Fundamental Constants Meeting, 2015

SPECTROSCOPIC DETERMINATION OF THE BOLTZMANN CONSTANT

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Eltville, 4 February 2015

Outline

- DBT: Basic principles
- Present status of spectroscopic determinations of k_B
- The line shape problem
- The UniNA2 experiment on $H_2{}^{18}O$
- Uncertainty budget
- The 3rd generation experiment
- Conclusions and outlook

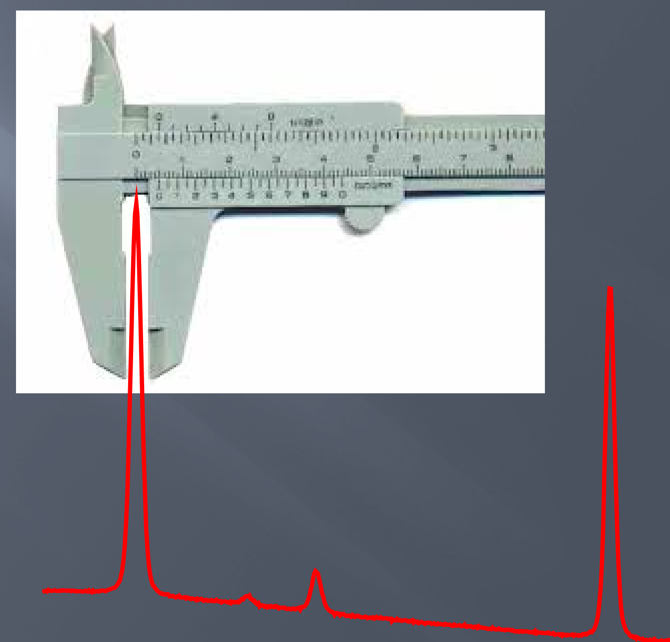
(for more details, please visit the poster)

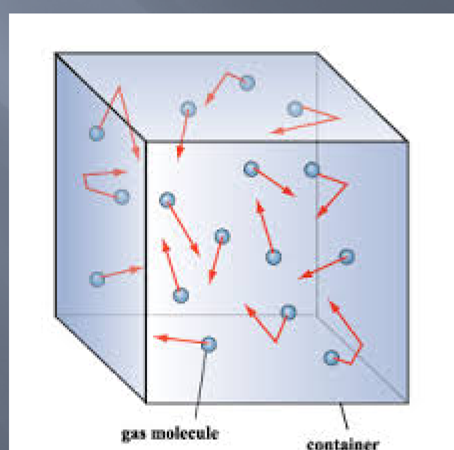
Basic principle

Proposed by Ch. J. Bordé, Metrologia **39,** 435 **(2002)**

The method consists in measuring very precisely the Doppler width of an absorption profile corresponding to an isolated atomic or molecular spectral line in a gas at thermodynamic equilibrium

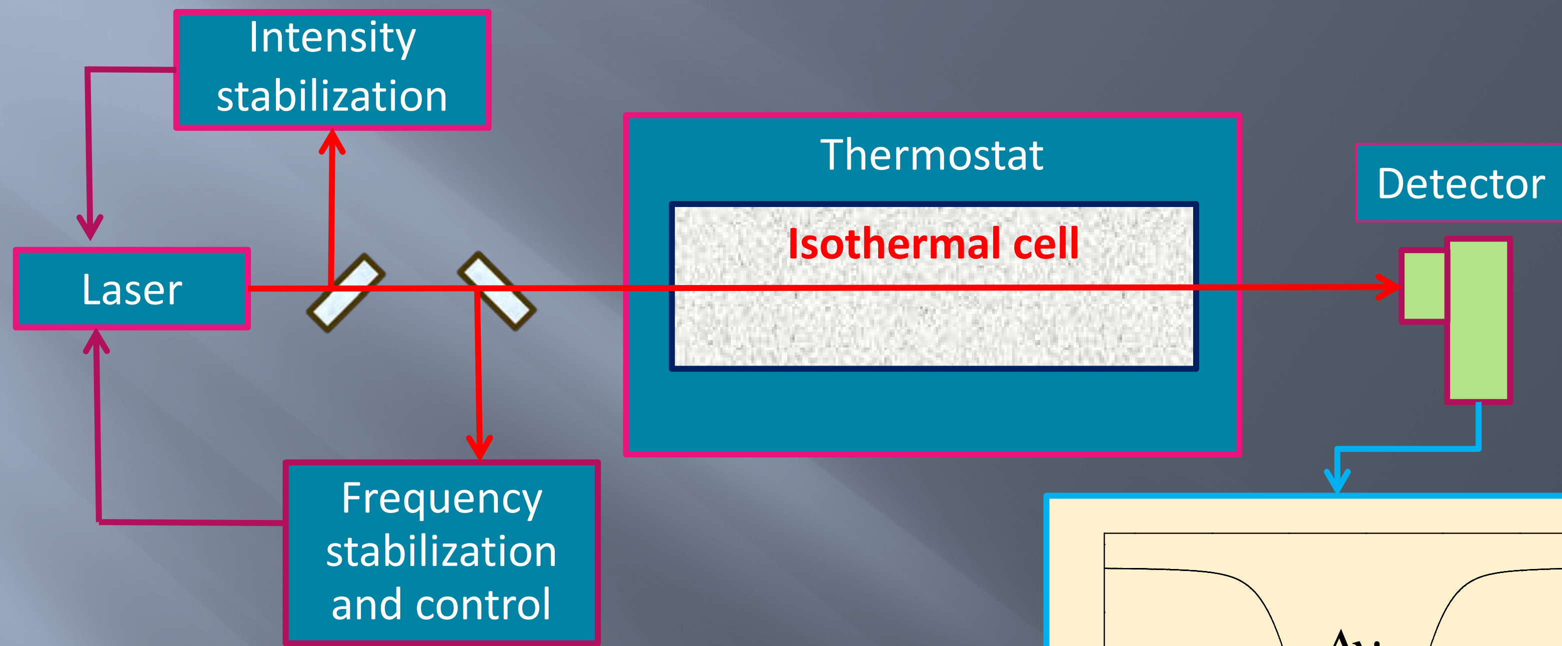
$$\Delta \nu_D = \sqrt{\ln 2}\,\frac{\nu_0}{c}\sqrt{2\frac{k_B T}{M}}$$

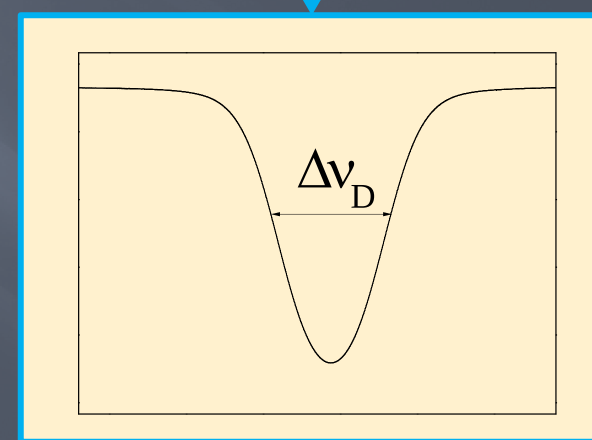




$$N(v)dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left[-\frac{mv^2}{2kT}\right]dv$$

DBT's ingredients and requirements





$$I_t(\nu) = I_0 e^{-\alpha(\nu-\nu_0)L}$$

Absolute and highly reproducible frequency scale underneath each absorption spectrum

Main requirements:
- ✓ isolated line
- ✓ high spectral fidelity
- ✓ refined line shape model

Present status of DBT

Group	Value (10^{-23} J/K)	Relative (global) uncertainty (ppm)	Relative deviation (ppm)	Gas	Year
Paris 13	1.380 65	190	+1	NH_3	2007
Paris 13	1.380 704	50	+39	NH_3	2010/2011
Paris 13	1.380 80	144	+109	NH_3	2011
Naples 2	1.380 58	160	-50	CO_2	2008
Naples 2	1.380 631	24	-13	$H_2{}^{18}O$	2013
Western Australia	1.381 04	410	+280	^{85}Rb	2011
Lethbridge Canada	1.380 660	87	+8	C_2H_2	2014
Western Australia	1.380 545	71	-75	Cs	2015

@ 296K

Atomic or molecular sample?

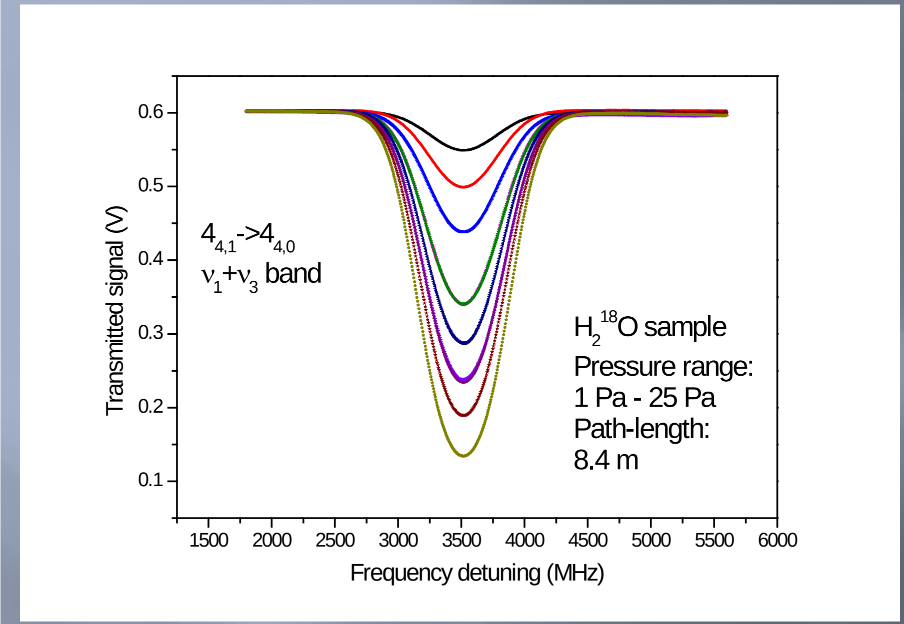
Alkali-metal and alkali-earth metal atoms:

Advantages	Disadvantages
Very low-pressures (10^{-5} – 10^{-4} Pa)	Hyperfine structure
No perturbation from collisions	Pertubation from magnetic fields
	Optical pumping effects
	Different species for different temperatures
	Natural broadening

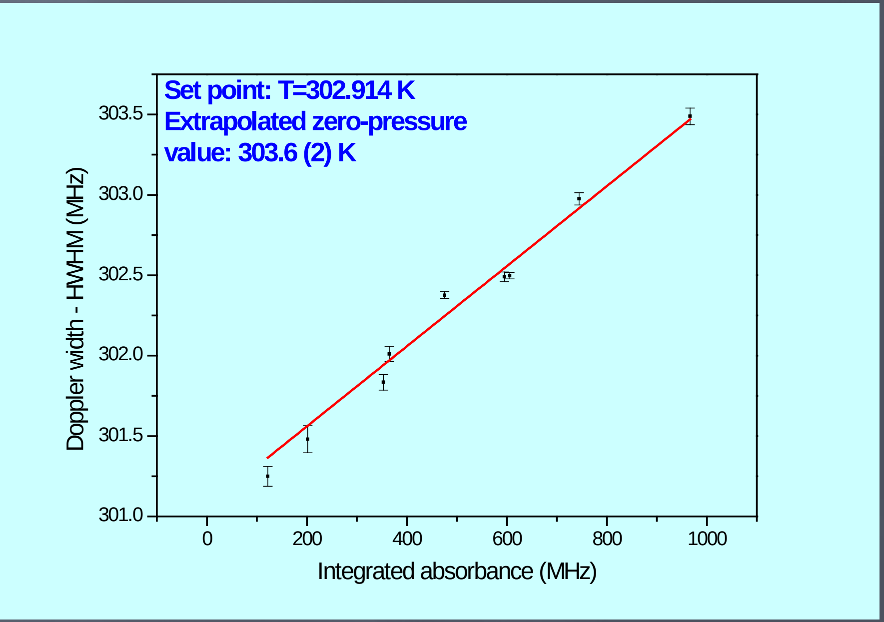
Molecules:

Advantages	Disadvantages
No perturbation from magnetic fields (diamagnetic molecules)	Collisional line-shape perturbations
Negligible non-linear effects	Hyperfine structure (depending on the molecule)
One species for broad T-range	
Negligible natural broadening (vibration-rotation transitions)	

A first example of DBT operation and measurements



$\Delta\nu_D$ extrapolation from Gaussian fits

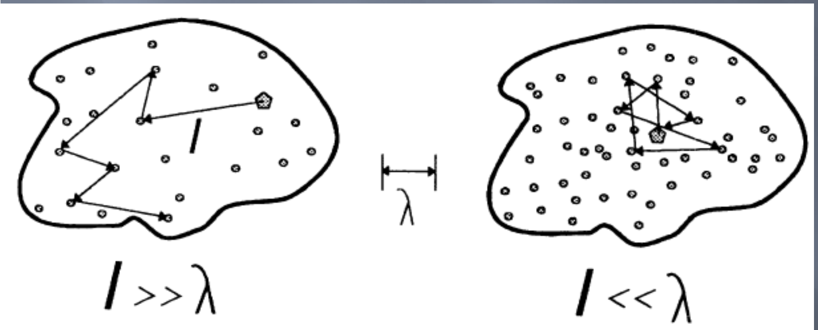


From kinetic theory (rigid spheres):

$l \sim 1.2$ mm >> λ

Statistical uncertainty = 0.07%

Systematical deviation = +0.22 %



Dependence on the pressure:

Collisional broadening should be considered!

