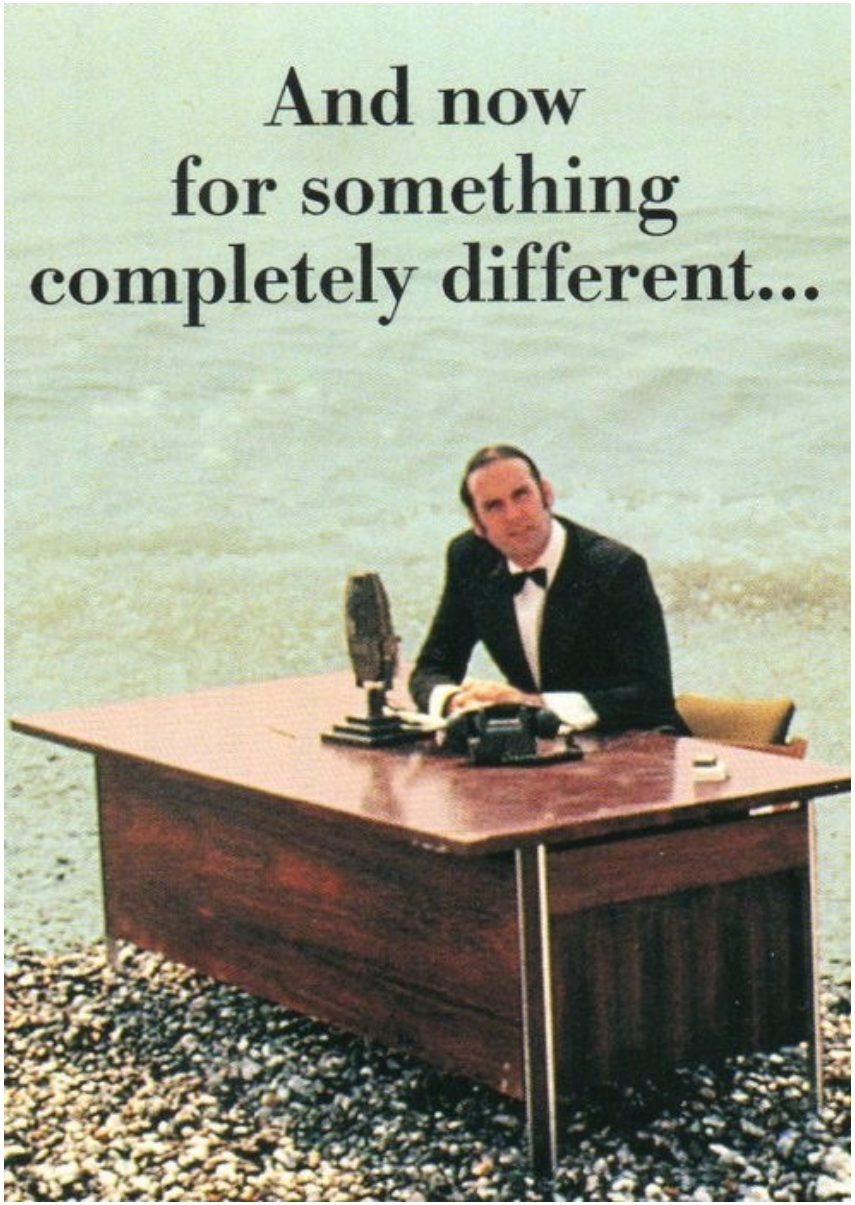
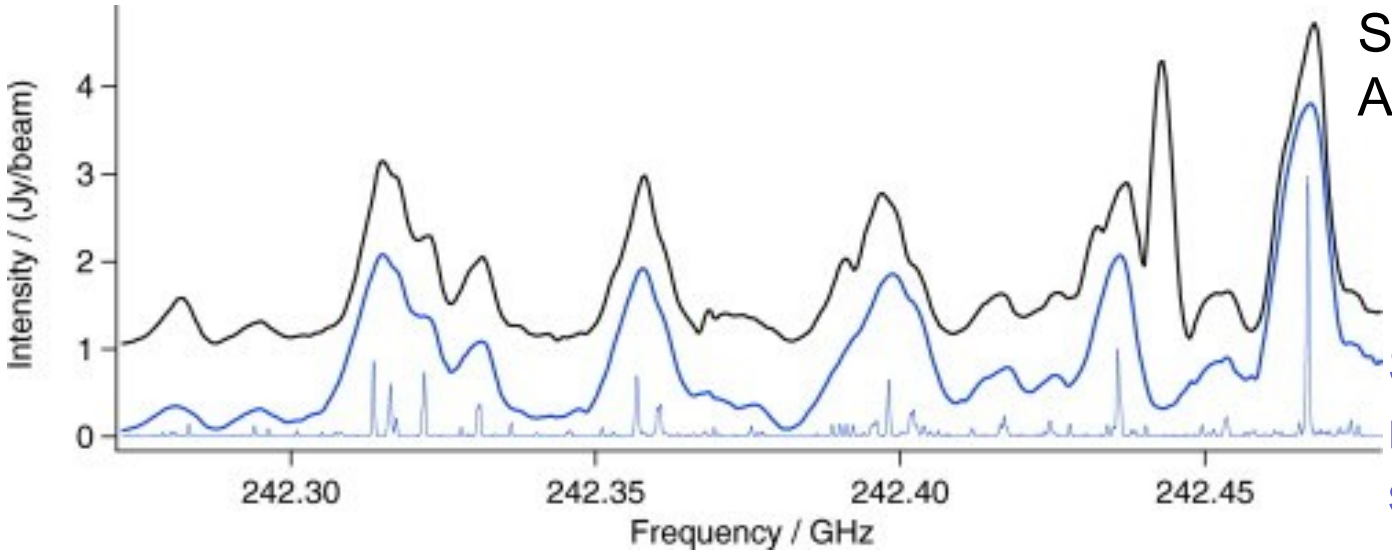


ALMA and molecular spectroscopy

(Picture courtesy of Python M)

ALMA and molecular spectroscopy…



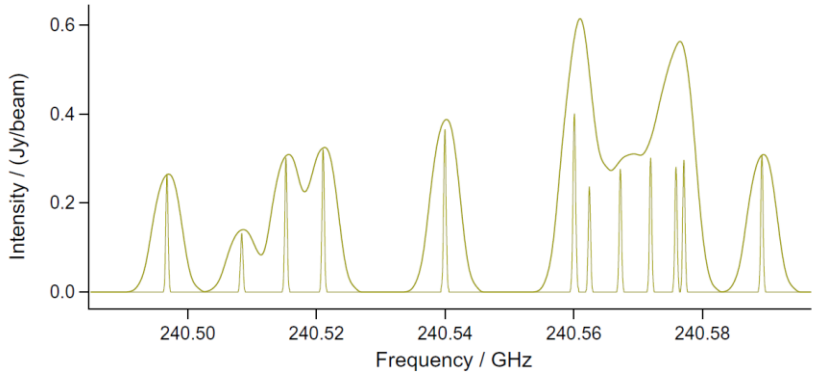
Spectrum from ALMA (Orion KL)

Spectrum from molecular spectroscopy

Analysis/Interpretation/Understanding/Assignment of ALMA spectra by comparison with „molecular spectroscopy“ (MS) spectra.

S. M. Fortman, J. P. McMillan, C. F. Neese, S. K. Randall, A. J. Remijan, T. L. Wilson, F. C. De Lucia, *Journal of Molecular Spectroscopy* **280** (2012) 11–20

How can we generate MS spectra for comparison with ALMA?



