# Laser-induced luminescence spectroscopy of $Gd^{3+}$ ions in aqueous solution and its application to portable monitoring system

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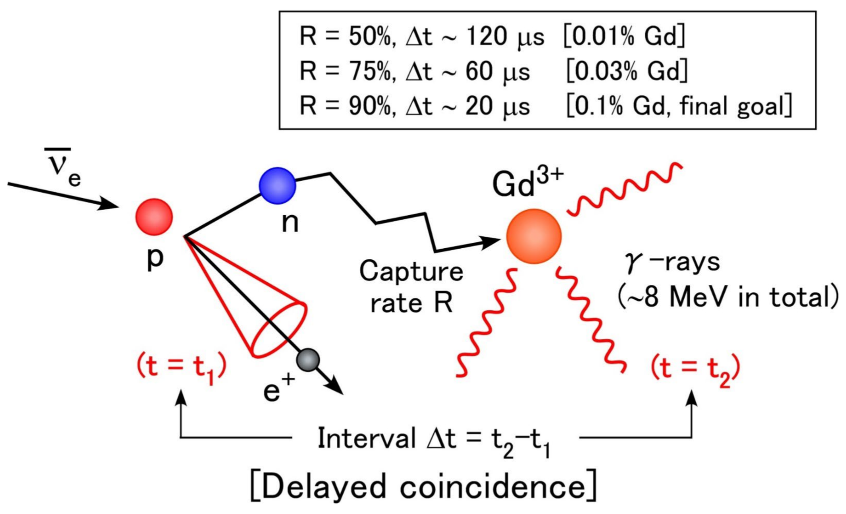
## 1. Introduction

### ■ SK-Gd experiment

The SK-Gd experiment is currently ongoing where gadolinium (Gd) sulfate is dissolved in a water Cherenkov detector to increase the detection sensitivity of supernova relic neutrino events.

- Delayed coincidence technique for $\overline{\nu}_e$ detection
- Large neutron absorption cross section of Gd
- Gd concentration: 0.01% → 0.03% → 0.1%

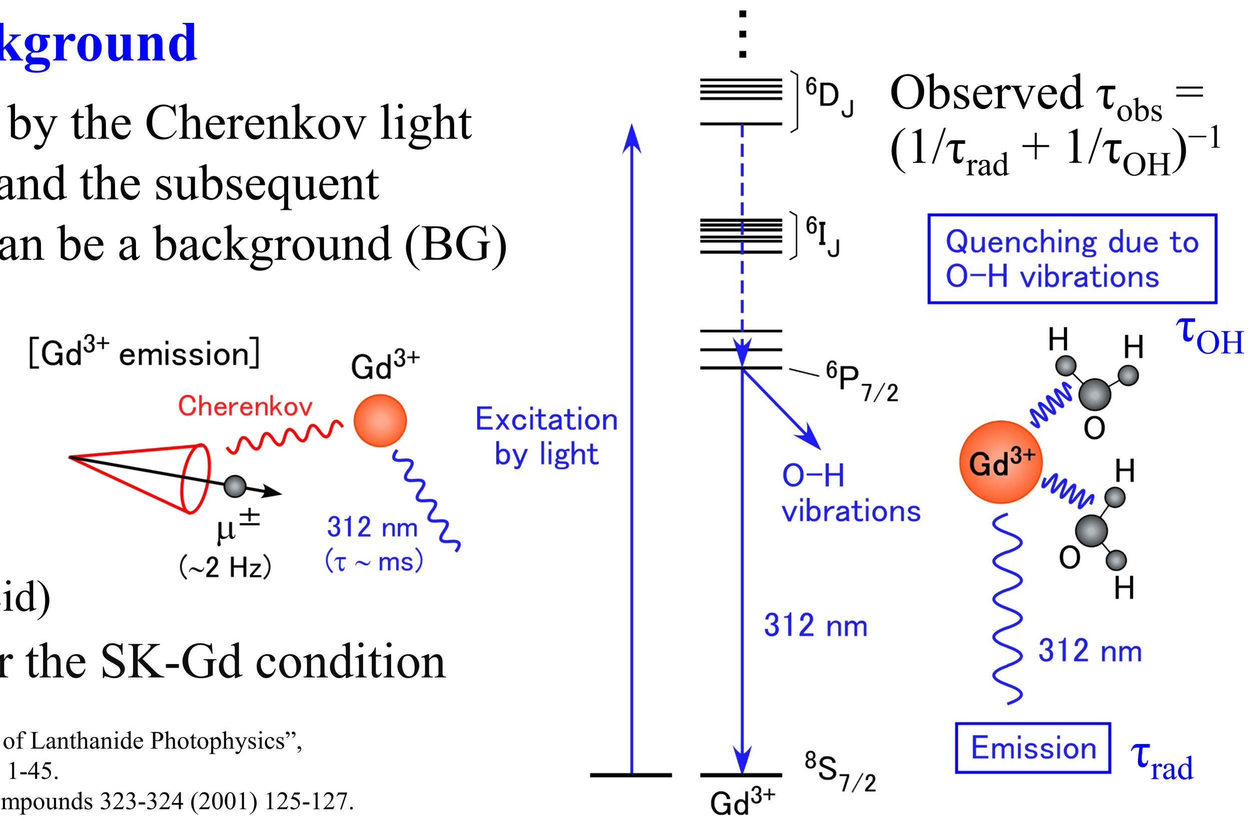
current status (0.03% Gd)




