^{17}O and ^{33}S Fourier Transform NMR Studies in Thiosulfate and Thiomolybdate Solutions

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Fourier Transform NMR measurements of ^{17}O and ^{33}S are reported for several aqueous sulfate, thiosulfate, molybdate and thiomolybdate solutions. Using informations from ^{17}O signals, ^{33}S NMR lines are assigned. Experimental parameters, chemical shifts and linewidths are given.

Introduction

The detection of NMR signals of quadrupolar nuclei and their assignment to molecular structure is sometimes not quite easy because of the large broadening of the lines, even if the chemical shifts are large for nuclei with higher atomic number. The chlorine NMR studies in inorganic or organic compounds [1–3] are a well known example.

Since sulfur is a highly significant element in chemistry, NMR investigations of the quadrupolar ^{33}S, the only sulfur isotope with a spin, are very important. Only a few NMR investigations of ^{33}S are reported [4, 5]; this fact is due to the low natural abundance of 0.74% and the sometimes unexpected widths of the NMR lines which are often broadened beyond the possibility of detection [6].

If a multi-nuclei-spectrometer is available the observation of a further nucleus of an element in the same group of the periodic table may sometimes help to assign the observed signals. For the VI a element sulfur ^{17}O NMR investigations are obvious since a good deal of information is available [7–9] and the lines are usually not very broad due to the favourable ratio of $\frac{2I+3}{I^2(2I-1)}(eQ)^2$ (see Reference [10]).

In the following communication ^{33}S NMR lines have been identified using also informations from ^{17}O NMR lines in equivalent compounds: ^{17}O and ^{33}S were observed in aqueous solutions of thiosulfates and thiomolybdates.

Experimental

The NMR measurements were performed with a commercial multinuclei Bruker pulse spectrometer SXP 4 – 100 in a magnetic field of 2.11 T produced by a Bruker high resolution 15″ magnet system. The magnetic field was externally stabilized by the Bruker B-SN 15 NMR stabilizer. An appropriate

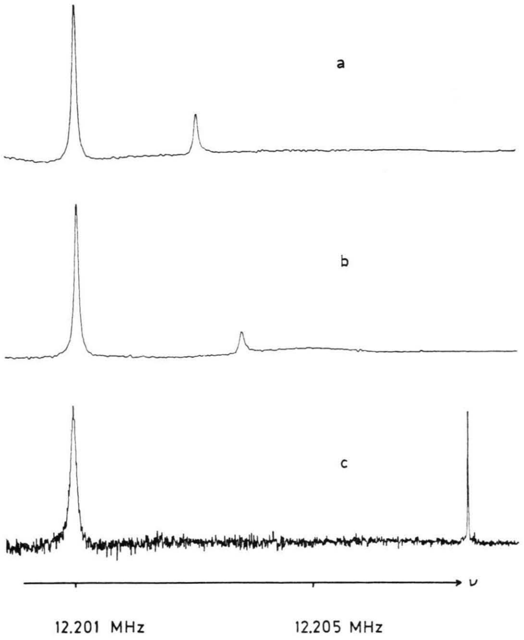

Fig. 1. Natural abundant ^{17}O FT NMR spectra of aqueous solutions of oxyanions at about 12.201 MHz: a) 4.0 molal $(NH_4)_2SO_4$ in H_2O, b) 4.0 molal $(NH_4)_2S_2O_3$ in H_2O, c) 2.6 molal K_2MoO_4 in H_2O. — The strong signals at low frequency are the ^{17}O lines in water, the signals at higher frequencies are due to the oxyanions. The chemical shifts and line widths are given in Table 1. — Experimental parameters: For a) through c): volume: 1.5 ml; plotted spectrum width: 8700 Hz; experimental spectrum width: 12500 Hz. Pulse repetition frequency: a) 20 Hz, b) 20 Hz, c) 2.5 Hz. — Number of pulses: a) 40000, b) 40000, c) 20000. Total measuring time: a) 33.3 min, b) 33.3 min, c) 132 min. For a) and b) 1 K data points were accumulated and trapezoidal multiplication (no line broadening) followed by 3 K of zero-filling was applied before Fourier transformation, whereas for c) 4 K data points were accumulated and no data managing was performed. This is the reason for the lower signal to noise ratio.

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number of free induction decays[11, 12] of ^{17}O and ^{33}S were accumulated and Fourier transformed by a Bruker BNC 12 data unit.

