

# Laboratory spectroscopy at DLR

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## Background

- Group established in 1990
- Emphasis on quantitative spectroscopy of atmospheric trace gases to support atmospheric remote sensing
- Initial focus on far infrared but soon extended to mid and near infrared
- Participation in several EU-, ESA-, nationally-funded projects
- Member of HITRAN scientific advisory committee

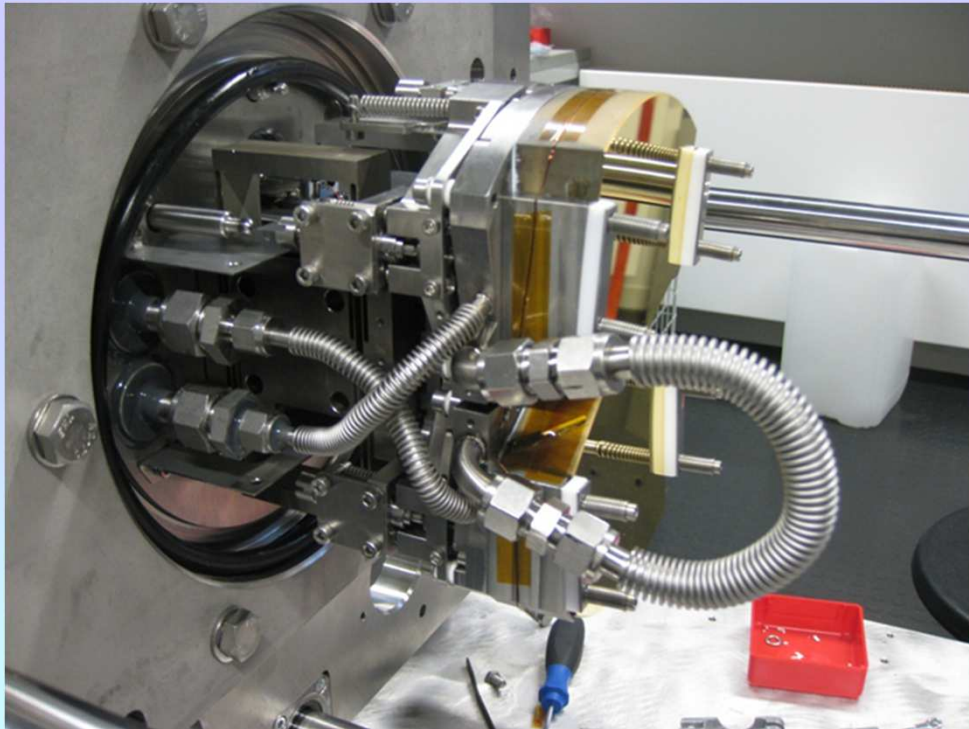
## Infrastructure

- Bruker IFS125 HR Fourier-Transform spectrometer, range 10-40000  $\text{cm}^{-1}$
- Coolable(195K), heatable(950K) cells, 130 m multireflection cell
- Lab equipment for production/handling of stable/instable species



