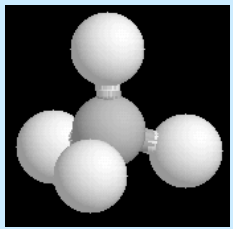
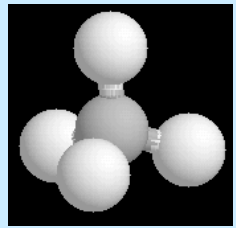
Infrared Laboratory Spectroscopy of CH_4 and CH_3D for Atmospheric Studies

Linda R. Brown



Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

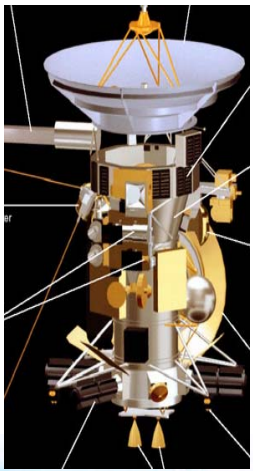


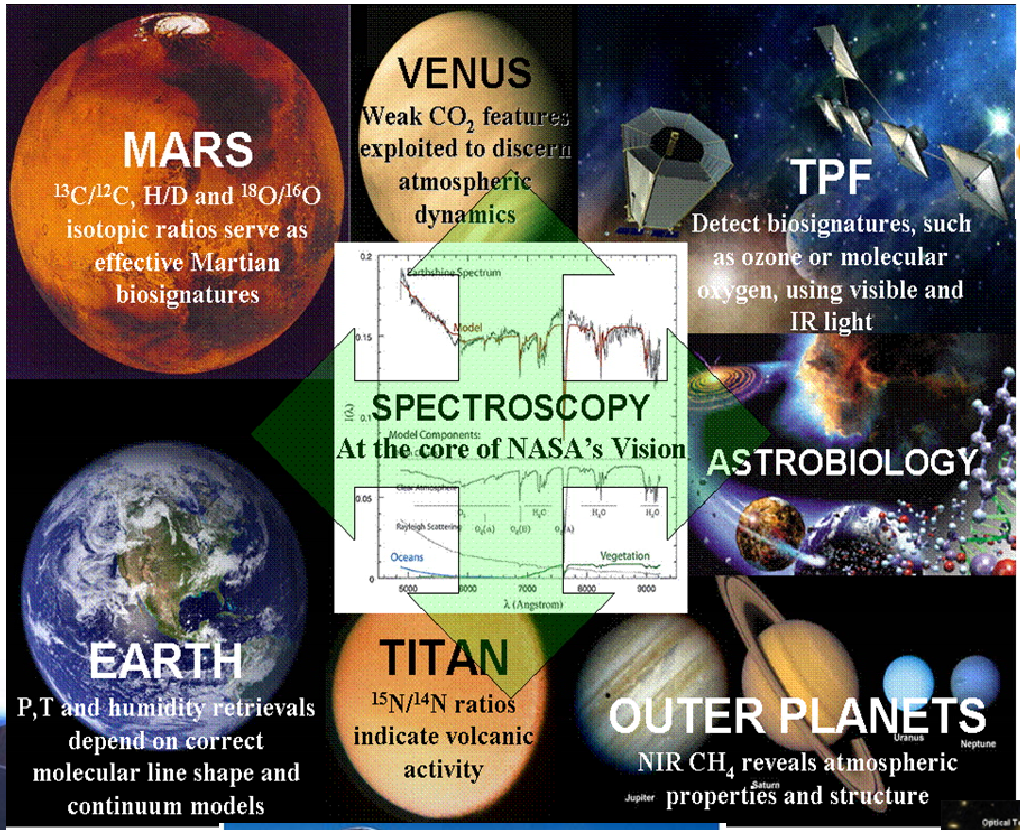
linda.brown@jpl.nasa.gov

The part of the research was performed at the Jet Propulsion Laboratory (JPL), California Institute of Technology under contract with the National Aeronautics and Space Administration

with many enthusiastic co-investigators

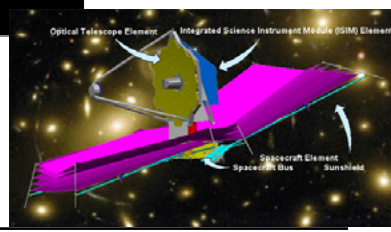
ASTRONOMICAL REMOTE SENSING





IRS Pocket Guide v3.1 (January 2005)

SPITZER SPACE TELESCOPE



Basic transition line parameters

- **Line position** (or center frequency)
- **Line intensity @ 296 K**
- **Lower state energy** (for temperature dependence)
- Vibrational - rotational quantum assignment

Line shape parameters

- **Pressure-broadened widths** **(usually Voigt)**
  & temperature dependence.
- **Line mixing**
- **Pressure-induced frequency shifts**
- **Self-broadened widths**
- Continua: collision-induced absorption (CIA)
  (given as cross section files)

Line-by-line parameters should be COMPLETE and ACCURATE (ENOUGH)

ACCURACIES NEEDED FOR MANY APPLICATIONS

ν **Positions:** **0.00001 - 1.0 cm^{-1}** \

E'' **Lower states energies (from assignments): ≈ ½%**

S **Line intensities:** → **0.2 to 10%**

γ **Pressure-broadening widths:** → **0.2 to 20 %**

η **Temperature dependence of widths:** **10 to 40%**

δ **pressure-induced shifts:** **??**

METHODS TO OBTAIN SPECTROSCOPIC PARAMETERS

- **Calculations based on successful theoretical modeling (good for positions and intensities, but not line shapes)**
- **Predictions based on limited data and/or poorer theoretical modeling (warning: extrapolations very poor!)**
- **Empirical data retrieved line-by-line with some known assignments (warning: no weak lines, larger uncertainties!)**
- **Absorption cross sections from lab spectra, sometimes at different temperatures (for unresolved heavy species and continua)**

Near-IR CH_4 (and CH_3D): Positions and Intensities:

Difficult to model because energy levels perturb each other.

Triacontad: **intractable:**
empirical linelist with 1% assigned.

