Anomalous Temperature Dependence of the ^{127}I Quadrupole Interaction in Tetraethylstiboniummetaperiodate $(C_2H_5)_4SbIO_4$

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^{127}I solid state NMR studies revealed second order quadrupole effects in $(C_2H_5)_4SbIO_4$ with anomalous positive temperature coefficients of the quadrupole coupling constants. This anomaly is caused by a continuous change of the axes of the electric field gradient tensor.

Key words: ^{127}I NMR Quadrupole Splitting, Periodates

1. Introduction

Extensive ^{127}I solid state NMR investigations of metaperiodates with alkyl- or arylsubstituted cations of main group V indicated second order quadrupole effects with quadrupole coupling constants in the range of 2 to 7 MHz at room temperature [1, 2]. The temperature dependence of the ^{127}I quadrupole coupling constants showed normal behaviour with negative temperature coefficients $\bar{\alpha}$ for the metaperiodates $(C_2H_5)_4PIO_4$ and $(C_2H_5)_4AsIO_4$ [2].

By way of contrast we observed anomalous positive temperature coefficients $\bar{\alpha}$ for the arylsubstituted metaperiodates $(C_6H_5)_4EIO_4$ (E = P, As, Sb) [1] and an unusual temperature behaviour for $(C_2H_5)_4SbIO_4$, where in addition to the anomalous value $\bar{\alpha} > 0$ of the quadrupole coupling constants the asymmetry parameter η reveals negative temperature dependence $(\partial\eta/\partial T)_p < 0$.

Presently a comprehensive theory of the anomalous temperature dependence fails, because special intra- and intermolecular interactions appear to be the reason of this phenomenon. The most important examples considered until now are summarized in our previous publications [1, 2]. With these main mechanisms the anomalous temperature effect of tetraethylstiboniummetaperiodate data will be discussed.

2. Experimental

2.1. *Instrumentation*

The measurements of the ^{127}I NMR powder spectra were taken by a Bruker FT-NMR CXP 200 spectrometer equipped with a superconducting magnet ($B_0 = 4.698$ T). The suitable ^{127}I Larmor frequency was 40.30 MHz. For temperature dependence experiments the thermostat Bruker B-VT 1000 with a temperature tolerance $\Delta T = \pm 1$ K was used. Experimental errors of the reported quadrupole coupling constants are in the order of $\Delta e^2 qQ/h = \pm 0.03$ MHz and those of the asymmetry parameter η amount to $\Delta\eta = \pm 0.02$.

2.2. *Preparation of $(C_2H_5)_4SbIO_4$*

The quarternary stibonium salt $(C_2H_5)_4SbI$ prepared by literature method [3] was dissolved in water and then the hydroxide $(C_2H_5)_4Sb^+OH^-$ was synthesized by application of a strong basic anion exchanger (Merck, Exchanger III). The neutralization of this basic solution with pure, solid periodic acid gives the desired metaperiodate. After evaporation of the solvent and drying of the white polycrystalline salt in high vacuum at room temperature $(C_2H_5)_4SbIO_4$ is accessible in a yield of about 90%. The determination of the melting point was not tried to avoid violent explosion. The analytical data are as follows [4]:

$C_8H_{20}O_4ISb$ (428.90)

calc. %:	C 22.40	H 4.70	O 14.92	I 29.59	Sb 28.39
found %:	C 23.04	H 4.76	O 14.86	I 28.55	Sb 28.41

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3. Results

For the first time polycrystalline $(C_2H_5)_4SbIO_4$ was studied by ^{127}I solid state NMR in the temperature range of 217 K to 301 K. Figure 1 shows the typical second order quadrupole splitting $\Delta\nu$ of the central ^{127}I NMR transition ($m = +1/2 \leftrightarrow m = -1/2$) in the case of a non axialsymmetric asymmetry parameter η. A comparison of this powder pattern with the theoretical lineshape functions for the central transition of the NMR of a half-integral nuclear spin (see Fig. 2) points at an asymmetry parameter $\eta > 1/3$ [5, 6].

