Real-time optical characterization of ammonia (NH_3) by UV absorption spectroscopy

Nikolaus Dietz and Vincent Woods

Department of Physics & Astronomy

Georgia State University; Atlanta GA

http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html

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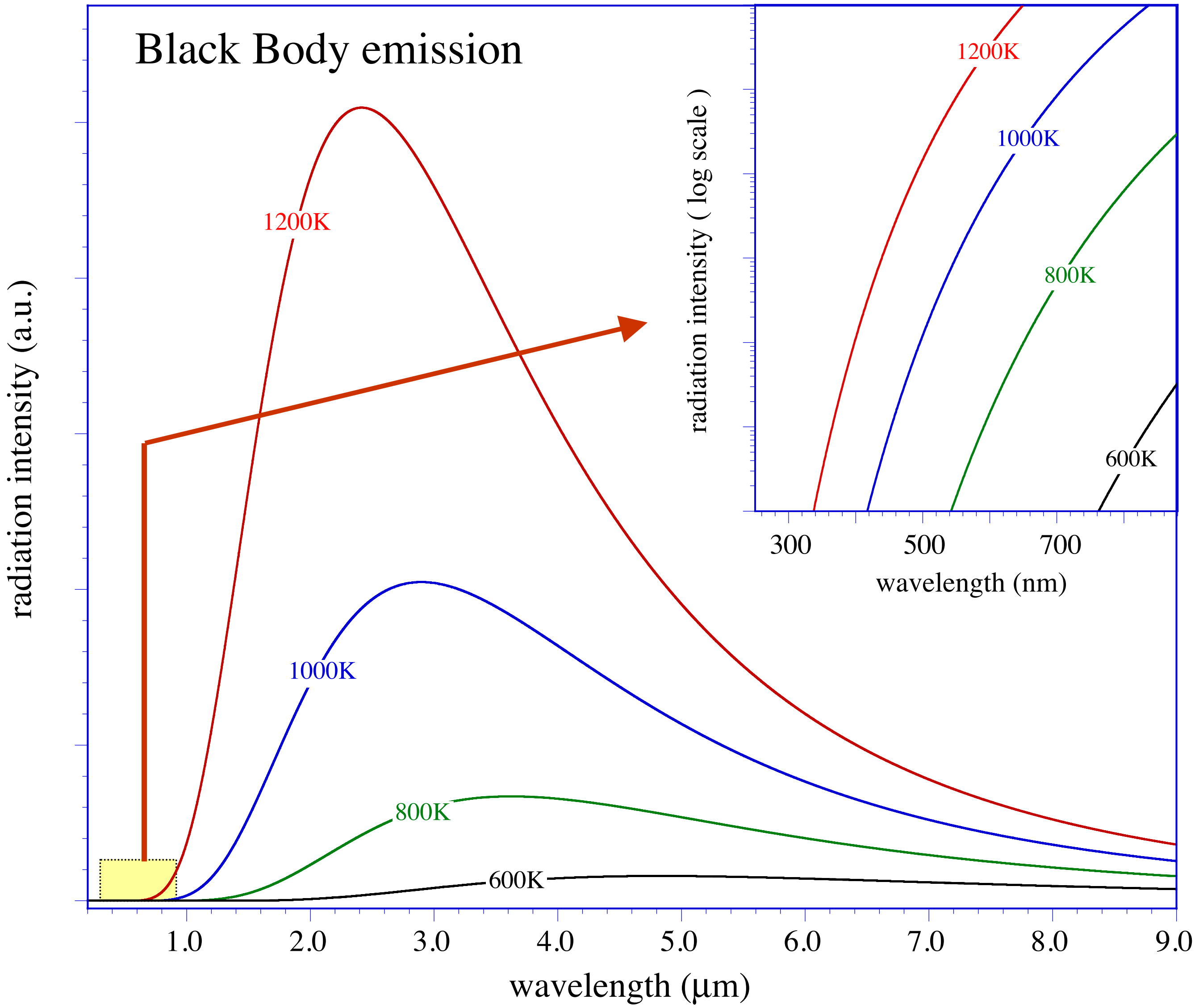
Dept. Physics & Astronomy

Advantage of UV spectroscopy to study precursor decomposition dynamics



- optical detection below 400 nm eliminates interference with radiation from heated substrate / gas phase:
  - UV absorption
  - *Luminescence*
  - Raman spectroscopy
  - Light Scattering

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Ammonia (NH_3) Characterization

- *NH_3 UV-transmission spectra*
- *Continuous NH_3 flow: Sensitivity*
- *Decomposition of NH_3*
- *Pulsed NH_3 flow*

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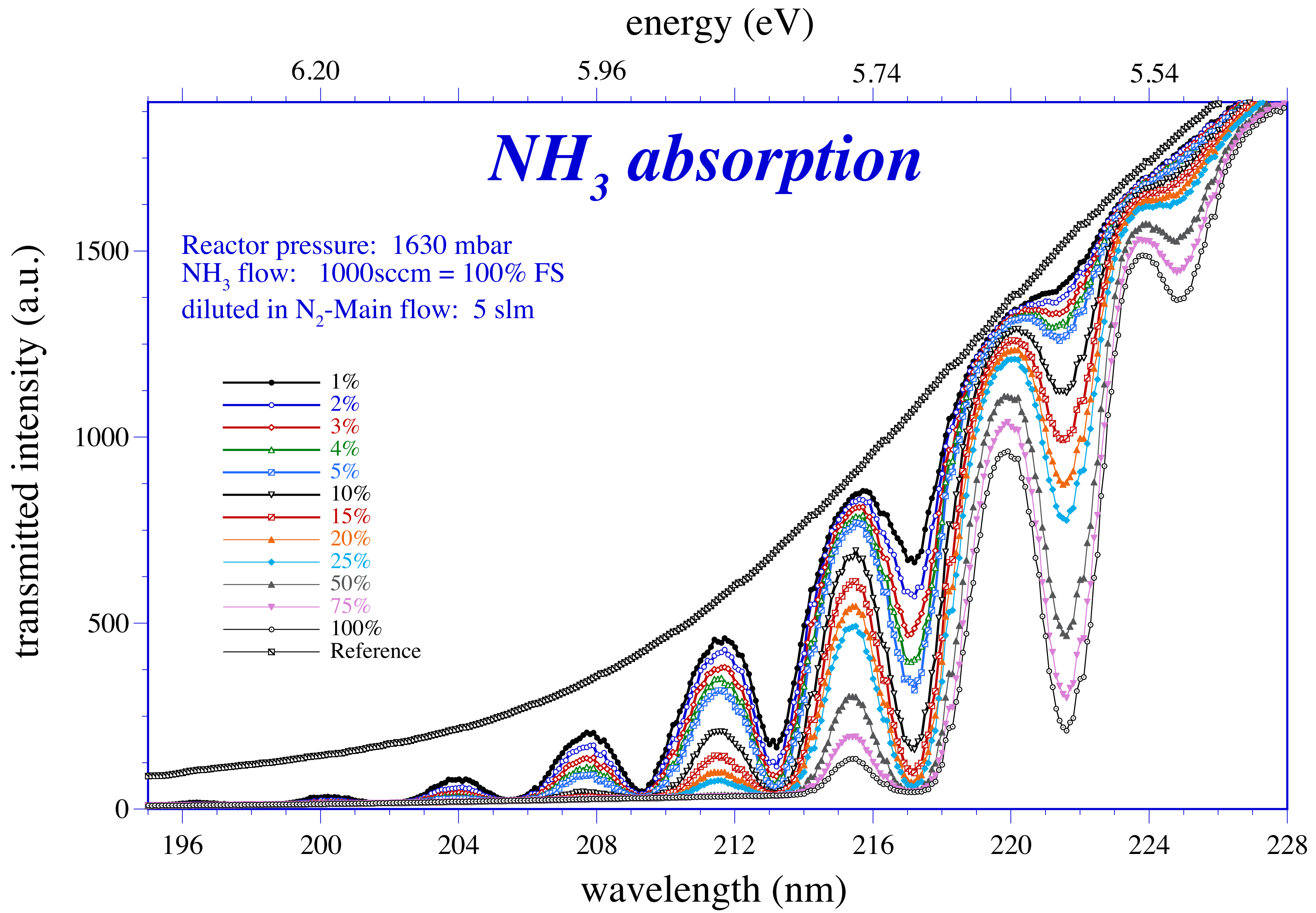
Characterization of NH_3 UV-absorption



