

Analyzing the Performance of Plasmonic Resonators for Dielectric Sensing

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The frequency shift of the plasmon resonances of metallic nanostructures upon changes in the surrounding bulk refractive index, coating with dielectric layers, and attachment of dielectric spheres is investigated. A general figure of merit (FOM) for the sensing capability of a given resonator is introduced and applied to those three situations. It is based on statistical analysis and an analytical expression for the resonance change. The latter is derived in a perturbation approach and yields a direct connection between the field localization and the resonator response. The scaling of this FOM with the size of the resonator and the analyte are discussed. We show that the optimal resonator strongly depends on the analyte under consideration. These concepts and their limitations are illustrated based on full numerical simulations of surface-supported crescent-shaped gold nanostructures.

Introduction

Optical sensors based on localized surface plasmon resonances of metal nanoparticles are promising candidates for pushing the limits of label free detection down to the ultimate limit of real time single molecule sensitivity. This sensing technique employs the resonant oscillations of the quasi-free electrons in metal particles which can be observed as characteristic peaks in their extinction and scattering spectra. The spectral position of these peaks is highly dependent on the dielectric properties of the resonators immediate surrounding, which may change upon binding of any analyte under study. Since the first use of metal colloids for the determination of affinity constants,¹ researchers are now able to measure the scattering spectra of single nanoparticles.^{2,3} Both monitoring of changes in the local surrounding bulk refractive index and detection of biomolecules has been demonstrated.^{4,5} The ultimate goal in terms of sensing with plasmonic resonators would be the label-free detection of the binding and unbinding of an individual biomolecule to an individual resonator.⁶ In order to further push the detection limit toward such single molecule sensitivity, a systematic optimization of material, size, and shape of the plasmonic resonator must be done. For this purpose, it is advantageous to use well-defined model analytes which mimic a biomolecule binding event. Then, different resonators can be benchmarked by comparing their response to this standard. Here, we derive a set of requirements which an ideal plasmonic resonator has to fulfill. We notice that during the review process of our work, a study of Nusz et al. was published which aims at the same question.⁷ Since we focus on different aspects of the problem, the two publications complement each other. Our results do not contradict their findings and vice versa.

The paper is organized as follows. First a figure of merit (FOM) is derived, based on a perturbative approach combined with a statistical analysis of the uncertainty in measuring the spectral resonance position. Three model analytes, namely the change of the surrounding bulk refractive index, a coating with a dielectric layer and attachment of a dielectric sphere are studied. Next, simple scaling laws for plasmonic resonators are

derived and their limits are discussed. Finally, these concepts are illustrated using crescent-shaped metal structures. This geometry is one of several shapes that have a high field localization^{8,9} and are therefore more sensitive to bulk refractive index changes than simple Mie spheres.¹⁰ They support multiple plasmonic resonances with different sensing volumes.¹¹

Definition of a FOM

We consider a plasmonic resonator with a resonance which is detected as a peak in some spectroscopic experimental setup. Upon attachment of an analyte this peak shifts in frequency by $\Delta\omega$. Then, a straightforward definition for the FOM is

$$\text{FOM} \propto \frac{\Delta\omega}{\Delta\omega_{\text{un}}} \quad (1)$$

where $\Delta\omega_{\text{un}}$ is the uncertainty of the determination of the resonance position.

Different Sources for Noise. The experimental uncertainty depends on various details of the measuring instrument and is limited by the noise. The achievable noise level is ultimately limited by the counting statistics of the spectral measurement but can also be limited by instrumental imperfections. In the following we therefore introduce the limiting cases “signal noise”, “instrument noise”, and “background noise”.

We first assume a signal error which is Poisson distributed and a signal noise which dominates the background noise. This represents the ideal situation of a perfectly stable experiment with the ultimate experimental accuracy which is only limited by photon statistics. The statistical analysis of this scenario, the “signal noise regime” (SN), is given by Bobroff¹² (eq 14a therein), arriving at an uncertainty of

$$\Delta\omega_{\text{un}} = \Delta\omega_{\text{SN}} = \frac{\Gamma}{\sqrt{S}} f \quad (2)$$

where Γ is the full width at half-maximum of the peak under consideration, S is the peak signal strength above background, and f is a function of the desired confidence level, the shape of

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the resonance peak, and several details of the experimental setup but is independent from the resonator. Typically $0.1 < f < 1$; for example, for a Gaussian line shape sampled with 100 points and a confidence level of 63%, $f = 0.25$. Then, at a signal-to-noise level of one, the uncertainty in the peak position is 0.25 its line width.

In the instrument noise regime imperfections in the instrumental setup dominate the error which is then independent from the light intensity. One may consider, for example, drifts in the optical alignment, in particular the focus position or in the spectrum of a light source. If these effects yield a much larger error than $\Delta\omega_{\text{SN}}$ in eq 2, the signal strength does not contribute to the uncertainties in fitting. No general equation exists for $\Delta\omega_{\text{un}}$ in that case and the most practical way to determine it is by experiment.

As a third case we consider the background noise regime, where an uncorrelated background noise σ_{B} is the main error source. In particular for very small resonators one quickly arrives at the situation where less photons from the object under investigation than from other sources are detected where in turn the statistics of the latter ones dominates the experimental error. Here, according to Bobroff¹² the uncertainty is

$$\Delta\omega_{\text{un}} = \Delta\omega_{\text{B}} = \frac{\Gamma}{S/B}f \quad (3)$$

In this background noise regime the signal-to-noise ratio S/B has to be maximized. We note that in eq 2 \sqrt{S} is the signal-to-noise ratio in the signal noise regime which indicates that in general the signal-to-noise ratio has to be maximized.

For the scattering spectroscopy considered here the signal strength S is proportional to the intensity of the illumination source I , the cross section σ at resonance, the cumulative transmittance T of the entire optical setup, the detector sensitivity P , and the measuring time t .

$$S = PTI\sigma t \quad (4)$$

Depending on the type of experiment, σ may represent either a scattering cross section σ_{s} or an extinction cross section σ_{ext} . In most cases measuring time as well as illumination intensity is limited so it is desirable to optimize the cross section of the resonator.

