N.M.R. and the Periodic Table*

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1 Introduction

This article is intended to show the wide scope for the use of n.m.r., viewed from the standpoint of the Periodic Table, particularly for inorganic chemistry. There is, perhaps, a need to balance the recent overemphasis on ^{13}C n.m.r. It is not intended that this discussion should reflect roughly the amount of work done on each nucleus. Indeed, the article might well have been entitled 'N.M.R. Studies with Less Popular Nuclei', since it will largely ignore the vast amount of research reported for the nuclei ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P. Moreover, there is no attempt to give a comprehensive set of references to the study of any particular nucleus. It is, on the other hand, hoped that at least one reference is given to each nucleus which has been the subject, during the 1970's, of a *chemical* n.m.r. study (*i.e.* excluding work on metals themselves, alloys, the solid state in general, and other studies which may be classified as physics). For keeping abreast of the appropriate literature on an annual basis the reader is referred to the Chemical Society's Specialist Periodical Reports on 'Spectroscopic Properties of Inorganic and Organometallic Compounds' and on 'Nuclear Magnetic Resonance'.

N.m.r. spectroscopy has been used in chemistry for about 25 years, but the overwhelming majority of its applications have been with a single isotope, the proton. This is because the ^{1}H nucleus is ideal for n.m.r. in at least three ways: (i) it has spin quantum number $I = \frac{1}{2}$, and therefore normally gives sharp lines in solution-state spectra, (ii) it exists in *ca.* 100% natural abundance, and (iii) it has a relatively high magnetic moment. These factors result in a more favourable signal-to-noise ratio than found for other nuclei. After ^{1}H, the two most popular nuclei have been ^{19}F and ^{31}P. These have the same three favourable characteristics, though for ^{31}P the magnetic moment is only *ca.* 40% that of ^{1}H. In fact apart from these nuclei there are only three other isotopes in the whole Periodic Table with $I = \frac{1}{2}$ in *ca.* 100% natural abundance, namely ^{89}Y, ^{103}Rh, and ^{169}Tm. For obvious chemical reasons neither yttrium nor thulium has become popular for n.m.r., and although rhodium offers greater scope it has a very low magnetic moment and it has been little used.

Consequently, in order to assess the potential of n.m.r. throughout the Periodic Table one must turn to nuclei either of $I > \frac{1}{2}$, or of natural abundance $< 100\%$. Many such nuclei have indeed been studied from the earliest days of n.m.r.,

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but in most cases only sporadically, although ^{11}B n.m.r. has been reasonably popular and has yielded significant chemical results.[1]

For many nuclei the principal problem is one of sensitivity. The signal strength is proportional to the concentration of the appropriate spins, and (at constant applied field B_0) to the *cube* of the nuclear magnetic moment, μ, concerned. Peak heights also depend greatly on relaxation times, on nuclear spin quantum numbers, and, of course, on radiofrequency powers. In fact the dependence on μ^3 is based on the assumption that the *optimum* r.f. power is used, *i.e.* that which gives the maximum signal strength, but it would be normal to use significantly lower powers to avoid saturation broadening. When comparing the suitability of various nuclei for n.m.r. it is useful to calculate the quantity $\gamma^3 NI(I + 1)$, which will be designated here the *receptivity** of the nucleus, and to refer it to the corresponding property for the proton. In this expression γ is the magnetogyric ratio and N is the % natural abundance. Obviously the receptivity should only be taken as a rough guide to signal strengths; the expression given above assumes simple relaxation behaviour with $T_1 = T_2$. Table 1 lists the relative receptivities for the most useful spin-$\frac{1}{2}$ nuclei of the Periodic Table. A total of 21 elements are represented; the lanthanides and actinides have been excluded, as have radioactive isotopes. It may be seen that apart from hydrogen and fluorine only thallium has a spin-$\frac{1}{2}$ isotope with a greater magnetic moment than ^{31}P.† Even ^{31}P is only *ca.* 6.6% as receptive as the proton, and many nuclei of potential n.m.r. interest are four or more orders of magnitude less receptive than ^{1}H. The important ^{13}C nucleus has a relative receptivity of only 1.76×10^{-4}. Clearly considerable experimental finesse is required in

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* It should be noted that the equation for this property is based on considerations of continuous-wave n.m.r. spectroscopy, not Fourier transform.

† He also has a larger magnetic moment than ^{31}P, but since it is radioactive, in extremely low natural abundance, and not useful chemically it has not been included in Table 1.

[1] (*a*) W. G. Henderson and E. F. Mooney, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 219; (*b*) G. R. Eaton and W. N. Lipscomb, 'N.M.R. Studies of Boron Hydrides and Related Compounds', Benjamin, New York, 1969.

[2] (*a*) G. C. Levy and G. L. Nelson, '^{13}C N.M.R. for Organic Chemists', Wiley-Interscience, New York 1972; (*b*) J. B. Stothers, '^{13}C N.M.R. Spectroscopy', Academic Press, New York, 1972.

[3] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135.

[4] 'Nitrogen N.M.R.', ed. M. Witanowski and G. A. Webb, Plenum Press, New York, 1973.

[5] J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 1.

[6] C. H. Dungan and J. R. Van Wazer, 'Compilation of reported ^{19}F N.M.R. Chemical Shifts, 1951 to Mid-1967', Wiley–Interscience, New York, 1970.

[7] G. C. Levy, J. D. Cargioli, P. C. Juliano, and T. D. Mitchell, *J. Amer. Chem. Soc.*, 1973, **95**, 3445.

[8] R. K. Harris and B. J. Kimber, *J. Organometallic Chem.*, 1974, **70**, 43.

[9] (*a*) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, '^{31}P N.M.R' (*Topics in Phosphorus Chem.*, Vol. 5), Interscience, 1967; (*b*) G. Mavel, *Ann. Reports N.M.R. Spectroscopy*, 1973, **5B**, 1.

[10] A. Schwenk, *J. Magn. Resonance*, 1971, **5**, 376.

[11] S. Gronowitz, I. Johnson, and A.-B. Hornfeldt, *Chem. Scripta*, 1973, 3, 94.

[12] M. A. Lardon, in 'Organic Selenium Compounds: their Chemistry and Biology', ed. D. L. Klayman, Wiley, New York, 1973, p. 933.

[13] C.-W. Burges, R. Koschmieder, W. Sahm, and A. Schwenk, *Z. Naturforsch.*, 1973, **28a**, 1753.

