SELF- AND AIR-BROADENED LINE PARAMETERS OF METHANE IN THE 4100-4300 WAVENUMBER RANGE

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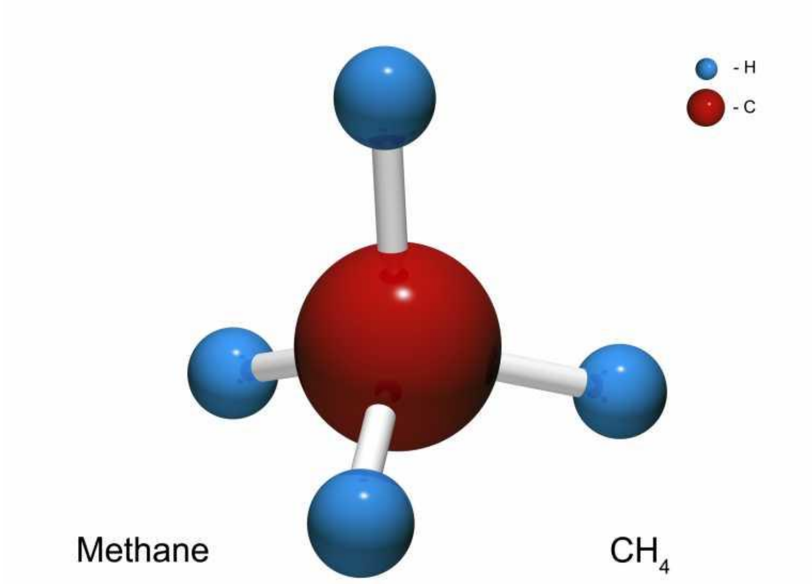
Motivation

Methane:

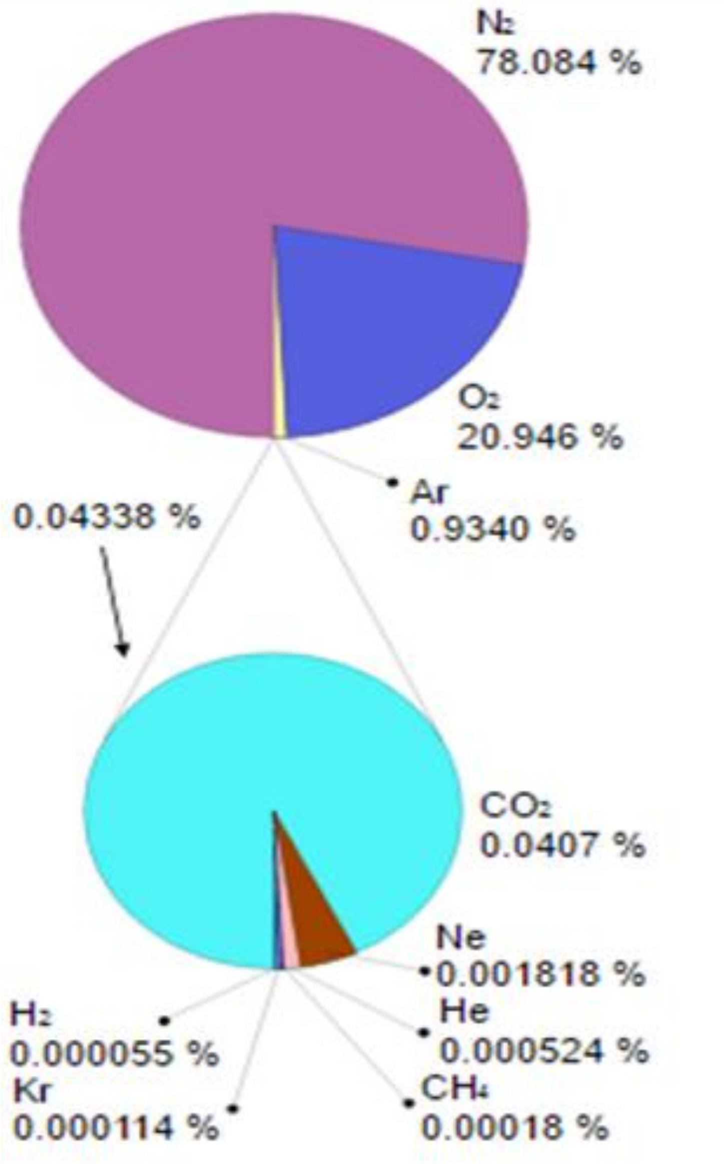
- Atmospheric trace gas [1,800 ppb]
- Second most important anthropogenic green house gas
- Global warming potential ~ 86 times that of CO_2
- Present also in outer planets



HITRAN molecule #6

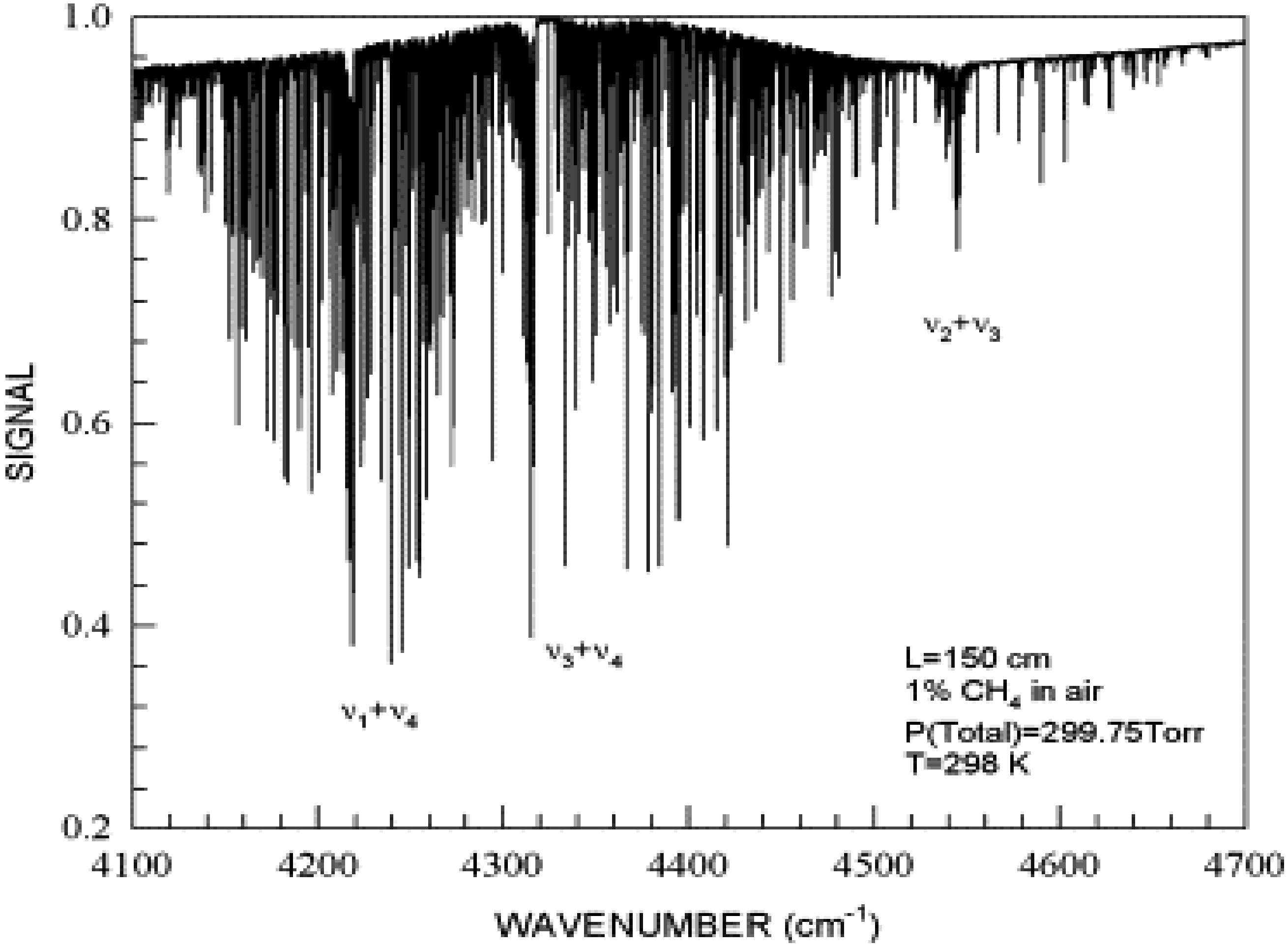
Geometry: Tetrahedral T_d symmetry

Earth Atmosphere



Source: *Wikipedia-Atmosphere of earth*

Methane Octad Band



Total 8 interacting combination and overtone bands:

(i) $3\nu_1$, (ii) $\nu_2+2\nu_4$, (iii) $\nu_1+\nu_4$, (iv) $\nu_3+\nu_4$, (v) $2\nu_2+\nu_4$, (vi) $\nu_1+\nu_2$, (vii) $\nu_2+\nu_3$, (viii) $3\nu_2$

Most intense:

$\nu_1+\nu_4 \sim 4220\ cm^{-1}$
$\nu_3+\nu_4 \sim 4320\ cm^{-1}$
$\nu_2+\nu_3 \sim 4540\ cm^{-1}$

A. Predoi-Cross, M. Brawley-Tremblay, Linda R. Brown, V. Malathy Devi, D. Chris Benner, *Multispectrum analysis of $^{12}CH_4$ from 4100 to 4635 cm^{-1} : Air-broadening coefficients (Widths and shifts)*, J. Mol. Spectrosc. 236 (2006) 201–215.

Previous Studies on Methane

- Room temperature;
- Only one speed-dependent analysis

1. *Spectroscopic line parameters of $^{12}CH_4$ for atmospheric composition retrievals in the 4300-4500 cm^{-1} region* **(in the 4300–4500 cm^{-1} region)** R. Hashemi *et al.* J. Quant. Spectrosc. Radiat. Transfer 186 (2017) 106–117.

2. *Self- and air-broadened line shape parameters in the $\nu_2+\nu_3$ band of $^{12}CH_4$: 4500–4630 cm^{-1}* **(in the 4500–4630 cm^{-1} region)** V.M. Devi *et al*. J. Quant. Spectrosc. Radiat. Transfer 152 (2015) 149-165.

3. *Line mixing effects in the $\nu_2 + \nu_3$ band of methane* **(Room-temperature study)** A. Predoi-Cross *et al*. J. Mol. Spectrosc. 246 (2007) 65-76.

4. *Multispectrum analysis of $^{12}CH_4$ from 4100 to 4635 cm^{-1}: II. Air-broadening coefficients* **(Air-broadening, room-temperature study)** A. Predoi-Cross *et al.* J. Mol. Spectrosc. 236 (2006) 201-215.

5. *Multispectrum analysis of $^{12}CH_4$ from 4100 to 4635 cm^{-1}: I. self-broadening coefficients (widths and shifts)*, **(Self-broadening, room-temperature study)** A. Predoi-Cross *et al*. J. Mol. Spectrosc 232 (2005) 231-246.

6. *Measurements of Air-broadening and pressure-shifting of methane lines in the 2.3 μm region* **(Room temperature study)** V. Malathy Devi *et al*. J. Mol. Spectrosc 157 (1993) 95-111.

7. **Temperature dependence of Lorentz air-broadening** *and pressure shift coefficients of CH_4 lines in the 2.3 μm spectral region* V. Malathy Devi *et al*. J. Quant Spectrosc Radiat. Transfer 51 (1994) 439-465.

<u>**Objectives**</u>

Determination of line parameters of $(\nu_1 + \nu_4)$ **band :**

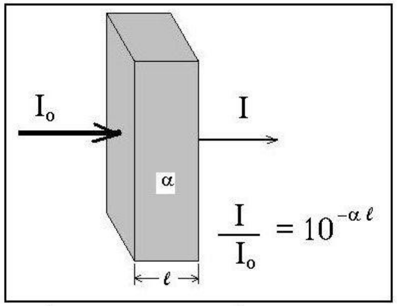
- CH_4-CH_4 and CH_4-air <u>**half width and pressure-shift**</u> coefficients along with their temperature dependences
- Retrievals of <u>**speed-dependence**</u> parameters
- Measurements of <u>**line-mixing coefficients**</u> for 49 strongest pairs of transitions using the off-diagonal relaxation matrix element formalism

Comparison of:

- Observed line position and intensities with calculated values and with GEISA 2015, HITRAN 2012 database results
- Broadening and shift coefficients with available database results
- Line mixing coefficients with previous published results

Applications of this type of research: Earth Radiation Budget, Radiative Forcing and Remote Sensing

Theoretical Background



The Beer Lambert Law

$$A = \log_{10} \frac{I_o}{I} = \varepsilon l c$$

A = absorbance of sample
C = concentration (mol/L)
ε = molar absorptivity (L mol^{-1} cm^{-1})

$$I(v) = I_0(v) e^{-K(v)L}$$

Spectral absorption coefficient, $K(v) = p\chi_{abs} S(T) F(v - v_0)$

F(ν) = line-shape function
p = pressure
χ_{abc} = mole fraction
S(T) = line strength

Line-shape profiles:

- Doppler (dominant at **low p**)
- Lorentz (dominant at **high p**)
- Voigt (convolution of both)

- We assumed Speed-Dependent Voigt Profile (SDVP)

Equations

- A spectral line is characterized by:

  Lorentz half width at half maximum

$$b_L(p,T) = p\left[b_L^0(air)(p_0,T_0)(1-\chi)\left[\frac{T_0}{T}\right]^{n1} + b_L^0(self)(p_0,T_0)\chi\left[\frac{T_0}{T}\right]^{n2} \right]$$

Pressure-shift of the line from its center

$$\nu = \nu_0 + p\left[\delta^0(air)(1-\chi) + \delta^0(self)\chi\right] \qquad \delta^0(T) = \delta^0(T_0) + \delta'\left[T - T_0\right]$$

$\boldsymbol{b_L^0}$ = pressure broadening coefficient (cm^{-1} atm^{-1}) of the spectral line

$\boldsymbol{\delta^o}$ = pressure-induced shift coefficient (cm^{-1} atm^{-1})

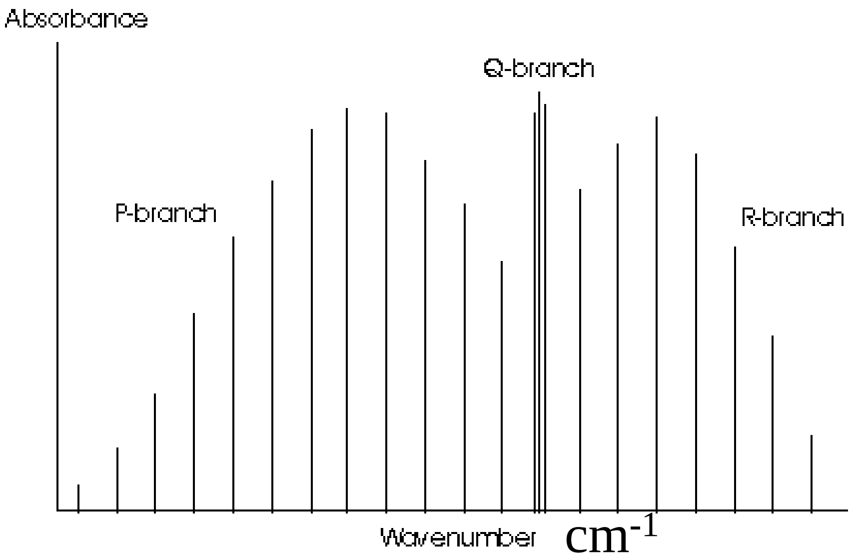
$\boldsymbol{b_L(p, T)}$ = Lorentz halfwidth (cm^{-1}) at p and T

