Accuracy Validation of a Spectroscopic Gas Analyzer using Gravimetric Standard Gas Mixtures

– Impact of Background Gas Composition on CO_2 Measurement by Cavity Ring-Down Spectroscopy

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Jeongsik Lim and Jeongsoon Lee

KRISS (Korea Research Institute of Standards and Science)

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INDEX

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PART 1

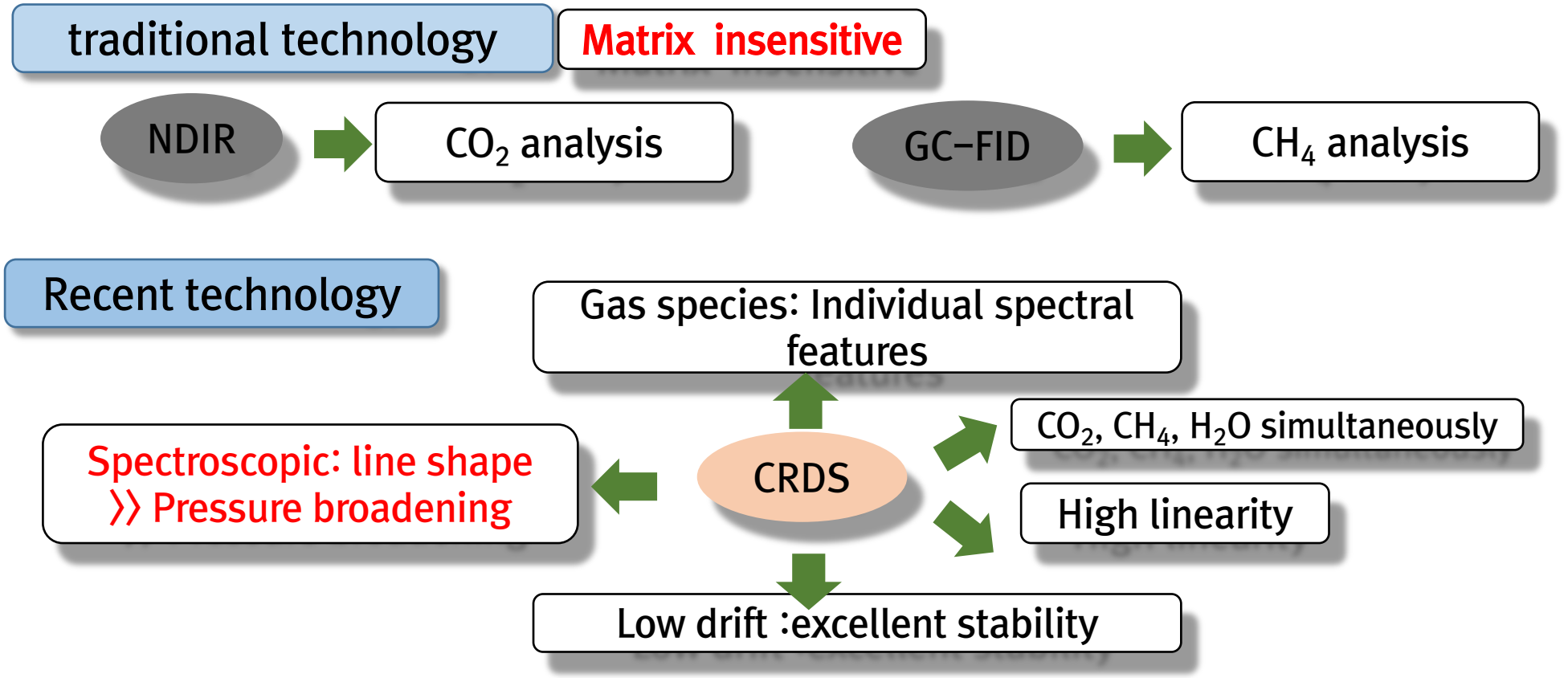
Pressure Broadening CO_2

1. Background
2. CRDS: Pressure broadening on CO_2 line
3. Measurement of broadening coefficients
4. summary

Background

- High precision and accurate of CO_2 &CH_4 measurement by the researcher investigating global climate change
- Target precision (WMO)

  CO_2 : 0.1 μmol mol^{-1}, CH_4 : 0.002 μmol mol^{-1}(alleviate)

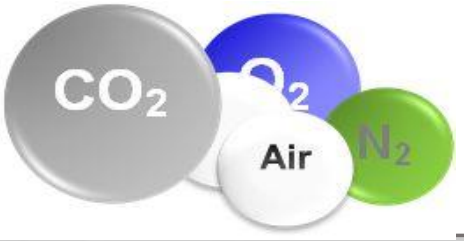


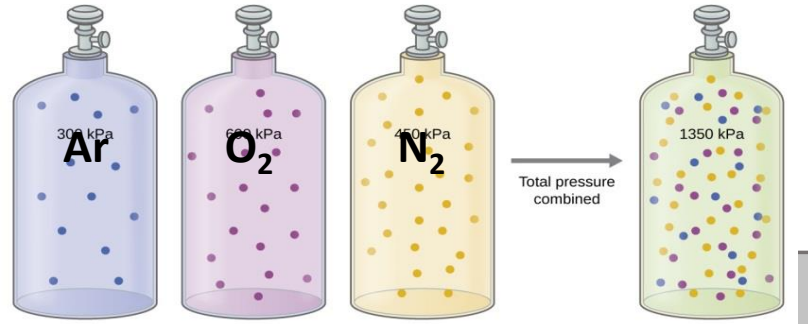
Well prepared standard mixtures

Amount of CO_2 Mole fractions of the gas mixtures.

