

# Improved Version of a Microwave Fourier Transform Spectrometer in the Frequency Band from 26 to 40 GHz

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We report the design and performance of an improved version of a microwave Fourier transform spectrometer in the frequency region between 26 and 40 GHz for the investigation of rotational spectra. The performance is illustrated by rotational transitions of allene- $d_4$  and isotopomers of carbonyl sulfide in natural abundance. The high sensitivity of the spectrometer allows the measurement of very weak lines in only a few minutes.

## Introduction

We improved the sensitivity of our recently described [1] microwave Fourier transform (MWFT) spectrometer substantially. This improvement was achieved by replacing the sample cell of square cross section by a circular waveguide and using the  $H_{01}(TE_{01})$  mode in this new cell.

## Experimental Set Up

The sample cell (30) in Fig. 2 of [1] was replaced by a circular waveguide with 0.797" (2.02 cm) inner diameter and 12 m length, as shown in Figure 1. The tapers (29) and (31) in Fig. 2 of [1] were replaced by Marie transducers, which transform the  $H_{10}(TE_{10})$  mode of a rectangular waveguide into the  $H_{01}(TE_{01})$  mode of circular waveguide [2]. In addition, a mode filter was inserted in front of the detection system.

The advantage of this set up is the lower wall attenuation in the circular waveguide and the larger sample volume. The square waveguide of 3.2 m length has an attenuation of 6.6 dB with its tapers, the circular waveguide of 12 m length has an attenuation of 2 dB maximum with its transducers and filter. The sample volume increases from 205 cm<sup>3</sup> to 3384 cm<sup>3</sup>.

The disadvantage of the circular waveguide is the possible occurrence of other modes (see Table 1). Our mode filter attenuates the unwanted  $H_{11}(TE_{11})$  mode by 15 dB. We observed no sharp resonances due to those modes. In some frequency regions, decaying

signals from reflected pulses were observed. They increase when the mode filter is omitted. We conclude that the mode filtering should be improved to allow a shorter delay between the end of the polarizing pulse and the begin of the measuring period. The connection to the vacuum and sample filling system is made by a sequence of four slits, 0.6 mm wide and 10 mm long, along the circumference of the circular waveguide. On both sides of the cell 6 sequences of slits are positioned with distances varying from 4 to 8 mm. They also act as a mode filter.

## Experimental Tests and Results

In Fig. 2 we present the recording of the  $J_K \leftarrow J'_K$ ,  $= 2_0 \leftarrow 1_0$  transition of allene- $d_4$  in the vibrational

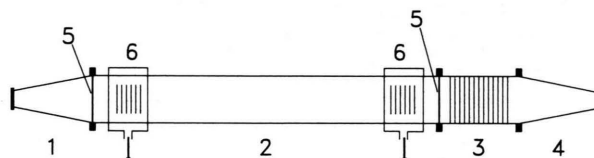


Fig. 1. Set up of the circular waveguide sample cell. This cell replaces parts 29, 30, 31 of Fig. 2 in [1].

- 1 Marie transducer from  $H_{10}(TE_{10})$  rectangular waveguide mode to  $H_{01}(TE_{01})$  circular waveguide mode, Gamma Corporation MT 28-800 M, mode purity 20 dB, insertion loss 0.13 dB max., VSWR 1:1.3 max.
- 2 Sample cell, brass, Evered and Co., Type C 104, diameter 0.797" (2.02 cm), length 12 m, volume 3384 cm<sup>3</sup>.
- 3 Mode filter, Gamma Corporation 28-800,  $H_{11}(TE_{11})$  mode suppression 15 dB, insertion loss 0.2 dB max., VSWR 1:1.2 max.
- 4 see 1.
- 5 Vacuum tight windows.
- 6 Connection to vacuum and sample filling system.

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Table 1. Cut off frequencies  $\nu_c$  of different propagation modes in circular wave guides derived from [2], Table 1.1. Transmission is possible for frequencies  $\nu > \nu_c$ .  $D$ : inner diameter of the wave guide. The mode designations translate as:  $TE_{mn} \cong H_{mn}$ ,  $TM_{mn} \cong E_{mn}$ .

