

Scattering of infrared light by dielectric core-shell particles

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We study the scattering of infrared light by small dielectric core-shell particles taking an Al_2O_3 sphere with a CaO core as an example. The extinction efficiency of such a particle shows two intense series of resonances attached, respectively, to in-phase and out-of-phase multipolar polarization-induced surface charges buildup, respectively, at the core-shell and the shell-vacuum interface. Both series, the character of the former may be labeled bonding and the character of the latter antibonding, give rise to anomalous scattering. For a given particle radius and filling factor, the Poynting vector field shows therefore around two wave numbers the complex topology of this type of light scattering. Inside the particle, the topology depends on the character of the resonance. The dissipation of energy inside the particle also reflects the core-shell structure. It depends on the resonance and shows strong spatial variations.

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I. INTRODUCTION

Nanoparticles with a core-shell structure are of interest for various fields of applied research. They are routinely fabricated [1,2] and have applications ranging from nanophotonics [3,4] to medical treatment [5]. In the field of plasmonics [6], for instance, recent attention has been paid to nanoparticles having a metallic core and a dielectric shell [7–9] or vice versa [3,10]. The reason is the added tunability of the optical response due to the geometry and composition of the particle. One of the most remarkable properties of coated nanoparticles is that they may induce transparency in a certain range of wave numbers due to the interplay of the dipole radiations of the core and the shell [11].

We are interested in the scattering of light by particles with a dielectric core and a dielectric coat (shell) where both materials show a strong transverse optical phonon resonance giving rise to anomalous scattering in the infrared occurring for wave numbers λ^{-1} where the complex dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$ has $\varepsilon' < 0$ and $\varepsilon'' \ll 1$ [12,13]. In our previous work [14], we analyzed the extinction efficiency of this type of core-shell particle with an eye on using it in a low-temperature plasma as an electric probe with an optical readout. The idea, originally put forward for homogeneous dielectric particles [15,16], is to utilize the blue-shift of the anomalous dipole resonance due to the surplus electrons collected from the plasma as a diagnostics from which the charge of the particle and thus the floating potential at the particle's position in the plasma can be determined. Whereas for homogeneous particles the charge-induced shift is most probably too small to be of practical importance, core-shell particles show a much larger blue-shift. In particular, the position of what we called shell resonance is very charge sensitive. Its blue-shift should be measurable for particle radii up to $0.5 \mu\text{m}$ by infrared attenuation spectroscopy as it is typically used in plasma diagnostics [17]. We also proposed to use dielectric particles scattering infrared light in the anomalous regime as grains in dusty plasmas and to replace traditional force-balance techniques [18,19] of determining the charge of the grains by an optical technique.

The dielectric core-shell particles suggested for an optical charge measurement contain a core with negative and a

shell with positive electron affinity. This particular choice of electron affinities results in a potential well which localizes the surplus electrons in the shell of the particle. Compared to a homogeneous particle, where the surplus electrons are spread out over the whole particle, the volume charge density of surplus electrons is thus enhanced. It is this localization effect which already yields larger charge-induced shifts for the anomalous resonances of the core. More important, however, is that the core-shell structure leads also to an additional resonance not present in a homogeneous particle [20,21]. Within the hybridization model for the optical response of complex nanostructures [22,23], the additional resonance can be understood as the antibonding split-off of the anomalous resonance of the shell due to its mixing with a cavity mode supported by the core. The bonding partner is located at smaller wave numbers with the splitting between the bonding and the antibonding resonances controlled by the filling factor $f = b/a$ which is the core radius b measured in units of the particle radius a . In our investigations of charged core-shell particles we found the position of the antibonding dipole resonance (which we called shell resonance) to be particularly charge sensitive.

The purpose of this work is to analyze the bonding and antibonding resonances showing up in dielectric core-shell particles in more detail using a neutral Al_2O_3 particle with a CaO core as an example. In addition to the results for this particular physical particle, we also show results for a dissipationless model particle where the scattering anomalies can be more clearly identified. We demonstrate that the bonding as well as the antibonding resonances scatter light in the anomalous regime. This can be deduced from the inverse hierarchy of the partial extinction cross sections and the topology of the Poynting vector field [12]. In contrast to the hybridization model [22,23], we do not use the electrostatic approximation. Instead, we solve the full Mie equations [24–27] for the core-shell particle [28]. We can thus gain further insight into the hybridization scenario [22,23] by investigating specifically in the dipole regime the energy flux inside and outside the particle by the methods previously used for homogeneous particles [29–33]. From the spatial distribution of the dissipation, we can moreover identify regions inside the particle where most of the energy is deposited which may

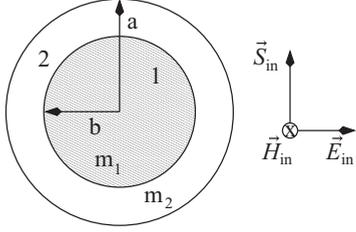


FIG. 1. Illustration of the scattering geometry. The incident electromagnetic plane wave is characterized by a Poynting vector \vec{S}_{in} , an electric field \vec{E}_{in} , and a magnetic field \vec{H}_{in} . It propagates along the z axis with an electric field polarized along the x axis. The index of refraction in the core ($i = 1$) and the shell ($i = 2$) of the particle is $m_i = \sqrt{\varepsilon_i}$, where ε_i is the complex dielectric function in region i . The total radius of the particle is a while the radius of the core is b .

be of technological interest [33]. Dissipation depends on the character of the resonance, bonding or antibonding, and is for both cases highly inhomogeneous, varying by two orders of magnitude from one position to another.

The remaining paper is organized as follows. In the next section, we recall briefly the Mie theory of light scattering by core-shell particles relegating mathematical details necessary to fix our notation to an Appendix. In Sec. III, we present our results, discussing first the hierarchy of the two series of extinction resonances and then, in the dipole regime, the topology of the Poynting vector field, the magnitude and orientation of the electric field, and the dissipation of energy inside the particle. Concluding remarks with a summary of our main findings are given in Sec. IV.

II. THEORETICAL BACKGROUND

In Fig. 1, we show the geometry of the scattering problem we consider. An electromagnetic wave, linearly polarized in the x direction and propagating in the z direction, hits a core-shell particle located at the center of the coordinate system. The particle is embedded in vacuum. It has a total radius a and a core radius $b = fa$ where f is the filling factor of the particle. In the limit $f \rightarrow 1$, the particle has thus no shell whereas for $f \rightarrow 0$ it has no core. The core ($i = 1$) and the shell ($i = 2$) of the particle are made out of different dielectric materials characterized by magnetic permeabilities $\mu_i = 1$ and dielectric functions $\varepsilon_i(\lambda^{-1}) = \varepsilon'_i(\lambda^{-1}) + i\varepsilon''_i(\lambda^{-1})$ giving rise to refractive indices $m_i(\lambda^{-1}) = \sqrt{\varepsilon_i(\lambda^{-1})}$, where $\lambda^{-1} = \nu/c$ is the wave number of the incident infrared radiation, ν is its frequency, and c is the speed of light. In the formulas given in the following and in the Appendix we will use $\omega = 2\pi\nu$ and $k = 2\pi\lambda^{-1}$ instead of ν and λ^{-1} , the abbreviation $k_i = km_i$, and the size parameters $x = 2\pi\lambda^{-1}b$ and $y = 2\pi\lambda^{-1}a$.

The theory of light scattering by a homogeneous spherical particle worked out originally by Mie [24] has been extended to a core-shell particle by Aden and Kerker [28] a long time ago. Since then, the approach has been applied extensively [20,21] and it has also found its way into many textbooks [25–27]. Mathematically, the Maxwell equations for the scattering problem shown in Fig. 1 are solved by expanding the electromagnetic fields in the three regions of interest, the outer space, the shell, and the core, in terms of spherical vector

harmonics and determining the expansion coefficients from the boundary conditions at the two interfaces.

Outside the particle there is the incident and the scattered wave. In terms of vector harmonics, the fields of the incident wave can be written as [27]

$$\vec{E}_{\text{in}} = \sum_{n=1}^{\infty} E_n (\vec{M}_{o1n}^{(1)} - i\vec{N}_{e1n}^{(1)}), \quad (1)$$

$$\vec{H}_{\text{in}} = -\frac{kc}{\omega\mu_m} \sum_{n=1}^{\infty} E_n (\vec{M}_{e1n}^{(1)} + i\vec{N}_{o1n}^{(1)}) \quad (2)$$

with expansion coefficients

$$E_n = i^n E_0 \frac{2n+1}{n(n+1)}, \quad (3)$$

where E_0 is the strength of the incident electric field, eventually used as the unit for the field strength, $\mu_m = 1$ is the vacuum permeability, and the superscript (1) denotes that the radial dependence of the fields is given by the Bessel function j_n . The expansions for the fields of the scattered wave are

$$\vec{E}_s = \sum_{n=1}^{\infty} E_n (ia_n \vec{N}_{e1n}^{(3)} - b_n \vec{M}_{o1n}^{(3)}), \quad (4)$$

$$\vec{H}_s = \frac{kc}{\omega\mu_m} \sum_{n=1}^{\infty} E_n (ib_n \vec{N}_{o1n}^{(3)} + a_n \vec{M}_{e1n}^{(3)}) \quad (5)$$

with a superscript (3) indicating that the Bessel function h_n describes now the radial dependence of the fields.

Inside the particle, the fields in the shell and the core have to be distinguished. Inside the shell,

$$\vec{E}_2 = \sum_{n=1}^{\infty} E_n (f_n \vec{M}_{o1n}^{(1)} - ig_n \vec{N}_{e1n}^{(1)}) \quad (6)$$

$$+ v_n \vec{M}_{o1n}^{(2)} - iw_n \vec{N}_{e1n}^{(2)}, \quad (7)$$

$$\vec{H}_2 = -\frac{k_2 c}{\omega\mu_2} \sum_{n=1}^{\infty} E_n (g_n \vec{M}_{e1n}^{(1)} + if_n \vec{N}_{o1n}^{(1)}) \quad (8)$$

$$+ w_n \vec{M}_{e1n}^{(2)} + iv_n \vec{N}_{o1n}^{(2)}, \quad (9)$$

while inside the core

$$\vec{E}_1 = \sum_{n=1}^{\infty} E_n (c_n \vec{M}_{o1n}^{(1)} - id_n \vec{N}_{e1n}^{(1)}), \quad (10)$$

$$\vec{H}_1 = -\frac{k_1 c}{\omega\mu_1} \sum_{n=1}^{\infty} E_n (d_n \vec{M}_{e1n}^{(1)} + ic_n \vec{N}_{o1n}^{(1)}) \quad (11)$$

with the superscripts (1) and (2) indicating, respectively, to use the Bessel function j_n and y_n for the radial dependence of the fields. The expansion coefficients $a_n, b_n, c_n, d_n, f_n, g_n, v_n$, and w_n have to be determined from the boundary conditions at the core-shell and the shell-vacuum interface giving rise to a system of eight equations for eight unknowns [27]. Once the expansion coefficients are known, quantities of physical interest can be computed. In the following, we focus on the extinction efficiency, the Poynting vector field, and the dissipation of energy inside the particle.

