127I, 185Re and 187Re Solid State NMR Measurements on 
(CH$_3$)$_4$AsIO$_4$ and (CH$_3$)$_4$AsReO$_4$

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Rhenium, Iodine, Solid State NMR, Quadrupole Effects, Phase Transitions

Tetramethylarsionium-metaperiodate shows 127I solid state NMR signals without any visible quadrupole splitting. Due to the very large nuclear quadrupole moments of the rhenium isotopes 185, 187Re, the analogous Re compound exhibits the expected second order quadrupole NMR effects. The measured 185, 187Re NMR powder spectra contain superimposed signals arising from two different types of ReO$_4$ tetrahedra, indicating that part of the ReO$_4^-$ anions deviate only slightly from tetrahedral symmetry, while the other part are nearly undistorted ReO$_4^-$ anions.

The temperature dependence of the solid state NMR spectra reveals phase transitions for both compounds, which are confirmed also by DSC analyses. Furthermore, the DSC analysis of the Re compound again proves the existence of the two different types of ReO$_4^-$ tetrahedra in the lattice of the high temperature modification.

1. Introduction

Several different kinds of 127I solid state NMR spectra of metaperiodates with alkyl-substituted cations of main group V have been found so far. The spectra manifest second order quadrupole interactions with quadrupole coupling constants in the range of 2—15 MHz at room temperature [1—3].

In the 127I solid state NMR spectra of tetraethylammonium- and tetramethylphosphonium-metaperiodate, resolved first or second order quadrupole effects cannot be detected [4]. Compared to the 127I-nucleus, with a nuclear quadrupole moment Q = —0.7 barn, the 185Re and 187Re isotopes possess extremely large nuclear quadrupole moments Q(185Re) = 2.8 barn and Q(187Re) = 2.6 barn. Therefore we calculated the maximum values of the quadrupole coupling constants for the isomorphous metaperrhenates [4]. On measuring the 185Re and 187Re solid state NMR spectra of the corresponding compounds, we observed a different behaviour. No quadrupole interactions are visible in the 185Re and 187Re powder NMR spectra of (C$_2$H$_5$)$_4$NReO$_4$. By contrast, the 185Re and 187Re NMR spectra of (CH$_3$)$_4$PReO$_4$ show the expected quadrupole interaction with quadrupole coupling constants in the calculated range of 20 MHz at room temperature.

The present paper describes for the first time 127I, 185Re and 187Re solid state NMR spectra of tetramethylarsionium-metaperiodate (1) and the analogous metaperrhenate (2). The quadrupole disturbed line shapes of the 185Re and 187Re spectra are of high complexity and will be discussed in terms of second order quadrupole splitting. From the temperature dependence of the quadrupole interaction the very small deviations Δβ from tetrahedral symmetry of the ReO$_4^-$ anions are calculated. Moreover, we observed phase transitions for both compounds. The phase transitions are discussed on the basis of NMR and DSC investigations.

2. Experimental

2.1. Instrumentation

The 127I, 185Re and 187Re powder spectra were obtained with a Bruker FT-NMR CXP 200 spectrometer equipped with a superconducting magnet (B$_0$ = 4.698 T). Temperature dependent experiments were carried out using a Bruker B-VT 1000 thermostat with a temperature tolerance ±1 K. Experimental errors of the reported quadrupole coupling constants are in the order of Δe’QH = ±0.2 MHz.

The DSC measurements were done with a Perkin Elmer differential scanning calorimeter Model DSC-2 [5].

2.2. Preparation of the compounds (1) and (2)

The starting compound trimethylarsine was synthesized following the procedure of Zingaro and Merijanian [6]. Addition of methyl iodide gave the quaternary arsonium salt [7]. The hydroxide (CH$_3$)$_4$AsOH was synthesized by application of a

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strongly basic anion exchanger (Merck, Exchanger III). Neutralization of the basic solution with the equivalent amount of pure periodic acid gave the desired metaperiodate (1). The metaperrhenate (2) was prepared analogously by using an aqueous solution of perrhenic acid. This acid was obtained from KReO₄ using a strong acid cation exchanger (Merck, Exchanger I).

