^{53}Cr Fourier Transform Nuclear Magnetic Resonance Studies

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In various alkali chromate solutions in H_2O and D_2O the dependence of the Larmor frequency of ^{53}Cr on the concentration of the solutions was measured by Fourier transform NMR and a large solvent isotope effect on the chemical shift of ^{53}Cr was found. Further in potassium chromate solutions the chemical shifts of ^{39}K were observed and in a 2.2 molal solution of K_2CrO_4 in D_2O a ratio of the Larmor frequencies of ^{53}Cr and of ^{39}K was measured with high accuracy. Using the concentration dependence of the Larmor frequencies of ^{53}Cr and of ^{39}K, an extrapolated ratio $\nu(^{53}Cr)/\nu(^{39}K)_{\text{extrapol.}}$ in infinitely diluted K_2CrO_4 in D_2O is given. From this ratio a value of the magnetic moment of ^{53}Cr in the chromate ion is derived.

In chromium hexacarbonyl the ^{53}Cr signal was observed and the chemical shift is given.

I. Introduction

Using the Fourier-Transform NMR method [1, 2] systematic investigations of nearly all stable isotopes with a nuclear spin are possible, also of the isotopes of the transition elements in their diamagnetic compounds. For transition elements usually very large chemical shifts are observed [3] and, since most of the isotopes have quadrupole moments, the linewidths have a large range, f.e. in Mn compounds [4]. Therefore one of the first problems is to choose an appropriate reference compound.

To proceed with NMR investigations in different groups of the periodic table we have studied ^{53}Cr NMR signals. The 9.5% naturally abundant ^{53}Cr is the only chromium isotope which has a nonzero spin $I=3/2$. In a 1 molal solution of K_2CrO_4 in H_2O the relative sensitivity of ^{53}Cr is $7.9 \cdot 10^{-7}$ compared with 1 for the proton NMR signal in this solution without considering the relaxation times. This is the reason that for ^{53}Cr only a few NMR measurements are known [5–11]. The magnetic moment of ^{53}Cr in the chromate ion was determined in two different experiments in 1953 [5, 6]. Woonton and Dyer [7] got a value of the magnetic moment of ^{53}Cr in a MgO crystal by an ENDOR experiment. The accuracy of these magnetic moments is about $1 \cdot 10^{-4}$ or worse. By comparing the intensity of the ^{53}Cr NMR signal in a Na_2CrO_4 solution with the intensity of the ^{2}H signal in D_2O Halbach [8] verified, that the nuclear spin of ^{53}Cr is 3/2.

In an other ^{53}Cr NMR experiment Egozy and Loewenstein [9] measured the exchange rate in the chromate-dichromate system. Further Barnes and Graham [10, 11] determined the Knight shift of ^{53}Cr in pure chromium metal and in V – Cr alloys, relative to the Na_2CrO_4 solution given in Reference 6.

In this work the dependence of the Larmor frequency of ^{53}Cr on the concentration of diverse alkali chromates in H_2O and D_2O was investigated. The chemical shift of ^{53}Cr in chromium-hexacarbonyl in tetrahydrofuran was determined and the NMR signals of ^{53}Cr of some various chromate-dichromate systems were observed. Further a ratio of the Larmor frequencies of ^{53}Cr and of ^{39}K in a K_2CrO_4 solution was measured. By these results a new value of the magnetic moment of ^{53}Cr in a $CrO_4{}^{2-}$ ion surrounded only by water molecules can be given. Solutions of Na_2CrO_4 or K_2CrO_4 are proposed as reference standards for the ^{53}Cr NMR investigations.

II. Experimental

The ^{53}Cr measurements were done with a commercial multinuclei Bruker pulse spectrometer SXP 4-100 in a magnetic field of 2.1 T produced by a Bruker 15″ magnet system. The magnetic field was externally stabilized by the Bruker NMR stabilizer B-SN 15. The free induction decays of ^{53}Cr and of ^{39}K were accumulated and Fourier transformed by the Bruker BNC 12 computer.

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The Larmor frequency of ^{53}Cr was approximately 5.0875 MHz, that of ^{39}K about 4.1999 MHz. Both Larmor frequencies can be observed with the described spectrometer by retuning without apparative alterations.

The ratio of the Larmor frequencies $\nu(^{53}\text{Cr})/\nu(^{39}\text{K})$ was measured in a 2.2 molal K_2CrO_4 solution in D_2O in a rotating cylindrical sample tube of 10 mm outer diameter. Most of the chemical shift measurements were performed in nonrotating cylindrical tubes (10 mm outer diameter). Only for the measurements of K_2CrO_4 solutions in D_2O nonrotating cylindrical and spherical tubes of 10 mm outer diameter were used.

