

Fourier Transform Nuclear Magnetic Resonance Studies of ^{25}Mg and ^{43}Ca

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The ratios of the Larmor frequencies of ^{25}Mg and ^{37}Cl and of ^{43}Ca and ^{37}Cl have been measured in aqueous solutions and nuclear magnetic moments are given for these nuclei in the hydrated ions. ^{25}Mg and ^{43}Ca chemical shifts have been investigated at natural abundance of these isotopes in solutions of the chlorides, bromides, nitrates, perchlorates in H_2O and D_2O . The signal intensities are large enough to study within reasonable time these nuclei at natural abundance down to low concentrated solutions, e. g. 8 millimolar for ^{25}Mg . For ^{25}Mg very small chemical shifts have been observed whereas for ^{43}Ca remarkable shifts to higher frequencies are found for halide solutions and to lower frequencies for the oxyanion solutions. Linewidths of only some Hz have been observed for both isotopes.

I. Introduction

Nuclear magnetic resonance studies of ions in aqueous and non-aqueous solutions have proven to be a useful tool in investigating structural phenomena (see for example Ref.¹) All of the very interesting earth alkaline elements have at least one isotope which is accessible to nuclear magnetic resonance studies. But there are only a few NMR investigations of these nuclei in solutions: ^9Be ^{2, 3}, ^{25}Mg ^{4–7}, ^{43}Ca ^{8–10}, ^{87}Sr ^{11, 12}, ^{135}Ba ¹³. The reasons for this are the mostly very low NMR signals of these nuclei due to their small gyromagnetic ratios and the low natural abundance of the isotopes.

Continuing our systematic investigations in the various groups of the periodic table we have done NMR investigations of ^{25}Mg and ^{43}Ca at natural abundance. Naturally occurring magnesium contains 10.13% of the ^{25}Mg isotope which has a nuclear spin of $5/2\hbar$. ^{43}Ca has a natural abundance of 0.129%, a nuclear spin of $7/2\hbar$ and as far as we know a nuclear quadrupole moment of yet unknown size. The sensitivity in a 1 molal aqueous solution is for ^{25}Mg about $2.2 \cdot 10^{-6}$ and for ^{43}Ca about $8 \cdot 10^{-8}$ compared with the sensitivity of the proton at the same field. These low NMR sensitivities are the reason for the few studies of ^{25}Mg and ^{43}Ca in natural abundance in solutions.

For nuclei with poor NMR results, systematic investigations of the following aspects are necessary: ratio of the Larmor frequency to the Larmor frequency of a standard nucleus, nuclear magnetic

moment, chemical shifts and linewidths in aqueous and non-aqueous solutions, NMR-signals at low concentrations at natural abundance, NMR standards, and solvent isotope effects. Since magnesium and calcium also are of important interest in biological systems the knowledge of the behaviour of NMR-signals of these elements is useful for further applications in these fields, since only some few papers have been published on biological systems of these nuclei at natural abundance^{6, 7}.

In the following the results of our work on some of the mentioned aspects are described.

II. Experimental

The NMR-investigations of the ^{25}Mg , ^{43}Ca and ^{37}Cl signals have been done with a multi-nuclei Fourier transform spectrometer: the magnetic field of 1.807 T is externally stabilized by a Li-NMR probe¹⁴, the frequency range of 4–62 MHz is accessible by a Bruker pulse spectrometer BKR 322 s, the NMR pulse responses are accumulated by a time averaging computer (Signal Analyzer 5480 A of Hewlett Packard) and Fourier-transformed on the CDC 3300 of the Zentrum für Datenverarbeitung der Universität Tübingen using the procedures described by Schwenk^{15, 16}. Some essential features of the observed nuclei are given in Table 1.

For the ^{25}Mg , ^{37}Cl and a part of the ^{43}Ca investigations the free induction decay was observed whereas for the most of the ^{43}Ca measurements the QFT-method¹⁶ was used.

The chemical shifts are given: $\delta = \nu_{\text{sample}} - \nu_{\text{reference}}$, a positive value means a shift to higher frequency at constant field. The shifts are measured relative to an external reference by the sample

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Table 1. Important properties for NMR-investigations of ^{25}Mg , ^{37}Cl and ^{43}Ca .

