"Molecular physics challenge for exoplanet studies"

UCL

Line lists for hot hydride molecules

Jonathan Tennyson
Physics and Astronomy
University College London

ExoMol

Calculated molecular line lists
for the opacity of exoplanets,
cool stars and other hot atmospheres

Hydride Toolbox
Paris
December 2016

Image credit Shutterstock

"Molecular physics challenge for exoplanet studies"

UCL

Line lists for hot hydride molecules and their friends

Jonathan Tennyson
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Calculated molecular line lists
for the opacity of exoplanets,
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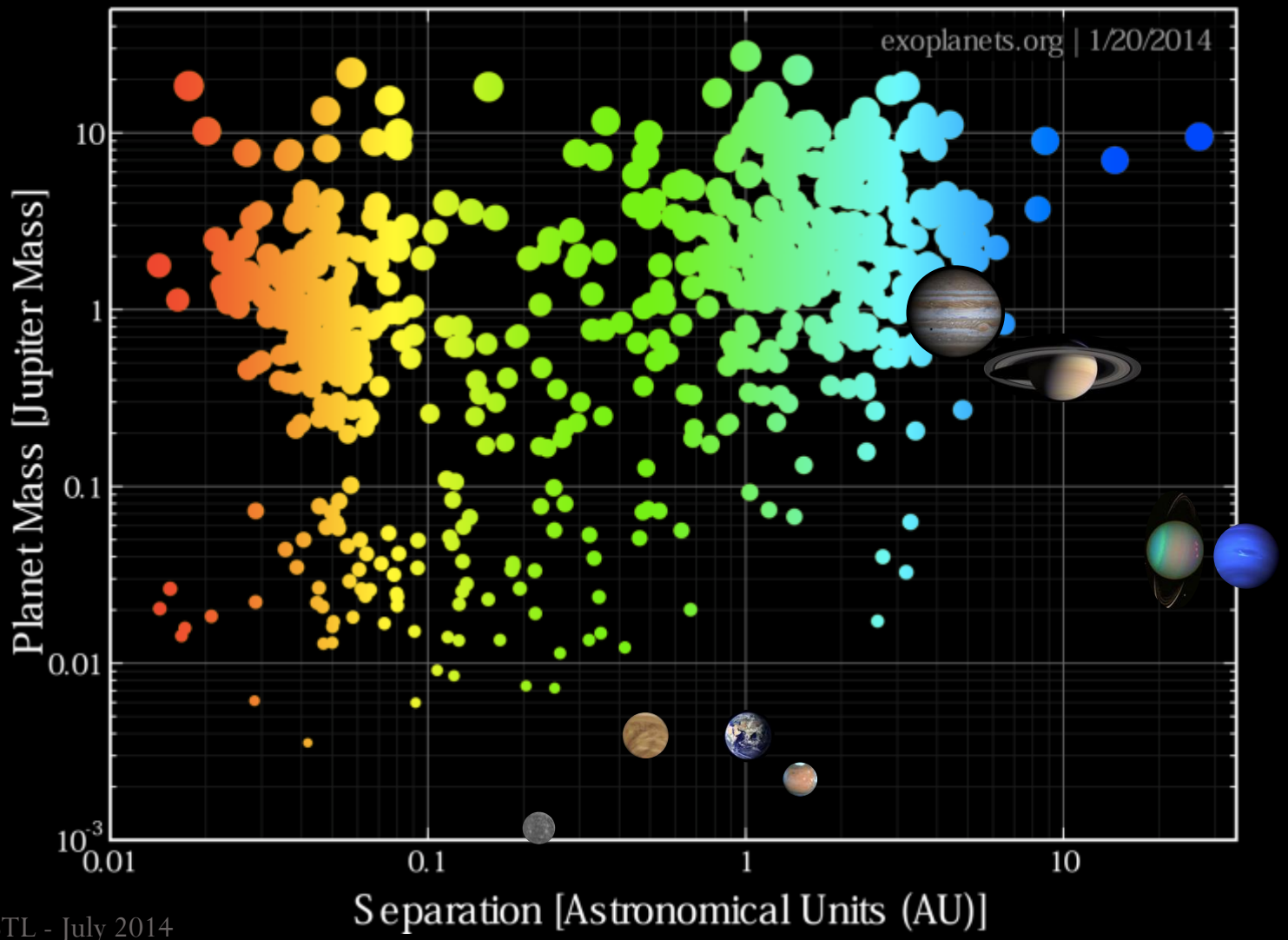
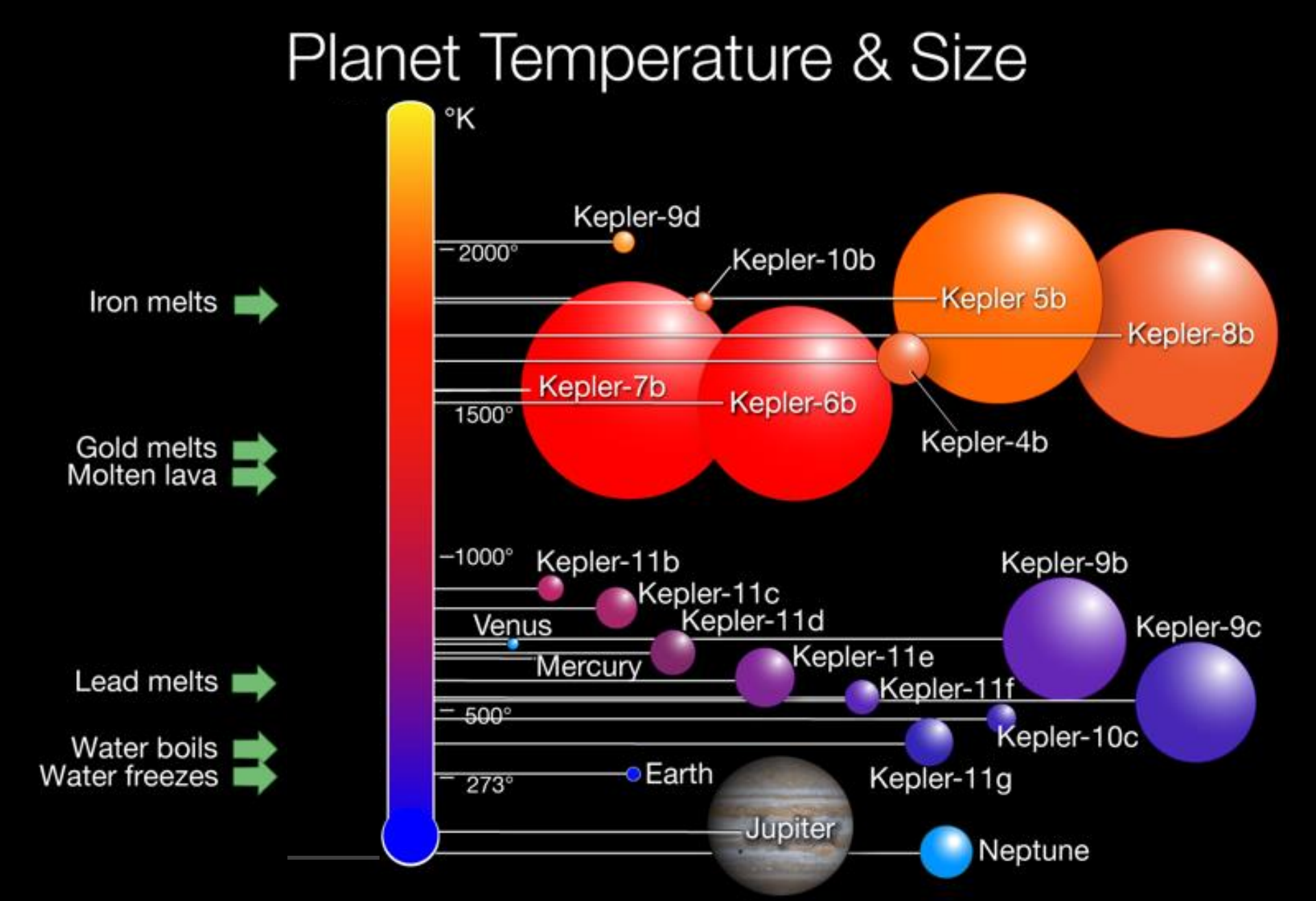
Hydride Toolbox
Paris
December 2016

Image credit Shutterstock

The Exoplanet Revolution

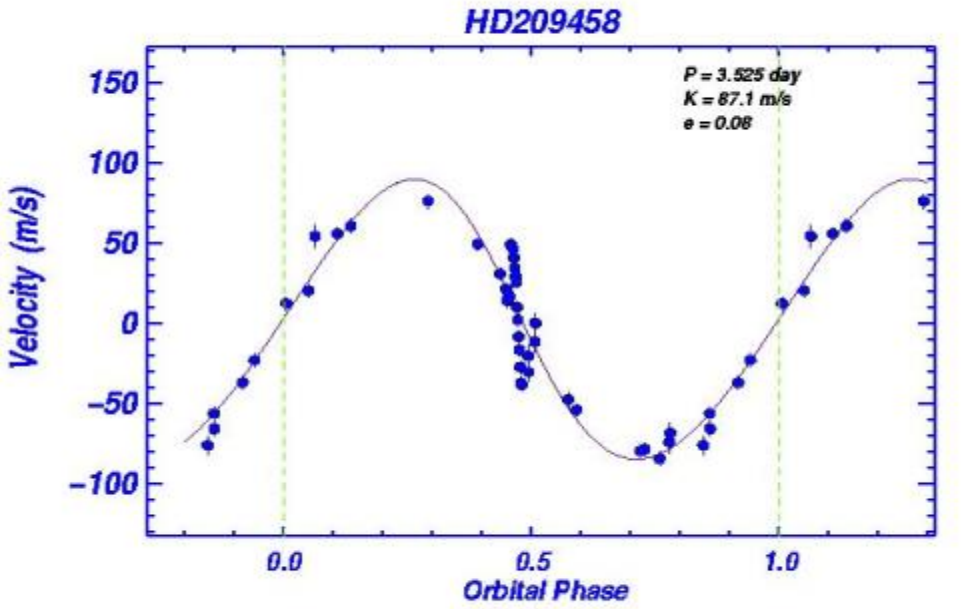
9 to > 3000 in 20 years!

