High-temperature emission spectra and updated calculated spectroscopic database of methane

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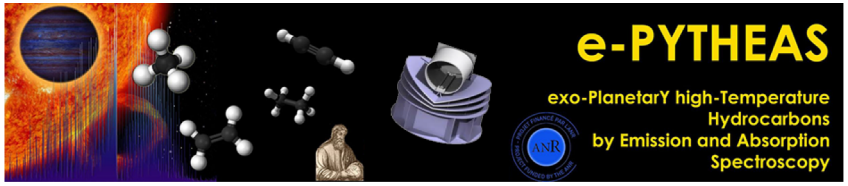
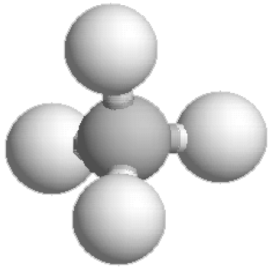
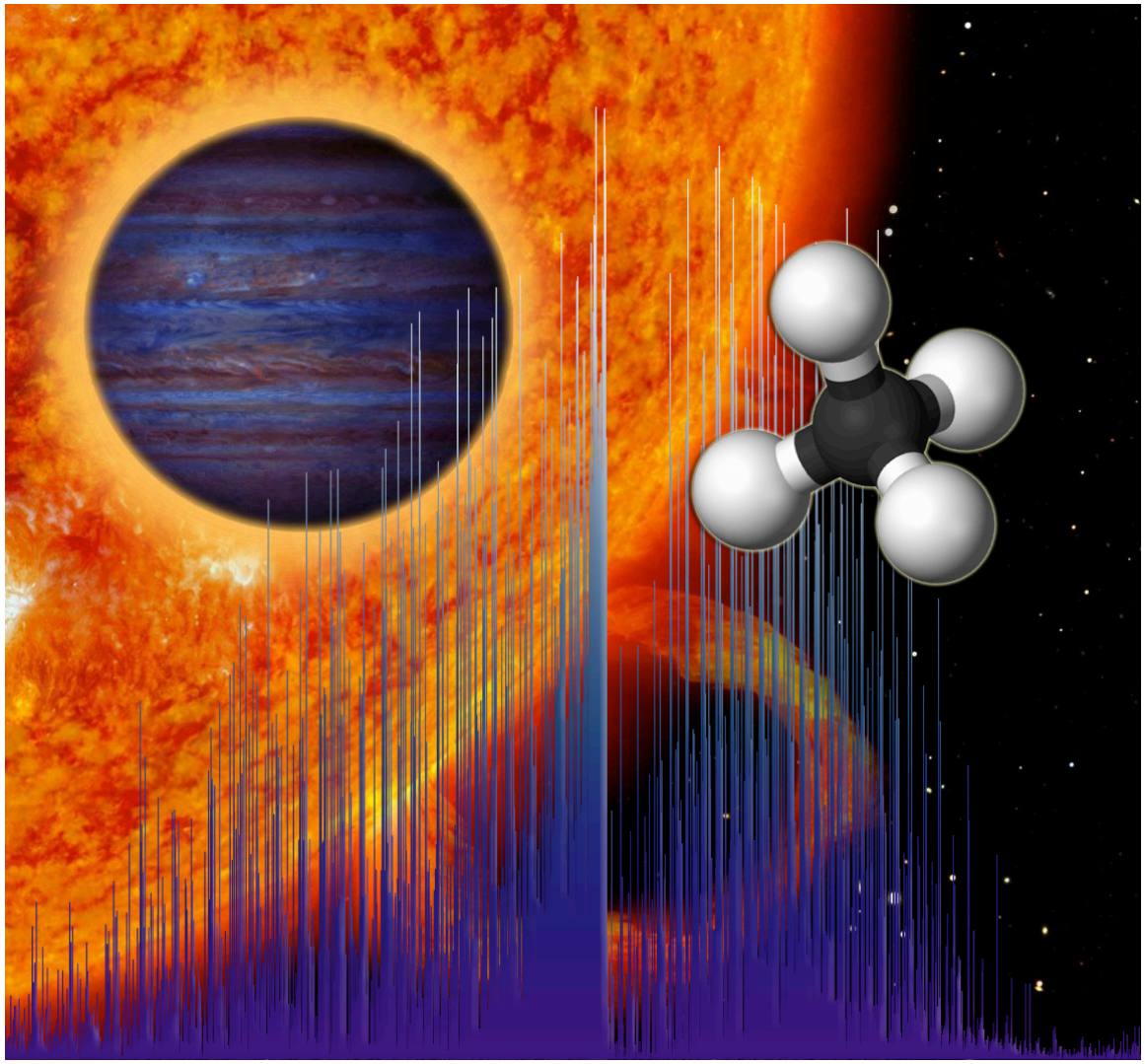


PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR



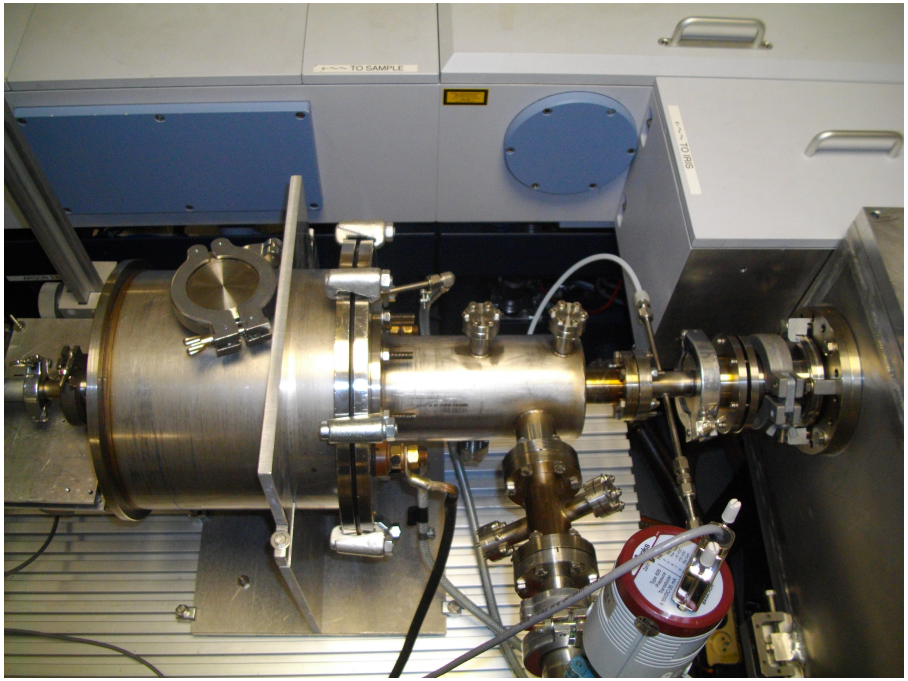
Context and method

- **Methane (CH_4) at high temperature** (up to 3000 K) in the atmosphere of giant **exoplanets** (« hot Jupiters ») and **brown dwarfs**
- Study of « **hot bands** »
- Very high **complexity** of the spectrum of CH_4 in **highly excited states**