Nucleus	^{25}Mg	^{37}Cl	^{43}Ca
Natural abundance (%)	10.13	24.47	0.129
Spin (\hbar)	5/2	3/2	7/2
Quadrupole moment (10^{-24} cm^2)	0.22	-0.062	?
NMR-sensitivity in 1 molal aqueous solution (proton=1)	$2.2 \cdot 10^{-6}$	$6.0 \cdot 10^{-6}$	$8.0 \cdot 10^{-8}$
Larmor frequency at 1.807 T (MHz)	4.710	6.275	5.178

replacement method. The reference solutions were a 2.0 molal solution of $\text{Mg}(\text{ClO}_4)_2$ in H_2O and a 7.2 molal solution of CaCl_2 in H_2O for ^{25}Mg and ^{43}Ca respectively. Rotating and not rotating cylindrical samples of 10 mm outer diameter were used. No bulk susceptibility corrections were made, since they are smaller than the other errors. The temperature for all measurements was $(303 \pm 3) \text{ K}$.

III. Ratios of the Larmor Frequencies

The ratios of the Larmor frequencies of ^{37}Cl and ^{25}Mg and ^{43}Ca respectively have been determined. The Larmor frequencies of ^{37}Cl and of the earth alkaline nuclei are close together and further the Larmor frequency of ^{37}Cl is well known in terms of that of ^2H and ^1H .

The Larmor frequencies of ^{25}Mg and ^{37}Cl and of ^{43}Ca and ^{37}Cl were measured alternately in the same probe and sample by changing the excitation frequency. For ^{43}Ca the result is:

$$\nu(^{43}\text{Ca})/\nu(^{37}\text{Cl}) = 0.825\,1753(16).$$

The sample consisted of 11.72 mol% CaCl_2 , 41.36 mol% D_2O and 46.92 mol% H_2O . 4 runs at different days with together $n = 64$ measurements have been performed. The given error is two times the standard deviation S^* . The linewidth of ^{43}Ca was 70 Hz due to the QFT-technique, that of ^{37}Cl was the natural width of 330 Hz. Signal-to-noise ratios are always better than 40 within 12 min.

For ^{25}Mg the following ratio was found:

$$\nu(^{25}\text{Mg})/\nu(^{37}\text{Cl}) = 0.749\,838\,65(24).$$

The sample consisted of 3.4 mol% $\text{Mg}(\text{ClO}_4)_2$ and 96.6 mol% H_2O . At 4 different days 70 ratios were

$$* \text{ standard deviation: } S = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (l_i - \bar{l})^2}.$$

measured, the given error is two times the standard deviation. A rotating sample was used since the linewidths are only 6 Hz, they are nearly equal for both nuclei in this solution. Measuring times of 5 min are used for signal-to-noise ratios of more than 90.

For calculating a magnetic moment, the dependence of the NMR-signal on the concentration of the samples used must be investigated.

IV. Chemical Shifts of ^{25}Mg and ^{43}Ca

^{25}Mg and ^{43}Ca resonance lines of diverse salts have been observed at various concentrations in aqueous solution. Figure 1 shows a typical NMR-signal of ^{25}Mg in a 2.0 molal aqueous solution of magnesiumperchlorate and Fig. 2 the ^{43}Ca signal of a 3 molal solution of calciumchlorid. Typical experimental conditions are given in the figure captions.

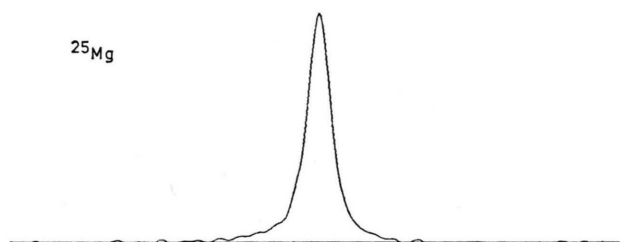


Fig. 1. Absorption signal of ^{25}Mg in a 2.0 molal aqueous solution of $\text{Mg}(\text{ClO}_4)_2$. Larmor frequency: 4.709 765 MHz, linewidth: 4 Hz, spectrum width: 80 Hz, pulse repetition frequency: 3.3 Hz, accumulation time: 5.5 min, rotating cylindrical sample: 10 mm outer diameter, sample volume: 1 ml.

