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

2017 CAP Congress
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May 29 - June 2, 2017
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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
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:

$v_1 + v_4 \sim 4220 \text{ cm}^{-1}$
$v_3 + v_4 \sim 4320 \text{ cm}^{-1}$
$v_2 + v_3 \sim 4540 \text{ cm}^{-1}$

Previous Studies on Methane

- Room temperature;
- Only one speed-dependent analysis


5/28/2017
Objectives

Determination of line parameters of \( (v_1 + v_4) \) band:

- \( \text{CH}_4 \)-\( \text{CH}_4 \) and \( \text{CH}_4 \)-\( \text{air} \) half width and pressure-shift coefficients along with their temperature dependences
- Retrievals of speed-dependence parameters
- Measurements of line-mixing coefficients 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

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

$A = \log_{10} \left( \frac{I_0}{I} \right) = \varepsilon l c$

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

Spectral absorption coefficient,

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

F(v) = line-shape function
p = pressure
$\chi_{abc}$ = 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

\[ b_L(p, T) = \rho \left[ b_L^0(\text{air})(p_0, T_0)(1 - \chi) \left( \frac{T_0}{T} \right)^{n_1} \right] + b_L^0(\text{self})(p_0, T_0) \chi \left( \frac{T_0}{T} \right)^{n_2} \]

Pressure-shift of the line from its center

\[ \nu = \nu_0 + \rho \left[ \delta^0(\text{air})(1 - \chi) + \delta^0(\text{self})\chi \right] \quad \delta^0(T) = \delta^0(T_0) + \delta'[T - T_0] \]

- \( b_L^0 = \) pressure broadening coefficient (cm\(^{-1}\) atm\(^{-1}\)) of the spectral line
- \( \delta^0 = \) pressure-induced shift coefficient (cm\(^{-1}\) atm\(^{-1}\))
- \( b_L(p, T) = \) Lorentz halfwidth (cm\(^{-1}\)) at \( p \) and \( T \)
- \( \chi = \) 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
- \( \delta' = \) Temperature dependence of the pressure-induced shift coefficient
P branch: ($\Delta J = -1$)
Q branch: ($\Delta J = 0$)
R branch: ($\Delta J = +1$)

$\nu = 0$, vibrational ground state
$\nu = 1$, 1$^{\text{st}}$ vibrational excited state

**Experimental Conditions**

<table>
<thead>
<tr>
<th>Gas sample</th>
<th>CH$_4$ Volume mixing ratio</th>
<th>Total Pressure (Torr)</th>
<th>Temp. (K)</th>
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<td>$^{12}$CH$_4$</td>
<td>1.0</td>
<td>385.0</td>
<td>298.4</td>
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<td>22.20, 121.51</td>
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<td>148.4</td>
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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

Residual = observed – calculated

SDVP

Global Std. Dev= 0.085%

Bottom: 14 experimental spectra that were fitted simultaneously.


Lorentz Half Width Coefficients

\[ |m| = \text{lower state J for P and Q transition} \]

\[ = \text{upper state J for R branch transition} \]
Temperature Dependence of Broadening Coefficients

Temperature dependent CH$_4$-Air broadening coefficient (cm$^{-1}$ atm$^{-1}$ K$^{-1}$)

| $|m|$ | 0 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 |
|-----|---|---|---|---|---|----|----|----|----|
| $\nu_1 + \nu_4$ band | | | | | | | | | |

Temperature dependent CH$_4$-CH$_4$ broadening coefficient (cm$^{-1}$ atm$^{-1}$ K$^{-1}$)

| $|m|$ | 0 | 2 | 4 | 6 | 8 | 10 | 12 | 14 |
|-----|---|---|---|---|---|----|----|----|
| $\nu_1 + \nu_4$ band | | | | | | | | | |

Legend:
- Present study, F
- Present study, E
- Present study, A
- HITRAN-2012

F Species
- E Species
- A Species
Air- and Self-Shift Pressure Induced Coefficients

\[ \nu_1 + \nu_4 \text{ band} \]

- CH4-Air shift coefficient (cm^{-1} atm^{-1})
- CH4-CH4 shift coefficient (cm^{-1} atm^{-1})

- Present study, F
- Present study, E
- Present study, A
- GEISA-2015
- HITRAN-2012

- F Species
- E Species
- A Species
Temperature Dependence of Air- and Self-Shift Coefficients

Temperature dependent CH$_4$-Air shift coefficient (cm$^{-1}$ atm$^{-1}$ K$^{-1}$)

$\nu_1+\nu_4$ band

Temperature dependent CH$_4$-CH$_4$ shift coefficient (cm$^{-1}$ atm$^{-1}$ K$^{-1}$)

$\nu_1+\nu_4$ band
Comparison of Line Mixing Coefficients

Off-diagonal relaxation matrix

Element coefficients (cm$^{-1}$ atm$^{-1}$)

$|m|$
Comparison of Line Mixing Coefficients

Off-diagonal relaxation matrix

Element coefficients (cm\(^{-1}\) atm\(^{-1}\))

- Present study (\(v_1 + v_4\) band)
- Devi et al. (\(v_2 + v_3\) band)
- Predoi-Cross et al. (\(v_2 + v_3\) band)
- Smith et al. (\(v_4\) band)
- Smith et al. (\(v_4\) band)
- Smith et al. (\(v_2\) band)
- Devi et al. (2\(v_3\) band)
- Hashemi et al. (\(v_3 + v_4\) band)
Comparison of Line Position

$v_1+v_4$ band

Ratios of line position

Obs. / Theory
Obs. / GEISA-2015
Obs. / HITRAN-2012
Comparison of Percentage Intensity Difference

Percentage difference in intensity (%)

- Theoretical
- HITRAN-2012
- GEISA-2015

\( v_1 + v_4 \) band

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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
Thank you for your kind attention