Self- and Air-Broadened Line Shape Parameters of Methane in the 2.3 Microns Region

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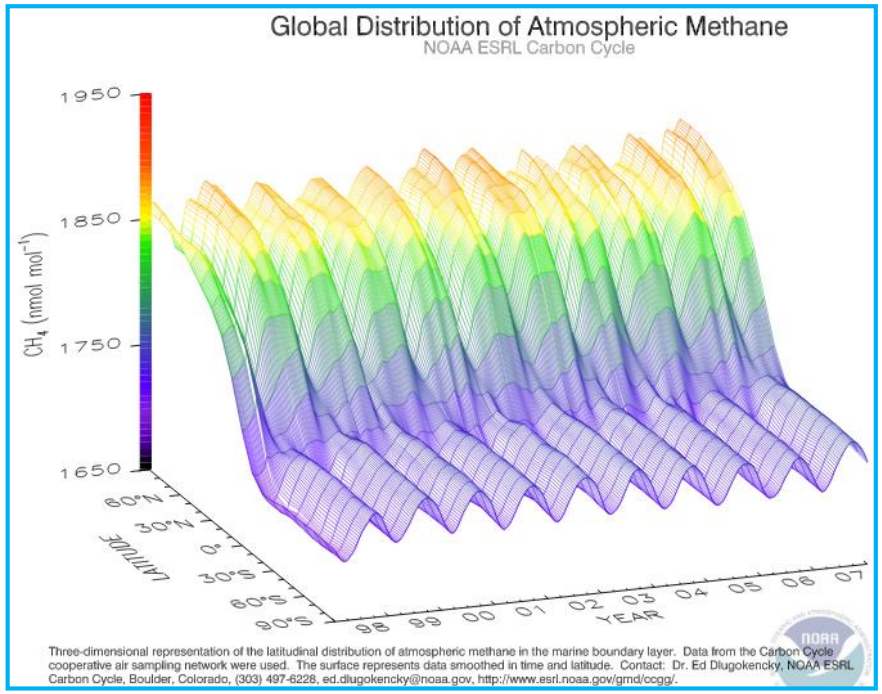
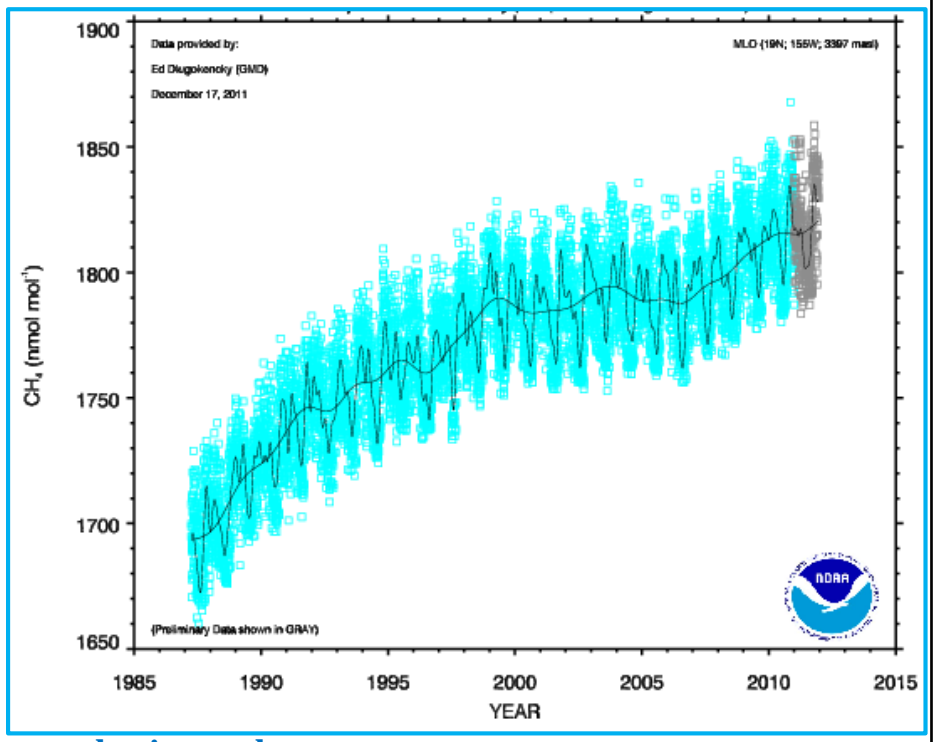
Overview of Presentation

1. Motivation for this spectroscopic study and the current status of knowledge
2. Experimental Details
3. Spectroscopic analysis
4. Data interpretation and comparisons with other studies
5. Conclusions and directions for future work
6. Acknowledgements

Motivation for this spectroscopic study





Source: http://www.ask.com/wiki/Atmospheric_methane

Methane is a trace atmospheric gas and one of most potent greenhouse gases. Due to its importance in the global Carbon Cycle, methane has received a lot of interest from both experimentalists and theoreticians alike. The management of greenhouse gases relies on the accuracies with which these gases can be measured in the terrestrial atmosphere. The spectral region located at 2.3-μm region is referred to as the "methane octad". Overlapping with the methane bands are spectra of other atmospheric constituents such as CO and HF .

Motivation for this spectroscopic study

- Knowledge of the temperature-dependences of air-broadened line widths and shifts is crucial for the correct interpretation of ~~such~~ infrared spectra such as those being recorded by instruments on various spacecraft (ASCENDS (Active Sensing of CO2 Emissions over Nights, Days and Seasons), MOPITT (Measurements Of Pollution In The Troposphere)) retrievals or by ground-based instruments.

- We have measured the self- and air-broadened Lorentz widths, shifts and line mixing coefficients along with their temperature dependences for methane absorption lines in the 2.3 μm region between room temperature and 150 K. A multi-spectrum fitting technique to include speed dependent Voigt profile and full line mixing is applied to fit several spectra (room and cold) simultaneously.

