Anomalous Temperature Dependence of the ^{127}I-Quadrupole Coupling in $(C_6H_5)_4PIO_4$, $(C_6H_5)_4AsIO_4$ and $(C_6H_5)_4SbIO_4$

Paul K. Burkert and Dagmar G. Klobasa

Anorganisch-chemisches Institut der Technischen Universität München

Z. Naturforsch. **40 a,** 274 – 278 (1985); received December 20, 1984

On measuring second order quadrupole effects in ^{127}I solid state NMR, new anomalous temperature coefficients of the quadrupole interaction were observed in tetraphenylphosphonium-, tetraphenylarsonium- and tetraphenylstibonium metaperiodate. The relevance of possible mechanisms like breakdown of $d_\pi - p_\pi$ backbonding, negative pressure coefficients, charge transfer, orientational change of the electric field gradient tensors, and influence of reorientational motions is discussed for these compounds.

Key words: NMR Quadrupole Splitting, Periodates

1. Introduction

A small number of substances shows NQR frequencies ν or quadrupole coupling constants $e^2 q Q/h$ with positive temperature coefficients $\alpha = (1/\nu)\,(\partial \nu/\partial T)_p$ in certain temperature ranges. This behaviour, which is in contradiction to the original Bayer theory [1], is called anomalous temperature dependence. The initial theory [1] neglects all temperature dependent volume effects. Although the most important parameters of this theory, particularly the moments of inertia and the lattice frequencies depend on volume, the isochoric term $(\partial \nu/\partial T)_V$ is there described only.

Kushida, Benedek and Bloembergen (KBB) [2] finally found the correlation between the temperature dependence of the NQR frequencies ν at constant volume, the so called Bayer term $(\partial \nu/\partial T)_V$, and the term at constant pressure $(\partial \nu/\partial T)_p$, which is experimentally much more easily accessible than the Bayer term:

$$\left(\frac{\partial \nu}{\partial T}\right)_p = -\frac{\alpha_p}{\chi_T}\left(\frac{\partial \nu}{\partial p}\right)_T + \left(\frac{\partial \nu}{\partial T}\right)_V \quad (1)$$

with $\alpha_p = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$ thermal expansion coefficient,

$\chi_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T$ isothermal compressibility coefficient.

Difficulties using this theory are arising, however, because for many NQR investigations most of the necessary parameters are not available or only accessible by considerable experimental effort.

Presently a comprehensive discussion of the anomalous temperature coefficients of quadrupole coupling constants is not possible because special intra- and intermolecular interactions appear to be the origin of these effects. The most important possibilities considered until now are:

(a) the breakdown of $d_\pi - p_\pi$ backbonding [3, 4]
(b) the occurrence [5] of sufficiently large negative pressure coefficients $(\partial \nu/\partial p)_T$
(c) charge transfer from π- to σ-orbitals of adjacent atoms [6, 7]
(d) continuous orientational change of the principal axes system of the electric field gradient (EFG) tensors $\tilde{q}_{ik}$ [8 – 12]
(e) influence of reorientational motions [13 – 18].

On measuring second order quadrupole effects in ^{127}I solid state NMR we observed new anomalous temperature coefficients of tetraphenylphosphonium- (**1**), tetraphenylarsonium- (**2**), and tetraphenylstibonium metaperiodate (**3**). The compounds (**1**) and (**2**) show this anomalous behaviour after a phase transition detected by the typical change of the quadrupole coupling constants in the ^{127}I NMR powder spectra. (**3**) has no phase transition in the whole temperature range measured.

With the main mechanisms listed above the anomalous temperature effects will be discussed.

2. Experimental

2.1. *Instrumentation*

The quadrupole coupling constants $e^2 q Q/h$ of the compounds $Ph_4E^+IO_4^-$ (E = P, As, Sb; Ph = C_6H_5)

Reprint requests to Dr. Paul K. Burkert, Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstr. 4, D-8046 Garching.

0340-4811 / 85 / 0300-0274 $ 01.30/0. – Please order a reprint rather than making your own copy.

