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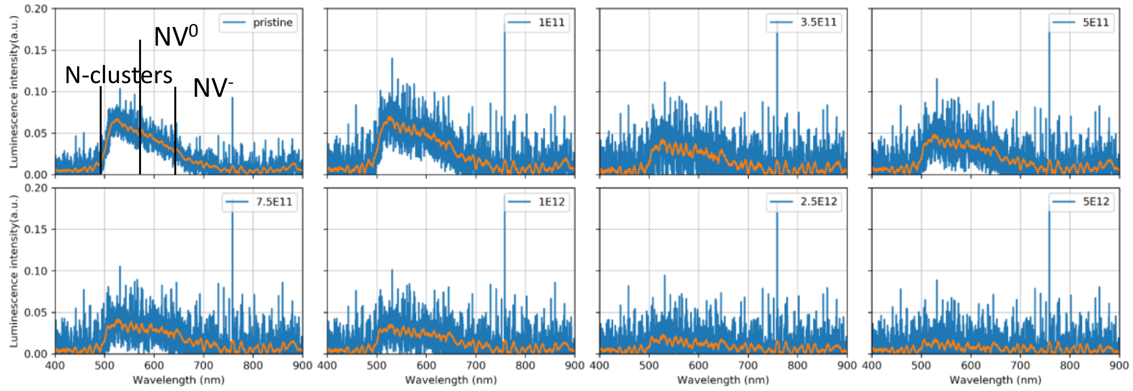
New results on beam-induced color centers in nitrogen containing diamonds

2nd Annual Meeting of ARIES WP17

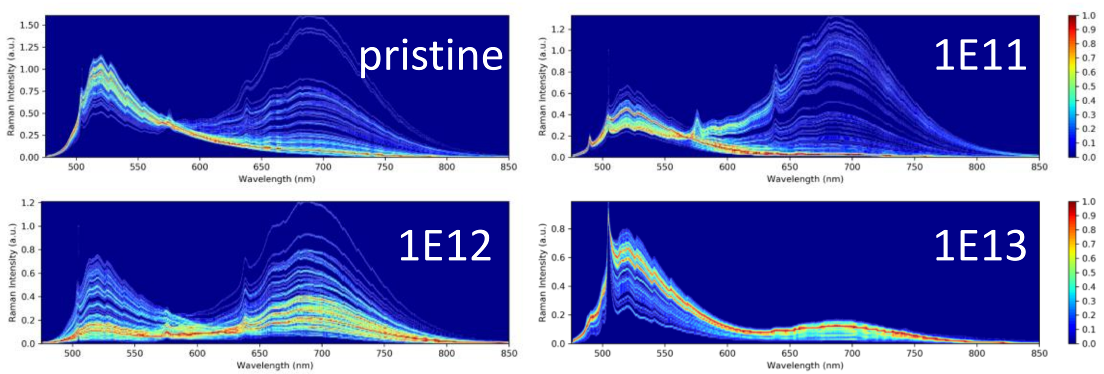
P. Simon, M. Tomut (GSI) D. Grech, M. Kitzmantel (RHP)

Recap of 1st Annual Meeting in Malta

- Measured first iono-luminescence (IL) spectra in 2018 on Diamond/Titanium-matrix composites:



- Raman/PL measurements on composites is not straight forward:



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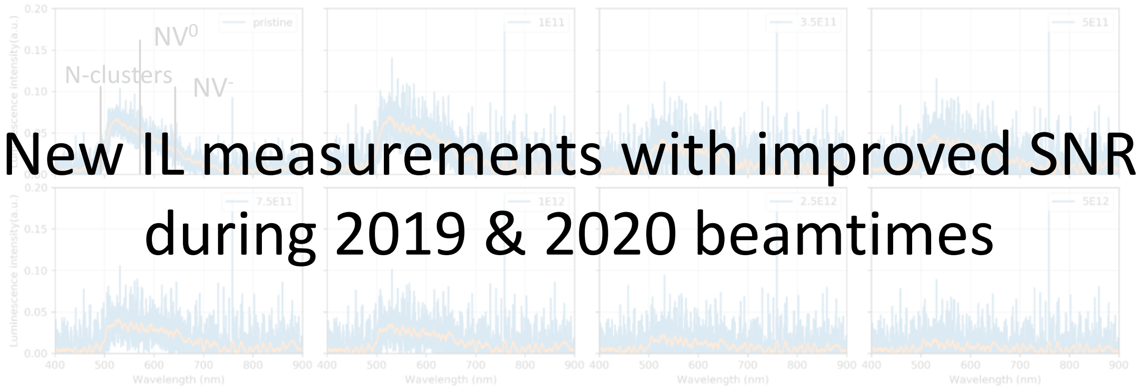

New IL measurements with improved SNR during 2019 & 2020 beamtimes

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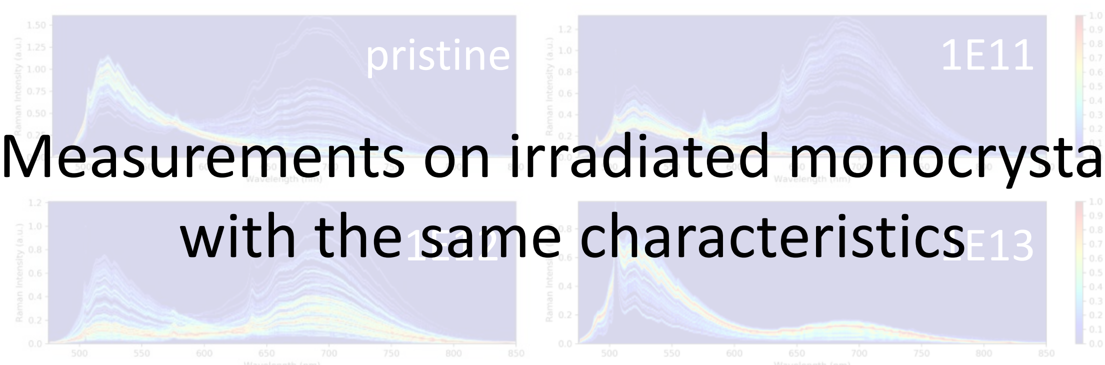

