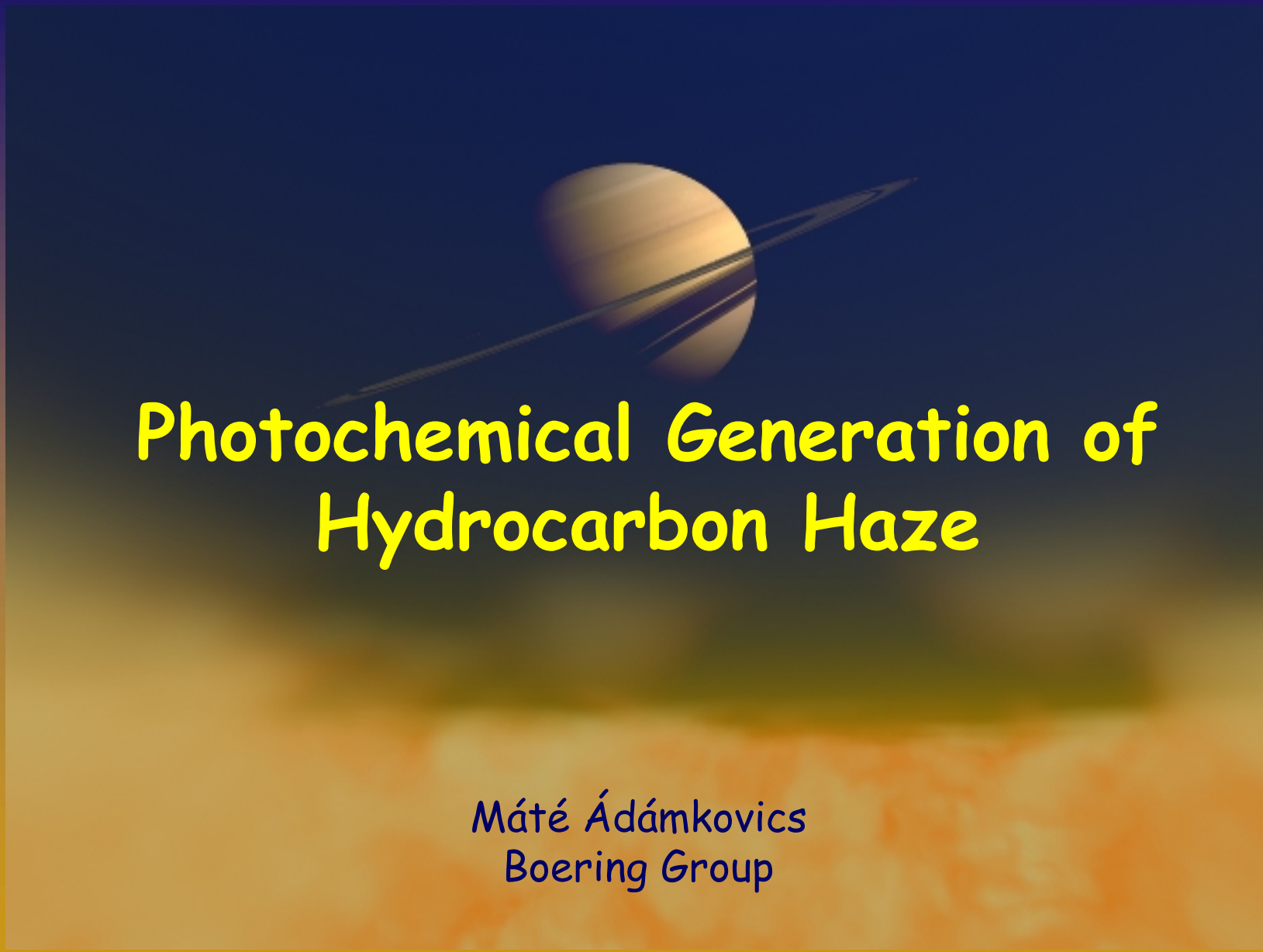


Photochemical Generation of Hydrocarbon Haze

Máté Ádámkovics
Boering Group

Overview

The Problem:

explain presence of liquid H_2O on >3.8 Ga Earth

The Explanations:

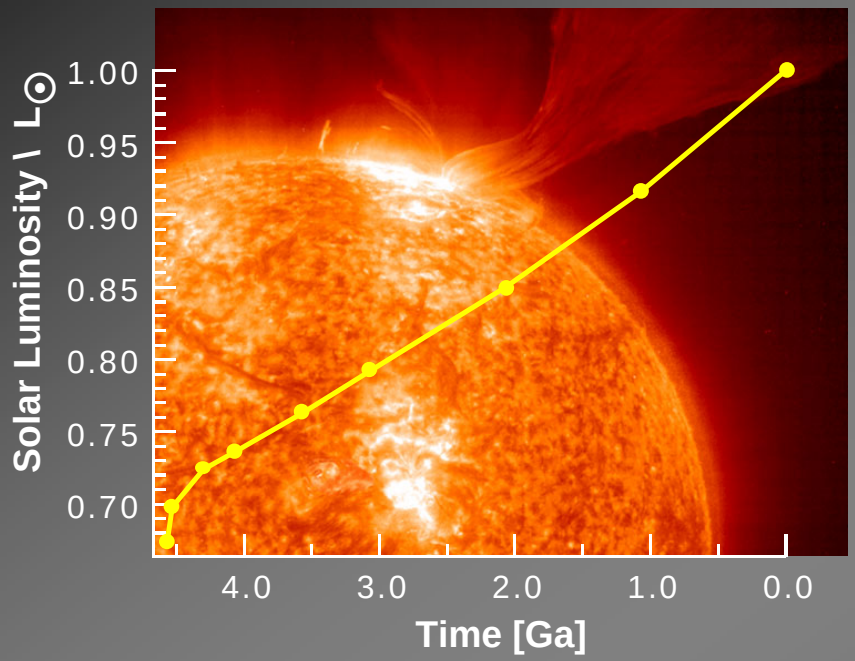
Accepted (and other) hypotheses

The Chemistry:

An experiment to quantitatively test a reasonable explanation

Solar Evolution and Temperatures on Earth

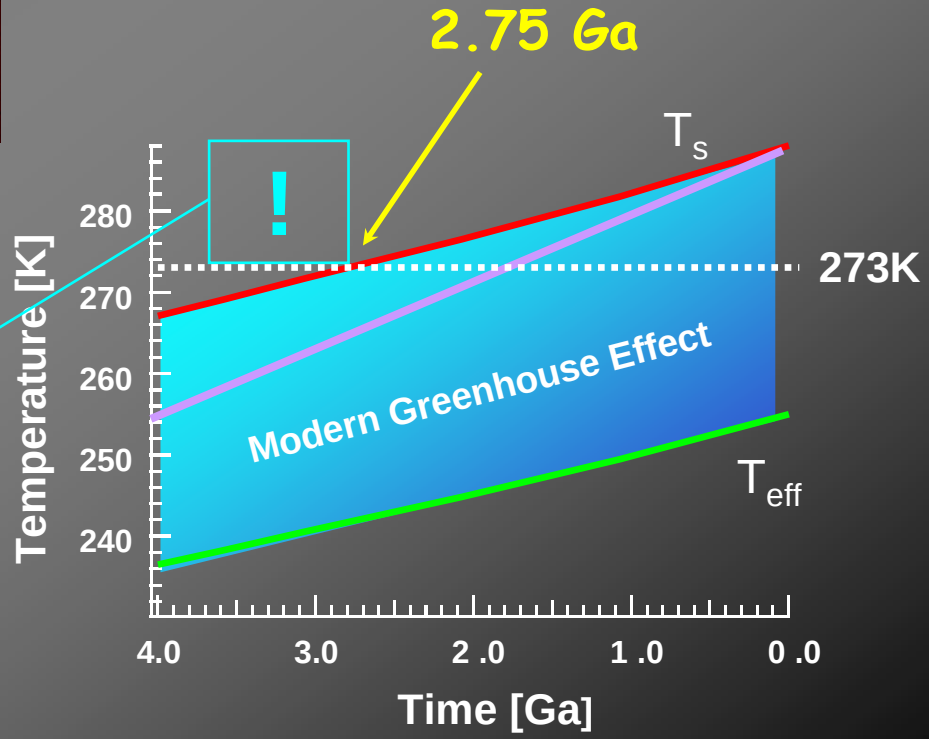
The Faint Young Sun



Bahcall, J.N. and Pinsonneault, M.H., *Rev. Mod Phys.* (1995)