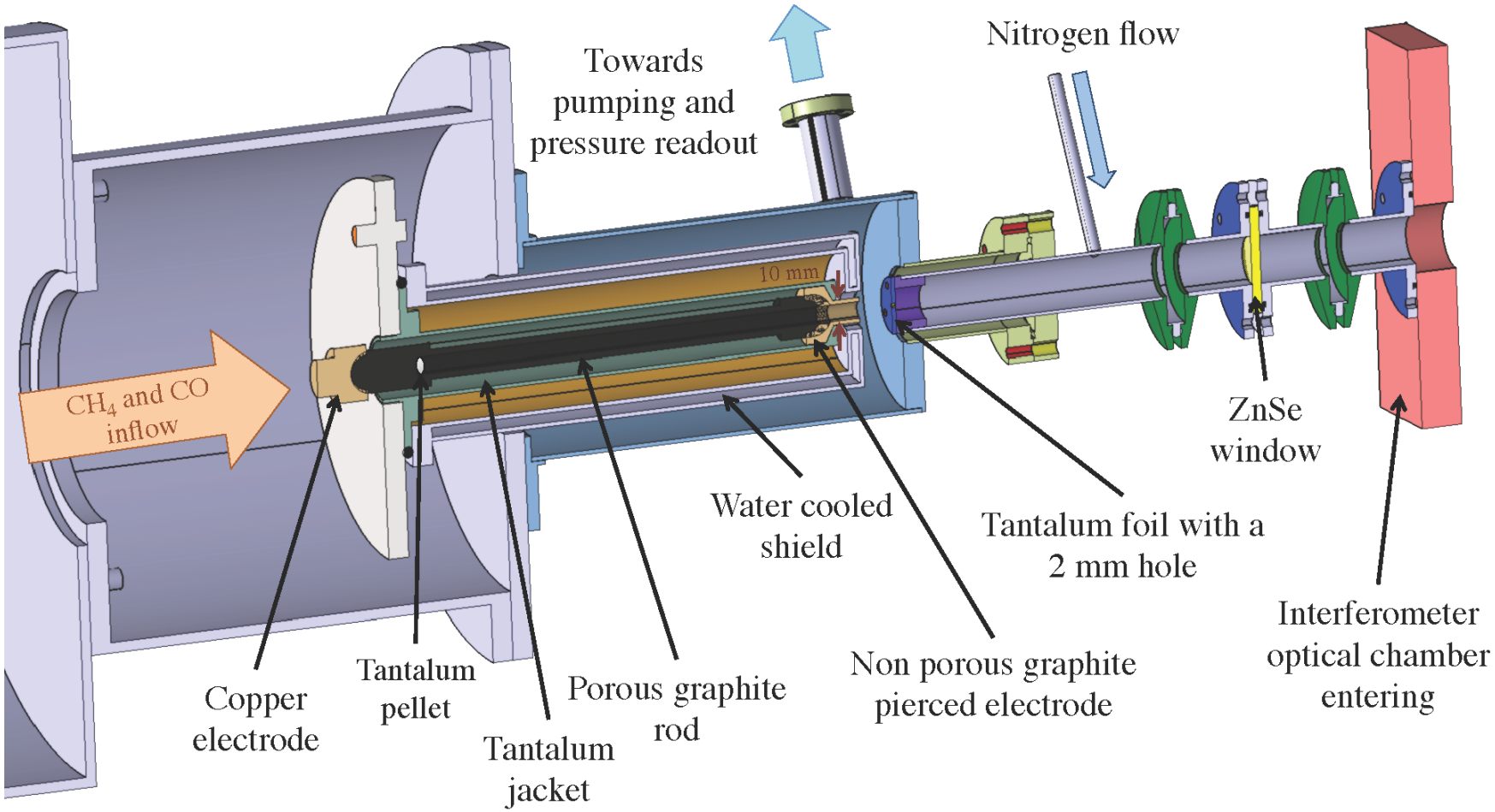
- **Emission spectra** using a high-enthalpy heating source, coupled to a FTIR spectrometer
- **Stretching pentad region** in the 2600–3300 cm^{-1} region

I. Experiment

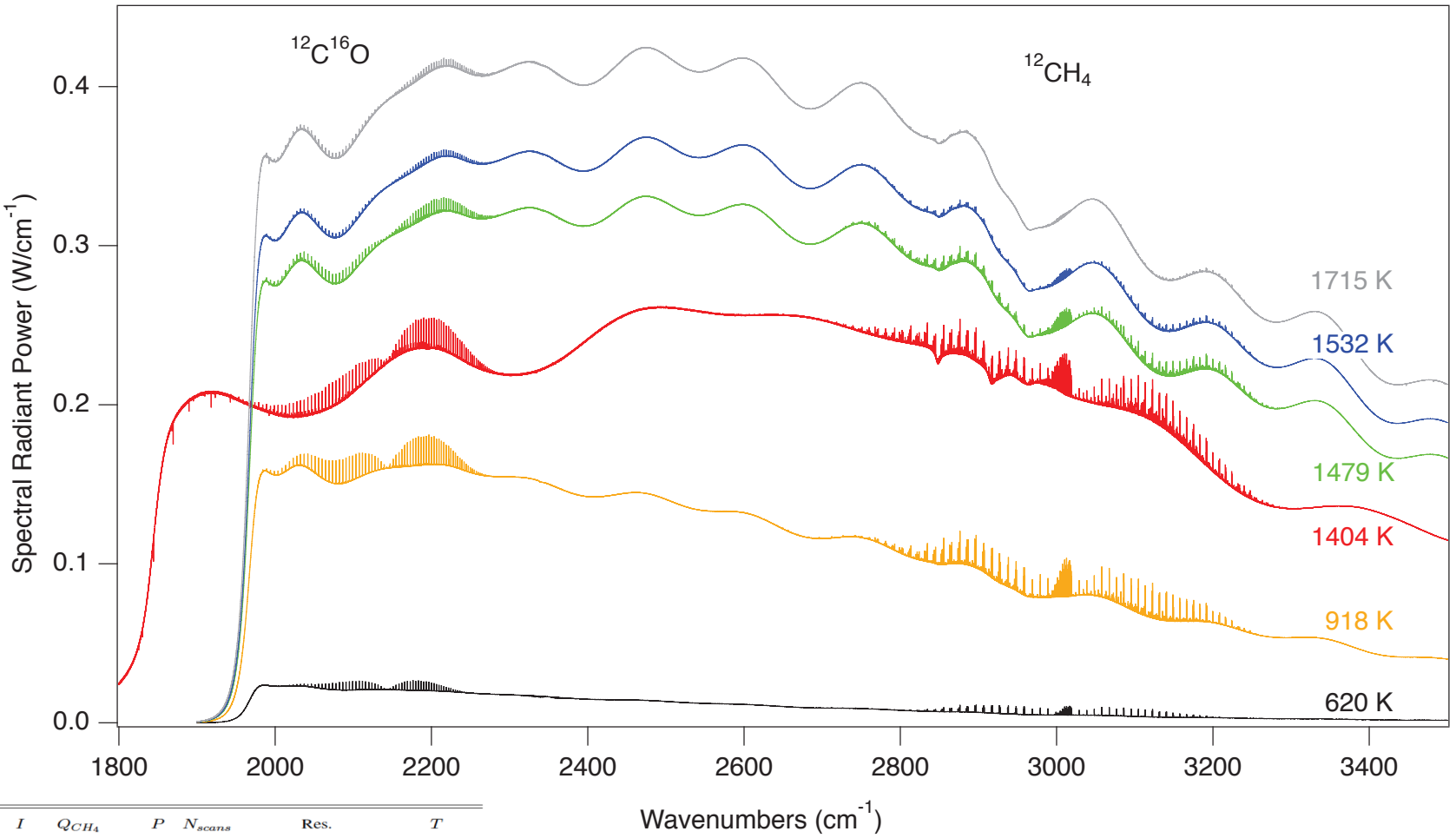


Hot emission spectra

(*Experiment: Institut de Physique de Rennes*)



Hot emission spectra



No.	I	Q_{CH_4}	P	N_{scans}	Res.	T
	A	l_n/min	Pa		cm^{-1}	K
1	20	3	6.93	2500	0.012	620 (5)
2	50	3	7.20	1200	0.012	918 (5)
3	80	3	8.12	2000	0.008	1404 (10)
4	100	3	8.80	2000	0.020	1479 (12)
5	130	3	10.66	2000	0.020	1532 (20)
6	130	1.5	9.33	1800	0.020	1715 (25)

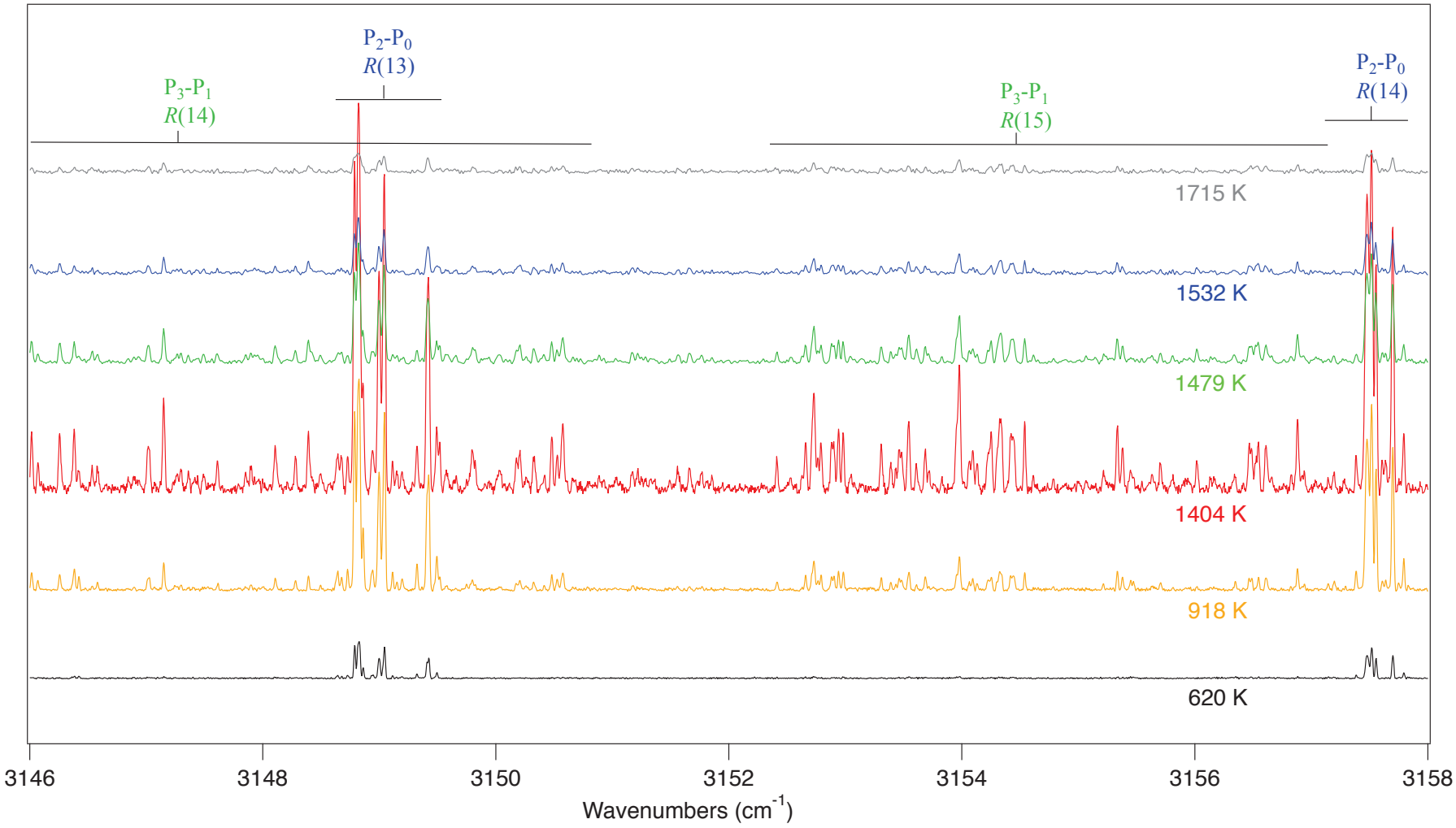
I : Electric current
Q_{CH_4}: Mass flow rate of methane (normal liter per minute)
P: Pressure of the vacuum chamber
N_{scans}: Number of interferograms averaged
Res.: Spectral resolution
T: Gas temperature

