A database for water transitions from experiment and theory

Jonathan Tennyson
Department of Physics and Astronomy
University College London

HITRAN meeting
Harvard
June 2006

The Earth seen in water vapour by NASA's GOES satellite

Why water vapour?

- Molecule number 1 in HITRAN
- Major (70%) atmospheric absorber of incoming sunlight
- Even $H_2{}^{18}O$ is fifth biggest absorber
- Largest (60%) greenhouse gas
- Atmospheres of cool stars
- Combustion
- Life !?

UCL strategy for a reliable, complete (300K) linelist

- Strong lines:
  water-air spectra, variable path-length
- Weak lines:
  water vapour spectra, longest path-length & integration times possible
- Isotopologues:
  Isotopically enhanced samples (Kitt Peak, CRDS)
- Completeness/assignments:
  High quality variational calculations

IUPAC Task group

A database of water transitions from experiment and theory

- Water lines at room temperature (HITRAN)
- Hot water
- Isotopologues
- Line profiles
- Theory
- Validation
- Database

Meet room P226 "Tea Room"
Weds from 2.30 pm
Thurs until lunch

Scope

- transitions 0 – 30,000 cm^{-1}.
- linelist for room temperature (**C**, 296 K) & hot (**H**) water.
- **C** complete for intensities > 10^{-29} cm $molecule^{-1}$ in natural abundance.
- Singly & doubly substituted isotopologues: $HD^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $D_2{}^{16}O$, $HD^{17}O$, and $HD^{18}O$. No triply substituted isotopologues, no tritium.
- Line profiles: **function form?**
  Broadening parameters γ and δ.
  Dependence: pressure (0 – 3 atm), temperature (200 – 300 K)
  Experimental & computational data.
  Parameters for self- , N_2, O_2, air, and H_2 broadening.

Database

- Master database to be prepared for each isotopologue.
- Should capture origin & time-dependence of measured and computed values.
- Both ‘old’ and ‘new’ data archived and accessible.
- Flexible in terms of data structures
- HITRAN “button”

Master file strategy

- Use most complete (not necessarily best) as Master file eg BT2
- Augment with data from other sources: expt, other theory
- Store all known data: use error analysis to combine
- Clear data history
- Files structured by function: levels, transitions (+ mixings?)
- Distributed data?
- Some functionality in-built eg HITRAN button

New BT2 linelist

Barber et al, Mon. Not. R. astr. Soc. 368, 1087 (2006).

http://www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/BT2/

- 50,000 processor hours.
- Wavefunctions > 0.8 terabites
- 221,100 energy levels (all to J=50, E = 30,000 cm^{-1})
  14,889 experimentally known
- 506 million transitions (PS list has 308m)
  >100,000 experimentally known with intensities
- → Partition function 99.9915% of Vidler & Tennyson's value at 3,000K

Comparison with Experimental Levels

	BT	PS
Agreement:	%	%
Within 0.10 cm^{-1}	48.7	59.2
Within 0.33 cm^{-1}	91.4	85.6
Within 1 cm^{-1}	99.2	92.6
Within 3 cm^{-1}	99.9	96.5
Within 5 cm^{-1}	100.0	97.0
Within 10 cm^{-1}	100.0	98.1

Number of Experimental Levels: 14,889

Raw spectra from DVR3D program suite

1	7	1	54	7	0	33	9003.892	7003.799	2000.092	4.01E-03	2.78E-22	3.89E-04	6.71E-01
1	3	0	38	3	1	17	9098.530	7098.116	2000.415	1.56E-03	1.01E-22	1.41E-04	5.59E-01
1	7	0	84	6	0	47	10486.138	8485.481	2000.657	4.69E-02	1.12E-21	1.56E-03	7.84E+00
1	6	0	77	6	1	45	10939.532	8938.685	2000.848	4.83E-03	8.33E-23	1.16E-04	9.34E-01
1	6	1	11	5	1	5	4407.221	2406.299	2000.922	2.77E-02	5.25E-20	7.34E-02	5.35E+00
0	6	0	16	5	0	5	4407.355	2406.297	2001.058	3.26E-02	2.06E-20	2.88E-02	6.30E+00
1	4	1	60	4	0	46	11384.245	9383.183	2001.062	6.66E-03	8.35E-23	1.17E-04	1.86E+00
1	6	0	78	7	0	60	10955.914	8954.726	2001.188	1.69E-02	2.88E-22	4.03E-04	3.27E+00
0	7	1	19	7	0	9	6034.992	4033.695	2001.297	7.29E-04	1.43E-22	2.00E-04	1.22E-01
1	5	1	104	5	0	75	12912.871	10911.526	2001.344	3.36E-02	1.40E-22	1.96E-04	7.68E+00

Energy file: N J sym n E/cm^{-1} v_1 v_2 v_3 J K_a K_c

A	B	C	D	E	F	G	H	I	J	K
N	J	sym	n	E/cm^{-1}	v_1	v_2	v_3	J	K_a	K_c
43432	11	1	50	**8730.136998**	0	2	1	**11**	3	8
43433	11	1	51	**8819.773962**	0	4	0	**11**	6	6
43434	11	1	52	**8918.536215**	0	0	2	**11**	2	10
43435	11	1	53	**8965.496130**	0	2	1	**11**	5	6
43436	11	1	54	**8975.145175**	2	0	0	**11**	4	8
43437	11	1	55	**9007.868894**	1	0	1	**11**	3	8
43438	11	1	56	**9082.413891**	1	2	0	**11**	6	6
43439	11	1	57	**9170.343871**	1	0	1	**11**	5	6
43440	11	1	58	**9223.444158**	0	0	2	**11**	4	8
43441	11	1	59	**9264.489815**	2	0	0	**11**	6	6
43442	11	1	60	**9267.088316**	0	5	0	**11**	2	10
43443	11	1	61	**9369.887722**	0	2	1	**11**	7	4
43444	11	1	62	**9434.002547**	0	4	0	**11**	8	4
43445	11	1	63	**9457.272655**	1	0	1	**11**	7	4
43446	11	1	64	**9498.012728**	0	0	2	**11**	6	6
43447	11	1	65	**9565.890023**	1	2	0	**11**	8	4

Transitions file:

12.8 Gb

Divided into
16 files by frequency
For downloading

N_f	N_i	A_{if}
144848	146183	3.46E-04
115309	108520	7.42E-04
196018	198413	1.95E-04
7031	7703	1.13E-02
149176	150123	1.69E-04
81528	78734	2.30E-01
80829	78237	8.83E-04
209672	210876	2.51E-01
207026	203241	2.72E-04
188972	184971	1.25E-01
152471	153399	1.12E-02
39749	37479	1.46E-07
10579	15882	6.90E-05
34458	35617	1.15E-03

Master file strategy:
Inclusion of Experimental (+ other theoretical) **data**

Added to record. Data classified:

Property of level → Energy File

- Experimental levels (already included)
- Alternative quantum numbers (local modes)

Property of transition → Transition File

- Measured intensities or A coefficients
- Line profile parameters

Line mixing as a third file? Location of partition sums?

Linelists available for Master databases

	Author	Potenial	E_{max}/cm^{-1}	J_{max}	transitions	avaiable
$H_2{}^{16}O$	BT2	Shirin (2003)	30000	50	✔	✔
$H_2{}^{17}O$	Shirin	FIS3 (2006)	26000?	**10**	✔	✔
$H_2{}^{18}O$	Shirin	FIS3 (2006)	26000?	**10**	✔	✔
HDO	Tashkun	PS (1997)	26000	?	✔	**?**
$D_2{}^{16}O$	Zobov	Shirin (2004)	**14000**	30	✔	✔
$HD^{18}O$					✘	✘
$HD^{17}O$					✘	✘

Main characteristics (poster by Attila Csaszar)