A first example using the Voigt model

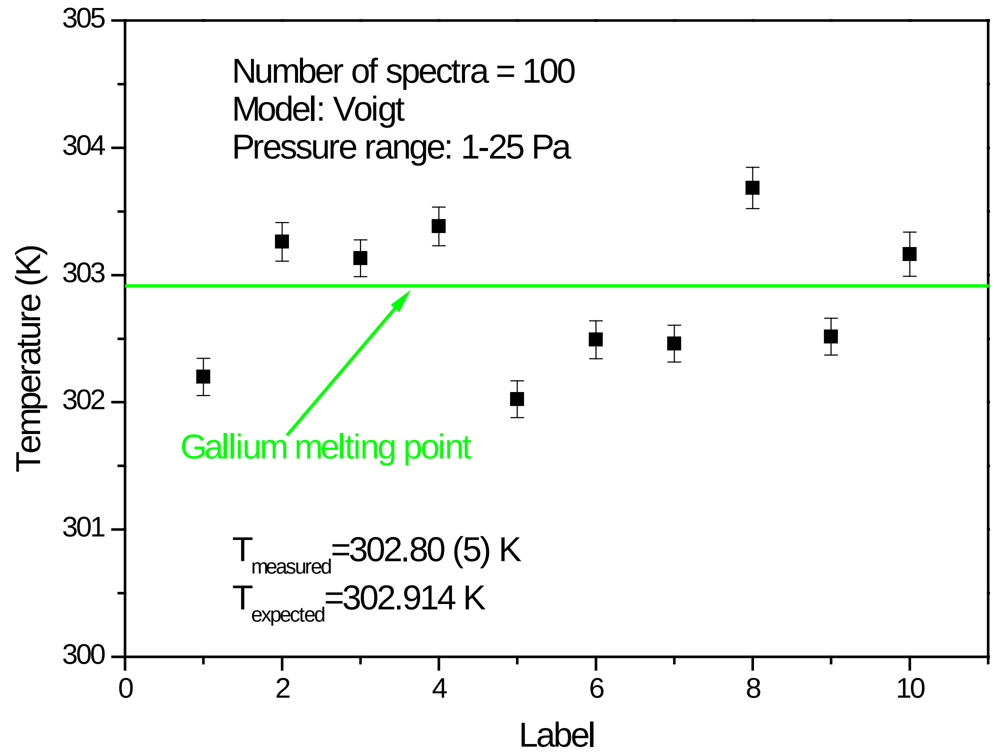
T = 302.80 (5) K

Precision = 160 ppm

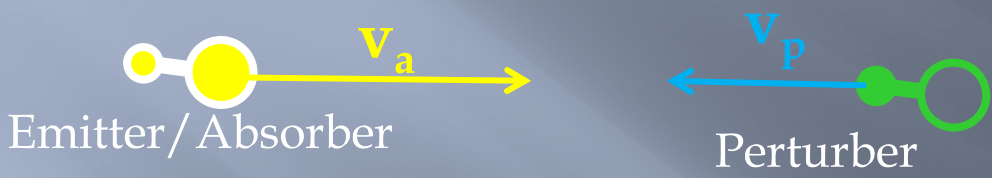
Systematical shift = -380 ppm

Apart from the Dicke effect, is there any further norrowing?

$\Delta\nu_D$ extrapolation from Voigt fits



Speed-dependence of collisional broadening



$$\Gamma\left(\vec{v}_a\right) = \Gamma\left(v_a\right) = \int_0^{\infty} \mathrm{d}\, v_r \, . \, f\left(v_r \middle| v_a\right) . \Gamma\left(v_r\right)$$

Classical collisional theories (such as the formalism of Robert and Bonamy) lead to a dependence of the relaxation rate on the relative velocity!
Since these results can hardly be translated into a fitting procedure for the analysis of experimental line shapes, approximations must be used.

Berman and Pickett theory

Empirical collisional interaction potential of the form $\boldsymbol{V(R) \propto R^{-q}}$

Power-law dependence on the relative speed of the absorber/perturber system
$\Gamma(v_r) \propto (v_r)^m$, with $m = (q-3) / (q-1)$

$$\Gamma(v_a) = \frac{\Gamma_0}{(1+m_p/m_a)^{m/2}} \cdot M\left[-\frac{m}{2};\frac{3}{2};-\frac{m_p}{m_a}\left(\frac{v_a}{v_{a0}}\right)^2\right]$$

$$\Delta(v_a) = \frac{\Delta_0}{(1+m_p/m_a)^{n/2}} \cdot M\left[-\frac{n}{2};\frac{3}{2};-\frac{m_p}{m_a}\left(\frac{v_a}{v_{a0}}\right)^2\right]$$

$n = -3/(q-1)$

Speed-dependent Voigt profile

$$I_{SDVP}(\omega) = \frac{1}{\pi}\int f_M(\vec{v}) \frac{d\vec{v}}{\Gamma(v) - i[\omega - \omega_0 - \Delta(v) - \vec{k}\cdot\vec{v}]}$$

In general it is not symmetric and is narrower than the ordinary Voigt profile.

Expansion of $\Gamma(v_a)$ in the vicinity of the mean quadratic speed :

$$\Gamma(v_a) = \Gamma_0 + \Gamma_2 \left[\left(\frac{v_a}{v_{a0}} \right)^2 - \frac{3}{2} \right]$$

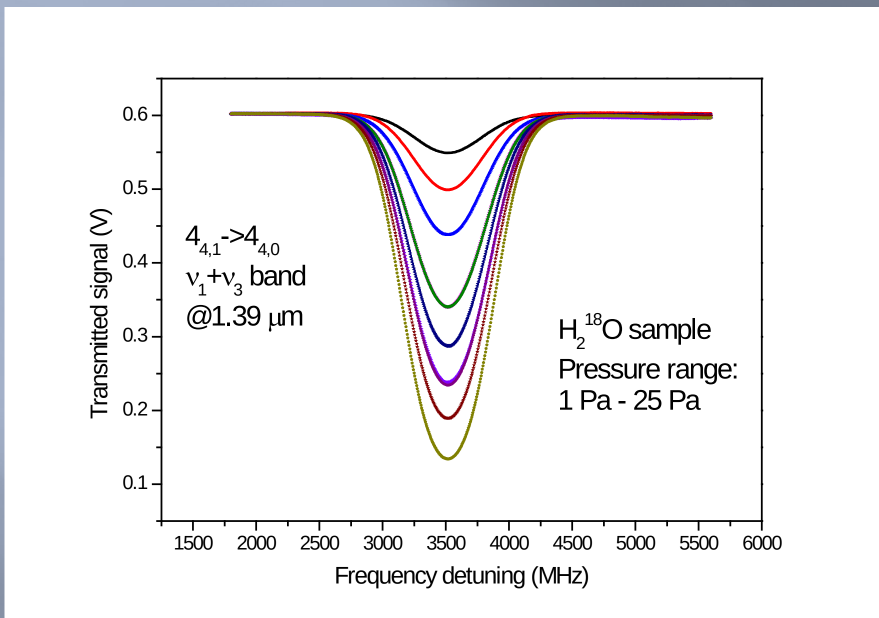
$$\Gamma_2 \sim 0.1\,\Gamma_0$$

F. Rohart, H. Mäder, H.-W. Nicolaisen, J. Chem. Phys. 101, 6475-6486 (1994).

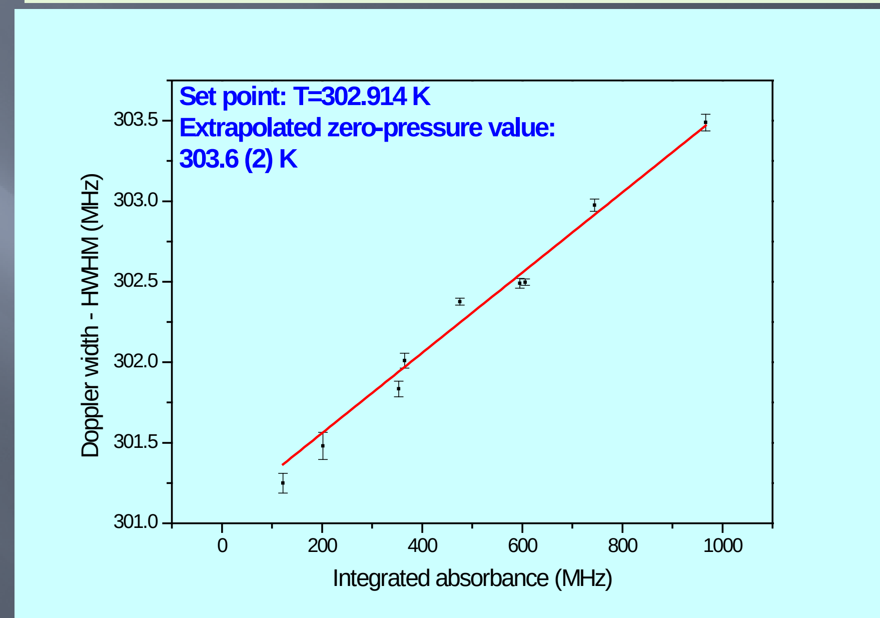
M.D. De Vizia, F. Rohart, A. Castrillo, E. Fasci, L. Moretti, and L. Gianfrani, Phys. Rev. A 83, 052506 (2011).
M. D. De Vizia, A. Castrillo, E. Fasci, L.Moretti, F. Rohart, and L. Gianfrani, Phys. Rev. A 85, 062512 (2012).
M. D. De Vizia, A. Castrillo, E. Fasci, P. Amodio, L. Moretti, L. Gianfrani, Phys. Rev. A 90, 022503 (2014).

