Determination of Quadrupole and Spin-Rotation Coupling in the Rotational Spectrum of Carbonylsulfide-^{33}S and -^{17}O

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The quadrupole and spin rotation coupling constants are determined by analysis of the $J = 0 - 1$ and $J = 1 - 2$ transitions of OC^{33}S and ^{17}OCS in natural abundance. The data are compared with those obtained from molecular beam electric resonance and very recent pulsed beam microwave Fourier transform spectroscopy.

In the past several years we have contributed to the development of microwave Fourier transform (MWFT) spectroscopy [1 – 5] of static molecular gases in thermodynamic equilibrium as a spectroscopic tool with high resolution and sensitivity. For critical evaluation of its limits, it is necessary to compare results gained with static gas MWFT spectroscopy with those from spectroscopic methods with inherently higher resolution. We present a comparison with the hyperfine structure (hfs) of carbonylsulfide- ^{33}S, OC^{33}S, and carbonylsulfide- ^{17}O, ^{17}OCS. Reinartz and Dymanus [6] determined the nuclear quadrupole coupling constant eqQ and the spin rotation constant C_I with molecular beam electric resonance spectroscopy from the $J = 0 - 1$ transition in the $v_2 = 0$ and $v_2 = 1$ vibrational states. Very recently Lovas and Suenram [7] investigated both isotopic species with a pulsed beam MWFT spectrometer with 1% OCS in Argon. Their values for the $J = 0 - 1$ transitions are reproduced in Tables 1 and 2. We investigated the $J = 0 - 1$ and $1 - 2$ transitions. We measured the hfs of both isotopes in natural abundance (0.75% for ^{33}S and 0.04% for ^{17}O). The frequencies are given in Table 1. For ^{17}OCS the line frequencies were corrected with a line shape analysis [8]. Figure 1 provides a representative measurement. For OC ^{33}S it was not necessary because the triplet is widely split. For OC ^{33}S we succeeded to measure the $J = 2 - 3$ line with a new MWFT-spectrometer [9]. As the quality of the spectra is not yet comparable with those of lower frequency ranges, the components of the line were not included in the fit. The hfs was analysed according to [10, 11].

Table 1. Quadrupole hyperfine structure of rotational transitions of carbonylsulfide -^{33}S and -^{17}O. ν: measured frequencies [MHz], $\Delta \nu_{\mathrm{hfs}}$: splittings referred to the hypothetical unsplit line [MHz], $\delta = \Delta \nu_{\mathrm{hfs}} - \Delta \nu_{\mathrm{calc}}$, $\Delta \nu_{\mathrm{calc}}$: splittings calculated with the constants of Table 2. Components of $J = 2 - 3$ not included in the fit.

OC^{33}S $J - J'$	$F - F'$	ν	$\Delta \nu_{\mathrm{hfs}}$	δ	ν [7]
0 – 1	3/2 – 1/2	12017.105	7.279	0	12017.101(8)
	3/2 – 5/2	12011.285	1.458	0	12011.287(4)
	3/2 – 3/2	12004.002	– 5.824	0	12003.998(4)
1 – 2	3/2 – 1/2	24032.725	13.101	0	
	3/2 – 3/2	24025.448	5.824	0	
	3/2 – 5/2 5/2 – 7/2	24020.249	0.625	0 – 1	
	1/2 – 1/2	24019.625	0.001	3	
	5/2 – 5/2	24012.964	– 6.660	– 2	
	1/2 – 3/2	24012.345	– 7.279	0	
2 – 3	3/2 – 3/2	36035.162	5.796	– 23	
	5/2 – 5/2	36033.123	3.757	15	
	7/2 – 9/2 5/2 – 7/2	36029.712	0.346	– 2 – 1	
	1/2 – 3/2 3/2 – 5/2	36027.900	– 1.466	– 8	
	3/2 – 3/2	36022.448	– 6.918	– 8	
				19	
^{17}OCS					
0 – 1	5/2 – 3/2	11767.532	0.193	– 5	11767.531(6)
	5/2 – 7/2	11767.400	0.061	2	11767.402(6)
	5/2 – 5/2	11767.132	– 0.207	3	11767.135(4)
1 – 2	5/2 – 3/2	23534.976	0.329	6	
	5/2 – 5/2	23534.774	0.127	2	
	5/2 – 7/2 7/2 – 9/2	23534.678	0.031	– 16 10	
	3/2 – 3/2	23534.557	– 0.090	– 5	
	7/2 – 7/2	23534.427	– 0.220	2	
	3/2 – 5/2	23534.364	– 0.283	0	