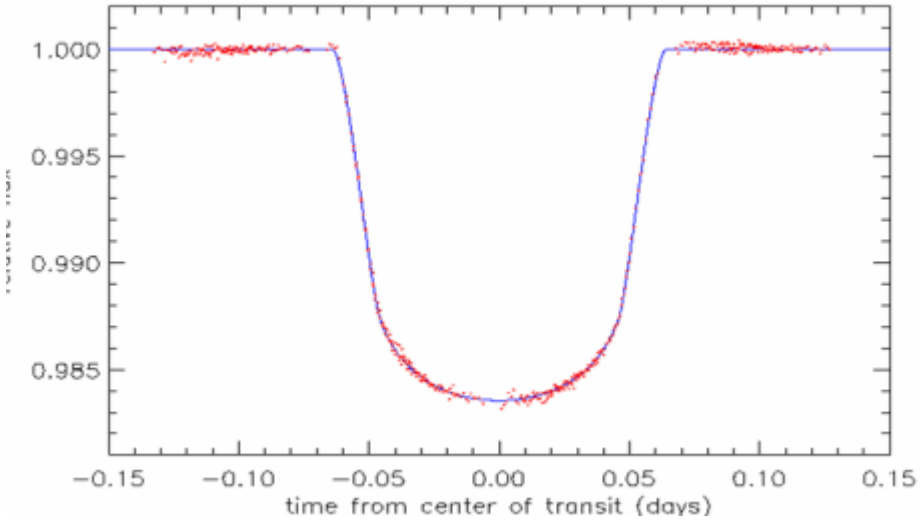




Courtesy of Kepler's team

HD 209458b





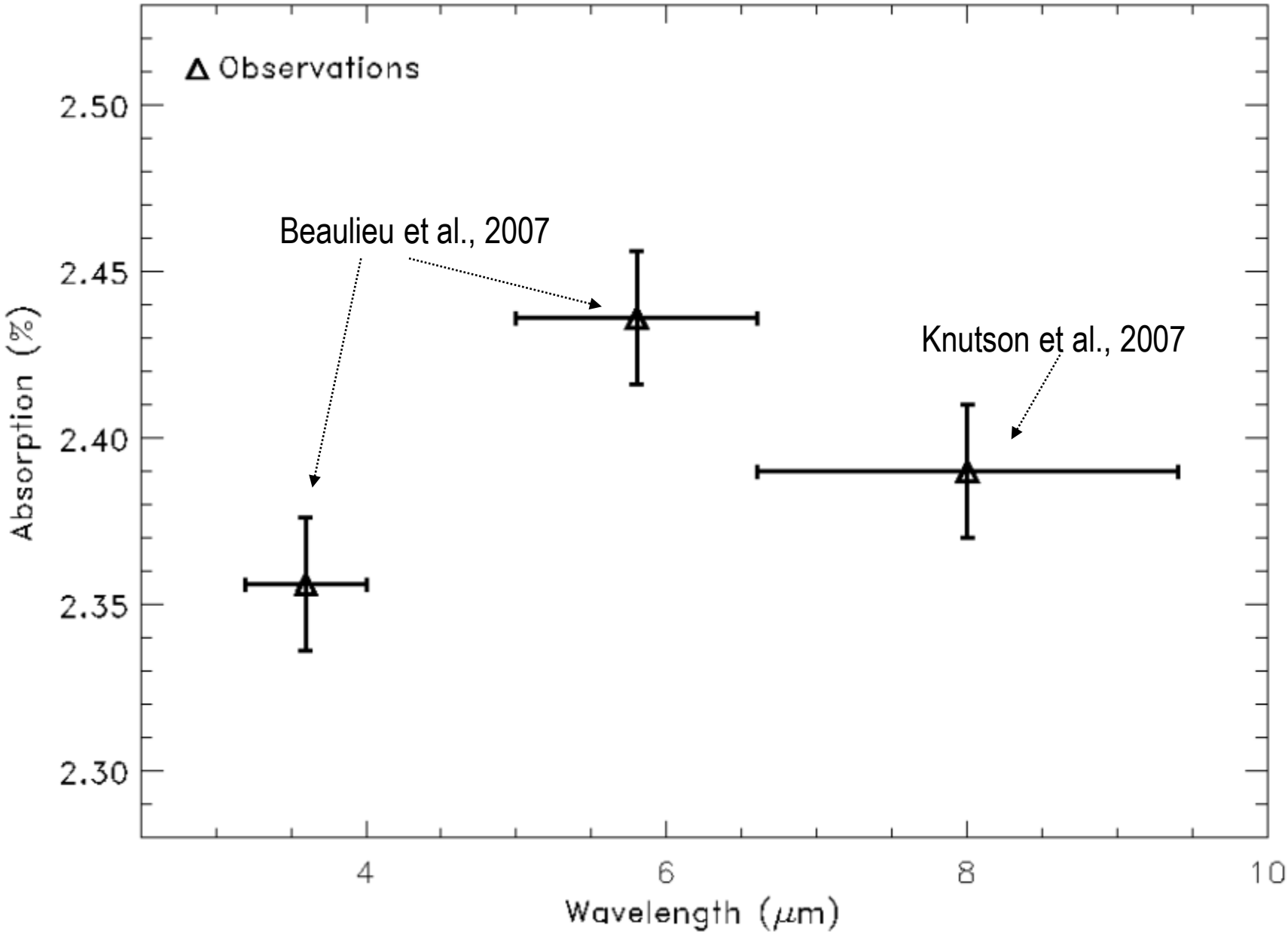
Period = 3.52 days

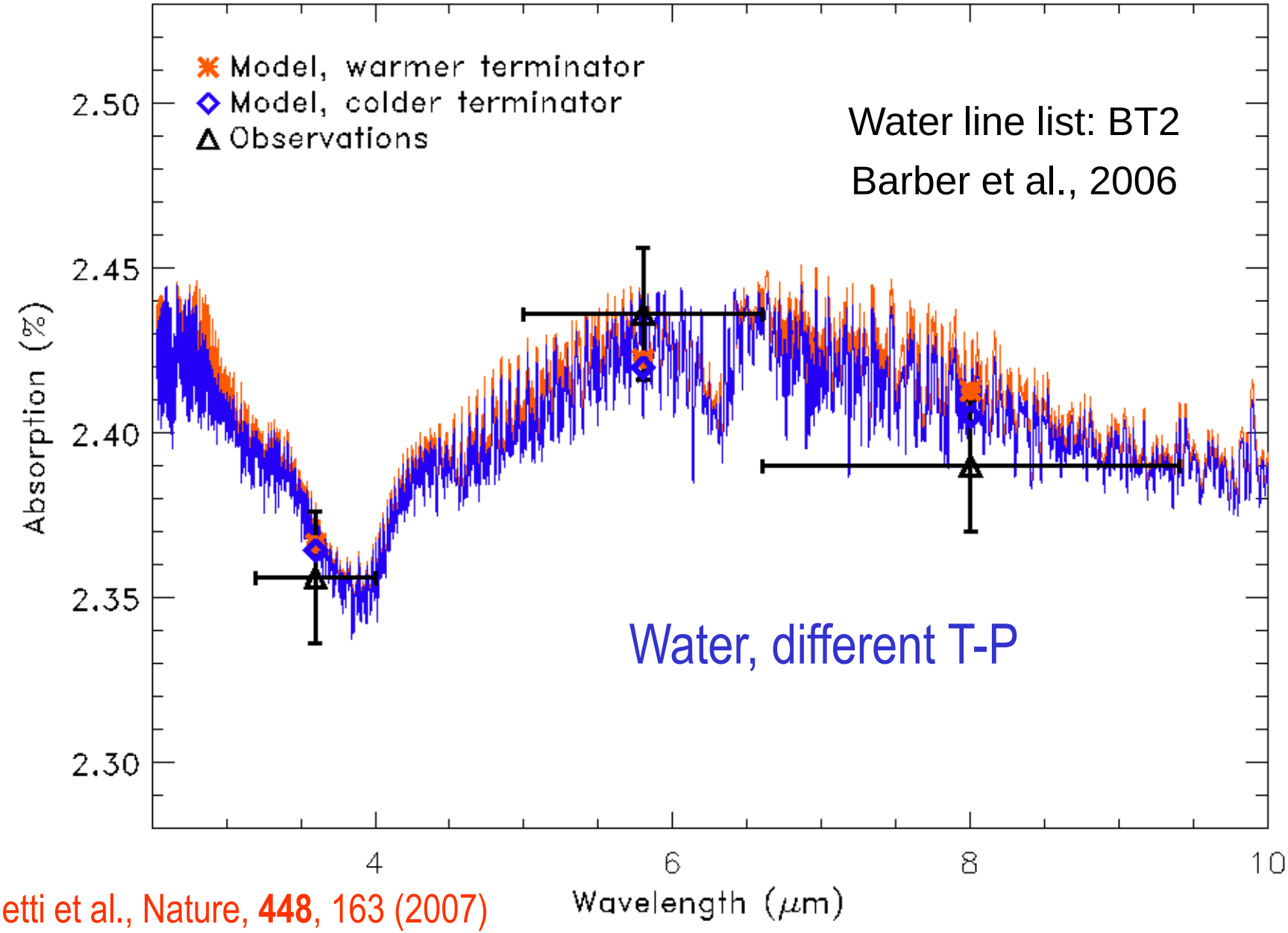
Mass = 0.69 ±0.05 $M_{Jupiter}$

Radius = 1.35 ±0.04 $R_{Jupiter}$

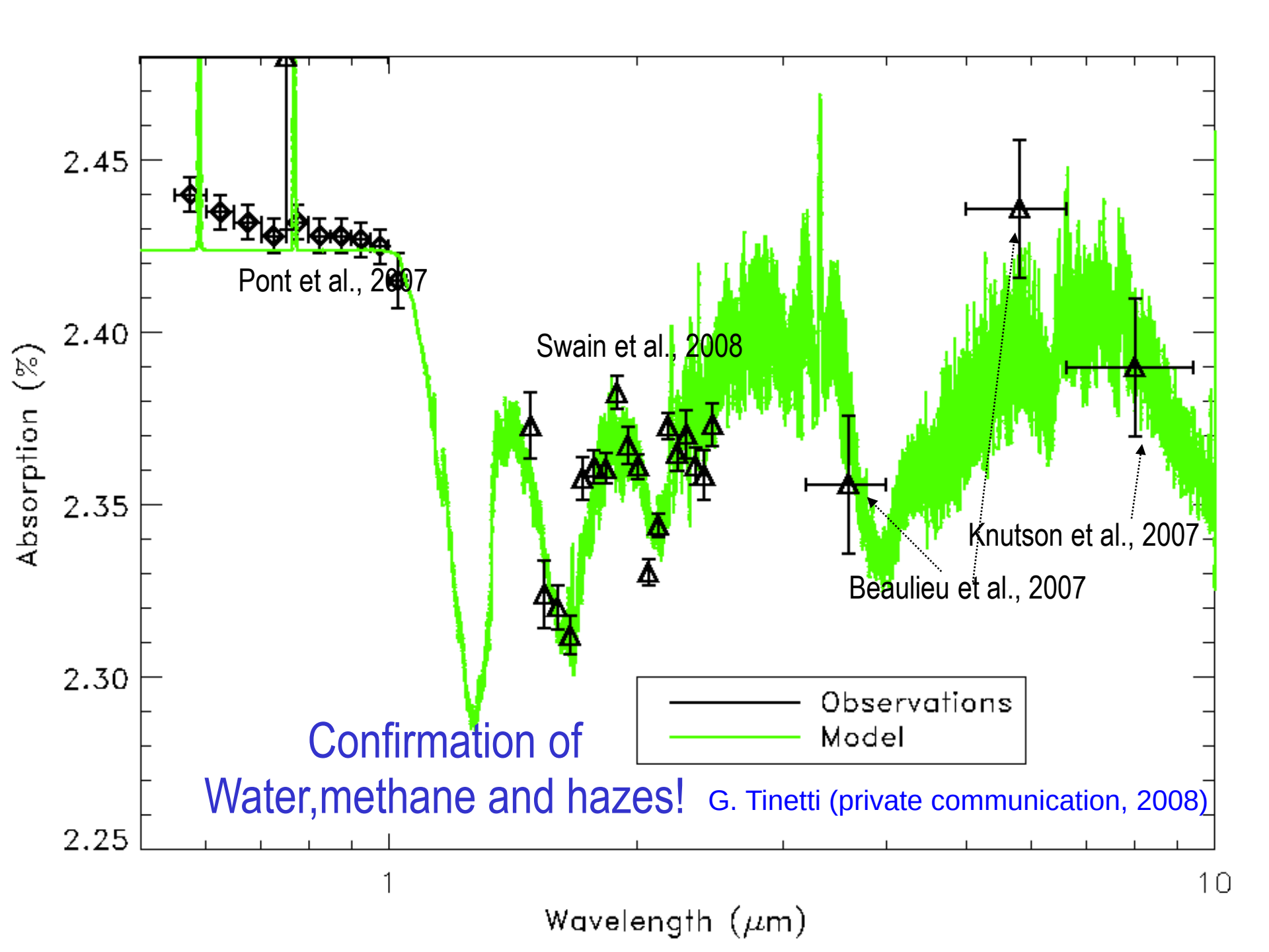
Density = 0.35 ±0.05 g/cm^3

HD189733b: Primary transit with Spitzer

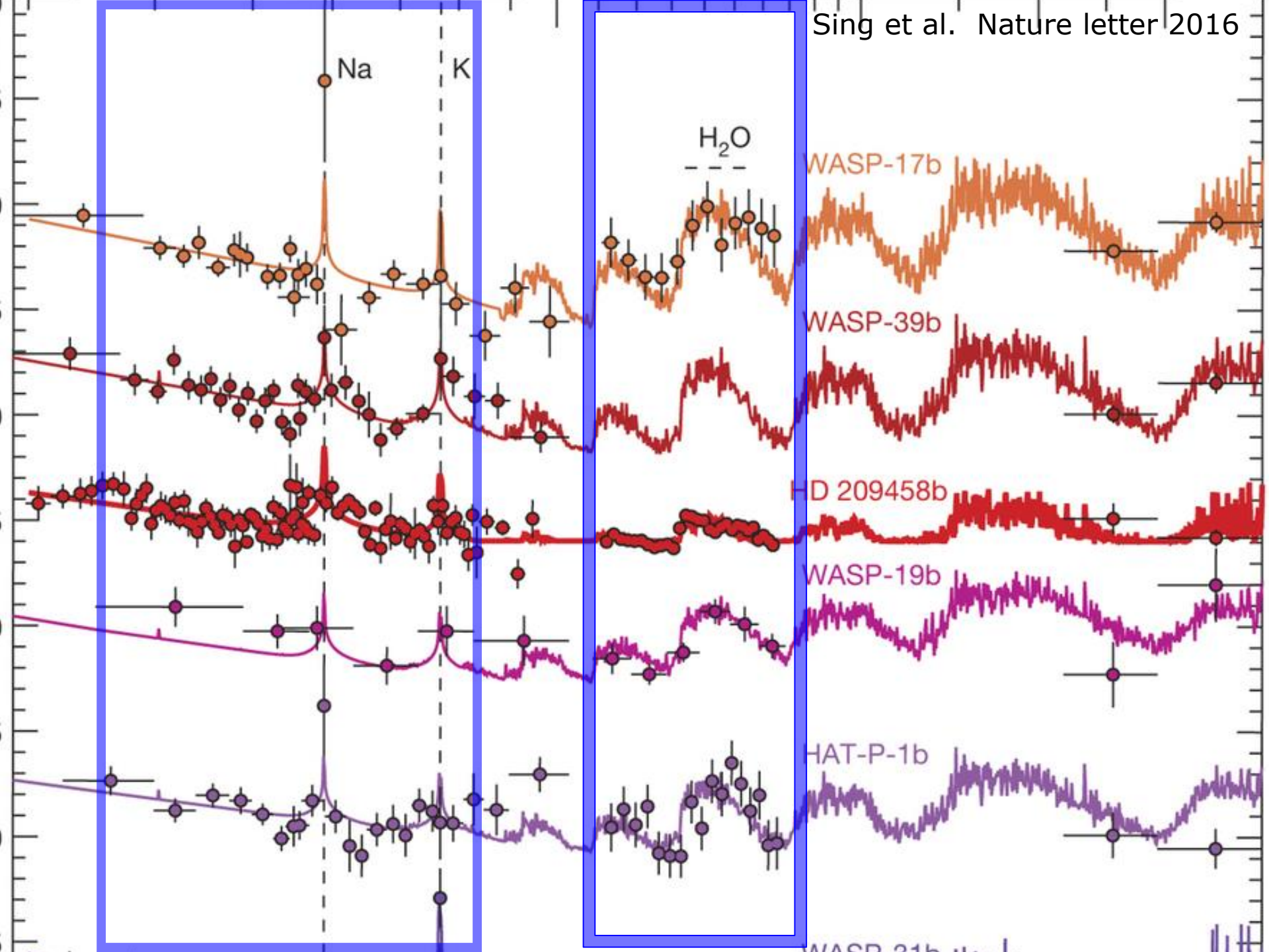




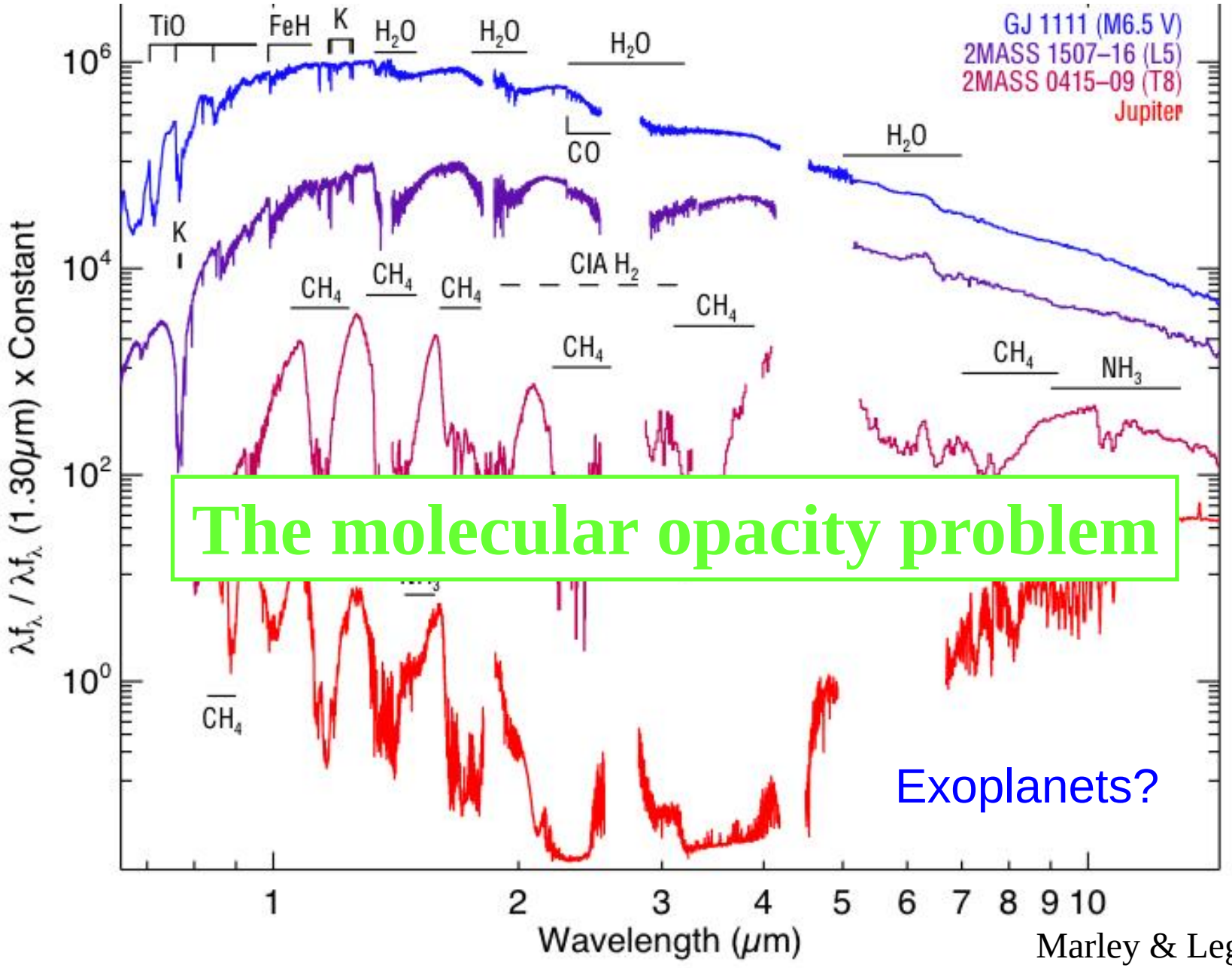
Tinetti et al., Nature, **448**, 163 (2007)


Pont et al., 2007
Swain et al., 2008
Knutson et al., 2007
Beaulieu et al., 2007
Observations
Model
Confirmation of
Water,methane and hazes!
G. Tinetti (private communication, 2008)
Absorption (%)
2.45
2.40
2.35
2.30
2.25
1
10
Wavelength (μm)

Sing et al. Nature letter 2016



Cool atmospheres: dominated by molecular absorption



The molecular opacity problem

M Dwarf

Brown Dwarfs

Planet

Exoplanets?

Marley & Leggett (2008)

ExoMol

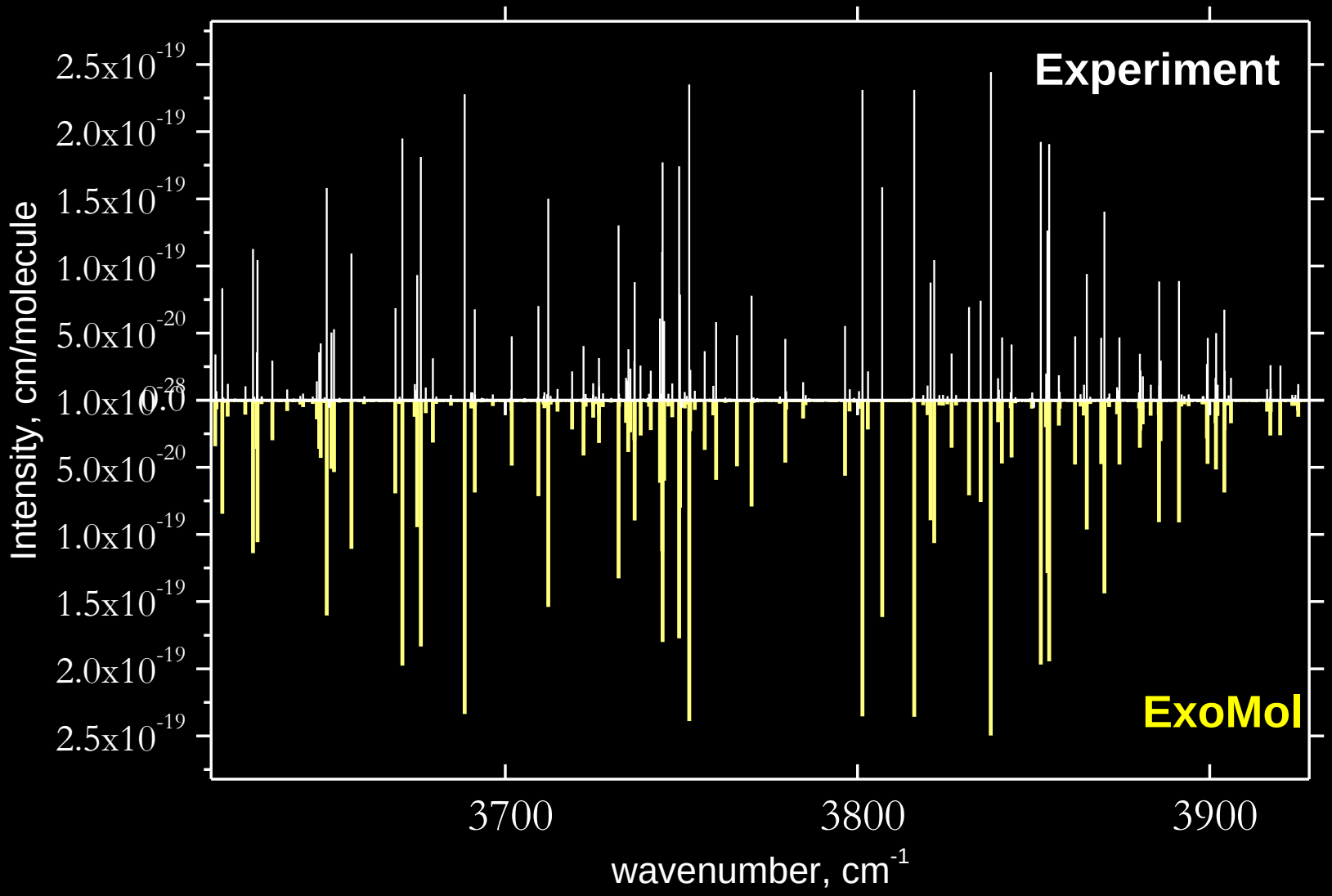
- 5 year project: 2011-16
- Provide data for all molecular transitions important for exoplanet atmospheres
- Methodology: first principles quantum mechanical calculations, informed by experiment

J Tennyson and S.N. Yurchenko, MNRAS, 425, 21 (2012).

erc

Science & Technology Facilities Council

Line list = line positions + line intensities



This is our 2016-line list for water

Frontier Problems in Exoplanet Characterization

- Non-equilibrium processes in exoplanet atmospheres

  (Stevenson et al. 2010; Madhusudhan & Seager 2011; Moses et al. 2013) CH_4, CO, NH_3

- Constraints on thermal inversions in hot Jupiters

  (Fortney et al. 2008; Spiegel et al. 2009) TiO, VO, H_2S

- C/O ratios and Carbon-rich atmospheres

  (Fortney et al. 2008; Spiegel et al. 2009) H_2O, CO, HCN, CH_4, C_2H_2, TiH, FeH

- Constraints on exoplanet formation conditions

  (Madhusudhan et al. 2011; Oberg et al. 2011) H_2O, CO, CH_4

- Atmospheres and interiors of super-Earths

  (Bean et al. 2011; Desert et al. 2011; Miller-Ricci Kempton et al. 2011) H_2O, CO_2

Slide courtesy of N Madhusudhan (Cambridge)

ExoMol list of molecules

Molecular line lists for exoplanet & other atmospheres

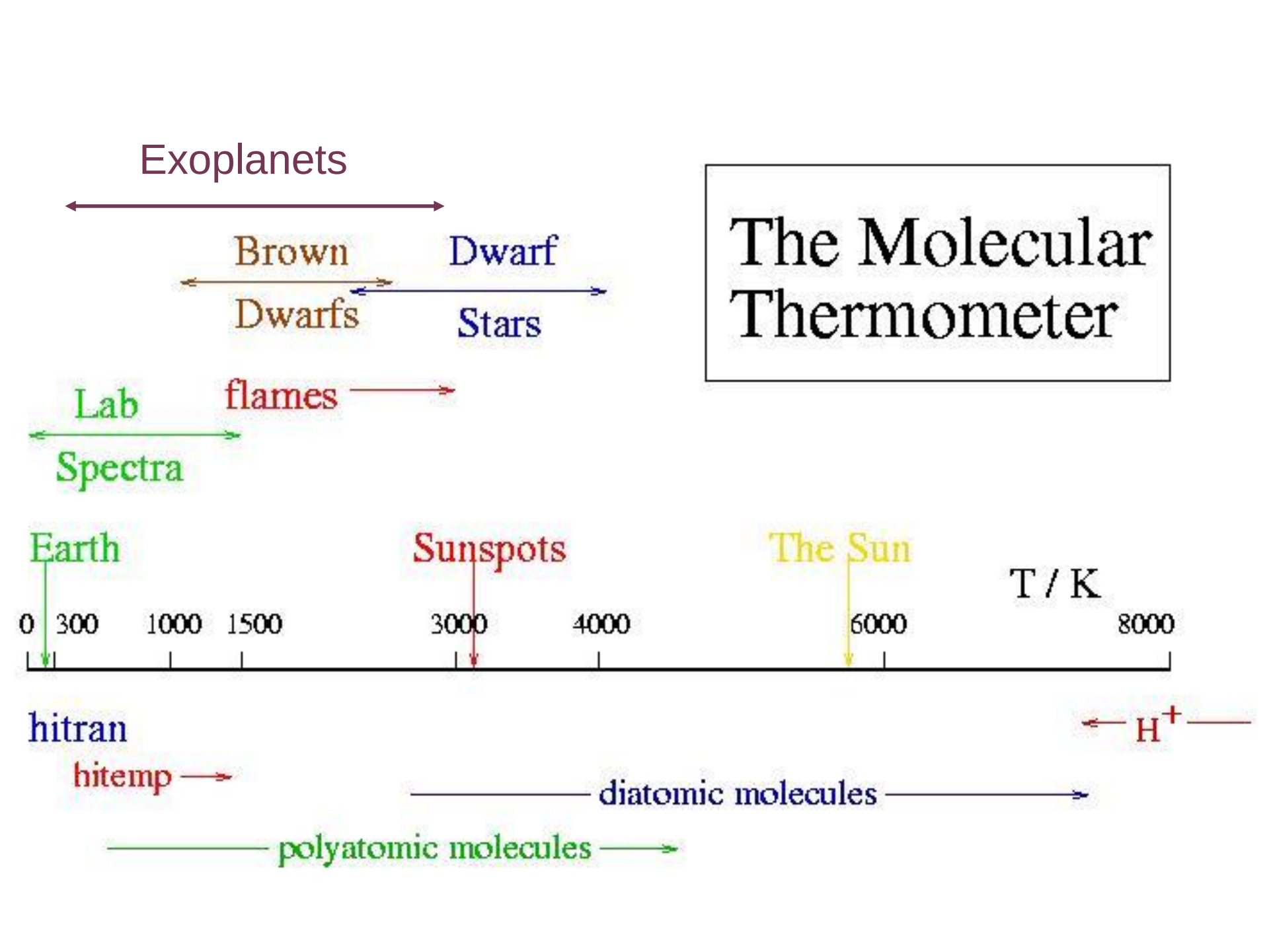
	Primordial (Metal-poor)	Terrestrial Planets (Oxidising)	Giant-Planets & Cool Stars (Reducing atmospheres)
Already available	H_2, LiH **HeH^+, H_3^+** **H_2D^+**	OH, CO_2, O_3, NO **H_2O, HDO, NH_3**	H_2, CN, CH, CO, **CO_2**, TiO **HCN/HNC, H_2O, NH_3,**
ExoMol		**O_2, CH_4, SO_2, SO_3 HOOH, H_2CO, HNO_3**	**CH_4, PH_3, C_2, C_3, HCCH, H_2S, C_2H_6, C_3H_8, VO, O_2, AlO, MgO,** **CrH, MgH, FeH, CaH, AlH, SiH, TiH, NiH, BeH, YO**