The temperature was (299 ± 2) K.

Signal-to-noise ratios of about 40 were achieved for ^{53}Cr within 5 minutes of measuring time and for ^{39}K signal-to-noise ratios of 100 within about 1 minute in the 2.2 molal K_2CrO_4 solution in D_2O. A typical absorption curve is given for ^{53}Cr in Figure 1.

The linewidths were about 11 Hz for ^{53}Cr and 12 Hz for ^{39}K in this solution.

The chemical shift is given by $\delta = \nu_{\text{sample}} - \nu_{\text{reference}}$, a positive value means a shift to higher frequency at a constant field.

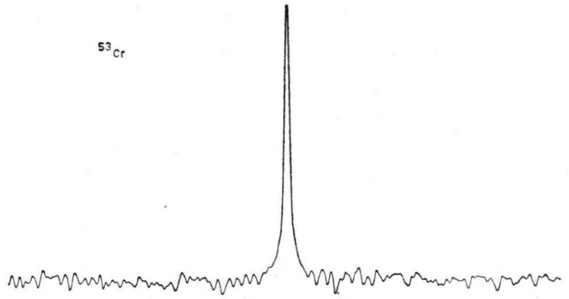

Fig. 1. Absorption signal of ^{53}Cr in a 2.2 molal solution of K_2CrO_4. Larmor frequency: 5.087 519 MHz, line width: 11 Hz, spectrum width: 1000 Hz, pulse repetition frequency: 3.3 Hz, accumulation time: 5 min, number of pulses: 1000, rotating cylindrical sample: 10 mm outer diameter, sample volume: 1.5 ml.

III. Results and Discussion

a) Chemical shifts of ^{53}Cr in aqueous solutions of alkali chromates

The dependence of the Larmor frequency of ^{53}Cr on the concentration of the alkali chromates in aqueous solutions, excepted the lithium chromate because of its small solubility in water, has been investigated. The results are given in Figure 2.

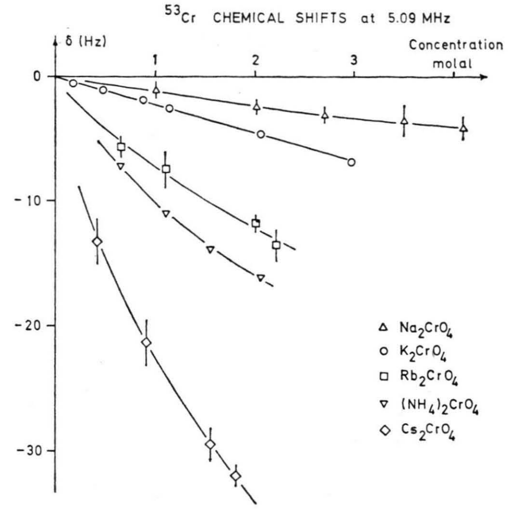

Fig. 2. Chemical shifts of ^{53}Cr in diverse aqueous solutions of chromium salts as a function of concentration. Cylindrical samples of 10 mm outer diameter were used. The shifts are referenced to the extrapolated frequency of the infinite dilution resonance of ^{53}Cr in the chromate ion for water. No bulk susceptibility corrections were made.

The shifts are referenced to the extrapolated frequency of the infinite dilution resonance of ^{53}Cr for H_2O. Increasing the concentration of the solutions one gets shifts to lower frequencies. Further the amount of the shifts is increasing in the sequence of the cations: Na^+, K^+, Rb^+, NH_4^+, Cs^+.

Comparing these results with measurements at other nuclei in oxy-anions one finds a similar behaviour in the case of ^{35}Cl in ClO_4^- [12] and of ^{55}Mn in MnO_4^- [13]. Because of the small sensitivity of the ^{33}S [14] and of the ^{183}W NMR signal [15] the accuracy of the results in the corresponding oxy-anions SO_4^{2-} and WO_4^{2-} is too small to show differences of the Larmor frequencies in solutions containing different alkali cations.

For getting the influence of the bulk susceptibility the chemical shifts of K_2CrO_4 in D_2O have been measured as well in spherical as in cylindrical sample tubes. The results are given in curve c and b of Figure 3. The Larmor frequency in a spherical tube is shifted to lower frequency and the gradient is a little smaller than in the cylindrical sample tubes. But there is still a dependence of the Larmor frequency of ^{53}Cr on the concentration of the K_2CrO_4 solution. It seems reasonable, to take solutions of Na_2CrO_4 or K_2CrO_4 in H_2O as reference standards for further ^{53}Cr NMR investigations, because in these solutions only small chemical shifts must be taken into consideration and because in these solutions relatively strong and small NMR signals can be achieved.

