Optical resonances of gold nanoparticles on a gold surface: quantitative correlation of geometry and resonance wavelength

A Rueda, M Stemmler, R Bauer, K Müllen, Y Fogel and M Kreiter

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany
E-mail: kreiter@mpip-mainz.mpg.de

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Abstract. The optical resonance of gold nanoparticles placed at nanometre distances from a gold surface by means of a dielectric spacer was investigated. Different types of molecules, 2-aminoethanethiol and shape-persistent polyphenylene dendrimers were used as spacers and compared. Furthermore, the gold nanoparticle size and the ambient medium were varied. The influence of all these parameters on the resonance wavelength of the system was determined. Based on a simple analytical model, a quantitative analysis was developed and surprisingly good agreement of this model with our experiment without any adjustable parameters was found.

1 Author to whom any correspondence should be addressed.
1. Introduction

Metal nanoparticles placed next to a metal surface exhibit unique optical properties. Analytical calculations of the optical response of this system in the sub-wavelength, quasi-static regime \[1\]–\[4\] show that for nanometre distances between the sphere and the plane the interaction cannot be regarded as a dipole on a mirror problem. At such small distances higher multipole orders have to be taken into account and the system becomes resonant with the incoming field at wavelengths which are highly red-shifted with respect to the resonance of the isolated sphere. In resonance, the incoming field is greatly enhanced in the gap between the sphere and the plane, an effect that led to the term ‘gap resonances’ \[3\]. A complementary approach to explain the sphere-on-plane interaction was recently developed by Nordlander and Prodan \[5\] and Prodan et al \[6\]. They described the gap resonance as a hybridized mode due to the interacting resonance of the sphere and the continuum of surface excitations on the plane metal surface, in close analogy to the hybridization of atomic orbitals in molecules.

The key feature ascribed to sphere-on-plane systems is a very large electromagnetic field localized in a volume of a few cubic nanometres. This localized electromagnetic field plays an important role in many physical effects involving emission and collection of light, for example light emission from scanning tunneling microscopes (STM) \[7\], scanning near field optical microscopy (SNOM) \[8\] and surface enhanced raman scattering (SERS) \[9\]. Furthermore it can be used in biosensing and chemical sensing \[10\]–\[12\] or as an optical tweezer \[13\].

Estimates of the field enhancement are based on quasi-static calculations of the fields in an ideal geometry. The nanoparticle is modeled as a sphere surrounded by a homogeneous...
medium on a perfectly flat plane (ambient-colloid (AC) model, see figure 1(a)). The resonator is described by the sphere radius \( R \) and the spacer thickness \( d_{sp} \). Furthermore, the dielectric functions \( \varepsilon_{sm} \) for the surrounding medium, and \( \varepsilon_{Au} \) for the metal (gold) constituting the plane and the sphere must be specified. Experimentally, a spacer layer is needed to suspend the nanoparticle on top of the plane ideally leading to the geometry shown in figure 1(b) (ambient-spacer-colloid (ASpC) model). Now, the dielectric constant of the spacer layer \( \varepsilon_{sp} \) must be specified in addition. Realistic experimental systems though, may vary significantly from the ideal geometry. Figure 1(c) shows a sketch to scale of how a realistic system could look like. The gold surface is not flat but owns considerable roughness. Here, the gold surface topography was taken from an atomic force micrograph of a typical evaporated gold surface [14]. The spacer layer is sketched as an assembly of particles with a diameter of 3 nm. Gold nanoparticles generally resemble rather polyhedra than spheres and many different shapes are possible. Here, we sketch an icosahedron according to Buffat et al [15] with an approximate diameter of 60 nm. We note that in such a realistic geometry significant deviations of the entire geometry and in particular of the contact area from the ideal case occur. These deviations should affect the optical response. Calculations of rectangular particles on planes show that simultaneously increasing contact areas and gap distances may leave the resonance wavelength unchanged [16] and may yield identical values to a sphere-on-plane system. A further assumption in the ideal model is the description of the metal in terms of a bulk dielectric function. On the length scales under consideration, which are typically in the range from 5Å to 30Å, nonlocal effects and surface states are expected to play a role leading to a deviation of the dielectric function of the metal from the bulk values. A quantitative understanding of the influence of these factors on the field enhancement calculations is therefore important if their magnitude is to be taken as realistic. A direct measurement of the field enhancement is not possible but the signature of the sphere-on-plane resonance in the far field response of the system can be studied and promises some insight on the electromagnetic effects taking place on these very small length scales.

Experiments to systematically investigate the dependence of the gap resonances on the resonator geometry were done using different types of systems. Kume et al [17]–[19] investigated silver particles embedded in a SiO\(_2\) matrix, deposited on an aluminum substrate. Later, organic spacer layers between the sphere and the plane were used to design better defined geometries [10, 11], [20]–[22]. The standard way to study the optical answer of the sphere-on-plane systems is absorption spectroscopy [21, 22]. Okamoto et al managed to show clearly the gap resonances in the extinction spectrum and investigated the effect of the sphere diameter on the resonance wavelength. Tsuboi et al [22] investigated also sphere-on-plane systems using different kinds of organic spacers. Le et al [23] investigated the influence of the finite thickness of the supporting gold layer.