Of central importance for the characterization of the scattering process is the extinction efficiency, that is, the scattered and absorbed energy per second divided by the incident energy flux per unit area. It is given by [27]

$$Q_t = \sum_{n=1}^{\infty} Q_t^{(n)} \quad (12)$$

with

$$Q_t^{(n)} = \frac{2}{y^2} \text{Re}[(2n+1)(a_n + b_n)] \quad (13)$$

the partial extinction efficiency for the multipole resonance of order n where $n=1$ denotes the dipole resonance, $n=2$ the quadrupole resonance, and so on.

Whereas Q_t is of relevance only in the outer space, the time-averaged Poynting vector field is of interest in the whole space. It can be obtained for the outer and the inner regions by inserting the expansions for the fields given above into the standard expression [25]

$$\vec{S} = \frac{1}{2} \frac{c}{4\pi} \text{Re}[\vec{E} \times \vec{H}^*]. \quad (14)$$

Likewise, the dissipation of energy inside the particle can be obtained from [34]

$$W = \frac{1}{2} \frac{\omega}{4\pi} \varepsilon'' |\vec{E}|^2 \quad (15)$$

using for the electric field and the imaginary part of the dielectric function the values applicable to the region under consideration.

Outside the particle, only the scattered and incident fields $\vec{E}_{s,\text{in}}$ and $\vec{H}_{s,\text{in}}$ are present. For the calculation of the extinction efficiency and the outside Poynting vector field, the coefficients a_n and b_n are thus sufficient. In order to obtain, however, the dissipation and the Poynting vector field inside the particle, the fields $\vec{E}_{1,2}$ and $\vec{H}_{1,2}$ and hence the coefficients c_n, d_n, f_n, g_n, v_n , and w_n are also required. In the notation of Bohren and Huffman [27] we list therefore all eight coefficients in the Appendix.

III. RESULTS

We discuss the scattering of infrared light by neutral dielectric core-shell particles with filling factor $f=0.7$ for two particular cases: (i) a physical CaO/Al₂O₃ particle and (ii) an idealized model particle. For the former we take realistic bulk dielectric functions for the CaO core [35] and the Al₂O₃ shell [36,37] to be found in our previous work [14] and plotted at the bottom of Fig. 2, while for the model particle the dielectric functions of the core and the shell are given by

$$\varepsilon' = \varepsilon_{\infty} + \lambda_{\text{TO}}^{-2} \frac{\varepsilon_0 - \varepsilon_{\infty}}{\lambda_{\text{TO}}^{-2} - \lambda^{-2}}, \quad \varepsilon'' = 0 \quad (16)$$

with $\lambda^{-1} = \nu/c$ the wave number of the electromagnetic wave, λ_{TO}^{-1} the wave number of the transverse optical phonon, and ε_0 and ε_{∞} the dielectric constants at low and high frequency, respectively. The values taken for the core and the shell are listed in Table I.

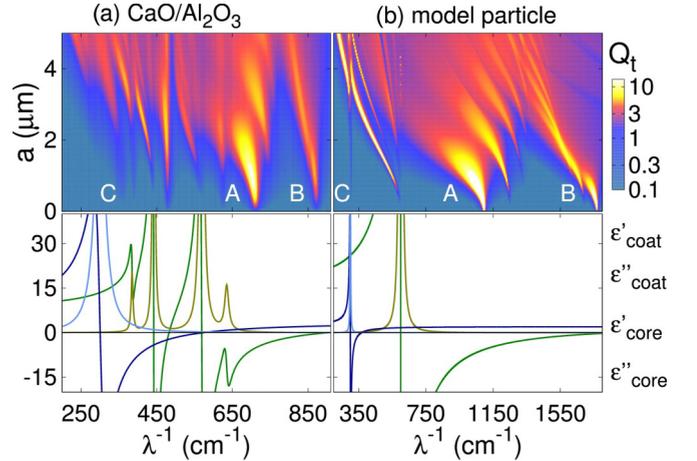


FIG. 2. (Color online) Top: Extinction efficiency Q_t as a function of the wave number λ^{-1} and the particle radius a for filling factor $f=0.7$. The anomalous resonance of the core is indicated by C while the two resonances appearing in the surface phonon regime of the shell are denoted by A and B. Bottom: Real and imaginary parts of the dielectric functions used for the CaO/Al₂O₃ particle and the model particle, respectively.

In contrast to the dielectric function of the physical CaO/Al₂O₃ particle, the dielectric function of the model particle is real. The model particle has thus no damping. Since by definition anomalous resonances occur for wave numbers for which $\varepsilon' < 0$ and $\varepsilon'' \ll 1$, that is, in situations where dissipative losses are much smaller than radiative losses [12], the model particle displays the properties of anomalous resonances more clearly than the CaO/Al₂O₃ particle which of course has dissipation. In particular, the disentangling of the complex topology of the energy flux is at first easier for the model particle.

A. Hierarchy of anomalous resonances

We start with the extinction spectrum in the far field of the particle. In Fig. 2, the extinction efficiencies Q_t of the CaO/Al₂O₃ and the model particle are shown as a function of wave number λ^{-1} and particle radius a together with the dielectric functions of the particles. Here and in the figures following, the filling factor f is always 0.7. In the dipole regime, for very small radii, three resonances A, B, and C can be identified for both kinds of particles. Resonance C, which we will not discuss in detail, is the anomalous dipole resonance of the core while resonance B is the one we proposed to use as a charge diagnostics [14]. The resonances A and B are of particular interest because they belong to a series of resonances lying in the surface phonon regime of the shell, that is, in the spectral region between $\lambda_{\text{TO},2}^{-1}$ and $\lambda_{\text{LO},2}^{-1}$, where $\lambda_{\text{TO}(LO),2}^{-1}$ is the

TABLE I. Parameters for the model particle.

Model	λ_{TO}^{-1} (cm ⁻¹)	ε_0	ε_{∞}
Core	300	3	2
Shell	600	20	2

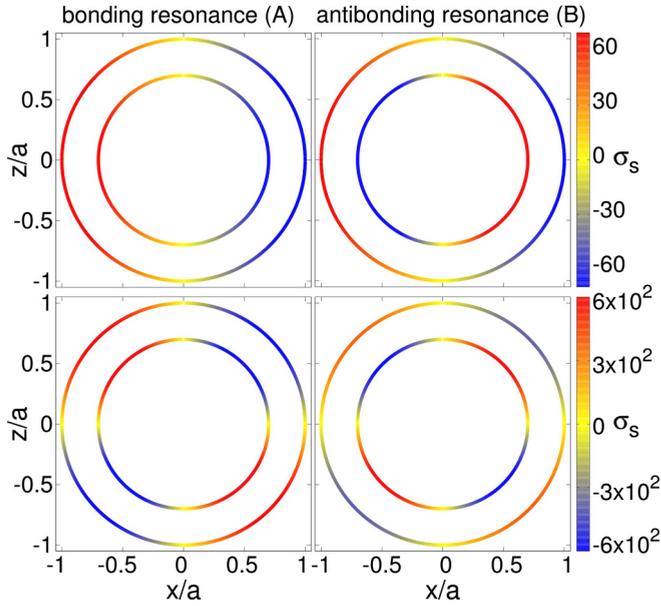


FIG. 3. (Color online) Polarization-induced surface charges build up at the core-shell and the shell-vacuum interface of the model particle to satisfy the boundary conditions of the Maxwell equations for the dipole (upper two panels) and the quadrupole resonances (lower two panels). For the bonding resonances, the multipolar surface charges of the two interfaces are in phase, whereas for the antibonding resonances they are out of phase. The wave numbers are always slightly above the resonance: $\lambda^{-1} = 1095.669 \text{ cm}^{-1}$ (bonding dipole), $\lambda^{-1} = 1767.293 \text{ cm}^{-1}$ (antibonding dipole), $\lambda^{-1} = 1241.95 \text{ cm}^{-1}$ (bonding quadrupole), and $\lambda^{-1} = 1682.42 \text{ cm}^{-1}$ (antibonding quadrupole). The particle radius $a = 0.1 \text{ }\mu\text{m}$ for the dipole and $a = 0.6 \text{ }\mu\text{m}$ for the quadrupole resonances with filling factor $f = 0.7$ in both cases.

wave number of the transverse (longitudinal) optical phonon of the shell. The goal of our work is to investigate the physical properties of these two series.

From the viewpoint of the hybridization model [22,23], the two series arise from the mixing of a surface mode of a hypothetical particle with radius a made out of shell material with a surface mode of a hypothetical cavity of radius b made out of core material and embedded into a junk of shell material leading in each multipole order to a bonding and an antibonding mode. The hybridization scenario is buried in the Mie equations, but it can be made explicit by plotting the difference of the normal components of the polarization $\vec{P} = \epsilon_0(\epsilon - 1)\vec{E}$ at the core-shell and the shell-vacuum interface; $\epsilon_0 = 1$ is the dielectric function of the vacuum. As can be seen in Fig. 3 for the particular case of the dipole and quadrupole resonances of the model particle, the polarization-induced surface charges required to satisfy the boundary conditions of the Maxwell equations at the two interfaces are for the bonding resonances in phase and for the antibonding resonances out of phase. The two dipole resonances, for instance, can thus be understood in terms of an inner and an outer dipole which are oriented either parallel or antiparallel. In the vicinity of these two resonances, the electric field outside the particle is thus the effective field of two parallel or antiparallel dipoles. Inside the particle, the field is more complex (see following).

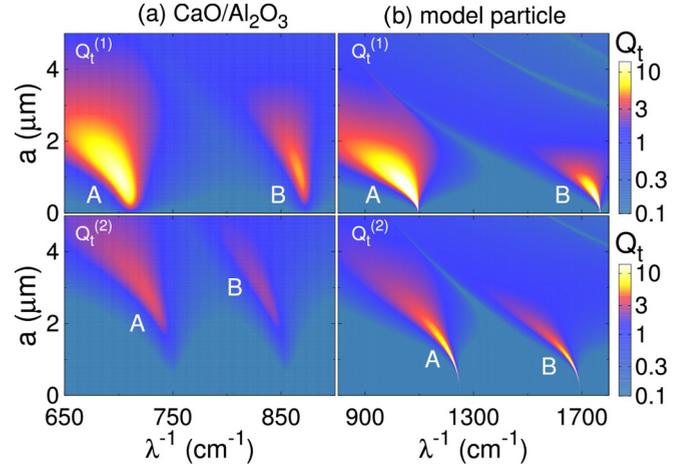


FIG. 4. (Color online) Partial extinction efficiency $Q_t^{(n)}$ in the vicinity of the bonding (A) and antibonding resonance (B) as a function of the wave number λ^{-1} and the particle radius a . The superscripts (1) and (2) indicate the dipole and the quadrupole modes. Higher multipole modes appearing at larger radii are weaker and cannot be seen on the scale used for the plot. The filling factor $f = 0.7$.

Similarly, the bonding and antibonding quadrupole resonances originate from quadrupole surface polarization charges at the two interfaces which are either in or out of phase.

The parameters of the dielectric functions of the model particle have been chosen in such a way that the series of antibonding resonances can be also clearly identified. Both the bonding and antibonding series stop at the third multipole order, that is, at the octupole, as it is also the case for the $\text{CaO}/\text{Al}_2\text{O}_3$ particle. But, it is conceivable to have material combinations and perhaps filling factors for which the series of sharp resonances continues to higher order. The question then arises as to whether the two series of resonances scatter light anomalously. In particular, it would be interesting to know whether the sharp resonances signal the resonant excitation of a particular surface mode of the shell and whether the hierarchies of extinction cross sections to which the two series give rise to are inverted as it would be the case for homogeneous particles made out of either the shell or the core material.

