Temperature dependence of the spectroscopic parameters for the magnetic dipole transitions in the 1.27 µm O_2 band

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Context: traditional use of 0.76µm band

Column-averaged mole fraction XCO_2

$$XCO_2 = \frac{CO_2^{col}}{O_2^{col}/0.2095}$$

0.76µm: O_2 *A*-band
$(b^1\Sigma_g^+ (v=0) - X\,^3\Sigma_g^-(v=0))$

Well-established : used in SCIAMACHY, OCO-2, TCCON, MicroCarb

But drawbacks:

- Largely saturated
- Fairly far from the 1.6 µm band of CO_2

1.27µm: O_2 *a*-band
$(a^1\Delta_g(v=0) - X\,^3\Sigma_g^-(v=0))$

Advantages: weaker & closer to 1.6 µm

But: intense dayglow emission
Now well modelled by Sun et al. in GRL (2018)

MicroCarb is a test mission: both bands will be used and compared

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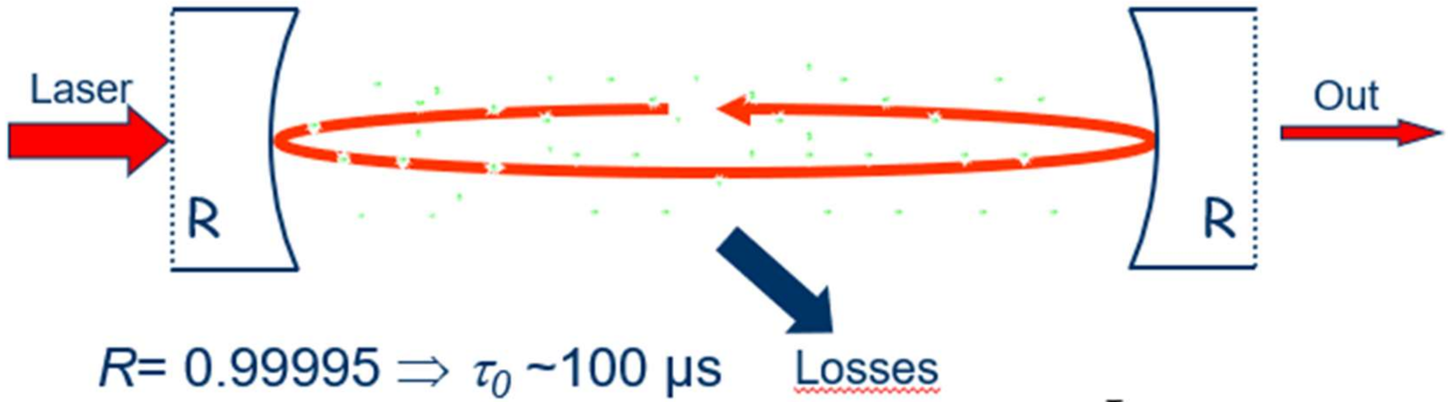
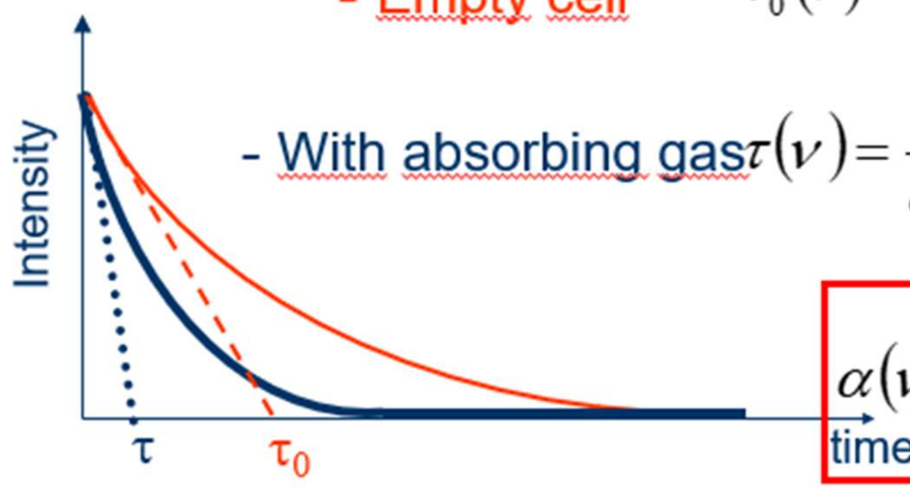
The CRDS technique



$R = 0.99995 \Rightarrow \tau_0 \sim 100\ \mu s$

- Empty cell $\tau_0(\nu) = \dfrac{L_{cav}}{c(1 - R(\nu))}$

- With absorbing gas $\tau(\nu) = \dfrac{nL_{cav}}{c(1 - R(\nu) + \alpha L_{cav})}$

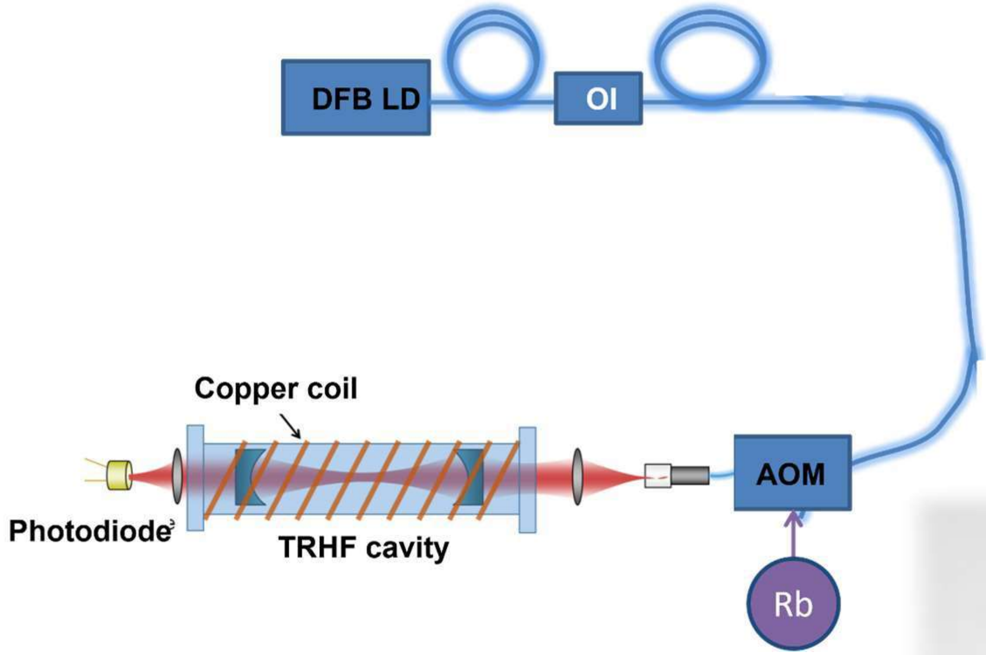


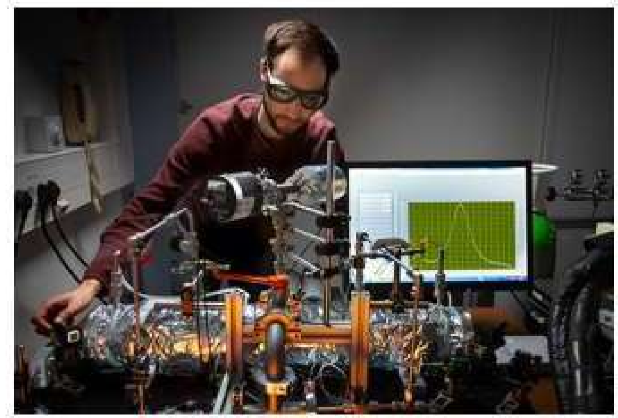
$$\alpha(\nu) = \frac{1}{c}\left(\frac{n}{\tau(\nu)} - \frac{1}{\tau_0(\nu)}\right)$$

