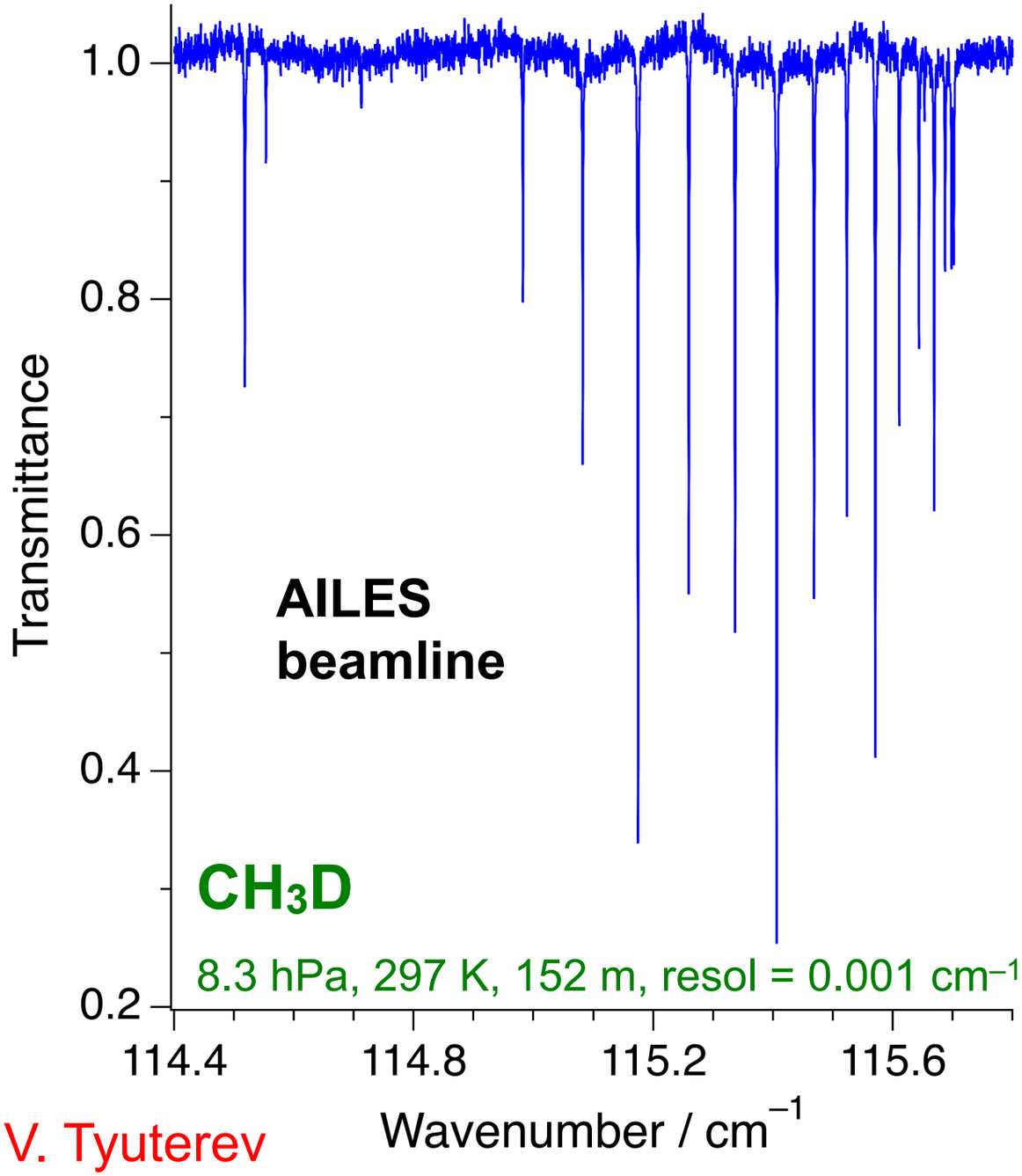
Line intensities and broadening coefficients from high-resolution far infrared spectra

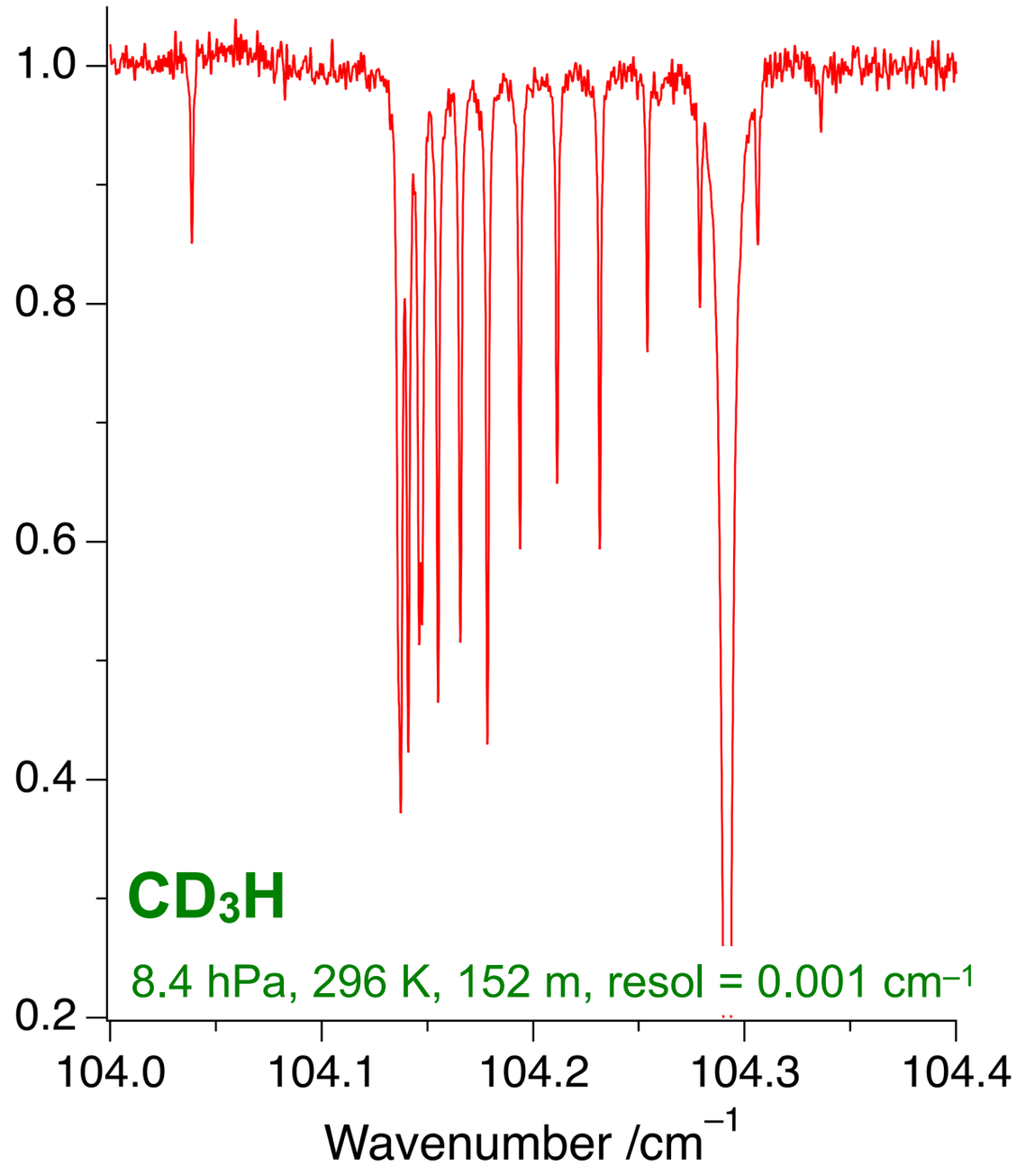
J. Vander Auwera

Service de Chimie Quantique et Photophysique
Université Libre de Bruxelles

Introduction

From laboratory spectra ...

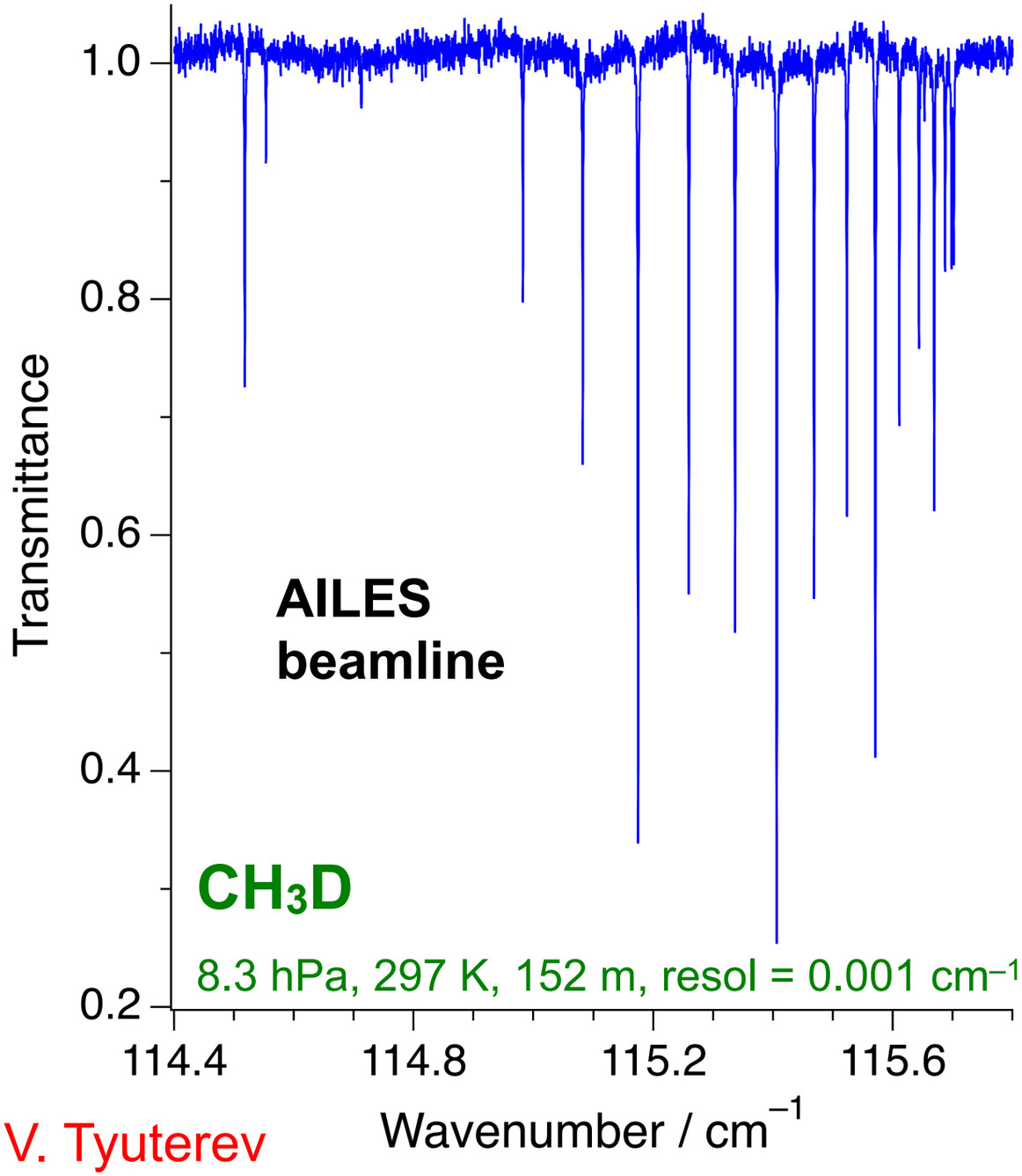


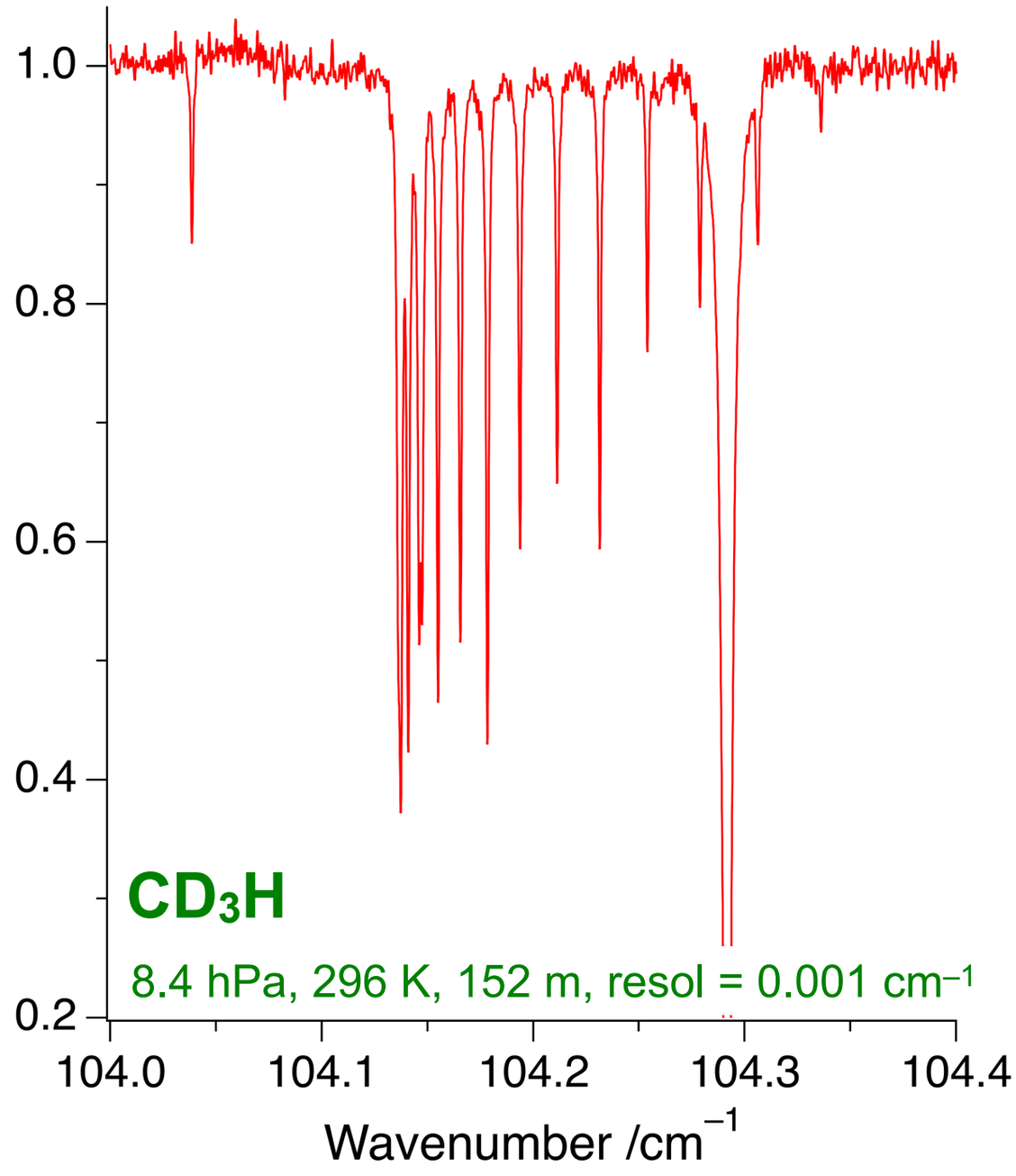


V. Tyuterev

Introduction

From laboratory spectra ... → *to line parameters* (positions, intensities, widths...)





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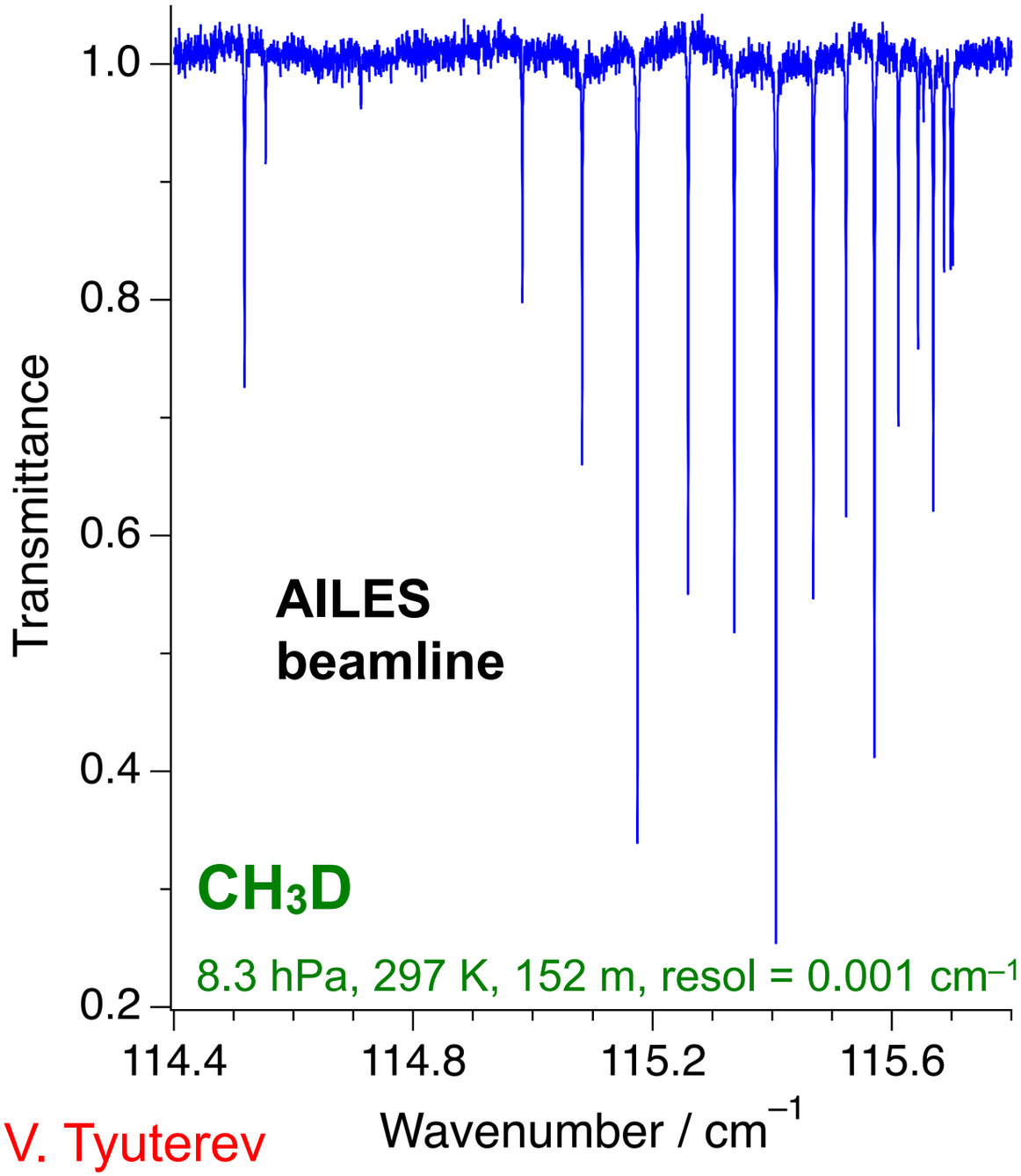

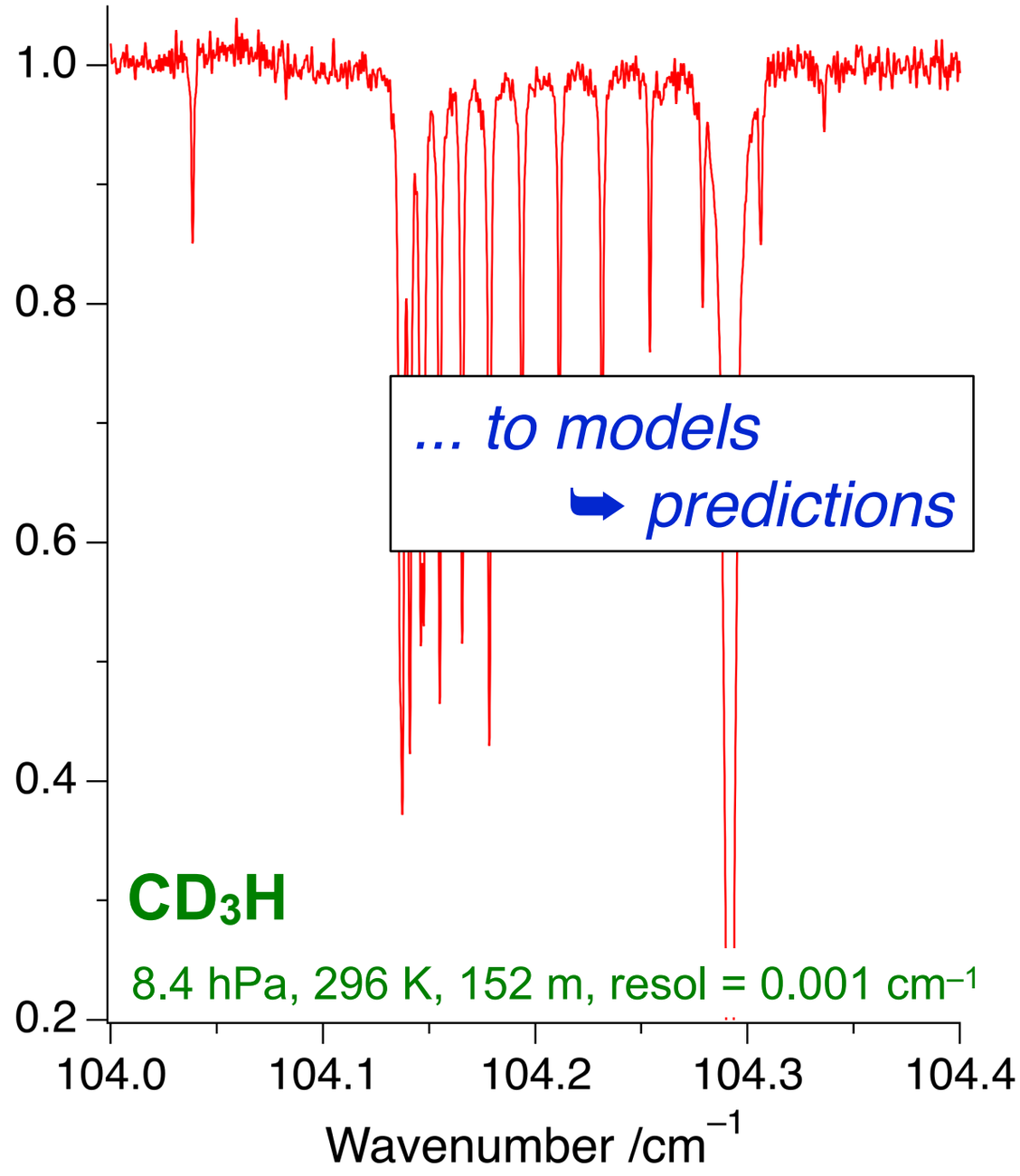

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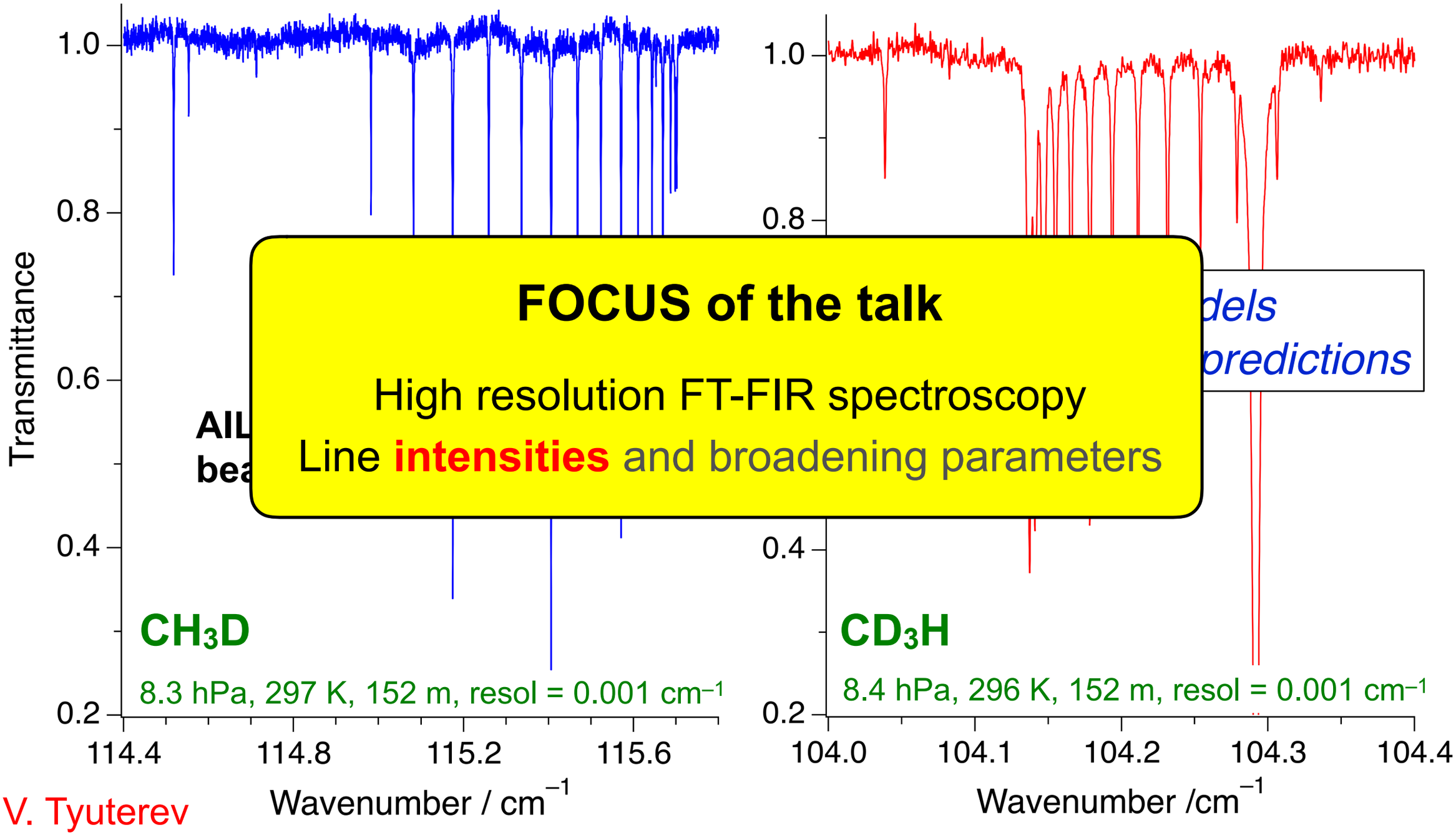


