Terahertz Spectrum of Trioxane

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The pure rotational spectrum of trioxane, $(H_2CO)_3$ the trimer of formaldehyde, has been recorded with high resolution in the frequency range between 326 and 947 GHz for the main isotopomer, the ^{13}C, and the ^{18}O isotopic species in the vibrational ground state. These new high J and K data reveal that the molecule is fairly rigid. For the constants determinable from the recorded high J and K spectra ($J = 90$ and $K = 75$) the rotational constant

$$B = 5273.257\ 180(33)\ \text{MHz},$$

the two quartic centrifugal distortion constants D_J, and D_{JK}, and the three sextic constants H_J, H_{JK}, and H_{KJ} are needed in the fit to reproduce the measured spectra within experimental accuracy. In addition, for the ^{13}C isotopomer the sextic constants H_{JK} and H_{KJ} are determined as well as the off-diagonal parameters d_1 and d_2.

Introduction

Although the microwave spectrum of the lowest three R branch transitions of trioxane have been measured in 1963 by Oka et al. [1], and several medium J transitions ($J = 47$) of the millimeter and submillimeter wave spectrum by Gadhi et al. [2], it remains interesting to measure spectra of a heavy molecule like trioxane at very high J values to study the behaviour of centrifugal distortion effects in a ring molecule. With the new terahertz spectrometer at Cologne we have the possibility to measure line positions very precisely (~10 kHz) near 1 THz and above.

The rather heavy ring molecule 1, 3, 5 - trioxane, $(H_2CO)_3$, the cyclic trimer of formaldehyde, serves as an example of a fairly rigid molecule. Since trioxane is an oblate top, the population of the energy levels at room temperature allow not only high J transitions to be measured, but also high K transitions. These measurements are very valuable in determining the centrifugal distortion constants D_{JK}, H_{JK}, and H_{KJ} as well as higher terms if required.

Trioxane possesses two low lying bending vibrational states, the degenerate vibration $\nu_{20}= 307\ \text{cm}^{-1}$ and the vibration $\nu_7= 467\ \text{cm}^{-1}$. Although the associated rotational spectra have been measured in the respective 1st excited vibrational states, they will not be discussed here. The purpose of the present note is to present these measurements of the main isotopomer of trioxane and its ^{13}C and ^{18}O isotopomers in the ground vibrational state in the terahertz frequency region.

Experimental details

The Cologne terahertz spectrometer has been described in some detail in [3, 4]. For the present measurements, which were carried out parallel to the measurement of the formaldehyde terahertz spectrum [5], we have used high-frequency and broadband tunable backward wave oscillators (BWOs) as radiation sources up to 1 THz. Supplied by the ISTOK Research and Production Company, these BWOs were digitally frequency and phase locked to a commercially available 78 - 118 GHz synthesizer from the Institute of Electronic Measurements, KVARZ, Nizhnii Novgorod, Russia. The measurement accuracy at 1 THz for unblended lines is estimated to be better than 10 kHz.

As detector we used a magnetically tuned hot electron InSb bolometer supplied by the Queen Mary College, London, UK.

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Tab. I. Observed Ground State Rotational Transitions of Trioxane in MHz.

