Angular Interrogation of Surface Plasmon Resonance

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Surface plasmon resonance (SPR) refers to the phenomenon of the coupling of an incident light wave with the coherent oscillations of electrons present at a metal/dielectric interface. In the bulk of a metal, free electrons oscillate with an eigen frequency known as the plasma frequency ω_p, with energies close to 10 eV. However, at its inteface with a dielectric, these oscillations occur with a lower energy, giving rise to a longitudinal charge density wave (coherent electron oscillations) propagating along the interface. This charge density wave is called a surface plasmon. The coupling of an electromagnetic wave with this charge density wave corresponds to SPR excitation and results in an electromagnetic wave propagating along the interface known as a surface plasmon polariton (SPP)[1].

The study of this optical resonance phenomenon has given birth to a field known as Plasmonics which has several applications in areas such as bio-sensing, data recording, microscopy, refractometry, solar cells among others [2][3][4]. The distinguishing feature of this phenomenon is that it leads to subwavelength confinement of light, resulting in high sensitivity of the associated parameters to local changes in refractive index.

In this experiment, we will first simulate the conditions required for SPP excitation on an air/gold interface with the aid of a theoretical model. We will then verify this simulation experimentally through angular interrogation of the reflectivity for such an interface. Through the experiment, students are expected to learn concepts fundamental to electromagnetic wave propagation, dielectric properties of materials and the electromagnetic boundary conditions applicable at the interface between two media.

KEYWORDS

Plasmon Resonance · Reflectivity · Boundary Conditions · Thin Films · Dispersion Relation · Complex Dielectric Constant ·

APPROXIMATE PERFORMANCE TIME 1 week.

1 List of Equipment

1. Intensity stablized laser diode, L635P005, Thorlabs

2. Laser diode mount, TCLDM9, Thorlabs

3. Mounted Geltech aspheric lens, X230TME-B, Thorlabs

4. Laser diode driver and temperature controller, LDTC2/2, Wavelength Electronics

5. D.C power supply, HY5003, V&A Instruments

6. Optical chopper system, MC2000, Thorlabs

7. Linear polarizer, LPVISE050-A, Thorlabs

8. Motorized rotation stages, PRM1Z8, Thorlabs

9. Stage controllers, TDC001, Thorlabs

10. High speed silicon photodetector, DET36A, Thorlabs

11. Lock-in amplifier, SR-850, Stanford Research Systems

12. Terminal block, NI SCC-68, National Instruments

13. Data acquisition card, NI PCI-6221, National Instruments

14. Right angle prism 5 mm, PS909, Thorlabs

15. Bionano gold microscope slides, 30020011, Phasis

16. BK-7 index matching liquid, 19586, Cargille Laboratories

17. Optical breadboard 90 x 60 x 6 cm, PBI51506, Thorlabs

18. Optical rail 60 cm, RLA600/M, Thorlabs

19. Rail carriers 2.5 cm, RC1, Thorlabs

20. Post holders 7.6 cm long, PH3/M, Thorlabs

21. Mounting base 25 x 75 x 10 mm, BA1/M, Thorlabs

22. M6 and M4 screws, Thorlabs

2 Experimental Objectives

The experimental objectives include:

1. Simulating a reflectivity vs angle of incidence curve for a thin film system and identifying the maximum and minimum in reflectivity—corresponding to total reflection and plasmon resonance.

2. Experimentally generating a reflectivity vs angle of incidence curve for an real thin film system and identifying therein the location of resonance excitation.

3. Comparing experimental and theoretical results.

References and Essential reading

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[6] C. A. Bennett, "Principles of Physical Optics", Chapter 3, pp. 109, John Wiley and Sons, Inc, 2008.

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[8] "Introduction to the Lock-in Amplifier", LUMS School of Science and Engineering, 2010.

