Precision Measurements of Magnetic Moments of Nuclei with weak NMR Signals

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Two NMR spectrometers were combined and a special probe assembly was constructed in order to enable a simultaneous measurement of the signals of ^{2}H and any nucleus, the gyromagnetic ratio of which is $<1.4\cdot10^7\ \mathrm{T^{-1}\,sec^{-1}}$. The Larmor frequencies of ^{39}K, ^{73}Ge, and ^{109}Ag in well defined samples were referred very accurately to the resonance of ^{2}H in D_2O. It was possible now, to refer the Lamor frequencies of the nuclei ^{41}K, ^{57}Fe, ^{87}Sr, ^{107}Ag, ^{183}W, ^{187}Os, which were previously referred to the resonance of one of the nuclei mentioned above, to the Larmor frequencies of the deuteron and the proton in D_2O or H_2O.

The magnetic moments of all these nuclei are given.

1. Introduction

The gyromagnetic ratio of all nuclei reported in this work are $\gamma<1.4\cdot10^7\ \mathrm{T^{-1}\,sec^{-1}}$, i. e. the Larmor frequencies are below 4 MHz in our field $B_0\approx$ 1.807 Tesla. In this range of Larmor frequencies there is no standard nucleus, i. e. a nucleus the Larmor frequency of which has been referred to that of the proton with an uncertainty of less than 1 ppm. The resonance frequencies of all standard nuclei are essentially higher, e. g. the deuteron has a Larmor frequency of 11.8 MHz in our field.

A few years ago in our laboratory a NMR pulse spectrometer was constructed especially for nuclei with extremely weak NMR signals [3]. With this instrument the NMR signals of a number of nuclei were detected for the first time or an accurate Larmor frequency was measured in a well defined sample [1–12].

In order to refer these Larmor frequencies to that of the deuteron, two different NMR spectrometers had to be used [4–6]. Because the nuclei under investigation and the standard nuclei had to be measured alternately, the probe assemblies together with the samples had to be replaced. Considerable systematic errors are caused by this technique: There is no guarantee that the different samples are placed accurately at the same locus in the magnetic field, moreover, the two different probe assemblies are constructed with different diamagnetic materials. Therefore, a slightly different shielding of the field B_0 may result. Fluctuations of the field B_0 in time may cause further uncertainties. These systematic errors taken together are estimated to be about 5 ppm.

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To avoid these uncertainties a probe assembly was developed which enables a simultaneous measurement of the NMR signals of deuterium at 11.8 MHz and of any nucleus in the range 1.4 . . . 4 MHz in the same sample. All sources of uncertainties of the measured ratios of Larmor frequencies as mentioned above are avoided by this technique.

In the following the probe assembly, the two combined spectrometers and the results achieved with this apparatus are described.

2. Experimental

In order to detect the weak NMR signals in the frequency range below 4 MHz our own pulse spectrometer, described in [3], and, for the ^{2}H resonance, the commercial Bruker pulse spectrometer B-KR 322 s were used. This apparatus, originally developed to measure relaxation times, was employed for Fourier-spectroscopy with various nuclei. Both spectrometers use single-coil-arrangements to irradiate the rf field and to receive the NMR signal.

In the Bruker spectrometer the rf signal during the pulse is fed by a 50 Ω coaxial line to the probe assembly. In the probe circuit the rf signal is transformed to high impedance. By pairs of diodes the receiver is decoupled from the probe circuit during the rf pulses as well as the transmitter during the time interval of reception of the NMR signal. The preamplifier for the NMR signal is not switched and, therefore, overdriven during the pulses. It is situated just outside the magnetic field and is connected with the probe assembly by a short coaxial

line, the capacity of which is part of the probe circuit.

In our pulse spectrometer for lower frequencies, the rf signal during the pulse is coupled inductively to the probe circuit. The capacity of the circuit as well as the pulsed transmitter and the gated preamplifier are mounted near the probe assembly and connected by three coaxial lines.

In Fig. 1 a schematic circuit diagram of the combined probe assembly is given. The lines on the left side of this assembly are connected to the Bruker spectrometer, while on the right side there are the connections to our own spectrometer.

