^{39}K, ^{40}K and ^{41}K Nuclear Magnetic Resonance Studies

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The NMR lines of ^{39}K and ^{41}K have been investigated in solutions of many potassium salts in H_2O, D_2O, methanol and ethylenediamine and also in solid potassium halides. The NMR signal of the rare isotope ^{40}K was detected for the first time. The ratio of the Larmor frequencies of ^{39}K and ^{41}K has been measured in various samples: $\nu(^{30}\mathrm{K})/\nu(^{41}\mathrm{K}) = 1.821\,873\,1(9)$. No primary isotopic effect was to be detected within these limits of error (0.5 ppm). The concentration dependence of the chemical shift of the ^{39}K resonance frequencies was determined. Using this dependence, the ratios of the Larmor frequencies of the nuclei ^{39}K, ^{40}K, and ^{41}K for infinite dilution relative to the resonance frequency of ^{2}H in D_2O are given. The magnetic moments of the $^{39}\mathrm{K}^+$, $^{40}\mathrm{K}^+$, and $^{41}\mathrm{K}^+$ ions purely surrounded by water molecules are $\mu(^{39}\mathrm{K}^+) = 0.390\,952\,9(24)\,\mu_\mathrm{N}$, $\mu(^{40}\mathrm{K}^+) = -1.296\,262(9)\,\mu_\mathrm{N}$, $\mu(^{41}\mathrm{K}^+) = 0.214\,588\,4(13)\,\mu_\mathrm{N}$ without diamagnetic corrections. Comparison of these values with the results of atomic beam magnetic resonance experiments yields the hyperfine structure anomalies of all pairs of potassium isotopes and also the shielding of potassium nuclei by water molecules around the ions; the shielding constant is $\sigma^*(\mathrm{K}^+ \text{ in } H_2O \text{ vs. K atom}) = -0.000\,105\,2(8)$. For the liquid samples the relaxation times T_2 and for the solid ones the relaxation times T_1 and the line widths are given.

1. Introduction

There are three potassium isotopes in the natural mixture: ^{39}K, ^{40}K and ^{41}K. Their properties most important for NMR-investigations are given in Table 1.

Tab. 1.

Isotope	Natural abundance	Spin I	Quadrupole moment in barn (a)	NMR-sensitivity (b)	Larmor frequency at 1.807 Tesla
^{39}K	93.1%	3/2	0.055	$4.7 \cdot 10^{-4}$	3.590 MHz
^{40}K	0.012%	4	−0.07	$6.2 \cdot 10^{-7}$	4.464 MHz
^{41}K	6.88%	3/2	0.067	$5.8 \cdot 10^{-6}$	1.971 MHz

a) Data from Nuclear Data Tables Vol. 5, No. 5–6, March 1969.

b) Referred to the proton NMR-signal of H_2O at the same magnetic field B_0 and with the same probe volume; with regard to the percentage of the isotope in the natural mixture. Calculated with the formula Signal $\sim N_0\,\mu^3 (I+1)/I^2$ (N_0 is the number of nuclei under investigation per volume).

There are former NMR-measurements of the magnetic moments of ^{39}K and ^{41}K [1–5]. The measurements were done on aqueous solutions of some potassium salts, the dependence of the Larmor frequency on the concentration of the sample was not taken into consideration in any of the experiments. The uncertainties of the ratios of the Larmor frequencies, used to calculate the magnetic moments, are $\geqq 5$ ppm for ^{41}K and $\geqq 10$ ppm for ^{39}K [1–3]. These accuracies are by more than one order of magnitude lower than the accuracies of the magnetic moments of ^{39}K and ^{41}K as obtained by atomic beam magnetic resonance techniques [6]. As actual NMR techniques yield results with uncertainties far below 1 ppm, a comparison of the previous NMR results with the moments obtained by atomic beam techniques is not reasonable.

Two investigations on the dependence of the chemical shifts of the resonances of ^{39}K on the concentration of the sample were done [7, 8], but in both experiments the ^{39}K Larmor frequencies are not referred to a well known standard. Up untill now there are no NMR investigations of the isotope ^{40}K. The reason for this may be the extremely weak NMR signal, which results from the small percentage of the radioactive isotope ^{40}K in the natural mixture.

For all other alkali elements there exist very accurate NMR investigations [9–11] as well as atomic beam magnetic resonance [12, 13] or optical pumping experiments [14, 15], which yield accurate values of the absolute shielding of the alkali ions in water as well as of the hyperfine structure anomalies. In the present work the corresponding values for the potassium isotopes will be given.

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2. Experimental

2.1 *Apparatus*

Our measurements were performed with two pulse spectrometers, a commercial Bruker B-KR 322 s spectrometer for the frequency range 4 ... 62 MHz and one especially developed to detect weak NMR signals in the range 1.4 ... 4 MHz. This spectrometer is described in [16, 17]. In the probe assemblies of both spectrometers a one-coil-arrangement is used. The magnetic field $B_0 = 1.807$ Tesla is stabilized with a ^{7}Li-NMR-probe [18]. The spatial homogeneity is achieved by special nickel-shims. The measurements at ^{39}K and ^{41}K were done with a probe assembly which permits a sample rotation up to 250 rps. The temperature of the sample was held constant within ± 1 K by a thermostat. All measurements were done at a temperature of the sample of 298 K.

