Nuclear Quadrupole Resonance: The Present State and Further Development*

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The importance of nuclear electric quadrupole interactions in chemistry, both present and future, depends very much on their power to resolve problems in electronic structure and molecular dynamics. Fortunately, the subject, by its very nature, is "multinuclear"; even if the ground state of a given nucleus is non-quadrupolar, there often exist excited nuclear states which are, an example being ^{19}F, for which quadrupole coupling constants are now being published from angular correlation measurements. Other new techniques are constantly extending the range of the experiments, recent examples being the use of SQUID magnetometers to detect acoustic ^{121}Sb and ^{123}Sb quadrupole resonance in antimony metal and Fourier transform quadrupole resonance spectroscopy based on fast field cycling to measure ^{2}H quadrupole interactions in powders. Recently, much work on quadrupole interactions in solids of half-integral spin nuclei such as ^{17}O or ^{27}Al has been pursued in two different ways; by quadrupole double resonance in natural abundance, and nuclear magnetic resonance in very high magnetic fields, for which enrichment of low-abundance nuclei such as ^{17}O is often required. In the liquid phase, measurements are now sufficiently reliable for comparisons of changes in the nuclear electric quadrupole tensor from gas to liquid and solid phases to be made. The new methods of partial alignment of polar molecules in the liquid phase in strong electric fields, or magnetically anisotropic molecules in high magnetic fields, seem certain to contribute to these developments.

The present state and the future of any branch of radiofrequency spectroscopy depends very much on where one stands. For the experimental chemist, whose viewpoint is very much dominated by the study of molecular structure and dynamics, the significance of quadrupole interactions depends on their ability to give him reasonably unequivocal answers to his problems and the prospect of new techniques which increase the range of his understanding. In one respect nuclear quadrupole resonance has always had one advantage, being truly "multinuclear". This is certain to become an increasing characteristic of much future work. The past two years have seen new studies of such nuclei as ^{6}Li, ^{83}Kr, ^{93}Nb, ^{139}La, ^{167}Er, ^{181}Ta and ^{209}Bi, some by conventional quadrupole [1] or magnetic resonance methods [2], and others by new techniques. Among the latter the most remarkable development within the past decade has been that of perturbed angular correlation measurements [3]. These fulfill the criterion of extending our understanding of nature, since they have, at last, brought the fluorine nucleus into the ambit of quadrupole resonance spectroscopy.

The principle is to excite a nucleus with a spin-1/2 ground state to an excited nuclear state in which it possesses an electric quadrupole moment. Since these states last for only a short time, typically 10^{-7} s, conventional methods of measuring quadrupole interactions do not apply; the interaction of the nuclear moments with external fields is therefore detected by an analysis of the spatial anisotropy of the radiation which is emitted when the excited nucleus returns to its ground state. For ^{19}F, for example, the nuclear energy level scheme (Fig. 1) shows two excited states, one of which has a lifetime of 128 ns and a nuclear spin 5/2, and is therefore quadrupolar (Q is about 0.07 barn).

In time-differential perturbed angular distribution experiments (TDPAD), the excited nuclear states are produced by bombardment of the sample at 15 K with a pulsed beam of accelerated particles, e.g. 0.5 MeV protons for ^{19}F; the γ-rays of the decaying level are counted by two detectors at 90° and 180° to the proton beam axis, and the coincidence rates

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$N(180°, t)$ and $N(90°, t)$ reduced according to the equation

$$R(t) = 2\left\{\frac{N(180°, t) - N(90°, t)}{N(180°, t) + 2N(90°, t)}\right\}. \quad (1)$$

In the presence of a nuclear coupling, e.g. to an external electric field gradient, there occurs a perturbation of the angular dependence; this causes a modulation of the exponential decay curve, so that $R(t)$ shows oscillatory behaviour with time (Fig. 2), which may be represented as the sum of a number of Legendre polynomials whose coefficients depend on the quadrupole coupling constant (e^2qQ/h) and asymmetry parameter (η) of the excited nuclear state [3]. In CF_4, for example [4], the best fit to Fig. 2 (the continuous line) gives $e^2qQ/h = 59.7_3$ MHz, $\eta = 0$, compared with a value of 127.2 MHz in solid fluorine. The carbon tetrahalide series is thus complete, as Table 1 shows.

The way is open to compare ^{19}F quadrupole coupling constants with values for the other halogens in related series of molecules. In a recent paper on compounds of the type $BF_3 \cdot NH_x(CH_3)_{3-x}$ ($x = 1, 2, 3$) [5] ^{19}F TDPAD results were combined with ^{14}N quadrupole double resonance measurements and ^{11}B quadrupole-split magnetic resonance measurements to provide a remarkably complete picture of the electron distribution in these three molecules.