Icosad: **almost intractable; one strong band studied,** empirical list

Tetradecad: mostly unassigned; no public prediction; empirical linelist

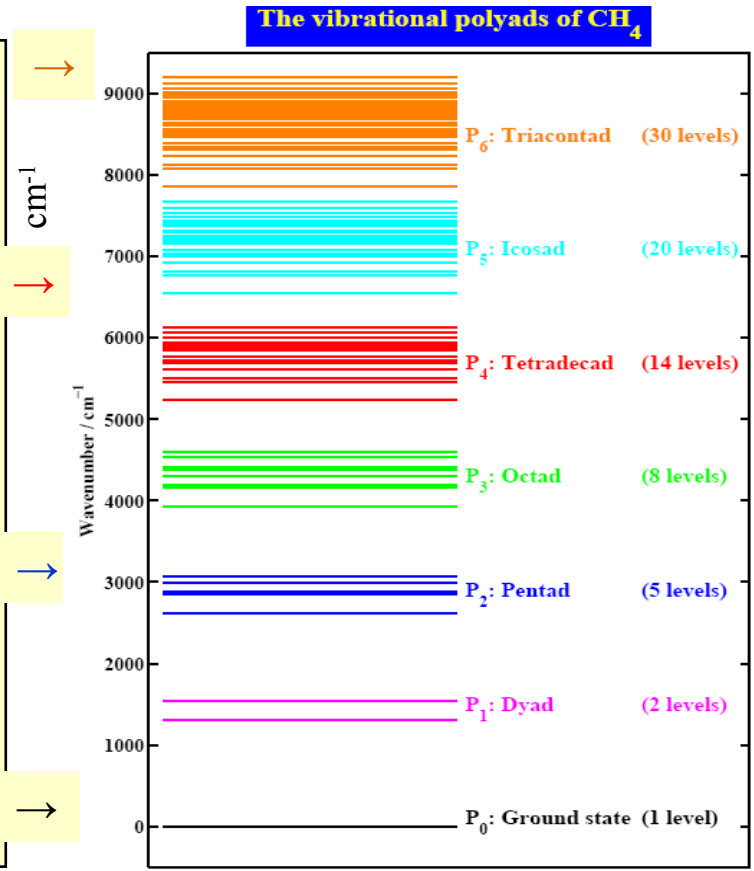
Octad: **new predictions coming for main isotope only.**

CH_3D overtones/combination →

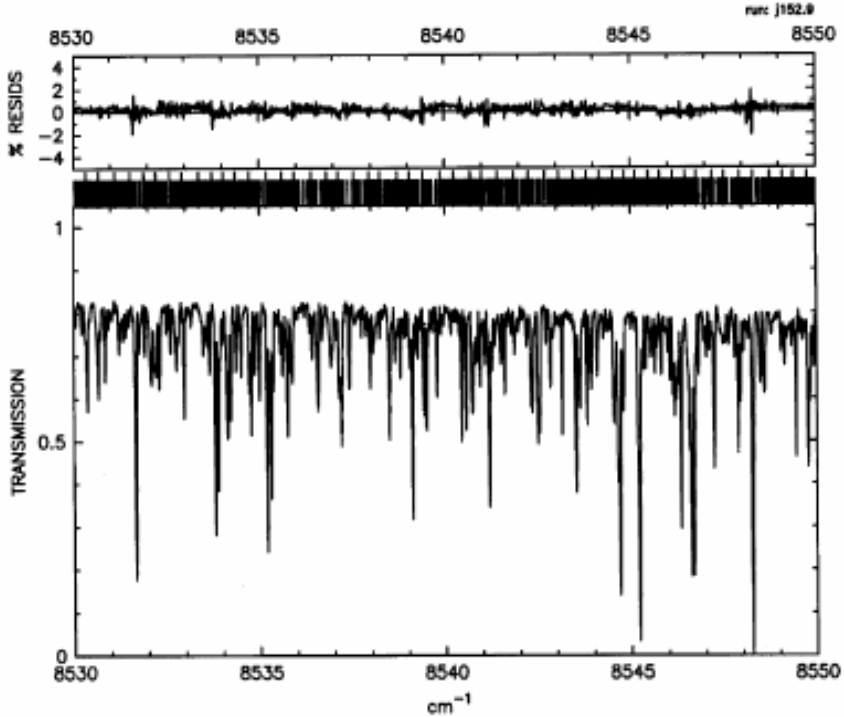
Pentad: 3 isotopes **(fundamentals and overtones)** modeled;
Hot bands intensities are estimated.

Dyad: 3 isotopes good. Hot bands intensities modeled to 8%.

GS: Intensities low by 15%.
CH_3D prediction is old.



Triacontad



Room temperature methane lab spectrum at 0.022 cm^{-1} resolution

Retrieved 537 positions and intensities Line-by-line

Bottom panel is observed spectrum overlaid with synthetic; top is difference plot.

No known assignments: can not compute spectra at other temperatures or attach broadening coefficients as a function of quantum numbers

Oyanagi et al.

THE JOURNAL OF CHEMICAL PHYSICS **124**, 064311 (2006)

Highly accurate potential-energy and dipole moment surfaces for vibrational state calculations of methane

- **Vibrational configuration-interaction calculations of energy levels and the absorption intensities up to 9000 cm^{-1}**
- **full-dimensional ab initio potential-energy surface (PES) and dipole moment surface for methane**
- **Predicted energy levels within 10 cm^{-1} of observed**

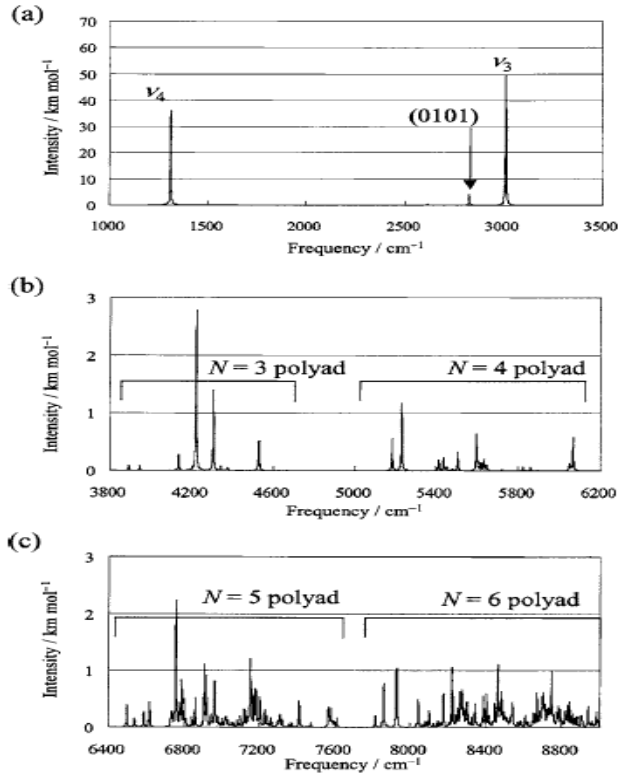


FIG. 2. Theoretical vibrational spectra obtained from VCI calculations using the MSI(4th) potential-energy functions and dipole moment surfaces. Panels (b) and (c) are scaled up for clarity.

