Fourier Transform NMR Investigations of ^{77}Se in Aqueous Solutions

W. Koch, O. Lutz, and A. Nolle
Physikalisches Institut der Universität Tübingen

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In solutions of H_2SeO_3, Na_2SeO_3, $NaHSeO_3$ and Na_2SeO_4 in H_2O NMR signals of ^{77}Se have been observed. In these solutions chemical shifts were determined. In a 4 molal solution of Na_2SeO_3 the ratio of Larmor frequencies $\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H})$ has been measured with a high-resolution probe. A value of the magnetic moment of ^{77}Se in Na_2SeO_3 at infinite dilution in H_2O is given: $|\mu(^{77}\mathrm{Se})| = 0.533\,299\,6(7)\mu_N$. Relaxation times T_1 have been measured by the inversion-recovery method. In a 4 molal solution of Na_2SeO_3 in H_2O a NOE enhancement of 0.4(1) could be observed.

Introduction

At least one isotope of the stable chalcogenide elements is accessible to NMR-studies. Of these ^{17}O and ^{33}S are quadrupolar nuclei, whereas ^{77}Se, ^{123}Te and ^{125}Te are nuclei with the favourable nuclear spin 1/2. In liquids NMR studies of ^{17}O are well known [1], whereas for ^{33}S [2, 3] and ^{123}Te, ^{125}Te [4, 5] only few data have been reported. In the last time, the interest in NMR-studies of ^{77}Se grows up [6—18], since selenium has been found to play an important role in biochemistry [11—18].

^{77}Se has a natural abundance of 7.6%, a spin $I = 1/2$ and a Larmor frequency of 17.2 MHz in a magnetic field of 2.11 T. The receptivity is three times stronger than that of ^{13}C in the same magnetic field. The range of chemical shifts in organic compounds is large, about 1500 ppm [7]. ^{77}Se-^{1}H spin-spin coupling constants of about 47 Hz have been reported [13]. Investigations at low concentrations may be limited by long relaxation times, only some data have recently been given [7, 17]. Since the magnetic moment of ^{77}Se is positive an enhancement of signals due to a nuclear Overhauser effect (NOE) might be possible between ^{77}Se and ^{1}H.

In the following we describe ^{77}Se NMR experiments in inorganic selenium salt solutions. Since very few data are available in this area [6, 7], the ratio of the Larmor frequency of ^{77}Se to a reference nucleus, the magnetic moment of ^{77}Se, chemical shifts as a function of concentration, spin-lattice relaxation times T_1 and NOE-enhancement will be reported.

Experimental

For the NMR measurements of ^{1}H, ^{23}Na and ^{77}Se we used a Bruker pulse spectrometer SXP 4-100 at a magnetic field of 2.114 T. With a B-NC 12 computer the free induction decays were accumulated and Fourier transformed.

For the measurements of the ratio of the Larmor frequencies $\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H})$ and of the chemical shifts of ^{77}Se, a high resolution probe with internal ^{1}H stabilization (B-SN 20 with ^{1}H extension unit) was used. The measurements of the spin-lattice relaxation times T_1 were performed with a high-power probe and external ^{1}H stabilization B-SN 15. Typical signals of an inversion-recovery experiment are shown in Figure 1. For proton decoupling in NOE experiments we used the decoupler and power unit B-SV 3 BP and a high-resolution probe with external ^{2}H stabilization B-SN 20.

All measurements were performed with cylindrical sample tubes with 10 mm outer diameter. The temperature was (298 ± 2) K. The Na_2SeO_3 and H_2SeO_3 were delivered from Merck, Darmstadt, the $NaHSeO_3$ from Serva, Heidelberg and the Na_2SeO_4 from ICN Pharmaceuticals INC., Plainview, N.Y. All samples were used without further purification.

According to Reference [19] the chemical shift is given as

$$\delta(^{77}\mathrm{Se}) = [(\nu_{\mathrm{sample}} - \nu_{\mathrm{ref.}})/\nu_{\mathrm{ref.}}] \cdot 10^6 ,$$

where $\nu_{\mathrm{ref.}}$ is the Larmor frequency of ^{77}Se in an infinitely diluted solution of Na_2SeO_3 in H_2O.

