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Dielectric interlayers increasing the transparency of metal films for mid-infrared attenuated total reflection spectroscopy

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By depositing a continuous, thin metal film on a substrate coated with a mid-infrared (IR) transparent dielectric film that fulfils the role of an index-matching, anti-reflective coating for the metal, the transparency of the metal in the IR wavelength range can be significantly enhanced. Here, this effect is used to yield enhanced absorption in attenuated total internal reflection infrared (ATR-IR) spectroscopy in the presence of continuous, flat thin metal films. The main limit of the ATR technique when using continuous metal films is the low transparency of metals, especially for infrared light. Computations and experiments show an enhancement in the absorbance of a sample in contact with the metal at certain wavenumbers when the dielectric interlayer is present. The realization of the setup is the stratified system zinc selenide - germanium ($\sim 1\mu\text{m}$) - gold (40 nm and 20 nm) using the organic solvent acetonitrile as sample. Enhancement is stronger in s-polarisation than in p-polarisation. In s-polarisation, enhancement factors of up to 4 have been observed so far, but calculations show a route to higher enhancements. In addition to the increased absorption, the absorbance spectra show interference fringes which are due to a mismatch in the real part of the refractive index of the sample in contact with the metal film compared to a reference measurement.

1 Introduction

While the understanding of solid surface has made enormous progress over the past decades, the detailed understanding of solid/liquid interfaces is less developed. The main reason is the lack of applicability of many experimental characterisation techniques in condensed matter. Optical spectroscopy in general is not limited by a sample form. It can be used to study chemical structures and transformations in liquids, solids and gases and is furthermore applicable to the study of interfaces. In the latter case, at least one of the examined media needs to be transparent at the wavelengths employed. A further issue is the separation of signals originating from the bulk from signals originating from the interface.

The method of attenuated total internal reflection (ATR) spectroscopy is a well-established nondestructive, interface-sensitive method frequently used for studying organic molecules on solid surfaces^{1–3}. It is particularly powerful in the mid-infrared (IR) wavelength range, because of the large number of possible vibrational transitions which can be excited for molecules. The use of the evanescent wave created in ATR experiments is advantageous in cases where an interface of an IR-absorbing solvent with a solid is probed, because no propagation through the absorbing sample medium is needed.

In its normal configuration, ATR-IR spectroscopy uses an

infrared transparent, high refractive index internal reflection element (IRE) as medium of incidence. Examples include germanium, silicon, and zinc selenide^{1,2}. The angle of incidence is chosen to be above the critical angle of total internal reflection. Frequently, however, samples near metal/(complex) liquid interfaces need to be investigated. Such studies can be conducted with high sensitivity using surface enhanced infrared reflection absorption (SEIRA) spectroscopy on rough metal island films^{4,5}, or specially designed structured surfaces⁶. Certain questions, especially the study of self-assembly and self-organisation processes require, however, the use of a smooth surface^{7,8} which can also be used for the application of a uniform electrochemical potential to the interface under study. In these cases, a thin, continuous metal film is deposited on the IRE. Continuous films have further advantages as the results can be quantified, and the orientation of molecules can be determined². Because metals are not transparent in the IR range, the sensitivity of the method is thus considerably reduced. Metals can be considered as near ideal mirrors for electromagnetic waves, representing a serious obstacle for a surface sensitive analysis of the sample.

Designing a metal layer for these experiments, one needs to take into account several factors. Metals show a bulk-like electronic structure above a certain thickness only. Usually, therefore, continuous films with a thickness $> 5 - 10$ nm need to be used. Thin metals often grow in island structures, which close only above a certain thicknesses. Furthermore, in studies where metal reactions are under investigation, as, e.g. in

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corrosion studies, the initial thickness of the films place limits on the experiments. The aforementioned reasons all imply that the metal layer should be as thick as possible, while the lack of optical transparency calls for layers as thin as possible.

Recently, in a work on increasing the transparency of tunnelling barriers for light, a configuration using dielectric interlayer has been realised in the visible, enabling an increase of transmission of light through deposited metal films in a symmetric configuration⁹.

