INFRARED ABSORPTION CROSS SECTIONS OF ClOOCl - LABORATORY WORK AND APPLICATION IN MIPAS-B MEASUREMENTS

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Introduction (1)

POLAR OZONE DEPLETION
Nobel Lecture, December 8, 1995
by
MARIO J. MOLINA

…

In 1987 we proposed a mechanism involving the self reaction of ClO to form chlorine peroxide [12], a compound which had not been previously characterized:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
$$Cl_2O_2 + h\nu \rightarrow 2\,Cl + O_2$$
$$2\,(Cl + O_3 \rightarrow ClO + O_2)$$
$$\text{Net: } 2\,O_3 + h\nu \rightarrow 3O_2$$

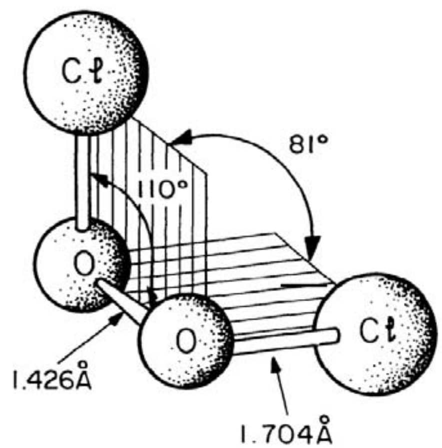


Fig. 4: Structure of chlorine peroxide [14].

…

The structure of the product formed in the termolecular ClO self reaction has been shown by both theory [13] and experiment [14] to be indeed ClOOCl, rather than ClOClO (see Figure 4).

…

14. Birk, M., R.R. Friedl, E.A. Cohen, H.M. Pickett, and S.P. Sander, *The Rotational Spectrum and Structure of Chlorine Peroxide*, J. Chem. Phys., 91, 6588-6597 (1989).

Introduction (2)

- But: No direct measurement and thus experimental proof for this species in the atmosphere existed until recently. Reason: weak infrared absorption and spectroscopic database missing
- Recent new UV absorption cross section measurements by JPL even created doubt in the ClOOCl cycle

- 1999/2000 MIR absorption cross sections have been measured at DLR within the national Ozone Research Programme but not published until 2010 together with first remote sensing observation of ClOOCl