$$F = \sigma T^4$$

$$T_{eff} = [\, F\,(1-\alpha)/\sigma\,]^{1/4}$$



1-H_2O present on Earth

Evidence for liquid water: sedimentary rocks >3.8 Ga

Nutman, A.P. *et al., Geochim. Cosmochim. Acta* (1997)

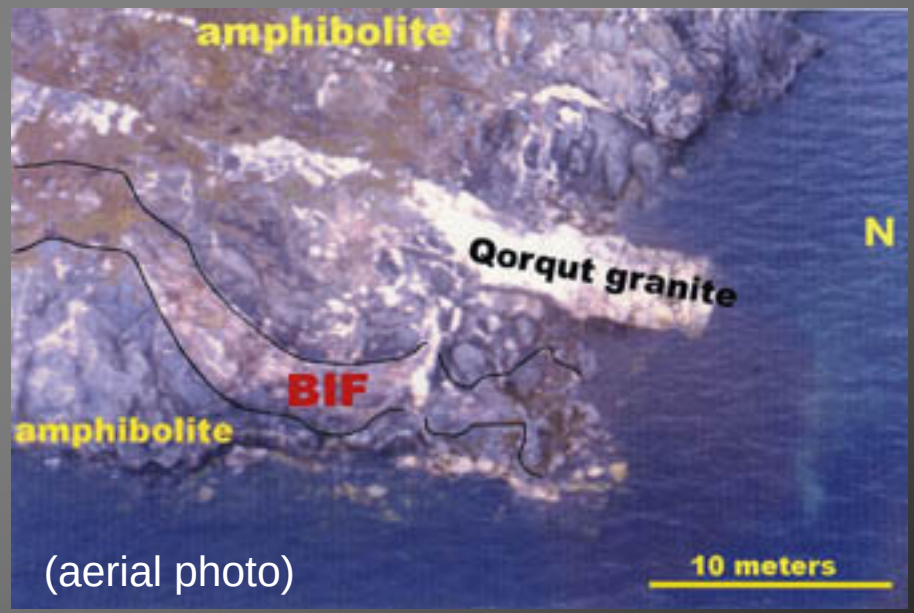
Direct Evidence:

- Banded Iron Formation (BIF) indicates sedimentary rock
- U-Pb isotope ratio dating of zircon via SHRIMP

Ample indirect evidence:

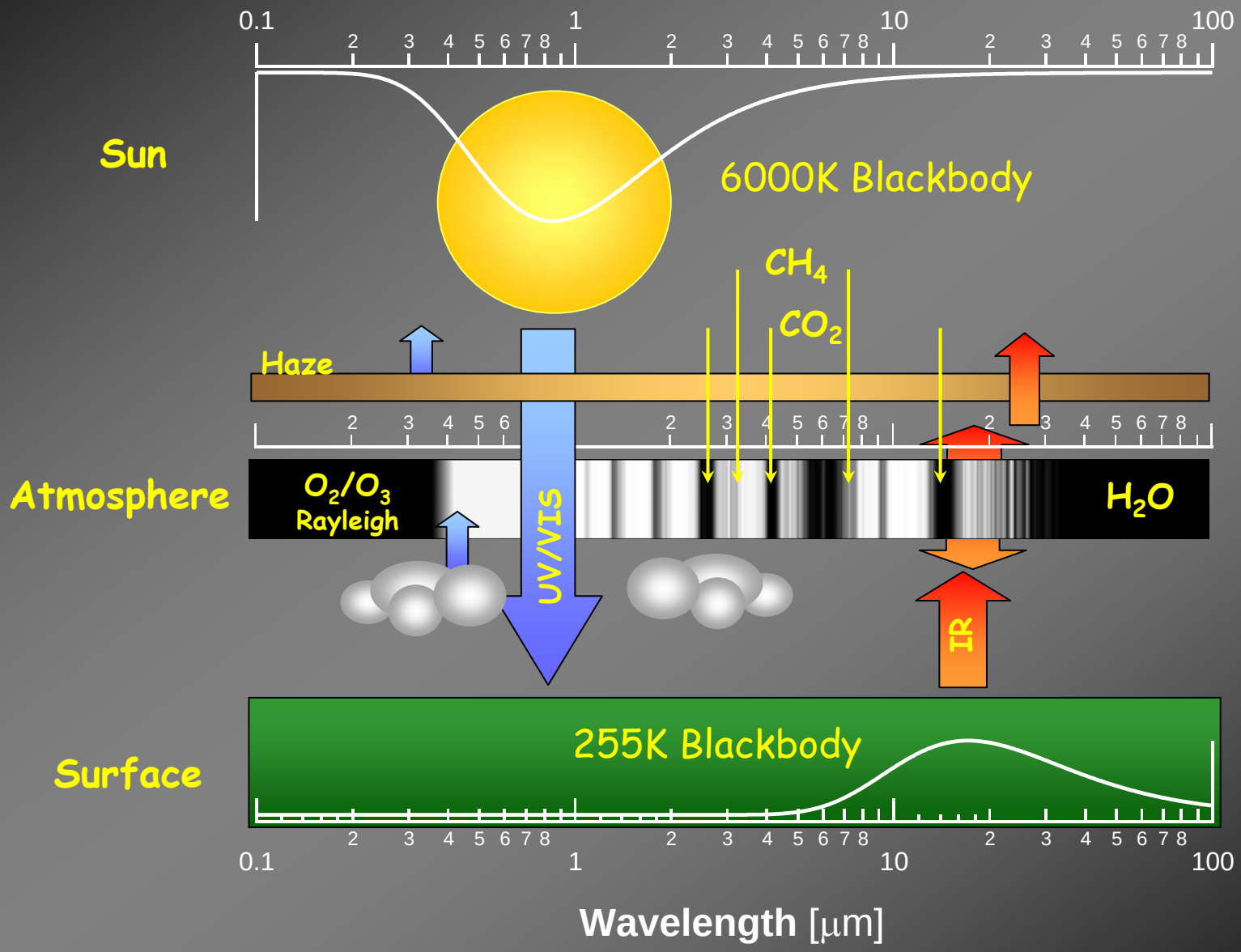
- metamorphic rocks

Island of Akilia, southern West Greenland



Mojzsis, S.J, *et al.*, (2000)

The Greenhouse effect basics



Analysis of Proposed Solutions

Hypothesis	Advantages	Disadvantages	Conclusion
Decrease Albedo	Very Simple	Not sufficient flux increase with α=0	not sufficient
Alter Earth's Inclination	Well modeled, no climate change	Can't explain current inclination	more data necessary
Increase CO_2	Simple effect	Contradicts geological record	contributing effect
Increase CH_4	Simple effect	Large flux necessary is unphysical	contributing effect
Form Haze Layer	Corresponds with existing data	Difficult to quantify net effect	lab data required