The measurements on ^{40}K were done with our commercial spectrometer, as the Larmor frequency of this nucleus is above 4 MHz. Special efforts were made to improve the Q of the probe circuit. To determine the ratio of the Larmor frequencies of ^{39}K and ^{2}H both spectrometers were combined. A special probe assembly with two coils was used [19]; the one – connected with the commercial spectrometer – was tuned to the deuteron resonance frequency 11.81 MHz and the other – connected with our highly sensitive spectrometer – was tuned to the Larmor frequency of ^{39}K. This assembly, combined with both spectrometers allows the simultaneous irradiation of rf-pulses for both nuclei mentioned, and it allows also the simultaneous detection of the NMR signals of both nuclei. By this technique all uncertainties are eliminated which are either caused by the use of two probe assemblies at perhaps slightly different loci in the magnetic field B_0 or caused by fluctuations of the field B_0 in time.

The free induction decay NMR signal was accumulated in a time averaging computer (Signal Analyzer 5480 of Hewlett-Packard) to improve the signal/noise-ratio.

2.2 *Measuring Technique and Evaluation of the NMR Signals*

The measurements of the NMR signals of ^{40}K were performed with the Quadriga Fourier Transform technique (QFT) [20]. This is a steady state free precession technique of high sensitivity with periodical irradiation of equal rf-pulses. The pulses are spaced by $T \ll T_1, T_2$. The shape of the NMR line obtained by the QFT is given by

$$I(\nu) = \sin 2\pi T(\nu_L - \nu)/2\pi T(\nu_L - \nu) ;$$

ν_L is the Larmor frequency. The halfwidth of this line $\Delta\nu_{1/2} = 0.6/T$ is independent of the natural width of the NMR line.

The measurements of the ^{39}K and ^{41}K-NMR signals were done in such a manner that the NMR signal decayed completely during the time interval between the rf-pulses. The Fourier-transform of the free induction decay NMR-signal following the rf-pulses is a Lorentzian line with the halfwidth $\Delta\nu_{1/2} = 1/\pi T_2$ in the case of an exponentially decaying NMR-signal. T_2 is the transverse relaxation time.

By a rotation of the sample with a frequency of 50 rps the influence of the inhomogeneity of the field B_0 perpendicular to the axis of rotation is suppressed. The remaining inhomogeneous broadening of the NMR-line is due to the gradient of B_0 parallel to the axis of rotation. For the case of a constant field gradient one has [21]

$$(\Delta\nu^*)^2 = (\Delta\nu)^2 + (\Delta\nu_B)^2$$

with the measured line width $\Delta\nu^*$, the natural line width $\Delta\nu$, and the line width $\Delta\nu_B$ due to this field gradient.

The signal stored in the time averaging computer is transferred by punched tape to a computer (CDC 3300 of the Zentrum für Datenverarbeitung, Tübingen) to calculate the Fourier Transform or the QFT respectively.

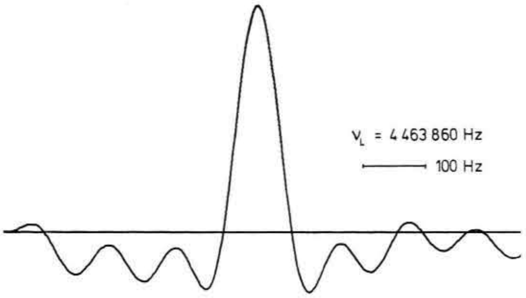

Fig. 1. ^{40}K NMR signal of the reference sample. Total measuring time 10 hours. The pulse period was $T = 11.1$ msec, i. e. the pulse repetition rate was 90 Hz; altogether $3.2 \cdot 10^6$ pulses were applied.

Figure 1 shows the QFT-NMR-line of ^{40}K in the reference sample (see Section 2.3). In Fig. 2 the free induction decay signal and the absorption curve of ^{39}K in a 1.5 molal K_3 [$Fe(CN)_6$] aqueous solution are plotted. This solution is paramagnetic. Measurements of the chemical shifts were done by the sample replacement method.

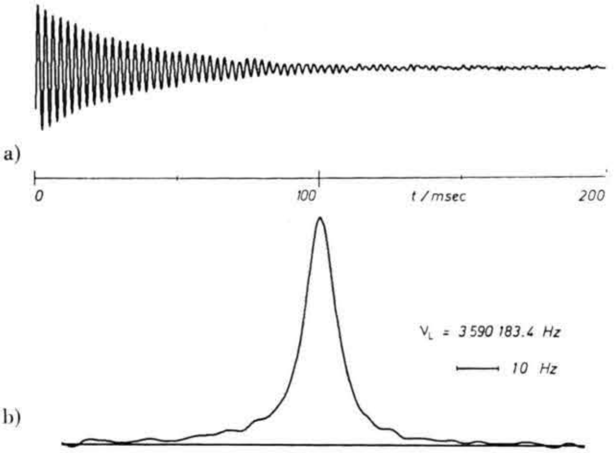

Fig. 2. a) Free induction decay of the ^{39}K NMR signal after a 90°-pulse. b) Absorption signal (Cosine Fourier-Transform of the free induction decay signal). The sample was a 1.5 molal aqueous solution of paramagnetic potassium-hexacyanoferrate (III) in a sphere of 8 mm internal diameter. The pulse spacing is $T = 222$ msec i. e. the pulse repetition rate 4.5 Hz. In a total measuring time of 10 minutes 2,700 pulses were applied.