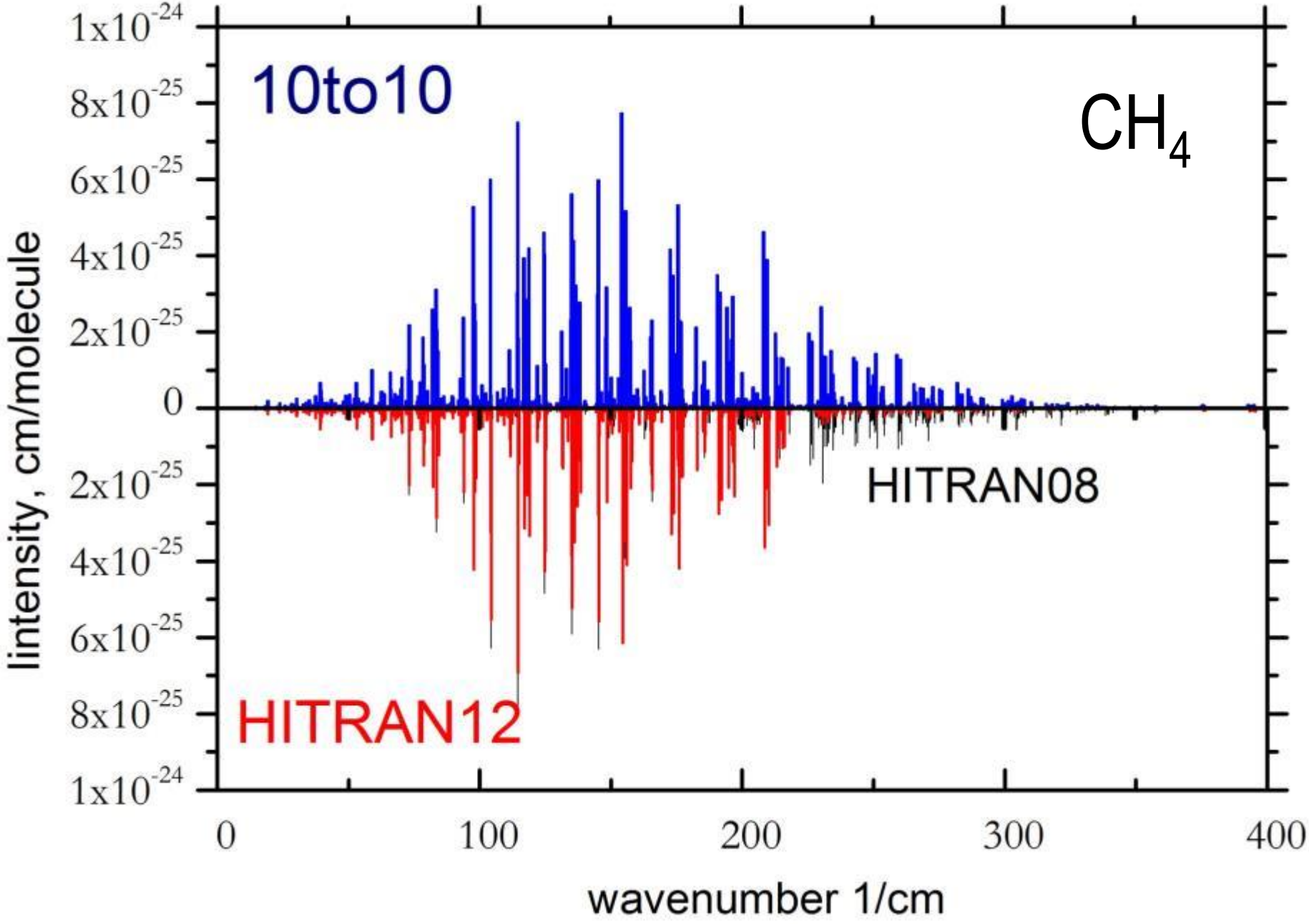
Available from elsewhere
Already calculated at UCL
Will be calculated during the ExoMol project

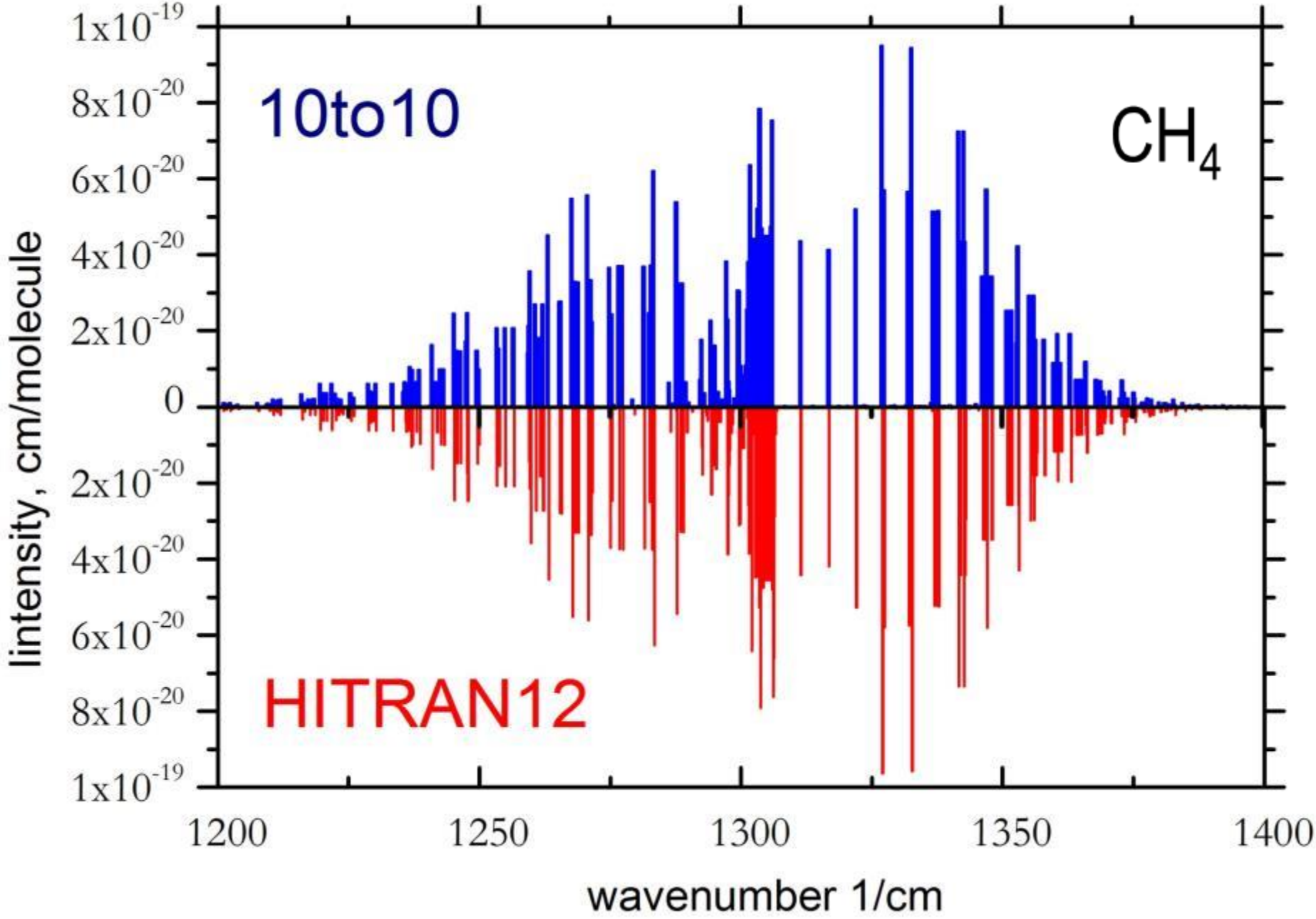
Full details:
J. Tennyson and S.N. Yurchenko, MNRAS, 425, 21 (2012)

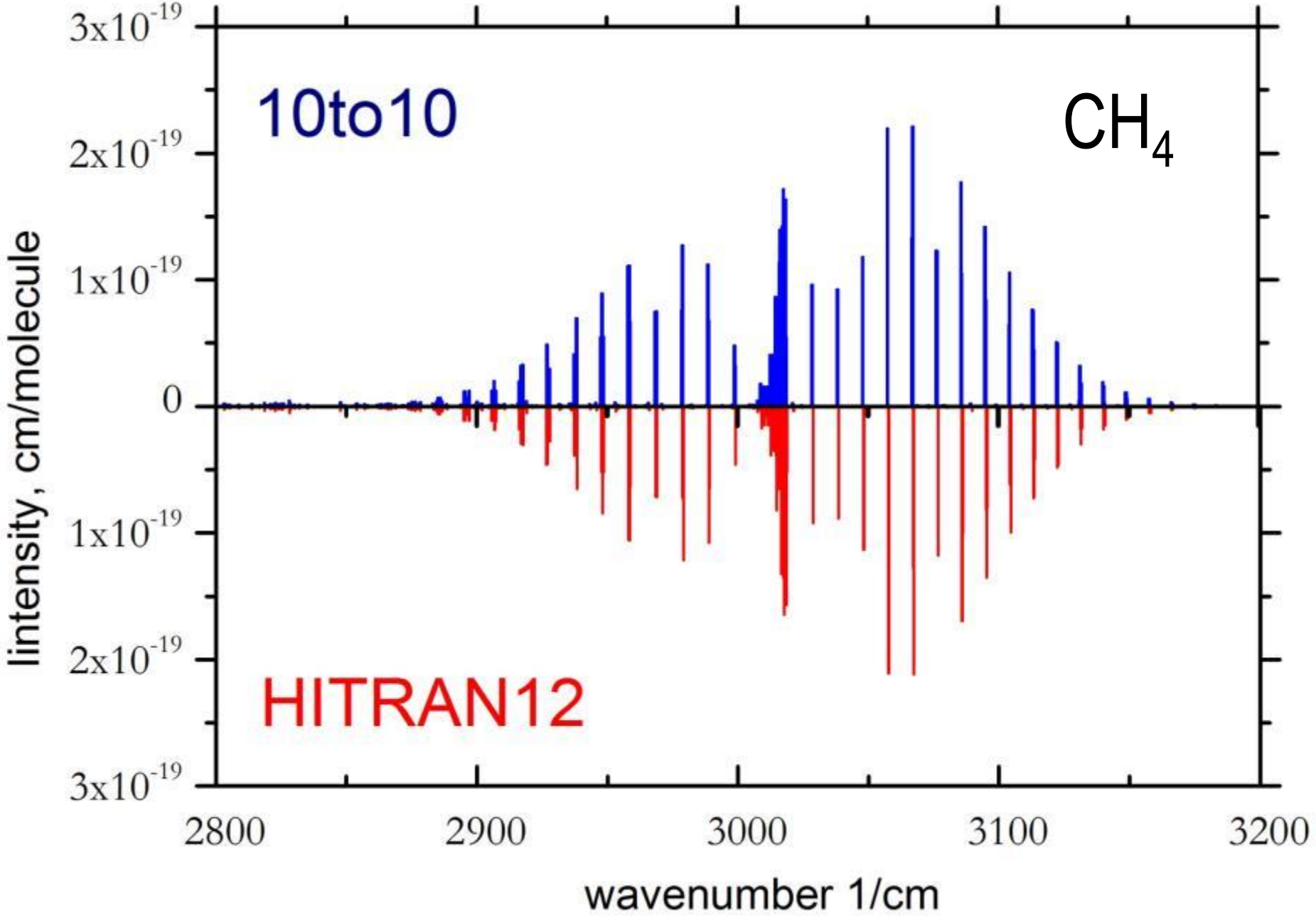
www.exomol.com

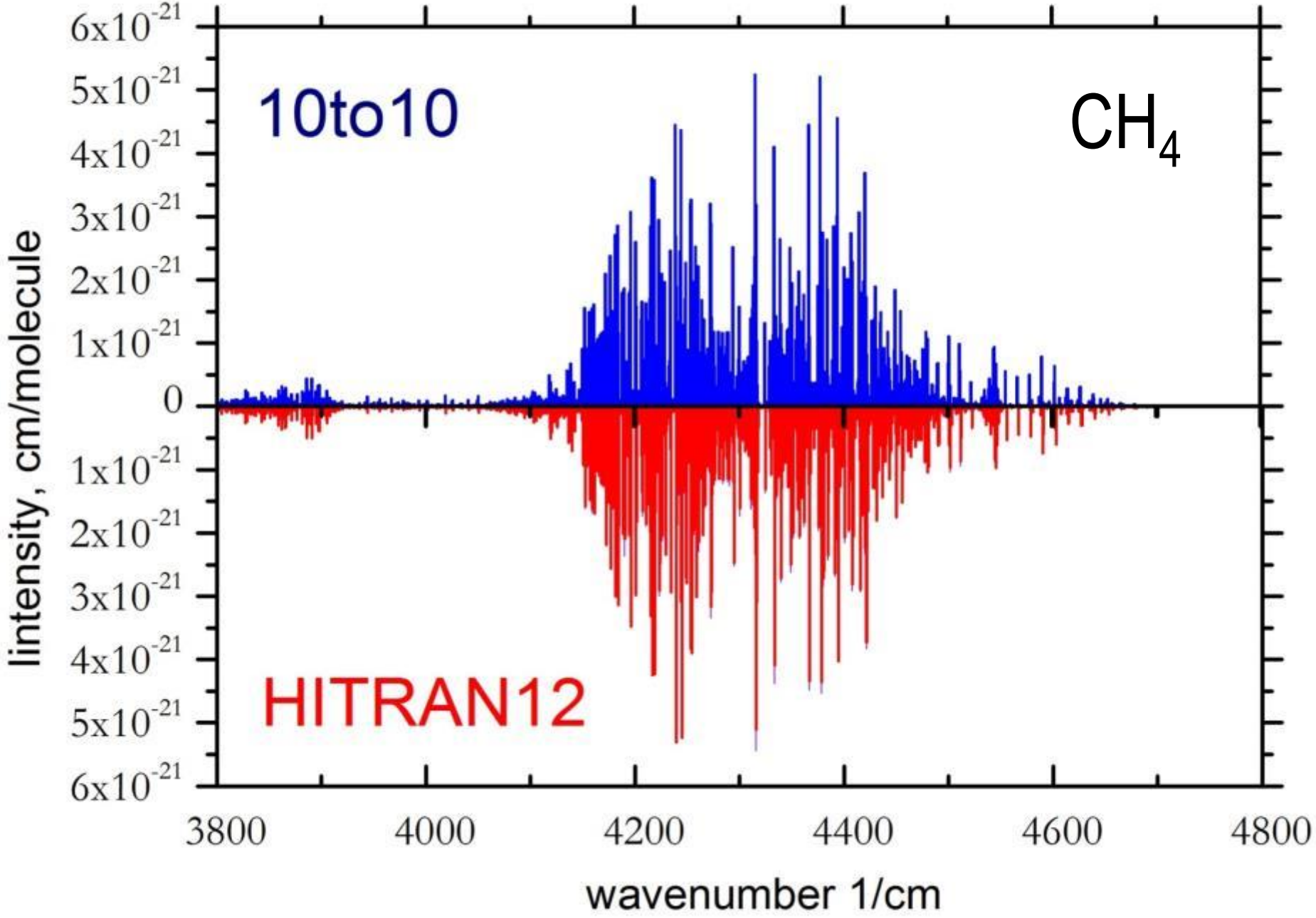
Why theory, not experiment?

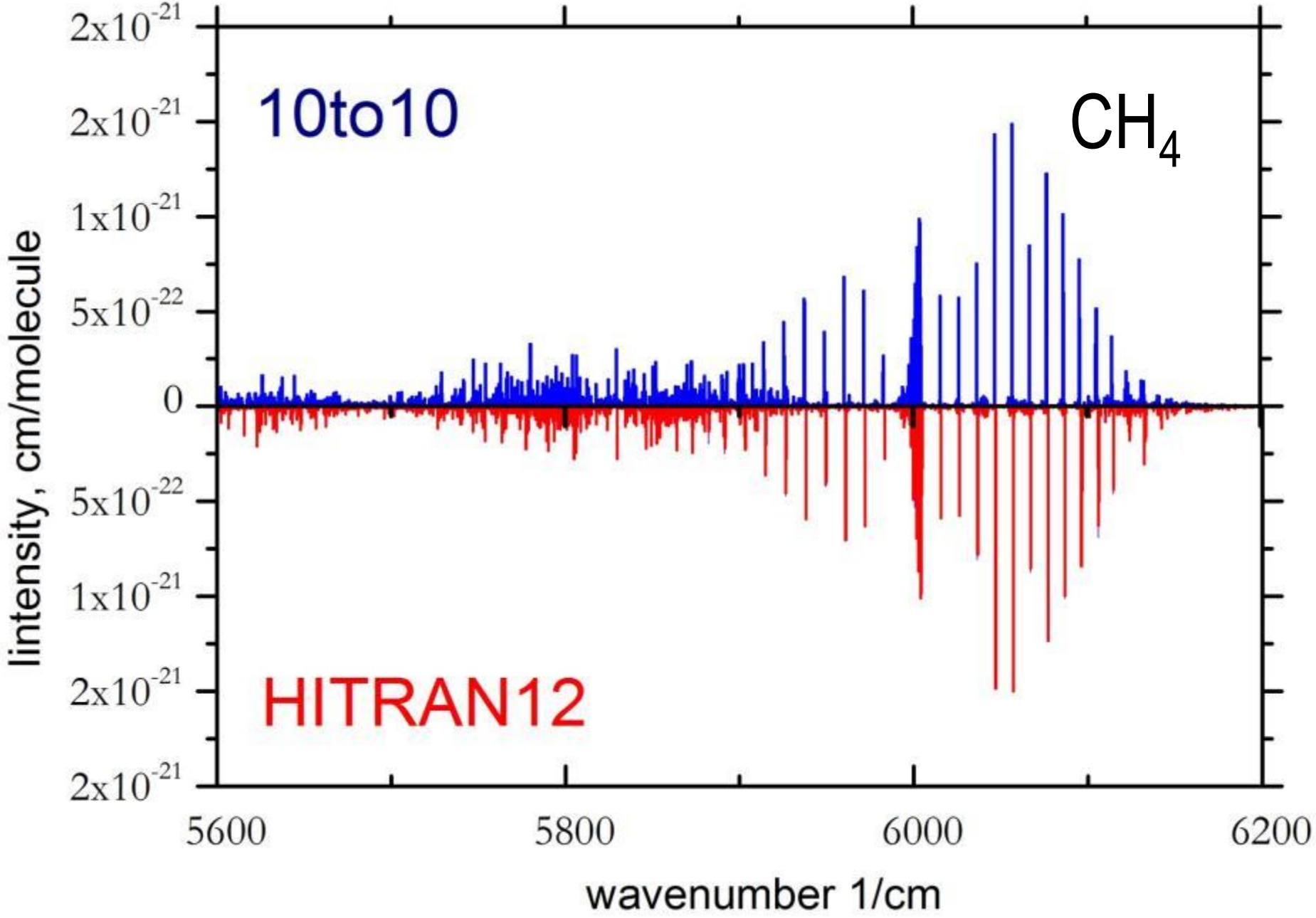

Exoplanets
Brown Dwarfs
Dwarf Stars
The Molecular Thermometer
Lab Spectra
flames
Earth
Sunspots
The Sun
T / K
0
300
1000
1500
3000
4000
6000
8000
hitran
hitemp
H+
diatomic molecules
polyatomic molecules


10to10
CH_4
HITRAN08
HITRAN12
intensity, cm/molecule
wavenumber 1/cm
1x10-24
8x10-25
6x10-25
4x10-25
2x10-25
0
2x10-25
4x10-25
6x10-25
8x10-25
1x10-24
0
100
200
300
400

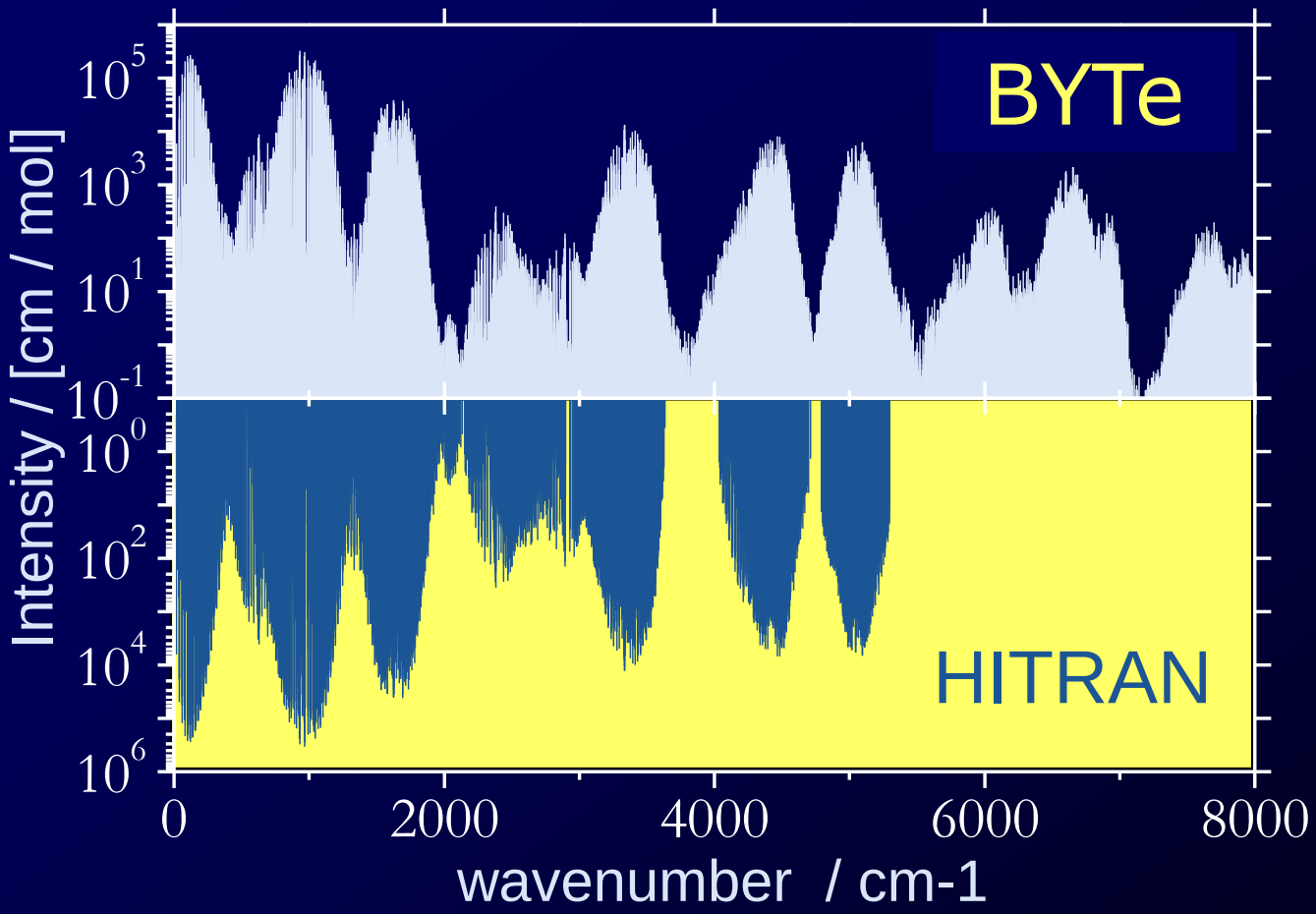

10to10
CH_4
HITRAN12
intensity, cm/molecule
wavenumber 1/cm
1x10^-19
8x10^-20
6x10^-20
4x10^-20
2x10^-20
0
2x10^-20
4x10^-20
6x10^-20
8x10^-20
1x10^-19
1200
1250
1300
1350
1400


