Electric Field Nuclear Magnetic Resonance (Application to Nuclear Quadrupole Coupling) *

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The technique of electric field NMR is outlined in terms of theoretical approach and of experimental method. As an illustration, new and recent values for quadrupole coupling constants measured in the liquid state are reported. They are compiled together with observations from the solid and the gas. A discussion concerning the differences between the phases is briefly given. Experimental results of quadrupole coupling constants for all of the three phases are still scarce.

Introduction

Nuclear magnetic resonance of partially oriented liquids and liquid solutions offers a method to study anisotropic molecular properties. The orientation in liquid systems can be achieved in several ways. Well-known is the use of liquid crystal solvents, which acquire their orientation by interaction of their anisotropic magnetic susceptibility with the magnetic field of the NMR spectrometer; dissolved probe molecules are partially oriented by intermolecular interactions with the ordered solvent. Diamagnetic anisotropic molecules in isotropic solvents are oriented in the field of high-field spectrometers. In this case, the anisotropic spin interactions can be related to the principal components of the magnetic susceptibility tensor. The degree of orientation in normal liquids is ~ 100,000 times less than in liquid crystal solvents. A third orientation mechanism is found in the interaction of a strong electric field with the effective molecular dipole moment. This technique, called electric field NMR (EFNMR), has been used to study nuclear quadrupole interactions in the liquid state. The investigations deal with ^{14}N, ^{2}H, ^{17}O and ^{33}S quadrupole couplings. Since the orientation of the electric dipole moment in the molecule is usually known, EFNMR often allows the assignment of the principal components of the quadrupole coupling tensor (qct) to a specific molecular axis. It shares this advantage with (single crystal) NQR and NMR spectroscopy and microwave techniques. A recent review dealing with electric (and magnetic) field alignment effects in normal liquid state NMR has been published [1].

The present availability of high field multinuclear NMR spectrometers gives access to EFNMR of low sensitive, less common nuclei, e.g. ^{17}O [2] and ^{33}S [3]. In this account we will deal with general aspects of EFNMR, and the technique will be illustrated by recent and some new results.

General Experimental Aspects of EFNMR

To be able to apply a strong electric field to the sample in the NMR spectrometer, the normal glass sample tube is replaced by a specially constructed EFNMR sample cell. This cell is in fact a parallel plate capacitor mounted in a well insulating housing. With the liquid in between, one of the plates is earthed, the other (at 2 – 5 mm) is set at a high voltage (20,000 – 50,000 volts). The sample will not be a perfect insulator and a small electric current will arise. This current should be kept as low as possible to prevent heating, electrical breakthrough and inhomogeneity of the electric field. Carefull purification (deionization, drying) and electrodialytic membranes (in situ) are helpful tools to minimize electric conduction. Samples are restricted to aprotic, non-ionic compounds. The inherent construction of the cell and the fact that it cannot rotate both lead to a limited magnetic field homogeneity

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compared to the situation reached with normal, spinning sample tubes (the typical ^2H line-width in the latter case is ~ 0.2 Hz, compared to 4–5 Hz in EFNMR). Line-width problems can be reduced by appropriate digital resolution enhancement techniques or by observation of zero quantum NMR transitions [4].

Theory

For quadrupolar nuclei the part of interest of the spin Hamiltonian is the term H_Q, describing the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) at the nucleus. This term, treated as a first order perturbation to the Zeeman energy in the presence of a strong magnetic field, may be written [5]

$$H_Q = \frac{3}{2}\,\frac{eQ}{6I(2I-1)}\,V_{z'z'}\,[3I_{z'}^2 - I^2]\,.$$

eQ is the nuclear quadrupole moment, I the nuclear spin quantum number, $I_{z'}$ and $V_{z'z'}$ are the components of the spin and the EFG along the magnetic field direction (z'). If the alignment is dominated by the interaction of a strong electric field E (also along z') with the effective molecular dipole moment (along the molecular z axis), $V_{z'z'}$ can be expressed in V_{zz}:

$$V_{z'z'} = \langle \tfrac{3}{2}\cos^2\theta_{zz'} - \tfrac{1}{2}\rangle_E\, V_{zz}\,,$$

where $\langle\ldots\rangle_E$ is the motionally averaged molecular alignment induced by E. The splitting $\Delta\nu$ (in Hz) between two adjacent lines of the multiplet of $2I$ lines arising upon alignment is

$$\Delta\nu = \frac{3}{2I(2I-1)}\,\frac{eQV_{zz}}{h}\,\langle \tfrac{3}{2}\cos^2\theta_{zz'} - \tfrac{1}{2}\rangle_E\,.$$

