^{123}Te and ^{125}Te Fourier Transform NMR Investigations

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The NMR signals of ^{123}Te and ^{125}Te have been observed in solutions of K_2TeO_3 and Na_2TeO_3 in D_2O. In these solutions the ratios of Larmor frequencies $\nu(^{125}Te)/\nu(^{123}Te)$, $\nu(^{125}Te)/\nu(^{2}H)$ and $\nu(^{125}Te)/\nu(^{23}Na)$ have been determined with high accuracy. With the measured chemical shifts of ^{2}H, ^{23}Na, ^{125}Te relative to infinitely diluted solutions the ratios of the Larmor frequencies are extrapolated and values of the magnetic moments are given. The relaxation times T_1 and T_2 are very different for ^{125}Te in TeO_3^{2-}: a ratio T_1/T_2 of 8.2 ± 0.4 has been found. No nuclear Overhauser effect due to dipole-dipole interaction of ^{125}Te with the water protons has been detected.

Introduction

All stable chalcogenide elements have at least one isotope which is accessible to NMR studies: ^{17}O and ^{33}S are quadrupole nuclei, whereas ^{77}Se, ^{123}Te and ^{125}Te have the spin 1/2. All these isotopes have been studied by the nuclear magnetic resonance method (see for instance Reference [1]). For ^{123}Te and ^{125}Te only a few direct NMR data are known [2–4], despite of their relatively large receptivity (see Table 1).

Table 1. For NMR investigations important data of tellurium.

Nucleus	Natural abundance %	Larmor frequency at 2.11 T in MHz	Spin	Receptivity
^{123}Te	0.87	23.592	1/2	$1.6 \cdot 10^{-4}$
^{125}Te	6.99	28.442	1/2	$2.2 \cdot 10^{-3}$

In the following we describe the investigations of some elementary NMR data of ^{123}Te and ^{125}Te, which must be available for further applications of tellurium NMR.

Experimental

The NMR measurements of ^{2}H, ^{17}O, ^{23}Na, ^{123}Te and ^{125}Te were performed using a Bruker pulse spectrometer SXP 4-100 at a magnetic field of 2.114 T, which can be stabilized externally by a Bruker B-SN 15 unit or internally by a Bruker B-SN 20 unit. The free induction decays were accumulated and Fourier transformed by the BNC 12 computer. A high resolution probe with ^{2}H internal stabilization (HR-probe) and also a multinuclei high power probe with external ^{1}H-stabilization (HP-probe) — both manufactured by Bruker — were available. For the measurements of the relaxation times spherical sample tubes and for the other measurements cylindrical sample tubes with 10 mm outer diameter were used. The temperature was (300 ± 2) K. Typical signals with experimental parameters for both isotopes are given in Figure 1. The K_2TeO_3 was purchased from Merck, Darmstadt and the Na_2TeO_3 from ICN Pharmaceuticals, Inc., Plainview, N.Y., and used without further purification. The solutions were all strongly basic. According to the convention of presentation of NMR data of heteronuclei [5] the chemical shifts are given as

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

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Results

a) Ratio of the Larmor Frequencies $\nu(^{125}Te)/\nu(^{123}Te)$

In a 4 molal solution of K_2TeO_3 in D_2O, the ratio of the Larmor frequencies of ^{125}Te and ^{123}Te was measured at different days using the HR-probe:

$$\nu(^{125}\mathrm{Te})/\nu(^{123}\mathrm{Te}) = 1.205\,581\,816\,(48)\ *.$$

This is in good agreement with the ratios given by Pfister and Dreeskamp [6]:

$$\nu(^{125}\mathrm{Te})/\nu(^{123}\mathrm{Te}) = 1.205\,581\,84\,(12) \text{ in } \mathrm{Te(CH_3)_2}$$

and

$$\nu(^{125}\mathrm{Te})/\nu(^{123}\mathrm{Te}) = 1.205\,581\,70\,(24) \text{ in } \mathrm{Te_2(CH_3)_2}$$

obtained by a heteronuclear double resonance experiment. Hence the primary isotope effect of the