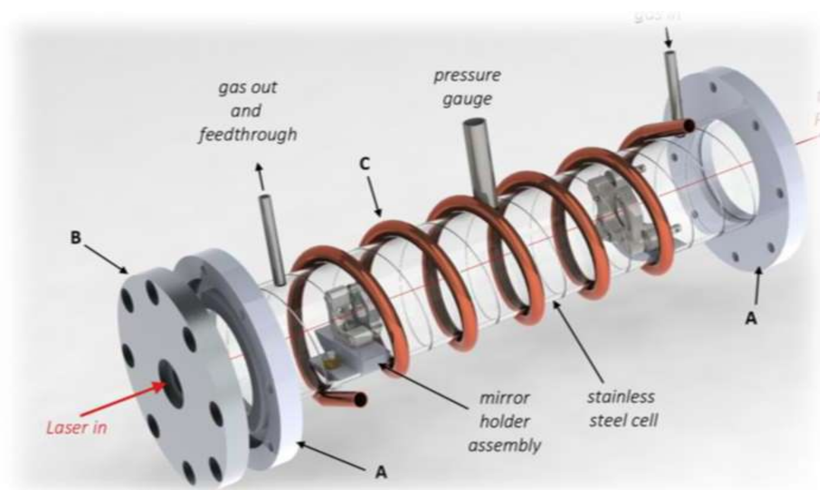
CRDS set-up

L_{abs_eq} ~ 16.5 km

High sensitivity α_{min}~ 5×10^{-11} cm^{-1}





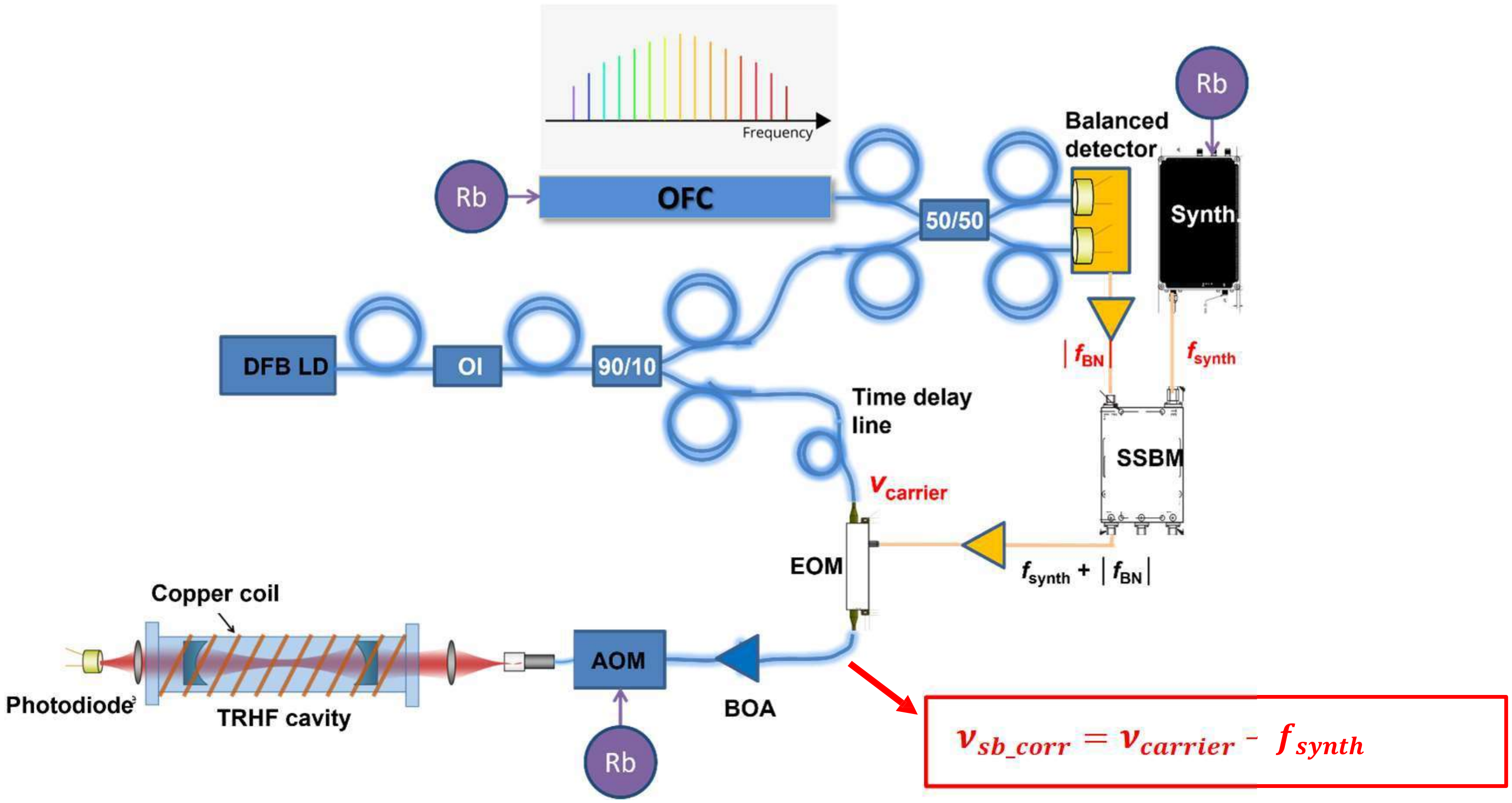


Temperature range:

243 to 333 K

ΔT_{max}< 0.1 K

Comb coherence transfer approach



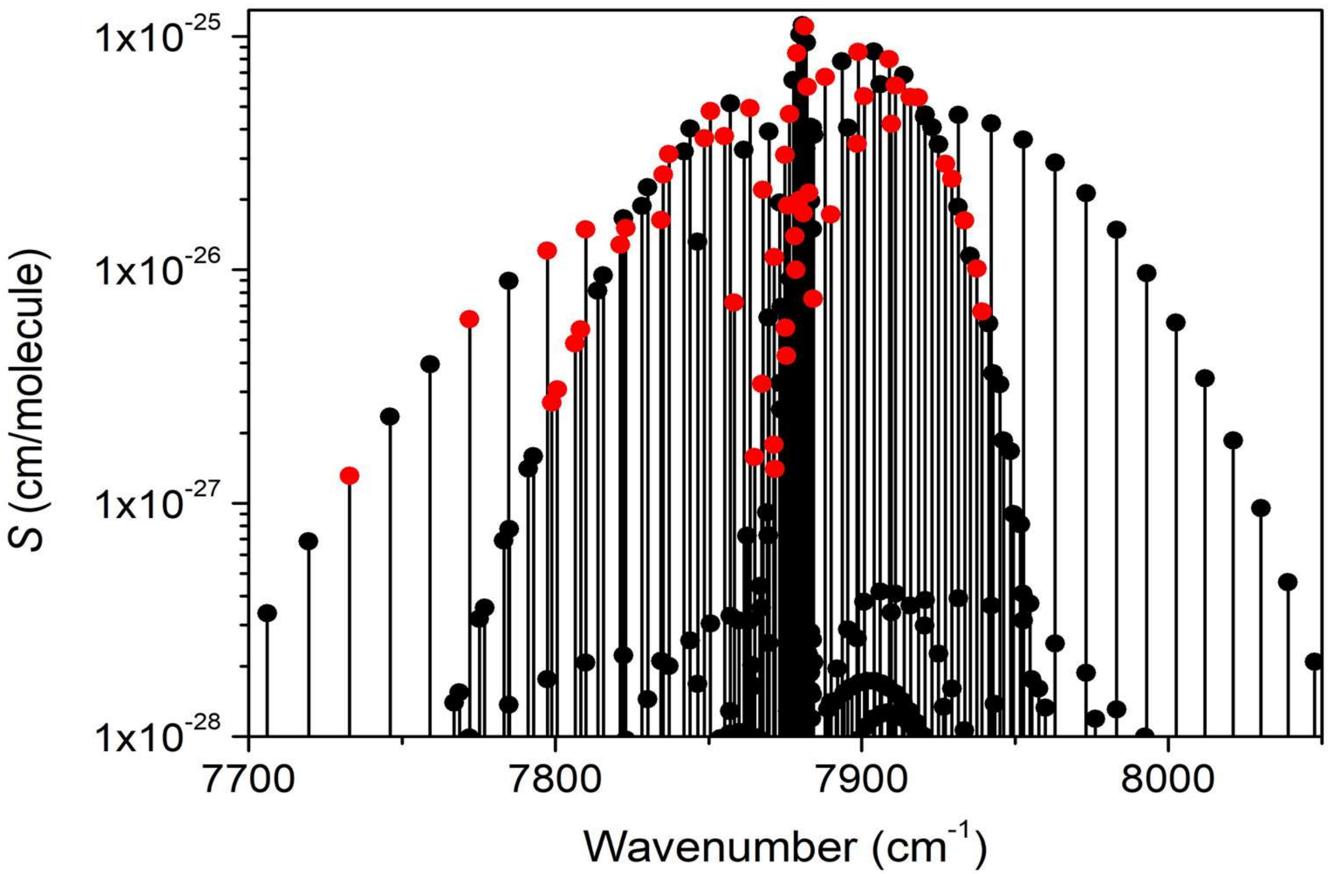
Direct coherence transfer of the comb tooth (low phase noise laser)

- RF locked comb (30 to 50 kHz)

Advantages:

- Efficient injection of the HF cavity (2 kHz)
- Tuning agility

The 1.27 µm O_2-band



Measured 55 transitions depicted in red

Dry air with 1% of Argon

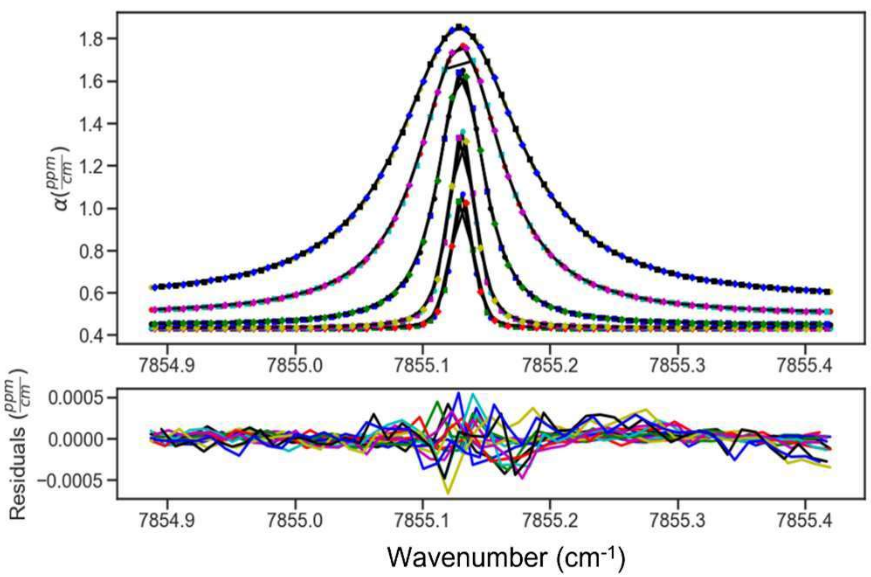
Temperature depency: 3 temperatures (250, 275, 333 K)

At each Temperature: 5 pressures (50, 100, 250, 500, 750 Torr)

P(9)P(9) transition @ 253 K

Example for fitting of the measured data

MATS fitting program from NIST



QF	Std. Dev. (cm^{-1})
9346	6.80×10^{-11}
9178	6.58×10^{-11}
10149	5.85×10^{-11}
13417	6.92×10^{-11}
11719	7.69×10^{-11}
13712	6.43×10^{-11}
9928	1.21×10^{-10}
10193	1.17×10^{-10}
10535	1.11×10^{-10}
10991	1.14×10^{-10}
7305	1.62×10^{-10}
9819	1.27×10^{-10}
6674	1.87×10^{-10}
7062	1.77×10^{-10}
7508	1.65×10^{-10}

Profile: qSDNG (+ LM)

Globally fitted param.:
ν_0, γ_{air}, δ_{air}, a_w, a_s, β, ζ

Param. fitted for each spectrum:
S + base line

Std. Dev.: $1.11\text{x}10^{-10}$ to $7.69\text{x}10^{-11}$ cm^{-1}
QF: 7062 – 13712
-> High S/N ratio