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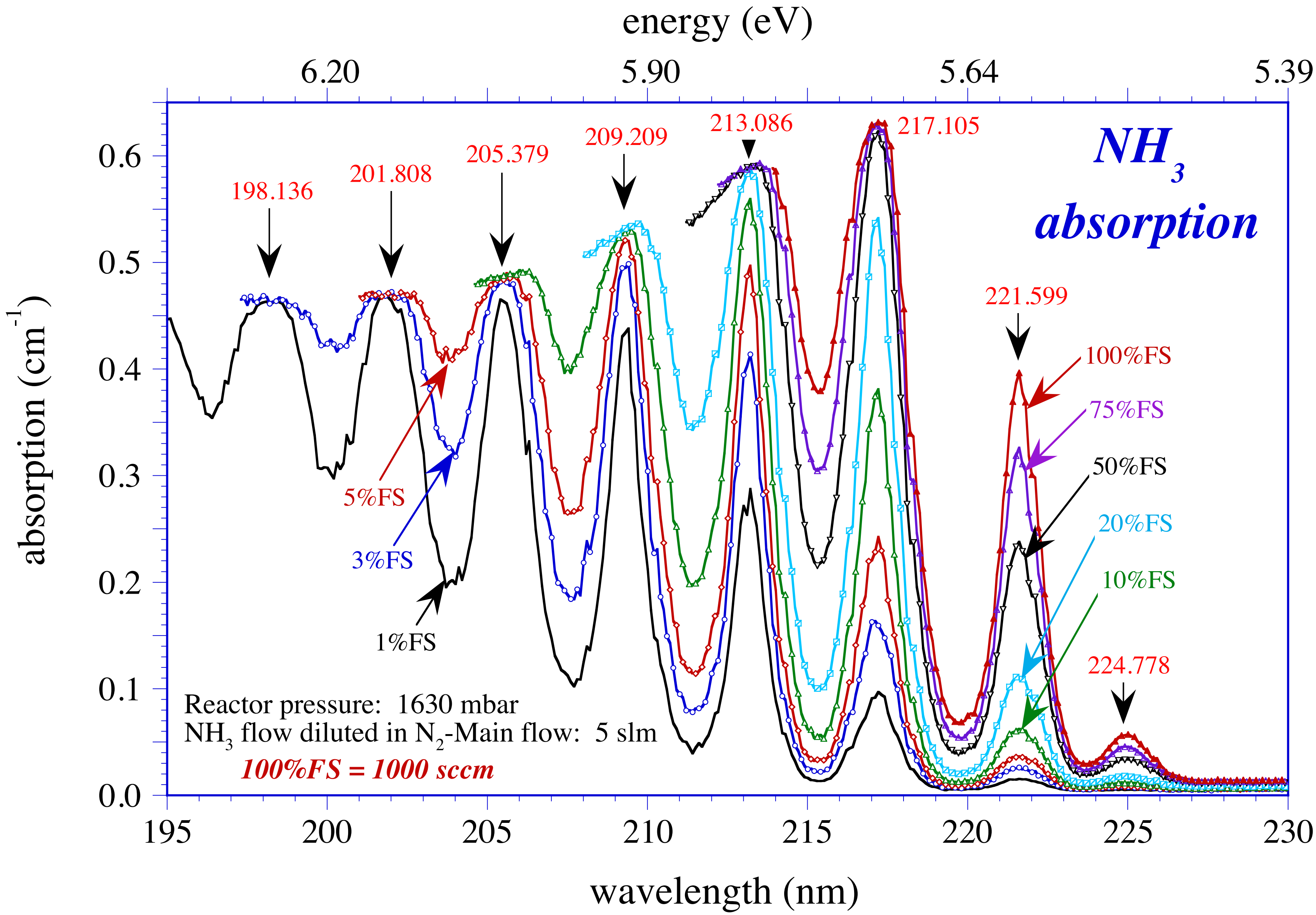
Characterization of NH_3 UV-absorption : MFC-I