* The given errors are the standard deviation.

chemical shift is smaller than $1 \cdot 10^{-7}$ and therefore chemical shift data of ^{125}Te and ^{123}Te are equivalent.

b) Ratio of the Larmor Frequencies $\nu(^{125}\mathrm{Te})/\nu(^{2}\mathrm{H})$ and $\nu(^{125}\mathrm{Te})/\nu(^{23}\mathrm{Na})$

In the 4 molal solution of K_2TeO_3 in D_2O, the ratio of the Larmor frequencies of ^{125}Te and ^{2}H was measured at different days with the HR-probe. For ^{2}H the centre band signal of the reference channel at 13.8145833 MHz was used. The result is: $\nu(^{125}\mathrm{Te})/\nu(^{2}\mathrm{H}) = 2.058\,849\,71\,(15)$.

In a further experiment, ^{23}Na was used as reference nucleus since its Larmor frequency is not far away from that one of ^{125}Te. In a 3 molal solution of Na_2TeO_3 in D_2O the Larmor frequencies of ^{125}Te and ^{23}Na were measured with the HP-probe:

$$\nu(^{125}\mathrm{Te})/\nu(^{23}\mathrm{Na}) = 1.194\,798\,21\,(7)\,.$$

The linewidth of the ^{23}Na signal is 34 Hz and decreases with decreasing concentration of the solutions.

c) Dependence of the Larmor Frequencies on Concentration

The Larmor frequencies of ^{2}H, ^{23}Na and ^{125}Te depend on the concentration of the aqueous solution. In the given solutions the Larmor frequencies of all the nuclei decrease with decreasing concentration. The shifts are about $\delta(^{2}\mathrm{H}) = 1$, $\delta(^{23}\mathrm{Na}) = 2$ and $\delta(^{125}\mathrm{Te}) = 2$ referred to infinite dilution. The dependence of the Larmor frequency has been measured and has been found to be nearly linear for these nuclei.

d) Larmor Frequencies at Vanishing Concentration and Magnetic Moments

From the chemical shift data and the ratios of the Larmor frequencies the following ratios for vanishing concentration in D_2O can be derived:

$$\nu(^{125}\mathrm{Te})/\nu(^{2}\mathrm{H})\,|_{\mathrm{extrapol.}} = 2.058\,849(1)\,,$$

$$\nu(^{125}\mathrm{Te})/\nu(^{23}\mathrm{Na})\,|_{\mathrm{extrapol.}} = 1.194\,7994(7)\,.$$

The magnetic moments of ^{125}Te and ^{123}Te are derived for both ratios using

$$\nu(^{2}\mathrm{H})/\nu(^{1}\mathrm{H}) = 0.153\,506\,086\,(6) \text{ of Nolle}^{7},$$

$$\nu(^{23}\mathrm{Na})/\nu(^{2}\mathrm{H}) = 1.723\,174\,6\,(4) \text{ of Lutz}^{8}$$

and the magnetic moment of the proton in water, $\mu_p = 2.792\,7740\,(11)\,\mu_N$ (Reference [9]). The results are for tellurium in TeO_3^{2-} at infinite dilution:

$$|\mu(^{125}\mathrm{Te})| = 0.882\,6446\,(6)\,\mu_N\,,$$

$$|\mu(^{125}\mathrm{Te})| = 0.882\,6442\,(8)\,\mu_N\,,$$

$$|\mu(^{123}\mathrm{Te})| = 0.732\,1316\,(5)\,\mu_N\,,$$

$$|\mu(^{123}\mathrm{Te})| = 0.732\,1311\,(6)\,\mu_N\,.$$

These results are not corrected for diamagnetism. Using the ratios $\nu(^{125}\mathrm{Te})/\nu(^{23}\mathrm{Na})$ and $\nu(^{123}\mathrm{Te})/\nu(^{23}\mathrm{Na})$ of Weaver[2] for a solution of TeO_2 in HCl one gets values of the magnetic moments, the amount of which is for both nuclei about 200 ppm smaller. This difference indicates a chemical shift of 200 ppm, as in both measurements no paramagnetic catalysts were used. The sign of the magnetic moments is negative[2].