List of line shape parameters

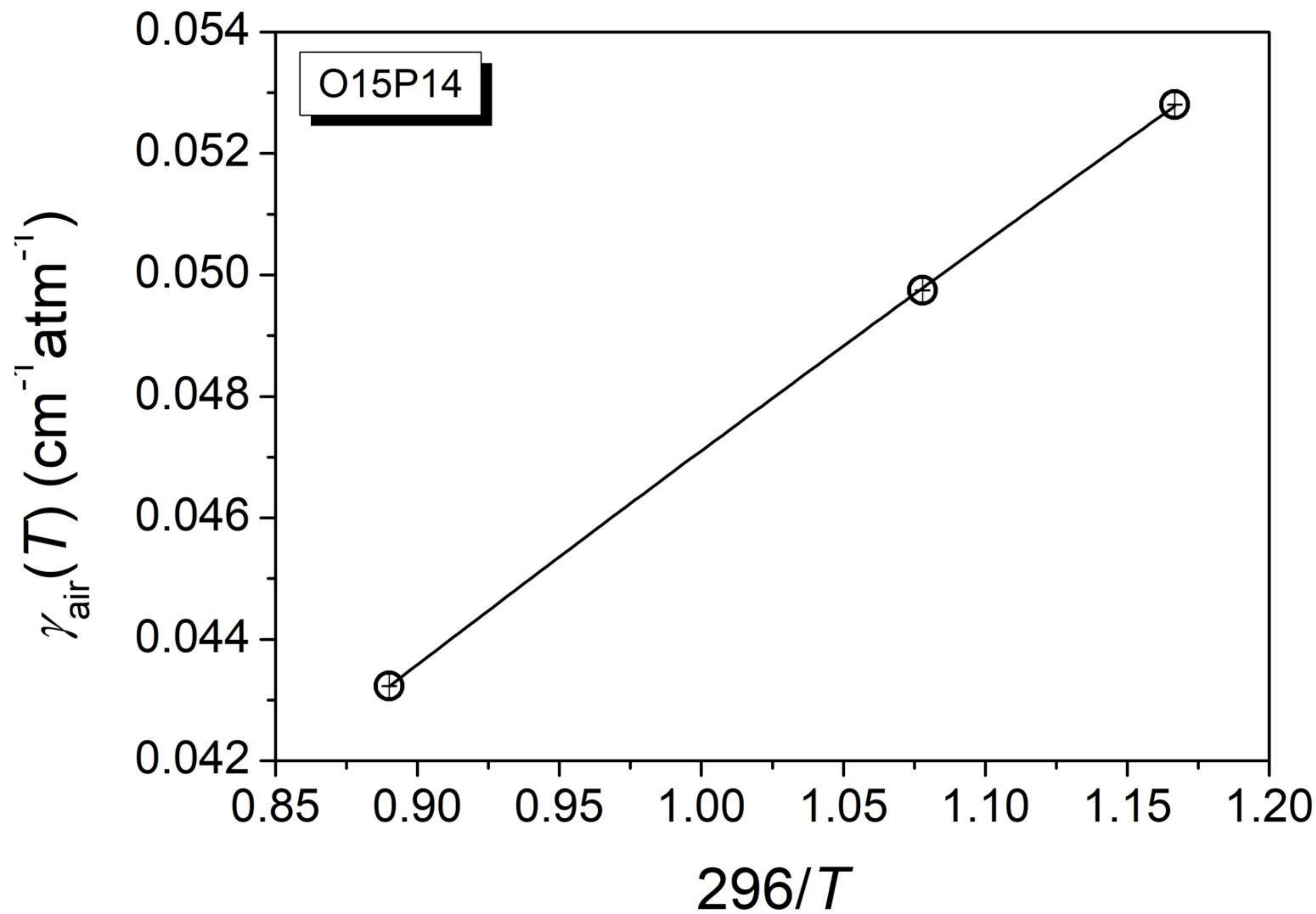
- Line-shape parameters and their temperature dependence determined for 55 transitions from high S/N CRDS spectra with reduced uncertainties

Table 1. *Spectroscopic parameters obtained at 296 K for the transitions studied in this work. A qSDNG profile is used in the multi-spectrum fit procedure. One-sigma uncertainties are given in parenthesis in the unit of the last digit. Here, a_w and a_s correspond to $\gamma_{2air}/\gamma_{0air}$ and $\delta_{2air}/\delta_{0air}$, respectively. ν_0 values are given in cm^{-1} ; S_0 values are in 10^{27} cm/molecule ; γ_{0air}, δ_{0air}, β values are given in $10^{-3}\ cm^{-1}atm^{-1}$; δ' values are given in $10^{-6}\ cm^{-1}atm^{-1}K^{-1}$ and ζ values are given in $10^{-3}\ atm^{-1}$.*

	$\nu_0^{a,d}$	$S_0^{b,d}$	γ_{0air}	$n_{\gamma 0air}$	δ_{0air}	δ'	β	n_β	$a_w(\times 10^3)$	$n_{\gamma 2air}$	a_s	δ'_2	ζ	n_ζ
O(25)P(24)	7732.859612	1.298	36.96(5)	0.601(14)	-2.70(5)	8.4(14)	5.10(20)	0.17(46)	107.00(300)	1.02(32)				
O(19)P(18)	7772.029465	6.146	43.14(2)	0.689(4)	-2.57(2)	8.5(5)	3.49(2)	1.38(6)	88.70(30)	0.28(3)				
O(15)P(14)	7797.419002	12.030	47.10(2)	0.738(4)	-2.46(1)	8.6(3)	2.98(4)	1.70(10)	80.30(20)	0.11(3)	-0.085(2)	0.12(19)		
P(25)P(25)	7798.845866	2.686	36.08(2)	0.557(5)	-2.64(1)	8.4(1)	4.90(28)	2.05(50)	111.30(300)	0.15(27)	-0.057(16)			
P(25)Q(24)	7800.633628	3.065	36.18(1)	0.562(3)	-2.54(1)	8.0(1)	3.82(7)	2.08(15)	111.70(10)	0.22(1)	-0.062(1)			
P(23)P(23)	7806.421861	4.838	38.21(1)	0.605(3)	-2.54(1)	8.2(2)	4.43(8)	1.56(16)	103.70(10)	0.33(1)	-0.061(11)			
P(23)Q(22)	7808.227444	5.570	38.22(3)	0.604(7)	-2.45(1)	7.9(1)	3.58(10)	1.99(25)	102.00(100)	0.16(9)	-0.044(10)			
O(13)P(12)	7809.894152	14.894	48.95(5)	0.756(8)	-2.37(1)	8.4(4)	2.65(10)	1.70(30)	76.50(90)	0.08(10)	-0.116(1)	-0.43(5)		
P(19)P(19)	7821.110627	12.831	42.18(3)	0.682(6)	-2.39(1)	7.6(1)	3.89(3)	1.44(6)	90.40(40)	0.21(4)	-0.050(7)	3.36(111)		
P(19)Q(18)	7822.952614	15.133	42.23(2)	0.687(3)	-2.31(1)	8.1(4)	3.01(2)	1.40(4)	90.40(10)	0.28(1)	-0.061(2)	-1.00(30)		
O(9)P(8)	7834.401703	16.346	52.47(5)	0.773(7)	-2.02(8)	6.8(2)	2.20(10)	2.40(40)	71.00(80)	0.00(9)	-0.130(70)		2.40[e]	1.08[e]
P(15)P(15)	7835.182403	25.740	45.88(2)	0.738(4)	-2.23(1)	8.7(1)	3.32(5)	1.45(13)	79.60(60)	0.30(6)	-0.097(12)	-2.58(113)		
P(15)Q(14)	7837.062483	31.436	45.99(4)	0.728(7)	-2.20(1)	7.4(1)	2.36(9)	2.36(31)	81.50(70)	0.04(7)	-0.062(5)	0.78(69)		
P(11)P(11)	7848.636477	36.799	49.26(3)	0.767(6)	-2.07(1)	7.1(4)	3.03(6)	1.30(20)	71.80(50)	0.14(6)	-0.113(3)	0.56(23)		
P(11)Q(10)	7850.558223	47.968	49.25(3)	0.767(5)	-2.05(2)	6.8(6)	2.42(5)	1.70(20)	71.90(50)	0.07(5)	-0.550(9)	0.39(146)		
P(9)P(9)	7855.131201	37.484	50.91(4)	0.771(7)	-1.90(1)	6.4(4)	2.59(9)	1.60(30)	73.10(80)	0.08(9)	-0.154(7)	0.44(40)		
O(5)P(4)	7858.323962	7.248	58.30(4)	0.784(5)	-1.46(1)	5.9(2)	2.56(3)	0.01(8)	69.60(80)	0.73(10)	-0.236(1)	-0.54(3)		
P(7)Q(6)	7863.443990	49.385	52.75(1)	0.766(1)	-1.84(3)	6.1(10)	2.25(1)	1.52(4)	73.40(70)	0.21(8)	-0.035(21)	1.00(510)	0.76[e]	1.29[e]

