Optical micro-spectroscopy of single metallic nanoparticles: Quantitative extinction and transient resonant four-wave mixing

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CONTENTS

S1. POLARISABILITY OF A NON-SPHERICAL GOLD NANOPARTICLE

As stated in the paper, we describe a non-spherical particle as a metallic ellipsoid with three orthogonal semi-axes a, b and c. In the particle reference system the polarisability tensor $\widehat{\alpha}$ is diagonal, and its eigenvalues are given by[1] $\alpha_i = 4\pi abc\frac{\epsilon-\epsilon_{\mathrm{m}}}{3\epsilon_m+3L_i(\epsilon-\epsilon_{\mathrm{m}})}$. ϵ is the dielectric constant of gold, ϵ_{m} is the dielectric constant of the medium surrounding the NP, and L_i with $i = a, b, c$ are dimensionless quantities defined by the particle geometry as follows:

$$\begin{aligned} L_1 &= \frac{abc}{2}\int_0^{+\infty}(a^2+q)^{-3/2})(b^2+q)^{-1/2}(c^2+q)^{-1/2})dq \\ L_2 &= \frac{abc}{2}\int_0^{+\infty}(a^2+q)^{-1/2})(b^2+q)^{-3/2}(c^2+q)^{-1/2})dq \\ L_3 &= \frac{abc}{2}\int_0^{+\infty}(a^2+q)^{-1/2})(b^2+q)^{-1/2}(c^2+q)^{-3/2})dq \end{aligned} \tag{1}$$

It should be noted that only two out of three geometrical factors are independent, as for any ellipsoid $L_1 + L_2 + L_3 = 1/3$. In some special cases, the integrals in Eq. 1 can be solved analytically. For a spherical particle with $a = b = c$ we have

$$L_1 = L_2 = L_3 = \frac{a^3}{2}\int_0^{+\infty}(a^2+q)^{-5/2})dq = \frac{1}{3}; \tag{2}$$

for a prolate spheroid with $a > b = c$ we have

$$L_1 = \frac{1-e^2}{e^2}, e^2 = 1 - \frac{b^2}{a^2}; \tag{3}$$

and for a oblate spheroid with $a = b > c$ we have

$$L_1 = \frac{g\left(e\right)}{2e^2}\left[\frac{\pi}{2} - \tan^{-1} g\left(e\right)\right], g\left(e\right) = \left(\frac{1-e^2}{e^2}\right)^{1/2}, e^2 = 1 - \frac{c^2}{a^2}. \tag{4}$$

In the most general case, we calculated the integrals in Eq. 1 using Matlab and its numerical integration function `integral`.

For an arbitrary particle orientation in the laboratory system, the polarizability tensor is transformed as:

$$\widehat{\alpha} = \widehat{A}^{-1}\widehat{\alpha}'\widehat{A}, \tag{5}$$

where $\widehat{A} = (a_{ij})$ is the rotation matrix transforming the particle reference system into the laboratory system and α' is the polarizability tensor in the laboratory system. The absorption, scattering and total cross-sections are calculated following Ref. [1]. The absorption cross-section in the laboratory system along the x-axis is given by (x,y,z corresponds to 1,2,3):

$$\sigma_{\mathrm{abs,X'}} = k\Im(\alpha_1 a_{11}^2 + \alpha_2 a_{21}^2 + \alpha_3 a_{31}^2), \tag{6}$$

and similarly for the other axes ($k = 2\pi n/\lambda$ with λ wavelength in vacuum and n refractive index of the surrounding medium). The scattering cross-section along the x-axis is:

$$\sigma_{\mathrm{sca,X'}} = \frac{k^4}{6\pi}\left(|\alpha_1|^2 a_{11}^2 + |\alpha_2|^2 a_{21}^2 + |\alpha_3|^2 a_{31}^2\right), \tag{7}$$

and the total extinction cross section is the sum:

$$\sigma_{\mathrm{ext,X'}} = \sigma_{\mathrm{abs,X'}} + \sigma_{\mathrm{sca,X'}} \tag{8}$$

If the polarization of light is parallel to one of the principal axes of the particle, the total cross-section is given by:

$$\sigma_{\mathrm{ext},m} = k\Im(\alpha_m) + \frac{k^4|\alpha_m|^2}{6\pi}, \tag{9}$$

where $m = 1, 2, 3$. If we rotate the particle by an angle γ in the laboratory xy plane around the z-axis, and keep the electric field polarization along the laboratory x-axis, the total extinction cross-section will be:

$$\sigma_{\mathrm{ext},\gamma} = \sigma_{\mathrm{ext,1}}\cos^2\gamma + \sigma_{\mathrm{ext,2}}\sin^2\gamma \tag{10}$$

