CDSD
(Carbon Dioxide Spectroscopic Databank):

Updated and Enlarged Version for Atmospheric Applications

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History of CDSD

- **1992 Phenomenological effective Hamiltonian model, *JMS*, *156, 48 (1992)***
- **1995 Phenomenological effective dipole moment model, *JMS, 171, 48***
- **1998-1999 Global fittings of $^{12}C^{16}O_2$ observed positions and intensities, *JQSRT 60, 785 (1998) JQSRT 62, 571 (1999)***
- **2003 CDSD-1000, the high-temperature carbon dioxide spectroscopic databank, *JQSRT, 82, 165 (2003)***
- **2004 CDSD-1000 and CDSD-296 were opened for the Internet access: ftp.iao.ru /pub/CDSD-1000 and /pub/CDSD-296**
- **2008 updated and new versions CDSD-296, CDSD-1000 and CDSD-Venus ftp.iao.ru /pub/CDSD-2008/**

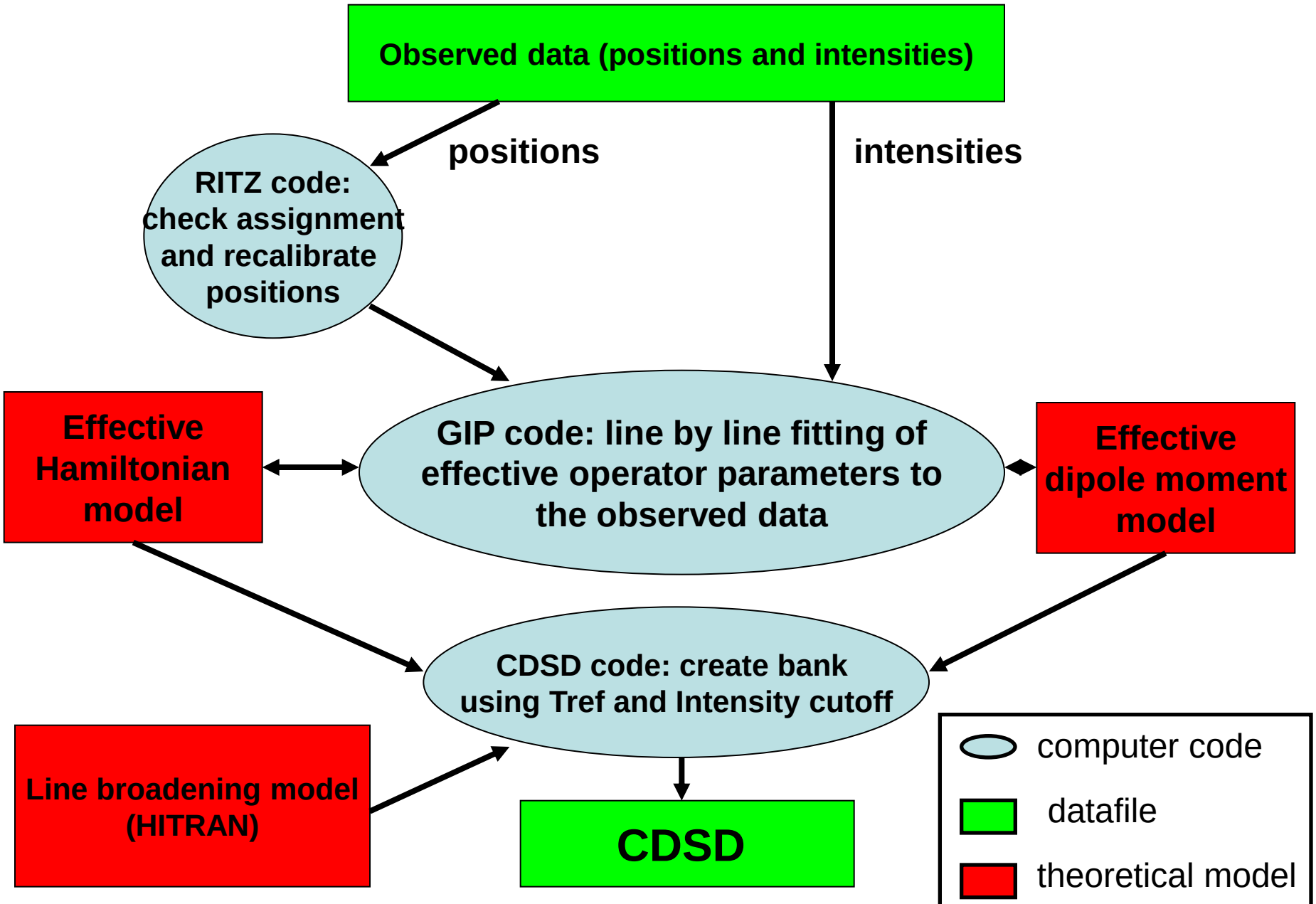
Motivation

- During last five years a lot of high quality measured CO_2 data appeared (Campargue and co-workers, Toth and co-workers)

- It is just time to refit all observed data available from the literature and to obtain more accurate models of effective Hamiltonians and effective dipole moment

- and to create updated and enlarged versions of CDSD (Carbon Dioxide Spectroscopic Databank) for atmospheric and high temperature applications