SD-effects in the NIR spectrum of water

A first example of DBT operation and measurements



$\Delta\nu_D$ extrapolation from Gaussian fits



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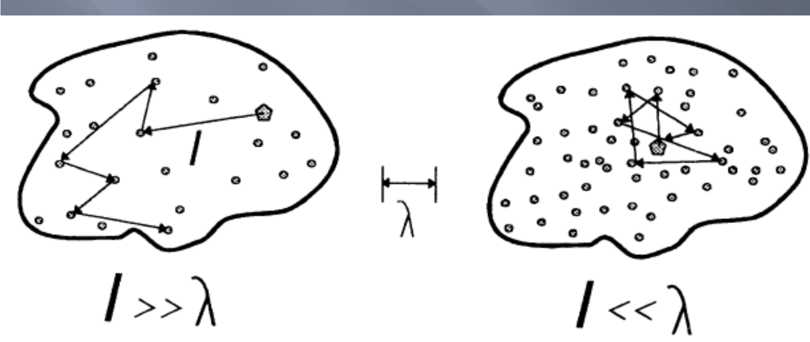
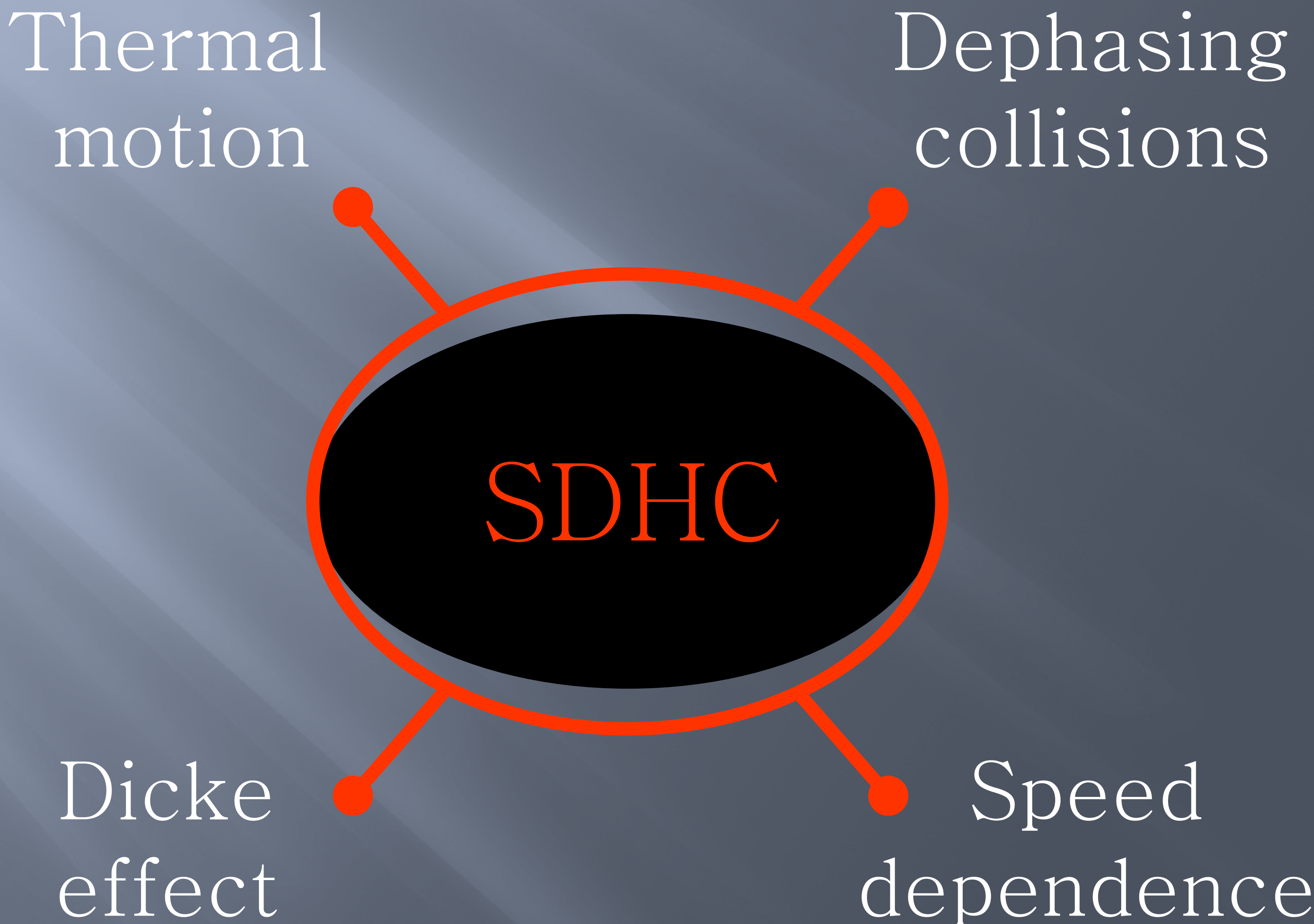


Statistical uncertainty = 0.07%
Systematical deviation = +0.22 %

$\Delta\nu_D/\Gamma_0 \sim 300$ $\Delta\nu_D/\Gamma_2 \sim 3000$

A realistic model for H_2O-H_2O collisions



The pcSDHC model

In addition to the speed-dependent and Dicke (hard-collision) effects on the shape, the pcSDHC model takes into account the correlation between collisions that produce a dephasing of the molecular dipole and those producing a change of the absorber velocity.

$$pCSDHC(\omega) = \frac{1}{\pi}\mathrm{Re}\left\{\frac{G(\omega)}{1-H(\omega)}\right\} \quad \text{with}$$

$$G(\omega) = \int_{-\infty}^{+\infty} d\mathbf{v} \frac{W_M(\mathbf{v})}{\left[\beta_V(v)+\beta_{VD}(v)+\gamma_D(v)-i(\omega-\omega_0-\delta_D(v)-\mathbf{k}\cdot\mathbf{v})\right]}$$

$$H(\omega) = \int_{-\infty}^{+\infty} d\mathbf{v} \frac{W_M(\mathbf{v})\left[\beta_V(v)+\beta_{VD}(v)-\gamma_{VD}(v)-i\delta_{VD}(v)\right]}{\left[\beta_V(v)+\beta_{VD}(v)+\gamma_D(v)-i(\omega-\omega_0-\delta_D(v)-\mathbf{k}\cdot\mathbf{v})\right]}$$

$$\beta(v) = \beta_V(v)+\beta_{VD}(v)$$
$$\gamma(v) = \gamma_D(v)+\gamma_{VD}(v)$$
$$\delta(v) = \delta_D(v)+\delta_{VD}(v)$$

$$W_M(\mathbf{v}) = \left(\sqrt{\pi}\bar{v}\right)^{-3}\exp\left(-v^2/\bar{v}^2\right) \qquad \bar{v} = \sqrt{2k_BT/m}$$

$$\eta = \frac{\gamma_{VD}}{\gamma} = \frac{\delta_{VD}}{\delta},\ \eta \text{ is the correlated fraction}$$

$$\frac{\gamma(v)}{\gamma_0} = \frac{\delta(v)}{\delta_0} = \frac{\beta(v)}{\beta_0} \propto v_r^p \text{ with } \ p = \frac{(q-3)}{(q-1)}$$

assuming that the potential interaction is $V(r) \propto r^{-q}$

Reference: A. S. Pine, *"Asymmetries and correlations in speed-dependent Dicke-narrowing line shapes of argon-broadened HF"*, JQRST **62**, 397-423 (1999).

What about relativistic effects?

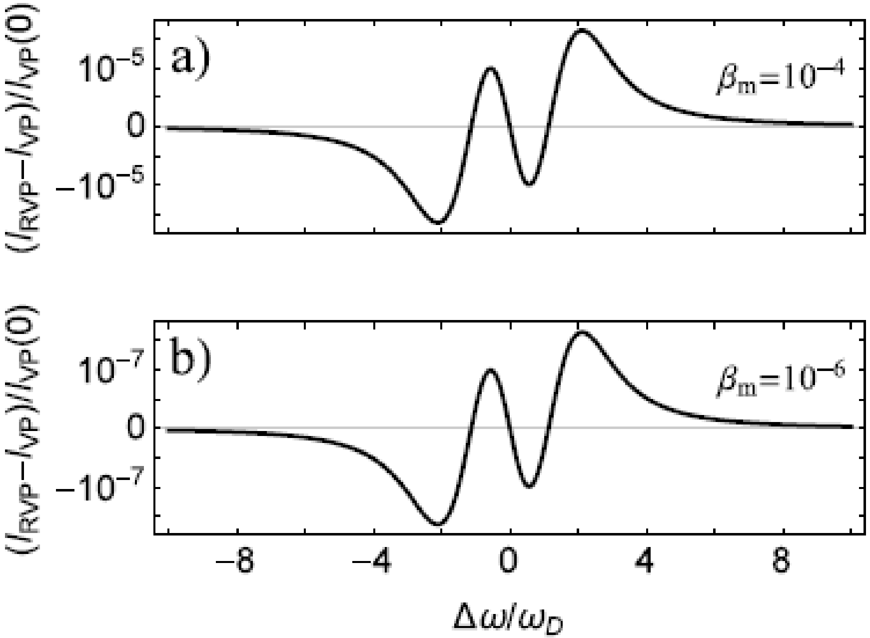
Relativistic formulation of the Voigt profile

P. Wcisło,[1] P. Amodio,[2] R. Ciuryło,[1] and L. Gianfrani[2]

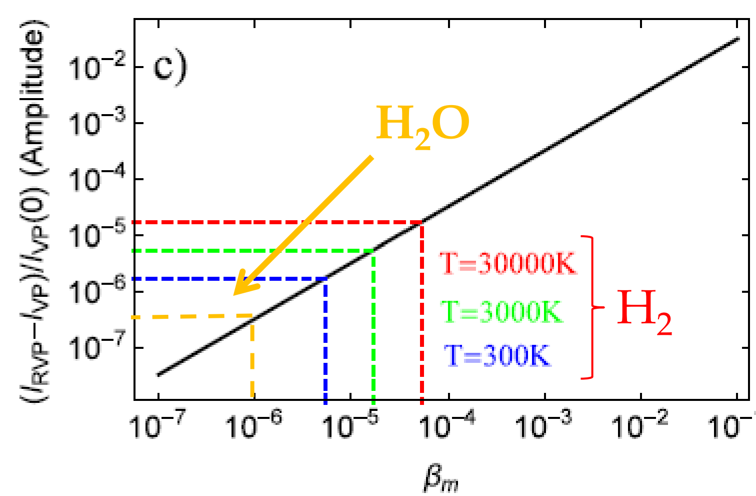
[1] *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

[2] *Department of Mathematics and Physics, Second University of Naples, Viale Lincoln 5, 81100 Caserta, Italy*

(Dated: January 17, 2015)

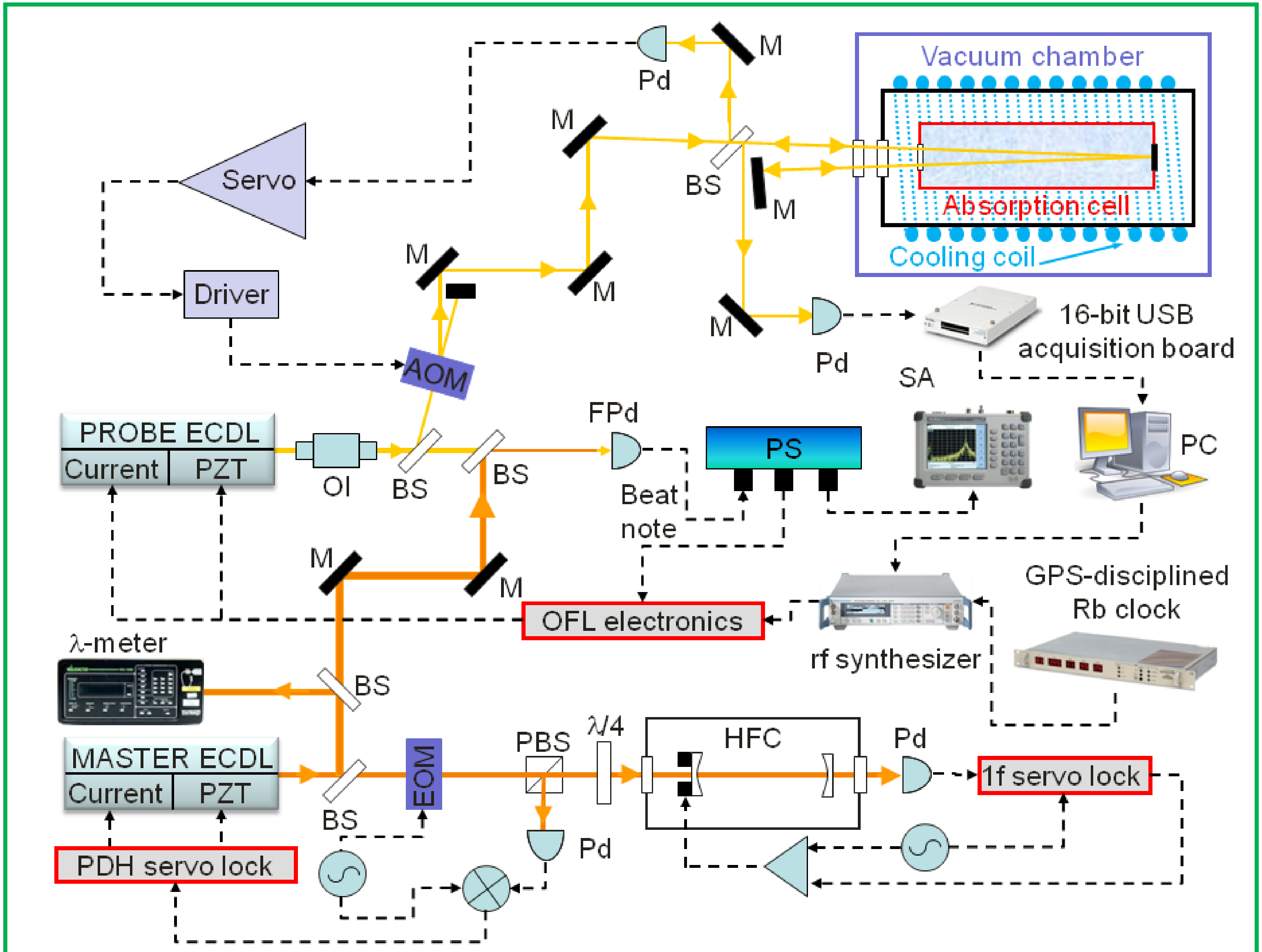


Physical Review A, in press.