Frequency Shift. Next we have to find an analytical expression which connects the frequency change $\Delta\omega$ in eq 1 with the resonator properties. If an analyte with dielectric constant ϵ_{a} is attached to the resonator, it occupies a sensing volume V_{a} and changes the dielectric constant in this volume about $\Delta\epsilon = \epsilon_{\text{a}} - \epsilon_{\text{s}}$. Here ϵ_{s} is the dielectric constant of the surrounding. From perturbation theory (see Appendix A) the resulting response $\Delta\omega$ of a resonant mode with field \vec{E} can be approximated in the limit of weak dielectric contrast and small volume as

$$\Delta\omega = -\frac{\omega}{2} \frac{\Delta\epsilon \int_{V_{\text{a}}} |\vec{E}|^2 dV}{\int_{\text{nearfield}} \epsilon_{\text{eff}} |\vec{E}|^2 dV} \approx -\omega \frac{\Delta n}{n} \frac{\int_{V_{\text{a}}} \epsilon_{\text{s}} |\vec{E}|^2 dV}{\int_{\text{nearfield}} \epsilon_{\text{eff}} |\vec{E}|^2 dV} = -\omega \frac{\Delta n}{n} C \quad (5)$$

Here $\Delta\epsilon \approx \epsilon_{\text{s}} 2\Delta n/n$ is expressed in terms of the relative change in refractive index $\Delta n/n$ and assumed to be constant in the sensing volume. For practical reasons, the near field is considered as all field around the resonator with an field enhancement greater than two. This definition was chosen since it is easy to implement in simulations. ϵ_{eff} equals the dielectric constant ϵ for the bare resonator for nonabsorbing media. In lossy materials, that is, inside the metal, a modified expression must be used, compare Appendix A. It turns out that the exact definition of the near-field cutoff does not significantly influence the computational results. In this equation it can be seen that the sensitivity is a function of frequency ω and the confinement factor C which is a measure how strong the electrical field is localized to the sensing volume. Details of the validity of this equation are discussed in Appendix A. Here we just want to point out, that this equation is not strictly valid but follows from perturbation theory for nonlossy and non radiating resonators. Still it gives an intuitive insight in the interaction of the analyte with the resonator. A quantitative analysis is possible but requires a more complex mathematical treatment.

Expression for the FOM. Next, we combine the expressions for frequency shift and noise to arrive at an expression for the FOM. With eq 2, which applies for the signal noise (SN) regime, in combination with eqs 4 and 5, the FOM reads as

$$\text{FOM} \propto \frac{\Delta n}{n} \cdot \frac{\sqrt{PTI}t}{f} \cdot \frac{\omega C \sqrt{\sigma}}{\Gamma} \quad (6)$$

The first term in this equation can be attributed to the analyte, the second to the instrument used to investigate the resonator, and the last to the resonator itself. The FOM for particle optimization becomes

$$\text{FOM}^{\text{SN}} = \frac{\omega}{\Gamma} C \sqrt{\sigma} \quad (7)$$

This expression implies that the optimal resonator should have a small relative resonance line width Γ/ω , high field confinement to the analyte volume and a high scattering or extinction cross section. While intuition would have led to similar conclusions in terms of quantities that have to be maximized or minimized, we have a quantitative expression, allowing to judge the weight of different parameters. The relative change in refractive index ($\Delta n/n$) is excluded in the definition of the FOM since it is no property of the resonator. From eq 5 it can be seen that in the limit of weak dielectric contrast the peak displacement is a linear function of Δn .

In the instrument noise regime, the errors are independent of the illumination intensity and lead to random displacements of the whole spectrum. From another viewpoint this noise can be regarded as an effect which lowers the effective cross section of the resonator. Because this lowered effective cross section is now a property of the instrumental setup and not the resonator it drops out of eq 6. In this case the FOM becomes

$$\text{FOM}^{\text{IN}} = \frac{\omega}{\Gamma} C = \text{FOM}^{\text{SN}} \sigma^{-0.5} \quad (8)$$

And in the background noise regime we obtain, using now eq 3 for $\Delta\omega_{\text{un}}$ together with eqs 4 and 5

$$\text{FOM}^{\text{BN}} = \frac{\omega}{\Gamma} C \sigma = \text{FOM}^{\text{SN}} \sigma^{0.5} \quad (9)$$

The expressions for the different noise regimes differ only in their dependence on the cross-section σ , and for the further discussion is it convenient to use the general expression

$$\text{FOM} = \frac{\omega}{\Gamma} C \sigma^\alpha \quad (10)$$

where we have introduced the exponent α which equals 0, 0.5, and 1 for the instrument noise, signal noise and background noise, respectively.

Dependence on the Type of Analyte. Clearly, the field confinement C and therefore the FOM strongly depends on the geometry of the analyte that is to be investigated. In the next part we therefore investigate three experimental situations namely change in bulk refractive index, growth of a thin layer on the resonator and the change of refractive index in a spherical volume close to the resonator. Frequently immersion experiments are performed and thus the bulk refractive index of the surrounding is changed.^{6,13} In this case, the analyte volume V_a in eq 4 corresponds to all space accessible for the surrounding liquid. For this case, a $\text{FOM}_{\text{B,Lit}} = m/\Gamma$ is introduced in literature⁶ with the bulk sensitivity factor $m = d\omega/dn$, which, from eq 5, equals

$$\text{FOM}_{\text{B,Lit}} = \frac{\omega}{\Gamma} = \frac{\omega}{\Gamma} \frac{C}{n} \quad (11)$$

which, by comparison with eq 10 with $\alpha = 0$, is readily identified as the expression for changes in bulk refractive index in the instrument noise regime up to a constant prefactor n^{-1} . At this point, we want to stress that this frequently used FOM exclusively applies to this particular experimental situation while sensing refractive index changes other than bulk or other dominating error sources corresponding to different noise regimes have to be treated in a different way.

