Nuclear spin symmetry conservation in H_2O investigated by direct absorption FTIR spectroscopy of water vapor cooled down in supersonic expansion

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Introduction

o Nuclear spin conversion of water in the gas phase is still an open question

o Intramolecular processes in an individual water molecule can not lead to spin conversion.

o However an interaction between a water molecule and a water cluster has been evoked as a possible route towards ortho-para conversion (Manca Tanner et al 2013).

o Water clusters can be formed in an adiabatic expansion. However, ortho-para conversion in condensed phase occurs on a timescale of milliseconds (Limbach et al 2006; Abouaf-Marguin et al 2007; Sliter et al 2011). Is the "interaction time" long enough in a supersonic expansion to lead to nuclear spin conversion?

Previous work done by Manca Tanner et al. JPCA 2013

R($1_{1,0}$)
ortho

R($1_{1,1}$)
para

R($2_{1,2}$)
ortho
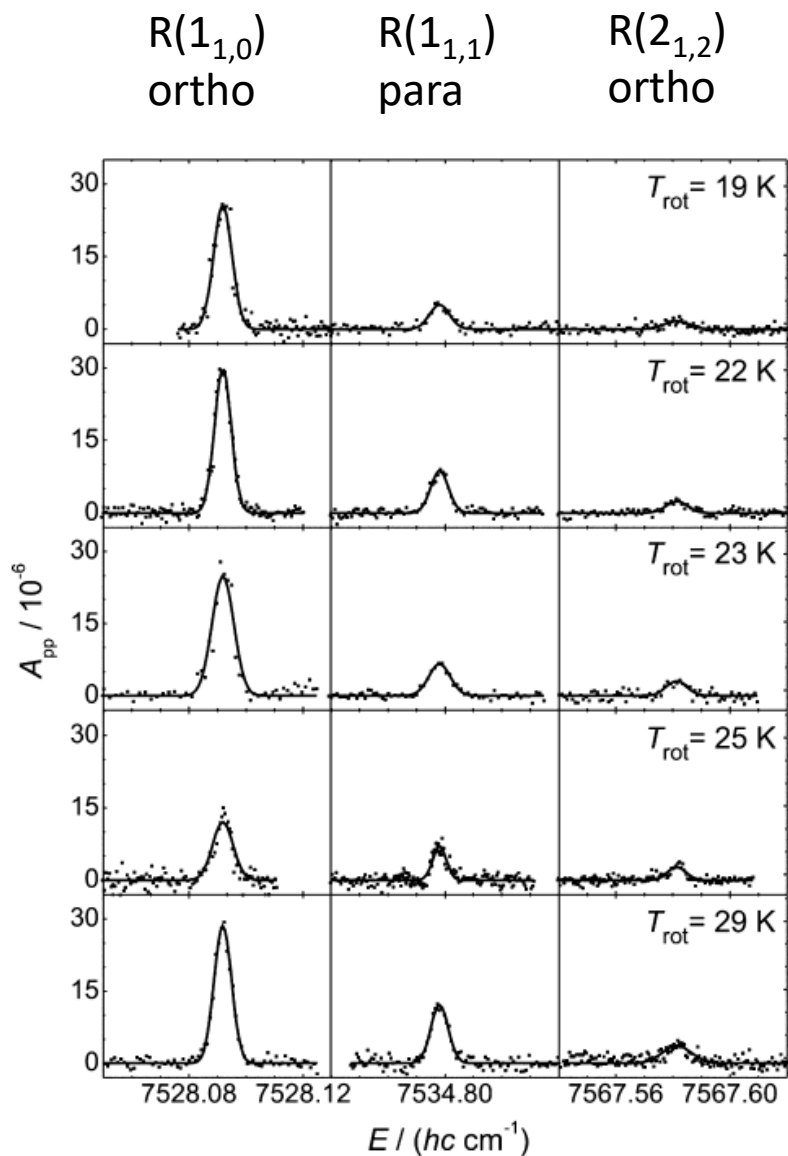
o CRDS + Slit jet expansion
o 2OH stretching range
o 3 rovibrational lines are observed
o Detection of water clusters not possible
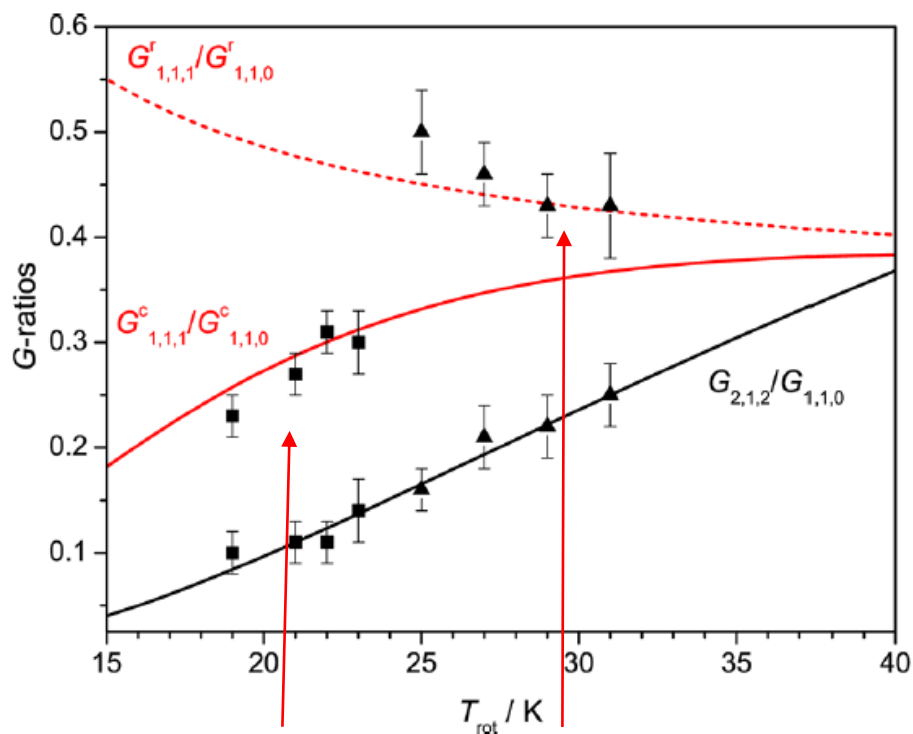
No conversion
(weak clustering)

Conversion !
(strong clustering)

Our objectives

o   Is the experiment performed by Manca Tanner *et al.* **reproducible**?

o   The **number of observed water transitions** has to be increased in order to get a reliable conclusion and to confirm (or to infirm) the results obtained by Manca Tanner *et al.*

o   Is it possible to detect **water clustering** which is supposed to play a major role in the nuclear spin conversion? What is the proportion of water molecules condensing in the jet?

o   Can we characterize the flow expansion accurately?

Rotational states associated to para- and ortho-H_2O

The Pauli exclusion principle states that the total wave function of H_2O must be antisymmetric under hydrogen atoms (fermions) exchange

$\Rightarrow$ Ortho- and para- molecules have different Rotational states

In the present study:
- Ground electronic state (symmetric wave function)
- Ground vibrationnel state (symmetric wave fucntion)

$$\psi_{Tot} = \psi_{elec} \times \psi_{vib} \times \underline{\psi_{rot} \times \psi_{ns}}$$

The symmetry of ψ_{Tot} depends on the symmetry of ψ_{rot} et ψ_{ns}

Rotational states associated to para- and ortho-H_2O

	K_aK_c	e,e	o,e	e,o	o,o
Γ_{rot}	C_{2v}	A_1	B_2	B_1	A_2
	M_{S4}	A^+	B^+	B^-	A^-
Γ_{ns}	M_{S4}	B^+	A^+	A^+	B^+
g		1	3	3	1

A symmetric rotational wave function [A^+/e,e or A^-/o,o] must correspond to an antisymmetric nuclear spin wave function [B^+], that is to say to para-H_2O with a statistical weight $g_{NS} = 1$.

An antisymmetric rotational wave function [B^+/o,e or B^-/e,o] must correspond to a symmetric nuclear spin wave function [A^+], that is to say to ortho-H_2O with a statistical weight $g_{NS} = 3$.