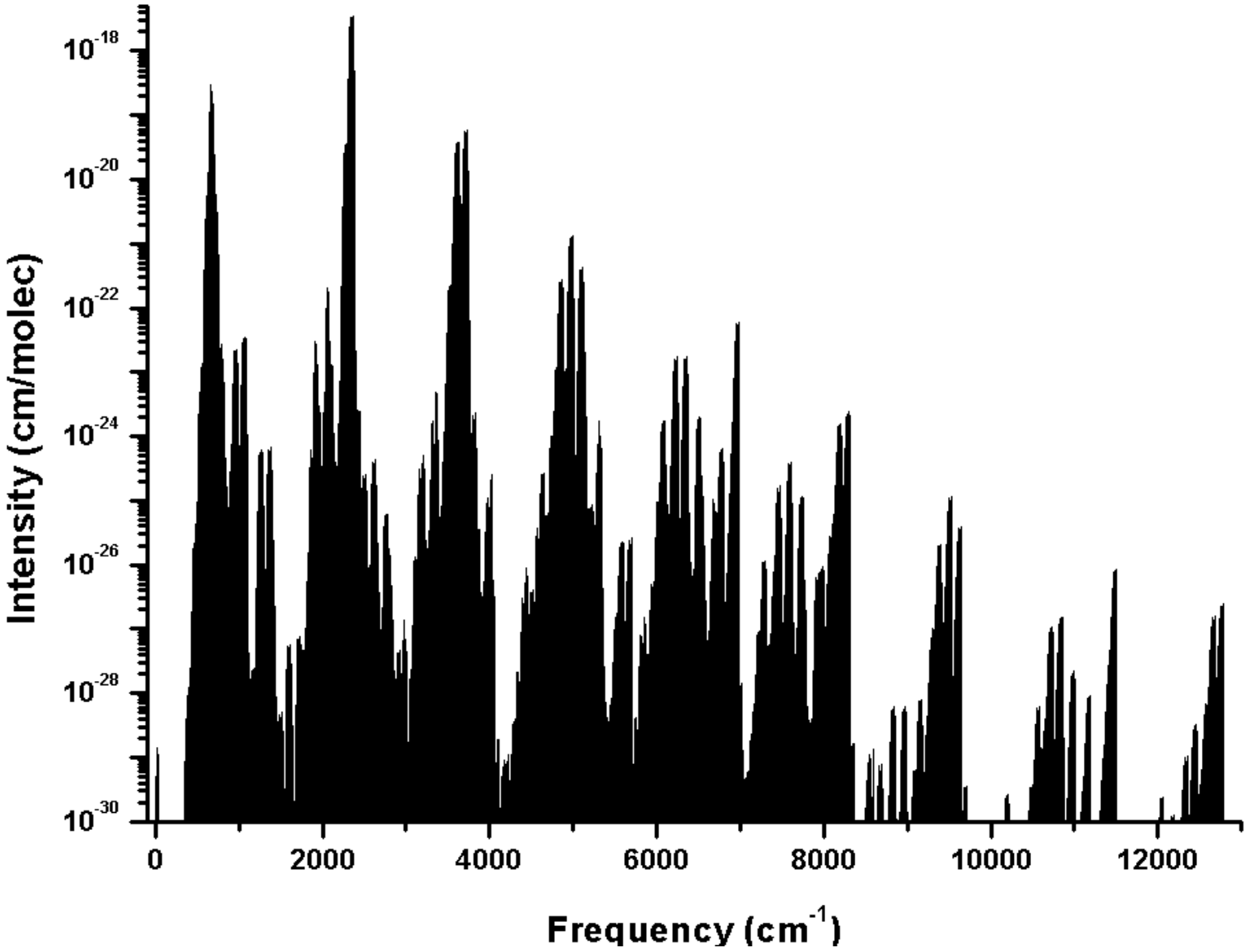
How CDSD is created

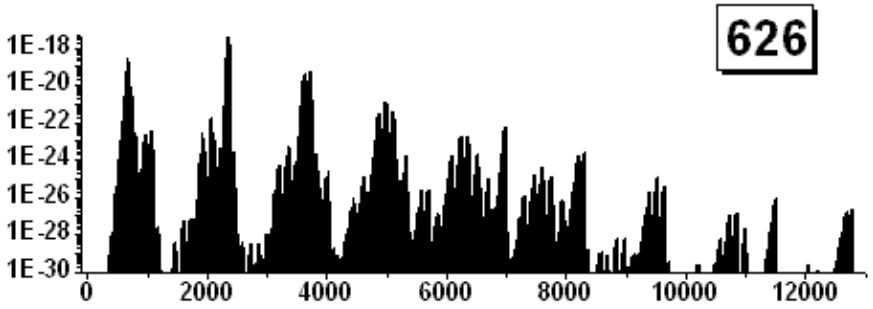


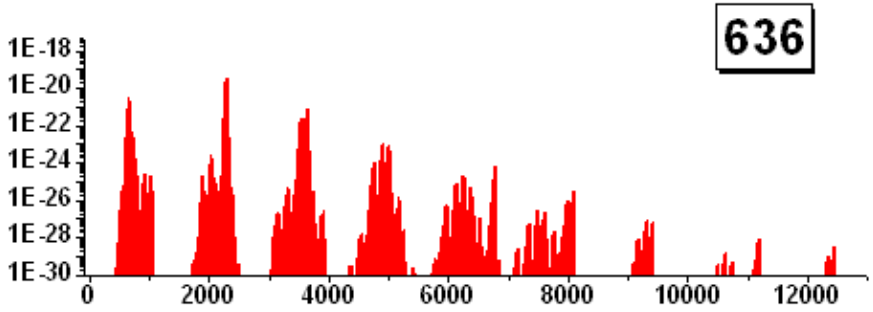
CDSD-296: ftp.iao.ru /pub/CDSD-2008

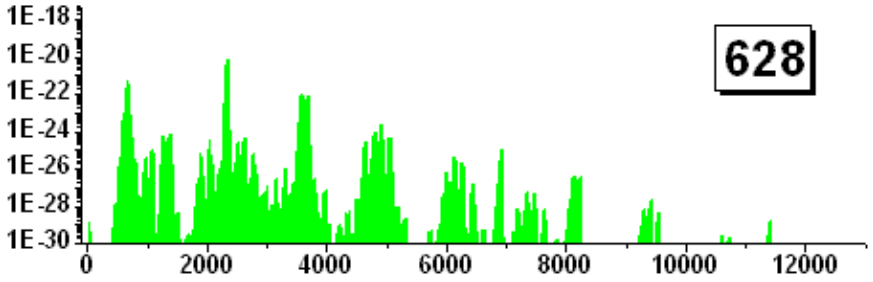
version	2003	2008
bank format	HITRAN-1996	HITRAN-2004
isotopes	4	7
T_{ref} (K)	296	296
Intensity cutoff (cm/molec)	10^{-27}	10^{-30}
range (cm^{-1})	436 – 8 310	5 – 12 784
lines	66717	419 610

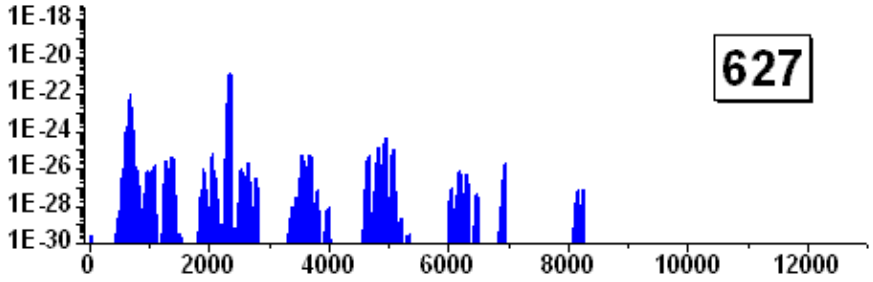
Graphical overview of CDSD-296

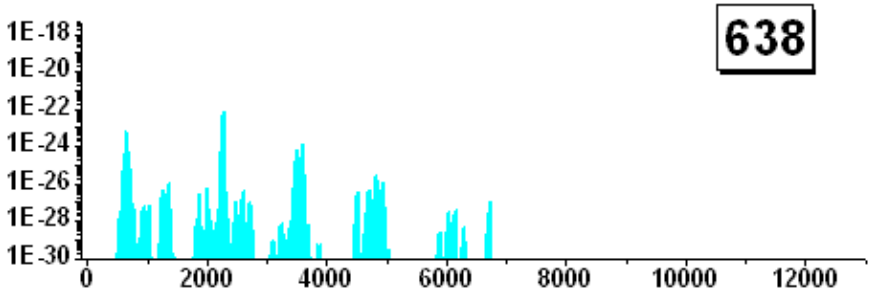


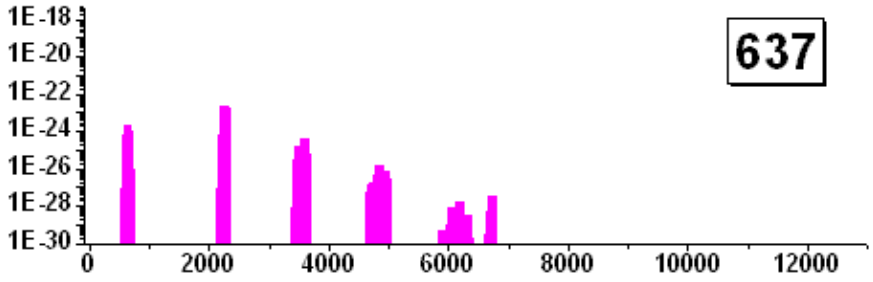


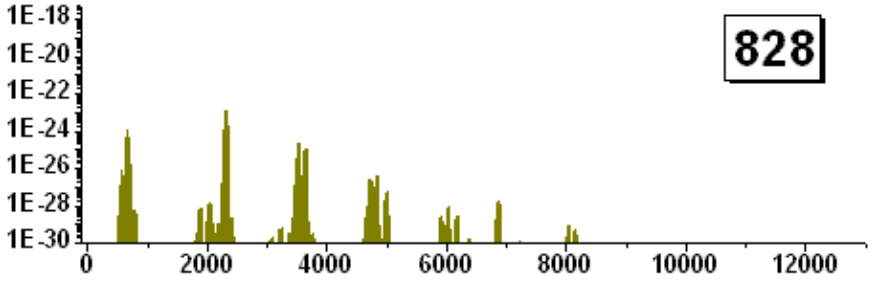












Isotopic composition of CDSD-296

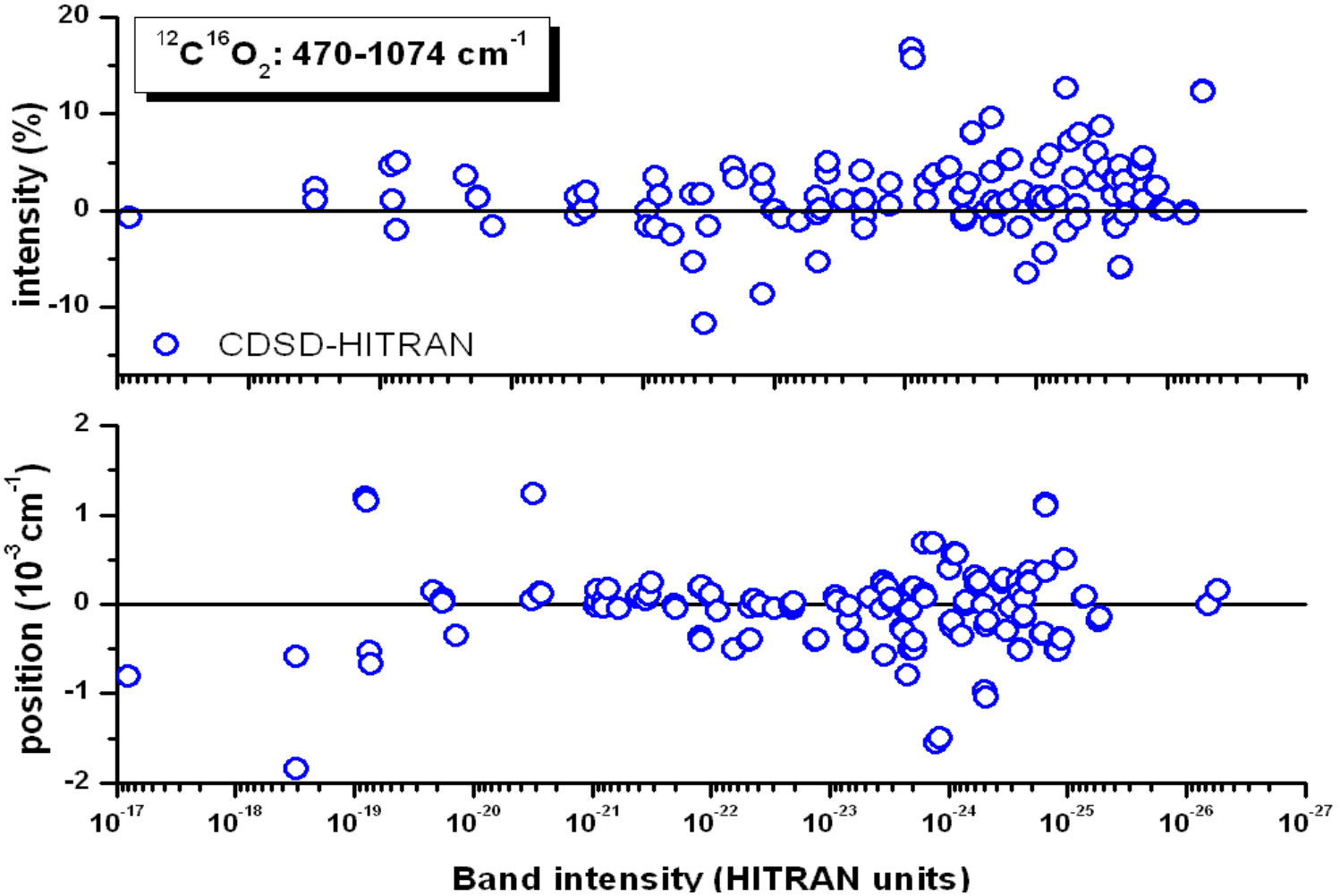
Overview of existing CO2 databanks aimed at atmospheric applications, Tref = 296 K

