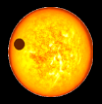


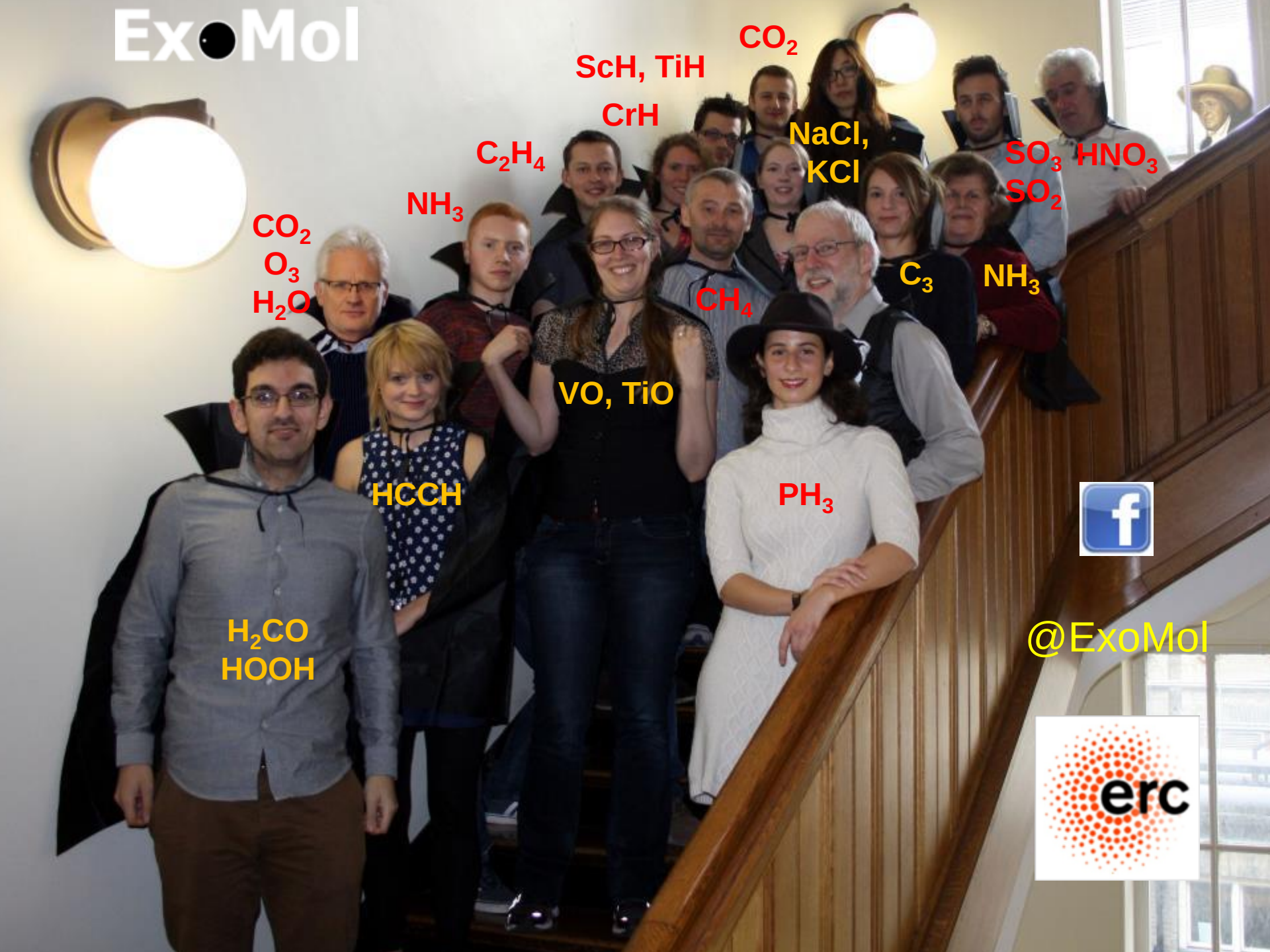
UCL

Molecular spectroscopy from first principles

Sergey Yurchenko

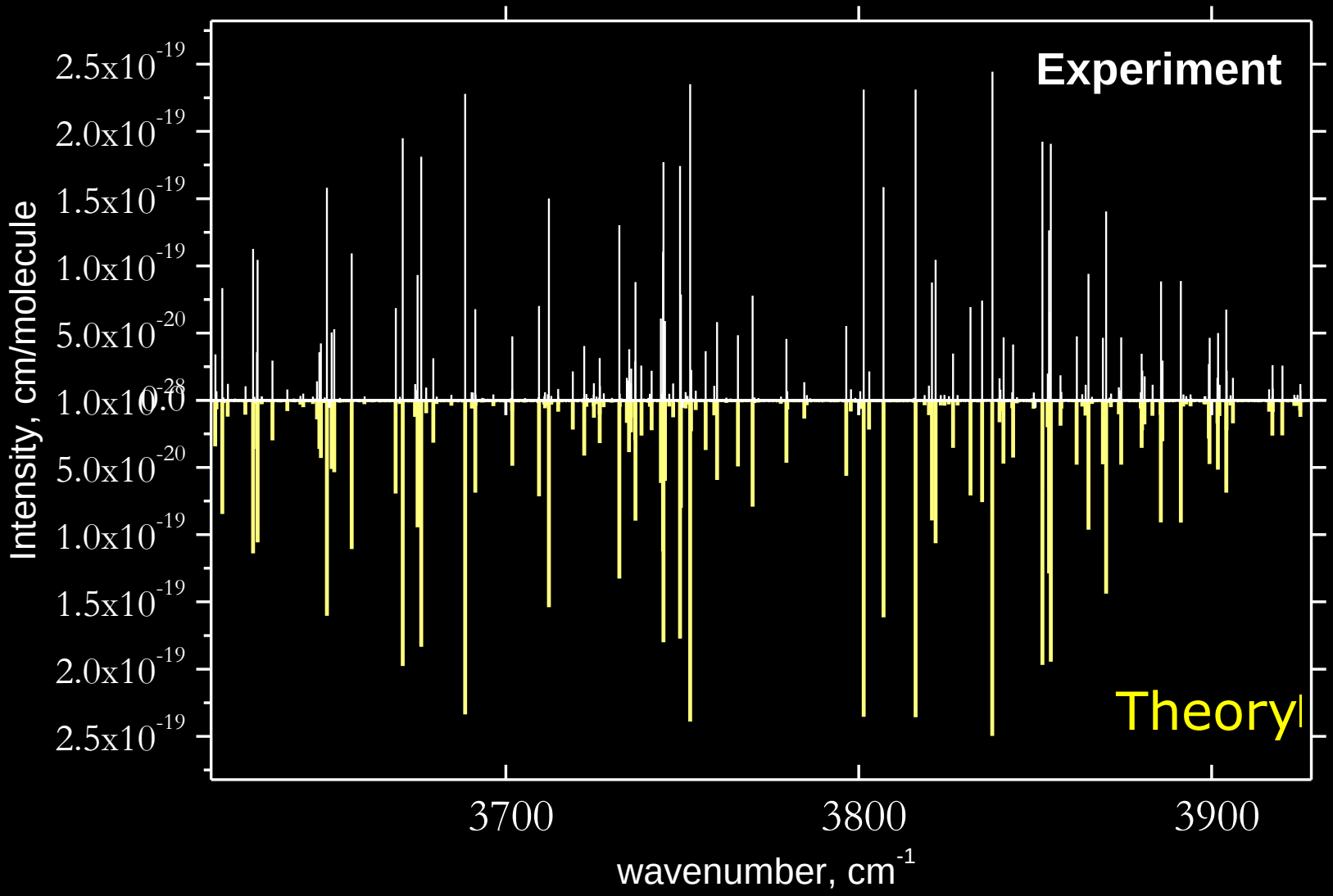

Science & Technology
Facilities Council


ExoMol
www.exomol.com
@ExoMol
erc

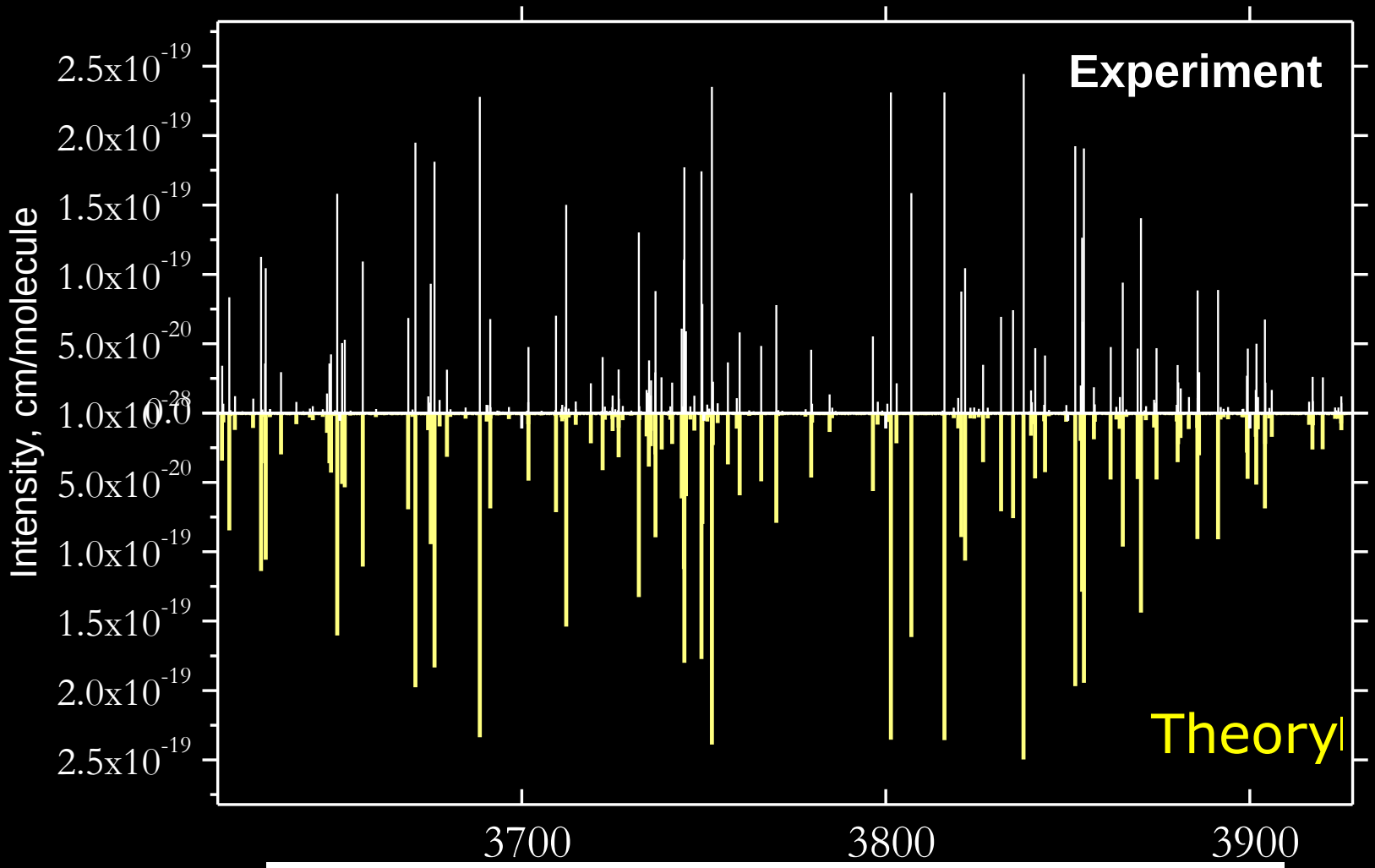

ExoMol
CO_2
ScH, TiH
CrH
C_2H_4
NaCl,
KCl
SO_3
HNO_3
SO_2
NH_3
CO_2
O_3
H_2O
C_3
NH_3
CH_4
VO, TiO
HCCH
PH_3
H_2CO
HOOH
@ExoMol
erc


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-Refaie
@ExoMol
erc

Theoretical spectroscopy



Theoretical spectroscopy



This is our 2018-line list for water

Recipe

How to make do accurate
ab intiio spectra

Electronic structure = solving Schrödinger equation for electrons

Electronic structure = solving Schrödinger equation for electrons

in the Born-Oppenheimer approximation

Really ab initio can be only microwave spectra

Accurate equilibrium structure using ab initio and vibrational corrections

This is for (almost only) pure rotational spectra of molecules, even very large molecules

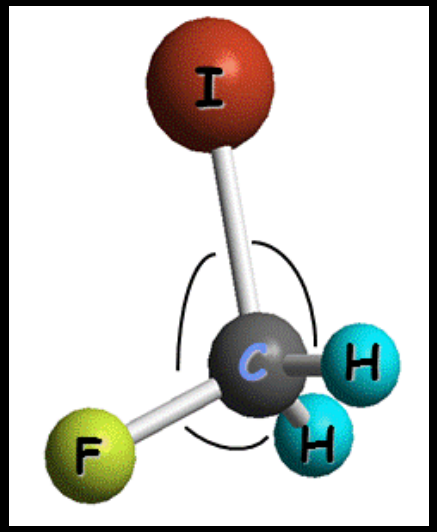
… where you start from
accurate equilibrium structure

… which provides A_e, B_e, C_e

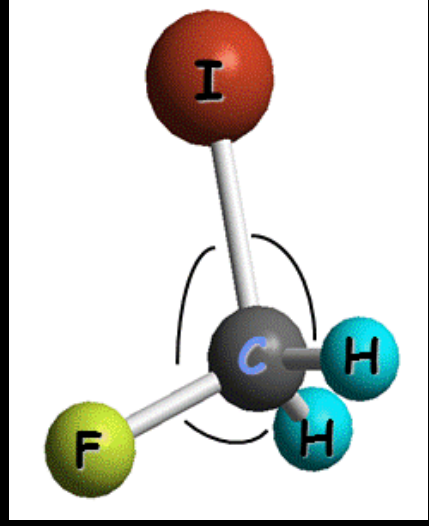
… and estimate centrifugal distortion constants α_e as vibrational corrections

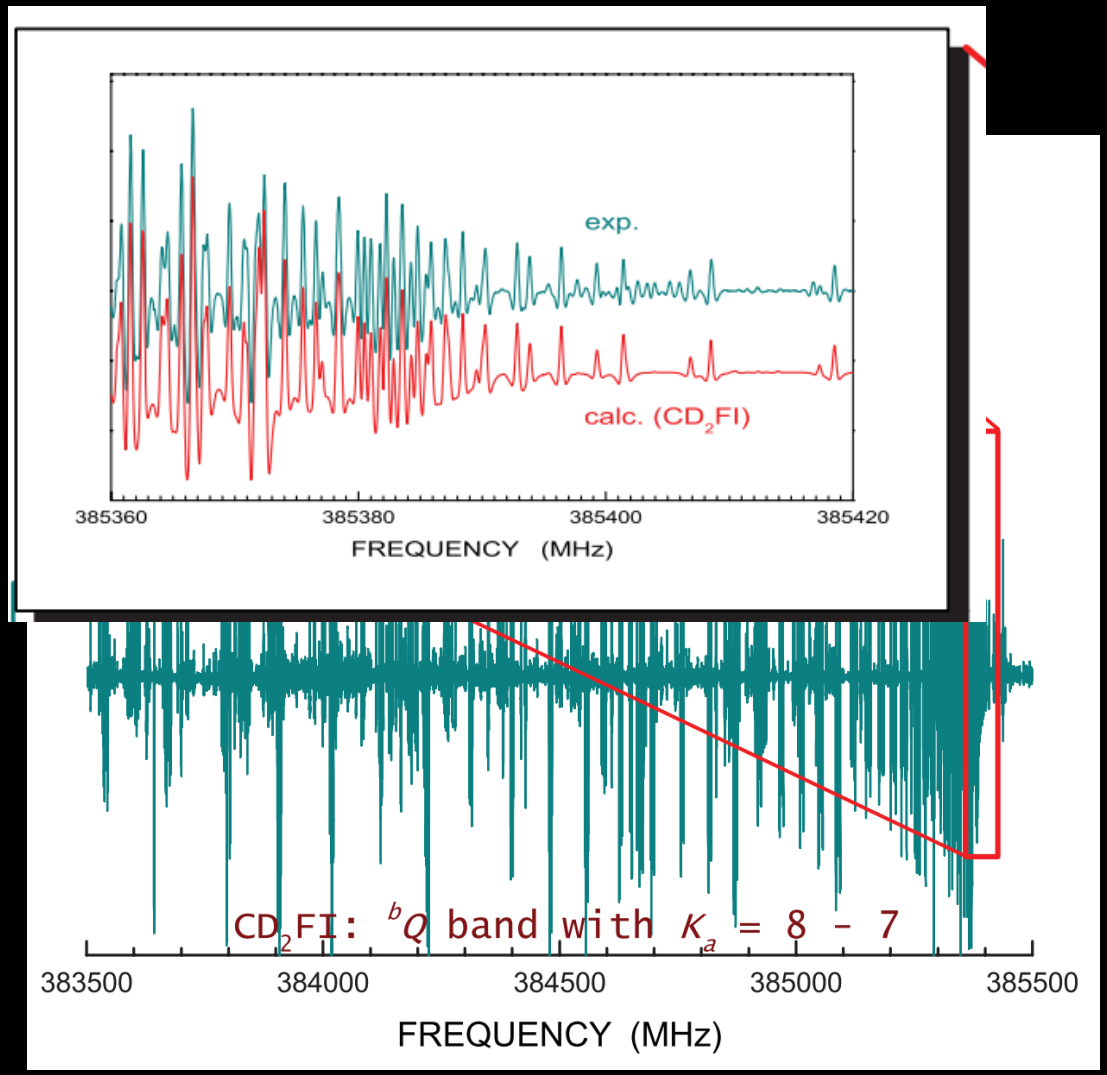
$$E_{Jv} = B_e\, J(J+1) - \alpha_e\, J(J+1)\left(v + \frac{1}{2}\right) + \cdots$$

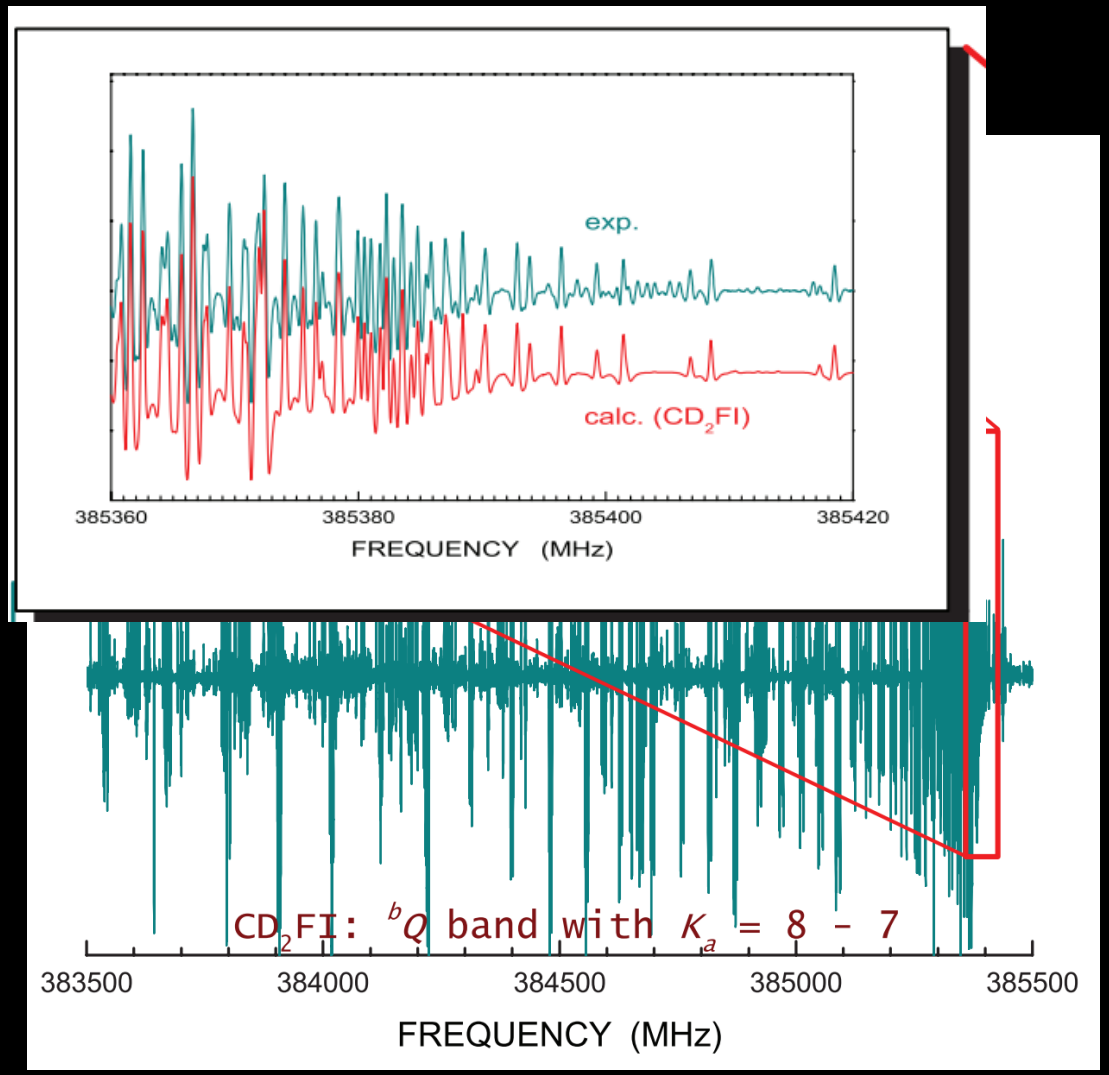
CH_2FI: Microwave spectrum

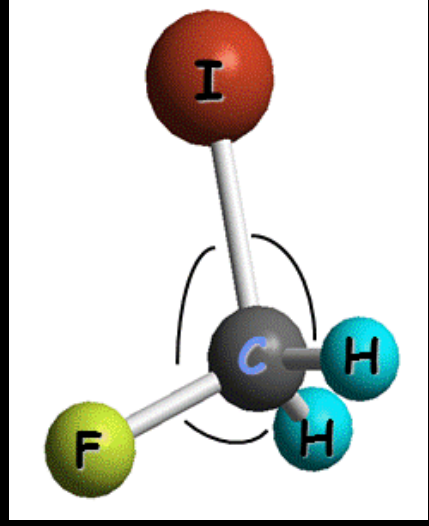


C. Puzzarini …. J. Gauss et al. J. Chem Phys. 134, 174312 (2011)


I
C
H
H
F


exp.
calc. (CD2FI)
385360
385380
385400
385420
FREQUENCY (MHz)
CD2FI: bQ band with Ka = 8 - 7
383500
384000
384500
385000
385500
FREQUENCY (MHz)





Level of ab initio theory

CCSD(T)/cc-pwCVQZ(-PP) level augmented by vibrational corrections at the MP2/cc-pVTZ(-PP) level, quartic, and sextic centrifugal-distortion constants at the MP2/cc-pVTZ(-PP) level, nuclear quadrupole-coupling constants at the SFDC-CCSD(T)/unc-ANO-RCC level, and spin-rotation constants at the MP2/unc-ANO-RCC level of theory

No cheating!

… the equilibrium structure (A,B,C) can be refined using experimental values …

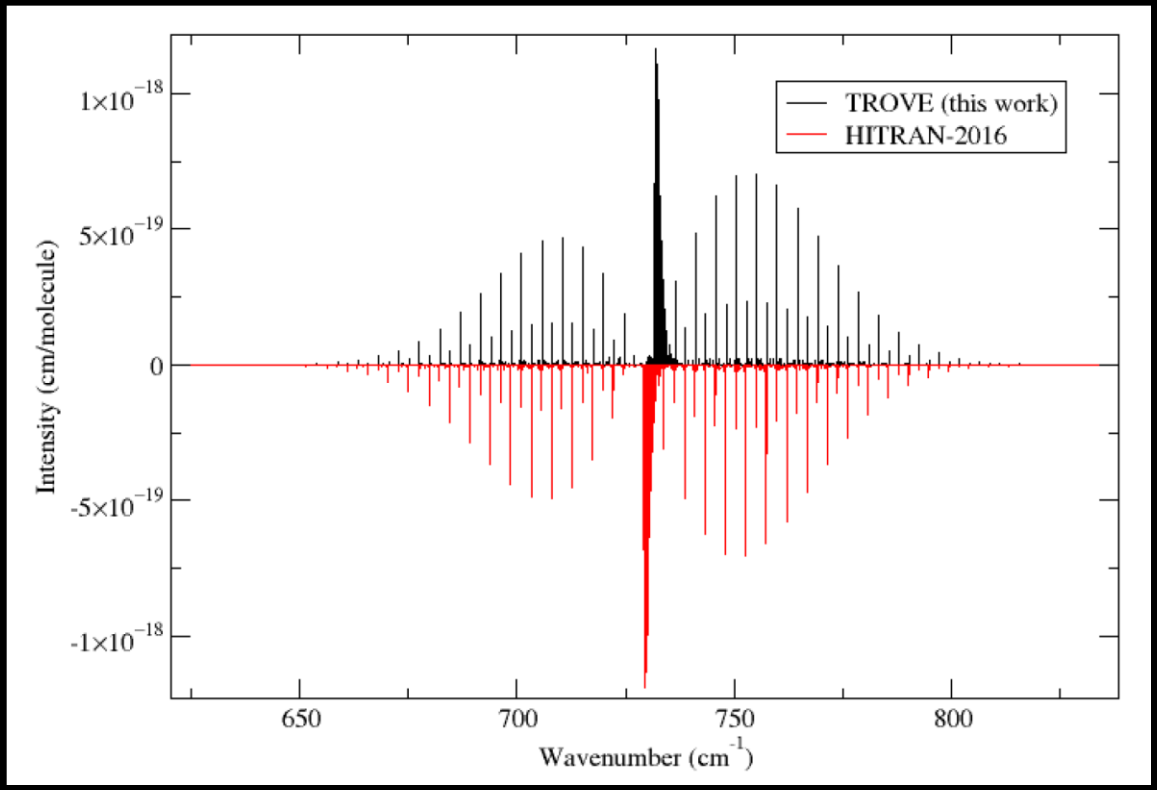
… leads to amazing quality of the ab initio rotational spectroscopy

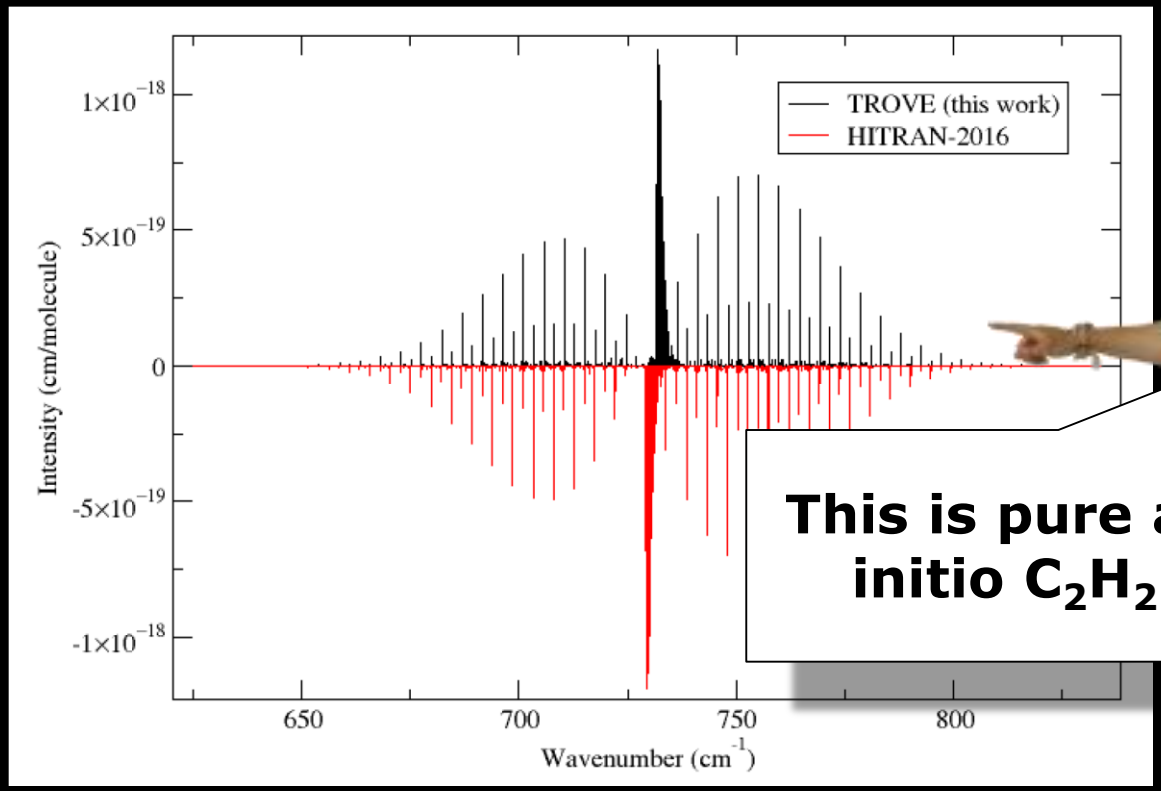
Vibrational motion however is much more complicated for ab initio methods

Qualitative description of ro-vibrational spectra by standard ab initio methods is reasonable

Qualitative description of ro-vibrational spectra by standard ab initio methods is reasonable

… but not perfect


TROVE (this work)
HITRAN-2016
1×10^-18
5×10^-19
0
-5×10^-19
-1×10^-18
Intensity (cm/molecule)
650
700
750
800
Wavenumber (cm^-1)



This is pure ab initio C_2H_2

How accurate ab initio line positions?

As accurate as ab initio PESs

Typically 1-5 cm^{-1}
for the fundamentals
using standard CCSD(T)-F12
methods

For example CH_4

THE JOURNAL OF CHEMICAL PHYSICS **145**, 104305 (2016)

A highly accurate *ab initio* potential energy surface for methane

Alec Owens,[1,2,a)] Sergei N. Yurchenko,[1] Andrey Yachmenev,[1] Jonathan Tennyson,[1] and Walter Thiel[2]

[1]*Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom*

[2]*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*

(Received 24 June 2016; accepted 24 August 2016; published online 9 September 2016)

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Mode	Sym.	Experiment	Calculated	Obs−calc
ν_4^1	F_2	1310.76	1310.24	0.52
ν_2^1	E	1533.33	1533.04	0.29
$2\nu_4^0$	A_1	2587.04	2585.74	1.30
$2\nu_4^2$	F_2	2614.26	2613.04	1.22
$2\nu_4^2$	E	2624.62	2624.08	0.54
$\nu_2^1 + \nu_4^1$	F_2	2830.32	2829.71	0.61
$\nu_2^1 + \nu_4^1$	F_1	2846.07	2845.44	0.63
ν_1	A_1	2916.48	2917.16	-0.68
ν_3^1	F_2	3019.49	3020.57	-1.08
$2\nu_2^0$	A_1	3063.65	3063.04	0.61
$2\nu_2^2$	E	3065.14	3064.53	0.61
$3\nu_4^1$	F_2	3870.49	3869.18	1.31
$3\nu_4^1$	A_1	3909.20	3907.11	2.09

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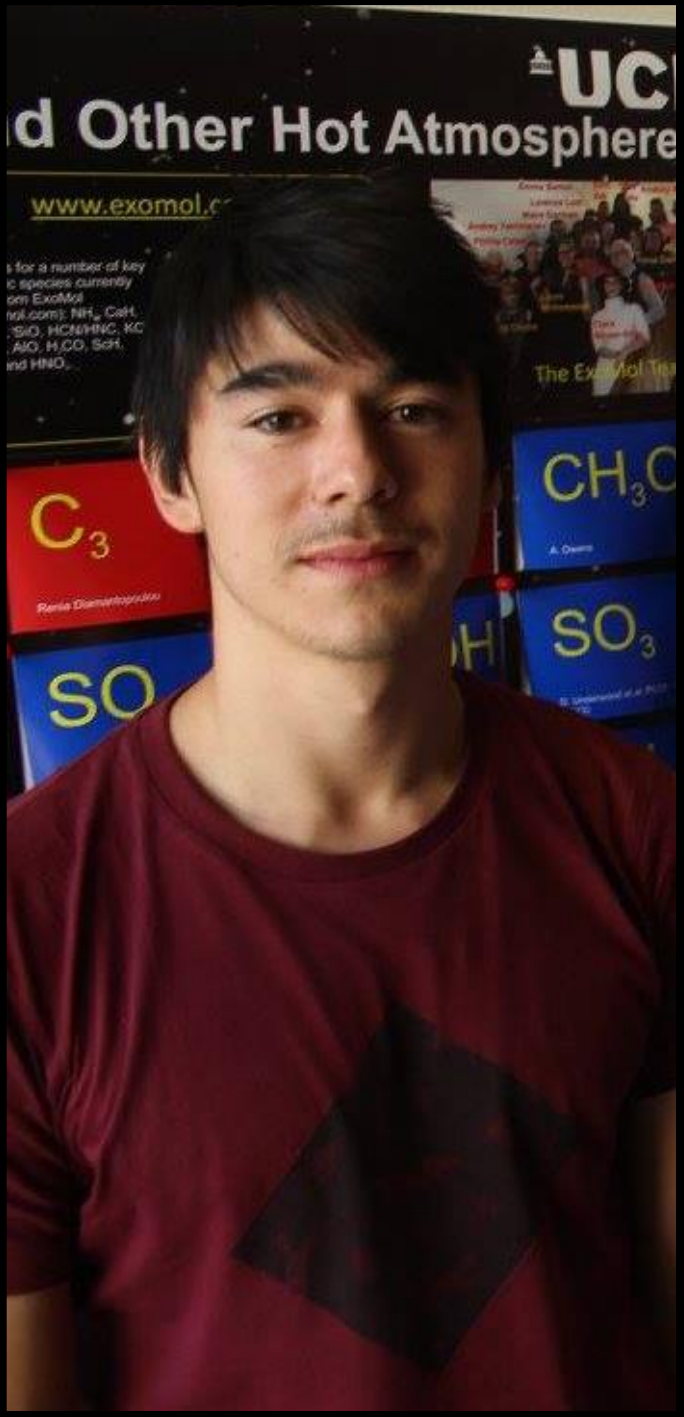
$3\nu_4^1$	A_1	3909.20	3907.11	2.09

This is still not good enough

You can do a better ab initio if
you push really hard …



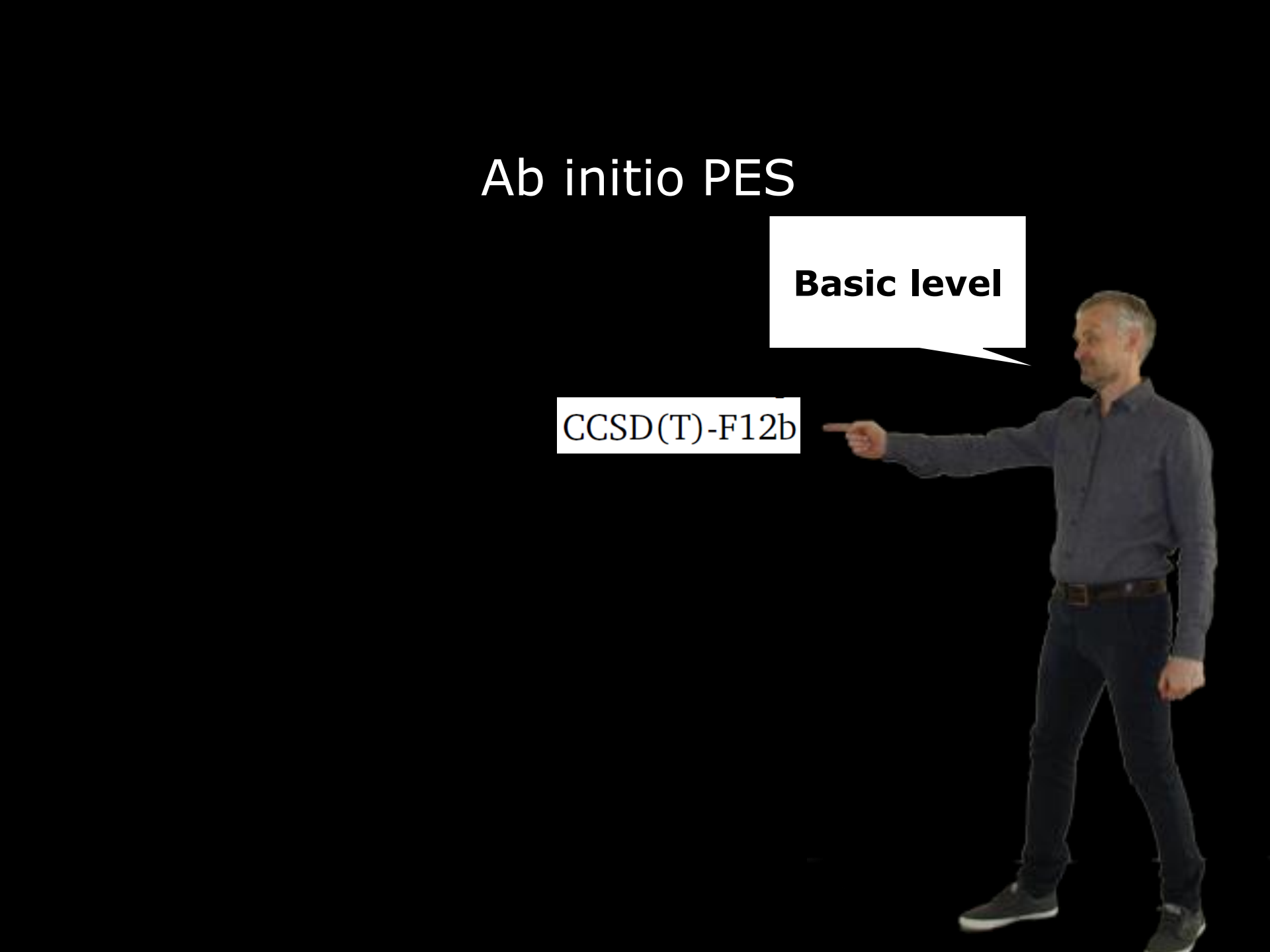
… for example pure ab initio (no cheating) spectrum of CH_3F

Ab initio PES

Ab initio PES

CCSD(T)-F12b

Ab initio PES



Ab initio PES

Basic level

CCSD(T)-F12b

Douglas-Kroll-Hess

Ab initio PES

Basic level

CCSD(T)-F12b

Douglas-Kroll-Hess

$$E_{\mathrm{tot}} = E_{\mathrm{CBS}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{HO}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{DBOC}}.$$

Ab initio PES

High Order

CCSD(T)-F12b

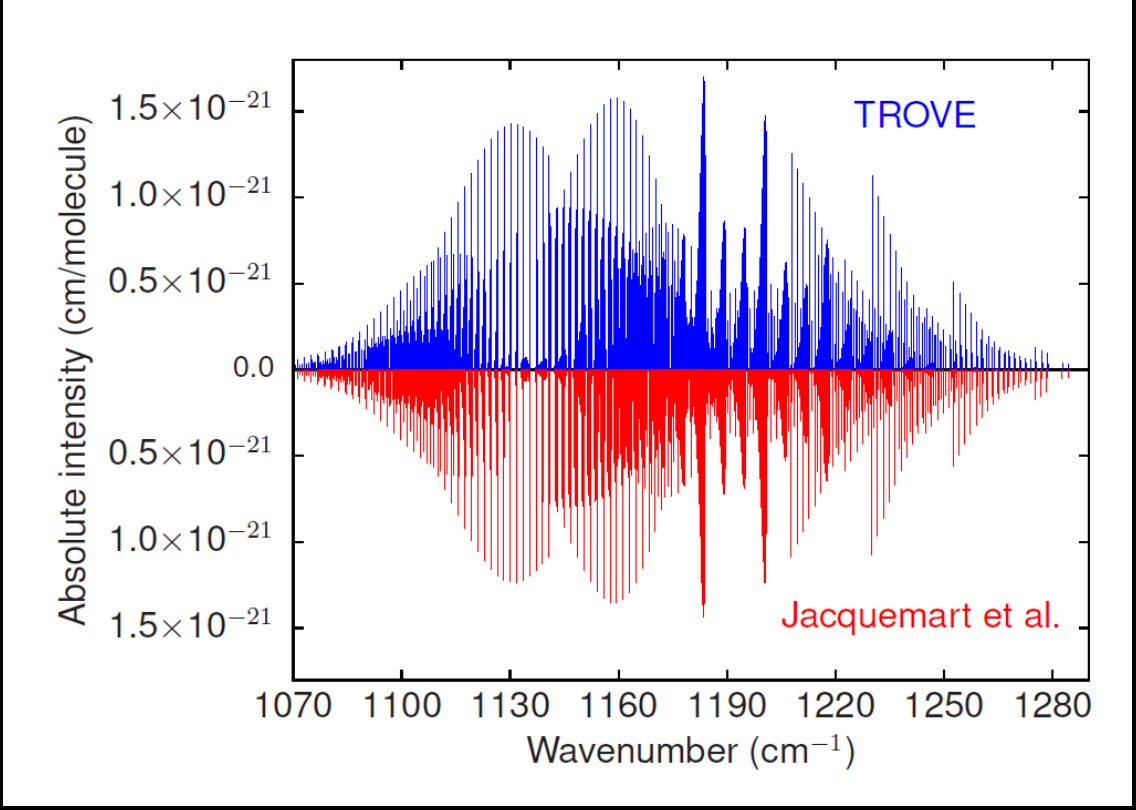
Douglas-Kroll-Hess

CCSD(T), CCSDT, and CCSDT(Q)

$$E_{\mathrm{tot}} = E_{\mathrm{CBS}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{HO}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{DBOC}}.$$

Then ab initio results can be really good

CH_3F



PCCP

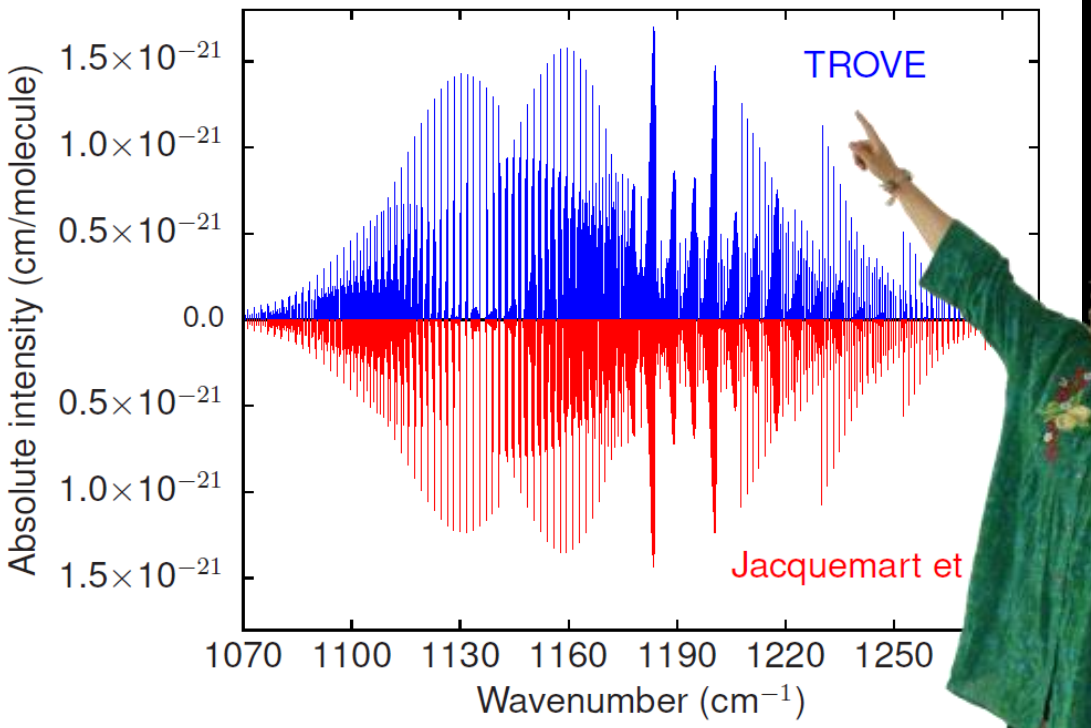
PAPER

The rotation–vibration spectrum of methyl fluoride from first principles†

Cite this: DOI: 10.1039/c8cp01721b

Alec Owens, *[ab] Andrey Yachmenev,[ab] Jochen Küpper,[abc] Sergei N. Yurchenko[d] and Walter Thiel[e]

CH_3F



Theory

PCCP

PAPER

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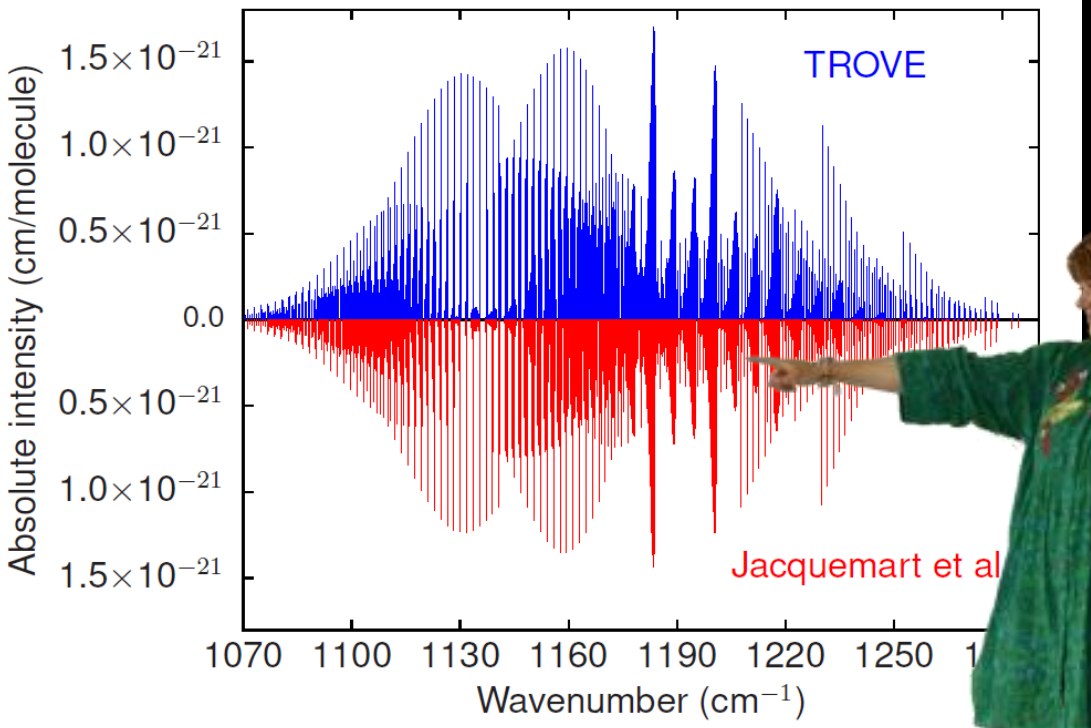
CH_3F



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DMS is also ab initio

DMS is also ab initio

CCSD(T)-F12b/aug-cc-pVTZ

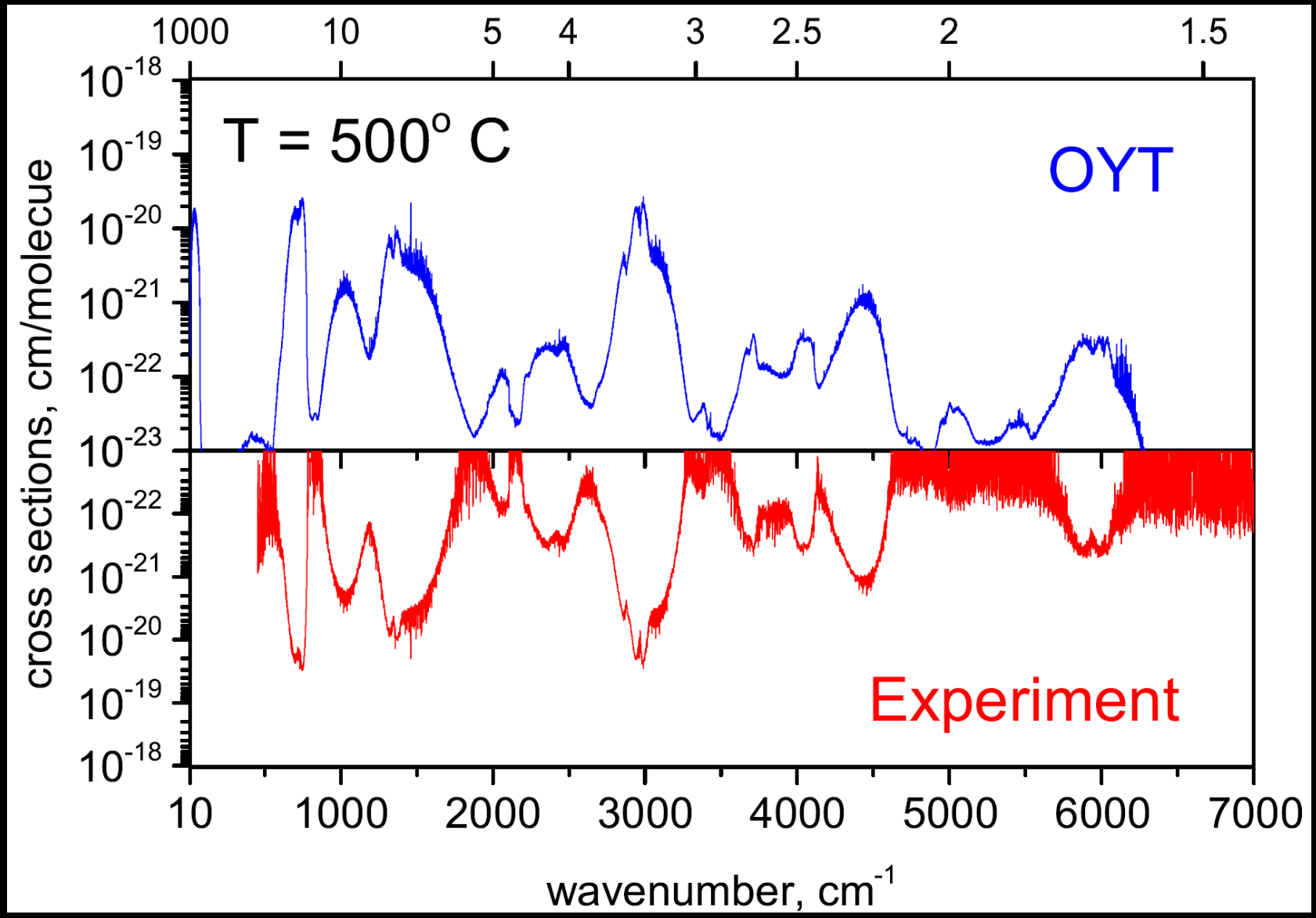
In fact intensities are (almost)
always ab initio!

