

Sub-Doppler Measurements and Terahertz Rotational Spectrum of $^{12}\text{C}^{18}\text{O}$

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The five lowest rotational transitions of $^{12}\text{C}^{18}\text{O}$ ($J = 2 \leftarrow 1$ to $J = 6 \leftarrow 5$) have been measured by saturation dip spectroscopy with an experimental accuracy of 1 to 1.5 kHz, employing phase-stabilized backward-wave oscillators. The five J rotational transitions cover the frequency range between 219 and 658 GHz. In addition, we have measured in the Doppler limited mode the rotational transitions $J = 1 \leftarrow 0$, $J = 7 \leftarrow 6$ and $J = 8 \leftarrow 7$. The accuracy achieved for the individual frequencies ranges between 5 and 20 kHz. Moreover the three rotational transitions $J = 16 \leftarrow 15$ to $J = 18 \leftarrow 17$ in the frequency region 1.7–2.0 THz were measured with an accuracy of 15 to 30 kHz by using the Cologne sideband spectrometer for terahertz applications COSSTA.

Key words: Sub-Doppler Measurement; Rotational Spectrum.

Introduction

Highly accurate rotational transition frequencies of CO have been in demand since they serve in the laboratory as an easy but important calibration standard, covering the millimeter wave to the far infrared region. In a continuing effort to provide the most accurate center frequencies for the various isotopomers of CO throughout the millimeter- and submm wave region, we used saturation dip spectroscopy at frequencies below 1 THz for the following CO isotopomers $^{12}\text{C}^{16}\text{O}$ [1], $^{13}\text{C}^{16}\text{O}$ [2] and $^{13}\text{C}^{18}\text{O}$ [3]. The literature on the determination of laboratory rest frequencies of CO has always reflected the most recent advances in technological developments concerning measurement accuracy. In contrast to the main isotopomer of carbon monoxides $^{12}\text{C}^{16}\text{O}$, only a few publications of laboratory measurements were reported in the literature for $^{12}\text{C}^{18}\text{O}$. Mainly three groups worked on the topic $^{12}\text{C}^{18}\text{O}$. Winnewisser et al. [4] published spectra of six different CO isotopomers in the submm-wave region up to 576 GHz. This work includes the determination of accurate frequencies of the five lowest rotational transitions of $^{12}\text{C}^{18}\text{O}$ with a statistical measurement uncertainty between 6 and 33 kHz. In 1983 Guelachvili et al. [5] published Dunham coefficients of CO based on Fourier Transform measurements of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ of vibrational spectra between 1205 and 6335 cm^{-1} . A third line of

work concerns Doppler limited measurements from de Natale et al. [6] employing a Fourier Transform spectrometer. The accuracy achieved for these transitions is about 1.2 MHz. For calibration of the spectrometer they used $^{12}\text{C}^{16}\text{O}$ rotational transitions.

Experimental Details

Two spectrometers were used for the present measurements: the Cologne terahertz spectrometer [7] and the Cologne sideband spectrometer for terahertz appli-

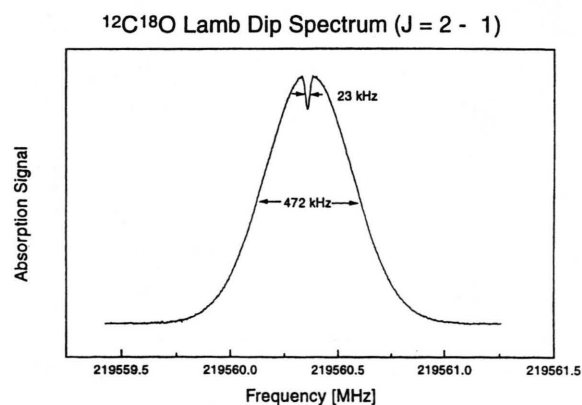


Fig. 1. Lamb dip spectrum of the $J = 2 \leftarrow 1$ transition of $^{12}\text{C}^{18}\text{O}$ at 219 GHz on the top of the Doppler-profile.