Chemical mechanisms: $CH_4 \rightarrow C_2H_m$

Methane Branching Ratios for $h\nu$ = Lyman α

$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$		$q_1 = 0.41$
$CH_2 + 2H$		$q_2 = 0.51$
$CH + H + H_2$		$q_3 = 0.08$
$CH_3 + H$		$q_4 = 0.00$

Photofragment Reactions (a)

$$2(CH_4 + h\nu \rightarrow {}^1CH_2 + H_2)$$
$$2({}^1CH_2 + H_2 \rightarrow CH_3 + H)$$
$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$$
$$net \quad 2\ CH_4 \rightarrow C_2H_6 + 2H$$

Net Reactions

$$2\ CH_4 \rightarrow C_2H_6 + 2H \qquad \text{(a)}$$

Chemical mechanisms: $CH_4 \rightarrow C_2H_m$

Methane Branching Ratios for $h\nu$ = Lyman α

$CH_4 + h\nu \rightarrow$	$^1CH_2$	+	H_2		$q_1 = 0.41$
	CH_2	+	$2H$		$q_2 = 0.51$
	CH	+	H	+ H_2	$q_3 = 0.08$
	CH_3	+	H		$q_4 = 0.00$

Photofragment Reactions (b)

$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$$
$$CH_4 + h\nu \rightarrow CH_2 + 2H$$
$$^1CH_2 + H_2 \rightarrow CH_3 + H$$
$$CH_2 + CH_3 \rightarrow C_2H_4 + H$$
$$\text{net } 2\ CH_4 \rightarrow C_2H_4 + 4H$$

Net Reactions

$$2\ CH_4 \rightarrow C_2H_6 + 2H \quad \text{(a)}$$
$$2\ CH_4 \rightarrow C_2H_4 + 4H \quad \text{(b)}$$

Chemical mechanisms: $CH_4 \rightarrow C_2H_m$

Methane Branching Ratios for $h\nu$ = Lyman α

$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$	$q_1 = 0.41$
$CH_2 + 2H$	$q_2 = 0.51$
$CH + H + H_2$	$q_3 = 0.08$
$CH_3 + H$	$q_4 = 0.00$

Photofragment Reactions (c)

$$2(CH_4 + h\nu \rightarrow CH_2 + 2H)$$
$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2$$
$$\text{net} \quad 2\ CH_4 \rightarrow C_2H_2 + 2H$$

Net Reactions

$2\ CH_4 \rightarrow C_2H_6 + 2H$	(a)
$2\ CH_4 \rightarrow C_2H_4 + 4H$	(b)
$2\ CH_4 \rightarrow C_2H_2 + 2H$	(c)

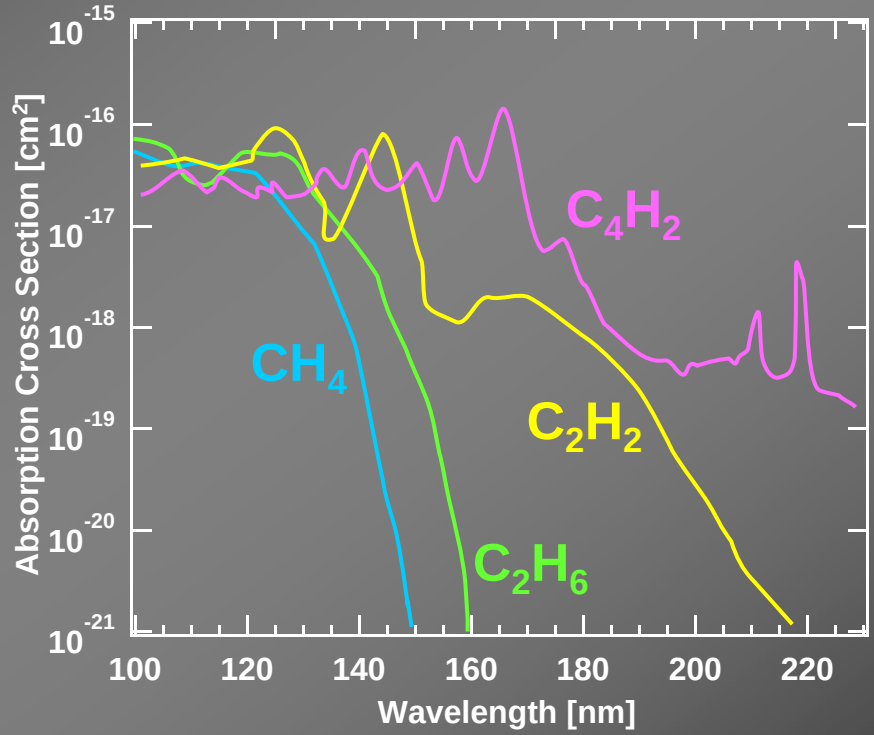
Photosensitized Dissociation and Larger Hydrocarbons

Photosensitized Dissociation

$$C_2H_2 + h\nu \rightarrow C_2H + H$$
$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$$
$$\textit{net} \quad CH_4 \rightarrow CH_3 + H$$

C_2 to C_4: An Example

$$C_2H_2 + h\nu \rightarrow C_2H + H$$
$$C_2H + C_2H_2 \rightarrow C_4H_2 + H$$
$$\textit{net} \quad 2C_2H_4 \rightarrow C_4H_2 + 2H$$



In General for Polyynes

$$C_2H_2 + h\nu \rightarrow C_2H + H$$
$$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H$$
$$\textit{net} \quad C_2H_2 + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + 2H$$

A small problem with current quantitative models

$$x\ C_nH_m\ (\text{gas}) \xrightarrow{k} y\ C_{n'}H_{m'}\ (\text{solid}) \qquad k = ?$$

"the species C_3H_4, C_4H_2 and HC_3N were allowed to go to soot at an arbitrary rate"

Zahnle, K., *JGR*, **91**, 2819, **(1986)**

"at CH_4/CO_2 ratios lower than this critical value [unity], most of the CH_4 undergoes oxidation, rather than polymerization, so organic haze does not form."