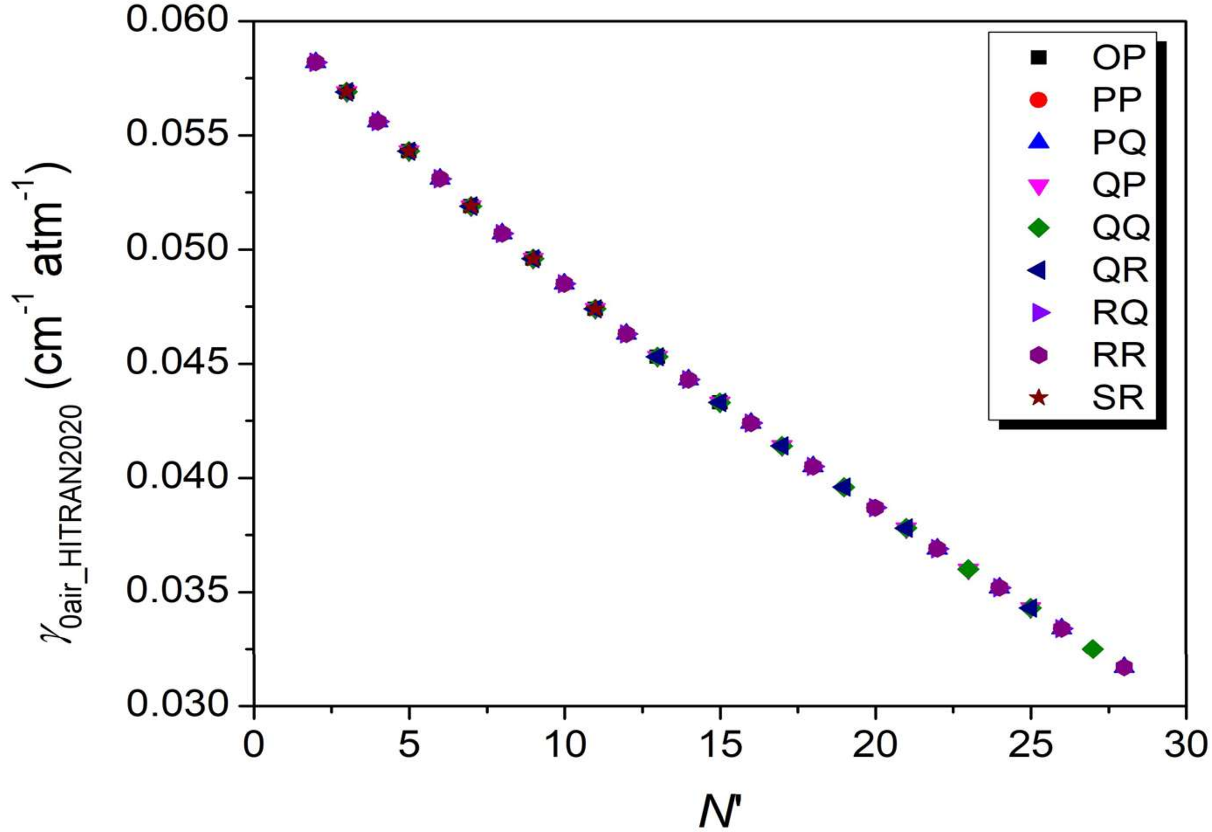
Example of temp. dep for the O15P14 transition for air-broadening coefficient γ_{air}

