

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Nuclear electric hexadecapole coupling in the caesium cation

A. S. Tracey^a; K. Radley^a

^a Department of Chemistry, Simon Fraser University, Burnaby, Canada

To cite this Article Tracey, A. S. and Radley, K.(1989) 'Nuclear electric hexadecapole coupling in the caesium cation', *Liquid Crystals*, 6: 3, 319 – 323

To link to this Article: DOI: 10.1080/02678298908029082

URL: <http://dx.doi.org/10.1080/02678298908029082>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Nuclear electric hexadecapole coupling in the caesium cation

by A. S. TRACEY† and K. RADLEY‡

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia,
Canada V5A 1S6

(Received 10 February 1989; accepted 2 May 1989)

Caesium N.M.R. spectra of the caesium ion have been measured in a nematic lyotropic liquid-crystalline solution prepared from caesium decylsulphate/decanol/water. The contributions of an asymmetry parameter, a second order quadrupole coupling and a hexadecapole coupling to the spectra have been discussed. The N.M.R. spectra was shown to be consistent with the occurrence of a hexadecapole interaction in the quadrupole split spectrum. The ratio $\Delta\tilde{\nu}_Q : \Delta\tilde{\nu}_M = 1:0.000034$ was obtained.

1. Introduction

Nuclei with spin, I , greater than $1/2$ generally give rise to quadrupole splitting in the nuclear magnetic resonance spectrum if that nucleus is contained in an anisotropic environment such as that provided in many solids or in anisotropic liquids. Should the nuclear spin be 2 or greater, the occurrence of a hexadecapole coupling is possible. Compared to the quadrupole splitting, simple theoretical estimates indicate that the hexadecapole interaction should be reduced by a factor of about 10^7 from the quadrupole splitting [1, 2]. Experimental evidence indicates that the reduction factor is about 10^4 , at least for antimony [3], although other work has indicated the absence of an observable hexadecapole coupling for a variety of nuclei.

The quadrupole coupling shifts the unperturbed Zeeman energy levels in a way which can be calculated from the quadrupolar hamiltonian [2]

$$\mathcal{H}_Q = \frac{e^2 q Q (3I_z - I(I+1) + \eta(I_x^2 - I_y^2))}{4I(2I-1)h} \quad (1)$$

where $e^2 q Q/h$ is the quadrupole coupling constant; Q the nuclear electric quadrupole moment; eq , the principal component of the electric field gradient tensor and η is the asymmetry parameter which for systems with axial symmetry is zero. The hexadecapole coupling introduces an additional shift in the energy levels which can be evaluated from the spin hamiltonion

$$\mathcal{H} = \frac{e^2 M m (35I_z^4 - 30I_z^2 I(I+1) + 25I_z^2 - 6I(I+1) + 3I^2(I+1)^2)}{384I(I-1)(2I-1)(2I-3)h}. \quad (2)$$

In this equation axial symmetry is assumed; $e^2 M m/h$ is the hexadecapole coupling constant and M is the nuclear electric hexadecapole moment. The quadrupole and

† This paper was presented in part at the Waterloo N.M.R. Summer Institute, 4-7 June 1987.

‡ Present address: 12 New Street, Skelmanthorpe, Huddersfield, W. Yorkshire, England. HD8 9BL.