Pavlov *et al.*, *JGR*, *105*, 11981, **(2000)**

The Experiment

1) Photochemical production of particulates

reactants: CH_4 and CO_2

He carrier gas

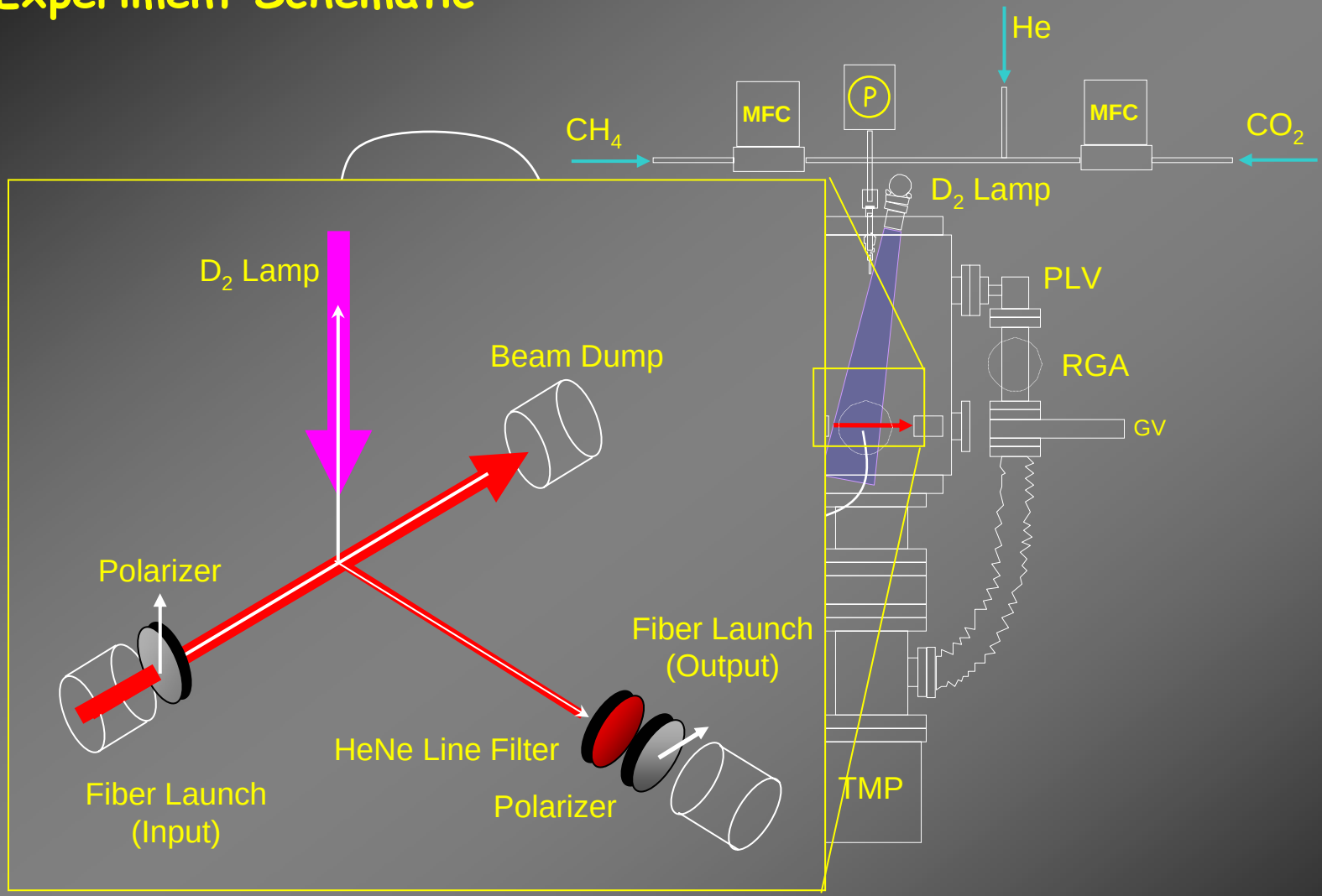
120-230nm photolysis with D_2 arc lamp

2) *in situ* Optical Detection/Characterization

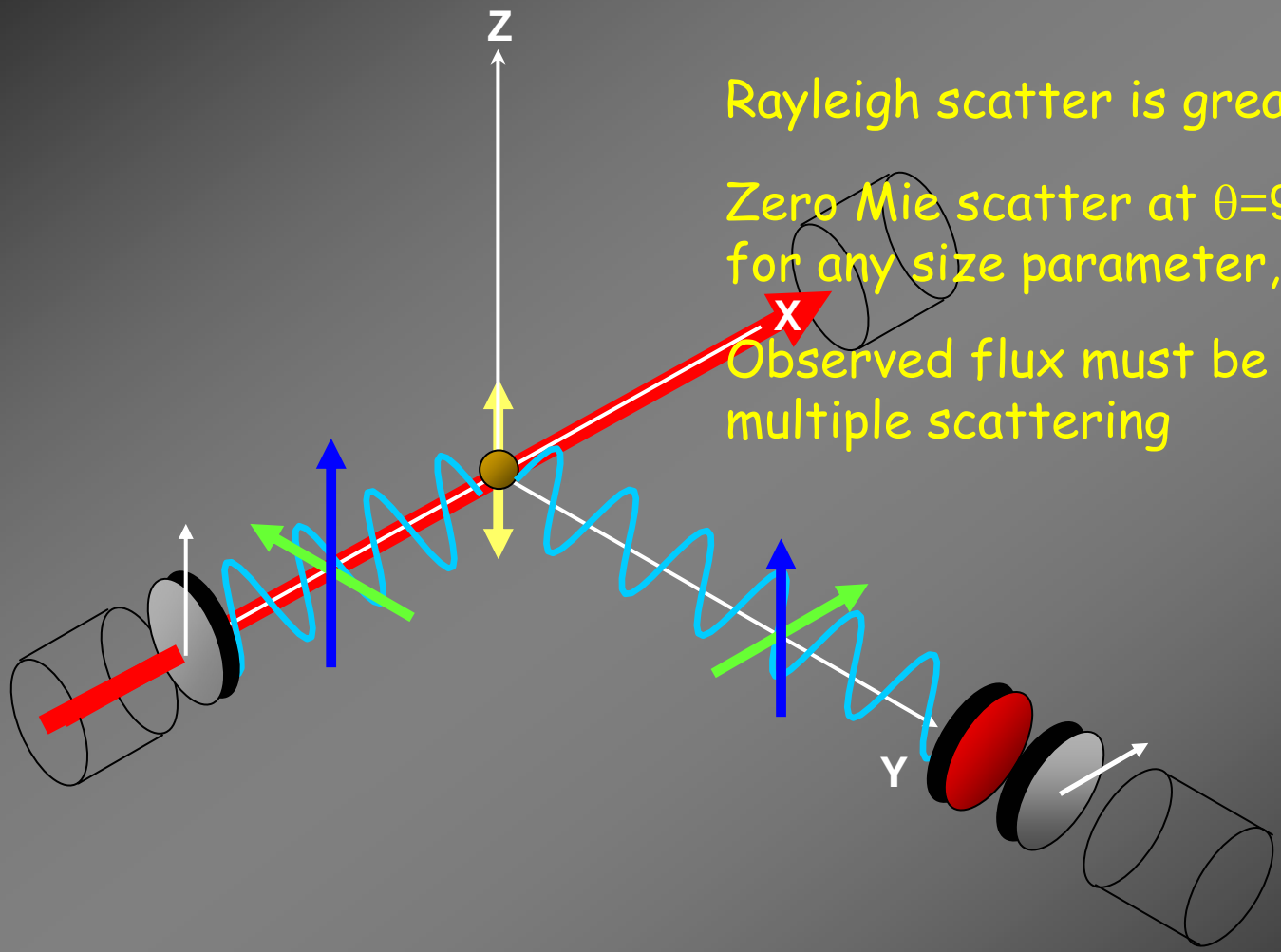
Detect 632.8nm scatter/reflection from particulates

