

Remote Raman detection of chlorine gas

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*OSA - Optical Sensors
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Knowledge for Tomorrow

Motivation

- Remote measurements to detect chlorine gas

- Chlorine gas exposure:



- **Industrial**
manufacturing
storage
handling



Karun petrochemical
plant, Iran 2020



MGPI plant, Kansas, 2016

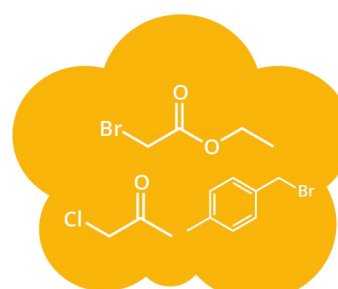
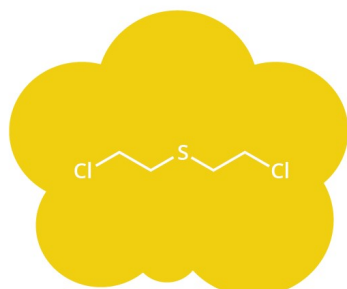
Changzhou, China 2021



Motivation

- Chlorine gas exposure:

- **Warfare agent** - chlorine, mustard gas, bromine and phosgene



- Lethal doses:

Chlorine	6000 [mg min /m ³] - 2070 ppm min
Mustard gas	900 [mg min /m ³] - 230 ppm min
Tear gasses	30 mins temporary effect
Phosgene	3000 [mg min /m ³] - 740 ppm min