Results and Discussion

a) Ratios of the Larmor Frequencies

The ratio of the Larmor frequencies of ^{77}Se and ^{1}H was measured in a 4 molal solution of Na_2SeO_3 in H_2O, by using a high-resolution probe with ^{1}H

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

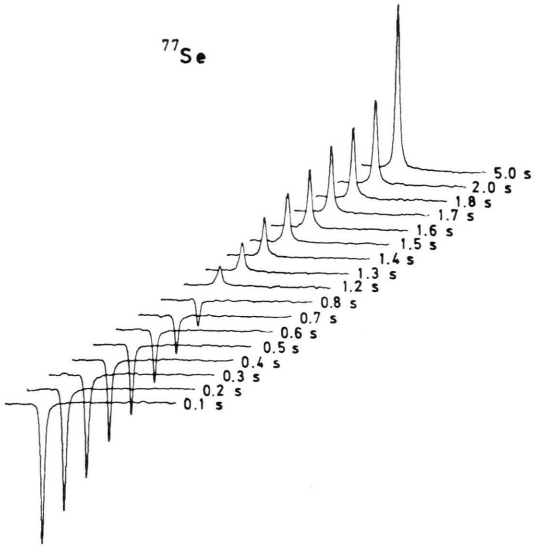

Fig. 1. Absorption signals of ^{77}Se at 17.188 MHz in a 4 molal solution of H_2SeO_3 in D_2O, measured by the inversion-recovery Fourier method [24]
$(180° - \tau_i - 90° - T)_{NS}$.
In the figure different waiting times τ_i between the 180° and 90° pulse are given. The recovery time was for all measurements $T = 5$ s. For each τ_i, NS = 100 scans were accumulated, yielding a total measuring time of about 4 h. The resulting relaxation time is $T_1 = 1.4(1)$ s. The plotted spectrum width of a single spectrum is 260 Hz. The signals were observed with a high-power probe and external ^{1}H-lock using 10 mm nonrotating cylindrical sample tubes.

internal stabilization. The ^{1}H lock-frequency is given in Table 1. The result of these measurements, which were performed at several days, is:

$$\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H}) = 0.190957382(6)\,.$$

To verify this result, in an other experiment ^{23}Na was used as a reference nucleus. The Larmor frequencies of ^{23}Na and ^{77}Se were measured in the same solution with a high-power probe with external ^{1}H stabilization B-SN 15:

$$\nu(^{77}\mathrm{Se})/\nu(^{23}\mathrm{Na}) = 0.7220172(2)\,.$$

The given errors are the standard deviation.

b) Chemical Shifts

The Larmor frequency of ^{77}Se was observed in a series of inorganic compounds in aqueous solution: Na_2SeO_3, Na_2SeO_4, $NaHSeO_3$ and H_2SeO_3. The solutions were all acid, with p_H values between 1 and 4. The results of the chemical shift are given in Table 1. The Larmor frequencies of ^{77}Se in the Na_2SeO_3, $NaHSeO_3$, Na_2SeO_4 and H_2SeO_3 solutions are rather different. The dependence of the Larmor frequency on the concentration of the solutions is very small. This behaviour has already been observed in other oxyanions e.g. for ^{33}S in SO_4^{2-} [3] and for ^{125}Te in TeO_3^{2-} [5]. According to Birchall et al. [7] the selenium (VI) compounds have lower Larmor frequencies than the selenium (IV) compounds, this is also true for the ^{77}Se signal in the $NaHSeO_3$ solutions, which is shifted about 50 ppm to higher frequency than the Na_2SeO_3 signal.

Table 1. ^{77}Se chemical shifts referred to Na_2SeO_3 at infinite dilution and spin-lattice relaxation times T_1. The chemical shifts were measured with the high-resolution probe with ^{1}H internal stabilization and corrected for the chemical shifts of the ^{1}H signal, which was determined in a separate measurement. The Larmor frequency of ^{77}Se in Na_2SeO_3 at infinite dilution was 17 189 707(9) Hz and the ^{1}H-lock-frequency was 90 018 750 Hz.

Sample	Concentration (molal in H_2O)	Chemical shift δ	Relaxation time T_1/s
Na_2SeO_4	0.5	-227.9 ± 0.5	10.2 ± 0.8
	1.0	-227.6 ± 0.6	—
	1.6	-227.3 ± 0.6	—
Na_2SeO_3	0.5	0.8 ± 0.5	—
	1.0	1.5 ± 0.5	10.7 ± 0.6
	2.0	1.9 ± 0.5	—
	3.0	2.3 ± 0.5	—
	4.0	2.7 ± 0.5	5.0 ± 0.5
H_2SeO_3	0.4	28.7 ± 0.5	—
	1.0	28.5 ± 0.5	—
	1.9	28.5 ± 0.5	—
	3.0	28.7 ± 0.5	—
	4.0	28.9 ± 0.5	1.1 ± 0.1
	5.2	29.3 ± 0.5	—
	4.0 in D_2O	—	1.4 ± 0.1
$NaHSeO_3$	0.5	46.4 ± 0.6	—
	1.0	47.2 ± 0.6	—
	2.0	48.4 ± 0.6	—
	3.0	49.3 ± 0.5	—
	4.0	50.7 ± 0.5	0.34 ± 0.05
	5.0	51.2 ± 0.5	—

The chemical shift of ^{1}H in the 4 molal Na_2SeO_3 solution in H_2O relative to a solution with vanishing concentration of Na_2SeO_3 is $\delta(^1\mathrm{H}) = 0.5 \pm 0.1$ and that of ^{23}Na: $\delta(^{23}\mathrm{Na}) = 2.3 \pm 0.2$.

