Indirect Spin-Spin Coupling Between ^{17}O and Other Quadrupolar Nuclei in Oxyanions

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Fourier transform NMR studies of ^{17}O, ^{35}Cl, ^{51}V, ^{53}Cr, ^{55}Mn and ^{95}Mo are reported for aqueous solutions of the oxyanions ClO_4^-, VO_4^{3-}, CrO_4^{2-}, MnO_4^-, and MoO_4^{2-}, partly enriched in ^{17}O. The indirect spin-spin coupling constant between ^{17}O and the quadrupolar central nucleus is determined:

$J(^{17}O-^{35}Cl) = (81.4 \pm 4.0)$ Hz, $J(^{17}O-^{51}V) = (61.6 \pm 2.5)$ Hz, $J(^{17}O-^{53}Cr) = (10 \pm 2)$ Hz, $J(^{17}O-^{55}Mn) = (28.9 \pm 2.8)$ Hz and $J(^{17}O-^{95}Mo) = (40.5 \pm 0.8)$ Hz.

A linear dependence of the reduced coupling constants on the atomic number of the central nucleus in the isoelectronic series VO_4^{3-}, CrO_4^{2-} and MnO_4^- was found.

Introduction

Indirect scalar spin-spin coupling is a well known phenomenon in NMR investigations of nuclei with spin 1/2. If the spin of the nucleus under consideration is greater than 1/2 the interaction of the associated electric quadrupole moment with electric field gradients produces an effective nuclear relaxation mechanism causing wide lines. Hence, the splitting due to spin-spin coupling with other magnetic nuclei and especially with other quadrupolar nuclei is seldom observable. At least the ratio

$$\frac{2I+3}{I^2(2I-1)}\,(eQ)^2$$

must be favourable for the quadrupolar nuclei. This is the case for ^{2}H, ^{17}O and ^{133}Cs. Disregarding ^{2}H, the quadrupole moment of which is extremely small, splittings due to spin-spin coupling involving two quadrupolar nuclei in liquids have been resolvable by our knowledge only in perchlorate[1], permanganate[2], molybdate[3] and pentaborane[4] solutions.

In the following some further examples of spin-spin coupling between quadrupolar nuclei in aqueous solutions of oxyanions observing both ^{17}O and the central nucleus are reported. It was one of the aims of this work to get informations on the systematic behaviour of spin-spin coupling constants in the isoelectronic series VO_4^{3-}, CrO_4^{2-} and MnO_4^-.

Experimental

The measurements were done with a multinuclei Bruker pulse spectrometer SXP 4-100 in a magnetic field of 2.114 T produced by a high resolution Bruker 15″ magnet system, externally stabilized by the Bruker NMR stabilizer B-SN 15. The free induction decays were accumulated and Fourier transformed by the Bruker BNC 12 computer. Some essential features of the observed nuclei ^{17}O, ^{35}Cl, ^{51}V, ^{53}Cr, ^{55}Mn and ^{95}Mo are given in Table 1.

Rotating and nonrotating cylindrical and spherical samples of 10 mm outer diameter were used. The temperature for all measurements was (299 ± 2) K.

Further experimental details are given in the figures. Chemical shifts are given by $\delta = [(\nu_{\text{sample}}/\nu_{\text{reference}}) - 1]$.

The procedure of the preparation of the enriched samples was the following: At first the respective salt was dissolved in water, which was enriched in ^{17}O. After a waiting time of a few hours the ap-

Table 1. For NMR investigations important properties of ^{17}O, ^{35}Cl, ^{51}V, ^{53}Cr, ^{55}Mn and ^{95}Mo.

Nucleus	^{17}O	^{35}Cl	^{51}V	^{53}Cr	^{55}Mn	^{95}Mo
Natural abundance in %	0.037	75.53	99.76	9.55	100	15.72
Spin	5/2	3/2	7/2	3/2	5/2	5/2
Larmor-Frequency at 2.114 T in MHz	12.205	8.827	23.661	5.087	22.315	5.865
Receptivity in a 1 molal aqueous solution (protons = 1)	$1\cdot10^{-7}$	$3\cdot10^{-5}$	$4\cdot10^{-3}$	$8\cdot10^{-7}$	$2\cdot10^{-3}$	$5\cdot10^{-6}$

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propriate base was added to the vanadate, chromate and molybdate solutions. No base was added to the $KMnO_4$ solution. The signal of this solution was observed a few days after the preparation. In all these solutions a total exchange of the oxygen isotopes between the solvent and the solute did happen. This could easily be verified by the observation of the ^{17}O signal of the solvent and the solute. Only in perchlorate solutions no exchange occurs [5]. Therefore the measurements in the perchlorate solution were performed at naturally abundant ^{17}O.