The second frequently encountered situation is the detection of a thin layer which adsorbs on the resonator surface. Here, one has to specify a fixed layer thickness d for which the FOM is evaluated. For very thin layers the field does not vary strongly along a path perpendicular to the resonator surface inside the layer and $\text{FOM}(d)$ becomes a linear function of d . In this regime one may alternatively state a FOM_L that is normalized by this value

$$\text{FOM}_L = \frac{\omega}{\Gamma} \frac{C}{d} \sigma^\alpha = \frac{\omega}{\Gamma} C_L \sigma^\alpha \quad (12)$$

effectively avoiding the choice of an arbitrary d by definition of $C_L = C/d$. This equation shows the importance of a field which is strongly confined to the surface. For this situation, we now want to discuss the connection between the FOM for layer and bulk sensing. It is based on the empirical expression for layer sensing^{6,11}

$$\Delta\omega = m\Delta n(1 - e^{-2d/l_d}) \quad (13)$$

with an effective decay length l_d which yields for very thin layers

$$\frac{\Delta\omega}{\Delta n} = \frac{2m}{l_d} d \quad (14)$$

A direct comparison to the established definition of the FOM⁶ is possible if we introduce a shift factor for layers, $m_L = 2m/l_d$, in analogy to m used for bulk. Then, we arrive for the instrument noise regime ($\alpha = 0$) at a FOM for layers which is formally equal to the established definition for bulk refractive index changes, FOM_B (eq 11) with m being replaced by m_L . This expression is identified with the FOM for layers proposed here (eq 12) up to a factor n^{-1} , if the instrument noise ($\alpha = 0$) is considered

$$\text{FOM}_{L,\text{Lit}} = \frac{m_L}{\Gamma} = \frac{\omega}{\Gamma} \frac{C}{d} \frac{1}{n} = \frac{1}{n} \text{FOM}_L^{\text{IN}} \quad (15)$$

We draw the important conclusion that for layer sensing a modified shift factor should be used that takes into account the typical decay length of the near field: Highly confined fields are advantageous. This intuitively clear modification implies that resonators which have been optimized for bulk refractive index sensing will in general not be the ideal choice for the sensing of thin layers and vice versa.

In order to define a FOM for single-object sensing, both shape and position of the analyte under study must be specified. The latter quantity can be eliminated if one assumes that the analyte is placed such that the FOM is maximized. Here, we focus on dielectric spheres with a fixed radius r as test objects with an easy geometry. Very similar to the situation for layers, for sufficiently small r $\text{FOM}(r)$ will become linear in r^3 as soon as the field is approximately constant over the sensing volume and we may define

$$\text{FOM}_S = \frac{\omega}{\Gamma} \frac{C}{r^3} \sigma^\alpha = \frac{\omega}{\Gamma} C_S \sigma^\alpha \quad (16)$$

It is now instructive to see how the quantities which constitute the FOM scale with the size of the metal resonator under consideration. First, no simple scaling can be given for the relative line width Γ/ω and a detailed analysis is required for each specific resonator. For some resonators, for example, spheres, the resonance line width is broadening for increasing resonator size but frequently the size-dependence of this quantity is moderate.

Experimentally, both a scattering cross section and an extinction cross section may be considered. This quantity strongly depends on resonator size. In the quasi-static limit they scale with r_{mp}^6 and r_{mp}^3 where r_{mp} is the linear dimension of the metal resonator. Already for small resonator sizes retardation effects lead to deviations from these simple laws. They generally decrease the cross section, but due to the simultaneous redshift of the resonance, the details depend on the precise functional dependence $\varepsilon(\lambda)$. Still the quasistatic approximation may be used as a rule of thumb to estimate trends.

The second quantity that varies strongly with resonator size is the confinement factor C . Here, different dependencies apply for the three sensing configurations under discussion. If we assume Γ/ω to be constant and the quasi-static values for the cross sections to be valid, we can derive some simple scaling laws for the FOM. The dependence of the FOM on resonator size is summarized in Table 1.

TABLE 1: Dependence of the FOM on Resonator Size for Different Dominating Sources of the Noise and Different Analyte Geometries^a

	bulk	layers	particles
instrument noise FOM $\propto \sigma^0 \propto r_{mp}^0(r_{mp}^0)$	FOM $\propto C_{bulk} \propto r_{mp}^0$	FOM $\propto C_{layer} \propto r_{mp}^{-1}$	FOM $\propto C_s \propto r_{mp}^{-3}$
signal noise FOM $\propto \sigma^{0.5} \propto r_{mp}^{1.5}(r_{mp}^3)$	r_{mp}^0	r_{mp}^{-1}	r_{mp}^{-3}
background noise FOM $\propto \sigma^1 \propto r_{mp}^3(r_{mp}^6)$	$r_{mp}^{1.5}(r_{mp}^3)$	$r_{mp}^{0.5}(r_{mp}^2)$	$r_{mp}^{-1.5}(r_{mp}^0)$
	$r_{mp}^3(r_{mp}^6)$	$r_{mp}^2(r_{mp}^5)$	$r_{mp}^0(r_{mp}^3)$

^a In each entry, absorption and extinction cross sections are considered, the latter are given in brackets.

We find for bulk refractive index measurements C is constant, and therefore, in the signal noise regime (eq 6), large resonators should be preferred for their large scattering and absorption cross sections. In the instrument noise regime, the FOM is only dependent on the relative line width. These results agree with earlier predictions that indicated that the relative sensitivity $\Delta\omega/\omega$ is constant for a given resonator shape.¹⁴

For very thin layers, C scales with r_{mp}^{-1} and thus increases with decreasing resonator size. In the instrument noise regime, small particles are advantageous since their confinement is increased and the cross section has no effect on the FOM. Though, including the scaling of the cross sections in the signal noise regime, FOM^{SN} scales with $r_{mp}^{0.5}$ and r_{mp}^2 for scattering and extinction experiments, suggesting that increasing resonator size is advantageous. The background noise regime favors large resonators even stronger. Remarkably, depending on the dominating source of noise, either increasing or decreasing particle size will improve the performance of the sensor. As a consequence, the true optimum will be found right at the resonator size where the transition between the instrument noise regime and the signal or background noise occurs. This can be understood as a change in the weight of the two different optimization goals, first maximize the frequency shift and second minimize the detection uncertainty. As long as the instrument noise dominates the primary goal is to increase the frequency shift which is determined by the confinement, while in the signal noise regime minimizing the detection uncertainty is more important.

