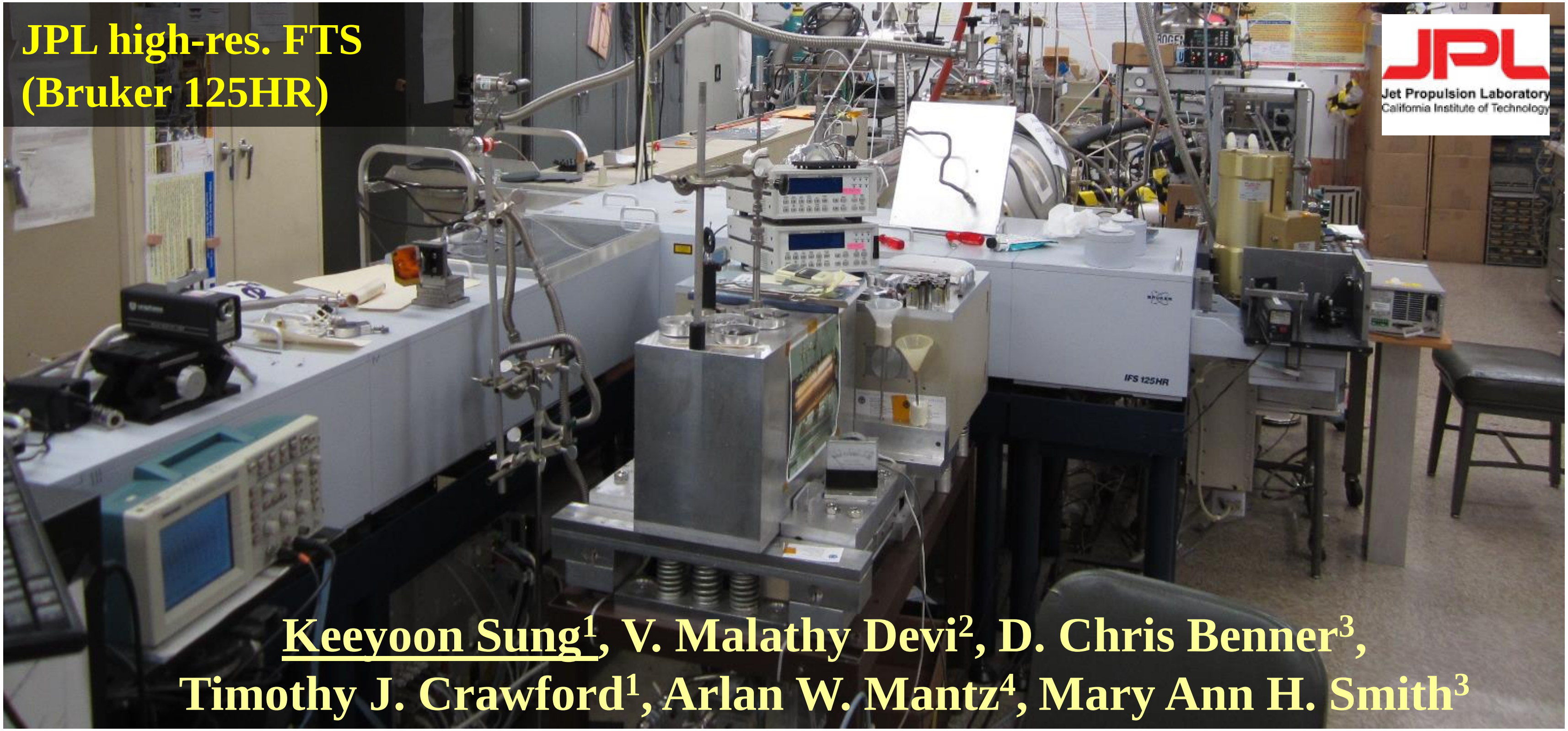
Progress in the measurement on temperature-dependence of H_2-broadening of cold and hot CH_4



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Motivation and Objectives

❖ Significance of H_2 pressure broadening

- H_2 : dominant atmospheric constituent in the giant gaseous bodies
- Cold Jovian planets, Hot Jupiter exoplanets, low mass brown dwarfs
- Key spectroscopic parameter in atmospheric opacity calculations
- Characterization of exoplanets

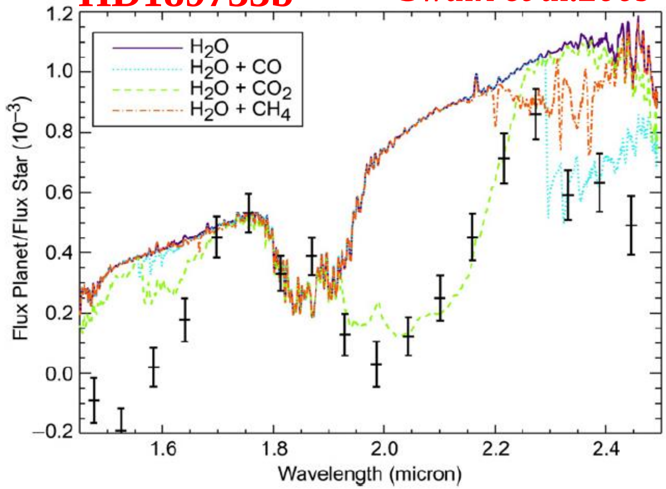
❖ Measurements of line shape parameters

- Broad temperature range: 80 – 400 K
- Study of their temperature dependence
- Check the validity of the power law for width
- Provide constraints for theoretical model for line widths
- T-dep. up to ~2000 K will be covered by the model calculations

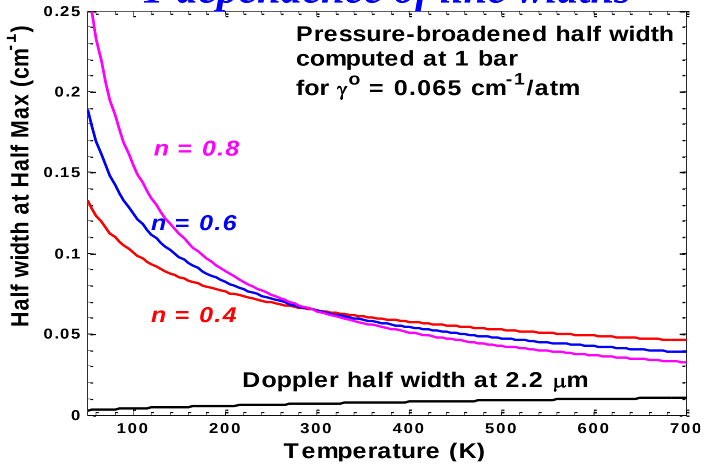
❖ In support of various NASA missions

TEXES, SOFIA, HST, JWST, etc.