Figure 1. (a) Model used for analytical calculations. (b) Idealized sample architecture. (c) Schematic of a realistic sample architecture.
The experiments were described [21, 22] by the simple analytical AC model although the experiments used a high-refractive index spacer which ideally would correspond to the ASpC model. The key problem in the analysis is the ambiguity in the choice of the gap distance and the surrounding dielectric function for the calculations. It was found that, assuming $\varepsilon_{\text{sm}} = 1$, the gap distances required to model the experiments were much smaller than the gap size expected for the spacer molecules used. It remains unclear whether this discrepancy was due to the mathematical simplification by using the AC model instead of the ASpC model, or due to the imperfect geometry (compare figure 1(c)). We note that, for example, larger contact areas due to the polyhedral nanoparticles and the rough plane are expected in a realistic geometry which would give a similar far-field response but considerably less field enhancements in the gap. Therefore, true quantitative experiments are important to resolve the ambiguity in the choice of the gap distance and gap dielectric function and obtain a realistic picture of the system.

In this paper, we lay a solid experimental basis for a quantitative analysis of sphere-on-plane systems by variation of three central parameters. Firstly, to investigate the influence of the spacer on the gap resonances, sphere-on-plane systems were fabricated using three different kinds of spacers. In addition to the commonly used alkanethiols, polyphenylene dendrimers were used as a versatile class of spacer molecules. Secondly, for each spacer, different systems with gold nanoparticle radii in the range between 11 nm and 80 nm were fabricated. Thirdly, the optical properties of the systems were investigated in surrounding media with different refractive indices, namely air, water and heptane.

Based on these experiments, we develop a way to interpret systems with spacer layers (ASpC-systems) using the analytical AC model which treats homogeneous environments (figure 1(a)), avoiding sophisticated numerical calculations. Together with surface plasmon spectroscopy, we resolve the ambiguity in the determination of the system geometry and, to our own surprise, find no strong evidence of geometrical and material imperfections as suggested in figure 1(c).

2. Experimental

A schematic representation of the sample architecture is shown in figure 2(a). Firstly, a thin ($\sim 2$ nm) chromium layer was deposited onto a BK7 (Menzel–Gläser, for the measurements in air) or a LaSFN9 (Hellma Optik, for the measurements in liquid) objective slide by thermal evaporation (Edwards FL 400), it serves as adhesion promoter. Subsequently, a gold layer (approximately 50 nm thick) was evaporated. One of these samples was kept as ‘Au’ reference. To create the small gaps needed to separate the gold colloids from the gold plane three different molecules were used: 2-aminoethanethiol (AET, cysteamine hydrochloride HPLC grade, Fischer Scientific) and two types of functional polyphenylene dendrimers (PPDs) PDIG$_2$ and TdG$_2$ shown in figure 3(a). To create the spacer layer, the slides were submerged in a solution containing the spacer molecule. One of these samples was kept as ‘Au+ spacer’ for later reference measurements. For 2-aminoethanethiol the submersion time was 16 h in a 1 mM solution in ethanol (HPLC grade, Fischer Scientific). The slides were then rinsed in ultra clean water (Milli-Q Gradient A10) and dried with an air gun. For TdG$_2$ and PDIG$_2$ the submersion time was 10 to 15 min in a 2 $\mu$M solution of the dendrimer molecule in tetrahydrofuran (HPLC grade, Sigma Aldrich). The slides were then rinsed in tetrahydrofuran and dried with an air gun.
Gold nanoparticle sols were prepared using the citrate reduction method \cite{24, 25}. In a 250 ml two-neck round-bottom flask, 100 ml of a 0.25 mM solution of HAuCl$_4$·3H$_2$O (Sigma Aldrich) was heated to reflux, and 2 ml of a solution of trisodium citrate (Sigma Aldrich) in water was injected quickly. For 20 nm, 40 nm, 60 nm and 150 nm diameter nanoparticles a concentration of 0.090 M, 0.026 M, 0.015 M and 0.010 M trisodium citrate solution was used respectively. Two different methods was used to attach the nanoparticles to the spacer. In the first method, the slide was submerged in the suspension. The submersion time depends on the spacer used. For AET 3–6 h was used. For TdG$_2$ and PDIG$_2$ the submersion time needed was 5–7 days. This is due to the hydrophobic nature of the surface after addition of the dendrimer molecule. The slides were then rinsed in water and dried with an air gun. Because of the long submersion time needed, an alternative method was used to attach the gold nanoparticles to the dendrimer spacer.

The slide was submerged in the gold nanoparticle sol. A potential was applied for 15 min between the gold surface and the gold nanoparticle sol to promote the attachment of the negatively charged gold nanoparticles. By varying the potential in the range between 0.1 V and 0.7 V different nanoparticle concentrations on the surface could be achieved. SEM images of the samples were taken with a commercial low voltage, high resolution SEM (1530 Gemini Leo).