FOCUS of the talk

High resolution FT-FIR spectroscopy

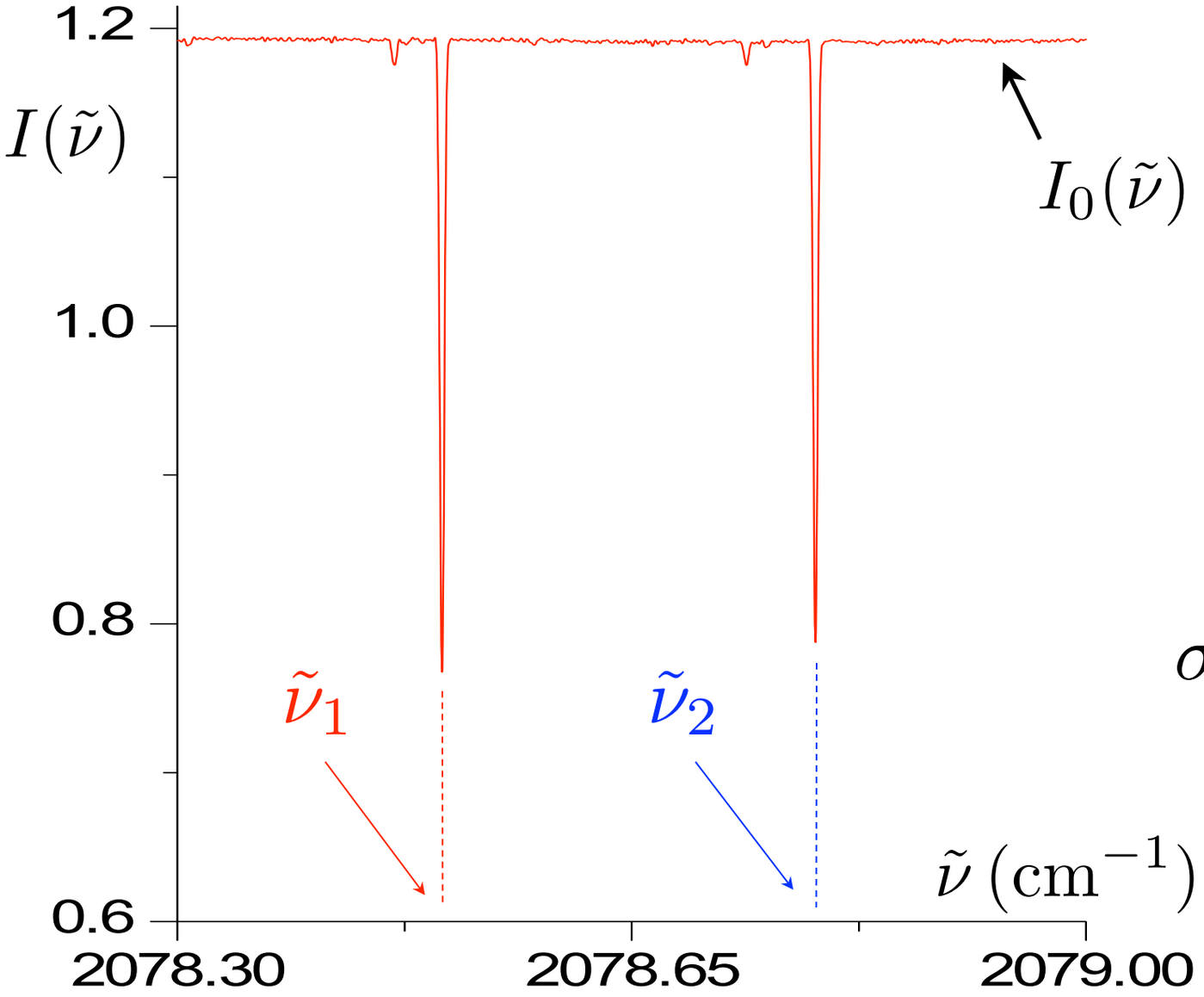
Line **intensities** and broadening parameters

V. Tyuterev

Modeling FT-FIR absorption spectra

Conventional and synchrotron sources

Modeling molecular absorption spectra



$I_0(\tilde{\nu})$ = polynome

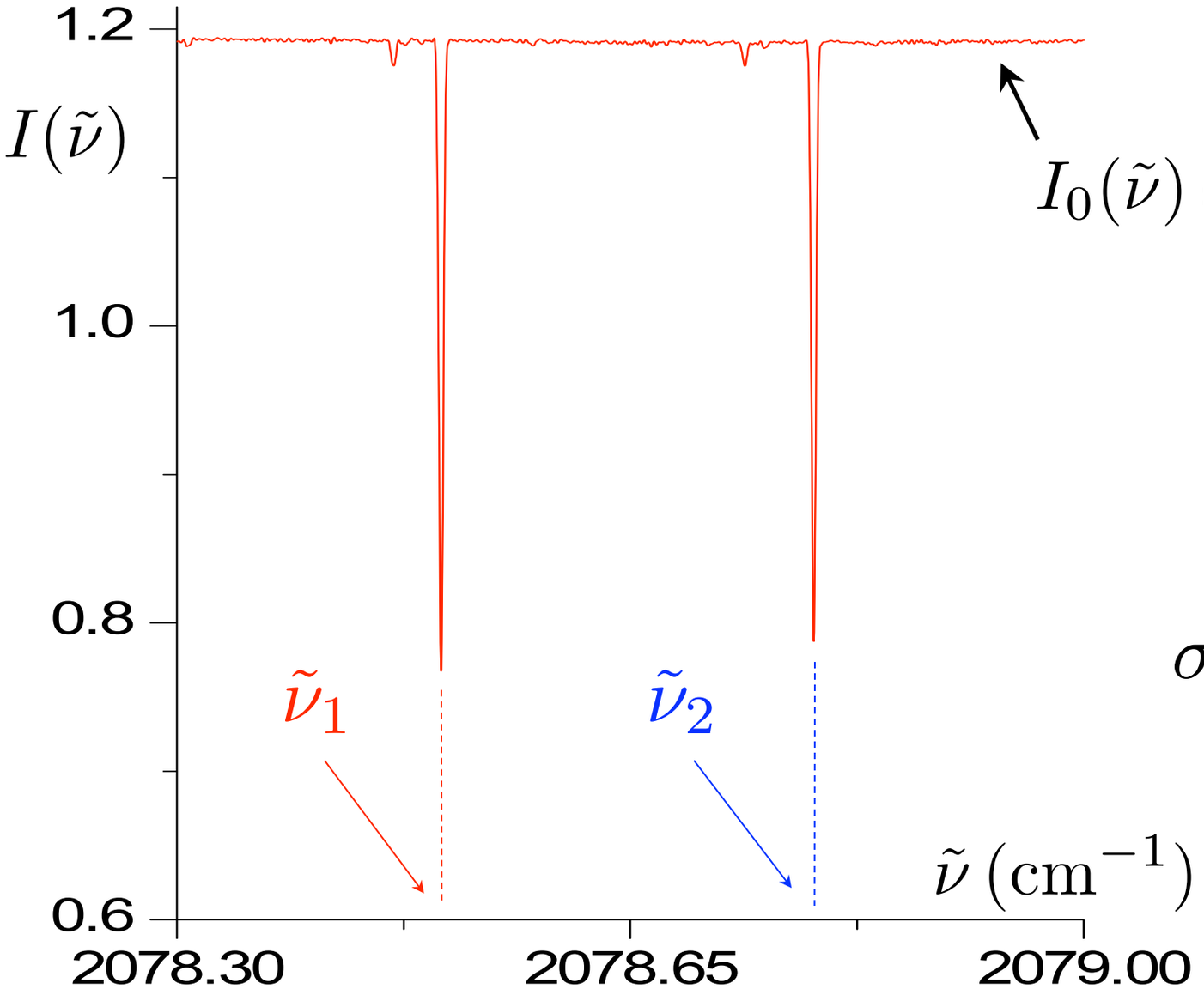
"Intensity"

$$\sigma_i(\tilde{\nu}-\tilde{\nu}_i) = \sigma_i^{int} g(\tilde{\nu}-\tilde{\nu}_i)$$

line profile

$$I(\tilde{\nu}) = [I_0(\tilde{\nu})\exp\{-\ell N[\sigma_1(\tilde{\nu}-\tilde{\nu}_1)+\sigma_2(\tilde{\nu}-\tilde{\nu}_2)]\}]$$

Modeling molecular absorption spectra



$I_0(\tilde{\nu})$ = polynome × "channeling"

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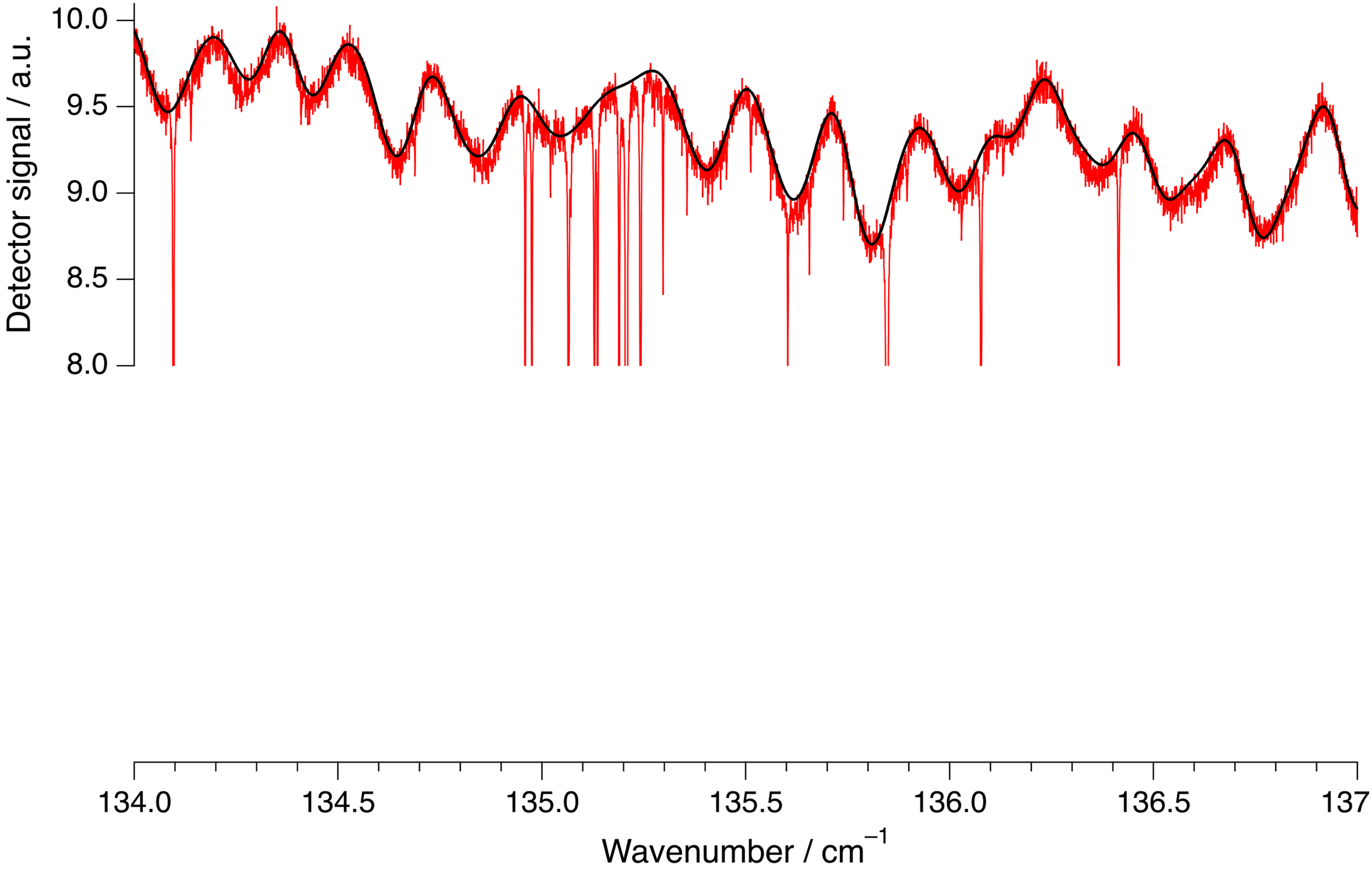
Reproducibility of the baseline at AILES



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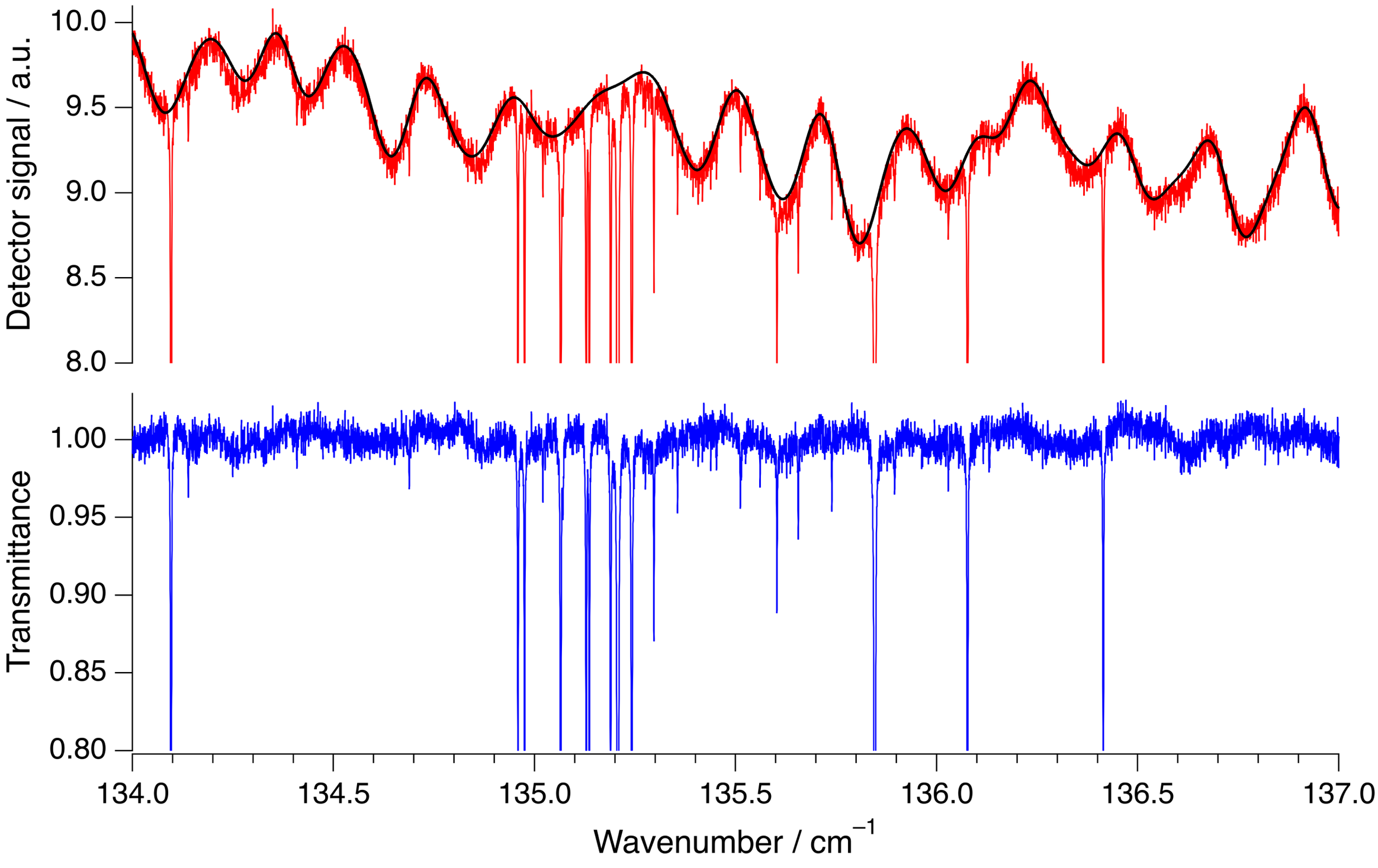
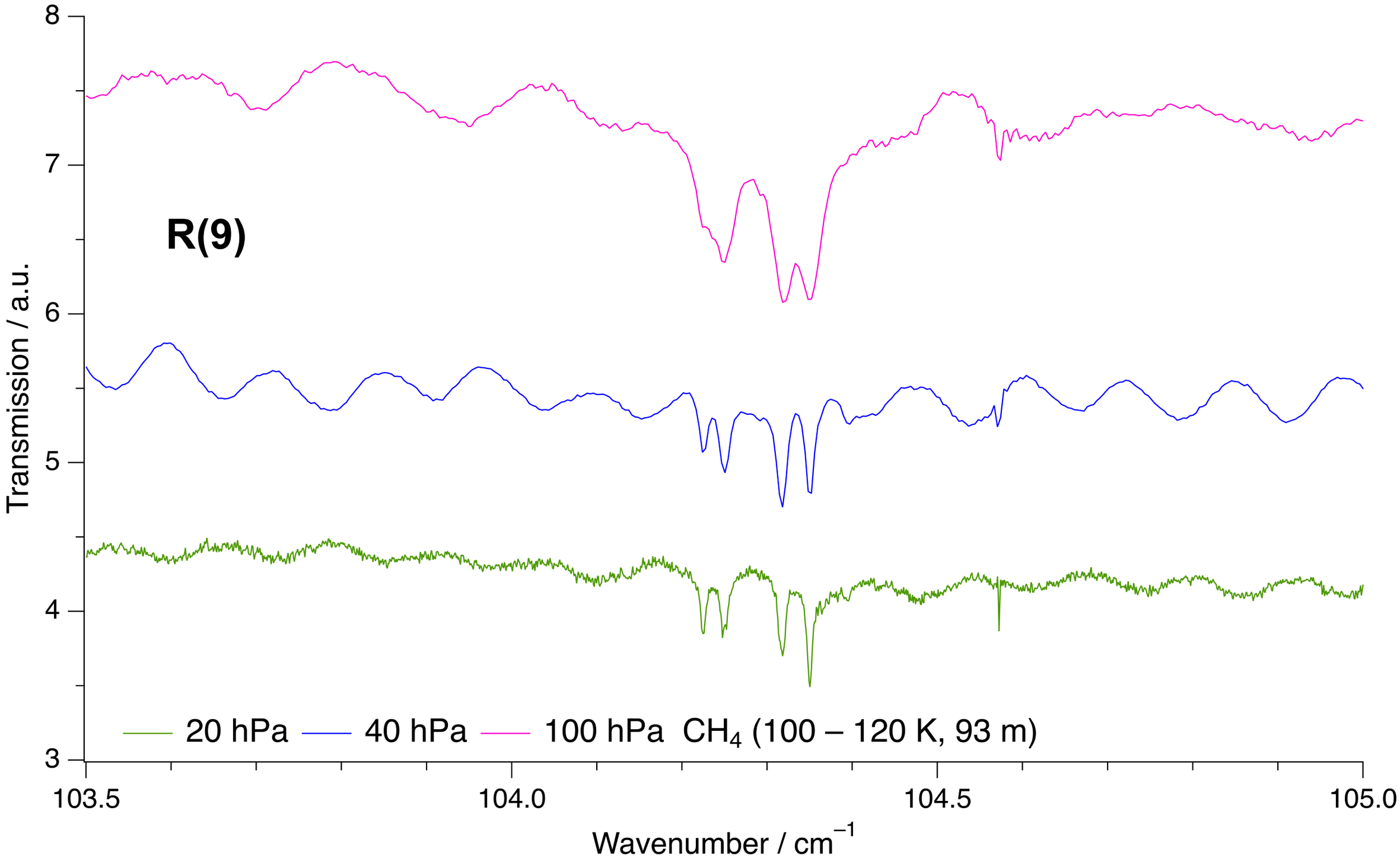
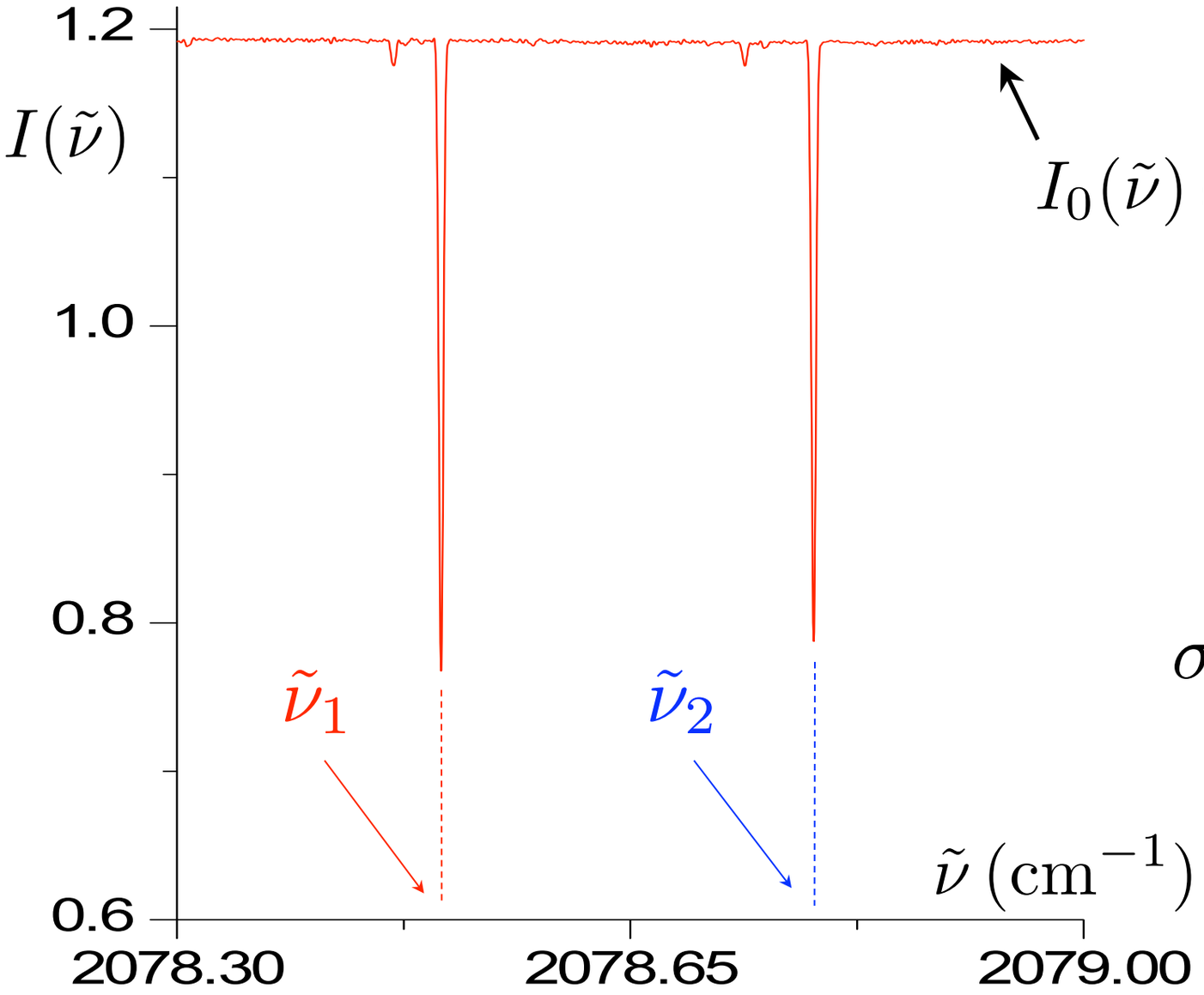