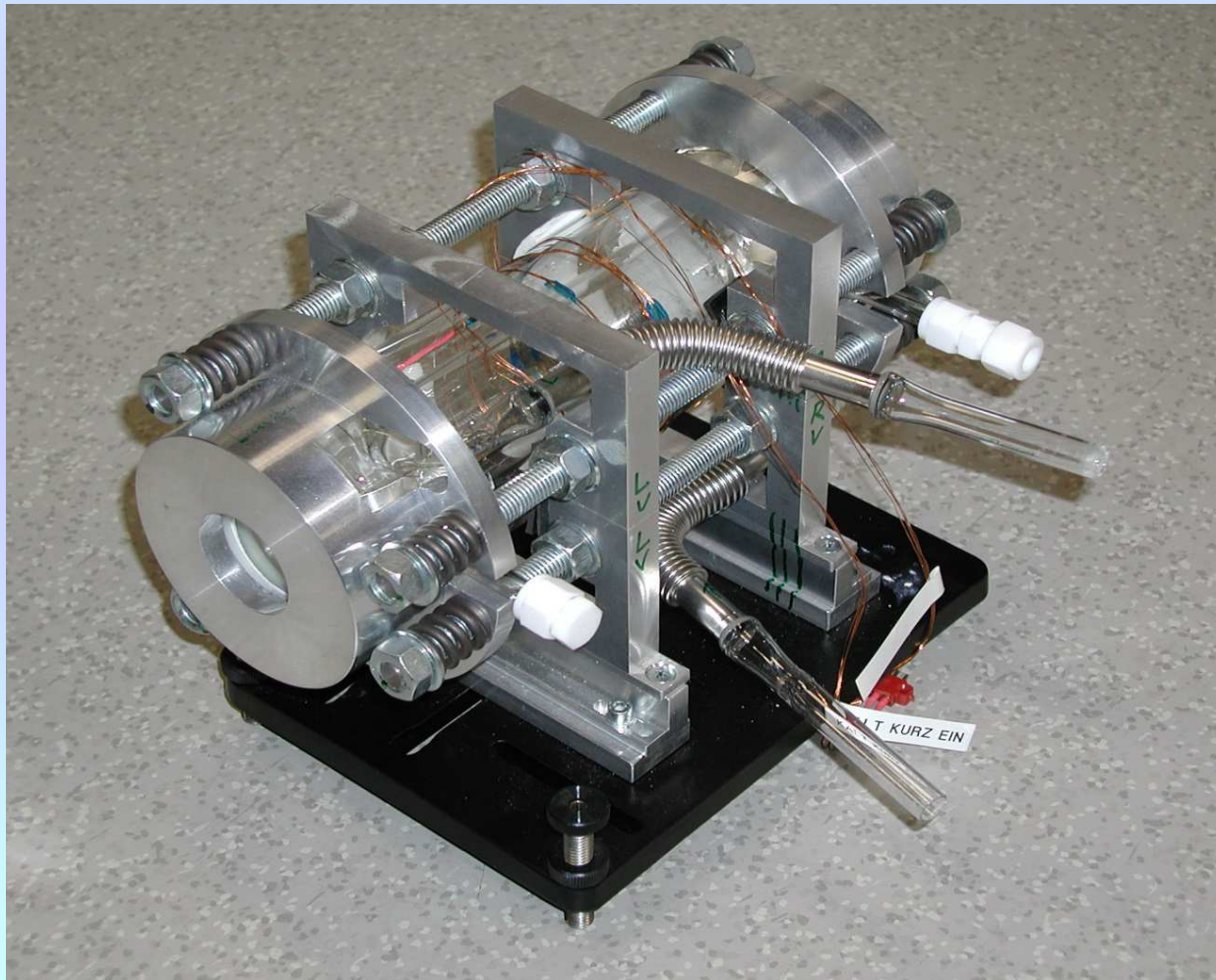
## Multireflection cell

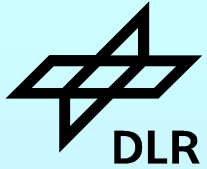
- Designed at DLR
- 80 cm baselength, up to 130 m absorption path
- Coolable down to 200 K
- Equipped for flow experiments with unstable species
- Cell was completely refurbished in 2012/2013 for better mirror alignment, higher absorption path, and temperature homogeneity