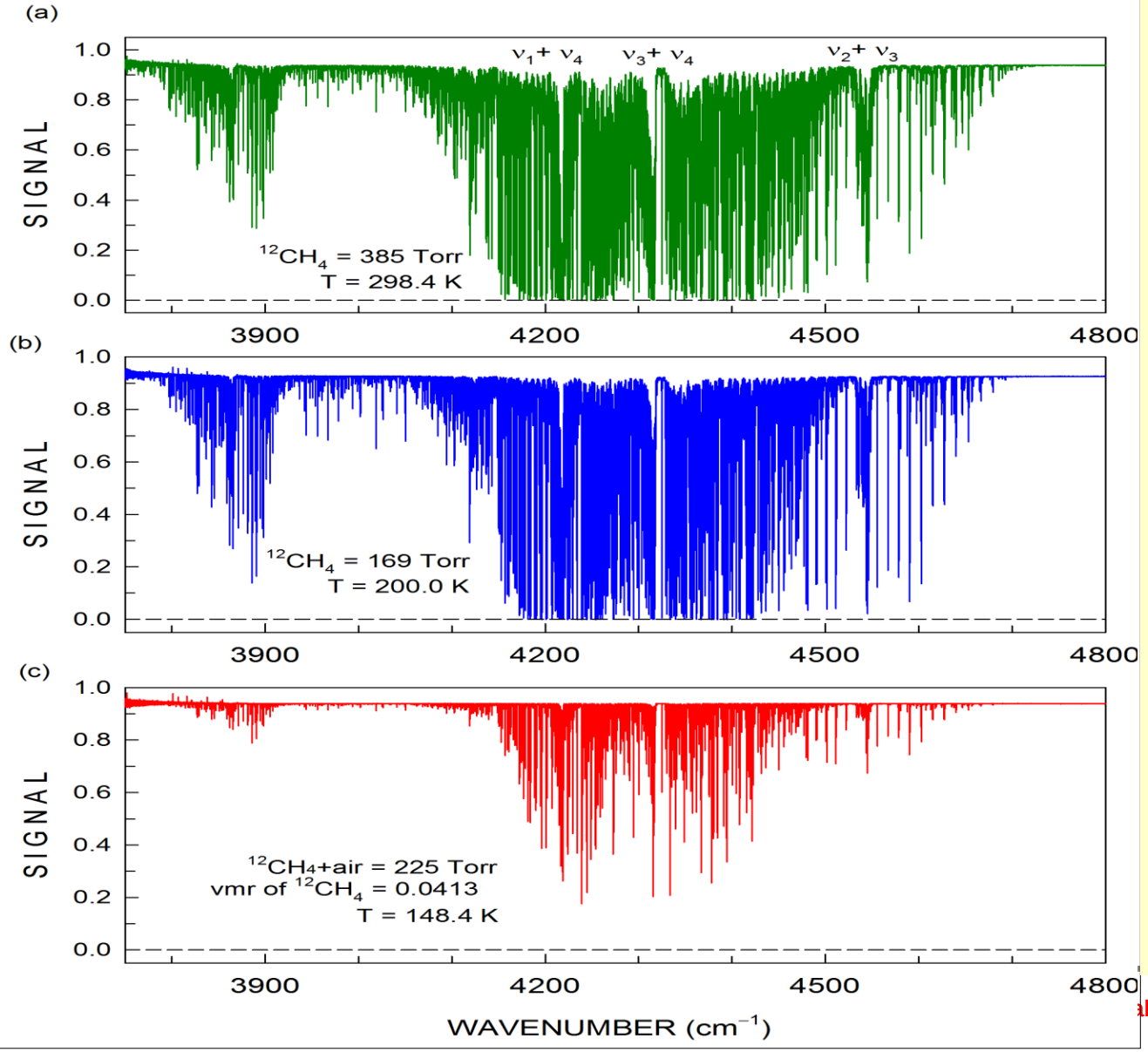
•Enhance knowledge of $^{12}CH_4$ spectra from 4100 - 4500 cm^{-1} and provide complete measurements (P, Q, and R branches) for the following bands:

- $\nu_1+\nu_4$ at 4220 cm^{-1} (3-fold degenerate) F2 vibrational symmetry
- $\nu_3+\nu_4$ at 4320 cm^{-1} (9-fold degenerate) F2 + F1 + E + A1 vibrational symmetry.

Current status of Knowledge in the Methane Octad Spectral Region

- Self- and air-broadened line shape parameters in the $\nu_2+\nu_3$ band of $^{12}CH_4$: 4500–4630 cm^{-1} V.M. Devi *et al.* J. Quant. Spectrosc. Radiat Transfer 152 (2015) 149-165.
- Multispectrum analysis of $^{12}CH_4$ in the 4100-4635 cm^{-1}(Air-broadening) A. Predoi-Cross *et al.* J. Mol. Spectrosc 236 (2006) 201-215.
- Multispectrum analysis of $^{12}CH_4$ in the 4100-4635 cm^{-1}(Self-broadening) A. Predoi-Cross *et al.* J. Mol. Spectrosc 232 (2005) 231-246.
- Line mixing effects in the $\nu_2+\nu_3$ band (Only air-broadening and room-temperature data). A. Predoi-Cross *et al.* J. Mol. Spectrosc. 246 (2007) 65-76.
- Air-broadening and pressure shifts in the 2.3 μm region (room temperature) V. Malathy Devi *et al.* J. Mol. Spectrosc 157 (1993) 95-111.
- Temperature dependences of Lorentz air-broadening and pressure shifts in the 2.3 μm region. V. Malathy Devi *et al.* J. Quant Spectrosc Radiat Transfer 51 (1994) 439-465.

Example of Three of the 14 Spectra Analyzed in this Study



Cell path length = 20.38 cm

(a) Self-broadened $^{12}CH_4$ spectrum with 385 Torr at 298.4 K

(b) Self-broadened $^{12}CH_4$ spectrum with 169 Torr at 200 K

(c) $^{12}CH_4$+air with 225 Torr total pressure and methane volume mixing ratio of 0.04

Experimental Conditions

Configuration and conditions	JPL Bruker IFS 125HR FTS
Spectrum Band pass (cm^{-1})	3750-5200
Light Source	Globar
Beam Splitter	CaF2
Detector	InSb
Resolution (cm^{-1}) (unapodized)	0.005
Maximum Optical Path Difference (cm)	1000
Focal length of the collimator (mm)	418
Aperture diameter (mm)	1.0
Sample pressure Pure CH_4 (Torr)	4.5-385
Total pressure (Torr) for CH_4+air	95-300
VMR of CH_4 in air-broadened spectra	0.004-0.097
Gas temperature (K)	298.4-150
Absorption Path length (cm)	20.38
Cell windows	ZnSe
Scanning time (h)	3-4
Signal-to-noise	~2000-2500
Calibration standards used	H_2O, CO, CH_4

JPL High Resolution Infrared Spectroscopy Laboratory

Source: **V.M. Devi, D.C. Benner, M.A.H.Smith, A.W.Mantz, K. Sung, T.J.Crawford, A. Predoi-Cross , JQSRT, 152(2015)149–165**

Coolable single path gas cell available at the JPL High Resolution Spectroscopy Laboratory