databank	HITRAN-2004	TOTH-2008	CDSD-2008
bank format	HITRAN-2004		HITRAN-2004
isotopes	8	9	7
Intensity cutoff (cm/molec)	10^{-27*}	10^{-30}	10^{-30}
range (cm^{-1})	0 – 12 784	4300 - 6989	5 – 12 784
lines	62 913	28 530	419 610
source	www.hitran.com	JQSRT 109, 906 (2008), supplementary material	ftp.iao.ru

*) microwave transitions of 628 and 627 have intensities as low as 10^{-35}

CDSD vs HITRAN: band by band comparison for $^{12}C^{16}O_2$

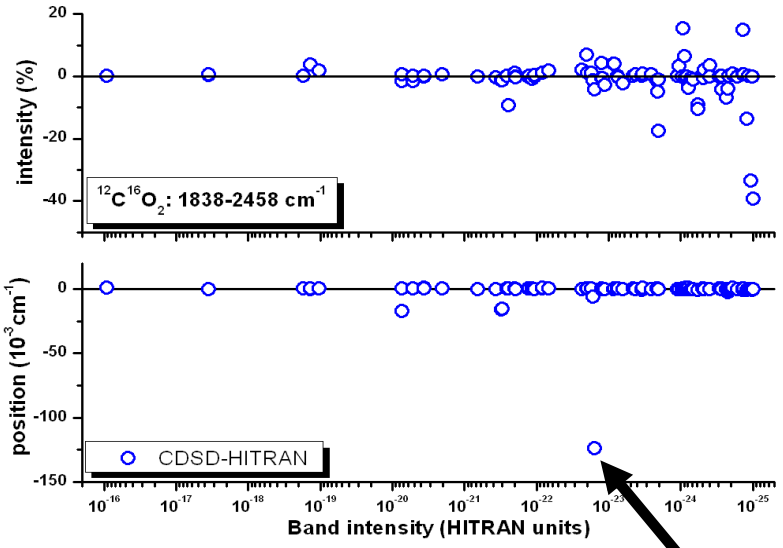
Intensity cutoff 10^{-27} cm/molecule



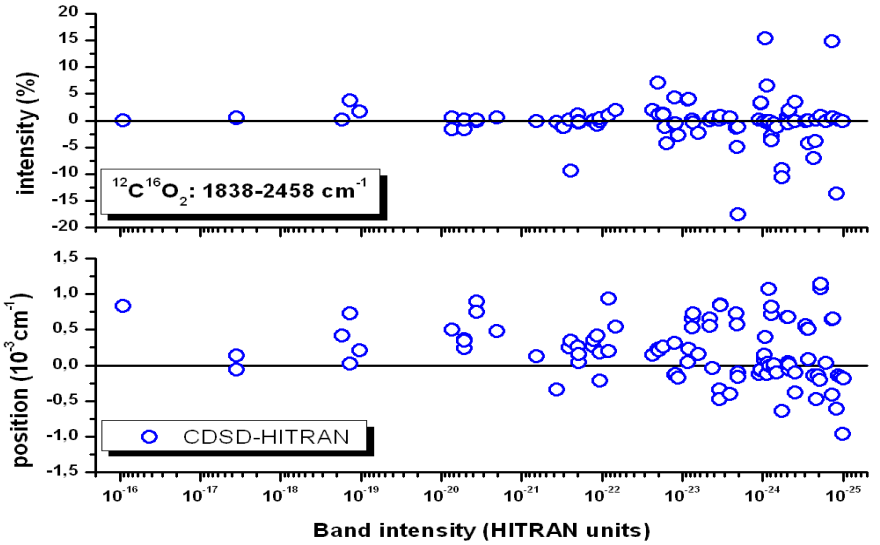
$$\text{position} = \frac{1}{N}\sum_i (\nu_i^{CDSD} - \nu_i^{HITRAN})$$

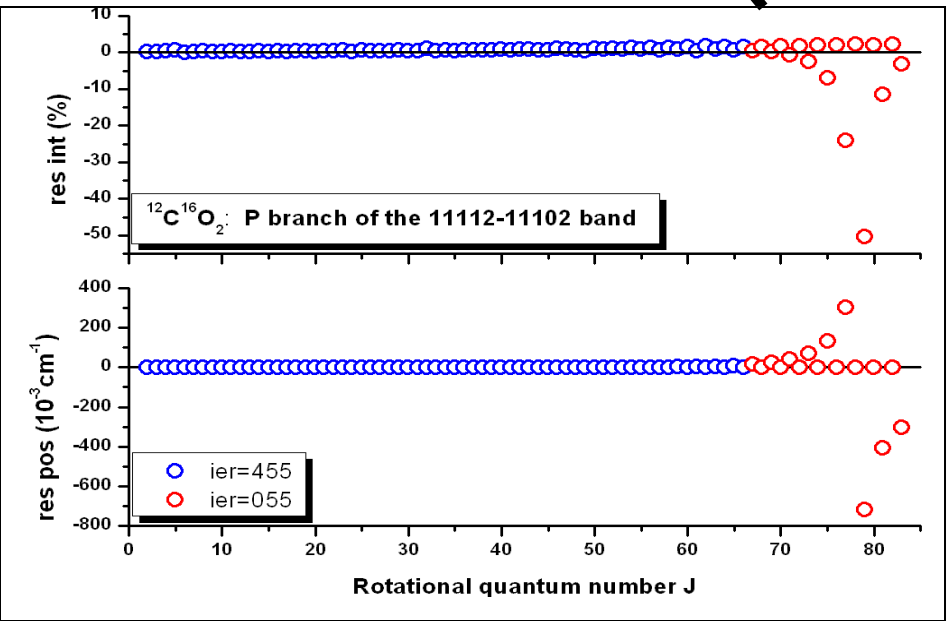
$$\text{intensity} = \frac{100\%}{2N}\sum_i \left(\frac{I_i^{CDSD}}{I_i^{HITRAN}} - \frac{I_i^{HITRAN}}{I_i^{CDSD}}\right)$$