The specular reflectivity of the samples was measured in a home-made surface plasmon spectrometer in Kretschmann configuration \cite{26, 27} shown schematically in figure 2(b). A halogen lamp and a monochromator (Chromex 250SM scanning monochromator) served as a tunable light source. The beam divergence was controlled by two aperture holes. The beam had a divergence of 0.24° and a diameter of 6 mm at the sample position. The incident light was transverse-magnetically polarized as required for surface plasmon excitation. The reflected light was detected with a photomultiplier (Hamamatsu H6240-01) in photon counting mode. For each wavelength an angular scan was taken.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Schematic representation of the sample architecture. (b) Schematic representation of the experimental setup.}
\end{figure}
Figure 3. (a) Three different molecules used as spacers: 2-aminoethanethiol (AET), PDIG$_2$ and TdG$_2$. (b) SEM of selected samples.

To change the surrounding medium a teflon fluid cell was integrated in the sample holder. Through the cell’s aperture holes liquids can be injected and extracted without changing the spot measured. The reflectivity of the samples was measured first in air, then in ultra clean water (Milli-Q Gradient A10) and then in heptane (n-heptane 99% p.a. WTL Laborbedarf GmBH).

3. Experiment: variation of the sphere-on-plane resonator parameters

3.1. Variation of the spacer

3.1.1. Spacer molecules. To create the small gaps needed to separate the gold colloids from the gold plane three small organic molecules were used. Theoretically, the gaps need to be of the order of 1 nm to 3 nm for the gap resonances to arise (see section 4.1). The alkanethiol

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2-aminoethanethiol (AET) (cysteamine hydrochloride HPLC grade, Fischer Scientific, compare figure 3(a)) was chosen because of its small size (less than 1 nm) and simple chemistry. Hereby the thiol group binds to the gold surface and the positively charged amino group to the gold nanoparticles. 2-Aminoethanethiol has been used previously for the assembly of sphere-on-plane systems [20]–[22] and as such the experimental procedures are well established.

A more versatile type of molecules in the above context, are dendrimers decorated with peripheral functional groups with high gold affinity. This class of molecules has a hyperbranched, more or less spherical structure allowing to induce multiple binding sites into the system. A special case among these hyperbranched molecules are polyphenylene dendrimers [28]–[36]. The molecular structure of these materials, consisting exclusively of phenyl–phenyl linkages furnishes these molecules with an outstanding rigidity and as such shape persistency [37]. These spacer molecules can have distances up to 28 nm [38, 39]. Moreover their straightforward, modular synthesis permits the easy design and production of nanoparticles with complex functionality [40].

Two types of functional polyphenylene dendrimers were employed in the present study. The first one, which will be called dendrimer PDIG$_2$ (shown in figure 3(a)) was designed to fulfill two different experimental demands: on one side the 16 peripheral dithiolane groups establish the necessary affinity towards gold [41]. On the other hand, a fluorophore unit was embedded into the core of the dendrimer in form of a perylene diimide dye (PDI). As such using PDIG$_2$ the fluorophore can be placed exactly in the gap between the gold nanoparticles and the gold plane and can be used as a probe for near field enhancements in future applications. Here, as a first step in this direction, we focus on the possibility to employ it as spacer for sphere-on-plane systems. The other dendrimer used is a second generation dendrimer and will be called TdG$_2$ (shown in figure 3(a)). It is built upon a tetraphenyl methane core and decorated with 16 dithiolane units at the periphery. Whereas the synthesis of TdG$_2$ is already documented in the literature [28] and was employed for the built-up of sensor arrays [33, 42] in the case of PDIG$_2$ a new synthetic protocol had to be followed which is given in the appendix.

3.1.2. Estimations of the gap thickness from the molecular structure. One can estimate an approximate value for the spacer thickness $d_{sp}$ by calculating the length of the molecule. Nevertheless, the spacer layer thickness is not necessarily given by this length. The actual arrangement of the spacer molecule when adsorbing to form a layer is generally not known and the configuration can change when the gold nanoparticle is bound.

For AET Barkowski and Hedberg [43] determined the length of the conformers in gaseous 2-aminoethanethiol by means of electron diffraction. Michota et al [44] found that when adsorbed to a gold surface two conformations are possible. In one conformation called the trans conformer only the thiol group binds to the surface, in the other conformation, called the gauche conformer, the thiol and the amino group bind to the surface. If the amino group binds to the surface, it is not free to bind to the gold nanoparticle which means that locally, for a sphere-on-plane resonator, only the length of the trans conformer is playing a role. The length lies in the range of 0.6 nm to 0.7 nm. In the case of TdG$_2$, a distance of 3.2 nm between the endgroups of any two straight all-para branches was determined by molecular modeling [45] resulting in a vertical distance of 2.6 nm. A diameter of approximately 3.8 nm was determined by light scattering experiments and atomic force microscopy methods [31]. In the case of PDIG$_2$ there are to our knowledge no molecular modeling calculations. A size similar to TdG$_2$ can be anticipated since the four branches, which dominate the total size of the molecule, are identical.
3.1.3. Estimations of the gap thickness from surface plasmon spectroscopy. Surface plasmon spectroscopy is a way to determine the spacer layer thickness \( d_{sp} \) experimentally [46]. Importantly, thickness and dielectric function of a thin dielectric layer cannot be determined simultaneously [47] and thus one has to be determined independently to state the other. Figure 4 shows the values for \( d_{sp} \) obtained assuming different values for \( \varepsilon_{sp} \). The values shown are averages over several wavelengths measured. The error bars take into account the variations from sample to sample.

