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# Incidence angle dependence of enhancement factor in attenuated total reflection surface enhanced infrared absorption spectroscopy studied by numerical solution of the vectorial Maxwell equations<sup>†</sup>

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The finite element method (FEM) was used to solve the time-harmonic Maxwell equations in a study of the effect of incidence angle of infrared light on the surface enhancement caused by colloidal gold particles in attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS). The spectral enhancement factor was obtained from computations of absorbance from a thin organic layer in the presence and absence of the metal nanostructure. For computations of an isolated particle the enhancement factor is high around the critical angle and decreases with increase in incidence angle. This trend was also observed in experiments performed with gold particles immobilised on a silane modified silicon ATR crystal. Computations where gold particles are touching each other show low enhancement factors around the critical angle and an increase with increasing incidence angle. These two opposing trends are analysed based on the electric field distribution around the particle.

# **1** Introduction

Surface enhanced infrared absorption spectroscopy (SEIRAS) has become a useful tool to investigate structures and reactions at interfaces. To study reactions at solid/liquid interfaces, the technique is frequently employed in attenuated total reflection (ATR) configuration, where a rough metal island film is placed on a high index, IR-transparent substrate, which is then put into contact with the liquid medium under study. The technique is particularly useful in the analysis of biomolecules at interfaces, in catalysis, and in electrochemistry. A number of review text are available covering various aspects of the application of SEIRAS  $^{1-6}$ 

Traditionally, the SEIRAS experiment is describes theoretically using the analytical solution of the Maxwell equations, which are available for stratified structures.<sup>7,8</sup> Within this framework, the layer containing the metal nanostructures is described as "effective medium" with an effective thickness and a dielectric function depending on the composition.<sup>1,2,4</sup> Enormous progress has been made in treating the metal island film as an effective medium of metal spheres, ellipsoids, and ellipsoids with a size distribution.<sup>4,9–11</sup> While the treatment within the effective medium approximation has been found to describe many aspects of SEIRAS consistent with experiments,<sup>1,2,9,10,12</sup> the model has been noted to contain "large simplifications".<sup>2</sup> Simplifications in this context means that local details of the morphology are not adequately described. For an understanding of, e.g., local electromagnetic interactions between neighbouring particles within the metal nanostructure film, these simplifications need to be overcome. A rational, knowledge-based design of structures for SEIRAS experiments is only possible with detailed knowledge of the spatial distribution of the electric field in the metal films. The difficulties in absolute physical quantification of SEIRAS experiments can also be tackled by a rigorous description of the electric fields in the layer yielding surface enhancement.<sup>9,10</sup>

The aforementioned simplifications in the description of SEIRAS, in particular ATR-SEIRAS, can be overcome by a rigorous electromagnetic treatment of the layer. Mie-based analytical treatments for electric fields, scattering and extinction cross-sections for spheres and aggregates of spheres have been developed, <sup>13–15</sup> and an overview over applications to surface-enhanced Raman scattering (SERS) has been given recently.<sup>16</sup> For more detailed insight into the structure of the electric field and its interaction with absorbing substances, a rigorous solution of the Maxwell equations for complex geometries is needed, which up to now was impossible to achieve analytically. In recent years, several numerical methods have been used to solve electromagnetic problems rigorously for linear optical media. These techniques include the finite difference time domain method, <sup>17</sup> the boundary element method,<sup>18,19</sup> and the finite element method (FEM).<sup>20</sup> The latter offers the advantage that the dielectric function of

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Full set of electric field distribution pictures. Electron micrographs of the particles used in the study. See DOI: 10.1039/b000000x/

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real metals can easily be incorporated, arbitrarily shaped geometries can be calculated, and the effect of interfaces can be studied. The drawbacks are relatively long computation times and rather low overall system size which can be studied.

Despite these limitations in system size, important morphological elements, which occur in real SEIRAS surfaces can be studied computationally in a reductionist approach. By selecting specific morphological elements from a surface, the influence of these on the overall, average, experimental enhancement can be obtained. Several classes of metal films are described as yielding surface enhancement, vacuum evaporated films, electrochemically deposited films, and adsorbed metal colloid films.<sup>2</sup> While not necessarily the most popular geometry in SEIRAS experiments, adsorbed metal colloids are well suited for principle studies of electromagnetic interactions at the interface, because metal colloids can be prepared with well–defined size and uniform size distribution.