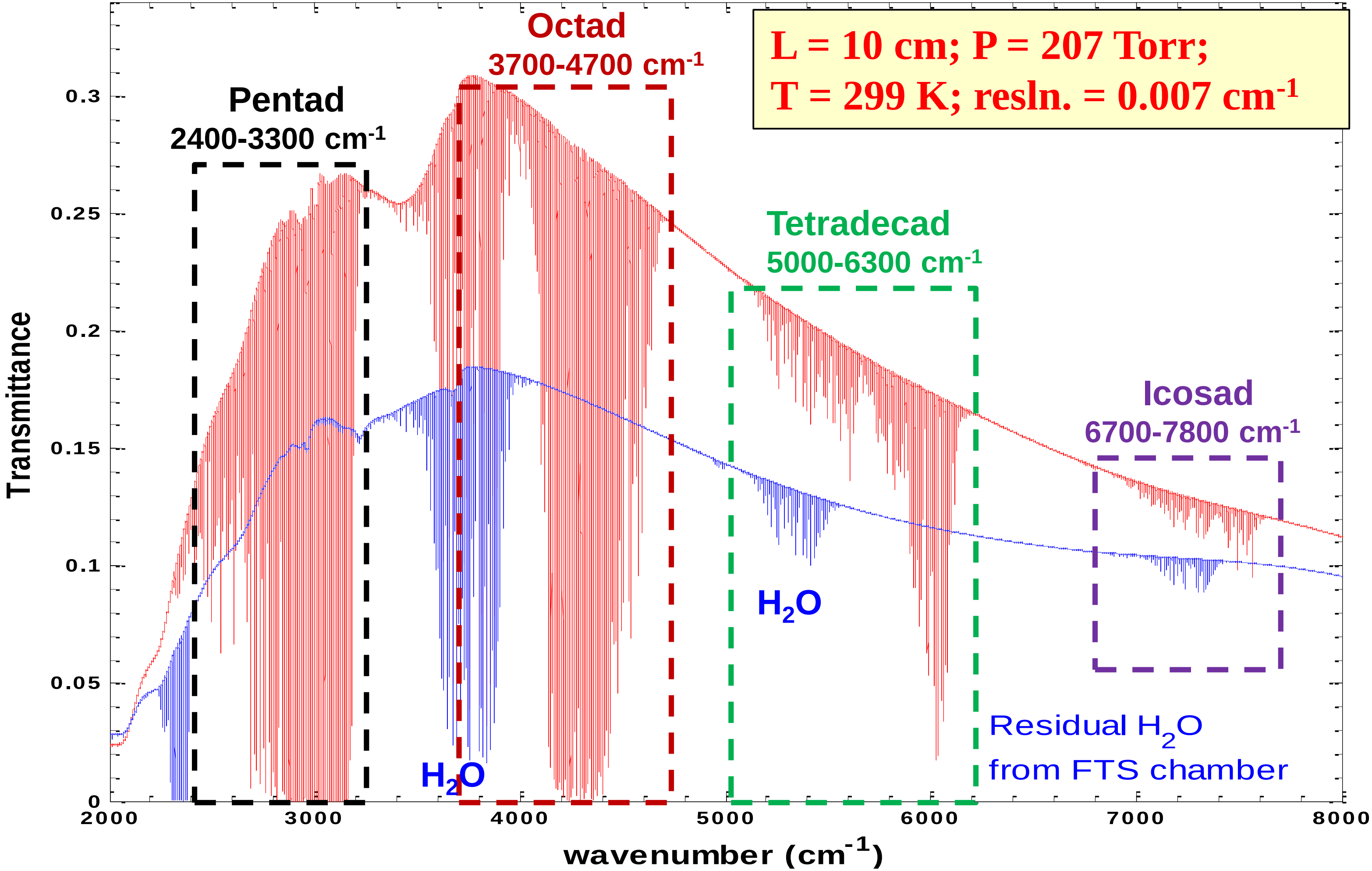
HD189733b *Swain et al.2009*



T-dependence of line widths



Overview of Infrared CH_4 spectrum

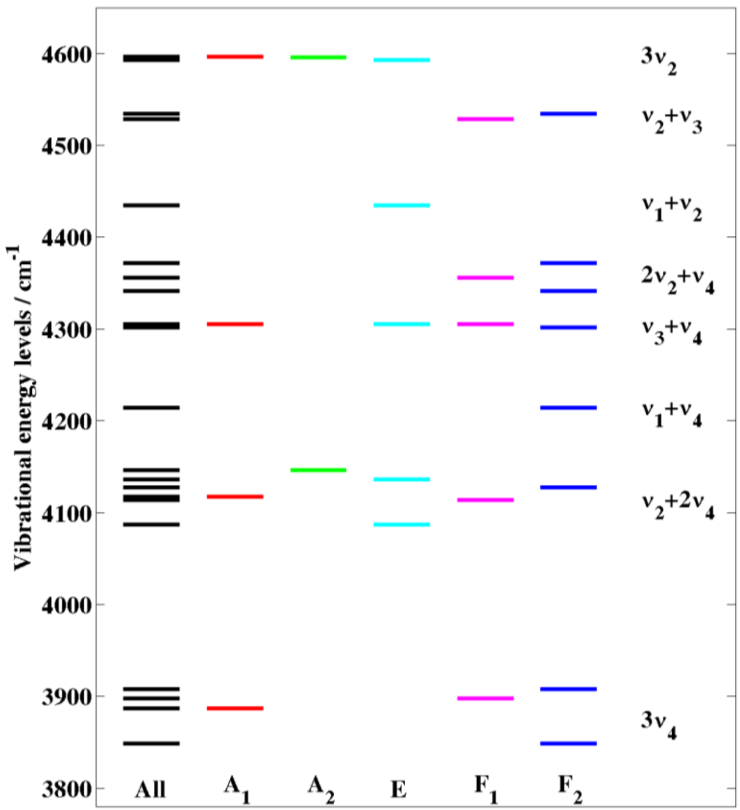


Methane Polyads

❑ Vibrational States

Polyads, P_n and name		Range (cm^{-1})	# vib levels	*# sub-levels*
P_0	GS	< 200	1	1
P_1	Dyad	1200 – 1700	2	2
P_2	Pentad	2400 – 3200	5	9
P_3	Octad	3700 – 4700	8	24
P_4	Tetradecad	5000 – 6200	14	60
P_5	Icosad	6500 – 7700	20	134