$$\gamma_{air}(T)=\gamma_{air}(296\ K)(296/T)^{n\_\gamma air}$$



HITRAN2020 values of $\gamma_{0air} = \gamma_{air}(296\ K)$

$$\gamma_{air}(T)=\gamma_{air}(296\ K)(296/T)^{n\_\gamma air}$$

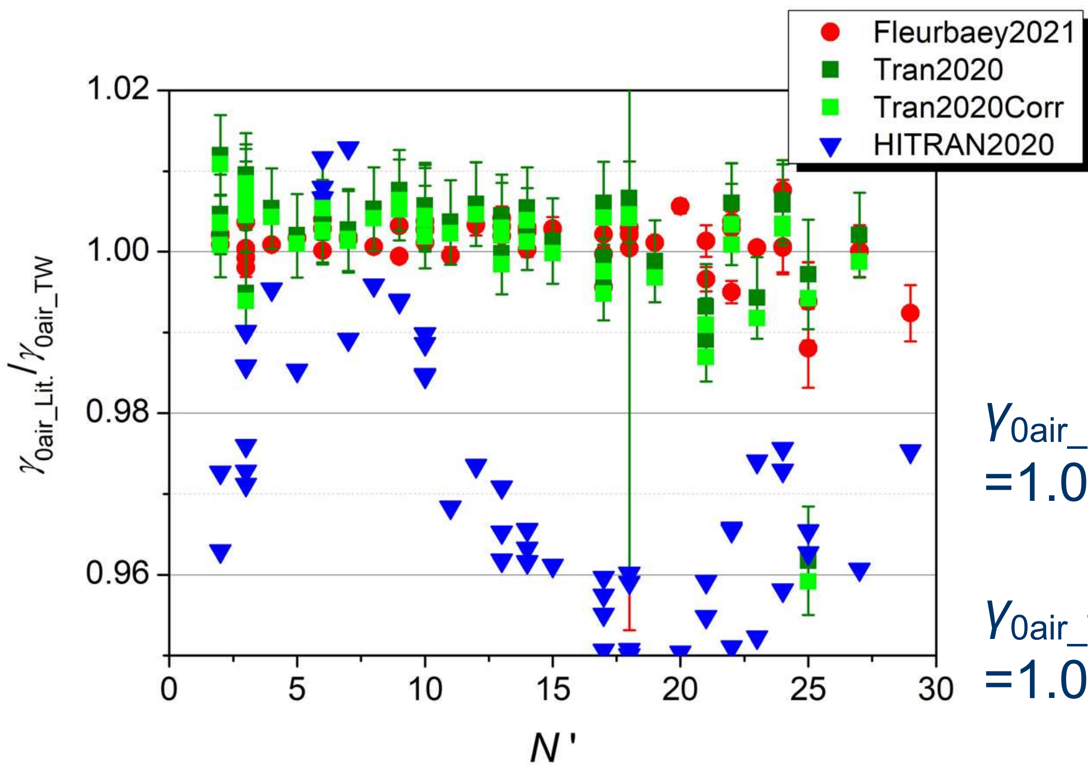


N' is the total orbital angular momentum of the upper state

Almost no branch dependence

Comparison of γ_{0air} to Fleurbaey2021, Tran2020 and HITRAN2020

$$\gamma_{air}(T)=\gamma_{air}(296\ K)(296/T)^{n\_\gamma air}$$



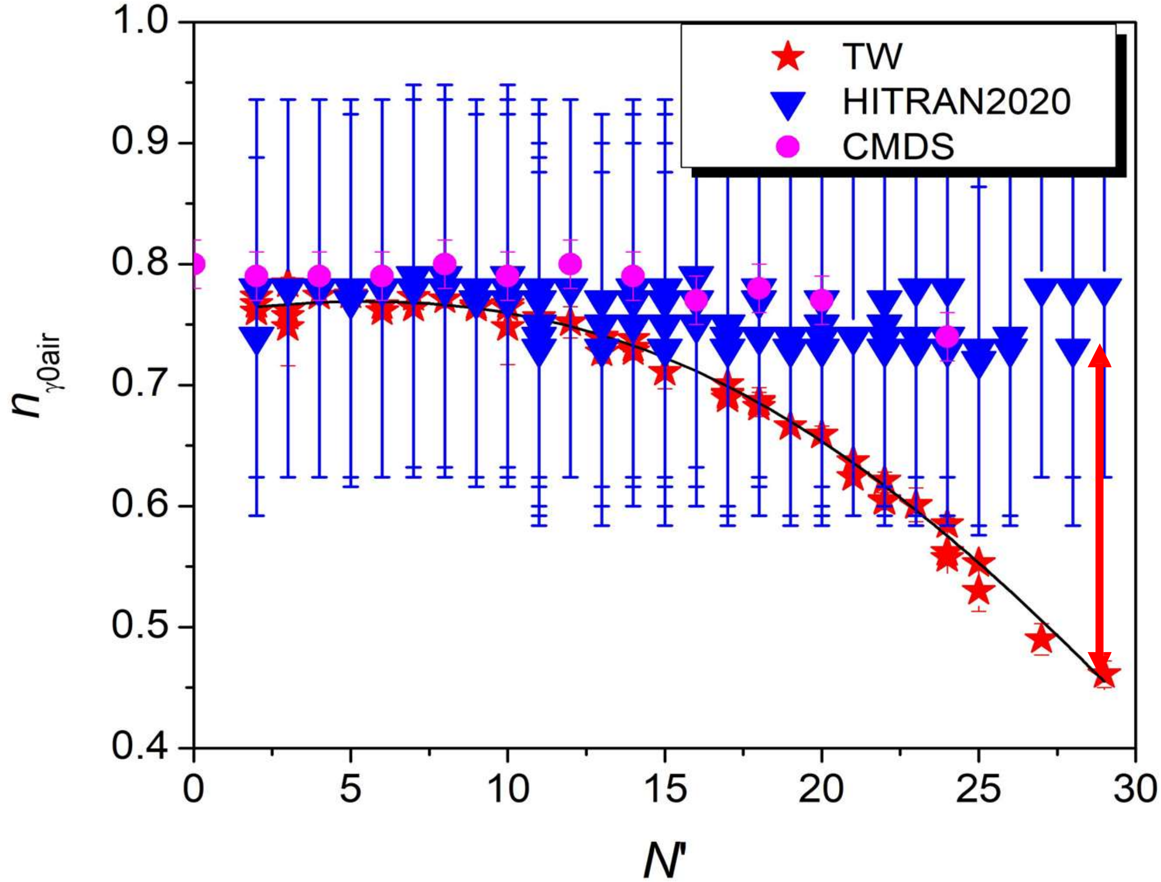
$\gamma_{0air\_Fleurbaey2021}/\ \gamma_{0air\_TW}$ $=1.0009\pm0.0033$ ($N_{trans}=53$)

$\gamma_{0air\_Tran2020}/\ \gamma_{0air\_TW}$ $=1.0017\pm0.0045$ ($N_{trans}=45$)

=> Mutual validation of the datasets with Fleurbaey2021 and Tran2020 at the 3 to 4‰ level (=>*N'*=27)