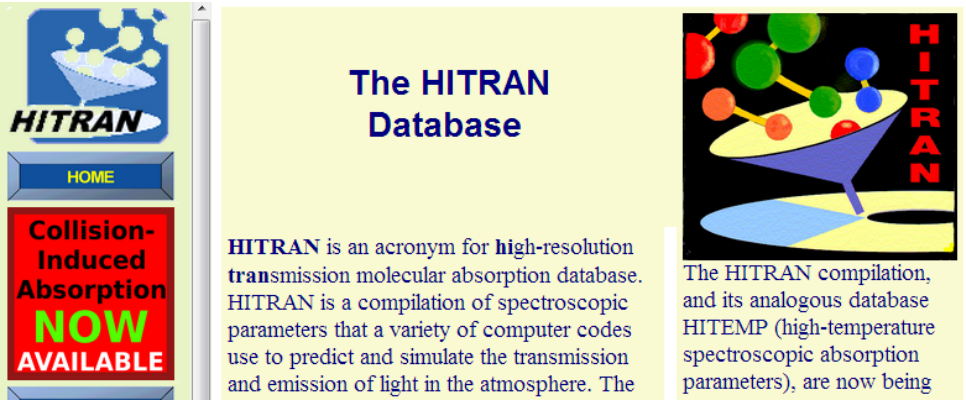
MS (CES) spectrum from S. M. Fortman, J. P. McMillan, C. F. Neese, S. K. Randall, A. J. Remijan, T. L. Wilson, F. C. De Lucia, *Journal of Molecular Spectroscopy* **280** (2012) 11–20

1. Experiment

2. Theory

1a. Assigned experimental spectra
Example: HITRAN
2b. Unassigned experimental spectra
Example: CES

Quantum mechanically (QM) simulated spectra
Example: TROVE



http://www.cfa.harvard.edu/hitran/

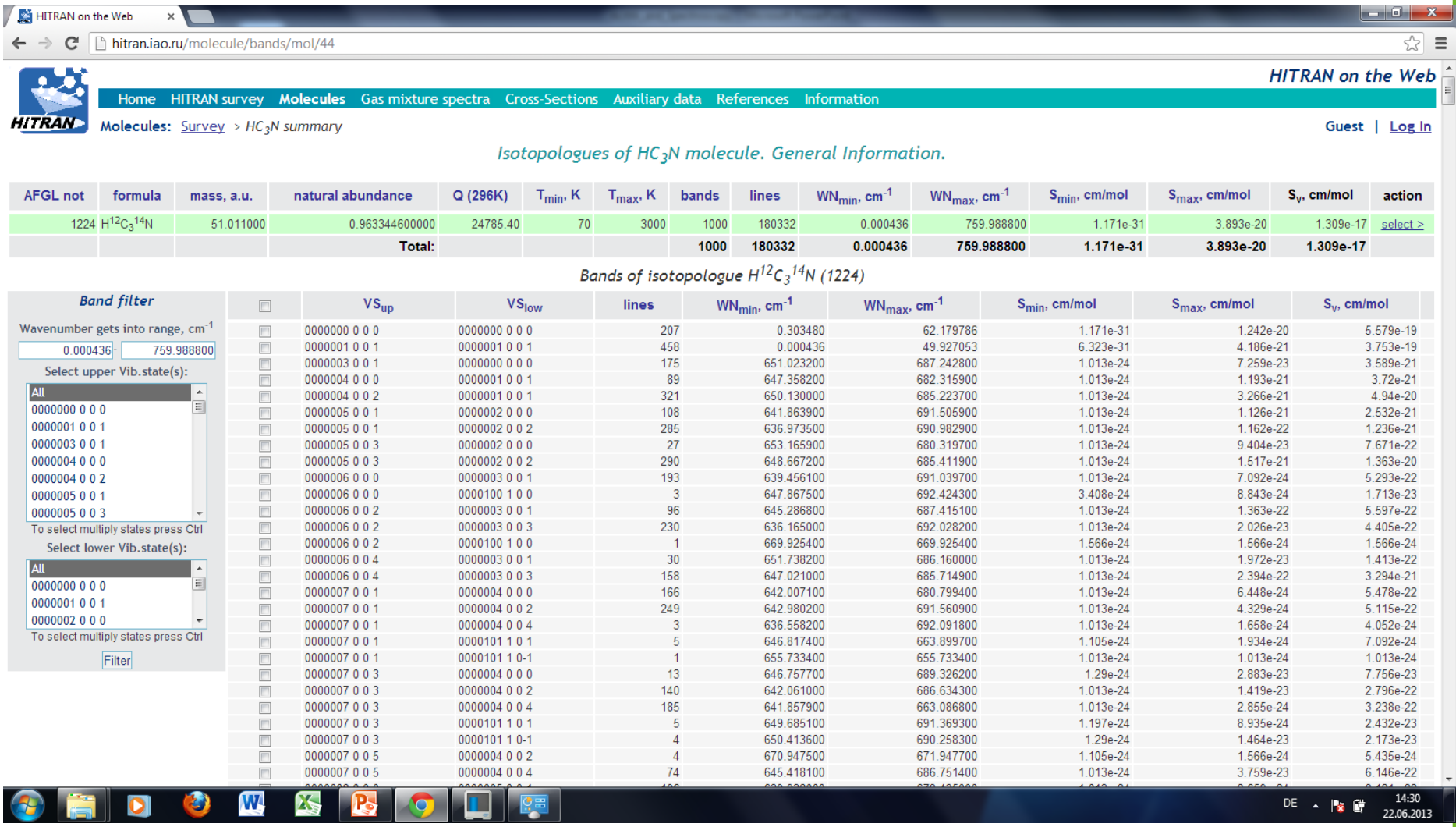
- Developed for atmospheric applications.
- Intensities available.

L.S. Rothman, I. E. Gordon, A. Barbe, D. Chris Benner, P. F. Bernath, M. Birk, V. Boudon, L. R. Brown, A. Campargue, J.-P. Champion, K. Chance, L.H. Coudert, V. Dana, V. M. Devi, S. Fally, J.-M. Flaud, R. R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W. J. Lafferty, J.-Y. Mandin, S.T. Massie, S.N. Mikhailenko, C. E. Miller, N. Moazzen-Ahmadi, O. V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C. P. Rinsland, M. Rotger, M. Šimečková, M. A. H. Smith, K. Sung, S. A. Tashkun, J. Tennyson, R. A. Toth, A. C. Vandaele, J. Vander Auwera, *Journal of Quantitative Spectroscopy & Radiative Transfer* **110** (2009) 533–572

Generating a „traditional“, experimentelly derived „line list“

- Record laboratory spectrum.
- Manually assign quantum numbers to initial and final state of each transition.
- Manually determine area under line (integrated intensity); proportional to Einstein *A* coefficient (Ph.D. student required).
- Publish list of the above, transition by transition, preferably on the web.

Example



HITRAN on the Web

hitran.iao.ru/molecule/bands/mol/44

HITRAN on the Web

Home | HITRAN survey | Molecules | Gas mixture spectra | Cross-Sections | Auxiliary data | References | Information

Molecules: Survey > HC_3N summary

Guest | Log In

Isotopologues of HC_3N molecule. General Information.

AFGL not	formula	mass, a.u.	natural abundance	Q (296K)	T_{min}, K	T_{max}, K	bands	lines	WN_{min}, cm^{-1}	WN_{max}, cm^{-1}	S_{min}, cm/mol	S_{max}, cm/mol	S_v, cm/mol	action
1224	$H^{12}C_3{}^{14}N$	51.011000	0.963344600000	24785.40	70	3000	1000	180332	0.000436	759.988800	1.171e-31	3.893e-20	1.309e-17	select >
			Total:				**1000**	**180332**	**0.000436**	**759.988800**	**1.171e-31**	**3.893e-20**	**1.309e-17**	

Bands of isotopologue $H^{12}C_3{}^{14}N$ (1224)

Band filter

Wavenumber gets into range, cm^{-1}: 0.000436 - 759.988800

Select upper Vib.state(s):

All
0000000 0 0 0
0000001 0 0 1
0000003 0 0 1
0000004 0 0 0
0000004 0 0 2
0000005 0 0 1
0000005 0 0 3

To select multiply states press Ctrl

Select lower Vib.state(s):