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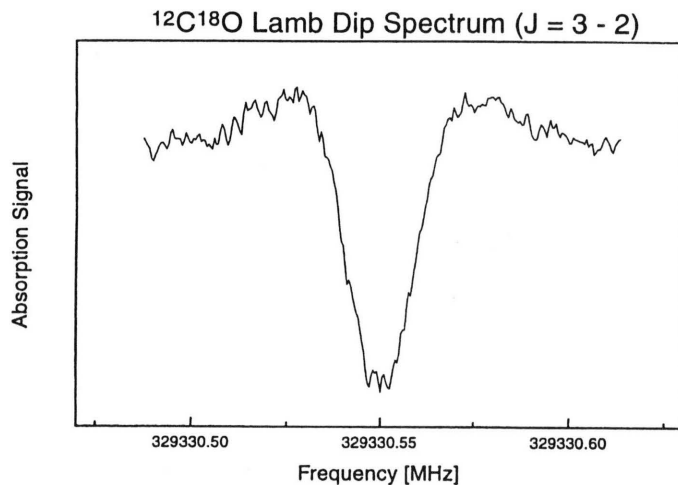


Fig. 2. Lamb dip spectrum of the $J=3 \leftarrow 2$ transition of $^{12}\text{C}^{18}\text{O}$ at 329 GHz.

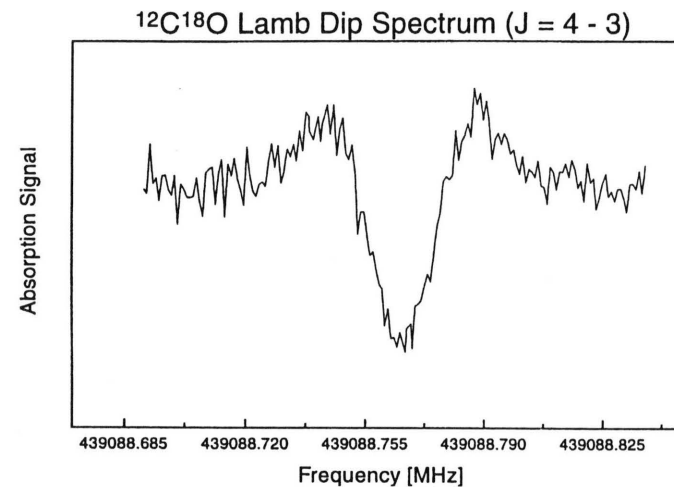


Fig. 3. Lamb dip spectrum of the $J=4 \leftarrow 3$ transition of $^{12}\text{C}^{18}\text{O}$ at 439 GHz.

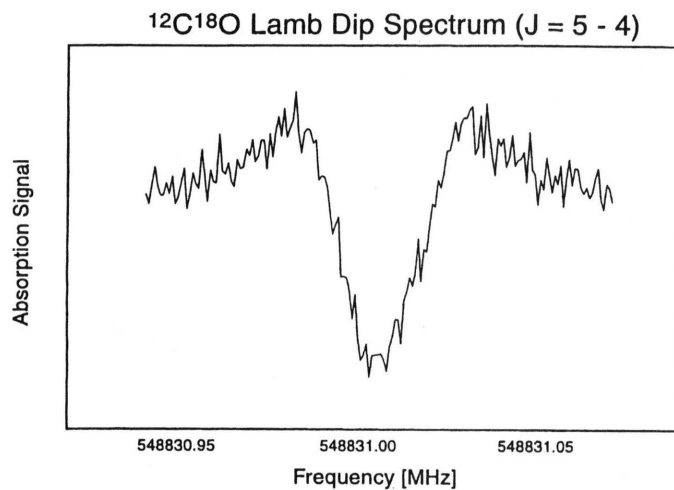


Fig. 4. Lamb dip spectrum of the $J=5 \leftarrow 4$ transition of $^{12}\text{C}^{18}\text{O}$ at 548 GHz.