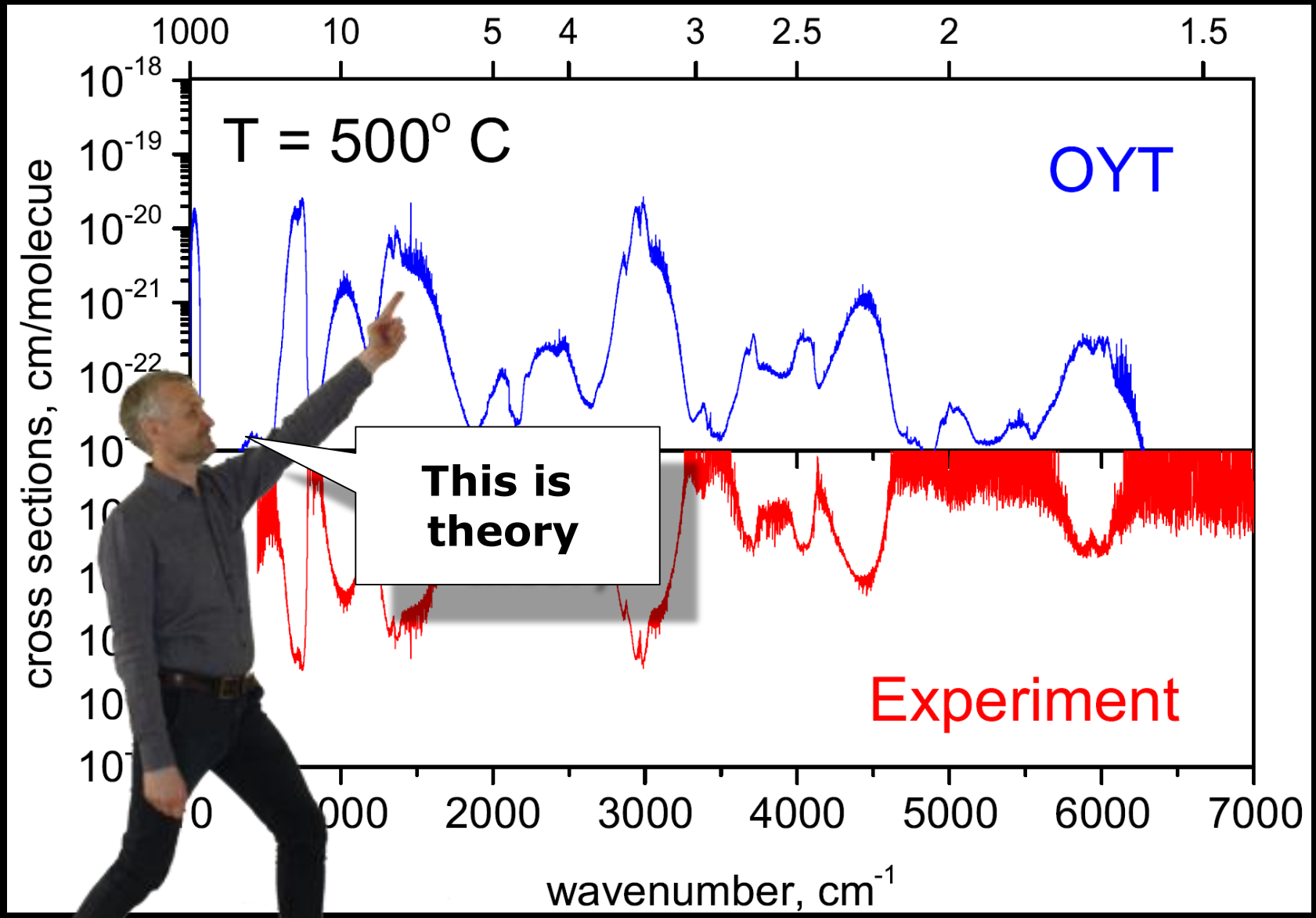
Accuracy of 10-20% is common for a reasonable level of theory

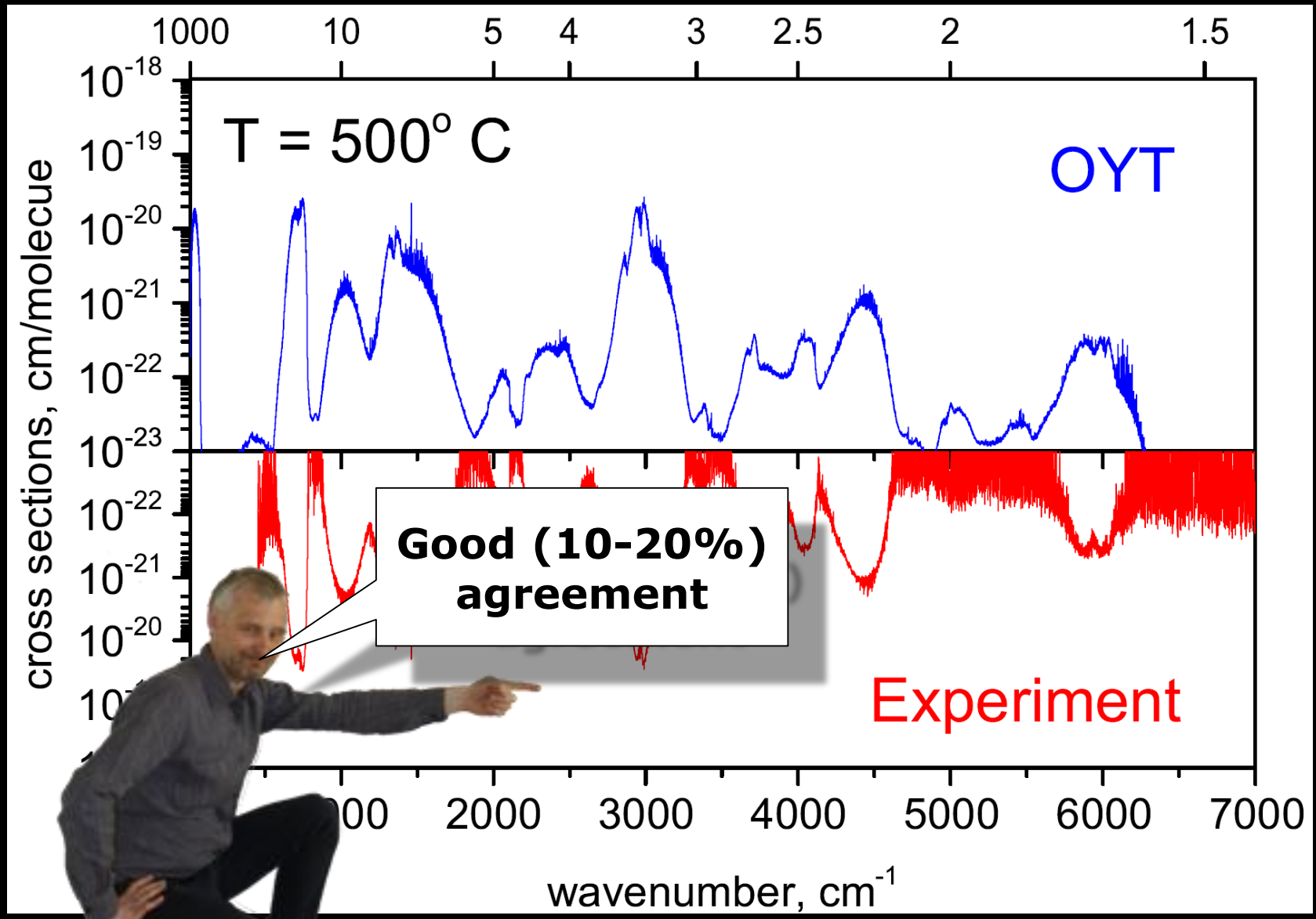
Ab initio dipole with the standard level of theory CCSD(T)/aug-cc-pVQZ

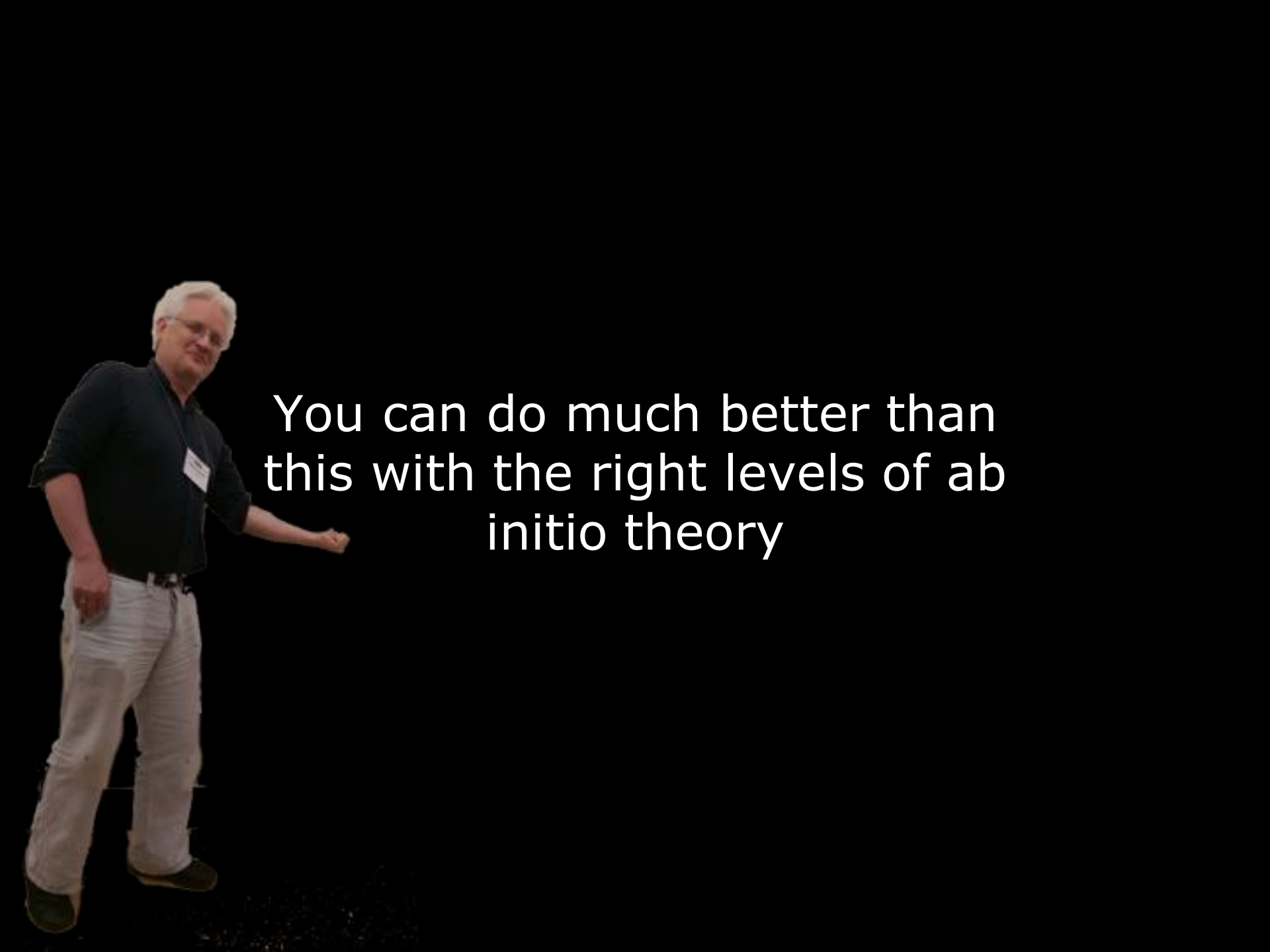
Comparing to high temperature experiments

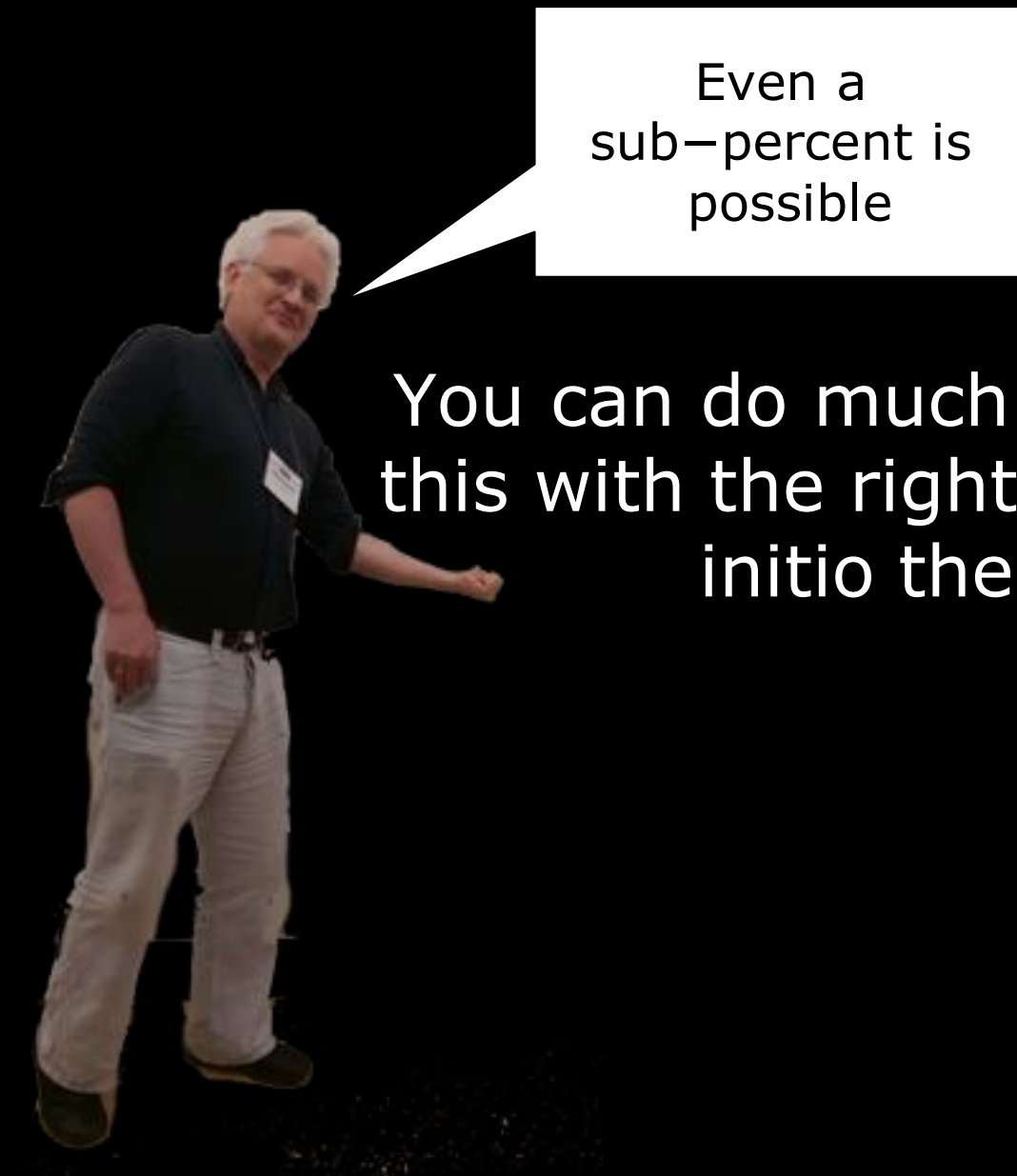
$T = 500^{o}C$


1000
10
5
4
3
2.5
2
1.5
T = 500° C
OYT
Experiment
cross sections, cm/molecue
wavenumber, cm-1
10-18
10-19
10-20
10-21
10-22
10-23
10
1000
2000
3000
4000
5000
6000
7000


1000
10
5
4
3
2.5
2
1.5
T = 500° C
OYT
This is theory
Experiment
cross sections, cm/molecue
wavenumber, cm-1
2000
3000
4000
5000
6000
7000

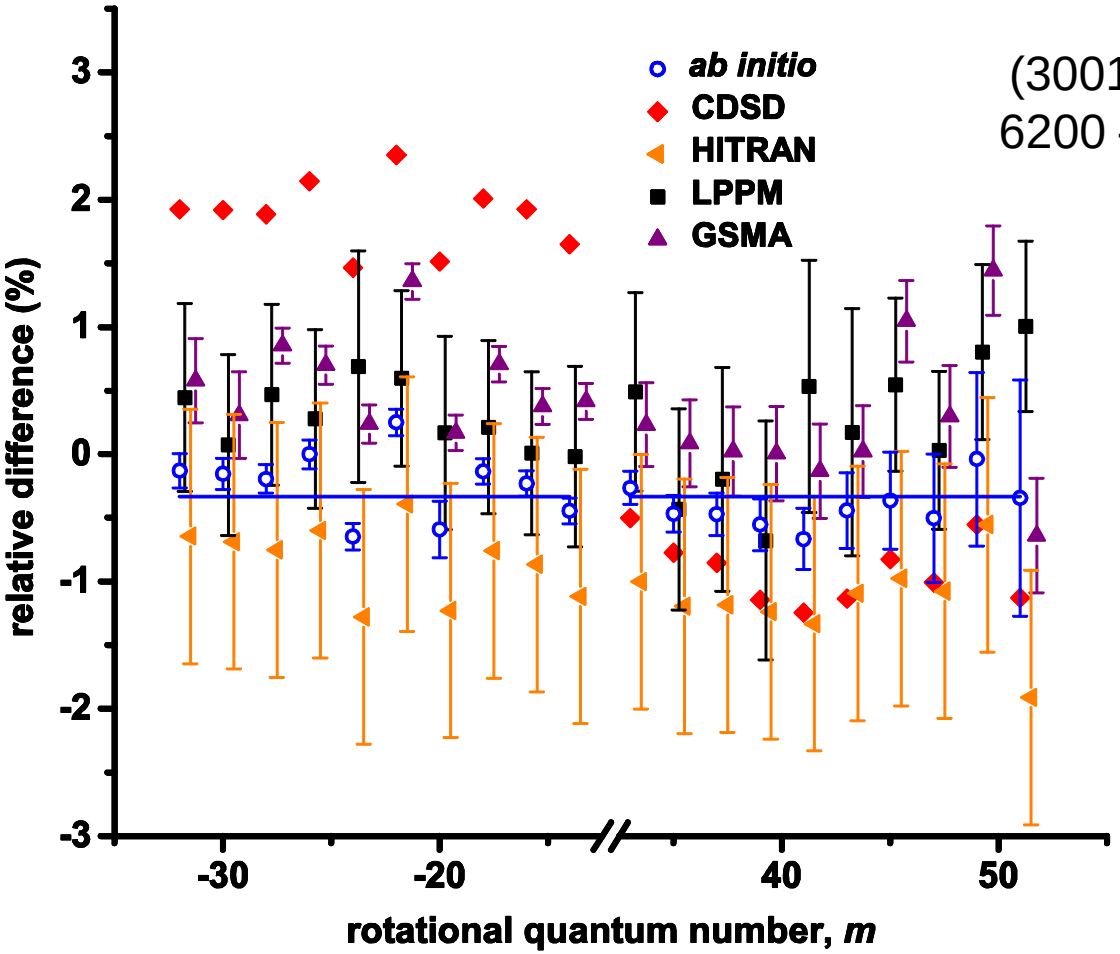

1000
10
5
4
3
2.5
2
1.5
T = 500° C
OYT
Experiment
Good (10-20%) agreement
cross sections, cm/molecue
wavenumber, cm-1
2000
3000
4000
5000
6000
7000


You can do much better than this with the right levels of ab initio theory



You can do much better than this with the right levels of ab initio theory

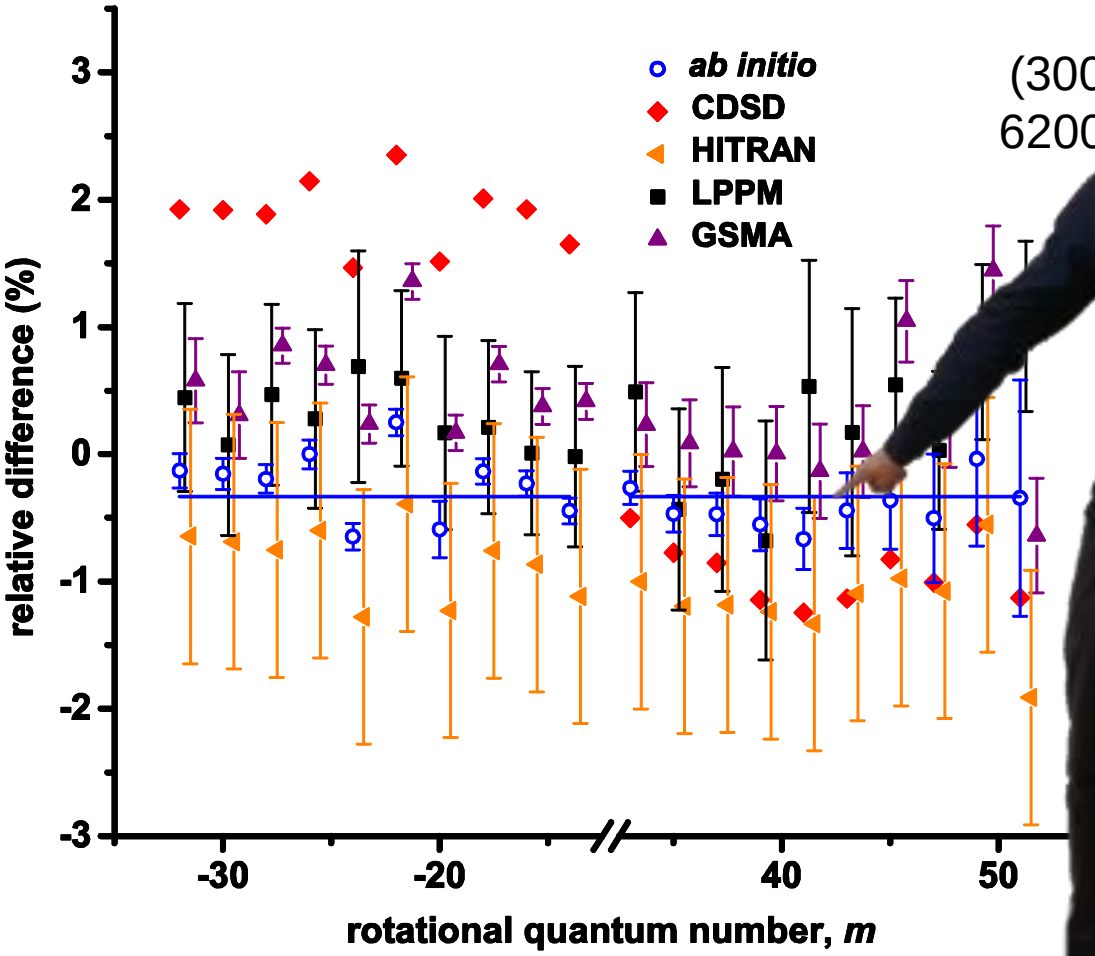
Example:
Carbon dioxide intensities
from Polyansky, Tennyson,
Zak and CO_2-mpany



(30013 – 00001)
6200 – 6258 cm^{-1}

:

OL Polyansky eta al Phys Rev Letts 114, 243001 (2015)

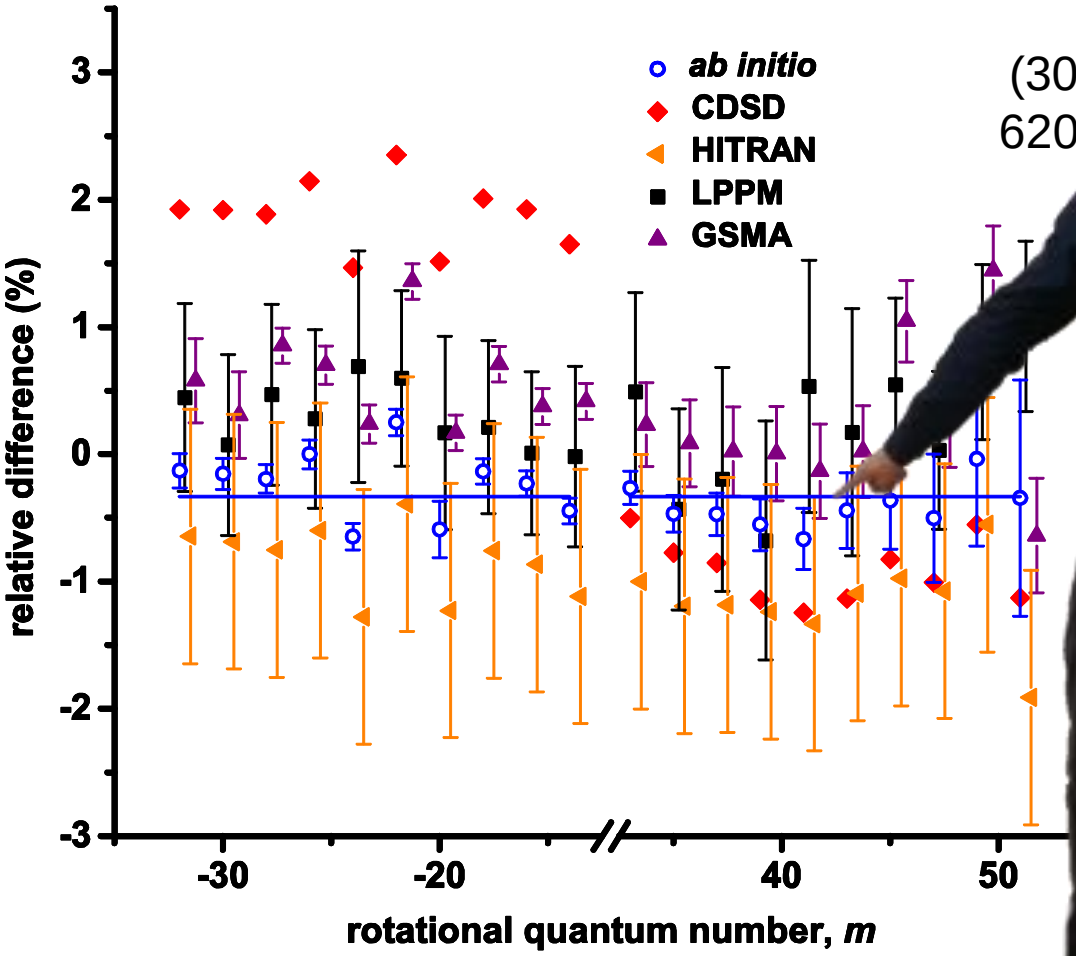


(30013 – 001)
6200 – 6 cm^{-1}

Blue is ab initio intensiies

:

OL Polyansky eta al Phys Rev Letts 114, 243001 (2015)



(30013 – 00 1)
6200 – 6 cm^{-1}

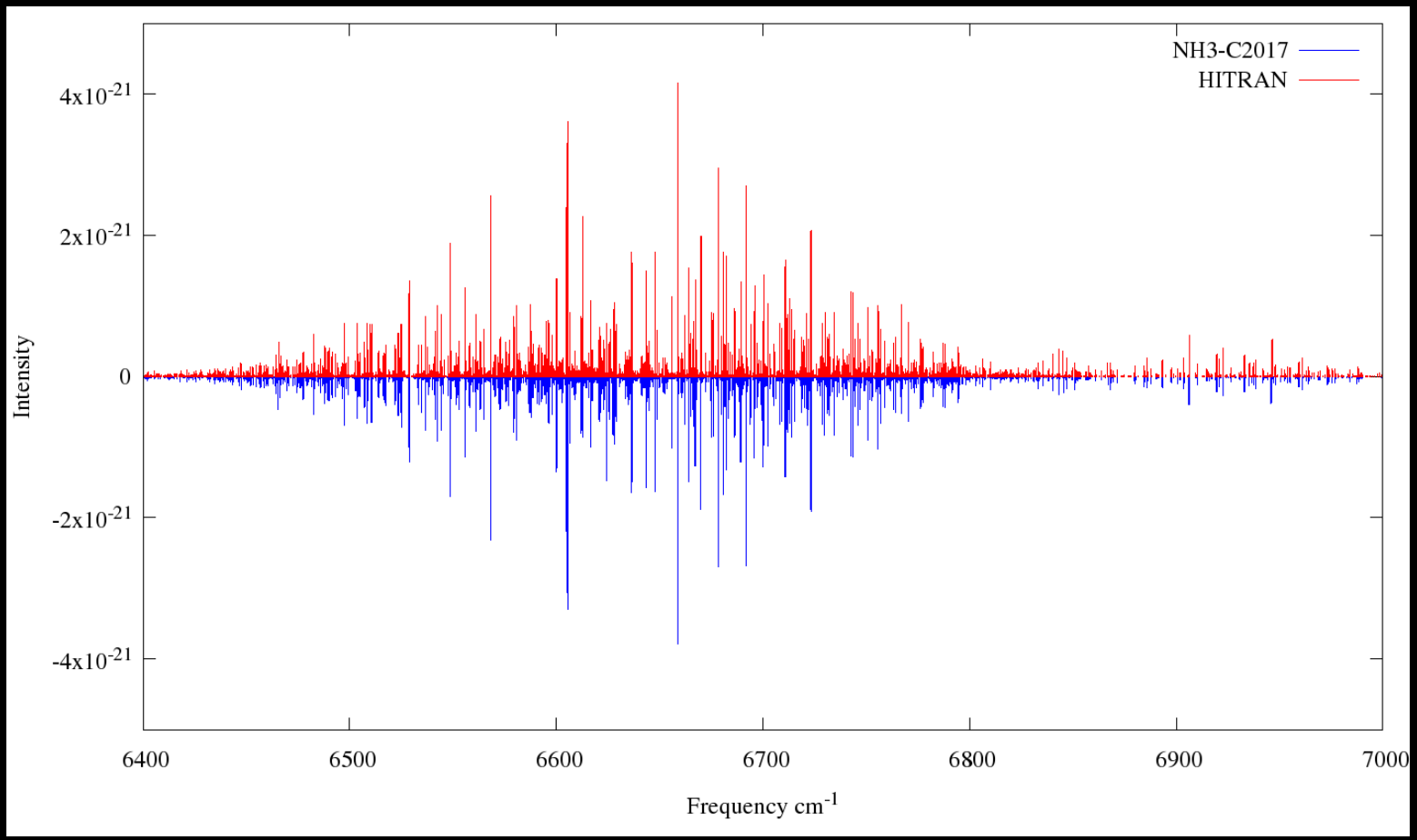
Amaizing
Sub−percents

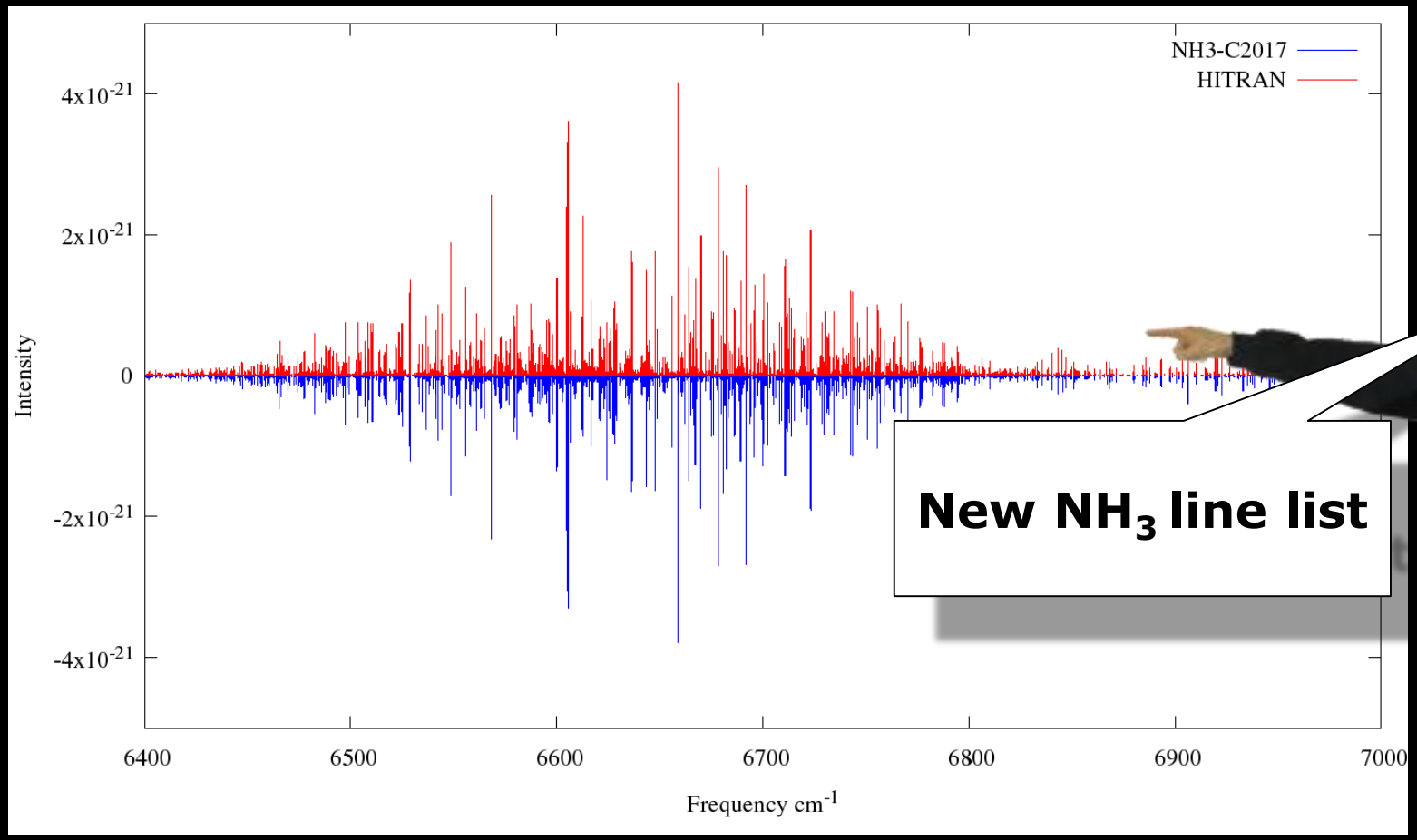
Blue is ab
initio
intensiies

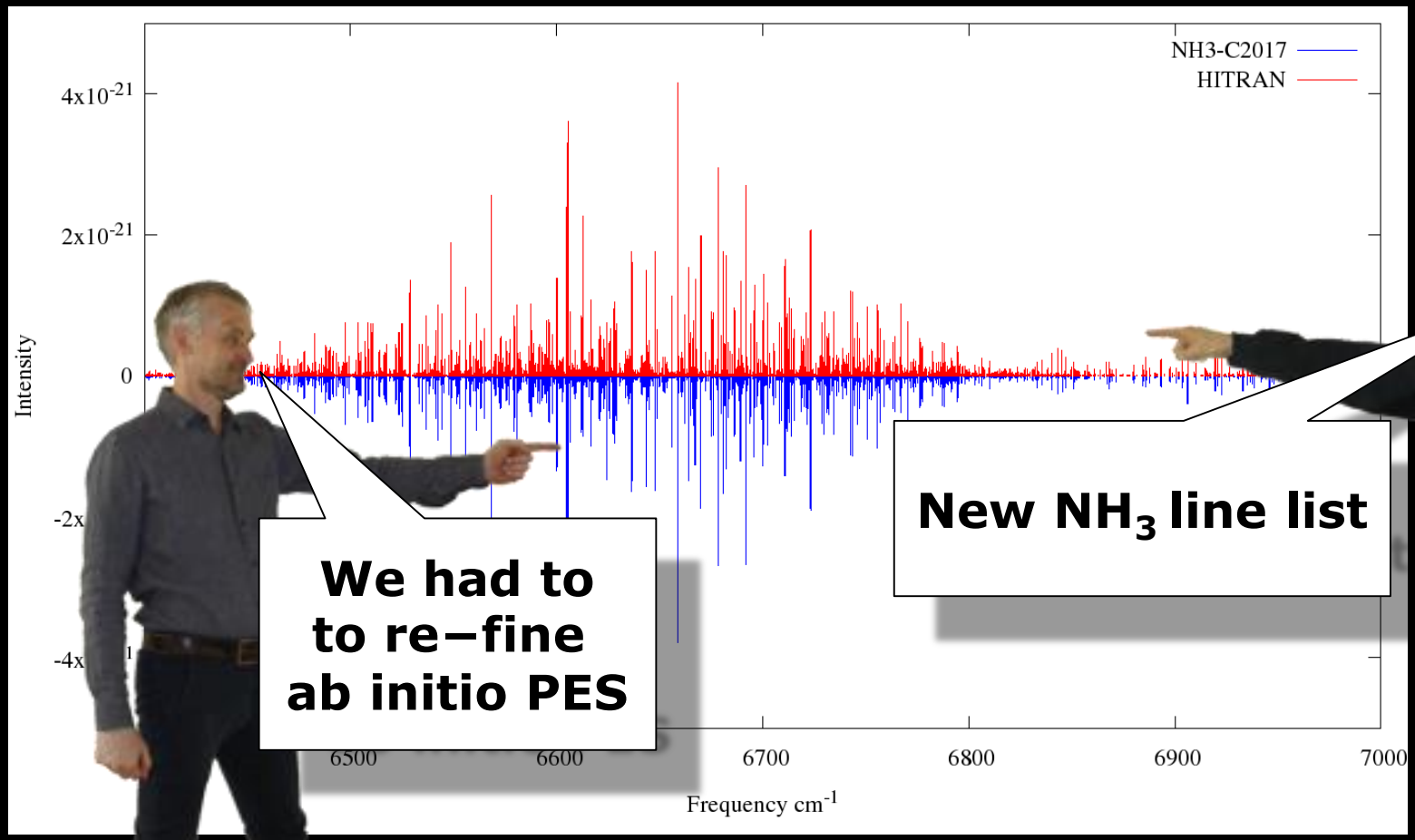
:

OL Polyansky eta al Phys Rev Letts 114, 243001 (2015)

Accurate ro-vibrational line positions?


NH3-C2017
HITRAN
4x10-21
2x10-21
0
-2x10-21
-4x10-21
Intensity
6400
6500
6600
6700
6800
6900
7000
Frequency cm-1


NH3-C2017
HITRAN
4x10-21
2x10-21
0
-2x10-21
-4x10-21
Intensity
6400
6500
6600
6700
6800
6900
7000
Frequency cm-1
New NH3 line list


NH3-C2017
HITRAN
4x10-21
2x10-21
0
-2x
-4x
Intensity
6500
6600
6700
6800
6900
7000
Frequency cm-1
We had to to re−fine ab initio PES
New NH3 line list

Method

Method

DIATOMICS

Solve Schrödinger equations

Solve Schrödinger equations

…. using Born-Oppenheimer approximation for motions of electrons and nuclei

Single electronic state example

Ab initio Spectra (SiO)

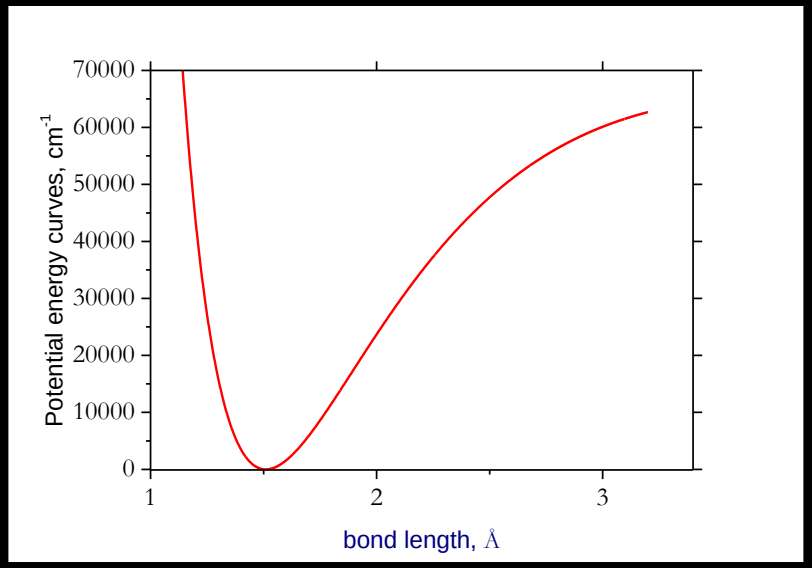
1. Ab initio Potential Energy Curve

2. Ab initio Dipole Moment Curve

3. Solution of Schrödinger equation (Energies and Wavefunctions)

4. Calculation of Intensities (Einstein coefficients)

Ab initio Spectra (SiO)



2. Ab initio Dipole Moment Curve

3. Solution of Schrödinger equation (Energies and Wavefunctions)

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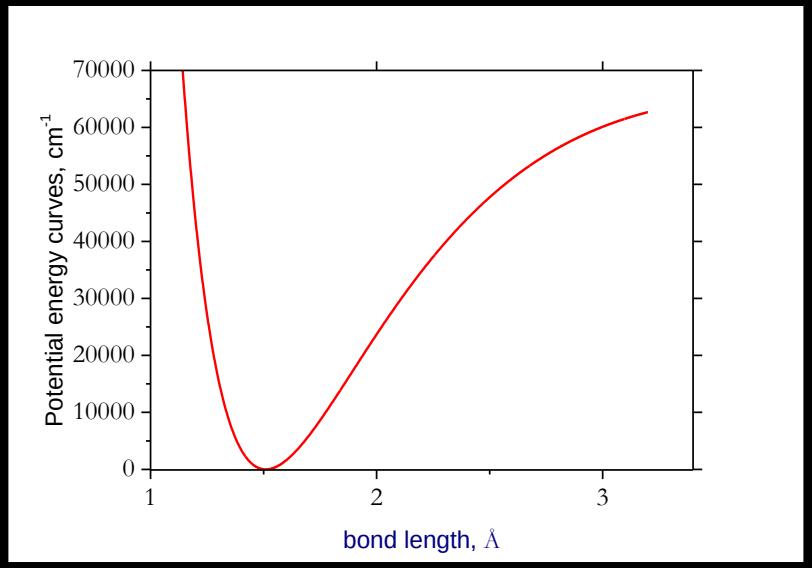
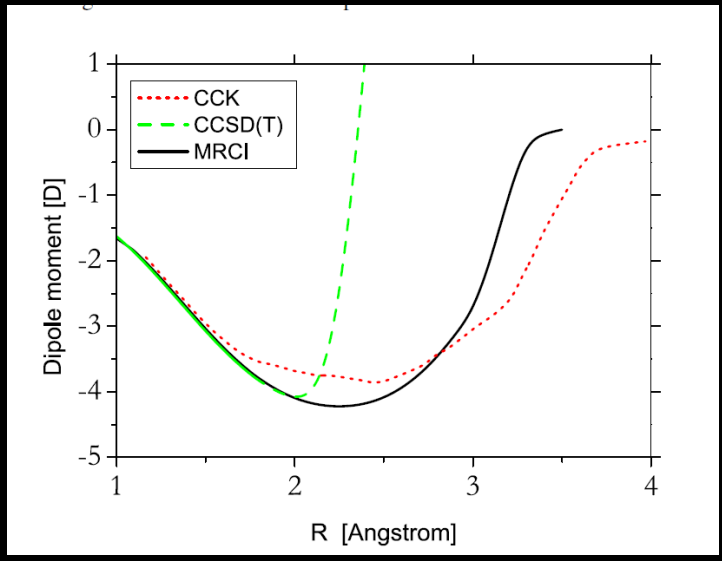
Ab initio Spectra (SiO)





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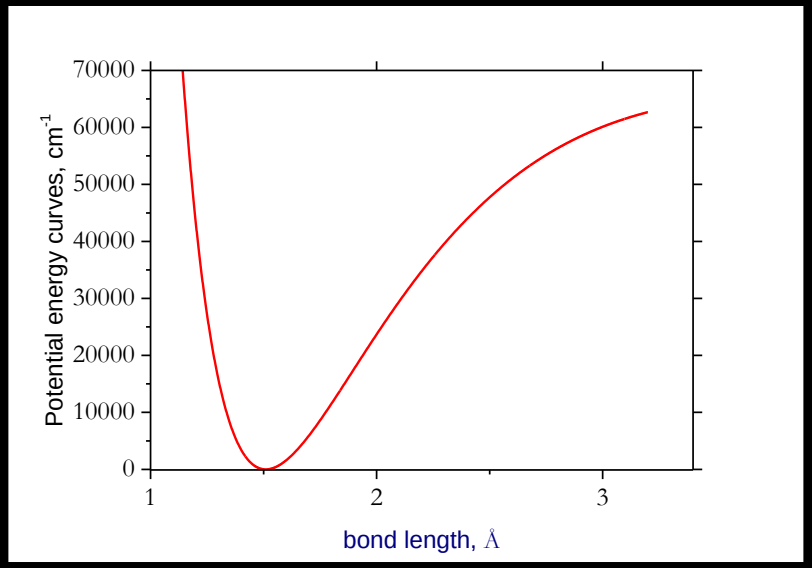
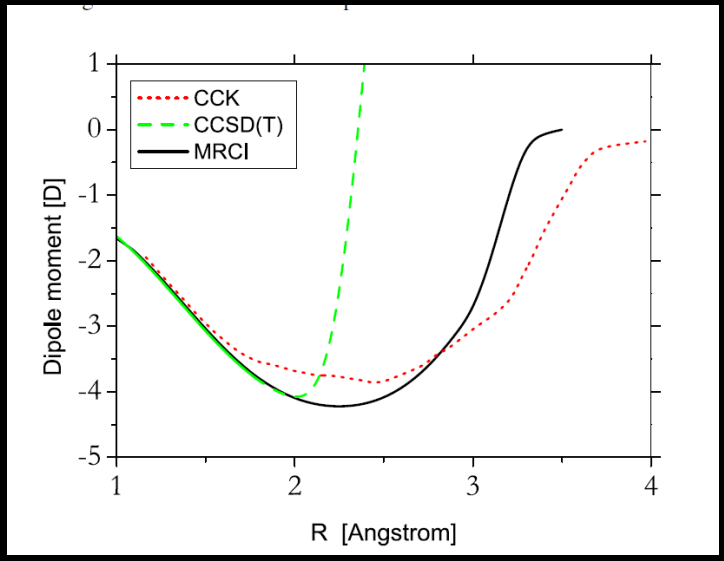


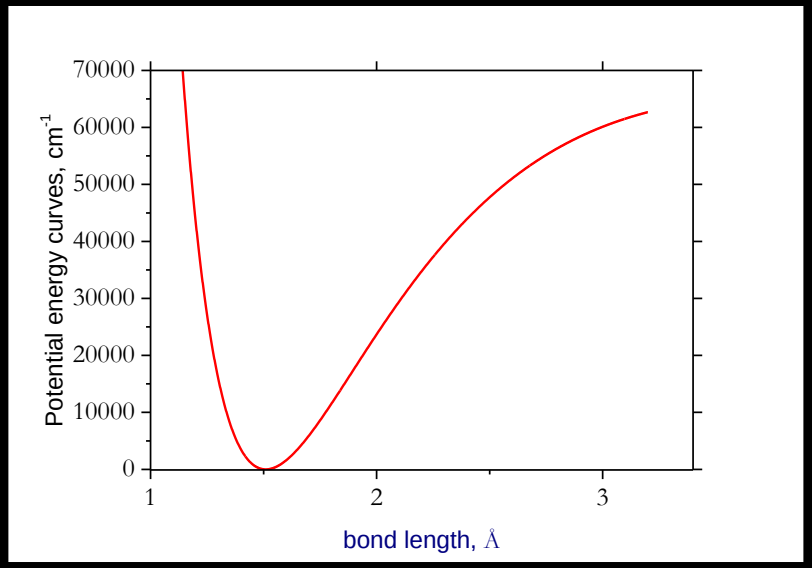


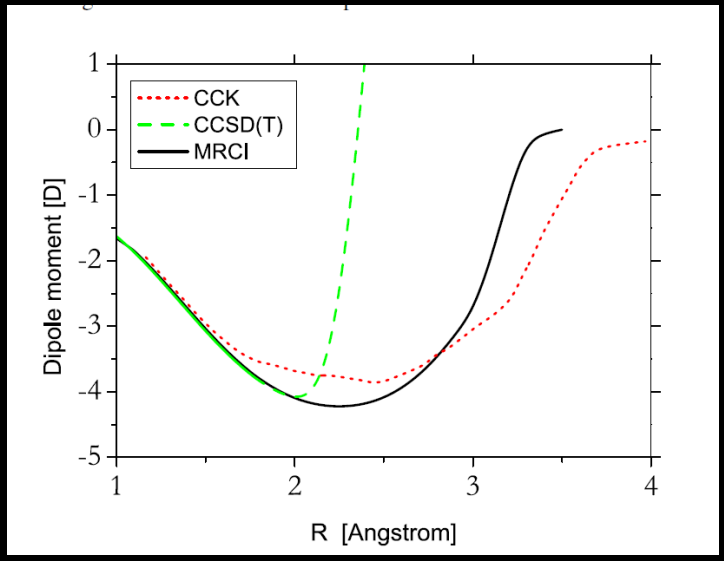
$$\frac{\hbar^2}{2\mu r^2}J(J+1) - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V(r)\Psi = E\Psi$$

LEVEL 8.0
R. Le Roy, Waterloo, Canada
Our Duo program

4. Calculation of Intensities (Einstein coefficients)

Ab initio Spectra (SiO)





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LEVEL 8.0
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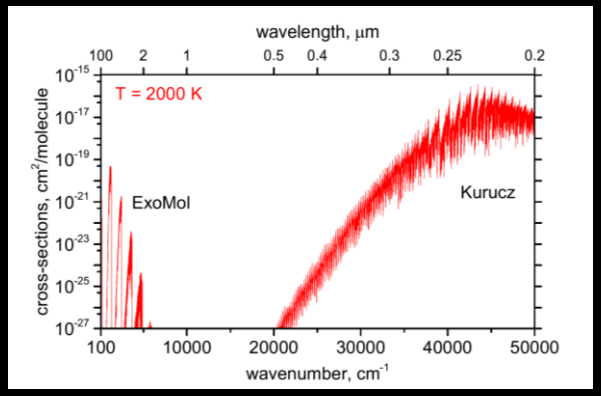
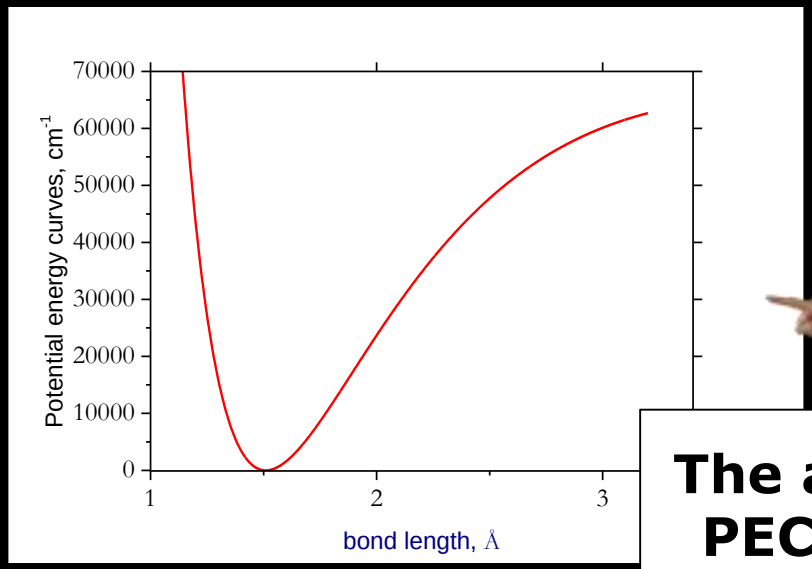
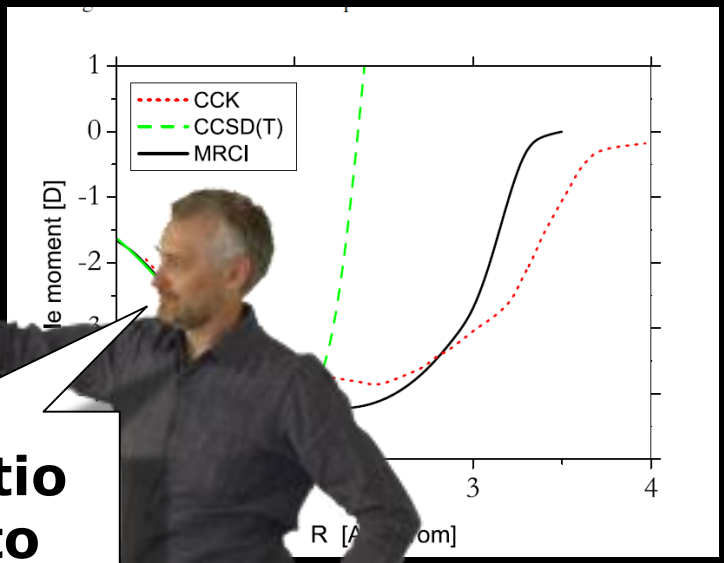


Ab initio Spectra (SiO)





The ab initio PEC has to be refined

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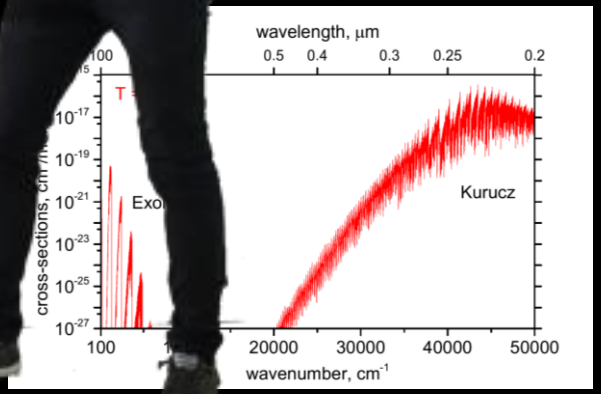


LEVEL 8.0

R. Le Roy, Waterloo, Canada

Our Duo program

Most of the systems are not single-state

Ab initio spectrum (MgO)

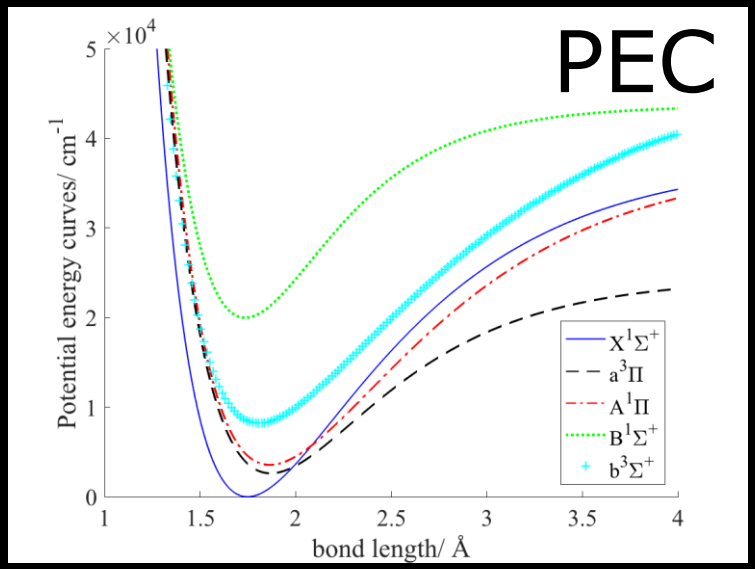
1. Ab initio Potential Energy Curves

2. Ab initio Dipole Moment Curves

3. Spin-Orbit couplings

4. Electronic angular momenta couplings

Ab initio spectrum (MgO)



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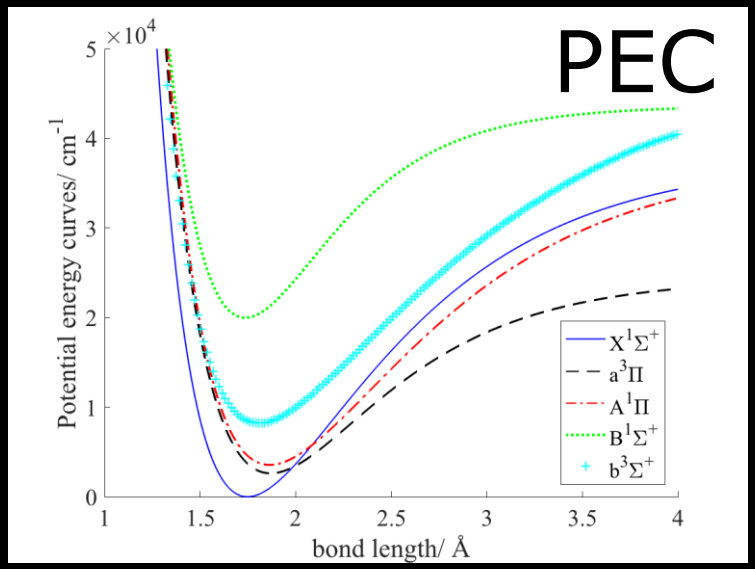
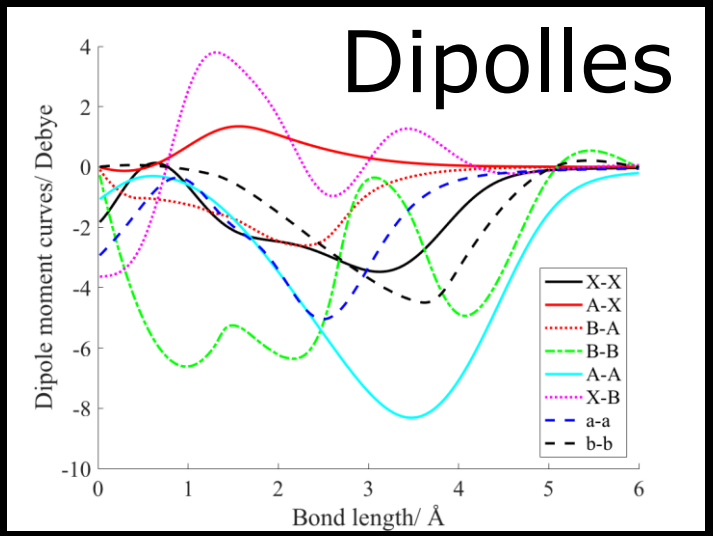
Ab initio spectrum (MgO)

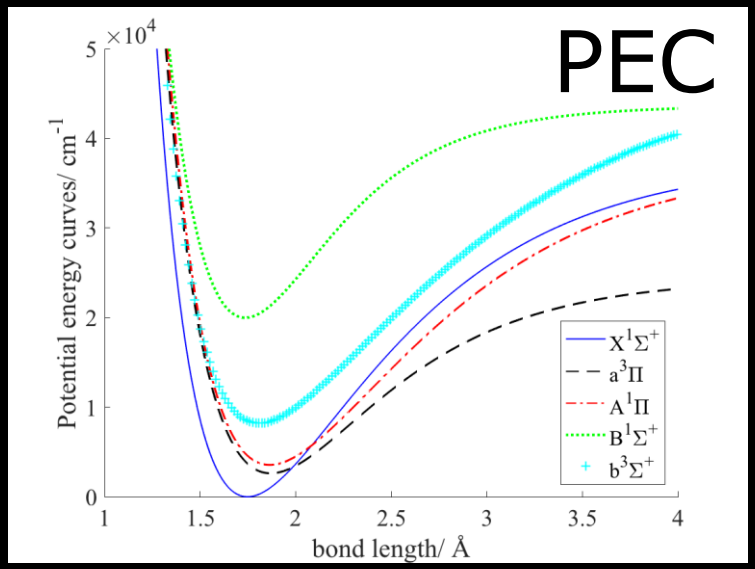


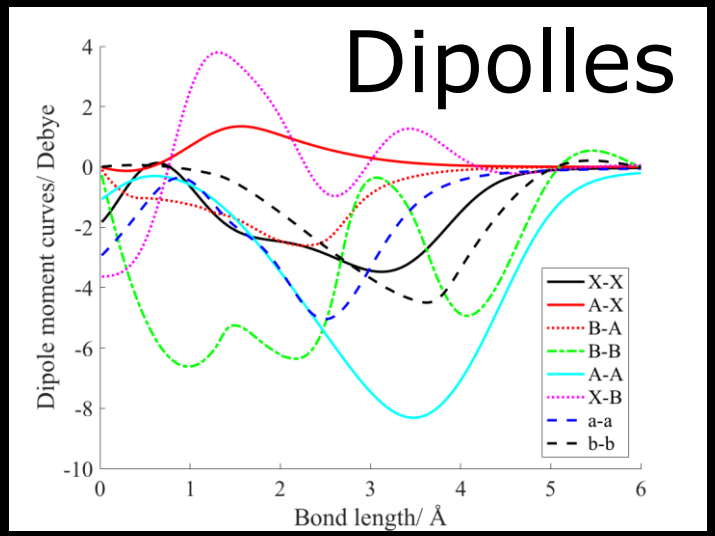


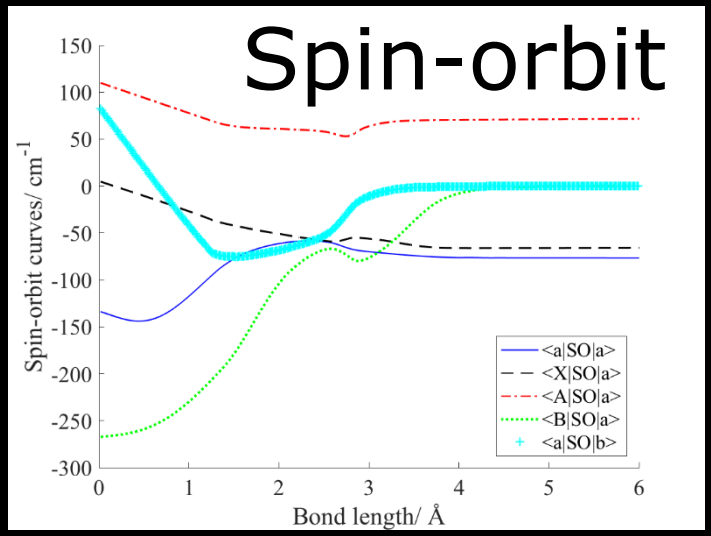
3. Spin-Orbit couplings

4. Electronic angular momenta couplings

Ab initio spectrum (MgO)