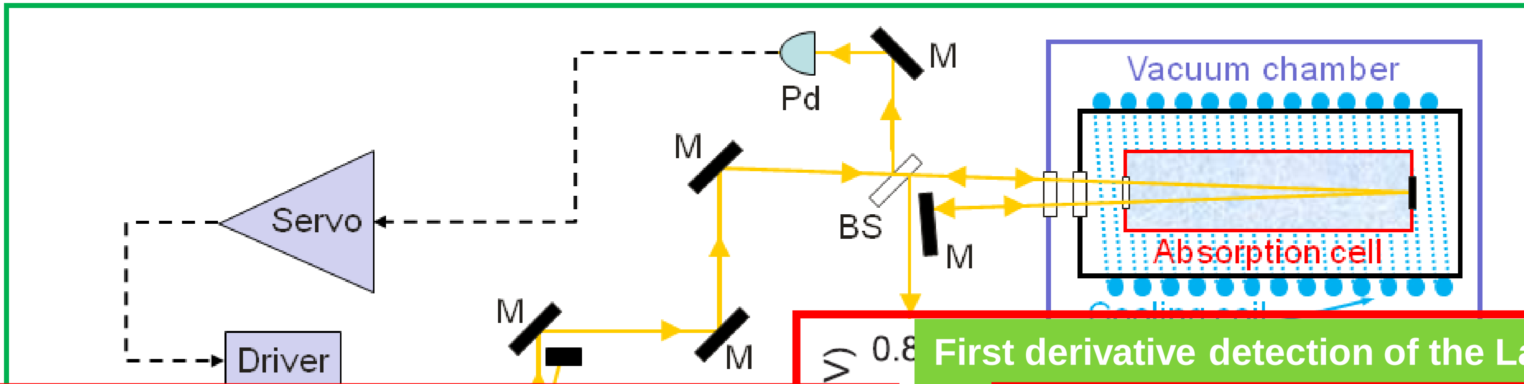


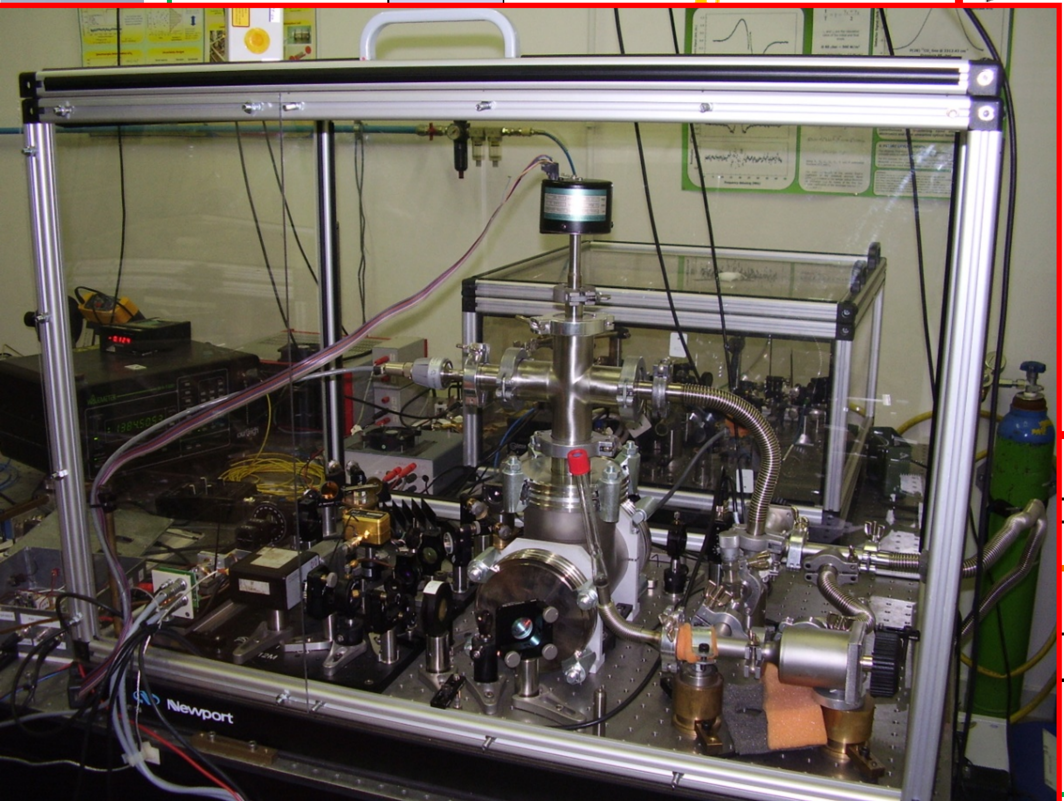
$$V \approx 500\ \mathrm{m/s} \rightarrow \beta \approx 1.6\ 10^{-6} \rightarrow \gamma - 1 \approx 10^{-12}$$

The dual-laser water spectrometer

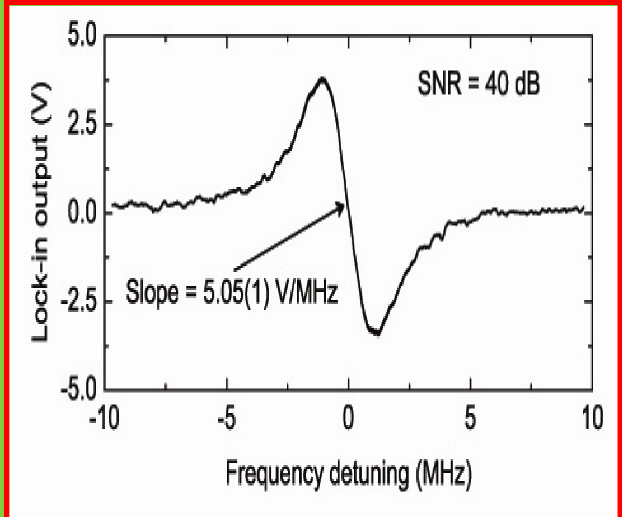


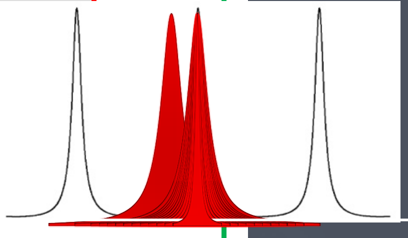
The dual-laser water spectrometer



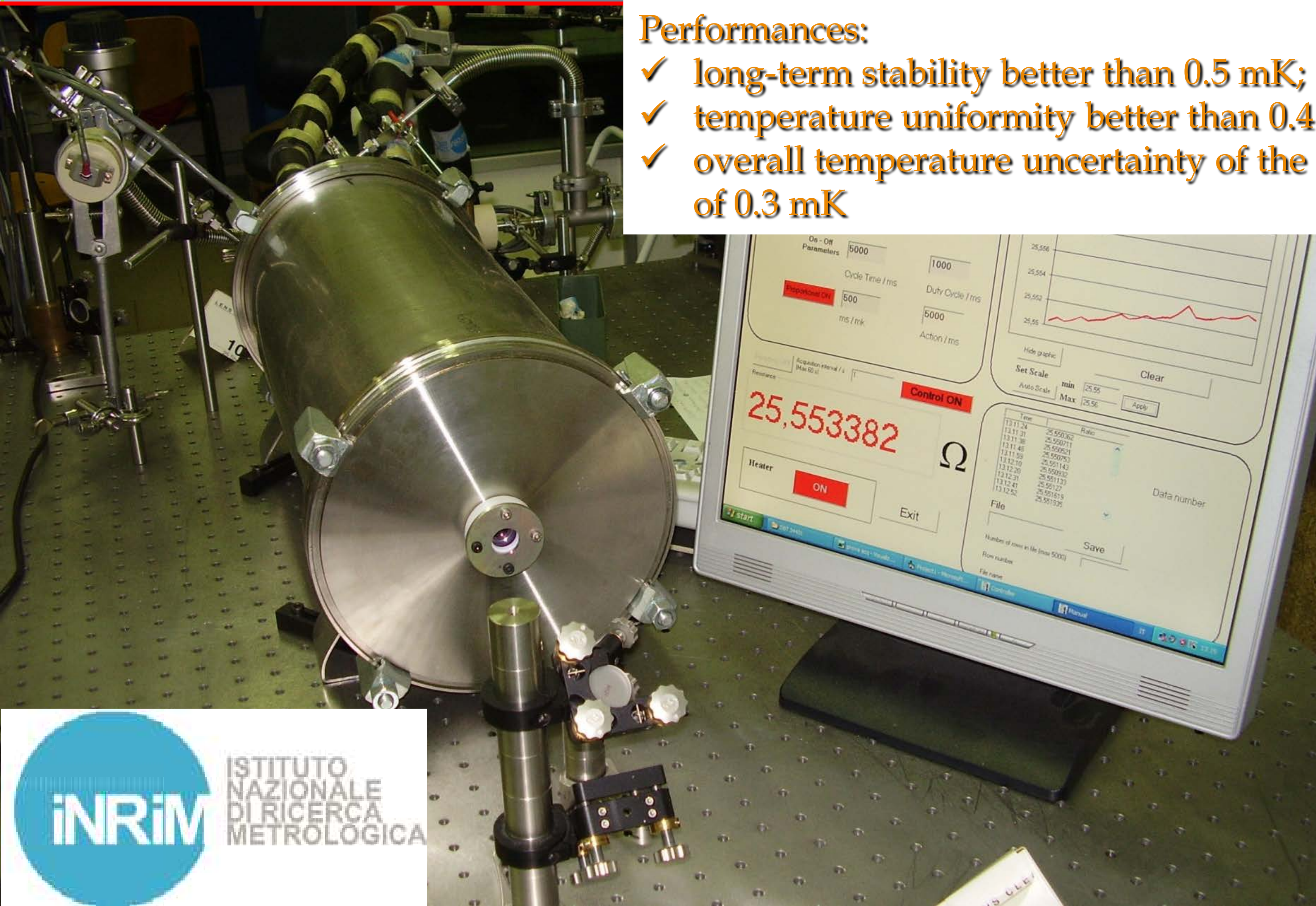


First derivative detection of the Lamb dip





The dual-laser water spectrometer



Performances:

- ✓ long-term stability better than 0.5 mK;
- ✓ temperature uniformity better than 0.4 mK;
- ✓ overall temperature uncertainty of the order of 0.3 mK