❑ Octad vibrational states for $^{13}CH_4$

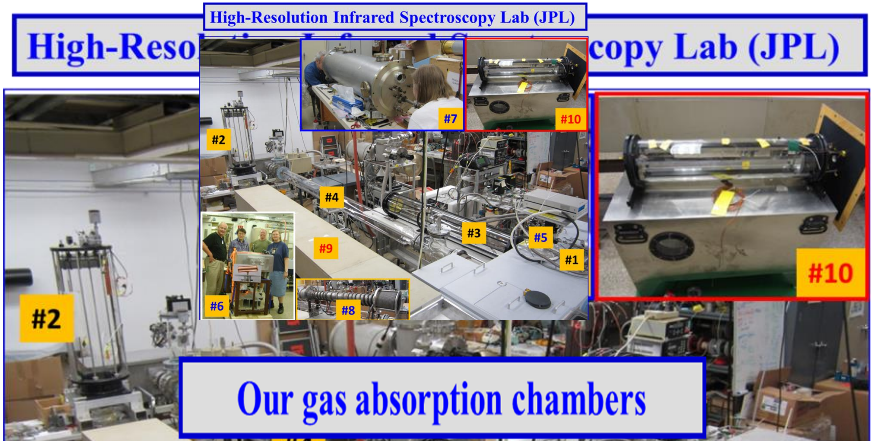


Brown et al. (MJ14) ISMS 2015

❑ Some characteristics

- Eight different vibrational bands
- Most have multiple components of vib. sym.species. (*i.e.*, ***A*, *E*, *F***)
- Only F_2 is inherently IR active.
- All others borrow intensities through interactions.
- ***A*** tends to borrow less while F_1 and ***E*** borrows more.

Data acquisition at JPL



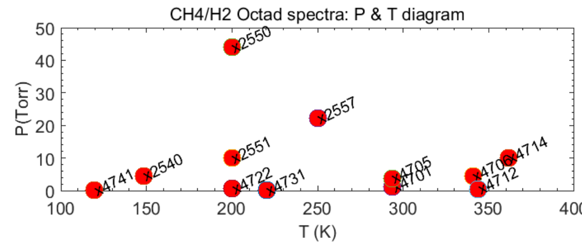
Our gas absorption chambers

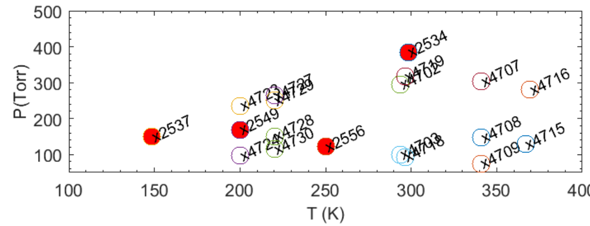
Cells	path lengths (in meters)	Temperatures	Wavelength
1	0.02, 0.06, 0.15, 0.20, 0.25 (fixed path)	T ~ 296 K (room)	2 – 50 μm
2	6.6 – 32.5 multipass	T ~ 296 K (room)	0.7 – 50 μm
3	20 – 180 multipass	T ~ 296 K (room)	0.7 – 1.6 μm
4	3.9 m + (0.76 or 0.35 m) *two color* (fixed)	T ~ 296 K (room)	IR *and* MW
5	0.204 (fixed)	80 < T < 297 K	1.6 – 15 μm
6	21 – Herriott (fixed)	30 < T < 250 K	1.6 – 8 μm
7	4 – 52 multipass	20 < T < 296 K	15 – 500 μm
8	0.8 (fixed)	180 < T < 296 K	0.7 – 18 μm
9	Extra vacuum chamber (using Emission port)	230 < T < (420 K)	0.7 – 15 μm
10	Heatable multipass 2.2 – 22 m (*to be installed*)	296 < T < 420 K	0.7 – 8 μm

❑Experimental conditions for CH_4+H_2 spectra

Gas sample	$^{12}CH_4$
Spectral region	4100 – 4750 cm^{-1}
Resolution(B)	0.0044 cm^{-1}
Total pressures	130 – 300 Torr
Path lengths	20.4 cm – 22 m
mixing ratios	0.002 - 1.000
Temperatures	80 – 370 K

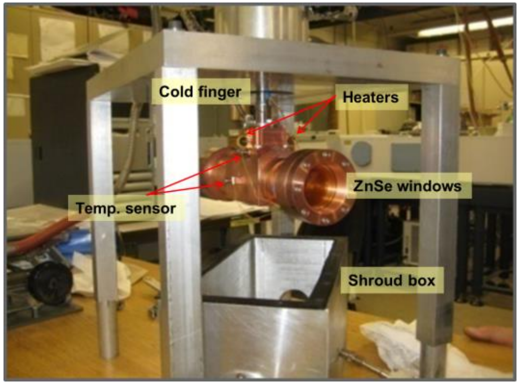
❑ P&T distribution of the observed spectra





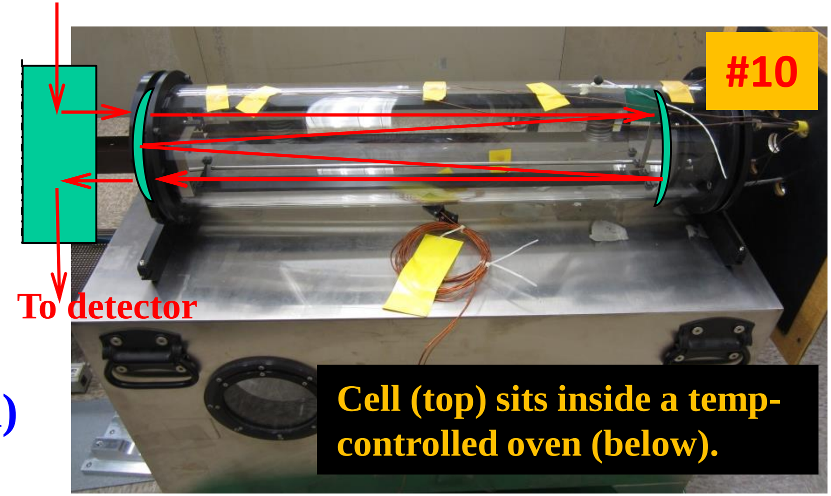
Two cold and one hot gas cells for this study

(1) Short cold cell (20.38 cm)



(2) Cryogenic Herriott cell (20.94 m, fixed)

(3) White-type hot cell (2.2 – 22 m)