FEM was recently applied to compute ATR-SEIRAS spectra, to identify trends with particle size, separation and shape. The electric fields around the particles at the interface have been obtained and analysed.<sup>21</sup> To further evaluate the approach presented there, a variation of the angle of incidence can be performed, which is the topic of this work. Variation of the angle of incidence was discussed before for SEIRAS in external reflection geometry,<sup>9</sup> as well as for ATR-SEIRAS.<sup>1,1,2,22,23</sup> In all previous reports, the effective medium approximation was used to explain the obtained data. For the case of SERS, a recent study reports on the angle-dependent polarisation, including a theoretical analysis of the Raman tensor.<sup>24</sup> In this manuscript, FEM is used on the computational side to study the dependence of enhancement on the angle of incidence. Simulations are accompanied by experiments.

# 2 Methods

#### 2.1 Computations

Simulations were carried out using JCMsuite (JCMWave GmbH, Berlin, Germany, www.jcmwave.com), a commercially available FEM-based solver of Maxwell's equations with adaptive multigrid meshing.<sup>25</sup> It permits to calculate numerical solution of the time-harmonic Maxwell equations in scattering problems, propagating or resonance modes for waveguides or resonators in one-, two- and three-dimensional geometries and has been used successfully for solving electromagnetic problems with complex geometries.<sup>26–28</sup>

The interaction between two particles was investigated using computational domains in two dimensions (2D) using Cartesian coordinates. On an interface between two semiinfinite half-spaces, circular metal particles with a certain separation were placed. In a three-dimensional (3D) world, this situation corresponds to infinite cylinders aligned on a surface with the cylinder long axis perpendicular to the direction of propagation of the electromagnetic plane wave. The solutions obtained here should be a good approximation for cylinders whose length is much larger than the wavelength of the incident light. In this case, parallel to the interface, periodic boundary conditions have been used. Three-dimensional geometries with rotational symmetry have been investigated using cylindrical coordinates, in which a computation in two dimensions is possible. Using this approach, the construction of individual spherical particles at the interface are possible. Computational domains in 2D Cartesian and cylindrical coordinate systems have been explained in detail elsewhere.<sup>21</sup>

In all cases, the medium of incidence had a refractive index  $n_2 = 3.3$ , equivalent to silicon, and the exit medium is air with  $n_1 = 1.0$ . Incidence and exit medium were bordering a perfectly matched layer (PML) as a pseudo-transparent boundary condition. For the particles placed at the silicon/air interface, the frequency-dependent optical constants of gold between wavelengths  $\lambda$  of 2.5 and 10  $\mu$ m were approximated by a polynomial.<sup>29</sup> A sample substance with the optical constants of poly(ethylene) is considered here,<sup>30</sup> which is expected to mimic the CH-stretching mode region of a number of substances with long aliphatic chains.

In all cases the source originates from the PML/silicon interface with unit field strength. Field images displayed in this work always show the field strength as multiples of this unit field strength. The plane wave impinges at the silicon/air interface under an angle of incidence  $\theta$ .

In simulations in 2D Cartesian coordinates, for each  $\lambda$ , the reflected electric field amplitude  $E_{refl}$  has been obtained from JCMsuite for a certain incident electric field amplitude  $E_{inc}$  at the two perpendicular linear polarisations. For each  $\lambda$ , a reflectivity *R* was calculated as

$$R = \frac{|E_{\text{refl}}|^2}{|E_{\text{inc}}|^2}.$$
 (1)

In the computations with rotational symmetry using cylindrical coordinates, in addition to the reflected field, a scattered field is encountered. In these cases, the law of reflection was used to isolate the reflected light, *i.e.*  $E_{\text{refl}}$  was obtained as the field in the direction of the reflected beam. In that way, the reflected field also contains the forward scattered electric field, as in the experiment. Typically, the scattered amplitude in different directions than the specularly reflected beam was found to be at least 7 orders of magnitude smaller than  $E_{\text{refl}}$ .