10to10
CH_4
HITRAN12
3x10^-19
2x10^-19
1x10^-19
0
1x10^-19
2x10^-19
3x10^-19
intensity, cm/molecule
2800
2900
3000
3100
3200
wavenumber 1/cm


10to10
CH_4
HITRAN12
intensity, cm/molecule
wavenumber 1/cm
6x10-21
5x10-21
4x10-21
3x10-21
2x10-21
1x10-21
0
1x10-21
2x10-21
3x10-21
4x10-21
5x10-21
6x10-21
3800
4000
4200
4400
4600
4800


10to10
CH_4
HITRAN12
intensity, cm/molecule
wavenumber 1/cm
2x10-21
2x10-21
1x10-21
5x10-22
0
5x10-22
1x10-21
2x10-21
2x10-21
5600
5800
6000
6200

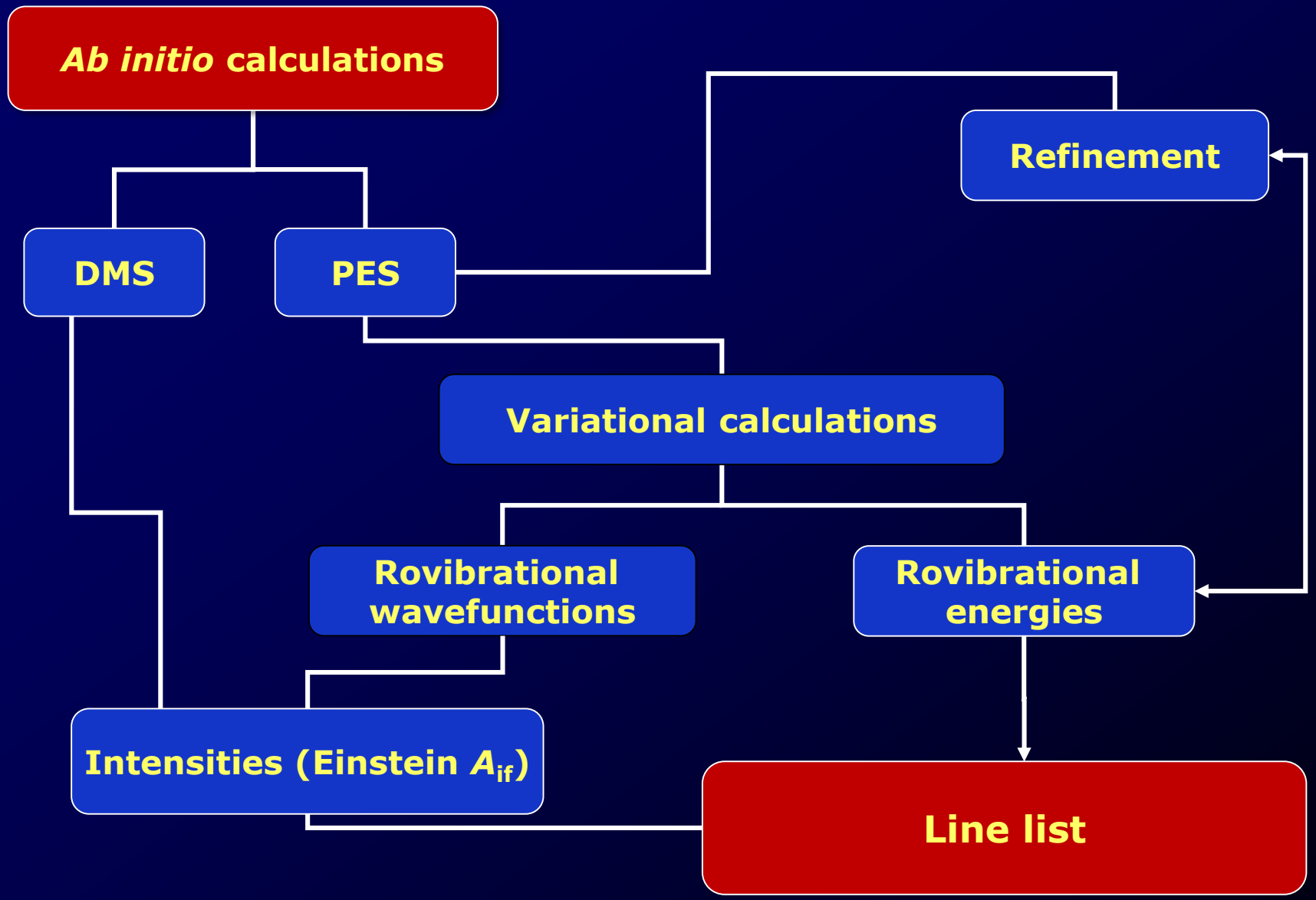
Completeness: Absorption of ammonia (T=300 K)



Less than 30,000 NH_3 lines known experimentally:
BYTe contains 1.1 billion lines, about 40,000 times as many!

S.N. Yurchenko, R.J. Barber & J. Tennyson, Mon. Not. R. astr. Soc., 413, 1828 (2011)

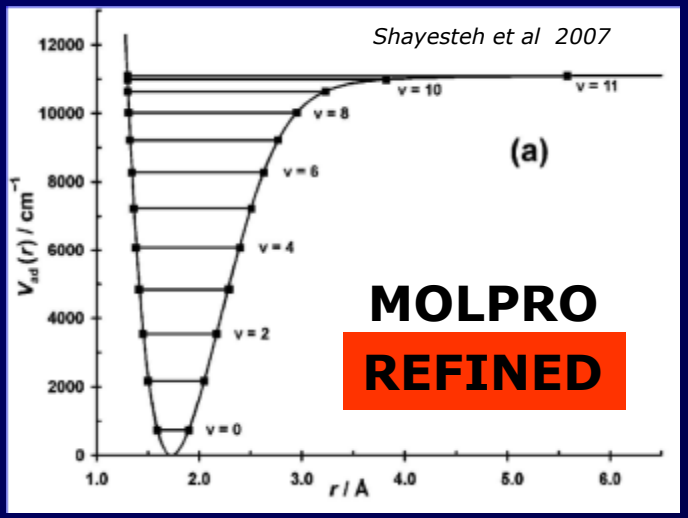
Method: Spectrum from the “first-principles”



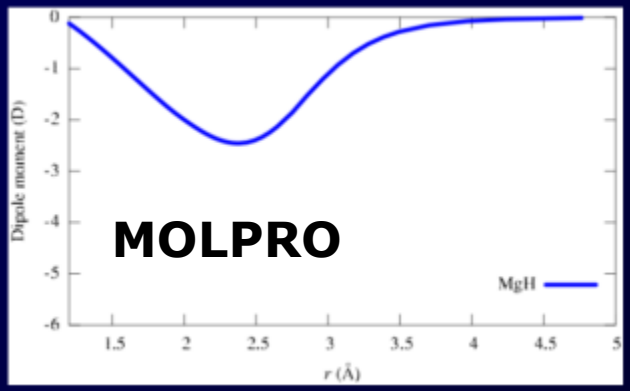
Ab initio: solve for motion of electrons

Line list: MgH

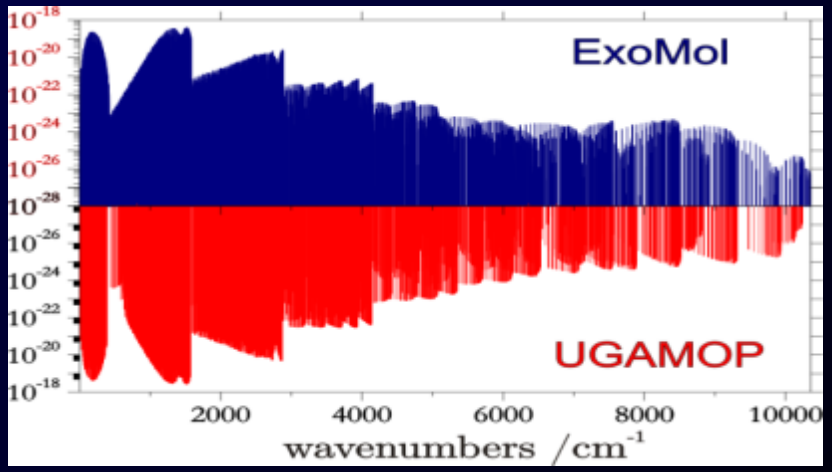
Potential energy curve



Dipole moment curve



Line list: 6690 lines, N_{max}=60



Solve for the motion of the nuclei

LEVEL 8.0
R. Le Roy,
Waterloo, Canada

B Yadin et al, MNRAS 425, 34 (2012)

New general diatomic code

Duo

Freely available from CCPforge

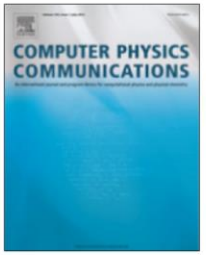
ccpforge.cse.rl.ac.uk

Computer Physics Communications 202 (2016) 262–275

Contents lists available at ScienceDirect

Computer Physics Communications

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



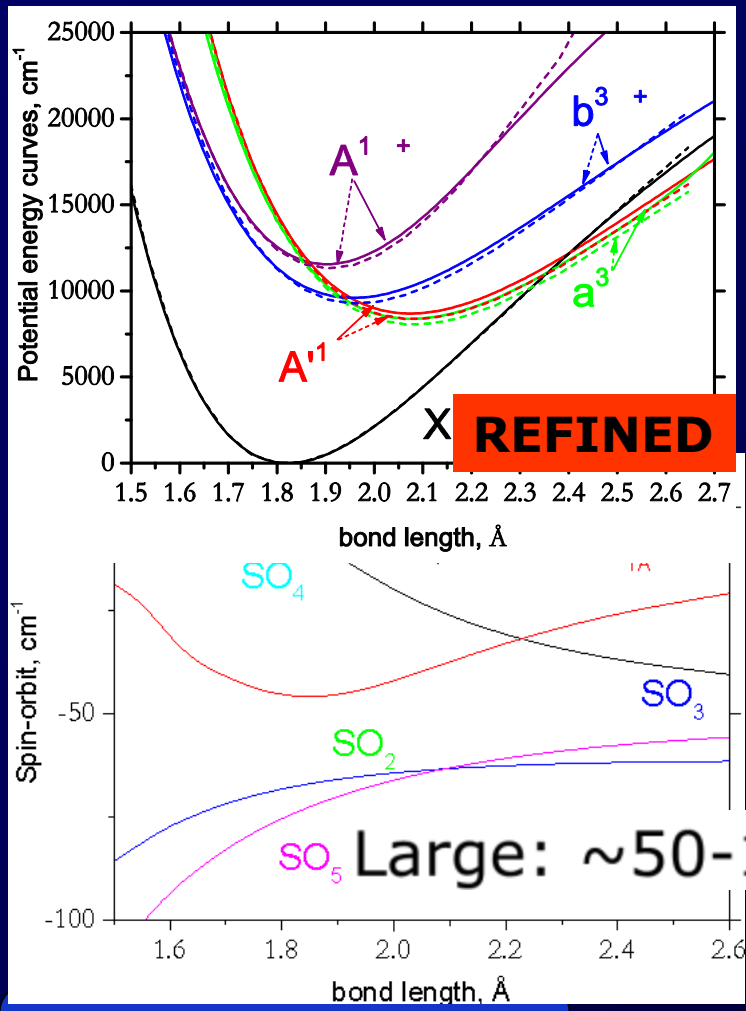
Duo: A general program for calculating spectra of diatomic molecules☆

Sergei N. Yurchenko[a,*], Lorenzo Lodi[a], Jonathan Tennyson[a], Andrey V. Stolyarov[b]

[a] Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom
[b] Department of Chemistry, Lomonosov Moscow State University, Leninskiye gory 1/3, 119992 Moscow, Russia

Line list: CaO

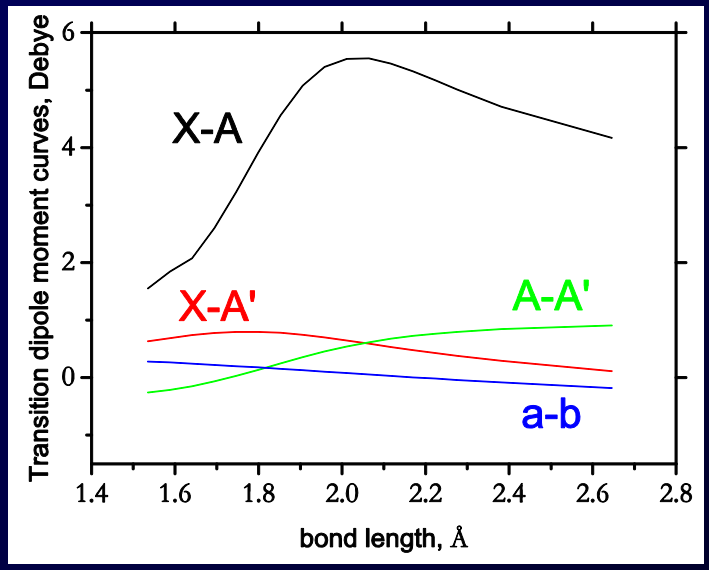
Potential energy



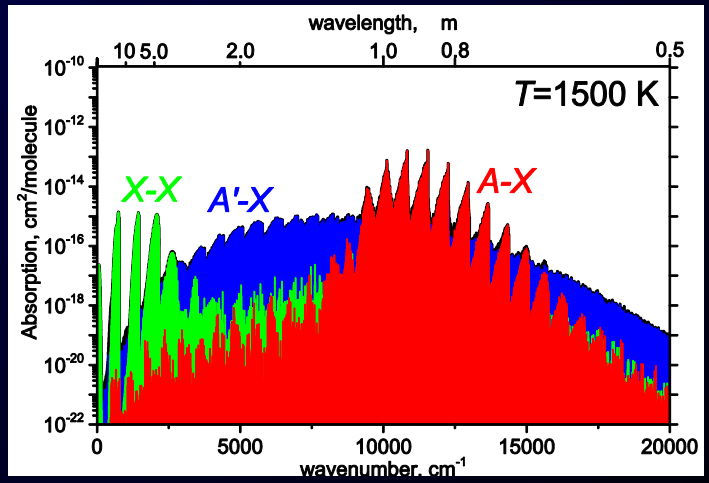
REFINED

Khalil et al (2011)

Dipole moment



Line list: 22 M lines

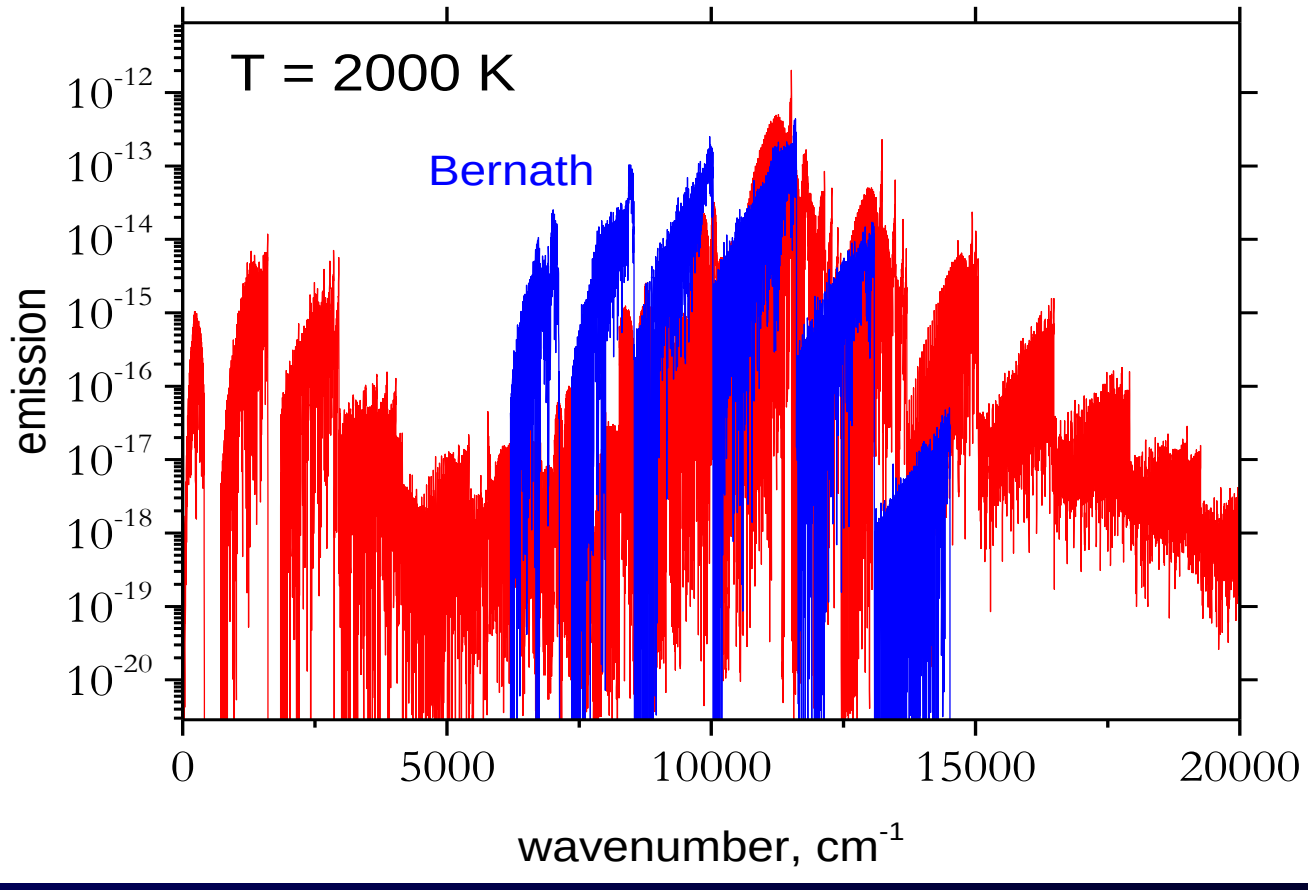


Large: ~50-100 cm^{-1}

Solve for the motion of the nuclei

Duo

SN Yurchenko et al, MNRAS 456, 4524 (2016)



CrH

Maire N. Gorman, PhD UCL (2016)

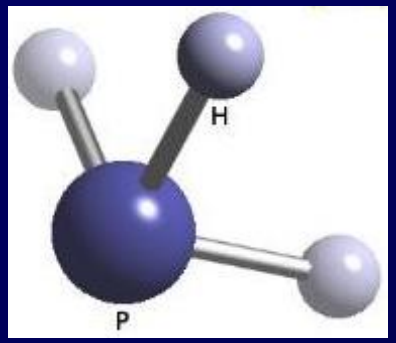
PH_3

Potential energy

Ab initio PES
[CCSD(T)/aug-cc-pV(Q+d)Z]

R. I. Ovsyannikov et al.
J. Chem. Phys 129, 044309 (2008).

Refined using lab spectra



Tunneling motion neglected

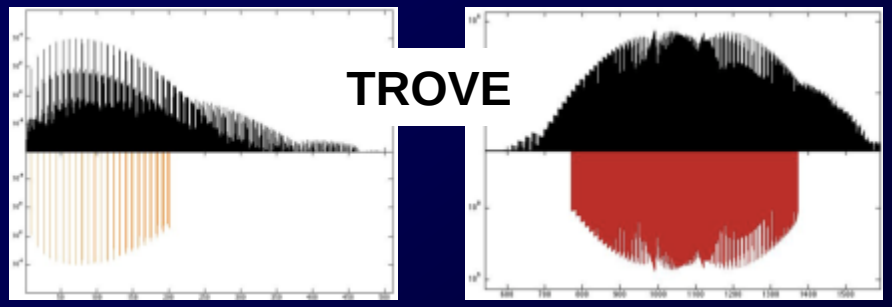
Dipole moment

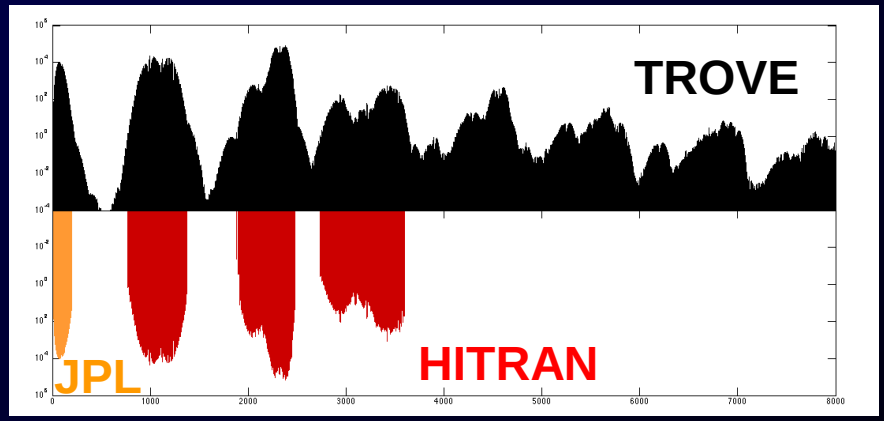
Ab initio:
CCSD(T)/aug-cc-pVTZ

S.N. Yurchenko et al.
J. Mol. Spectrosc 239, 71 (2006).