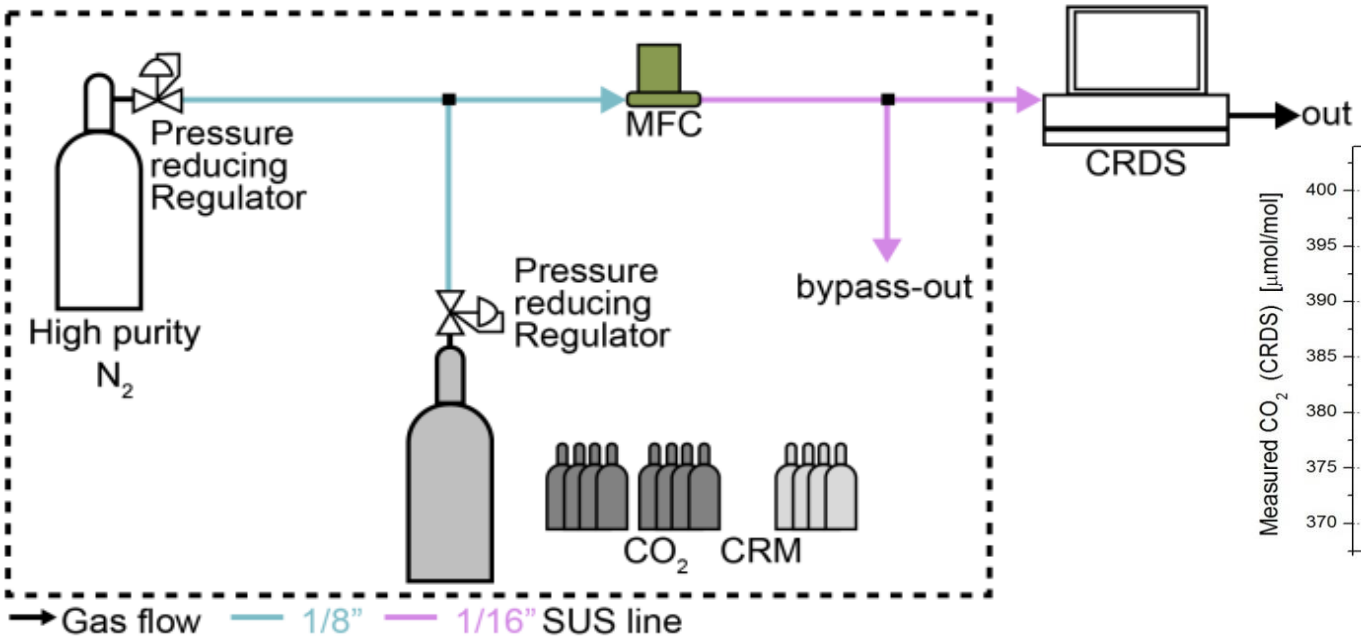
Cylinder #	Gas composition (%mol/mol)				Preparation method
	CO_2	N_2	O_2	Ar	
DF4560	400.61 (0.02%)	99.96	-	-	gravimetry
EB0011591	351.78 (0.10%)	83.45	16.48	0.04	manometry
EB0011528	353.08 (0.10%)	80.97	18.19	0.81	manometry
ME5590	386.94 (0.02%)	78.33	21.63	-	gravimetry
EB0006391	406.40 (0.10%)	78.16	20.87	0.93	manometry
ME0434	402.25 (0.02%)	78.07	21.03	0.87	gravimetry
ME5502	384.35 (0.02%)	77.57	20.53	1.86	gravimetry
ME5537	385.35 (0.02%)	70.98	18.85	10.12	gravimetry

- Gravimetrically
- manometrically

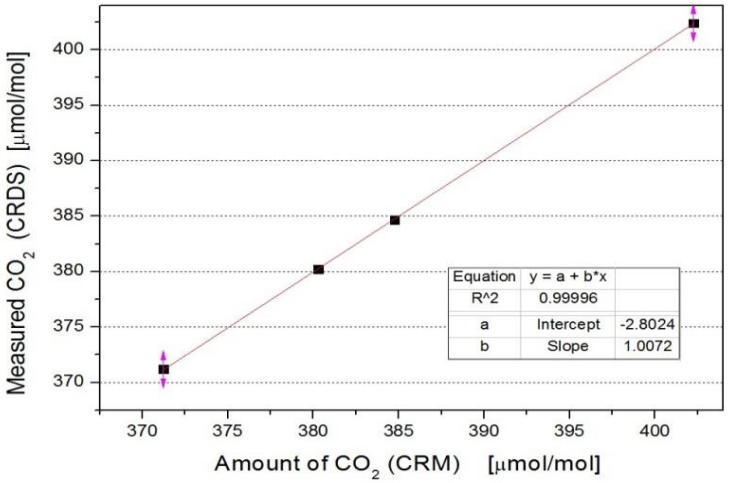




Experimental setting and calibration



WS-CRDS analyzer calibration with air



Schematic diagram: for gas plumbing to the WS-CRDS analyzer

(WS-CRDS, G-1301, Picarro, USA)

- CO_2 at a wavelength of 1.603 µm
  : R(1) of the (3 00 1)III ← (0 0 0) CO_2 band

Cylinder #	CO_2 mole fraction [µmol/mol]			Difference[D]	
	CRM assigned	before CRDS cal	after CRDS cal	[µmol/mol]	[%]
ME0424	371.22	371.18	371.29	0.07	0.0193
ME0485	380.31	380.23	380.28	−0.03	−0.0088
ME5552	384.76	384.66	384.67	−0.09	−0.0222
ME0434	402.25	402.41	402.30	0.05	0.0117

Differences

- Differences between the measured (corrected) and assigned concentrations are also listed.
  - CO_2 concentrations determined by gravimetry, measured using the well-calibrated CRDS
  - Before correction by considering **N_2-induced pressure** broadening
  - Against the assigned values, excess N_2 exhibited a negative CRDS response, whereas excess Ar showed a positive deviation.

