Oxygen Isotope Effects in ^{55}Mn and ^{95}Mo NMR Spectra of the Permanganate and Molybdate Ion

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By Fourier transform NMR spectroscopy the ^{55}Mn and ^{95}Mo resonance lines in the different permanganate and molybdate species $\text{Mn}^{16}\text{O}_4-n^{18}\text{O}_n^-$ and $\text{Mo}^{16}\text{O}_4-n^{18}\text{O}_n^{2-}$ ($n = 0, 1, 2, 3, 4$) have been resolved in aqueous solutions of potassium permanganate and sodium molybdate. An isotopic effect on the Larmor frequency for ^{55}Mn of $(0.59 \pm 0.02)\text{ppm}$ and for ^{95}Mo of $(0.25 \pm 0.01)\text{ppm}$ to lower frequency has been found for the substitution of one ^{16}O atom by one ^{18}O atom. The relaxation rates $1/T_1$ of ^{55}Mn in the different lines of the permanganate solution are equal within the limits of error. The oxygen exchange rate for the water-permanganate system has been evaluated.

Introduction

Modifications of the chemical environment of a nucleus under observation result in changes of the Larmor frequency and of the relaxation rates. Such a modification can be obtained for instance by substituting other ligands, by changing the oxidation state or by choosing other solvents. Investigations of these effects are known for both nuclei ^{55}Mn (Ref. ^{1–3}) and ^{95}Mo (Ref. ^{4–6}). It is a very interesting question, whether isotopic substitution — the minimum modification of a molecule — affects the Larmor frequency or the relaxation rates.

Intramolecular isotopic effects on the Larmor frequency induced by the replacement of protons by deuterons are well known for many nuclei ^{7–10}, but an effect induced by heavier nuclei has been observed only in the NMR spectra of ^{13}C (Ref. ¹¹), ^{19}F (Ref. ^{12–14}), and ^{59}Co (Ref. ^{15, 16}). Preliminary measurements of ^{55}Mn are published in Reference ¹⁷. The effect is usually smaller than 1 ppm and can be observed only for nuclei in compounds which yield very small linewidths.

The nuclei ^{55}Mn and ^{95}Mo have narrow lines in their tetrahedral oxyanions. On the other hand large chemical shifts are observable for both nuclei if the chemical environment is changed. Hence it has been of great promise to investigate ^{55}Mn in MnO_4^- and ^{95}Mo in MoO_4^{2-} under high resolution conditions. From the investigation of the scalar spin-spin coupling constants between ^{95}Mo and ^{17}O and between ^{55}Mn and ^{17}O (Ref. ¹⁸) it is known, that an exchange

between the oxygen of the solvent and the solute occurs, but it is also known, that this exchange is slow compared to the coupling constant. Otherwise no well resolved spectra could have been observed. That means, that only a few molecules change their isotopic composition during the measuring time of about 1 sec.

Further the spectra showing the scalar spin-spin coupling in Ref. ¹⁸ seem systematically asymmetrical, indicating an intramolecular isotopic effect. But so far only the spectra of ^{55}Mn in permanganate and of ^{95}Mo in molybdate yielded well resolved spectra so that a splitting due to an isotopic effect could be observed.

In the following we report on these oxygen isotope effects.

Experimental

The ^{55}Mn and ^{95}Mo NMR spectra were observed at 2.11 T with a multinuclei Bruker spectrometer SXP 4–100 MHz in rotating spherical samples of 10 mm outer diameter at $(300 \pm 2)\text{K}$. The magnetic field was externally stabilized by the B-SN 15. The free induction decays were accumulated and Fourier transformed by the Bruker BNC 12 data unit.

^{95}Mo has a spin 5/2, the Larmor frequency in the given field is 5.865 MHz and the receptivity is 2.9 compared with 1 for ^{13}C . The corresponding data for ^{55}Mn are: $I = 5/2$, Larmor frequency: 22.311 MHz and receptivity: 1000.

The isotopic substitution was performed by dissolving naturally abundant permanganate or molybdate in water, enriched in ^{17}O or ^{18}O . In these solutions an exchange of the oxygen between the water and the oxyanions occurs.

The relaxation rate of ^{55}Mn was measured using the inversion recovery method¹⁹.

Positive values of the chemical shift mean shifts to higher frequencies at constant magnetic field.