For a homogeneous particle, Tribelsky and Luk'yanchuk [12] have shown that if the size parameter is at the resonance wave number of the order one or smaller, the main contribution to this resonance comes from one resonantly excited surface mode. This selectivity remains for a core-shell particle, as we will now demonstrate. For that purpose, we plot in Fig. 4 for the physical and the model particle the extinction efficiencies due to the dipole mode $Q_t^{(1)}$ and the quadrupole mode $Q_t^{(2)}$ separately. As can be seen, each mode has its own distinct set of particle radii and wave numbers at which it is resonantly excited. Off resonance, the partial multipole extinction efficiencies provide only a homogeneous background to the overall extinction efficiency. Thus, it is possible to relate to the lowest resonance in Fig. 2 an excited dipole mode and to the second lowest resonance an excited quadrupole mode. For a given particle radius, a core-shell particle gives thus rise to two wave numbers at which a dipole mode or a quadrupole mode can be excited.

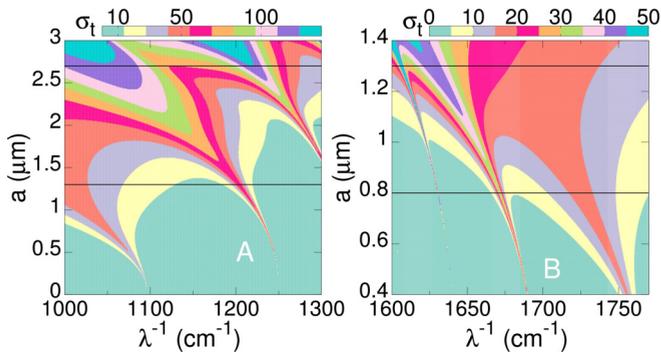


FIG. 5. (Color online) Inverse hierarchy of the extinction cross section σ_t in units of πa^2 for the model particle in the vicinity of the bonding (A) and the antibonding resonance (B). Horizontal lines indicate radii where the local maximum of the cross section shifted from a lower to a higher mode. The filling factor $f = 0.7$.

This is in contrast to a homogeneous particle where only one wave number exists.

Having identified the multipole order of the resonances, we can now turn to the extinction cross section $\sigma_t = \pi a^2 Q_t$ and study its hierarchy. For a homogeneous particle σ_t shows in the anomalous regime an inverse hierarchy, that is, for a given particle radius the cross section due to a higher multipole is larger than the cross section due to a lower multipole [12,13].

In Fig. 5, we see for the model particle that the series of bonding and antibonding resonances arising in core-shell particles display the same behavior. At the bonding resonance (left panel) for particle radii smaller than $a = 1 \mu\text{m}$ the cross section σ_t of the dipole resonance at $\lambda^{-1} \approx 1050 \text{ cm}^{-1}$ is dominant, at $a = 1.3 \mu\text{m}$ on the other hand, the maximum of the cross section shifted to the quadrupole resonance at $\lambda^{-1} \approx 1200 \text{ cm}^{-1}$. Yet another shift occurred for $a = 2.7 \mu\text{m}$, where the maximum of the cross section is now at the octupole resonance. This inverse hierarchy can also be seen for the antibonding resonance (right panel). At the particle radius $a = 0.8 \mu\text{m}$ the cross-section maximum has shifted from the dipole mode around $\lambda^{-1} \approx 1740 \text{ cm}^{-1}$ to the quadrupole mode around $\lambda^{-1} \approx 1680 \text{ cm}^{-1}$. The next shift of the cross-section maximum is indicated at $a = 1.3 \mu\text{m}$ where the octupole resonance is the most pronounced in the cross section. Since the inverse hierarchy is a direct consequence of the series of resonances in the extinction efficiency [12,13], the real $\text{CaO}/\text{Al}_2\text{O}_3$ particle shows the same inverted hierarchy of resonances in the cross section (not shown in Fig. 5).

Both the series of bonding and the series of antibonding resonances fulfill therefore the criteria of anomalous light scattering as spelled out by Tribelsky and Luk'yanchuk [12,13]. Each series consists of strong narrow resonances which are determined by a single resonantly excited bonding or antibonding mode and which moreover give rise to extinction cross sections increasing for fixed radius with the order of the multipole. The different physical origin of the two series, in-phase versus out-of-phase polarization-induced surface charges at the two interfaces, is reflected in the way the two series shift in wave number with increasing

multipole order. Whereas the bonding resonances shift to higher wave numbers, the antibonding resonances shift in the other direction. The antibonding quadrupole resonance is thus excited at lower wave numbers than the antibonding dipole resonance.

B. Topology of the Poynting vector field

In the previous section, we showed that the series of bonding and antibonding resonances have anomalous properties. We now investigate in the vicinity of the two lowest resonances the bonding and antibonding dipole resonances, the energy flux outside and inside the core-shell particle, and compare it with the results Tribelsky and Luk'yanchuk obtained for a homogeneous particle [12]. In particular, we consider a model particle with radius $a = 0.1 \mu\text{m}$ and a $\text{CaO}/\text{Al}_2\text{O}_3$ particle with radius $a = 0.4 \mu\text{m}$ keeping the filling factor in both cases fixed to $f = 0.7$. As can be deduced from Fig. 4, only the dipole resonances are then excited. For the model particle they are, respectively, at $\lambda_{b,1}^{-1} \approx 1095.669 \text{ cm}^{-1}$ and $\lambda_{ab,1}^{-1} \approx 1767.293 \text{ cm}^{-1}$, where the subscript stands for bonding/antibonding (b/ab) dipole ($n = 1$) resonance, while for the $\text{CaO}/\text{Al}_2\text{O}_3$ particle $\lambda_{b,1}^{-1} \approx 709.63 \text{ cm}^{-1}$ and $\lambda_{ab,1}^{-1} \approx 871.62 \text{ cm}^{-1}$.

Tribelsky and Luk'yanchuk [12] investigated the Poynting flux in the vicinity of an anomalous resonance of a homogeneous particle and identified its singular points. Due to the large changes in the modulus and phase of the scattering coefficients in this spectral region, the position and the occurrence of the singular points is very sensitive to little changes in the wave number of the incident light. A singular point is characterized by $|\vec{S}| = 0$ [30]. For the scattering geometry shown in Fig. 1, which is also the one used by Tribelsky and Luk'yanchuk [12], the singular points are located in the xz plane. Since in this plane $S_\phi(x,z) = 0$ they are given by the intersection of the isoclines $S_r(x,z) = 0$ and $S_\theta(x,z) = 0$. In the dipole regime, only the coefficients a_n , d_n , g_n , and w_n are resonant. Hence, the orientation of the electric and magnetic fields in space is in all three regions determined by the vector harmonics $\vec{N}_{e1n}^{(\dots)}$ and $\vec{M}_{e1n}^{(\dots)}$, respectively. The difference is in the radial dependence, signaled by the superscript (\dots) which may stand for (1), (2), or (3) depending on the field under consideration.

We also identify the type of the singular point which in vacuum, where $\nabla \cdot \vec{S} = 0$, can be only a center, a saddle, a saddle focus, or a saddle node [29]. For that purpose we (i) carefully analyze the field lines around the singularity as each type of singularity shows a characteristic field distribution and (ii) we check the behavior of the magnetic field $H_y(x,z) = |H(x,z)|e^{i\phi(x,z)}$ as suggested by Schouten [30]. At a center or a focus singularity, the amplitude of the magnetic field vanishes $|H(x,z)| = 0$, while a saddle or node point is characterized by $\nabla\phi(x,z) = 0$. Singular points due to anomalous resonances all lie in the near field since the characteristic spatial scales are smaller than the wavelength of the radiation [12]. For instance, for the model particle, the largest distance of singular points due to the antibonding dipole resonance is about $r = 1.5 \times 10^{-4} \text{ cm}$ while the wavelength of the incident light is $\lambda = 5.7 \times 10^{-4} \text{ cm}$. Similarly, for the bonding dipole resonance, $r = 2.5 \times 10^{-4} \text{ cm}$ and $\lambda = 9.13 \times 10^{-4} \text{ cm}$.

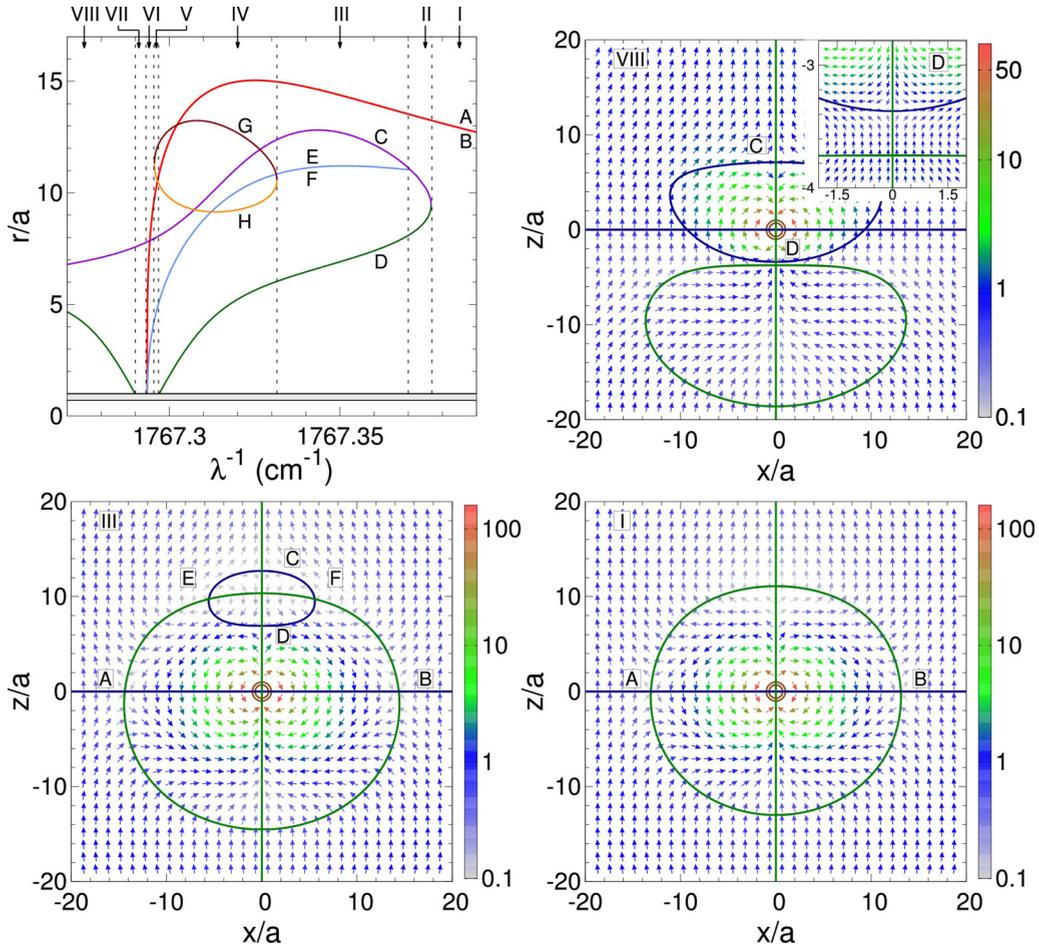


FIG. 6. (Color online) Top left: Position of the outside singular points in the Poynting field (Arabic letters) of the model particle with $f = 0.7$ and $a = 0.1 \mu\text{m}$ near the antibonding resonance at $\lambda_{\text{ab},1}^{-1} \approx 1767.293 \text{ cm}^{-1}$ as a function of wave number. For the bonding resonance, the results are similar. Spectral regions with a fixed topology are indicated by Roman numbers and the shaded area denotes the shell. The other three panels show the Poynting field for three fixed wave numbers. The color of the arrows gives the modulus of the Poynting vector normalized to the flux of incident energy. The intersections of the isoclines $S_{\theta}(r, \theta) = 0$ (green) and $S_r(r, \theta) = 0$ (blue) determine the singular points. The shell and the core of the particle are indicated by brown circles.