Absorbance  $A_{\rm smp}$  was computed from two values of R,  $R_{\rm smp}$  obtained in the presence of the metal particles and sample substance, and  $R_{\rm ref}$  as the reflectivity of the bare silicon/air interface. Above the critical angle  $\theta_{\rm cr} \approx 18^{\circ}$  for the situation used here, ideally  $R_{\rm ref} = 1$ . This condition was numerically well

fulfilled, deviations were in the order of  $10^{-7}$ . For each  $\lambda$ ,

$$A_{\rm smp} = -\log_{10}\frac{R_{\rm smp}}{R_{\rm ref}}.$$
 (2)

An example of the resulting absorbance spectrum of  $A_{smp}$  is shown as a straight line in Fig. 1 (main figure). To obtain re-



**Fig. 1** Spectra to compute *EF*. Main Figure: Absorbance spectra in the presence (--) and absence (--) of an organic layer over a metal particle. Inset: Baseline corrected spectrum (-) and spectrum in the absence of metal particle (....) around the resonant absorption.

liable spectral enhancement factors, two more simulations of  $R(\lambda)$  were carried out. First,  $R_{so}$  was computed in the presence of the sample substance, but in the absence of the metal particles, leaving the geometry of the sample substance unchanged compared to the case when metal particles were present.  $R_{so}$  was subsequently used to compute the absorbance  $A_{so}$  (Fig. 1, inset, dotted line) in the absence of metal using the same  $R_{ref}$ . Second, due to the steep baselines encountered in the presence of metal nanostructures, which originate from the strong frequency dependence of the dielectric function of the metal particles but in the absence of the sample substance. An absorbance  $A_{met}$  was calculated from  $R_{met}$  with the same  $R_{ref}$  and is shown as dashed line in Fig. 1 (main figure).

A baseline–corrected sample absorbance spectrum  $A_{\rm sbc}$  was then obtained as  $A_{\rm sbc} = A_{\rm smp} - A_{\rm met}$ . Absorbance was set to 0 far away from the resonant absorption of the sample substance to remove a baseline offset present after the computation. An example for the obtained spectrum is shown in the inset in Fig. 1 as straight line. The obtained spectrum is then analysed, and for simplicity will be referred to as absorbance spectrum  $A(\lambda)$ , leaving out all the indices, for the remainder of this work.

The spectral enhancement factor EF due to the presence of the metallic nanostructures was obtained by comparing the so-obtained absorbance spectra in the presence and absence of



Fig. 2 The two different sample geometries. In (A), the sample layer is placed on the planar surface underneath the particle, while in (B), the sample layer is placed as a coating on the spherical particle. (A) contains the incident light through the substrate and defines the angle of incidence  $\theta$ . (B) contains the coordinate system used throughout this work.

the metal nanostructures using

$$EF = \frac{A_{\rm sbc}}{A_{\rm so}},\tag{3}$$

where the maximum value of the absorbance spectrum at 2920  $\text{cm}^{-1}$  was used, which originates from the antisymmetric CH<sub>2</sub> stretching mode. The inset in Fig. 1 shows the two spectra which are compared for determination of *EF*.

A layer of sample substance of 1 nm thickness (unless noted otherwise) is placed in two different positions, drawn schematically in Fig. 2. In some cases, the sample substance is placed on the silicon/air interface, and the particles are present on top of the layer of sample substance (Fig. 2, geometry A). For other investigations, the sample substance is placed as a thin shell of 1 nm thickness around the particles (Fig. 2 geometry B).

The coordinate system used throughout this work is the same as used previously,<sup>21</sup> and is shown in Fig. 2(B). The *x*-axis is parallel to the interface along the direction of propagation, the *y*-axis perpendicular to the *x*-axis along the normal vector of the silicon/air interface, and the *z*-axis is located such that a right–handed Cartesian coordinate system is formed. Fig. 2(A) also schematically depicts the linear polarisations in this coordinate system. In p-polarisation, the electric field vector has components in *x* and *y* directions, while using s-polarisation, the electric field vector has components in *z* direction only.

#### 2.2 Experiments

IR spectroscopy measurements in the ATR geometry were carried out using a Biorad Excalibur FTS3000 (Biorad, Palo Alto, CA, USA; now part of Agilent Technologies) FTIR spectrometer with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The Harrick Seagull variable angle reflection unit (Harrick Scientific, Pleasentville, NY, USA) was used as it is suitable for varying  $\theta$ . A hemispherical silicon prism (Crystaltechno, Moscow, Russia) was mounted on the standard Seagull sample mount. The incident beam was set to maximum width, so that the illuminated sample area in experiments is close to the maximum available sample area. With the beam size along the beam direction being on the order of the crystal size, the sampled surface area becomes independent of the angle of incidence. Hence, no correction of the absorbance for the angle of incidence was performed. The angle of incidence was varied from 18° to 50°. The reflected light passes through a polariser, by which measurements in both s and p polarisation were carried out.