Results and Discussion

a) ^{55}Mn Isotopic Shift in Permanganate

In Figure 1 the ^{55}Mn spectrum of a 0.4 molal solution of naturally abundant KMnO_4 in enriched H_2O (61.4% ^{16}O , 10.9% ^{17}O , and 27.7% ^{18}O) is

Fig. 1. ^{55}Mn spectrum of a 0.4 molal solution of natural abundant KMnO_4 in H_2O (61.4% ^{16}O , 10.9% ^{17}O , 27.7% ^{18}O) half a year after the preparation of the sample at 22.311 MHz. Starting from the right the different lines are due to the permanganate ions $\text{Mn}^{16}\text{O}_{4-n}\text{O}_n^-$ ($n = 0, 1, 2, 3$). The magnified spectrum shows the unresolved multiplet of the scalar spin-spin coupling between ^{55}Mn and ^{17}O . — *Experimental parameters*: excitation frequency: 22.310830 MHz; experimental spectrum width: 1000 Hz; plotted spectrum width: 233 Hz; pulse repetition frequency: 1.67 Hz; number of pulses: 100; measuring time: 1 min; rotating spherical sample with 10 mm outer diameter; 1 K data points were accumulated followed by 7 K of zero-filling before Fourier-transformation.

given at a time half a year after the preparation of the sample. The different lines are due to the permanganate ions $\text{Mn}^{16}\text{O}_{4-n}\text{O}_n^-$ for $n = 0, 1, 2, 3$. A signal for $n = 4$ is not observable. The isotopic effect on the shielding is $-(0.59 \pm 0.02)$ ppm for the substitution of an ^{16}O atom by an ^{18}O atom. This value is in good agreement with an earlier reported one¹⁷.

Because of the contents of the ^{17}O isotope a scalar spin-spin coupling between ^{55}Mn and ^{17}O is observable. The ^{55}Mn spectrum shows no resolved lines of the spin-spin multiplet, as they are smeared out by the isotopic effect, but only a structureless broad

and very weak signal. The frequency separation of the two edges of this signal is about 160 Hz. This is in agreement with the coupling constant $J(^{17}\text{O} - ^{55}\text{Mn}) = (28.9 \pm 2.8)$ Hz, which has been determined by ^{17}O NMR (Ref. 18), if one takes into account the isotopic effect.

In Figure 2 the ^{55}Mn spectrum in a 0.27 molal solution of naturally abundant KMnO_4 in enriched

Fig. 2. ^{55}Mn spectrum of a 0.27 molal solution of natural abundant KMnO_4 in H_2O (enriched 99% in ^{18}O) measured 95 days after preparation. Starting from the right the different lines are due to the permanganate ions $\text{Mn}^{16}\text{O}_{4-n}\text{O}_n^-$ ($n = 1, 2, 3, 4$). — *Experimental parameters*: excitation frequency 22.310800 MHz; experimental spectrum width: 1000 Hz; plotted spectrum width: 300 Hz; pulse repetition frequency: 1 Hz; number of pulses: 100; measuring time: 100 sec; rotating spherical sample with 10 mm outer diameter; 1 K data points were accumulated followed by 7 K of zero-filling before Fourier-transformation.

H_2O (1% ^{16}O , 99% ^{18}O) is given, which was observed 95 days after the preparation of the sample. The oxygen isotopes are not statistically distributed. Because of the isotopic composition of the sample nearly all permanganate ions will contain four ^{18}O isotopes in the final stage. The development of the distribution of the different oxygen atoms with time can be described in analogy to the differential equations of radioactive series. Until now the following values of the mean-life were evaluated: $\tau_{0,1} = (6.5 \pm 0.8)$ days, $\tau_{1,2} \approx 32$ days, $\tau_{2,3} \approx 80$ days. The values of $\tau_{1,2}$ and $\tau_{2,3}$ are estimated values, for $\tau_{3,4}$ no value can be given until now. A 0.33 molal sample prepared in the same solvent but with another KMnO_4 solute gives very different time constants: $\tau_{0,1}$ can be estimated to be 54 days. The origin of this effect is not yet known but will be studied in more detail.

b) ^{95}Mo Isotopic Shift in Molybdate

In Figure 3 two different spectra of ^{95}Mo are given. The upper one was found in a 1 molal solution of naturally abundant Na_2MoO_4 in enriched H_2O (61.4% ^{16}O , 10.9% ^{17}O and 27.7% ^{18}O). By addition of a small amount of NaOH the solution