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3   Introduction

When light is incident from one medium onto the interface with another medium, typically part of it is reflected and part of it is transmitted into the second medium. However, under certain conditions that depend on the dielectric properties of the two media, the angle of incidence and the optical polarization, light can become coupled to the surface plasmons existing on the interface and propagates only in a direction parallel to the interface. The propagation constants in the direction perpendicular to interface are imaginary and, hence, there is zero reflection and transmission. These conditions are known as resonance conditions and correspond to SPP excitation. This phenomenon is illustrated in Figure 1.
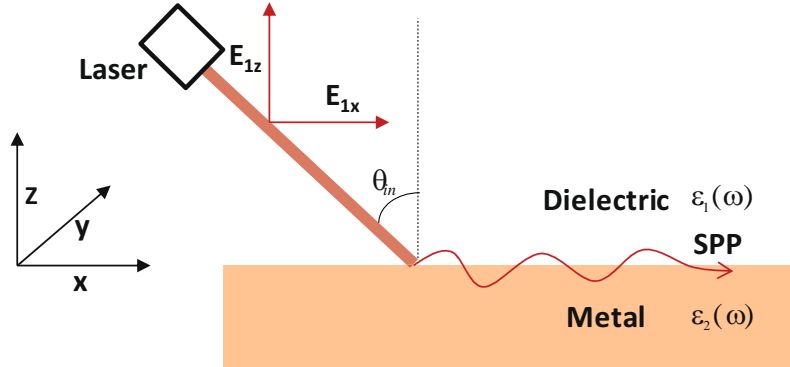

Figure 1: Surface plasmon polariton excitation and propagation. Incident light is P-polarized, having electric field components in the x and z directions, as shown. θ_{in} is the angle of incidence of light. Under the right conditions, an SPP is excited by the incident light.

3.1   Dispersion Relation of an SPP

As shown in Figure 1, it is assumed that the incident light is P-polarized. We can formulate plane wave expressions for the field present in each medium as:

$$\vec{E}_1(r) = (E_{1x}\hat{x} + E_{1z}\hat{z})e^{i(k_{1x}x + k_{1z}z)} \quad \text{and} \quad \vec{E}_2(r) = (E_{2x}\hat{x} + E_{2z}\hat{z})e^{i(k_{2x}x + k_{2z}z)}. \tag{1}$$

Assuming the relative permeabilities μ_1 and μ_2 are both unity, when the electromagnetic boundary conditions are applied at the interface, the following solutions are yielded for the propagation constants in the two media [1]:

$$k_{1x}^2 = k_{2x}^2 = k_x^2 = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1(\omega)\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}} \tag{2}$$

$$k_{1z}^2 = \frac{\omega^2}{c^2}\frac{\varepsilon_1^2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)} \quad \text{and} \quad k_{2z}^2 = \frac{\omega^2}{c^2}\frac{\varepsilon_2^2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}, \tag{3}$$

where ω represents the angular frequency of the incident light and c is the free space speed of light.

SPP excitation requires a wave that propagates only parallel to the interface. We, there-fore, require k_x to be real, k_{1z} to be positive imaginary and k_{2z} to be negative imaginary. Imaginary z-direction propagation constants imply exponential decay in the plane wave am-plitude with distance travelled away from the interface. The rate of this decay is determined by the propagation constants k_{1z} and k_{2z}. Since Equation (2) establishes the relationship between the angular frequency ω of the SPP and its propagation constant k_x, it is referred to as the dispersion relation of the SPP.

Q 1. Using Figure 1 and your knowledge of electromagnetic boundary conditions, derive Equations (2) and (3).

Q 2. Referring to Equations (2) and (3) explain what requirements are imposed on the dielectric constants ε_1 and ε_2 for the existence of SPP excitation? You may assume that both dielectric constants are real.

In our experiment, we use an air/gold interface—hence medium 1 is air and medium 2 is gold. Air is a non-dispersive medium, meaning ε_1 is relatively invariant with the frequency of incident light. Gold, on the other hand, is a dispersive medium; ε_2 varies strongly with the frequency of incident light and can be rougly approximated using the Drude-Sommerfeld Model for metals as [1]:

$$\varepsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\Gamma\omega} \tag{4}$$

where

$$\omega_p = \sqrt{\frac{Ne^2}{m^*\varepsilon_0}} \quad \text{and} \quad \Gamma = \frac{Ne^2}{m^*\sigma}. \tag{5}$$

N is the density of conduction electrons in the metal, m^* is the effective mass of each con-duction electron, e is the elementary charge, σ is the DC conductivity of the metal and ε_0 is the free space permittivity. For gold, $\omega_p = 1.36 \times 10^{16}$ rad/s and $\Gamma = 1.0 \times 10^{14}$ rad/s. The Drude Sommerfield model approximates the motion of the free electrons in a metal by considering them as an ideal negatively charged gas surrounding positively charged atomic cores. ω_p, known as the plasma frequency, is the eigenfrequency at which these free electrons oscillate. The real part of the dielectric constant of the metal is zero at the plasma frequency, negative below this frequency and positive above it. Γ refers to the mean collision rate of these free electrons with the atomic cores. It captures the damping effect on the motion of the free electrons due to these collisions [5].

