Spectroscopic Study of Self- and Air-broadened Methane in the 4100-4300 cm^{-1} Region

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Objectives

The methane band system in the 2.3-μm region is of interest not only for measurements of CH_4 atmospheric profiles, but also because it overlaps the spectra of other atmospheric molecules such as CO and HF

The level of accuracy for line shape parameters in the Octad region (2.3-μm region) of both $^{12}CH_4$ and $^{12}CH_4$ is less than in the lower polyads (Dyad and Pentad).

The information available in this spectral region does not meet the desired accuracy requirements to support remote sensing applications such as **ASCENDS** (**A**ctive **S**ensing of **C**O_2 **E**missions over **N**ights, **D**ays and **S**easons) retrievals.

Our ongoing laboratory effort has been to measure the temperature dependences of Lorentz self- and air-broadened halfwidth, pressure-induced shift and line mixing (off-diagonal relaxation matrix elements) coefficients for Octad transitions of $^{12}CH_4$. Previous studies of the same set of spectra have resulted in parameters for the **4500-4630 cm^{-1}** [Malathy Devi et al., JQSRT 152 (2015) 149-166] and the **4300-4500 cm^{-1}** [Hashemi et al., JQSRT 186 (2017) 106-117] regions.

A multispectrum fitting technique including the speed dependent Voigt profile and full line mixing is applied to fit several spectra (room temperature and colder) simultaneously.

Our prior $^{12}CH_4$ line shape studies in the 4100-4300 cm^{-1} region

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

Temperature dependence of Lorentz air-broadening and pressure-shift coefficients of $^{12}CH_4$ lines in the 2.3-μm spectral region, V. Malathy Devi et al., J. Quant. Spectrosc. Radiat. Transfer 51 (1994) 439-465.

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

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

Other research groups are investigating the N_2-broadened line shape parameters for the Octad bands.

Experimental setup and gas 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)	100
Focal length of the collimating lens (mm)	418
Source aperture diameter (mm)	1.0
Sample pressures of pure CH_4 (Torr)	4.5-385
Total sample pressure (Torr) for CH_4+air	95-300
Volume mixing ratio of CH_4 in air-broadened spectra	0.04-0.097
Gas sample temperature (K)	298-150
Absorption Path length (cm)	20.38
Cell windows	ZnSe
Vacuum box windows	KBr (wedged)
Scanning time (h)	3-4
Signal-to-noise	~2000-2500
Calibration standards used	H_2O^a, CO^b,CH_4^b

760 Torr = 1 atm (101.325 kPa= 1.01325 bar)

[a] Relative calibration of wavenumber scales with respect to ν_3 H_2O lines from residual gas in FTS chamber

[b] Absolute calibration with respect to CH_4 lines [Predoi-Cross *et al.*, J. Mol. Spectrosc. 232 (2005) 231-246]

Experimental Conditions of the Spectra Analyzed

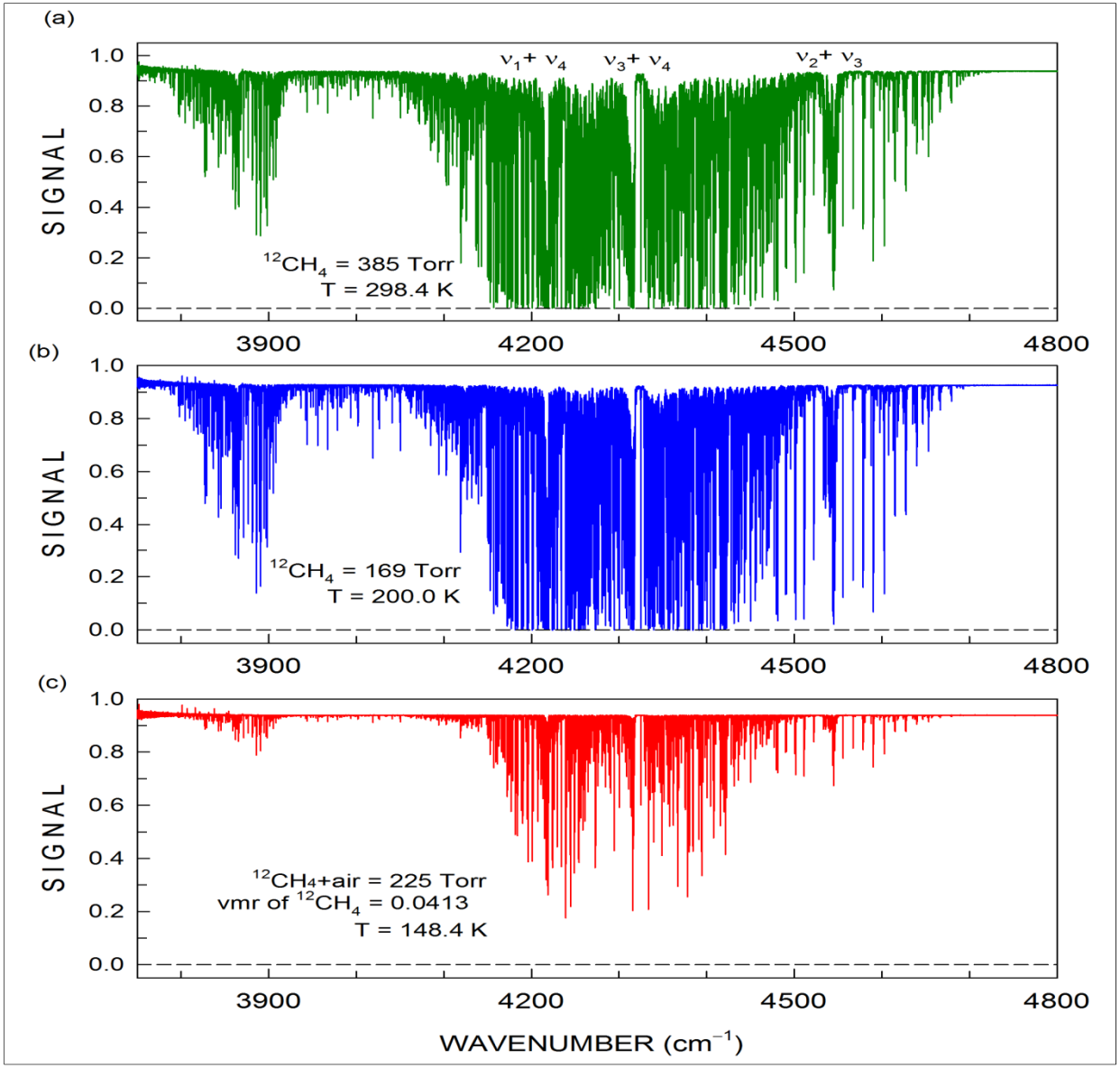
Spectrum #	Gas sample	Volume mixing ratio	Pressure (Torr)	T (K)	Calibration Correction
bk2534	$^{12}CH_4$	1.00	385.0	298.4	0.9999999885
bk2557	$^{12}CH_4$	1.00	22.20	250.0	0.9999998113
bk2556	$^{12}CH_4$	1.00	121.61	250.0	0.9999998275
bk2551	$^{12}CH_4$	1.00	9.90	200.0	0.9999998140
bk2550	$^{12}CH_4$	1.00	42.95	200.0	0.9999998070
bk2549	$^{12}CH_4$	1.00	169.00	200.0	0.9999997685
bk2540	$^{12}CH_4$	1.00	4.52	148.4	0.9999998142
bk2537	$^{12}CH_4$	1.00	149.06	148.5	0.9999997806
bk2560	$^{12}CH_4$+air	0.058	112.60	250.0	0.9999998276
bk2559	$^{12}CH_4$+air	0.058	254.58	250.0	0.9999998276
bk2554	$^{12}CH_4$+air	0.076	148.49	200.0	0.9999998418
bk2553	$^{12}CH_4$+air	0.076	299.95	200.0	0.9999998269
bk2543	$^{12}CH_4$+air	0.102	95.07	148.4	0.9999998048
bk2544	$^{12}CH_4$+air	0.043	225.37	148.4	0.9999998232

