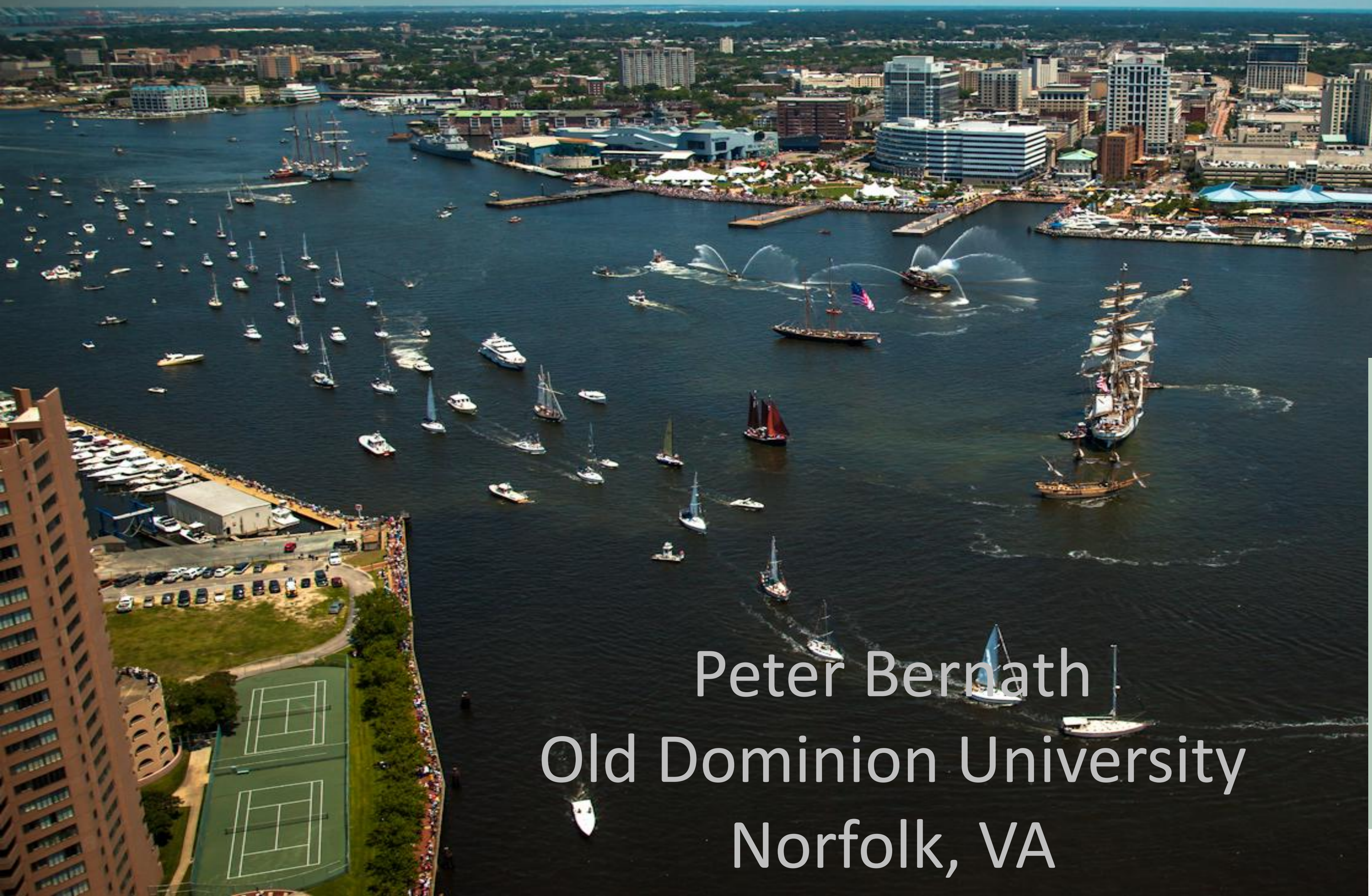
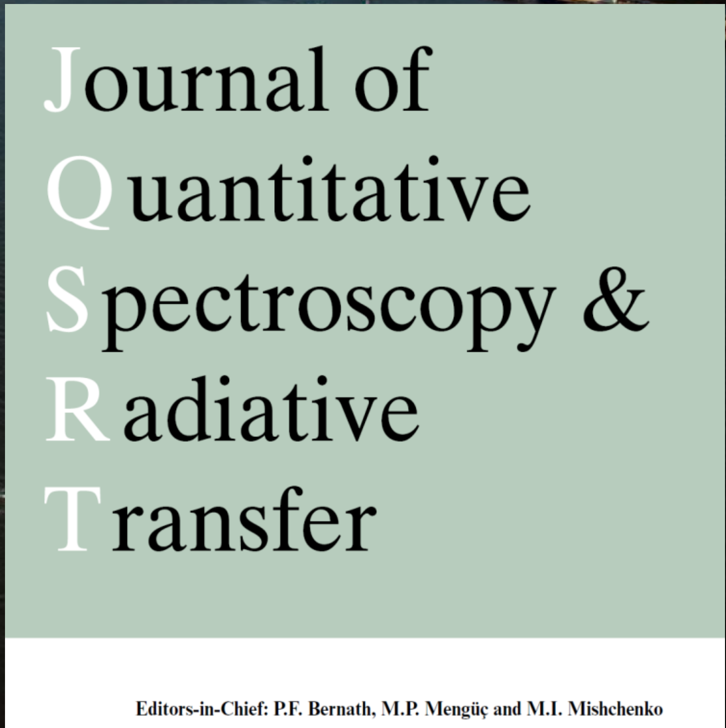
Laboratory Astrophysics for Cool Stars and Exoplanets



Peter Bernath
Old Dominion University
Norfolk, VA

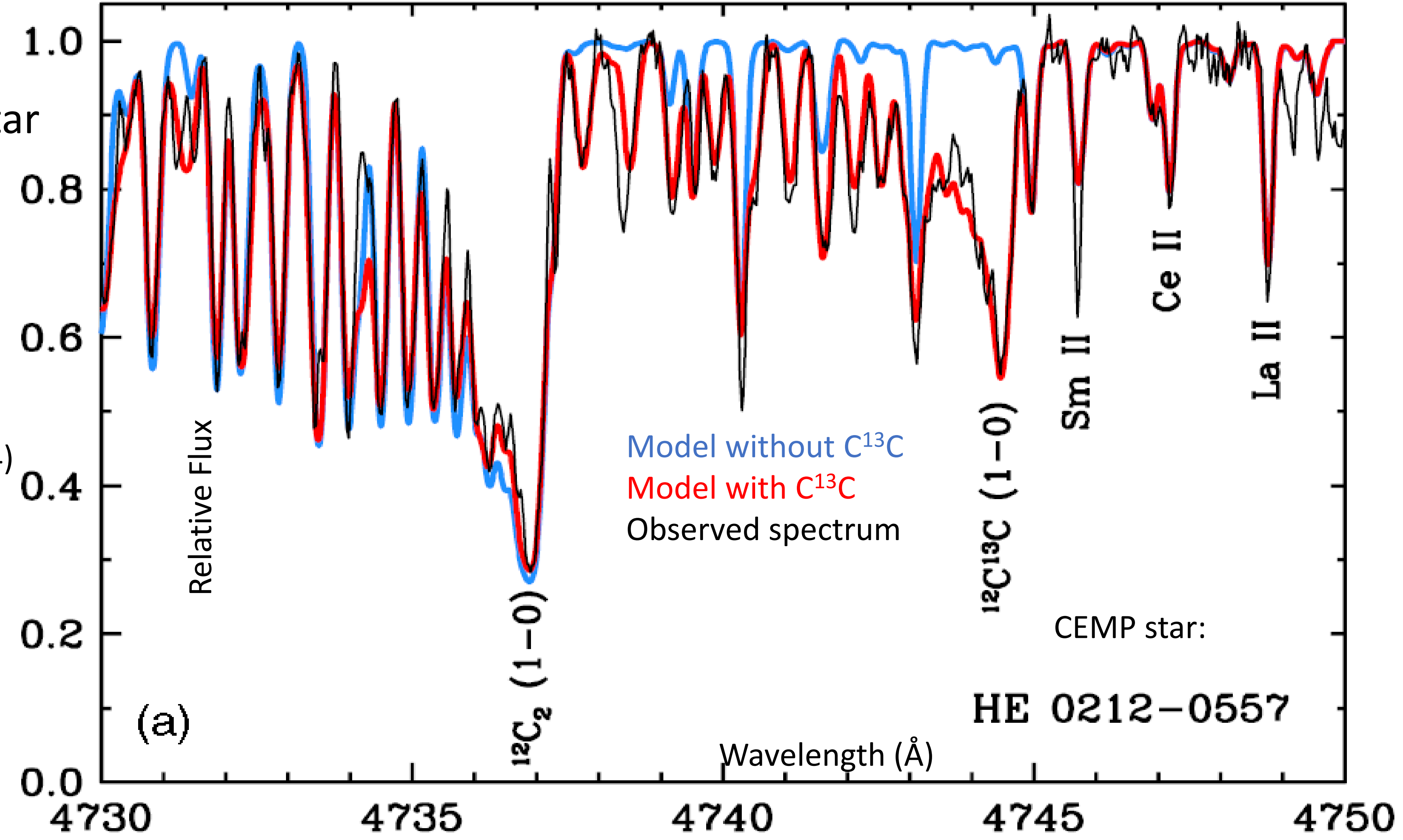


Molecules in Cool Stars, $C^{13}C$

C_2 Swan System in a carbon-enhanced metal-poor (CEMP) star

Terrestrial ^{13}C isotope abundance is 1%.

Line list:
Ram *et al*. ApJS **211**, 5 (2014)

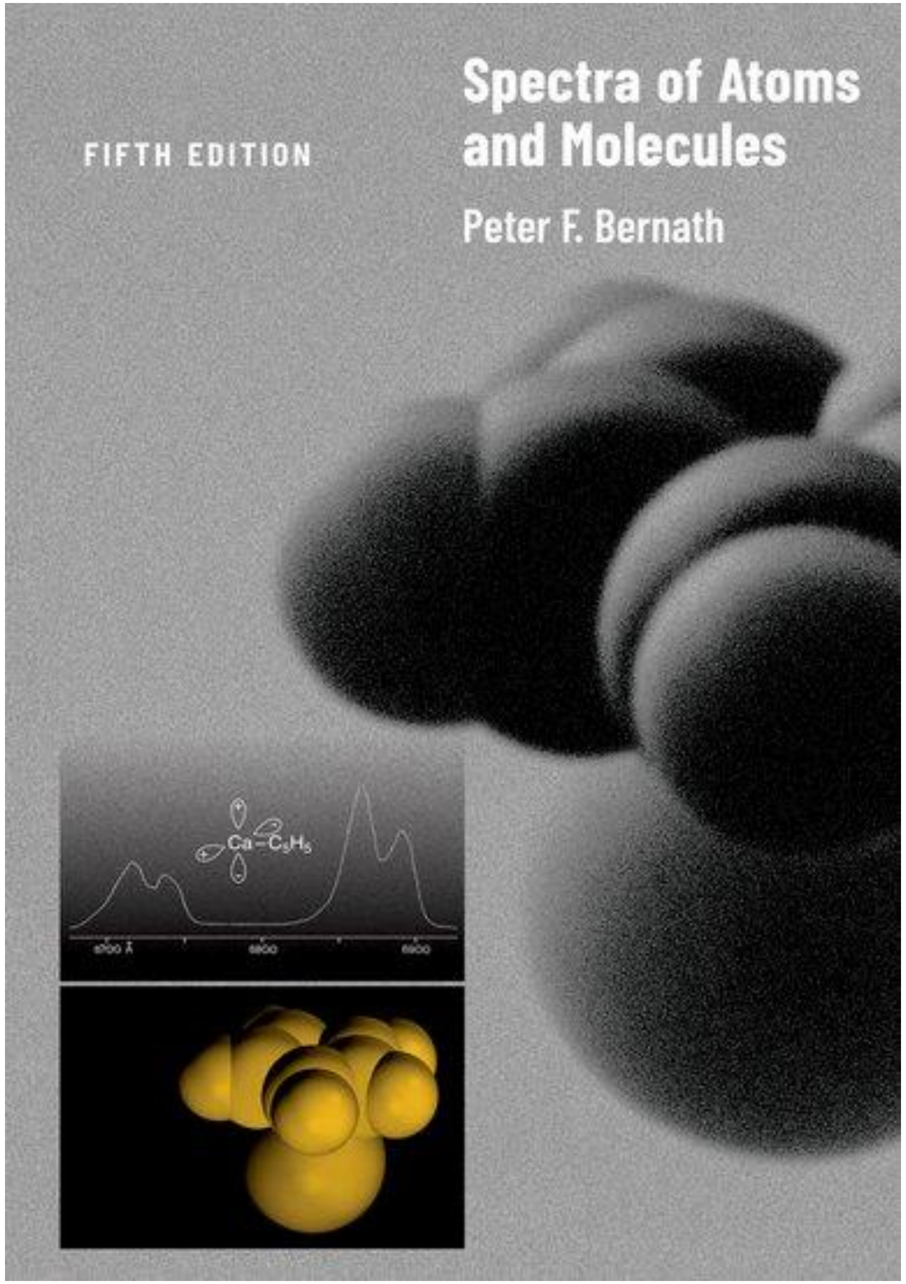


It's All Spectroscopy

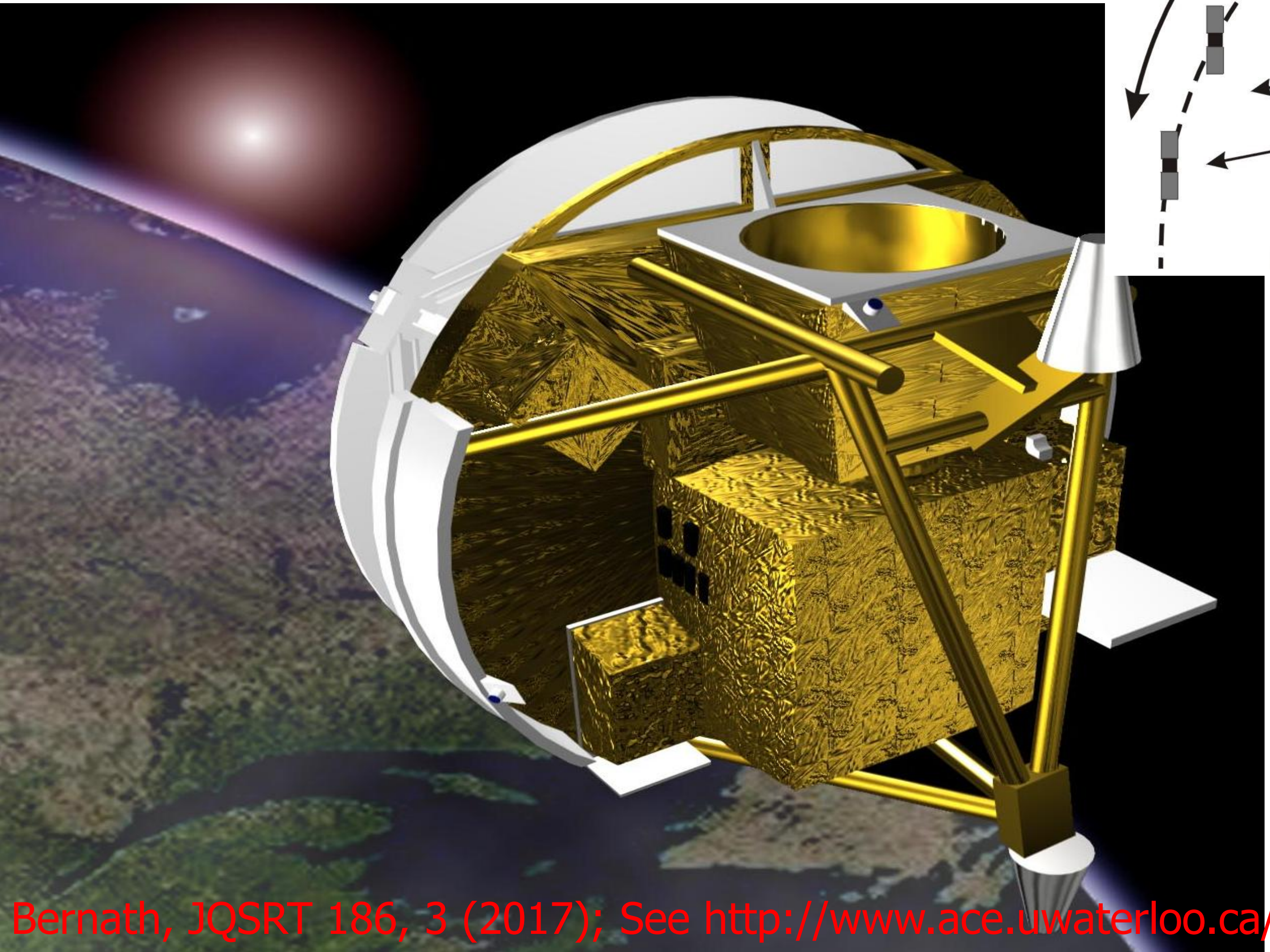
Spectra of Atoms and Molecules, Oxford University Press