Table 1 *N.m.r. properties of spin-½ nuclei*[a]

Isotope	*Natural abundance* $N\%$	*Magnetic moment*[b] μ/μ_N	*Magnetogyric ratio* $\gamma/10^7$ rad T^{-1} s^{-1}	*N.m.r. frequency*[c] Ξ/MHz	*Relative receptivity*[d]	*References*
^{1}H[e]	99.98	4.8371	26.7510	100.000	1.000	—
^{13}C	1.11	1.2162	6.7263	25.144	1.76×10^{-4}	2, 3
^{15}N	0.37	−0.4901	−2.7107	10.133	3.85×10^{-6}	4
^{19}F	100	4.5506	25.1665	94.077	0.8328	5, 6
^{29}Si	4.70	−0.9609	−5.3141	19.865	3.69×10^{-4}	7, 8
^{31}P	100	1.9581	10.8290	40.481	0.0663	9
^{57}Fe	2.2	0.1563	0.8644	3.231	7.39×10^{-7}	10
^{77}Se	7.6	0.9223	5.1008	19.068	5.26×10^{-4}	11, 12
^{89}Y	100	−0.2370	−1.3106	4.899	1.18×10^{-4}	—
^{103}Rh	100	−0.1523	−0.8420	3.148	3.12×10^{-5}	—
^{107}Ag[f]	51.8	−0.1957	−1.0825	4.047	3.43×10^{-5}	13
^{113}Cd[g]	12.3	−1.0730	−5.9342	22.183	1.34×10^{-3}	14
^{119}Sn[h]	8.6	−1.8029	−9.9707	37.272	4.44×10^{-3}	15, 16
^{125}Te[i]	7.0	−1.5284	−8.4525	31.597	2.21×10^{-3}	—
^{129}Xe	26.4	−1.3380	−7.3995	27.661	5.60×10^{-3}	17
^{183}W	14.4	0.2013	1.1131	4.161	1.04×10^{-5}	18
^{187}Os	1.64	0.1114	0.6161	2.303	2.00×10^{-7}	19
^{195}Pt	33.8	1.0400	5.7512	21.499	3.36×10^{-3}	20
^{199}Hg	16.8	0.8623	4.7690	17.827	9.54×10^{-4}	21
^{205}Tl[j]	70.5	2.7914	15.4375	57.708	0.1355	22
^{207}Pb	22.6	1.0120	5.5968	20.922	2.07×10^{-3}	23

[a] A complete list excluding radioactive nuclei, lanthanides, and actinides. The data are modified from those collated by K. Lee and W. A. Anderson (1967) and published in reference 24. p. E–75. [b] Given by $\mu/\mu_N = g_N[I(I+1)]^{\frac{1}{2}} = \gamma\hbar[I(I+1)]^{\frac{1}{2}}/\mu_N$ where g_N is the nuclear g-factor. [c] Scaled such that ^{1}H resonance is at 100 MHz (strictly the symbol Ξ should reference the frequencies to that of the protons in tetramethylsilane[25]). [d] At constant magnetic field; relative to the receptivity of the proton. Receptivity is defined here as $\gamma^3NI(I+1)$. It is assumed that $T_1 = T_2$ (see also the text). [e] Also ^{3}H (radioactive), $\mu/\mu_N = 5.1594$, $\gamma = 28.5336 \times 10^7$ rad T^{-1} s^{-1}, $\Xi = 106.664$ MHz. [f] Also ^{109}Ag, $N = 48.2$. [g] Also ^{111}Cd, $N = 12.8$. [h] Also ^{117}Sn, $N = 7.6$, and ^{115}Sn, $N = 0.4$. [i] Also ^{123}Te, $N = 0.9$. [j] Also ^{203}Tl, $N = 29.5$.

order to obtain n.m.r. information about many of the nuclei in the list.

There are several methods of overcoming the signal-to-noise problem, some of which have been in use for a considerable time. Four of these are mentioned below.

(*a*) Isotopic enrichment. This has proved to be a useful technique, which has been applied, in particular, to ^{2}H, ^{15}N, and ^{17}O (these have natural abundances 0.016, 0.36, and 0.037 % respectively), but it is tedious to prepare particular compounds from the starting materials likely to be available. It is also normally expensive, and is therefore only likely to be used in special cases.

(*b*) Increase in sample volume. There are obvious limits to the feasibility of this procedure (*e.g.* the size of the magnet–pole gap), especially as electronic efficiency operates against improvement in signal-to-noise, but 20 mm n.m.r. tubes have been used with success.[26]

(*c*) Observation of coupled nuclei. Clearly, coupling-constant information concerning a low-receptivity nucleus may be obtained from the spectrum of a high-receptivity nucleus to which it is coupled. In the case of ^{13}C, its low natural abundance results in the appearance[27] of so-called '^{13}C satellites' in ^{1}H (or ^{19}F resonance). Since one is observing a nucleus of high γ, the fact that ^{13}C has a relatively low γ is no longer of relevance, but the low natural abundance is still a handicap, especially since the ^{1}H (or ^{19}F) signal from molecules without ^{13}C will be strong and may obscure some of the lines due to the ^{13}C-containing species. Of course, a similar situation exists for any other low-abundance nucleus. Figure 1 shows[28] the '^{15}N satellites' in the ^{19}F resonance of 2,6-difluoro-3,4,5-trichloropyridine. In this case, the principal species present contains the quadrupolar ^{14}N nucleus, and the main ^{19}F resonance is thus very broad, enabling the '^{15}N satellites' to be clearly distinguished.

(*d*) Heteronuclear double resonance. The information available from observation of coupled nuclei is powerfully increased if the weak nucleus is simultaneously irradiated (its resonance does not need to be detected). There are a

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[14] (*a*) R. J. Kostelnik and A. A. Bothner-By, *J. Magn. Resonance*, 1974, **14,** 141; (*b*) A. A. Cardin, P. D. Ellis, J. O. Odom, and J. W. Howard, jun., *J. Amer. Chem. Soc.*, 1975, **97,** 1672.

[15] A. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *Mol. Phys.*, 1971, **21,** 179.

[16] P. J. Smith and L. Smith, *Inorg. Chim. Acta, Rev.*, 1973, **7,** 11.

[17] K. Seppelt and H. H. Rupp, *Z. anorg. Chem.*, 1974, **409,** 331, 338.

[18] J. Banck and A. Schwenk, *Z. Phys.* (*B*), 1975, **20,** 75.

[19] W. Sahm and A. Schwenk, *Z. Naturforsch.*, 1974, **29a,** 1763.

[20] C. Brown and B. T. Heaton, 3rd International Meeting on N.M.R. Spectroscopy, St. Andrews, July, 1975.

[21] G. E. Maciel and M. Borzo, *J. Magn. Resonance*, 1973, **10,** 388.

[22] S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, 1974, **96,** 404.

[23] G. E. Maciel and J. L. Dallas, *J. Amer. Chem. Soc.*, 1973, **95,** 3039.

[24] 'Handbook of Chemistry and Physics', ed. R. C. West, Chemical Rubber Co., Cleveland, 55th Edn., 1974.

[25] W. McFarlane, in 'Determination of Organic Structures by Physical Methods,' ed. F. C. Nachod and J. J. Zuckerman, Academic Press, New York, 1971, Chap. 3.