For AET these variations are small. For PDIG\(_2\) and TdG\(_2\) they constitute the major contribution to the error showing that in this case a thickness cannot be accurately determined. If the values obtained from the surface plasmon analysis for AET are compared with the estimated values based on the molecular structure \( d_{sp} \approx 0.6 \) nm, a value for \( \varepsilon_{sp} = 2.0 \pm 0.3 \) can be estimated. In the following, we will assume this value for all spacers. This assumption will be justified later.

3.2. Variation of the gold nanoparticle radius

The gold nanoparticle radius was tuned by changing the trisodium citrate concentration during the preparation. Gold nanoparticles with radii in the range from 11 nm to 80 nm were prepared yielding different sample architectures. Figure 3(b) shows scanning electron micrographs of different examples proving a good coverage of the gold surface predominantly by individual nanoparticles. Some nanoparticle aggregations are seen which are expected to have an optical response that is different from individual sphere-on-plane resonators due to mutual coupling. Since more than 80% of all particles are isolated, we expect the signal from aggregates to be dominated by the one from the individuals. These scanning electron micrograph images allow for a direct measurement of the gold nanoparticle radius \( R \) by determining the area \( A \) of the white objects from image processing and identification of this area with the one expected for the projection of a sphere; \( A = \pi R^2 \). A dispersion of about 5 nm for radii smaller than 75 nm and of about 10 nm for the bigger radii is found. The sample name convention used is: ‘spacer-radius’ where for spacer, the spacer name: AET, PDIG\(_2\) or TdG\(_2\) is used and the radius of the gold nanoparticles is given in nanometres.
3.2.1. Polarizability of the sphere-on-plane resonators with air as a surrounding medium. From the measured reflectivity a polarizability $\alpha$ per unit area $A$: $\alpha/A$ was extracted for each sample following a routine as described earlier [48]. Briefly, a fit of the reflectivity was made using a transfer-matrix algorithm [49]. The sample was modeled as a multilayer system assuming that the sphere-on-plane resonators form an effective layer for which the Clausius–Mossotti relationship [50] can be used. Figure 5 shows the real and imaginary part of the extracted complex polarizability for a representative selection of samples.

The extracted polarizability shows clear resonances which resemble the form of a Lorentz-type resonator [51]. The resonances are seen with all three different spacers. Furthermore, depending on the nanoparticle radius and spacer the position of the resonance can be tuned to shift to wavelengths longer than the resonance wavelength of the sphere ($\sim$ 510 nm). Figure 5(a) shows that for a 19 nm radius nanoparticle and the spacer TdG$_2$, the resonance is seen at around 600 nm. Changing the spacer to AET (figure 5 (b)) makes the resonance shift into the red to around 700 nm. Using very big nanoparticles like those shown in figure 5(c) with 80 nm
radius shifts the resonance further into the red to around 800 nm. Since the experimentally accessible wavelength range is restricted to $550 \text{ nm} < \lambda < 800 \text{ nm}$ [48], the resonance of the isolated sphere cannot be seen.

3.3. Variation of the surrounding medium

A great advantage of surface plasmon spectroscopy is the possibility to measure in liquids. Contrary to extinction experiments, where transmission through a highly absorbing gold film and through the liquid has to be measured, in surface plasmon spectroscopy no light has to propagate through the liquid. Therefore, the dielectric response of the surrounding medium can be varied experimentally by immersion in liquids.

Any changes in the system architecture such as solvent-induced swelling of the spacer introduce variations in the response of the sphere on plane resonators which are not alone due to the refractive index change due to the new surrounding medium. To experimentally exclude this systematic error, the optical response of the sample was measured in air once more after the measurements in air, water and heptane had been performed. The minimum position of the reflectivity dip was seen to return to the same place as measured before indicating that the sample did not irreversibly change its optical response.

Nevertheless, this does not exclude the possibility of reversible changes. To experimentally test this, besides water ($\varepsilon = 1.77$), a nonpolar solvent: heptane ($\varepsilon = 1.86$) was used. No significant difference was noticed when comparing the measurements in both solvents. It is not probable that these two chemically very different liquids affect the sphere-on-plane resonators on the molecular level in the same way. Thus, the observed shift can be interpreted in terms of the increase in refractive index of the surrounding medium.