Here, we extend this concept into the mid-IR wavelength range, with the aim of using it for analytical spectroscopy. Our goal is to show that by adding a dielectric interlayer in between a thin metal film and an IRE, an enhanced absorption of the sample is achieved.

2 Modelling

Hooper et al. showed in increased transmission of visible light through a silver film when introducing zinc sulphide interlayers in a symmetric configuration $\text{SiO}_2 - \text{ZnS} - \text{Ag} - \text{ZnS} - \text{SiO}_2$, compared to $\text{SiO}_2 - \text{Ag} - \text{SiO}_2$ ⁹. As opposed to there, we shall focus on the use of reflected rather than transmitted light, as this is advantageous for use in analytical spectroscopy of near-surface regions in bulk liquids. Furthermore, half of the symmetric configuration needs to be replaced by the sample, making it asymmetric. The comparison of an ATR configuration of a metal film directly on the IRE with the configuration using the interlayer as introduced here is shown in Fig. 1. In the mid-IR, both real and imaginary part of the refractive index are rather high, which is why the interlayers need to consist of materials with a high refractive index in order to increase transmission of light through the metal. The highest refractive index in common IR-transparent materials is 4.0 for germanium¹⁰. For ideal impedance matching, an even higher index is desirable, but to our knowledge there is a lack of transparent materials showing a higher index.

The metal under study here is gold. Most other metals have similar optical properties and a likewise behaviour is to be expected. Gold has been chosen because it is inert, well-characterised in deposition, and often the metal of choice for electrochemical experiments. Different media of incidence have been investigated to study the effect of the incidence medium's refractive index on the resulting reflectivity spectra.

Fig. 2 shows examples of computed reflectivity spectra, based on optical multilayer theory^{11–13} for different incidence media with a germanium interlayer of thickness $d_{\text{Ge}} = 1000\text{ nm}$ and a gold layer of thickness $d_{\text{Au}} = 20\text{ nm}$. Literature values for the optical constants have been used¹⁰. Compared to the results for bare gold, the presence of an interlayer on all media of incidence leads to certain wavenumbers with distinctly lower reflectivity, in the examples chosen, around 1800,

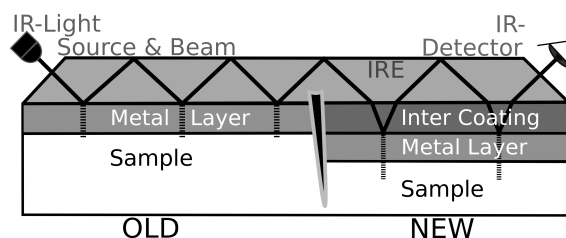


Fig. 1 Schematic view of both the extended system introduced here and the simple configuration. In the simple configuration (left), IR light enters an IRE, onto which a metal film is deposited. Introduced here is the addition of a transparent interlayer between IRE and metal (right).

3000, and 4200 cm^{-1} . The minimum values in the reflectivities decrease with decreasing refractive index of the incidence medium. The most extreme case of air as medium of incidence leads to the lowest reflectivity. It is worth noting that both CaF_2 and air do not show internal reflection under the conditions studied here in the absence of the metal layer. However, as pointed out previously, metals act as tunnelling barriers for light at all angles of incidence⁹. The reason for the occurrence of the minima has been mentioned previously⁹: within the interlayer there is constructive interference, leading to a higher tunnelling probability of the photons through the metal layer at certain wavelengths. At these wavelengths, light can penetrate the metal more efficiently in the presence of the interlayer, leading to a stronger absorption inside the metal, but also to a higher intensity of light at the metal/(gas or liquid) interface. Consequently, for use in absorption spectroscopy, the minima of the reflectivity curves are where enhanced absorption from the sample in contact with the metal film is to be expected.

A special situation arises for p-polarisation on CaF_2 as medium of incidence. The reason is that the angle of incidence of 45° is the critical angle of total internal reflection for the CaF_2/air interface at $\approx 3000\text{ cm}^{-1}$. As the behaviour near the critical angle is always special, this substrate will not be discussed here any further.