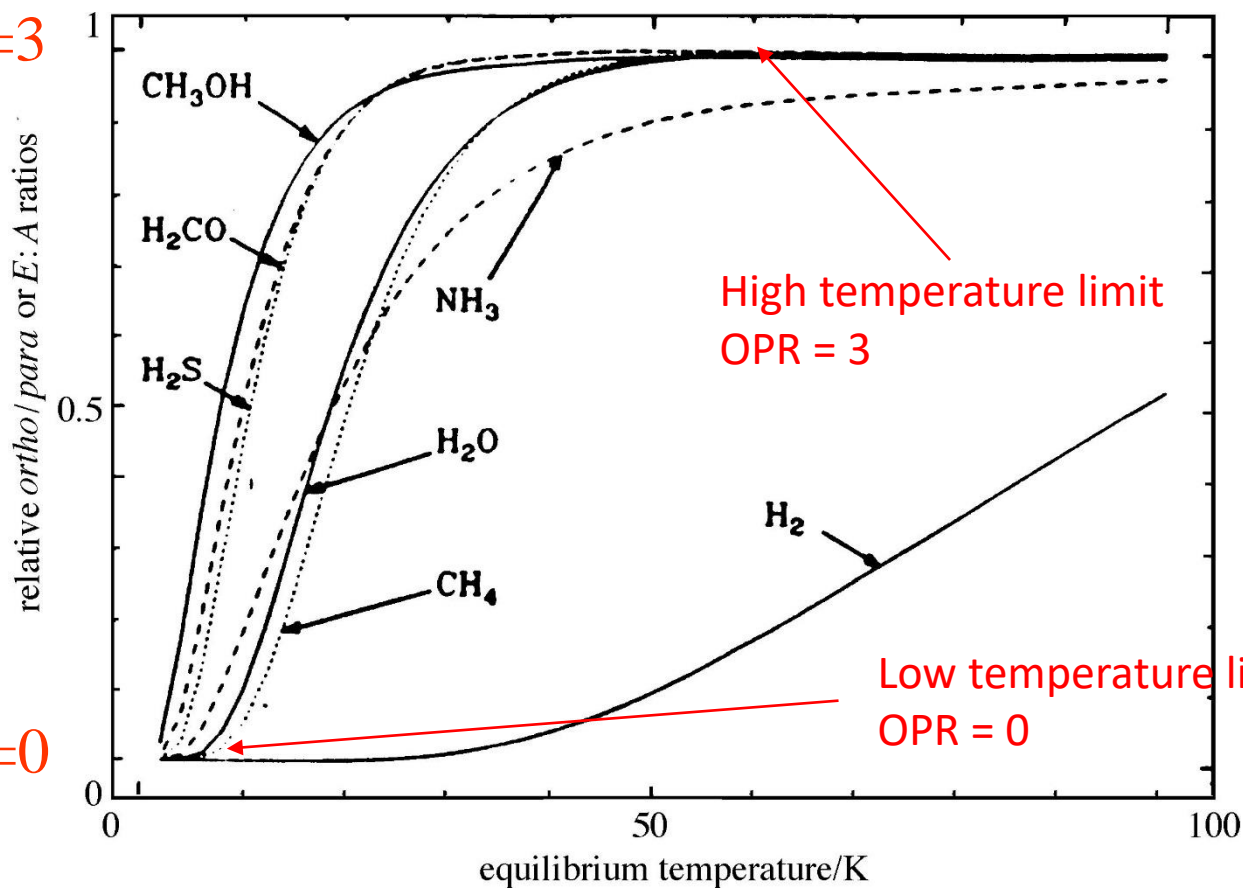# *Rotational states associated to para- and ortho-H$_2$O*
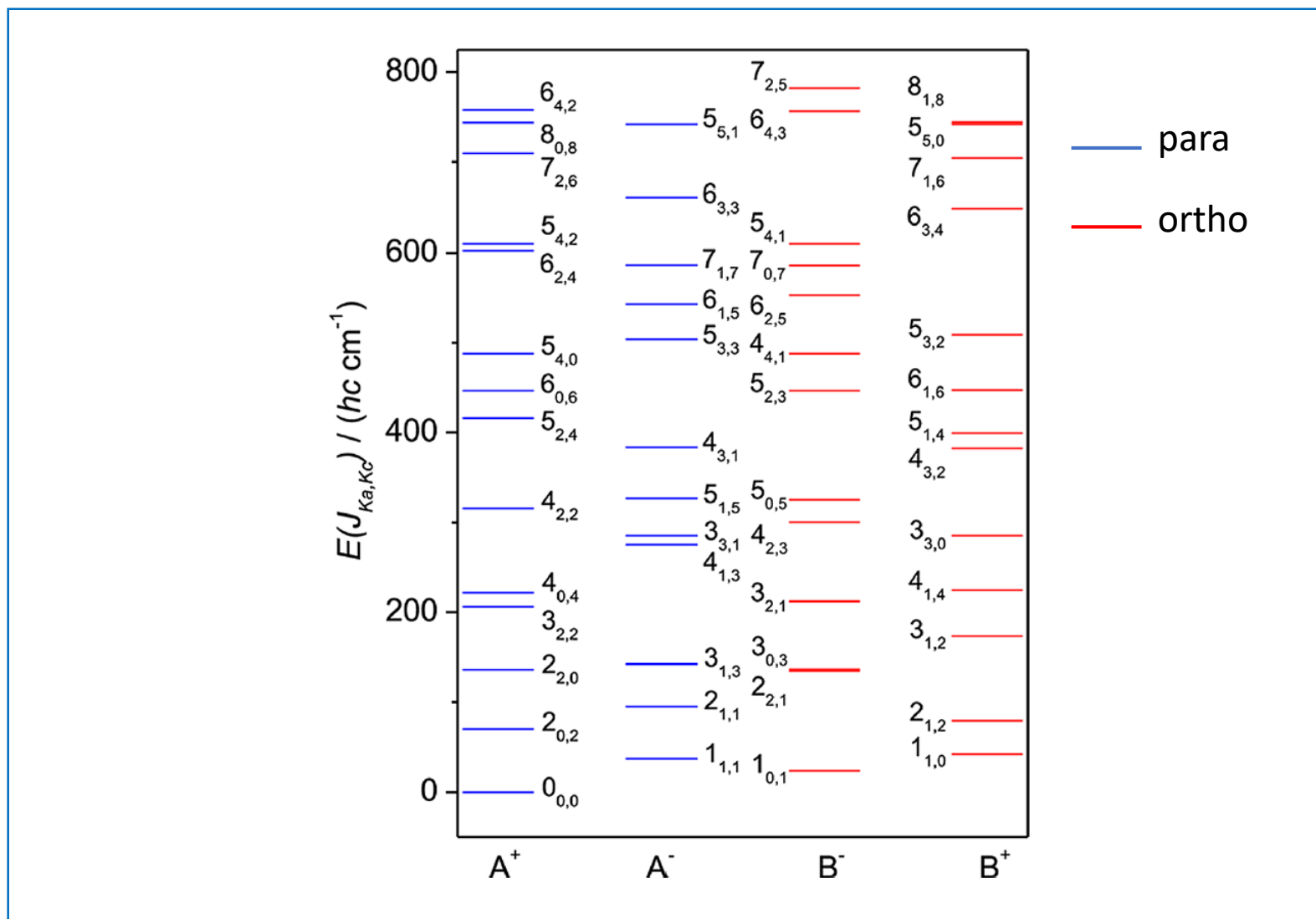
From Manca Tanner *et al*. JPCA 2013

Ortho-to-Para Ratio (OPR)

$$OPR(T) = \frac{\sum g_{NS}(\text{ortho})g_J(\text{ortho})\exp(-\frac{hcE_{\text{ortho}}}{kT})}{\sum g_{NS}(\text{para})g_J(\text{para})\exp(-\frac{hcE_{\text{para}}}{kT})}.$$

o/p=3

o/p=0

From Crovisier
Faraday Discuss.,
109, 437 (1998)

relative *ortho/para* or *E : A* ratios

CH$_3$OH

H$_2$CO

H$_2$S

NH$_3$

H$_2$O

CH$_4$

H$_2$

High temperature limit
OPR = 3

Low temperature limit (0 K)
OPR = 0

equilibrium temperature/K

The two limiting cases in a supersonic expansion

1. Instantaneous nuclear spin conversion (equilibrium)

    The OPR adapts instantly to the equilibrium curve as the temperature of the gas expansion evolves

$$OPR(T) = 3\frac{\sum g_J(\text{ortho})\exp(-\frac{hcE_{\text{ortho}}}{kT})}{\sum g_J(\text{para})\exp(-\frac{hcE_{\text{para}}}{kT})}.$$