CDSD vs HITRAN: band by band comparison for $^{12}C^{16}O_2$



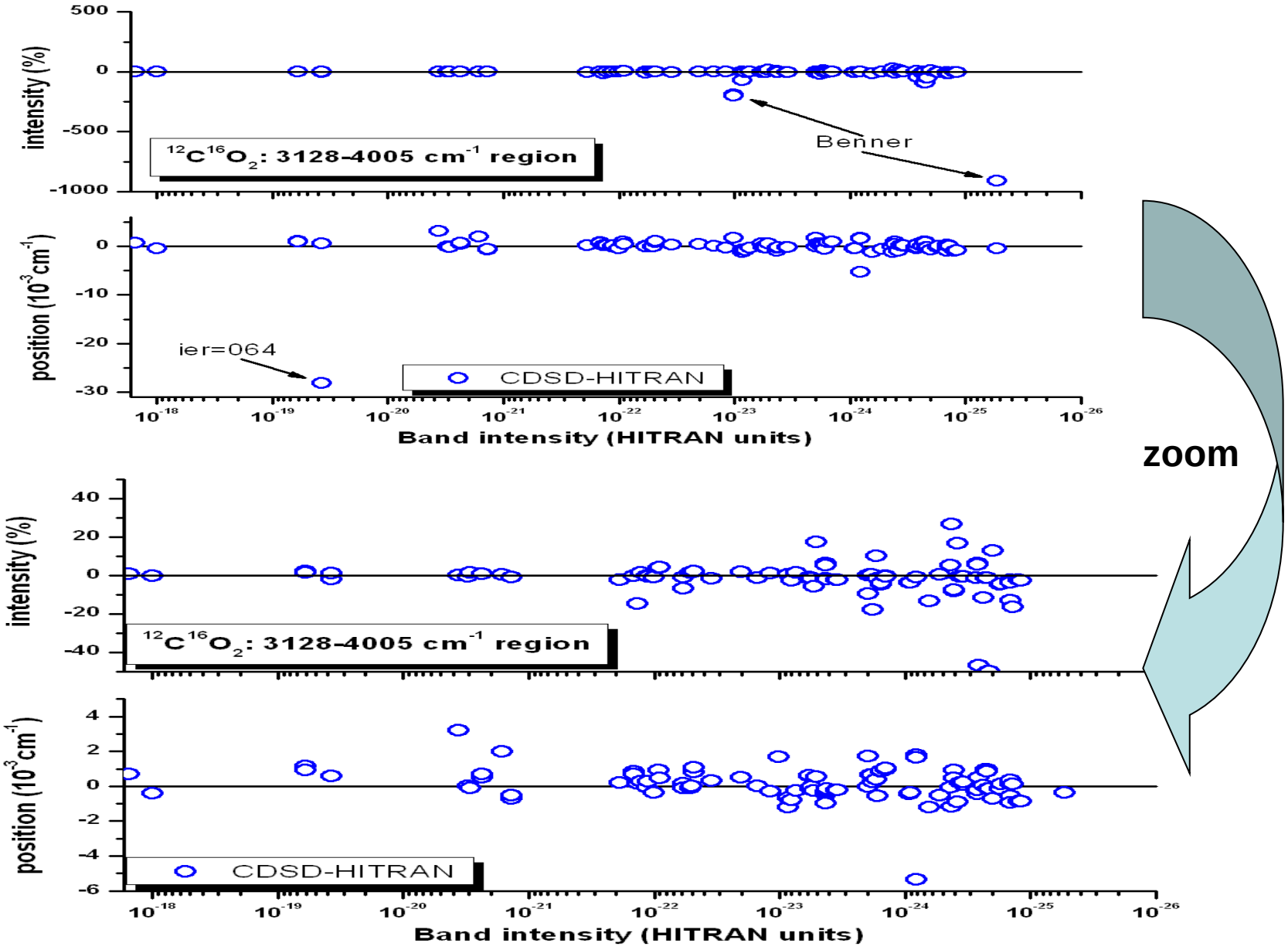
zoom



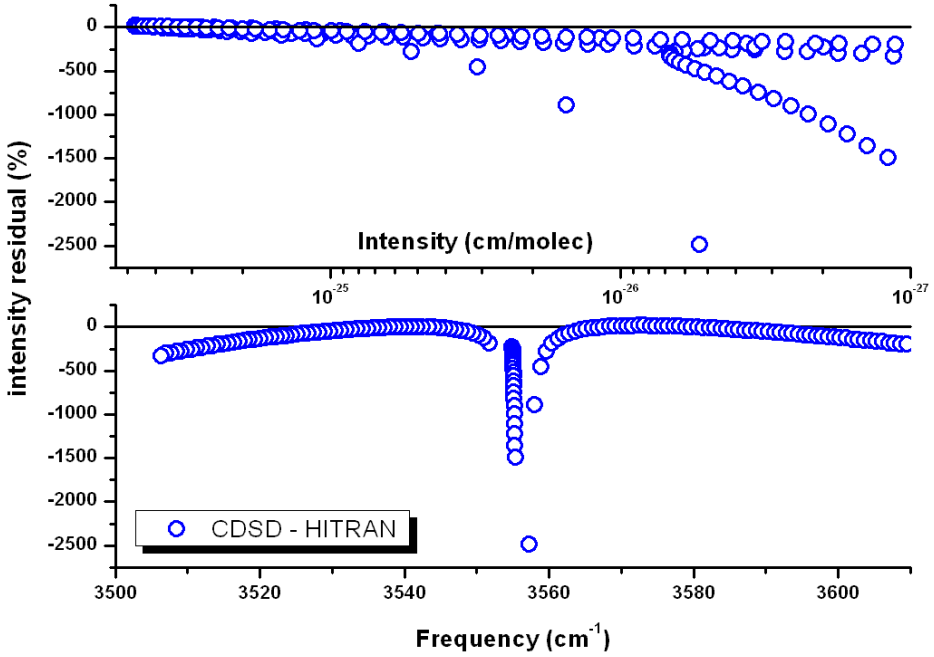


Usage of spectroscopic constants for extrapolation of rotational line positions of a band is dangerous

CDSD vs HITRAN: band by band comparison for $^{12}C^{16}O_2$



CDSD vs HITRAN: the 23301-02201 band



Number of lines 152

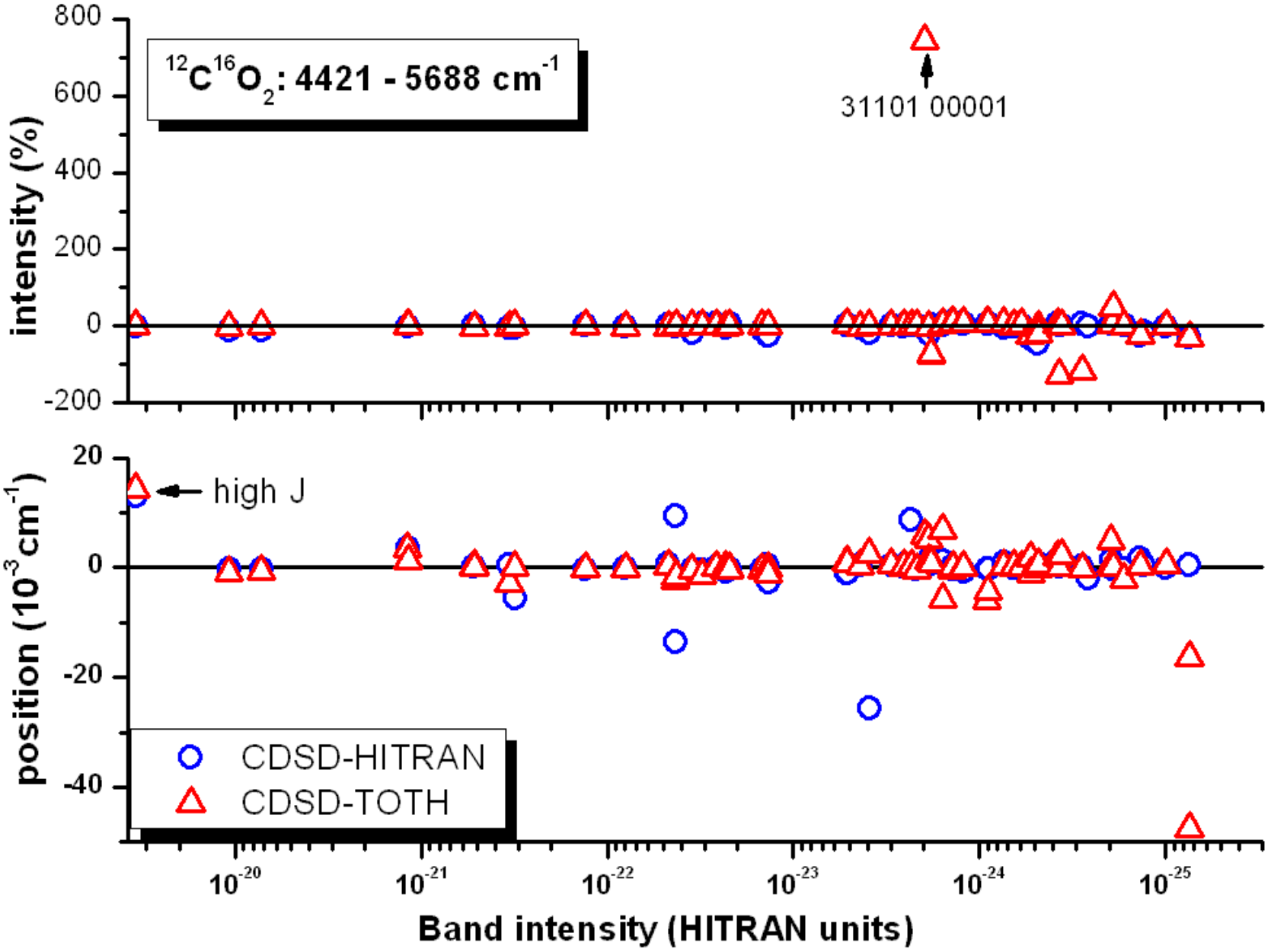
HITRAN intensities from: D.Chris Benner, College of William and Mary, private communication (2003).