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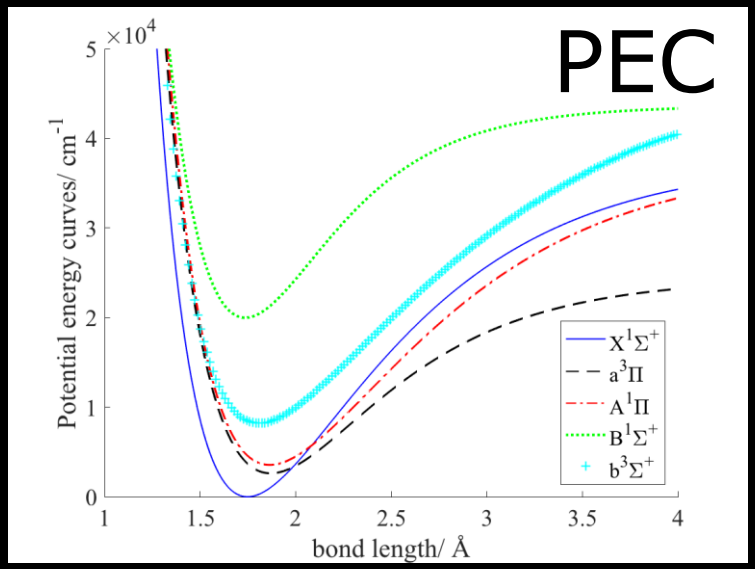
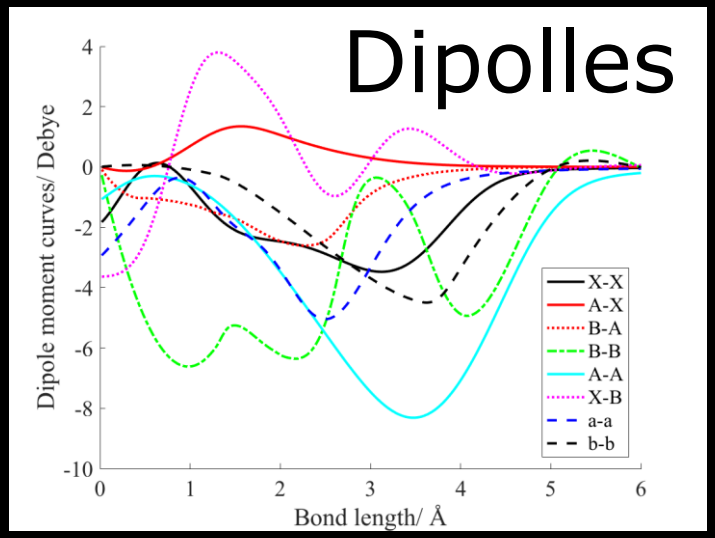
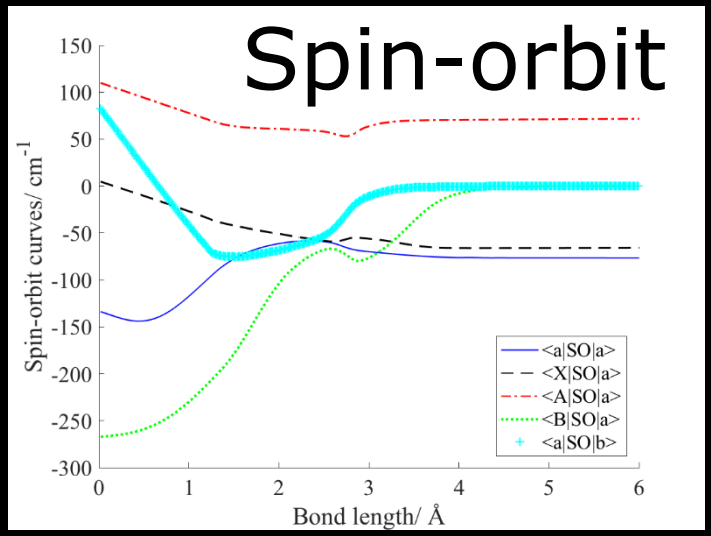
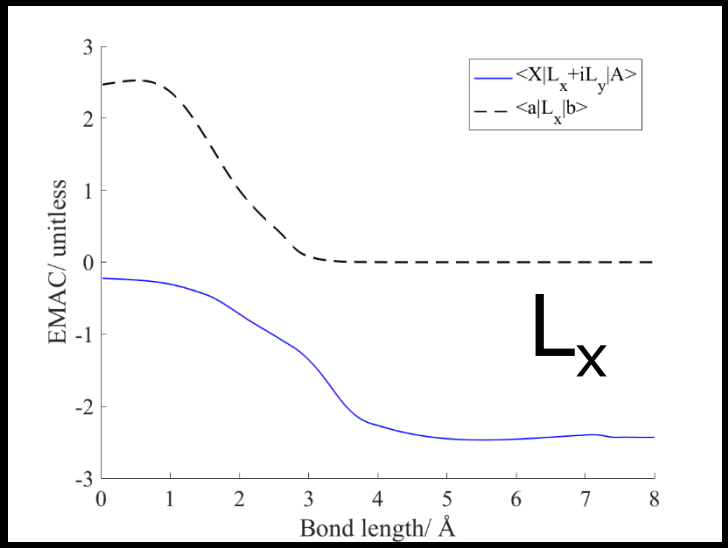
Ab initio spectrum (MgO)

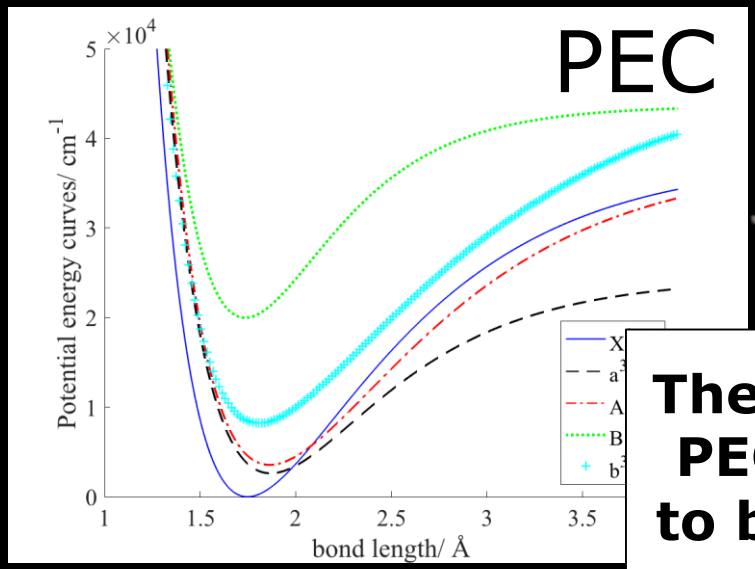


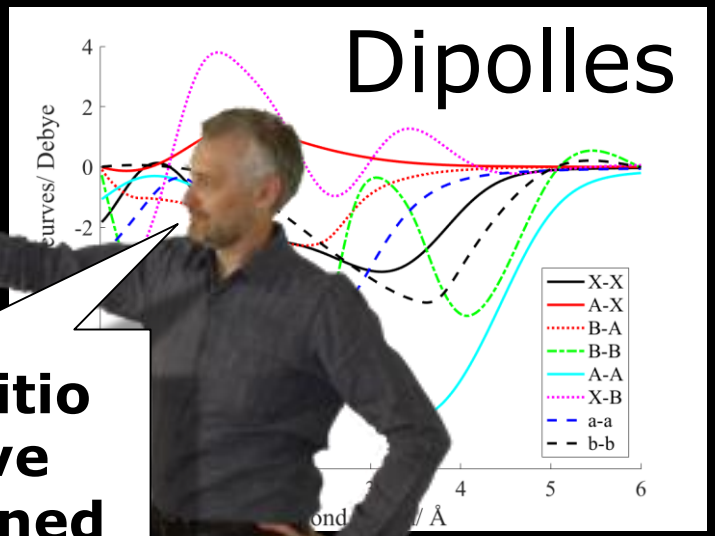




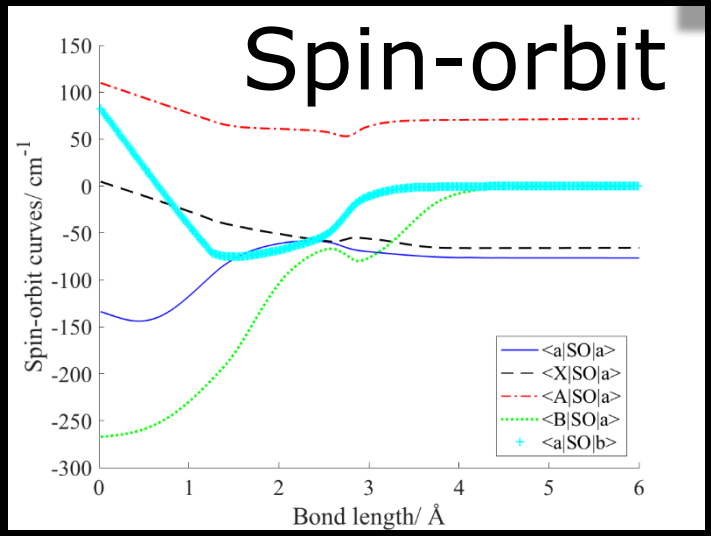


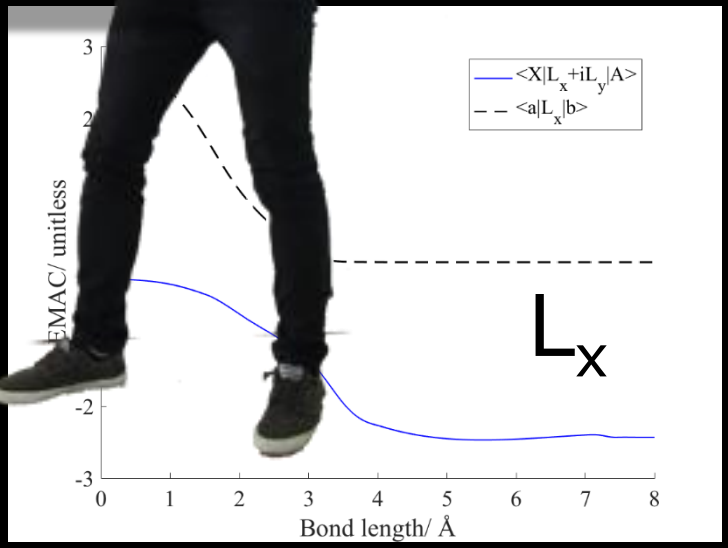
Ab initio spectrum (MgO)



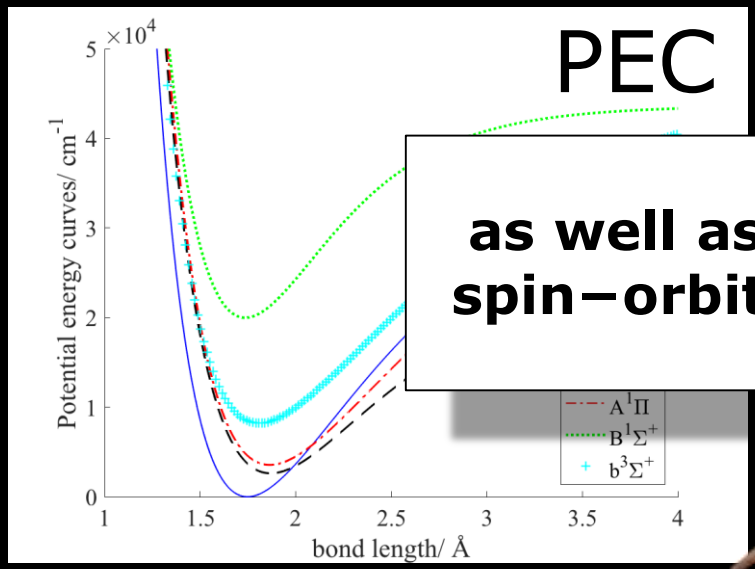


The ab initio PECs have to be refined

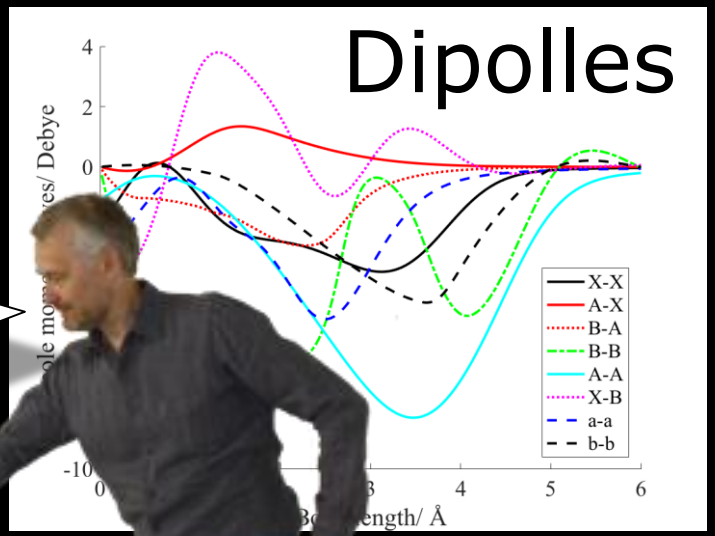


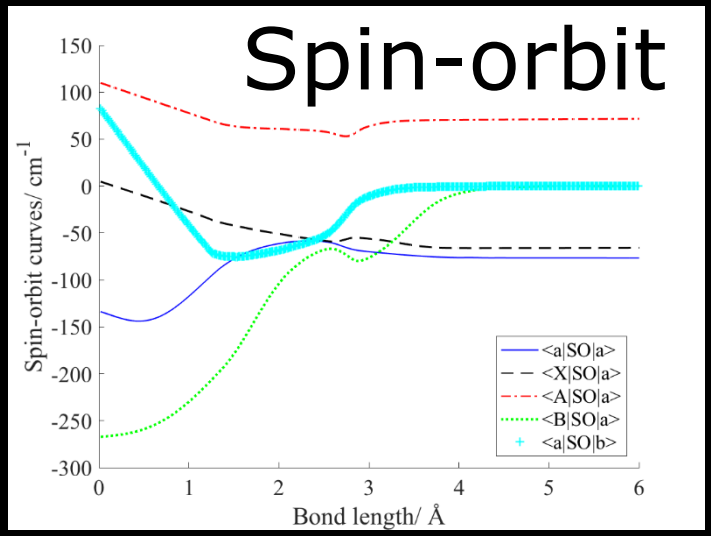


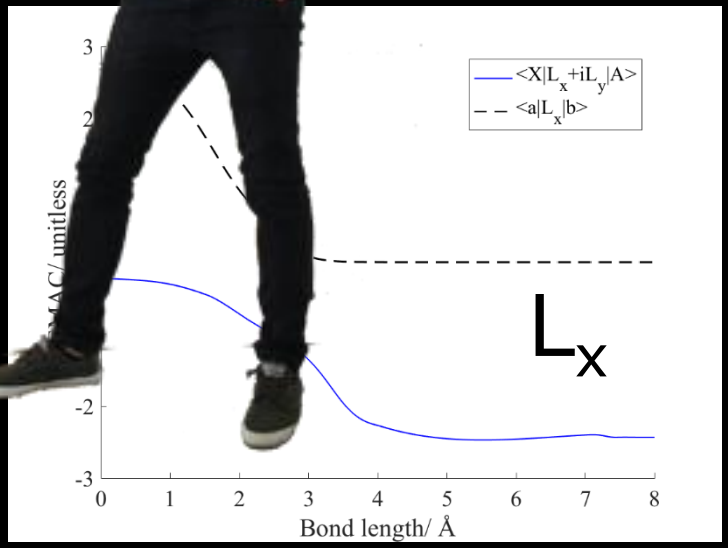
Ab initio spectrum (MgO)



as well as spin–orbits







A more sophisticated code for
a coupled system is required

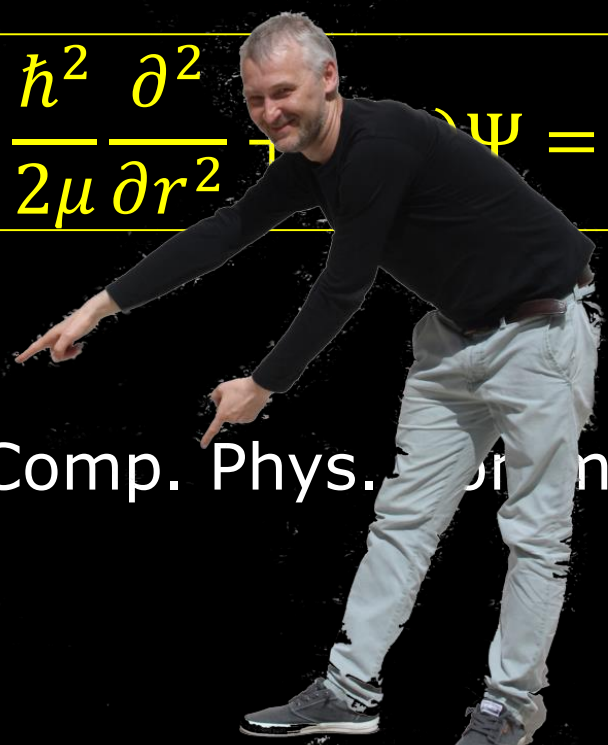
$$\frac{\hbar^2}{2\mu r^2}\hat{R}^2 - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V(r)\Psi = E\Psi$$

Our code Duo

Yurchenko et al Comp. Phys. Comm. (2016)

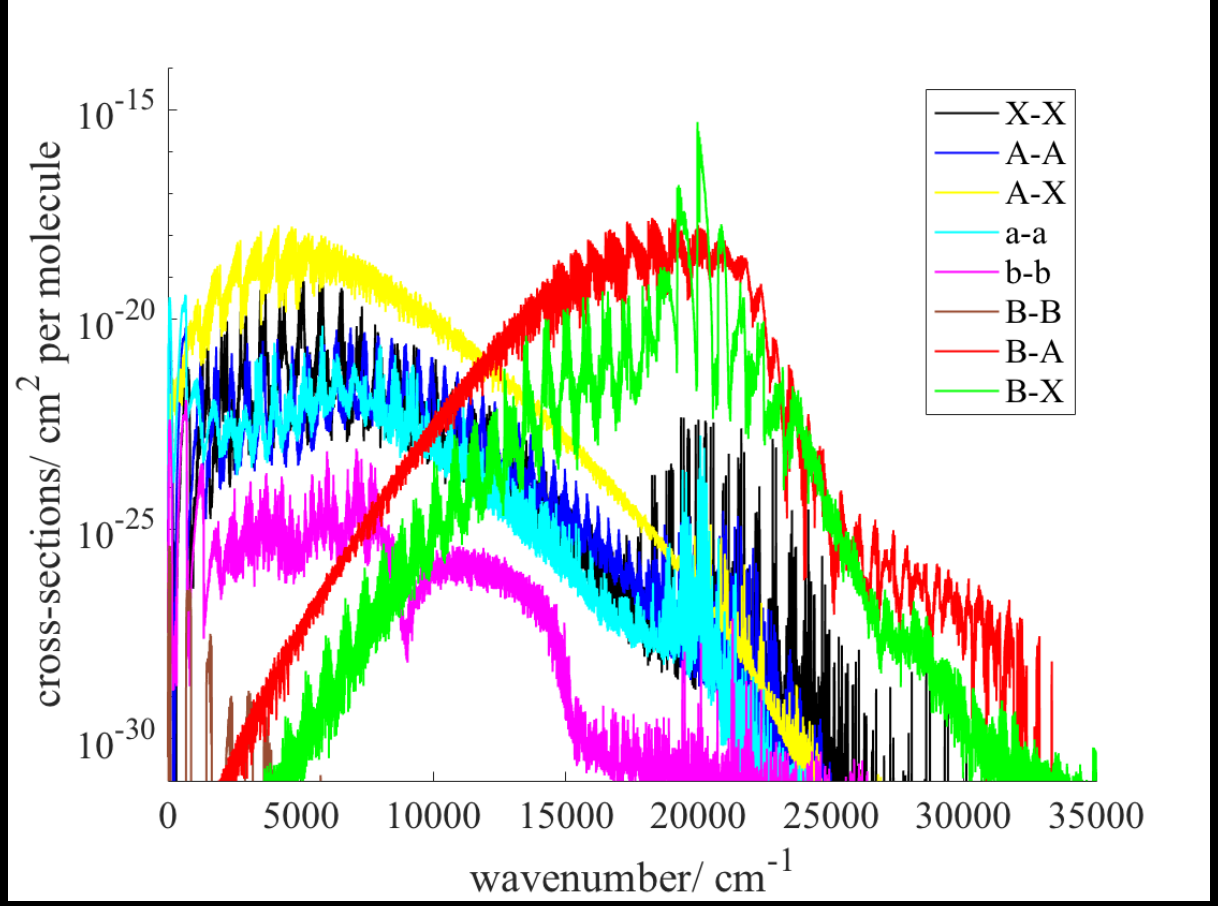
A more sophisticated code for
a coupled system is required

$$\frac{\hbar^2}{2\mu r^2}\hat{R}^2 - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \ldots \Psi = E\Psi$$

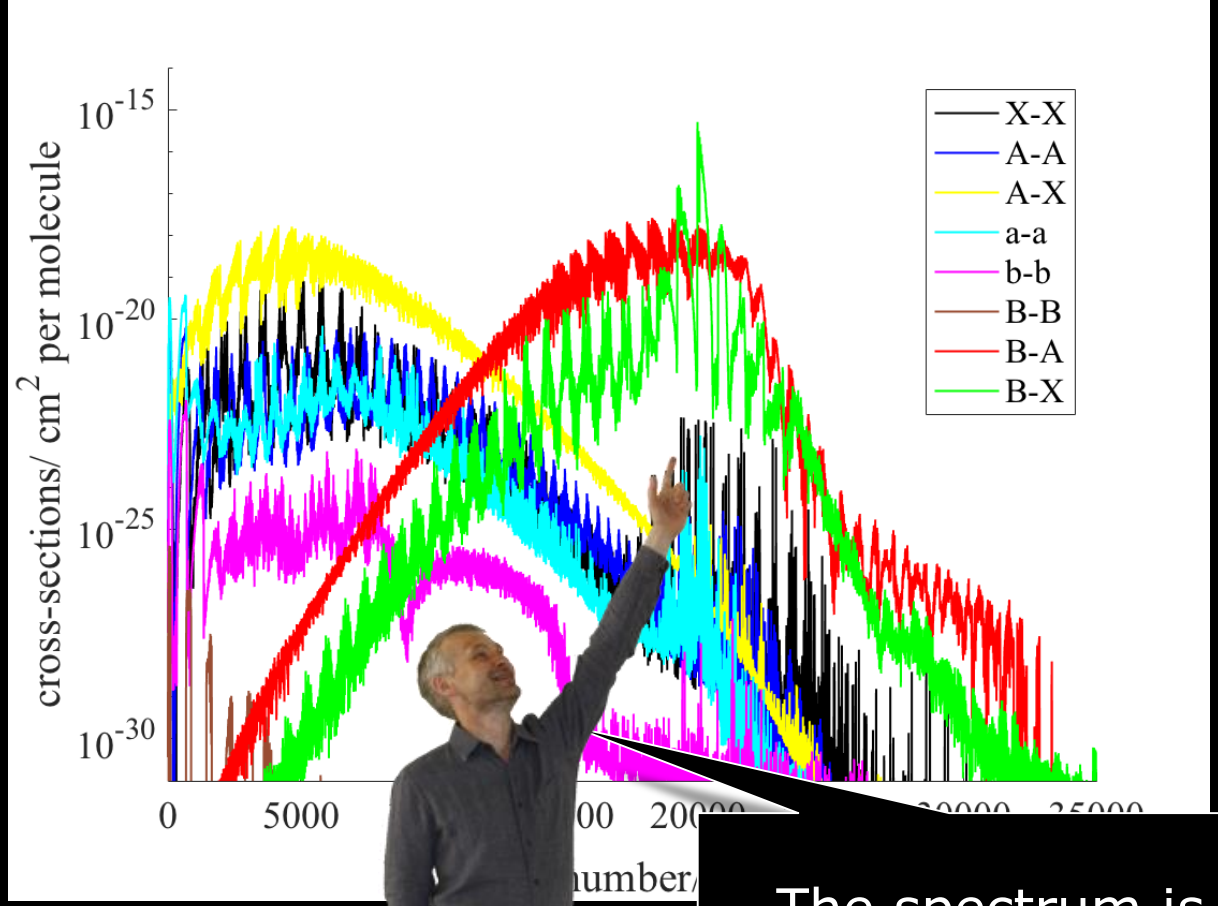


Our code Duo

Yurchenko et al Comp. Phys. [illegible] n. (2016)


cross-sections/ cm^2 per molecule
10^{-15}
10^{-20}
10^{-25}
10^{-30}
0
5000
10000
15000
20000
25000
30000
35000
wavenumber/ cm^{-1}
X-X
A-A
A-X
a-a
b-b
B-B
B-A
B-X

MgO



MgO

The spectrum is more complex, with multiple interacting electronic bands

In fact:
for diatomics pure ab initio calculations is almost never good enough

In fact:
for diatomics pure ab initio calculations is almost never good enough

… at least for practical applications

Example: CrH ab initio spectra

CrH ab initio absorption at T=2000 K

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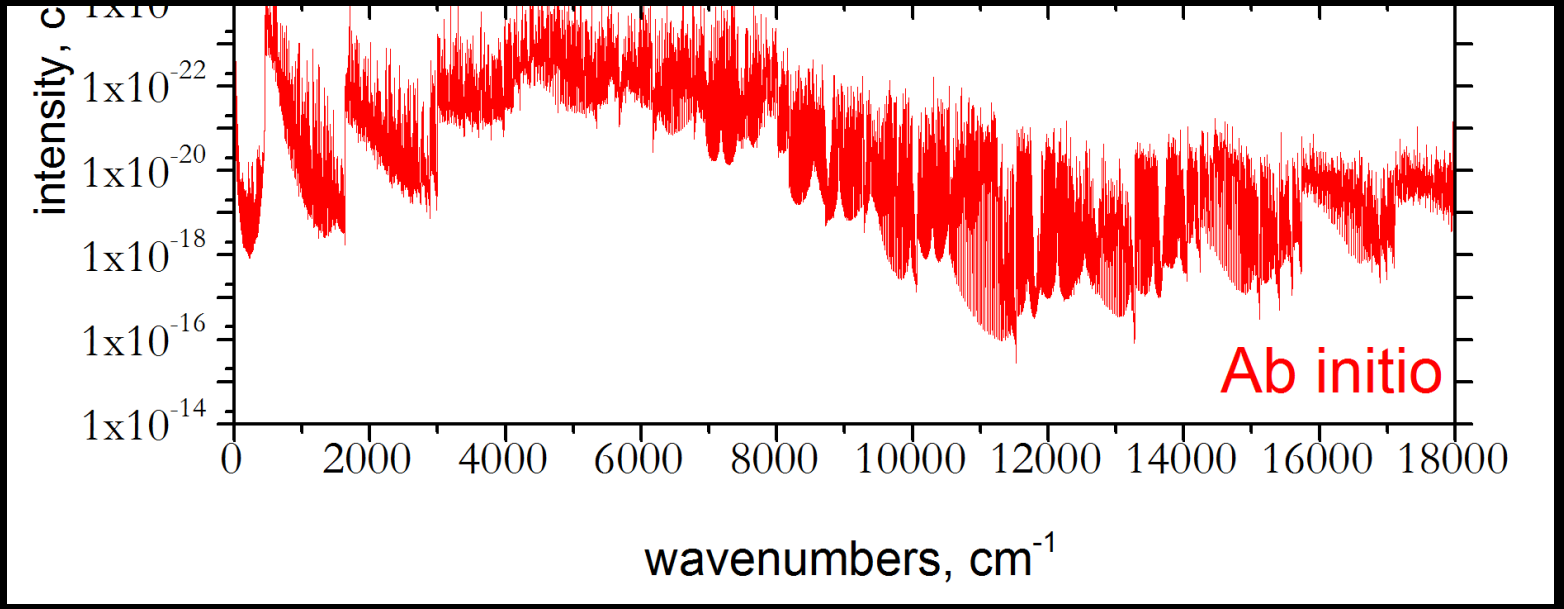
High level ab initio
ic-MRCI/aug-cc-pV5Z

CrH ab initio absorption at T=2000 K

High level ab initio
ic-MRCI/aug-cc-pV5Z



CrH ab initio absorption at T=2000 K

High level ab initio
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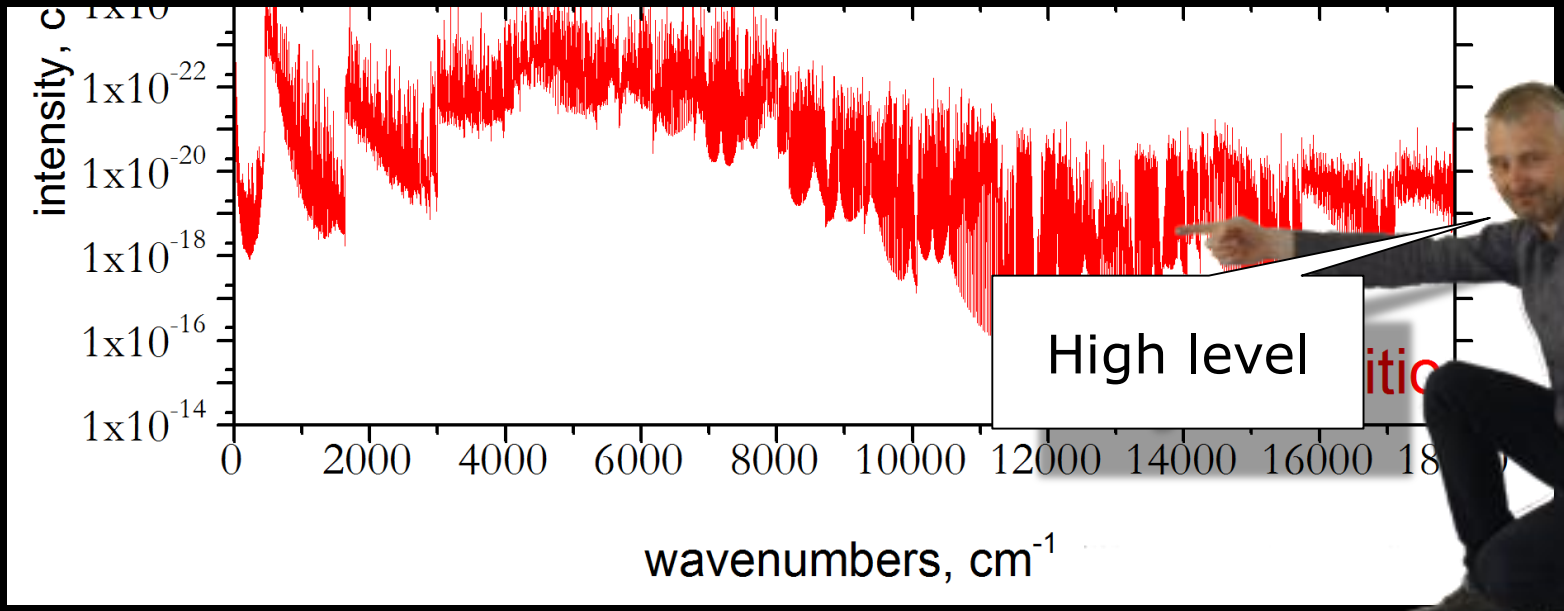
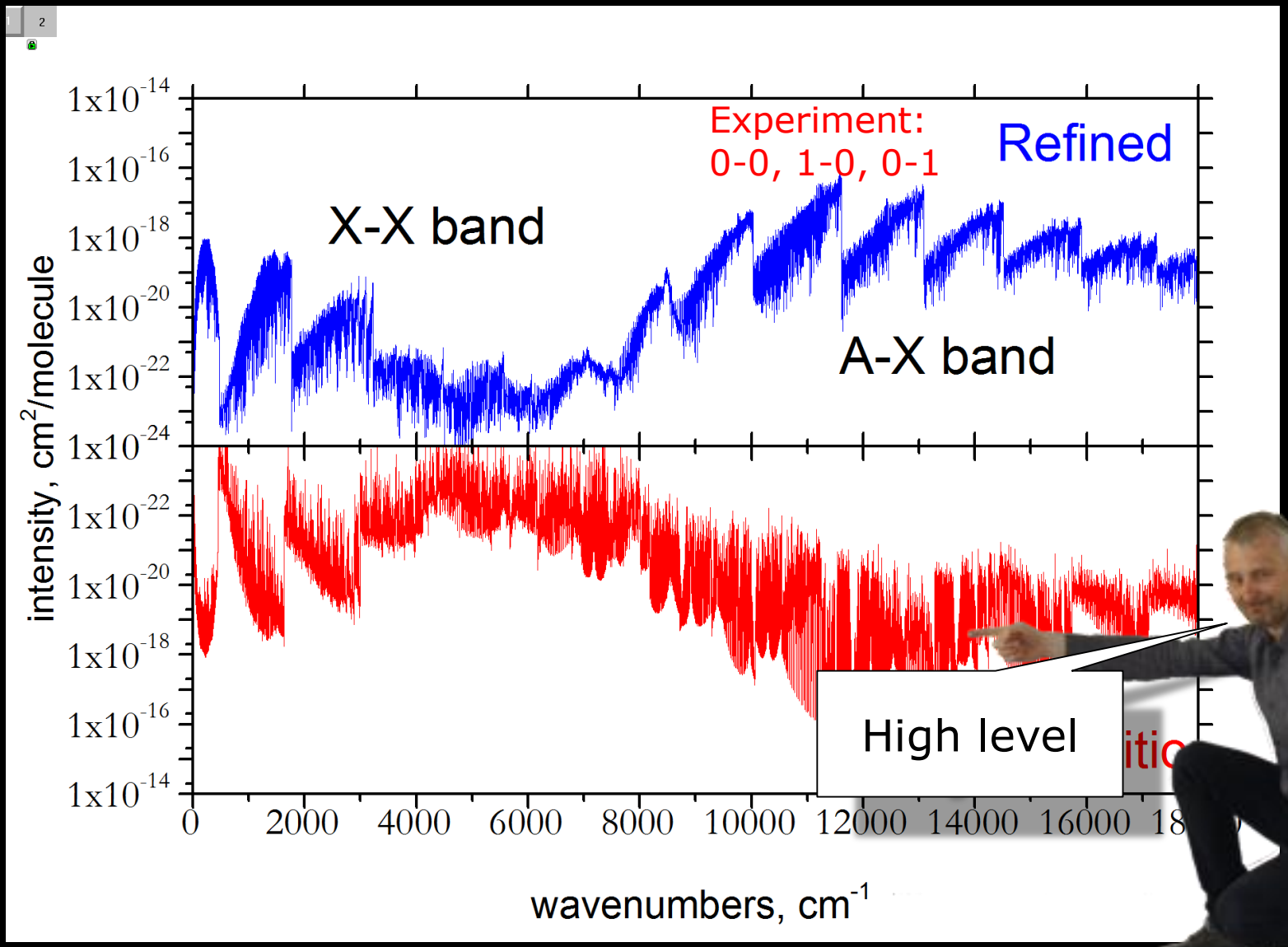
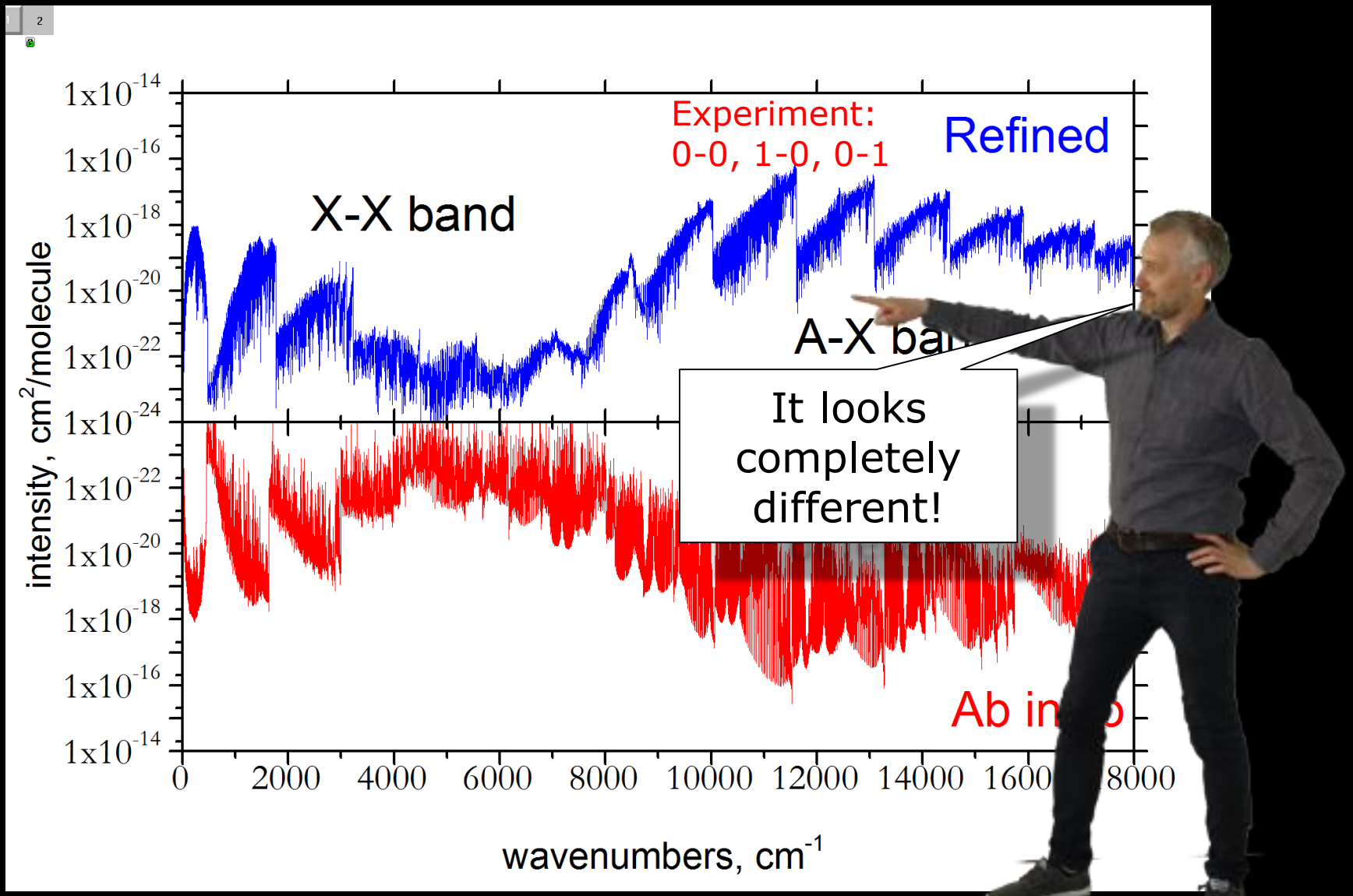


CrH ab initio absorption at T=2000 K

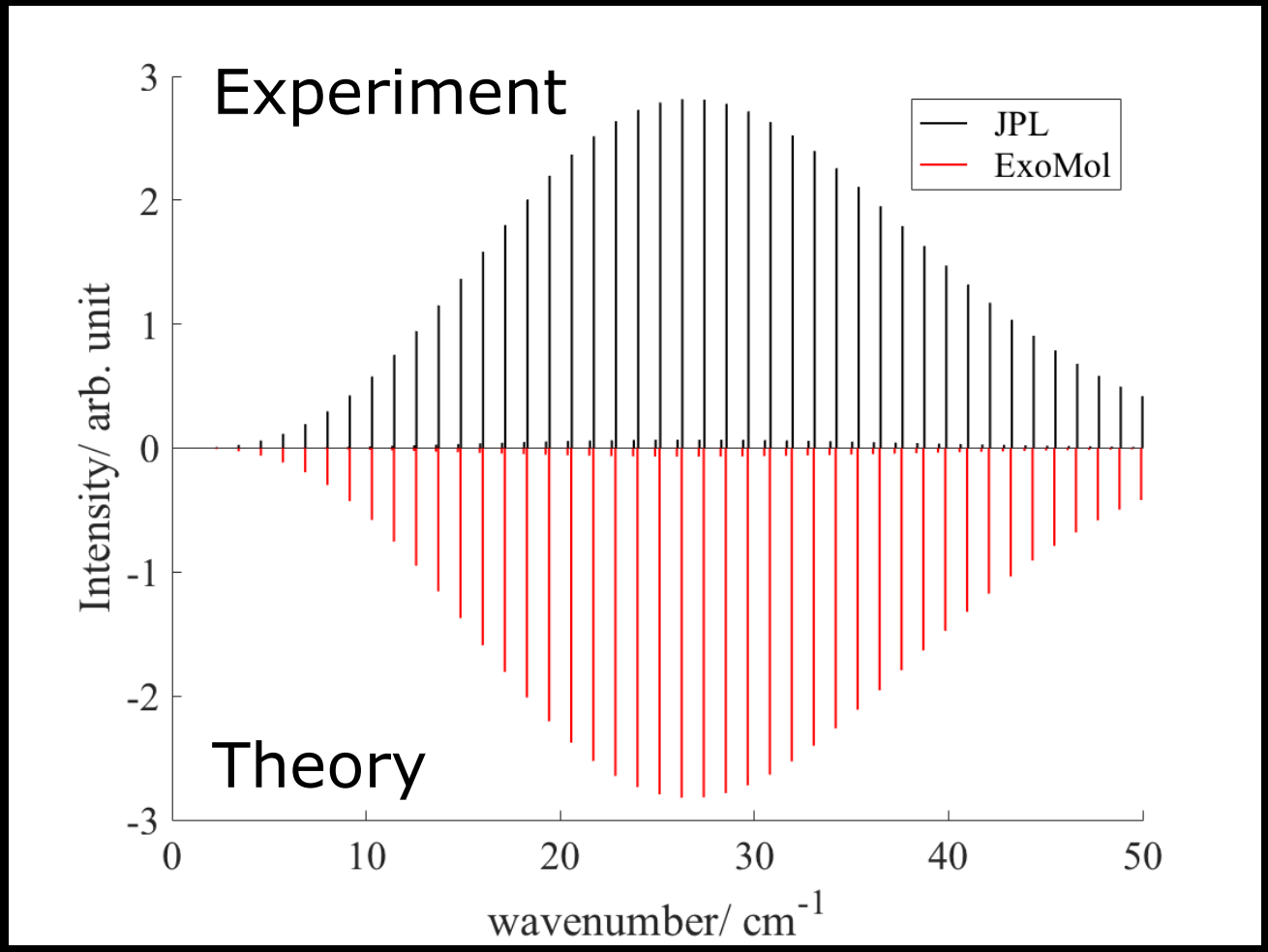


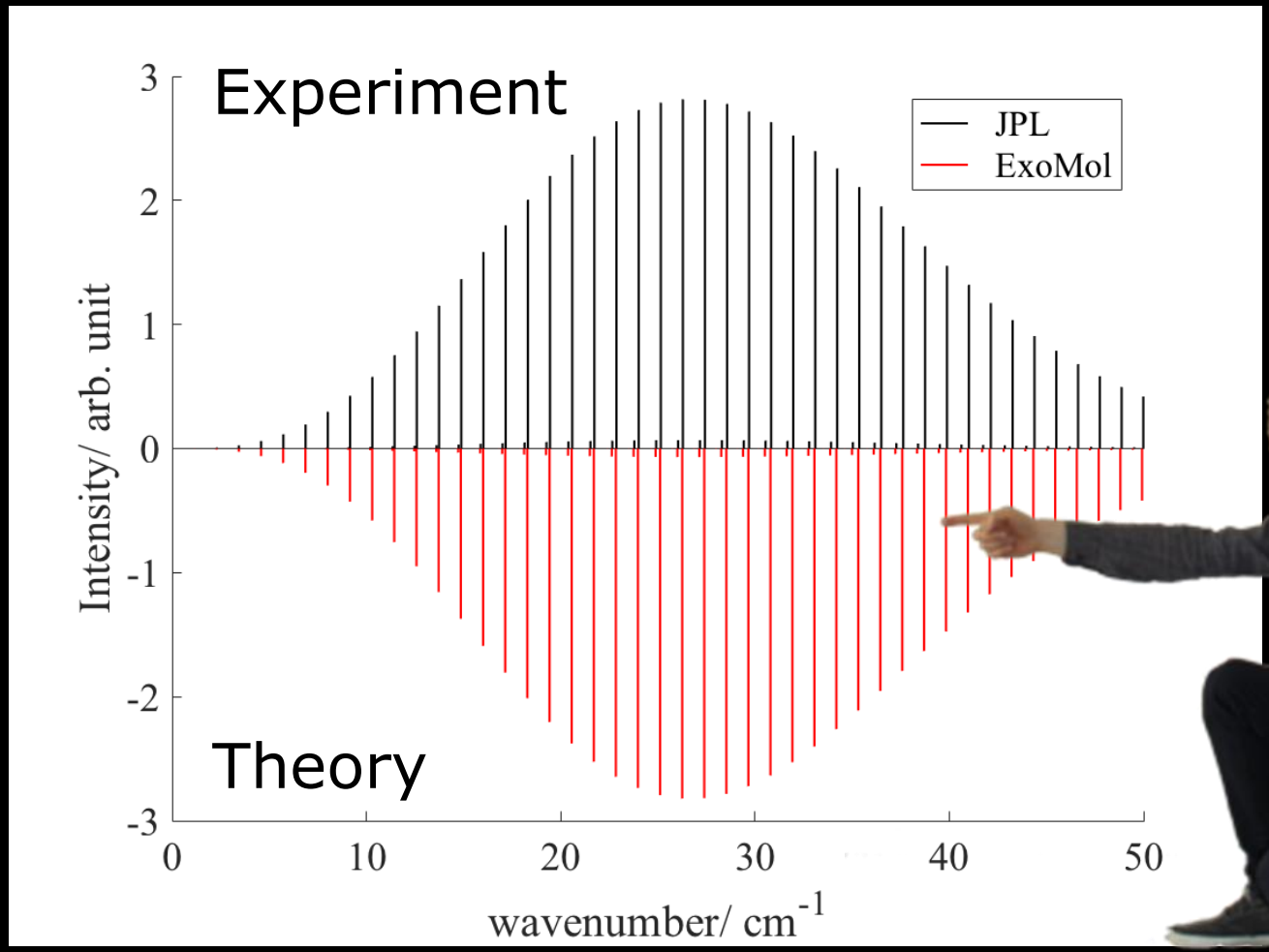
CrH ab initio absorption at T=2000 K



Refinement of our pure theoretical model to experiment is always mandatory

How accurate are we?


Experiment
Theory
JPL
ExoMol
Intensity/ arb. unit
wavenumber/ cm-1
3
2
1
0
-1
-2
-3
0
10
20
30
40
50



MgO: Only after refinement

For most of hot diatomics
no experimental intensities
or lifetimes are available
but hugely needed!

More on diatomics: see my presentation this afternoon

More on diatomics: see my presentation this afternoon

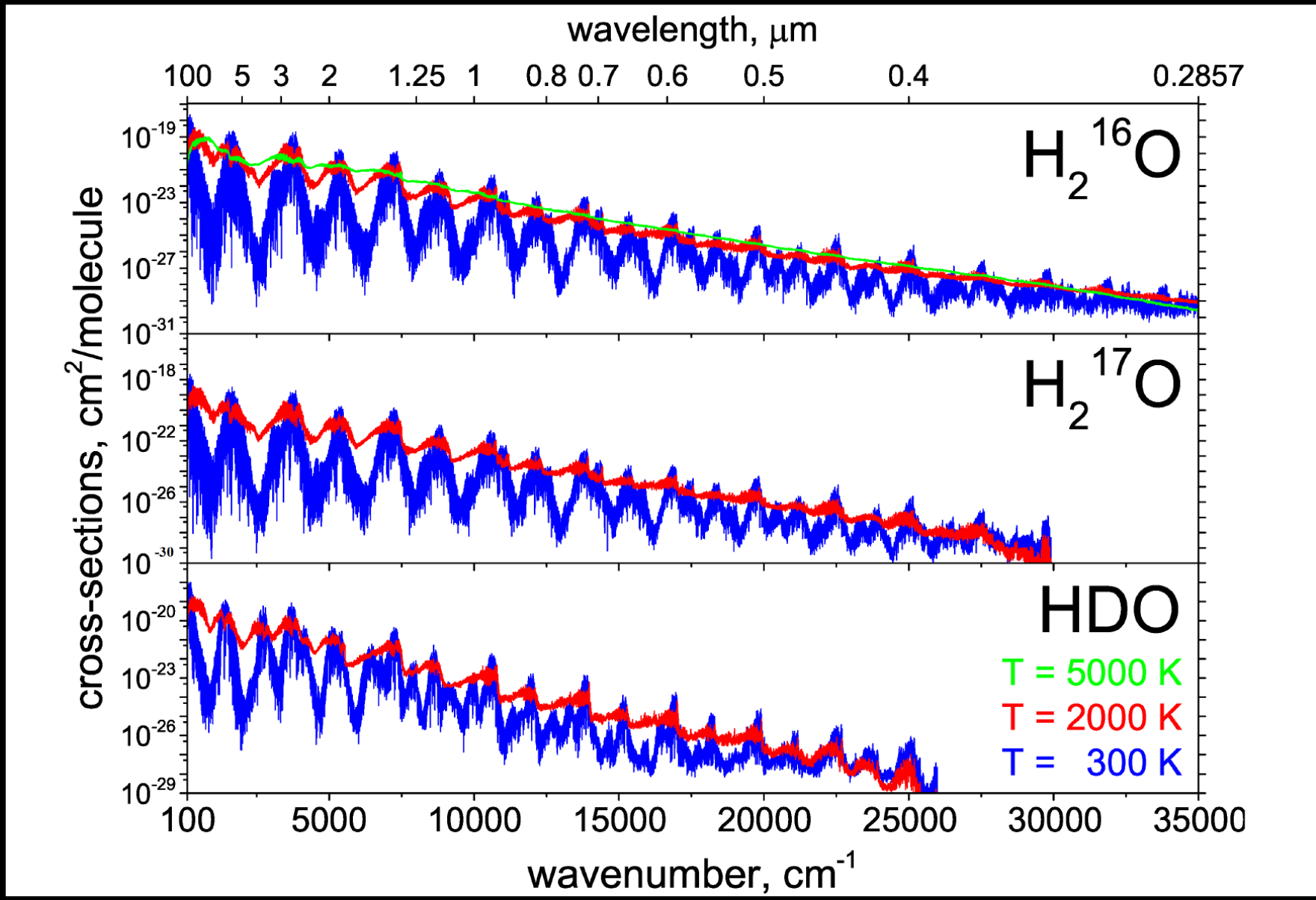
WH05 (small molecules) at 14:53

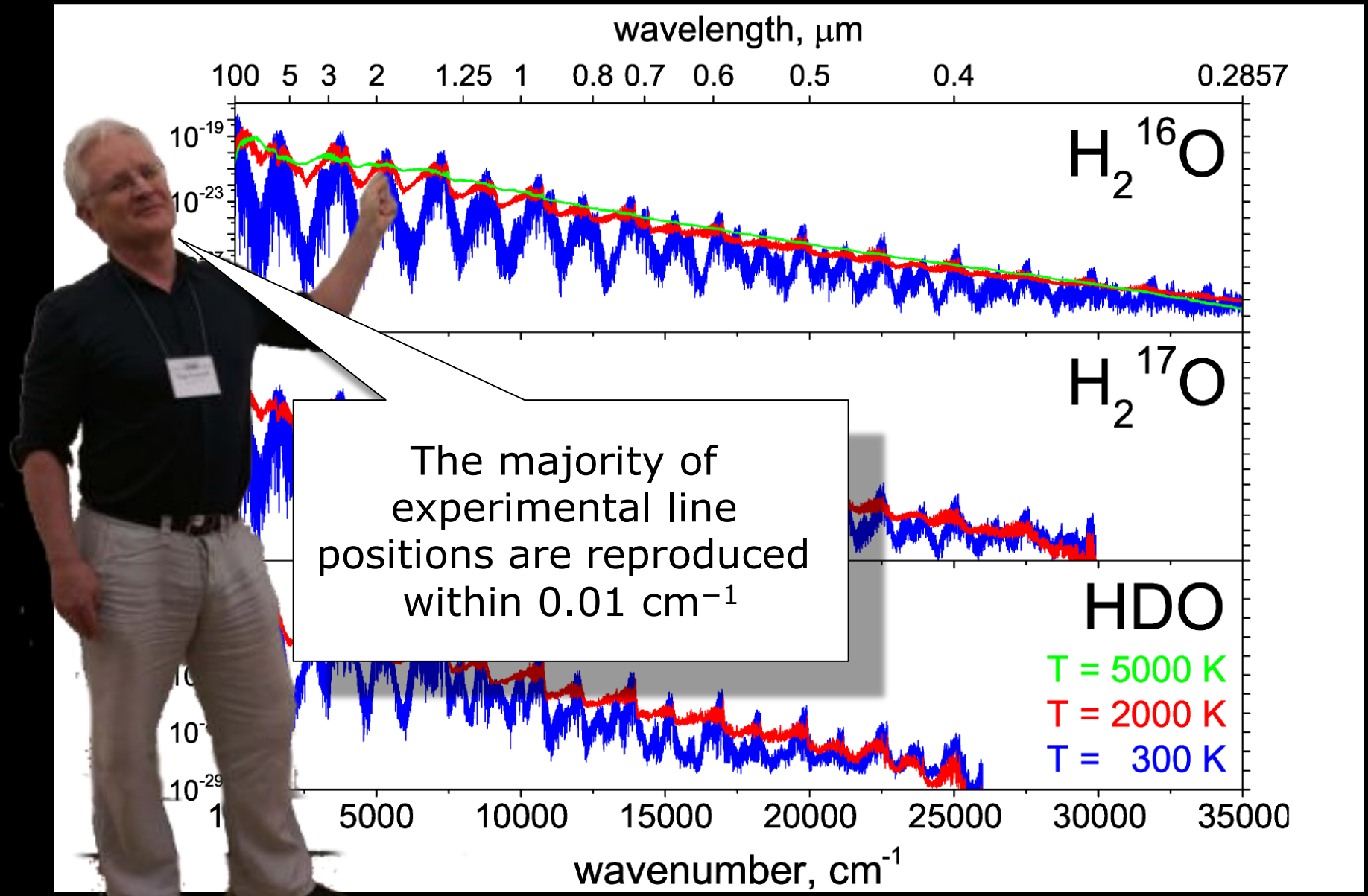
Polyatomic molecules

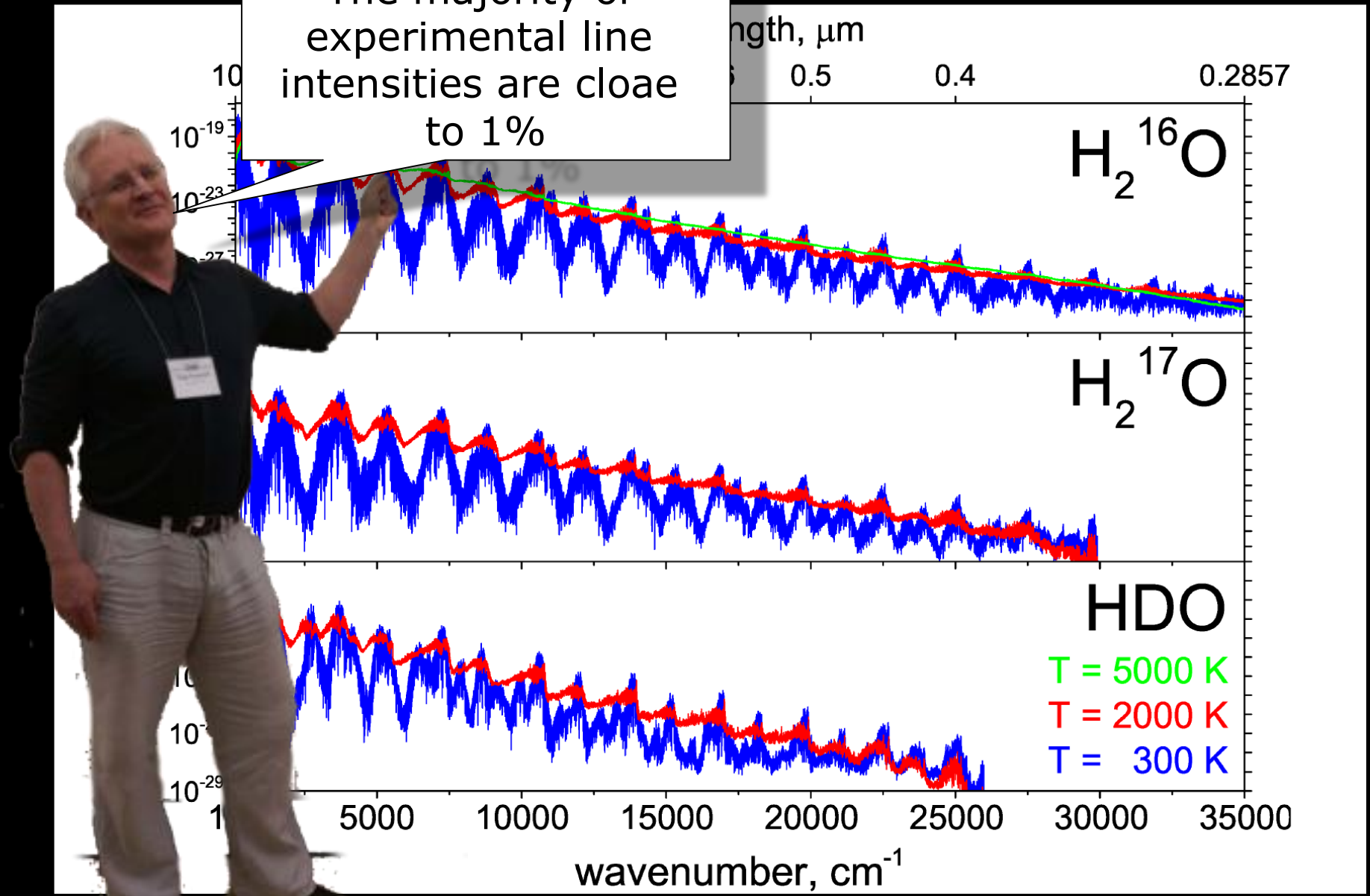
We have produced a new water line list POKAZATEL, fully complete and more accurate

