OSA CONTINUUM

Plasmon resonances of metal nanoparticles in an absorbing medium

MICHAEL I. MISHCHENKO[1,*] AND JANNA M. DLUGACH[2]

[1]NASA Goddard Institute for Space Studies, 2880 Broadway, New York, NY 10025, USA
[2]Main Astronomical Observatory of the National Academy of Sciences of Ukraine, 27 Zabolotny Str., 03143, Kyiv, Ukraine
[*]michael.i.mishchenko@nasa.gov

Abstract: We study the behavior of plasmon resonances of metal nanospheres embedded in an absorbing medium. First-principles far-field computations based on the general Lorenz–Mie theory show that increasing absorption in the host medium broadens and suppresses plasmon resonances in the extinction and effective scattering efficiency factors and suppresses resonance features in the phase function. These effects of absorption are analogous to those on the morphology-dependent resonances of dielectric particles with large size parameters.

© 2019 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

1. Introduction

The subject of electromagnetic scattering by particles embedded in an absorbing host medium has attracted much attention (see, e.g., [1–23] and numerous references therein). In [22,23], the effect of absorption on morphology-dependent resonances of monodisperse spherical particles was studied. It was concluded that increasing absorption in the host medium suppresses (and eventually eradicates) the morphology-dependent resonances and makes them broader. This effect is similar to that of increasing absorption in a spherical particle embedded in a nonabsorbing medium.

Another prominent type of scattering resonances are plasmon resonances exhibited by nanoparticles made of Drude and noble metals [24–26]. So far these resonances have mostly been analyzed by assuming that the host medium is nonabsorbing. However, this assumption can be invalid in many cases. Therefore, the purpose of this short communication is to apply a first-principles computer program developed recently for far-field computations of electromagnetic scattering based on the general Lorenz–Mie theory and study how plasmon resonances of monodisperse metal nanospheres behave with increasing absorption in the host medium.

2. Computations

We study the scattering of a homogeneous plane wave by a spherical particle embedded in an infinite homogeneous host medium. The materials of the medium and the particle are assumed to be linear, isotropic, and nonmagnetic. Consistent with [27–29], we imply the $\exp(-\mathrm{i}\omega t)$ time-harmonic dependence of all electromagnetic fields, where $\mathrm{i} = (-1)^{1/2}$, ω is the angular frequency, and t is time. We define the scattering problem in terms of the particle radius R, the wavelength in a vacuum λ, and the complex refractive indices of the host, m_1, and the particle, m_2, given by

$$m_1 = m_1' + \mathrm{i}m_1'' \tag{1}$$

and

$$m_2 = m_2' + \mathrm{i}m_2'', \tag{2}$$

where $m_1'>0$, $m_1'' \geq 0$, $m_2'>0$, and $m_2'' \geq 0$.

As discussed in [27], the only far-field optical observables inherent to the particle (i.e., those depending only on R, λ, and the relative refractive index $m = m_2/m_1$) are the extinction cross

#379482 https://doi.org/10.1364/OSAC.2.003415
Journal © 2019 Received 2 Oct 2019; revised 8 Nov 2019; accepted 8 Nov 2019; published 25 Nov 2019

OSA CONTINUUM

section $C_{\rm ext}$ entering Eq. (31) of [27] and the 4×4 Stokes scattering matrix $\mathbf{F}(\Theta)$ entering Eq. (30) of [27], where $\Theta \in [0,\pi]$ is the scattering angle. In particular, these quantities are independent of the distance from the particle as well as of the size and shape of a volume of space for which the radiation energy budget is evaluated (cf. Section 7.5.1 of [26]). We will therefore focus on the computation and analysis of these intrinsic optical observables. For convenience of displaying numerical results, we will represent the scattering matrix as follows:

$$\mathbf{F}(\Theta) = \frac{C_{\rm sca}^{\rm eff}}{4\pi}\tilde{\mathbf{F}}(\Theta), \tag{3}$$