Baseline examples



Modeling molecular absorption spectra



$I_0(\tilde{\nu})$ = polynome × "channeling"

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$$\sigma_i(\tilde{\nu}-\tilde{\nu}_i) = \sigma_i^{int} g(\tilde{\nu}-\tilde{\nu}_i)$$

line profile

$$I(\tilde{\nu}) = [I_0(\tilde{\nu})\exp\{-\ell N[\sigma_1(\tilde{\nu}-\tilde{\nu}_1)+\sigma_2(\tilde{\nu}-\tilde{\nu}_2)]\}] \otimes f_{ils}(\tilde{\nu})$$

Instrument Line Shape of a FTS

- No apodization (boxcar)

  ➥ sinc function

Instrument Line Shape of a FTS

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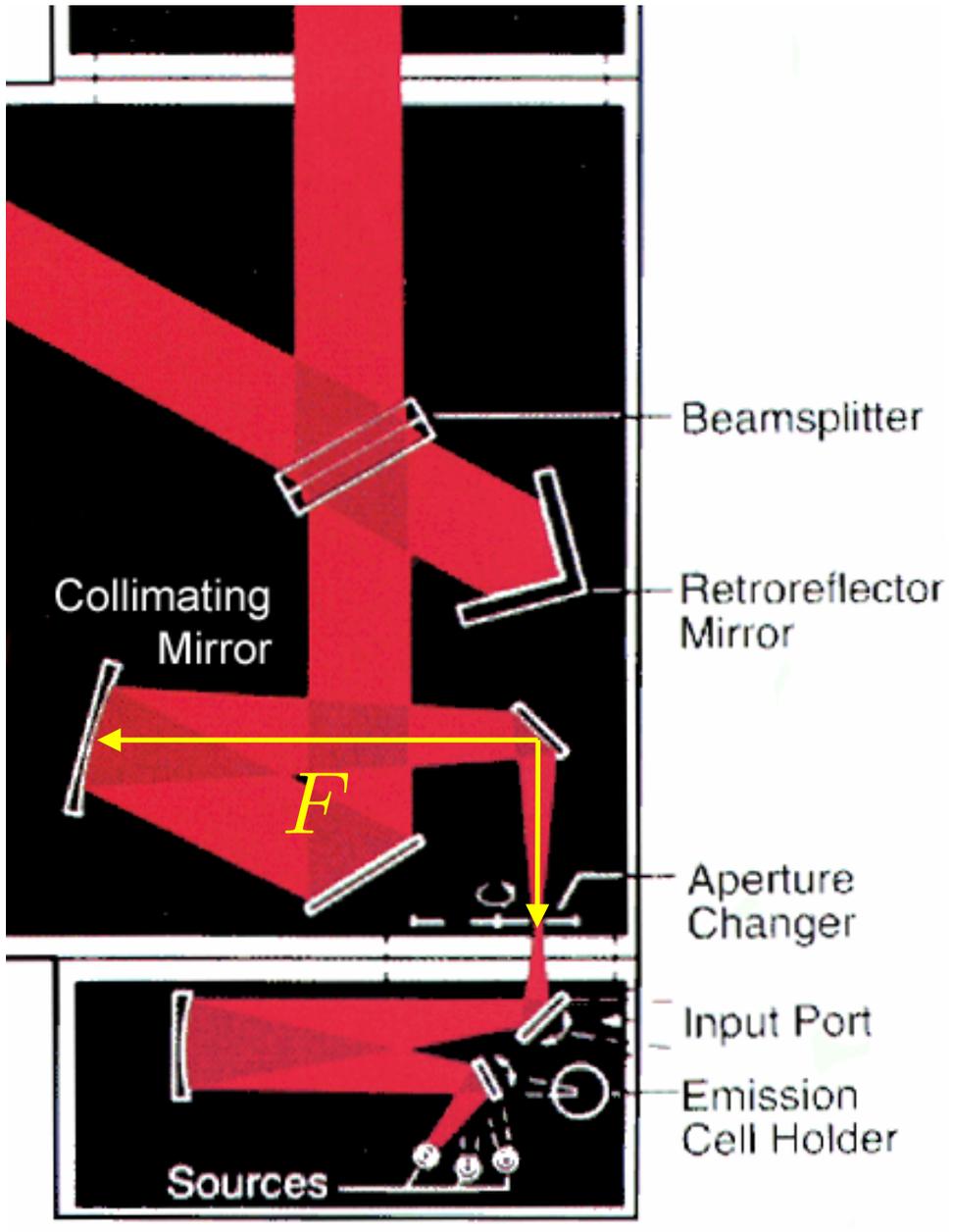
  ➥ sinc function

- Aperture broadening

  ➥ Apodization by

Optical Path Difference

$$I(\delta) \propto \mathrm{sinc}\left(\frac{\pi d^2 \tilde{\nu} \delta}{8F^2}\right)$$



Instrument Line Shape of a FTS

- No apodization (boxcar)

  ➥ sinc function

- Aperture broadening

  ➥ Apodization by

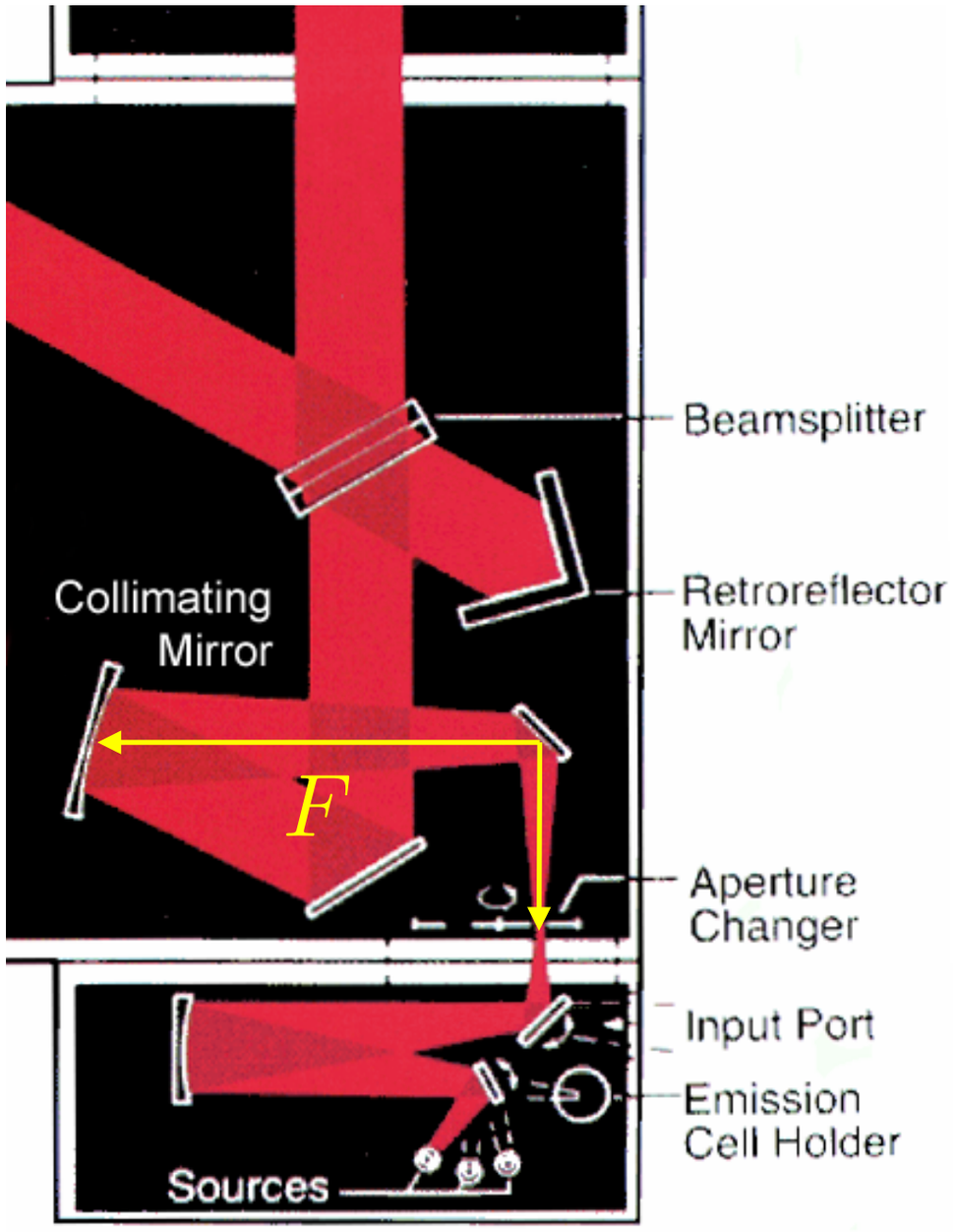
Optical Path Difference

$$I(\delta) \propto \mathrm{sinc}\left(\frac{\pi d^2 \tilde{\nu} \delta}{8F^2}\right)$$

Source = synchrotron beam

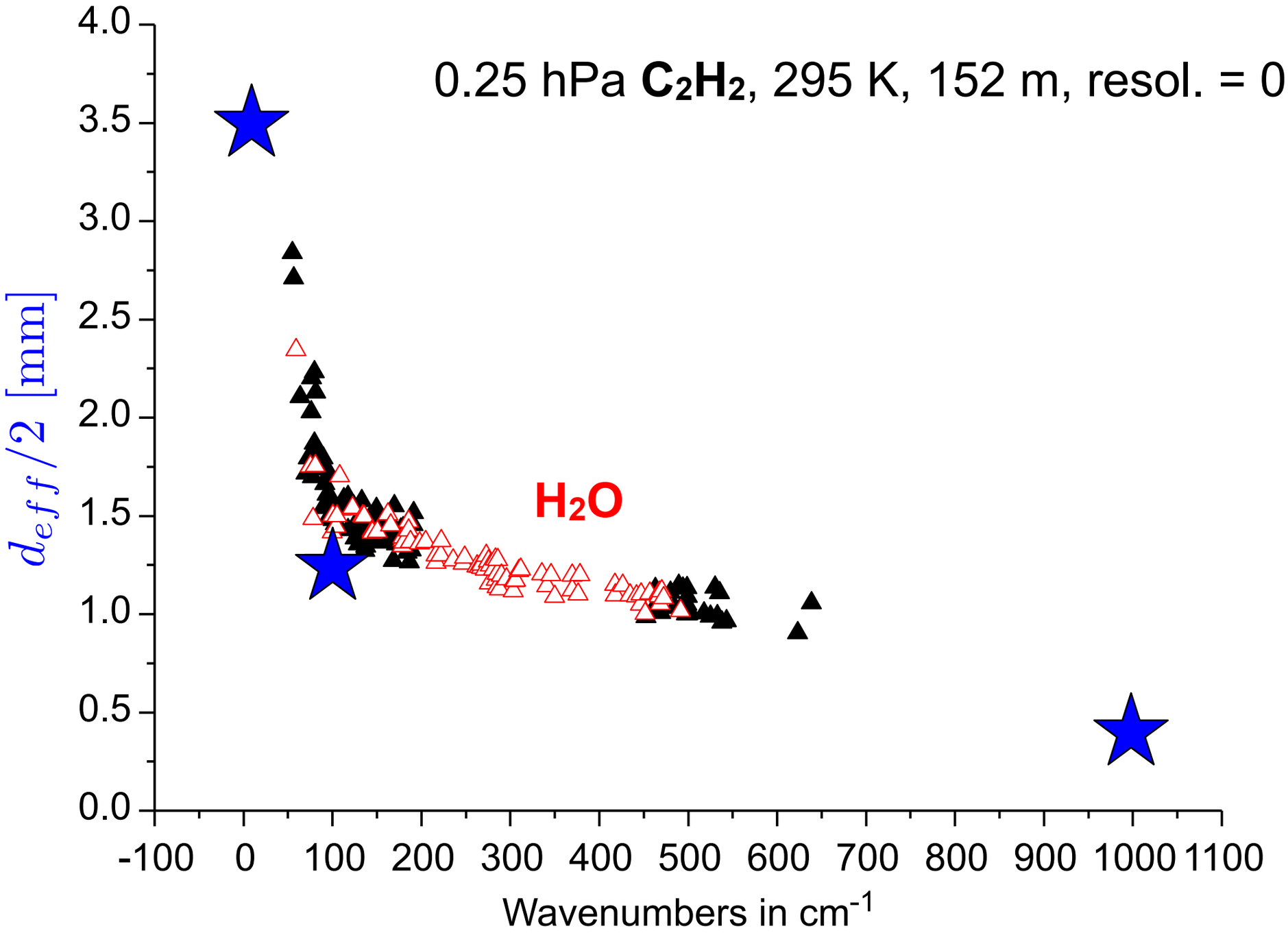
$$d_{eff}\,[\mathrm{mm}] = 0.8\sqrt{\frac{1000}{\tilde{\nu}}}$$

Roy *et al.*, Infr. Phys. Technol. 49 (2006) 139



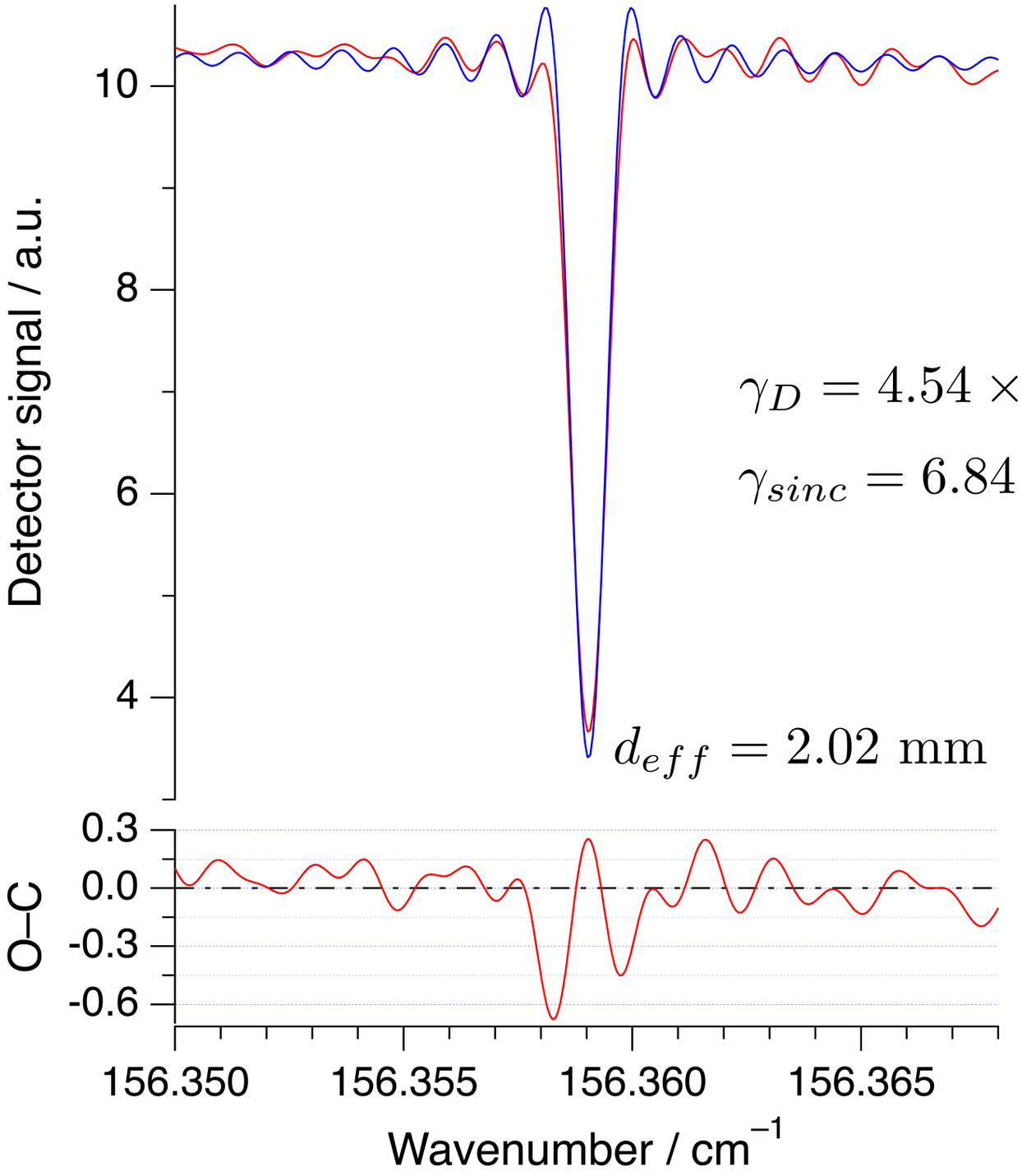
Synchrotron beam diameter – *Continued*

Jacquemart *et al.*, JQSRT 119 (2013) 95



Synchrotron beam diameter – *Continued*

H_2O in empty cell (152 m path)

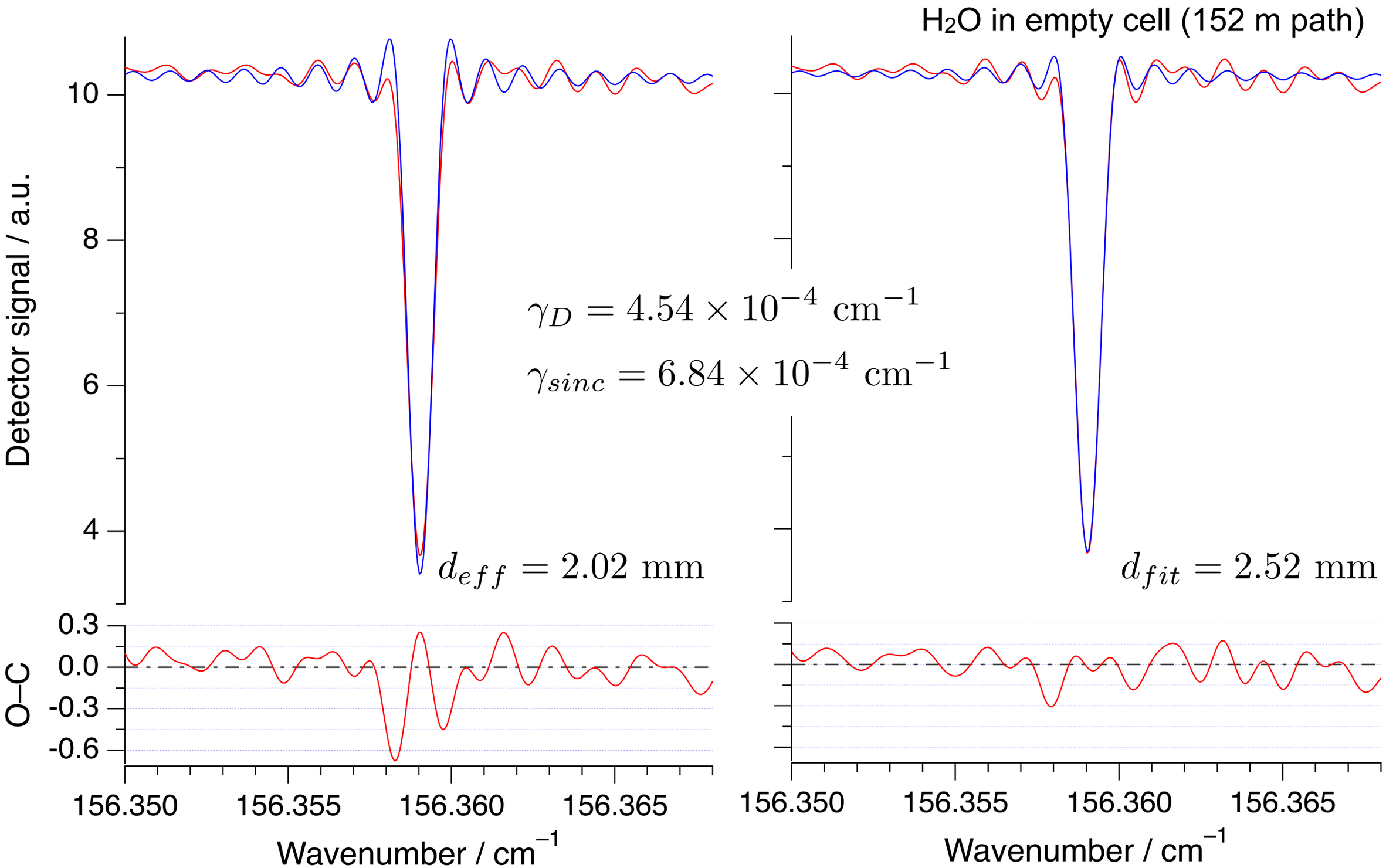


$$\gamma_D = 4.54 \times 10^{-4}\ \mathrm{cm}^{-1}$$

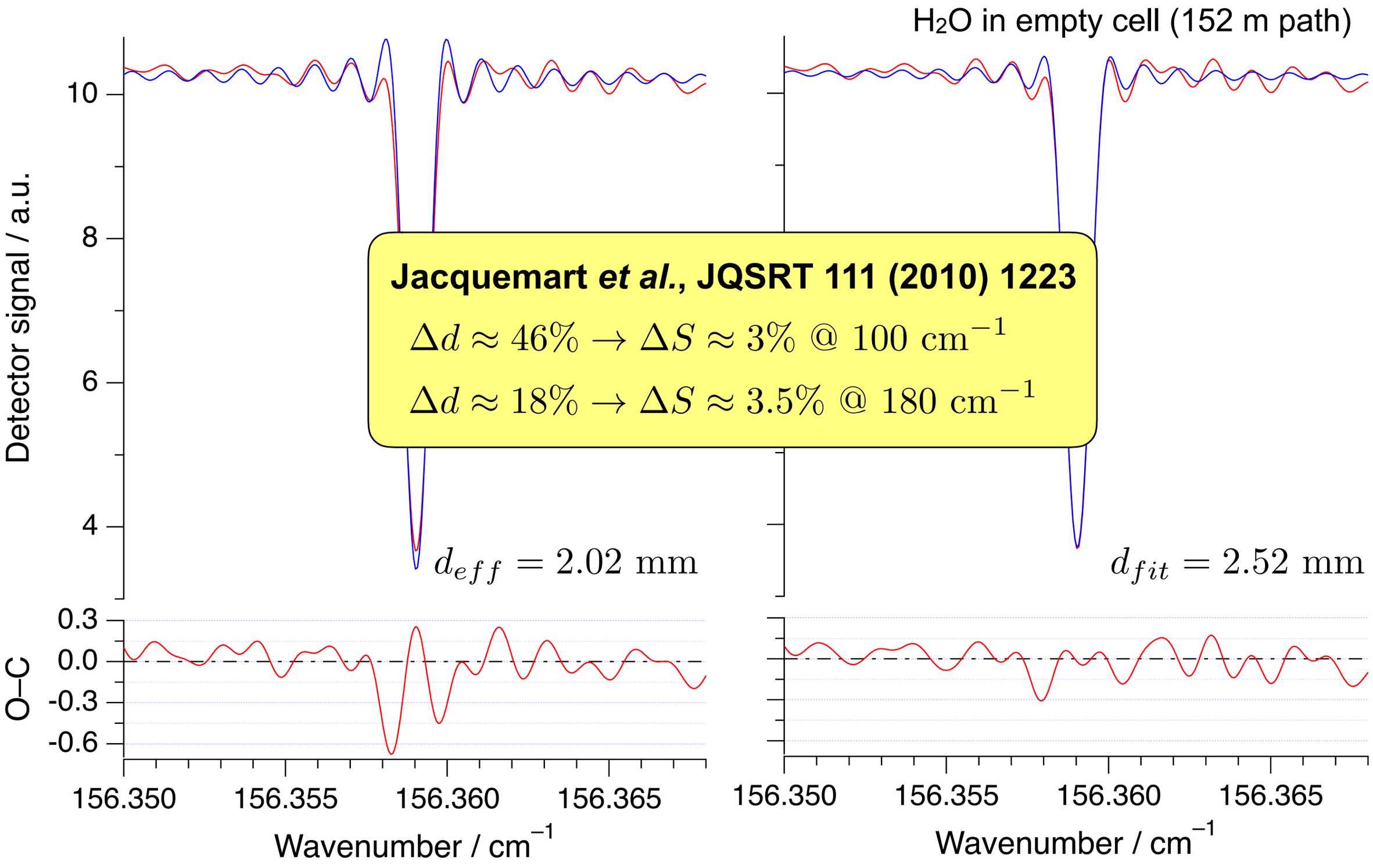
$$\gamma_{sinc} = 6.84 \times 10^{-4}\ \mathrm{cm}^{-1}$$