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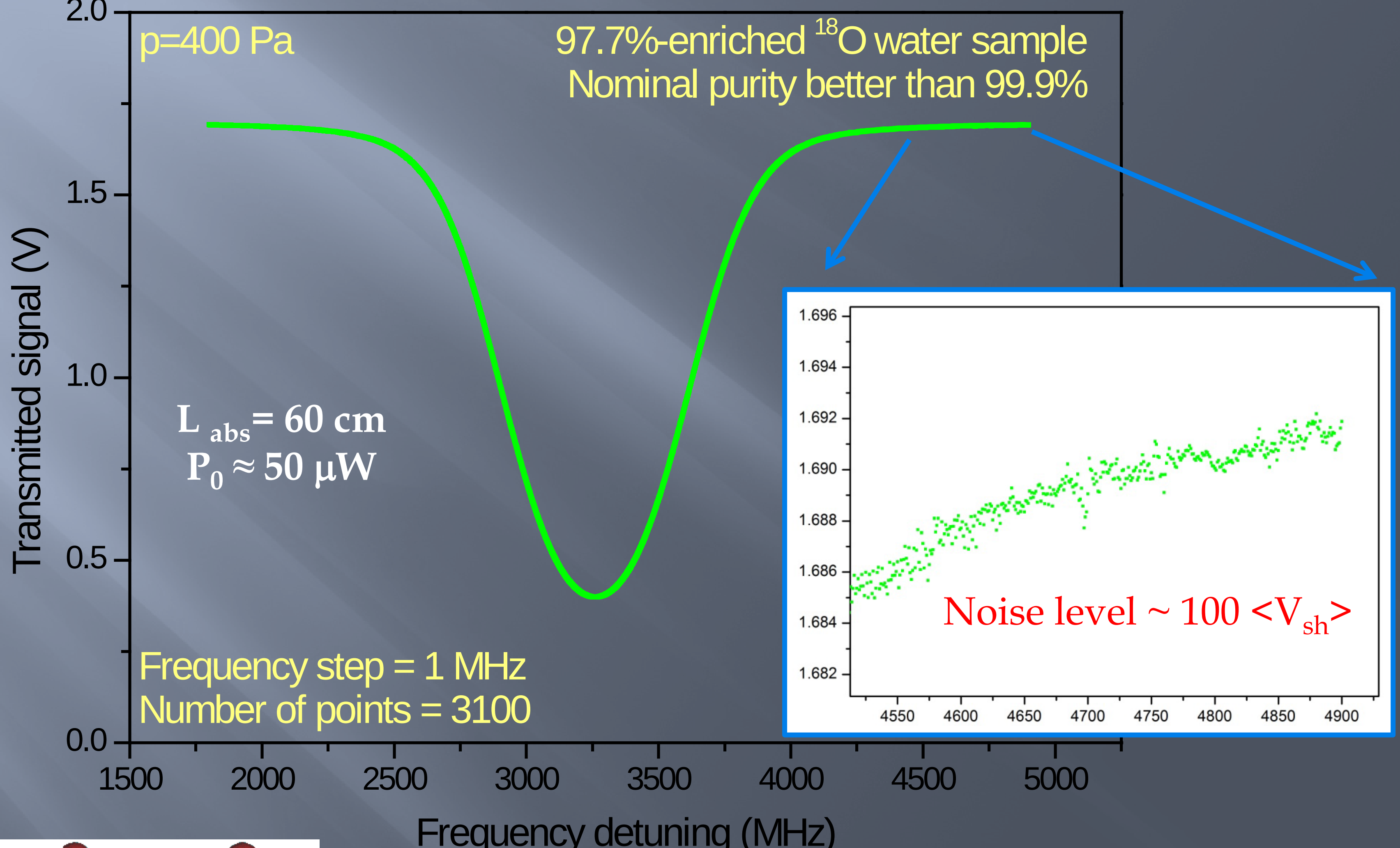
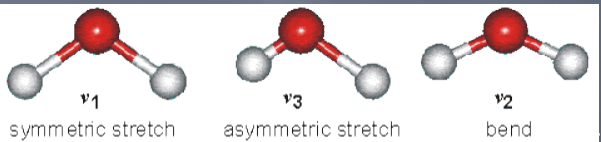
Example spectrum



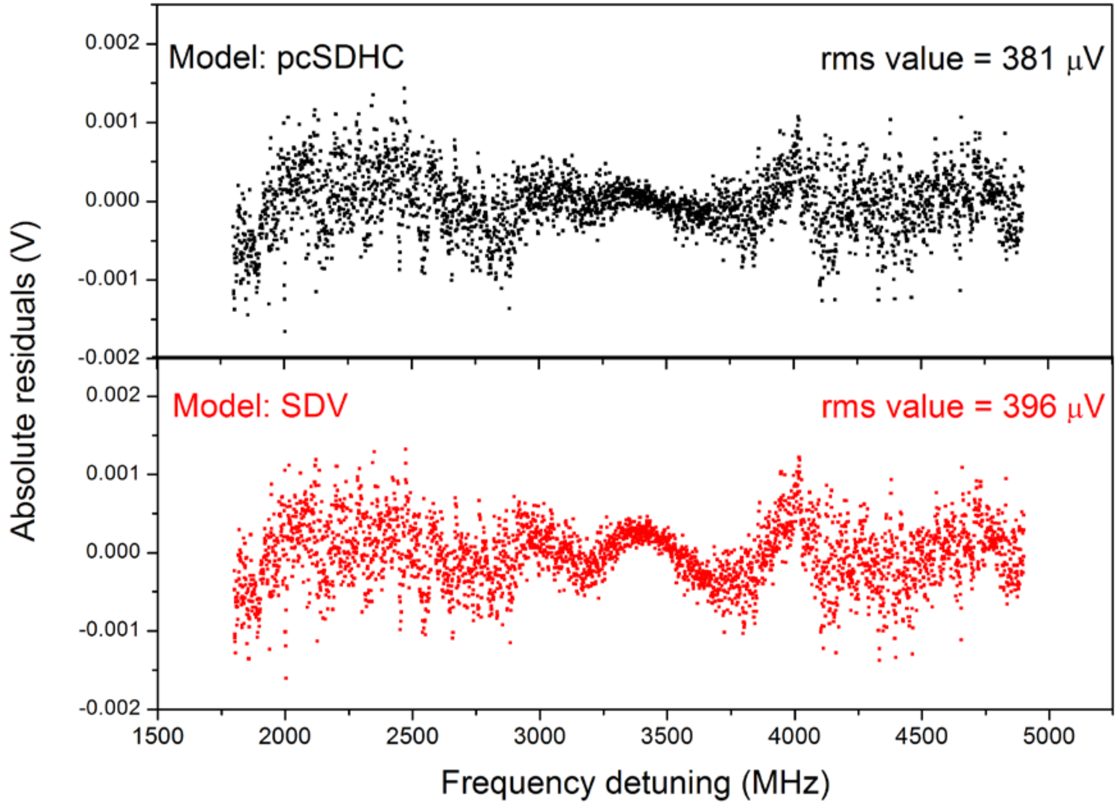


$4_{4,1}$->$4_{4,0}$ line of the $H_2^{18}O$ $\nu_1+\nu_3$ band at T=273.16 K

Example of individual line fitting

p=400 Pa

$$P(\nu) = (P_0 + P_1 \upsilon) \exp\left[-Ag(\upsilon - \upsilon_0)\right]$$



Nonlinear least squares fits under MATLAB environment using trust region optimization algorithm.

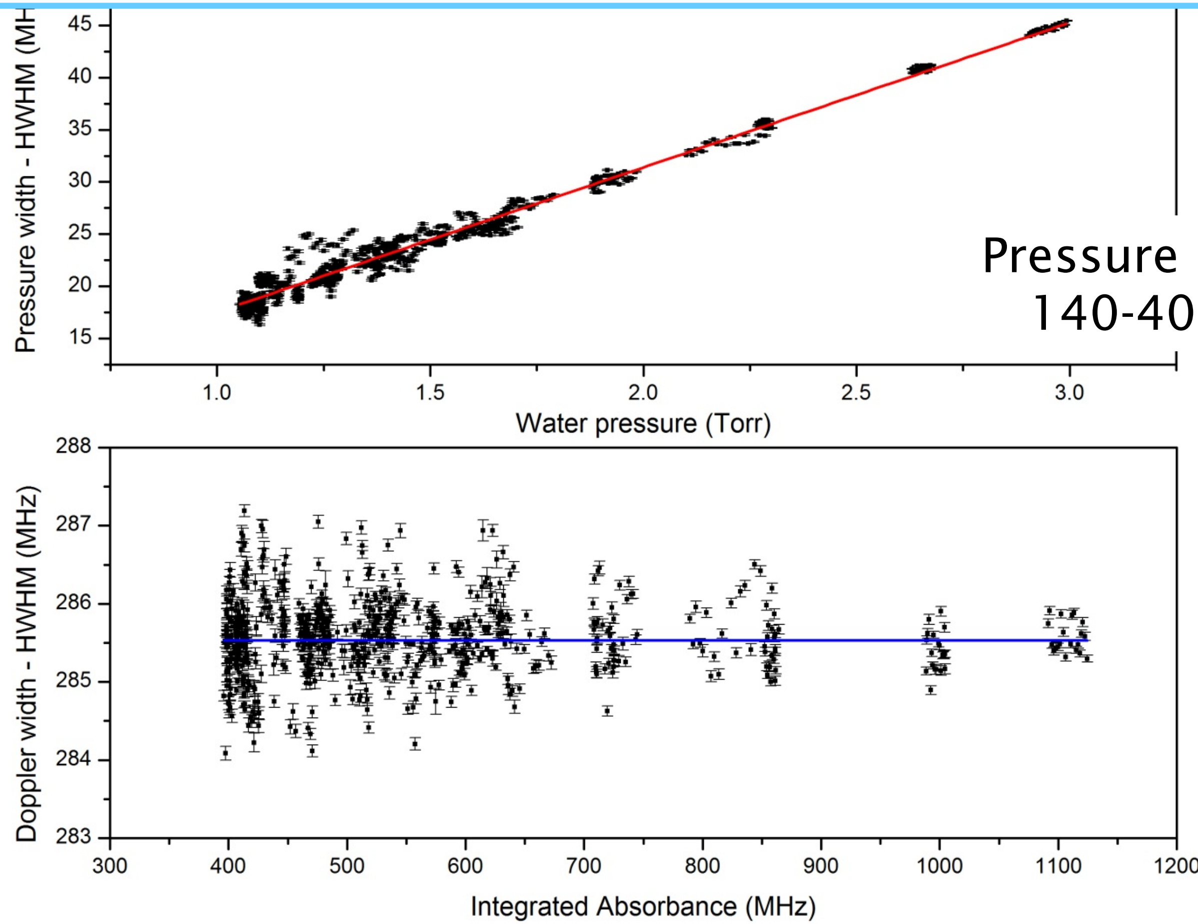
Free parameters:

ν_0, A, P_0, P_1, Γ_0, β_0, $\Delta\nu_D$

Please note: pressure measurements are not needed!

Retrieved widths

Pressure broadening coefficient = 13.86 (6) MHz/Torr
HITRAN database: 14.0 (7) MHz/Torr



Pressure range:
140-400 Pa

Number of spectra = 718 Model: pcSDHC $q=5.017 \pm 0.017$ $\eta=0.2$

Our value

$$k_B = (1.380631 \pm 0.000033)\ \times 10^{-23}\ \text{J/K}$$

L. Moretti, A. Castrillo, E. Fasci, M.D. De Vizia, G. Casa, G. Galzerano, A. Merlone, P. Laporta, and L. Gianfrani, Phys. Rev. Lett. 111, 060803 (2013).
APS Synopsis: http://physics.aps.org/synopsis-for/print/10.1103/PhysRevLett.111.060803

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Synopsis: Laser Spectroscopy Refines Boltzmann Constant

iStockphoto/tcsaba

Determination of the Boltzmann Constant by Means of Precision Measurements of $H_2{}^{18}O$ Line Shapes at 1.39 μm

L. Moretti, A. Castrillo, E. Fasci, M. D. De Vizia, G. Casa, G. Galzerano, A. Merlone, P. Laporta, and L. Gianfrani

Phys. Rev. Lett. **111**, 060803 (2013)

Published August 8, 2013

In 2011, the General Conference on Weights and Measures (CGPM) resolved to find a better definition of the kelvin. Currently, the unit is defined as $1/273.16$ of the triple point of water, a standard that works well for thermometers operating near room temperature but causes inaccuracies in those designed for extreme conditions (such as a ceramic furnace or a liquid helium bath). CGPM argued that the kelvin should instead be defined in terms of the Boltzmann constant, a fundamental constant that relates the average mechanical energy in a particle to temperature. Researchers have since sought new ways to measure the constant with a high level of accuracy. Now, Luigi Moretti at the Second University of Naples, Italy and colleagues report in *Physical Review Letters* a sixfold reduction in the uncertainty of the Boltzmann constant when it is determined using laser spectroscopy.