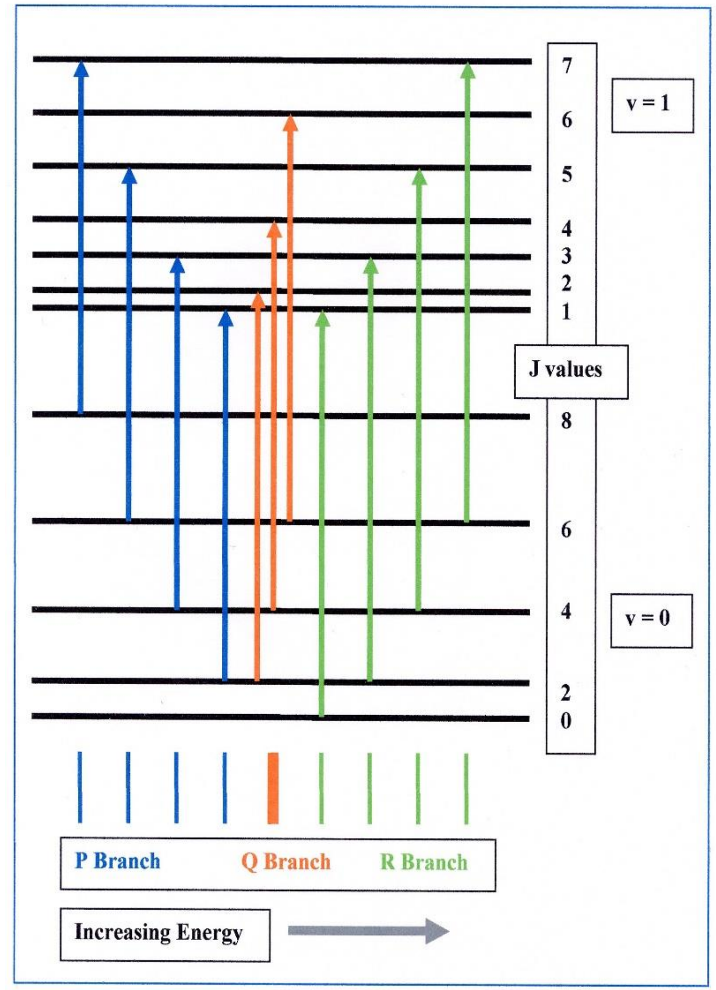
χ = ratio of partial pressure of CH_4 to total sample pressure

n_1 and n_2 = T dependence exponents for air- and self-broadened widths

δ' = Temperature dependence of the pressure-induced shift coefficient

Rotation-Vibration Transition





P branch: $(\Delta J = -1)$

Q branch: $(\Delta J = 0)$

R branch: $(\Delta J = +1)$

Source: *Wikipedia*

$\nu = 0$, vibrational ground state

$\nu = 1$, 1st vibrational excited state

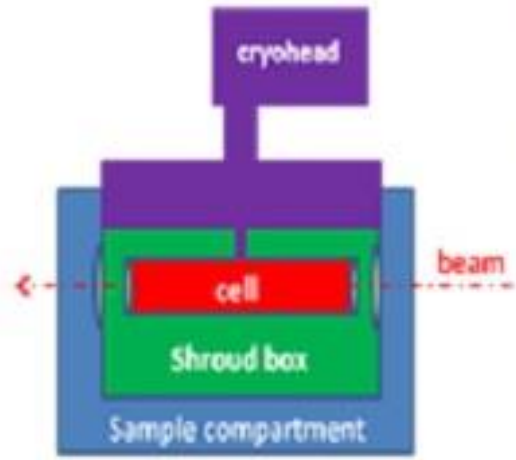
Experimental Conditions

Gas sample	CH_4 Volume mixing ratio	Total Pressure (Torr)	Temp. (K)
$^{12}CH_4$	1.0	385.0	298.4
$^{12}CH_4$	1.0	22.20, 121.51	250.0
$^{12}CH_4$	1.0	9.90, 43.95, 169.00	200.0
$^{12}CH_4$	1.0	4.52	148.4
$^{12}CH_4$	1.0	149.06	148.5
$^{12}CH_4$+Air	0.055	112.60	250.0
$^{12}CH_4$+Air	0.057	254.58	250.0
$^{12}CH_4$+Air	0.073	148.49	200.0
$^{12}CH_4$+Air	0.074	299.95	200.0
$^{12}CH_4$+Air	0.0965	95.07	148.4
$^{12}CH_4$+Air	0.0413	225.37	148.4

Absorption path length = 20.38 cm

Experimental Setup

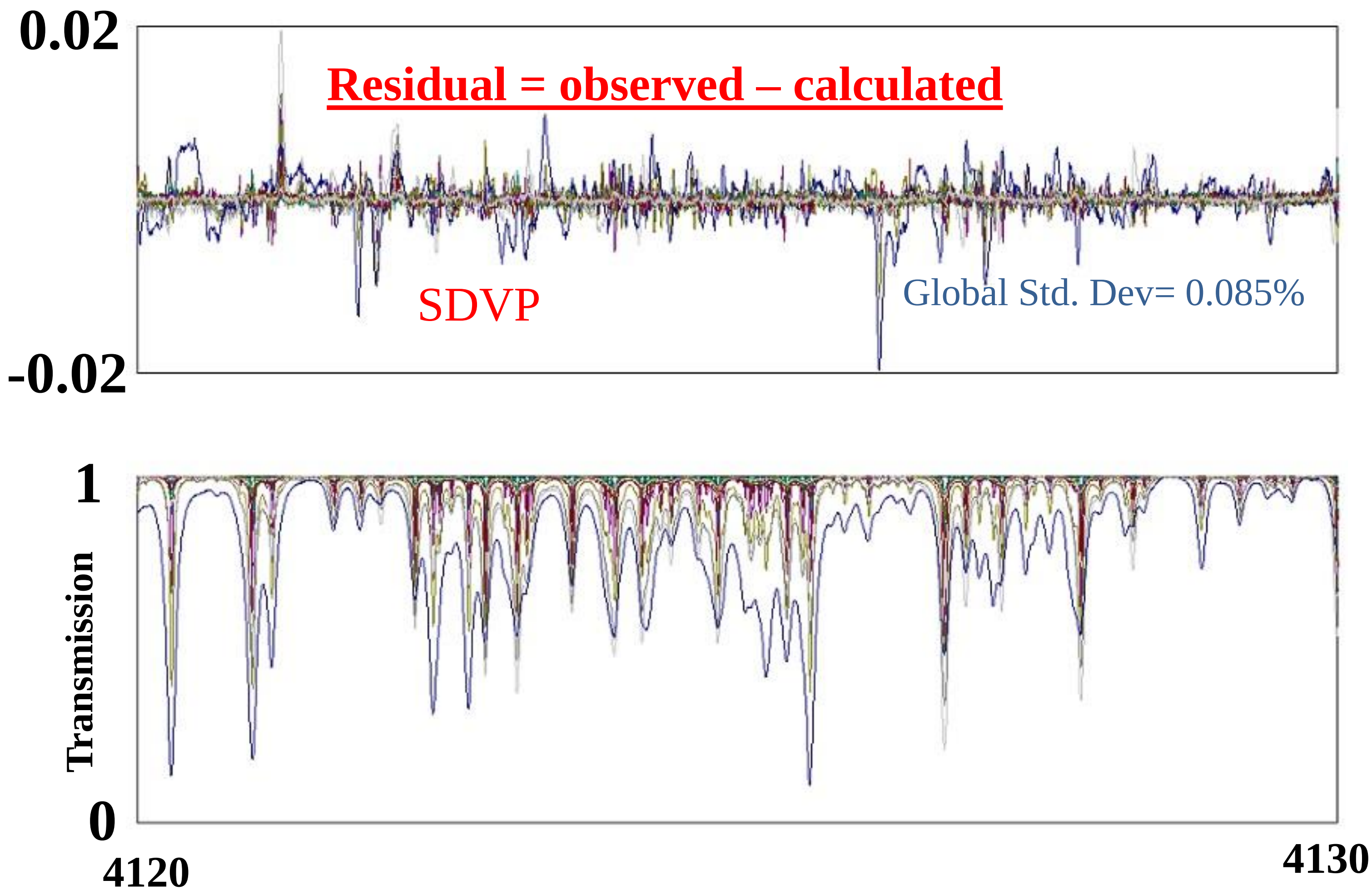
- Absorption spectra recorded with the **Bruker IFS 125HR FTS** (Fourier Transform Spectrometer) located at JPL, California.
- **Light Source:** Globar **Detector:** InSb
- **Absorption path length:** 20.38 cm **Resolution:** (0.005 cm^{-1})
- **Band pass:** 3750 to 5200 cm^{-1} **Scanning time:** 5-7 h / each
- **SNR:** 2000 to 2500 **Aperture Diameter:** 1 mm
- **Temperature:** 298-148 K **Total sample pressure:** 4.5-385 Torr
- 99.95% Enriched ^{12}C methane samples