‘ … as to the 23301 <- 02201 band, again we measured only 16 lines (from P39 to R31) and the interaction between 23301 and 12212 is not well constrained at high Js. Our residuals for the line positions in these bands were all less than 0.001 cm-1…’

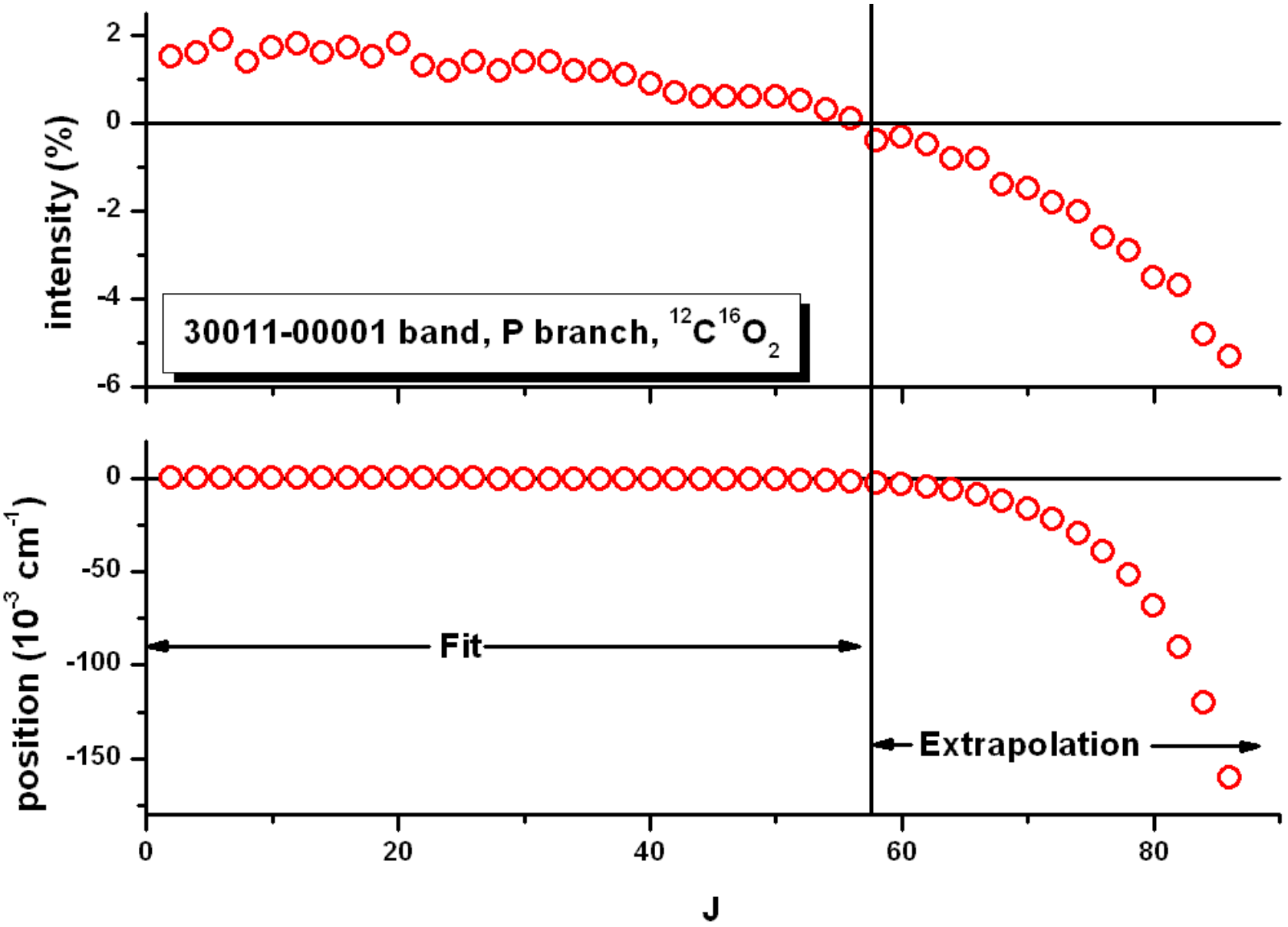
D.C. Benner, private communication (2005)

Usage of spectroscopic constants for extrapolation of line intensities of a band is dangerous

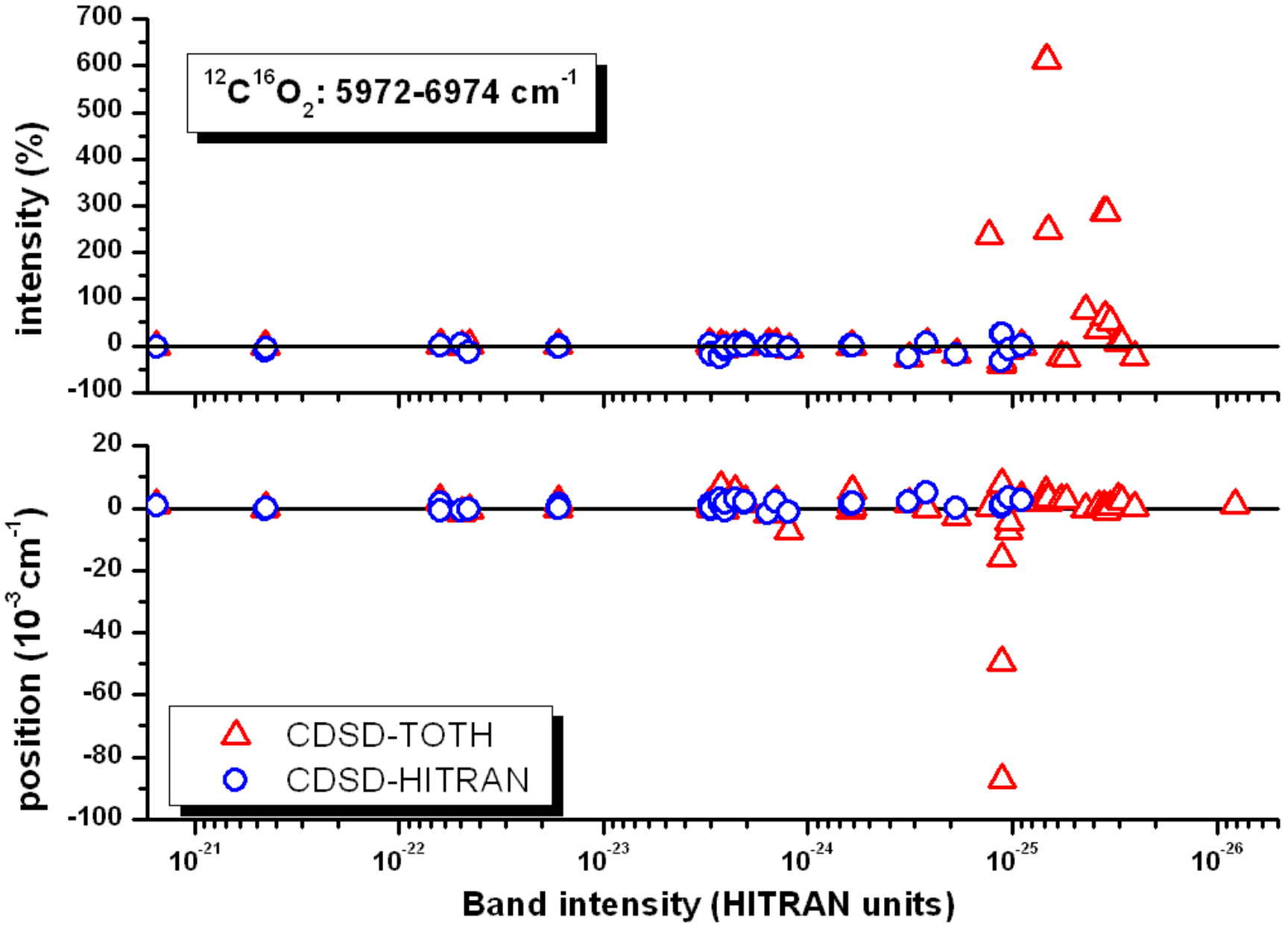
CDSD vs HITRAN and TOTH: band by band comparison for $^{12}C^{16}O_2$



