WMO –

Ozone Theme Meeting 2009

Ozone UV absorption cross section at 253.65 nm revisited and simultaneous UV-IR measurements

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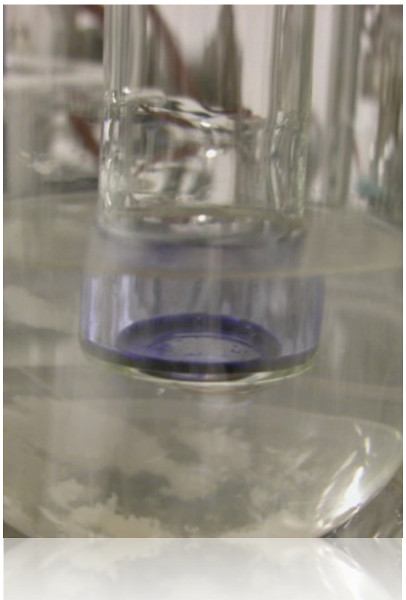
Outline

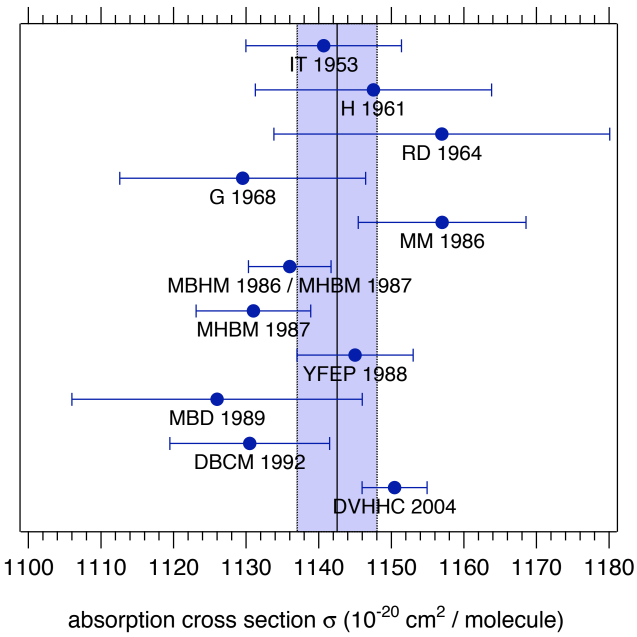


- Introduction
- Absolute measurements in the UV (@ 253.65 nm)
  - Method
  - Experimental details
  - Preliminary results
- Simultaneous UV - IR (10 µm) measurements ?

Why remeasure O_3 at 253.65 nm ?

- O_3 Standard
  - tropospheric measurements (air quality monitoring)
  - recommended value has sizable uncertainty
  - dominant uncertainty factor in modern UV photo spectrometers
  - standard for measurements in other wavelength regions
  - additional sources of systematic bias have been identified
- Discrepancy between UV and IR data (~ 5%) ?
  - requires multi-wavelength comparisons
  - re-determination of absolute values

Review Measurements



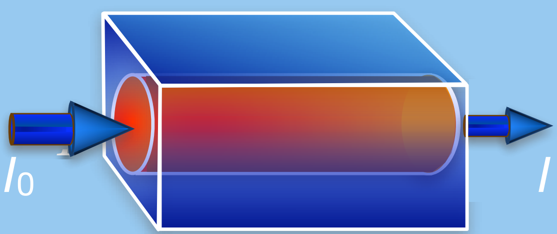
IT 1953	-	Inn & Tanaka
H 1961	-	Hearn
RD 1964	-	Raper & DeMore
G 1968	-	Griggs
MM 1986	-	Molina & Molina
MBHM 1986	-	Mauersberger et al.
MHBM 1987	-	Mauersberger et al.
YFEP 1988	-	Yoshino et al.
MBD 1989	-	Malicet et al.
DBCM 1992	-	Daumont et al.
DVHHC 2004	-	Dufour et al.