2.3 Samples

Cylindrical samples of 9 mm internal diameter and 18 mm length as well as spheres of 8 mm and 18 mm internal diameter were used.

The potassium salts were delivered by E. Merck AG, Darmstadt. Most of these salts were analytical grade, whereas KCl, KBr and KI were Suprapur reagents. The water used as solvent had a conductivity of less than $10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. The other solvents were analytical grade (ethylenediamine) and Uvasol solvents (D_2O and methanol).

The concentrations of the solutions were determined by weighing salt and solvent. The solutions of some very hygroscopical potassium salts were produced by dilution of concentrated solutions, the concentration of which was determined by measuring their density.

A 31 molal solution of KNO_2 in D_2O was used as reference sample. This solution is particularly suited for reference as it yields a very good signal/noise-ratio within a relatively short measuring time, and as the KNO_2 solutions show a very small dependence of the chemical shift on the concentration; moreover the width of the NMR-line of this reference sample is narrow (see Section 3.9).

3. Results

3.1 The Ratio of the Larmor Frequencies of ^{39}K and ^{41}K

To determine the ratio $\nu(^{39}\mathrm{K})/\nu(^{41}\mathrm{K})$ the following five samples were used:

No. 1 Aqueous solution 16 molal in KF,
No. 2 Aqueous solution 10.3 molal in KOH,
No. 3 Aqueous solution 20 molal in KOH,
No. 4 Aqueous solution 31 molal in KNO_2,
No. 5 31 molal solution of KNO_2 in D_2O (Reference sample, see Section 2.3).

Altogether 58 ratios of the Larmor frequencies of the potassium isotopes were measured. The result obtained is:

$$\nu(^{39}\mathrm{K})/\nu(^{41}\mathrm{K}) = 1.821\,873\,1\,(9)\ .$$

The error of 0.5 ppm is three times the r.m.s. error. The results obtained from the five samples are all within these limits of error. This means that a possible primary isotopic effect is surely less than 0.5 ppm. Therefore, the measurements of the dependence of the chemical shift of the potassium NMR on the concentration of the sample must be done only for the isotope ^{39}K, which delivers the strongest NMR signal; all results hold in the same manner for the two other potassium isotopes ^{40}K and ^{41}K.

The only former NMR result of the ratio of the Larmor frequencies of ^{39}K and ^{41}K by Brun et al.[2]

$$\nu(^{39}\mathrm{K})/\nu(^{41}\mathrm{K}) = 1.821\,96\,(27)$$

is in agreement with the value above.

Recently, Beckmann, Böklen and Elke[6] measured the g_I-factors of ^{39}K and ^{41}K using the atomic beam magnetic resonance method. From their values for g_I one arrives at:

$$g_I(^{39}\mathrm{K})/g_I(^{41}\mathrm{K}) = 1.821\,873\,7\,(23)\ .$$

The agreement with the present NMR value is very good.

3.2 Concentration Dependence of the Chemical Shift and Solvent Effects

The chemical shift of ^{39}K in aqueous solutions of $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, KBr, KCl, $K_2C_2O_4$, $KHSO_4$, KNO_3, KI, KOH, KF and KNO_2 has been measured as a function of the concentration from 0.25 molal up to saturated solutions. For each sample about 10 measurements were performed alternately with the reference sample described in Section 2.3.

In the range up to 9 molal some of these salts were investigated by Deverell and Richards[7] and also by Bloor and Kidd[8].

Moreover, KNO_2 dissolved in D_2O was investigated to study the solvent isotopic effect of the potassium ion. Further samples were solutions of KI in ethylenediamine ($C_2H_8N_2$) and KOH in methanol (CH_3OH). All samples were measured in cylindrical probes and the results corrected for bulk susceptibility, except the measurements in organic solvents. The corrections for the diamagnetic salts are small (less than 0.3 ppm), in contrast to the paramagnetic $K_3[Fe(CN)_6]$. Here the correction for a 1.5 molal aqueous solution was determined experimentally by a comparison of the shifts of cylindrical and spherical samples. There is the shift $\delta_{\text{sphere}} - \delta_{\text{cyl.}} = 3.43(20)$ ppm. From this result a molar susceptibility of $K_3[Fe(CN)_6]$ in H_2O is calculated by using the Wiedemann law: $\chi_m = 2.6(3) \cdot 10^{-3}$ cm^3/mole. Within the limits of error there is agreement with the susceptibility $\chi_m = 2.3 \cdot 10^{-3}$ cm^3/mole[22] for solid $K_3[Fe(CN)_6]$. On that measured susceptibility the calculation of the susceptibilities of all other $K_3[Fe(CN)_6]$ samples, by applying the Wiedemann law, was based.

In Figs. 3 – 5 the results are given. On the ordinate the shifts are plotted in relative units: $\delta = (\nu_{\text{sample}} - \nu_0)/\nu_0$ where ν_0 is the Larmor frequency of K^+ at infinite dilution. A positive value of the shift means a shift to higher frequencies at a constant field. The shift of the cylindrical reference sample is $\delta_{\text{cyl}} = -3.1(2)$ ppm and the corrected value $\delta = -3.0(2)$ ppm. Typical errors are 0.2 ppm (three times the r.m.s. error).