❑ **Three gas absorption cells**

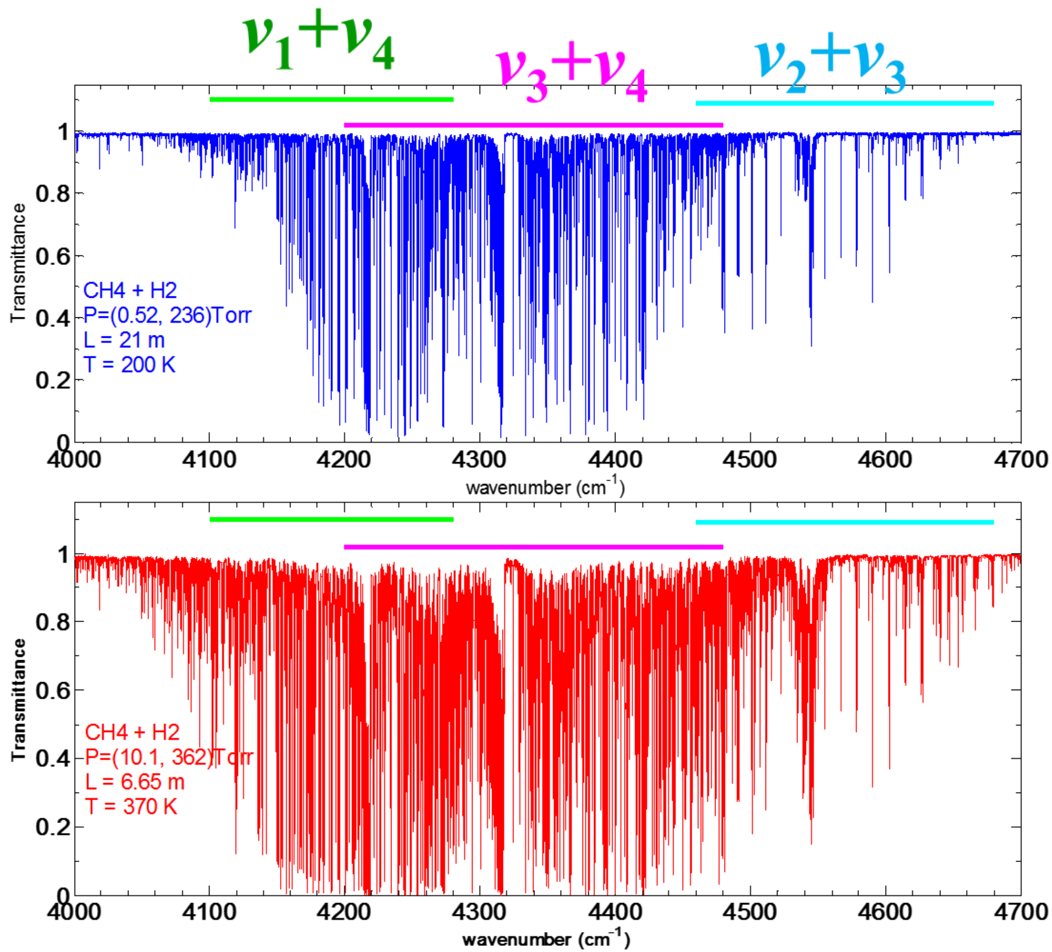
- **Variable pathlength, 0.2038 cm - 22 m**
- **Temperature, 80 – 500 K**
- **Spectral coverage, 0.7 – 8 μm**
- **Transfer optics designed & developed**
  - **Beam intercept and guiding**
  - **Heat-insulated stainless steel tubing**

Three bands observed in this work

◙ CH_4+H_2 mixture spectra
4000 – 4700 cm^{-1}.
200 – 370 K

◙ Three bands:
$\nu_1+\nu_4$ (*strong*),
$\nu_3+\nu_4$ (*strong*),
$\nu_2+\nu_3$ (*weak*)

◙ Atmospheric H_2O & CO_2 overlap with $\nu_1+\nu_4$.



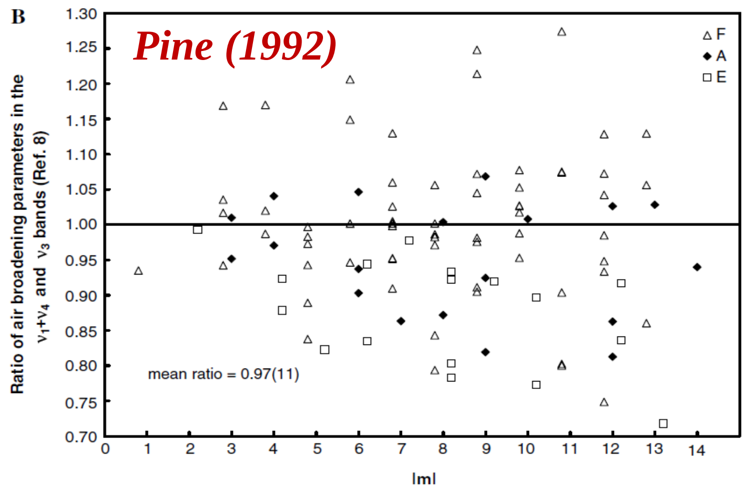
Early studies on Line shape parameters

❖ $^{12}CH_4$ in the Octad

- Positions and intensities
- Broadening (Self, Air, O_2, N_2) [*Pine, 1992*]
- Model calculations of the widths

❖ H_2-broadening of $^{12}CH_4$

- First measurements on $\nu_1 + \nu_4$ [*Margolis (1993)*]
- Calculations [*R.Gamache, T. Garbard, H. Tran*]
- Compilations [HITRAN 2016]



❖ Various dependences

- Vibrational dependence – [*Margolis, 1993*]
- Temperature dependence
- Symmetry dependence

❖ Line mixing

- Measurements and calculations

Some basic equations for spectrum descriptions

- **Transmittance:** $\tau(\nu;\nu_o) = \exp[-k(\nu)\cdot N\cdot\xi\cdot l]$
- **Line shape profile(Voigt):**

$$f(\nu-\nu_0)=V(x,y)=\frac{1}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}}\frac{y}{\pi}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{y^2+(x-t)^2}dt$$

$$x=\frac{\left[\sqrt{ln2}\cdot|\nu-\nu_o|\right]}{\gamma_D};\; y=\sqrt{ln2}\cdot\gamma_L/\gamma_D;$$

- **Temperature dependence of the line shape parameters:**

$$\gamma_{p,T}=P\times\gamma^{o}_{p_0,T_0}\left(\frac{T_0}{T}\right)^n \qquad \delta_{p,T}=P\times\left[\delta^{o}_{p_0,T_0}+\delta'\times(T-T_0)\right]$$

- **Voigt profile, represented by Fadeeva function,**

$$W(z)=\frac{i}{\pi}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{z-t}dt \qquad K(x,y)=\frac{\sqrt{\ln 2}}{\lambda_D\sqrt{\pi}}\cdot\mathrm{Re}[W(z)]$$