760 Torr = 1 atm =101.325 kPa = 1.01325 bar

The $^{12}CH_4$ sample was 99.95% enriched in ^{12}C; cell length was 20.38 cm.

Additional spectra for background and calibration were recorded but not listed here

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 at 148.4 K and methane volume mixing ratio of 0.04

Equations used to retrieve Lorentz self- and air-broadened widths, shifts and their temperature dependences

The self- and air-broadened Lorentz half widths, self- and air- pressure-induced shift coefficients and their temperature dependences were measured on a line-by-line basis in the constrained multispectrum fits defined in the following Eqs.

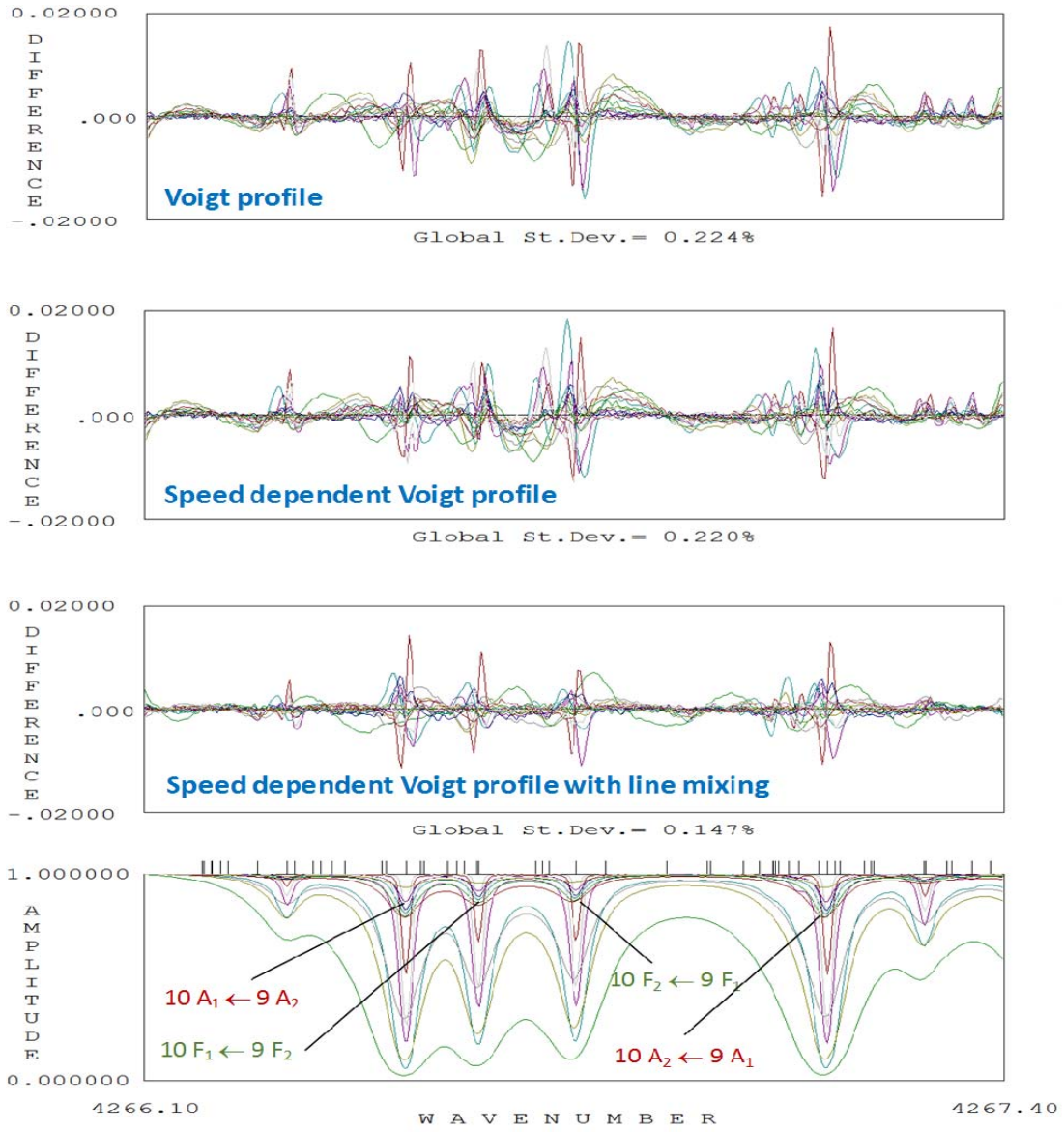
$$b_L(p,T) = p\left[b_L^0(air)(p_0,T_0)(1-\chi)\left[\frac{T_0}{T}\right]^{n1} + b_L^0(self)(p_0,T_0)\chi\left[\frac{T_0}{T}\right]^{n2}\right]$$

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

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

b_L^0 and δ^0 represent pressure broadening and pressure-shift coefficients (in cm^{-1} atm^{-1} at 296 K), respectively. $b_L(p,T)$ is the Lorentz half width (in cm^{-1}) of the spectral line at pressure p and temperature T, $b_L^0(Gas)(p_0,T_0)$ is the Lorentz half width coefficient of the line at the reference pressure p_0 (1 atm) and temperature T_0 (296 K) of the broadening gas (either air or CH_4), and χ is the ratio of the partial pressure of CH_4 to the total sample pressure in the cell. Temperature dependences of air- and self-broadened half width and pressure-induced shift coefficients were determined separately for each transition within the same fit.

Example: Multispectrum fit of R(9) in the $\nu_1+\nu_4$ band



(Top panel) Weighted (obs-calc) fit residuals for the **Voigt line profile**

(Panel 2) Weighted (obs-calc) fit residuals for the **Speed dependent Voigt line profile**

(Panel 3) Weighted (obs-calc) fit residuals for the **Speed dependent Voigt line profile with Line mixing**

(Bottom panel) The 14 observed spectra. *The short vertical lines at the top mark positions of transitions included in the fit.*
The two pairs of lines mixing in this manifold are annotated in red (A species) and green (F species).