2. Absence of nuclear spin conversion

    The number of ortho- and para- molecules remains what it was initially in the room temperature reservoir (OPR is fixed to 3)

$$OPR(T) = \left(\frac{g_{\text{NS}}(\text{ortho})}{g_{\text{NS}}(\text{para})}\right)_{\text{Slow}} \frac{\sum g_J(\text{ortho})\exp(-\frac{hcE_{\text{ortho}}}{kT})}{\sum g_J(\text{para})\exp(-\frac{hcE_{\text{para}}}{kT})} = 3$$
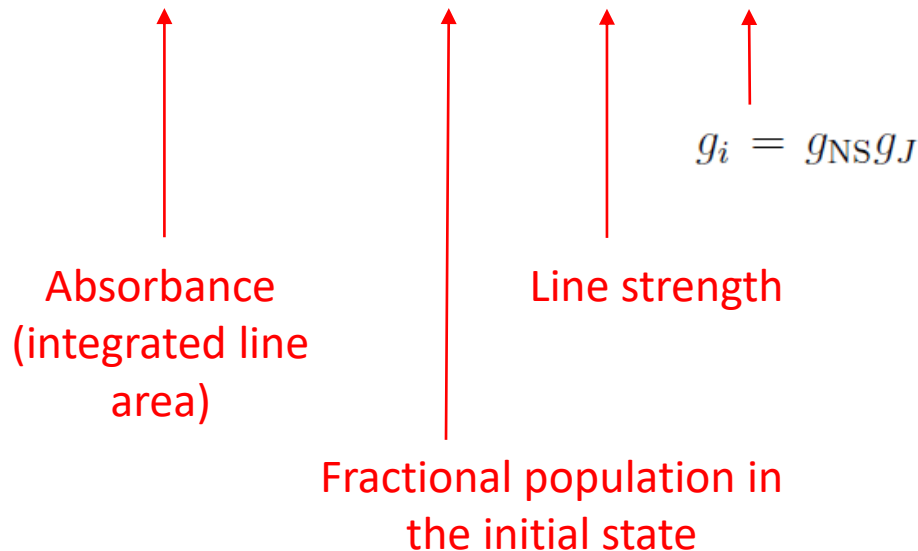
In that case, we have to consider an effective nuclear spin statistical weight

$$\left(\frac{g_{\text{NS}}(\text{ortho})}{g_{\text{NS}}(\text{para})}\right)_{\text{Slow}} = 3 \bigg/ \left(\frac{\sum g_J(\text{ortho})\exp(-\frac{hcE_{\text{ortho}}}{kT})}{\sum g_J(\text{para})\exp(-\frac{hcE_{\text{para}}}{kT})}\right)$$
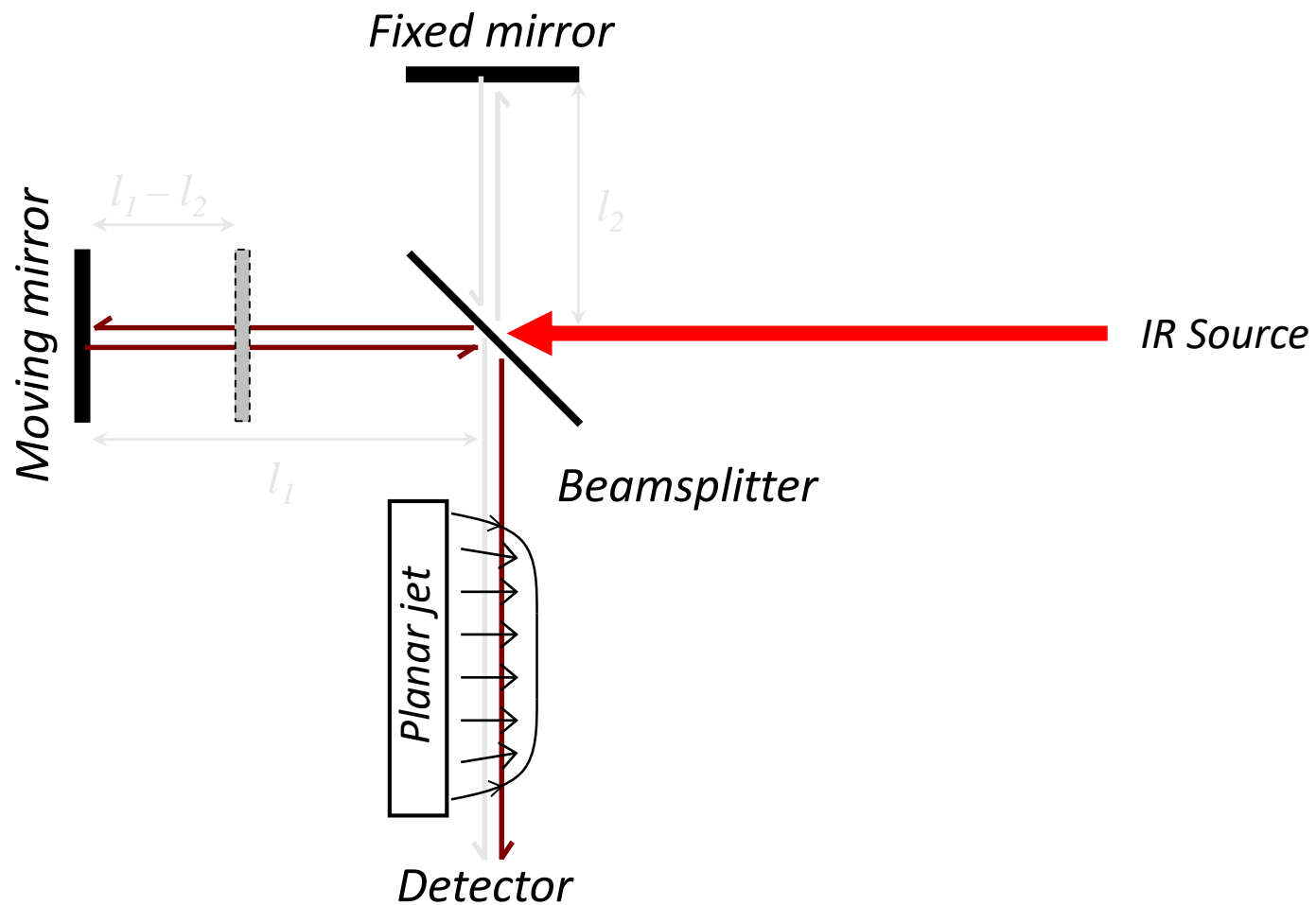
How to access to the number of nuclear spin isomers?

