Angle-Tunable Enhanced Infrared Reflection Absorption Spectroscopy via Grating-Coupled Surface Plasmon Resonance

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Supporting Information

**ABSTRACT:** Surface enhanced infrared absorption (SEIRA) spectroscopy is an attractive method for increasing the prominence of vibrational modes in infrared spectroscopy. To date, the majority of reports associated with SEIRA utilize localized surface plasmon resonance from metal nanoparticles to enhance electromagnetic fields in the region of analytes. Limited work has been performed using propagating surface plasmons as a method for SEIRA excitation. In this report, we demonstrate angle-tunable enhancement of vibrational stretching modes associated with a thin poly(methyl methacrylate) (PMMA) film that is coupled to a silver-coated diffraction grating. Gratings are fabricated using laser interference lithography to achieve precise surface periodicities, which can be used to generate surface plasmons that overlap with specific vibrational modes in the polymer film. Infrared reflection absorption spectra are presented for both bare silver and PMMA-coated silver gratings at a range of angles and polarization states. In addition, spectra were obtained with the grating direction oriented perpendicular and parallel to the infrared source in order to isolate plasmon enhancement effects. Optical simulations using the rigorous coupled-wave analysis method were used to identify the origin of the plasmon-induced enhancement. Angle-dependent absorption measurements achieved signal enhancements of more than 10-times the signal in the absence of the plasmon.

Surface plasmon resonance (SPR) is well established as a versatile, sensitive, and label-free optical sensing method that can be used to monitor binding events at surfaces and characterize thin films. An overview of SPR and other sensors based on evanescent electromagnetic waves can be found in several review articles and books. While many plasmonic applications use prisms in the Kreschmann configuration to couple incident photons to surface plasmons, diffraction gratings can also be used as SPR sensing platforms. Although grating coupler-based SPR sensors are typically less sensitive than prism coupled sensors, gratification exhibit a variety of other advantages. In reflection measurements, for example, precise control of the metal film thickness, which is necessary for prism coupling, is not required for gratings. Gratings also provide additional control and flexibility. One can tune the location of the plasmon resonance by selection of the grating pitch or also by real-time adjustment of the incident angle. In addition, gratings are an information rich sensing platform in that one can excite several surface plasmons simultaneously through the multiple diffractions emerging from a diffraction grating. Gratings are also a very cost-effective platform. They can be fabricated by injection molding of plastics or produced by optical lithography. Effective grating couplers have been fabricated from such commonplace sources as compact discs (CDs) and digital versatile discs (DVDs). Diffraction gratings also lend themselves to clean experiments, as no refractive index matching fluid is needed as typical in prism-coupled configurations.

While a great deal of SPR sensor research has focused on the visible and near-infrared portions of the spectrum, the infrared spectral region has also seen interesting implementations of SPR. Prism-coupled SPR sensors in the mid-IR have taken advantage of the long plasmon decay lengths in that region to monitor larger structures, such as the interior of living cells. IR spectrometers have been modified to allow for variable angle, prism-coupled SPR reflectance experiments. Improved performance at infrared frequencies due to a sharper resonance curve has also been demonstrated for enhanced detection sensitivity and imaging at these conditions.

Infrared reflection-absorption spectroscopy (IRRAS) is a popular technique used to characterize thin films and has been widely used to deduce the structure and composition of ultrathin monolayer and polymer films. The fact that film thickness and coverage are commonly determined by SPR makes it a nice complement to IRRAS measurements. Indeed, in a previous publication, we demonstrated how SPR and IRRAS can be combined to allow for simultaneous thickness and compositional characterization of alkanethiolate monolayers.