Speed dependence

We used the quadratic implementation of the speed-dependent Voigt profile [Rohart et al., J. Mol. Spectrosc. 168 (1997) 222-233]. In this approach, the Lorentz half width can be related to the mean speed of the molecules, v_m, the most probable speed, v_p, and the speed of the molecules at collision, v, using the expression:

$$b_L^o = b_L^o(v_m)\left\{1 + S\left[\left(\frac{v}{v_p}\right)^2 - c\right]\right\}$$

The speed dependence parameter is S, and $c = \frac{3}{2}$.

- The default value for the speed dependence parameter in HITRAN2016 is **0.08** for all methane transitions in the 4100-4300 cm^{-1} region.
- We used as the initial default value the speed-dependence parameter calculated by the algorithm introduced by **V. Kochanov [JQSRT 189 (2017) 18-23]** assuming $q = 6$ in the effective potential $V \sim r^{-q}$ (where r is the displacement from equilibrium position) for a mixture of methane and dry air; this value was ***S* = 0.172**.
- Examining the results from our preliminary fits, we noticed that the average value of retrieved speed-dependence parameters was 0.13, which is close to the value of **0.132** obtainable using a parameter $q = 5$. The final fits assumed this default value for all transitions where S could not be retrieved.

Line Mixing

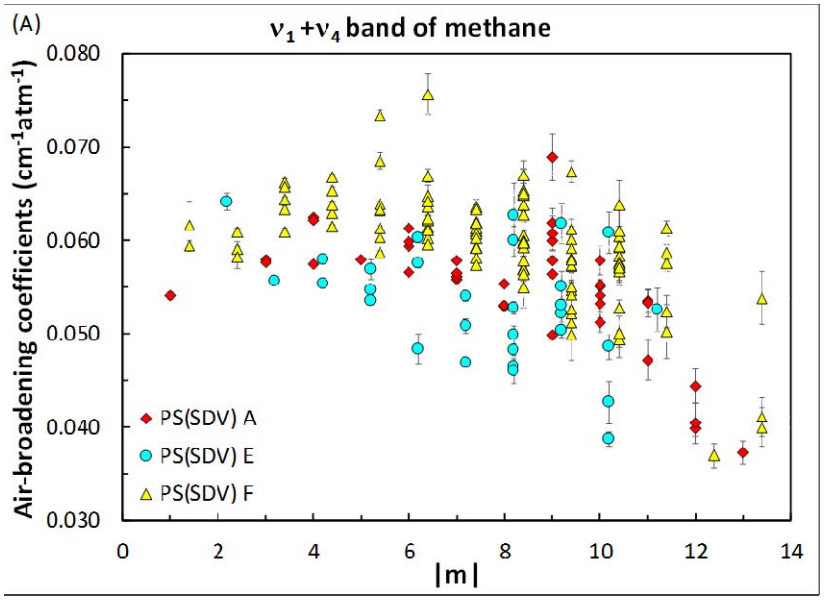
Line mixing is modeled in our multispectrum fitting software using the off-diagonal relaxation matrix elements first introduced by Levy *et al.* [in K. Narahari Rao and A. Weber, eds., *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*, Boston, MA: Academic Press (1992) pp. 261-337], where the physical state of the molecules at a given moment is related to the elements of the **relaxation matrix**, ***W***. The off-diagonal elements of ***W*** quantify the coupling between pairs of absorption lines.

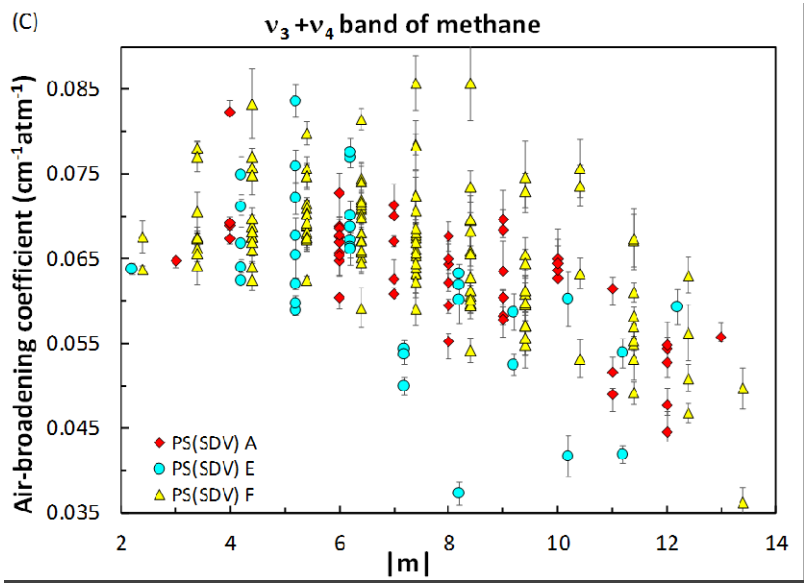
The units for the off-diagonal relaxation matrix elements (ORME) are the same as for Lorentz widths and pressure shifts (cm^{-1} atm^{-1} at 296 K).

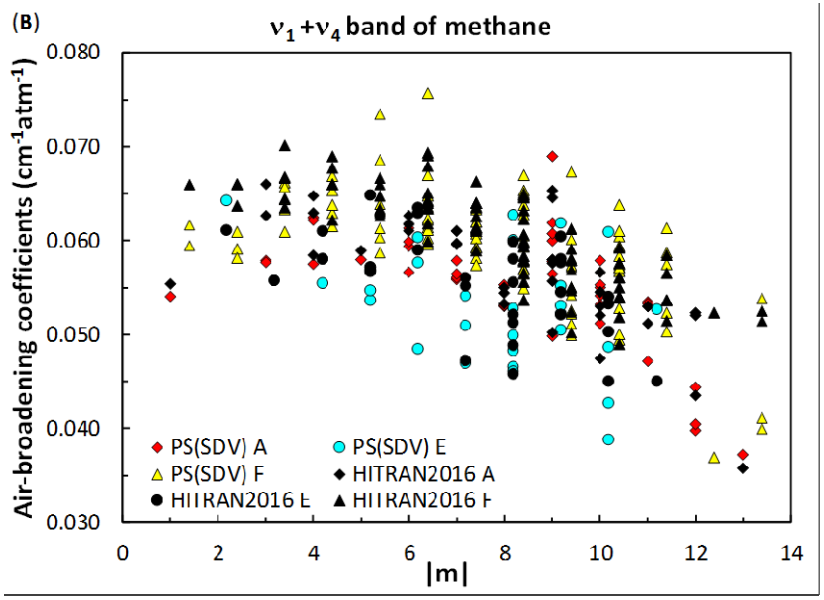
The temperature-dependence law for ORME is considered to be the same as for the Lorentz half-widths with the **temperature-dependence exponent 0.8** for methane, as recommended by Malathy Devi *et al.* [JQSRT 152 (2015) 149-165].

