Pressure dependent line intensity and continuum absorption for pure CO_2: experimental results

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HRMS 2023, Dijon

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Introduction

- Radiative transfer models: Line intensities are pressure-independent
- Intensity decrease with increasing pressure known for HF in Xe 2%/atm [Kouzov 2000] and HCl in Ar 1%/atm [Boulet 2004]
- Recent confirmation by Tran, 2023, pure HCl 3%/atm, HCl in CO_2 3%/atm, HCl in air 0.8% - no intensity decrease for HCl in He
- CO in N_2 only 0.3%/atm, no effect for CO in He [Reed 2023]
- Strong rotational quantum number dependence, largest decrease for low J
- Confirmation of intensity decrease by re-quantized Classical Molecular Dynamics Simulations (rCMDS)

- Is there any intensity decrease for the atmospheric relevant molecule CO_2?
- If yes, how does this affect the CO_2 retrieval?

- Experimentally „easy“ situation: pure CO_2

CO_2 1.6 µm range measurement conditions

Source	Halogen lamp
Spectrometer	Bruker IFS 125 HR
Cell	Multireflection, 80 cm base length
Optical filter	1.5 µm high-pass
Detector	Internal InGaAs, cut-on 5800 cm^{-1}
Maximum optical path difference	100 cm

#	p_{CO2}(mbar)	$p_{CO2,equiv}$(mbar)	l(cm)	T(K)	t_{meas}(min)	SNR_{RMS}
1	10.0002(62)	10.0007	1456.40(29)	294.23(10)	880	14000
2	30.115(20)	30.119	1456.40(29)	294.23(10)	82	4700
3	75.227(24)	75.256	1456.40(29)	294.23(10)	82	4900
4	151.443(24)	151.561	1456.40(29)	294.22(10)	82	5000
5	298.696(24)	299.158	1456.40(29)	294.22(10)	82	4800
6	503.693(40)	505.011	1456.40(29)	294.23(10)	82	4900
7	749.742(60)	752.670	1456.40(29)	294.23(10)	82	4900
8	982.351(79)	987.390	1456.40(29)	294.23(10)	82	4900
9	10.0052(62)		11695.92(98)	294.23(10)	1017	14000
10	100.721(24)		11695.92(98)	294.23(10)	82	4000

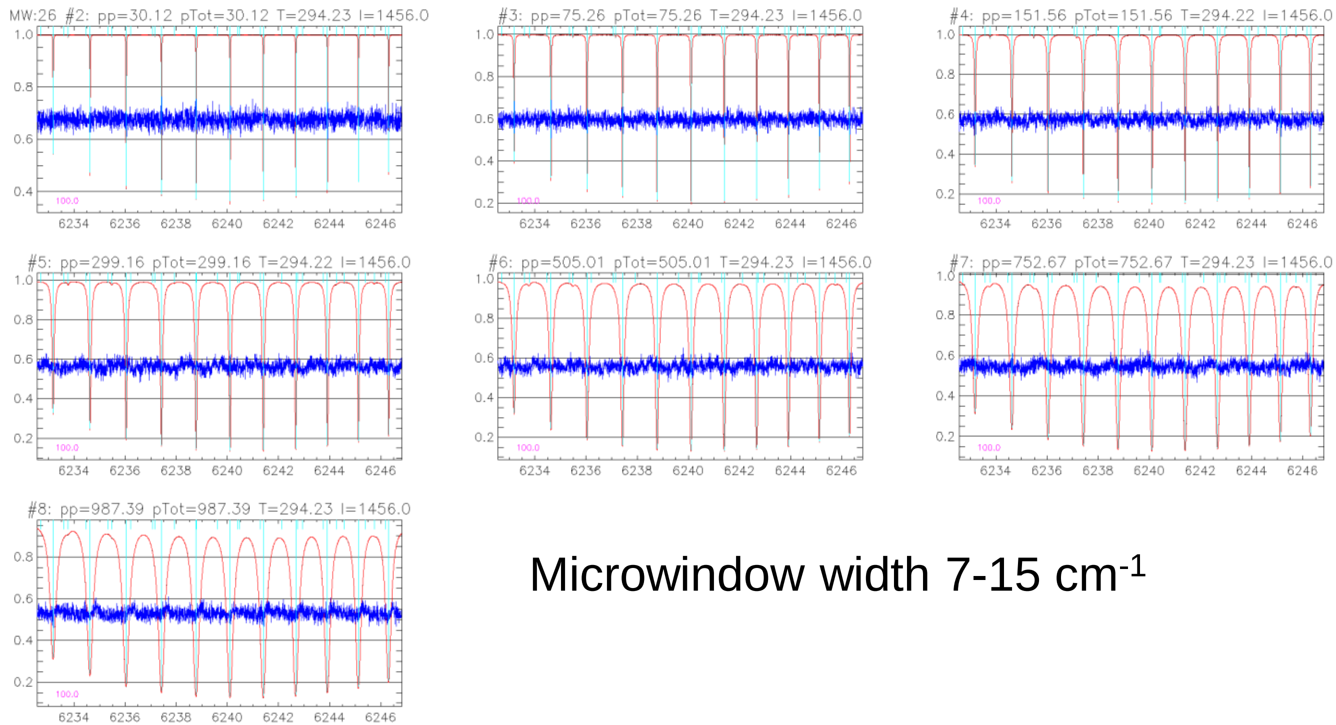
#	p_{CO2} (mbar)	$p_{CO2,equiv}$ (mbar)	l (cm)	T (K)	T_{fit} (K)	Inhom (%)	t_{meas} (min)	SNR_{RMS}
11	9.9989(62)	9.9989	1456.33 (29)	210.25(10)	210.03(10)	0	880	15000
12	518.928(42)	522.681	1456.33 (29)	210.26(10)	211.75(30)	2.1	54	3800
13	749.619(60)	757.409	1456.33 (29)	209.99(10)	212.36(30)	3.2	54	4000
14	998.961(80)	1012.725	1456.33 (29)	210.32(10)	212.95(30)	3.6	54	3800

