School of Chemistry
FACULTY OF MATHEMATICS AND PHYSICAL SCIENCES

UNIVERSITY OF LEEDS

Low Temperature Gas Phase Reaction Rate Coefficient Measurements: Toward Modeling of Stellar Winds

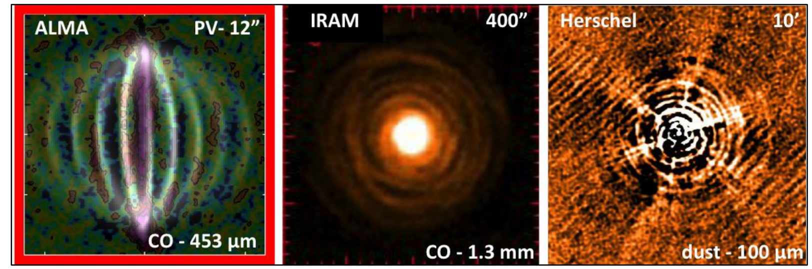
Dr. Niclas West

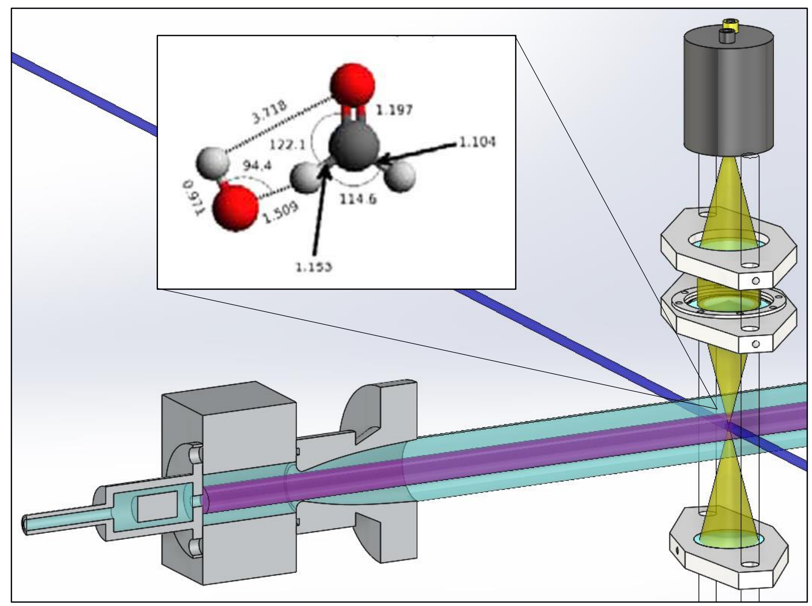
Heard Research Group

29/06/2018

Talk Outline

- Motivation:
  - Astrochemistry
- Background:
  - Low T Reactions
- Method:
  - Laval Nozzle + PLP-LIF
- Results:
  - $OH + CH_2O \rightarrow H_2O + CHO$
- Conclusions

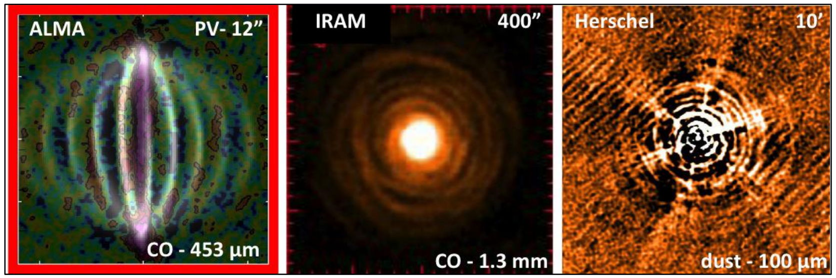




Decin, L. et al. A&A, submitted (2014)
Menut, J.-L. et al. MNRAS, 376, L6–L10 (2007)
Decin, L. et al. A&A, 534, A1 (2011)
Vu, N. G. et al. J. Phys. Chem. A, 117, 12208 (2013)

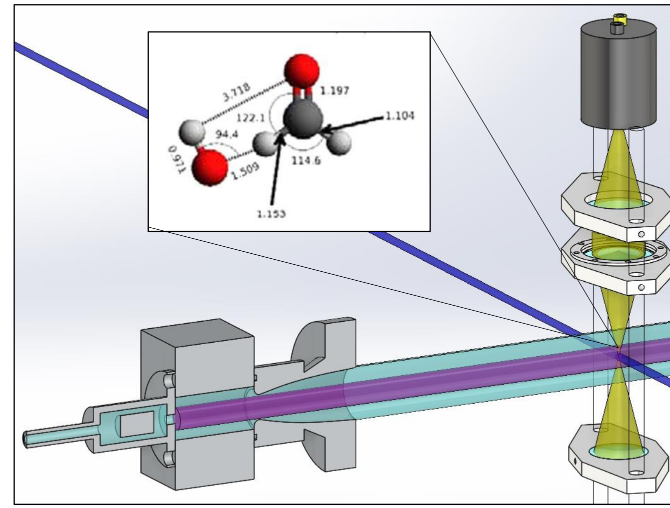
Motivation: Astrochemistry/Astrophysics Overview

Spatial and wavelength-resolved measurement



Data ↓ ↑ Next target

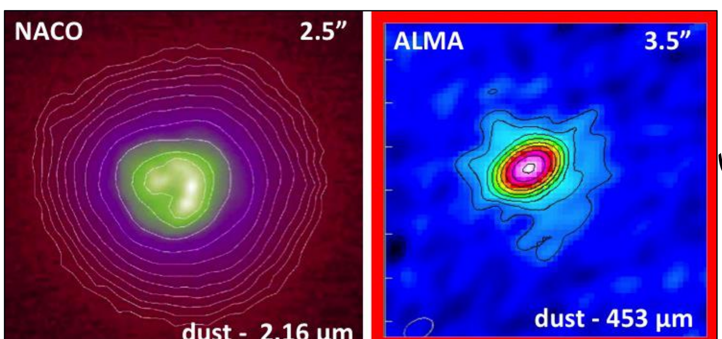
Low T gas phase kinetics



Rates

Next species (Sensitivity Analysis)

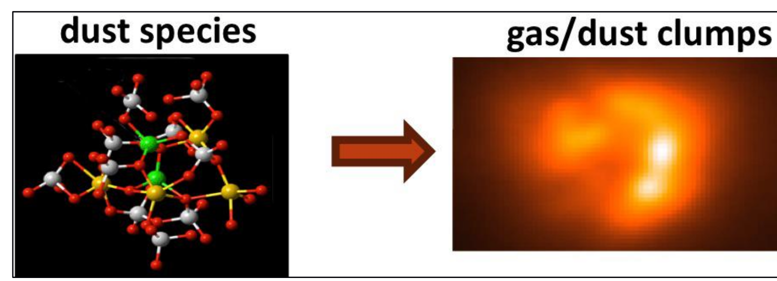
Modeling of kinetics and dynamics



Rates

Next species

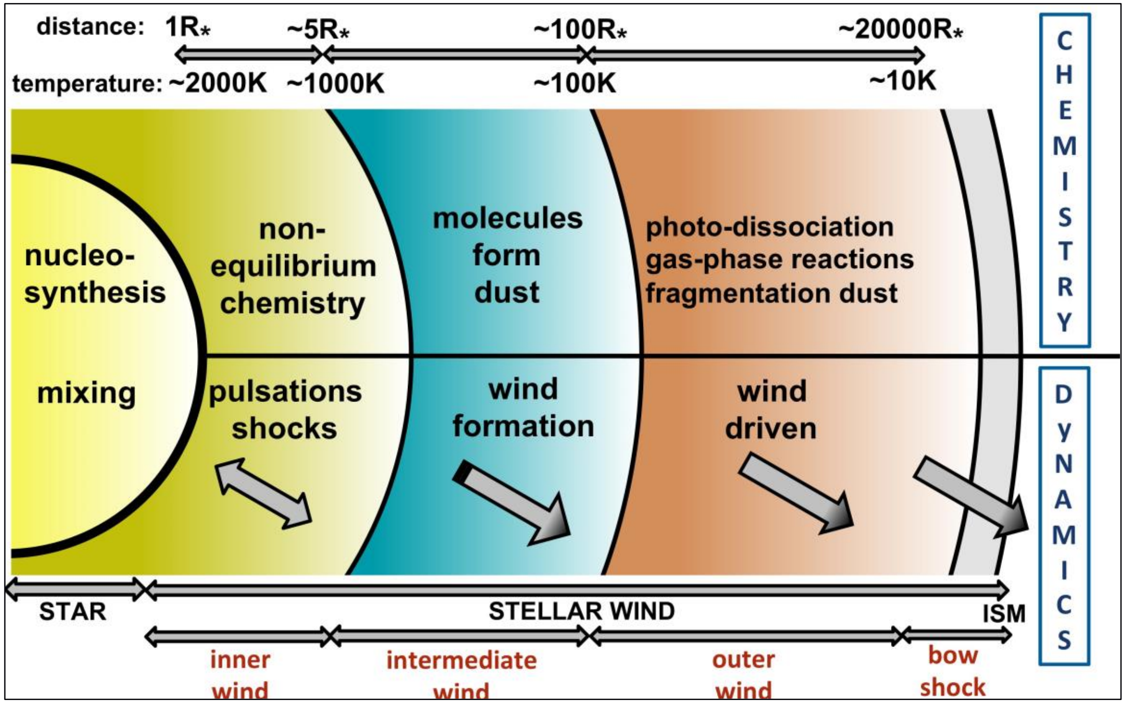
Gas-grain kinetics



Decin, AEROSOL (AstrochEmistRy of Old Stars: direct prObing of unique chemical Laboratories). European Research Council (ERC): 2014; pp 1-21.

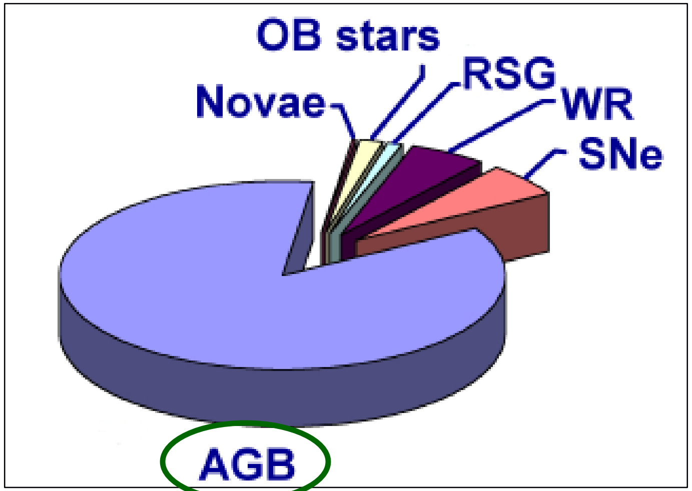
Motivation: From Stellar Atmosphere to ISM

Asymptotic Giant Branch (AGB) [~Red Giant] Star

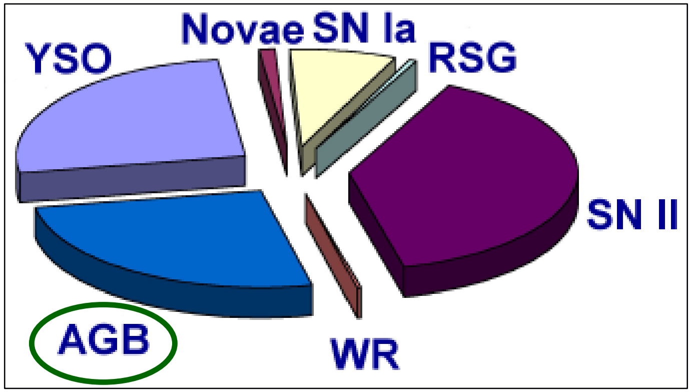


AGB stars are a major source of ISM species. The dynamics of the stellar winds determine the composition of these species.

Sources of ISM Gas



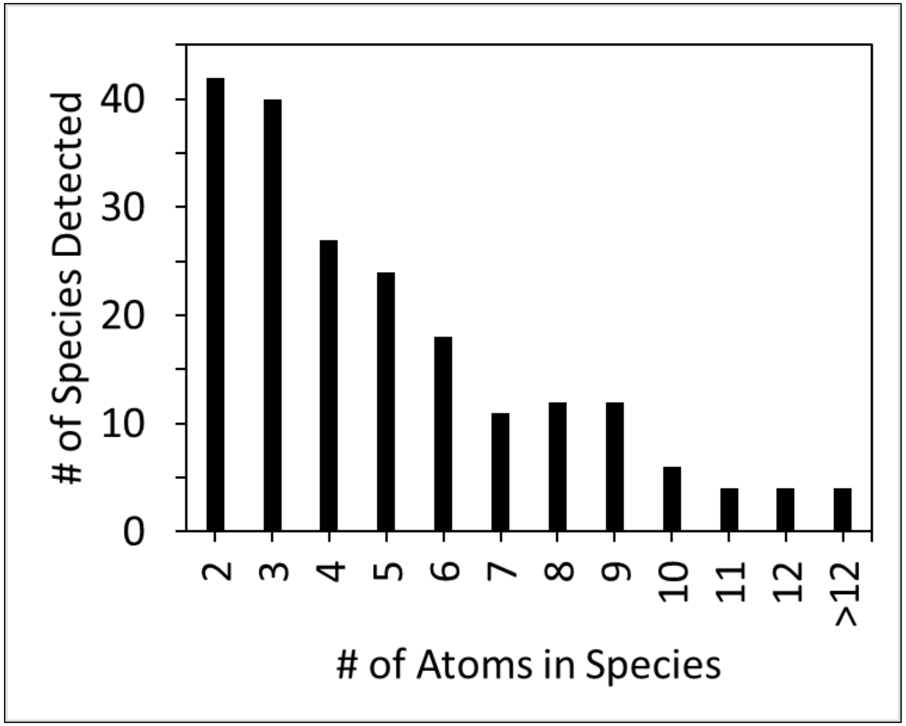
Sources of ISM Dust



Decin, AEROSOL (AstrochEmistRy of Old Stars: direct prObing of unique chemical Laboratories). European Research Council (ERC): 2014; pp 1-21.