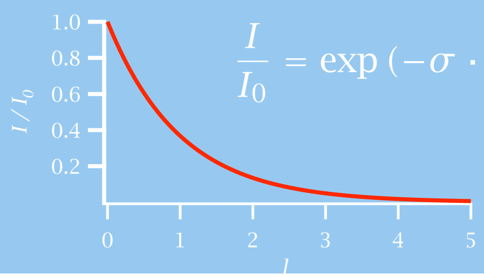
Absolute Measurements at 253.65 nm

Part I

Measurement Principle

Beer Lambert Law

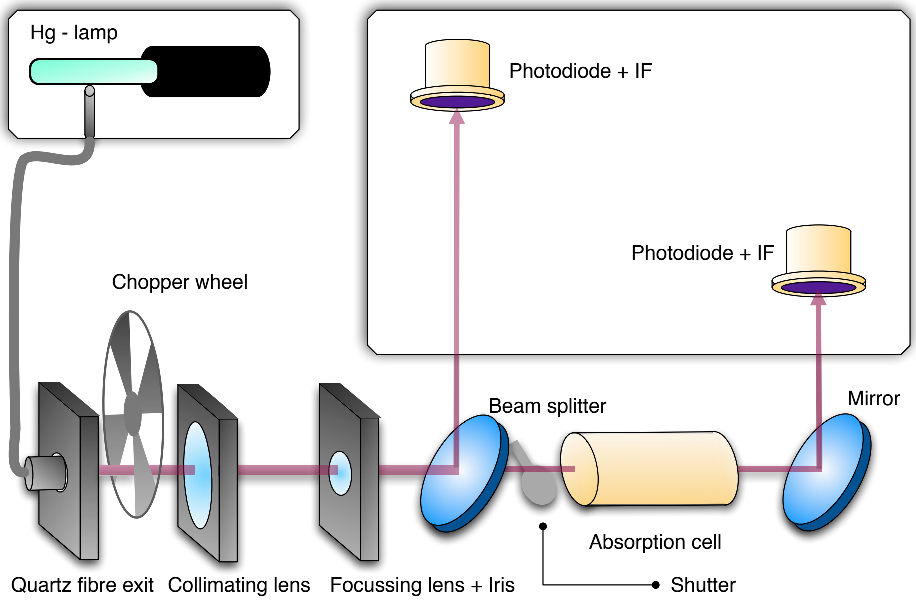




$$\frac{I}{I_0} = \exp\left(-\sigma \cdot n \cdot l\right)$$

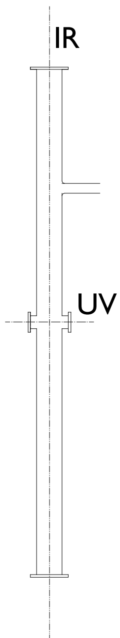
Measure
I, I_0, and *L directly;*
n through *p* and *T*

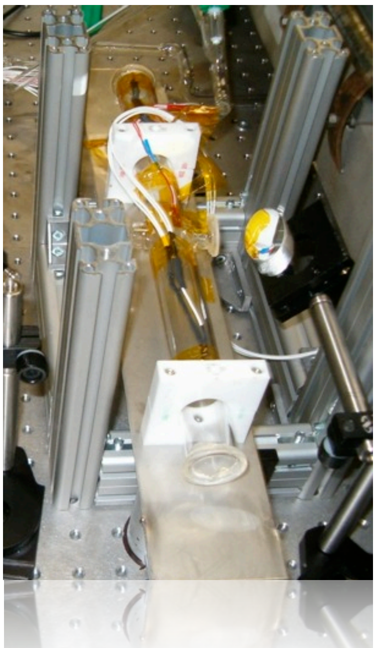
Experimental Setup



Experimental Setup (Crossed UV/IR Beam Arrangement)

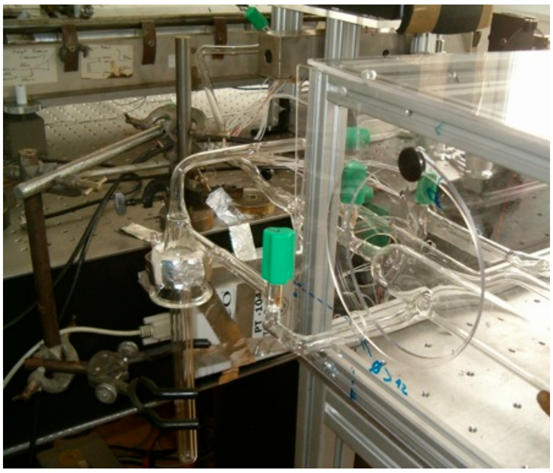
- Crossed beam arrangement for simultaneous UV - IR (10 µm) measurements
- All pyrex, BaF_2 windows, all teflon valves
- windows inclined by 3°
- ozone decomposition : ~ 2‰ / h, 4‰ / h (UV off, on)
- T (PT 100) = (21.31 ± 0.26)°C
- MS investigation of sample and residues