All
0000000 0 0 0
0000001 0 0 1
0000002 0 0 0

To select multiply states press Ctrl

Filter

VS_{up}	VS_{low}	lines	WN_{min}, cm^{-1}	WN_{max}, cm^{-1}	S_{min}, cm/mol	S_{max}, cm/mol	S_v, cm/mol
0000000 0 0 0	0000000 0 0 0	207	0.303480	62.179786	1.171e-31	1.242e-20	5.579e-19
0000001 0 0 1	0000001 0 0 1	458	0.000436	49.927053	6.323e-31	4.186e-21	3.753e-19
0000003 0 0 1	0000000 0 0 0	175	651.023200	687.242800	1.013e-24	7.259e-23	3.589e-21
0000004 0 0 0	0000001 0 0 1	89	647.358200	682.315900	1.013e-24	1.193e-21	3.72e-21
0000004 0 0 2	0000001 0 0 1	321	650.130000	685.223700	1.013e-24	3.266e-21	4.94e-20
0000005 0 0 1	0000002 0 0 0	108	641.863900	691.505900	1.013e-24	1.126e-21	2.532e-21
0000005 0 0 1	0000002 0 0 2	285	636.973500	690.982900	1.013e-24	1.162e-22	1.236e-21
0000005 0 0 3	0000002 0 0 0	27	653.165900	680.319700	1.013e-24	9.404e-23	7.671e-22
0000005 0 0 3	0000002 0 0 2	290	648.667200	685.411900	1.013e-24	1.517e-21	1.363e-20
0000006 0 0 0	0000003 0 0 1	193	639.456100	691.039700	1.013e-24	7.092e-24	5.293e-22
0000006 0 0 0	0000100 1 0 0	3	647.867500	692.424300	3.408e-24	8.843e-24	1.713e-23
0000006 0 0 2	0000003 0 0 1	96	645.286800	687.415100	1.013e-24	1.363e-22	5.597e-22
0000006 0 0 2	0000003 0 0 3	230	636.165000	692.028200	1.013e-24	2.026e-23	4.405e-22
0000006 0 0 2	0000100 1 0 0	1	669.925400	669.925400	1.566e-24	1.566e-24	1.566e-24
0000006 0 0 4	0000003 0 0 1	30	651.738200	686.160000	1.013e-24	1.972e-23	1.413e-22
0000006 0 0 4	0000003 0 0 3	158	647.021000	685.714900	1.013e-24	2.394e-22	3.294e-21
0000007 0 0 1	0000004 0 0 0	166	642.007100	680.799400	1.013e-24	6.448e-24	5.478e-22
0000007 0 0 1	0000004 0 0 2	249	642.980200	691.560900	1.013e-24	4.329e-24	5.115e-22
0000007 0 0 1	0000004 0 0 4	3	636.558200	692.091800	1.013e-24	1.658e-24	4.052e-24
0000007 0 0 1	0000101 1 0 1	5	646.817400	663.899700	1.105e-24	1.934e-24	7.092e-24
0000007 0 0 1	0000101 1 0-1	1	655.733400	655.733400	1.013e-24	1.013e-24	1.013e-24
0000007 0 0 3	0000004 0 0 0	13	646.757700	689.326200	1.29e-24	2.883e-23	7.756e-23
0000007 0 0 3	0000004 0 0 2	140	642.061000	686.634300	1.013e-24	1.419e-23	2.796e-22
0000007 0 0 3	0000004 0 0 4	185	641.857900	663.086800	1.013e-24	2.855e-24	3.238e-22
0000007 0 0 3	0000101 1 0 1	5	649.685100	691.369300	1.197e-24	8.935e-24	2.432e-23
0000007 0 0 3	0000101 1 0-1	4	650.413600	690.258300	1.29e-24	1.464e-23	2.173e-23
0000007 0 0 5	0000004 0 0 2	4	670.947500	671.947700	1.105e-24	1.566e-24	5.435e-24
0000007 0 0 5	0000004 0 0 4	74	645.418100	686.751400	1.013e-24	3.759e-23	6.146e-22

DE 14:30 22.06.2013

- Is quantum number assignment of MS spectra necessary for comparison with ALMA spectra?
- Not really, it would seem.
- Can it be avoided?

Journal of Molecular Spectroscopy 280 (2012) 11–20

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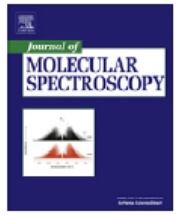
journal homepage: www.elsevier.com/locate/jms



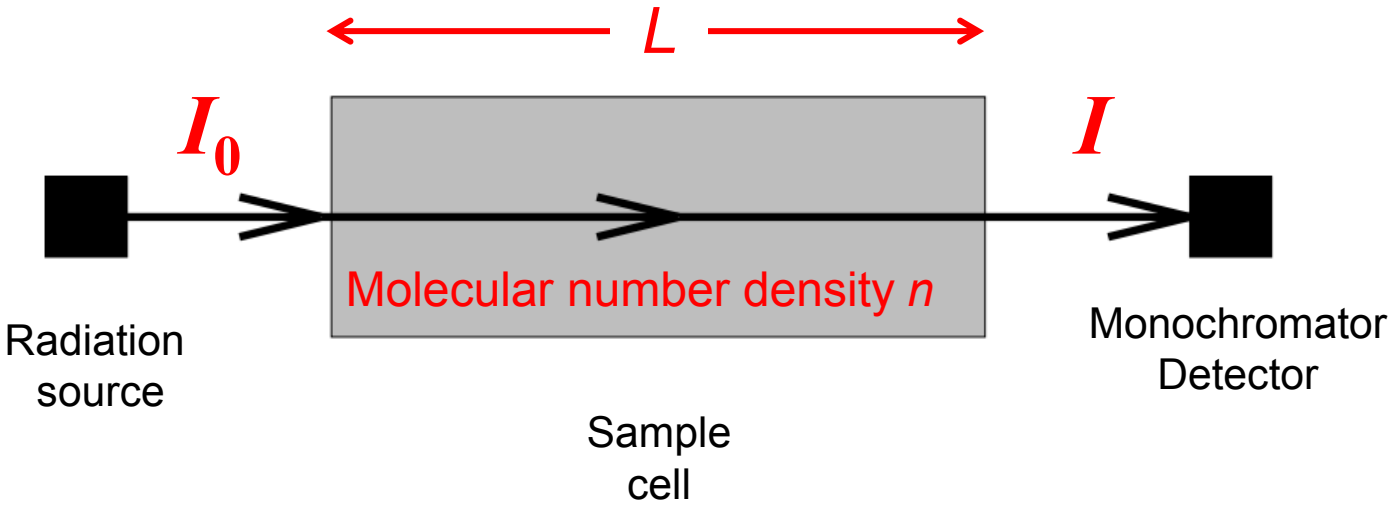
An analysis of a preliminary ALMA Orion KL spectrum via the use of complete experimental spectra from the laboratory

CES

Sarah M. Fortman [a], James P. McMillan [a], Christopher F. Neese [a], Suzanna K. Randall [b], Anthony J. Remijan [c], T.L. Wilson [d], Frank C. De Lucia [a,*]

[a] Department of Physics, Ohio State University, 191 W. Woodruff Ave., Columbus, OH 43210, USA
[b] European Space Agency, Karl-Schwarzschild-Str. 2, 85748 Garching, Germany
[c] National Radio Astronomy Observatory, 520 Edgemont Road, Charlottesville, VA 22903-2475, USA
[d] Naval Research Laboratory, Code 7210, Washington, DC 20375, USA

Basic quantitative spectroscopy

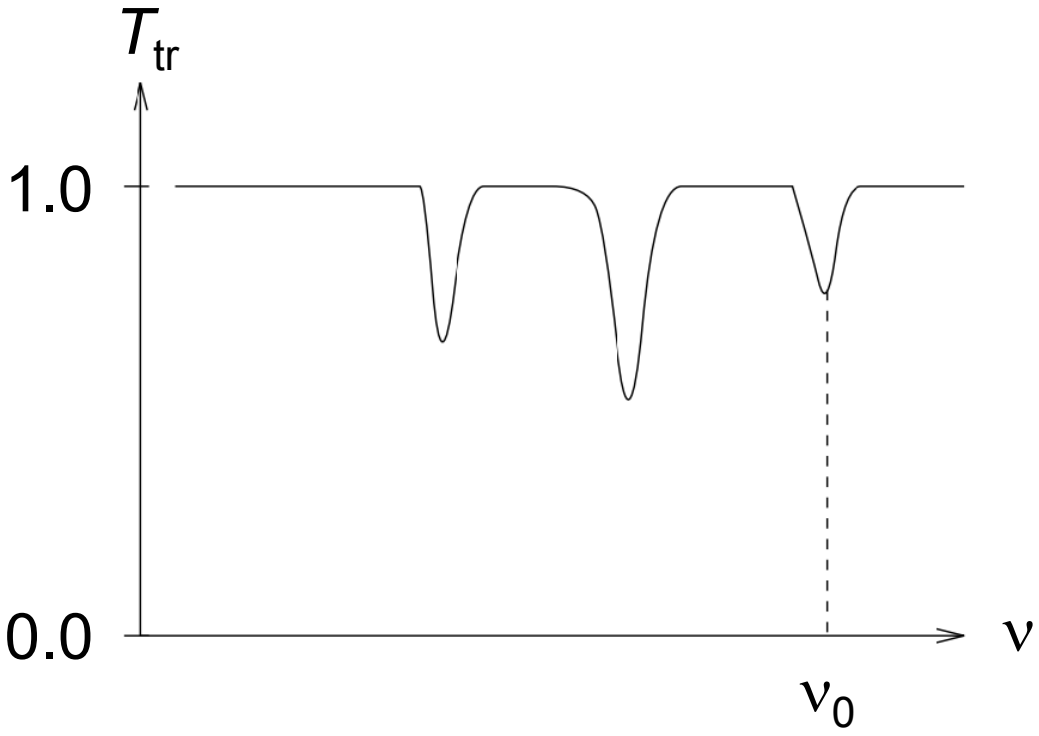


Lambert-Beer law:

$$\text{Transmittance } T_{tr} = \frac{I}{I_0} = \exp(-nL\varepsilon(\nu))$$

$\varepsilon(\nu)$: Absorption coefficient

Transmission spectrum

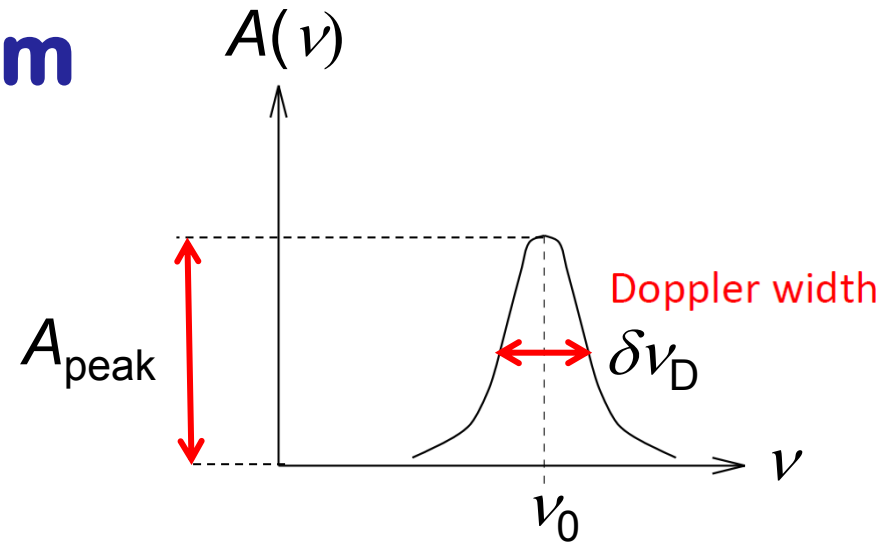


Absorbance

$$A = -\ln(T_{tr}) = -\ln\left(\frac{I}{I_0}\right) = nL\varepsilon$$

Absorbance spectrum

$$A = -\ln(T_{tr}) = -\ln\left(\frac{I}{I_0}\right) = nL\varepsilon$$



Basic CES equation

$$A_{peak} = L\alpha_{peak}(T) = \frac{nL}{Q}\frac{8\pi^3}{3ch}(1 - e^{-h\nu_0/kT})S_{ij}\mu^2 e^{-E_l/kT}\sqrt{\frac{\ln(2)}{\pi}}\frac{\nu_0}{\delta\nu_D}$$

Q: Partition function

E_ℓ: Energy of lower state

T: Temperature

$S_{ij}\mu^2$: Line strength

Rearrange basic equation to

$$\frac{A(\nu)}{nL/Q} = \frac{8\pi^3}{3ch}\sqrt{\frac{\ln(2)}{\pi}}\frac{1}{W}\frac{(1-e^{-\frac{h\nu_0}{kT}})}{\sqrt{T}} S_{ij}\mu^2 e^{-\frac{E_l}{kT}} e^{-\frac{\ln(2)}{W^2 T}(1-\frac{\nu}{\nu_0})^2}$$

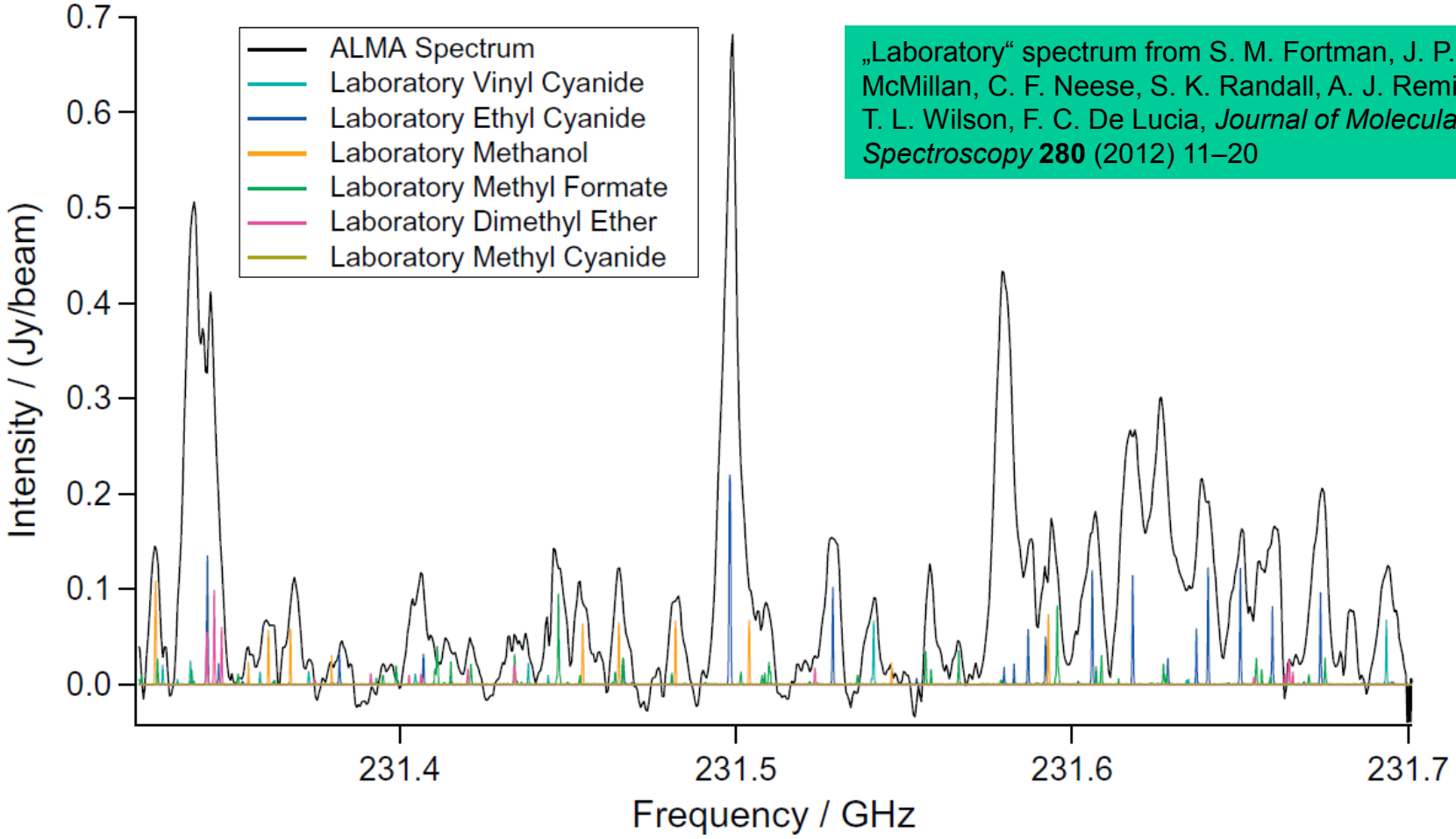
$$= K\frac{(1-e^{-\frac{h\nu_0}{kT}})}{\sqrt{T}}\tilde{S}_{ij}\mu^2 e^{-\frac{\tilde{E}(\nu)}{kT}}$$

with

$$\tilde{E}(\nu) = E_L + k\frac{\ln(2)}{W^2}\left(1-\frac{\nu}{\nu_0}\right)^2 \quad \text{and} \quad \delta\nu_D = \sqrt{\frac{2N_a k\ln(2)}{Mc^2}}\sqrt{T}\nu_0 = W\sqrt{T}\nu_0$$

- *nL/Q* and *T* determined from experimental spectrum and theoretical values of $S_{ij}\mu^2$ and ν_0 (QM list).
- Each line characterized by values of $\tilde{S}_{ij}\mu^2$ and $\tilde{E}(\nu)$.
- These are determined „automatically“, no assignment.