The three coils of the probe assembly are wound on three plexiglass cylinders arranged concentrically. To achieve the best filling factor, the inner coil (12 mm ϕ, 6 mm long, 12 windings) is part of the tunable probe circuit of our spectrometer for weak signals. The outer coil (20 mm ϕ, 8 mm long, 18 + 6 windings) belongs to the probe circuit of the Bruker spectrometer, which is tuned to the resonance frequency of ^{2}H (about 11.8 MHz). The excitation coil for the lower frequencies (16 mm ϕ, 7 mm long, 10 windings) is found in the middle. To avoid mechanical resonances – i.e. ringing after rf pulses as described by Clark [13] – the coils are embedded in polyester resin.

Since the two probe circuits are tuned to strongly different frequencies, there is only a weak coupling, and the tuning of one circuit hardly affects the other.

The pulse lengths necessary for a 90-°pulse are e.g. 45 μsec for ^{39}potassium at about 3.6 MHz and 135 μsec for the deuterium resonance (this relatively long time is due to the large volume of the outer probe coil).

The probe assembly is built for samples with a maximum outer diameter of 10 mm. A rotation of the sample up to 250 rps can be achieved with an air turbine.

In Fig. 2 a simplified block diagram of the two combined spectrometers is given. All frequencies for the two rf pulses are deduced from the master oscillator (frequency standard XSB of Rohde & Schwarz), which also drives the pulse generator. Both spectrometers work in almost the same manner: Short rf pulses of the appropriate frequencies (1.4 . . . 4 MHz resp. 11.8 MHz) are generated by two gates and applied to the sample at the same time. Between these pulses the two NMR signals of the nuclei under investigation and the deuterons are received, amplified and mixed with the irradiation frequencies. The amplifiers of the Bruker-spectrometer (left side of the diagram) are overdriven during the rf pulses; they are constructed for fast recovery.

The simultaneously received NMR signals, mixed into the LF range, are transferred via active low pass filters to the time averaging computer (Signal analyzer 5480 A of Hewlett-Packard). The memory of this computer is split into two halves (odd and even channel numbers). In each of these halves the NMR signal of one species of nuclei is stored and summed. For further evaluation, these signals are transferred by punched tape to the computer CDC 3300 of the Zentrum für Datenverarbeitung Tübingen. One gets the Larmor frequencies by calculating the Fourier-transform or the Quadriga Fourier-transform [14].

3. Results

With the apparatus described above the Larmor frequencies of ^{39}K, ^{73}Ge, and ^{109}Ag were referred to that of ^{2}H in D_2O. The results are given in Table 1. The measurement of the ratio of the Larmor frequencies of ^{73}Ge in $GeCl_4$ and of ^{2}H in D_2O was performed with samples contained in rotating

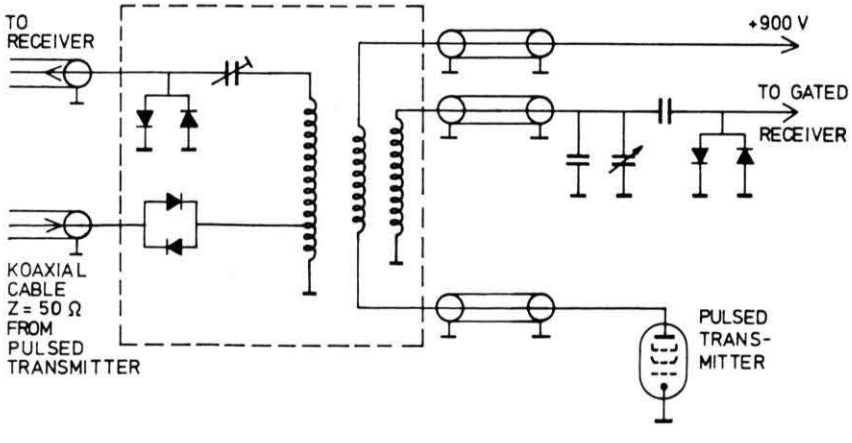

Fig. 1. Circuit diagram of the special probe assembly to be connected to the Bruker spectrometer (left side) and also to our pulse spectrometer for weak NMR signals (right side).

