LETTER TO THE EDITOR

Sub-Doppler Measurements on the Rotational Transitions of Carbon Monoxide

G. Winnewisser, S. P. Belov, Th. Klaus, and R. Schieder

I. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany

The six lowest rotational transitions of CO have been measured to an accuracy of ±500 Hz. Highly accurate rotational transition frequencies of CO have always been in demand since they serve in the laboratory as an easy but important secondary calibration standard, covering the millimeter to the far infrared region. Astrophysically, CO is a ubiquitous interstellar molecule, and also an important trace constituent of planetary atmospheres. For both cases, precise laboratory rest frequencies are required for accurate velocity determinations.

The literature on laboratory rest frequency determinations of CO has always reflected the most recent advances in technological developments concerning measurement accuracy. This is illustrated by recent work from two groups on this topic. One line of work, by Varberg and Evenson (*1*), concerns the determination of accurate far-infrared rotational frequencies of CO employing the laser sideband technique and its most recent revision (*2*) using improved CO_2 frequencies (*3*). The accuracy achieved for the individual frequencies ranges between 10 and 43 kHz in the frequency region 600–4340 GHz. A second line of work concerns the precise Doppler-limited measurements of the three CO rotational transitions $J = 2 \leftarrow 1$, $3 \leftarrow 2$, and $4 \leftarrow 3$ by Belov *et al.* (*4*) using the Nizhnii Novgorod based RAD-2 spectrometer. This technique achieved an accuracy of 1–2 kHz (1σ uncertainty) on the appropriate line center positions, when pressure shift effects were taken into account.

The purpose of the present Letter is to report Lamb-dip measurements carried out on CO with the Cologne terahertz spectrometer (*5*) operating in the saturation mode (*6–8*). This spectrometer has been used recently for sub-Doppler resolution measurements on a variety of molecules. Among the molecular spectra studied is the rotation–inversion spectrum of ammonia in its ground (*6*) and first excited vibrational states (*7*), with the aim of resolving its nuclear hyperfine structure. For the ground state of NH_3 we have resolved for the first time the hyperfine structure of the $(J, K) = s(1, 0) - a(0, 0)$ rotation–inversion transition and determined its unsplit line center frequency to be 572 498.163 MHz with an accuracy of 10 kHz (*8*). The quoted uncertainty is not determined by the ultimately reachable measurement accuracy of the spectrometer, but rather reflects possible pressure shift contributions. For CO, it has been shown that self-pressure shift effects are negligibly small not only for the $J = 2 \leftarrow 1$ and $3 \leftarrow 2$ transitions (*4*), but even for the $1 \leftarrow 0$ line, as has been confirmed recently by Mäder *et al.* (*9*). In the case of negligible contributions from pressure shifts— and this should normally be so for a number of molecules—the expected accuracy of the Lamb-dip measurements is estimated to be about 1 kHz for isolated strong lines. In favorable cases the achieved measurement precision of a transition frequency can even be better.

Figure 1 shows the Lamb-dip of the $J = 4 \leftarrow 3$ transition of CO recorded in the second derivative form. The full linewidth of the Lamb-dip is close to 40 kHz and consists of about 30 measured points. The frequency step can be as small as 100 Hz multiplied by the number of harmonics (*n*) of the KVARZ synthesizer (*n* = 4 or 5 in this case). During the measurements,

special efforts were taken to ensure that frequency shifts, which can appear from optical misalignment or other sources such as baseline problems, were inside the frequency reproducibility of each measured transition. The experimental uncertainties for the Lamb-dip frequencies were then estimated to be not larger than 500 Hz.