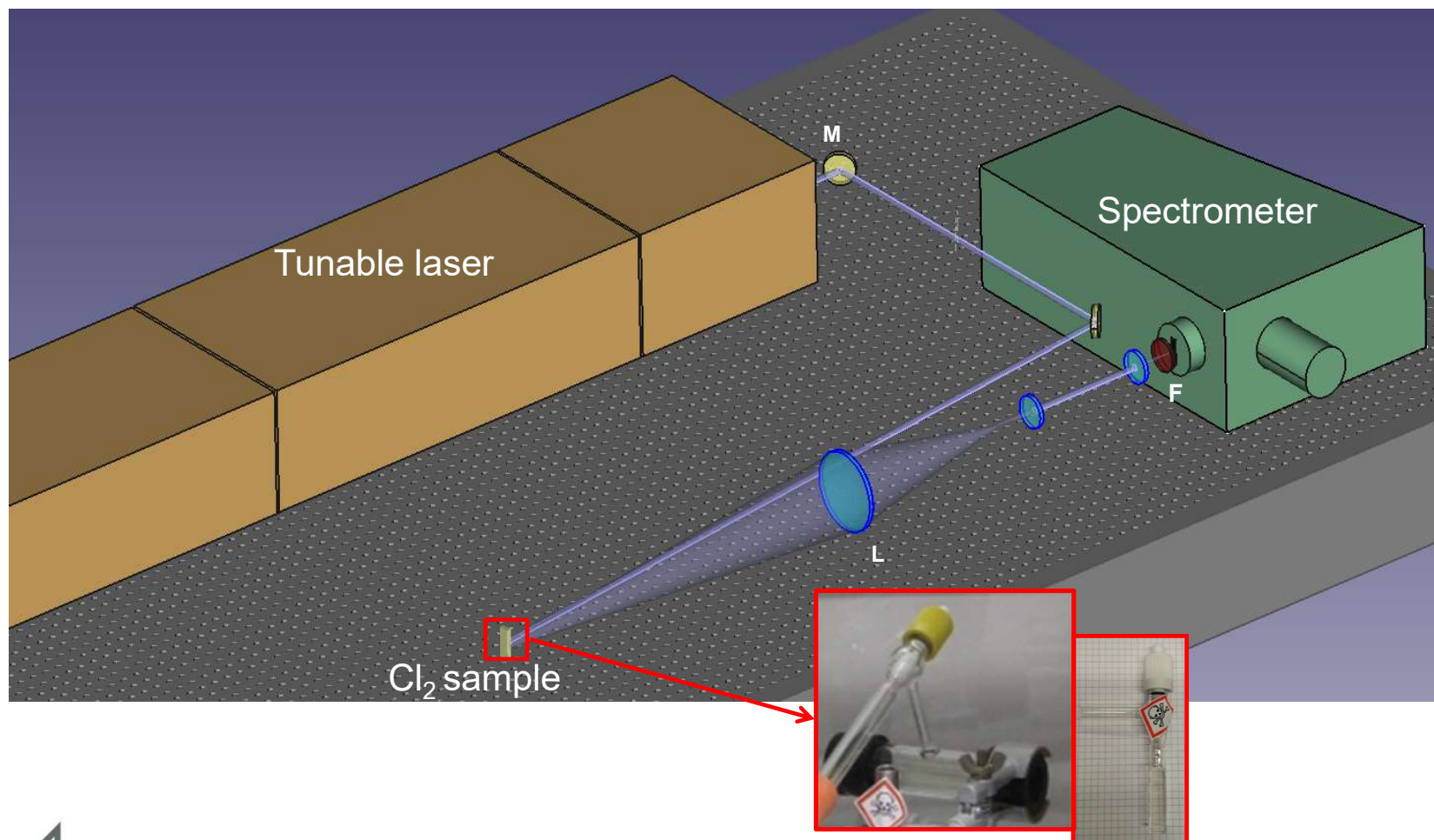


Introduction

- Remote detection set up optimized (distance of 60 cm)
- Changed excitation WL in the deep UV => To maximize Cl₂ signal
- Detection limits in acquisition times
- Solution for background interference => Lab test: Cl₂ must be enclosed
- **SYSTEM SETUP**
- **SAMPLE SETUP**
- **RESULTS**
- **CONCLUSION AND FUTURE DEVELOPMENTS**



System setup

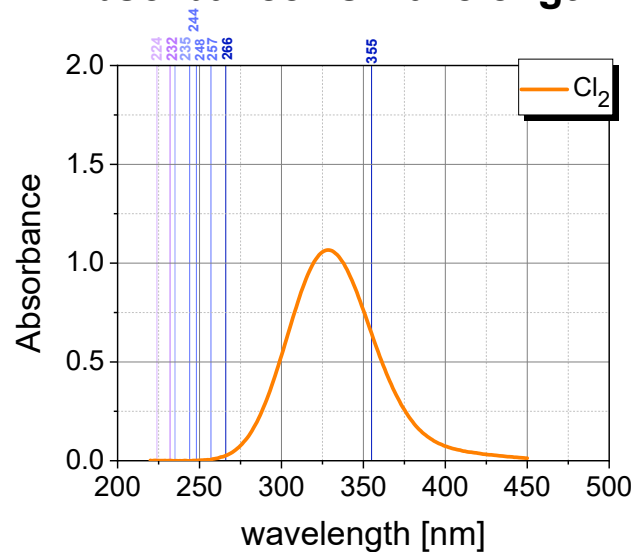


- Nd:YAG laser
- dye laser
- mixing unit
- 190-900 nm,
1 mJ/pulse, 10Hz
- Liq. N₂ cooled spectr.
2400 grooves/mm
- 60 cm remote
distance detection
- Laser filter
- Cl₂ 35.94%



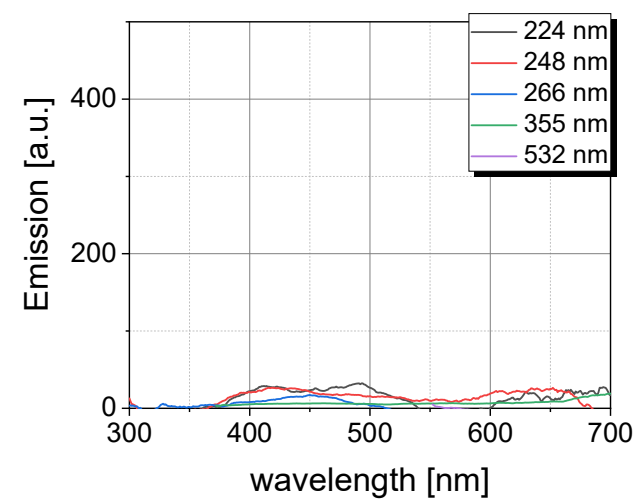
Results

Absorbance vs wavelength



- Edinburgh Instruments FS5 Spectrofluorometer
- 1nm step, 0.5 s sample time per wavelength
- max at 330 nm, FWHM 60 nm
- molar extinction coefficient, path length:
[Cl₂] = 36%