Example of simulated ALMA spectrum



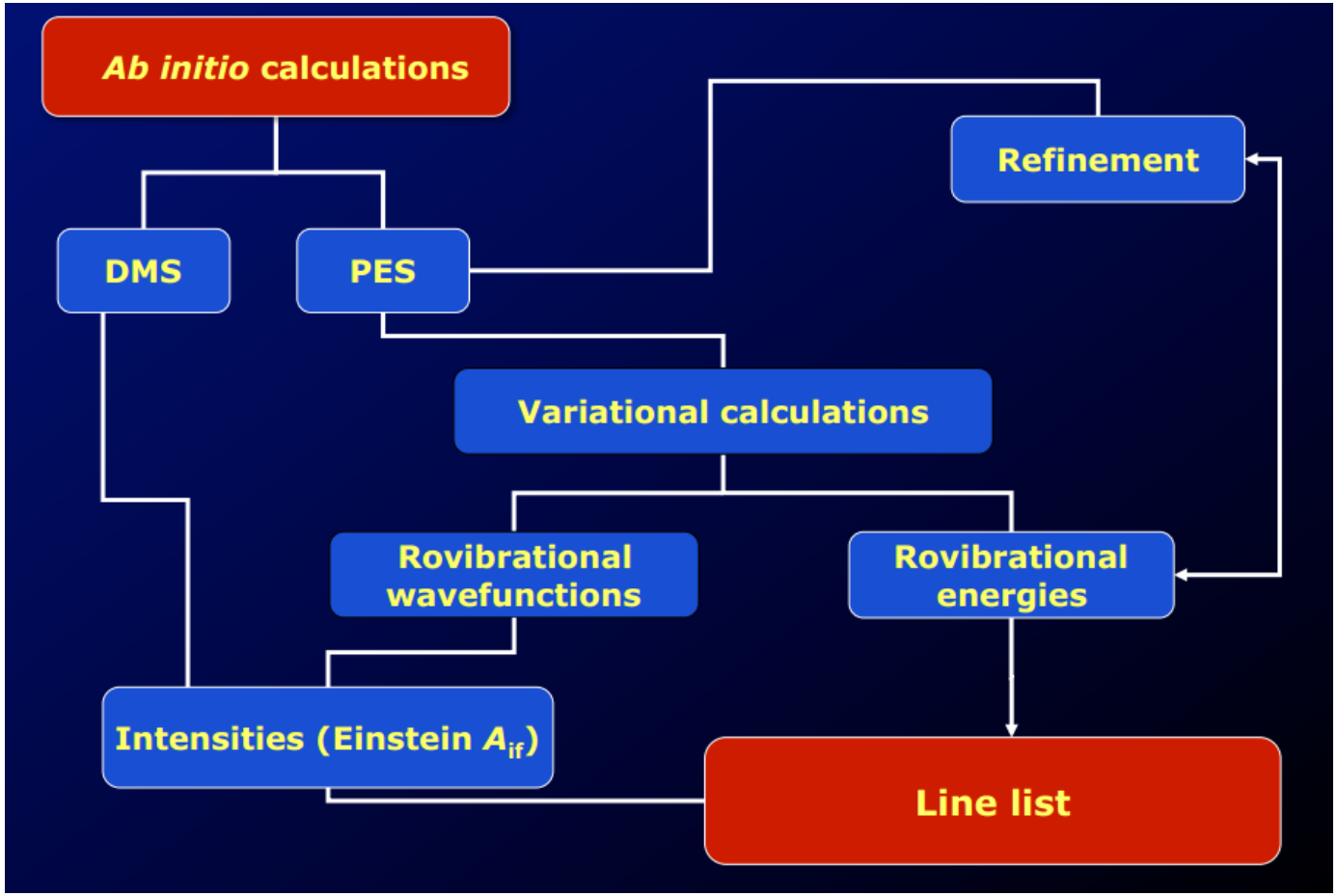
„Laboratory“ spectrum from S. M. Fortman, J. P. McMillan, C. F. Neese, S. K. Randall, A. J. Remijan, T. L. Wilson, F. C. De Lucia, *Journal of Molecular Spectroscopy* **280** (2012) 11–20