$$d_{eff} = 2.02\ \mathrm{mm}$$

Synchrotron beam diameter – *Continued*

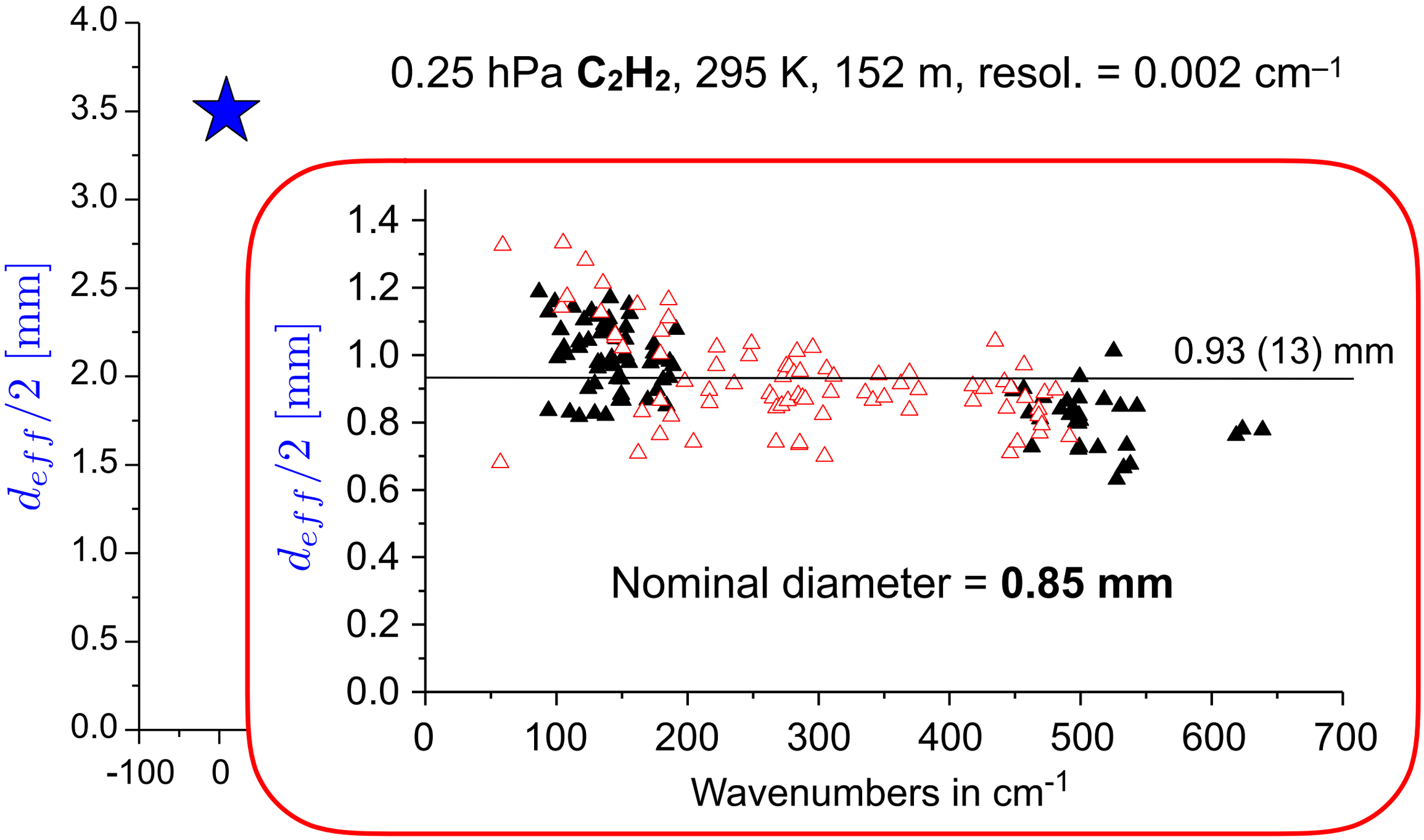


Synchrotron beam diameter – *Continued*

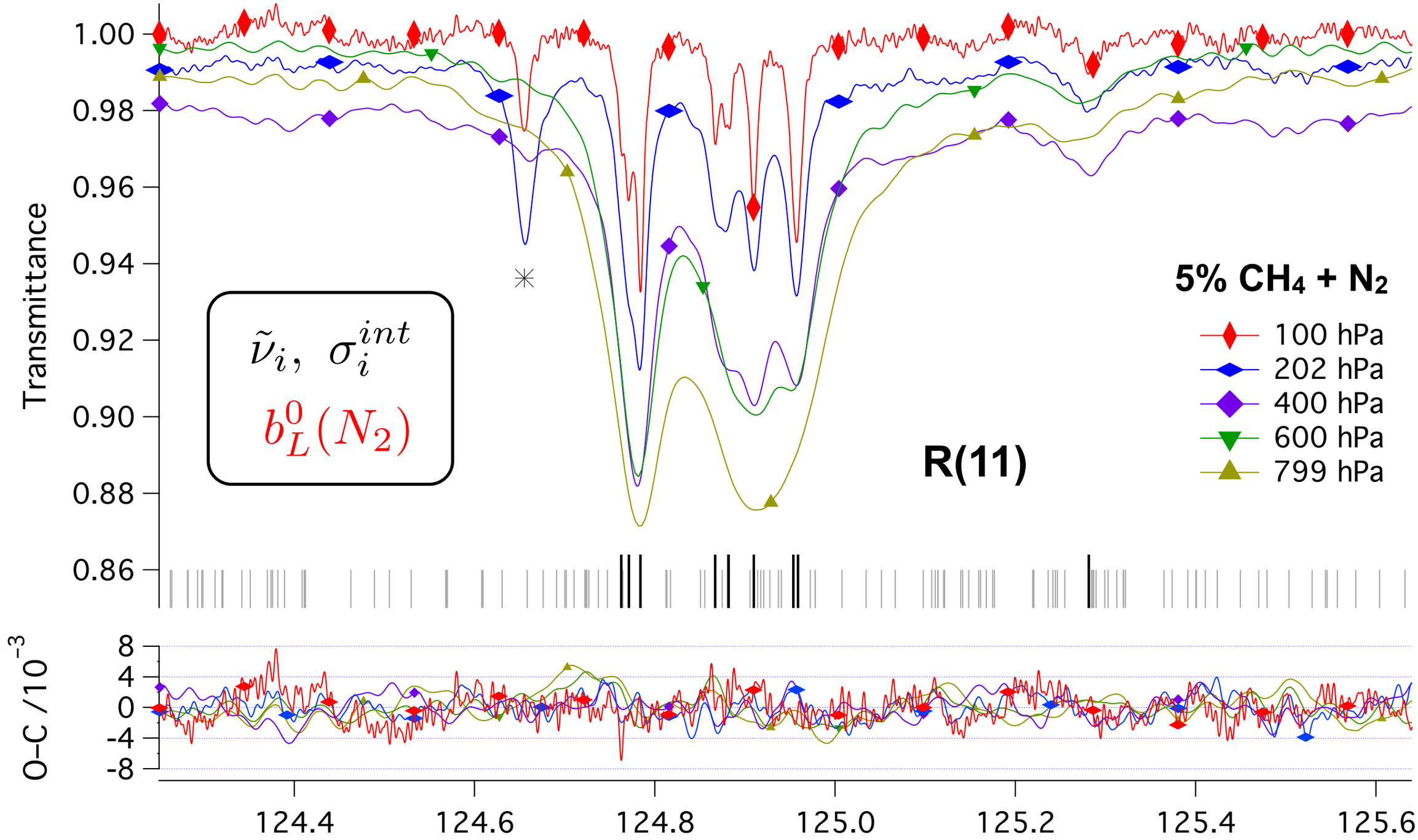


Synchrotron beam diameter – *Continued*

Jacquemart *et al.*, JQSRT 119 (2013) 95



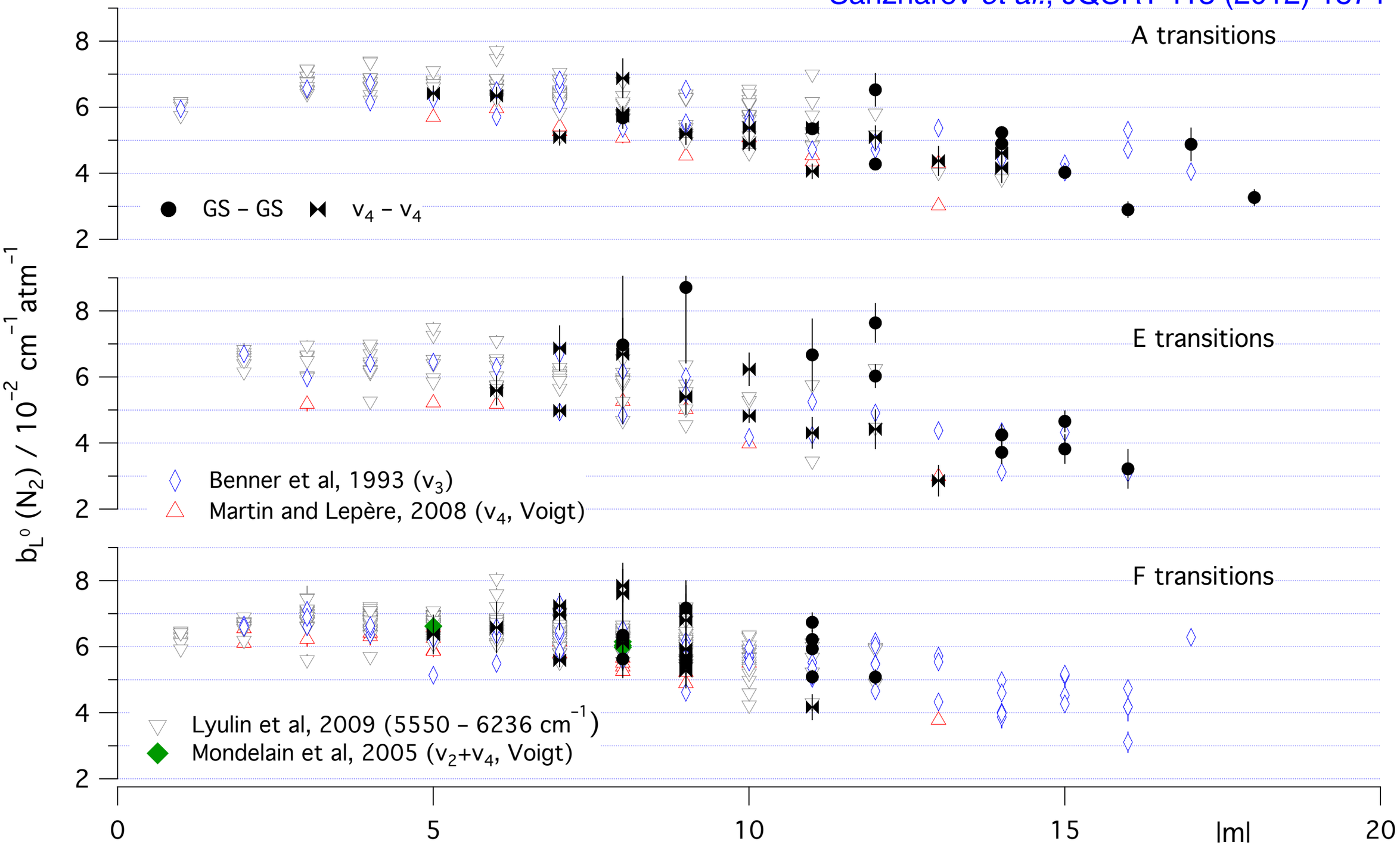
Broadening of pure rotation lines of $^{12}CH_4$



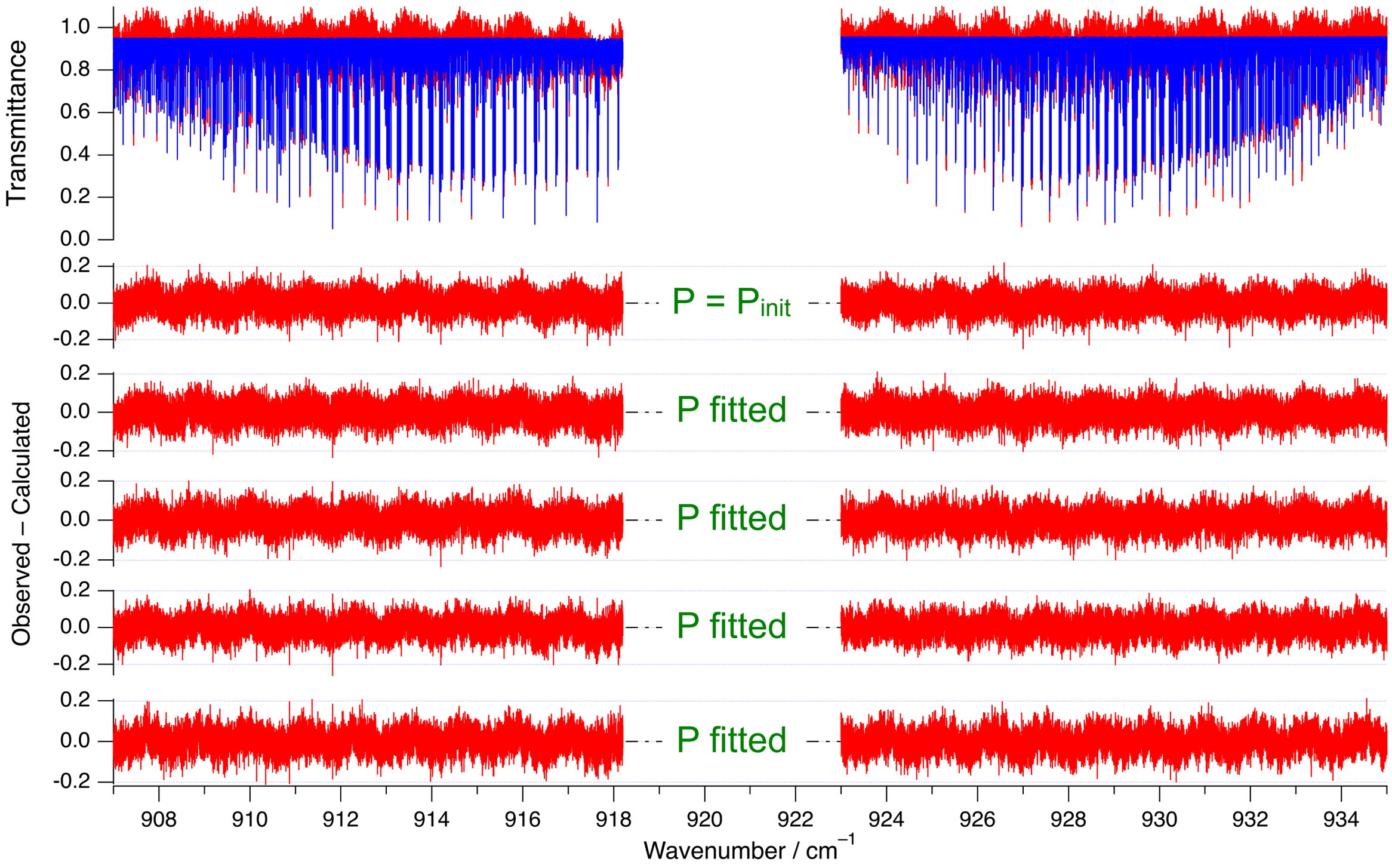
AILES beamline, 152 m, 296 K

Pure rotation of $^{12}CH_4$: N_2 broadening

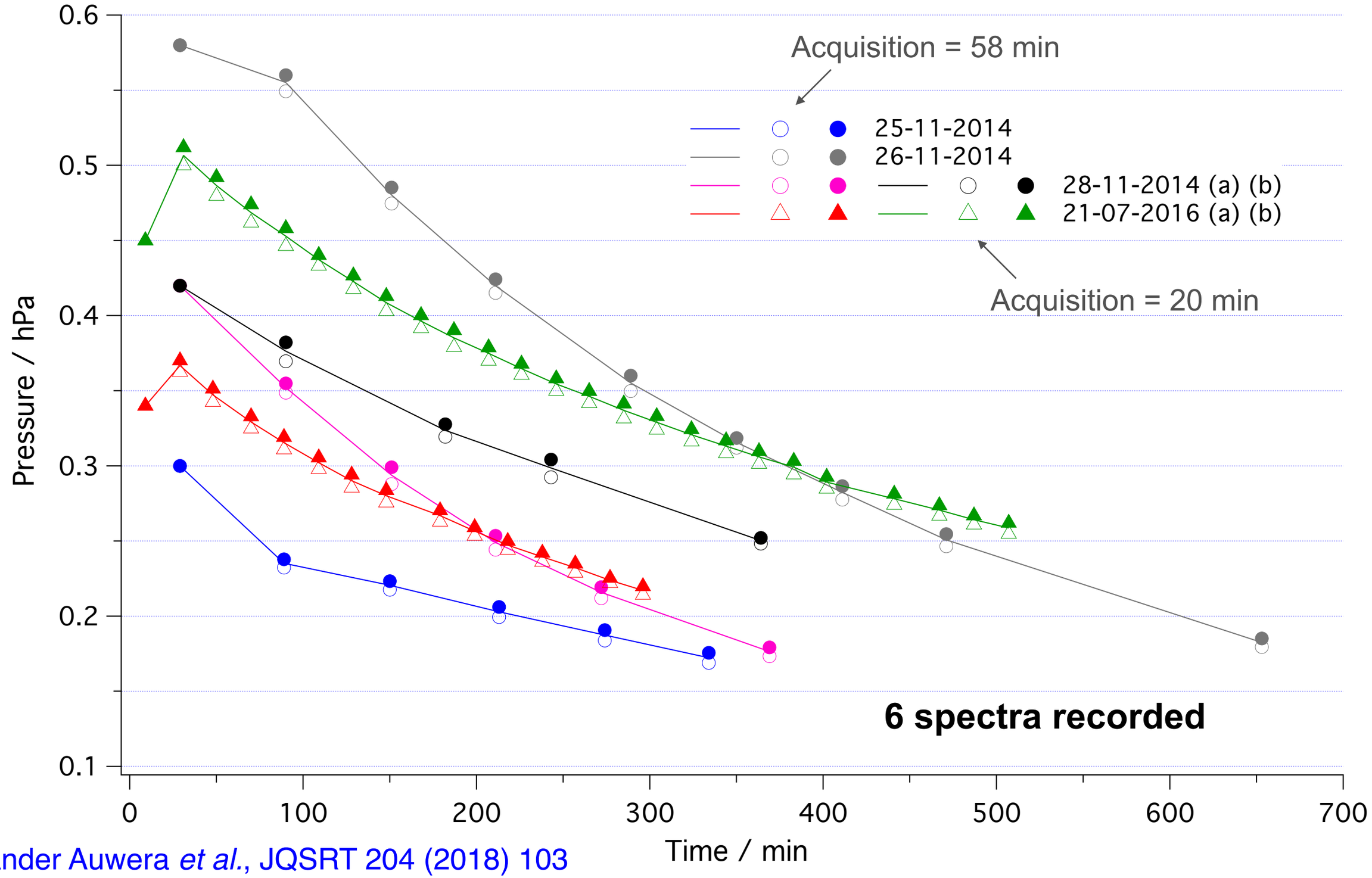
Sanzharov *et al.*, JQSRT 113 (2012) 1874



Multi-spectra analysis (ν_3 band of $^{102}RuO_4$)

