Article

The Radiofrequency NMR Spectra of Lithium Salts in Water; Reevaluation of Nuclear Magnetic Moments for ^{6}Li and ^{7}Li Nuclei

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Abstract: LiCl and LiNO$_3$ water solutions in the presence of small amounts of 3-helium have been investigated by means of multinuclear resonance spectroscopy. The resulting concentration dependences of the ^{3}He, ^{6,7}Li$^+$, ^{14}NO$_3{}^-$ and ^{35}Cl$^-$ resonance radiofrequencies are reported in the infinite limit. This data along with new theoretical corrections of shielding lithium ions was analyzed by a known NMR relationship method. Consequently, the nuclear magnetic moments of ^{6}Li and ^{7}Li were established against that of the helium-3 dipole moment: μ(^{6}Li) = +0.8220457(50)μ$_N$ and μ(^{7}Li) = +3.256418(20)μ$_N$. The new results were shown to be very close to the previously obtained values of the (ABMR) atomic beam magnetic resonance method. This experiment proves that our helium method is well suited for establishing dipole moments from NMR measurements performed in water solutions. This technique is especially valuable when gaseous substances of the needed element are not available. All shielding constants of species present in water solutions are consistent with new nuclear magnetic moments and these taken as a reference. Both techniques—NMR and ABMR—give practically the same results provided that all shielding corrections are properly made.

Keywords: ^{6}Li and ^{7}Li nuclear magnetic moments; NMR liquid-phase studies; nuclear magnetic shielding constants

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1. Introduction

The electromagnetic moments of nuclei, dipole and quadrupole, have great significance for theory of nuclear structure. The magnetic moments are of prime importance for all nuclei with spin number $I \geq 1/2$. They were established for the first time in the famous molecular beam experiments carried out by Rabi (1939) [1] and, afterwards, improved values were experimentally determined by means of NMR bulk experiments e.g., by Walchli (1954), for the sequence of nuclear moments from lithium up to thallium [2]. The method relies on the accurate measurements of two frequencies for different nuclei placed in one sample at the same magnetic field. One of these frequencies should belong to the nucleus with a well-known magnetic moment and can be taken as a reference. The main problem with this procedure lies in ensuring that the shielding effects of nuclei in the particular experimental conditions are known with enough accuracy. The spectacular growth of quantum theoretical methods in this field provided new impetus for improving existing data. Several such works were performed in the Laboratory of NMR Spectroscopy at the University of Warsaw. We utilize the gas phase conditions as a rule, because of the importance of the shielding results for the isolated molecules when extrapolation to the zero-pressure limit is possible [3,4]. Unfortunately, we do not have any stable gaseous substances at normal conditions available for several elements (e.g., Li, Be, Na, K, Sc). Instead of gaseous species, the liquid solutions should be used in these cases. In this work, water solutions of common salts of lithium were applied—LiCl and LiNO$_3$ in the presence of dissolved ^{3}He atoms. This procedure has

several advantages: very narrow NMR signals, good sensitivity and well-known shielding parameters of different ions in liquid samples.

Without a doubt, lithium nuclei are of great account from the point of view of nuclear physics. Accurate and precise experimental values of nuclear properties are of prime importance in this case. There are eight lithium isotopes ranging from ^{4}Li up to ^{11}Li; only two of them are stable: ^{6}Li (7.59(4)%) and ^{7}Li (92.41(4)%) [5]. Both these nuclei possess different moments, electric quadrupole and dipole magnetic, connected with magnetic numbers $I^\pi = 1^+$ (with three neutrons) and $I^\pi = 3/2^-$ (with four neutrons), respectively. Since the two isotopes vary by a single spin-1/2 neutron, they exhibit different quantum statistics: ^{6}Li is a composite fermion while a ^{7}Li nucleus is a composite boson particle. In these circumstances, they represent one of the smallest objects, whose nuclear parameters could be precisely calculated in the near future. Interestingly, in spite of different mass numbers, the charge radius in ^{7}Li is smaller, which indicates the valuable differences in the magnetic distribution inside both nuclei [6].

