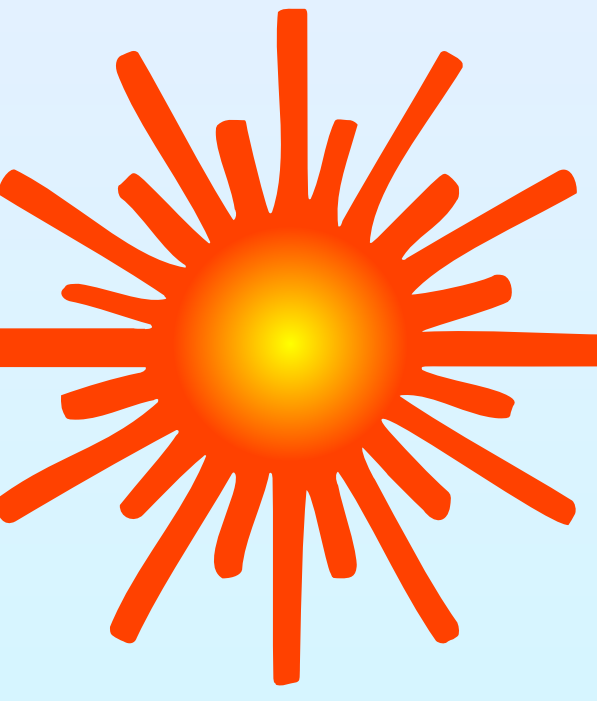


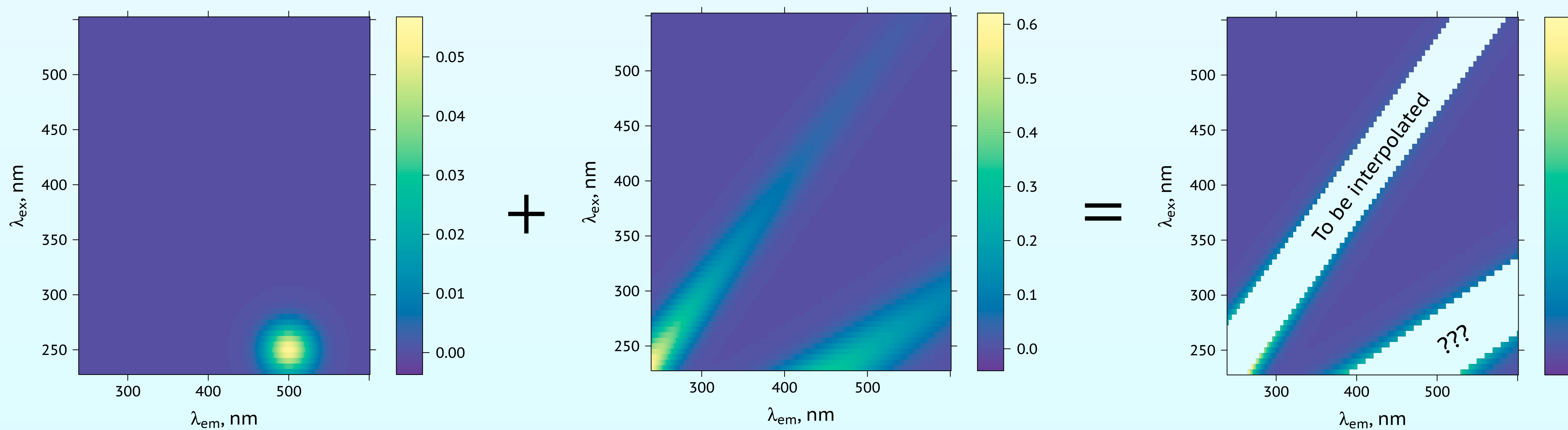
Modelling of scattering signal for direct PARAFAC decompositions of excitation-emission matrices