(The 1404 K spectrum is scaled by a factor 0.7)

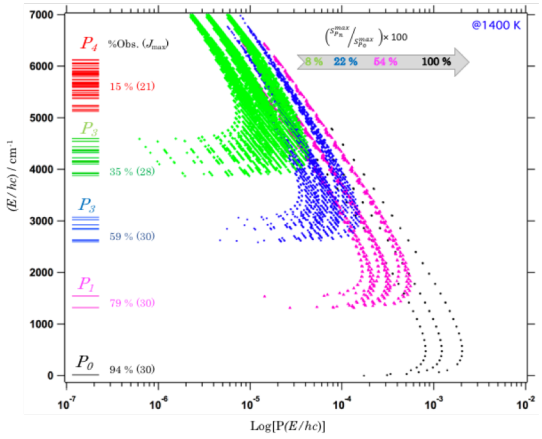
CO is used as a thermometer

Hot emission spectra

(*Detail in the Pentad's R branch*)



II. Theory & model



Tensorial formalism for line-by-line approach

Systematic expansion of effective Hamiltonian and transition moment up to any order and for any polyad scheme, thanks to group theory and tensorial methods

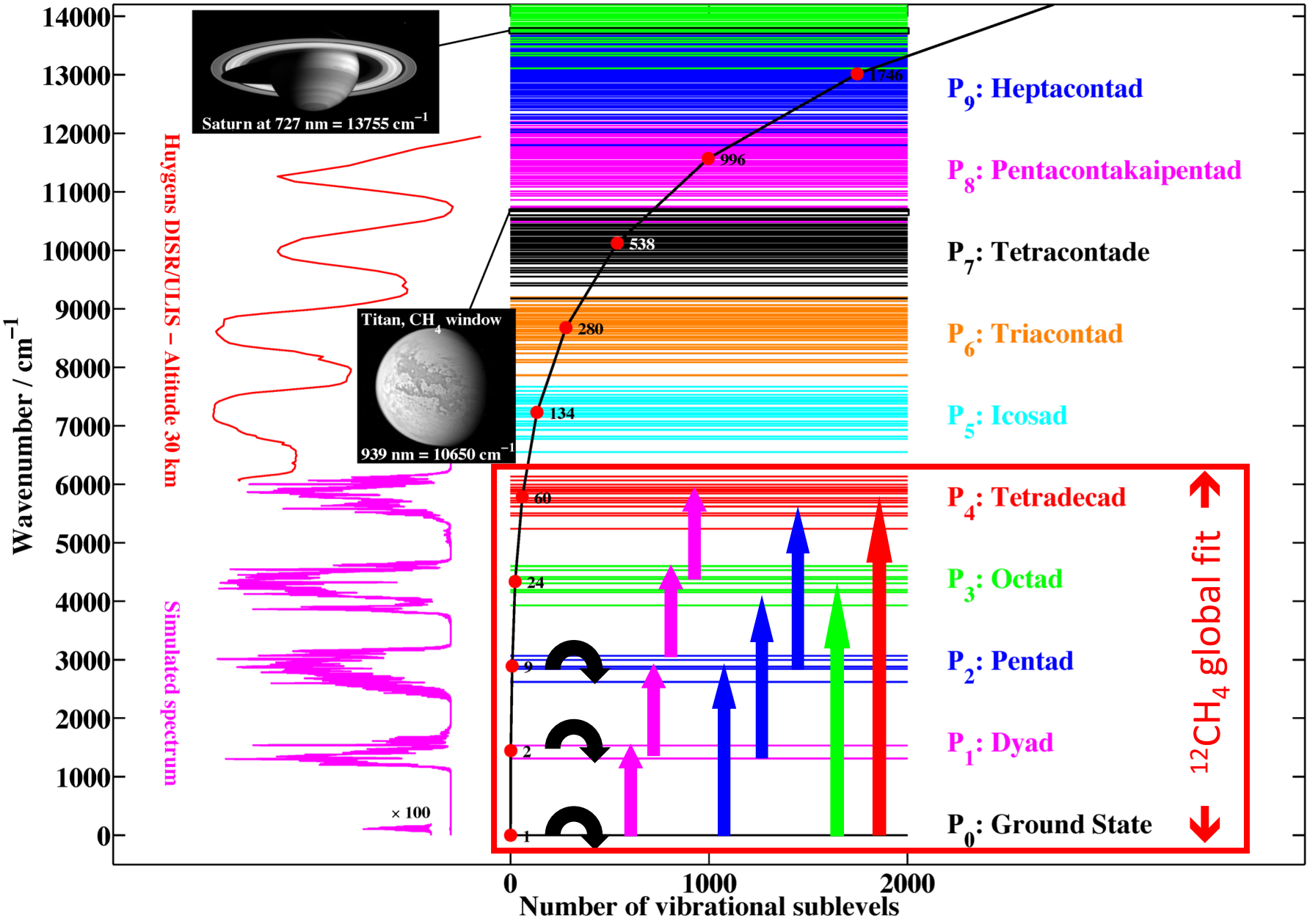
$$\mathcal{H}_{\{P_k\}} = \sum_{\text{all indexes}} \underbrace{t^{\Omega(K,n\Gamma)\Gamma_v\Gamma_{v'}}_{\{s\}\{s'\}}}_{\text{Parameters}} \beta\Big[\underbrace{R^{\Omega(K,n\Gamma)}}_{\text{Rotation}} \otimes \underbrace{{}^{\varepsilon}V^{\Gamma_v\Gamma_{v'}(\Gamma)}_{\{s\}\{s'\}}}_{\text{Vibration}} \Big]^{(A_{1g})}$$