From the measured reflectivity the polarizability per unit area $\alpha/A$ was extracted for each sample analogous to the measurements in air. The Clausius–Mossotti relationship was modified to account for a different surrounding medium:

$$\frac{\alpha}{A} = 3\varepsilon_0 \frac{\varepsilon_f/\varepsilon_{sm} - 1}{\varepsilon_f/\varepsilon_{sm} + 2} d_f$$

with $\varepsilon_0$ the permittivity of free space, $\varepsilon_f$ and $d_f$ the dielectric function and thickness of the effective film formed by the sphere-on-plane resonators and $\varepsilon_{sm}$ the dielectric function of the surrounding medium. $\varepsilon_{sm}$ is extracted by adjusting the position of the total reflection edge of the reference sample when measured in water or heptane, respectively. $\varepsilon_f$ and $d_f$ are extracted as explained in [48]. Figure 6 shows the real and imaginary parts of $\alpha/A$ for three samples in air (circles), water (triangles) and heptane (squares). The resonance in air for AET-23 is quite weak in $\text{Im}(\alpha/A)$ but it can be seen in $\text{Re}(\alpha/A)$. In all cases a red-shift of approximately 40 nm was measured. The redshift in heptane is slightly bigger due to its higher index of refraction. A small offset in the magnitude of the polarizability arises when comparing air with water and heptane. This may be due to slight changes in the optical response of the gold surface or the spacer layer when immersed in liquid. The offset in water or heptane is positive for AET-23 and TdG$_2$-23 and negative for PDIG$_2$-29.

3.4. Summary of results

Figure 7 shows the resonance wavelength $\lambda_{SOP}$, defined as the wavelength for which $\text{Im}(\alpha/A)$ reaches its maximum, as a function of $1/R$. $\lambda_{SOP}$ was extracted by estimating the approximate
Figure 6. Polarizability per unit area $\alpha / A$ for some of the samples investigated. (a) AET-23, (b) PDIG$_2$-29 and (c) TdG$_2$-23 with air (circles), water (triangles) and heptane (squares) as surrounding media.

Figure 7. Summary of the wavelength of resonance $\lambda_{SOP}$ as a function of $1/R$ for (a) AET, (b) PDIG$_2$ and (c) TdG$_2$.

position of the maximum from the calculated polarizability. In the case of PDIG$_2$-19 and TdG$_2$-19, two different samples prepared simultaneously were measured denoted as PDIG$_2$-19-1 and PDIG$_2$-19-2 in figure 7(b) and correspondingly for TdG$_2$-19 in figure 7(c). The samples PDIG$_2$-80 and PDIG$_2$-78 showed the same resonance wavelength and can therefore not be distinguished. For each individual spacer, i.e. a fixed gap distance, the bigger
the radius the longer the wavelength of resonance. For the samples AET-23, PDIG$_2$-29 and TdG$_2$-23 a red-shift of the resonance occurs when immersed in liquid.

4. Theory

4.1. The AC model

The dependence of $\lambda_{\text{SOP}}$ on $R$, $d_{sp}$, the dielectric function of the surrounding medium $\varepsilon_{\text{sm}}$ and $\varepsilon_{\text{Au}}$ can be treated analytically using the AC model (figure 1(a)). Different mathematical formalisms for this problem are known [1]–[4]. Apart from the choice of the coordinate system they are equivalent [21]. An analytical expression for the polarizability per resonator area $\alpha/A$ can be calculated provided that the entire system is significantly smaller than the wavelength of light. Furthermore, it is assumed that the bulk dielectric function of gold describes the dielectric response of the nanosphere and that the gold plane is semi-infinite. We chose the model of Wind et al [4] to calculate $\alpha/A$.

In the following, we discuss some properties of this model which are required for the description of our experiments. First, we note that in the static approximation, the sphere-on-plane system is scale invariant depending only on the gap/radius ratio [52]. Then, the normalized complex polarizability $\alpha$ is a function of three parameters: $\alpha(\varepsilon_{\text{sm}}, d_{sp}/R, \lambda)$. Figure 8 gives an overview of the functional dependence of $\alpha$ on these parameters. Figure 8(a) shows $\alpha$ as a function of $\lambda$ for $\varepsilon_{\text{sm}}=1.0$ and $d_{sp}/R=0.02$. The calculations were done using $\varepsilon_{\text{Au}}$ obtained from the interpolation of the data from Johnson and Christy [53]. Two resonances are seen at $\lambda=535$ nm and $\lambda=635$ nm, both resemble Lorentz-type resonators. In figure 8(b) the imaginary part of $\alpha$ is shown as a function of $\lambda$ keeping $\varepsilon_{\text{sm}}=1.0$ fixed and varying $d_{sp}/R$. For $d_{sp}/R=1$ only one resonance is observed at $\lambda=510$ nm. For this $d_{sp}/R$ ratio the sphere is far away from the plane and the resonance corresponds to that of the sphere alone. As the $d_{sp}/R$ ratio is decreased a second resonance appears, the gap resonance, which progressively shifts into the red. For $d_{sp}/R=0.01$ a third resonance exists at $\lambda=560$ nm due to higher order modes of the system [5, 6]. It should be noted that for the gap resonances to appear, $d_{sp}/R=0.1$ or smaller is needed. Figure 8(c) shows the influence of $\varepsilon_{\text{sm}}$ for a fixed $d_{sp}/R$ ratio. All resonances shift further into the red as $\varepsilon_{\text{sm}}$ is increased. The change in $\varepsilon_{\text{sm}}$ induces a greater shift in the gap resonances than for the resonance of the sphere alone.

