The ^{33}S Nuclear Quadrupole Hyperfine Coupling in the Rotational Spectrum of ^{33}S Dimethylsulfoxide

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The rotational spectrum of the ^{33}S dimethylsulfoxide in natural isotopic abundance has been studied using molecular beam Fourier transform microwave spectroscopy. Rotational and quadrupole coupling constants could be extracted from the spectra. They were found to be $A = 7017.5456(16)$ MHz, $B = 6894.5117(17)$ MHz, $C = 4218.14115(84)$ MHz, $\chi_{aa} = -15.720(18)$ MHz, $\chi_{bb} = -17.045(23)$, and $\chi_{cc} = 32.765(25)$ MHz.

Introduction

First studies on dimethylsulfoxide, DMSO, were made by Dreizler et al. [1], [2]. They investigated the spectra of $(CH_3)_2SO$ and $(CD_3)_2SO$ by Stark modulation microwave spectroscopy and presented a centrifugal distortion analysis. In a further publication [3] r_0 and r_s structures of DMSO were derived from the spectra of seven isotopic species. Later, Typke [4], [5] improved the centrifugal distortion analysis. The last work on DMSO was published by Fliege et al. [6]. Higher resolution of Fourier transform microwave spectroscopy (FTMW) allowed to resolve the internal rotation splitting in the rotational transitions of the torsional ground state and to determine the internal rotation barrier V_3. In the course of our studies on ^{33}S nuclear quadrupole coupling we have become interested in the coupling constants of dimethylsulfoxide, as sulfur is bonded differently in comparison to the hitherto investigated molecules [7]. The sulfur is bonded to two carbon and one oxygen atom.

Experimental

A sample of DMSO (purity 99%) was obtained from Aldrich-Chemie, Steinheim. The spectra were recorded using a molecular beam MB-FTMW spectrometer [8] in the frequency range from 8 to 20 GHz. In order to increase sensitivity and resolution of the spectrometer, the molecular beam was pulsed through one of the mirrors along the resonator axis [9].

The free induction decay was downconverted to an intermediate frequency ν_{IF} of 10 MHz. Because of the low vapour pressure of DMSO (0.6 hPa at 20 °C) it was necessary to fill the substance into a small container upstream the nozzle. The argon stream was lead over the reservoir. The backing pressure was 50 kPa. So the concentration of DMSO can be assumed to be 0.12%. The natural abundance of ^{33}S is 0.76%, so the concentration of ^{33}S DMSO amounts to approximately 9 ppm. The time domain signals were recorded sampling 16 k data points at intervalls of 10 ns. The frequencies were calculated using a Fourier transformation. Up to 30 k averaging cycles, taking approximately 30 minutes, were necessary to get a sufficient signal-to-noise ratio for ^{33}S dimethylsulfoxide. We measured the spectra up to the angular momentum quantum number $J = 2$.

Spectral Analysis

We started our investigation by searching for the $J_{K-,K+} = 1_{1,1} - 0_{0,0}$ and $2_{0,2} - 1_{1,1}$ transitions using the automatic scan mode of the MB-FTMW spectrometer. In Fig. 1 a scan over the $J_{K-,K+} = 1_{1,1} - 0_{0,0}$ transition is given. Because of the large intensity differences between the ^{32}S, ^{34}S, and ^{33}S isotopomers the intensity scale is logarithmic. We found all three hyperfine (hfs) components of the transition. For this scan we averaged 2048 cycles for each frequency point to get a sufficient signal to noise ratio. High resolution is not necessary in the scan mode, so we recorded only 2 k data points at a sample intervall of 10 ns. The frequency step was 1 MHz. For the whole scan we needed 136 minutes.