Another instrument which seems certain to find increasing application in magnetic resonance spectroscopy is the SQUID magnetometer (Superconducting Quantum Interference Device). The instrument is based on a Josephson junction at 4.2 K and has an extraordinarily high sensitivity to changes in magnetic susceptibility or magnetic flux which has

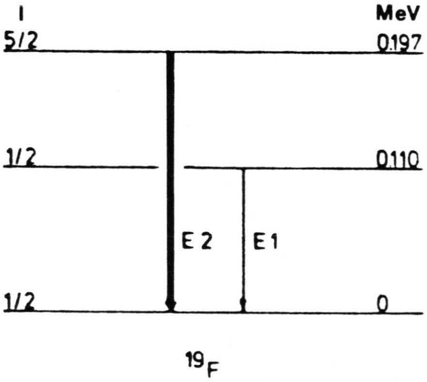


Fig. 1. Nuclear energy-level diagram for ^{19}F; the γ-decay marked "E2" has a lifetime of 129 ns.

Table 1. Halogen quadrupole coupling constants (MHz) in the diatomic halogen molecules and carbon tetrahalides.

Nucleus		e^2qQ/h (MHz)	T/K		e^2qQ/h (MHz)	T/K
^{19}F	CF_4	59.73	15.5	F_2	127.2	15.5
^{35}Cl	CCl_4	81 [a]	20	Cl_2	108.5 [b]	77
^{79}Br	CBr_4	640 [a]	77	Br_2	765.0 [b]	77
^{127}I	CI_4	2130.33	77	I_2	2157.2	77

[a] Average value. – [b] Assuming $\eta = 0$.

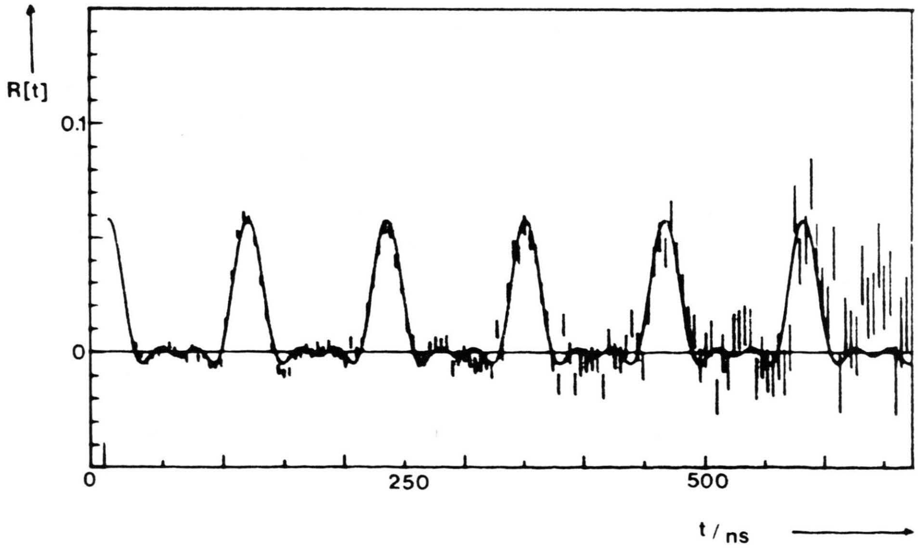


Fig. 2. Reduced counting-rate $R(t)$ for ^{19}F γ-ray emission in solid CF_4 at 15.5 K as a function of the decay time.

recently been used to detect acoustic nuclear quadrupole resonance and spin-lattice relaxation of ^{121,123}Sb in antimony metal [6]. The experiment required a $1.32 \times 1.87 \times 0.738$ cm^3 single crystal of antimony, and was conducted in magnetic fields (H) between 0.5 and 146.7 mT and at a temperature of 4.2 K; the ^{121,123}Sb spin populations are changed by the acoustic energy transmitted to the sample by a transducer connected to an r.f. source and the resulting changes (both positive and negative) in M_z (the z-component of the magnetisation) cause changes in the flux threading the pick-up coil connected to the SQUID (Figure 3). Such changes can be detected at frequencies as high as 100 MHz and with a noise figure of about $\frac{1}{4}$ dB. For zero asymmetry parameter, the energies of the Sb levels are given by the well-known first-order expression for $m_I > 1/2$

$$E_m = \gamma \hbar\, H\, m_I \cos\theta + \frac{e^2 qQ}{4I(2I-1)}\,[3m_I^2 - I(I+1)], \tag{2}$$

where θ is the angle between H and q_{zz}, the maximum principal component of the electric field gradient. For $m_I = \pm 1/2$, the states are mixed by the magnetic field to give two new states $|\pm 1/2\rangle'$: transitions from these to the states $|\pm 3/2\rangle$ are then observed as four transitions near 7 MHz (Fig. 3) with opposite signs for the lower pair relative to the upper pair. The transitions are generated by transverse waves, which can thus excite both $\Delta m_I = \pm 1$ and $\Delta m_I = \pm 2$ processes whose intensities depend on the magnitude of the dynamic quadrupole coupling between the nuclear electric quadrupole moment and the transverse and longitudinal acoustic waves, information of considerable relevance to solid state studies. The resonant intensities decay, once acoustic power is removed, with a time constant equal to the spin-lattice relaxation time, T_1, typically 0.94 ± 0.50 s for ^{121}Sb in a magnetic field of 50 mT.