Single pass cold cell assembly, Helium-cooled refrigerator system

Results

- **Fitting Software:** Labfit

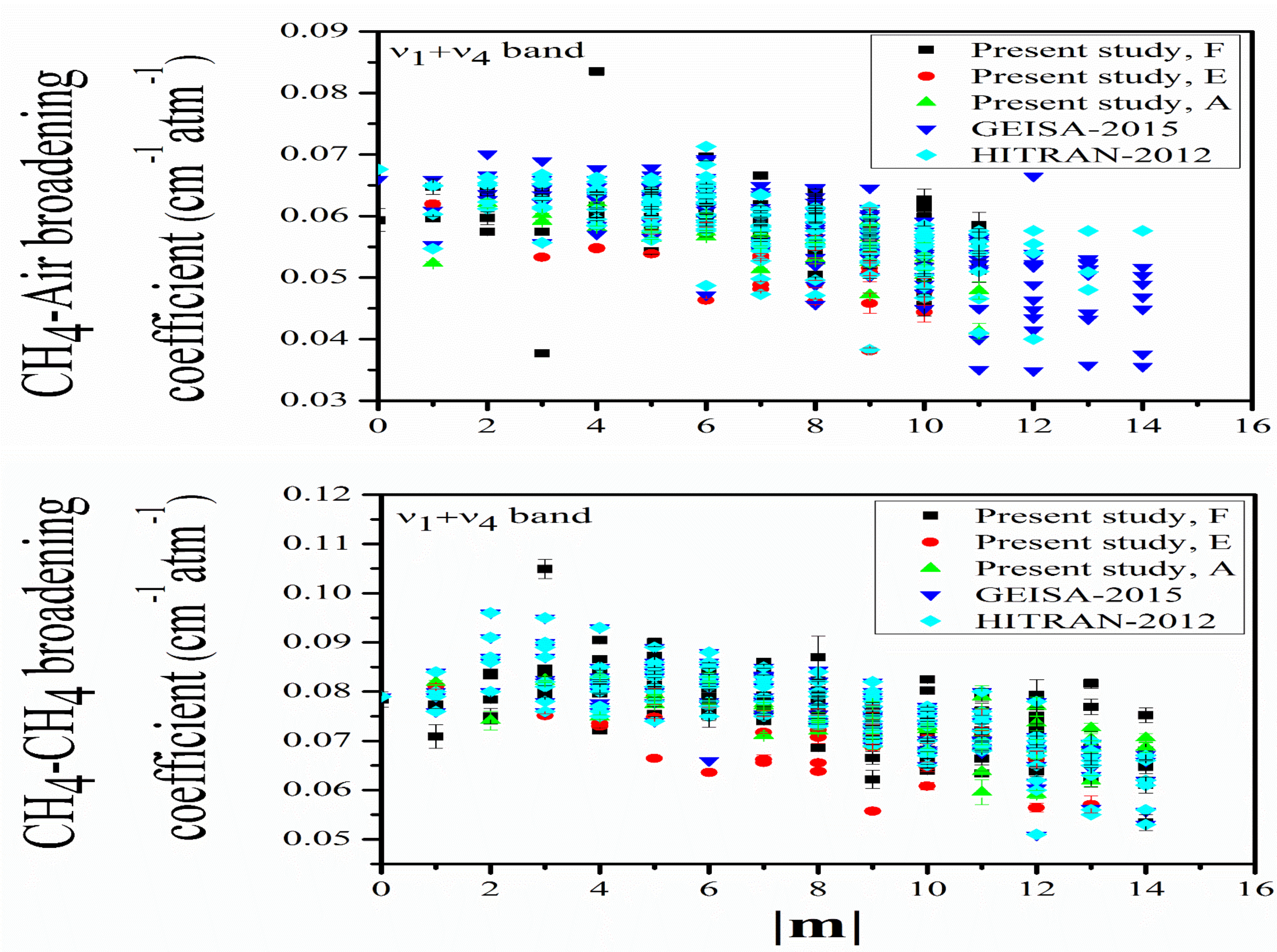


Bottom: 14 experimental spectra that were fitted simultaneously.

D.C. Benner, C.P. Rinsland, V. Malathy Devi, M.A.H. Smith, D. Atkins, *A multispectrum nonlinear least-squares fitting technique.* J. Quant. Spectrosc. Radiat. Transfer 53 (1995) 705-721

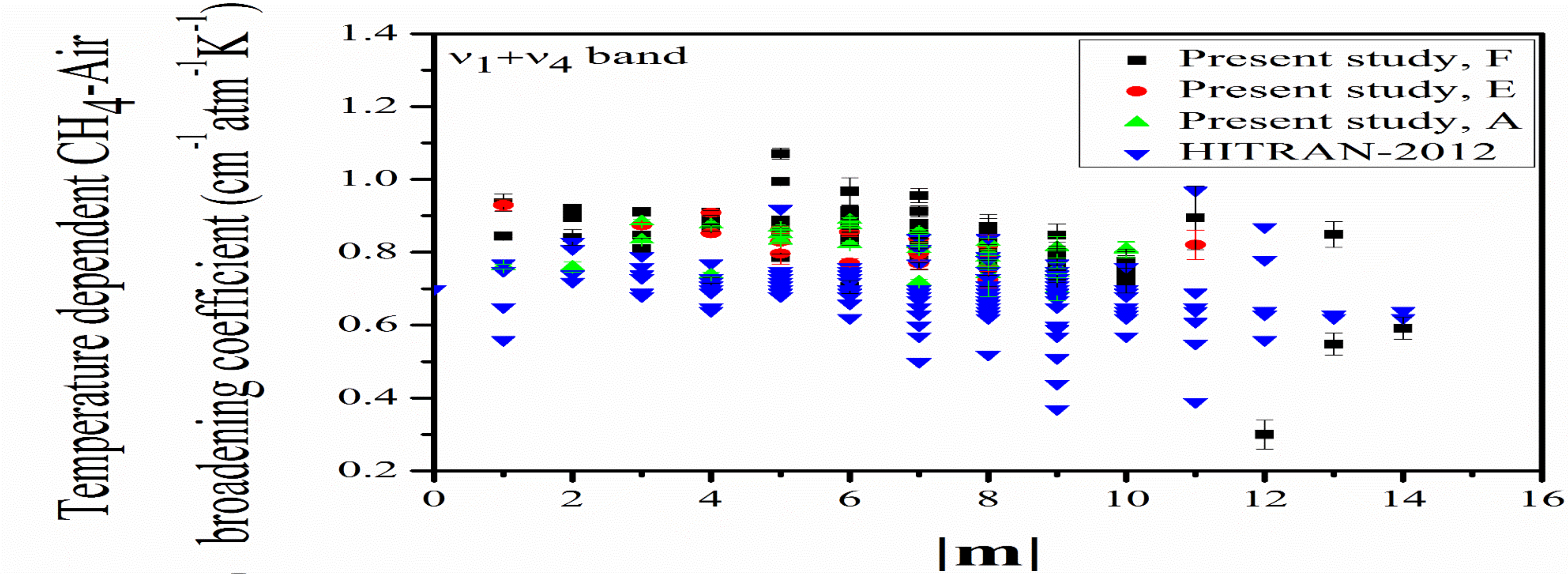
Letchworth KL, Benner DC. *Rapid and accurate calculation of the Voigt function.* J. Quant. Spectrosc. Radiat. Transfer 107 (2007) 173 – 192.