Figure 5 shows the concentration dependence of the chemical shift of two potassium salts in organic solvents. Pettit and Bruckenstein[23] made a cryoscopic study of KI in ethylenediamine (EDA) in the concentration range 0.02 – 0.1 molar and found potassium iodide to be present as undissociated monomer. The shift of KI in EDA at infinite dilution is δ(KI in EDA) = 30.7(4) ppm. That of KOH in methanol is δ(KOH in methanol) = −10.0(4) ppm. In D_2O the potassium NMR resonance of KNO_2 is shifted to lower frequencies by $\delta = -0.15(10)$ ppm, which is nearly independent of the concentration of the salt.

3.3 *The Ratio of the Larmor Frequencies of ^{39}K and ^2H*

To determine this ratio, the two Larmor frequencies $\nu(^{39}K)$ and $\nu(^2H)$ in the reference sample were measured simultaneously using our two-spectro-

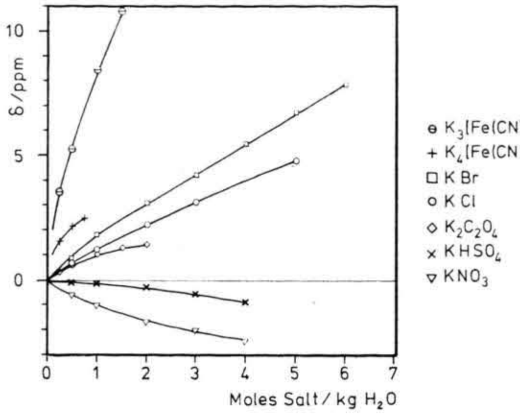

Fig. 3. Potassium chemical shift in aqueous solutions of well soluble potassium salts. The errors of the measurements are smaller than the symbols indicating the measuring points.

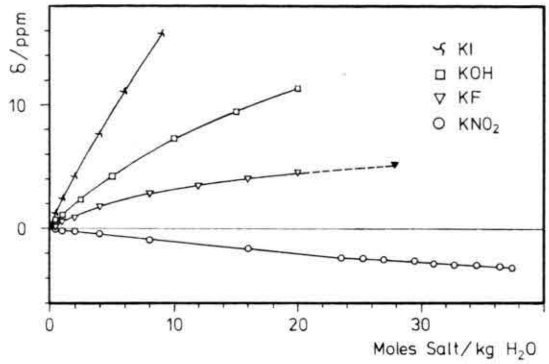

Fig. 4. Potassium chemical shifts in aqueous solutions of very well soluble potassium salts. The symbol ▼ indicates $KF \cdot 2\,H_2O$ which has a melting point of 319 K. For our measurements this sample was undercooled.

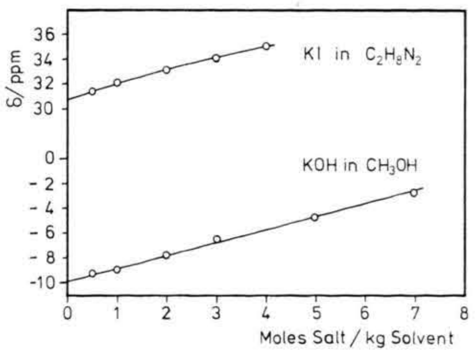

Fig. 5. Potassium chemical shift of KI in ethylenediamine and of KOH in methanol. The shifts are referred to K^+ in H_2O at infinite dilution. The errors of these measurements are typically 0.4 ppm.

meter-combination[19]. The samples were contained in cylinders as well as in spheres. The result of 26 measurements is the following ratio:

$$\{\nu(^{39}\mathrm{K})/\nu(^{2}\mathrm{H})\}_{\mathrm{ref.\,sample}} = 0.303\,984\,154(22)\ .$$

Between the deuteron resonance frequencies in the reference sample and in pure D_2O there is a shift of (0.7 ± 0.2) ppm, the ^{2}H-Larmor frequency of D_2O is shifted to higher frequencies. On the other hand, the shift of the ^{39}K resonance frequencies of the reference sample and the K^+ ion only surrounded by water molecules is $\delta_{\mathrm{ref}} = (-3.0 \pm 0.2)$ ppm (see Section 3.2). Taking these two shifts into consideration the ratio of the Larmor frequencies of ^{39}K in the K^+ ion in H_2O and of ^{2}H in pure D_2O results to be

$$\nu(^{39}\mathrm{K}^+)/\nu(^{2}\mathrm{H\ in\ D_2O}) = 0.303\,984\,85(9)\ .$$

3.4 *The Ratio of the Larmor Frequencies of ^{40}K and ^2H*

The Larmor frequency of ^{40}K in the reference sample was determined with the Bruker pulse spectrometer and referred to the Larmor frequency of ^{37}Cl in 4.5 molal solution of NaCl in D_2O. The ^{37}Cl resonance can be received with the same probe assembly also suitable for the ^{40}K NMR-signal. The result of 20 measurements with cylindrical samples is

$$\{\nu(^{40}\mathrm{K})/\nu(^{37}\mathrm{Cl})\}_{\mathrm{cyl}} = 0.711\,402\,0(18)\ .$$

A very accurate frequency ratio $\nu(^{37}\mathrm{Cl})/\nu(^{2}\mathrm{H})$ in this 4.5 molal solution of NaCl in D_2O is given in [24]. With this ratio, with the shift of the ^{2}H resonances in this NaCl solution and in pure D_2O[24], as well as with the shift of the potassium resonance of the reference sample (see Sect. 3.2), the ratio of the Larmor frequencies of ^{40}K (K^+ ion in H_2O extrapolated to infinite dilution) and of ^{2}H in pure D_2O is obtained to be

$$\nu(^{40}\mathrm{K}^+)/\nu(^{2}\mathrm{H}) = 0.377\,965\,0(10)\ .$$

This result is corrected for bulk susceptibility to the spherical shape of the sample.