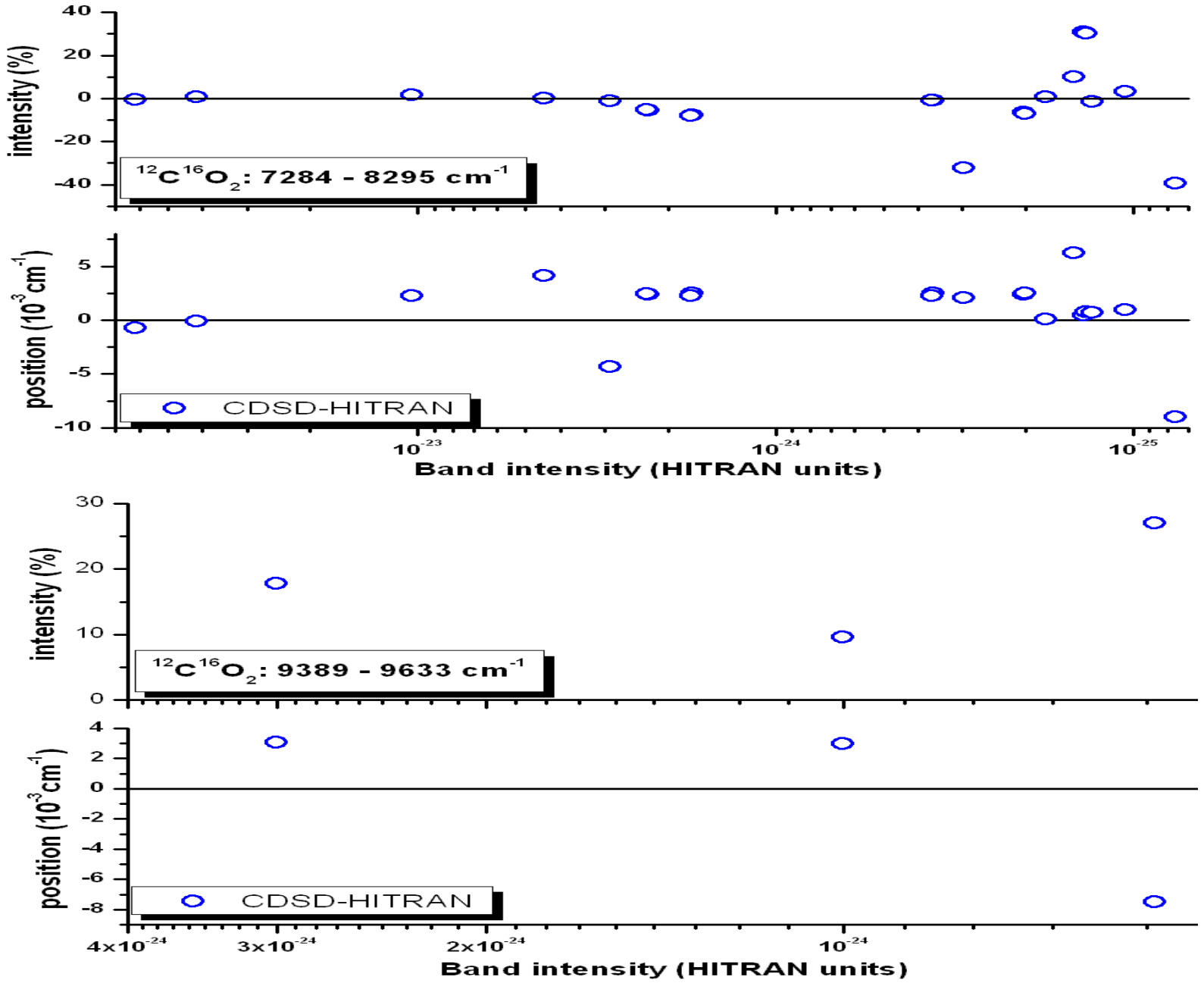
Danger of long range extrapolations (cutoff 10^{-30}cm/molec)



CDSD vs HITRAN and TOTH: band by band comparison for $^{12}C^{16}O_2$

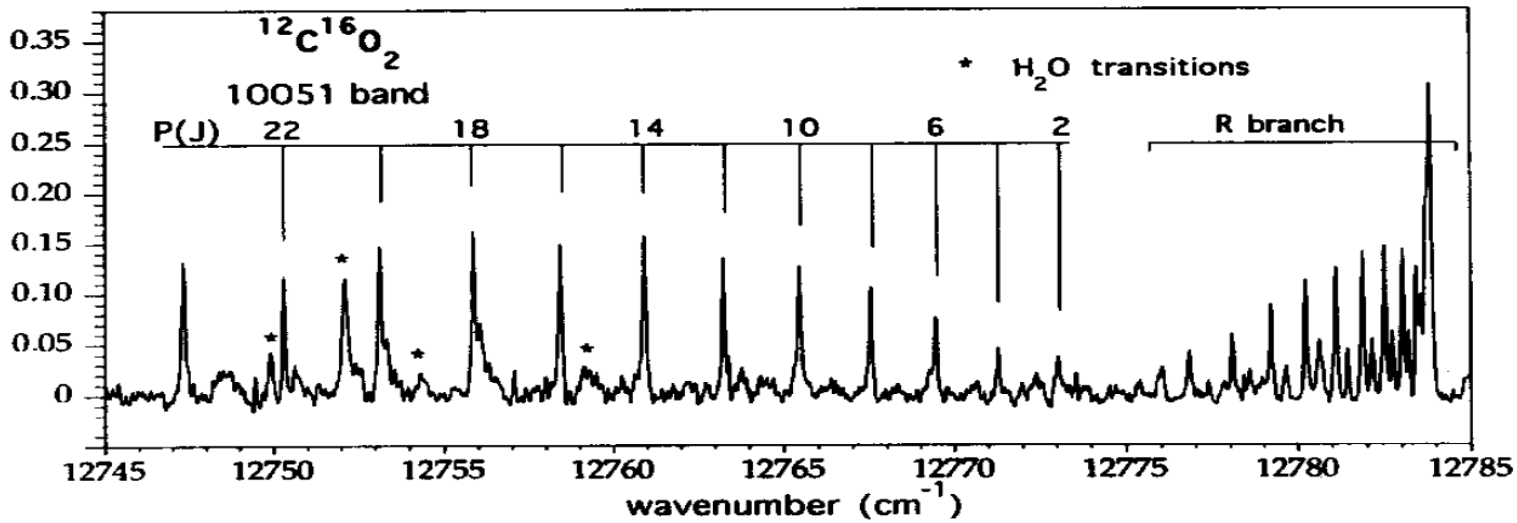


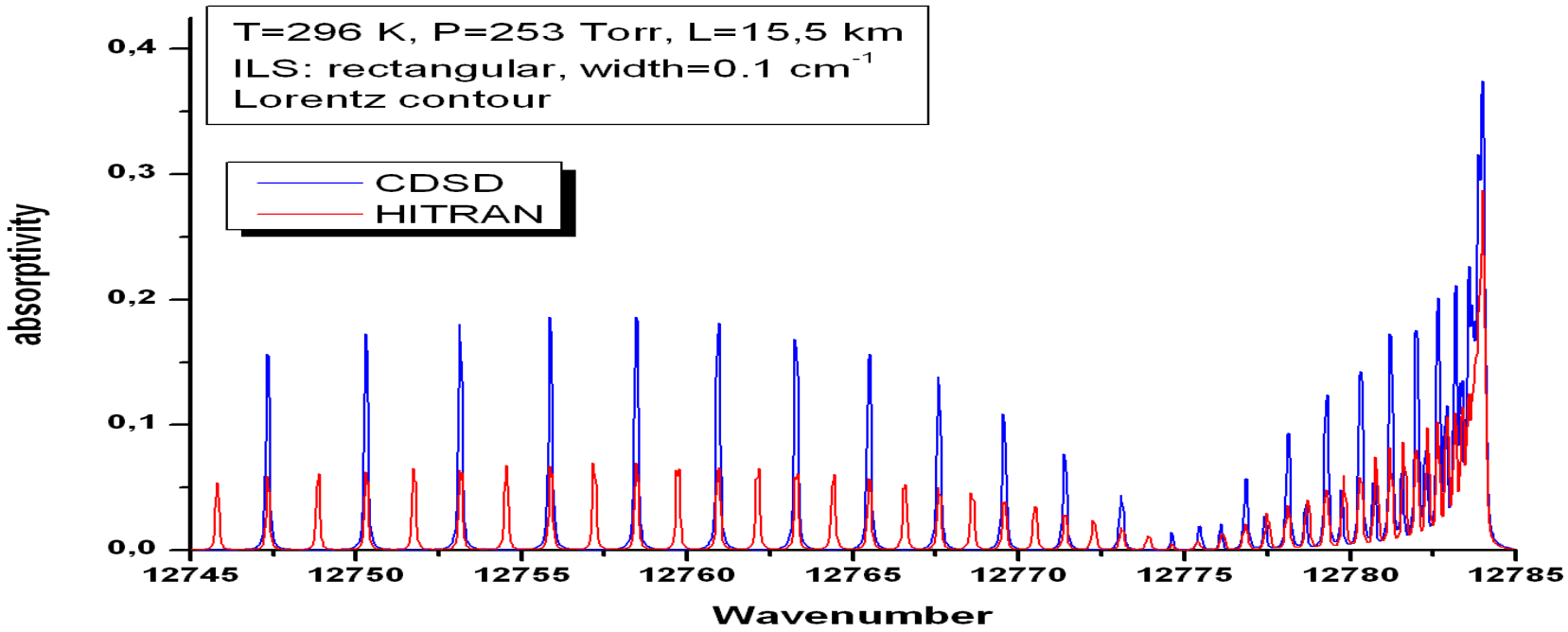
CDSD vs HITRAN: band by band comparison for $^{12}C^{16}O_2$



CDSD vs HITRAN: 12000-12800 cm^{-1} region

A.Campargue *et al*, Chem. Phys. Lett., 223, 567 (1994)





Other versions of CDSD

- **CDSD-1000**: version for high-temperature applications. Tref=1000 K, cutoff=10^{-27} cm/molec, near 4 million of lines