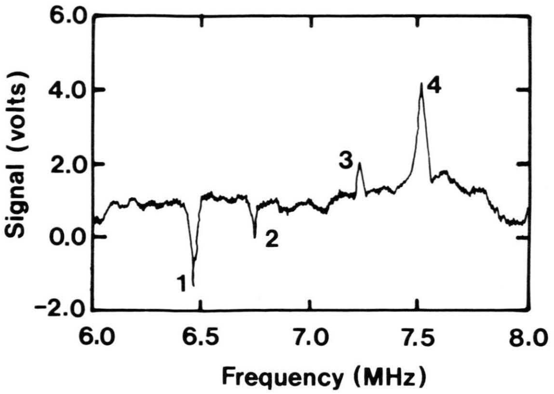
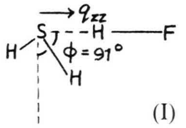


Fig. 3. ± 1/2 → ± 3/2 Zeeman quartet ($H = 50.4$ mT) for ^{123}Sb acoustic nuclear quadrupole resonance in a single crystal of antimony metal at 4.2 K, as detected by a SQUID magnetometer.

More conventional methods still have an important role to play, and the high sensitivity of most super-regenerative or pulsed spectrometers in the HF and UHF ranges ensures them a firm future. The applications of such instruments can still throw light on unusual structural problems. A recent example is the study by ^{35}Cl pulsed quadrupole resonance of graphite layer compounds of $SnCl_4$ and Cl_2 [7]. In a sample of composition $C_{54}SnCl_6$, "free" $SnCl_4$ and Cl_2 ^{35}Cl signals are observed near 24 and 54 MHz respectively, together with a new line at 15.635 MHz ($T = 77$ K), comparable in frequency with $SnCl_6^{2-}$ signals at 15.63 MHz in Rb_2SnCl_6 and 15.73 MHz in K_2SnCl_6, and with a short (but unquoted) spin-lattice relaxation time. The compound is thus formulated as $[C_{54}]^{2+}SnCl_6^{2-}$, with the carbon layer acting as a collective cation.

The use of higher fields from superconducting magnetic systems has meant that more quadrupole nuclei can now be studied by nuclear magnetic resonance techniques and quadrupolar splitting resolved in polycrystalline samples. In ^{27}Al ($I = 5/2$), for example, whose quadrupole coupling constants in many zeolites range from 1 to 3 MHz, the central (− 1/2 → + 1/2) transition and ± 1/2 → ± 3/2 sidebands can both be resolved in sufficiently strong magnetic fields, and correlated in two-dimensional Fourier transform experiments [8]. Under selective excitation conditions, in which only the central component is observed, the powder patterns depend on the on-resonant pulse width [9], a dependence which can also be exploited to derive values for the ^{27}Al quadrupole coupling constants in zeolites. With several over-lapping lines, however, these methods lose much of their power.

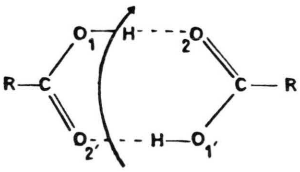
A nucleus which has been unjustly neglected in both traditional and new experiments is ^{33}S. The first pure quadrupole resonance signals in rhombic sulphur were observed over thirty years ago in a remarkable paper by Dehmelt [10]; since then, little further work has been published, and no double resonance detection has been reported, except a possible sighting in solid $KHSO_4$, which is alleged [11] to show a doublet ^{33}S frequency near 2.33 MHz at 291 K. But more and more ^{33}S magnetic resonance studies are being reported [12] from investigations with modern high-field spectrometers and there is now an urgent need for information on a wider range of ^{33}S quadrupole coupling constants. Microwave investigations mean that we now have a better idea of where to look; thus in gaseous $H_2{}^{33}S$ [13], $e^2qQ/h = 40$ MHz and $\eta = 0.6$ with q_{zz} perpendicular to the molecular plane and $q_{xx} = -8$ MHz along the C_2 axis, whereas in the $H_2{}^{33}S \ldots HF$ hydrogen-bonded complex (I), it drops to 32.785 MHz [14], due largely to zero-point oscillations of mean amplitude 20° about an



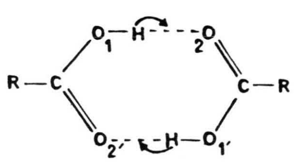
(I)

average value of φ of 91°. Thioformaldehyde has also been investigated [15], and the $C{=}^{33}S$ group found to have a ^{33}S quadrupole coupling constant of + 49.9 MHz and $\eta = 0.531$; interestingly, q_{zz}, the maximum principal component, lies along the in-plane perpendicular to the C=S bond, and q_{xx}, the minimum component (− 11.7 MHz) lies along the bond, just as for ^{17}O in formaldehyde, where the corresponding values are + 12.37 MHz and − 1.89 MHz [16].