Comparison of $n_{\gamma air}$ of this work to HITRAN2020 and CMDS

$\gamma_{air}(T)=\gamma_{air}(296\ K)(296/T)^{n\_\gamma air}$



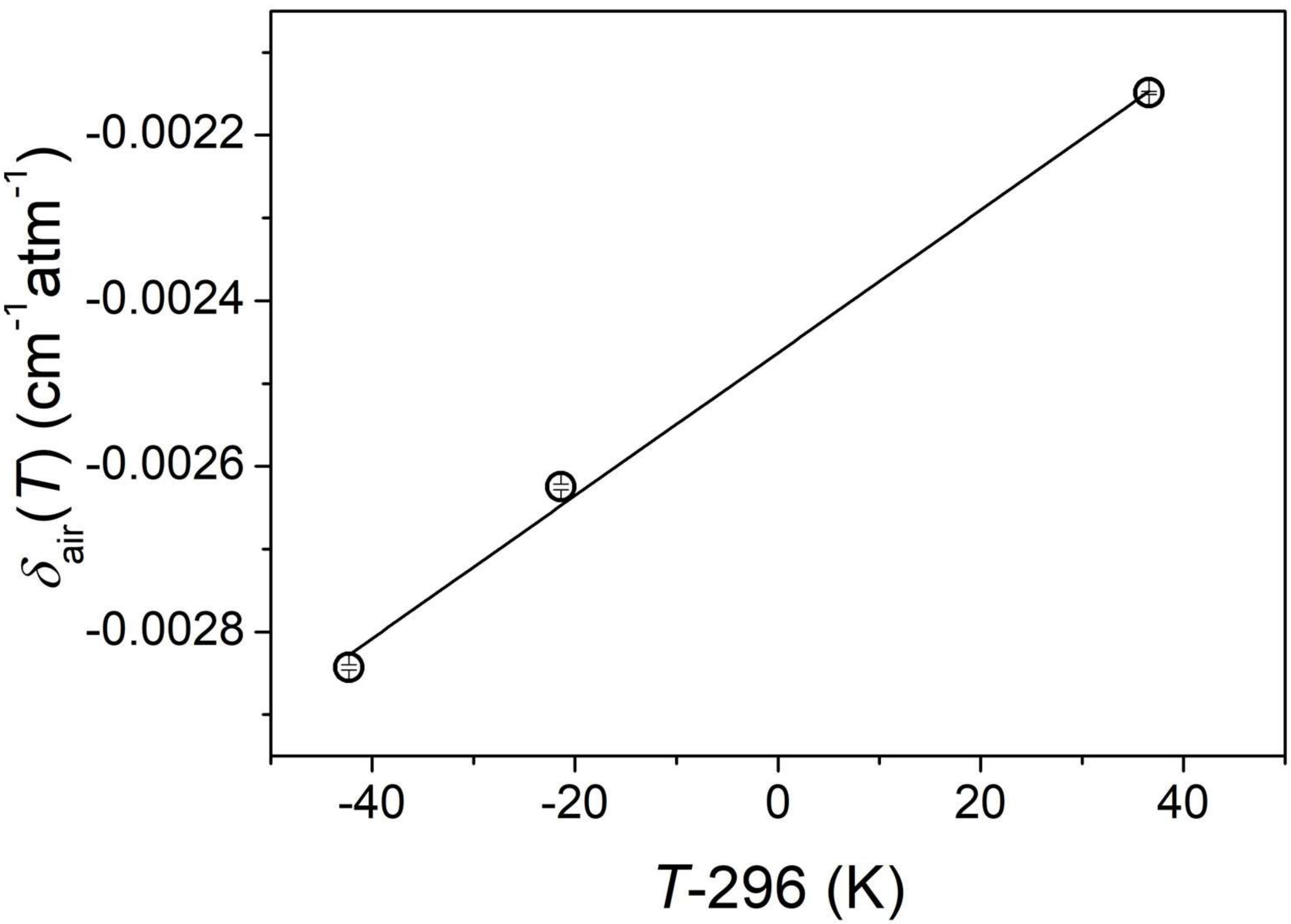
Classic molecular dynamic simulations (CMDS) done by Ha Tran and published in Tran2019

Large discrepancy compaired to HITRAN and CMDS

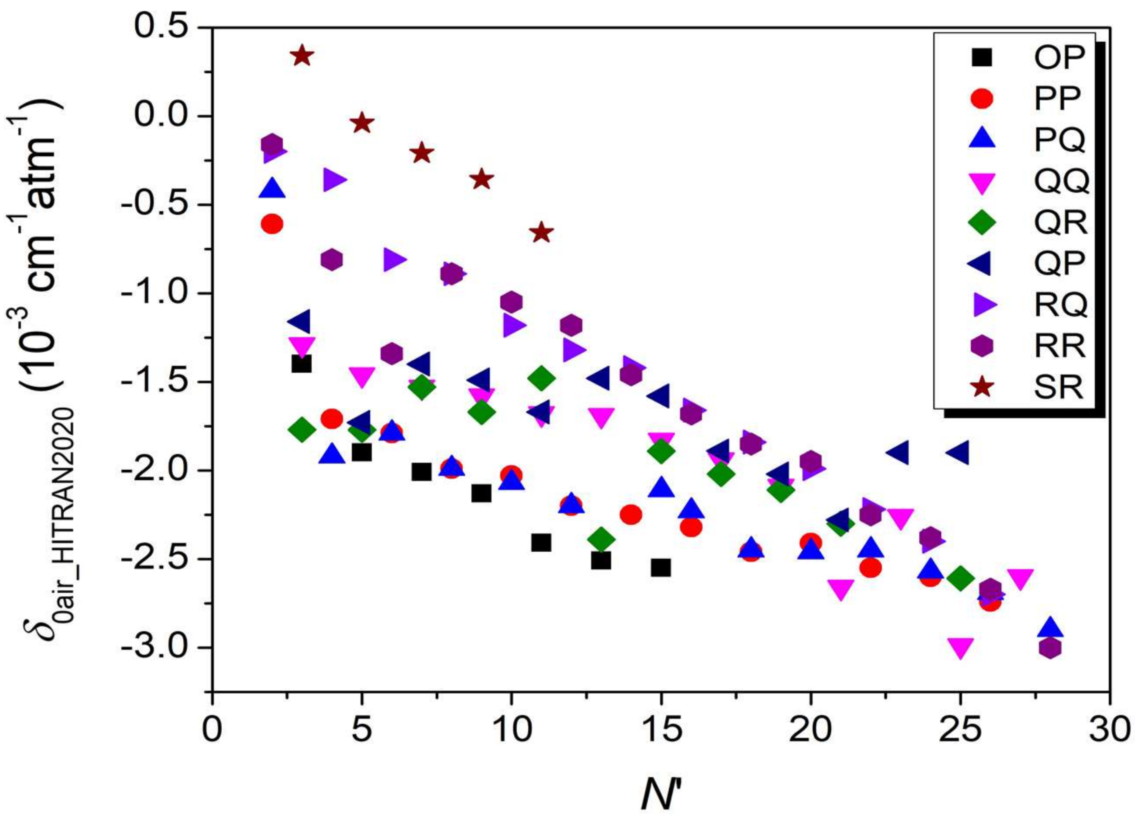
Example of temp. dep for the O(15)P(14) transition for air-pressure shift coefficient δ_{air}

$$\delta_{air}(T) = \delta(296) + \delta'(T - 296)$$

O(15)P(14)