Monitor reservoir of gas to constrain chemistry

Experiment Schematic



Observed Scatter and Reflectance Signal

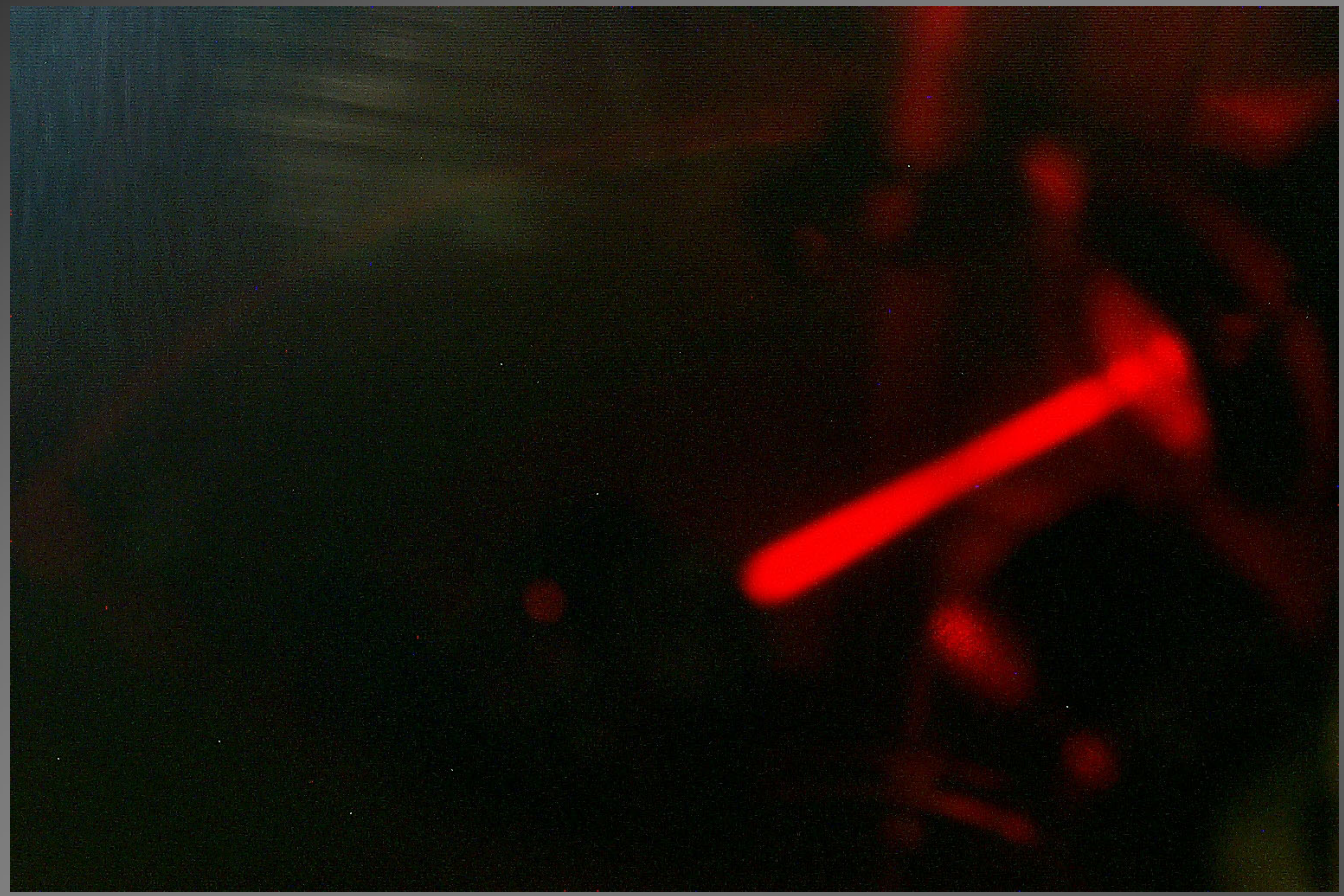


Rayleigh scatter is greatly reduced

Zero Mie scatter at θ=90
for any size parameter, $\chi = r/\lambda$