The present measurements are probably the most precise absolute line frequency determinations achievable to date in the millimeter- and submillimeter-wave region. It is therefore desirable to have the line center positions of the lower *J* rotational transitions of CO brought up to the level of accuracy obtainable by saturation-dip spectroscopy. Accordingly, we have remeasured these transitions and studied the $J = 5 \leftarrow 4$ and $J = 6 \leftarrow 5$ transitions. Tables 1 and 2 summarize both the far-infrared data of Evenson (*2*) and the CO transitions measured with the Cologne terahertz spectrometer operating in the saturation mode up to 800 GHz and in the conventional Doppler-limited mode up to 1.3 THz. The line center frequencies were derived from the experimental data points by fitting them to a parabolar function. For these measurements the pressure was maintained near 1 μbar in a 3.9-m free space absorption cell. The highest frequency Lamb-dip spectrum recorded for CO is displayed in Fig. 2. The accuracy of the Lamb-dip measurements is estimated to be within ±500 Hz as already mentioned above, whereas the Doppler-limited transition frequencies of the Cologne spectrometer can be trusted to ±5 kHz. These levels of accuracy are substantiated not only by the quality of the fit of these lines, but also by internal consistency with previous microwave measurements. The internal consistency checks include the following:

1. The four lowest *J* rotational transitions have been measured to rather high precision by several laboratories with different types of spectrometers. All previous results are, within their quoted uncertainty, in excellent agreement with our present Lamb-dip data (Table 1). In particular, our recent Doppler-limited submillimeter CO measurements (*12*) agree to within 1 kHz with our new sub-Doppler results.

2. The statistics on the calculated $J = 1 \leftarrow 0$ line position using different data sets can be used to gain some insight into the residual systematic error and thus into the internal consistency of the measurements. For example, our fit of the new data together with far infrared data from (*2*) (Table 2) yielded 115271.20202 (6) MHz for the calculated frequency of the $J = 1 \leftarrow 0$ transition both when the measured frequency of this transition was included in the fit and when it was not included. A similar result was obtained when the frequencies of the first four transitions in Table 2 were replaced in the fit by the data reported by Winnewisser *et al.* (*10*).[1] In this latter case, $\nu_{calc} = 115271.20200(7)$ MHz when we kept the uncertainty of the remaining two Lamb-dip measurements. When their uncertainty was