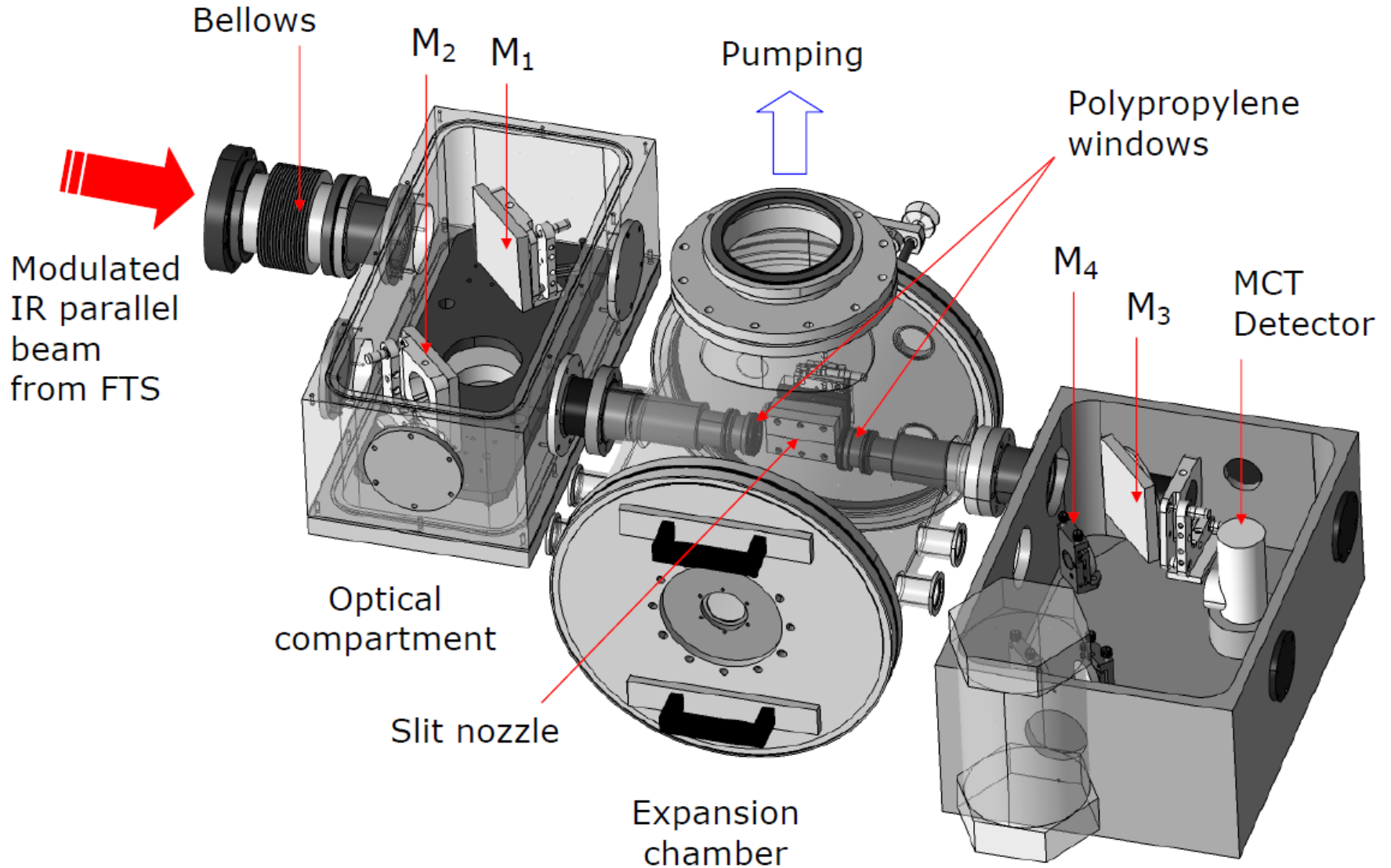This information is extracted from the absorption line intensities (absorbances)

$$\frac{A_{fi}}{A_{f'i'}} = \frac{F_{fi}^N}{F_{f'i'}^N} \times \frac{n_i}{n_{i'}} = \frac{F_{fi}^N}{F_{f'i'}^N} \times \frac{g_i}{g_{i'}} \exp\left(-\frac{hc(E_i - E_{i'})}{kT}\right)$$
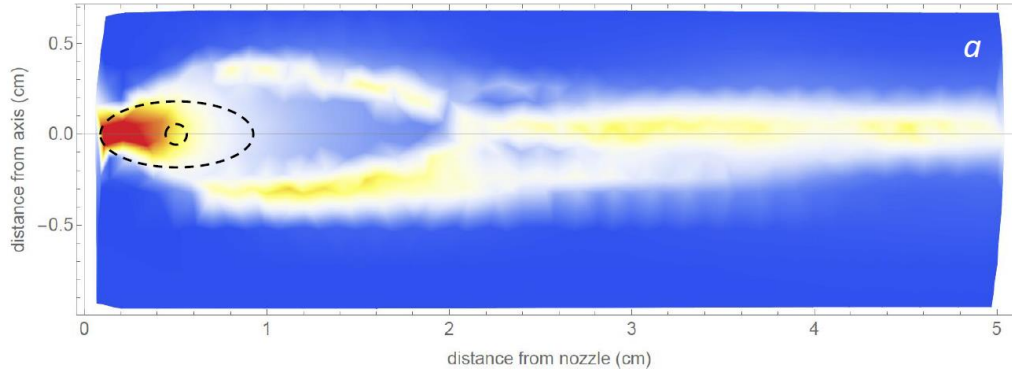
$$g_i = g_{\text{NS}} g_J$$

Absorbance (integrated line area)

Fractional population in the initial state

Line strength

Direct absorption FTIR spectroscopy

Jet-AILES apparatus

Bellows

M₂ M₁

Pumping

Polypropylene windows

Modulated IR parallel beam from FTS

M₄ M₃ MCT Detector

Optical compartment

Slit nozzle

Expansion chamber

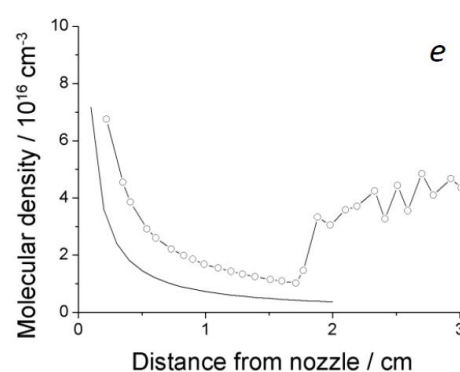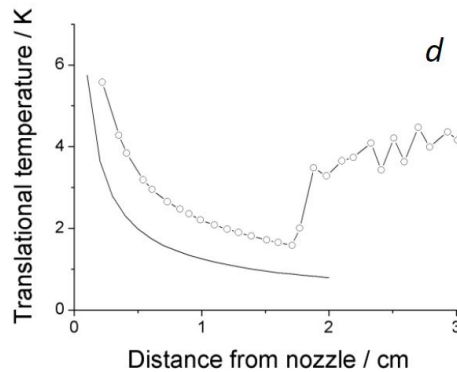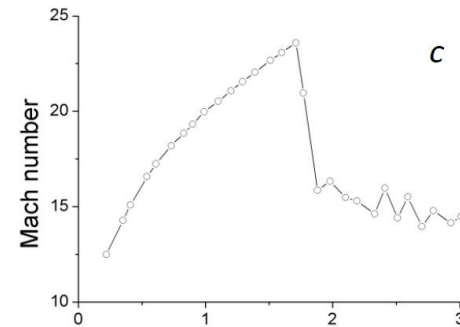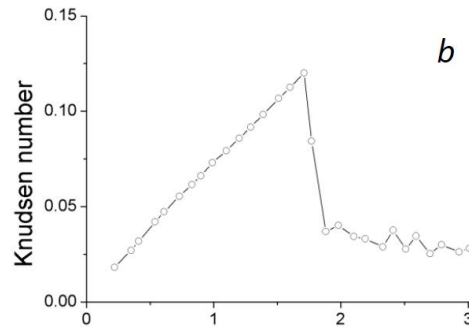# Supersonic slit-jet expansion (characterized by Pitot probe)