In order to investigate the effect of absorption from a sample in contact with the gold layer, two reflectivity computations have been performed, mimicking the experimental procedure. First, the layer system with air was simulated as a reference (R_{ref}). Following the simulation with air, air was replaced by the liquid sample (R_{smp}). The sample chosen was acetonitrile, because of the spread of its absorption modes throughout the IR range¹⁴. Optical constants from the literature were used in the calculations¹⁴. Mimicking the measurement process, the absorbance A was calculated as

$$A = -\log_{10} \frac{R_{\text{smp}}}{R_{\text{ref}}} \quad (1)$$

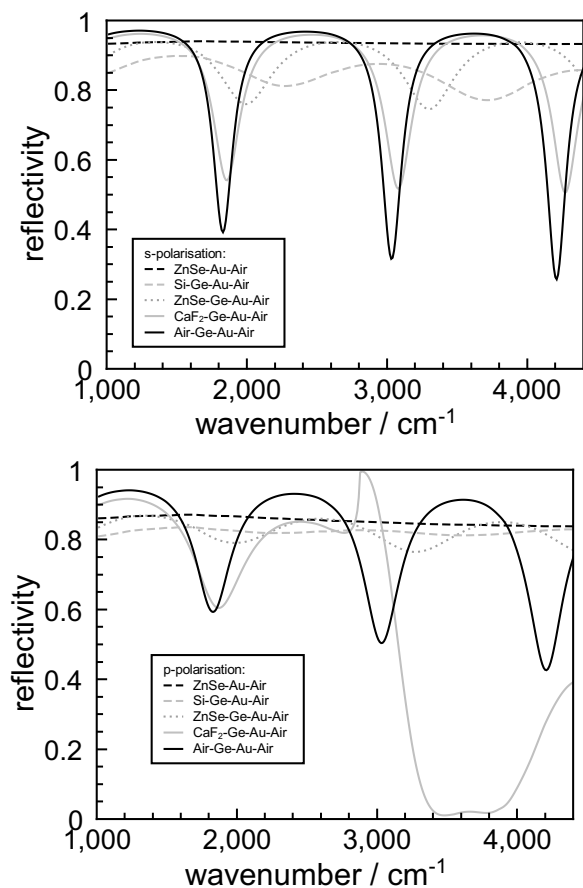


Fig. 2 Computed reflectivities for the proposed systems with different media of incidence at 45° incidence angle for $d_{\text{Ge}} = 1000\text{ nm}$ and $d_{\text{Au}} = 20\text{ nm}$ for parallel (p; bottom) and perpendicular (s; top) linear polarisations.

The results of the simulation for the absorbance of the system ZnSe-Ge-Au-acetonitrile are displayed in Fig. 3. The thickness of the germanium interlayer was chosen as 900 nm, where the minimum in the reflectivity curve is near the frequency of the nitrile stretching modes, which are located at ~ 2250 and $\sim 2290\text{ cm}^{-1}$. Comparing the spectra with and without interlayers reveals first of all a significant difference because of the presence of interference fringes in the calculation done with the interlayer. The presence of these fringes is caused by a mismatch of refractive indices of sample ($n_{\text{Acetonitrile}} \approx 1.34$) and background reference ($n_{\text{air}} \approx 1$). The “absorbance” values of the fringe structure therefore allows the deduction of the presence of a non-absorbing sample.

On top of the fringe structure, the spectra show the absorption modes of acetonitrile. In order to compare the absorption due to the CN stretching modes at ~ 2250 and $\sim 2290\text{ cm}^{-1}$, the “wave-like” baseline in the systems with interlayer was

subtracted. The resulting absorption in the system with interlayers is increased by a factor of 3.8 for s-polarisation and by a factor of 1.5 for p-polarisation with respect to the system without interlayers.

On the other hand, the CH stretching modes at ~ 2940 and $\sim 3000\text{ cm}^{-1}$, which are far away from the reflectivity minimum, are almost unaffected by the presence of the interlayer.