3.5 *Nuclear Magnetic Moments of ^{39}K, ^{40}K and ^{41}K*

From the ratios of the Larmor frequencies reported in Sects. 3.1, 3.3 and 3.4 the nuclear magnetic moments of ^{39}K, ^{40}K and ^{41}K ions surrounded solely by water molecules can be calculated using the frequency ratio of ^{2}H in heavy water and ^{1}H in light water of Smaller[25], the magnetic moment of the proton in H_2O (uncorrected for diamagnetism) of Taylor et al.[26] and the nuclear spins of Table 1. In Table 2 these values are listed together with the frequency ratios and g_I-factors, which are calculated by using the relation

$$|g_I| = 0.466\,963\,42(20)\cdot 10^{-3}\,\{\nu(\mathrm{K})/\nu(^{2}\mathrm{H})\}_{\mathrm{NMR}}$$

from Reference[6]. This g_I-factor is defined by $\mu_I/\mu_B = g_I \cdot I$. The numerical factor in this equation is calculated by the formula

$$g_I(K) = \{g_I(\mathrm{K})/g_I(^{2}\mathrm{H})\}_{\mathrm{NMR}} \cdot \{g_I(^{2}\mathrm{H})/g_I(^{1}\mathrm{H})\}_{\mathrm{NMR}} \cdot \{g_I(^{1}\mathrm{H})/g_J(^{1}\mathrm{H})\} \cdot \{g_J(^{1}\mathrm{H})/g_e\} \cdot g_e$$

using the experimental values $g_I(^2\mathrm{H})/g_I(^1\mathrm{H})$ of Smaller[25], $g_I(^1\mathrm{H})/g_J(^1\mathrm{H})$ of Lambe[27], g_e of Weseley and Rich[28] and the theoretical value for $g_J(^1\mathrm{H})/g_e$ of Grotch and Hegstrom[29]. One gets from this equation the nuclear g_I-factors related to the Bohr magneton μ_B. One gets the values given in Table 2 with the known signs of the magnetic moments (see e. g. References[6] and [13]).

The present results will now be compared with those of previous measurements. Our results agree with the values $\mu(^{39}\mathrm{K}) = 0.390\,94(7)$ of Collins[1] $\mu(^{39}\mathrm{K}) = 0.390\,948(5)$ of Brinkman[3], but disagree with the value $\mu(^{39}\mathrm{K}) = 0.390\,873(13)$ of Brun et alias[2]. The difference between this result and the value of Table 2 is about 200 ppm. This difference is more than 7 times the uncertainty given by these authors. This discrepancy cannot be explained by chemical shifts. For ^{40}K no previous NMR measure-

Tab. 2. Nuclear magnetic moments and g_I-factors of the potassium ions surrounded only by water molecules, and Larmor frequency ratios. The errors given here result from the uncertainties of the frequency ratios measured (three times the r.m.s. errors), the uncertainty of extrapolation to infinite dilution (see sect. 3.2), and the uncertainties of the values cited as given by these authors. All these errors are added quadratically.

	$\nu(\mathrm{K})/\nu(^{2}\mathrm{H})$	$\nu(\mathrm{K})/\nu(^{1}\mathrm{H})$	$g_I \cdot 10^3$	μ_I/μ_N
$^{39}K^+$	0.303 984 85(9)	0.046 663 524(22)	−0.141 949 80(7)	0.390 952 9(24)
$^{40}K^+$	0.377 965 0 (10)	0.058 019 93 (16)	0.176 495 8 (5)	−1.296 262 (9)
$^{41}K^+$	0.166 852 92(9)	0.025 612 938(18)	−0.077 914 21(6)	0.214 588 4(13)

ment to determine the nuclear magnetic moment is known.

The nuclear magnetic moment of ^{41}K given by Brun et al.[2] $\mu(^{41}\mathrm{K}) = 0.214\,53(3)$ also disagrees with our value by more than 270 ppm, which is two times the error given in [2]. Previous determinations of the ratio of the resonance frequencies of ^{41}K and ^{2}H by Lutz and Schwenk[4] and also by Kaufmann et al.[5] were performed with a 9 molar or 10.6 molal aqueous KF solution. Taking into consideration the chemical shift of the ^{41}K resonance in this solution δ (9 molar KF) $= 3.2(3)$ ppm the present measurements yield the ratio

$$\nu(^{41}\mathrm{K}\text{ in 9 molar KF})/\nu(^2\mathrm{H}\text{ in }\mathrm{D_2O}) = 0.166\,853\,46(20).$$

This value corresponds nicely with the results given in [4] and [5].