K	$J = 31 \leftarrow 30$	O–C	$J = 58 \leftarrow 57$	O–C	$J = 85 \leftarrow 84$	O–C	$J = 90 \leftarrow 89$	O–C
3	326783.029	0.018						
4	326783.904	0.020	610654.636	–0.017	893170.938	–0.006		
5	326785.003	–0.003	610656.749	0.005	893173.979	–0.004		
6	326786.378	–0.001	610659.301	0.002	893177.680	–0.017	945297.752	–0.016
7	326787.998	–0.003	610662.316	–0.002	893182.086	–0.000	945302.380	–0.027
8	326789.867	–0.005	610665.797	–0.005	893187.147	–0.004	945307.761	0.000
9	326791.991	–0.003	610669.775	0.023	893192.892	–0.000	945313.813	–0.014
10	326794.362	–0.003	610674.221	0.055	893199.310	0.001	945320.614	0.004
11	326796.980	–0.006	610679.046	0.001	893206.411	0.010	945328.046	–0.058
12	326799.851	–0.005	610684.382	–0.006	893214.166	–0.002	945336.299	–0.015
13	326802.972	–0.005	610690.198	0.000	893222.598	–0.015	945345.231	–0.007
14	326806.343	–0.004	610696.483	0.012	893231.714	–0.019	945354.873	–0.004
15	326809.964	–0.003	610703.213	0.002	893241.532	0.002	945365.214	–0.017
16	326813.833	–0.004	610710.411	–0.003	893251.982	–0.020	945376.296	–0.003
17	326817.955	–0.002	610718.074	–0.010	893263.152	–0.000	945388.051	–0.032
18	326822.324	–0.003	610726.251	0.030	893274.977	–0.002	945400.584	0.001
19	326826.956	0.008	610734.817	–0.005	893287.597*	0.114	945413.795	–0.002
20	326831.814	–0.004	610743.883	–0.006	893300.666	0.002	945427.640	–0.057
21	326836.935	–0.004	610753.407	–0.015	893314.526	0.003	945442.369	–0.005
22	326842.307	–0.004	610763.420	–0.002	893329.072	0.013	945457.734	–0.003
23	326847.932	–0.001	610773.886	–0.002	893344.265	–0.007	945473.829	0.012
24	326853.803	–0.002	610784.821	0.000	893360.059*	–0.105	945490.647	0.034
25	326859.928	–0.001	610796.213	–0.006	893376.757	0.022	945508.112	–0.013
26	326866.303	–0.000	610808.083	–0.002	893393.987	0.002	945526.348	–0.007
27	326872.925	–0.003	610820.407	–0.011	893411.881	–0.031	945545.317	0.013
28	326879.800	–0.004	610833.218	–0.001	893430.517	–0.003	945564.972	0.002
29	326886.928	–0.003	610846.488	0.001	893449.775	–0.032	945585.357	0.003
30	326894.307	–0.002	610860.220	–0.002	893469.777	0.002	945606.442	–0.014
31			610874.415	–0.011	893490.214*	–0.208	945628.271	–0.007
32			610889.100	0.002	893511.751	0.000	945650.218*	–0.601
33			610904.238	0.000	893533.734	–0.025	945674.097	0.017
34			610919.433*	–0.413	893556.451	0.000	945698.069	0.008
35			610935.922	–0.002	893579.800	–0.022	945722.766	0.003
36			610952.476	0.004	893603.870	–0.006	945748.207	0.022
37			610969.484	–0.003	893628.627	0.013	945774.337	0.009
38			610986.976	0.002	893654.054	0.021	945801.191	–0.002
39			611004.924	–0.005	893680.170	0.034	945828.798	0.017
40			611023.356	0.000	893706.910	–0.011	945857.105	0.014
41			611042.247	–0.005	893734.292*	–0.100	945886.143	0.010
42			611061.615	–0.005	893762.549	0.000	945915.908	0.022
43			611081.459	–0.001	893791.386	–0.002	945946.361	–0.006
44			611101.764	–0.006	893821.010	0.055	945977.591	0.029
45			611122.549	–0.004	893851.130	0.002	946009.507	0.009
46			611143.805	–0.003	893882.018	–0.007	946042.156	0.002
47			611165.539	0.003	893913.616	0.004	946075.512	–0.024
48			611187.737	0.001	893945.884	–0.001	946109.651	0.005
49			611210.407	–0.002	893978.854	0.007	946144.507	0.025
50			611233.560	0.003	894012.493	–0.003	946180.063	0.017
51			611257.163	–0.015	894046.835	–0.001	946216.348	0.009
52			611281.278	0.004	894081.862	–0.003	946253.352	–0.007
53			611305.850	0.005	894117.580	–0.004	946291.113	0.002
54			611330.902	0.011	894153.987	–0.008	946329.604	0.011
55			611356.422	0.010	894191.092	–0.005	946368.781	–0.023
56			611382.424	0.014	894228.883	–0.008	946408.754	0.005
57			611408.898	0.011	894267.371	–0.007	946449.426	0.001
58					894306.548	–0.010	946490.238*	–0.595
59					894346.423	–0.009	946533.001	0.024
60					894386.997	–0.004	946575.864	0.010
61					894428.254	–0.012	946619.468	0.003
62					894470.217	–0.009	946663.799	–0.013
63					894512.876	–0.007	946708.887	–0.009
64					894556.234	–0.004	946754.792	0.074
65					894600.277	–0.013	946801.249	–0.026
66					894645.038	–0.004	946848.557	–0.016
67					894690.275*	–0.218	946896.607	–0.003
68					894736.639	–0.006	946945.391	0.003
69					894783.490	–0.007	946994.900	–0.005
70					894831.047	–0.005	947045.162	–0.003
71					894879.307	–0.002	947096.167	–0.000
72					894928.267	–0.002	947147.896	–0.019
73					894977.934	–0.000	947200.391	–0.013
74					895028.301	–0.003	947253.629	–0.010
75					895079.397	0.017	947307.615	–0.006
76					895131.169	0.007		
77					895183.677	0.025		