If we finally consider attachment of a small dielectric sphere, the confinement scales with r_{mp}^{-3} . As a consequence small resonators are advantageous as well if the instrument noise dominates. For scattering the FOM^{SN} is independent of resonator size but in extinction experiments it scales with $r_{mp}^{-1.5}$ and small resonators may be advantageous in the signal noise regime. Again, background noise strongly favors large resonators. Similar to layer sensors, the optimum resonator will correspond to the transition between two different noise regimes.

We point out that this analysis did not yet take into account variations in resonator shape. For the sensing of very small analytes the field confinement to the analyte volume is important, and the main effort should be to develop metal particles which support resonances with large cross sections together with fields confined to small volumes. Additionally maximizing the field confinement could also lead to a smaller line width, because the fraction of the field inside the absorbing metal is minimized. For a full optimization, size-induced variations in Γ/ω as well as deviations from these simple scaling laws must be included.

Numerical Calculations

Bare Resonator. In the following, we will present numerical calculations of the response of crescent shaped metal particles as one example for a plasmonic resonator to illustrate the concepts discussed before. These calculations serve as a basis to evaluate the approximate expression for the resonance shift

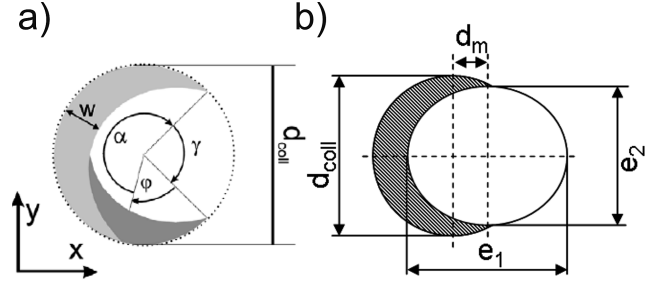


Figure 1. (a) Sketch of the geometry of the crescent fabricable by nanosphere lithography on a glass support. (b) Construction of the crescent in the simulation.

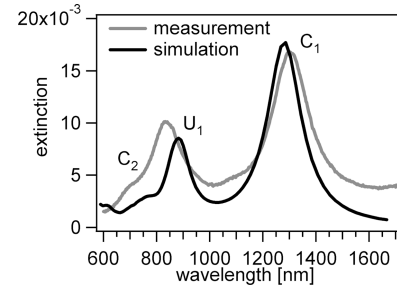


Figure 2. Extinction of a layer of crescents.

upon attachment of an analyte given by eq 5. Although the most straightforward examples would be a simple sphere we choose this particular geometry because previous experiments have shown already that the sensing capabilities of this geometry are superior.^{10,11} Also we limited our discussion to the simplest case of a crescent shaped resonator to keep it in limits.

Figure 1 shows a sketch of such a resonator as it can be experimentally realized by colloidal lithography.⁸ For an ideal process its 3-dimensional shape is described in a unique way by four parameters: The evaporation angle Θ determines the width w while the diameter d_{coll} is determined by the size of the colloids used as a mask. Furthermore, the thickness t of the structure in the z -direction is determined by the amount of evaporated metal and, for double evaporation, additionally the turning angle φ can be adjusted to tune the opening γ .

For the simulations the particle shape was approximated by a circle which is cut by an ellipse (Figure 1b). The parameters to describe this geometry were obtained by a fit to scanning electron micrographs of fabricated crescents. This representation of the geometry avoids hard edges along the inner perimeter of the crescent and is described by a simple equation which facilitates the setup of the simulation. Vertical sidewalls are assumed in the present model. This simple shape reproduces well the behavior of real structures, while calculations of even more realistic shapes show only minute differences.¹⁵

The observed resonances are named according to their polarization as “C” or “U” resonances. A “C” resonance corresponds to an excitation E-field polarization parallel to the y -axis of Figure 1 while a “U” resonance is excited with polarization parallel to the x -axis. The resonances are named in

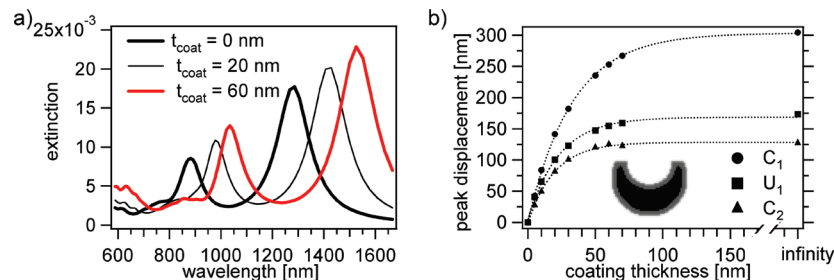


Figure 3. (a) Calculated extinction spectra for 3 representative t_{coat} . (b) shift of the resonance peaks when covered by a thin layer of a dielectric with $n = 1.5$ with varying the coating thickness. The lines are fitted exponential functions. The inset shows a cut through a coated crescent (gray = coating with $n = 1.5$).

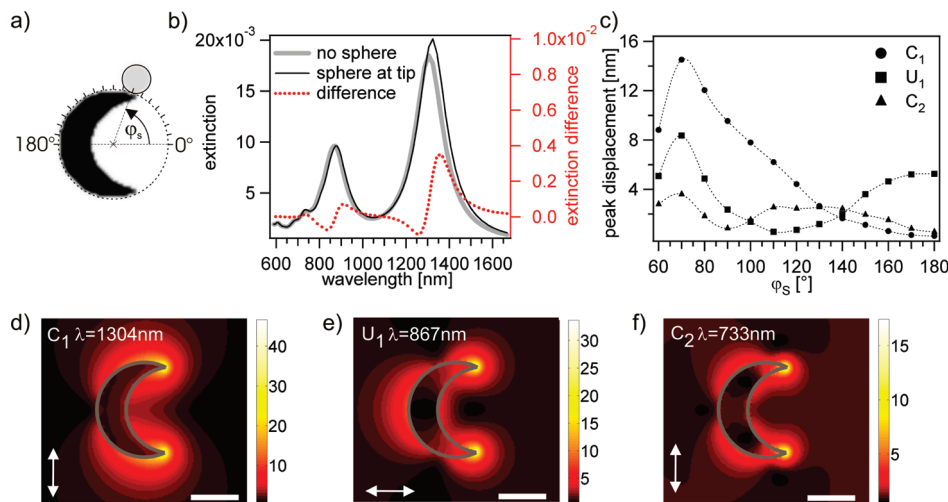


Figure 4. (a) Geometry of the crescent with attached colloid and (b) extinction spectra with and without colloid ($\varphi_s = 70^\circ$). (c) Response of the crescent as a function of sphere position. (d–f) Field enhancements ($|E|/|E_{\text{incident}}|$) for the resonance peaks at a cut through the middle of the crescent thickness ($z = 20$ nm). The scale bar is 100 nm. Note that the color scale is not the standard “yellow hot” scale but logarithmically scaled.