Identification of hot band transitions of CH_4 near 3000 cm^{-1}

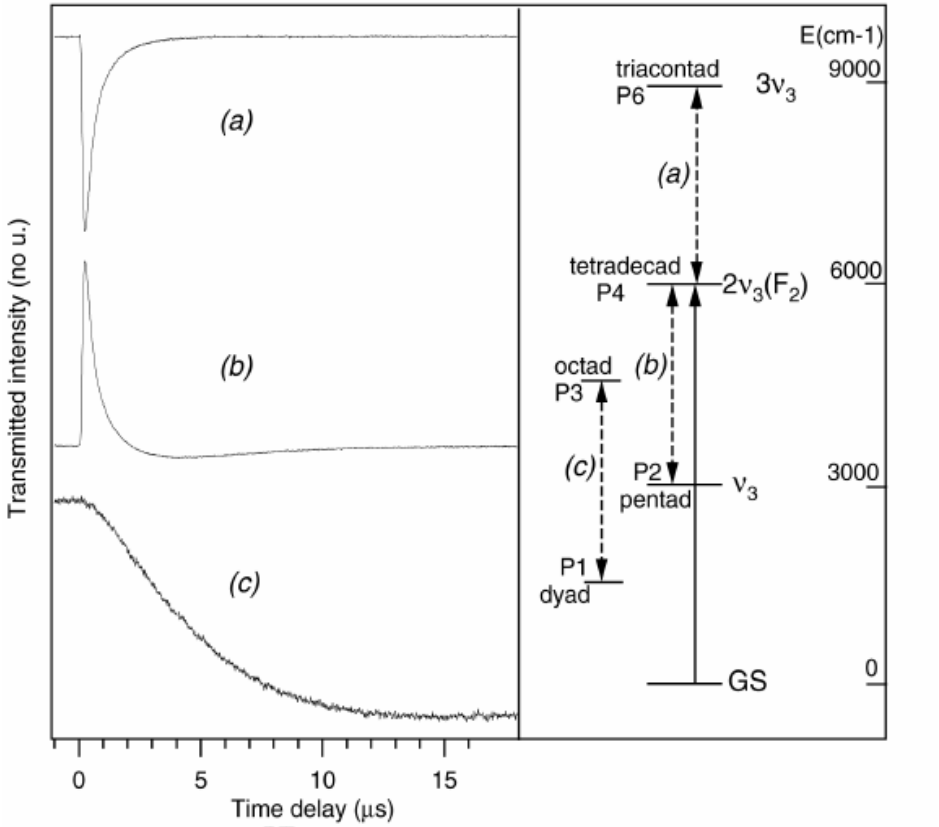
C. Boursier*, J. Menard, A. Marquette, F. Menard-Bourcin

Figure 1

Double resonance experiment

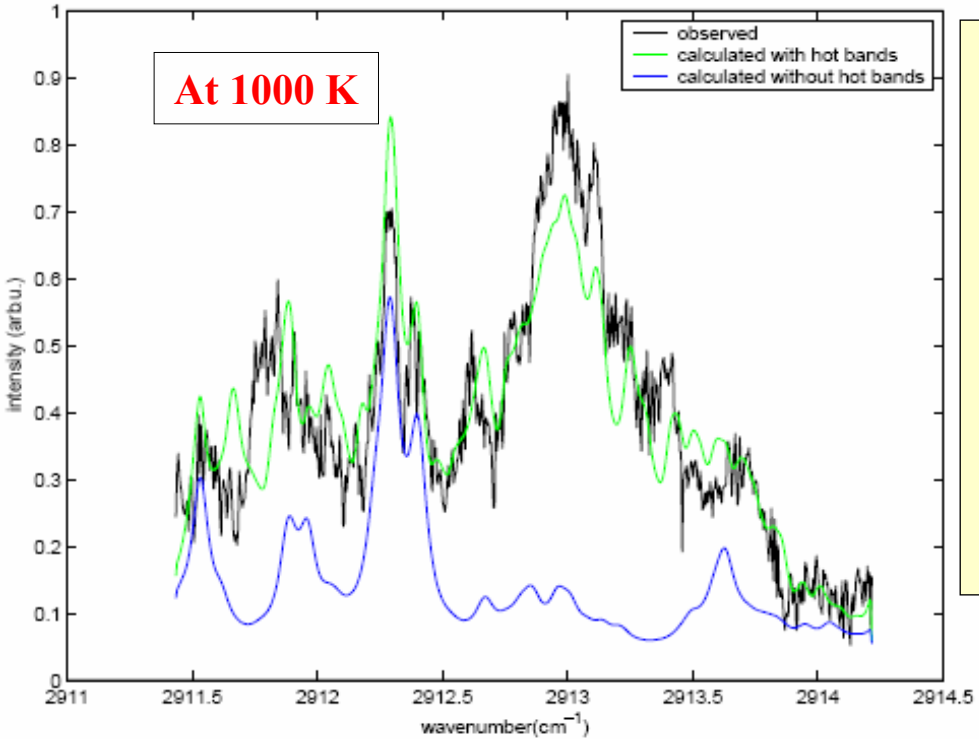
Assign higher states via hot band transitions.

Accepted J. Mol. Spectrosc.



◆Methane Hot bands Are Important

The methane Raman spectrum from 1200 to 5500 cm^{-1}: A first step toward temperature diagnostic using methane as a probe molecule in combustion systems



Jourdanneau et al.

J. Mol. Spectrosc.

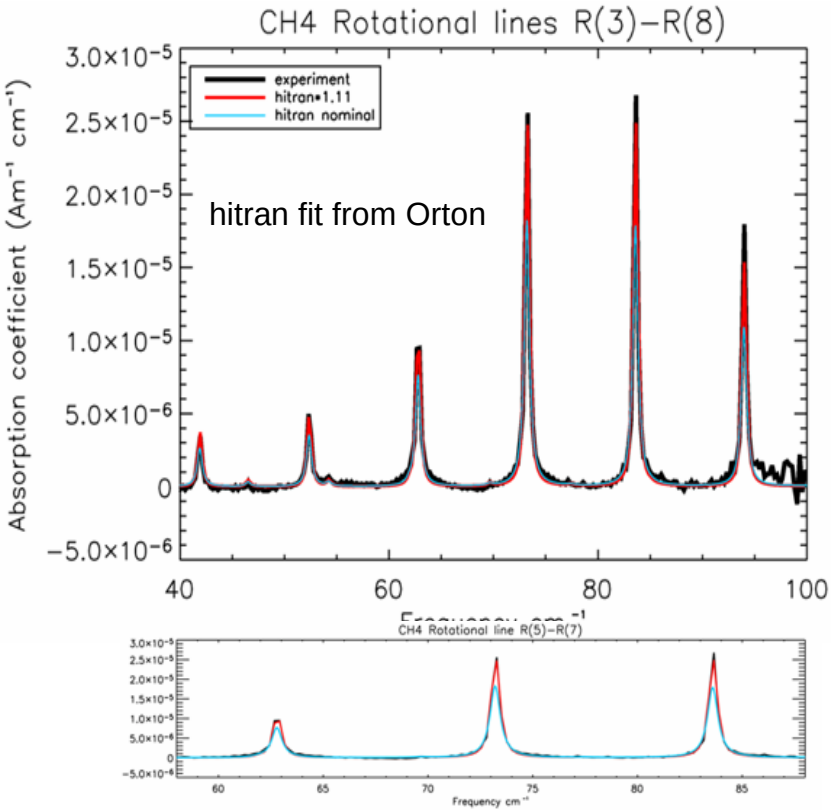
Vol. 233

Pgs 219-231

(2005)

Fig. 10. Simulation without, and with hot bands in the region 2911–2914 cm^{-1}. The band centered at 2913 cm^{-1} is $\nu_1 + \nu_4 - \nu_4$.