e) Relaxation Times

Since both tellurium isotopes have the spin 1/2, long relaxation times are expected. Weaver[2] estimated a ratio of the relaxation times of T_1/T_2 of 12 in a 3.1 molar solution of TeO_2 in HCl. This fact could be a limitation for further applications. Linewidths of about 2 Hz were observed (see Figure 1). For the 4 molal solution of K_2TeO_3 in D_2O the relaxation time T_1 of ^{125}Te has been measured by

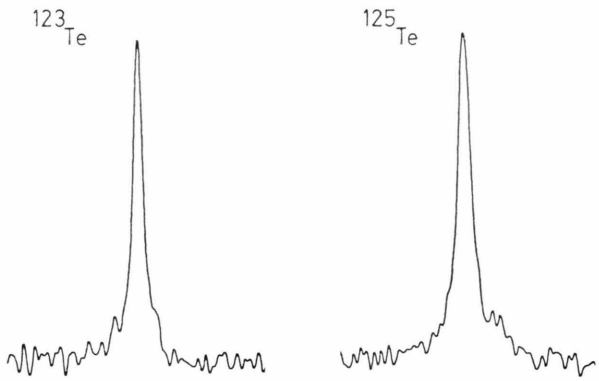

Fig. 1. Absorption signals of ^{123}Te at 23.592 MHz and of ^{125}Te at 28.442 MHz in a 4 molal solution of K_2TeO_3 in D_2O using 10 mm cylindrical sample tubes. The signals were observed with a high resolution probe working in the multi-nuclei mode (17 MHz–38 MHz) and an internal ^{2}H-lock.

^{123}Te: number of scans: 500; total measuring time: 25 min, linewidth: 2.0 Hz.

^{125}Te: number of scans: 20; total measuring time: 1.5 min, linewidth: 2.7 Hz.

The plotted spectrum width is for both signals 43 Hz. For each spectrum 400 data points were accumulated followed by 3696 points of zero filling before the Fourier transformation of 4 K points.

the inversion recovery Fourier transform method: the result is: $T_1 = 2.50(10)$ s. Since the observed linewidths were somewhat broadened by the inhomogeneity of the magnetic field, T_2 was determined by measuring T_1/T_2 using the method of Kronenbitter and Schwenk[10]. The result was $T_1/T_2 = 8.2 \pm 0.4$, which gives for the transversal relaxation time of ^{125}Te $T_2 = 0.31(2)$ s. The difference between T_1 and T_2 is presumably due to exchange phenomena in the tellurite solutions. This fact is also supported by ^{17}O NMR. In these solutions no separate signals for H_2O and the tellurite oxyanion were observed even in a sample, which was enriched in ^{17}O. Only a single 220 Hz broad ^{17}O line was detected, which is much broader than the ^{17}O signal in pure water.

Irradiation of the water proton frequency during the measurement of ^{125}Te in a solution in H_2O did not change the intensity of the tellurium signal (NOE = 0). Therefore only a very small contribution of dipole-dipole relaxation due to the water protons to the relaxation mechanisms of ^{125}Te can be assumed.

Conclusions

For NMR investigations ^{125}Te is a favourable spin-1/2-nucleus, which has a rather large receptivity, despite of the low natural abundance. The signals in aqueous solutions are narrow and the longitudinal relaxation times are in the range of seconds. Therefore the often occurring serious problems of waiting times are avoidable. All these properties indicate that the nuclear magnetic resonance method can be employed for investigations of tellurium in liquid and solid state physics and chemistry.

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