- **Speed-dependent narrowing profile**

$$K_s(x,y,s,H)=\frac{2}{\pi}\int_{-\infty}^{\infty}v\cdot e^{-v^2}\cdot\tan^{-1}\left(\frac{x+v}{y(\tilde{v})[1+s(v^2-1.5)]+H}\right)dv$$

Line mixing in Labfit

❑ Full Line mixing

$$I(v) = (1/\pi)\cdot \mathrm{Im}[\mathbf{X}^T\mathbf{G}^{-1}\boldsymbol{\rho}\mathbf{X}]$$

$$G(v) = (v - v_0) - i\mathbf{W},$$

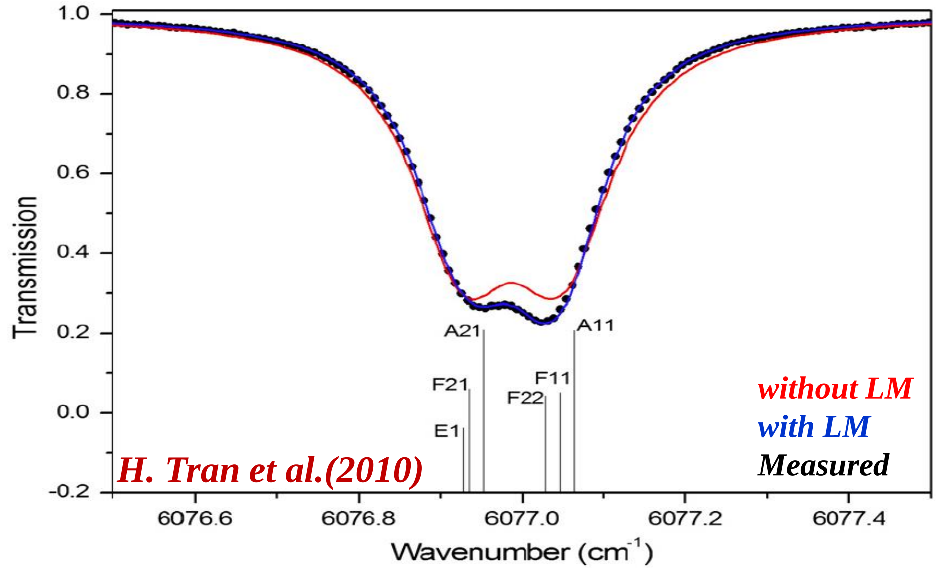
$$W_{ii} = \gamma_{Li} + i\delta_i$$

$$X_i = \sqrt{[(S_i/\rho_i)]}$$

$$\rho_i = (2J+1)\exp(-C_2E''_i/T)$$

C_2 = 2nd boltzman constant

Effect of line mixing: $CH_4(2v_3)$ R(6)



❑ Labfit to solve for W_{ik}, the off-dia. Relaxation Matrix

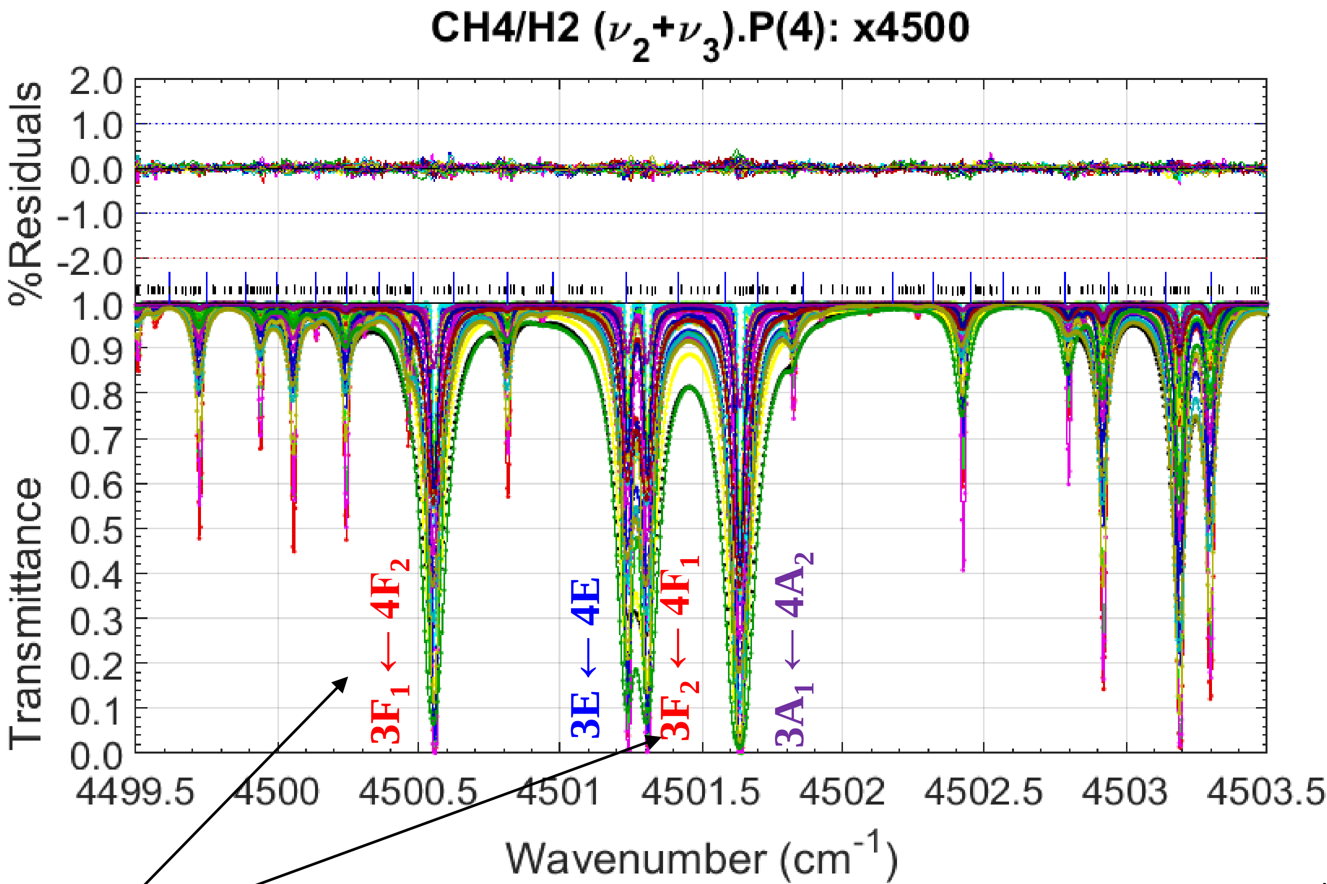
(Assumed linear P & exponential T dependences)

$$W_{ik} = p\sum_{j}^{Ngases}\frac{g_k}{g_i}W^0_{ikj}\chi_j\left(\frac{T_o}{T}\right)^{m_j}$$