Recrystallization from water/ethanol gave analytically pure compounds. The data of the elemental analyses are as follows:

C₄H₁₂AsIO₄ (1)
Calcd C 14.74 H 3.71 As 22.99 O 19.63 138.93,
Found C 14.73 H 3.76 As 22.94 O 19.49 138.72.

C₄H₁₂AsReO₄ (2)
Calcd C 12.47 H 3.14 As 19.45 O 16.61 Re 48.33,
Found C 12.37 H 3.01 As 19.21 O 16.61 Re 48.74.

3. Results

3.1. ¹²⁷I Solid state NMR spectra of (CH₃)₄AsIO₄ (1)

For the first time polycrystalline (CH₃)₄AsIO₄ (1) was studied by ¹²⁷I solid state NMR spectroscopy. The temperature dependent spectra are shown in Fig. 1.

On lowering the temperature compound 1 shows chemical shift effects. The temperature dependent results are summarized in Table I and Fig. 2.
The line width of the dipolar broadened $^{127}$I NMR resonance amounts to 2.5 kHz. This value is independent on temperature. At temperatures below 260 K, $^{127}$I solid state NMR measurements of 1 give no signals. The DSC analysis shows a single peak for both temperature rise and temperature down measurements. This indicates a first order phase transition of 1 at $T = 254(3)$ K (s. Fig. 3) [8, 9].

3.2. $^{185}$Re and $^{187}$Re Solid state NMR spectra of (CH$_3$)$_4$AsReO$_4$

In agreement with our calculations [4], $^{185}$Re and $^{187}$Re solid state NMR spectra of compound 2 could be detected. Fig. 4 shows the powder pattern obtained at $T = 380$ K with NaReO$_4$ in aqueous solution as a reference.

The natural abundance of the rhenium nuclei ($^{185}$Re: 37.1%, $^{187}$Re: 62.9%) and the difference in the Larmor frequencies, $v_L$ ($v_L(^{185}$Re) = 45.028 MHz, $v_L(^{187}$Re) = 45.489 MHz), are very advantageous as the two isotopes can be observed simultaneously in the NMR spectra. The left part of the spectrum (at high frequency) shows $^{185}$Re quadrupole splitting $\Delta v_{T=380\text{K}} = 22.5$ kHz $\pm$ 1 kHz manifested by the outward frequency edges.

The quadrupole splitting of the $^{185}$Re nucleus is larger ($\Delta v_{T=380\text{K}} = 25.4$ kHz $\pm$ 1 kHz) as a consequence of the larger quadrupole moment of this Re isotope ($Q(^{185}$Re) = 2.8 barn, $Q(^{187}$Re) = 2.6 barn). Moreover, the distance between these two resonance signals is exactly equal to the difference in the Larmor frequencies of $^{185}$Re and $^{187}$Re.

<table>
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<tr>
<th>$T$ [K]</th>
<th>$v_o$ [MHz]</th>
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Table I. Temperature dependent frequencies, $v_o$, of the $^{127}$I NMR powder spectra of (CH$_3$)$_4$AsIO$_4$; the spectra are depicted in Fig. 1.
The temperature dependent $^{187}$Re solid state NMR spectra of 2 are depicted in Fig. 5.

The $^{185,187}$Re powder spectra of 2 have additional signals arising from two different types of ReO$_4^-$ tetrahedra in the lattice. The frequency edges B arise from a second order quadrupole splitting $\Delta v$ of the central $^{185,187}$Re NMR transition ($m = +1/2 \leftrightarrow m = -1/2$) associated with an axial symmetric asymmetry parameter $\eta \approx 0$. The quadrupole coupling constants can be determined by applying equation (1).

$$e^2qQ/h = 4\sqrt{2} \sqrt{\Delta v} v_L$$

with $v_L$: Larmor frequency
$\Delta v$: quadrupole splitting

The temperature dependence of the data is summarized in Table II and Fig. 6.