where

$$C_{\rm sca}^{\rm eff} = 2\pi \int_0^{\pi} {\rm d}\Theta\, \sin\Theta\, F_{11}(\Theta) \tag{4}$$

is the so-called effective scattering cross section and $\tilde{\mathbf{F}}(\Theta)$ is the dimensionless so-called normalized scattering matrix. The latter satisfies the normalization condition

$$\frac{1}{2}\int_0^{\pi} {\rm d}\Theta\, \sin\Theta\, \tilde{F}_{11}(\Theta) = 1, \tag{5}$$

where $\tilde{F}_{11}(\Theta)$ describes the angular distribution of the scattered intensity in the case of unpolarized incident light and is traditionally called the phase function.

The extinction and effective scattering cross sections and the normalized scattering matrix are computed using the FORTRAN program described in [27,28]. This program is based on the first-principles theory of far-field scattering by particles in an absorbing medium [17] and the general Lorenz–Mie theory applicable to any m_1'' [29], has been thoroughly tested, and is available at https://www.giss.nasa.gov/staff/mmishchenko/Lorenz-Mie.html.

All computations have been performed for Au, Ag, Al, and Na particles assuming that their radius is fixed at $R = 10$ nm. The spectral refractive indices of these metals are taken from [30–32] and are depicted in Fig. 1. The refractive index of the host medium has been assumed to be spectrally independent.

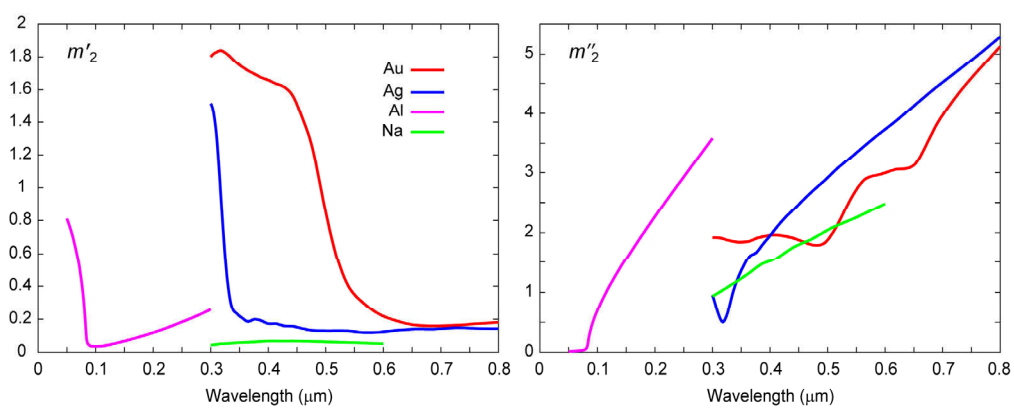

Fig. 1. The real (left-hand panel) and imaginary (right-hand panel) parts of the spectral refractive indices of the four metals used in this study.