3.6 Hyperfine Structure Anomalies

By comparing NMR measurements for the ratios of the g_I-factors with the ratios of the A-factors of two potassium isotopes one gets the hyperfine structure anomaly, which is defined by

$$^1\Delta^2 = (A_1/A_2)/(g_{I_1}/g_{I_2}) - 1 = \frac{\Delta\nu_1}{\Delta\nu_2}\cdot\left(\frac{\nu_2}{\nu_1}\right)_{\mathrm{NMR}}\cdot\frac{2I_2+1}{2I_1+1} - 1\,.$$

$\Delta\nu$ is the hyperfine structure separation of the isotope in question. $(\nu_2/\nu_1)_{\mathrm{NMR}}$ is the ratio of the Larmor frequencies of the two isotopes from NMR measurements.

Beckmann et al.[6] have determined the hfs-separation in the $^2S_{1/2}$ ground state with high accuracy by an atomic beam magnetic resonance experiment

$$\Delta\nu(^{39}\mathrm{K}) = 461.719\,720\,2(14)\ \mathrm{MHz}\,,$$
$$\Delta\nu(^{41}\mathrm{K}) = 254.013\,872\,0(20)\ \mathrm{MHz}\,.$$

For ^{40}K the corresponding value was measured by Eisinger et al.[13] using the same technique:

$$\Delta\nu(^{40}\mathrm{K}) = 1285.790(7)\ \mathrm{MHz}\,.$$

These values and our ratios

$$\nu(^{39}\mathrm{K})/\nu(^{41}\mathrm{K}) = 1.821\,873\,1(9)\ \text{(see Sect. 3.1)}\,,$$
$$\nu(^{40}\mathrm{K})/\nu(^{39}\mathrm{K}) = 1.243\,367\,9(33)\,,$$
$$\nu(^{40}\mathrm{K})/\nu(^{41}\mathrm{K}) = 2.265\,259(6)$$

calculated with the ratios given in Sect. 3.3 and 3.4 yield the following hfs-anomalies of the potassium isotopes in the $^2S_{1/2}$ ground state:

$$^{39}\Delta^{41} = -0.229\,34(5)\ \%\,,$$
$$^{39}\Delta^{40} = 0.459\,4(6)\ \%\,,$$
$$^{40}\Delta^{41} = -0.685\,6(6)\ \%\,.$$

These values agree with those reported in [6]

$$^{39}\Delta^{41} = -0.229\,36(14)\ \%$$

and in [13]

$$^{39}\Delta^{40} = 0.466(19)\ \%\,.$$

These two values are based exclusively on results of atomic beam magnetic resonance experiments.

3.7 The Shielding Constant of K^+ Ions in Water

Performing a NMR experiment in a static magnetic field B_0, at the positions of the nuclei under investigation there is a magnetic field strength

$$B = (1-\sigma)\,B_0\,,$$

as the applied field is shielded by the electrons and other molecules surrounding those nuclei under investigation. The Larmor frequency of these nuclei may be calculated in two different ways:

$$\omega_{\mathrm{L}} = 2\pi\,\nu_{\mathrm{L}} = \gamma_{\mathrm{NMR}}\cdot B_0 = \gamma_{\mathrm{nucl}}\cdot B\,.$$

γ_{NMR} is the gyromagnetic ratio measured with the NMR method and γ_{nucl} the gyromagnetic ratio of the bare nucleus. The shielding constant can be evaluated from this:

$$\sigma = 1 - \gamma_{\mathrm{NMR}}/\gamma_{\mathrm{nucl}} = 1 - \mu_{I,\mathrm{NMR}}/\mu_{I,\mathrm{nucl}} = 1 - g_{I,\mathrm{NMR}}/g_{I,\mathrm{nucl}}\,.$$

The magnetic moments and g_I-factors are defined in the same manner as the corresponding gyromagnetic ratios. To evaluate this shielding constant, two independent measurements must be performed; a NMR experiment and an experiment with bare nuclei. Such an experiment is not possible at the present time, whereas the g_I-factors can be measured on free atoms or ions, e. g. with the atomic beam magnetic resonance or the optical pumping technique. For this reason another shielding constant may be defined:

$$\sigma^*(\mathrm{K^+}\text{ in }\mathrm{H_2O}\text{ vs. K-atom}) = 1 - \frac{\mu_I(\mathrm{K^+}\text{ in }\mathrm{H_2O})}{\mu_I\text{ (atomic beam)}} = 1 - \frac{g_I(\mathrm{K^+}\text{ in }\mathrm{H_2O})}{g_I\text{ (atomic beam)}}\,.$$

This constant describes the shielding of the magnetic field B_0 by the water molecules and ions surrounding the $\mathrm{K^+}$ ion under investigation, except for the small difference in the shielding of the nucleus by the electrons of the atom and the ion; this difference is – for the potassium isotopes – below the experimental uncertainty [30, 31].