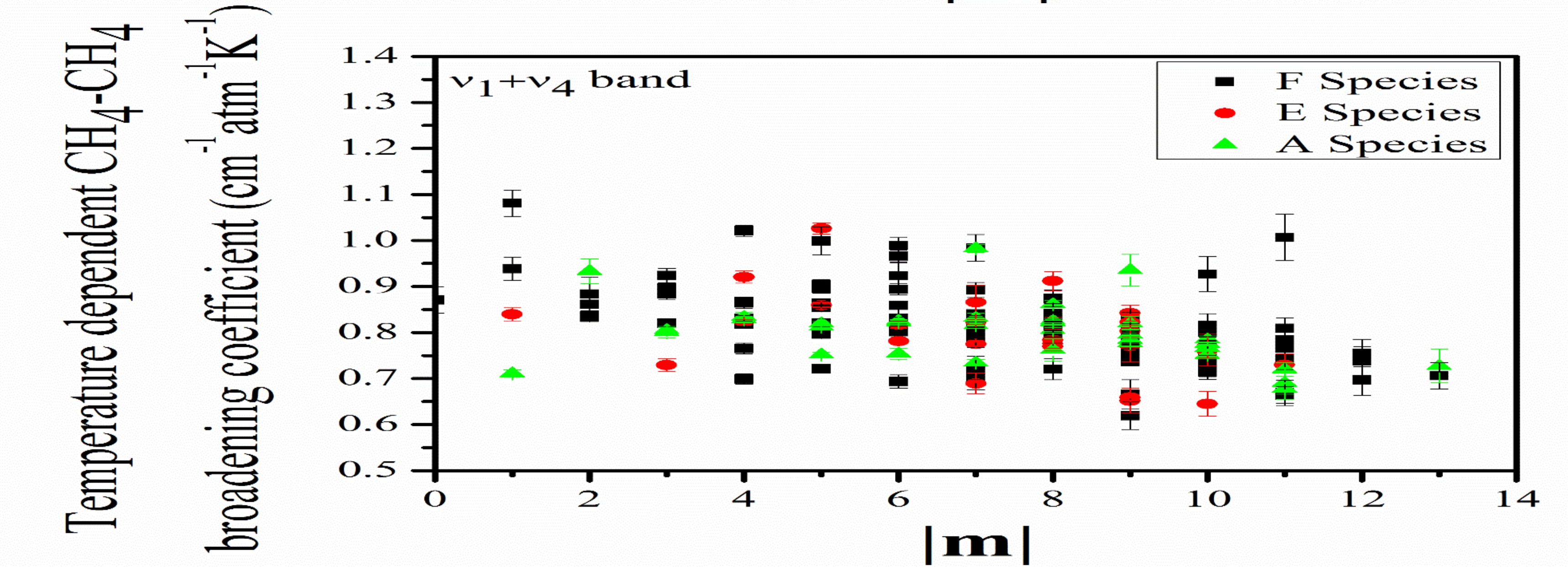
Lorentz Half Width Coefficients



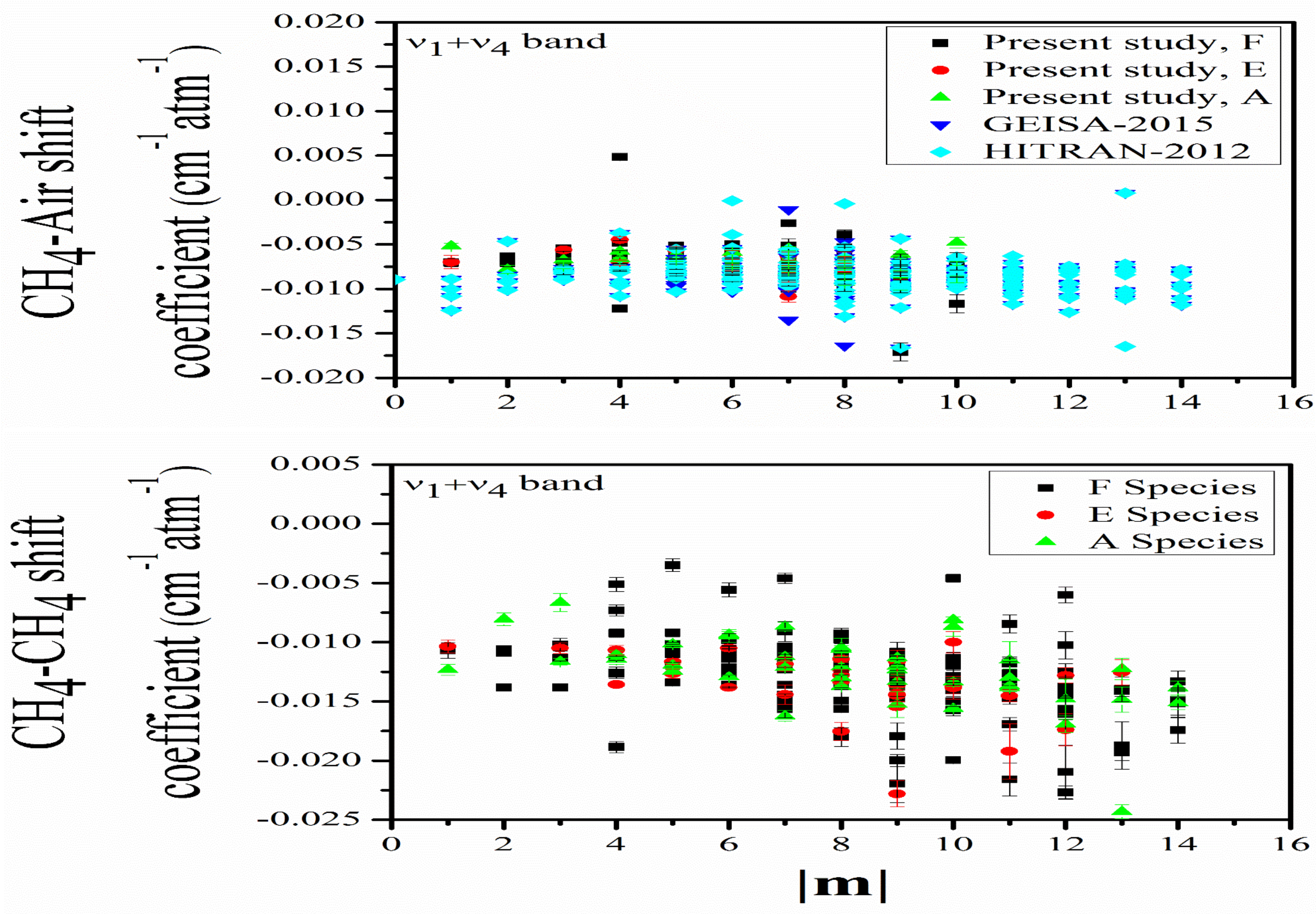
|m| = lower state J for P and Q transition
= upper state J for R branch transition