Measurements on irradiated monocrystals with the same characteristics

Irradiation campaigns 2019 & 2020

- Irradiation with 4.8 MeV/n ^{48}Ca and ^{197}Au
- Beamtime 2019 (composites & yellow diamonds):
  - Improved IL measurements with peltier-cooled moving-grating CCD spectrometer (up to $5 \cdot 10^{13}$ i/cm^2)
    - Sensitivity beyond beam diagnostic cameras
  - In-situ FT-IR measurements (up to $5 \cdot 10^{13}$ i/cm^2)
  - First irradiation of monocrystalline diamonds (irregular geometry)

- Beamtime 2020 (composites, CVD diamonds & yellow diamonds):
  - IL with fast CCD spectrometer and on-line flux measurement
  - In-situ UV/c absorption spectroscopy at 50 K and RT
  - Irradiation of monocrystalline diamonds with regular geometry

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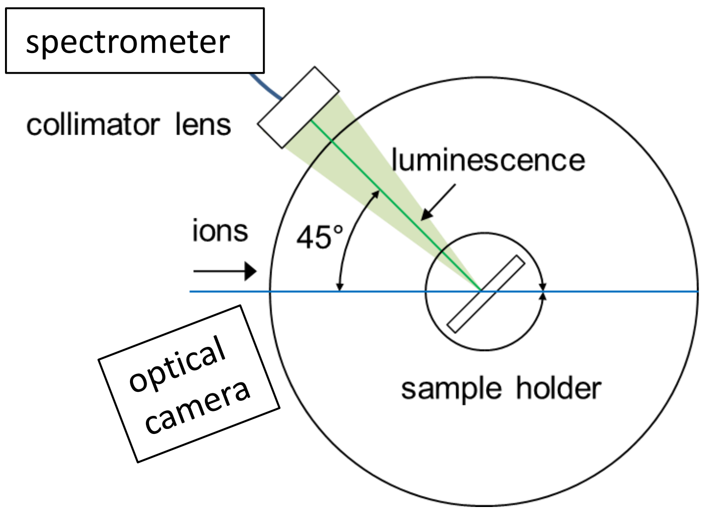
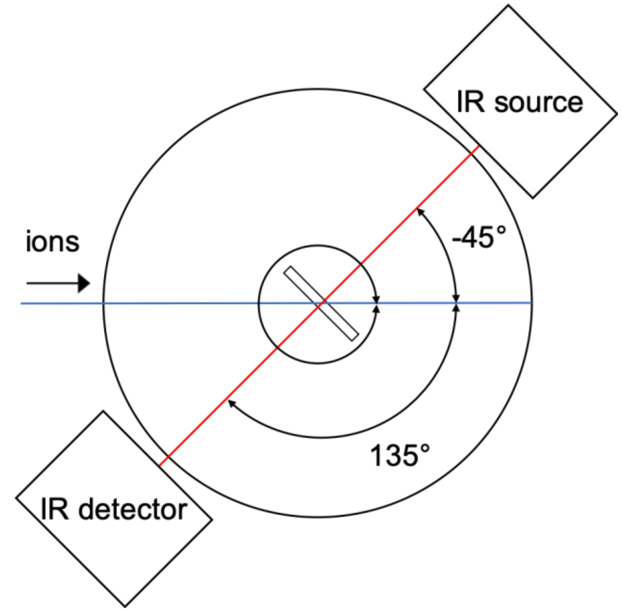
IL + FT-IR measurements 2019

- On-line iono-luminescence:



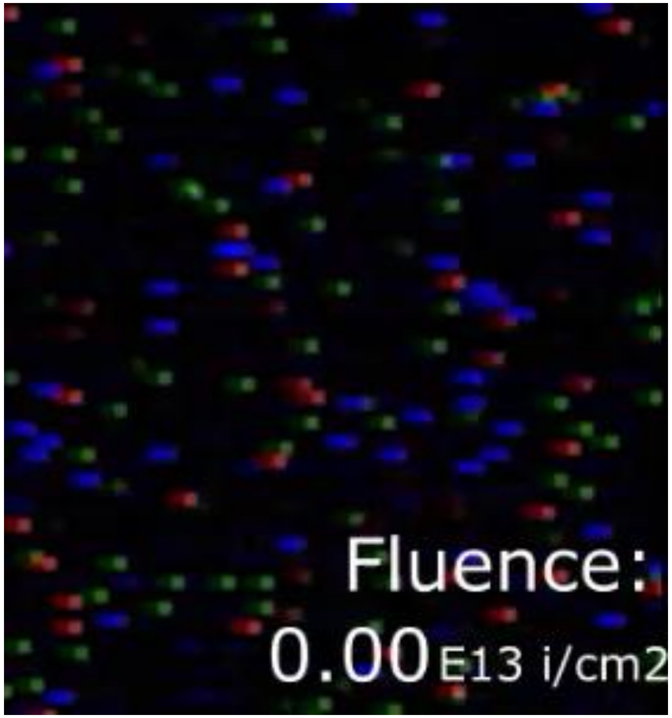
- Horiba iHR320
- Integration time: 5-120 s

- In-situ FT-IR:



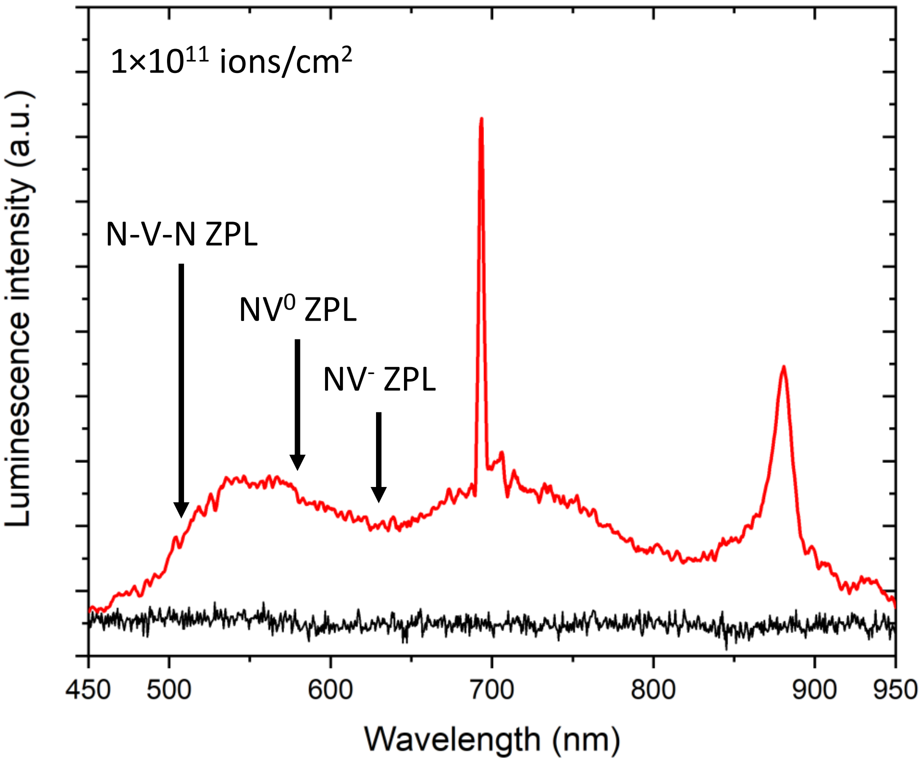
- Thermo Fisher Nicolet 6700
- 2 cm^{-1} resolution