1. Topology outside the particle

We start with the outside energy flux. For both the model and the $\text{CaO}/\text{Al}_2\text{O}_3$ particle, only the dipole resonances are excited. Since outside the particles the topology of the energy flux in the vicinity of the bonding and antibonding (dipole) resonances turn out to be qualitatively the same, we discuss only results for the latter.

Figure 6 summarizes for the model particle the topology of the outside Poynting vector field in the vicinity of the antibonding dipole resonance ($a = 0.1 \mu\text{m}$, $f = 0.7$, $\lambda_{\text{ab},1}^{-1} \approx 1767.293 \text{ cm}^{-1}$). Note the dramatic modifications in the topology of the Poynting field due to very small changes in the wave number. The top left of the figure shows the position of the singular points, labeled by Arabic letters, with respect to the particle center. The Roman numerals on the top indicate regions with a fixed topology. The remaining three panels show the Poynting flux outside the particle, symbolized by the two brown circles in the center of the plots, for wave numbers representative for the indicated topological region. The arrows show the direction of the Poynting vector, while the colors correspond to the modulus of the Poynting flux normalized

to the incident flux of light. In addition, the $S_r = 0$ isocline and $S_{\theta} = 0$ isocline are indicated by blue and green lines. The singular points are given by the intersection of two differently colored isoclines.

For wave numbers $\lambda^{-1} < \lambda_{\text{ab},1}^{-1}$, for instance, in region VIII, the Poynting flux in the vicinity of the particle shows a dipole radiation oriented opposite to the incident light which is propagating in the z direction. As an illustration of this behavior, we plotted in the upper right panel of Fig. 6 the Poynting flux for $\lambda^{-1} = 1767.28 \text{ cm}^{-1}$. It contains two singular points, one in the upper and one in the lower half of the xz plane. At the saddle point D in the lower half-plane (replotted on a magnified scale in the inset) it can be nicely seen that the energy flux emitted by the particle due to the excited dipoles is oriented oppositely to the incident energy flux. The field lines emitted by the particle (positive S_r component) and the field lines from the incoming wave (negative S_r component) meet at this point and then bend over to flow towards plus or minus x . In the upper half-plane, that is for $z \geq 0$, the Poynting flux either passes by or is reabsorbed by the particle. This can be seen at point C, which is the

Bohren saddle point [29], where the field lines coming from $\pm x$ are going behind the particle (positive S_r component) or towards it (negative S_r component). The saddle points C and D reflect the strength of the energy flow of the resonant excitation relative to the strength of the energy flow of the incoming light. Thus, these points can disappear if the dipoles are not emitting enough energy, as it can happen if the damping inside the particle is too large.

On the high-energy side of the resonance, for wave numbers $\lambda^{-1} > \lambda_{ab,1}^{-1}$, the dipoles radiate energy parallel to the incident light. The Poynting flux thus gets more complicated. For example, in the topological region III, at $\lambda^{-1} = 1767.35 \text{ cm}^{-1}$, six singular points, four saddle points A, B, C, D, and two foci points E and F (in three dimensions these are saddle-focus points) arise, all located in the upper half of the xz plane (see lower left panel of Fig. 6). There are no singular points anymore for $z < 0$. Since the excited dipoles changed simultaneously their directions, the S_r component of the Poynting vector is always negative for $z < 0$, that is, the energy flux along the z axis is oriented towards the particle. One of the $S_r = 0$ isoclines at which a change of sign in the S_r component occurs is located above the particle at $z > 0$ and so is now the saddle point D. At this point, the field lines emitted by the particle and thus having a positive S_r component and the field lines coming from the foci points E and F and heading towards the particle owing to the negative S_r component meet and take their way towards plus and minus x . This is quite similar to the situation at point D in region VIII since the foci points can be regarded as sources of energy in the xz plane [29]. At the Bohren saddle point C the field lines come together from the left and right focus and then they either go behind the particle or towards it, as they did in region VIII. At $z = 0$ there are two saddle points A and B. To understand their functioning, let us take a look along the $S_\theta = 0$ isocline. For $z < 0$ field lines which cross the $S_\theta = 0$ isocline enter the particle, while field lines crossing the $S_\theta = 0$ isocline for $z > 0$ leave the particle. Thus, at the singular points A and B field lines leaving or entering the particle come close together and form a saddle point.

Some wave numbers away from $\lambda_{ab,1}^{-1}$, in region I, only the saddle points A and B remain as can be seen in the panel on the lower right of Fig. 6 where the Poynting flux is plotted for $\lambda^{-1} = 1767.38 \text{ cm}^{-1}$. If we would plot separatrices inside the circle defined by the $S_\theta = 0$ isocline, we would find Tribelsky ears [29]. For $z < 0$, the Poynting flux has not changed qualitatively compared to region III. But for $z > 0$, the $S_r = 0$ isocline disappeared. As a result, there are no further singular points other than A and B.

A comparison of our results for the Poynting flux near the antibonding dipole resonance of a core-shell particle with the results found by Tribelsky and Luk'yanchuk [12] near the anomalous resonance of a homogeneous particle shows that the topologies are the same. The same pattern arises also around the bonding dipole resonance. Hence, the changes in the anomalous topology of the Poynting flux appear for a core-shell particle around two wave numbers. By just looking at the energy distribution outside the particle, one could not distinguish between a core-shell and a homogeneous particle. Although in the first case two dipoles emit energy, which may have parallel or antiparallel orientation, depending on whether

one is close to the bonding or close to the antibonding dipole resonance, whereas in the second case the energy is emitted only by one dipole.

2. Topology inside the particle

The core-shell structure of the particle reveals itself in the energy flux inside the particle. The reason is the relative orientation of the inner and the outer dipole. It is parallel for the bonding and antiparallel for the antibonding resonance. Following, we will verify the orientation of the dipoles explicitly by looking at the electric field lines. At present, it suffices to recall the polarity of the surface polarization charges shown in Fig. 3 from which the orientation of the dipoles can be also deduced. Unlike the Poynting flux outside the particle, which arises from the superposition of the incoming field with an effective overall dipole field of the particle, inside the core-shell particle the energy fluxes of two dipoles which are either parallel (bonding) or antiparallel (antibonding) mix.

As explained at the beginning of this section, in the dipole regime the singular points of the Poynting flux are all located in the xz plane. The figures summarizing the results for the Poynting flux inside the particle are thus constructed in analogy to Fig. 6. We will show the position of the singular points with respect to the particle center and for representative wave numbers the topology of the energy flux. The only difference is that the radial distance of the singular points from the center is now less than the particle radius a .

3. Antibonding dipole resonance

The inside topology of the Poynting flux near the antibonding dipole resonance of the model core-shell particle is presented in Fig. 7. On the scale of this figure, the localized surface electromagnetic modes characteristic for the type of light scattering we discuss in this paper can be clearly identified. They are associated with the optical whirlpools [31] in the Poynting flux which are indicated by light blue circles. The energy is rotating around whirlpools and thus $S_r = 0$. However, since S_θ has a maximum [32] at these points, whirlpools are not ordinary singularities. At the two interfaces, the whirlpools are oriented in the opposite direction. It is instructive to trace the direction of the whirlpools to the orientation of the inner and the outer dipole. The polarity of the surface charges at the two interfaces as well as the electric field lines to be presented in Sec. III C show that at the antibonding resonance, the two dipoles are antiparallel. Hence, in the shell region the electric field lines belonging to the outer and the inner dipole are parallel. In the vicinity of the whirlpools, this leads then to a rectifying Poynting flux inside the shell, with Poynting field lines separated by a $S_r = 0$ isocline.

We now go through Fig. 7 step by step. The antibonding dipole resonance is at $\lambda_{ab,1}^{-1} \approx 1767.293 \text{ cm}^{-1}$. A representative topology of the Poynting vector field for $\lambda^{-1} < \lambda_{ab,1}^{-1}$ is the one of region VIII shown in the upper right panel of Fig. 7 for the particular wave number $\lambda^{-1} = 1767.289 \text{ cm}^{-1}$. Like before, the singular points are the intersection points between two lines of different color corresponding, respectively, to the $S_r = 0$ and $S_\theta = 0$ isoclines. Very close to horizontal $S_r = 0$ isoclines (blue) in the negative xz half-plane is also a $S_\theta = 0$ isocline (green). Both come from the outside and have

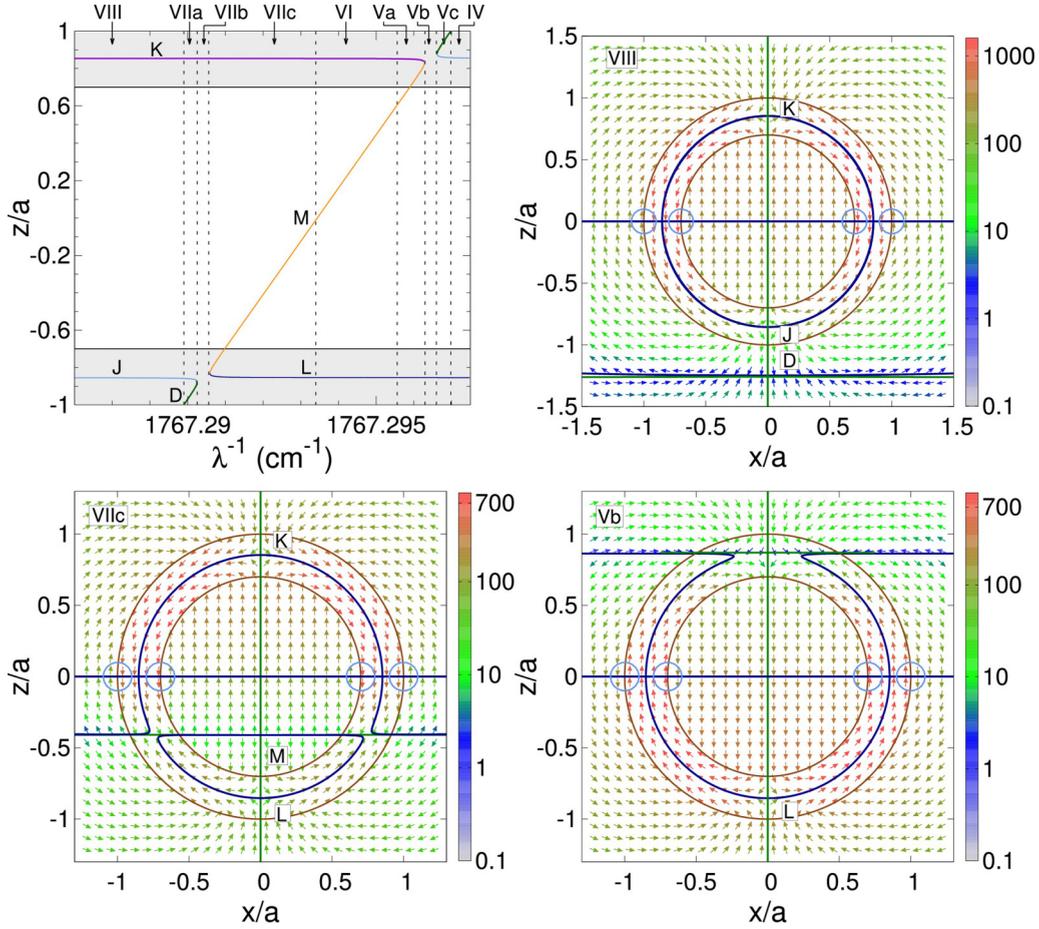


FIG. 7. (Color online) Top left: Position of the singular points (Arabic letters) occurring in the Poynting field inside the model particle ($f = 0.7$ and $a = 0.1 \mu\text{m}$) in the vicinity of the antibonding dipole resonance at $\lambda_{ab,1}^{-1} \approx 1767.293 \text{ cm}^{-1}$. The different topologies are indicated by Roman numbers and the shaded regions denote the shell. The other three panels show the Poynting flux for three wave numbers, each one is representative for a certain topology. The arrows show the direction of the Poynting flux at each point, while the modulus of the Poynting vector normalized to the incident flux of energy is encoded by the color of the arrows. The intersections of the isoclines $S_\theta(r, \theta) = 0$ (green) and $S_r(r, \theta) = 0$ (blue) determine the singular points. The shell and the core are again indicated by brown circles and the optical whirlpools are marked by light blue circles.