Cylinder #	CO_2 mole fraction [µmol/mol]		Difference	
	$A_{assigned\ value}$	$B_{CRDS\ measured}$	(B-A) [D] [µmol/mol]	(B-A)% [E] (=(B-A)/A*100)
DF4560	400.61	390.84	−9.77	−2.44
EB0011591	351.78	349.62	−2.16	−0.61
EB0011528	353.08	352.05	−1.03	−0.29
ME5590	386.94	386.51	−0.43	−0.11
EB0006391	406.40	406.39	−0.01	0.00
ME0434	402.25	402.34	0.09	0.02
ME5502	384.35	384.80	0.45	0.12
ME5537	385.35	390.71	5.36	1.39

Line shapes

Types of line broadening

1. Natural broadening ($\Delta\nu_u$): Result of finite radiative lifetime
2. **Collisional/pressure broadening ($\Delta\nu_C$): Finite lifetime in quantum state owing to collisions**
3. Doppler broadening ($\Delta\nu_D$): Thermal motion
4. Voigt profile ($\Delta\nu_V$): Convolution of Lorentzian to Gaussian

$$\gamma_{TPBC} = \gamma_{N_2} p_{N_2} + \gamma_{O_2} p_{O_2} + \gamma_{Ar} p_{Ar}$$

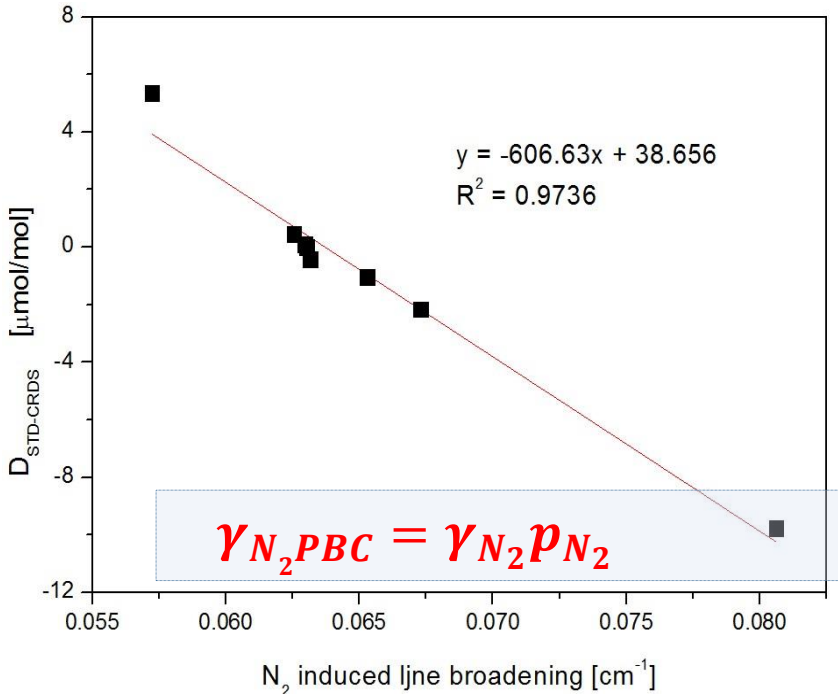
	Pouchet et al.	Nakamichi et al.	HITRAN
γ_{N_2}	0.0721	0.08064	0.0778
γ_{O_2}	0.0660	0.06695	0.0702
γ_{Ar}	-	0.06312	-
γ_{air}	-	0.078	0.0758

- ✓ Pouchet I., et al. (2004), Diode laser spectroscopy of CO_2 in the 1.6 µm region for the in situ sensing of the middle atmosphere, J. Quant. Spectrosc. Radiat. Transfer, 83(3-4), 619–628, doi: 10.1016/S0022-4073(03)00108-0.
- ✓ Nakamichi S., et al., (2006), Buffer-gas pressure broadening for the (3 0(0) 1)III <-- (0 0 0) band of CO_2 measured with continuous-wave cavity ring-down spectroscopy, Phys. Chem. Chem. Phys., 8(3), 364–368, doi: 10.1039/b511772k.
- ✓ Rothman L. S., et al. HITRAN 2004

Differences

III
N2 induced

- Differences between the measured (corrected) and assigned concentrations are also listed.
  - CO_2 concentrations determined by gravimetry, measured using the well-calibrated CRDS;
  - After correction by considering **N_2-induced pressure** broadening
  - $y_{corrected} = y_{CRDS} - \left(-606.63 \cdot \gamma_{N_2} \cdot p_{N_2} + 38.656\right)$



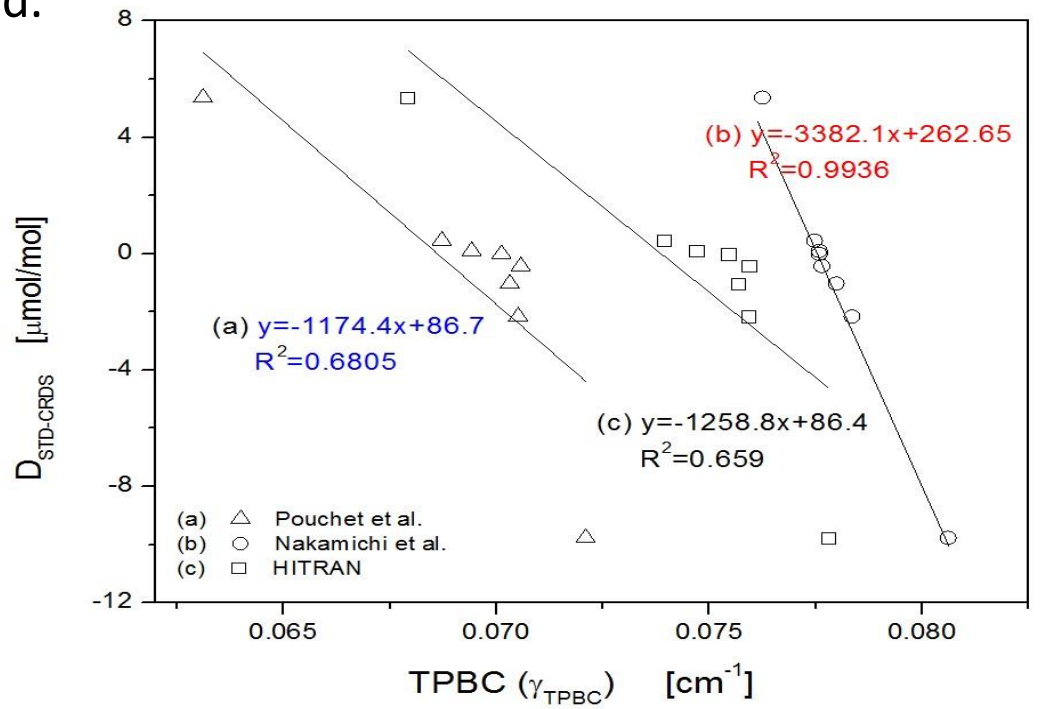
Cylinder #	CO_2 mole fraction [µmol/mol]		Difference
	$A_{assigned\ value}$	$C_{PBC\ (N2)\ corrected}$	(C-A)% F (=(C-A)/A*100)
DF4560	400.61	401.09	0.12
EB0011591	351.78	351.79	0.00
EB0011528	353.08	353.00	−0.02
ME5590	386.94	386.17	−0.20
EB0006391	406.40	405.97	−0.11
ME0434	402.25	401.87	−0.09
ME5502	384.35	384.09	−0.07
ME5537	385.35	386.78	0.37