---

[1] In addition to $^{12}C^{16}O$, the lowest rotational transitions of the following CO isotopomers have been measured (*10*): $^{12}C^{17}O$, $^{12}C^{18}O$, $^{13}C^{16}O$, $^{13}C^{17}O$, and $^{13}C^{18}O$.
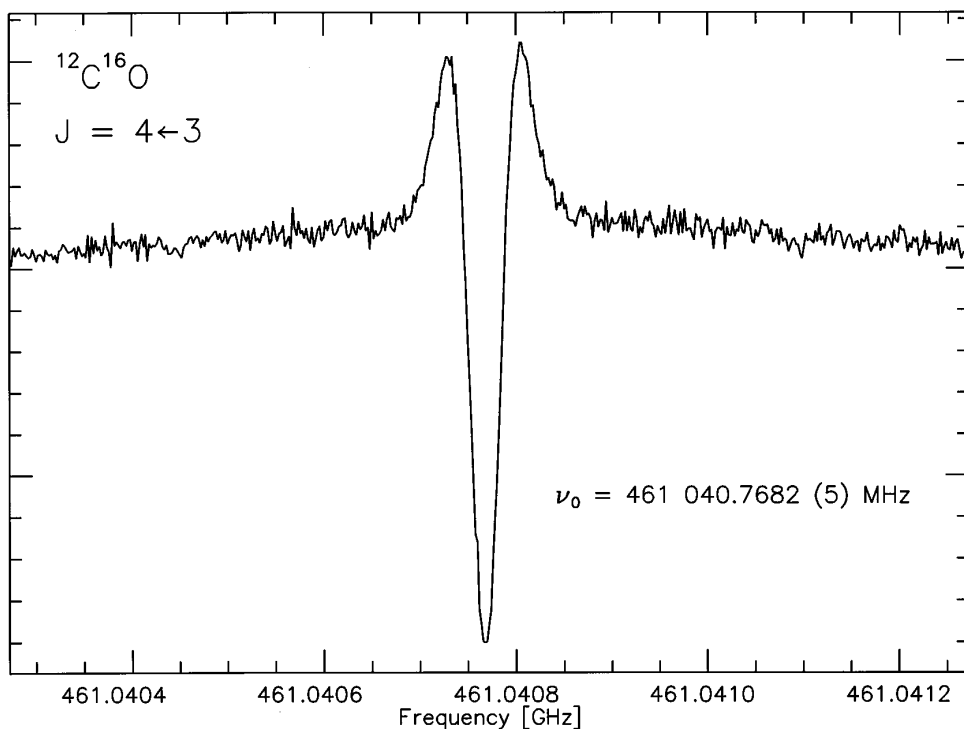
FIG. 1. The Lamb-dip spectrum of the $J = 4 \leftarrow 3$ transition of CO at 461 040.7682 MHz. The width of the scan is 1 MHz which corresponds to the full Doppler linewidth. The Lamb-dip signal is resolved with about 30 measured data points within the full linewidth of about 40 kHz.
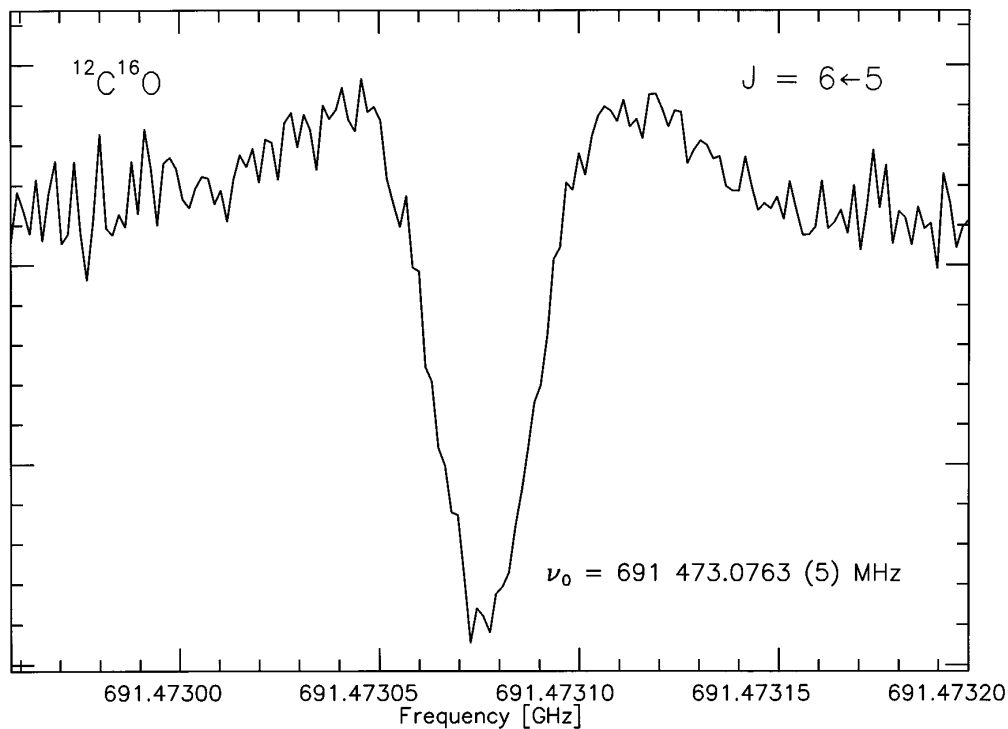

FIG. 2. This 240 kHz scan shows the Lamb-dip of the $J = 6 \leftarrow 5$ transition of CO at 691 473.0763 MHz. The linewidth is about 30 kHz and the total scan consists of 150 points.