Multispectrum fit

- Line model: Hartmann-Tran + Rosenkranz line mixing
- Quadratic baseline
- Consecutive fit: Ambient temperature, 212 K
- Depletion parameter: $S(p)=S(p=0)*[1-d_{self}*p(atm)]$

Parameter	# of lines
σ	1178
S	1169
$d_{self,294K}$	202
$\gamma_{0,self}$	1193
$\gamma_{2,self}$	346
ν_{VC}	62
$Y_{self,294K}$	255
$\delta_{0,self}$	1198
$\delta_{2,self}$	80
$d_{self,212K}$	194
n_{self}	632
$n_{\gamma2,self}$	113
$Y_{self,212K}$	298
$T\delta_{0,self}$	234

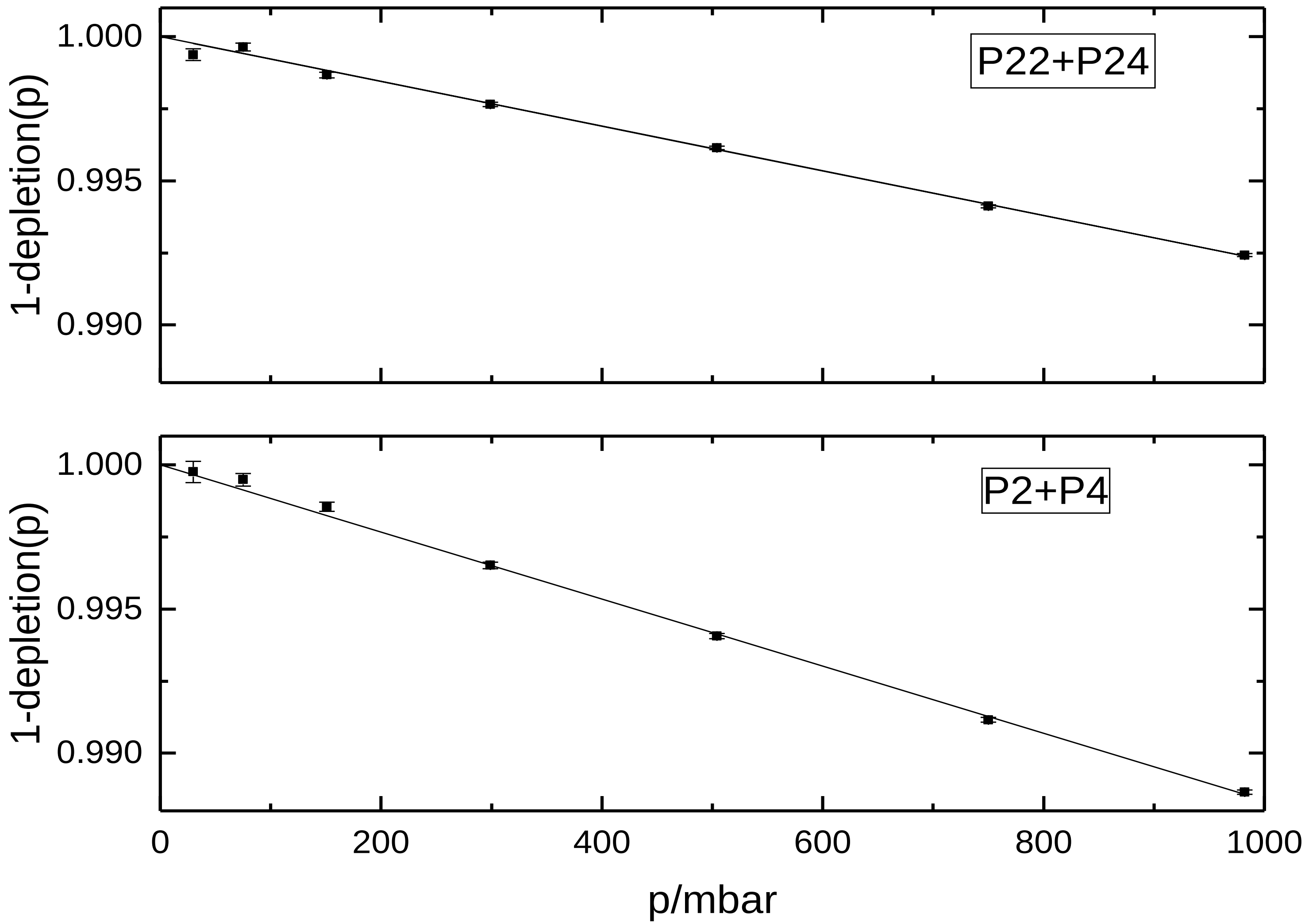
Example of microwindow with ambient temperature spectra