Gold particles in colloidal solution were prepared following a standard method with slight modifications.<sup>31</sup> A 50 mL aqueous solution of HAuCl<sub>4</sub> (0.25 mM) was prepared in a threeneck flask equipped with a reflux condenser, and the solution was heated in an oil bath to boil while being stirred. Then, 0.05 mL 5 wt% aqueous sodium citrate solution was added. The reaction was continued until the solution became wine red coloured thus indicating that the reaction was completed.

A silane layer was adsorbed on the oxide-covered silicon on which the gold particles could later be deposited. Following a procedure which was described in detail elsewhere,<sup>32</sup> the silicon crystal was immersed in a solution of 2.0 mM (3-aminopropyl)-triethoxysilane (APTES) (ABCR, Karlsruhe, Germany) in CHCl<sub>3</sub> for 30 min. The crystal was then subjected to an ammonia atmosphere overnight and finally was rinsed with deionized water to remove excess unbound silane. Using the spectroscopic ellipsometer SE-800 (Sentech Instruments, Berlin/Krailling, Germany), the change in the ellipsometric parameter  $\Delta$  before and after the surface modification was correlated to a layer thickness of  $(0.7 \pm 0.1)$  nm using the instrument's fitting software assuming a layer with a refractive index of 1.420.

Initially, single-channel IR spectra of the Si prism modified with an APTES layer were recorded. Subsequently, the prism's sampling surface was put in contact with the aqueous gold particle dispersion for 15 min, rinsed with water, dried, and spectra with adsorbed particles were recorded. Scanning electron micrographs of the particles immobilised on a silicon wafer prepared according to the same procedure are shown in the ESI<sup>†</sup> (Fig. 8-11). Predominantly, the observed particles are isolated, with only few clusters visible on the micrograph. The average diameter of the particles is  $\approx$ 70 nm. The SEM images show slight deviations from the spherical shape used for the computations, which is not supposed to lead to qualitatively different results, as the electric field distribution around spheroids are very similar to those around spheres. <sup>33–36</sup> Particles of a relatively large diameter have been chosen to avoid surface effects on the dielectric function of the gold particles. 37-39

# **3** Results and Discussion

#### 3.1 Interaction between two particles

The angle dependence of EF of two metal particles separated by a certain distance was studied for several separation distances. Here, simulations were carried out using a 2D Cartesian coordinate setup. The spacing distance between adjacent particles was varied from 0 - 10 nm in cases where a 1 nm organic layer was placed either as a shell around the particle (Fig. 2, (B)) or as a layer on the substrate under an uncoated particle (Fig. 2, (A)). A separation of 0 nm for a coated particle means that the coatings of two particles are touching each other, with the metal cores still separated by the thickness of the coatings (here, 2 nm). Only p-polarisation was investigated here, as in s-polarisation the electric field contains components in z-direction only, which is not explicitly defined in the 2D geometry used in these computations.

Results are displayed in Fig. 3. The general trend for all the spacing distances is that the enhancement factor has a low value at  $\theta_{cr}$  and increases with increasing incidence angle. For geometry A, EF is continuously increasing with  $\theta$  (Fig. 3a). As reported before, EF is highest if the metal structures are closer to each other.<sup>21</sup> As in this geometry, there is no organic layer around the particles, a distance of 0 nm between the particles means that the metal structures are actually touching. In this case, the highest EF are also found if the sample substance is located away from the main hot spot between the touching particles. The fact that the metal parts touch make the structure at 0 nm separation qualitatively different from the other structures. Results for this separation are also most prone to numerical errors, which is why the minimum in EF at  $\theta = 19^{\circ}$  should not be discussed here in further detail. Higher EF are obtained in case of a shell around the particles (geometry B), where maximum  $EF \approx 70$  (Fig. 3b), because here the organic layer is placed in the centre of the region with highest electric field. For this geometry, there is a limiting value of *EF*, which is reached at  $\theta > 30^{\circ}$ .