Observed flux must be from multiple scattering

Inside the reaction chamber

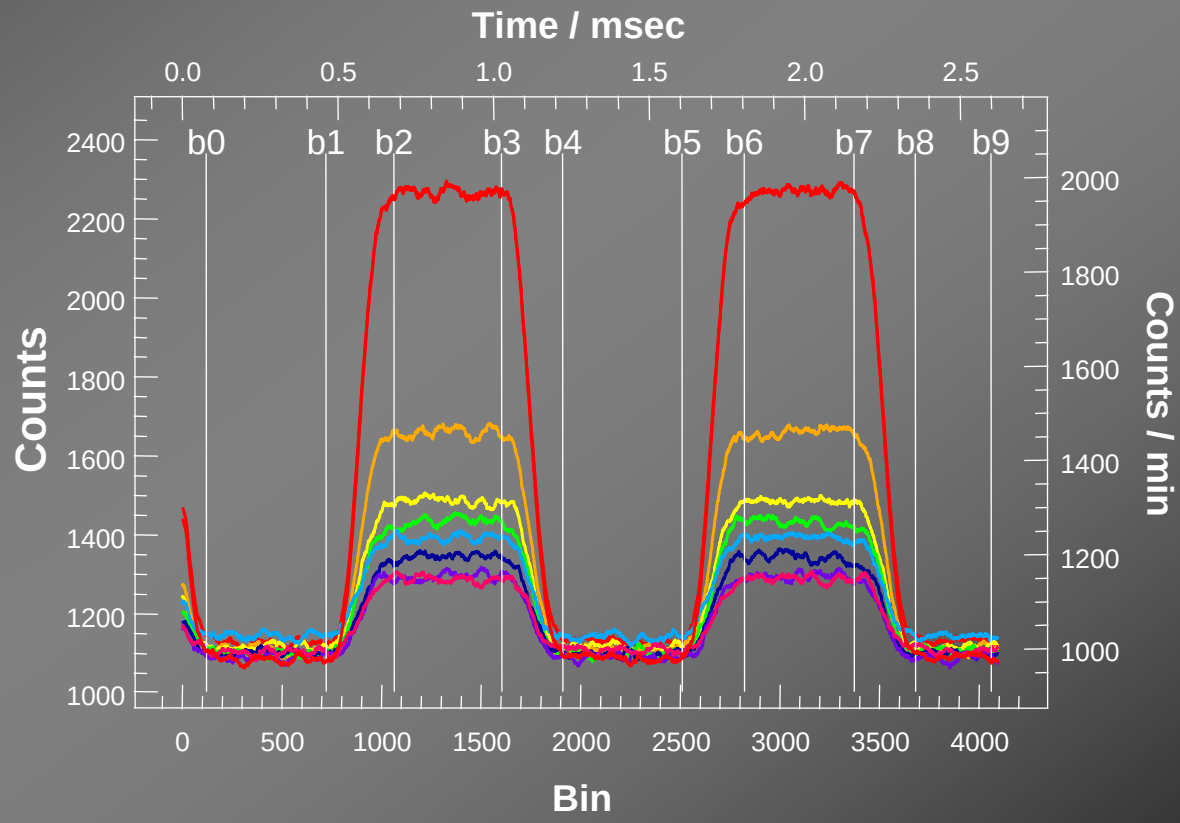


Output from Multi-Channel Scaler

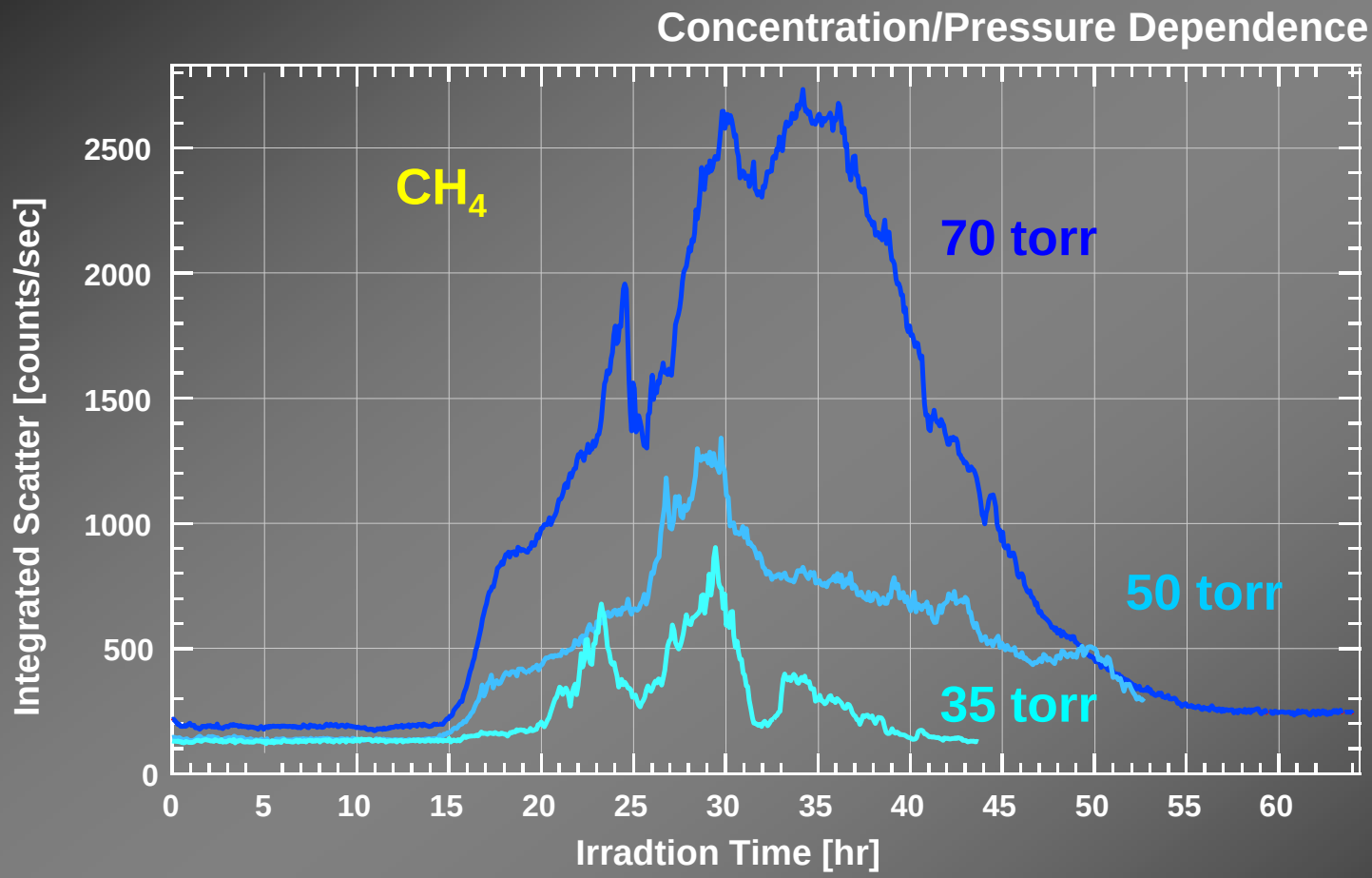
2.6ms scan with 1kHz optical modulation

30K scans averaged per dataset

Rise/fall times excluded

