Fourier Transform Nuclear Magnetic Resonance Studies of ^{67}Zn

B. W. Epperlein, H. Krüger, O. Lutz, and A. Schwenk

Physikalisches Institut der Universität Tübingen, Germany

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^{67}Zn nuclear magnetic resonance studies of various solutions of diverse zinc salts in H_2O and D_2O are reported. In the solutions of ZnI_2, $ZnBr_2$ and $ZnCl_2$ a remarkable chemical shift to higher frequency is observable, whilst for $Zn(ClO_4)_2$, $Zn(NO_3)_2$ and $ZnSO_4$ no shift is detectable. The ^{67}Zn shifts in zinc halide solutions depend on the isotopic composition of the solvent. The substitution of hydrogen by deuterium in the solvent yields for the ^{67}Zn line an anomalous solvent isotope effect to higher frequency. Moreover for increasing temperature a linear increase of the shift and a nonlinear decrease of the linewidth for the zinc halide solutions were observed.

The ratio of the Larmor frequencies of ^{67}Zn and ^{37}Cl has been measured in an aqueous zinc perchlorate solution, and a magnetic moment has been calculated for ^{67}Zn. The shielding constant for the hydrated zinc ion has been evaluated:

$$\sigma^* (\text{hydrated } ^{67}\text{Zn}^{++} \text{ versus } ^{67}\text{Zn atom}) = -(6.9 \pm 0.1) \cdot 10^{-4} .$$

I. Introduction

The first NMR measurement of ^{67}Zn was made 1953 by Weaver[1]. In this work the ratio of the Larmor frequencies of ^{67}Zn and ^{14}N has been measured in a not well defined aqueous solution of $Zn(NH_3)^{++}$ with an accuracy of $1.2 \cdot 10^{-5}$, and a magnetic moment of ^{67}Zn has been calculated. Bennet[2] detected the NMR signal of the ^{67}Zn nucleus in the Zintl intermediate phase LiZn. No further NMR measurements of ^{67}Zn in condensed matter are known.

The reason for this is the relatively small NMR signal of ^{67}Zn, which has a natural abundance of 4.11%, a small nuclear magnetic moment[3], a nuclear spin $I = 5/2$ (see[4]), and a quadrupole moment $Q = 0.18 \cdot 10^{-24}$ cm^2 (see[5]). The Larmor frequency of ^{67}Zn in our magnetic field $B = 1.807$ Tesla is about 4.814 MHz. The ^{67}Zn NMR signal in a 1 molal aqueous solution of a Zn salt is about 10^{-6} times weaker than the proton signal in this solution at the same magnetic field.

This work is part of an extensive NMR study of the nuclei of the IIb group elements of the periodic system. The behaviour of the ^{111}Cd resp. ^{113}Cd NMR lines in aqueous solution has been reported earlier[6, 7]. Further, a shielding constant of

$$\sigma^* (\text{hydrated } ^{111}\text{Cd versus } ^{111}\text{Cd atom}) = -(11.06 \pm 0.04) \cdot 10^{-4}$$

was determined. The results of the similar ^{199}Hg NMR studies[8] will be published soon[9].

In this paper we describe the measurement of ^{67}Zn NMR chemical shifts and line widths in aqueous solutions as a function of their concentration, temperature and isotopic composition of the solvent. Furthermore the ratio of the Larmor frequencies of ^{67}Zn and ^{37}Cl has been measured in an aqueous solution of $Zn(ClO_4)_2$ with high accuracy, and a magnetic moment has been calculated for ^{67}Zn. This value may be compared with the magnetic moment determined in the $^1S_0$ ground state of the Zn atom by Spence and McDermott[3] by means of optical pumping. As a result the shielding constant σ^* is evaluable, which is defined as $\sigma^* = 1 - g_{\text{I, NMR}}/g_{\text{I, atom}}$ (s. Ref.[10]). This shielding constant yields a general atomic reference scale for all experimental chemical shifts.