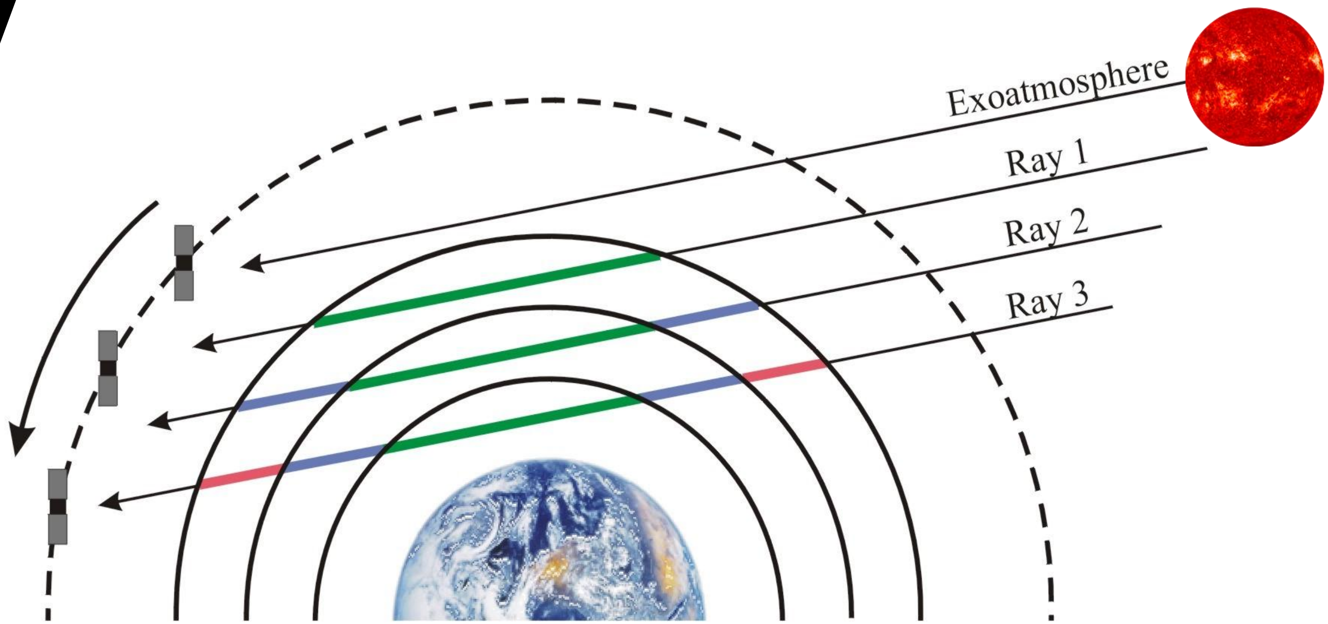
Textbook aimed at graduate students and senior undergrads. Particularly useful treatment of the confusing topic of line intensities needed for remote sensing. 4th edition added chapters on atmospheric and astronomical spectroscopy.

5th edition (2025) has a chapter added on the new spectroscopy of clouds and aerosols from ACE satellite data.



Atmospheric Chemistry Experiment (ACE) Satellite



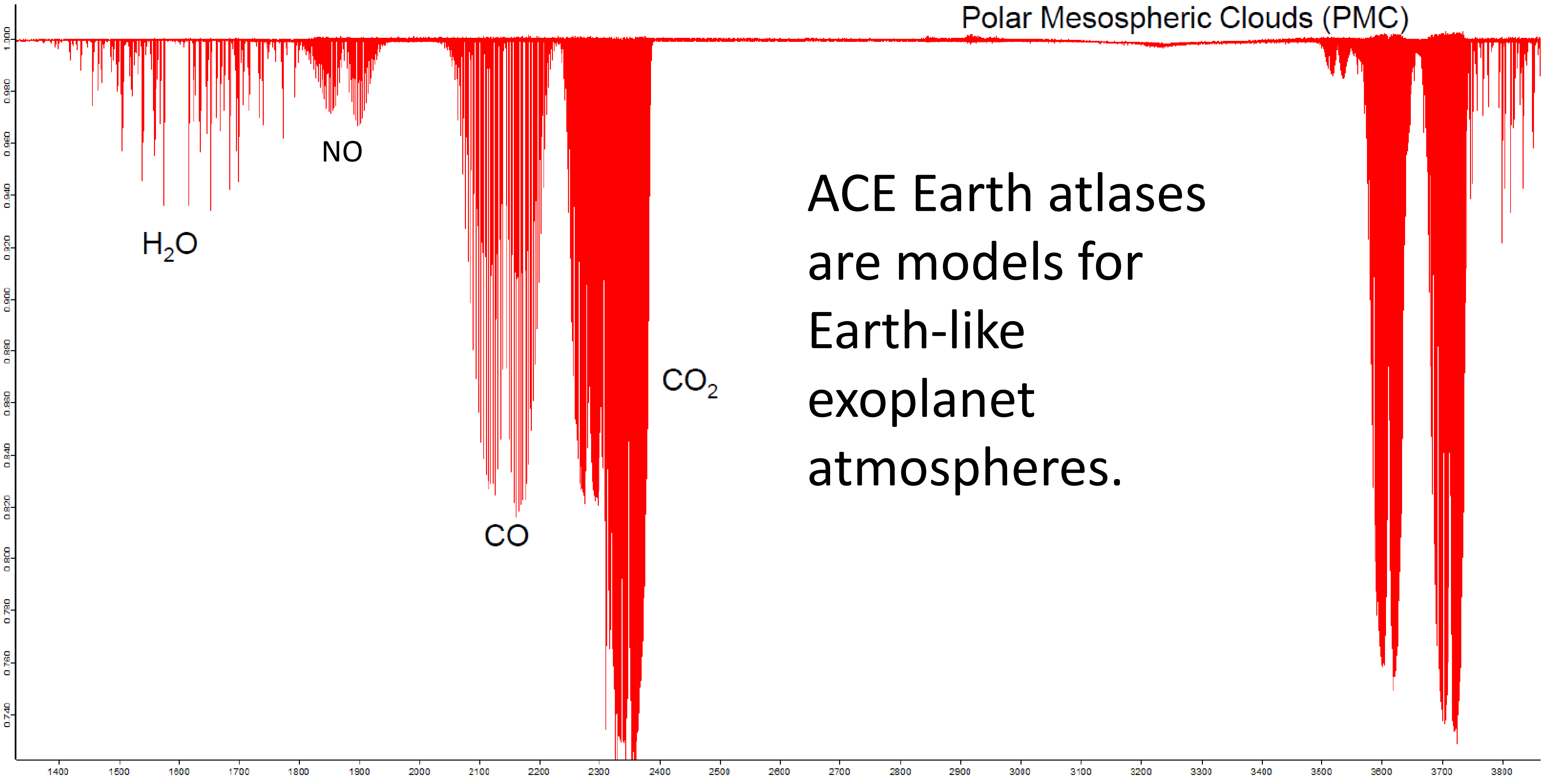


Solar occultation has the same limb geometry as exoplanet transit (transmission) spectroscopy.

Bernath, JQSRT 186, 3 (2017); See http://www.ace.uwaterloo.ca/

New ACE Infrared Earth Atlases

85 km Spectra - Arctic Summer



ACE Earth atlases are models for Earth-like exoplanet atmospheres.

Line List Requirements

Molecular data at high spectral resolution for samples at low and high temperatures.

Although observations may be at low spectral resolution, underlying radiative transfer is at high resolution.

From Beer-Lambert law: $$I = I_0 \exp\left[-S' g(\nu - \nu_{10}) Nl\right]$$

Need a lineshape function $g(\nu-\nu_{10})$ (assumed to be Voigt; H_2, He and CO_2 pressure broadening parameters needed) and a line strength S' in SI units, from Bernath, *Spectra of Atoms and Molecules*:

$$S' = \frac{2\pi^2 \nu_{10} S_{J'J''}}{3\varepsilon_0 hc Q_T} \exp\left(-\frac{E_{low}}{kT}\right)\left[1-\exp\left(-\frac{h\nu_{10}}{kT}\right)\right]$$

Line list requirements 1. line position, ν_{10}, 2. partition function, Q_T (calculated, $Q(T)=\Sigma g_i \exp(-E_i/kT)$), 3. line intensity, $S_{J'J''}$ (or S'), and 4. lower state energy, E_{low}.

Molecular Opacities

Create line list and then compute opacity tables (absorption cross-section as a function of wavelength) suitable for a range of temperatures, pressures and compositions.

Line lists (ν_{10}, S', E_{low}) can be created by:

1. Ab initio calculation. Solve the electronic Schrödinger equation ($H\psi=E\psi$) to obtain potential energy functions and (transition) dipole surfaces, then vibration-rotation Schrödinger equation for each electronic state to obtain energy levels (transitions) and wavefunctions (intensities).
2. Experimental measurement.
3. Combination of 1 and 2.

Ab initio calculations provide the large number of transitions needed at high temperature, but line position accuracy is too low. Experimental measurement has required accuracy, but not the millions (billions) of lines needed. However, calculated line intensities can be as good as experiment for small molecules.

MoLLIST Website

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

MoLLIST: Molecular Line Lists, Intensities and Spectra

Peter F. Bernath

Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA

A R T I C L E I N F O

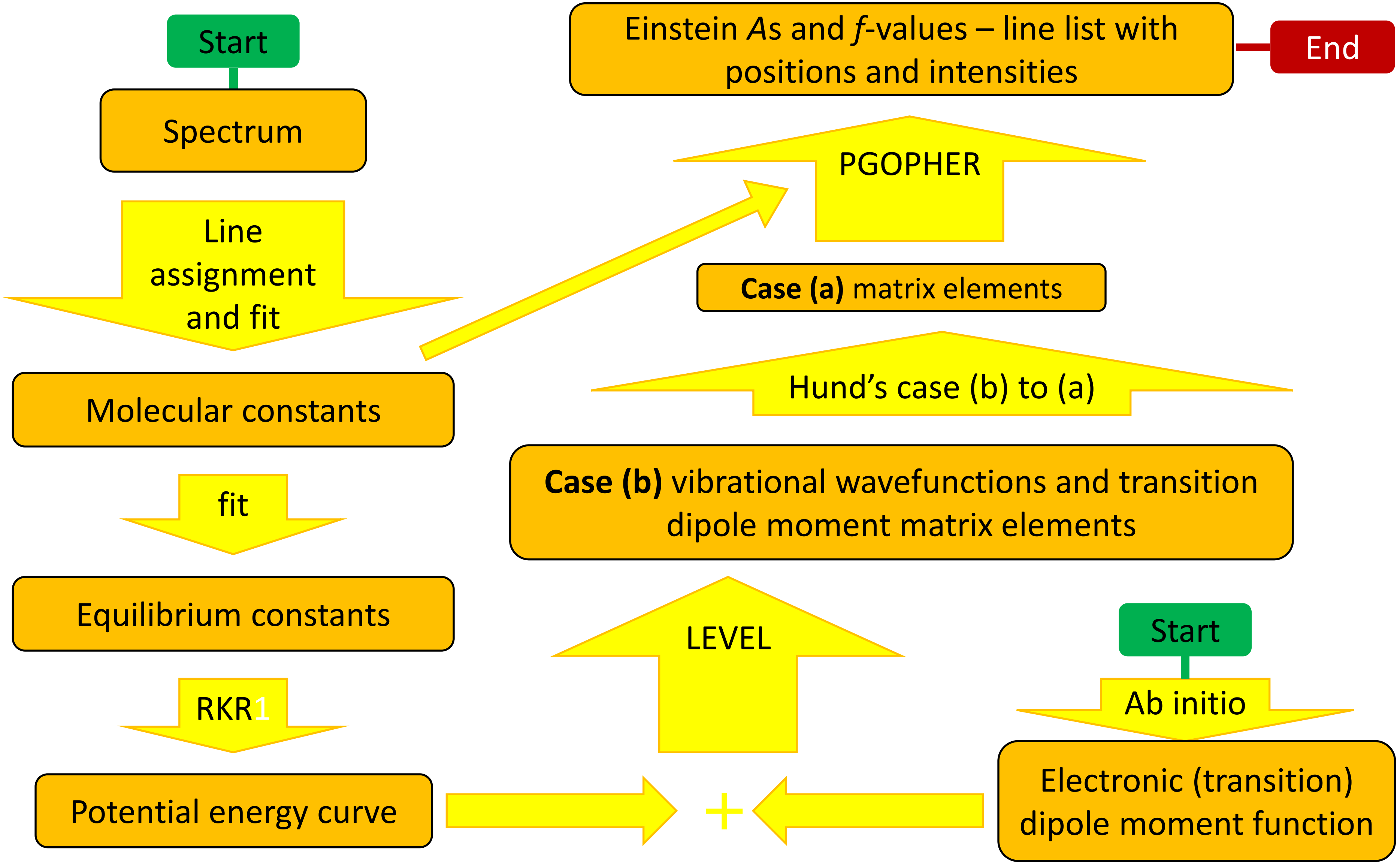
Article history:
Received 11 September 2019
Revised 6 October 2019
Accepted 6 October 2019
Available online 8 October 2019

Keywords:

A B S T R A C T

The simulation of astronomical spectra of cool stars, brown dwarfs and exoplanets requires high resolution line lists and absorption cross sections of many molecules. Similar data sets are needed for the Earth's atmosphere and other planets in our solar system. The requirements for line lists are reviewed and methods used to create them are discussed. Equations to convert between different units are provided. The MoLLIST (Molecular Line Lists, Intensities and Spectra) data compilation is presented and used as an example.