The first hints about the ^{7}Li nuclear magnetic moment were made by Goudsmit and Young [7] and soon after deduced by Granath [8] as the nuclear spin 3/2 and magnetic moment possess 3.29 times the theoretical magnetic moment of the proton ($\mu_N = e\hbar/2m_p$, where e is the elementary charge and m_p is the proton's mass). A further investigation into the magnetic properties of lithium isotopes was carried out by Rabi's molecular/atomic beam MR experiments in the resonance absorption method. The determination of the nuclear spin and magnetic moment of lithium isotopes was obtained for LiCl, LiF and Li_2 molecules [9,10]. Next, more precise results were received by NMR measurements performed in water solutions of lithium salts and calculated against the deuterium NMR reference [11,12]. Soon after, precise lithium nuclei dipole moments were measured by the atomic beam magnetic resonance method [13]. These last results were cited later in the most pronounced tabulated compilations of magnetic moments for stable nuclei [14–16]. All of the remaining lithium nuclei are radioactive and have very short half-lives (^{4}Li-4.9–8.9 × 10^{-23} s, ^{5}Li-5.4 × 10^{-22} s, ^{8}Li-0.84 s, ^{9}Li-0.178 s, ^{10}Li-5.5 × 10^{-22}–5.5 × 10^{-21} s and ^{11}Li-0.0087 s) [5].

The aim of this work is twofold. Firstly, precise NMR measurements of frequencies for LiCl and $LiNO_3$ in water solutions were performed and analysis of new ^{6}Li/^{7}Li NMR data collected for water solutions at low concentrations was performed and compared to the results for ^{3}He dissolved in the same samples. Up to now, the addition of helium ingredients has only been carried out in our lab only in the gas phase. We are now trying to extend our method to the liquid samples. As a second step, the nuclear magnetic moments of ^{6}Li and ^{7}Li nuclei were recalculated using new shielding constants of lithium cations solvated in water solutions [17]. New magnetic moments measured in our work were compared with these established before by the atomic beam method. It is obvious that accurate values of the nuclear ground-state properties of isotopes, such as the magnetic dipole and electric quadrupole moments, are ideal tools for testing the validity of nuclear structure models. Subsequently a comparison of different experimental and purely theoretical results was made.

2. Results and Discussion

2.1. NMR Experiments in Water Solutions

Lithium has NMR spectroscopy based on two different nuclei. Both are quadrupolar, then the interaction with the electric field gradient at the nucleus is important by definition. It is worth noting anomalous, very small quadrupolar moment of ^{6}Li (0.00082(2) barn, 1 barn = m^2) [15] (contrary to that of ^{7}Li-0.0406(8) barn), which as a consequence yields rather sharp resonance signals. The chemical shift range of both nuclides is small and reaches only ~30 ppm. Fortunately, lithium cation shows a high symmetric structure characterized by a small electric field gradient and its line width for reference solution (9.7 M LiCl in D_2O) not even achieving ~0.1 Hz. For this reason, water solutions of lithium salts seem to be ideal for precise measurements.

For the derivation of the lithium nuclear magnetic moments we have used the usual form of equation, which connects two observed frequencies at the zero concentration of lithium salts and

nuclear dipole moments. They should be corrected for shielding values of Li^+ and ^3He measured in aqueous solutions:

$$\Delta\mu_{Li}^z = \frac{\nu_{Li}}{\nu_{He}} \cdot \frac{(1-\sigma_{He})}{(1-\sigma_{Li})} \cdot \frac{I_{Li}}{I_{He}}\Delta\mu_{He}^z, \tag{1}$$

where ν_{Li} and ν_{He} mean appropriate radiofrequencies extrapolated to the infinite diluted solutions. I_x are magnetic quantum numbers of measured nuclei, and $\sigma_{He,Li}$ are also shielding corrections for nuclei in the experimental conditions. The above equation makes it possible to calculate the magnetic moment μ_{Li} when all other quantities are known. The experimental results of NMR measurements are shown in Table 1. The suitable concentration dependencies of specific extrapolations are illustrated in Figures 1 and 2. In general, the concentration dependences of chemical shifts/shielding for cations or anions should not be linear, particularly at higher concentrations. For uniformity, all analyses were done by single-variable quadratic functions. It is known that virial expansions can be used for models of aqueous ionic solutions [18]. All coefficients are shown in Table 1 as δ [ppm], δ_1 [ppm × mL × mol^{-1}] and δ_2 [ppm × mL × mol^{-2}]. The course of the functions (Figures 1 and 2) reflects the magnetic susceptibility effect of solutions and a complex intermolecular forces arising during rapidly equilibration of solvent-separated cations and anions.

A crucial role in the estimations of lithium nuclear magnetic moments has been played by knowledge of the diamagnetic corrections for helium atoms and lithium cations. As the reference point of helium measurements was chosen very precise shielding value of single atom nuclei $\sigma_0(^3He) = 59.96743(10)$ ppm calculated with relativistic corrections, QED (Quantum Electrodynamics) corrections and nuclear mass effects [19]. At the beginning, we measured the ^3He NMR signal against that of gaseous systems; the difference is 2.7675(25) ppm in the chemical shift category, independently on the concentration of helium in water. It corresponds to the 0.2384(5) ppm deshielding effect when going from isolated molecule in gaseous state to the liquid water solution. This value was used to correct the helium frequency by electron screening. For comparison, the chemical shift corrected for the susceptibility of ^3He in water solution against that of gaseous sample (1-atm gas sample used for the gas reference) was measured previously by Jokisaari [20] $\Delta\delta = 0.297(39)$ ppm.