Oleg Polyansky et al MNRAS re-submitted (2018)

All bound states up to dissociation


wavelength, μm
100 5 3 2 1.25 1 0.8 0.7 0.6 0.5 0.4 0.2857
cross-sections, cm²/molecule
H2 16O
H2 17O
HDO
T = 5000 K
T = 2000 K
T = 300 K
100 5000 10000 15000 20000 25000 30000 35000
wavenumber, cm-1


wavelength, μm
100 5 3 2 1.25 1 0.8 0.7 0.6 0.5 0.4 0.2857
$H_2{}^{16}O$
$H_2{}^{17}O$
HDO
T = 5000 K
T = 2000 K
T = 300 K
The majority of experimental line positions are reproduced within 0.01 cm^{-1}
5000 10000 15000 20000 25000 30000 35000
wavenumber, cm^{-1}


The majority of experimental line intensities are cloae to 1%
ngth, μm
0.5
0.4
0.2857
$H_2{}^{16}O$
$H_2{}^{17}O$
HDO
T = 5000 K
T = 2000 K
T = 300 K
5000
10000
15000
20000
25000
30000
35000
wavenumber, cm^{-1}

This summarises our main goals…

Accurate line positions

Accurate line intensities

To be complete for high excitations and hot spectra

These goals however are not always compatible

It is too difficult or even impossible to be accurate and complete

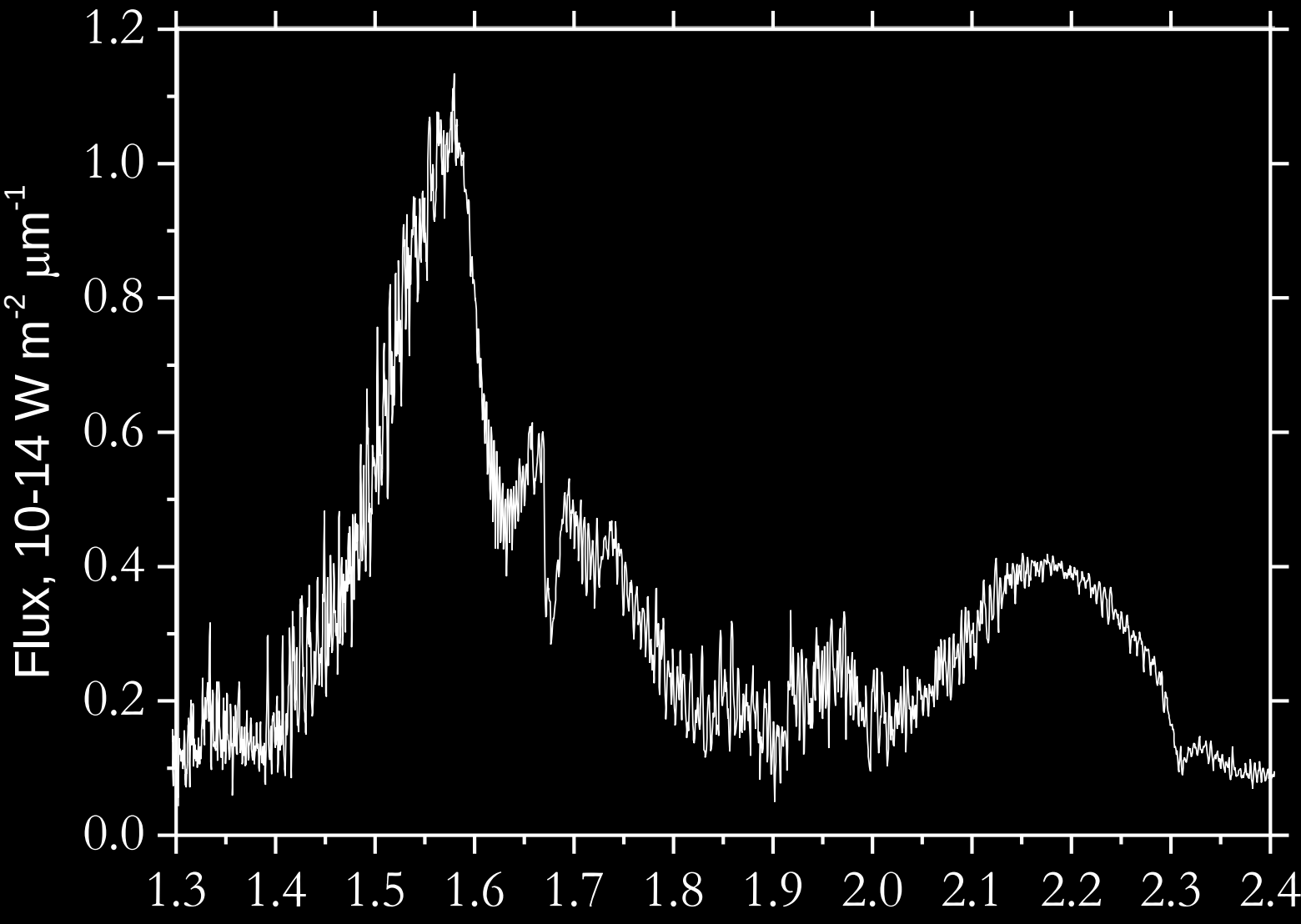
Luckily, most of applications require to be either accurate or complete

For example, the microwave spectral applications must be accurate but not so much complete

Most of the opacity applications (atmospheric retrievals) require to be complete not so much accurate

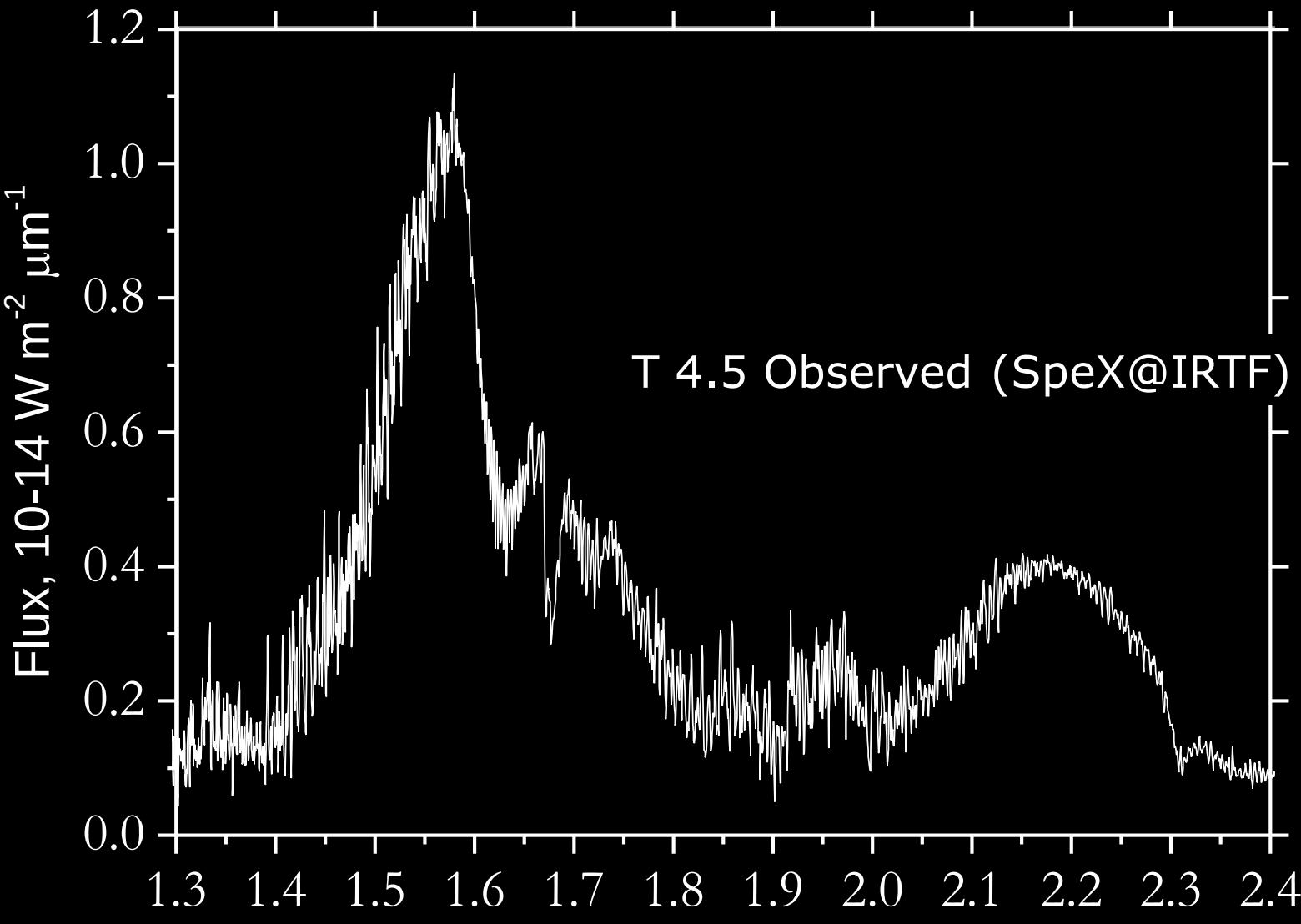
Example: brown dwarf spectra

T4.5 Brown dwarf 2MASS 0559-14



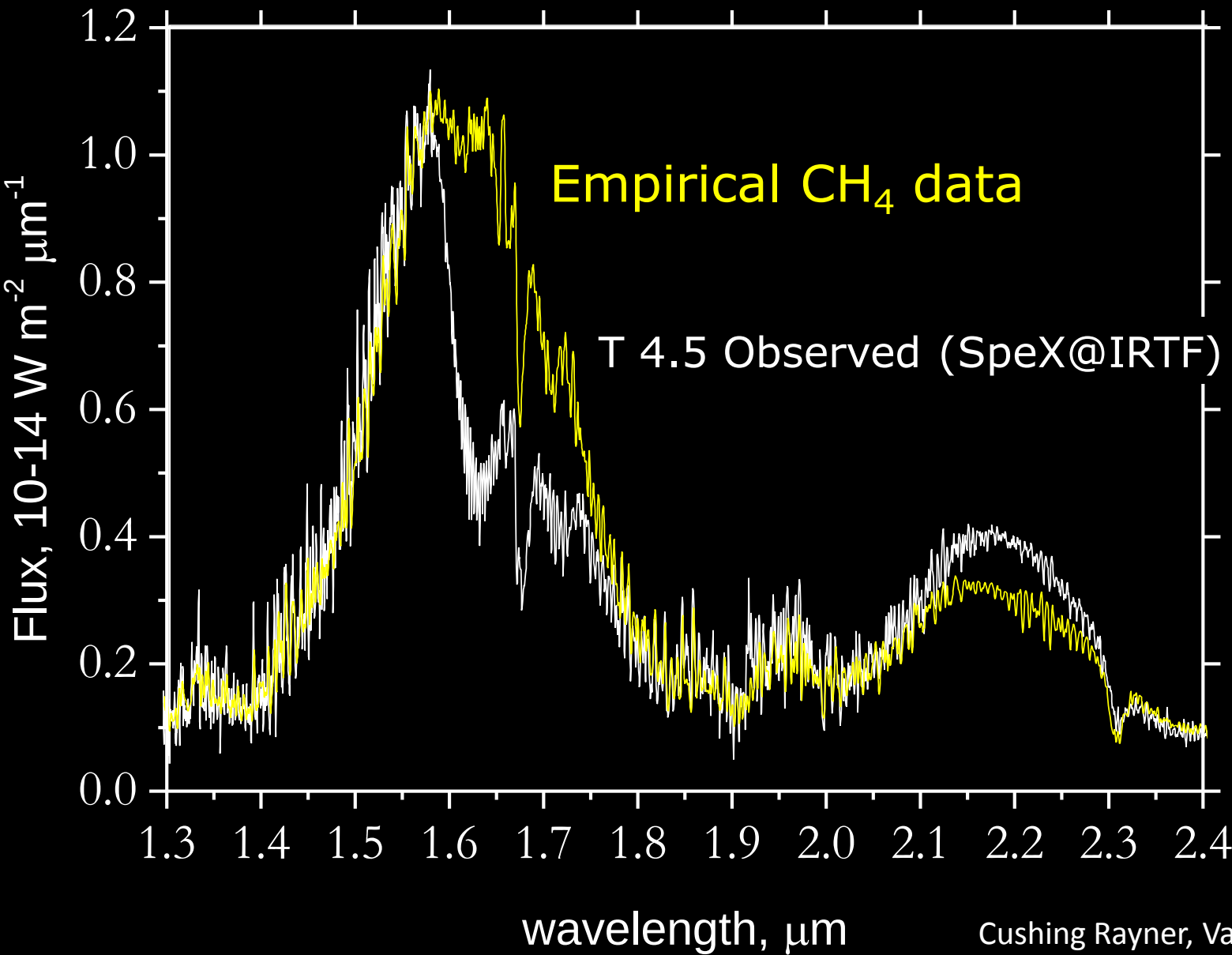
Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14



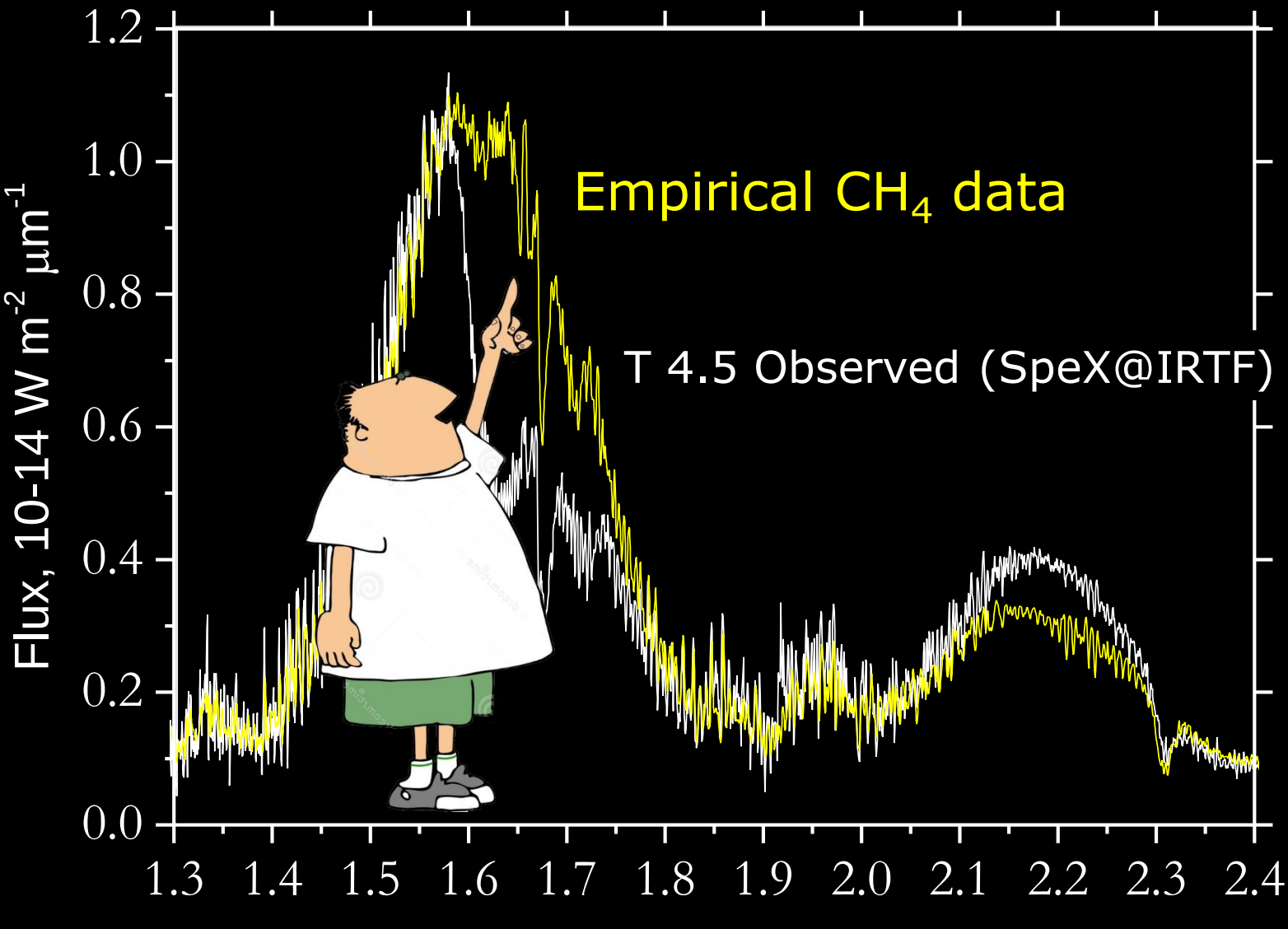
Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14



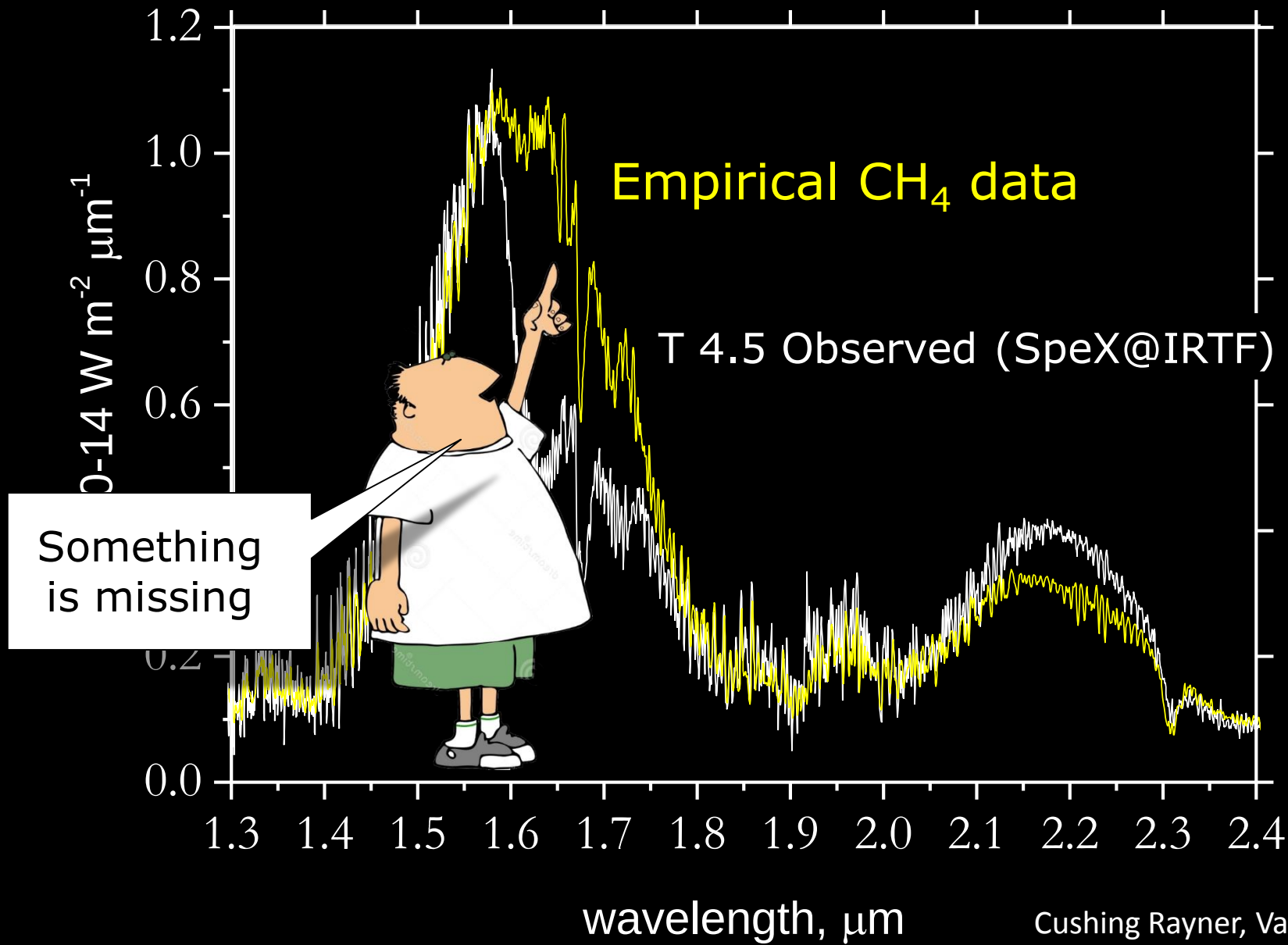
Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14

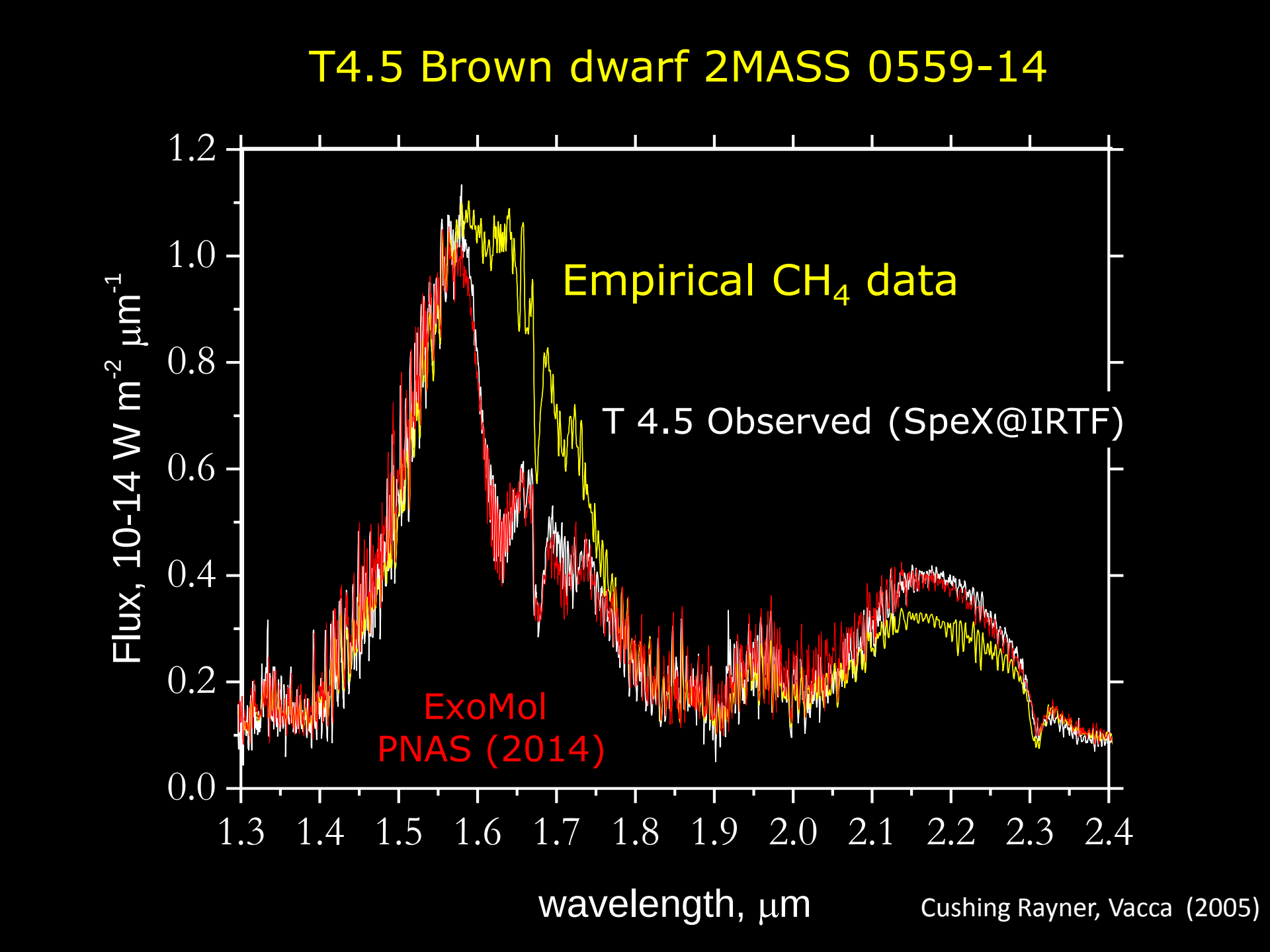


Cushing Rayner, Vacca (2005)

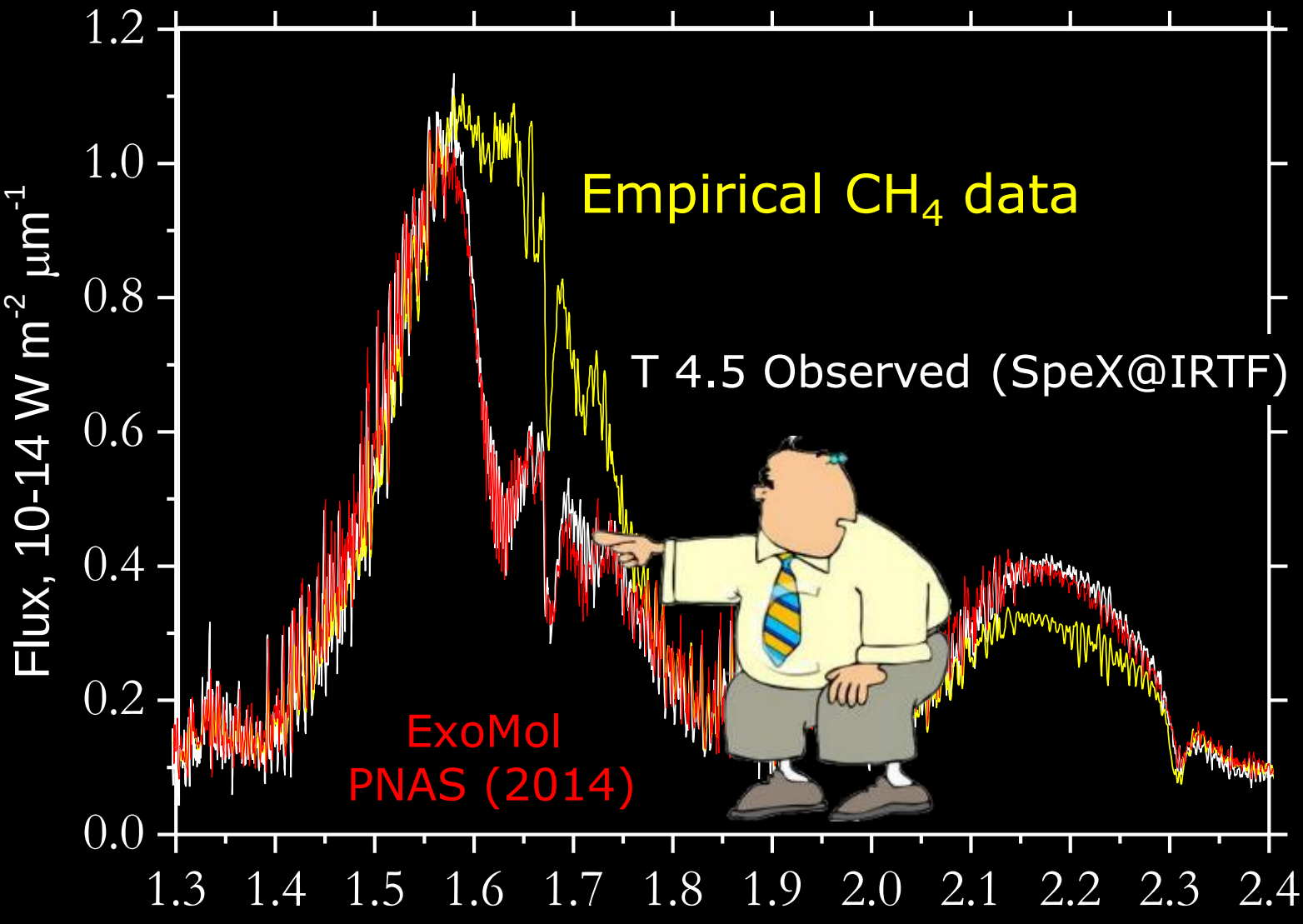
T4.5 Brown dwarf 2MASS 0559-14



Cushing Rayner, Vacca (2005)

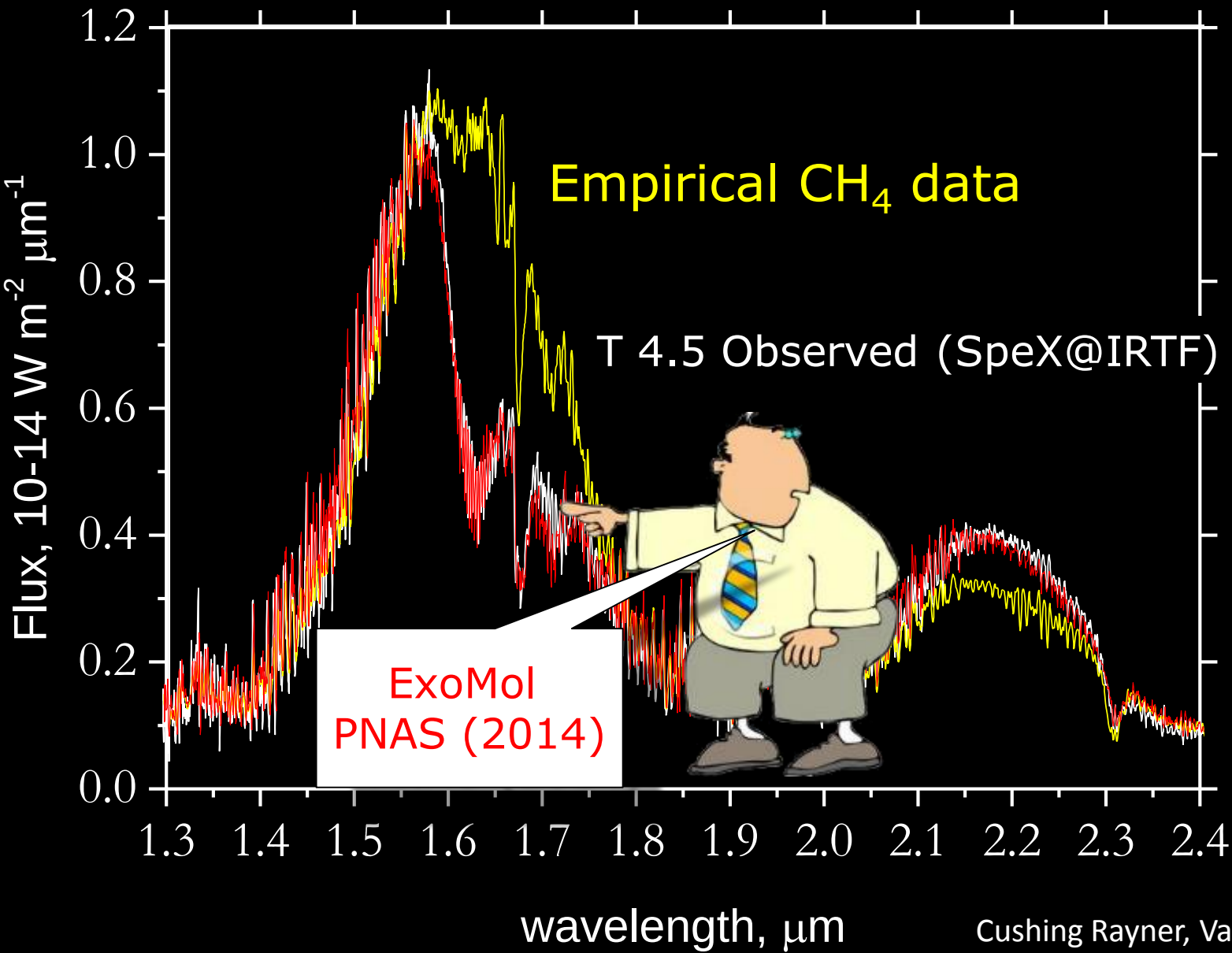

T4.5 Brown dwarf 2MASS 0559-14
Empirical CH_4 data
T 4.5 Observed (SpeX@IRTF)
ExoMol
PNAS (2014)
Flux, 10-14 W m^{-2} μm^{-1}
wavelength, μm
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4
Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14



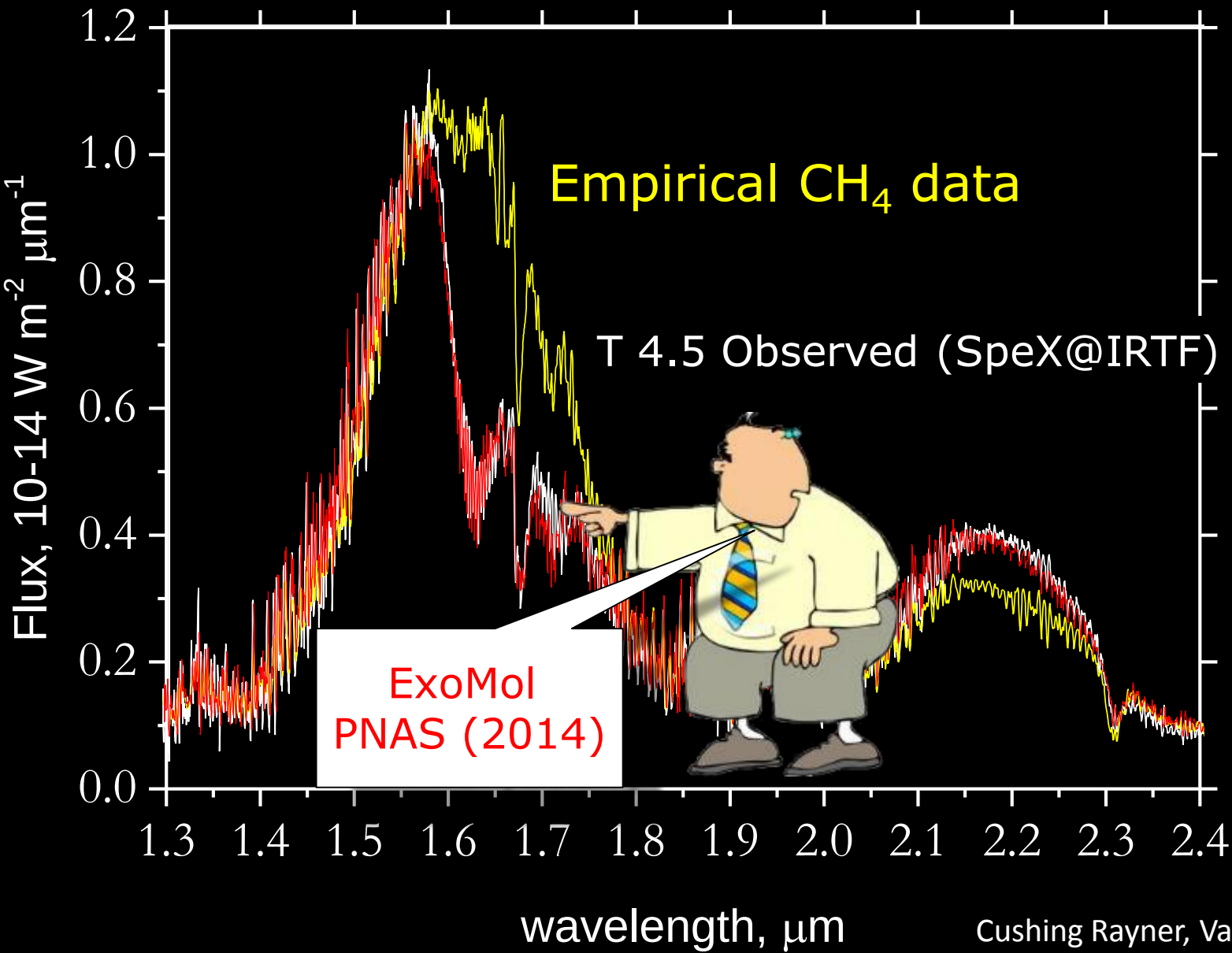
Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14



Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14



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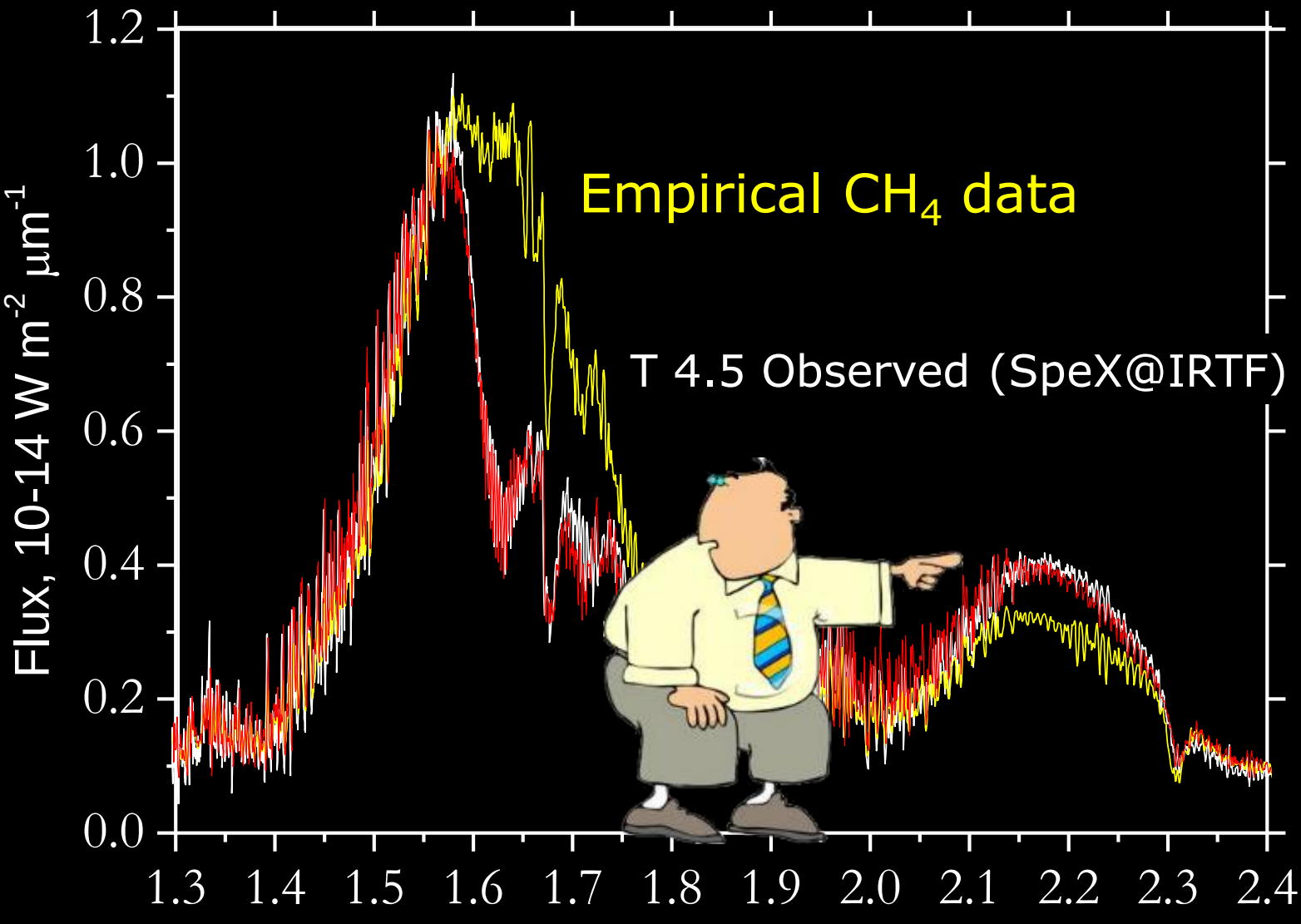
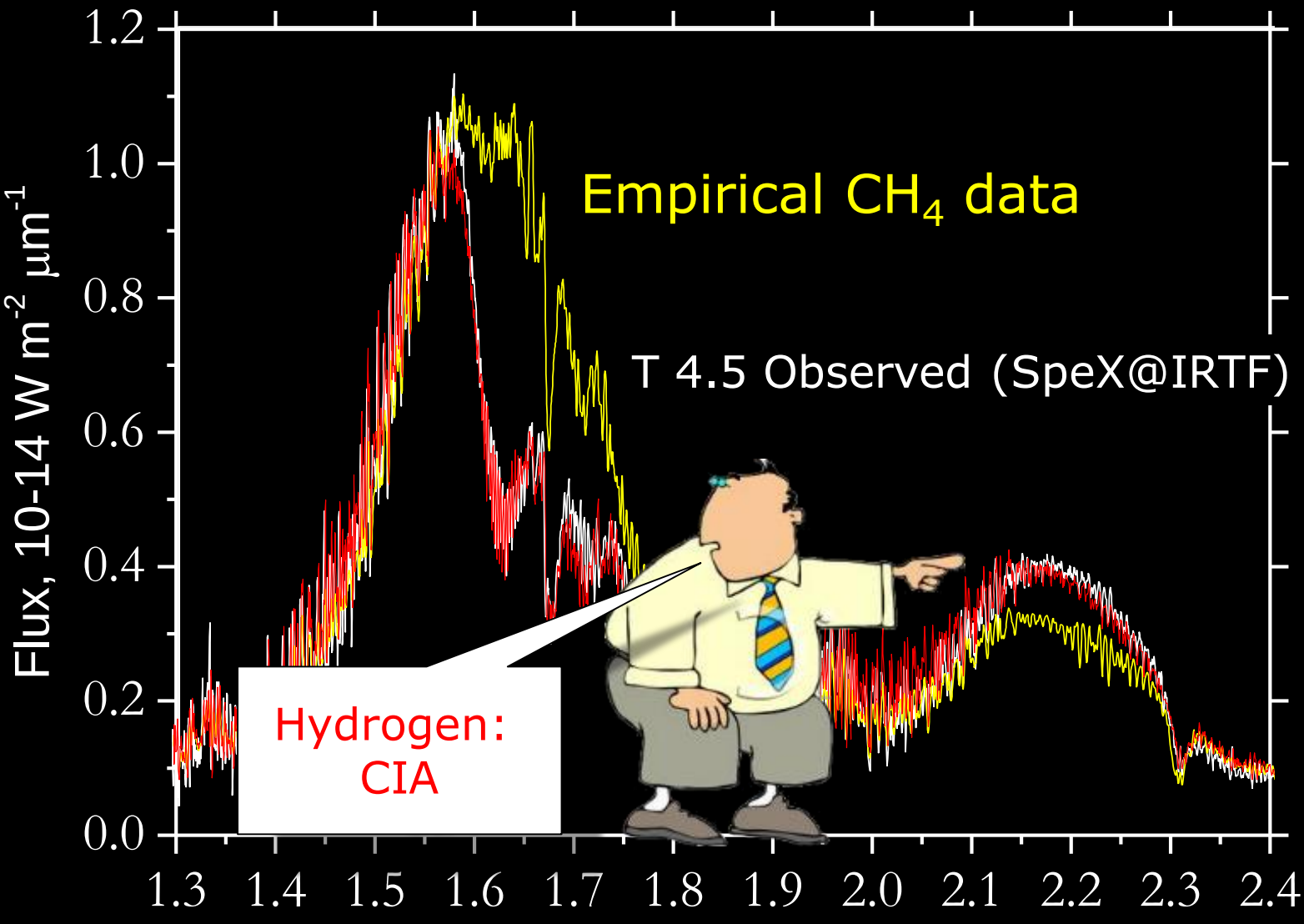
T4.5 Brown dwarf 2MASS 0559-14

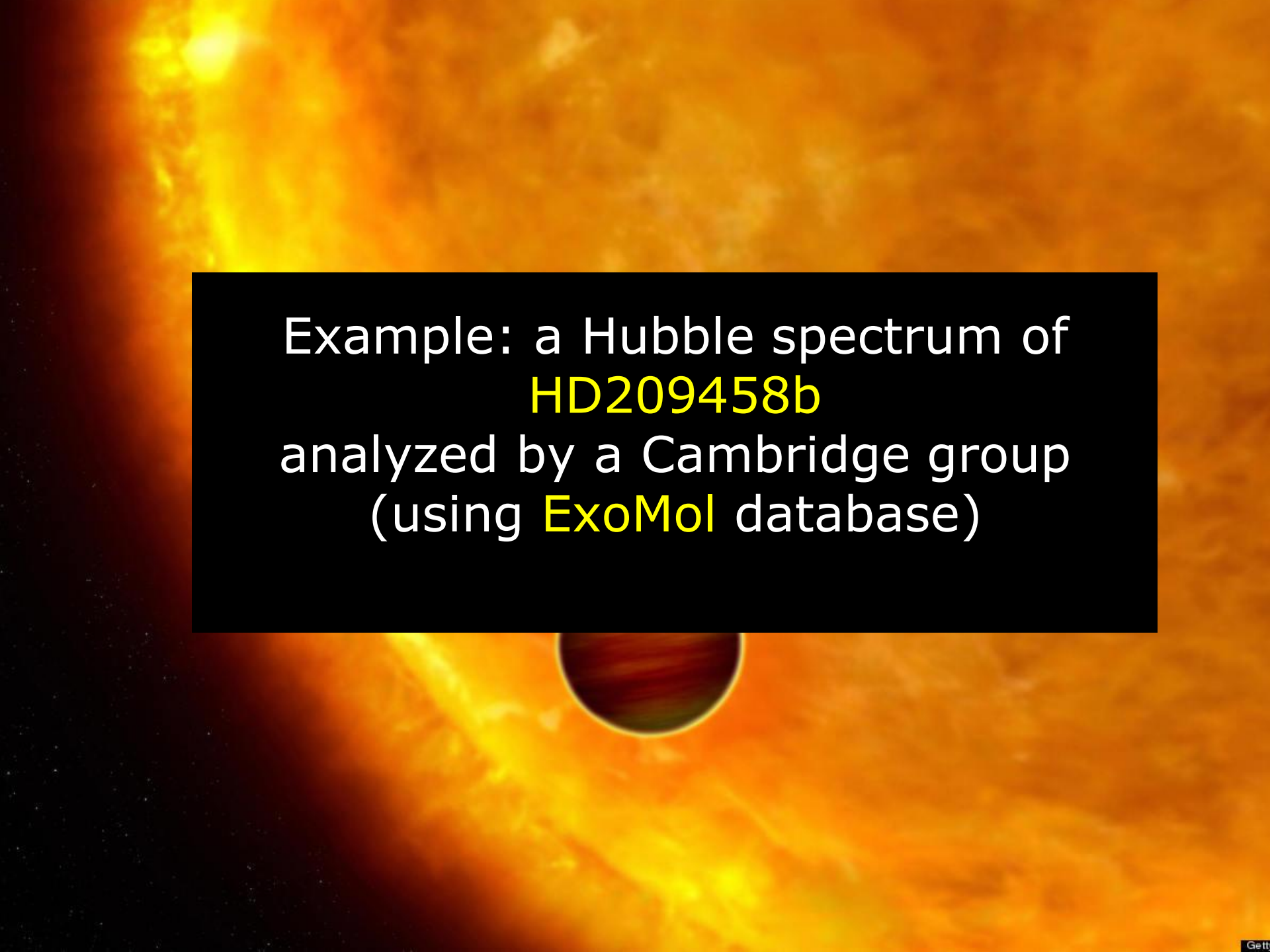


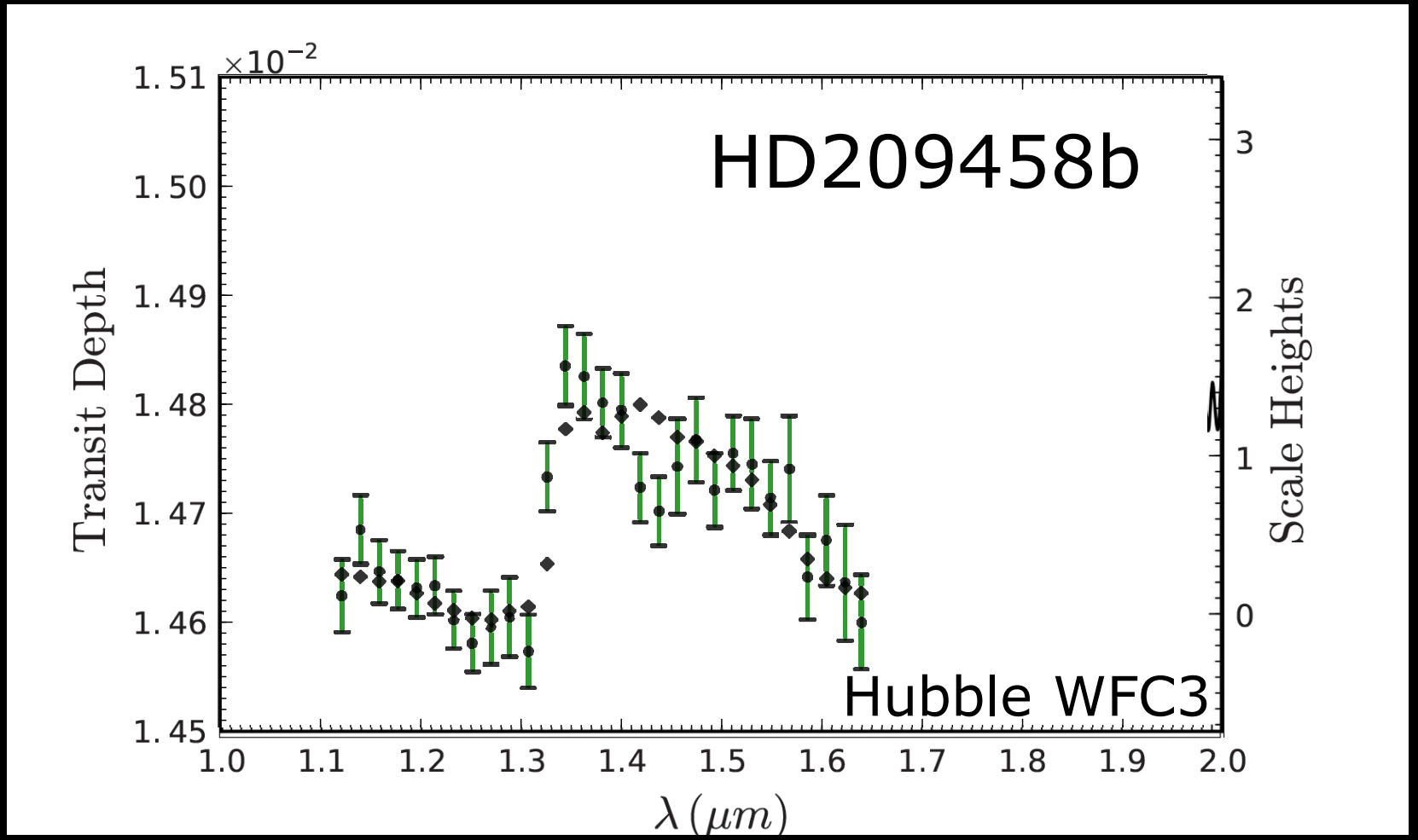
Cushing Rayner, Vacca (2005)

T4.5 Brown dwarf 2MASS 0559-14

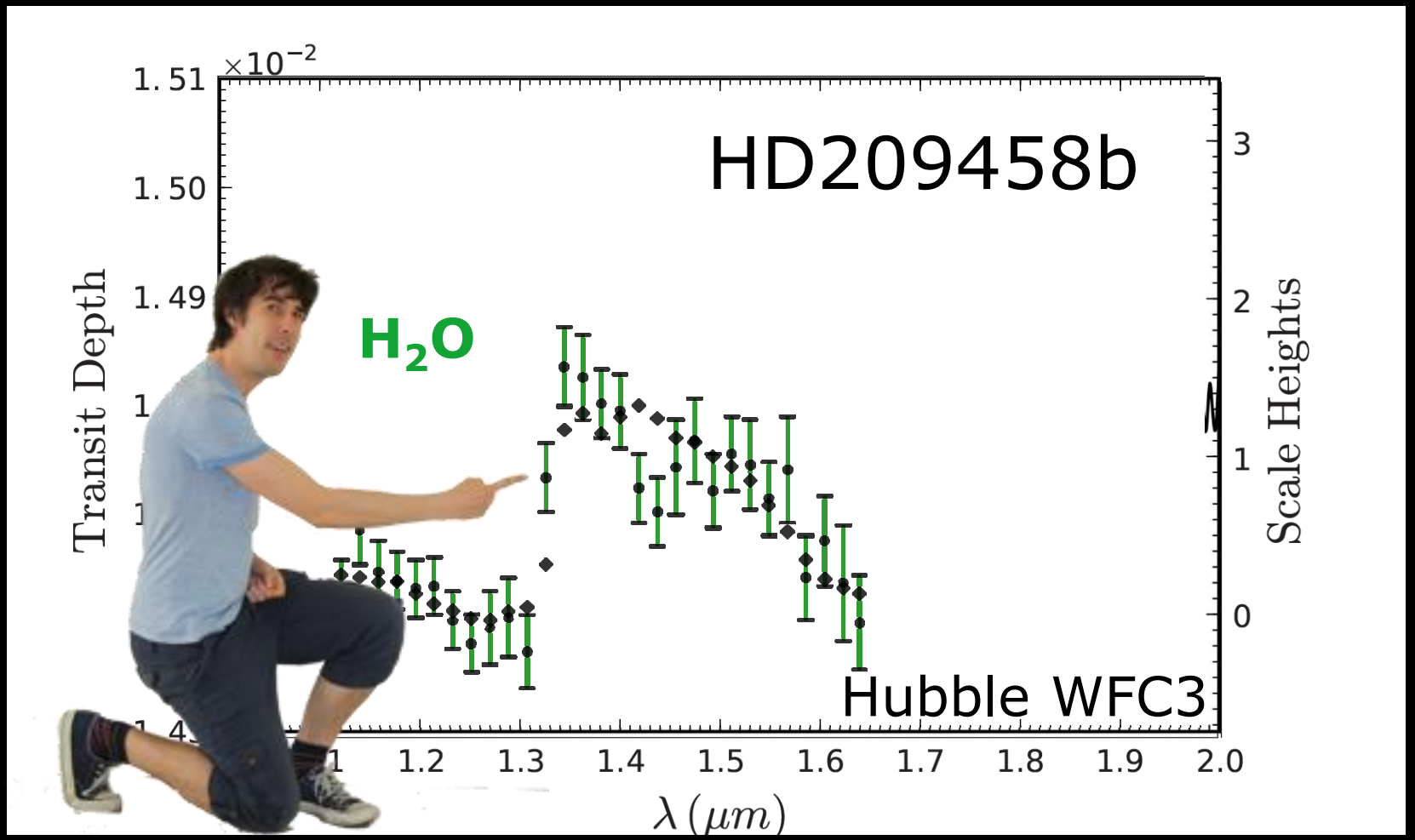


Cushing Rayner, Vacca (2005)

