{r}) = \mathbf{E}_a(\mathbf{r}) e^{-i\omega_At} + c.c,
\]
and
\[
\mathbf{H}_a(\mathbf{r}) = \mathbf{H}_a(\mathbf{r}) e^{-i\omega_At} + c.c,
\]
with
\[
\mathbf{E}_a(\mathbf{r}) = \frac{\omega_A^2}{4\pi\epsilon_0} \left( (\hat{\mathbf{r}} \times \mathbf{\mu}^A(\mathbf{R}_a)) \times \hat{\mathbf{r}} \right) \frac{e^{i\omega_A(r-r\cdot\mathbf{R}_a)n_A^4}}{r},
\]
and
\[
\mathbf{H}_a(\mathbf{r}) = \frac{c\omega_A^2}{4\pi} (\hat{\mathbf{r}} \times \mathbf{\mu}^A(\mathbf{R}_a)) \frac{e^{i\omega_A(r-r\cdot\mathbf{R}_a)n_A^4}}{r}.
\]
[42], where \( \hat{\mathbf{r}} \) is a unit vector in the direction of \( \mathbf{r} \). The total scattered fields are the sums of the fields scattered from all the molecules,
\[
\mathbf{E}(\mathbf{r}) = \sum_{a=1}^{N} \mathbf{E}_a(\mathbf{r}),
\]
and
\[
\mathbf{H}(\mathbf{r}) = \sum_{a=1}^{N} \mathbf{H}_a(\mathbf{r}).
\]
The time averaged Poynting vector is
\[
\mathbf{S}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) \times \mathbf{H}^*(\mathbf{r}) + \mathbf{E}^*(\mathbf{r}) \times \mathbf{H}(\mathbf{r}),
\]
and Eqs. (6.10), (6.11), and (6.12) give the radiated power per unit solid angle as
\[
\frac{dP}{d\Omega} = r^2 \hat{\mathbf{r}} \cdot \mathbf{S}(\mathbf{r}) = \frac{c\omega_A^2}{8\pi^2\epsilon_0} \sum_{a=1}^{N} \sum_{b=1}^{N} \Gamma_{free} : \mathbf{\mu}^A(\mathbf{R}_a) \mathbf{\mu}^A(\mathbf{R}_b) e^{i\omega_A(\mathbf{R}_a-\mathbf{R}_b) \times \hat{\mathbf{r}} n_A^4},
\]
where \( \Gamma_{free} = (\delta^{ij} - r^i r^j/r^2) \) and a colon product as \( T^{ij} A^i B^j = T : A B \) have been defined. I Insert \( \mathbf{\mu}^A(\mathbf{R}) \) from Eq. (6.9) and write the slowly varying electric field amplitudes \( \mathbf{E}_P(\mathbf{R}) \) and \( \mathbf{E}_S(\mathbf{R}) \) in terms of dimensionless envelope functions \( f_P(\mathbf{R}) \) and \( f_S(\mathbf{R}) \) (peaking at unity), constant real amplitudes \( \mathcal{E}_P \) and \( \mathcal{E}_S \), and complex polarization vectors
\( e_{p}^{in} \) and \( e_{s}^{in} \),

\[
\begin{align*}
E_{P}(R) &= \mathcal{E}_{P} f_{P}(R) e_{p}^{in}, \\
E_{S}(R) &= \mathcal{E}_{S} f_{S}(R) e_{s}^{in}.
\end{align*}
\] (6.14)

In a more realistic treatment an incident finite beam is a superposition of many plane waves with slightly different wave vectors and polarization vectors. I neglect the small differences between the polarization vectors of the components in the superposition and take the beam to be approximately polarized along the polarization vector of the central component. I define a characteristic length \( l_{CARS} \) corresponding to the oscillation amplitude of the harmonic oscillator driven at resonance. From Eq (6.6), at resonance the amplitude of the oscillations at the peak of the envelope functions is

\[
l_{CARS} = \frac{2\alpha_{1}}{m\gamma_{0}} \mathcal{E}_{P} \mathcal{E}_{S}.
\] (6.15)

Combining Eqs. (6.9), (6.13), (6.14), and (6.15),

\[
\frac{dP}{d\Omega} = \frac{\tilde{\omega}_{A}^{2} n_{1}^{2} \alpha_{1}^{2}}{32\pi^{2} \epsilon_{0}} \left( l_{CARS} \right)^{2} \rho^{2} \mathcal{E}_{P}^{2} \mathcal{E}_{S}^{2} \left| e_{p}^{in} \cdot e_{s}^{in*} \right|^{2} \left( \Gamma_{\text{free}} : e_{p}^{in*} e_{p}^{in} \right) \times \left| \int dR e^{i\Delta \kappa \cdot R} f_{P}^{2}(R) f_{S}(R) \right|^{2},
\] (6.16)

where \( \Delta \kappa = \kappa_{A} - (2\kappa_{P} - \kappa_{S}) \) and \( \kappa_{A} \) is the projection of the anti-Stokes wavevector, \( \mathbf{k}_{A} = n_{1}^{1} \tilde{\omega}_{A} \mathbf{r} \), into the \( xy \) plane. I have assumed that the density of molecules on the sheet is sufficiently large that the sums in Eq. (6.13) can be converted into integrals, using \( \sum_{a=1}^{N} \rightarrow \rho \int d\mathbf{R} \). Eq. (6.16) can be further simplified by considering an experimental scenario in which the pump and Stokes fields are \( s \)-polarized and collinear in the same plane of incidence (\( \hat{k}_{P} = \hat{k}_{S} \)). I define the angle between \( \mathbf{k}_{P} \) (or equivalently \( \mathbf{k}_{S} \)) and the \( z \) axis as \( \theta_{i} \), and the angle between \( \mathbf{k}_{A} \) and the \( z \) axis as \( \theta \). I denote the polarization vector of the pump field by \( \hat{s}_{P} \), choose the \( x \) axis such that \( \hat{x} = \hat{z} \times \hat{s}_{P} \) is parallel to \( \hat{k}_{P} \), and define the angle between the \( x \) axis and \( \mathbf{k}_{A} \) as \( \beta \) (see Fig. 6.1). I assume that the pump and Stokes fields have Gaussian envelope functions in the \( xy \) plane,

\[
f(x, y) = \exp\left(-\frac{x^{2} \cos^{2} \theta_{i} + y^{2}}{2\Delta^{2}}\right),
\] (6.17)

where \( \Delta \) is the FWHM of the beam divided by \( 2\sqrt{\ln 2} \). Eq. (6.16) then simplifies to
Figure 6.1: (a) A thin layer of \( N \) molecules with a uniform areal density \( \rho \) at \( z = 0 \). The \( \hat{S}_P \) is the unit polarization vector of the pump (and Stokes) field, perpendicular to the x axis. The angle between \( \hat{z} \) and the anti-Stokes wavevector, \( k_A \), is defined as \( \theta \). (b) The angle between \( \kappa_P \) (\( \hat{x} \)) and \( \kappa_A \) is defined as \( \beta \).

\[
\frac{dP}{d\Omega} = \frac{\omega_A n_i^4 c \alpha_1^2 (l_{CARS})^2 \rho^2 A^2 \mathcal{E}_P^2}{72\pi^2\epsilon_0 \cos^2 \theta_i} \left( 1 - (\sin \beta \sin \theta)^2 \right) \\
\times \exp \left( -\frac{\Delta^2}{3} \left( \frac{(\Delta \kappa_x)^2}{\cos \theta_i^2} + (\Delta \kappa_y)^2 \right) \right),
\]

(6.18)

where

\[
\Delta \kappa_y = \hat{y} \cdot \Delta \kappa = \kappa_A \sin \beta, \\
\Delta \kappa_x = \hat{x} \cdot \Delta \kappa = \kappa_A \cos \beta - (2\kappa_P - \kappa_S),
\]