[26] A. Allerhand, R. F. Childers, and E. Oldfield, *J. Magn. Resonance*, 1973, **11,** 272.

[27] J. H. Goldstein, V. S. Watts, and L. S. Rattet, *Progr. N.M.R. Spectroscopy*, 1971, **8,** 103.

[28] A. V. Cunliffe and R. K. Harris, *Mol. Phys.*, 1968, **15,** 413.

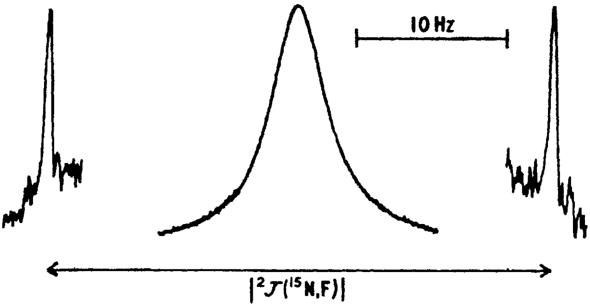

Figure 1 *The* 94.1 MHz ^{19}F *spectrum of* 2,6-*difluoro*-3,4,5-*trichloropyridine, showing the weak, sharp* '^{15}N *satellites' (at increased amplitude) on either side of the intense broad resonance due to molecules containing* ^{14}N

number of ways of achieving this and the reader is referred to relevant reviews[25,29] for the details, but the following points need to be emphasized:

(i) The only equipment needed is a frequency synthesizer, plus modifications to double-tune the probe.

(ii) The equipment will suffice to obtain information about *all* types of nucleus (within the range of the double-tuning), *provided* they are coupled to the observed nucleus.

(iii) The INDOR method[25,29] will enable the complete spectrum of the weak nucleus to be recorded indirectly *via* the strong nucleus.

(iv) Therefore the chemical shifts and all coupling constants [not just those to the strong nucleus, as is the case for (*c*) above] of the weak nucleus may be obtained.

(v) The 'tickling' experiment[25,29] allows the determination of the relative signs of coupling constants.

(vi) The sensitivity of the *strong* nucleus is used. This is emphasized by the example of Me_2PPMe_2–^{13}C as illustrated diagrammatically in Figure 2. It is feasible to obtain the position of the very weak ^{31}P band marked I indirectly by observing the proton band marked II under ^1H–$\{^{31}P\}$ heteronuclear double-resonance conditions.[30] It does not prove feasible to observe band I directly even under conditions of proton noise-decoupling (band I is only 0.1% of the total ^{31}P spectrum, and of course the molecule containing ^{13}C is in only *ca.* 4% natural abundance).

The power of the heteronuclear double-resonance method has been amply illustrated by McFarlane,[29] who has used it to observe indirectly ^{13}C, ^{15}N, ^{29}Si, ^{31}P, ^{77}Se, ^{103}Rh, ^{119}Sn, ^{125}Te, ^{183}W, ^{195}Pt, and ^{199}Hg.

The heteronuclear double-resonance method was the best technique for

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[29] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 135.
[30] E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **13**, 65.

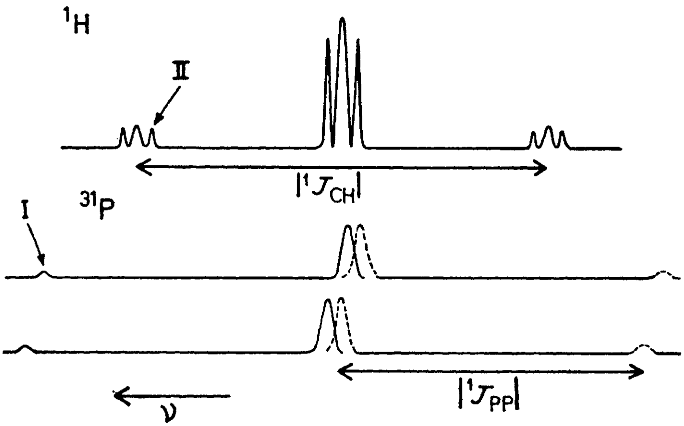

Figure 2 *Diagrammatic* ^{1}H *and* ^{31}P *spectra of tetramethyldiphosphine-*^{13}C. *The intensities and frequency separations are not to scale. All* (^{13}C, H) *and* (^{31}P, H) *coupling constants except for* $^1J_{CH}$ *have been ignored in the* ^{31}P *spectrum for the sake of clarity. The two subspectra of the* ^{31}P *spectrum are drawn separately; dashed lines are used for half of each subspectrum. The bands marked* I *and* II *are discussed in the text*

obtaining information about less-receptive nuclei in the period 1965—70. Recent advances in instrumental techniques, however, have caused a resurgence of *direct* n.m.r. studies for a wide range of nuclei, and there is little doubt that this area will continue to expand rapidly in the next few years. There will be considerable repercussions in inorganic and organometallic chemistry. This is therefore an appropriate time to survey the Periodic Table to see the full potential of n.m.r. The new techniques already have had widespread effect in organic chemistry[2] and biochemistry,[31] through their application to ^{13}C n.m.r. This is not the place to discuss in any detail the recent instrumental advances, but they may be summarized as follows:

(i) the concept of multiscan averaging, whereby noise levels are reduced;

(ii) heteronuclear double resonance, whereby spectra may be greatly simplified by the removal of splittings due to spin–spin coupling—^{1}H noise decoupling is particularly useful;

(iii) the advent of Fourier transform (FT) spectroscopy,[32] which uses pulses of radiofrequency to obtain information about all parts of a spectral region simultaneously, thus saving time [which may be traded for sensitivity according to (i) above].

It may be noted that the prerequisite for advances (i) and (iii) has been the advent of small computers that may be interfaced to n.m.r. spectrometers.

The net effect of the new techniques is to increase the signal-to-noise ratio, and it is now feasible to study directly all the nuclei listed in Table 1. Even the

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[31] G. A. Gray, *Critical Rev. Biochem.*, 1973, **1**, 247.

[32] T. C. Farrar and E. D. Becker, 'Pulse and Fourier Transform N.M.R.; Introduction to Theory and Methods', Academic Press, New York, 1971.

two least receptive spin-½ nuclei, ^{57}Fe and ^{187}Os, have recently been observed directly.[10,19] Heteronuclear double resonance is now best regarded as the poor man's FT, since it is a relatively cheap method, but in nearly every instance direct observation of a nuclear resonance is preferable.