Theoretical (QM) line list

Ab initio: Solve Schrödinger equation for electrons

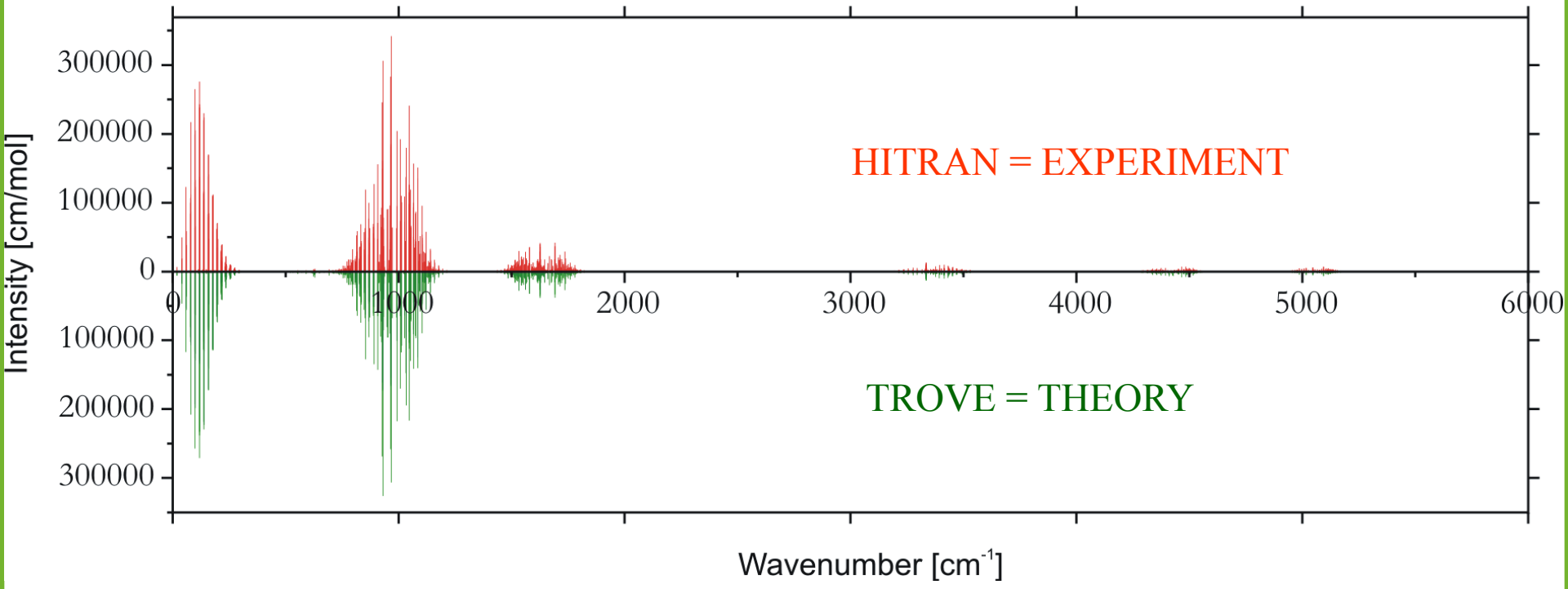
PES: Potential energy surface

DMS: Dipole moment surface



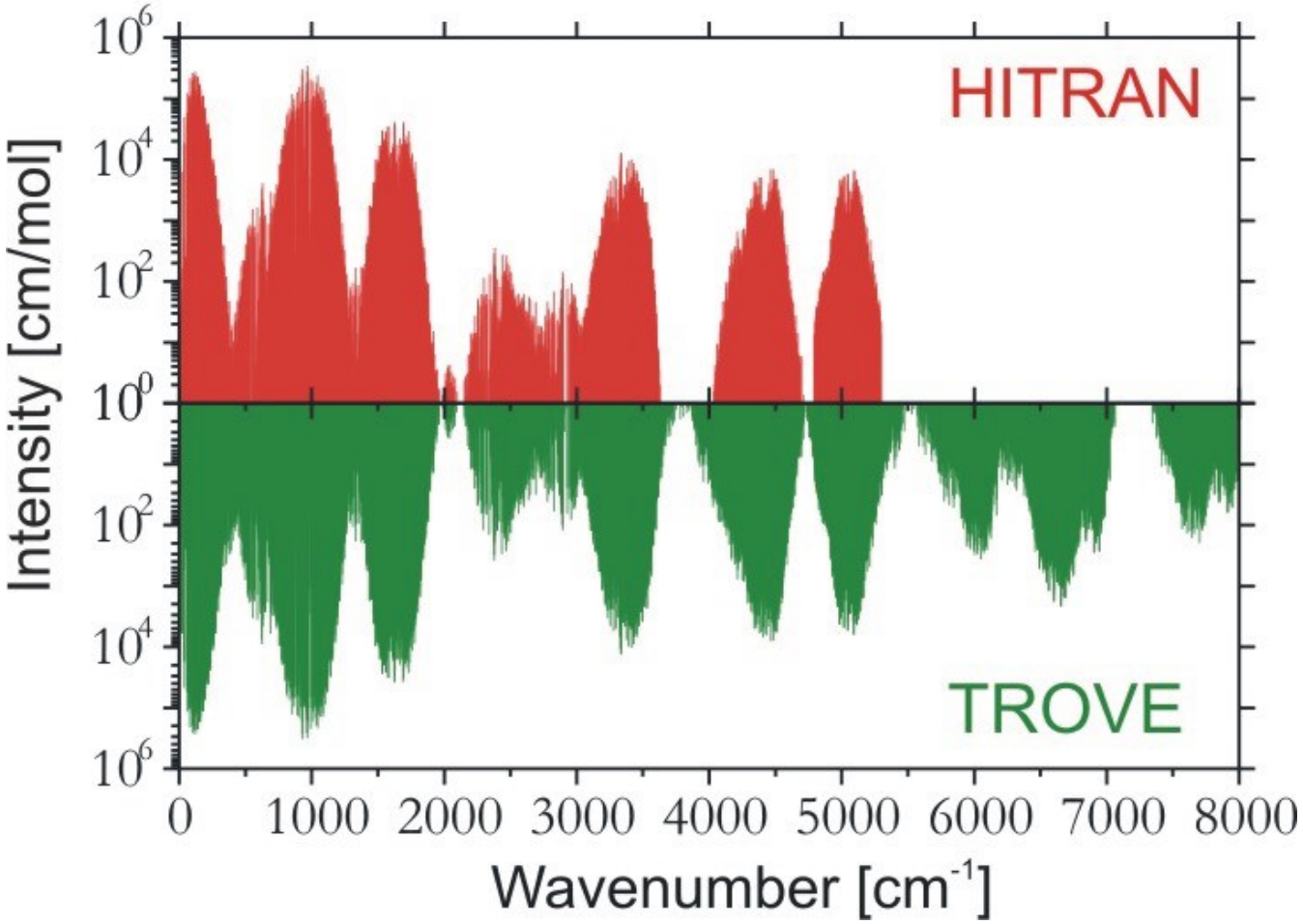
Source: Website of Jonathan Tennyson, UCL, London

TROVE for NH_3: Absorption intensities at *T*=300K, 3.25 million transitions



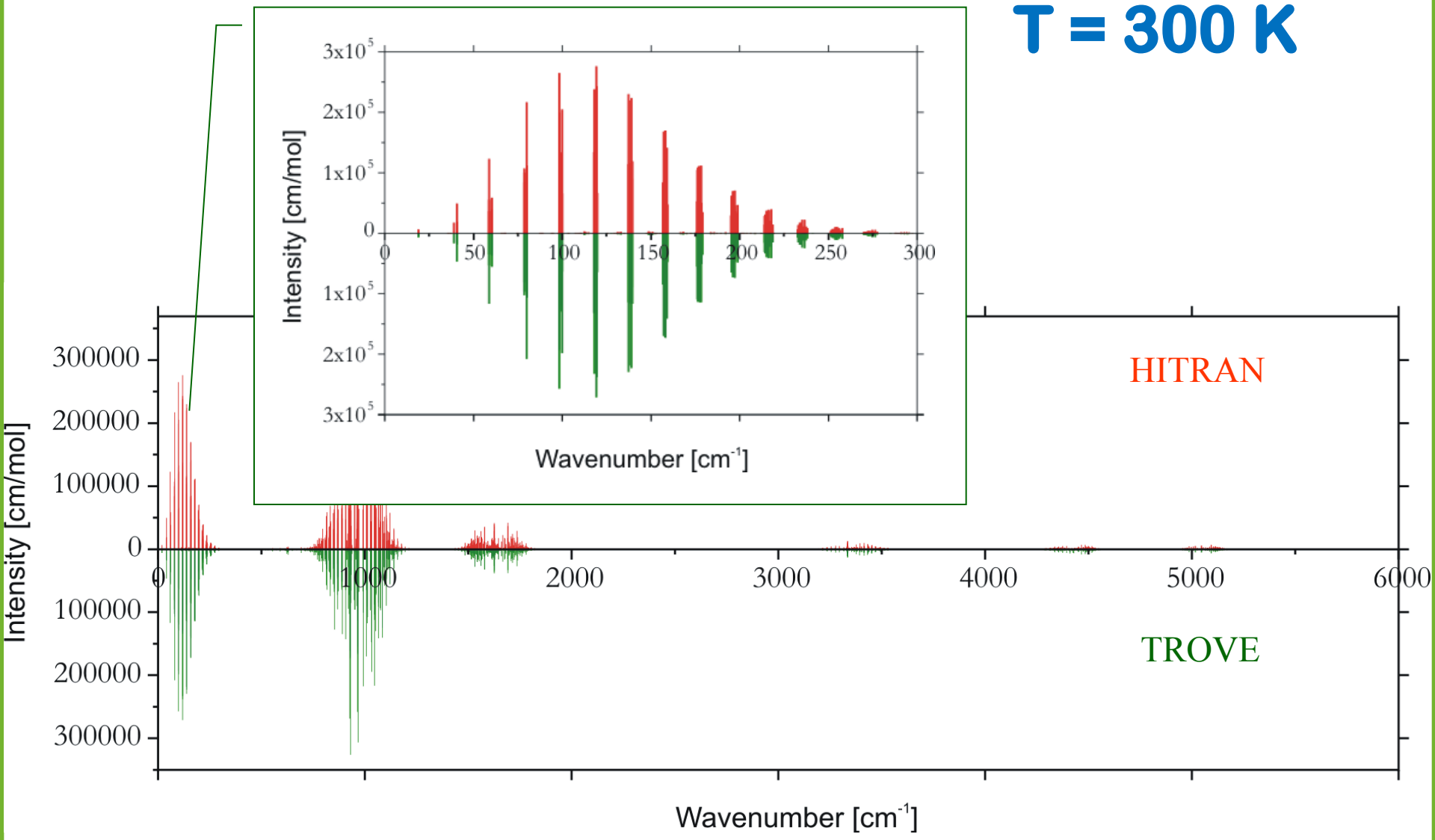
S. N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* **245**, 126-140 (2007).
S. N. Yurchenko, R. J. Barber, A. Yachmenev, W. Thiel, P. Jensen, and J. Tennyson. *J. Phys. Chem. A* **113**, 11845-11855 (2009).