The study of the nature and mechanism of phase transitions and order-disorder processes in solids has always provided an important motivation for studying the temperature dependence of nuclear quadrupole resonance frequencies and relaxation times; some of this material has been summarized in a recent review [17]. Nuclear quadrupole resonance studies are most helpful in two circumstances. Firstly, when they can throw further light on an established mechanism: for example, ^{127}I quadrupole resonance in $4\text{-}RC_6H_4NH_3^+I^-$ ($R = H$, CH_3, C_2H_5, F) shows clearly that the upper phase transition (II → I) in all these iodides is connected with a freezing-in of the rotation of the $-NH_3^+$ group [18]. Secondly, when they can distinguish clearly between two or more possible mechanisms, particularly where other methods fail. A recent example occurs in the study of carboxylic acid dimers by ^{17}O quadrupole resonance. It has been widely recognised for some years that the acidic hydrogen atoms in these dimers are disordered, the degree of disorder increasing with temperature; the first evidence came from infra-red spectroscopy [19] and was reinforced by X-ray and neutron diffraction studies of benzoic acid [20] and ^1H (dipolar) and ^{13}C magnetic resonance spectroscopy of single crystals of partially-deuterated p-toluic acid [21] and benzoic acid [22] respectively. The mechanism for the proton disorder is thought to be fast, concerted, two-proton jumps (III) within an asymmetric double-potential well, but it has been pointed out [23] that the effects of this motion are indistinguishable from those of a molecular rotation about the C ... C axis (II) on the basis of the nuclear magnetic resonance evidence alone (e.g. from the magnetic resonance spectrum of the carboxylic ^{13}C nucleus). The two mechanisms, however, do differ in their effect on the ^{17}O quadrupole resonance frequencies obtained from double resonance spectroscopy [24]. This is most obvious if we consider model (III); the new ^{17}O principal quadrupole tensor of the $C^{17}OH$ group (or its centrosymmetrically-related neighour in the dimer) in the disordered crystal is simply derived by averaging the "ordered" $C^{17}OH(\mathbf{D}_1)$ and $C{=}^{17}O \ldots H(\mathbf{D}_2)$ tensors in a common frame of reference



(II)



(III)

$$\mathbf{D} = (1 - \alpha)\,\mathbf{D}_1 + \alpha\,\mathbf{D}_2\,, \tag{3}$$

where α is the degree of mixing, and re-diagonalizing the new tensor $\mathbf{D}$. If the tensors $\mathbf{D}_1$ and $\mathbf{D}_2$ vary little with temperature or environment, the consequence is that as α increases, e.g. by increasing the temperature or by suitable changes in the group R, the $C^{17}OH$ and $C^{17}O \ldots H$ frequencies will be observed to move together, finally becoming identical, or nearly so, when $\alpha = 0.5$. This is not true in model (II), for which the $C^{17}OH$ and $C{=}^{17}O \ldots H$ tensors are *separately* averaged by the motion, and their frequencies do not therefore converge. Figure 4 shows a plot of e^2qQ/h and η for ^{17}O in nine

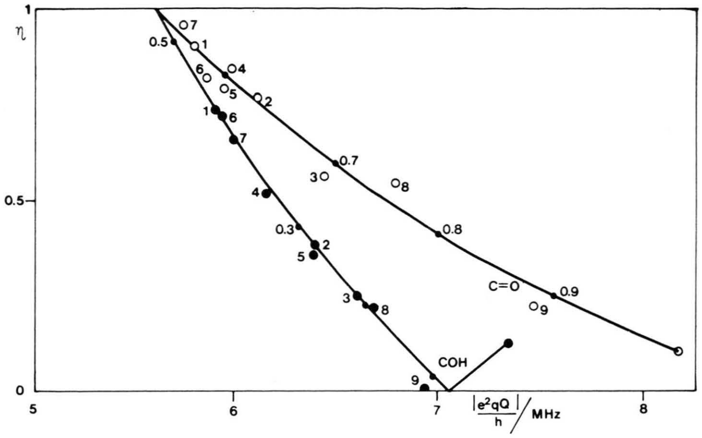


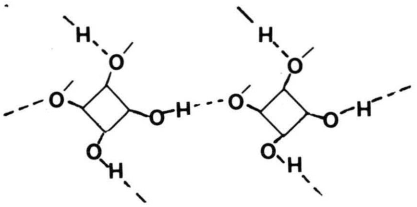
Fig. 4. A plot of the ^{17}O quadrupole coupling constant against asymmetry parameter for carboxylic acids at room temperature; open circles: $C{=}^{17}O \ldots H$, closed circles: $C^{17}OH$. The experimental data are plotted for benzoic acid (1), *p*-chlorobenzoic acid (2), *m*-chlorobenzoic acid (3), *p*-nitrobenzoic acid (4), *m*-nitrobenzoic acid (5), *p*-hydroxybenzoic acid (6), *m*-hydroxybenzoic acid (7), acetylsalicylic acid (8) and *β*-oxalic acid (9).

different carboxylic acid dimers at room temperature, using tensors $\mathbf{D}_1$ and $\mathbf{D}_2$ for the $C^{17}OH$ and $C^{17}O \ldots H$ groups inferred from previous ^{17}O measurements on ordered systems [24]; values of α are placed along the theoretically derived curve from (3) at intervals of 0.1. The result is a good fit between theory and experiment, with the $C^{17}OH$ and $C^{17}O \ldots H$ values almost coinciding for benzoic acid, points (1), which is known to be almost completely disordered at room temperature [20, 22]. It seems fairly certain, from similar evidence, that similar disorder occurs in $KHCO_3$ at room temperature; this salt also contains centrosymmetric $(HCO_3)_2^{2-}$ ions, as in (III) with R = O.

