

High-Temperature Non-LTE and LTE Cavity Ringdown Spectroscopy using SMAUG experimental setup

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Astronomical observations

Experimental data

Analysis & interpretation of
the radiative properties of
hot gaseous media

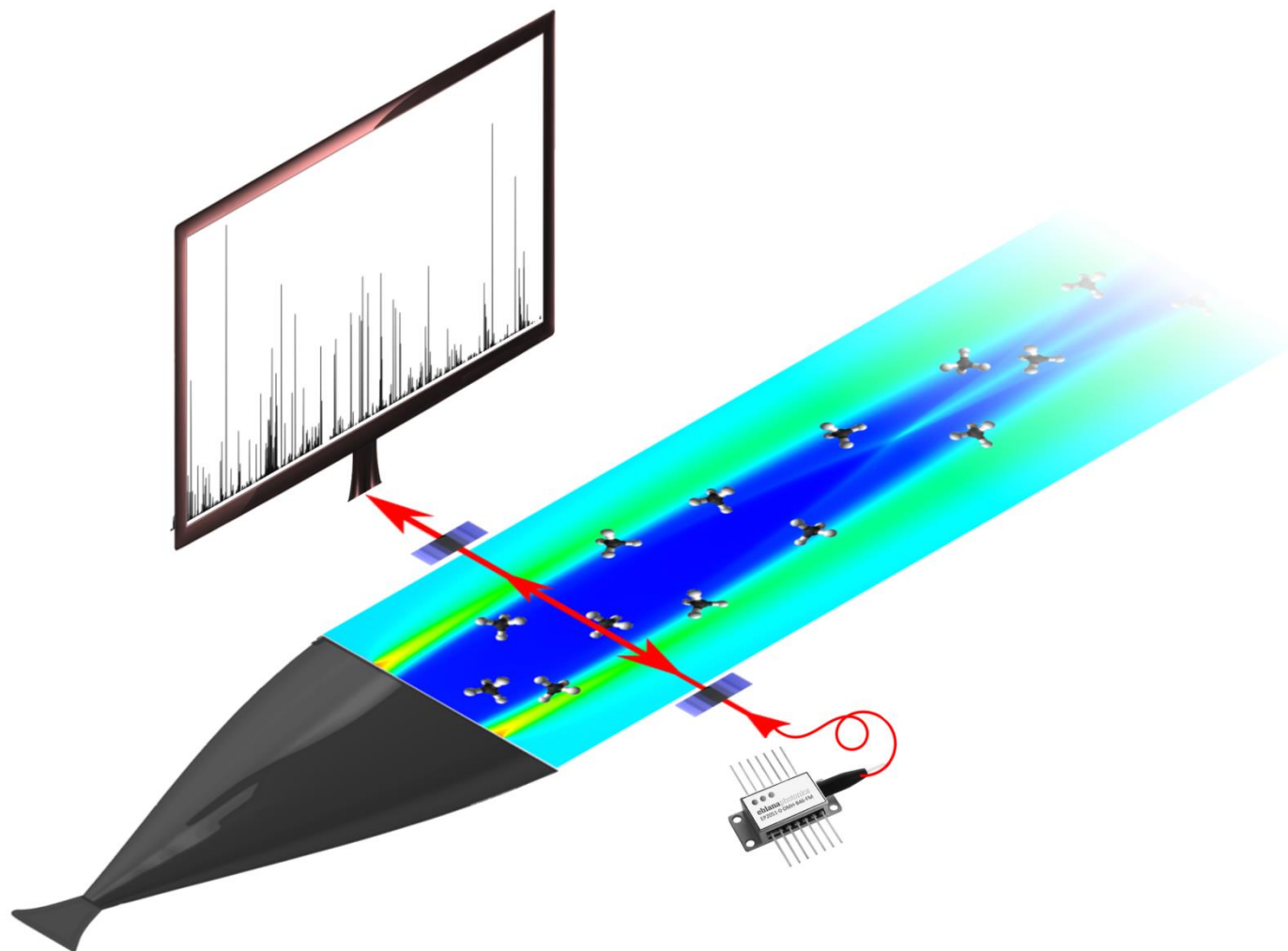
Theoretical
molecular
model

Atmospheric
modelling

e-PYTHEAS project

SMAUG

Spectroscopy of Molecules Accelerated in Uniform Gas flows



SMAUG

Spectroscopy of Molecules Accelerated in Uniform Gas flows

Mission: record high temperature, high-resolution IR spectral data

- ❖ small hydrocarbons (CH_4 , C_2H_2 , C_2H_4 , C_2H_6)
- ❖ in controlled conditions

Challenges: HT spectra

- ❖ create the hot environment
- ❖ overcrowded for polyatomic molecules
- ❖ line-by-line analysis very difficult

Our approach: two complementary working regimes

- ❖ hypersonic jet CRDS → non-LTE spectra
- ❖ post-shock CRDS → LTE spectra

Essence of SMAUG

Adiabatic expansion:

$$c_P T_0 = c_P T + \frac{1}{2} u^2$$

non-LTE:

$$\begin{aligned} T &\rightarrow 0 \\ u &\rightarrow u_{lim} \end{aligned}$$

LTE:

$$\begin{aligned} T &\rightarrow T_0 \\ u &\rightarrow 0 \end{aligned}$$

Hypersonic jet CRDS: non-LTE spectra

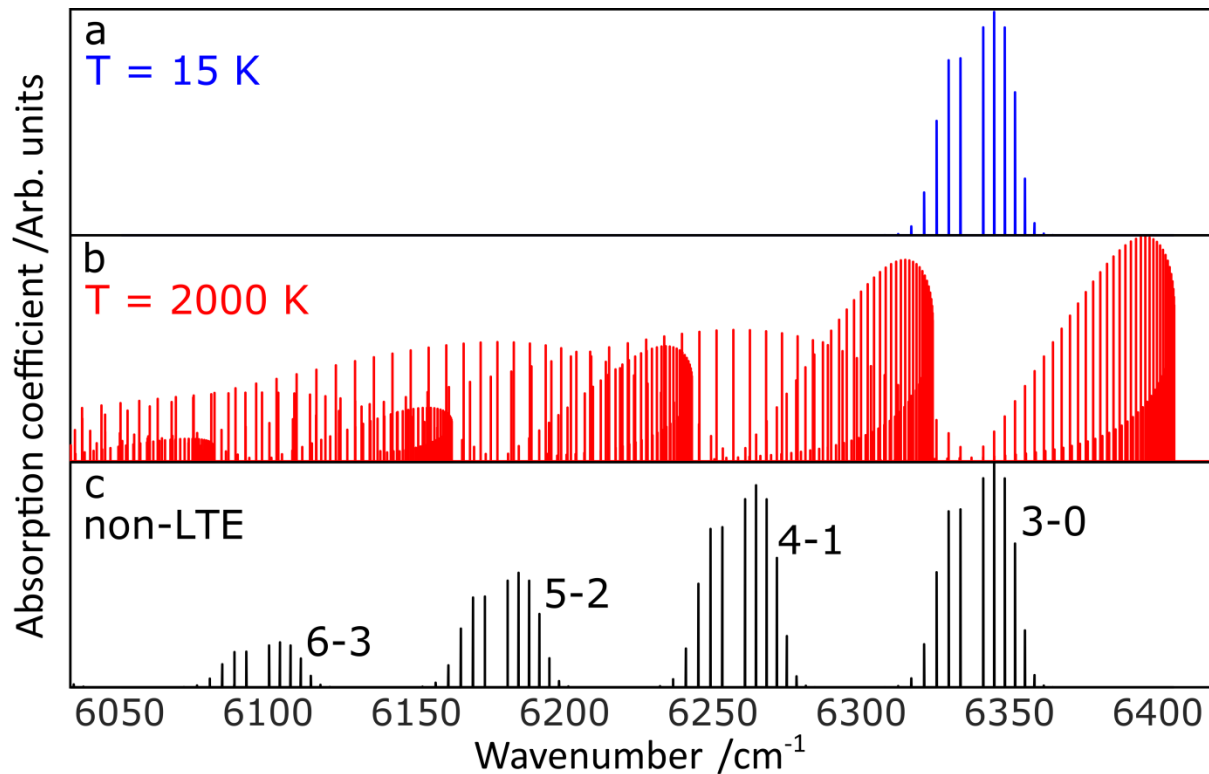
- few molecular collisions
 - low energy transfer V-T & V-R
 - decoupled internal degrees of freedom