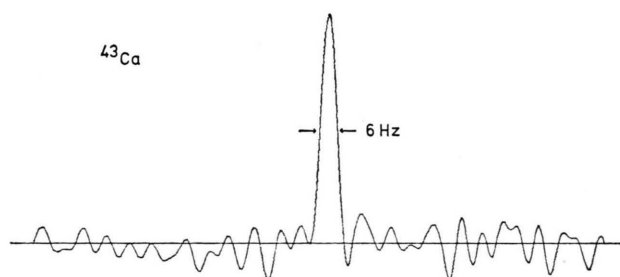


Fig. 2. Absorption signal of ^{43}Ca in a 3.0 molal aqueous solution of CaCl_2 . Larmor frequency: 5.177 866 MHz, linewidth: 6 Hz, spectrum width: 198 Hz, pulse repetition frequency: 3.3 Hz, accumulation time: 20 min, rotating cylindrical sample: 10 mm outer diameter, sample volume: 1 ml.

^{25}Mg chemical shifts:

^{25}Mg chemical shifts have been measured as a function of concentration of the following salts in aqueous solution: $\text{Mg}(\text{NO}_3)_2$, $\text{Mg}(\text{ClO}_4)_2$, MgBr_2 and MgCl_2 . The results are given in Figure 3.

The chemical shifts are very small and the whole range is only about 1 ppm. The differences between the various salts are nearly vanishing in contrast to the results of Ellenberger et al.⁵, who found shifts up to 3 ppm. Their lines are also broader and the signal to noise ratio much smaller.

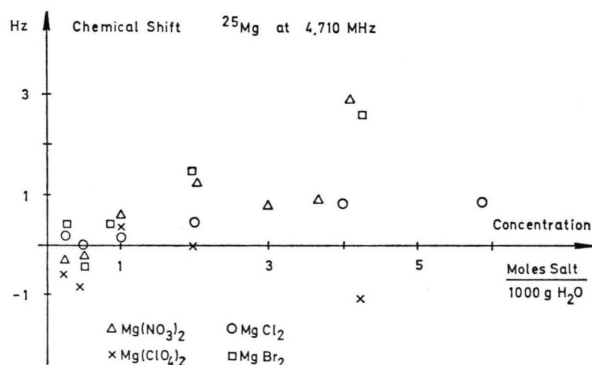


Fig. 3. Chemical shifts of ^{25}Mg at a Larmor frequency of 4.710 MHz in diverse aqueous solutions of magnesium salts as a function of concentration. Rotating cylindrical samples of 10 mm outer diameter were used. Reference: 2.0 molal solution of magnesium-perchlorate, typical error: about ± 1 Hz, bulk susceptibility correction smaller than this error.

 ^{43}Ca chemical shifts:

Chemical shift investigations have been done in aqueous and some non-aqueous solutions of CaCl_2 , CaBr_2 , $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Ca}(\text{HCOO})_2$ and $\text{CaC}_6\text{H}_5\text{O}_6$. Results are given in Figure 4.

In the halide solutions, the Larmor frequency is shifted to higher frequency, whereas oxyanions give negative chemical shifts. The two formate and lactate solutions show a shift $\delta = -31(7)$ Hz and $\delta = -45(6)$ Hz. The whole range in the studied aqueous solution was found to be about 20 ppm for ^{43}Ca .

The shifts of ^{25}Mg and ^{43}Ca can be compared with those of ^{87}Sr ¹². The range of the chemical shift increases from about 1 ppm for ^{25}Mg to 40 ppm for ^{87}Sr a behaviour which has been found also in alkali and IIb-group investigations^{1, 17-20}. Calcium ion shifts follow the same trend with changing anion

that has been previously observed by Banck and Schwenk¹² for strontium.

The shift of a 1.7 molal solution of calcium-chlorid in methanol was (90 ± 4) Hz compared with a 1.7 molal solution in H_2O . Similar shifts in methanol have been observed for the NMR-signals of potassium¹⁷ and cesium²¹.