Far-IR CH_4 Intensities for ground state transitions in HITRAN and GEISA low by 15% ± ?



Lab Spectra of Far-IR CH4 (Wishnow)

HITRAN intensities for Far IR set by one "indirect method", (calc.) [Hilico et al., J Mol Spec, 122, 381 (1987)] with claim of accuracy of ± 30%.

Cassam-Chenai, [JQSRT, 82,251(2003)] predicts ab initio Q branch based on Stark measurements [Ozier et al. Phys Rev Lett, 27, 1329, (1971)].
The intensities are 15% higher than HITRAN values.

Lab data (left) confirms a higher value for R branch manifolds.

Models for Collision-Induced Continua

- http://www.astro.ku.dk/~aborysow/programs/

  Borysow & Frommhold calculate collision-induced spectra at different temperatures and then form model spectra of cross sections.

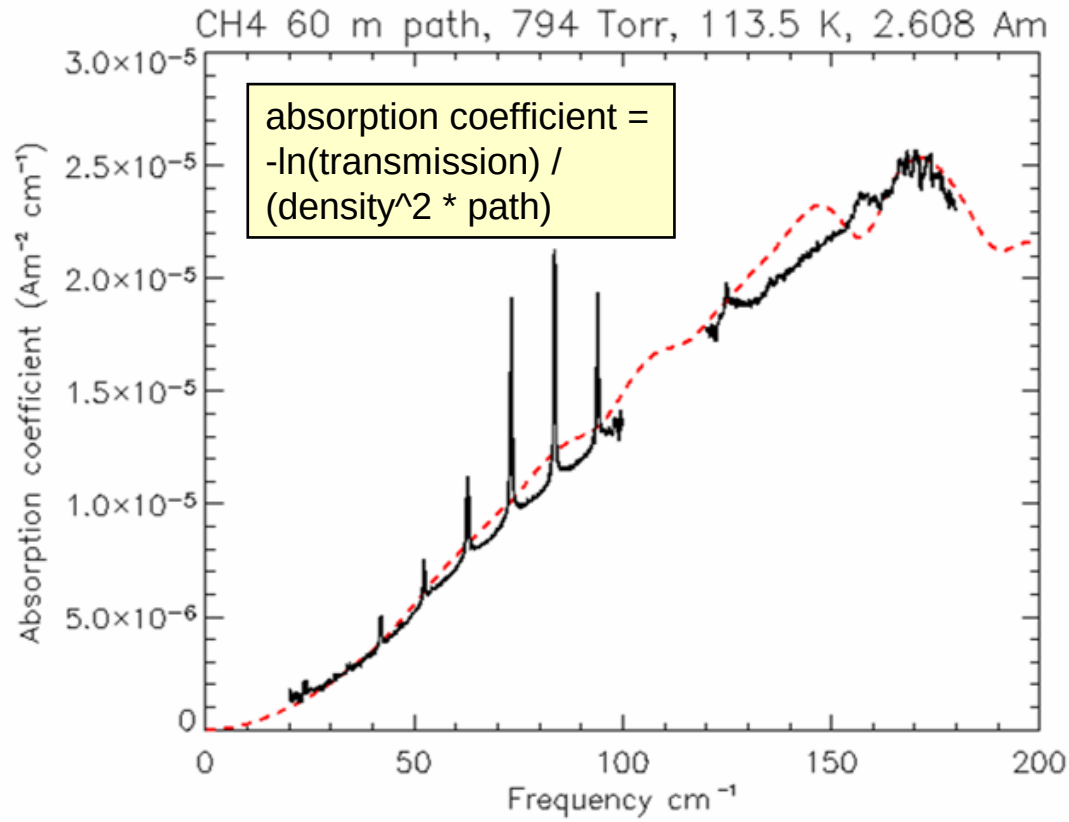
- Very useful models and software available for generating synthetic spectra

  H_2-H_2, H_2-He, H_2-CH_4, H_2-Ar, N_2-N_2,

  CH_4-CH_4, N_2-CH_4, CH_4-Ar, CO_2-CO_2

New work in progress for H_2-H_2 by Gustafsson and Frommhold

Low temperature spectrum of methane



First observation of R(3)-R(7) lines

Wishnow, Leung, Gush, Rev. Sci. Inst., 70, 23 (1999) at 0.24 and 0.06 cm^{-1} resolution

Ground State transitions with calc. Collision-Induced absorption shows need to improve the CIA parameters