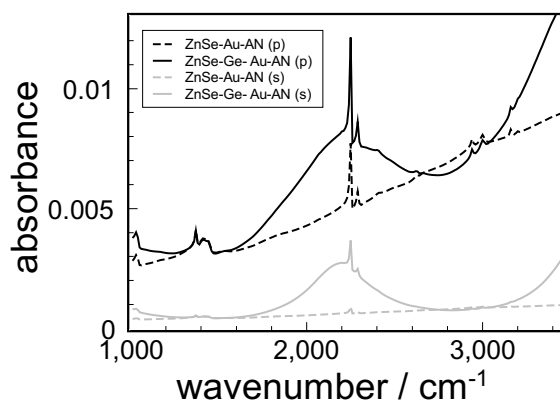


Fig. 3 Comparison of calculated absorbance spectra in the presence and absence of the germanium interlayer on ZnSe with $d_{\text{Ge}} = 900\text{ nm}$, $d_{\text{Au}} = 20\text{ nm}$ and incidence angle 45°. The polarisation (s and p) is indicated in brackets in the graph.

The layer thickness of the interlayer determines the wavenumbers of the minima in the reflectivity spectra, consequently determining the wavenumber regions with an increased absorption of the sample.

3 Materials and methods

Using a high vacuum physical vapour deposition chamber (Leybold Univex 450) working at $\sim 5 \times 10^{-6}$ mbar, germanium (Umicore, Balzers, Liechtenstein) was evaporated using the electron-beam technique, with an evaporation rate of approximately 3 Å/s on a ZnSe prism with an angle of 45° (Crystaltechno, Moscow, Russia). Thicknesses were monitored by a quartz crystal micro-scale.

On top of the Ge layer, a gold (Wieland Dental, Pforzheim, Germany) layer was evaporated using thermal evaporation with an evaporation rate of approx. $2\text{--}3\text{ Å/s}$. In control experiments, the gold was directly evaporated onto the ZnSe prism without Germanium interlayers.

The crystals with an evaporated layer were subsequently placed into a Pike VeeMax II ATR setup (Pike Technologies, Watertown, WI, USA) which was placed inside the sample chamber of a commercial Fourier transform infrared

spectrometer Biorad FTS3000 (Varian, Palo Alto, CA, USA) equipped with a middle band liquid nitrogen cooled mercury cadmium telluride (MCT) detector. A schematic view of the setup is shown in Fig. 4.

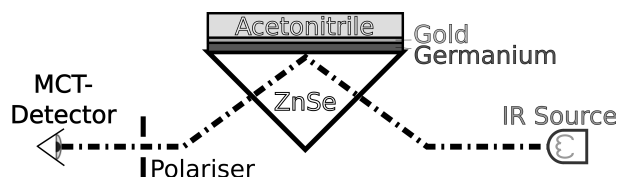


Fig. 4 A schematic view of the setup used in the experiment.

As a sample, standard laboratory solvent acetonitrile (*pro analysi*; VWR International) was used and placed in direct contact with the gold layer on top of the ATR crystal. The whole setup was purged with nitrogen for at least an hour before measurement. Spectra were recorded with a resolution of 2 cm^{-1} , averaging 1000 scans for each background and sample.

Layers prepared were characterised by a scanning electron microscope (SEM) type Zeiss Leo 1550VP Gemini (Carl Zeiss SMT AG, Germany). Here, secondary electron contrast is used to obtain images, using an acceleration voltage of 7-10 keV with a working distance of approximately 7 mm.

4 Experimental results

4.1 ZnSe-Ge-Au-acetonitrile, $d_{\text{Ge}} = 900\text{ nm}$ and $d_{\text{Au}} = 40\text{ nm}$

To exploit the limits of the interlayer concept, a (for optical experiments) quite thick gold layer with $d_{\text{Au}} = 40\text{ nm}$ was deposited first and investigated with and without the germanium interlayer. The thickness of the germanium interlayer was chosen to be $d_{\text{Ge}} = 900\text{ nm}$, which is expected to yield an absorbance enhancement in the region of $2200\text{--}2400\text{ cm}^{-1}$, where the acetonitrile CN stretching modes are located.