Temperature Dependence of Broadening Coefficients

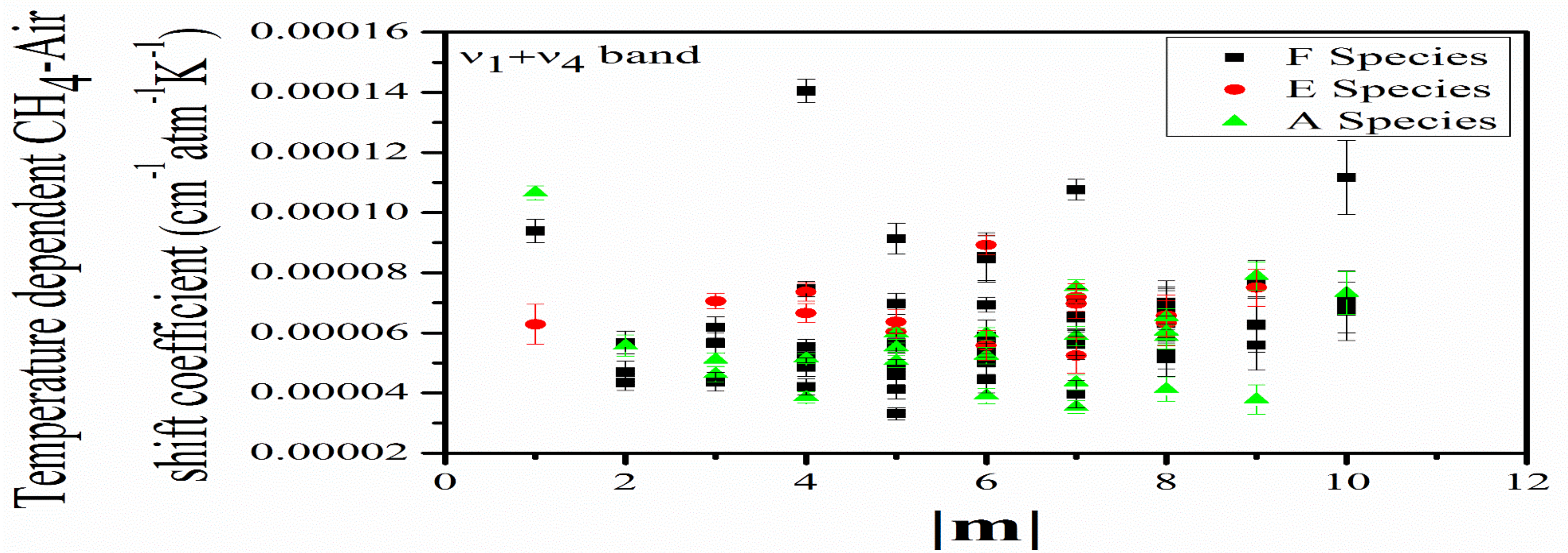


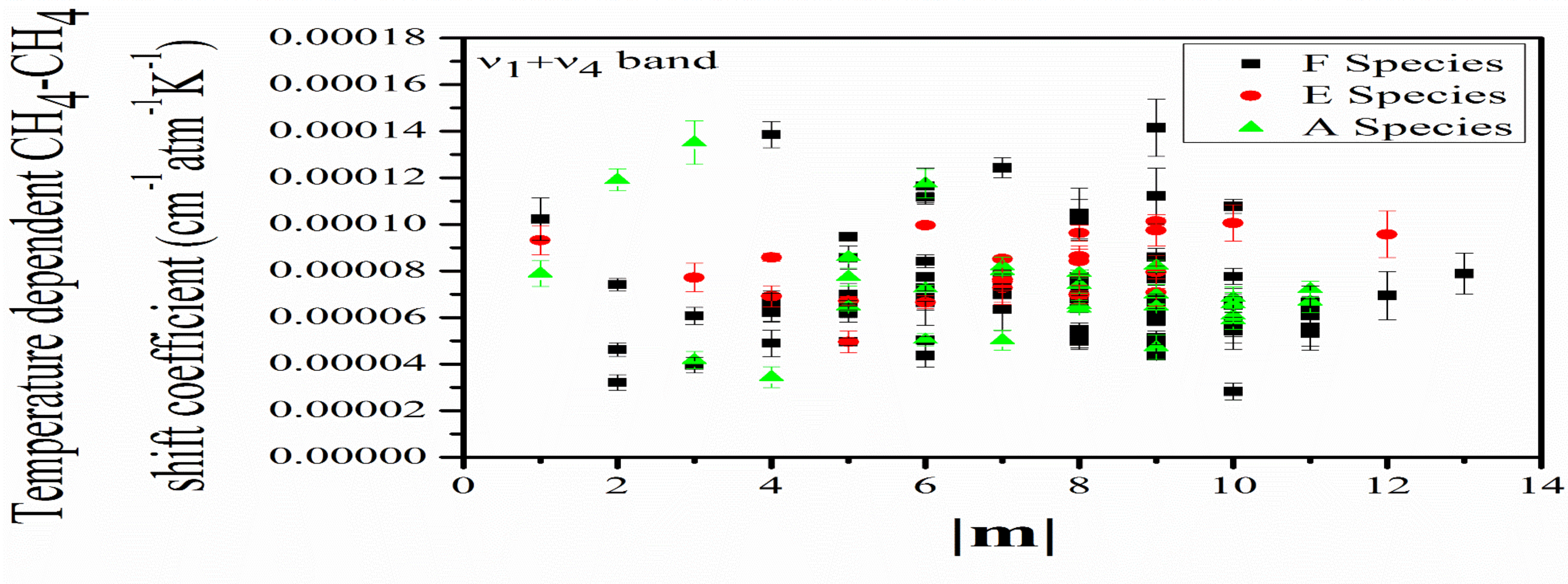


Air- and Self-Shift Pressure Induced Coefficients

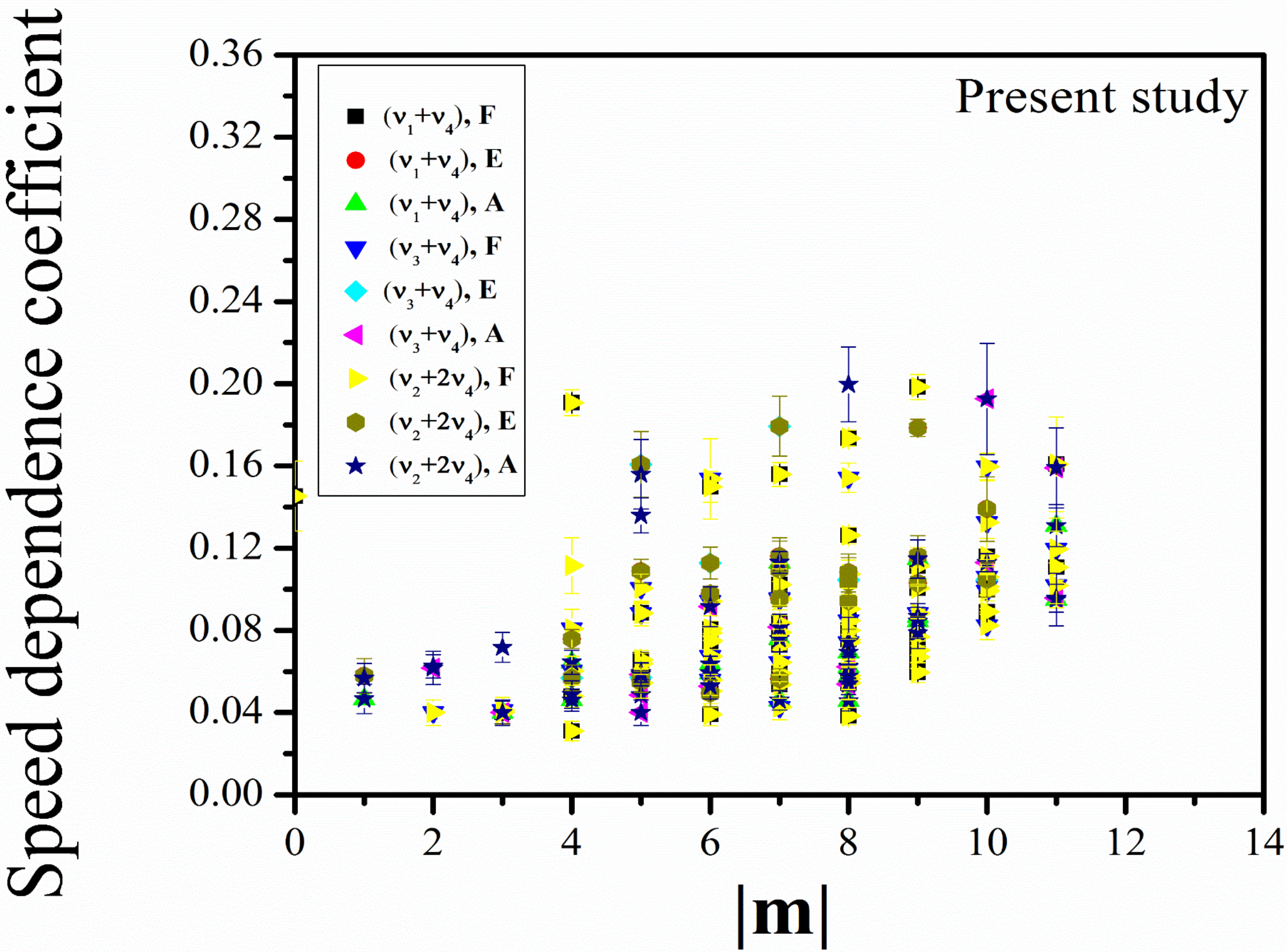


Temperature Dependence of Air- and Self- Shift Coefficients

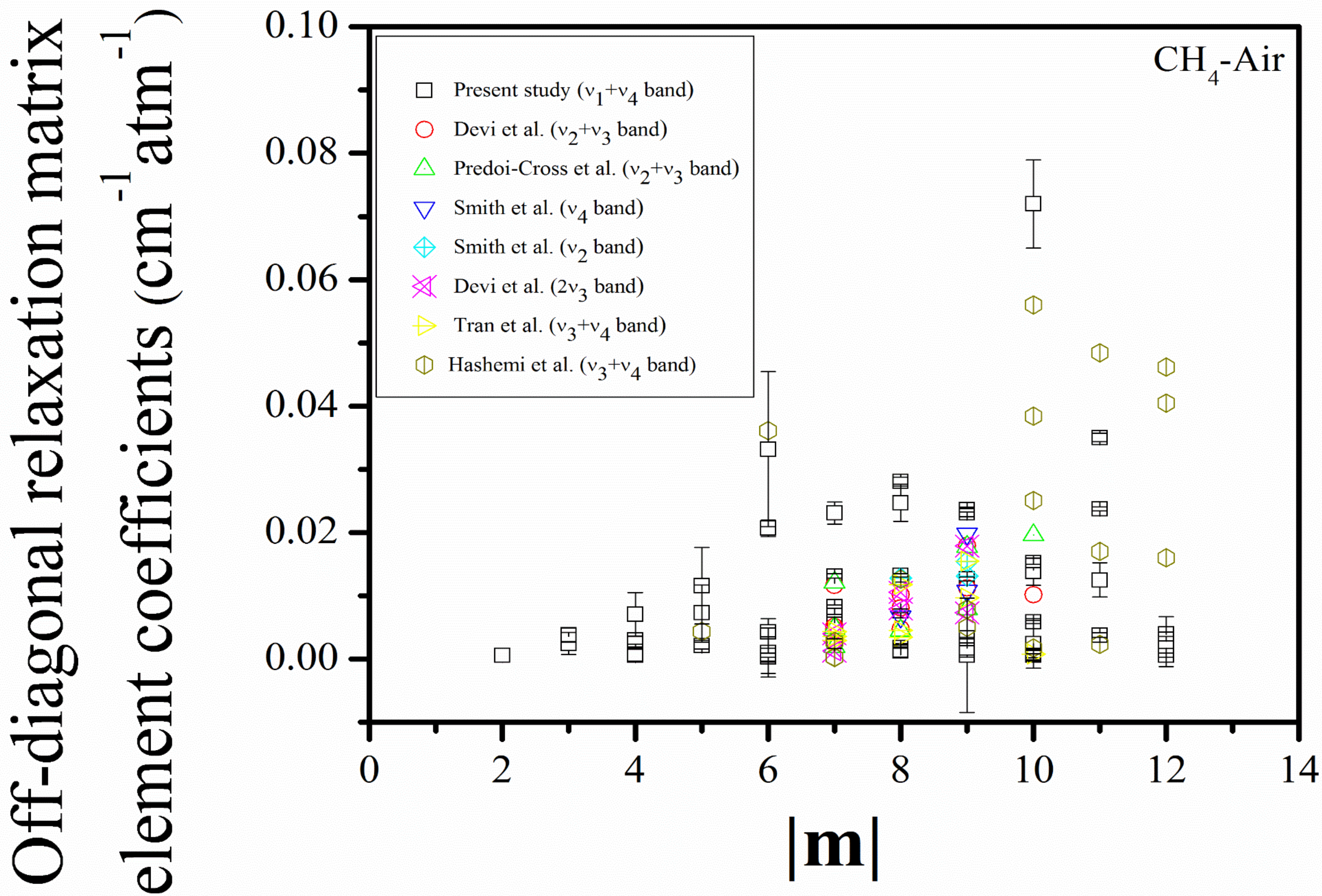




Speed Dependence Parameter



Comparison of Line Mixing Coefficients



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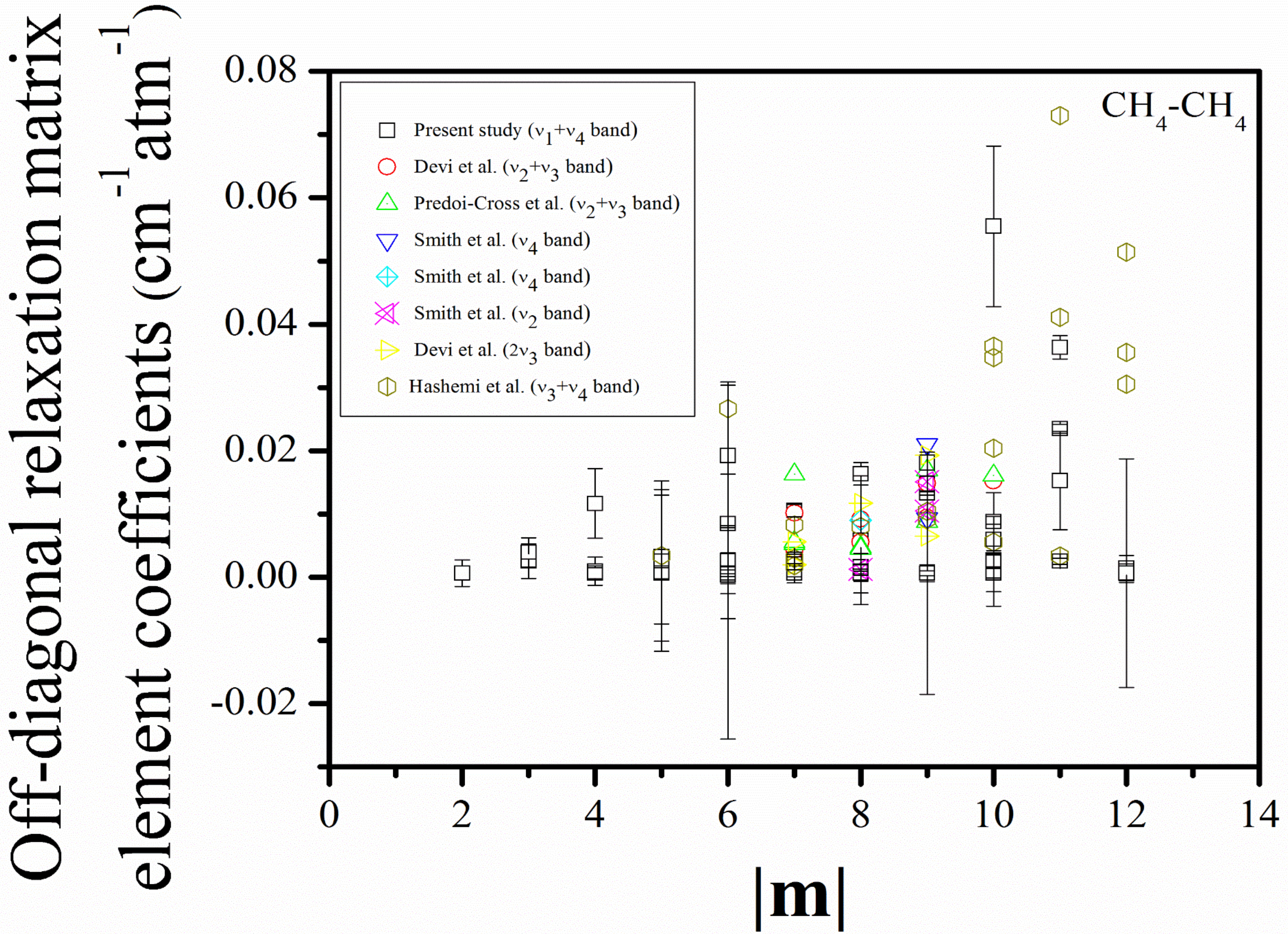