Table 1. NMR parameters measured in LiCl and LiNO$_3$ water solutions*. Shielding results of $^6Li^+$ and $^7Li^+$ cations calculated for: (a) six-coordinated and (b) four-coordinated water complexes.

Water Solution	Nuclide	ν_0 (Radiofrq.) MHz	δ/ppm	δ_1/ppm mL mol^{-1} δ_2/ppm mL mol^{-2}	σ/ppm	Reference
LiCl						
	$(^6Li^+)_{aq.}$	73.6695828(2)	−0.1472	−0.0632 0.0148	90.89(300) (a) 91.69(300) (b)	[17]
	$(^7Li^+)_{aq.}$	194.5544573(2)	−0.1469	−0.0632 0.0148	90.89(300) (a) 91.69(300) (b)	[17]
	$^{35}Cl^-$	49.0491386(10)	4.7125	0.9358 −0.0461	998.28(500)	[21] (This work)
	^3He	381.3564690(5)	−2.7675	−0.0478 0.0102	59.729(1)	[19] (This work)
LiNO$_3$						
	$(^6Li^+)_{aq.}$	73.6695829(2)	−0.147	−0.003 −0.0059	90.89(300) (a) 91.69(300) (b)	[17]
	$(^7Li^+)_{aq.}$	194.5544571(2)	−0.147	−0.003 0.0059	90.89(300) (a) 91.69(69) (b)	[17]
	$^{14}NO_3^-$	36.1752096(10)	−5.595	−0.107 0.0165	−132.14	[4] (This work)
	^3He	381.3564691(5)	−2.7676	−0.0045 −0.004	59.729(1)	(This work)