Slit dimension
Width either 18 or 36 μm
Length 60 mm

Hydrodynamic time
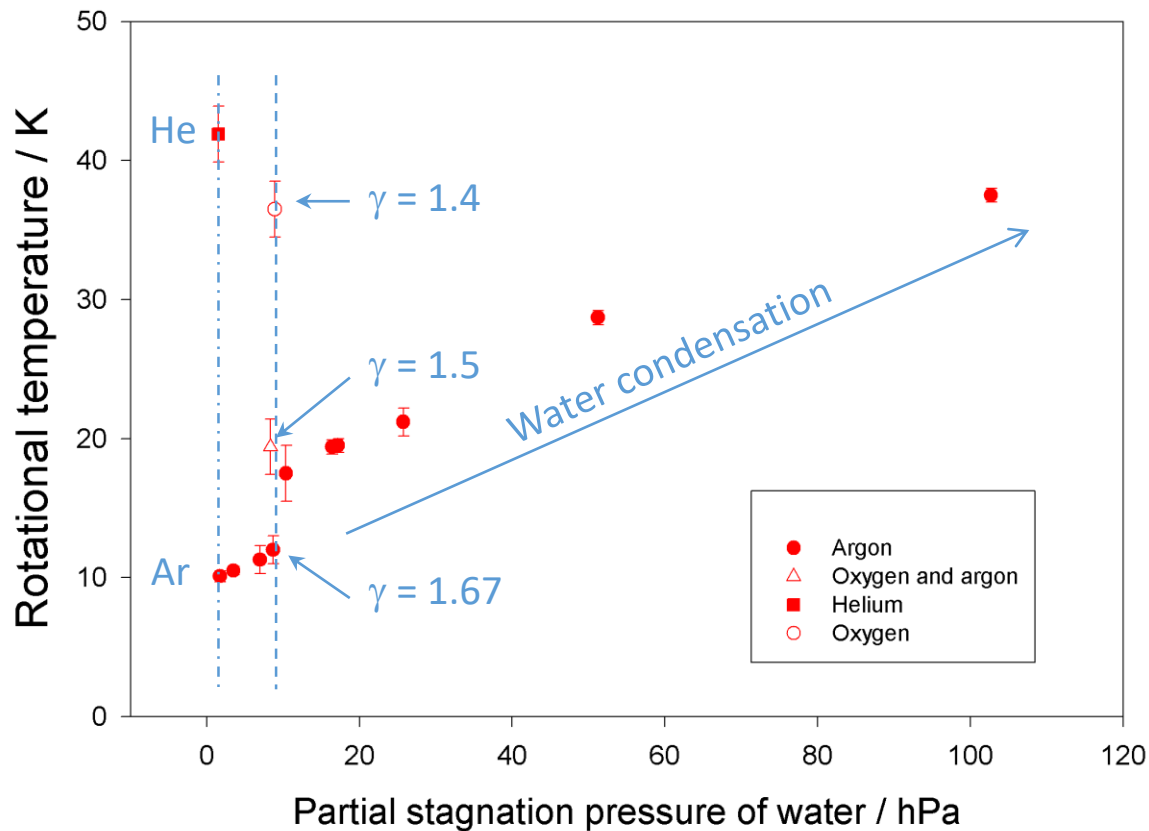between 3 (He) and 9 (Ar) μs

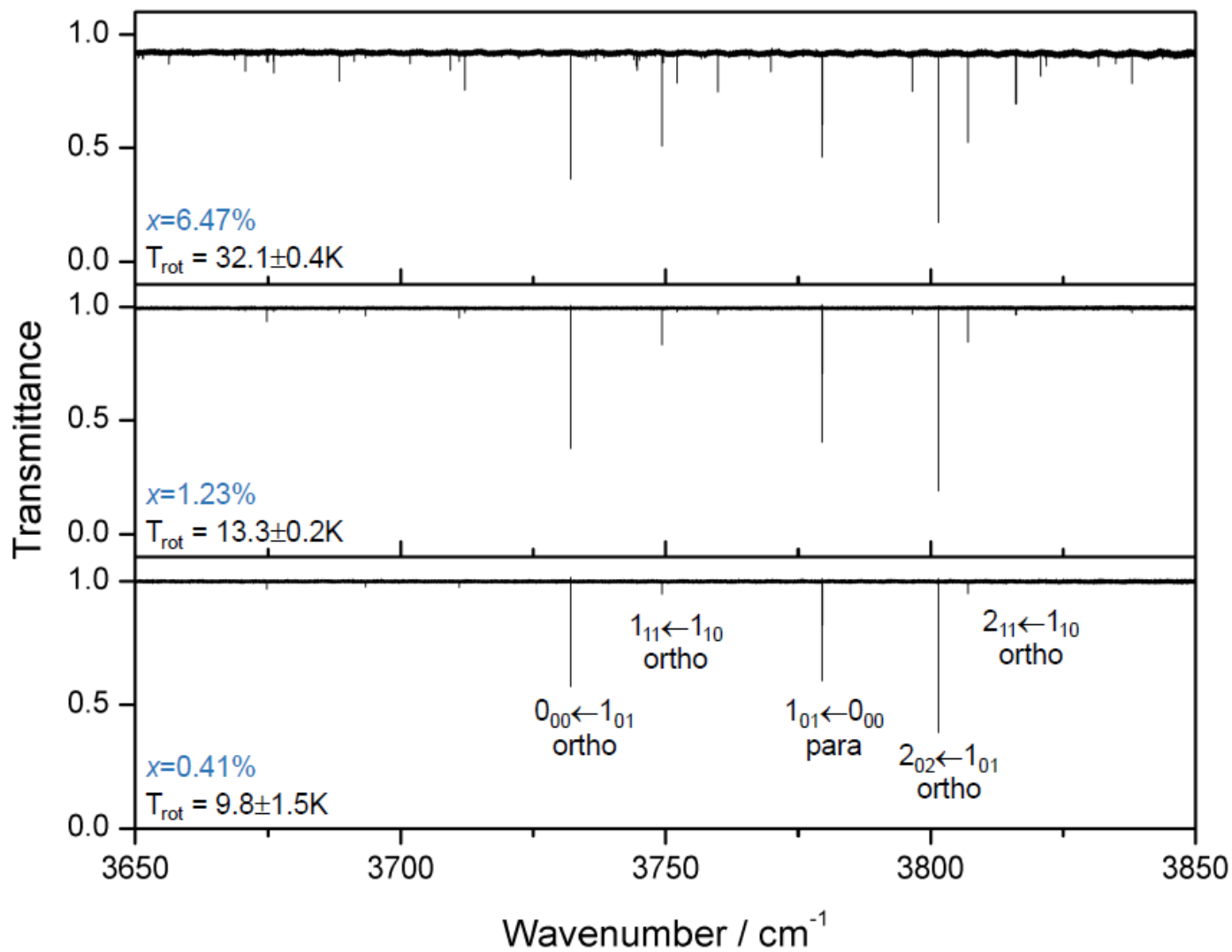The **gas concentration** can be easily estimated from these measurements

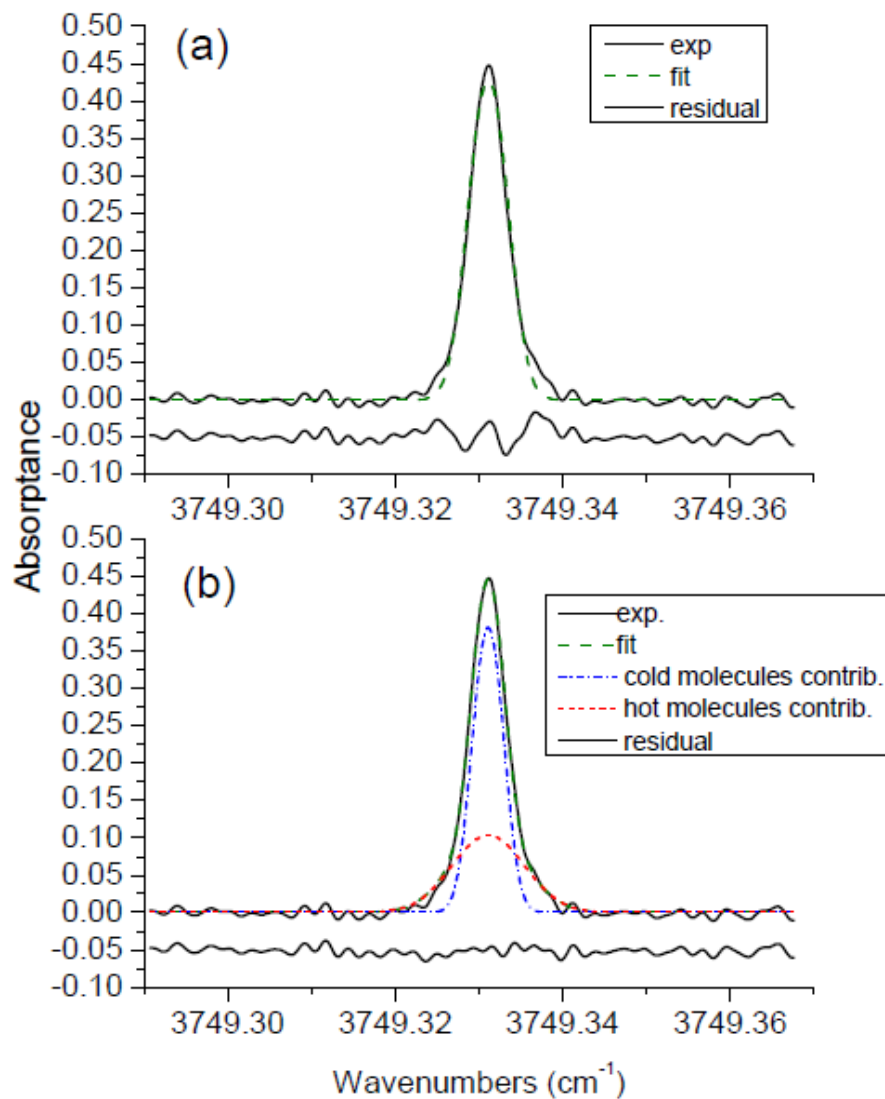# *Tuning of the temperature*

Temperature is tuned by:
o   condensing a fraction of the water vapor in the expansion
o   changing the specific heat ratio of the carrier gas
o   changing the rotational relaxation efficiency of the carrier gas