II. Experimental

The NMR signals of ^{67}Zn and ^{37}Cl have been measured with our multi-nuclei Fourier transform NMR spectrometer[10] in an externally stabilized magnetic field of 1.807 Tesla[11]. For getting a reasonable signal-to-noise ratio a sufficient number of pulse responses has been summed by a Hewlett Packard signal analyzer type 5480 A. Always an appropriate rf-pulse spacing was used, so that the NMR signal following a rf-pulse had totally decayed before the next pulse. The fourier transformations were calculated by the CDC 3300 computer of the Zentrum für Datenverarbeitung der Universität Tübingen. All measurements were made in cylindrical sample tubes of 10 mm external diameter. The temperature of the samples was (303 ± 3) K, except for the temperature dependence measurements. These measure-

Reprint requests to Dr. O. Lutz, Physikalisches Institut der Universität Tübingen, *D-7400 Tübingen*, Morgenstelle.

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ments were made with the temperature control unit Bruker B-ST 100/700. Figure 1 shows a typical NMR absorption line of ^{67}Zn in a 2.3 molal $Zn(ClO_4)_2$ solution in H_2O at a Larmor frequency of 4.813773 MHz. The line width is about 62 Hz and the measuring time 5 min.

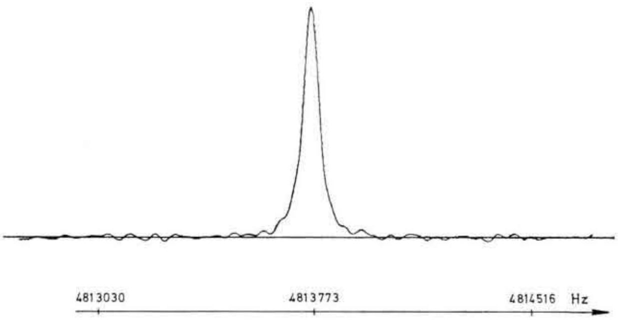

Fig. 1. Typical ^{67}Zn NMR absorption line of a 2.3 molal aqueous $Zn(ClO_4)_2$ solution in a 10 mm cylindrical sample at a Larmor frequency of 4.813 773 MHz. Line width 62 Hz, measuring time 5 min, pulse repetition rate 20 Hz.

The chemical shifts were measured relative to an external standard by the sample exchange method. This external standard was a 2 molal aqueous solution of $Zn(ClO_4)_2$. The chemical shift is given by $\delta = \nu_{\text{sample}} - \nu_0$, a positive value means a shift to higher frequencies at constant field. No bulk susceptibility corrections were made, since they are smaller than the other errors.

III. Results and Discussion

a) ^{67}Zn Chemical Shift in Aqueous Solutions

The ^{67}Zn NMR of the zinc ion in aqueous solution of the zinc salts ZnI_2, $ZnBr_2$, $ZnCl_2$, $Zn(ClO_4)_2$, and $ZnSO_4$ at various concentrations has been investigated. The results are given in Figure 2. The measured shifts are adjusted so that they refer to the ^{67}Zn ion at infinite dilution as standard, positive values correspond to decreased shielding. The measuring errors are smaller than ± 1 ppm, therefore smaller than the prints used in the diagram.

Zinc halides: The dependence of the shift on concentration is strongly nonlinear; the resonance lines are shifted to higher frequencies with increasing concentration. For comparison the second element of the IIb group of the periodical system, cadmium, shows a similar behaviour [7]. The shift for a 1 molal aqueous solution of $ZnCl_2$ is +62 ppm relative to vanishing concentration, the appropriate result for ^{111}Cd is about +100 ppm.