* are not weighted in the fit

Table 2. Molecular Constants for the Vibrational Ground State of Trioxane (The values in parentheses are the standard deviations in units of the last digit).

B (MHz)	5273.257180(33)
D_{JK} (kHz)	–2.016295(17)
D_J (kHz)	1.3438797(80)
H_{KJ} (Hz)	0.0027408(34)
H_{JK} (Hz)	–0.0020978(15)
H_J (Hz)	0.00049061(55)

Spectra

Symmetric Species

As a rather heavy oblate symmetric top with a relatively large dipole moment of 2.07 D, trioxane displays fairly strong R-branch transitions, which are spaced at nearly regular frequency intervalls of ~ $2B = 10.5$ GHz. The lines of different K for the same J transition are separated by centrifugal distortion, i. e. by the effect of D_{JK}, H_{JK} and H_{KJ}. For an oblate symmetric top this K-structure can be observed up to very high K values ($J \geq K$). In the case of the $J = 84 \leftarrow 85$ transition, we have observed the entire K-structure up to the $K = 77$ transition. The rotational frequencies of the R-branch transitions including sextic centrifugal distortion terms can be written

$$\begin{aligned}\nu_{J+1\leftarrow J} &= \frac{E_{J+1,K} - E_{J,K}}{h} \\ &= 2B(J+1) - 4D_J(J+1)^3 \\ &\quad - 2D_{JK}(J+1)K^{2} \\ &\quad + H_J(J+1)^3[(J+2)^3 - J^3] \\ &\quad + 4H_{JK}(J+1)^3K^{2} + 2H_{KJ}(J+1)K^{4}.\end{aligned}$$

The newly observed lines for the ground state of the main isotopomer of trioxane are listed in Table 1. A total of 4 new R-branch transitions were measured, which together with the K-structure lines amounts to a total of 220 lines. These new data were fitted in a least squares analysis together with the previously measured lines [2]. It is interesting to note that in the fitting procedure no higher than sextic terms are required, a manifestation that the structure of trioxane is fairly rigid. The newly determined constants (Table 2) agree well with those of Gadhi et al. [2], but are more accurate, particularly the sextic constants.

The first few K-lines at the band head of each J transition are blended due to Doppler broadening and