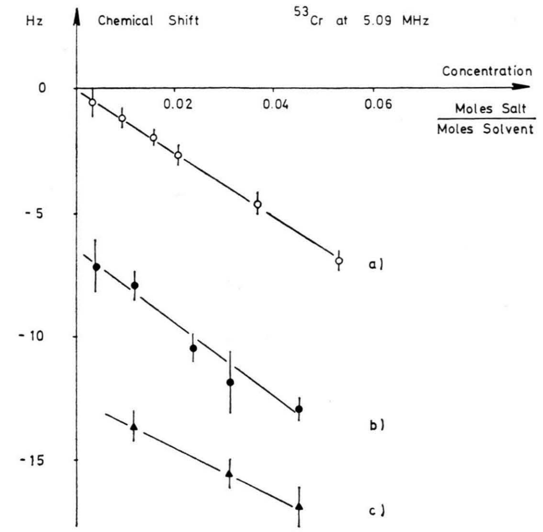

Fig. 3. Chemical shifts of ^{53}Cr in different potassium chromate solutions as a function of concentration. The measurements of the curves a and b were performed in cylindrical samples of 10 mm outer diameter in H_2O respectively in D_2O. The points of curve c were measured in spherical samples of 10 mm outer diameter. The shifts are referred to the Larmor frequency of ^{53}Cr in the chromate ion surrounded only by H_2O molecules.

b) Solvent Isotope Effect

The Larmor frequency of a nucleus in aqueous solutions usually depends on the isotopic composition of the solvent. Curves a and b of Fig. 3 show the difference of the Larmor frequencies of solutions of K_2CrO_4 in H_2O and D_2O for cylindrical sample tubes. This difference of the Larmor frequencies depends only a little on the concentration of the solution and one gets for infinitely diluted solutions: $[\nu(^{53}\text{Cr in } D_2O)/\nu(^{53}\text{Cr in } H_2O)] - 1 = (1.3 \pm 0.3)$ ppm. This solvent isotope effect shows a negative sign, as it is usually observed[16], and the amount is comparable with the solvent isotope effect of ^{55}Mn in $KMnO_4$ solutions[13].

c) Chromate-Dichromate System

The linewidths of ^{53}Cr in aqueous alkali chromate solutions are in the range of $10-15$ Hz and depend only slightly as well on the CrO_4^{2-} concentration as on the alkali cations, but the linewidths are very sensitive to variations of the p_H-value: The p_H-value of a 2 molal solution of K_2CrO_4 is about 9. If acid is added, $Cr_2O_7^{2-}$ is formed and the observed linewidth is increasing to a value of 80 Hz for $p_H = 6.9$. The ^{53}Cr NMR line in a 2 molal $Na_2Cr_2O_7$-solution ($p_H = 3.5$) was not detected. Similar results were found by Egozy and Loewenstein[9]. A remarkable shift of the Larmor frequency was not observed in solutions with different p_H-values.

d) Chemical Shift of ^{53}Cr in chromium-hexacarbonyl

The ^{53}Cr signal has been found not only in the oxidation state $+6$ in the CrO_4^{2-} ion but also in the oxidation state 0 in the $Cr(CO)_6$ compound. In Figure 4 an absorption signal of ^{53}Cr in this compound is given. The chemical shift of a 0.14 molal solution in tetrahydrofuran relative to the chromate ion in infinite dilution in H_2O is $-(1795 \pm 3)$ ppm. Measurements of other chromium complexes are running.

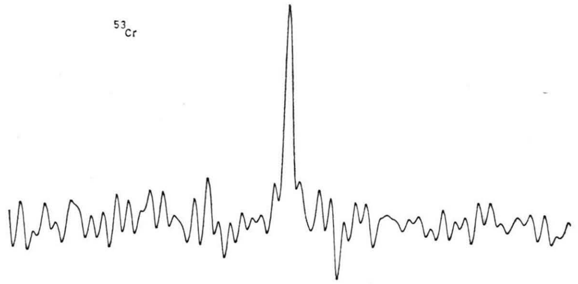

Fig. 4. Absorption signal of ^{53}Cr in a 0.14 molal $Cr(CO)_6$ solution in tetrahydrofuran. Larmor frequency: 5.078 290 MHz, line width: 17 Hz, spectrum width: 1000 Hz, pulse repetition frequency: 10 Hz, accumulation time: 3.3 h, number of pulses: 120 000, cylindrical sample of 10 mm outer diameter, sample volume: 1.5 ml.