(**1**) – (**3**) were determined from second order quadrupole splittings of the ^{127}I solid state NMR spectra. For these measurements the FT-NMR spectrometer Bruker CXP 200 equipped with a superconducting magnet ($B_0 = 4.698\,T$) was used. The resulting ^{127}I Larmor frequency ν_L was 40.19 MHz. Temperature dependent experiments were carried out using the thermostat Bruker B-VT 1000 with a temperature tolerance $\Delta T = \pm 1$ K. Experimental errors of the reported quadrupole coupling constants are in the range of $\Delta\,(e^2 q\,Q/h) = \pm\,0.05$ MHz mainly caused by dipolar broadening of the quadrupole split ^{127}I NMR powder patterns.

2.2. Preparation of the compounds (1) – (3)

Starting with the commercially available compounds $Ph_4E^+X^-$ (E = P, As, Sb; X = Cl, Br; Ph = C_6H_5) prepared by literature methods [19, 20], the hydroxides $Ph_4E^+OH^-$ (E = P, As, Sb; Ph = C_6H_5) were synthesized by application of a strong basic anion exchanger (Merck, Ionenaustauscher III) in aqueous solutions. Neutralisation of these basic solutions with the equivalent amount of pure, solid periodic acid gives the desired periodates (**1**) – (**3**). After evaporation of the solvent and drying of the white polycrystalline compounds in high vacuum at room temperature they are accessible in a yield of 70% – 80%. For further purification they are recrystallized from ethanol to give analytically pure samples. Heating of these compounds just to determine their melting points was avoided to prevent violent explosions. The analytical data are presented in the following.

$C_{24}H_{20}O_4IP$ (530.30)

calc. %:	C 54.36	H 3.80	I 23.93
found %:	C 54.12	H 3.82	I 23.83

$C_{24}H_{20}O_4IAs$ (574.25)

calc. %:	C 50.20	H 3.51	I 22.10	As 13.05
found %:	C 49.75	H 3.45	I 22.00	As 12.90

$C_{24}H_{20}O_4ISb$ (621.07)

calc. %:	C 46.41	H 3.25	O 10.30	I 20.43
found %:	C 46.15	H 3.28	O 10.42	I 20.29

3. Results

The typical second order ^{127}I quadrupole splittings $\Delta\nu$ of the central ^{127}I NMR transition ($+1/2 \leftrightarrow -1/2$) dependent on temperature are depicted in Figure 1. For polycrystalline substances the dependence of the quadrupole splitting $\Delta\nu$ upon the spin quantum number I and the asymmetry parameter η [21, 22] is given by

$$\Delta\nu = \frac{\nu_Q^2}{144\,\nu_L}\left[I\,(I+1) - \tfrac{3}{4}\right] f(\eta) \qquad (2)$$

with $\nu_Q = \dfrac{e^2 q\,Q}{h}\,\dfrac{3}{2I\,(2I-1)}$

and $f(\eta) = 16\,(1-\eta) + (3-\eta)^2$ for $\eta \leqq 0.33$.

A comparison of these ^{127}I NMR powder spectra with earlier measurements of scheelite-structured