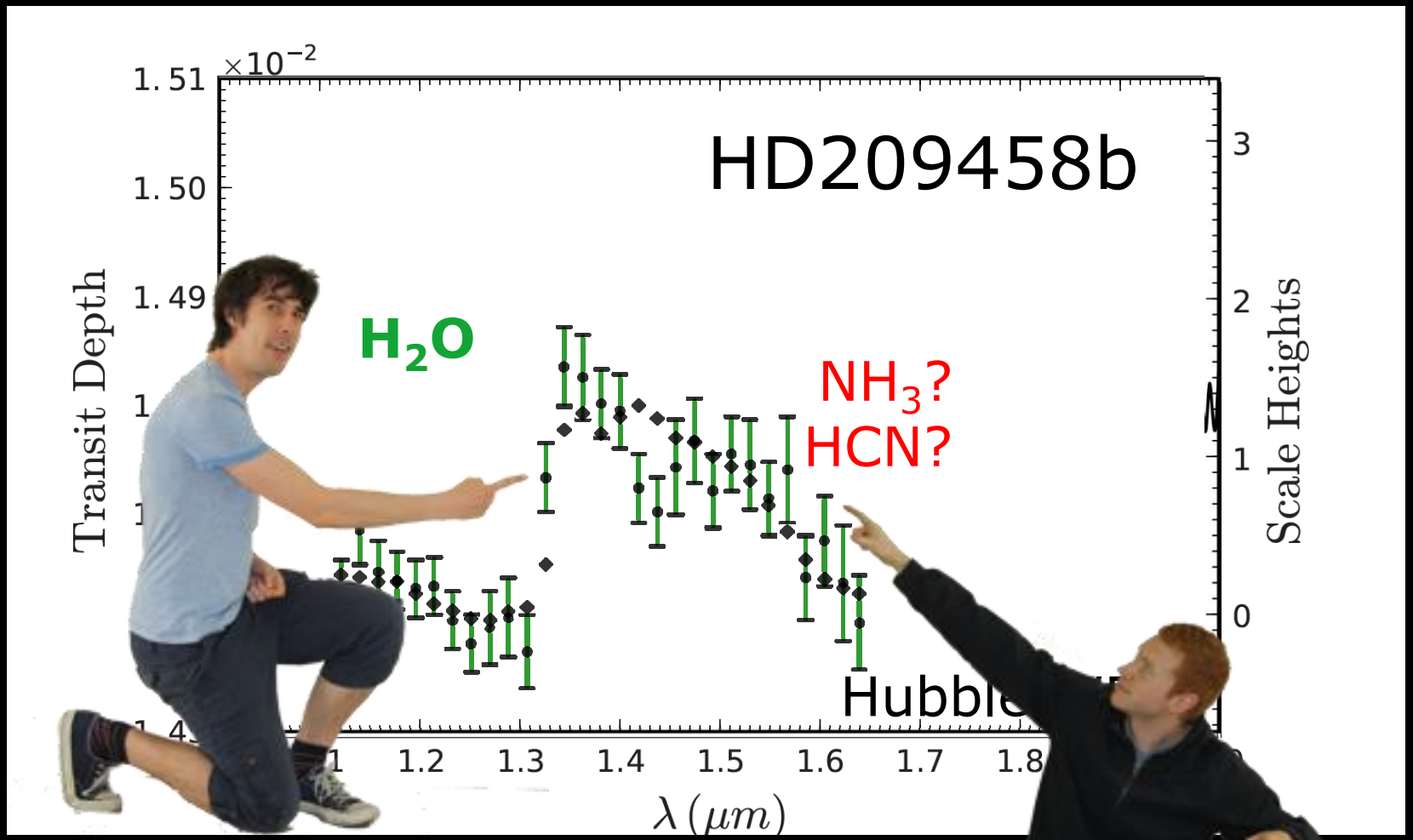

Example: a Hubble spectrum of
HD209458b
analyzed by a Cambridge group
(using ExoMol database)



MacDonald and Madhusudhan (2017)

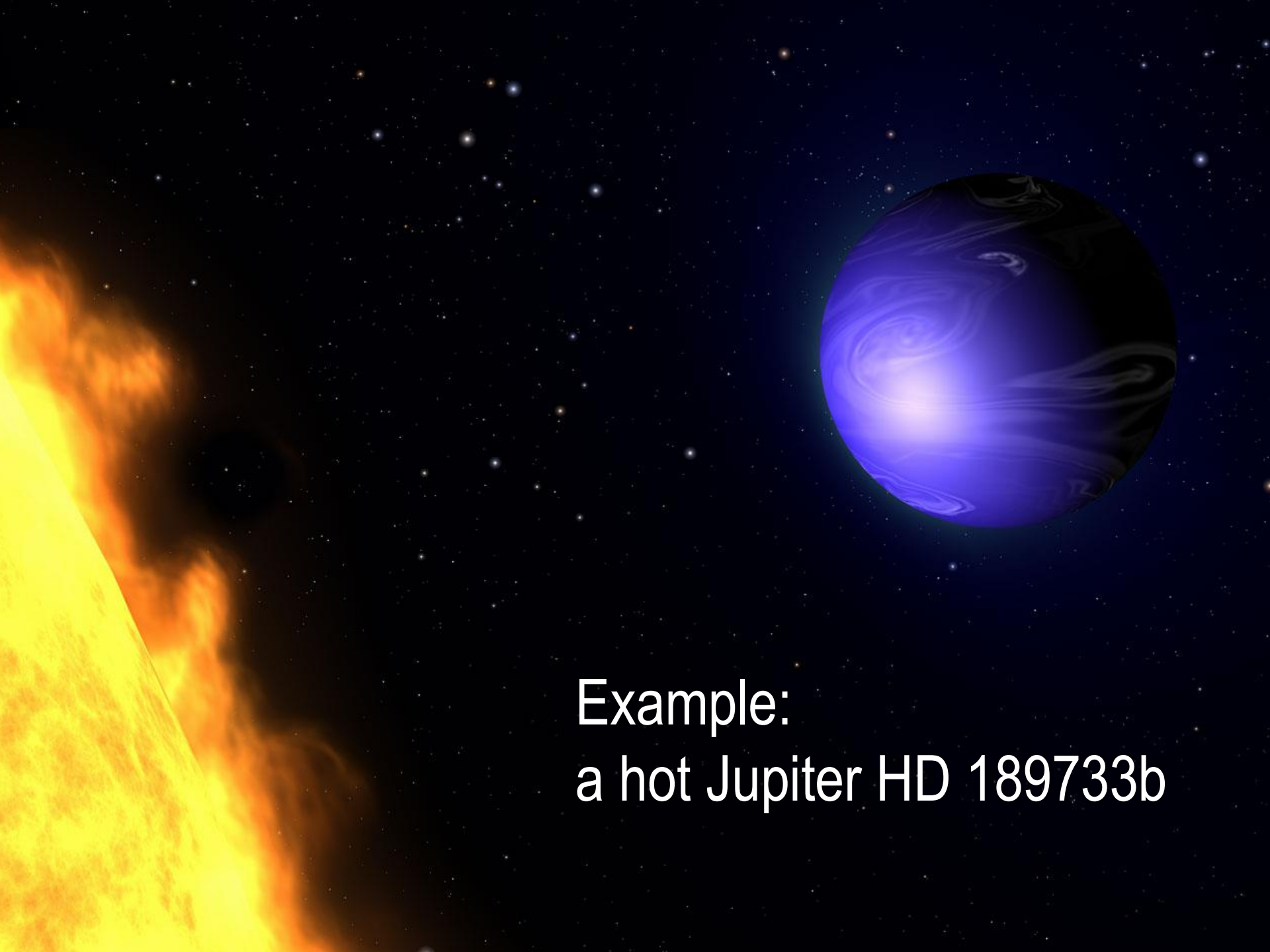


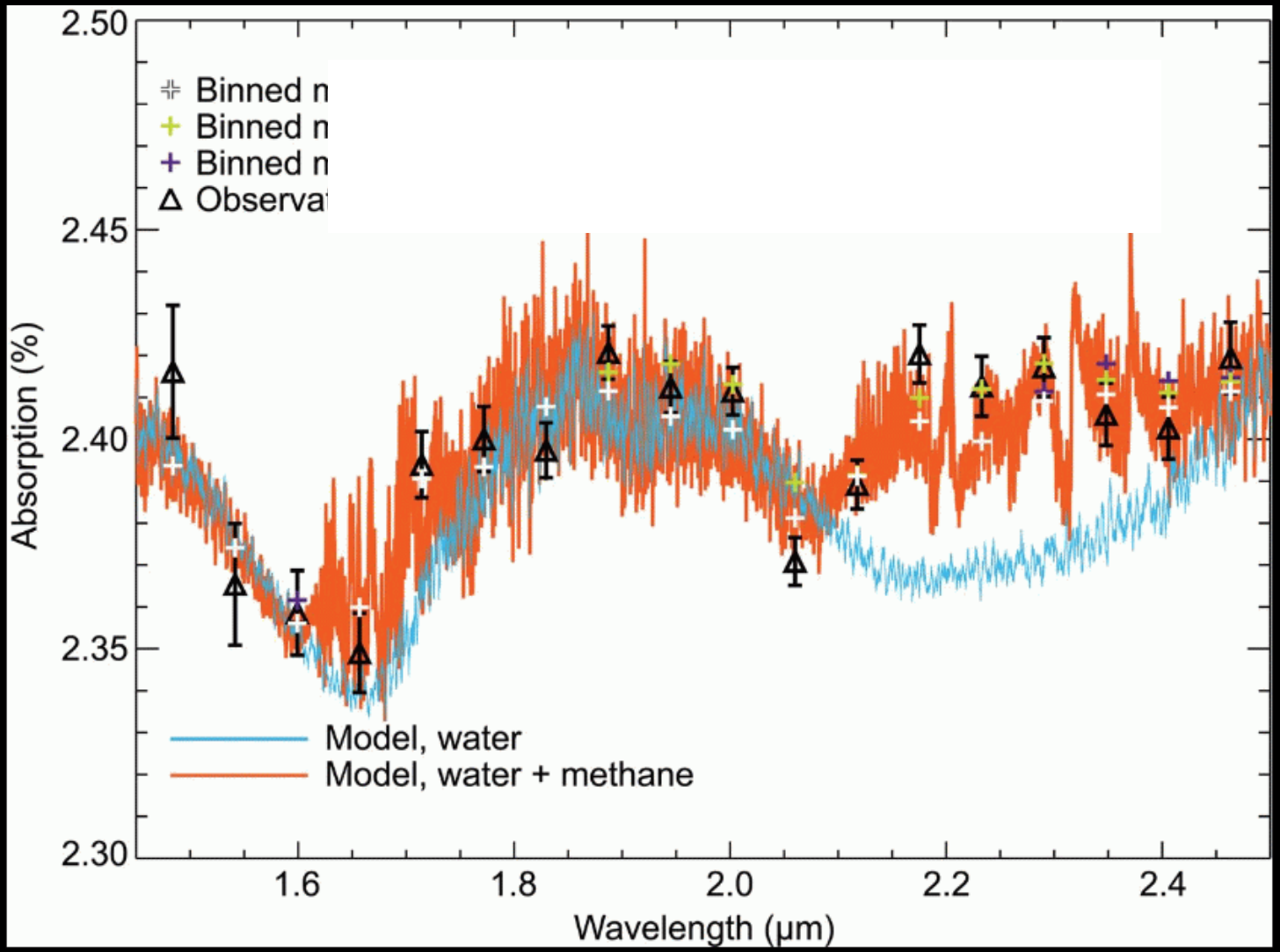
MacDonald and Madhusudhan (2017)



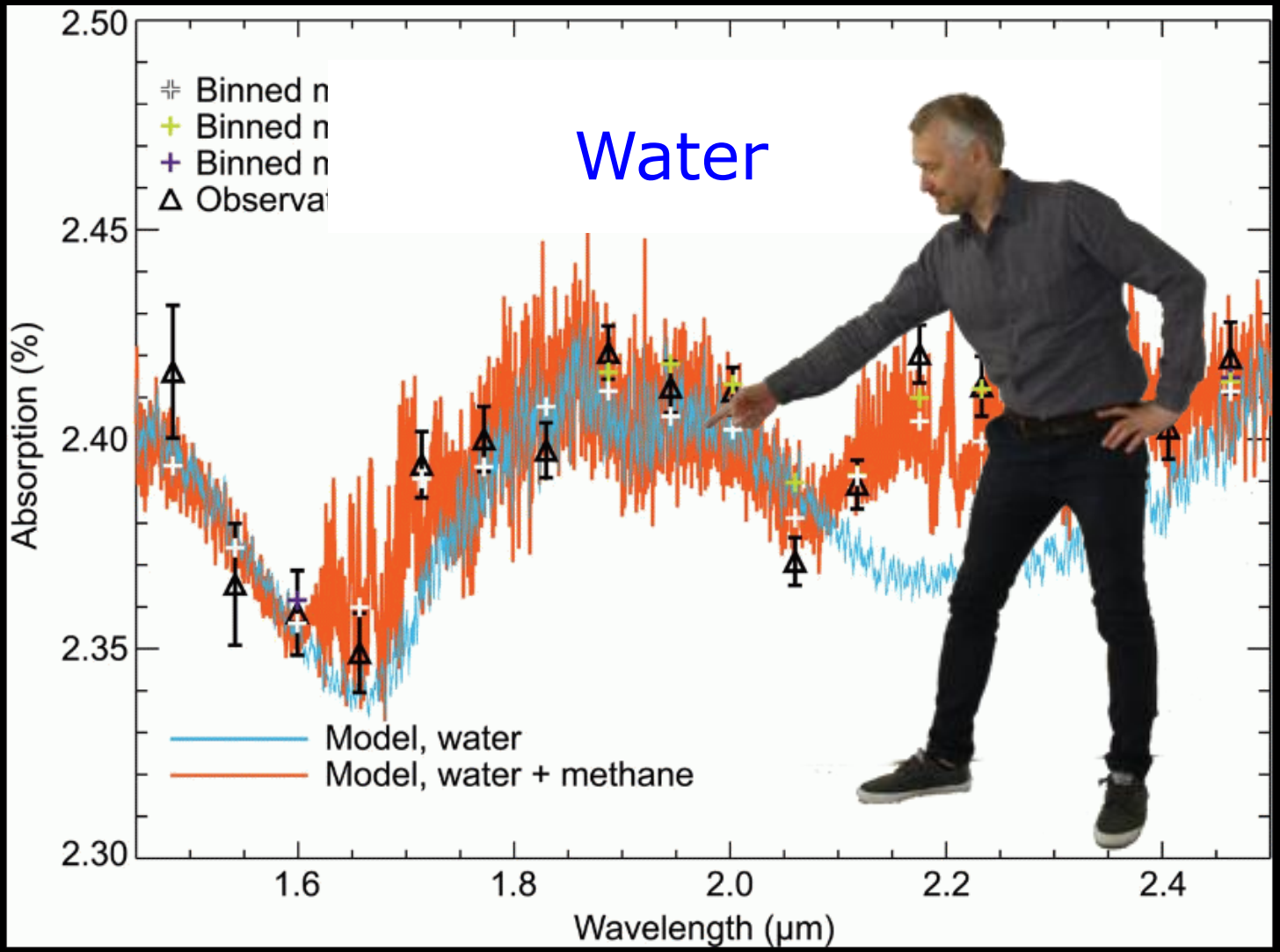
MacDonald and Madhusudhan (2017)

Water and Methane are
usually first to find

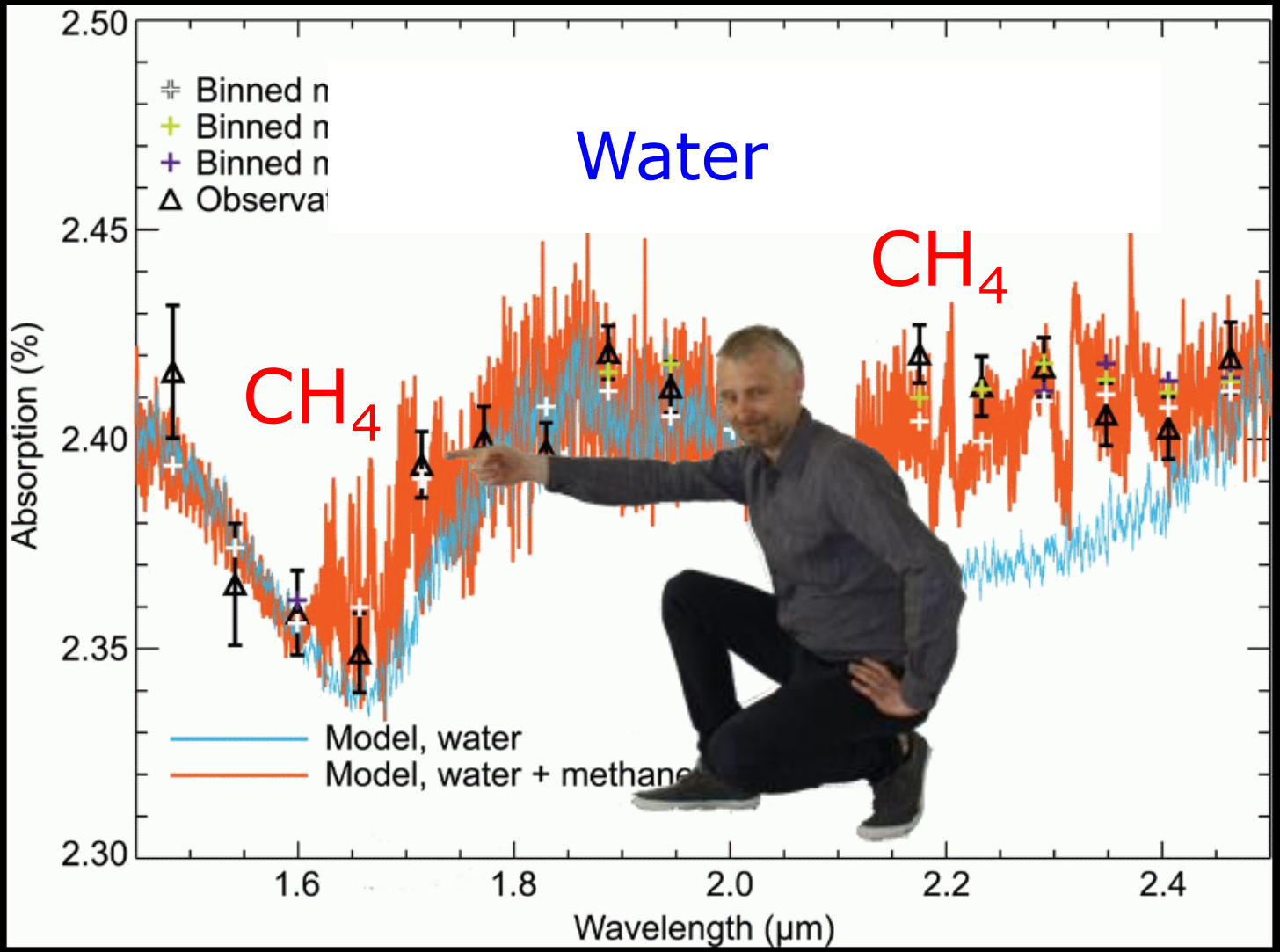

Example:
a hot Jupiter HD 189733b



Swain et al Nature **452**, 329-331 (2008)



Swain et al Nature **452**, 329-331 (2008)



Swain et al Nature **452**, 329-331 (2008)

Polyatomics: Method for solving the nuclear motion Schrödinger equation

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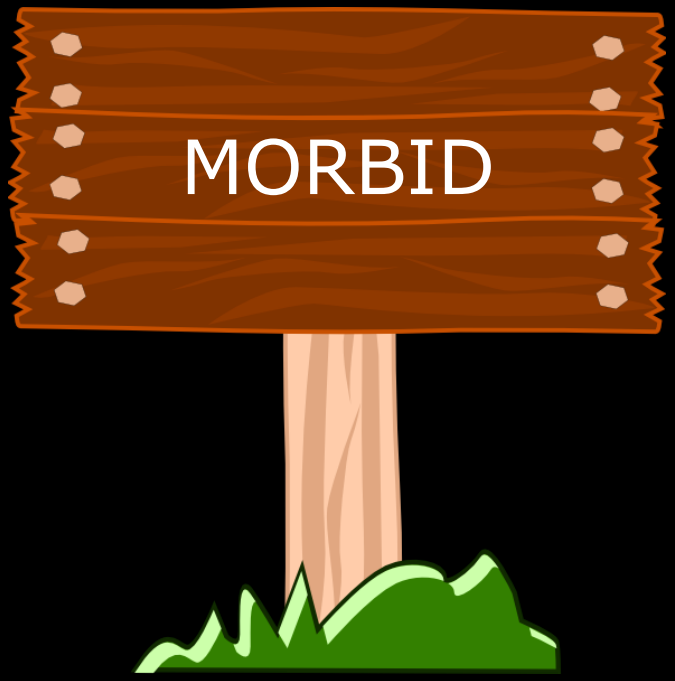
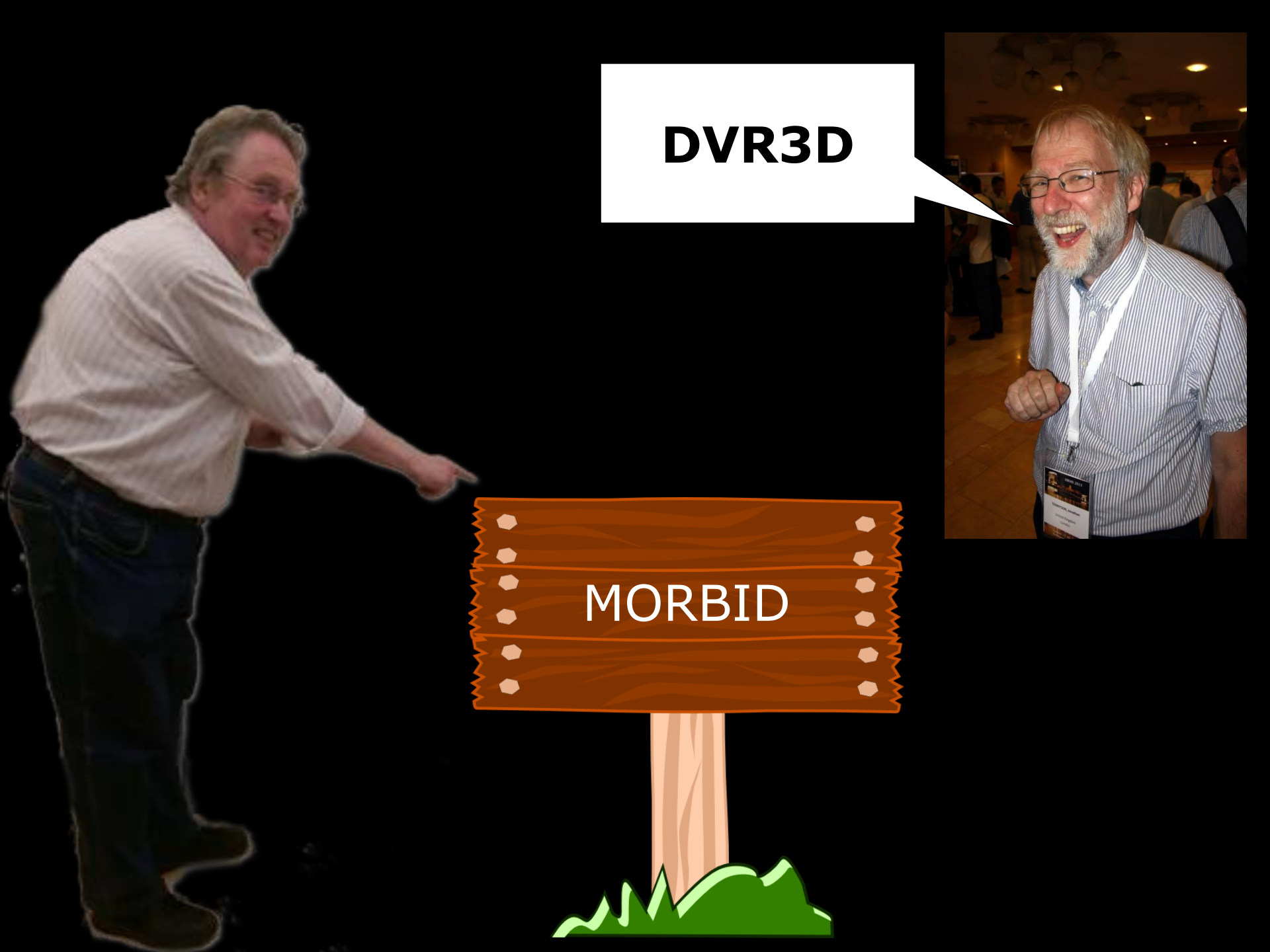
TROVE


MORBID


MORBID


DVR3D
MORBID

Ingredients and calculation steps are essentially the same as for diatomics

1. Accurate ab initio potential energy surface

…computed with
CCSD(T)-F12b/aug-cc-pVQZ-DK
MOLPRO

+ corrections:
cc-pCVTZ, CCSD(T),
CCSDT, and CCSDT(Q)
CFOUR

2. Accurate ab inition Dipole Moment Surface

2. Accurate ab inition Dipole Moment Surface

Typical Dipoles:
CCSD(T)/aug-cc-pVQZ
using finite fields

3: Solve Schrödinger equation

$$H\Psi = E\,\Psi$$

3: Solve Schrödinger equation

… variationally in the matrix representation:

$$\langle \phi_1 \phi_2 \phi_3 \ldots | H | \phi'_1 \phi'_2 \phi'_3 \ldots \rangle$$

The Hamiltonian has to be transferred to the body-fixed system which makes complicated

$$\hat{H} = \sum_{i,j} \frac{\partial}{\partial q_i} G_{ij}(\bar{q}) \frac{\partial}{\partial q_j} +$$

$$+ \sum_{i,\alpha} \frac{\partial}{\partial q_i} G_{i\alpha}(\bar{q})\, \hat{J}_\alpha - \hat{J}_\alpha\, G_{i\alpha}(\bar{q}) \frac{\partial}{\partial q_i} +$$

$$+ \sum_{\alpha,\beta} \hat{J}_\alpha\ G_{\alpha\beta}(\bar{q})\, \hat{J}_\beta +$$

$$+ U(\bar{q}) + V(\bar{q})$$

The most known and widely used is Watsonian

Simplification of the molecular vibration–rotation hamiltonian

JAMES K. G. WATSON

Department of Chemistry, The University, Reading, Berkshire, England

(*Received 5 September 1968*)

By use of the commutation relations and sum rules, the Darling–Dennison vibration–rotation hamiltonian for a nonlinear molecule is rearranged to the form:

$$H = \tfrac{1}{2}\sum_{\alpha\beta}(\Pi_\alpha - \pi_\alpha)\mu_{\alpha\beta}(\Pi_\beta - \pi_\beta) + \tfrac{1}{2}\sum_k P_k^2 - \tfrac{1}{8}\hbar^2\sum_\alpha \mu_{\alpha\alpha} + V.$$

The order of the factors in the first term is immaterial, on account of the relation:

$$\sum_\alpha \pi_\alpha \mu_{\alpha\beta} = \sum_\alpha \mu_{\alpha\beta}\pi_\alpha.$$

A simple expansion is given for the $\mu_{\alpha\beta}$ tensor in terms of the normal coordinates.

1. Introduction

On the basis of the classical expression given by [illegible] Wilson and Howard [1], Darling and Dennison [2]

$$U = -\tfrac{1}{8}\hbar^2\sum_\alpha \mu_{\alpha\alpha}. \qquad (3)$$

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TROVE approach is to *numerically* expand the kinetic energy operator in the sum-of-product form

$$G_{ij}(\bar{q}) = \sum_{n_1 n_2 n_3} G^{(ij)}_{n_1 n_2 n_3} \, q_1^{n_1} q_2^{n_2} q_3^{n_3}$$

$$G_{ij}(\bar{q}) = \sum_{n_1 n_2 n_3} G^{(ij)}_{n_1 n_2 n_3} \, q_1^{n_1} q_2^{n_2} q_3^{n_3}$$

Obtained numerically

$$G_{ij}(\bar{q}) = \sum_{n_1 n_2 n_3} G^{(ij)}_{n_1 n_2 n_3} \, q_1^{n_1} q_2^{n_2} q_3^{n_3}$$

Obtained numerically

$$V(\bar{q}) = \sum_{n_1 n_2 n_3} F_{n_1 n_2 n_3} \, q_1^{n_1} q_2^{n_2} q_3^{n_3}$$

$$G_{ij}(\bar{q}) = \sum_{n_1 n_2 n_3} G^{(ij)}_{n_1 n_2 n_3} \, q_1^{n_1} q_2^{n_2} q_3^{n_3}$$

Obtained numerically

$$V(\bar{q}) = \sum_{n_1 n_2 n_3} F_{n_1 n_2 n_3} \, q_1^{n_1} q_2^{n_2} q_3^{n_3}$$

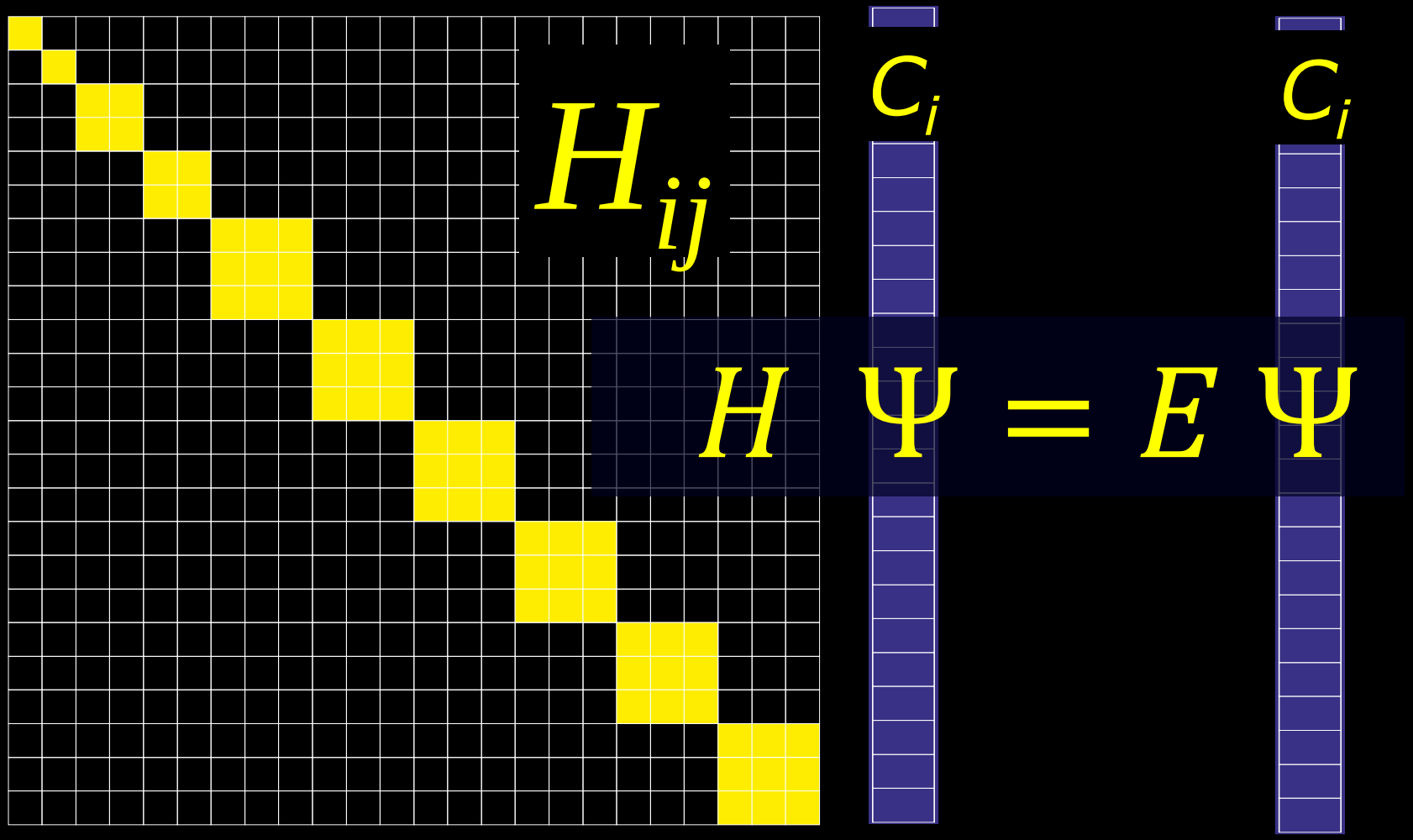
Obtained numerically

… which is good for product-type basis set representations

… which is good for product-type basis set representations

$$\Phi = |J, k, m\rangle|v_1\rangle|v_2\rangle|v_3\rangle \ldots$$

We use a symmetry adapted basis so that the Hamiltonian matrix is block-diagonal


H_{ij}
c_i
c_i
$H\ \Psi = E\ \Psi$

In fact last year we published a paper on an automatic symmetrisation procedure we use

JCTC Journal of Chemical Theory and Computation

Article

pubs.acs.org/JCTC

Symmetry-Adapted Ro-vibrational Basis Functions for Variational Nuclear Motion Calculations: TROVE Approach

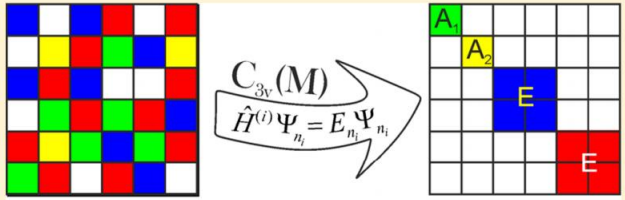
Sergei N. Yurchenko,*[,†] Andrey Yachmenev,[‡] and Roman I. Ovsyannikov[¶]

[†]Department of Physics and Astronomy, University College London, London, WC1E 6BT, United Kingdom

[‡]Center for Free-Electron Laser Science (CFEL), DESY, Notkestrasse 85, 22607 Hamburg, Germany

[¶]Institute of Applied Physics, Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod, Russia 603950

ABSTRACT: We present a general, numerically motivated approach to the construction of symmetry-adapted basis functions for solving ro-vibrational Schrödinger equations. The approach is based on the property of the Hamiltonian operator to commute with the complete set of symmetry operators and, hence, to reflect the symmetry of the system. The symmetry-adapted ro-vibrational basis set is constructed numerically by solving a set of reduced vibrational eigenvalue



Symmetry adaptation without symmetry operations

JCTC Journal of Chemical Theory and Computation

Article

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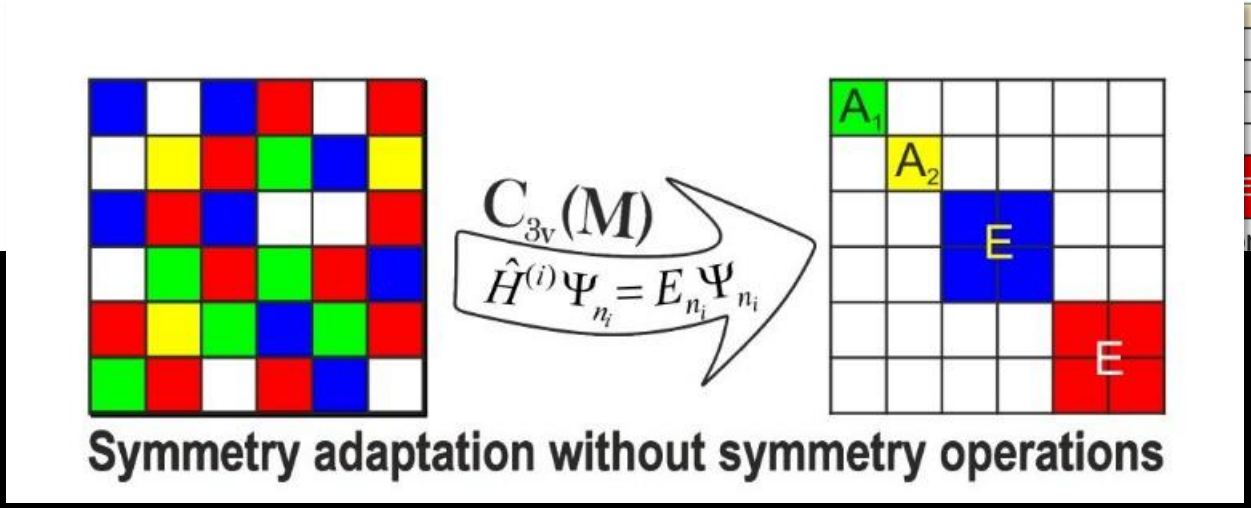

JCTC Journal of Chemical Theory and Computation

Article

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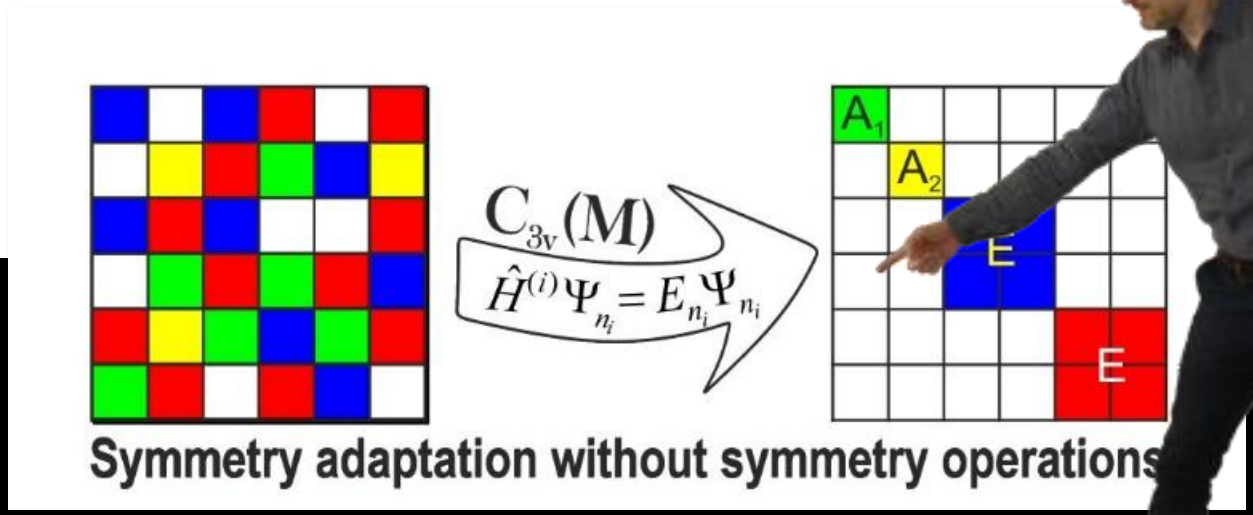
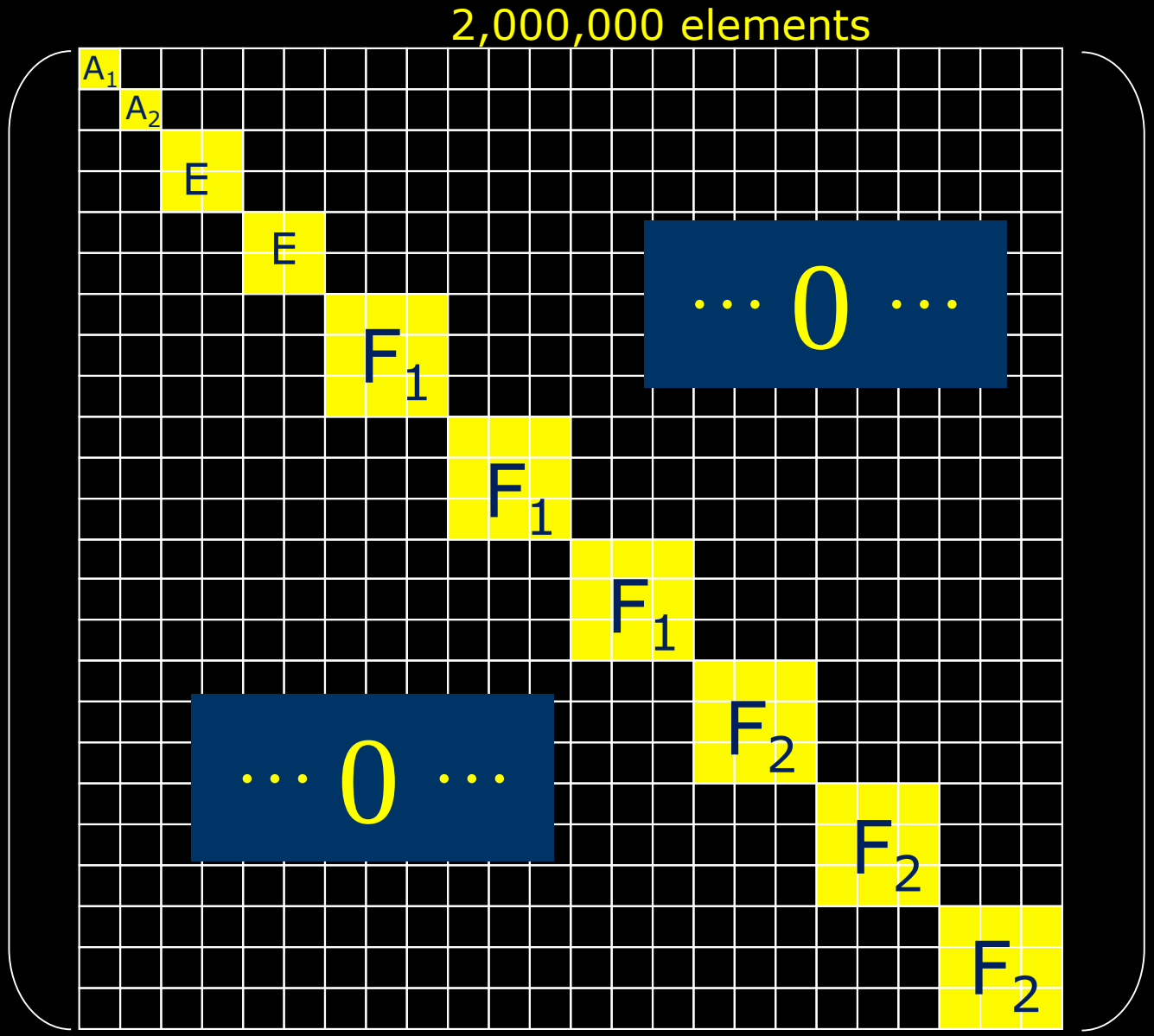


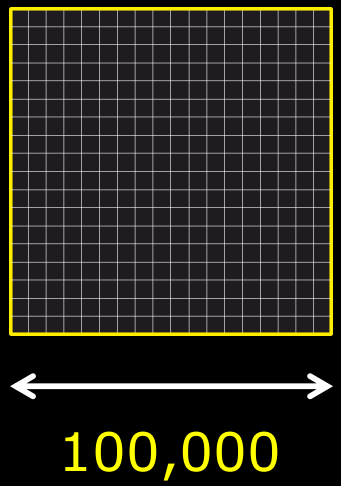
Symmetries help to reduce the dimension

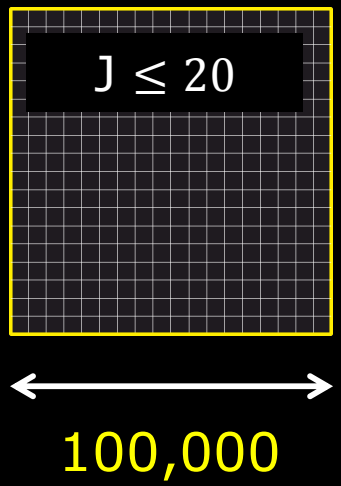
$T_d(M)$

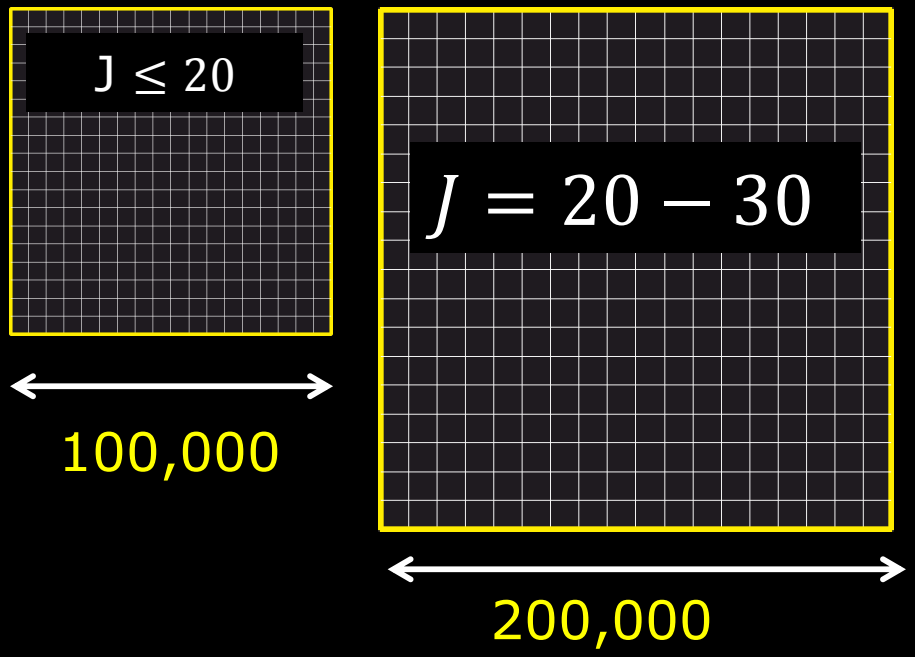

2,000,000 elements
2,000,000 elements
A1
A2
E
E
F1
F1
F1
F2
F2
F2
… 0 …
… 0 …

… and obligatory for intensity calculations

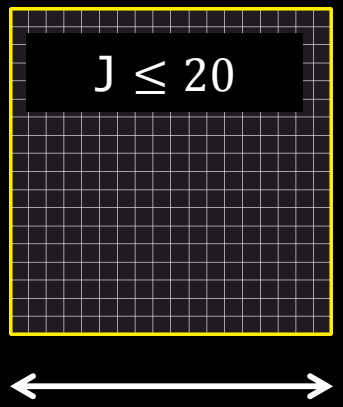
Then we diagonalize the Hamiltonian matrices


100,000

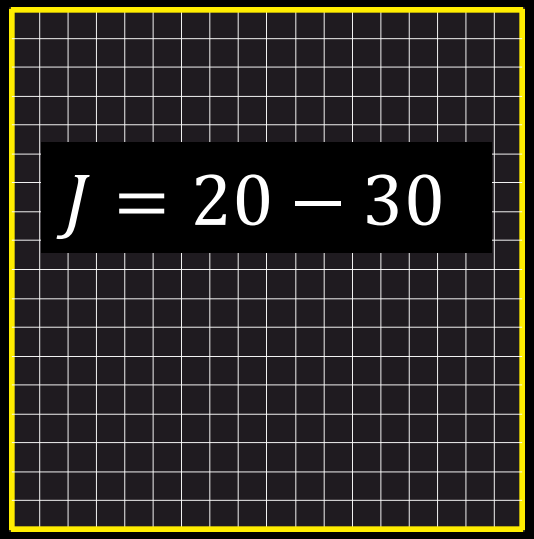

J ≤ 20
100,000


J ≤ 20
100,000
J = 20 – 30
200,000

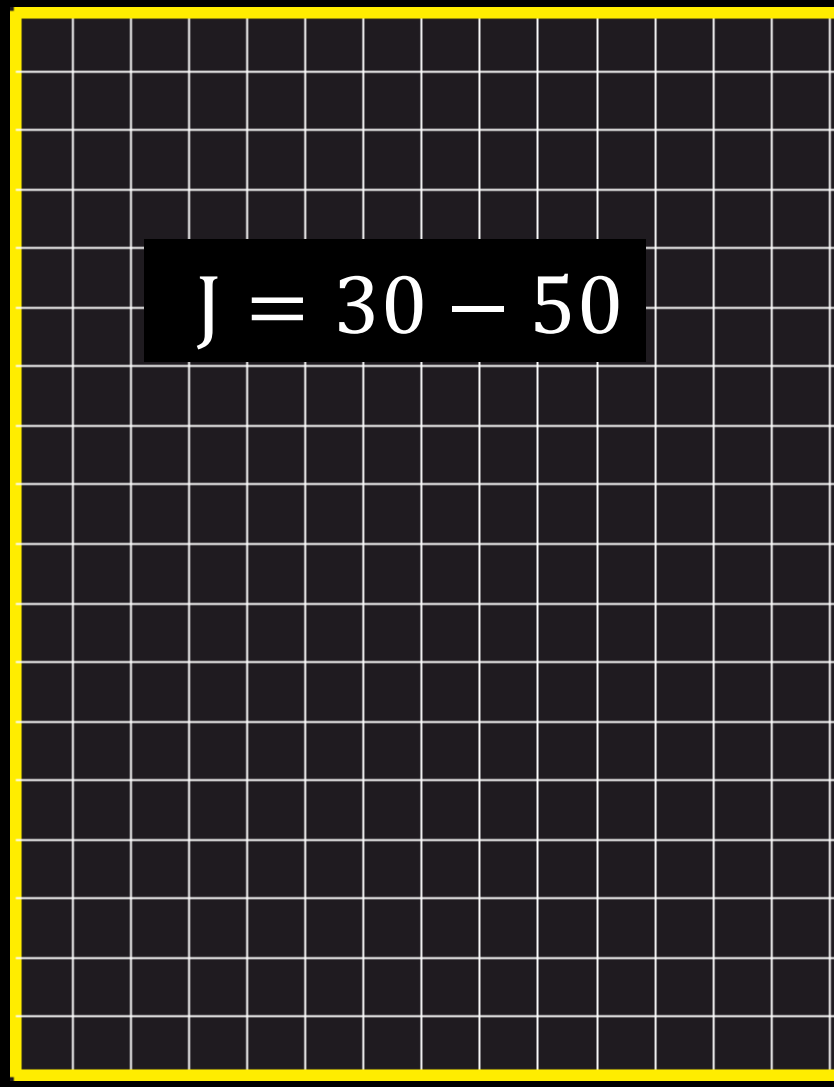
1-2 M CPUh total



100,000



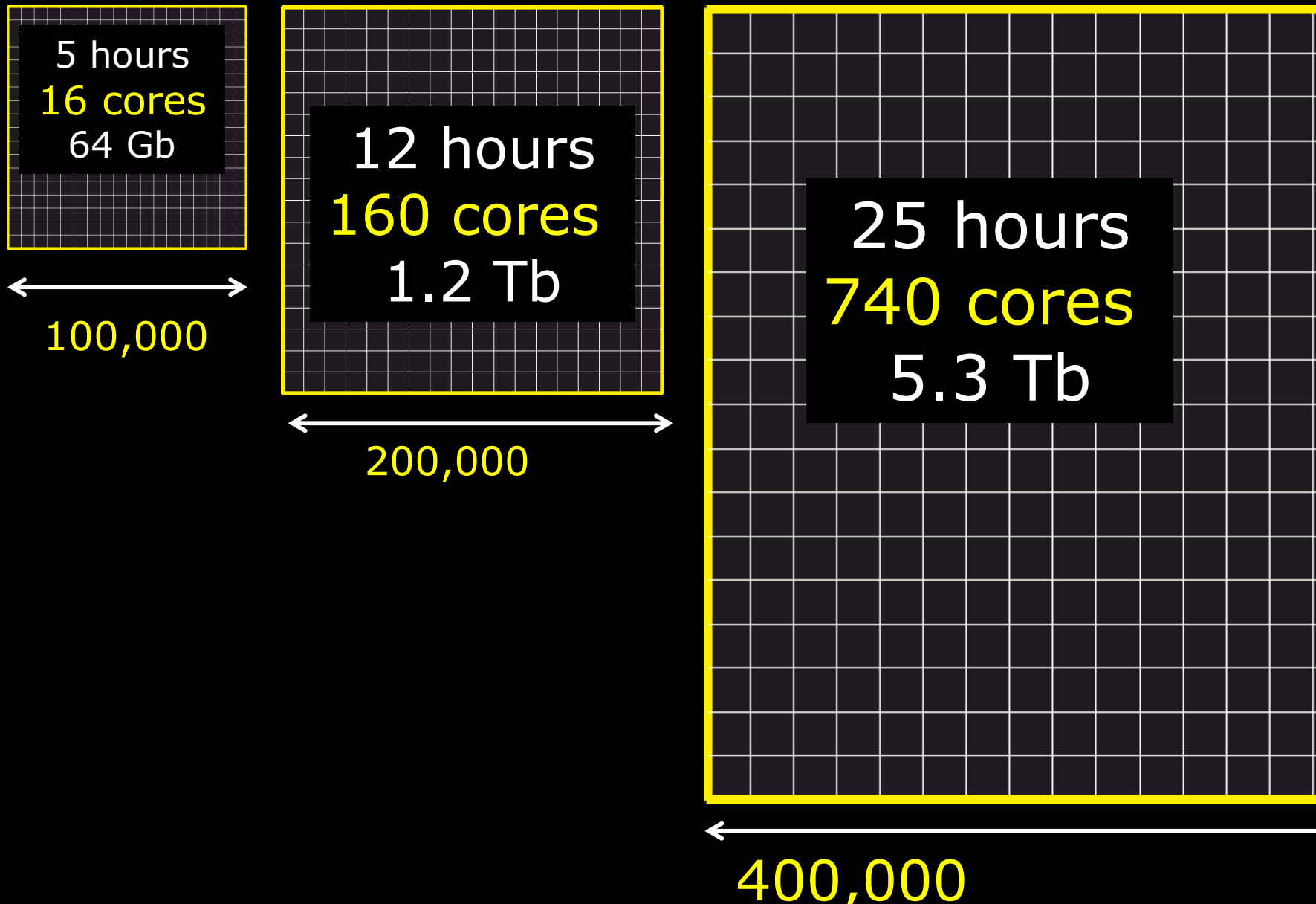
200,000

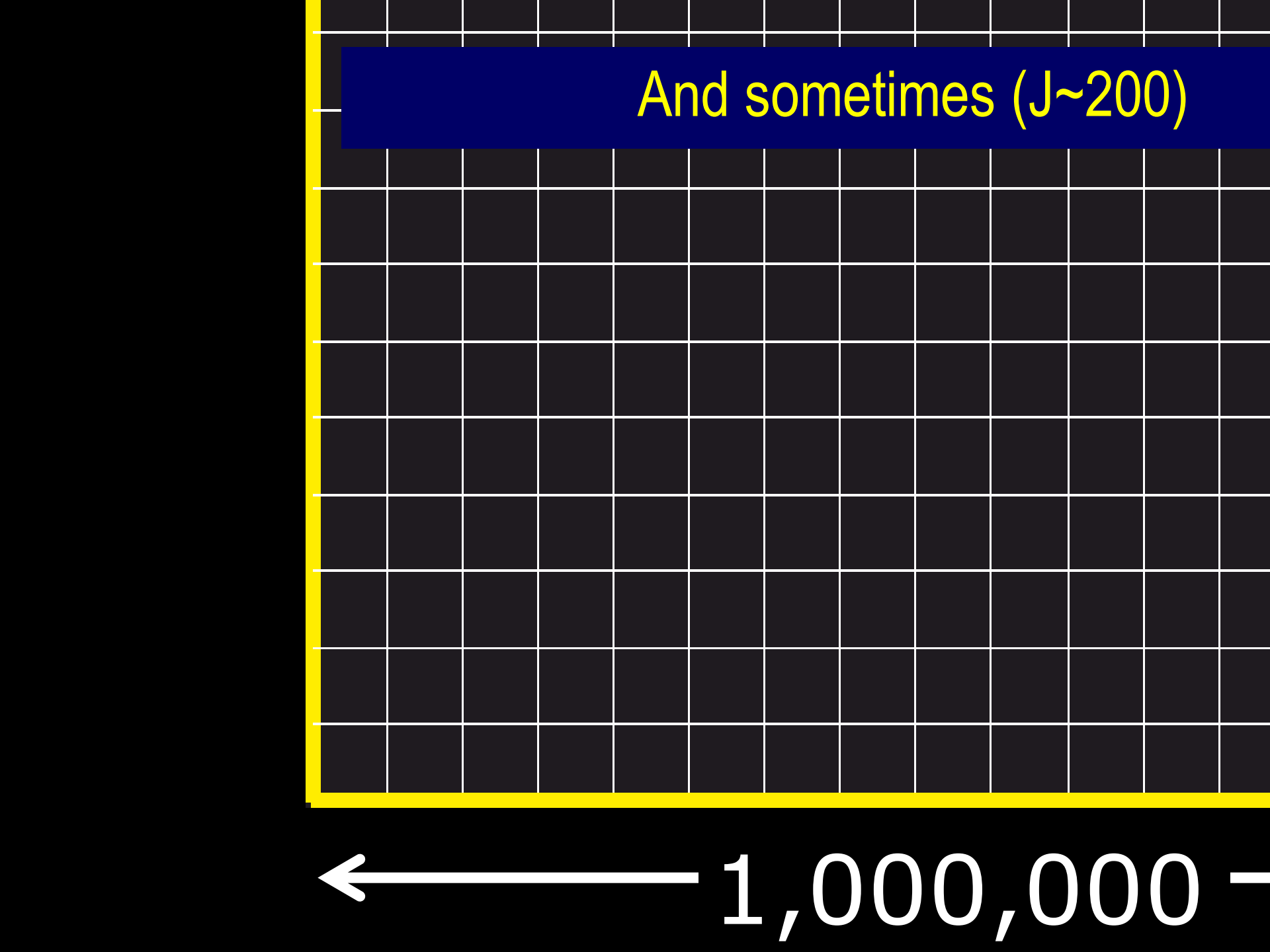


400,000

Diagonalization: Time vs size

1-2 M CPUh total




And sometimes (J~200)
1,000,000

And sometimes (J~200)