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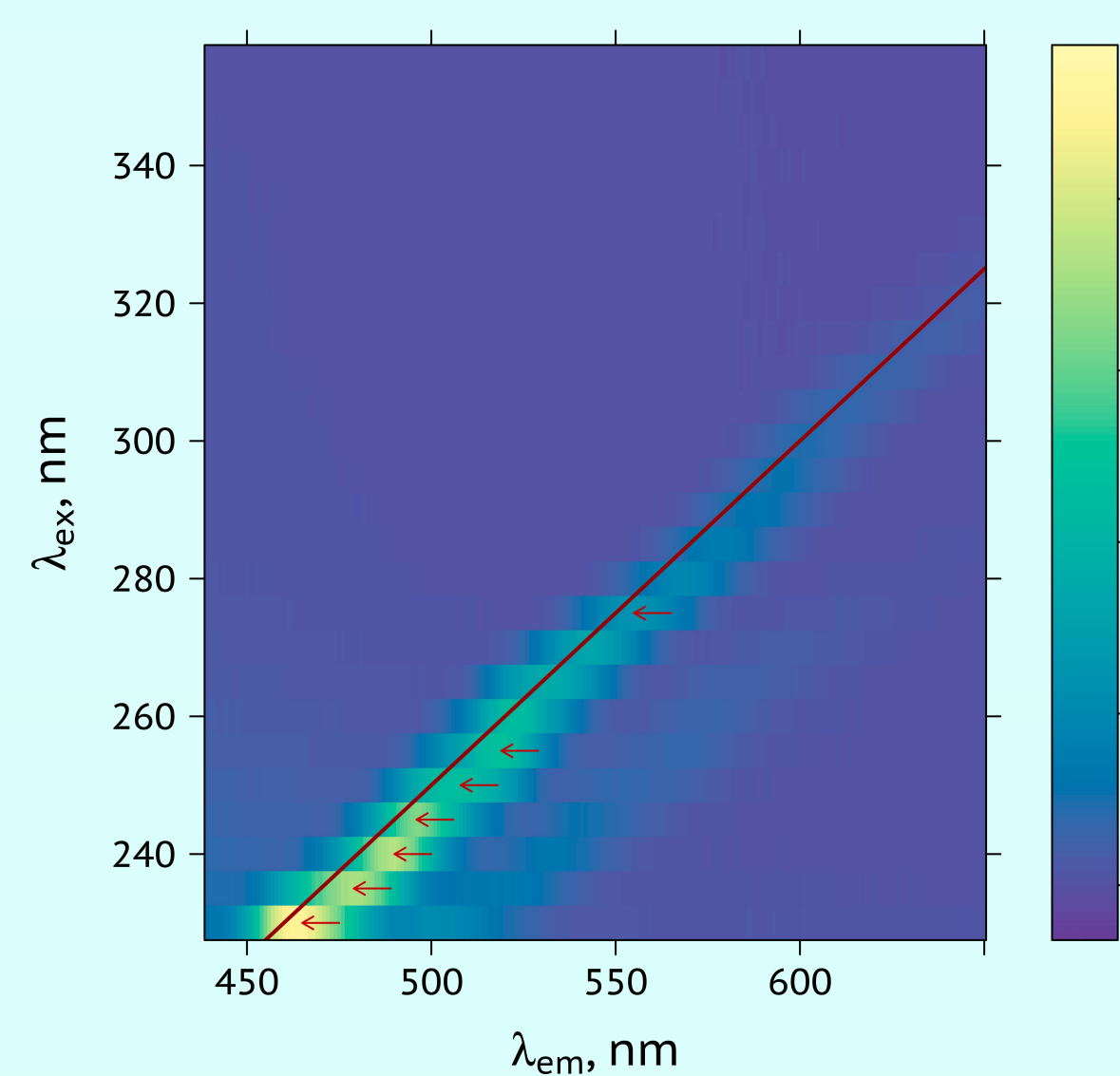
Motivation