TABLE 1
Measured Lamb-Dip Frequencies for Rotational Transitions of $^{12}C^{16}O$ and Comparison with Data from Other Works

	Cologne THz Spectrometer			RAD	Microwave		FTMW
$J' \leftarrow J''$	ν_{exp} [MHz]	$\Delta\nu_{exp}$[a] [kHz]	O–C [kHz]	$\nu_{exp}-\nu_{obs}$[b] [kHz]	$\nu_{exp}-\nu_{obs}$[c] [kHz]	$\nu_{exp}-\nu_{obs}$[d] [kHz]	$\nu_{exp}-\nu_{obs}$[e] [kHz]
$1 \leftarrow 0$	115 271.2018	0.5	−0.22	−0.2(20)[e]	−3.3(52)	−2.2(50)	1.8(50)
$2 \leftarrow 1$	230 538.0000	0.5	0.04	0.0(10)	−1.6(50)		
$3 \leftarrow 2$	345 795.9899	0.5	0.05	−1.1(10)	−0.7(36)		
$4 \leftarrow 3$	461 040.7682	0.5	0.22	−0.8(20)	3.0(38)		
$5 \leftarrow 4$	576 267.9305	0.5	−0.51				
$6 \leftarrow 5$	691 473.0763	0.5	0.21				

[a] Estimated experimental uncertainties of the Cologne Lamb-dip frequencies ν_{exp}.

[b] ν_{obs} measured by Belov *et al.* (4). The experimental uncertainties for all observed frequencies, ν_{obs}, are given in brackets in units of the last quoted digits.

[c] ν_{obs} measured by Winnewisser *et al.* (10).

[d] ν_{obs} measured by Rosenblum *et al.* (11).

[e] ν_{obs} measured by Mäder *et al.* (9).

increased 10 times (up to 5 kHz) the result was $\nu_{calc} = 115271.20208(25)$ MHz. If only our Lamb-dip data were fitted, the calculated frequency was 115271.20209(15) MHz. Finally, the Lamb-dip data together with the Doppler limited lines from Belov *et al.* (*12*) resulted in a frequency of 115271.20200(12) MHz. From these various fit results, we conclude that the residual systematic error in our Lamb-dip measurements should be less than 100 Hz.

In addition to the internal consistency checks, the quality of the least-squares fits to our Lamb-dip data, carried out separately (rms = 0.24 kHz) and together with our Doppler-limited lines up to $J = 11 \leftarrow 10$ from Belov *et al.* (*12*) (rms[2] = 0.26 kHz), confirm that the Cologne terahertz spectrometer has reached an accuracy in the sub-kHz level when operated in the sub-Doppler mode. It should be noted that the CO data presented here are in very close agreement with the earlier data set compiled by Varberg and Evenson (*1, 2*). The result of a least-squares fit to all presently available rotational transition frequencies (up to $J = 38 \leftarrow 37$) is presented in Table 2. It was found that the L_0-term in the centrifugal distortion expansion is not required, resulting in a revised set of molecular constants for CO in its ground vibrational state (Table 3). The B_0, D_0, and H_0 terms are in good agreement with the previous values given by Varberg and Evenson (*1*).

The best signal-to-noise ratio reached in our experiments (Fig. 1) and the narrowest full linewidths of the Lamb-dips (16 kHz at 230 GHz, 25 kHz at 461 GHz, and 32 kHz at 691 GHz) are limited mainly by the parameters of the KVARZ synthesizer's (78-118 GHz) output signal, which was used as a local oscillator to feed the harmonic-mixer in the BWO

phase-lock loop. Thus, there is still room for considerable improvement of the parameters of the saturation-dip, such as the linewidth and signal-to-noise ratio, so as to increase the accuracy of the frequency determination.

It might be of interest to use precise Lamb-dip data for secondary frequency calibration in line spectroscopy. The removal of systematic errors of line position measurements in pulsed beam Fourier-transform microwave spectrometers (FTMW) serves as one purpose for the proposed calibration. This type of spectrometer provides very high sensitivity, permits the observation of molecular lines with a full linewidth of 2–5 kHz, and allows a determination of line positions with a reproducibility of about 500 Hz (see, e.g., Lovas *et al.* (*13*)). But, as mentioned by Mäder *et al.* (*9*), the systematic errors of measurements with FTMW spectrometers are considerably larger than statistical errors and these really limit the measurement accuracy.