In these dimeric systems, the increasing disorder is not accompanied by any related phase transitions. In other systems involving proton jumps within a double-potential well, this is not necessarily the case. Two recent instances are squaric acid and the alkali metal dihydrogen phosphates. In the former [25], which forms (at room temperature) ordered layers of $C_4O_4H_2$ molecules, each with two distinct kinds of oxygen nuclei, "near" (O) or "far" (O′) according to the O−H distance, the two sets of frequencies move together as the phase transition at 95 °C is approached, but only finally coalesce (after a brief disappearance) above 130 °C. In another hydrogen-bonded system, that of the alkali metal dihydrogen phosphates, which also show proton jumps in a double potential well, the ^{17}O quadrupole double resonance frequencies show a neat contrast. In KH_2PO_4 [26] all protons move in a double potential well above T_C, the Curie temperature, and freeze into one of the two equilibrium sites below; in CsH_2PO_4 [27] however, there are two different kinds of hydrogen-bonded ^{17}O nuclei in the structure (A and B in Fig. 5) each with three frequencies (for $I = 5/2$)

$$\pm 1/2 \rightarrow \pm 3/2, \quad \pm 3/2 \rightarrow \pm 5/2, \quad \pm 1/2 \rightarrow \pm 5/2$$

but only one set (A) collapses as T_C (at − 60 °C) is approached, the other (B) remains ordered through the transition, to which it makes very little contribution. The set (A) frequencies follow an equation similar to that of (3) but with α replaced by p, defined as the order parameter. Once again, the nuclear quadrupole resonance measurements provide a distinction of mechanism; they are, for example, inconsistent with a displacive model, in which the proton is centered above T_C but displaced off-centre below, for then the high temperature tensor would not be the weighted mean of the two low-temperature ones.



The great advantage of ^{17}O quadrupole double resonance techniques is that the sample does not require isotopic enrichment. To measure the same couplings by nuclear magnetic resonance in very high fields does, by up to 40%: the ^{17}O magnetic resonance spectra at 67.8 MHz of some oxides (Fig. 6) show typical quadrupole structure for the

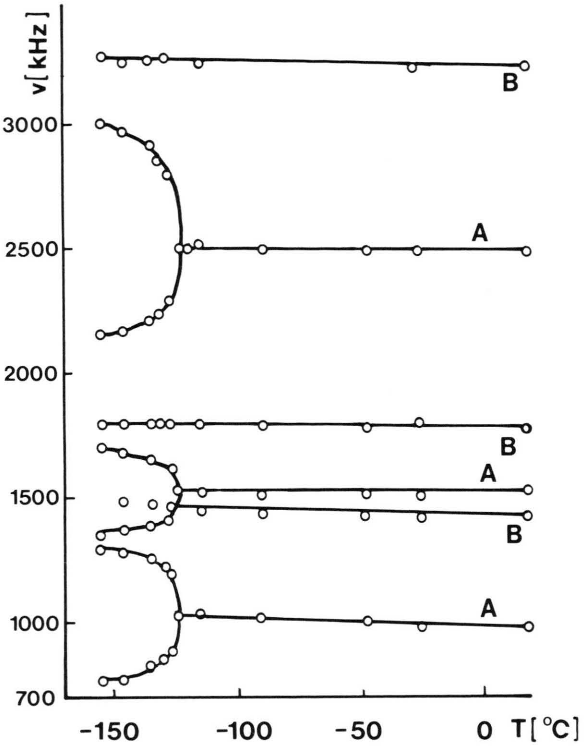


Fig. 5. The ^{17}O quadrupole double resonance frequencies in CsH_2PO_4 as a function of temperature.

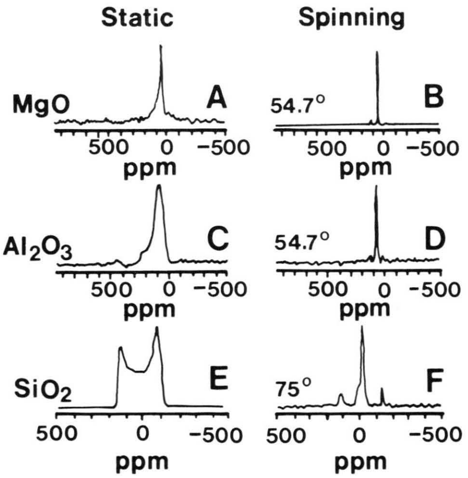


Fig. 6. ^{17}O magnetic resonance spectra ($-1/2 \rightarrow \pm 1/2$) at 67.8 MHz of three oxides; the left-hand spectra are for static samples, the right-hand spectra for spinning samples at (B, D) or close to (F) the "magic angle".

central transition and spinning sidebands when the sample is spun at, or close to, the "magic angle" [28]. Quadrupole coupling parameters can be deduced by simulated line-shape studies: in the figure, SiO_2 for example shows a typical second-order powder pattern in which the splitting (for spin 5/2) is roughly equal to

$$\Delta = \frac{1}{32\nu_L}\left(\frac{e^2qQ}{h}\right)^2,$$

where ν_L is the ^{17}O Larmor frequency, giving a quadrupole coupling constant of about 5.8 MHz. At present, the simpler double resonance techniques seem to have the edge on these elaborate and expensive pulsed magnetic resonance methods.