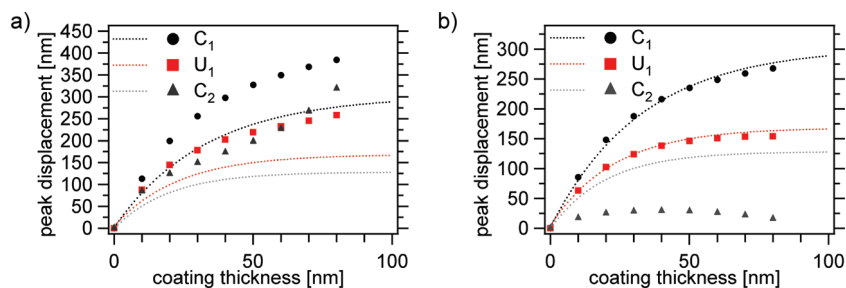


Figure 5. Peak displacement as a function of coating thickness calculated by perturbation theory (a) quasistatic (eq 5) and (b) theory of Lai. The dashed lines correspond to the exponential fit to the shifts calculated with FDTD.

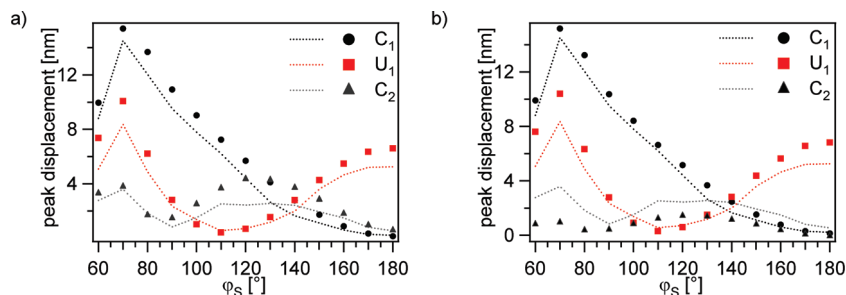


Figure 6. Peak displacement for attachment of a colloid by perturbation theory (a) quasistatic (eq 5) and (b) theory of Lai. The dashed lines correspond to the values calculated with FDTD.

ascending order starting at C_1 or U_1 for the resonance with the longest wavelength.⁸ Numerical simulations were performed using the finite difference time domain method as explained in detail in Appendix B.

The particles considered here have the fabrication parameters $\varphi = 0^\circ$, $\Theta = 30^\circ$, $t = 40$ nm, $d_{\text{coll}} = 205$ nm. These parameters are used throughout the following discussion. From the calculated extinction cross section, a Vis–NIR absorption measure-

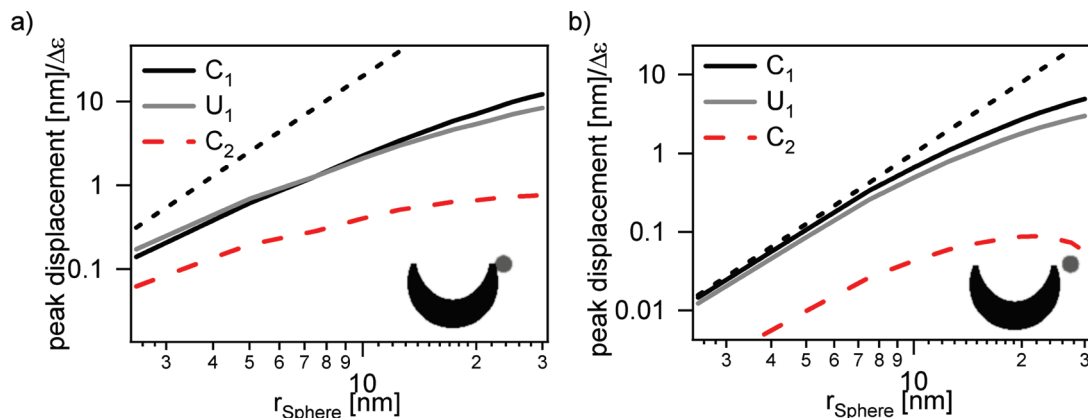


Figure 7. Peak displacement as a function of sphere radius. (a) At the position of highest field ($\varphi_s = 70^\circ$ attached to the tip) and (b) in a more uniform field ($\varphi_s = 70^\circ$ 12 nm away from tip), the dashed black lines correspond to a cubic polynomial. The insets show the position of the sphere. The displacement is normalized to the dielectric contrast and applies to all possible combinations of analyte and surrounding.

ment can be modeled and compared to measured spectra up to a constant prefactor which is given by the surface coverage. The latter was extracted from SEM micrographs and found to be around 1%. The comparison is shown in Figure 2 and is quite good. We take this as a proof that our simulation accurately describes the response of real gold nanocrescents for longer wavelengths. Below 800 nm where the C_2 resonance occurs, deviations are seen which are due to several problems:

First, the dielectric function of gold is not accurately described by a Drude–Lorentz model at smaller wavelength, as discussed below, so the dielectric function of the gold in the simulation deviates from the experiment. Second, the regular discretization which leads to a staircasing approximation of the curved interfaces of the particle affects the smaller wavelengths stronger at a given spatial discretization. Third, a nonperfect absorbing boundary leads to small computational errors around 800 nm due to resonances in the fictitious box used for the simulation. In particular the weak C_2 resonance is sensitive to these errors. Beside this there is also inhomogeneous broadening due to the size distribution of resonators in the experiment making the experimentally observed resonances slightly broader than the simulated ones. Also at 1100 nm a small peak can be seen in the experimental spectra but not in the simulated ones. This peak comes from aggregates which form during the fabrication process and was discussed earlier.⁸