Characterization of NH_3 UV-absorption: MFC-II

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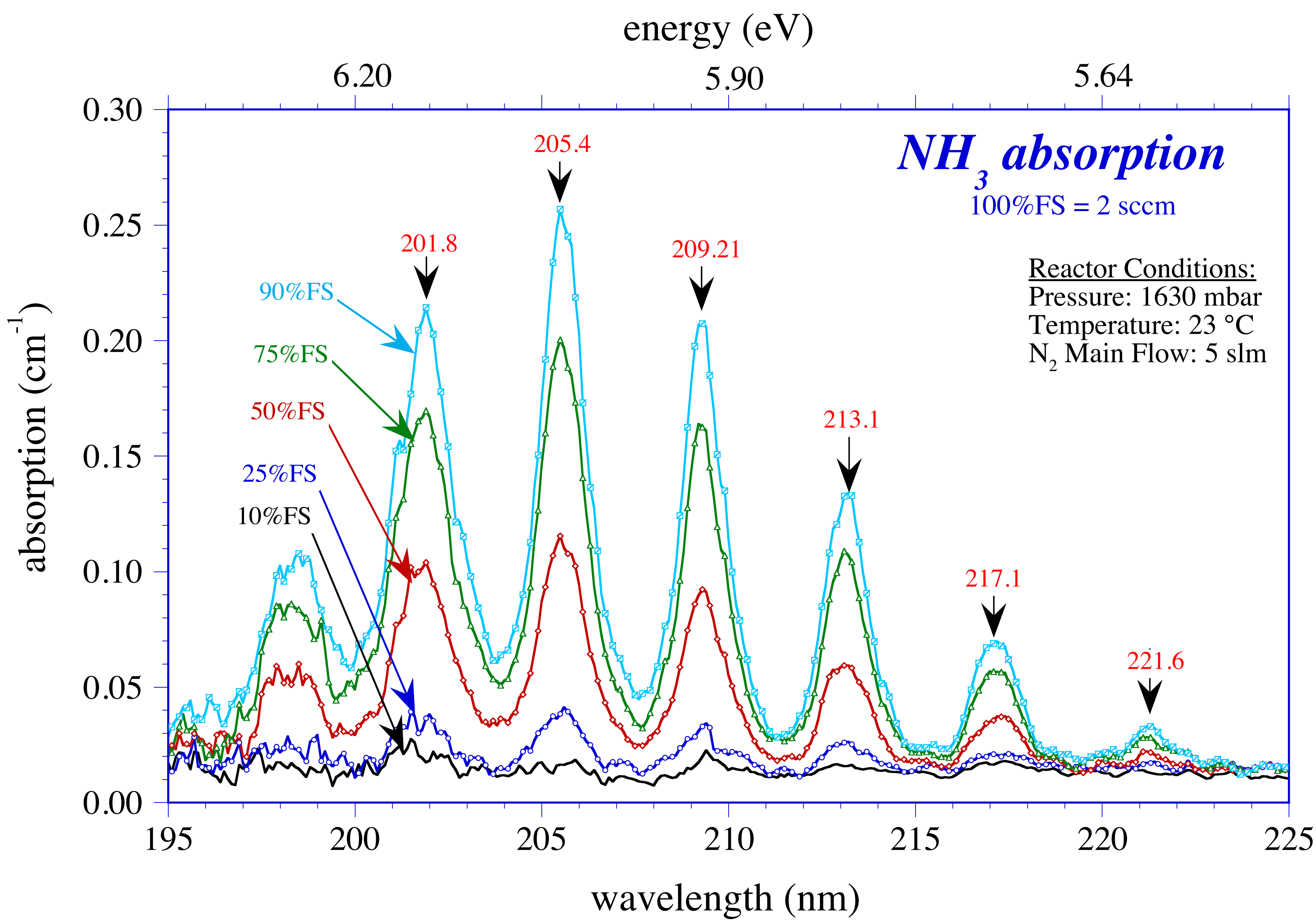

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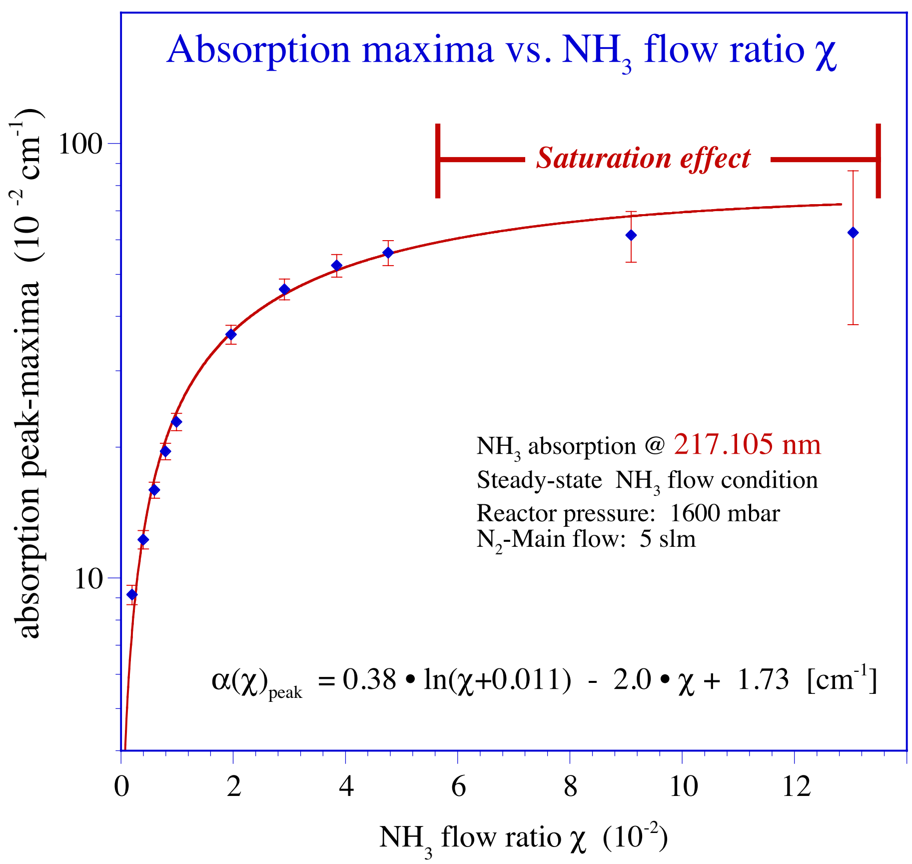
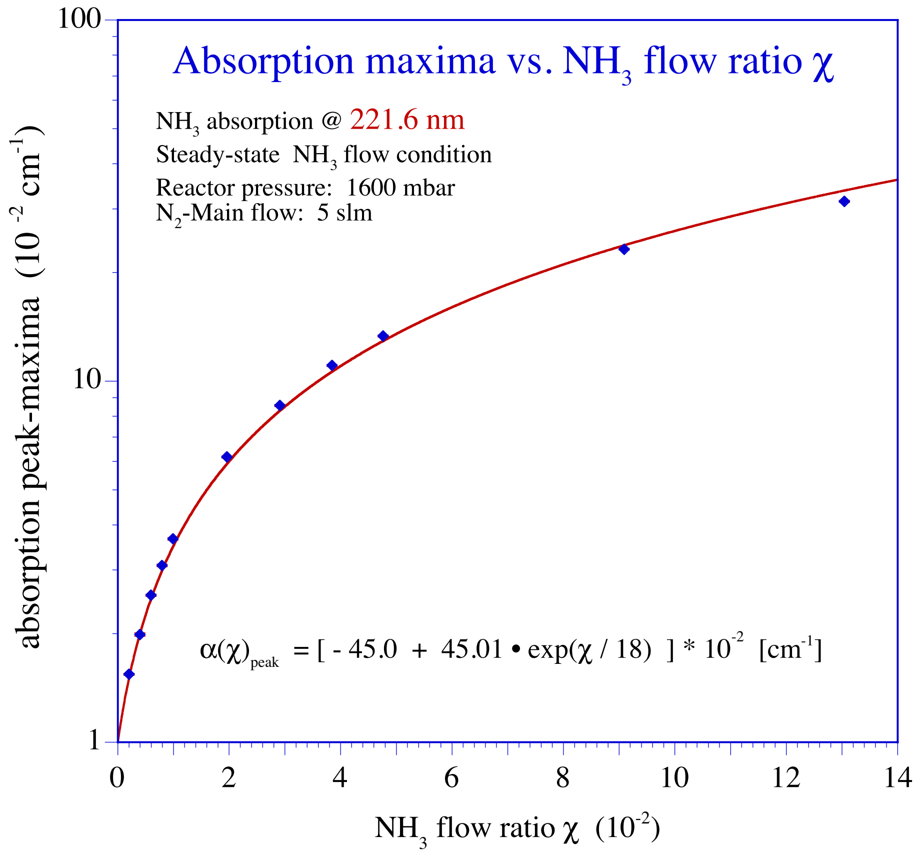
NH_3 characterization: Absorption maxima

The total flow of gases through the HPCVD reactor is given by $F = F_{Main\_N_2} + F_{NH_3} = 0.5 \cdot z + 1 \cdot 10^{-2} \cdot y$ [slm]

The molar ammonia flow ratio χ through the reactor is given by $\chi = \frac{n_{NH_3}}{n_{total}} = \frac{n_{NH_3}}{n_{Main\_N_2} + n_{NH_3}} = \frac{y}{50 \cdot z + y}$

where z and y are the percentage of flow full scale (FS) with 50 slm and 1 slm, respectively.





