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

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(Z. Naturforsch. 31 a, 1046—1050 [1976]; received June 21, 1976)

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 $\text{ClO}_4^-$, $\text{VO}_4^{2-}$, $\text{CrO}_4^{2-}$, $\text{MnO}_4^-$, and $\text{MoO}_4^{2-}$, partly enriched in $^{17}$O. The indirect spin-spin coupling constant between $^{17}$O and the quadrupolar central nucleus is determined:

$$I(\text{H} - \text{Cl}) = (81.4 \pm 4.0) \text{ Hz}, \quad I(\text{H} - \text{V}) = (61.6 \pm 2.5) \text{ Hz}, \quad I(\text{H} - \text{Cr}) = (10 \pm 2) \text{ Hz}, \quad I(\text{H} - \text{Mn}) = (28.9 \pm 2.8) \text{ Hz} \quad \text{and} \quad I(\text{H} - \text{Mo}) = (40.5 \pm 0.6) \text{ Hz}.$$

A linear dependence of the reduced coupling constants on the atomic number of the central nucleus in the isoelectronic series $\text{VO}_4^{2-}$, $\text{CrO}_4^{2-}$ and $\text{MnO}_4^-$ was found.

**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 NM R 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 $(299 \pm 2) \text{ K}$. 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>
<thead>
<tr>
<th>Nucleus</th>
<th>$^{17}$O</th>
<th>$^{35}$Cl</th>
<th>$^{51}$V</th>
<th>$^{53}$Cr</th>
<th>$^{55}$Mn</th>
<th>$^{95}$Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural abundance in %</td>
<td>0.037</td>
<td>75.53</td>
<td>99.76</td>
<td>9.55</td>
<td>100</td>
<td>15.72</td>
</tr>
<tr>
<td>Spin</td>
<td>5/2</td>
<td>3/2</td>
<td>7/2</td>
<td>3/2</td>
<td>5/2</td>
<td>5/2</td>
</tr>
<tr>
<td>Larmor-Frequency at 2.114 T in MHz</td>
<td>12.205</td>
<td>8.827</td>
<td>23.661</td>
<td>5.087</td>
<td>22.315</td>
<td>5.865</td>
</tr>
<tr>
<td>Receptivity in a 1 molal aqueous solution (protons = 1)</td>
<td>$1 \cdot 10^{-7}$</td>
<td>$3 \cdot 10^{-3}$</td>
<td>$4 \cdot 10^{-3}$</td>
<td>$8 \cdot 10^{-7}$</td>
<td>$2 \cdot 10^{-3}$</td>
<td>$5 \cdot 10^{-6}$</td>
</tr>
</tbody>
</table>

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

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propionate base was added to the vanadate, chromate and molybdate solutions. No base was added to the KMnO₄ 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 ¹⁷O signal of the solvent and the solute. Only in perchlorate solutions no exchange occurs⁵. Therefore the measurements in the perchlorate solution were performed at naturally abundant ¹⁷O.

**Results**

A) Indirect spin-spin coupling between ¹⁷O and ⁵¹V in the VO₄³⁻ ion

The indirect spin-spin coupling between ¹⁷O and ⁵¹V was observed in a 0.9 molal solution of NaVO₃ in D₂O (enriched to 12% in ¹⁷O) at a pH value greater than 13. At this high concentration of OD⁻ only the two species of vanadate ions VO₂₃⁻ and VO₄³⁻ exist⁶⁻⁸. In Fig. 1 the absorption signal of ¹⁷O in the described solution is given. The frequency increases from the right to the left. The signal at lower frequency is due to the VO₄³⁻ ion and that one at higher frequency is due to the VO₂₃⁻ ion. The chemical shift of the ⁵¹V signal in the VO₂₃⁻ ion relative to the VO₄³⁻ ion is 18.5 ppm.

The signal of ⁵¹V in the VO₄³⁻ ion is composed of a signal of such ions, which contain no ¹⁷O isotope and which therefore show no scalar coupling, and further of a signal of ions, which contain one ¹⁷O.

![](image1.png)

Fig. 1. Absorption signal of ¹⁷O at 12.208 MHz in a 0.9 molal solution of NaVO₃ in D₂O at pH greater 13, 12% enriched in ¹⁷O. Experimental parameters: Experimental spectrum width: 10000 Hz, plotted spectrum width: 2500 Hz, pulse repetition frequency: 16.7 Hz, number of pulses: 60000, 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.

¹⁷O in the described solution is given. The frequency increases from the right to the left. The signal at lower frequency is due to the VO₄³⁻ ion and that one at higher frequency is due to the VO₂₃⁻ ion. The chemical shift of the ¹⁷O signal in the VO₂₃⁻ relative to the VO₄³⁻ signal is 132 ppm. The signal of ¹⁷O in VO₂₃⁻ is shifted 568 ppm relative to the water signal in the same sample.

The total linewidth of the two multiplets is 400 Hz for the VO₂₃⁻ and 470 Hz for the VO₄³⁻. The scalar coupling between ¹⁷O and ⁵¹V is obscured in the VO₂₃⁻ ion by chemical exchange effects⁹.

The lineshape of the VO₄³⁻ ion is given ratio of the intensities and of the linewidths given in Fig. 1 for VO₂₃⁻. For VO₄³⁻ the lineshape of the Vo₂₃⁻ 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 ⁵¹V 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 VO₂₃⁻ ion and that one at higher frequency is due to the VO₄³⁻ ion. The chemical shift of the ⁵¹V signal in the VO₂₃⁻ ion relative to the VO₄³⁻ ion is 18.5 ppm. The signal of ⁵¹V in the VO₄³⁻ ion is composed of a signal of such ions, which contain no ¹⁷O isotope and which therefore show no scalar coupling, and further of a signal of ions, which contain one ¹⁷O.