From the calculations, the wavelength of maximum Im($\alpha$) can be extracted. This sphere-on-plane resonance wavelength is a function of two parameters $\lambda_{\text{AC}}(\varepsilon_{\text{sm}}, d_{sp}/R)$, shown in figure 8(d). In color, the lines of constant $\lambda_{\text{AC}}$ from $\lambda_{\text{AC}}=600$ nm to $\lambda_{\text{AC}}=1100$ nm in 100 nm steps are shown. Each value of $\lambda_{\text{AC}}$ can be achieved by a whole set of $(\varepsilon_{\text{sm}}, d_{sp}/R)$ combinations. The dependency of $\lambda_{\text{AC}}$ on $\varepsilon_{\text{sm}}$ is approximately linear (figure 8(e)) whereas the relationship between $\lambda_{\text{AC}}$ and $d_{sp}/R$ is nonlinear (figure 8(f)).

4.2. The ASpC model

To include the influence of the spacer on $\lambda_{\text{SOP}}$, we use the idealized ASpC model shown in figure 1(b). In the ASpC model $\lambda_{\text{ASpC}}=f(\varepsilon_{sp}, \varepsilon_{sm}, d_{sp}/R)$. Hence, for a full description of the ASpC system, the whole plane spanned by $(\varepsilon_{sp}, \varepsilon_{sm})$ is important. Although the AC model can only calculate $\varepsilon_{sp}=\varepsilon_{sm}$ it can be used to determine a range of possible values for $d_{sp}/R$ if the following assumption is made: for a fixed $d_{sp}/R$, the resonance wavelength $\lambda_{\text{ASpC}}$
Figure 8. (a) Complex polarizability $\alpha$ as function of the wavelength $\lambda$. (b) Influence of $d_{sp}/R$ on the imaginary part of $\alpha$. (c) Influence of $\varepsilon_{sm}$ on the imaginary part of $\alpha$. (d) $\lambda_{SOP}^{AC}$ as a function of $d_{sp}/R$ and $\varepsilon_{sm}$. (e) $\lambda_{SOP}^{AC}$ as a function of $\varepsilon_{sm}$. (f) $\lambda_{SOP}^{AC}$ as a function of $d_{sp}/R$.

increases monotonically when somewhere in the surrounding medium the dielectric function increases. This property can be shown rigorously for resonances in lossless structures [54] and is expected to be valid for the system under study. In particular, we can start increasing the dielectric function first in the gap area, i.e. only increase me $\varepsilon_{sp}$, until the spacer layer is formed and then continue increasing the dielectric function, now only in the surrounding medium, until the entire system is surrounded by spacer. This path in the $(\varepsilon_{sm}, \varepsilon_{sp})$ plane is sketched in figure 9(a). Only when $\varepsilon_{sm} = \varepsilon_{sp}$ (dotted line in figure 9(a)) we can use the AC model to calculate $d_{sp}/R$. Figure 9(b) sketches $\lambda_{SOP}^{ASpC}$ along this path. A monotonic increase of the resonance wavelength when either $\varepsilon_{sm}$ or $\varepsilon_{sp}$ is increased, directly leads to the inequality:

$\lambda_{SOP}^{AC}(\varepsilon_{sm}, d_{sp}/R) < \lambda_{SOP}^{ASpC}(\varepsilon_{sm}, \varepsilon_{sp}, d_{sp}/R) < \lambda_{SOP}^{AC}(\varepsilon_{sp}, d_{sp}/R)$. 

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Instead of using the AC model, the influence of the spacer could be taken into account by numerical calculations as it has been done for silver nanoparticle dimers [55] and for rectangular nanoparticles on a plane [56]. However, firstly: it is not trivial to calculate this system numerically due to problems encountered when discretizing the small gap. Secondly, the central experimental problem: the ambiguity in the determination of the spacer thickness and its refractive index remains also when comparing with full numerical models.

5. Quantitative analysis: determining a gap thickness interval

In the following, the measured values of $\lambda_{SOP}$ for the samples AET-23, PDIG$_2$-29 and TdG$_2$-23 in the different surrounding media together with the calculated dependence of $\lambda_{SOP}$ on $d_{sp}/R$ and $\varepsilon_{sm}$ will be used to determine a gap thickness interval if a value for $\varepsilon_{sp}$ is assumed. We will use exemplarily $\varepsilon_{sp} = 2.00$ which is reasonable for non-close-packed organic molecules as estimated in section 3.1.3. However, this analysis works for any $\varepsilon_{sp}$ and gives comparable results for all reasonable choices $1.77 < \varepsilon_{sp} < 2.5$.

