Atomic Reference Scale for Chemical Shifts of Rubidium

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With a multi-nuclei Fourier transform NMR spectrometer the ratio of the Larmor frequencies of $^{85}$Rb and $^1$H in a solution of RbCl in D$_2$O has been measured with high accuracy. The concentration dependence of the $^{85}$Rb NMR signals has been determined in solutions of rubidium salts in H$_2$O and D$_2$O. Using this dependence, the ratio of the Larmor frequencies of the $^{85}$Rb nuclei for infinite dilution relative to $^1$H in pure D$_2$O is given. From this a $g$-factor for $^{85}$Rb has been derived and has been compared with the $g$-factor of an optical pumping experiment. The difference in the $g$-factors results from the shielding of the rubidium nuclei by the water molecules around the ions. The shielding constant is $\sigma\left(^{85}\text{Rb}\right) = -2.11(2) \times 10^{-4}$. This yields a general atomic reference scale for the chemical shift of rubidium in the liquid and solid states and the possibility of comparing experimental and theoretical shielding constants.

I. Introduction

Chemical shifts in NMR spectroscopy are usually referred to an internal or external standard, for which an intensive NMR line, which is as narrow as possible, will be chosen; the choice is somewhat arbitrary. This procedure yields relative chemical shifts very well, but the absolute shift is not known. An absolute chemical shift or absolute shielding constant had to be referred to a bare nucleus. Contrary to that of a free atom, the Larmor frequency of a bare nucleus is not simple to measure for light or heavy nuclei at this time. Therefore a shielding constant $\sigma$ is defined in the following way: $\sigma$ is the difference between the Larmor frequency of a free atom or ion and the Larmor frequency of an atom or ion in a particular chemical surrounding, devided by the first. The difference between the definitions using either the bare nucleus or the free atom or ion is only the diamagnetic shielding of the atom or ion, which can be calculated fairly well. Such a shielding constant yields a general atomic reference scale for experimental chemical shifts which can be compared now with calculated results.

By comparing the nuclear $g$-factors of the free atom or ion derived from atomic beam or optical pumping techniques with NMR measurements of the $g$-factor of the ion in a particular molecular environment, the shielding constant can be determined. The following shielding constants have been quoted:

- $^7\text{Li}$ (Ref. 1), $^{14}\text{N}$ (Ref. 2), $^{19}\text{F}$ (Ref. 2), $^{23}\text{Na}$ (Ref. 2), $^{85}\text{Rb}$ (Refs. 4, 5), $^{133}\text{Cs}$ (Ref. 5), and $^{209}\text{Pb}$ (Ref. 6).

In this paper we describe the evaluation of the shielding constant of $^{85}$Rb; for this nucleus a $g$-factor measured by the optical pumping method is available 7. A comparison between $\sigma\left(^{85}\text{Rb}\right)$ and $\sigma\left(^{85}\text{Rb}^+\right)$ could perhaps elucidate an isotopic effect on the shielding constant.

II. Experimental

$^{85}$Rb has a natural abundance of 72.15%, the Larmor frequency at 18.07 kOe is about 7.428 MHz, and the relative sensitivity in a 0.1 molal solution of RbNO$_3$ in water is about $7 \times 10^{-6}$ for $^{85}$Rb compared with 1 for the protons in this solution. To study the NMR signals of this nucleus, Fourier transform spectroscopy is the most appropriate method.

The NMR signals of $^1$H and $^{85}$Rb have been observed with a Bruker B-KR 322s pulse spectrometer in a magnetic field of 18.07 kOe, which is held constant with the aid of a $^7\text{Li}$ NMR probe 8. An appropriate number of free induction decays is summed by a Hewlett-Packard signal analyzer type 5480A. The Fourier transformations were calculated with programs of A. Schwenk by the CDC 3300 computer of the Zentrum für Datenverarbeitung Tübingen.