## Short absorption path cell

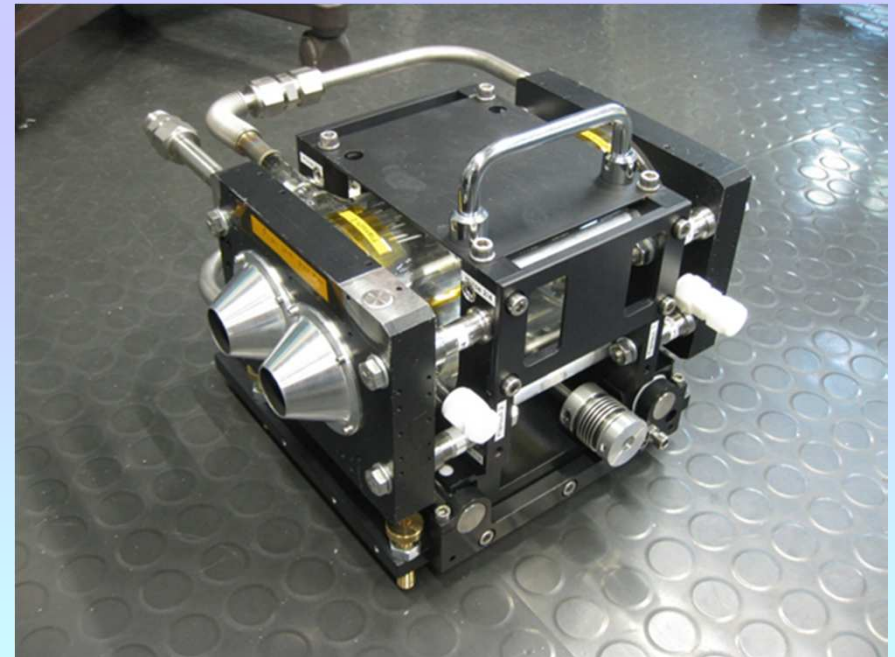
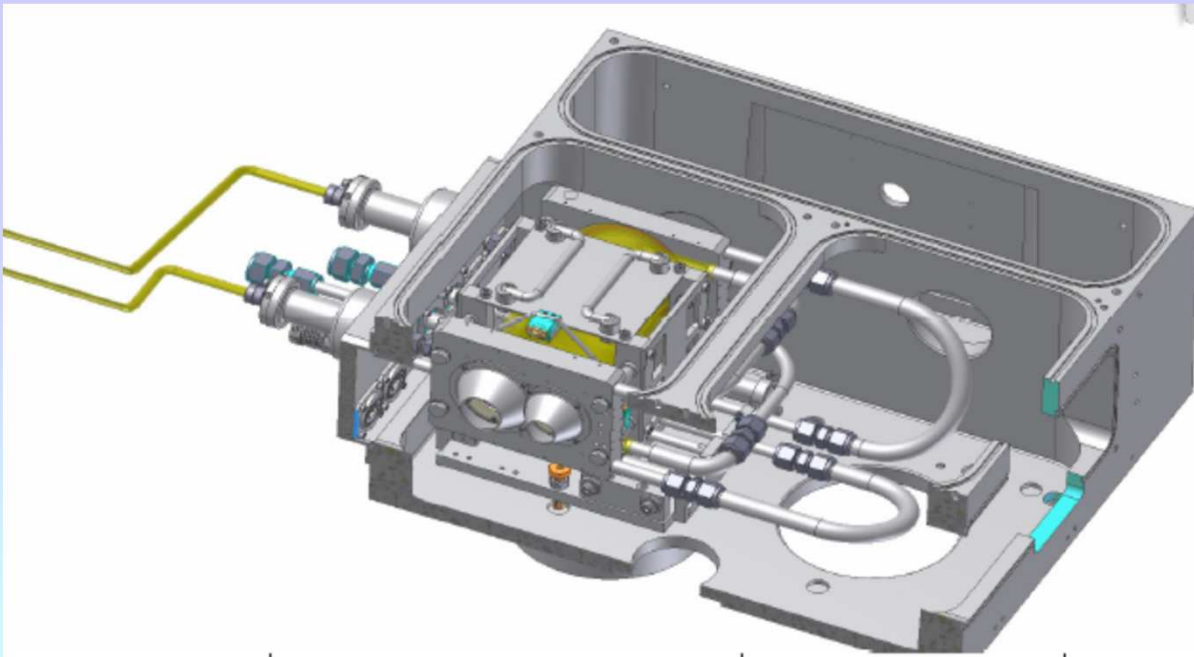
- Designed at DLR
- 25 cm absorption path
- Coolable to 195 K
- High temperature homogeneity





## New short absorption path cell

- 22 cm absorption path
- Coolable to 190 K
- Two window pairs allowing UV+MIR, MIR+FIR, UV+FIR quasisimultaneously
- High temperature homogeneity ( $<0.1$  K)
- Path length accuracy 0.1% - requires raytracing!





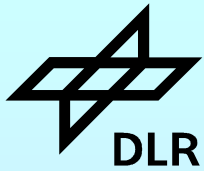
## Spectroscopic database work at DLR

Species	FIR	MIR	Purpose/Application	Remark
O <sub>3</sub>	S, $\gamma(T)$	$\sigma$ , S, $\gamma(T)$ , $\alpha(T,p)$	database improvement	
ClONO <sub>2</sub>		$\alpha(T,p)$	database improvement, MIPAS	difficult synthesis
N <sub>2</sub> O <sub>5</sub>		$\alpha(T,p)$	database improvement, MIPAS	
OH/HO <sub>2</sub>	$\sigma$		new methodology	extremely unstable
BrO	$\sigma$ , $\gamma(T)$		database improvement, MASTER/SOPRANO	extremely unstable
ClO	$\sigma$ , $\gamma(T)$	$\sigma$ , S	database improvement, MASTER/SOPRANO	unstable
ClOOCl	$\sigma$	$\alpha(T,p)$	remote sensing MIPAS	sample preparation difficult
HOCl	$\sigma$		FIR database	
CO	S, $\gamma(T)$	S, $\gamma(T)$	error characterisation, high temperature database, Q/A	<1% radiometric accuracy
CO <sub>2</sub>		$\alpha(T,p)$	high temperature database	
H <sub>2</sub> O		$\sigma$ , S, $\gamma(T)$ , MIR+NIR	high temperature database improvement, climate, MIPAS, IASI, WALES	sample preparation difficult
NO		$\sigma$ , S, $\gamma(T)$	high temperature database, engine emissions	
NO <sub>2</sub>		$\alpha(T,p)$	high temperature database, engine emissions	



