Nuclear Magnetic Shielding and Quadrupole Coupling of ^{133}Cs in Cesium Salt Powders

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NMR signals of ^{133}Cs have been measured in CsI, CsBr, CsCl, Cs_2CO_3, Cs_2SO_4, $CsNO_3$ and Cs_2CrO_4 powders relative to a 0.5 molal aqueous solution of CsCl. Combining these results with the shielding constant of the solution, which has been determined in former measurements, the nuclear magnetic shielding of ^{133}Cs in the crystalline powders can be given in an atomic reference scale. The theoretical values of the shielding constant of ^{133}Cs in CsCl, CsBr and CsI agree only in the order of magnitude with the experimental ones. For ^{133}Cs in Cs_2SO_4 a first-order quadrupole pattern has been observed.

Introduction

The absolute size of the nuclear magnetic shielding or of the chemical shift of nuclei in condensed matter is not easy to evaluate neither by theory nor by experiment, because of the unknown absolute magnetic shielding of the reference compound usually used for the measurement of the relative chemical shift of the compound in question.

For the alkali nuclei, however, the magnetic shielding of the nuclei in the hydrated alkali ions is now well known: ^{6}Li (Ref. [1]), ^{7}Li (Ref. [1]), ^{23}Na (Ref. [1]), ^{39}K (Ref. [2]), ^{40}K (Ref. [2]), ^{41}K (Ref. [1, 2]), ^{85}Rb (Ref. [3]), ^{87}Rb (Ref. [4–7]), ^{133}Cs (Ref. [7, 8]). Therefore the magnetic shielding of ^{133}Cs in cesium salts can be given and can be compared with the magnetic shielding in cesium halides calculated by Hafemeister and Flygare [9] and also by Ikenberry and Das [10].

In the following we describe measurements of ^{133}Cs in powdered cesium compounds which allowed to evaluate the shielding constant of ^{133}Cs and in one case to derive a quadrupole coupling constant. A comparison with theoretical values [9, 10] is given. Some conclusions for the concentration dependence of the ^{133}Cs NMR lines in aqueous solutions can be drawn.

Experimental

The NMR measurements of ^{133}Cs were performed on a Bruker pulse spectrometer SXP 4 – 100 in a magnetic field of 2.11 T, produced by a Bruker magnet system which was externally stabilized. The free induction decays near the Larmor frequency of 11.81 MHz were accumulated and Fourier transformed by the Bruker B-NC 12 data unit. For large spectral widths the Bruker transi-store BC-104 was used.

The ^{133}Cs signals in well dried powders of Cs_2CrO_4, $CsNO_3$, Cs_2SO_4, Cs_2CO_3, CsCl, CsBr and CsI were measured at (300 ± 3) K in 10 mm spherical sample tubes. As reference sample a 0.5 molal solution of CsCl in H_2O without paramagnetic catalysts was used. The chemical shift of this reference sample taken from Ref. [7] is $\delta(^{133}\text{Cs}) = 6.1 \pm 0.1$ versus the infinite dilution of Cs-ions in H_2O, where δ is defined by $\delta(^{133}\text{Cs}) = \{(\nu_{\text{sample}} - \nu_{\text{ref.}})/\nu_{\text{ref.}}\} \cdot 10^6$. About 10 differences were measured for the powder samples by the sample exchanging method. Since spherical samples were used, no susceptibility correction was necessary. A typical signal with the experimental parameters is shown in Figure 1.

Magnetic Shielding

The Larmor frequency of a nucleus in a diamagnetic free atom or ion is proportional to the external magnetic field $\boldsymbol{B}_0$:

$$\boldsymbol{\omega} = \gamma_{\text{atom}} \cdot \boldsymbol{B}_0$$

where γ_{atom} denotes the gyromagnetic ratio of the nucleus resulting from a measurement of $\boldsymbol{B}_0$ and ω. γ_{atom} is affected by the diamagnetic shielding of the electrons. If the same experiment is made using a nucleus in condensed matter – the usual NMR experiment – the Larmor frequency is also proportional to the external magnetic field $\boldsymbol{B}_0$:

$$\boldsymbol{\omega} = \gamma_{\text{NMR}} \cdot \boldsymbol{B}_0$$

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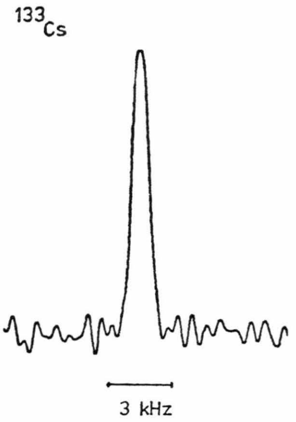