Mode	$H_{11}$	$E_{01}$	$H_{21}$	$E_{11}$ $H_{01}$	$H_{31}$	$E_{21}$	$H_{41}$	$H_{12}$	$E_{02}$	$E_{31}$	$H_{51}$	$H_{22}$	$E_{12}$ $H_{02}$
$\nu_c D \cdot 10^{10}$ [cm s <sup>-1</sup> ]	1.757	2.296	2.913	3.656	4.008	4.899	5.073	5.090	5.269	6.093	6.118	6.392	6.692
$\nu_c$ [GHz] for $D = 2$ cm	8.786	11.478	14.567	18.280	20.040	24.493	25.363	25.449	26.344	30.467	30.591	31.961	33.459

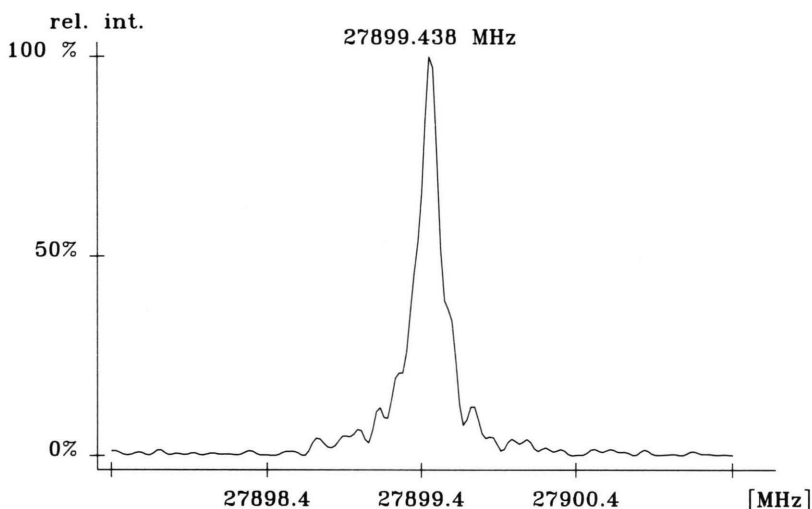


Fig. 2. A 4 MHz section out of a 50 MHz scan of the rotational power spectrum of the  $J_K \leftarrow J'_K$   $= 2_0 \leftarrow 1_0$  transition of allene-d<sub>4</sub> in the vibrational state  $\nu_{11} = 1$ . Sample interval 10 ns\*, 1024 data points supplemented with 3072 zeros prior to Fourier transformation\*, temperature 21 °C\*, pressure 7 mTorr (0.9 Pa), polarization frequency 27 899.4 MHz, 1600 k averaging cycles (22 s measuring time).

\* these conditions also apply to Figs. 3, 4, and 5.

state  $\nu_{11} = 1$ . It was recorded with 1600 k averaging cycles. We measured the same transition with our previous set up (Fig. 4 of [1]) and needed 83 200 k averaging cycles to reach a comparable signal to noise ratio\*. In Fig. 3 we give two transitions of carbonylsulfide, the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{12}\text{C}^{34}\text{S}$  in the vibrational state  $\nu_1 \nu_2^l \nu_3 = 1\ 0^0\ 0$  and the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{13}\text{C}^{34}\text{S}$  in the vibrational ground state. Both isotopes are measured in natural abundance. Kisiel and Millen [3] calculated the absorption coefficients of these transitions as  $\alpha = 1.9 \cdot 10^{-10} \text{ cm}^{-1}$  and  $\alpha = 1.3 \cdot 10^{-10} \text{ cm}^{-1}$ . We estimate the sensitivity of the spectrometer from the signal to noise ratio  $S/N \approx 20/1$  of these transitions to be  $\alpha \approx 5 \cdot 10^{-11} \text{ cm}^{-1}$ , that is ten times the sensitivity we achieved with our preceding set up [1]. It should be mentioned that coherent perturbations (P in Fig. 3) caused by averager switching frequencies contribute to the limitation of sensitivity. There are in addition many unassigned

lines in the spectrum (see for example Figure 3). We do not report weaker transitions here because the observed lines are more than 100 kHz off the predictions, thus the assignments are not sure. The spectra of the isotopomers of carbonylsulfide should be studied with higher precision.