NH_3 flow: Concentration & Sensitivity

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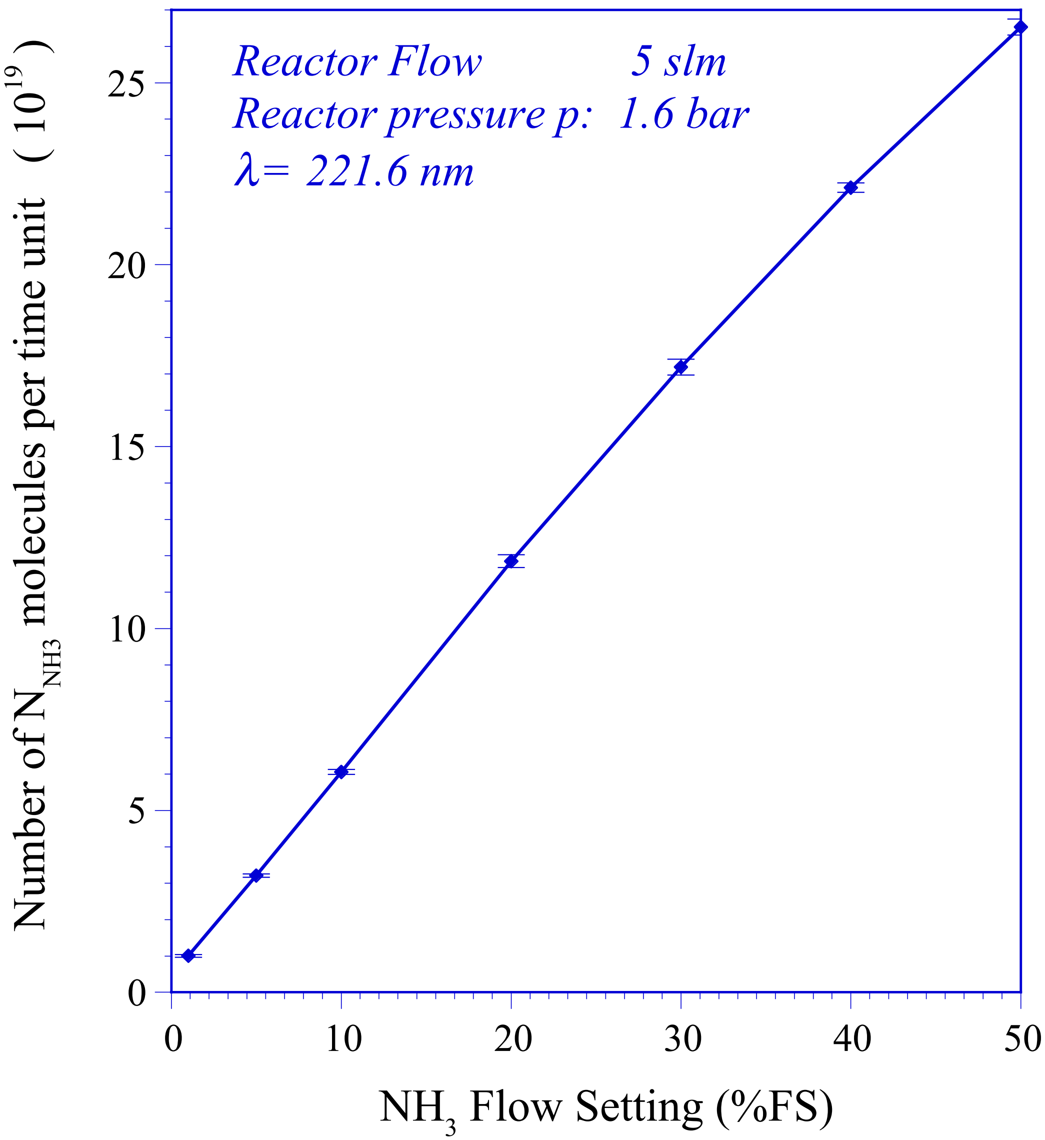

The number concentration of NH_3 molecules per time unit as function of the observed absorption *at* $\lambda = 221.6\ nm$

$$N_{NH_3(\lambda=221.6nm)} = \frac{7.17 \cdot 10^{21} \cdot z \cdot \ln\alpha'}{1 - 32 \cdot \ln\alpha'} \quad [s^{-1}]$$

with $$\alpha' = \frac{\alpha_{@221.6nm} - 80}{80.01}$$

Absorption line at λ = 221.6 nm sensitive for NH_3 concentrations in the range: $10^{+19} - 10^{+21}$