The dependence of the quadrupole splitting $\Delta\nu$ on the spin quantum number I and the asymmetry parameter η [5, 6] is given by

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

with

$$\nu_Q = \frac{e^2 qQ}{h}\,\frac{3}{2I(2I-1)} \qquad (\nu_L = \text{Larmor frequency})$$

and

$$f(\eta) = 8(1-\eta^2) + 16(1-\eta) \quad \text{for } \eta > 1/3.$$

With regard to the location of the shoulders the following distance $\overline{AB}$ results from Fig. 2:

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

with

$$g(\eta) = -16(1-\eta) + 16(1+\eta).$$

For the nuclear spin $I = 5/2$ follows from the ratio $\overline{A'A}$ to $\overline{AB}$:

$$\frac{\overline{A'A}}{\overline{AB}} = \frac{-\eta^2 - 2\eta + 3}{4\eta}. \qquad (3)$$

Because of the restriction $0 \leqq \eta \leqq 1$ only one η-value is reasonable. Dependent on η the corresponding quadrupole coupling constant e^2qQ/h can be calculated by

$$\frac{e^2 qQ}{h} = \sqrt{\frac{25\,\nu_L \overline{AB}}{\eta}}. \qquad (4)$$

For $(C_2H_5)_4SbIO_4$ the values of e^2qQ/h and η are listed in Table 1. Their temperature dependence is shown in Figs. 3 and 4.

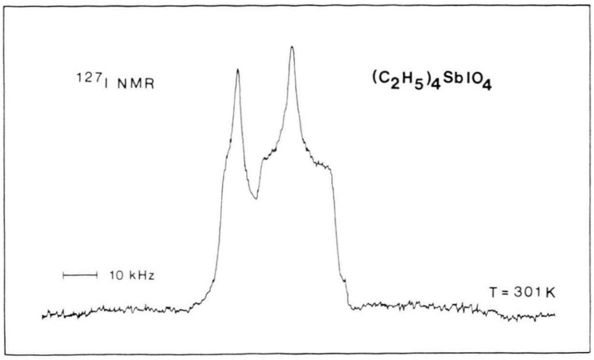

Fig. 1. ^{127}I NMR spectrum of polycrystalline $(C_2H_5)_4SbIO_4$. Larmor frequency: $\nu_L = 40.30$ MHz; sweep range: SW = 151.5 kHz; pulse program: one cycle pulses; pulse width: 5 µs; recycle time: 20 ms.

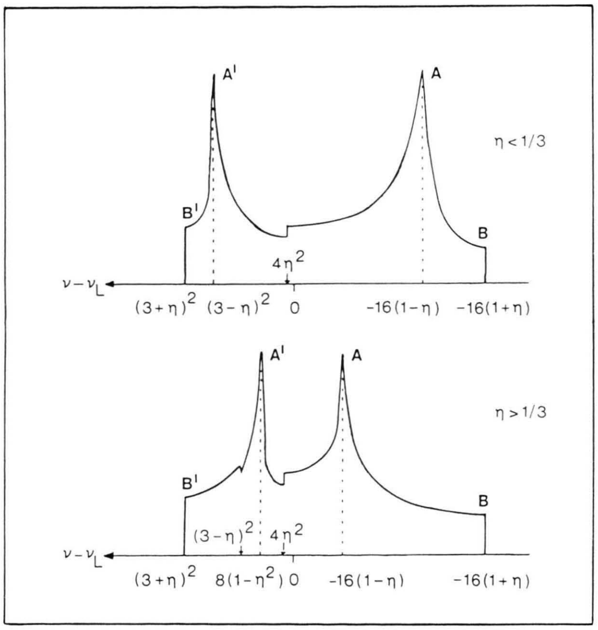

Fig. 2. NMR powder pattern for the central transition ($m = +1/2 \leftrightarrow m = -1/2$) of a half-integral nuclear spin in the case $\eta \neq 0$ [5, 6].