(6.19)

and \( A = \pi \Delta^2 \). Eq. (6.18) shows that the radiated anti-Stokes power depends quadratically on the number of illuminated molecules and is mainly distributed as a Gaussian function, with its maximum at \( \Delta \kappa_x = \Delta \kappa_y = 0 \), the phase matching condition. According to the first of Eq. (6.19) the phase matching condition is satisfied when \( \beta = 0 \) corresponding to the anti-Stokes wavevector in the plane of incidence of the pump and Stokes fields. The second of Eq. (6.19) becomes zero when \( \kappa_A = 2\kappa_P - \kappa_S = \kappa_A^{PM} \). I denote the \( \kappa_A \) that satisfies this condition by \( \kappa_A^{PM} \), where the superscript \( PM \) stands for phase matching. The angular width of the CARS radiation is proportional to the inverse of the incident beam width, so for large incident beams the CARS signal is significant only over a small angular range, while for small incident beams the CARS signal is radiated over a wide range of angles. Consider a special case in which the pump and Stokes beams are normal to the plane of the molecule (as in CARS microscopy), and therefore \( \theta_i = 0 \) and
\( \kappa_P = \kappa_S = 0 \). Thus the radiated CARS power is

\[
\frac{dP}{d\Omega} = \frac{\tilde{\omega}_A n_1^4 \alpha_i^2}{72\pi^2 \epsilon_0} (l_{CARS})^2 \rho^2 A^2 \mathcal{E}_P^2 \left( 1 - (\sin \beta \sin \theta)^2 \right) \exp \left( - \frac{\Delta^2}{3} (\kappa_A)^2 \right).
\]

At normal incidence the phase matching condition reduces to \( \kappa_A = 0 \), meaning that the CARS signal has its maximum at \( \theta = 0 \) (along the +z direction) and at \( \theta = \pi \) (along the –z direction). To find the total collected power, we can integrate (6.20) over all the solid angles,

\[
P = \int_0^{2\pi} \int_0^{\pi} \frac{dP}{d\Omega} \sin \theta d\theta d\beta.
\]

The total CARS power is

\[
P = \frac{\tilde{\omega}_A n_1^4 \alpha_i^2}{72\pi^2 \epsilon_0} (l_{CARS})^2 \rho^2 A^2 \mathcal{E}_P^2 \left( \frac{1}{a^2} + \frac{\sqrt{\pi e^{-a^2}}}{2a^3} (2a^2 - 1) \frac{\text{Erf}(ia)}{i} \right),
\]

where \( a = \tilde{\omega}_A n_1^4 \Delta / \sqrt{3} \) and \( \text{Erf} \) is the error function. For \( a \geq 2 \),

\[
\frac{\sqrt{\pi e^{-a^2}}}{2a^3} (2a^2 - 1) \frac{\text{Erf}(ia)}{i} \approx \frac{1}{a^2},
\]

and Eq. (6.22) simplifies such that the average collected CARS power in each of forward or backward directions becomes

\[
P_{\text{free, CARS}} \simeq \frac{\tilde{\omega}_A^2 \alpha_i^2}{48\epsilon_0^2 n_1^2} \rho^2 (l_{CARS})^2 P_P,
\]

assuming \( n_1^4 \simeq n_P^4 \simeq n_S^4 = n_1 \). The \( P_P = I_P A D \) is the average pump power with \( I_P = 2c\epsilon_0 n_1^P \mathcal{E}_P^2 \) the pump peak intensity, and \( D \) is the duty cycle (the ratio between the pulse duration and the period) of the pump and Stokes lasers. The \( a \geq 2 \) condition is satisfied when FWHM \( \geq 0.7\lambda_A \), where FWHM is the full width half maximum of the pump and Stokes beams.

### 6.3 Molecules on a planar structure

Now I place the molecules at \( z = 0 \) a distance \( d \) above an arbitrary planar structure with a substrate of refractive index \( n_N(\omega_i) = n_N^i \), where \( i \) is P for pump, S for Stokes, or A for anti-Stokes (see Fig. 6.2). Consider a configuration in which the pump and Stokes fields are incident from the substrate and the fields in the substrate are described by Eqs. (6.4) and (6.14). The field at the position of molecule \( a \) located at \( \mathbf{r}_a = \mathbf{R}_a \) can be expressed...
as

\[ E^L(R_a, t) = E^L_P(R_a) e^{i(\kappa_P \cdot R_a - \omega_P t)} + E^L_S(R_a) e^{i(\kappa_S \cdot R_a - \omega_S t)} + c.c, \]  

(6.25)

with \( E^L_P(R) = g_P(R) \mathcal{E}_P \) and \( E^L_S(R) = g_S(R) \mathcal{E}_S \), where \( \mathcal{E}_P \) and \( \mathcal{E}_S \) are the real constant amplitudes of the pump and Stokes fields in the substrate, and \( g_P(R) \) and \( g_S(R) \) are dimensionless envelope functions of the pump and Stokes fields at \( z = -d \). The \( g_P(R) \) and \( g_S(R) \) can be related to the pump and Stokes fields envelope functions in the substrate (taken to be \( f_P(R) \) and \( f_S(R) \)) [81,85]. The complex vectors \( \mathbf{e}^L_P \) and \( \mathbf{e}^L_S \) contain polarization vectors and their associated Fresnel transmission coefficients. If the pump and Stokes fields are \( s- \) polarized, these vectors are simply

\[ \mathbf{e}^L_P = T^s_P N_1 e^{i\omega^P_0 d} \hat{s}_P, \]
\[ \mathbf{e}^L_S = T^s_S N_1 e^{i\omega^S_0 d} \hat{s}_S, \]

(6.26)

where \( \hat{s}_P \) and \( \hat{s}_S \) are the polarization vectors of the pump and Stokes fields, respectively, \( T^s_P N_1 \) and \( T^s_S N_1 \) are Fresnel transmission coefficients (from the substrate to the cladding) of the pump and Stokes fields for \( s- \) polarization, and superscript \( j \) is \( P \) for pump, \( S \) for Stokes, or \( A \) for anti-Stokes field.

Figure 6.2: A thin layer of \( N \) molecules with a uniform areal density \( \rho \) at a distance \( d \) above an arbitrary planar structure, extended from \( z = -d \) to \( z = -D - d \). The pump and Stokes fields are incident from the substrate.

The anti-Stokes dipole moment induced in molecule \( a \) is

\[ \mu^A(R_a, t) = \mu^A(R_a) e^{-i\omega_A t} + c.c, \]

where

\[ \mu^A(R_a) = \frac{i \alpha^2}{m} \frac{E^L_P(R_a) \cdot E^L_A(R_a)}{\gamma \omega_0} \mathcal{E}_P(R_a) e^{i(2\kappa_P - \kappa_S) \cdot R_a}, \]

(6.27)

as follows from Eq. (6.8). The radiated fields into the substrate and far from the dipole
source are

\[
\begin{align*}
\mathbf{E}_a(r) & \sim \frac{\tilde{\omega}_A^2}{4\pi\epsilon_0} \left( \hat{s}_N \mu_\text{sN}(R_a) + \hat{p}_N - \mu_\text{pN}(R_a) \right) e^{i\tilde{\omega}_A(r - \hat{r} \cdot R_a) n_A^a}, \\
\mathbf{H}_a(r) & \sim \frac{n_A^c \omega_A^2}{4\pi} \left( \hat{s}_N \mu_\text{sN}(R_a) - \hat{p}_N - \mu_\text{pN}(R_a) \right) e^{i\tilde{\omega}_A(r - \hat{r} \cdot R_a) n_A^a},
\end{align*}
\] (6.28)

with

\[
\begin{align*}
\mu_\text{sN}(R_a) &= \gamma_{sN} \cdot \mu(A)(R_a), \\
\mu_\text{pN}(R_a) &= \gamma_{pN} \cdot \mu(A)(R_a),
\end{align*}
\] (6.29)

and \(\gamma_{sN}\) and \(\gamma_{pN}\) are given by (4.45). All the \(\kappa\) dependent quantities in (6.28) are evaluated at \(\tilde{\kappa} = \tilde{\omega}_A n_A^1 (\hat{x} + \hat{y} \cdot \hat{r}) \cdot \hat{r}\). The unit polarization vectors of the radiated electric field are defined according to (2.7), and the \(T_s^A\) and \(T_p^A\) are Fresnel transmission coefficients (from the cladding to the substrate) for \(s\)- and \(p\)-polarizations of the anti-Stokes field, respectively. Eqs. (6.11), (6.12), and (6.28) give

\[
\frac{dP_{\text{sub}}}{d\Omega} = \frac{c n_A \omega_A^4}{8\pi^2\epsilon_0} \sum_{a=1}^N \sum_{b=1}^N \Gamma_{\text{sub}} : \mu^A (R_a) \mu^A (R_b) e^{i\tilde{\omega}_A (R_a - R_b) \cdot \hat{r} n_A^a},
\] (6.30)