The nuclear magnetic moments and the g_I-factors of ^{39}K, ^{40}K and ^{41}K in the atom are known from Refs. [6] and [13] respectively:

$$\mu_I\,(^{40}\mathrm{K}, \text{atom}) = -1.296\,4\,(4)\ \mu_N\,,$$
$$g_I\,(^{39}\mathrm{K}, \text{atom}) = -0.141\,934\,89\,(12)\cdot 10^{-3}\,,$$
$$g_I\,(^{41}\mathrm{K}, \text{atom}) = -0.077\,906\,00\,(8)\ \ \cdot 10^{-3}\,.$$

Therefore, the shielding of the potassium ions by the surrounding water is

$$\sigma^*\,(^{39}\mathrm{K}^+) = -0.105\,1\,(10)\cdot 10^{-3}\,,$$
$$\sigma^*\,(^{40}\mathrm{K}^+) = \ \ 0.1\,(3)\cdot 10^{-3}\,,$$
$$\sigma^*\,(^{41}\mathrm{K}^+) = -0.105\,4\,(12)\cdot 10^{-3}\,.$$

As there is no primary isotopic effect of the shielding constant within the accuracy of 0.5 ppm, a weighted value is derived from these results:

$$\sigma^*\,(K^+ \text{ in } \mathrm{H_2O} \text{ vs. K-atom}) = -0.105\,2\,(8)\cdot 10^{-3}.$$

The shielding constants of the other alkali elements are well known [6, 10, 15]. The results of all alkali ions are plotted in Fig. 6: the shielding of the alkali ions solely by the surrounding water is a nearly linear function of the atomic number.

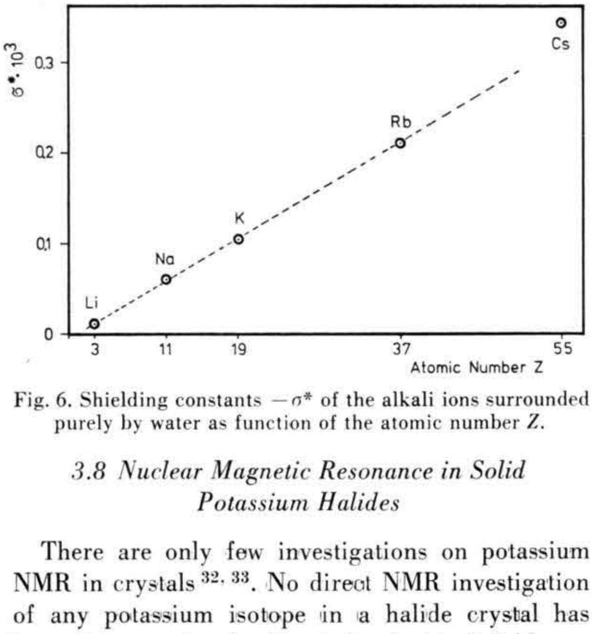

Fig. 6. Shielding constants $-\sigma^*$ of the alkali ions surrounded purely by water as function of the atomic number Z.

3.8 Nuclear Magnetic Resonance in Solid Potassium Halides

There are only few investigations on potassium NMR in crystals [32, 33]. No direct NMR investigation of any potassium isotope in a halide crystal has been done previously. To study electrical field gradients, Hartland [34] detected in a double resonance experiment with a Na$^+$ doped KF single crystal the NMR signals of all three potassium isotopes by observing the ^{19}F resonance. The values for the ratios of the resonance frequencies calculated from the approximate Larmor frequencies given in Ref. [34] agree with the results given in Section 3.6.

We were able to observe the NMR signals of all four potassium halides KF, KCl, KBr, and KI. The samples were crystalline powder as described in Sect. 2.3 in spherical glass bulbs with an internal diameter of 18 mm. Each spectrum consists of one line with a halfwidth of less than 210 Hz, agreeing with the cubic symmetry of the potassium environment, i. e. the vanishing field gradient tensor.

The shift of ^{39}K in the halides, together with the line widths and the longitudinal relaxation times T_1 (see Sect. 3.9) are presented in Table 3.

Tab. 3. The ^{39}K shifts in polycrystalline potassium halides, line-widths and longitudinal relaxation times T_1. The shifts are referred to the ^{39}K$^+$ ion at infinite dilution in H_2O.

Salt	Chem. shift δ/ppm	Line width $\Delta\nu_{1/2}$/Hz	T_1/sec
KF	23.0 ± 3.0	156(16)	1.71(9)
KCl	49.6 ± 1.0	109(10)	1.28(4)
KBr	57.6 ± 3.0	210(20)	1.56(10)
KI	62.5 ± 1.6	197(16)	1.34(10)

3.9 Relaxation Times and Line Widths

From all measurements with liquid and solid samples the transverse relaxation times T_2 or the line widths were evaluated respectively.

From the Lorentzian shape of the absorption line of the liquid samples and particularly from their halfwidth, the relaxation times T_2 were calculated and corrected for inhomogeneity of the field B_0 parallel to the axis of rotation as described in Section 2.2. The line width $\Delta\nu_B$ resulting from this field gradient was obtained with the reference sample, the natural line width of which was evaluated from more than 100 measurements in a particularly adjusted field B_0: $\Delta\nu = (12\pm1)$ Hz. The resulting corrections of the measured line widths are relatively small (less than 10% in all cases).