- Pressure broadenings for the investigated gas mixtures based on various pressure broadenings coefficients from different references
- Furthermore, this correction linearly drifted the CRDS responses for a wide extent of TPBC ranging 0.064 to 0.081 cm^{-1} atm^{-1}.

$$\gamma_{TPBC} = \gamma_{N_2} p_{N_2} + \gamma_{O_2} p_{O_2} + \gamma_{Ar} p_{Ar}$$

Cylinder #	Pouchet et al.(a)	Nakamichi et al.(b)	HITRAN (c)
DF4560	0.0721	0.08061	0.0778
EB0011591	0.0710	0.07835	0.0765
EB0011528	0.0704	0.07798	0.0758
ME5590	0.0708	0.07765	0.0761
EB0006391	0.0701	0.07759	0.0755
ME0434	0.0702	0.07758	0.0755
ME5502	0.0695	0.07747	0.0748
ME5537	0.0636	0.07625	0.0685

- Total pressure broadening vs. difference between the measured value by CRDS and the assigned value of the standard gas mixture
- (a) and (c): Because of the lack of γ_{Ar}, the correlations to the fitted line are poor
- In practice, *Huang and Yung* [2004] reported that the Lorentzian width responds in a direction opposite to the peak value of the Voigt function for a fixed Gaussian width. According to the results shown in the Figure, as the TPBC increased, the differences, $D_{STD\text{-}CRDS,}$ decreased.



- ✓ Gravimetric gas mixtures of ambient air composition were utilized as calibration standards for CO_2 measurement by CRDS
- ✓ A linear shift of CRDS response was observed as a function of total pressure broadening coefficient (TPBC) ranging over 0.05 cm^{-1} atm^{-1}
- ✓ TPBC-corrected CRDS response agreed with the gravimetric concentration of the attempted gas mixtures within 0.15% (±0.6 µmol/mol)

Cylinder #	CO_2 mole fraction [µmol/mol]		Difference	
	Sample assigned value [A]	TPBC Correction value [B]	(B – A) [C] [µmol/mol]	((B-A)/A*100) [D] %
DF4560	400.61	400.82	0.21	0.05
EB0011591	351.78	351.97	**0.19**	**0.05**
EB0011528	353.08	353.15	**0.07**	**0.02**
ME5590	386.94	386.47	−0.47	−0.12
EB0006391	406.40	406.15	**−0.25**	**−0.06**
ME0434	402.25	402.09	**−0.16**	**−0.04**
ME5502	384.35	384.17	**−0.18**	**−0.05**
ME5537	385.35	385.95	0.60	0.16

Summary

- the effect of background composition on CO_2 measurement has been investigated using wavelength-scanned cavity ring-down spectrometry (WS-CRDS), taking a spectral line centered at the R(1) of the $(3\ 0^0\ 1)_{III} \leftarrow (0\ 0\ 0)$ band.
  - For this purpose, eight cylinders with various compositions were gravimetrically and manometrically prepared with $1\sigma = 0.1\%$
  - Depending on the gas composition, the deviations between the CRDS responses and gravimetrically (or manometrically) assigned CO_2 concentration ranged from −9.77 to 5.36 µmol/mol.
  - The total pressure broadening coefficient (TBPC) based on the composition of N_2, O_2, and Ar corrected the deviations to up to 0.15%.
- To obtain accurate measurements using intensity-based optical measurement techniques such as WS-CRDS, it is imperative to calibrate the instrument based on TBPC (use air mixture within moderate composition)
- accurate CO_2 line pressure broadening coefficients can be obtained from experimental broadening measurement of accurate standard mixtures

CRMs for Greenhouse Gas Analysis

substance	Range of Certified Values in Reference Materials	Uncertainty (k=2) [U=2*u=2*]	Dissemination	ref
CO_2	above 10 µmol/mol	**0.08 at 380 µmol/mol**	Air / Air modified	CCQM-K3, 52, 120
CH_4	above 100 nmol/mol	0.005 at 1.9 µmol/mol		CCQM-P41, 82
N_2O	above 50 nmol/mol	0.2 at 320 nmol/mol		CCQM-K68
CO	above 100 nmol/mol	0.3 at 350 nmol/mol		CCQM –K84
SF_6 NF_3	above 6 pmol/mol for SF_6 above 1 nmol/mol for NF_3 (0.5 pmol/mol after 2011)	0.06 at 6 pmol/mol for SF_6 0.01 at 1 nmol/mol for NF_3		CCQM-K15,
PFCs	above 10 pmol/mol for CF_4 above 100 µmol/mol for C_2F_6 (50 pmol/mol after 2013)	0.5 at 10 pmol/mol for CF_4		CCQM-K15,
HFCs, CFCs HCFCs	µmol/mol~50 pmol/mol for CFC 11,12,113	0.2 at 50 pmol/mol for CFC		CCQM-K83

- Standard gas mixtures

❖ CRMs for Greenhouse Gas Analysis

- Carbon dioxide, methane, nitrous oxide in nitrogen or air
- F-compounds in nitrogen or air: Semiconductor, Display, Chiller
- Stable Isotope (CNOHS) in greenhouse