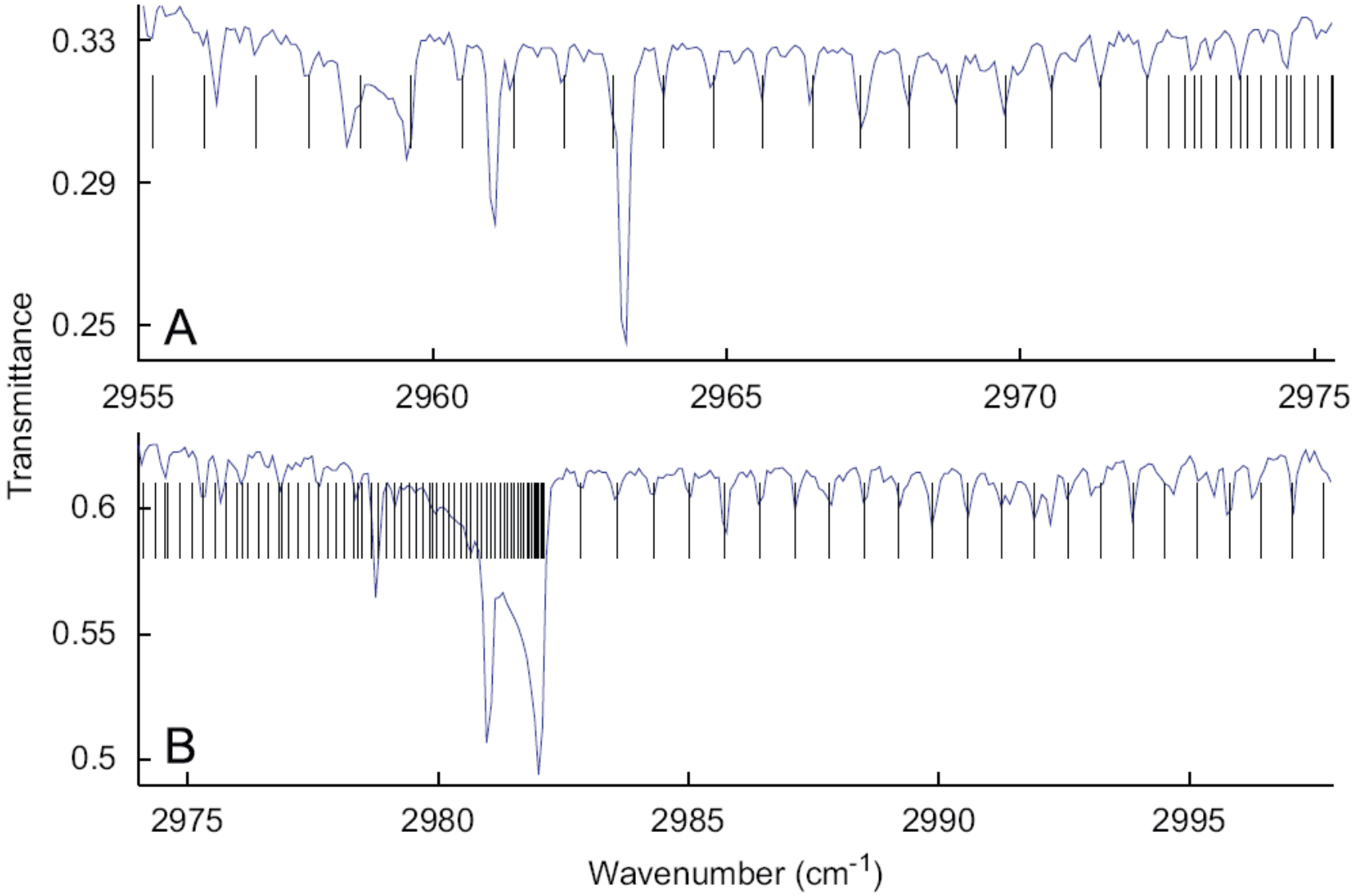
- **CDSD-Venus**: version to study of Venus atmosphere. Tref=750 K, cutoff=10^{-30} cm/molec, near 12 million of lines

- All versions of CDSD are accessible via the Internet: ftp.iao.ru folder /pub/CDSD-2008