Few spectra (OH stretching region)
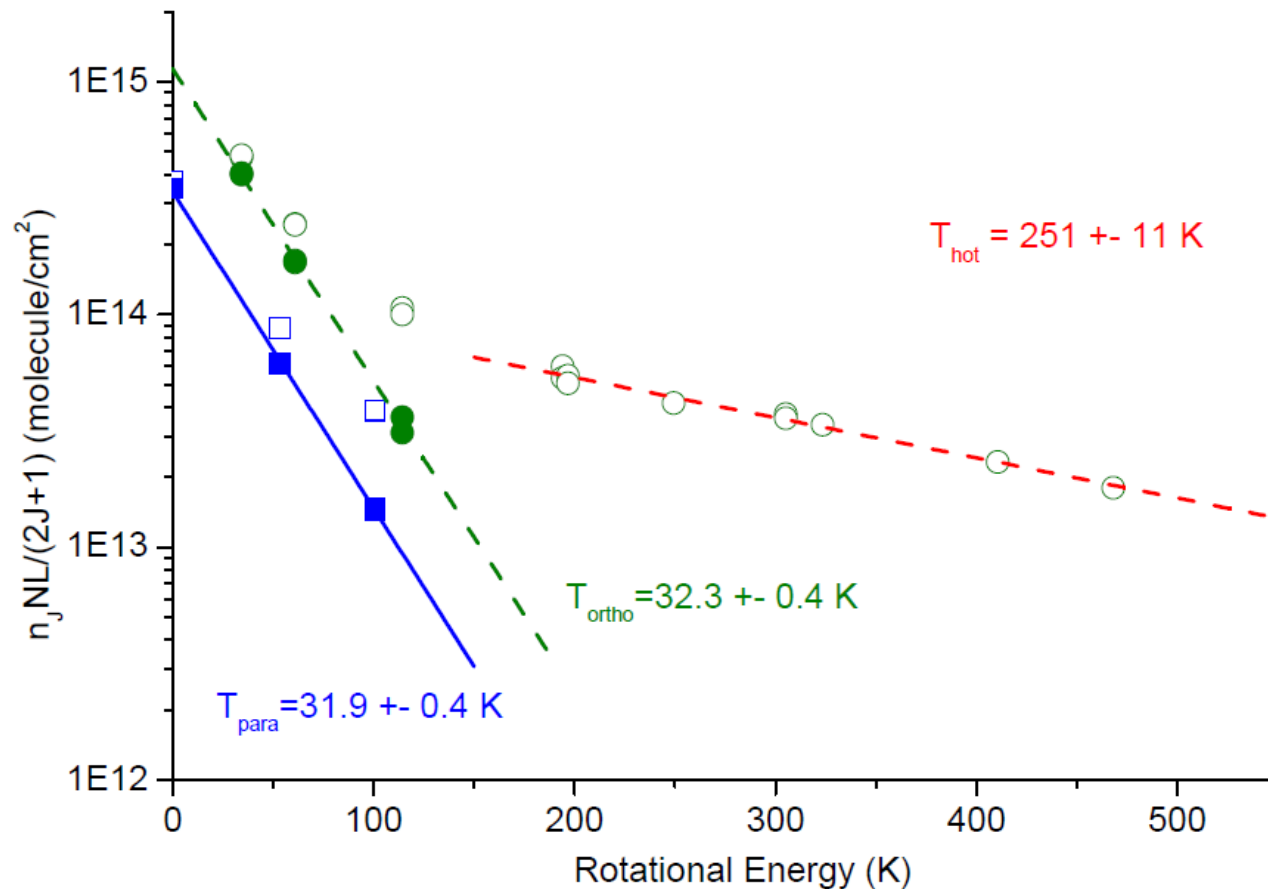
Few spectra (OH stretching region)

Instrumental resolution: 0.002 cm^{-1}

Rotational temperature

o Example of **"Boltzmann plot"** used to extract the rotational temperature from the absorbance spectra
o Ortho and para lines are treated separately
o The low temperature is corrected from the warm gas contribution

Experimental conditions

Carrier gas			H₂O			P_{H_2O}	P_0^b	P_{ch}^c	d^{*d}	$T_{rot}(O/P)^e$	NL_{cold}^f 10^{14}	T_{hot}^g	NL_{hot}^f 10^{14}	τ_{hyd}^h	x_{cond}^i
Ar	He	O₂	g/h	slm	x^a%	hPa	hPa	hPa	µm	K	molec/cm²	K	molec/cm²	µs	%
	slm														
20			2	0.041	0.21	1.73	843	0.71	36	10.7±1.6 / -	1.1±0.3	-	-	8.8	75
20			4	0.083	0.41	3.46	843	0.71	36	9.8±0.6 / -	3.0±0.5	-	-	8.8	65
20			8	0.166	0.82	6.94	843	0.71	36	11.6±0.3 / 13.4±2.7	4.3±0.3	288±50	5.2±0.1	8.8	75
20			10	0.238	1.04	8.68	843	0.71	36	12.0±0.6 / 12.7±0.5	4.8±0.2	167±13	5.6±0.1	8.8	78
20			12	0.249	1.23	10.37	843	0.71	36	13.0±0.6 / 13.3±0.1	6.0±0.6	176±30	5.6±1.0	8.8	77
20			20	0.415	2.03	17.15	845	0.71	36	20.2±0.5 / 18.9±0.4	11.8±1.3	225±25	10.2±1.4	8.8	72
20			30	0.622	3.01	25.68	853	0.72	36	22.4±0.3 /24.1±1	15.3±0.7	257±15	17.6±2.4	8.8	76
30			20	0.415	1.36	16.35	1202	1.04	36	18.9±1.3 / 18.7±0.4	8.8±0.8	-	-	8.8	78
30			50	1.037	3.34	51.20	1533	1.09	18	25.3±0.6 / 25.7±1.3	13.5±1.5	237±13	28.4±2.2	8.8	79
30			100	2.074	6.47	102.74	1588	1.11	18	32.3±0.4 / 31.9±0.4	22.2±1.7	251±11	53.5±1.7	8.8	83
		20	8	0.166	0.82	8.88	1083	0.69	18	31.3±0.5 / 30.4±4	10.4±0.1	-	-	6.6	0
20		20	8	0.166	0.41	8.25	2013	1.33	18	21.8±2 /18.0±4	7.8±1.2	-	-	7.6	0
	30		4	0.083	0.28	1.54	549	1.11	36	41.8±3 / 39.7±4	3.8±0.2	-	-	2.8	0