Iono-luminescence



Iono-luminescence Spectrum

- No nitrogen-related ZPLs!
  - [N-V-N]: 502 nm
  - NV0: 575 nm
  - NV-: 638 nm



ZPL: zero-phonon line
PSB: phonon sideband
HPHT: High pressure / high temperature

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- Broad bands:
  - 500 – 650 nm
    - [N-V-N] PSB?
    - Intrinsic „A“ radiation band?
  - 650 – 800 nm
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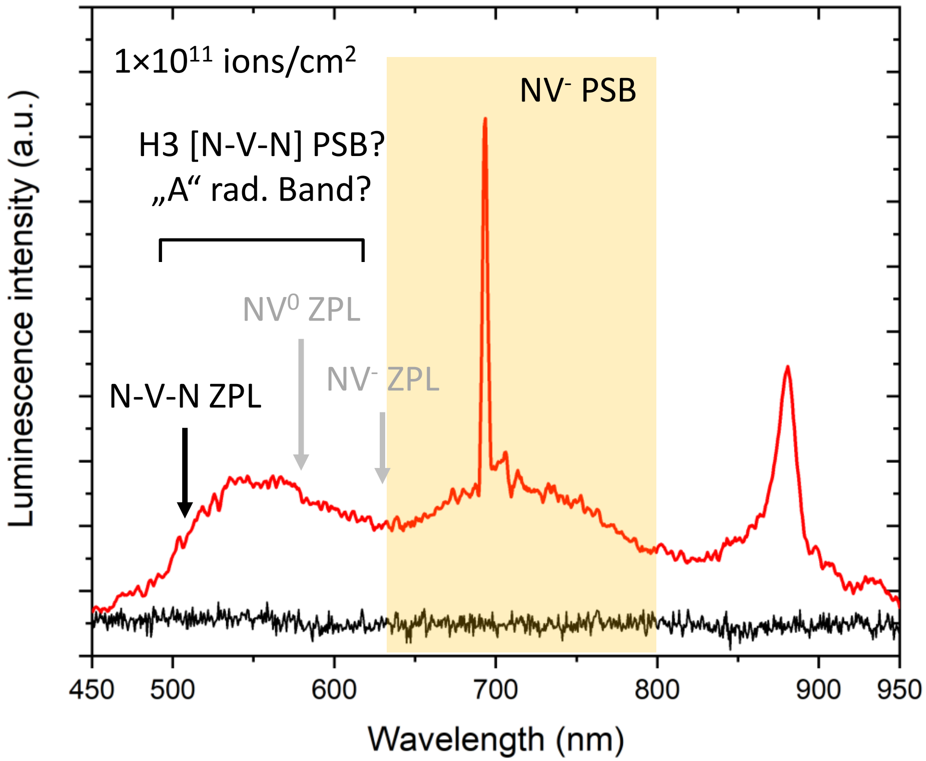

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  - 500 – 650 nm
    - [N-V-N] PSB?
    - Intrinsic „A“ radiation band?
  - 650 – 800 nm
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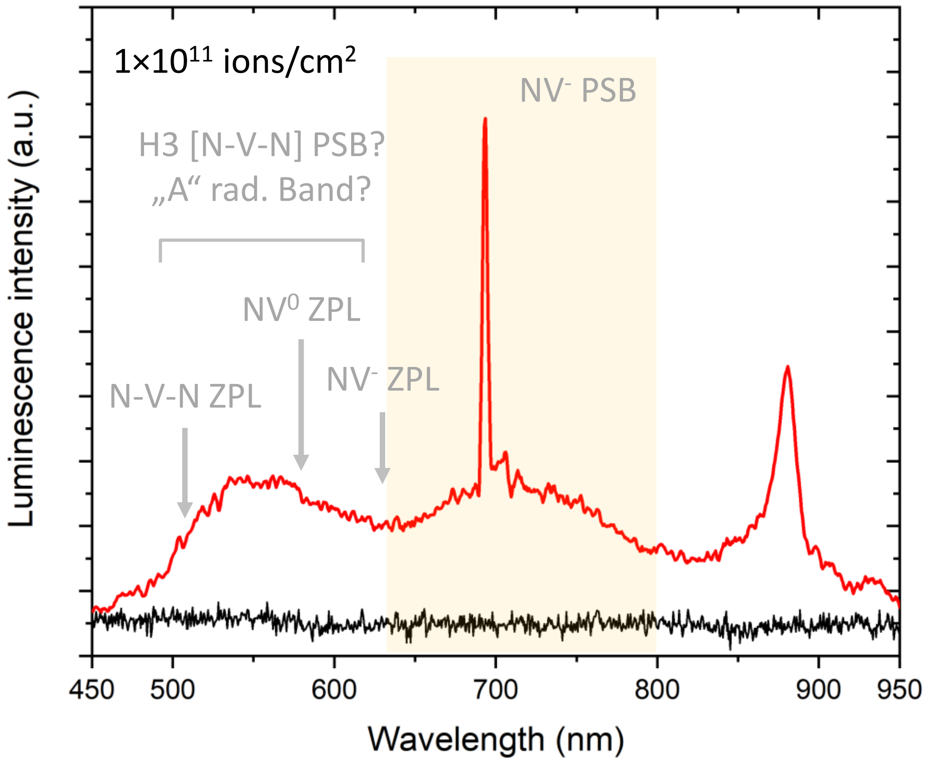
- ZPLs:
  - ~690 nm
    - Al_2O_3 (nat. oxide layer on sample holder)
  - ~884 nm
    - Nickel-related (precursor during HPHT)