Response to Attached Layers. Next, we turn our attention to the attachment of thin dielectric layers. All further discussion is done for air as the surrounding medium, but could be easily extended to other surroundings. Layers are experimentally easy to achieve and for the sample under study, experimental data is available.¹¹ In this simulation the response of the crescent to an applied thin dielectric coating with thickness t_{coat} and refractive index $n = 1.5$ was studied. The coating is defined by all space that has a smaller distance to the crescent than the coating thickness and is not part of the supporting substrate (see inset in Figure 3b). The results are shown in Figure 3. The attachment of a thin nonabsorbing layer results in a clear red shift of the observed peaks in the spectrum. Lower order peaks shift more than higher order peaks which leads to better separation of C_2 from U_1 . A general increase of the extinction at lower wavelengths is also observed. Figure 3b) summarizes the shifts from several calculations like Figure 3a) for varying t_{coat} . For a layer thickness below 20 nm, the peak shift is approximately linear in t_{coat} , for thicker dielectric coatings the shift saturates.

An effective penetration depth of the electric field may be obtained from fitting of the peak displacement curves to an

TABLE 2: Comparison of Simulated and Experimental Decay Constants

	C_1 (nm)	U_1 (nm)	C_2 (nm)
simulation	33	23	19
experiment	29.1	21	10

exponential function (eq 13). The result is shown in Table 2. Except for the C_2 peak we find perfect agreement between the theory and experiment.¹¹ Although very high field gradients exist at the tips, the overall response is well modeled by an exponential decay.

Response to Attached Colloids. If single-molecule sensing is to be pursued, one has to consider the response to the attachment of individual objects rather than coating with films or changes in the overall dielectric surrounding. We chose a sphere diameter of 60 nm and a refractive index of $n = 1.5$ which is small compared to the resonator dimensions but still large compared to molecules. This size is suited for benchmarking because it is large enough to yield a measurable response and is easy to manipulate in experiment. An experiment done like this and showing the local response of the crescents was published separately.¹⁵ For the simulation, the sphere was placed on the substrate and touching the crescent. Because the diameter of the sphere is bigger than the height of the crescent the center of the sphere is displaced 10 nm relative to a plane through the middle of the crescent. The spectral response was calculated as a function of its position along the outer perimeter described by the angle φ_s , compare Figure 4a. To keep the discussion simple, other possible attachment positions like the inner side or the top of the crescent are not discussed. Slight variations of the analyte position do not have a large effect as long as the binding occurs next to the tip as was investigated recently in more detail.¹⁵ Figure 4b shows a typical spectrum of the crescent with and without a sphere directly attached to the tip. A small red shift can be observed which is best represented in the difference spectrum. Figure 4c shows this shift as a function of φ_s . Two effects can be observed. First the shift is strongest directly at the tip, which was expected because the highest field enhancement occurs there. Second the shift shows a different dependence on the position of the sphere for each resonance. The physical reason for this effect is directly obvious when comparing this shift with the near field distributions of the three resonances under study which are shown in Figure 4d–f. The shift magnitude corresponds to the field strength at the analyte position and in particular no shift is seen if particles are placed in field minima of a certain resonance.

Thus multipolar resonances reveal information of the position where a particle is bound. Binding at $\varphi_s = 110^\circ$ for example leads only to shifts of the C_1 and C_2 resonances while the U_1 resonance is unaffected because the field is very low at that position. Similar effects are seen at all positions allowing in principle for a localization of the binding event.

Calculations Based on Perturbation Theory in Comparison to Exact Calculations

Next, we want to demonstrate that the semianalytical equation that relates field distribution and resonance shift (eq 4) is appropriate for the description of the crescents optical response to the attachment of a dielectric sphere and a layer.

Response to Attached Layers. In Figure 5a the result of a perturbative calculation for the growth of a layer in comparison to the full numerical analysis is shown. Only qualitative agreement can be seen. In general eq 5 overestimates the response of the resonator and breaks down completely when the perturbation extends out of the enhanced near field, which can be seen for example at the response of the C_2 resonance going up again. An improved perturbation theory where the contribution of radiation is taken into account has been proposed by Lai et al.¹⁶ and is discussed in Appendix A. It gives very good results for the C_1 and U_1 resonance. The response of the C_2 resonance does not agree, due to the aforementioned numerical problems and therefore wrong normalization.

Response to Attached Colloids. The same analysis was done for the attachment of a colloid to the resonator and the results are shown in Figure 6. Both perturbation theories agree well with the exact calculations. For the C_2 resonance the same problem as discussed before is present in the normalization of the improved perturbation theory but not in the near field approximation. The result shows that eq 5 can give good results for very small perturbations in the near field.

Finally we investigate how the peaks of this particular structure shift as a function of an attached spheres size. The sphere is placed at the position of highest field and touching the crescent resonator. The resulting peak displacement normalized by the change in the dielectric constant is shown in Figure 7a. At a radius of 2.5 nm still a shift of 0.15 nm for the C_1 and U_1 resonance is observed, a value which is reported to be resolvable by state of the art instruments.¹⁷ This size corresponds to the size of a single macromolecule, that is, streptavidin which is frequently used to evaluate sensing schemes can be described approximately as a sphere with a diameter of $d = 5$ nm and a refractive index of 1.52.^{17,18} Of course one has to take into account that the dielectric contrast is 5 times lower in aqueous solution which lowers the response also 5 times. Still we expect that further optimization should allow for detection of single attached molecules given a big enough dielectric contrast. By comparing the slope of the peak displacement with that of a cubic polynomial we see that even the smallest modeled spheres do not experience a nearly uniform field where a slope proportional to r^3 is expected. When moving the sphere 12 nm away from the tip (at the same angular position φ_s) into a more uniform field, the slope approaches the expected cubic polynomial (Figure 7b). We expect the same result for smaller spheres directly at the tip, but this cannot be tested because of the finite discretization of the simulation.