Dashed line: **CH_4 Collision-Induced Absorption (CIA) from Borysow.**

Air- and Self-broadened Widths of Methane

5 Bands of the OCTAD: 4100 to 4635 cm^{-1}

Widths vary as a function of quanta and band symmetry

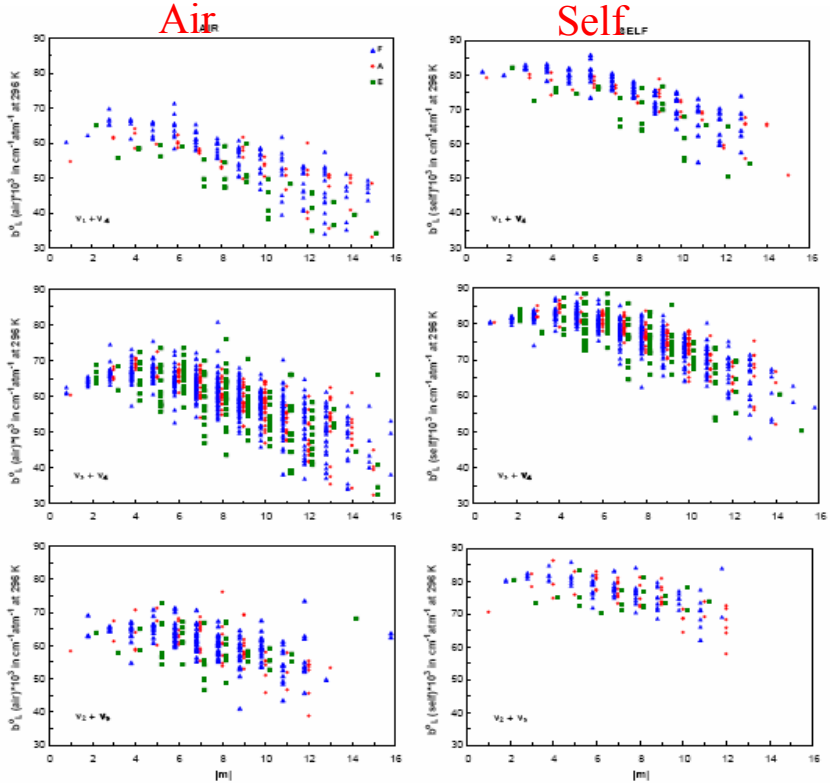


Fig. 3. Measured air-broadening and self-broadening coefficients, b_L^o (in cm^{-1} atm^{-1} at 296 K), in the three strongest bands ($\nu_1 + \nu_4$, $\nu_3 + \nu_4$, and $\nu_2 + \nu_3$) of the octad polyad plotted as a function of $|m|$, where $|m|$ is the lower state J for P and Q transitions and the upper state J for R branch lines. The error bars are not plotted to allow a better observation of the trends in broadening coefficients as a function of $|m|$.

$\nu_1+\nu_4$ at 4220 cm^{-1}:

3-fold degenerate (F2).

These widths are within 4% of ν_3 values (at 3020 cm^{-1}) and other bands with a 3-fold vibrational symmetry (F2).

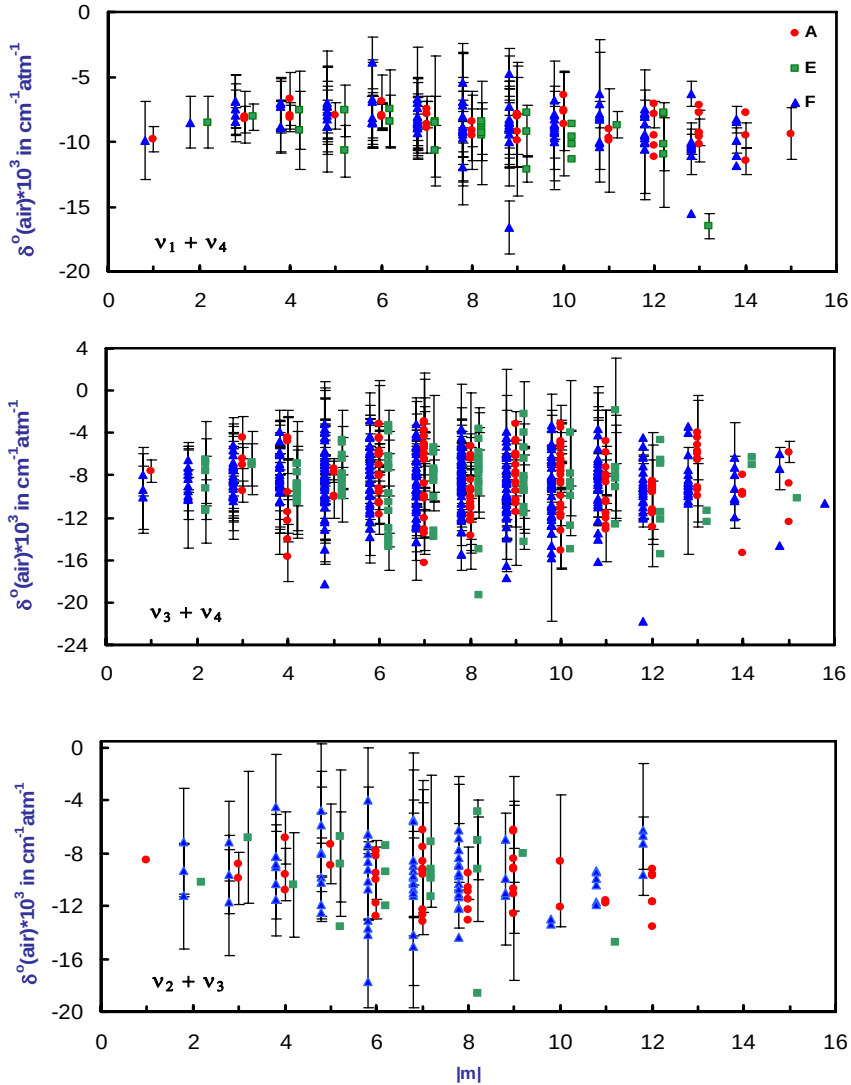
$\nu_3+\nu_4$ at 4310 cm^{-1}:

9-fold degenerate band: variation of widths at each J is much greater.

$\nu_2+\nu_3$ at 4530 cm^{-1}:

6-fold degenerate band: some variation of widths at each J.

Predoi-Cross et al. J. Mol. Spect.



Air-broadened pressure shifts: δ

NO obvious patterns vs quantum numbers

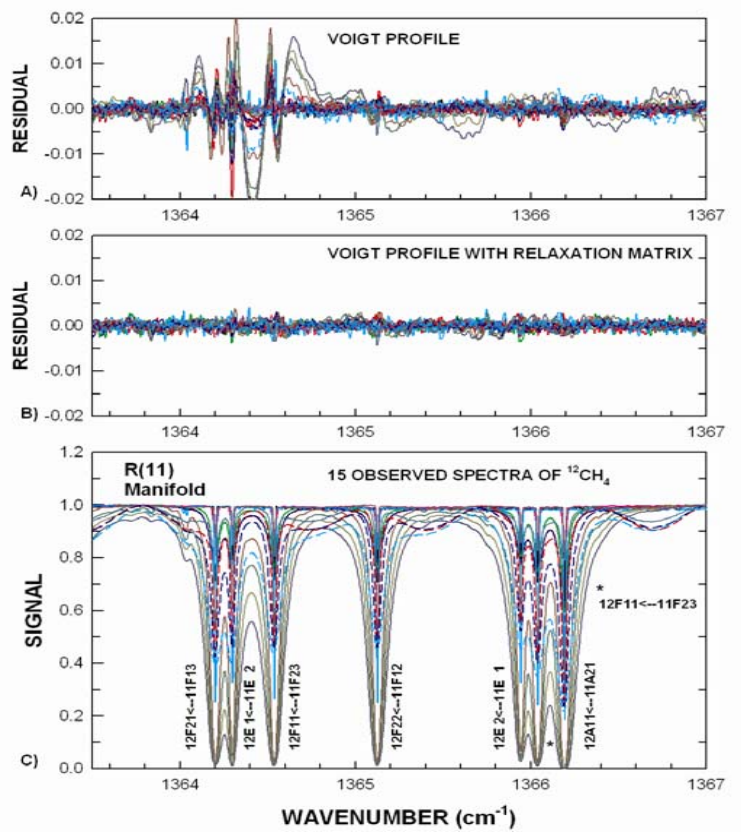
Pressure shifts can be estimated with a simple linear expression:

$$\delta \sim -1.97(24) \times 10^{-6} \times \nu$$

where ν is the vibrational band center.