^{a}water vapor/carrier gas molar ratio; ^{b}stagnation pressure; ^{c}residual pressure in the expansion chamber; ^{d}nozzle width (the slit length is 60 mm); ^{e}rotational temperature extracted from *ortho* (O) or *para* rovibrational lines (P); ^{f}column densities for hot and cold gases (see text for details); ^{g} rotational temperature of the warm residual gas in shear layers; ^{h}hydrodynamic time; ^{i}fraction of condensed water vapor.
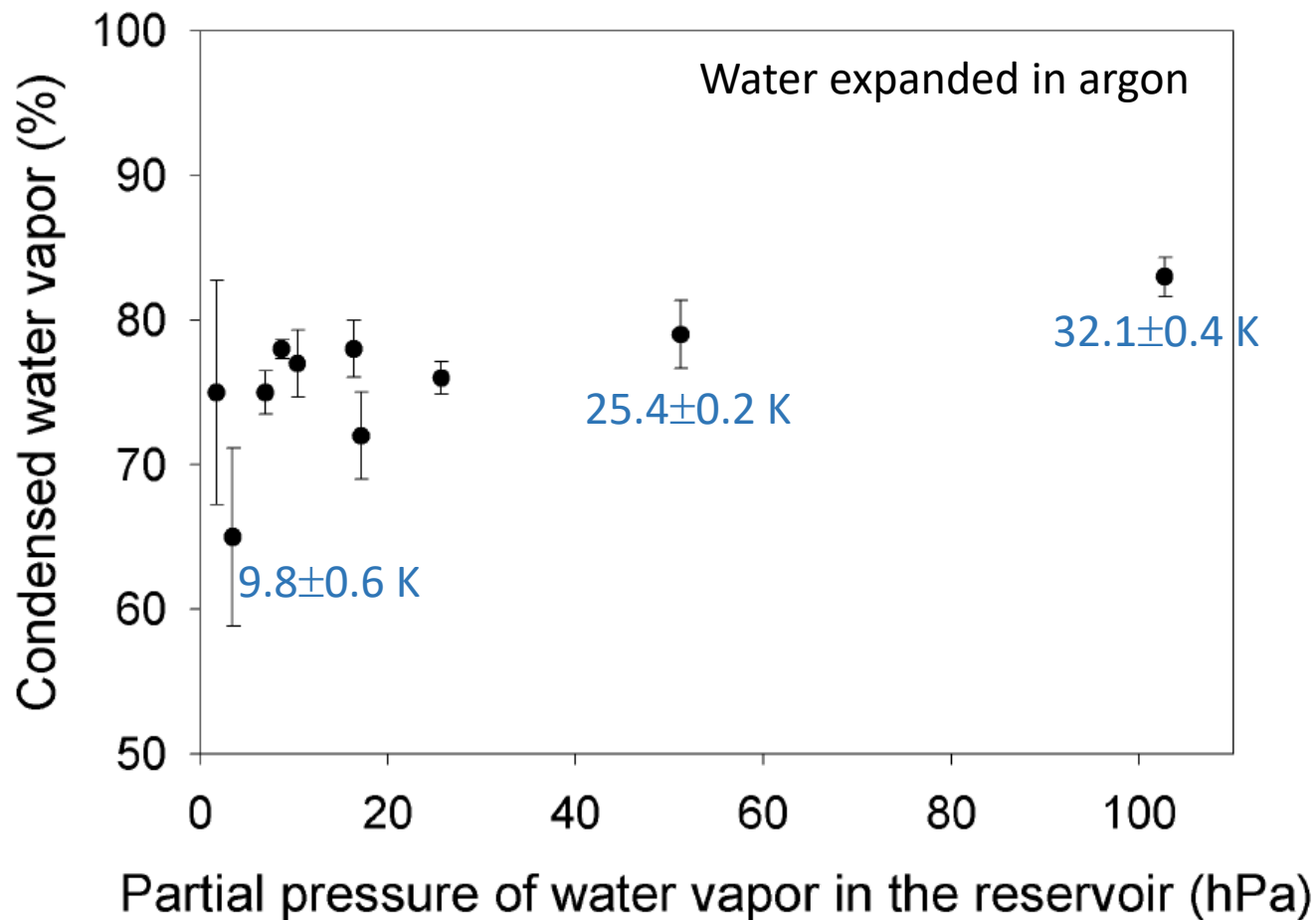
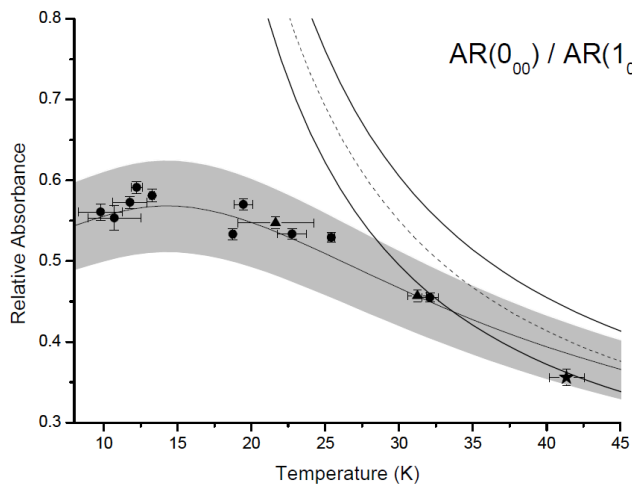# Water clusters signature
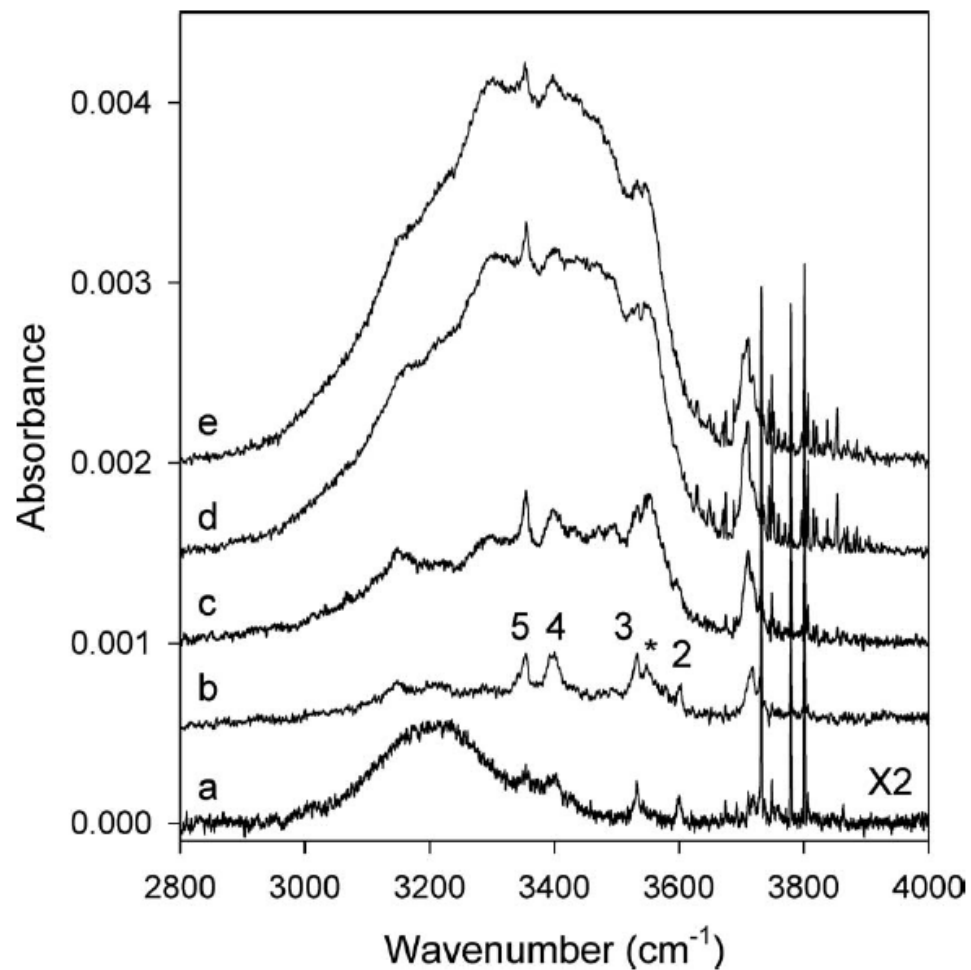
Water clustering
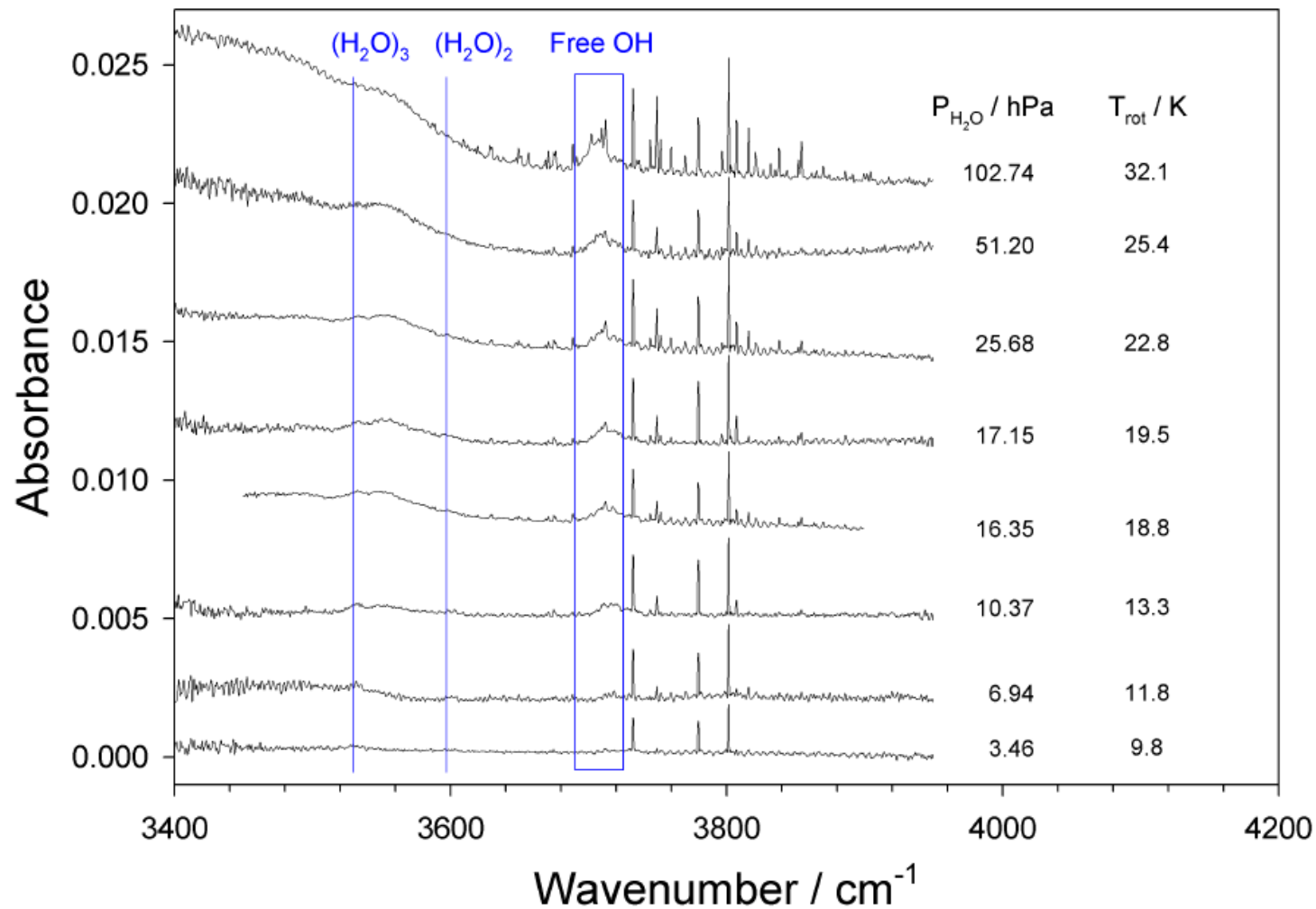
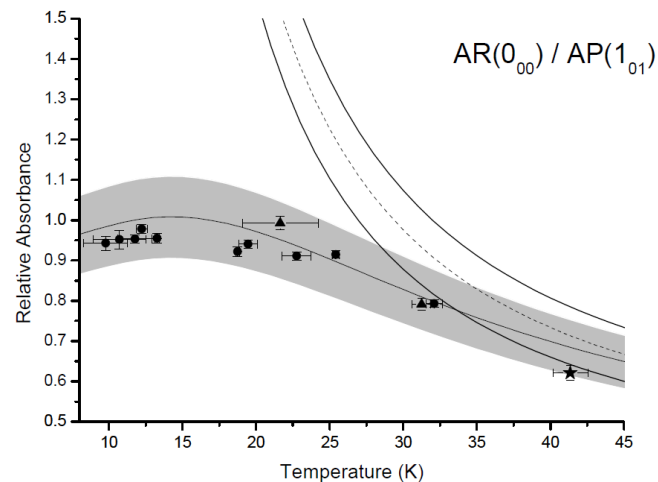Intrum. Resolution
1 cm^{-1}