Fig. 1. ^{133}Cs absorption signal in CsI powder at 11.808 MHz: experimental spectrum width: 50 kHz, number of pulses: 11, measuring time: 11 minutes, nonrotating spherical sample tubes of 10 mm outer diameter were used. 200 data points were accumulated followed by 7992 points of zerofilling before the Fourier transformation of 8 K points.

but with an other gyromagnetic ratio γ_{NMR}. This gyromagnetic ratio of the nucleus is influenced not only by the electron of the atom or ion under observation itself but also by the interaction with the environment. This is the well known phenomenon of chemical shift. From both relations a shielding constant σ^* for the nucleus in condensed matter relative to the free atom can be defined by

$$\sigma^* = (\gamma_{\mathrm{NMR}} - \gamma_{\mathrm{atom}}) / \gamma_{\mathrm{atom}} \,.$$

If γ_{atom} is available with the necessary accuracy the chemical shift in all measured environments can be referred to this atomic shielding scale, which is for theoretical comparisons a much better scale than that usually used in NMR specroscopy basing on a rather arbitrary chemical compound. This shielding constant σ^* of a compound is connected by the diamagnetic shielding of the free atom σ_{d} with the absolute shielding σ of this compound referred to the bare nucleus:

$$\sigma = \sigma_{\mathrm{d}} + \sigma^*$$

σ_{d} and σ are defined by the relations

$$\boldsymbol{\omega} = \gamma_{\mathrm{I}}(1 - \sigma_{\mathrm{d}}) \boldsymbol{B}_0$$

for free atoms or ions and

$$\boldsymbol{\omega} = \gamma_{\mathrm{I}}(1 - \sigma) \boldsymbol{B}_0$$

for condensed matter. γ_{I} is the gyromagnetic ratio of the bare nucleus; σ_{d} can be calculated with reasonable accuracy for free atoms and ions [11, 12].

Some years ago there have been made some efforts to calculate σ^* for alkali nuclei in alkali halides and infinitely dilute aqueous solutions of alkali halides by Ikenberry and Das [10, 13, 14] and Hafemeister and Flygare [9] modifying the Kondo-Yamashita [15] formalism starting from wave functions of the free ions. These authors found that σ^* is proportional to a sum of squares of overlap integrals between the alkali metal orbitals and the orbitals of the neighbour ions divided by the mean excitation energy.

A comparison of the theoretical values of σ^* for ^{133}Cs in cesium halides given by Ilkenberry and Das [14] with experimental values was not possible since chemical shifts of ^{133}Cs in cesium halides have not been available in the atomic reference scale. The chemical shifts of ^{133}Cs measured by several authors [16–19] were given relative to ambiguously defined aqueous solutions or aqueous solutions which contained paramagnetic ions [18].

The shielding of the cesium by water and by the other ions in concentrated aqueous solutions or by paramagnetic ions was unknown [§] and was usually underestimated. The shielding constant of Cs$^+$ ions in infinitely diluted aqueous solution is

$$\sigma^* (^{133}\mathrm{Cs}^+, \text{ inf. dil. } \mathrm{H_2O}) = (-344.0 \pm 1.5) \cdot 10^{-6}$$

from measurements of γ_{NMR} by Lutz [5, 7] and γ_{atom} by White et al. [8]. This value is not at all negligible compared with the shielding constants of the crystalline powders.

The shielding of our reference sample is also known:

$$\sigma^* (^{133}\mathrm{Cl}^+ \text{ in 0.5 molal CsCl in } \mathrm{H_2O}) = (-350.1 \pm 1.5) \cdot 10^{-6} \text{ (Ref. }^{7}) \,.$$

Accurate measurements of the chemical shift $\delta(^{133}\mathrm{Cs})$ of cesium salts yield the shielding constant for the cesium salts $\sigma^*_{\text{cryst, exp}}(^{133}\mathrm{Cs})$ which can be compared with theoretical values of

$$\sigma^*_{\text{cryst, theor}}(^{133}\mathrm{Cs}) \,.$$

[§] Baron [18] used as reference sample a 5 molal solution of CsBr which contained $4.5 \cdot 10^{22}$ Mn^{2+} ions/cm^3. During earlier investigations [7] the chemical shift of such a solution versus infinite dilution was measured in spherical tubes, $\delta(^{133}\mathrm{Cs}) = 233$, and in cylindrical tubes, $\delta(^{133}\mathrm{Cs}) = 201$, indicating that Baron's results are strongly influenced by his reference samples.

Results

a) Shielding Constants

The results of the ^{133}Cs measurements are given in Table 1. The measured ^{133}Cs shifts in the powder samples relative to the liquid reference sample are listed in column 2. It is remarkable that the ^{133}Cs$^+$ ion in powder samples of $CsNO_3$ and Cs_2CrO_4 and in $CsNO_3$ and Cs_2CrO_4 solutions [7, 20–22] shows a Larmor frequency which is lower than that in the infinitely dilute aqueous solution.