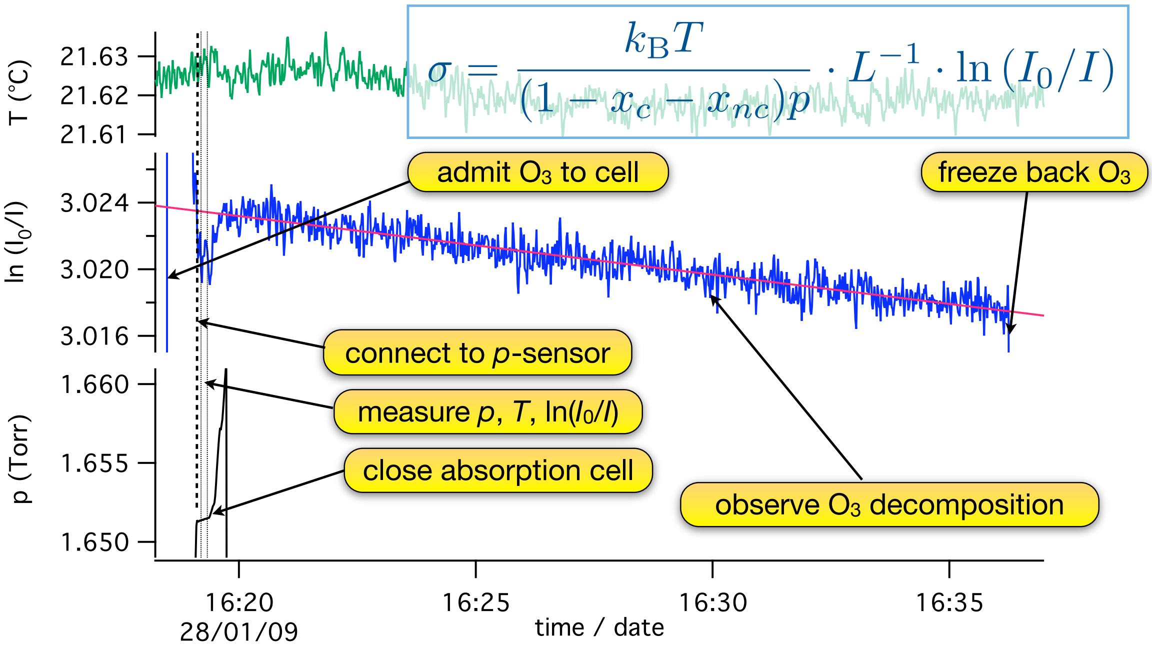
Experimental Setup (Ozone Generation & Handling)

- 1. Electric discharge
- 2. Ozone purification / recovery
- 3. Pressure measurement



Measurement Principle - Sample Run

$$\sigma = \frac{k_{\mathrm{B}}T}{(1 - x_c - x_{nc})p} \cdot L^{-1} \cdot \ln(I_0/I)$$