presently no physical consequences. In region VIII, there are two singular points inside the shell, K and J, and, as discussed before (see Fig. 6), two singular points outside the particle, C and D, from which only D is within the range of Fig. 7. The Poynting flux shows that the particle is emitting and reabsorbing light to-and-fro the outside region. In the vicinity of the core, the Poynting flux in the shell resembles the flux around an excited dipole. The core is emitting energy into the shell and is also reabsorbing energy from it. The singular points inside the shell arise therefore from an interference between the electromagnetic fields of an inner and an outer dipole.

In region VIII, the saddle point K arises from field lines emitted from and reabsorbed by the outer dipole meeting field lines which are emitted from the inner dipole. The field lines take then their way to the left and right, that is, to $\pm x$, causing thereby a rectified energy flux. At the saddle point J, on the other hand, the rectified energy flux is divided, some field lines are reentering the core and some are leaving the particle. In the shell region, the points J and K operate thus analogously to the points C and D in the outside region of the particle (cf.

region VIII of Fig. 6). One can hence interpret the reabsorbed energy flow of the outer dipole as light which is incident on the core and interacting there with the inner dipole.

For wave numbers closer to the resonance, the outside saddle point D enters the shell region, as can be seen in the top left panel of Fig. 7, where for $\lambda^{-1} \approx 1767.29 \text{ cm}^{-1}$ the green line corresponding to the singular point D is coming up from $z/a = -1$. In the top left panel of Fig. 6, on the other hand, the green line disappears for that wave number at $r/a = 1$. The point D is caused by the intersection of the $S_r = 0$ isocline (blue line) with the $S_\theta = 0$ isocline (green line), which lies on the z axis. With the point D the $S_r = 0$ isocline is also entering the particle. There has to be thus an avoided crossing with the $S_r = 0$ isocline already existing inside the shell because isoclines are solutions of the differential equation $\frac{dr}{d\theta} = r \frac{S_r}{S_\theta}$ and a crossing would violate the uniqueness of the solution [29]. As a result (see the top left panel of Fig. 7), there is only one singular point, the point K, in region VIIb, where $\lambda^{-1} < \lambda_{ab,1}^{-1}$, and one singular point, the point L, in region Vb, where $\lambda^{-1} > \lambda_{ab,1}^{-1}$. The Poynting flux for the latter is shown in the lower right panel of Fig. 7 and will be discussed in a moment.

The avoided crossing occurs also in region VIIc; the Poynting flux of it is plotted in the bottom left panel of Fig. 7. The $S_r = 0$ isocline entering the shell from the outside goes around it taking its way through the upper half of the xz plane and causing thereby the saddle point K. While the $S_r = 0$ isocline inside the shell enters the core to prevent a crossing and causes thereby the saddle-node point M inside the core and the saddle point L inside the shell. The saddle point L has the same function as the saddle point K. The emitted field lines of the outer dipole are reabsorbed in the shell and meet there the emitted field lines of the inner dipole. The saddle point M, on the other hand, distinguishes between a region where both the inner and the outer dipole have already changed their directions from a region where they have not. In the xz plane, this point is a singularity line. Thus, to visualize the Poynting flux around this saddle point one would have to look at the yz plane.

The topology of the Poynting flux in region Vb is plotted in the lower right panel of Fig. 7 for $\lambda^{-1} = 1767.2965 \text{ cm}^{-1}$. The singular point L can be clearly seen. Since $\lambda^{-1} > \lambda_{ab,1}^{-1}$, both dipoles have changed their direction as can be also inferred from the orientation of the energy whirlpools at $z = 0$. For wave numbers well above $\lambda_{ab,1}^{-1}$, the topology of the energy flux inside the particle is the one of region IV. There are now two saddle points L and J corresponding to the singular points K and J in region VIII, respectively. The topology before and after the resonance is thus in fact the same only upside down because the inner and the outer dipole changed simultaneously their direction.

Up to this point, we discussed the Poynting flux near the antibonding dipole resonance of the dissipationless model particle. Since the dielectric functions for the core and the shell are real [see Eq. (16)], only radiative damping is thus accounted for so far. In a real particle, however, dissipative losses occur as well. The dielectric functions for the core and the shell of the CaO/Al₂O₃ particle plotted in the left bottom panel of Fig. 2 have imaginary parts. From the work of Wang and co-workers [29] we know that the topology of the Poynting vector is very sensitive to dissipation. We

expect therefore the Poynting flux of the CaO/Al₂O₃ particle to deviate from the Poynting flux of the model particle. Indeed, for the antibonding resonance we found by artificially adding an imaginary part to the dielectric function of the model particle that large imaginary parts of the core and the shell dielectric functions lead in the shell region to a dominance of the inner dipole and to a strong damping of the outer dipole. Since the saddle points are an outgrowth of the relative strength of the two dipoles, it is clear that not all the singular points of the dissipationless model particle may appear for a particle with dissipation. For the particular case of a CaO/Al₂O₃ particle, this can be seen in Fig. 8, where we plot for wave numbers near the antibonding dipole resonance in panel (a) the positions of the outer singular points and in panel (b) the positions of the inner singular points. Compared to the model particle, many outer singular points are missing, while most of the inner singular points are still present.

4. Bonding dipole resonance

Let us return to the model particle and discuss the topology of the Poynting vector field near the bonding dipole resonance at $\lambda_{b,1}^{-1} \approx 1095.669 \text{ cm}^{-1}$. The results are summarized in Fig. 9. As it was the case for the antibonding resonance, optical whirlpools appear at the core-shell and the shell-vacuum interface. They correspond to surface-localized electromagnetic modes. However, since at the bonding resonance the inner and the outer dipole are oriented parallel, the whirlpools at the two interfaces rotate now in the same direction. For $\lambda^{-1} < \lambda_{b,1}^{-1}$, for instance, in region VIIa, the whirlpools at $x/a = -1, z/a = 0$ and $x/a = -0.7, z/a = 0$ both rotate clockwise while the whirlpools at $x/a = 0.7, z/a = 0$ and $x/a = 1, z/a = 0$ both rotate anticlockwise. Behind the resonance, that is, for $\lambda^{-1} > \lambda_{b,1}^{-1}$, for instance, in region VIIc the situation is reversed.

In the vicinity of two rectified optical whirlpools energy flows in the opposite direction. As a result, the singular points N and O appear in regions VIIa and VIIIb. They are caused by a $S_\theta = 0$ isocline inside the shell, indicated by a green line, which forms a circle around the core. The two singular

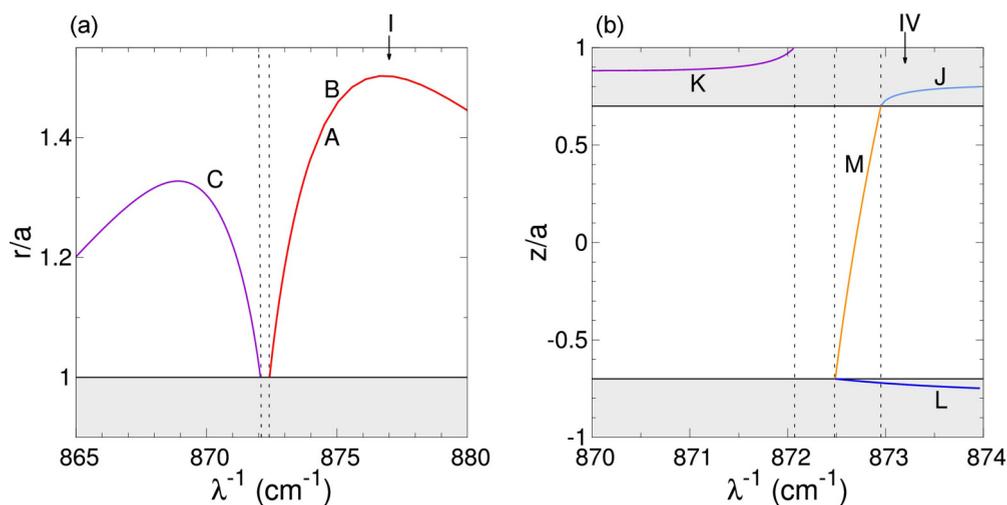


FIG. 8. (Color online) Position of singular points (Arabic letters) in the Poynting field outside (a) and inside (b) a CaO/Al₂O₃ particle with $f = 0.7$ and $a = 0.4 \mu\text{m}$ for wave numbers near the antibonding resonance at $\lambda_{ab,1}^{-1} \approx 871.62 \text{ cm}^{-1}$. Roman numerals indicate regions with fixed topology which were also found for the model particle. The shaded regions denote the shell.