❑Cell characteristics

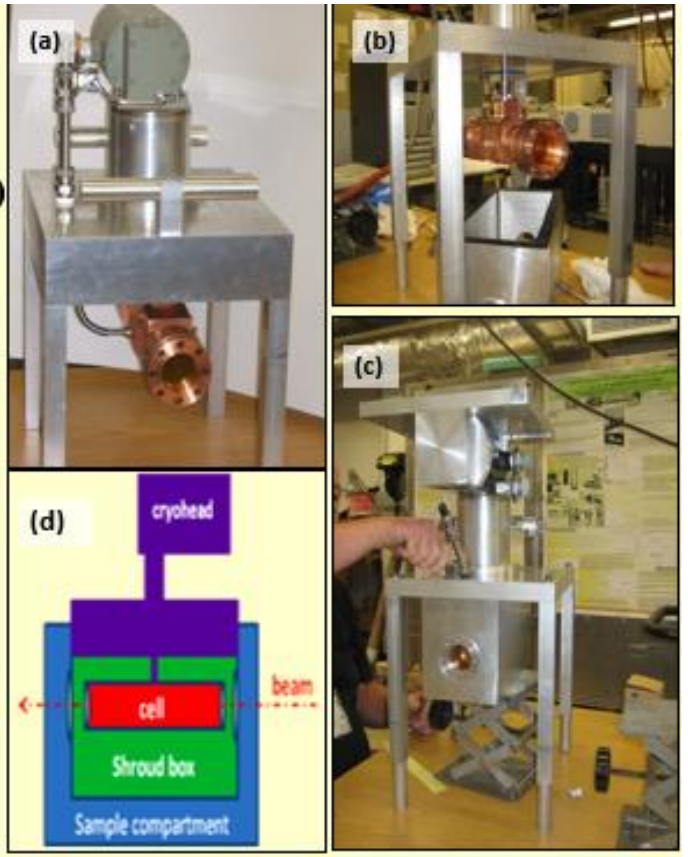
- Single pass coolable cell
- Path length: 20.38 cm (with shroud box)
- Body: copper (oxygen free high conductivity)
- Cell windows: ZnSe (25mm dia. wedged)
- Vacuum box windows (KBr wedged)
- Cold finger: Closed cycle He refrigerator
- Temp-sensors: two Si-diodes
- Heater: two heaters; 25 Ω / 25 W each

•Performance

- Temp achieved so far: 80 – 300 K
- Temp stability: ≤ 0.01 K (for 24 hours)

•Improvement by adding a vacuum box

✓Minimized buildup of ice layers on the windows
✓Achieved measurements at temperatures relevant to planetary atmospheres (300 – 80 K).
✓Increased dramatically the holding time of the cell and improved temperature stability.
✓Shortened time required to cool from room temperature



▲Fig. Coolable cell for Bruker FTS
(a) Initial version of cell prior to modification
(b) Redesigned cell with vacuum box (detached)
(c) The cell with the vacuum box
(d) A schematic diagram of the cell assembly placed inside the sample compartment

Table: Summary of spectra analyzed

Gas sample	VMR of $^{12}CH_4$	Pressure (Torr)	T (K)	Calibration
$^{12}CH_4$	1.00	385.0	298.4	0.9999999885
$^{12}CH_4$	1.00	22.20	250.0	0.9999998113
$^{12}CH_4$	1.00	121.61	250.0	0.9999998275
$^{12}CH_4$	1.00	9.90	200.0	0.9999998140
$^{12}CH_4$	1.00	42.95	200.0	0.9999998070
$^{12}CH_4$	1.00	169.00	200.0	0.9999997685
$^{12}CH_4$	1.00	4.52	148.4	0.9999998142
$^{12}CH_4$	1.00	149.06	148.5	0.9999997806
$^{12}CH_4$+air	0.055	112.60	250.0	0.9999998276
$^{12}CH_4$+air	0.057	254.58	250.0	0.9999998276
$^{12}CH_4$+air	0.073	148.49	200.0	0.9999998418
$^{12}CH_4$+air	0.074	299.95	200.0	0.9999998269
$^{12}CH_4$+air	0.0965	95.07	148.4	0.9999998048
$^{12}CH_4$+air	0.0413	225.37	148.4	0.9999998232

Reference: V.M. Devi, D.C. Benner, M.A.H.Smith, ArlanW.Mantz, K. Sung, T.J.Crawford, A. Predoi-Cross , JQSRT, 152(2015)149–165

Spectroscopic Analysis

- All spectra were fitted simultaneously using the multi-spectrum fitting technique of Benner *et al.* using Voigt profile [1,2]. This program also has the ability to apply speed-dependent Voigt (SDV) profile and quantify line mixing via off-diagonal relaxation matrix formalism [3]. The spectral line parameters to initiate the least-squares fittings were taken from the HITRAN2012 database [4]. Spectral backgrounds, zero transmission levels, FTS phase error, FTS instrumental function were appropriately modeled. Positions calibration: the low pressure methane spectra referenced to residual water lines.

- The following expressions were assumed to determine the self broadening and pressure shift coefficients:

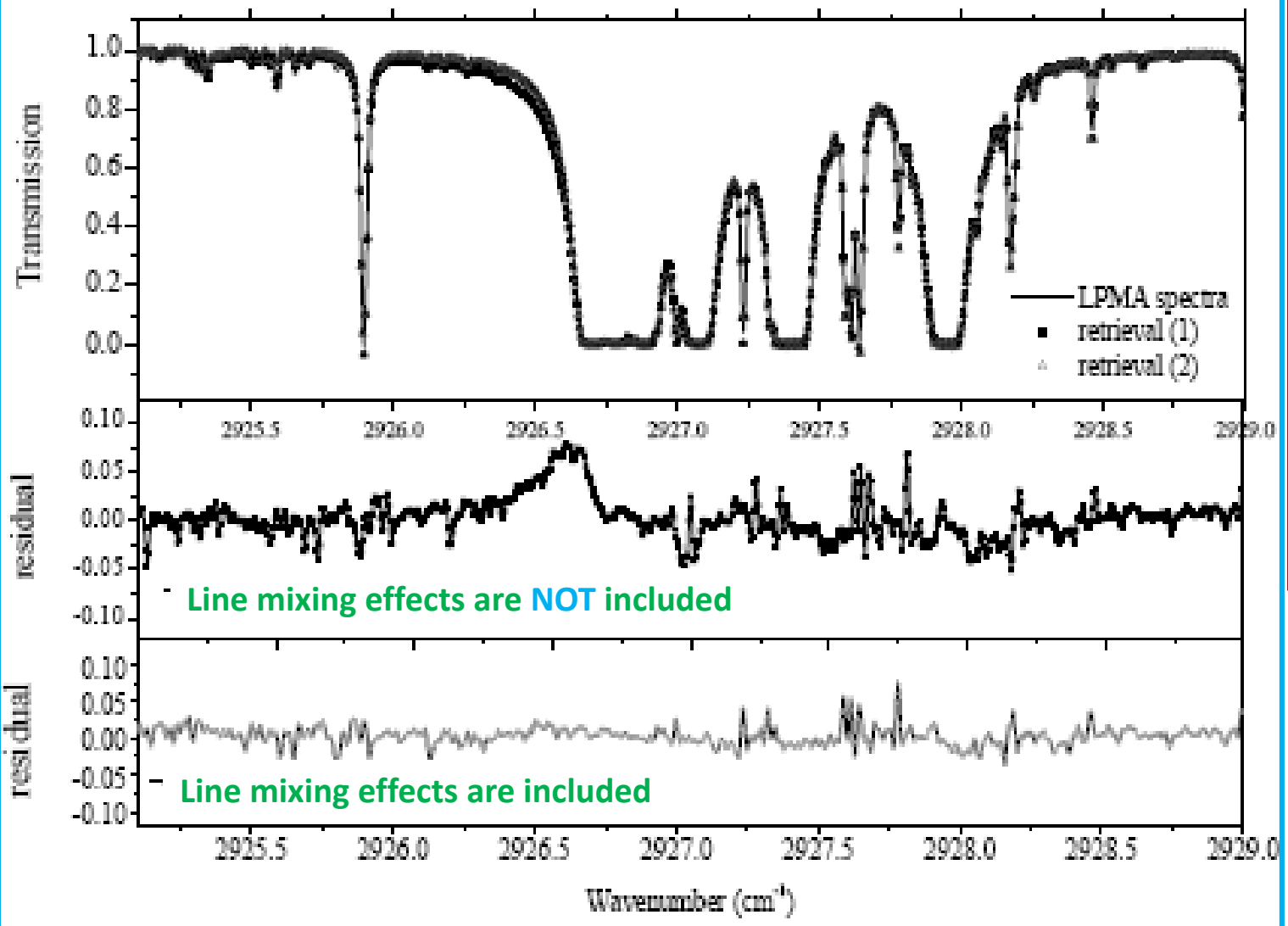
$$b_L(p,T) = p\left[b_L^0(air)(p_0,T_0)(1-\chi)\left[\frac{T_0}{T}\right]^{n1} + b_L^0(self)(p_0,T_0)\chi\left[\frac{T_0}{T}\right]^{n2}\right] \quad (1)$$