The increase in *EF* with increasing  $\theta$  is understood by analysing the electric field distribution around the particles as shown in Fig. 4. For particles whose coatings are touching (0 nm) and at a distance of 5 nm, at  $\theta = 18^{\circ}$  the field distribution shows two maxima, one in the region in direct contact with the incidence medium, and the second on the opposite side of the particle, facing the free exit medium. This field distribution is special to  $\theta_{cr}$ , where the penetration depth of the evanescent wave diverges. With increasing  $\theta$ , the field maxima move out of the region between incidence medium and particle. In general, at  $\theta > \theta_{cr}$ , a field distribution similar to an oscillating dipole distorted by the surface is found.<sup>21</sup> For all separations at  $\theta = 40^{\circ}$  the field maximum is therefore in between adjacent particles, where it is enhanced by the presence by a confine-



**Fig.** 3 *EF* in p-polarisation as function of  $\theta$  for varying spacing distance (0–10 nm) between neighbouring gold particles (a) on an organic layer on the substrate (geometry A) and (b) enclosed in an organic shell (geometry B). Distances between particles are indicated in the plot.



**Fig. 4** Electric field strength at 3200 cm<sup>-1</sup> in *x*-*y*-plane at  $\theta = 18^{\circ}$  (a, b) and  $\theta = 40^{\circ}$  (c, d) for two coated gold particles with a diameter of 30 nm and a coating shell of 1 nm touching each other (a, c) and separated by a distance of 5 nm (b, d).

ment effect similar to a gap mode between the particles, which is naturally stronger for particles with lower separation.<sup>40–43</sup>

### 3.2 Single spherical particle

The angle dependence of EF from the organic material either as a shell around or as a layer underneath an individual, isolated spherical particle of 30 nm diameter was studied using the 2D cylindrical coordinate setup describing a spherical particle between silicon and air. Results are shown in Fig. 5 for both polarisations.

In case of particles with coating (geometry B), the trend for both polarisations is opposite, however, EF is almost angleindependent for s-polarisation. EF has its maximum at  $\theta_{cr}$ and reduces with increasing  $\theta$ . This behaviour is caused by the larger spatially averaged electric field at  $\theta_{cr}$  compared to other  $\theta$ . For the scenario where the organic material is present as a layer under the particle (geometry A), s- and p-polarisations have similar trends. In s-polarisation, EF is again almost angle-independent, but decreases slightly with increasing  $\theta$ . Though the trend in p-polarisation is similar to geometry B, the maximum EF is 2.7 for the layer on the substrate, compared to 1.8 for a shell around the particle. The different maxima can be explained by an inspection of the respective field images, Fig. 6 for geometry B and Fig. 1 of the ESI<sup>†</sup> for geometry A. In both cases, the maximum fields reach the same value in the region between metal and substrate. In the case of geometry A, selectively only this region is probed by the



**Fig.** 5 *EF* vs.  $\theta$  in p-polarisation (•, scale on left) and s-polarization (**■**, scale on right) for an isolated gold particle of 30 nm diameter with an organic layer (a) on the substrate (geometry A) and (b) as a shell around the particle (geometry B).



**Fig. 6** Total electric field amplitude in *x*-*y*-plane (incident p-polarisation) at 3200 cm<sup>-1</sup> around a single coated gold particle (geometry B) of diameter 30 nm with varying  $\theta$ : 18° (a), 20° (b), 40° (c) and 60° (d). Each  $\theta$  has a different colour scale; a plot with all a uniform colour scale for all  $\theta$  is included in ESI Fig. 2<sup>†</sup>.

sample substance, while in geometry B, other regions around the particle contribute to the enhancement, but to a smaller extent. The electric field amplitude in *z*-direction — relevant for the excitation of dipole transitions in s-polarisation — is not affected by changes in  $\theta$ . (Rather, changing  $\theta$  affects the balance between the amplitude in *x* and *y*-directions only, relevant for p-polarisation). Hence, to first approximation, absorbance in s-polarisation is not supposed to show any angle– dependence. The observed change of  $\approx 1 \%$  over the angular range investigated here can be attributed to slight differences in the scattering contribution to the absorbance.

At  $\theta_{cr}$ , the penetration depth goes to infinity, which is why large absorbance is found for bulk samples.<sup>44</sup> Both s- and ppolarisation are equally affected by the variation in penetration depth.<sup>44</sup> Under the conditions used here, the penetration depth is, however, larger than the overall size of the structure at all  $\theta$ : at the highest  $\theta$ , the penetration depth is  $\approx 150$  nm.<sup>44</sup> The observed high *EF* at  $\theta_{cr}$  is therefore not caused by the divergence of the penetration depth around  $\theta_{cr}$ .

