Quantitative measurement of EXTINCTION, SCATTERING and ABSORPTION by metallic nanoparticles

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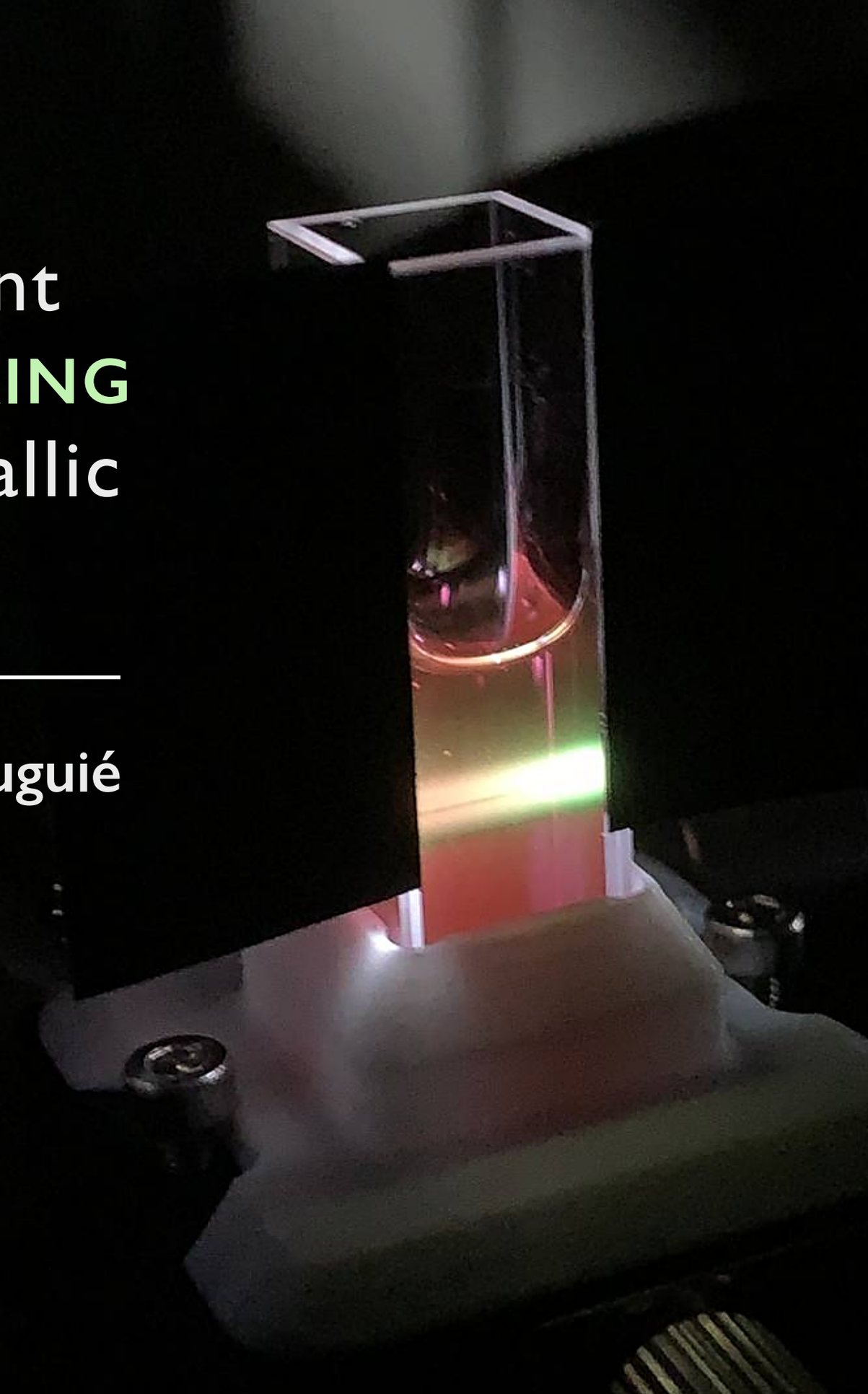
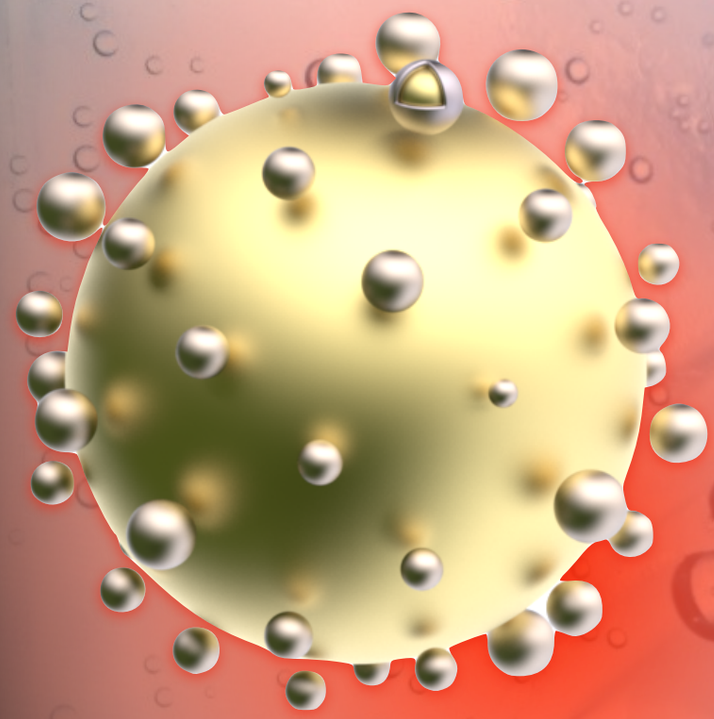


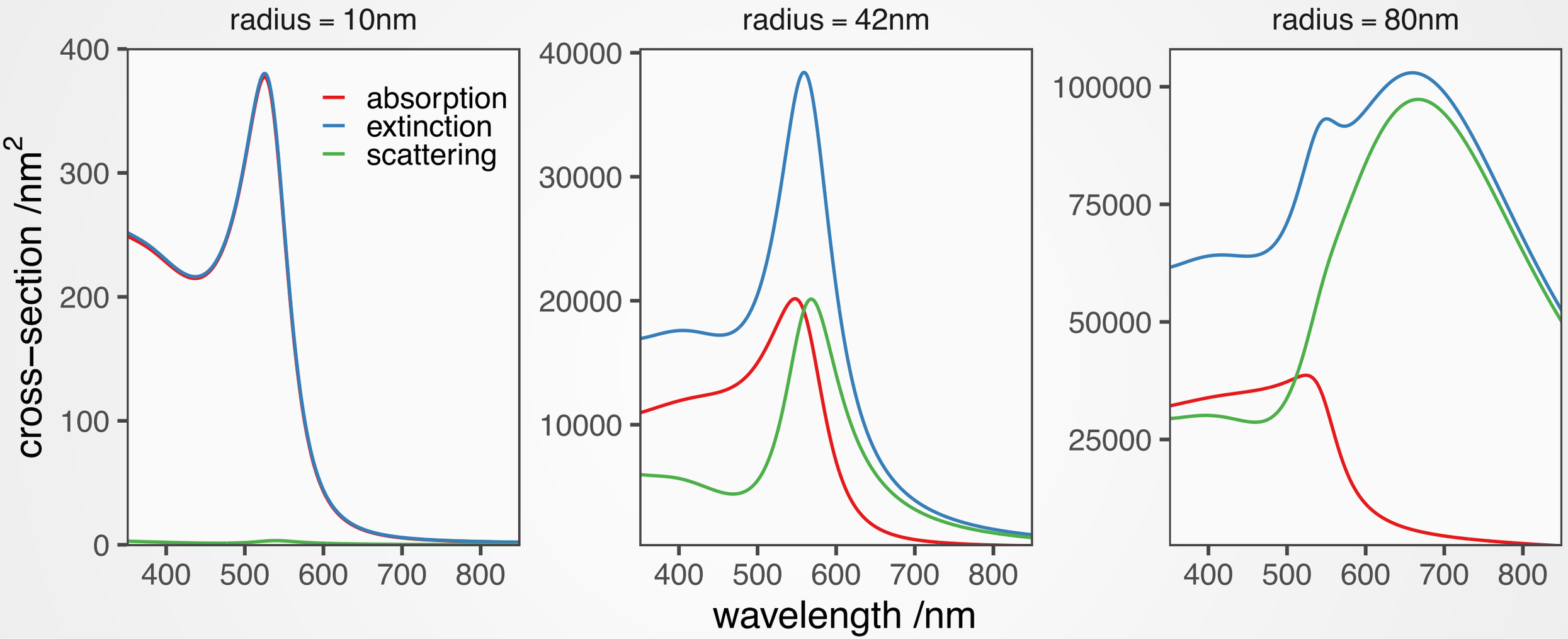
ABSORPTION, SCATTERING: DIFFERENT INFORMATION