The chemical shifts were measured relative to an external standard by the sample exchange method. The chemical shift is given by $\delta = \nu_{\text{sample}} - \nu_i$; a positive value means a shift to higher frequency at a constant field. Cylindrical samples of 10 mm diameter were used; no bulk susceptibility corrections were made since they are smaller than the errors shown in Figure 1. Concentrations are given as moles salt per moles solvent. The temperature for the $^{85}$Rb measurement was (28 ± 2) °C. Further experimental conditions are given in Table 1.
Table 1. Experimental conditions employed for recording the rubidium and deuterium resonances at a field of 18.07 kOe.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>Larmor frequency</th>
<th>linewidth</th>
<th>pulse rep. time</th>
</tr>
</thead>
<tbody>
<tr>
<td>^2H</td>
<td>11.810 MHz</td>
<td>30 b Hz</td>
<td>0.9 Hz</td>
</tr>
<tr>
<td>^85Rb</td>
<td>7.428 MHz</td>
<td>180 Hz</td>
<td>90 Hz</td>
</tr>
</tbody>
</table>

a 10.7 mol% RbCl and 89.3 mol% D$_2$O.
b The linewidth of the $^2$H resonance is due to the inhomogeneity of the magnetic field.

III. The Ratio of the Larmor Frequencies of $^{85}$Rb and $^2$H

In a defined solution of RbCl in D$_2$O the ratio of the Larmor frequencies, $\nu(^{85}$Rb+)/$\nu(^2$H), was measured. The solution consisted of 10.7 mol% RbCl and 89.3 mol% D$_2$O (99.75% deuterium). The Larmor frequencies were measured alternately in the same probe at constant field only by varying the excitation frequency. This frequency was controlled by a frequency counter during the addition of the free induction decays. 49 measurements of the ratio were carried out on different days. A signal to noise ratio of 100 was achieved for the $^{85}$Rb signal. The experimental conditions are given in Table 1.

The result is:

$$\nu(^{85}$Rb+)/\nu(^2$H) = 0.628 973 6(3).$$

The uncertainty * is due to three times the rms error (0.1 ppm) and a systematic error (0.4 ppm); the systematic error arises from the partial asymmetry of the absorption signals, due to the inhomogeneity of the magnetic field.

BLUMBERG et al. 9 found a value

$$\nu(^{85}$Rb+)/\nu(^2$H) = 0.628 978 90(38)$$
in a saturated solution of RbCl; they observed the NMR signals of $^2$H and $^{85}$Rb in different probes at different locations in the magnetic field. The results cannot be compared because of the strong concentration dependence of the Larmor frequency of the $^{85}$Rb.

IV. Concentration Dependence

Measurements of the chemical shift of $^{85}$Rb NMR signals in aqueous solutions have not been carried out whereas the chemical shift of $^{87}$Rb has been studied by DEVERELL and RICHARDS 10 and LUTZ 4, 5 in several Rb$^+$-solutions. Therefore we have measured the chemical shift of $^{85}$Rb$^+$ in aqueous solutions of RbCl, Rb$_2$CO$_3$, Rb$_2$SO$_4$, and RbNO$_3$. The results are given in Figure 1. The measured shifts are adjusted so that they refer to the rubidium ion at infinite dilution as standard. The error of the extrapolation was assumed to be ±5.0 Hz. The influence of the anions on the chemical shift of the $^{85}$Rb ions is smaller than in the case of the $^{133}$Cs (Ref. 5), but the sequence in the influence is the same.

![Fig. 1. $^{85}$Rb chemical shifts in aqueous solutions of rubidium salts. Positive values are to higher frequencies. The measured shifts were adjusted so that they refer to the $^{85}$Rb$^+$ ion at infinite dilution as standard. Cylindrical probes (9 mm inner diameter) were used; no bulk susceptibility correction was made.](image)

The chemical shift of the solution, in which the ratio of the Larmor frequencies has been measured, relative to a solution of infinite dilution is:

$$\delta(^{85}$Rb$^+) = (143 \pm 6) \text{ Hz}.$$  

The Larmor frequency of $^2$H is also dependent on the concentration of the solution of RbCl in D$_2$O. A shift of −(3.2 ± 1.0) Hz was found for this solution referred to pure D$_2$O.