➔ All interactions are automatically included

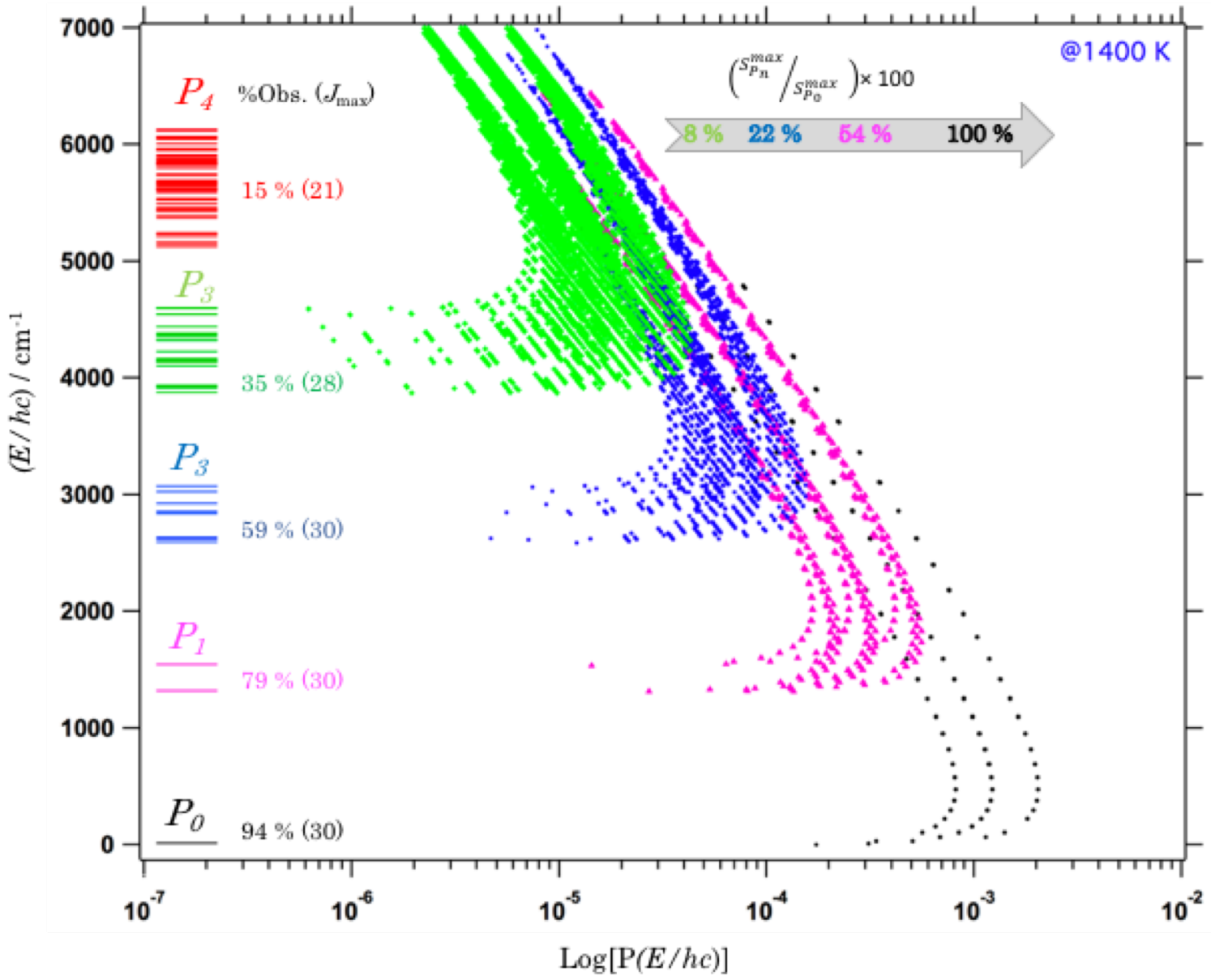
➔ Vibrational extrapolation

➔ Global analyses

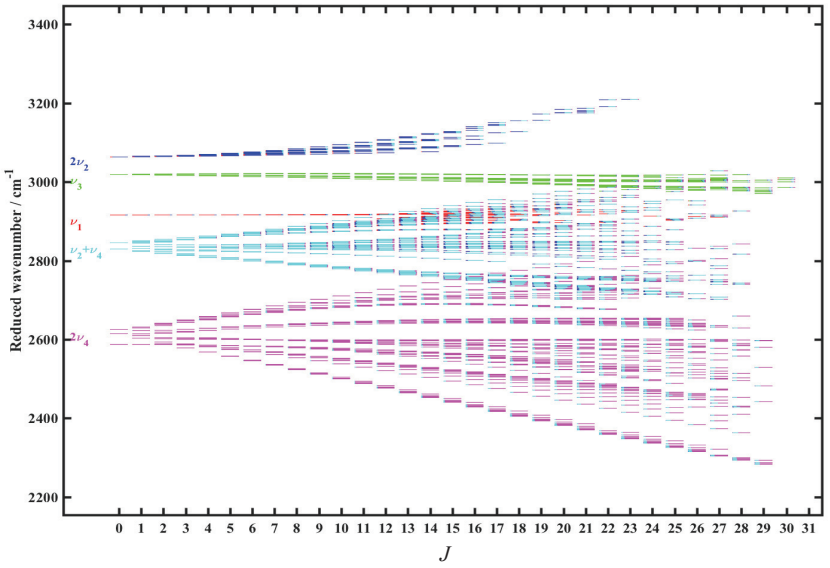
The polyads of methane



Level population & hot band contributions



III. Global fit



Line position fit details

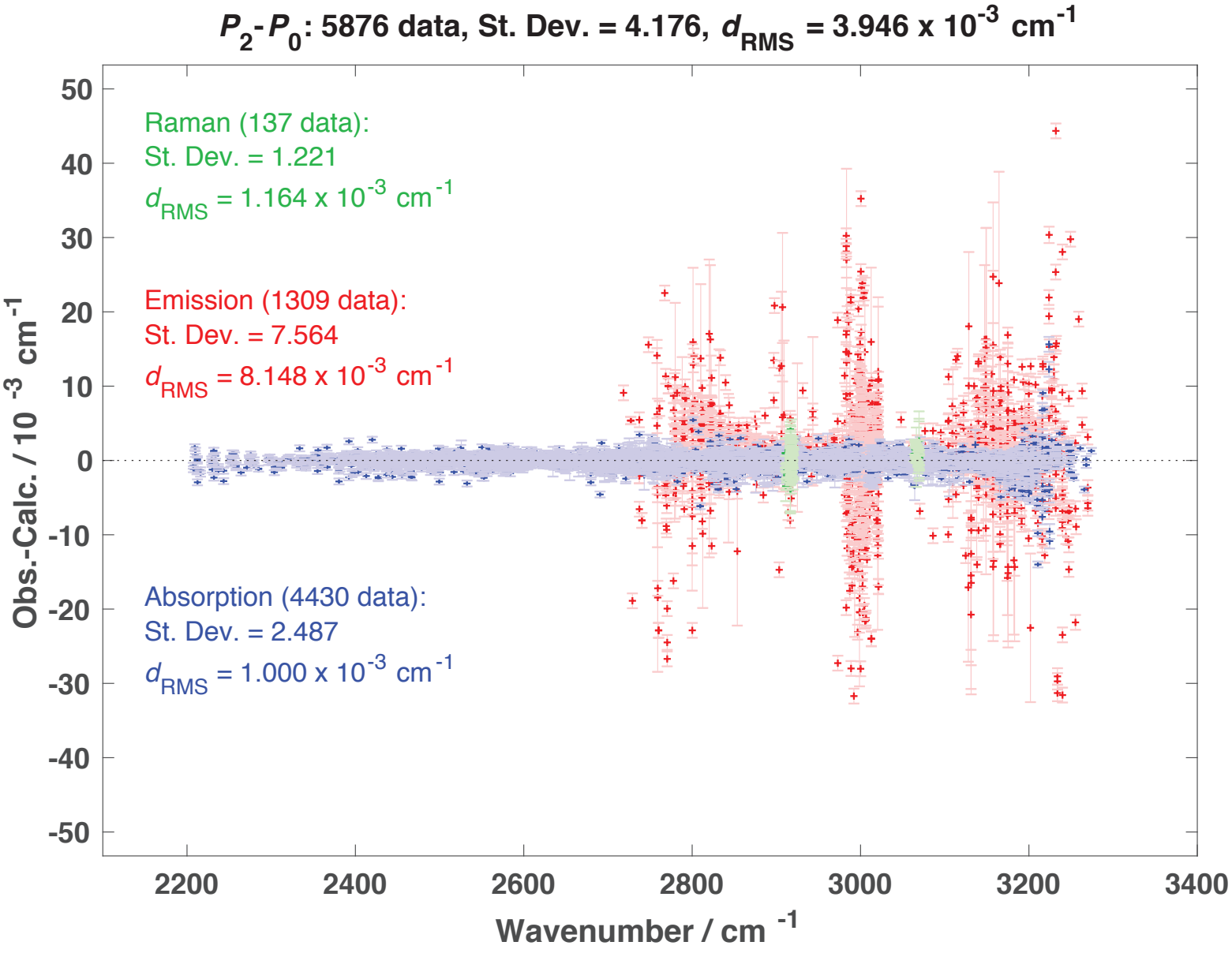
$\mathcal{H}_{\{\text{GS}\}}$, $\mathcal{H}_{\{\text{Dyad}\}}$, $\mathcal{H}_{\{\text{Pentad}\}}$, $\mathcal{H}_{\{\text{Octad}\}}$, $\mathcal{H}_{\{\text{Tetradecad}\}}$ expanded to order 6, 6, 6, 5, 5, respectively.