* Lock system tuned to $\nu(D_2O) = 76.8464$ MHz
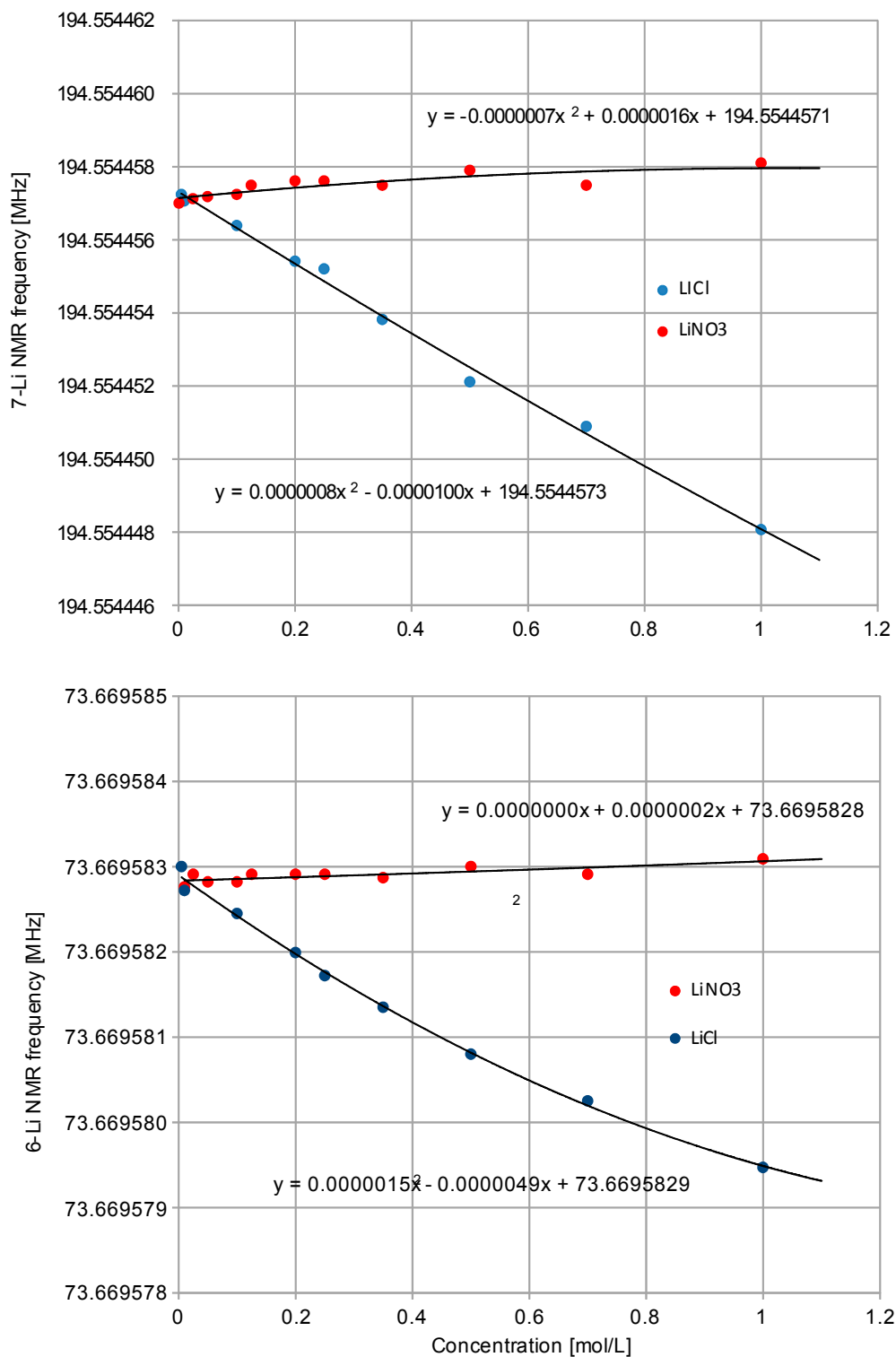
Figure 1. ^{6}Li and ^{7}Li NMR frequencies versus concentration of LiCl and LiNO$_3$ in water solutions.
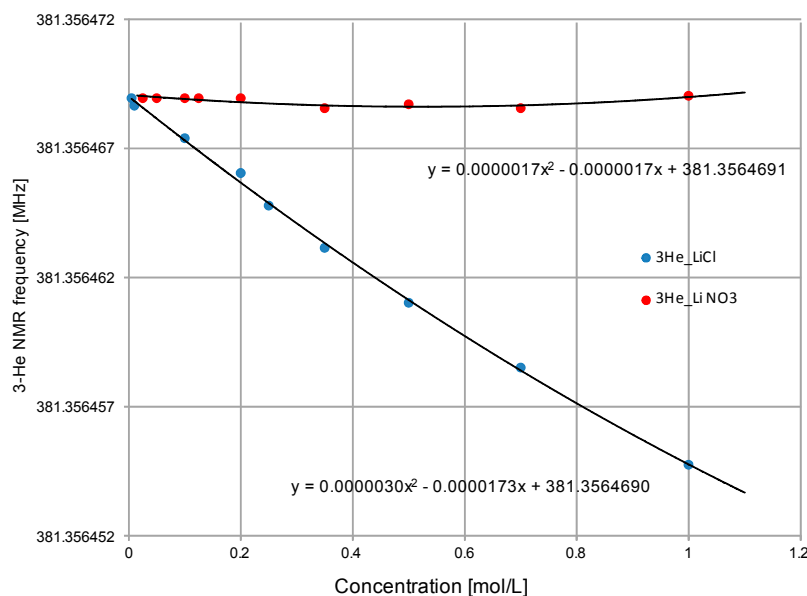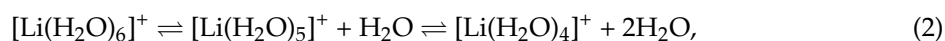
Figure 2. The ^{3}He NMR frequencies of helium atoms dissolved in water solutions of LiCl (lover curve) and LiNO$_3$ (upper curve) against salt concentration. Intersection of the axis represents frequency value at infinite dilution.

More significant correction is needed in the case of lithium nuclei. The ^{6,7}Li$^+$ cation's solvation properties in water solutions were actively studied in many theoretical simulations [22,23] and experimental research used different spectroscopy techniques [24–26]. The structure of the water complex is the subject of many controversies. The Li$^+$ cation in water solution has the smallest ionic radius of 90 pm (as 4-coordinated) and 76 pm (as-6-coordinated), and the highest positive charge density compared to other alkali metals. The stability of four, five or six water molecules in the inner shell of Li$^+$ ion is still under consideration. Most of this data refers to strong solutions in which there are very few water molecules that are not in the primary hydration spheres of the lithium cation, which may account for some of the solvation number variations with solute concentration. In the lithium aqueous ions have been found to have the solvation numbers of 3–6 and solvation numbers less than 4 can be suitable when the formation of contact ion pairs is possible. In the infinite dilution, we can exclude the possibility of interaction between a solvated cation and an anion and forming an ion pair. It is clear that the measured solvation number is a time-averaged value in the water solutions. The primary solvation number seen is fractional; there are two or more species with integral solvation numbers present in equilibrium with each other:

$$[\text{Li}(\text{H}_2\text{O})_6]^+ \rightleftharpoons [\text{Li}(\text{H}_2\text{O})_5]^+ + \text{H}_2\text{O} \rightleftharpoons [\text{Li}(\text{H}_2\text{O})_4]^+ + 2\text{H}_2\text{O}, \tag{2}$$