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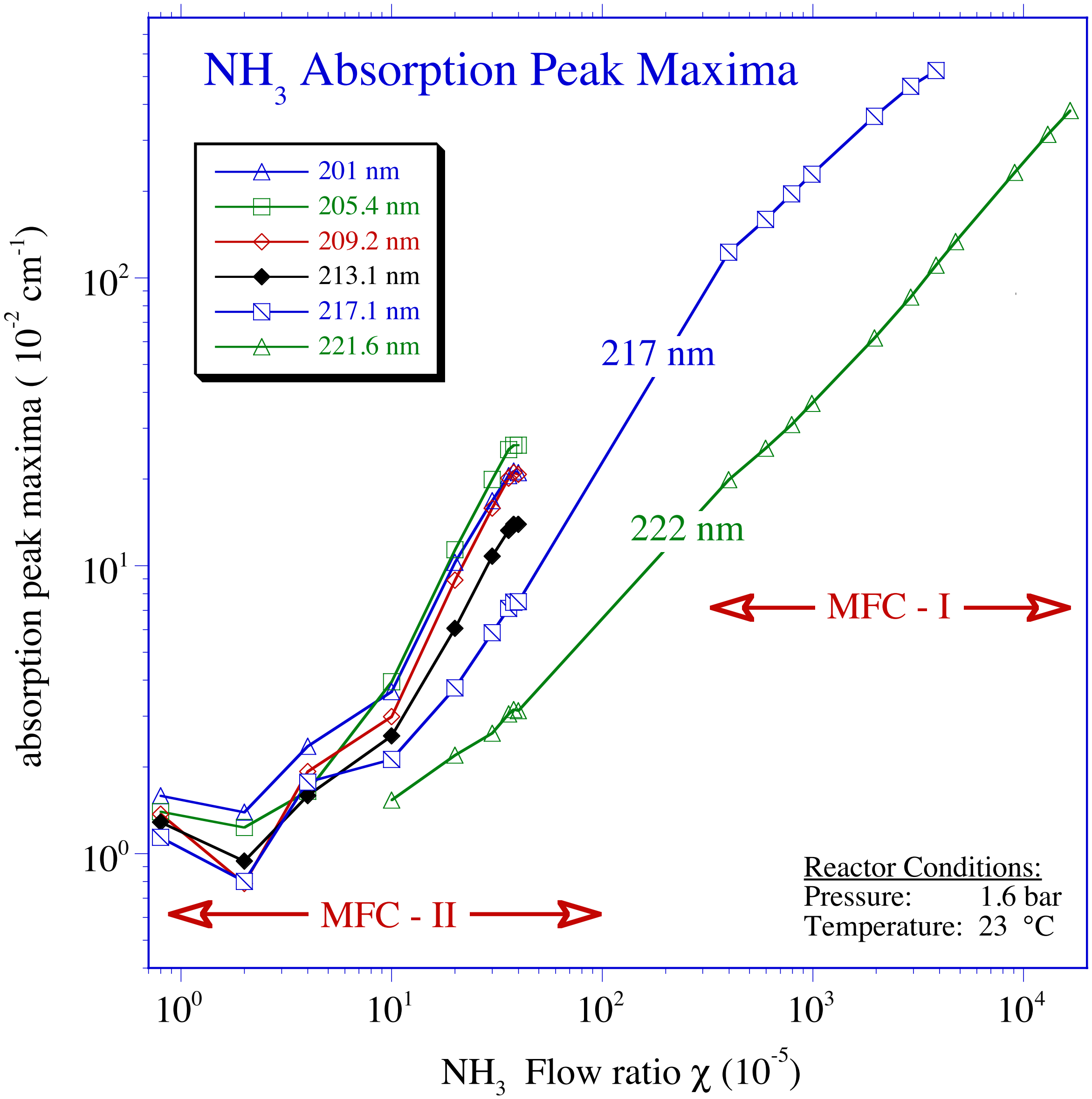
NH_3 flow: Concentration & Sensitivity



Absorption peak maxima correlate linearly with NH_3 flow ratio χ in a double log scale!

Sensitivity to NH_3 concentrations

λ = 224.8 nm (10^{+21} - 10^{+24})

λ = 221.6 nm (10^{+18} - 10^{+21})

λ = 217.1 nm (10^{+17} - 10^{+19})

λ = 213.07 nm (10^{+16} - 10^{+18})

λ = 209.21 nm (10^{+15} - 10^{+17})

λ = 205.38 nm (10^{+14} - 10^{+17})

λ = 201.81 nm (? - 10^{+16})

λ = 198.14 nm (? - 10^{+16})

λ = 194.62 nm (? - 10^{+15})

Decomposition of NH_3

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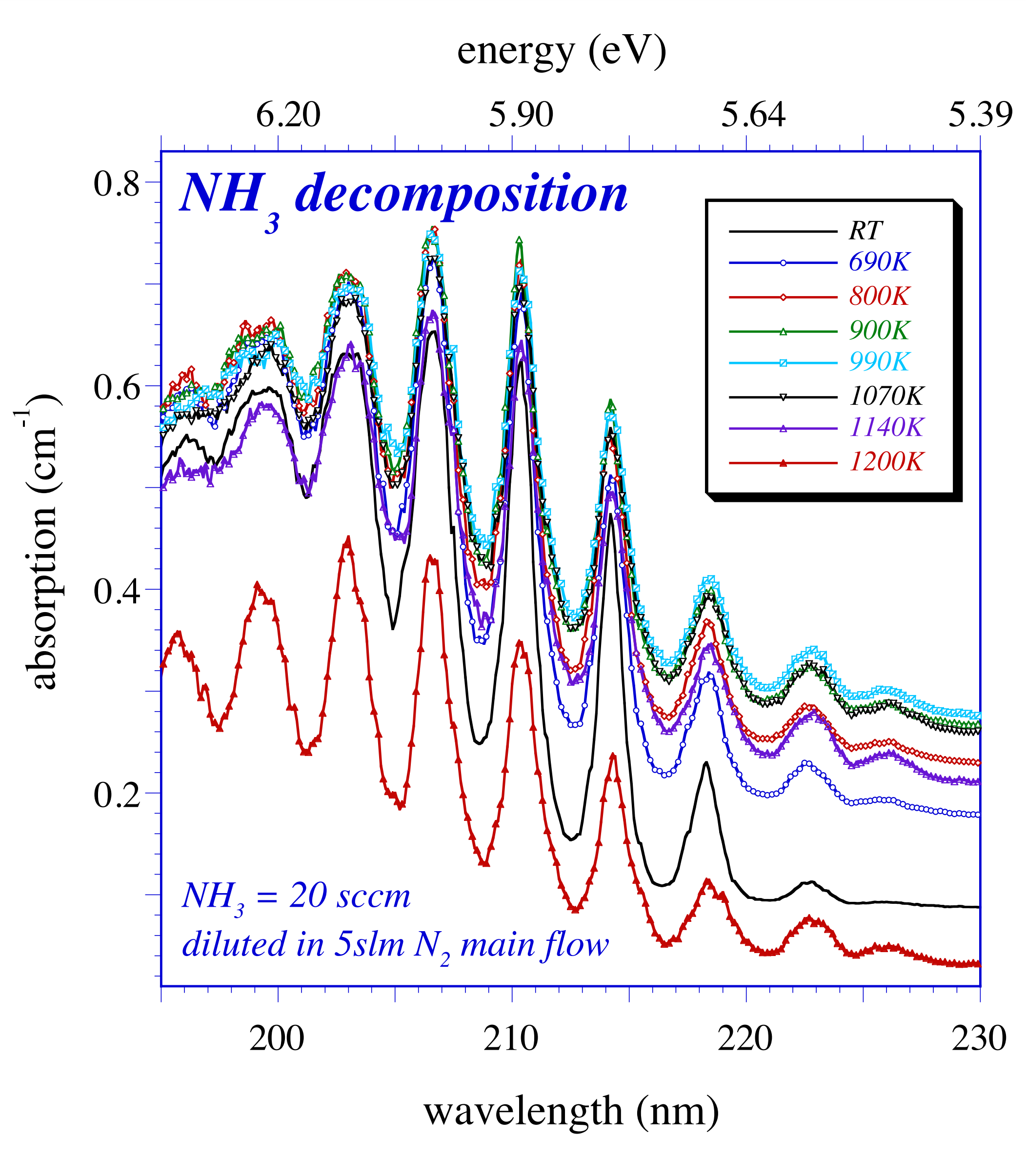