LOEWENSTEIN et al. 11 found for $^{87}$Rb$^+$ in H$_2$O and D$_2$O a solvent isotope effect of (0.29 ± 0.06)
ppm. We have measured the chemical shift of $^{85}$Rb$^+$ in solutions of RbCl and RbNO$_3$ in D$_2$O. The values for RbCl are given in Fig. 1, the values for RbNO$_3$ in D$_2$O are omitted for clarity. Our error is about 0.5 ppm, and within this limit we observed no solvent isotope effect.

V. Ratio of the Larmor Frequencies for Infinite Dilution

Using the dependence of the Larmor frequencies on concentration, the ratio of the Larmor frequencies which were measured in the somewhat arbitrary solution were transferred to a general base. The ratio of the Larmor frequency of the $^{85}$Rb nucleus at vanishing concentration to the Larmor frequency of $^2$H in pure D$_2$O is chosen as this general base:

$$\frac{\nu(^{85}\text{Rb}^+)}{\nu(2\text{H})} \text{extrapol.}$$

The result is:

$$\frac{\nu(85\text{Rb}^+)}{\nu(2\text{H})} \text{extrapol.} = 0.6289614(5).$$

The additional error is due to the uncertainty of the extrapolation to zero concentration.

From this ratio, a nuclear magnetic moment can be derived, using $\nu(2\text{H})/\nu(1\text{H}) = 0.153506083(60)$ of SMALLER$^{12}$ and the uncorrected magnetic moment of the proton in water $\mu_p = 2.792709(17) \mu_N$ of TAYLOR et al.$^{13}$.

The result is:

$$\mu(85\text{Rb}^+ \text{in D}_2\text{O}) = 1.3481717(15) \mu_N.$$  

The moment is affected by the uncertainty of the magnetic moment of the proton and is not corrected for the ionic diamagnetism. The magnetic moment, determined by the NMR method in the described manner, is influenced merely by the electrons of the ion itself and by the surrounding water molecules, which interact with the ion.

VI. The Shielding Constant of $^{85}$Rb$^+$ Ions in Water

In the performance of a NMR experiment in a solution in a static magnetic field $H_0$, the magnetic field, which the nucleus under investigation experiences, is not $H_0$; the influence of the surrounding ions or molecules gives rise to an additional magnetic field, which varies rapidly in time.

The Larmor frequency is

$$\omega = 2\pi \nu = \frac{g_I \mu_N}{\hbar} H = \gamma H = \gamma (1 - \sigma) H_0$$

$$= \gamma_{\text{NMR}} H_0.$$  

From this equation follows:

$$\sigma = 1 - \frac{\gamma_{\text{NMR}}}{\gamma} = 1 - \frac{g_{1\text{NMR}}}{g_I},$$

where $\gamma$ is the gyromagnetic ratio, and $g_I$ the nuclear $g$-factor of the atom not corrected for diamagnetism, $\gamma_{\text{NMR}}$ the gyromagnetic ratio and $g_{1\text{NMR}}$ the nuclear $g$-factor resulting from NMR experiments.

For evaluating $\sigma$, $g_{1\text{NMR}}$ and $g_I$ must be determined in independent experiments. $g_I$ can be measured on free atoms or ions with for example the atomic beam magnetic resonance or the optical pumping technique; $g_{1\text{NMR}}$ is measured on the ion in aqueous solutions by the NMR method.

If all methods use ions, the diamagnetic shielding of the ion needs not be accounted for further. If one of the methods uses atoms, a correction for the small difference between the diamagnetic shielding of the atom and that of the ion has to be made. For the size of this difference in the case of Rb see References$^{14, 15}$.