Motivation: Astrochemistry of Stellar Winds and ISM

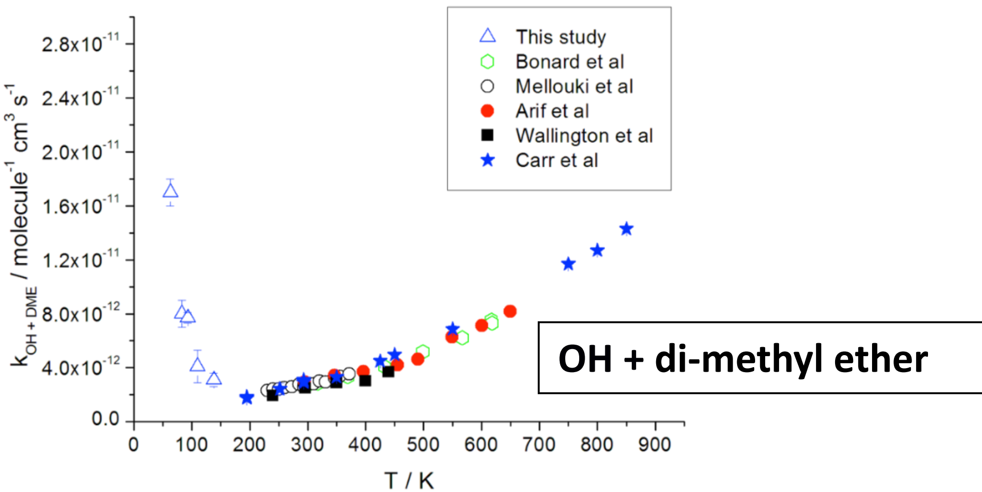
- InterStellar Medium (ISM): Space between stars in a galaxy

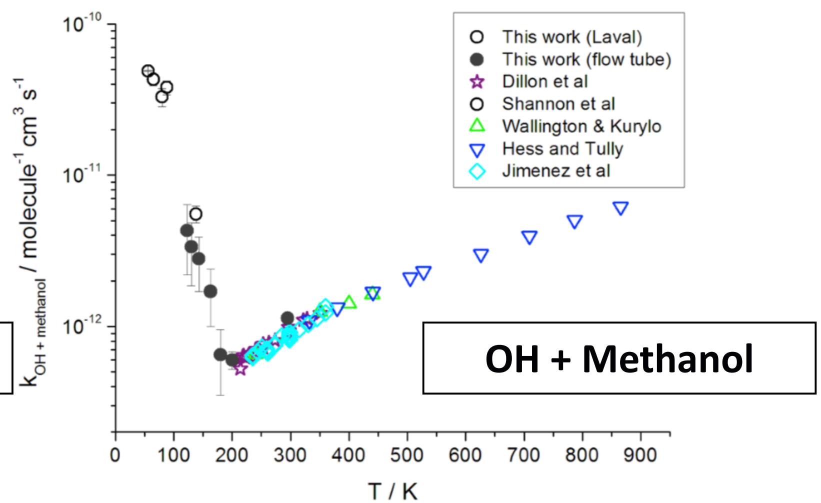


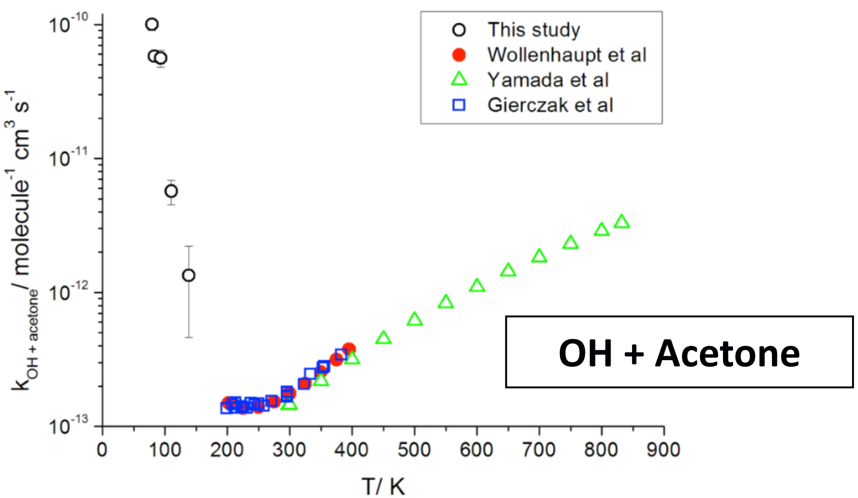
- How are complex molecules formed in low T (~10 K) stellar winds?
  - Pinpoint dominant chemical pathways (Elements → Simple hydrocarbons → Complex/Biomolecules)
- Reaction rates at T ≲ 250 K:
  - Often dramatically increase with decreasing temperature
  - Are scarce due to experimental difficulties

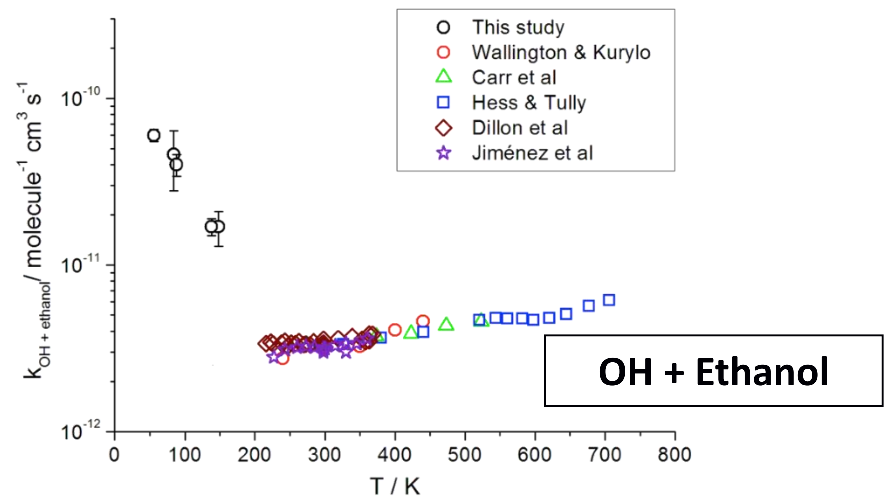
Decin, AEROSOL (AstrochEmistRy of Old Stars: direct prObing of unique chemical Laboratories). European Research Council (ERC): 2014; pp 1-21.

Background: Heard Group Low T Reaction Rates (all have barriers to reaction)



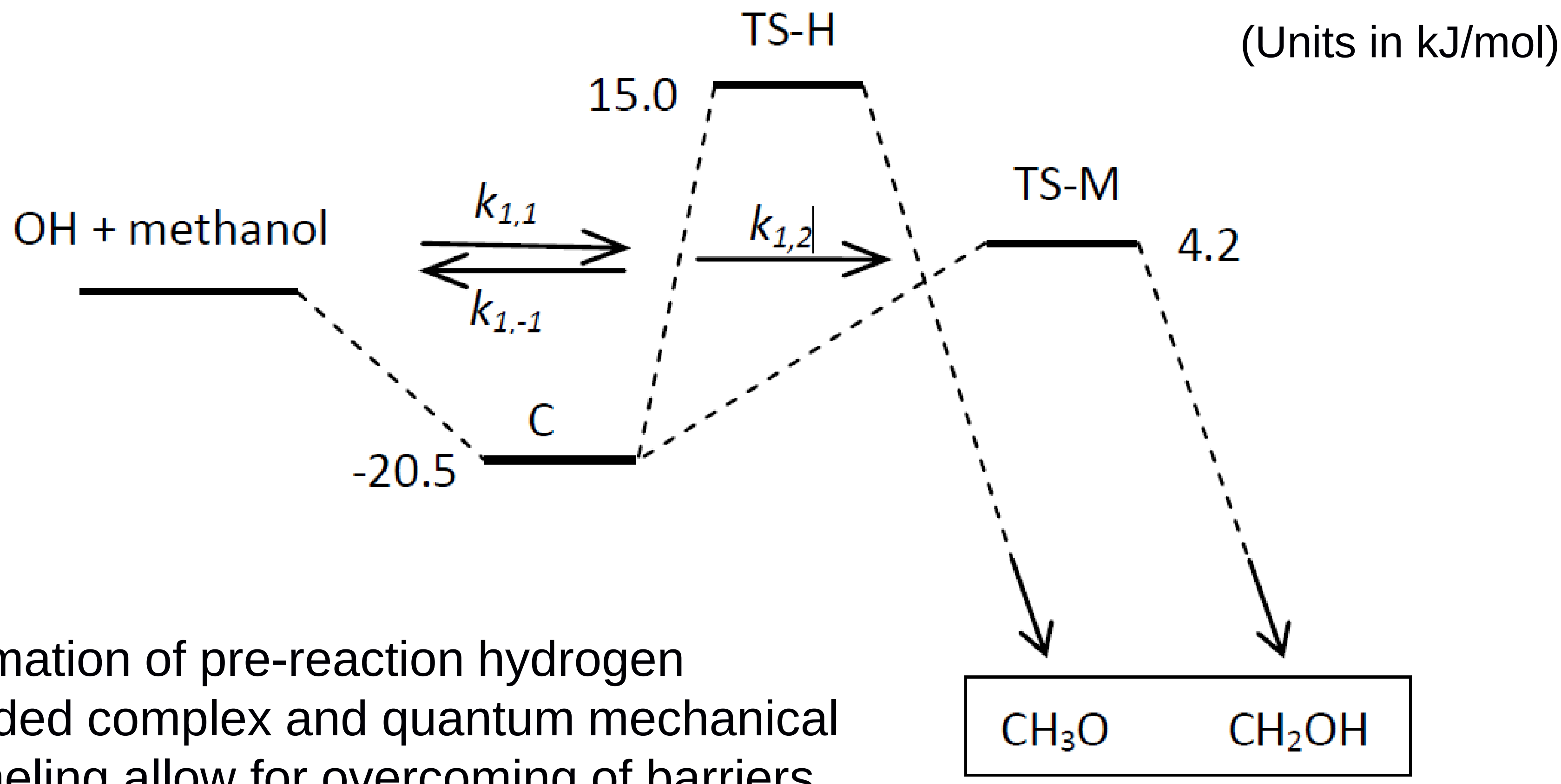






Shannon et al., 2013; 2014; Caravan et al., 2014; Gomez-Martin et al., 2014

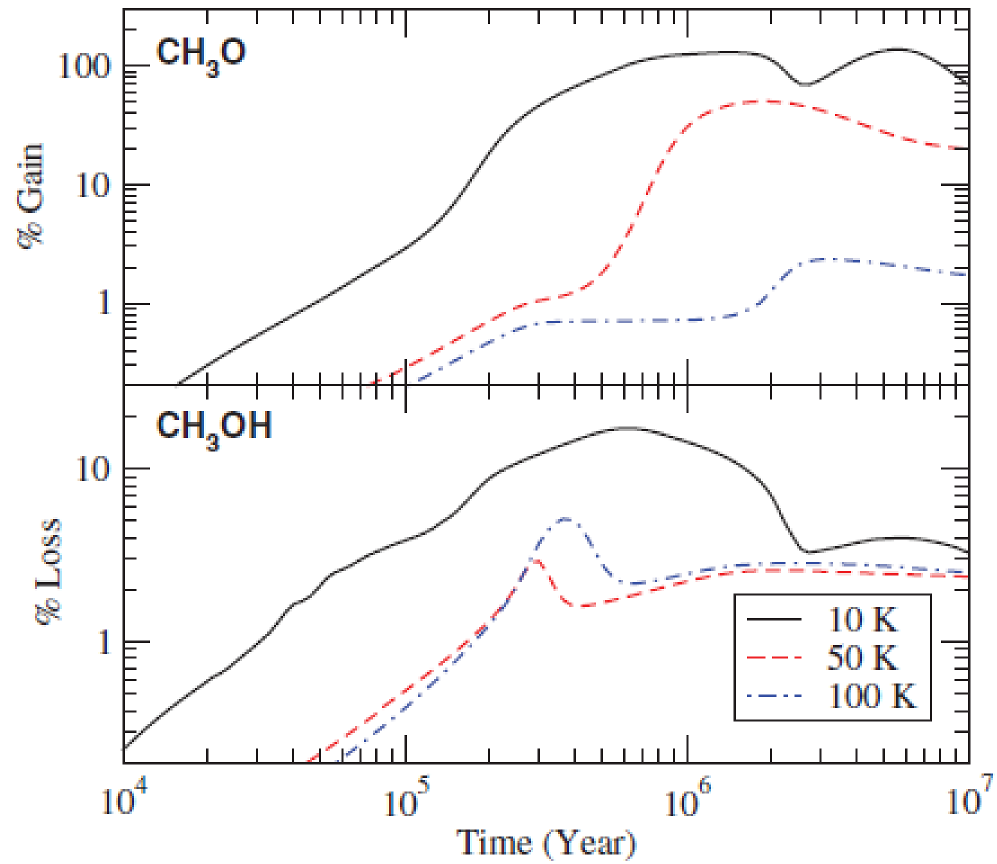
Background: Overcoming Reaction Barriers at Low T



Formation of pre-reaction hydrogen bonded complex and quantum mechanical tunneling allow for overcoming of barriers.

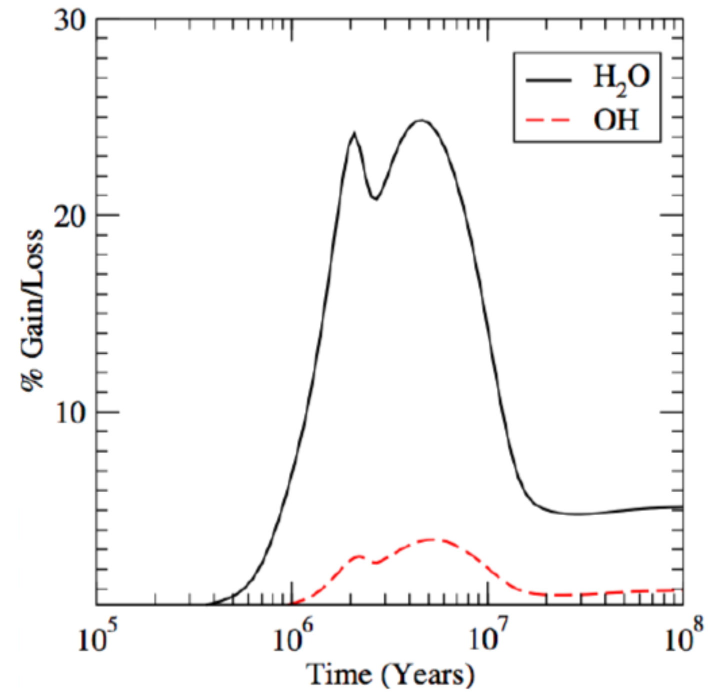
Shannon et al., 2013; 2014; Caravan et al., 2014; Gomez-Martin et al., 2014

Impact of $OH + CH_3OH \rightarrow CH_3O + H_2O$ in Dense Interstellar Clouds Via Astrochemical Modelling



Gas-grain model
(12,000 reactions, OSU and KIDA databases)

Acharyya et al., Mol. Phys. 2015



Eric Herbst (U of Virginia)

Method: Generalized Reaction for Laval PLP-LIF

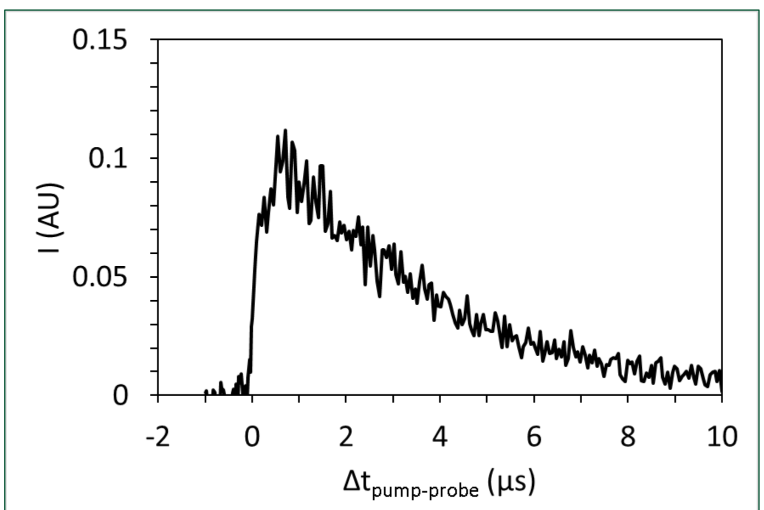
10[Precursor] ≲ [A] => Pseudo 1st Order

- Precursor + $h\nu_{UV}$ → B (k_{rel})

Probe (We can often monitor reactants or products)

- A+ B → C + D (k_r)
- B → Loss (Diffusion, Quenching, Etc.)