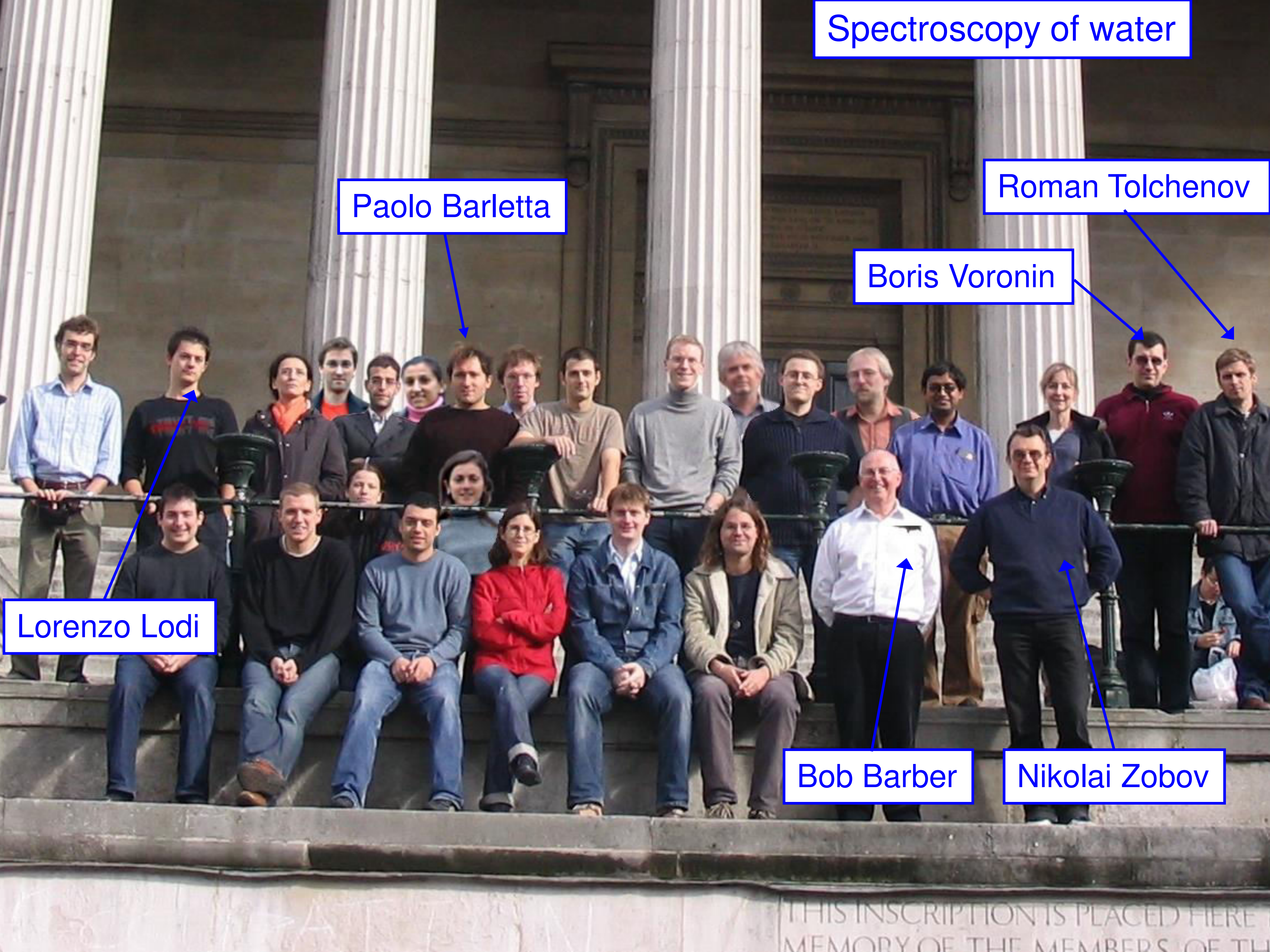
- Dual database of rovibrational energy levels and rovibrational transition with well-defined uncertainties
- Complete collection and storage of all relevant spectroscopic data for all major isotopologues of water
- Critical evaluation of data which will always carry their own pedigree (*e.g.*, bibliographical references, important measurement conditions, metadata)
- Inclusion of intensities, line widths, and line broadenings in the database, possibly including refinement of relevant parameters
- Global multi-dataset optimization
- Curation, organizational, data-mining and displaying tools
- Allow immediate (and automatic) consistency analysis of newly reported data before data deposition
- Allow „experiments" with what-if scenarios (important in order to predict what extra information new experiments might provide
- All supporting programs written in C++ and Java
- Sensitivity analysis of uncertainties
- Reproduce all known and well-defined experimental data (time-dependence)
- Predictions are rigorously quantified by their respective uncertainty bounds
- Minimal chance of leaving feasible regions of parameters
- HITRAN „button" to produce the best available data in HITRAN form for modeling studies

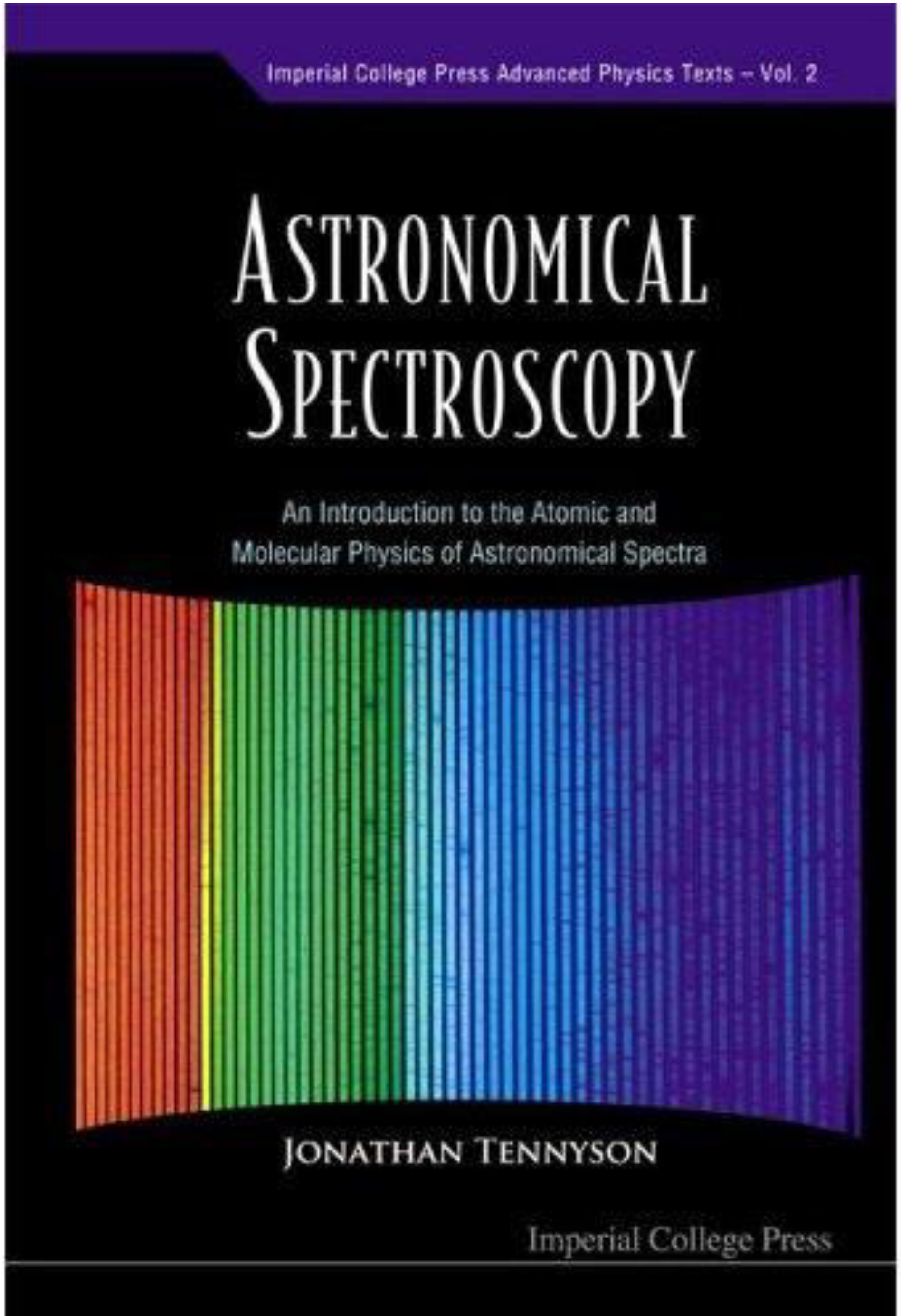
IUPAC Task group

A database of water transitions from experiment and theory

MEMBERS:

Peter Bernath (Waterloo, Canada); Alain Campargue (Grenoble, France); Michel Carleer (Brussels, Belgium); Attila Császár (Budapest, Hungary); Robert Gamache (Lowell, U.S.A.); Joseph Hodges (NIST, U.S.A.); Alain Jenouvrier (Reims, France); Olga Naumenko (Tomsk, Russia); Oleg Polyansky (Ulm, Germany); Laurence Rothman (Harvard, U.S.A.); Jonathan Tennyson (London, U.K.); Robert Toth (JPL, U.S.A.); Ann Vandaele (Brussels, Belgium); Nikolai Zobov (Nizhny Novgorod, Russia)