where \(\Gamma_{\text{sub}} = \gamma_{sN} \gamma_{sN} + \gamma_{pN} \gamma_{pN}\). I use Eq. (6.27) along with the definition of \(E_L(R_a)\) and convert the sums in Eq. (6.30) into integrals assuming a large density of molecules. The radiated power into a unit solid angle in the substrate results as

\[
\frac{dP_{\text{sub}}}{d\Omega} = \frac{\omega_A^4 n_A^c \alpha_0}{2\pi^2\epsilon_0} (l_{\text{CARS}})^2 \rho^2 \varepsilon_0^2 \left| E_L^* (R) \cdot E_S (R) \right|^2 (\Gamma_{\text{sub}} : E_L^* E_P)
\times \left| \int dRe^{i\Delta \kappa \cdot R} g^2_P (R) g_S (R) \right|^2,
\] (6.31)

where \(l_{\text{CARS}}\) is given by (6.15) and is not the amplitude of molecular oscillations in the presence of the planar structure that will be introduced later. In a similar approach the radiated power into the cladding is

\[
\frac{dP_{\text{clad}}}{d\Omega} = \frac{\omega_A^4 n_A^c \alpha_0}{2\pi^2\epsilon_0} (l_{\text{CARS}})^2 \rho^2 \varepsilon_0^2 \left| E_L^* (R) \cdot E_S (R) \right|^2 (\Gamma_{\text{clad}} : E_L^* E_P)
\times \left| \int dRe^{i\Delta \kappa \cdot R} g^2_P (R) g_S (R) \right|^2,
\] (6.32)

where \(\Gamma_{\text{clad}} = \gamma_{s1} \gamma_{s1} + \gamma_{p1} \gamma_{p1}\) and \(\gamma_{s1}\) and \(\gamma_{p1}\) are given by (4.25). Compared to Eq.
(6.16), Eq. (6.32) contains the modification of the pump and Stokes field at the position of the molecules and the change in the radiation pattern due to the presence of the multilayer structure.

We are interested in planar structures that support resonant modes such as Bloch surface waves. As discussed in chapter 4, these resonances are usually very narrow in the $\kappa$ space, so the incident beam must be large enough to couple to the modes efficiently. Consider the limit of a large beam, $\kappa_I \Delta \gg 1$, where $\kappa_I$ and $\Delta$ are proportional to the width of the resonance and the spatial width of the incident beam, respectively. In this limit, as showed in Eq. (4.64),

$$g(x, y) \approx f(x, y) - (\kappa_I)^{-1} \partial f(x, y) \partial x + \ldots \approx f(x - (\kappa_I)^{-1}, y), \quad (6.33)$$

implying that in the limit of large beams the incident beam experiences a spatial shift of $\kappa_I^{-1}$. We can neglect this small shift and take $g(x, y) \approx f(x, y)$.

Consider a situation where the pump and Stokes beams come from the substrate at the angles $\theta_P$ and $\theta_S$ with the $z$ axis, respectively, and are in the same plane of incidence ($\hat{k}_P = \hat{k}_S$). Take the fields to be $s-$ polarized with Gaussian envelop functions in the $xy$ plane. When (6.33) and (6.26) are inserted into (6.31),

$$\frac{dP_{\text{sub}}^{\text{sub}}}{d\Omega} = \frac{\omega^A n^A_0 \alpha^A_1}{72\pi^2\epsilon_0 c^2 (v_{\text{CARS}})^2 \rho^2 A^2 \mathcal{E}_P^2}$$

$$\times \left| T_{1N}^{sP} \right|^4 \left| T_{1N}^{sS} \right|^2 \left( \left| T_{1N}^{sA} \cos \beta \right|^2 + \left| T_{1N}^{pA} \sin \beta \right|^2 \right)$$

$$\times \left( \frac{w^A_1}{w^s_1} \exp \left( i(2w^P_1 - w^s_1 + w^A_1) d \right) \right)^2$$

$$\times \exp \left( - \frac{\Delta^2}{3} \left( \frac{(\Delta \kappa_x)^2}{C^2} + (\Delta \kappa_y)^2 \right) \right), \quad (6.34)$$

where $\beta$ is the angle between the $x$ axis and $\hat{k}_A$, as in Fig. 6.1, and $C^2 = (2 \cos^2 \theta_P + \cos^2 \theta_S)/3$, which compared to (6.18) refers to a more general case where the pump and Stokes beams are not collinear.

We are interested in structures that support guided modes at the anti-Stokes frequency. If the structure has a resonance at the anti-Stokes frequency for $s-$ polarization, the transmission coefficient $T_{1N}^{sA}$ will have a pole at a complex wavenumber $\kappa_{\text{res}}^A$

$$T_{1N}^{sA} \approx \frac{\tau_{1N}^{sA}}{\kappa - \kappa_{\text{res}}^A}, \quad (6.35)$$
for $\kappa$ close to $\kappa^{A}_{R}$, where $\kappa^{A}_{res} = \kappa^{A}_{R} + i\kappa^{A}_{I}$ and $\tau^{A}_{N}$ is complex and has units of wavenumber [81]. The total collected power can be estimated by inserting (6.35) into (6.34), and integrating over all the solid angles. From (6.34) and (6.19), it is clear that the CARS signal is peaked at $\beta = 0$ with an angular width proportional to the inverse of the incident beam width. For sufficiently large incident beams the radiated CARS power is significant only over a small range of $\beta$, so we can expand $\beta$ around zero and approximate $\sin \beta \simeq \beta$ and $\cos \beta \simeq 1$. I will design the planar structure such that the Gaussian function in (6.34) and the Lorentzian function in (6.35) have their maximum at the same $\kappa$, so that $\kappa^{P}_{A} = 2\kappa - \kappa = \kappa^{A}_{R}$. In the large beam limit, $\kappa\Delta \gg 1$, the width of the Gaussian function ($\propto 1/\Delta$) is much smaller than the width of the Lorentzian function ($\propto \kappa^{A}_{I}$), and therefore the Lorentzian function can be assumed to be uniform over the range the Gaussian function is significant. Thus, the integrated power is

$$P_{CARS}^{ML} \simeq \frac{2\alpha_{1}^{2}}{48\varepsilon_{0}n_{1}^{2}} \rho^{2} (l_{CARS}^{ML})^{2} P_{P}^{ML} \times \frac{n_{1}}{n_{N} \cos \theta_{PML}} \left| \frac{w^{A}_{N} T_{s} e^{i\omega_{1} d}}{w^{A}_{1}} \right|^{2},$$

(6.36)

where the quantities with superscript $A$ are evaluated at $\kappa^{A}_{R}$. The amplitude of molecular oscillations in the presence of the multilayer structure can be characterized with a new parameter, $l^{ML}_{CARS}$, where

$$l^{ML}_{CARS} = \frac{2\alpha_{1}}{m_{\gamma} \omega_{0}} \left( |T_{N1}^{P} e^{i\omega_{1} d}| \langle \mathcal{E}_{P} \rangle |T_{N1}^{S} e^{i\omega_{1} d}| \langle \mathcal{E}_{S} \rangle \right),$$

(6.37)

differs from $l_{CARS}$ (the amplitude of oscillations in a uniform medium), as it depends on the modified pump and Stokes field amplitudes in the presence of the multilayer structure. The $|T_{N1}^{P} e^{i\omega_{1} d}|$ and $|T_{N1}^{S} e^{i\omega_{1} d}|$ factors take into account the modification of the pump and Stokes fields, respectively, due to the transmission through the multilayer structure and the distance $d$ above the structure. The $P_{P}^{ML}$ is the average probe (taken to be the same as pump) power at the position of the molecules, and is also modified due to the presence of the structure as

$$P_{P}^{ML} = |T_{N1}^{P} e^{i\omega_{1} d}|^{2} P_{P}$$

(6.38)

with $P_{P}$ the average probe (pump) power in the substrate and $|T_{N1}^{P} e^{i\omega_{1} d}|^{2}$ takes into account the modification of the probe (pump) power, due to the transmission through the multilayer structure and the distance $d$ above the structure. The scattered CARS signal reaches the substrate by passing through the distance $d$ and the multilayer structure, and therefore the collected power in the substrate is modified by a factor of $|T_{1N}^{A} e^{i\omega_{1} d}|^{2}$. 
6.4 A planar resonant structure

So far I have derived an expression for the CARS power in terms of the Fresnel coefficients for the pump, Stokes, and anti-Stokes fields. The Fresnel coefficients can be very large when the fields are coupled to the (leaky) resonant modes of the structure. In order to obtain maximum enhancement of the CARS signal, the structure should support resonant modes at all the pump, Stokes, and anti-Stokes frequencies. The energy conservation in CARS implies that

$$\omega_A - \omega_P = \omega_P - \omega_S,$$

(6.39)

and as showed in Sec. 6.3, when the incident pump and Stokes beams are in the same plane of incidence, the maximum anti-Stokes signal is obtained when

$$\kappa_A^{PM} - \kappa_P = \kappa_P - \kappa_S,$$

(6.40)

which can be understood as the momentum conservation. The above equations imply that $(\kappa_P, \omega_P), (\kappa_S, \omega_S),$ and $(\kappa_A^{PM}, \omega_A)$ lie on a line. This limits the structures fulfilling the triple resonance criteria, since the dispersion relations of most well known resonances, such as waveguide modes, do not follow a linear trend over a reasonably large Stokes shift range. However, structures with more design degrees of freedom support resonances with dispersion relations that can be tailored more conveniently.