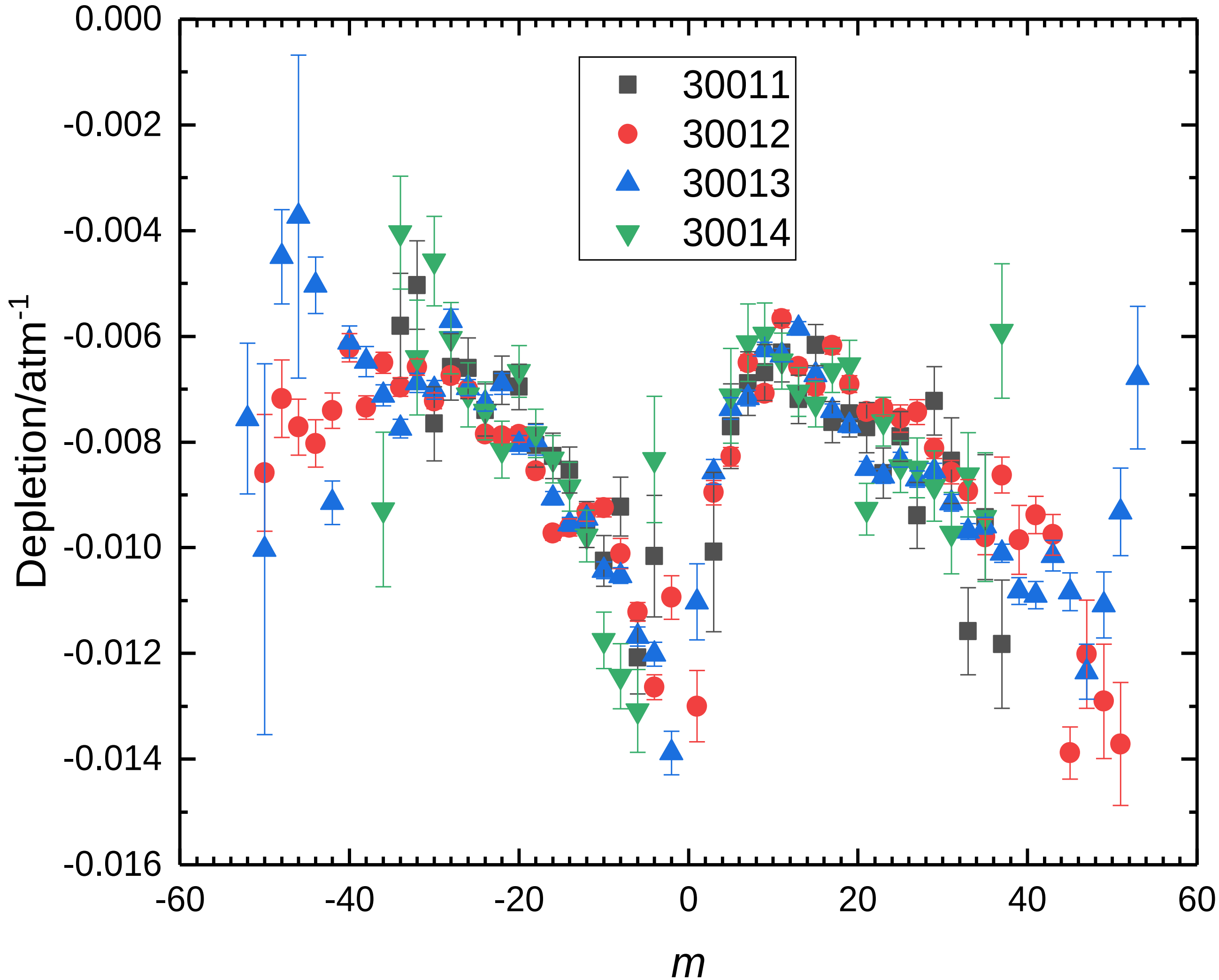
Microwindow width 7-15 cm^{-1}

Linearity of intensity depletion vs. Pressure