Another compelling analytical application of plasmonic sensing involves the coupling of SPR with molecular resonances. Several publications have focused on the interaction of SPR with molecular resonances in the visible spectrum. At infrared frequencies, a technique entitled surface enhanced infrared absorption (SEIRA) has been demonstrated in which localized SPR (LSPR) from metal island films and other metallic nanostructures has been exploited to enhance the signal associated with vibrational spectroscopy. Several LSPR-based schemes have been developed in which localized surface plasmon resonance (LSPR) from metal island films and other metallic nanostructures has been exploited to enhance the signal associated with vibrational spectroscopy.
used for SEIRA, including various configurations of metal nanoparticles,\textsuperscript{33} nanoantennae,\textsuperscript{34,35} split ring resonators,\textsuperscript{36} and nanoshells.\textsuperscript{37} Recently, a strip grating coated with a thin gold layer atop a CaF\textsubscript{2} substrate was utilized to enhance absorption of the C=O stretching vibration in poly(methyl methacrylate) (PMMA).\textsuperscript{38} This was one of the few experimental examples of SEIRA that made use of propagating surface plasmons instead of LSPR. A distinct advantage of propagating surface plasmons based upon grating couplers for SEIRA is that gratings provide the ability to directly tune the plasmonic response through manipulation of the excitation angle.

In this work, we exploit the inherent angle-tunability of diffraction grating couplers to explore the interactions of surface plasmon polaritons (SPPs) with infrared vibrational modes in PMMA films. Laser interference lithography is used to fabricate sinusoidal grating couplers with precise control of the grating pitch. Incident angle is varied to manipulate the SPR response to desired locations within the IR spectrum. We present IRRAS spectra obtained using silver-coated gratings as substrates for poly(methyl methacrylate) (PMMA) films at a range of incident angles. Experimental data show plasmon-enhanced infrared absorption resulting from interactions of SPPs with C–H and C=O vibrational modes. Modeling results aid in the characterization of the experimentally observed behavior of grating coupler-PMMA samples and to assist in elucidating the origins of this signal enhancement.

![Scheme 1. Lloyd’s Mirror Interferometer Apparatus, Showing Laser Source, Objective Lens, Pinhole, and Rotatable Sample Stage](image)

### EXPERIMENTAL SECTION

#### Materials and Reagents.

Toluene and glass microscope slides were obtained from Fisher (Waltham, MA). Poly(methyl methacrylate) (PMMA, 120 000 MW) was purchased from Aldrich (St. Louis, MO). Silver wire (99.995%) and tungsten wire baskets for evaporation were from Ted Pella (Redding, CA). Microposit S1813 Positive photoresist and Microposit 352 developer were obtained from Rohm and Haas Electronic Materials LLC (Philadelphia, PA). UV curable optical adhesive (NOA 81, Norland) and polydimethylsiloxane silicone elastomer kit (SYLGARD 184, Dow Corning, Midland, MI) were used as received. Deionized water with electrical resistivity exceeding 18 M\(\Omega\) cm was used for cleaning and rinsing of samples (NANOPure, Barnstead, Dubuque, IA).

**Grating Fabrication.** Nanostructured diffraction gratings of specific pitch values were fabricated on glass slides using laser-interference lithography (LIL) in a Lloyd’s mirror configuration.\textsuperscript{39–41} Briefly, a positive photoresist was coated onto clean glass slides at 4 000 rpm for 60 s using a model WS-650MZ-23NPP spin coater (Laurell Technology Corp., North Wales, PA). Samples were postbaked at 90 °C for 1 min and then cooled with air to room temperature. A custom built Lloyd’s mirror apparatus, as shown in Scheme 1, was employed in conjunction with a 405 nm diode (Oxxius, Lannion, France) or 532 nm YAG (Coherent, Santa Clara, CA) laser to expose a sinusoidal interference pattern into the photoresist layer. Average grating pitch was controlled by adjusting the angle of the Lloyd’s mirror. After developing the photoresist, the grating surface was rinsed with DI water and dried in a stream of nitrogen gas. The pitch was then determined by measuring the vertical displacement of transmitted diffracted orders of a 632 nm laser beam over a lateral distance of 6 feet. Once the desired pitch was obtained through tuning of the Lloyd’s mirror apparatus, a silicone elastomer kit (SYlgard 184, Dow Corning, Midland, MI) was used to transfer the LIL grating topology to a PDMS master. Several replicas of each grating were fabricated from each PDMS master by sandwiching a drop of UV-curable polymer (NOA 81, Norland Products, Inc., Cranbury, NJ) between the PDMS surface and a clean glass slide and exposing with a UV lamp for 20 min. The gratings on the glass slides released cleanly from the PDMS, which allowed the same nanostructure to be reproduced several times without noticeable degradation of the structure. A 160 nm coating of silver was then deposited at a rate of 1–1.5 Å/s on the grating by thermal evaporation (Denton Benchtop Turbo III, Denton Vacuum, LLC, Moorestown, NJ). Silver film thickness was monitored in situ using a quartz crystal resonator. The grating fabrication process is illustrated in Scheme 2.