❖ CRMs for Environmental Gas Analysis

- Automobile emission test gases
- Air pollution monitoring gases: NOx, SOx, CO, O_3
- Volatile organic compounds in atmospheric air and indoor air

❖ CRMs for Industrial Gas Analysis

- Natural gases, pipeline natural gases
- Inorganic gases for atomic power plant
- Process gas for industry application

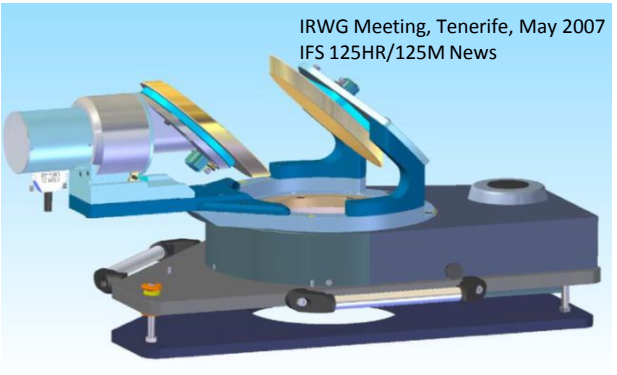
PART 2
KRISS FTS–Sun tracking observation

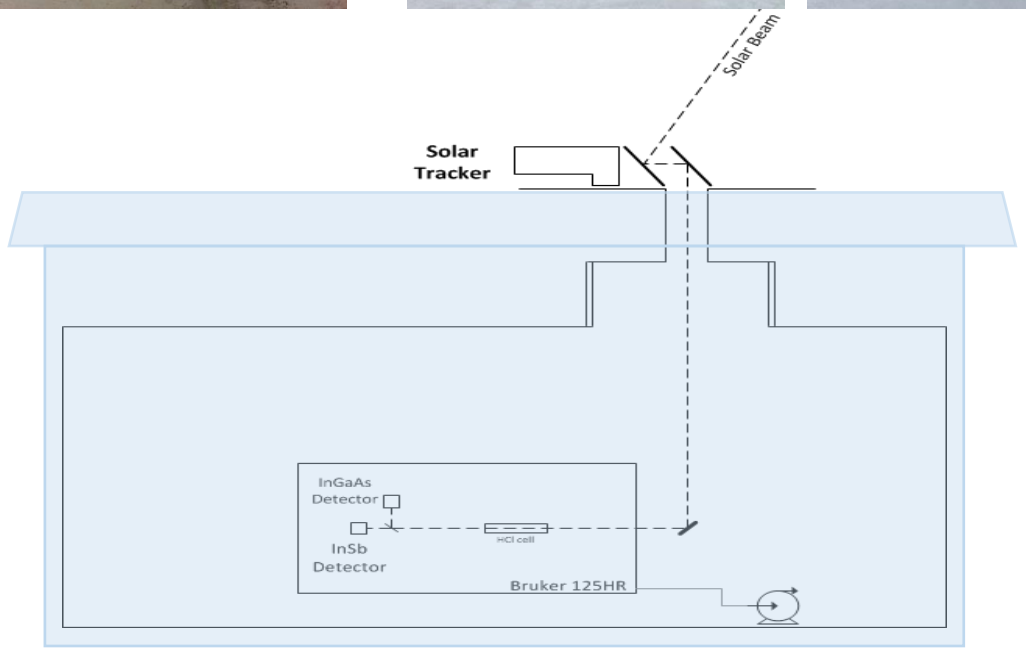
1. Site: instrument, location, observation
2. Calibration: x(spectral), y(irradiation)

Part2: KRISS FTS-Sun tracking observation

- Site: instrument, location, observation
- Calibration: x(spectral), y(irradiation)
- Pressure broadening measurement