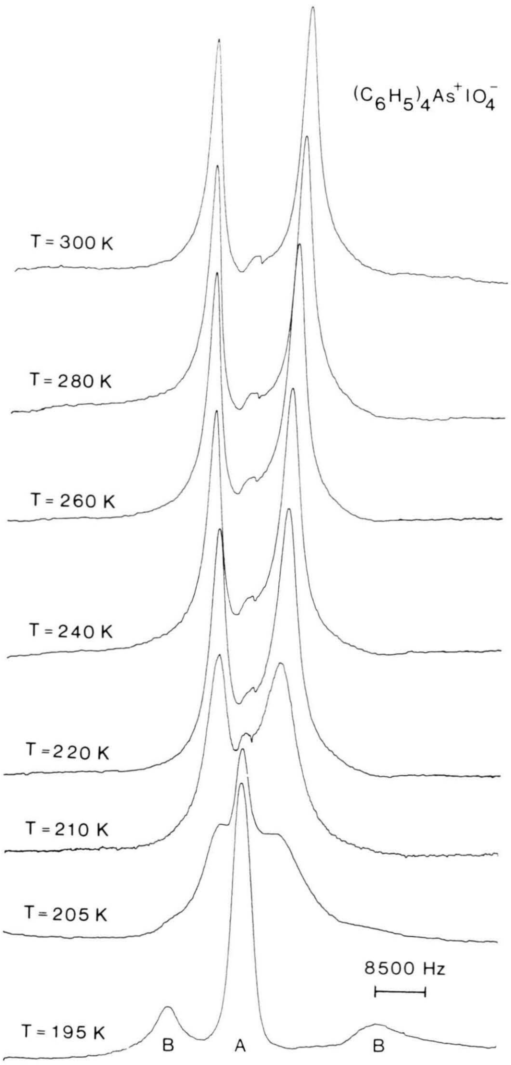

Fig. 1. Temperature dependence of the ^{127}I NMR spectra of polycrystalline $(C_6H_5)_4AsIO_4$ with second order quadrupole splitting $\Delta\nu$. Larmor frequency: $\nu_L = 40.1885$ MHz; sweep range: SW = 83.3 kHz; pulse program: one cycle pulses; pulse width: 4 µs; recycle time: 60 ms.

Table 1. Temperature dependence of second order ^{127}I NMR quadrupole splitting $\Delta\nu$ of $(C_6H_5)_4E^+IO_4^-$ (E = P, As, Sb). The quadrupole coupling constants e^2qQ/h are calculated from (3).

$(C_6H_5)_4PIO_4$			$(C_6H_5)_4AsIO_4$			$(C_6H_5)_4SbIO_4$		
T [K]	$\Delta\nu$ [kHz]	e^2qQ/h [MHz]	T [K]	$\Delta\nu$ [kHz]	e^2qQ/h [MHz]	T [K]	$\Delta\nu$ [kHz]	e^2qQ/h [MHz]
293	15.53	4.47	297	15.95	4.53	302	5.91	2.76
288	15.14	4.41	277	15.14	4.41	293	5.37	2.63
283	14.84	4.37	257	14.08	4.26	288	5.08	2.56
278	14.55	4.33	238	13.02	4.09	283	4.79	2.48
273	14.36	4.30	218	11.56	3.86	278	4.49	2.40
268	14.06	4.25	213	10.90	3.75	273	4.20	2.32
263	13.77	4.21	208	10.25	3.63	268	3.96	2.26
259	13.38	4.15	204	9.52	3.50	263	3.66	2.17
256	13.18	4.12	203	16.28	4.58	258	3.37	2.08
253	17.48	4.74	201	29.46	6.16	253	3.08	1.99
248	20.46	5.13	200	31.25	6.34	248	2.78	1.89
243	22.66	5.40	197	33.37	6.55	243	2.44	1.77
238	24.07	5.56	194	34.99	6.71	238	2.05	1.62
233	24.90	5.66	191	37.11	6.91	233	1.71	1.48
228	25.39	5.71	188	38.17	7.01	228	1.47	1.37
			185	41.26	7.28			
			182	41.83	7.33			
			179	42.81	7.42			

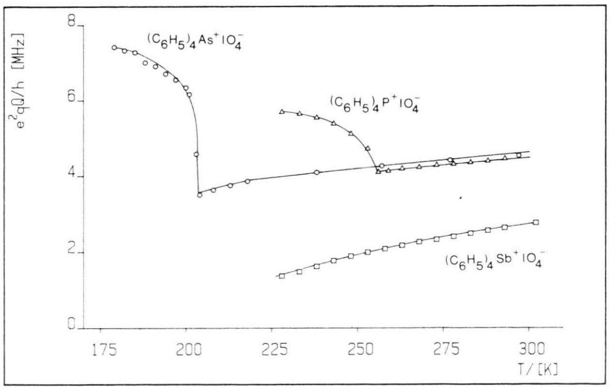

Fig. 2. Temperature dependence of ^{127}I quadrupole coupling constants e^2qQ/h measured by second order quadrupole effects in ^{127}I NMR powder spectra of $(C_6H_5)_4E^+IO_4^-$ (E = P, As, Sb); values of e^2qQ/h from Table 1.