Shielding constants $\sigma^*_{\text{cryst, exp}}$ (^{133}Cs, cesium salt) calculated from the shifts in column 2 and σ^* of the reference sample are presented in column 3.

For cubic cesium halide salts only a single symmetrical resonance signal was found. These linewidths and the widths of the central line for the noncubic salts, which have also been measured, are given in column 5.

Hafemeister and Flygare [9] have calculated shielding constants using the relations given by Ikenberry and Das [10] and the overlap integrals of Reference [23]. These theoretical results in column 4 agree in the order of magnitude but do not increase in the same order from CsCl to CsI as the experimental ones do. Using more recent values of the mean excitation energies [24] there is no considerable change of the shielding constants.

A comparison of the present results with that of older measurements in some of the salts [16–19] is not reasonable because of the not well defined reference solutions of the older measurements and the strong dependence of the ^{133}Cs resonance frequency on the concentration of aqueous salt solutions.

The measured shielding constants are given in Fig. 2 in the atomic scale. It is remarkable that the shielding constant of ^{133}Cs in water is about half that of ^{133}Cs in CsI which has the largest amount of shielding. Further, $CsNO_3$ and Cs_2CrO_4 are situated in the opposite direction of ^{133}Cs in water. Therefore it is very dangerous to draw conclusions from measurements which used aqueous reference solutions if the shielding of the latter is not known.

Further in Fig. 2 the shielding of ^{133}Cs in the dimer Cs_2, which recently has been measured by Huber et al. [25] is given. These authors also tried to determine the difference between the shielding of the ^{133}Cs in the free atom and the free monovalent ion. The contribution of the single valence electron to the diamagnetic shielding is very small as expected. The value of Ref. [25] is:

$$\sigma\,(\text{free Cs-atom}) - \sigma\,(\text{free Cs}^+\text{-ion}) = (14 \pm 13) \cdot 10^{-6}\,.$$

The difference between the diamagnetic shielding in the free atom and the free ion can be estimated to be about $1 \cdot 10^{-5}$ for the high atomic number element cesium in agreement with the calculated values [11, 12]. This small amount does not influence the comparison of the experimental and theoretical shielding in cesium salt powders. But this fact has to be kept in mind using the shielding data of this work which are basing on the definition given above if the accuracy is increased considerably.

b) Quadrupole Coupling

For some noncubic salts, the ^{133}Cs line of which has been investigated in aqueous solutions earlier [7, 20–22], the ^{133}Cs powder signal has been observed; the chemical shifts are given in Table 1. Usually one symmetrical line was observed, the linewidths are given in Table 1.

In the case of Cs_2SO_4, which has the symmetry group V_h^{16}, P_{nma} a first-order quadrupole pattern was observed with 6 small satellites due to

Table 1. Chemical shift δ, shielding constant σ^*_{cryst} and linewidths of ^{133}Cs in crystalline cesium salts. The shift of the reference sample, a 0.5 molal solution of CsCl in H_2O, versus infinite dilution is $\delta(^{133}\text{Cs}) = +6.1 \pm 0.1$. The shielding constant of the hydrated Cs$^+$ in H_2O is $\sigma^*(^{133}\text{Cs}) = (-344.0 \pm 1.5) \cdot 10^{-6}$. The chemical shift δ in the usual convention is connected with the shielding constant by $\delta = -\sigma_{\text{sample}} \cdot 10^6$ resulting in the relation $\sigma^*_{\text{cryst, exp}} = \sigma_{\text{sample}} + \sigma^*_{\text{reference}}$. The errors result from the linewidths and are rounded up for the values given in column 3.

Salt	δ	$\sigma^*_{\text{cryst, exp}}/10^{-6}$	$\sigma^*_{\text{cryst, theory}}/10^{-6}$	Linewidth/Hz
Cs_2CrO_4	$-\ 61.3 \pm 9.0$	-289 ± 10	—	2300 ± 100
$CsNO_3$	$-\ 14.9 \pm 3.0$	-335 ± 4	—	700 ± 50
Cs_2SO_4	$+\ 91.7 \pm 6.0$	-442 ± 7	—	1400 ± 85
Cs_2CO_3	$+152.7 \pm 9.0$	-503 ± 10	—	2200 ± 25
CsCl	$+228.1 \pm 4.0$	-578 ± 5	-270 (Ref. [9])	1045 ± 25
CsBr	$+260.3 \pm 4.0$	-610 ± 5	-260 (Ref. [9])	1100 ± 25
CsI	$+274.3 \pm 4.0$	-624 ± 5	-250 (Ref. [9])	935 ± 25

the spin $I=7/2$. The quadrupole coupling constant $(3\,e^2\,q\,Q)/[2\,I(2\,I-1)\,h]=(38.0\pm0.6)\,\text{kHz}$ was derivable. This is a small coupling constant, but it is not unreasonable since the quadrupole moment of ^{133}Cs is very small: $Q=-0.0036\cdot10^{-24}\,\text{cm}^2$ (Reference[26]). To our knowledge no other quadrupole coupling constant is known for cesium salts. Earlier, Bloembergen and Sorokin[17] failed to observe ^{133}Cs in sulfate, nitrate and carbonate.