In order to understand the mechanism of the spectral enhancement at the different  $\theta$ , the electric field distribution around the particle at several  $\theta$  is shown in Fig. 6 with incident p-polarisation and in Fig. 7 with incident s-polarisation. In Fig. 6a, at  $\theta = 18^{\circ}$ , the electric field strength value for p-polarisation reaches a value of ~50 at the point of highest field



**Fig. 7** Total electric field amplitude in *y*-*z*-plane (incident s-polarisation) at 3200 cm<sup>-1</sup> around a single coated gold particle (geometry B) of diameter 30 nm for  $\theta = 18^{\circ}$  (a) and  $\theta = 60^{\circ}$  (b).

strength. When  $\theta$  is changed to 20°, only slightly away from  $\theta_{cr}$ , the maximum field strength reaches only 23 (Fig. 6b). At  $\theta > \theta_{cr}$ , such as 40° (d) and 60° (e) the maximum field strength encountered continuously decreases. A close inspection of the field pattern reiterates a simple physical fact, which in the view of the authors is often neglected in the discussion of field enhancement. As

$$A \propto |E|^2, \tag{4}$$

the relevant field is the field inside the sample substance, which is weakened compared to the electric field in vacuum by the real part of the dielectric constant  $\varepsilon$  of the sample substance.<sup>7</sup> Therefore, using the electric field  $E_0$  in vacuum as a base,

$$A \propto \operatorname{RE}(\varepsilon)^{-2} |E_0|^2.$$
(5)

Here,  $\text{Re}(\varepsilon) \approx 2.25$ . The spectral enhancement factor *EF* discussed here is a spatial average over the local spectral enhancement factor  $EF_{\text{loc}}(x, y, z)$ , which is a function of position,  $EF = \langle EF_{\text{loc}}(x, y, z) \rangle_{xyz}$ .  $EF_{\text{loc}}$  can be directly related to the field enhancement. From eqs. 3 and 4,

$$EF_{\text{loc}} \simeq \frac{1}{\text{Re}(\varepsilon)^2} \left(\frac{|E|_{\text{met}}}{|E|_0}\right)^2,$$
 (6)

neglecting the effect of scattered light on the total absorbance, and treating the electric fields in air (exit medium in this work) and vacuum as equal.  $|E|_{met}$  is the field in the presence of the metal particle. The ratio  $\frac{|E|_{met}}{|E|_0}$  is the field enhancement factor, which is frequently discussed in the SERS literature. In eq. 6, for ATR-SEIRAS,  $|E|_0$  depends only on the *y* coordinate, i.e. the distance of the point under consideration from the interface where the evanescent wave is generated. For the further discussion of  $EF_{loc}$ ,  $|E|_0$  from the reference computations is used, while  $|E|_{met}(x, y, z)$  is taken from the computations which lead to the respective field image. It must be pointed out that the computation of full spectra using FEM, as

performed in this work, goes beyond the simple statement of eq. 6, as effects from scattering of the evanescent wave by the particles are fully included in the FEM treatment and hence in the obtained averaged EF.

At all  $\theta$  shown in Fig. 6, the region with high electric field strength is relatively small. Nevertheless its strong contribution to the absorbance implies that the overall trend in angle dependence follows the trend in the maximum fields observed. At the point with highest electric field at  $\theta_{cr}$ , where an incident electric field with unit amplitude in air is enhanced  $\approx$ 50-fold,  $EF_{loc} \approx 130$  is obtained. It must be pointed out that such regions are especially prone to nonlinear optical effects, which is why there is no further analysis of such regions with extremely high local fields in this work. The region between particle and incidence medium overall shows a  $\approx$ 30-fold enhanced electric field, which still corresponds to  $EF_{loc} \approx$ 50. Though only relatively small in spatial extension, in the computational experiment reported here, this region dominates the absorbance spectrum.

At higher  $\theta$ , as shown in Fig. 6c and 6d the electric field distribution becomes more uniform. Here, extended areas parallel to the interface show an increase in electric field strength of  $\approx$ 3, corresponding to  $EF_{\text{loc}} \approx$ 2.1, which is close to the overall average EF.