Spectroscopy of water
Paolo Barletta
Roman Tolchenov
Boris Voronin
Lorenzo Lodi
Bob Barber
Nikolai Zobov
THIS INSCRIPTION IS PLACED HERE



www.worldscibooks.com/physics/p371.html

Labelling BT2 energy levels

J=25	J=26	J=27	J=28	J=29	J=30	J=31
e	e	e	e	e	e	e
8	8	8	8	8	8	8
6,171.595	6,647.059	7,139.12	7,647.650	8,172.487	8,713.483	9,270.484
7,026.716	7,533.369	8,055.92	8,594.168	9,147.872	9,716.787	10,300.639
7,715.449	8,187.439	8,675.83	9,180.833	9,702.386	10,240.435	10,794.934
7,729.146	8,262.554	8,811.35	9,375.052	9,953.431	10,546.255	11,153.286
8,297.771	8,860.800	9,437.28	10,027.243	10,630.630	11,247.231	11,876.321
8,668.232	9,174.105	9,695.15	10,231.128	10,781.645	11,346.330	11,925.255
8,679.039	9,278.621	9,892.85	10,519.907	11,158.558	11,773.137	12,333.738
9,041.386	9,628.654	10,200.59	10,706.821	11,230.920	11,808.105	12,468.284
9,240.960	9,712.024	10,236.40	10,864.548	11,512.638	12,179.577	12,748.026
9,417.429	9,951.830	10,500.80	11,064.101	11,641.403	12,201.871	12,836.462
9,560.232	10,139.880	10,658.50	11,157.111	11,671.777	12,233.013	12,865.287
9,709.826	10,176.031	10,737.08	11,283.245	11,799.695	12,332.023	12,880.080
9,830.647	10,298.575	10,782.82	11,351.598	11,983.277	12,632.014	13,297.793
10,003.358	10,570.613	11,150.02	11,741.339	12,341.648	12,919.546	13,487.796
10,147.816	10,728.503	11,301.88	11,831.223	12,376.627	12,969.282	13,596.429
10,283.872	10,786.030	11,325.91	11,939.687	12,569.512	13,186.455	13,758.743
10,380.255	10,978.414	11,558.74	12,086.274	12,628.900	13,215.060	13,876.022
10,549.891	11,046.594	11,593.38	12,206.875	12,751.210	13,310.619	13,884.951

J=31			o8				J=32			o8			
9270.484	0	0	0	31	1	31	9843.328	0	0	0	32	1	32
10300.639	0	0	0	31	3	29	10899.132	0	0	0	32	3	30
10794.935	0	1	0	31	1	31	11365.856	0	1	0	32	1	32
11153.293	0	0	0	31	5	27	11774.277	0	0	0	32	5	28
11876.839	0	0	0	31	7	25	12507.258	0	1	0	32	3	30
11925.277	0	1	0	31	3	29	12528.734	0	0	0	32	7	26
12333.738	0	2	0	31	1	31	12912.970	0	2	0	32	1	32
12487.133	0	0	0	31	9	23	13151.952	0	0	0	32	9	24
12748.027	1	0	0	31	1	31	13309.624	1	0	0	32	1	32
12837.108	0	1	0	31	5	27	13443.559	0	0	1	32	0	32
12880.079	0	0	1	31	0	31	13454.795	0	1	0	32	5	28
13019.639	0	0	0	31	11	21	13697.050	0	0	0	32	11	22
13487.823	0	2	0	31	3	29	14067.285	0	2	0	32	3	30
13574.239	0	0	0	31	13	19	14236.728	0	1	0	32	7	26
13598.867	0	1	0	31	7	25	14253.538	0	0	0	32	13	20
13758.746	1	0	0	31	3	29	14345.561	1	0	0	32	3	30
13884.951	0	0	1	31	2	29	14473.887	0	0	1	32	2	30

Room temperature $H_2^{16}O$ lines

- Strong line data about 9000 cm^{-1}
- Compatability between mid and near infrared intensities
- Weak lines throughout whole spectrum
- Far infrared?

Solution strategy

largely experimental plus careful analysis?

Hot water (up to T=3000+ K)

- New complete linelist available from UCL
  Accuracy?
- Experimental assignments
- New experiments?
- $H_2{}^{16}O$ only?
  (Some experiment for HDO and D_2O)
- Line profiles?

Solution strategy:

largely theoretical with validation by experiment

Isotopologues

- $H_2{}^{18}O$, $H_2{}^{17}O$, HDO lines patchy in visible
- $D_2{}^{16}O$ not well known above 10000 cm^{-1}
- Any interest in other isotopologues?
- Room T only?
- Line profiles?

Solution strategy

Isotopically enhanced experiments

Line profiles

- Broadening by which species?
  water, O_2, N_2, air, H_2,.....?
- T dependence?
- P dependence? (up to 10 atm?)

Solution strategy

Theory validated by high quality experiment?

Validation

- between experiments
- atmospheric spectra
- Theory vs experiment
- other

Distribution and storage

- HITRAN
- Web database

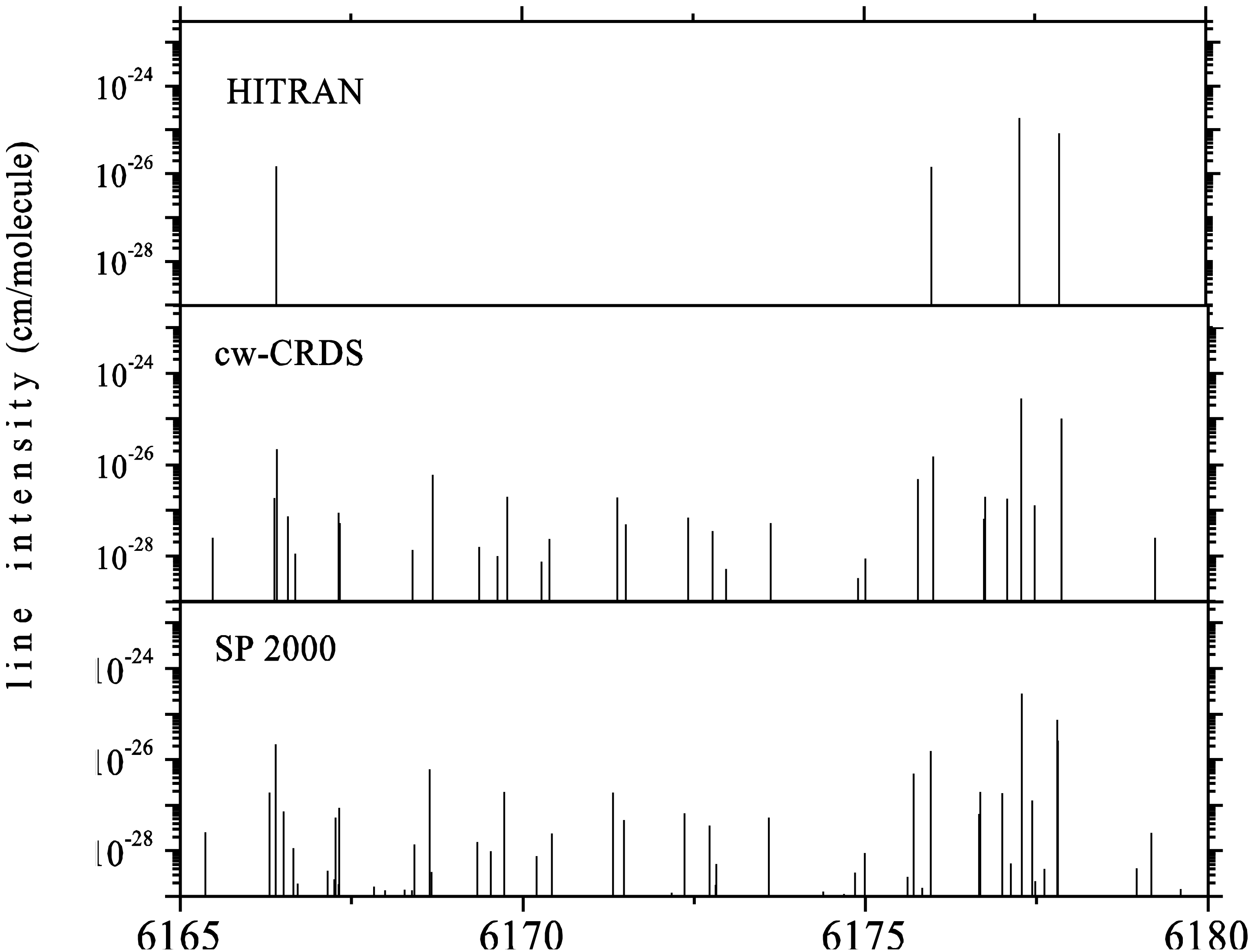
  eg Spectroscopic databank at Tomsk
- Publication or other means of distribution?

So what is the problem?