(k_{obs})



Yields data of multi-exponential form where the total growth rate (k_{rel}) and the total decay rate (k_{obs}) are fit.

Method: OH + CH_2O Reaction

10[CH_2O] ≲ [t-BuOOH] => Pseudo 1st Order

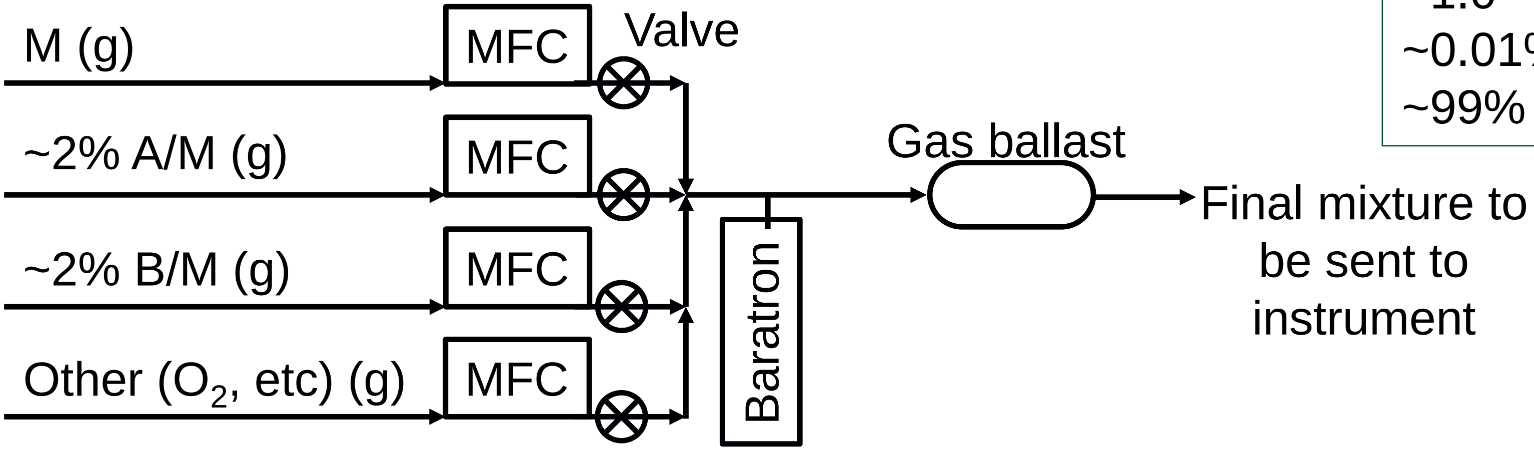
- t-BuOOH + hv_{308nm} → OH(J*,v*) + OH
- OH(J*,v*) → OH (k_{rel})

Probe (~308 nm, ~240 nm, 121 nm)

- CH_2O + OH → CHO + H_2O (k_r)
- CH_2O + OH → H + CO + H_2O
- CH_2O + OH → H + HC(O)OH
- OH → Diffusion loss

(k_{obs})

Method: Gas Mixture Preparation/Limitations



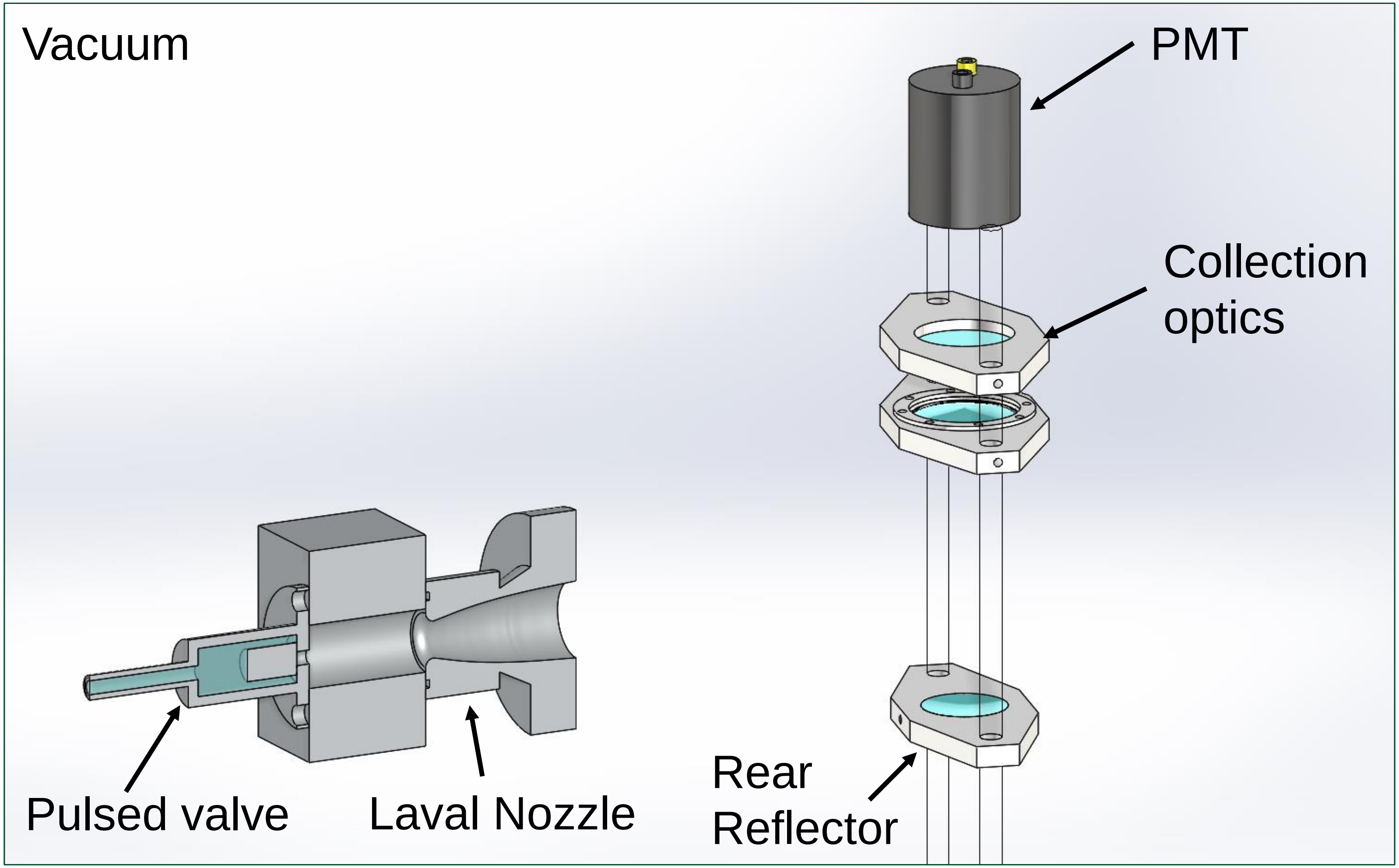
~1.0 - 0.1% A
~0.01% B
~99% M (g)

Where: A and B = Reagents/Precursors 1 and 2,

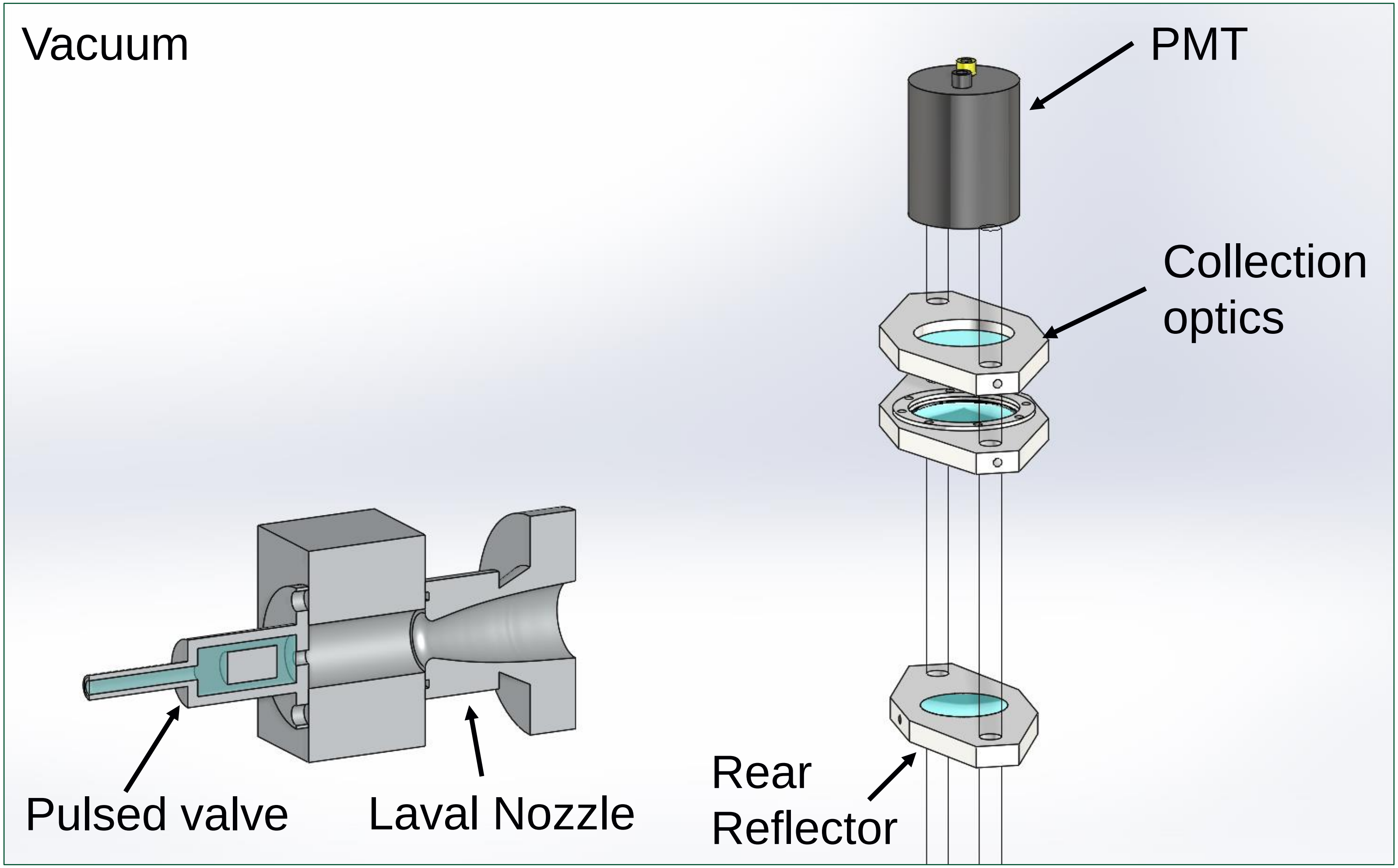
M = Bath gas (He, N_2, etc)

(At ⪆ 1% reagents often quickly dimerize at low T)