  – due to over-commitment

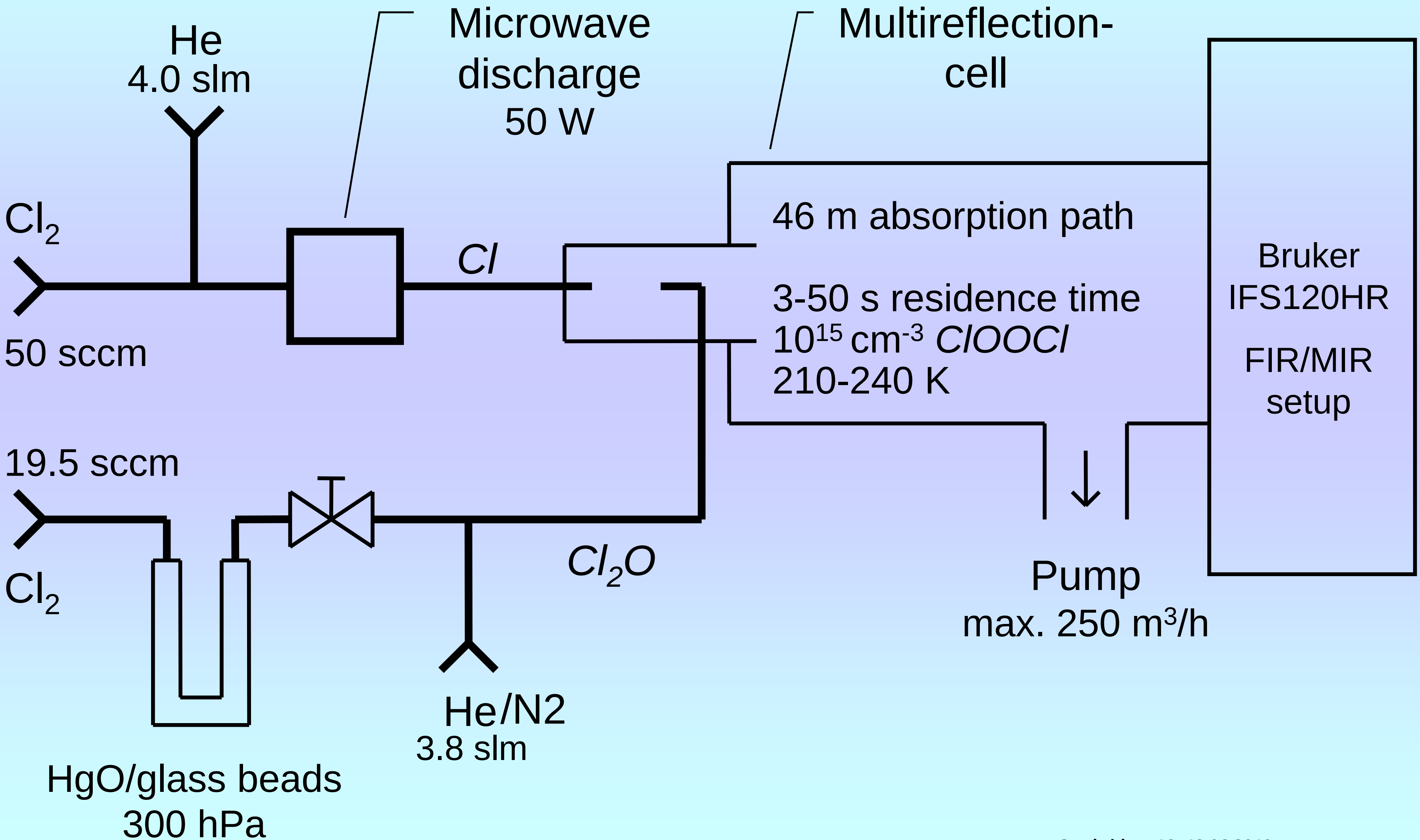
Laboratory measurements of ClOOCl

- Two targets:
  - MIR absorption cross sections (ACS) of ClOOCl, number density from FIR pure rotational lines
  - Percentage conversion of ClO into ClOOCl at stratospheric temperatures

- FIR linestrengths:
  - Permanent electric dipole moment measured 1990 (unpublished results)

  - Linestrengths of $^{35}ClOO^{35}Cl$, $^{35}ClOO^{37}Cl$, $V_{torsion}=0,1$ calculated for JPL catalogue
  - Problem: Uncertainty of torsional fundamental (127±20 cm^{-1}) introduces linestrength uncertainty of 11%
  - Other fundamentals (328, 443, 560, 653, 752 cm^{-1}) <5% uncertainty for 50 cm^{-1} fundamental error

Experimental Setup



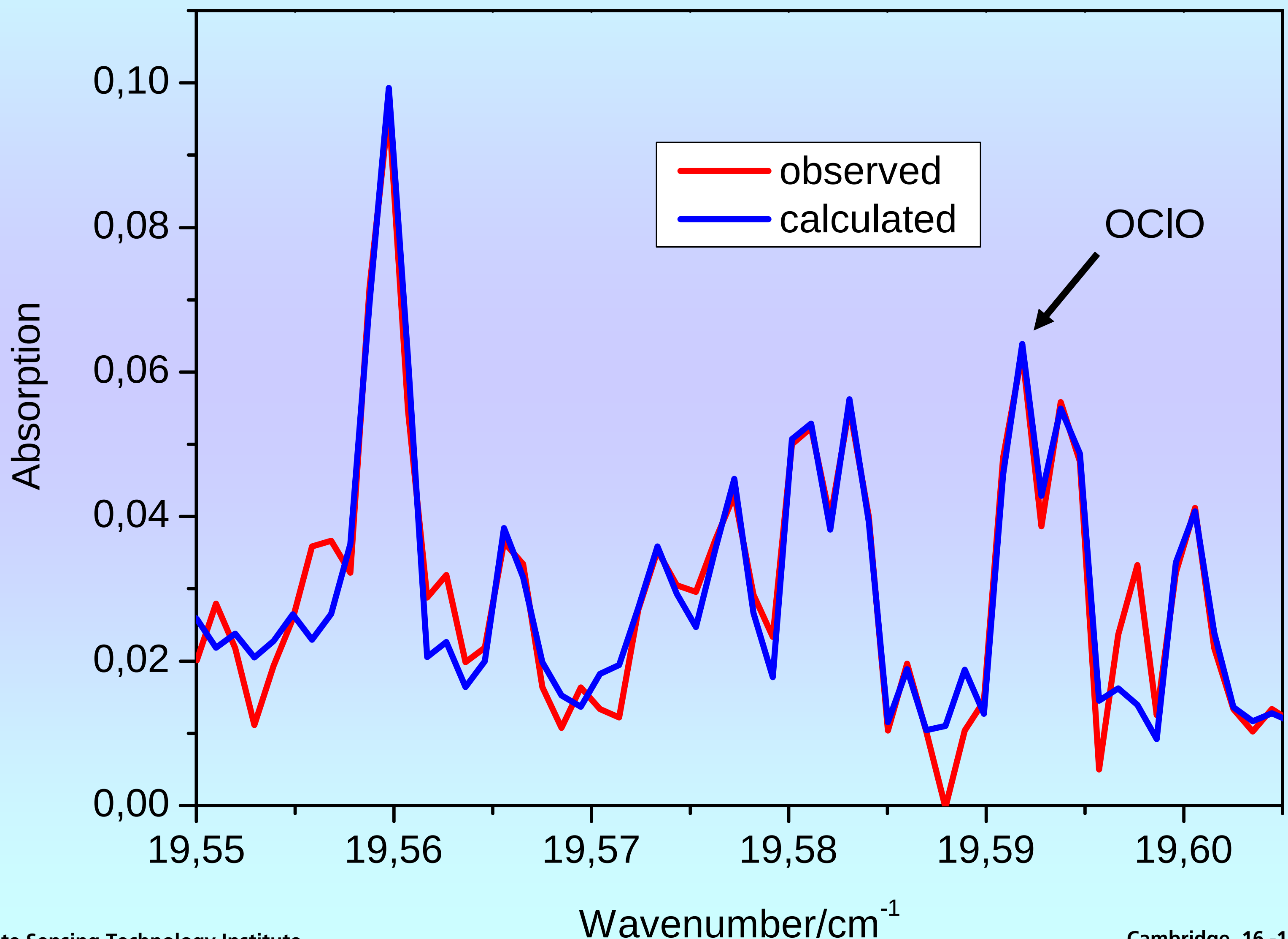
Improvement of rotational centrifugal distortion constants