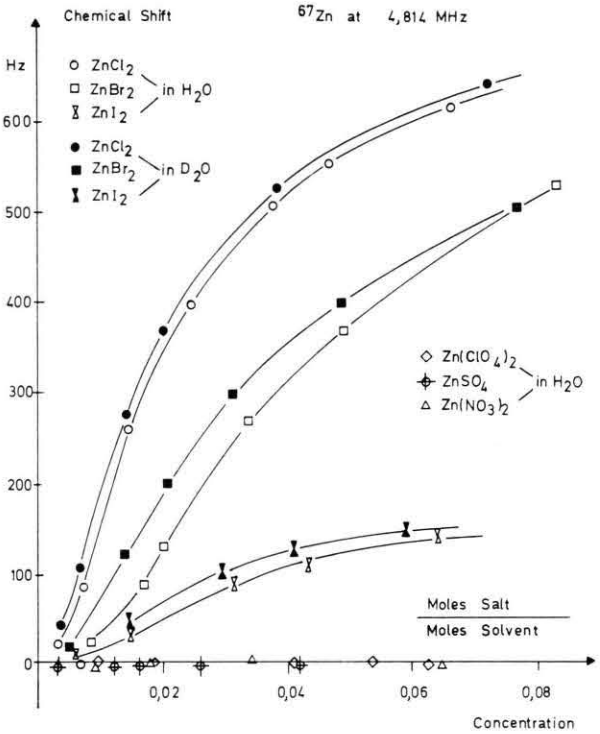

Fig. 2. Chemical shifts of ^{67}Zn in diverse zinc salts in aqueous solutions as a function of concentration. Positive values correspond to decreased shielding. Measuring errors < ± 1 ppm.

The reason for this large shift is the strong complexation of zinc halides. The structure of aqueous zinc halide solutions has been investigated in many preliminary reports with the methods of X-ray diffraction and Raman spectroscopy [12–15]. For a dilute aqueous solution of $ZnCl_2$ these reports indicate the following composition: $Zn(H_2O)_6^{++}$, $ZnCl_4^{--}$ and a small amount of $ZnCl^+(aq)$. The large NMR shift is probably caused by an increasing substitution of H_2O by Cl^- in the octahedral $Zn(H_2O)_6^{++}$, resulting in a $ZnCl_4^{2-}$-ion, which is energetically more favourable than the intermediate $ZnCl_4(H_2O)_2^{--}$ (Ref. [15]). Zinc bromide and iodide show a similar behaviour as $ZnCl_2$ but the shifts are smaller, since the large Br^--ions and more the I^--ions are less able to form complexes. The same effects were observed for ^{111}Cd in aqueous cadmium halide solutions [7, 16].

Zinc perchlorate, nitrate and sulfate: For these salts no chemical shift is detectable within our error of less than ± 1 ppm. This indicates that the great oxyanions do not strongly affect the stable $Zn(H_2O)_6^{++}$-complex. For comparison $^{111}Cd - Cd(ClO_4)_2$ and $CdSO_4$ solution show a very small chemical shift, whereas for $Cd(NO_3)_2$ a remarkable shift to lower frequency was found [7, 16].

b) Anomalous Solvent Isotope Effect

Special attention has been called to the change of the ^{67}Zn chemical shifts which are caused by substitution of hydrogen by deuterium in the solvent water. Earlier reports on other nuclei indicate a solvent isotope effect to lower frequency on changing from H_2O to D_2O solutions [10, 17–22]. The largest effect was observed for ^{207}Pb in aqueous lead nitrate solutions [23]. The difference between the shielding in H_2O and D_2O is $\sigma(H_2O) - \sigma(D_2O) = -(31 \pm 3)$ ppm for a concentration of 0.004 moles lead nitrate per mole solvent.

For ^{111}Cd a first indication for a shift to higher frequencies or lower field was found in a cadmium chloride solution [7], whereas in perchlorate and nitrate solution the usual solvent isotope effect was observed.

^{67}Zn chemical shift in zinc halides at various concentrations in solutions of H_2O and D_2O are measured. The results are plotted in Fig. 2 (tabulated values see Reference [24]). For all these salts an anomalous shift to higher frequencies was found for the solutions in D_2O, compared with those in H_2O. The difference between the shieldings in H_2O and D_2O is e. g. $\sigma(H_2O) - \sigma(D_2O) = (13.1 \pm 0.7)$ ppm for a concentration of 0.02 moles zinc bromide per mole solvent.