Figures 2 and 3 show the extinction efficiency factor

OSA CONTINUUM

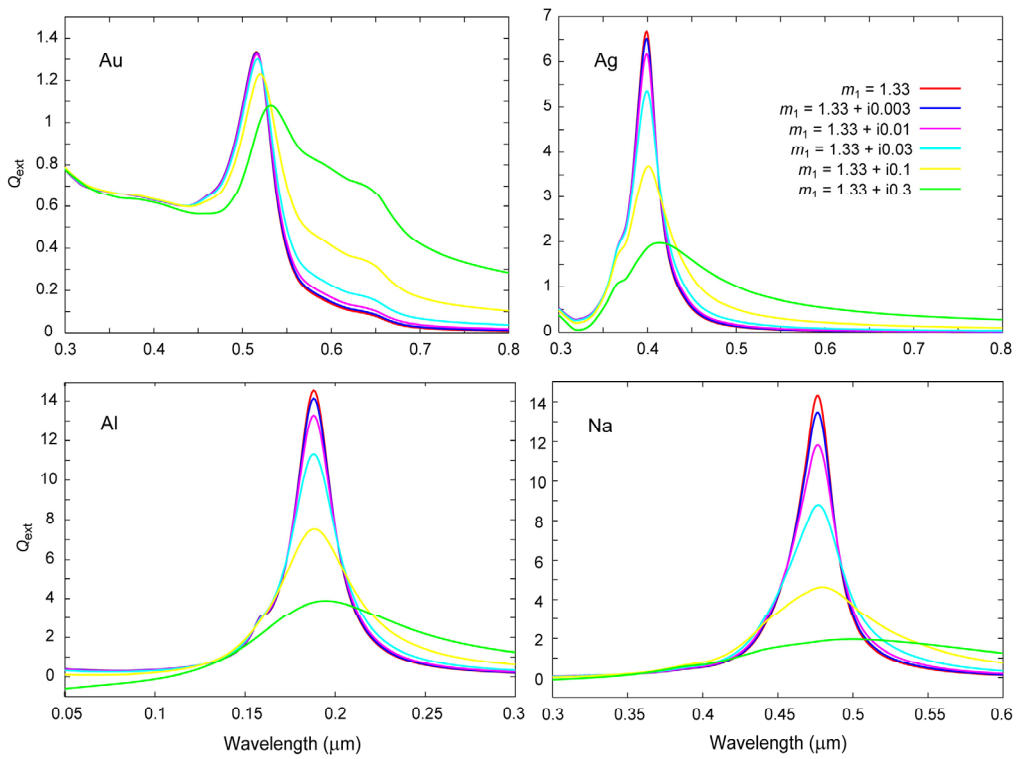

Fig. 2. Spectral extinction efficiency factors of 10-nm spherical particles made of noble and Drude metals.

$$Q_{\text{ext}} = \frac{C_{\text{ext}}}{\pi R^2} \tag{6}$$

and the effective scattering efficiency factor

$$Q_{\text{sca}}^{\text{eff}} = \frac{C_{\text{sca}}^{\text{eff}}}{\pi R^2} \tag{7}$$

as functions of the vacuum wavelength for m_1' fixed at 1.33 and m_1'' ranging from 0 (nonabsorbing host) to 0.3 (strongly absorbing host). Both efficiency factors are dimensionless. To analyze the effect of the real part of the refractive index of the host medium, Fig. 4 shows both efficiency factors for the Na particle computed by assuming that m_1' is fixed at 1.5. Finally, Fig. 5 depicts the phase functions for the Al particle computed by assuming that $m_1 = 1.33$ and $m_1 = 1.33 + \text{i}0.3$.