The transversal relaxation times of ^{39}K in the potassium salts are plotted in Figures 7, 8 and 9. The relaxation times T_2 of KNO_2 in D_2O are lower than those of KNO_2 in H_2O by a constant amount of 4 msec and independent of the concentration of the salt. For infinite dilution of these salts the following relaxation times result:

$$T_2\,(^{39}\mathrm{K}^+ \text{ in } \mathrm{H_2O}) \quad = (56\pm6)\ \text{msec}\,,$$
$$T_2\,(^{39}\mathrm{K}^+ \text{ in } \mathrm{D_2O}) \quad = (52\pm5)\ \text{msec}\,,$$
$$T_2\,(^{39}\mathrm{KI} \text{ in EDA}) \quad = (10\pm1)\ \text{msec}\,,$$
$$T_2\,(^{39}\mathrm{KOH} \text{ in } \mathrm{CH_3OH}) = (30\pm6)\ \text{msec}\,.$$

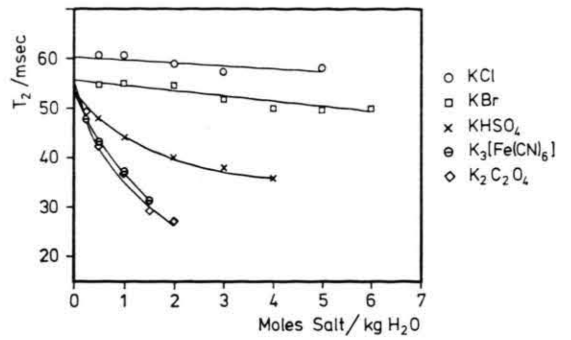

Fig. 7. ^{39}K transverse relaxation times T_2 as a function of the concentration of potassium salts for well soluble salts. The uncertainty of the given relaxation times is smaller than 10%. Within these limits of error the T_2 values of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ are in agreement.

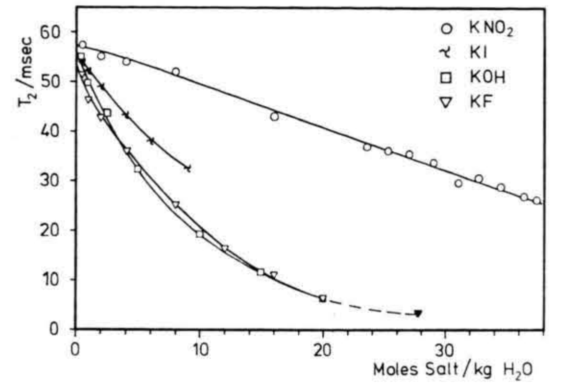

Fig. 8. ^{39}K transverse relaxation times as function of the concentration for very well soluble salts. The symbol ▼ indicates molten and undercooled $KF \cdot 2\,H_2O$.

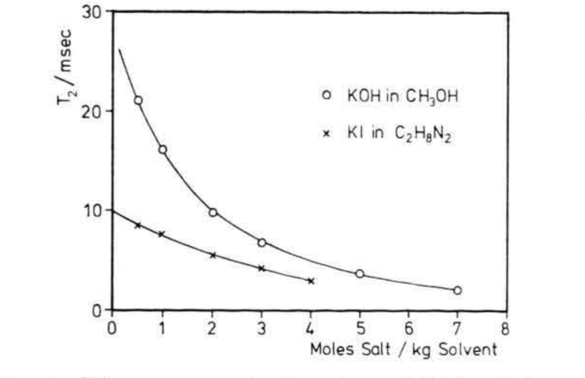

Fig. 9. ^{39}K transverse relaxation times of KI in ethylenediamine and of KOH in methanol. KI in ethylenediamine is undissociated at low concentrations [23].

The uncertainties given here are estimated from the plots. The temperature of all samples was (298 ± 2) K.

The transverse relaxation times T_2 of ^{41}K were measured in three different samples. In Table 4 the results are compared with those of ^{39}K and the ratios $T_2(^{39}K)/T_2(^{41}K)$ are given. The mean value of these ratios is $T_2(^{39}K)/T_2(^{41}K) = 1.36(20)$. If the contribution to the relaxation due to magnetic dipole interaction may be neglected in comparison with the contribution due to quadrupole interaction one gets [35]

Tab. 4. Transverse relaxation times T_2 of ^{39}K and ^{41}K in various samples.

Sample	$T_2(^{41}K)$ /msec	$T_2(^{39}K)$ /msec	$T_2(^{39}K)/T_2(^{41}K)$
KNO_2 31 molal in D_2O	19.6 ± 3.0	26.6 ± 2.0	1.36(20)
KF 16 molal in H_2O	7.6 ± 1.3	11.1 ± 0.2	1.46(25)
KOH 10.3 molal in H_2O	15.0 ± 1.7	19.0 ± 0.4	1.27(14)

$$T_2(^{39}K)/T_2(^{41}K) \approx T_1(^{39}K)/T_1(^{41}K) = Q^2(^{41}K)/Q^2(^{39}K) = 1.48$$

with the quadrupole moments of Table 1. This value has a positive correlation with the experimental result of the present work.

A further hint to the predominance of the quadrupole relaxation is the agreement of the T_2 values of the paramagnetic $K_3[Fe(CN)_6]$ with those of the diamagnetic $K_4[Fe(CN)_6]$. The measurements of the spin-lattice relaxation time T_1 of the polycrystalline potassium halide samples were made with the progressive saturation method. From the exponentially increasing NMR signal as a function of the pulse spacing T $(S \sim 1 - \exp\{-T/T_1\})$, the relaxation time T_1 may be evaluated by a least square fit routine. The results are given in Table 3.

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