The Larmor frequency of ^{17}O was approximately 12.201 MHz, that one of ^{33}S 6.908 MHz. Chemical shifts are given by $\delta = (\nu_{\text{sample}} - \nu_{\text{reference}}) / \nu_{\text{reference}}$. A positive δ means a shift to higher frequency at a constant field. The shifts are measured relative to an external reference by the sample replacement method or sometimes in the case of ^{17}O to the internal water line. The temperature was (299 ± 2) K. Non rotating cylindrical sample tubes with 10 mm outer diameter were used.

Typical spectra of ^{17}O and ^{33}S are given in Fig. 1 and 2. The experimental data have been chosen so, that the frequency scales are the same for each figure. For exact measurements of the chemical shifts and line widths the experimental parameters were individually adjusted to the appropriate problem.

Results

a) Chemical Shifts and Line Widths of ^{17}O

Chemical shifts of ^{17}O signals in aqueous solutions of inorganic compounds containing oxygen atoms were reported earlier[8, 9, 13–16]. An extremely narrow ^{17}O NMR line was recently found by Vold and Vold[17] in the MoO_4^{2-}-ion.

To get further information ^{17}O signals were detected in aqueous solutions of sulfates, thiosulfates and molybdates. Some results for line widths and chemical shifts are given in Table 1 and Figure 1.

The ^{17}O line in the SO_4^{2-}-ion is much broader than in the MoO_4^{2-}-ion; surprisingly the line width found in the thiosulfate ion is nearly the same as in the sulfate ion.

The substitution of an oxygen atom by a sulfur atom results in a change of the chemical shift from (166.1 ± 1.4) ppm for the SO_4^{2-}-ion to (227.5 ± 0.5) ppm for the $S_2O_3^{2-}$-ion. The signal in the molybdate was found at the known position[17].

The concentration dependence of the ^{17}O signals in the oxyanions in D_2O is small: in cesium sulfate solutions (1.5 ± 0.3) ppm/mol, in ammonium thiosulfate solutions (0.4 ± 0.3) ppm/mol and in sodium molybdate solutions (0.2 ± 0.6) ppm/mol were found. This means, that the influence of the ions and solvent molecules on the positions of the NMR line in the oxyanions is rather small. The ^{17}O NMR line of D_2O in solutions of oxyanions is also shifted[14, 16]: In cesium sulfate solutions (1.4 ± 0.4) ppm/mol, in ammonium thiosulfate solutions (1.3 ± 0.2) ppm/mol and in sodium molybdate solutions $-(0.8 \pm 0.4)$ ppm/mol were found. Finally it should be mentioned, that the ^{17}O line of water in the aqueous solutions is broader in D_2O than in H_2O (see Table 1) contrary to the line widths in pure D_2O and H_2O (see Reference[9]).

b) Chemical Shifts and Line Widths of ^{33}S

Due to the low NMR receptivity of the ^{33}S signal which in a 1 molal aqueous Cs_2SO_4-solution is about $2 \cdot 10^{-7}$ of that of the proton, very few NMR data of ^{33}S are known[4, 5]. As ^{33}S reference line the signal in the sulfate ion was proposed[5] because of its narrow line (see Figure 2 a).

Searching for further ^{33}S NMR signals only one line was found in thiosulfate solutions (see Fig. 2 b), this line is shifted (34.5 ± 0.2) ppm to higher frequency and has a line width of 36 Hz. First of all this signal was assigned to the central sulfur in the thiosulfate ion[18]. But due to the relatively narrow signal of ^{17}O in the thiosulfate this shifted ^{33}S line was suspected of being the sulfur in the thio-position. Fortunately from a NMR work on ^{95}Mo[19]

Table 1. ^{17}O chemical shifts and line widths in aqueous solutions of oxyanions. The reference was a pure H_2O sample. For avoiding susceptibility corrections spherical samples were used for the final comparison of the water lines.