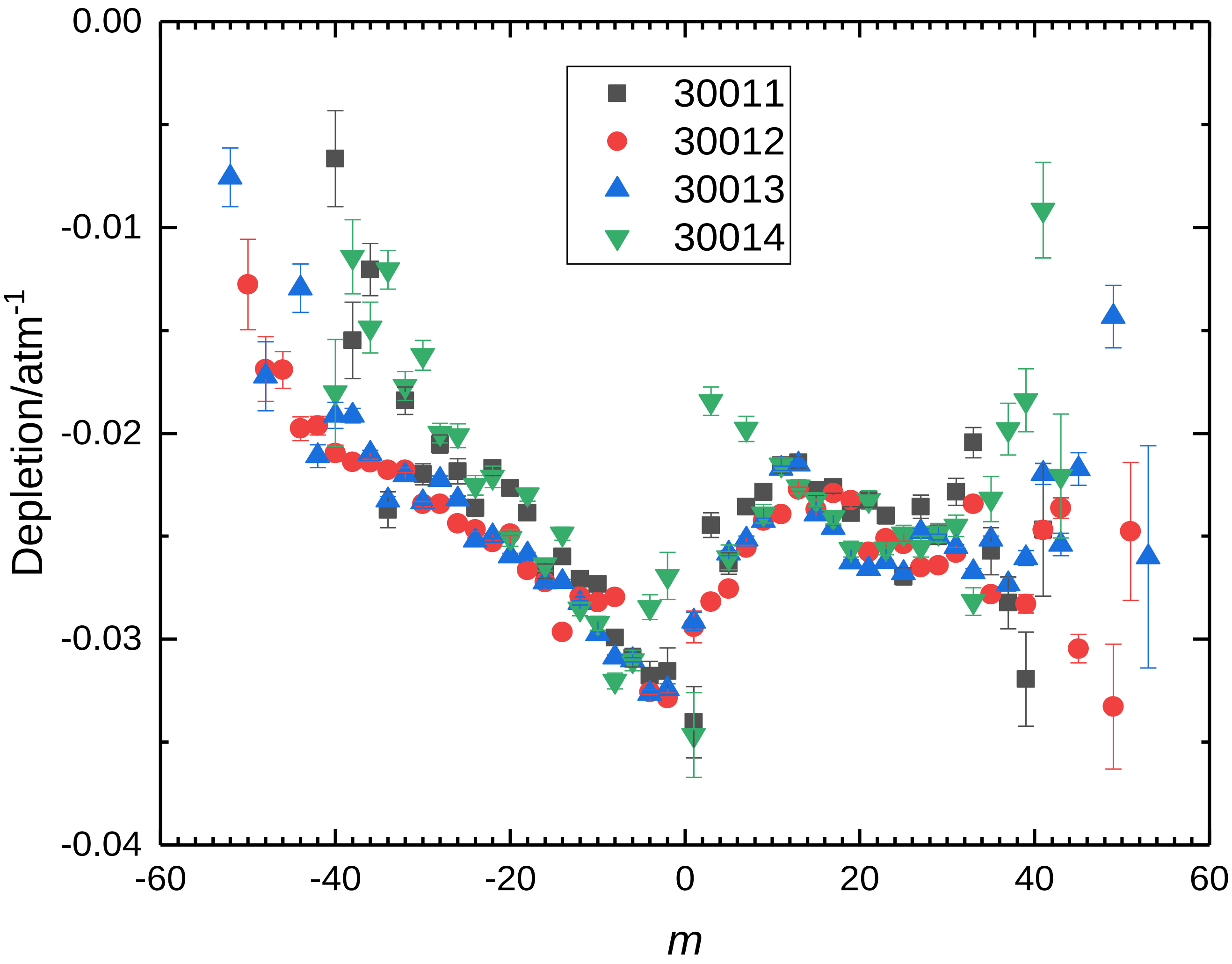
Symbols: depletion for individual measurements, line $1+d_{self} \cdot P$