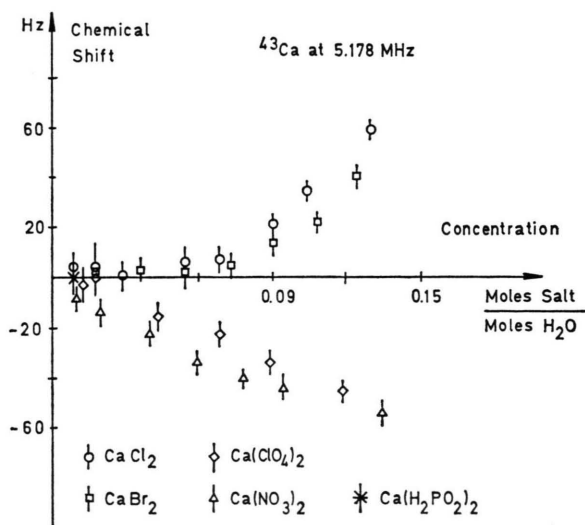


Fig. 4. Chemical shifts of ^{43}Ca at a Larmor frequency of 5.178 MHz in diverse aqueous solutions of calcium salts as a function of concentration. Cylindrical samples of 10 mm outer diameter were used. Reference: 7.2 molal solution of calciumchlorid. Plotted data, however, are referenced to the extrapolated frequency of the infinite dilution resonance for water, bulk susceptibility correction smaller than the measuring errors.

Further a solvent isotope effect of ^{43}Ca in solutions of some salts in H_2O and D_2O was searched for. The results for some equally concentrated solutions are given in Table 2. The size of the solvent isotope effect is always smaller than the experimental error but all the observed resonance lines in H_2O are situated at higher frequency also for the not

Table 2. Solvent isotope effect on chemical shift of ^{43}Ca .

Salt	Concentration moles salt moles solvent	^{43}Ca chemical shift $\nu(\text{H}_2\text{O}) - \nu(\text{D}_2\text{O})$	H_2O due to water of crystalliza- tion in D_2O samples
CaCl_2	0.018	9 ± 11	6.5%
CaBr_2	0.018	5 ± 10	3.2%
$\text{Ca}(\text{ClO}_4)_2$	0.018	7 ± 7	6.5%
$\text{Ca}(\text{NO}_3)_2$	0.020	4 ± 7	7.0%

given results obtained for $\text{Ca}(\text{NO}_3)_2$ -solutions as a function of concentration.

V. NMR-signals at low Concentration

In systems of biological relevance, the concentrations are situated in the range of some millimoles solute/kg solvent. From the measurements at higher concentrations the signal-to-noise ratio suggests that millimolar concentrations of at least magnesium compounds can be studied within reasonable time.

In order to confirm this point the ^{25}Mg and ^{43}Ca signals were observed at low concentration. A typical example with experimental conditions is given in Fig. 5, which shows the ^{25}Mg absorption line in a 8 millimolar $\text{Mg}(\text{ClO}_4)_2$ -solution. Within 190 min. a signal-to-noise ratio of 7:1 was achieved. For ^{43}Ca the conditions are less favourable.

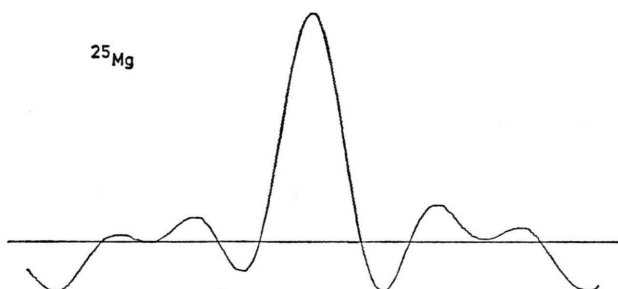


Fig. 5. Absorption signal of ^{25}Mg in a 8 millimolar solution of $\text{Mg}(\text{ClO}_4)_2$. No paramagnetic catalysts were added. Larmor frequency: 4.709 762 MHz, spectrum width: 100 Hz, pulse repetition frequency: 5 Hz, accumulation time: 190 min, rotating cylindrical sample: 10 mm outer diameter, sample volume: 1 ml.

VI. Linewidths

Since ^{25}Mg and ^{43}Ca have a nuclear spin of $5/2\hbar$ and $7/2\hbar$ respectively, these nuclei have quadrupole moments, the size of which is yet unknown for ^{43}Ca as far as we know. Due to the small magnetic moment, quadrupole relaxation seems to be the dominant contribution to the linewidths. There is only few information on linewidths in aqueous solution for these nuclei^{5, 7}.