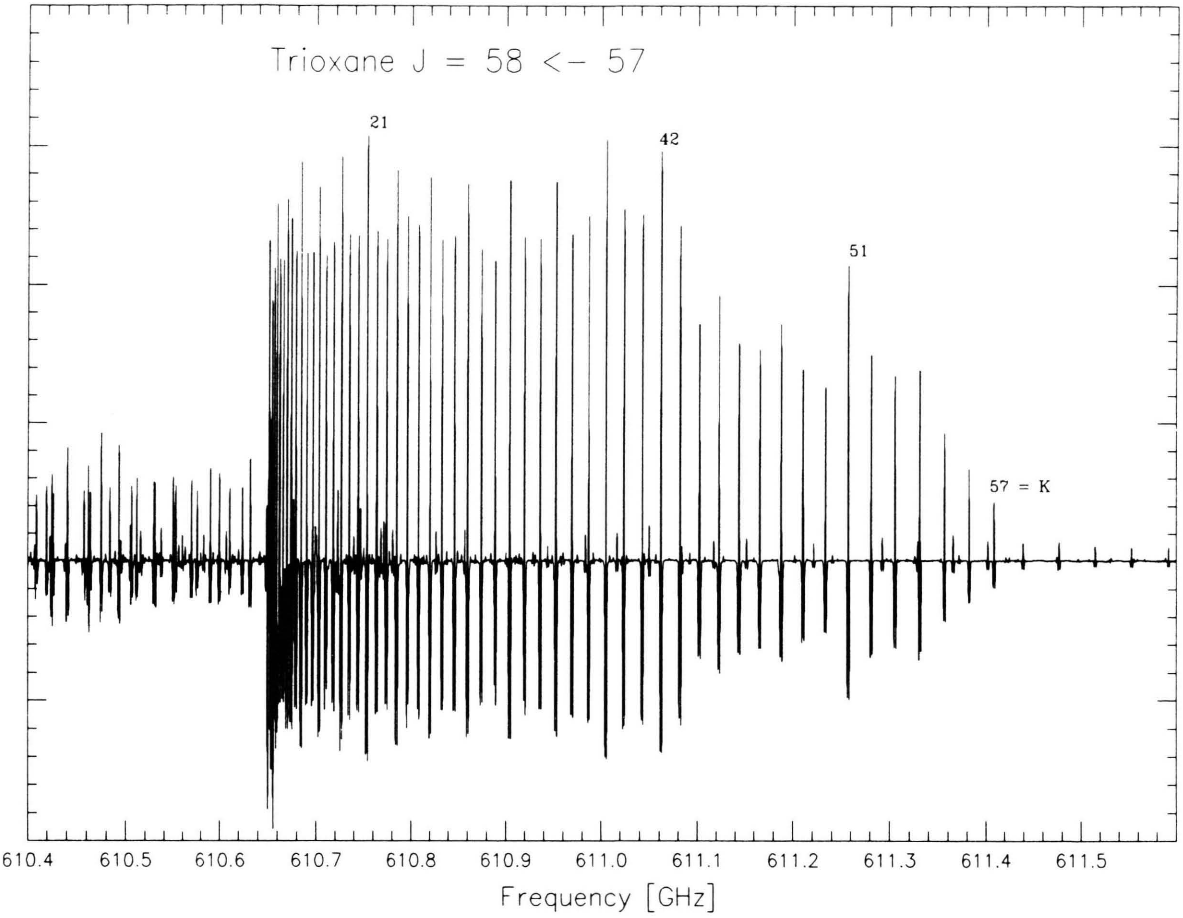

Fig. 1. Complete *K*-structure of the $J = 58 \leftarrow 57$ transition at 611 GHz. The spectrum was recorded in the second derivative form using source frequency modulation.

can not be resolved by the spectrometer when operated in the Doppler limited mode, as is seen in Fig. 1 for the $J = 58 \leftarrow 57$ transition. This blending is increasingly true for higher *J*-transitions, as can be seen in the case of the $J = 85 \leftarrow 84$ transition (Fig. 2 a,b) and the $J = 90 \leftarrow 89$ transition (Figure 3). For the assignment of the individual *K* lines, the intensity alternation due to the nuclear spin statistics is of importance also for the assignment process. In the case of trioxane all *K* lines with a multiple of 3, i. e. $K = 3n$, carry the nuclear spin weight 48, whereas all lines with $K \neq 3$ have the weight 40, where n is not 0. Thus all lines divisible by 3 are by a factor 1.2 stronger in intensity than the other *K* lines. This fact is clearly visible in all displayed spectra (Figs. 1, 2a, 2b and 3). For the non-symmetric isotopomers of trioxane, i. e. the ^{13}C and ^{18}O the intensity alternation is lost as seen in Figure 4.

Isotopomers $(H_2CO)_2(H_2{}^{13}CO)$ and $(H_2CO)_2(H_2C^{18}O)$

By substitution of one ^{12}C by ^{13}C or one ^{16}O by ^{18}O, the corresponding isotopomers of trioxane are only slightly asymmetric, with values for Ray's asymmetry parameter $\kappa = 0.919$ for $(H_2CO)_2(H_2{}^{13}CO)$ and $\kappa = 0.843$ for $(H_2CO)_2(H_2C^{18}O)$ (see Table 3). Thus the asymmetry-splitting for both isotopomers is fairly small, and only a few low K_c asymmetry doublets could be resolved. Since for both isotopomers the direction of the dipole moment is hardly changed in comparison to its direction for the main isotopomer,