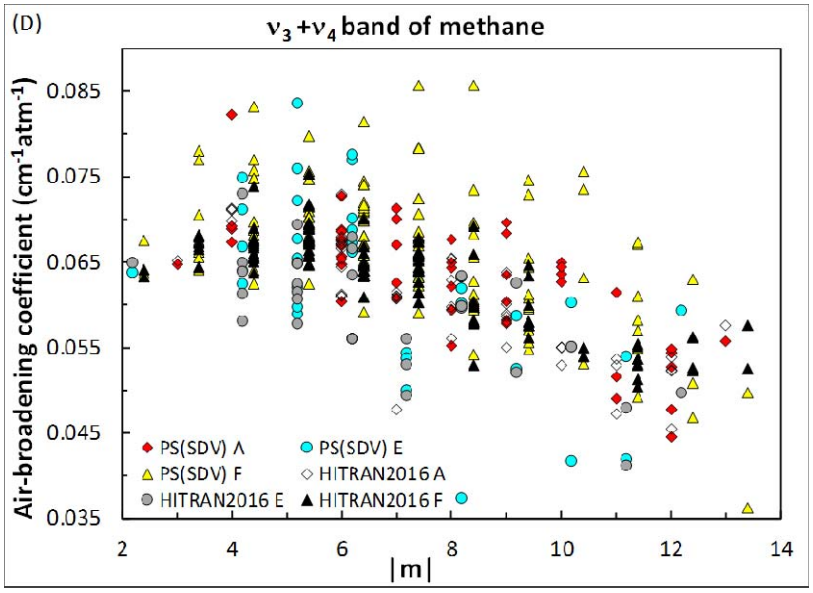
From our multispectrum fits we have determined ORME for 21 pairs of methane transitions (both self- and air-broadened) in the 4100-4300 cm^{-1} spectral region.