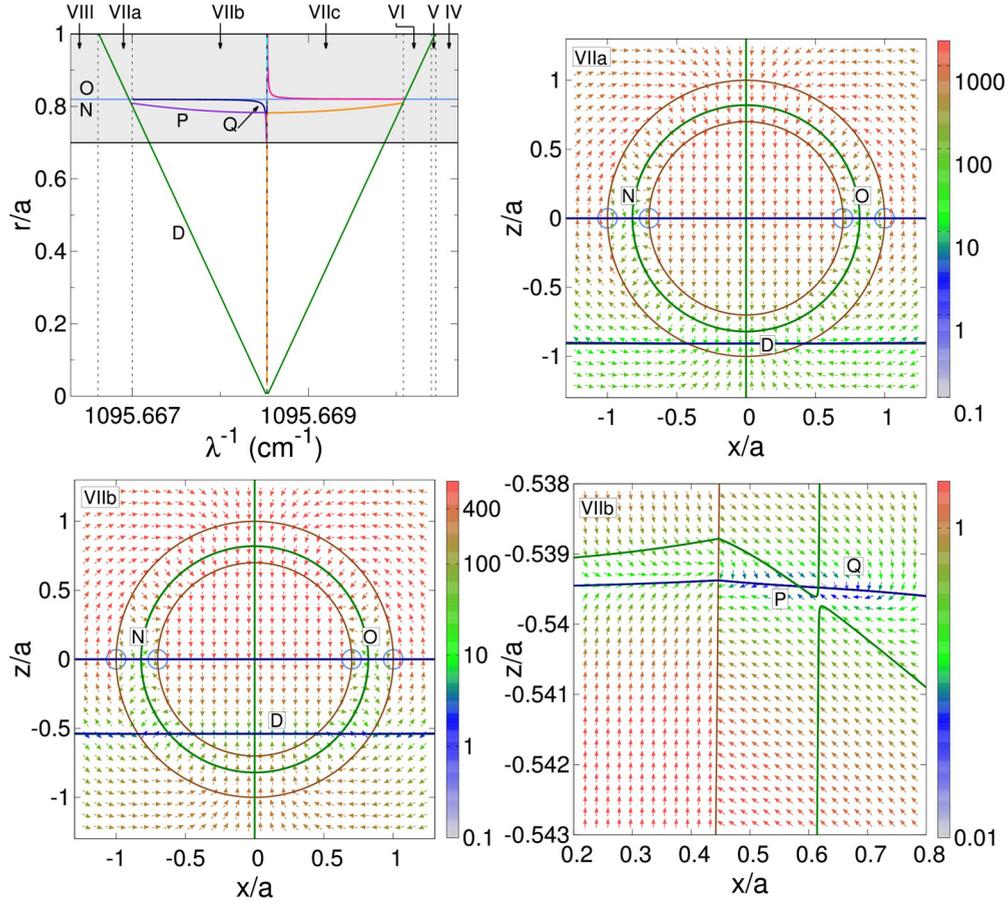


FIG. 9. (Color online) Top left: Position of the inside singular points (Arabic letters) in the Poynting field of the model particle ($f = 0.7$ and $a = 0.1 \mu\text{m}$) in the vicinity of the bonding resonance at $\lambda_{b,1}^{-1} \approx 1095.669 \text{ cm}^{-1}$. Roman numbers indicate spectral regions with a fixed topology while the shaded area denotes the shell. The upper right and the lower left panels show the Poynting field for two representative wave numbers whereas the panel on the lower right is just a zoom-in into the panel to its left. The modulus of the Poynting vector normalized to the flux of incident energy is encoded in the color of the arrows. The intersections of the isoclines $S_\theta(r, \theta) = 0$ (green) and $S_r(r, \theta) = 0$ (blue) determine the singular points. The shell and the core are indicated by brown circles and the optical whirlpools are shown as light blue circles.

points N and O, which separate the field lines entering the core from the field lines leaving the particle, operate thus in the same way as the two singular points A and B of region I outside the particle (see lower right panel in Fig. 6) which separate the field lines entering the particle from the ones leaving it.

In addition to the points N and O for wave numbers close to the resonance the saddle point D appears inside the particle. The closer the wave number is to the resonance, the more D moves inside the particle. In region VIIa D is inside the shell, while in region VIIb D is inside the core. Underneath the $S_r = 0$ isocline at $z < 0$ is moreover hidden another $S_\theta = 0$ isocline which is coming from the outside. Hence, if the saddle point D is deep enough inside the particle an avoided crossing occurs between the two $S_\theta = 0$ isoclines. In the lower left panel of Fig. 9, only the $S_\theta = 0$ isocline encircling the core is visible. To clarify the situation, we replotted it therefore on a magnified scale in the lower right panel. There it can be seen that the $S_\theta = 0$ isocline coming from the outside of the particle is going downwards in the shell, while the other $S_\theta = 0$ isocline is going towards the core. As a result, the singular points Q and P appear. While the point Q is an unstable foci, that is, an energy sink in the xz plane, the point P is a saddle point. In

region VI, where $\lambda^{-1} > \lambda_{b,1}^{-1}$, the saddle point D is still inside the shell but lies now above the $S_\theta = 0$ isocline existing in the shell and encircling the core. The topology in this region is the same as in region VIIa, but upside down and with different orientation of the optical whirlpools, since the inner and outer dipole simultaneously changed directions.

Having discussed for the dissipationless model particle the topology of the inside Poynting vector field near the bonding dipole resonance, we now comment on the energy flux near such a resonance in a real particle with finite dissipation, taking again the $\text{CaO}/\text{Al}_2\text{O}_3$ particle as an example. For the bonding resonance, we empirically found by varying the imaginary parts of the dielectric function the outer dipole to be rather stable, even for large values of $\epsilon''_{1,2}$. The inner dipole, however, disappears. As a result, there are also no surface-localized electromagnetic modes at the core-shell interface anymore. The results for the bonding dipole resonance of the $\text{CaO}/\text{Al}_2\text{O}_3$ particle shown in Fig. 10 are consistent with these empirical findings. Whereas almost all singular points in the Poynting flux outside the particle are preserved because of the robustness of the outer dipole, inside the shell most of the singularities disappeared. The situation is thus just reversed to the one we found for the antibonding resonance.

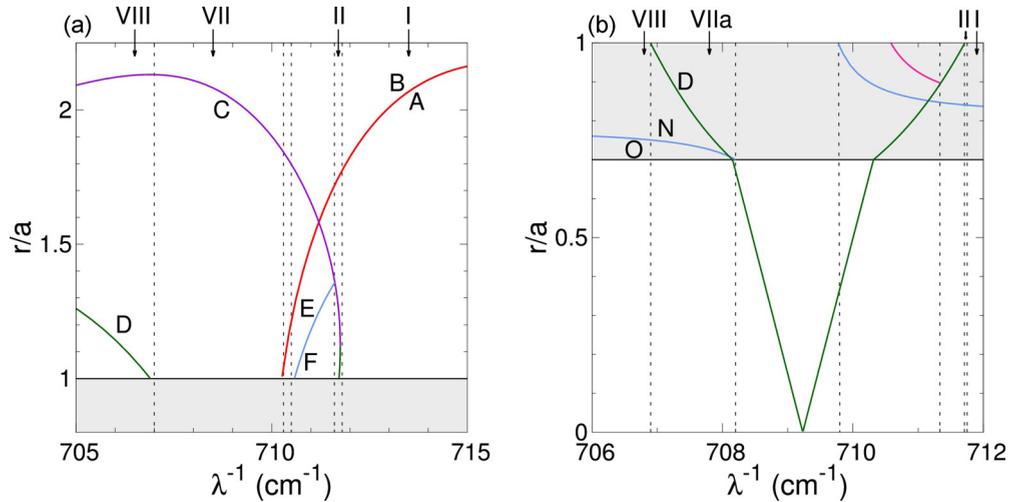


FIG. 10. (Color online) Position of the singular points (Arabic letters) of the Poynting field outside (a) and inside (b) of a $\text{CaO}/\text{Al}_2\text{O}_3$ particle with filling factor $f = 0.7$ and radius $a = 0.4 \mu\text{m}$ in the vicinity of the bonding resonance at $\lambda_{b,1}^{-1} \approx 709.63 \text{ cm}^{-1}$. Roman numbers indicate regions with a fixed topology which were also found for the model particle and the shaded regions denote the shell.

C. Electric field

We now investigate for the model particle the electric field for wavelengths in the vicinity of the bonding and the antibonding dipole resonance and contrast it with the field in the vicinity of the core resonance. For comparison, we also include the field near the anomalous resonance of a homogeneous particle. For all four resonances, we calculate the electric field amplitude $|\vec{E}|^2$ and the real part of the electric field $\text{Re}(\vec{E})$ for wave numbers where the topology of the Poynting flux is of type I shown in Fig. 6: For the homogeneous particle $\lambda^{-1} = 1406.5 \text{ cm}^{-1}$, while for the core-shell particle $\lambda^{-1} = 306.026 \text{ cm}^{-1}$ (core resonance), $\lambda^{-1} = 1095.74 \text{ cm}^{-1}$ (bonding resonance), and $\lambda^{-1} = 1767.375 \text{ cm}^{-1}$ (antibonding resonance).

The results for the electric field are summarized in Fig. 11, where the value of the electric field amplitude is encoded in colors and the direction of the real part of the electric field is given by black arrows. The electric field of the incident wave is polarized in the x direction. Hence, the induced charge displacements are also in the x direction.

Let us first discuss the field for the anomalous resonance of the homogeneous particle shown in Fig. 11(a). From the electric field structure outside the particle it is clear that a dipole mode is excited. The field lines by definition go from positive to negative charges, but the dipole of course points towards positive charges. Hence, the excited dipole is oriented in negative x direction implying polarization-induced surface charges to be positive for the $x < 0$ hemisphere and negative for the $x > 0$ hemisphere. As can be seen from the linear scale of the plot, the variation of the electric field amplitude inside the homogeneous particle is very small. Yet, a shallow minimum occurs at the center of the particle.

The electric field for the core-shell particle is plotted in Figs. 11(b) to 11(d) for the core, the bonding, and the antibonding resonance, respectively. Inside the core, the electric field resembles for all three resonances the field of a homogeneous particle. On the logarithmic scale used for the plots, this cannot be seen but a linear scale would reveal an

onionlike structure similar to the one depicted in Fig. 11(a). Only for the core resonance [Fig. 11(b)], however, would the minimum of the field still be at the center of the particle, whereas for the bonding and antibonding resonances the field at the center is in fact maximal. The core resonance [Fig. 11(b)] has most in common with the anomalous resonance of the homogeneous particle [Fig. 11(a)] because it arises from the resonance condition of the core dielectric function. Only a single dipole is thus excited as can be seen from the field lines. They originate from the $x < 0$ hemisphere of the core-shell interface and terminate in its $x > 0$ hemisphere, signaling positive and negative polarization-induced surface charges, respectively. At the shell-vacuum interface the field lines are only refracted, leading to an inhomogeneous field inside the shell which is in most parts much smaller than in the core.