The angle dependence also shows that at each  $\theta$  in ppolarisation, there is a "blind spot", *i.e.* a region around the particle where the electric field strength is almost 0, hence no absorption of light from this region can be observed. This spot correspond to the nodes in the field pattern in the harmonic oscillator. These nodes revolve around the particle if  $\theta$  is changed. Such a behaviour has interesting consequences for experimental studies, as it shows that depending on  $\theta$ , different portions of the interfacial region can be excluded from contributing to the observed spectrum.

Using the language of gap modes, the field pattern characteristic for  $\theta_{cr}$  directly excites the gap mode between particle and incidence medium. At higher  $\theta$ , the nodes move into the gap region, thus decreasing the observed absorbance. However, at the same time, these modes move into regions between adjacent particles, leading to the observations discussed in section 3.1.

In s-polarisation, as shown in Fig. 7, the field distribution around the particle in *y*-*z*-direction is quite homogeneous, with almost no change with  $\theta$ . Only the magnitude of the total field changes, not the field distribution. Therefore, no angle dependence of the absorbance is found. As for incident light with s-polarisation, the electric field vector oscillates solely in *z*direction and no change in a field component (other then scattered light) is found with changing  $\theta$ . Hence no angle dependence of the field pattern and absorbance is expected in first approximation. Overall, there is no  $\theta$  at which a sample in the gap between metal and incidence medium can be detected in



Fig. 8 Absorbance with varying  $\theta$  for computations (scale on the right) and experiments (scale on the left), both in p-polarisation.

s-polarisation, neither can a sample facing the open incidence medium be detected in s-polarisation.

Comparing the field images in s- and p-polarisation shows that at  $\theta_{cr}$ , the field maxima are rotated by 90° with respect to each other (Fig. 6a vs. Fig. 7a). Such a constellation means that at  $\theta_{cr}$ , regions to which s-polarisation is particularly sensitive are not at all detected in p-polarisation, and *vice versa*. At higher  $\theta$ , the pattern in p-polarisation more and more approaches the pattern in s-polarisation. At  $\theta = 60^{\circ}$ , the fields in both polarisations look very similar (Fig. 6d vs. Fig. 7b). Therefore, under these conditions, the ATR-SEIRAS experiment probes similar regions around the particles.

A full set of field images, with inclusion of less relevant planes, can be found in the  $\text{ESI}^{\dagger}$  Fig. 3 to 7.

#### 3.3 Experiments

To study the incidence angle variation of EF in experiments, the absorbance of a thin organic layer in the presence and in the absence of the gold nanostructure needs to be measured. A geometry close to geometry A has been used experimentally, to exclude the influence of the high field region between adjacent particles. Geometry A is more tolerant to the presence of clusters of metal particles.<sup>21</sup> However, using a single reflection setup as needed in experiments varying the angle of incidence over a large range, the absorbance of the monolayer in the absence of gold particles was below the noise level of the spectra. Hence a direct calculation of EF for comparison with the plot in Fig. 5a was not possible.

Instead, both in experiments as well as in computations, absorbance was calculated by taking the spectra with the organic layer but without particles as reference (as  $R_{ref}$  in eq. 2), and using the spectra in the presence of the particles as a sample spectrum (as  $R_{smp}$  in eq. 2).

Parameters for the computational setup (using an individual particle as in Section 3.2, therefore excluding particle interactions) were extracted from experiments. Layer thickness of the organic layer was 0.7 nm and diameter of the particles was 70 nm. An oxide layer of thickness 1.5 nm and n = 1.45 was included to represent the native oxide layer on the silicon substrate. The citrate layer has been included as non-absorbing in the wavelength range under consideration. As discussed previously,<sup>21</sup> computations show that the thickness of the citrate layer varied in the computational experiment between 1 and 10 nm has only a meager influence on EF, and no difference in the general trend is observed. The results of experiments and computations are compared in Fig. 8. The values of absorbance are orders of magnitude different, because computations represent one individual particle, while in experiment a collection of predominantly isolated particles is present, with  $\sim 0.9 \,\mu\text{m}^2$  per particle.<sup>21</sup> Therefore, only the trend with  $\theta$  can be compared.