We assumed in the beginning that the incident light is P-polarized. This is because, if the above procedure is repeated for S-polarized light, for unity μ_1 and μ_2 the boundary conditions do not yield a solution that is a surface mode (where light propagation is only along the interface). Hence, for S-polarized light, resonance cannot be excited.

Q 3. Using Equations (3) and (4) calculate the decay lengths perpendicular to the air/gold interface (distance in the z-direction required for field intensity to drop to 1/e of its initial value) in both air and gold at wavelength $\lambda = 635$ nm.

Q 4. Find ω_p and Γ for:

1. aluminum with density 2.70 g/cm^3, 27.0 g/mole, one conduction electron per atom and a conductivity of 3.77×10^7 Ω/m.

2. silver with density 10.49 g/cm^3, 108 g/mole, one conduction electron per atom and conductivity of 6.30×10^7 Ω/m.

(Taken from [6])

3.2 Excitation of the SPP

From the previous discussion, it may seem that the appropriate choice of ε_1 and ε_2 is all that is needed to excite an SPP. However, one further consideration that needs to be made is that the coupling of two electromagnetic waves requires conservation of both energy $\hbar\omega$ and momentum $\hbar\vec{k}$ of the incident wave. The projection of the incident light wave vector along the x-axis is:

$$k_{in,x} = n_1 \frac{\omega}{c} \sin(\theta_{in}) \tag{6}$$

where n_1 is the refractive index of medium 1. For momentum conservation, Equation (6) must equal Equation (2). This results in the condition,

$$n_1 \sin(\theta_{in}) = \sqrt{\frac{\varepsilon_1(\omega)\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}}. \tag{7}$$

Hence, the best way to determine whether an SPP excitation is possible is to plot simultaneously on an ω vs k_x graph, both Equations (2) and (6) and see if they intersect.

Q 5. Plot Equation (6) for incidence through:

1. air

2. glass

on a single ω vs k_x graph. Take $\theta_{in} = 45^0$.

On the same graph plot Equation (2) for the air/gold interface. You may use the Drude-Sommerfeld model to determine the variation of ε_2 with ω.

From your plots you will readily recognize that k_x values in air are too small to allow the requisite coupling. The value of k_x needs to be increased and this is achieved by allowing incidence through glass. Your graph will show that a point of intersection between the dispersion relations of glass and the SPP is in fact possible. This generally occurs at θ_{in} greater than the critical angle of glass— when there is attenuated total reflection and an evanescent wave is present inside the gold. This is precisely why we chose $\theta_{in} = 45^0$ in the above plots as that is larger than the critical angle for most glasses. In our experiment, we achieve SPP excitation using a prism in what is commonly known as the Kretschmann-Raather configuration [3].
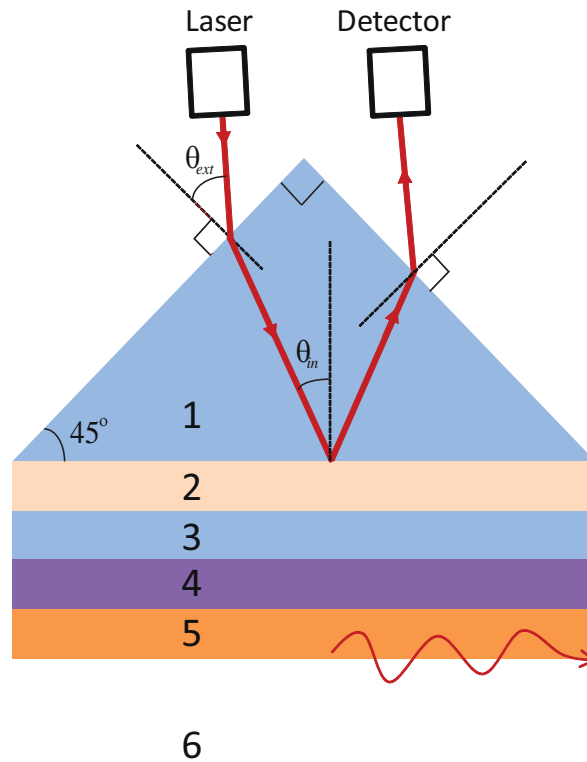
Laser   Detector

θ_{ext}

$45°$

θ_{in}

1
2
3
4
5

6

Figure 2: Sample thin film system used in the current experiment: (1) Prism (2) Index matching fluid (3) Glass slide (4) Titanium (5) Gold (6) Air.