$$\nu = \nu_0 + p\left[\delta^0(air)(1-\chi) + \delta^0(self)\chi\right] \quad (2)$$

$$\delta^0(T) = \delta^0(T_0) + \delta'(T - T_0) \quad (3)$$

- In the below equations, $b_L(p,T)$ is the Lorentz half-width at pressure p and temperature T, and δ^0 represent the pressure-induced shift coefficient (in $cm^{-1}\,atm^{-1}$), respectively. b^0_L is the Lorentz half-width of the line at the reference pressure p_0(1 atm) and temperature T_0 (296 K) [5].

Atmospheric spectroscopy – challenges



Observed line mixing for transitions that share the same J″:

A1 → A2 will mix with A2 → A1

E+ → E- will mix with E- → E+

F1 → F2 will mix with F2 → F1

Atmospheric retrievals for the P9 branch of ν_3 band of methane. Mondelain *et al.* JMS (2007).

Relaxation matrix and its elements

W= Relaxation Matrix

W_{jj} is function of Lorentz widths and pressure shifts

W_{jk} (line mixing coefficients = off diagonal elements)

W_{jk} and W_{kj} related by energy density ρ calculated assuming detailed balance via Boltzmann terms where

E'' = lower state energy

C_2 = 2nd radiation constant = 1.4387 K/cm^{-1}

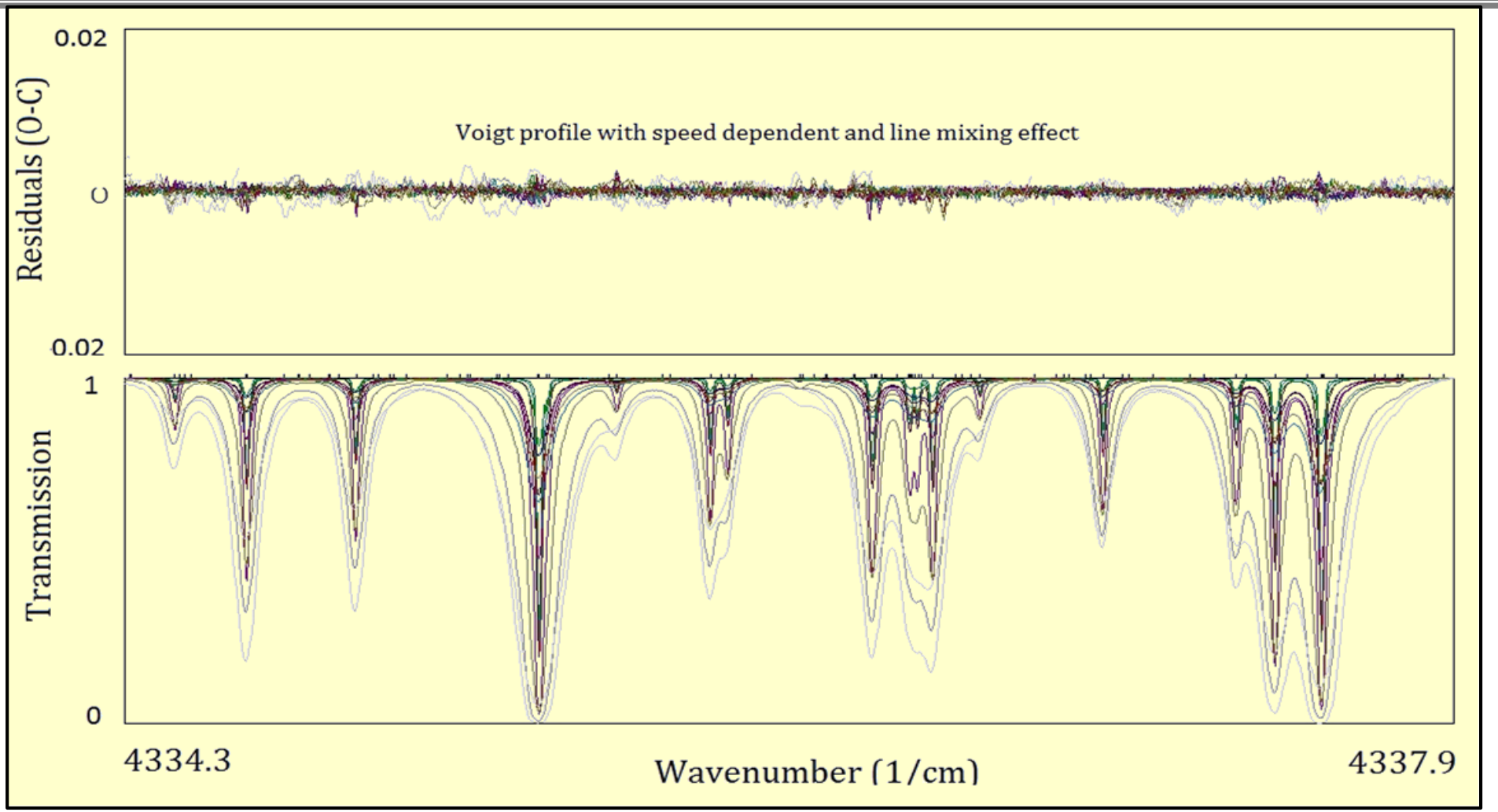
$$W_{jj} = \alpha_{Lj} + i\,\delta_j$$

$$W_{jk} = W_{kj}\frac{\rho_j}{\rho_k}$$

where

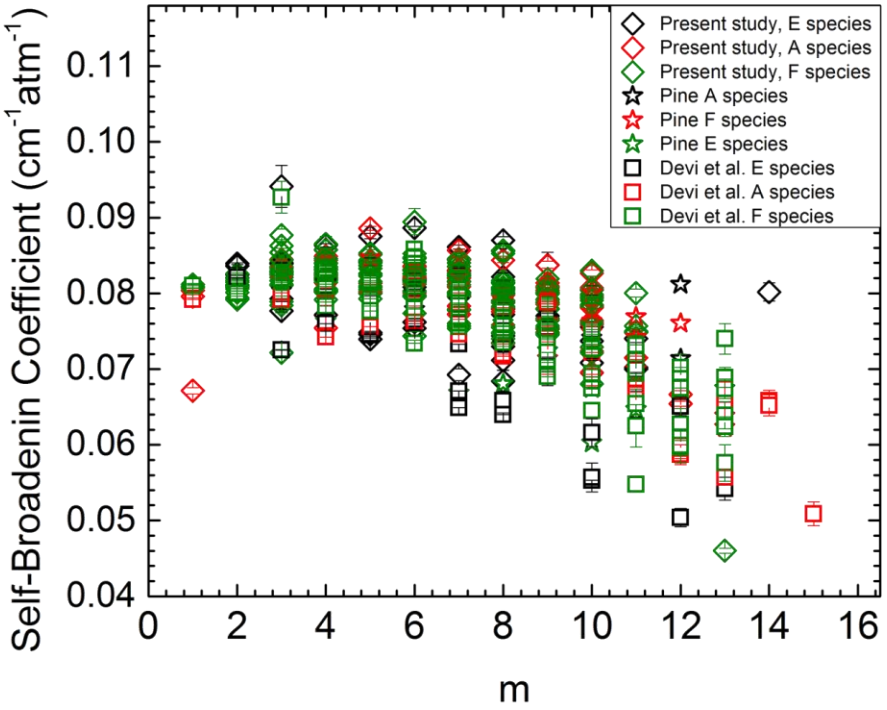
$$\frac{\rho_j}{\rho_k} = \frac{(2J_j''+1)\exp\left[\frac{-C_2E_j''}{T}\right]}{(2J_k''+1)\exp\left[\frac{-C_2E_k''}{T}\right]}$$

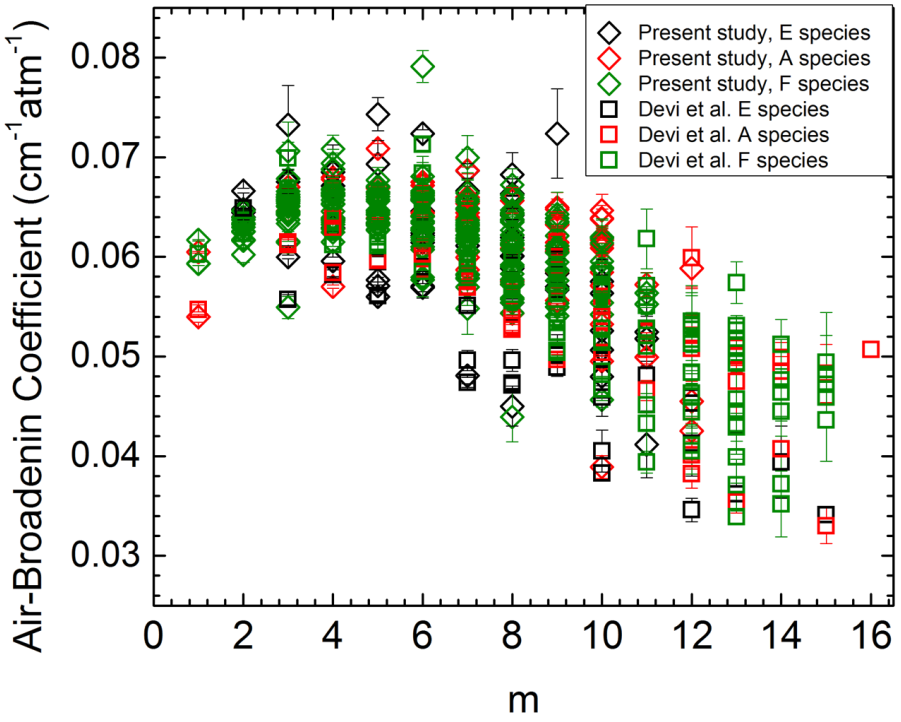
The objective of this analysis of a new set of experimental data is to retrieve line parameters for the $\nu_1+\nu_4$ band, the $\nu_3+\nu_4$ band and for nearby bands in the methane octad region.