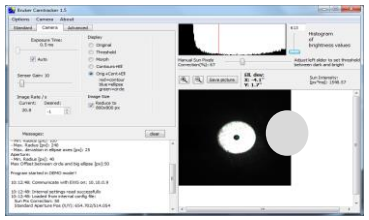
KRISS FTIR solar tracker

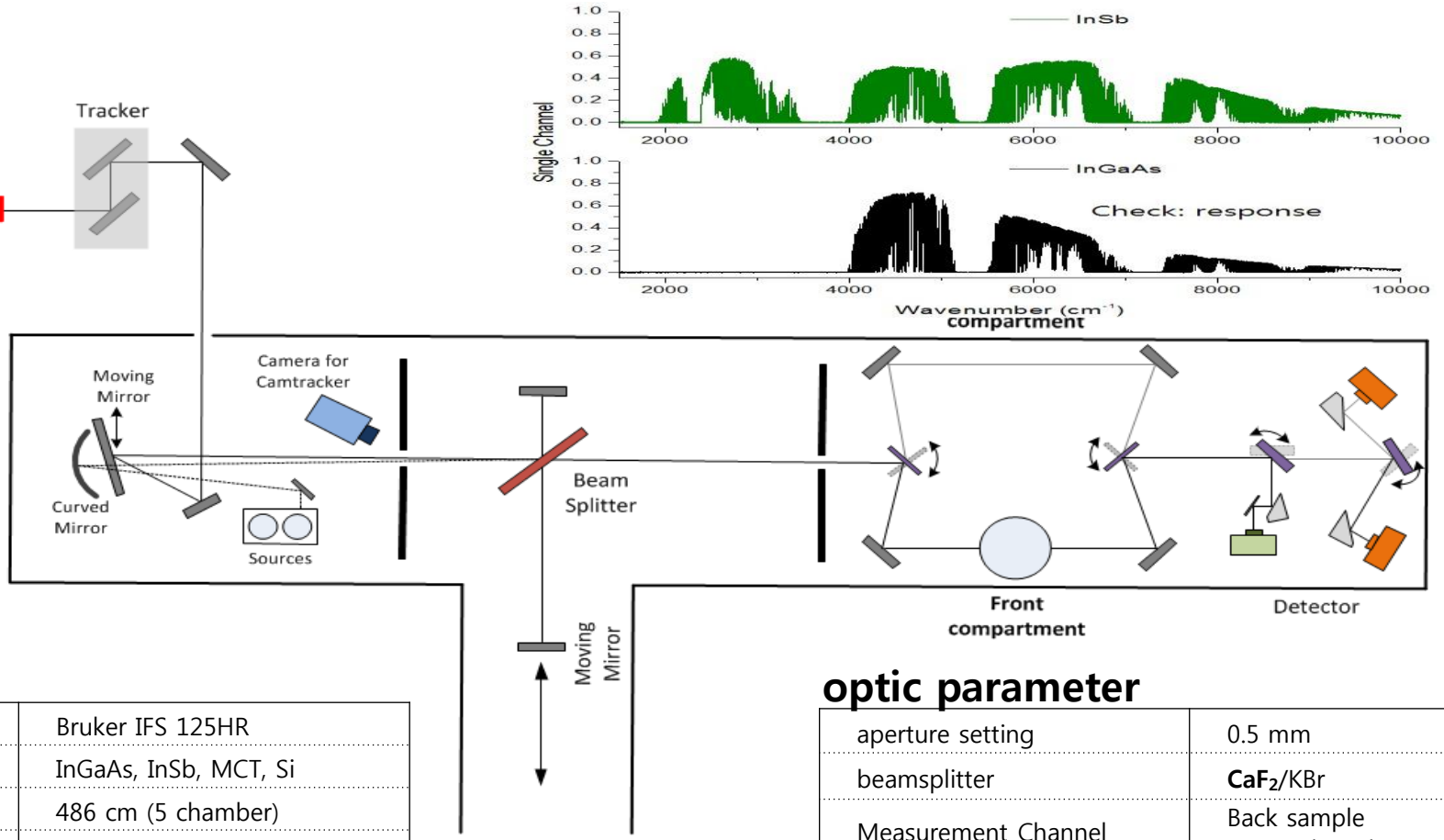




KRISS analyzer system:
Sun tracker(A547N) + FTS(IFS120HR-upgraded)
installed since Dec. 2012

KRISS FTIR solar tracker





KRISS FTS

FTS	Bruker IFS 125HR
Detector	InGaAs, InSb, MCT, Si
Max. OPD	486 cm (5 chamber)
Spectral Max resolution	~ 0.002/cm
He:Ne reference laser	15798.02/cm
Softwear	OPUS 7.0