**Scanning Electron Microscopy (SEM).** A Quanta 250 field emission SEM (FEI, Hillsboro, OR) was used to collect scanning electron micrographs normal to the grating surface and in cross-section. Cross-sectional images were acquired by scoring samples with a scribe and then immersing in liquid nitrogen for 5 min before fracturing. Sample surfaces were then sputter-coated with 2–5 nm of iridium before imaging. Images were collected at high vacuum using an Everhart-Thornley secondary electron detector.

**Atomic Force Microscope (AFM) Imaging.** A Dimension 3100 scanning probe microscope with Nanoscope IV controller (Veeco Metrology, LLC, Santa Barbara, CA) was utilized to obtain height profiles of the grating surface. Imaging was conducted in tapping mode using silicon TESP7 AFM tips (Veeco Metrology, LLC, Santa Barbara, CA) with a spring constant of 79 N/m and resonance frequency of 258 kHz.

**Spin Coating of Thin Polymer Films.** Polymer films of thicknesses ranging from 30 to 300 nm were spun onto silver-coated gratings. PMMA was dissolved overnight in toluene at 2 wt %. Initial tests were performed to determine spin speeds resulting in the desired PMMA thickness for each grating. After spinning, the samples were placed in a vacuum chamber evacuated to 10 psig for several hours or overnight to remove any remaining solvent. Polymer film thicknesses were confirmed with a combination of atomic force microscopy and cross-sectional SEM.
Infrared Reflection Absorption Spectroscopy (IRRAS). IRRAS spectra were collected using a Fourier transform infrared spectrometer (FTIR) ( Nicolet MAGNA 750, Thermo Scientific) equipped with a specular reflectance accessory (Pike Vee-Max II, Pike Technologies, Madison, WI). The reflectance accessory allowed for spectra to be obtained at a range of incident angles between 55° and 80° and under both s- and p-polarized illumination. Spectra were measured for PMMA-coated and uncoated gratings relative to a flat silver mirror at the same incident angle and polarization. Gratings were also rotated in-plane to acquire spectra with the grating direction both perpendicular and parallel to the incident light.

Method for Calculating SPR-Enhancement of Vibrational Modes. The magnitude of the plasmon-enhancement of vibrational modes was considered by comparing the size of the vibrational peaks in the presence of the plasmon relative to the p-polarized absorption of the same film with the grating direction aligned parallel to the source light (no plasmon excitation). We collected the peak heights at 2994, 2950, and 807 cm⁻¹ relative to a horizontal baseline for each spectrum. For each sample and incident angle, the height for the perpendicular spectrum (no plasmon) was divided by the amplitude with weak absorption signal. The increase in signal due to enhancement was then expressed as an enhancement factor, defined as a multiple of the unenhanced absorption signal.

Optical Modeling. The rigorously coupled wave analysis (RCWA) method was used to simulate the optical response of the sample gratings, as described previously. A custom-built code was written in Matlab to perform the modeling. Diffraction efficiencies were computed for multiple orders of reflected light using both transverse magnetic (TM) and transverse electric (TE) incident light as a function of wavelength and angle of incidence. The grating geometry was approximated based upon fitting AFM images of the grating surface and SEM cross sections of the layer structure. RCWA simulations were performed at a given incident angle using a 5 nm wavelength step and a 5 nm layer thickness; optical constants for silver and PMMA were from the literature and our measurements, respectively.