Is the scatter evidence of line mixing?

Studies to Understand Line Mixing in CH_4



Multispectrum fitting of line mixing in self- and air-broadened ν_4 methane (M. Devi)

Line Mixing Rules

A1 ↔ A2 **but not** A2 ↔ A2

F1 ↔ F2 **but not** F2 ↔ F2

E ↔ E

Sum of mixing coefficients = 0.

First noticed in Raman spectra

Stimulated Raman $2\nu_2$ Q-branch, (Millot et al. 1991)

Most absorption studies at 3000 cm^{-1}

1992-2003: Pine - measurements

1999-2001: Pieroni et al. - theory

2001-2002: Grigoriev – high pressure

2006: Tran, Hartmann et al.

(Two papers in press JQSRT)

Models at very high pressure in both ν_4 and ν_3 **with software and database for air, N_2, H_2, Ar & He**

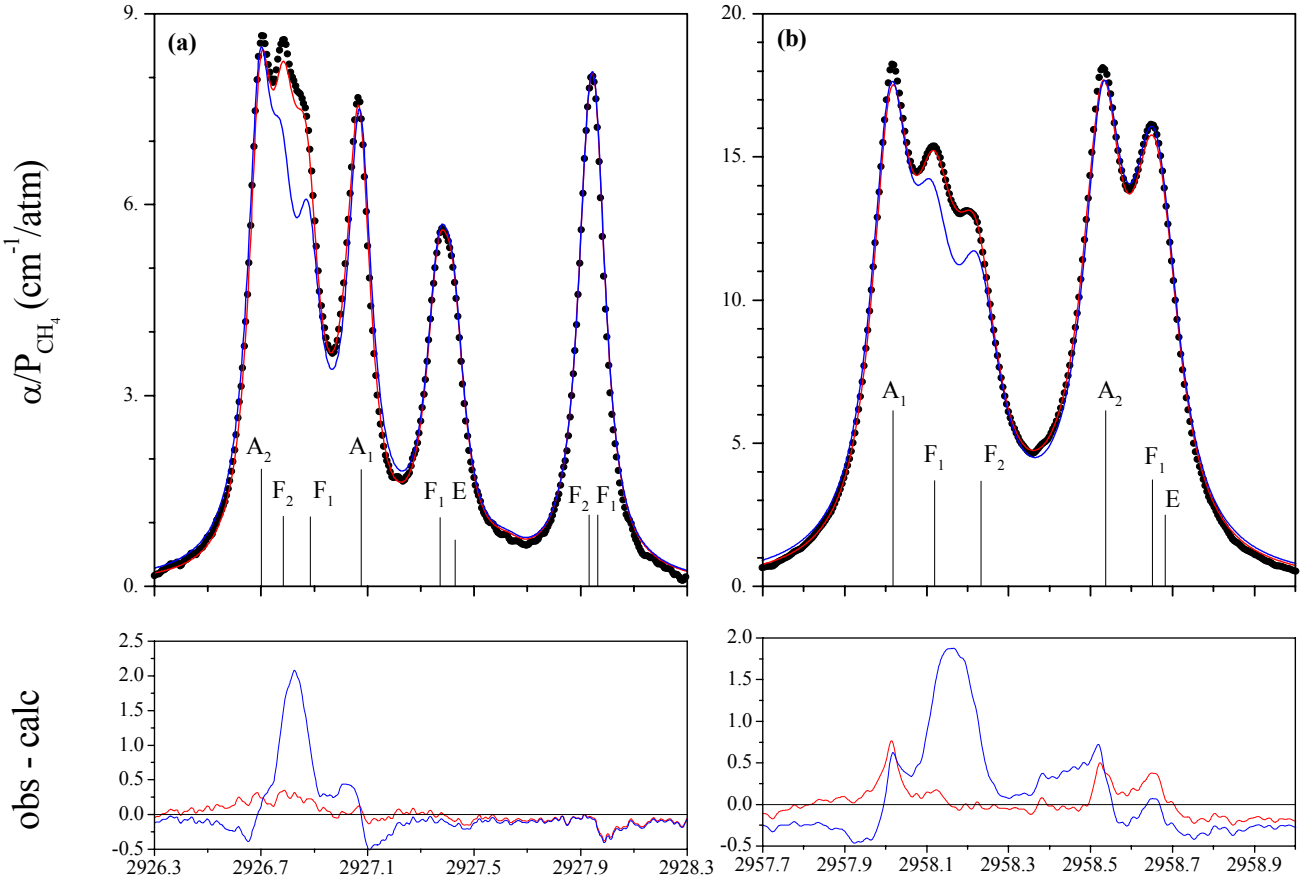
Collisional effects in CH_4 spectra, IR, Raman, and Atmospheres

Jean-Michel Hartmann,

Laboratoire de PhotoPhysique Moléculaire

- Individual IR line shapes
- Shapes of IR manifolds
- Shapes of IR branches and bands
- The IR wings
- The case of Raman spectra
- Collision induced absorption
- Effects on atmospheric transmission
- Effects on Jovian Emission