NH_3 line list simulations, T = 300 K

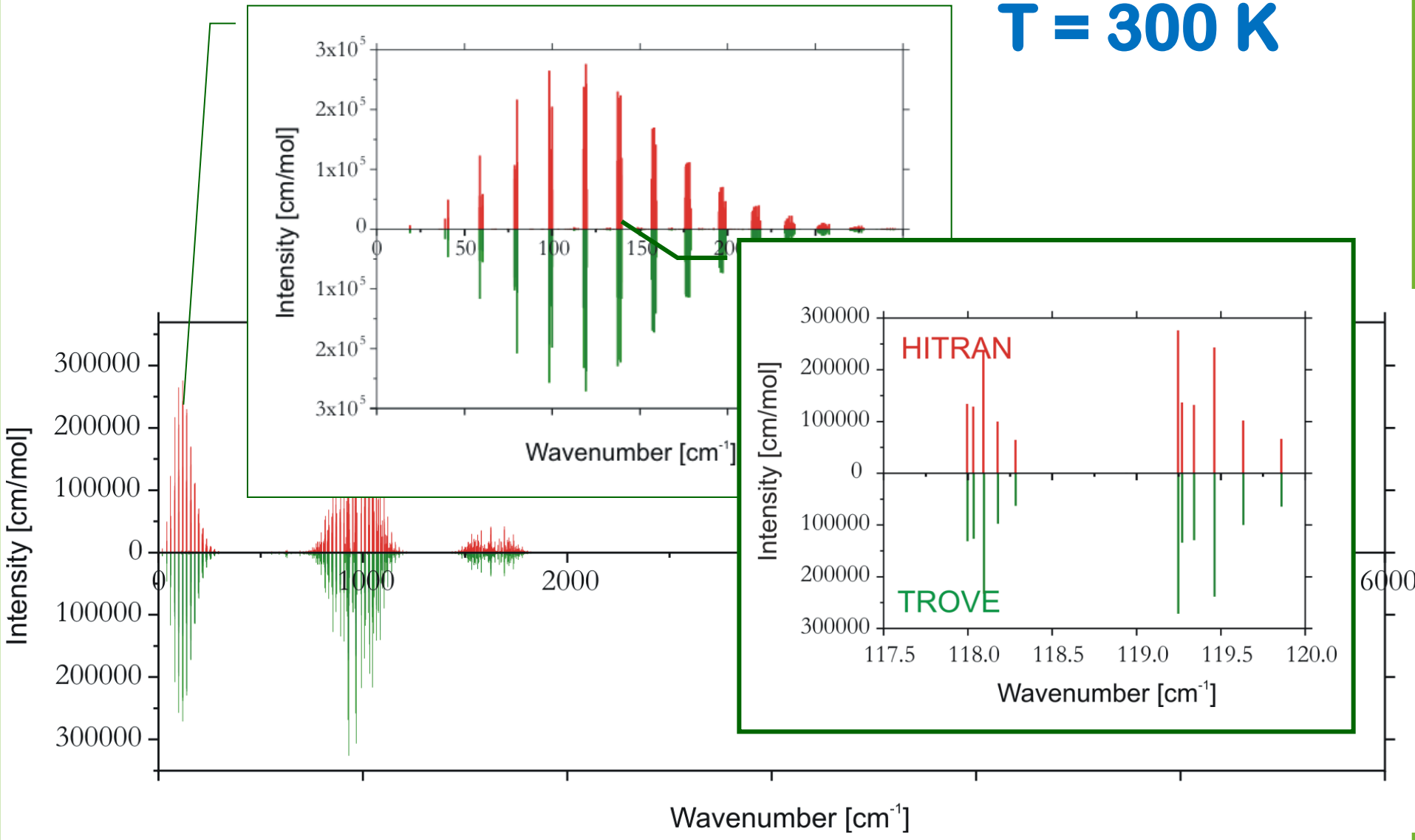


S. N. Yurchenko, R. J. Barber, A. Yachmenev, W. Thiel, P. Jensen, and J. Tennyson. *J. Phys. Chem. A* **113**, 11845-11855 (2009).

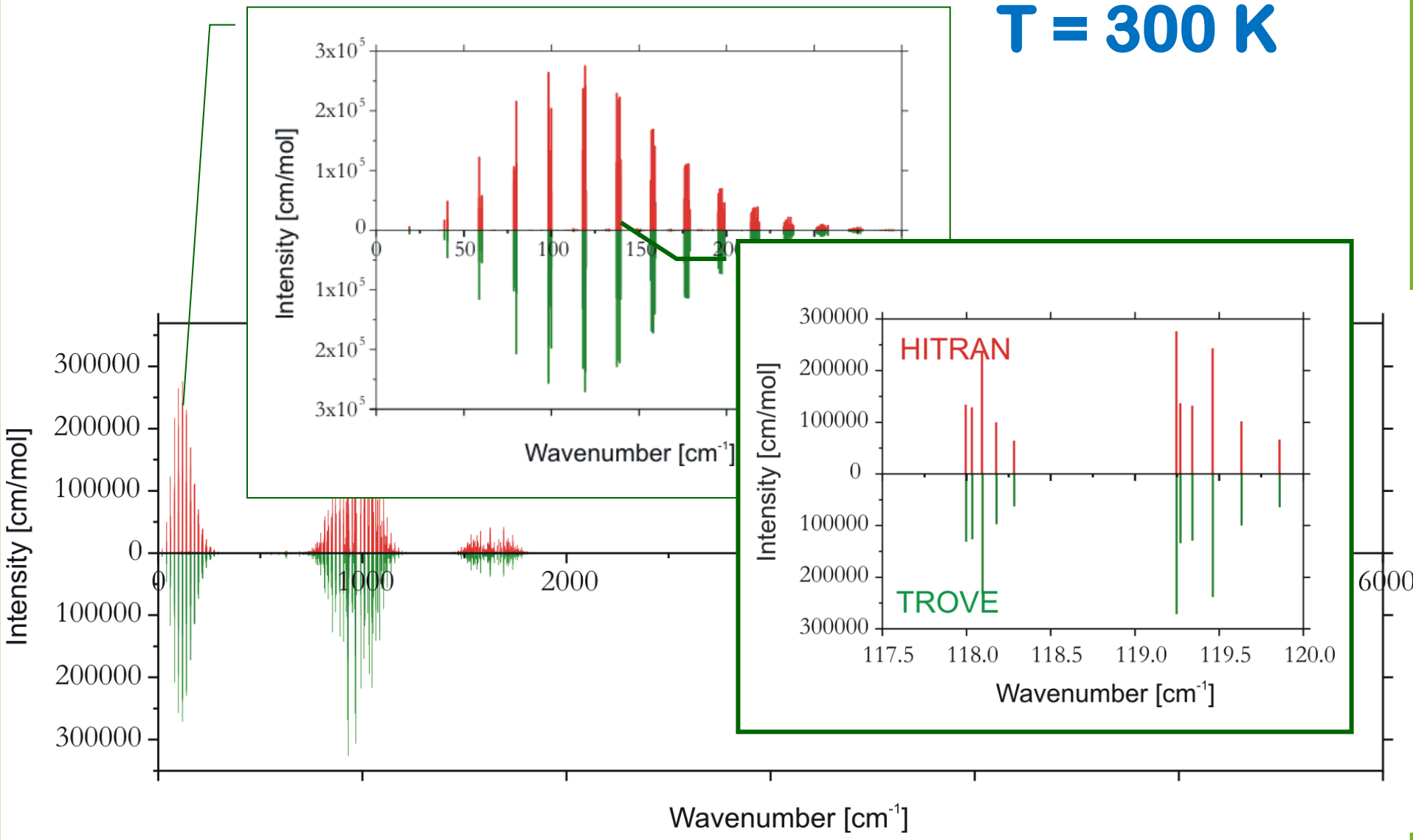
Absorption spectrum of NH_3 at T = 300 K