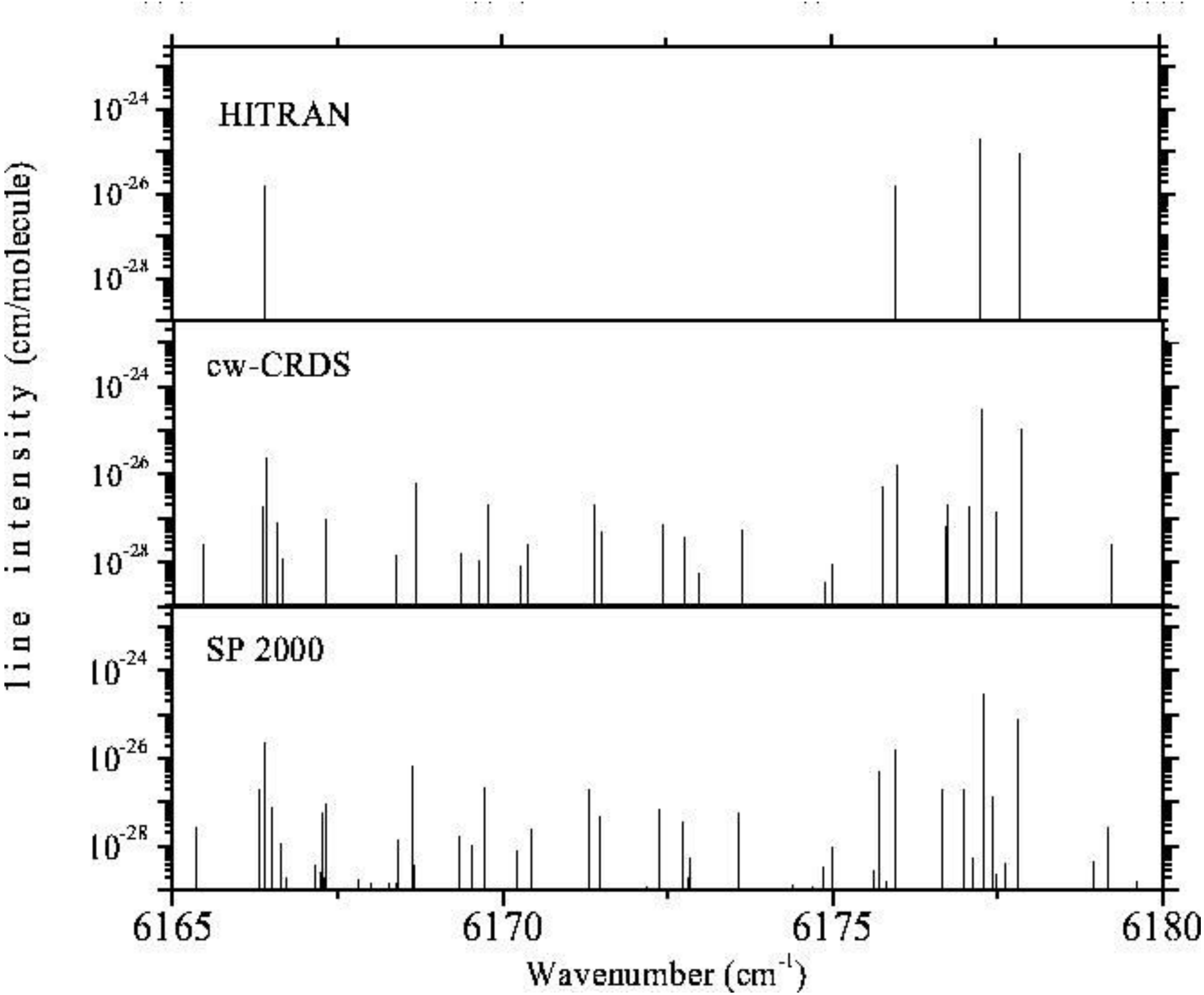
Water is well studied (30,000+ lines in HITRAN)

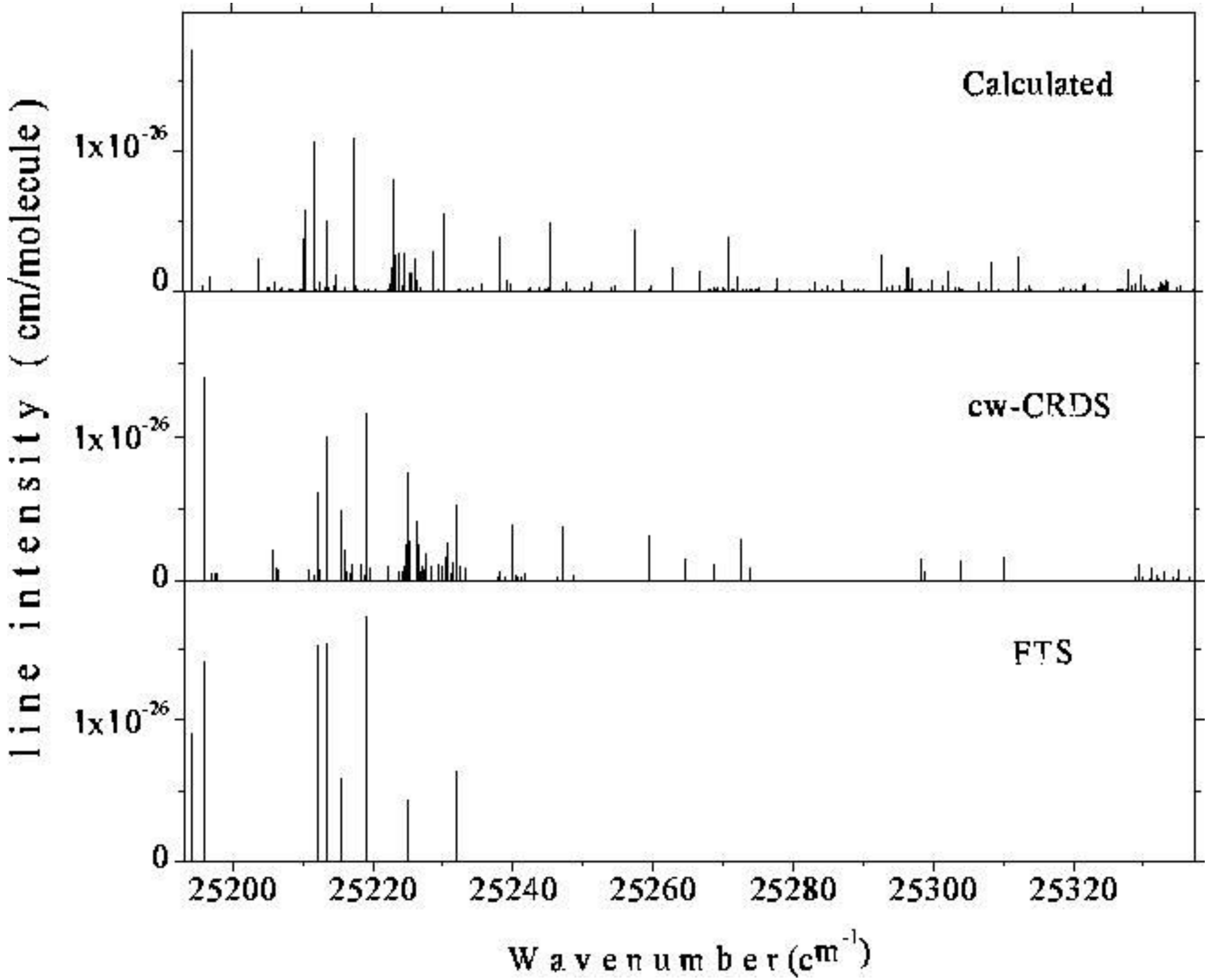
But

- Water spectra have huge dynamic range
- Difficult to work with experimentally
- Spectra very dense: baseline hard to characterise
- Strong lines usually saturated (water-air spectra)
- Line profiles important (water-air & water-water)
- Weak lines can be significant (pure water spectra)
- Line assignment difficult (Variational Methods)



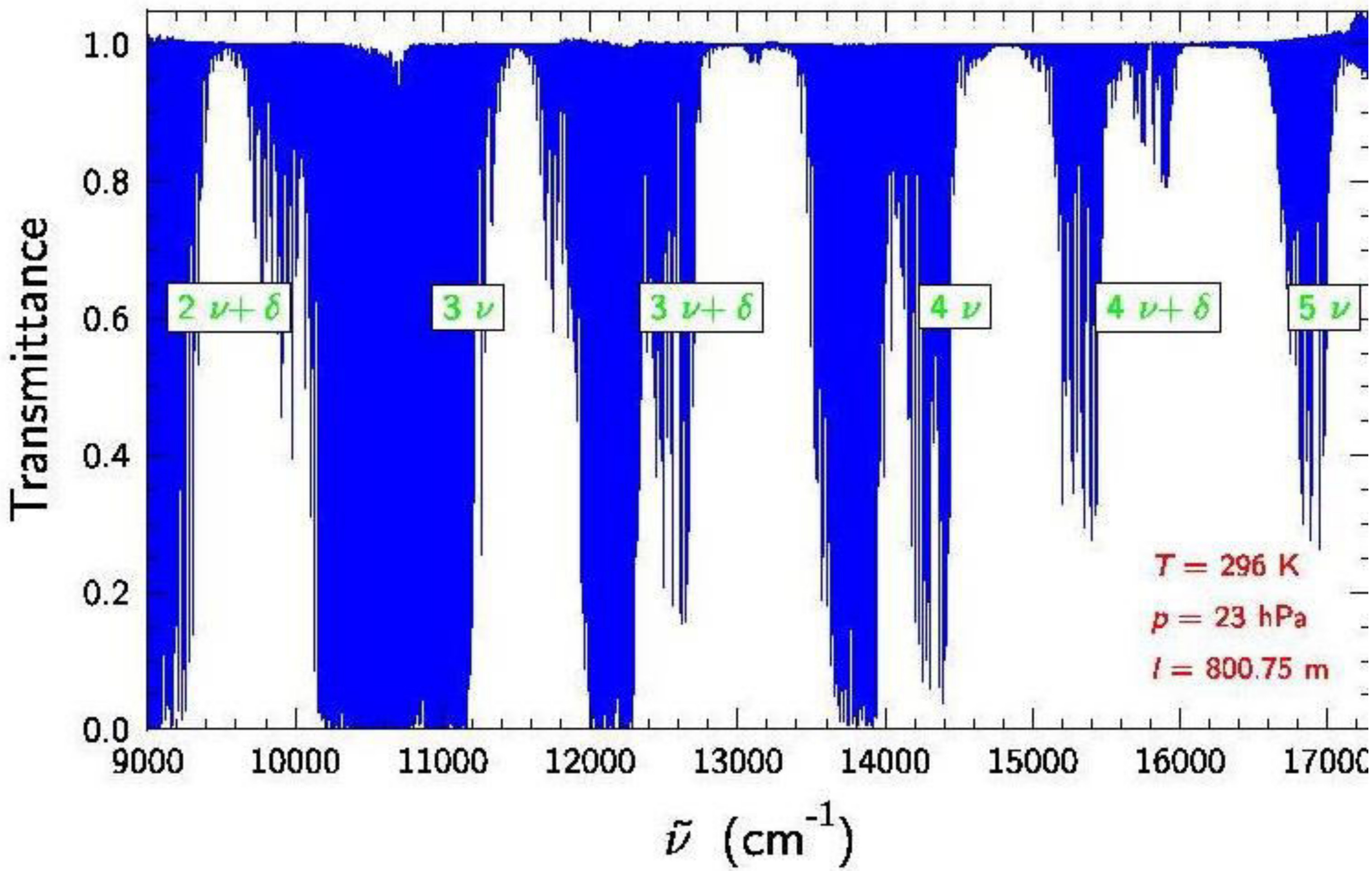
HITRAN
cw-CRDS
SP 2000
line intensity (cm/molecule)
10-24
10-26
10-28
6165
6170
6175
6180