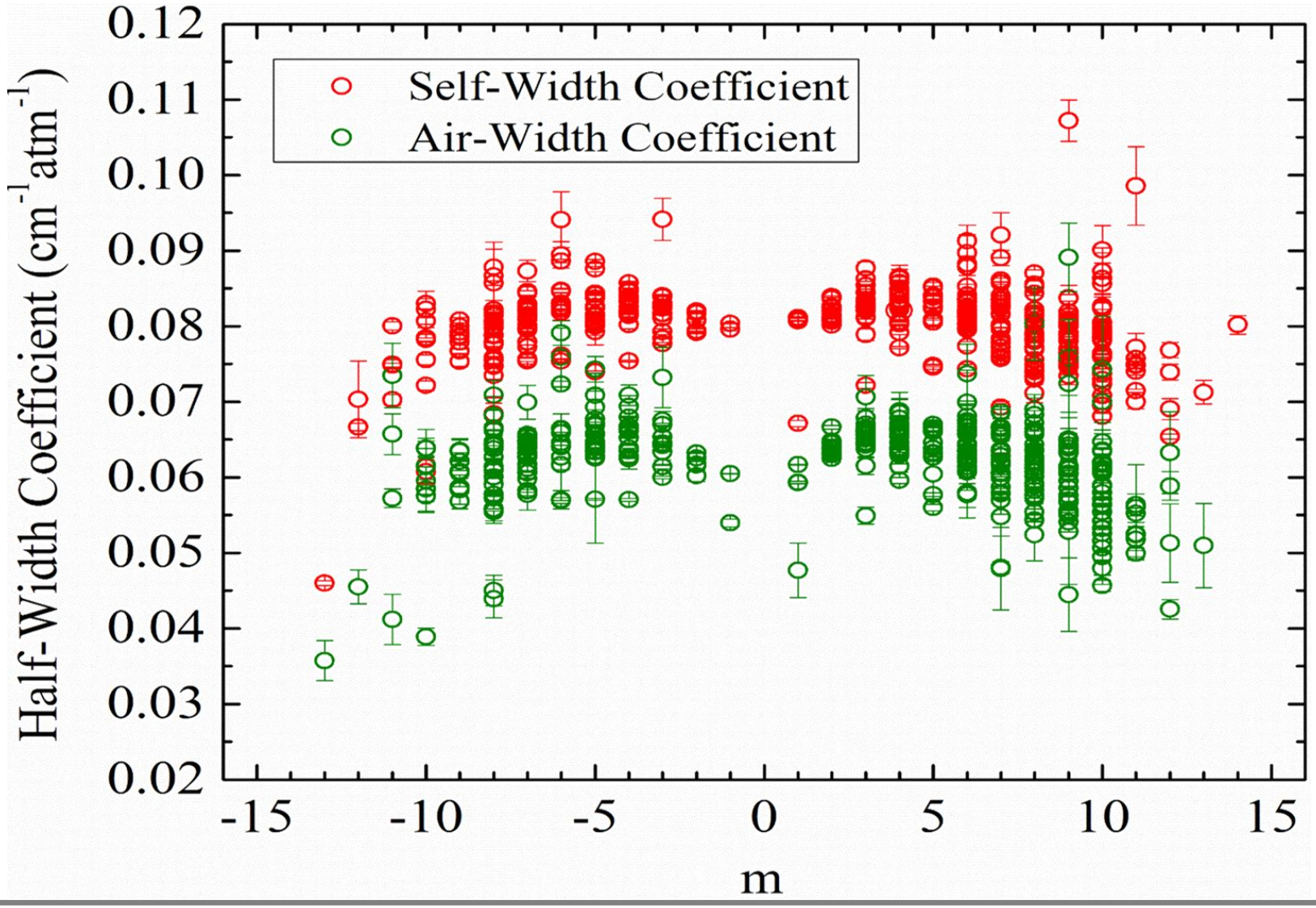
Multispectrum fit in the $\nu_1+\nu_4$ band. Observed spectra and weighted (observed–calculated) residuals resulting from simultaneous fitting of 14 self- and air-broadened spectra.

Measured half-width Coefficients in the range between 4300 and 4400 cm^{-1} plotted as a function of m .