## Focus: Spectroscopic data with specified uncertainties

- Methods for optimum adjustment of FTS
- Methods for detection and minimisation of instrumental errors
- Detailed calculation and propagation of instrumental errors, sample errors, etc
- Quality assurance methods for validation of errors
- Line modelling including Dicke/collisional narrowing



# OZONE

## Problem

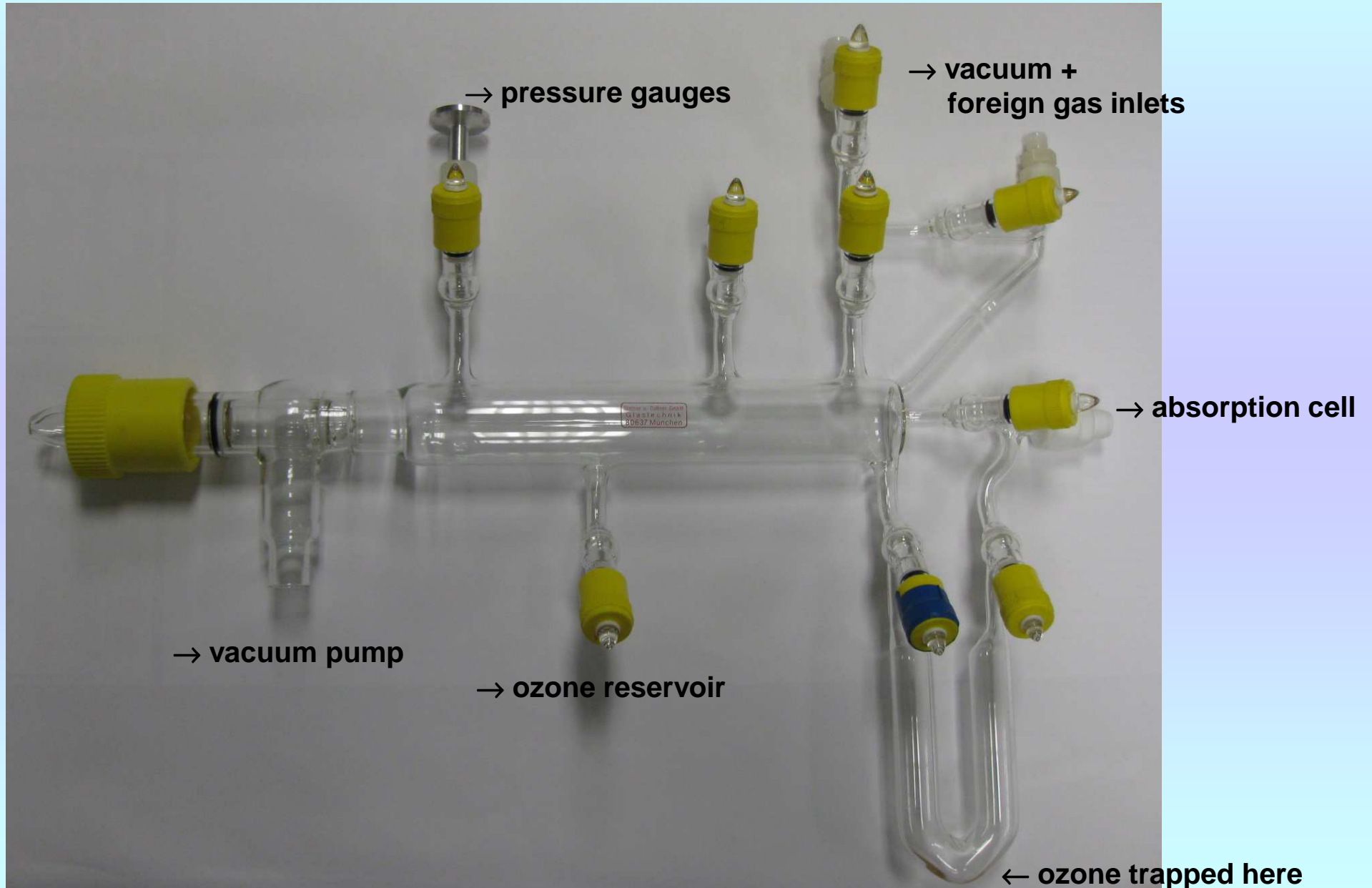
Ozone is a slightly unstable molecule since it decomposes into oxygen or oxydises organic matter