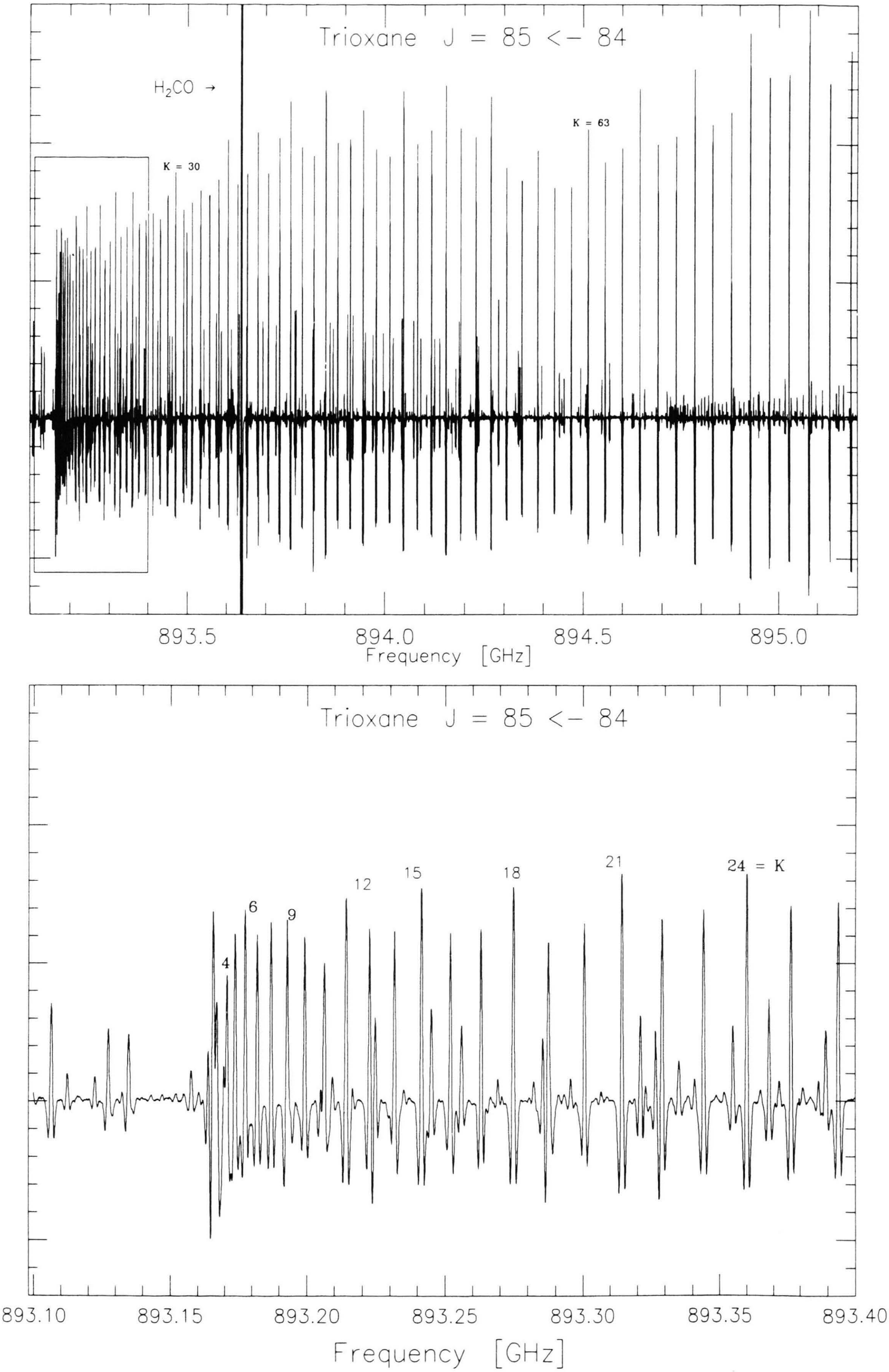

Fig. 2. a) Part of the *K*-structure of the transition $J = 85 \leftarrow 84$ from $K = 0$ up to $K = 77$ at 894 GHz. Also shown is a strong absorption line of formaldehyde in the excited vibrational state $v_2=1$.
b) Magnification of the marked section in Figure 2a. The beginning of the *K*-structure of the transition $J = 85 \leftarrow 84$ is shown. The intensity alternation due to nuclear spin statistics for lines with $K = 3n$ is clearly noticeable.