metaperiodates [16, 18] gives evidence of the case $\eta \to 0$. From (2) the quadrupole coupling constant results to be

$$e^2qQ/h = 4\sqrt{2}\sqrt{(\Delta\nu)\cdot\nu_L}\,. \tag{3}$$

The values of e^2qQ/h listed in Table 1 were calculated from (3). Their temperature dependence is shown in Figure 2.

Figure 2 evidences the phase transitions of the compounds (**1**) and (**2**) at (255 ± 1) K and (203 ± 1) K, respectively, and the three anomalous positive temperature coefficients α of the quadrupole coupling constants. Compound (**3**) does not show a phase transition in the measured temperature range. Measurements of the second order quadrupole splitting $\Delta\nu$ at temperatures below 228 K for compound (**3**) are not possible because the quadrupole splitting $\Delta\nu$ of (**3**) becomes of the order of the dipolar broadening and therefore cannot be resolved from the ^{127}I NMR signals. The same reason prevents the measurement of possibly present quadrupole effects in the ^{127}I NMR signal component A of the compounds (**1**) and (**2**) in their respective low temperature modifications (see Figure 1).

4. Discussion

4.1. Phase transitions

Figures 1 and 2 show the phase transitions of the compounds (**1**) and (**2**) at $T = 255 \pm 1$ K and $T = 203 \pm 1$ K, respectively. Below these transitions of the two compounds the ^{127}I NMR spectra consist of a signal component B with a large quadrupole splitting $\Delta\nu$ and a signal component A with no visible quadrupole splitting (see Figure 1). At the transition point the component B runs through a minimum of the quadrupole interactions and then shows the anomalous temperature coefficient $\bar{\alpha} > 0$ in the high temperature modification. The component A of the respective compounds (**1**) and (**2**) disappears at this point. This means that in the low temperature modification a part of the IO_4^--tetrahedra suffers a very small distortion by insertion in the lattice. The other IO_4^--tetrahedra have a comparatively large EFG. Moreover, the flat descent of the frequency edges suggests the occurrence of an asymmetry parameter $\eta \neq 0$ for the component B. This refers to a lowering of the symmetry at these IO_4^--tetrahedra. No phase transition is found for compound (**3**). Its room temperature modification stays also in the range 228 K $\leqq T \leqq$ 200 K, however, at $T = 225$ K the quadrupole splitting of the ^{127}I signals is reduced to the order of the dipolar broadening and therefore cannot be resolved.

4.2. Anomalous temperature coefficients

The anomalous temperature coefficients of the quadrupole coupling constants are summarized in

Table 2. Compounds with anomalous temperature coefficients $\bar{\alpha}$ as representatives of the different mechanisms in comparison with the coefficients of $(C_6H_5)_4E^+IO_4^-$ (E = P, As, Sb). The average temperature coefficient of the high temperature modification is given by

$$\bar{\alpha} = \frac{2}{e^2qQ/h(T_1) + e^2qQ/h(T_2)} \, \frac{e^2qQ/h(T_2) - e^2qQ/h(T_1)}{T_2 - T_1}$$