Solve for the motion of the nuclei

TROVE: Yurchenko, Thiel, Jensen

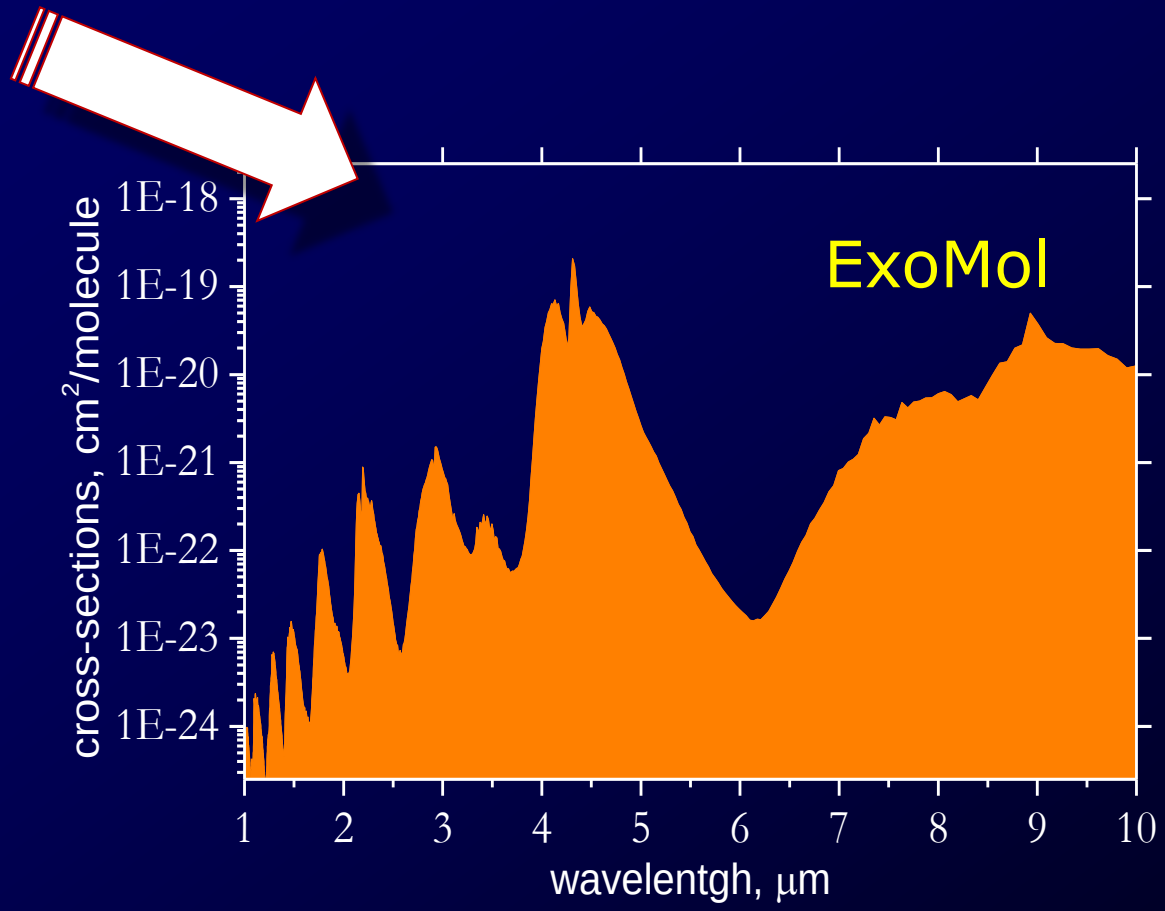




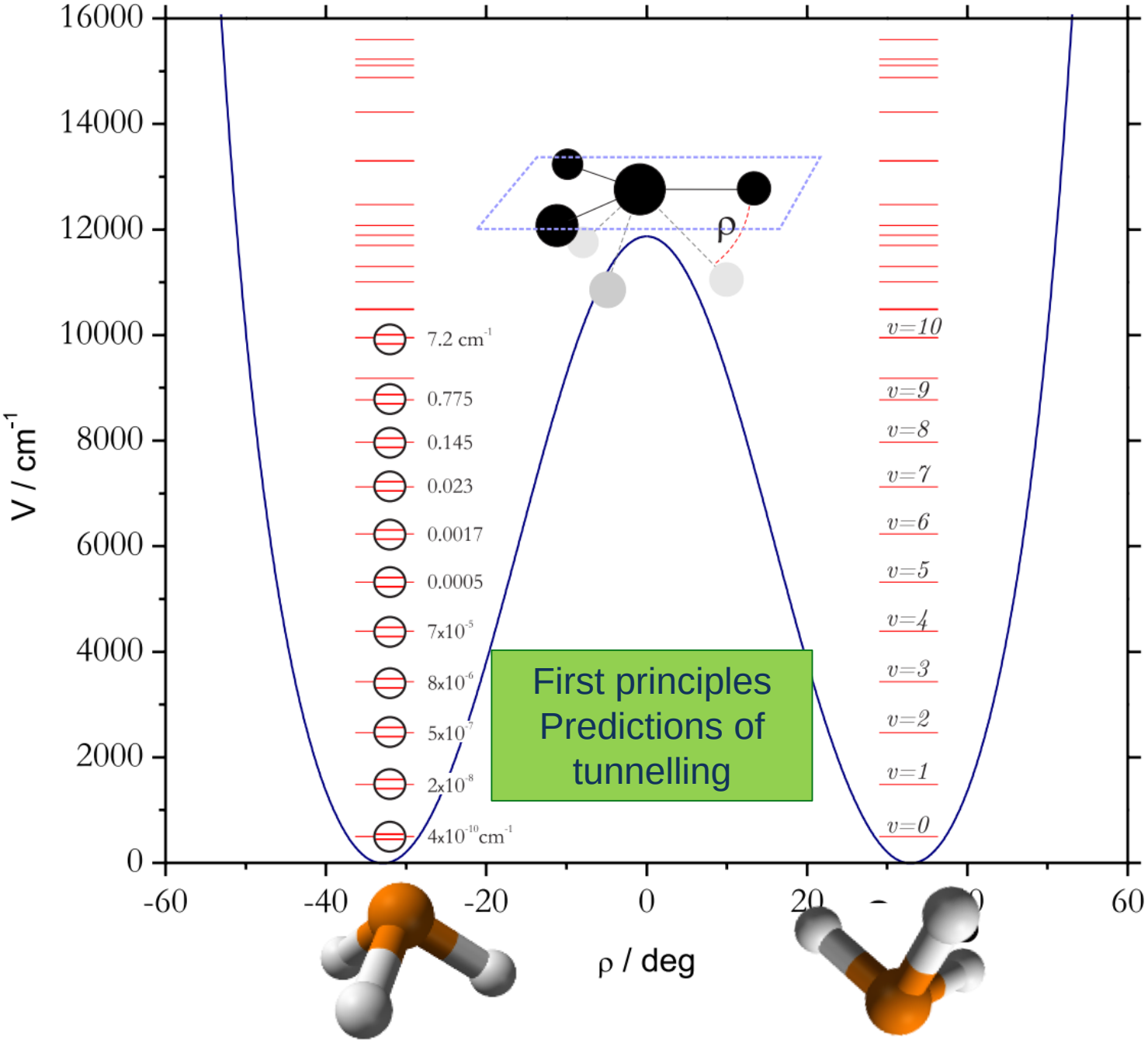
C Sousa-Silva et al, MNRAS, 446, 2337 (2015)

16.8 billion transitions for T up to 1500 K

It has a nice strong feature at 4.5 μm



No detection yet of phosphine on exoplanets

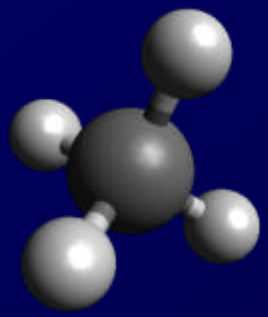


C. Sousa-Silva et al, J Chem Phys 145, 091102 (2016)

Ab initio: solve for motion of electrons

CH_4

Potential energy



Dipole moment

9D surface
130 000
geometries

MOLPRO
CCSD(T)-f12/QZ

Ab initio
10 electrons
Ground
electronic state

Three 9D surfaces
130 000
geometries

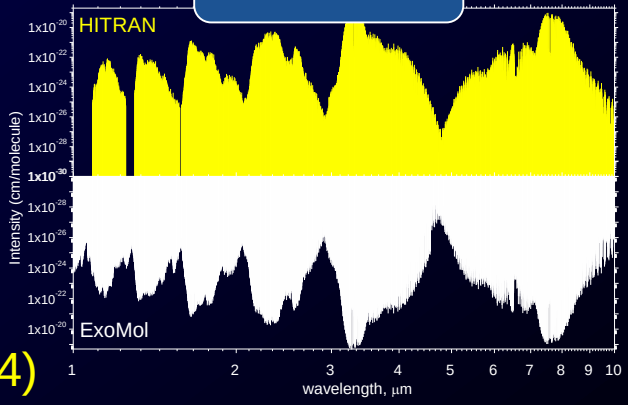
MOLPRO
CCSD(T)-f12/QZ

Solve for the motion of the nuclei

TROVE
Yurchenko, Thiel, Jensen

10to10

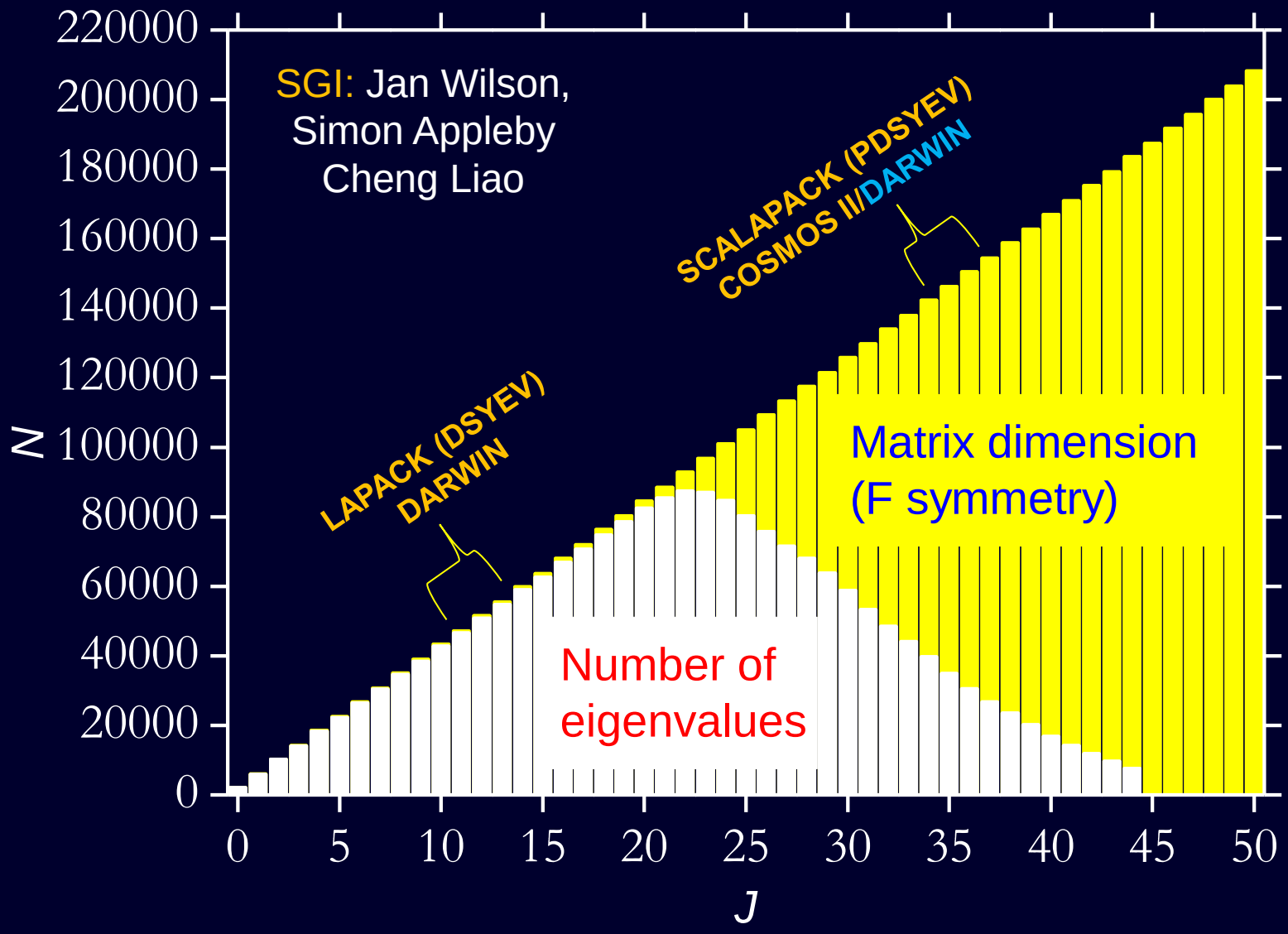
Line list:



9.8 Billion transitions

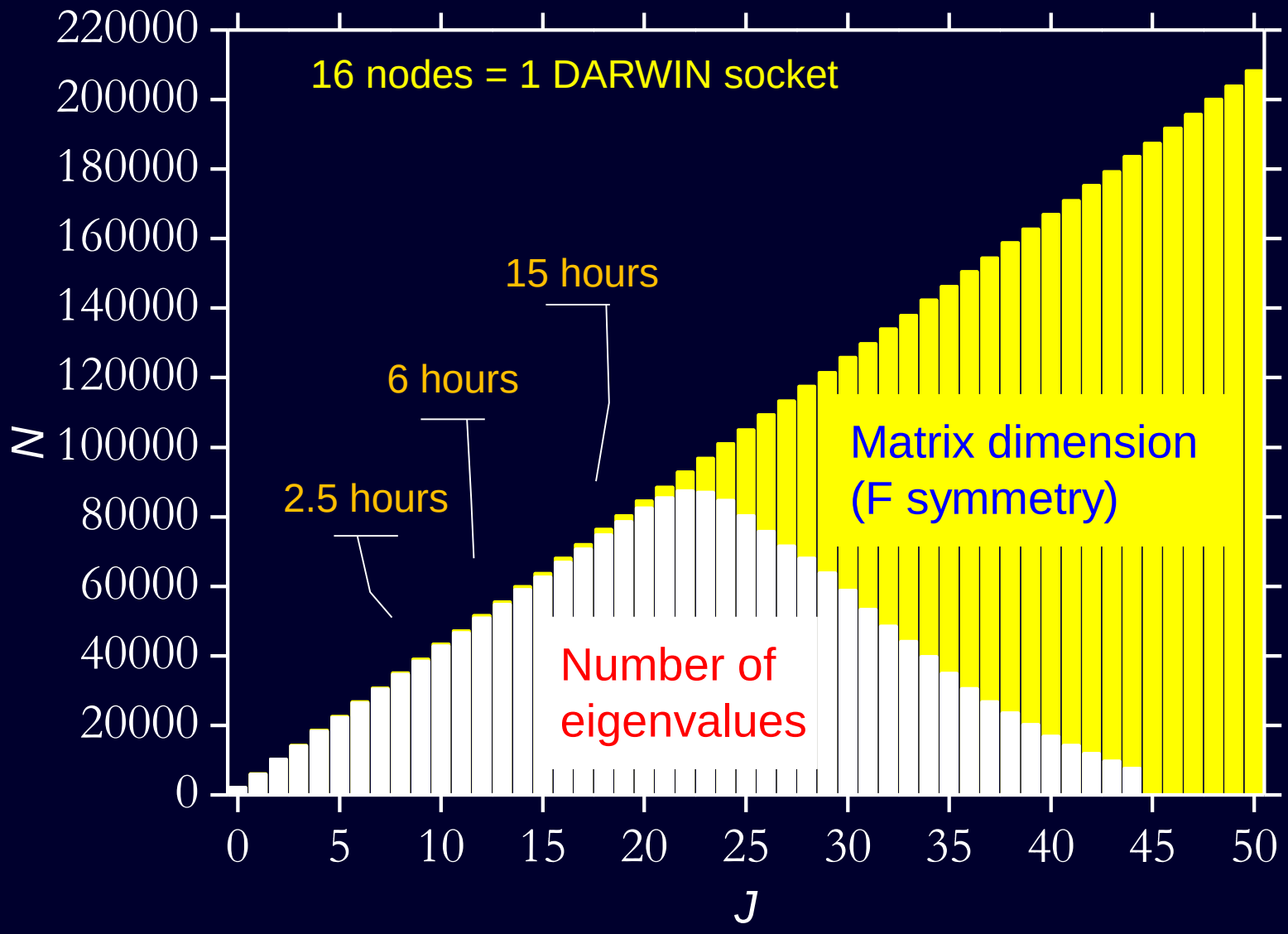
SN Yurchenko & J Tennyson, MNRAS 440, 1649 (2014)