The principal experimental difficulty in any nuclear quadrupole resonance experiments involving irradiation of the spin system lies in transmitting the maximum amount of power to the tank circuit over a wide range of frequencies, while at the same time ensuring that the small signals thereby generated are passed on to the receiver as swiftly and with as little loss as possible. To some extent, double resonance methods alleviate this problem, since the signal is detected at one frequency (usually ^1H), which remains invariant as the experiment is conducted. The simplest quadrupole resonance spectrum however would be one in which the free evolution of the spin system was studied in zero field, without the perturbing effects of any radiation. A close approximation to this situation is obtained in recent field cycling experiments, in which Fourier transform nuclear quadrupole free precession is developed in zero field, and detected by fast field cycling to high magnetic fields [29]. The method is most suited to the determination of low quadrupole resonance frequencies, provided that the magnetic field is changed in a time shorter than the inverse of the characteristic resonance frequencies, e.g. for a few hundred kHz, in a time of 1 μs. Experimentally this is achieved [30] by switching in two steps (Fig. 7), the first by sample transfer from the large magnetic field of a superconducting magnetic ($H_0 = 4.2$ T) to the much smaller field ($H = 0.03$ T) of a solenoid, which is then switched off for a variable time t, before the cycle is reversed. Fourier transformation of the ^2H magnetization measured in high field as a function of the time t spent in zero field, then gives the pure quadrupole resonance

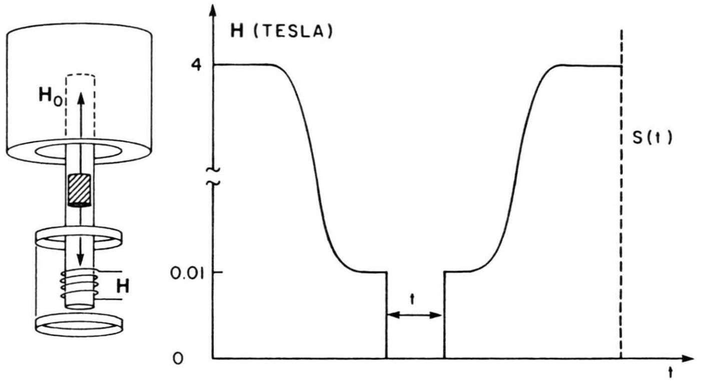


Fig. 7. Magnetic field cycle used in Fourier transform nuclear quadrupole resonance spectroscopy.

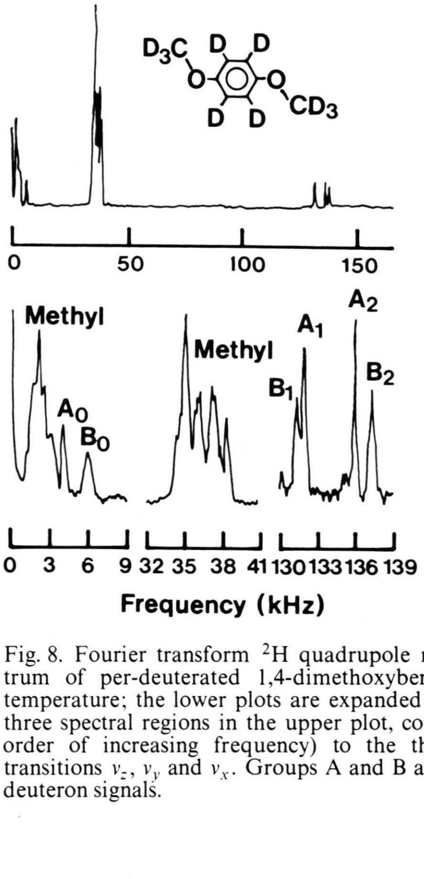


Fig. 8. Fourier transform ^2H quadrupole resonance spectrum of per-deuterated 1,4-dimethoxybenzene at room temperature; the lower plots are expanded versions of the three spectral regions in the upper plot, corresponding (in order of increasing frequency) to the three groups of transitions ν_z, ν_y and ν_x. Groups A and B are the aromatic deuteron signals.

spectrum, limited of course in quality by the sampling rate. For ^2H, e.g., t was stepped in intervals of 3 µs up to a maximum value of 500 to 1,000 µs. The spectra are sharp, as in Fig. 8, which shows the ^2H spectrum of polycrystalline per-deuterated 1,4-dimethoxybenzene; all three transitions for this spin-1 nucleus are observed, e.g. note the two sets of aromatic ^2H frequencies labelled A_2, A_1, A_0 ($e^2qQ/h = 178.5$ kHz, $\eta = 0.045$) and B_2, B_1, B_0 ($e^2qQ/h = 179.1$ kHz, $\eta = 0.067$). The disadvantage for ^2H is that a high degree of enrichment is required, since it is the ^2H magnetisation in high field which is sampled, but this is not a drawback for other more abundant nuclei, such as ^7Li and ^{27}Al, where the method has considerable power for quadrupole coupling constants in the range of 10–200 kHz [30, 31].