Compound	Nucleus	$\bar{\alpha}$ [K^{-1}]	Literature Comments Mechanism
K_2ReCl_6	^{35}Cl	$+0.0936 \cdot 10^{-4}$	[3], [4] Breakdown of the $d_\pi - p_\pi$ backbonding
K_2WCl_6	^{35}Cl	$+0.4305 \cdot 10^{-4}$	
K_2ReBr_6	^{81}Br	$+0.2484 \cdot 10^{-4}$	
$TiBr_4$	^{79}Br	$+0.067 \cdot 10^{-4}$	[5] Negative pressure coefficient $(\partial \nu/\partial p)_T < 0$
α-ICl	^{35}Cl	$+2.1 \cdot 10^{-4}$	[6], [7] Only one of the two inequivalent Cl-atoms anomalous Charge transfer
Re_2CO_{10}	^{187}Re	$+1.37 \cdot 10^{-4}$	[8], [9], [10], [11], [12] Only ν_2 (± 3/2 ↔ ± 5/2) anomalous Change of the EFG-tensor axes
$(CH_3)_3GeOReO_3$	^{187}Re ^{185}Re	$+0.6 \cdot 10^{-4}$	
NH_4ReO_4	^{187}Re	$+0.15 \cdot 10^{-2}$	[13], [14], [15], [16] Reorientational motions of the cation
ND_4ReO_4	^{187}Re	$+0.15 \cdot 10^{-2}$	
NH_4IO_4	^{127}I	$+1.6 \cdot 10^{-2}$	
$(C_6H_5)_4PIO_4$	^{127}I	$+0.2 \cdot 10^{-2}$	see discussion
$(C_6H_5)_4AsIO_4$	^{127}I	$+0.2 \cdot 10^{-2}$	
$(C_6H_5)_4SbIO_4$	^{127}I	$+0.8 \cdot 10^{-2}$	

Table 2 for the compounds (**1**) – (**3**) and compared with other important examples presently known.

(a) In their MO calculation, Haas and Marram [4] explain the positive temperature coefficients of the ^{35}Cl and ^{81}Br NQR frequencies observed in K_2ReCl_6, K_2WCl_6 and K_2ReBr_6 [3] by a temperature dependent breakdown of the intra-ionic $d_\pi - p_\pi$ backbonding in these complex anions. The effective mechanism appears to be the increase of the bending vibrations between the metal and the ligands whereby the population numbers of the halogen ligand orbitals increase at higher temperature.

In the case of (**1**) – (**3**), these π-backbonding effects cannot be responsible for the anomalous temperature coefficients $\bar{\alpha} > 0$, because otherwise all measured metaperiodates [18] should show this phenomenon. That is not the case except for NH_4IO_4 [18].

(b) For the compound $TiBr_4$ the explanation of the positive temperature coefficient $\bar{\alpha}$ of the ^{79}Br NQR frequencies [5] is related with the appearance of a sufficiently large negative pressure coefficient $(\partial \nu/\partial p)_T$ (compare (1)). This effect could contribute to the positive temperature coefficient $\bar{\alpha} > 0$ of the compounds (**1**), (**2**) and (**3**), because their cations are very voluminous and therefore can have a pressure dependent influence on the EFG's. Additional investigations in this field call for high experimental efforts and are planned together with the group of Brown and Segel [23].

(c) ^{185}Re and ^{187}Re NQR measurements of Re_2CO_{10} proved a positive temperature coefficient for the NQR transitions ν_2 (± 3/2 ↔ ± 5/2) in the temperature range $77\ K \leqq T \leqq 200\ K$, whereas the other NQR transitions ν_1 (± 1/2 ↔ ± 3/2) showed a normal dependence [8, 9, 10]. According to Mooberry, Spiess and Sheline [8] the orientational change of the principal axes of the EFG-tensors $\tilde{q}_{ik}$ is the reason for this remarkable behaviour. Schmidbaur, Koth and Burkert [11, 12] observed similar phenomena of the ^{185}Re and ^{187}Re NQR transitions in the compound $(CH_3)_3GeOReO_3$ due to the same effect.

In the obtained ^{127}I NMR spectra (see Fig. 1) of (**1**) – (**3**) the form of the ^{127}I NMR signals with second order quadrupole interactions does not give any indication for a change of the asymmetry parameter η in the range of the anomalous temperature coefficient α and therefore there is no evidence for an orientational change of the EFG-tensors $\tilde{q}_{ik}$. Rather all second order quadrupole splittings $\Delta\nu$ of the ^{127}I NMR signals are characteristic of the case $\eta \to 0$ (see (2)) in the range of the anomalous temperature dependence.