The higher solvation numbers may be interpreted in terms of water molecules in a tetrahedron coordination [Li(H$_2$O)$_4$]$^+$ or even higher coordinated complexes e.g., an octahedral aqua ions which are revealed by molecular dynamic simulations. The final suggestion of P.E. Mason et al. [25] shows that an infinitely diluted water solution at room temperature is mainly composed of 4 coordinated lithium complexes of great stability. Without pre-empting composition at the infinite dilution we decided to calculate lithium moments when tetrahedral or/and octahedral coordination take place. If the coordination number of central lithium cation varies, its shielding values change, starting from 95.30–95.41 ppm for an isolated ion up to 90.18 ppm in the hexacoordinated complex [17]. In the last case the small correction of 0.8 ppm for 2 water molecules, which distorts the first tetrahedral solvation shell of lithium ion, was applied [27]. The final shielding effect, with the small relativistic term 0.08 ppm calculated by the CCSD/utA,tz (Coupled Cluster) quantum method, was then 90.89 ppm. If four coordinating lithium cations are present then shielding constant 91.69 ppm should be valid [17].

Taking into account of the ν_{Li}/ν_{He} frequency ratio (see Table 1) and both shielding corrections for ^{3}He and ^{6,7}Li nuclei we can deduce the nuclear magnetic dipole moments of ^{6}Li and ^{7}Li nuclei (see Table 2). Two values in the table were quoted for different shielding corrections for the lithium nucleus (90.89 and 91.69 ppm) as the lower and upper limit for the magnetic moment. It is worth noting that both results are in good agreement with previously results used in establishing the absolute lithium shielding scale by J.Mason [28], see also [13]: 90.0(8) ppm (^{6}Li) and 90.4(7) ppm (^{7}Li). In any case, the effect is small and will be used as reference against ABMR results (see Table 3).

Table 2. $^{6/7}$Li nuclear magnetic shielding values calculated from Equation (3) and selected nuclear magnetic moments. Theoretical results for hexa- and tetra-coordinated water complex.

$\mu(^7Li)/\mu_N$	Method/Reference	Nucleus	$\sigma(^7Li^+)_{aq.}/ppm$
	Theory/[17]		$90.89 \div 91.69(300)$
3.2564169(98)	NMR/(This work)	$^{35}Cl^-$	91.16
		$^{14}NO_3{}^-$	90.36
3.2564195(98)	NMR/(This work)	$^{35}Cl^-$	91.53
		$^{14}NO_3{}^-$	90.73
3.2564157(30)	ABMR/[13], (This work)	$^{35}Cl^-$	90.76
		$^{14}NO_3{}^-$	89.96
3.2564625(4)	NMR/[15]	$^{35}Cl^-$	105.13
		$^{14}NO_3{}^-$	104.33
$\mu(^6Li)/\mu_N$			$\sigma(^6Li^+)_{aq.}/ppm$
	Theory/[17]		$90.89 \div 91.69(300)$
0.8220453(25)	NMR/(This work)	$^{35}Cl^-$	91.09
		$^{14}NO_3{}^-$	90.30
0.8220459(25)	NMR/(This work)	$^{35}Cl^-$	91.82
		$^{14}NO_3{}^-$	91.03
0.8220445(10)	ABMR*/[13], (This work)	$^{35}Cl^-$	90.12
		$^{14}NO_3{}^-$	89.32
0.822567(3)	NMR/[15]	$^{35}Cl^-$	725.27
		$^{14}NO_3{}^-$	724.47

2.2. ABMR Experiments for Atoms

An extensive ABMR (atomic beam magnetic resonance) experiment was carried out to examine ^{6,7}Li nuclear magnetic moments [13]. Several improvements to the original technique were made to avoid all systematic errors involved in this approach. The method of separated oscillatory fields with triple resonance technique and special calibration of the magnetic field offered very precise final results. For a proper comparison of our results with ABMR values, several new corrections were applied to the original quantities, i.e., proton-to-electron mass ratio m_p/m_e = 1836.15267389(17) [29] and diamagnetic correction factor in Li atom $(1-\sigma_{Li})^{-1}$ = 1.0000101472 [30]. This last value is very consistent with previous received theoretical results -101.4 and 101.45 ppm [31,32]. The g_J factor for the $2^2S_{1/2}$ state was taken from the original work-2.002301100(64), which agrees very closely with the purely theoretical data, 2.00230101 [33]. The final, corrected magnetic moments established by Beckmann et al. [13] are shown in Table 2 as ABMR* results. The differences between nuclear magnetic moments measured in our NMR investigation and the ABMR method are then of the order 0.8–1.5×10^{-4}%. Remarkably, our refine results are much closer to the ABMR results than those cited in several current specifications [14–16] received from previous NMR measurements performed in aqueous solutions. It is certainly not without significance that the final results are more closely related to the ABMR results when shielding lithium cations were used for the strictly hexacoordinated water complex.