Results

A) Indirect spin-spin coupling between ^{17}O and ^{51}V in the VO_4^{3-} ion

The indirect spin-spin coupling between ^{17}O and ^{51}V was observed in a 0.9 molal solution of $NaVO_3$ in D_2O (enriched to 12% in ^{17}O) at a pD value greater than 13. At this high concentration of OD^- only the two species of vanadate ions $V_2O_7^{4-}$ and VO_4^{3-} exist [6–8]. In Fig. 1 the absorption signal of ^{17}O in the described solution is given. The frequency increases from the right to the left. The signal at lower frequency is due to the VO_4^{3-} ion and that one at higher frequency is due to the $V_2O_7^{4-}$ ion. The chemical shift of the ^{17}O signal in the $V_2O_7^{4-}$ relative to the VO_4^{3-} signal is 132 ppm. The signal of ^{17}O in VO_4^{3-} is shifted 568 ppm relative to the water signal in the same sample.

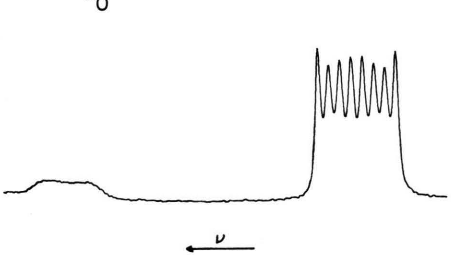

Fig. 1. Absorption signal of ^{17}O at 12.208 MHz in a 0.9 molal solution of $NaVO_3$ in D_2O at pD greater 13, 12% enriched in ^{17}O. Experimental parameters: Experimental spectrum width: 10 000 Hz, plotted spectrum width: 2500 Hz, pulse repetition frequency: 16.7 Hz, number of pulses: 60 000, measuring time: 1 h, nonrotating spherical sample: 10 mm outer diameter, sample volume: 0.3 ml. 1 K data points were accumulated followed by 3 K of zero-filling before Fourier transformation.

The total linewidth of the two multiplets is 400 Hz for the $V_2O_7^{4-}$ ion and 470 Hz for the VO_4^{3-} ion. The scalar coupling between ^{17}O and ^{51}V is obscured in the $V_2O_7^{4-}$ ion by chemical exchange effects [9], a coupling constant for the VO_4^{3-} ion can be given: $J(\underline{^{17}O}-{}^{51}V) = (61.6 \pm 2.5)$ Hz *. The lineshape of the ^{17}O signal in VO_4^{3-} is mainly due to the quadrupolar relaxation of the ^{51}V nucleus. The ratio of the reciprocal intensities of the single components of the multiplet and their linewidths for ^{17}O due to quadrupolar relaxation of the ^{51}V nucleus is: 1008 : 1872 : 1728 : 1440 : 1440 : 1728 : 1872 : 1008 (see Ref. [10, 11]). To get by a computer program a similar lineshape as that one given in Fig. 1 for ^{17}O in the VO_4^{3-} ion one has to take into account the given ratio of the intensities and of the linewidths and a further broadening, unspecific for the different lines of the multiplet.

In Fig. 2 the absorption signal of ^{51}V in the mentioned sample is given. The frequency increases now from the left to the right. The signal at lower frequency is due to the $V_2O_7^{4-}$ ion and that one at higher frequency is due to the VO_4^{3-} ion. The chemical shift of the ^{51}V signal in the $V_2O_7^{4-}$ ion relative to the VO_4^{3-} ion is − 18.5 ppm.