Results: Air-broadened half widths

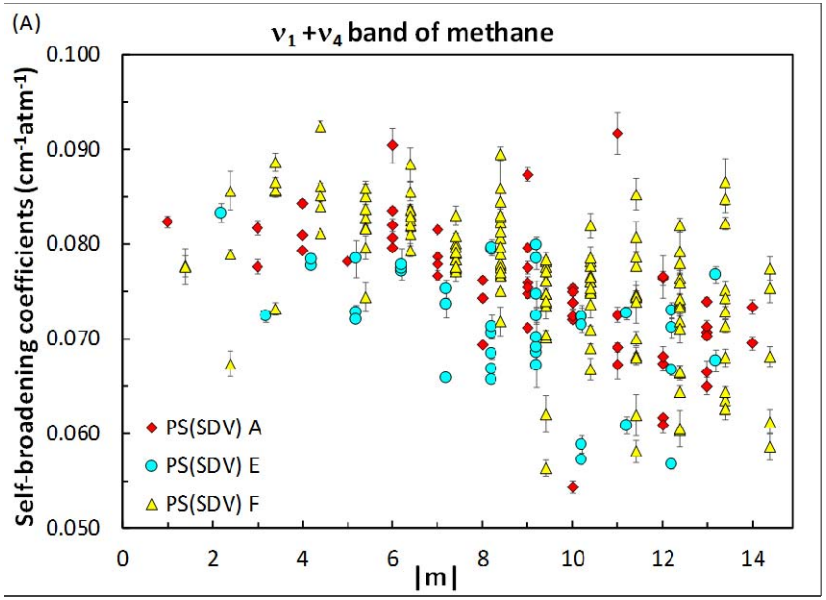


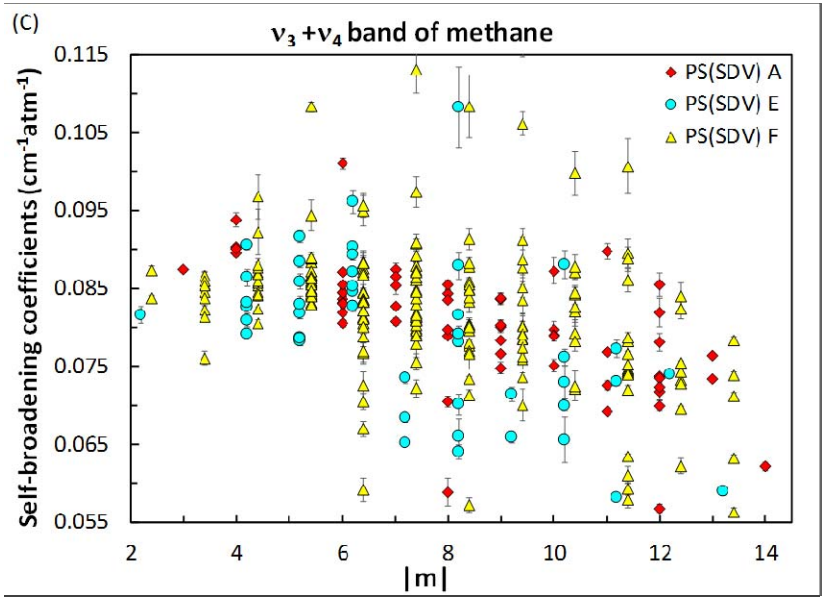


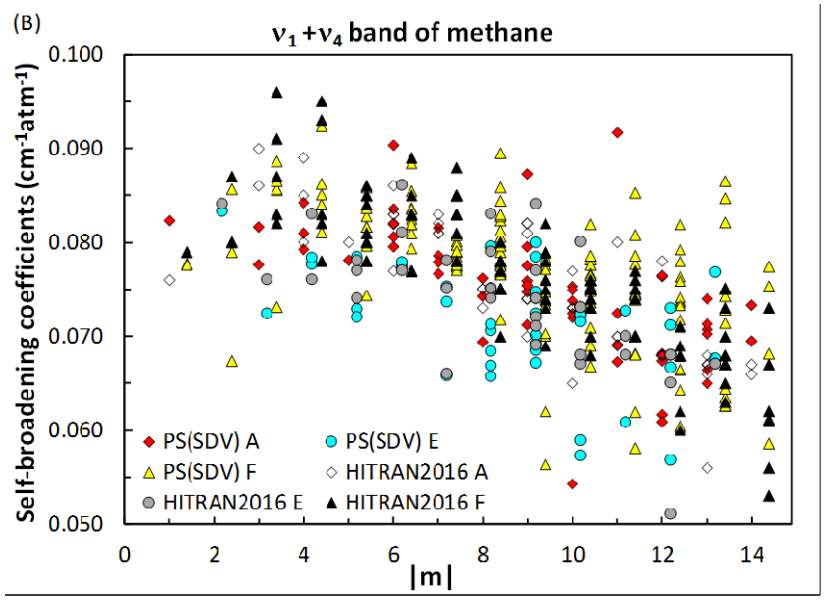


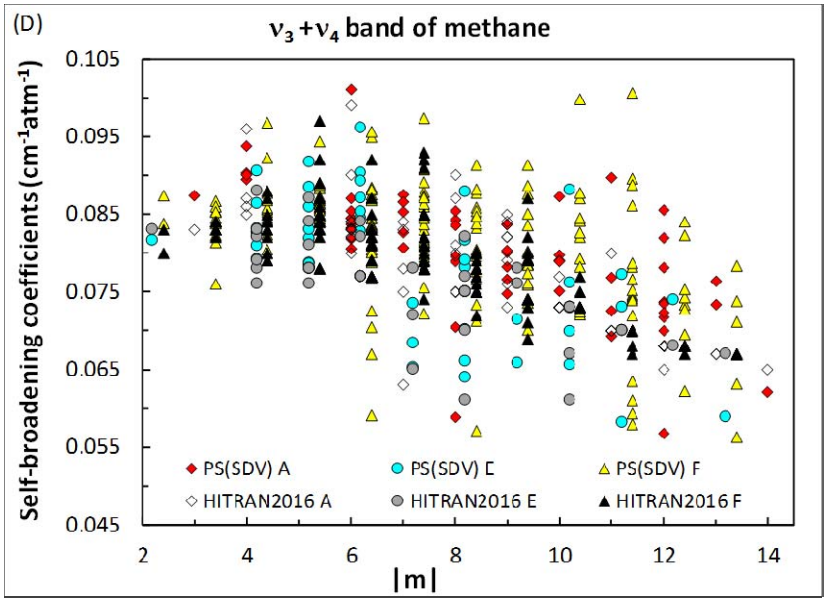


Results: Self-broadened half widths

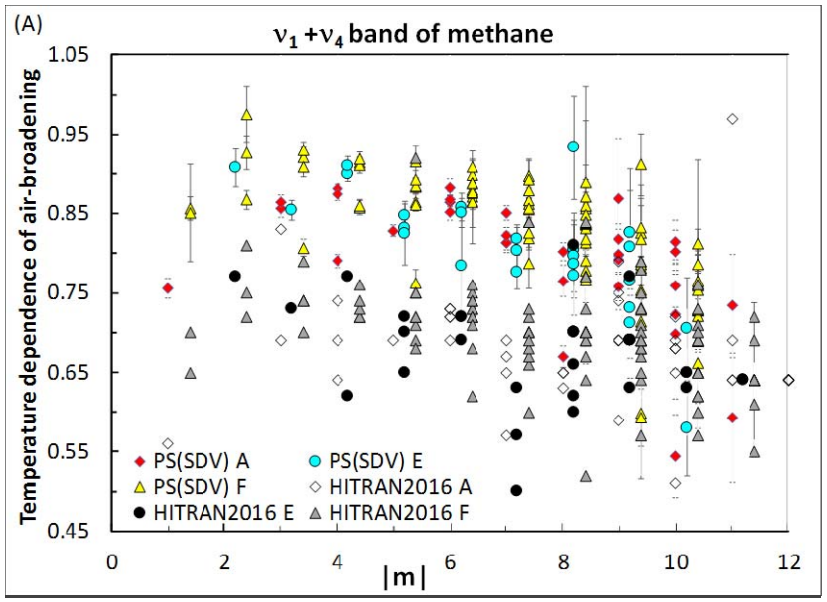


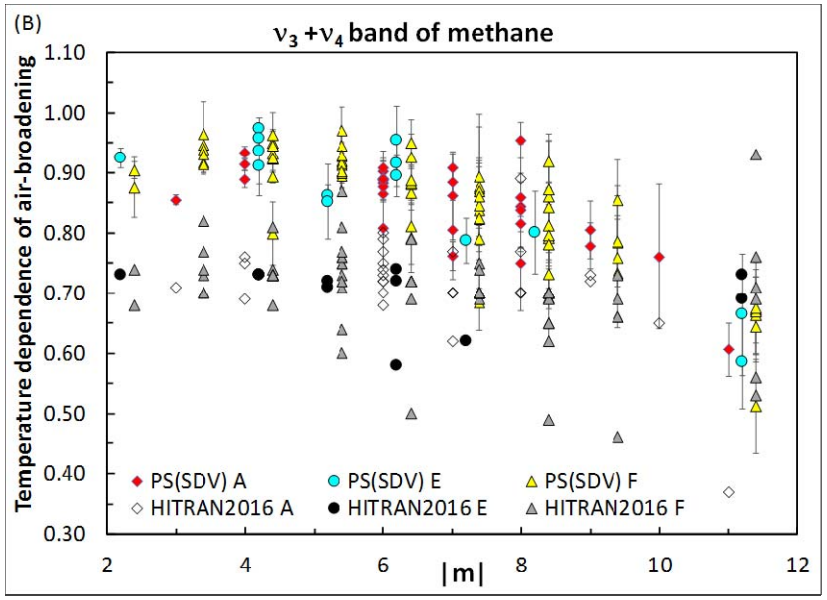




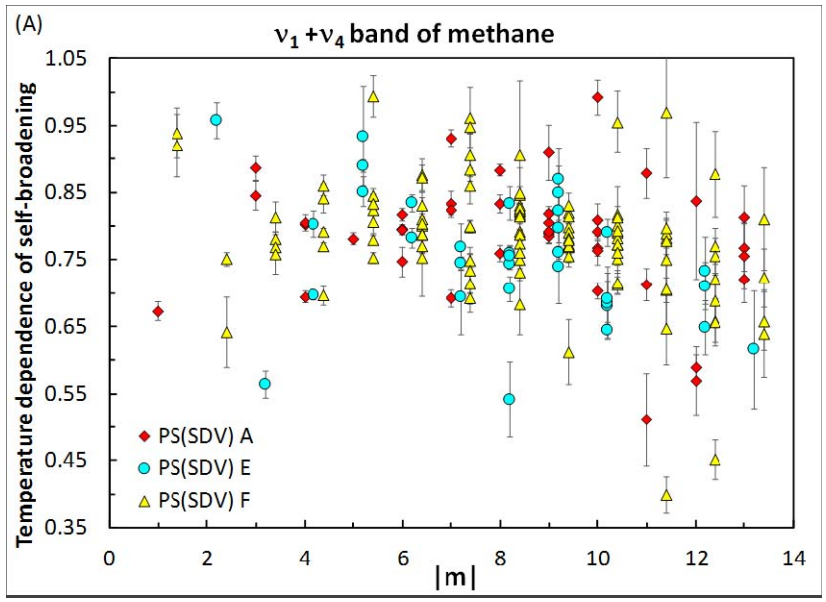


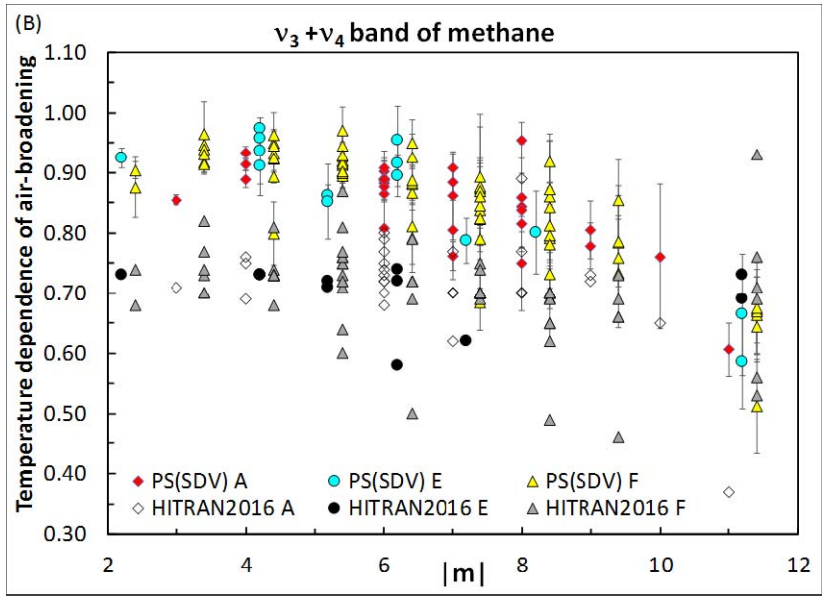
Air-width temperature dependences



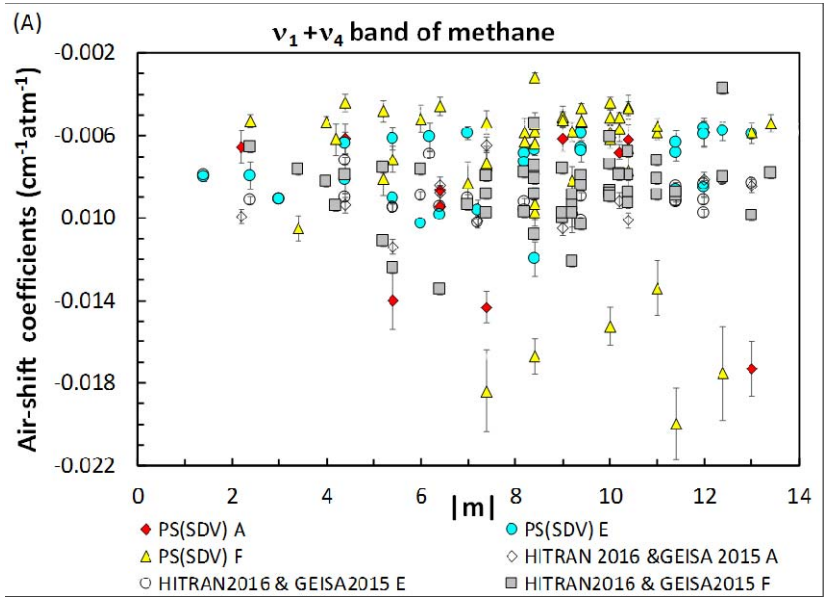


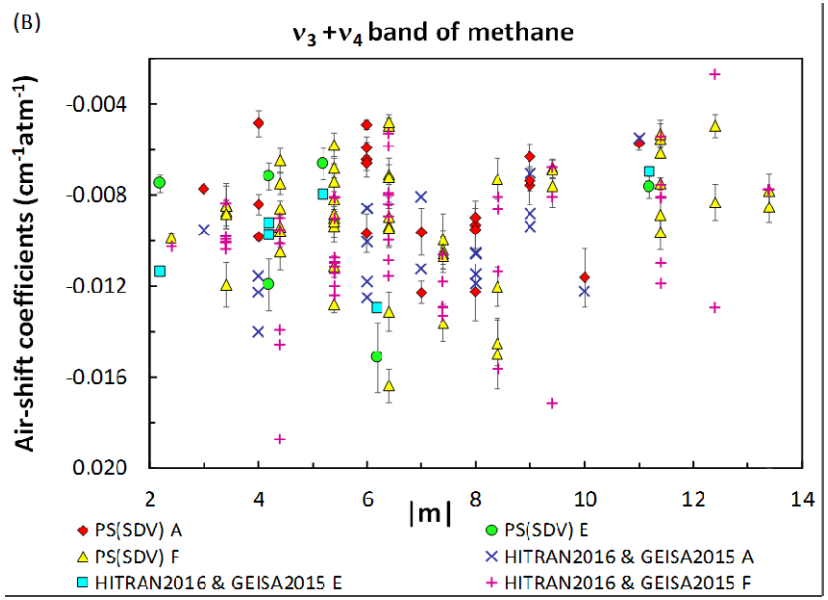
Self-width temperature dependences



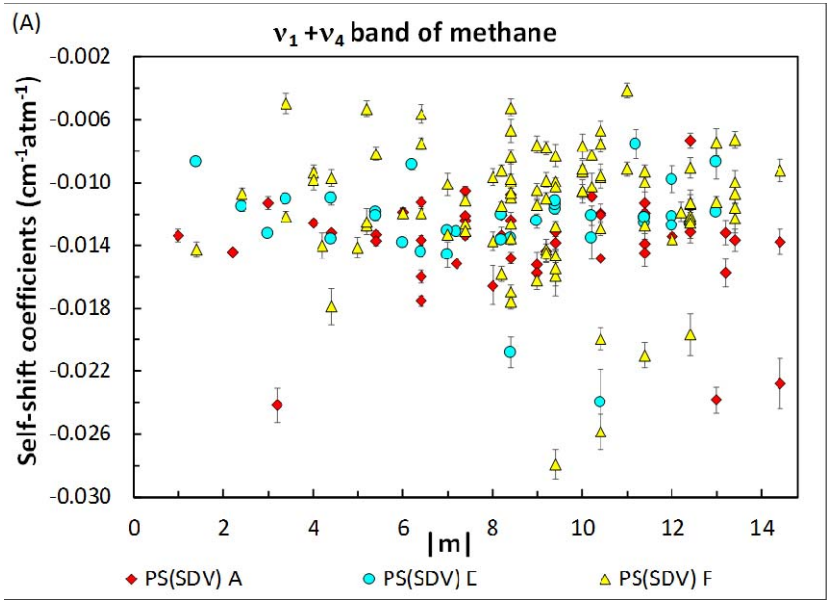


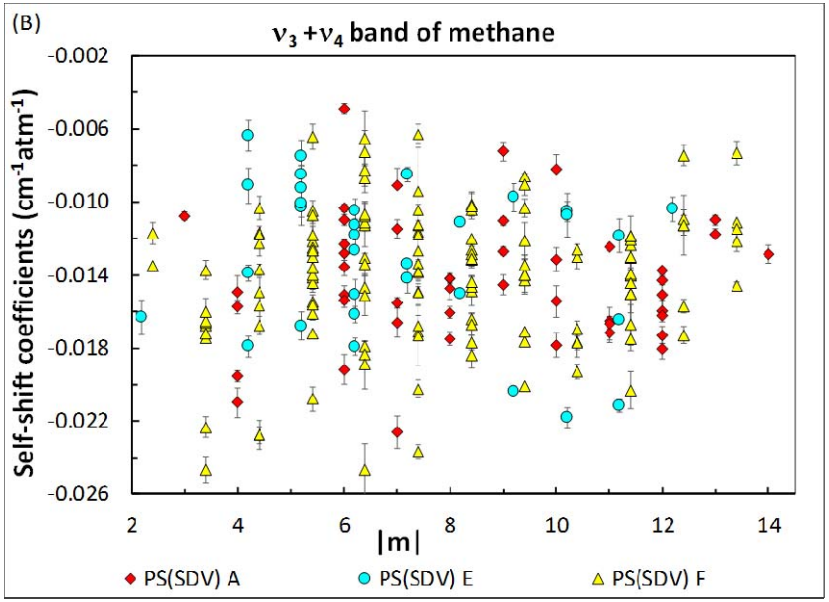
Air-shift Coefficients



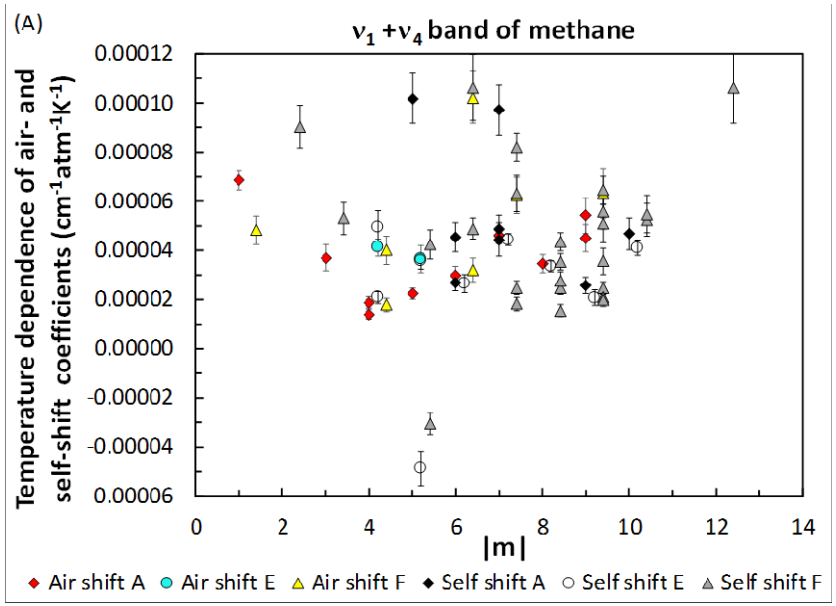


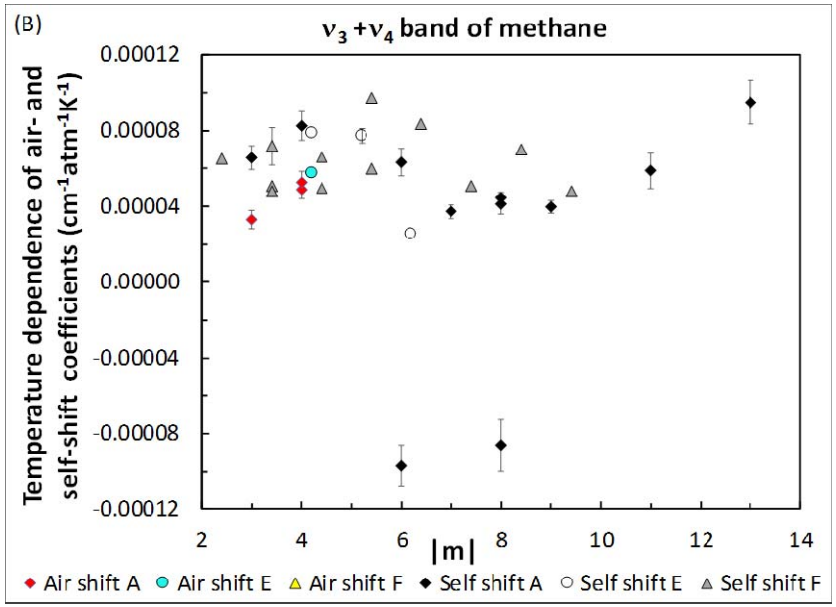