HITRAN
cw-CRDS
SP 2000
line intensity (cm/molecule)
10^-24
10^-26
10^-28
6165
6170
6175
6180
Wavenumber (cm^-1)



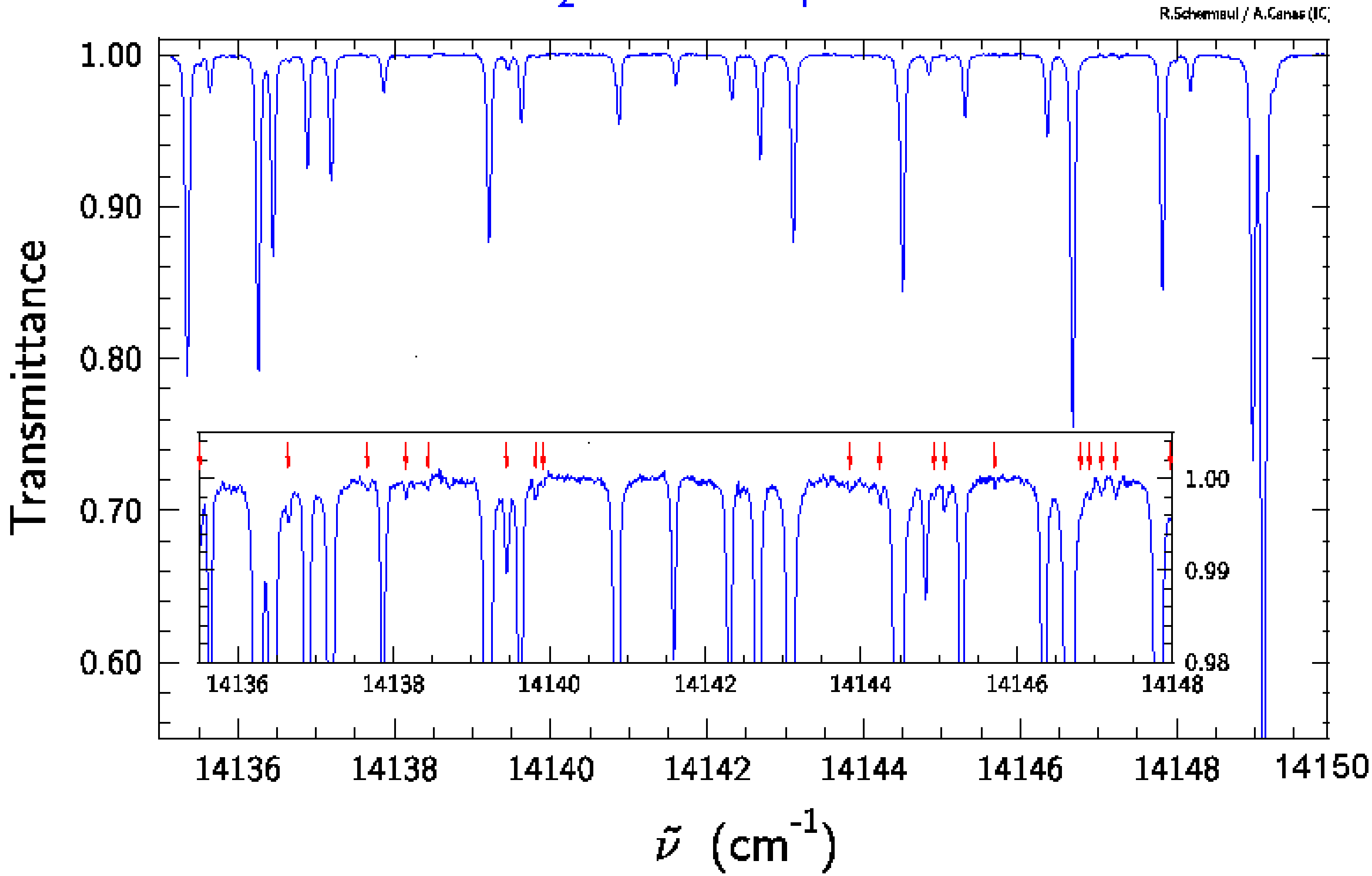
P. Dupre, T. Germain, A. Campargue, N.F. Zobov, O.L. Polyansky, S.V. Shirin, R.N. Tolchenov and J. Tennyson, *J. Molec. Spectrosc*. (to be submitted).

Polyad structure in water absorption spectrum



Long pathlength Fourier Transform spectrum recorded by R Schmeraul

H_2O Visible Spectrum



Weak lines: new experimental measurements

Weak water lines → **Very difficult to record**

→ **Only a few weak lines in HITRAN**

MSF data (NERC) : 8m cell, pure water vapour

- **Schermaul, Learner et al.**
- Bruker F.T.S.
- Range : 9000-12 700 cm^{-1}
- T : 295.7 K
- $p(H_2O)$: 22.93 hPa
- pathlength ~ 800.8 m
- Number of lines : 7923
- Number of new lines : 1082

- **Schermaul, Learner et al.**
- Bruker F.T.S.
- Range :11 700-14 750 cm^{-1}
- T : 294.4 K
- $p(H_2O)$: 23.02 hPa
- pathlength ~ 800.8 m
- Number of lines : 5316
- Number of new lines : 1534

Also data in 6000 - 9000 cm^{-1} region

Weak lines: new experimental measurements

REIMS data, 50 m cell, pure water vapor (also water-air)

- **Coheur et al., Fally et al.**
- Bruker F.T.S
- Range :13 000 - 25 020 cm^{-1}
- T : 291.3 K
- $p(H_2O)$: 18.32 hPa
- pathlength ~ 602.32 m
- Number of lines: 9353
- Number of new lines : 2286

- **Merienne et al.**
- Bruker F.T.S
- Range : 9 250 - 13 000 cm^{-1}
- T : 292 K
- $p(H_2O)$: 23.02 hPa
- pathlength ~ 602.32 m
- Number of lines : 7061
- Number of new lines : small

HDO !