Summary

In summary, we analyzed how plasmonic resonators should be optimized for detection of very small changes in the dielectric environment. We developed a simple figure of merit from

perturbation theory and a statistical analysis of the spectral measurement of resonances. The most important finding is, that mainly the field confinement determines the sensing capability and optimization should aim to increase it. For example, geometries with thin gaps as can be obtained by a slightly modified crescent preparation or bowties are expected to be superior sensors. We derived simple scaling laws from our figure of merit. We used our findings to analyze the sensing capabilities of crescent shaped resonators in detail for different sensing situations. While good agreement with already available experimental data is found, we showed that for spherical detection volumes these resonators should be able to sense the change of refractive index in spheres as small as 2.5 nm in radius. We expect that based on our figure of merit resonators with improved sensitivity will be identified enabling the detection of single molecules in real time with future plasmonic sensors.

Appendix A: Perturbation Theory

A well-known result of Hermitian first order perturbation theory, derived in many books (e.g., ref 19), is

$$\frac{\Delta\omega}{\omega} = -\frac{1}{2} \frac{\int_{V_s} \Delta\epsilon |\vec{E}|^2 dV}{\int_{\text{all space}} \epsilon |\vec{E}|^2 dV} \quad (\text{A.1})$$

Here $\Delta\omega/\omega$ is the relative change in frequency, ϵ is the space dependent permittivity, $\Delta\epsilon$ the dielectric contrast, and E the electrical field.

This equation connects a small change in permittivity with the change of the eigenfrequency of an eigenmode

$$\vec{E} = \vec{E}_0(\vec{r})e^{-i\omega t} \quad (\text{A.2})$$

which is a solution to the vectorial wave equation

$$L\vec{E} + \frac{\epsilon}{c^2}\vec{E} = 0 \quad \text{with} \quad L\vec{E} = \nabla \times (\nabla \times \vec{E}) \quad (\text{A.3})$$

A nice interpretation of the perturbation result was shown by Joannopoulos et al.²⁰ When $\Delta\epsilon$ is approximated by $\Delta\epsilon \approx \epsilon_s 2\Delta n/n$ where Δn is the refractive index change, n is the refractive index and the perturbation is assumed constant over the perturbed volume

$$\frac{\Delta\omega}{\omega} = -\frac{\Delta n}{n} \frac{\int_{V_s} \epsilon |\vec{E}|^2 dV}{\int_{\text{all space}} \epsilon |\vec{E}|^2 dV} \quad (\text{A.4})$$

For transparent materials the term in the integral can be interpreted as the energy density of the field so this shows that the relative change in frequency is proportional to the relative change in refractive index and the fraction of the energy within the detection volume where the change takes place.

This theory is only strictly valid when the resonator is not lossy and does not radiate energy, hence the problem is Hermitian. However the interpretation above suggests that we can use the same formula and just substitute the correct formulation for the energy if these assumptions do not apply. We assume that the radiated field does not contribute to the

change in frequency, because once it is radiated away it does not interact with the resonator again. For a weakly radiating resonator we may therefore neglect radiation by restricting the integral in the denominator to a volume where the near field dominates. Here we define the near field as all field around the resonator which has a field enhancement greater than 2. Other definitions exist, but we choose this for the particularly simple evaluation of the integrals. The integration is not sensitive to the exact number of the field enhancement chosen for this definition.

The field energy inside the metal is

$$W = |\vec{E}|^2 \left(\epsilon_{\infty} + \frac{1}{2} \frac{\Delta\epsilon}{\Gamma^2 + \omega^2} \right) = \epsilon_{\text{eff}} |\vec{E}|^2 \quad (\text{A.5})$$

where the kinetic energy of the electrons was considered with a Drude model (eq B.1) and the Lorentz term of B.1 is neglected because out of resonance its contribution is small. This leads to eq 5 which might be called quasi static perturbation theory. The value of this equation is that it gives some insight into the nature of the problem and can be used to optimize the particle. It must be stressed, though, that it cannot be used for quantitative calculations because its errors can be in the order of the signal itself. We found factors of up to 2 between experiment and theory. The assumption of a small perturbation is not valid in particular for changes in bulk refractive index. In this case, the energy confinement C would be close to one which would give a sensitivity of

$$\frac{\Delta\omega}{\Delta n} \approx -\frac{\omega}{n} \quad (\text{A.6})$$

which would mean that the frequency shift per refractive index unit equals the resonant frequency itself. Experimentally usually smaller shifts are observed.^{10,21} Generally the smaller the perturbed volume the better the theory should work which means that it gives good estimates in the case of very small local changes such as binding of single molecules.

A more quantitative theory was developed by Lai et al.¹⁶ Their finding was that the normalization of the modes contains an additional surface term which accounts for the outgoing waves and that the integral has to be carried out over the scalar product of the electrical field with itself and not its magnitude, resulting in complex quantities

$$\frac{\Delta\omega}{\omega} = -\frac{1}{2} \frac{\int_{V_s} \Delta\epsilon \vec{E}^2 dV}{\int_{\text{all space}} \epsilon \vec{E}^2 dV + \frac{ic}{2\omega} \int_{\text{Boundary}} \vec{E}^2 dA} \quad (\text{A.7})$$

This formula is expected to yield exact results in the case of vanishing small $\Delta\epsilon$. Apart from the surface integral being a less intuitive quantity than the energy densities considered in eq (A.5), there are some difficulties in the use of this formula. While it was shown¹⁶ that the integral in the denominator of eq A.7 converges this proof was only valid for extension of the integral to the far field. To obtain the field in such a big area FDTD calculations would be very inefficient or require complicated postprocessing. In our case the computational box is between 0.55λ and 0.95λ depending on the resonance under study. Numerical experiments for a metal sphere where the

integral is easy to solve, show that at 0.55λ good convergence with an error in the order of 5% can be expected. A second approximation we do is to approximate the field of the resonance by the scattered field at the maximum extinction cross section. This means that we approximate the complex ω of the eigensolution with the real ω of the exciting wave. As a consequence the scattered fields do not satisfy the interface condition for the electrical field normal to the boundary of the resonator.