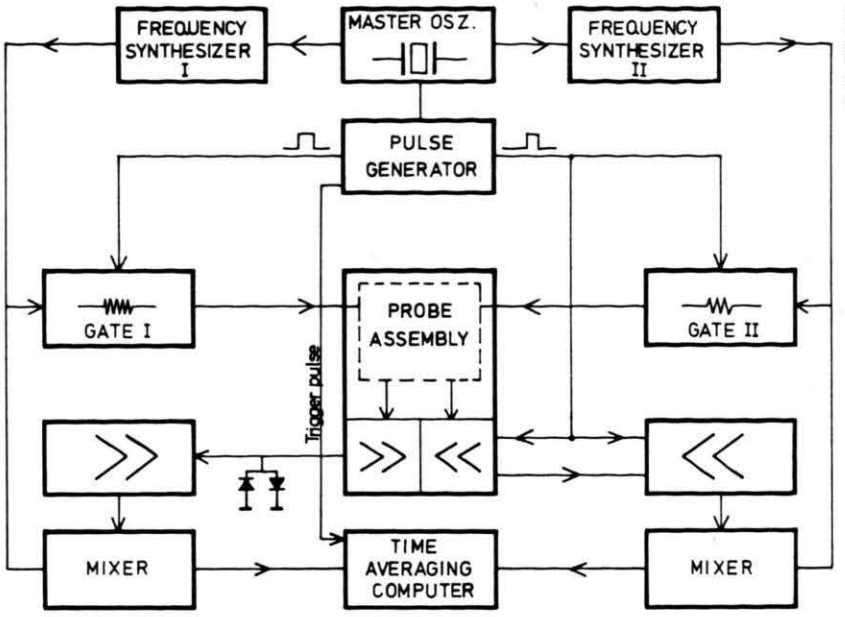

Fig. 2. Block diagram of the apparatus combined by two NMR spectrometers to enable the simultaneous measurement of the Larmor frequencies of two nuclear species.

Tab. 1. In the first three lines the ratios of the Larmor frequencies of ^{39}K, ^{73}Ge, ^{109}Ag and of the deuteron measured with our special apparatus are given. The uncertainties are three times the rms errors. Below, the Larmor frequencies of other nuclei and of other samples are referred to those of the proton and of the deuteron in D_2O and H_2O respectively, on the basis of the results above.

Nucleus x	Sample	$\nu(x)/\nu(^2H)$	$\nu(x)/\nu(^1H)$	$\mu(x)/\mu_N$
^{39}K	31 molal KNO_2 in D_2O	0.303 984 154 (22)		
^{73}Ge	liquid $GeCl_4$	0.227 248 66 (5)		
^{109}Ag	14 molal $AgNO_3$ in a solution of 90 Wt.-% CH_3CN + 10 Wt.-% D_2O	0.303 199 37 (18)		
^{39}K	K^+-ion in aqueous	0.303 984 85 (9)	0.046 663 524 (22)	0.390 952 9 (24)
^{41}K	solution at infinite dilution	0.166 852 92 (9)	0.025 612 938 (18)	0.214 588 4 (13)
^{57}Fe	liquid $Fe(CO)_5$	0.210 921 6 (2)	0.032 377 75 (4)	0.090 421 6 (6)
	1,5 molar $Fe(C_5H_5)_2$ in benzene	0.211 249 2 (3)	0.032 428 04 (5)	0.090 562 1 (6)
^{73}Ge	liquid $GeCl_4$		0.034 884 052 (16)	−0.876 789 (6)
^{87}Sr	ions in aqueous	0.282 321 15 (34)	0.043 338 01 (6)	−1.089 274 (7)
^{107}Ag	solution at infinite dilution	0.263 694 96 (35)	0.040 478 78 (6)	−0.113 045 5 (7)
^{109}Ag		0.303 154 14 (50)	0.046 536 01 (8)	−0.129 961 5 (8)
^{183}W	liquid WF_6	0.271 110 6 (2)	0.041 617 13 (4)	0.116 224 5 (7)
^{187}Os	molten OsO_4	0.148 680 20 (13)	0.022 823 315 (22)	0.063 738 9 (4)

cylinders with an inner diameter of 9 mm. The results were corrected for bulk susceptibility. As the $GeCl_4$ sample does not contain deuterium, the sample replacement technique had to be used. The pulse repetition rate was 0.9 Hz. It was chosen to achieve a total decay of the free precession NMR signal between two consecutive pulses.