4. Discussion

For $(C_2H_5)_4SbIO_4$ no phase transition is observed in the measured temperature range. But Fig. 3 and Table 1 indicate an anomalous temperature behaviour of the ^{127}I quadrupole interaction with a positive temperature coefficient $\bar{\alpha} = 9.0 \cdot 10^{-4}\,K^{-1}$. By contrast with the already published examples [1,

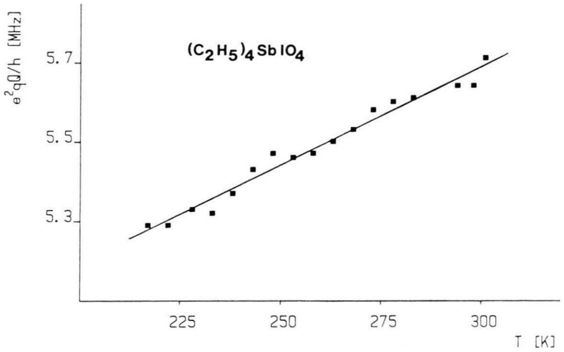

Fig. 3. Temperature dependence of the ^{127}I quadrupole coupling constants for $(C_2H_5)_4SbIO_4$ in the case $\eta \neq 0$. Accuracy: $\Delta e^2 qQ/h = \pm 0.03$ MHz.

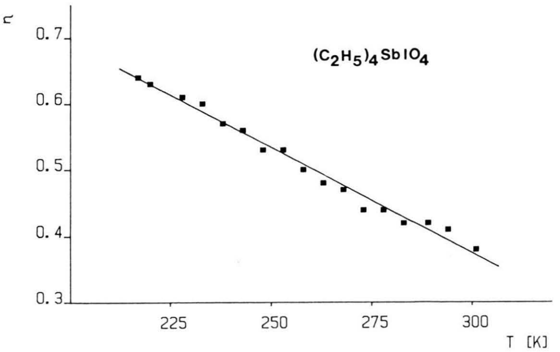

Fig. 4. Temperature dependence of the asymmetry parameter η for $(C_2H_5)_4SbIO_4$. Accuracy: $\Delta\eta = \pm 0.02$.

Table 1. Temperature dependence of the determined quadrupole coupling constants e^2qQ/h and the asymmetry parameter η for $(C_2H_5)_4SbIO_4$. The values are calculated with (3) and (4).

T [K]	$\overline{A'A}$ [kHz]	$\overline{AB}$ [kHz]	η	e^2qQ/h [MHz]
301	17.02	12.28	0.38	5.71
294	15.98	12.87	0.41	5.64
289	15.83	13.17	0.42	5.64
283	15.54	13.17	0.42	5.61
278	15.09	13.61	0.44	5.60
273	14.80	13.76	0.44	5.58
268	14.06	14.20	0.47	5.53
263	13.61	14.50	0.48	5.50
258	13.02	14.94	0.50	5.47
253	12.73	15.24	0.51	5.46
248	12.28	15.83	0.53	5.47
243	11.54	16.42	0.56	5.43
238	10.95	16.42	0.57	5.37
233	10.21	16.87	0.60	5.32
228	10.06	17.16	0.61	5.33
222	9.47	17.46	0.63	5.29
217	9.03	17.90	0.64	5.29

2] the following mechanisms explaining $\bar{\alpha} > 0$ can be excluded:

a) Influence of the Reorientational Motions

Reorientational motions of the cation as found in the ammonium salts of ReO_4^- and IO_4^- [7−10] cause larger anomalous temperature coefficients in the order of $+10^{-2}$ K^{-1}, and no displacement of the electric field gradient tensors is observed in these cases. The same order of the anomalous temperature coefficients $\bar{\alpha}$ results for the samples $(C_6H_5)_4EIO_4$ (E = P, As, Sb) [1]. For $(C_2H_5)_4SbIO_4$ the calculated $\bar{\alpha}$-value is much smaller.

b) Breakdown of $d_\pi - p_\pi$-backbonding

If intra-ionic π-backbonding effects would be responsible for the positive temperature coefficient $\bar{\alpha}$ all measured metaperiodates should show this phenomenon.

c) Effect of the Radii

Further the ratio of the anionic and cationic radii or the elementary cell volume can be eliminated, because comprehensive studies of sheelite-structured metaperiodates [9−11] prove that these parameters are not responsible for $\bar{\alpha} > 0$ in these compounds.

From these considerations two possible mechanisms remain for $\bar{\alpha} > 0$: the occurrence [12] of a sufficiently large negative pressure coefficient $(\partial \nu / \partial p)_T$ in the Kushida-Benedek-Bloembergen (KBB) theory [13] or a continuous orientational change of the principle axes system of the electric field gradient tensor $\tilde{q}_{ik}$ [14−18].