5.1. Interval analysis

Figure 10(a) shows the dependency of $\lambda_{SOP}^{AC}$ on $d_{sp}/R$ calculated for different values of $\varepsilon_{sm}$ (solid lines). Two values for $d_{sp}/R$ can be calculated for a fixed $\lambda_{SOP}$: those given by assuming the system is completely embedded in spacer $\varepsilon_{sm} = 2.00$ and those assuming that the system is totally surrounded by air ($\varepsilon_{sm} = 1$) or water ($\varepsilon_{sm} = 1.77$). In both cases, intervals of possible $d_{sp}/R$ are obtained which are indicated as black and blue solid lines for air and water, respectively. Given that the radius can be estimated, an interval for $d_{sp}$ is obtained. Figure 10(b) shows these intervals using air and water as surrounding media.
Figure 10. (a) $d_{sp}/R$ interval in water and in air determined by the measured $\lambda_{SOP}$. (b) Intervals for $d_{sp}$ calculated using the experiments in air, water and with the extrapolation approach (see section 5.2) assuming $\varepsilon_{sp} = 2.00$.

Due to the huge uncertainty of about 60%, the measurements in air do not provide very valuable information. The immersion experiments yield new values for $d_{sp}$, the limits being given now by the surrounding medium water and the spacer. The values fall into the range calculated before in air and the uncertainty is reduced.

5.2. $d_{sp}/R$ from extrapolation approach

Next, we introduce as a further assumption that the values measured for $\lambda_{SOP}$ in air, water and heptane can be linearly extrapolated to a certain value of $\varepsilon_{sm}$. For example, if we extrapolate to the value of the spacers’ dielectric response $\varepsilon_{sp}$, we arrive at a situation that can be modeled analytically. In this way, we replace a full analytical ASpC model by an empirical extrapolation. The linear extrapolation approach is justified by the fact that in the AC model the dependence of $\lambda_{SOP}$ is approximately linear. Calculations on more complex geometries yield similar linear dependencies [16]. Figure 11(a) shows the $\lambda_{SOP}$ obtained from the immersion experiments in air, water and heptane for the three different spacers. The shaded area delimitates the possible $\lambda_{SOP}$ when the values are linearly extrapolated. The $\lambda_{SOP}$ ($\varepsilon_{sm}$) extracted from the extrapolation determine a unique $d_{sp}/R$ value with an error which is due to experimental uncertainty in the measured $\lambda_{SOP}$ as illustrated exemplarily for TdG$_2$-23 in figure 11(b). The interval of possible $d_{sp}/R$ values for any $\varepsilon_{sp}$ is directly read from this graph. If again $\varepsilon_{sm} = 2.00$ is assumed, we obtain a better estimate for $d_{sp}/R$ which agrees with the earlier analysis (see figure 10(b)).

5.3. Scale invariant representation of the results

With these $(d_{sp}, \varepsilon_{sp})$ combinations, the measured $\lambda_{SOP}$ can be related with the gap/radius ratio of the sample. Figure 12 shows the results obtained using the values obtained in section 5.2.

Within the error, all resonances lie between the values predicted by the theory using either air or spacer as surrounding medium. They seem not to behave as if the system were completely embedded in the surrounding medium or in spacer but in a mixture of both environments with similar weight of $\varepsilon_{sp}$ and $\varepsilon_{sm}$. This result is reasonable, since much more surrounding medium than spacer is surrounding the sphere (compare figure 1(b)) but the field concentration in the gap

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Figure 11. (a) \( \lambda_{\text{SOP}} \) for \( \varepsilon_{\text{sm}} = 1 \) (air), \( \varepsilon_{\text{sm}} = 1.77 \) (water) and \( \varepsilon_{\text{sm}} = 1.86 \) (heptane). The shaded regions show the possible range for \( \lambda_{\text{SOP}} \) taking into account the error bars in the extrapolation. (b) The \( \lambda_{\text{SOP}} \) determined from (a) for TdG\(_2\)-23 is shown as a solid contour line which determines a \( d_{\text{sp}}/R(\varepsilon_{\text{sm}}) \). The dotted contour lines show the regions of uncertainty when determining \( d_{\text{sp}}/R(\varepsilon_{\text{sm}} = 2.00) \).

Figure 12. \( \lambda_{\text{SOP}} \) as a function of \( d_{\text{sp}}/R \). The calculations using the AC model for air and spacer as surrounding media are shown for comparison.

gives more weight to the dielectric response there. For small \( d_{\text{sp}}/R \) a tendency to a dominating \( \varepsilon_{\text{sp}} \) is observed but this could be due to the breaking of the quasi-static condition for the large nanoparticle radii. Only the values for PDIG\(_2\)-26 and PDIG\(_2\)-19-2 lie outside the trend line. In general the experimental results agree very well with the simple analytical model.
Figure 13. $d_{sp}$ as a function of $\varepsilon_{sp}$ for (a) AET-23, (b) PDIG$_2$-29 and (c) TdG$_2$-23 using surface plasmon spectroscopy (empty symbols) and using the extrapolated values for $\lambda_{SOP}$ from the immersion experiments and the theory of Wind et al (filled symbols). The solid lines connect the symbols as a guide to the eye.

Importantly, independent of the thickness of the three different spacers used the results can be described with this type of master curve. This indicates that at least down to the gap distances investigated here, no significant influence of corrections due to the very small length scales involved play a big role.