Self-shift Coefficients



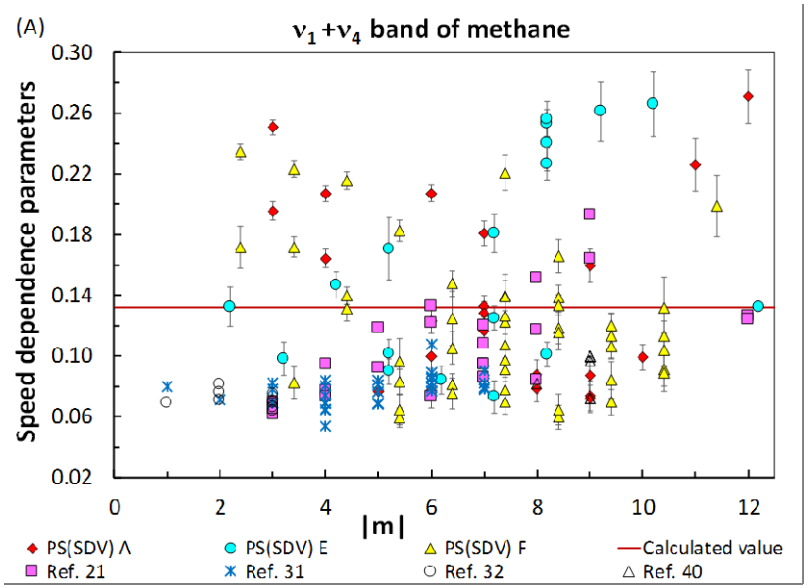


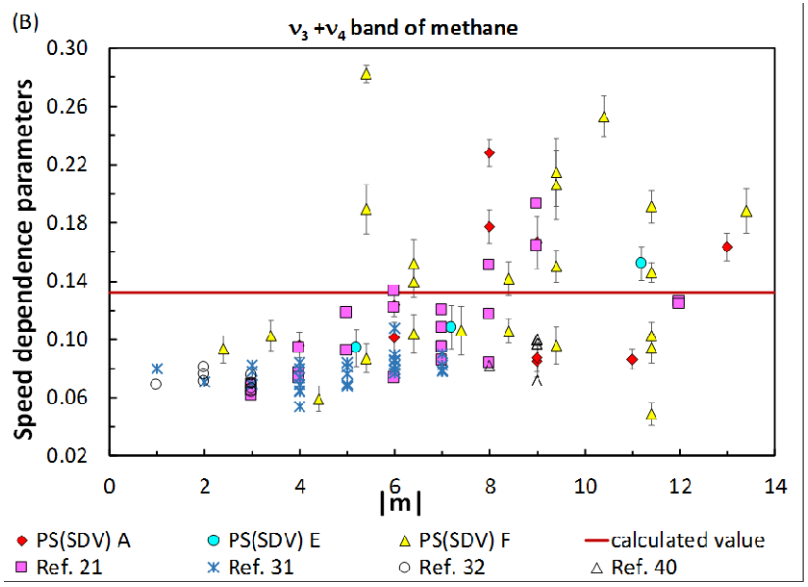
Pressure-Shift Temperature Dependences





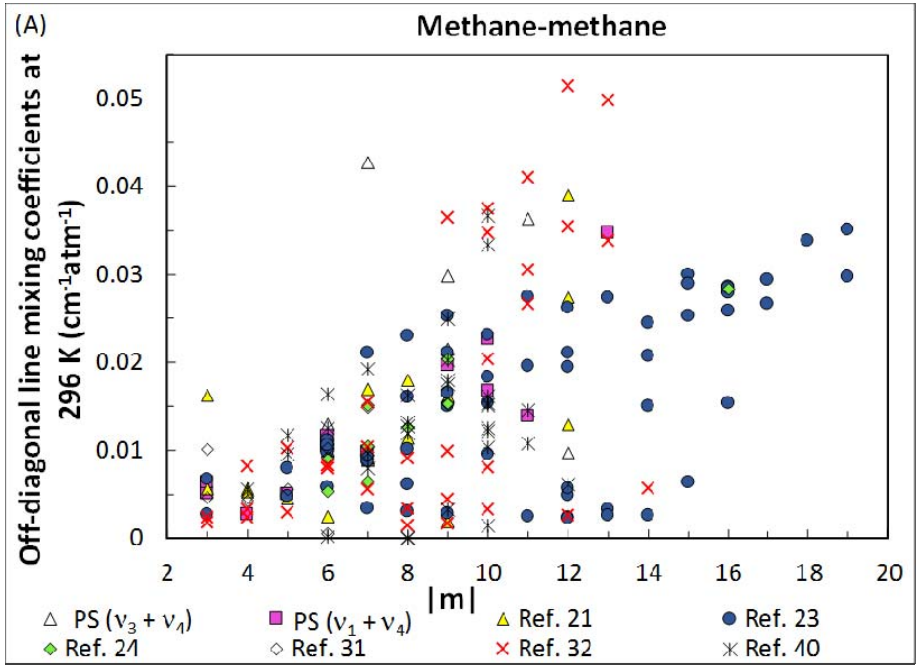
Speed Dependence Parameters

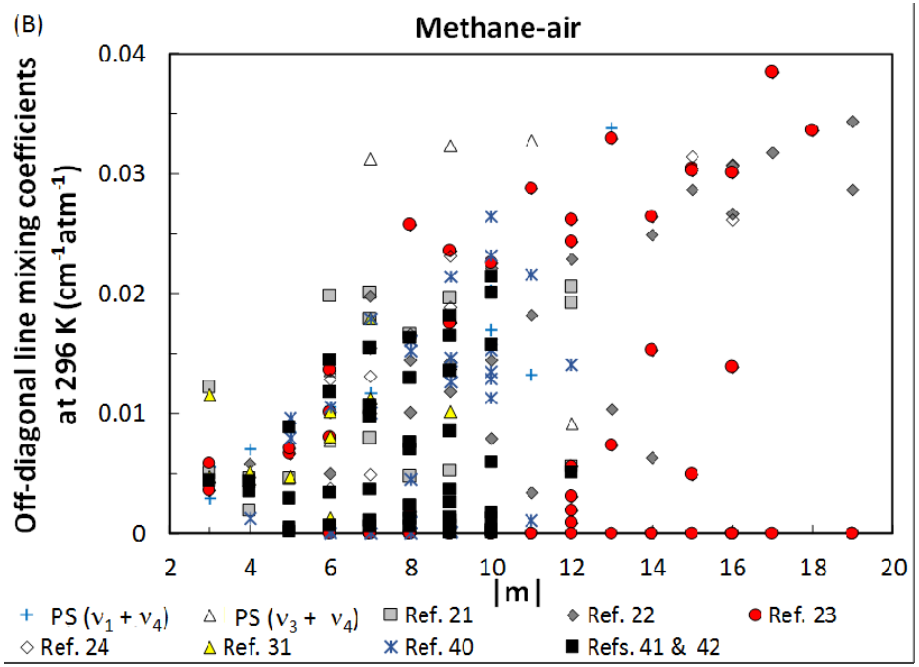




Previous meas.: Refs.21&31: $\nu_2+\nu_3$; Ref. 32: $\nu_3+\nu_4$ R; Ref. 40: $2\nu_3$

Line Mixing Parameters





Previous measurements: Refs.21&31: $\nu_2+\nu_3$; Refs. 22&23: ν_4; Ref. 24: ν_2; Ref. 32: $\nu_3+\nu_4$ R branch; Ref. 40: $2\nu_3$
Calculations: Refs. 41&42: ν_3 , ν_4

Totals of measured methane line parameters in the 4100-4300 cm^{-1} region

Self/Air	Position	Intensity	Lorentz width	Pressure shift	*n* (width)	*δ′* (shift)	ORME	Speed Dependence