c) Aqueous Solution

The behaviour of the ^{133}Cs resonance in aqueous solutions has been investigated earlier[7, 20–22] for the following salts: CsF, CsCl, CsBr, CsI, $CsNO_3$, Cs_2CO_3, Cs_2SO_4, Cs_2CrO_4. For increasing concentration the Larmor frequencies are shifted to higher frequencies for all salts with the exception of $CsNO_3$ and Cs_2CrO_4 (References[7, 20–22]).

In Fig. 2 these chemical shifts or magnetic shieldings are given in the atomic reference scale. It is obvious that the magnetic shielding found in the powder samples reflects directly the behaviour of the ^{133}Cs resonance in cesium salt solutions. It should be emphasized that the influence of the NO_3^- and CrO_4^{2-} ions on the ^{133}Cs shift is smaller than that of the water molecules.

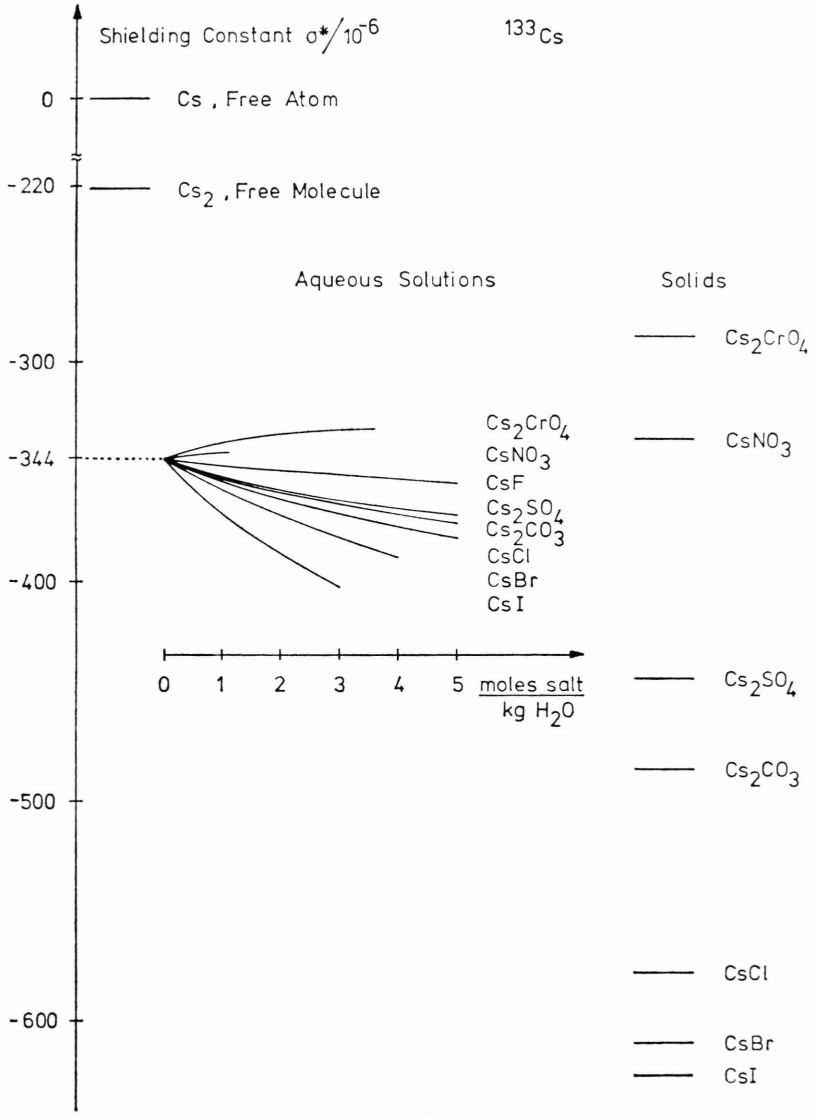

Fig. 2. Atomic reference scale of the nuclear magnetic shielding of ^{133}Cs. The following data were used: free atom: Ref.[8], free molecule Cs_2: Ref.[25], aqueous solutions: Ref.[7, 20–22], solid samples: this work.

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