RESULTS AND DISCUSSION

The pitch of the fabricated gratings was controlled by tuning the angle of the Lloyd’s mirror interferometer. Target pitch values were calculated using the SPR matching condition for grating-based coupling:

$$\frac{2\pi}{\lambda} n_d \sin \theta + m \frac{2\pi}{\Lambda} = \pm \Re \left( \frac{2\pi}{\lambda} \sqrt{\epsilon_d \epsilon_m} \right)$$

where λ is the wavelength, n_d is the refractive index of the dielectric medium, θ is the incident angle relative to the grating surface normal, m is the diffracted order, Λ is the grating pitch, and ε_d and ε_m are the permittivities of the dielectric and metal, respectively. For a metal–air interface at infrared frequencies, the permittivity of the metal is much larger than that of air, and the matching condition simplifies to eq 2 below.

$$\sin \theta + m \frac{\lambda}{\Lambda} = \pm 1$$

Using this relation (eq 2), target pitch values of ~1700 and 3000 nm were determined by equating the –1 diffracted order to the respective locations of the C–H and C=C=O stretching modes in PMMA (2950 cm⁻¹, 2994 cm⁻¹, and 1739 cm⁻¹). These locations were chosen in order to overlap the surface plasmon with that of the vibrational modes of the PMMA.

The grating amplitude was impacted by the laser exposure dose and subsequent photoresist development time. Insufficient laser exposure and development time resulted in small grating amplitudes with weak diffraction efficiencies, while excess exposure dose and/or development time often resulted in complete removal of the photoresist layer. Typical exposures were ~5 s for the 405 nm laser, which translates to a dose of ~30 mW s cm⁻² at a power level of 30 mW and an exposure area of ~5 cm².

Imaging with SEM and AFM combined with optical diffraction were used to determine the dimensions of the gratings and to measure the thickness and uniformity of the silver and PMMA coatings. Figure 1A depicts a typical cross-sectional SEM image of a completed sample. The image shows a multilayer structure consisting of a UV-curable polymer substrate, a silver film, and a PMMA layer. The three different layers are noted in the image as well as the sinusoidal surface profile that is achieved with laser lithography. AFM profiles of the upper grating surface of the two different sized gratings confirm pitch values of 1710 and 3025 nm (Figure 1B,C). SEM images acquired in plan view show that the top grating surfaces exhibit uniform ordering of grating ridges over large length scales (Figure S1, Supporting Information).

IRRAS (p-polarized) spectra for both the 1710 nm (Figure 2A) and 3025 nm (Figure 2B) pitch gratings with just the silver coatings exhibit a distinct and very large absorbance associated with the excitation of a surface plasmon. For both gratings, the plasmon is excited by coupling incident light to the –1 diffracted order (eq 2). For the 1710 nm pitch grating, this absorbance appears in the neighborhood of 3000 cm⁻¹ (Figure 1B) and at 1700 cm⁻¹ for the 3025 nm pitch grating (Figure...
Both sets of spectra shift to larger wavenumbers with decreasing incident angle, as expected by angle-dependence of the SPR matching condition. Adjusting the location of the plasmon within a range of wavelengths can be done by making gratings of varying pitch as reported elsewhere or by variation of the angle of incidence. Notably, an angle-based tuning approach allows a wide range of wavenumbers to be interrogated with one grating sample. The ability to easily produce gratings of a given pitch combined with the angle-tunable response of each grating allows measurements to be performed over large expanses of the infrared spectrum.

SEIRA using metal nanoparticles has been previously shown to occur when SPR is excited in the same spectral region as a molecular vibration. In this mode of SEIRA, the size of the nanoparticles is used to dictate the location of the SPR response. Using the grating-coupled method described here, we can change the incident angle to manipulate the location of the SPR maximum to allow a precise overlay of the SPR response and vibrational modes. We have chosen to investigate this phenomena using a PMMA film, which shows strong vibrational features associated with C–H and C═O moieties and can be readily coated to a controlled thickness via spin coating.