ν_3 band, P(9) and P(6) manifold, CH_4-N_2 at 300 K, 1 atm



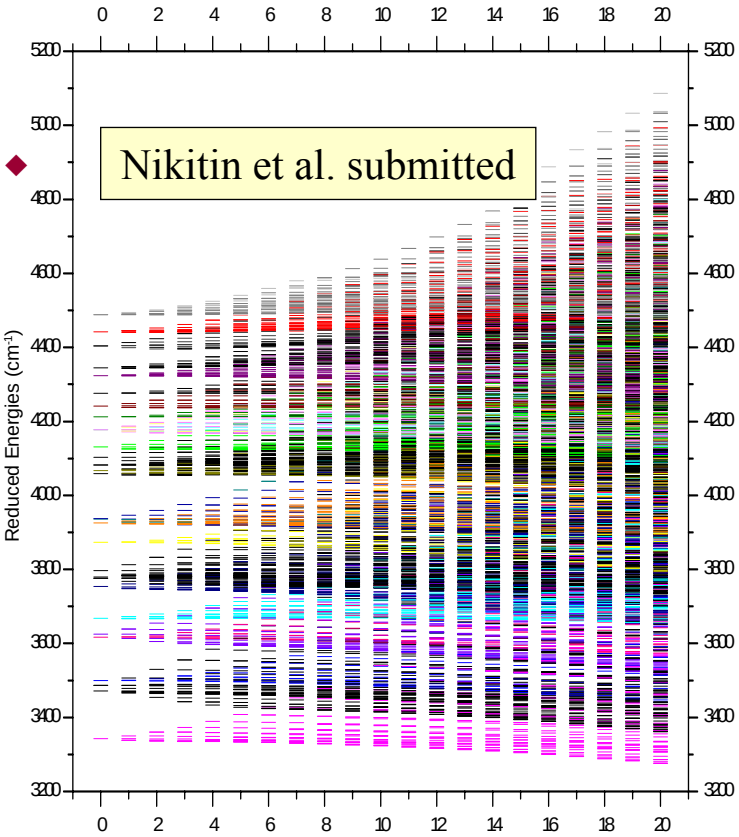
The "Enneadecad" of CH_3D: 3300 to 4900 cm^{-1}

A. Nikitin, Laboratory of Theoretical Spectroscopy, Tomsk RUSSIA
L.R. Brown, Jet Propulsion Laboratory, Pasadena USA
J.P. Champion, Laboratoire de Physique, Dijon France

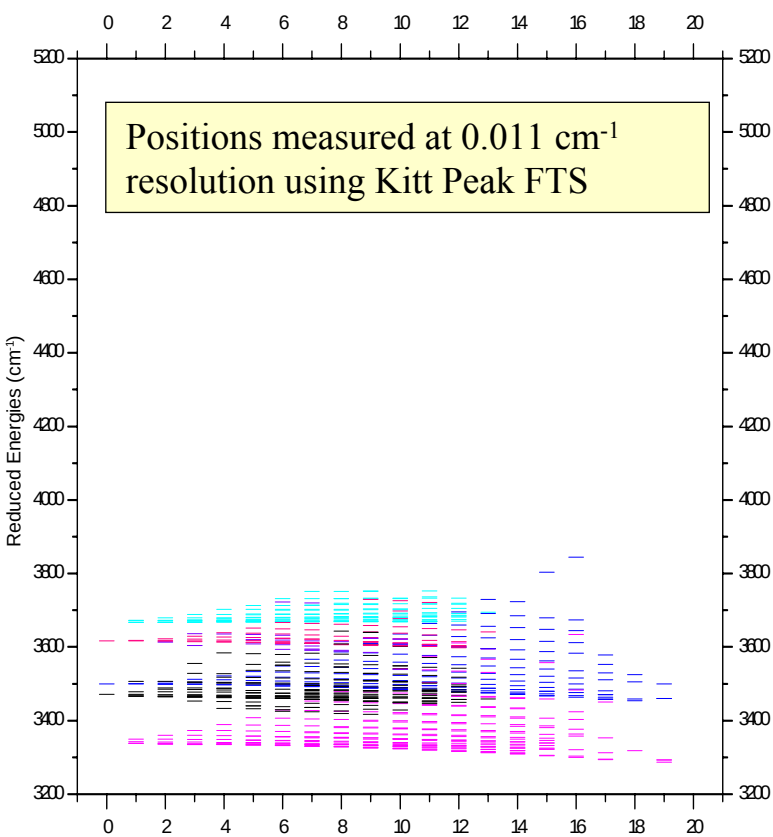
- Enneadecad = 19 vibrational states (37 vibrational sublevels)
- Global analysis of 8 sublevels at 2.9 μm & hot bands at 3.3 μm
- Measured Intensities between 3300 – 3700 cm^{-1}
- 441 effective Hamiltonian parameters fixed to values known from prior analyses of the Ground State, Triad and Nonad of CH_3D
- 144 extra effective Hamiltonian parameters fitted using newly assigned "Enneadecad" and "Enneadecad – Triad" hot transitions
- 0.0008 cm^{-1} Fit of positions (6^{th} order) : 2702 cold & hot band transitions
- 4.5 % Fit of intensities (3^{rd} order) : more than 850 measurements