To obtain a value for eQV_{zz}/h from the spectrum, the last term on the rhs should be known. Fortunately, it can often be calculated from the deuteron line-splitting in the deuterated analogue of the molecule under investigation, and knowledge of eQV_{zz}/h for this nucleus:

$$\frac{eQ}{h}V_{zz} = \frac{eQ}{h}\big[(\tfrac{3}{2}\cos^2\alpha_{zz''} - \tfrac{1}{2}) - \tfrac{1}{2}\eta\sin^2\alpha_{zz''}\cos 2\beta_{z^*y''}\big]\,V_{z''z''}\,,$$

where $(eQ/h)\,V_{z''z''}$ is the major principal component of the (deuteron) qct (normally called the qcc), $\alpha_{zz''}$ is the angle between the dipole moment and the major principal axis of the qct, $\beta_{z^*y''}$ is the angle between the projection (z^*) of z on the $x''\,y''$ plane and the y'' axis, and η is the asymmetry parameter of the qct. As a good approximation, the z'' axis can be associated with the C–D bond and η can be taken zero. The error thus introduced will be not more than 5 percent. The ^2H qcc is often known, and $\alpha_{zz''}$ can be calculated from the molecular structure, known from other sources.

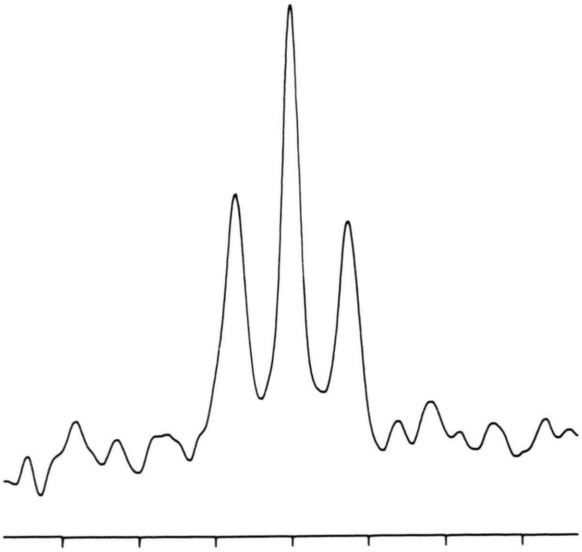

Fig. 1. ^{33}S EFNMR spectrum of sulfolane, partially oriented by an electric field of 8.3×10^6 V m^{-1}, showing a triplet, as expected for an $I = 3/2$ nucleus. The scale is 100 Hz div^{-1}.

To give an impression of the EFNMR spectra, the ^{33}S spectrum of sulfolane, observed with an applied orienting electric field, is represented in Figure 1. Though not a very sensitive nucleus, NMR of ^{33}S in natural abundance can be observed without much difficulty with modern high field Fourier transform spectrometers.

Recent Results, Discussion

Some recent and preliminary results on nuclear quadrupole couplings, observed in liquids with EFNMR, are tabulated in Table 1. As far as available, observations from NQR and microwave spectroscopy are also represented. The table contains

Table 1. Quadrupole coupling constants from EFNMR (liquid phase); comparison with results in the solid state (from NQR spectroscopy) and in the gas phase (from microwave spectroscopy).