So far, this survey has been concerned with quadrupole tensors obtained entirely in the solid or gaseous phases. However, in the past twenty years, an increasing number of values has been forthcoming from experiments on liquids. It seems certain that this trend will continue into the future. Measurements of partially-oriented molecules dissolved in mesophases provide some of the most interesting examples and have been the subject of a recent review [32]. In ordinary liquids, however, all quadrupole splittings are expected to vanish, and one must then have recourse to line width and relaxation time measurements. A typical procedure is illustrated by a recent analysis [33] of hexamethylenetetramine and its deuterated analogue in solutions in CCl_4 and $CDCl_3$; the ^1H and ^{13}C spin-lattice relaxation times are used to derive consistent values of the correlation time, τ_c, the nuclear Overhauser enhancement for ^{13}C being used to check that its relaxation is exclusively dipolar. The ^2H and ^{14}N line-widths (at half-height, $\Delta\nu_{1/2}$) are then measured and related to the correlation time by the equation (for $I = 1$)

$$\frac{1}{T_2} = \pi \Delta\nu_{1/2} = \frac{3\pi^2}{2}\left(\frac{e^2 qQ}{h}\right)^2 (1 + \eta^2/3)\,\tau_c . \tag{4}$$

Knowing τ_c, and assuming η to be zero, gives a "solution" value for e^2qQ/h. In this example, the ^{2}H quadrupole coupling constant comes to 168 kHz in CCl_4 and 170 kHz in $CHCl_3$, which is close to that measured in the solid phase (162 kHz). The situation at nitrogen is less clear-cut; the ^{14}N quadrupole coupling constants come to 4.17 MHz and 4.31 MHz respectively in the same pair of solvents, both substantially less than the solid state value of 4.408 MHz at room temperature, and more comparable with values of 4.0 to 4.3 MHz found at hydrogen-bonded nitrogen sites in complexes of hexamethylenetetramine. It is then not immediately obvious why the lower value should be found in CCl_4, a solvent incapable of hydrogen bonding. Another example where the differences between solid and solution are even larger is the case of the ^{27}Al quadrupole coupling in $Al(acac)_3$. In the solid state at room temperature, the experimental situation is clear; the small departure from full octahedral symmetry at the ^{27}Al site (point symmetry D_3) gives rise in nuclear quadrupole double resonance experiments to three frequencies at values of 460, 890, 1350 kHz [34] with line shapes typical of thermal mixing spectra (the unexpected strength of the latter seems to be a typical feature of double resonance experiments on half-integral spin nuclei). The ^{27}Al quadrupole coupling constant is thus 2.98_3 MHz and the asymmetry parameter 0.16. In high magnetic fields, with an ^{27}Al magnetic resonance frequency of 23.5 MHz, a typical second-order splitting of the $+1/2 \rightarrow -1/2$ transition is observed [35] (compare the ^{17}O magnetic resonance spectrum of SiO_2 in Fig. 6) from which a quadrupole coupling constant of 2.85 MHz is deduced assuming an asymmetry parameter of zero. The problems once again arise in solution; if the ^{27}Al spin-lattice (T_1) and spin-spin (T_2) relaxation times are dominated by the modulation of the non-zero quadrupole interaction caused by fast isotropic reorientation, then (4) still applies. η is taken to be zero, which introduces little error; τ_c is estimated from the ^{13}C spin-lattice relaxation time, assumed (from the nuclear Overhauser effect) to be dominated by the $^{13}C-{}^1H$ dipole-dipole interaction. In toluene solution, at six different temperatures between 25 and 72 °C, and with $1/T_2$ derived from the ^{27}Al magnetic resonance line width at 23.5 MHz, a constant value of 0.49 MHz is derived. It is concluded that the "higher quadrupole coupling constant in the solid state may originate from a higher degree of deviation from octahedral symmetry, resulting from crystal packing, or from electric field gradients caused by neighbouring molecules", but the latter could not reasonably account for a factor of five difference. We seem therefore to have a genuine case of a difference in structure or motion, or both, between solution and solid state.

In recent years, a new technique has been added to the chemist's armoury, in which quadrupole splittings are observed in polar liquids (or solutions thereof) partially aligned in a strong electric field [36], or of strongly magnetically anisotropic molecules (e.g. $C_6H_5NO_2$) in very high magnetic fields [37]. The principle of the electric field experiments is to have nuclei such as ^{2}H and ^{14}N both present in the molecule of interest, e.g. pyridine or pyrimidine: a 20% solution in diethylether is placed between gold electrodes, 3 mm apart, and inserted into the probe of a wide-bore superconducting spectrometer; in this case, the magnetic field strength was 4.2 T, giving ^{14}N frequencies of 12.99 MHz and ^{2}H of 27.6 MHz. An electric field of between 5 to 8×10^6 V m^{-1} gives, for $I = 1$, a doublet splitting (Figure 9). In the magnetic case, a