CH_4 diagonalization: Size of the problem

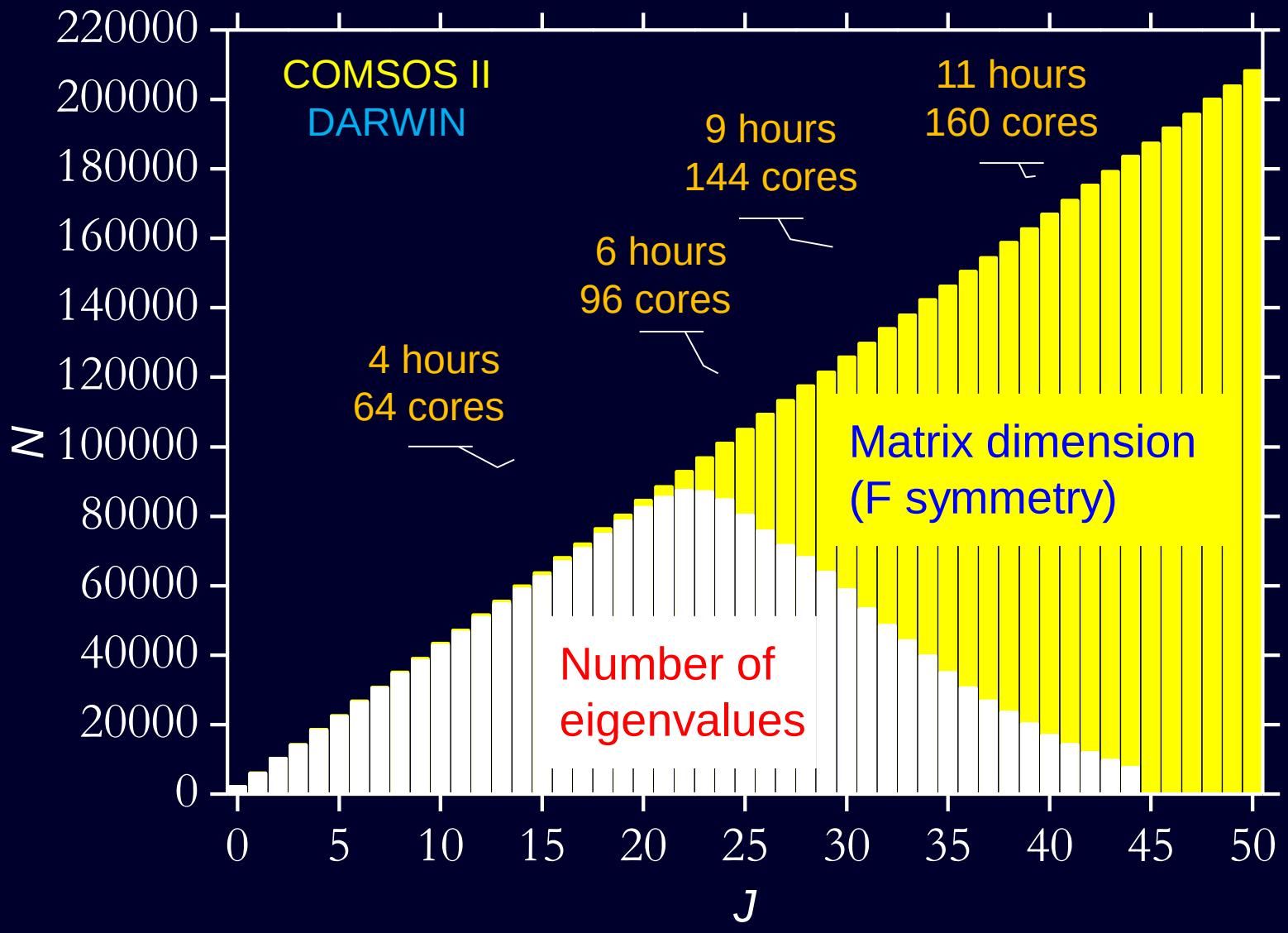


Acknowledgment: Andrey Kaliazin Dirac/COSMOS

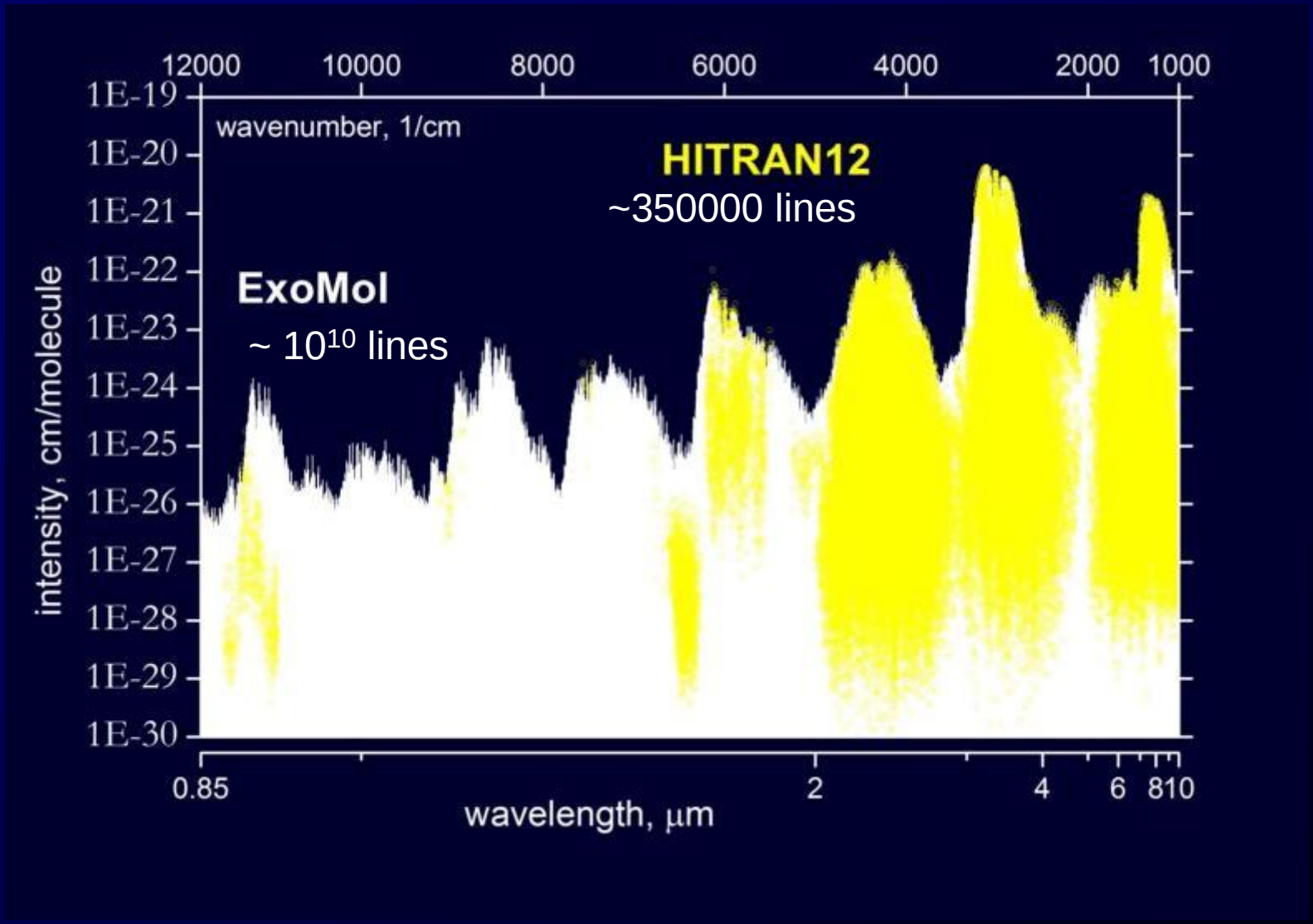
CH_4 diagonalization: Size of the problem

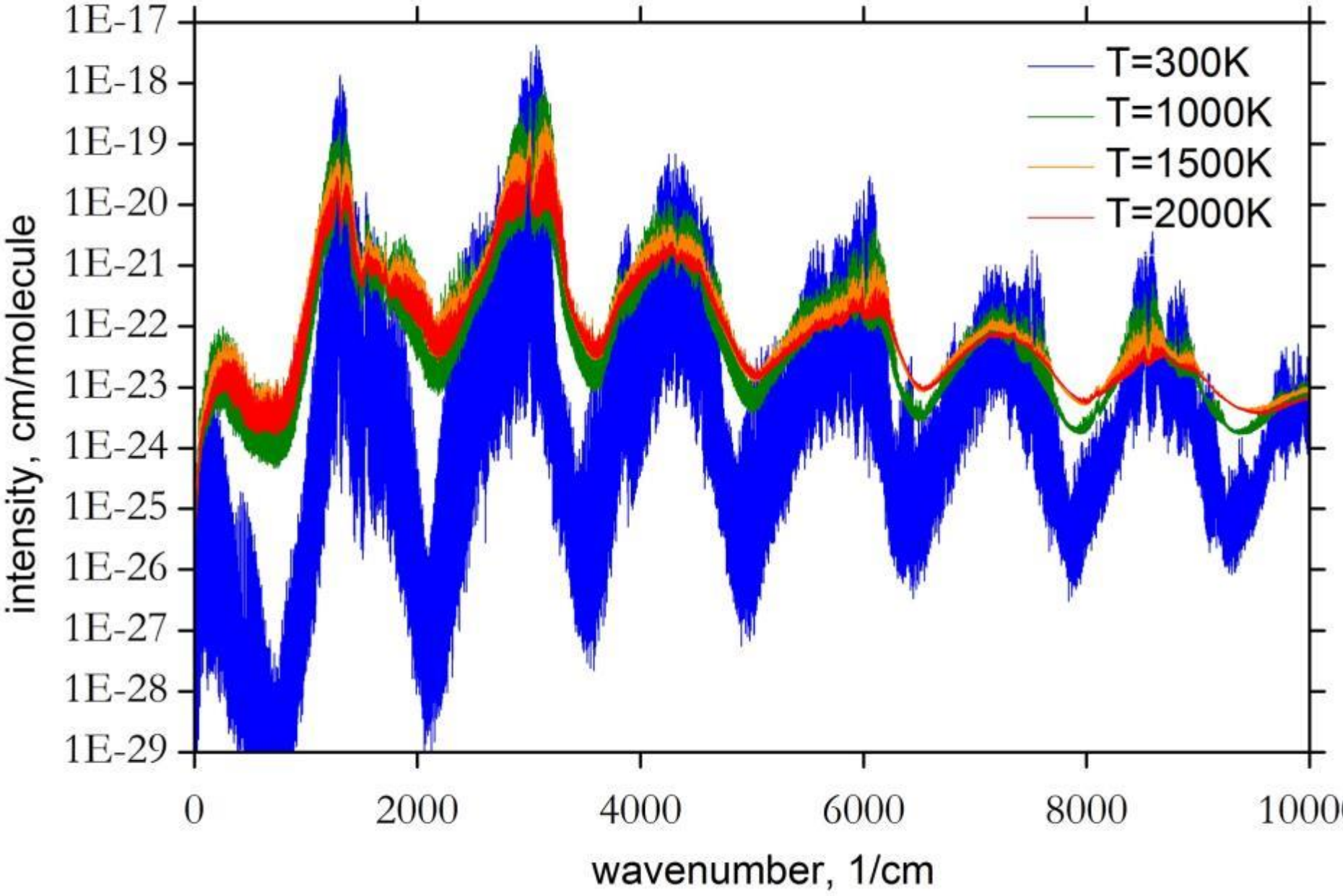


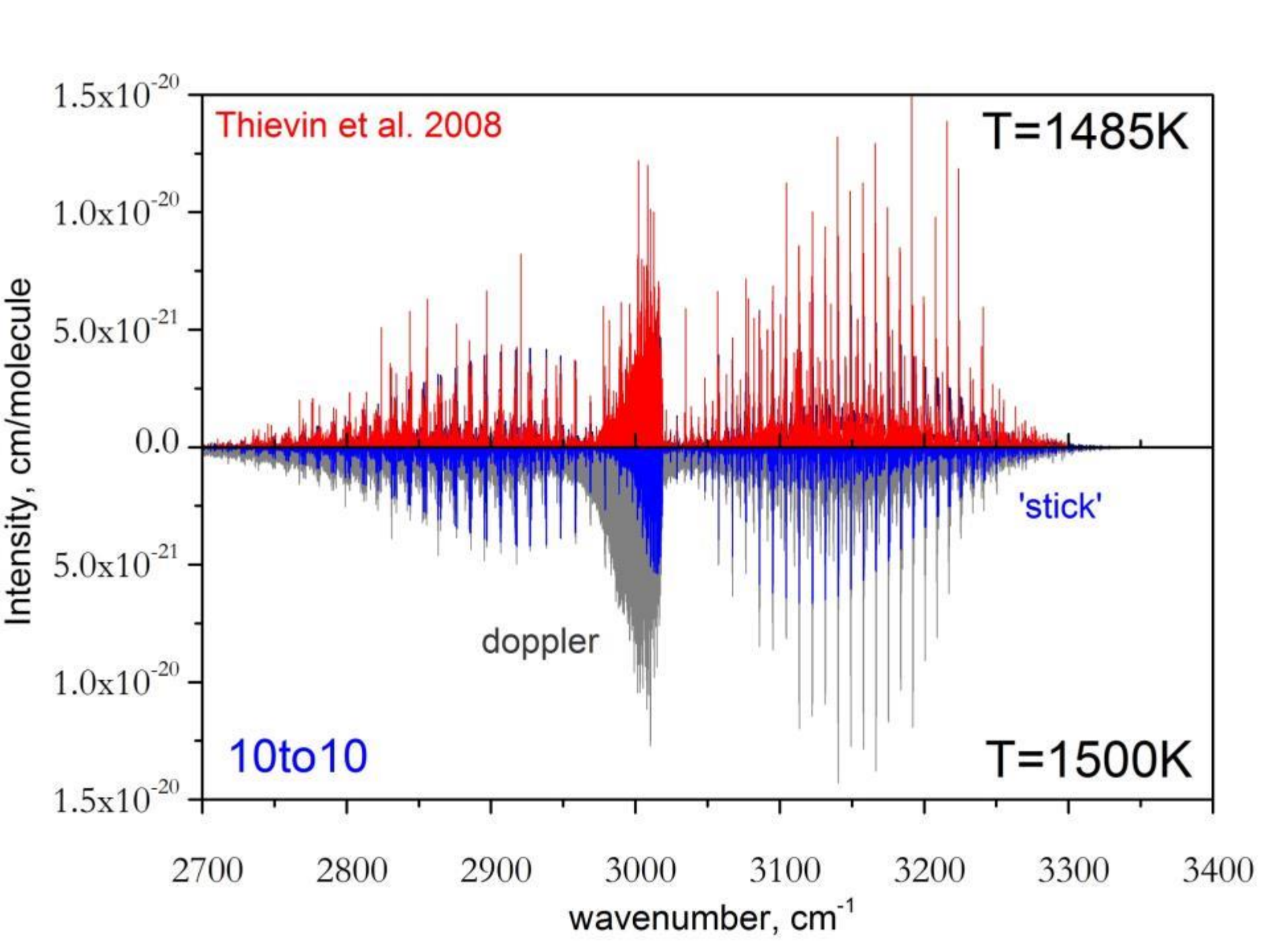
CH_4 diagonalization: Size of the problem

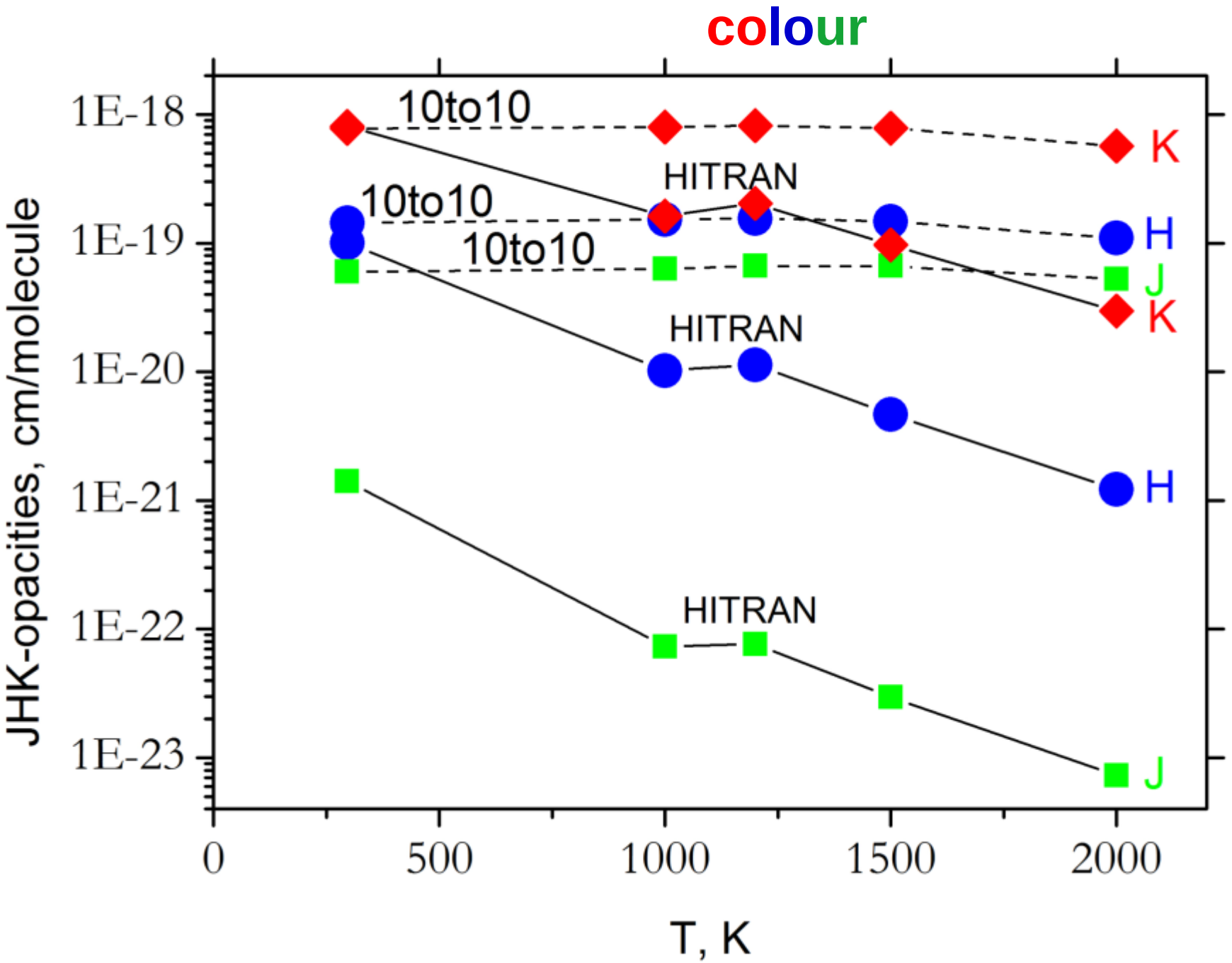


Absorption spectra of CH_4: from experimental line list

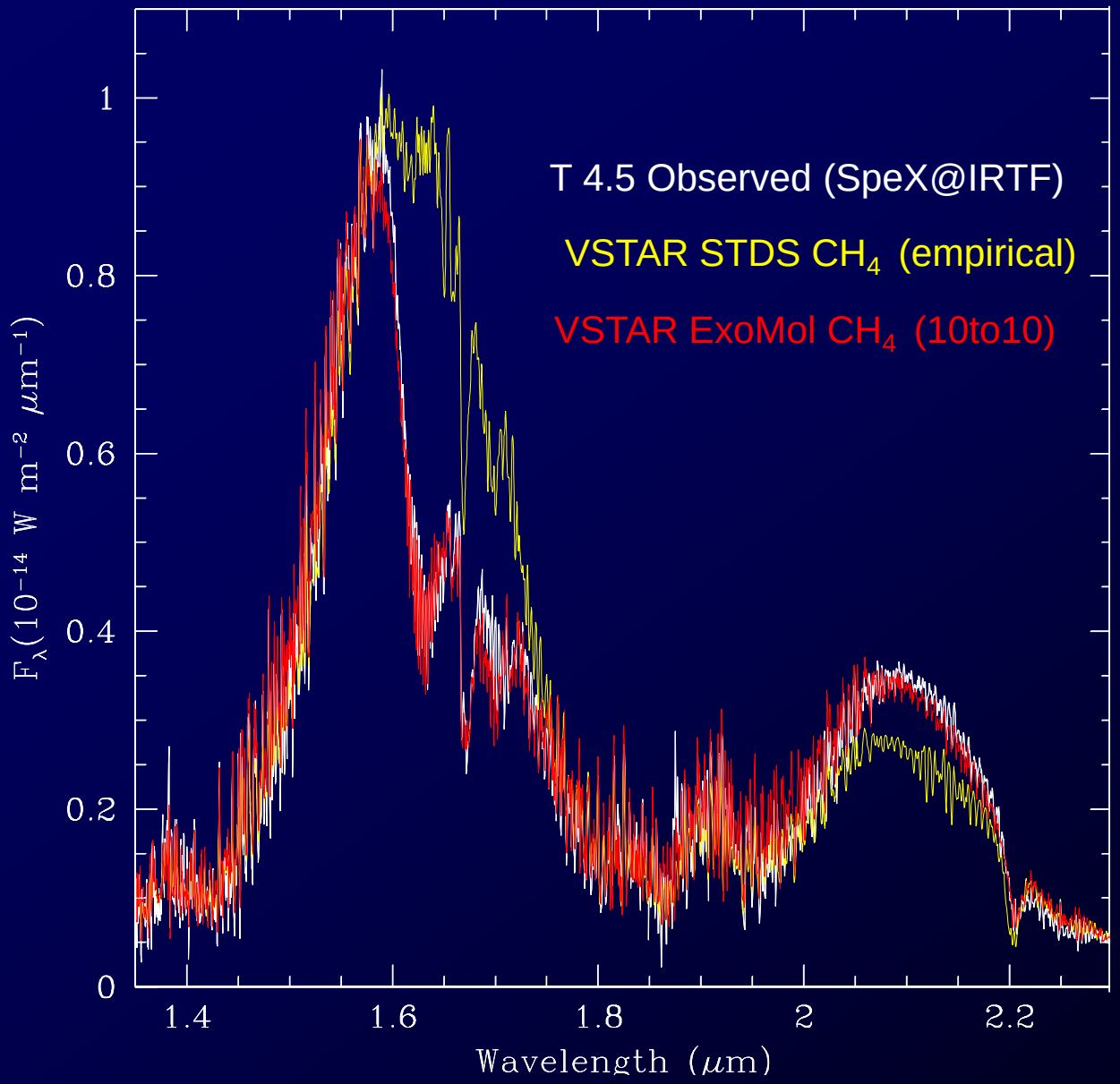



1E-17
1E-18
1E-19
1E-20
1E-21
1E-22
1E-23
1E-24
1E-25
1E-26
1E-27
1E-28
1E-29
intensity, cm/molecule
T=300K
T=1000K
T=1500K
T=2000K
0
2000
4000
6000
8000
10000
wavenumber, 1/cm


Thievin et al. 2008
T=1485K
'stick'
doppler
10to10
T=1500K
Intensity, cm/molecule
wavenumber, cm-1
1.5x10-20
1.0x10-20
5.0x10-21
0.0
5.0x10-21
1.0x10-20
1.5x10-20
2700
2800
2900
3000
3100
3200
3300
3400


colour
10to10
HITRAN
10to10
10to10
HITRAN
HITRAN
K
H
J
K
H
J
1E-18
1E-19
1E-20
1E-21
1E-22
1E-23
JHK-opacities, cm/molecule
0
500
1000
1500
2000
T, K

VSTAR spectra of the T4.5 brown dwarf: a “methane dwarf”



2MASS 0559-14

SN Yurchenko, J Tennyson, J Bailey, MDJ Hollis, G Tinetti, PNAS, 111, 9379 (2014)

Cushing ,Rayner, Vacca (2005)

ExoMol

Hot line lists

Published in MNRAS

I. BeH, MgH, CaH
II. SiO
III. HCN/HNC
IV. CH_4
V. NaCl, KCl
VI. PN
VII. PH_3
VIII. H_2CO
IX. AlO
X. NaH
XI. HNO_3
XII. CS
XIII. CaO
XIV. SO_2
XV. HOOH
XVI. H_2S
XVII. SO_3
XVIII. VO

(Virtually) Complete

XIX. $H_2{}^{18}O$, $H_2{}^{17}O$
XX. H_3^+
XXI. $H_2{}^{16}O$
XXII. NO
XXIII. TiO

- NS
- CrH

In progress

- C_3
- PH, PO, PS
- TiH
- MnH
- NaO
- SH
- AlH
- C_2H_4
- SiH
- HCCH
- SrH
- CH_3Cl
- SiH_4