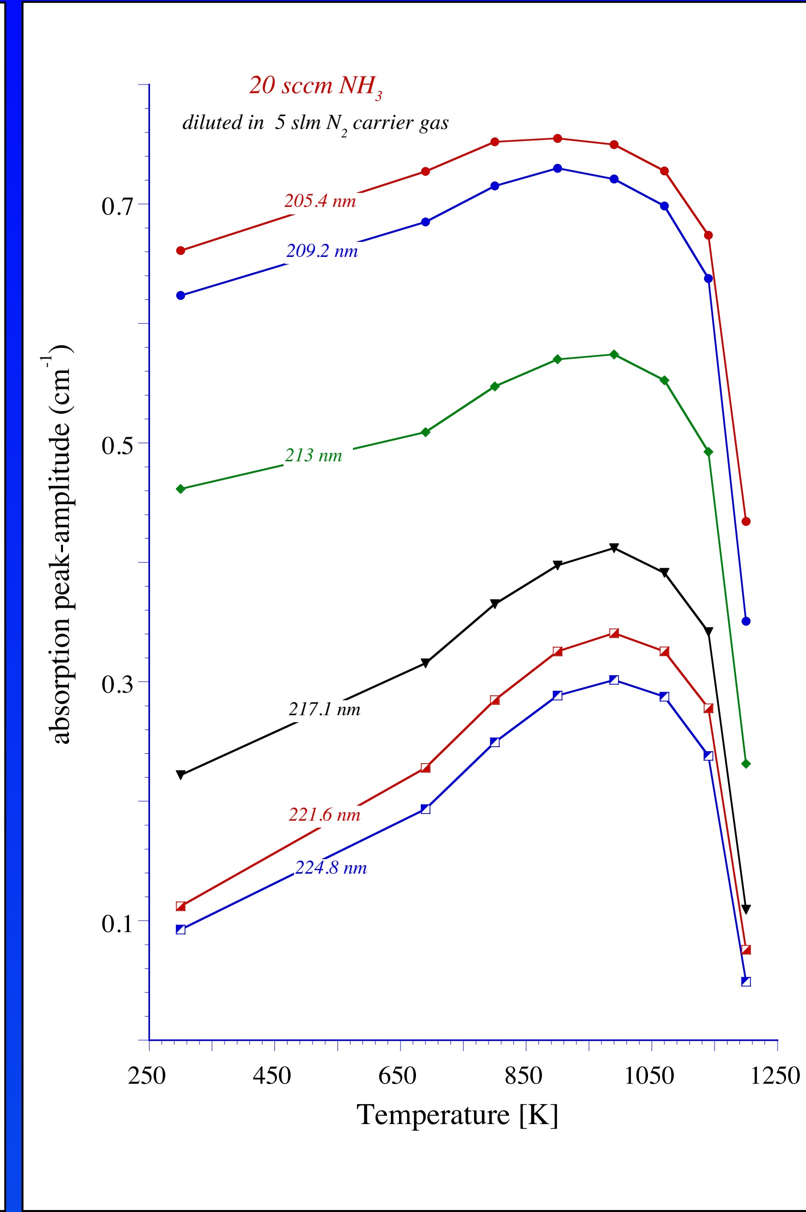

NH_3 flow characterization: Pulsed Injection

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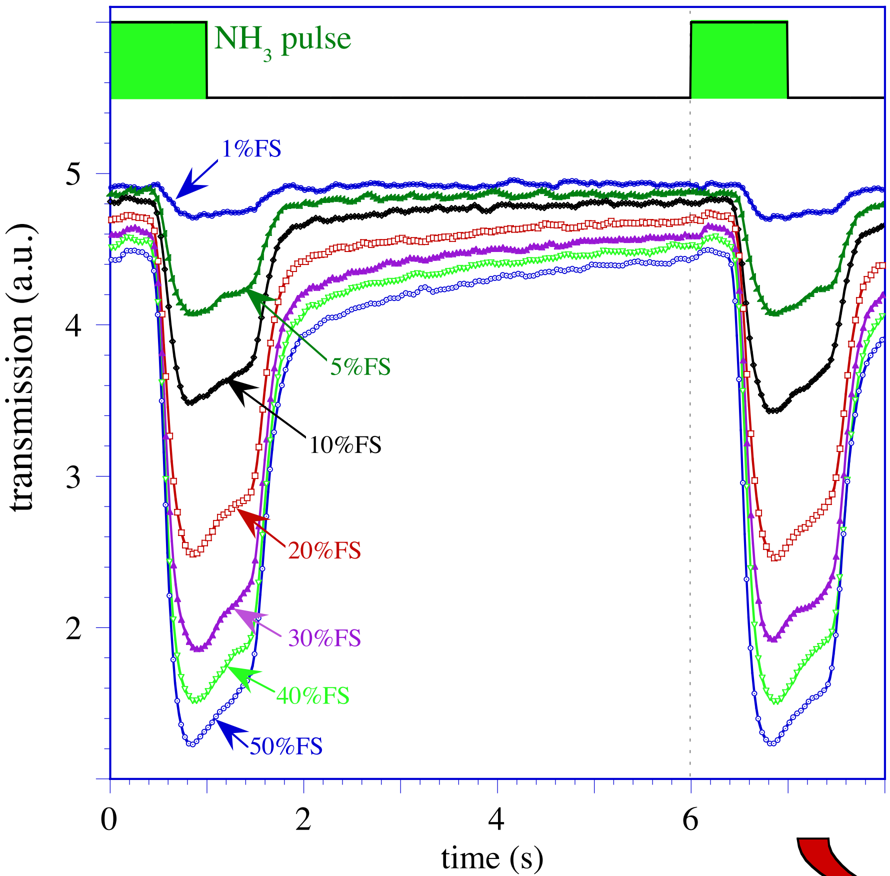