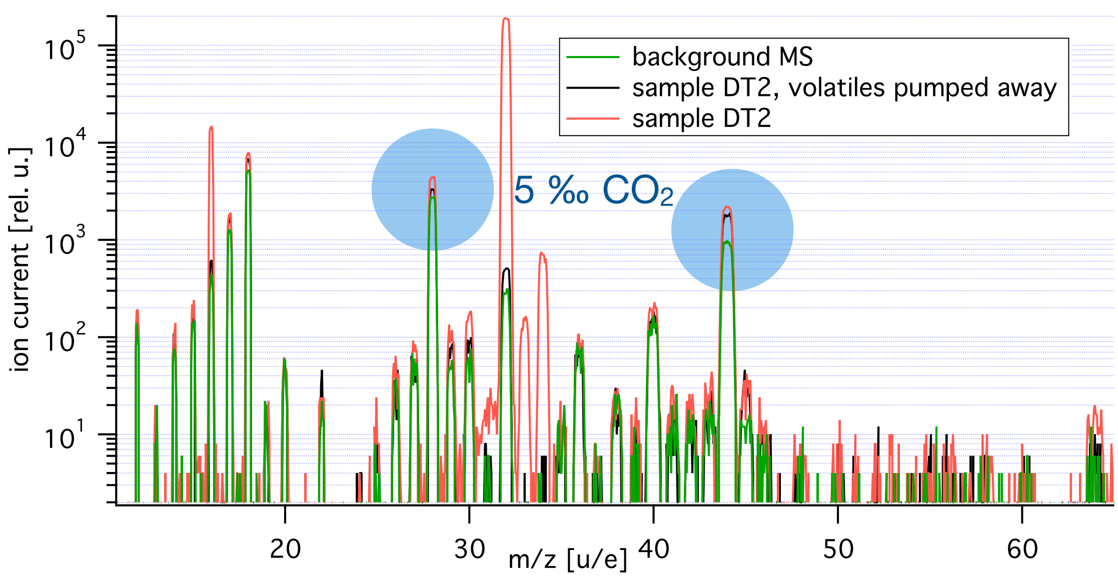


Uncertainty Budget

$$\sigma = \underbrace{\frac{k_B T}{(1 - x_c - x_{nc})p}}_{n^{-1}} \cdot L^{-1} \cdot \ln\left(I_0/I\right)$$

y		*u*(*y*)	*u*(*y*)/*y* (%)
Cell Length (*L*)	49.495 mm	0.027 mm	0.05
Temperature (*T*)	294.46 K	0.05 K	0.02
Pressure (*p*)	76 - 393 Pa		0.08
$\ln(I/I_0)$	1.1 - 5.4		0.05
Impurity (x_c)	≲ 0.005		≃ 100
Impurity (x_{nc})	1 - 4 ‰		~ 7