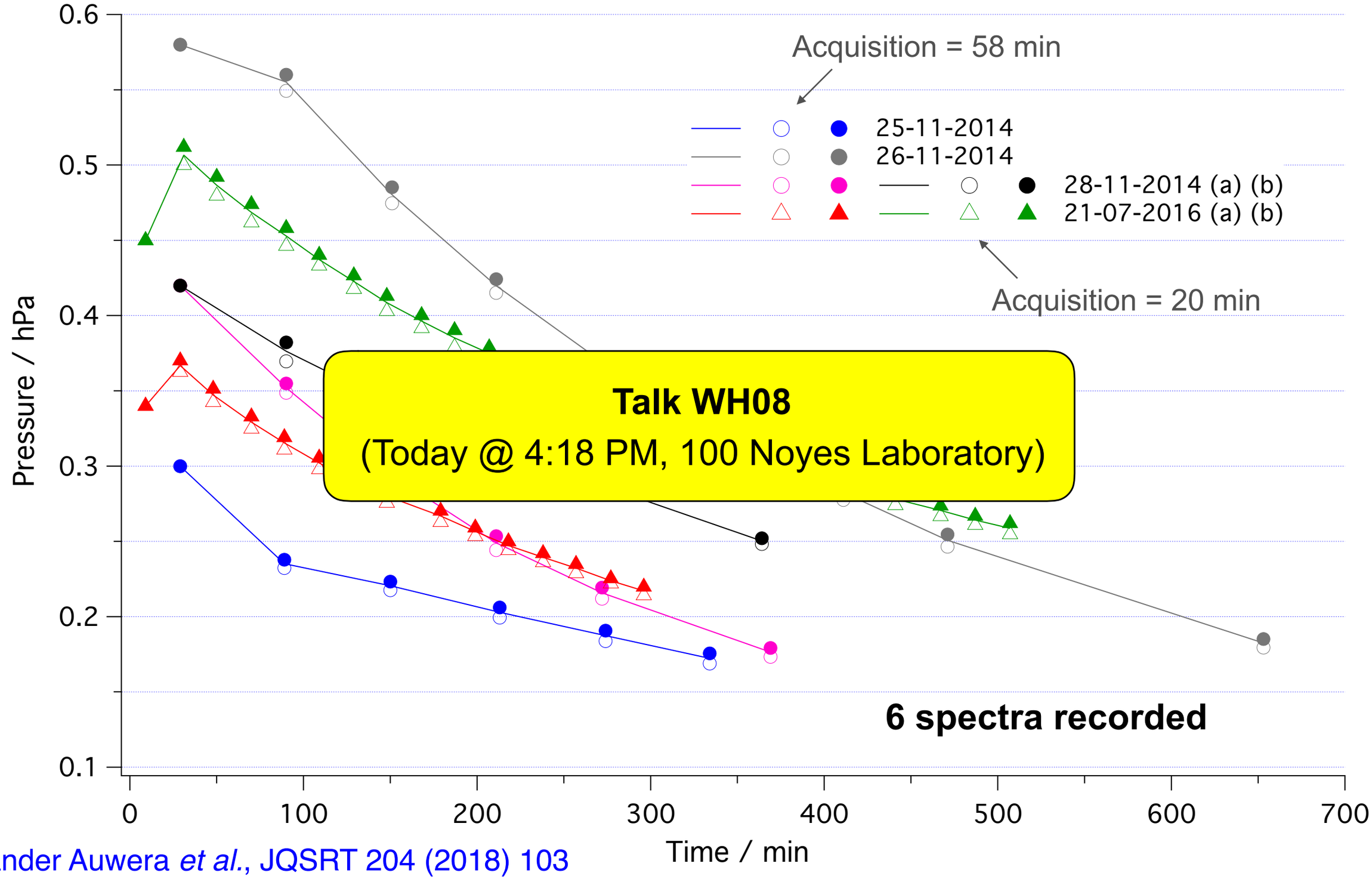


Evolution of the pressure of $^{102}RuO_4$



Vander Auwera *et al.*, JQSRT 204 (2018) 103

Evolution of the pressure of $^{102}RuO_4$

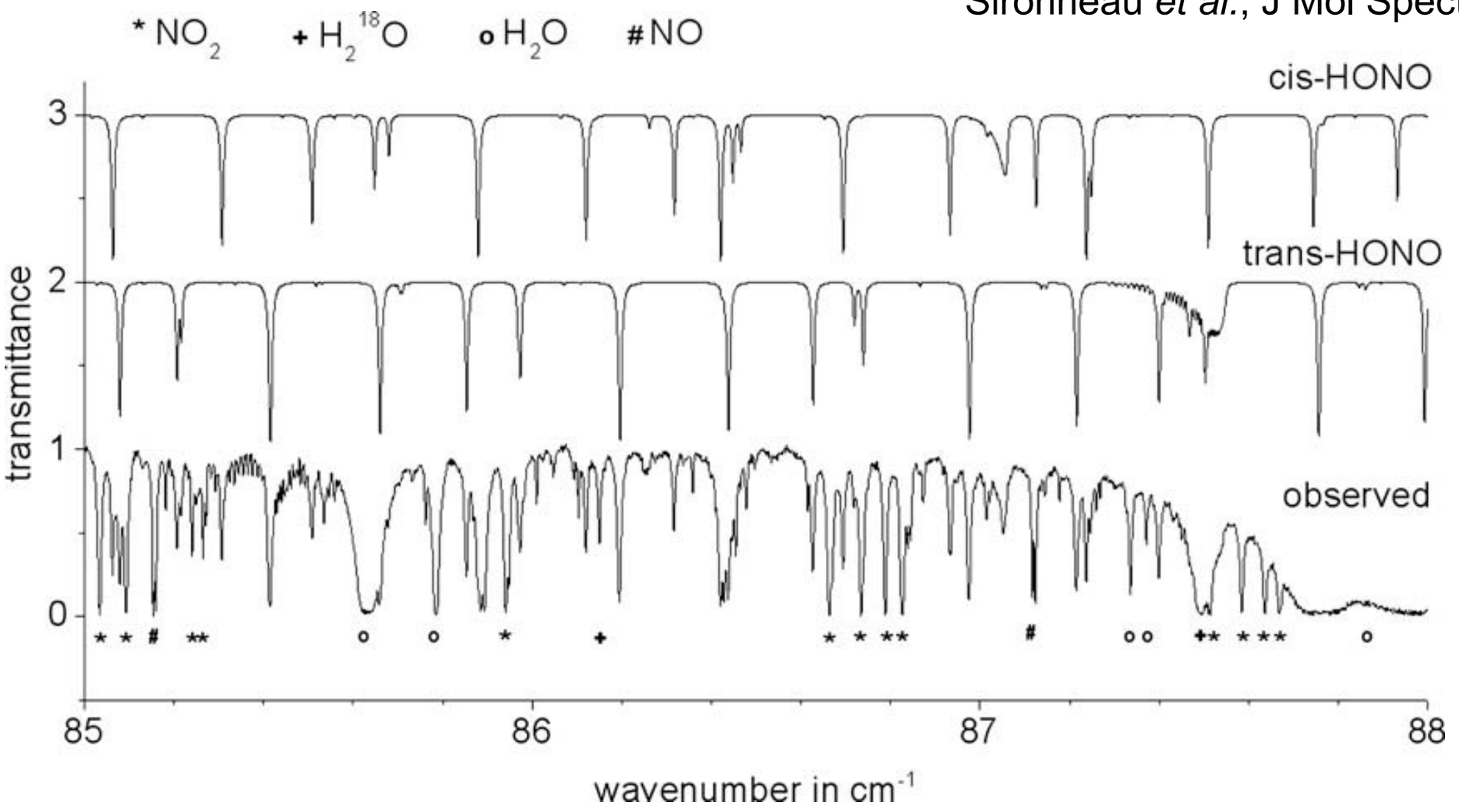


Vander Auwera *et al.*, JQSRT 204 (2018) 103

Measurements

FT-FIR spectroscopy ➔ pure rotation

Sironneau *et al.*, J Mol Spectrosc 259 (2010) 100



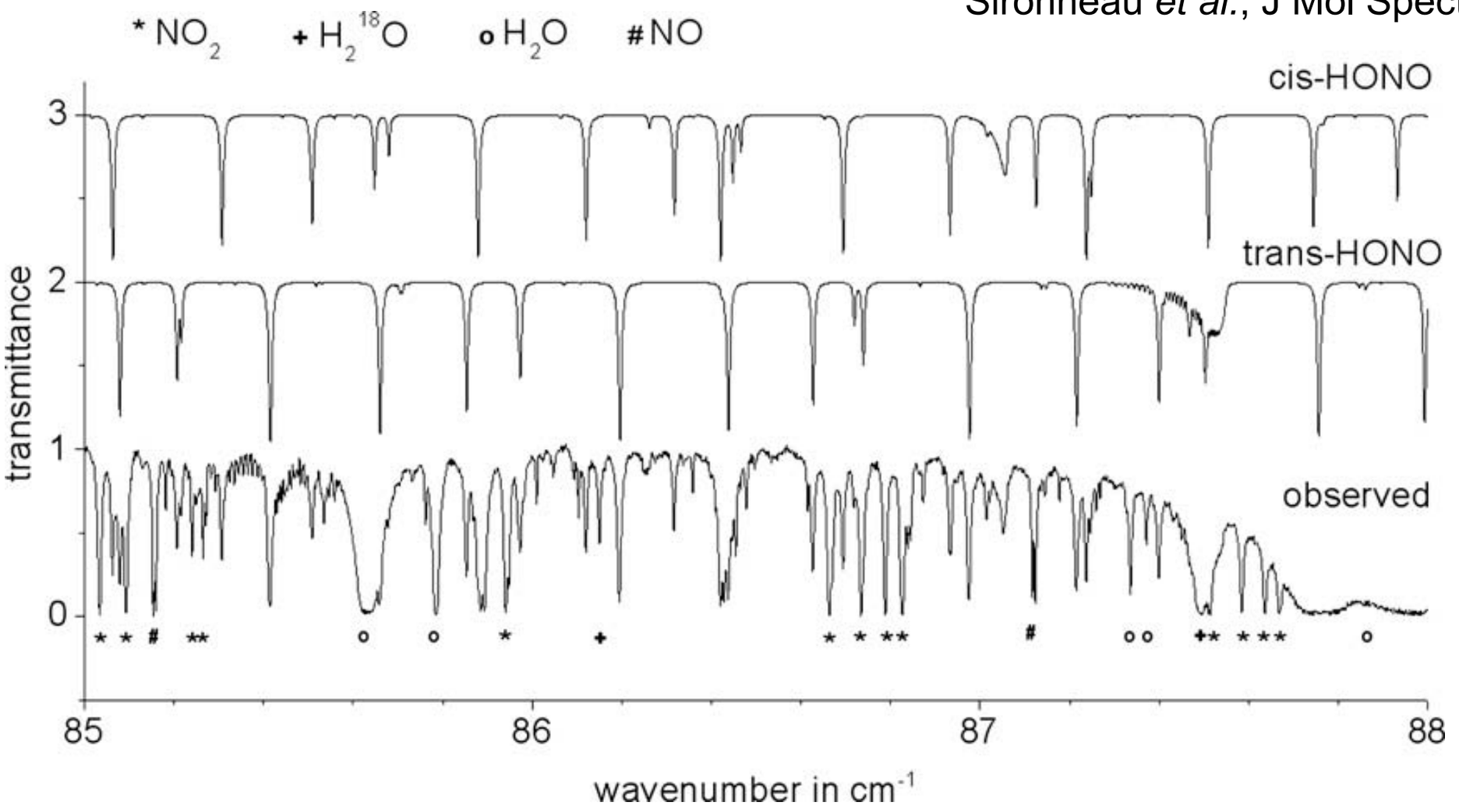
J/Ka = 9/5 – 41/21

J/Ka = 9/6 – 43/22

nitrous acid

FT-FIR spectroscopy ➔ pure rotation

Sironneau *et al.*, J Mol Spectrosc 259 (2010) 100



J/Ka = 9/5 – 41/21

J/Ka = 9/6 – 43/22

nitrous acid

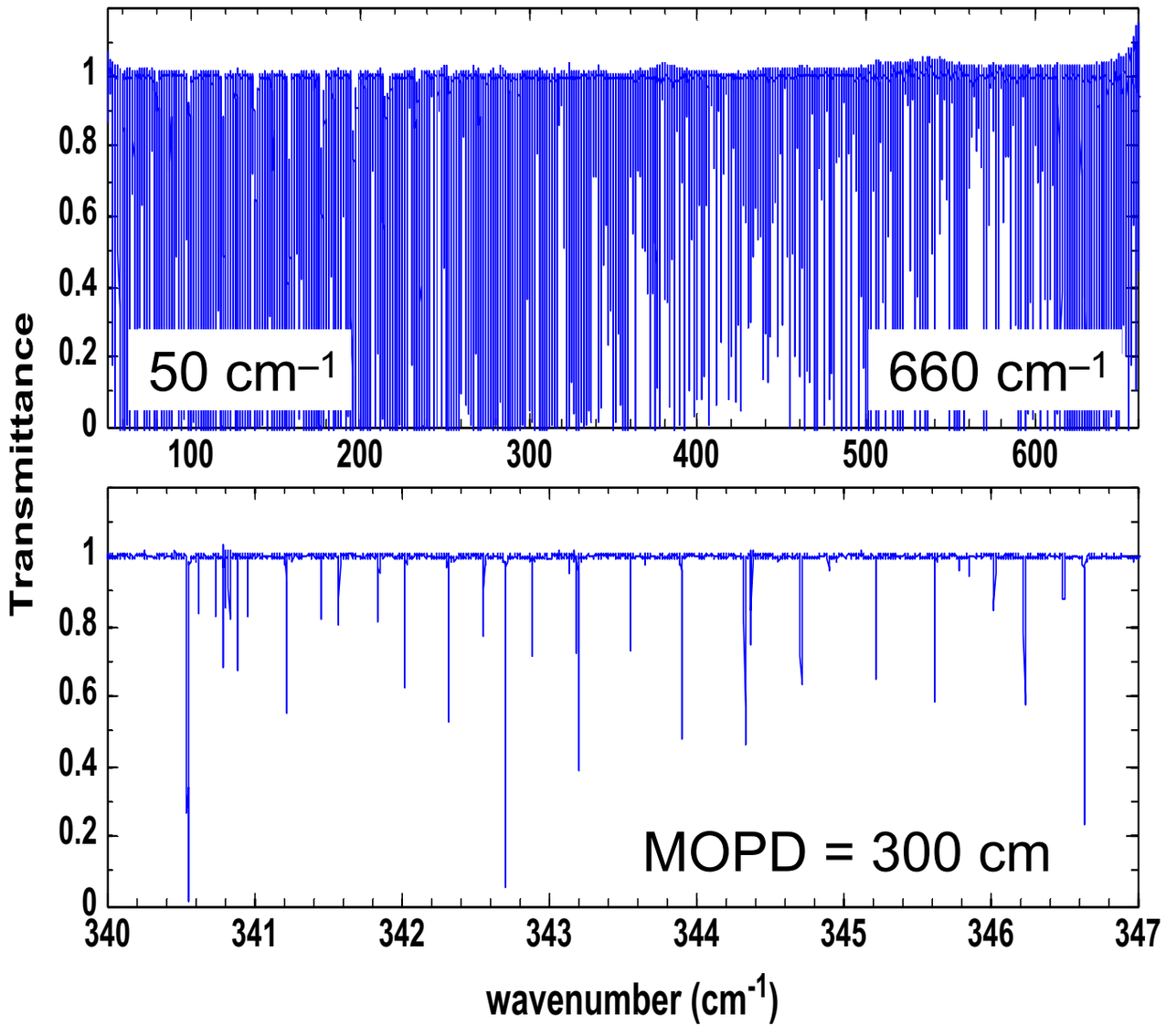
Herman-Wallis dependence

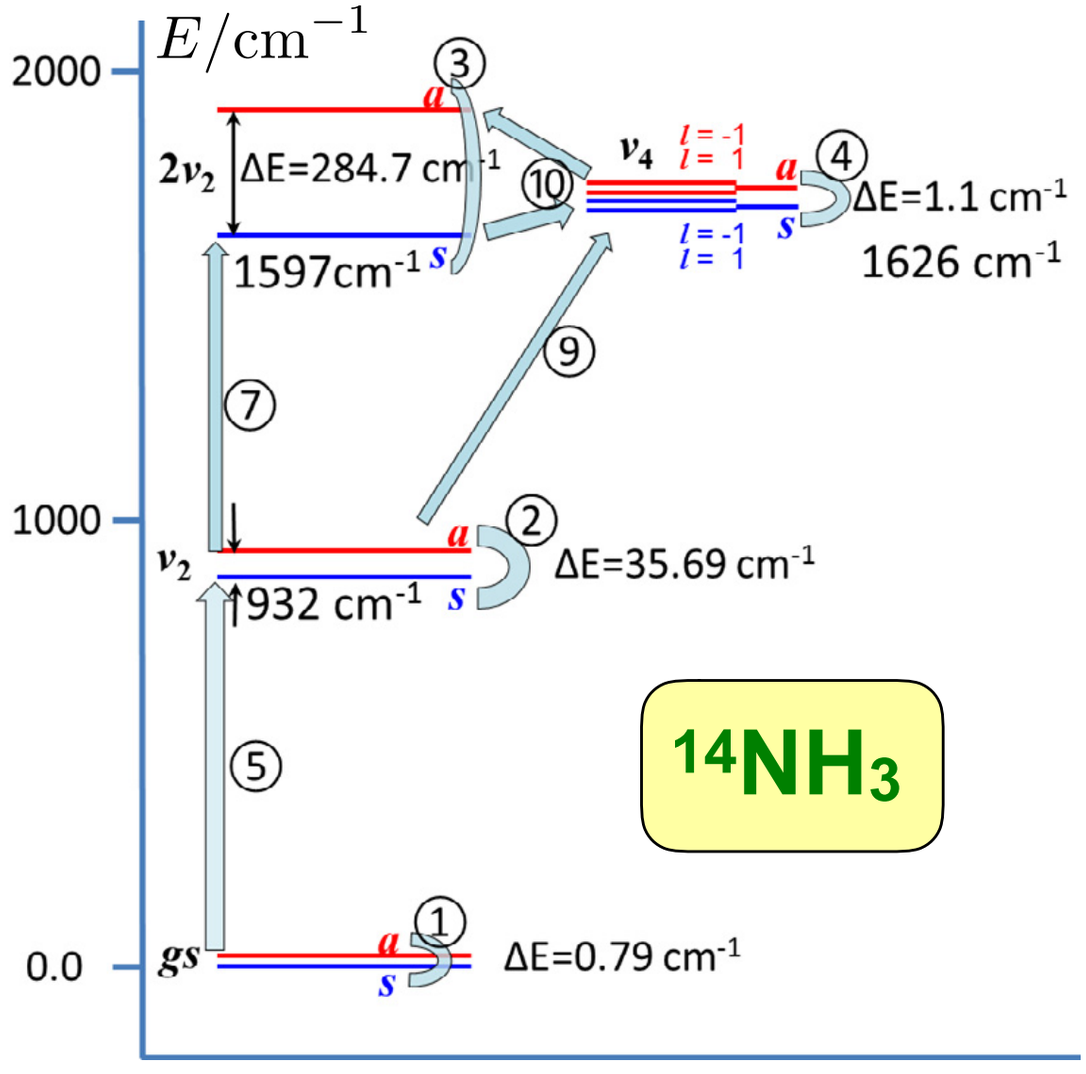
$$\Delta E(cis - trans) = 107\,(26)\ \mathrm{cm}^{-1}$$

FT-FIR spectroscopy

→ Large amplitude motion

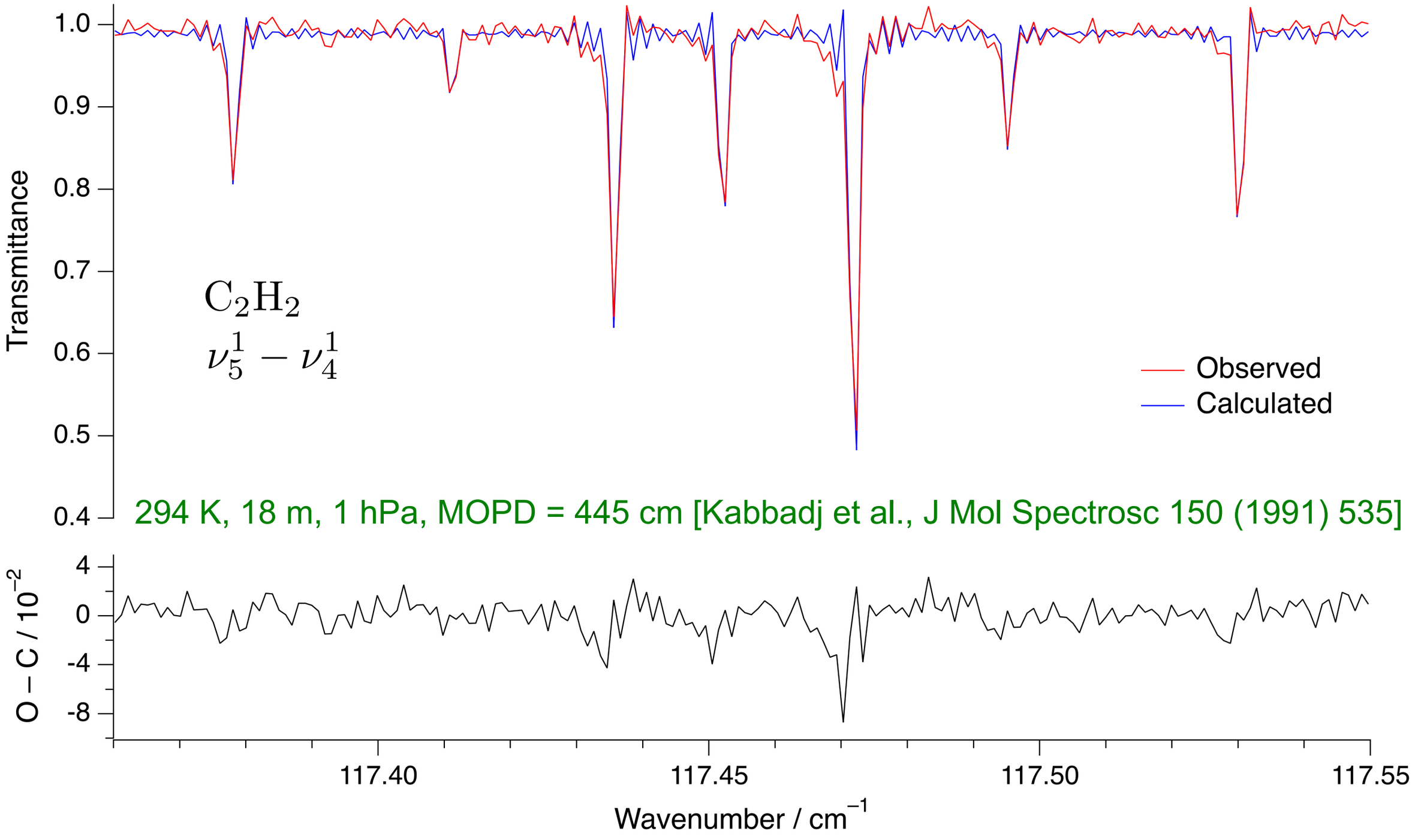
Line positions and intensities for inversion-rotation and rovibrational spectra





Sung *et al.*, J Mol Spectrosc 327 (2016) 1

Far infrared spectroscopy ➔ Hot bands



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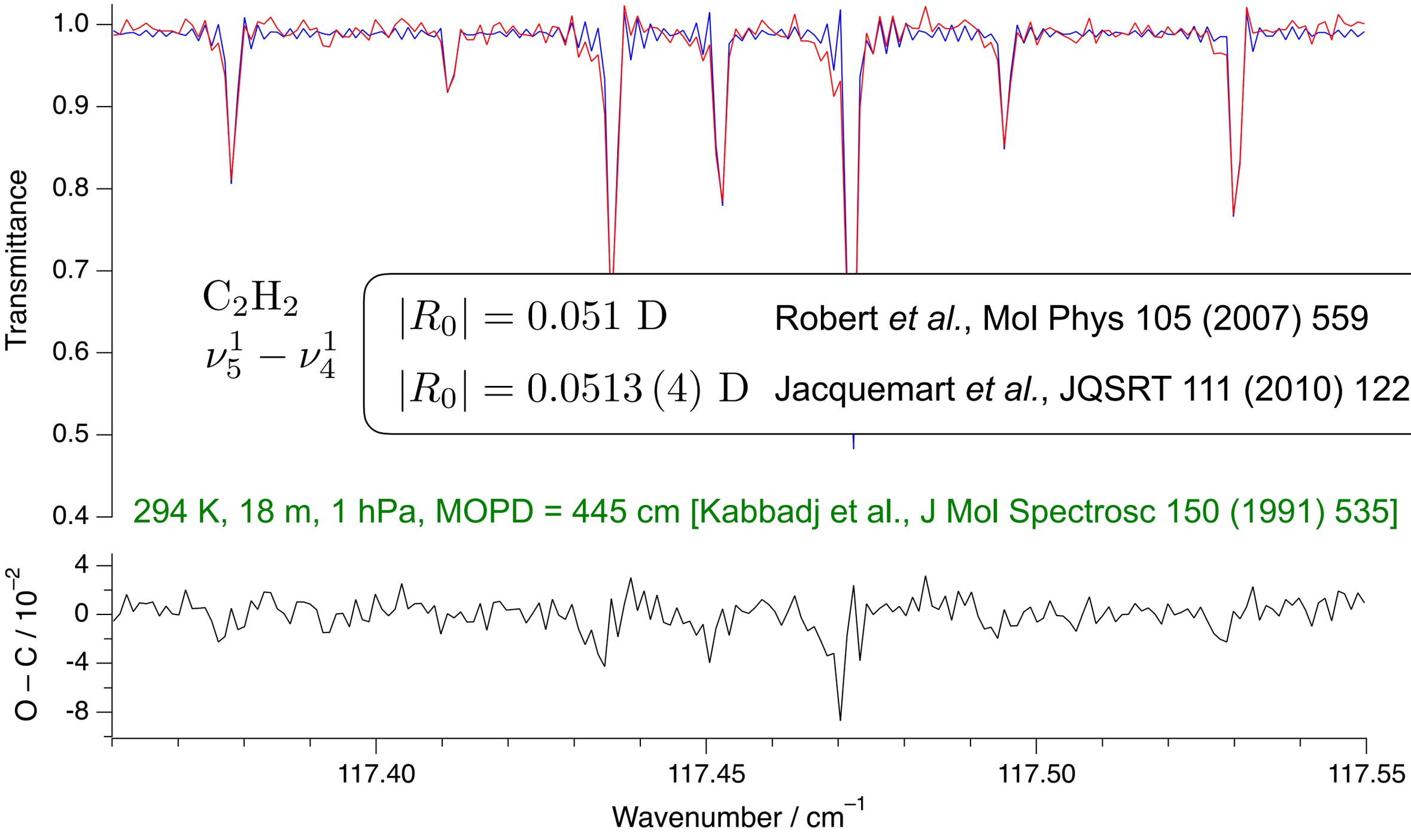
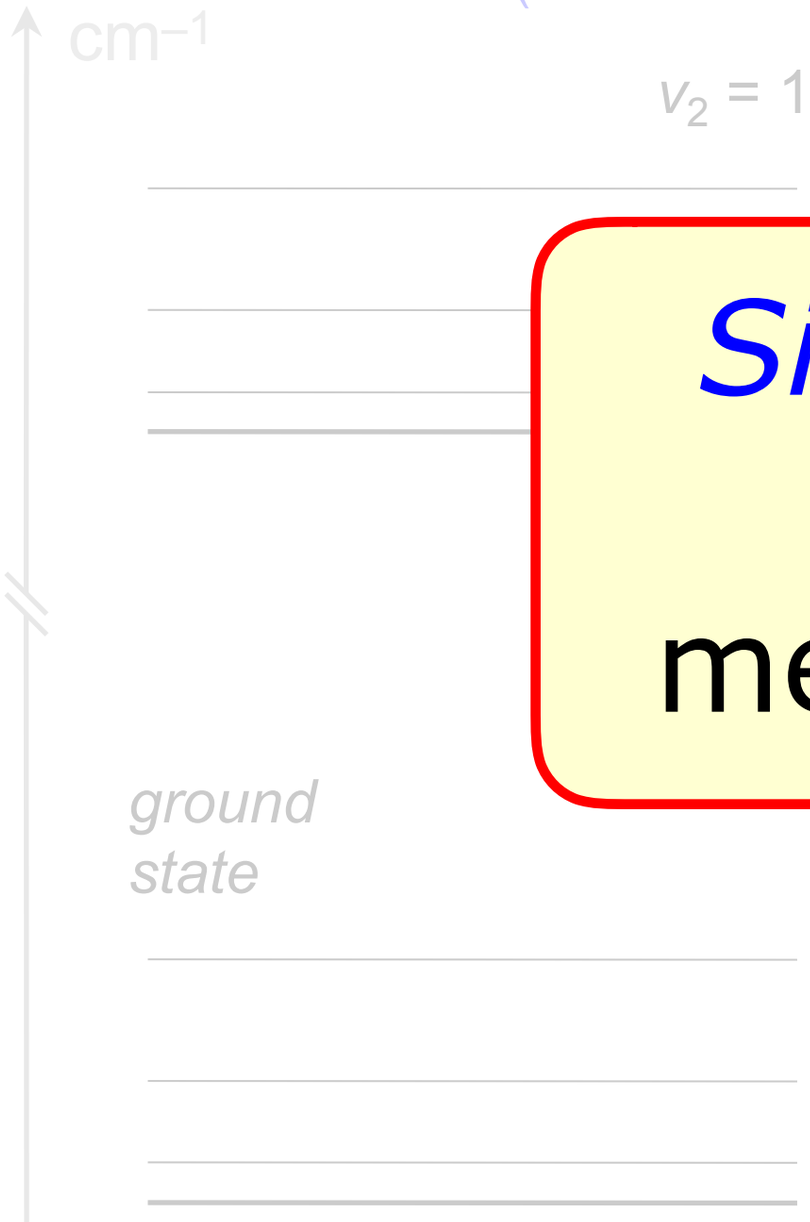