4 The Experiment

4.1 Sample Thin Film System

The sample we are going to use for our experiment has a multi-layered structure and is illustrated in Figure 2. The right angle prism (layer 1) is bonded to the glass end of the gold coated glass slide (layer 3) by using the BK-7 index matching fluid (layer 2). Layers 1,2 and 3 have closely matched refractive indexes and, hence, effectively act as a single glass layer. As discussed in Section 3.2, the purpose of this layer is to provide the additional momentum along the interface (additional k_x) required for SPP excitation. The other end of the glass slide is coated with a layer of titanium (layer 4) which in turn is coated with a layer of gold (layer 5). The titanium buffer serves as an adhesive to keep the gold layer bonded onto the glass.

As discussed in Section 3.2 and illustrated in Figure 2, an evanescent wave, generated due to attenuated total reflection, can be used to excite an SPP on the air/gold interface. This evanescent wave has to travel through layers 4 and 5 before it is allowed to excite an SPP at the air/gold interface. Since these are highly absorbing metallic layers, their thicknesses need to be considerably less than the typical decay length of the evanescent wave, which is a few hundred nanometers. In our case, the thicknesses of titanium and gold are 5 nm and 50 nm, respectively—considerably smaller than the typical decay length.

4.2 Simulating SPP Excitation

In the first part of this experiment, we will simulate the excitation of the SPP. For this purpose, we have designed, in MATLAB, a Graphic User Interface (GUI) for multi-layered thin film systems such as our six-layer system (Figure (2)). A screen shot of the GUI is shown in Figure 3. An SPP excitation in our thin film system will correspond to a minimum in both transmission and reflectivity of light incident on layer 2 of the system. However, since the angle of incidence θ_{in} at resonance is always greater than the critical angle, in the range of θ_{in} we will be probing, we need only look for a minimum in reflectivity since transmission will already be at a minimum. Hence, our simulation is composed of generating a curve of reflectivity vs θ_{in} for an approximate model of our thin film system. The reflectivity is calculated by using Fresnel's equations for a multi-layer thin-film system [7]. It is assumed that each layer is atomically flat (no surface roughness) and has uniform dielectric properties. According to Fresnel's equations, the reflectivity depends on the thicknesses and dielectric constants of each layer. These are provided in Table 1.

Progress through the following steps to perform the simulation:

1. Open the **n_layer_fresnel.m** MATLAB file located on the desktop and run it. A window similar to the one shown in Figure 3 should open.

2. Enter the wavelength of light in the appropriate text-input box. We will be using a wavelength of 635 nm for our experiment. Make sure you use the right units. You will notice that the dielectric constant of gold at the entered wavelength appears in an adjacent box.

3. Select the number of layers. A graphical model of our thin film system should subsequently appear.

4. Using Table 1 fill in the information for the dielectric constants and thickness of each layer in the respective text-input boxes, using the correct units. The boxes accept string inputs. Please keep the following points in mind while entering information.

    (a) Enter numbers in MATLAB's string scientific notation. For example 10 nm should be written as 10E-9 m.

    (b) While entering complex numbers use the 'a + i*b' form.

5. Press the Generate Curve button. You should observe a reflectivity vs angle of incidence curve.

6. The angle of incidence at both maximum and minimum reflectivity will be shown in text boxes next to the curve. Note down these two values in your notebook. MATLAB determines these values by traversing through the array containing the reflectivity values and determining the indexes corresponding to maximum and minimum reflectivity. The angle of incidence at minimum reflectivity is the angle at which SPP excitation occurs, which we will denote as θ_{res}.

7. Now increase the number of layers to 7. Consider a modification to our thin film system where a 10 nm layer of dielectric (refractive index $n_{\text{dielectric}} = 1.40$) has been added between the gold and air layers. Generate a reflectivity curve for this system. Note down the change in θ_{res} produced by the addition of this layer.