OSA CONTINUUM

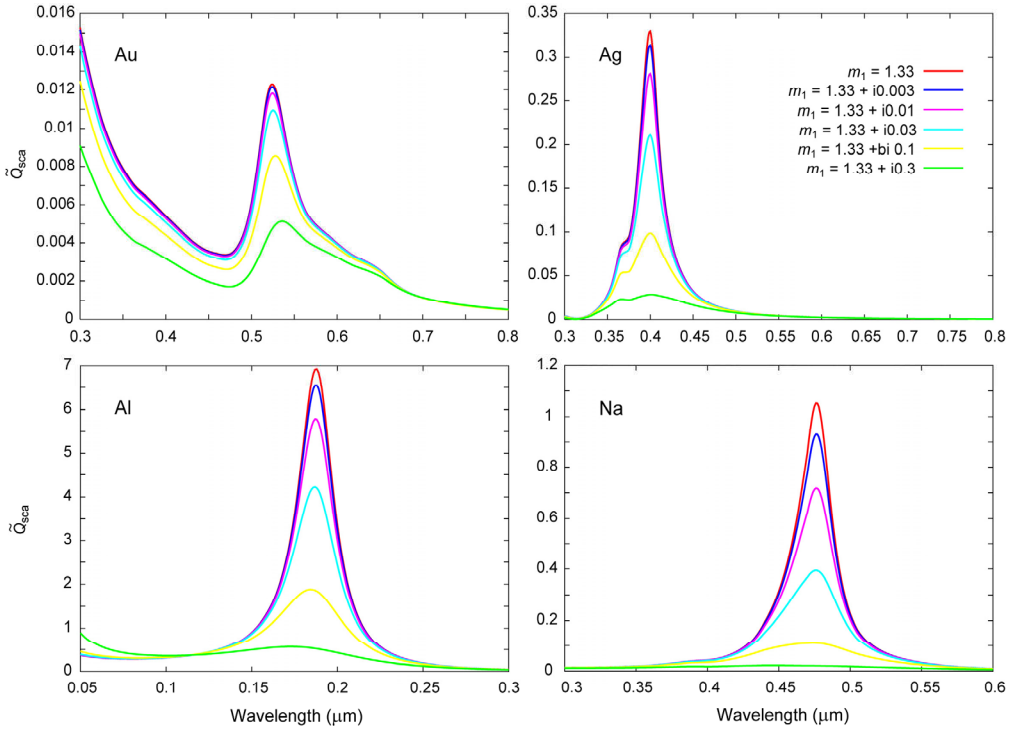

Fig. 3. Spectral scattering efficiency factors of 10-nm spherical particles made of noble and Drude metals.

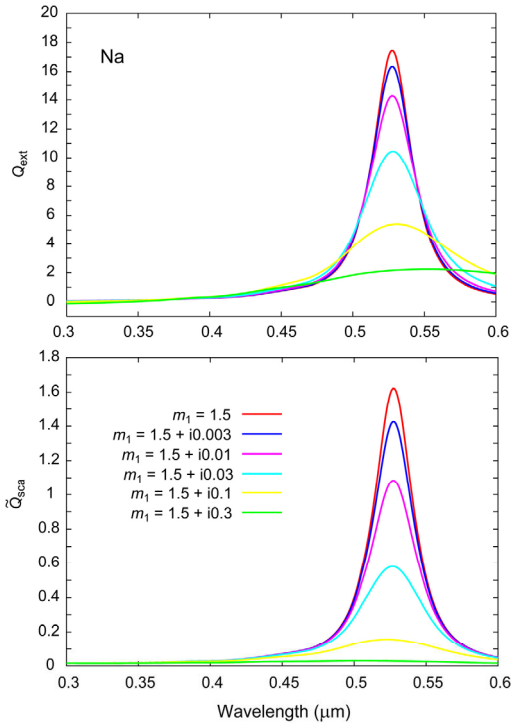

Fig. 4. Spectral extinction and effective scattering efficiency factors of the 10-nm spherical Na particle.

OSA CONTINUUM

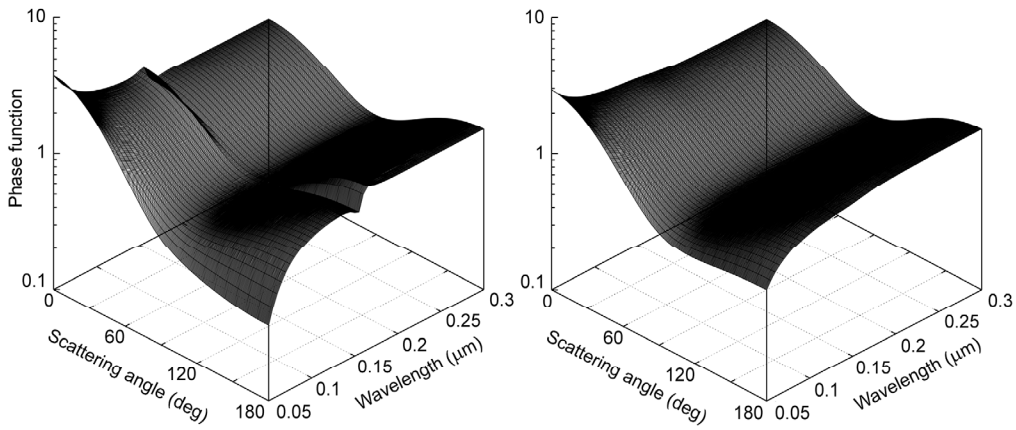

Fig. 5. Spectral dependence of the phase function of the 10-nm spherical Al particle. The refractive indices of the host medium are $m_1 = 1.33$ (left-hand panel) and $m_1 = 1.33 + \mathrm{i}0.3$ (right-hand panel).