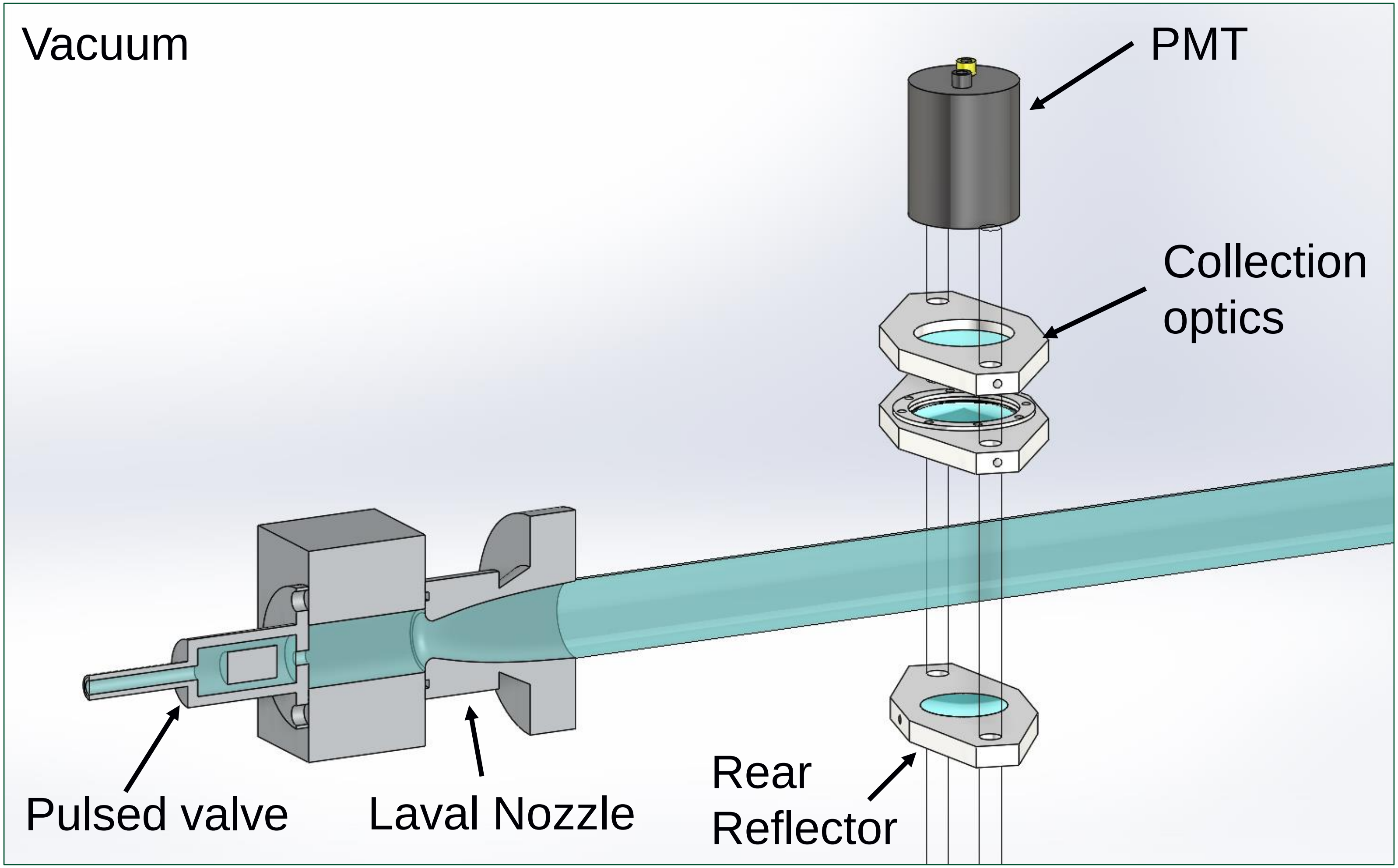
Method: Laval Nozzle and PLP-LIF



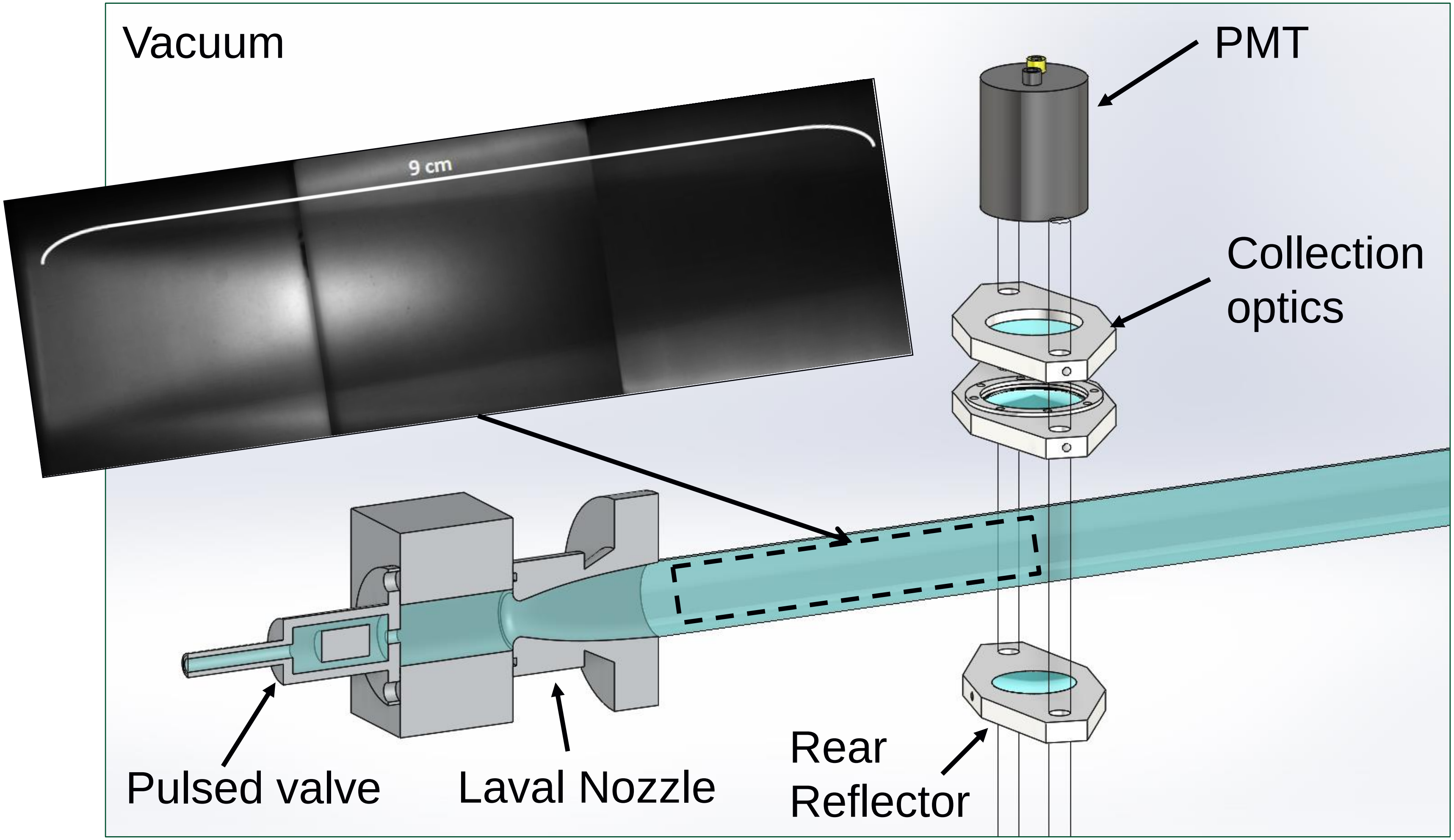
Method: Laval Nozzle and PLP-LIF



Method: Laval Nozzle and PLP-LIF

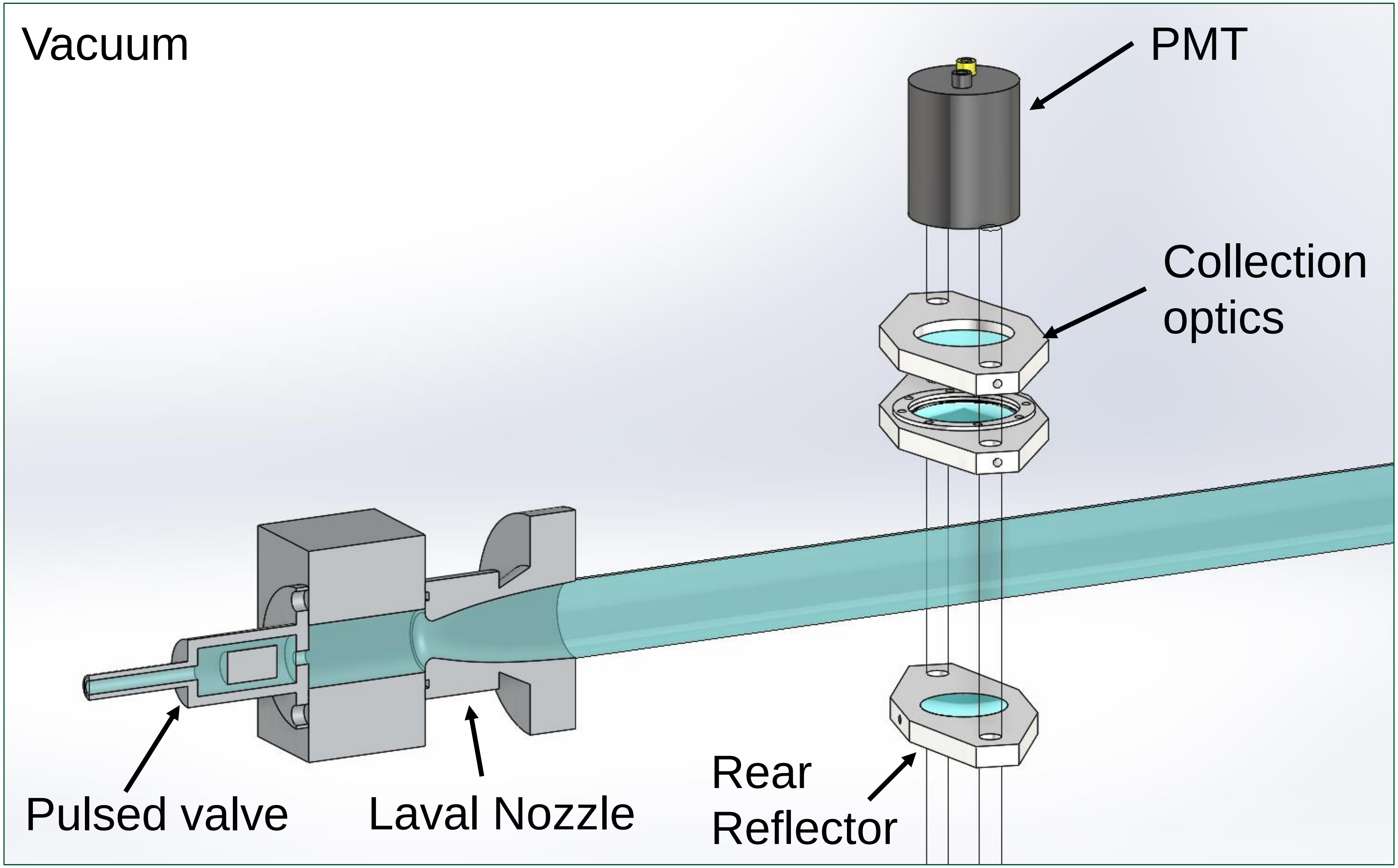


Method: Laval Nozzle and PLP-LIF



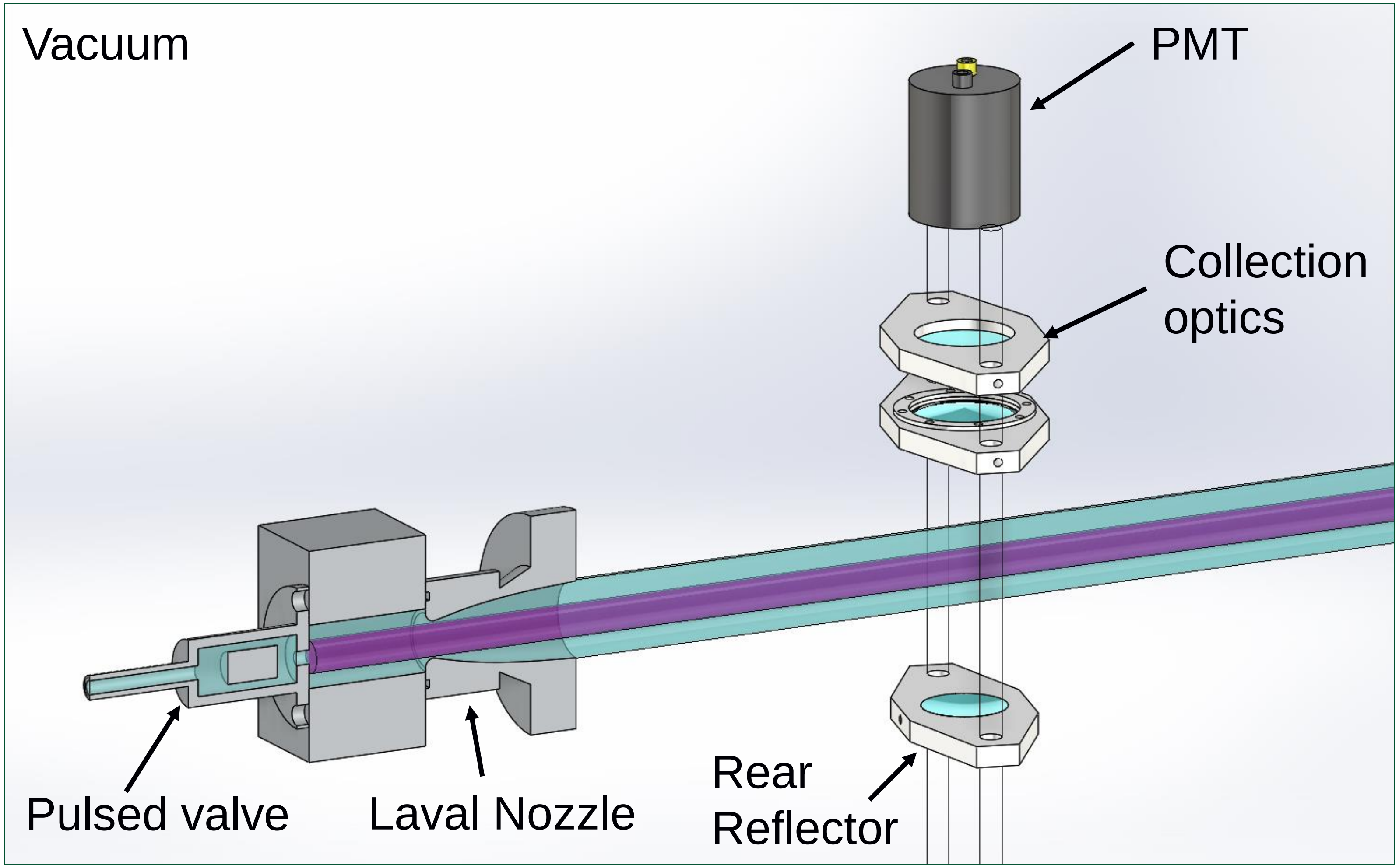
Sanchez-Gonzalez, R., *Advanced laser diagnostics development for the characterization of gaseous high speed flows*. Texas A&M University: 2012.

Method: Laval Nozzle and PLP-LIF

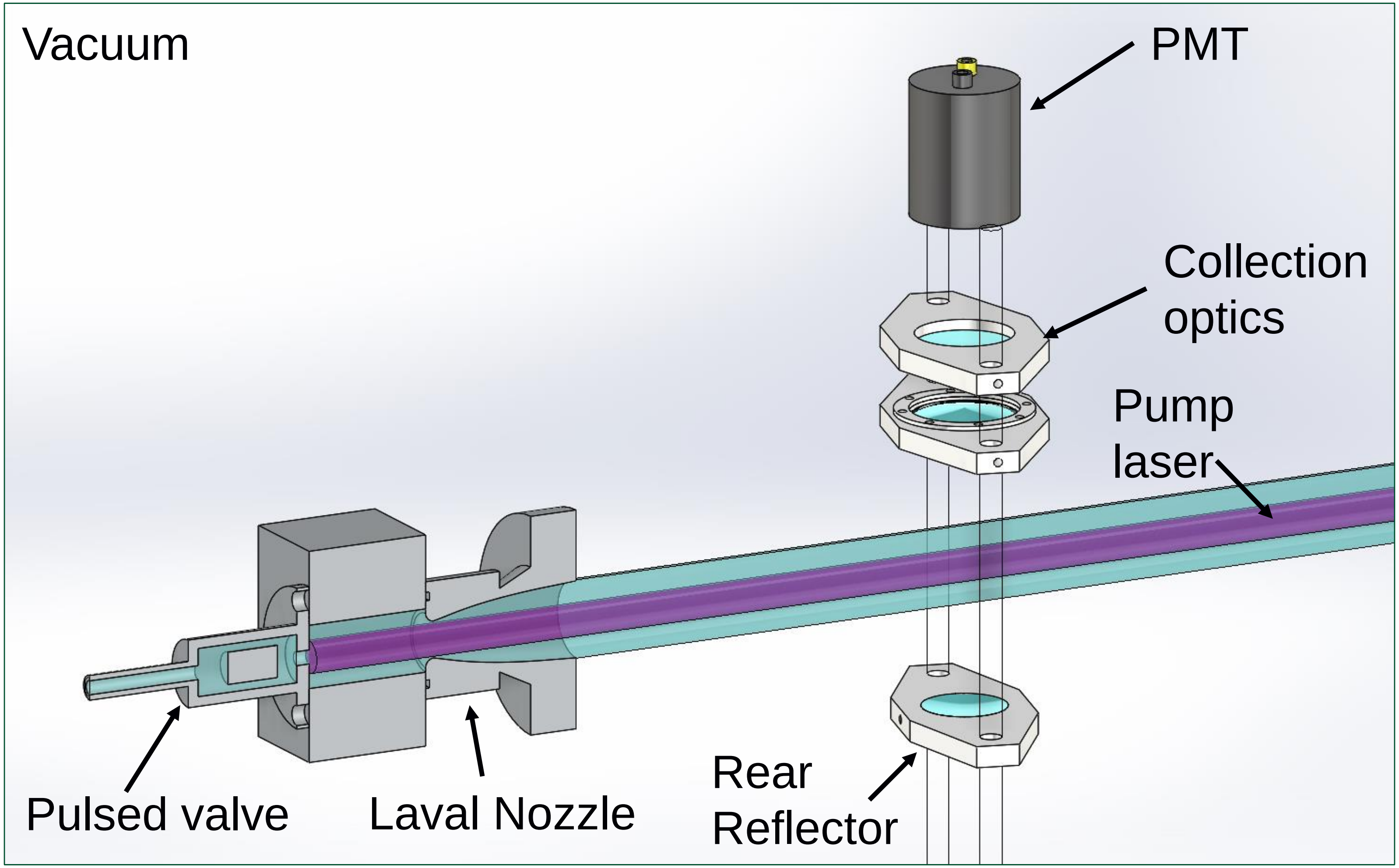


Sanchez-Gonzalez, R., *Advanced laser diagnostics development for the characterization of gaseous high speed flows*. Texas A&M University: 2012.