Table 3. Electromagnetic properties of lithium, chlorine, nitrogen, helium and deuterium nuclei.

Nuclide	I^π	Q Barn	Abundance %	μ/μ_N	Diamagnetic Correction	g_I Factor	$\gamma_I \times 10^7$	Reference
^{6}Li	1^+	0.00082(2)	7.59(4)	0.8220453(25)	1.00009089	0.822045(3)	3.93712(1)	(This work)
				0.8220459(25)	1.00009169			
				0.8220445(10)	1.000101472			[13]
				0.832; 0.835				[34]
				0.843(5); 0.843(2)				
^{7}Li	$3/2^-$	0.0406(8)	92.41(4)	3.2564169(98)	1.00009089	2.170945(7)	10.39756(3)	(This work)
				3.2564195(98)	1.00009169			
				3.2564157(2)	1.000101472			[13]
				2.993; 3.036				[34]
				3.01(2); 3,02(2)				
^{35}Cl	$3/2^+$	0.0850(11)	75.78(4)	0.821721(5)		0.547814(3)	2.62371(1)	[21]
^{14}N	1^+	0.02001(10)	99.632(7)	0.4035729(45)		0.403573(5)	1.93288(2)	[4]
^{3}He	$1/2^+$		0.000137	2.127625308(25)	1.00005973	4.25525061(5)	20.3801680(2)	[29]
^{2}H(D)	1^+	0.00286(2)	0.0156	0.8574382311(48)		0.857438231(5)	4.1066289(1)	[29]

2.3. Shielding Factors

The new nuclear magnetic moments from NMR and ABMR experiments (Table 2) can certainly be tested, because a few shielding constants of different additional nuclei present in the solution are known with great precision. The concentration dependencies for $^{35}Cl^-$ and $^{14}NO_3^-$ anions are shown in Figure 3.

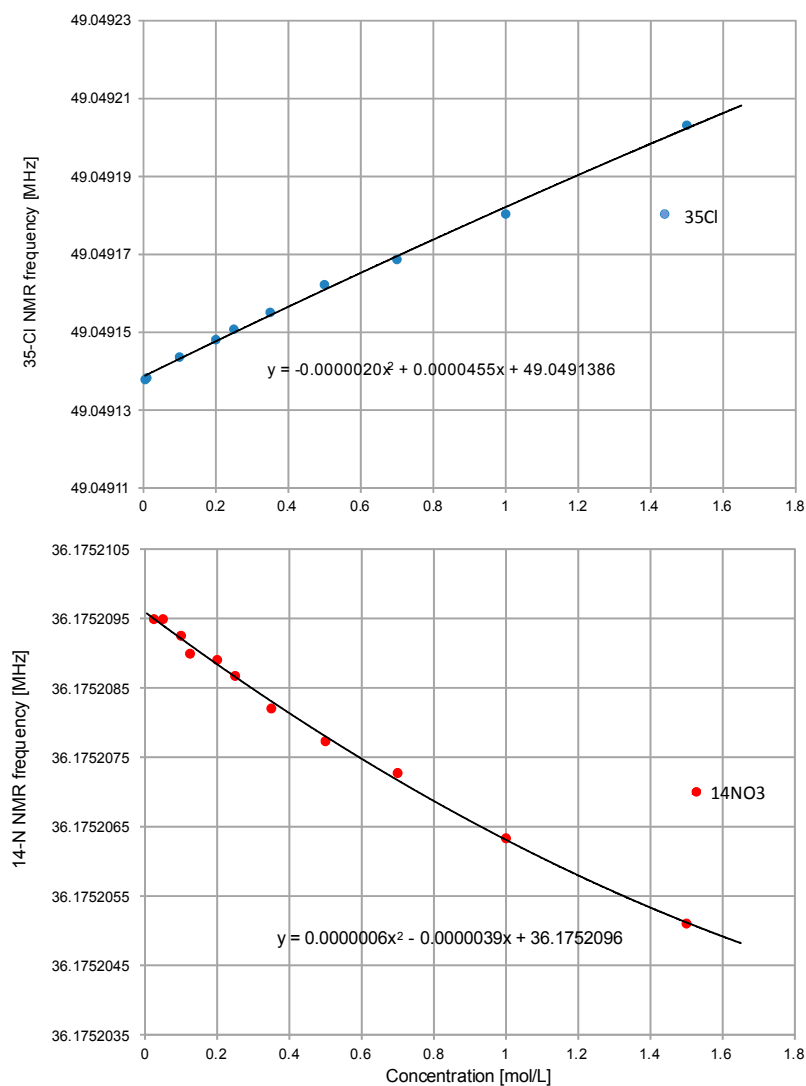**Figure 3.** The ^{14}N and ^{35}Cl NMR frequencies of Cl^- and NO_3^- anions as function of LiCl and LiNO$_3$ concentration in water solutions. Intersection of the axis represents frequency value at infinite dilution.