Fitting residuals from Labfit: P(4)

- ❖ **Some statistics**
- ➢ **29 spectra**
- ➢ **8 at RT**
- ➢ **5 at 200 K**
- ➢ **5 at 220 K**
- ➢ **2 at 250 K**
- ➢ **9 at T = 340-370K**

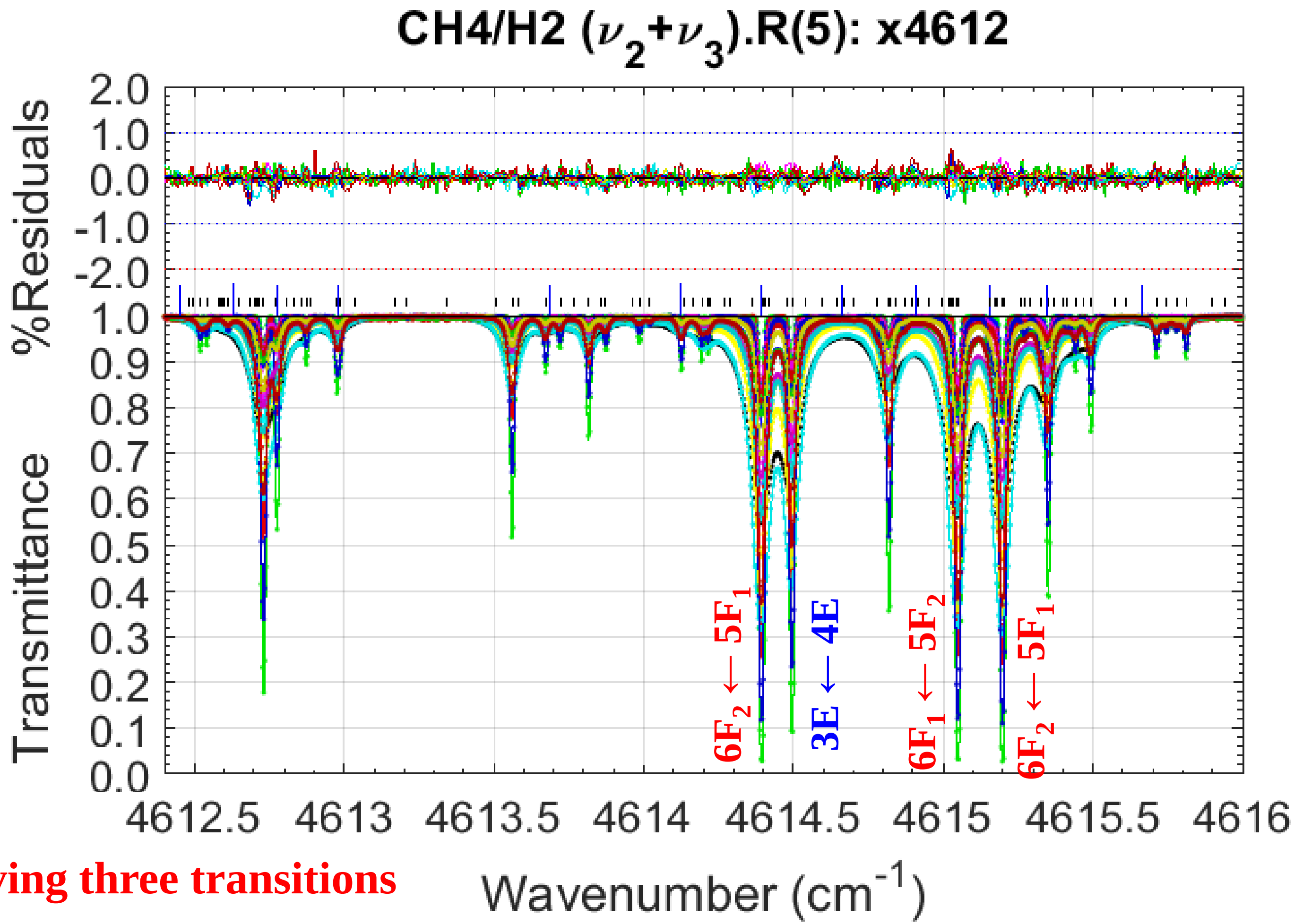
- ➢ **288 transitions**
- ➢ **positions,**
- ➢ **intensities,**
- ➢ **widths & T-dep**
- ➢ **shifts & T-dep**
- ➢ **speed-dep.**
- ➢ **one pair of line mixing**



Fitting residuals from Labfit_GUI: R(5)

❖ Some statistics
- ➢ 19 spectra
- ➢ 5 at RT
- ➢ 5 at 200 K
- ➢ two at 220 K
- ➢ two at 200 K
- ➢ 5 at T=340-370K

- ➢ 142 transitions
- ➢ positions,
- ➢ intensities,
- ➢ widths & T-dep
- ➢ shifts & T-dep
- ➢ speed-dep.
- ➢ line mixing involving three transitions