An atom at rest absorbs light at sharp, well-defined frequencies, but these frequencies shift if the atom moves toward or away from the light source. An absorption line measured in a gas of warm, moving atoms will therefore be smeared out in frequency—an effect called Doppler broadening that varies with the square root of the Boltzmann constant. Moretti *et al.* used a pair of frequency-stabilized lasers to carefully measure this broadening around an infrared absorption line in water held at the triple point, and they determined the constant to be $1.380631 \pm 0.000024 \times 10^{-23}$ joules/kelvin. Though this value has an uncertainty 20 times greater than the best measurement reported to date, Moretti *et al.* foresee improvements by summing up larger number of spectra and using more refined models to fit the shape of the atomic absorption line. – *Jessica Thomas*

Previous synopsis | Next synopsis

L. Moretti, A. Castrillo, E. Fasci, M.D. De Vizia, G. Casa, G. Galzerano, A. Merlone, P. Laporta, and L. Gianfrani, Phys. Rev. Lett. 111, 060803 (2013).

APS Synopsis: http://physics.aps.org/synopsis-for/print/10.1103/PhysRevLett.111.060803

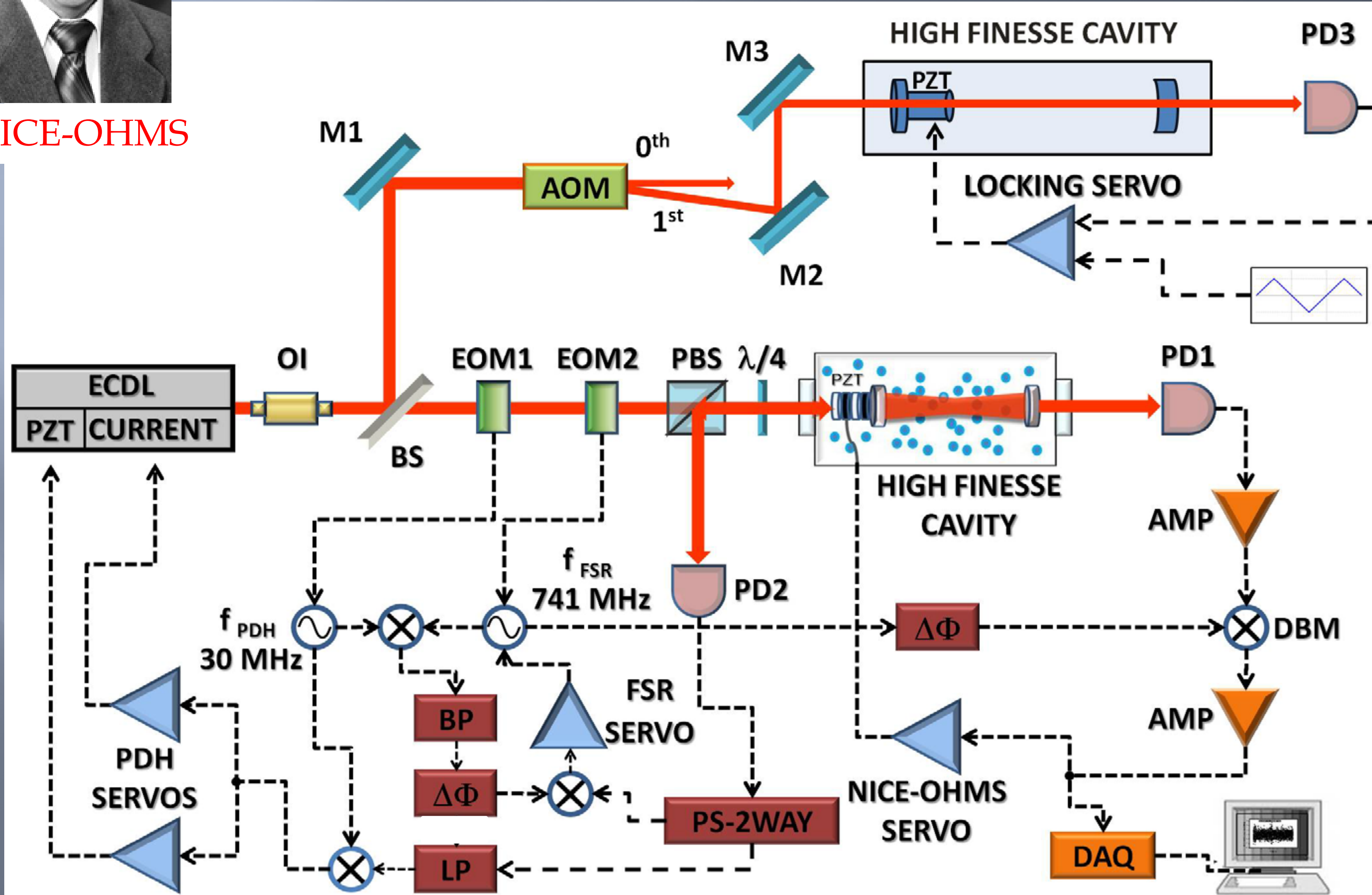
Uncertainty budget

Component	**Type A**	**Type B**
Statistical uncertainty	15.7×10^{-6}	
Frequency scale		$< 2 \times 10^{-6}$
Line-center frequency		0.278×10^{-6}
Line emission width and FM broadening		~~10×10^{-6}~~
Optical saturation effects		Negligible
Detector nonlinearity		$< 2 \times 10^{-6}$
AM modulation effects		Negligible
Relativistic effects		Negligible
Finite detection bandwidth		$< 10^{-9}$
Cell’s temperature	3.7×10^{-8}	1.1×10^{-6}
Hyperfine structure effects (*Ortho* transitions)		$< 10^{-6}$
Line shape model		14.9×10^{-6}
Combined relative uncertainty = 24×10^{-6}		

A. Castrillo, L. Moretti, E. Fasci, M.D. De Vizia, G. Casa and L. Gianfrani, J. Molecular Spectroscopy 300, 131-138 (2014).

The new reference laser

NICE-OHMS



The new reference laser

2200 OPTICS LETTERS / Vol. 39, No. 7 / April 1, 2014

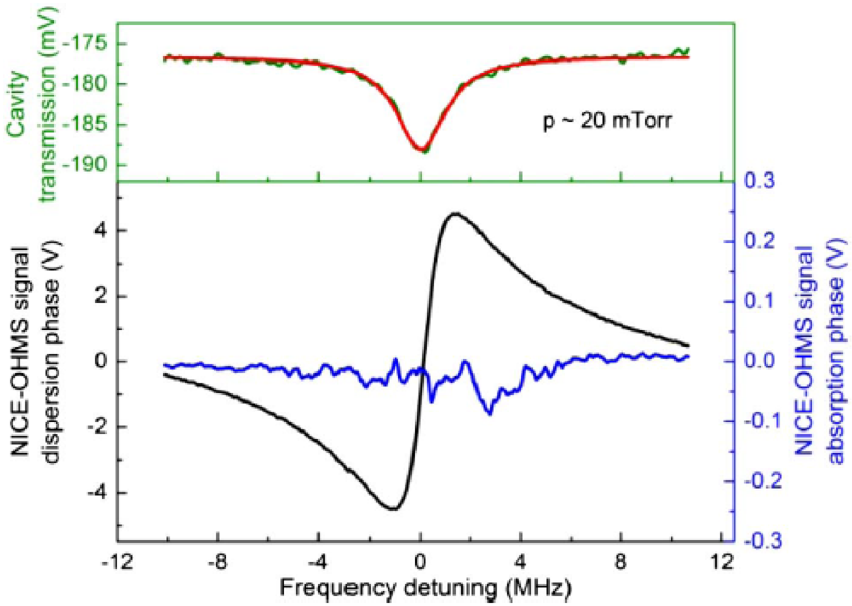


Fig. 2. Example of saturated absorption spectroscopy. The upper plot shows the Lamb dip for the $4_{4,1} \rightarrow 4_{4,0}$ line of the $H_2{}^{18}O$ $\nu_1 + \nu_3$ band at $\lambda = 1389.0839$ nm, along with the fit to a Lorentzian profile (red line) at a pressure ~2.7 Pa (20 mTorr). The lower plot gives the NICE-OHMS profile in the dispersion regime of operation. The blue trace, in a magnified scale, represents the NICE-OHMS signal, as recorded in the absorption regime.

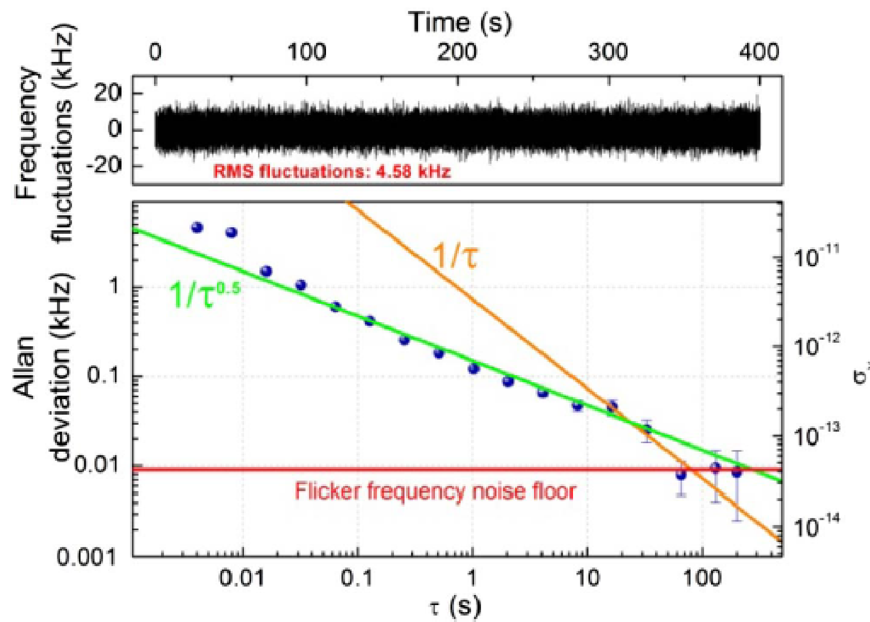
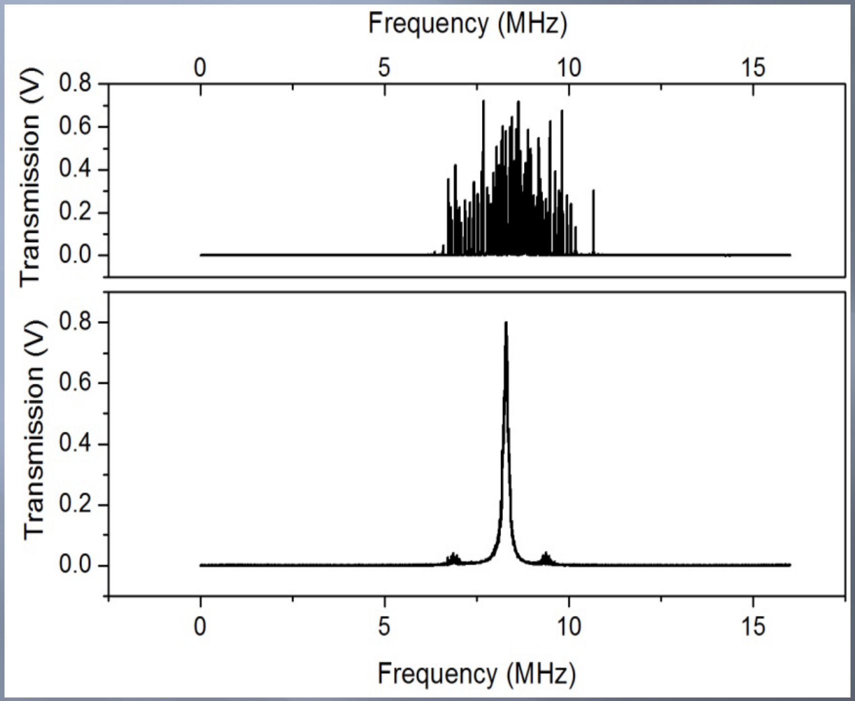
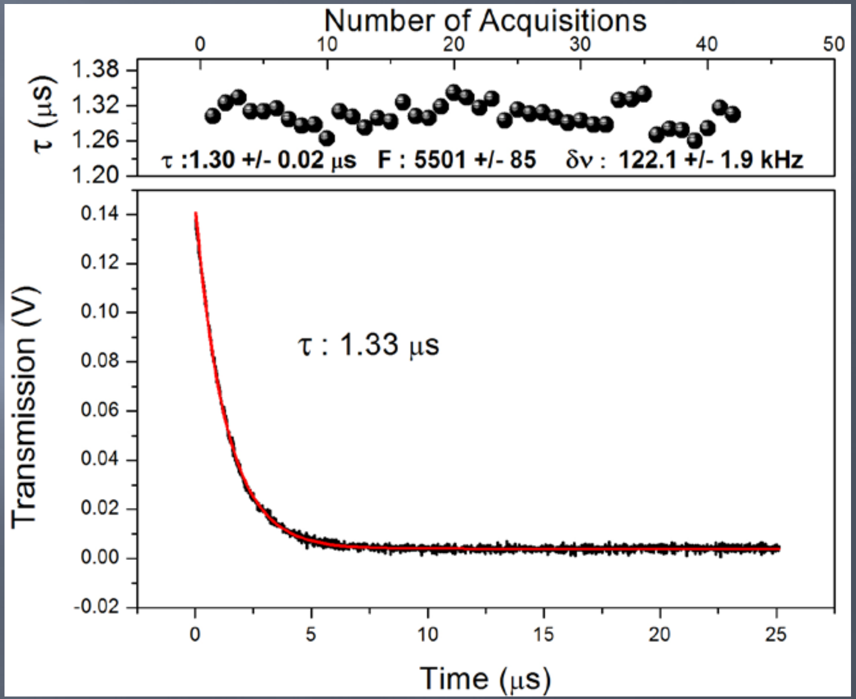