The optical properties of PMMA in the infrared region have been previously reported. For our purposes, these were also measured. The infrared absorbance spectrum of a PMMA film was used to determine the optical constants of PMMA (Figure S2, Supporting Information). Kramers–Kronig analysis was then applied to compute the complex refractive index \( n \) and extinction coefficient \( k \) of PMMA over a range of wavenumbers from 3500 cm\(^{-1}\) to 1500 cm\(^{-1}\). The results of this calculation provide the refractive index \( n \) (Figure 3A) and extinction coefficient \( k \) (Figure 3B) for PMMA. The vibrational signatures associated with the C–H and C═O modes are evident in both the refractive index and the extinction coefficient. The extinction coefficient \( k \) attains a maximum value of 0.42 at 1739 cm\(^{-1}\), corresponding to the C═O stretching peak. C–H stretching modes exhibit two
absorption peaks at 2950 and 2994 cm\(^{-1}\), with \(k\)-values of 0.041 and 0.023, respectively. As expected, the refractive index \(n\) undergoes inflections at both of these spectral regions.

Infrared measurements were then taken of PMMA-coated gratings under various experimental configurations. Figure 4 illustrates IRRAS measurements for the 1710 nm pitch grating following deposition of a 300 nm PMMA film. The data reflects measurements at several different grating orientations, light polarization states, and angles of incidence. For all experimental configurations in this work, the reference blank was a flat silver mirror measured at the same angle of incidence and polarization. Figure 4A depicts three different curves corresponding to different forms of the IRRAS measurement for a PMMA-coated grating, including (i) p-polarized light with the grating direction perpendicular to the light path, (ii) p-polarized light with the grating direction parallel to the light path, and (iii) s-polarized light with the grating direction perpendicular to the light path. In all three cases, a signal associated with the primary C–H vibrational modes is observed. The plasmon can be removed by using s-polarized light at this same orientation or by using p-polarized light with the grating rotated by 90° so that the grating grooves are parallel to the incident radiation. For s-polarized light in the perpendicular orientation (profile iii), a very weak absorption signal for the PMMA C–H stretching modes is observed. A marginally stronger signal is observed with p-polarized light in the parallel orientation. Therefore, it is clear that the enhancement in the vibrational signals is associated with the presence of the surface plasmon for profile i.

Figure 4B contains a full set of spectra obtained for incident angles between 55° and 80° under p-polarized light oriented perpendicular to the grating direction. The large absorbance associated with the surface plasmon is evident in all of these images. Notably, as the plasmon changes position with variation in the incident angle, the two peaks associated with the C–H stretching vibrations are enhanced by varying degrees. The most intense enhancement occurs at ~65° where, presumably, there is the strongest overlap between the surface plasmon and the vibrational modes. Dashed vertical lines are included in the figure at the two C–H stretching peaks (2994 and 2950 cm\(^{-1}\)) to guide the eye. If one compares the angle-dependent result for the perpendicular orientation to that of p-polarized light in the parallel orientation where there is no surface plasmon, there is only a small increase in signal intensity with increasing angle of incidence, as would be expected for a typical IRRAS measurement (Supporting Information, Figure S3) but no significant enhancement.

An analogous set of results for the 3025 nm pitch grating is presented in Figure 5. These results are focused in the spectral region near the location of the C=O vibrational mode. p-Polarized spectra in Figure 5A show the C=O stretching vibration measured at 65° incidence with the grating direction parallel (no plasmon) and perpendicular (plasmon present) to
the incident light source. An enhancement is also seen in this case where surface plasmon is present (curve i) over data in the absence of the surface plasmon (curve ii). While the increase in the absorption signal is not as dramatic as that seen for the C-H stretching vibrations in Figure 4, enhancement is still observed. As before, the incident light angle can be tuned to manipulate the degree of interaction between the surface plasmon and the vibrational mode. The angle-driven shift of the plasmon response through the C=O stretching region is shown in Figure 5B. A maximum in enhancement is again observed at angles, between 65° and 75°, where the overlap between the surface plasmon peak and that of the vibrational mode appear the strongest. Enhanced absorption with a definite angle dependence was observed for both C-H and C=O stretching modes (Figure 6). Enhancement of the C-H stretching vibrations on the 1710 nm pitch grating (Figure 6A) was significant, reaching a magnitude of over 10-fold enhancement. The largest enhancement factor for the 2994 cm⁻¹ mode was 11.25 at 65° incidence, while the 2950 cm⁻¹ mode achieved its largest enhancement of 8.92-fold at 70°. It should be noted that the angles where the maximum occurs is somewhat arbitrary since both the incident angle and the grating pitch impact the plasmon location. Presumably, the maximum enhancement of the vibrational peak occurs where the interaction between the plasmon peak (and its associated electric field) and the vibrational mode are maximized. Similarly, enhancement of the C=O peak was angle dependent (Figure 6B). The maximum enhancement factor in the 1739 cm⁻¹ peak was over 1.9, and this value was observed at ~65° angle of incidence. The origin of the enhancement observed in this work can be considered in terms of the interaction of the surface plasmon with the vibrational modes in the PMMA film. Clearly, the surface plasmon is associated with an enhanced electric field at the metal–dielectric interface. Thus, when the spectral location of the surface plasmon overlaps a particular vibrational mode, the enhanced field results in a larger vibrational signal. In addition, one can consider the interaction between the surface plasmon and the vibrational mode in terms of the surface plasmon’s propagation length, L. The propagation length, as defined in eq 3, describes the spatial extent of the plasmon on the metal surface and is related to the dielectric properties of the interface, including both metal and film.\(^4\)