1,000,000

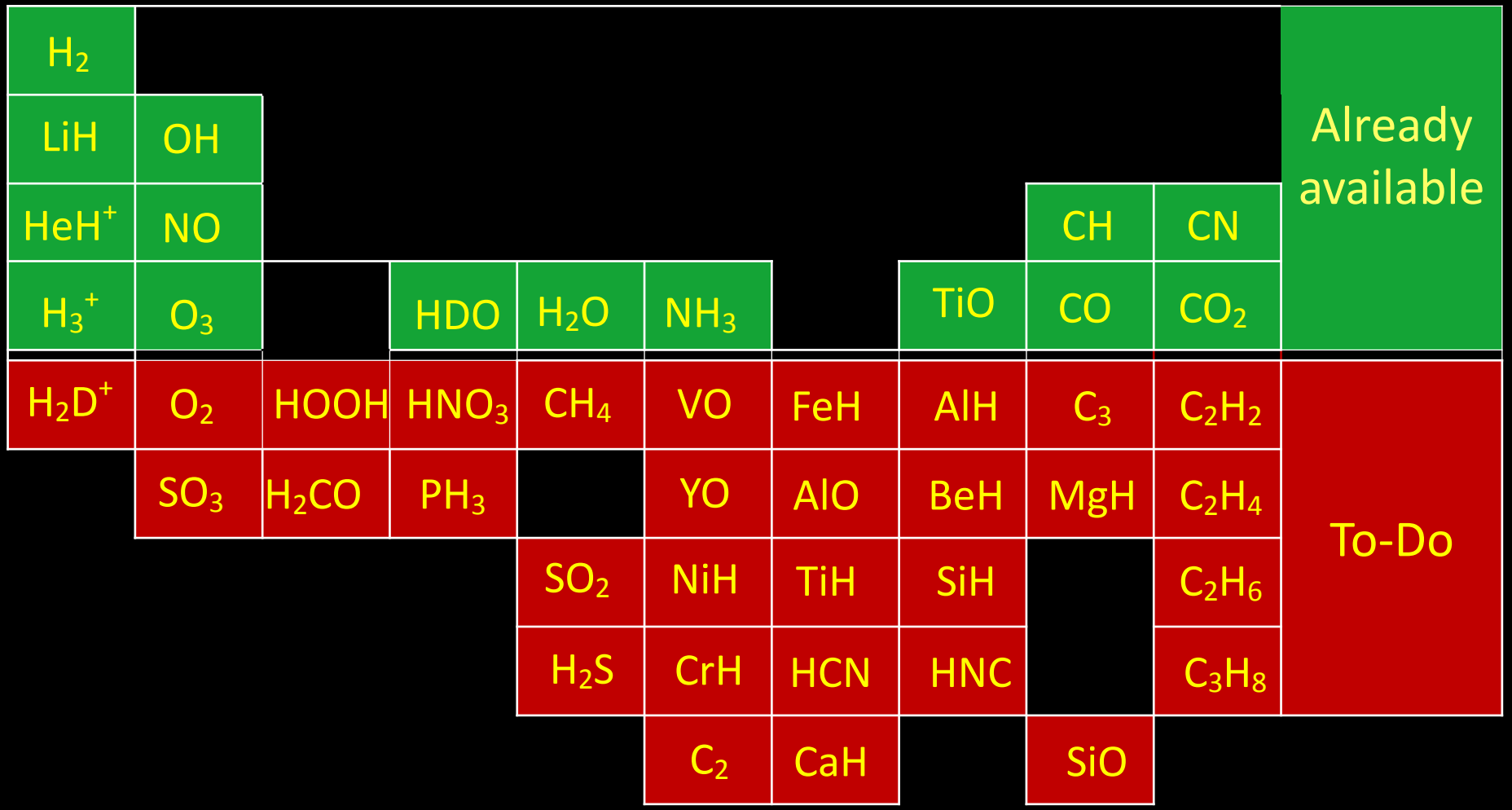
We have constructed an efficient machinery for accurate production of molecular spectra

We have constructed an efficient machinery for accurate production of molecular spectra

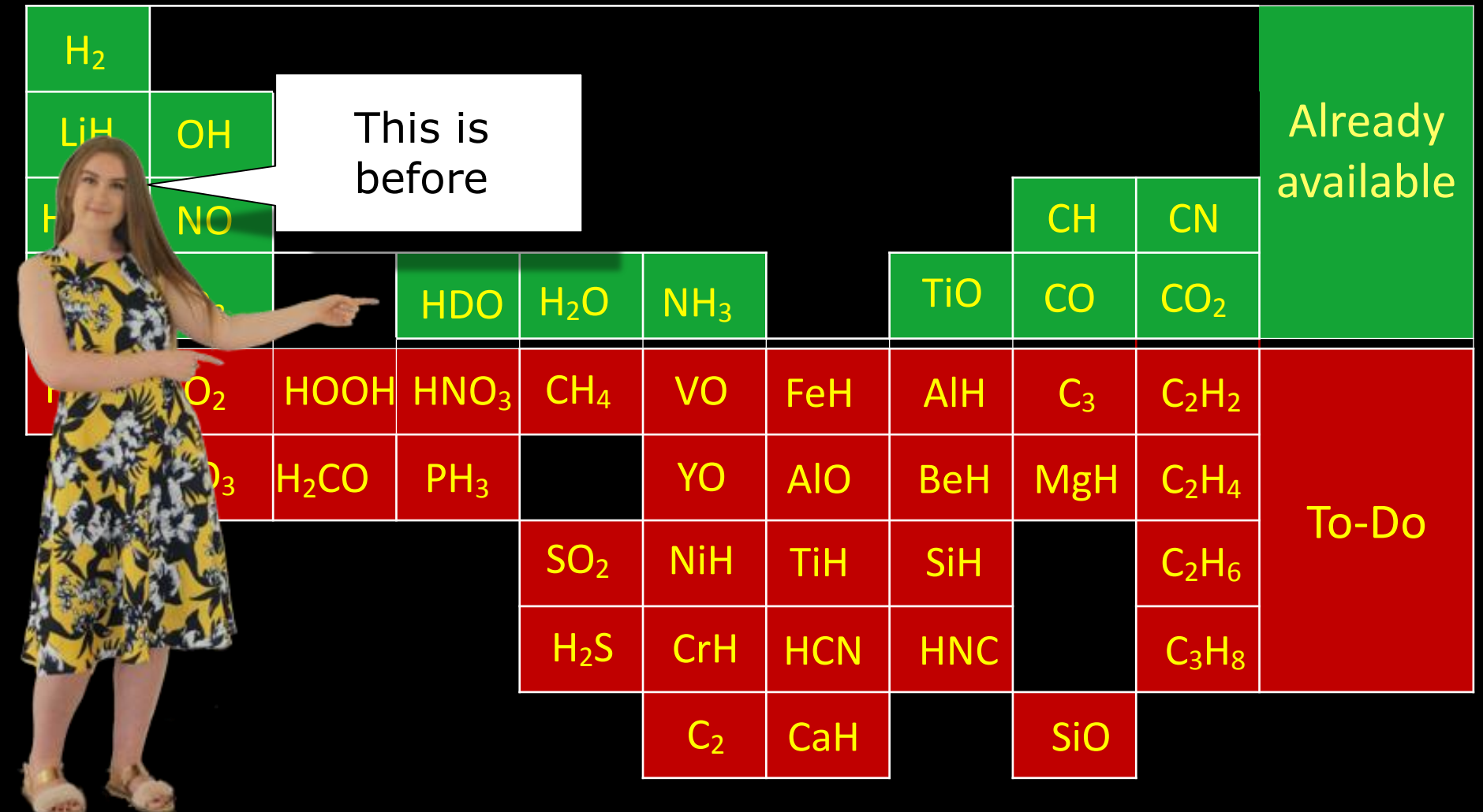
for atmospheric applications (stars and exoplantes)

This is where we started

2011


H_2
LiH
OH
HeH^+
NO
CH
CN
H_3^+
O_3
HDO
H_2O
NH_3
TiO
CO
CO_2
Already available
H_2D^+
O_2
HOOH
HNO_3
CH_4
VO
FeH
AlH
C_3
C_2H_2
SO_3
H_2CO
PH_3
YO
AlO
BeH
MgH
C_2H_4
SO_2
NiH
TiH
SiH
C_2H_6
H_2S
CrH
HCN
HNC
C_3H_8
To-Do
C_2
CaH
SiO

2011


H_2
LiH
OH
NO
HDO
H_2O
NH_3
TiO
CH
CN
CO
CO_2
Already available
O_2
HOOH
HNO_3
CH_4
VO
FeH
AlH
C_3
C_2H_2
O_3
H_2CO
PH_3
YO
AlO
BeH
MgH
C_2H_4
SO_2
NiH
TiH
SiH
C_2H_6
H_2S
CrH
HCN
HNC
C_3H_8
C_2
CaH
SiO
To-Do
This is before

2018

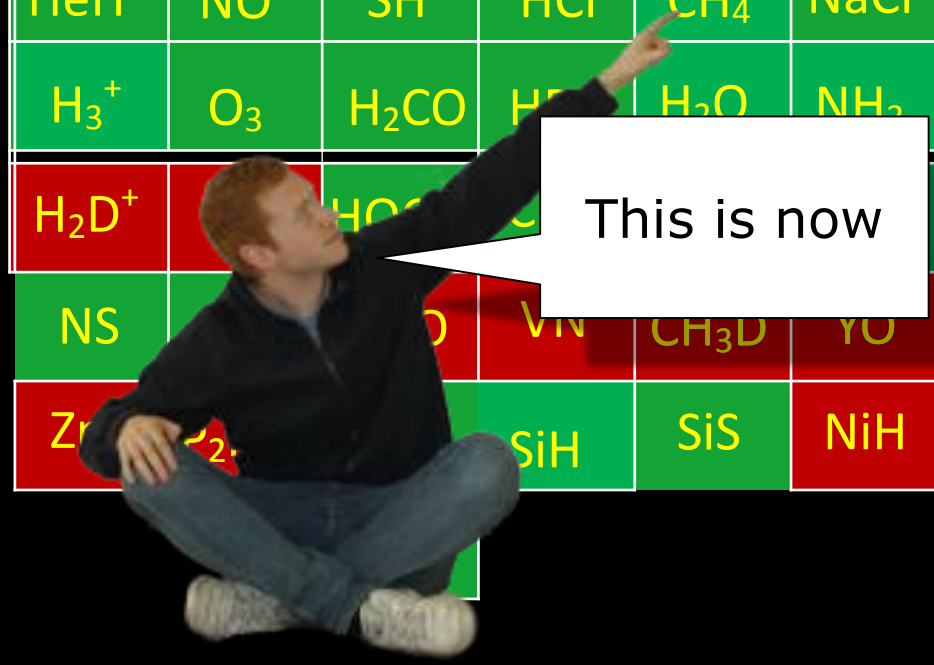
ExoMol

H_2	PH_3	AlO	AlH	CS	HNO_3	PN	H_2S	CrH	ScH	Done
LiH	OH	SO_2	CH_3Cl	C_2	BeH	PS	KCl	HCN	HNC	
HeH^+	NO	SH	HCl	CH_4	NaCl	SiO	MgH	CH	CN	
H_3^+	O_3	H_2CO	HDO	H_2O	NH_3	CaH	SO_3	CO	CO_2	
H_2D^+	O_2	HOOH	CH_3F	TiO	VO	FeH	CaO	C_3	C_2H_2	To-Do
NS	NaH	BaO	VN	CH_3D	YO	SiH_4	PH	SH	C_2H_4	
ZnS	P_2H_2	SO	SiH	SiS	NiH	TiH	MgO	CH_3Cl	C_2H_6	
		PO				SiC		PS	C_3H_8	

2018

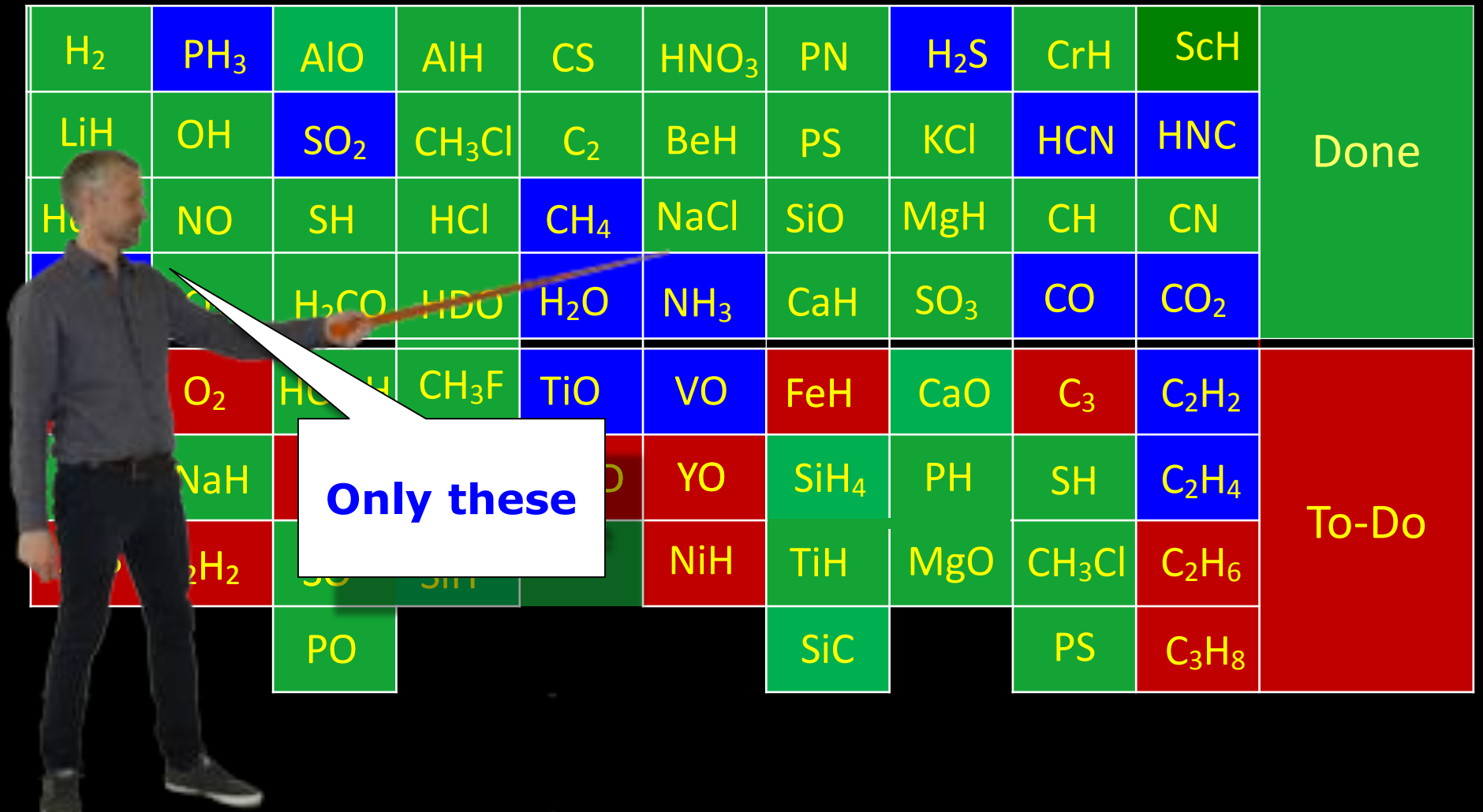
ExoMol

H_2	PH_3	AlO	AlH	CS	HNO_3	PN	H_2S	CrH	ScH	Done
LiH	OH	SO_2	CH_3Cl	C_2	BeH	PS	KCl	HCN	HNC	
HeH^+	NO	SH	HCl	CH_4	NaCl	SiO	MgH	CH	CN	
H_3^+	O_3	H_2CO	H[illegible]	H_2O	NH_3	CaH	SO_3	CO	CO_2	
H_2D^+		HO[illegible]	[illegible]			FeH	CaO	C_3	C_2H_2	To-Do
NS		[illegible]O	VN	CH_3D	YO	SiH_4	PH	SH	C_2H_4	
Zr[illegible]		[illegible]$_2$	SiH	SiS	NiH	TiH	MgO	CH_3Cl	C_2H_6	
						SiC		PS	C_3H_8	



Not all of them are actively used for retrievals yet

ExoMol 2018

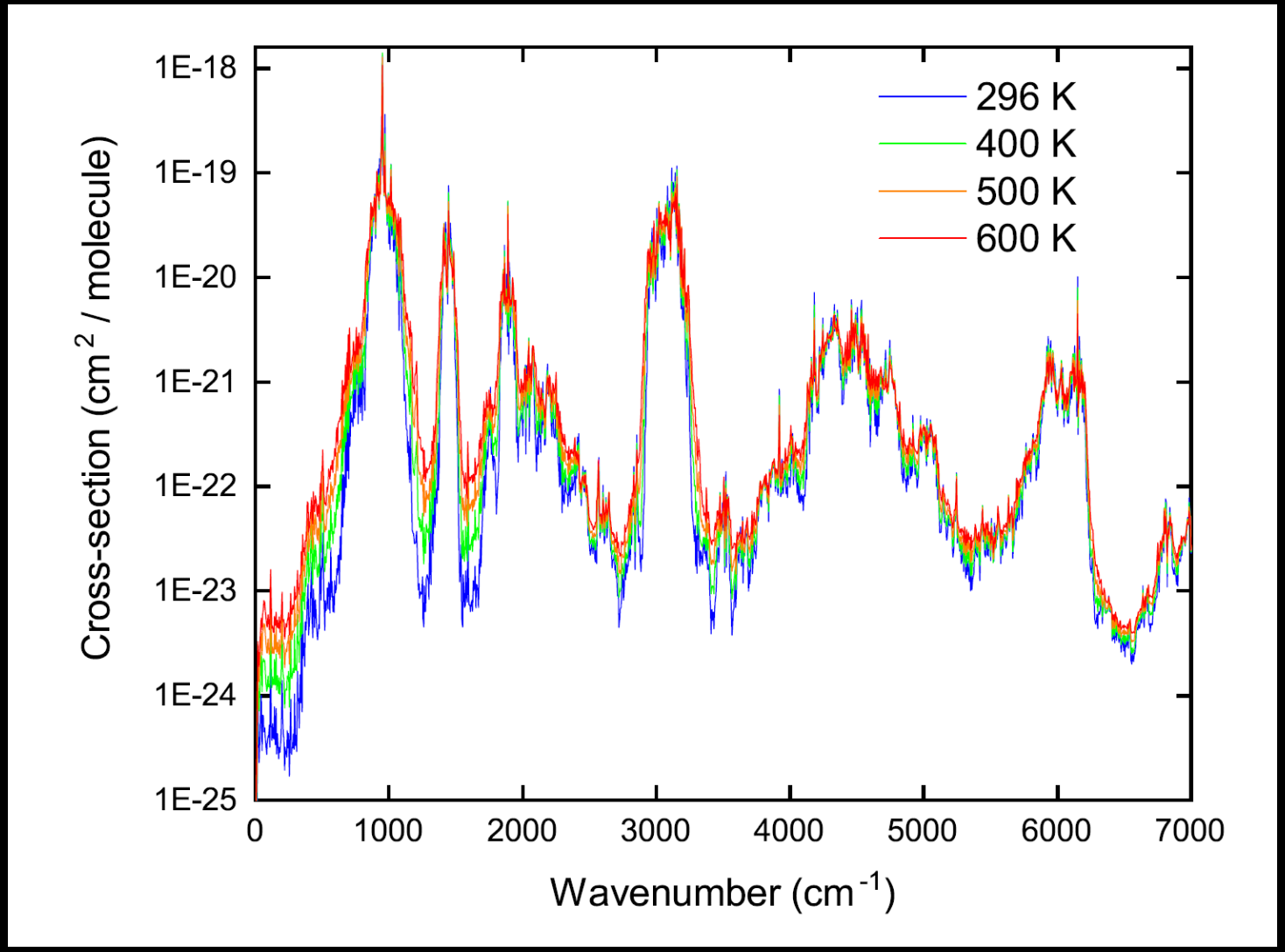

H_2
PH_3
AlO
AlH
CS
HNO_3
PN
H_2S
CrH
ScH
LiH
OH
SO_2
CH_3Cl
C_2
BeH
PS
KCl
HCN
HNC
NO
SH
HCl
CH_4
NaCl
SiO
MgH
CH
CN
H_2CO
HDO
H_2O
NH_3
CaH
SO_3
CO
CO_2
O_2
CH_3F
TiO
VO
FeH
CaO
C_3
C_2H_2
NaH
YO
SiH_4
PH
SH
C_2H_4
NiH
TiH
MgO
CH_3Cl
C_2H_6
PO
SiC
PS
C_3H_8
Done
To-Do
Only these

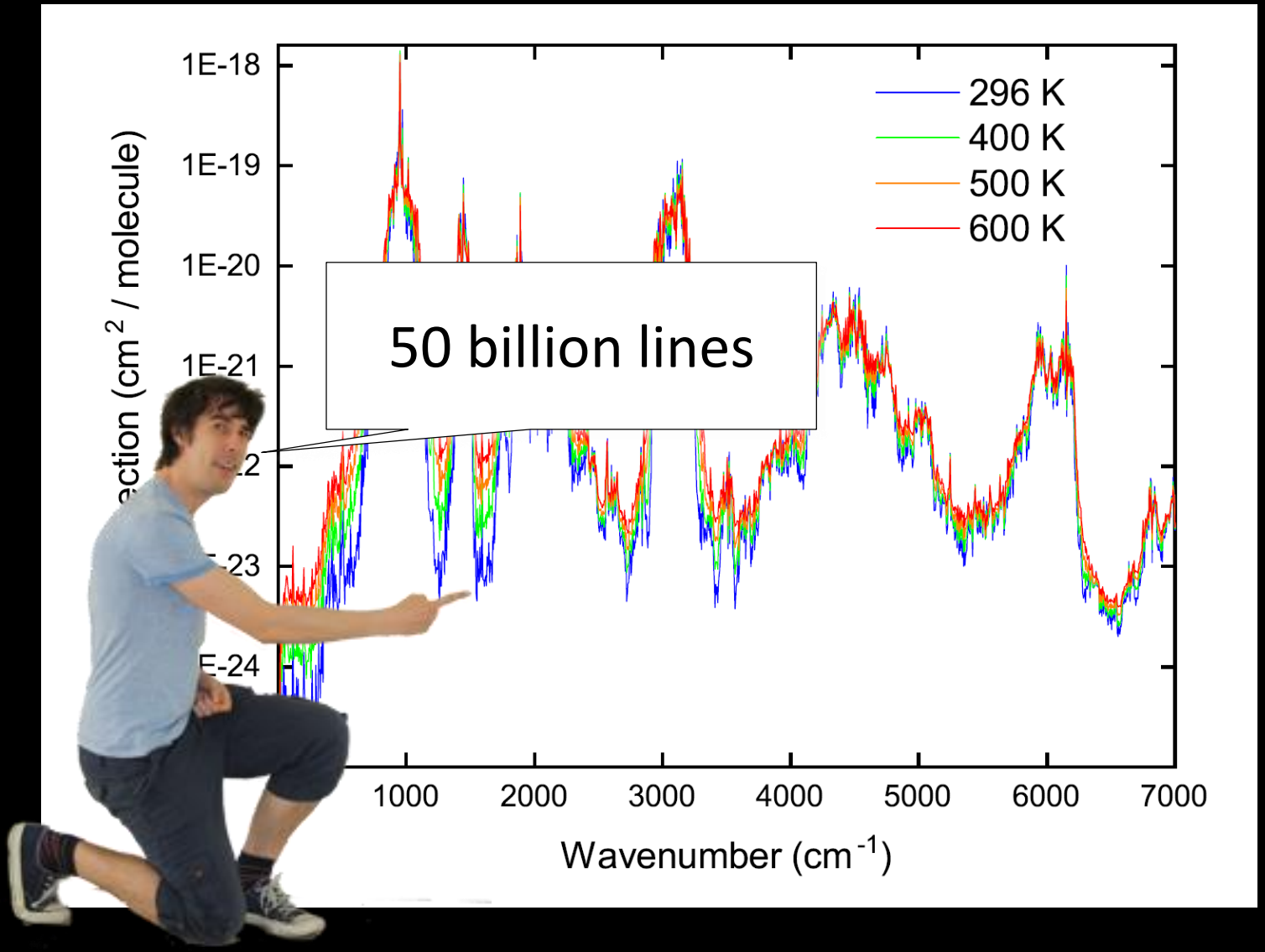
Larger molecules

Barry Mant

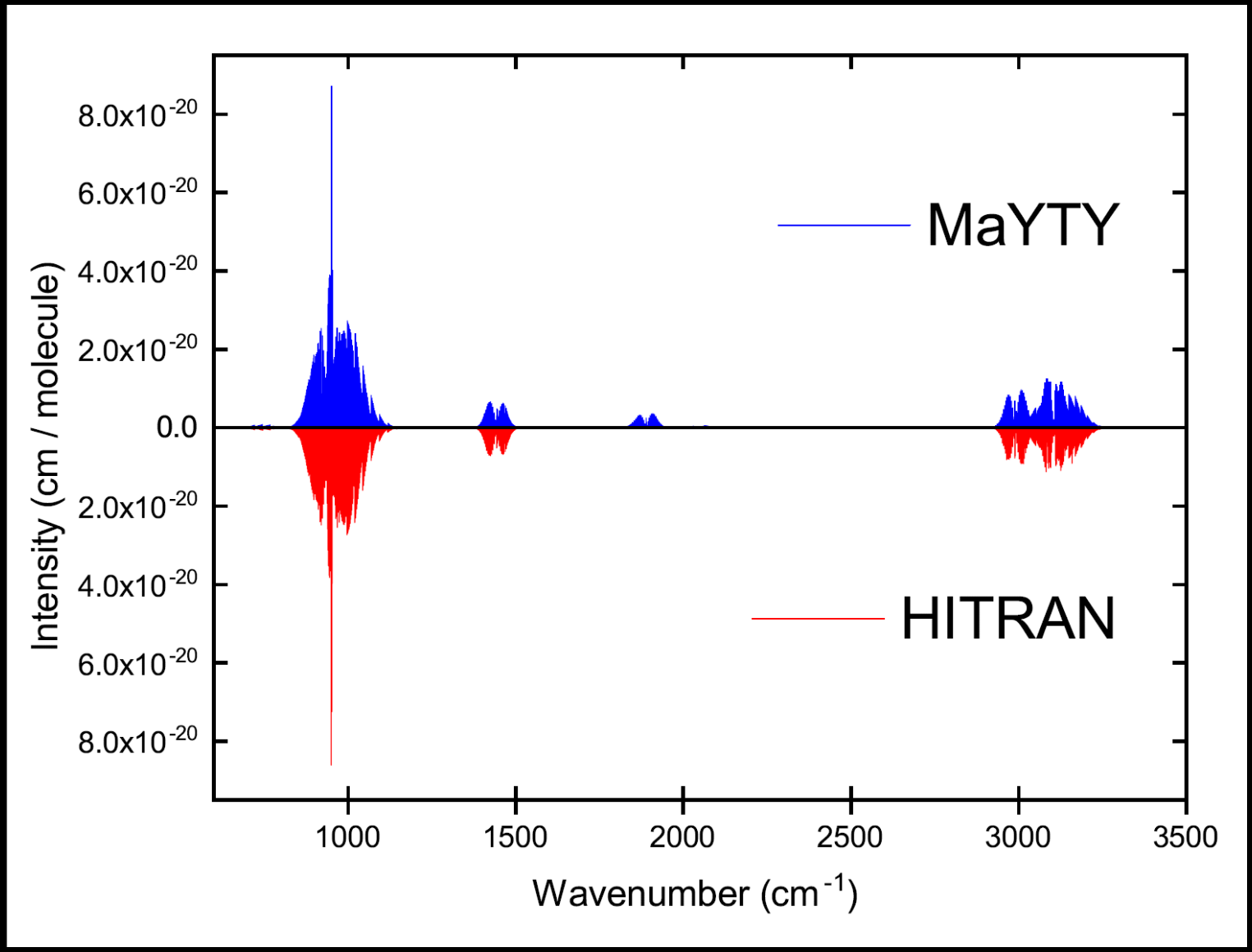
Ethylene:
new ExoMol ~~song~~ line list

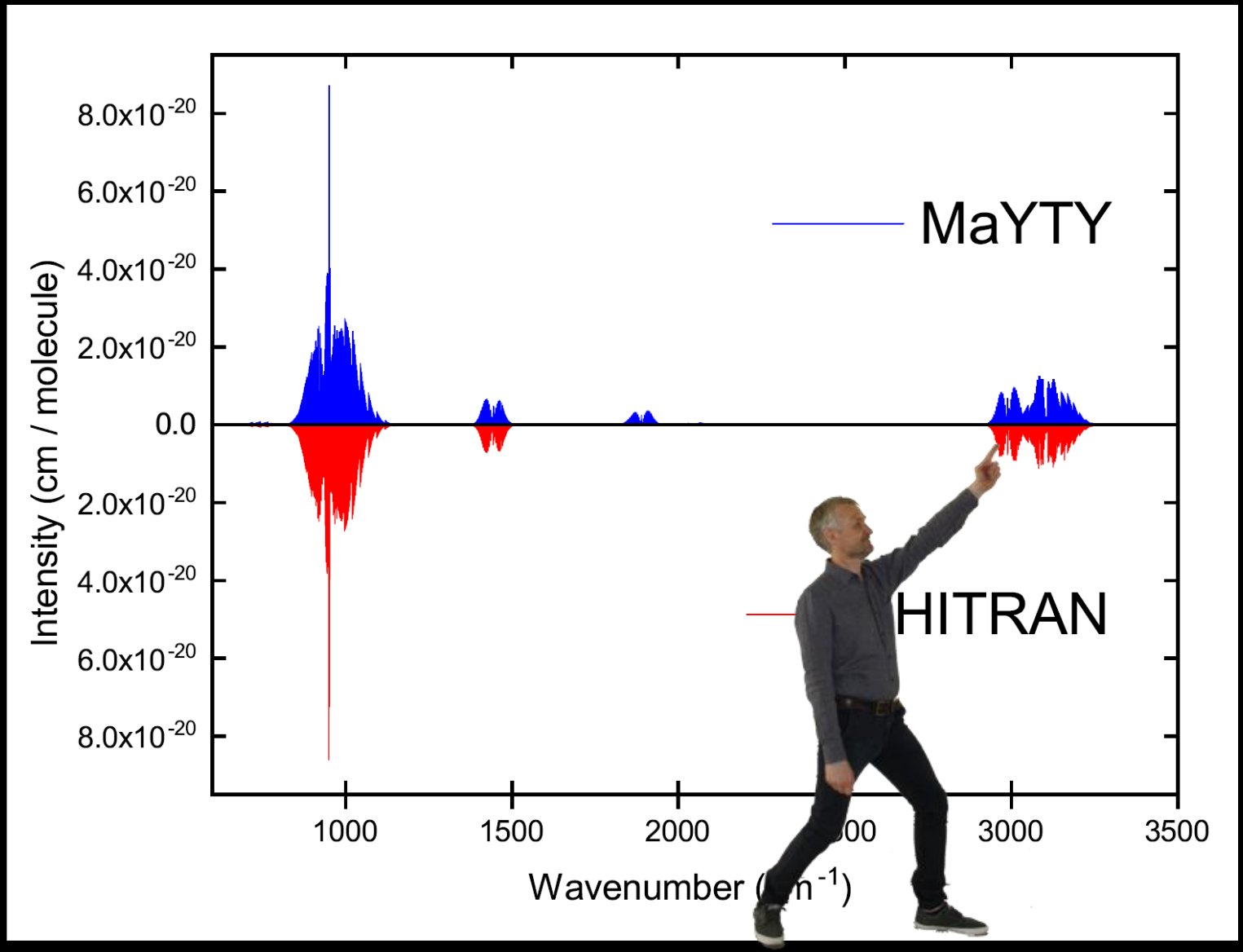
Barry Mant

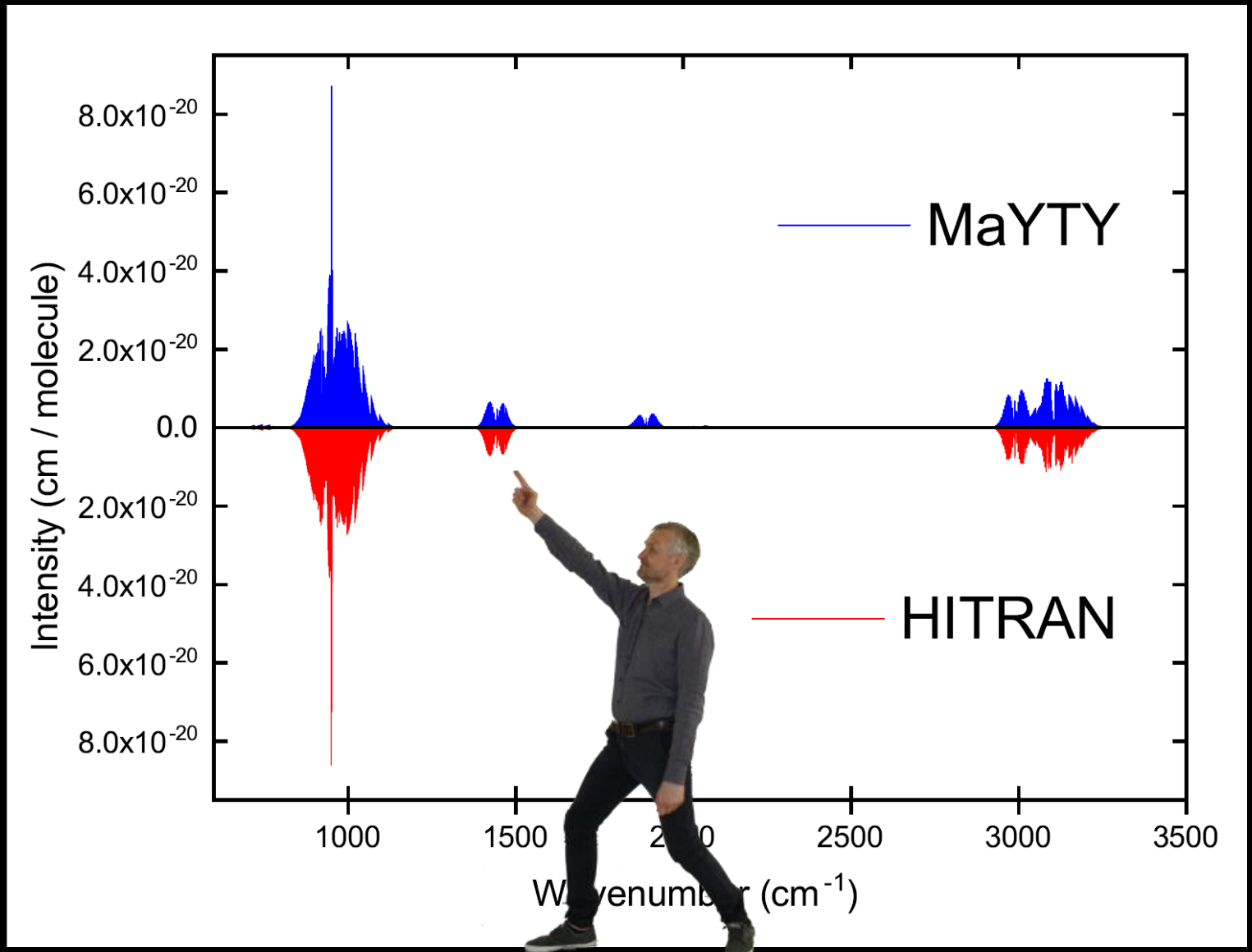

Cross-section (cm^2 / molecule)
1E-18
1E-19
1E-20
1E-21
1E-22
1E-23
1E-24
1E-25
0
1000
2000
3000
4000
5000
6000
7000
Wavenumber (cm^{-1})
296 K
400 K
500 K
600 K

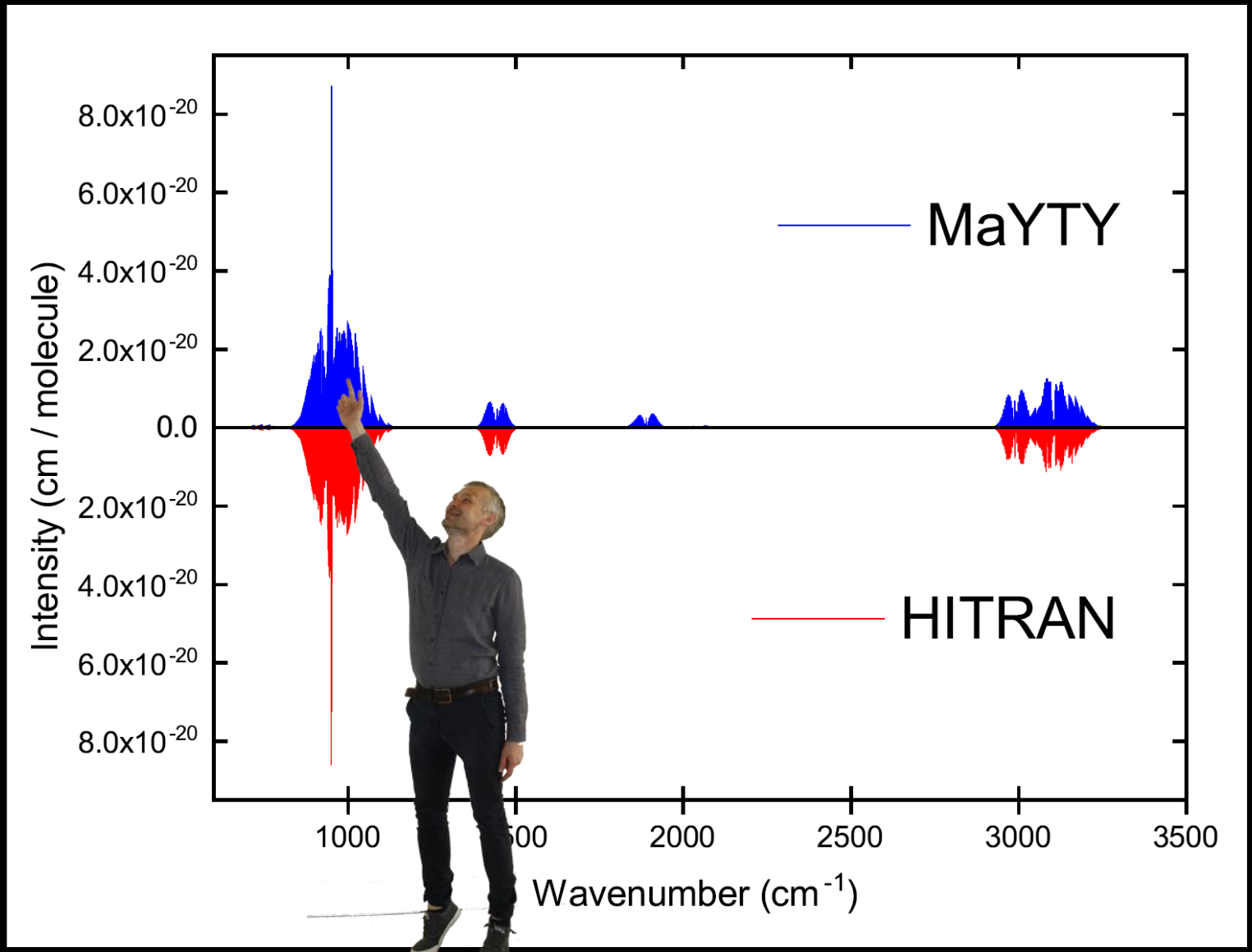

1E-18
1E-19
1E-20
1E-21
296 K
400 K
500 K
600 K
50 billion lines
1000
2000
3000
4000
5000
6000
7000
Wavenumber (cm-1)

3 band model:
Vibrational spectrum of C_2H_4

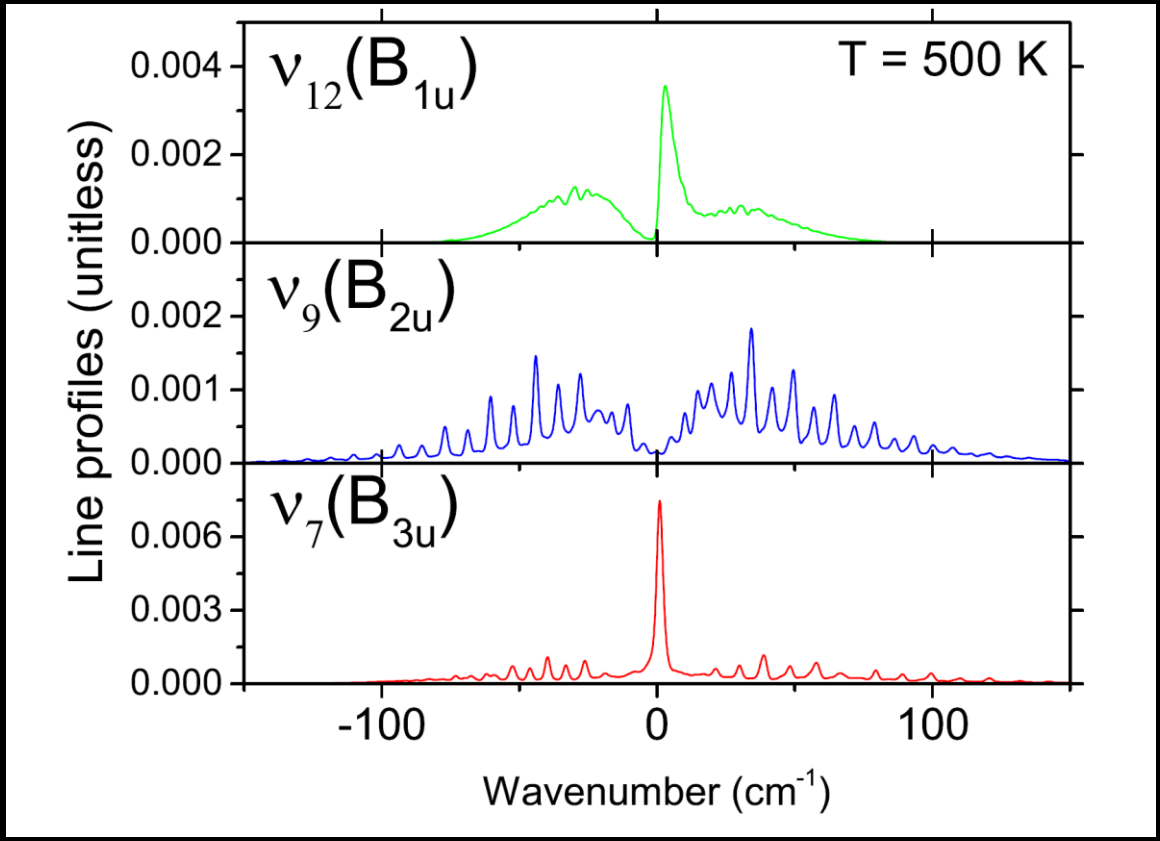

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
2500
3000
3500
Wavenumber (cm-1)

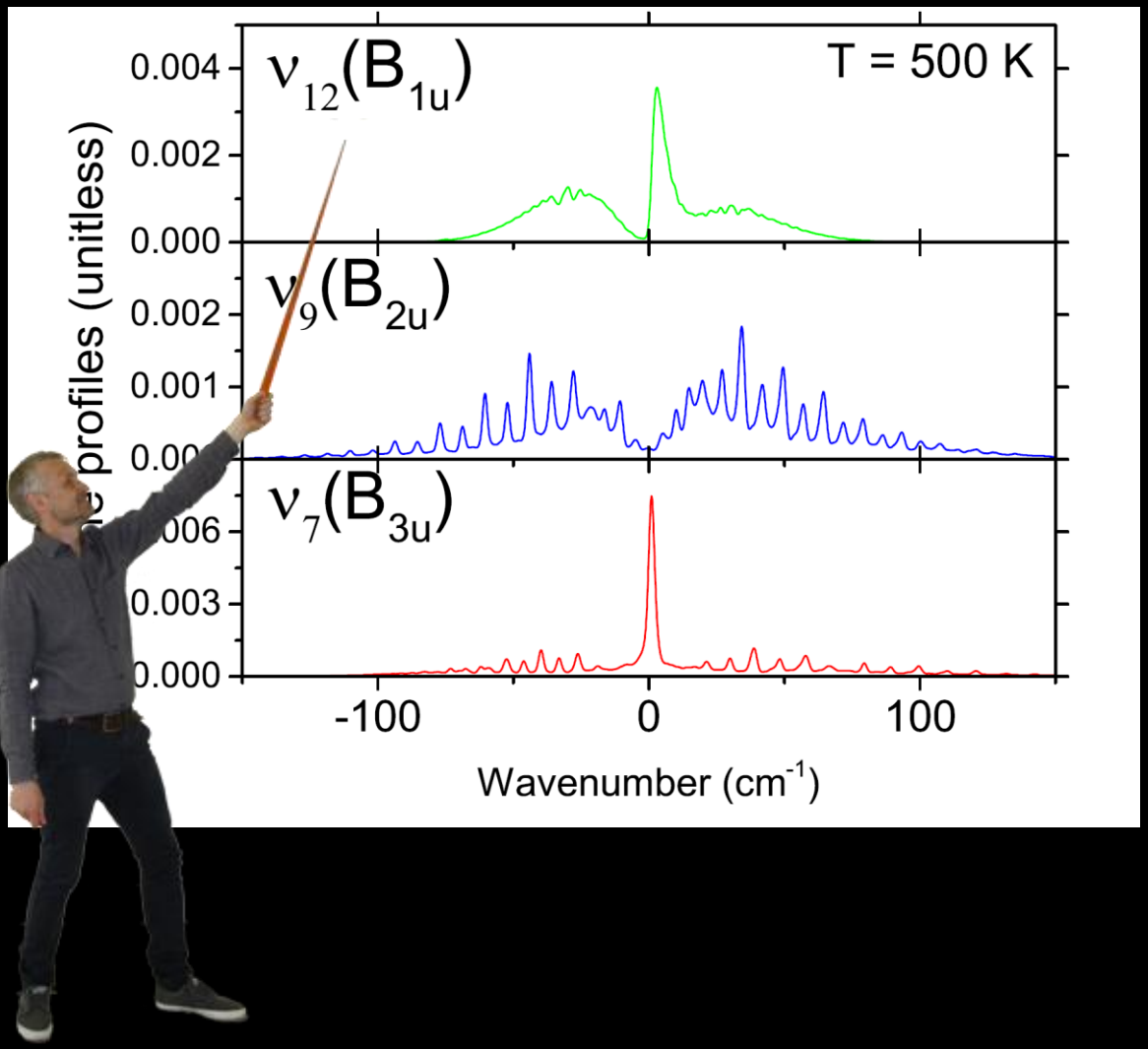

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

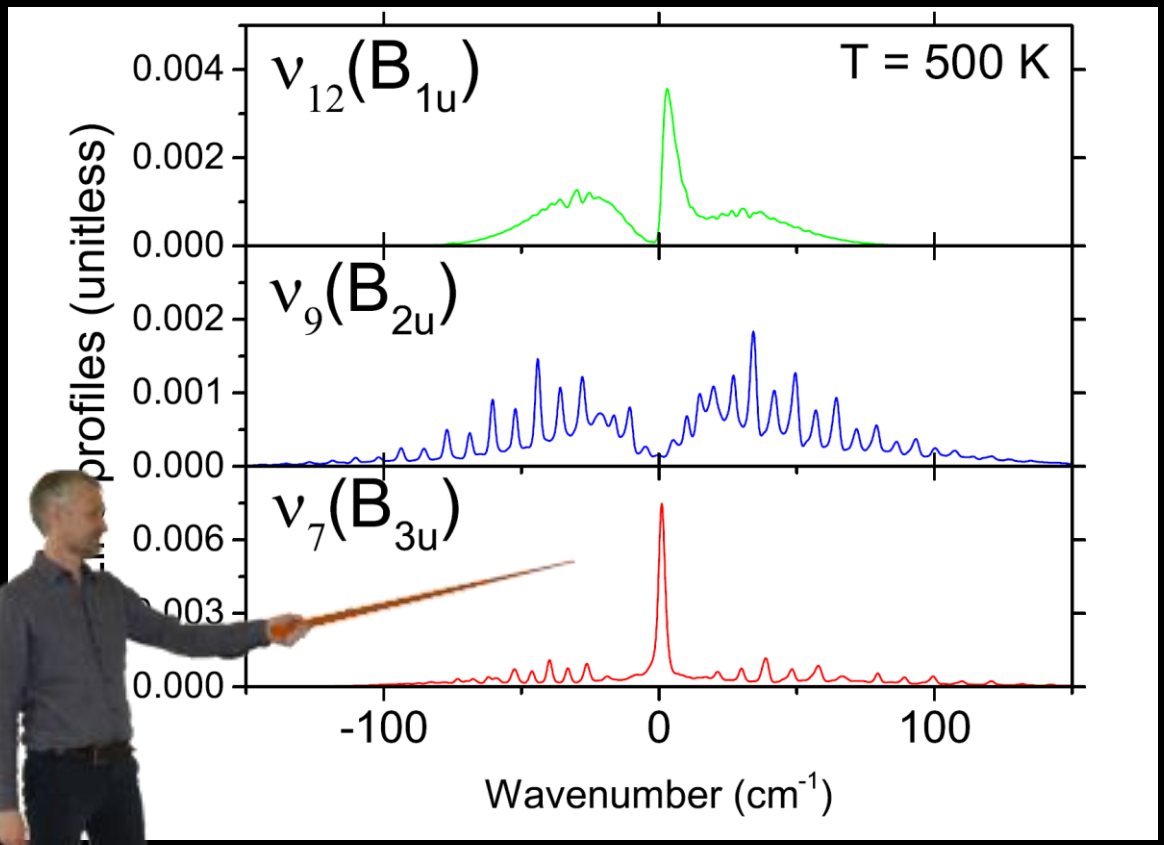

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2500
3000
3500
(cm-1)


8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
2000
2500
3000
3500
Wavenumber (cm-1)

Extract their shapes


ν12(B1u)
T = 500 K
ν9(B2u)
ν7(B3u)
Line profiles (unitless)
0.004
0.002
0.000
0.002
0.001
0.000
0.006
0.003
0.000
-100
0
100
Wavenumber (cm-1)


ν12(B1u)
T = 500 K
ν9(B2u)
ν7(B3u)
0.004
0.002
0.000
0.002
0.001
0.00
006
0.003
0.000
-100
0
100
Wavenumber (cm-1)
profiles (unitless)


ν12(B1u)
T = 500 K
ν9(B2u)
ν7(B3u)
0.004
0.002
0.000
0.002
0.001
0.000
0.006
0.000
-100
0
100
Wavenumber (cm-1)