Starting at  $\theta_{cr}$ , absorbance decreases with increase in  $\theta$  in both experiments and computations. The value recorded at  $\theta_{cr}$ is the highest throughout the experiments in both simulations and experiment. In both cases, the absorbance goes through a minimum around 22–25° and increases at higher  $\theta$ . It should be noted that the trend in absorbance is not identical to the trend in *EF* in Fig. 5b as *EF* is a ratio of two absorbances in presence and absence of the metal particles. Above 35°, the computed absorbance continues to increase gradually before reaching a peak around 50° and proceeds to decrease afterwards. This behaviour is not observed in the experiments where the absorbance begins to decrease above 35° and proceeds to decrease further with increase in  $\theta$ . The deviations at high angles could be due to multiple reflections or the lens effect from the hemispherical crystal used in the experiments.

As reported in section 3.2, absorbance in s-polarisation shows no angle dependence, neither in experiment, nor in computations.

#### 3.4 Comparison with literature reports

Previous reports on the angle dependence of ATR-SEIRAS have analysed metal films prepared by gas-phase deposition. <sup>1,12,22,23</sup> Films with a effective layer thickness above few nm show a maximum in absorbance at high angles of incidence, as opposed to the observation here for deposited colloidal particles. On the other hand, at low effective layer thickness, a behaviour similar to the behaviour reported here is observed, especially the maximum in absorbance around the critical angle, which coincides with the maximum average electric field over the metal/organic composite film. <sup>1,12</sup> At low effective thickness, the morphology of the resulting films is expected to be more islands–like, hence resembling the colloidal particles investigated here. <sup>45</sup> Films with larger effective

thickness show reflectivity curves which more closely resemble the curves obtained for stratified media including a homogeneous metal layer, which is why the optical properties, including the absorbance of organic species on such structures, are more film–like.<sup>1</sup>

One important difference between the colloidal particle films as studied here and gas-phase deposited films is the likely absence of the high-field region between particle and incidence medium, as the morphologies for gas-phase deposited films resemble hemispheres. To the knowledge of the authors, there is no report in the literature about hollow structure obtained from gas-phase deposition.

### 4 Summary and Conclusions

In previous work,<sup>21</sup> two different regions were identified, where high fields dominate contributions to SEIRA spectra: regions of high fields between particle and substrate, and regions of high field between neighbouring particles. The results presented here show two different trends in the effect of incidence angle on surface enhancement from the two high field regions. In addition, around  $\theta_{cr}$  as a third region, the part of a particle pointing away from the surface into the exit medium can be probed with high sensitivity.

Isolated particles show the largest enhancement around  $\theta_{cr}$  both in experiment as well as in computations. At  $\theta_{cr}$ , the field pattern around the particles has its maxima in the region between particle and incidence medium and on top of the particle. The relatively strong field between particle and incidence medium is making optimum use of the gap region between metal and incidence medium. The high field region between particle and substrate is therefore set to dominate the spectrum at incidence angles near  $\theta_{cr}$ . With increasing incidence angle, this maximum in electric field moves out of the region between particle and surface into a region parallel to the interface, where it can be enhanced by the presence of second nanostructure in the vicinity of the first.

This high field region between two particles in the vicinity of each other is, on the other hand best used at higher angles of incidence, as the field pattern around the particles in these cases show a minimum on the particle top, while they show maxima "parallel" to the interface. These maxima are enhanced by the presence of a second particle in the vicinity. The high field region in the gaps between particles is therefore likely to dominate the spectrum at larger angles of incidence. In almost all experimental studies reported in the literature, angles of incidence are used which favour this second mechanism.

Angle dependence is a phenomenon of spectra in ppolarisation only, as in general enhancement is predominantly found in p-polarisation.

The results here show that by varying  $\theta$ , in p-polarisation

different regions of the nanostructures at the interface contribute to the spectra, and some regions can be selectively excluded. For practical use of this property of the experiment, the overall morphology of a surface must be known. Spectra in s-polarisation are more promising for quantification, as they depend less on different surface parameters. However, these spectra barely show any surface enhancement at all, and some surface regions never contribute to the spectrum at any  $\theta$ .

An interesting consequence of this work is that experiments, in which the material in contact with the "free" solution is to be probed, *e.g.* when studying adsorption of complex molecules, should best be conducted near the critical angle of total reflection. Otherwise, the region in between the particles is predominantly probed.

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# **Graphical Abstract**



The finite element method is used to simulate the effect of incidence angle in surface-enhanced ATR-IR spectra.