Line intensities for the ν_2 band of HOCl

(measurements in Wuppertal)



$Cl_2O + H_2O$

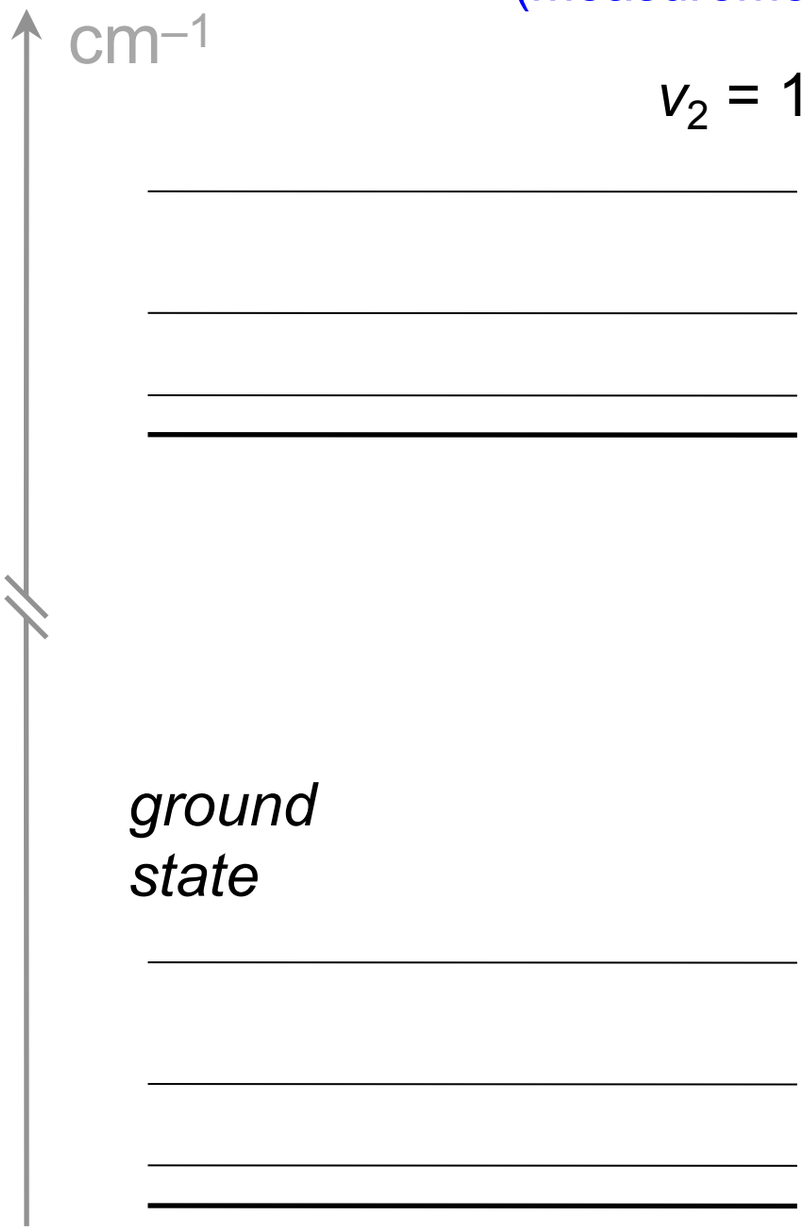
Simultaneous

FIR – IR

measurements

Line intensities for the ν_2 band of HOCl

(measurements in Wuppertal)



HOCl = Cl_2O + H_2O

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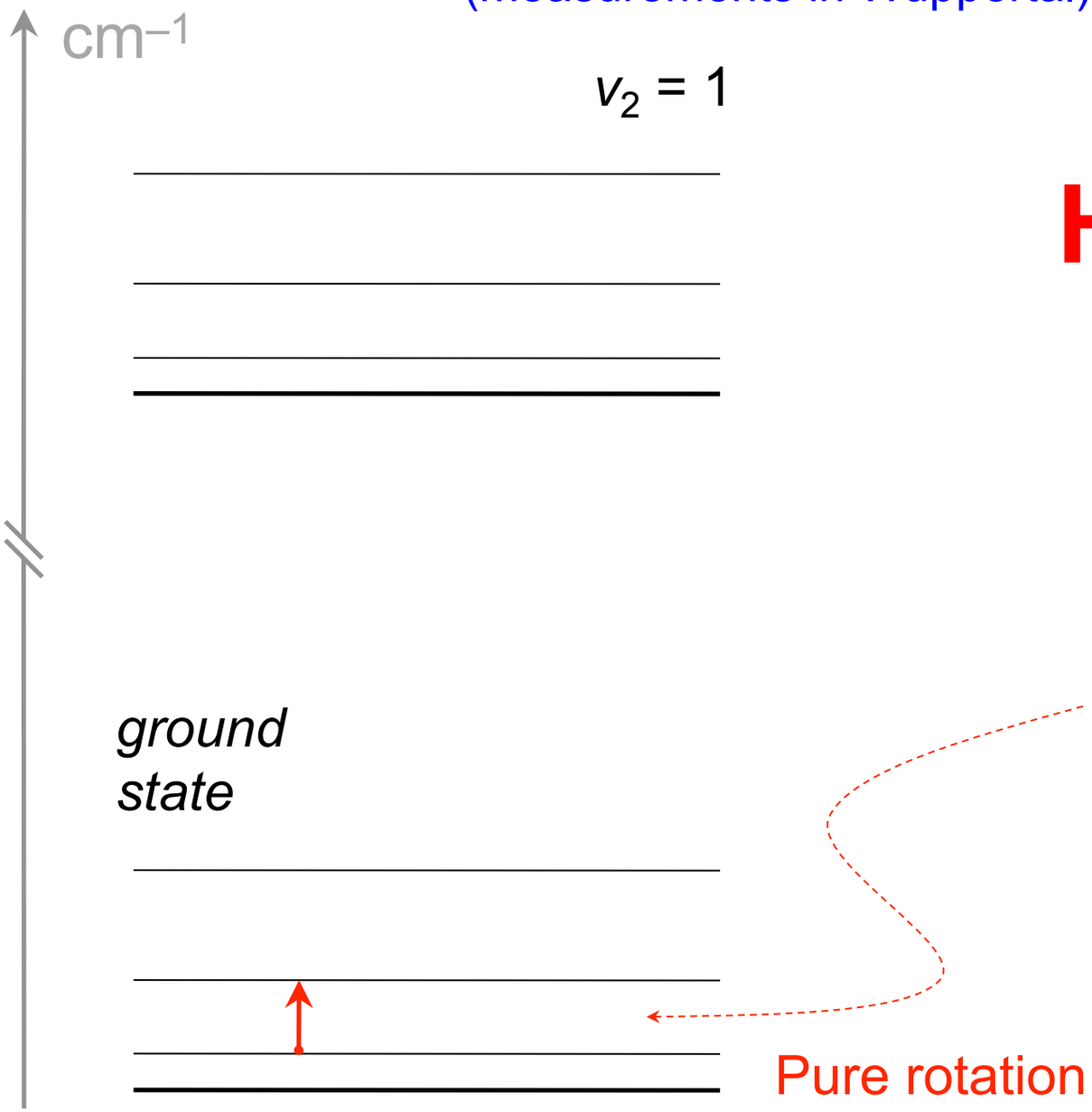
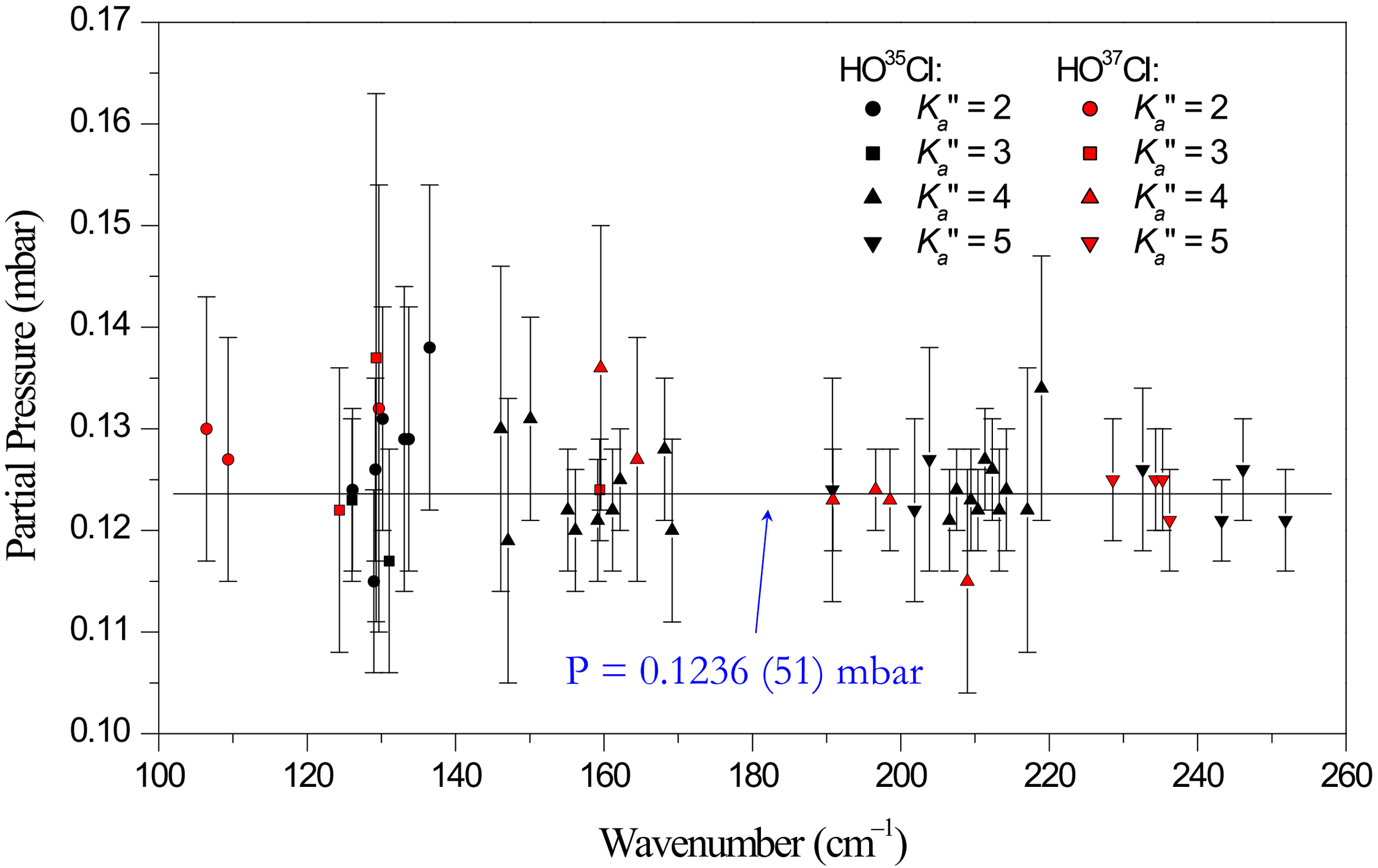


HOCl = Cl_2O + H_2O

Pressure of HOCl from FIR line intensities

Vander Auwera *et al.*, J Mol Spectrosc 204 (2000) 36



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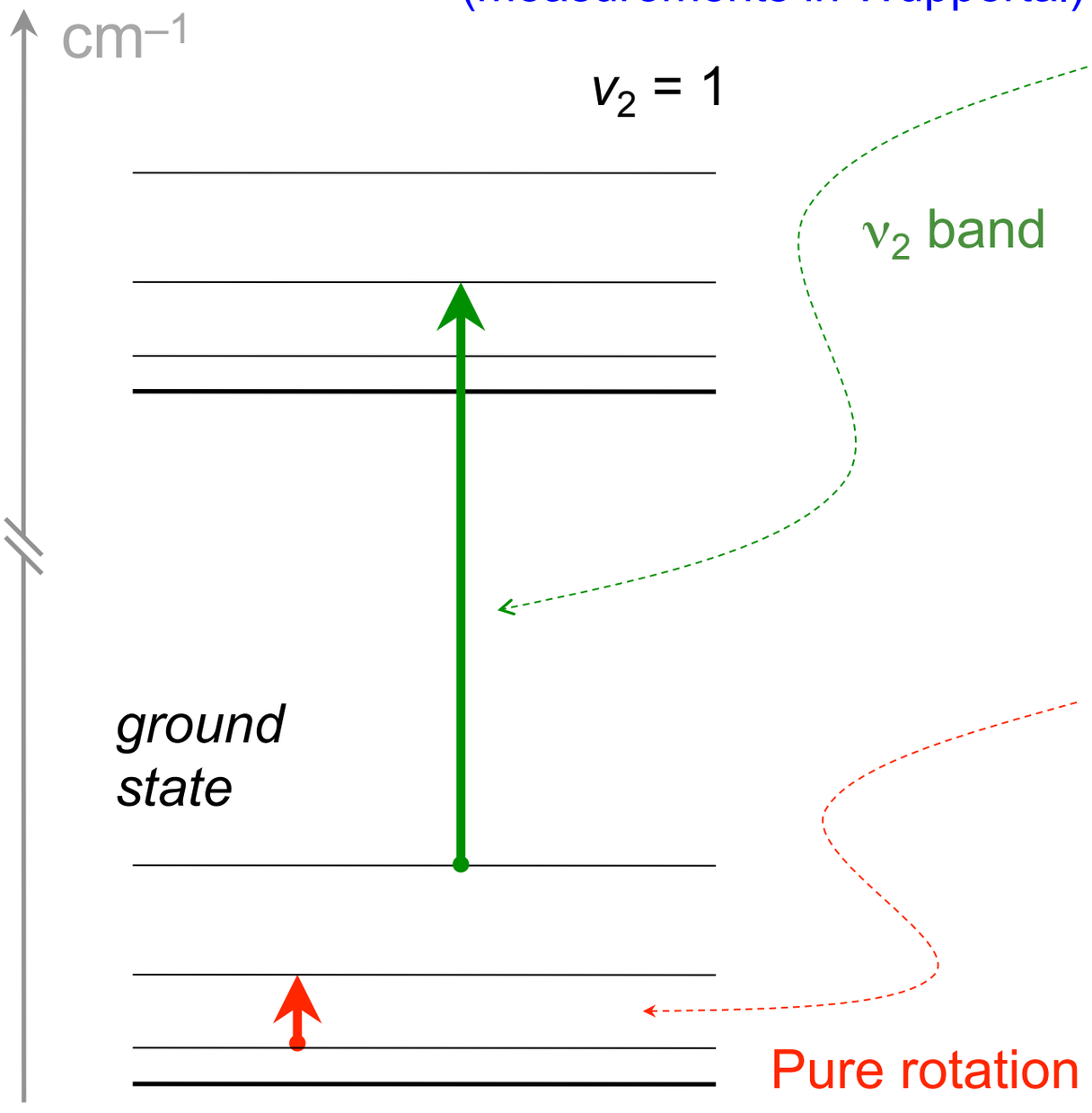
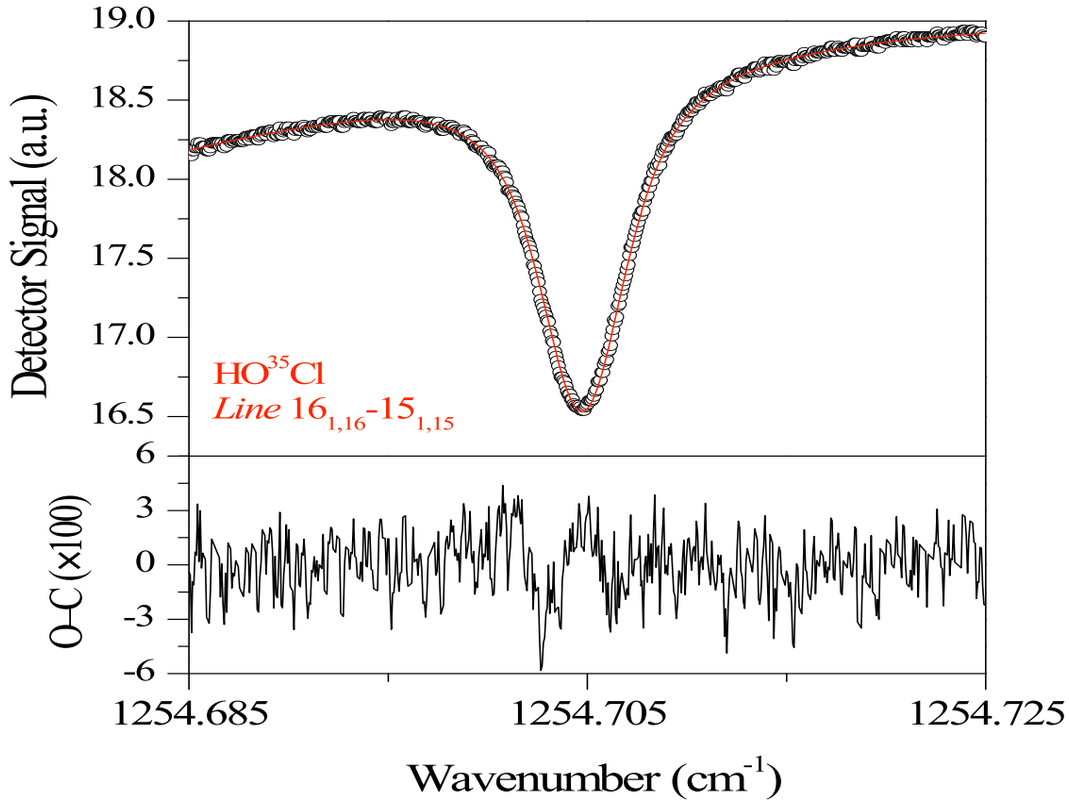
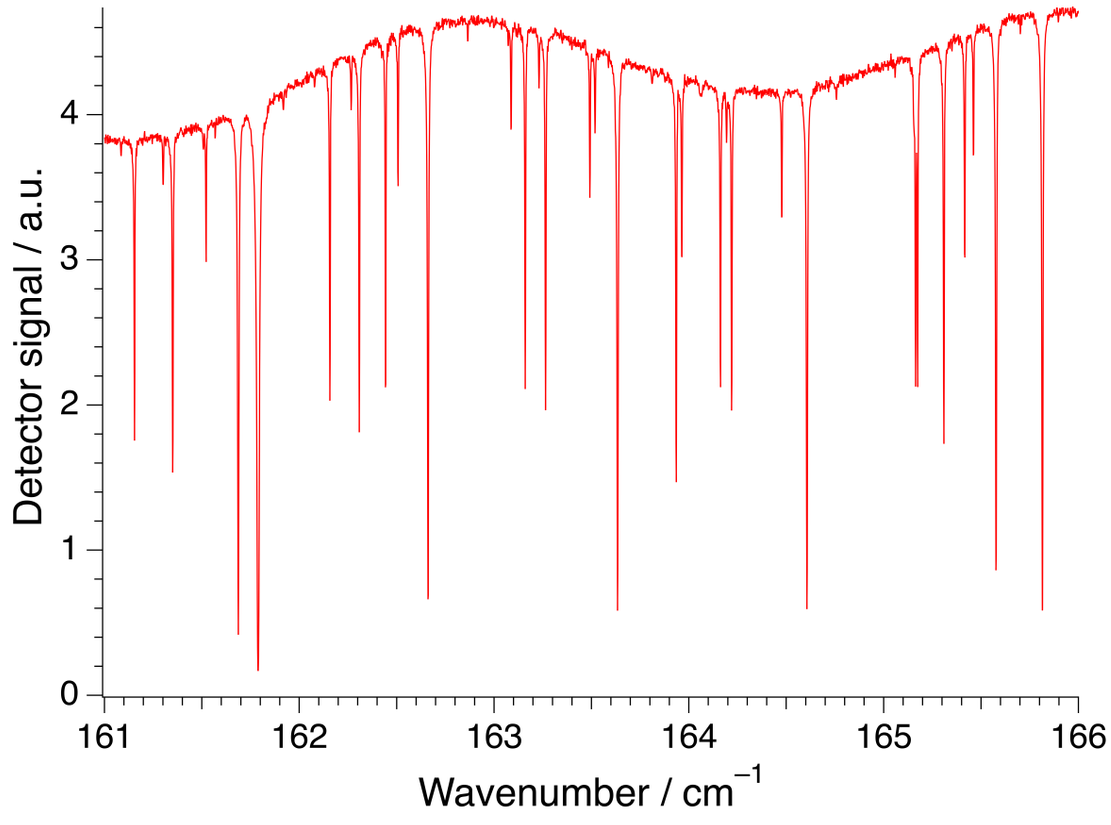
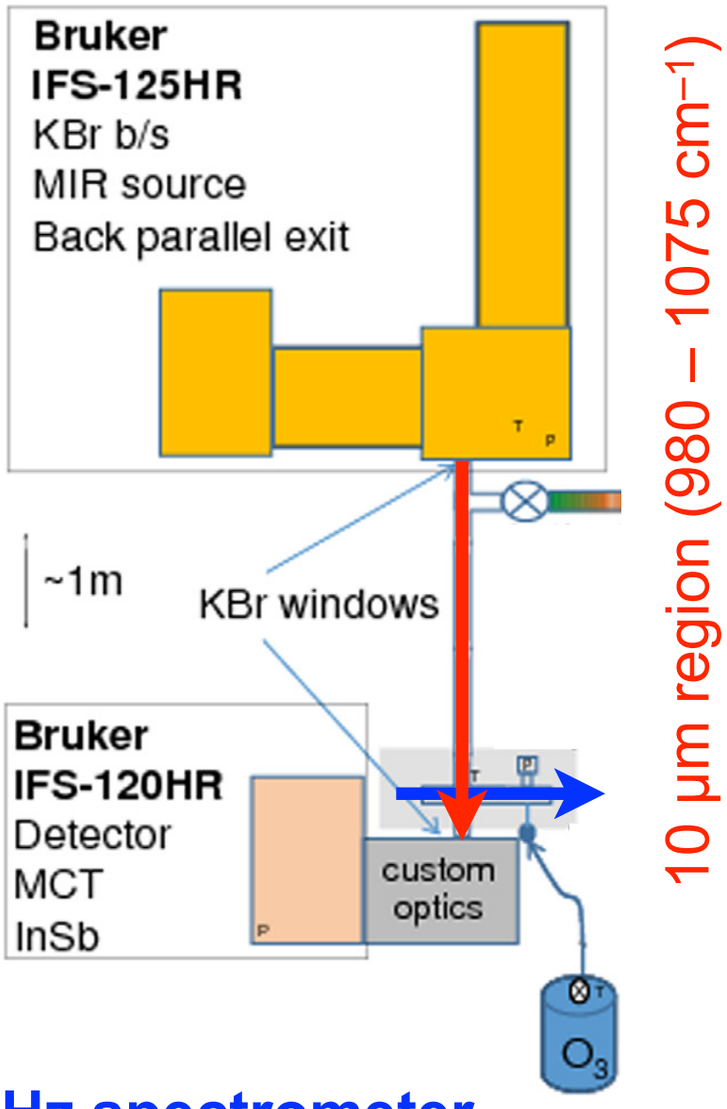