Hypersonic jet CRDS: non-LTE spectra

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 - decoupled internal degrees of freedom
- high vibrational levels thermally populated
- high- J rotational levels thermally de-populated

Hypersonic jet CRDS: non-LTE spectra

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simplified rotational structure

Hypersonic jet CRDS: non-LTE spectra

non-LTE:

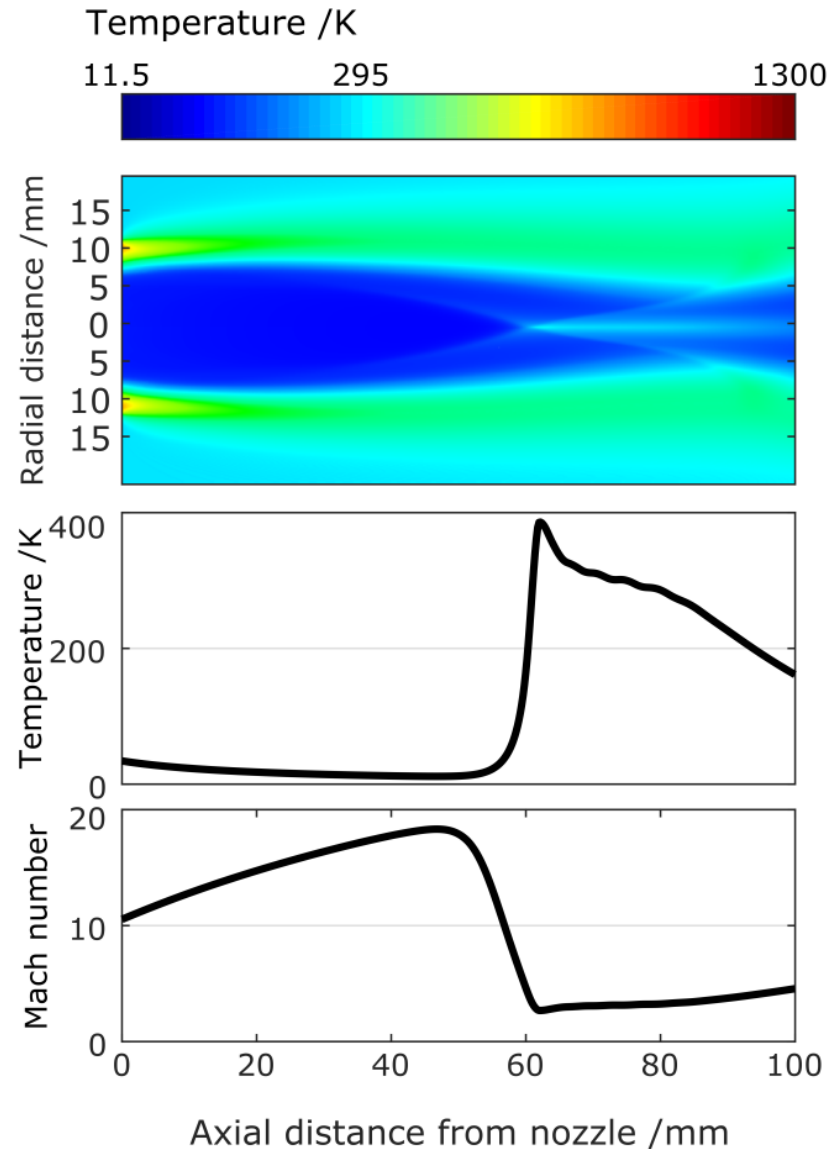
$$T \rightarrow 0$$

$$u \rightarrow u_{lim}$$

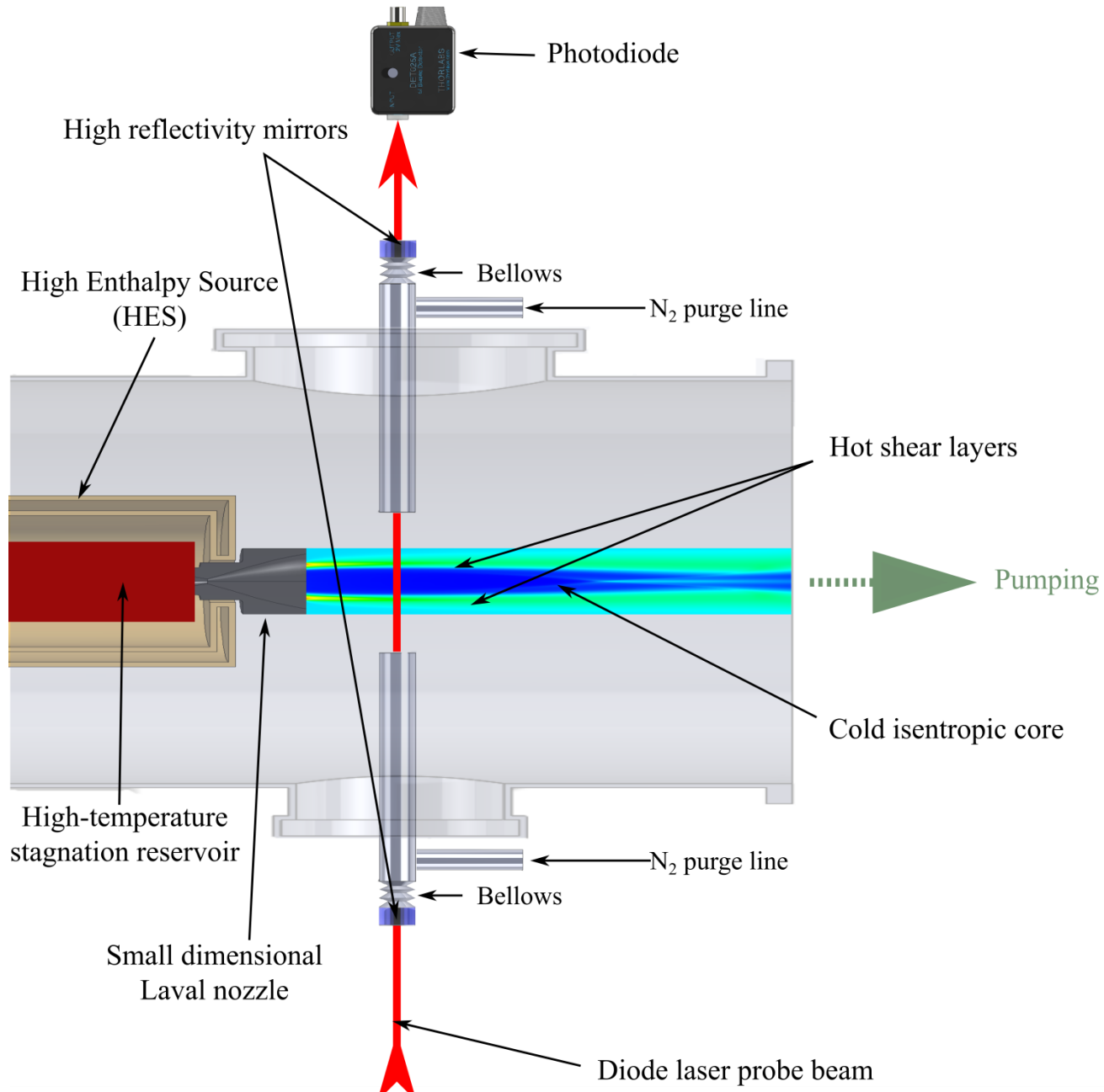
Simulation:

$$T_0 = 1300 \text{ K} \rightarrow T_{min} = 11.5 \text{ K}$$

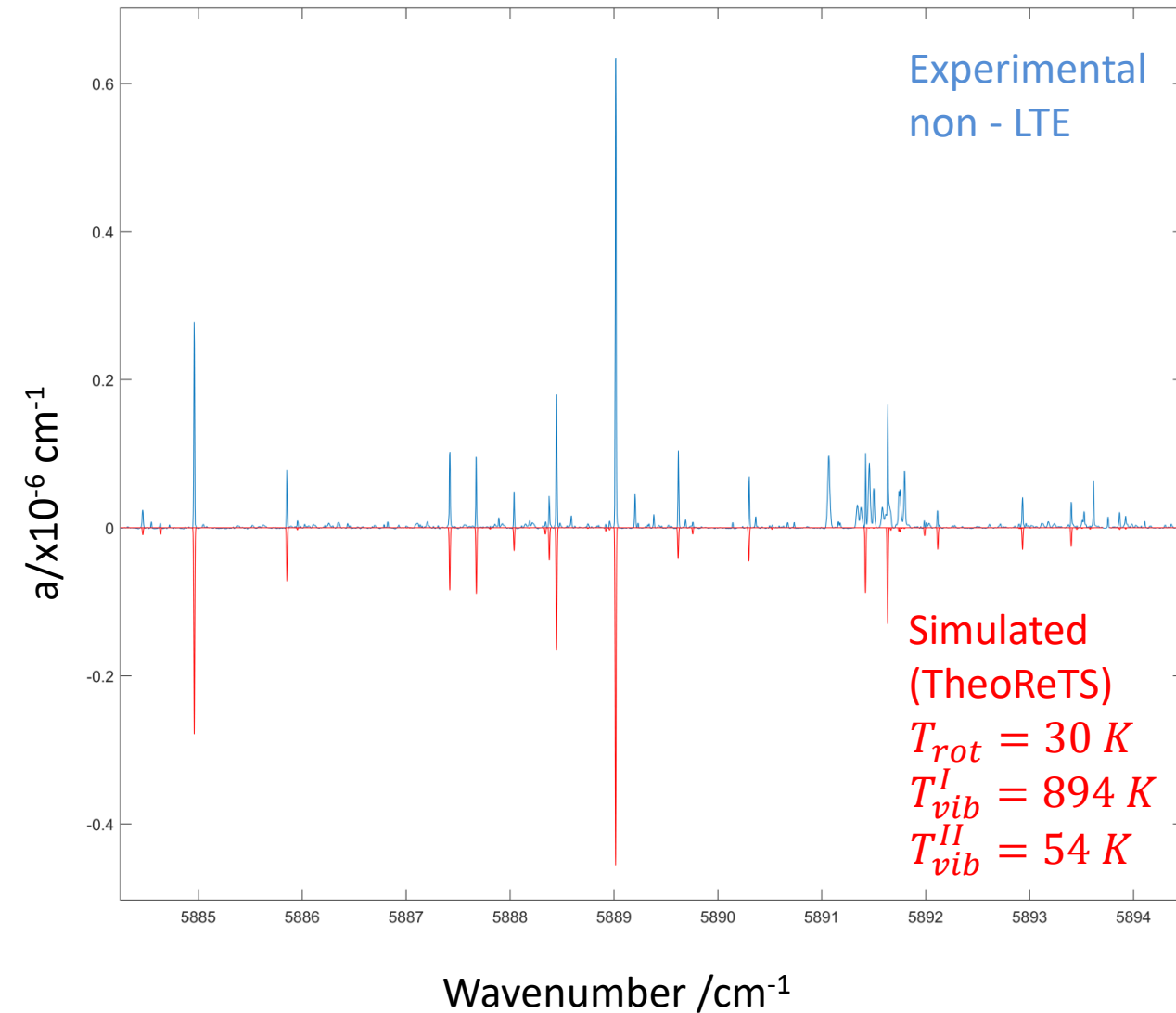
$$u \rightarrow u_{lim} = 1230 \text{ m.s}^{-1}$$



SMAUG Experimental setup



Hypersonic jet CRDS: non-LTE spectra



CH₄ non-LTE conditions:

$$T_{rot} = 30 (1) K$$

$$T_{vib}^I = 894 (47) K$$

$$T_{vib}^{II} = 54 (4) K$$

Hypersonic jet CRDS: non-LTE spectra



Found the position of the **hot bands**
Identify low- J lines



Missing the **high- J rotational lines**

Post-shock CRDS: LTE spectra

How to probe hot gases in SMAUG?

- the graphite rod is not accessible for CRDS

Adiabatic expansion:

$$c_P T_0 = c_P T + \frac{1}{2} u^2$$

Post-shock CRDS: LTE spectra

How to probe hot gases in SMAUG?

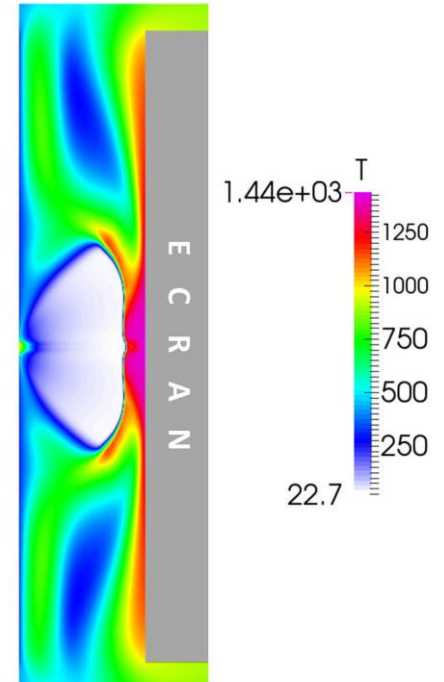
- the graphite rod is not accessible for CRDS

Adiabatic expansion:

$$c_P T_0 = c_P T + \frac{1}{2} u^2$$

Shockwave:

- thin region in a flow: few mean free paths thick
- supersonic \rightarrow subsonic flow
- TOTAL energy is conserved
- velocity \rightarrow zero
- temperature, pressure & density rapidly increase

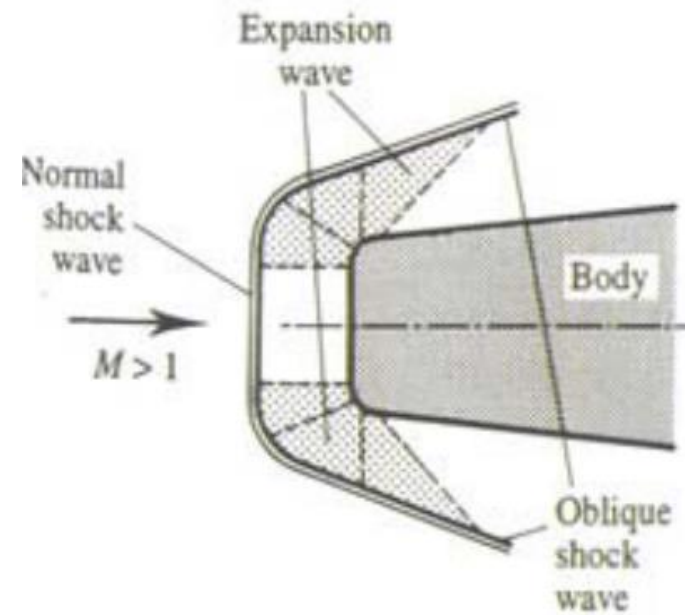


Post-shock CRDS: LTE spectra

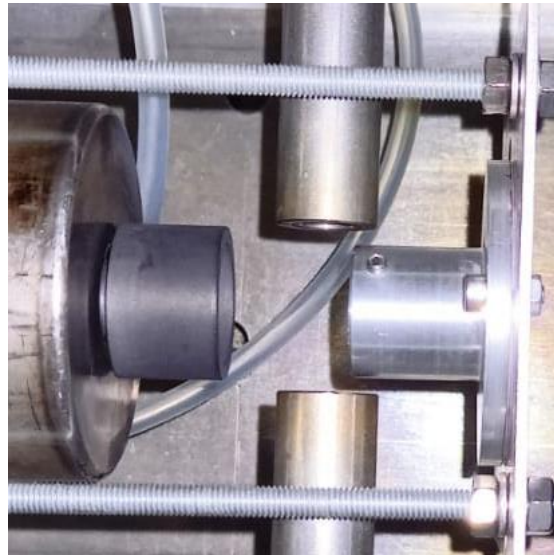
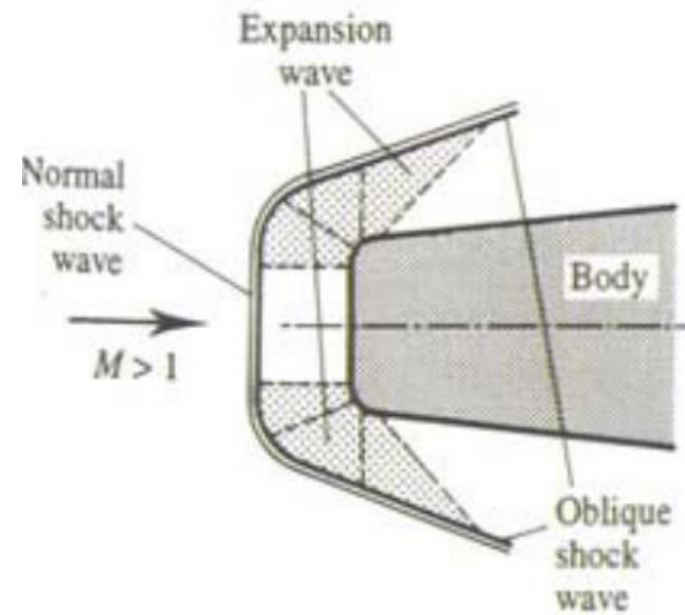
LTE:

$$T \rightarrow T_0$$

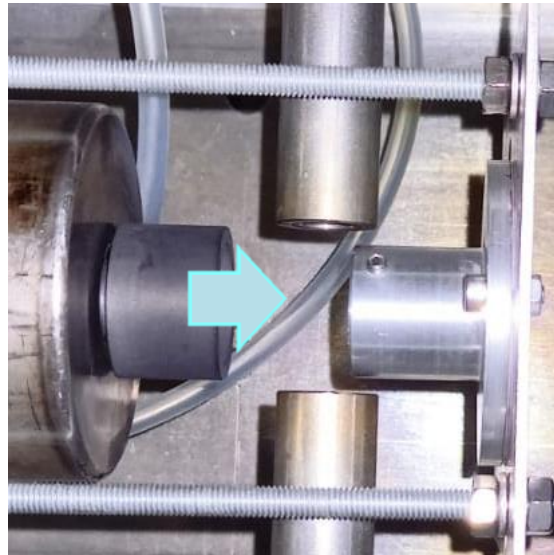
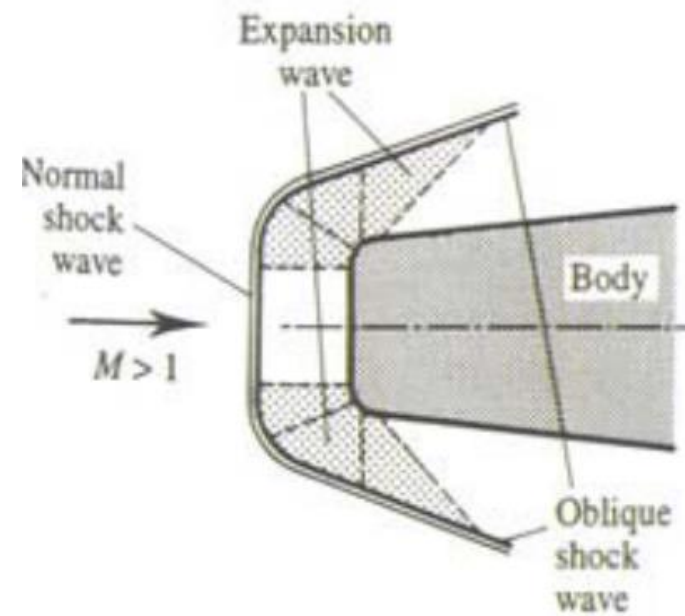
$$u \rightarrow 0$$