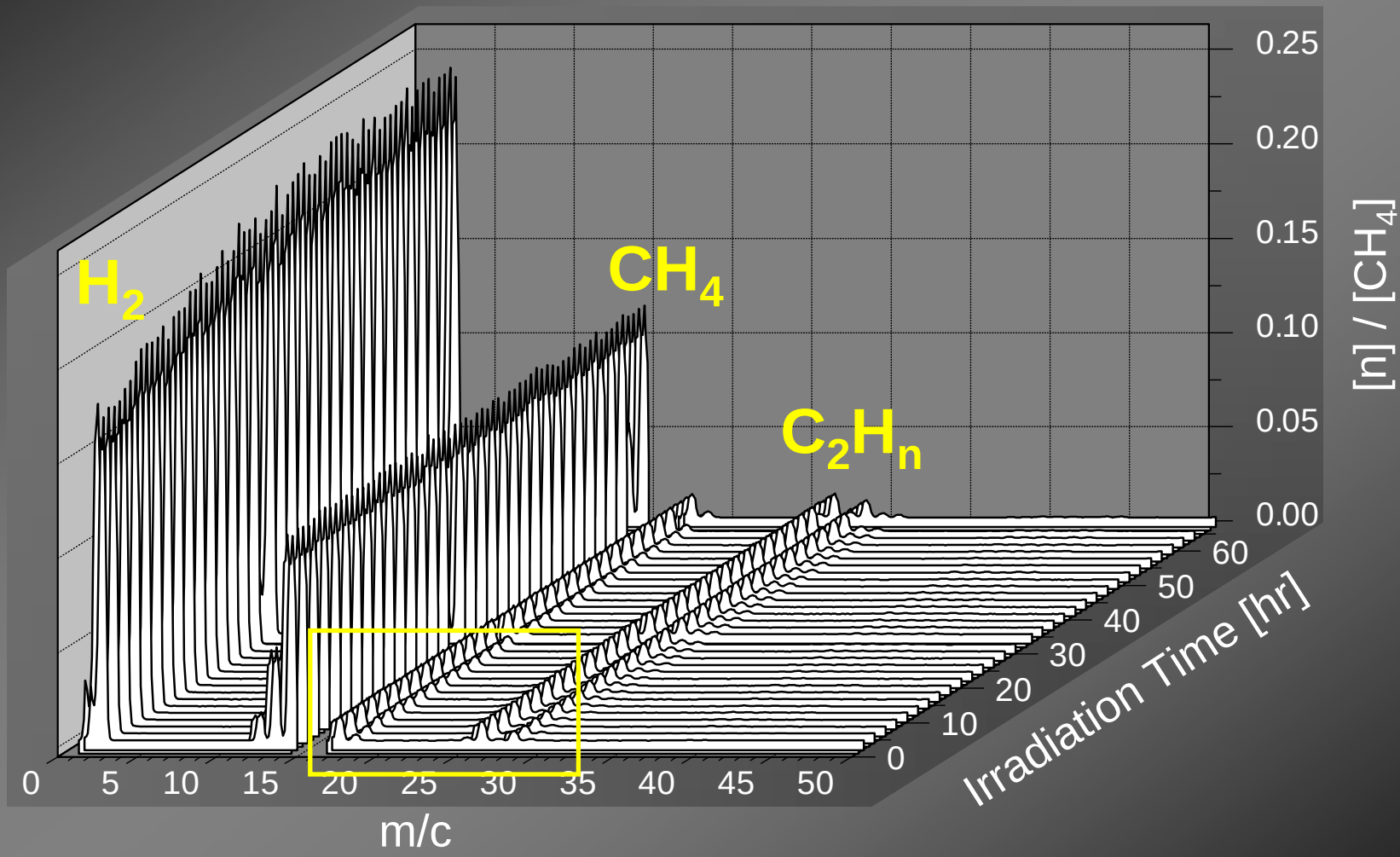


Hydrocarbon Formation with CH_4

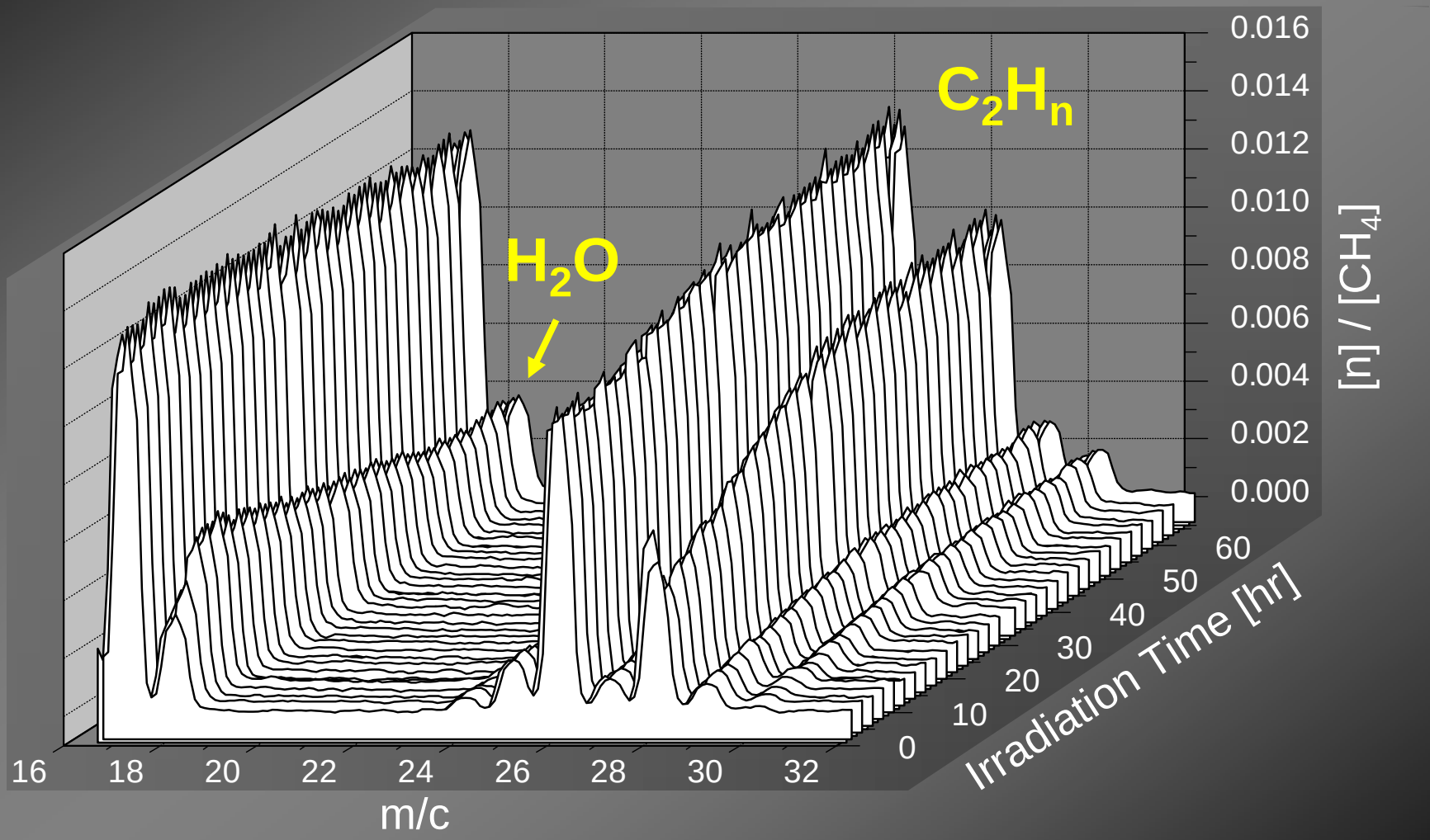


- Reproducibility of signal
- Similar formation timescale

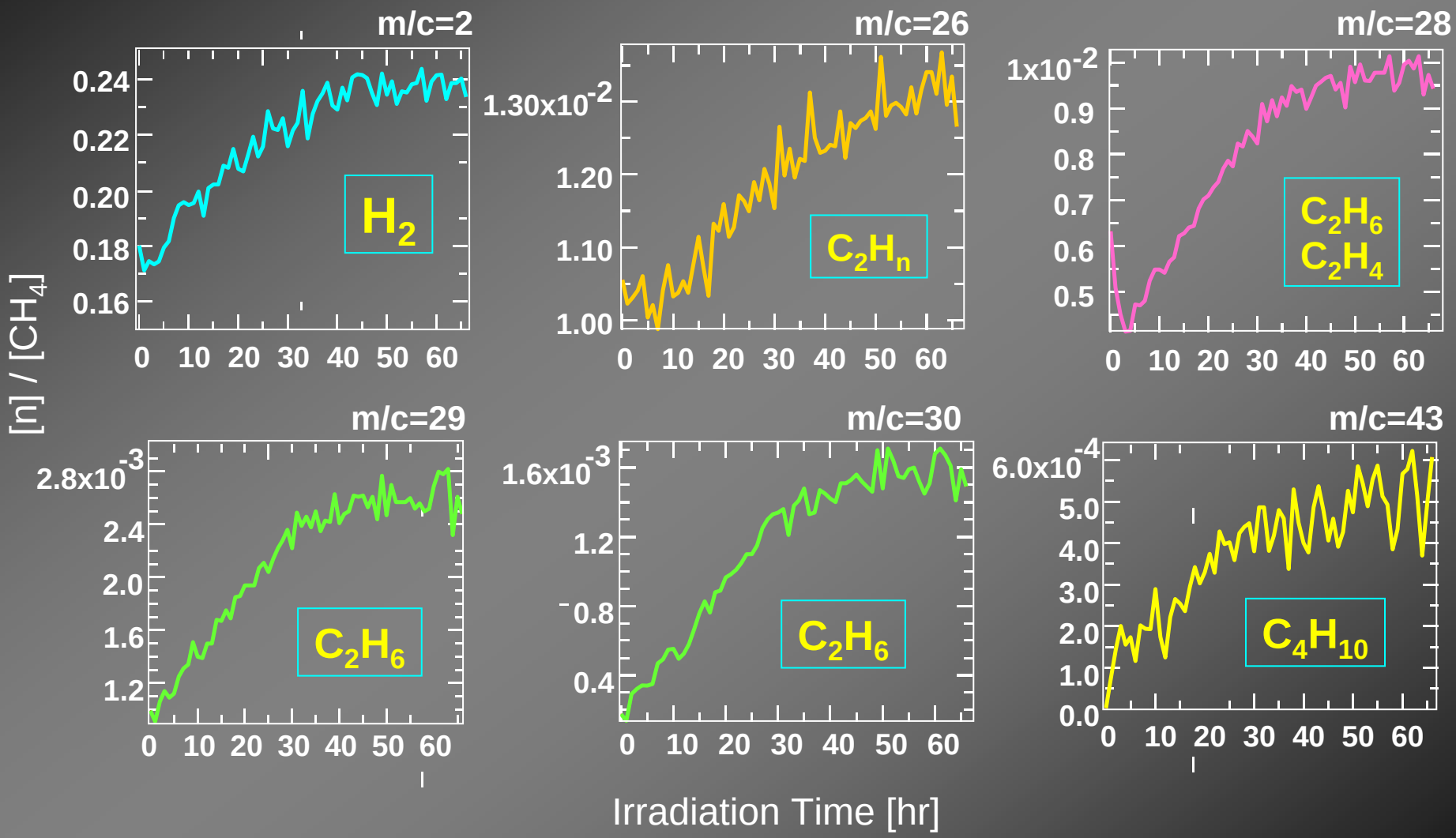
Time Series RGA-MS Data: $[CH_4]$ = 70 torr