Absolute line intensities for O_3 at 10 μm

Drouin *et al.*, JQSRT 203 (2017) 282

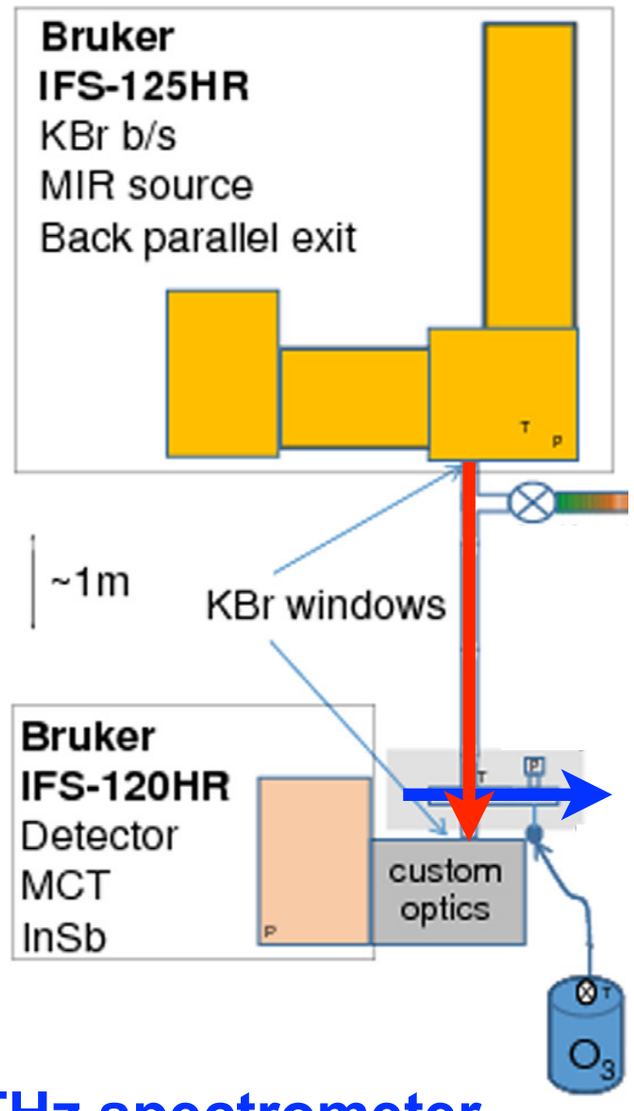


THz spectrometer

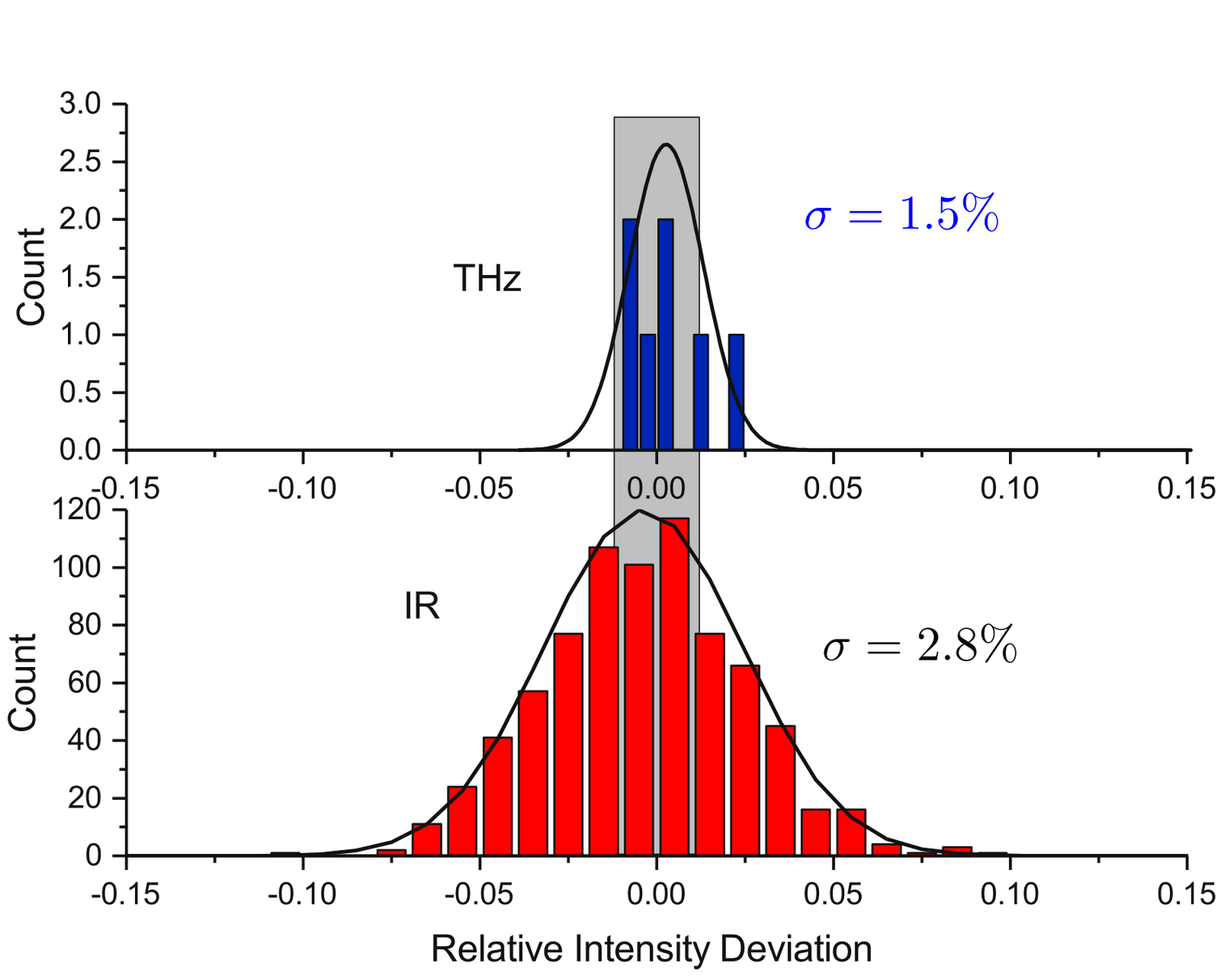
7 pure rotation lines of O_3
(692 – 779 GHz)

Absolute line intensities for O_3 at 10 μm

Drouin *et al.*, JQSRT 203 (2017) 282



10 μm region (980 – 1075 cm^{-1})



THz spectrometer

7 pure rotation lines of O_3
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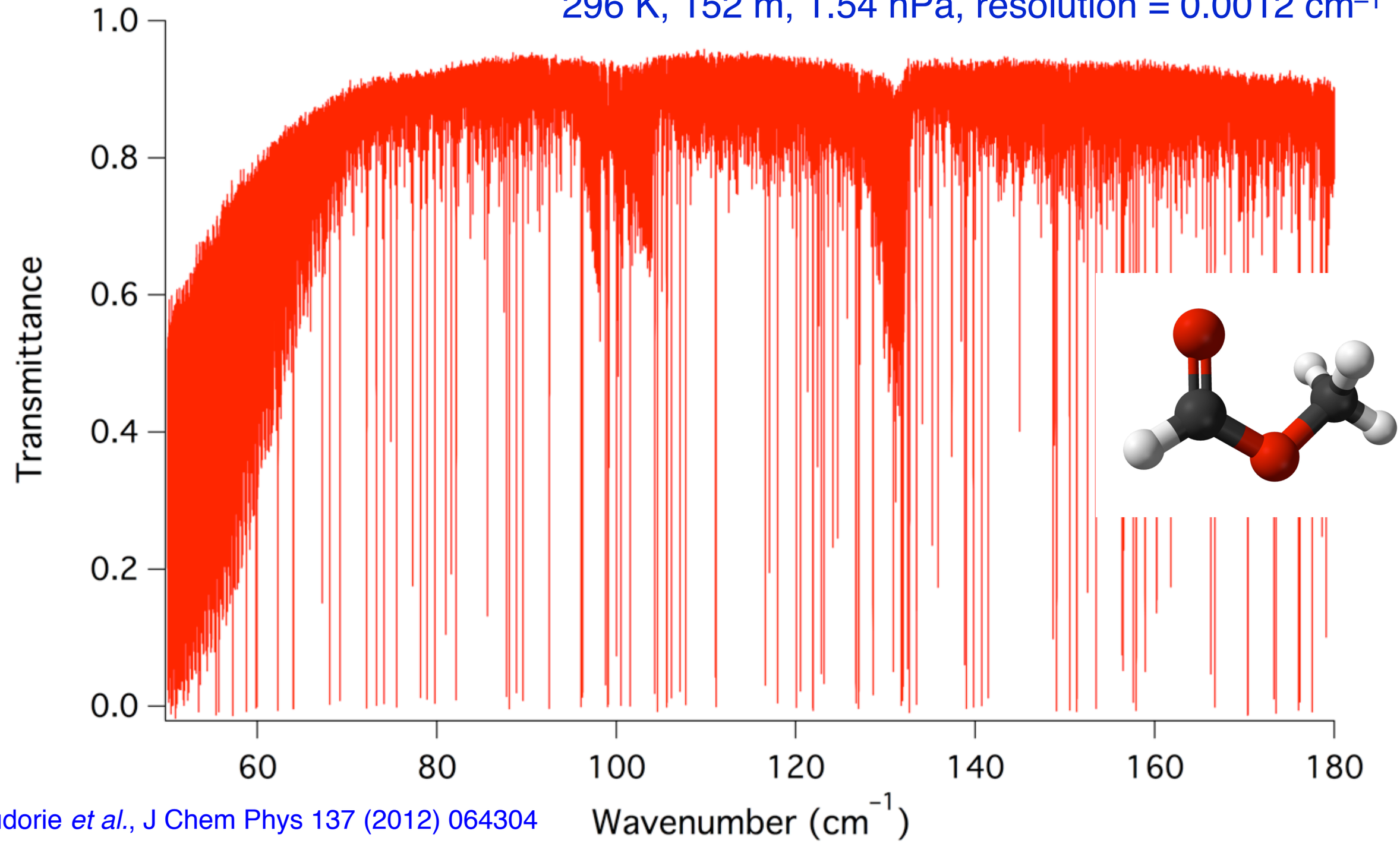
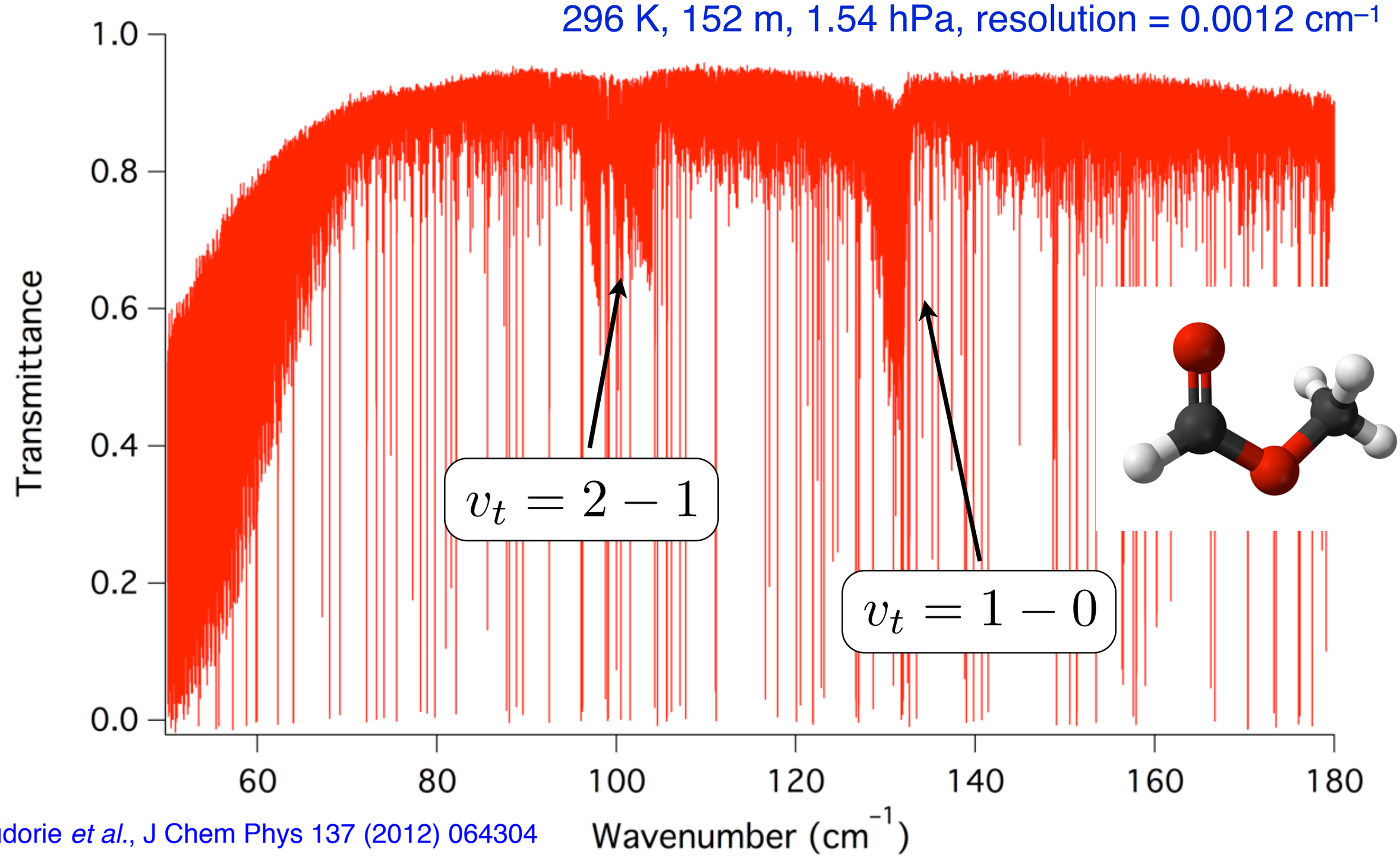
FIR spectroscopy of *cis*-methylformate

296 K, 152 m, 1.54 hPa, resolution = 0.0012 cm^{-1}



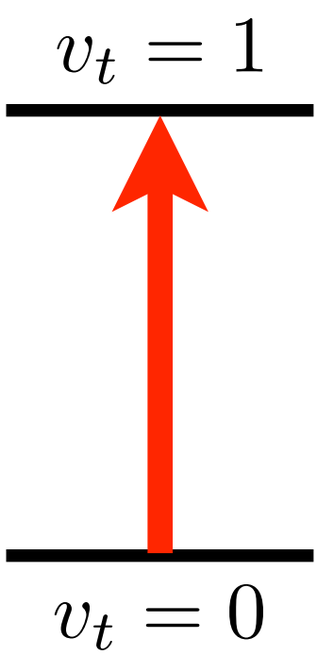
Tudorie *et al.*, J Chem Phys 137 (2012) 064304

FIR spectroscopy of *cis*-methylformate



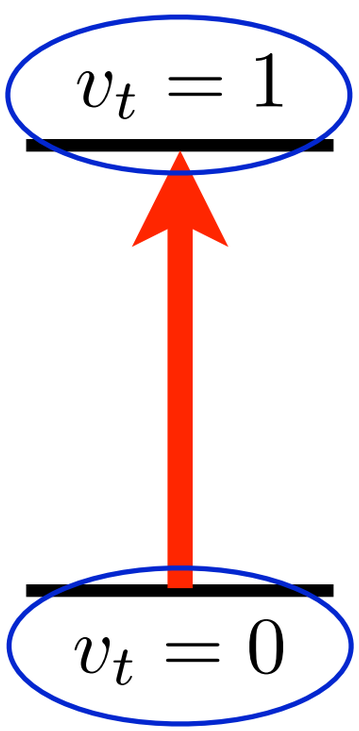
Tudorie *et al.*, J Chem Phys 137 (2012) 064304