Following the formalism of WHITE et al.$^7$ we write:

$$g_{1\text{NMR}}(^{85}\text{Rb}^+) = g_{1\text{NMR}}(^{85}\text{Rb}^+) \cdot g_{1\text{NMR}}(2\text{H})$$

$$g_{I}(^{85}\text{Rb}) \cdot g_{I}(^{85}\text{Rb}) \cdot g_{I}(2\text{H}) \cdot g_{I}(2\text{H}) = g_{I}(^{85}\text{Rb}) \cdot g_{I}(^{85}\text{Rb}) \cdot g_{I}(2\text{H}) \cdot g_{I}(2\text{H}).$$

In addition to our value Eq. (1), the appropriate ratios of Refs.$^7, 12, 16, 17$ were used.

The result is:

$$\sigma(^{85}\text{Rb}^+ \text{in D}_2\text{O vs. } ^{85}\text{Rb}) = -2.11 (2) \cdot 10^{-4};$$

LUTZ$^5$ gives for the shielding constant of the $^{87}$Rb nucleus:

$$\sigma(^{87}\text{Rb}^+ \text{in D}_2\text{O vs. } ^{87}\text{Rb}) = -2.0 (2) \cdot 10^{-4}.$$  

and more recently WHITE et al.$^7$ calculated with the extrapolated ratio of LUTZ$^5$:

$$\sigma(^{87}\text{Rb}^+ \text{in D}_2\text{O vs. } ^{87}\text{Rb}) = -2.116 (12) \cdot 10^{-4}.$$  

These values are in good agreement with our

$$\sigma(^{85}\text{Rb}^+ \text{in D}_2\text{O vs. } ^{85}\text{Rb}).$$

There is no difference in the shielding constant of the $^{85}$Rb$^+$ and $^{87}$Rb$^+$ ions within the accuracy of the
experiment. With the correction for the difference of the diamagnetic shielding of the Rb atom and the Rb\(^+\) ion \(^{14,15}\) we get from Equation (2)

\[
\sigma(\text{Rb}\text{ }\text{in } D_2\text{O vs. } ^{85}\text{Rb}^+) = -2.15(2) \times 10^{-4}.
\]

IKENBERRY and DAS \(^{18}\) have calculated the shielding constant of a Rb\(^+\) ion, surrounded by 6 H\(_2\)O molecules, using the formalism of KONDO and YAMASHITA \(^{19}\). Their result is:

\[
\sigma(\text{Rb}\text{ }\text{in } H_2\text{O vs. } \text{Rb}^+) = -0.65(3) \times 10^{-4}. \tag{3}
\]

The large difference between the experimental and the theoretical value shows, that the theoretical model to explain the shielding constant is not yet accurate.

The good agreement of DEVERELLS \(^{20}\) value using the relation between the concentration dependence of quadrupolar relaxation and the shielding constant is encouraging but must be proved at further nuclei.

**VII. Atomic Reference Scale for Chemical Shifts**

With our value for the shielding constant of the Rb\(^+\) ions in water we are able to establish an atomic reference scale for all chemical shifts of rubidium in the liquid and solid states using the relative chemical shifts, which are quoted in literature \(^{10,21}\). These results are given in Figure 2. All rubidium chemical shifts measured further relative to aqueous solutions or other references can be given absolutely within this scale.

In the same manner an atom related Knight shift \(K_a\), i.e. the Knight shift relative to the free atom, can be evaluated. This is useful because one gets the real influence of the metallic state on the Larmor frequency of the nucleus by this procedure. The shifts \(K_a\) given in Fig. 2 result from the ratios of Chapter VI, the ratios of BLUMBERG et al. \(^{9}\) and the ratios of WHITE et al. \(^{7}\).

The results are:

\[
K_a(\text{Rb}) = -0.6767(3)\%,
\]

\[
K_a(\text{Rb}) = -0.6742(1)\%.
\]

It is worth mentioning, that the values of the Knight shifts of the two rubidium isotopes differ. This fact is due to the large hyperfine structure anomaly of the \(^{85}\text{Rb}\) and \(^{87}\text{Rb}\) isotopes \(^{9}\).