Semi-empirical Method (James Brooke)



Special Issue: JQSRT Jan 2017

Colin Western 1957-2021

Journal of Quantitative Spectroscopy & Radiative Transfer 186 (2017) 221–242

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

PGOPHER: A program for simulating rotational, vibrational and electronic spectra

Colin M. Western

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom

RKR1: A computer program implementing the first-order RKR method for determining diatomic molecule potential energy functions

Robert J. Le Roy Journal of Quantitative Spectroscopy & Radiative Transfer 186 (2017) 158–166

LEVEL: A computer program for solving the radial Schrödinger equation for bound and quasibound levels

Robert J. Le Roy Journal of Quantitative Spectroscopy & Radiative Transfer 186 (2017) 167–178

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Bob LeRoy 1944-2018

TiO

Key molecule for classifying M stars by their optical spectra

Found in stratospheres of hot Jupiter exoplanets: responsible for stratosphere formation (temperature inversion)

Complex spectra typical of transition metal oxides (open d-shell)

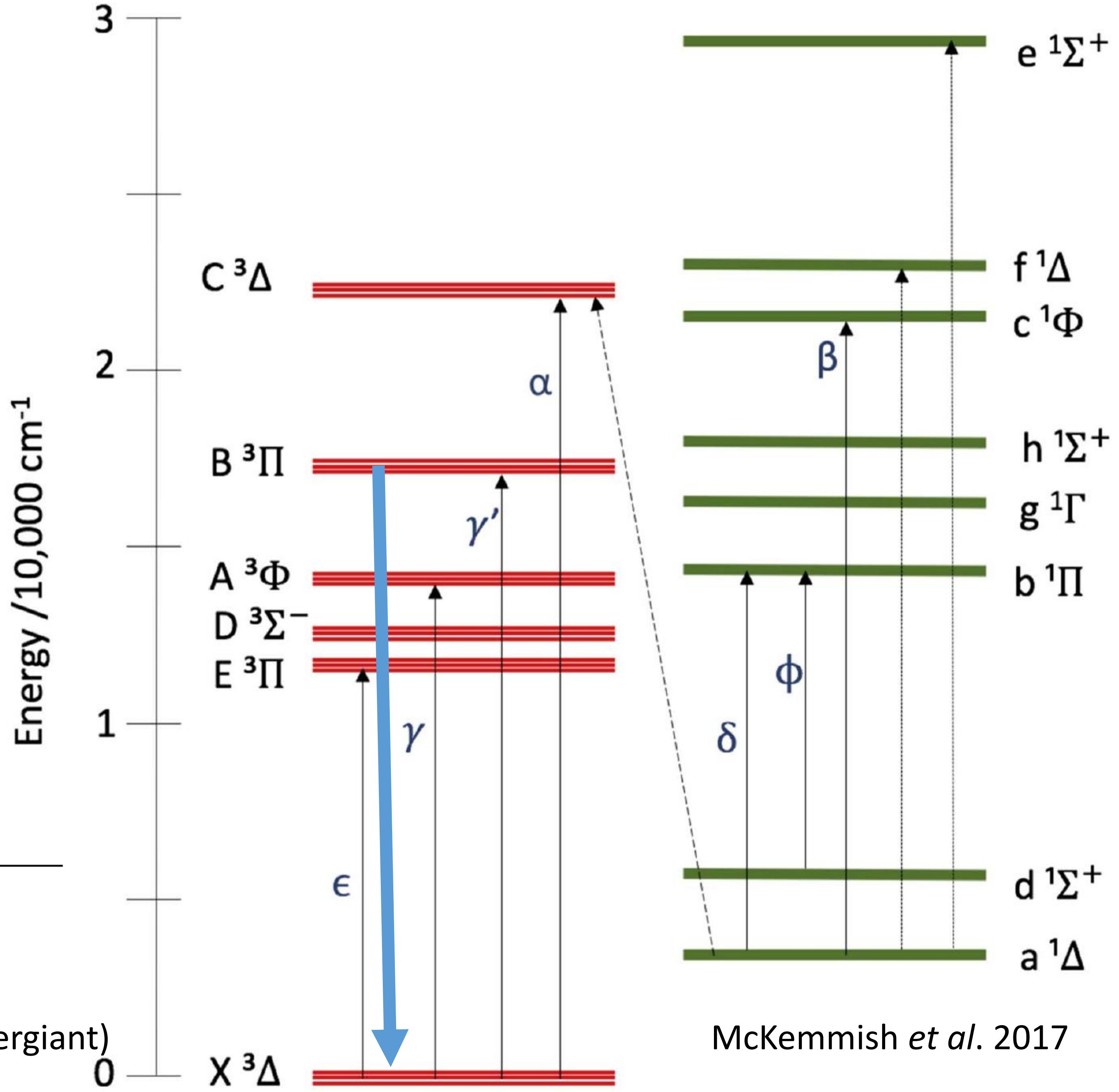
PROCEEDINGS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Fowler 1907

The Fluted Spectrum of Titanium Oxide

A. Fowler

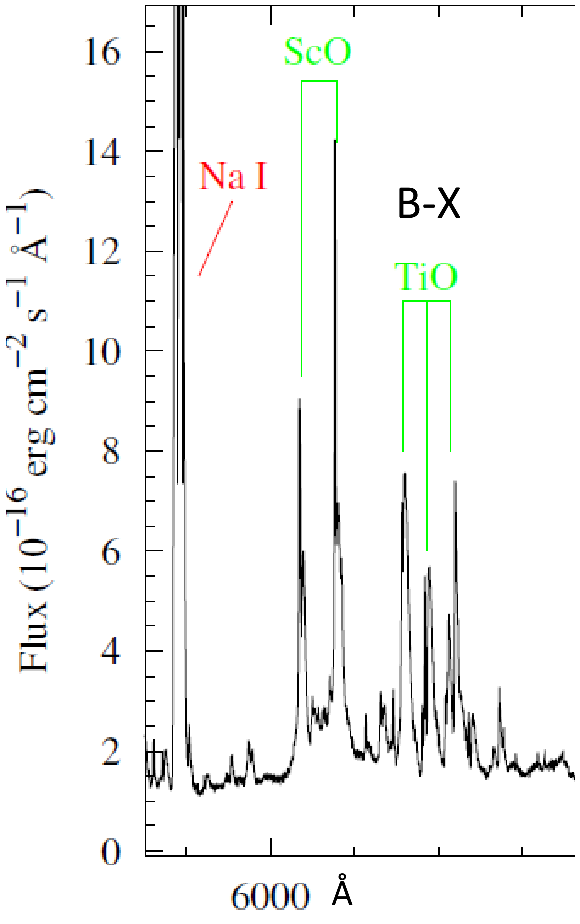
Proc. R. Soc. Lond. A 1907 **79**, 509-518
doi: 10.1098/rspa.1907.0059



Antares M1.5I (M supergiant)

McKemmish *et al.* 2017

TiO Spectroscopy



Tylenda *et al*. 2015
V4332 Sgr: stellar merger

M Star Opacities: The $B^3\Pi$ - $X^3\Delta$ Band System of TiO

PETER F BERNATH[1,2] MANISH BHUSAL[2] AND MIREK R SCHMIDT[3]

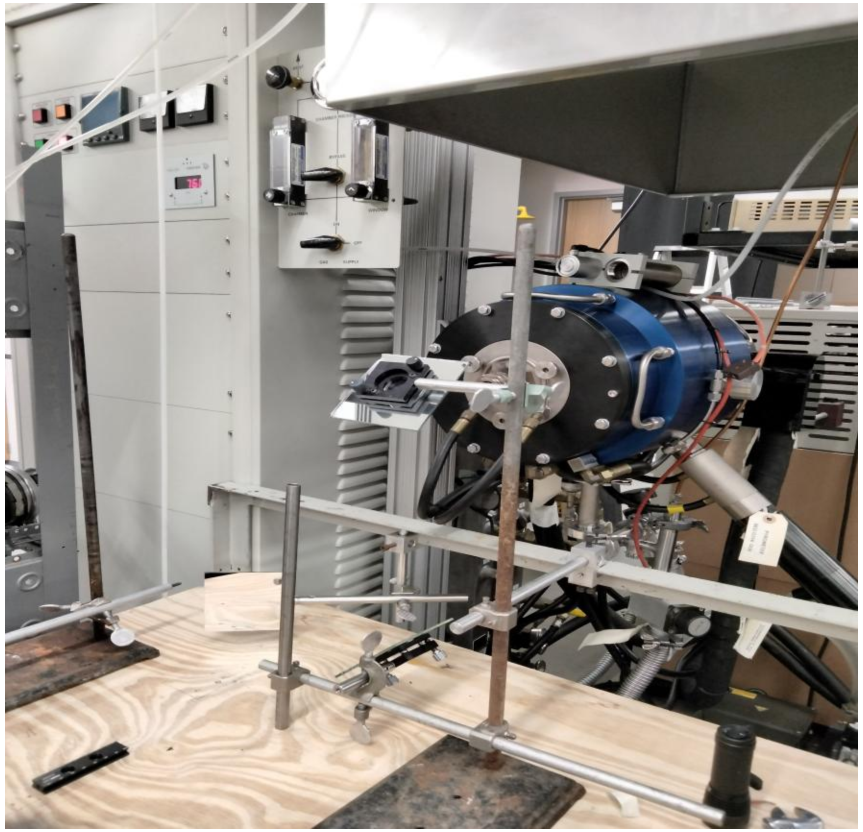
[1] *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA*
[2] *Department of Physics, Old Dominion University, Norfolk, VA 23529, USA*
[3] *Nicolaus Copernicus Astronomical Center, ul. Rabiańska 8, 87-100 Toruń, Poland*

In press Astrophys. J.

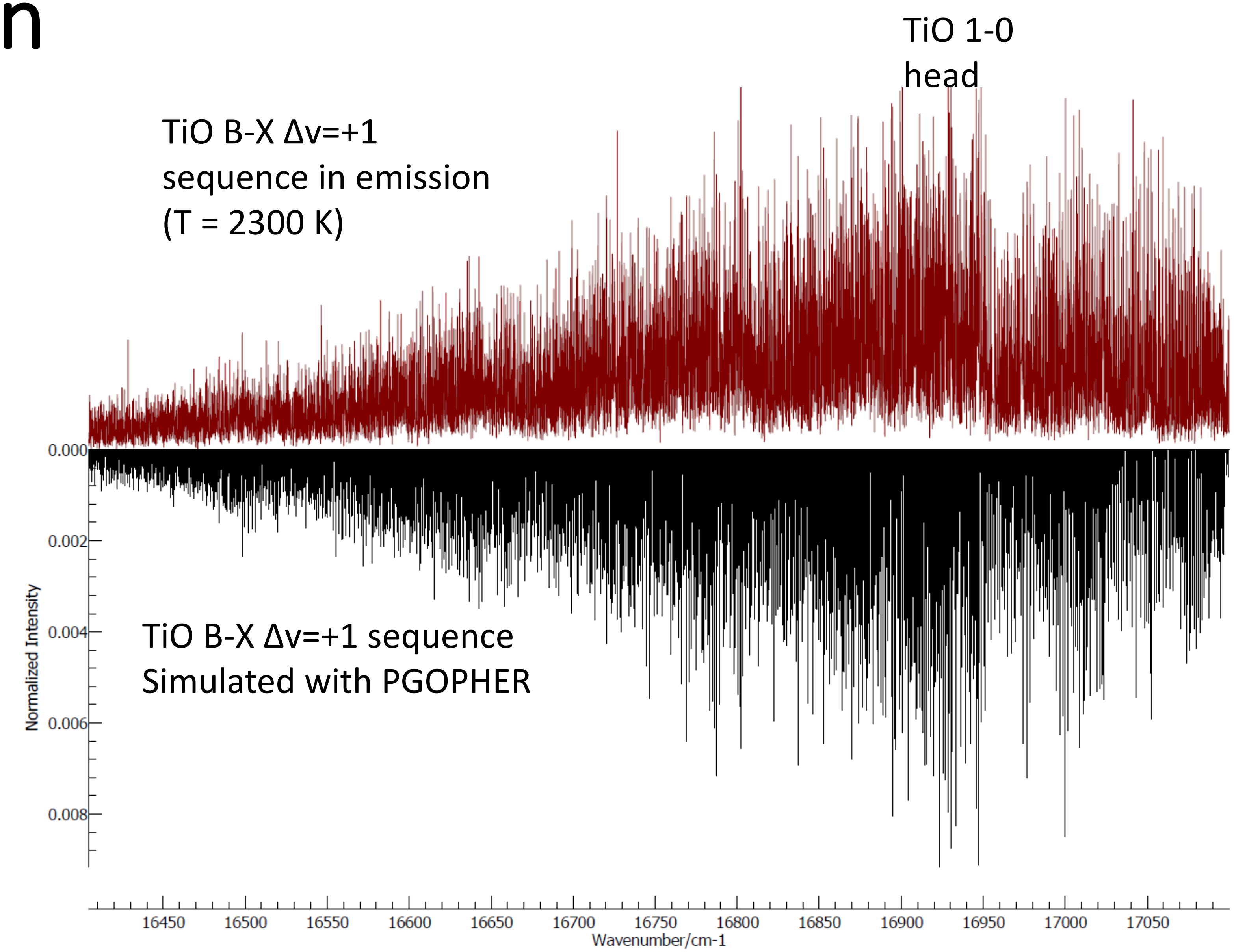
ABSTRACT

The spectra of titanium monoxide (TiO) are used to classify M stars. TiO experimental cross sections based on a high-resolution emission spectrum recorded with a Fourier transform spectrometer at the National Solar Observatory are used for the analysis of the TiO $B^3\Pi$ - $X^3\Delta$ transition (γ' system). The 3-2 and 4-3 vibrational bands are analyzed for the first time and the analysis of the 2-1 band is revised. The transition dipole moment function from an ab initio calculation has been used to calculate the band strengths. These band strengths are used to produce a $B^3\Pi$ - $X^3\Delta$ line list for v=0-4 suitable for simulation of astronomical spectra.