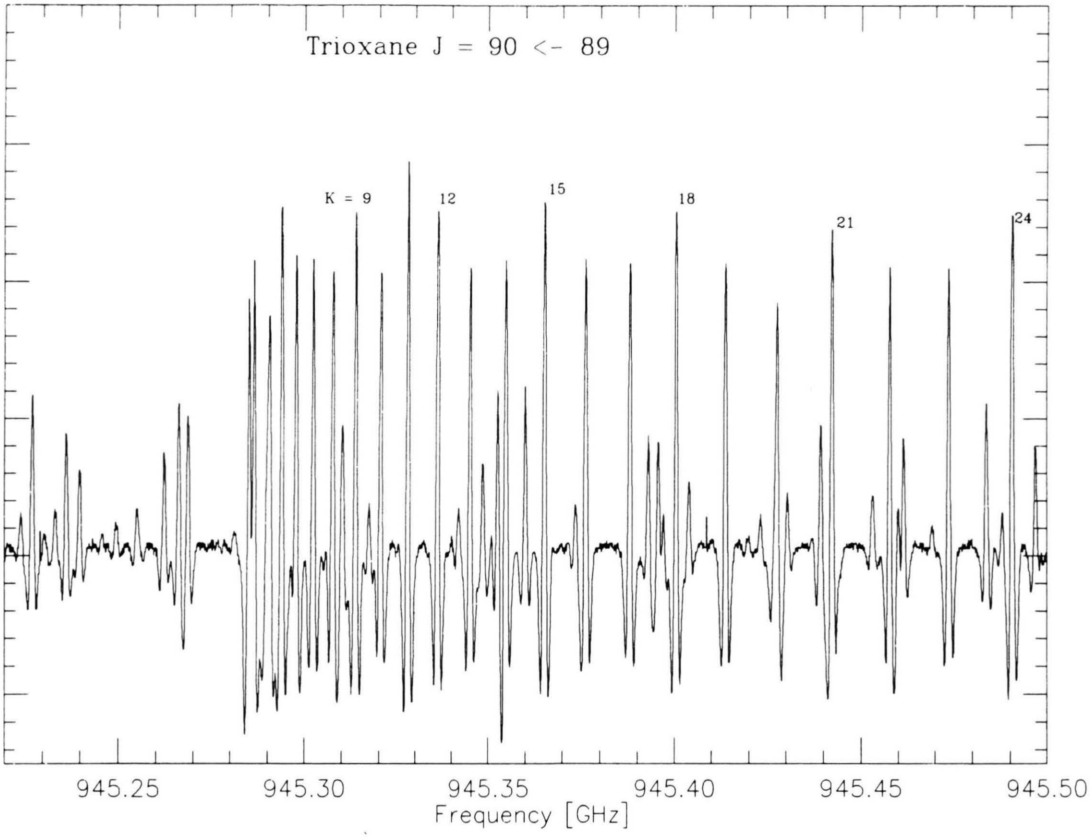

Fig. 3. The beginning of the K-structure of the highest recorded frequency transition $J = 90 \leftarrow 89$ at 945 GHz. Lines with $K = 3n$ are again easy to recognize.

Table 3. Molecular Constants for the Vibrational Ground State of Isotopic Species of Trioxane (The values in parentheses are the standard deviations in units of the last digit).

	$(H_2CO)_2(H_2{}^{13}CO)$	$(H_2CO)_2(H_2C^{18}O)$
A (MHz)	5271 .1051(21)	5267 .9951(14)
B (MHz)	5176 .4084(18)	5080 .4556(13)
C (MHz)	2904 .24(11)	2875 .401(35)
D_J (kHz)	1 .318132(30)	1 .29427(39)
D_{JK} (kHz)	-1 .98347(30)	-1 .94472(39)
d_1 (Hz)	-7 .98(12)	
d_2 (Hz)	-2 .425(94)	
H_{JK} (Hz)	-0 .001927(47)	
H_{KJ} (Hz)	0 .002779(29)	
κ	0 .9199813(40)	0 .8432333(25)

only c-type R-branch transitions with $\Delta K_c = 0$ and $\Delta K_a = \pm 1$ were observed. The appropriate new measurements of $(H_2CO)_2(H_2{}^{13}CO)$ between 313 and 615 GHz are available from the authors upon request. The only substantial difference to the spectra of the main isotopomer is the loss of the symmetry axis, and consequently the disappearance of nuclear spin weights noted as line intensity effects.