… and apply to all other bands

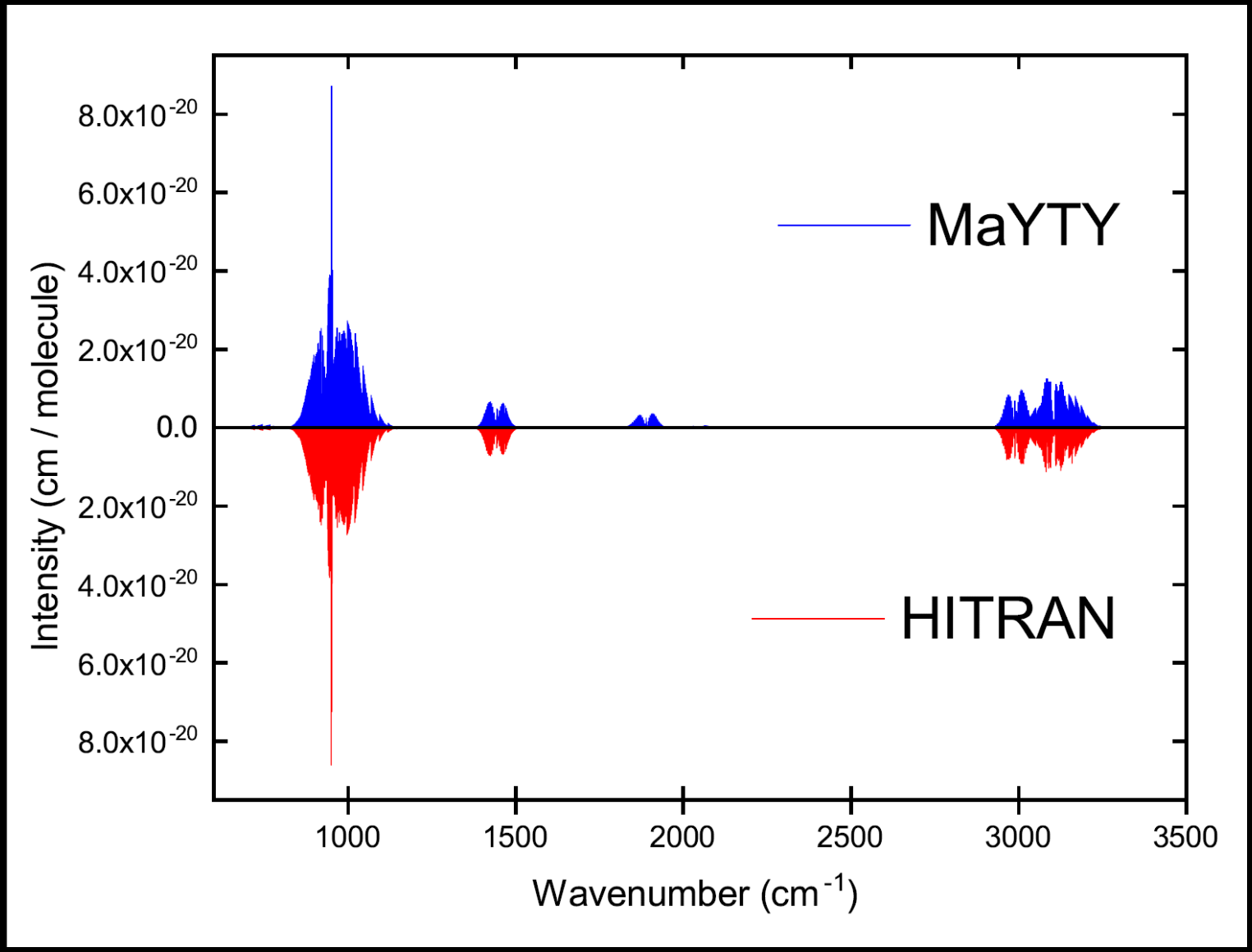
… and apply to all other bands

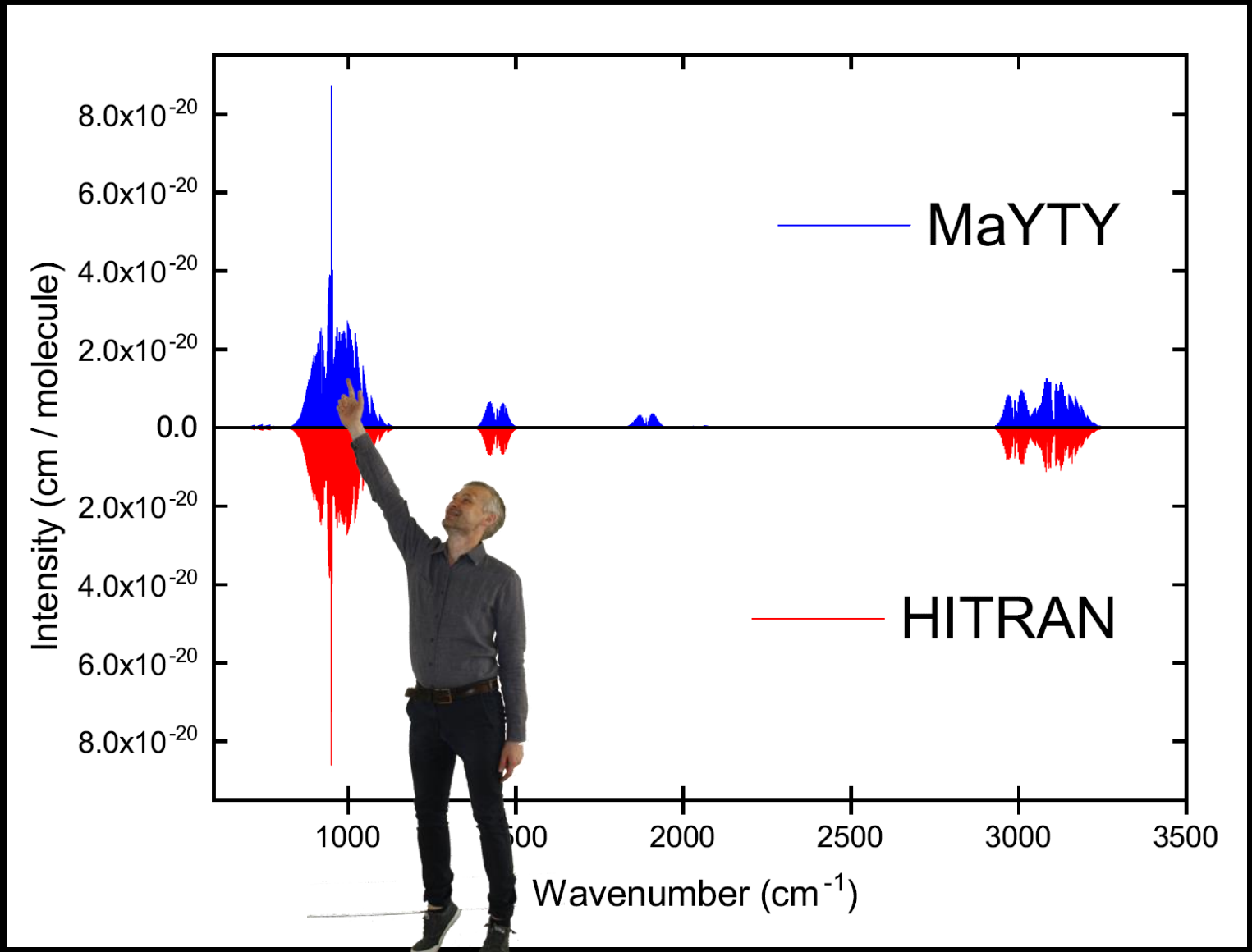
Low cost vibrational
band intensities

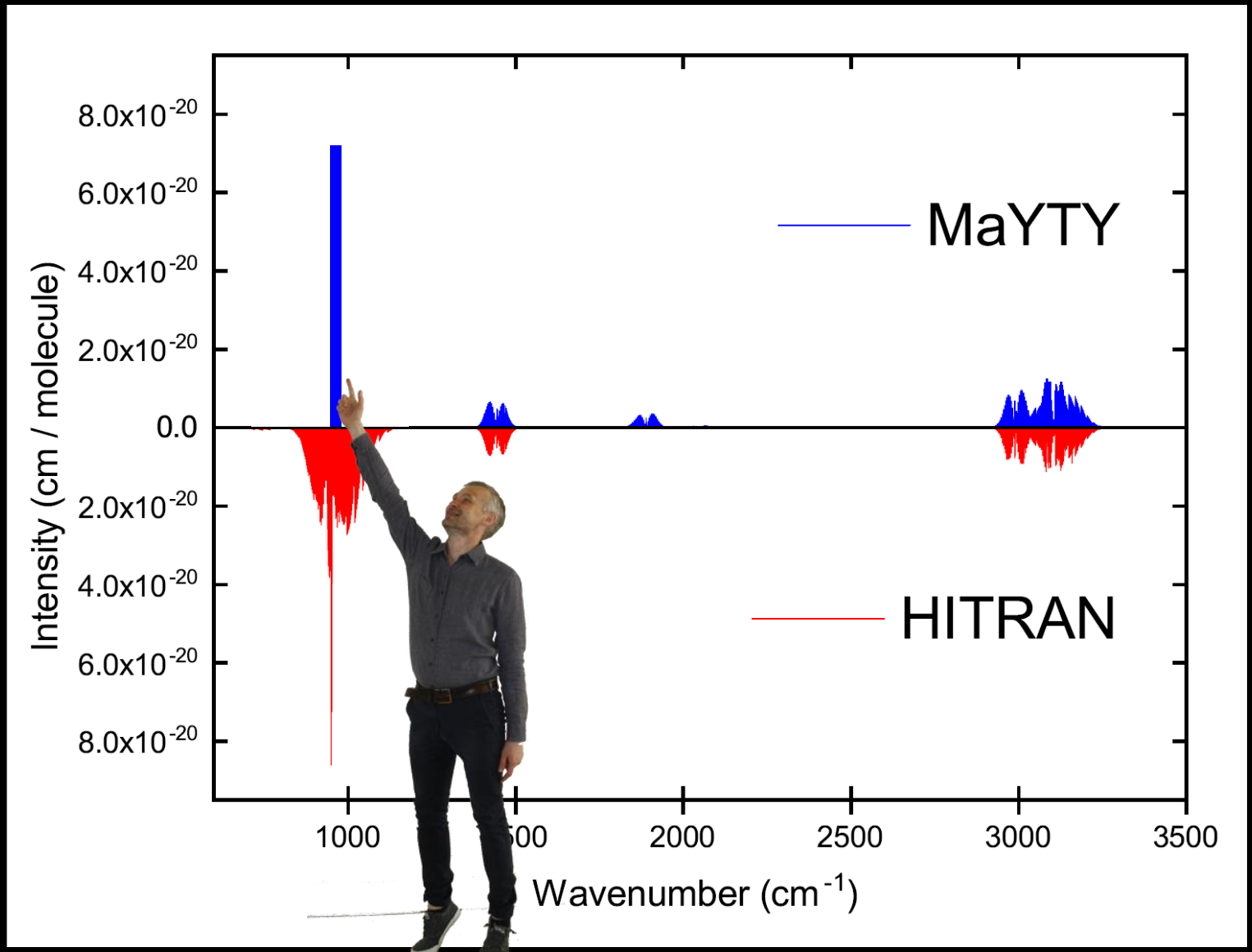
Cheating on variational calculations

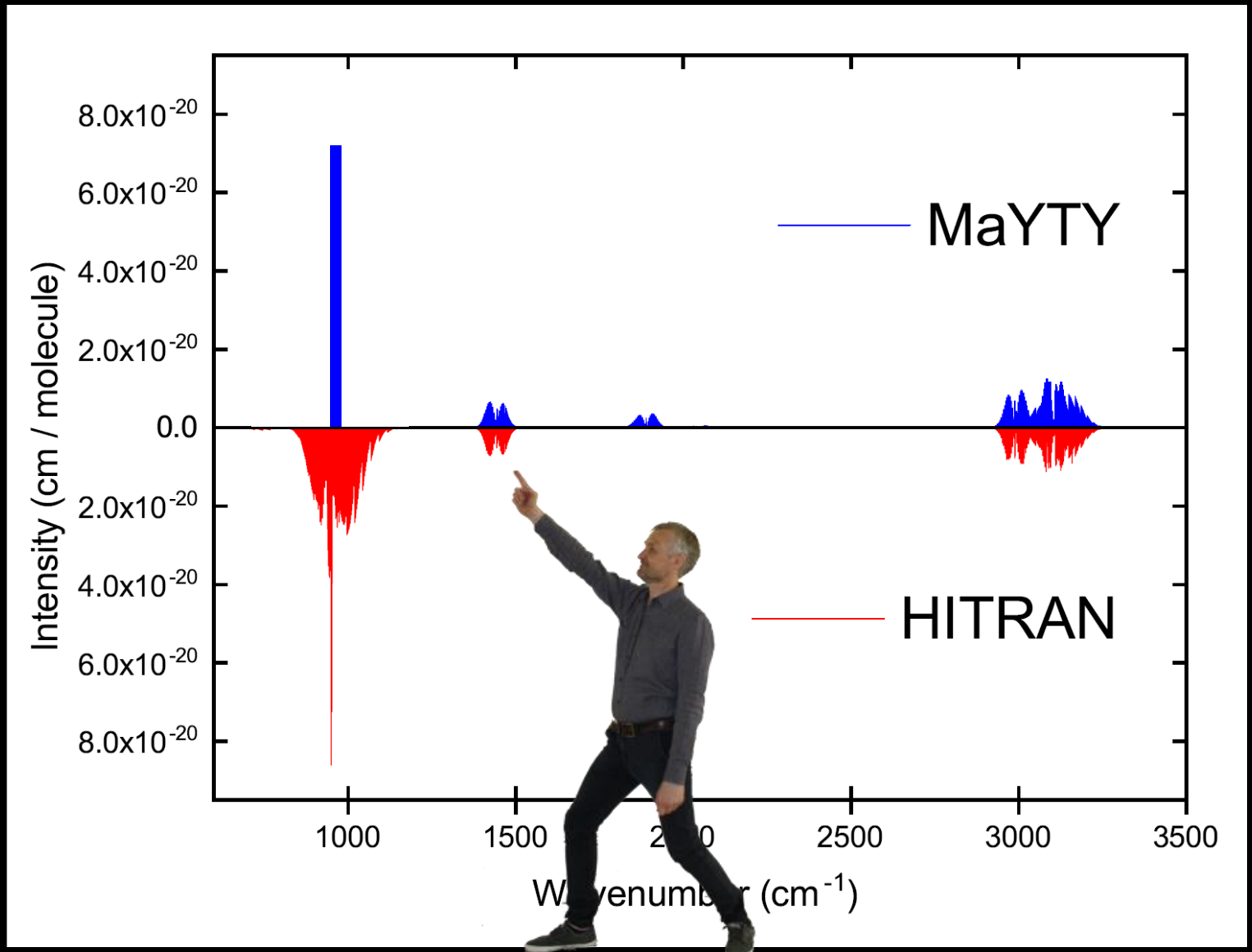
… and apply to all other bands

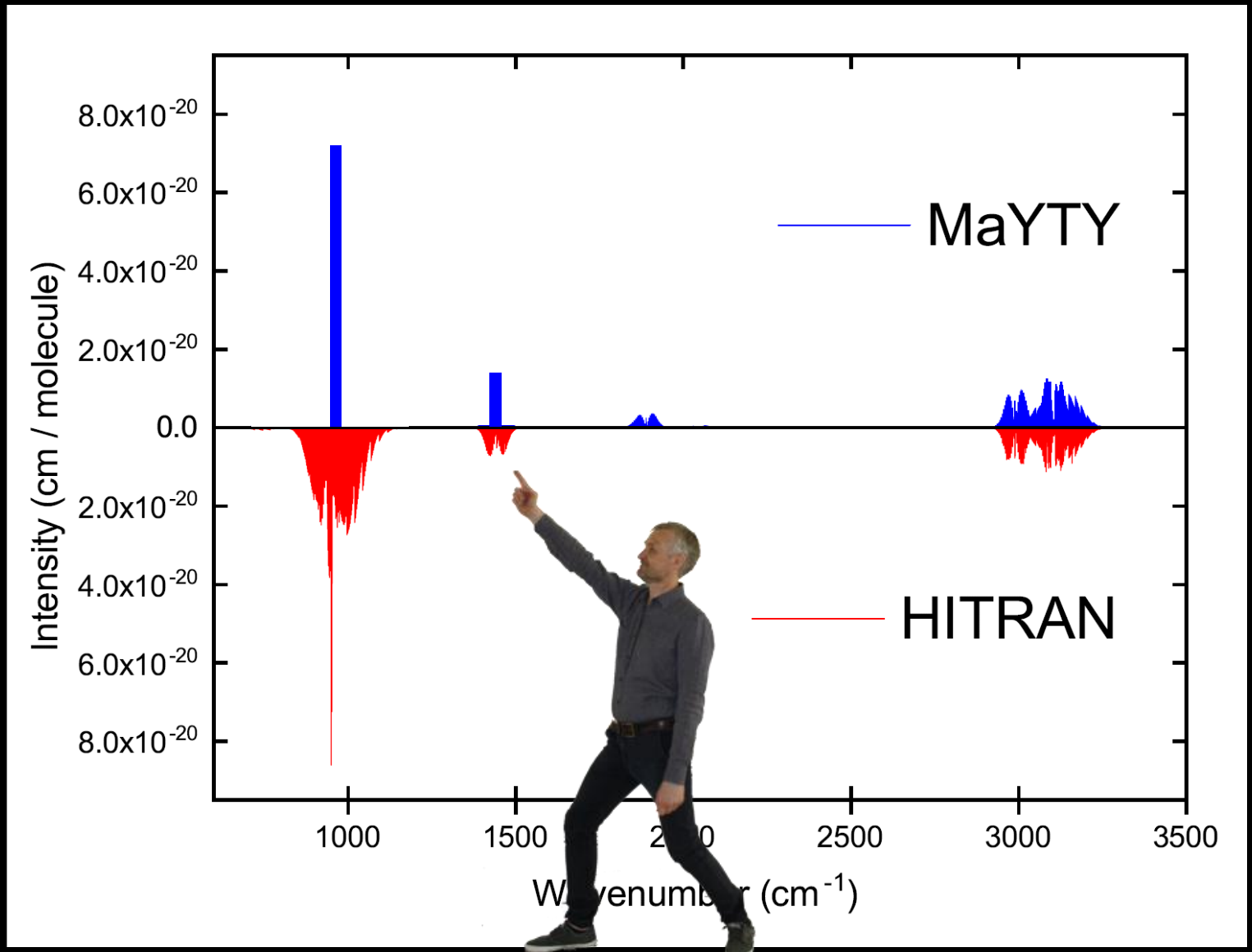
Low cost vibrational band intensities

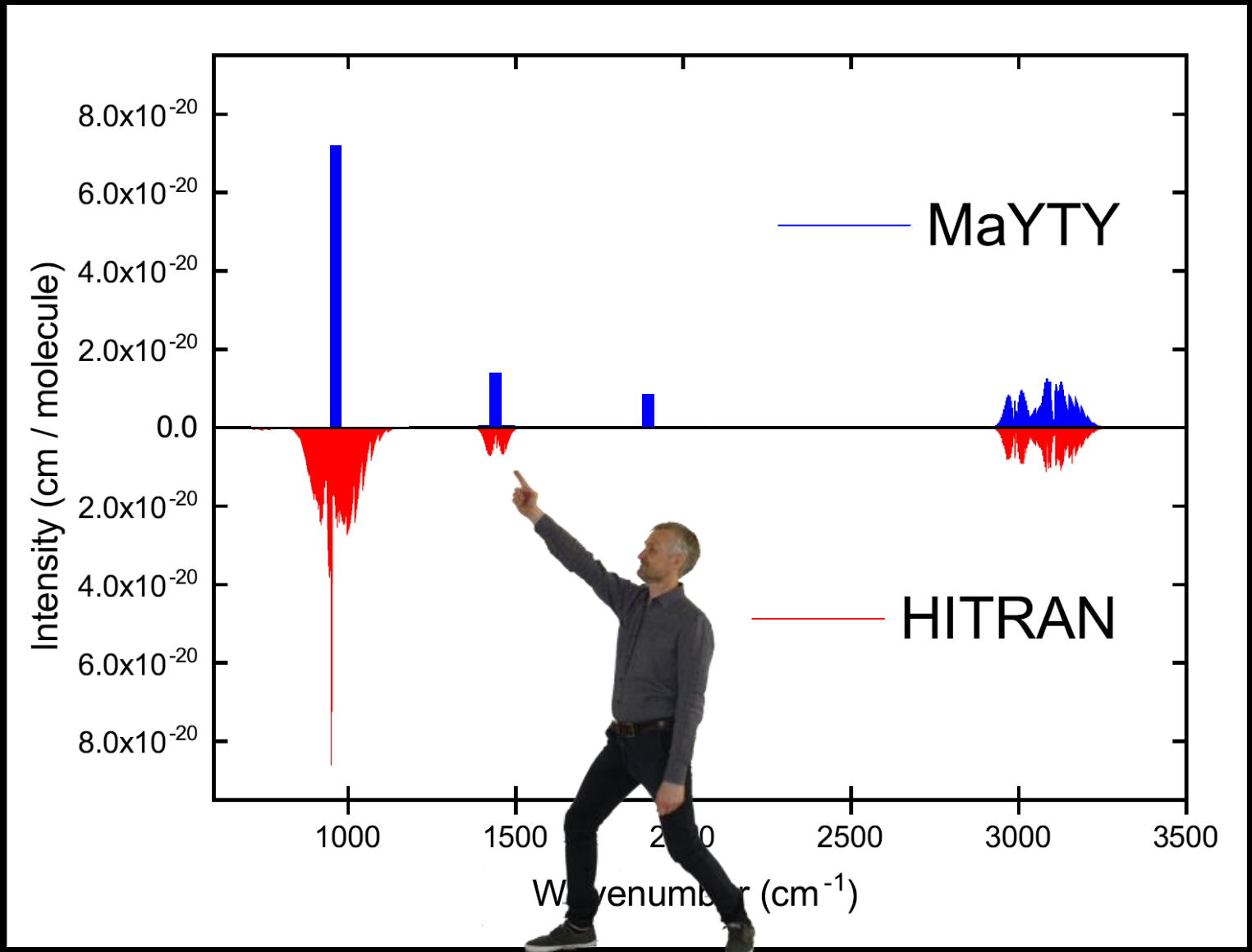

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
2500
3000
3500
Wavenumber (cm-1)

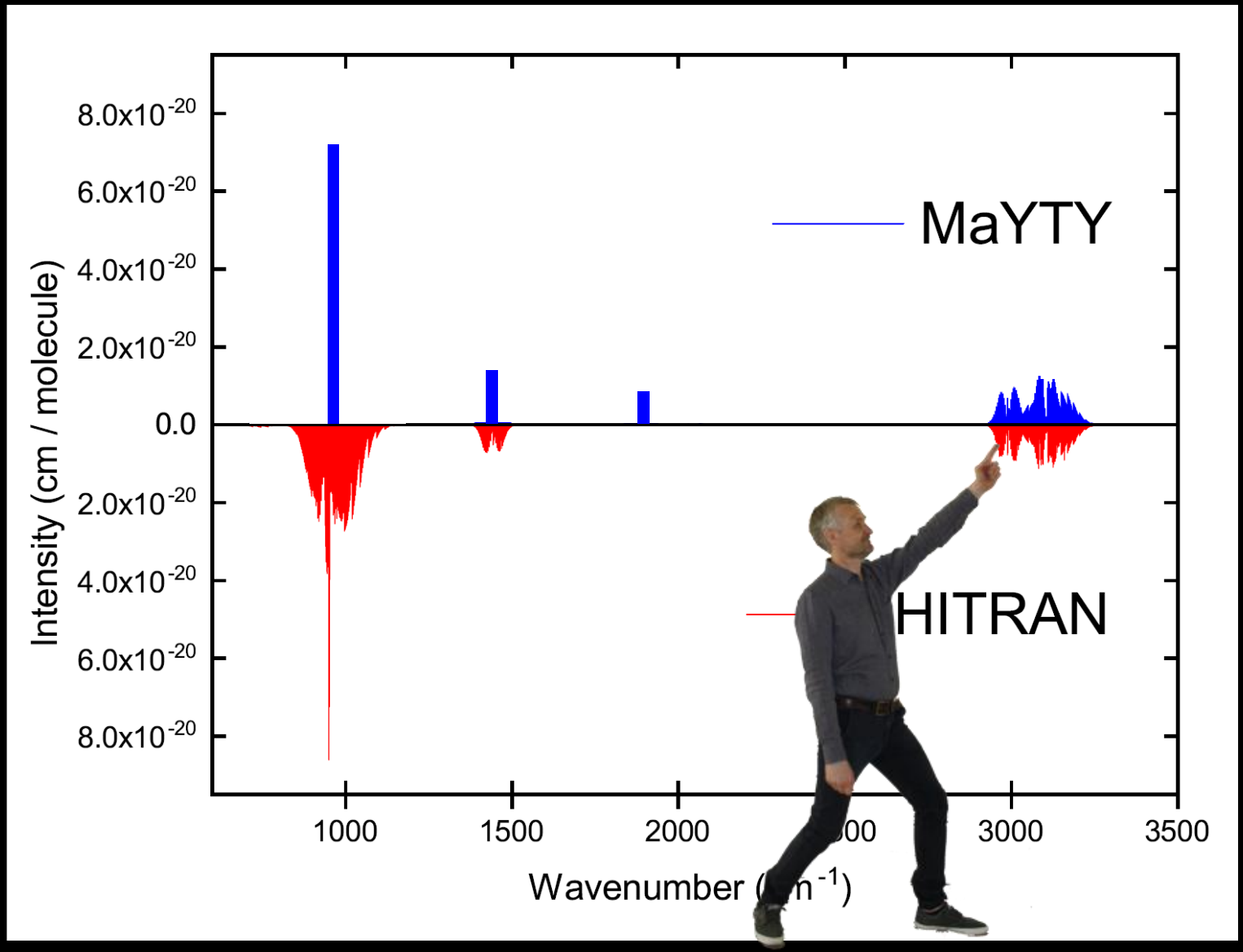

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
2000
2500
3000
3500
Wavenumber (cm-1)

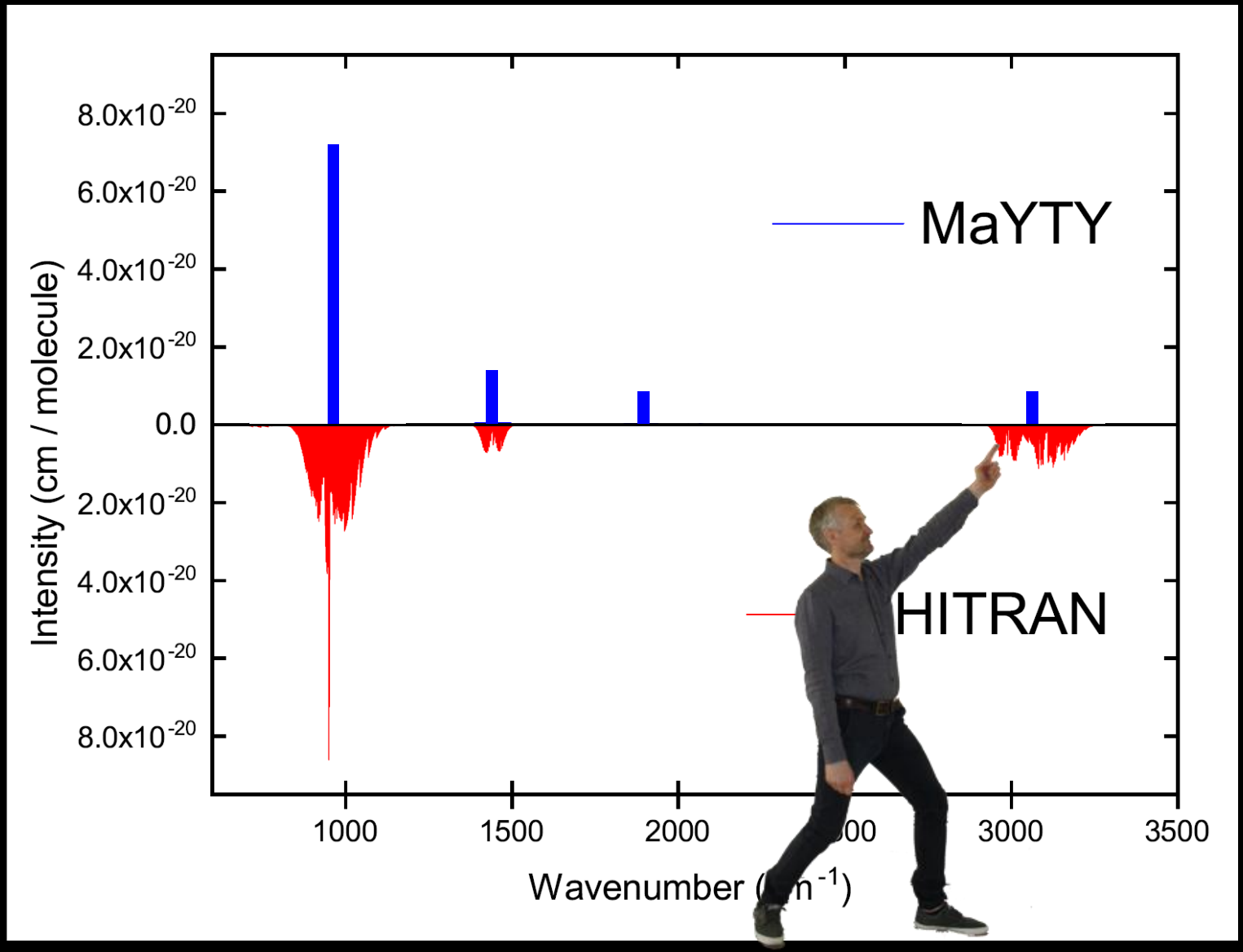

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
2000
2500
3000
3500
Wavenumber (cm-1)

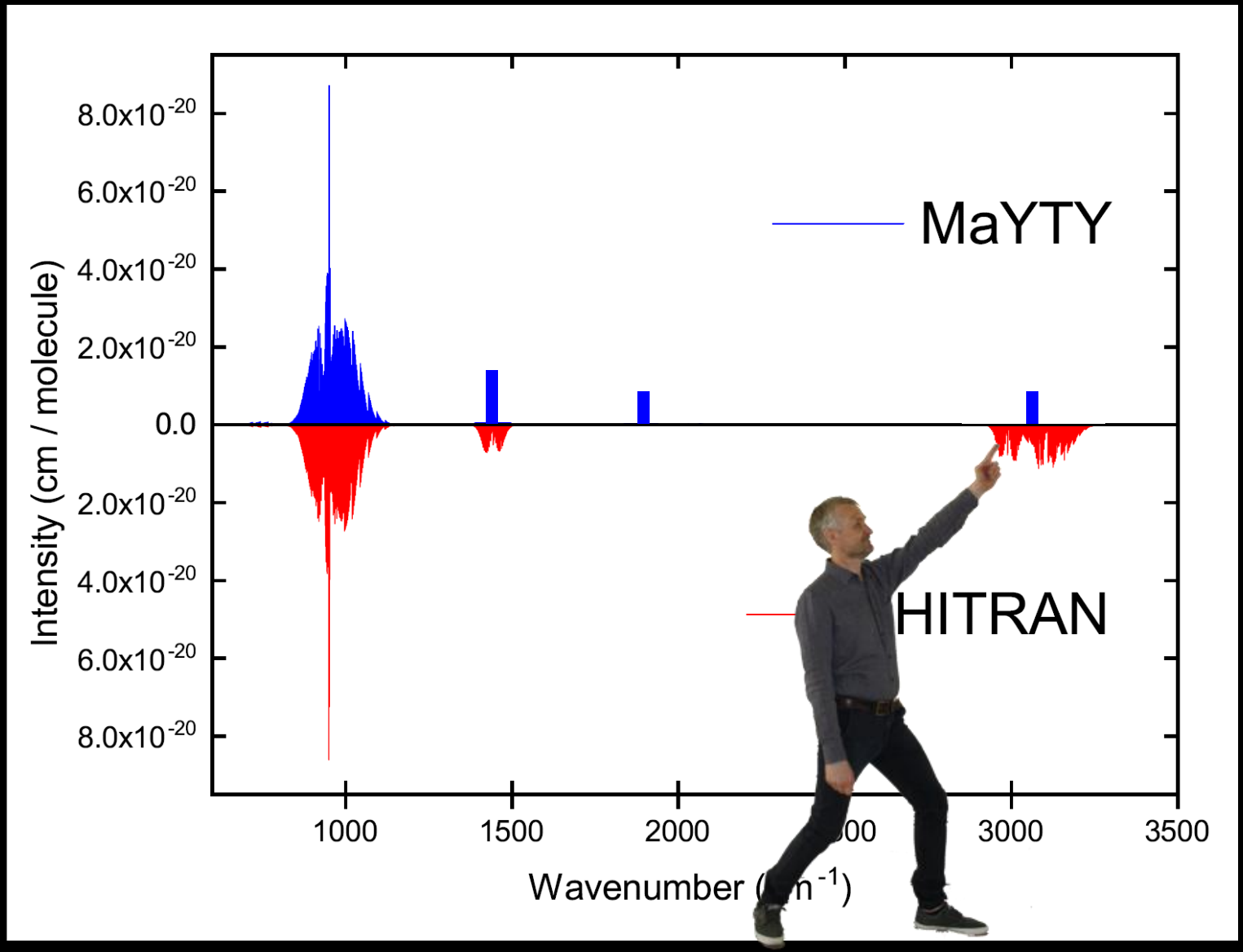

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2500
3000
3500
(cm-1)

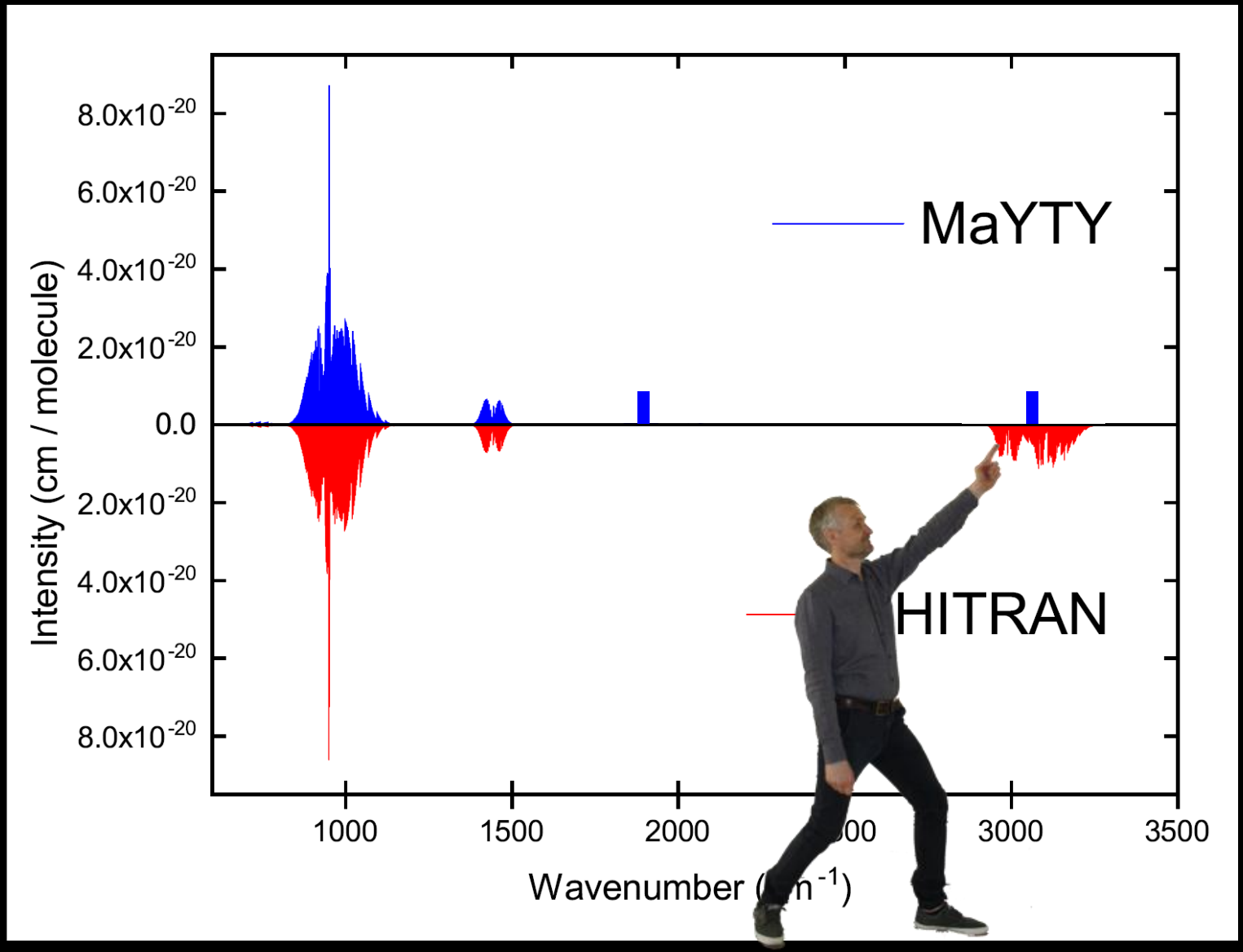

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2500
3000
3500
(cm-1)

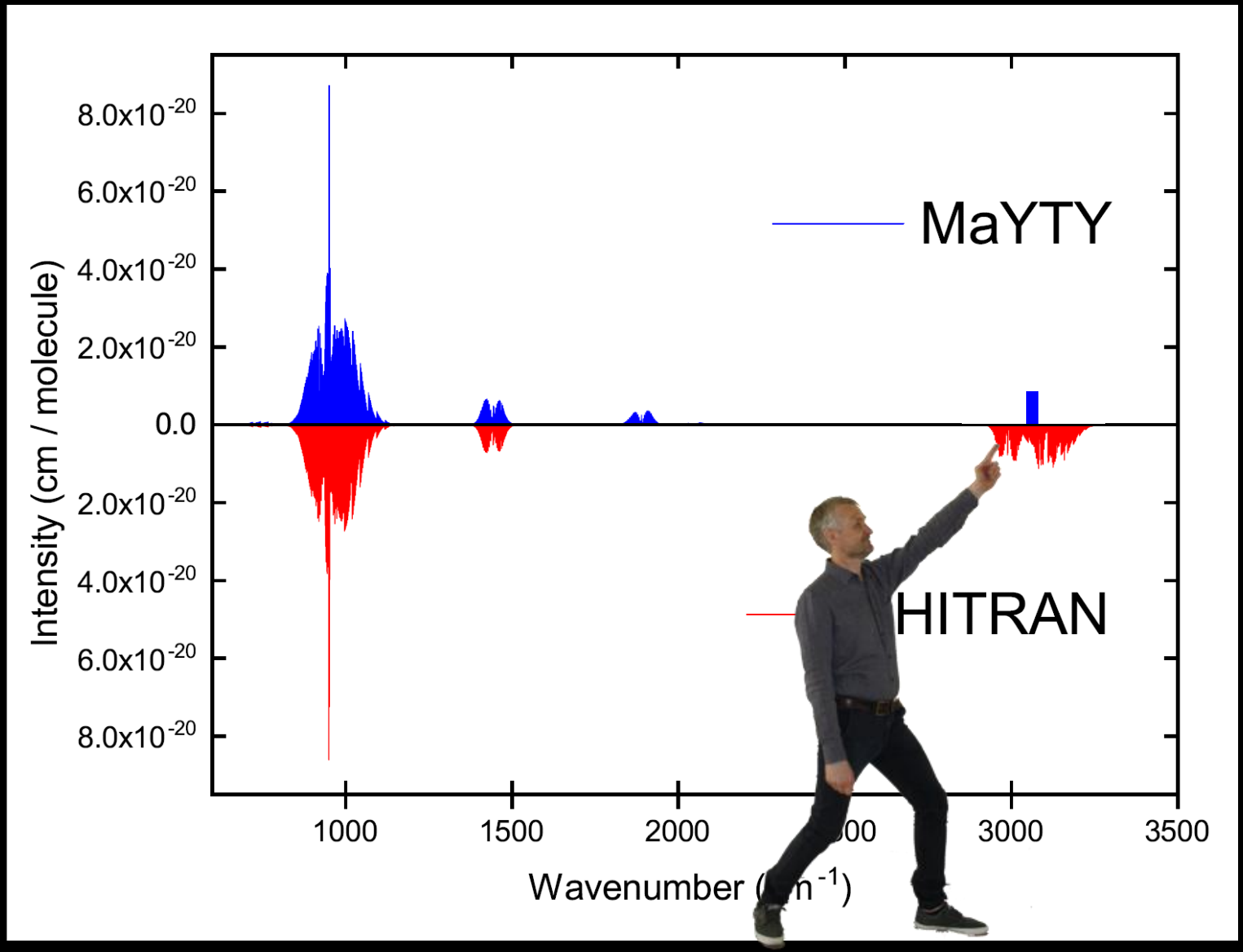

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2500
3000
3500
(cm-1)

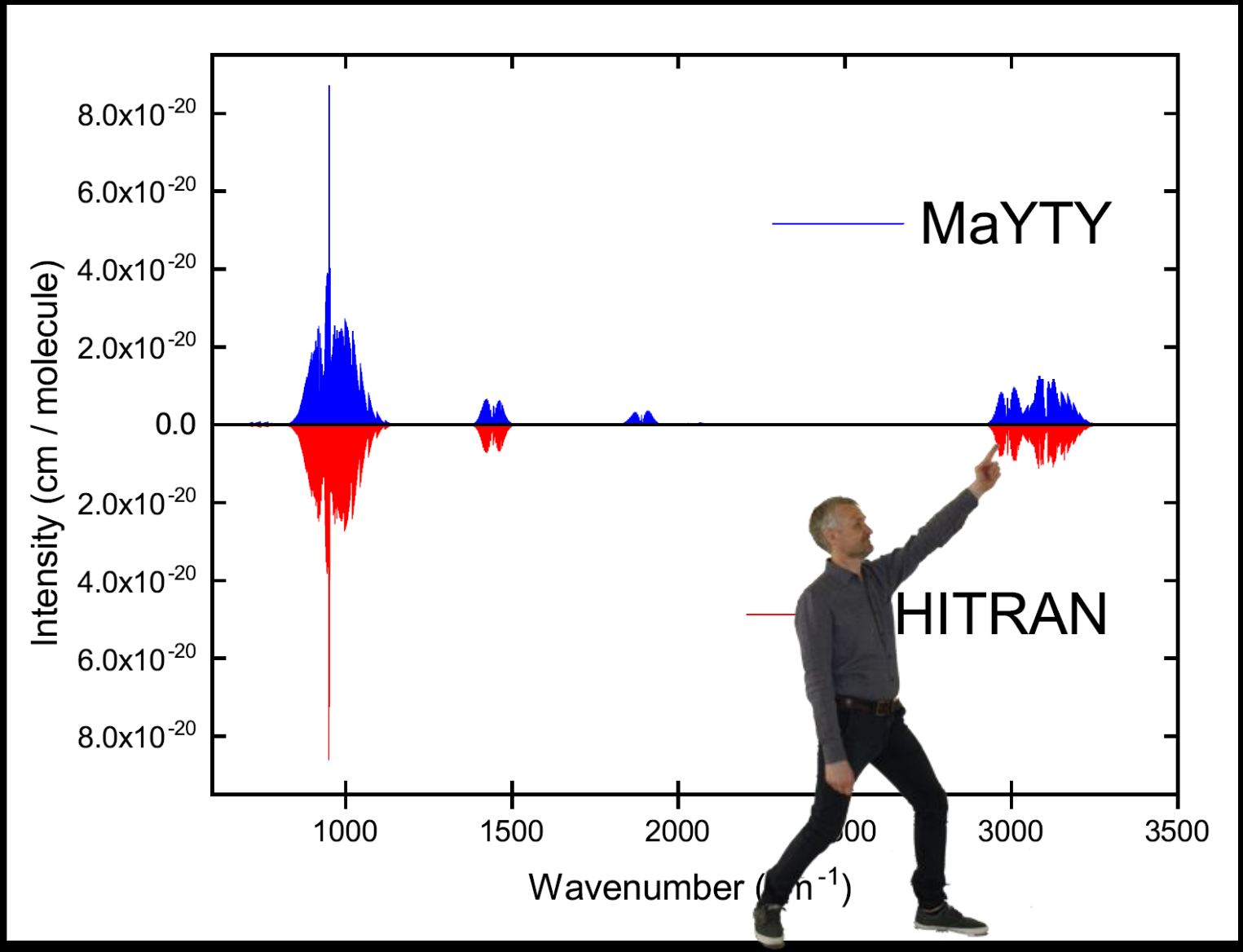

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

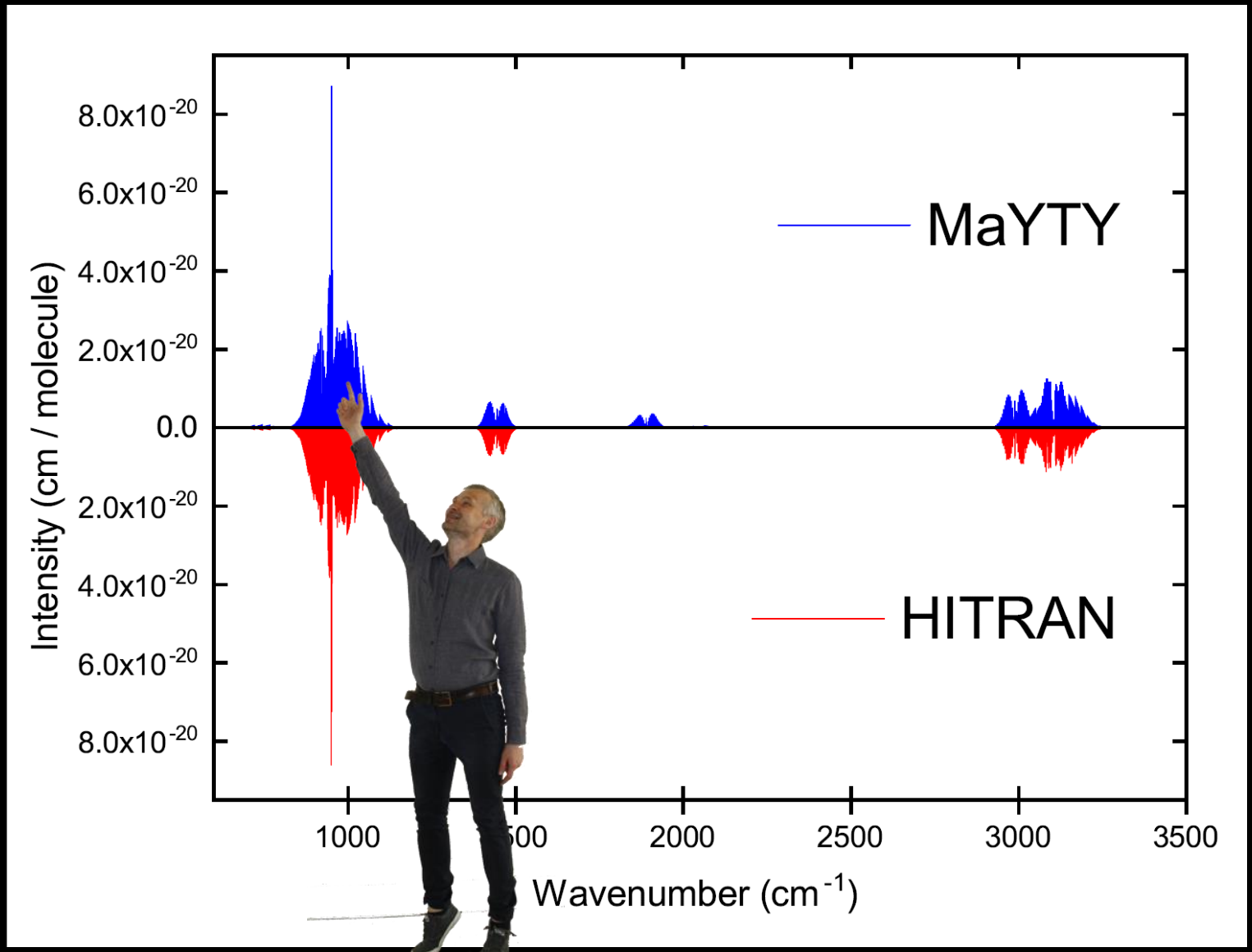

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

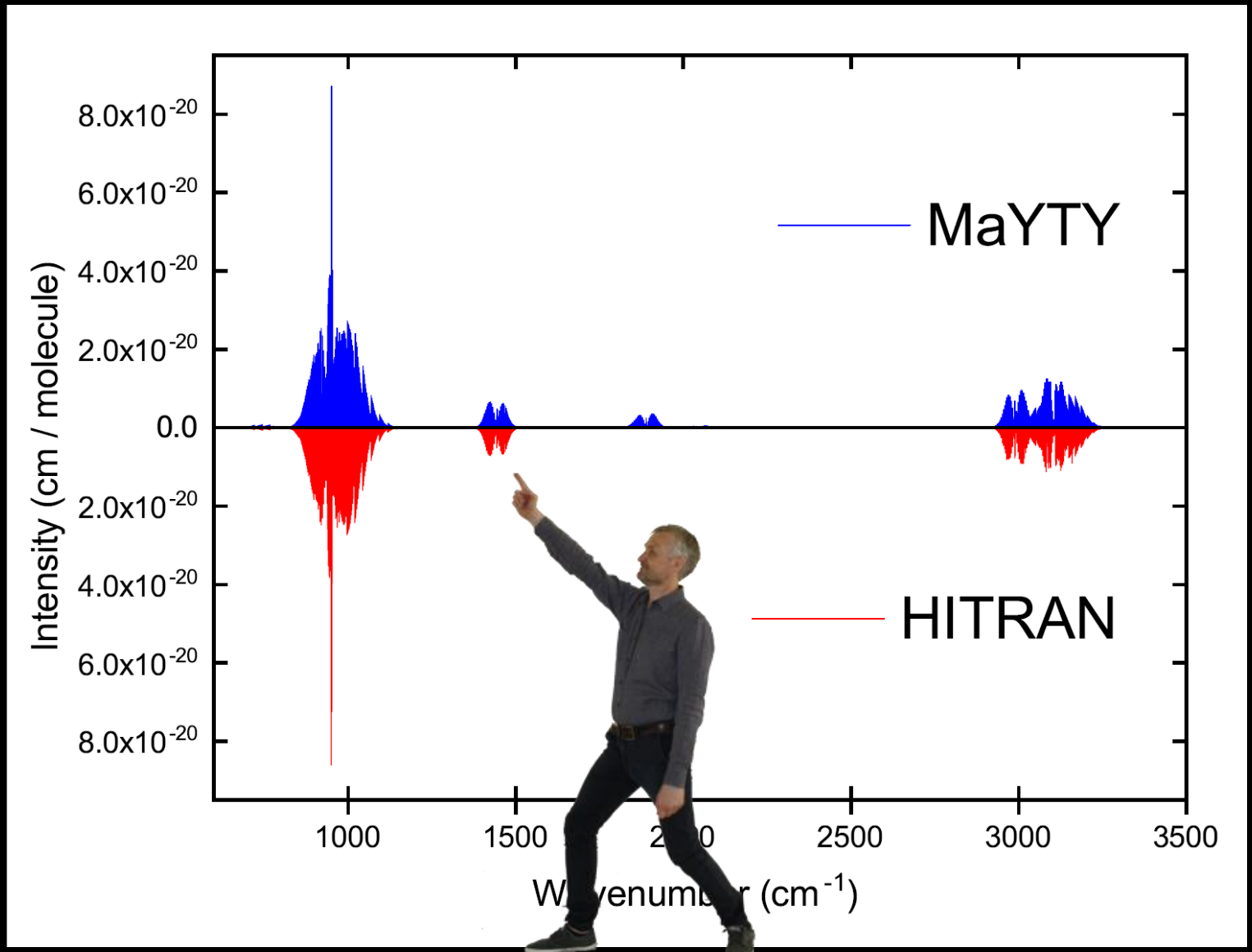

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

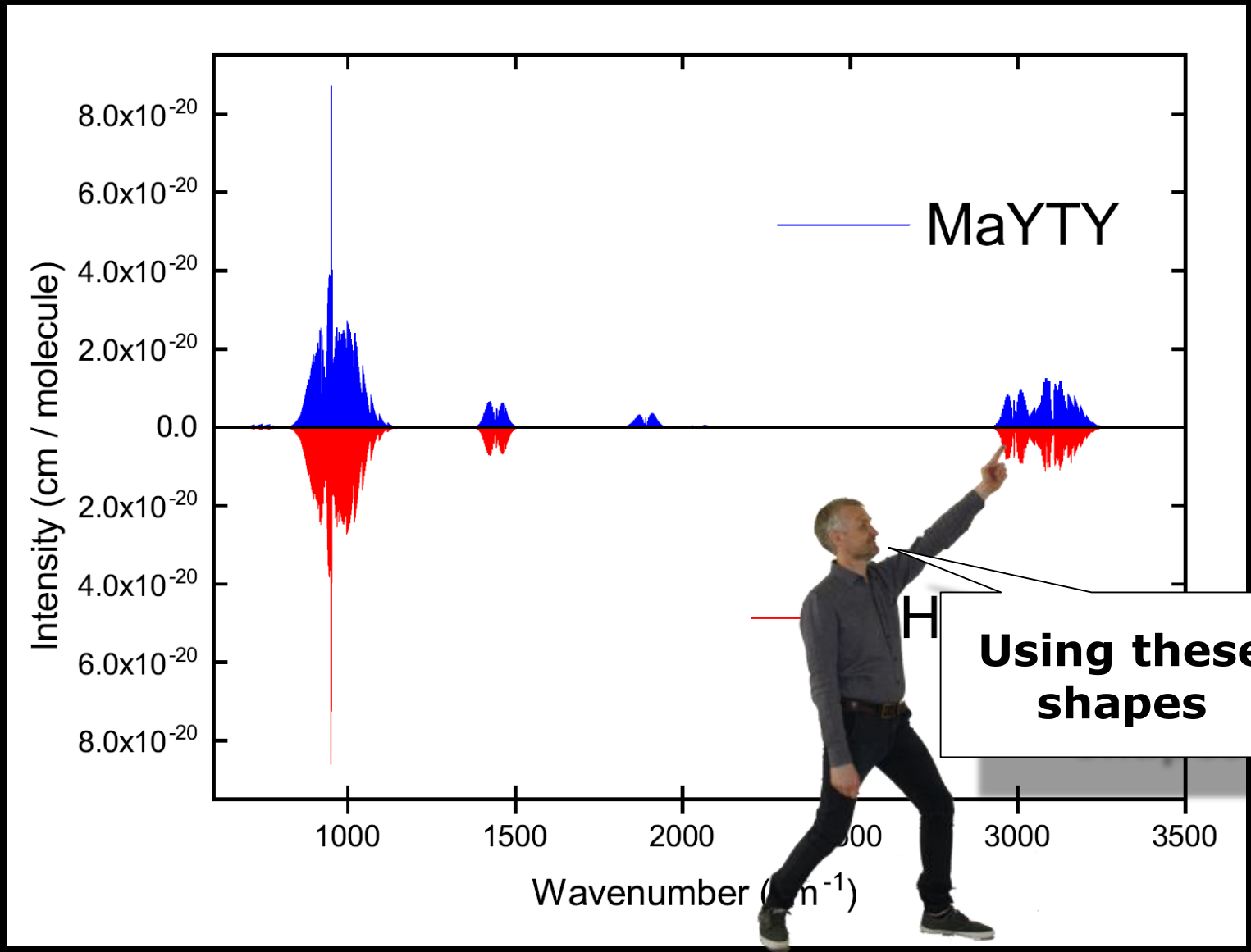

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

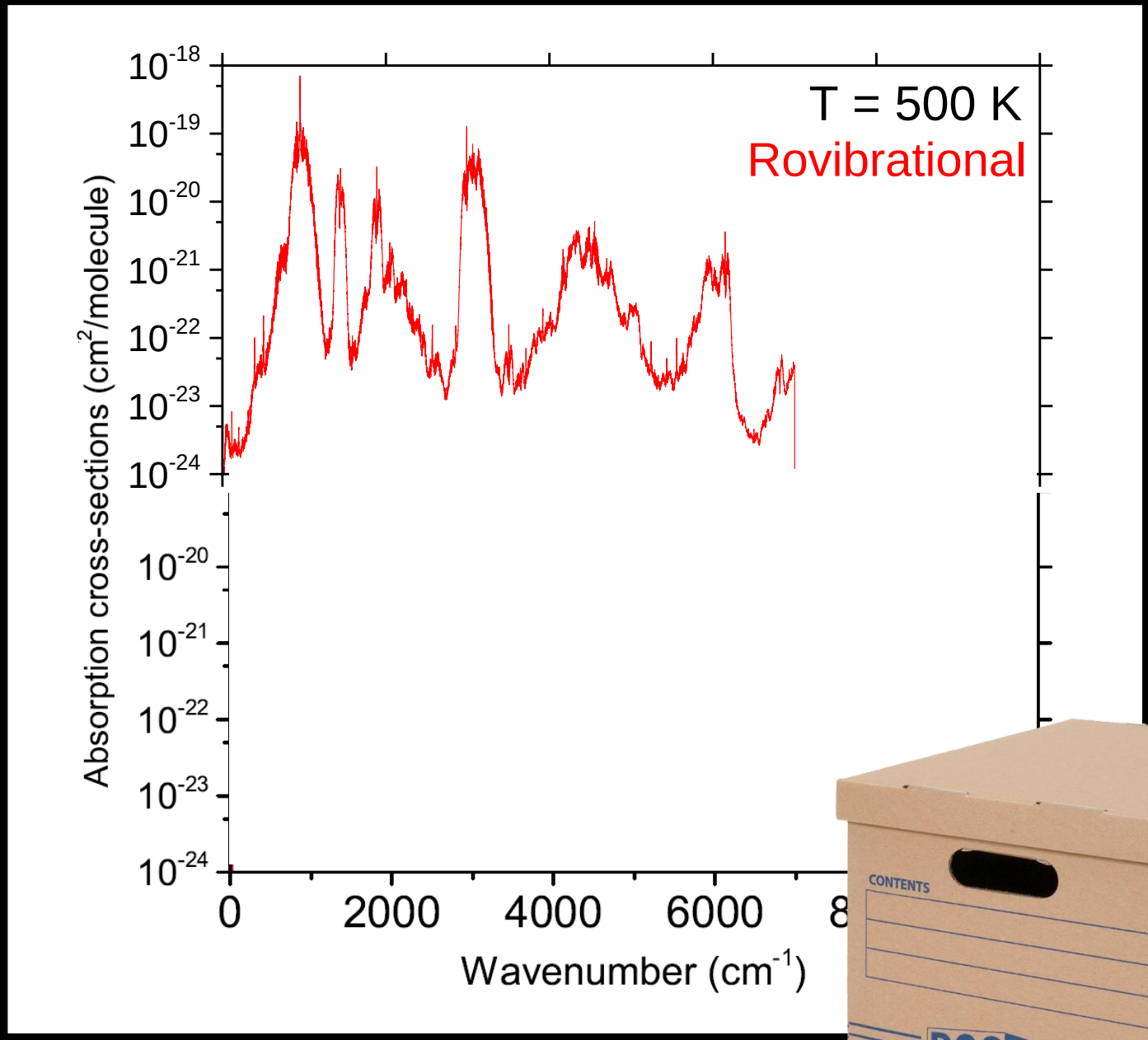

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

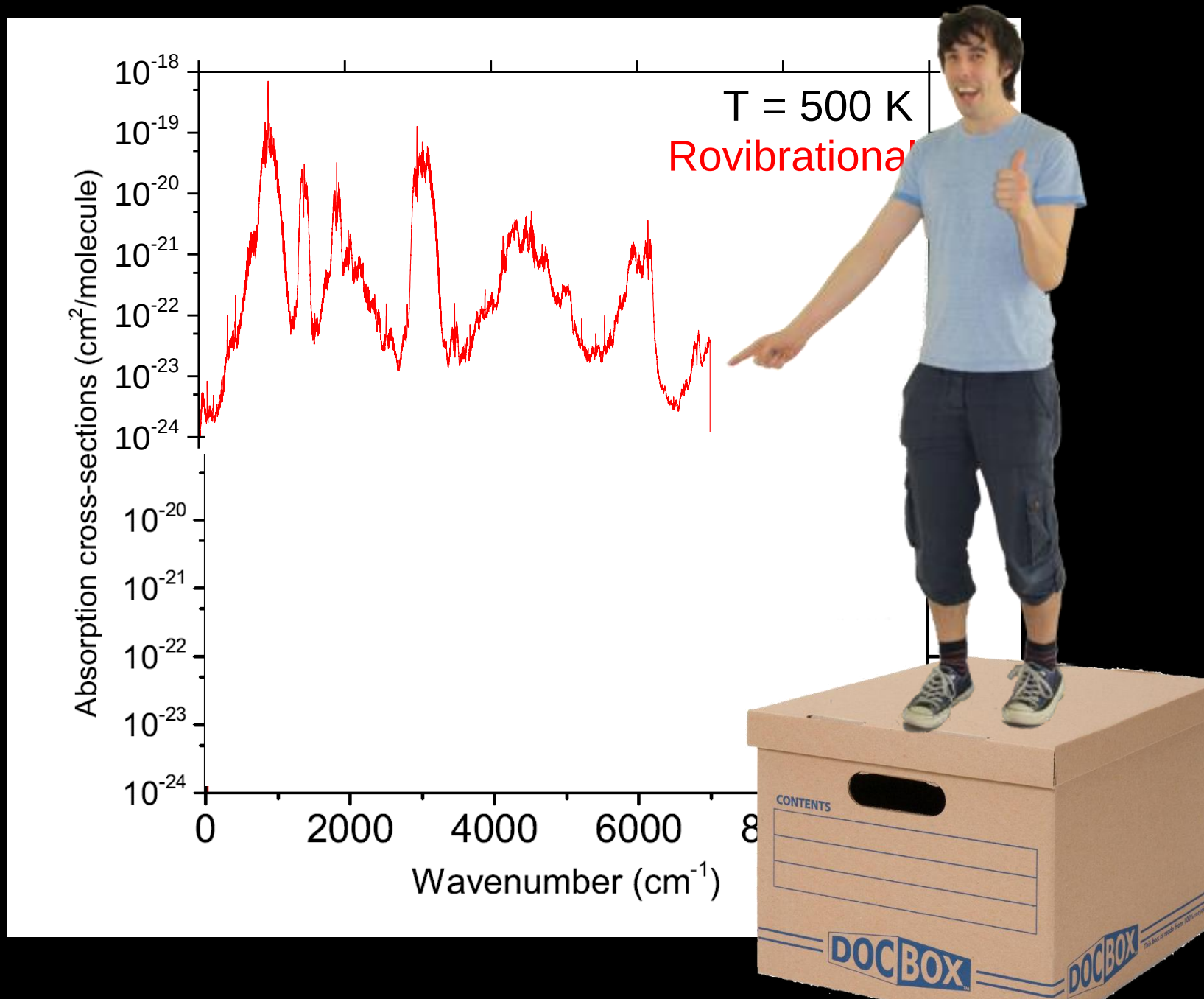

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2000
3000
3500
Wavenumber (cm-1)