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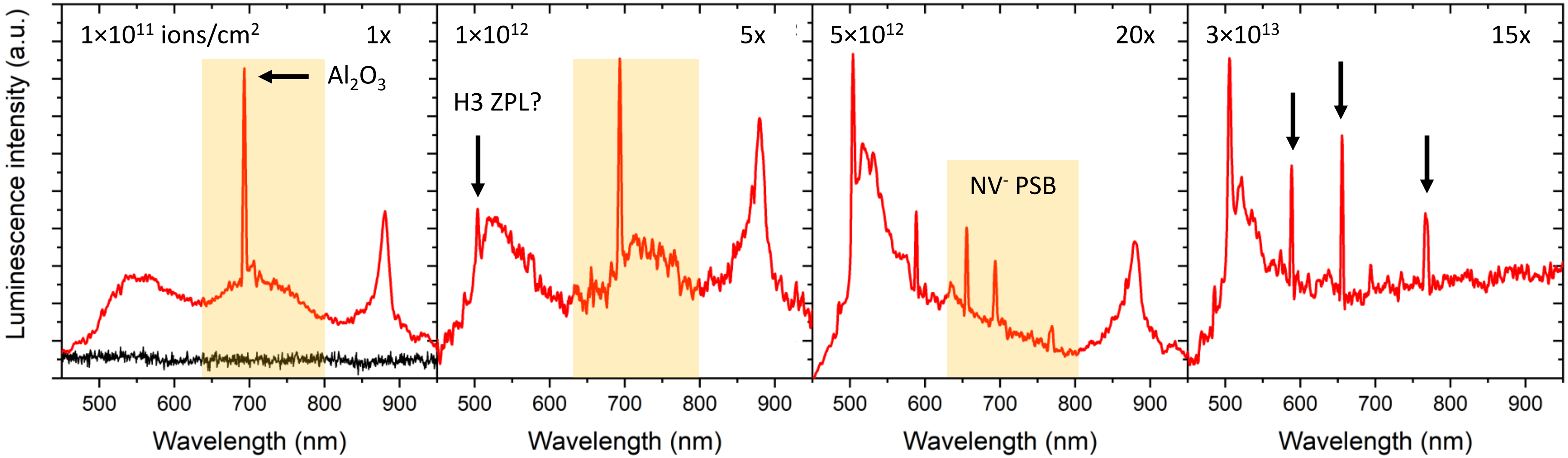
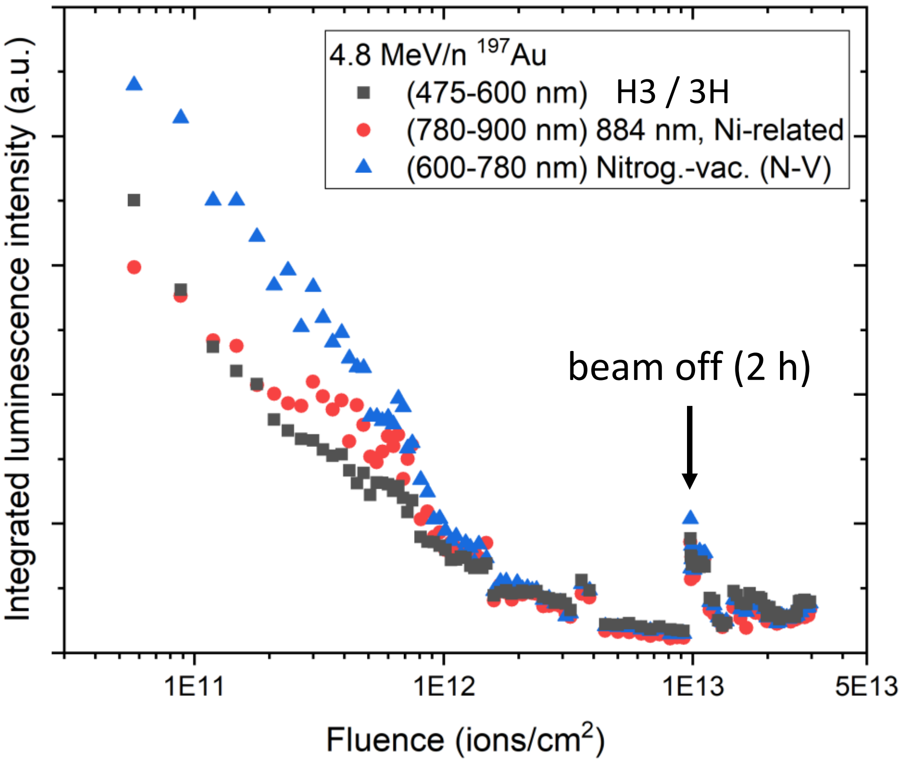
Iono-luminescence Spectra Evolution



- Evolution of ZPL at ~500 nm
  - H3 [N-V-N]: 503.2 nm
  - 3H (intrinsic): 503.4 nm
- Strong decrease of integrated IL signal
- Possible ZPLs at ~590, ~660 & 760 nm → **No clear identification possible**

Integrated IL signal

- Exponential decay of IL sigal with increasing fluence
- Only 5% of initial signal preserved at final fluence
  - Close to detection limit of spectrometer
- No significant contribution of beam-induced defects