Fluorescence vs wavelength

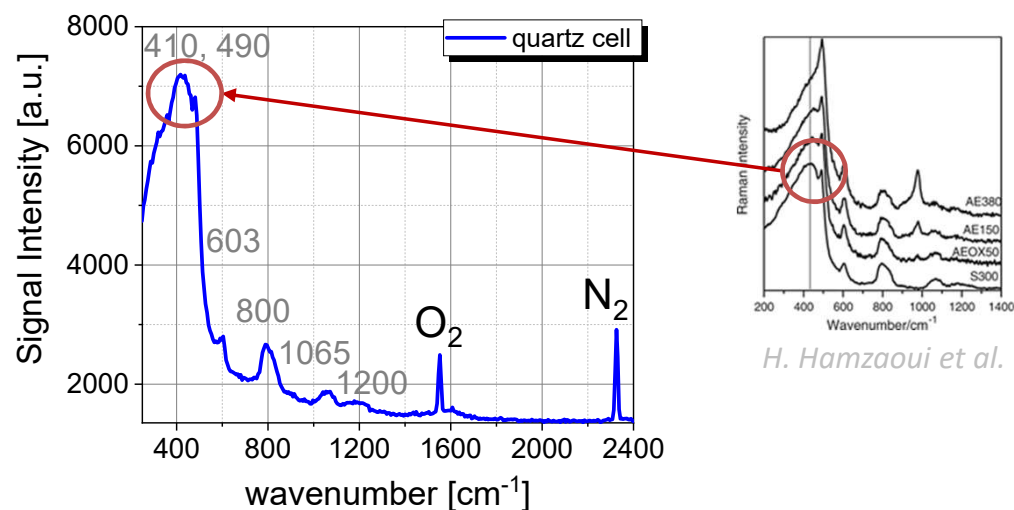


- standard UV laser sources
- negligible fluorescence



Results

- Quartz background signal



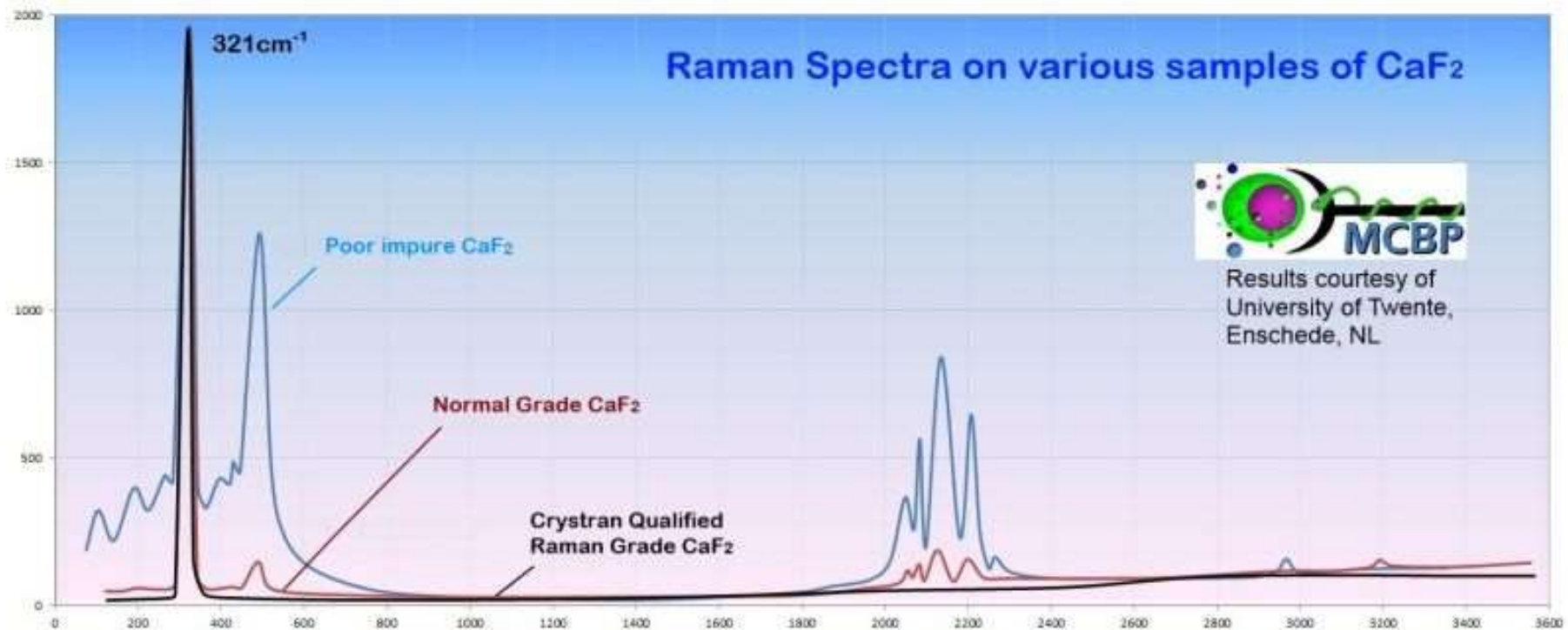
empty quartz glass cell
as ref. background

- laser energy density below 6 mJ/cm²
- 224, 232, 235 nm tested to maximize signal