In the other zinc salts, like perchlorate, nitrate, and sulfate, contrarily to cadmium salts, no solvent isotope effect was observed within an experimental error of ± 1 ppm. No bulk susceptibility correction was made, since the given errors are larger than this correction.

These shielding differences are presumably due to the different vibronic states of the H_2O and D_2O molecules surrounding the ions [17]. The substitution of the heavy D_2O-molecules cause a decrease of energie of the vibronic states. This gives a shift of the resonance line to lower frequencies. The reason for the difference between the normal and anomalous solvent isotope effect must be looked for in the stable halide complexes which are found in zinc and cadmium solutions.

Investigations of the ^{199}Hg nucleus, the third element of the IIb group of the periodical system, show a similar behaviour [8, 9].

c) Temperature Dependence of the ^{67}Zn Chemical Shift

The ^{67}Zn resonance of solutions of $ZnCl_2$, $ZnBr_2$ and $Zn(ClO_4)_2$ with a concentration of about 2 molal was investigated in the temperature range from 253 K to 343 K. Figure 3 shows, that the Larmor frequency in $Zn(ClO_4)_2$ is independent on the temperature contrarily to $ZnCl_2$ and $ZnBr_2$:

$ZnCl_2$	2 molal	3.4 Hz/K	or	0.70 ppm/K
$ZnCl_2$	4 molal	2.3 Hz/K	or	0.48 ppm/K
$ZnBr_2$	1.9 molal	2.9 Hz/K	or	0.61 ppm/K
$Zn(ClO_4)_2$	2.2 molal	0.0 Hz/K	or	0.00 ppm/K

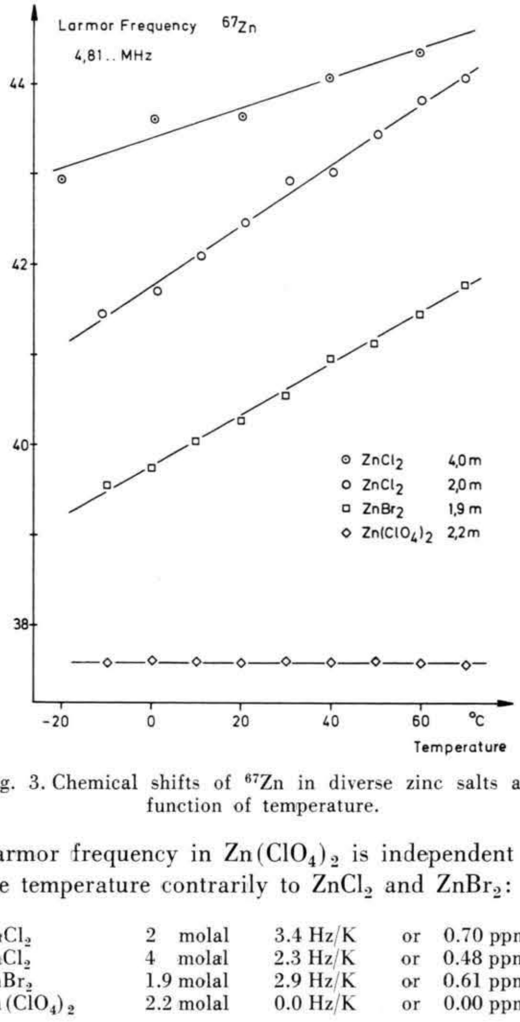

Fig. 3. Chemical shifts of ^{67}Zn in diverse zinc salts as a function of temperature.