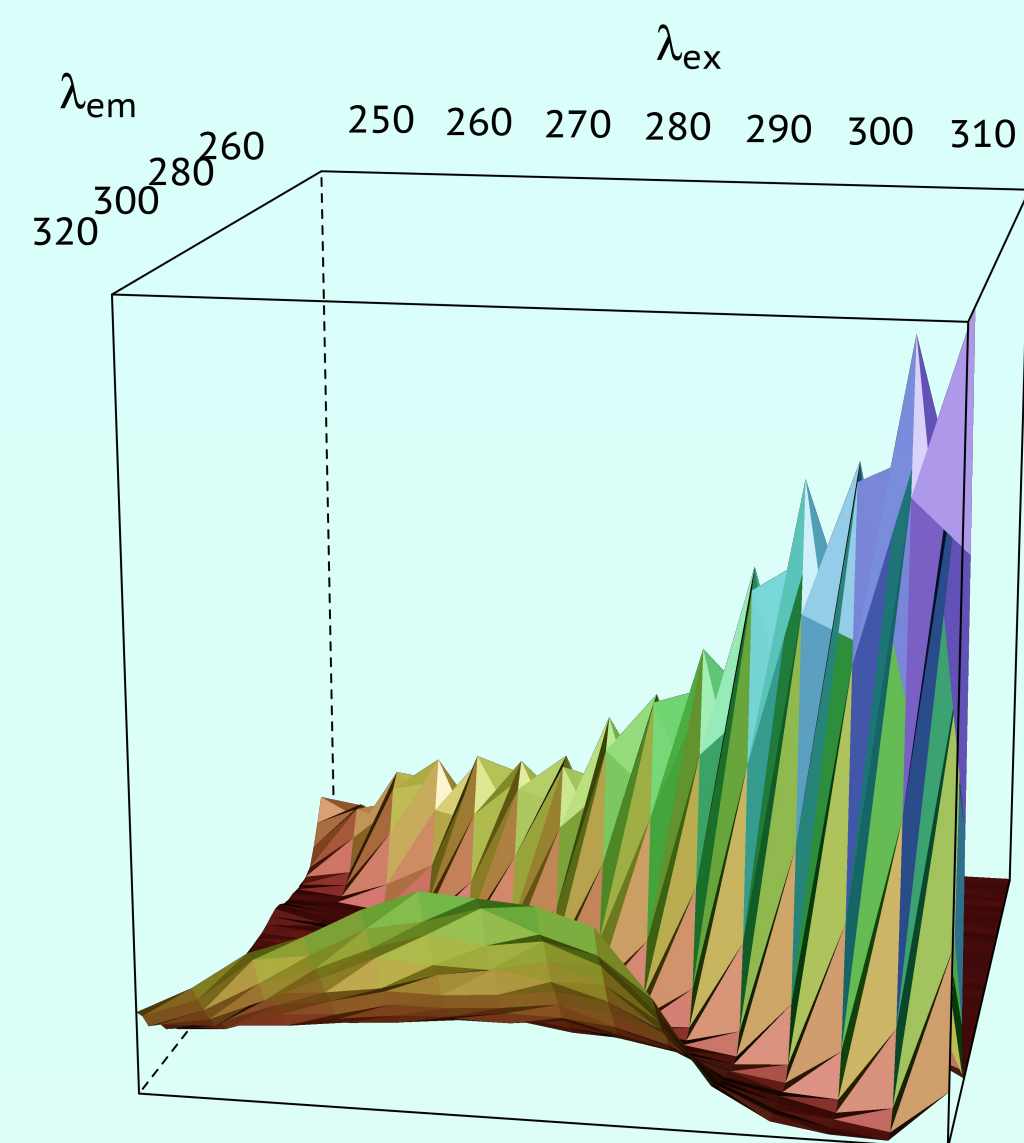
- PARAFAC is widely used in fluorescence spectroscopy
- Scattering signal doesn't adhere to PARAFAC assumptions
- Interpolation [1] of scattering areas is lossy
- Could scattering be modelled together with fluorescence?