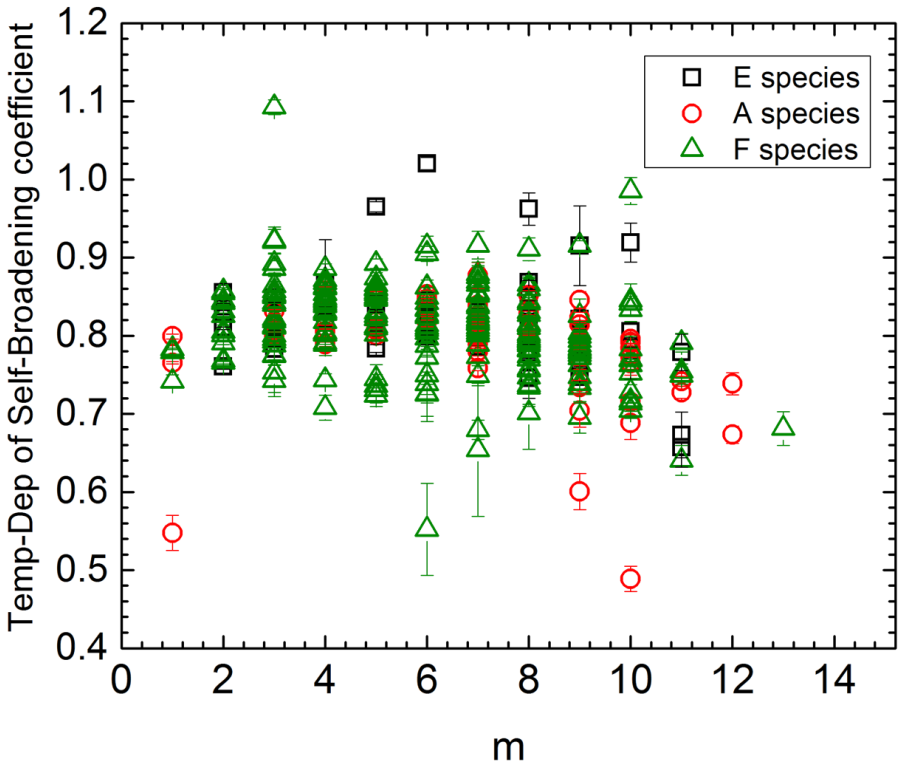


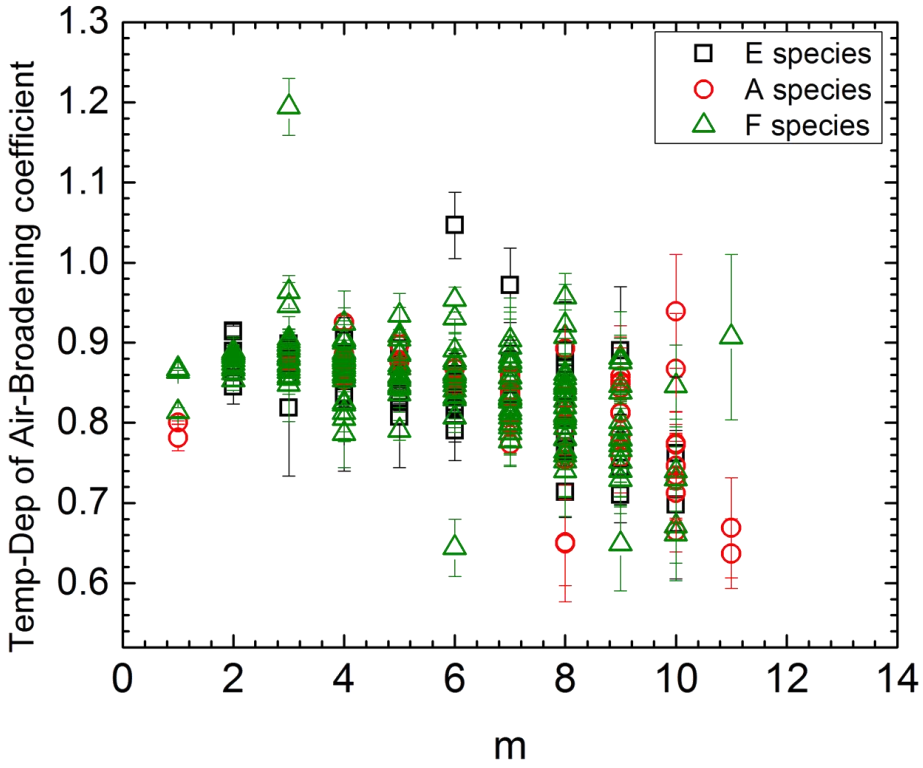


Comparison of Self-Width and Air-Width Coefficients

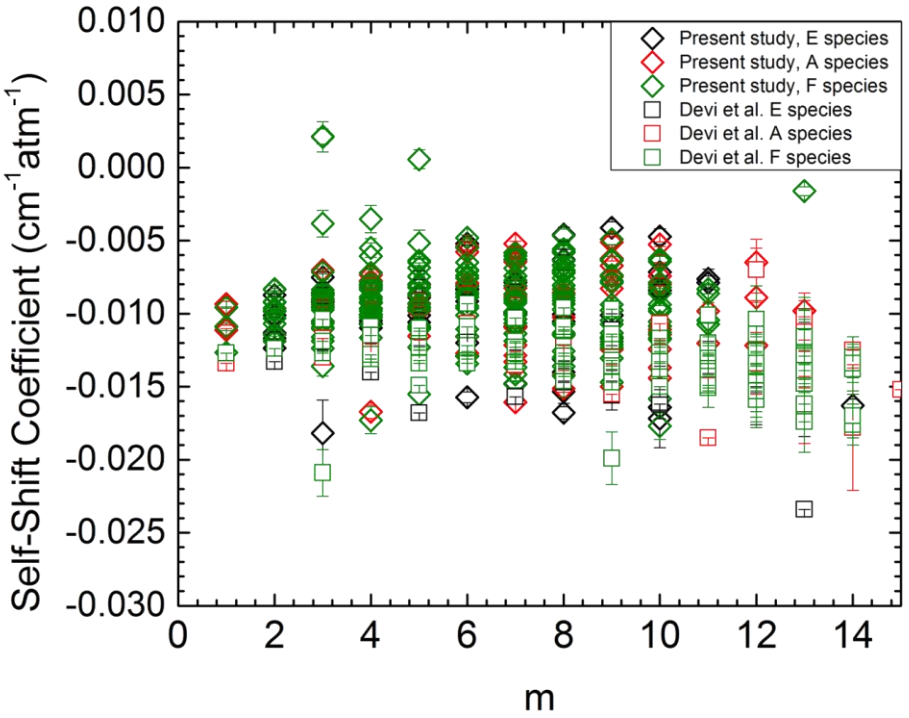


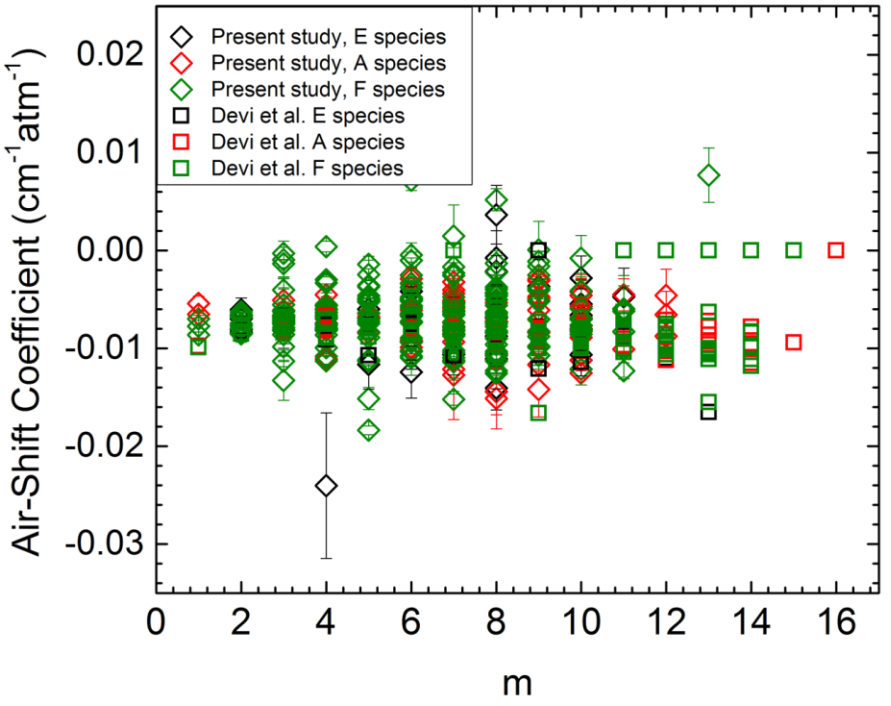
Temperature dependences of half-width coefficients vs. m