Lycurgus vase



Photocatalysis

QUANTITATIVE VALIDATION OF EXT = ABS + SCA



- Testing what we think we know: quantitative comparison
- Surprisingly few work in this area

  Collings *et al* J. Phys. Chem. B 103, 1999 • Micali *et al* Anal. Chem. 73, 2001 • Bin Ren *et al* Anal. Chem. 87, 2015

(COMMON) LINEAR OPTICAL SPECTROSCOPY

- UV–vis transmission (**extinction**)
- integrating sphere (**absorption**)

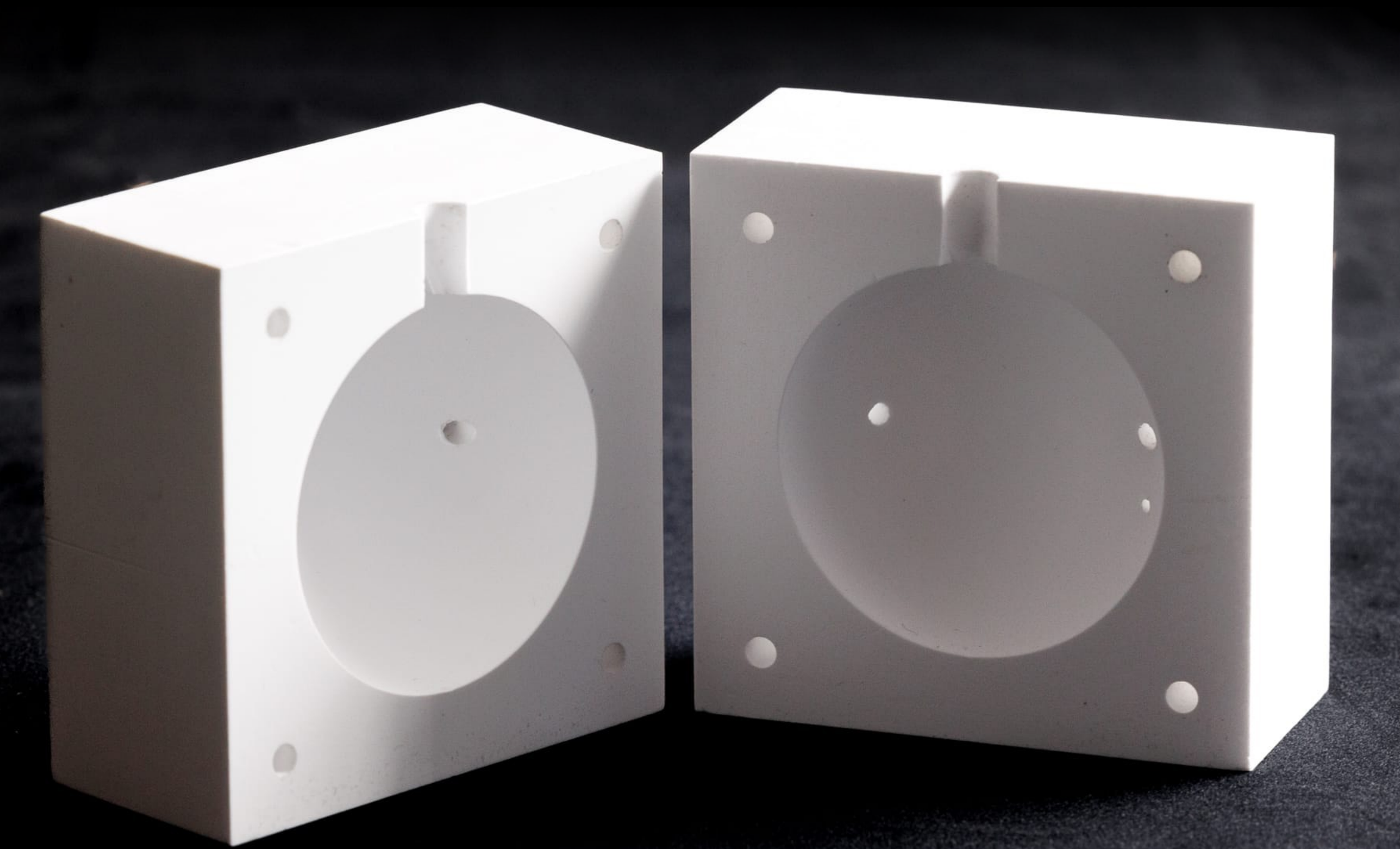
} *bulk samples*

- dark field (**scattering**)
- photoacoustic (**absorption**)