m-dependence of depletion, d_{self}, at ambient temperature

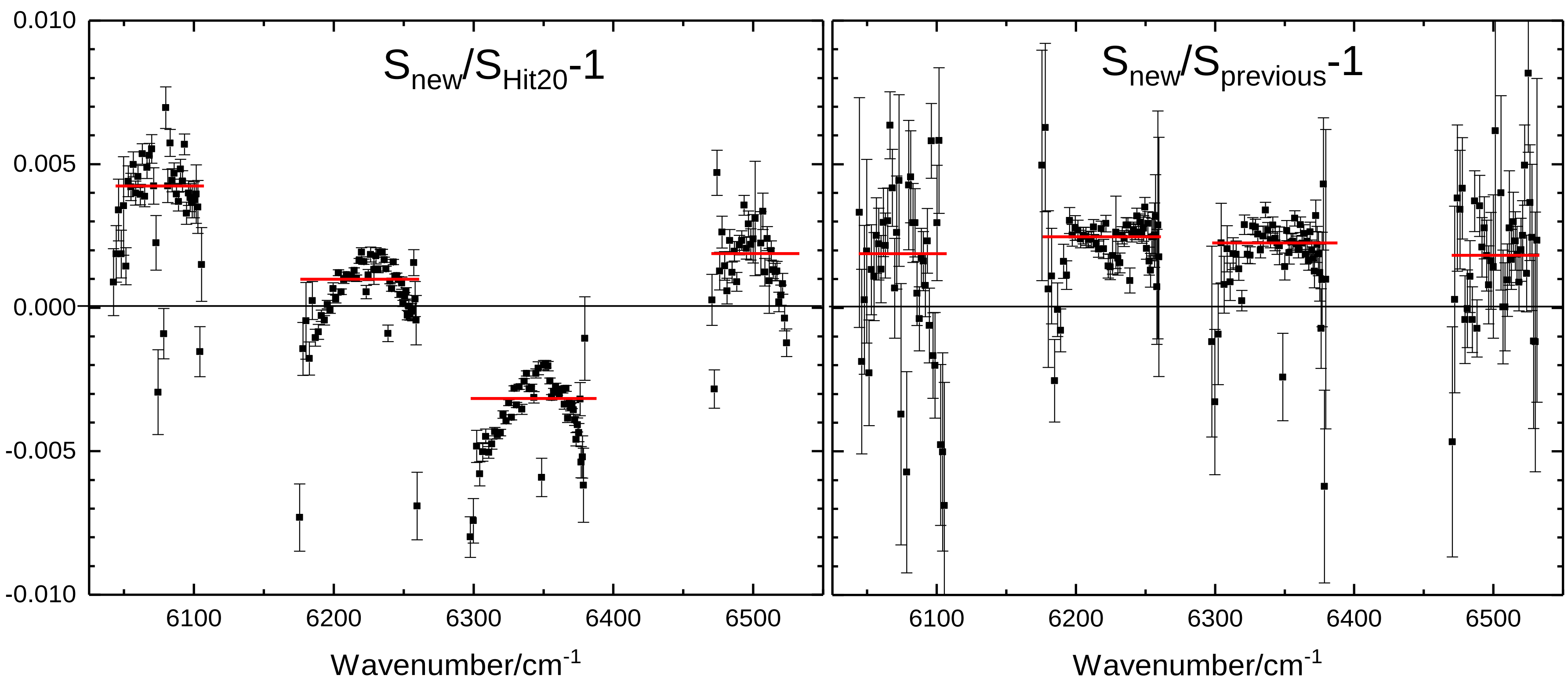


m-dependence of depletion, d_{self}, at 212 K



Improved line intensities: Systematic uncertainty <0.06%

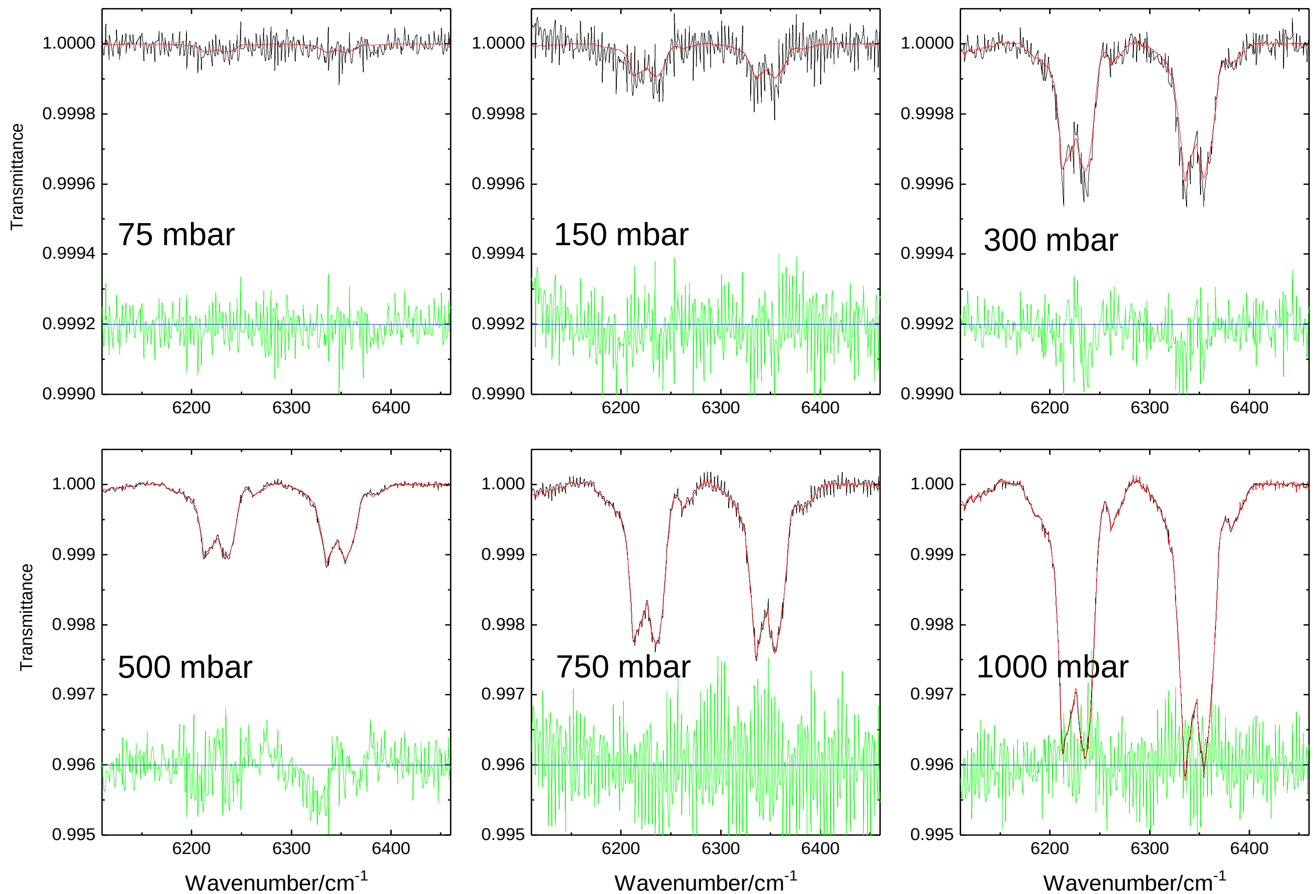
- Previous work: Birk et al., “High accuracy CO2 Fourier transform measurements in the range 6000–7000 cm^{-1}”, JQSRT 2021, systematic uncertainty 0.15%
- New intensities 0.2% larger than previous
- m-dependent differences to HITRAN20 spanning 0.4%



Fit of in-band self continuum

- From fitted baselines of multispectrum fit, spectra cut in 3 cm^{-1} wide microwindows (method see Birk et al., „3 µm water vapor self- and foreign-continuum: New method for determination and new insights into the self-continuum”, JQSRT 2020).
- Advantage: line parameters and continuum from same spectra