What scattering may be

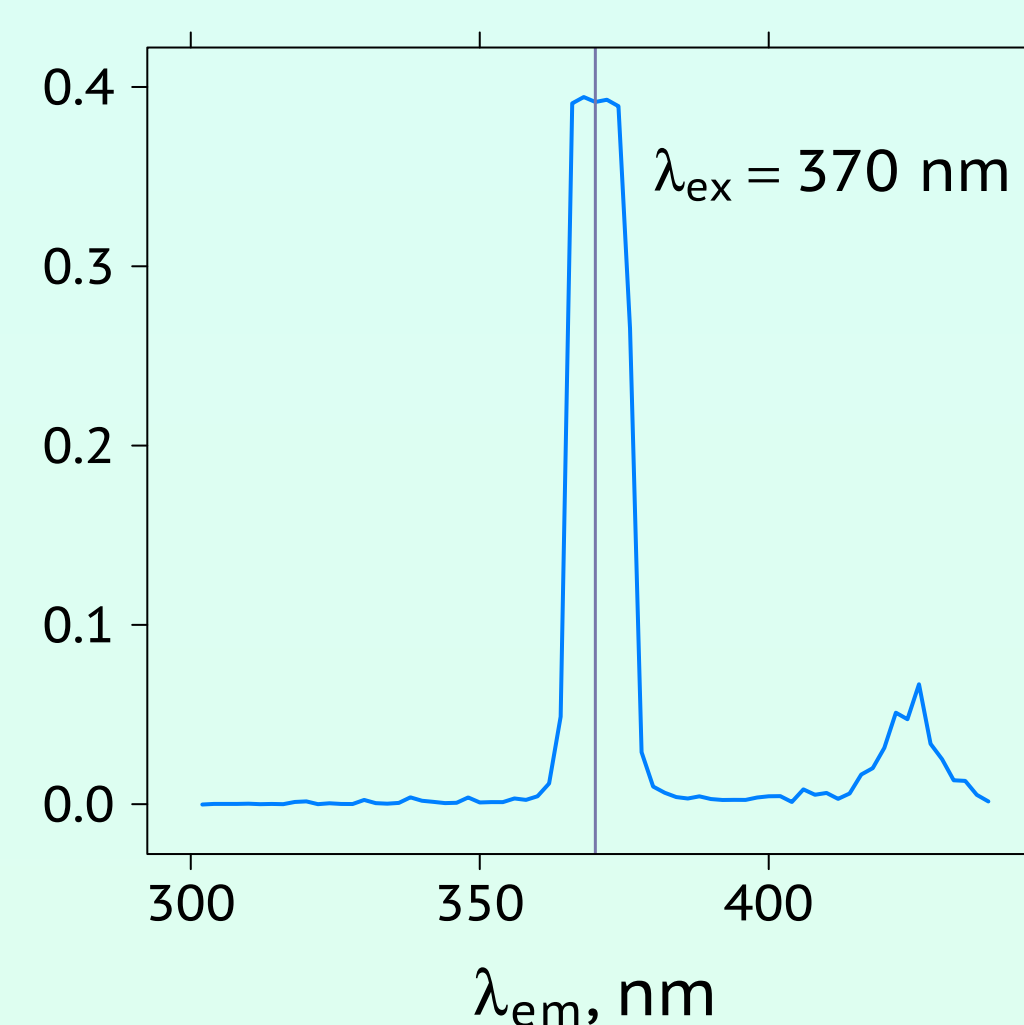
$$I(\lambda_{em}, \lambda_{ex}) = \underbrace{P(\lambda_{em} - \lambda_{center}, w)}_{\text{peak function}} \times \underbrace{\lambda_{ex}^{-4}}_{\text{physics}} \times \text{const} ?$$



- Not a smooth line: wavelengths slightly miscalibrated
- Doesn't matter for fluorescence



- Not λ^{-4} : not calibrated for spectral sensitivity
- Unknown function of λ_{ex}