The signal of ^{51}V in the VO_4^{3-} ion is composed of a signal of such ions, which contain no ^{17}O isotope and which therefore show no scalar coupling, and further of a signal of ions, which contain one ^{17}O

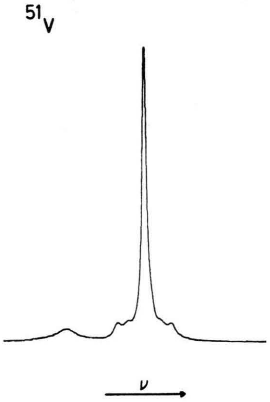

Fig. 2. Absorption signal of ^{51}V at 23.661 MHz in a 0.9 molal solution of $NaVO_3$ in D_2O at pD greater 13, 12% enriched in ^{17}O. Experimental parameters: Experimental spectrum width: 5000 Hz, plotted spectrum width: 1500 Hz, pulse repetition frequency: 1 Hz, number of pulses 200, measuring time: 3.3 min, nonrotating spherical sample: 10 mm outer diameter, sample volume: 0.3 ml. 1 K data points were accumulated followed by 3 K of zero filling before Fourier transformation.

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* The underlined isotope designates the nucleus, which has been observed to determine the indirect spin-spin coupling constant.

isotope. The first kind of ions produces the central line with a measured linewidth of 27 Hz and the second kind causes the wings of the signal. From this signal a coupling constant can be given by a computer program: $J(^{17}\text{O}-\underline{^{51}\text{V}}) = (63 \pm 5)$ Hz. The error is an estimated one. Values of the coupling constant outside of these limits give clearly different lineshapes. The linewidth of the hardly resolved satellites is about 50 Hz. The small asymmetry of the wings may be due to a small isotopic effect.

The signal of ^{51}V in the $V_2O_7{}^{4-}$ ion shows no fine structure. The linewidth is 125 Hz. As in the ^{17}O spectrum the chemical exchange is so fast, that without further experiments no coupling constant can be given.

In less basic solutions ($p_{\text{H}} \approx 12.5$) one gets mainly two variations in both spectra: first the signal of the $V_2O_7{}^{4-}$ is as intensive as the signal of the $VO_4{}^{3-}$ ion [6-8] and second the resolution is worse in the multiplets of the $VO_4{}^{3-}$ ion. The chemical shift of both nuclei in the two compounds depends on the p_{H} value, too.

B) Indirect spin-spin coupling between ^{17}O and ^{53}Cr in the $CrO_4{}^{2-}$ ion

The indirect spin-spin coupling between ^{17}O and ^{53}Cr was observed in a 2.6 molal basic solution of K_2CrO_4 in H_2O, enriched to 35% in ^{17}O. The absorption signal of ^{53}Cr in this solution is given in Figure 3. Again, this pattern results from different components. First, chromate ions, which contain no ^{17}O isotope, give a central line with a linewidth of about 10 Hz [12]. Second, about 42% of the chromate ions contain one ^{17}O isotope; because of the scalar coupling between ^{17}O and ^{53}Cr one gets a multiplet of 6 lines, which is unresolved and superimposed on the central line. Third, about 30% of the chromate ions contain two or more ^{17}O isotopes. For two ^{17}O isotopes in one chromate ion one gets 11 different lines with varying intensity. With the computer program, which has been used to evaluate the ^{51}V spectrum, this ^{53}Cr signal has been fitted, too. Fairly good results could be achieved under the following conditions: The same linewidth of 9 Hz was assumed for the central line and for all satellites, further equal intensity for all 6 satellites was used. The ratio of the intensities of chromate ions with no ^{17}O isotope to those with one ^{17}O to those with two ^{17}O isotopes was determined from the isotopic composition of the sample. The result for the coupling constant is: $J(^{17}\text{O}-\underline{^{53}\text{Cr}}) = (10 \pm 2)$ Hz. The error is an estimated one.