In order to verify the conformity of the nuclear shielding values of lithium nuclei in water solution a different form of Equation (1) was used:

$$\sigma_X = 1 - \frac{\nu_X}{\nu_Y} \cdot \frac{\Delta\mu_Y}{\Delta\mu_X} \cdot \frac{I_X}{I_Y}(1 - \sigma_Y), \tag{3}$$

Formula (3) was carried out for each pair of nuclei: $^{6,7}Li/^{14}N$ and $^{6,7}Li/^{35}Cl$ present in our samples of H$_2$O solutions. ^{14}N nuclear shielding in the NO$_3^-$ anion at infinite dilution was calculated from nuclear magnetic shielding of liquid CH$_3$NO$_2$, which is equal to -132.14 ppm [4]. ^{35}Cl nuclear shielding in the Cl$^-$ anion was calculated against shielding value in 0.1 M NaCl/D$_2$O solution, which is equal to 998.28 ppm [21]. From the results collected in Table 2, it is clear that only our new $^{6,7}Li$ nuclear

magnetic moments are consistent with shielding calculations against D_2O, $^{35}Cl^-$ and $^{14}NO_3{}^-$ species accordingly to Equation (3).

Subsequently, the uncertainty error of lithium shielding is much less then suggested by theoretical predictions (± 3 ppm) [17] and possibly remains ± 1.5 ppm an order of magnitude.

It is worth noting that measurements of lithium dipole moments, contrary to many heavier isotopes, depend on diamagnetic corrections of NMR frequencies only in limited degree. This is a consequence of the relatively narrow spectral ranges of all nuclei in magnetic resonance studies ($^{6,7}Li$, ^2H, ^3He) and the small screening factors. It means that $^{6,7}Li$ magnetic moments belong to the class of most precise and accurately known dipole moments for all elements in the whole periodic table.

The lithium nuclei are very promising objects in the theoretical quantum calculation field. It is known that pure theoretical methods are still a long way from the precision of resonance experiments. Formerly performed calculations are valid to the three or four digit numbers, i.e., $\mu(^6Li) = 0.832\mu_N$ and $\mu(^7Li) = 2.993\mu_N$ or $\mu(^6Li) = 0.835\mu_N$ and $\mu(^7Li) = 3.036\mu_N$ [34]. On the other hand the lithium magnetic moments of another isotopes are still a subject of great interest. New developments have also involved short living isotopes: $^{8,9,11}Li$ nuclei. The investigation into magnetic moments for stable isotopes forms only a part of the studies, which include the short living isotopes at different excitation levels. The nuclear moments of $^8Li(1.653560(18))\mu_N$, $^9Li(3.43682(5))\mu_N$ and $^{11}Li(3.6712(5))\mu_N$ were measured by β-NMR experiments with major precision [35].

3. Materials and Methods

$LiNO_3$ (Sigma-Aldrich, Saint Louis, MO, USA, 99.99%) and LiCl (Sigma-Aldrich, 99.998%, anhydrous) were used for preparing water solutions at total densities in the range 0.25–1.2 mol/L. Samples of 0.3 mL in Pyrex tubes (4 mm o.d. and 56 mm long) were frozen in liquid nitrogen and pumped to a pressure of ~10^{-3} mmHg. Small amounts of ^3He (Chemgas, Boulogne, France, 99.9%) $\leq 3.0 \times 10^{-3}$ mol/L were then added before sealing the ampoules by torch. Only a small amount of helium can be dissolved in water solutions (~0.0015 g/kg in pure H_2O at room temperature). These ampoules were fitted into standard 5 mm o.d. NMR test tubes (Wilmad-LabGlass Co., Vineland, NJ, USA) 548-PP or 10 mm tubes with liquid D_2O in the annular space. The reference samples were 0.1 M NaCl in D_2O for $^{35,37}Cl$ NMR spectra ($\Delta_{1/2} = 0.38$ Hz) and 0.1 M LiCl for $^{6,7}Li$ NMR spectra. The lock system, operated at 76.8464 MHz, allows the same magnetic field $B_0 = 11.7570$ T to be preserved. All measurements were performed at a constant temperature of 300 K. The small isotope effect when H_2O was changed by D_2O was equal to 0.02 ppm in 1 M lithium chloride solution. The rise of temperature causes deshielding effect of the lithium-7 signal by 0.0076 ppm/deg in the range 288.8–328.8 K.