- JPL catalogue based on rotational transitions in the range 9.5-14.5 cm^{-1}
- Measured FIR lines 17-24 cm^{-1}, calibration 7 ClO lines (15-28 cm^{-1})
- Thus: Predictions from JPL catalogue far off
- Refit of rotational constants including FIR lines:

Isotopologue	Torsional state	Submmw lines	FIR lines	Constants fitted/total
$^{35}ClOO^{35}Cl$	0	81	143	14/14
$^{35}ClOO^{37}Cl$	0	59	78	12/13
$^{35}ClOO^{35}Cl$	1	40	76	9/13
$^{35}ClOO^{37}Cl$	1	28	14	9/13

- Improved constants were never reported to JPL

Excerpts of modelled and measured ClOOCl.
Contaminants (Cl_2O_3, ClO, HOCl and OClO) also modelled
Instrumental resolution: 0.0013cm^{-1}=1/(2MOPD), P_{tot}=5 mb



Determination of torsional fundamental

- Use FIR spectrum with high Cl_2O titration (cell temperature 213.2 K)
- Determine contamination by Cl_2O, ClO, OClO, HOCl, Cl_2O_3, remove Cl_2O contamination by subtraction of pure Cl_2O spectrum
- Retrieve line intensities of rotational lines assuming torsional fundamental to be 127 cm^{-1}, taking into account contaminations
- Perform number density/temperature fit of ground state rotational lines (ca. 400) → gas temperature 225.1(8.7) K
- Perform number density fit of first excited torsional state rotational lines (ca. 200), fixing temperature at 225.1 K
- Calculate new torsional fundamental from number density ratio → 111.5(8.5) cm^{-1}

- Number density error

Determination of number density for MIR/FIR/MIR measurement

- Consecutive MIR/FIR/MIR measurements with constant flow conditions. Proof: MIR spectrum does not change. P_{tot} 5.4 mb, resolution FIR 0.0013 cm^{-1}, MIR 0.056 cm^{-1}
- FIR number density accuracy:
  - Dipole moment 2%
  - Partition sum 5%
  - Temperature 7%
  - Statistical error 4%
  - **Total (rss) 10%**
  - **ClOOCl number density 0.98(10)×10^{15} molec/cm^3**
- Cl_2O titration 30% -> Maximum ClOOCl number density 1.2x10^{15} molec/cm^3
- **Percentage conversion of ClO into ClOOCl: 80(10)%**