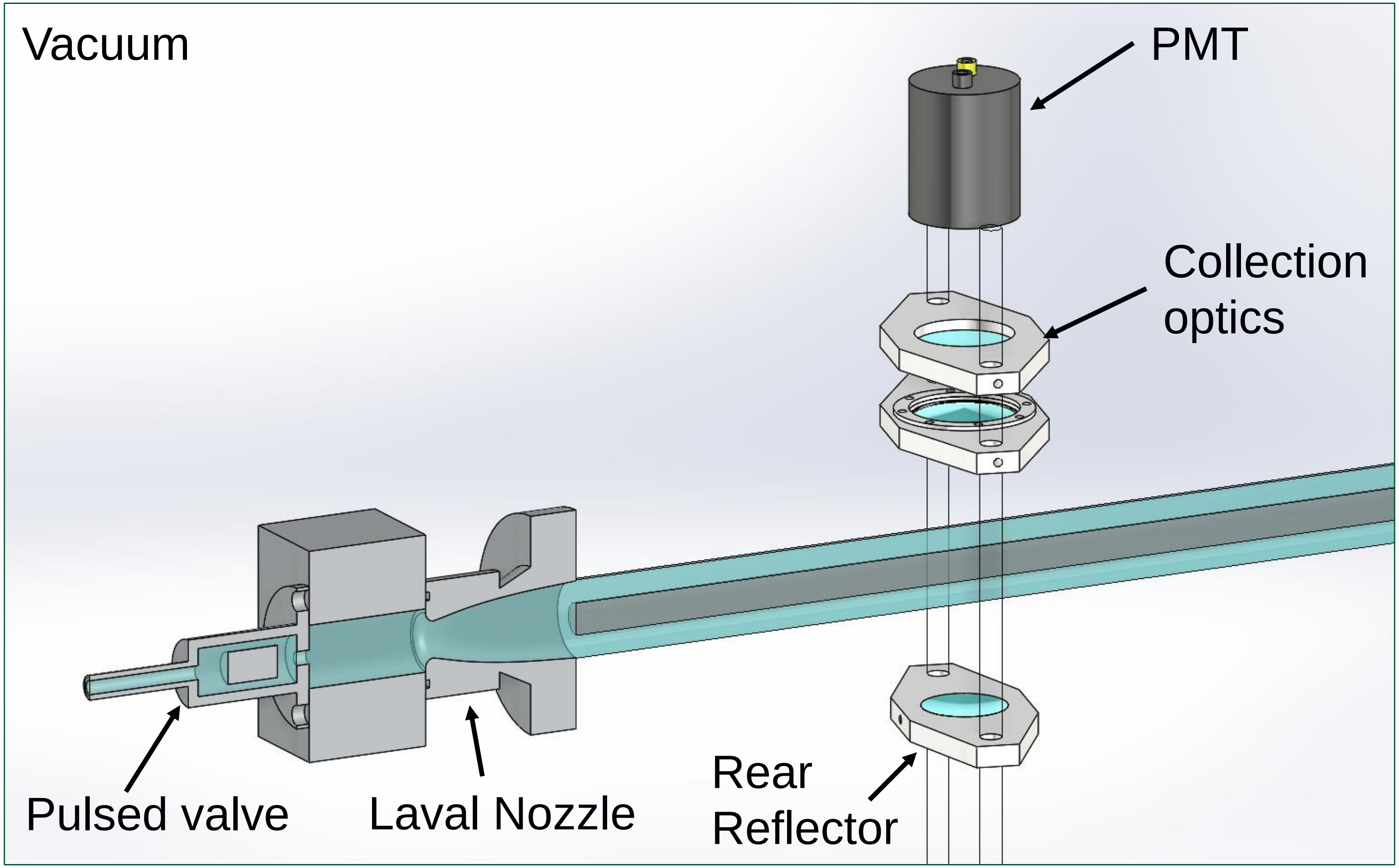
Method: Laval Nozzle and PLP-LIF



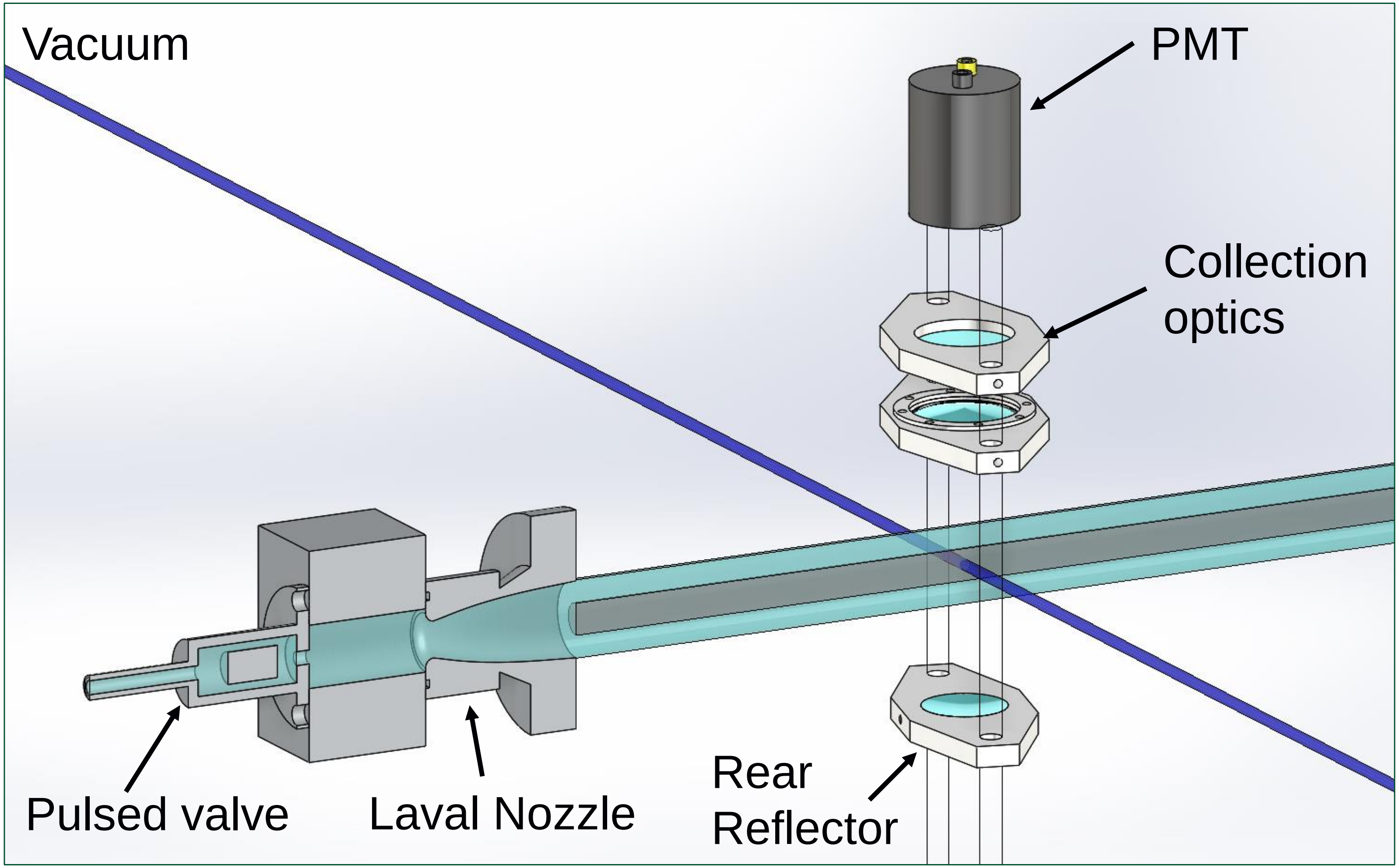
Method: Laval Nozzle and PLP-LIF



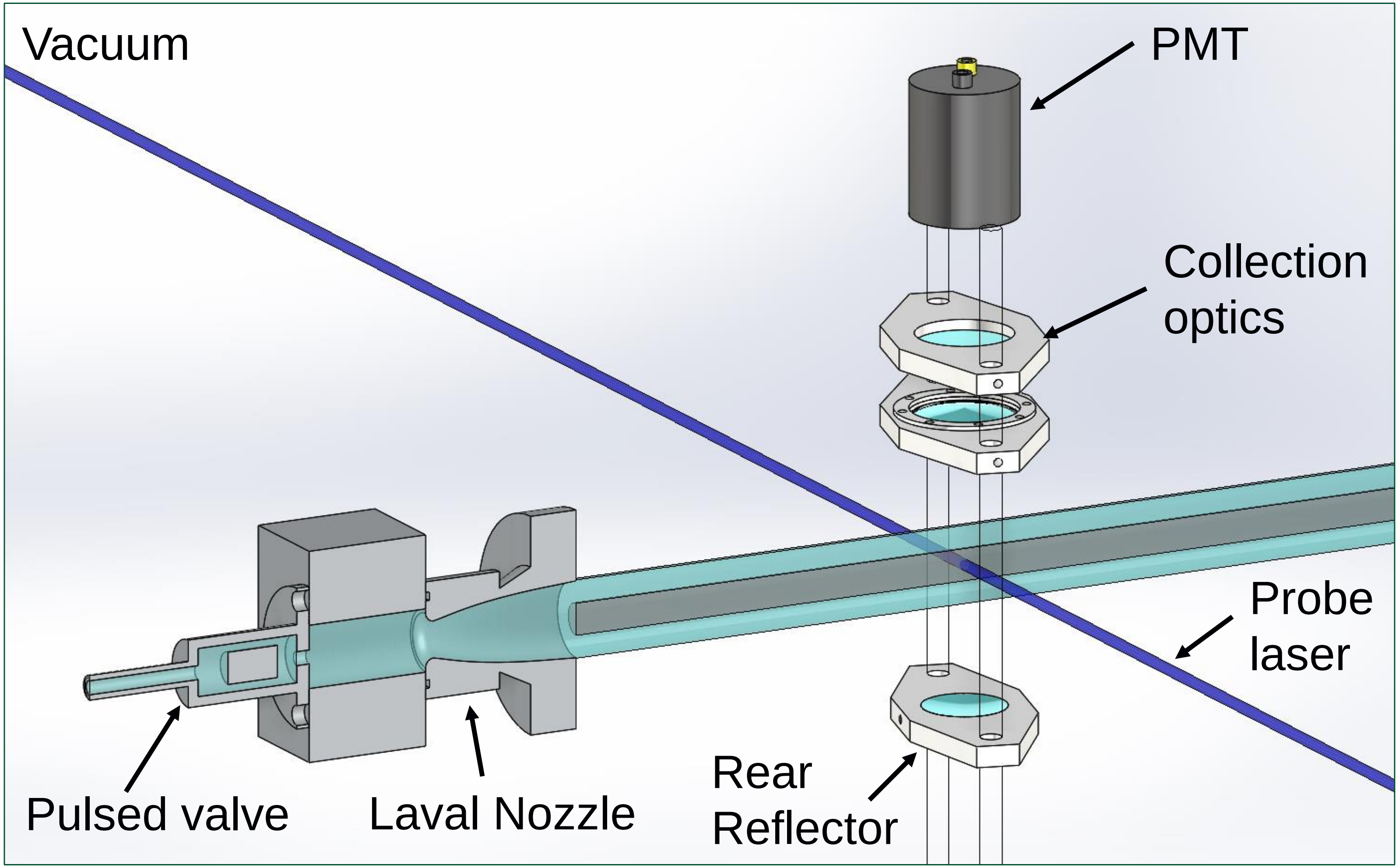
Method: Laval Nozzle and PLP-LIF



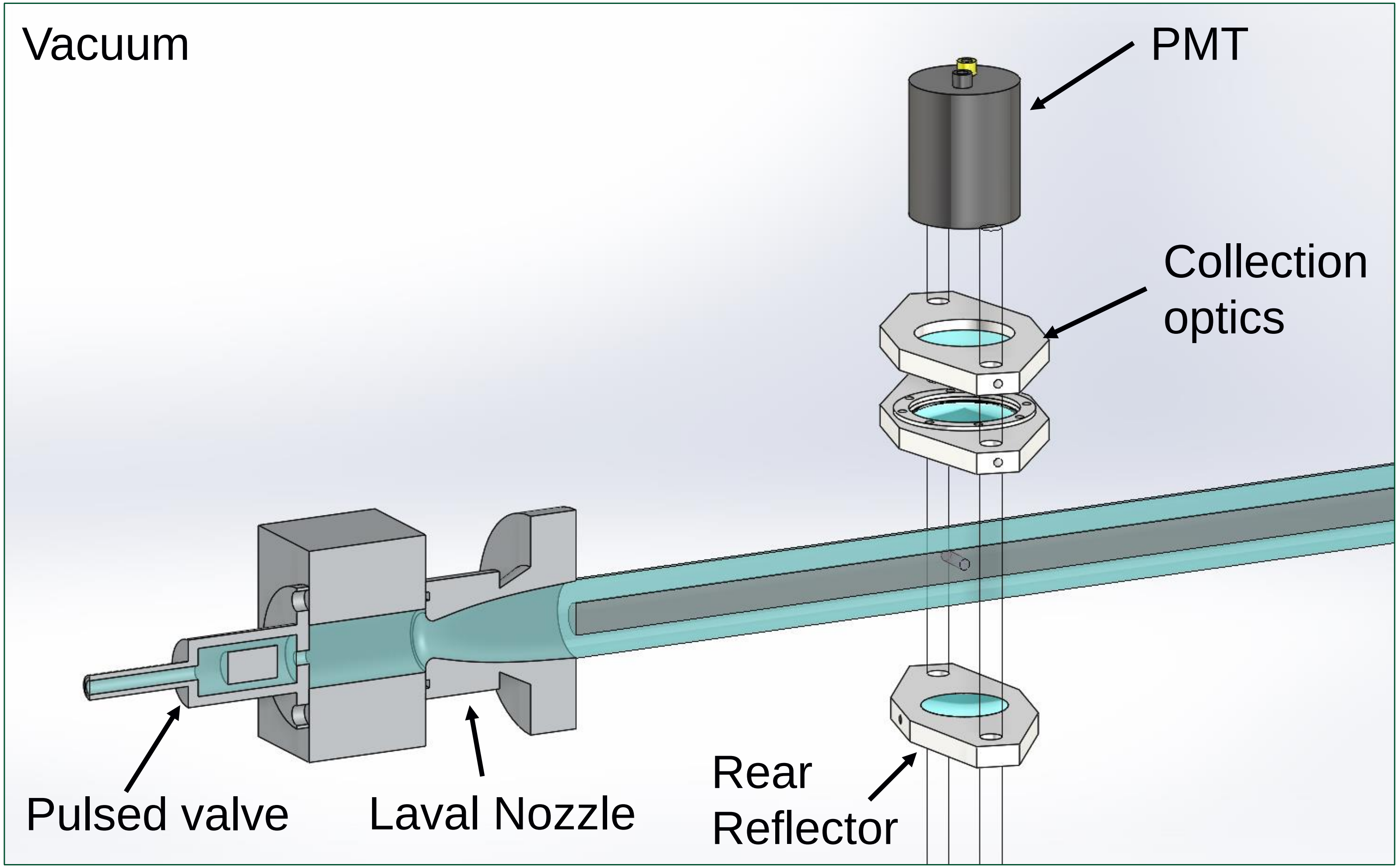
Method: Laval Nozzle and PLP-LIF



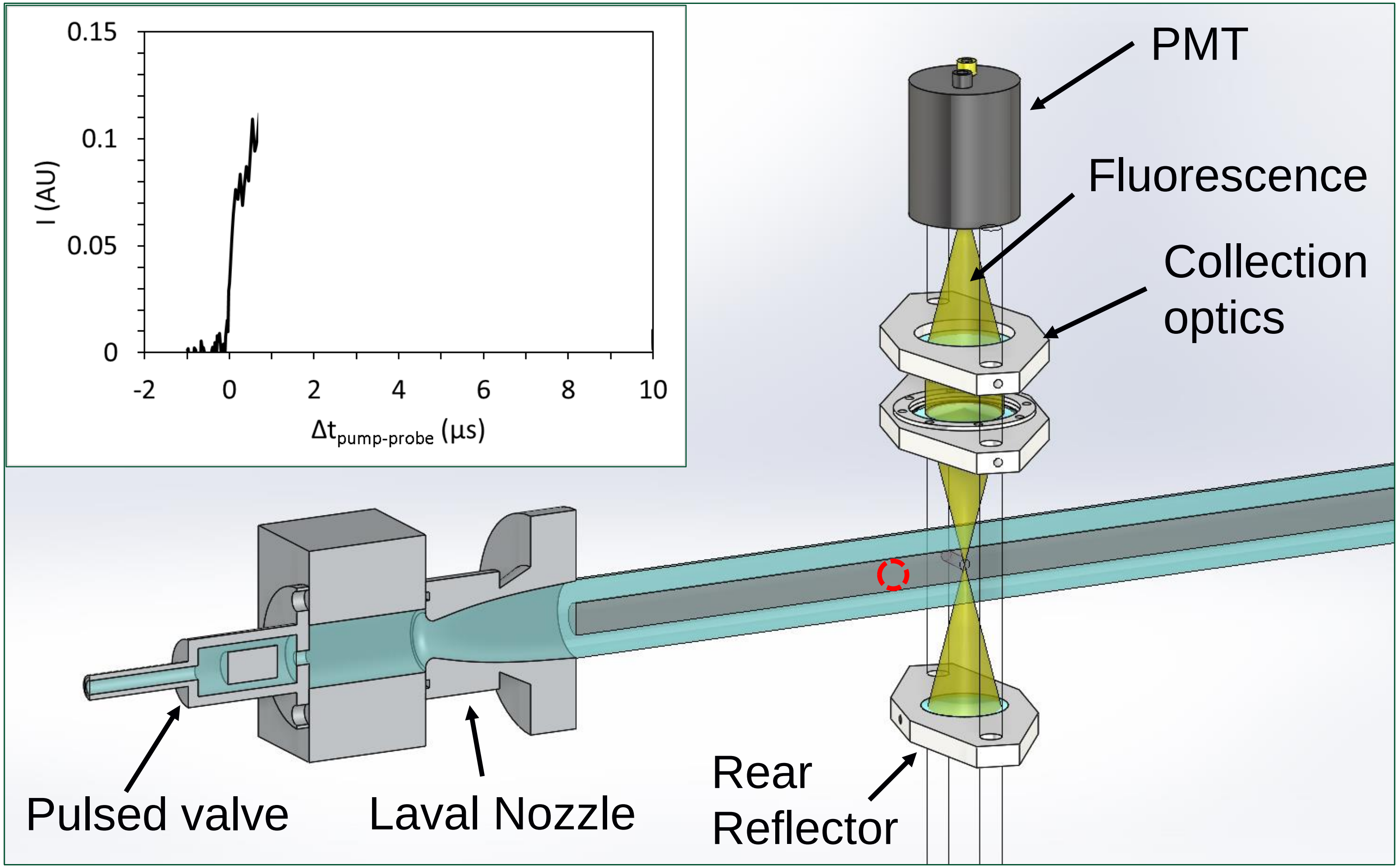
Method: Laval Nozzle and PLP-LIF