(d) Until now the largest anomalous temperature coefficients α of quadrupole coupling constants were found in ammonium perrhenate (NH_4ReO_4) and ammonium metaperiodate (NH_4IO_4) [13–16]. At present the reason of these anomalous effects is not clarified completely, but reorientational motions of the ammonium ions appear to be of importance. A suitable model of Negita, Nakamura and Chihara [17] gives evidence of corresponding reorientational correlation times. Indeed static effects seem to contribute, too. Quite recently we could demonstrate for the tetragonal ammonium salts that there is a direct correlation between the observed anomalies of the temperature behaviour of the lattice parameter a and the anomalous temperature dependence of the ^{185}Re, ^{187}Re and ^{127}I quadrupole coupling constants [18].

For the compounds (**1**) – (**3**) dynamic effects within the lattice, like hindered torsion vibrations, change of the corresponding vibration axes in the cations and analogous static effects as in NH_4ReO_4 and NH_4IO_4, cause the main contribution to the anomalous temperature coefficients. For solving these problems further experiments should be done in connection with the measurements of the pressure coefficients [23].

Acknowledgement

We wish to express our gratitude to Professor H. P. Fritz, Institute of Inorganic Chemistry, Technical University of Munich, for financial support of this research.

[1] H. Bayer, Z. Physik **130,** 227 (1951).
[2] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104,** 1364 (1956).
[3] R. Ikeda, D. Nakamura, and M. Kubo, J. Phys. Chem. **69,** 2101 (1965).
[4] T. E. Haas and E. P. Marram, J. Chem. Phys. **43,** 3985 (1965).
[5] R. G. Barnes and R. D. Enghardt, J. Chem. Phys. **29,** 248 (1958).
[6] T. Kiichi, N. Nakamura, and H. Chihara, IV. Int. Symp. on NQR Spectroscopy, Osaka 1977.
[7] H. Chihara, and N. Nakamura, Adv. in NQR (ed.: J. A. S. Smith), Vol. 4, 51, Heyden, London 1980.
[8] E. S. Mooberry, H. W. Spiess, and R. K. Sheline, J. Chem. Phys. **57,** 813 (1972).
[9] S. L. Segel and R. G. Barnes, Phys. Rev. **107,** 638 (1969).
[10] S. L. Segel and L. A. Anderson, J. Chem. Phys. **49,** 1407 (1968).
[11] H. Schmidbaur, D. Koth, and P. K. Burkert, Chem. Ber. **107,** 269 (1974).
[12] P. K. Burkert, D. Koth, and H. Schmidbaur, Z. Naturforsch. **31 b,** 149 (1976).
[13] P. K. Burkert and M. F. Eckel, Z. Naturforsch. **28 b,** 5 (1973).
[14] P. K. Burkert and M. F. Eckel, Z. Naturforsch. **28 b,** 379 (1973).
[15] P. K. Burkert and F. M. Hutter, Z. Naturforsch. **32 b,** 15 (1977).
[16] P. K. Burkert, Z. Naturforsch. **35 b,** 1349 (1980).
[17] K. Negita, N. Nakamura, and H. Chihara, Chem. Phys. Lett. **63,** 187 (1979).
[18] P. K. Burkert, J. Mol. Struct. **58,** 307 (1982).
[19] H. H. Willard, L. R. Perkins, and F. F. Blicke, J. Amer. Chem. Soc. **70,** 737 (1948).
[20] F. F. Blicke and E. Monroe, J. Amer. Chem. Soc. **57,** 720 (1935).
[21] G. H. Stauss, J. Chem. Phys. **40,** 1988 (1964).
[22] J. F. Baugher, P. C. Taylor, T. Oja, and P. J. Bray, J. Chem. Phys. **50,** 4914 (1969).
[23] R. J. C. Brown and S. L. Segel, private comm. 1984.