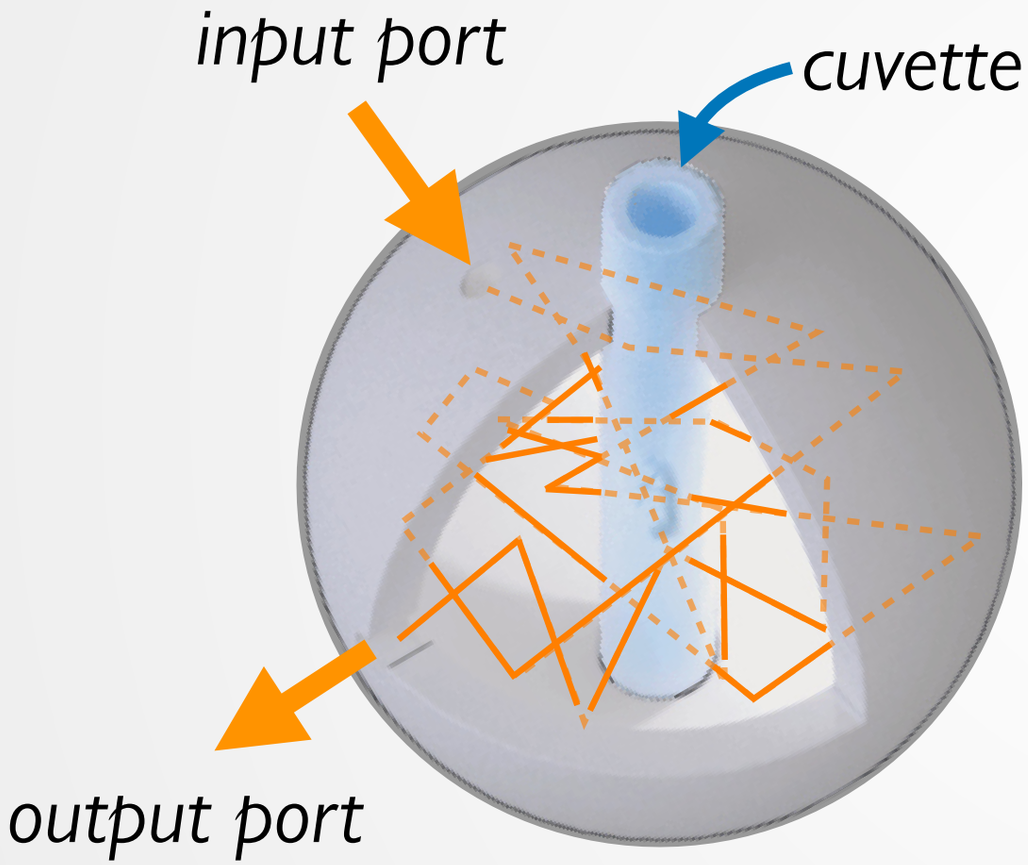
} *bulk or single-particle*

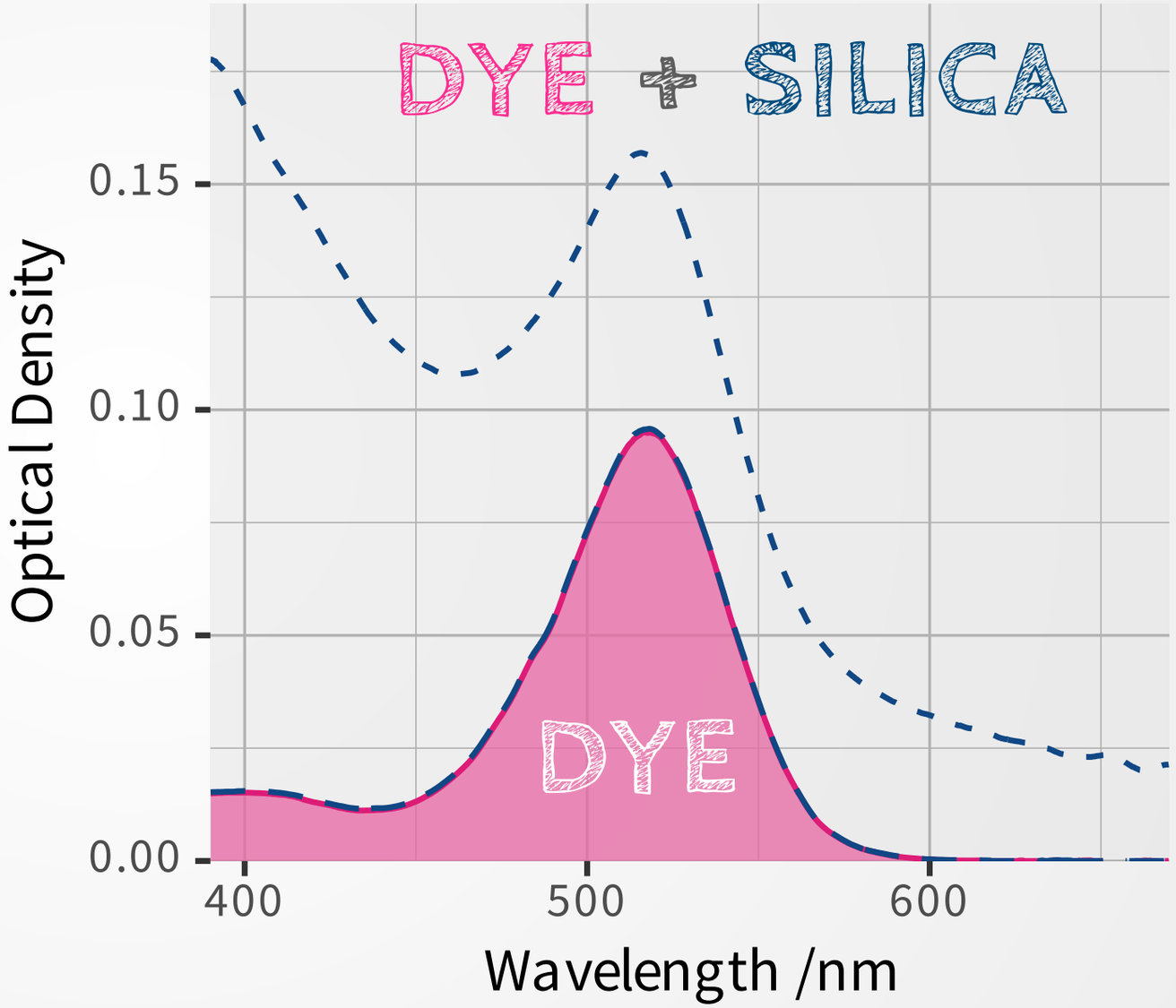
- spatial modulation (**extinction**) – *Del Fatti, Vallée*
- interferometry (**scattering**) – *Sandoghdar*
- interferometry (**extinction**, **absorption**) – *Berg, Oulton*
- ...