Here the focus is on multilayer structures (see Fig. 6.3a) supporting Bloch surface waves. I have designed a structure with a linear dispersion relation for Stokes shifts up to 2100 cm$^{-1}$ for a pump at 1064 nm. The unit cell of the structure consists of one layer of SiO$_2$ with $d_{SiO_2}=104$ nm and one layer of TiO$_2$ with $d_{TiO_2}=212$ nm. To adjust the BSW dispersion relation, two additional top layers with $d_{SiO_2}=153$ nm and $d_{TiO_2}=67.5$ nm were added. The top layer is 10 nm of SiO$_2$, and is introduced to provide better chemical functionalization. I have assumed a water cladding, since in most biosensing applications the molecules are in solutions, and have optimized the BSW dispersion relation considering a 5 nm molecular layer with an index of 1.46 (typical thickness and index of lipids, which as I discuss later are our target molecules). Fig. 6.3b shows the dispersion relation for $s-$ polarized BSW supported by the above structure, taking into account the frequency dependence of refractive indices [94]. As expected, the BSWs are within the photonic bandgap region (evanescent in the multilayer) and to the right of the light line of water (evanescent in the cladding). I choose a Gadolinium Gallium Garnet (GGG) prism substrate with an index of refraction of $n_N=1.94$ at the pump frequency to couple the propagating fields into the resonant modes in a Kretschmann geometry [6]. I
choose a GGG prism, since with water cladding a high index prism substrate is required in order to fit the BSW dispersion line between the cladding and substrate light lines.

The incident pump and Stokes fields couple to the BSWs when their angles of incidence are $\theta_P = \sin^{-1}\left(\frac{\kappa_P^{BSW}}{\tilde{\omega}_P n_P^N}\right)$ and $\theta_S = \sin^{-1}\left(\frac{\kappa_S^{BSW}}{\tilde{\omega}_S n_S^N}\right)$, with $\kappa_P^{BSW}$ and $\kappa_S^{BSW}$ the BSW wavenumbers for the pump and Stokes frequencies, respectively. The excitation of the surface waves results in large pump and Stokes fields in the cladding at the molecules positions, which then lead into a larger driving force as well as a larger probe field to be scattered off the molecules. Fig. 6.4a shows $|T_{N1}^{P2}|$ and $|T_{N1}^{S2}|$, where the intensity enhancements for the pump and Stokes fields at $\kappa_P^{BSW}$ and $\kappa_S^{BSW}$ are clear. The width of these resonances ($\Delta\kappa_{res}$), which are indicative of the coupling losses, are very small and increase by decreasing the number of periods in the periodic structure. I choose 3.5 periods such that $\Delta\kappa_{res} \geq 6 \text{mm}^{-1}$ for the pump and Stokes frequencies, and therefore an incident beam with $\Delta_{2nm} = 2 \text{mm}$ gives $\Delta_{2nm} \Delta\kappa_{res} \simeq 12$ and can couple to the resonant modes efficiently. Incident beams with significantly smaller beam diameters have larger $\kappa$ spreads and only a small fraction of the beams can couple to the resonant modes. The frequency width of the pump and Stokes resonances is greater than 0.1 ps$^{-1}$, and therefore pulses with a time duration of $\tau = 10$ ps, which are considered in the next section, can efficiently couple to the resonant modes.

The structure has been designed to support a BSW at the anti-Stokes frequency at a wavenumber equal to the anti-Stokes wavenumber that satisfies the phase matching
Figure 6.4: (a) The Fresnel transmission coefficients (from substrate to cladding) of the pump and Stokes fields, for the multilayer structure discussed in the text. The $\kappa_0$ is $\kappa_{BSW}^P$ for the pump and $\kappa_{BSW}^S$ for the Stokes. (b) The Fresnel transmission coefficients (from cladding to substrate) of the anti-Stokes field, for the multilayer structure discussed in the text. The BSW resonance wavenumber is the same as the phase matching wavenumber, $\kappa_{PM}^A$.

condition, $\kappa_{BSW}^A = \kappa_{PM}^A$. Therefore, the phase matched anti-Stokes signal automatically couples to a BSW. The $|T_{nN}^{sA}|^2$ plotted in Fig.6.4b shows the intensity enhancement of the scattered anti-Stokes signal when coupled to the BSW. The width of the anti-Stokes BSW, $\Delta \kappa_{res} \simeq 4 \text{ mm}^{-1}$, ensures that the surface wave does not travel any farther than 250 $\mu$m.

So far I have shown that a multilayer structure can be designed to allow coupling of all fields involved in the CARS process to BSW resonances. In the next section I calculate the CARS power from molecules on this structure, and compare it with spontaneous Raman scattering power and CARS power in the absence of the resonant structure.

### 6.5 Comparisons

In spontaneous Raman scattering the Raman signal and the fluorescence background [104] are both red shifted with respect to the pump, while in coherent anti-Stokes Raman scattering the CARS signal is blue shifted with respect to the pump separating it from the red shifted fluorescence background. CARS power depends quadratically on the density of molecules instead of linearly as in spontaneous Raman scattering, so the CARS signal is expected to be stronger than the spontaneous Raman signal for bulk samples. This section compares the CARS and spontaneous Raman scattering powers for thin layers of molecules. The CARS power for thin layers of molecules (Eqs. (6.20) and (6.34)) is
maximized at certain directions in space and the width of the power distribution scales by the inverse of the width of the pump and Stokes beams, and therefore is very narrow for large incident beam spot sizes. Collection of such a directional signal is more efficient, especially compared to the spontaneous Raman scattering where the scattering signal is emitted over a large range of angles. The CARS signal is usually masked with a non-resonant background [24], but the unwanted non-resonant signal can be removed using one of the various proposed methods such as polarization sensitive [64], time resolved [65], frequency modulated [55], or interferometric CARS [66].

For the calculations in this section I consider lipid bilayers as candidate molecules. Lipids are rich in CH\textsubscript{2} stretches with Raman shifts about 2800-3000 cm\(^{-1}\), which allow them to be distinguished from other chemical species [56,57]. However, since the CH\textsubscript{2} vibrational frequencies of different lipid molecules are very similar, specific lipid molecules can not be differentiated. To spectrally distinguish different lipid molecules, the CH\textsubscript{2} groups can be replaced by CD\textsubscript{2} groups (when the molecules are deuterated), changing their Raman shift to about 2100 cm\(^{-1}\) [57]. The multilayer structure that I have designed supports BSW with a linear dispersion for Raman shifts up to 2100 cm\(^{-1}\), and therefore deuterated lipids are appropriate molecules to be studied with our designed multilayer structure. A typical lipid molecule has about 30 CD\textsubscript{2} bonds and the area per molecule is about 70 Å\(^2\) [120], so the areal density of the vibrational oscillators is \(\rho \sim 43/\text{nm}^2\). The Raman cross section per C-D bond is about \(\sigma^S_0 \sim 2 \times 10^{-29} \text{ cm}^2\) [121] and their homogeneous linewidth is about 5-10 cm\(^{-1}\) [122] corresponding to \(\gamma = \Delta \omega \sim 1 \text{ ps}^{-1}\).