Sample	^{17}O in the oxyanions		^{17}O in water	
	Chemical shift ppm	Line width Hz	Chemical shift ppm	Line width Hz
4 molal $(NH_4)_2SO_4$ in H_2O	167.0 (0.1)	84 (10)	3.0 (0.2)	85 (2)
4 molal $(NH_4)_2SO_4$ in D_2O	166.1 (1.4)	101 (5)	0.1 (1.4)	107 (8)
4 molal $(NH_4)_2S_2O_3$ in H_2O	227.9 (0.6)	89 (13)	5.1 (0.2)	77 (2)
4 molal $(NH_4)_2S_2O_3$ in D_2O	227.5 (0.5)	105 (7)	2.5 (0.4)	89 (11)
1.9 molal Na_2MoO_4 in H_2O	532.4 (0.5) *	<5 Hz	−0.5 (0.4)	93 (6)
1.9 molal Na_2MoO_4 in D_2O	531.2 (0.6) *	<5 Hz	−4.1 (0.6)	128 (7)

* In good agreement with the values given in Reference[17].

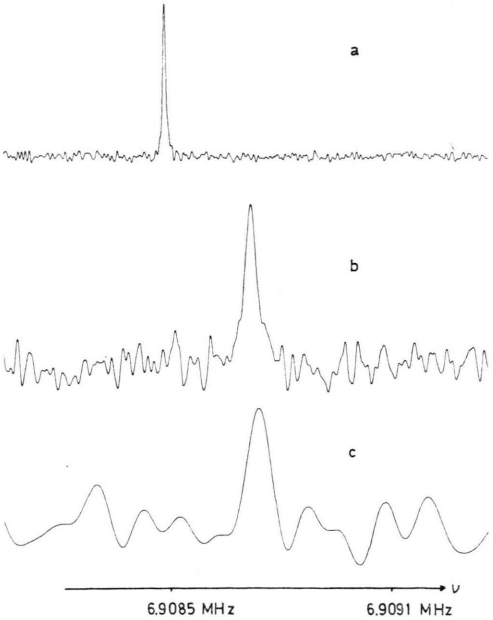

Fig. 2. Natural abundant ^{33}S FT NMR signals at about 6.908 MHz of a) 4.0 molal $(NH_4)_2SO_4$ in H_2O, b) 4.0 molal $(NH_4)_2S_2O_3$ in H_2O, c) 1.1 molal K_2MoS_4 in H_2O. The chemical shifts are for b) (34.5 ± 0.2) ppm and for c) (33.4 ± 1.6) ppm referred to the sulfate signal in 4 molal ammonium sulfate. The line widths (non rotating samples) increase from 10 Hz for a) to 36 Hz for b) to 61 Hz for c), the latter resulting partly from rapid pulsing. Experimental parameters: a) through c): 1.5 ml; plotted spectrum width: 1310 Hz. — Experimental spectrum width: a) 2000 Hz, b) 2000 Hz, c) 50000 Hz. Pulse repetition frequency: a) 2 Hz, b) 3,3 Hz, c) 50 Hz. Number of pulses: a) 5000, b) 10000, c) 75000. Total measuring time: a) 41.6 min, b) 50 min, c) 25 min. For a) and b) 1 K data points were accumulated and trapezoidal multiplication (no line broadening) followed by 3 K zero-filling was applied before Fourier transformation whereas for c) 1 K data points were accumulated followed by 7 K of zero-filling before Fourier transformation without data managing.

samples of potassium tetrathiomolybdate were available *. The ^{33}S signal in a 1.1 molal aqueous solutions of this salt is given in Fig. 2 c: the shift of this thio-signal is (33.4 ± 1.6) ppm, the line width is about 61 Hz. This fact strongly encourages us to assign the single line in the thiosulfate to the sulfur in the thio-position. For the sulfur in the central position a broadening beyond detection must be assumed. Further investigations support this assumption: no ^{33}S NMR signals could be detected ** in aqueous solutions of the following sulfur containing inorganic salts: Na_2S, $Na_2S_2O_4$, $(NH_4)_2S_2O_8$, Na_2SO_3, $NaHSO_4$, $Na_2S_2O_5$, $K_2S_4O_6$, NH_4SCN.

The electric field gradient seems to be so large that the ^{33}S signal is strongly broadened; very broad signals have been found also earlier [4, 5], for instance in concentrated H_2SO_4. This fact is certainly a severe limitation to the applicability of ^{33}S NMR in inorganic and organic chemistry for elucidation of molecular structure.

Conclusions

^{33}S NMR investigations show surprising features, the applicability is limited. NMR signals of ^{17}O in equivalent positions can help to assign the found signals. This indicates the utility of multinuclei spectrometers; but they must have a high sensitivity for such less receptive nuclei at natural abundance.

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[**] Performed with the NMR spectrometer also used in Reference [5].

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