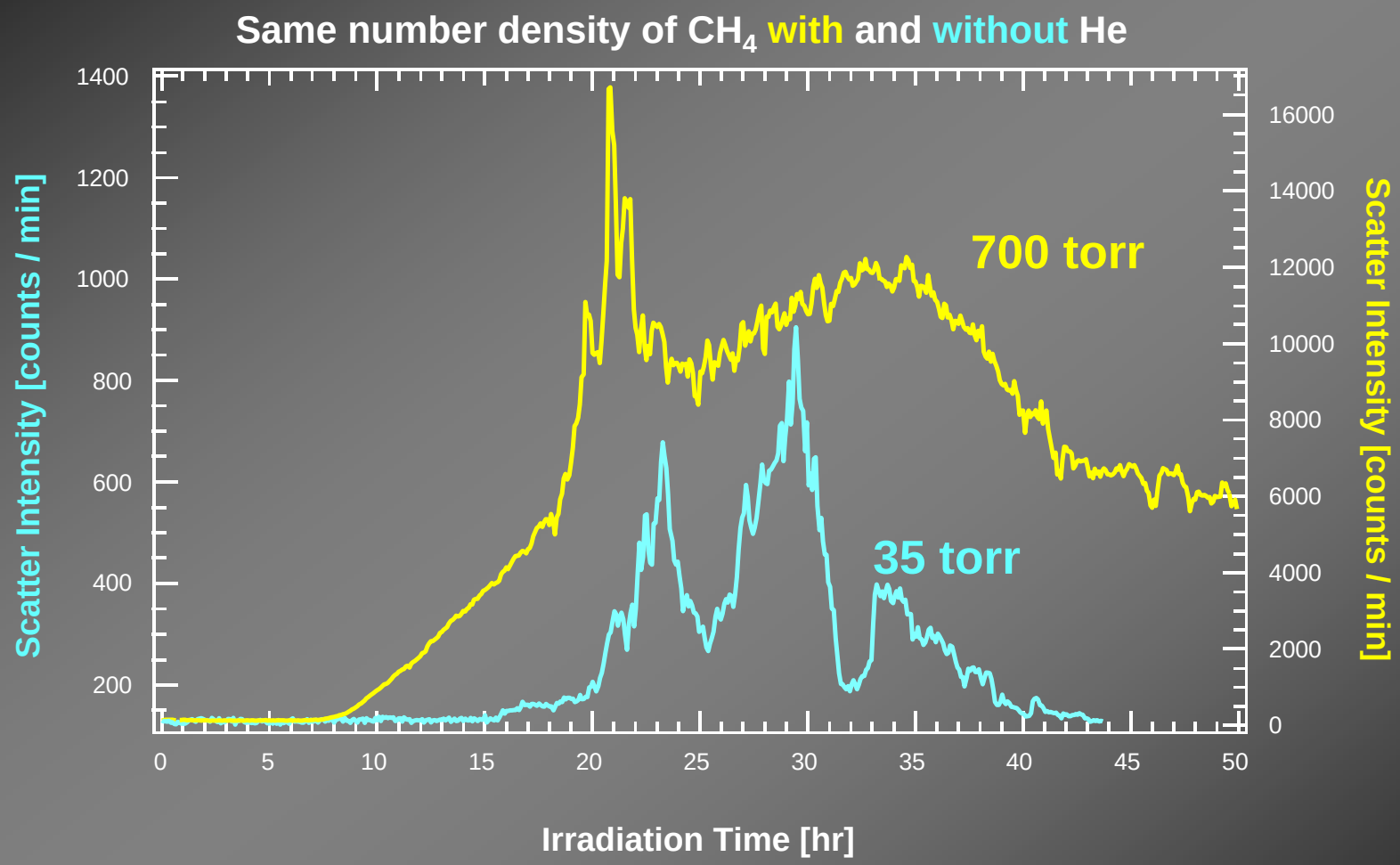
Time Series RGA-MS Data: [CH_4] = 70 torr



Time Series RGA-MS Data: [CH_4] = 70 torr

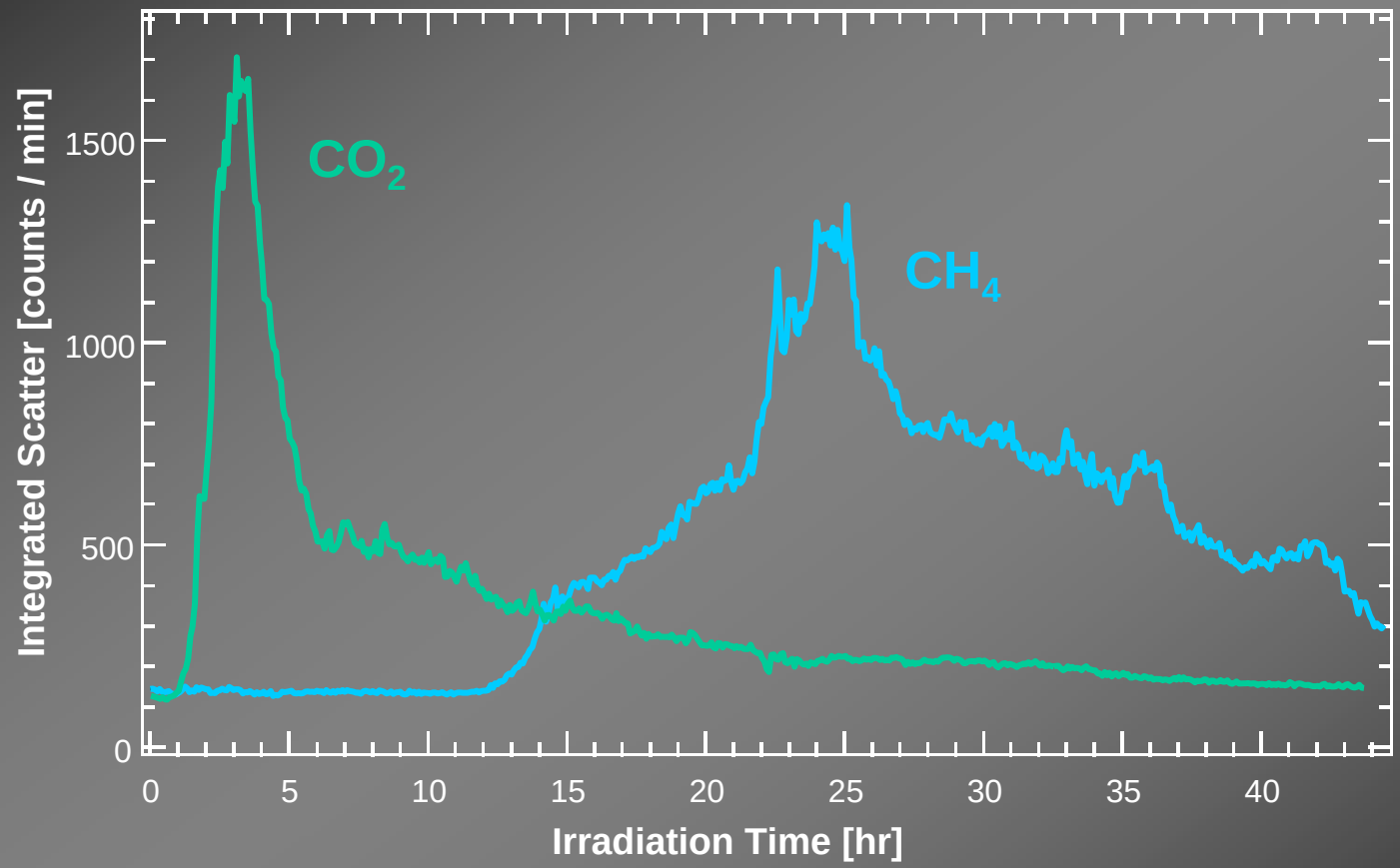


CH_4 Pressure Dependence



- Order of magnitude larger signal at 700 torr
- Can be kinetic or microphyical effect

Particulate formation with *both* CO_2 and CH_4



- Comparable optical scatter
- Notable difference formation timescale

Modelling the observed signal

Microphysics and Kinetics

Rate of Scatter increase:

- **chemical reaction rates**
  - for C_nH_m species up to n=4:
    - 74 photodissociation reactions
    - 194 chemical reactions (31 3-body reactions)
- **nucleation properties**
  - (particle size distribution function)

Rate of Scatter decrease:

- **depletion of reactants**
- **decrease in VUV flux**
  - coating surface of MgF_2 window
  - shielding from haze formation
- **nucleation**

Summary

Designed, assembled, and tested photochemistry reaction chamber

Observed formation of particulate haze with CH_4 and preliminarily with CO_2

Started models and experiments to determine the kinetics pertinent to haze formation

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