In turn, the extinction cross-section for an incident polarized light at an angle θ with respect to the laboratory x-axis is:

$$\sigma_{\mathrm{ext}}(\theta) = \sigma_{\mathrm{ext,1}}\cos^2(\gamma-\theta) + \sigma_{\mathrm{ext,2}}\sin^2(\gamma-\theta) \tag{11}$$

This represents a sinusoidal dependence of the measured extinction cross-section versus θ, which can be rewritten as

$$\sigma_{\mathrm{ext}}(\theta) = \bar{\sigma}(1 + \alpha_{\mathrm{P}}\cos[2(\theta-\gamma)]) \tag{12}$$

with

$$\bar{\sigma} = \frac{\sigma_{\mathrm{ext},1} + \sigma_{\mathrm{ext},2}}{2}, \alpha_{\mathrm{P}} = \frac{\sigma_{\mathrm{ext},1} - \sigma_{\mathrm{ext},2}}{\sigma_{\mathrm{ext},1} + \sigma_{\mathrm{ext},2}} \tag{13}$$

In order to link α_{P} and $\bar{\sigma}$ to the particle ellipticity $\rho = 1 - b/a$ and the particle volume $V = (4/3)\pi abc$, we calculated $\sigma_{\mathrm{ext},1}$ and $\sigma_{\mathrm{ext},2}$ as a function of ρ and V using $a > b$, $c = \sqrt{ab}$ and varying ρ from 0 to 0.9 and V from $5.23 \times 10^2\,\mathrm{nm}^3$ to $5.23 \times 10^5\,\mathrm{nm}^3$ (effective radius from 5 nm to 50 nm). In the calculations we assumed a surrounding medium of refractive index 1.515. $\sigma_{\mathrm{ext},1}$ and $\sigma_{\mathrm{ext},2}$ were calculated as spectral averages over the R (570-650 nm), G (480-580 nm), and B (420-510 nm) filters of the Canon color camera, and the corresponding α_{P} and $\bar{\sigma}$ versus ρ and V were evaluated. α_{P} calculated for all available volumes, plotted as a function of ellipticity, for the R, G and B filters is shown in Fig. S1.

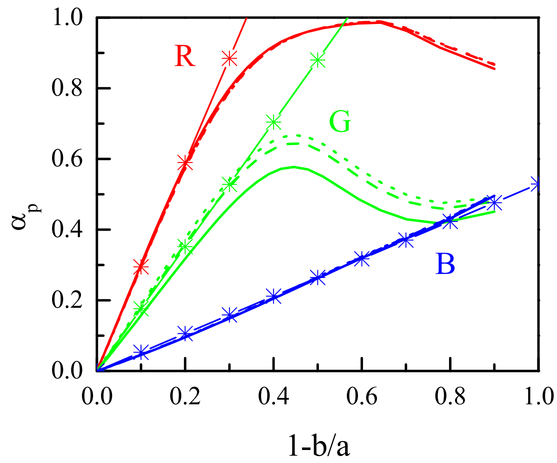

FIG. S1. Asymmetry parameter α_{P} versus particle ellipticity, using calculated cross-sections $\sigma_{\mathrm{ext},1}$ and $\sigma_{\mathrm{ext},2}$ as spectral averages over the R, G, and B filters of the color Canon camera in the experiment. Different curves with the same color show calculations for three different particle volumes (solid line: $523\,\mathrm{nm}^3$; dashed line: $2.62 \times 10^5\,\mathrm{nm}^3$, and dotted line: $5.23 \times 10^5\,\mathrm{nm}^3$). Lines with star symbols show the linear approximation using the mean K parameters (see text).

We observe that α_{P} is linear in ρ in the range $\alpha_{\mathrm{P}} < 0.5$. By fitting these curves in the linear regime as $\rho = K\alpha_{\mathrm{P}}$ we find a value of K only weakly dependent on volume. In the R channel, we can define a mean dimensionless $K = 0.339$ with a standard deviation (from the volume dependence) of 2×10^{-3} (i.e. less than 1%). In the G channel we find $K = 0.568$ with standard deviation 3×10^{-2}, and in the B channel $K = 1.89$ with standard deviation 6×10^{-3}.