Full assignment nearly complete

Water vapour spectrum: new assignments in the blue

Band			Previous		This work		
local	normal	ν_0(cm^{-1})	lines	levels	lines		levels
					obs	cal	
(3,0)+4	340	16534			33	15	26
(3,0)−4	241	16546.324			42	16	33
(2,1)+4	142	16795			76	4	33
(4,0)−2	321	16821.635	131	54	34		3
(4,0)+2	420	16823.321	39	22	63	9	26
(5,0)+0	500	16898.271	114	56	66	2	8
(5,0)−0	401	16898.842	203	76	50		
(2,1)−4	043	16967			8	8	11
(3,1)+2	222	17227	2	2	38	12	26
(3,1)−2	123	17312.539	53	32	18	2	6
(4,1)+0	302	17458.354	88	43	48	3	8
(4,1)−0	203	17495.528	137	57	72		4
(3,2)+0	104	17748.134	5	4	48	25	41
(4,0)−3	331	18265.819	52	28	60	6	22
(4,0)+3	430		2	1	6		3
(2,1)−5	053	18350			18	3	11
(5,0)−1	411	18393.314	62	27	71	2	24
(5,0)+1	510	18392.974	15	7	50	4	27
(3,1)−3	133	18758.634			24	13	24
(2,2)+3	034	18977			10	3	8
(5,0)−1	411	18989.961	20	11	66	8	34
(4,0)−4	341	19679.196	6	4	54	6	32
(2,1)−6	063	19720			6		3
(6,0)−0	501	19781.105	88	39	59	2	15
(6,0)+0	600	19782	29	17	51	5	18
(5,0)−2	421	19863			19	8	16
(5,0)+2	520	19864			27	1	11
(4,1)−2	223	20441.882			20	5	11
(5,1)+0	402	20534			23	15	25
(5,1)−0	303	20543.137	25	14	32	7	18
(6,0)−1	511	21221.828	25	11	21	1	11
(6,0)+1	610	21221.569	9	6	4	2	4
(5,0)−3	431	21312			16	2	11

Long pathlength FTS

M. Carleer, A. Jenouvrier, A.-C. Vandaele,

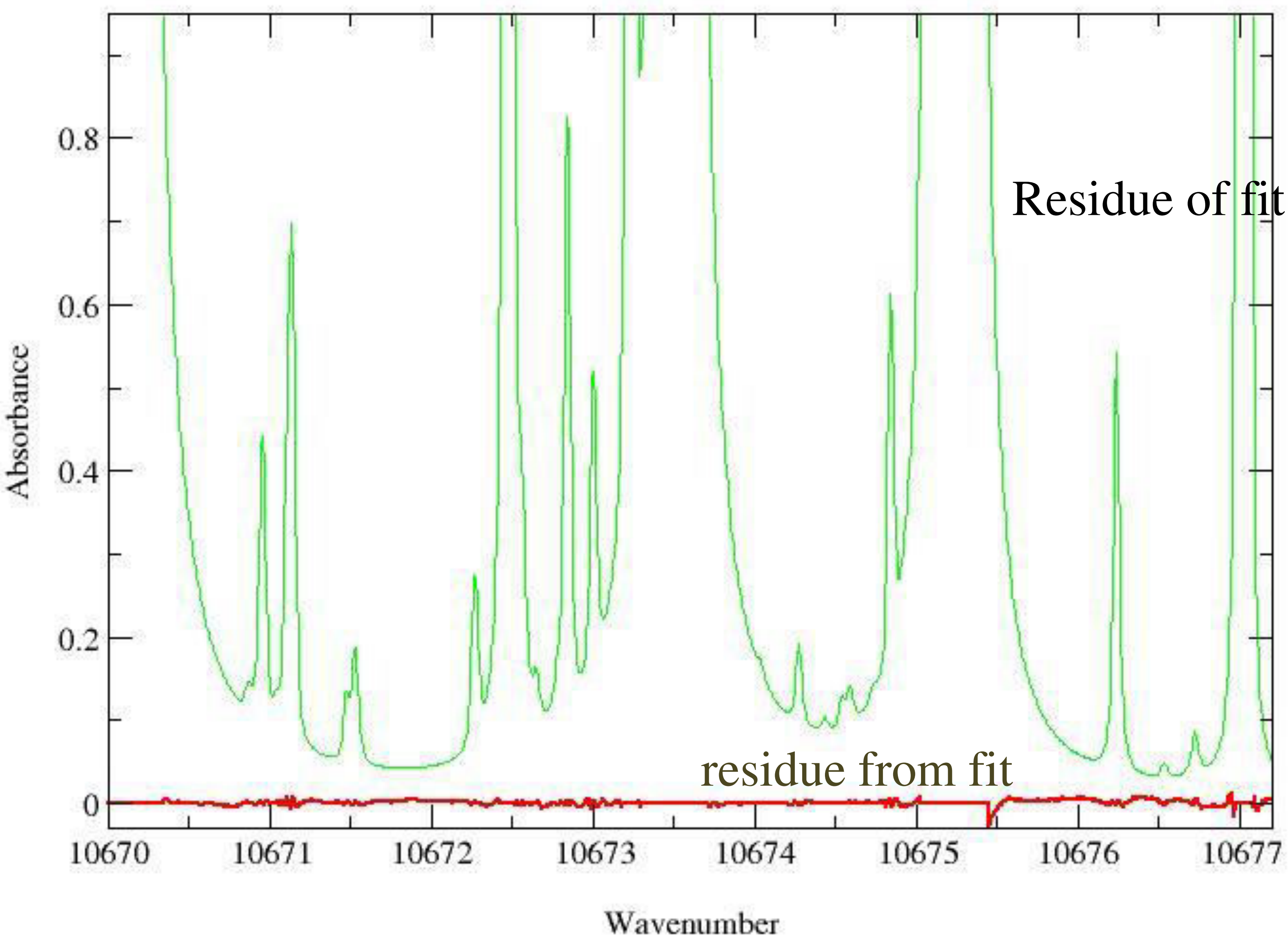
P.F. Bernath, M.F. Marienne, R. Colin,

N.F. Zobov, O.L. Polyansky,

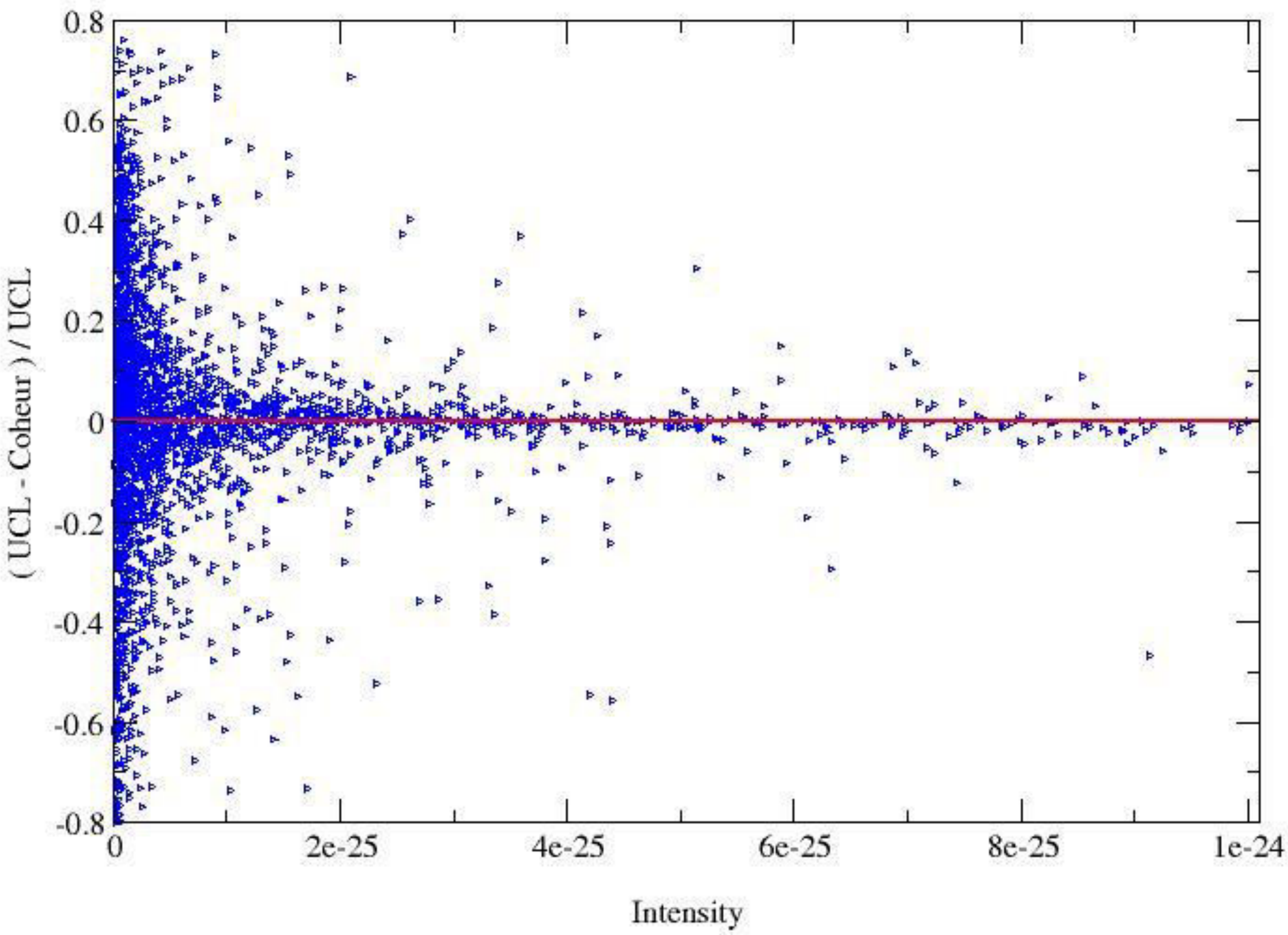
J. Tennyson & V.A. Savin

J. Chem. Phys., **111**, 2444 (1999)

MSF spectra: line parameter retrieval using GOBLIN



Intensity comparison for weak lines: MSF vs Rheims



Reliable intensities required for satellite retrievals

MSF data (ESA) : 8m cell, water-air spectra

- **Schermaul, Learner, Brault, Newnham et al.**
- Bruker F.T.S.
- Range : 9000 – 12 700 cm^{-1}
- T : 295.7 K (also 253 K)
- $p(H_2O)$: 10.03 hPa
- Pathlength: SPAC 4.938 m