INTEGRATING SPHERE ABSORPTION SPECTROSCOPY



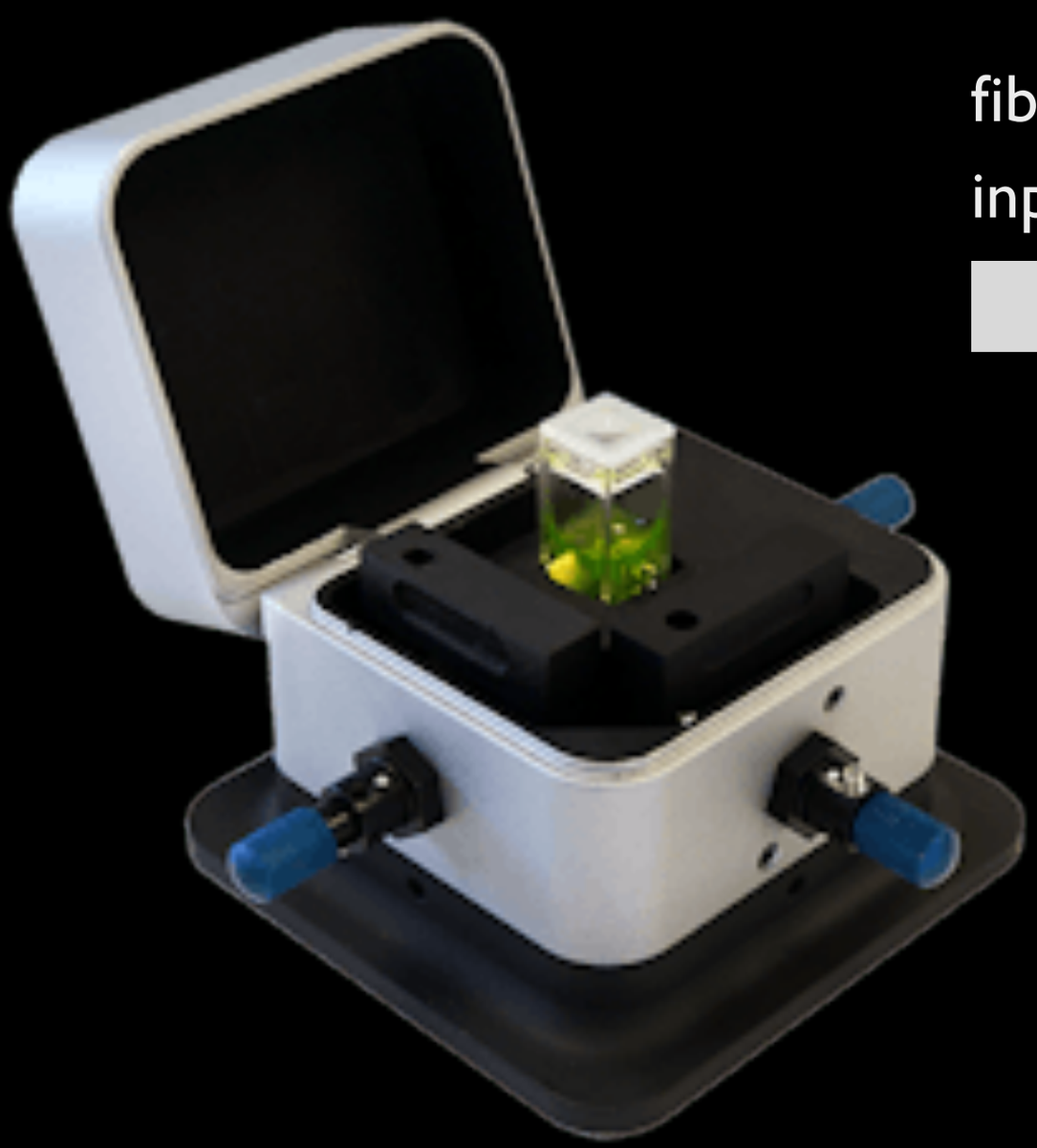
INTEGRATING SPHERE ABSORPTION

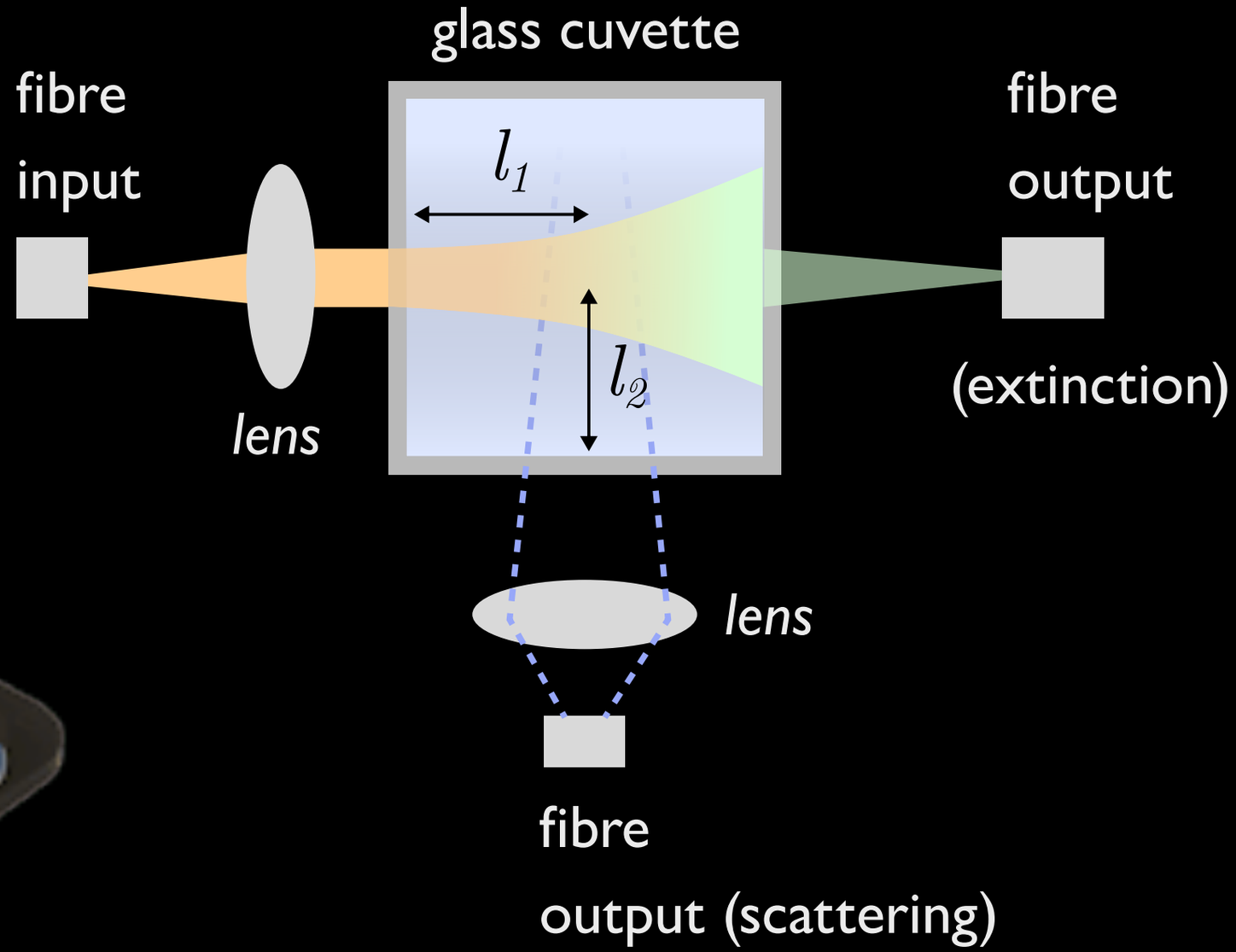




Modified optical absorption of molecules on metallic nanoparticles at sub-monolayer coverage – Nat. Photon. 10, 40–45 (2016)