Planned

- NH_3
- MgO
- NiH
- FeH

- Larger hydrocarbons

J. Tennyson et al, 327, 73, J. Mol. Spectrosc. (2016)

Updated data structure
New functionality

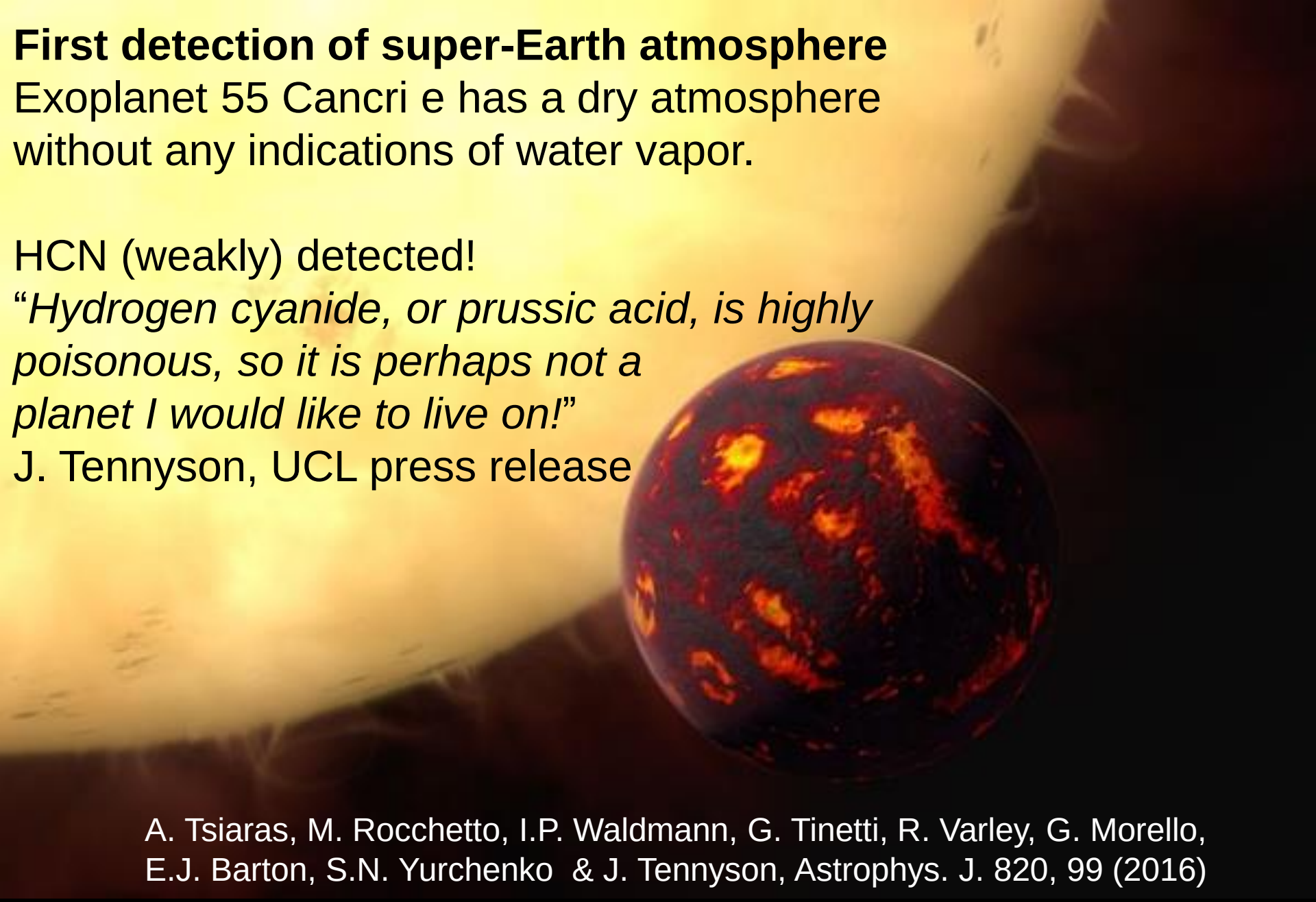
ExoMol

Other features:

1. Lifetimes (Tennyson et al, J Phys B, 49, 044002 (2016))
2. Lande g-factors (Semenov et al, J Molec Spectrosc (2016))
3. Pressure broadening (Barton et al, JQSRT (2017) + submitted)
   H_2 and He
   J and T dependence (only)
4. Dipoles for molecular control/orientation effects
   (A Yachmenev, RichMol project)

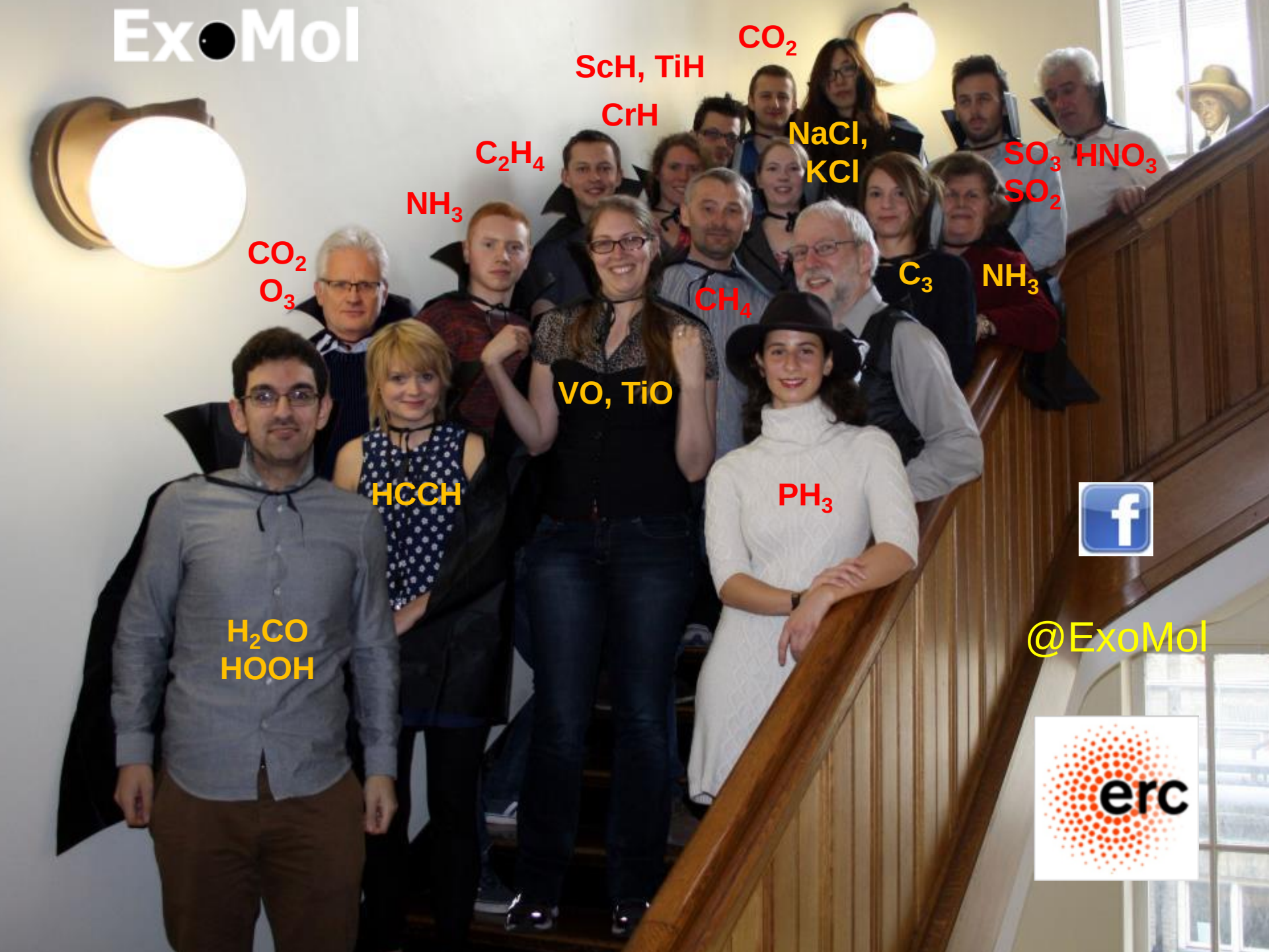
First detection of super-Earth atmosphere
Exoplanet 55 Cancri e has a dry atmosphere without any indications of water vapor.

HCN (weakly) detected!
"*Hydrogen cyanide, or prussic acid, is highly poisonous, so it is perhaps not a planet I would like to live on!*"
J. Tennyson, UCL press release

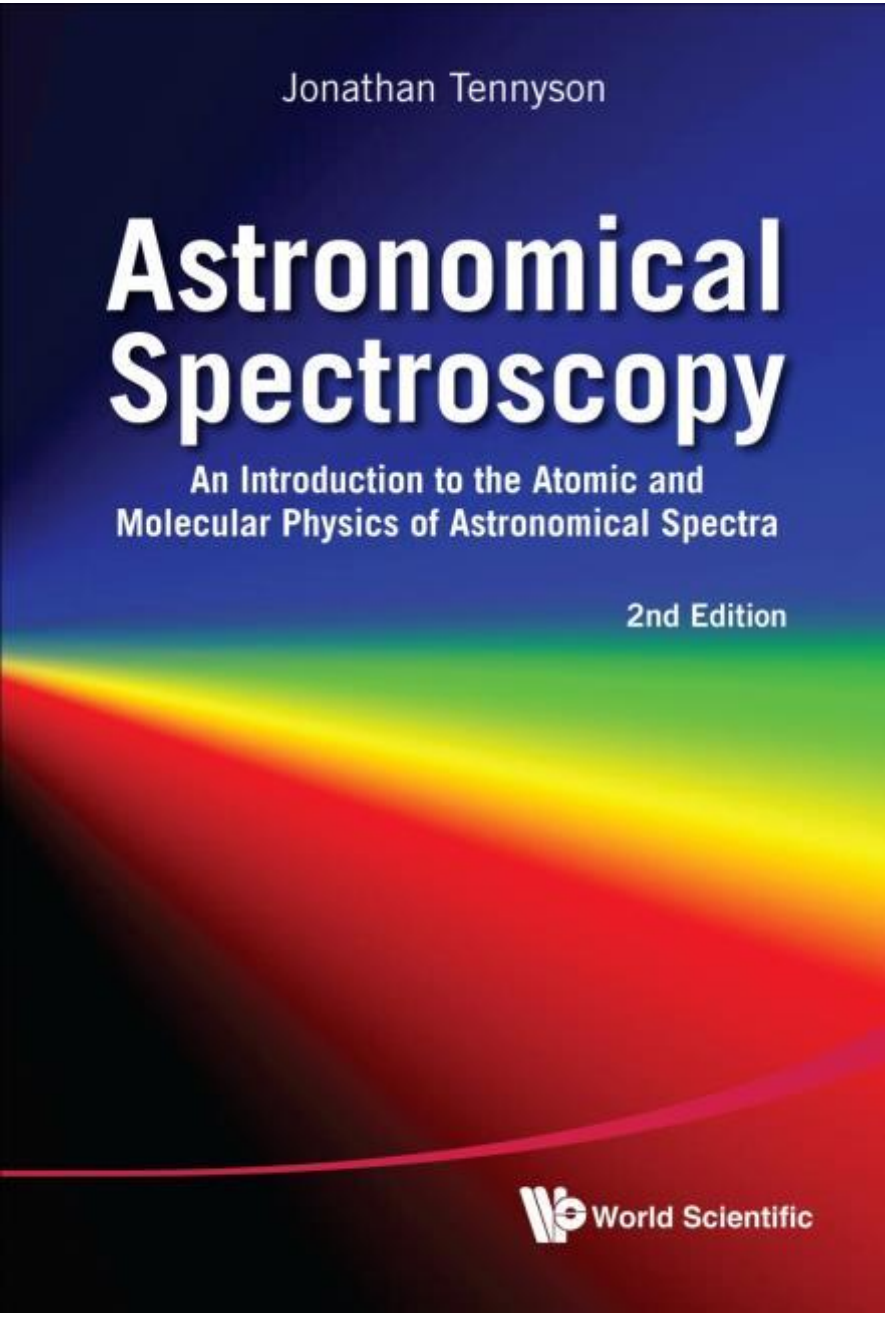


A. Tsiaras, M. Rocchetto, I.P. Waldmann, G. Tinetti, R. Varley, G. Morello, E.J. Barton, S.N. Yurchenko & J. Tennyson, Astrophys. J. 820, 99 (2016)


ExoMol
www.exomol.com
@ExoMol
erc


ExoMol
CO_2
ScH, TiH
CrH
C_2H_4
NaCl,
KCl
SO_3
HNO_3
SO_2
NH_3
CO_2
O_3
C_3
NH_3
CH_4
VO, TiO
HCCH
PH_3
H_2CO
HOOH
@ExoMol
erc


ExoMol
Emma Barton
Emil Zak
"Zoe" Na
Anatoly Pavlyuchko
Lorenzo Lodi
Maire Gorman
Andrey Yachmenev
Dan Underwood
Phillip Coles
Afaf Al-Derzi
Renia Diamantopoulou
Oleg Polyansky
Sergey Yurchenko
Laura McKemmish
Katy Chubb
Clara Sousa-Silva
Ahmed Al-Rafaie
@ExoMol
erc



www.worldscibooks.com/physics/7574.html

About the first edition
"The best book for anyone who is embarking on research in astronomical spectroscopy"
Contemporary Physics (2006)

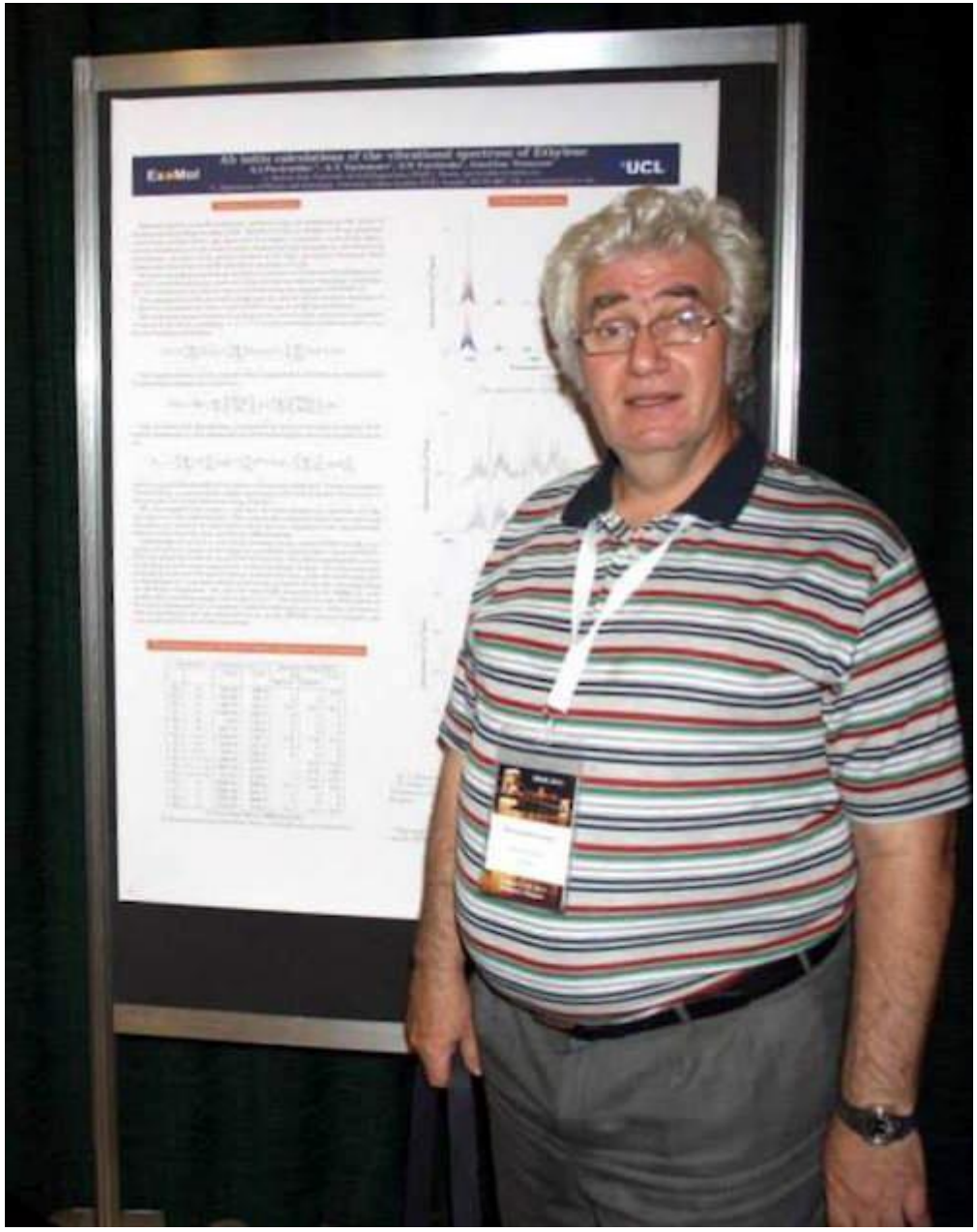
Published 2011

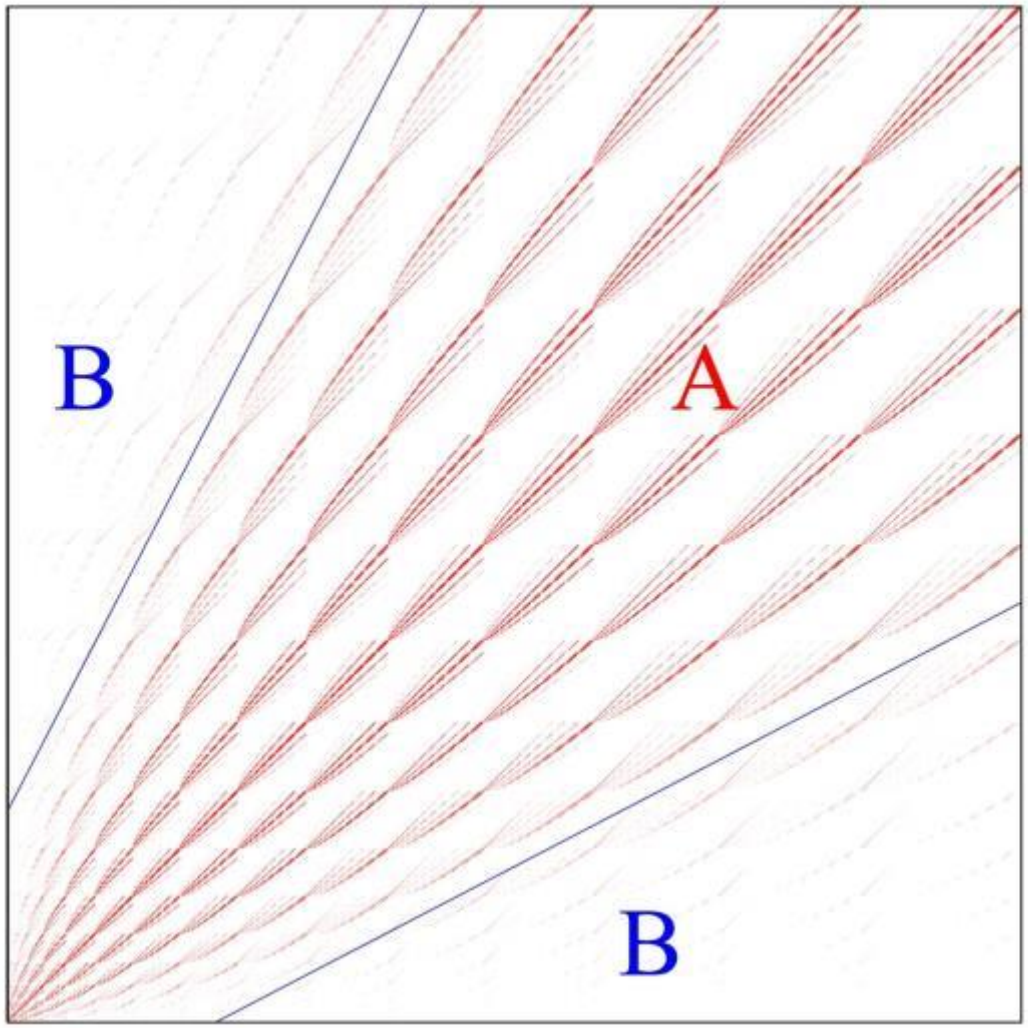
Anatoly Pavlyuchko (1956-2015)

A hybrid variational-perturbation method for calculating rovibrational energy levels of polyatomic molecules, Mol. Phys., 113, 1559 (2015)

A hybrid variational-perturbation calculation of the ro-vibrational spectrum of nitric acid, J. Chem. Phys., 142, 094309 (2015)

ExoMol molecular line lists XII: A Hot Line List for nitric acid, MNRAS, 452, 1702 (2015).