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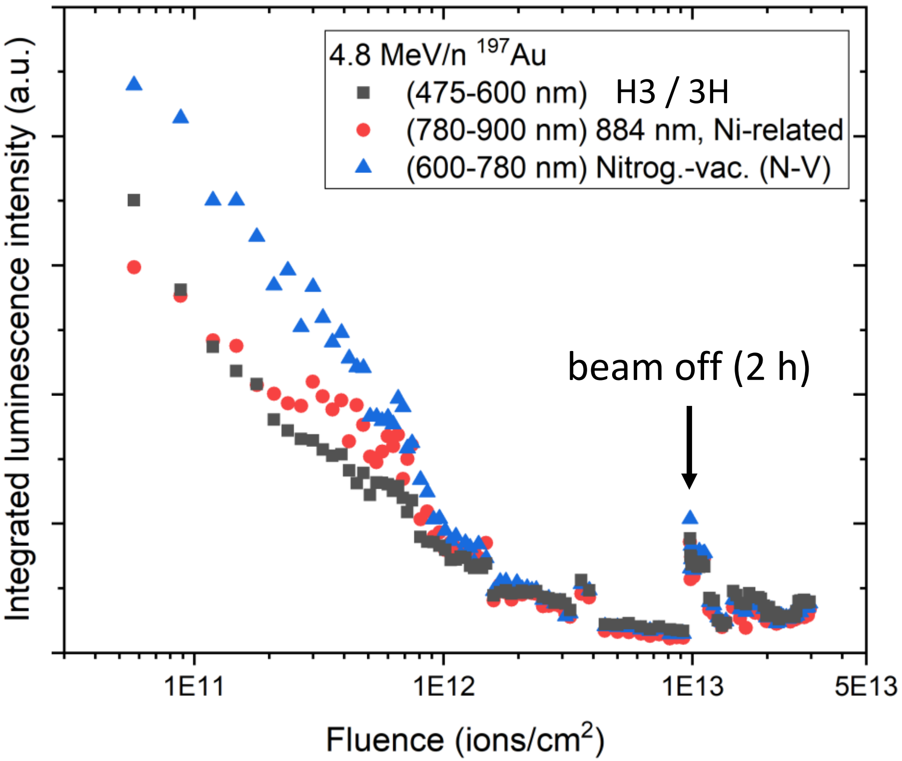
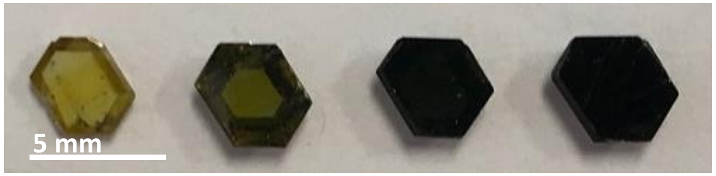
- ... And what about transmission?

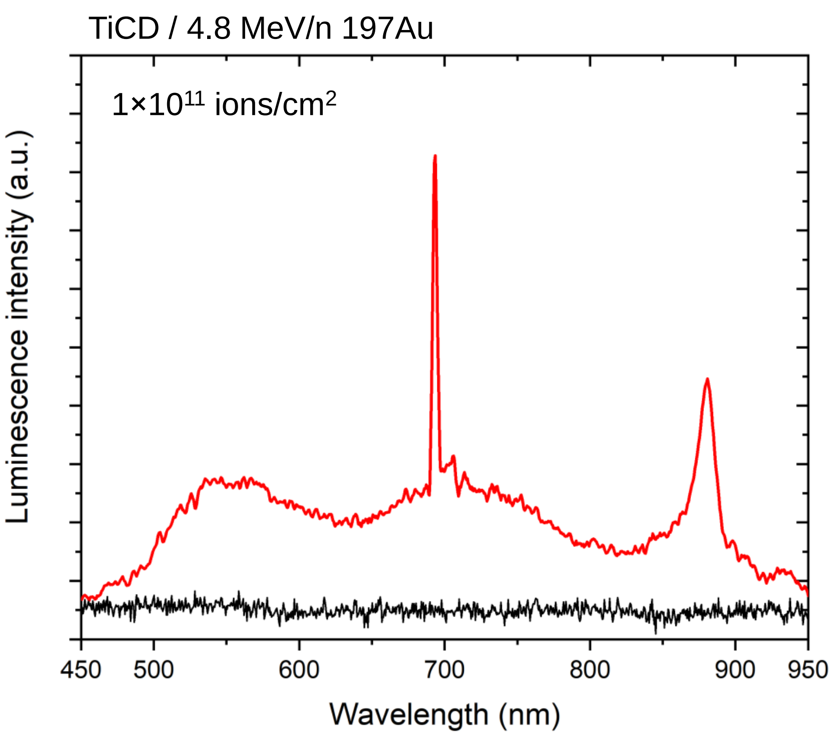


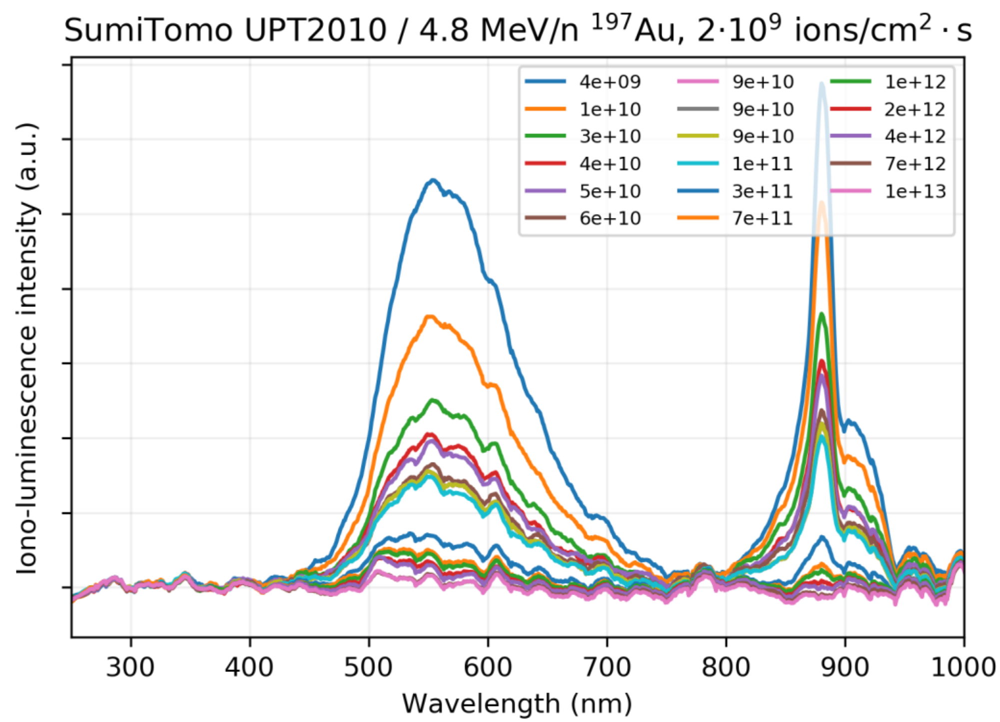
After irradiation with 4.8 MeV/n ^{197}Au:



1×10^{11} 1×10^{12} 5×10^{12} 1×10^{13} ions/cm^2

IL signal / composite vs. monocrystal





- Commercially available (10-100 €/pc., up to 3x3x1 mm) HPHT diamonds with ~200 ppm N_s
- Measurements with new (fast) CCD spectrometer set-up

Good agreement between old & new IL set-up!
Monocrystals behave virtually identical to composites!