Figure 3 shows the Periodic Table with elements marked according to their n.m.r. properties. Spin-½ nuclei normally give sharper lines than spin > ½ nuclei because of the quadrupolar properties of the latter, so that resolution and signal-to-noise are better for spin-½ cases (other factors being equal). The type of information obtained from n.m.r. studies of any nucleus is analogous to that given by ^1H n.m.r., *i.e.* (i) chemical shifts, (ii) coupling constants, (iii) relaxation times, (iv) exchange lifetimes, and (v) intensities. It is clear that spin-½ nuclei are normally best for obtaining (i) and (ii) accurately (especially for small splittings). On the other hand, the spin–spin relaxation time T_2 may often be obtained very conveniently from linewidths for quadrupolar nuclei, and in such cases the dominant relaxation mechanism is known to be quadrupolar. The spin–lattice relaxation time T_1 may be measured by FT methods for spin-½ nuclei, but the process is often time-consuming, and further experiments are usually required to ascertain the dominant relaxation mechanism. Consequently, quadrupolar nuclei find their greatest use in studies of molecular motion based on relaxation information.

Two further points are worthy of note. Firstly, the nuclear-spin quantum number does not show any tendency to increase with atomic number; spin-½ nuclei, for example, may be found in all the rows of the Periodic Table in an apparently random fashion. Secondly, linewidths (*i.e.* spin–spin relaxation rates, T_2^{-1}) do not normally increase as the spin quantum number increases; indeed, there is a tendency for the reverse to be true.[33]

2 Spin-½ Nuclei

As mentioned above, 21 elements (excluding lanthanides and actinides) may be studied by n.m.r. using spin-½ nuclei. Table 1 gives some of their n.m.r. properties and a selection of references to recent studies (except for ^1H). In the cases of ^{13}C, ^{15}N, ^{19}F, and ^{31}P review articles or books are quoted. In addition there are some more general reviews[34–36] for less popular nuclei. The spin-½ nuclei may be grouped as follows:

Non-metals:	H, C, N, F, Si, P, Se, Te, Xe
Group A metals:	Sn, Tl, Pb
Transition metals:	Fe, Y, Rh, Ag, Cd, W, Os, Pt, Hg

There is little doubt that the first category will continue to provide the overwhelming majority of n.m.r. applications. Carbon-13, of course, already vies with ^1H as the most useful n.m.r. nucleus (in spite of its low natural abundance), and, as mentioned above, ^{19}F and ^{31}P are particularly favourable for n.m.r.

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[33] J. W. Akitt, *J. Magn. Resonance*, 1970, **3**, 411.

[34] R. H. Cox, *Magn. Resonance Rev.*, 1972, **1**, 271; 1974, **3**, 207.

[35] P. R. Wells, in 'Determination of Organic Structures by Physical Methods', ed. F. C. Nachod and J. J. Zuckerman, Academic Press, New York, 1971, Chap. 5.

[36] P. L. Corio, S. L. Smith, and J. R. Wasson, *Analyt. Chem.*, 1972, **44**, 407R.

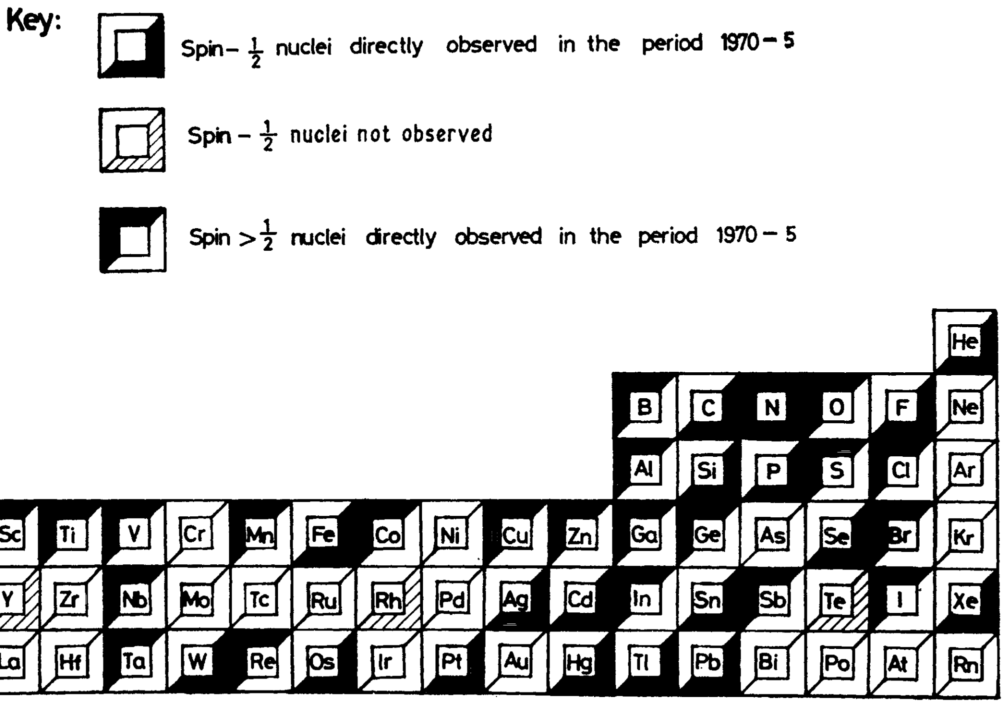


Figure 3 *The Periodic Table (excluding the lanthanides and actinides) showing n.m.r. nuclei of recent importance*

Unfortunately the potentially very useful ^{15}N nucleus is in very low natural abundance (see below). The Group A metals Sn and Pb, together with Si, are also of considerable importance, in part because they are in the same group of the Periodic Table as carbon, and also because they have relatively high magnetic moments. Since they are in Group IV, interpretation of n.m.r. parameters is somewhat simplified because of the absence of lone-pair effects for the four-co-ordinate state. Thallium has a very favourable magnetic moment and is relatively easy to study. On the other hand, although some of the spin-$\frac{1}{2}$ transition metals undoubtedly have considerable n.m.r. potential (especially Cd, Pt, and Hg), others have very low relative receptivities, and it is unlikely that they will be much used for n.m.r.—in such cases the use of indirect methods (c) and (d) (see above) may be preferred to direct observation (especially for Rh and W). The striking feature of the list of spin-$\frac{1}{2}$ nuclei is the total absence of any alkali or alkaline earth metals, and the inclusion of only one halogen (fluorine).