In conclusion, the rotational transitions of the CO molecule, with a relatively small dipole moment of 0.1 Debye, have been measured with saturation-dip spectroscopy for the first time. At present, sub-Doppler saturation spectroscopy provides the most precise method for absolute line position measurements (⩽500 Hz) and can be applied to a large number of molecules in the millimeter- and submillimeter-wave region.

---

[2] rms value given only for the six Lamb-dips.

TABLE 2
Observed and Calculated Frequencies for Rotational Transitions of Carbon Monoxide

J'	$\leftarrow$	J''	ν_{exp}[a] [MHz]	$\Delta\nu_{exp}$[b] [kHz]	ν_{calc} [MHz]	σ_{calc}[c] [kHz]	O−C [kHz]
1	$\leftarrow$	0	115 271.2018	0.5	115 271.20202	0.06	-0.22
2	$\leftarrow$	1	230 538.0000	0.5	230 537.99996	0.11	0.04
3	$\leftarrow$	2	345 795.9899	0.5	345 795.98985	0.16	0.05
4	$\leftarrow$	3	461 040.7682	0.5	461 040.76798	0.21	0.22
5	$\leftarrow$	4	576 267.9305	0.5	576 267.93101	0.25	-0.51
6	$\leftarrow$	5	691 473.0763	0.5	691 473.07609	0.29	0.21
7	$\leftarrow$	6	806 651.806	5	806 651.8010	0.3	5
8	$\leftarrow$	7	921 799.700	5	921 799.7042	0.4	-4
9	$\leftarrow$	8	1 036 912.393	5	1 036 912.3852	0.5	8
10	$\leftarrow$	9	1 151 985.452	11	1 151 985.4442	0.6	8
11	$\leftarrow$	10	1 267 014.486	5	1 267 014.4828	0.8	3
12	$\leftarrow$	11	1 381 995.105	13	1 381 995.1036	1.0	1
13	$\leftarrow$	12	1 496 922.909	12	1 496 922.9108	1.2	-2
14	$\leftarrow$	13	1 611 793.518	11	1 611 793.5099	1.5	8
15	$\leftarrow$	14			1 726 602.508	2	
16	$\leftarrow$	15	1 841 345.506	11	1 841 345.514	2	-8
17	$\leftarrow$	16	1 956 018.139	11	1 956 018.139	3	0
18	$\leftarrow$	17	2 070 615.993	14	2 070 615.995	3	-2
19	$\leftarrow$	18	2 185 134.680	13	2 185 134.698	4	-18
20	$\leftarrow$	19	2 299 569.842	10	2 299 569.863	5	-21
21	$\leftarrow$	20	2 413 917.113	11	2 413 917.112	6	1
22	$\leftarrow$	21	2 528 172.060	11	2 528 172.065	6	-5
23	$\leftarrow$	22			2 642 330.347	7	
24	$\leftarrow$	23	2 756 387.584	17	2 756 387.586	8	-2
25	$\leftarrow$	24	2 870 339.407	13	2 870 339.411	10	-4
26	$\leftarrow$	25	2 984 181.455	14	2 984 181.455	11	0
27	$\leftarrow$	26	3 097 909.361	17	3 097 909.354	12	7
28	$\leftarrow$	27			3 211 518.748	14	
29	$\leftarrow$	28			3 325 005.279	15	
30	$\leftarrow$	29	3 438 364.611	10	3 438 364.594	17	17
31	$\leftarrow$	30	3 551 592.361	10	3 551 592.342	19	19
32	$\leftarrow$	31			3 664 684.177	20	
33	$\leftarrow$	32	3 777 635.728	16	3 777 635.755	22	-26
34	$\leftarrow$	33	3 890 442.717	13	3 890 442.738	25	-21
35	$\leftarrow$	34			4 003 100.791	27	
36	$\leftarrow$	35	4 115 605.585	22	4 115 605.584	29	1
37	$\leftarrow$	36			4 227 952.790	32	
38	$\leftarrow$	37	4 340 138.112	43	4 340 138.088	35	24

[a] Observed frequencies ν_{exp} from this work, from Belov *et al.* (<u>12</u>), and from Evenson (<u>2</u>).
[b] Experimental uncertainties.
[c] 1σ standard errors of the calculated frequencies.