ClOOCl MIR absorption cross section
213 K, 40 mb

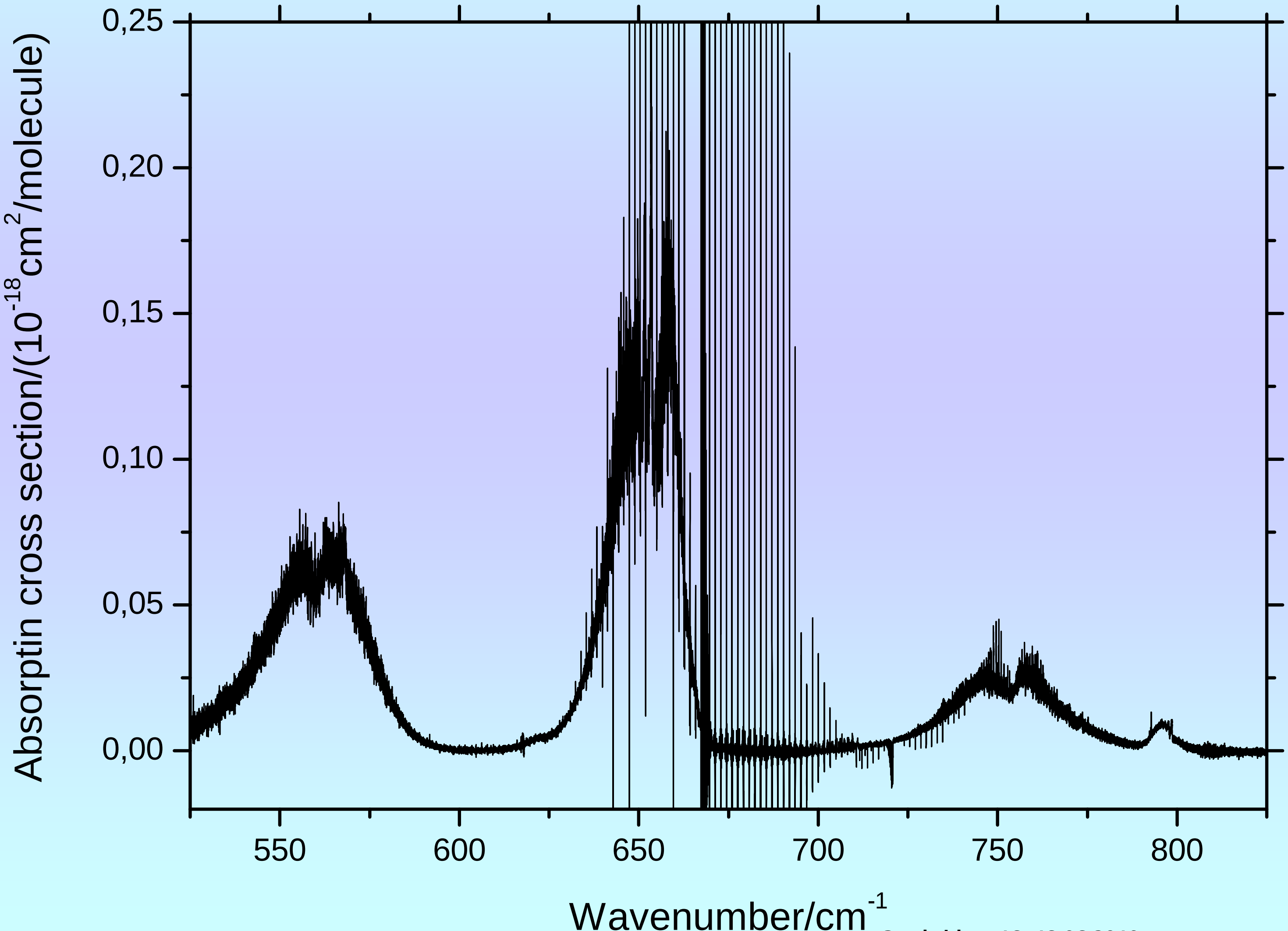
Total error 12%

Only other published cross sections factor 3 smaller!