For the bonding and the antibonding resonance, the situation is different because now two dipoles are involved. From the polarization-induced surface charges shown in Fig. 3 we already know that for the bonding resonance the dipoles are orientated parallel, whereas for the antibonding resonance they are orientated antiparallel. The field lines shown in Figs. 11(c) and 11(d) verify this. Let us first look at Fig. 11(c) displaying the field for the bonding dipole resonance. The shell-core interface in the $x < 0$ hemisphere is a source for field lines, indicating positive charges, whereas the shell-core interface in the $x > 0$ hemisphere is a sink for field lines, indicating negative charges. At the shell-vacuum interface, the situation is the same. Both the inner and the outer dipole are thus oriented in the negative x direction. Inside the shell, the two dipole fields interfere which destroys the homogeneity of the field. For $z = 0$ and $x/a \approx \pm 0.9$ destructive interference occurs as the outgoing field lines from the inner dipole cancel the inner field lines of the outer dipole. At $z/a = \pm 0.9$ and $x = 0$, on the other hand, constructive interference occurs because outer field lines of the inner dipole and inner field lines of the outer dipole run parallel leading to a high electric field. At the antibonding resonance shown in Fig. 11(d), the shell-core interface in the $x < 0$ hemisphere is a sink for

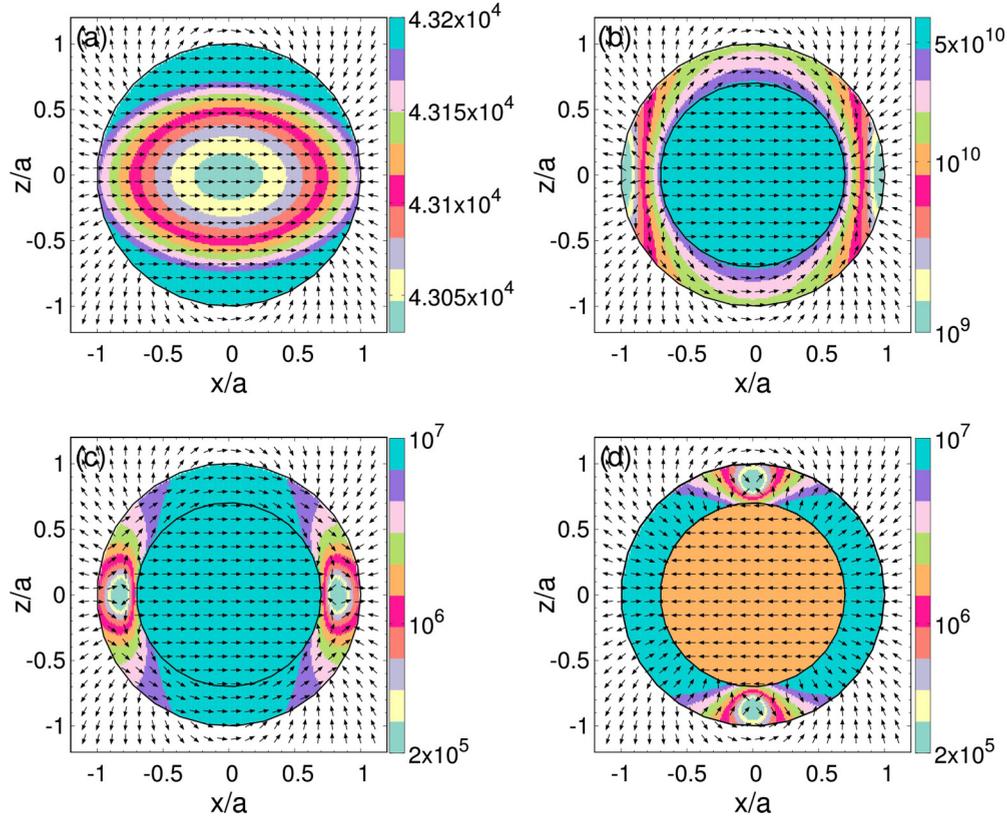


FIG. 11. (Color online) Electric field amplitude $|\vec{E}|^2$ and the direction of the real part of the electric field in the vicinity of the core (b), the bonding (c), and the antibonding (d) dipole resonance of the model particle ($f = 0.7$ and $a = 0.1 \mu\text{m}$). Panel (a) shows for comparison results for the dipole resonance of a homogeneous particle of the same size made out of the shell material. Black arrows denote the direction of the real part of the electric field while the colors give the field amplitude. The wave numbers used for the plots are given in the main text.

field lines while in the $x > 0$ hemisphere it is a source. The shell-vacuum interface, on the other hand, is a source for field lines in the $x < 0$ hemisphere and a sink $x > 0$ hemisphere. The inner and the outer dipole are thus oriented antiparallel. In the shell the inner field lines of the outer dipole interfere with the outer field lines of the inner dipole, leading at $z/a = \pm 0.9$ and $x/a = 0$ to a minimum in the field.

The electric field in core-shell particles differs therefore dramatically from the one in a homogeneous particle. Whereas the latter is homogeneous, the former is very inhomogeneous, varying in the shell for the bonding and the antibonding resonance over almost two orders of magnitude. At the bonding resonance, the field amplitude is also high in the core, but for the antibonding resonance it is one order of magnitude smaller in the core than in most parts of the shell. The inhomogeneity of the electric field can be used to control the dissipation of energy inside a core-shell particle by varying the wavelength of the incident light. For the model particle discussed in this section there is of course no dissipation since the dielectric functions of the core and the shell are purely real, but for physical particles the dielectric functions are complex and a control mechanism is conceivable.

D. Dissipation

In this section, we present results for the dissipation of energy inside a $\text{CaO}/\text{Al}_2\text{O}_3$ particle. According to Eq. (15), it depends on the imaginary parts of the dielectric functions as

well as on the amplitude of the electric field. Since the latter is strongly enhanced in the vicinity of anomalous resonances, even small imaginary parts of the dielectric functions may thus lead to a huge dissipation [33]. The field enhancement in a core-shell particle is moreover rather inhomogeneous, and there will be hence spots inside it where dissipation is strong and spots where it will be rather weak, irrespective of the magnitude of the (spatially homogeneous) imaginary parts of the dielectric functions.

In Fig. 12, we show the electric field and the dissipation for the $\text{CaO}/\text{Al}_2\text{O}_3$ particle near the bonding and the antibonding dipole resonance. The wave numbers are in both cases in the topological region I where the Poynting flux outside the particle displays Tribelsky ears. For the bonding resonance $\lambda^{-1} = 715 \text{ cm}^{-1}$ leading to $\varepsilon_1'' = 0.104$ and $\varepsilon_2'' = 0.304$, while for the antibonding resonance $\lambda^{-1} = 877 \text{ cm}^{-1}$ giving rise to $\varepsilon_1'' = 0.0492$ and $\varepsilon_2'' = 0.0657$.

The electric field inside the $\text{CaO}/\text{Al}_2\text{O}_3$ particle shown in the upper two panels of Fig. 12 is inhomogeneous as it was for the model particle discussed in the previous section. Due to constructive and destructive interference of the electric fields of the excited dipoles inside the shell, there are points where the amplitude of the electric field is enhanced and points where it is very small. For the bonding resonance [Fig. 12(a)], the field amplitude inside the core is high and more or less homogeneous, whereas inside the shell the field amplitude varies over two orders of magnitude reaching at $x/a = \pm 0.9$ and $z/a = 0$ its smallest value which is two

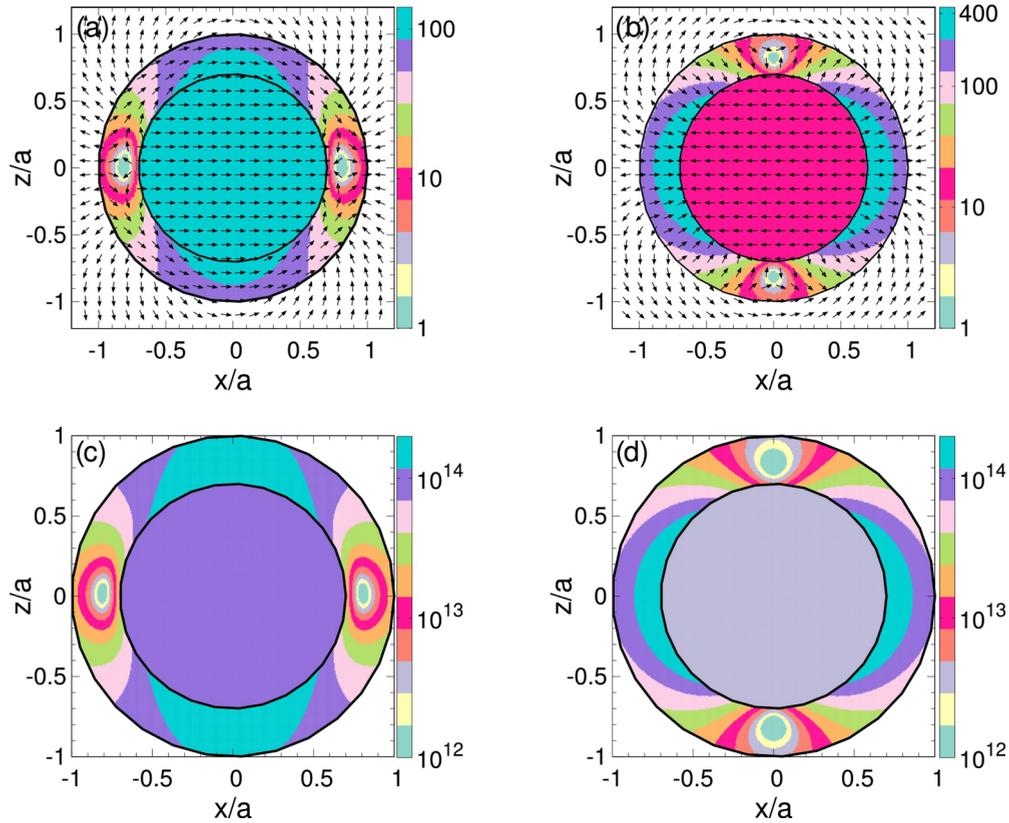


FIG. 12. (Color online) The top two panels show the electric field amplitude $|\vec{E}|^2$ and the direction of the real part of the electric field in the vicinity of the bonding (a) and the antibonding (b) dipole resonances of a CaO/Al₂O₃ particle with $f = 0.7$ and $a = 0.4 \mu\text{m}$. The wave numbers are, respectively, $\lambda^{-1} = 715 \text{ cm}^{-1}$ and $\lambda^{-1} = 877 \text{ cm}^{-1}$. The two bottom panels depict the dissipation inside the particle for the bonding (c) and antibonding (d) dipole resonances, respectively. Black arrows in the upper two panels denote the direction of the real part of the electric field, while colors indicate the electric field amplitude (upper two panels) or the dissipation (lower two panels).

orders of magnitude lower than inside the core. Compared to the dissipationless model particle the electric field inside the core of the CaO/Al₂O₃ particle is no longer symmetric along the x axis and it reaches its maximum no longer in the center of the particle but around $z/a = 0.7$ and $x/a = 0$. On the logarithmic scale this cannot be seen, but a linear scale would reveal these features. The spatial distribution of the dissipation near the bonding resonance [Fig. 12(c)] parallels more or less the field distribution. It is homogeneous inside the core, where it is also rather high, and varies strongly inside the shell reaching its smallest value at $x/a = \pm 0.9$ and $z/a = 0$. The results for the antibonding resonance, given in Figs. 12(b) and 12(d), show the same overall trend. Inside the core, the field and the dissipation are homogeneous whereas in the shell strong variations occur. In contrast to the bonding resonance, the electric field inside the core is now, however, smaller than in most parts of the shell where destructive and constructive interference lead moreover to a strongly varying field. This feature is also preserved in the spatial distribution of the dissipation. It varies strongly within the shell and is in most parts of it two orders of magnitude higher than inside the core. There are, however, also narrow regions where dissipation is strongly suppressed.

The spatial inhomogeneities of the electric field in the shell of the model particle can thus be also found in the shell of the CaO/Al₂O₃ particle. Since the dielectric functions of the

latter have finite imaginary parts, the field inhomogeneities lead now, however, also to inhomogeneities in the dissipation. Within the shell, the dissipation of energy varies for both the bonding and the antibonding resonance over almost two orders of magnitude giving rise to extended regions of high dissipation and well-localized cold spots where dissipation is rather low although the dielectric function of the shell is spatially homogeneous.