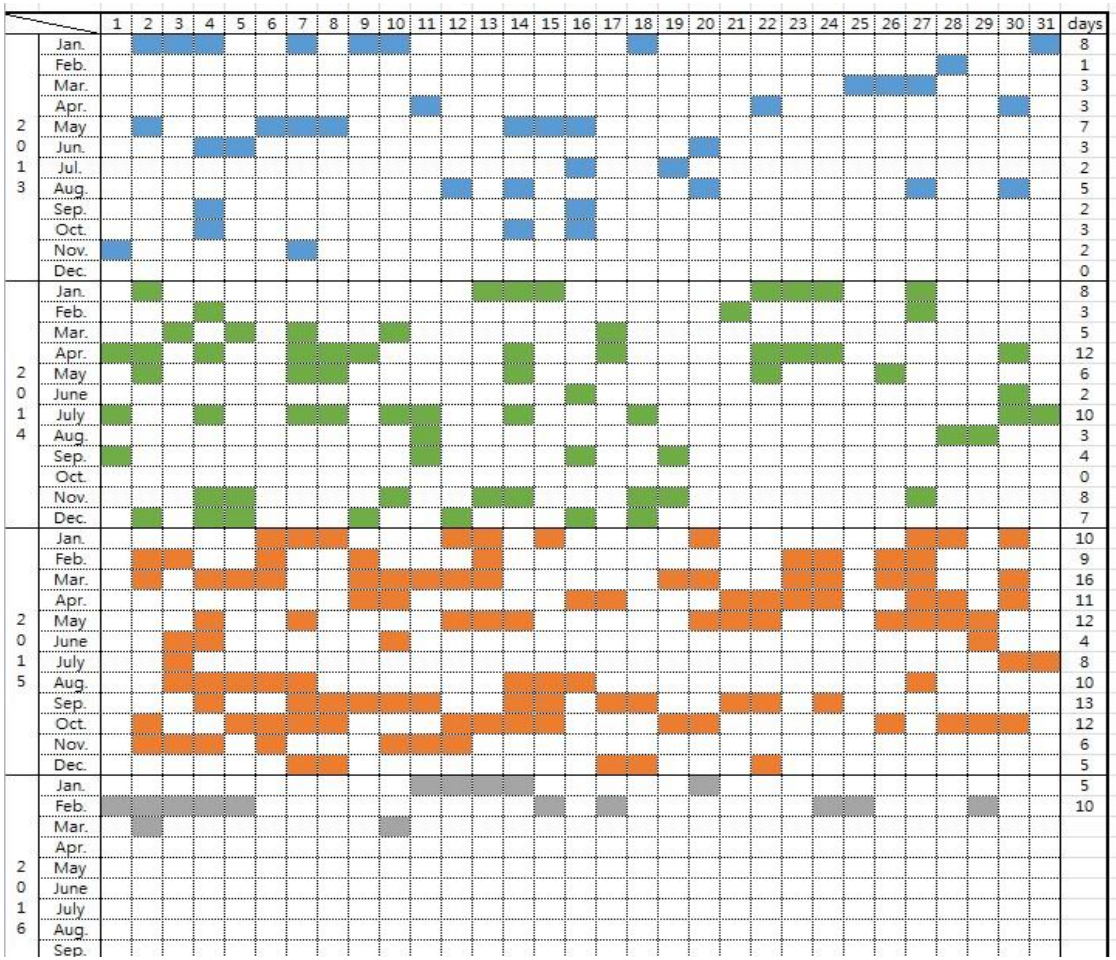
optic parameter

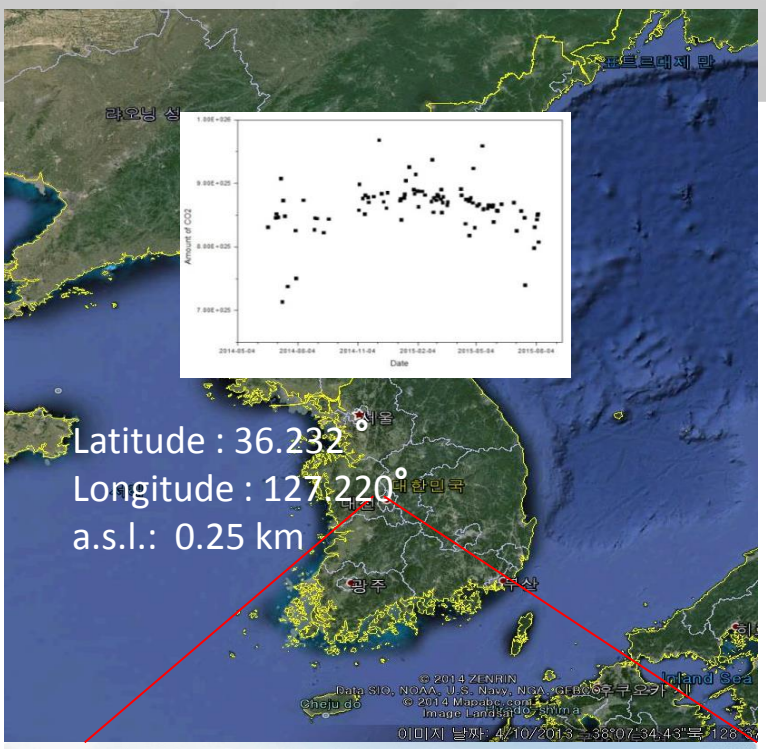
aperture setting	0.5 mm
beamsplitter	**CaF_2**/KBr
Measurement Channel	Back sample compartment
Spectral resolution	~ 0.014/cm
Apodization function	Boxcar
Focal length	418 mm

➢ KRISS analyzer system: Sun tracker(A547N) + FTS(IFS125HR) installed since Dec. 2012

KRISS Site

- KRISS FTIR observation dates





1. Daily average CO2 result of FTIR observations
   - A total of 85 days (2014/6 - 2015/9; 16 month)
   - Preliminary result: vertical mixing ratio per daily average)

Current status of the FTIR system

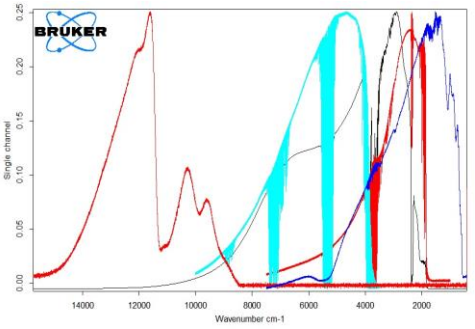
- Spectral Range : 700 ~ > 14000 cm^{-1}

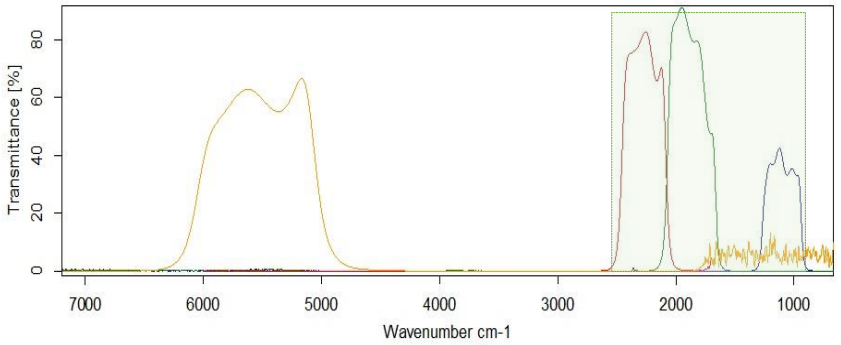
FTIR: New detector is installed in Jan. 2016

Detector	Source	Beam splitter
Si	Tungsten	CaF_2
InGaAs	Globar	KBr
InSb		Quartz
MCT		

FTIR: optical Filters

NDACC Filter	Wavenumber (cm^{-1})	Availability : KRISS FTIR
1	4000 - 4300	Not-Available
2	2900 - 3500	Not-Available
3	2400 - 3100	Not-Available
4	2000 - 2700	Available
5	1500 - 2200	Available
6	750 - 1350	Available