Scanning electron micrographs of the obtained layers are shown in Fig. 5. They show, as desired, a rather dull image without major features except a few bubble-like objects. Therefore, these images prove that the obtained gold layers are closed, i.e. have no holes. The origin of the bubble-like objects is not clear. For optimum performance, the number of these objects must be minimised.

Resulting absorbance spectra in the CN stretching mode region are shown in Fig. 6, comparing the spectra with and without the germanium interlayer for both s- and p-polarisation. For p-polarisation, the absorbance of the CN stretching mode at $\tilde{\nu} = 2250\text{ cm}^{-1}$ with the interlayer is by a factor of two higher compared to the absorbance without interlayer. The result for s-polarisation shows the presence of the peak in the

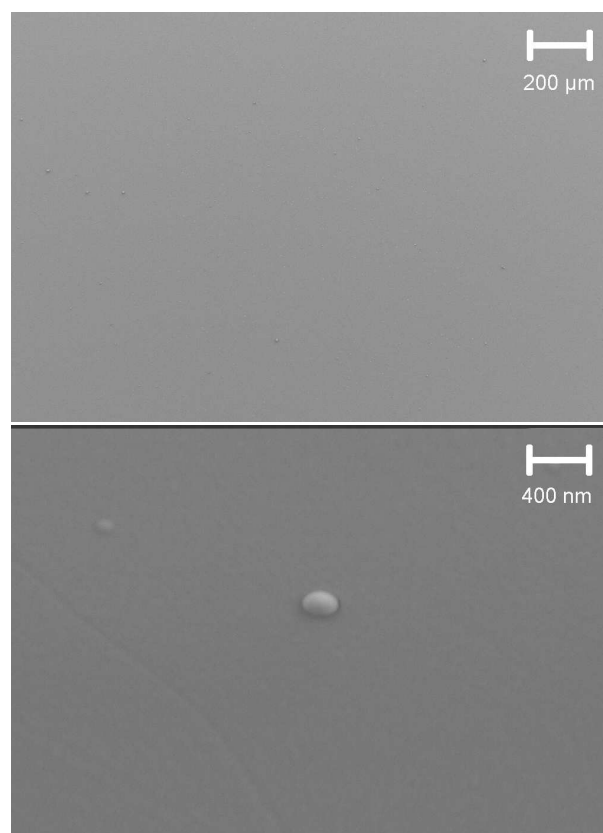


Fig. 5 Scanning electron micrographs of the ZnSe-Ge(900 nm)-Au(40 nm) on two different length scales.

spectra of the system with the Ge interlayer, while the absorption is below the level of the noise for s-polarisation. Both spectra show residual peaks of the uncompensated CO_2 absorptions at wavenumbers $> 2270\text{ cm}^{-1}$.

The overall absorbance of the bulk liquid in contact with 40 nm Au is in the order of 10^{-4} , which is rather low. It reflects the limits of IR absorption spectroscopy through thin metal films. An absorbance like that will, however, be too low to conduct experiments where monolayer sensitivity is needed. In these cases, thinner layers are needed.

4.2 ZnSe-Ge-Au-acetonitrile, $d_{\text{Ge}} = 1350\text{ nm}$ and $d_{\text{Au}} = 20\text{ nm}$

As an example for thinner layers, an Au layer of $d_{\text{Au}} = 20\text{ nm}$ has been placed on top of a germanium layer of $d_{\text{Ge}} = 1350\text{ nm}$. They are not compared to a reference system, as gold films deposited on ZnSe without germanium used to form an island structure, and therefore no suitable reference system without germanium could be produced. These findings indicate that germanium on ZnSe also works as adhesion promoter for metals such as gold. Due to the lack of a suitable reference

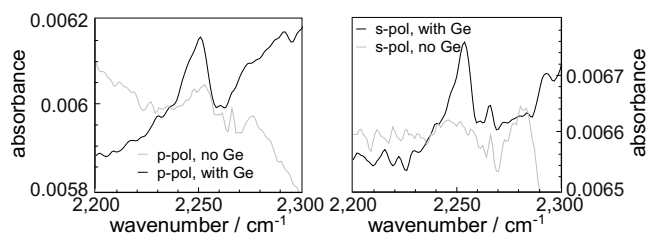


Fig. 6 Absorbance (left: p-polarisation, right: s-polarisation) of acetonitrile on a ZnSe prism coated with germanium, $d_{\text{Ge}} = 900\text{ nm}$ and gold $d_{\text{Au}} = 40\text{ nm}$ in comparison to a system without germanium.

system, we decided to compare the resulting spectra to computed spectra.