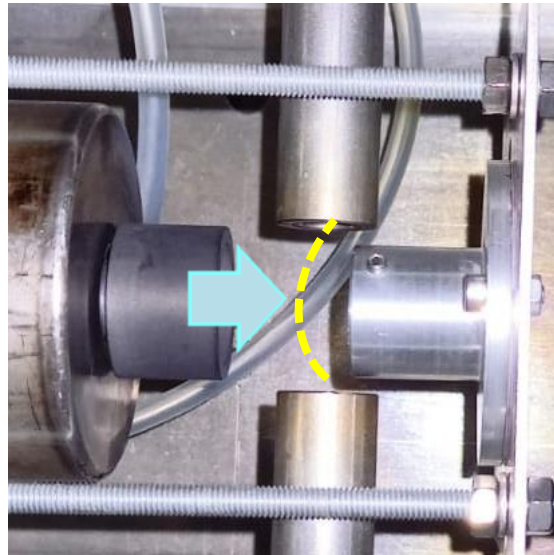
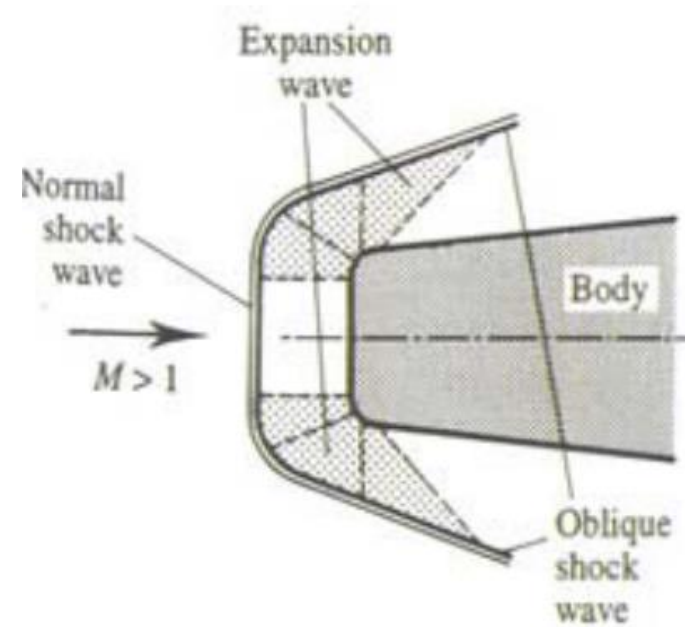
Post-shock CRDS: LTE spectra



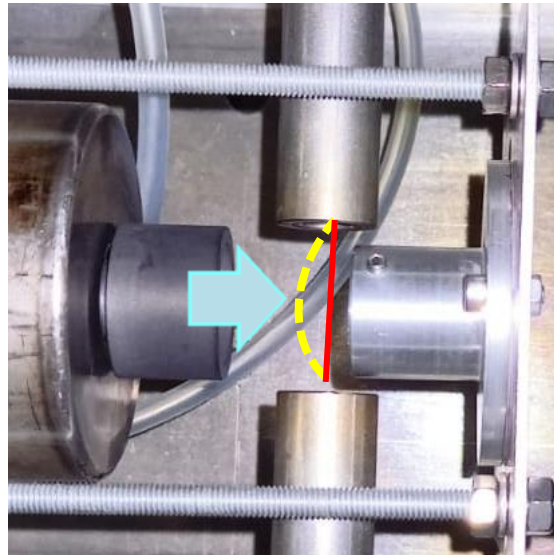
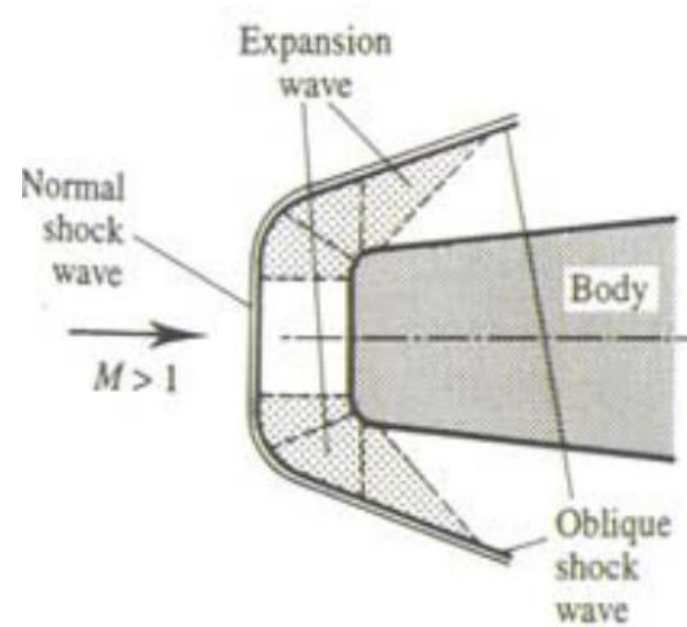
Post-shock CRDS: LTE spectra



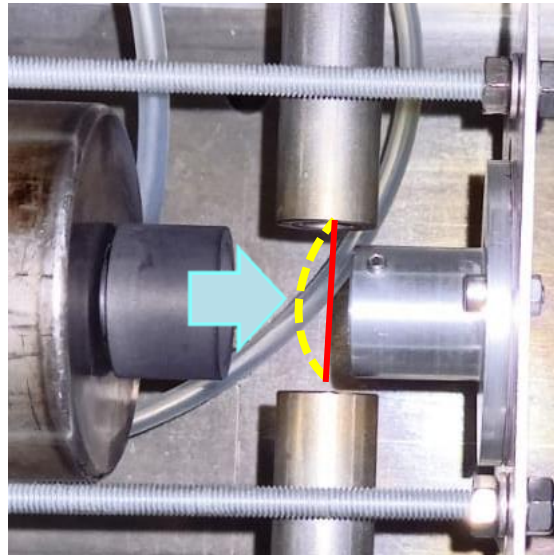
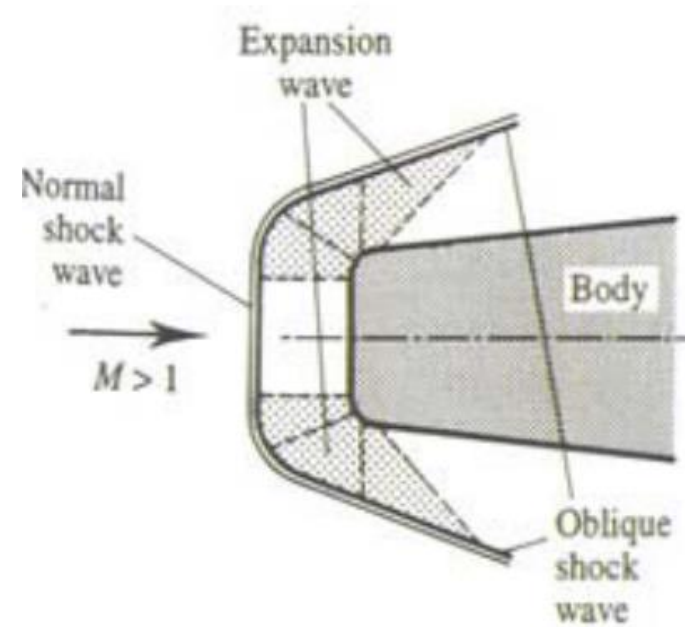
Post-shock CRDS: LTE spectra