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Equation (7) summarizes the conditions needed for resonance excitation. It can be inferred that the right-hand side of the equation depends on the dielectric properties in the vicinity of the SPP interface whereas the left-hand side depends on the refractive index of the exciting glass layer and the angle of incidence. Growing an additional layer of dielectric on the gold surface changes the dielectric properties in the vicinity of the interface. Since the right side of the equation changes, the resonance condition is fulfilled at a different θ_{res}. This provides us with a means for carrying out thin-film sensing. By monitoring the shift in θ_{res} we can determine whether an additional layer of thin-film has been adsorbed or grown on the gold surface. This technique has been applied in bio-sensing applications, where, for example, selective adsorption of a protein can be detected by monitoring the change in θ_{res} it produces [2].
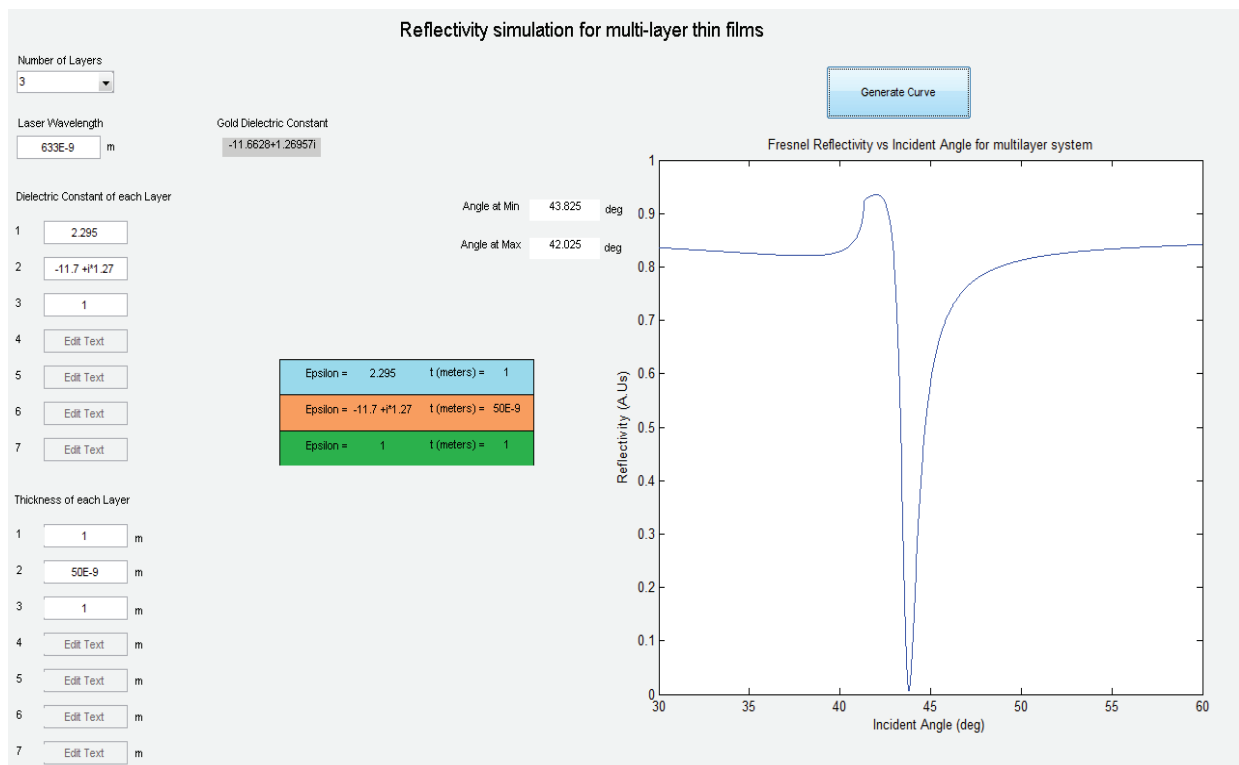

Figure 3: Screenshot of the GUI for simulating the reflectivity of the sample thin film system.

Table 1: Dielectric constant and thickness of each layer

Layer	Dielectric Constant	Thickness (m)
1	2.295	arbitrary
2	2.300	1E-5
3	2.271	1E-3
4	-3.9039 + i12.5560	5E-9
5	Given in GUI	50E-9
6	1	arbitrary

9

4.3   Experimental arrangement

Figure 4 illustrates our experimental setup. An intensity stabilized laser diode ($\lambda = 635$ nm), housed in a TCLDM9 mount, acts as the light source, whose intensity is stabilized by a feedback controller (LDTC2/2). The controller stabilizes both the current through the laser diode and its temperature by using the feedback signals from a photodiode and thermistor present in the TCLDM9 mount. Light from the laser passes through an optical chopper, which modulates the intensity of light at a certain frequency, so that its signal may be tuned into by a lock-in amplifier. The laser light then passes through a polarizer before impinging on the surface of the prism (layer 1 in our sample). The sample is placed on the motorized rotation stage S1. A photodetector, mounted on another motorized stage S2, is used to track the trajectory of light reflected from our sample. Hence, S1 is used to change the angle of incidence θ_{in} while S2 ensures the reflected intensity is measured for each θ_{in} by the photodetector.