TiO B-X Transition



Carbon furnace at ODU



Stellar TiO B-X

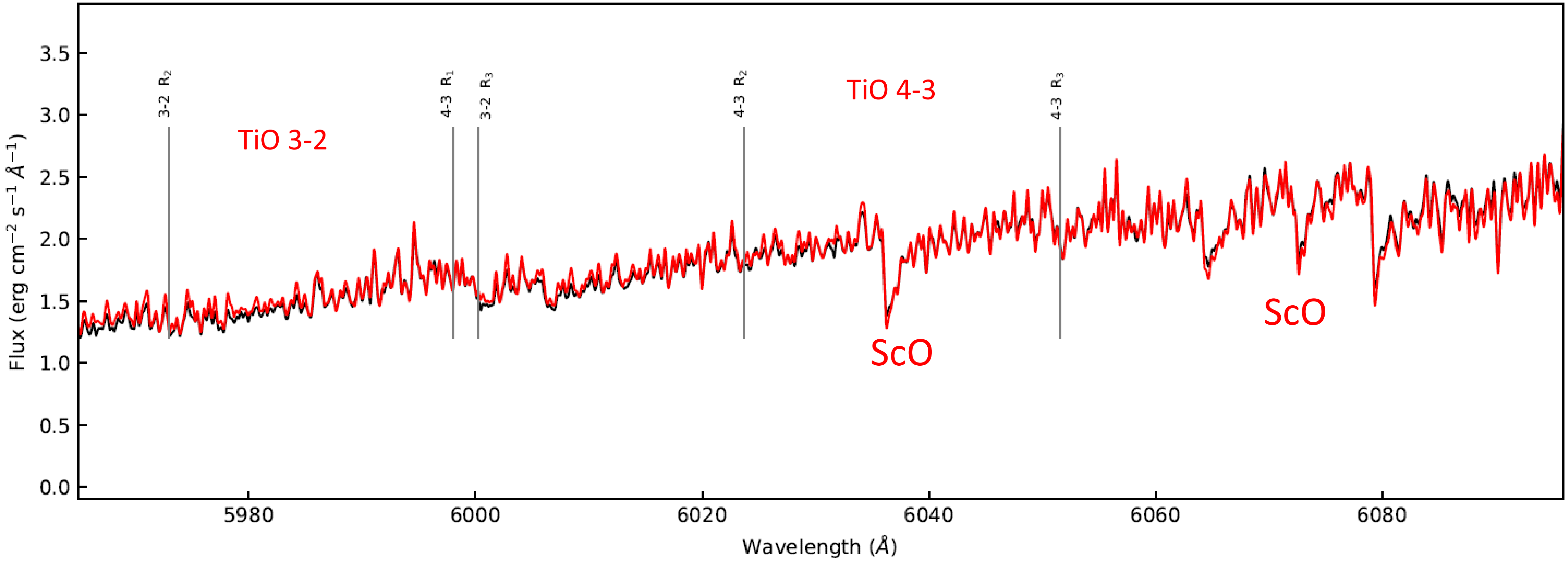
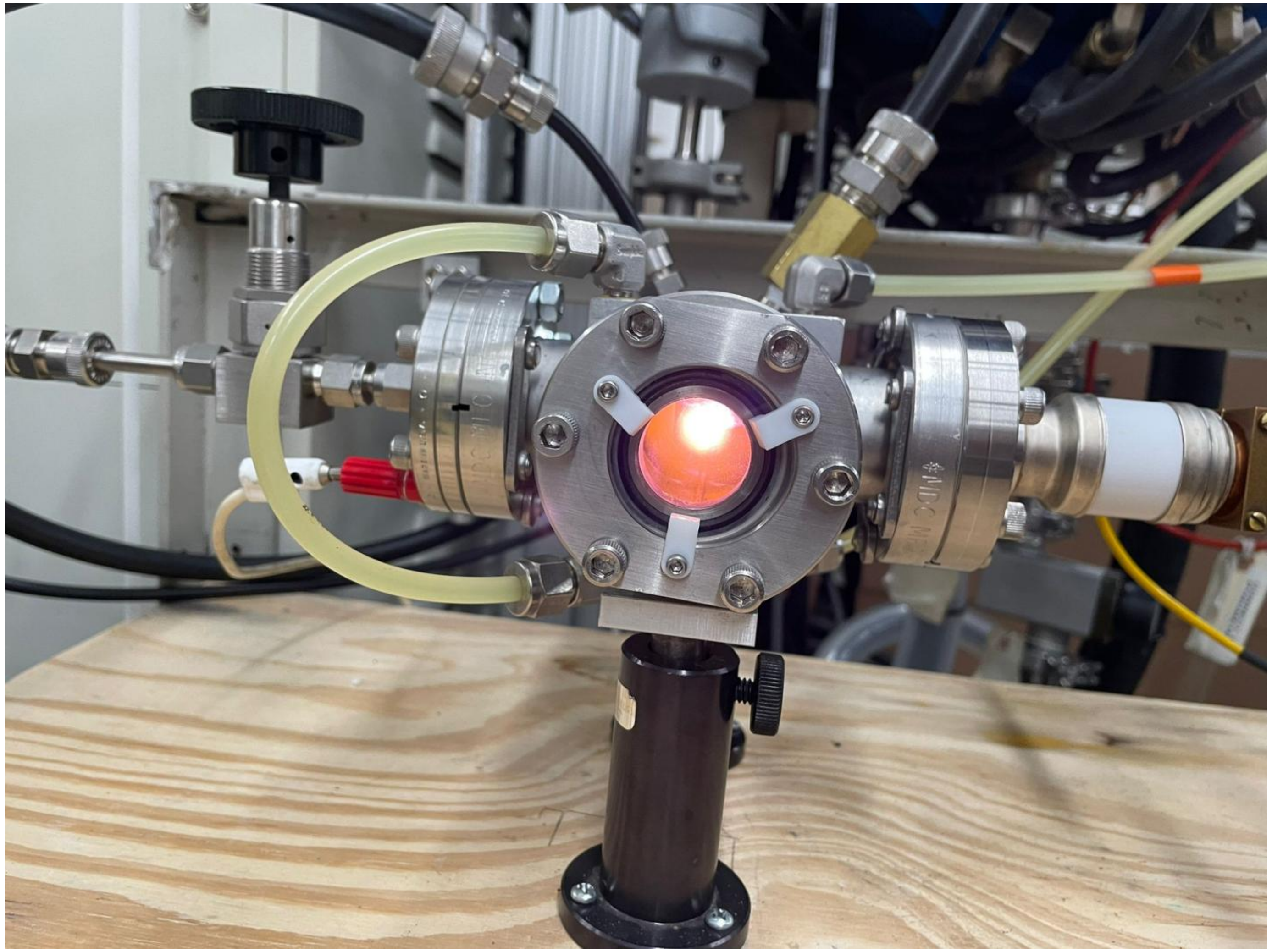


Figure 4. MELCHIORS spectrum of 30 Her (M6 III) in black is compared with the synthetic spectrum as described in the text. The positions of the TiO $B^3\Pi$ - $X^3\Delta$ R-heads of main branches are marked with vertical lines. The deep absorptions are formed by heads of the ScO $A^2\Pi$ - $X^2\Sigma^+$ 0-0 and 1-1 bands.

30 Her (M6 III); obs. (back), TiO B-X calc. red; Vertical lines, TiO band heads

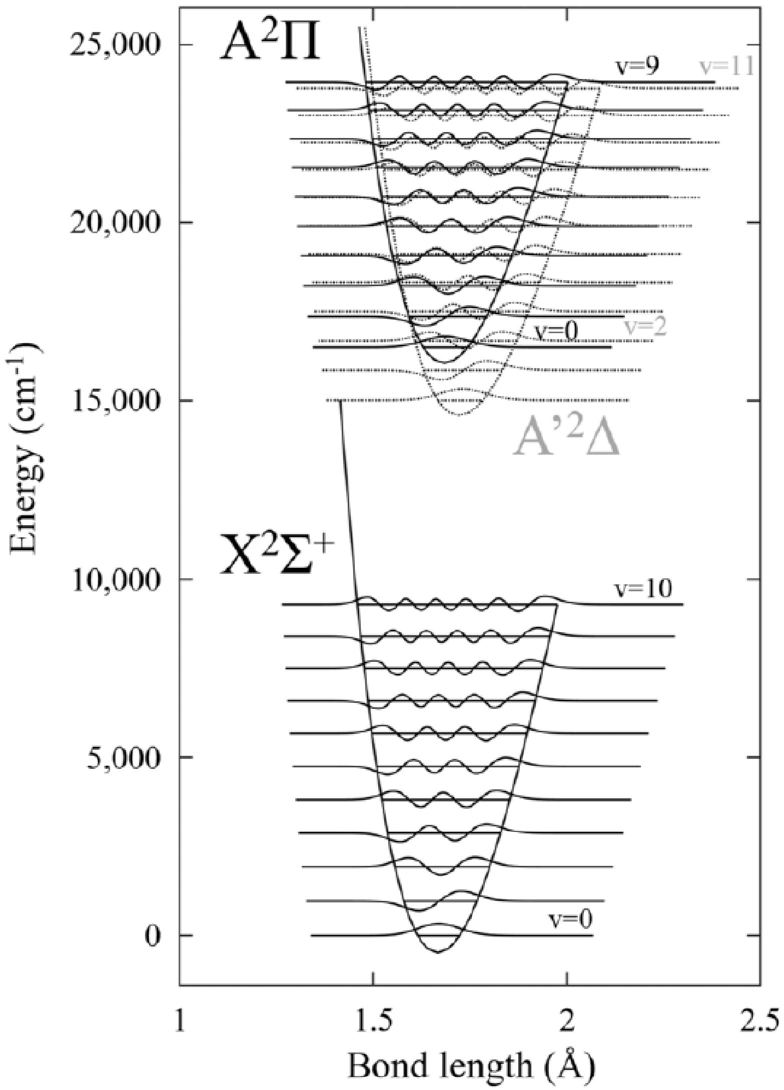
Deep absorptions: ScO $A^2\Pi$-$X^2\Sigma^+$ band heads (ScO based on L. Lavy, *et al*. 2024)

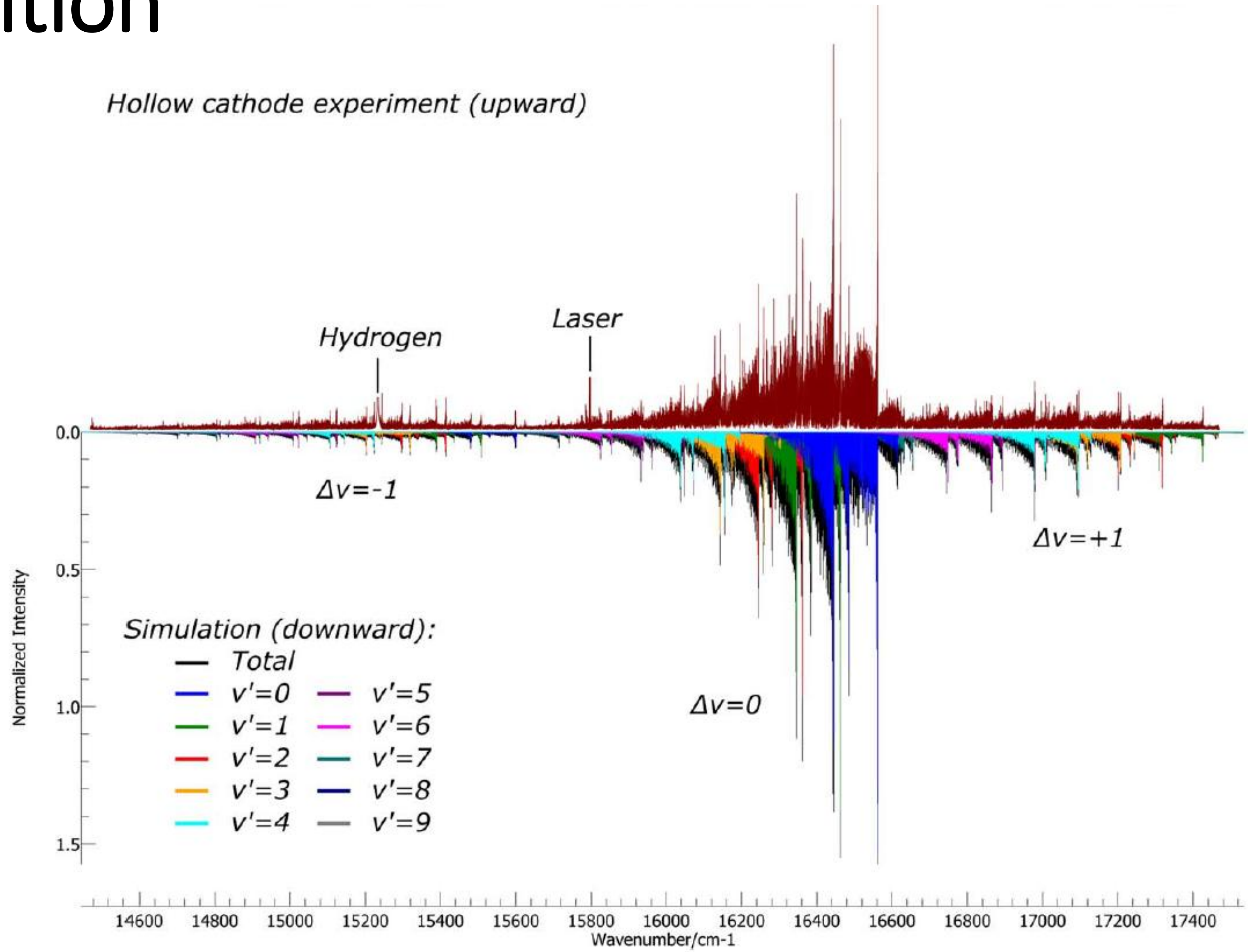
ScO Hollow Cathode Emission Spectrum



Composite wall (Sc_2O_3/Cu) hollow cathode lamp; Ar carrier gas with 0.8 A current

ScO $A^2\Pi$-$X^2\Sigma^+$ Transition





L. Lavy, A. Pastorek, P. F. Bernath, The $A^2\Pi-X^2\Sigma^+$ band system of ScO for M-type star spectral analysis, *ApJ* **975**, 180 (2024).

$^2\Pi$-$^2\Delta$ Perturbations

Lines are all doubled by hyperfine structure.

$A'^2\Delta_{3/2}(v+2) \sim A^2\Pi_{3/2}(v)\ (\boldsymbol{L}\cdot\boldsymbol{S})$

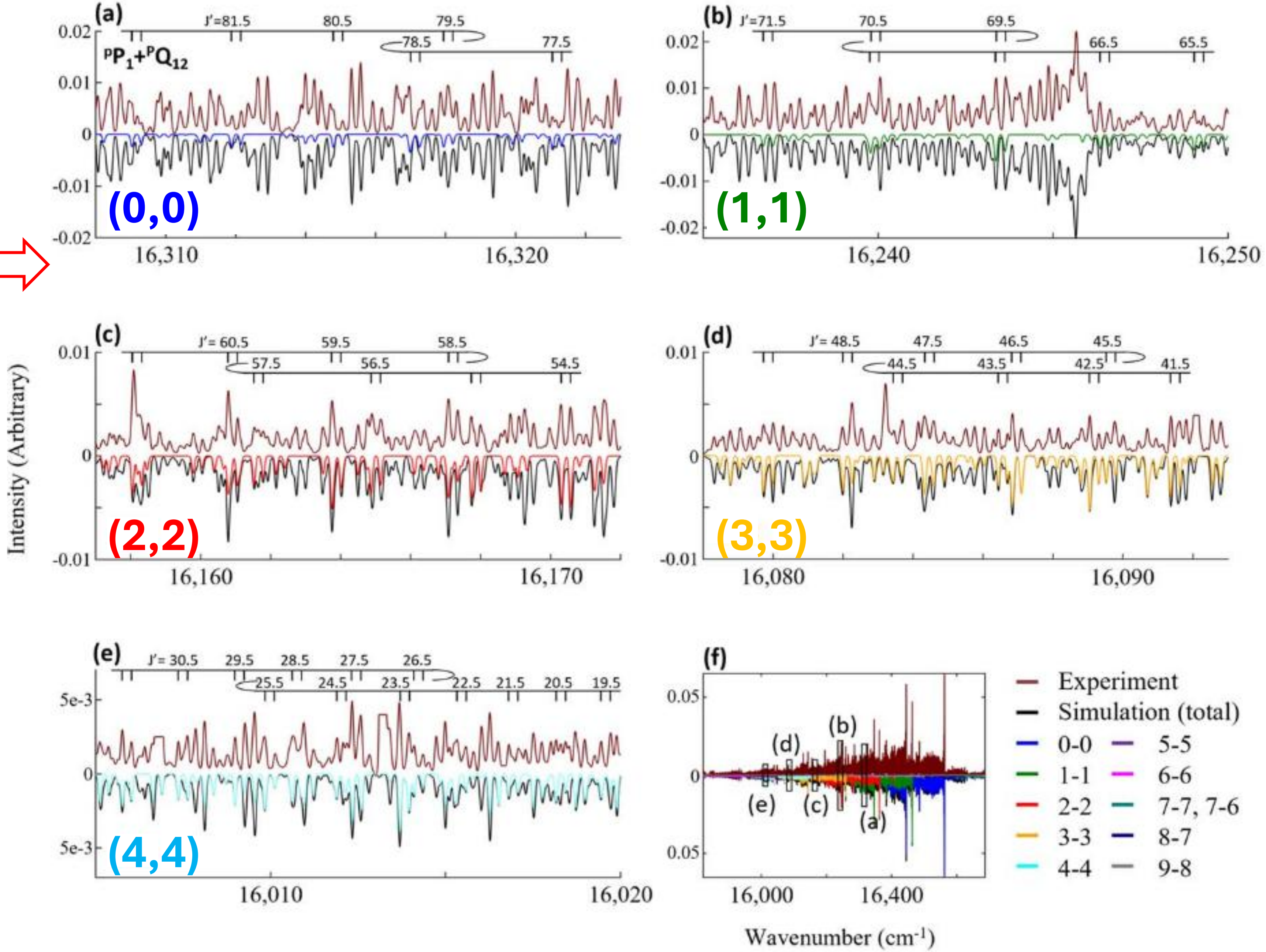
$A'^2\Delta_{3/2}(v+2) \sim A^2\Pi_{1/2}(v)\ (\boldsymbol{J}^{+}\cdot\boldsymbol{L}^{-})$

$A'^2\Delta_{5/2}(v+2) \sim A^2\Pi_{3/2}(v)\ (\boldsymbol{J}^{+}\cdot\boldsymbol{L}^{-})$

spin–orbit coupling

rotation-orbit coupling

Reported previously by R. Stringat *et al*. (1972) for v = 0 and by S. F. Rice *et al*. (1989) for v = 1.