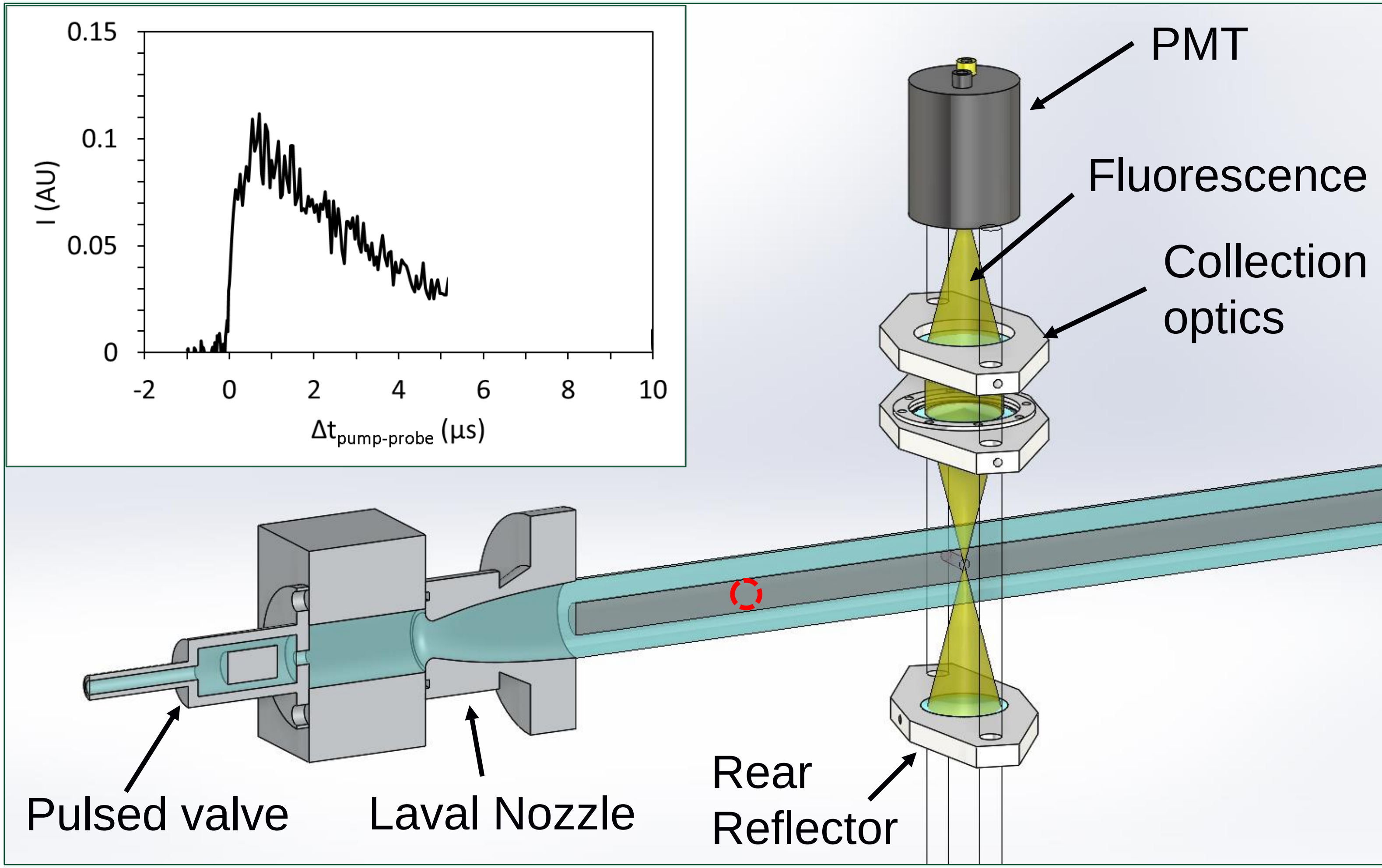
Method: Laval Nozzle and PLP-LIF



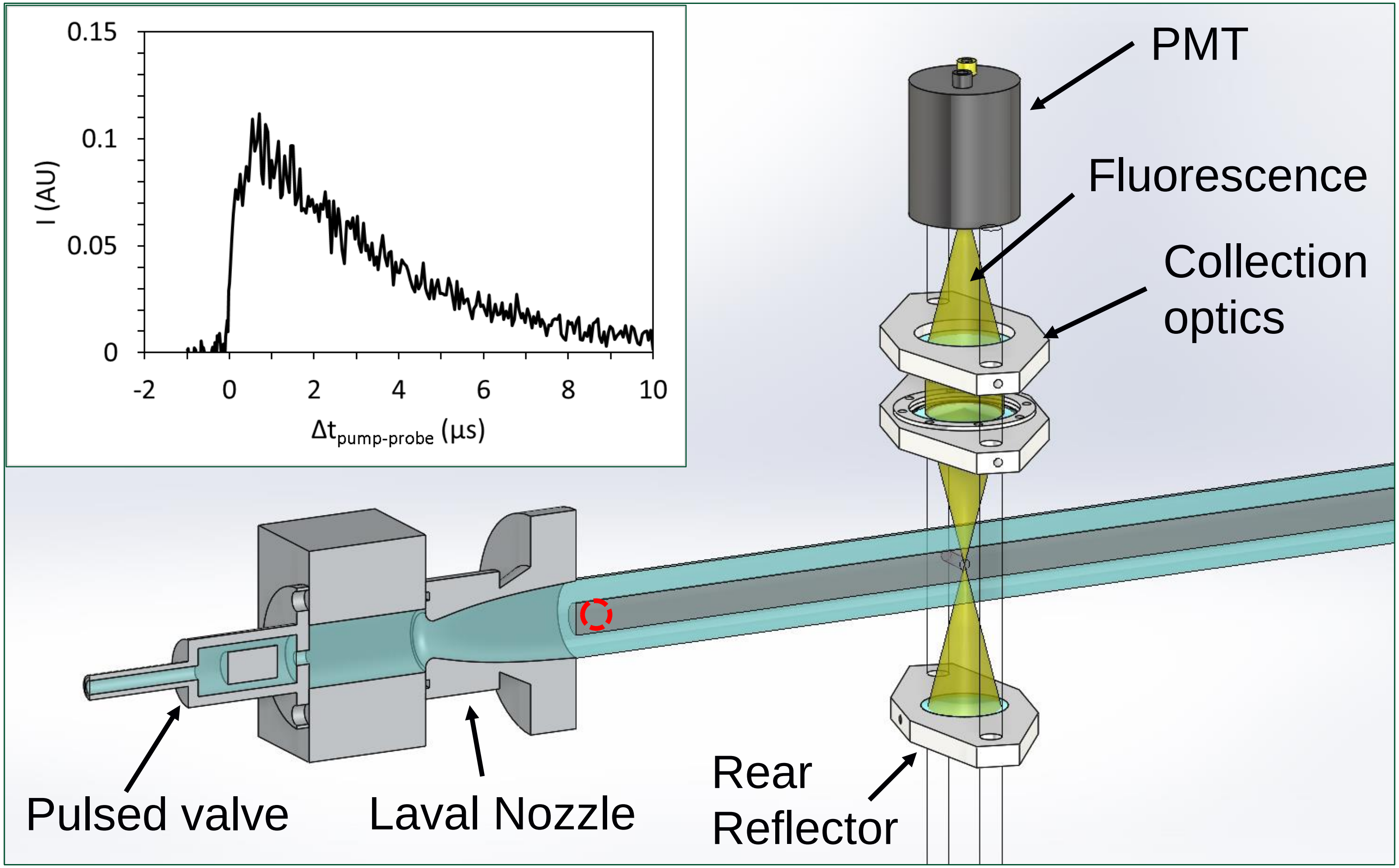
Method: Laval Nozzle and PLP-LIF



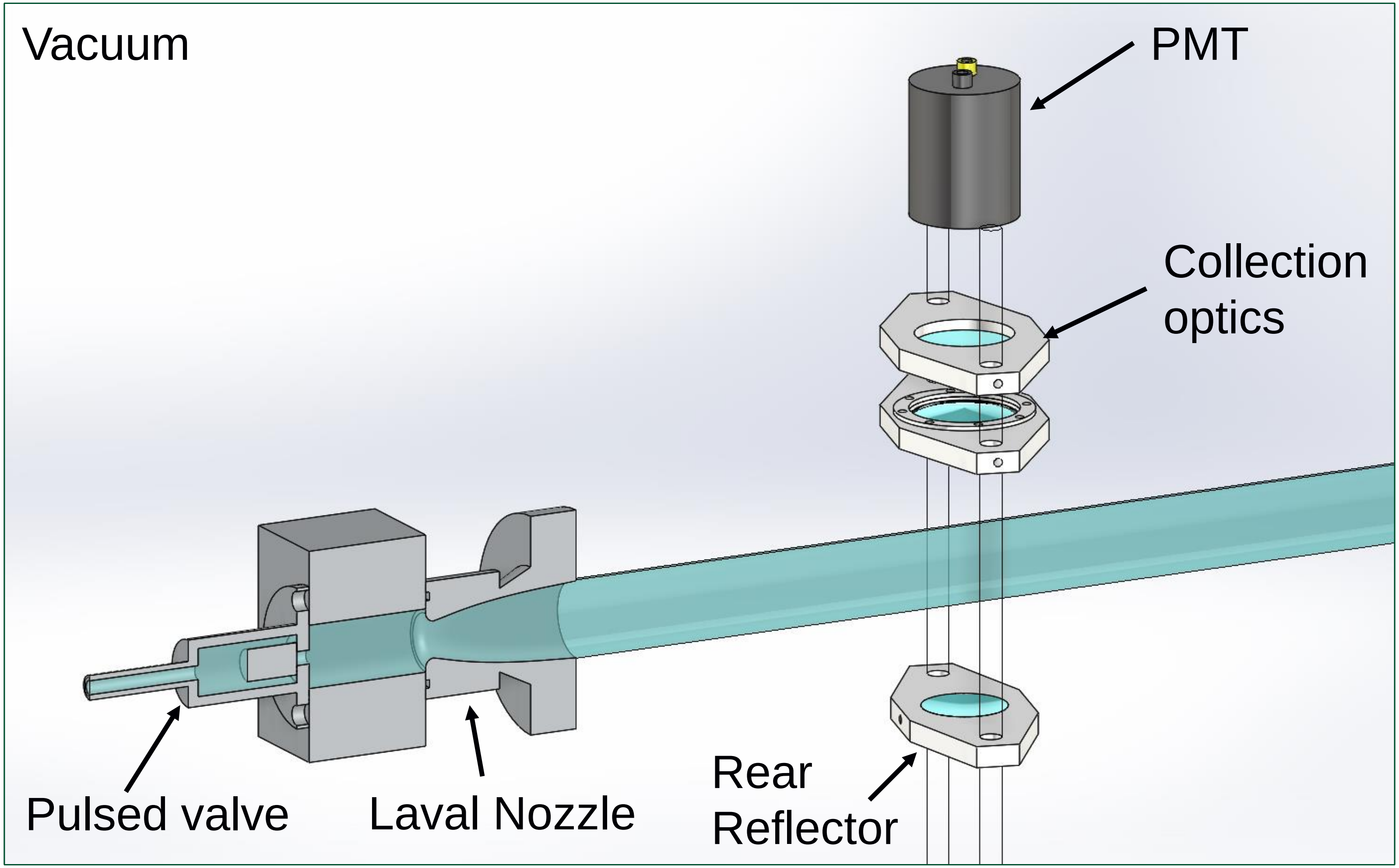
Method: Laval Nozzle and PLP-LIF



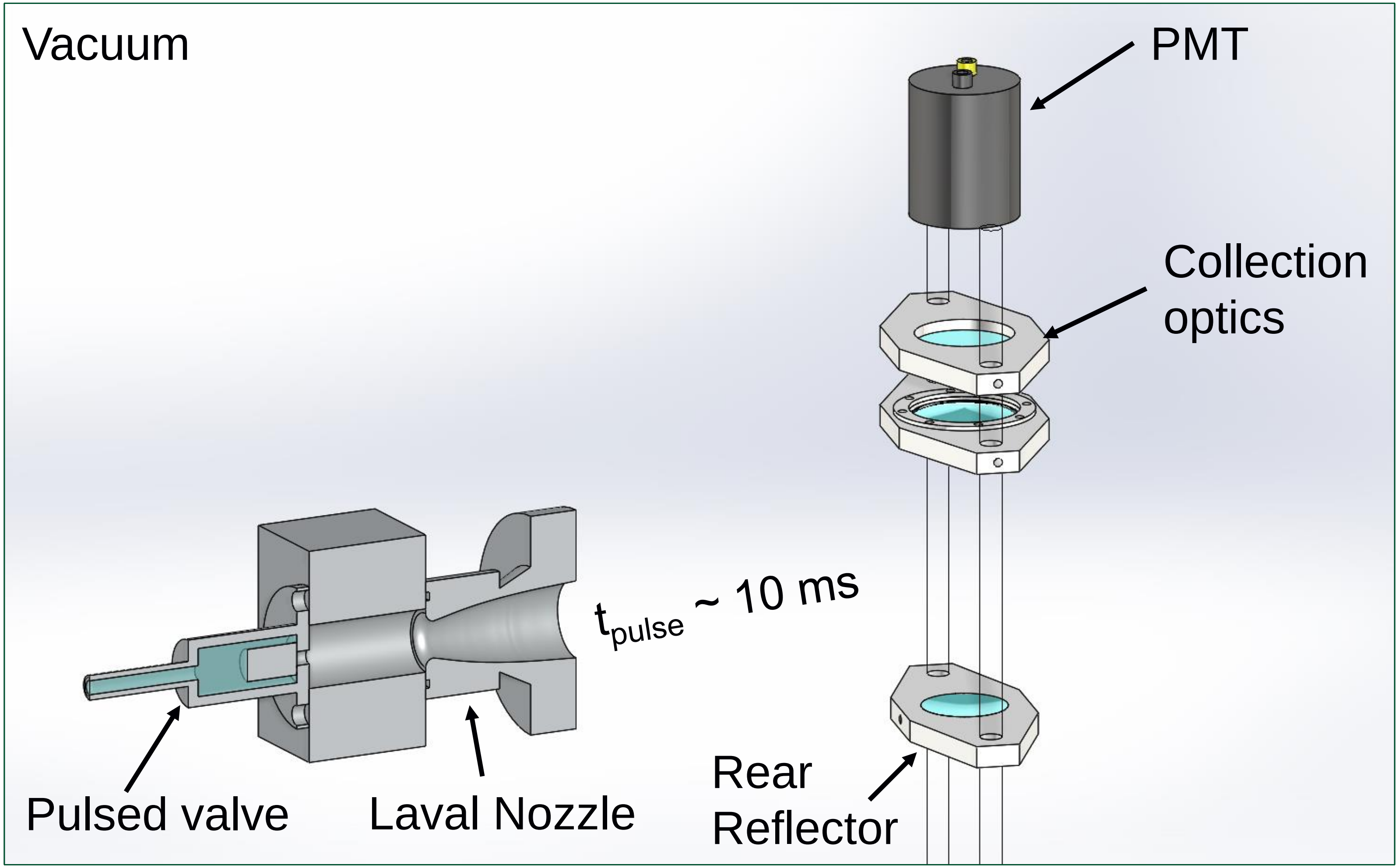
Method: Laval Nozzle and PLP-LIF



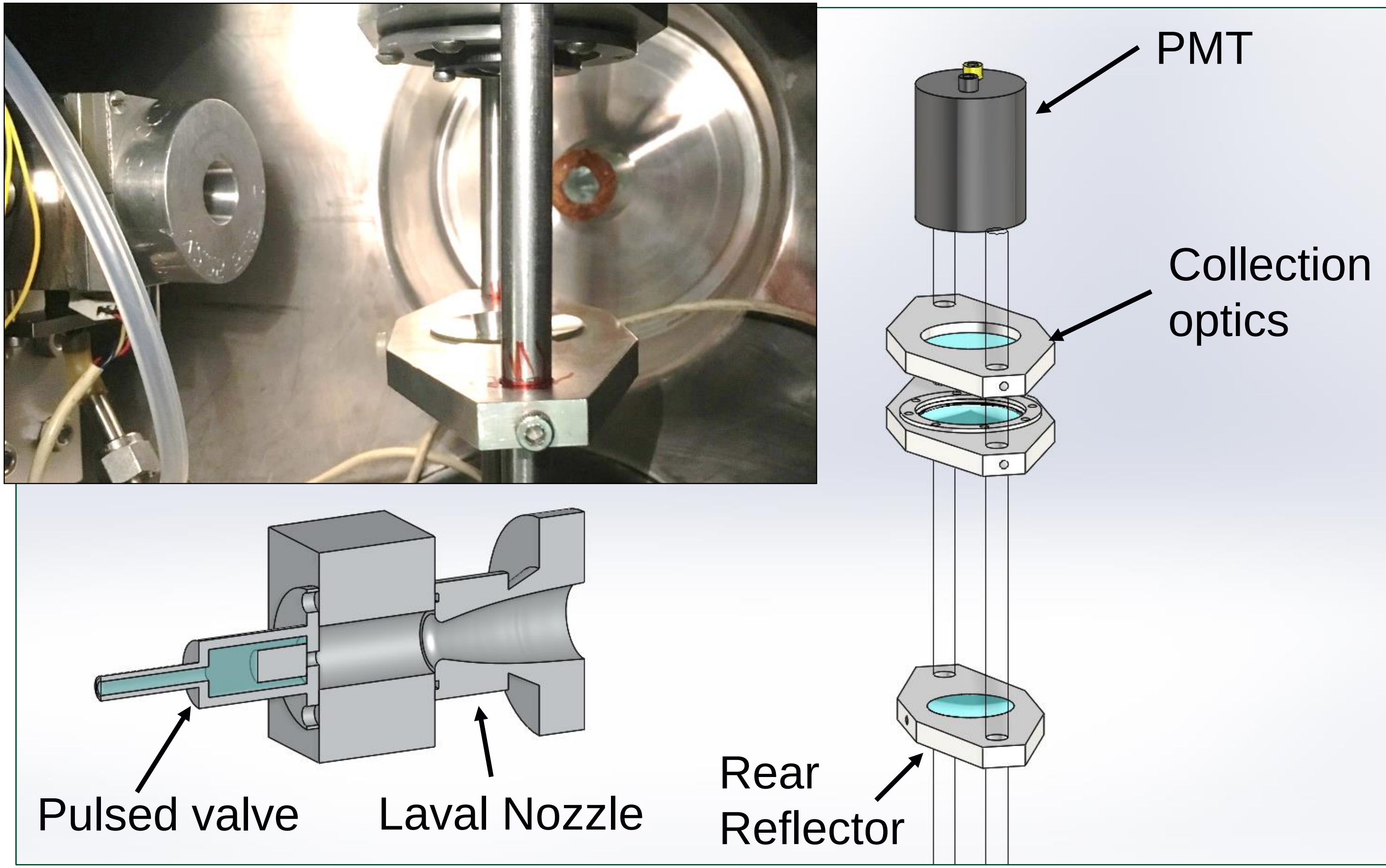
Method: Laval Nozzle and PLP-LIF



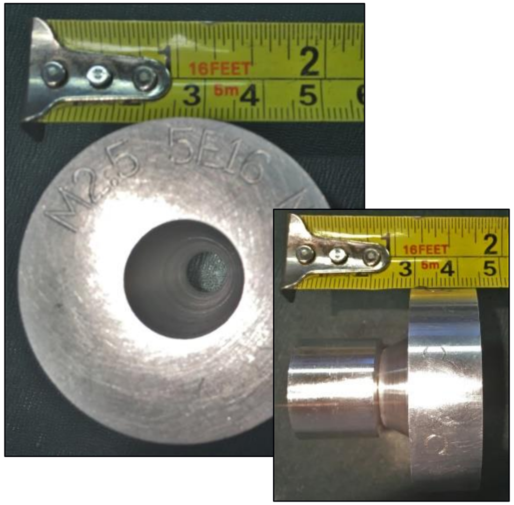