Order	$\widetilde{H}^{\langle\text{Tetradecad}\rangle}_{\{\text{GS}\}}$		$\widetilde{H}^{\langle\text{Tetradecad}\rangle}_{\{\text{Dyad}\}}$		$\widetilde{H}^{\langle\text{Tetradecad}\rangle}_{\{\text{Pentad}\}}$		$\widetilde{H}^{\langle\text{Tetradecad}\rangle}_{\{\text{Octad}\}}$		$\widetilde{H}^{\langle\text{Tetradecad}\rangle}_{\{\text{Tetradecad}\}}$		$\widetilde{H}^{\langle\text{Tetradecad}\rangle}$	
0	1	(1)	2	(2)	2	(2)	0	(0)	0	(0)	5	(5)
1	0	(0)	2	(2)	5	(5)	0	(0)	0	(0)	7	(7)
2	2	(2)	6	(6)	21	(21)	13	(12)	7	(7)	49	(48)
3	0	(0)	6	(6)	35	(35)	57	(56)	36	(30)	134	(127)
4	3	(3)	13	(13)	71	(71)	183	(181)	219	(113)	489	(381)
5	0	(0)	11	(11)	94	(94)	343	(331)	672	(126)	1120	(562)
6	4	(4)	22	(22)	154	(150)	0	(0)	0	(0)	180	(176)
Total	10	(10)	62	(62)	382	(378)	596	(580)	934	(276)	1984	(1306)
Prev. work[†]	10	(10)	62	(62)	228	(218)	596	(539)	934	(267)	1830	(1096)

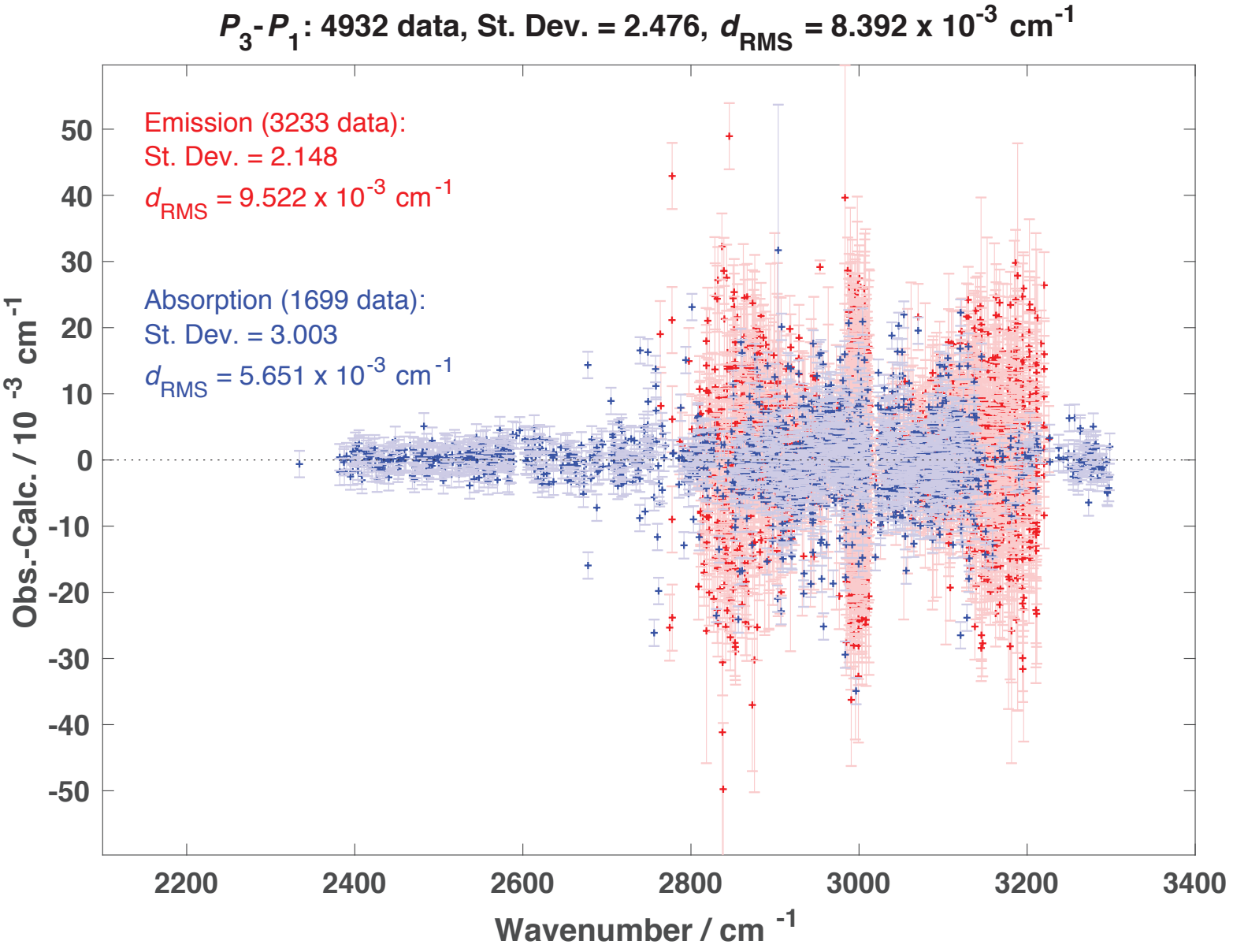
Total: 39,614 data (MW, IR, Emission, Raman)

[†]B. Amyay, M. Louviot, O. Pirali, R. Georges, J. Vander Auwera, and V. Boudon, *J. Chem. Phys.* **144**, 24312 (2016).

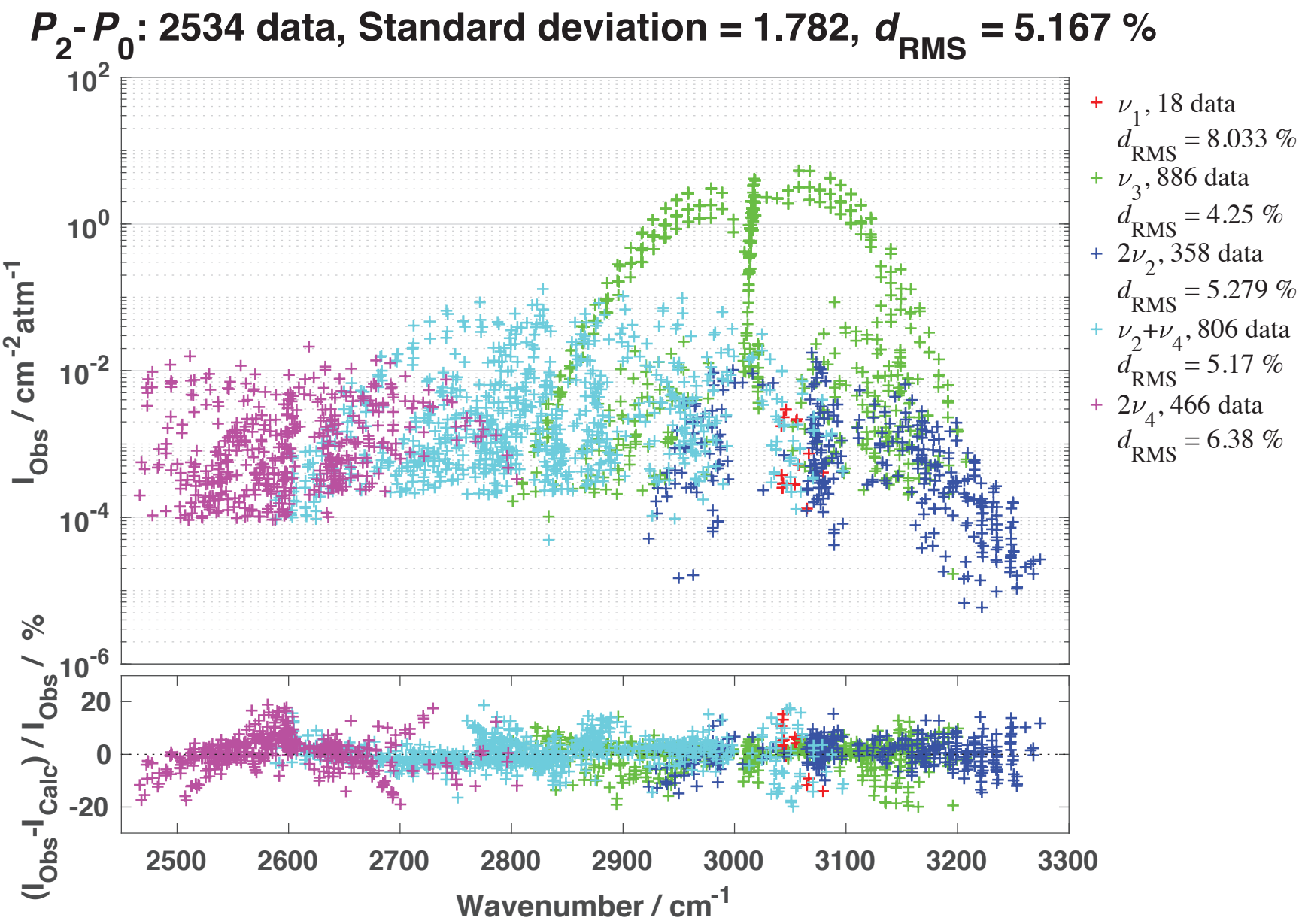
Fit residuals for line positions (Pentad)