RESULTS

	$A^2\Pi_{1/2}$	$A^2\Pi_{3/2}$	$A'^2\Delta_{3/2}$	$A'^2\Delta_{5/2}$
$A^2\Pi_{1/2}$	$A^2\Pi$		sym.	sym.
$A^2\Pi_{3/2}$			sym.	sym.
$A'^2\Delta_{3/2}$	$bf(J)$	$-a/\sqrt{3}$	$A'^2\Delta$	
$A'^2\Delta_{5/2}$	0	$bg(J)$		

Size of the perturbation $A'^2\Delta(v+2) \sim A^2\Pi(v)$

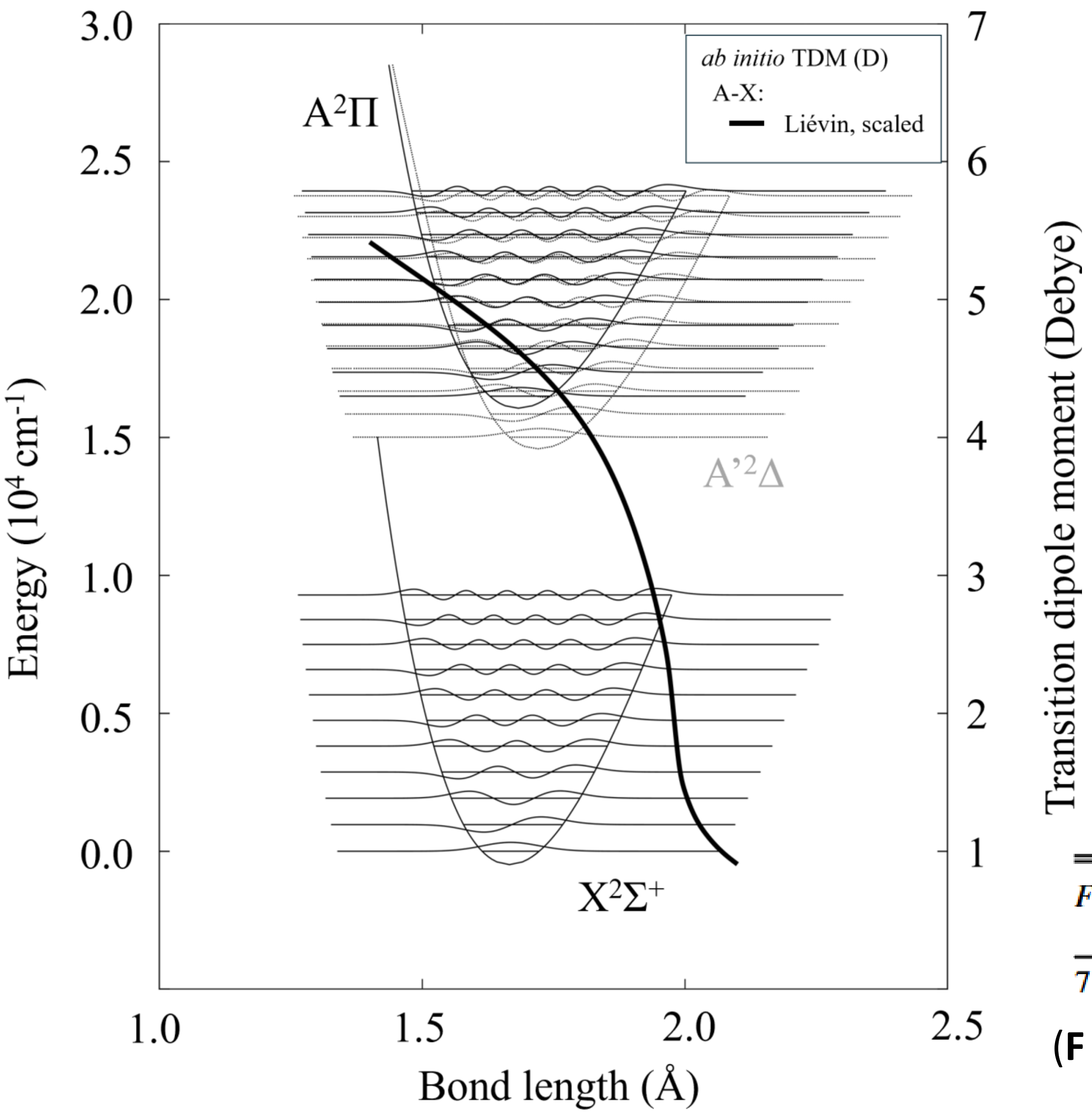
v	a	b
0	−1.5038(73)	−0.035016(42)
1	−2.7007(27)	−0.062733(29)
2	−3.8326(66)	−0.088786(21)
3	−4.8804(80)	−0.112382(21)
4	−5.8584[g]	−0.133017(65)
5	−6.7609[g]	−0.151772[g]
6	−7.5889[g]	−0.168027[g]
7	−8.3423[g]	−0.181908[g]
8	−9.0212[g]	−0.193415[g]
9	−9.6255[g]	−0.202547[g]

Fit of the $A'^2\Delta$ state that we see only through the perturbation of A-X

$A'^2\Delta$ spectroscopic constants

v	T_v	B_v	$10^7 D_v$	A_v	$10^4 A_{Dv}$
2	16681.385(51)	0.471621(10)	6.205[f]	47.508(23)	−1.070[f]
3	17502.4294(919)	0.4686560(267)	6.205(15)	47.5412(918)	−1.070(216)
4	18315.1863(461)	0.4656830(147)	6.205[f]	47.5793(68)	−1.070[f]
5	19119.787(12)	0.4626143(65)	6.205[f]	47.6142[d]	−1.070[f]
6	19915.709(15)	0.459600(25)	6.205[f]	47.6498[d]	−1.070[f]
7	20703.502[d]	0.456512[d]	6.205[f]	47.6855[d]	−1.070[f]
8	21482.976[d]	0.453389[d]	6.205[f]	47.7211[d]	−1.070[f]
9	22254.134[d]	0.450232[d]	6.205[f]	47.7568[d]	−1.070[f]
10	23016.975[d]	0.447042[d]	6.205[f]	47.7924[d]	−1.070[f]
11	23771.500[d]	0.443818[d]	6.205[f]	47.8281[d]	−1.070[f]

Reported previously by R. Stringat et al. (1972) for v = 0 and by S. F. Rice et al. (1989) for v = 1.



A-X transition dipole matrix elements (debye)

v′ \ v″	0	1	2	3	4	5	6	7	8	9	10
0	**4.675**	**0.91**	0.202	0.029	3.90E-03	2.10E-06	-1.40E-04	-4.10E-05	-1.70E-05	-7.70E-06	1.00E-05
1	**-1.208**	**4.37**	**1.27**	0.352	0.059	8.60E-03	-1.90E-04	-4.80E-04	-1.70E-04	-3.40E-05	-8.50E-06
2	0.149	**-1.731**	**4.029**	**1.522**	0.499	0.095	0.014	-8.90E-04	-1.20E-03	-4.40E-04	-9.60E-05
3	8.40E-03	0.292	**-2.134**	**3.652**	**1.702**	0.639	0.136	0.02	-2.50E-03	-2.50E-03	-1.00E-03
4	-9.00E-03	6.80E-03	0.462	**-2.46**	**3.243**	**1.821**	0.769	0.178	0.025	-5.90E-03	-5.10E-03
5	2.20E-03	-1.90E-02	-6.60E-03	0.658	**-2.722**	**2.806**	**1.881**	0.886	0.221	0.028	-0.013
6	-1.90E-04	5.90E-03	-0.031	-0.036	0.878	**-2.92**	**2.345**	**1.884**	0.982	0.258	0.025
7	-8.40E-05	-7.50E-04	0.012	-0.043	-0.085	1.116	**-3.054**	**1.867**	**1.829**	1.052	0.283
8	4.40E-05	-1.70E-04	-2.00E-03	0.02	-0.052	-0.158	1.368	**-3.119**	**1.381**	**1.713**	1.085
9	-8.70E-06	1.40E-04	-2.20E-04	-4.30E-03	0.031	-0.056	-0.259	1.627	**-3.112**	**0.891**	**1.536**

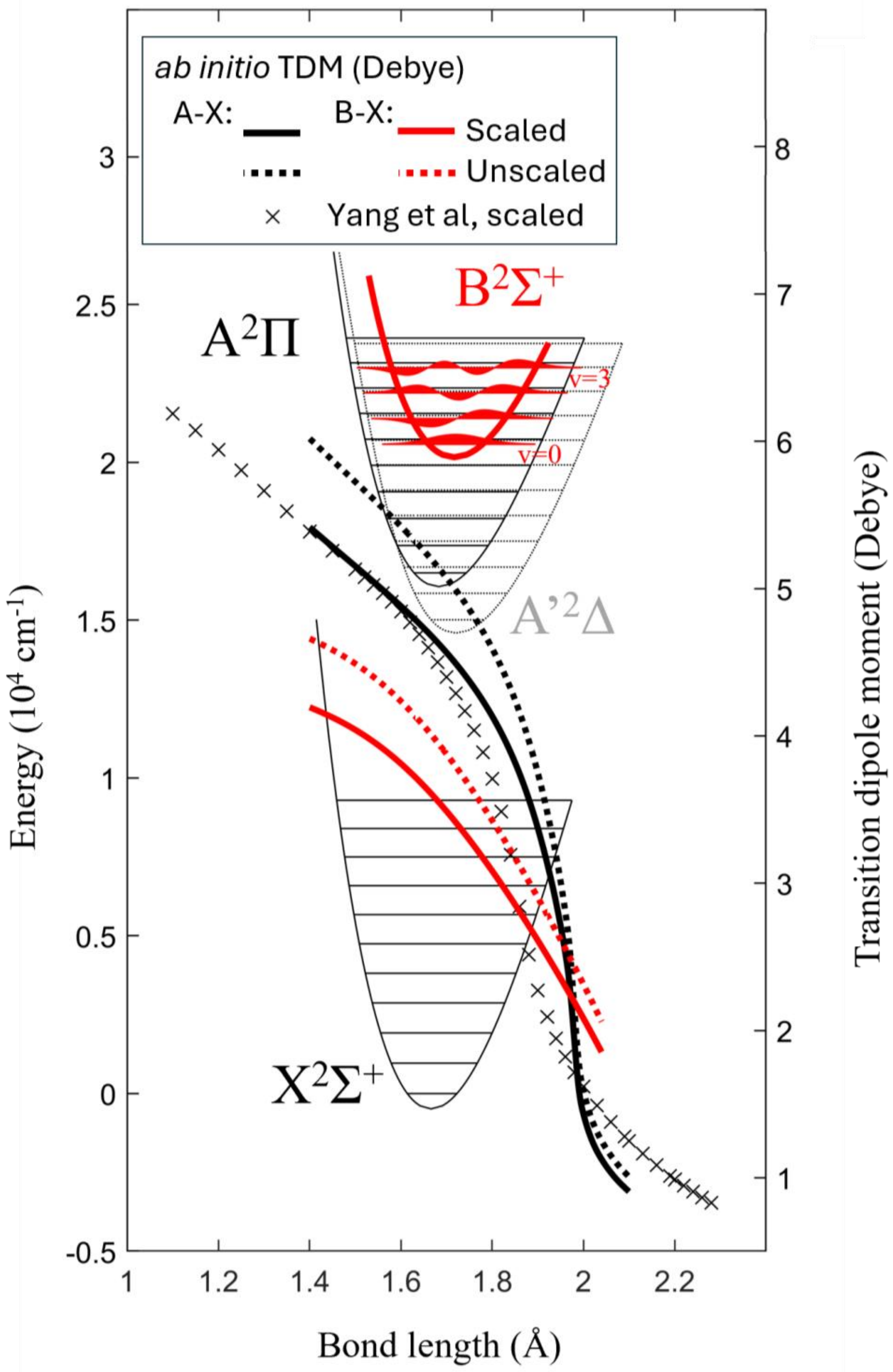
Line list

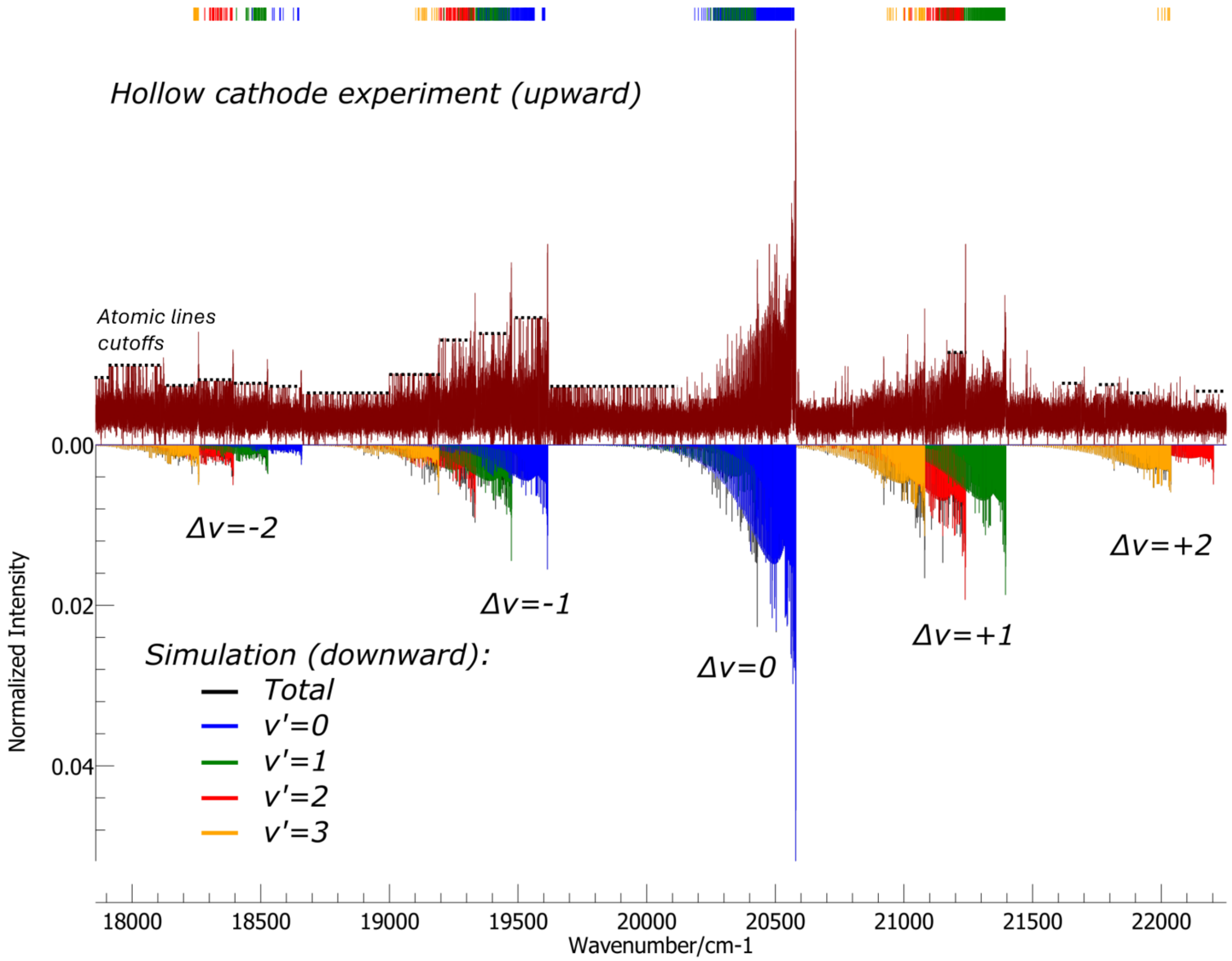
F'	p'	F''	p''	Position (cm^{-1})	E_{upper} (cm^{-1})	E_{lower} (cm^{-1})
7	e	8	e	16420.42545	16500.62349	80.19804