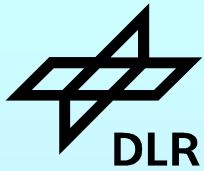
⇒ not easy to quantify amount in absorption cell

DLR developed (patented) method to generate ozone/air mixtures with defined number densities in absorption cell



# Vacuum apparatus for ozone





## Method for generation of defined ozone/air mixtures

- Absorption cell connected to vacuum apparatus – only glass/teflon surfaces, minimum amount of metal (pressure gauge)

### Conditioning of vacuum apparatus and cell

1. Store small amount of pure ozone in trap at 77K
2. Evaporate ozone into cell and vacuum apparatus, measure total pressure
3. Freeze out ozone again, measure pressure of residual oxygen, then pump away oxygen
4. Redo steps 2. And 3. Calculate decomposition per cycle from a) difference in total pressure and b) residual oxygen pressure over liquid ozone. Redo until decomposition is not decreasing anymore and decompositions from a) and b) are the same: conditioning ready



## Method for generation of defined ozone/air mixtures

With conditioned vacuum apparatus and cell:

- Measure decomposition of vacuum apparatus + cell and vacuum apparatus alone
- The decomposition per cycle (vacuum apparatus + cell) gives maximum initial decomposition of ozone in cell
- Monitor decomposition in cell spectroscopically
- After spectroscopic measurement trap ozone from cell and measure decomposition by cycling, check agreement with spectroscopic result
- If foreign gas added, check effect on line intensities (before/after) to quantify effect on ozone number densities. Careful selection of spectral features measurement conditions for line intensity determination (opacity, instrumental lineshape influence, ...)

## Method for generation of defined ozone/air mixtures

The method allows to determine ozone number densities better than 1%

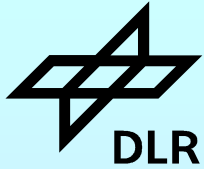
Proof: Experimental linestrengths of far-infrared pure rotational transitions of ozone and comparison to theoretical linestrengths from permanent electric dipole moment (small HWF): Birk, M., Wagner, G., and Flaud, J.-M., „Experimental Linestrengths of Far-Infrared Pure Rotational Transitions of Ozone“, J. Mol. Spectrosc. 163, 245-261 (1994)

Same method used for measurement of MIR linestrengths: agreement with other laboratories in the 1% range:

Wagner, G., Birk, M, Schreier, F, Flaud, J.-M., „Spectroscopic database for ozone in the fundamental spectral regions“, J. Geophys. Res. 107, D22, 4626 (2002), doi:10.1029/2001JD000818

Flaud, J.M., Wagner, G., Birk, M., Camy-Peyret, C., Claveau, C., De Backer-Barilly, M.R., Barbe, A., Piccolo, C., “The ozone absorption around 10  $\mu\text{m}$ ”, J. Geophys. Res., 108, (2003), S. ACH X-1-ACH X-3

Rinsland, C.P., Flaud, J.-M., Perrin, A., Birk, M., Smith, M.A.H., Wagner, G., Goldman, A., Malathy Devi, V., Benner, D.C., Barbe, A., Schreier, F., Tyuterev, V., Chance, K.V., Stephen, T.M., Mikhailenko, S., “Spectroscopic Parameters for Ozone and Its Isotopes: Recent Measurements, Outstanding Issues, and Prospects for Improvements to HITRAN”, JQSRT 82, 207-218 (2003)



## Capabilities for ozone spectroscopy

- Infrastructure and knowledge available for generating defined ozone/air mixtures with column amount knowledge inside the cell better than 1%
- Short and multipath cell available with high temperature homogeneity (200-300 K) for quasi-simultaneous measurements of ozone/air mixtures in FIR/MIR, MIR/UV, and FIR/UV
- FIR: Pure rotational transitions -> absolute line intensities known from dipole moment
- MIR/UV: Discrepancy between MIR and UV ozone intensities can be solved
- UV: High resolution Bruker + available gas cells are capable of solving any spectroscopic task for ozone