Table 2. ^{33}S and ^{17}O quadrupole coupling eQq and spin rotation constant C_I of OC^{33}S and ^{17}OCS in the vibrational ground state. Standard error in units of the last digit in brackets. – not determined

	eQq [MHz]	C_I [kHz]	Ref.
OC^{33}S	– 29.1184(12)	0.87(5)	[6]
	– 29.11(4)	–	[7]
	– 29.122(3)	1.1(4)	this work
^{17}OCS	– 1.30(3)	–	[7]
	– 1.333(22)	– 3.3(13)	this work

From the data it is clearly seen that the beam electric resonance method is superior in precision. The data agree roughly in one standard error. Both MWFT methods appear equivalent in this application. Experience indicates that MWFT spectroscopy is applicable to a greater variety of molecules, especially to larger ones.

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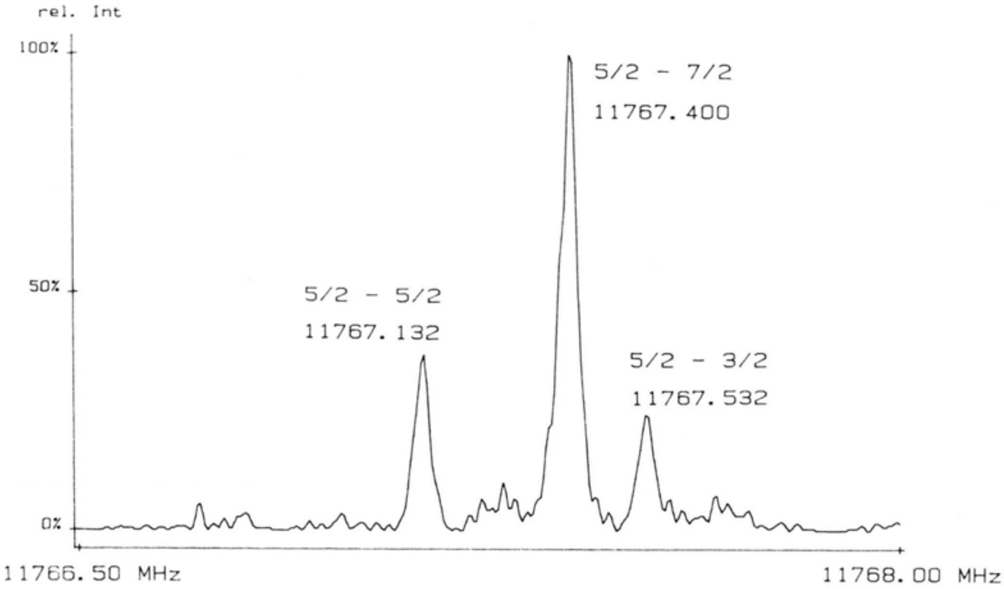

Fig. 1. Rotational transition $J = 1 - 0$ of carbonylsulfide- ^{17}O, ^{17}OCS, showing ^{17}O-hfs. Polarisation frequency 11768.000 MHz, temperature $-30\,°$C, pressure 1.9 mTorr (0.25 Pa), $4 \cdot 10^7$ averaging cylces, 1024 data points supplementend by 3072 zeros prior to Fourier transformation, sampling interval 50 ns.

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