Fig. 3. Allan deviation analysis of the residual frequency fluctuations of the stabilized ECDL. The upper plot results from the time behavior of the NICE-OHMS error signal, as recorded with a sampling time of 4 ms. Calculated Allan deviations as a function of the integration times are shown in the lower plot (with absolute values on the left axis and relative ones on the right axis). The relative stability is 5×10^{-13} for an integration time of 1 s. Colored lines do not correspond to a fit of the data.

H. Dinesan, E. Fasci, A. Castrillo, and L. Gianfrani, Optics Letters 39, 2198-2201 (2014)

The new reference laser





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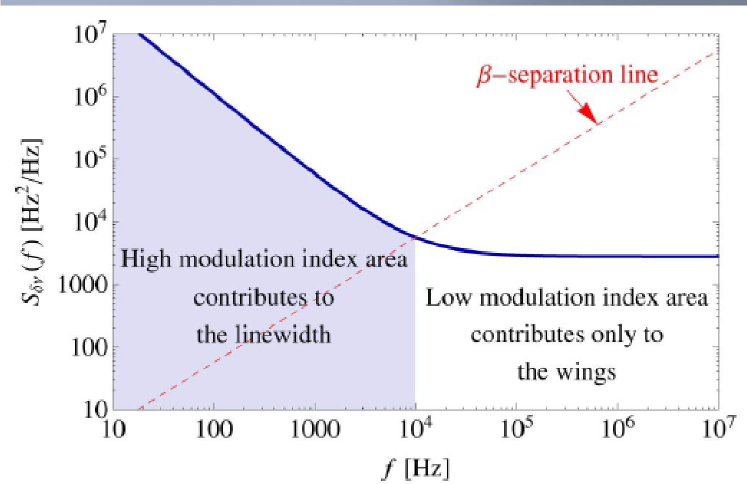


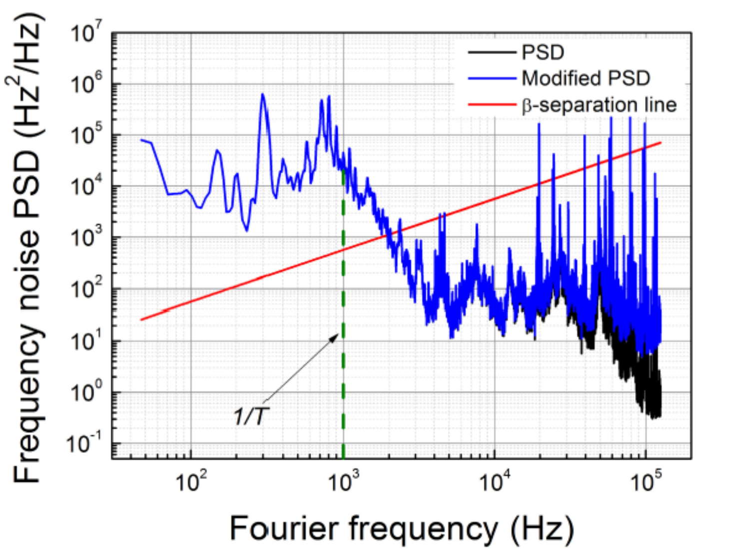


Fig. 4. Frequency-noise power spectral density, as measured from the cavity-transmitted signal with the cavity side-locked to the laser. The β-line is also shown, along with the indication of a cut-off frequency of 1 kHz corresponding to an observation time of 1 ms. For Fourier frequencies larger than 100 kHz, the frequency noise is clearly smaller than 1 Hz^2/Hz. The spectrum has been modified (see the blue trace) to take into account the 122 kHz cavity cutoff.

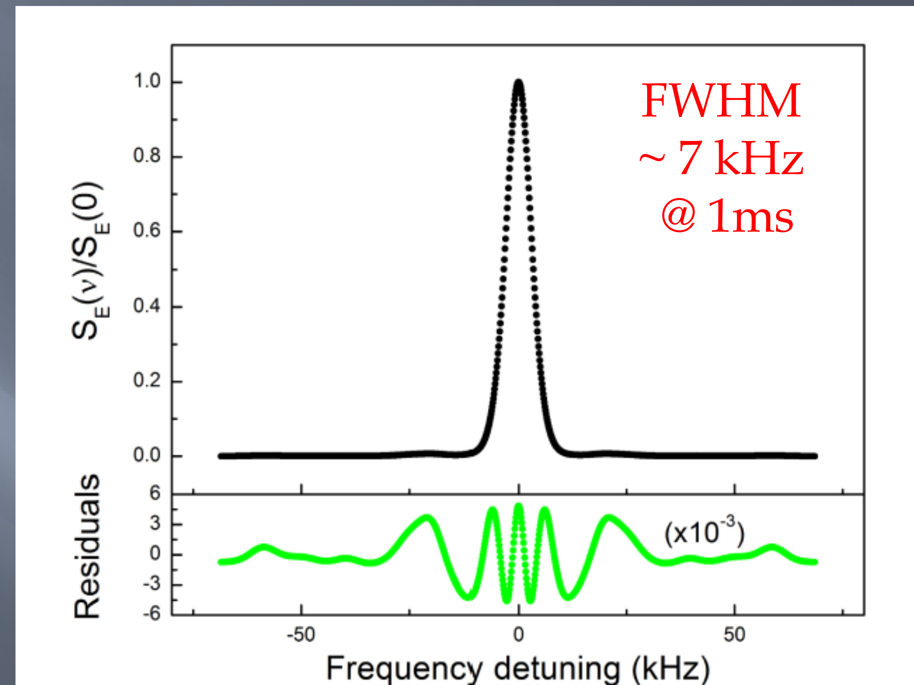
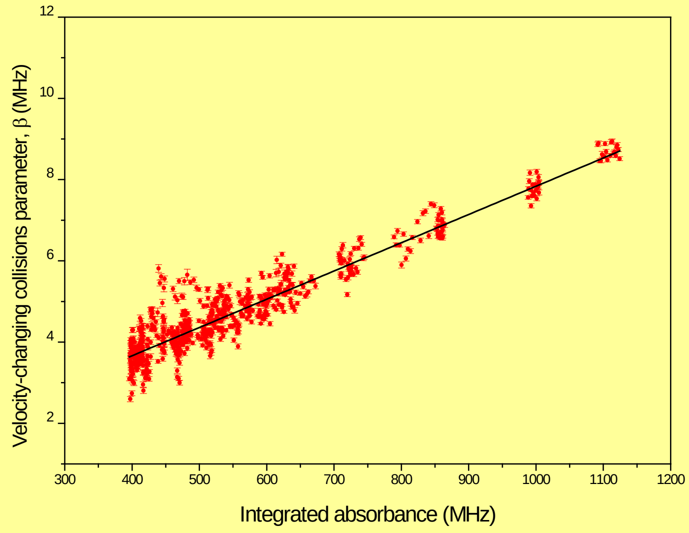


Fig. 6. The laser emission profile (in terms of relative intensity) reconstructed from the frequency-noise power spectral density of Fig. 4, by using numerical integrations of Eqs. (2) and (3). The profile is reproduced by a Voigt convolution with a satisfactory agreement, as demonstrated by a nonlinear least-squares fit, whose residuals are shown in the bottom plot.

$$S_{\delta\nu}(f) = 8\ln(2)f/\pi^2$$

H. Dinesan, E. Fasci, A. D'Addio, A. Castrillo, and L. Gianfrani, Optics Express 23, 1757-1766 (2015).

Statistical correlation



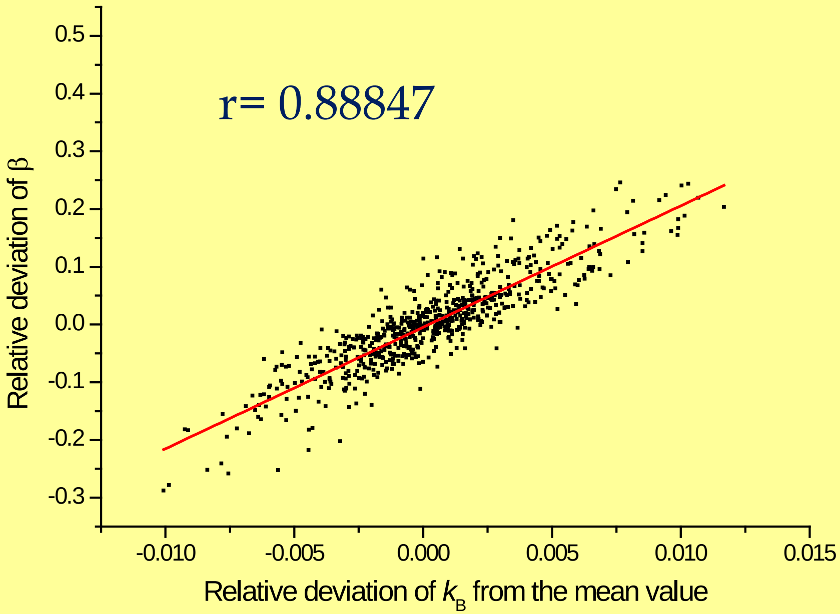
$\beta \leq k_B T / (2\pi m_a D)$

D → mass diffusion coefficient

For H_2O molecules, @ T = 296 K and p = 1 atm, $D = 1.7 \times 10^{-5}\ m^2/s$

CMDS:
N. H. Ngo, H. Tran, and R. R. Gamache, J. Chem. Phys. **136,** 154310 (2012);

Experiment:
L. R. Fokin and A. N. Kalashnikov, High temperature **46, 614** (2008).