6. Resolving the ambiguity in $\varepsilon_{sp}/d_{sp}$

In section 5, we have described a way to determine a set of possible pairs ($d_{sp}$, $\varepsilon_{sp}$) for arbitrary $\varepsilon_{sp}$. Thus, if $d_{sp}/R$ is known $\varepsilon_{sp}$ is determined in a unique way and vice versa. Since neither of those quantities is determined from the sphere-on-plane resonance alone, an independent experiment is required to resolve this ambiguity. In surface plasmon spectroscopy a very similar situation is found and only a set of possible ($d_{sp}$, $\varepsilon_{sp}$) combinations but no unique values are obtained (compare section 3.1.3). The combination of the information from the two techniques though, resolves this ambiguity as shown in figure 13 for three samples. The pairs ($d_{sp}$, $\varepsilon_{sp}$) that agree with both experiments are readily determined as crossing points.

Due to the small errors in the determination of $d_{sp}$ for AET, a precise determination of $\varepsilon_{sp} = 1.9 \pm 0.1$ and $d_{sp} = (0.6 \pm 0.1)$ nm is possible. This determination without free parameters, but assuming a perfect ASpC system yields exactly the layer thickness as estimated from the molecular structure indicating no sign of an imperfect geometry as suggested in figure 1(c). Although this may be a coincidence, the agreement remains remarkable. For PDIG$_2$ and TdG$_2$ large errors in the surface plasmon spectroscopy experiments do not allow for a very precise conclusion but reasonable estimates for ($\varepsilon_{sp}$, $d_{sp}$) are obtained. For TdG$_2$ we find $\varepsilon_{sp} = 2.3 \pm 0.5$ and $d_{sp} = (2.0 \pm 0.5)$ nm. Again agreement with the size of the spacer molecule is found. For PDIG$_2$ we find $\varepsilon_{sp} = 2.0 \pm 0.3$ and $d_{sp} = (1.8 \pm 0.3)$ nm. The most probable thickness found for PDIG$_2$ is slightly smaller than expected from the molecular structure (around 2.6 nm). Taking into account the error in both the size estimate for the molecule and of the optical thickness determination, we consider this deviation to be still in agreement with our simple model. The results show that this alternative class of larger spacer molecules is well suited for further investigations on sphere-on-plane systems, in particular utilizing the option to combine a surface
functionalization which guarantees a strong affinity to noble metals with other functions. Apart from the chromophore in PDIG$_2$, specific binding sites for biomolecules or electrochemically active species could be envisaged, allowing for the study of luminescence enhancement, specific binding events and electrochemical processes in highly confined optical fields.

7. Conclusions

Sphere-on-plane resonators were fabricated using three different kinds of spacers. In particular, we succeeded in fabricating these systems using the polyphenylene dendrimers PDIG$_2$ and TdG$_2$ which possess different physical and chemical properties and allow for further functionalization making them a more versatile type of spacer than the commonly used alkanethiols. By combining the three different spacers and varying the nanoparticle radius the gap resonance wavelength could be tuned in the range between 550 nm and 850 nm. The dielectric response of the surrounding medium was varied by immersion in water and heptane. The influence of the dielectric function of spacer and surrounding medium on the resonance wavelength was found to be roughly equal in spite of the considerably smaller volume of the spacer. A spacer thickness interval was determined using an A$\text{Sp}$C system based on the analytical calculations of an AC system. In combination with surface plasmon spectroscopy the gap distance and spacer dielectric function could be determined without adjustable parameters. To our surprise the gap distance is in agreement with an estimate from the molecular structure. No evidence of geometrical imperfections or modifications to Maxwell’s equations for continuous media on the sub-nanometre scale is seen in our experiments. Further experiments should show if this remarkably good agreement with a simple theory applies as well to the local field enhancements and other measurable quantities or if it is pure coincidence.

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Appendix A. Synthesis of PDIG$_2$

The polyphenylene dendrimer PDIG$_2$ was synthesized as follows. The first step in which the first generation dendrimer (3) (see figure A.1) is synthetized was taken from [57].

The perylene diimide core (PDI) (1) was prepared according to [58, 59]. Starting from this fluorescent core the first generation dendrimer (3) bearing ethynyl groups was prepared by Diels–Alder addition of the cyclopentadienone (2) substituted with ethynyl groups deactivated by silyl substituents followed by deprotection [60]. For the building up of the second generation an eightfold Diels–Alder cycloaddition of the methoxy-functionalized tetraphenylcyclopentadienone (4) was done to obtain the dendrimer having 16 methoxy-groups at its periphery. The same solvents as for the formation of the first generation are employed. Subsequently these methoxy groups underwent a multiple ether cleavage reaction in the presence of an excess of PBr$_3$ leading to the sixteenfold hydroxyl-functionalized polyphenylene dendrimer (6). The latter was then used in a dicyclohexylcarbodiimide-coupling sequence together with
Figure A.1. Synthesis of the polyphenylene dendrimer 8 (PDIG$_2$) with a PDI core and 16 dithiolane units $R$ at the periphery.

Thioctic acid (5-[1,2]dithiolan-3-ylpentanoic acid) (7) leading to the final target molecule (8). All final compounds and intermediates resembled the characteristic properties of polyphenylene dendrimers and were unambiguously identified by routine analytical methods.

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