MS - Analysis

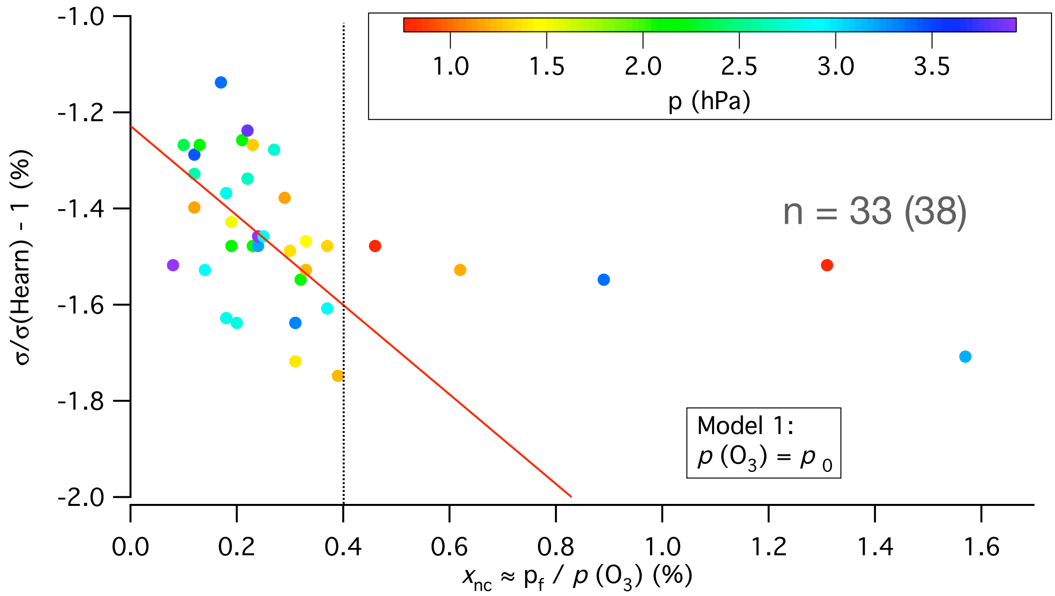


MS - Analysis

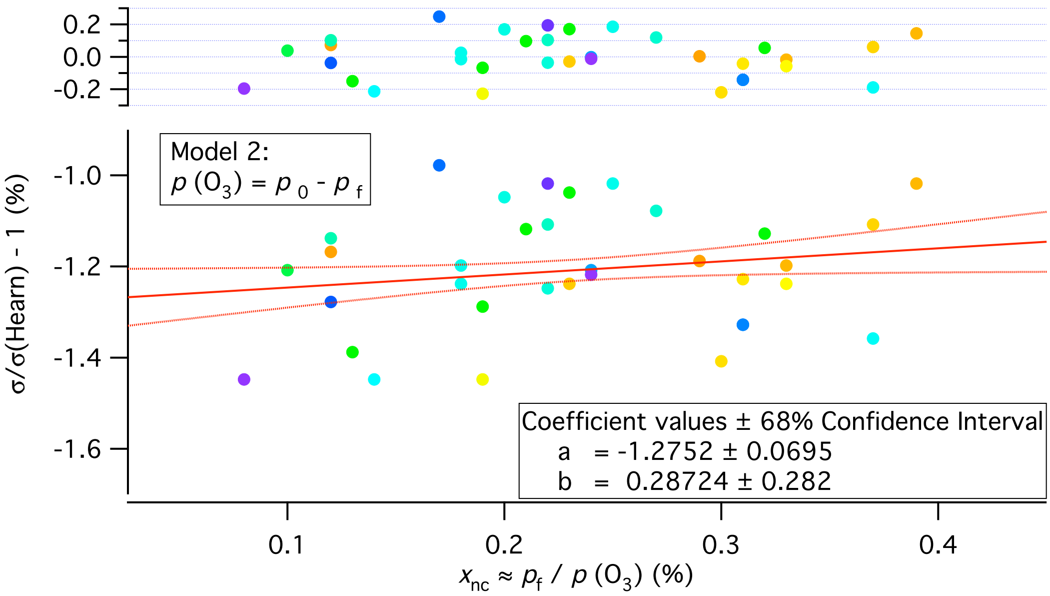
Origin of CO_2 ?

- Transfer dip-tubes (stainless steel) have previously been used for the analysis of stratospheric CO_2 samples. Check for contamination.
- Several cleaning cycles with high concentrations of O_3 have lowered the maximum content of CO_2 down to 0.5 ‰, when O_3 was produced in a similar apparatus.
- 1 ‰ of uncertainty due to impurities seems to be possible.
- Need to verify for UV samples.