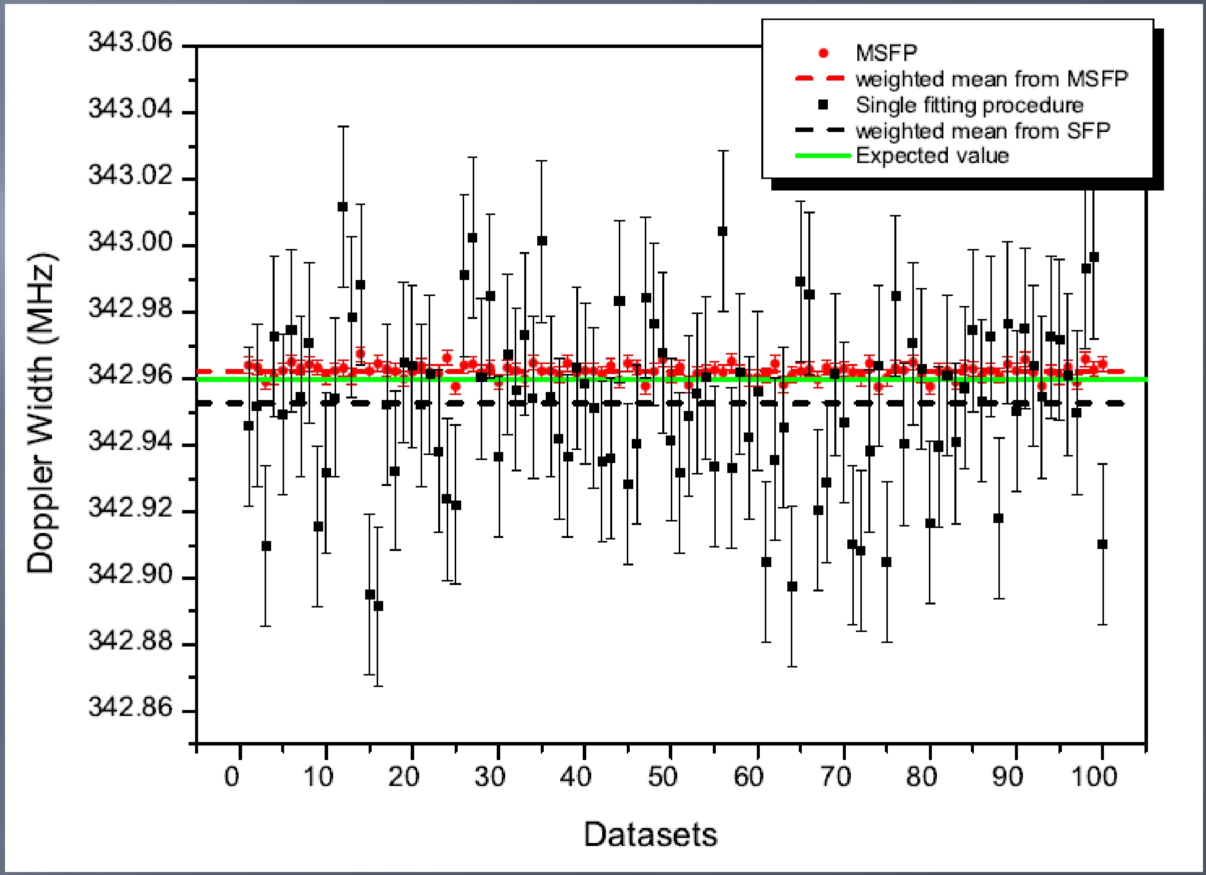


Solving the correlation issue….

Global fitting approach, tested on numerically simulated spectra

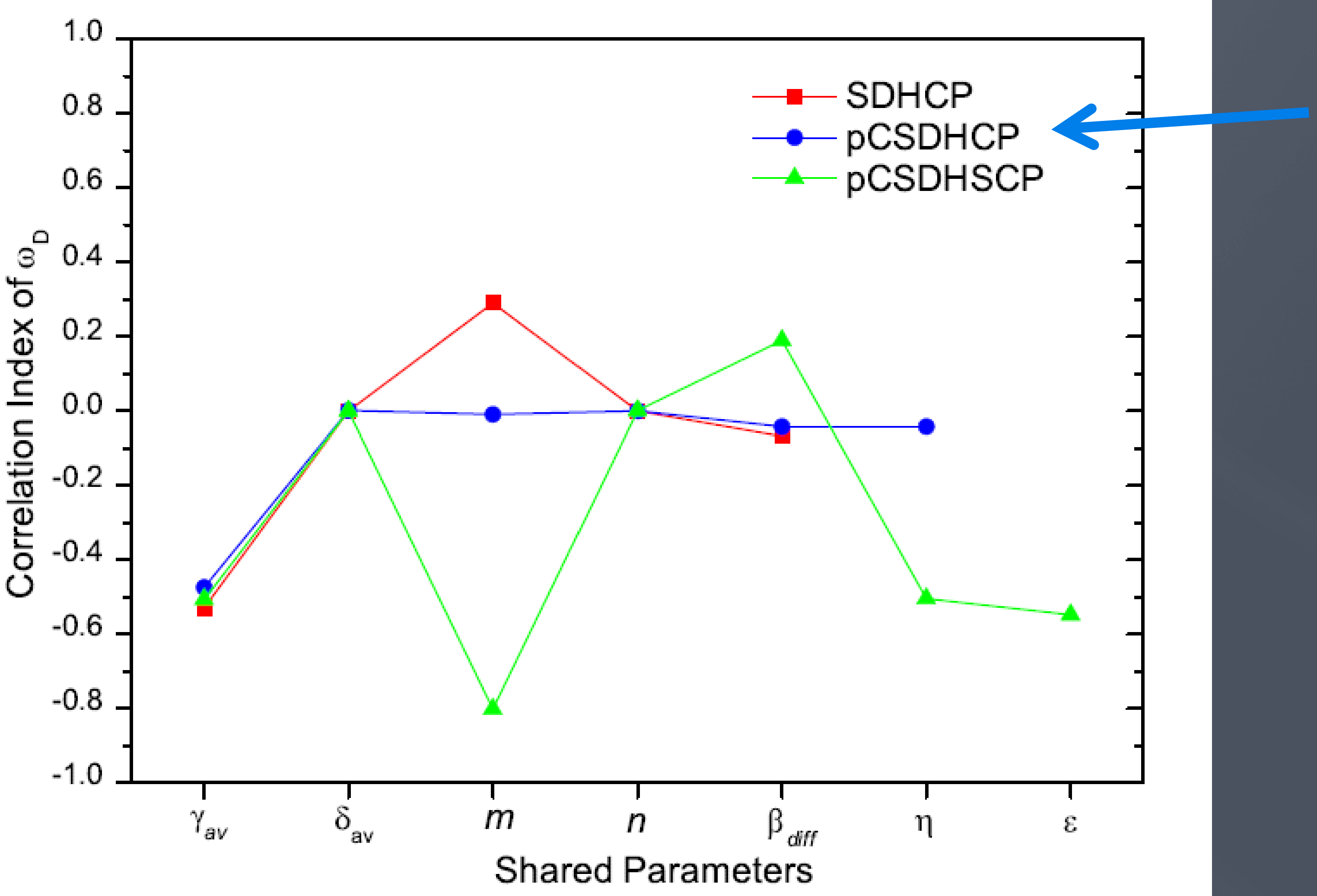
Individual fits:
Statistical uncertainty = 8 ppm
Systematical deviation = 21 ppm

Global fit:
Statistical uncertainty = 0.7 ppm
Systematical deviation = 6.7 ppm

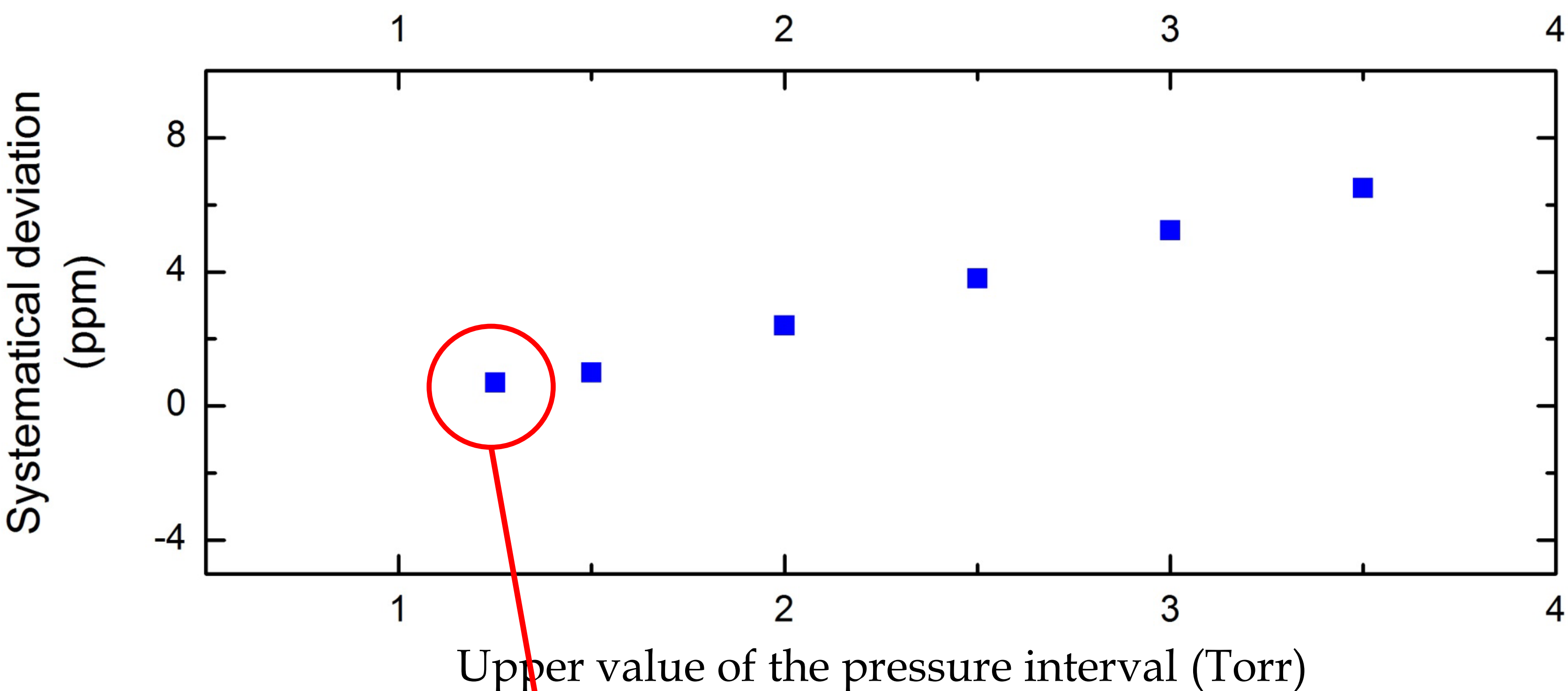


Total number of simulated spectra: 1000
S/N= 10000 T=273.16 K
Pressure range ($H_2{}^{18}O$): 10 – 460 Pa
Model (simulations): Partially Correlated Speed-Dependent Keilson-Stoner
Model (fits): Speed-Dependent Hard Collision

Correlation coefficients



Prospect for a determination at the ppm-level



0.7 ppm

It seems convenient to lower the pressure!

Conclusions and future work

- DBT is a very general and theoretically transparent approach to measure the thermodynamic temperature of a gaseous medium;
- It has the potential to contribute to the new definition of the unit kelvin;
- The choice of the lineshape model is crucial for a successful DBT experiment;

- By using the pcSDHC model we could provide a spectroscopic determination of k_B with a combined uncertainty of 24 ppm;
- Further improvements are still possible;

- NICE-OHMS has been developed for an improved stabilization of the MASTER laser;
- The probe laser is now phase-locked to the reference laser
- We have implemented a long path-length technique to lower the pressure;

- The 3rd generation experiment is in progress (please, visit the poster)!

The MPM Group at UniNA2

Seconda Università degli Studi di Napoli SUN

Thank you for the kind attention!

EURAMET
European Association of National Metrology Institutes

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union