Optimal laser parameters for CARS have been discussed in [55], where picosecond pulses with energies about 1 nJ per pulse have been recommended. I choose the pulse duration \(\tau \sim 10 \text{ ps}\) for the pump and Stokes pulses, so that the bandwidth of the excitation pulses (\(\sim 1 \text{ cm}^{-1}\)) is much smaller than the homogeneous linewidth of the molecules (\(\sim 5-10 \text{ cm}^{-1}\)), and therefore the molecular vibrations can be driven efficiently. The picosecond pulses are also advantageous (compared to femtosecond pulses) for minimizing the non-resonant background, since they mainly contain frequency components that can resonantly drive the molecular vibrations. The bandwidth of 10 ps pulses is also smaller than the linewidth of the resonant modes (\(\sim 4 \text{ cm}^{-1}\)) in the resonant multilayer structure introduced in the last section, and therefore they can also couple to BSW resonances efficiently.

The pump and Stokes intensities must be below the molecular damage threshold. The damage threshold intensity varies for different biological molecules and is determined by the pulse duration, repetition rate, and excitation wavelength [123]. The studies of cell and tissue photodamage by Yakovlev et al. shows that the damage threshold intensity
can be approximated as

\[ I_t \simeq 1.5 \times 10^{11} \text{W/cm}^2 \sqrt{\frac{1 \text{ps}}{\tau}} \]  \hspace{2cm} (6.41)

in the wavelength region around 1000 nm, and it is mainly due to multiphoton absorption [124,125]. For 10 ps pulses the above expression gives \( I_t \sim 5 \times 10^{10} \text{ W/cm}^2 \).

Unless otherwise stated, the above parameters are used for the rest of the calculations in this section.

A. CARS or spontaneous Raman? (uniform medium)

The average CARS power from a thin layer of molecules in a uniform medium was calculated in Sec. 6.2. In a similar approach (see chapter 4), the spontaneous Raman scattering power (in half space) can be calculated to be

\[ P_{\text{free Spont.}} \sim \frac{\tilde{\omega}_S^4 \alpha^2}{48 \pi \epsilon_0} \rho (l_{\text{Spont.}}^S)^2 P_P, \]  \hspace{2cm} (6.42)

where \( P_P \) is the average power of the pump field, and \( l_{\text{Spont.}}^S \) is the characteristic length corresponding to the oscillation amplitude of the quantum harmonic oscillator (Eq. (4.14)). From Eqs. (6.24) and (6.42),

\[ \frac{P_{\text{free}}^\text{CARS}}{P_{\text{free}}^\text{Spont.}} \sim \frac{1}{4 \pi n_1} \left( \frac{\tilde{\omega}_A}{\tilde{\omega}_S} \right)^4 \left( \frac{l_{\text{CARS}}}{l_{\text{Spont.}}^S} \right)^2 \left( \frac{P_P^\text{CARS}}{P_P^\text{Spont.}} \right) \rho \lambda_A^2, \]  \hspace{2cm} (6.43)

where \( P_P^\text{CARS} \) and \( P_P^\text{Spont.} \) are the average pump power in CARS and spontaneous Raman, which I take to be the same. In terms of the known parameters of the molecule and pump and Stokes lasers, the squared ratio of the characteristic lengths of CARS and spontaneous Raman is

\[ \left( \frac{l_{\text{CARS}}}{l_{\text{Spont.}}^S} \right)^2 = \frac{96 \pi}{\tilde{\omega}_S n_1^2} \frac{1}{(hc\gamma(n + 1))^2} \sigma_0 \lambda_\text{CARS} \lambda_{\text{Spont.}}^C \]  \hspace{2cm} (6.44)

where \( \sigma_0^S \) is the Stokes cross section in a uniform medium discussed in chapter 4. Tightly focused beams of diameters about 1 \( \mu \text{m} \) are commonly used in CARS experiments to maximize the pump and Stokes intensities. Tightly focused beams with 10 ps pulses of 1 nJ energy per pulse have peak intensities about \( 10^{10} \text{ W/cm}^2 \). For a Stokes shift of 2100 \( \text{cm}^{-1} \), \( n=3 \times 10^{-5} \) at room temperature, and \( l_{\text{CARS}}/l_{\text{Spont.}}^S \approx 0.12 \). With an areal density of 43/nm\(^2\) of scatterers, \( \rho \lambda_\text{A}^2 \simeq 3 \times 10^7 \), and therefore
This means that for the lipid molecules with a large density of Raman active modes, the CARS power is much stronger than the spontaneous Stokes Raman scattering power. We can also compare CARS with spontaneous anti-Stokes Raman scattering. I find $l_{\text{CARS}}/l_{\text{Spont.}}^A \approx 21$, where $l_{\text{Spont.}}^A$ is the characteristic length associated with the anti-Stokes radiation (Eq. (4.14)). The ratio of the CARS power to the spontaneous anti-Stokes Raman scattering power, through an equation similar to Eq. (6.43), is

$$\frac{P_{\text{free}}^{\text{CARS}}}{P_{\text{free}}^{\text{Spont.}}} \approx 6 \times 10^8$$

(spontaneous anti-Stokes),

which is more than $10^3$ times larger than the ratio of the CARS power to the spontaneous Stokes Raman scattering power as a result of $l_{\text{Spont.}}^A \ll l_{\text{Spont.}}^S$.

**B. Tight focusing or resonant structure?**

We can compare CARS power from a thin layer of molecules on the resonant multilayer structure to the CARS power in a uniform medium. From Eqs. (6.24) and (6.36),

$$\frac{P_{\text{CARS}}^{\text{ML}}}{P_{\text{CARS}}^{\text{free}}} \approx \frac{n_1}{n_N \cos \theta_P} \frac{n^A_N T^A_N}{w_1} \left| \frac{w_A^N T^A_N \text{e}^{iw_A} d}{l_{\text{CARS}}^A} \right|^2 \left( \frac{P_{\text{ML}}^{\text{CARS}}}{P_{\text{P}}^{\text{free}}} \right).$$

(6.45)

Considering 10 ps pulses of 1 nJ of energy per pulse, and 2 mm and 1 μm beams for the multilayer structure and uniform medium, respectively (see Fig. 6.5), the pump and Stokes peak intensities at the position of the molecules are about $4 \times 10^6$ W/cm$^2$ and $8 \times 10^5$ W/cm$^2$ for the multilayer structure, and are about $10^{10}$ W/cm$^2$ in the uniform medium (below the typical damage threshold of $5 \times 10^{10}$ W/cm$^2$ [124]). This gives $l_{\text{CARS}}^{\text{ML}}/l_{\text{CARS}} \approx 10^{-4}$ and the ratio of CARS powers is

$$\frac{P_{\text{CARS}}^{\text{ML}}}{P_{\text{CARS}}^{\text{free}}} \approx 0.1$$

(1 μm beams in free space).

Even though the resonant structure enhances the pump, Stokes, and anti-Stokes fields due to coupling to resonant modes, and a larger number of the molecules are illuminated by the larger incident beams, the CARS signal is stronger in the uniform medium where the incident beams are tightly focused and larger field intensities at the molecules positions are achieved.
Figure 6.5: (a) A thin layer of molecules on a resonant structure illuminated with a 2 mm beam. (b) A thin layer of molecules in the uniform medium, illuminated with a 1 μm beam.