S1 and S2 share a common axis of rotation and are USB interfaced to a computer through their respective motor controllers.

The motion of these two stages is controlled by a LABVIEW program. The photodetector voltage is measured using the SR-850 lock-in amplifier. The reference signal for the lock-in amplifier is provided by the controller of the optical chopper. The channel 1 output of the lock-in amplifier is interfaced to the computer using NI's data acquisition hardware. The photodetector voltage is, hence, also observable in LABVIEW. Since both stages and the photodetector output are interfaced with LABVIEW, the curve between θ_{in} and reflected intensity can be obtained by running a scan. The LABVIEW code, written for this experiment, runs this scan automatically.

Before we can run the scan, however, we need to bear in mind that S1 will control the value of θ_{ext} rather than θ_{in}. Our final curve, however, needs to be plotted on reflectivity vs θ_{in} axes.

Q 6.   Derive the relationship between θ_{ext} and θ_{in} using the information given in Figure 2.
Q 7.   What are the particular advantages of using a lock-in amplifier in this experiment?

Q 8.   Why is it important to keep the intensity of the laser diode light constant?
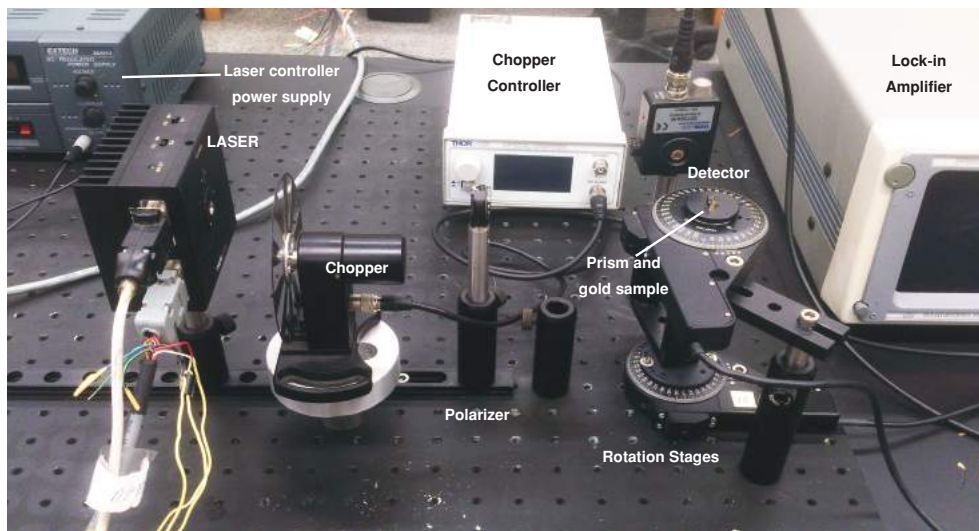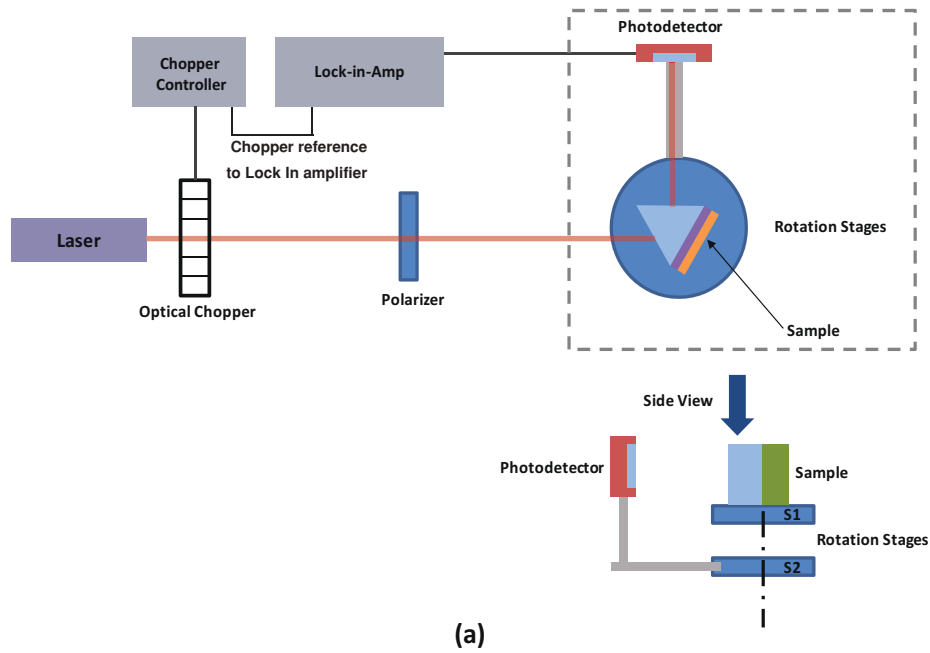
(a)

(b)

Figure 4: (a) Schematic diagram of the experimental setup (b) Photograph of the setup.