Compound	Nucleus	Solid state [MHz]	Gas phase [MHz]	Liquid phase [MHz]	Reference
Nitromethane	^{14}N	1.6946*	– 1.18*	1.75 ± 0.05	[2, 6, 7]
Nitromethane	^{17}O	8.2[a]	–	9.1 ± 0.4	[2]
Nitrobenzene	^{14}N	1.4249*	–	1.52 ± 0.06	[1, 6]
Pyridine	^{14}N	4.5845*	– 4.88 ± 0.04	5.1 ± 0.3	[9, 10, 11]
Acetonitrile	^{14}N	3.738*	– 4.2244 ± 0.0015	4.2 ± 0.2[b]	[12, 13]
Sulfolane	^{33}S	–	–	1.34 ± 0.03	[3]
Acrylonitrile	^{14}N	–	– 4.21 ± 0.04	4.49 ± 0.25	[4, 14]
Benzene	^{2}H	0.193 ± 0.0013	0.223 ± 0.012[e] 0.240 ± 0.020[c,e]	0.186 ± 0.006[d]	[15, 16]
Fluorobenzene	^{2}H	–	0.253 ± 0.021[c,e]	0.186 ± 0.006[d]	

[a] Component of the ^{17}O qct along the molecular moment; solid state value calculated from NQR data on nitrobenzene [8], assuming the ONO angle to be the same for the two compounds (125°). – [b] Unpublished result.

[c] From NMR of magnetic field aligned gaseous sample [17].

[d] Quoted best average value [18]; no EFNMR observation.

[e] Note that the vapour phase value is substantially higher than the condensed phase value.

* No explicit indication concerning the error in the original literature; next digit probably uncertain.

additional information to a recent compilation [19]. Well-documented examples of compounds with their quadrupole coupling investigated in the three states of aggregation are becoming more abundant, but are still scarce. In liquids, data concerning other nuclei than ^{2}H and ^{14}N are increasing in number.

As a general rule, solid state values are lower than gasphase values [20]. Interestingly, for ^{14}N in nitromethane the solid (and liquid) state value is much higher than that in the gasphase. Though not listed in the table, a similar behaviour is said to be found for molecular nitrogen (N_2) [21 a] (2.52 MHz in the gas vs. 4.65 MHz in the solid); it should be noted, however, that the gas phase value refers to an excited electronic metastable state [21 b], and it can therefore not be compared to the ground state NQR value, as is done in [21 a].

As can be seen in the table, the EFNMR results suffer, in some cases, from a limited accuracy. Low sensitivity and/or broad lines (compared to the splittings to be observed) are responsible. Taking into account the quoted errors, the EFNMR results are closer to the gasphase values than to those in the solid state (except for ^{14}N in nitromethane).

In the solid state, lattice effects have been studied extensively (see [22a] for a review). Unique in the crystal are the different crystallographic sites and the lattice vibrations, which may lead to differences with respect to the gaseous state. Calculations by Bersohn [22b] of the effect of intermolecular electric fields in the lattice indicate that a decrease as well as an increase relative to the gasphase is possible.

In liquids, a different apporach is required. Since reaction field theory [23] has been very successful in describing dielectric phenomena in liquids, it is tempting to consider its implications for quadrupole coupling. The reaction field (R) at the site of the dipole (which generates this field) is, within the limitations of the model, always parallel to the dipole. Several aspects of R can be envisaged. First, R may polarize the bond of which the nucleus under investigation makes part. This effect will generally increase the ionic character of the bond and decrease the quadrupole coupling. Secondly, R may polarize the core electrons, thus affecting the electric field gradient at the nucleus. Thirdly, R is inhomogeneous if the dipole is non-ideal, an assumption better describing reality than an ideal dipole. It is clear that the gradient adds to the intramolecular gradient. Finally, even an ideal dipole, located eccentrically in the (spherical or ellipsoidal) cavity, generates an inhomogeneous reaction field, which can, as in the preceeding case, augment or decrease the quadrupolar coupling. These effects are absent in the gas phase: at sufficiently low pressure, R is zero.

In the above discussion we have refrained from taking into consideration the anomalous values of the quadrupole coupling constants of ^{2}H and ^{14}N of molecules dissolved in liquid crystals. To mention two examples: the ^{2}H qcc of nitromethane-d$_3$ in EBBA is 111.7 kHz [24] and the ^{14}N qcc of methylisocyanide in ZLI 1167 is 178 kHz [25]. The "regular" values are 165 kHz and 489 kHz, respectively [2, 25]. It remains to be investigated, whether these anomalies can be explained by the reaction field model.

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