C. CARS or spontaneous Raman? (resonant structure)

The presence of the resonant structure enhances both the spontaneous Raman and CARS signals. In chapter 4 the spontaneous Raman scattering from molecules on resonant structures was discussed. If the structure supports resonant modes for the pump and Stokes fields, the average Stokes power in the substrate is

\[
P_{\text{ML Spont.}}^{\text{ML}} \approx \frac{\omega_S^2 \alpha_1^2}{48 \pi \varepsilon_0} P_{\text{Spont.}}^2 P_C^{\text{ML}}
\]

\[
\times \frac{3 \pi \tan \theta_S}{4 \cos \theta_P} \frac{\kappa_P^S}{\omega_S} \left| \frac{w_N^S}{w_I^S} T_{1N} e^{i \omega_1^S d} \right|^2,
\]

where \( \theta_S \) is the Stokes resonance angle, and the quantities with superscript S are evaluated at the Stokes resonance angle (wavenumber). Similar to CARS the modification of the scattered field in the presence of the planar structure is determined by the Fresnel coefficients. From Eqs. (6.42) and (6.46)

\[
\frac{P_{\text{ML Spont.}}^\text{ML}}{P_{\text{Spont.}}^\text{free}} \approx \frac{3 \pi \tan \theta_S}{4 n_1 \cos \theta_P} \left( \frac{\kappa_P^S}{\omega_S} \right) \left| \frac{w_N^S}{w_I^S} T_{1N} e^{i \omega_1^S d} \right|^2,
\]

and the ratio is about \( 10^4 \) for the multilayer structure studied here. Comparing CARS and spontaneous Raman scattering in the presence of the multilayer structure,

\[
\frac{P_{\text{ML CARS}}^{\text{ML}}}{P_{\text{ML Spont.}}^\text{ML}} = \frac{P_{\text{ML CARS}}^\text{ML}}{P_{\text{CARS}}^\text{free}} \cdot \frac{P_{\text{CARS}}^\text{free}}{P_{\text{Spont.}}^\text{ML}} \cdot \frac{P_{\text{Spont.}}^\text{ML}}{P_{\text{Spont.}}^\text{free}}.
\]

For 10 ps pump and Stokes pulses of 1 nJ energy per pulse and beam diameters of 2 mm

\[
\frac{P_{\text{ML CARS}}^\text{ML}}{P_{\text{ML Spont.}}^\text{ML}} \approx 1.
\]
suggesting that with the resonant multilayer structure the enhancement of the CARS power and the spontaneous Raman scattering powers are similar. The reason is due to the fact that with the resonant structure the maximum achievable intensities at the surface of the structure is limited by the minimum beam area that allows efficient coupling of the pump and Stokes fields to the resonant modes. The ratio of the characteristic oscillation lengths $l_{CARS}^{ML}/l_{Spont.}^{S} \approx 10^{-5}$ is so small that even the quadratic dependence of the CARS power on the density of oscillators can not compensate for it. The complexity of the CARS experiment compared to the spontaneous Raman scattering experiment is a disadvantage for CARS, while the blue shifting of the anti-Stokes signal is an advantage for CARS.

### 6.6 Conclusion

I have studied coherent anti-Stokes Raman scattering from thin layers of molecules on planar structures. I have considered resonant structures supporting Bloch surface waves for all the fields involved in the CARS process, and found expressions for the CARS power in terms of the Fresnel coefficients of the structure. I have shown that despite the limitations enforced by the phase matching condition, the dispersion relation of BSW can be engineered such that all the fields including the radiated anti-Stokes field couple to surface waves. In particular, I have designed a structure that supports BSW with a linear dispersion relation for Stokes shifts up to 2100 cm$^{-1}$. I have compared the CARS power to the spontaneous Raman scattering power in a uniform medium and in the presence of the multilayer structure. To have an estimation of these quantities in typical experimental scenarios, I have considered lipid bilayers as candidate molecules. The CD$_2$ bonds in deuterated lipids have a Raman shift about 2100 cm$^{-1}$, and therefore these molecules are appropriate for use on the multilayer structure proposed in this chapter.

For the lipid molecules with a damage threshold intensity about $5 \times 10^{10}$ W/cm$^2$, in the uniform medium the CARS power is about $10^6$ times greater than the spontaneous Raman scattering power. On the resonant multilayer structure the spontaneous Raman scattering power is enhanced about $10^4$ and the CARS power is of the same order of magnitude as the spontaneous Raman scattering power. The complexity of the CARS instrumentation is a disadvantage, however, CARS has the advantage of the signal being blue shifted with respect to the pump field, and therefore it offers a more efficient separation from the fluorescence background. I have considered pump and Stokes beams with diameters 2 mm and 1 $\mu$m in the resonant structure case and uniform medium, respectively, and found that the CARS power from molecules on the structure is about 0.1
of the CARS power from molecules in the uniform medium. Therefore, with the resonant multilayer structure, even though all the incoming and outgoing fields are enhanced due to the coupling to the resonant modes, and despite a larger number of molecules being illuminated by the pump and Stoke beams, the power of the anti-Stokes signal in the presence of the resonant structure is smaller than the one from molecules in the uniform medium. The large beam size in the multilayer structure case limits the maximum achievable intensity at the surface of the structure and the maximum driving force on the molecules.

Compared to CARS in a uniform medium, CARS on the resonant structure has the advantage of the potential for integration as a compact device. Moreover, since the width of the anti-Stokes radiation is inversely proportional to the width of the pump and Stokes beams, the radiated power is highly directional in the presence of the structure, while with the tightly focused beams the anti-Stokes signal comes out over a wide range of angles. In CARS with tightly focused beams only a small section of the sample is illuminated with the small incident beams and scanning through the whole sample makes the process slow. Using the resonant multilayer structure with beams that have an area about $10^6$ larger, a significantly larger part of the sample is illuminated at once, and therefore the process can be significantly faster.
Chapter 7

Conclusion

Ultrasensitive detection of biological molecules is a powerful tool in medical diagnostics. Optical biosensing techniques and devices have attracted great interest in the last few decades, because of their selectivity in molecular detection and possibility of multiplexing and compact design.

In surface plasmon resonance biosensors the small propagation length of surface plasmons limits the performance of these devices. Metal films or stripes in symmetric configurations support LRSP resonances with longer propagation lengths. In many biosensing applications the physical implementation of such symmetric structures is challenging or even impossible. An alternative solution is designing asymmetric layered structures supporting similar LRSP modes. Chapter 3 presented a systematic strategy for designing asymmetric multilayer structures that support LRSPs. I showed that a multilayer structure can be designed to support a LRSP mode at a wavenumber close to the LRSP resonance wavenumber in a symmetric configuration and with a propagation length slightly larger than the propagation length of the LRSP in the symmetric structure (ignoring scattering losses due to surface roughness). I presented a protocol for designing such periodic multilayer structures, obtained a rough estimation of the structure parameters using a model system without loss, and determined the exact parameters by including the loss in the final design. For a specific structure composed of a gold film and SiO$_2$ and TiO$_2$ layers, the dependence of the mode losses on the thickness of the periodic multilayer structure was studied and it was shown that these losses are minimum if the multilayer structure thickness is about or greater than 30 μm.

I derived a semi-analytic expression for a standard surface sensing parameter that characterizes the sensitivity of arbitrary planar resonant structures. For thin molecular layers on such structures the resulted semi-analytic expression shows the dependence of the sensing parameter on the dielectric constant and thickness of the molecular layer and
the pole strength of the resonance in the bare resonant structure. For molecular layer thicknesses less than about 5 nm there is a good match between the semi-analytic expressions and the exact results, and for molecular layer thicknesses up to 10 nm corrections about 10% apply. I found that (in an end-fire coupling configuration) the surface sensing parameter of the asymmetric multilayer structure is $G = 1.28 \text{ nm}^{-1}$ and is larger than the surface sensing parameter of the symmetric structure, $G = 1.09 \text{ nm}^{-1}$. Compared to the previous studies, the asymmetric structures in this thesis have the advantage of being fully periodic, less lossy, more stable, and easier to fabricate. The main contribution from this thesis, however, is the new design strategy that can be applied to structures involving other metals or other materials for the multilayers.

Another optical sensing technique studied in this thesis is Raman scattering that provides specific information about the vibrational structure of molecules, and therefore allows for better selectivity of chemical and biological species. The weak Raman scattering signal is significantly enhanced when molecules are located in the vicinity of resonant structures and the incident and scattered fields are coupled to resonant modes. In this thesis the enhancement of Raman scattering from molecules on resonant dielectric structures, including multilayers supporting BSW resonances, has been studied. The BSW structures do not suffer from absorption losses and can be designed to support BSWs over a wide spectral range, and the BSW dispersion relation can be easily tuned by varying the parameters of the multilayer structure.

Chapter 4 presented a systematic study of spontaneous Raman scattering cross section for molecules on arbitrary planar structures and calculated Raman cross sections in terms of the Fresnel coefficients of the structure. This allows for identification of any resonances as well as derivation of semi-analytic expressions for the scattering power when the scattered fields are coupled to resonant modes. The Kretschmann configuration was considered to couple propagating fields to resonant modes, since this coupling scheme reduces the interaction of the scattered fields with the molecules on the surface of the structure and allows for implementation of microfluidic channels and multiplexing. For a Stokes shifts of 3000 cm$^{-1}$, I compared the numerical calculations of the differential Raman cross sections in the BSW structures, waveguide structures, and surface plasmon structures. A maximum enhancement of about $10^6$ was found for the BSW structures corresponding to excitation of a BSW by the Stokes radiation. The enhancement of the integrated Stokes cross section (up to $10^3$ for the dielectric structures) is a result of the enhancement of the pump field and the excitation of the resonant modes at the Stokes frequency only results in a redistribution of the radiated power. I confirmed that the presented plane wave analysis is valid in a more realistic scenario of excitation by a finite
pump beam, if the beam diameter is larger than a few millimeters.