In Fig. 4 we present the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{12}\text{C}^{34}\text{S}$  in the vibrational state  $\nu_1 \nu_2^l \nu_3 = 0\ 1^1\ 0$  with an absorption coefficient  $\alpha = 8.3 \cdot 10^{-10} \text{ cm}^{-1}$ . We needed 225 seconds measuring time to reach a signal to noise ratio  $S/N \approx 125/1$ . Kisiel and Millen needed 2040 seconds to record the same transition with a signal to noise ratio  $S/N \approx 2/1$  using a Hewlett Packard MW spectrometer. In Fig. 5 we give a comparison of the sensitivity of our new spectrometer and of the previous spectrometer described in [1]. In the upper trace we show the transition  $J \leftarrow J' = 3 \leftarrow 2$  of  $^{18}\text{O}^{12}\text{C}^{32}\text{S}$  in the vibrational state  $\nu_1 \nu_2^l \nu_3 = 0\ 2^0\ 0$  recorded with our previous set up at a temperature of  $-50\ ^\circ\text{C}$  in 48 000 k averaging cycles. In the lower trace we show the same transition recorded with our

\* *Erratum*: All numbers of averaging cycles in [1] must be multiplied by 32, e.g. 2600 k must be replaced by  $2600 \cdot 32$  k.

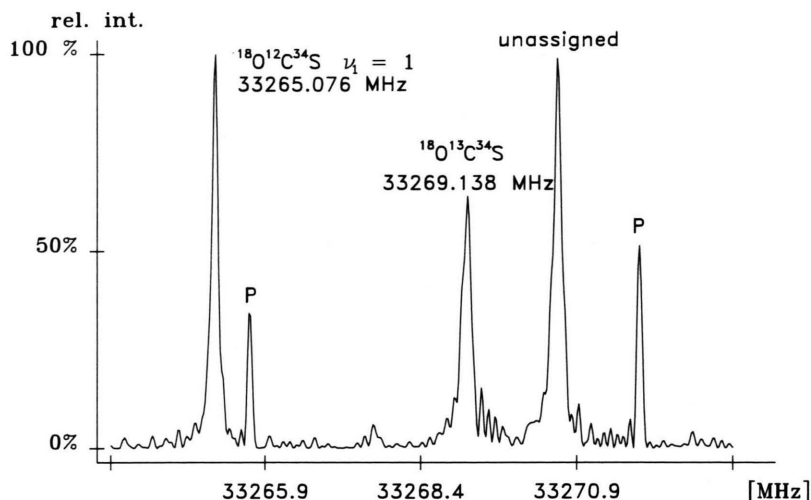


Fig. 3. A 10 MHz section out of a 50 MHz scan of the rotational power spectrum of the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{12}\text{C}^{34}\text{S}$  in the vibrational state  $v_1 v_2 v_3 = 1 0^0 0$  and the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{13}\text{C}^{34}\text{S}$  in the vibrational ground state. Absorption coefficients are  $\alpha = 1.9 \cdot 10^{-10} \text{ cm}^{-1}$  and  $\alpha = 1.3 \cdot 10^{-10} \text{ cm}^{-1}$  [3]. Pressure 5 mTorr (0.65 Pa), polarization frequency 33 269.2 MHz, 64 000 k averaging cycles (854 s measuring time). P: Coherent perturbations caused by averager switching frequencies.

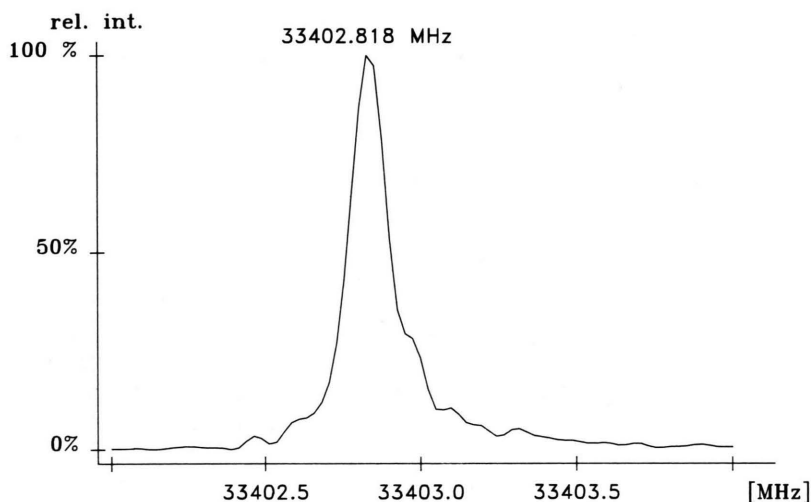


Fig. 4. A 2 MHz section out of a 50 MHz scan of the rotational power spectrum of the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{12}\text{C}^{34}\text{S}$  in the vibrational state  $v_1 v_2 v_3 = 0 1^1 0$ . The absorption coefficient is  $\alpha = 8.3 \cdot 10^{-10} \text{ cm}^{-1}$  [3]. Pressure 5 mTorr (0.65 Pa), polarization frequency 33 403 MHz, 16 864 k averaging cycles (225 s measuring time). Compare this with Fig. 1 of [3].