Figures 7 and 8 compare the measured absorbance spectra for a system with $d_{\text{Ge}} = 1350\text{ nm}$ and $d_{\text{Au}} = 20\text{ nm}$ for both s- and p-polarisation with the calculated spectra of the respective configuration.

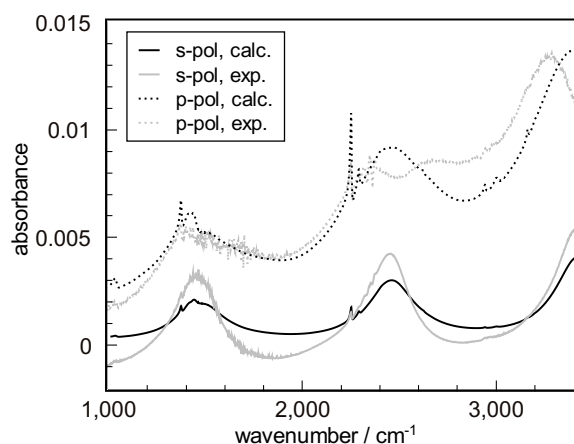


Fig. 7 Comparison of measured spectra (exp.) and calculations (calc.) with both s- and p-polarisation as indicated in the graph for the ZnSe-Ge($d_{\text{Ge}} = 1350\text{ nm}$)-Au($d_{\text{Au}} = 20\text{ nm}$)-acetonitrile system at 45° angle of incidence.

The overall comparison between calculated and experimental spectra is shown in Fig. 7. The measurements for p-polarisation show qualitative agreement between theory and experiment for the extrema positions but not for the exact height of the maxima. The agreement for s-polarisation is better - the extrema positions do quantitatively match. Still the exact heights are slightly different. The differences between simulations and measurements are attributed to a minor spread in angle of incidence. Small inhomogeneities in both layers also contribute to the discrepancies. One expects p-polarised

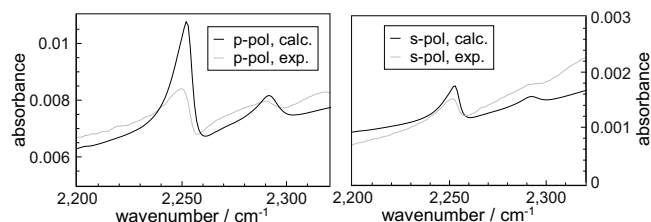


Fig. 8 Detailed comparison of measurement and calculation in the region of the acetonitrile CN stretching mode for p-polarisation (left) and s-polarisation (right).

spectra to be affected stronger by the inhomogeneities. It is worth noting that no baseline correction or treatment has been applied to the spectra, and the differences in the baselines for both polarisations predicted by computations are reproduced by the experiments.

In the experiment, residual absorptions from atmospheric CO_2 are present at 2340 and 2360 cm^{-1} . The vibrational modes of the acetonitrile are present in the spectra as expected. A detailed view of the region of the CN stretching mode at $\sim 2250\text{ cm}^{-1}$ is presented in Fig. 8. The CN stretching mode is in the shoulder of one of the interlayer interference fringes, therefore an increase in absorption is expected when compared to a situation where the germanium layer is absent. For p-polarisation, the agreement is not so good, the measured absorbance reaches half of the calculated value. For s-polarisation, the measured absorbance is of the same magnitude as the predicted absorbance.

The agreement in the absorbance between simulation and experiment for s-polarisation proves the presence of the enhancement due to the introduction of the interlayer in between the internal reflection element and metal layer.