3. Discussion and conclusions

For simplicity, we have restricted our study to host media with spectrally independent refractive indices. This implies that the spectral variability of the relative refractive index $m = m_2/m_1$ entering the far-field Lorenz–Mie computation is fully defined by that of the refractive index of the particle.

Figures 2–4 strongly suggest that irrespective of m_1', the general effect of increasing absorption in the host medium is to broaden and suppress the plasmon resonances in the extinction and scattering efficiency factors of noble and Drude nanoparticles and sometimes eradicate them completely. Interestingly, in the case of the Au nanosphere the broadening effect of absorption on the extinction efficiency factor is much more pronounced than that for the other metal particles.

The phase functions of the 10-nm Au, Ag, and Na particles turn out to be Rayleigh-like irrespective of m_1 and λ and hence are not shown. The size parameter $x = 2\pi R/\lambda$ of the aluminum particle at ultraviolet wavelengths is large enough to cause non-Rayleigh phase-function features in the left-hand panel of Fig. 5. This includes the transition from the Rayleigh regime to that typical of wavelength-sized scatterers (a pronounced forward-scattering enhancement and reduced backscattering) as well as noticeable resonance behavior at wavelengths around 0.18 μm. However, the suppressing effect of absorption in the host medium is also obvious in the right-hand panel of Fig. 5.

These suppressing/broadening effects of absorption in the host medium on the plasmon resonances appear to be similar to those on the morphology-dependent resonances of dielectric particles [22].

Our results based on the far-field Lorenz–Mie theory may seem to be inconsistent with the conclusions reached in [33], according to which increasing absorption can substantially enhance plasmon resonances and make them narrower. The specific origin of this apparent disagreement remains uncertain to us. On one hand, it is not quite obvious what definitions of the optical cross sections were used in [33] and how they were computed. On the other hand, unlike in our study, the absorption in the host medium was assumed in [33] to be spectrally dependent. This, of course, added to the spectral variability of the relative refractive index $m = m_2/m_1$ entering the electromagnetic-scattering computation and may have affected the outcome of the computations and the resulting conclusion. This issue warrants further clarification and analysis.

OSA CONTINUUM

One of the reviewers of this paper offered the following qualitative explanation. In the quasi-static model, a plasmon resonance occurs when the relative permittivity of the nanosphere is minus twice that of the surrounding medium: $\varepsilon_1(\lambda) = -2\varepsilon_2(\lambda)$. This is a pole in the complex plane. The faster $\varepsilon_1(\lambda)$ and $\varepsilon_2(\lambda)$ approach and recede from this pole in the complex plane as the wavelength varies, the narrower the resonance. Then dispersion in both the real and imaginary parts of the permittivities contributes to narrowing the resonance. So, if we had an absorbing material that had a large drop in absorption at the resonance wavelength, this should cause a narrow plasmonic resonance. This is what might be happening to cause a narrow resonance in the gold and P3HT system. The absorption of P3HT very rapidly drops near the plasmon resonance peak.

Another reviewer suggested that perhaps the source of the discrepancy between our results and those in [33] may come from the fact that Eq. (3) in [33] is actually incorrect since the quasi-static approximation formula for the extinction is used and mistaken as absorption. Given the formula in Eq. (2) in [33] for the scattering cross section, there appears to be a violation of the optical theorem.