For comparison: $\Delta\nu\,(^{111}Cd)/\Delta T = 0.5$ ppm/K in 2 molal $CdSO_4$ solution [25] and $\Delta\nu(^{207}Pb) = 2$ ppm/K in 1 molal $Pb(NO_3)_2$ solution [23]. Deverell at al. [17] have found a shift $\Delta\nu(^{19}F)/\Delta T = -0.05$ ppm/K for an aqueous 5.5 molar KF solution. These authors explain the negative shift with a slight decrease in the vibrational frequency with increasing temperature due to a weakening of the fluorine ion water interaction. For zinc halides we have a shift to higher frequencies or higher shielding. This shift is presumably due to the strong halide complexes.

d) Line widths

The observed line widths are very sensitive to variations of concentration, anions, pH-value and temperature. The widths are in the range between 20 Hz for a 0.3 molal ZnI_2 solution at 303 K, partly due to field inhomogeneity and 600 Hz for a 4 molal $ZnCl_2$ solution at 253 K. The dependence of the ^{67}Zn line widths on temperature are plotted in Figure 4. The widths $\Delta\nu_{1/2}$ for diverse anions (concentration always 2 molal, temperature 303 K) are:

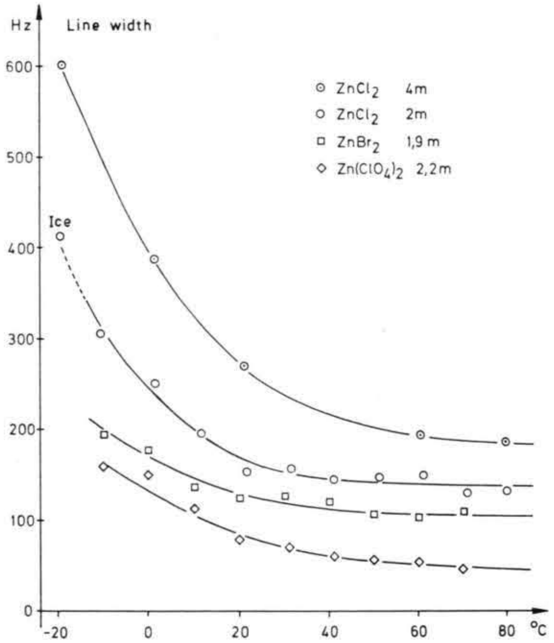

Fig. 4. Line widths of ^{67}Zn of diverse zinc salts as a function of temperature.

ZnI_2	35 Hz	$Zn(ClO_4)_2$	50 Hz
$ZnBr_2$	80 Hz	$ZnSO_4$	65 Hz
$ZnCl_2$	110 Hz	$Zn(NO_3)_2$	83 Hz

In the zinc halide solutions the pH-value was adjusted by adding a very small amount of hydrochloric acid. In less concentrated solutions (<2 molal) without added acid, zinc tends to precipitate as the hydroxide. Because of the hydrolysis more concentrated solutions are strongly acidic, e. g. a 6 molal solution of $ZnCl_2$ has a $p_H \approx 1$. The line widths are smaller with a little amount of added acid, since more of the ^{67}Zn nuclei are in the same complex.

Because of the large line widths it is difficult to registrate ^{67}Zn signals in $ZnCl_2$ solutions of concentrations greater than 12 molal with our spectrometer.

Further, no ^{67}Zn resonance line was observable in solutions of $ZnCl_2$ and $ZnBr_2$ in ethanol, dimethylether, and acetone. In a mixture of 95% water and 5% ethanol, the line width for a 1.8 molal $ZnBr_2$ solution was 115 Hz. For comparison the line width in the same solution without ethanol was 75 Hz.

e) The Ratio of the Larmor Frequencies of ^{67}Zn and ^{37}Cl

The Larmor frequencies of ^{67}Zn and ^{37}Cl were measured alternately in the same sample of aqueous zinc perchlorate at (303 ± 3) K only by varying the excitation frequency. The sample consisted of 72.28 mol% D_2O, 23.76 mol% H_2O and 3.96 mol% $Zn(ClO_4)_2$. The line widths are about 55 Hz for the zinc and 40 Hz for the chlorine resonance. For zinc the signal-to-noise ratio is greater than 35 within a measuring time of 5.5 min. The result is:

$$\nu(^{67}\mathrm{Zn})/\nu(^{37}\mathrm{Cl}) = 0.766\,394\,32\,(55)\,.$$

The given error is twice the standard deviation.

f) The Magnetic Moment of ^{67}Zn^{++} hydrated by Water *

The ^{67}Zn and the ^{37}Cl (22) resonance lines show a small dependence on the concentration of the aqueous perchlorate solutions. Extrapolating this ratio to vanishing concentration of zinc perchlorate, we obtain the Larmor frequencies of ^{67}Zn in the zinc ion and of ^{37}Cl in the perchlorate ion, which are influenced only by the surrounding water molecules:

$$[\nu(^{67}\mathrm{Zn})/\nu(^{37}\mathrm{Cl})]_{\mathrm{extrapol.}} = 0.766\,392\,3\,(9)\,.$$

The error results from the uncertainty of the extrapolation to zero concentration.