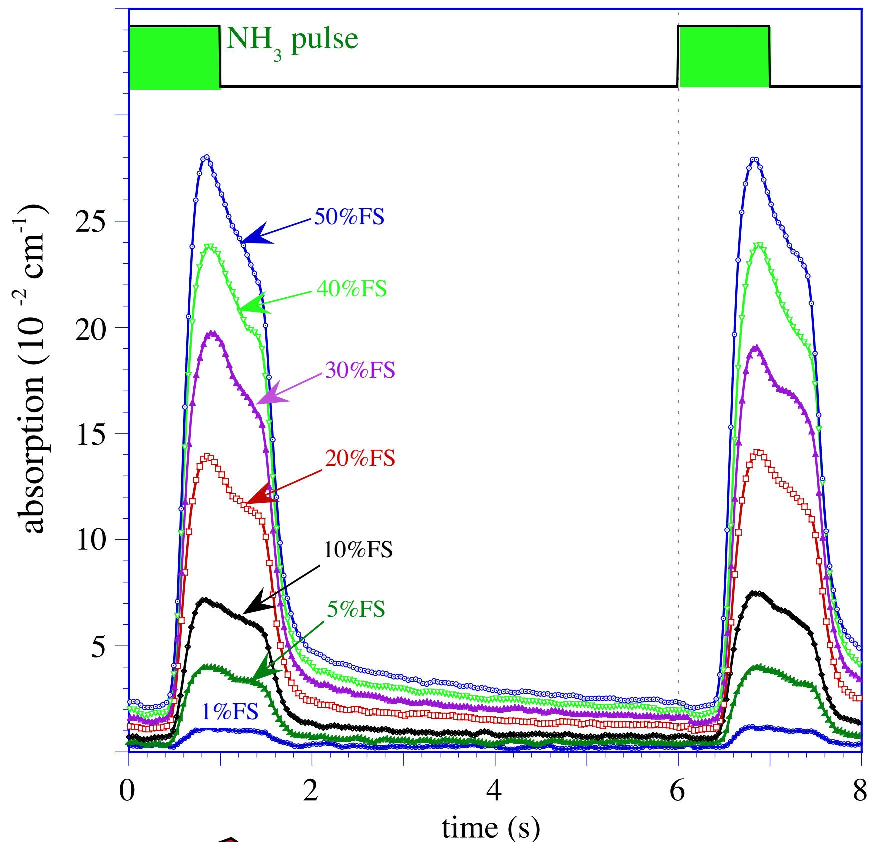

Absorption traces for 1 sec NH_3 pulses injected 6 s apart

Transmission traces monitored at *λ = 221.6 nm* during NH_3 precursor pulse injection in the reactor at *1.6 bar* and a total flow through the reactor of 5slm. The NH_3 flow was varied from 10 – 500 sccm (1 - 50%FS). The cycle sequence is 6 s with a 1 s NH_3 pulse width.

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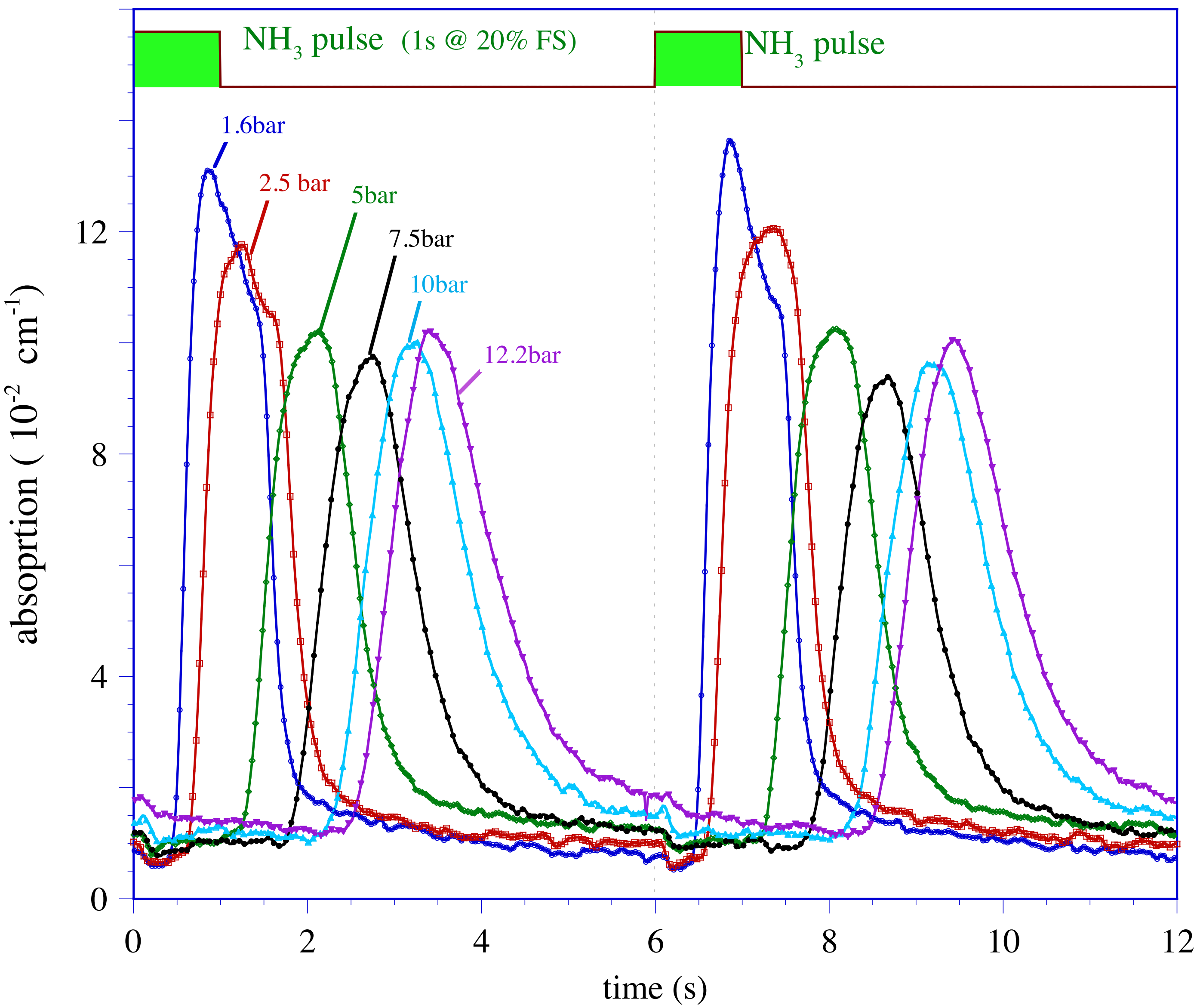
NH_3 flow characterization: Pulsed Injection



Absorption traces monitored at

λ = 221.6 nm

Reactor main flow:

5slm

NH_3 flow through the reservoir:

200 sccm

Reactor pressure:

1bar - 12.5 bar

Distinct features:

- *a systematic shift in the pulse arrival time,*
- *a systematic NH_3 pulse broadening,*
- *a change in NH_3 absorption cross section for p > 8 bar.*