The spin-$\frac{1}{2}$ nuclei may be grouped in a different way for a discussion of experimental methods:

(i) Nuclei of natural abundance $\geqslant 90\%$: ^{1}H, ^{19}F, ^{31}P, ^{89}Y, ^{103}Rh

(ii) Nuclei of natural abundance $\leqslant 10\%$: ^{13}C, ^{15}N, ^{29}Si, ^{57}Fe, ^{77}Se, ^{119}Sn, ^{125}Te, ^{187}Os

(iii) Nuclei of natural abundance between 10 and 90%: ^{107}Ag, ^{113}Cd, ^{129}Xe, ^{183}W, ^{195}Pt, ^{199}Hg, ^{205}Tl, ^{207}Pb

This division is particularly relevant when considering the complexity of spectra for molecules containing several nuclei of the species observed. Low natural abundance is a disadvantage as far as signal-to-noise is concerned, but it is a great boon for spectral simplicity, since the probability of having two such nuclei in the same molecule is very small and can normally be ignored. It is thus the great advantage of ^{13}C n.m.r. that effects from (^{13}C, ^{13}C) coupling need not be considered, and each peak in the proton-decoupled spectrum arises from a different isotopomer. On the other hand, the spectra for high-abundance nuclei may be more complex and difficult to assign, but they do yield the extra coupling information. The worst situation as far as spectral complexity is concerned is probably in category (iii). However, by a stroke of good fortune, the nuclei most likely on chemical grounds to be found in several positions in a molecule, *i.e.* the non-metals (particularly ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, and ^{31}P), have natural abundances either $\geqslant 90\%$ or $\leqslant 10\%$. The possibility of coupling to other isotopes of the same element must also be considered. Again by chance, it happens that the principal non-metals do not have more than one spin-$\frac{1}{2}$ nucleus in comparable natural abundance; however, this is a potential problem with $^{107}Ag/^{109}Ag$, $^{113}Cd/^{111}Cd$, $^{119}Sn/^{117}Sn$, and $^{205}Tl/^{203}Tl$. The existence of ^{14}N ($I = 1$, natural abundance 99.6%) is not normally a problem in ^{15}N n.m.r. because splittings due to $J(^{15}N, ^{14}N)$ are collapsed by ^{14}N quadrupolar relaxation.

The experimental techniques for nuclei in category (i) are as for ^{1}H and are well known, and will not be discussed here except to note that the noise decoupling, multiscan averaging, and FT methods all lead to an appreciable improvement in the ease of obtaining good spectra for these nuclei as well as for those in low natural abundance. The advantages in terms of signal-to-noise and/or time of FT spectroscopy are well displayed[37] for ^{31}P in Figure 4, which shows

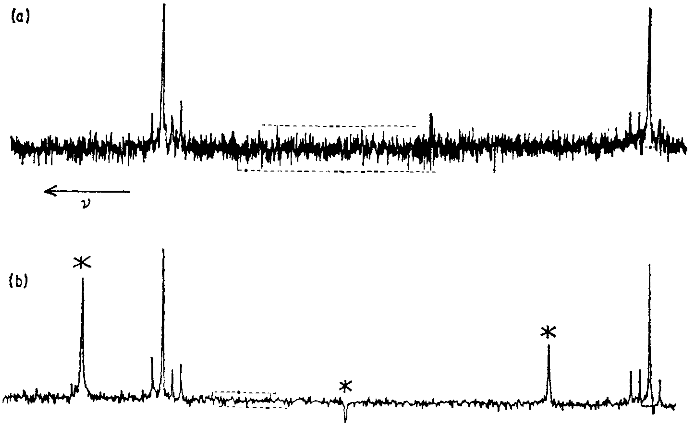
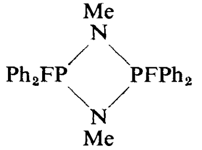


Figure 4 *The* ^{31}P *n.m.r. spectrum of the tetraphenyldifluorodiazadiphosphetidine* (1) *under conditions of proton noise decoupling.* (a) *Continuous wave spectrum* (36 *scans, sweep time* 1000 s, *total time* ≈ 10 h, *S/N** ≈ 7.5); (b) *Fourier transform spectrum* (777 *pulses, acquisition time* 4 s, *total time* ≈ 52 min, *S/N** ≈ 26). *The peaks marked by asterisks are due to impurities, arising from decomposition during the time interval* (ca. *three months*) *between recordings* (a) *and* (b)



(1)

spectra of the tetraphenyldifluorodiazadiphosphetidine (1). The signal-to-noise ratio of the continuous wave (CW) spectrum is appreciably worse than that of the FT spectrum even though the former took much longer to acquire. It may be noted that since ^{31}P is a high-abundance species the (P, P) coupling constant may be obtained from the spectrum.

Experimental methods for category (ii) nuclei are as for ^{13}C and are also well documented. However, some remarks will be made here about spectra of nuclei with negative magnetic moments (*i.e.* anti-parallel to the spin angular momentum, as for the electron but in contrast to ^{1}H, ^{13}C, *etc.*). Spin-$\frac{1}{2}$ nuclei in this category are ^{15}N, ^{29}Si, ^{89}Y, ^{103}Rh, ^{107}Ag, ^{113}Cd, ^{119}Sn, ^{125}Te, and ^{129}Xe. This causes problems when spectra are run under proton noise-decoupled conditions,

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* Using the customary practical definition of S/N (see ref. 38, page 117).

[37] R. K. Harris and M. I. M. Wazeer, unpublished work.

[38] R. R. Ernst, *Adv. Magn. Resonance*, 1966, **2**, 1.

since the nuclear Overhauser effect (NOE)[39] will normally cause a *reduction* in signal intensity, instead of an enhancement as is the case for ^{13}C. The NOE for an experiment in which nucleus Z is observed while species X is irradiated may be defined as the total intensity under double-resonance conditions divided by the corresponding total intensity under single-resonance conditions. It may be shown[39] that:

$$\text{NOE} = 1 + \frac{\gamma_X}{2\gamma_Z}\,\frac{T_1{}^Z}{T_1{}^Z{}_{DD}}$$

where $T_1{}^Z$ and $T_1{}^Z{}_{DD}$ are the total spin–lattice relaxation time of the Z nucleus and the contribution to it of (X, Z) dipolar interactions, respectively. It may be seen that the NOE reduces signal intensity if $T_1{}^Z{}_{DD}$ is a significant contribution to $T_1{}^Z$ and if *either* γ_X *or* γ_Z is negative. If the (X, Z) dipolar contribution to $T_1{}^Z$ is dominant, the maximum effect is observed, and

$$\text{NOE}_{\text{max}} = 1 + \gamma_X/2\gamma_Z$$

Therefore if $|\gamma_X| > |2\gamma_Z|$ and either γ_X or γ_Z is negative, the signal itself may be negative. In the case of a ^{29}Si–$\{^1\text{H}\}$ experiment, since $|\gamma_{^1\text{H}}| \approx 5\,|\gamma_{^{29}\text{Si}}|$, $\text{NOE}_{\text{max}} = -1.5$. Such a situation is illustrated in Figure 5, which shows ^{29}Si spectra for triphenylsilane under both coupled and decoupled conditions;[40] the NOE in this case is -1.4.