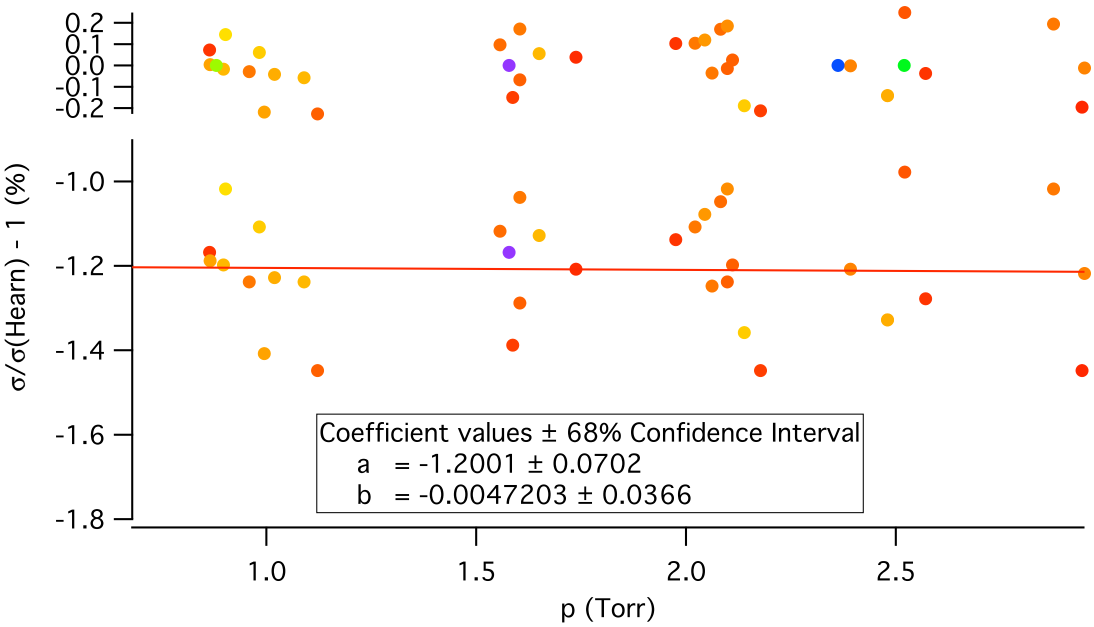
Results - Impurities added after



Results - Impurities already present



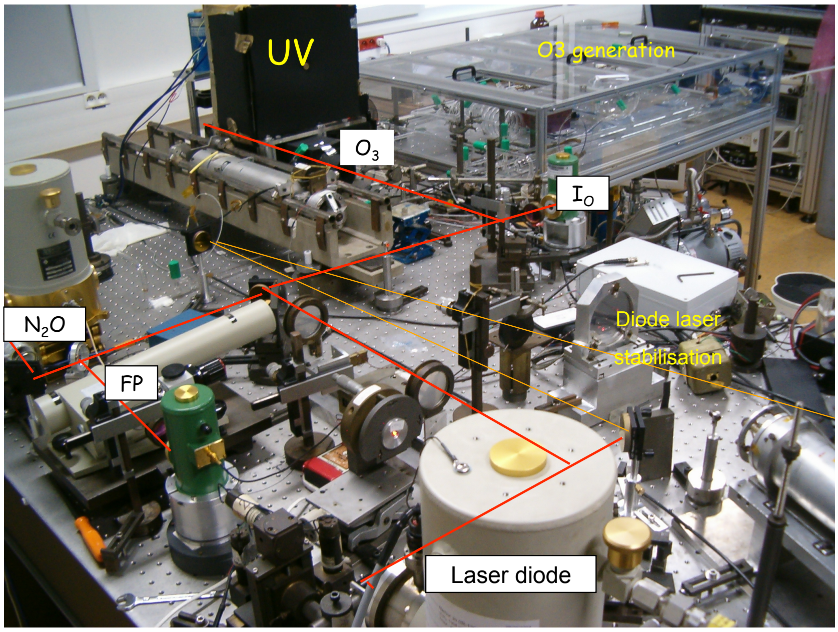
Results - Linearity of BLL



IR measurements at 10 µm

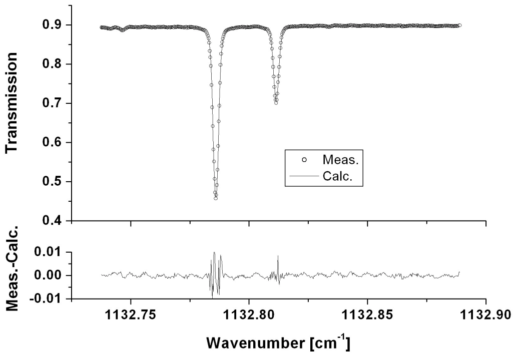
Part II

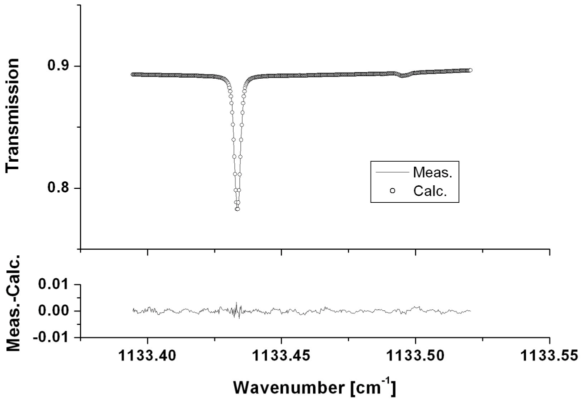
LPMAA Interferometer Controlled TDLAS



IR Ozone Measurements

in the 1032.5 - 1033.5 cm^{-1} range





Line Positions in the (100←000) Band

#	J', K'$_a$, K'$_c$ ← J", K"$_a$, K"$_c$	E" [cm^{-1}]	ν [cm^{-1}]	u(ν) [cm^{-1}]	ν - ν$_{HITRAN}$ [cm^{-1}]
1	16 3 13 ← 15 2 14	113.0870	1132.599228	3 10^{-5}	-4.2 10^{-5}
2	9 4 6 ← 8 3 5	58.4464	1132.603357	3 10^{-5}	-4.3 10^{-5}
3	35 2 34 ← 34 1 33	505.5065	1132.656978	3 10^{-5}	-0.3 10^{-5}
4	36 0 36 ← 35 1 35	510.2025	1132.785929	3 10^{-5}	-7.1 10^{-5}
5	19 3 17 ← 18 2 16	158.1653	1132.811396	3 10^{-5}	-4.4 10^{-5}
6	10 4 6 ← 9 3 7	66.0127	1133.433514	3 10^{-5}	-0.4 10^{-5}
7	18 2 16 ← 17 1 17	127.2639	1133.5868[illegible]	3 10^{-5}	-5.0 10^{-5}
8	38 1 37 ← 37 2 36	[illegible]	1133.631677	3 10^{-5}	-2.3 10^{-5}
9	37 1 37 ← 36 0 36	538.9365	1133.671119	3 10^{-5}	-8.1 10^{-5}
10	21 3 19 ← 20 2 18	191.7092	1133.724521	3 10^{-5}	-3.9 10^{-5}
11	42 2 40 ← 41 1 39	750.2643	1133.978509	3 10^{-5}	-12.0 10^{-5}
12	37 2 36 ← 36 1 35	563.9440	1134.02872	3 10^{-5}	-8.5 10^{-5}
13	11 4 8 ← 10 3 7	74.4314	1134.251439	3 10^{-5}	-3.1 10^{-5}
14	38 0 38 ← 37 1 37	568.5063	1134.453749	3 10^{-5}	-8.1 10^{-5}
15	23 3 21 ← 22 2 20	228.7342	1134.509712	3 10^{-5}	+1.2 10^{-5}

Our positions agree well with HITRAN 2004

Intensities in the (100←000) Band