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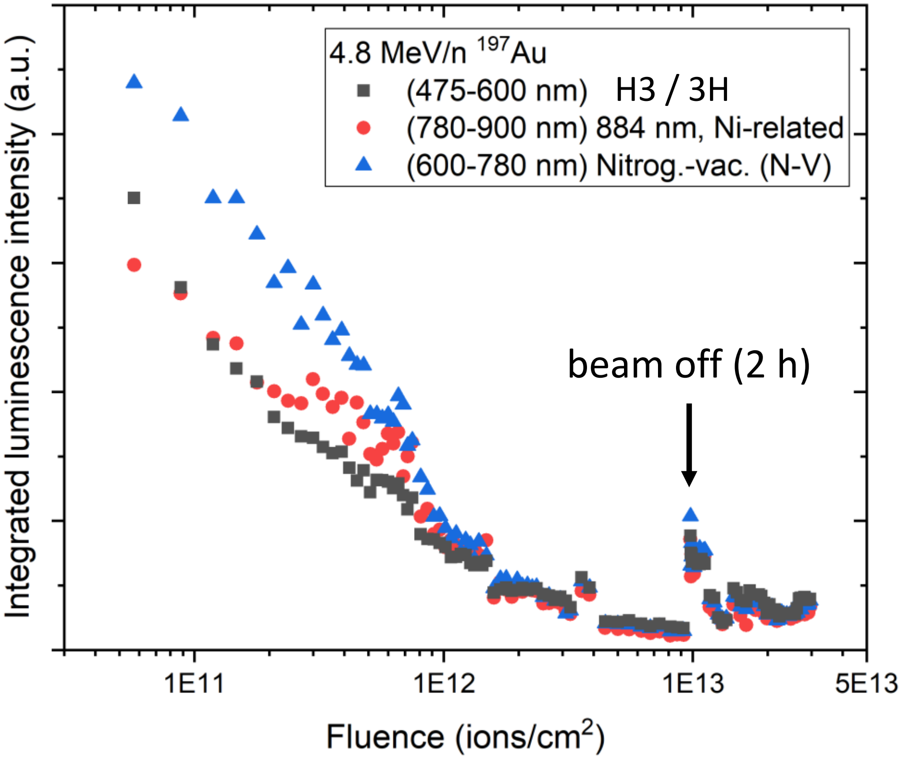

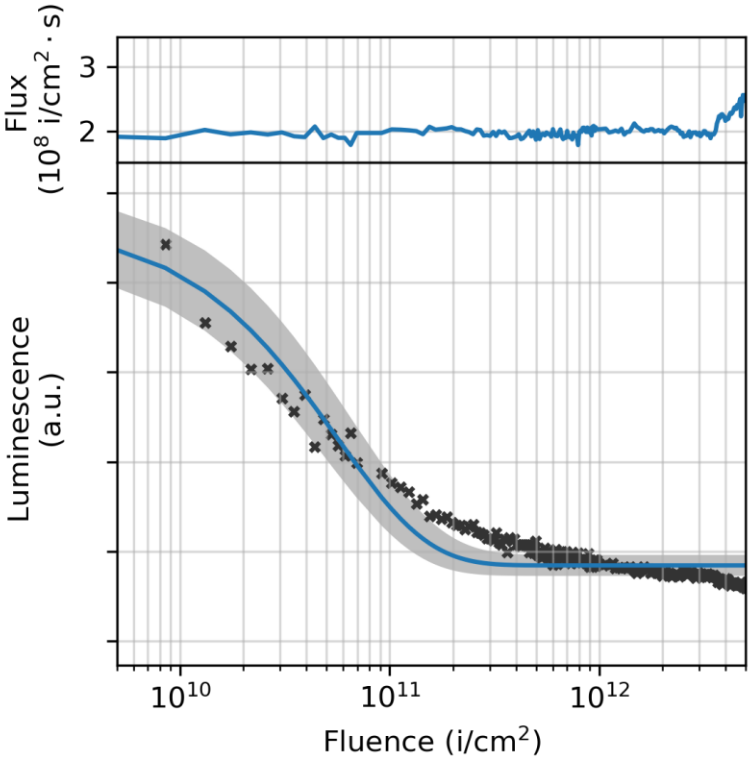

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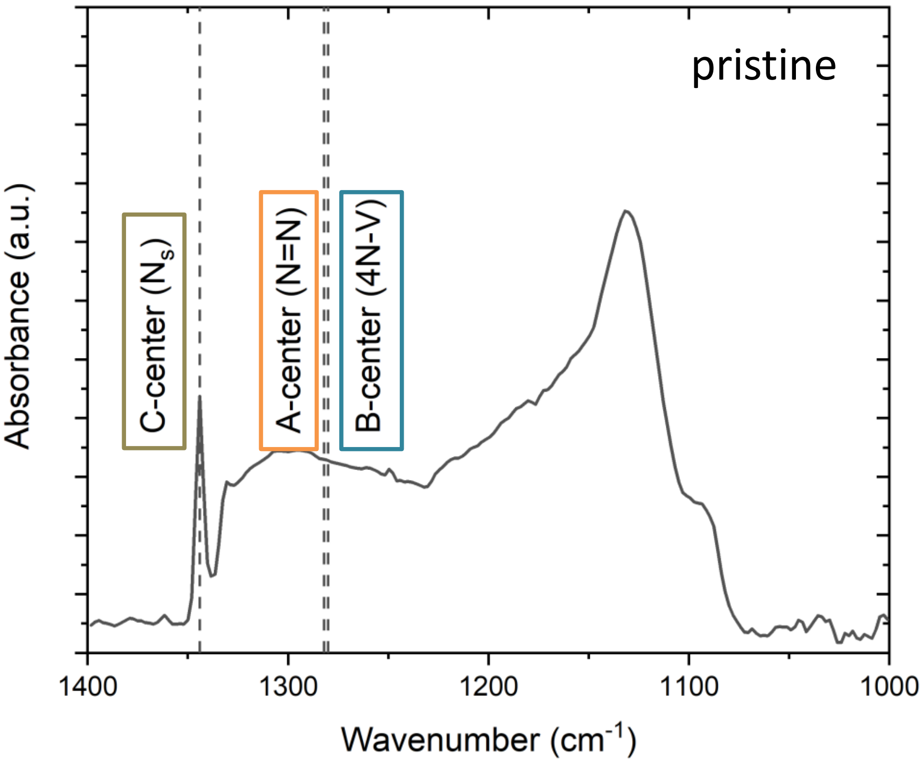
FT-IR spectroscopy of irr. diamond