5 Conclusions and Outlook

The enhancement of absorption in ATR spectroscopy through thin continuous metal films is possible with the introduction of a dielectric interlayer, inspired by the concept introduced by Hooper et al. for optical tunnelling⁹. The dielectric interlayer acts as a kind of anti-reflective layer for the metal when introduced into the system of IRE - metal - sample. Here, it has been shown that it is possible to calculate the behaviour of this multilayer system, and a system ZnSe-Ge-Au has been realised with germanium layer thicknesses of 1350 nm and 900 nm and gold layer thicknesses of 20 nm as well as 40 nm .

Under the conditions of having a gold layer thickness of 40 nm , the spectra for acetonitrile show an enhancement factor in p-polarisation up to ~ 2 . In s-polarisation, the absorption mode is recovered from the noise in the presence of the interlayer, while it is invisible in the interlayer's absence. Con-

sequently, the thickness range of metal films through which internal reflection spectroscopy is still possible is clearly extended through introduction of the interlayer.

The multilayer stack yields high enhancements directly in the minima of the reflectivity curves. While the wavenumber of these minima can be tuned by changing the thickness of the interlayer, the depth critically depends on the angle of incidence as well as the medium of incidence. Medium of incidence with lower refractive index should yield higher enhancement. Computations do furthermore show that a much higher enhancement is obtained when the refractive index of the interlayer is increased in order to match more closely the refractive index of the metal. Unfortunately, increasing the refractive index above 4.0 appears to be impossible with no non-absorbing materials. Nevertheless, further work will be done on optimising the enhancement.

A very important difference to surface-enhanced infrared absorption spectroscopy is that in the systems introduced here, the enhancement - though low - is uniform over the whole surface, i.e. there are no hot spots which yield high enhancement while other parts do not contribute to the signal at all. Such a behaviour is highly beneficial for quantitative studies, and enables the study of self-assembly processes on flat surfaces.

Furthermore, the presence of the interference fringes in the spectra bears additional information about the real part of the refractive index of a non-absorbing sample. Details of the information content from these structures will be worked out in future studies.

Overall, the method offers great potential in the study of adsorption processes to metal interfaces. One remarkable feature is the fact that the increase in absorbance in s-polarisation is stronger than the increase in absorbance in p-polarisation.

This property means a further softening of the surface selection rule, which is already not strictly valid for these thin metal films. With the strengthening of the signal in s-polarisation, the study of orientation of molecules in anisotropic films is expected to be greatly facilitated.

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References

- 1 N. J. Harrick, *Internal reflection spectroscopy*, Wiley, 1967.
- 2 E. Goormaghtigh, V. Raussens and J.-M. Ruysschaert, *Biochim. Biophys. Acta*, 1999, **1422**, 105–185.
- 3 C. Vigano, J.-M. Ruysschaert and E. Goormaghtigh, *Talanta*, 2005, **65**, 1132–1142.
- 4 R. F. Aroca, D. J. Ross and D. Concepcion, *Appl. Spec.*, 2004, 324A–338A.
- 5 K. Ataka and J. Heberle, *Anal. Bioanal. Chem.*, 2007, 47–54.
- 6 F. Neubrech, A. Pucci, T. W. Cornelius, S. Karim, A. García-Etxarri and J. Aizpurua, *Phys. Rev. Lett.*, 2008, **101**, 157403.
- 7 M. Boncheva and H. Vogel, *Biophys. J.*, 1997, **73**, 1056–1072.
- 8 A. Erbe, R. J. Bushby, S. D. Evans and L. J. C. Jeuken, *J. Phys. Chem. B*, 2007, **111**, 3515–3524.
- 9 I. R. Hooper, T. W. Preist and J. R. Sambles, *Phys. Rev. Lett.*, 2006, **97**, 053902.
- 10 E. D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, 1985.
- 11 J. Lekner, *Theory of reflection*, Kluwer, 1987.
- 12 M. Schubert, *Phys. Rev. B*, 1996, **53**, 4265–4274.
- 13 A. Erbe, *Reflcalc*, <http://home.arcor.de/aerbe/en/prog/a/reflcalc.html>.
- 14 J. E. Bertie and Z. Lan, *J. Phys. Chem. B*, 1997, **101**, 4111–4119.