Clearly the observed NOE results from competition between (X, Z) dipolar relaxation and other mechanisms. It is perfectly possible to get a near-zero

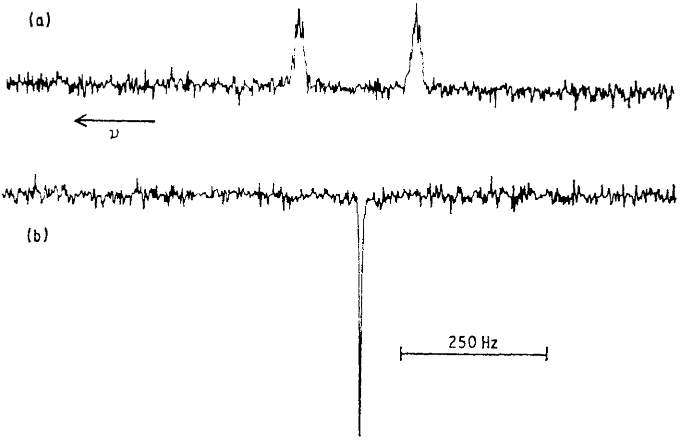

Figure 5 *The* 19.9 MHz ^{29}Si *n.m.r. spectrum of triphenylsilane.* (a) *Single-resonance (coupled) spectrum—the main splitting is due to* $^1J_{\text{SiH}}$*;* (b) *Proton noise-decoupled spectrum, showing the negative peak resulting from the nuclear Overhauser effect*

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[39] J. H. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect', Academic Press, New York, 1971.

[40] R. K. Harris and B. J. Kimber, unpublished work.

signal, as is illustrated[41] in Figure 6. One method of overcoming this difficulty is to change the balance of the relaxation mechanisms. This may be done by addition of a paramagnetic substance; even molecular oxygen may have a substantial effect, as is shown[40] in Figure 7. In certain circumstances it may be preferable to *remove* dissolved oxygen (thus increasing the magnitude of the NOE) by degassing or by bubbling nitrogen through the sample. As an alternative to oxygen a controlled addition of a paramagnetic metal salt, such as the trisacetylacetonate of chromium or of iron, may be used.[42] However, too much paramagnetic compound will cause line broadening—*ca.* 0.03 mol l^{-1} is optimum in many cases.

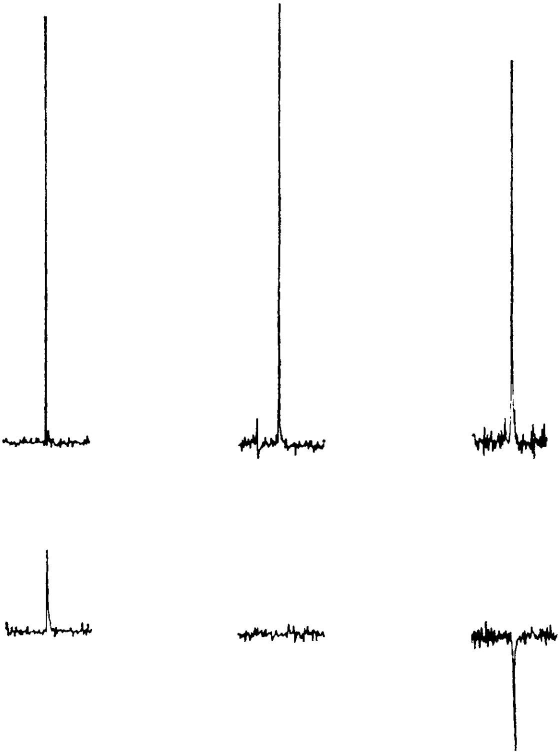

Figure 6 ^{29}Si-{^{1}H} *N.m.r. spectra of* (EtO)$_n$ SiMe$_{4-n}$. *The spectra at the left, in the middle, and at the right are due to the species with n* = 2, 3, *and* 4 *respectively. The three spectra above are without the* NOE (*obtained using the gated decoupling technique*[43]). *Those at the bottom are with the* NOE—*note the null signal for n* = 3

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[41] R. K. Harris and B. J. Kimber, *Org. Magn. Resonance*, 1975, **7**, 460.

[42] G. C. Levy, J. D. Cargioli, P. C. Juliano, and T. D. Mitchell, *J. Magn. Resonance*, 1972, **8**, 399.

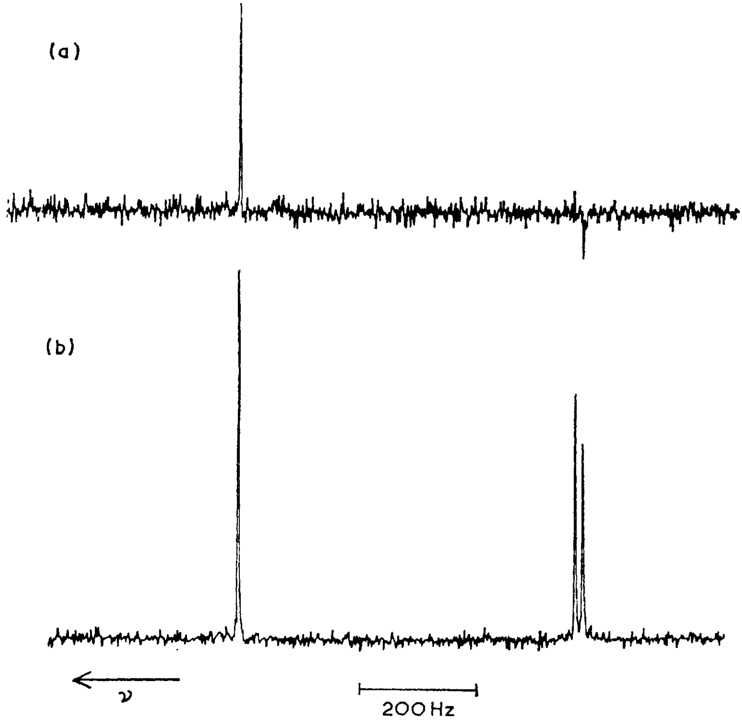

Figure 7 ^{29}Si-{^{1}H} *N.m.r. spectra of* $Me_3Si{\cdot}O{\cdot}[SiMe_2{\cdot}O]_4{\cdot}SiMe_3$. (a) *Using liquid straight from the bottle;* (b) *after bubbling* O_2 *through the liquid (partially suppressing the* NOE). *The intensity scales in* (a) *and* (b) *are not comparable*

This discussion illustrates the fact that proper use of FT spectroscopy depends on an understanding of relaxation phenomena. This is so not only because of the NOE but because the repetition rate for pulses can cause saturation (and hence weak signals) if it is appreciably greater than the relaxation rate. Unfortunately, ^{15}N and ^{29}Si relaxation times for most small molecules are rather long (usually over 20 s). Addition of a paramagnetic substance will reduce the overall values of T_1, and will allow more rapid pulsing. However, paramagnetic additives should be avoided when the highest resolution is required. An alternative is the use of the gated decoupling[43] technique, but this is rather time-consuming. Of course, if T_1 is dominated by mechanisms other than (X, Y) dipolar interactions (*e.g.* by spin–rotation interactions) the null-signal problem illustrated in Figure 6 does not arise.

Under proton-decoupled conditions, spectra for nuclei in category (ii) will not normally contain spin–spin coupling information unless such nuclei as ^{19}F or ^{31}P are present.