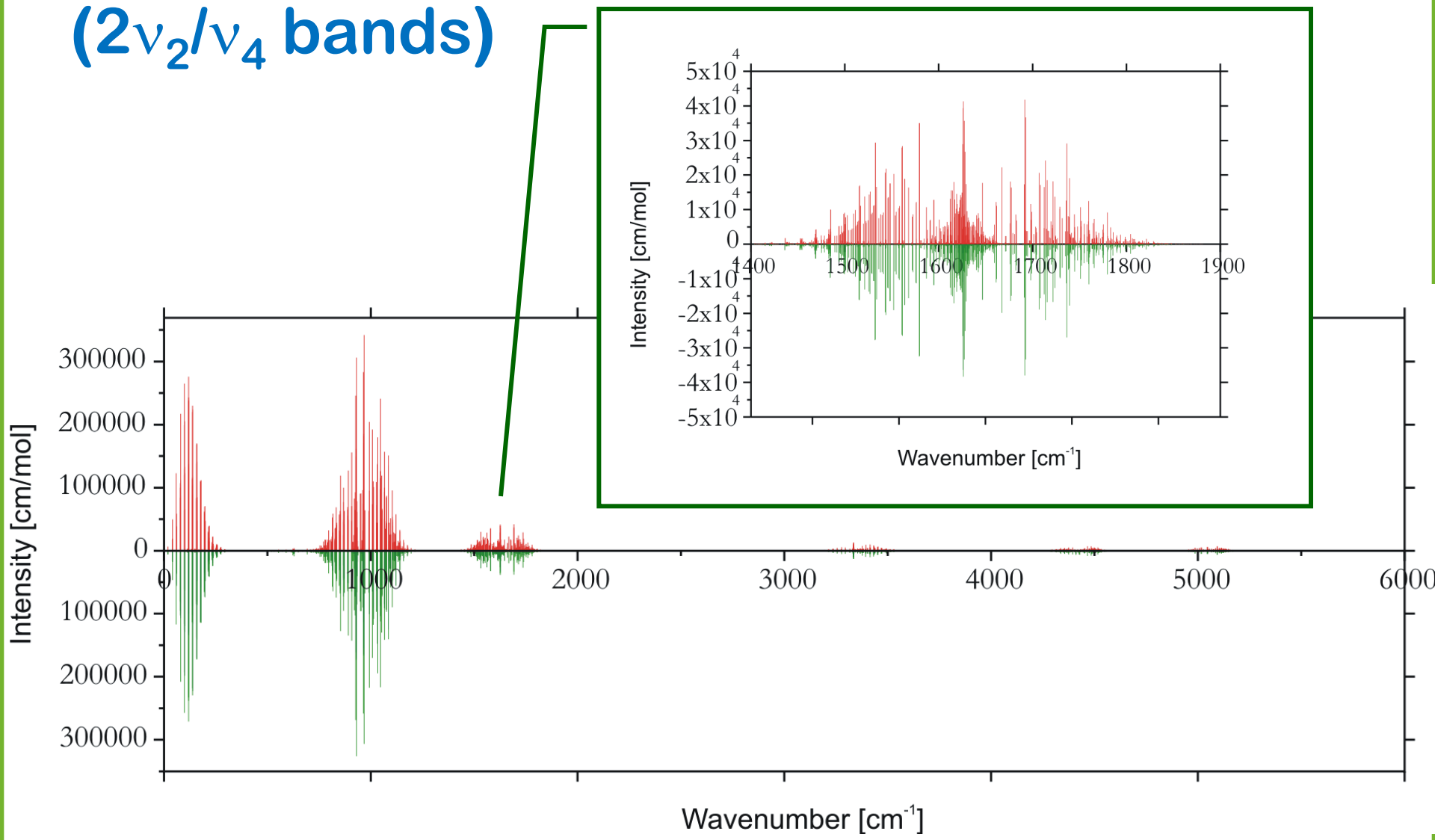
Absorption spectrum of NH_3 at T = 300 K



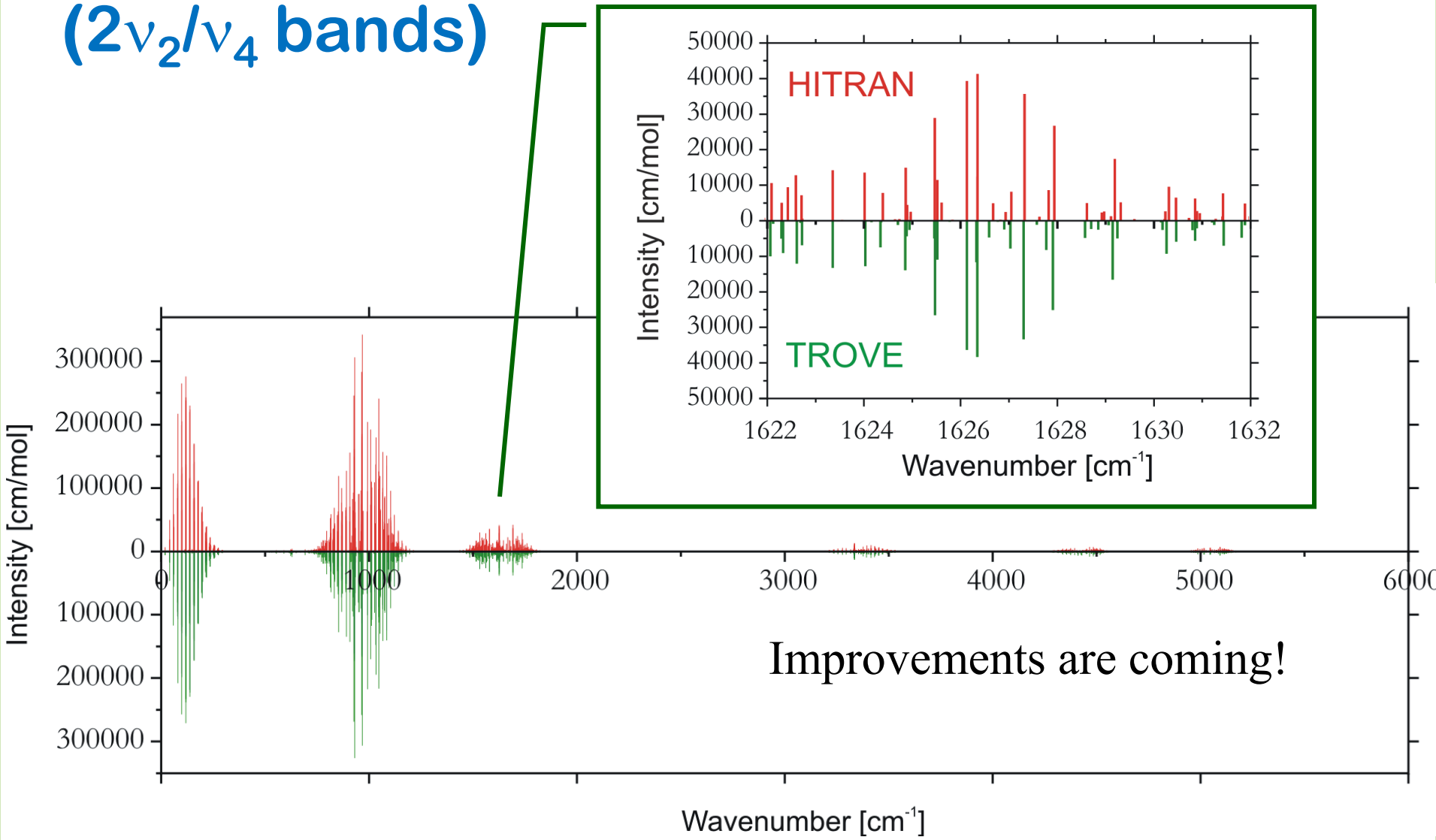
Absorption spectrum of NH_3 at T = 300 K



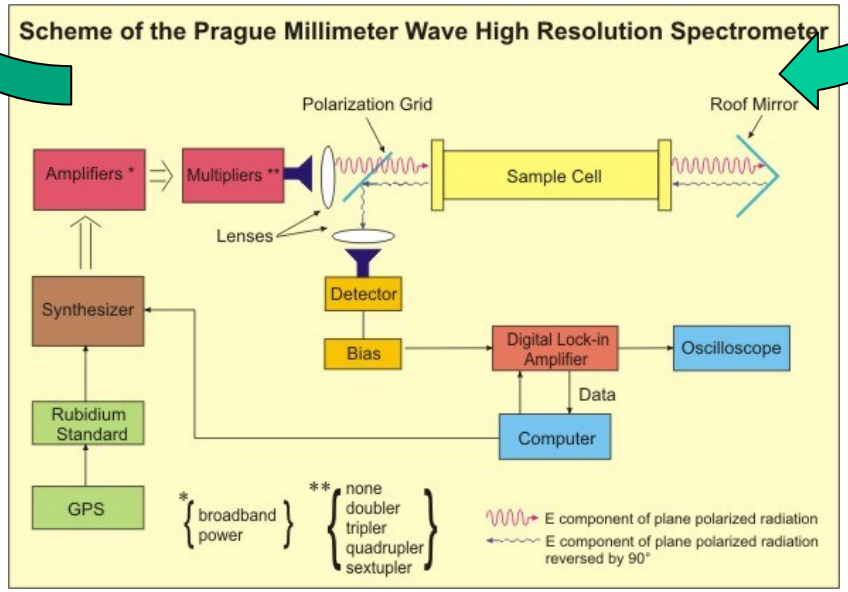
Absorption spectrum of NH_3 at T = 300 K ($2\nu_2/\nu_4$ bands)



Absorption spectrum of NH_3 at T = 300 K ($2\nu_2/\nu_4$ bands)



Improvements are coming!



We hope for mutual benefits…

… and I thank you for your attention!