Self	634	593	631	476	341	78	21	130
Air	634	593	442	191	260	25	21	

SUMMARY

14 room- and cold-temperature spectra were fitted simultaneously using a multispectrum fitting technique in the 4100-4300 cm^{-1} (Octad region containing transitions of the strong $\nu_1+\nu_4$ and $\nu_3+\nu_4$ bands, as well as some transitions of the $\nu_2+2\nu_4$, $2\nu_2+\nu_4$ and $3\nu_4$ bands).

First measurements of **temperature dependences** of **self-broadened** methane widths and shifts in this region, and a combined analysis of both self- and air-broadened spectra for all observed transitions.

On average, **temperature dependence** exponents for **air-broadened width** coefficients were ~10% **larger** than for **self-broadened width** coefficients for the same transitions.

Overall, for a given transition, the **temperature dependence** for the **self-shift** coefficient was **about the same** as that for the **air-shift** coefficient ($\nu_1+\nu_4$ and $\nu_3+\nu_4$ bands).

Line mixing parameters for both self- and air-broadening were determined for 21 pairs of transitions. Their temperature dependences could not be unambiguously determined in the present study, but the default temperature exponent of 0.8 determined from other methane spectral regions seems to be also valid for the 4100-4300 cm^{-1} region.

Speed dependence parameter was determined for 130 transitions, and an average default speed dependence parameter of 0.132 is recommended for transitions which could not be measured.