Quadrupole Splitting of Vanadium-51 N.M.R. Signals in Nematic Phases

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The ^{51}V n.m.r. spectra of vanadyl esters dissolved in nematic liquids show a seven line system which is due to a first order quadrupole interaction. Quadrupole splittings vary from 3.6 to 19.3 kHz.

Vanadyl esters and halides (neat or in solution) have recently been subject to n.m.r. investigations concerning the correlations between ^{51}V n.m.r. parameters (line width and chemical shift) and electronic features or solvent-solute interaction, respectively [1, 2]. In these systems, isotropic molecular motion restricts quadrupole interaction to quadrupole broadening of the n.m.r. signals. In anisotropic mesophases, however, splitting of the resonance signals, originating from interactions between the electric nuclear quadrupole moment tensor and local electrical fields described by the field gradient tensor will occur, which, if sufficiently small in contrast to the Zeeman splitting, can be expressed by a first order term [3]

$$\Delta\nu = \frac{3e^2qQS}{4hI(2I-1)}(3\cos^2\Theta - 1)\,.$$

S is an ordering factor describing the degree of anisotropy, and $\Delta\nu$ denotes the quadrupole splitting. For the vanadium nucleus (nuclear spin $I = 7/2\,\hbar$), seven equidistant signals are to be expected, with the central line corresponding to the $m = -1/2 \rightarrow m = +1/2$ transition and a chemical shift equal to that in isotropic media. This is verified in Figs. 1 and 2, showing the ^{51}V n.m.r. spectrum of vanadyltriisopropylate dissolved in a liquid crystal. The main anisotropy axis corresponds to a quadrupole splitting of 12.0 kHz. A weak, superimposed septett ($\Delta\nu = 3.6$ kHz) may be due to a secondary anisotropy axis, thus indicating a directional dependence of the ordering factor.

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Table 1. Quadrupole splittings of ^{51}V n.m.r. signals of vanadyl esters in nematic liquid crystals.

Ester	Phase[a]	Concentration w/w [%]	Temperature [K]	Splitting[b] [kHz]
$VO(OPr^i)_3$	NP 4	2.9	293	19.3
$VO(OPr^i)_3$	NP 4	5.8	293	14.9
$VO(OPr^i)_3$	NP 4	8.8	293	11.5
$VO(OPr^i)_3$	NP 4	11.6	293	10.2
$VOCl(OPr^i)_2$	NP 4	6.7	293	4.3
$VO(OPr^i)_3$	MBBA	8.3	293	12.0
$VO(OPr^n)_3$	MBBA	8.3	293	13.8
$VO(OBu^i)_3$	MBBA	8.3	293	14.1
$VO(OPr^i)_3$	NP 4	7.6	300	10.8
$VO(OPr^i)_3$	NP 4	7.6	295	12.8
$VO(OPr^i)_3$	NP 4	7.6	290	14.1
$VO(OPr^i)_3$	NP 4	7.6	285	16.5
$VO(OPr^i)_3$	NP 4	7.6	280	17.0

[a] NP 4 = Nematische Phase 4, Merck; MBBA 3 N-(p-Methoxibenzylidene)-p-n-butylanilin, Riedel-de Haen.

[b] Quadrupole splitting for the main anisotropy axis.

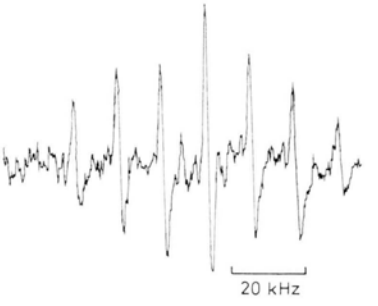

Fig. 1. 11.2 MHz n.m.r. spectrum of $VO(OPr^i)_3$, dissolved in the liquid crystal MBBA. External magnetic field = 0.995 T.

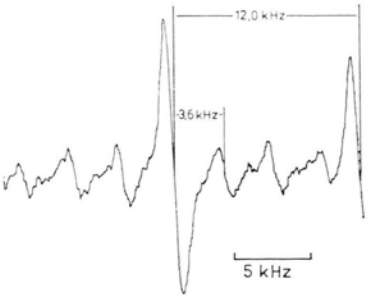

Fig. 2. Enlarged section of Fig. 1, showing a secondary anisotropic component.

The extent of quadrupole interaction (i.e. the extent of anisotropy) in nematic phases varies with the type of liquid crystal and vanadyl ester employed. Further, there is an apparent dependence upon concentration and temperature. Selected data are compiled in Table 1.

[1] D. Rehder, Z. Naturforsch. **32**b, 771 (1977).
[2] K. Paulsen, D. Rehder, and D. Thoennes, Z. Naturforsch. **33a**, 834 (1978).
[3] B. Lindman and S. Forsén in: P. Diehl, E. Fluck, and R. Kossfeld (Ed.), NMR — Basic Principles and Progress, Vol. 12, Springer-Verlag, Berlin 1976.