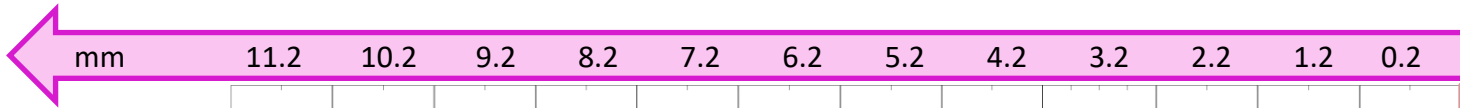
Post-shock CRDS: LTE spectra



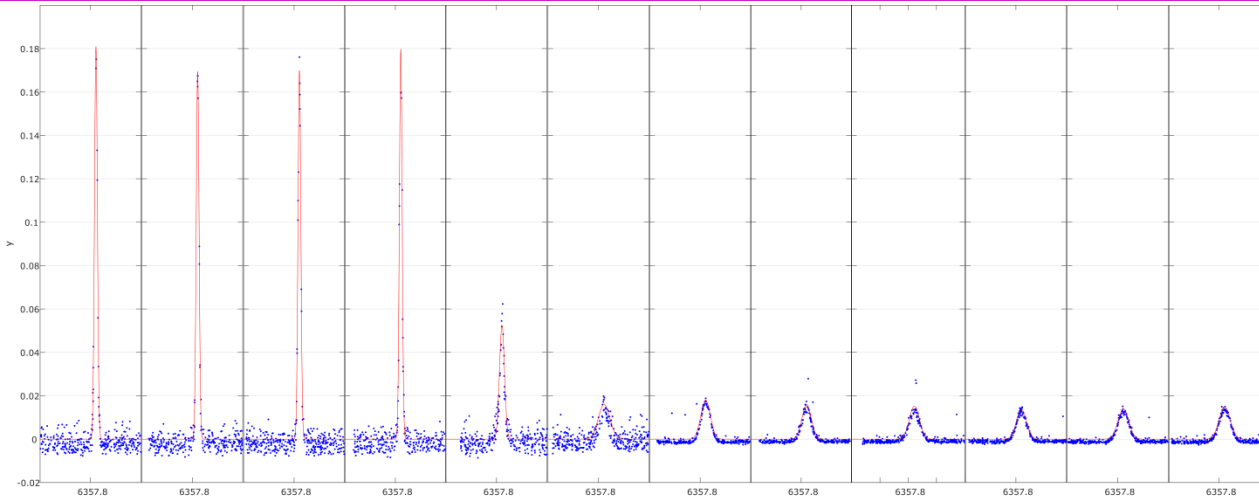
Post-shock CRDS: LTE spectra



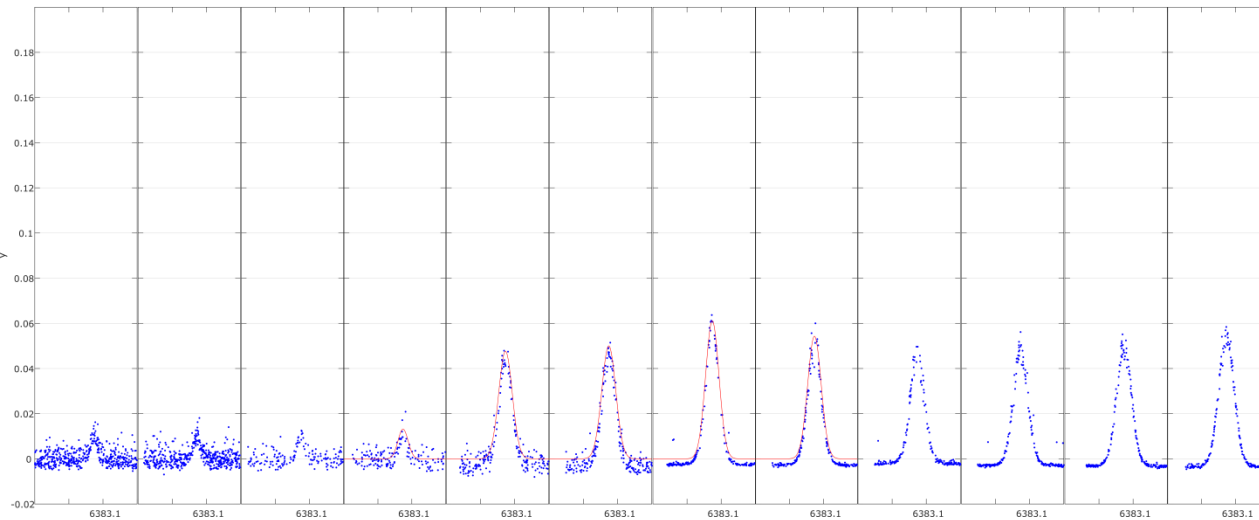
Study the shockwave with CO



R1 transition

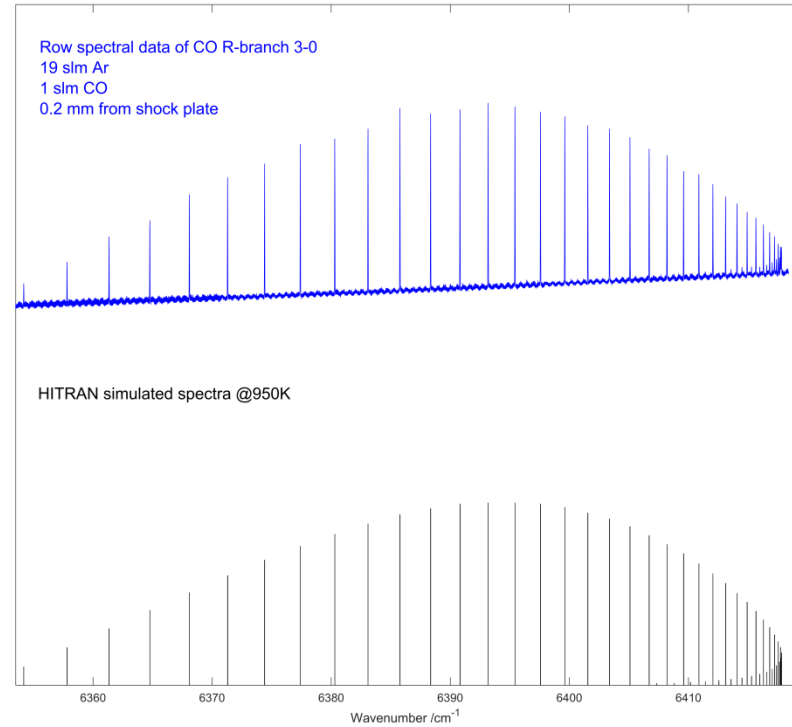
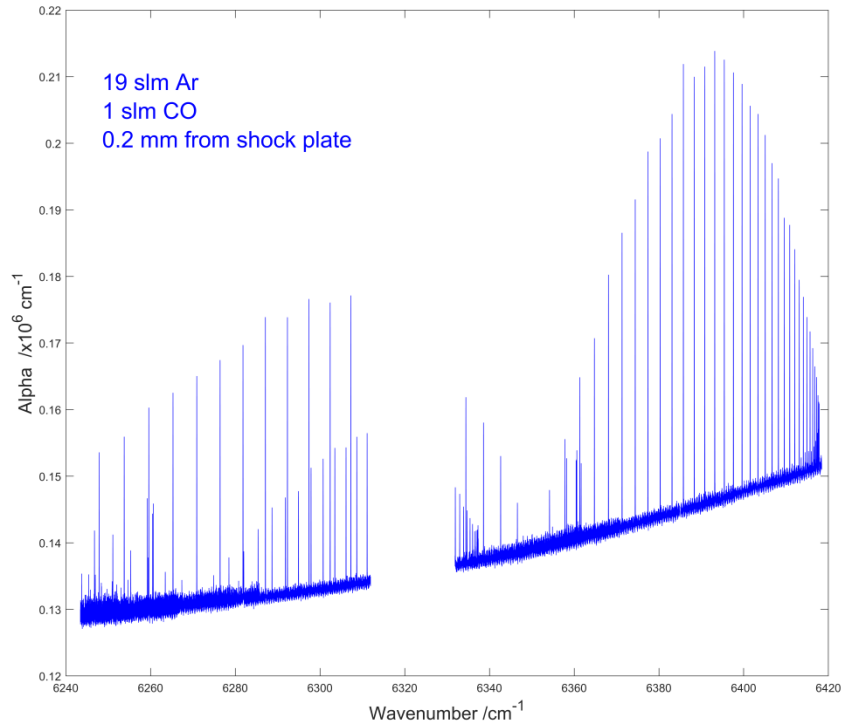