The observed linewidths for ^{25}Mg are given in Figure 6. The inhomogeneity of the magnetic field contributes about 2–3 Hz to the observed line-

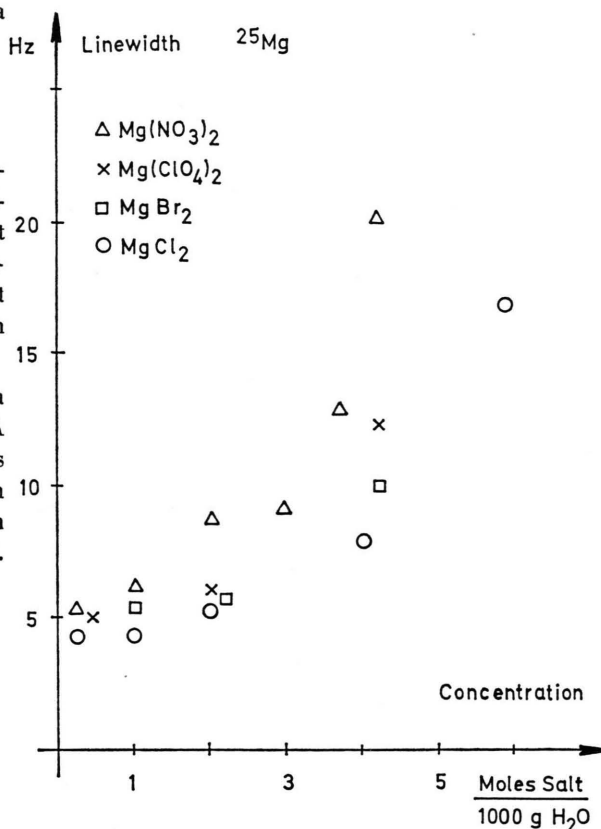


Fig. 6. Observed linewidths of ^{25}Mg of diverse magnesium salt solutions as a function of concentration. Measuring errors ± 1 Hz. The broadening of the natural NMR lines by the inhomogeneity of the field is about 2–3 Hz.

widths. The resonance lines are narrow in agreement with the observation of Bryant⁷ in a MgCl_2 -solution, and in disagreement with the broader lines found by Ellenberger and Villemin⁵.

Some typical linewidths observed for ^{43}Ca are given in Table 2. The contribution of the field in-

Table 3. Linewidths of ^{43}Ca in aqueous solutions.

Salt	Concentration moles salt per 1000 g H ₂ O	Linewidth * (observed) Hz
CaCl_2	3.0	6
CaCl_2	7.2	7
$\text{Ca}(\text{ClO}_4)_2$	3.8	6.5
$\text{Ca}(\text{ClO}_4)_2$	6.5	11

* The contribution of the inhomogeneity of the magnetic field is about 2–3 Hz.

homogeneity is also about 2–3 Hz. The linewidths increase with increasing concentration (and viscosity) and are greater for the oxyanions than for the halides. A similar behaviour was found for $^{87}\text{Sr}^{12}$, but for this nucleus the linewidths are 100–300 Hz.

The relatively small linewidths of ^{25}Mg and ^{43}Ca in these solutions give rise to the hope to detect NMR-signals of these nuclei if exchange processes are involved or if the nuclei are in binding sites with electrical field gradients, both aspects occur in biological systems.

VII. Magnetic Moments for the Hydrated Ions

The magnetic moments for nuclei in ions are given usually in aqueous solutions of vanishing concentration, since the shielding of the nuclei results in this case solely from the electrons of the ion itself and the surrounding water molecules. To proceed in this manner, the ratios of the Larmor frequencies and the dependence of the Larmor frequencies of salt and concentration of the preceding chapters are used together with the ratio $\nu(^{37}\text{Cl})/\nu(^2\text{H}) = 0.531\,294\,38(4)$ of Blaser et al.²² which was determined in a sample of 4.5 molal NaCl-solution in D_2O and the following further measurements:

$$\begin{aligned} &\nu(^{37}\text{Cl} \text{ in } 7.0 \text{ molal solution of } \text{CaCl}_2 \text{ in } \text{D}_2\text{O}) - \\ &\nu(^{37}\text{Cl} \text{ in } 4.5 \text{ molal solution of } \text{NaCl} \text{ in } \text{D}_2\text{O}) = \\ &= (193 \pm 10) \text{ Hz.} \end{aligned}$$