Fig. 3. ^{95}Mo spectra of natural abundant Na_2MoO_4 . a) 1 molal solution in H_2O (61.4% ^{16}O , 10.9% ^{17}O , 27.7% ^{18}O). — b) 0.87 molal solution in D_2O (72.5% ^{18}O , 27.5% ^{16}O). The different lines are due to the molybdate ions $\text{Mo}^{16}\text{O}_{4-n}\text{O}_n^{2-}$, the indices n are given in the figure for each line. — Experimental parameters: excitation frequency: 5.865278 MHz; experimental spectrum width 500 Hz; plotted spectrum width: 35 Hz; pulse repetition frequency: 0.33 Hz; number of pulses: 500; measuring time: 25 min; rotating spherical sample with 10 mm outer diameter; 1 K data points were accumulated followed by 15 K of zero-filling before Fourier-transformation.

was made basic. This sample was used to measure the scalar spin-spin coupling constant between ^{17}O and ^{95}Mo (Reference ¹⁸). In the nonrotating sample a central line with a linewidth of 5.5 Hz was found. Sample rotation reveals a fine structure, which is due to the isotopic composition of the molybdate ions $\text{Mo}^{16}\text{O}_{4-n}\text{O}_n^{2-}$ for $n = 0, 1, 2, 3, 4$. The ions which contain ^{17}O isotopes make no contribution to the

central line because of the scalar spin-spin coupling. From the given isotopic composition of the solution one can calculate the probabilities p_n for the occurrence of the different ions assuming statistically distributed oxygen isotopes: $p_0 : p_1 : p_2 : p_3 : p_4 = 0.23 : 0.41 : 0.28 : 0.08 : 0.01$. The ratios of the measured intensities differ from this calculation. Because of the overlapping lines these intensities must be corrected. It was assumed, that the lineshapes of the different lines are Lorentzian with the same linewidth. An estimated linewidth was used to calculate the contribution of the different lines to the neighbouring lines. The ratios of the corrected intensities I_n are: $I_0 : I_1 : I_2 : I_3 = 0.23 : 0.41 : 0.31 : 0.12$. The intensity I_4 is comparable to the noise and was not evaluated. By the adjustment $I_1 = p_1$ one gets amounts of the probabilities p_n and of the intensities I_n which are in good agreement. So the oxygen isotopes are statistically distributed. The ^{95}Mo NMR signal of the molybdate ion shows an isotopic effect on the magnetic shielding of $-(0.25 \pm 0.01)$ ppm, if a ^{16}O is replaced by a ^{18}O .

This isotopic effect was observed about half a year after the preparation of the sample. To get some information about the time constant of the exchange, another sample was prepared: a 0.87 molal solution of naturally abundant Na_2MoO_4 in enriched D_2O (72.5% ^{18}O and 27.5% ^{16}O). By addition of NaOH a p_D value of 11.5 ± 0.5 was achieved. The ratios of the probabilities of the different ions in this sample are:

$$p_0 : p_1 : p_2 : p_3 : p_4 = 0.02 : 0.12 : 0.32 : 0.37 : 0.16.$$

The NMR signal of ^{95}Mo in this sample was measured immediately after the preparation. The spectrum, which is given in the lower half of Fig. 3 was observed. The ratio of the corrected intensities is: $I_1 : I_2 : I_3 : I_4 = 0.16 : 0.35 : 0.37 : 0.17$. The probabilities and intensities were adjusted by $p_3 = I_3$. Further measurements at later times gave no change of the intensities. One recognizes, that the oxygen isotopes are statistically distributed after a time less or equal 5 minutes. The isotopic effect on the shielding is again $-(0.25 \pm 0.01)$ ppm, if a ^{16}O is replaced by a ^{18}O . The different position of the two patterns in Fig. 3 is due to the solvent isotope effect and due to the dependence of the Larmor frequency on the concentration of the solutions ⁵. The isotopic composition of the solvent has no influence on the intramolecular isotopic effect in the NMR spectrum of ^{95}Mo in molybdate.