The first possibility could be supported by pressure dependence experiments which still fail. But at the present state of knowledge we expect a positive or only very small negative pressure coefficient $(\partial \nu / \partial p)_T$ for $(C_2H_5)_4SbIO_4$, because the homologous compounds $(C_2H_5)_4EIO_4$ (E = P, As) possess positive or small negative pressure coefficients $(\partial \nu / \partial p)_T$ in the sense of the KBB theory [13] following from the measured normal temperature dependence of the ^{127}I quadrupole interaction [2], where obviously the isochor Bayer term $(\partial \nu / \partial T)_V$ in the KBB theory is dominating [13]. This presumption is based upon the fact that even in the presence of very anomalous α-values the pressure measurements of NH_4ReO_4 [19] and NH_4IO_4 [20] clearly pointed out positive values of the pressure coefficient $(\partial \nu / \partial p)_T$.

In conclusion, this discussion emphasizes that the remaining mechanism of a change of the electric field gradient tensor axes which explains $\bar{\alpha} > 0$ in the compounds Re_2CO_{10} [14–16] and $(CH_3)_3GeOReO_3$ [17, 18] is also dominant in $(C_2H_5)_4SbIO_4$. In Re_2CO_{10} and $(CH_3)_3GeOReO_3$ the temperature coefficients of the ^{185}Re and ^{187}Re NQR frequencies ν_1 ($\pm 1/2 \leftrightarrow \pm 3/2$) and ν_2 ($\pm 3/2 \leftrightarrow \pm 5/2$) differ in their temperature dependence. Consequently the asymmetry parameter η changes with temperature and brings about the anomalous temperature behaviour of the quadrupole coupling constants. In the case of $(C_2H_5)_4SbIO_4$ we also observe a temperature dependent change of the asymmetry parameter η (see Fig. 4) and a positive temperature coefficient $\bar{\alpha}$ of the ^{127}I quadrupole interaction. Therefore the anomalous temperature coefficient $\bar{\alpha} > 0$ is caused by reversible and probably continuous phase transitions connected with a continuous change of the axes of the electric field gradient tensor.

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[1] P. K. Burkert and D. G. Klobasa, Z. Naturforsch. **40a**, 274 (1985).
[2] D. G. Klobasa, P. K. Burkert, and G. Müller, Z. Naturforsch. **41a**, 330 (1986).
[3] B. J. Pullmann and B. O. West, Aust. J. Chem. **17**, 30 (1964).
[4] D. G. Klobasa, Thesis, Technical University Munich 1986.
[5] G. H. Stauss, J. Chem. Phys. **40**, 1988 (1964).
[6] J. F. Baugher, P. C. Taylor, T. Oja, and P. J. Bray, J. Chem. Phys. **50**, 4914 (1969).
[7] P. K. Burkert and M. F. Eckel, Z. Naturforsch. **28b**, 5 (1973).
[8] P. K. Burkert and M. F. Eckel, Z. Naturforsch. **28b**, 379 (1973).
[9] P. K. Burkert and F. M. Hutter, Z. Naturforsch. **32b**, 15 (1977).
[10] P. K. Burkert, Z. Naturforsch. **35b**, 1349 (1980).
[11] P. K. Burkert, J. Mol. Struct. **83**, 307 (1982).
[12] R. G. Barnes and R. D. Enghardt, J. Chem. Phys. **29**, 248 (1958).
[13] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).
[14] E. S. Mooberry, H. W. Spiess, and R. K. Sheline, J. Chem. Phys. **57**, 813 (1972).
[15] S. L. Segel and R. G. Barnes, Phys. Rev. **107**, 638 (1969).
[16] S. L. Segel and L. A. Anderson, J. Chem. Phys. **49**, 1407 (1968).
[17] H. Schmidbaur, D. Koth, and P. K. Burkert, Chem. Ber. **107**, 2697 (1974).
[18] P. K. Burkert, D. Koth, and H. Schmidbaur, Z. Naturforsch. **31b**, 149 (1976).
[19] R. J. C. Brown, J. Magn. Res. **18**, 558 (1975).
[20] S. L. Segel, R. J. C. Brown, and R. D. Heyding, J. Chem. Phys. **69**, 3435 (1978).