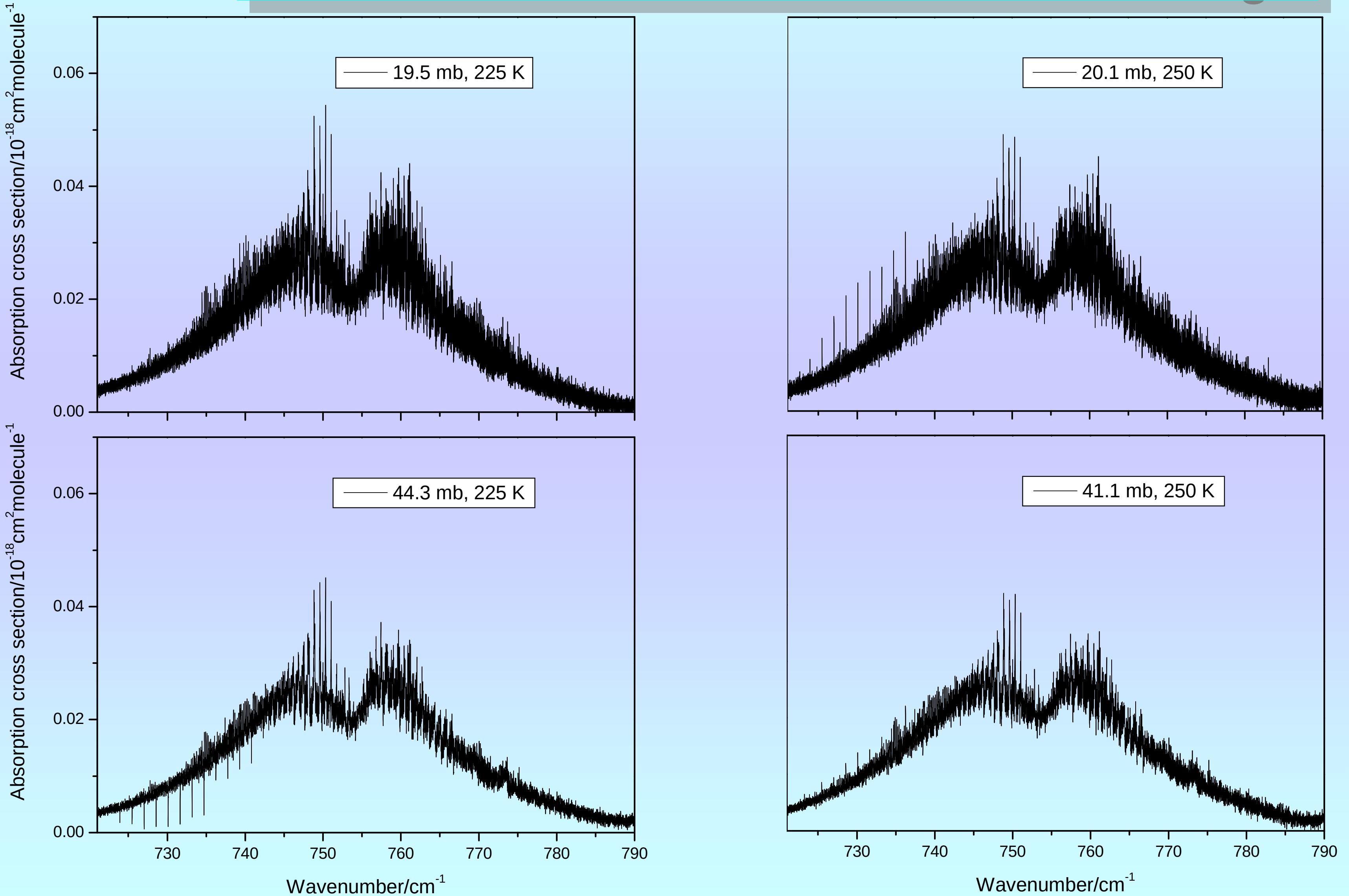
„Integrated IR band intensities of the ν5 and ν1 bands of ClOOCl“, *A. S. Brust, F. Zabel, and K. H. Becker*, Geophys. Res. Lett., 24, 1395-1398 (1997)