(F = J + I)

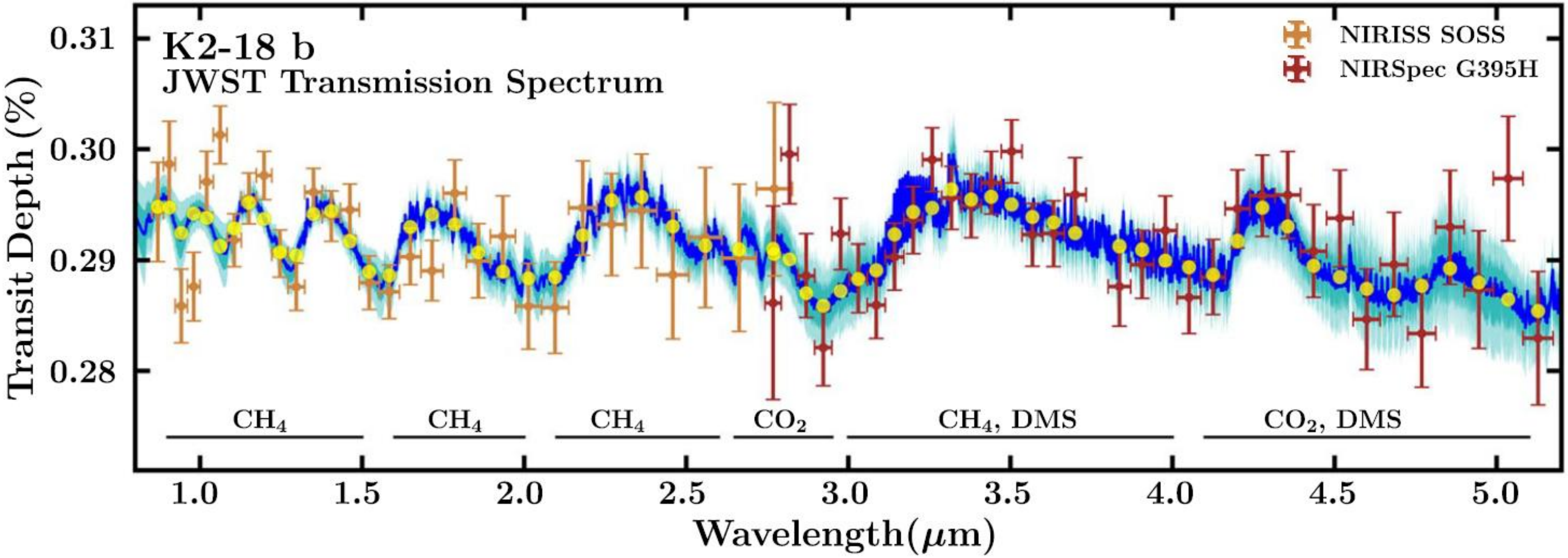
A (s^{-1})	f	Branch	Label
7.263E +06	3.563E-02	oP12(11.5)7,8	A $v = 0$ 10.5 10 F1f 7–X $v = 0$ 11.5 12 F2f 8

ScO $B^2\Sigma^+$ - $X^2\Sigma^+$ Transition





CH_4 in K2-18 b with JWST

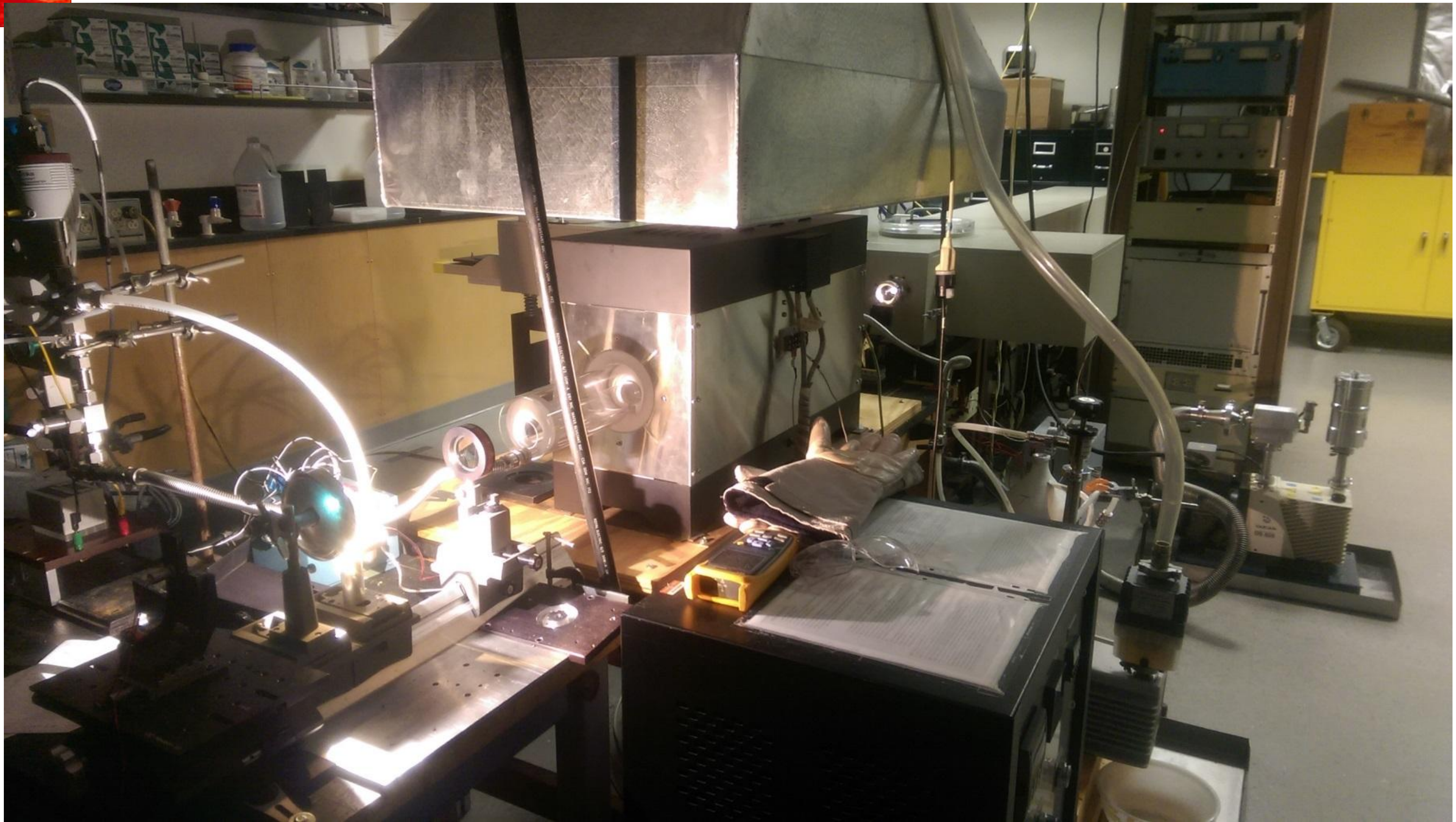


K2-18 b: M dwarf planet, 8.6 Earth masses, T_{equil} = 265 K

CH_4 data from HITEMP (Hargreaves *et al*. 2020)

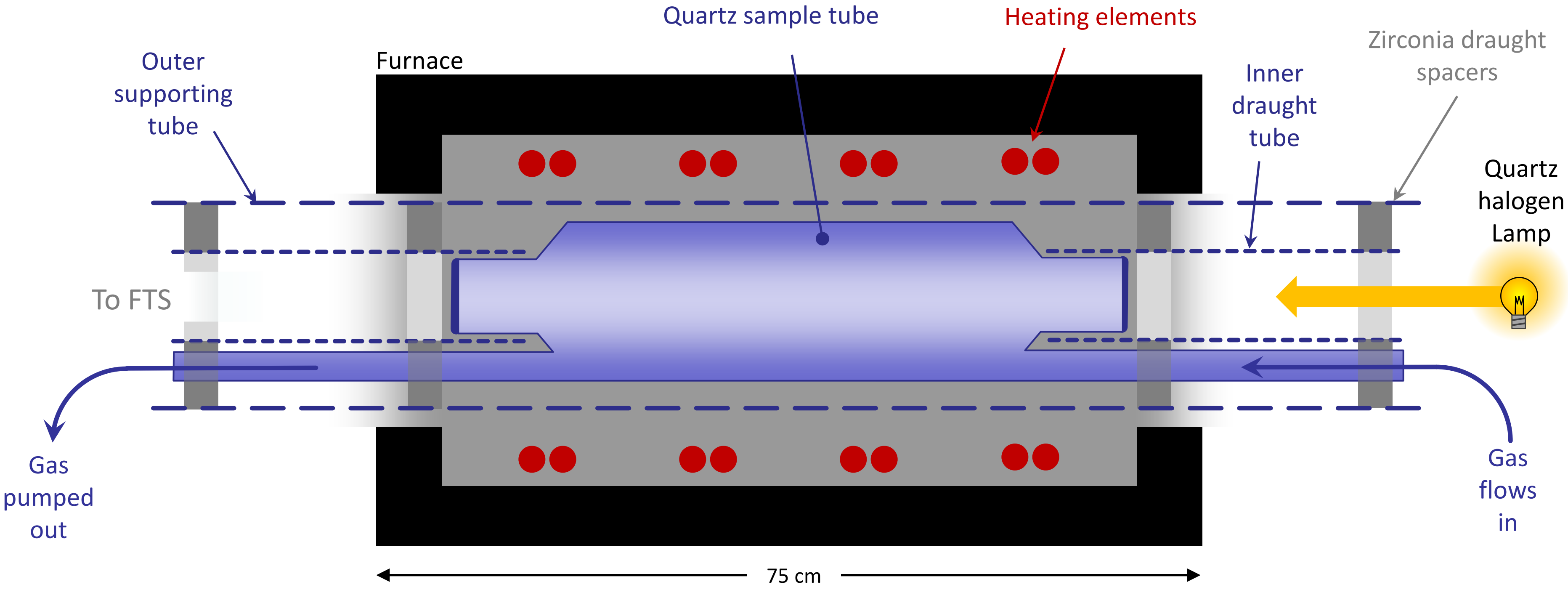
Madhusudhan *et al*. ApJL 956:L13 (2023)

Hot CH_4 Absorption

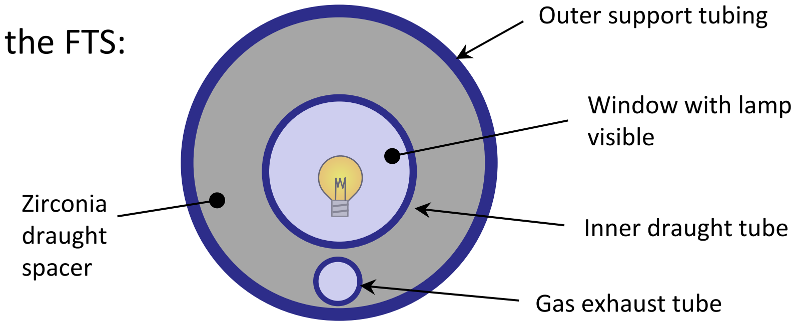


Absorption Cell

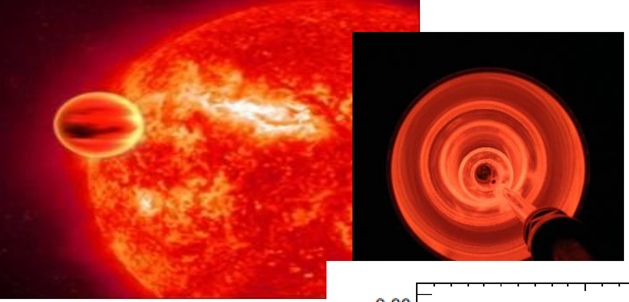
Profile from the side:



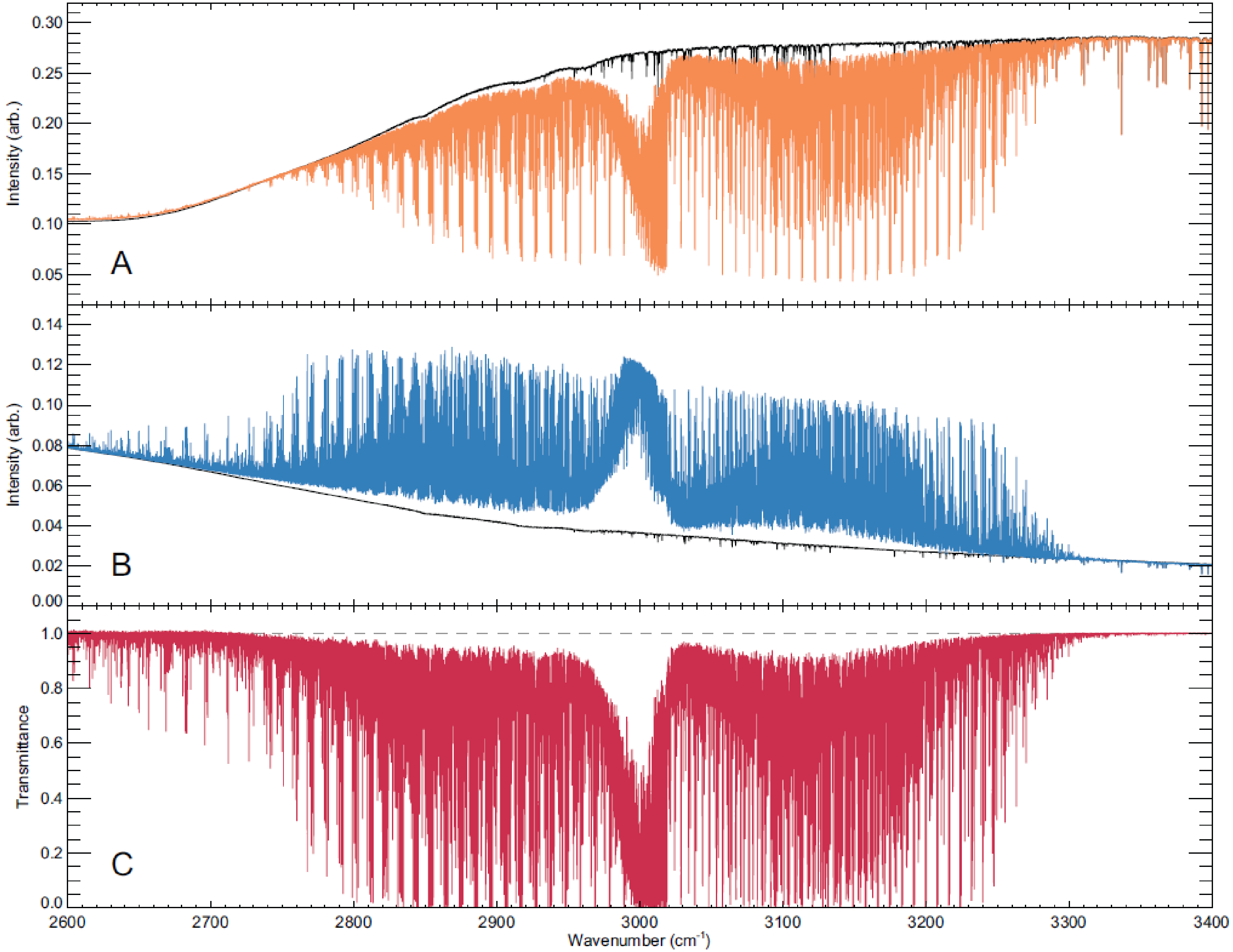
Looking from the FTS:



Hargreaves *et al.*
ApJ **813**, 12 (2015)



CH_4 Transmission (700°C)



1: Hot CH_4 + Lamp

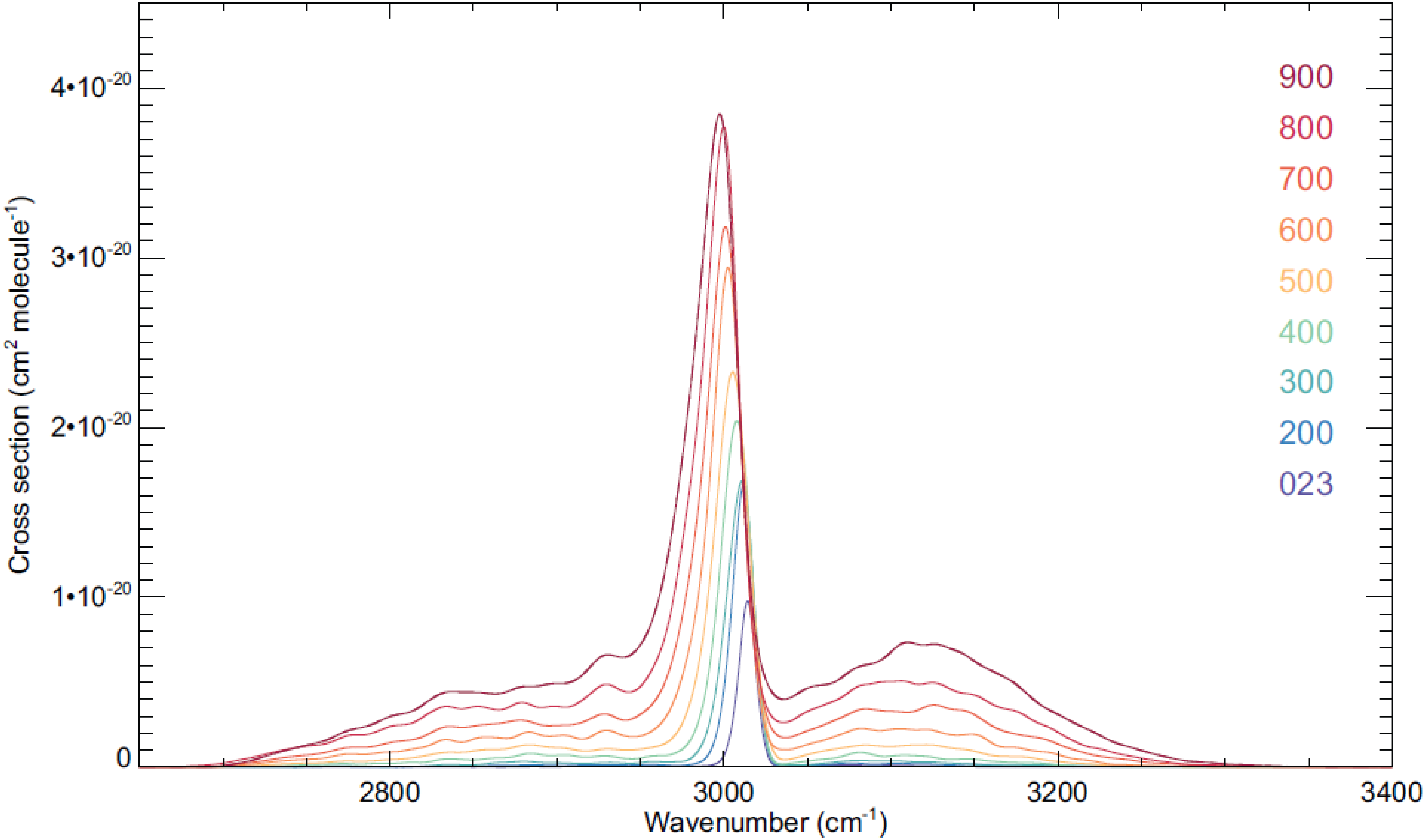
3: No sample + Lamp

2: Hot CH_4 + no lamp

4: No sample + no lamp

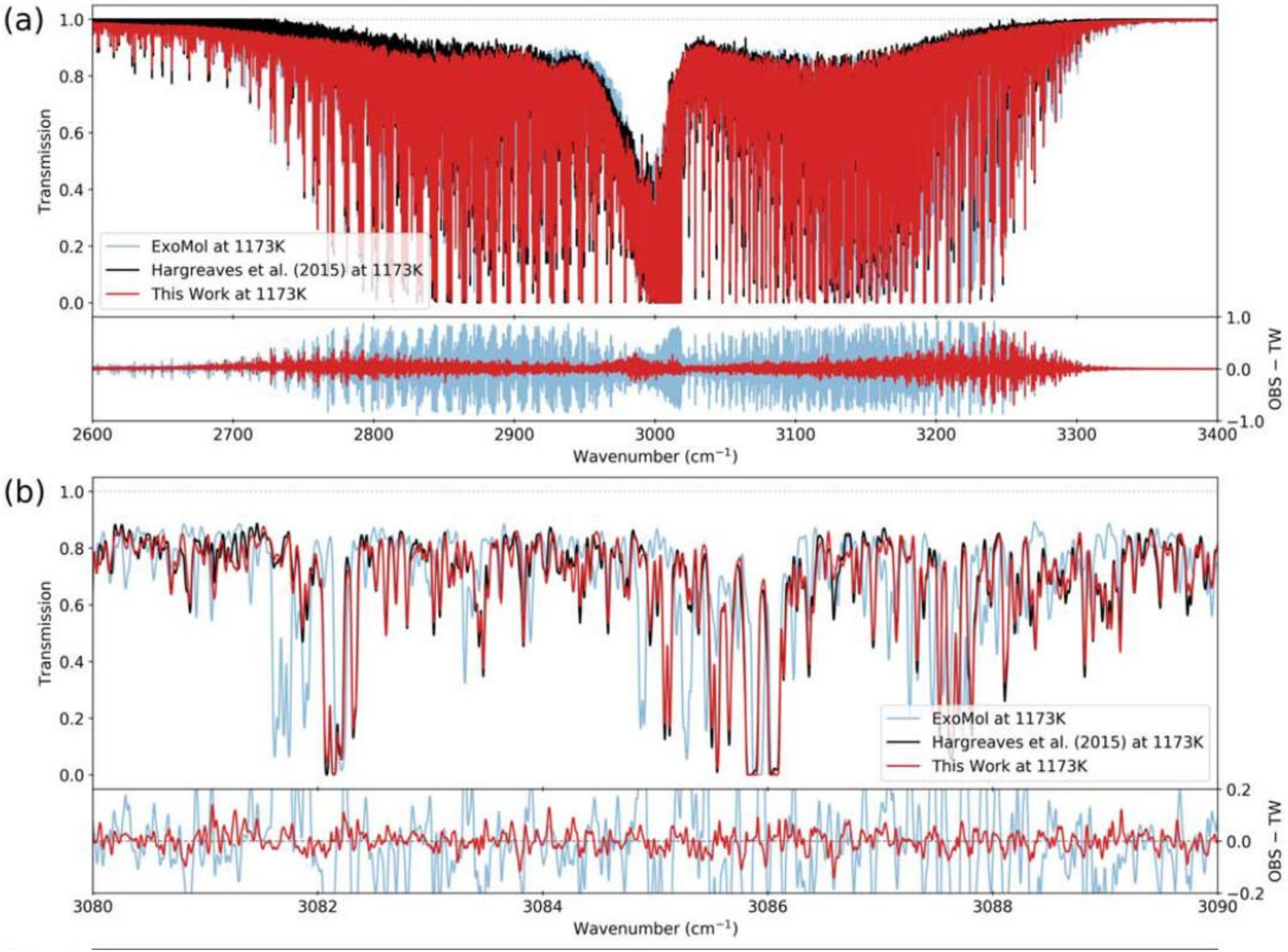
Transmission = (1-3)/2-4)

CH_4 Quasi-continuum



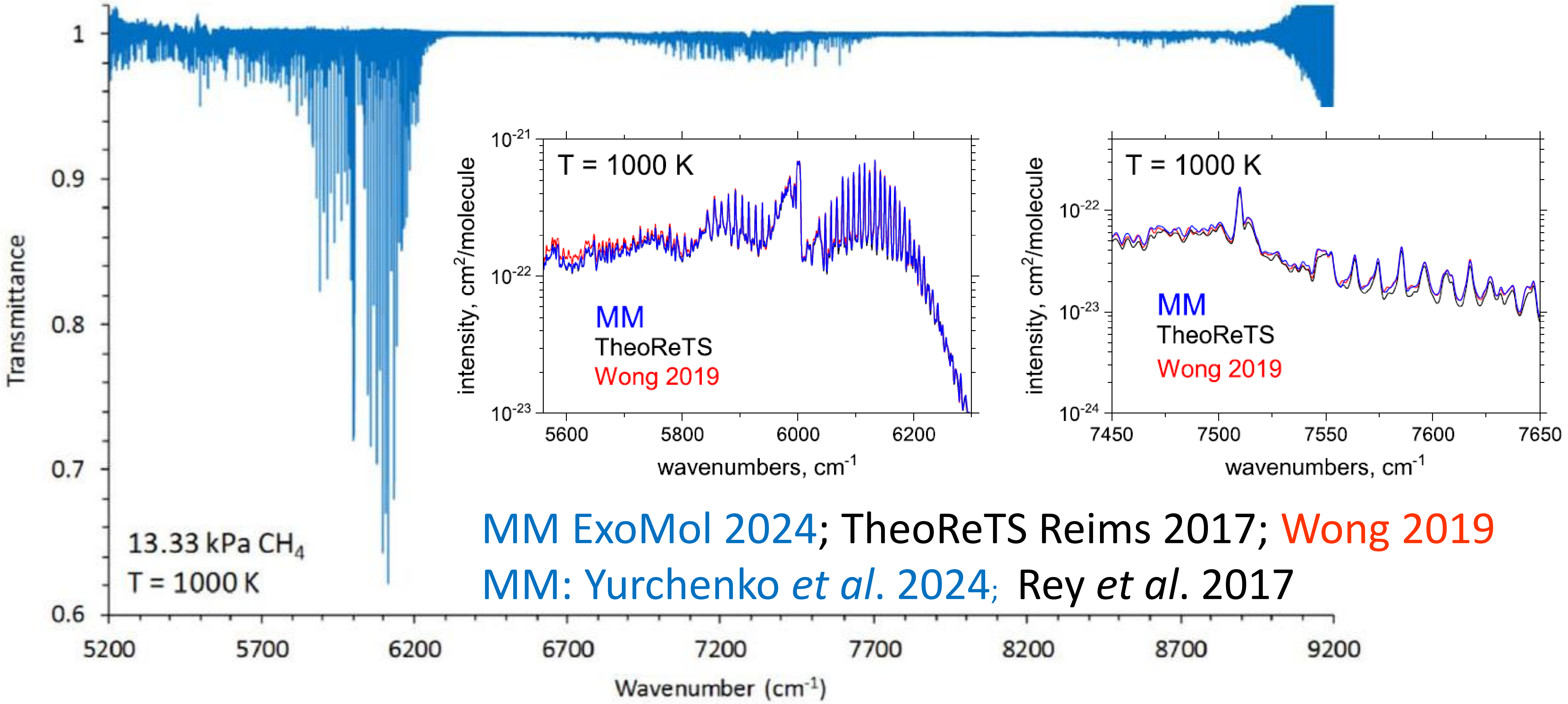
CH_4 Comparisons with HITEMP 2020 and ExoMol 2014

Hargreaves *et al*. 2020



Atlas of Experimental and Theoretical High-temperature Methane Cross Sections from $T = 295$ to 1000 K in the Near-infrared ApJS 240:4 (2019)

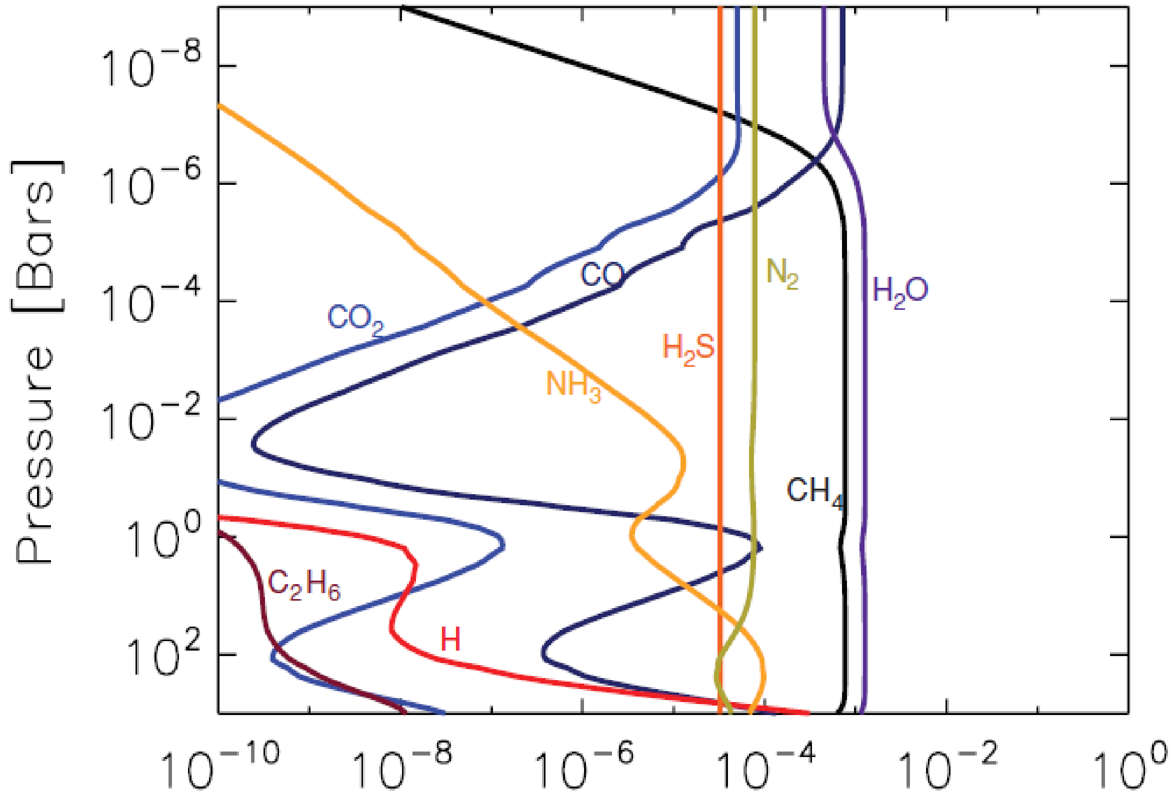
Andy Wong[1], Peter F. Bernath[1], Michael Rey[2], Andrei V. Nikitin[3,4], and Vladimir G. Tyuterev[2,4]