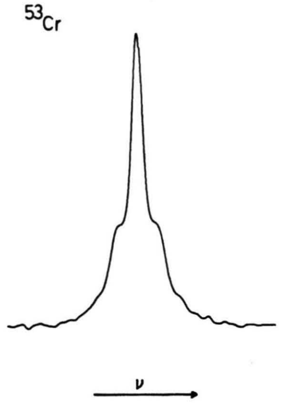

Fig. 3. Absorption signal of ^{53}Cr at 5.087 MHz in a 2.6 molal basic aqueous solution of K_2CrO_4, 35% enriched in ^{17}O. Experimental parameters: Experimental spectrum width: 2000 Hz, plotted spectrum width: 300 Hz, pulse repetition frequency: 1.7 Hz, number of pulses: 60 000, measuring time: 10 h, rotating cylindrical sample: 10 mm outer diameter, sample volume: 1 ml. 1 K data points were accumulated and trapezoidal multiplication (no line broadening) followed by 3 K of zero filling was applied before Fourier transformation.

The coupling between ^{53}Cr and ^{17}O could not be detected by ^{17}O NMR in the 35% ^{17}O enriched sample, because the linewidth of the ^{17}O signal in the chromate ions, which contain no ^{53}Cr isotopes, is about 20 Hz and because the ratio of the intensities of the central line to each line of the expected multiplet is 1 : 0.025.

The chemical shift of the ^{17}O signal of the chromate ion relative to the ^{17}O signal in pure water is 822.1 (0.5) ppm. This value is slightly different from the value given in Reference 13.

C) Indirect spin-spin coupling between ^{17}O and ^{95}Mo in the $MoO_4{}^{2-}$ ion

Recently the coupling constant $J(\underline{^{17}\text{O}}-{}^{95}\text{Mo})$ was determined by ^{17}O NMR by Vold and Vold [3] in the molybdate ion. In the present work the scalar coupling of ^{17}O and ^{95}Mo in molybdate was observed using either of both nuclei. The sample was a 1 molal basic solution of Na_2MoO_4 in H_2O, enriched to 11% in ^{17}O. In Fig. 4 the absorption signal of ^{95}Mo in this sample is given. The central line is due to the molybdate ions which contain no ^{17}O nuclei. Because of the nonrotating spherical sample the linewidth is about 5 Hz, though the natural line width is less than 1 Hz (Ref. [14-16]). The multiplet yields the coupling

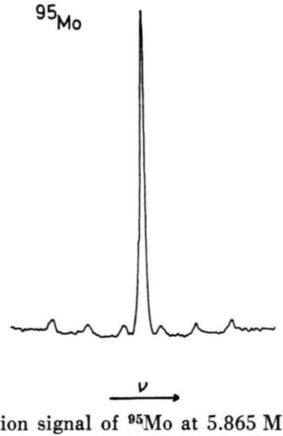

Fig. 4. Absorption signal of ^{95}Mo at 5.865 MHz in a 1 molal basic aqueous solution of $NaMoO_4$, 11% enriched in ^{17}O. Experimental parameters: Experimental spectrum width: 1000 Hz, plotted spectrum width: 300 Hz, pulse repetition frequency: 0.5 Hz, number of pulses: 30 000, measuring time: 16.6 h, nonrotating spherical sample: 10 mm outer diameter, sample volume: 0.3 ml. 1 K data points were accumulated and trapezoidal multiplication (no line broadening) followed by 3 K of zero filling was applied before Fourier transformation.

constant $J(^{17}\mathrm{O} - ^{95}\underline{\mathrm{Mo}}) = (40.5 \pm 0.8)$ Hz. The result is in good agreement with the results of the ^{17}O measurements: See Ref. [3] and the value of the present work given also in Table 2. In the ^{17}O NMR pattern, the multiplet is shifted a small amount to lower frequency relative to the central line. This small shift may be an isotopic effect. The ratio of the intensities of the central line and the satellites indicates, that only the coupling between ^{17}O and ^{95}Mo is observed. The quadrupole moment of ^{97}Mo is 11.4 times larger than that of ^{95}Mo (see References [14, 15]). Also by ^{97}Mo NMR no coupling between ^{97}Mo and ^{17}O was observable, only a single broad line with a width of about 50 Hz could be detected.

Table 2. Spin-spin coupling constants between ^{17}O and other quadrupolar nuclei in oxyanions. The results of this work are given in column 3 and 4. The known values (given in column 5) were all determined by ^{17}O NMR. The underlined isotope designates the nucleus which has been used to determine the coupling constant.