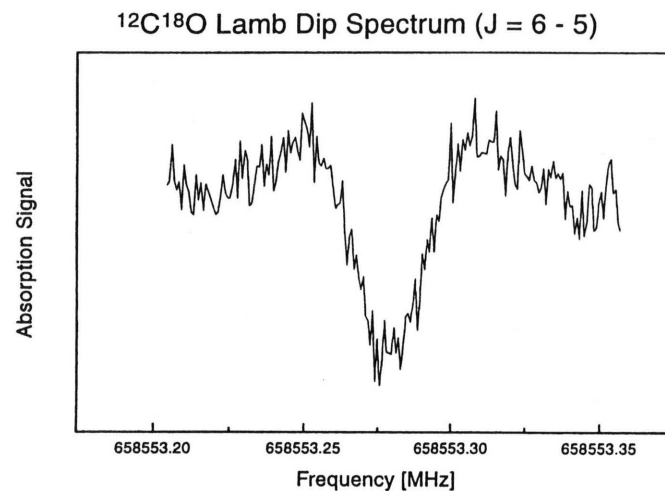


Fig. 5. Lamb dip spectrum of the $J=6 \leftarrow 5$ transition of $^{12}\text{C}^{18}\text{O}$ at 658 GHz.

cations, COSSTA [8]. Both spectrometers operate with phase-locked backward-wave oscillators (BWOs), and in case of the sideband spectrometer with a frequency-locked FIR laser. All reference frequencies are locked against a rubidium frequency standard. The Cologne terahertz spectrometer can be used up to about 1.6 THz [9], whereas the Cologne sideband spectrometer for terahertz applications can presently be tuned to frequencies between 1.7 to 2.0 THz. The present measurements on $^{12}\text{C}^{18}\text{O}$ are carried out with both spectrometers. With the Cologne terahertz spectrometer five lines were detected in sub-Doppler resolution ($J=2 \leftarrow 1$ to $J=6 \leftarrow 5$) and three lines in Doppler mode ($J=1 \leftarrow 0$, $J=7 \leftarrow 6$, $J=8 \leftarrow 7$). Lines measured with the sideband spectrometer were recorded in Doppler limited mode ($J=16 \leftarrow 15$, $J=17 \leftarrow 16$ and $J=18 \leftarrow 17$).

Results

The newly measured transitions are summarized together with the transitions reported by de Natale *et al.* [6] in Table 1. The line center frequencies were derived from the measured data points by fitting them to a parabolic function. The achieved measurement accuracies depend on the spectrometer used and on the mode employed. The differences in the accuracies of the Doppler-limited measurements depend on the achieved signal to noise ratio. Doppler lines with good signal to noise ratio can be trusted to 5 kHz, whereas the achievable accuracy for unblended, fully resolved Lamb dip measurements in the submillimeter wave region recorded with a good signal to noise ratio estimated to be around 500 Hz [1]. However, accuracies presented here are estimated to be between 1 to 1.5 kHz, depending on the signal to noise ratio.

Figure 1 shows the Lamb dip superimposed on the Doppler line profile. The linewidth of the Doppler profile is about 472 kHz, whereas the linewidth of the sub-Doppler line is about 23 kHz. In Figs. 2 to 5 we present a sequence of different rotational transitions recorded with sub-Doppler resolution. Whereas Fig. 6 demonstrates the highest frequency Doppler spectrum recorded in this study. The new set of data of $^{12}\text{C}^{18}\text{O}$ was subjected to a least-square fit in which each line was weighted proportionally to the inverse square of its experimental uncertainty. The σ of the fit is 2.5 kHz. The o-c values for the frequencies measured by de Natale *et al.* [6] stay in close agreement with the corresponding o-c values determined in the same reference. In Table 2 we give a

Table 1. Sub-Doppler and Doppler resolved rotational transitions of $^{12}\text{C}^{18}\text{O}$.