The theoretical values of the shielding constants in the liquid and solid states are not in good agreement with the experimental ones. For dilute solutions see Eq. (3); IKENBERRY and DAS \(^{18}\) found for the shielding of the Rb halide crystals values between \(-2.17 \times 10^{-4}\) and \(-2.11 \times 10^{-4}\) and TTERLIKIS et al. \(^{22}\) got \(K = -60 \times 10^{-4}\) for the \(^{85}\text{Rb}\) nucleus in Rb metal.

**Acknowledgement**

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Neutronenbeugungsuntersuchungen an der Mischkristallreihe $\text{Er}_x\text{Y}_{1-x}\text{Al}_2$

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Neutron Diffraction Measurements on Er$_x$Y$_{1-x}$Al$_2$

The magnetic properties of Er$_x$Y$_{1-x}$Al$_2$ have been studied by neutron diffraction measurements. The compounds exhibit ferromagnetic ordering for $x > 0.3$ with a linear dependence of the Curie temperature on $x$. ErAl$_2$ orders at 12.5 °K.

Einleitung

Im Rahmen eines Forschungsprogramms zur Untersuchung der magnetischen Eigenschaften und der Austauschmechanismen in Intermetallischen Verbindungen zwischen 3d-Übergangselementen und Seltenen Erden haben wir bisher über die magnetischen Strukturen und das magnetische Verhalten von ErAl$_2$, ErFe$_2$ und ErAl$_3$ berichtet. In Fortführung dieser Arbeiten berichten wir hier über Neutronenbeugungsuntersuchungen an Mischkristallen der Zusammensetzung Er$_x$Y$_{1-x}$Al$_2$.

Diese Kristalle ordnen sich ein in eine Gruppe von Verbindungen, die eine systematische Variation sowohl wichtiger kristallographischer Faktoren als auch der Austauschparameter enthält:

<table>
<thead>
<tr>
<th>Er$<em>x$Y$</em>{1-x}$Al$_2$</th>
<th>Laves-Phase, kubisch, AuCu$_2$-Typ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErAl$_2$</td>
<td>kubisch, (MgCu$_2$)-Typ</td>
</tr>
<tr>
<td>ErFe$_2$</td>
<td>hexagonal, 15 Schichten</td>
</tr>
</tbody>
</table>

ferro- bzw. ferri-magnetisch
Kristallfeld = klein
Austauschwechselwirkung positiv

er einer Neutronenwellenlänge von 0,971 Å. Die Absorption der Probe in der Zylindermitte wurde experimentell zu 18% bestimmt (Transmission = 82%). Bei der Auswertung der Kernstreuung zur Bestimmung der absoluten Skala für die Berechnung der magnetischen Momente wurden die Kernstreuamplituden $b_{\text{Er}} = 7,9 f$, $b_{\text{Al}} = 3,5 f$ und $b_{\text{Y}} = 7,85 f$ eingesetzt (1 f = 1 Fermi = 10$^{-13}$ cm). Die Streulänge von Yttrium wurde aus einer Neutronenbeugungsmessung von YAl$_2$ durch Ausgleichsrechnung neu bestimmt.


Kristallstrukturdaten

Die Er$_x$Y$_{1-x}$Al$_2$-Mischkristalle sind Laves-Phasen vom Stukurtyp C 15 (=MgCu$_2$). Sie kristallisieren in der Raumgruppe $O_h^-$-F d3m mit den Ionen in den folgenden Punktlagen

$\text{Er}, \text{Y}$ 8(a)  $\bar{4} \bar{3}m$  $0 \ 0 \ 0$, $\bar{1} \bar{1} \bar{1}$

$\text{Al}$ 16(d)  $\bar{3}m$  $\bar{1} \bar{1} \bar{1}$  $\bar{1} \bar{1} \bar{1}$  $\bar{1} \bar{1} \bar{1}$

Für Erbium und Yttrium nehmen wir statistische Besetzung der Punktlage 8(a) an. Die Kernstreudaten allein erlauben keine Differenzierung von Er und Y