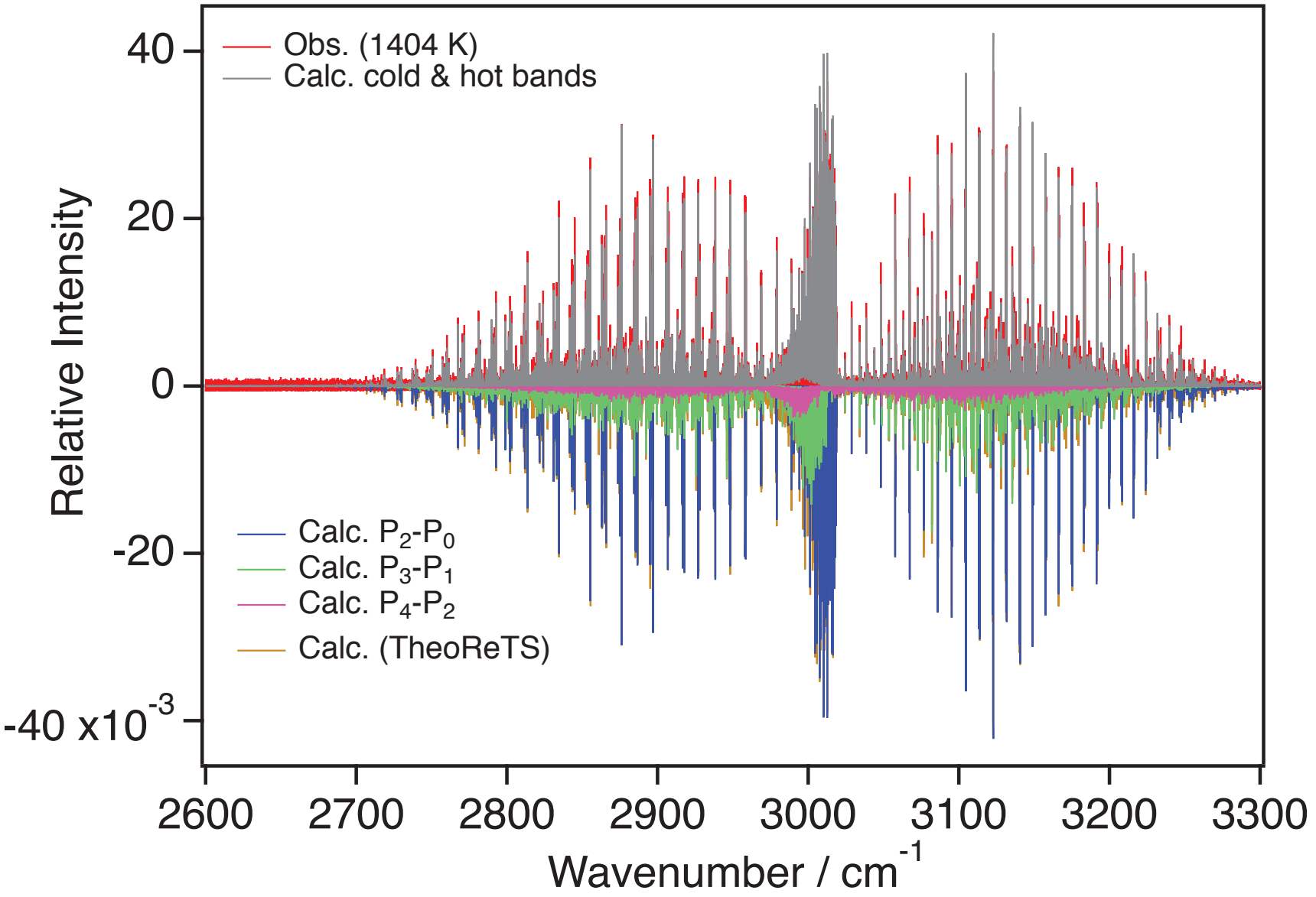
Fit residuals for line positions (Octad–Dyad)



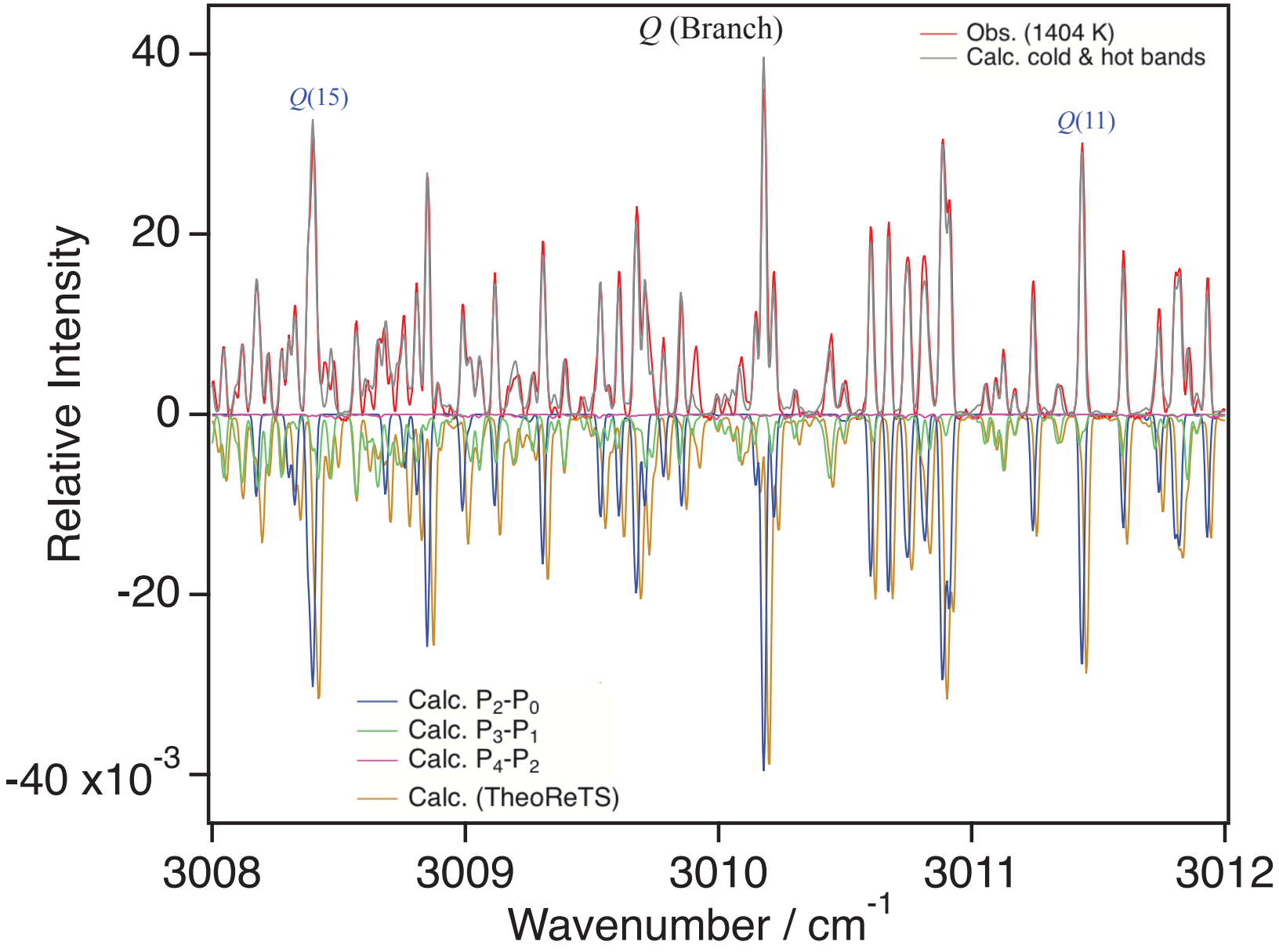
Fit residuals for line intensities (Pentad)