4.4   Sample and Detector Alignment

Prior to running the scan, we need to carry out some sample and detector alignment procedures. Perform the following steps.

1. To make sure that both the TDC001 controllers are powered on and connected to the computer via USB, run the **ATP CONFIG** software on the computer desktop. You should be able to see a list of their serial numbers and connected rotation stages.

2. Now Run the **ATP USER** software. The graphical stage controllers for both S1 and S2 should appear. A screenshot of the graphical controllers is shown in Figure 6.
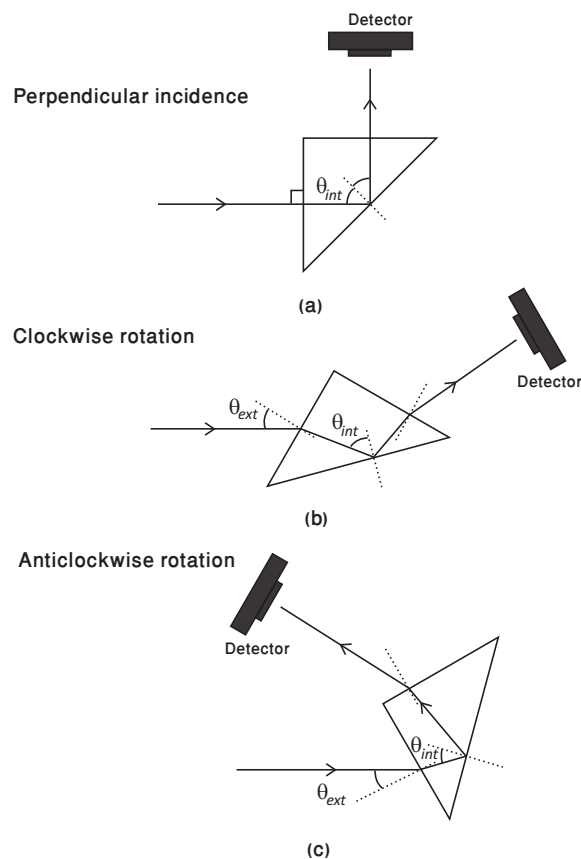
Figure 5: Convention for angle measurement: (a) for $\theta_{ext} = 0$, $\theta_{int} = 45^o$; change in θ_{ext} is considered positive for clockwise (b) and negative for anti-clockwise rotation (c) of the stage. The sense of rotation (clockwise or anticlockwise) is as viewed from the above.

3. The sample is already placed on S1. Using the graphical controller, move S1 until the laser light is normally incident on the prism surface. This corresponds to $\theta_{ext} = 0^o$. The way to check if the light is normally incident on the prism is to monitor the light reflected off its surface and see if it goes back to the laser source. You can do some fine tuning by using a small jog step size $(0.1^o$) in order to converge on the S1 position corresponding to $\theta_{ext} = 0^o$. Note down this S1 position in your notebook. Let's call it θ_{ext0}.

4. Rotate the stage S2, on which the detector is mounted, such that the reflected beam falls perpendicularly on the sensor. Note down this angle also as θ_{det0}.

5. The LABVIEW code is programmed to perform a scan of 10° by moving S1 and S2 counterclockwise (in the direction of decreasing θ_{ext} according to the frame of reference of the rotation stage). The minimum angle our system can resolve is 0.1^o. Based on the simulation carried out in Section 4.2 and the answer to Question 6, one can verify that a scan range of $5 \geq \theta_{ext} \geq -5$ is appropriate.