  LPAC 32.75m, 128.75m, 512.75m
- Number of lines : 7923
- Number of new lines : 1082

See poster by Tolchenov

Intensity data compared to HITRAN-96
by polyad for spectral region 8500 – 15800 cm^{-1}

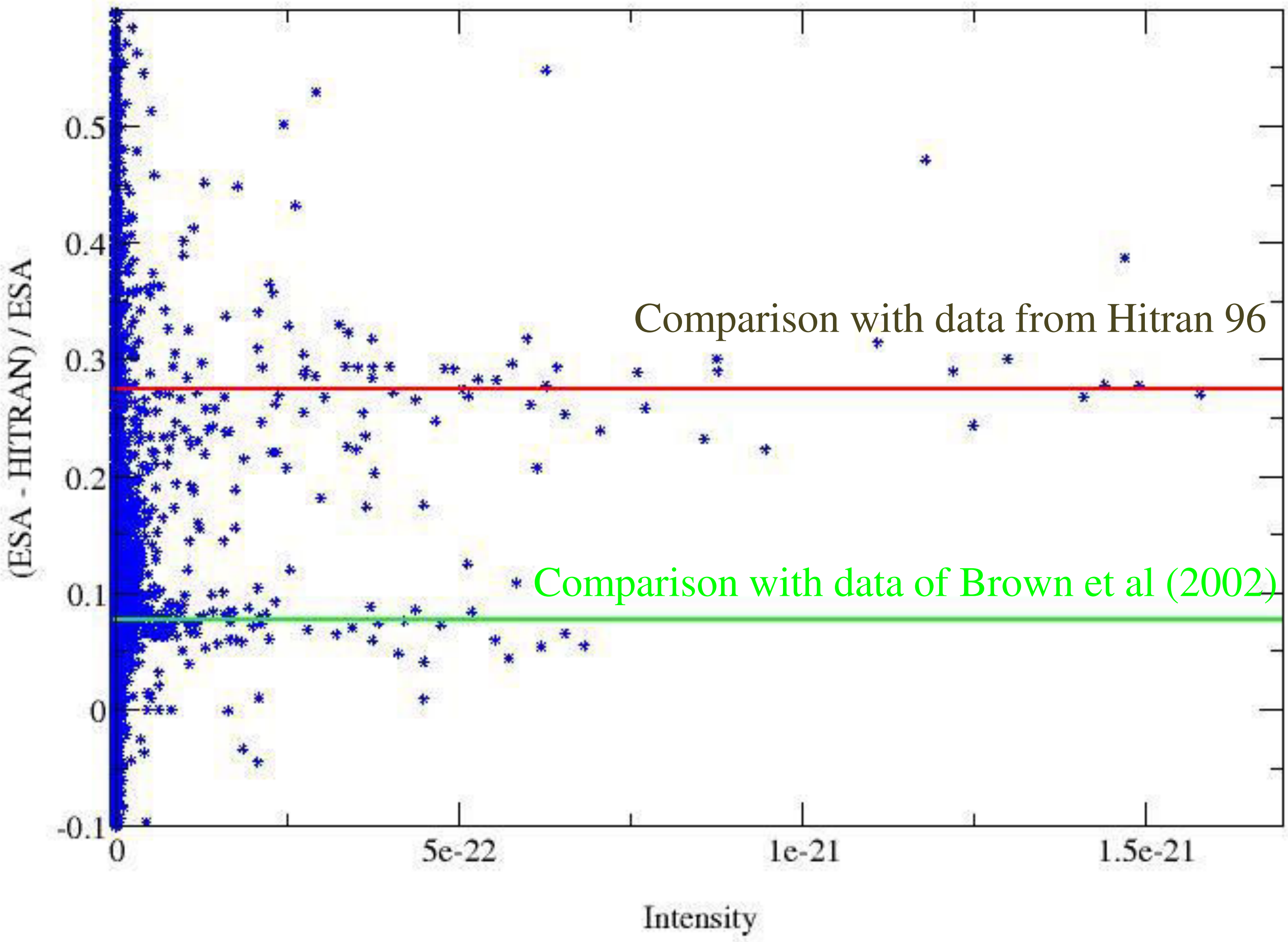
Polyad	Integrated absorbance	Spectral linefits	*Ab Initio* calculation	Correction Giver et al.
$2\nu+\delta$		1.26	1.31	0.92
3ν	1.19	1.21	1.04	1.14
$3\nu+\delta$	1.26	1.25	1.25	1.09
4ν		1.06	1.04	0.96

Numbers are ratio of total intensity to Hitran96

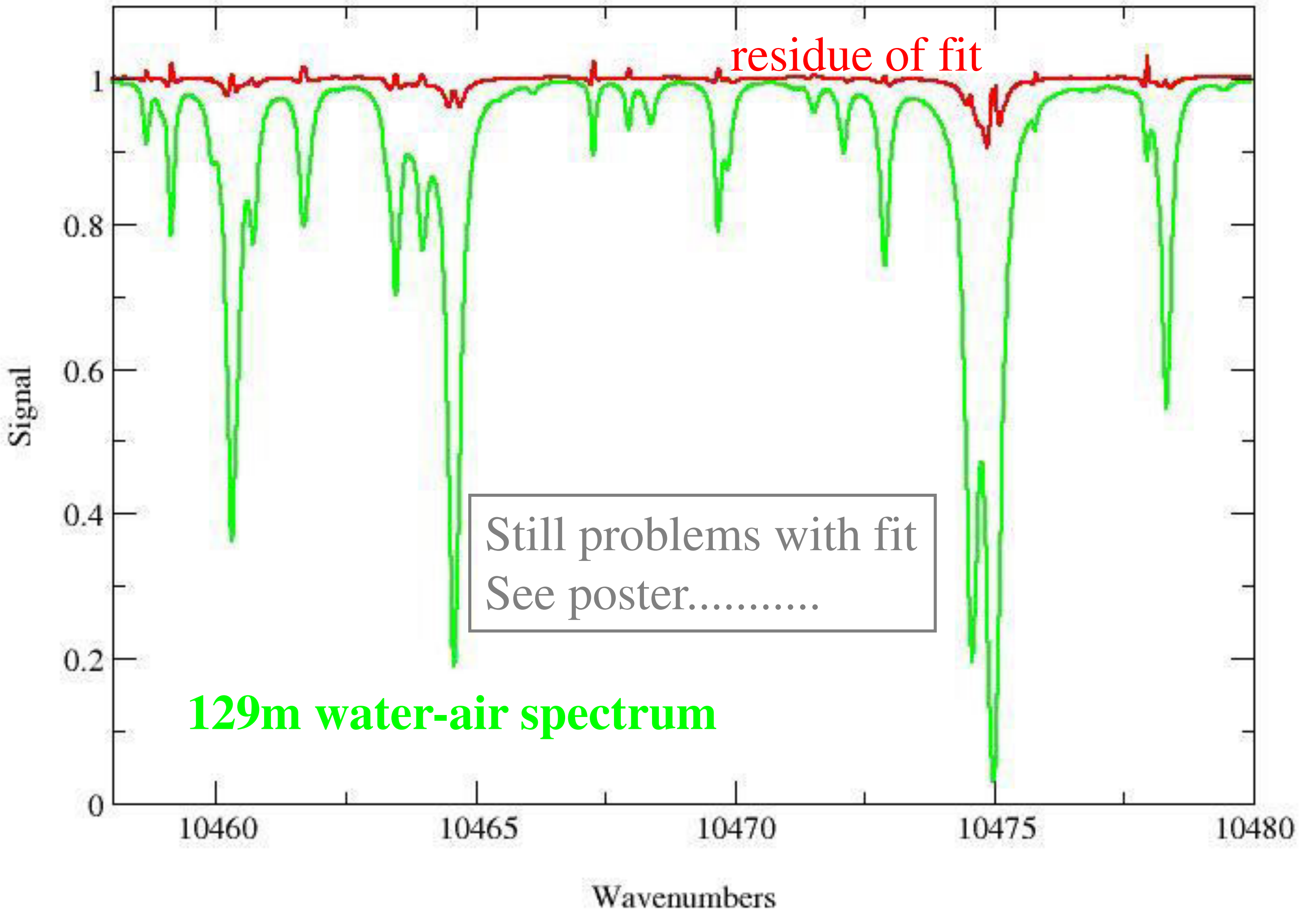
HITRAN underestimates intensity of strong lines!

D Belmiloud *et al*, *Geophys. Res. Lett.*, **27**, 3703 (2000).