The experimental realization of surface enhanced Raman scattering in dielectric multilayer structures supporting BSWs, presented in chapter 5, provided a proof of principle of the theoretical study. Our experimental colleagues showed that the Raman lines of acetone solution and sulphur powder on BSW structures are enhanced compared to the Raman line of molecules on bare prisms. While due to the absence of the Raman lines in the case of the bare prism it is not possible to estimate the real SERS enhancement factor, a lower bound of 50 is assumed by considering the noise amplitude in the bare prism measurements. Based on the theoretical studies presented in chapter 4, I predicted a SERS enhancement factor about 400 for the sample at visible. Our experimental colleagues observed an enhancement of the same order in a photoluminescence experiment with the sample in the visible, providing a better estimation of SERS enhancement factor. These enhancement factors are still less than those reported in traditional metallic SERS structures with localized SP resonances. However, addition of metallic nanoparticles on the surface of these dielectric structures can increase the SERS enhancement even further, and fabrication of additional guiding channels on these structures can lead to the confinement of the BSW in 1D.

Chapter 6 presented surface enhanced coherent anti-Stokes Raman scattering from thin layers of molecules on planar resonant structures. I focused on multilayer structures supporting resonant modes for all the pump, Stokes, and anti-Stokes fields, and derived expressions for the CARS power in terms of the Fresnel coefficients of the structure. The coupling of incident pump and Stokes fields to resonant modes enhances the pump and Stokes field intensities at the surface of the structure and as a result the molecular vibrations are driven more strongly. The radiated anti-Stokes field is peaked at specific directions, due to the phase matching condition, and it can couple to a resonant mode if the structure supports resonances with a linear dispersion relation. I designed a multilayer structure supporting BSWs with a linear dispersion relation for Stokes shifts up to 2100 cm$^{-1}$, which allows the pump, Stokes, and anti-Stokes fields to couple to BSWs.

I compared the CARS power and the spontaneous Raman scattering power in a uniform medium and in the presence of the multilayer structure, and presented numerical comparisons for deuterated lipid bilayers, which are rich in CD$_2$ bonds and have Raman shifts about 2100 cm$^{-1}$. In the uniform medium the CARS power is about $10^5$ times greater than the spontaneous Raman scattering power. On the resonant multilayer structure, the CARS power is of the same order as the spontaneous Raman scattering power and about 10 times weaker than the CARS power in the uniform medium. The area of the pump and Stokes beams is assumed to be more than six orders of magnitude
larger in the resonant structure case. This limits the maximum achievable intensity at the surface of the structure and the driving force on the molecules. Therefore, despite a larger number of molecules being illuminated by the large pump and Stoke beams the anti-Stokes signal is not stronger than the anti-Stokes signal in the uniform medium. However, the radiated anti-Stokes power is highly directional in the presence of the resonant structure, and such structures offer the potential for integration as a compact device enabling fast imaging or spectroscopy of thin samples in 2D. Compared to spontaneous Raman scattering, CARS has the advantage of the signal being blue shifted with respect to the pump field, and therefore it offers a more efficient separation from the fluorescence background. The CARS experiment instrumentation is, however, more complex and the anti-Stokes signal is masked by a nonresonant background signal. Nonetheless, the unwanted background signal can be removed using one of the previously proposed techniques.

The results presented in this thesis can be extended to study SERS from molecules on planar structures supporting LRSP. The asymmetric multilayer structure studied in chapter 3 can be used as a SERS substrate when the pump field is coupled to the LRSP excitation, and because of the good surface functionalization of the gold films these structures are expected to be more promising SERS substrates than fully dielectric multilayer structures. The Raman scattering cross section of molecules on such structures can be calculated using the approach presented in chapter 4. Another extension of the results presented in this thesis is studying LRSP in asymmetric multilayer structures coated with metal stripes, which allow field confinement in 1D and integration with microfluidic channels. Such structures can be designed and studied using commercial software.
Appendix A

The transfer matrix method

A.1 Formalism

In a multilayer structure, isotropic in the $xy$ plane, the electric field components for each of $s$– and $p$– polarizations can be related using $2 \times 2$ transfer matrices (here we follow the notation in [83,89]). For instance, if the fields in layer $N$ at $z = -D$ are $(E_{N+}e^{-iw_ND}, E_{N-}e^{iw_ND})$, the fields in layer 1 at $z = 0$ are

\[
\begin{pmatrix}
E_{1+} \\
E_{1-}
\end{pmatrix} = \begin{pmatrix}
a & b \\
c & d
\end{pmatrix} \begin{pmatrix}
E_{N+}e^{-iw_ND} \\
E_{N-}e^{iw_ND}
\end{pmatrix},
\]  

where $\mathcal{M}_{1N} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$ is the transfer matrix between $z = 0$ and $z = -D$, and the polarization labels are implicit. In order to determine the elements of the transfer matrix in terms of the parameters of the structure (dielectric constants, thickness of the layers), I start by relating the fields in the same medium $(i)$ between point $a$ at $z = z_a$ and point $b$ at $z = z_b$. The fields at points $a$ and $b$ are given by $e_i(z_a) = (E_{i+}e^{iw_i z_a}, E_{i-}e^{-iw_i z_a})$ and $e_i(z_b) = (E_{i+}e^{iw_i z_b}, E_{i-}e^{-iw_i z_b})$, respectively. A propagation transfer matrix defined as

\[
M_i(z_b - z_a) = \begin{pmatrix}
e^{iw_i(z_a-z_b)} & 0 \\
0 & e^{-iw_i(z_a-z_b)}
\end{pmatrix}
\]  

(A.2)

gives $e_i(z_a) = M_i(z_a - z_b)e_i(z_b)$. In particular, the matrix that propagates the fields from one interface to another is

\[
M_i(d_i) = \begin{pmatrix}
e^{iw_i d_i} & 0 \\
0 & e^{-iw_i d_i}
\end{pmatrix},
\]  

(A.3)
where \( d_i \) is the thickness of layer \( i \). At the interface of medium \( i \) and medium \( j \) at \( z = z_0 \) and with medium \( i \) taken to be above medium \( j \), the fields just above the interface and just below the interface are given by \( e_i(z_0^+) \) and \( e_j(z_0^-) \), respectively. Using the continuity condition at the interface, I find \( e_i(z_0^+) = M_{ij} e_j(z_0^-) \), with

\[
M_{ij} = \frac{1}{t_{ij}} \begin{pmatrix} 1 & r_{ij} \\ r_{ij} & 1 \end{pmatrix},
\]

(A.4)

where for \( s- \) polarization

\[
r_{ij}^s = \frac{w_i - w_j}{w_i + w_j},
\]

\[
t_{ij}^s = \frac{2w_i}{w_i + w_j},
\]

(A.5)

and for \( p- \) polarization,

\[
r_{ij}^p = \frac{w_i \varepsilon_j - w_j \varepsilon_i}{w_i \varepsilon_j + w_j \varepsilon_i},
\]

\[
t_{ij}^p = \frac{2n_i n_j w_i}{w_i \varepsilon_j + w_j \varepsilon_i}.
\]

(A.6)

The \( r_{ij} \) and \( t_{ij} \) are the Fresnel reflection and transmission coefficients, respectively, and satisfy the identities

\[
r_{ji} = -r_{ij},
\]

\[
t_{ij} t_{ji} - r_{ij} r_{ji} = 1.
\]

(A.7)

It also can be shown that \( M_{ik} M_{kj} = M_{ij} \) and consequently \( M_{ij} M_{ji} = M_{ii} = I \), with \( I \) the identity matrix. Using the propagation and interface transfer matrices given in Eqs. (A.3) and (A.4), the transfer matrix for any arbitrary layered structure can be constructed. For example, consider a simple structure consisting of medium with dielectric constant \( \varepsilon_1 \) for \( z \geq 0 \), medium with dielectric constant \( \varepsilon_2 \) for \( 0 > z > -D \), and medium with dielectric constant \( \varepsilon_3 \) for \( z \leq -D \). The fields in medium 1 are related to the fields in medium 3 through

\[
e_1(0) = M_{12} M_2(D) M_{23} e_3(-D),
\]