A portion of the K_c-structure of the transition $J = 59 \leftarrow 58$ is shown in Figure 4. In the region between 310 and 320 GHz, the K_c-structures of the transitions with lower $J = 29$ and 30 were also observed for $(H_2CO)_2(H_2C^{18}O)$. All observed lines were fitted by an S-reduced Hamiltonian in a least squares analysis together with all data available in the literature. The determined constants agree very well with those of Colmont et. al. [6], but are more accurate. For the first time the sextic constants of centrifugal distortion H_{JK} and H_{KJ}, as well as the parameters d_1 and d_2 are determined here for $(H_2CO)_2(H_2{}^{13}CO)$.

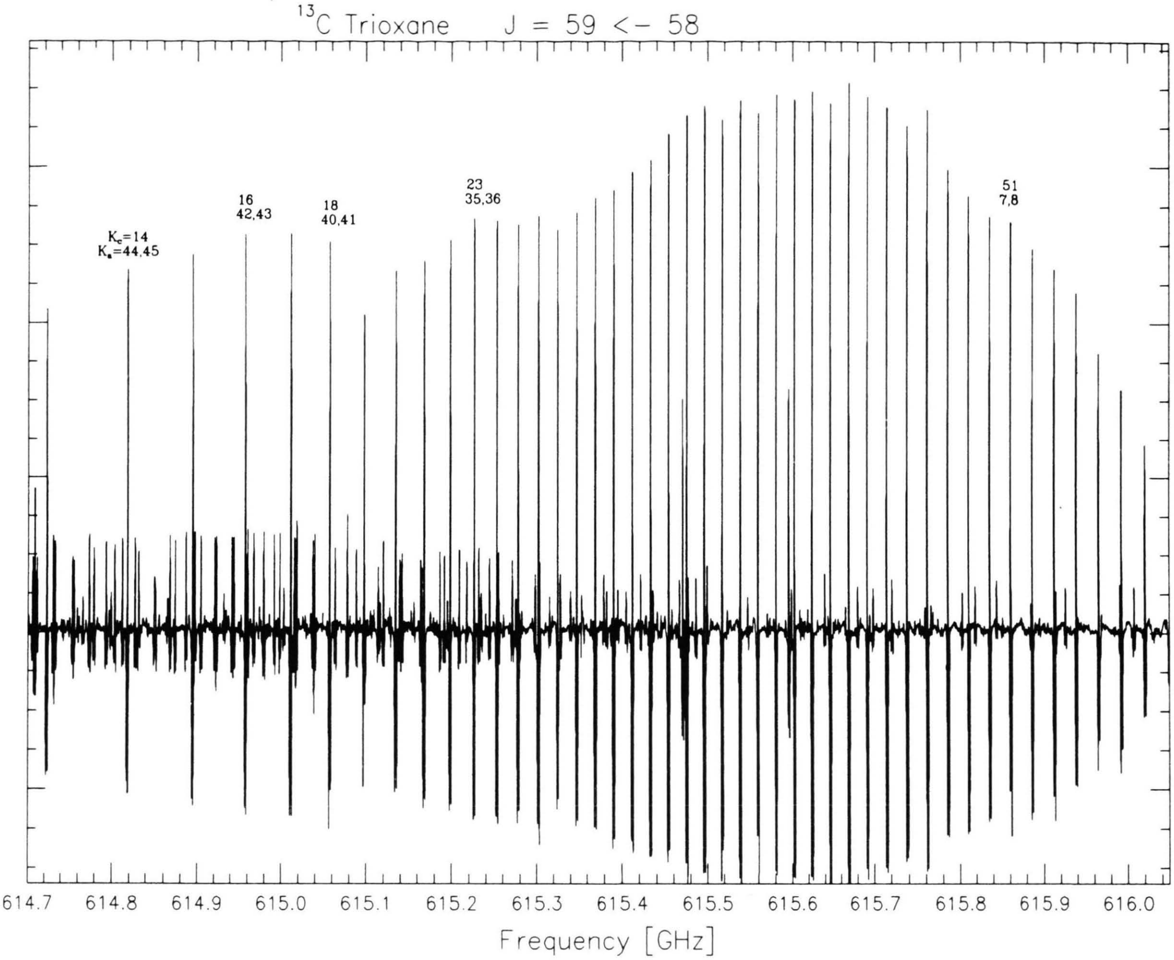

Fig. 4. The rotational spectrum of $(H_2CO)_2(H_2{}^{13}CO)$ at 615 GHz. Some measured R-branch lines of the transitions $J = 59 \leftarrow 58$ are shown, commencing with $K_c = 13$.

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