90 DEGREE SETUP

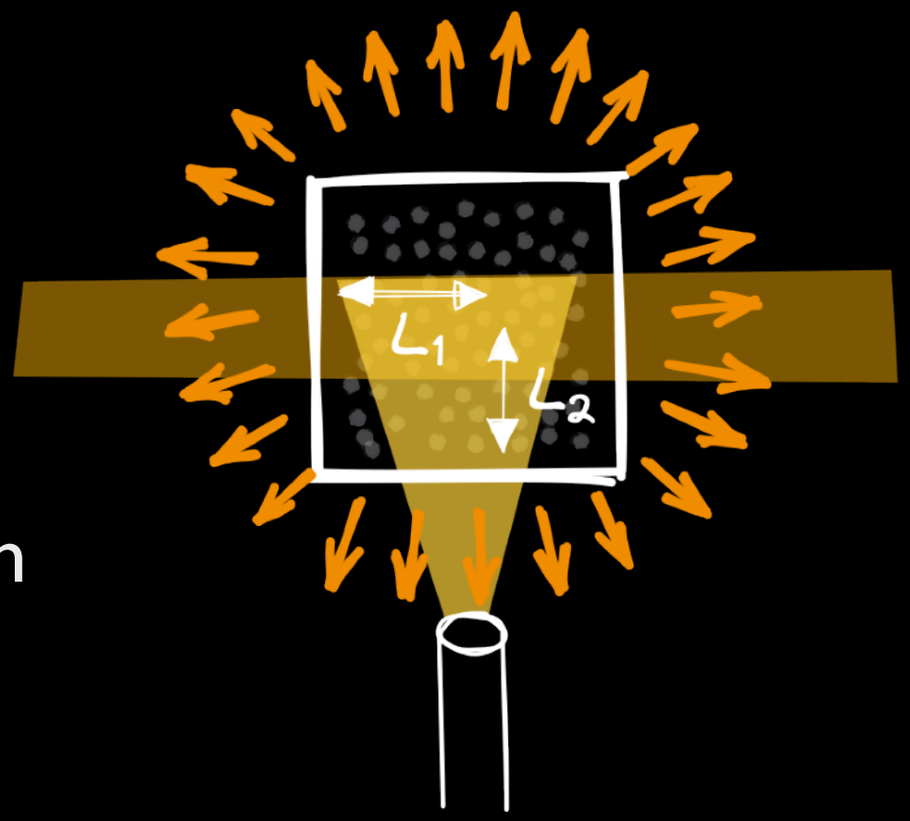





CROWN

CORRECTIONS TO THE SCATTERING SIGNAL

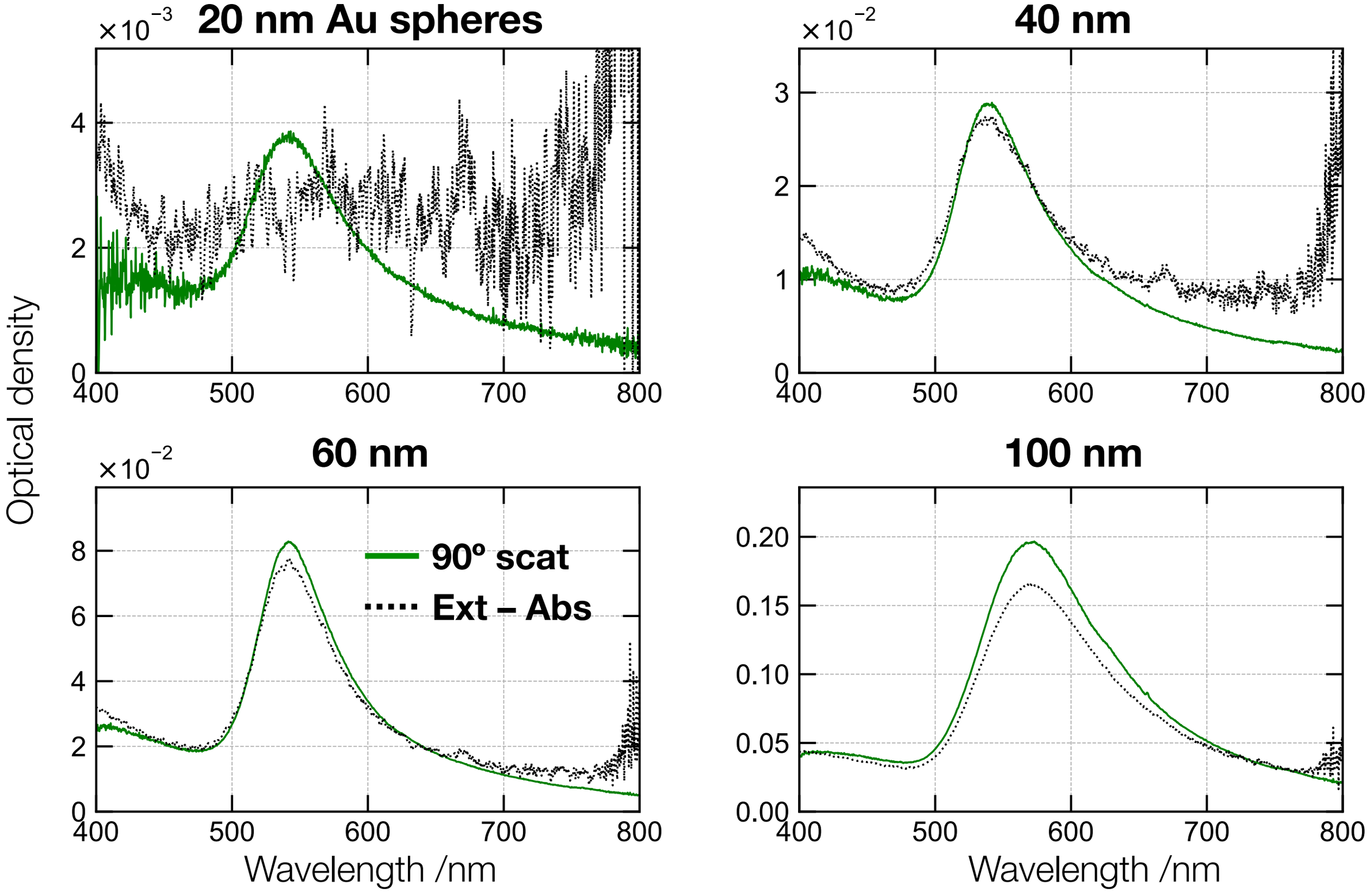
- we only collect a finite solid angle Ω
- **incident light** modified by extinction
- **scattered light** modified by extinction



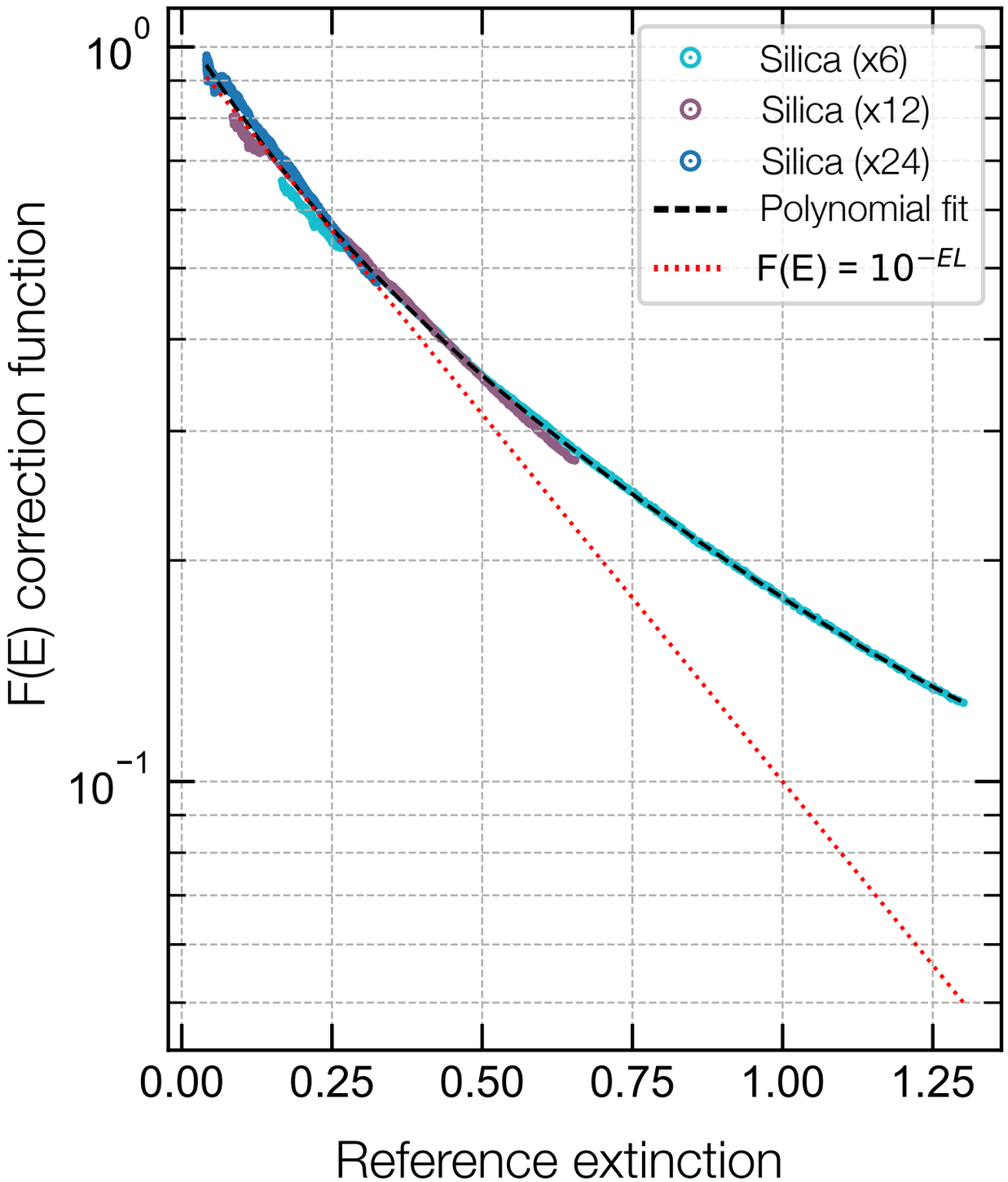
"Naive" model:

- geometrical scaling factor *K (calibration with standard UV–vis)*
- small (Rayleigh) scatterers – constant scattering profile
- Beer-Lambert type correction $I(L) = I_0 \times 10^{-E(L_1+L_2)}$

PRELIMINARY (INCONSISTENT) RESULTS



CALIBRATION CURVE ACCOUNTING FOR EXTINCTION



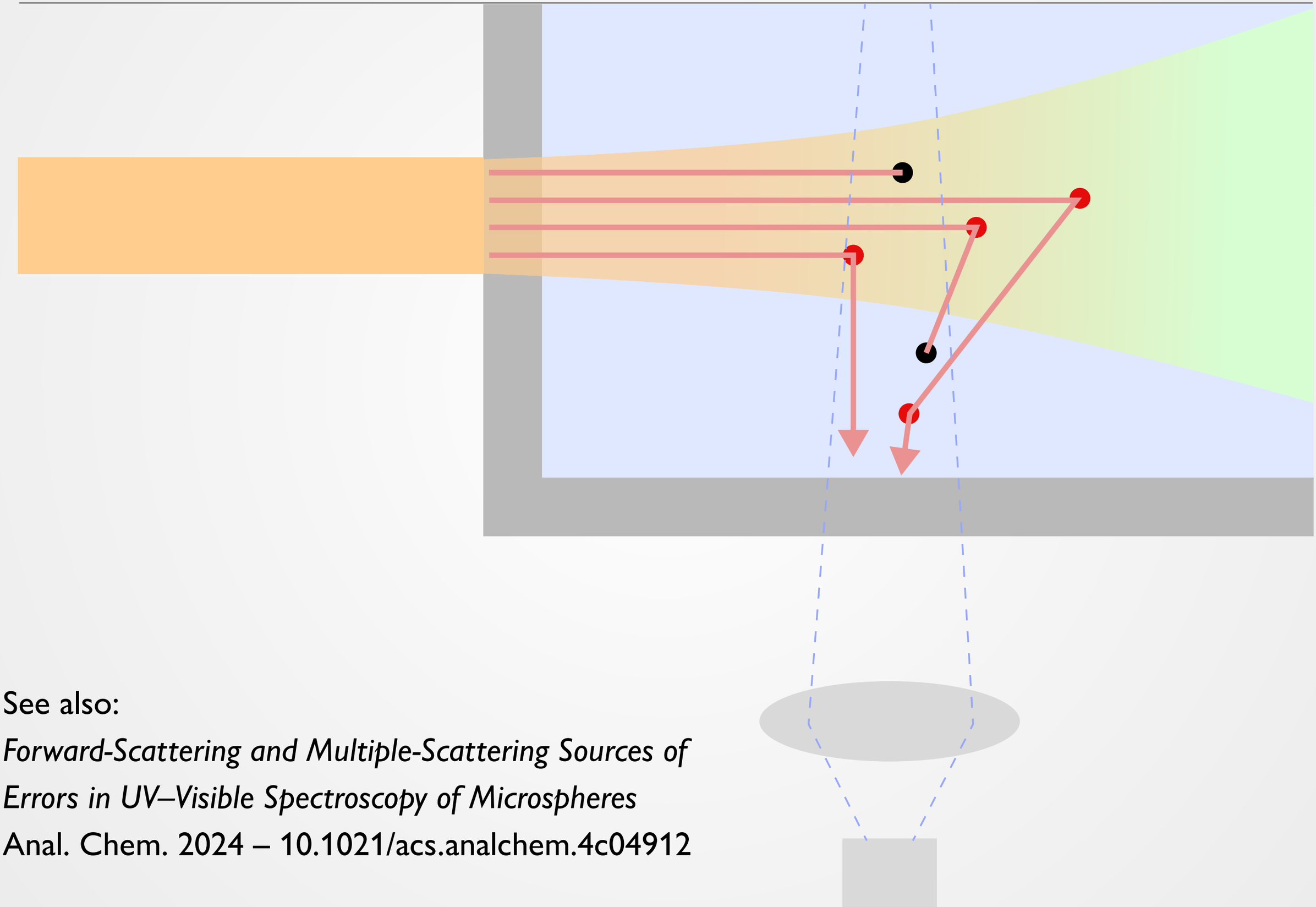
Calibration function F(E) retrieved from **silica nanoparticles** (non-absorbing)

$$E = S = K \frac{I_{\text{scat}}}{I_{\text{ref}}} \frac{1}{F(E)}$$

$$F(E) = K \frac{I_{\text{scat}}}{I_{\text{ref}}} \frac{1}{E}$$

- 10^{-EL} approximation off for E > 0.3
- Polynomial fit works well for silica
- Insufficient for gold nanoparticles

SCHEMATIC VIEW OF THE COMPLICATIONS



See also:

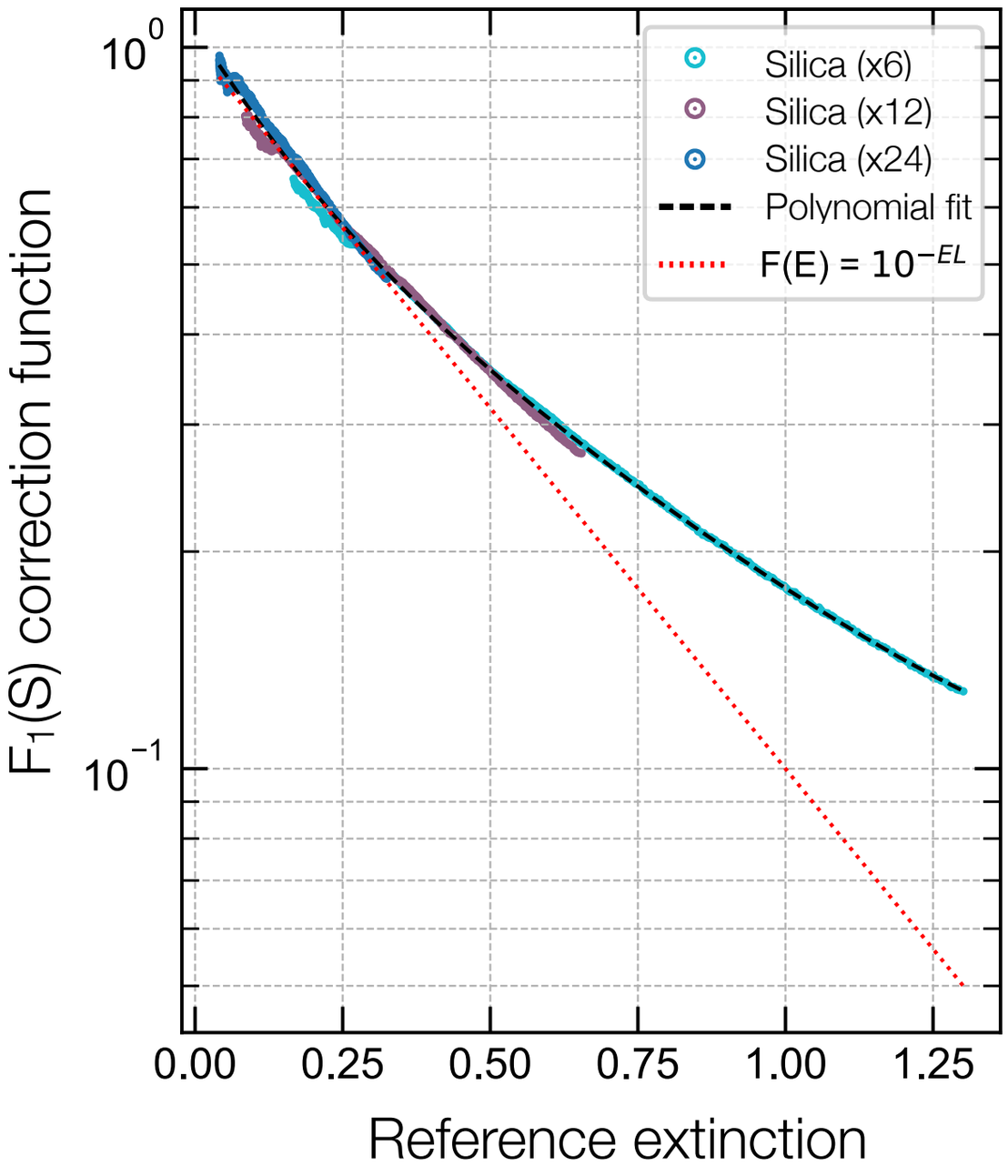
Forward-Scattering and Multiple-Scattering Sources of Errors in UV–Visible Spectroscopy of Microspheres