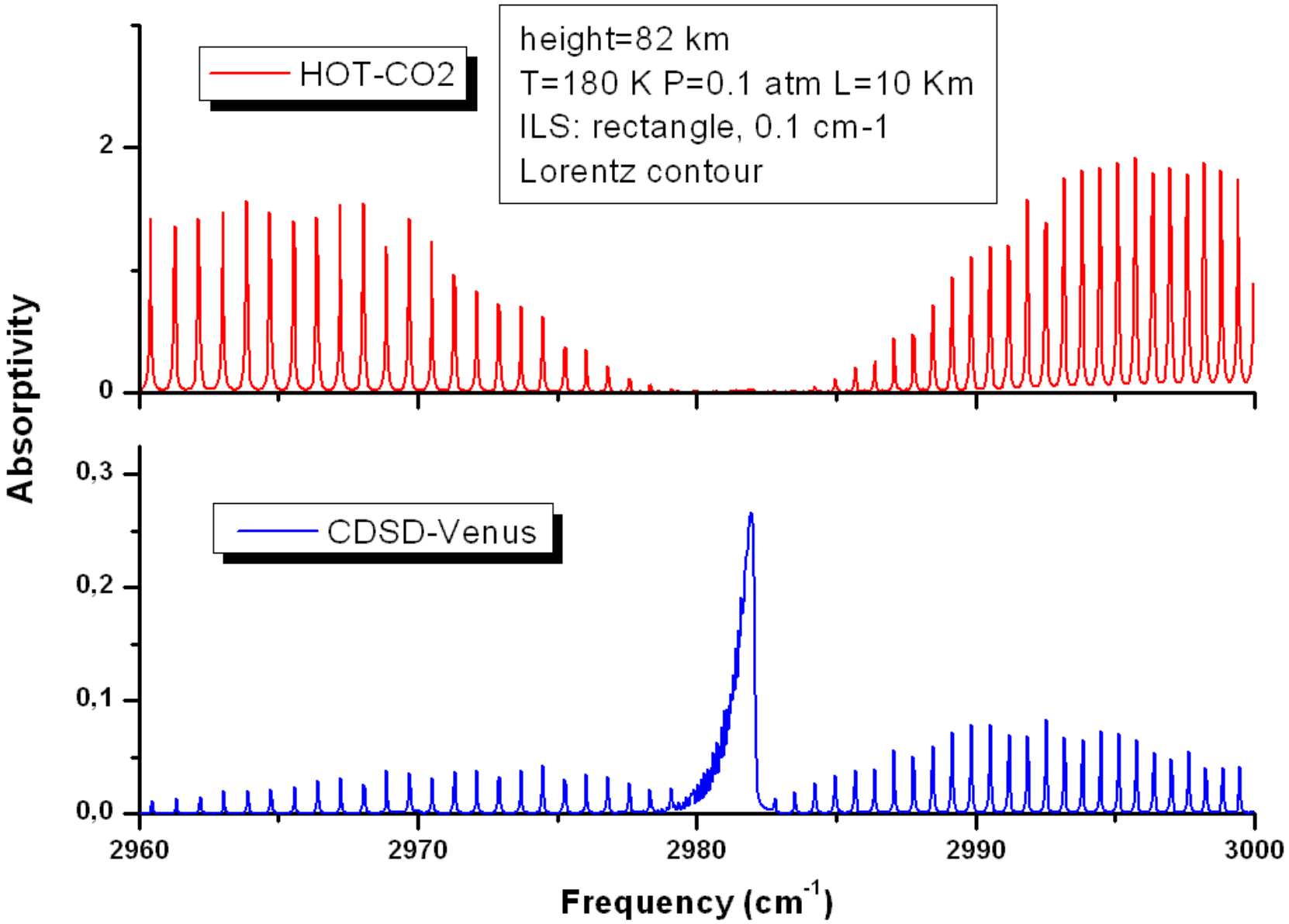
Venus and Mars

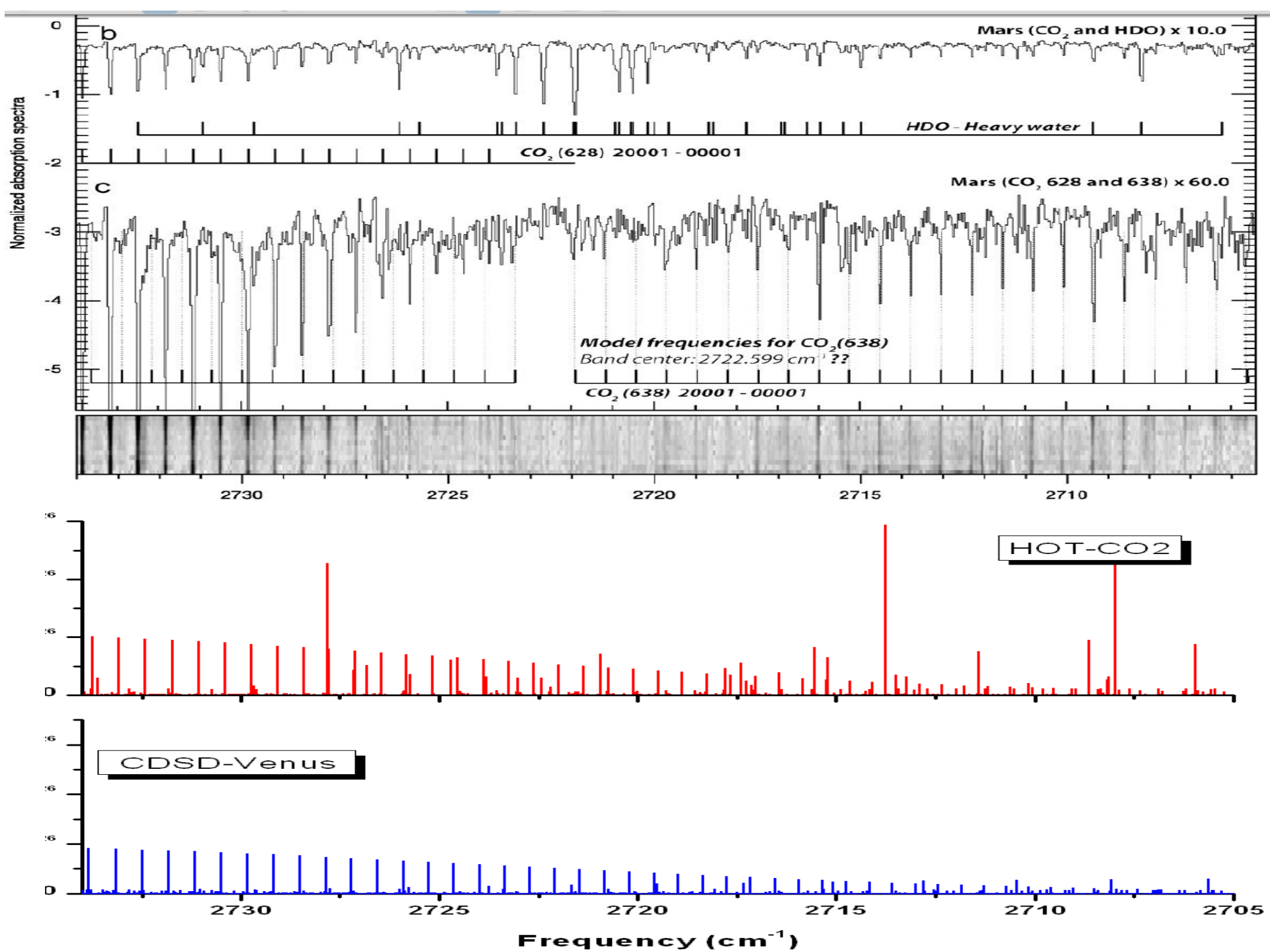
databank	HOT-CO2	CDSD-Venus
Tref	296 K	750 K
I_{min} at T=750 K	$8.54 \cdot 10^{-32}$	10^{-30}
data format	HITRAN-1996	HITRAN-2004
isotopes	1,2,3,5	1,2,3,4,5,6,7
range (cm^{-1})	21 - 12783	14 - 12784
lines	7 088 178	11 730 277

Line parameters for the 01111–00001 band of $^{12}C^{16}O^{18}O$ from SOIR measurements of the Venus atmosphere (V. Wilquet *et al*, JQSRT 109, 895 (2008)

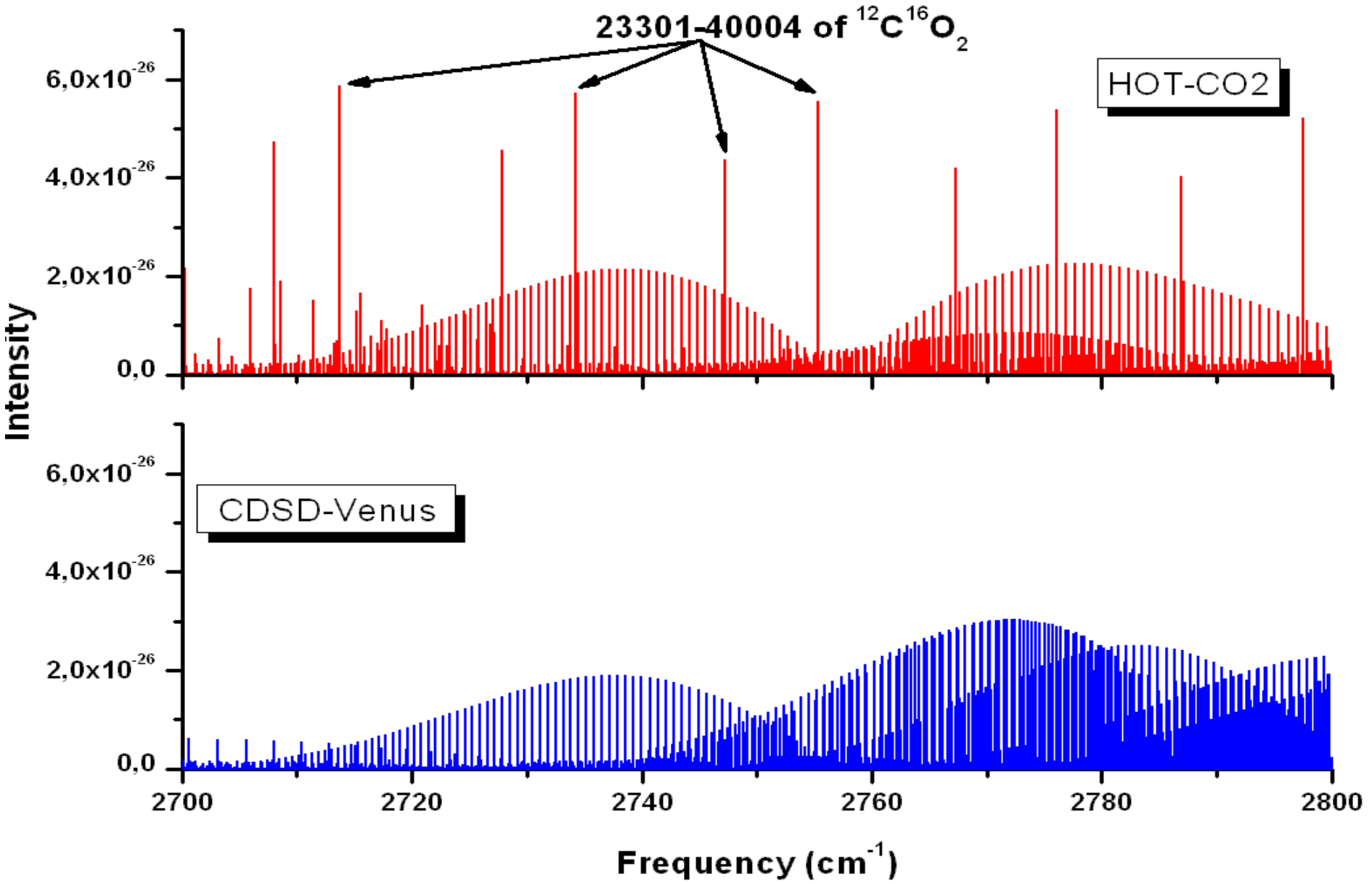


Simulation


HOT-CO2
height=82 km
T=180 K P=0.1 atm L=10 Km
ILS: rectangle, 0.1 cm-1
Lorentz contour
CDSD-Venus
Absorptivity
Frequency (cm-1)
0
2
0,0
0,1
0,2
0,3
2960
2970
2980
2990
3000


b
Mars (CO_2 and HDO) x 10.0
HDO - Heavy water
CO_2 (628) 20001 - 00001
c
Mars (CO_2 628 and 638) x 60.0
Model frequencies for CO_2(638)
Band center: 2722.599 cm^{-1} ??
CO_2 (638) 20001 - 00001
Normalized absorption spectra
0
-1
-2
-3
-4
-5
2730
2725
2720
2715
2710
HOT-CO2
CDSD-Venus
2730
2725
2720
2715
2710
2705
Frequency (cm^{-1})

G.L. Villanueva *et al,* JQSRT 109, 883 (2008), Fig. 5



G.L. Villanueva *et al,* JQSRT 109, 883 (2008), Table 2, 20001-00001 band of $^{16}O^{13}C^{18}O$

Villaneuva			CDSD-Venus			HOT-CO2
P	23	2705.639	2705.618	R	4	
P	22	2706.351	2706.356	R	5	2705.126
P	21	2707.085	2707.095	R	6	2705.864
P	20	2707.841	2707.834	R	7	2706.602
P	19	2708.572	2708.573	R	8	2707.340
P	18	2709.320	2709.312	R	9	2708.079
P	17	2710.055	2710.052	R	10	2708.817
P	16	2710.800	2710.792	R	11	2709.556
P	15	2711.528	2711.532	R	12	2710.296
P	14	2712.276	2712.273	R	13	2711.035
P	13	2713.019	2713.013	R	14	2711.775
P	12	2713.756	2713.755	R	15	2712.515
P	11	2714.501	2714.496	R	16	2713.255
P	10	2715.244	2715.238	R	17	2713.996
P	9	2715.982	2715.981	R	18	2714.737
P	8	2716.732	2716.724	R	19	2715.478
P	7	2717.469	2717.467	R	20	2716.220
P	6	2718.179	2718.211	R	21	2716.962
P	5	2718.958	2718.955	R	22	2717.705
P	4	2719.690	2719.699	R	23	2718.447
P	3	2720.404	2720.444	R	24	2719.191

Conclusions

- **$^{16}O^{12}C^{17}O$ and $^{16}O^{13}O^{17}O$ new laboratory measurements are urgently needed**
- **long range J extrapolations based on spectroscopic constants are extremely dangerous**
- **measured data should be given in publications along with calculated data**
- **HITRAN should have a person who will be responsible for support of present and future CO_2 data**

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