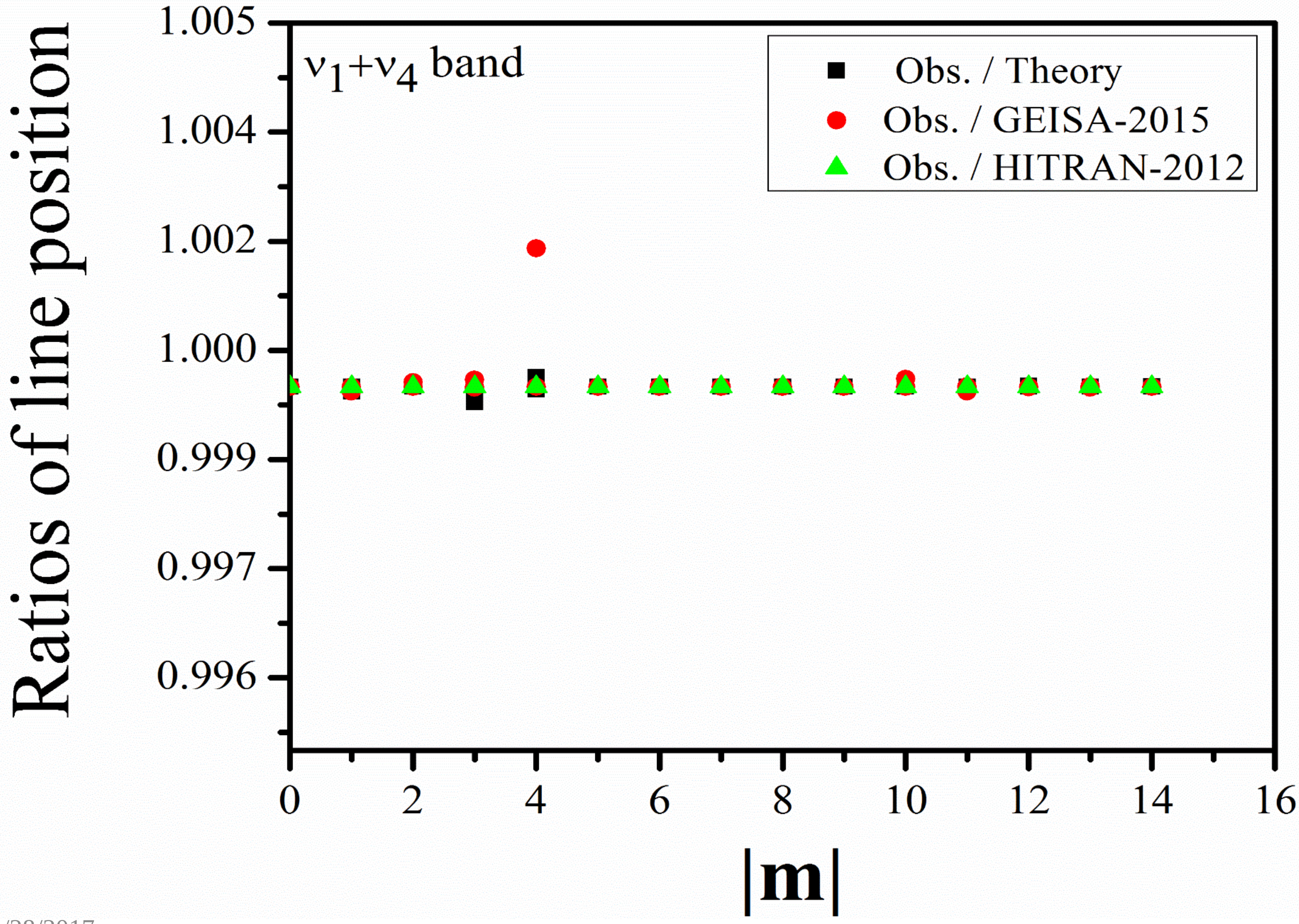
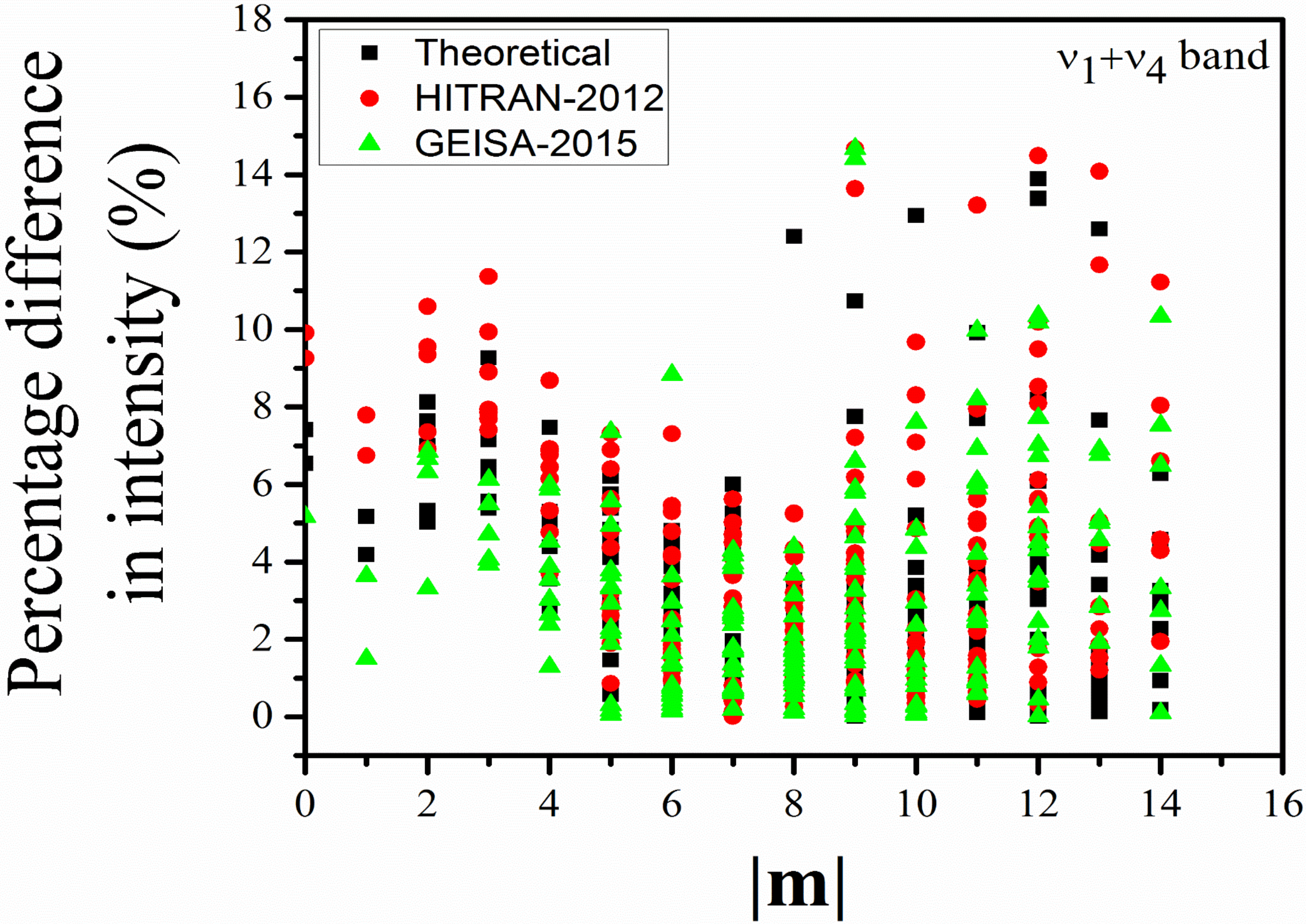


Comparison of Line Position



Comparison of Percentage Intensity Difference



Conclusion

- This work contributes to a better understanding of T-dependence of self- and air-broadening and pressure-shift of **(P, Q, R)** transitions in methane (4100-4300 cm^{-1}).

- We retrieved speed-dependent line parameters ~ **(0.0 to 0.2)**. The speed dependence parameters appeared to be independent of vibrational bands.

- Also retrieved are the line mixing coefficients given as off-diagonal relaxation matrix elements ~ **(0.00 to 0.07 $cm^{-1}atm^{-1}$ at 296 K)** with a slightly larger values in air-broadening case.

- The future plan is to study CH_4 broadened by **H_2** for applications such as the remote sensing of outer planets like Jupiter, Saturn, etc.

Acknowledgements

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Thank you for your kind attention