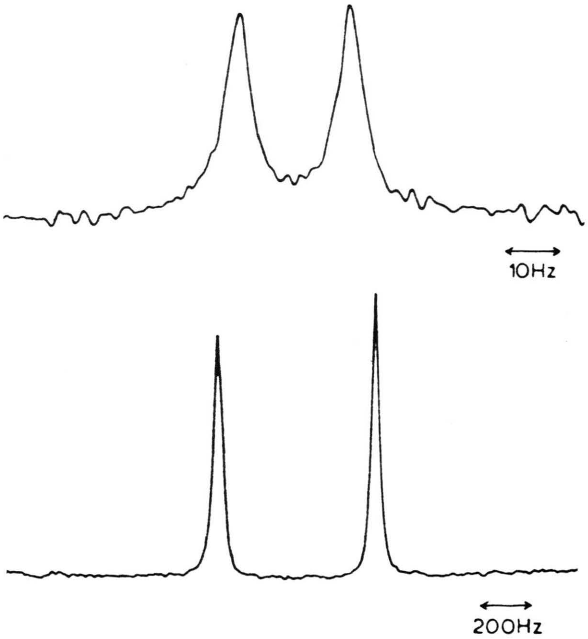


Fig. 9. ^{2}H (top) and ^{14}N (bottom) magnetic resonance spectra of neat nitromethane-d_3 in a magnetic field of 5.87 T and an electric field of 10^7 V m^{-1}.

similar structure, of splitting about 2 Hz, is observed in ^{2}H magnetic resonance spectra of neat nitrobenzene-d$_5$ at 76.8 MHz [37]. These splitting patterns follow from the high-field Hamiltonian, regarding the quadrupolar interaction as a small perturbation of the Zeeman term,

$$\hat{\mathscr{H}}_Q = \frac{3}{2}\left\{\frac{e^2 Q}{6I(2I-1)}\right\} q_{z'z'}(3\hat{I}_{z'}^2 - \hat{I}^2), \qquad (5)$$

where $q_{z'z'}$ the magnitude of the electric field gradient along the magnetic field, is related to its value q_{zz} in the direction of the molecular electric dipole moment by the equation

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

the average being over the random molecular reorientations which oppose the alignment induced by the applied electric field, E. The Hamiltonian in (5) gives rise to two frequencies, with a splitting of

$$\Delta\nu = \frac{3}{2}\left(\frac{e^2 Q}{h}\right) q_{zz}\langle \tfrac{3}{2}\cos^2\theta_{zz'} - \tfrac{1}{2}\rangle_E . \qquad (6)$$

The alignment factor in triangular brackets is calculated from the ^{2}H splitting, whose maximum principal component of the quadrupole coupling is assumed to equal 186 kHz and to lie along the C–D direction with $\eta = 0$. For pyridine, the electric dipole moment lies parallel to the C_2 axis, coincident with one of the principal axes (q_{ZZ}) of the electric field gradient; the analysis is straightforward, and gives $e^2qQ/h = \pm 5.10 \pm 0.28$ MHz, but no value for η (in the solid [38], the values are 4.58$_4$ MHz, $\eta = 0.396$, and in the gas [39], -4.88 MHz, $\eta = 0.414$). In pyrimidine, the two directions do not coincide, but the electric dipole moment may be assumed to lie in the molecular plane bisecting the $\widehat{\text{NCN}}$ angle, and the transformation angle to the in-plane components is then known if one of the ^{14}N principal components is assumed to lie along the $\widehat{\text{CNC}}$ bisector and to have the same magnitude as in pyridine (5.10 MHz). q_{zz} in (6) is then given by

$$q_{zz} = q_{ZZ}\cos^2\theta_{zZ} + q_{YY}\cos^2\theta_{yY} + q_{XX}\cos^2\theta_{xX}$$

where X, Y, Z denote the principal axes of the electric field gradient; a knowledge of the angles θ_{zZ}, θ_{yY}, θ_{xX} enables the second in-plane component to be calculated, giving values of e^2qQ/h (assumed) $= \pm 5.10 \pm 0.28$ MHz, $\eta = 0.56 \pm 0.04$ (in the solid [40], 4.43$_6$ MHz and $\eta = 0.386$). The agreement can be improved by slight adjustments in the transformation matrix, but is still insufficient to settle unequivocally any differences between solid and liquid. In fact, the tendency is to relate the liquid values to the gas phase ones, rather than those in the solid state. However, the potential of the method seems large, and must surely be capable of considerable development. Recently, ^{17}O magnetic resonance (in natural abundance) has been studied [41] in CD_3NO_2 in electric fields of 10^7 V m^{-1}; (5) predicts a quintet, as observed, with an intensity ratio of 5:8:9:8:5, but the numerical factor in (6) is now 3/20, and the separation between adjacent lines drops considerably compared to that of ^{14}N. The analysis is therefore less accurate. The ^{17}O quadrupole coupling constant, measured as 9.1 ± 0.4 MHz, is once again the component along the dipole moment axis, whereas the maximum principal component is in plane with respect to the C, N and 2O atoms, and perpendicular to the N–O bond. A transformation to the principal axes gives a value of 8.2 MHz, compared to a recent double resonance measurement in nitrobenzene [42] of 13.1 MHz ($\eta = 0.580$).

Measurements of this kind will no doubt be continued; hopefully, the reliability of the conclusions will improve. We may then have accurate measurements for the quadrupole parameters in gas, liquid (solution), and solid phases, an advance of some relevance to the study of the structure and dynamical behaviour of molecules. As we stated at the beginning, these should be among the objectives of all spectroscopic investigations.

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