The Enneadecad of CH_3D Energy Levels

Calculated

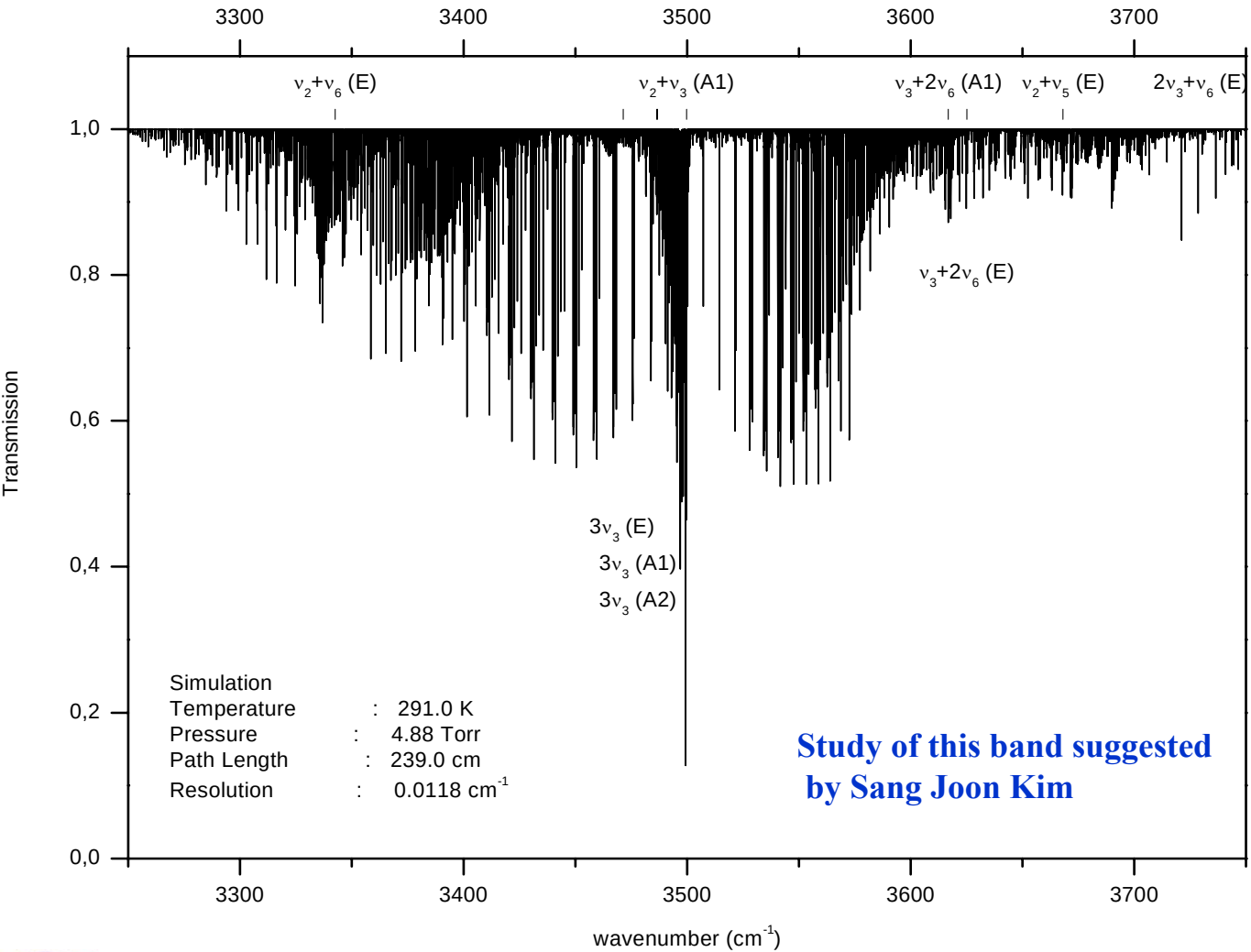


Observed



Reduced Upper State Energies (cm^{-1}) vs Quantum number J

Spectrum Overview (Simulation)



Recent Research: pressure broadening of CH_3D

Extensive measurements of four lowest fundamentals
Several broadeners: Self, O_2, N_2, air, H_2
Empirical expressions as a function of J,K
Theoretical calculations of widths beginning to match data

- **Measurements and theoretical calculations of N_2-broadening and N_2-shift coefficients in the ν_2 band of CH_3D, Predoi-Cross et al. J. Mol. Spectrosc. 235 (1): 35-53, 2006**
- **Measurements and theoretical calculations of self-broadening and self-shift coefficients in the ν_2 band of CH_3D, Predoi-Cross et al. J. Mol. Spectrosc. 234 (1): 53-74, 2005**
- **H_2-broadening coefficients in the ν_3 band of CH_3D at low temperatures Lerot et al. J. Mol. Spectrosc. 219 (2): 329-334, 2003**
- **Diode-laser measurements and calculations of H_2-broadening coefficients in the ν_3 band of CH_3D. Lerot et al. J. Mol. Spectrosc. 217 (1): 79-86, 2003**
- Self- and N_2-broadening, pressure induced shift and line mixing in the ν_5 band of CH_3D using a multispectrum fitting techniques. **Devi et al. J. Quant. Spectrosc. & Rad. Transfer 74 (1): 1-41, 2002 plus papers for air-broadening. Modeled with empirical expressions.**

Room-temperature broadening and pressure-shift coefficients in the ν_2 band of CH_3D–O_2: Measurements and semi-classical calculations

Adriana Predoi-Cross [a,*], Kyle Hambrook [a], Shannon Brawley-Tremblay [a], Jean-Pierre Bouanich [b], V. Malathy Devi [c], Mary Ann H. Smith [d]

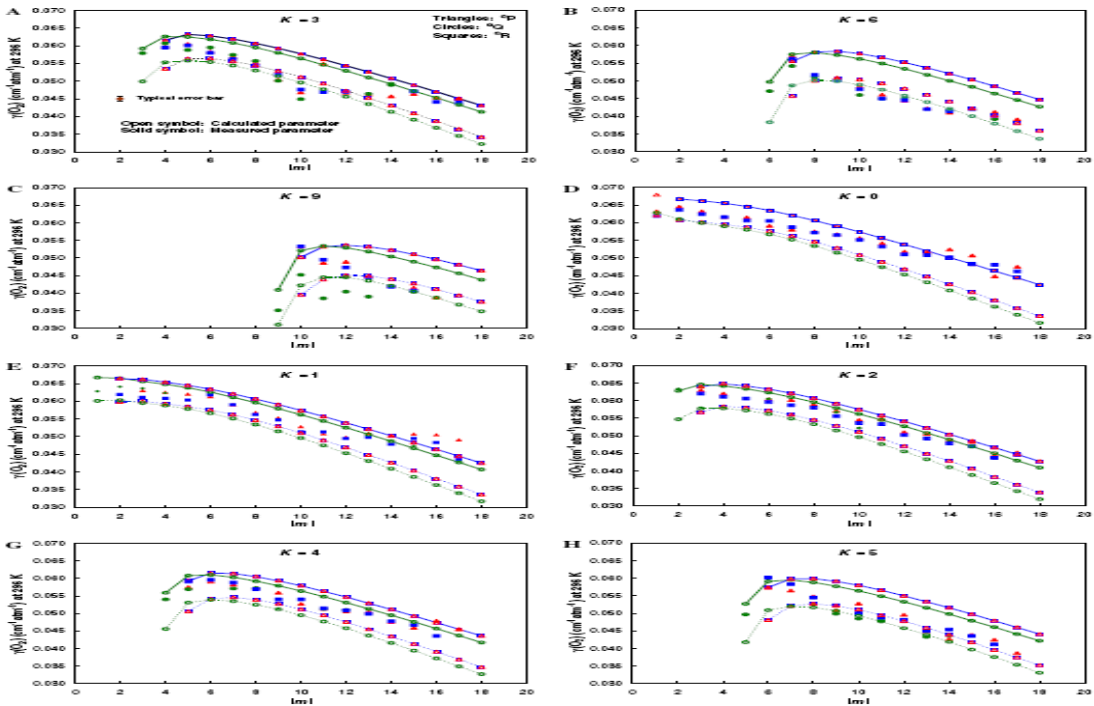


Fig. 5. Variation of measured, empirically derived, and theoretically calculated O_2-broadening coefficients with $|m|$ for (A) $K = 3$; (B) $K = 6$; (C) $K = 9$; (D) $K = 0$; (E) $K = 1$; (F) $K = 2$; (G) $K = 4$; and (H) $K = 5$. For a given $|m|$, the theoretical broadening coefficients for the ^QP and ^RR lines are very nearly the same. The broadening coefficients connected with smooth line are obtained using calculation 1 and those connected with dotted line are obtained using calculation 2.

Spectroscopy Needed for CH_4 and CH_3D

- **Far-IR:** Improved accuracy for line-by-line intensities
- **Far-IR:** Better models for CIA with different broadeners
- **Mid-IR:** Analysis of weaker hot bands (Octad-Dyad,….)
- **Near –IR:** Extensive analyses for all isotopes
- **IR:** Models for pressure broadening coefficients
- **Near-IR:** Extensive broadening measurements
- **IR:** Line mixing measurements and models