### ■ $Gd^{3+}$ emission background

$Gd^{3+}$ ions are excited by the Cherenkov light from cosmic muons, and the subsequent emission at 312 nm can be a background (BG) source.

- $\tau_{rad}$ = 10.9 ms[1] (calculation)
- $\tau_{obs}$ = 2300 μs[1], 1480 μs[2] (in perchloric acid)
- No $\tau_{obs}$ data under the SK-Gd condition

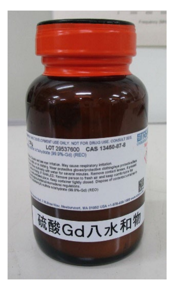


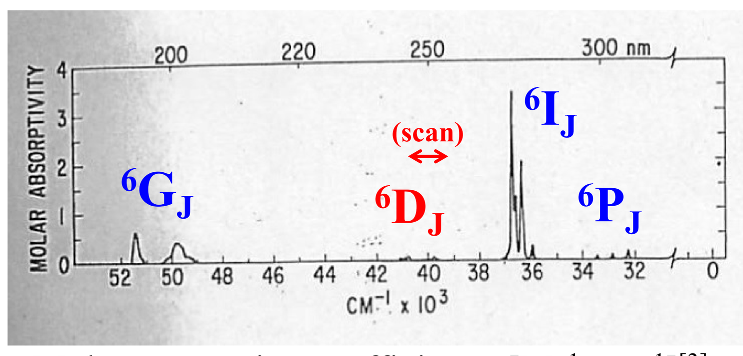

[1] J-C.G. Bünzli, S.V. Eliseeva, "Basics of Lanthanide Photophysics", Lanthanide Luminescence (2010) pp. 1-45.
[2] S. Lis et al., Journal of Alloys and Compounds 323-324 (2001) 125-127.

## 2. $Gd^{3+}$ ion emission measurement

### ■ Experimental setup

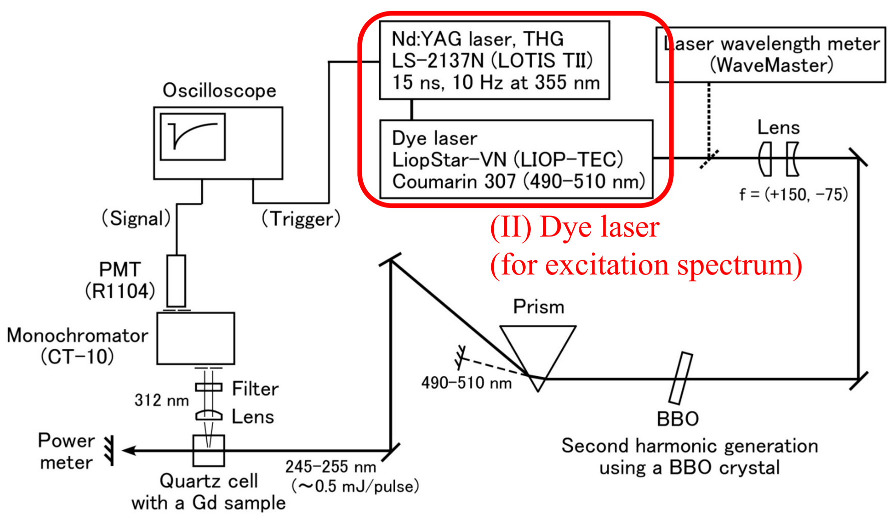
- Laser-induced luminescence spectroscopy of $Gd^{3+}$ ions in aqueous solution
- Commercially available $Gd_2(SO_4)_3 \cdot 8H_2O$ sample dissolved in
  (I) ultrapure water with 0.5-2.0 mol/l $SO_4^{2-}$ or $10^{-6}$-$10^{-4}$ mol/l $NO_3^-$ added for confirming the quenching effect, and
  (II) ultrapure water for measuring the excitation spectrum
- Excitation of $Gd^{3+}$ ions by frequency doubling of a pulsed
  (I) Nd: YAG laser at 532 nm, and
  (II) dye laser at 490-510 nm (tunable)
- PMT signal of $Gd^{3+}$ emission at 312 nm was observed with an oscilloscope.