The dependence of $\bar{\sigma}$ on volume for all investigated ellipticities is shown in Fig. S2. This dependence is well described by $\bar{\sigma} = H_1 V + H_2 V^2$. The coefficients H_1 and H_2 versus ellipticity ρ are shown in Fig. S3 for the R, G and B filter bandwidths. They are independent of ellipticity for small ρ. In the range $\rho \leq 0.1$ we have $H_1 = 1.39 \times 10^{-2}$/nm and $H_2 = 1.09 \times 10^{-7}/\text{nm}^4$ for R, $H_1 = 6.80 \times 10^{-2}$/nm and $H_2 = 2.11 \times 10^{-7}/\text{nm}^4$ for G, $H_1 = 4.54 \times 10^{-2}$/nm and $H_2 = 7.90 \times 10^{-8}/\text{nm}^4$ for B.

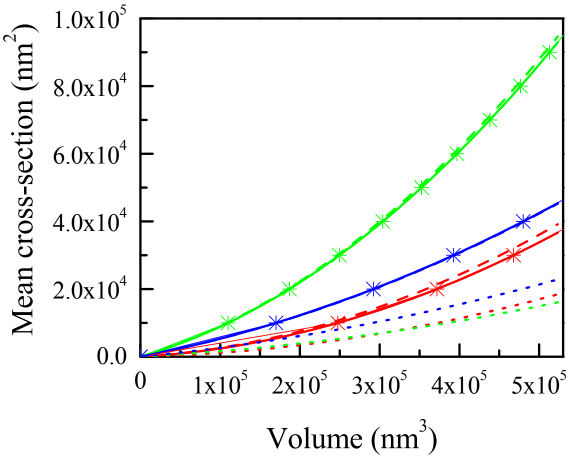

FIG. S2. Mean extinction $\bar{\sigma}$ versus particle volume using calculated cross-sections $\sigma_{\text{ext},1}$ and $\sigma_{\text{ext},2}$ as spectral averages over the R, G, and B filters of the color Canon camera in the experiment. Different curves with the same color show calculations for different ellipticities (solid line: 0; dashed line: 0.1; dotted line: 0.9). Lines with star symbols show the curves with mean H coefficients in the range of small ellipticities 0 to 0.1 (see text).

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[1] Bohren, C. F. & Huffman, D. R. *Absorption and Scattering of Light by Small Particles* (Wiley-VCH, 1998).

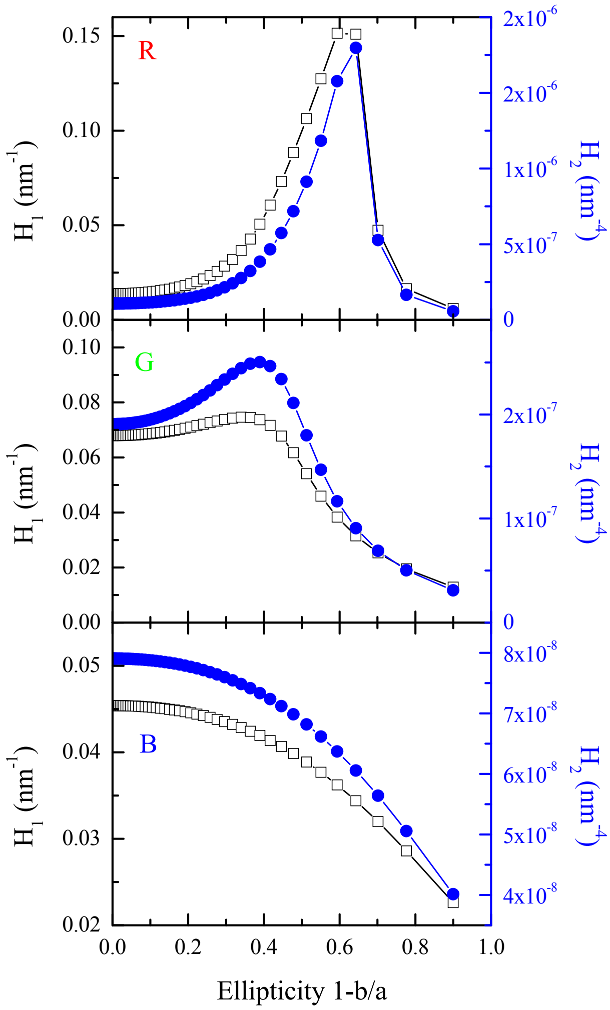

FIG. S3. Coefficients H_1 and H_2 versus ellipticity for the R, G and B filter bandwidths in the experiment, as indicated.