$J' \leftarrow J''$	Obs. Frequencies ^a [MHz]	o-c [kHz]
1 \leftarrow 0	109 782.172 (20) ^b	-3.4
2 \leftarrow 1	219 560.3541 (15) ^b	-3.0
3 \leftarrow 2	329 330.5525 (15) ^b	0.9
4 \leftarrow 3	439 088.7658 (10) ^b	0.6
5 \leftarrow 4	548 831.0055 (10) ^b	0.4
6 \leftarrow 5	658 553.2782 (10) ^b	-0.4
7 \leftarrow 6	768 251.5933 (50) ^b	-0.1
8 \leftarrow 7	877 921.9553 (60) ^b	-3.2
9 \leftarrow 8	987 560.2 (12) ^c	-182
10 \leftarrow 9	1 097 163.5 (12) ^c	625
11 \leftarrow 10	1 206 724.7 (12) ^c	-748
12 \leftarrow 11	1 316 244.4 (12) ^c	286
13 \leftarrow 12	1 425 715.4 (12) ^c	515
14 \leftarrow 13	1 535 133.3 (12) ^c	-476
15 \leftarrow 14	1 644 497.3 (12) ^c	497
16 \leftarrow 15	1 753 799.981 (30) ^d	-1.9
17 \leftarrow 16	1 863 039.359 (20) ^d	24.1
18 \leftarrow 17	1 972 210.870 (15) ^d	-9.5
19 \leftarrow 18	2 081 310.8 (12) ^c	161
20 \leftarrow 19	2 190 332.6 (12) ^c	-2037
21 \leftarrow 20	2 299 281.1 (12) ^c	2198
22 \leftarrow 21	2 408 138.2 (12) ^c	-1259
23 \leftarrow 22	2 516 913.5 (12) ^c	1158
24 \leftarrow 23	2 625 591.6 (12) ^c	-1981
25 \leftarrow 24	2 734 180.4 (12) ^c	1188

^a The errors in parentheses are 1σ and given in units of the last quoted digits.

^b Frequencies measured with the Cologne terahertz spectrometer. The frequencies of the first five transitions ($J=1 \leftarrow 0$) measured by Winnewisser *et al.* [4] in Doppler limited mode agree within quoted errors with the presented frequencies.

^c Observed frequencies taken from de Natale *et al.* [6].

^d Frequencies measured with the Cologne sideband spectrometer.

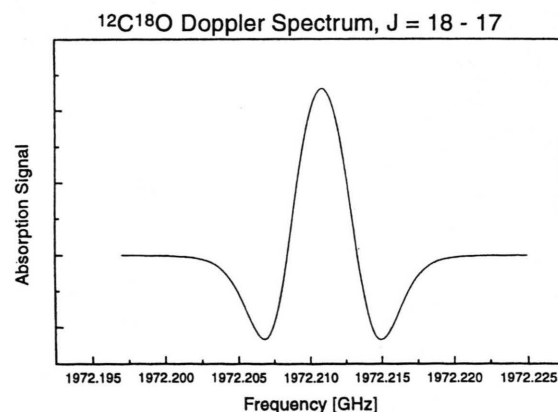


Fig. 6. Doppler spectrum of the $J=18 \leftarrow 17$ transition of $^{12}\text{C}^{18}\text{O}$ at 1972 GHz.

Table 2. Molecular constants of $^{12}\text{C}^{18}\text{O}$.

Con- stants	This work	M. Winnewisser et al. [4]	de Natale et al. [6]	Unit
B_0	54 891.41920 (10)	54 891.4212 (10)	54 891.422 (5)	MHz
D_0	166.4058 (27)	166.468 (27)	166.308 (12)	kHz
H_0	0.1458 (54)	0.1419 ^a	–	Hz

^a Values taken from G. Guelachvili et al. [5].

summary of the newly determined constants. The values of the three constants B_0 , D_0 and H_0 generally agree with the corresponding values quoted by Winnewisser et al. [4] and de Natale et al. [6]. On account of the precise sub-Doppler measurements the new constants could be determined more accurately. They reproduce the experimental data very well as can be seen by the o–c values given in Table 1. Because of the higher relative uncer-

tainties of the Fourier Transform measurements they were of lower influence to the overall result of the fit.

In summary, precise experimental frequencies of $^{12}\text{C}^{18}\text{O}$ could be determined by sub-Doppler spectroscopy. Accurate frequency predictions can be provided now with the improved molecular constants determined here. Calculated frequencies are available from the authors upon request or under www.ph1.uni-koeln.de.

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