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* A preliminary value is given in Reference [26].

Using the ratio of the Larmor frequencies of ^{37}Cl and ^{2}H for vanishing perchlorate concentration in D_2O

$$[\nu(^{37}\mathrm{Cl})/\nu(^{2}\mathrm{H})]_{\mathrm{extrapol.}} = 0.531\,829\,2(4)\ {}^{**}$$

derivable from the work of Blaser et al.[22],

$$\nu(^{2}\mathrm{H})/\nu(^{1}\mathrm{H}) = 0.153\,506\,083(60)$$

of Smaller[27], and the uncorrected magnetic moment of the proton in water $\mu = 2.792\,709(17)\,\mu_N$ of Taylor et al.[28], the magnetic moment of the zinc ion, which is hydrated by water is:

$$\mu(\text{hydrated } ^{67}\mathrm{Zn}^{++}) = 0.873\,664\,4(12)\,\mu_N\,.$$

This value is not corrected for the diamagnetism of the electrons of the ion and the surrounding water and is still in agreement with the less accurate result of Reference[1].

g) The Shielding Constant of ^{67}Zn Ions by Water

Spence and McDermott[3] have determined the Larmor frequency of ^{67}Zn in free atoms in the $^{1}S_0$ ground state by optical pumping techniques relative to the Larmor frequency of protons in H_2O:

$$\nu(^{67}\mathrm{Zn})_{\mathrm{opt.}}/\nu(^{1}\mathrm{H}) = 0.062\,524\,1(6)\,.$$

From our NMR measurements of the ratio of the Larmor frequencies of ^{67}Zn and ^{37}Cl in aqueous solution for infinite dilution follows with Ref.[22, 27]:

$$[\nu(^{67}\mathrm{Zn})/\nu(^{1}\mathrm{H})]_{\mathrm{NMR,\,extrapol.}} = 0.062\,567\,52(9)\,.$$

From both ratios the shielding constant is derivable:

$$\sigma^*(\text{hydrated } ^{67}\mathrm{Zn}^{++} \text{ versus } ^{67}\mathrm{Zn atom}) = -(6.9 \pm 0.1)\cdot 10^{-4}\,.$$

Spence and McDermott[3] gave the following value for the shielding constant of ^{67}Zn in the $\mathrm{Zn(NH_3)^{++}}$ ion, using the older measurement of Weaver[1]: $\sigma^* = -3.58(15)\cdot 10^{-4}$. A comparison is not possible, since the sample of Weaver's experiment is not given accurately.

For comparison, for the second element of the IIb group of the periodical system, a shielding constant of

$$\sigma^*(\text{hydrated } ^{111}\mathrm{Cd}^{++} \text{ versus Cd atom}) = -(11.06 \pm 0.04)\cdot 10^{-4}$$

was fouund[7]. Further, the shielding constant for ^{199}Hg is much larger, a preliminary value is given in Reference[8].

h) Atomic Reference Scale for ^{67}Zn Chemical Shifts

With the shielding constant of the zinc ions in water we are able to establish an atomic reference scale for all chemical shifts in the liquid, solid and metallic state, like in the case of ^{87}Rb[10] and ^{111}Cd[7]. For LiZn[2], the shielding constant is $\sigma^* = -26.9 \cdot 10^{-4}$. The predicted value for the Knight-shift in zinc metal is -0.20%[29].

Acknowledgement

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[**] Recalculated value; see Reference[26]. Change due to solvent isotope effect.

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