In the temperature range of $T < 310$ K no $^{185}$Re or $^{187}$Re NMR signal can be achieved. The DSC analysis proves a reversible first order phase transition at $T =$

<table>
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<tr>
<th>$T$ [K]</th>
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<th>$e^2qQ/h$ [MHz]</th>
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<td>11.62</td>
</tr>
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</table>

Table II. Temperature dependence of second order $^{187}$Re NMR quadrupole interactions of (CH$_3)_4$AsReO$_4$. 

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**Fig. 4.** $^{185}$Re–$^{187}$Re solid state NMR spectrum of (CH$_3)_4$AsReO$_4$ at $T = 380$ K with aqueous NaReO$_4$ solution as standard. Larmor frequency: $v_L = 45.25$ MHz; sweep range: SW = 1 MHz; pulse program: one cycle pulses; pulse width: DL$_1 = 5 \mu$s; recycle time: DL$_0 = 40$ ms; number of scans: NS = 30,000.

**Fig. 5.** Temperature dependence of the $^{187}$Re solid state NMR spectra of polycrystalline (CH$_3)_4$AsReO$_4$. Larmor frequency: $v_L = 45.455$ MHz; sweep width: SW = 357.1 kHz; pulse program: one cycle pulses; pulse width: DL$_1 = 5 \mu$s; recycle time: DL$_0 = 40$ ms; number of scans: NS = 100,000. The average temperature coefficient is given by

$$\alpha = \frac{2}{e^2qQ/h(T_f) + e^2qQ/h(T_i)} \cdot \left\{ e^2qQ/h(T_2) - e^2qQ/h(T_1) \right\}/(T_2 - T_1).$$
Fig. 6. Temperature dependence of $^{187}$Re quadrupole coupling constants $e^2 qQ/h$ measured by second order quadrupole effects in $^{187}$Re powder spectra of $(\text{CH}_3)_4\text{AsReO}_4$; values from Table II.

294 K for temperature down measurement and at $T = 301$ K for temperature rise measurement (s. Fig. 3).

4. Discussion

4.1. $^{127}$I Solid state NMR spectra of $(\text{CH}_3)_4\text{AsIO}_4$ (1)

The $^{127}$I powder spectra of 1 (s. Fig. 1) show the typical line shape for cases where dipolar coupling is the dominant solid state interaction in the lattice [10]. The presence of a very small quadrupole interaction hidden due to dipolar line broadening cannot be excluded.

From the line width the maximum value of the quadrupole coupling constant can be approximated to $e^2 qQ/h \leq 1.8$ MHz. The iodine atoms must possess a nearly spherical electric environment, as provided by nearly undistorted $\text{IO}_4^-$ tetrahedra. These results suggested that the analogous rhenium compound 2 should be suitable for NMR measurements.

4.2. $^{185}$Re and $^{187}$Re Solid state NMR spectra of $(\text{CH}_3)_4\text{AsReO}_4$

The $^{185}$Re and $^{187}$Re solid state NMR spectra of 2 (s. Fig. 4 and 5) show the characteristic features of a superposition of two different NMR resonances. This unusual line shape is a consequence of two different $\text{ReO}_4^-$ tetrahedra in the lattice. We could observe comparable spectra in the $^{127}$I solid state NMR spectra of tetraphenylarsonium-metaperiodate in a low temperature modification at $T \leq 205$ K [11, 12].