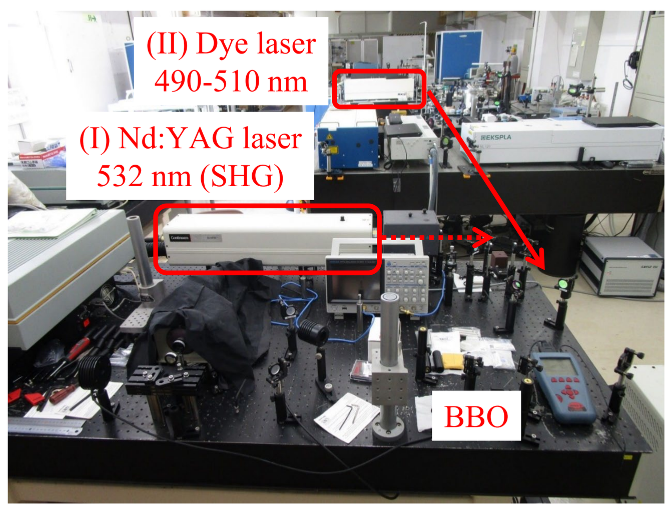





Molar attenuation coefficient ε [$M^{-1} \cdot cm^{-1}$][3] (M: mol/l)

[3] W.T. Carnall, "The absorption and fluorescence spectra of rare earth ions in solution", Handbook on the Physics and Chemistry of Rare Earths 3 (1979) pp. 171-208.

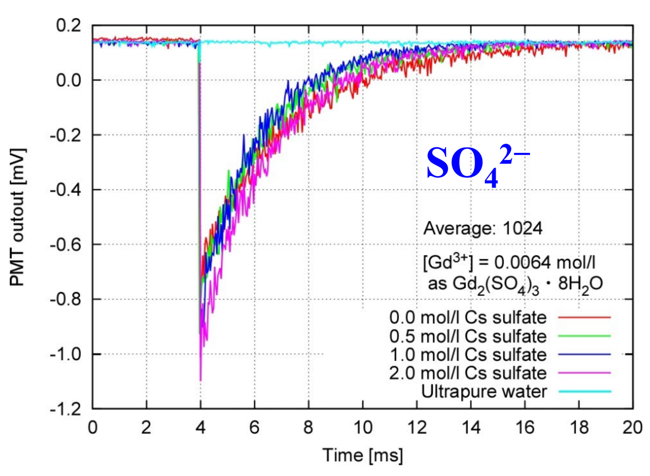


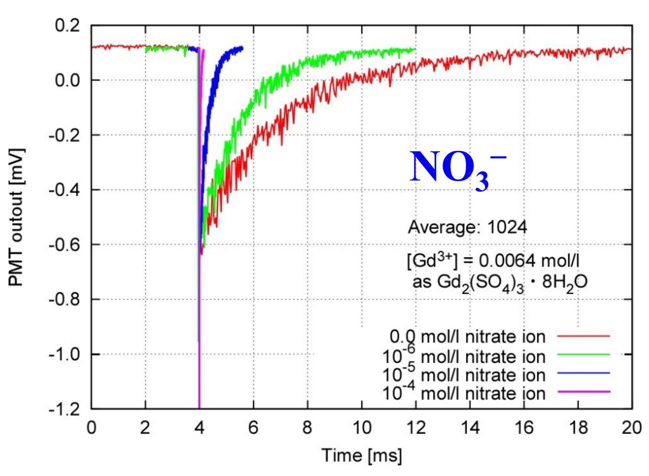




### ■ Quenching by anions (0.1% Gd)

[4] J-J Vuilleumier et al., J. Chem. Soc. Faraday Trans. 1 85(8) (1989) 2605-2613.