Number density from UV measurement

UV/MIR optical paths through cell orthogonal



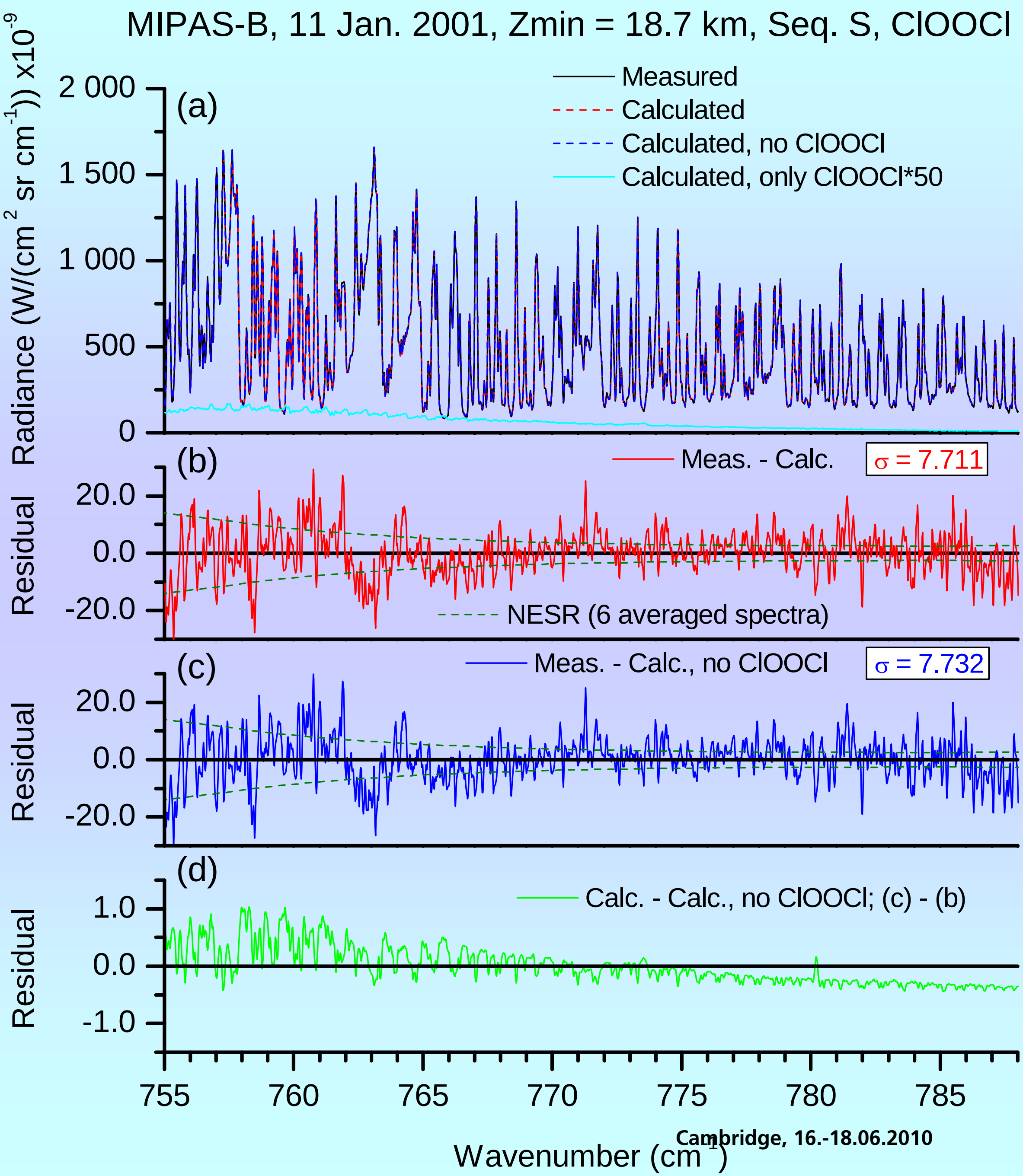
ClOOCl MIR absorption cross sections of weakest band used for remote sensing