[43] R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Magn. Resonance*, 1972, **7**, 327.

3 Choice between $I = \frac{1}{2}$ and $I > \frac{1}{2}$ Nuclei

It is an interesting fact that in the whole Periodic Table (excluding the lanthanides and actinides) there are only five elements which present a choice to the n.m.r. spectroscopist in that both $I = \frac{1}{2}$ and $I > \frac{1}{2}$ nuclei exist in sufficient natural abundance to make them feasible for study. These elements are hydrogen, nitrogen, xenon, osmium, and mercury. For the first two of these the choice of preferred nucleus is debatable.

Hydrogen.—Here the choice lies between ^{1}H ($I = \frac{1}{2}$, $N = 99.98\%$, $\Xi = 100$ MHz) and ^{2}H ($I = 1$, $N = 0.02\%$, $\Xi = 15.35$ MHz). At first sight all the advantages would seem to lie with ^{1}H. It has a very high receptivity and is thus easy to observe. A wealth of chemical information is available (and has been obtained) from ^{1}H n.m.r. However, there are two disadvantages that are not always sufficiently recognized:

(i) Because of the high natural abundance of ^{1}H and the variety of chemical situations for hydrogen, many spectra of large organic molecules and biomolecules are too complicated to interpret. This arises from the number of chemically shifted sites and the existence of (H, H) coupling.

(ii) Relaxation times are often not dominated by any particular mechanism or interaction and, in particular, intermolecular effects may be as important as intramolecular effects. This renders the use of T_1 measurements for molecular motional information somewhat difficult.

Of course the first of these problems can be removed by extensive deuteriation, followed by ^{2}H decoupling. But this is extremely time-consuming and expensive, and it becomes virtually impossible to build up a whole deuterium chemistry for biomolecules. However, selective deuteriation at one site only is relatively easy, and use may then be made of ^{2}H resonance, with ^{1}H noise-decoupling. The result is a single line with a readily determinable chemical shift which may be used for structural assignment. Indeed, with FT techniques it is possible to look at ^{2}H in natural abundance,[44] giving a ^{13}C-like situation in which there is a separate single signal (with ^{1}H noise decoupling and in the absence of other magnetic nuclei) for each different hydrogen site in the molecule. It is true that the chemical shifts, when measured in Hz, are smaller (by a factor of *ca.* 6) than in ^{1}H resonance, but this is more than offset by the spectral simplicity. The ^{2}H lines are not normally broadened too much by quadrupolar relaxation, so the resolution is reasonable. In any case relaxation-time data (of T_2 from linewidths, or of T_1 by FT methods) will usually be dominated by the quadrupolar mechanism, and thus they can be readily used to discuss molecular motion.[45] A further use of the simplicity of ^{2}H n.m.r. lies in the area of chemical-site exchange. The absence of coupling effects implies that spectra for exchange rates comparable to the n.m.r. timescale will give simple bandshapes (as in the

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[44] J. M. Briggs, L. F. Farnell, and E. W. Randall, *J.C.S. Chem. Comm.*, 1973, 70.

[45] H. H. Mantsch, H. Saito, L. C. Leitch, and I. C. P. Smith, *J. Amer. Chem. Soc.*, 1974, **96**, 256.

case of ^{13}C spectra), from which kinetic parameters may be readily extracted. Exchange rates may also be obtained by following intensity changes in appropriate peaks.[46]

It is also relevant to mention the possibility[47] of using ^{3}H n.m.r. The tritium nucleus is of spin-$\frac{1}{2}$ and is radioactive. It is the only nucleus with a higher magnetic moment than the proton (such that Ξ = 106.526 MHz). With ^{1}H noise decoupling, ^{3}H spectra have the advantage[47] of simplicity (as for ^{2}H) when selective substitution is employed, plus a high sensitivity and a relatively large chemical shift range in Hz (compared with ^{2}H spectra).

Nitrogen.—The situation with nitrogen is complementary to that with hydrogen in the sense that the quadrupolar nucleus (^{14}N, $I = 1$) is in high natural abundance ($N = 99.6\%$) whereas the spin-$\frac{1}{2}$ isotope, ^{15}N, is in low natural abundance ($N = 0.36\%$). Both have rather low magnetic moments and therefore have low n.m.r. frequencies (Ξ = 7.2 and 10.1 MHz for ^{14}N and ^{15}N respectively). The problem with ^{14}N resonance[4,48] is the large linewidths often encountered, due to quadrupolar relaxation. The widths, W, are given by $(\pi T_2)^{-1}$. For a spin-1 nucleus the spin–spin relaxation time is (for isotropic re-orientation in the extreme narrowing case):

$$T_2^{-1} = \frac{3}{8}\chi^2\left(1 + \frac{\eta^2}{3}\right)\tau_q$$

where χ is the nuclear quadrupole coupling constant (*ca.* 3—5 MHz for ^{14}N), and is given by $\chi = e^2 q_{zz}Q/h$. The quantity q is the electric field gradient at the nucleus, with q_{zz} as its biggest component, Q is the nuclear electric quadrupole moment ($\approx 1.55 \times 10^{-26}$ cm^2 for ^{14}N), η is the asymmetry parameter for q, *i.e.* it is $(q_{yy} - q_{xx})/q_{zz}$, and τ_q is the quadrupolar correlation time for molecular tumbling (usually in the range 1—10 ps for non-viscous liquids). The dependence on q_{zz} (which is clearly very low for T_d or O_h molecules) and on τ_q causes a wide variation in linewidths, as shown in Table 2.

Table 2 *Representative* ^{14}N *n.m.r. linewidths*[a]

Compound	*W*/Hz	*Compound*	*W*/Hz
MeNC	0.3	NMe_3	77
NMe_4^+	12	MeCN	88
$EtONO_2$	12	*N*-methylpyrrole	118
NO_3^-	18	$HCONMe_2$	160
$MeNO_2$	21	pyridine	215
MeNCO	35	PhCN	390
CN^-	52	aniline	1300

[a] Taken from the article by J. M. Lehn and J. P. Kintzinger in ref. 4.

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[46] L. S. Bresler, A. S. Khachaturov, and I. Ya. Poddubnyi, *J. Organometallic Chem.*, 1974, **64**, 335.

[47] J. Bloxsidge, J. A. Elvidge, J. R. Jones, and E. A. Evans, *Org. Magn. Resonance*, 1971, **3**, 127.

[48] J. P. Kintzinger and J. M. Lehn, *Helv. Chim. Acta*, 1975, **58**, 905.

