123Te and 125Te Fourier Transform NMR Investigations

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The NMR signals of 123Te and 125Te have been observed in solutions of K2TeO3 and Na2TeO3 in D2O. In these solutions the ratios of Larmor frequencies \( v(125\text{Te})/v(123\text{Te}) \), \( v(125\text{Te})/v(2\text{H}) \) and \( v(125\text{Te})/v(23\text{Na}) \) have been determined with high accuracy. With the measured chemical shifts of \( 2\text{H}, 23\text{Na}, 123\text{Te} \) 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 125Te in TeO22−: a ratio \( T_1/T_2 \) of 8.2 ± 0.4 has been found. No nuclear Overhauser effect due to dipole-dipole interaction of 125Te with the water protons has been detected.

Introduction

All stable chalcogenide elements have at least one isotope which is accessible to NMR studies: 170 and 33S are quadrupole nuclei, whereas 77Se, 123Te and 125Te have the spin 1/2. All these isotopes have been studied by the nuclear magnetic resonance method (see for instance Reference 1). For 123Te and 125Te 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.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural abundance %</th>
<th>Larmor frequency at 2.11 T MHz</th>
<th>Spin</th>
<th>Receptivity ( 10^{-4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>123Te</td>
<td>0.87</td>
<td>23.592</td>
<td>1/2</td>
<td>1.6 \times 10^{-4}</td>
</tr>
<tr>
<td>125Te</td>
<td>6.99</td>
<td>28.442</td>
<td>1/2</td>
<td>2.2 \times 10^{-3}</td>
</tr>
</tbody>
</table>

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

Experimental

The NMR measurements of \( 2\text{H}, 17\text{O}, 23\text{Na}, 123\text{Te} \) and 125Te 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 \( 2\text{H} \) internal stabilization (HR-probe) and also a multinuclei high power probe with external \( 1\text{H} \)-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 K2TeO3 was purchased from Merck, Darmstadt and the Na2TeO3 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 \( \delta(\text{Te}) = ([v_{\text{sample}} - v_{\text{ref.}}]/v_{\text{ref.}}) \times 10^6 \) .

Results

a) Ratio of the Larmor Frequencies \( v(125\text{Te})/v(123\text{Te}) \)

In a 4 molal solution of K2TeO3 in D2O, the ratio of the Larmor frequencies of 123Te and 125Te was measured at different days using the HR-probe:

\[ v(125\text{Te})/v(123\text{Te}) = 1.205581816(48) \]

This is in good agreement with the ratios given by Pfister and Dreeskamp\(^6\):

\[ v(125\text{Te})/v(123\text{Te}) = 1.20558184(12) \text{ in Te(CH}_3)_2 \]

and

\[ v(125\text{Te})/v(123\text{Te}) = 1.205581670(24) \text{ in Te}_2(\text{CH}_3)_2 \]

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 $^{125}\text{Te}$ and $^{123}\text{Te}$ are equivalent.

b) Ratio of the Larmor Frequencies $v(1^{25}\text{Te})/v(2\text{H})$ and $v(1^{25}\text{Te})/v(23\text{Na})$

In the 4 molal solution of $\text{K}_2\text{TeO}_3$ in $\text{D}_2\text{O}$, the ratio of the Larmor frequencies of $^{125}\text{Te}$ and $^2\text{H}$ was measured at different days with the HR-probe. For $^2\text{H}$ the centre band signal of the reference channel at 13.8145833 MHz was used. The result is:

$$v(1^{25}\text{Te})/v(2\text{H}) = 2.05884971(15)$$

In a further experiment, $^{23}\text{Na}$ was used as reference nucleus since its Larmor frequency is not far away from that of $^{125}\text{Te}$. In a 3 molal solution of $\text{Na}_2\text{TeO}_3$ in $\text{D}_2\text{O}$ the Larmor frequencies of $^{125}\text{Te}$ and $^{23}\text{Na}$ were measured with the HP-probe:

$$v(1^{25}\text{Te})/v(23\text{Na}) = 1.19479821(7)$$

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

c) Dependence of the Larmor Frequencies on Concentration

The Larmor frequencies of $^2\text{H}$, $^{23}\text{Na}$ and $^{125}\text{Te}$ 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 $\delta(^2\text{H}) = 1$, $\delta(^{23}\text{Na}) = 2$ and $\delta(^{125}\text{Te}) = 2$ 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 $\text{D}_2\text{O}$ can be derived:

$$v(1^{25}\text{Te})/v(^1\text{H})|_{\text{extrapol.}} = 2.058849(1)$$

$$v(1^{25}\text{Te})/v(^{23}\text{Na})|_{\text{extrapol.}} = 1.1947994(7)$$

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

$$v(^2\text{H})/v(^1\text{H}) = 0.153506086(6)$$

of Nolle\textsuperscript{7},

$$v(^{23}\text{Na})/v(^2\text{H}) = 1.7231746(4)$$

of Lutz\textsuperscript{8} and the magnetic moment of the proton in water,

$$\mu_p = 2.7927740(11)\mu_N$$

(Reference \textsuperscript{9}). The results are for tellurium in $\text{TeO}_3^2-$ at infinite dilution:

$$|\mu(^{125}\text{Te})| = 0.8826446(6)\mu_N$$

$$|\mu(^{123}\text{Te})| = 0.8826442(8)\mu_N$$

$$|\mu(^{125}\text{Te})| = 0.7321316(5)\mu_N$$

$$|\mu(^{123}\text{Te})| = 0.7321311(6)\mu_N$$

These results are not corrected for diamagnetism.

Using the ratios $v(1^{25}\text{Te})/v(^{23}\text{Na})$ and $v(1^{25}\text{Te})/v(^{23}\text{Na})$ of Weaver\textsuperscript{2} for a solution of $\text{TeO}_2$ in $\text{HCl}$ 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\textsuperscript{2}.

e) Relaxation Times

Since both tellurium isotopes have the spin $1/2$, long relaxation times are expected. Weaver\textsuperscript{2} estimated a ratio of the relaxation times of $T_1/T_2$ of 12 in a 3.1 molar solution of $\text{TeO}_2$ in $\text{HCl}$. This fact could be a limitation for further applications. Line-widths of about 2 Hz were observed (see Figure 1). For the 4 molal solution of $\text{K}_2\text{TeO}_3$ in $\text{D}_2\text{O}$ the relaxation time $T_1$ of $^{125}\text{Te}$ has been measured by

![Fig. 1](image-url) Absorption signals of $^{123}\text{Te}$ at 23.592 MHz and of $^{125}\text{Te}$ at 28.442 MHz in a 4 molal solution of $\text{K}_2\text{TeO}_3$ in $\text{D}_2\text{O}$ 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 $^2\text{H}$-lock.

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

$^{125}\text{Te}$: 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. 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 $\text{H}_2\text{O}$ 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 $\text{H}_2\text{O}$ 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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7. A. Nolle, to be published.