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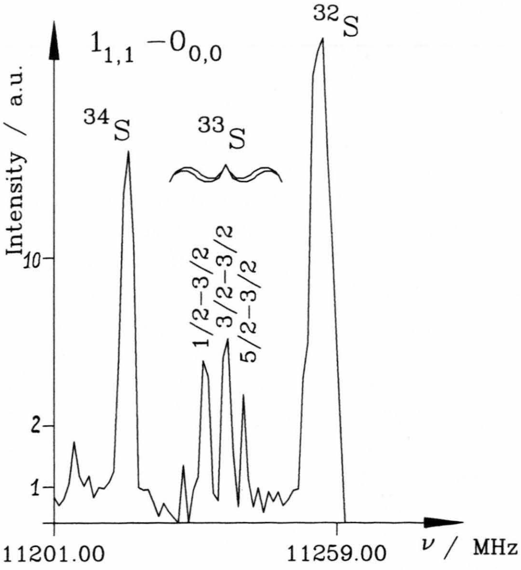

Fig. 1. Scan showing the $J_{K-,K+} = 1_{1,1} - 0_{0,0}$ transitions of ^{32}S, ^{34}S, and ^{33}S isotopomers of dimethylsulfoxide. The intensity in arbitrary units is drawn in logarithmic scale. Experimental conditions: frequency step 1 MHz, 2048 averaged cycles at each frequency, 2 k data points at a sample interval of 10 ns, polarisation time 0.5 μs, polarisation power 0.3 mW, time needed for the scan 136 min.

Then we remeasured both ^{33}S transitions in the high resolution mode of the spectrometer. A first analysis of the hyperfine structure of both lead to preliminary ^{33}S quadrupole coupling constants which allowed a better prediction for other transitions.

This enabled us to find finally the 18 hyperfine components in five rotational transitions given in Table 1. Measurements of transitions with a higher J were not feasible because, due to the minor occupation numbers in consequence of the low rotational temperature in the supersonic molecular beam, the low concentration of the ^{33}S isotopomer, and the splitting into several hfs components, there are not enough spectroscopically active molecules to get a sufficient signal. For analysis the program HFS [10], [11] was used, diagonalizing the Hamiltonian matrix containing rotation, nuclear quadrupole interaction, and centrifugal distortion effects according to the reduction of van Eijck [12]. Since only five rotational transitions were measured, the distortion constants had to be fixed to the values of the ^{32}S isotopomer derived by Fliege et al. [13]. The resulting rotational, centrifugal distortion, and quadrupole coupling constants are given in Table 2.

Table 1. Measured transitions of ^{33}S dimethylsulfoxide. ν_{obs} denotes the observed frequency, ν_{calc} the calculated frequency and $\Delta\nu_{obs} - \nu_{calc}$.

$J, K-, K+$	$J', K'-, K'+$	F	F'	ν_{obs}/MHz	$\Delta\nu$/kHz
1,1,1	0,0,0	5/2	3/2	11236.5272	−10.1
		3/2	3/2	11232.2589	−7.9
		1/2	3/2	11239.9269	−1.1
2,0,2	1,1,1	7/2	5/2	19546.1006	−3.7
		3/2	1/2	19540.3528	−6.6
		5/2	3/2	19542.1860	−2.7
		3/2	3/2	19548.0189	−9.9
		5/2	5/2	19537.9155	−11.6
2,1,2	1,0,1	7/2	5/2	19673.3948	15.4
		5/2	3/2	19669.1285	9.6
		3/2	1/2	19667.9077	12.8
		3/2	3/2	19674.9751	6.3
2,1,1	2,0,2	7/2	7/2	8029.7369	7.0
		5/2	5/2	8042.1723	2.7
		3/2	3/2	8033.2889	2.9
2,2,1	2,1,2	7/2	7/2	8394.8561	−1.2
		5/2	5/2	8406.9764	−3.0
		3/2	3/2	8398.3175	−5.2

Table 2. Rotational, van Eijck's centrifugal distortion (I^r representation), and quadrupole coupling constants of ^{33}S dimethylsulfoxide. * denotes derived constants, $^+$ parameters kept fixed in the fit. The standard deviation σ of the fit is 9.1 kHz.