\[
L = \frac{1}{2\text{Im}\left[\frac{2\pi}{\lambda} \sqrt{\epsilon_m^2 - \epsilon_f^2}\right]}
\]

In this case, the optical constants of the PMMA film impact the propagation length of the surface plasmon. Previous reports have shown that, in the presence of a strong absorbance (a large extinction coefficient), a surface plasmon is quenched, which results in severe attenuation of the propagation length.\(^4\) A similar phenomenon can be observed here. Indeed, as shown in Figure 7, the plasmon propagation length at a silver–PMMA interface experiences dramatic reductions at wavenumbers associated with the C–H and C=O stretching vibrations. Physically, this behavior can be explained in terms of the coupling between the plasmon and the vibrational mode, whereby the plasmon is quenched and the associated momentum is captured by the vibrational modes of the PMMA, leading to an enhanced absorption. It should also be noted that the optical properties of silver and PMMA at the frequencies in question produce evanescent field penetration depths on the order of several micrometers, so that the entirety of the PMMA film may be probed by SPPs in this configuration (Figure S4 in the Supporting Information).\(^5\)

Further verification of this coupling and enhancement can be seen by comparing these experimental results with an optical model of the grating interface. For this comparison, a rigorous coupled-wave analysis (RCWA) code was used to simulate the optical response of the 1710 nm pitch sample grating. A typical comparison between the model results and experimental data is shown in Figure 8, which depicts p-polarized light reflected at 65° from a 300 nm PMMA layer. Both model results and those from experiment exhibit a similar enhancement in the vibrational peaks. Subtle differences are likely the result of slight differences in the physical dimensions of the actual and simulated surface profile and component optical properties.

**CONCLUSIONS**

Surface enhanced infrared absorption is a useful analytical technique for increasing sensitivity and lowering limits of detection in IR spectroscopy. The majority of previous

![](image.png)

Figure 6. Angle-dependent enhancement for (A) C–H stretching vibrations at 2950 and 2994 cm⁻¹ and (B) C=O stretching vibration at 1739 cm⁻¹.
applications of SEIRA utilized nanoparticle-based localized surface plasmon resonance to provide increased electromagnetic fields. In this work, we demonstrated SEIRA using a grating coupler, which has the benefits of being robust, simple, and tunable via both the physical dimensions (pitch) or the grating and angle of the incident light. Adjustment of the incident angle allowed the location of the plasmon resonance to coincide with that of the vibrational modes, producing absorption increases of more than 11 times over the absorption of identical films in the absence of plasmon-enhanced enhancement. We anticipate that fine-tuning of the grating dimensions in terms of pitch, amplitude, and shape of the grating can be used to further increase the magnitude of the signal enhancement.

ASSOCIATED CONTENT

S Supporting Information
Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES


Figure 8. Comparison of experimental (solid line) and RCWA modeling results (dashed line) for a 1710 nm pitch, 340 nm amplitude grating with 300 nm PMMA coating atop a 160 nm silver film. Incident angle is 65°.