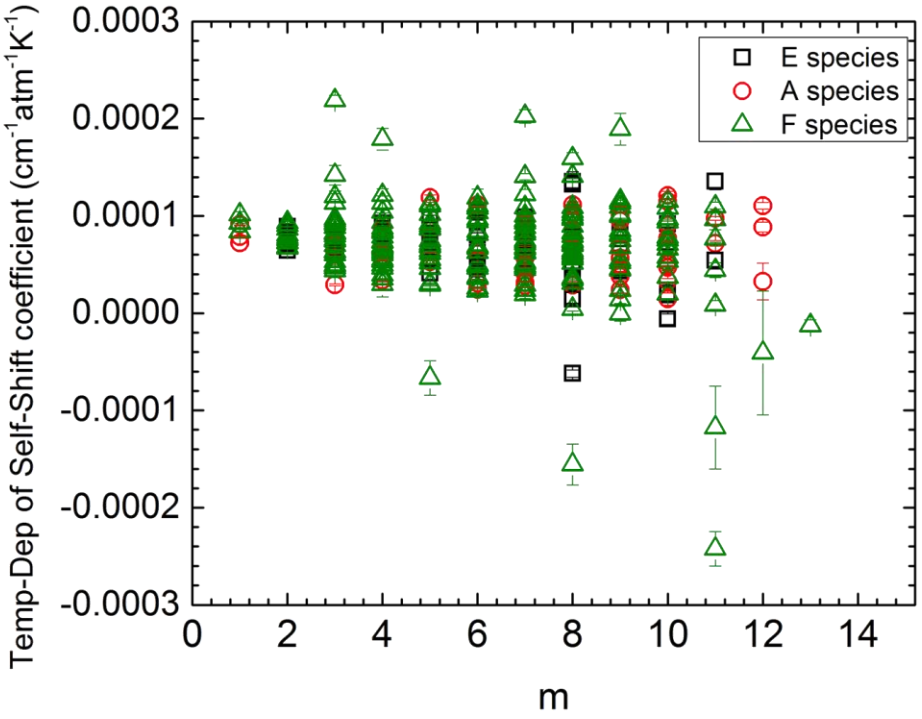


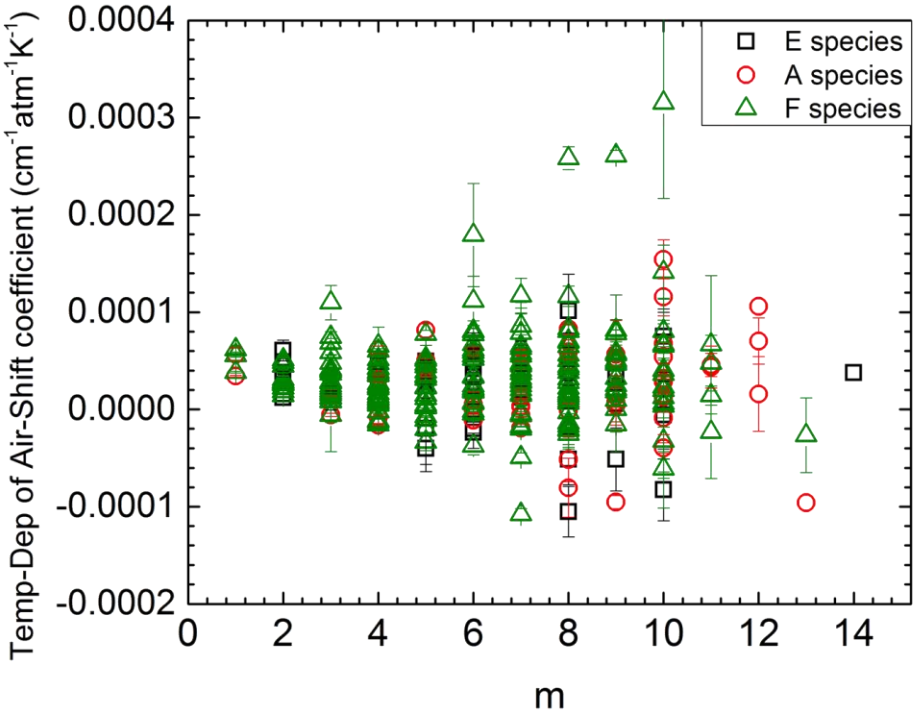
Measured Self- & Air-Shift Coefficients in the range between 4300 and 4400 cm^{-1} plotted as a function of m .





Temperature dependences of Self & Air-Shift Coefficients vs. m





Sample of measured line parameters

$J'\ C'\ n'^{a}$	$J''\ C''n''^{b}$	Positions	S^{c}	% err	$b_L^{0\,d}\times10^3$	% err	$n\ (b_L^0)^{e}\times10^3$	% err	$\delta^{0\,f}$	$\delta'^{g}\times10^5$	SD^{h}
2 A1 8	3 A2 1	4300.367139(3)	6.403	0.03	670	0.1	875	0.2	-0.00713(15)	1.9(1)	0.063(2)
3 F2 22	3 F1 1	4300.052054(4)	7.438	0.02	651	0.2	898	0.4	-0.00786(25)	4.1(2)	0.0438(2)
4 A2 11	4 A1 1	4313.180745(3)	1.563	0.08	678	0.5	925	0.8	-0.01107(52)	6.1(4)	0.0456(5)

[a] Upper state rotational quantum identifications; [b] Lower state rotational quantum identifications. [c] S corresponds to line intensities in units of 10^{-21} cm/molecule and the % errors are listed in the column next to it. [d] b_L^0 are the Lorentz half-width coefficients in cm^{-1} atm^{-1} at 296 K; self- width coefficients are given at the top of each row and air-width coefficients are listed at the bottom. The % errors are listed in the column adjacent to their values.[e] n (b_L^0) represents the temperature dependence exponents of Lorentz half-width coefficients. They have no units. The values at the top of each row correspond to the temperature dependence exponents for self-width coefficients while the bottom values for the air-width coefficients. The % errors are listed under the next columns.[f] δ^0 are the pressure-shift coefficients in cm^{-1} atm^{-1} at 296 K; self- shift coefficients are given at the top of each row and air-shift coefficients are listed at the bottom. The corresponding errors are given in parentheses next to their values.[g] δ' values are the temperature dependences of the pressure-shift coefficients expressed in cm^{-1} atm^{-1} K^{-1}. Values at top row correspond to self shift coefficients and the bottom for air shift coefficients.[h] Speed dependence and have no units.

Sample of measured off-diagonal relaxation matrix element coefficients in the $\nu_1+\nu_4$ band (in cm^{-1} atm^{-1})

The significant influence of line mixing is observed in atmospheric spectra recorded using remote sensing instrumentation. At elevated pressures the line mixing effect has to be taken into account. This effect is implemented in the fitting program according to the off-diagonal relaxation matrix element coefficients.

Identifi-cations	*Line mixing pairs*	*Line Position* (cm^{-1})	*Self-Mixing* ($cm^{-1}atm^{-1}$)	*Air-Mixing* ($cm^{-1}atm^{-1}$)	*T-dep. of self-mixing*	*T-dep. of air-mixing*
P(3)	2F1 ←3F2	4299.788	0.000753	0.00124	0.8(F)	0.8(F)
	2F2 ←3F1	4299.914				
Q(9)	9F1 ←9F2	4313.0702	0.008137	0.004516	0.82(F)	0.88(F)
	9F2 ←9F1	4313.1003				
Q(7)	7F2 ←7F1	4315.952	0.005023	0.010412	0.8(F)	0.8(F)
	7F1 ←7F2	4316.233				
Q(6)	6F1 ←6F2	4322.1569	0.001250	0.00125	0.8(F)	0.8(F)
	6F2 ←6F1	4322.1903				
Q(7)	7F2 ←7F1	4350.7085	0.004858	0.01174	0.8(F)	0.8(F)
	7F1 ←7F2	4350.9427				
R(9)	9A1 ←8A2	4355.749	0.011190	0.01302	0.8(F)	0.8(F)
	9A2 ←8A1	4355.765				

Conclusions

- This study reports temperature dependencies of self- and air-broadened half-width, pressure-induced shift and line mixing coefficients in the $\nu_1+\nu_4$ and $\nu_3+\nu_4$ bands of methane.

- 14 room- and cold-temperature spectra are fitted simultaneously using a multispectrum fitting technique in the 4500-4500 $cm^{-1.}$

- The measured temperature dependence exponents for self- and air-broadening were close, in the majority of cases. In general, the temperature dependence exponents for air-broadened width coefficients were slightly higher compared to those for self-broadened width coefficients. The temperature dependence for self-shift coefficients were much higher compared with those for air-shift coefficients.

- Even with data taken in the 150-298 K range we were unable to determine the temperature dependence exponents of line mixing.

References

[1] D.C. Benner *et.al. J. Quant. Spectrosc. Radiat. Transfer* **53** 705-721 (1995).
[2] Letchworth KL, Benner DC. *J Quant Spectrosc Radiat Transfer* **92** 107-173 (2007).
[3] A. Levy, N. Lacome, C. Chackerian, *MA: Academic Press* 261-337 (1992).
[4] L.S. Rothman *et al. J. Quant. Spectrosc. Radiat. Transfer* **130** 4-50 (2013).
[5] A. Predoi-Cross *et.al. J. Mol. Spectrosc.* **232** 231-246 (2005).

Acknowledgements

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