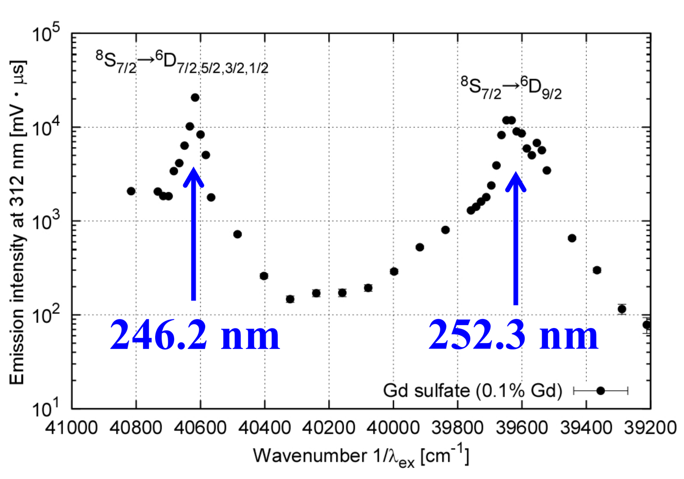
- Quenching by anions leads to shorter $\tau_{obs} = (1/\tau_{rad} + 1/\tau_{OH})^{-1}$.
- Quenching by $SO_4^{2-}$ ions is negligible, and the observed $\tau_{obs}$ ~ 2-3 ms.
- $NO_3^-$ ions show strong quenching, as reported in [4].



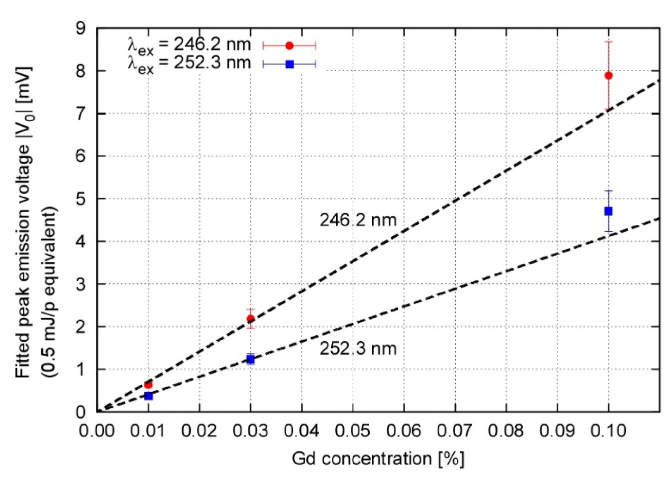




### ■ Excitation spectrum

- Emission increased ~$10^2$ times at 252.3 nm ($^6D_{9/2}$, ε ~ 0.1 $M^{-1} \cdot cm^{-1}$ [3]).
- FWHM ~ 100 $cm^{-1}$ and ε ~ 0.001 $M^{-1} \cdot cm^{-1}$ at non-resonant wavelengths are assumed in the simulation study.