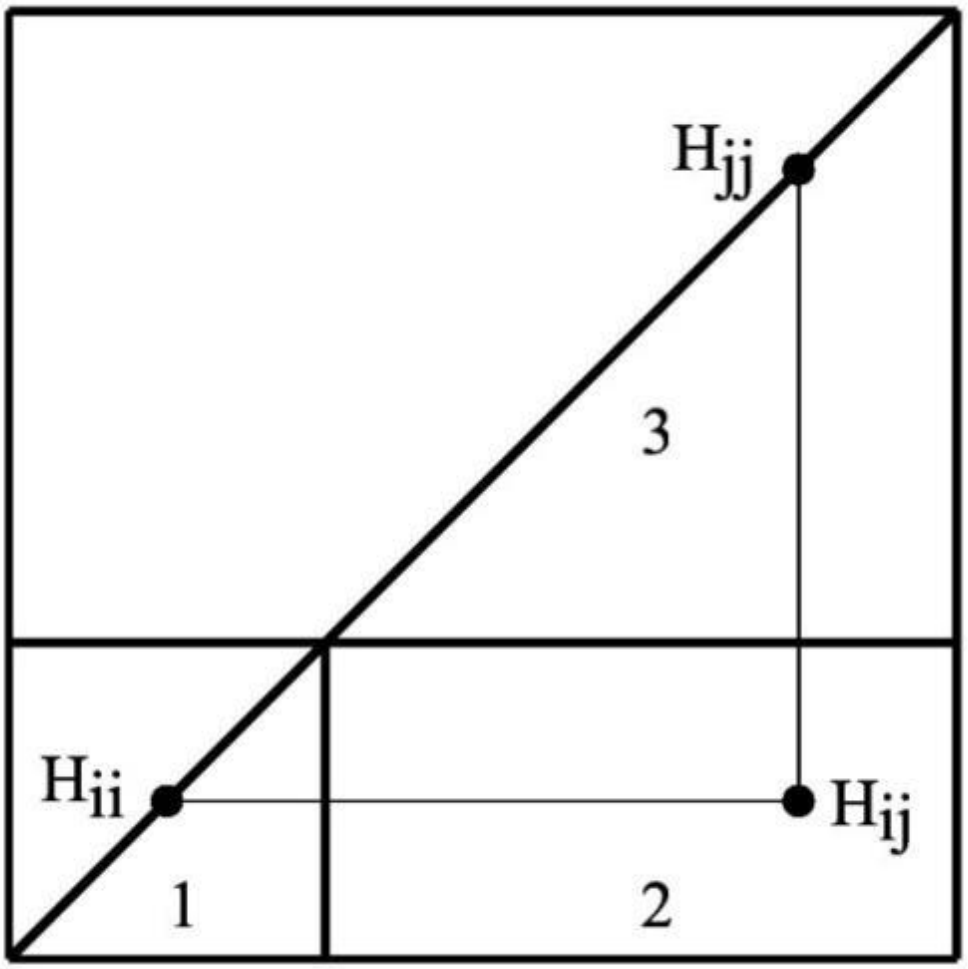




Vibrational Hamiltonian matrix:

A dense near the diagonal,

B sparse elsewhere

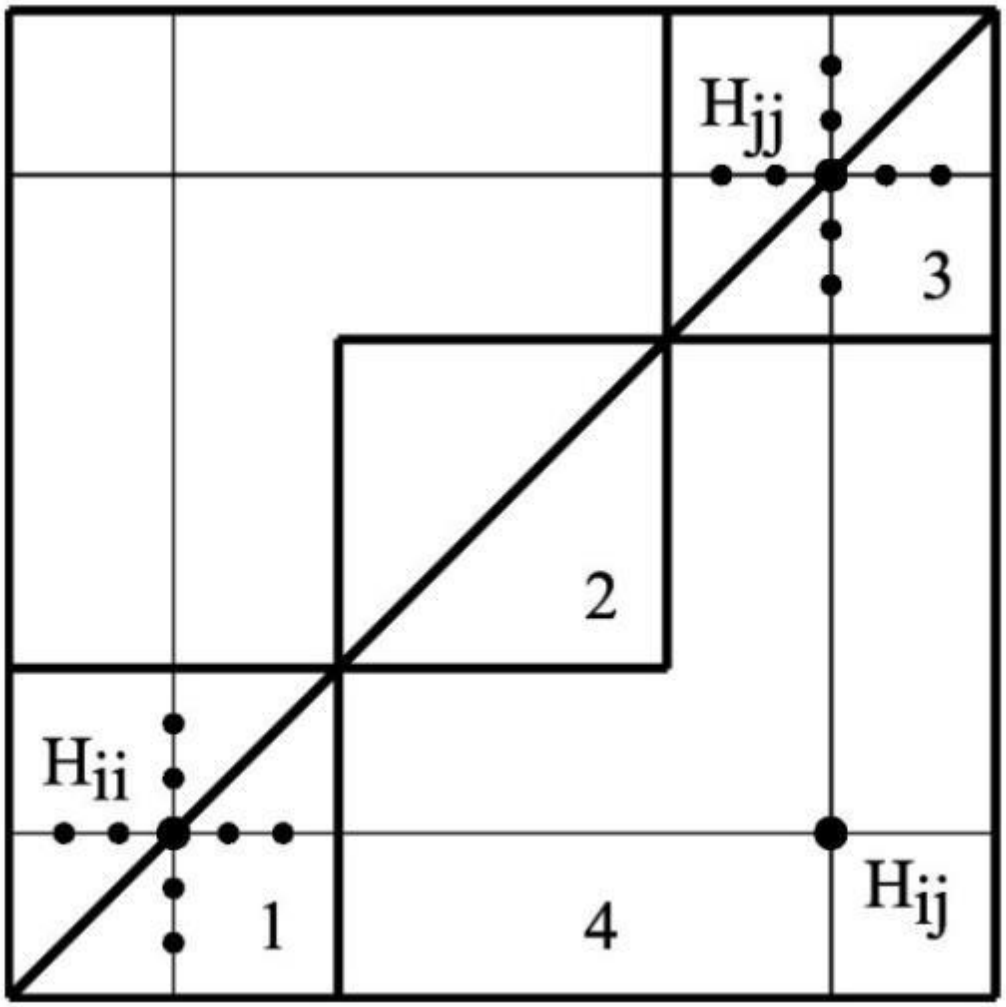


Vibrational Hamiltonian matrix:

Diagonalise region 1 only

Include effects of region 2 using perturbation theory

A.I. Pavlyuchko, S.N. Yurchenko & J. Tennyson, Mol. Phys., 113, 1559 (2015)



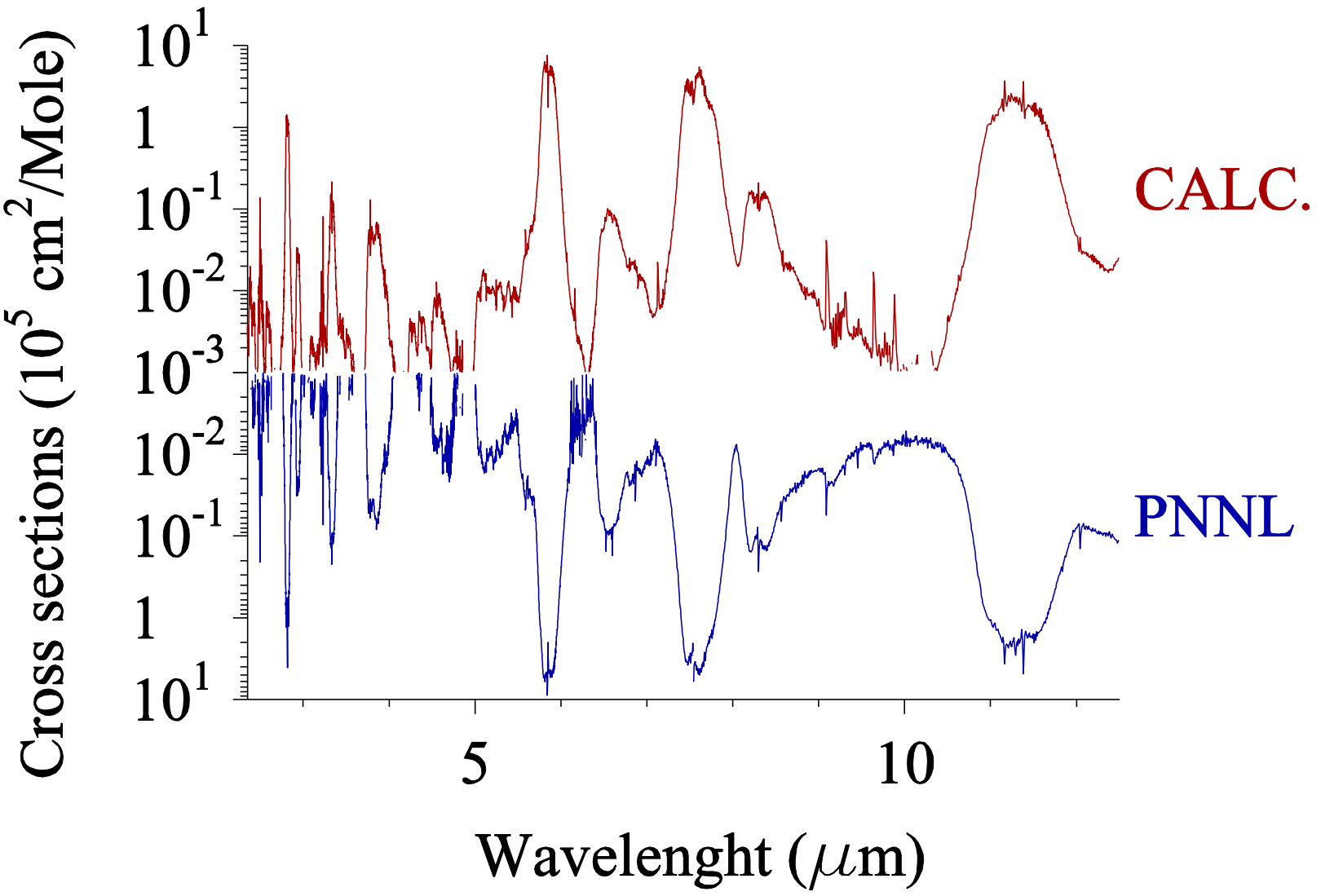
Rotation-Vibration Hamiltonian:

Treat vib state by vib state

Include Coriolis coupling via perturbation theory

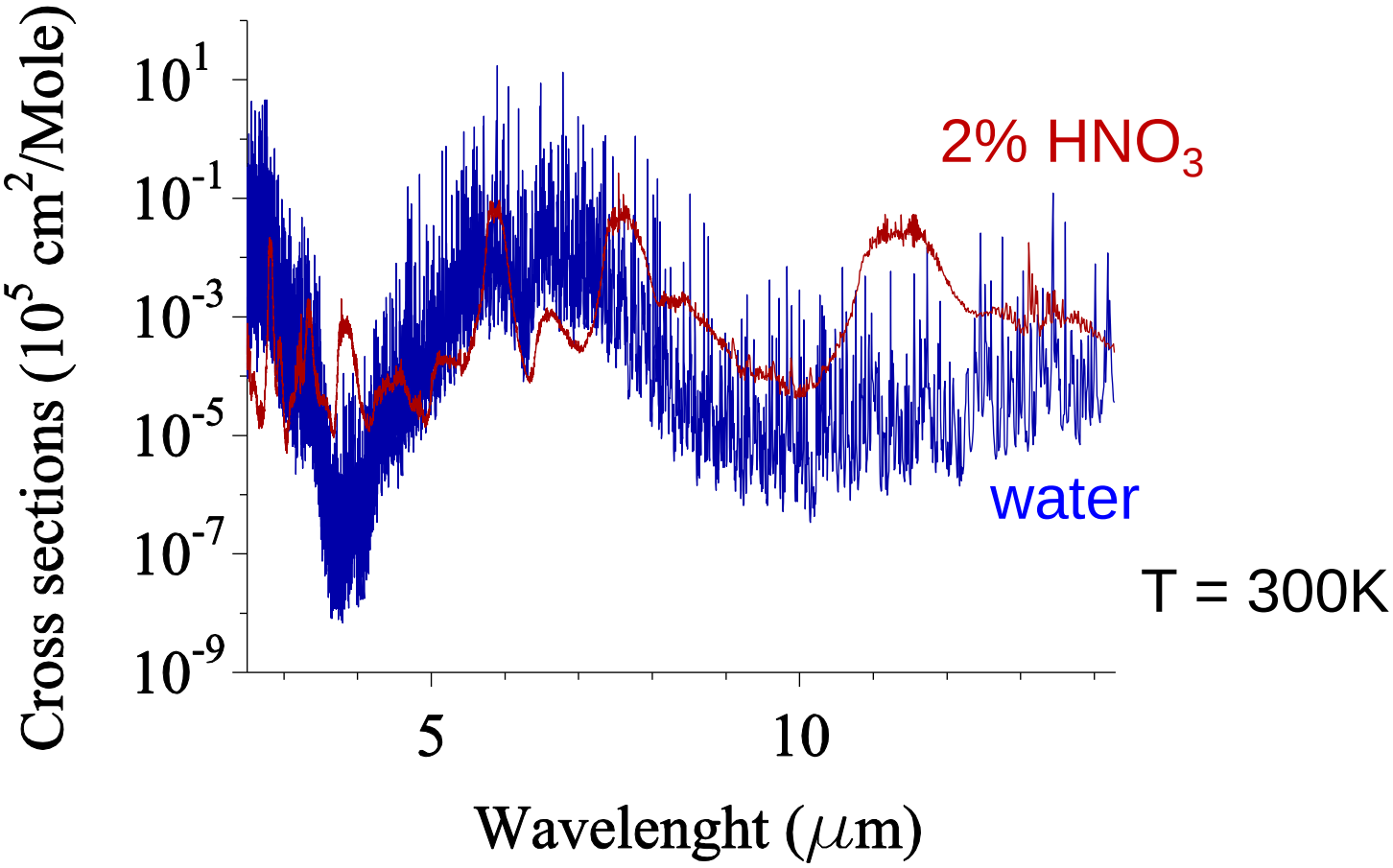
A.I. Pavlyuchko, S.N. Yurchenko & J. Tennyson, Mol. Phys., 113, 1559 (2015)

T =298 K spectrum of nitric acid (HNO_3)



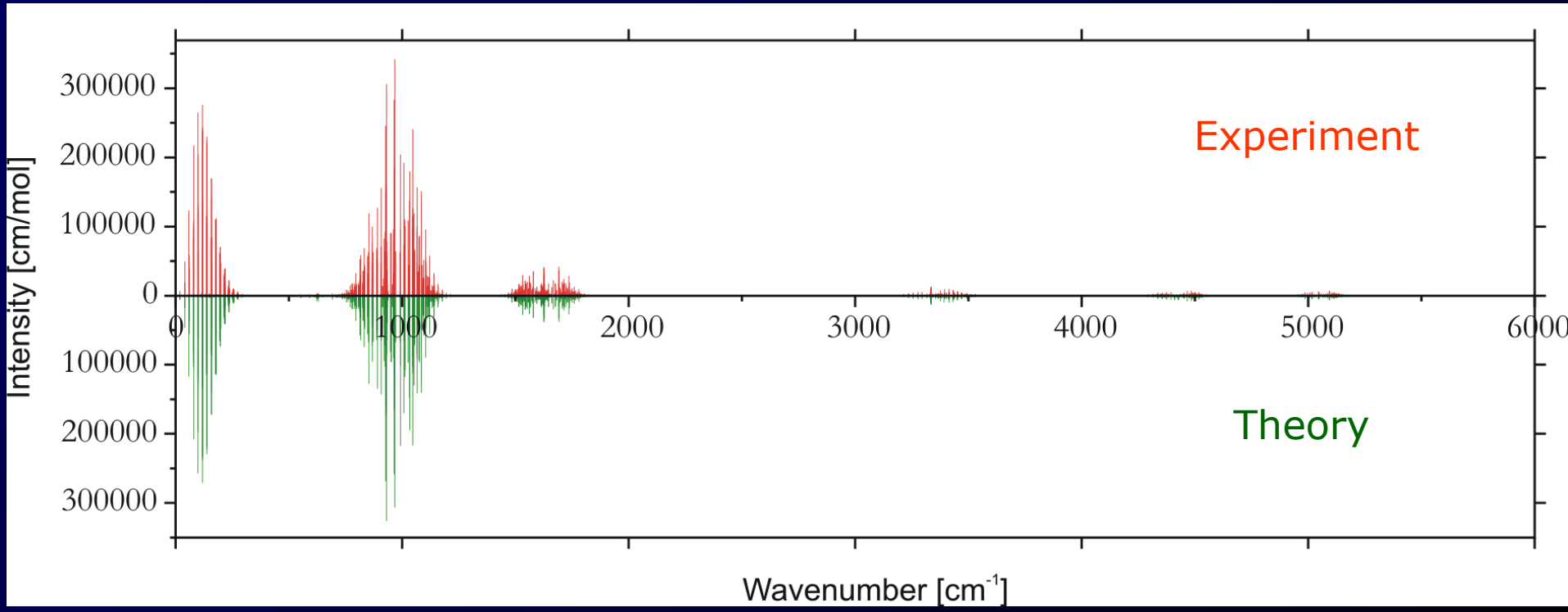
A.I. Pavlyuchko, S.N. Yurchenko & J. Tennyson, J. Chem. Phys., 42, 094309 (2015)

Nitric acid as a bio-signature?

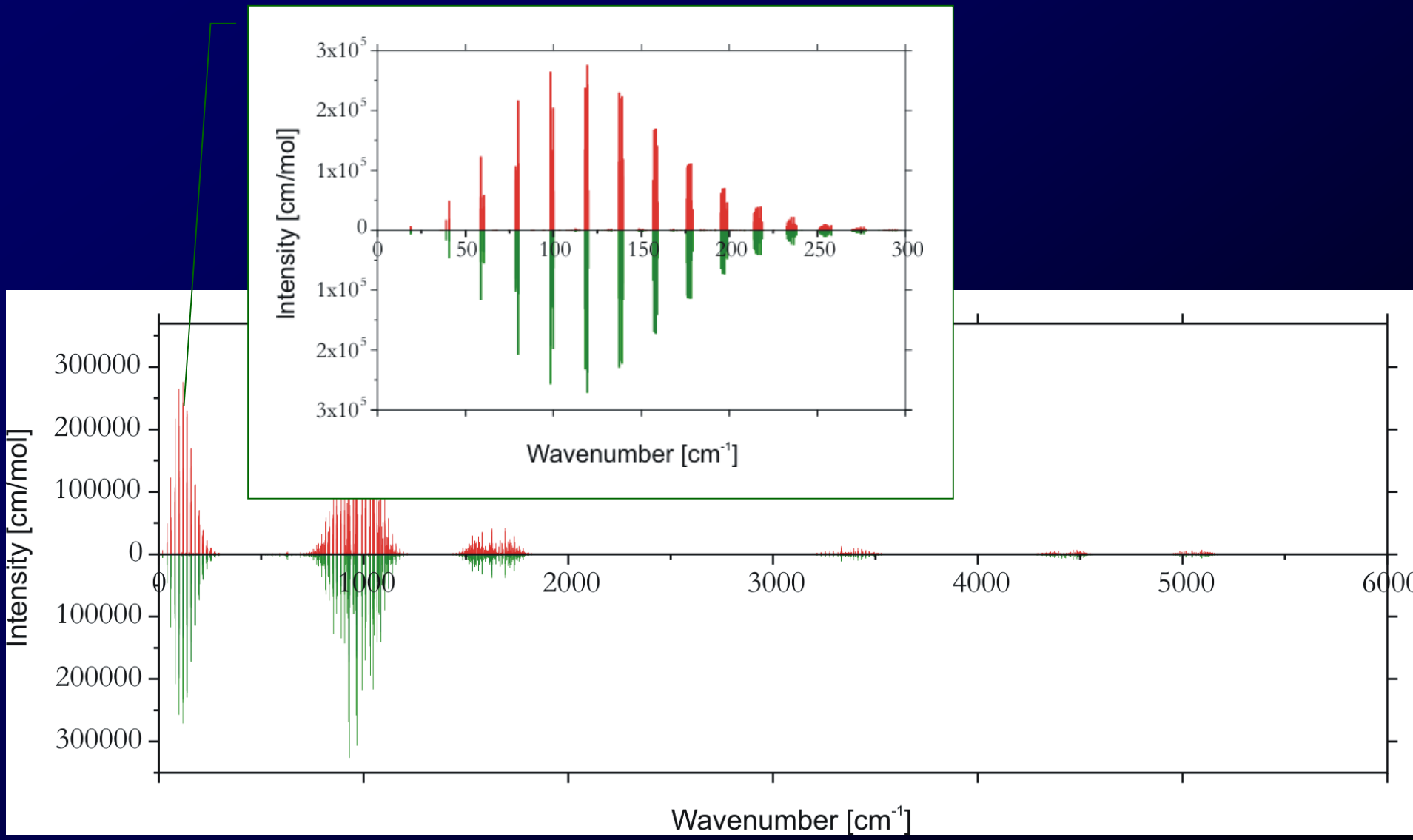


A.I. Pavlyuchko, S.N. Yurchenko & J. Tennyson, Mon. Not. R. astr. Soc., 452, 1702 (2015).

Absorption (T=300K) spectrum of NH_3: Accuracy



Absorption (T=300K) spectrum of NH_3: Accuracy



Absorption (T=300K) spectrum of NH_3: Accuracy