Method: Laval Nozzle and PLP-LIF

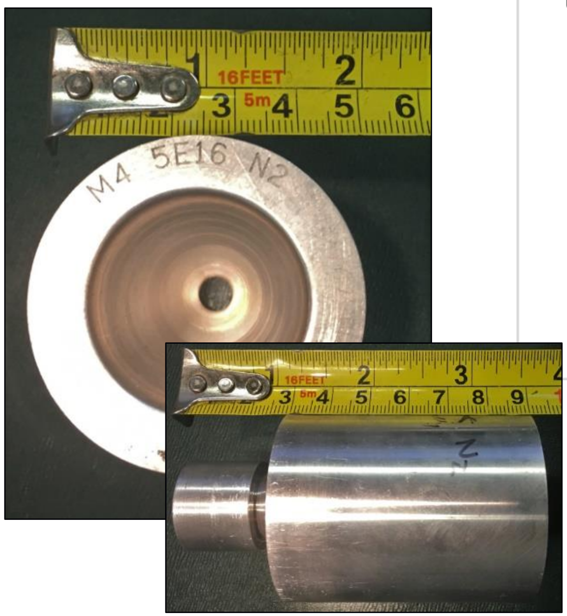


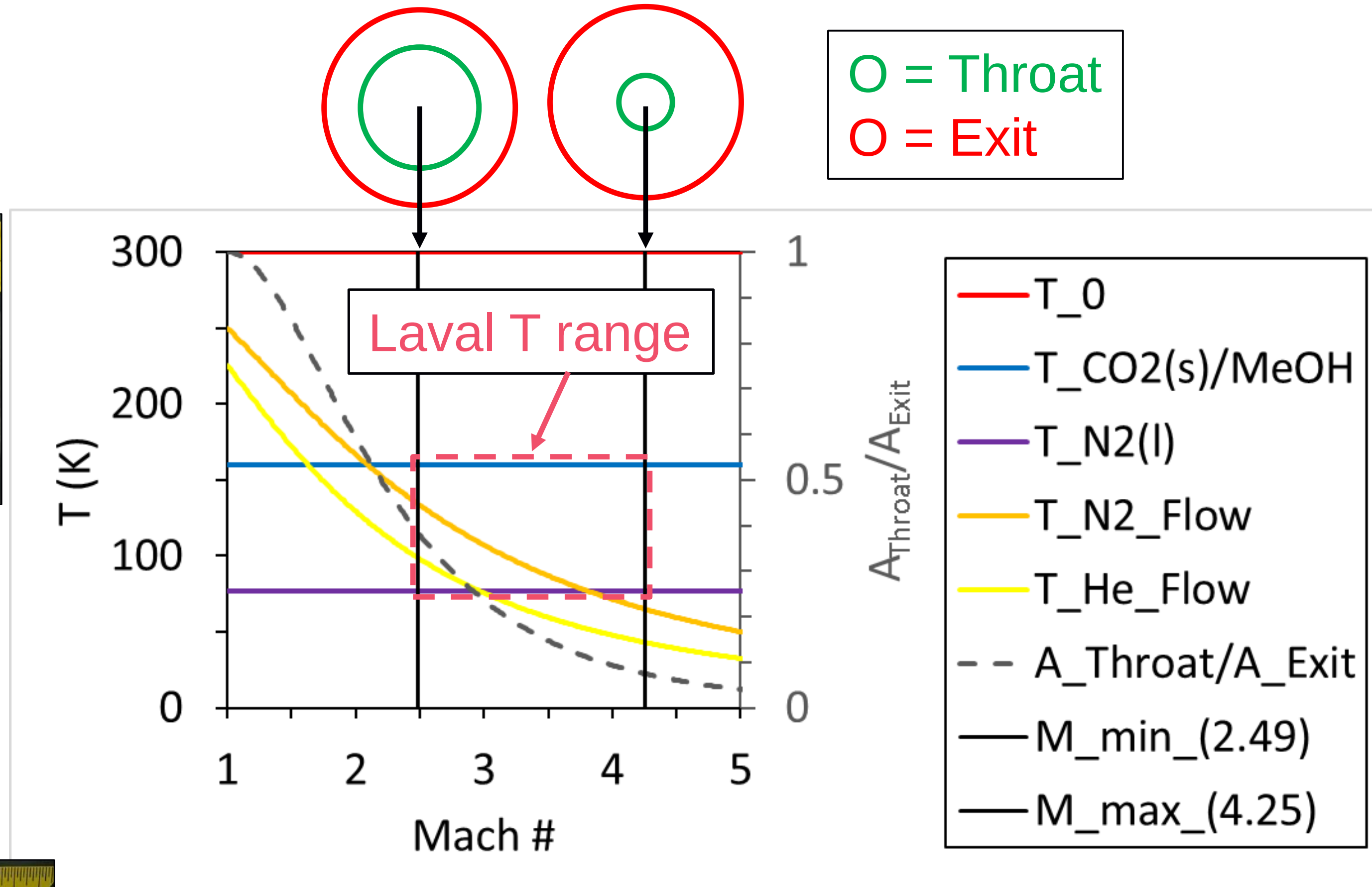
Method: Laval Nozzle and PLP-LIF



Method: Low T Through Laval Nozzle Design

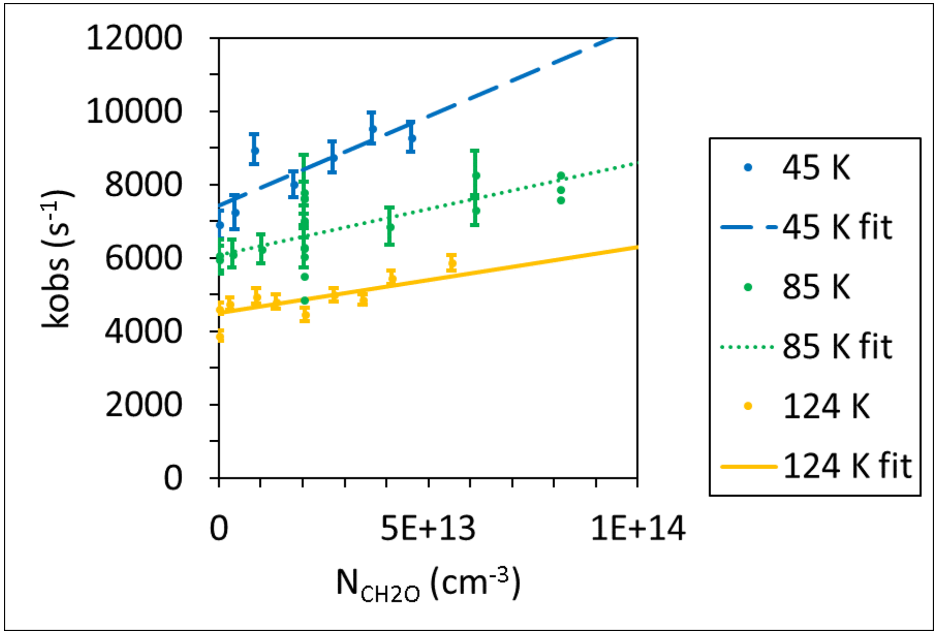


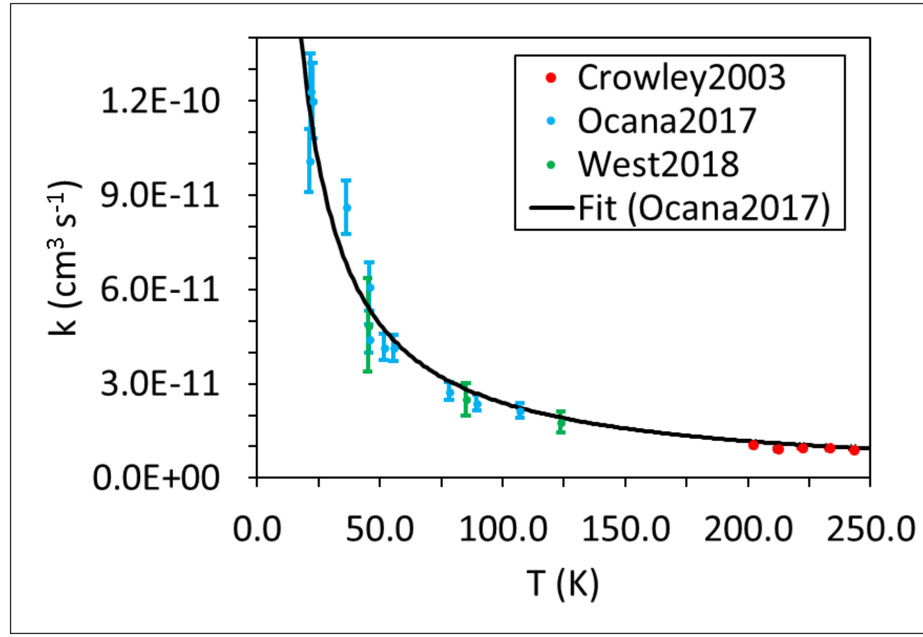




Switching between nozzles and bath gases allows for the generation of multiple temperatures.