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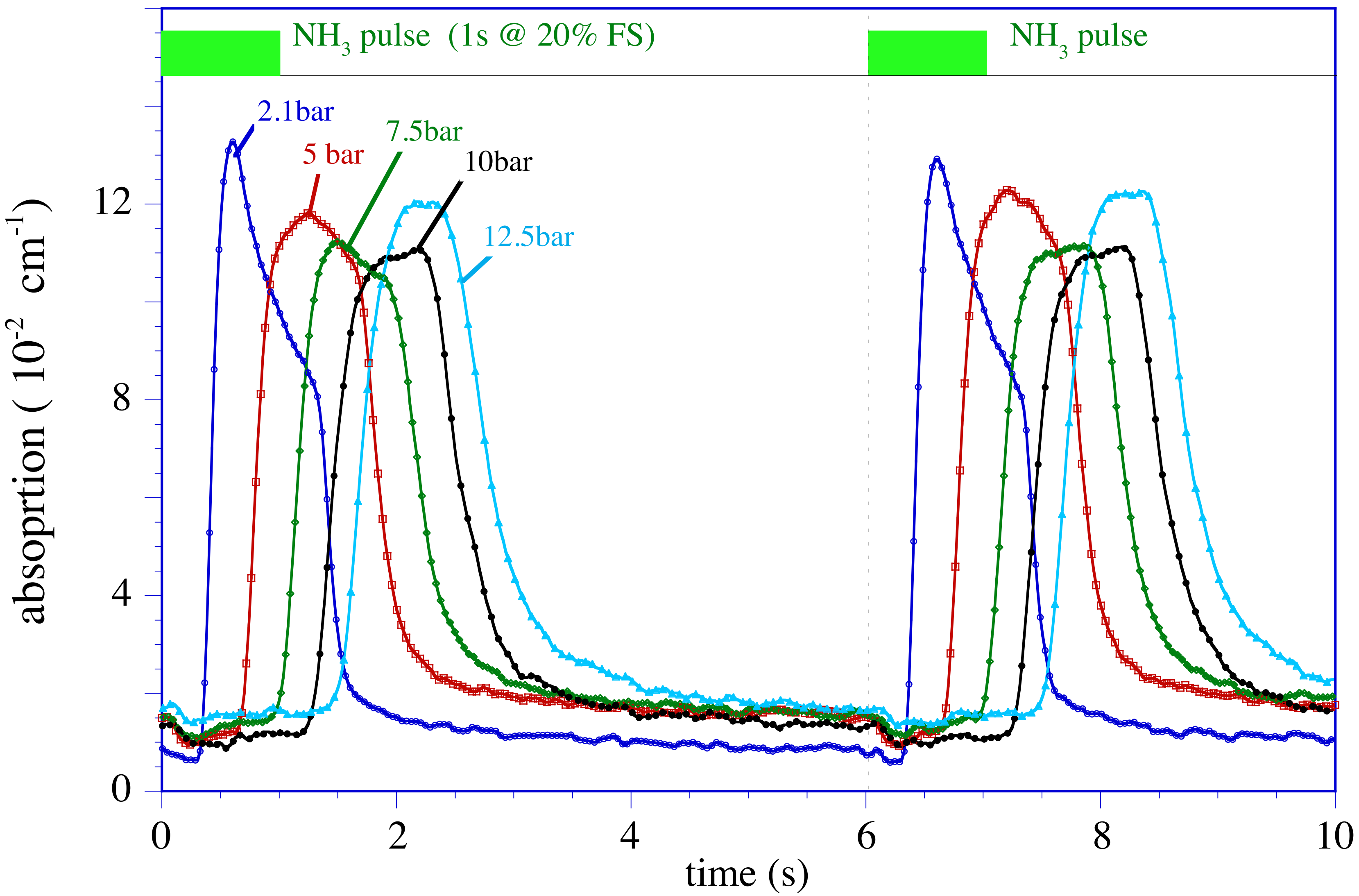

Main flow increased to 10 slm! ⇨ *NH_3 pulses sharpened*

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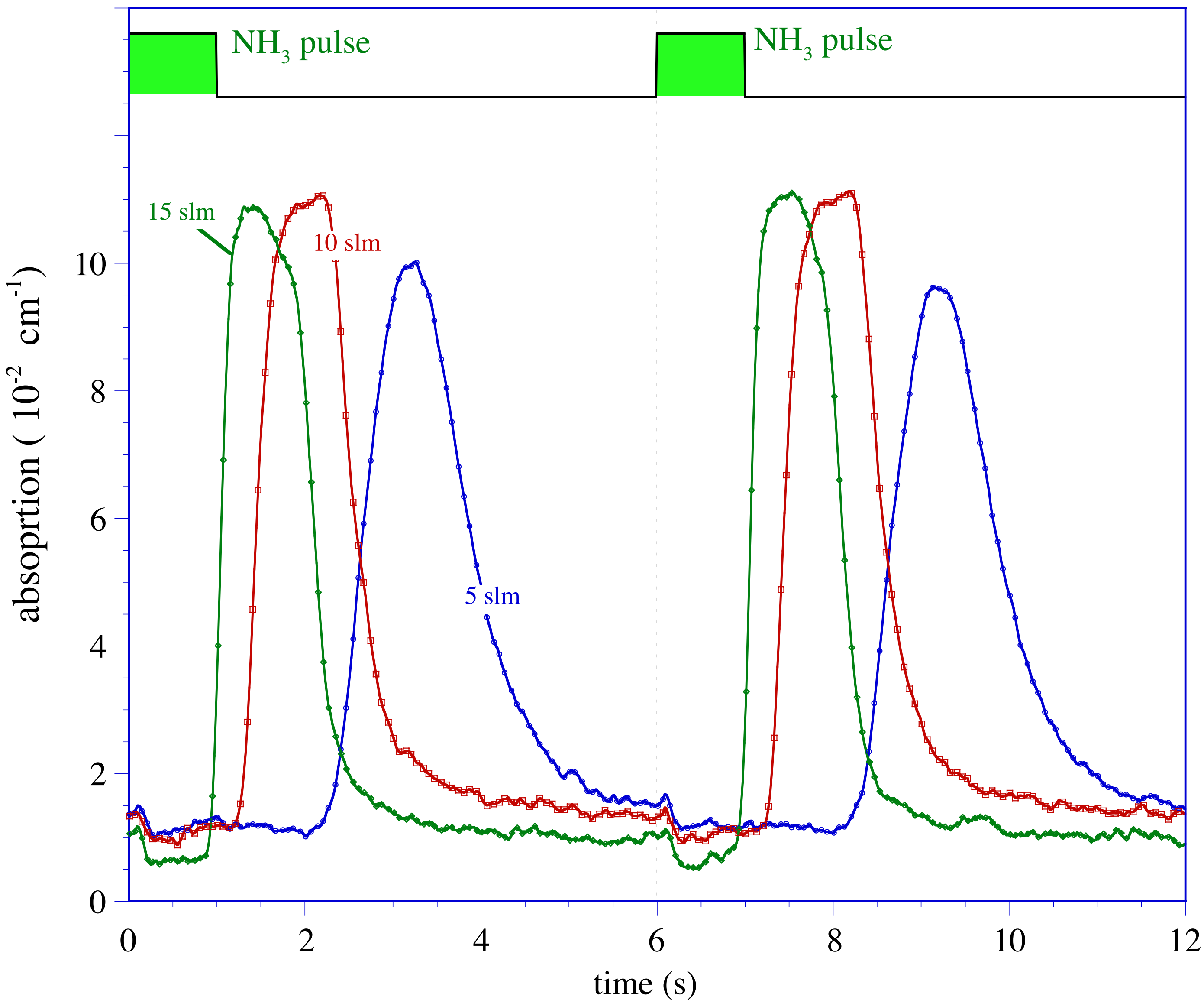

Precursor pulse delay / broadening as function of flow rate at constant reactor pressure

Monitoring:
λ = 221.6 nm

Cycle repetition rate:
6 sec

NH_3 pulse width:
1 sec

NH_3 flow:
20%FS = 200 sccm

Reactor pressure:
p = 10 bar

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References

[1] N. Dietz, M. Strassburg and V. Woods, "Real-time Optical Monitoring of Ammonia Decomposition Kinetics in InN Vapor Phase Epitaxy at Elevated Pressures", AVS 51st International Symposium, Anaheim, CA, Nov. 14-19, 2004.

[2] N. Dietz an V. Woods, unpublished results (2004).

refer to ***http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html***