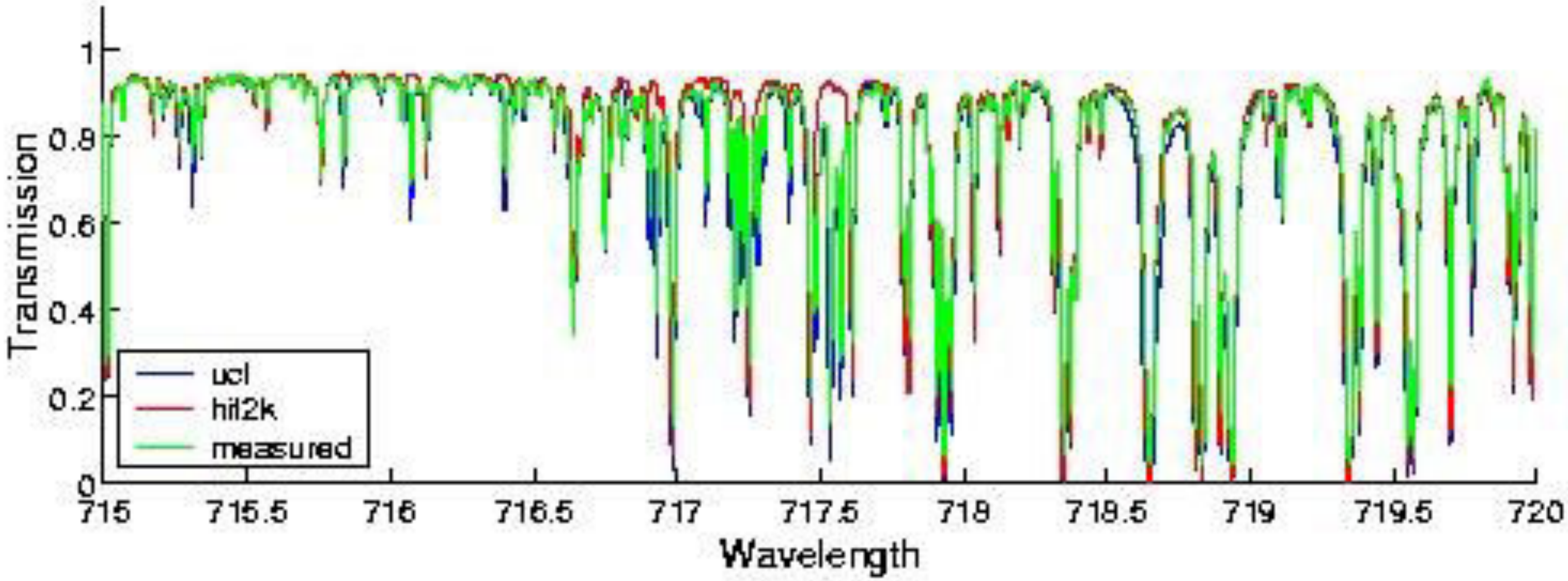
Intensity comparison for strong lines: ESA vs Hitran 2000



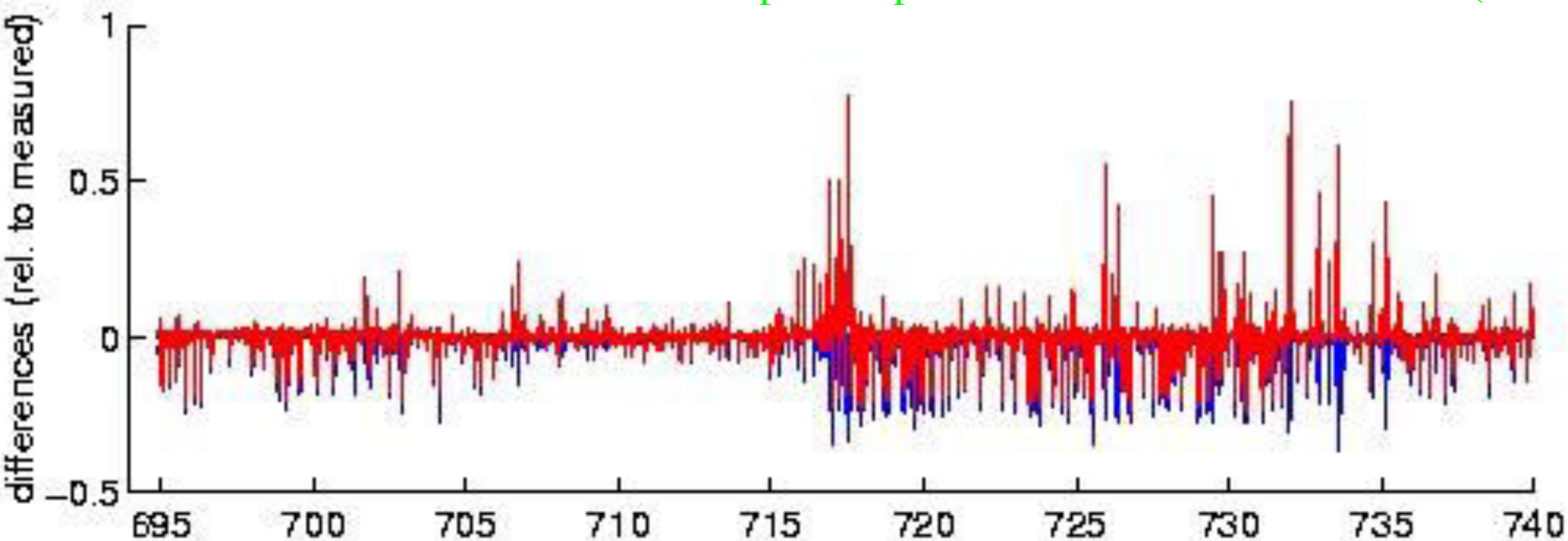
ESA spectra: line parameter retrieval



Validation using atmospheric spectra



Atmospheric spectra due to Newnham & Smith (RAL)



Water isotopmers in the visible

- Fourier transform spectra in Kitt Peak archive up to 15 000 cm^{-1}

$H_2{}^{18}O$: M. Tanaka, J.W. Brault and J. Tennyson, *J. Molec. Spectrosc.*, **216**, 77 (2002).

$H_2{}^{17}O$: M. Tanaka, O. Naumenko, J.W. Brault and J. Tennyson to be published

- Cavity ringdown spectra from Amsterdam about 17 000 cm^{-1}

$H_2{}^{18}O$: M. Tanaka, M. Sneep, W. Ubachs & J. Tennyson, J. Molec. Spectrosc., 226, 1 (2004).

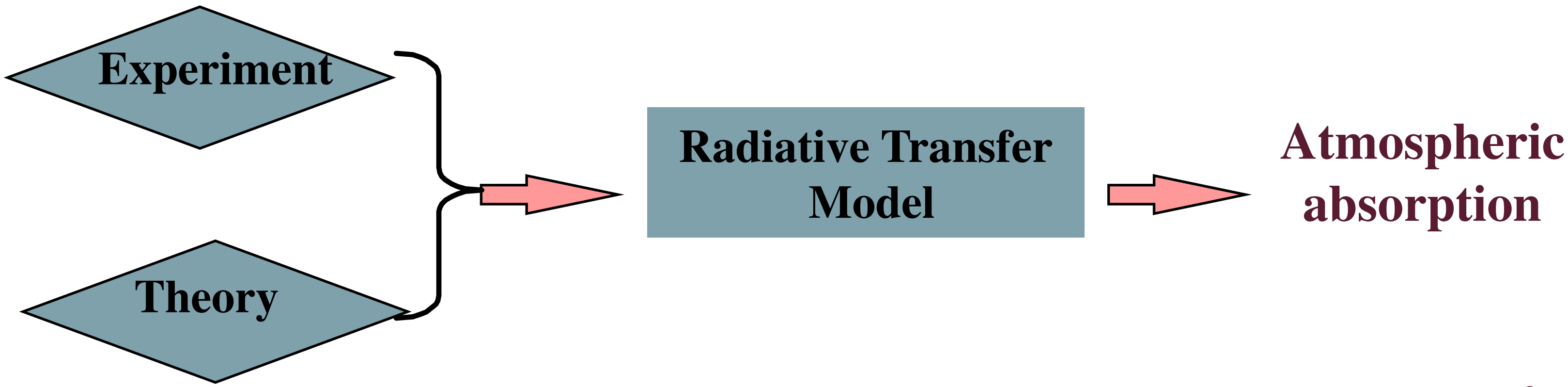
$H_2{}^{17}O$: being analysed at UCL

- **HDO**: Brussels/Rheims spectra of Coheur et al

being analysed in Tomsk

Missing absorption due to water: First estimates

- **In the red and visible :**



- **Unobserved weak lines have a significant effect : ~ 3 Wm^{-2}**
  - Estimated additional **2.5-3 %** absorption in the near I.R/Red.
  - Estimated additional **8-11 %** absorption in the 'Blue' ?
- **Underestimate of strong lines even more important : ~ 8 Wm^{-2}**
  - Estimated additional **8 %** absorption in the near I.R/Red.

Missing absorption due to water: Outstanding issues

- **In the near infrared and red:**
  - Contributions due to $H_2{}^{18}O$, $H_2{}^{17}O$ and HDO.
  - Possible role of water dimer $(H_2O)_2$.
- **In the blue and ultraviolet:**
  - Are $H_2{}^{16}O$ line intensities also underestimated?
  - Contribution due to weak lines