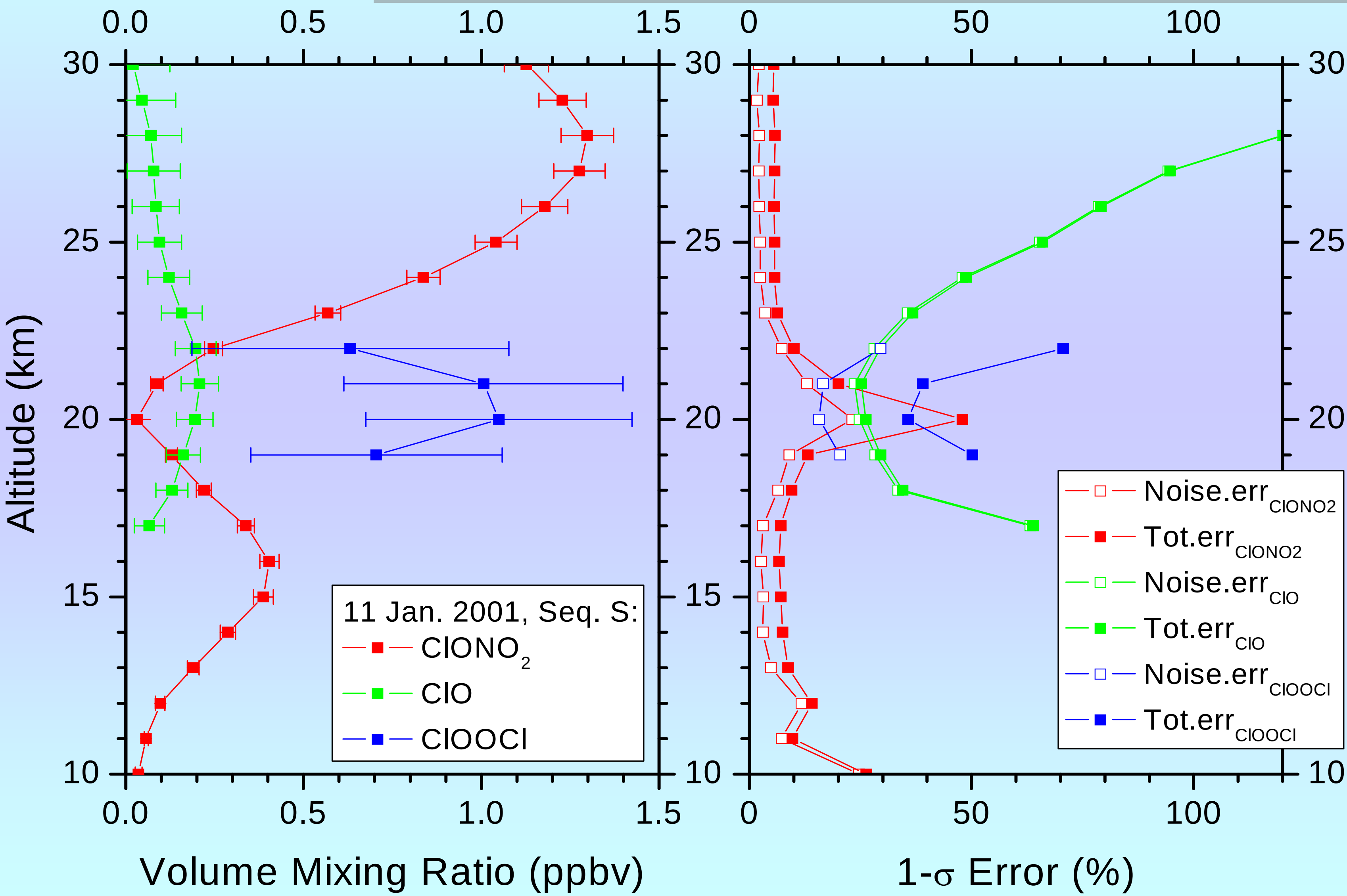
Excerpt of high resolution ClOOCl MIR spectrum
T=213 K, P_{tot}=5 mb, res=0.0013 cm^{-1}

MIPAS ClOOCl measurement in perturbed chemistry in Kiruna

G. Wetzel, H. Oelhaf, O. Kirner, R. Ruhnke, F. Friedl-Vallon, A. Kleinert, G. Maucher, H. Fischer, M. Birk, G. Wagner, and A. Engel, „First remote sensing measurements of ClOOCl along with ClO and ClONO2 in activated and deactivated Arctic vortex conditions using new ClOOCl IR absorption cross sections“, Atmos. Chem. Phys., 10, 931-945, 2010



First direct measurement of ClOOCl - in line with inorganic chlorine budget



MIPAS/TELIS balloon mission

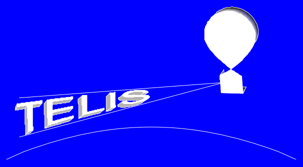
TELIS (cryogenic heterodyne spectrometer) species (limb sounding: height range 10-40 km, altitude resolution 2 km)

- DLR, 1830 ±40 GHz: OH, HO_2, HCl, NO, NO_2, O_3, H_2O, O_2, HOCl, $H_2{}^{18}O$, $H_2{}^{17}O$, HDO, CO
- RAL, 499 – 503 GHz: BrO, ClO, O_3, N_2O
- SRON, 450 – 660 GHz: ClO, BrO, O_3, O_2, HCl, HOCl, H_2O, HO_2, NO, N_2O, HNO_3, CH_3Cl, HCN, $H_2{}^{18}O$, $H_2{}^{17}O$, HDO