Finally, it is worth pointing out that in the case of $m_1'' = 0.3$, the extinction efficiency factor of the Al particle becomes negative at the shortest wavelengths (Fig. 2). The effect of negative extinction for dielectric particles with large size parameters was reported in [22,23] and has a rather transparent physical explanation. Indeed, the extinction cross section quantifies the difference in the readings of a forward-scattering detector taken with and without the particle. As was anticipated in [34], if the surrounding medium is absorbing, the presence of the particle can in fact make the detector signal stronger, thereby implying a negative extinction cross section. Of course, there is no violation of the energy conservation law since in this case the extinction cross section is not used to quantify the energy budget of a finite volume encompassing the particle [35]. The physical origin of possible negative extinction in the case of nanometer-sized metal particles requires further study. However, it appears to be consistent with the analysis of the small particle limit in [34].

Funding

Goddard Space Flight Center.

Acknowledgements

We thank three anonymous reviewers for valuable comments and suggestions.

Disclosures

The authors declare no conflicts of interest.

References

1. W. C. Mundy, J. A. Roux, and A. M. Smith, "Mie scattering by spheres in an absorbing medium," J. Opt. Soc. Am. **64**(12), 1593–1597 (1974).
2. P. Chýlek, "Light scattering by small particles in an absorbing medium," J. Opt. Soc. Am. **67**(4), 561–563 (1977).
3. C. F. Bohren and D. P. Gilra, "Extinction by a spherical particle in an absorbing medium," J. Colloid Interface Sci. **72**(2), 215–221 (1979).
4. P. Bruscaglioni, A. Ismaelli, and G. Zaccanti, "A note on the definition of scattering cross sections and phase functions for spheres immersed in an absorbing medium," Waves Random Media **3**(3), 147–156 (1993).
5. M. Quinten and J. Rostalski, "Lorenz–Mie theory for spheres immersed in an absorbing host medium," Part. Part. Syst. Charact. **13**(2), 89–96 (1996).
6. A. N. Lebedev, M. Gratz, U. Kreibig, and O. Stenzel, "Optical extinction by spherical particles in an absorbing medium: application to composite absorbing films," Eur. Phys. J. D **6**(2), 365–369 (1999).
7. W. Sudiarta and P. Chylek, "Mie-scattering formalism for spherical particles embedded in an absorbing medium," J. Opt. Soc. Am. A **18**(6), 1275–1278 (2001).