MM ExoMol 2024; TheoReTS Reims 2017; Wong 2019

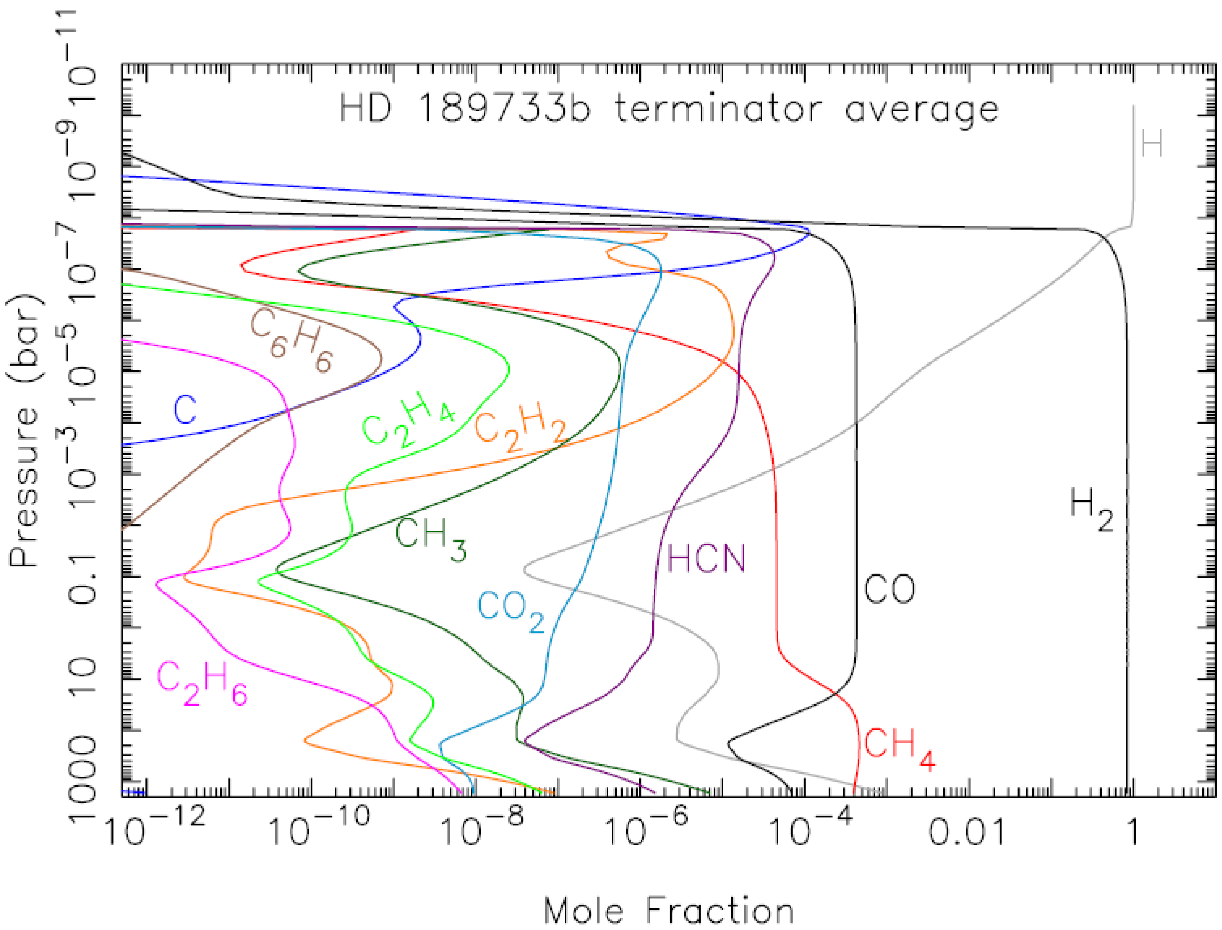
MM: Yurchenko *et al*. 2024; Rey *et al*. 2017

CH_4 and C_2H_6



Line *et al*. 2011, photochemical and thermodynamic model for hot Neptune, GJ436b

Moses *et al*. 2011, photochemical model for hot Jupiter, HD189733b



Possible Hycean conditions in the sub-Neptune TOI-270 d

Måns Holmberg and Nikku Madhusudhan

A&A, 683, L2 (2024)

M-dwarf planet, 4.8 Earth masses
T_{eq} = 340 K

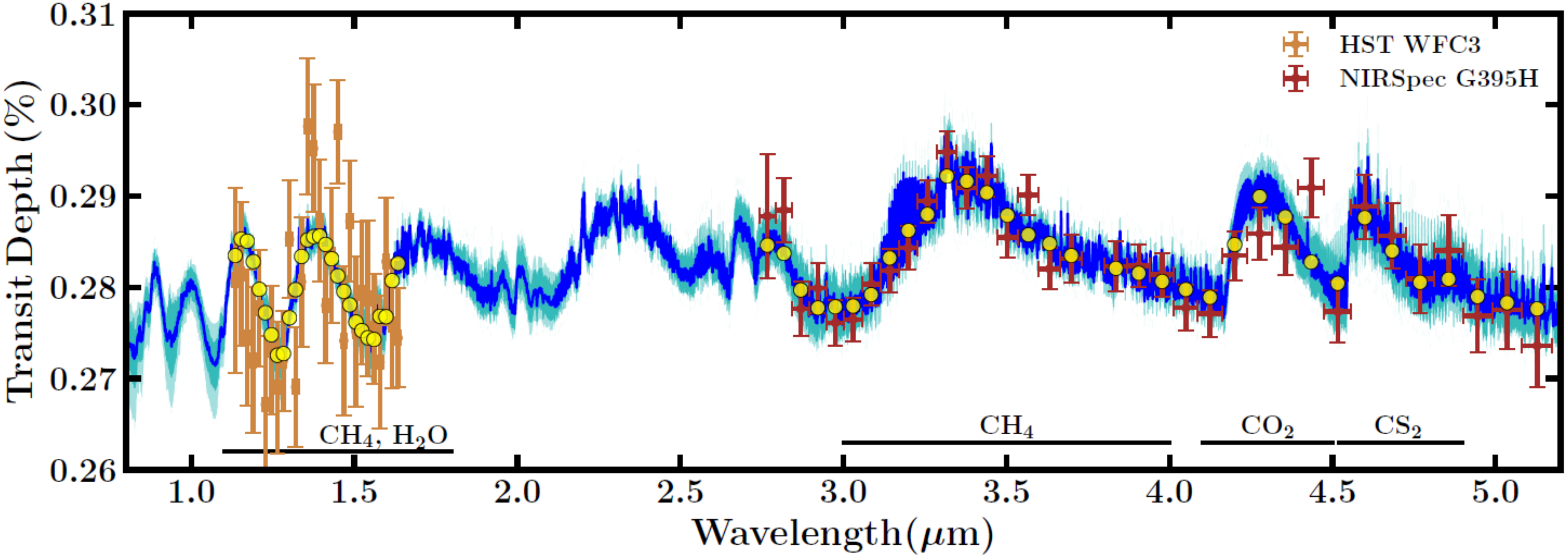
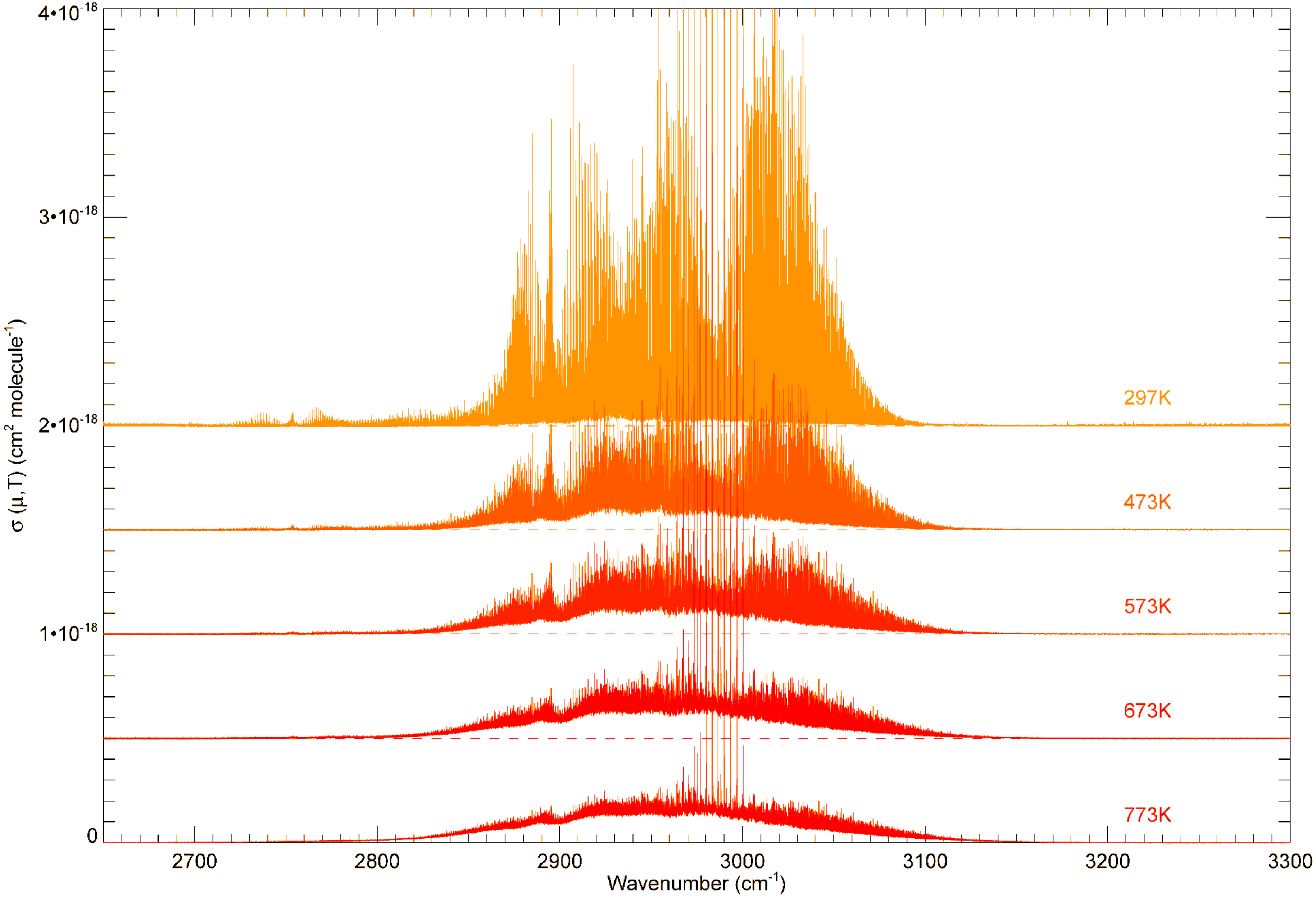


Fig. 2. Transmission spectrum of TOI-270 d observed with JWST/NIRSpec G395H and HST/WFC3. The NIRSpec G395H spectrum between 2.7–5.2 μm, from this work, is shown in dark red, binned to $R \approx 55$ for visual clarity. The WFC3 spectrum is shown in orange and spans 1.1–1.6 μm, reported by Mikal-Evans et al. (2023). The retrieval is performed using the native resolution NIRSpec G395H spectrum ($R \sim 2700$) and the WFC3 spectrum. The NIRSpec spectrum is vertically offset by −84 ppm, corresponding to the median retrieved offset in the canonical one-offset case. The blue curve shows the median retrieved model spectrum, while the medium- and lighter-blue contours denote the 1σ and 2σ intervals, respectively. Yellow points correspond to the median spectrum binned to match the observations. The prominent molecules responsible for the features in different spectral regions are labelled.

Holmberg and Madhusudhan: “we found potential hints of C_2H_6, at a lower significance of 1.8–2.3σ across the retrievals. C_2H_6 is known to be a photochemical byproduct of reactions involving CH_4”

Hot Ethane Cross-Sections (3.3 μm)

Hargreaves *et al.* 2015



Recent Line List Papers

1. P. Bernath, R. Johnson and J. Liévin, Line lists for $X^3\Sigma^-$ and $a^1\Delta$ vibration-rotation bands of SO, *J. Quant. Spectrosc. Rad. Transfer* **290**, 108317 (2022).
2. P. Bernath and D. Cameron, Line lists for TiO minor isotopologues for the $A^3\Phi$-$X^3\Delta$ electronic transition, *J. Quant. Spectrosc. Rad. Transfer* **310**, 108745 (2023).
3. P. F. Bernath, R. Dodangodage and J. Liévin, S-type stars: Line list for the $A^2\Pi$ - $X^2\Sigma^+$ band system of LaO, *Astrophys. J.* **953**, 181 (2023).
4. P. F. Bernath, M. Bhusal and J. Liévin, Opacities of S-type Stars: The Singlet $B^1\Pi$-$X^1\Sigma^+$, $B^1\Pi$-$A^1\Delta$, and $C^1\Sigma^+$-$X^1\Sigma^+$ Band Systems of ZrO, *Astrophys. J.* **960**, 23 (2024).
5. L. Lavy and P. F. Bernath, Molecules in cool stars: the $A^2\Pi$–$X^2\Sigma^+$ and the $B^2\Sigma^+$–$X^2\Sigma^+$ band systems of CaCl, *Astrophys. J.* **970**, 13 (2024).
6. P. F. Bernath, M. Bhusal and A. Pastorek, The $A^2\Pi$ - $X^2\Sigma^+$ Band System of YO, *Astrophys. J.* **974**, 53 (2024).
7. P. F. Bernath, M. Bhusal and J. Liéven, Visible Opacities of S-type Stars: The $d^3\Phi$ - $a^3\Delta$ Band System of ZrO, *Astrophys. J.* **975**, 154 (2024).
8. L. Lavy, A. Pastorek and P. F. Bernath, The $A^2\Pi$–$X^2\Sigma^+$ band system of ScO for M-type star spectral analysis, *Astrophys. J.* **975**, 180 (2024).
9. L. Lavy, P. F. Bernath and A. Pastorek, Line list for the $A^2\Pi$–$X^2\Sigma^+$ and the $B^2\Sigma^+$–$X^2\Sigma^+$ band systems of CaF, *Astrophys. J.* **979**, 19 (2025).
10. M. Bhusal, P. F. Bernath and J. Liéven, Visible Spectra of S-type Stars: The $f^3\Delta$ - $a^3\Delta$ (α system) and $e^3\Pi$ - $a^3\Delta$ (β system) Band Systems of ZrO, *Astrophys. J.* **982**, 156 (2025).
11. P. F. Bernath, M. Bhusal and M. R. Schmidt, M Star Opacities: The $B^3\Pi$ - $X^3\Delta$ Band System of TiO, *Astrophys. J.* (in press).

Acknowledgements

Robin

Chris Boone
Johnny Steffen
Mike Lecours
Matt Schmidt

Ryan Johnson
Randika Dodangodage
Jeffrey Pearson
Doug Cameron
Adam Pastorek
Leo Lavy
Rob Hargreaves

It's All Spectroscopy

Spectra of Atoms and Molecules, Oxford University Press

Textbook aimed at graduate students and senior undergrads. Particularly useful treatment of the confusing topic of line intensities needed for remote sensing. 4th edition added chapters on atmospheric and astronomical spectroscopy.

5th edition (2025) has a chapter added on the new spectroscopy of clouds and aerosols from ACE satellite data.