- broad peak 410 cm⁻¹ + sharp one 490 cm⁻¹, in agreement with literature



Results

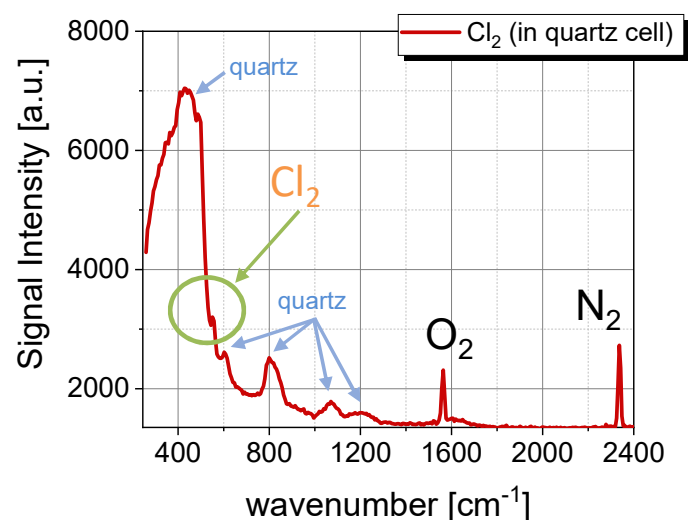
- **Special CaF₂ background signal**



Results

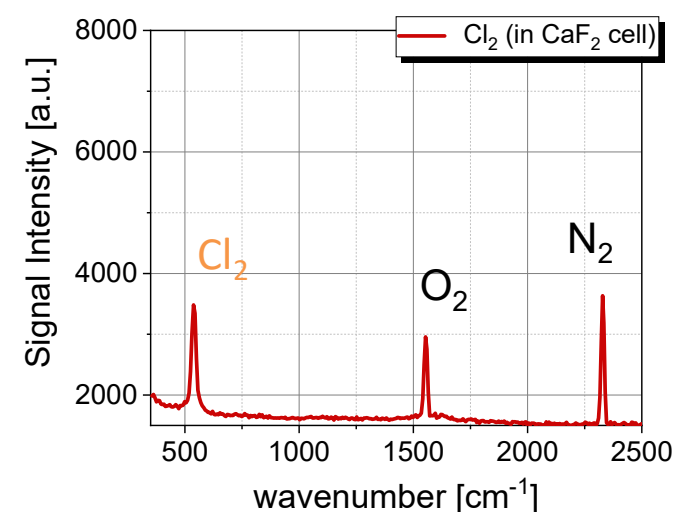
New windows material, new cell

Cl₂ signal (- quartz bknd)



vs

Cl₂ signal (- CaF₂ bknd)