Observed and calculated baselines from fitted continuum, 294 K.
Green: (obs-calc)x2 (upper graphs), x10 (lower graphs)



Depletion, continuum, and 2nd virial coefficient

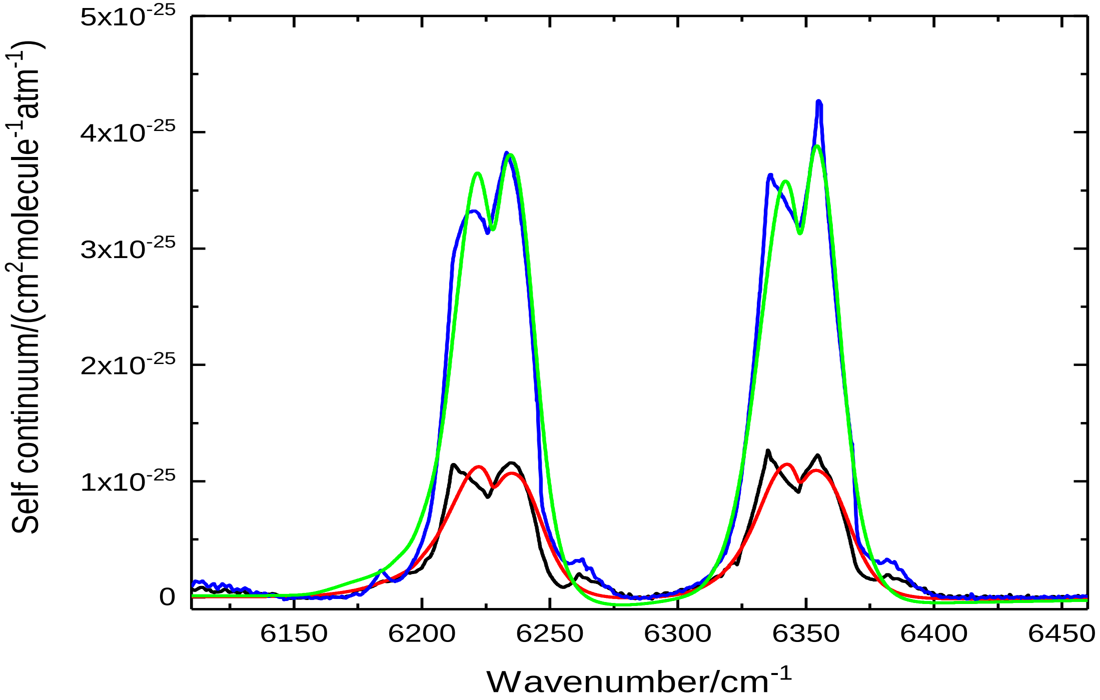
- Striking agreement for both temperatures and both bands between
  - intensity-weighted depletion,
  - continuum area at 1 atm divided by ΣS
  - depletion predicted from 2nd virial coefficient – fraction of monomers in pairs
- Depleted intensity is transferred to continuum – total band intensity pressure-invariant

	294 K		212 K	
	30012	30013	30012	30013
Intensity-weighted depletion [atm^{-1}]	**0.00948**	**0.00967**	**0.02751**	**0.02832**
Continuum area/ΣS	**0.01018**	**0.00978**	**0.02894**	**0.02747**
Real gas pressure correction	1.00525	1.00525	1.01423	1.01423
Predicted depletion from pressure correction	**0.01045**	**0.01045**	**0.02806**	**0.02806**

Continuum fitted from depleted intensities and pressure independent super-Lorentzians including line mixing

- Agreement indicates that only small contribution of bound dimers may be present – bound dimers: different band shapes + intensities

Fitted and measured continua
212 K measured
212 K calculated
294 K measured
294 K calculated



Fitted parameter	294 K	212 K
Global depletion scaling	1.035	1.041
Lorentz width @ m=0	1.33 cm^{-1}	1.90 cm^{-1}
Lorentz width increase/|m|	0.24 cm^{-1}	0.18 cm^{-1}
Rosenkranz parameter increase/m	-0.00294	-0.00323