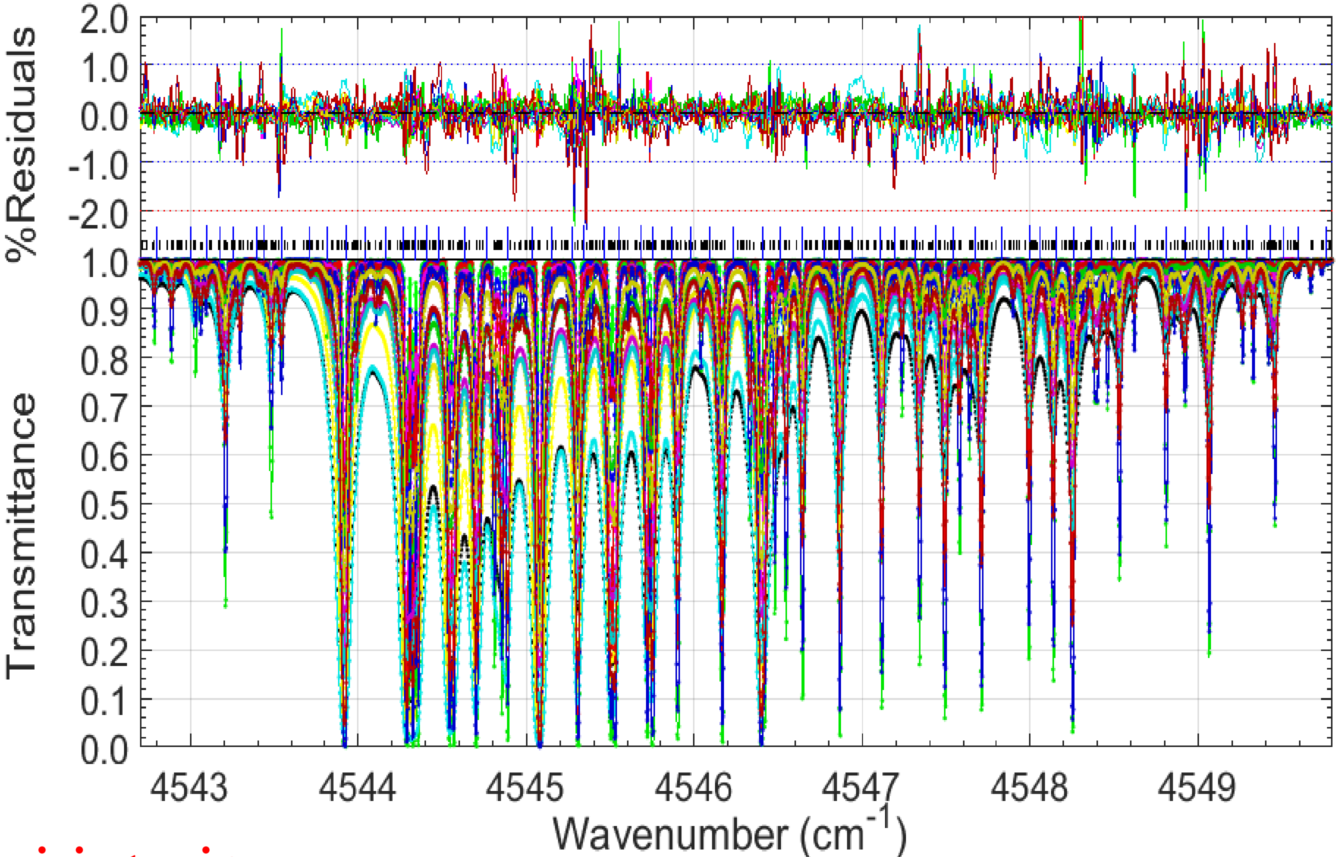


Fitting residuals for Q-branch

- ❖ **Some statistics**
- ➢ **19 spectra**
- ➢ **5 at RT**
- ➢ **5 at 200 K**
- ➢ **two at 220 K**
- ➢ **two at 200 K**
- ➢ **5 at T=340-370K**

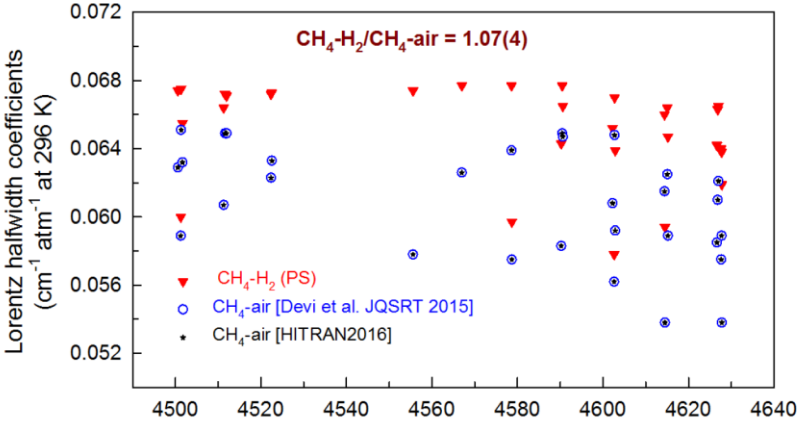
- ➢ **742 transitions**
- ➢ **positions,**
- ➢ **intensities,**
- ➢ **widths & T-dep**
- ➢ **shifts & T-dep**
- ➢ **speed-dep.**
- ➢ **three sets of line mixing pair**

$^{12}CH_4$ ($\nu_2+\nu_3$): $Q(1)$ – $Q(9)$

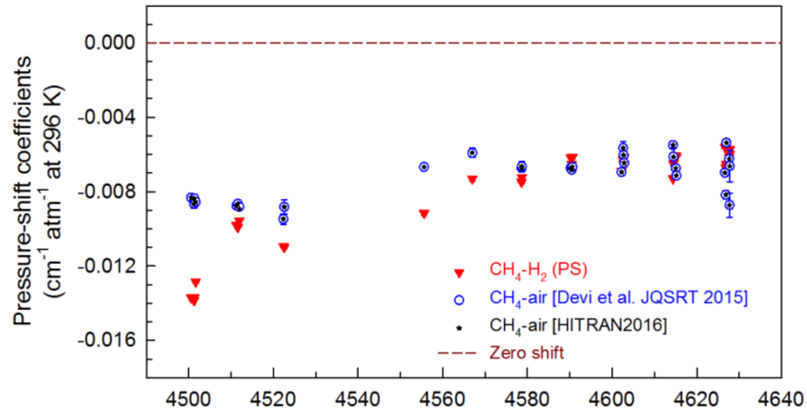


Preliminary results on widths and shifts

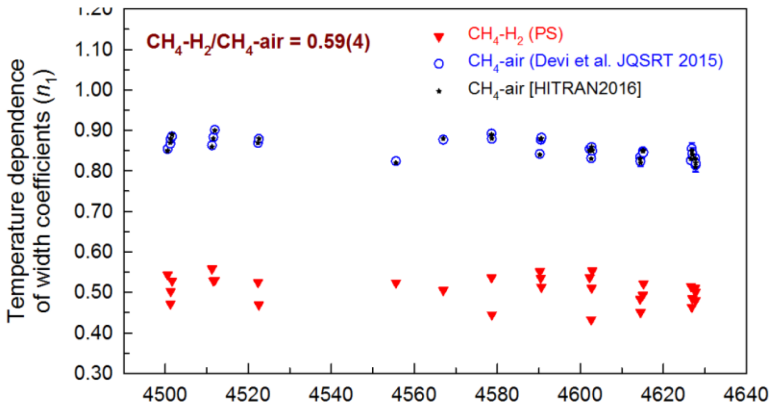
H_2-broadened width coefficients



H_2-pressure-induced freq. shift coefficients

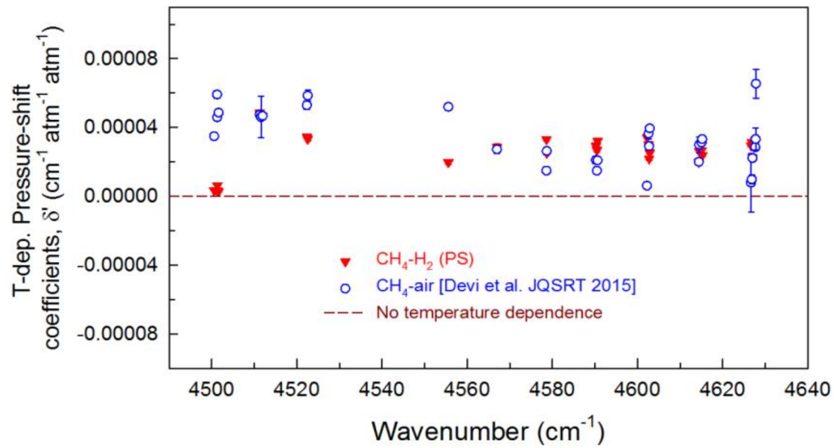


H_2-broadened width T-dep.