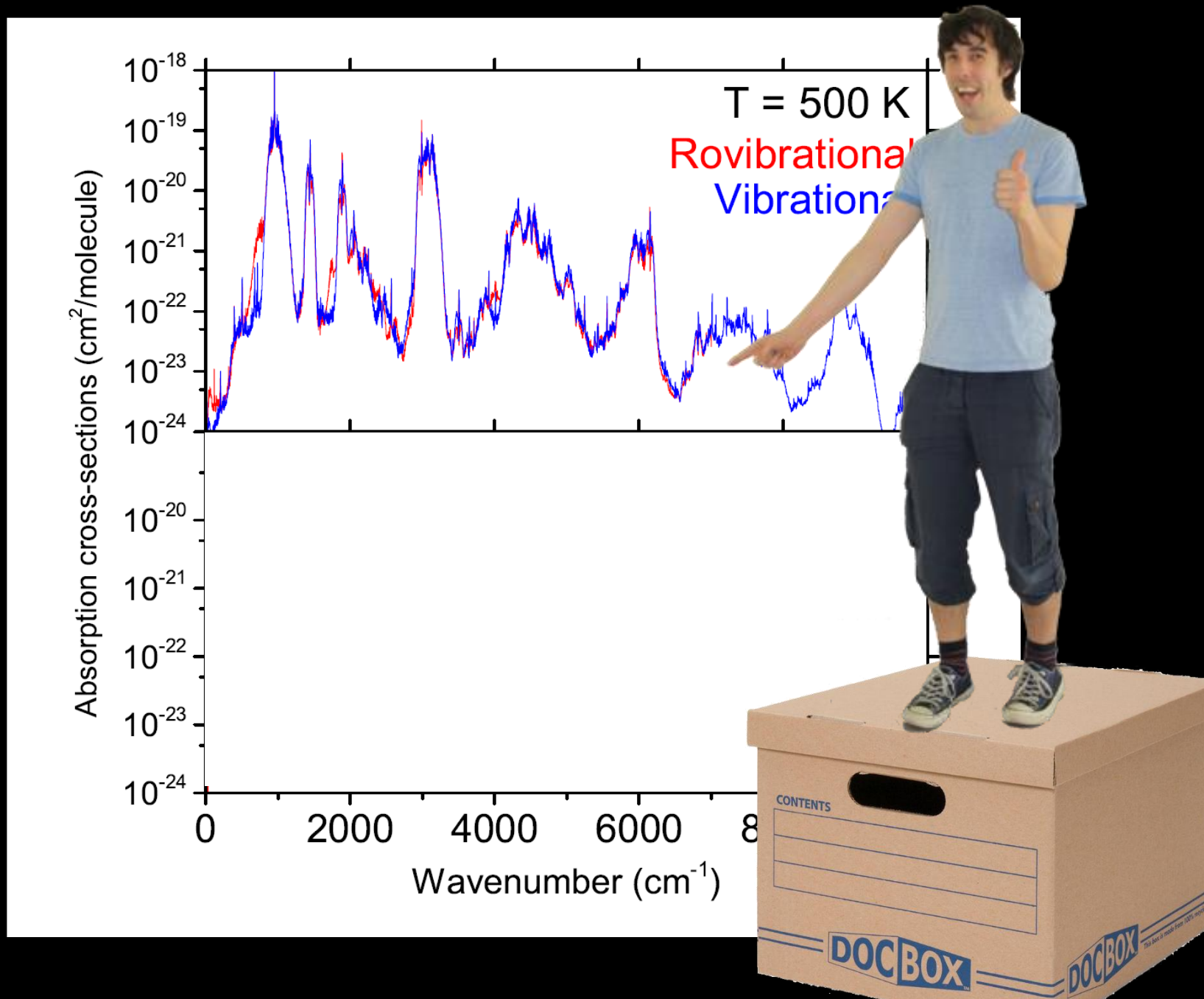

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
2000
2500
3000
3500
Wavenumber (cm-1)

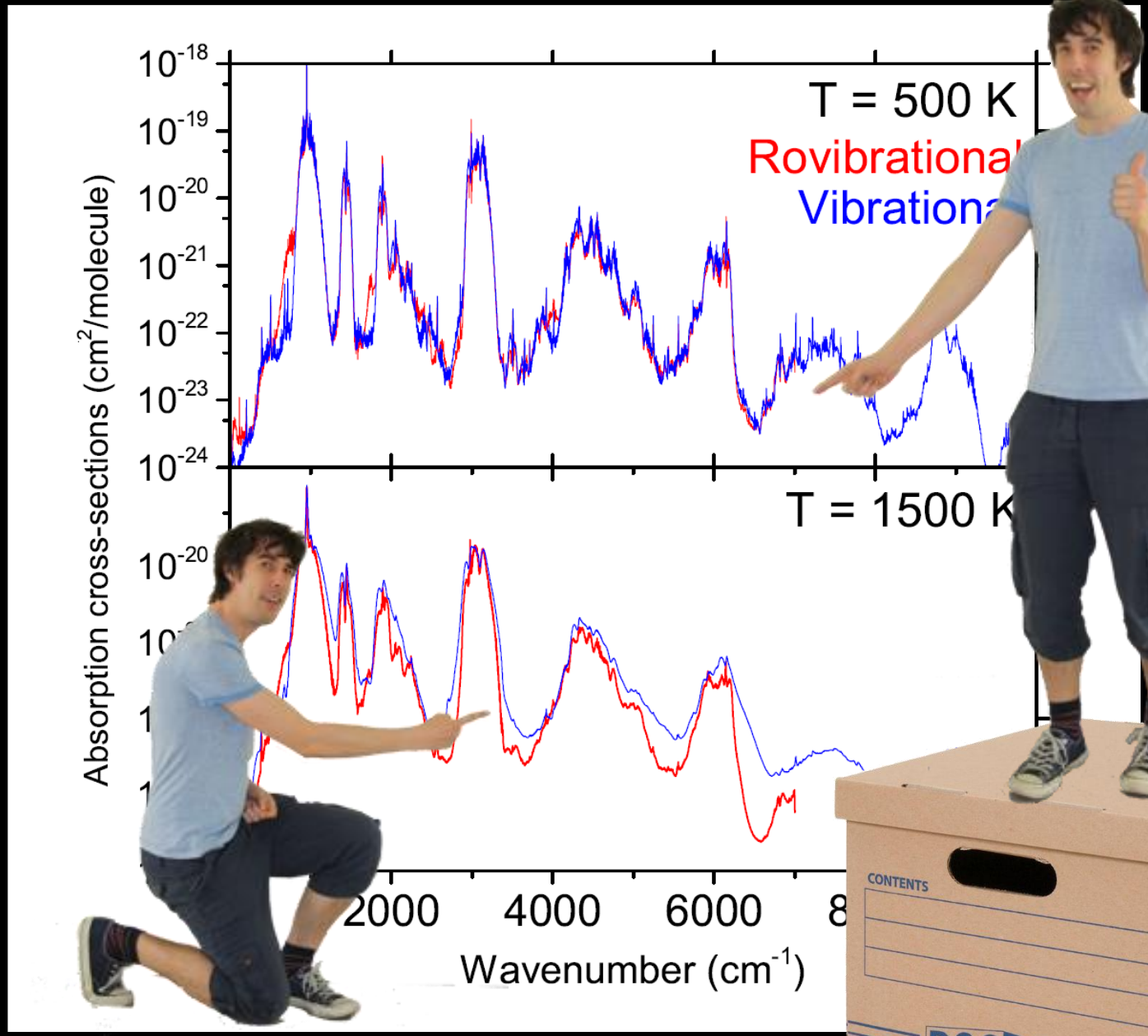

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
HITRAN
1000
1500
2500
3000
3500
(cm-1)

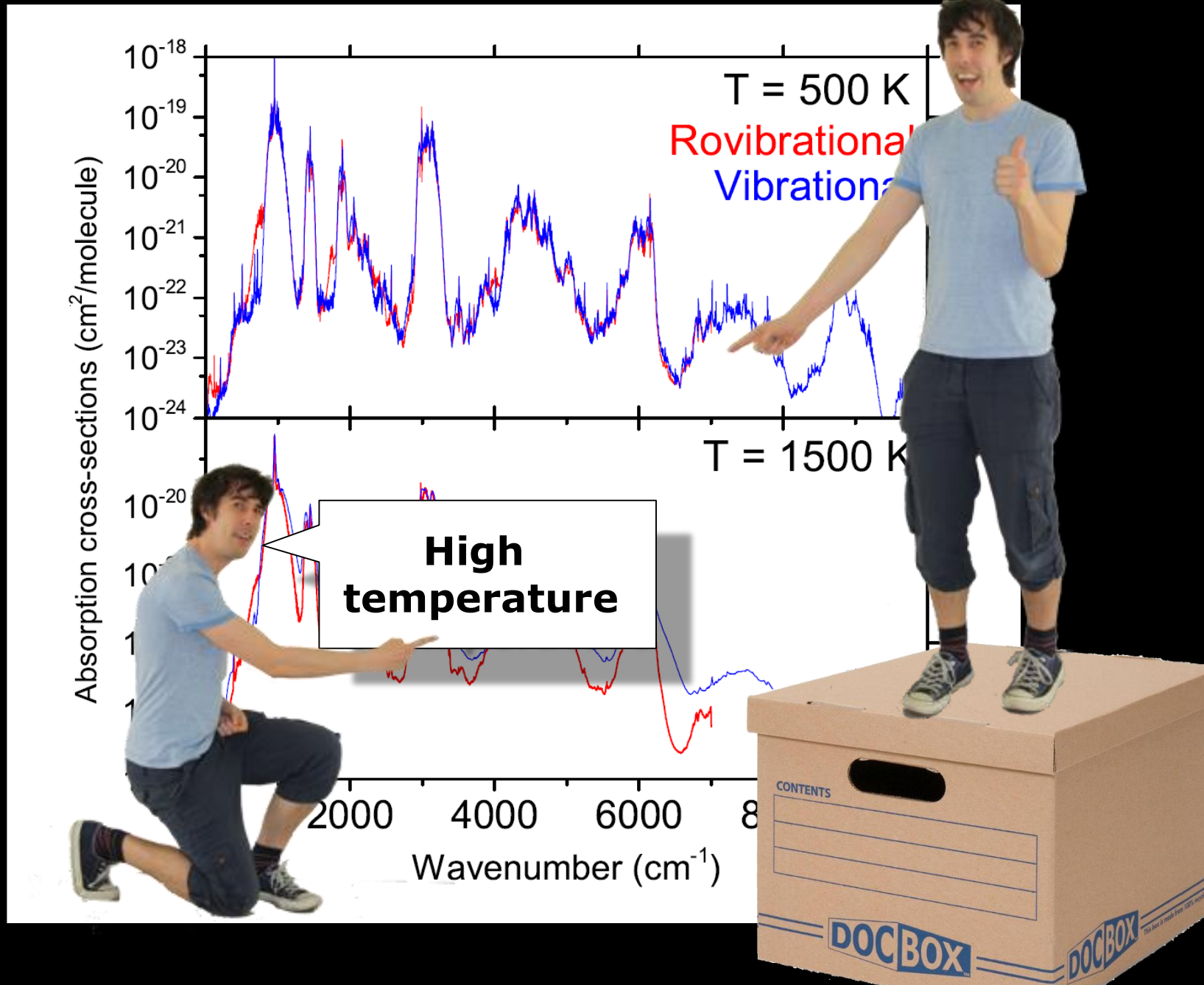

8.0x10-20
6.0x10-20
4.0x10-20
2.0x10-20
0.0
2.0x10-20
4.0x10-20
6.0x10-20
8.0x10-20
Intensity (cm / molecule)
MaYTY
1000
1500
2000
3000
3500
Wavenumber (cm-1)
Using these shapes


T = 500 K
Rovibrational
Absorption cross-sections (cm²/molecule)
10-18
10-19
10-20
10-21
10-22
10-23
10-24
10-20
10-21
10-22
10-23
10-24
0
2000
4000
6000
Wavenumber (cm-1)
CONTENTS
DOCBOX
DOCBOX


T = 500 K
Rovibrational
Absorption cross-sections (cm²/molecule)
10-18
10-19
10-20
10-21
10-22
10-23
10-24
10-20
10-21
10-22
10-23
10-24
0
2000
4000
6000
Wavenumber (cm-1)
CONTENTS
DOCBOX
DOCBOX

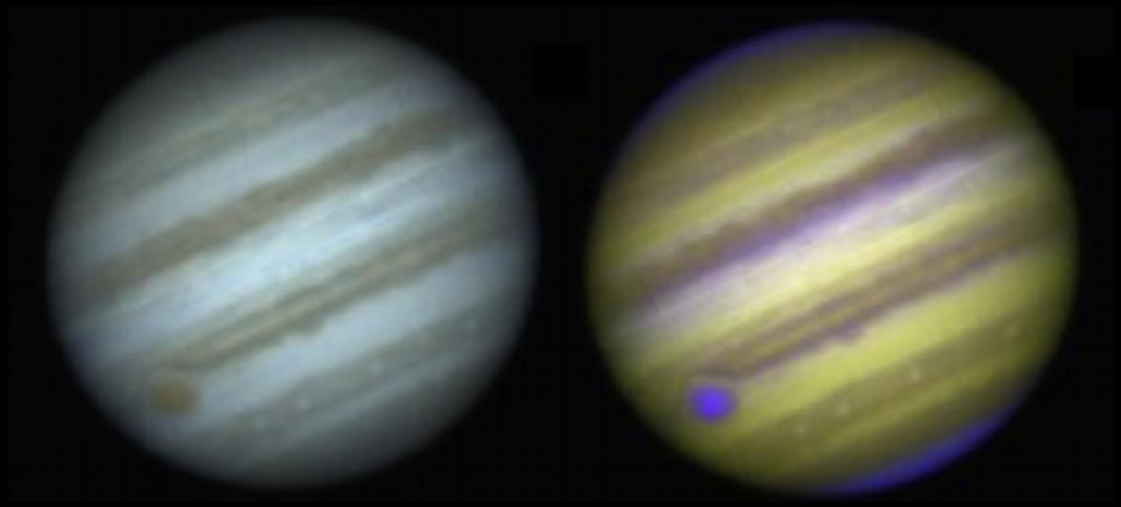

T = 500 K
Rovibrational
Vibrationa
Absorption cross-sections (cm²/molecule)
10^-18
10^-19
10^-20
10^-21
10^-22
10^-23
10^-24
10^-20
10^-21
10^-22
10^-23
10^-24
0
2000
4000
6000
Wavenumber (cm^-1)
CONTENTS
DOCBOX
DOCBOX


T = 500 K
Rovibrational
Vibrational
T = 1500 K
Absorption cross-sections (cm²/molecule)
10^-18
10^-19
10^-20
10^-21
10^-22
10^-23
10^-24
10^-20
2000
4000
6000
Wavenumber (cm^-1)
CONTENTS
DOCBOX
DOCBOX

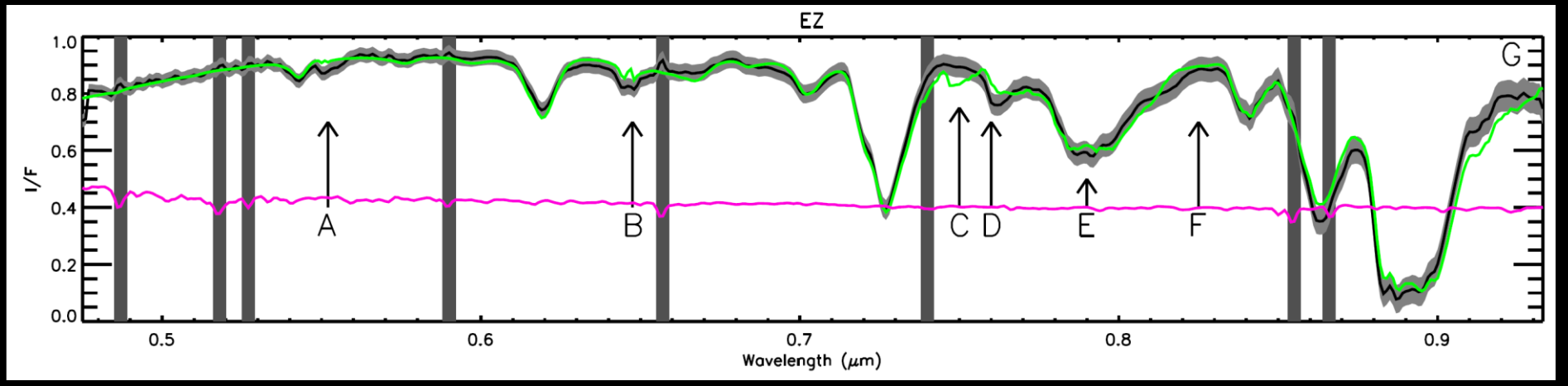

T = 500 K
Rovibrational
Vibrational
T = 1500 K
High temperature
Absorption cross-sections (cm²/molecule)
Wavenumber (cm⁻¹)
CONTENTS
DOCBOX

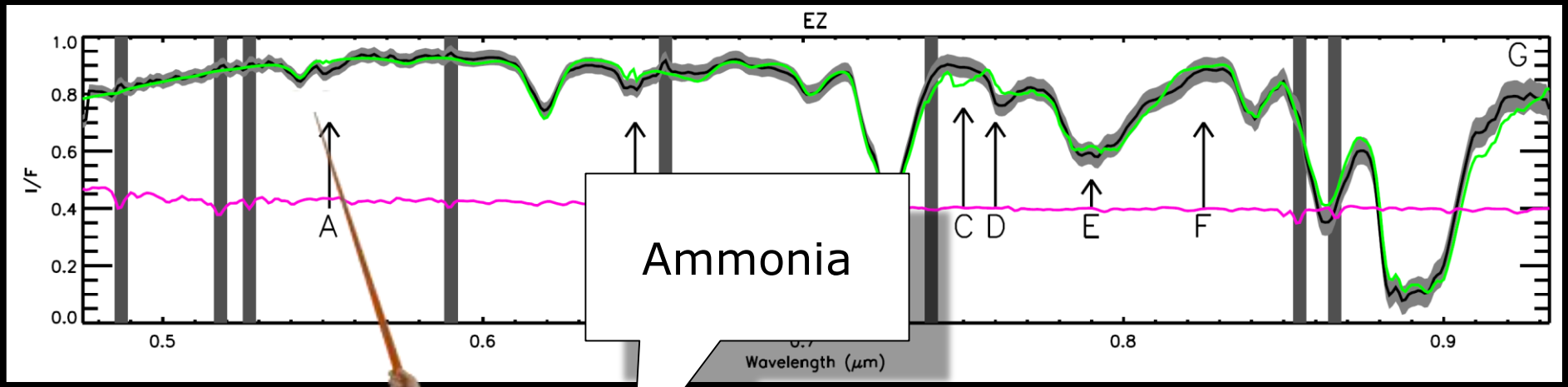
Ammonia

Very Large Telescope (VLT) Multi Unit Spectroscopic Explorer (MUSE) instrument in the spectral range 0.48–0.93 μm

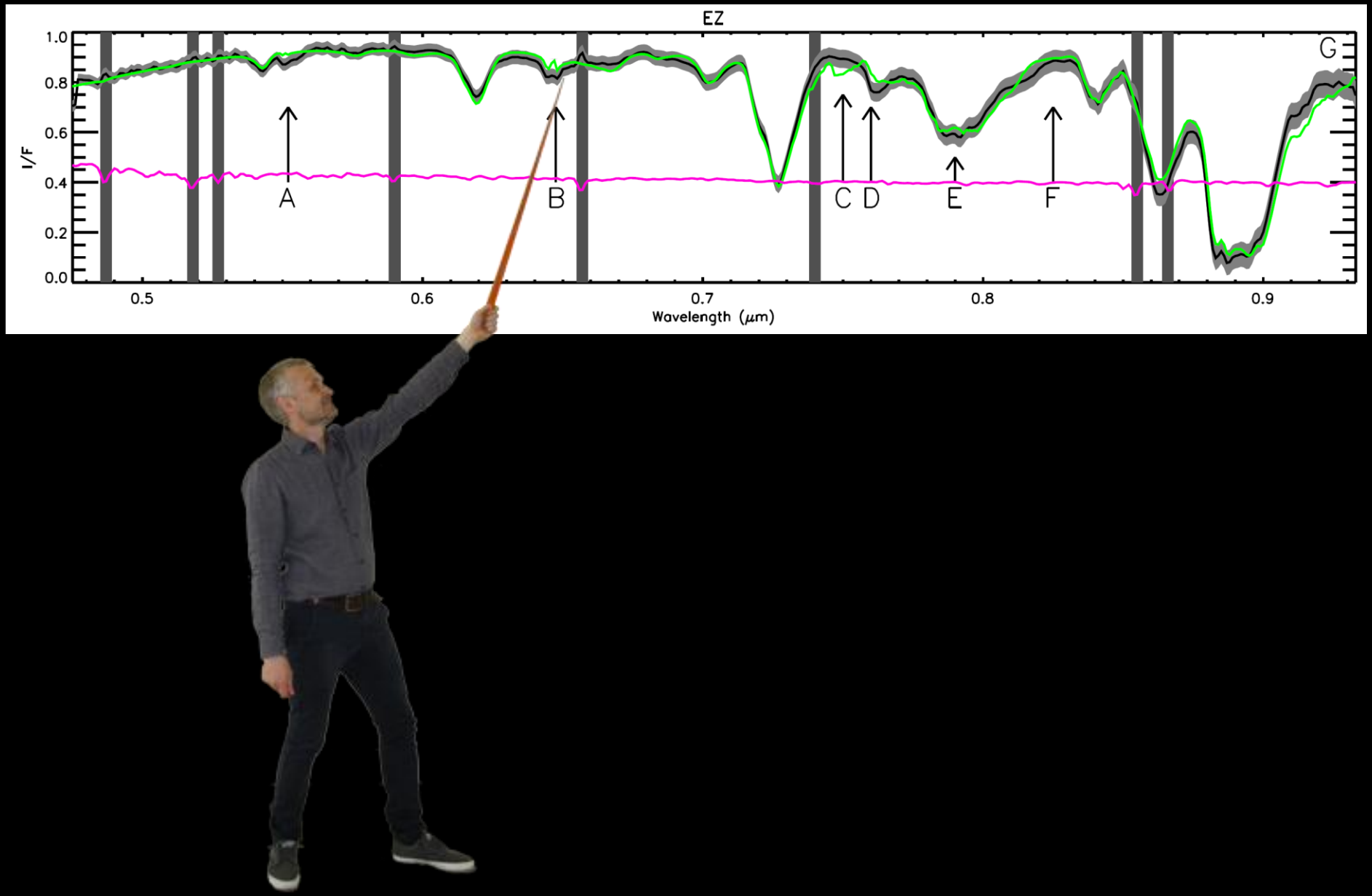


Visible spectrum of Jupiter:
Ammonia bands


EZ
1.0
0.8
0.6
0.4
0.2
0.0
I/F
0.5
0.6
0.7
0.8
0.9
Wavelength (μm)
A
B
C
D
E
F
G



Ammonia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I/F
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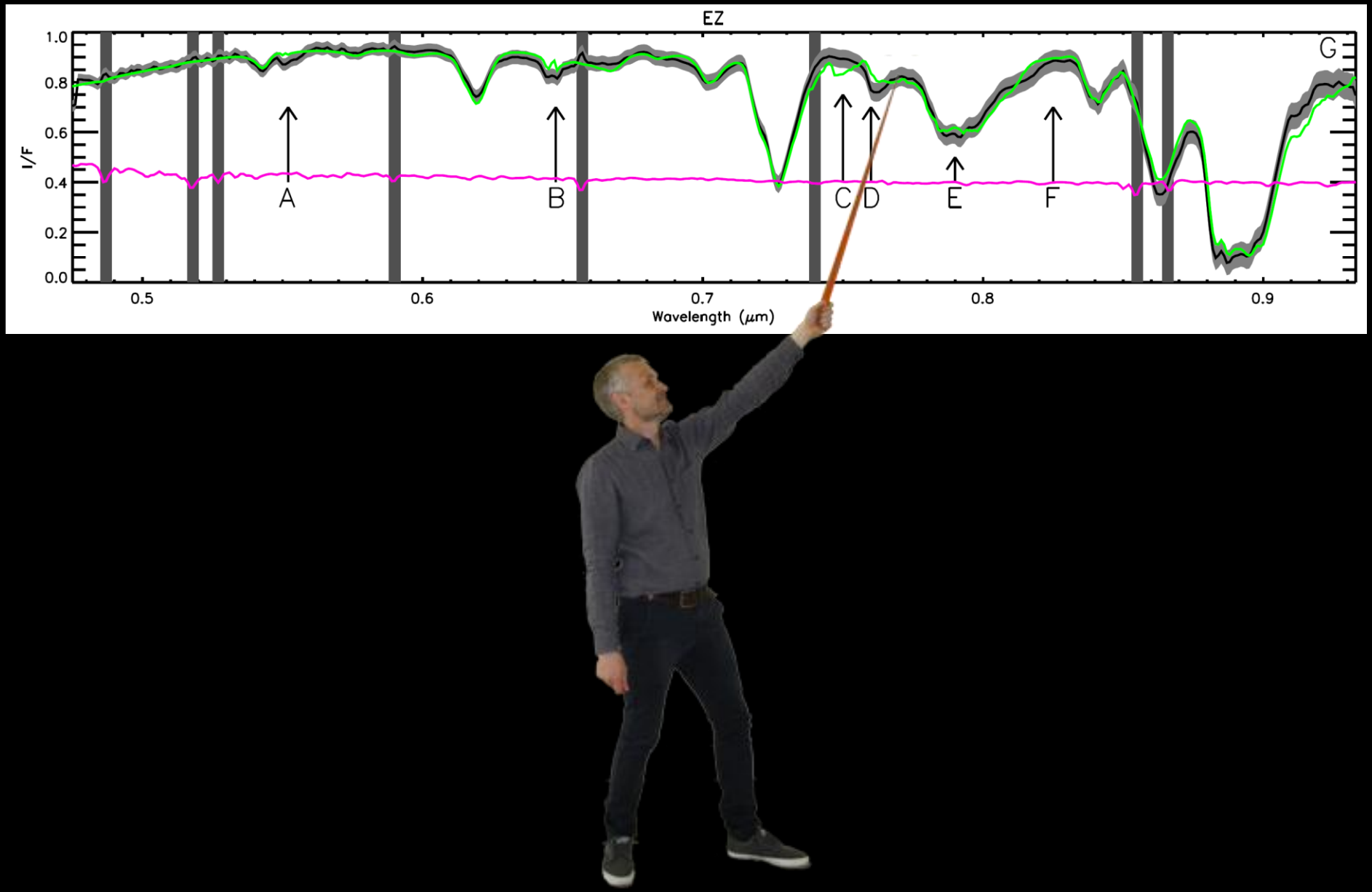
0.8
0.6
0.4
0.2
0.0
0.5
0.6
0.7
0.8
0.9
Wavelength (μm)
A
B
C
D
E
F
G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Wavelength (μm)
A
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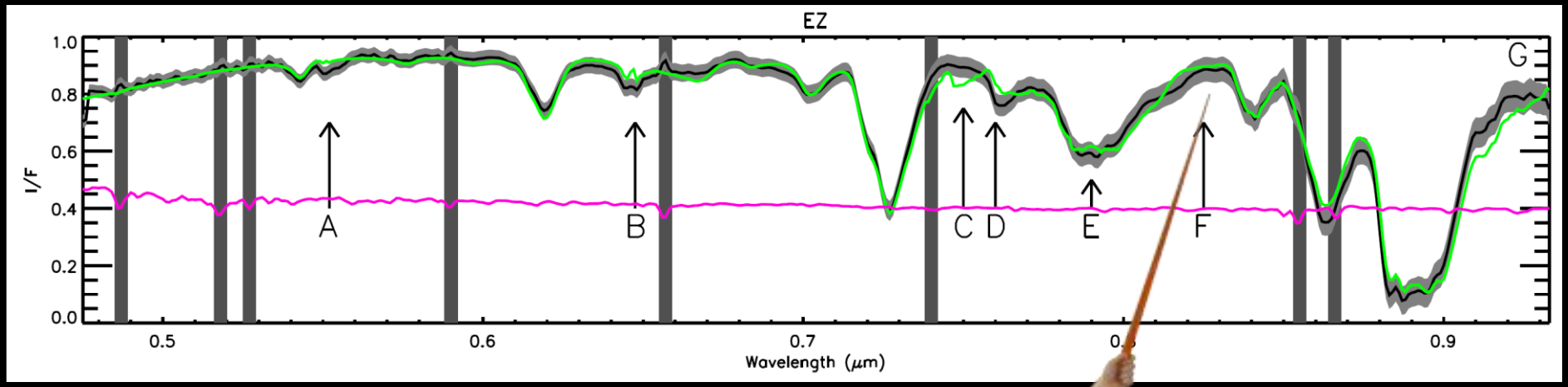
EZ
I/F
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Wavelength (μm)
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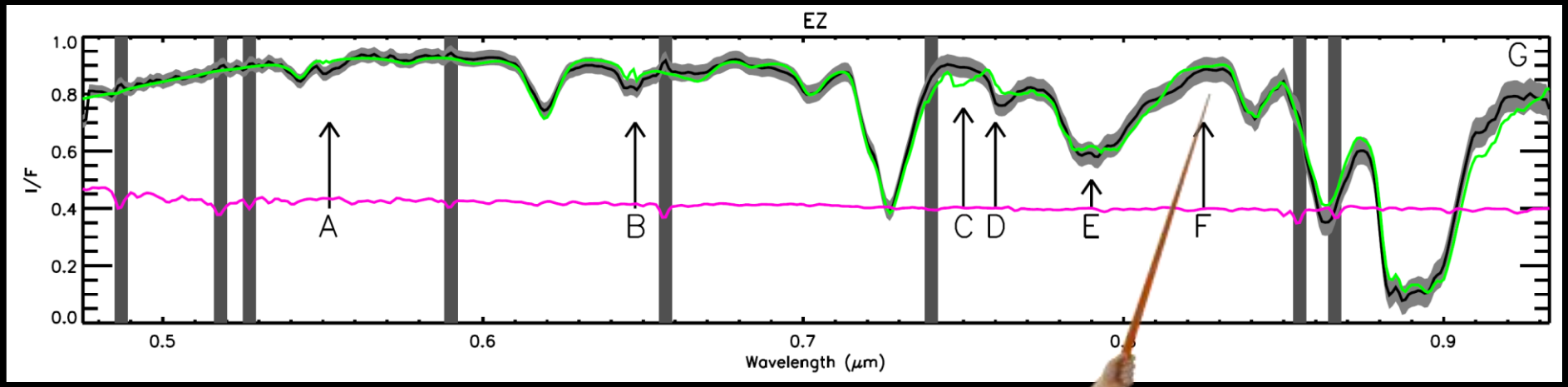

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Analysis of gaseous ammonia (NH_3) absorption in the visible spectrum of Jupiter

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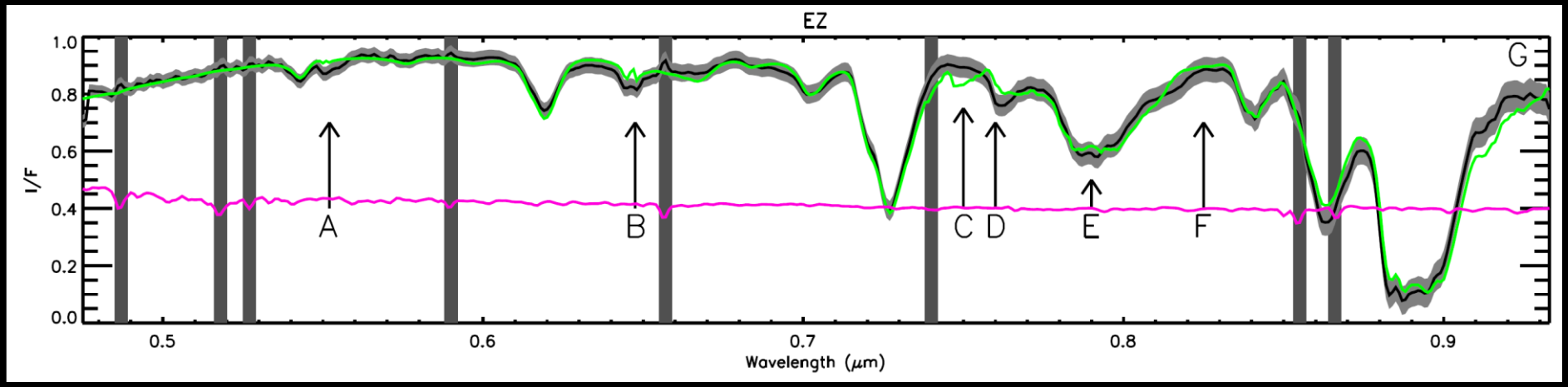
Department of Physics, University of Oxford, Parks Rd, Oxford OX1 3PU, UK



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They tried our new empirical line list for NH_3

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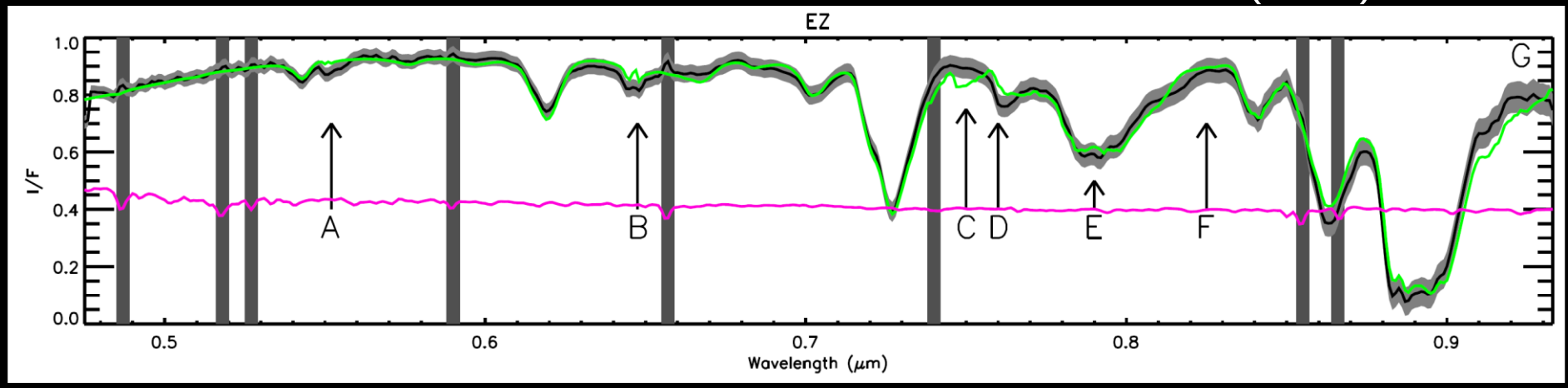

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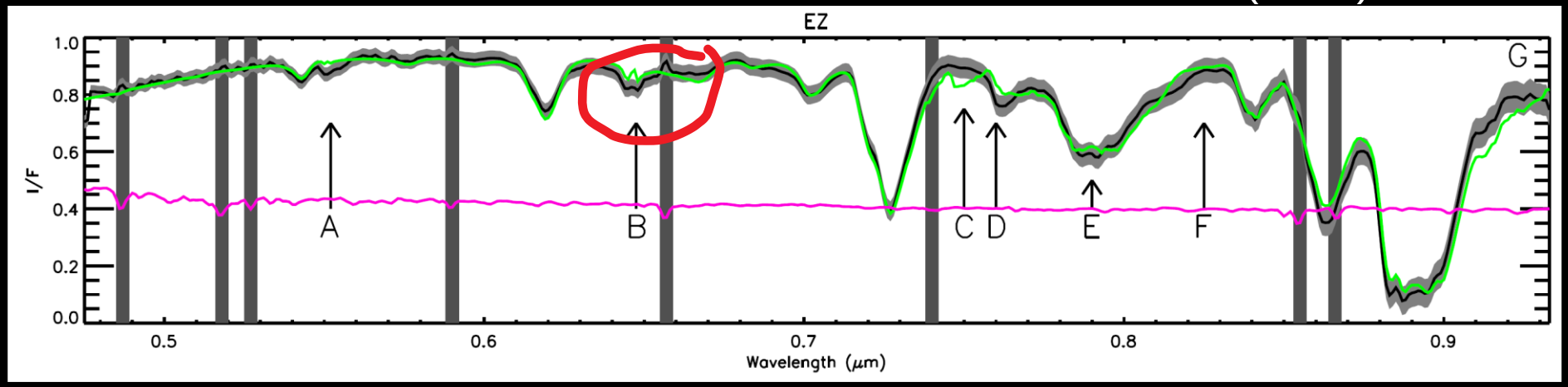

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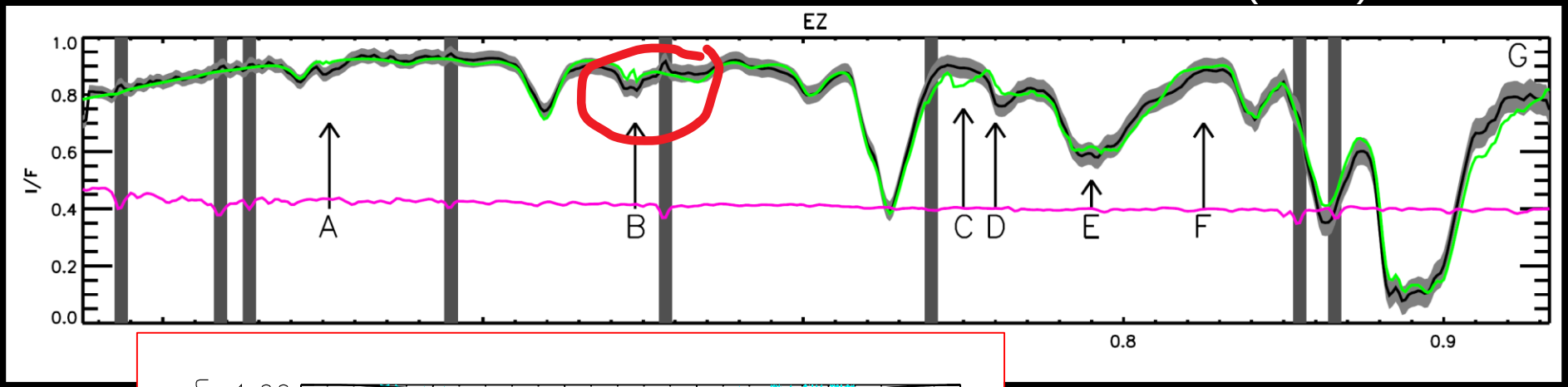

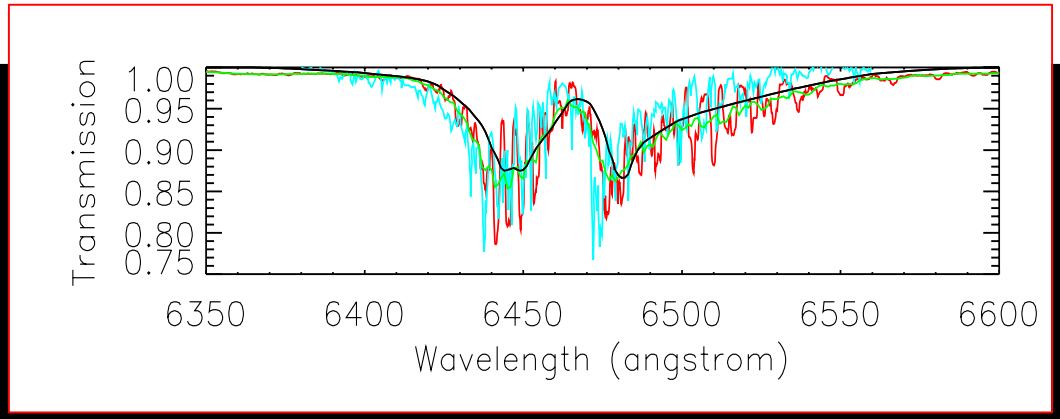

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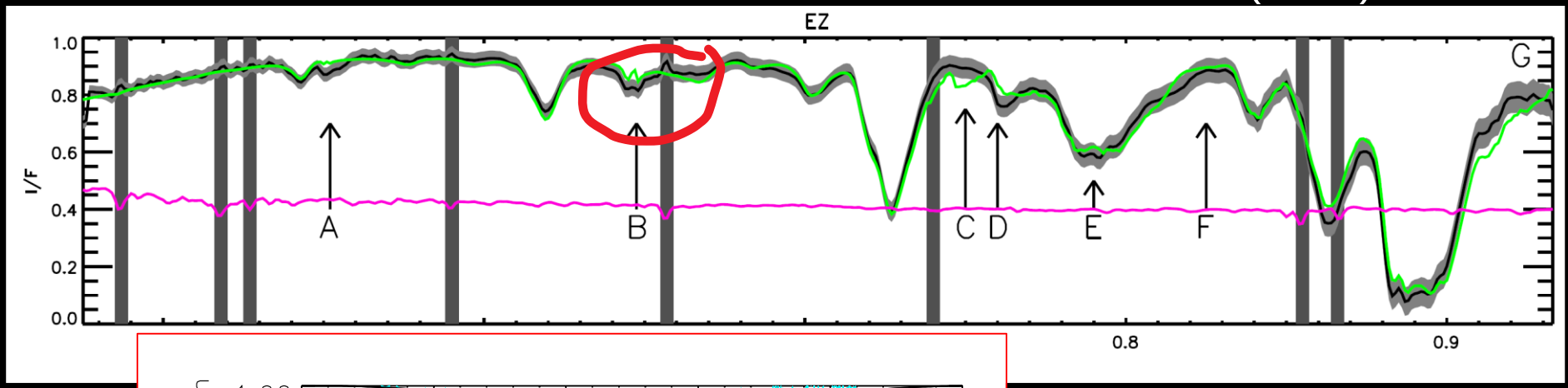

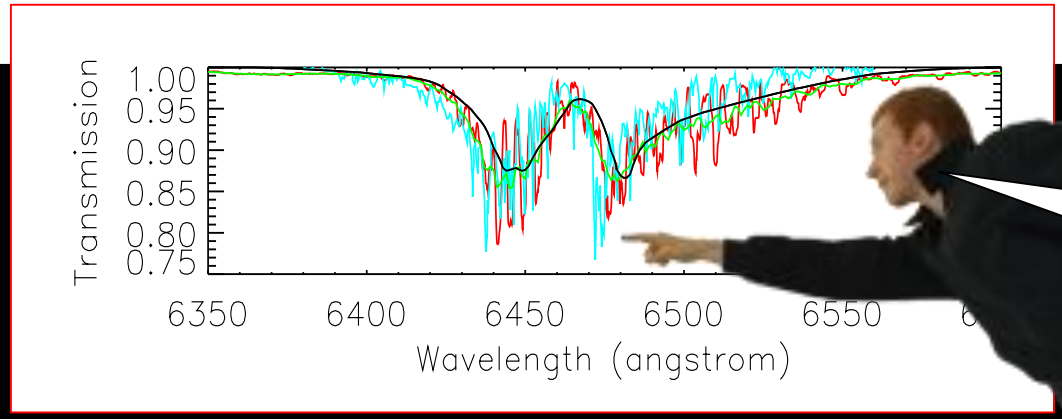

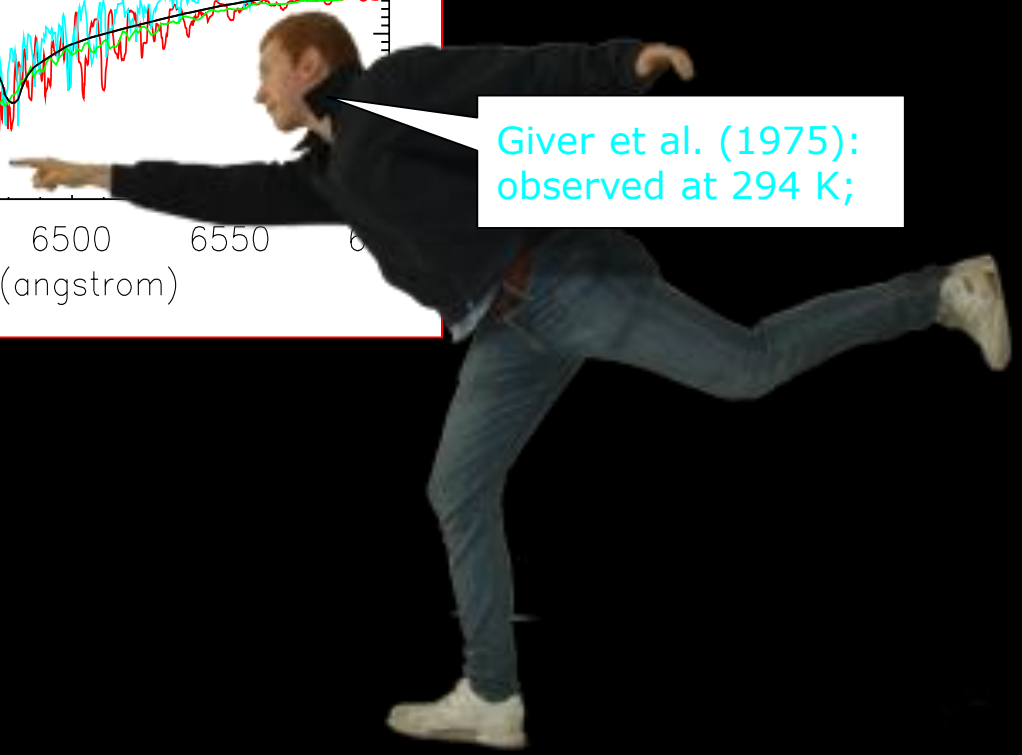

Giver et al. (1975): observed at 294 K;

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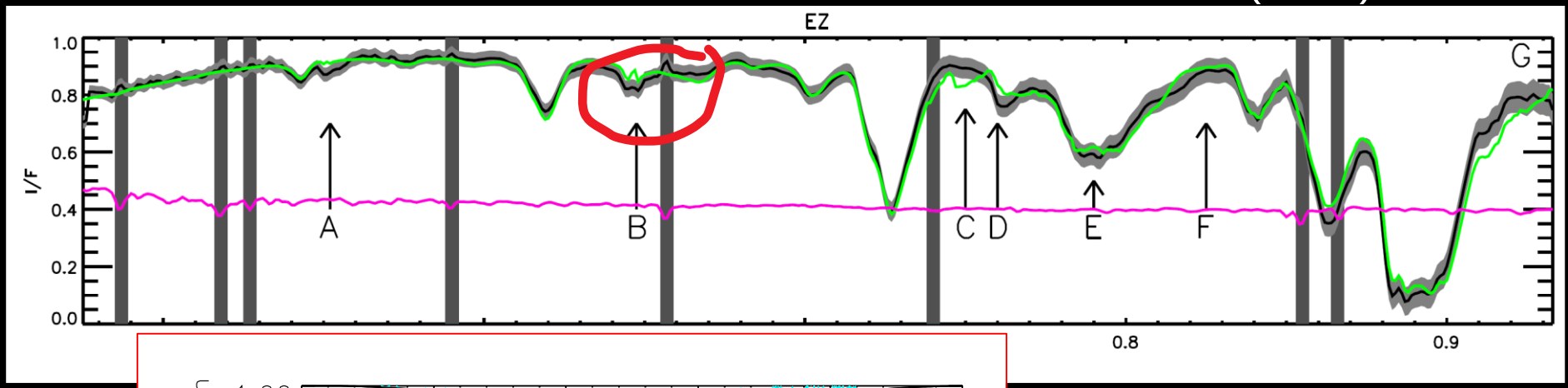

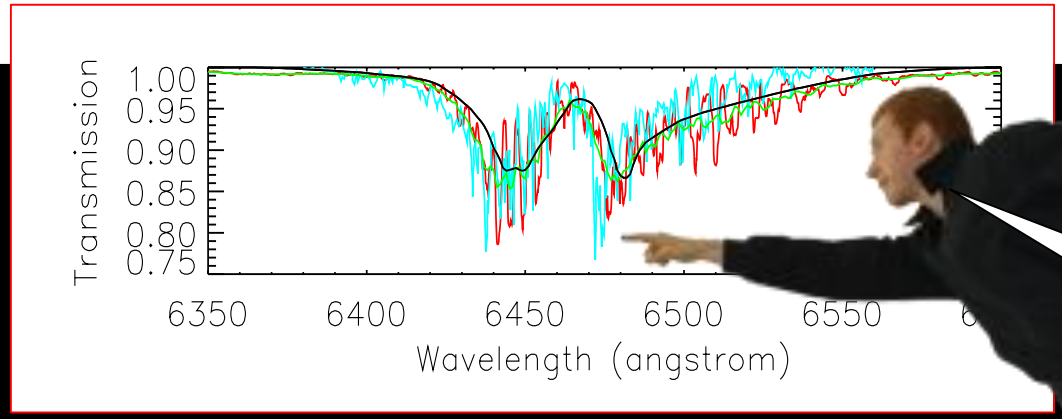

Lutz and Owen (1980): low resolution absorption coefficients.

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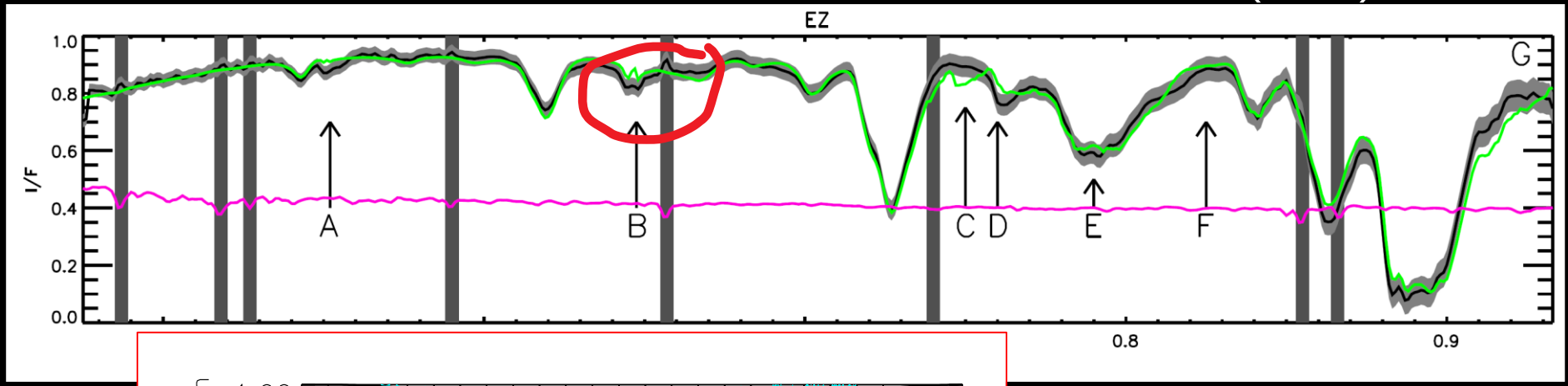

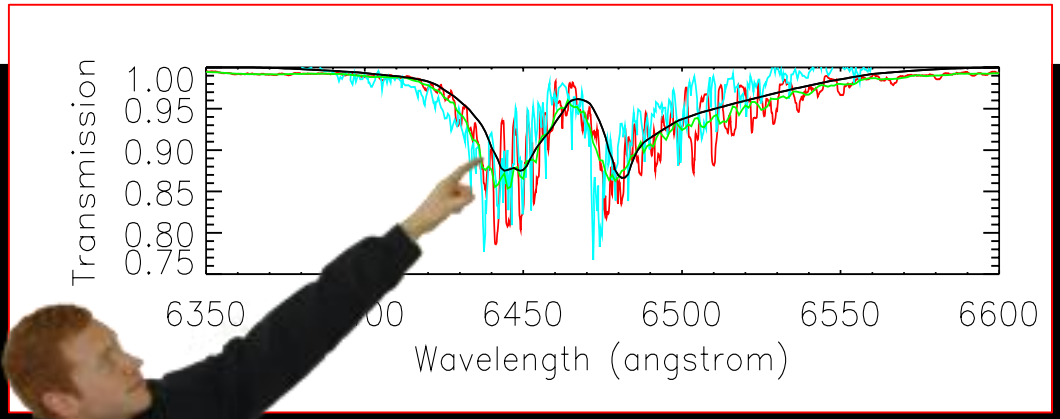

Our theoretical spectrum is represented by the green and red lines

Quasi-continuum

Methane line list contains 34 billion transitions


The End