Anal. Chem. 2024 – 10.1021/acs.analchem.4c04912

FACTORISED CALIBRATION FUNCTION $F_1(S) \times F_2(A)$

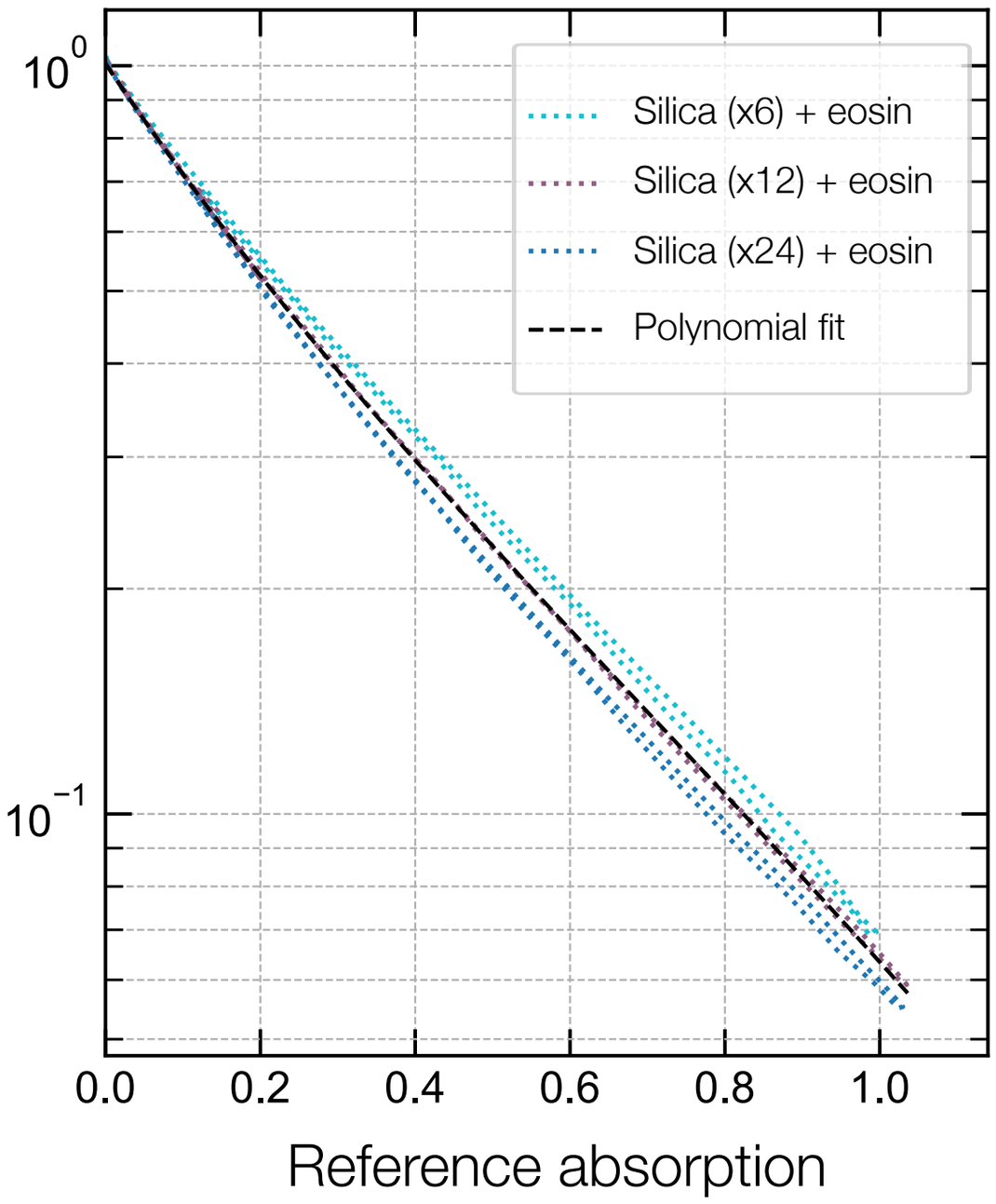
$F_1(S)$: silica nanoparticles

Extinction = Scattering

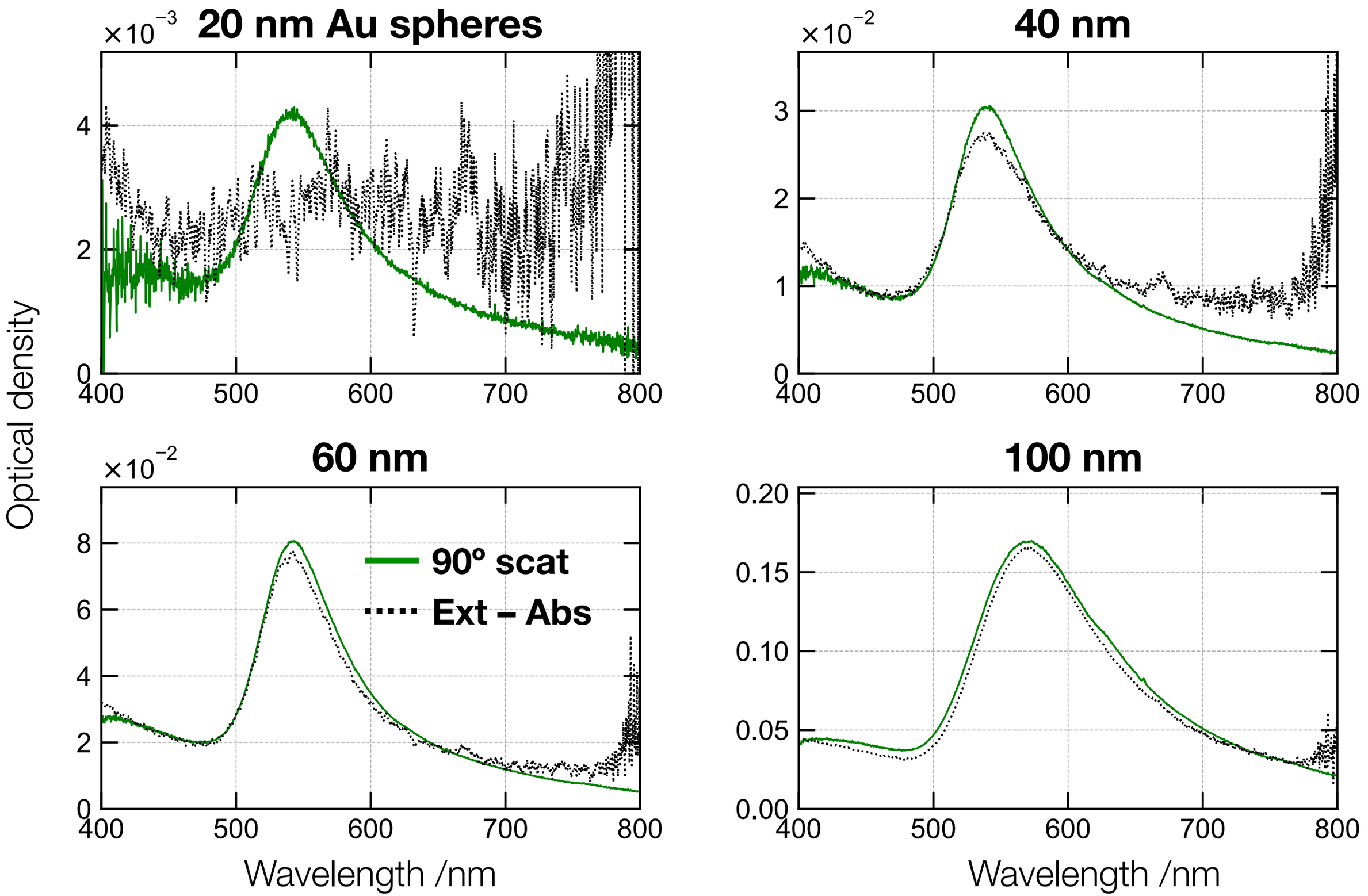


$F_2(A)$: silica + eosin dye

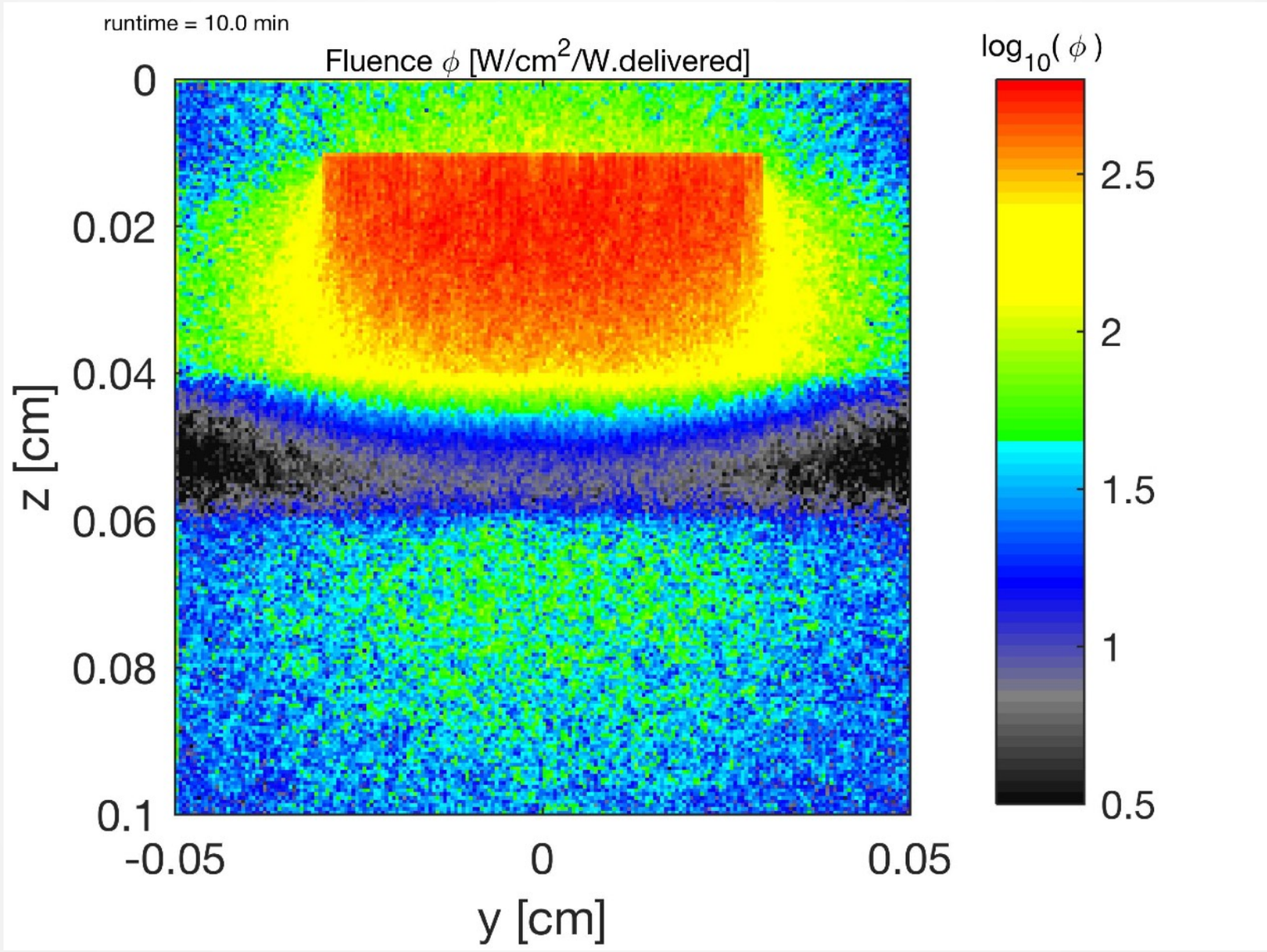
Extinction = Scattering + Absorption



RESULTS WITH $F_1(S) \times F_2(A)$ CORRECTION



NEXT STEPS



https://omlc.org/software/mc/mcxyz/

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