c) ^{55}Mn Nuclear Relaxation Rate in Permanganate

In a further experiment the longitudinal relaxation rates of ^{55}Mn in the 0.27 molal solution of naturally abundant KMnO_4 in enriched H_2O (1% ^{16}O and 99% ^{18}O) were measured 35 days after the preparation of the sample. The results are given in Figure 4. By a semilogarithmic plot one gets the following values:

$$(1/T_1)_0 = (11.9 \pm 1.2) \text{ sec}^{-1},$$

$$(1/T_1)_1 = (11.9 \pm 1.2) \text{ sec}^{-1},$$

$$(1/T_1)_2 = (12.3 \pm 1.2) \text{ sec}^{-1},$$

$$(1/T_1)_3 = (12.3 \pm 1.2) \text{ sec}^{-1},$$

$$(1/T_1)_4 = (13.9 \pm 1.4) \text{ sec}^{-1}.$$

The error was assumed to be 10%. It was tried to correct the intensities as described for the ^{95}Mo spectra. As the resolution in the spectra becomes

Fig. 4. ^{55}Mn inversion recovery Fourier transform spectra in a 0.27 molal solution of natural abundant KMnO_4 in H_2O (enriched 99% in ^{18}O) measured 35 days after preparation. Starting from the right the different lines are due to the permanganate ions $\text{Mn}^{16}\text{O}_4 - n^{18}\text{O}_n^-$ ($n = 0, 1, 2, 3, 4$). On the left the waiting time between the 180° and 90° pulse is given. — *Experimental parameters*: excitation frequency: 22.310700 MHz; experimental spectrum width: 1000 Hz; plotted spectrum width: 150 Hz; $180^\circ - 90^\circ$ -sequence repetition frequency: 0.5 Hz; number of pulses for each spectrum: 100; rotating spherical sample with 10 mm outer diameter; 1 K data points were accumulated followed by 7 K of zero-filling before Fourier-transformation.

worse in course of time, one has to choose different linewidths and lineshapes for each spectrum. Supposing Lorentzian lineshapes with equal linewidths for all spectra one gets changes in the relaxation rates. The assumed error is greater than 50% of these changes.

One can conclude, that if the relaxation rate of ^{55}Mn in the permanganate is dominated by quadrupole relaxation processes, the field gradient at the ^{55}Mn nucleus is only slightly changed by the substitution of an ^{16}O by an ^{18}O .

At 8.0 MHz Broze and Luz²⁰ have measured the relaxation rate of ^{55}Mn in MnO_4^- and found a value of $(19.0 \pm 1.9) \text{ sec}^{-1}$.

Conclusions

Intramolecular isotope effects due to small changes of the isotopic masses have been seldom observed^{11–17}. Extremely high resolution as in the case of ^{13}C (Ref. 11) or nuclei which show large chemical shifts^{12–17} are necessary.

A relatively good chance for detecting isotope effects exists obviously for the transition metal elements like ^{55}Mn (Ref. 17), ^{59}Co (Ref. 15, 16) and ^{95}Mo . The effects are usually smaller than 1 ppm, for ^{59}Co in the hexacyanocobaltate ion the carbon induced effect is 0.914 ppm per mass unit and the nitrogen induced effect amounts only to 0.197 ppm per mass unit. In the tetraoxanions of ^{55}Mn and ^{95}Mo the oxygen induced isotope effect is 0.295 ppm and 0.125 ppm per mass unit respectively. In all these cases the Larmor frequency of the central nucleus decreases with increasing mass of the ligands. Further if the NMR lines of the different molecular species are resolvable they are found to be equidistant.

For an estimation of the size of the isotope effect of ^{55}Mn in permanganate one can follow the treatise of Lauterbur¹⁵, who tried to calculate the ^{13}C induced isotope effect in ^{59}Co by considering the effects of changes in vibrational energies of the ground and excited electronic states of the hexacyanocobaltate ion. As a result of our calculation we get with data of Ref. 1, 15, 21–26 for the oxygen induced isotope effect in the $\text{Mn}^{18}\text{O}_4^-$ relative to the $\text{Mn}^{16}\text{O}_4^-$ ion a value of -7 ppm , which has to be compared with the experimental one of -2.4 ppm . The agreement is satisfactory, if one takes into account the uncertainties of the input data. A more detailed treatment will be compiled.

The ^{18}O isotope effect in oxyanions seems to be an interesting and very sensitive phenomenon for evaluating oxygen exchange rates in water-oxyanion systems. Further investigations in this field are running.

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