e) ^{39}K chemical shifts in K_2CrO_4 aqueous solutions

In the case of the ^{39}K resonance lines a nearly linear dependence of the Larmor frequency on the concentration of solutions of K_2CrO_4 in D_2O was found in cylindrical sample tubes. Relative to an infinitely diluted K_2CrO_4 solution the 2.2 molal solution, used for the measurements of the ratio of the Larmor frequencies $\nu(^{53}\text{Cr})/\nu(^{39}\text{K})$, showed a chemical shift of $-(8 \pm 1)$ Hz. By measuring the Larmor frequency of the standard probe * of Ref.[17], one

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* We thank Dr. W. Sahm and Dr. A. Schwenk for their ^{39}K standard sample, a 32 molal KNO_2 in H_2O.

finds, that the ^{39}K Larmor frequency in diluted K_2CrO_4 in D_2O is the same as that given for other infinitely diluted potassium solutions in D_2O in Reference 17. Bloor and Kidd[18] found a linear dependence of the Larmor frequency of ^{39}K in K_2CrO_4 of -0.25 ppm per moles $K^+/1000$ g solvent on the concentration. The result reported in this paper shows a negative sign too, but the amount is greater: $-(0.43 \pm 0.05)$ ppm per moles $K^+/1000$ g solvent.

f) Ratio of the Larmor frequencies of ^{53}Cr and ^{39}K

In a 2.2 molal solution of K_2CrO_4 in D_2O 63 measurements of the ratio of the Larmor frequencies $\nu(^{53}\mathrm{Cr})/\nu(^{39}\mathrm{K})$ were carried out on 4 different days.

The result is:

$$\nu(^{53}\mathrm{Cr})/\nu(^{39}\mathrm{K}) = 1.211\,327\,80(22).$$

The error is two times the standard deviation.

With the determined chemical shifts of ^{53}Cr $\delta = -(6 \pm 1)$ Hz and of ^{39}K $\delta = -(8 \pm 1)$ Hz in cylindrical sample tubes relative to an infinitely diluted K_2CrO_4 solution in D_2O one gets an extrapolated ratio of the Larmor frequencies:

$$\nu(^{53}\mathrm{Cr})/\nu(^{39}\mathrm{K})_{\mathrm{extrapol.}} = 1.211\,326\,92(42).$$

The additional error is due to the uncertainty of the extrapolation to zero concentration.

g) Magnetic moment of ^{53}Cr in the chromate ion

From the ratio $\nu(^{53}\mathrm{Cr})/\nu(^{39}\mathrm{K})_{\mathrm{extrapol.}}$ and with the aid of the ratios $\nu(^{39}\mathrm{K}^+ \text{ in } D_2O)/\nu(^2\mathrm{H})_{\mathrm{extrapol.}} = 0.303\,984\,80(10)$ given in Ref. 17 and $\nu(^2\mathrm{H})/\nu(^1\mathrm{H}) = 0.153\,506\,083(60)$ of[19] a ratio

$$\nu(^{53}\mathrm{Cr})/\nu(^1\mathrm{H}) = 0.056\,524\,773(34)$$

can be given.

Using this ratio and the value of the magnetic moment of the proton in H_2O $\mu_P = 2.792\,7740(11)$ μ_N of[20] one can derive a magnetic moment of ^{53}Cr in the CrO_4^{2-} ion. One gets $|\mu(^{53}\mathrm{Cr} \text{ in } CrO_4^{2-} \text{ in } D_2O)| = 0.473\,582\,75(34)\,\mu_N$. This magnetic moment is not corrected for the diamagnetism due to the electrons.

The two known values of $\mu(^{53}\mathrm{Cr})$ determined by NMR in the chromate ion have the same size of the magnetic moment but with different accuracy of $1.3 \cdot 10^{-4}$ (see [6]) and $1.5 \cdot 10^{-4}$ (see [5]). Only the latter value is in agreement with our result. By the ENDOR technique an other value of the magnetic moment of ^{53}Cr in a MgO crystal was determined: $\mu(^{53}\mathrm{Cr}) = -0.4751(5)\,\mu_N$ (see [7]). The difference of this value and the value given above is $(3.2 \pm 1.0) \cdot 10^{-3}$ and can be ascribed to the chemical shift due to the different chemical surroundings.

But this difference is much smaller than the difference between the magnetic moment of ^{55}Mn determined by NMR in MnO_4^- (see [13]) and of $^{55}Mn^{2+}$ determined by ENDOR[21].

Acknowledgement

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