Excitation spectrum

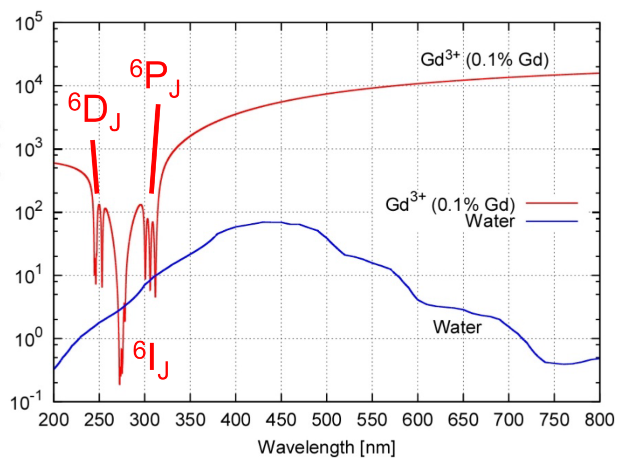


Gd concentration vs. peak voltage

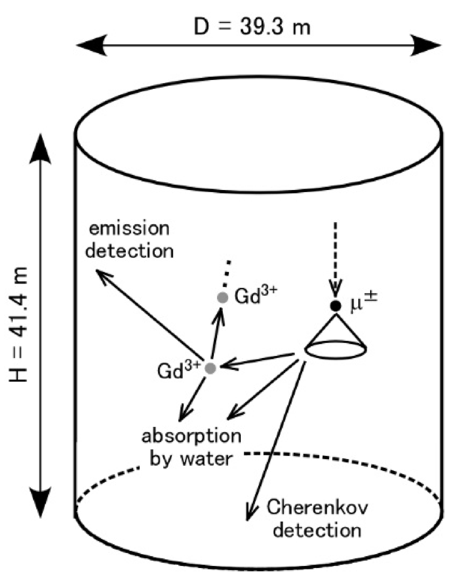
## 3. Simulation study

### ■ Simulation assumptions

- Cherenkov photon wavelength: 200-800 nm
- Attenuation length → Right figure
- $\tau_{rad}$ = 10.9 ms[1], $\tau_{obs}$ = 1, 3, 10 ms
- Normalization: ~$10^5$ pe of Cherenkov photons



Attenuation length

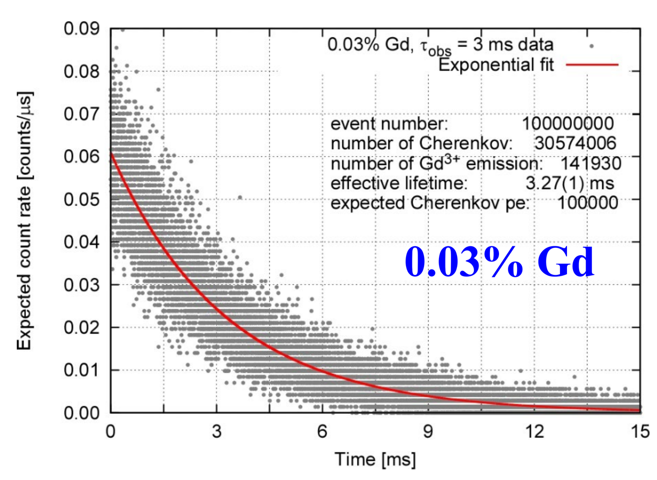


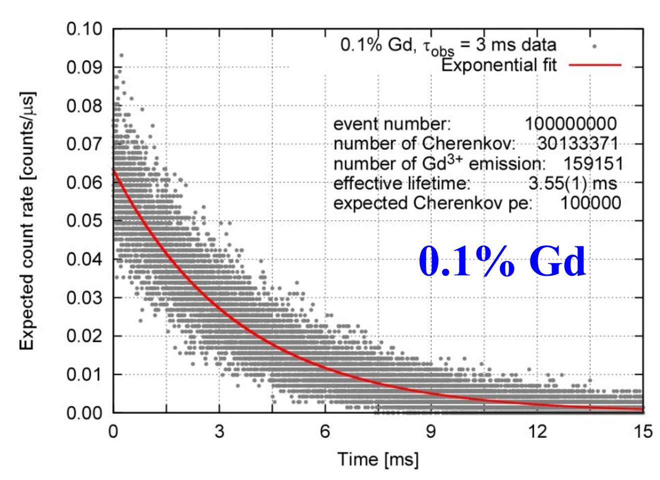

Simulation geometry

### ■ Calculation results ($\tau_{obs}$ = 3 ms)[5]

[5] Y. Iwata et al., Prog. Theor. Exp. Phys. 2022 (2022) 123H01.

- Reabsorption of emission at 312 nm by other $Gd^{3+}$ ions is considered to suppress the BG rate increase with higher Gd concentration.
- <0.1 pe/μs expected for Gd concentrations of up to 0.1%, which is sufficiently lower than the dark noise rate of PMTs.