Water condensation

o Water vapor condenses all the more as its partial pressure is high
o A maximum of 83% of condensation is achieved in argon
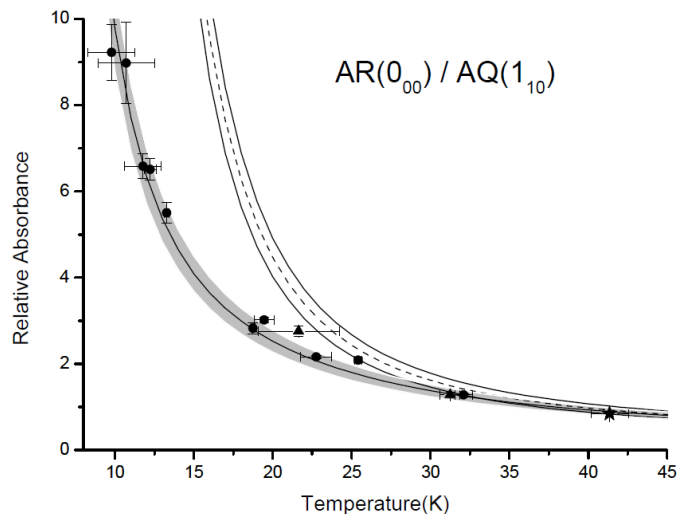o Condensation is responsible for a significant rise in temperature
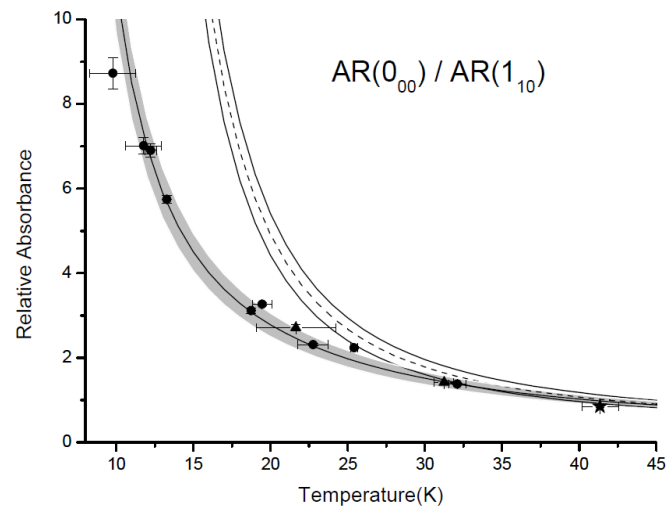
No nuclear spin conversion was observed…

AR(0$_{00}$) / AR(1$_{01}$)

$A_{1_{01}\leftarrow 0_{00}}/A_{2_{02}\leftarrow 1_{01}}$

AR(0$_{00}$) / AP(1$_{01}$)

$A_{1_{01}\leftarrow 0_{00}}/A_{0_{00}\leftarrow 1_{01}}$

AR(0$_{00}$) / AQ(1$_{10}$)

$A_{1_{01}\leftarrow 0_{00}}/A_{1_{11}\leftarrow 1_{10}}$

AR(0$_{00}$) / AR(1$_{10}$)

$A_{1_{01}\leftarrow 0_{00}}/A_{2_{11}\leftarrow 1_{10}}$

Conclusion

Unlike Manca Tanner's study, no nuclear spin conversion was observed in our supersonic expansion, despite:

- Similar jet conditions
- A very good signal-to-noise ratio
- A direct observation of water clusters
- A larger covered temperature range (10 – 42 K)
- A larger range of water mole fraction (0.2 – 6.5%)

Perspective   Use of de Laval nozzle uniform flows instead of free-jet expansions

- o Interaction time increased from few μs to ~1 ms
- o Intense clustering
- o Equilibrated translational and rotational temperatures