#	J', K'_a, K'_c ← J'', K''_a, K''_c	E'' [cm^{-1}]	S [cm^{-1}]	N	u(S)/S (%)	S/S_{HITRAN} -1 [%]
1	16 3 13 ← 15 2 14	113.0870	$4.096\ 10^{-22}$	7	0.8	3.4
2	9 4 6 ← 8 3 5	58.4464	$2.427\ 10^{-22}$	7	0.5	2.0
3	35 2 34 ← 34 1 33	505.5065	$9.436\ 10^{-22}$	8	0.5	3.7
4	36 0 36 ← 35 1 35	510.2025	$1.367\ 10^{-21}$	10	0.7	2.7
5	19 3 17 ← 18 2 16	158.1653	$4.906\ 10^{-22}$	10	0.9	1.6
6	10 4 6 ← 9 3 7	66.0127	$2.717\ 10^{-22}$	10	0.6	2.5
7	18 2 16 ← 17 1 17	127.2669	$1.413\ 10^{-22}$	10	0.8	2.8
8	38 1 37 ← 37 2 36	594.9334	$7.687\ 10^{-22}$	10	0.7	2.9
9	37 1 37 ← 36 0 36	538.9365	$1.280\ 10^{-22}$	9	0.5	3.9
10	21 3 19 ← 20 2 18	191.7092	$5.152\ 10^{-22}$	9	0.8	1.2
11	42 2 40 ← 41 1 39	750.2643	$3.126\ 10^{-22}$	9	0.5	2.6
12	37 2 36 ← 36 1 35	563.9440	$8.288\ 10^{-22}$	6	1.1	3.0
13	11 4 8 ← 10 3 7	74.4314	$2.974\ 10^{-22}$	6	0.6	1.8
14	38 0 38 ← 37 1 37	568.5063	$1.174\ 10^{-21}$	7	0.5	3.6
15	23 3 21 ← 22 2 20	228.7342	$5.339\ 10^{-22}$	7	0.8	1.5

Our intensities are 2.6 % higher than HITRAN 2004

Summary and Outlook

- Ozone cross section at 253.65 nm has been measured at 295 K
- Its value (1.133 ± 0.12%) 10^{-17}cm^2 is 1.3% smaller than Hearns.
- A difference of ~1% remains even if systematic impurity effects (CO_2) are considered. Note that the presence of multiple reflections would lead to an artificial increase of the observed value.
- Condensables still need better quantification
- Intensities of 15 strong lines in the 10 µm region are systematically (2.6(4)%) higher than HIITRAN 2004.
- Will measure the UV ozone cross section at lower pressure, longer path lengths and for individual isotopes ($^{16}O_3$, $^{16}O^{16}O^{18}O$, $^{18}O_3$).