The DSC analysis gives another hint at the existence of two different types of $\text{ReO}_4^-$ tetrahedra in the high temperature modification of 2. The temperature down measured DSC spectra (s. Fig. 3) unequivocally show two distinguishable maxima caused by the different loss of energy of the two $\text{ReO}_4^-$ tetrahedra by integration into the lattice of the low temperature modification.

i) Signal component A has no visible quadrupole coupling. The experimental line width can be approximated to 7 kHz. A maximum quadrupole interaction hidden under dipolar broadening can be calculated as $e^2 qQ/h \approx 3$ MHz. $^{127}$I NMR measurements on tetraphenylstibonium-metaperiodate show that quadrupole coupling constants in the range of $2 \text{ MHz} \leq e^2 qQ/h \leq 30$ MHz can be determined with our Bruker CXP 200 NMR spectrometer [11]. It appears therefore that this group of $\text{ReO}_4^-$ anions are not or very weakly distorted in the present lattice such that the electric field gradient almost disappears.

ii) Signal component B shows the two characteristic frequency edges of a second order quadrupole
splitting with a nearly axial-symmetric asymmetry parameter $\eta \approx 0$ [13, 14]. The frequency edges are broadened by dipole–dipole interactions. From Fig. 6 we can calculate a temperature coefficient $\tilde{\alpha} = -1.5 \times 10^{-2} \, \text{K}^{-1}$ in the temperature range of $290 \, \text{K} \leq T \leq 330 \, \text{K}$. This extremely negative value is in contradiction with the Bayer theory [15]. Obviously the occurrence of volume effects as defined by the Kushida-Benedek-Bloembergen (KBB) theory [16] cannot be neglected. Therefore the pressure coefficient $(\partial \nu / \partial P)_{T}$ corresponding to the KBB theory must possess a large positive value in order to yield an extremely negative value $(\partial \nu / \partial T)_{P}$.

From the temperature dependent quadrupole interactions we can gather a continuous change in the electric field gradient, which is caused by the distortion of the $\text{ReO}_{4}^{-}$ anion. With the aid of a point charge model for the $\text{ReO}_{4}^{-}$ ions it is possible to determine the deviation $\Delta \beta$ of the $\text{O}–\text{Re}–\text{O}$ angle from the tetrahedron angle $\beta = 109.47^\circ$ [17, 18]. The dependence of the quadrupole coupling constant upon $\Delta \beta$ is given by eq. (2):

$$ e^2 Q / h = Z e^2 Q / h \left(9 \cos^2 \theta - 1\right)(1 - \gamma \varepsilon) $$

with $Z$ : electric charge of the oxygen atom,
$\beta$ : O–Re–O angle,
$\gamma \varepsilon$ : Sternheimer polarization coefficient,
$r$ : Re–O distance [19].

The results, depending on bond ionization, are listed in Table III.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>$\Delta \beta$ (°)</th>
<th>ionic $(Z = -2)$</th>
<th>50% ionic $(Z = -1.25)$</th>
<th>covalent $(Z = -0.5)$</th>
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<tr>
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<td>0.45</td>
<td>1.15</td>
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</table>

The results, depending on bond ionization, are listed in Table III.

Depending on the electric charge of the oxygen atoms, the $\Delta \beta$ values lie in the range of $0.14–0.56^\circ$ at $T = 380 \, \text{K}$. These results demonstrate clearly the advantages of $^{185}\text{Re}$ and $^{187}\text{Re}$ solid state NMR spectroscopy. Quadrupole interactions are extremely sensitive to structural effects so that very small changes in the symmetry properties can easily be calculated. Even with X-ray measurements it is very difficult to determine deviations $\Delta \beta$ in the range of $\Delta \beta < 0.5^\circ$.

In the temperature range $294 \, \text{K} \leq T \leq 301 \, \text{K}$ we observe a reversible first order phase transition. It can be assumed that the quadrupole coupling constant of the low temperature modification is very large, which makes it accessible only by NQR methods, because it is impossible to achieve $^{185}\text{Re}$ or $^{187}\text{Re}$ NMR spectra in this temperature range. This kind of experiments is in progress, especially in order to examine if the phase transition is accompanied by a change in the temperature behaviour of the quadrupole coupling constant. Since this effect can be observed very often, we expect to have found another compound with an anomalous positive temperature coefficient $\tilde{\alpha}$ [1, 9, 10], measureable only by pure NQR methods.

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