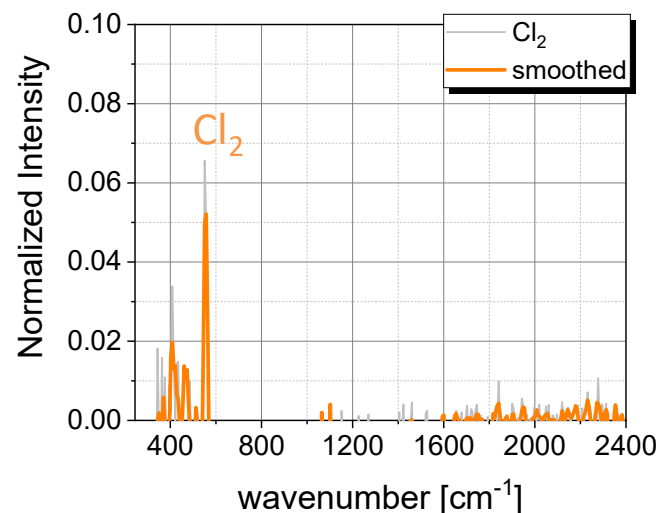
- quartz cell material overlapping with chlorine Raman signal
- Cl₂ sharp peak at 554 cm⁻¹ (15 cm⁻¹ FWHM)
- expected for Cl₂ at 554, 547, and 539 cm⁻¹



Results

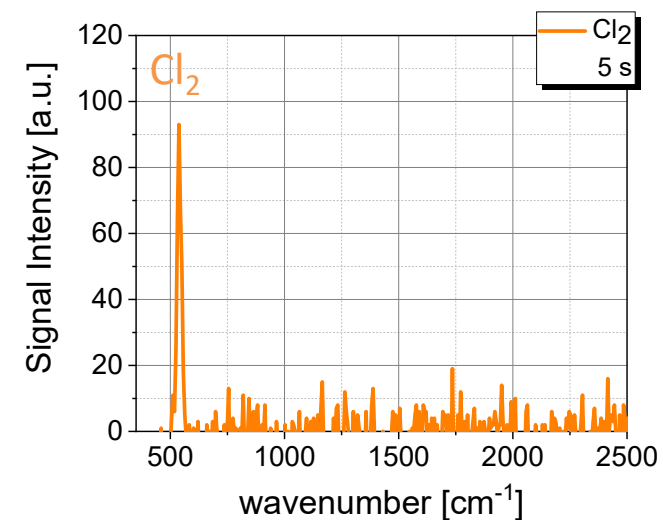
New windows material, new cell

Cl₂ signal (- quartz bknd)



vs

Cl₂ signal (- CaF₂ bknd)