R9 transition



Body to generate shockwave

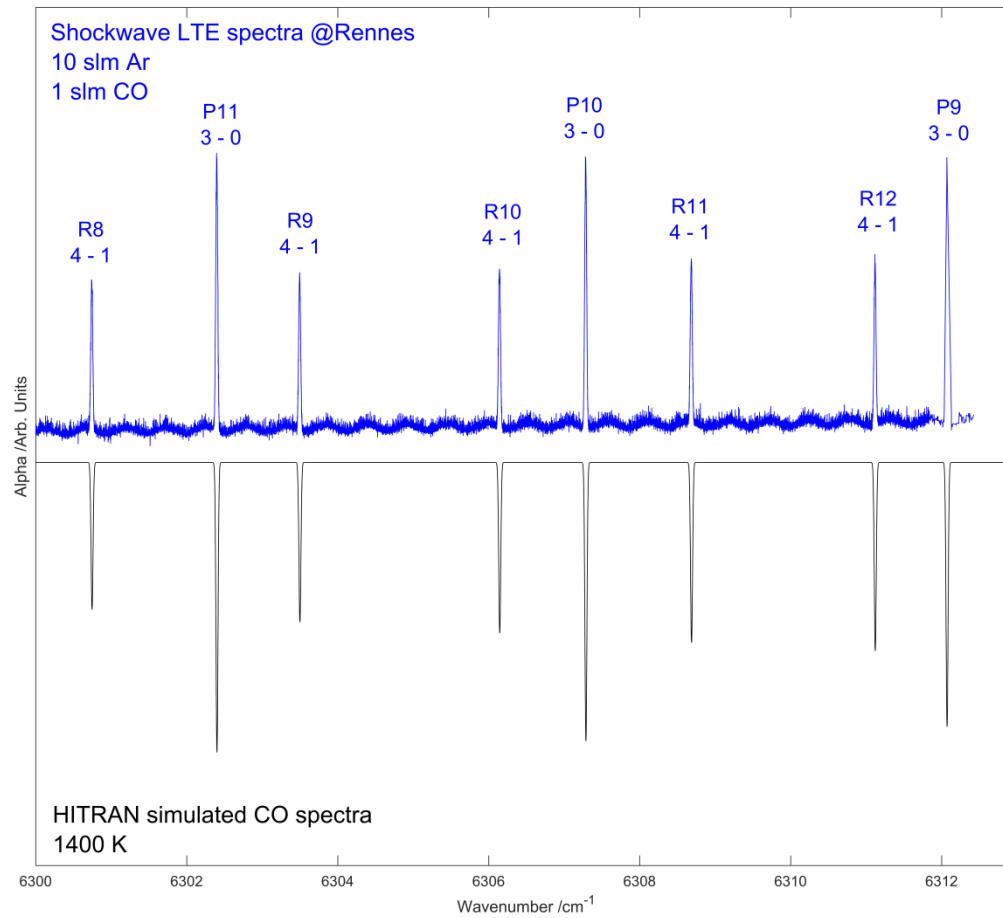
Determining the temperature with CO



1.7 km relative absorption length

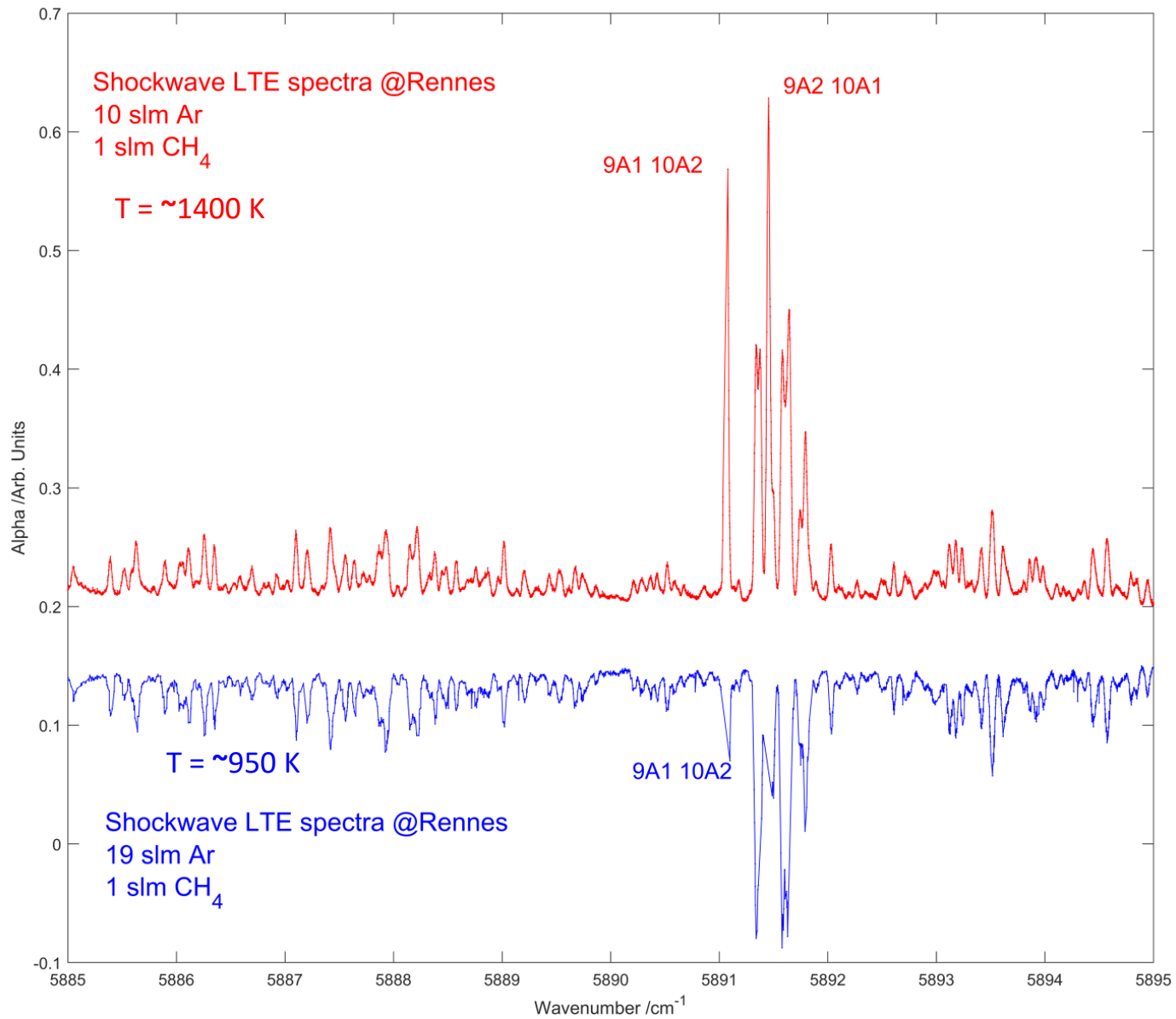
$T = \sim 950 \text{ K}$

Determining the temperature with CO

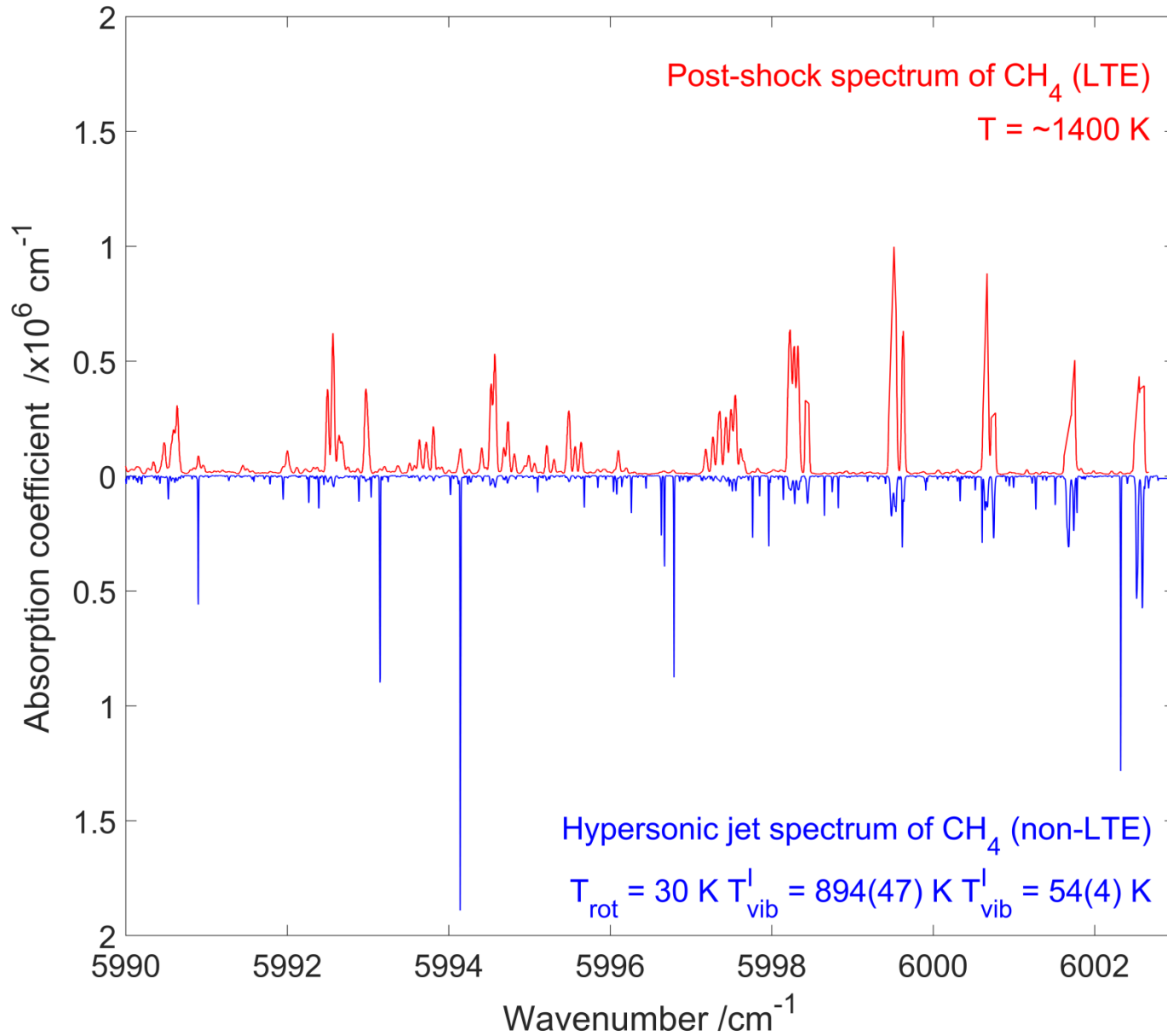


T = ~1400 K

Hot LTE spectra of CH₄



LTE vs non-LTE



Conclusions and perspectives

- SMAUG can operate according to two complementary working regimes: **non-LTE** and **LTE conditions**
- SMAUG was first applied to the spectroscopy of CH₄
 - other small hydrocarbons
- Collaboration with GSMA for the validation of the TheoReTS database

Limitations of the current experimental system:

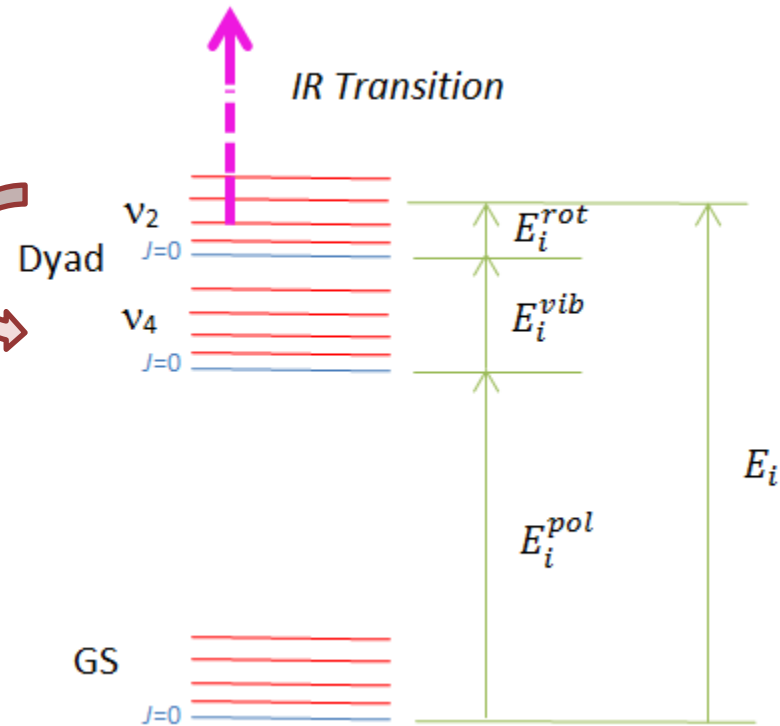
- $(T_0)_{\max} \sim 1400\text{K}$
- graphite heating element → limited variety of molecules can be studied

Temperature extraction – T_{vib}^I & T_{vib}^{II}

“interpolyad”
relaxation
 T_{vib}^I



“intrapolyad”
relaxation
 T_{vib}^{II}



$$\bar{\sigma}_{ij}(T_{rot}, T_{vib}^I, T_{vib}^{II}) = \bar{\sigma}_{ij}(T_0) \frac{Q_0(T_0)}{Q_{rot}(T_{rot}) \times Q_{vib}(T_{vib}^I) \times Q_{vib}(T_{vib}^{II})} \times \exp \left[\frac{E_i}{kT_0} - \frac{1}{k} \left(\frac{E_i^{pol}}{T_{vib}^I} + \frac{E_i^{vib}}{T_{vib}^{II}} + \frac{E_i^{rot}}{T_{rot}} \right) \right]$$

TheoReTS
database

Total Internal Partition Sum
(TIPS)

Prof. Robert Gamache