High resolution $^{6,7}Li$, ^{35}Cl and ^{14}N NMR spectra were recorded on a Varian-INOVA 500 spectrometer (Varian Inc., Palo-Alto, CA, USA) equipped with sw5 (switchable) and BB10 (broad band) probes operating at 194.5544 MHz, 73.6695 MHz, 49.0491 MHz and 36.1752 MHz, respectively. For the enhancement of ^6Li signals, the ^2H(D) filter was omitted in the detection circuit. The primary reference solutions—$^{6,7}LiCl$ (9.7 M in D_2O), $Na^{35}Cl$ (0.1 M in D_2O), $CH_3{}^{14}NO_2$ (liquid) were used for standardization of lithium, chlorine and nitrogen spectra. The ^3He NMR spectra in liquid water solutions were measured by a special, homemade (Helium) probe, relative to the gas phase result, received from the extrapolation of helium shielding in gaseous mixtures CF_4-^3He and C_2F_6-^3He to the zero-point density.

The observed line width of an NMR signal at half-height was different for particular nuclei: $\Delta_{1/2}(^7Li) = 0.30 \div 0.45$ Hz with digital resolution (d.r.) = 0.18 Hz, $\Delta_{1/2}(^6Li) = 0.18 \div 0.35$ Hz with (d.r.) = 0.18 Hz, $\Delta_{1/2}(^3He) = 0.55 \div 1.15$ Hz with (d.r.) = 0.38 Hz, $\Delta_{1/2}(^{14}N) = 2.24 \div 6.45$ Hz with (d.r.) = 0.23 Hz, $\Delta_{1/2}(^{35}Cl) = 8.0 \div 9.75$ Hz with (d.r.) = 0.61 Hz. All spectra were subjected to line broadening (l.b. = 0.1) and zero-filling procedures to improve of spectral quality.

The shielding susceptibility effect for water (3.006 ppm) was calculated treating the formula $\sigma_{1b} = -4\pi/3\chi_v$ and $\chi_v = \chi_M \cdot M_p/\varrho$ where $\chi_M = -12.97$, $M_p = 18.0002$ and $\varrho = 0.999865$ g/cm^3 [36].

4. Conclusions

The nuclear magnetic moment is a very important basic parameter of each nuclide, which is a fundamental measure of nucleus magnetic structure. The lithium isotopes belong to the most investigated nuclei of the past eight decades. NMR measurements offer the highest precision in relative measurements. In this work the dipole moments of ^{6}Li and ^{7}Li were found to be $\mu(^6\text{Li}) = +0.8220453(25) \div +0.8220459(25)$ and $\mu(^7\text{Li}) = +3.2564169(98) \div +3.2564195(98)$ in nuclear magnetons (μ_N). Our new results are more valuable than those previously established by NMR spectroscopy of lithium salts in water solvents. The results are very close to the earlier given numbers measured by the ABMR method: $\mu(^6\text{Li}) = +0.8220445(10)\mu_N$ and $\mu(^7\text{Li}) = +3.2564157(30)\mu_N$. Because both lithium nuclei differ by one only neutron this indicates significant differences in the magnetic distribution in ^{6}Li and ^{7}Li nuclei, which is confirmed by the nuclear theory.

The shielding constants received from theoretical calculations were verified by our experimental investigations against other shielding constants measured simultaneously in solutions. Both kinds of procedures lead to general agreement what means that nuclear shielding and magnetic moments built the orderly set of compatible data. This provided a very important check of the consistency and reliability of the magnetic properties of lithium nuclei. The limiting factor of the nuclear magnetic moments values is therefore diamagnetic corrections.

The applicability of the dissolved helium as a shielding reference in salt water solutions is then proved. Our new measurements did not solve the problem of the different kinds of lithium water complex ions present in solutions. Further investigations into these questions are strongly recommended. Nevertheless, our experimental findings can give new input towards the understanding of subnucleonic effects in magnetic moments when compared to new theoretical calculations involving higher-order corrections. I hope that the new "helium-3" method can be easily expanded to other alkali and alkaline earth metals to find their nuclear properties. The first attempts in this field are in progress.

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