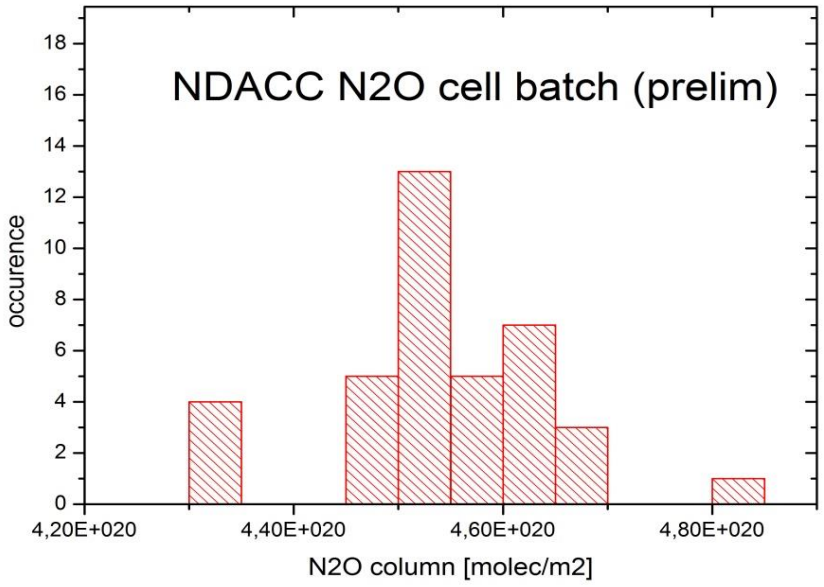


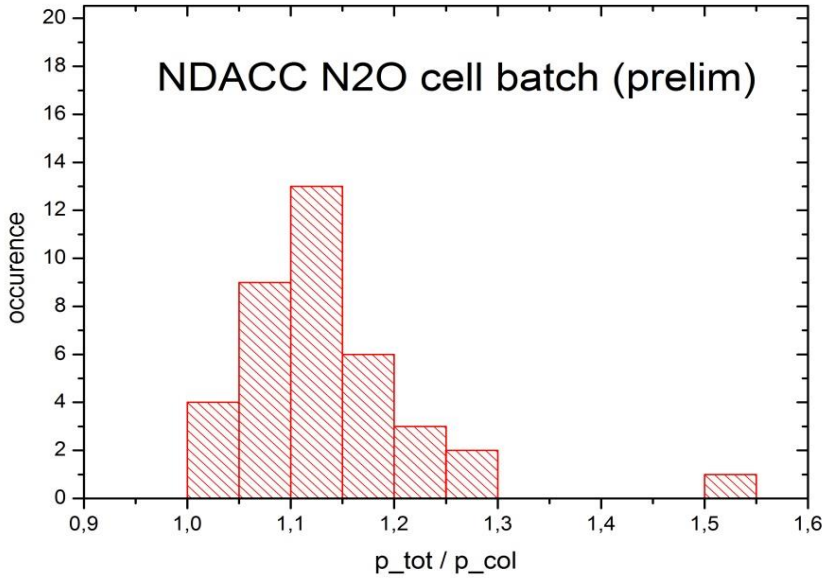
NDACC requirement

Spectral range: 700-4100 cm-1 (minimum),

Cell preparation: NDACC, Khe

- Results derived from spectra recorded in Khe



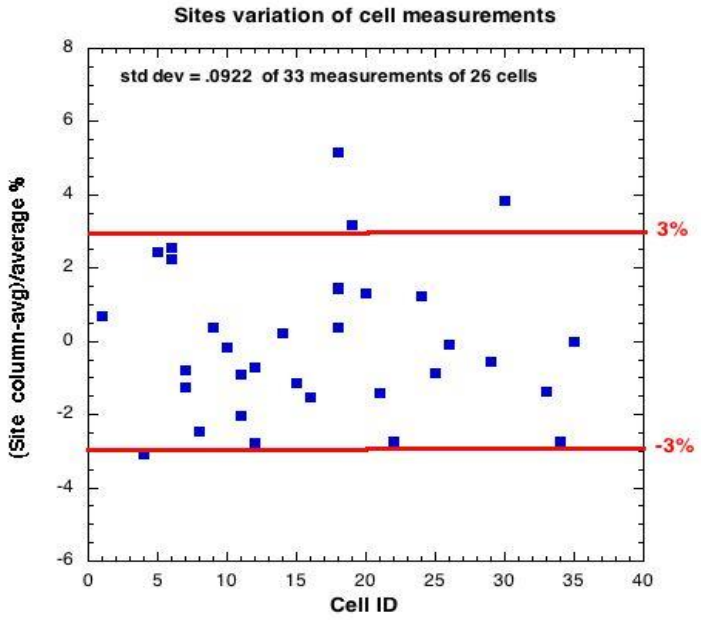


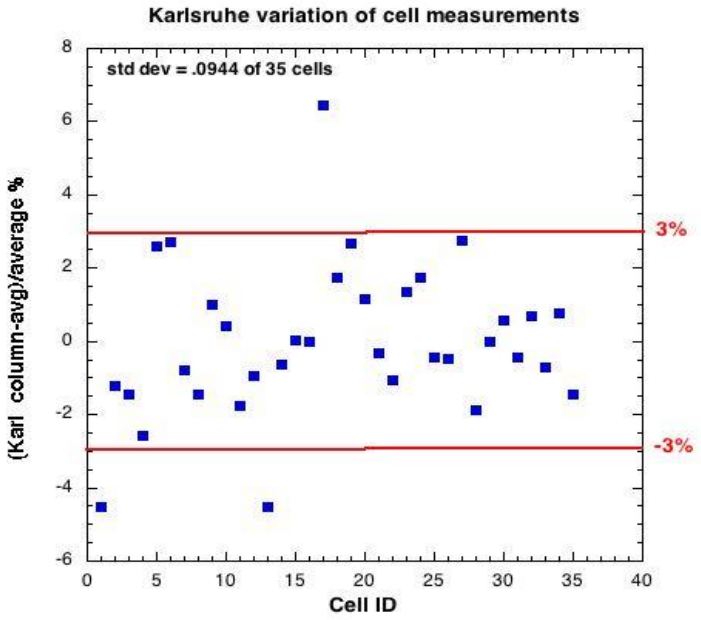
- Note: for the blind icomp column retrieval, the impurity of the cell content has been neglected (but consistently in distributed retrieval recipe & retrieved columns from Khe spectra).

NDACC cell exercise

Preliminary results

- NDACC cell comparison





N2O determined at IRWG sites 33 measurements made of 26 cells

N2o cell column amount determined by Frank Hase at Karlsrue

No #	Reference Cells ID	Laboratory Temperature	Fitted T	Fitted P	Fitted Column amount
1	N2O-21	297.9	298.42	0.9173	4.49067E+20
2	N20-22	297.1	296.39	0.962	4.43145E+20

PART 3

Future works

1. Summary & Future works

Summary & Future works

Enhancements of our FTIR analyzer performance

- Radiometric calibration: blackbody, cal. Tungsten lamp etc.
- Spectral calibration :
- ILS study
- Pressure broadening : HCl, HBr, N_2O etc.
- Data processing with GGG & PROFFIT and comparison with modeled data
  - 3 Dimensional atmospheric Chemical Transportation Model(GEOS-Chem)
  - Satellite data

Line broadening effect

- CRDS matrix effects on the line of CO_2
- Line broadening coefficients
- CO, CH_4

Thank you for attention!!