MIPAS-B (Fourier-transform spectrometer) species

O_3, NO, NO_2, HNO_3, HNO_4, N_2O_5, $ClONO_2$, ClOOCl, ClO, HOCl, $ClONO_2$, HDO, $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, N_2O, CH_4, CO, SF_6, CF_4, CCl_4, CFC-11, CFC-12, CFC-113, HCFC-22, CH_3Cl, NH_3, acetone, PAN, C_2H_6, C_2H_2, temperature

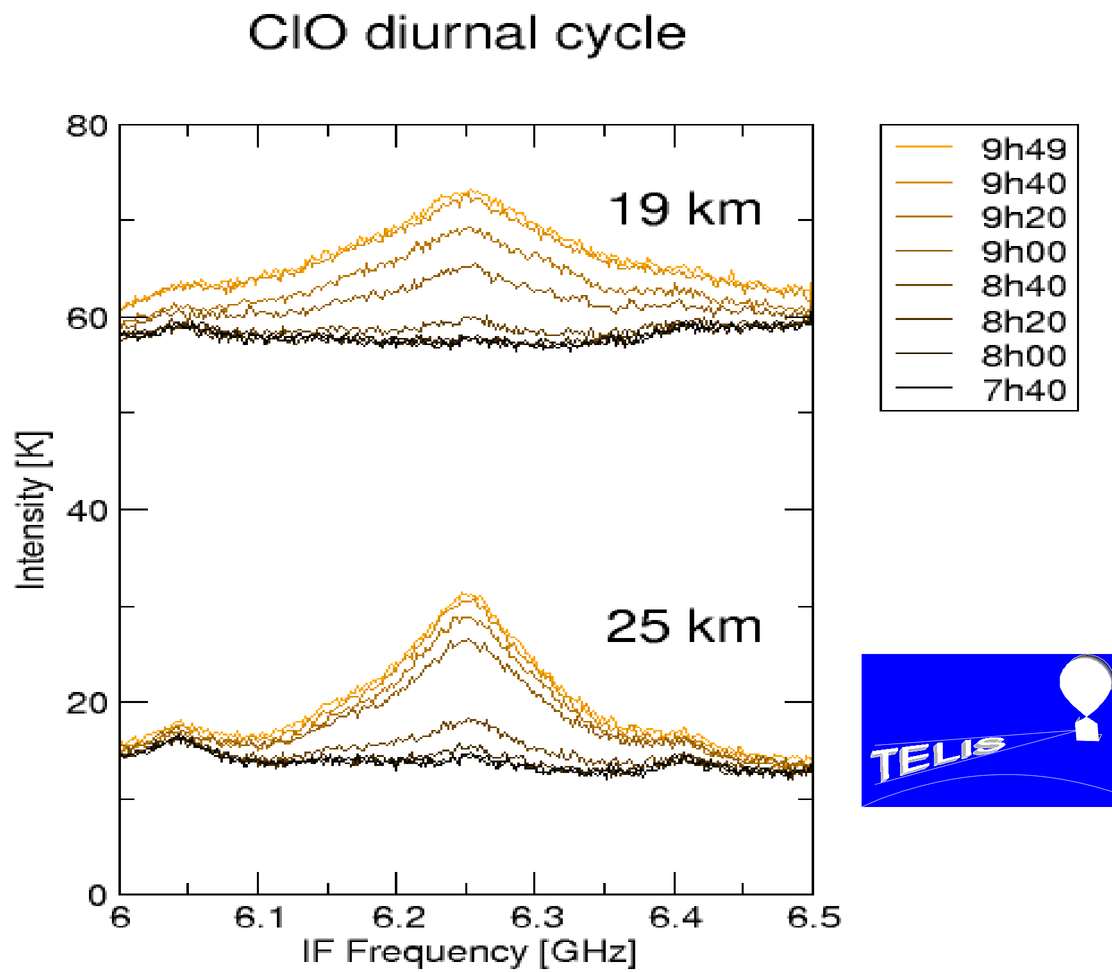
Species measured with MIPAS-B and TELIS
TELIS highlights
Sensitivity improved vs. MIPAS-B



MIPAS/TELIS gondola during roll-out, Kiruna 2009

TELIS measurement of ClO @ 501.27 GHz
Temporal evolution at two sample tangent heights

- Kiruna, January 2010
- Perturbed chemistry
- Balloon height 34 km
- Integrated receiver from SRON, T_{sys}=200 K



Together with MIPAS ClOOCl measurements photolysis rates of ClOOCl will result closing the gap in understanding the ozone hole