new set up at room temperature in 512 k averaging cycles. The signal to noise ratio is improved by a factor 3 and no coherent perturbation is visible as the molecular signal is stronger. We conclude that we achieve better results even when using only 1/100th of the measuring time necessary with our previous set up [1].

A further improvement may be possible by extending the cell length and better mode filtering. Both possibilities are investigated presently.

We noticed that the minimum achievable line width has not decreased compared to [1]. We remeasured the  $4_{04} \leftarrow 3_{13}$  transition of sulfur dioxide and found the same line width as given in Fig. 6 of [1].

First applications of the spectrometer were the investigation of hyperfine structures in vibrational excited states of  $^{16}\text{O}^{12}\text{C}^{33}\text{S}$  and in 1-bromo-2,2-difluoroethylene [4].

Future applications could include the fast measurement of nearly unpolar molecules.

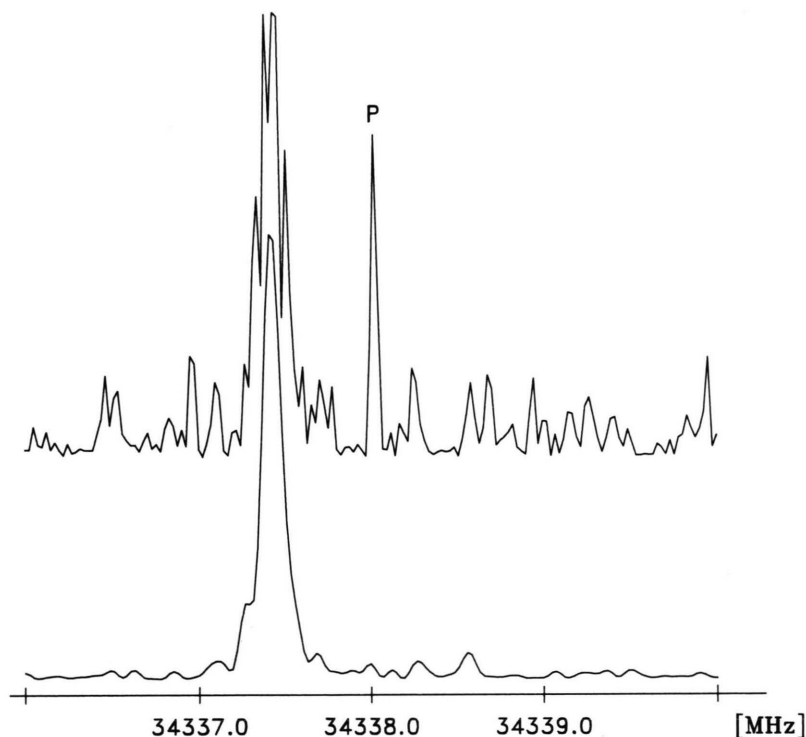


Fig. 5. A 4 MHz section out of a 50 MHz scan of the rotational power spectrum of the  $J \leftarrow J' = 3 \leftarrow 2$  transition of  $^{18}\text{O}^{12}\text{C}^{32}\text{S}$  in the vibrational state  $v_1 v_2 v_3 = 0 2^0 0$ . The absorption coefficient is  $\alpha = 7.3 \cdot 10^{-10} \text{ cm}^{-1}$  at  $-50^\circ\text{C}$  and  $\alpha = 1.7 \cdot 10^{-9} \text{ cm}^{-1}$  at room temperature. Polarization frequency 34 338 MHz. *Upper trace*: Measurement with spectrometer of [1], 48 000 k averaging cycles (640 s measuring time), temperature  $-50^\circ\text{C}$ . P: Coherent perturbation. *Lower trace*: Measurement with present set up, 512 k averaging cycles (7 s measuring time), temperature  $21^\circ\text{C}$ .

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