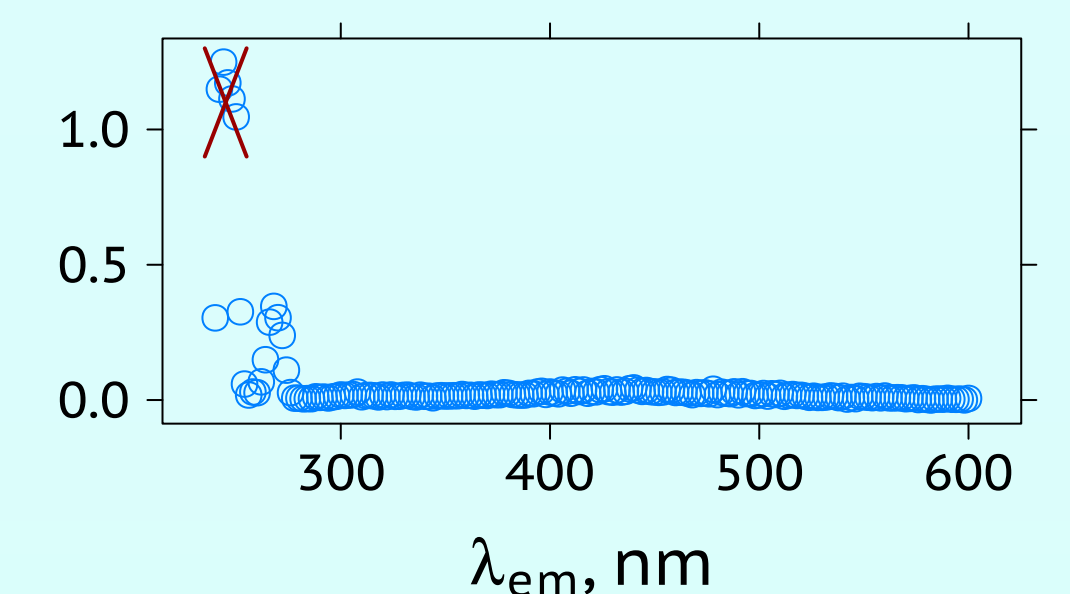
[1], Dogger bank dataset

- Not a Gauss/Lorentz/Voigt peak shape at all
- Scattering easily overflows detectors

How to model scattering?

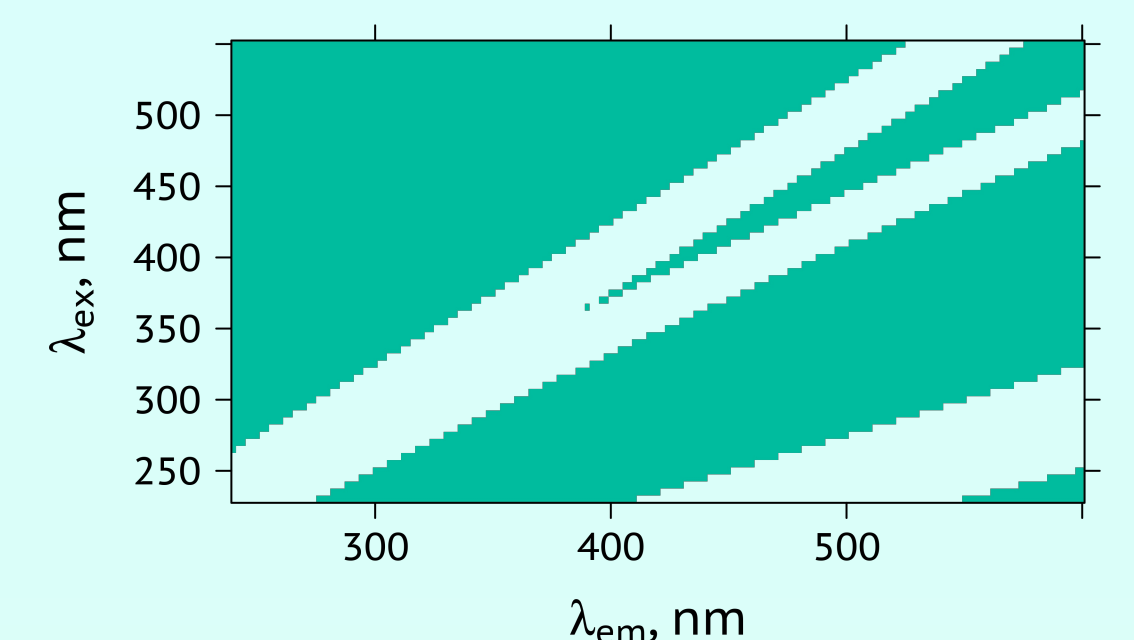
$$X_i(\lambda_j^{em}, \lambda_k^{ex}) = \underbrace{\sum_r A_{i,r} B_{j,r} C_{k,r}}_{\text{fluorescence, PARAFAC}} + \underbrace{\sum_r D_{i,r} S_{j,k,r}}_{\text{scatter, MCR}}$$