c) Larmor Frequencies at Vanishing Concentration and Magnetic Moment

The ratio of the Larmor frequencies $\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H})$ of a 4 molal Na_2SeO_3 solution can be extrapolated for a solution with infinite dilution: With the chemical shift data we get:

$$\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H})\big|_{\mathrm{extrapol.}} = 0.190\,956\,96(10)\,.$$

For ^{23}Na as reference nucleus the result is:

$$\nu(^{77}\mathrm{Se})/\nu(^{23}\mathrm{Na})\,|_{\mathrm{extrapol.}} = 0.721\,906\,2(4)\,.$$

With the ratio $\nu(^{23}\mathrm{Na})/\nu(^{2}\mathrm{H}) = 1.723\,174\,6(4)$ of Lutz [20] and $\nu(^{2}\mathrm{H})/\nu(^{1}\mathrm{H}) = 0.153\,506\,086(6)$ of Nolle [21] we get:

$$\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H})\,|_{\mathrm{extrapol.}} = 0.190\,957\,0(2)\,,$$

which is in good agreement with the upper value.

From the ratio $\nu(^{77}\mathrm{Se})/\nu(^{1}\mathrm{H})\,|_{\mathrm{extrapol.}}$ and the magnetic moment of the proton in water, $\mu_\mathrm{P} = 2.792\,744\,0(11) \cdot \mu_\mathrm{N}$ (Reference [22]) we derive for the magnetic moment of ^{77}Se in SeO_3^{2-} at vanishing concentration in H_2O:

$$|\mu(^{77}\mathrm{Se})| = 0.533\,299\,6(7)\,\mu_\mathrm{N}\,.$$

The result is not corrected for diamagnetism. There is a good agreement with former measurements of Weaver [6]:

$$\mu(^{77}\mathrm{Se}) = +\,0.533\,26(5)\,\mu_\mathrm{N}\,.$$

Because of the limited accuracy of this value of the magnetic moment, the chemical shift between the H_2SeO_3 solution with added paramagnetic catalysts of Weaver [6] and the SeO_3^{2-} ion at vanishing concentration of the present work, is not obvious. The sign of the magnetic moment of ^{77}Se is positive [6].

d) *Spin-lattice Relaxation Times and Nuclear Overhauser Effect*

^{77}Se spin-lattice relaxation in selenium oxyanions may arise from a variety of mechanisms: spin-rotation interaction, intramolecular and intermolecular dipole-dipole coupling, chemical shift anisotropy, scalar spin-spin coupling or chemical exchange. These different mechanisms can be separated by performing various experiments. In a first approximation we have measured in a few samples, which have been used for the chemical shift measurements, spin-lattice relaxation times of ^{77}Se with the inversion recovery method and a NOE enhancement. The results of the relaxation measurement are given in Table 1. For ^{77}Se in the SeO_4^{2-} and SeO_3^{2-} ions at low concentration relaxation times of 10 s occur, with increasing concentration the relaxation times of SeO_3^{2-} diminish to the half of this value. In $HSeO_3^-$ very short relaxation times have been found. For this solution with the high-resolution probe relatively broad signals of about 10 Hz have been measured. For ^{77}Se in a 4 molal solution of selenic acid in H_2O a value of T_1 of 1.1 s has been determined. Using D_2O as solvent for a selenic acid solution of the same concentration only a slight change is found. Wehrli reported for a non specified D_2SeO_3 solution a value $T_1 = 3.5$ s at 301 K [23]. Probably he used a less concentrated solution for his measurements.

Our NOE measurements indicate, that in aqueous solutions of selenium oxyanions the intermolecular dipole-dipole contribution to the relaxation times is small. In the 4 molal solutions of H_2SeO_3 and $NaHSeO_3$ and in the 1.6 molal solution of Na_2SeO_4 we found no NOE enhancement within an error limit of 10%. But for the 4 molal solution of Na_2SeO_3 in H_2O, an enhancement of 0.4(1) could be observed. For ^{77}Se a NOE enhancement up to 2.6 is possible. Because in H_2SeO_3 and $NaHSeO_3$ solutions no NOE was observed, even in these solutions the dipole-dipole contribution to spin-lattice relaxation is negligible.

These measurements show, that for the observed selenium compounds the dipole-dipole contribution to the spin-lattice relaxation plays only a minor role. This has also been observed by Dawson et al. [17] in organoselenic compounds, where no significant NOE could be observed as far as we know. Although long relaxation times and not the maximum nuclear Overhauser enhancement have been observed ^{77}Se NMR investigations will certainly find their way into various applications, since also at low concentrations which may occur in biochemical samples a reasonable signal intensity can be obtained as was shown for a 10 millimolal solution of Na_2SO_3 in H_2O. For about 1 ml in a 10 mm non-rotating cylindrical tube a signal-to-noise ratio of 4 was found within 26 hours.

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