Remote Raman detection of chlorine with deep UV excitation wavelengths

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Motivation

- Remote measurements to detect chlorine gas

- Chlorine gas exposure:

  - **Industrial**
  - manufacturing
  - storage
  - handling

MGPI plant, Kansas, 2016

DPC Enterprises, Missouri, 2002
Motivation

- Chlorine gas exposure:

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

- Lethal doses:
  - Chlorine: \(6000 \text{ [mg min } / \text{ m}^3]\) - 2070 ppm min
  - Mustard gas: \(900 \text{ [mg min } / \text{ m}^3]\) - 230 ppm min
  - Tear gasses: 30 mins temporary effect
  - Phosgene: \(3000 \text{ [mg min } / \text{ m}^3]\) - 740 ppm min
Introduction

• Remote detection set up optimized (distance of 60 cm)

• Change 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, 2.5 mJ/pulse, 10Hz
- Liq. N\textsubscript{2} cooled spectr. 2400 grooves/mm
- 60 cm remote distance detection
- Laser filter
- Cl\textsubscript{2} \sim 1 mg/ml
Sample setup

- Self-made system to fill a chlorine gas cell
- Chlorine pure gas tank 99.8%
- Vacuum pump below 0.4 bar
- Return line (chemical dechlorinators) sodium thiosulfate, sodium hydroxide, deionized water
- Local $\Delta P < 0.5$ bar to avoid window breaking limits
- Final sample concentration was 0.36 bar
Results

Absorbance vs wavelength

Fluorescence vs wavelength

- Edinburgh Instruments FSS Spectrofluorometer
- 1nm step, 0.5 s sample time per wavelength
- max at 330 nm, FWHM 60 nm
- molar extinction coefficient, path length: 
  \([\text{Cl}_2] = 0.36 \text{ bar}\)

- standard UV laser sources
- negligible fluorescence
Results

Background signal

- Laser energy density below 20 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

- 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
- 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

- Signal increases at higher excitation wavelengths for both cell material and Cl₂
- strong overlapping of the unwanted quartz material with chlorine at higher wavelengths

- Cl₂ growing increasing the incoming laser wavelength
- Increasing time increases signal by 24%
- 50 s detection limit (peak interference, not intensified camera)
Conclusions & Future Developments

- Chlorine gas was detected in a remote Raman configuration: not standard setup

- Collimated configuration, 60 cm detection distance,
  Total cell 1 mg/ml, probed volume (125 μg)
  laser energy density < 20 mJ/cm², acquisition time 50 s

- Reduce acquisition time using an ICCD detector

- Avoid strong quartz interference around region of interest (peaks overlapping) => Raman grade CaF₂, diamond
  New windows material required

- excitation wavelengths, concentration limits
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