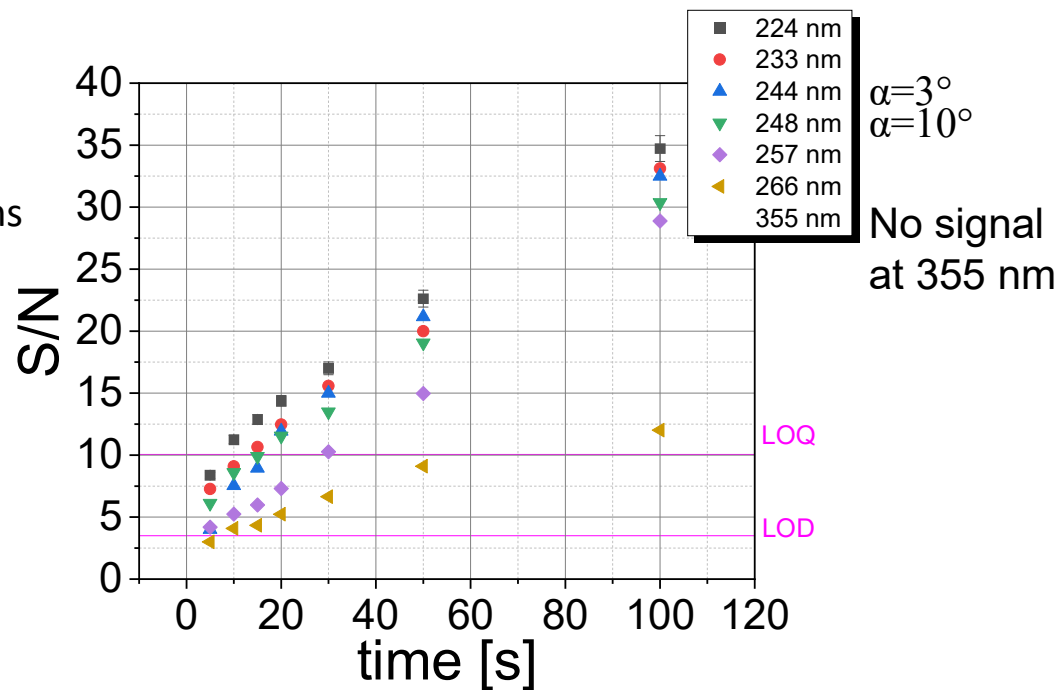
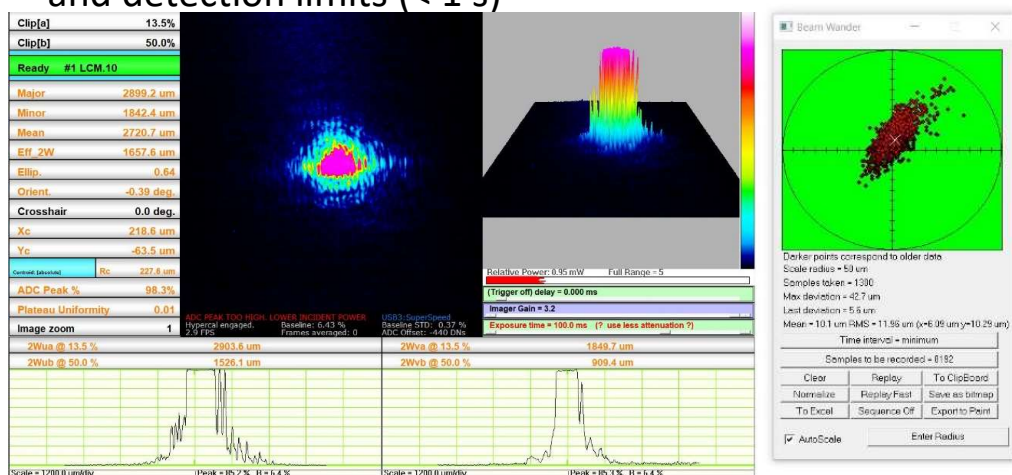


- broad peak quartz residual, in agreement with literature
- hard to separate the two
- remove cell not possible => change material



Results

- Avoid cell material interference around region of interest => Raman grade CaF₂, diamond
- detection limit lowered to **5s** (instead of 50 s)
- Raman peak interference removed changing material
- not intensified camera => possible to lower concentrations and detection limits (< 1 s)



Conclusions & Future Developments

- Chlorine gas was detected in a remote Raman configuration: not standard setup
- Collimated configuration, 60 cm detection distance, laser energy density $< 6 \text{ mJ/cm}^2$, acquisition time 5 s
- Solved quartz interference around region of interest (Raman peaks overlapping) => special Raman grade CaF_2 windows
- acquisition time reduced from 50 s to **5s** changing windows to CaF_2
- Excitation wavelengths (224, 235, 244, 248, 257, 266, 355 nm) at 1mJ
- Reduce acquisition time using an ICCD detector
- Concentration limits



Thank you!

Questions



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