6. Set the polarizer for p-polarization. A reading of 0° on the polarizer dial implies horizontal polarization.
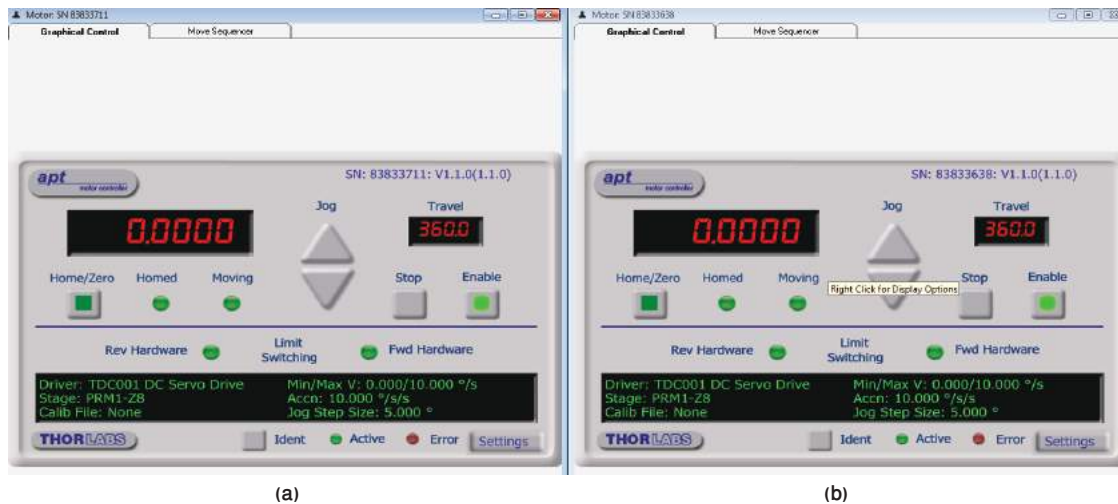
(a)　　　　　　　　　　　　　(b)

Figure 6: Graphical stage controllers in the ATP USER software for (a) S1 (b) S2.
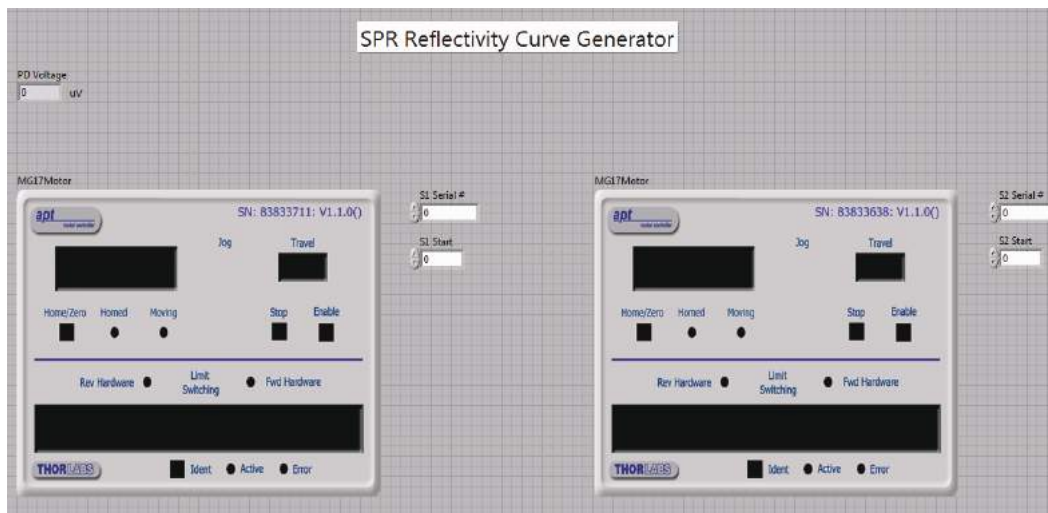
4.5 Performing the Scan

Figure 7: Screenshot of LABVIEW VI used for scanning the reflectivity of the sample.

Now carry out the following steps to perform the scan.

1. Download and open the **SPR_Scan** LABVIEW program.

2. The screen shown in Figure 7 should become visible. Enter the serial numbers of the two stages in the respective boxes. Also input the starting positions of S1 and S2. It can be inferred from step 5 of Section 4.4 that the starting position should be $\theta_{ext0} + 5$ for S1 and $\theta_{det0} + 10$ for S2.

3. Run the program. The stages will rotate to perform the scan automatically. It will take about 6-7 minutes for the scan to complete.

4. The folder where you want to save the results of the scan can be specified in the LabVIEW program.

5. Use the data from the scan to generate a curve of reflectivity vs θ_{in}. Bear in mind that you will have to convert the angles first into the respective values of θ_{ext} and then into those of θ_{in} (Please refer to Figure 5).

6. Determine the values of θ_{in} at both maximum and minimum reflectivity.

7. Changing the orientation of the polarizer to vertical, repeat the procedure for S-polarized light.

Q 9.   How do the theoretical and experimental values for θ_{in} at resonance compare? Account for any difference between the two values.