Example of simulation with “all” hot bands

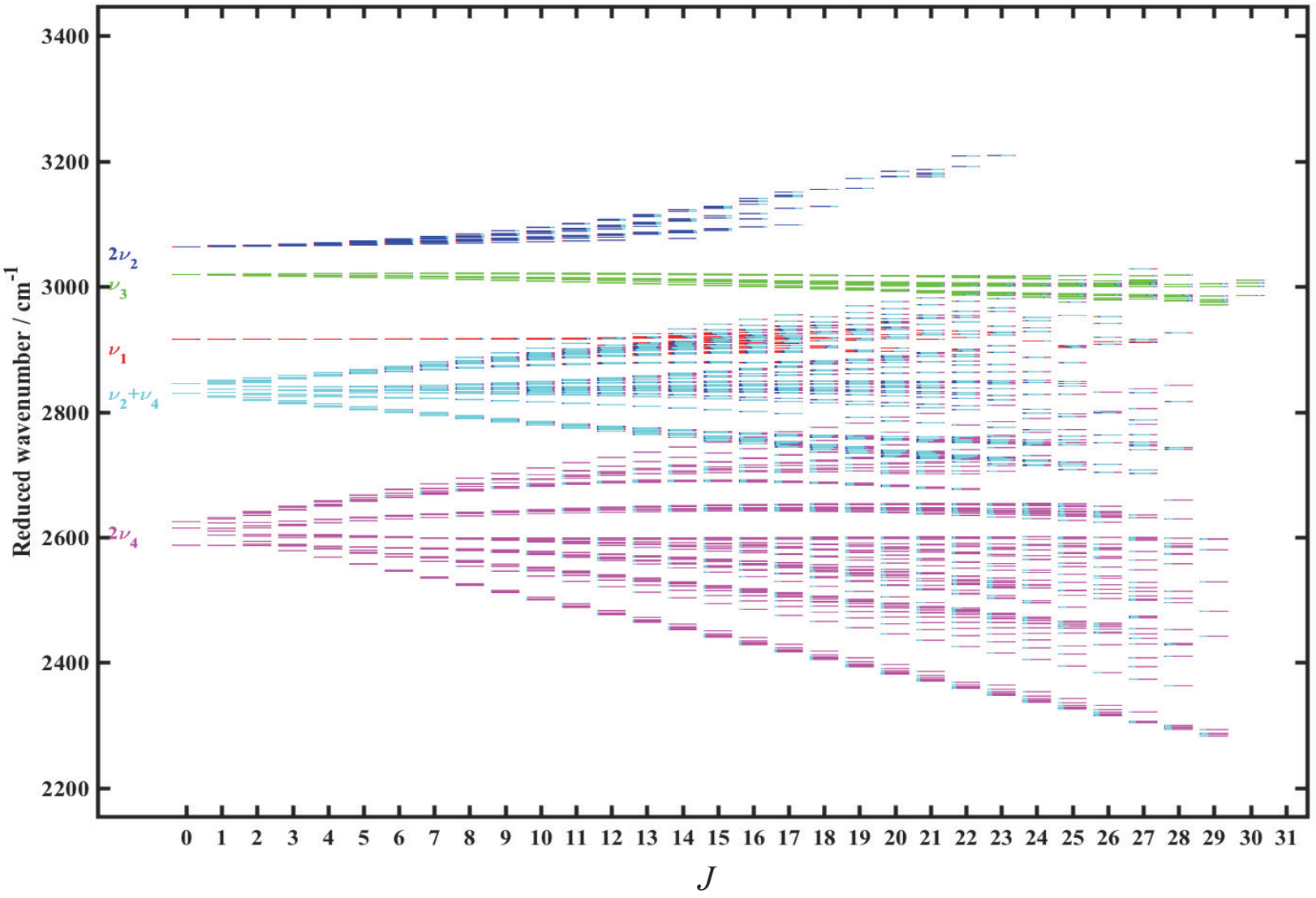


Example of simulation with “all” hot bands (detail)

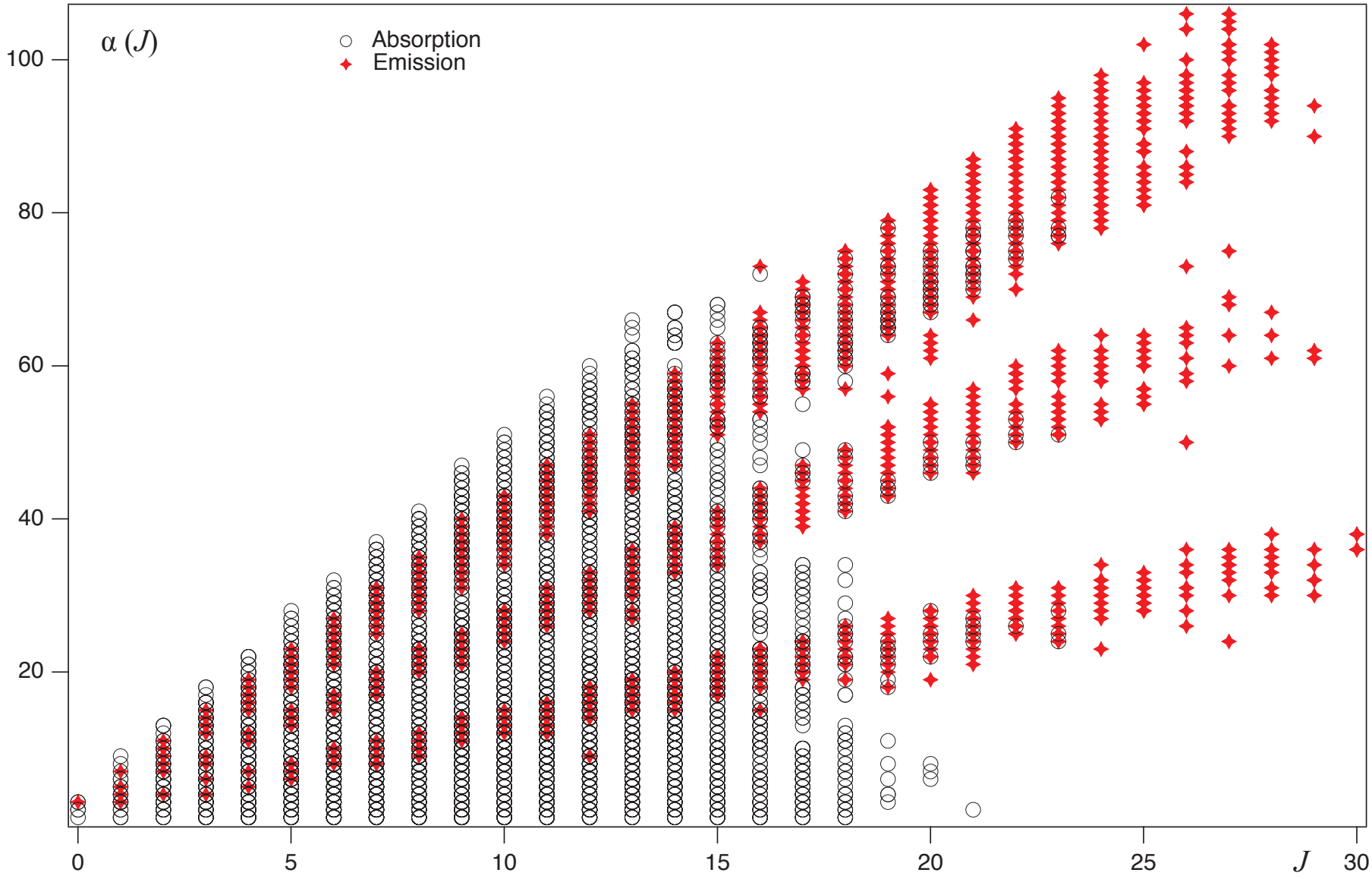


Assigned energy levels in the Pentad region

(*59 % of levels observed up to J = 30*)



Pentad: assigned absorption & emission lines



IV. Summary & CH_4 database

Status of Dijon line-by-line assignments ($^{12}CH_4$)

July 2018, including new assigments form emission spectra:
39,614 assigned positions, 9,396 assigned intensities

Polyad / Spectral region	Positions	Intensities
1 – *Ground state* **0–200 cm^{-1} (> 5.0 µm)**	$J \leq 24$ 2 hot bands	$J \leq 18$ 1 hot band
2 – *Dyad* **1000–1800 cm^{-1} (5.6–10.0 µm)**	$J \leq 30$ 3 hot bands	$J \leq 22$ 1 hot band
3 – *Pentad* **2200–3300 cm^{-1} (3.0–4.6 µm)**	$J \leq 30$ 2 hot bands	$J \leq 21$
4 – *Octad* **3700–4800 cm^{-1} (2.0–2.7 µm)**	$J \leq 28$	$J \leq 20$
5 – *Tetradecad* **5400–6300 cm^{-1} (1.6–1.9 µm)**	$J \leq 21$	$J \leq 14$
6 – *Icosad* **6600–7700 cm^{-1} (1.3 – 1.5 µm)**	Very partial analysis (3 band among 20)	No assignment
Upper polyads **> 7800 cm^{-1} (< 1.28 µm)**	No assignement	No assignement
Windows **(polyad far wings, all regions)**	No assignement	No assignement

The VAMDC/MeCaSDa database

http://vamdc.icb.cnrs.fr/PHP/methane.php
http://portal.vamdc.org

Calculated MeCaSDa line list extraction at 296K

Isotope(s)

- [x] 12CH4 [0.001 -> 6772.680 cm^{-1}]
- [ ] 13CH4 [0.000 -> 4741.874 cm^{-1}]
- [ ] 12CH3D [2014.584 -> 2337.647 cm^{-1}]

Characterisation

- (•) electric dipole [0.000e+0 -> 8.879e-18 cm^{-1}/(molecule cm^{-2})]
- ( ) polarizability [3.724e-21 -> 8.694e+0 arbitrary unit]

Type of Data

- (•) line by line
- ( ) cross sections with a step of: 1 cm^{-1}

Wavenumber Range

Lower wavenumber: 2400 cm^{-1}

Upper wavenumber: 3400 cm^{-1}

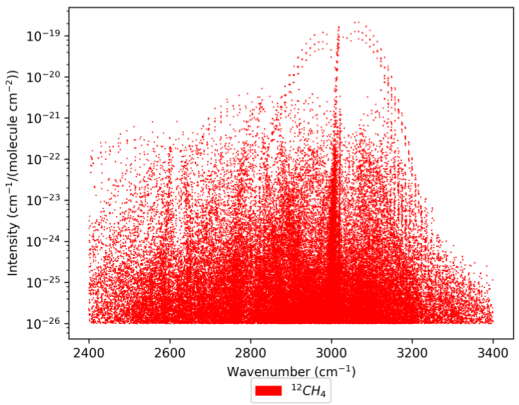
Intensity Threshold

Threshold: 1E-26

Extract — The extraction can last several minutes

Extracted line list here (66115 lines)

Extracted line file here (10.15 MB)



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Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. 49 (2016) 074003 (18pp)
doi:10.1088/0953-4075/49/7/074003

The virtual atomic and molecular data centre (VAMDC) consortium*

Home | VAMDC databases | Guided query | Advanced query | Saved queries | Disclaimer | Citation policy | Info | Tools — Welcome, vboudon! Logout