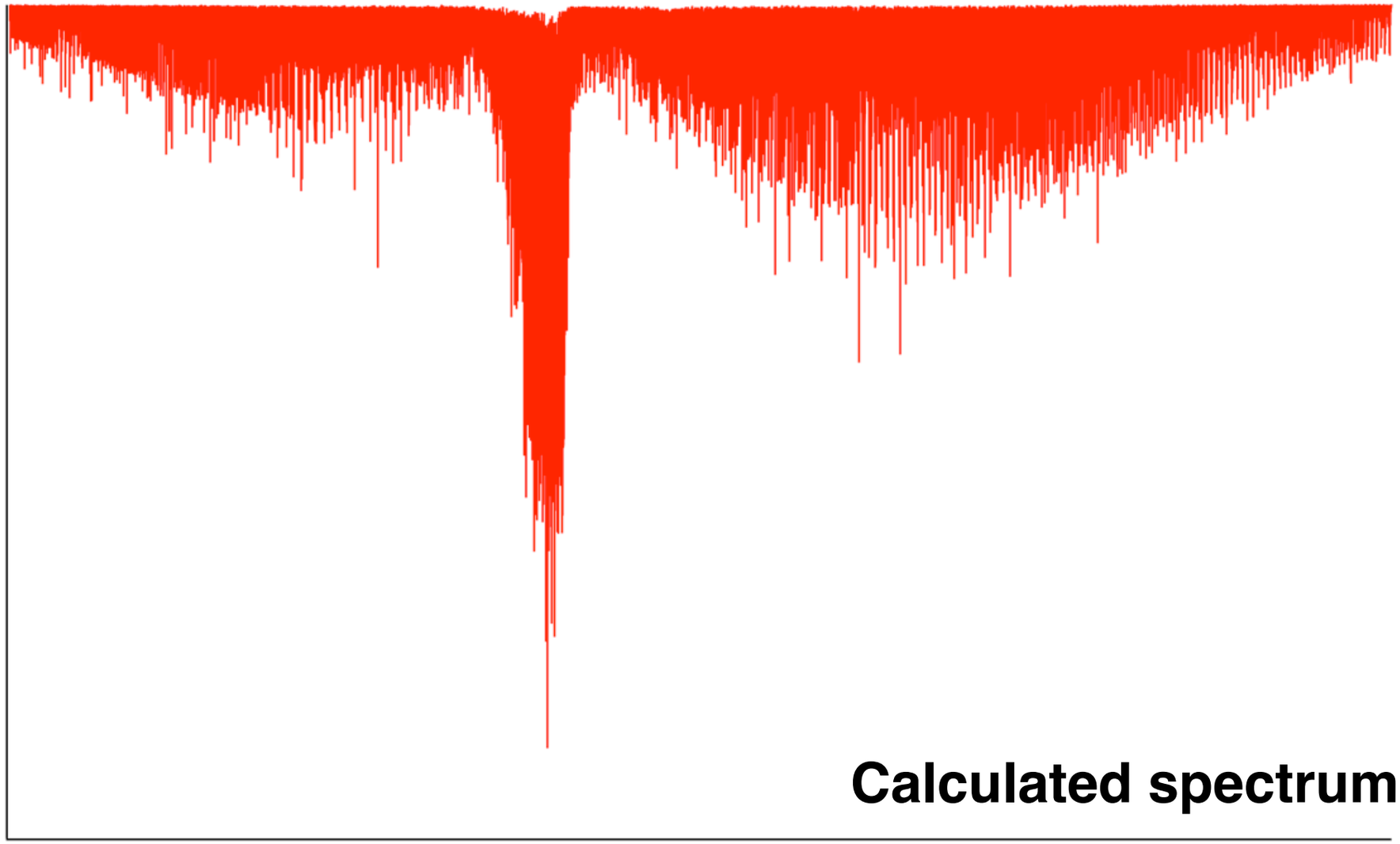
Objectives



Objectives

Extensive MW measurements

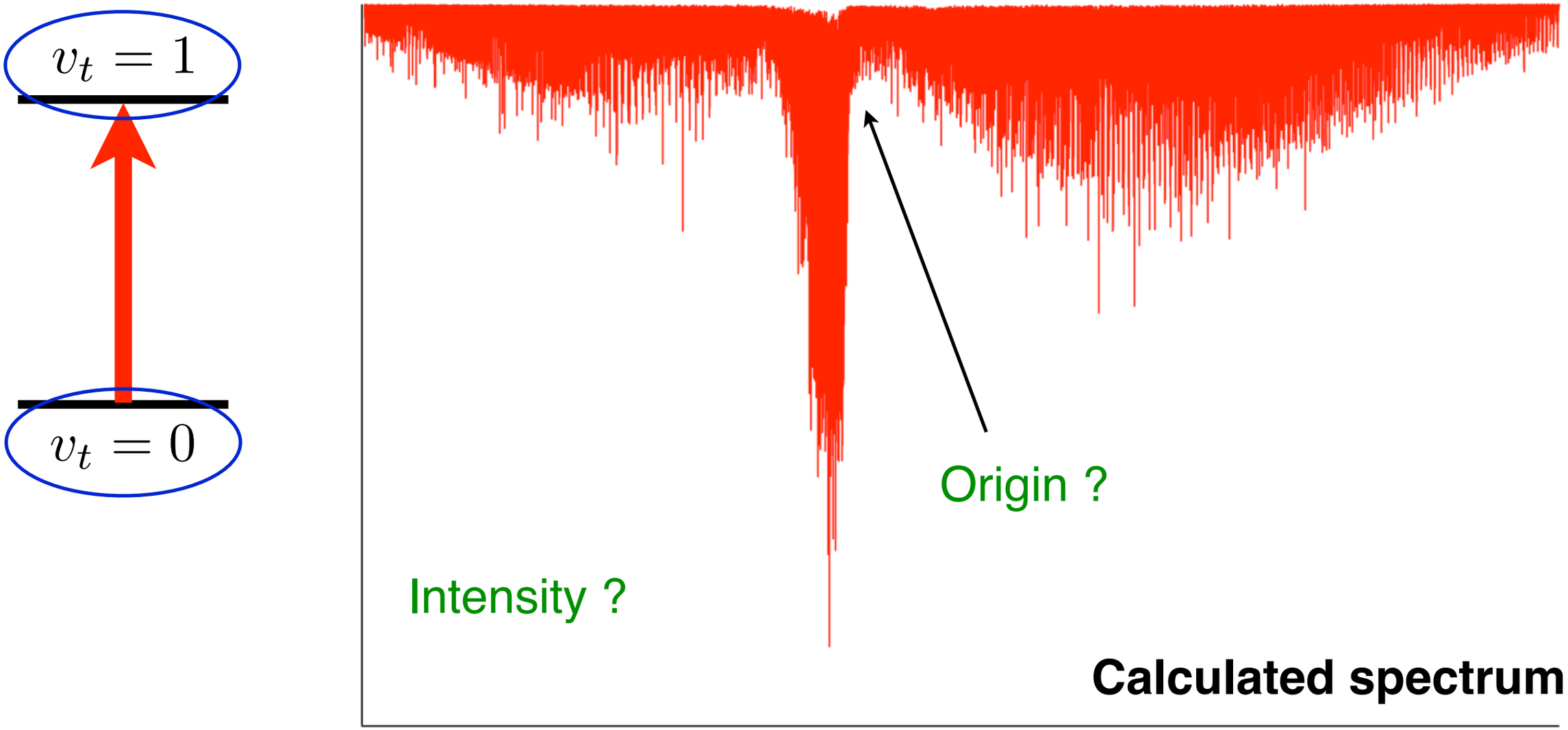




Ilyushin *et al.*, J Mol Spectrosc 255 (2009) 32

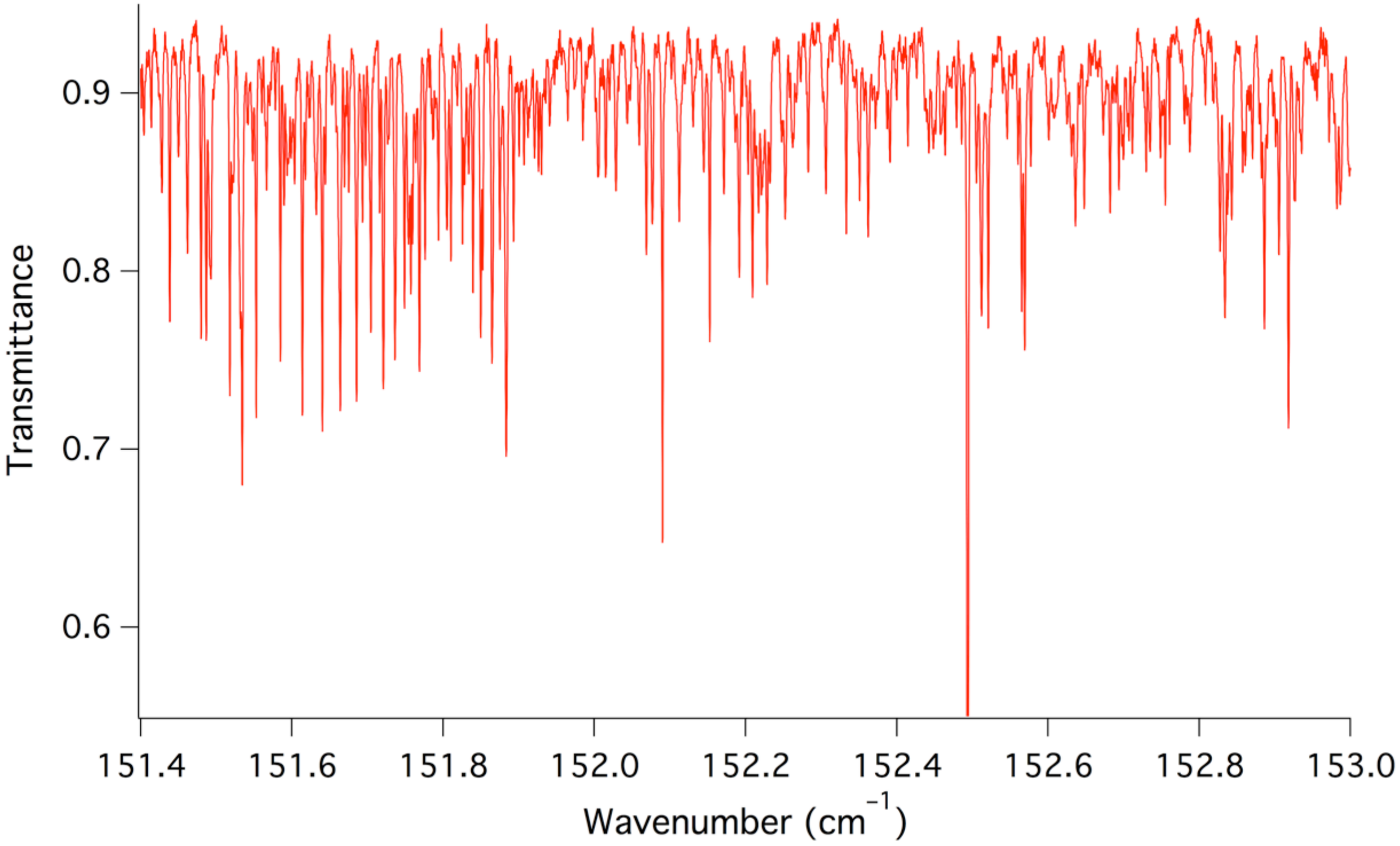
Objectives

Extensive MW measurements

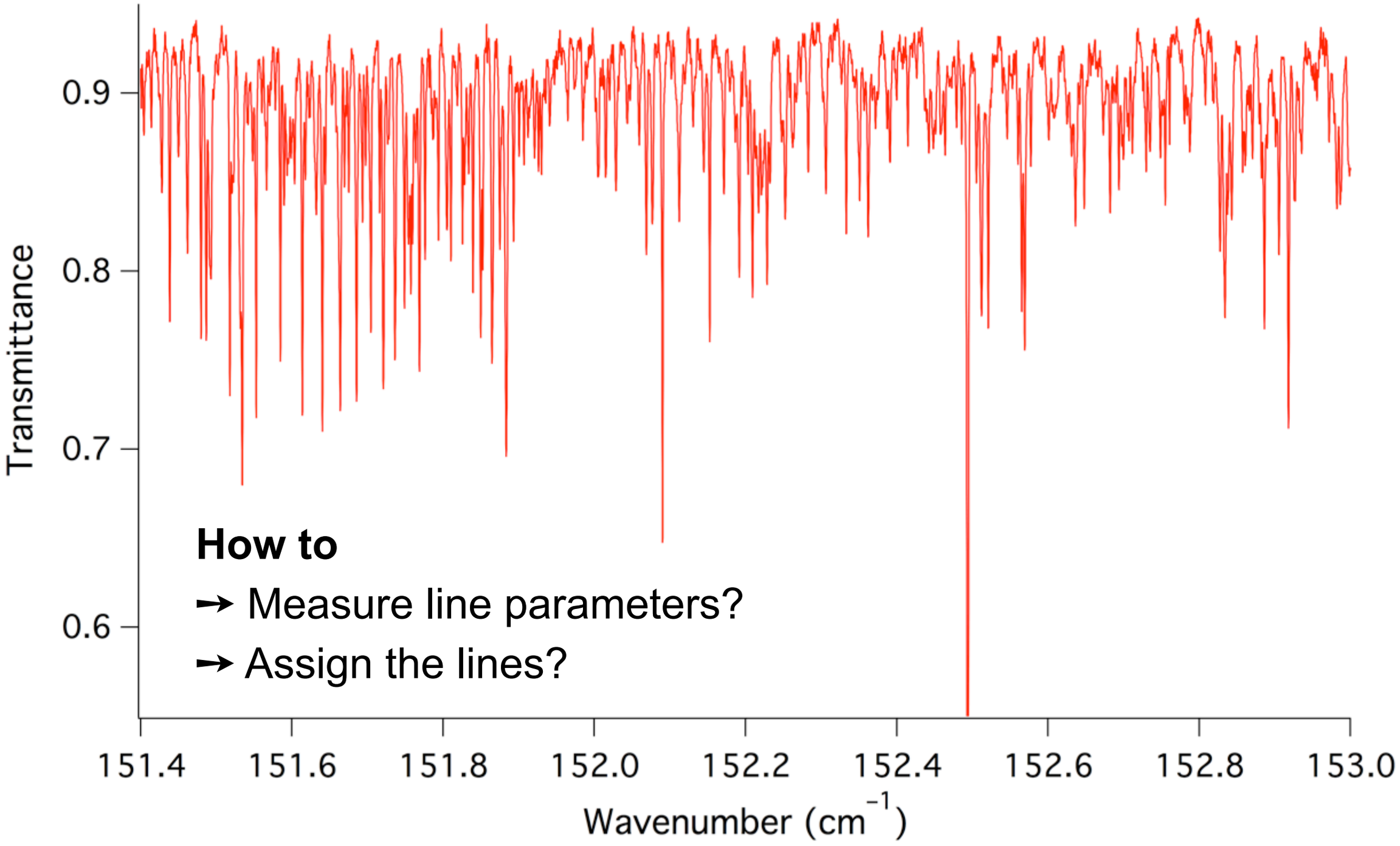


Ilyushin *et al.*, J Mol Spectrosc 255 (2009) 32

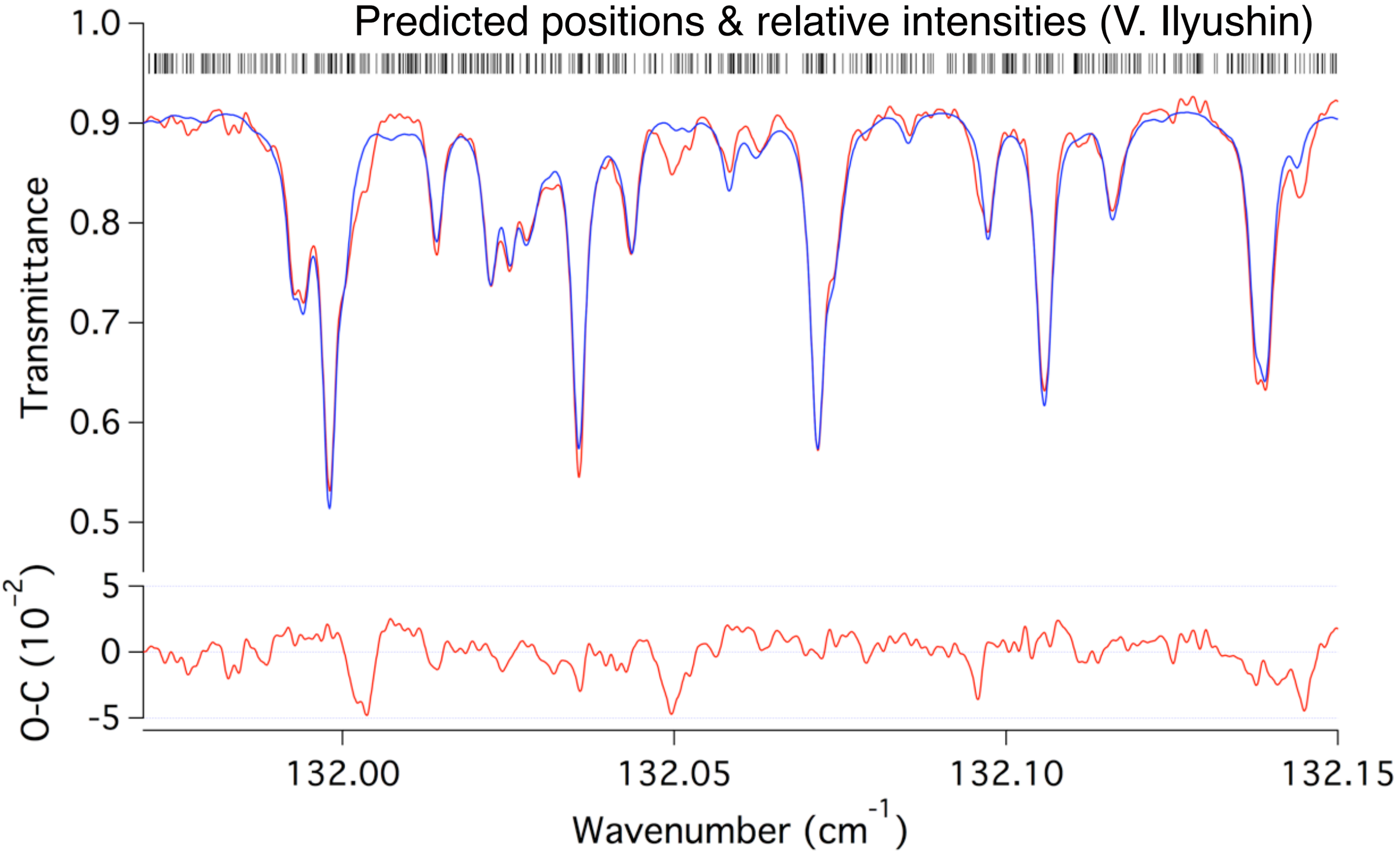
Dense spectrum



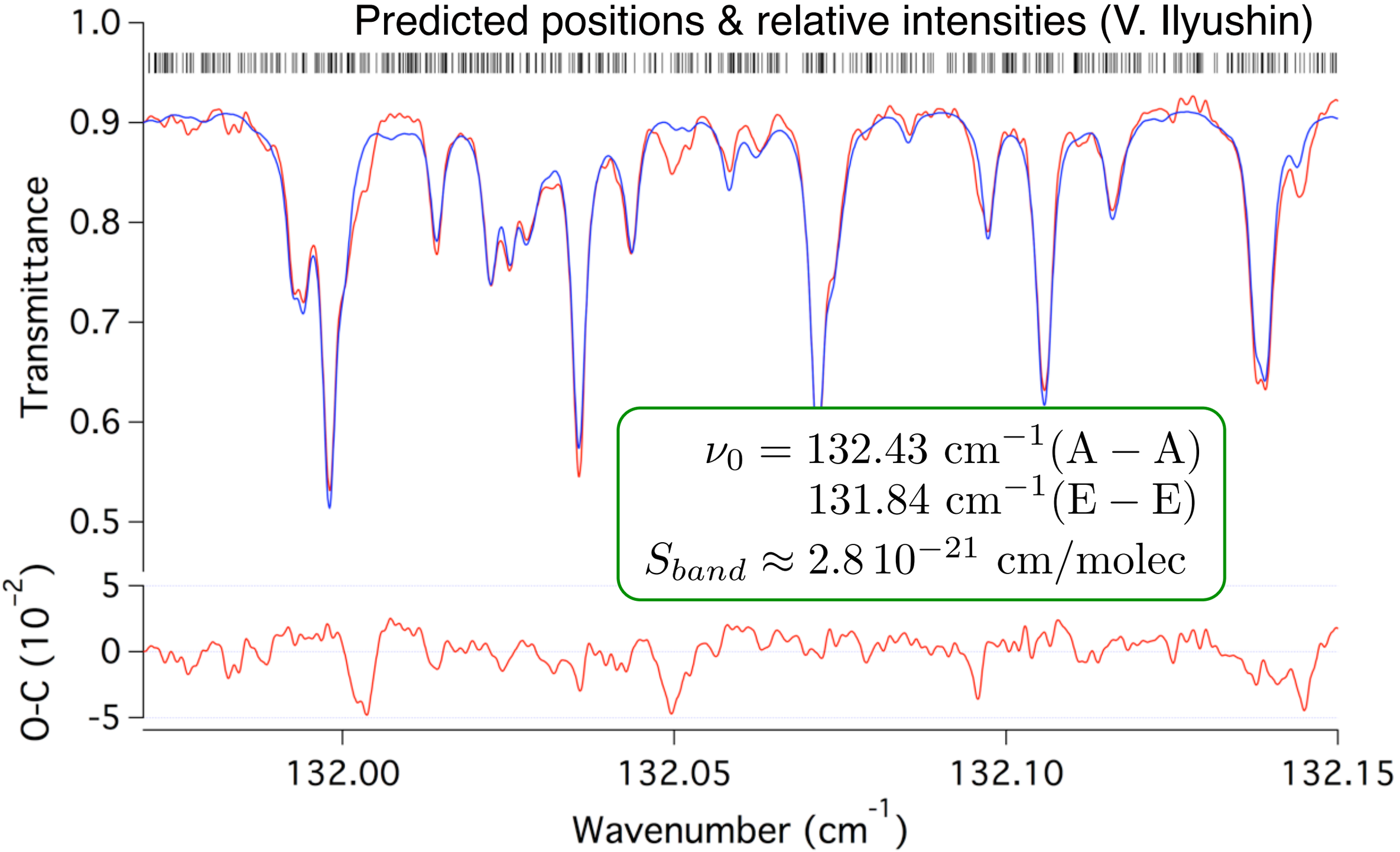
Dense spectrum



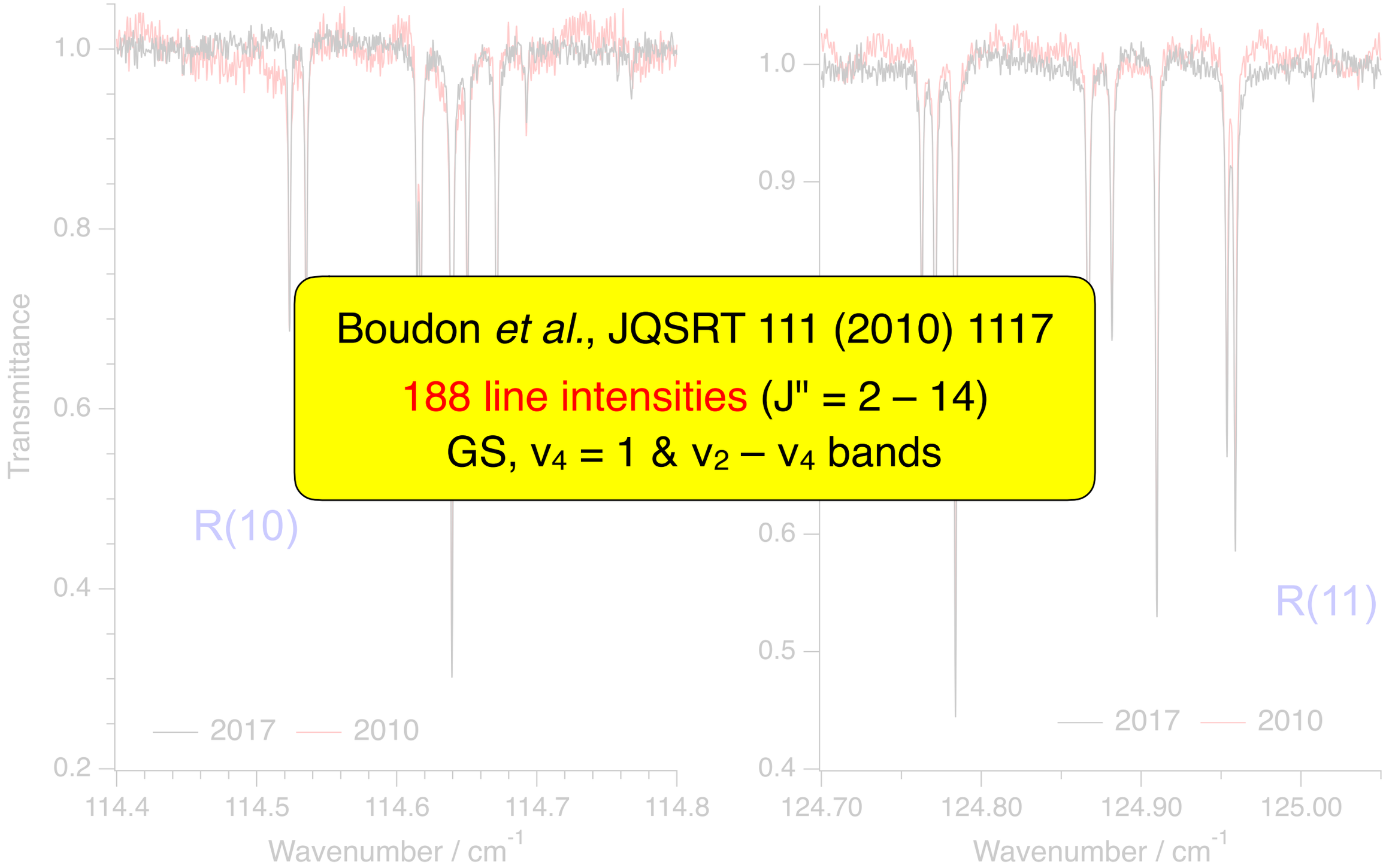
Fit using predicted linelist



Fit using predicted linelist



The FIR pure rotation spectrum of CH_4

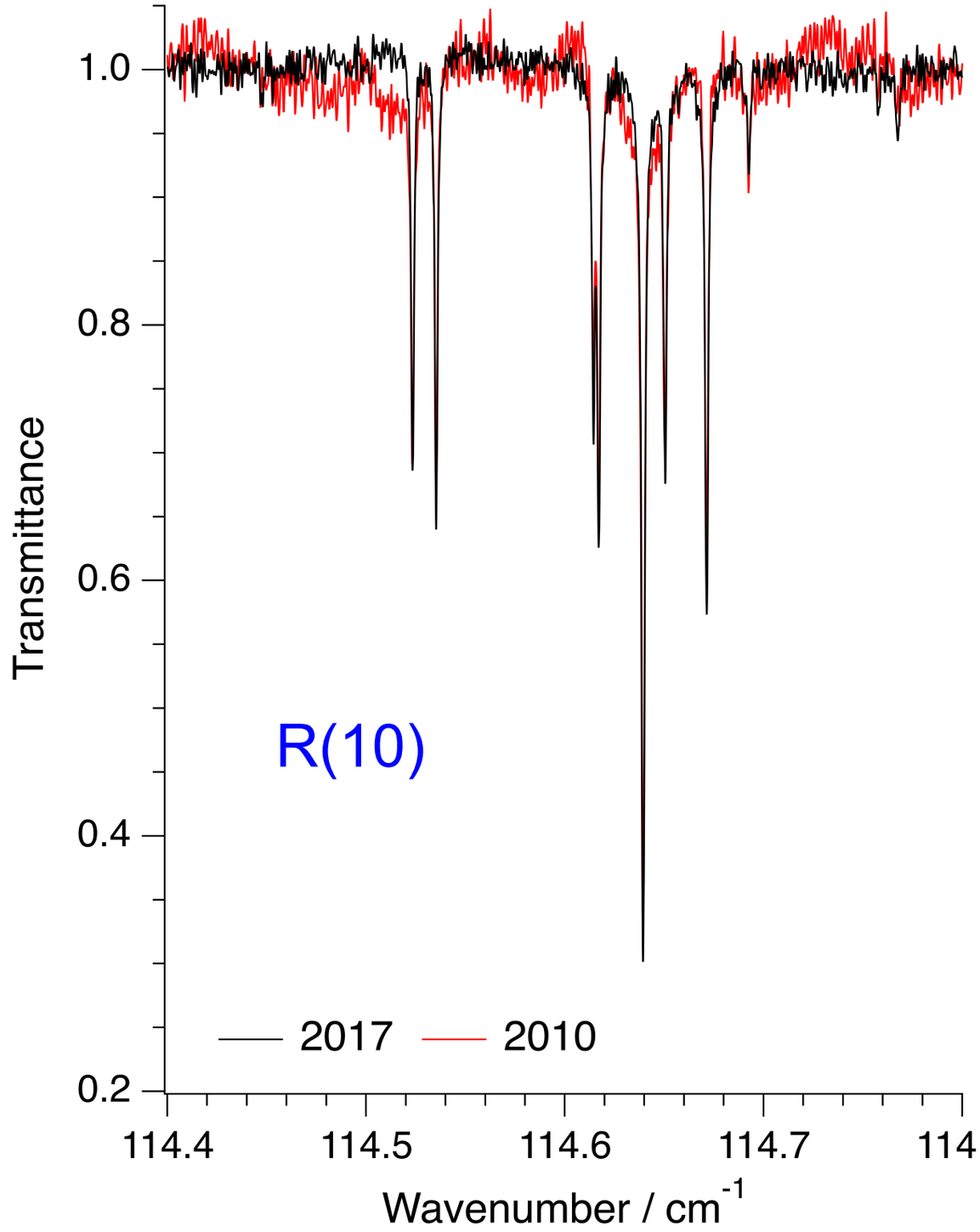


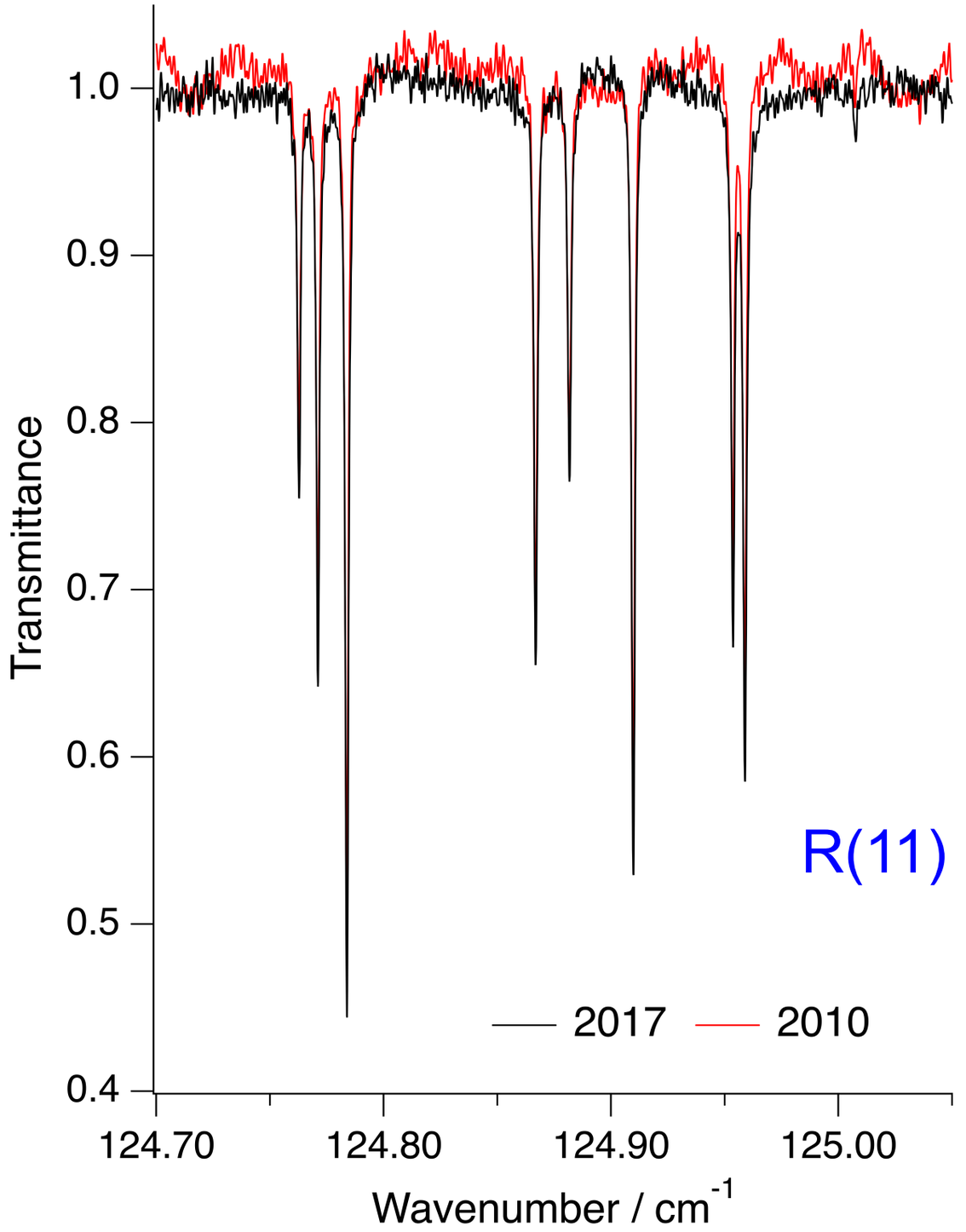
Boudon *et al.*, JQSRT 111 (2010) 1117

188 line intensities (J" = 2 – 14)

GS, $v_4 = 1$ & $v_2 - v_4$ bands

The FIR pure rotation spectrum of CH_4





Conclusion

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- Conventional and synchrotron sources
- Retrieval of line intensities and broadening coefs
- Determination of partial pressures
  - ➥ *intensities in other spectral ranges*

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- Lively field ➙ See following talks

Thank you!