$$\begin{aligned} &\nu(^2\text{H} \text{ in } 7.0 \text{ molal solution of } \text{CaCl}_2 \text{ in } \text{D}_2\text{O}) - \\ &\nu(^2\text{H} \text{ in } 4.5 \text{ molal solution of } \text{NaCl} \text{ in } \text{D}_2\text{O}) = \\ &= (9 \pm 3) \text{ Hz.} \end{aligned}$$

$$\begin{aligned} &\nu(^{37}\text{Cl} \text{ in } 2.0 \text{ molal solution of } \text{Mg}(\text{ClO}_4)_2 \text{ in } \text{H}_2\text{O}) - \\ &\nu(^{37}\text{Cl} \text{ in } 4.5 \text{ molal solution of } \text{NaCl} \text{ in } \text{D}_2\text{O}) = \\ &= (6315.3 \pm 1.0) \text{ Hz.} \end{aligned}$$

The following results were obtained for vanishing concentration:

$$\begin{aligned} &\nu(^{25}\text{Mg} \text{ in } \text{Mg}^{2+})/\nu(^{37}\text{Cl} \text{ in } \text{ClO}_4^-) \\ &= 0.749\,838\,24(31), \end{aligned}$$

$$\begin{aligned} &\nu(^{43}\text{Ca} \text{ in } \text{Ca}^{2+})/\nu(^{37}\text{Cl} \text{ in } \text{Cl}^-) \\ &= 0.825\,164\,9(38). \end{aligned}$$

Using the results of Blaser et al.²² the ratios of the Larmor frequencies of the earth alkaline nuclei at

vanishing concentration to the Larmor frequency of ^2H in D_2O are

$$\begin{aligned} \nu(^{25}\text{Mg})/\nu(^2\text{H}) &= 0.389\,785\,9(6), \\ \nu(^{43}\text{Ca})/\nu(^2\text{H}) &= 0.438\,418\,9(23). \end{aligned}$$

Using the ratio $\nu(^2\text{H})/\nu(^1\text{H}) = 0.153\,506\,083(60)$ of Smaller²³ and the uncorrected magnetic moment of the proton in water $\mu(^1\text{H} \text{ in } \text{H}_2\text{O}) = 2.792\,7740(11)\mu_N$ of Cohen and Taylor²⁴ the following magnetic moments were derived:

$$\begin{aligned} &|\mu(^{43}\text{Ca} \text{ in } \text{Ca}^{2+} \text{ hydrated by } \text{D}_2\text{O})| \\ &= 1.315\,675(7)\mu_N, \\ &|\mu(^{25}\text{Mg} \text{ in } \text{Mg}^{2+} \text{ hydrated by } \text{H}_2\text{O})| \\ &= 0.854\,813(1)\mu_N. \end{aligned}$$

The results can be compared with the following NMR-values from literature:

$\mu(^{25}\text{Mg}) = -0.854\,72(12)\mu_N$ of Alder and Yu⁴ determined by measuring the ratio of the Larmor frequencies of ^{25}Mg in a 4.6 molar aqueous solution of MgCl_2 and of ^{14}N in concentrated HNO_3 .

$\nu(^{43}\text{Ca})/\nu(^2\text{H}) = 0.438\,32(4)$ of Jeffries⁸ using a 0.7 molar aqueous solution of CaBr_2 isotopically enriched to 60% ^{43}Ca , which was 4.5 molar in MnCl_2 .

By keeping in mind the different solutions the agreements are good. The only measurement of the magnetic moments of the earth alkaline nuclei in free atoms is that by Olschewski²⁵ by optical pumping technique. Olschewski's result for ^{43}Ca is

$$\mu(^{43}\text{Ca} \text{ in free atom}) = -1.315\,37(60)\mu_N.$$

From this a shielding constant $\sigma^* = (\mu_{\text{atom}} - \mu_{\text{NMR}})/\mu_{\text{atom}}$ can be derived:

$$\begin{aligned} &\sigma^* (^{43}\text{Ca}^{2+} \text{ in } \text{D}_2\text{O} \text{ vs. } ^{43}\text{Ca} \text{ in free atom}) \\ &= -(2 \pm 5) \cdot 10^{-4}, \end{aligned}$$

the amount of this constant is smaller than the comparable value for $^{87}\text{Sr}^{12}$.

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