- 1344 cm^{-1}: C-center (N_s)
- 1282 cm^{-1}: A-center (N=N)
- 1280 cm^{-1}: B-center (4N=V)

- Tracking of radiation-induced defect dynamics



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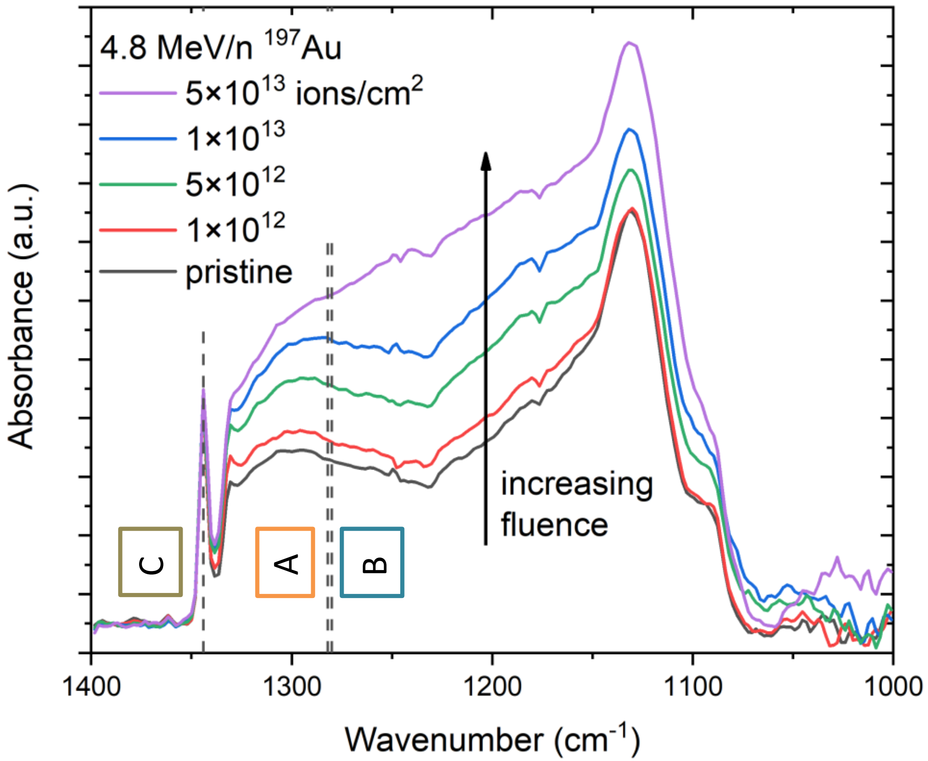

- Tracking of radiation-induced defect dynamics

- Non-luminescent defects that act as sinks for nitrogen:

$$N + V \rightarrow N\text{-}V + N \rightarrow N\text{-}V\text{-}N \rightarrow N{=}N + V$$

$\Delta E_b = 6.3$ eV $\Delta E_b = 4.5$ eV $\Delta E_b = 2.3$ eV

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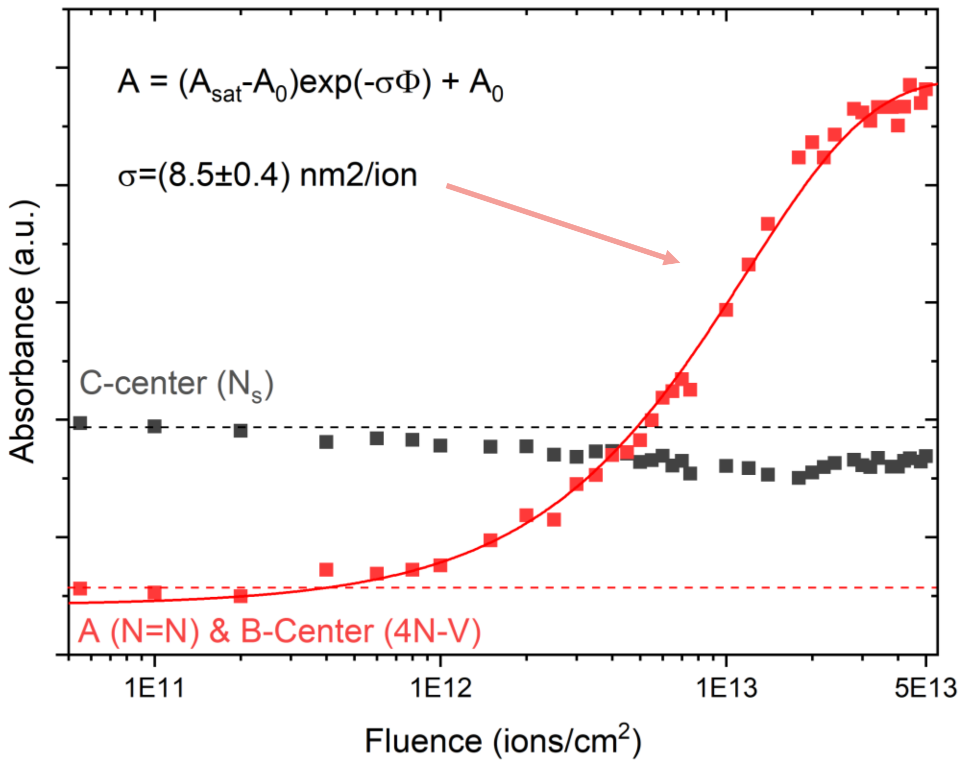
- C-center signal almost constant
  - Dominated by non-irradiated volume

