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

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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 $\alpha$ is diagonal, and its eigenvalues are given by

$$\alpha_i = 4\pi abc \frac{\varepsilon - \varepsilon_m}{3\varepsilon_m + 5L_i(\varepsilon - \varepsilon_m)},$$

$\varepsilon$ is the dielectric constant of gold, $\varepsilon_m$ 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:

$$L_1 = \frac{abc}{2} \int_0^{+\infty} (a^2 + q)^{-3/2}(b^2 + q)^{-1/2}(c^2 + q)^{-1/2}dq$$

$$L_2 = \frac{abc}{2} \int_0^{+\infty} (a^2 + q)^{-1/2}(b^2 + q)^{-3/2}(c^2 + q)^{-1/2}dq$$

$$L_3 = \frac{abc}{2} \int_0^{+\infty} (a^2 + q)^{-1/2}(b^2 + q)^{-1/2}(c^2 + q)^{-3/2}dq$$

Equation 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

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

Equation 2

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

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

Equation 3

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

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

Equation 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:

$$\tilde{\alpha} = \tilde{A}^{-1} \alpha' \tilde{A},$$  \hspace{1cm} (5)

where $$\tilde{A} = (a_{ij})$$ is the rotation matrix transforming the particle reference system into the laboratory system and $$\alpha'$$ 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):

$$\sigma_{\text{abs},X'} = \frac{k}{6\pi} \Im (\alpha_1 a_{11}^2 + \alpha_2 a_{21}^2 + \alpha_3 a_{31}^2),$$  \hspace{1cm} (6)

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

$$\sigma_{\text{sca},X'} = \frac{k^4}{6\pi} (|\alpha_1|^2 a_{11}^2 + |\alpha_2|^2 a_{21}^2 + |\alpha_3|^2 a_{31}^2),$$  \hspace{1cm} (7)

and the total extinction cross section is the sum:

$$\sigma_{\text{ext},X'} = \sigma_{\text{abs},X'} + \sigma_{\text{sca},X'}$$  \hspace{1cm} (8)

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

$$\sigma_{\text{ext},m} = k \Im (\alpha_m) + \frac{k^4 |\alpha_m|^2}{6\pi},$$  \hspace{1cm} (9)

where $$m = 1,2,3$$. If we rotate the particle by an angle $$\gamma$$ 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:

$$\sigma_{\text{ext},\gamma} = \sigma_{\text{ext},1} \cos^2 \gamma + \sigma_{\text{ext},2} \sin^2 \gamma$$  \hspace{1cm} (10)

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

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

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

$$\sigma_{\text{ext}}(\theta) = \bar{\sigma} (1 + \alpha_P \cos [2(\theta - \gamma)])$$  \hspace{1cm} (12)
with

$$\bar{\sigma} = \frac{\sigma_{\text{ext},1} + \sigma_{\text{ext},2}}{2}, \quad \alpha_p = \frac{\sigma_{\text{ext},1} - \sigma_{\text{ext},2}}{\sigma_{\text{ext},1} + \sigma_{\text{ext},2}}$$

(13)

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

![Figure S1](image.png)

FIG. S1. Asymmetry parameter $\alpha_p$ versus particle ellipticity, 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 three different particle volumes (solid line: 523 nm$^3$; dashed line: $2.62 \times 10^5$ nm$^3$, and dotted line: $5.23 \times 10^5$ nm$^3$). Lines with star symbols show the linear approximation using the mean $K$ parameters (see text).

We observe that $\alpha_p$ is linear in $\rho$ in the range $\alpha_p < 0.5$. By fitting these curves in the linear regime as $\rho = K \alpha_p$ 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 $2 \times 10^{-3}$ (i.e. less than 1%). In the G channel we find $K = 0.568$ with standard deviation $3 \times 10^{-2}$, and in the B channel $K = 1.89$ with standard deviation $6 \times 10^{-3}$.
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 $\rho$ are shown in Fig. S3 for the R, G and B filter bandwidths. They are independent of ellipticity for small $\rho$. In the range $\rho \leq 0.1$ we have $H_1 = 1.39 \times 10^{-2}/\text{nm}$ and $H_2 = 1.09 \times 10^{-7}/\text{nm}^4$ for R, $H_1 = 6.80 \times 10^{-2}/\text{nm}$ and $H_2 = 2.11 \times 10^{-7}/\text{nm}^4$ for G, $H_1 = 4.54 \times 10^{-2}/\text{nm}$ 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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FIG. S3. Coefficients $H_1$ and $H_2$ versus ellipticity for the R, G and B filter bandwidths in the experiment, as indicated.