OSA CONTINUUM

8. W. Sudiarta and P. Chylek, "Mie scattering efficiency of a large spherical particle embedded in an absorbing medium," J. Quant. Spectrosc. Radiat. Transfer **70**(4-6), 709–714 (2001).
9. P. Yang, B.-C. Gao, W. J. Wiscombe, M. I. Mishchenko, S. E. Platnick, H.-L. Huang, B. A. Baum, Y. X. Hu, D. M. Winker, S.-C. Tsay, and S. K. Park, "Inherent and apparent scattering properties of coated or uncoated spheres embedded in an absorbing host medium," Appl. Opt. **41**(15), 2740–2759 (2002).
10. G. Videen and W. Sun, "Yet another look at light scattering from particles in absorbing media," Appl. Opt. **42**(33), 6724–6727 (2003).
11. W. Sun, N. G. Loeb, and Q. Fu, "Light scattering by a coated sphere immersed in absorbing medium: a comparison between the FDTD and analytic solutions," J. Quant. Spectrosc. Radiat. Transfer **83**(3-4), 483–492 (2004).
12. Q. Fu and W. Sun, "Apparent optical properties of spherical particles in absorbing medium," J. Quant. Spectrosc. Radiat. Transfer **100**(1-3), 137–142 (2006).
13. J. Randrianalisoa, D. Baillis, and L. Pilon, "Modeling radiation characteristics of semitransparent media containing bubbles or particles," J. Opt. Soc. Am. A **23**(7), 1645–1656 (2006).
14. J. Yin and L. Pilon, "Efficiency factors and radiation characteristics of spherical scatterers in an absorbing medium," J. Opt. Soc. Am. A **23**(11), 2784–2796 (2006).
15. J. R. Frisvad, N. J. Christensen, and H. W. Jensen, "Computing the scattering properties of participating media using Lorenz–Mie theory," ACM Trans. Graph. **26**(3), 60 (2007).
16. S. Durant, O. Calvo-Perez, N. Vukadinovic, and J.-J. Greffet, "Light scattering by a random distribution of particles embedded in absorbing media: diagrammatic expansion of the extinction coefficient," J. Opt. Soc. Am. A **24**(9), 2943–2952 (2007).
17. M. I. Mishchenko, "Electromagnetic scattering by a fixed finite object embedded in an absorbing medium," Opt. Express **15**(20), 13188–13202 (2007).
18. S. Durant, O. Calvo-Perez, N. Vukadinovic, and J.-J. Greffet, "Light scattering by a random distribution of particles embedded in absorbing media: full-wave Monte Carlo solutions of the extinction coefficient," J. Opt. Soc. Am. A **24**(9), 2953–2962 (2007).
19. L. A. Dombrovsky and D. Baillis, *Thermal Radiation in Disperse Systems: An Engineering Approach* (Begell House, 2010).
20. R. Ceolato, N. Riviere, M. J. Berg, and B. Biscans, "Electromagnetic scattering from aggregates embedded in absorbing media," *Prog. Electromagn. Res. Symp. Proc. Taipei*, pp. 717–721 (2013).
21. B. Aernouts, R. Watté, R. van Beers, F. Delport, M. Merchiers, J. de Block, J. Lammertyn, and W. Saeys, "Flexible tool for simulating the bulk optical properties of polydisperse spherical particles in an absorbing host: experimental validation," Opt. Express **22**(17), 20223–20238 (2014).
22. M. I. Mishchenko, G. Videen, and P. Yang, "Extinction by a homogeneous spherical particle in an absorbing medium," Opt. Lett. **42**(23), 4873–4876 (2017).
23. M. I. Mishchenko and J. M. Dlugach, "Scattering and extinction by spherical particles immersed in an absorbing host medium," J. Quant. Spectrosc. Radiat. Transfer **211**, 179–187 (2018).
24. C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, 1983).
25. U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, 1995).
26. M. Quinten, *Optical Properties of Nanoparticle Systems* (Wiley-VCH, 2011).
27. M. I. Mishchenko and P. Yang, "Far-field Lorenz–Mie scattering in an absorbing host medium: theoretical formalism and FORTRAN program," J. Quant. Spectrosc. Radiat. Transfer **205**, 241–252 (2018).
28. M. I. Mishchenko, J. M. Dlugach, J. A. Lock, and M. A. Yurkin, "Far-field Lorenz–Mie scattering in an absorbing host medium. II: Improved stability of the numerical algorithm," J. Quant. Spectrosc. Radiat. Transfer **217**, 274–277 (2018).
29. J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, 1941).
30. P. B. Johnson and R. W. Christy, "Optical constants of the noble metals," Phys. Rev. B **6**(12), 4370–4379 (1972).
31. A. D. Rakić, "Algorithm for the determination of intrinsic optical constants of metal films: application to aluminum," Appl. Opt. **34**(22), 4755–4767 (1995).
32. N. V. Smith, "Optical constants of sodium and potassium from 0.5 to 4.0 eV by split-beam ellipsometry," Phys. Rev. **183**(3), 634–644 (1969).
33. R. L. Peck, A. G. Brolo, and R. Gordon, "Absorption leads to narrower plasmonic resonances," J. Opt. Soc. Am. B **36**(8), F117–F122 (2019).
34. C. F. Bohren and D. P. Gilra, "Extinction by a spherical particle in an absorbing medium," J. Colloid Interface Sci. **72**(2), 215–221 (1979).
35. M. I. Mishchenko and M. A. Yurkin, "Co- and counter-propagating wave effects in an absorbing medium," *J. Quant. Spectrosc. Radiat. Transfer* (2020).