2nd virial coefficient

- Fraction of monomers in pairs = fraction of depleted intensity
- These pairs undergo non-Markovian collisions resulting in super-Lorentzians – Theory see poster Ha Tran et al., „Pressure dependent line intensity and continuum absorption for pure CO_2: predictions by requantized molecular dynamics simulations", Poster O34
- Discrepancy to continuum theory [Serov 2017] where super-Lorentzians were regarded as characteristic of monomers only, not affecting the 2nd virial coefficient.
- 2nd virial coefficient B(T) can be calculated from intermolecular potential [e.g. Bock et al., 2000]:

$$B(T) = \frac{N_A}{2} \int \left\langle 1 - e^{-\beta V} \left[1 + \frac{\beta^2}{12} (H_0 V) \right] \right\rangle_{\omega_A \omega_B} dR,$$

- Both, the real gas correction as well as the non-Markovian collisions, are linked to the intermolecular potential V
- Potential minimum required for real gas pressure reduction as well as intensity depletion
- Notable fraction of bound dimers when potential minimum >kT (example H_2O self continuum)
- Whether continuum areas (in absence of bound complexes) and intensity depletions can be calculated from 2nd virial coefficient needs to be investigated for other pure gases and gas mixtures

Impact of depletion and continuum for remote sensing

- Example CO2M Mission requirements:
  global bias from spectroscopy <0.5%, differential error <0.1%, p-p residuals 1.6 µm 0.063%, 2µm 0.077%
- Retrieval simulations applying simplified modelled satellite observations
  - ☞Larger impact of continuum
  - ☞Continuum impact larger for opaque 2µm band
  - ☞Requirements not met in several cases

Global bias and residuals

	1.6 µm		2 µm	
Impact of	CO_2 col. dev./%	p-p residual/%	CO_2 col. dev./%	p-p residual/%
depletion	-0.47	0.036	-0.46	**0.143**
depletion+cont	+0.38	**0.195**	**+2.76**	**2.101**
cont	**+0.85**	**0.187**	**+3.22**	**2.046**

Differential errors

	1.6 µm		2 µm	
Impact of	TRO-SAW/%	TRO(0 km-2 km)/%	TRO-SAW/%	TRO(0 km-2 km)/%
depletion	**0.247**	-0.021	**0.314**	-0.006
depletion+cont	**-0.108**	0.025	**-0.878**	-0.094
cont	**-0.357**	0.045	**-1.197**	-0.087

Impact of depletion and continuum for remote sensing

- Example CO2M Mission requirements:
  global bias from spectroscopy <0.5%, differential error <0.1%, p-p residuals 1.6 µm 0.063%, 2µm 0.077%
- Retrieval simulations applying simplified modelled satellite observations
  - ☞Air continuum and depletion deduced from pure CO2 results + 2nd virial coefficients
  - ☞Larger impact of continuum
  - ☞Continuum impact larger for opaque 2µm band
  - ☞Requirements not met in several cases

Bias for tropical atmosphere and residuals

	1.6 µm		2 µm	
Impact of	CO_2 col. dev./%	p-p residual/%	CO_2 col. dev./%	p-p residual/%
depletion	-0.17	0.019	-0.17	0.036
depletion+cont	+0.29	**0.100**	**+1.48**	**1.078**
cont	+0.46	**0.097**	**+1.65**	**1.086**

Differential errors

	1.6 µm		2 µm	
Impact of	TRO-SAW/%	TRO(0 km-2 km)/%	TRO-SAW/%	TRO(0 km-2 km)/%
depletion	**0.128**	-0.001	**0.157**	-0.006
depletion+cont	-0.054	0.032	**-0.465**	-0.037
cont	**-0.183**	0.033	**-0.623**	-0.043

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Conclusion

- High accuracy pure CO_2 measurements for 294 K and 212 K, pressures up to 1 atm
- Multispectrum fitting of microwindows applying Hartmann-Tran profile with 1^{st} order Rosenkranz line mixing
- Improved spectroscopic database, line intensity accuracy better than 0.06%
- Intensity depletion detected, ca. 1%/atm at 294 K, 3%/atm at 212 K
- Continua determined, areas in agreement with depleted intensity at both temperatures
- Continua could be approximated as sum of pressure-independent super-Lorentzian+line mixing contributions applying depleted intensities
- Amount of monomer pairs calculated from real gas pressure correction applying 2^{nd} virial coefficient in agreement with average intensity depletion at both temperatures
- Continua theory stating that super-Lorentzian contributions are a characteristic of monomers not linked to the 2^{nd} virial coefficient may have to be reconsidered
- Continuum and depletion were found to have significant impact on satellite-based CO_2 retrievals
- Further investigations of other pure gases and mixtures regarding intensity depletion, continua, and 2^{nd} virial coefficients are needed

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