Appendix B: FDTD Simulations

For simulations the finite difference time domain method (FDTD) is used. Here Maxwells curl equations are approximated by finite differences on a regular grid in space. The electric and magnetic field are evolved in time using an explicit time marching scheme. FDTD is, beside errors that arise from the discretization, an exact method, which can solve in principle any wave propagation problem to any desired accuracy but is limited to the available computational resources. The method is described by Taflov²² and has been used earlier to calculate the electromagnetic properties of metallic nanoparticles.²³ For our investigation the freely available code meep²⁴ was applied. The simulation was set similar to the work of Oubre et al.,²³ a difference is that our particles are not placed in free space but on a substrate. The simulation area is surrounded by a perfectly matched layer (PML,²²) which absorbs the outgoing waves and for excitation a total field/scattered field (TFSF²²) boundary was used. Figure 8 shows a cut through the simulated space with source, absorbing boundary and the particle. At the TFSF boundary (red cuboid around the particle) currents are distributed in a way that without the particle inside the cuboid (volume 2) a x -polarized Gaussian light pulse with a center wavelength of 900 nm and a wavelength-bandwidth of 2400 nm propagates

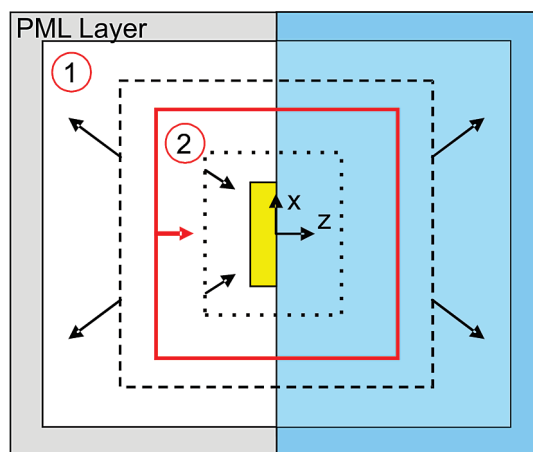


Figure 8. 2D cut along the x - z plane of the three-dimensional simulation space. The yellow object symbolizes the particle which lies on a glass surface. The TFSF-boundary is sketched as red line, surfaces for integration as black dashed and dotted lines.



Figure 9. Close-up of two discretized tips. Each pixel corresponds to a simulation cell (white corresponds to the permittivity of air, black to that of gold). The left configuration is used in all simulations presented here.

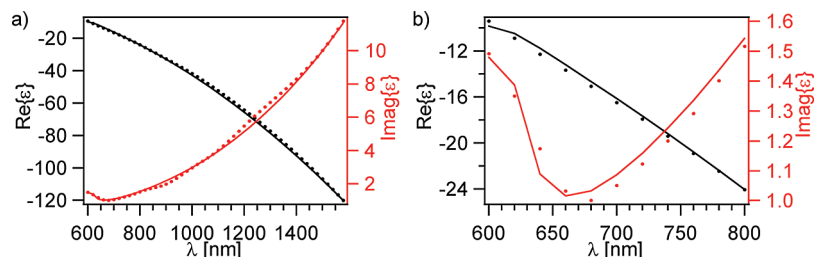


Figure 10. Dielectric function of gold from²⁷ (dots) and fitted dielectric function (lines). The values were obtained by fitting the data from²⁷ with a standard nonlinear least-squares routine.

in positive z direction and is partially reflected by the glass surface. Without the scattering particle, no field is present outside the cuboid (volume 1). The presence of a particle changes both the field inside and outside the TFSF boundary. Integration of the flux through a closed surface outside the TFSF boundary (dashed line) yields the total scattered flux and the scattering cross section. Absorbed flux and absorption cross section are obtained in an analogous way by integration over a closed surface inside the TFSF boundary (dotted line). The size of the computational area and the PML as well as the resolution was chosen such that convergence of the results was observed, indicating their independence of the mentioned parameters. A small residual error in the order of 5% remains due to reflections at a nonperfect PML and manifests itself as an overlaying oscillation of the cross sections especially at smaller wavelengths. Because this effect is small and is the same in all simulations with the same box/PML size it has only little influence on finding the resonances from the simulation. The computational box used here has the size $0.8 \times 0.8 \times 0.7 \mu\text{m}$, the PML is 100 nm thick around the whole box and the TFSF boundary is of $0.5 \times 0.5 \times 0.4 \mu\text{m}$ size.

The tips of the crescents deserve special attention. Theoretically, at an infinitely sharp tip the field diverges. Here, a tip radius of 5 nm is assumed. It is known that for gold nanoparticles which are smaller than this radius, the effective permittivity deviates from the bulk permittivity of gold due to several physical mechanisms summarized as finite size effects.^{25,26} They provide an approximate lower limit for feature sizes where the metal can be described by its bulk response. Figure 9c shows two possible discretizations for a tip for a pixel size of 5 nm. The tip was always constructed as shown on the left where an effective radius of 5 nm is approximately reproduced. Single pixels with metallic response as shown on the right were avoided by manual reshaping of the tip after the geometric construction.

For modeling the dielectric properties of the gold, a two oscillator Drude–Lorentz model was used. The first oscillator accounts for the contribution of the free electrons, while the second describes an interband transition of the gold. The formula for the dielectric function is

$$\varepsilon = \varepsilon_{\infty} + \frac{\Delta\varepsilon_1}{-\omega^2 - i\Gamma_1\omega} + \frac{\omega_2^2\Delta\varepsilon_2}{\omega_2^2 - \omega^2 - i\Gamma_2\omega} \quad (\text{B.1})$$

The values used are $\varepsilon_{\infty} = 9.17$, $\Delta\varepsilon_1 = 52.26$, $\Gamma_1 = 0.057$, $\omega_2 = 1.65$, $\Delta\varepsilon_2 = 0.068$, $\Gamma_2 = 0.062$. All dimensions are $2\pi c/\mu\text{m}$. The dielectric response as obtained with this model in

comparison to tabulated data is shown in Figure 10. For modeling the glass, a constant dielectric constant of 2.25 is used.

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