Oxyanion	Quadrupolar nuclei X	$J(^{17}\underline{\mathrm{O}}\text{-X})$ in Hz	$J(^{17}\mathrm{O}\text{-}\underline{\mathrm{X}})$ in Hz	$J(^{17}\underline{\mathrm{O}}\text{-X})$ in Hz (known values)
ClO_4^-	^{35,37}Cl	81.4 ± 4.0	—	85.5 ± 0.5 (Ref. [1])
VO_4^{3-}	^{51}V	61.6 ± 2.5	63 ± 5	—
CrO_4^{2-}	^{53}Cr	—	10 ± 2	—
MnO_4^-	^{55}Mn	28.9 ± 2.8	—	30.2 ± 3.0 (Ref. [2])
MoO_4^{2-}	^{95}Mo	40.3 ± 0.9	40.5 ± 0.8	40.3 ± 0.2 (Ref. [3])

D) Indirect spin-spin coupling between ^{17}O and ^{55}Mn in the MnO_4^- ion and between ^{17}O and ^{35,37}Cl in the ClO_4^- ion

The coupling constants between ^{17}O and ^{35,37}Cl and between ^{17}O and ^{55}Mn have already been measured both in enriched samples by ^{17}O NMR [1, 2]. In the present work only the coupling between ^{17}O and ^{55}Mn was observed in a 11% enriched sample, the coupling constant of ^{17}O and ^{35,37}Cl was measured at natural abundance.

In a 0.4 molal $KMnO_4$ solution in H_2O a coupling constant $J(^{17}\underline{\mathrm{O}} - ^{55}\mathrm{Mn}) = (28.9 \pm 2.8)$ Hz was found. This result is in good agreement with the value of Broze and Luz [2] (see Table 2). A lineshape was observed, which is mainly due to the quadrupolar relaxation of the ^{55}Mn nucleus, contrary to the lineshape reported in Reference [2]. This may result from the different Larmor-frequencies used in both experiments.

The ^{55}Mn signal in the mentioned sample shows a partly resolved pattern complicated by the isotopic composition of the water. Further experiments with this and other samples are running.

As already mentioned the exchange rate of the ^{17}O isotope between the water and the ClO_4^- is very small; therefore the coupling between ^{17}O and ^{35,37}Cl was measured by ^{17}O NMR at naturally abundant ^{17}O. The value is given in Table 2, it is in good agreement with the value of Alei [1].

By ^{35}Cl NMR the coupling between ^{17}O and ^{35}Cl was not observed though a signal-to-noise ratio of 6400 was achieved. Enriched samples in ^{17}O would give better intensity ratios between the main line and the satellites.

E) Correlation of the scalar spin-spin coupling constant with the atomic number in the isoelectronic series vanadate, chromate and manganate

Systematic investigations of indirect spin-spin coupling constants between ^{1}H or ^{19}F (indicated by A) and atoms of the same group of the periodic table or of isoelectronic atoms (indicated by B) in similar molecules show, that there is a linear correlation of the reduced coupling constant $[J(A-B)/\gamma_A \cdot \gamma_B]^{1/2}$ with the atomic number of B [17–20]. γ_A, γ_B are the gyromagnetic ratios of the respective nuclei.

It is interesting to test whether this empirical rule is valid only for ^1H and ^{19}F. In this work the coupling constants of ^{17}O with the central nuclei in the isoelectronic series VO_4^{3-}, CrO_4^{2-} and MnO_4^- has been measured. One finds that the reduced coupling constants, which one gets from the values of Table 2 and from the gyromagnetic ratios of ^{17}O and the corresponding nuclei ^{51}V, ^{53}Cr and ^{55}Mn, are consistent with a linear dependence on the atomic numbers of the metallic nuclei in the isoelectronic series VO_4^{3-}, CrO_4^{2-} and MnO_4^-.

Conclusions

Indirect spin-spin couplings between two quadrupolar nuclei in ligands are usually not easy to observe due to the broad lines and weak signals.

It is very useful to detect the NMR signals of both nuclei, which are connected by the spin-spin coupling for a selection of the most favourable nucleus for the evaluation of the coupling constant.

In the observed oxyanions the scale of the found patterns ranges from fully resolved spectra for both involved nuclei in MoO_4^{2-} to only a weakly structured line of ^{53}Cr and a single line of ^{17}O in the chromate ion.

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