TABLE 3
Rotational Constants for CO[a] in Comparison to the Values Reported by Varberg and Evenson (1)

Constant	Fitted Value[b]	Ref. (1)
B_0	57 635.968019 (28)	57 635.96826 (12)
D_0	0.18350489 (16)	0.18350552 (46)
H_0	1.7168 (10) $\cdot 10^{-7}$	1.7249 (59) $\cdot 10^{-7}$
L_0		-3.1 (23) $\cdot 10^{-13}$

[a] The fit includes all lines from Table 2. All values are given in MHz.

[b] Values in parentheses are 1σ standard errors.

Note added in proof. After completion of this Letter, we became aware of a paper by Beaky *et al.* (*14*) in which they report pressure broadening and line shift measurements of the $J = 1 \leftarrow 0$ and $2 \leftarrow 1$ transitions of CO in collision with helium between temperatures of 1 and 600 K. They found the line shift parameter due to pressure to be very small at room temperature but much larger at low temperatures. At 4.2 K they derived a line center frequency from their frequency shift vs pressure for the $J = 1 \leftarrow 0$ of 115271.202 MHz in close agreement with our Lamb-dip value. One possible error contribution for low temperature line frequency determinations is the zero calibration of the pressure measurement. Our Lamb-dip frequencies should be useful for a calibration of the zero pressure at very low temperatures.

REFERENCES

1. T. D. Varberg and K. M. Evenson, *Astrophys. J.* **385,** 763–765 (1992).
2. K. M. Evenson, private communication, 52nd Okazaki Conference, Okazaki, Japan, March 1995.
3. A. G. Maki, C. C. Chou, K. M. Evenson, L. R. Zink, and J. T. Shy, *J. Mol. Spectrosc.* **167,** 211–224 (1994).
4. S. P. Belov, M. Yu. Tretyakov, and R. D. Suenram, *Astrophys. J.* **393,** 848–851 (1992).
5. G. Winnewisser, *Vib. Spectrosc.* **8,** 241–253 (1995).
6. S. P. Belov, Th. Klaus, G. M. Plummer, R. Schieder, and G. Winnewisser, *Z. Naturforsch. A* **50,** 1187–1190 (1995).
7. S. P. Belov, Š. Urban, and G. Winnewisser, *J. Mol. Spectrosc.,* in press.
8. G. Winnewisser, S. P. Belov, Th. Klaus, and Š. Urban, *Z. Naturforsch. A* **51,** 200–206 (1996).
9. H. Mäder, A. Guarnieri, J. Doose, N. Nissen, V. N. Markov, A. M. Shtanyuk, A. F. Andrianov, V. N. Shanin, and A. F. Krupnov, *J. Mol. Spectrosc.* **180,** 183–187 (1996).
10. M. Winnewisser, B. P. Winnewisser, and G. Winnewisser, *in* ''Molecular Astrophysics, Series C'' (G. H. F. Diercksen, W. F. Huebner, and P. W. Langhoff, Eds.), Vol. 157, pp. 375–402. Reidel, Dordrecht, 1985.
11. B. Rosenblum, A. H. Nethercot, and C. H. Townes, *Phys. Rev.* **109,** 400–413 (1958).
12. S. P. Belov, F. Lewen, Th. Klaus, and G. Winnewisser, *J. Mol. Spectrosc.* **174,** 606–612 (1995).
13. F. J. Lovas, S. P. Belov, M. Yu. Tretyakov, W. Stahl, and R. D. Suenram, *J. Mol. Spectrosc.* **170,** 478–492 (1995).
14. M. M. Beaky, T. M. Goyette, and F. C. De Lucia, *J. Chem. Phys.* **105,** 3994–4004 (1996).