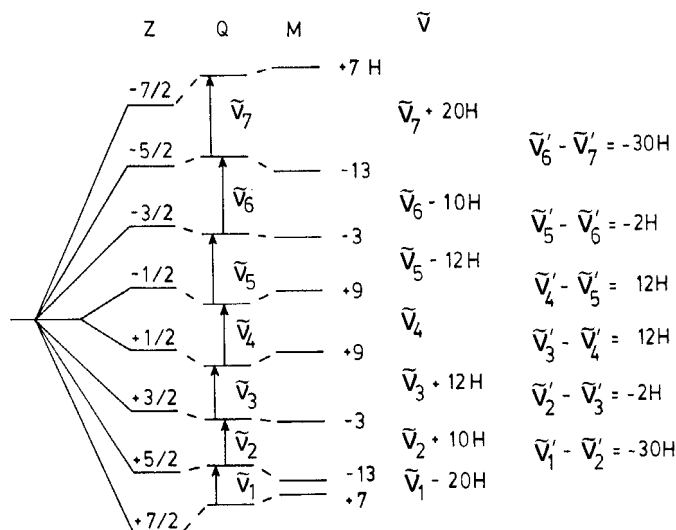


Figure 1. The effects of the quadrupole and hexadecapole interactions on the energy levels and transition frequencies of a spin 7/2 nucleus in the high field limit denotes the Zeeman splitting; Q quadrupole interaction; M , hexadecapole interaction; $H = e^2 Mm/1344h$.

hexadecapole couplings shift the energy levels of the nucleus as shown in figure 1 for a spin 7/2 system, the system of interest here. The intensity ratios for a N.M.R. quadrupole split seven line spectrum for a nucleus of spin $I = 7/2$ are 7:12:15:16:15:12:7. In figure 1, Z , Q and M represent the Zeeman interaction here is very large compared to the quadrupole interaction and H is given in units of $e^2 Mm/1344h$. The hamiltonians in the equations (1) and (2) are written in the principal axis system for the two interactions which are set in the molecule and not in the laboratory. In consequence the field is taken to be along the molecular Z axis.

It is well known that the use of liquid-crystalline phases provides a convenient method for observing quadrupole splittings [5]. The $^{133}\text{Cs}^+$ N.M.R. quadrupole splittings were first observed in an aqueous liquid crystal system many years ago [6]. The magnitude of such splittings are often considerably reduced from those expected of a solid because of motional averaging. However, the spectral lines tend to be sharp, and so the accuracy of measurement is often greatly improved over that obtained from solids. Even such nominally spherical entities as the alkali metal and halides ions provide quadrupole splittings in aqueous lyotropic liquid crystalline systems. These splittings are results from distortions caused by specific interactions between the ions and the micellar aggregates of the lyotropic medium [7, 8]. For such simple ions, the quadrupole coupling constant cannot be obtained because the extent of motional averaging and the distortions are unknown; however the quadrupole splitting can be measured. This provides the possibility of measuring the relative values of the partially averaged quadrupole and hexadecapole splittings.

2. Experimental

Figure 2 shows the caesium N.M.R. spectrum obtained at 52 MHz from a caesium decylsulphate liquid-crystalline material of composition caesium decylsulphate, 500 mg, decanol 60 mg, water (D_2O) 720 mg. This is a well-known lyotropic mesophase [9]. The linewidths obtained were about 2 Hz and 1 Hz line broadening was applied;

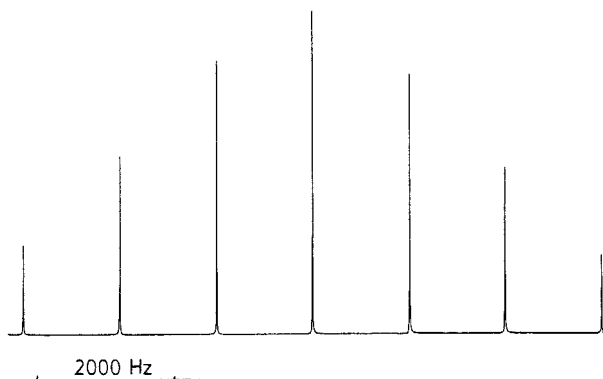


Figure 2. ^{133}Cs N.M.R. spectrum of the caesium cation in a caesium decylsulphate/decanol/water lyotropic nematic mesophase.

the digital resolution was 0.16 Hz for a 10 kHz sweep width. The computer listing for the transition frequencies relative to a zero reference of the central transition is given in the table. The asymmetries in the line positions were observed during a routine investigation of the caesium N.M.R. spectrum in an amphiphilic nematic liquid crystal. These asymmetries in the line positions could be due to the contributions of an asymmetry parameter, a second order quadrupole coupling, or a hexadecapole coupling to the spectral positions. The magnetic interactions are motionally averaged and so they must reflect the symmetry of the phase and not some local environment. The nematic phase is uniaxial about the director and so the asymmetry parameter must vanish. The nematic phase has a negative diamagnetic anisotropy which means that a second order quadrupole coupling is not possible.