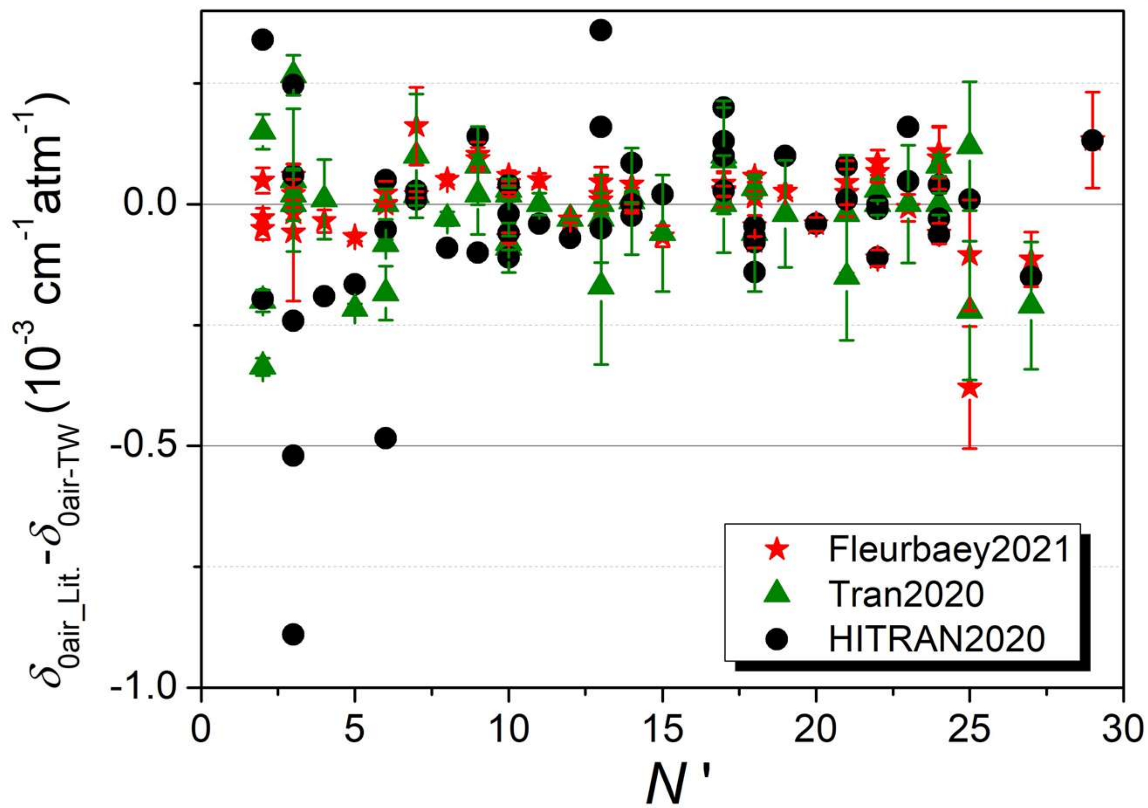
HITRAN2020 values of $\delta_{0air} = \delta(296\ K)$



A clear branch dependence is observed

Comparison of δ_{0air} to Fleurbaey2021, Tran2020 and HITRAN2020

$$\delta_{air}(T) = \delta(296) + \delta'(T - 296)$$



$\delta_{0air\_Tran2020} - \delta_{0air\_TW} = -2.0 \pm 11.1 \times 10^{-5}$ cm^{-1} atm^{-1}

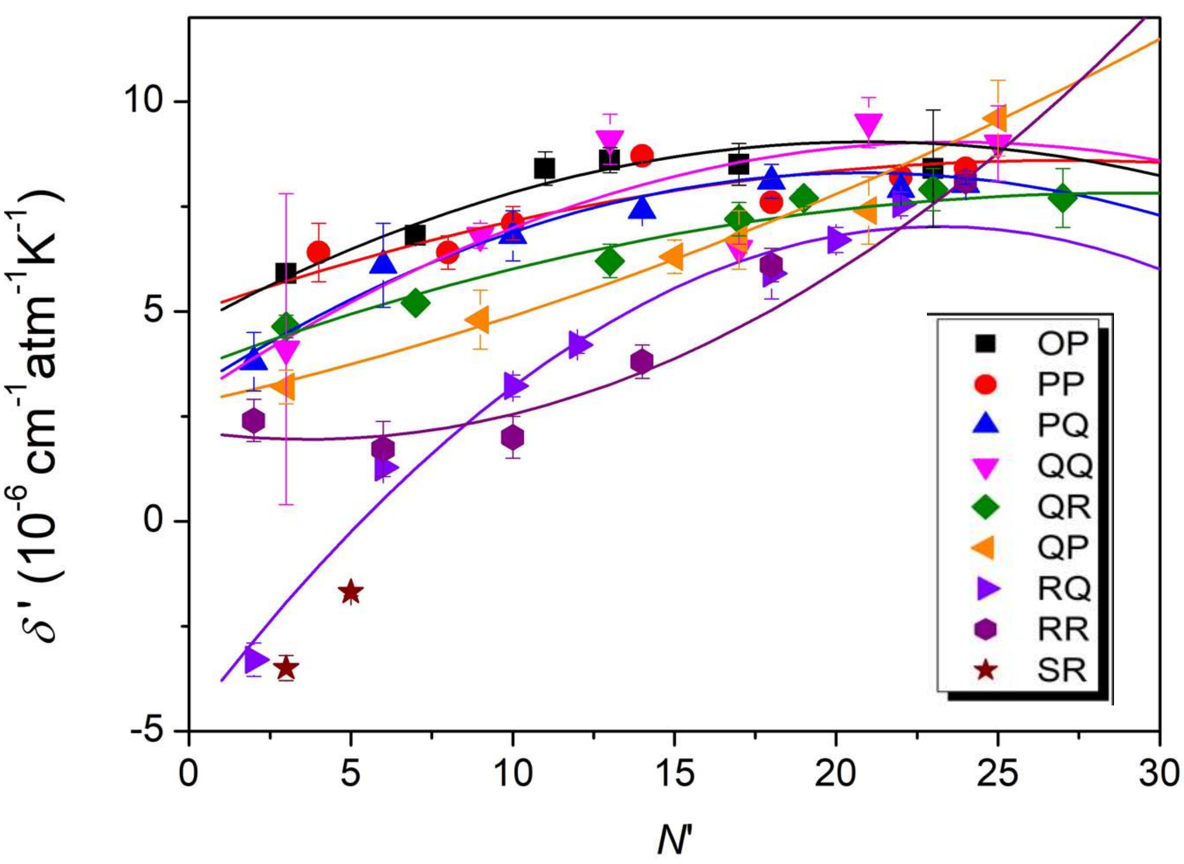
$\delta_{0air\_Fleurbaey2021} - \delta_{0air\_TW} = 0.5 \pm 8.1 \times 10^{-5}$ cm^{-1} atm^{-1}

Consistency of the three datasets

at the 1×10^{-4} cm^{-1}atm^{-1} level

Temp. dep. coefficient of air-pressure shift of our measurements δ'

$$\delta_{air}(T) = \delta(296) + \delta'(T - 296)$$



Summary and perspectives

- Results show good agreement with literature and high quality of the data(*i.e.* 3‰ unc. on γ_{0air})
- First time measured and reported values for temperature dependency of the line shape parameters
- HITRAN 2024 contribution:
  - Line shape parameters for reference Temperature at 296 K (together with Fleurbaey2021)
  - Temp. dep.
    - $n\gamma air$ and δ'
    - β, aw and as
    - $n\beta$, $n\delta 2air$, $n\gamma 2air$
    - Line-mixing parameter

Merci beaucoup Didier and LAME Team!