- A&B center signal increases with fluence
  - Damage cross-section: (8.5±0.4) nm^2/ion



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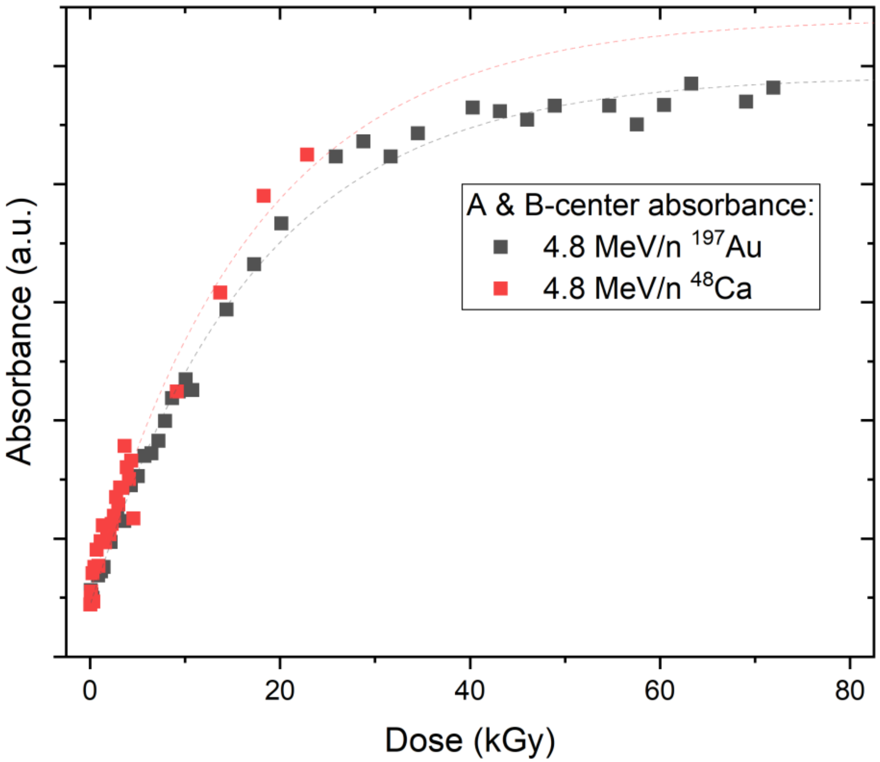
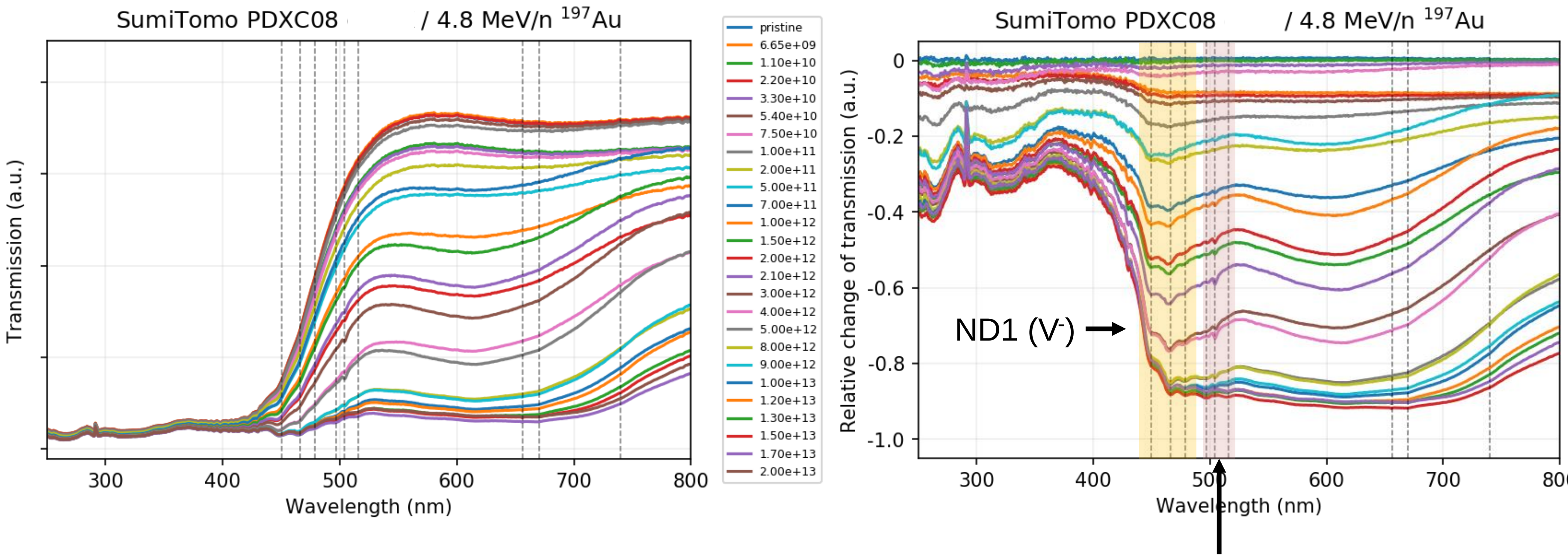


No effect of beam-induced macroscopic temperature!

Similar effect as annealing >1600°C & >5 GPa for several hours!

In-situ UV/c absorption spectroscopy



- Irradiation and measurement at both RT and 50 K
- Dramatic decrease in transmission
  - Already 30-40% loss of transmission at 1×10^{12} (>450 nm)
- Several absorption lines of color centers can be identified, mostly intrinsic

Summary

- IL signal drops down to 5% of initial signal with irradiation
- Optical camera shows change of main emission from „green“ to „blue“
  - Beam diagnostic cameras operate with a narrow filter
- FT-IR shows that complex non-luminescent nitrogen defects are forming
- Intrinsic degradation of transmission by irradiation
  - Additional process that degrades IL signal
- IL signal of diamond excited by swift heavy-ions might be an intrinsic process
  - Implications for potential optimization of the diamonds?