3. Results and discussion

When the results of this study were analysed with the assumption that the shift in the line positions result from a hexadecapole interaction, as outlined in figure 1, the inconsistency of this analysis did not occur. This can be seen in the table which provides various derived quantities of interest which can be solved for the two unknown parameters, $\Delta\tilde{\nu}_Q$, the quadrupole splitting and $\Delta\tilde{\nu}_H$, the hexadecapole contribution. The values obtained are $\Delta\tilde{\nu}_Q = 1397.99 \pm 0.0036$ Hz and $\Delta\tilde{\nu}_H = 0.0050 \pm 0.0036$ Hz. A second determination provided a value of $\Delta\tilde{\nu}_H$ of 0.0046 ± 0.0033 Hz which gives an average value from the two measurements of $\Delta\tilde{\nu}_H = 0.0048 \pm 0.0027$ Hz. The energy levels shown in figure 1 correspond to the situation when the magnetic field is along the symmetry axis of the magnetic interaction i.e. the Z axis, that is the director. The connection between the parameters in equations (1) and (2) and those relevant for the liquid system have been previously discussed [10]. For brevity and to avoid confusion equations (1) and (2) had been appropriately modified. Other factors including micelle shape, diamagnetic anisotropy and ion binding are not considered in the discussion.

From the values obtained from $\Delta\tilde{\nu}_H$ and $\Delta\tilde{\nu}_Q$ the ratio $\Delta\tilde{\nu}_H/\Delta\tilde{\nu}_Q$ of 1:0.0000034 is found. The ratio $\Delta\tilde{\nu}_H/\Delta\tilde{\nu}_Q$ is difficult to compare with other measurements because $\Delta\tilde{\nu}_Q$ is proportional to second rank order parameters while $\Delta\tilde{\nu}_H$ is proportional to fourth rank order Legendre parameters. The results of this study indicate that distortion of the nominally spherical caesium cation through ion/amphiphile

Table 1. The contributions of the quadrupole and hexadecapole interactions to the frequencies of the spin transitions for the caesium cation.

Transition	Experimental frequencies		Differences in transition frequencies		
	Frequency/Hz	Transitions	Difference	Contribution to hexadecapole interaction	
$\tilde{\nu}'_1$	-4193.88				
$\tilde{\nu}'_2$	-2796.03	$(\tilde{\nu}_1 - 20\Delta\tilde{\nu}_H) - (\tilde{\nu}_2 + 10\Delta\tilde{\nu}_H)$	-1397.85 - $30\Delta\tilde{\nu}_H$	-1397.85 + $\Delta\tilde{\nu}_Q = 30\Delta\tilde{\nu}_H$	$\Delta\tilde{\nu}_H = + 0.0064$
$\tilde{\nu}'_3$	-1398.00	$(\tilde{\nu}_2 + 10\Delta\tilde{\nu}_H) - (\tilde{\nu}_3 + 12\Delta\tilde{\nu}_H)$	-1398.03 - $2\Delta\tilde{\nu}_H$	-1398.03 + $\Delta\tilde{\nu}_Q = 2\Delta\tilde{\nu}_H$	$\Delta\tilde{\nu}_H = - 0.0024$
$\tilde{\nu}'_4$	0.00	$(\tilde{\nu}_3 + 12\Delta\tilde{\nu}_H) - \tilde{\nu}_4$	-1398.00 + $12\Delta\tilde{\nu}_H$	-1398.00 + $\Delta\tilde{\nu}_Q = - 12\Delta\tilde{\nu}_H$	
$\tilde{\nu}'_5$	1398.07	$\tilde{\nu}_4 - (\tilde{\nu}_5 - 12\Delta\tilde{\nu}_H)$	-1398.07 + $12\Delta\tilde{\nu}_H$	-1398.07 + $\Delta\tilde{\nu}_H = - 12\Delta\tilde{\nu}_H$	
$\tilde{\nu}'_6$	2796.04	$(\tilde{\nu}_5 - 12\Delta\tilde{\nu}_H) - (\tilde{\nu}_6 - 10\Delta\tilde{\nu}_H)$	-1397.97 - $2\Delta\tilde{\nu}_H$	-1397.97 + $\Delta\tilde{\nu}_Q = 2\Delta\tilde{\nu}_H$	$\Delta\tilde{\nu}_H = + 0.0071$
$\tilde{\nu}'_7$	4193.84	$(\tilde{\nu}_6 - 10\Delta\tilde{\nu}_H) - (\tilde{\nu}_7 + 20\Delta\tilde{\nu}_H)$	-1397.80 - $30\Delta\tilde{\nu}_H$	-1397.80 + $\Delta\tilde{\nu}_Q = 30\Delta\tilde{\nu}_H$	$\Delta\tilde{\nu}_H = + 0.0061$
Average of two spectra					
$\Delta\tilde{\nu}_N = 0.0048 \pm 0.0027$ Hz				$\Delta\tilde{\nu}_Q = 1397.99 \pm 0.04$ Hz	