- Set overflowed values to missing

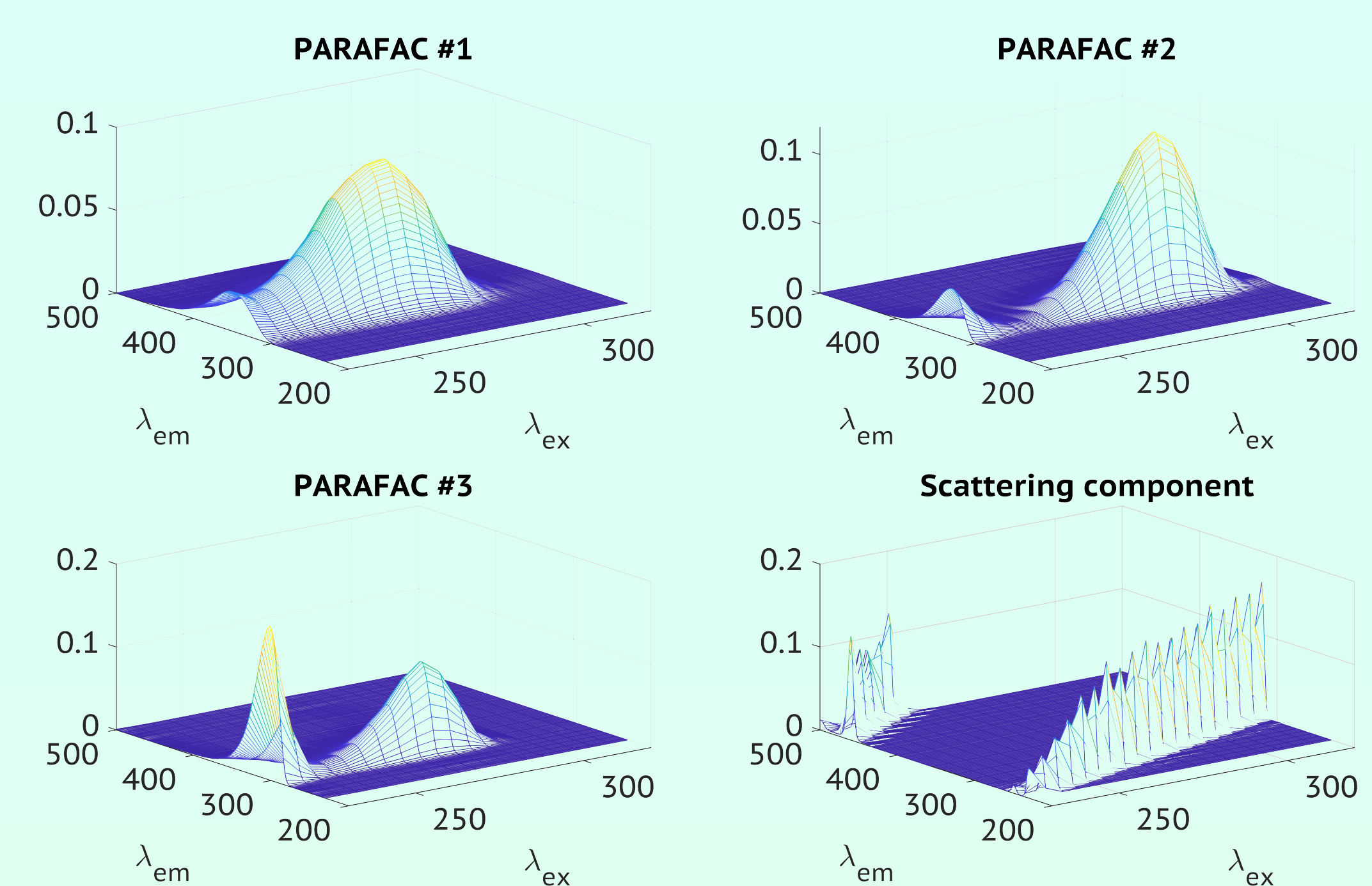


- Fit initial PARAFAC with scattering removed or interpolated

- Fix the MCR loadings to zeros outside scattering region



- Fit MCR and PARAFAC on each other's residuals, like [3]
- 1-3 MCR components needed, use MILES if needed



<http://models.life.ku.dk/fluorescence>

References

- [1] Bahram M.; Bro R.; Stedmon C.; Afkhami A.; Handling of Rayleigh and Raman scatter for PARAFAC modeling of fluorescence data using interpolation, Journal of Chemometrics. 2006, 20, 99–105.
- [2] Jordi R.; Bro R.; Jack-knife estimation of standard errors and outlier detection in PARAFAC models, Chemometrics and Intelligent Laboratory Systems, 2003, 65(1), 35–49.
- [3] Tauler R.; Marqués I.; Casassas E.; Multivariate curve resolution applied to three-way trilinear data: Study of a spectrofluorimetric acid–base titration of salicylic acid at three excitation wavelengths, Journal of Chemometrics, 1998, 12, 55–75.



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