Query Execution

Done

Modify query | Stop waiting | Save query

Comments

Your request

```
select * where (RadTransWavelength >= 35587.18861209964 AND
RadTransWavelength <= 35714.28571428572) AND ((InchiKey =
'VNWKTOKETHGBQD-UHFFFAOYSA-N'))
```

Results by node

Name	View data	Response	Last database update	Download	Species	States	Processes	Radiative	Collisions	Non Radiative
HITRANonline	-- Choose display --	OK	Not available	XSAMS file	1	219	504	504	0	0
MeCaSDa - Methane Calculated Spectroscopic Database	-- Choose display --	TRUNCATED (19% data returned)	Not available	XSAMS file	1	9875	10000	10000	0	0
JPL database: VAMDC-TAP service		EMPTY	04/07/2018 08:23		0	0	0	0	0	0
TOPbase : VAMDC-TAP interface		EMPTY	13/06/2016 00:00		0	0	0	0	0	0
CDMS		EMPTY	04/07/2018 08:23		0	0	0	0	0	0

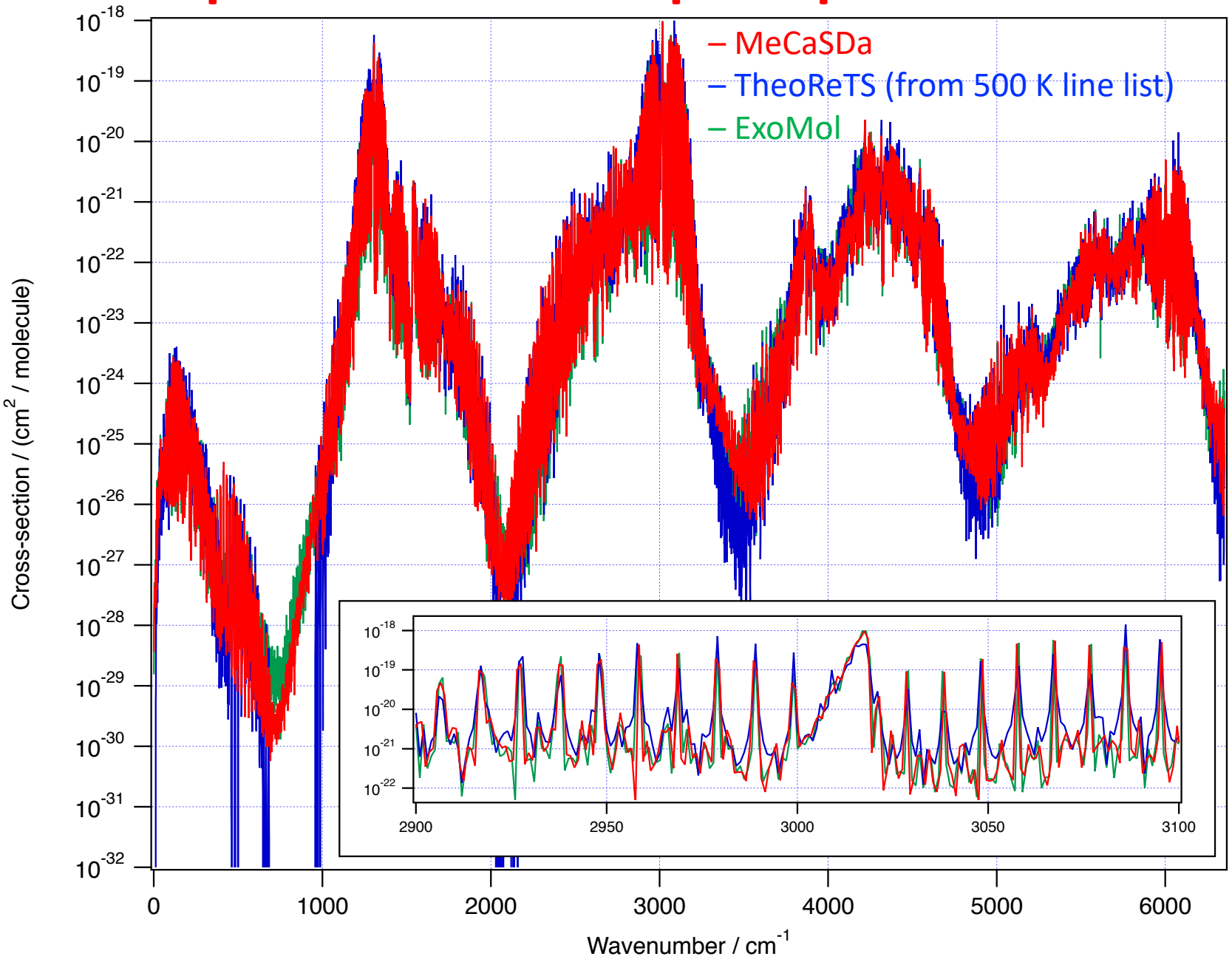
-- Choose display --
** XSAMS to Hitran
** BibTeX from XSAMS
** Table views of XSAMS
Collisional data XSAMS to HTML
Xsams2SME
Atomic spectroscopy XSAMS to HTML
Molecular spectroscopy XSAMS to HTML
XSAMS multiplexor

Journal of Quantitative Spectroscopy & Radiative Transfer 130 (2013) 62–68
Contents lists available at ScienceDirect
Journal of Quantitative Spectroscopy & Radiative Transfer
journal homepage: www.elsevier.com/locate/jqsrt

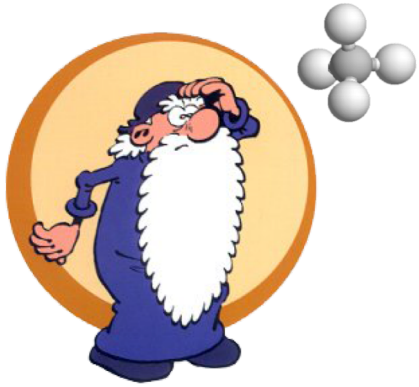
MeCaSDa and ECaSDa: Methane and ethene calculated spectroscopic databases for the virtual atomic and molecular data centre

VAMDC Virtual Atomic and Molecular Data Centre

Comparison with first-principles calculations



V. Conclusion and perspectives



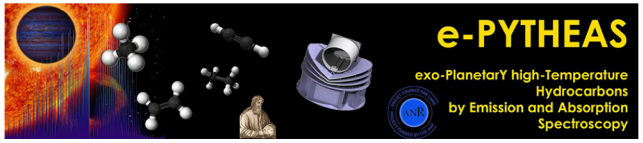
Conclusions

- **High temperature emission spectra**: many hot band lines
- **4,803 new assignments**: total up to 39 614!
- **1,525 new transitions (Tetradecad–Pentad)** identified
- **Global fit** of all assigned methane transitions
- **Improved line list** that corrects previous problems from HITRAN 2012 and MeCASDa
- **Update of MeCaSDa** (*Virtual Atomic and Molecular Data Centre)*

Perspectives for CH_4

- **Line-by-line analyses still have some role to play !**
  Hot bands at lower wavenumbers and high-*J*'s are assignable
- CRDS + hypersonic jet **out-of-equilibrium spectroscopy**

VAMDC consortium



http://e-pytheas.cnrs.fr

J. Chem. Phys. 148, 134306 (2018)

THE JOURNAL OF CHEMICAL PHYSICS **148**, 134306 (2018)

New investigation of the ν_3 C–H stretching region of $^{12}CH_4$ through the analysis of high temperature infrared emission spectra

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The ν_3 C–H stretching region of methane was reinvestigated in this work using high temperature (620-1715 K) emission spectra recorded in Rennes at Doppler limited resolution. This work follows our recent global analysis of the Dyad system $\Delta n = \pm 1$ (1000–1500 cm^{-1}), with n being the polyad number [B. Amyay *et al.*, J. Chem. Phys. **144**, 24312 (2016)]. Thanks to the high temperature, new assignments of vibration-rotation methane line positions have been achieved successfully in the Pentad system and some associated hot bands ($\Delta n = \pm 2$) observed in the spectral region 2600-3300 cm^{-1}. In particular, rotational assignments in the cold band [Pentad-ground state (GS)] and in the first related hot band (Octad-Dyad) were extended up to $J = 30$ and 27, respectively. In addition, 1525 new transitions belonging to the Tetradecad-Pentad hot band system were assigned for the first time, up to $J = 20$. The effective global model used to deal with the new assignments was developed to the 6th order for the first three polyads (Monad, Dyad, and Pentad), and to the 5th order for both the Octad and the Tetradecad. 1306 effective parameters were fitted with a dimensionless standard deviation $\sigma = 2.64$. The root mean square deviations d_{RMS} obtained are 4.18×10^{-3} cm^{-1} for the Pentad-GS cold band, 2.48×10^{-3} cm^{-1} for the Octad-Dyad, and 1.43×10^{-3} cm^{-1} for the Tetradecad-Pentad hot bands. *Published by AIP Publishing.* https://doi.org/10.1063/1.5023331