interactions in addition to the quadrupole splitting, gives rise to hexadecapole contributions to the transition frequencies of the seven line spectrum. The contribution is small and, in these experiments, is considerably less than the linewidth. Since the linewidth is dominated by quadrupolar relaxation, attempts to obtain a more reliable measure of this contribution will probably rely on mesophases which provide larger quadrupole splittings but do not significantly contribute to the line broadening. Quadrupolar relaxation effects on the N.M.R. lineshapes have been discussed many years ago [11, 12]. The effect of the quadrupolar moment of ^{133}Cs on the N.M.R. linewidths are apparently small.

4. Conclusion

A preliminary report of the measurement of the hexadecapole coupling in an amphiphilic nematic liquid crystal for caesium N.M.R. has been presented. It has already been noted that the effects are very small and only the order of magnitude could be determined. If the parameter is to give useful information about liquid crystals the accuracy of the measurements will have to be improved by either updating the electronics of the WP400 MHz Bucker spectrometer or by the use of a spectrometer with a larger magnetic field i.e. 500 MHz or 600 MHz.

Thanks are gratefully extended to the Natural Science and Engineering Council of Canada for its financial support of this work through operating grants to AST. Thanks also to Mrs Lynn Cook for word processing the manuscript.

References

- [1] SEGAL, S. L., 1979, *J. chem. Phys.*, **69**, 2423.
- [2] WANG, T. C., 1955, *Phys. Rev.*, **99**, 566.
- [3] GOTOU, H., 1983, *J. magn. Reson.*, **54**, 36.
- [4] MAHLER, R. J., 1966, *Phys. Rev.*, **152**, 325.
- [5] RADLEY, K., REEVES, L. W., and TRACEY, A. S., 1976, *J. phys. Chem.*, **80**, 174.
- [6] LINDHOLM, G., 1977, *Acta chem. scand.*, **25**, 2767.
- [7] BAILEY, D., BUCKINGHAM, A. D., FUJIWARA, F., and REEVES, L. W., 1975, *J. magn. Reson.*, **18**, 344.
- [8] WENNERSTROM, N., LINDMAN, B., LINDBLOM, G., and TIDY, G. J. T., 1979, *J. Chem. Soc. Faraday Trans. I*, **75**, 663.
- [9] RADLEY, K., and REEVES, L. W., 1975, *Can. J. chem.*, **53**, 2998.
- [10] FALLE, H. R., and LUCKHURST, G. R., 1979, *J. magn. Reson.*, **3** 161.
- [11] WATANABLE, H., TOTANI, T., and OHTSURU, M., 1968, *Molec. Phys.*, **14**, 367.
- [12] SUZUKI, M., and KUBO, R., 1963, *Molec. Phys.*, **7**, 201.