OH + CH_2O Results

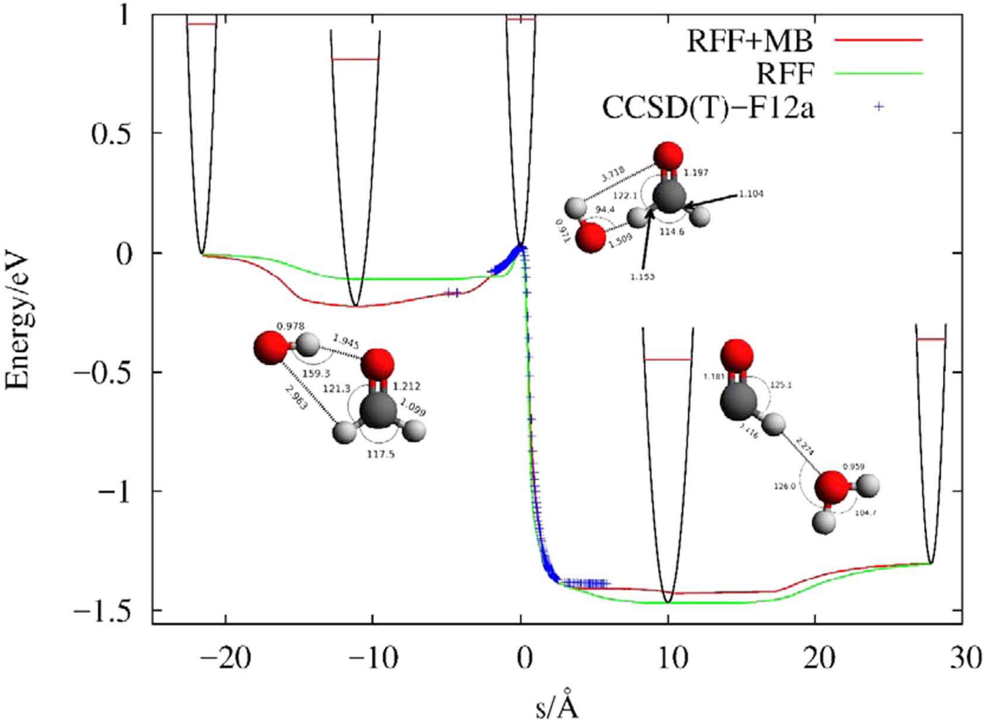




Unfortunately another group beat us to measuring OH + CH_2O in a Laval nozzle instrument, but we believe that we can add to this story as well as measure CH_2O + other co-reagents.

Ocana, A. J., et al., *Astrophys. J.* **2017,** *850* (1), 12.
Sivakumaran, V., et al., *Physical Chemistry Chemical Physics* **2003,** *5* (21), 4821-4827.

OH + CH_2O Reaction Mechanism



- A barrier (~2.4 kJ/mol) is present along the reaction pathway
- Inverse T dependence observed in QCT calculations
- long-range dipole–dipole interactions => formation of OH---CH_2O long-lived complex
- Reaction coordinate is strongly coupled to the orthogonal vibrations and can exchange enough energy to overcome the barrier

With this mechanism, can we put an upper limit on the reaction rate below 20 K?

Can we determine the rate of formation of the collision complex by measuring: OH(v=1,2,3) + CH_2O?

Ocana, A. J., et al., *Astrophys. J.* **2017,** *850* (1), 12.

Determining Upper Limit of OH---CH_2O Formation

$10[O_3] \lesssim [CH_2O]$ => Pseudo 1st Order

- $O_3 + hv_{UV} \rightarrow O(^1D) + H_2 \rightarrow$ OH(v = 0,1,2,3,4) + H (k_{rel})

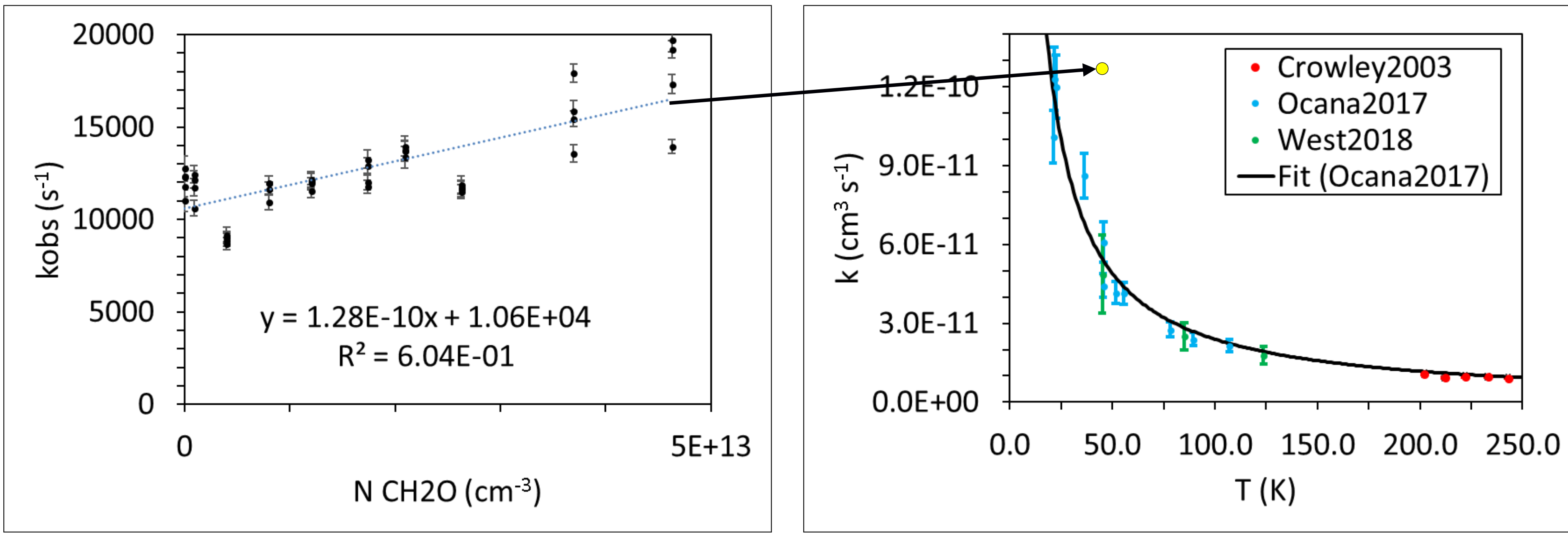
Probe

- OH(v*) + CH_2O → OH---CH_2O complex
- OH---CH_2O → OH(v) + CH_2O(v*, J*) ($k_{Coll.}$)
  → H_2O + CHO (k_{rxn})
- OH(v*) → Loss (Diffusion, Quenching, Etc.)

(k_{obs})

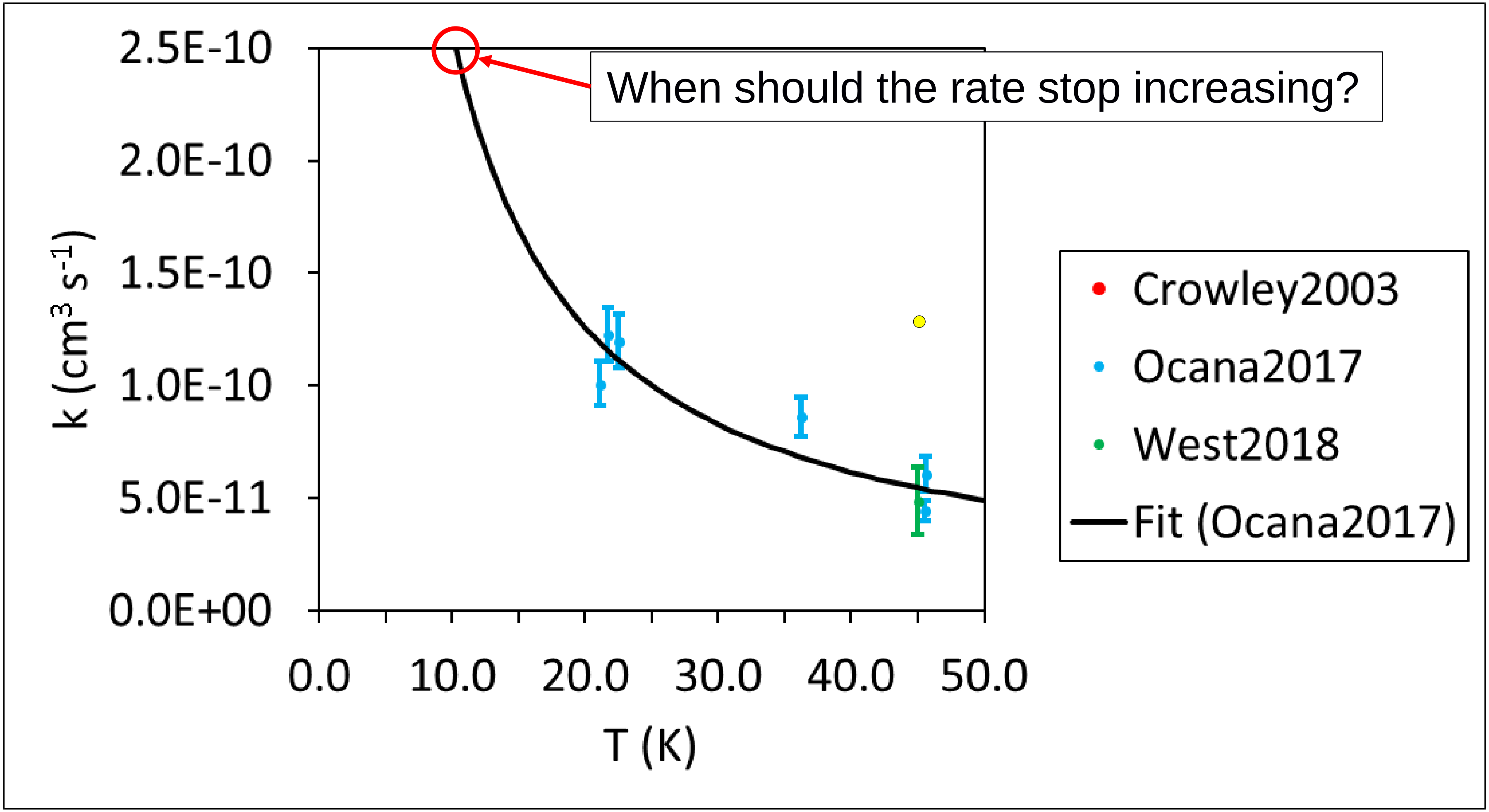
The slope of the plot of loss rate of OH(v*) vs [CH_2O] yields the rate of formation of the OH---CH_2O complex.

Preliminary 45 K OH(v = 3) + CH_2O Loss Rate Data



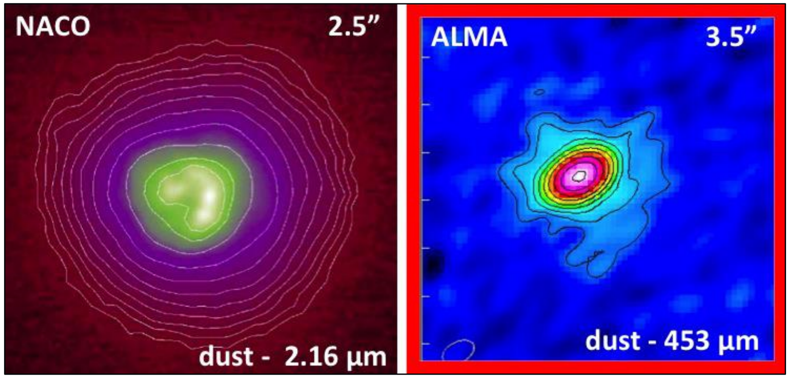
More measurements are needed at different temperatures in order to fit the temperature dependence of the rate of formation of the OH---CH_2O complex.

Predicting T < 20 K behavior

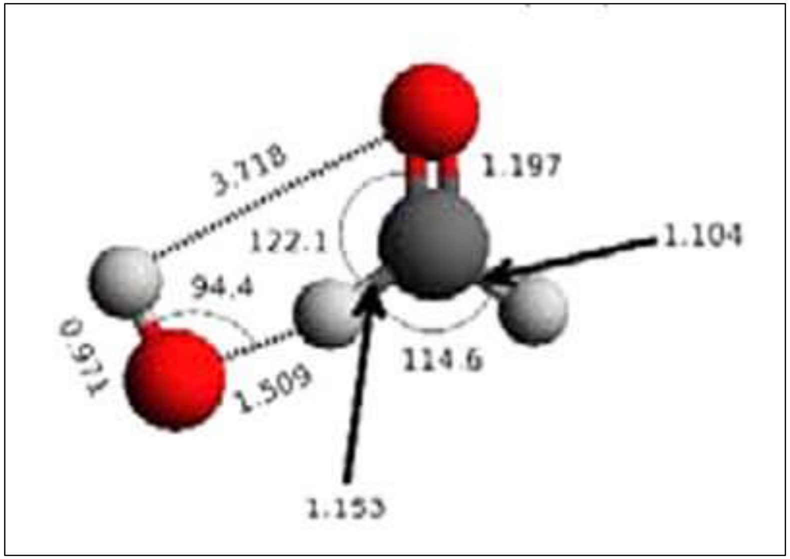


Conclusions

- Measurements of many key low temperatures gas phase reaction rate coefficients are still needed for accurate astrophysical/ astrochemical modeling.



- Sharp increases in reaction rate coefficients at low temperatures are difficult to predict. These sharp increases often involve the formation of a long-lived complex that allows for an otherwise improbable/infrequent process to occur.



Thank you!

- This research was supported by the ERC Consolidator Grant 2016-2021 (PI: Professor Leen Decin, University of Leuven)

- Heard group