For the ^{109}Ag measurements D_2O was used as internal standard. The sample was a 14 molal solution of $AgNO_3$ in a mixture of acetonitrile (90 Wt.% CH_3CN) and D_2O (10 Wt.%).

The NMR signal of this sample is considerably better than the signal of a sample containing Ag^+ ions. The reason for this is the more favourable ratio of the relaxation times T_1/T_2. Therefore this sample (in the following called Ref. 5) was taken as reference for our investigations of silver complexes presently running.

The sample was contained in a cylinder with an internal diameter of 9 mm. Because of the long relaxation times of the ^{109}Ag nucleus the Quadriga-technique [14] had to be used; the pulse repetition rate was 90 Hz.

The ^{39}K measurements are described in detail in Reference [7].

Taking into account the measured chemical shift of the ^{109}Ag resonance frequency in this sample (ref. No. 5) and in the reference sample No. 4 defined in Ref. [8]:

$$(\nu_{\text{ref. 5}} - \nu_{\text{ref. 4}})/\nu_{\text{ref. 4}} = (196.7 \pm 1) \text{ ppm},$$

the shift between the reference sample No. 4 and the Ag^+ ion in H_2O at infinite dilution [8] and also the chemical shift of the ^{2}H resonance in the sample ref. No. 5 and in pure D_2O

$$(\nu_{\text{ref. 5}} - \nu_{D_2O})/\nu_{D_2O} = 0.45\,(6) \text{ ppm},$$

the ratio of the Larmor frequencies of the $^{109}Ag^+$ ion surrounded solely by H_2O molecules and of ^{2}H in pure D_2O can be calculated.

The ratio $\nu(^{109}\text{Ag})/\nu(^2\text{H})$ given in Table 1 is a weighted mean value of this result and the value calculated with the ratios $\nu(^{109}Ag^+)/\nu(^{73}\text{Ge})$ of Ref. [8] and $\nu(^{73}\text{Ge})/\nu(^2\text{H})$ of the present work.

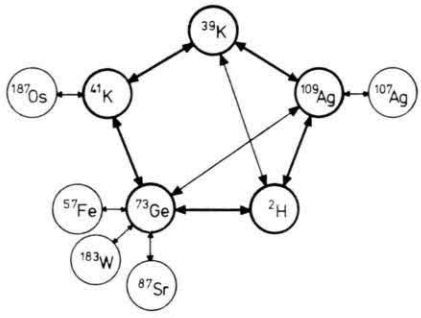

Fig. 3. Scheme of the measured ratios of Larmor frequencies of nuclei with weak NMR signal. Each pair of nuclei under investigation is linked by an arrow. The resonances of all nuclei pointed out in the inner pentagon are referred to the resonance of ^{2}H in more than one way, to prove the consistency of all measurements.

From previous work, accurate ratios of the Larmor frequencies of ^{39}K and ^{41}K [7], of ^{187}Os and ^{41}K [3], as well as of ^{107}Ag and ^{109}Ag [8] are known. The resonance frequencies of ^{57}Fe [9, 10], ^{87}Sr [11], and ^{183}W [13] are referred to that of ^{73}Ge. From these values and the results of the present measurements, the ratios of the Larmor frequencies of all nuclei mentioned above and that of the deuteron in D_2O can be calculated according to the scheme of Figure 3.

Using the ratio of the Larmor frequencies

$$\nu(^2\text{H in } D_2O)/\nu(^1\text{H in } H_2O) = 0.153\,506\,083\,(60)$$

of Smaller [15] and the magnetic moment of protons in water (uncorrected for diamagnetism)

$$\mu = 2.792\,709\,(17)\ \mu_N$$

of Taylor et al. [16], the magnetic moment of all nuclei mentioned here can be calculated.

The results are given in Table 1 together with the ratios of Larmor frequencies (referred to the deuteron in D_2O as well as to the proton in H_2O).

The uncertainties of the present results $\nu(x)/\nu(^2\text{H})$ (in the upper 3 lines of Table 1) are 3 times the rms errors of about 20 measured frequency ratios with each nucleus. The uncertainties of all other quantities are the square root of the sum of the squares from these errors and the uncertainties of previous measurements as given in the cited references.

Further details about the NMR of the nuclei mentioned here (e. g. chemical shifts, used samples etc.) are to be found in the papers cited here.

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