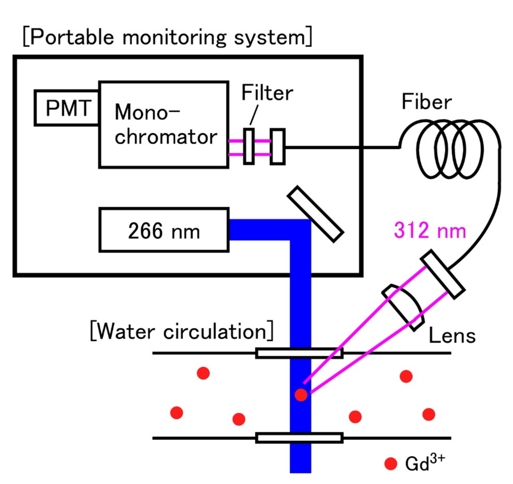


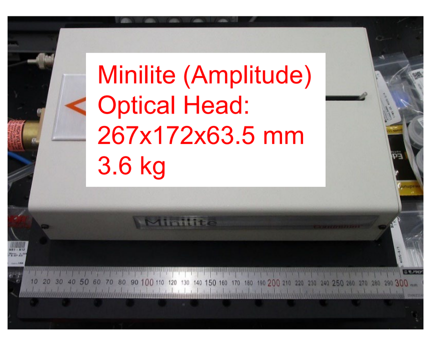




## 4. Portable monitoring system

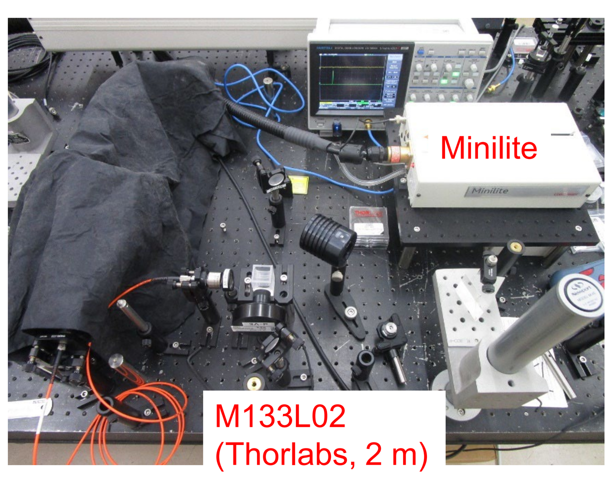
### ■ Characteristics and current progress

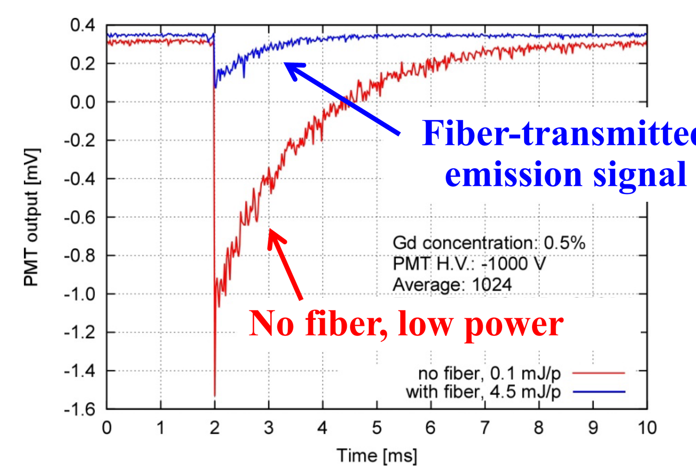
- Real-time measurements of $Gd^{3+}$ concentration and emission lifetime without contamination during water sampling
- Portable Nd:YAG laser available: Minilite
  → Compact and good power stability, but non-resonant 266 nm excitation
- High-OH multimode fiber (M133L02) for transmission of emission signals
- Transmission efficiency ~ 0.4% due to divergence of fiber output light etc.
  → A single filter is enough for BG (scattered 266 nm) suppression.








## 5. Conclusion

### ■ $Gd^{3+}$ ion emission in a water Cherenkov detector

- Quenching by $SO_4^{2-}$ ions is negligible, and the expected $Gd^{3+}$ emission BG rate from cosmic muons in SK-Gd is sufficiently lower than the dark noise rate of PMTs.
- A portable monitoring system for real-time measurements of $Gd^{3+}$ concentration and emission lifetime is currently under development.