![](image2.png)

Fig. 2. Absorption signal of ⁵¹V at 23.661 MHz in a 0.9 molal solution of NaVO₃ in D₂O at pH greater 13, 12% enriched in ¹⁷O. 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.

* 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: \(J(^{17}O - ^{53}V) = (63 \pm 5)\) 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 \(V_2O_4^{4-}\) 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 (\(p_H \approx 12.5\)) one gets mainly two variations in both spectra: first the signal of the \(V_2O_4^{4-}\) is as intensive as the signal of the \(V_2O_3^{3-}\) ion \(^8\) and second the resolution is worse in the multiplets of the \(V_2O_4^{3-}\) 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 \(^{55}Cr\) 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}O - ^{53}Cr) = (10 \pm 2)\) Hz. The error is an estimated one.

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 \(^{55}Cr\) 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 \(J(^{17}O - ^{95}Mo)\) 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
constant \( J(^{17}\text{O} - ^{95}\text{Mo}) = (40.5 \pm 0.8) \text{ Hz} \). The result is in good agreement with the results of the \(^{17}\text{O}\) measurements: See Ref. 3 and the value of the present work given also in Table 2. In the \(^{17}\text{O}\) 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 \(^{17}\text{O}\) and \(^{95}\text{Mo}\) is observed. The quadrupole moment of \(^{97}\text{Mo}\) is 11.4 times larger than that of \(^{95}\text{Mo}\) (see References 14, 15). Also by \(^{97}\text{Mo}\) NMR no coupling between \(^{97}\text{Mo}\) and \(^{17}\text{O}\) was observable, only a single broad line with a width of about 50 Hz could be detected.

**D) Indirect spin-spin coupling between \(^{17}\text{O}\) and \(^{55}\text{Mn}\) in the \(\text{MoO}_4^{2-}\) ion and between \(^{17}\text{O}\) and \(^{35,37}\text{Cl}\) in the \(\text{ClO}_4^{-}\) ion**

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

In a 0.4 molal KMnO\(_4\) solution in H\(_2\)O a coupling constant \( J(^{17}\text{O} - ^{55}\text{Mn}) = (28.9 \pm 2.8) \text{ Hz} \) 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 \(^{55}\text{Mn}\) nucleus, contrary to the lineshape reported in Reference 2. This may result from the different Larmor-frequencies used in both experiments.

The \(^{55}\text{Mn}\) 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 \(^{17}\text{O}\) isotope between the water and the \(\text{ClO}_4^{-}\)  is very small; therefore the coupling between \(^{17}\text{O}\) and \(^{35,37}\text{Cl}\) was measured by \(^{17}\text{O}\) NMR at naturally abundant \(^{17}\text{O}\). The value is given in Table 2, it is in good agreement with the value of Alei 1.

By \(^{35}\text{Cl}\) NMR the coupling between \(^{17}\text{O}\) and \(^{35}\text{Cl}\) was not observed though a signal-to-noise ratio of 6400 was achieved. Enriched samples in \(^{17}\text{O}\) 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 \(^1\text{H}\) or \(^{19}\text{F}\) (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 \( J(A - B)/\gamma_A \gamma_B^{1/2} \) with the atomic number of \(B^{17-20}. \gamma_A, \gamma_B \) are the gyromagnetic ratios of the respective nuclei.

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**Table 2. Spin-spin coupling constants between \(^{17}\text{O}\) 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 \(^{17}\text{O}\) NMR. The underlined isotope designates the nucleus which has been used to determine the coupling constant.

<table>
<thead>
<tr>
<th>Oxyanion</th>
<th>Quadrupolar nuclei X</th>
<th>( J(^{17}\text{O} - ^{57}\text{X}) ) in Hz</th>
<th>( J(^{17}\text{O} - ^{35}\text{X}) ) in Hz</th>
<th>( J(^{17}\text{O} - ^{37}\text{X}) ) in Hz (known values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{ClO}_4^{-})</td>
<td>(^{35,37}\text{Cl})</td>
<td>81.4 ± 4.0</td>
<td></td>
<td>85.5 ± 0.5 (Ref. 1)</td>
</tr>
<tr>
<td>(\text{VO}_4^{2-})</td>
<td>(^{51}\text{V})</td>
<td>61.6 ± 2.5</td>
<td>63 ± 5</td>
<td></td>
</tr>
<tr>
<td>(\text{CrO}_4^{2-})</td>
<td>(^{53}\text{Cr})</td>
<td></td>
<td>10 ± 2</td>
<td></td>
</tr>
<tr>
<td>(\text{MnO}_4^{2-})</td>
<td>(^{55}\text{Mn})</td>
<td>28.9 ± 2.8</td>
<td></td>
<td>30.2 ± 3.0 (Ref. 2)</td>
</tr>
<tr>
<td>(\text{MoO}_4^{2-})</td>
<td>(^{95}\text{Mo})</td>
<td>40.3 ± 0.9</td>
<td>40.5 ± 0.8</td>
<td>40.3 ± 0.2 (Ref. 3)</td>
</tr>
</tbody>
</table>
It is interesting to test whether this empirical rule is valid only for $^1$H 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.

**Acknowledgement**

We are indebted to Prof. Dr. H. Krüger for his continuous support of this work. We thank Dr. A. Schwenk for helpful discussions and the Deutsche Forschungsgemeinschaft for financial support.