IV. CONCLUSIONS

In our previous work, we proposed to use the antibonding dipole resonance of dielectric core-shell particles having a core with negative and a shell with positive electron affinity to determine by infrared attenuation spectroscopy the number of surplus electrons of the particle. Due to the particular choice of the electron affinities, the electrons would be confined to the shell region, leading to a high volume electron density which in turn would strongly affect the electric polarizability of the particle and hence the position of the extinction resonances. In particular, the maximum of the antibonding dipole resonance, which we initially called shell resonance since it is absent for homogeneous particles, turned out to be very charge sensitive. To understand the mechanism leading to this resonance and also to make contact to the field of plasmonics, we investigated in this work neutral dielectric

core-shell particles, using a CaO/Al₂O₃ particle as a physical example and a dissipationless model core-shell particle as an idealized system. The scattering of light is in both cases mediated by infrared transverse optical phonons.

We showed that the series of bonding and antibonding resonances arising in the surface mode regime of the shell are attached to in-phase and out-of-phase multipolar polarization-induced surface charges building up at the two interfaces to satisfy the boundary conditions of the Maxwell equations. For the series of bonding resonances the surface charges are in phase, whereas for the series of antibonding resonances they are out of phase. The inner and the outer dipole associated with the two lowest resonances are thus aligned parallel for the bonding and antiparallel for the antibonding resonance. We demonstrated that both series of resonances scatter light anomalously, that is, originate from selective excitation of surface modes giving then rise to an inverse hierarchy in the extinction cross section. We also analyzed the topology of the Poynting flux in the vicinity of the bonding and the antibonding dipole resonance. The outside Poynting flux near these two resonances is determined by an effective dipole describing the effective outer field of the inner and the outer dipole. The topology of the outside Poynting flux is thus for the bonding and the antibonding resonance similar to the Poynting flux of a homogeneous particle. Inside the particle, however, the Poynting flux is determined by the interplay of the outer field of the inner and the inner field of the outer dipole. As a result, the topology of the inside Poynting flux depends on the alignment of the two dipoles and is thus different for the bonding and the antibonding resonance.

Inside the particle, the Poynting flux, the electric field, and the dissipation of energy are highly inhomogeneous. Of particular interest, perhaps also from the technological viewpoint of laser heating, is the inhomogeneous dissipation near the antibonding dipole resonance. Inside the shell, there are broad banana-shaped hot spots where the dissipation is almost two orders of magnitude larger than in the core as well as rather localized cold spots where the dissipation is almost an order smaller. Although we do not expect the enhanced dissipation in the shell to be a problem for the optical charge measurement we proposed since the surplus electrons are bound by an energy on the order of the shell material's electron affinity, which is for technologically relevant dielectrics such as Al₂O₃ in the range of electron volts, the heating of the confined electron gas should be investigated in the future.

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APPENDIX

Using the orthogonality of the vector spherical harmonics [25,27], the eight expansion coefficients a_n , b_n , c_n , d_n , f_n , g_n , v_n , and w_n can be straightforwardly calculated from the core-shell boundary conditions at $r = b$,

$$(\vec{E}_2 - \vec{E}_1) \times \vec{r} = 0, \quad (\text{A1})$$

$$(\vec{H}_2 - \vec{H}_1) \times \vec{r} = 0, \quad (\text{A2})$$

and the shell-vacuum boundary conditions at $r = a$,

$$(\vec{E}_s + \vec{E}_{\text{in}} - \vec{E}_2) \times \vec{r} = 0, \quad (\text{A3})$$

$$(\vec{H}_s + \vec{H}_{\text{in}} - \vec{H}_2) \times \vec{r} = 0, \quad (\text{A4})$$

yielding eight equations for the eight unknowns.

The coefficients a_n and b_n determining the scattering components of the electromagnetic fields in the outer space, Eqs. (4) and (5), turn then out to be [27,28]

$$a_n = C_n^{-1} \{ \psi_n(y) [\psi'_n(m_2 y) - A_n \chi'_n(m_2 y)] - m_2 \psi'_n(y) [\psi_n(m_2 y) - A_n \chi_n(m_2 y)] \}, \quad (\text{A5})$$

$$b_n = D_n^{-1} \{ m_2 \psi_n(y) [\psi'_n(m_2 y) - B_n \chi'_n(m_2 y)] - \psi'_n(y) [\psi_n(m_2 y) - B_n \chi_n(m_2 y)] \} \quad (\text{A6})$$

with

$$A_n = \frac{m_2 \psi_n(m_2 x) \psi'_n(m_1 x) - m_1 \psi'_n(m_2 x) \psi_n(m_1 x)}{m_2 \chi_n(m_2 x) \psi'_n(m_1 x) - m_1 \chi'_n(m_2 x) \psi_n(m_1 x)}, \quad (\text{A7})$$

$$B_n = \frac{m_2 \psi_n(m_1 x) \psi'_n(m_2 x) - m_1 \psi_n(m_2 x) \psi'_n(m_1 x)}{m_2 \chi'_n(m_2 x) \psi_n(m_1 x) - m_1 \psi'_n(m_1 x) \chi_n(m_2 x)}, \quad (\text{A8})$$

$$C_n = \xi_n(y) [\psi'_n(m_2 y) - A_n \chi'_n(m_2 y)] - m_2 \xi'_n(y) \times [\psi_n(m_2 y) - A_n \chi_n(m_2 y)], \quad (\text{A9})$$

$$D_n = m_2 \xi_n(y) [\psi'_n(m_2 y) - B_n \chi'_n(m_2 y)] - \xi'_n(y) \times [\psi_n(m_2 y) - B_n \chi_n(m_2 y)]. \quad (\text{A10})$$

For the fields inside the core, Eqs. (10) and (11), the coefficients read as

$$c_n = -D_n^{-1} F_n m_2 m_1 \times \frac{[\psi_n(m_2 x) \chi'_n(m_2 x) - \chi_n(m_2 x) \psi'_n(m_2 x)]}{[m_1 \chi_n(m_2 x) \psi'_n(m_1 x) - m_2 \psi_n(m_1 x) \chi'_n(m_2 x)]}, \quad (\text{A11})$$

$$d_n = -C_n^{-1} F_n m_2 m_1 \times \frac{[\psi_n(m_2 x) \chi'_n(m_2 x) - \chi_n(m_2 x) \psi'_n(m_2 x)]}{[m_2 \chi_n(m_2 x) \psi'_n(m_1 x) - m_1 \psi_n(m_1 x) \chi'_n(m_2 x)]} \quad (\text{A12})$$

with

$$F_n = [\psi'_n(y) \xi_n(y) - \psi_n(y) \xi'_n(y)], \quad (\text{A13})$$

while for the fields inside the shell, Eqs. (7)–(9), the coefficients become

$$f_n = D_n^{-1} m_2 F_n, \quad (\text{A14})$$

$$g_n = C_n^{-1} m_2 F_n, \quad (\text{A15})$$

$$v_n = D_n^{-1} m_2 F_n B_n, \quad (\text{A16})$$

$$w_n = C_n^{-1} m_2 F_n A_n. \quad (\text{A17})$$

- [1] S. J. Oldenburg, R. D. Averitt, S. L. Westcott, and N. J. Halas, *Chem. Phys. Lett.* **288**, 243 (1998).
- [2] N. J. Halas, S. Lal, S. Link, W.-S. Chang, D. Natelson, J. H. Hafner, and P. Nordlander, *Adv. Mater.* **24**, 4842 (2012).
- [3] X. Fan, W. Zheng, and W. J. Singh, *Light: Sci. Appl.* **3**, e179 (2014).
- [4] P. N. Prasad, *Nanophotonics* (Wiley, Hoboken, NJ, 2004).
- [5] C. Loo, A. Lowery, N. Halas, J. West, and R. Drezek, *Nano Lett.* **5**, 709 (2005).
- [6] E. Ozbay, *Science* **311**, 189 (2006).
- [7] W. Liu, A. E. Miroshnichenko, D. N. Neshev, and Y. S. Kivshar, *ACS Nano* **6**, 5489 (2012).
- [8] W. Liu, A. E. Miroshnichenko, D. N. Neshev, and Y. S. Kivshar, *Phys. Rev. B* **86**, 081407(R) (2012).
- [9] L. Zhang, H. Jing, G. Boisvert, J. Z. He, and H. Wang, *ACS Nano* **6**, 3514 (2012).
- [10] M. I. Stockman, *Nat. Photonics* **2**, 327 (2008).
- [11] A. Alú and N. Engheta, *Phys. Rev. E* **72**, 016623 (2005).
- [12] M. I. Tribelsky and B. S. Luk'yanchuk, *Phys. Rev. Lett.* **97**, 263902 (2006).
- [13] M. I. Tribelsky, *Europhys. Lett.* **94**, 14004 (2011).
- [14] E. Thiessen, R. L. Heinisch, F. X. Bronold, and H. Fehske, *Eur. Phys. J. D* **68**, 98 (2014).
- [15] R. L. Heinisch, F. X. Bronold, and H. Fehske, *Phys. Rev. B* **85**, 075323 (2012).
- [16] R. L. Heinisch, F. X. Bronold, and H. Fehske, *Phys. Rev. Lett.* **109**, 243903 (2012).
- [17] J. Röpcke, J. Lombardi, G. Rousseau, and P. B. Davies, *Plasma Sources Sci. Technol.* **15**, S148 (2006).
- [18] J. Carstensen, H. Jung, F. Greiner, and A. Piel, *Phys. Plasmas* **18**, 033701 (2011).
- [19] V. E. Fortov, O. F. Petrov, A. D. Usachev, and A. V. Zobnin, *Phys. Rev. E* **70**, 046415 (2004).
- [20] R. Ruppin, *Surf. Sci.* **51**, 140 (1975).
- [21] C. Uberoi, *Phys. Lett. A* **76**, 69 (1980).
- [22] E. Prodan, C. Radloff, N. J. Halas, and P. Nordlander, *Science* **302**, 419 (2003).
- [23] T. C. Preston and R. Signorell, *Proc. Natl. Acad. Sci. USA* **108**, 5532 (2011).
- [24] G. Mie, *Ann. Phys. (Leipzig)* **330**, 377 (1908).
- [25] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).
- [26] M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic, New York, 1969).
- [27] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).
- [28] A. L. Aden and M. Kerker, *J. Appl. Phys.* **22**, 1242 (1951).
- [29] Z. B. Wang, B. S. Luk'yanchuk, M. H. Hong, Y. Lin, and T. C. Chong, *Phys. Rev. B* **70**, 035418 (2004).
- [30] H. F. Schouten, T. Visser, and D. Lenstra, *J. Opt. B: Quantum Semiclassical Opt.* **6**, S404 (2004).
- [31] M. V. Bashevoy, V. A. Fedotov, and N. I. Zheludev, *Opt. Express* **13**, 8372 (2005).
- [32] B. S. Luk'yanchuk, M. I. Tribelsky, and V. V. Ternovkij, *J. Opt. Technol.* **73**, 371 (2006).
- [33] B. S. Luk'yanchuk, A. E. Miroshnichenko, M. I. Tribelsky, Y. S. Kivshar, and A. Khokhlov, *New J. Phys.* **14**, 093022 (2012).
- [34] L. D. Landau and E. M. Lifschitz, *Electrodynamics of Continuous Media* (Butterworth-Heinemann, Amsterdam, 1984).
- [35] A. M. Hofmeister, E. Keppel, and A. K. Speck, *Mon. Not. R. Astron. Soc.* **345**, 16 (2003).
- [36] E. D. Palik, *Handbook of Optical Constants of Solids* (Academic, New York, 1985).
- [37] A. S. Barker, *Phys. Rev.* **132**, 1474 (1963).