Rotational constants:		^{33}S quadrupole coupling constants:	
A'/MHz	7017.5456(16)		
B'/MHz	6894.5117(17)	χ_{aa}/MHz	−15.720(18)
C'/MHz	4218.14115(84)	$\chi_{bb} - \chi_{cc}$/MHz	−49.811(28)
		χ_{bb}/MHz	−17.045(23)*
van Eijck's centrifugal distortion constants:		χ_{cc}/MHz	32.765(25)*
D'_J/kHz	5.93$^+$		
D'_{JK}/kHz	−8.912$^+$		
D'_K/kHz	3.86$^+$		
δ'_J/kHz	−0.1634$^+$		
R'_6/kHz	−0.272$^+$		

Discussion

We were able to determine the rotational and quadrupole coupling constants of DMSO. Due to the b, c mirror plane, the off-diagonal elements χ_{ab} and χ_{ac} of the quadrupole coupling tensor are zero. Since there is no near degeneracy between rotational levels of low J which are connected by matrix elements dependent on the in plane off-diagonal element χ_{bc} of the quadrupole coupling tensor, only diagonal elements could be extracted from the spectra. So the principal axes of the ^{33}S nuclear coupling tensor remain unknown.

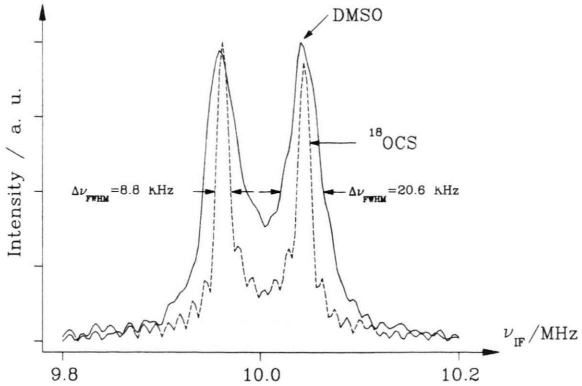

Fig. 2. Linewidth for dimethylsulfoxide. The amplitude spectra of the $J_{K_-,K_+}=2_{2,1}-1_{1,0}$, transition of ^{32}S DMSO and the $J-J'=2-1$, transition of ^{18}O carbonylsulfide are drawn on an intermediate frequency ν_{IF} scale of the detection system. ^{18}OCS illustrates the normal line width of our spectrometer. The linewidth of DMSO is more than two times larger due to unresolved internal rotation splitting and a possible spin-rotation coupling. The Doppler doubletts are almost completely resolved. Experimental conditions: 8 k data points at sample intervals of 10 ns, 32 k Fourier transformation, polarisation frequencies $\nu_{DMSO}=25\,328.38$ MHz and $\nu_{OCS}=22\,819.39$ MHz, polarisation power $P_{DMSO}=0.3$ mW and $P_{OCS}=10$ mW, polarisation time 0.5 μs.

It should be noted that the standard deviation of the fit, $\sigma=9.1$ kHz, is larger than usual [14], [15]. This is reasonable because the internal rotation splitting amounts to only a few kHz and could not be resolved. This leads, together with the spin-rotation coupling of the six hydrogen nuclei, to broad lines. The line width is nearly 20 kHz. In Fig. 2 we present the $J_{K_-,K_+}-J'_{K'_-,K'_+}=1_{1,1}-0_{0,0}$, $F-F'=3/2\text{-}3/2$ of DMSO and the $J-J'=2\text{-}1$ of ^{18}O carbonylsulfide (^{18}OCS). The full line width at half maximum of DMSO is $\Delta\nu_{FWHM}=20.6$ kHz and is more than two times larger than that of ^{18}OCS. The line widths were derived by a least squares fit of the free induction decay. Furthermore, the centrifugal distortion constants, which were kept fixed to the values of the ^{32}S isotopomer, are not the exact values of ^{33}S DMSO. So the large errors seem to be reasonable. An additional least squares fit of the hfs splittings alone leads to the same quadrupole coupling constants with a standard deviation of $\sigma_{hfs}=5.8$ kHz.

Since there exist no data on the ^{33}S nuclear quadrupole coupling of other molecules, where the sulfur is bonded to two carbon and one oxygen atom, no comparison is possible. The quadrupole coupling constants derived in this work should be a basis for quantumchemical calculations.

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