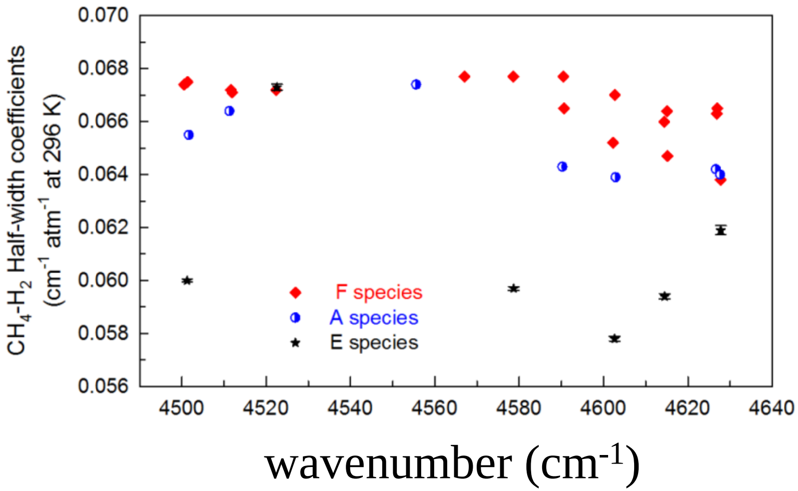
wavenumber (cm^{-1})

H_2-freq. shift T-dep.

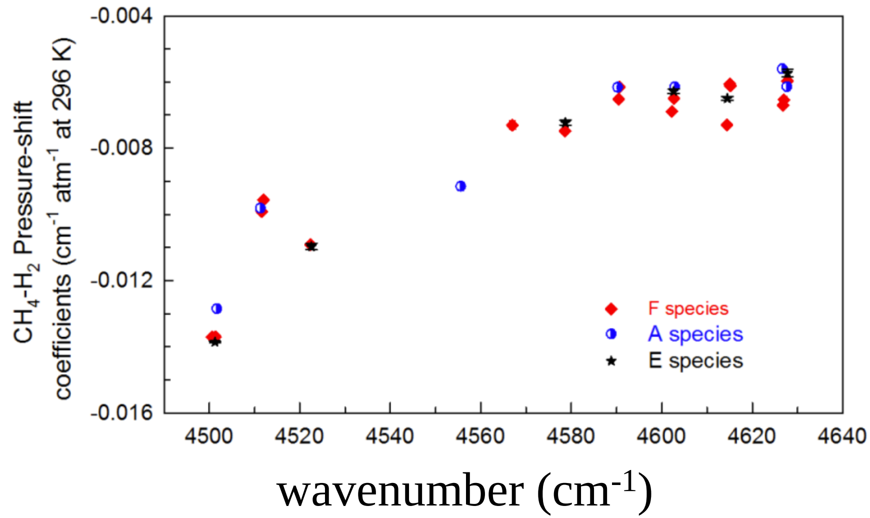


Preliminary results: Symmetry dependence

H_2-broadened width coefficients



H_2-pressure-induced freq. shift coefficients



Preliminary results on Line Mixing

Measured Off-diagonal Relaxation Matrix Element coefficients

Pairs	Line ID	Positions (cm^{-1})	ORME coefficients (cm^{-1}/atm at T_o = 296 K)	
P(4)	3F1 ← 4F2 3F2 ← 2F1	4500.555 4501.310	0.0065(2)	0.045(9)
P(3)	2F1 ← 3F2 2F2 ← 3F1	4511.595 4511.929	0.0055(1)	0.086(8)
Q(3)	3F2 ← 3F1 3F1 ← 3F2	4544.345 4544.701	0.0107(3)	0.8 (Fixed)
Q(6)	6F1 ← 6F2 6F2 ← 6F1	4545.900 4546.166	0.0077(3)	0.8 (Fixed)
Q(9)	9F2 ← 9F1 9F1 ← 9F2	4547993 4548.138	0.0156(5)	0.8 (Fixed)
R(3)	4F1 ← 3F2 4F2 ← 3F1	4590.463 4590.610	0.0058(1)	0.453(64)
R(4)	5F1 ← 4F2 5F2 ← 4F1	4602.228 4602.723	0.0065(3)	1.47(15)
R(5)	6F2 ← 5F1 6F1 ← 5F2 6F2 ← 5F1	4614.394 4615.049 4615.199	0.0007(1) 0.0100(3)	0.8 (Fixed) 0.8 (Fixed)
R(6)	7F2 ← 6F1 7F1 ← 6F2	4626.815 4626.934	0.0051(2)	2.80(15)

Summary and further work

❑ Measured line shape parameters of H_2-Pressure broadened CH_4 spectra

- Obtained a series of spectra at 80 – 370 K of CH_4 pure and mixtures with H_2.
- Used a new version of Labfit_GUI (Graphic User Interface) [*Drouin, Benner, et al.*]
- Retrieved widths and shifts along with their T-dep. for 40 transitions from the v_2+v_3 band for the first time.
  - Results show distinctive difference from Air-broadening
  - also, show *A/E/F* rotational symmetry species dependence for pressure broadening
- Retrieved Line mixing coefficients for 19 transitions from 9 manifolds, including Q-br.

❑ Future work

- Supplied this measurement to theoretical models
- Continue to include the spectra at T < 200 K for this band.
- Measure the line shape parameters for v_3+v_4 band
- Make comparison with theoretical calculations
- Suggest the parameters for high temperatures based on the combined efforts

Acknowledgements

Research described in this talk was performed under the National Aeronautics and Space Administration. We thank Drs. B. J. Drouin, A. Guillaume, M. Cich for the GUI version of the Labfit.