(A.8)

and therefore, the transfer matrix between medium 1 and medium 3 is simply \( \mathcal{M}_{13} = M_{12} M_2(D) M_{23} \), the product of the elementary interface and propagations transfer matrices. Thus from (2.14), the Fresnel reflection and transmission coefficients defined in
The transfer matrix method

(2.12) and (2.13) are

\[ T_{13} = \frac{t_{12} t_{23} e^{iw_2 D}}{1 - r_{21} r_{23} e^{2iw_2 D}}, \]
\[ R_{13} = r_{12} + \frac{t_{12} t_{23} r_{21} e^{2iw_2 D}}{1 - r_{21} r_{23} e^{2iw_2 D}}. \]  

(A.9)

The transfer matrix calculation can be generalized for a structure with \( N \) layers with thicknesses \( d_1, d_2, d_3, \ldots, d_N \). In particular,

\[ M_{1N} = M_{12} M_2(d_2) M_{23} M_3(d_3) \ldots M_{N-1,N}, \]

(A.10)

and

\[ M_{N1} = M_{N,N-1} M_{N-1}(d_{N-1}) \ldots M_2(d_2) M_{21}, \]

(A.11)

and these matrices can be calculated numerically.

A.2 Fresnel coefficients of a lossless multilayer structure

In this section I show that the Fresnel coefficient between cladding and a multilayer structure (with non-absorbing layers), \( \bar{R}_{1s} \) is real in the region where the fields are evanescent in the cladding and are in the bandgap of the multilayer structure. I assume an infinitesimally thin virtual layer (medium \( v \)) with dielectric constant \( \varepsilon_1 \), between the overlayers and the periodic part. Then \( \bar{R}_{1s} \) is

\[ \bar{R}_{1s} = R_{1v} + \frac{T_{1v} R_{vs} T_{v1}}{1 - R_{vs} R_{v1}}, \]

(A.12)

where \( R_{vs} \) is the reflection coefficient between the virtual layer and the periodic part. The \( R_{1v}, T_{1v}, R_{v1}, \) and \( T_{v1} \) are the Fresnel coefficients between the cladding and the virtual layer (both with dielectric constant \( \varepsilon_1 \)), and are the elements of the transfer matrix \( M_{1v} \),

\[ M_{1v} = M_{12} M_2(d_2) M_{23} M_3(d_3) M_{34} \ldots M_{ne}. \]

(A.13)

I use \( M_{ij} = M_{i1} M_{1j} \), and regroup the transfer matrices in (A.13) as

\[ M_{1v} = (M_{12} M_2(d_2) M_{21})(M_{13} M_3(d_3) M_{31}) \ldots (M_{1n} M_n(d_n) M_{nv}). \]  

(A.14)
If the fields are evanescent in the cladding, all the elements of \((M_{1i}M_i(d_i)M_{i1})\) are real (see Sec. A.3). Therefore, all the elements of the transfer matrix \(\mathcal{M}_{1v}\), including \(R_{1v}\), \(T_{1v}\), \(R_{v1}\), and \(T_{v1}\) are real. The reflection coefficient between the virtual layer and the periodic part of the multilayer structure, \(R_{vs}\), is

\[
R_{vs} = r_{va} + \frac{t_{va}R_{per}t_{av}}{1 - r_{av}R_{per}},
\]

where in the second line, I have used the Fresnel coefficients identities in (A.7). In the region of interest, \(|R_{per}| = 1\), and if the fields are propagating in medium \(a\) (which is the case for the structures in this thesis), then \(|r_{av}| = 1\), and therefore

\[
R_{vs} = \frac{1}{R_{per}^* - r_{av}} + \frac{1}{R_{per} - r_{av}^*},
\]

indicating that \(R_{vs}\) is real. Since all \(R_{vs}\), \(R_{1v}\), \(T_{1v}\), \(R_{v1}\), and \(T_{v1}\) are real, the Fresnel coefficient \(\bar{R}_{1s}\) in Eq. (A.12) is real as well.

### A.3 Transfer matrix of a symmetric structure

A symmetric structure is consisted of a layer of medium \(i\) with dielectric constant \(\varepsilon_i\) and thickness \(d_i\) sandwiched between two media with the same dielectric constant \(\varepsilon_s\). In this section, following the argument in [89], I show that the elements of the transfer matrix of this symmetric structure, \(\mathcal{M}_{ss} = M_{si}M_i(d_i)M_{is}\), are real, if the field is evanescent in medium \(s\). We have

\[
M_{si} = \frac{1}{t_{si}} \begin{pmatrix} 1 & r_{si} \\ r_{si} & 1 \end{pmatrix},
\]

and

\[
M_i(d_i) = \begin{pmatrix} e^{i\omega d_i} & 0 \\ 0 & e^{-i\omega d_i} \end{pmatrix},
\]

and

\[
M_{is} = \frac{1}{t_{is}} \begin{pmatrix} 1 & r_{is} \\ r_{is} & 1 \end{pmatrix},
\]
thus
\[ M_{ss} = \frac{1}{T} \begin{pmatrix} T^2 - R^2 & R \\ -R & 1 \end{pmatrix} , \] (A.20)

with
\[
T = \frac{t_{si} t_{is} e^{i w_{d_i}}}{1 - r_{is}^2 e^{2 i w_{d_i}}},
\]
\[
R = \frac{r_{si} + r_{is} e^{2 i w_{d_i}}}{1 - r_{is}^2 e^{2 i w_{d_i}}}. \] (A.21)

Using
\[
r_{si} = -r_{is},
\]
\[
1 + r_{si} r_{is} = t_{si} t_{is}, \] (A.22)

the \( T \) and \( R \) are simplified as
\[
T = \frac{1 - r_{is}^2}{e^{-i w_{d_i}} - r_{is}^2 e^{i w_{d_i}}}, \] (A.23)

and
\[
R = \frac{r_{is} e^{i w_{d_i}} - r_{is} e^{-i w_{d_i}}}{e^{-i w_{d_i}} - r_{is}^2 e^{i w_{d_i}}}. \] (A.24)

If there is no absorption in the structure (\( \varepsilon_i \) and \( \varepsilon_s \) are real) and the field is evanescent in medium \( s \), \( w_s = \sqrt{\omega^2 \varepsilon_s - k^2} = i q \), where \( q \) is real. Then
\[
r_{is} = \frac{w_i - w_s}{w_i + w_s} = \frac{w_i - i q}{w_i + i q}, \] (A.25)

and
\[
r_{is} = \frac{w_i \varepsilon_s - w_s \varepsilon_i}{w_i \varepsilon_s + w_s \varepsilon_i} = \frac{w_i \varepsilon_s - i q \varepsilon_i}{w_i \varepsilon_s + i q \varepsilon_i}, \] (A.26)

for \( s- \) and \( p- \) polarization, respectively. If the field is propagating in medium \( i \), then \( w_i \) is real and \( |r_{is}| = 1 \), and
\[
T = \frac{r_{is}^* - r_{is}}{r_{is}^* e^{-i w_{d_i}} - r_{is} e^{i w_{d_i}}}, \] (A.27)

and
\[
R = \frac{e^{i w_{d_i}} - e^{-i w_{d_i}}}{r_{is}^* e^{-i w_{d_i}} - r_{is} e^{i w_{d_i}}}. \] (A.28)

thus
\[
T = \frac{\text{Im}(r_{is})}{\text{Im}(r_{is} e^{i w_{d_i}})}, \] (A.29)
and

\[ R = \frac{\text{Im}(e^{-i\omega d_i})}{\text{Im}(r_{is}e^{i\omega d_i})}, \quad (A.30) \]

are real. If the field is evanescent in medium \( i \), \( \omega_i = \sqrt{\omega^2 \varepsilon_i - \kappa^2} = ip \), where \( p \) is real. Therefore, \( r_{is} \) and \( e^{\pm i\omega d_i} \) are real, meaning that \( T \) and \( R \) are real as well. This indicates that the elements of \( \mathcal{M}_{ss} \) are real, if the field is evanescent in medium \( s \).
Bibliography


[118] www.few.de.