Clearly, then, the choice between ^{14}N and ^{15}N must depend on the value of $\Delta\nu_{\frac{1}{2}}$ for ^{14}N and on the problem in hand. If high resolution is required (for measurement of coupling constants or small chemical shift differences) ^{15}N will be preferred, but if the chemical shift differences involved are large or if motional information is required, then ^{14}N will be chosen. It is in general easier to measure T_2 from ^{14}N linewidths than T_1 from FT experiments on ^{15}N (these are often very time-consuming). For some special cases no doubt ^{15}N isotopic enrichment will be used, as in many of the early studies[4] of ^{15}N n.m.r.

4 Quadrupolar Nuclei

Figure 3 shows some quadrupolar nuclei which have been studied recently; Table 3 (pp. 18 and 19) summarizes their n.m.r. properties (the list of such nuclei is not exhaustive) and gives recent references (49—76) to their use. The reviews mentioned earlier[34–36] together with that by Deverell,[77] are also relevant. Obviously there is a wide range of nuclei of greater or lesser suitability. A useful classification is as follows:

Non-metals: [^{2}H, ^{14}N**], B*, O, S
Halogens: Cl*, Br*, I**
Alkali and alkaline earth metals: Li*, Na**, K*, Rb*, Cs**, Be**, Mg, Ca, Sr (Ba is also feasible)
Group A metals and metalloids: Al**, Ga, Ge, In, Sb* (As and Bi are also feasible)

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[49] G. W. Canters and E. de Boer, *Mol. Phys.*, 1973, **26,** 1185.
[50] R. A. Kovar and G. L. Morgan, *J. Amer. Chem. Soc.*, 1970, **92,** 5067.
[51] B. L. Silver and Z. Luz, *Quart. Rev.*, 1967, **21,** 458.
[52] E. Lippmaa, M. Mägi, S. S. Novikov, L. I. Khmelnitzki, A. S. Prihodko, O. V. Levedev, and L. V. Epishina, *Org. Magn. Resonance*, 1972, 4, 153, 197.
[53] H. J. C. Berendsen and H. T. Edzes, *Ann. New York Acad. Sci.*, 1973, **204,** 459.
[54] R. G. Bryant, *J. Magn. Resonance*, 1972, **6,** 159.
[55] J. W. Akitt, *Ann. Reports N.M.R. Spectroscopy*, 1972, **5A,** 465.
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[57] H. L. Retcofsky and R. A. Friedel, *J. Amer. Chem. Soc.*, 1972, **94,** 6579.
[58] O. Lutz, A. Nolle, and A. Schwenk, *Z. Naturforsch.*, 1973, **28a,** 1370.
[59] C. Hall, *Quart. Rev.*, 1971, **25,** 87.
[60] H. Wennerström, B. Lindman, and S. Forsén, *J. Phys. Chem.*, 1971, **75,** 2936.
[61] O. Lutz, A. Schwenk, and A. Uhl, *Z. Naturforsch.*, 1973, **28a,** 1535.
[62] G. A. Melson, D. J. Olszanski, and E. T. Roach, *J.C.S. Chem. Comm.*, 1974, 229.
[63] R. G. Kidd, R. W. Matthews, and H. G. Spinney, *J. Amer. Chem. Soc.*, 1972, **94,** 6686.
[64] D. Rehder and J. Schmidt, *J. Inorg. Nuclear Chem.*, 1974, **36,** 333.
[65] G. M. Bancroft, H. C. Clark, R. G. Kidd, A. T. Bake, and H. G. Spinney, *Inorg. Chem.*, 1973, **12,** 728.
[66] D. Rehder and J. Schmidt, *Z. Naturforsch.*, 1972, **27b,** 625.
[67] A. Johnson and G. W. Everett, *Inorg. Chem.*, 1973, **12,** 2801.
[68] P. D. Ellis, H. C. Walsh, and C. S. Peters, *J. Magn. Resonance*, 1973, **11,** 426.
[69] B. W. Epperlein, H. Krüger, and O. Lutz, *Z. Naturforsch.*, 1974, **29a,** 660.
[70] S. F. Lincoln, *Austral. J. Chem.*, 1972, **25,** 2705.
[71] R. G. Kidd and H. G. Spinney, *J. Amer. Chem. Soc.*, 1973, **95,** 88.
[72] R. G. Kidd and H. G. Spinney, *Inorg. Chem.*, 1973, **12,** 1967.
[73] A. Fratiello, D. D. Davies, S. Peak, and R. E. Schuster, *Inorg. Chem.*, 1971, **10,** 1627.
[74] R. G. Kidd and R. W. Matthews, *J. Inorg. Nuclear Chem.*, 1975, **37,** 661.
[75] L. C. Erich, A. C. Gossard, and R. L. Hartless, *J. Chem. Phys.*, 1973, **59,** 3911.
[76] R. A. Dwek, Z. Luz, and M. Shporer, *J. Phys. Chem.*, 1970, **74,** 2232.
[77] C. Deverell, *Progr. N.M.R. Spectroscopy*, 1969, **4,** 235.

Transition metals: Sc**, Ti, V**, Mn**, Co**, Cu*, Zn, Nb**, Ta**, Re*

(A single asterisk indicates that the natural abundance of the favoured isotope is $> 50\%$, a double asterisk that N is *ca.* 100%).

The cases of hydrogen and nitrogen have already been discussed. Boron-11 is well-established[1] as a suitable nucleus for study, and many chemical applications have been reported. Oxygen and sulphur are mentioned below. Arsenic, antimony, and bismuth may become important in the future, since suitable quadrupolar nuclei exist, but they have not been greatly studied to date. Aluminium-27 has already received quite a lot of attention.[55,56] There is considerable scope for future work on transition metals (to date there has only been an appreciable amount of work on Mn and Co—see below), However, it is for the halogens, alkali metals, and alkaline earth metals that n.m.r. of quadrupolar nuclei is of the greatest importance, since these are the elements giving, *par excellence*, simple ions in aqueous solution.

Traditionally the experimental techniques used for quadrupolar nuclei have been somewhat different fron those for spin-$\frac{1}{2}$ nuclei. Broad-line spectrometers have been preferred, and often spectra have been obtained in the dispersion mode.[78] The question of the large linewidths (short T_2) often observed has been treated above during the discussion of ^{14}N resonance. Two points need to be made regarding FT spectroscopy of quadrupolar nuclei:

(i) Since the advantage of FT over CW depends on $(\Delta/W)^{\frac{1}{2}}$ where Δ is the full spectral width for the sample and W is an individual linewidth in the same units, the gain for quadrupolar nuclei is not so marked as for spin-$\frac{1}{2}$ nuclei because of the frequent large values of W for the former. Thus it is not necessarily advantageous (in terms, for instance, of cost efficiency) to use FT equipment for quadrupolar nuclei, particularly when a spectrum is expected to be a single line and/or when nuclei in *ca.* 100% natural abundance are being examined.

(ii) Since both T_1 and T_2 are usually short for quadrupolar nuclei, the interpulse spacing for FT can also be short without saturating the system, thus increasing the time-efficiency of obtaining spectra. This may, however, give rise to some difficulties involving the rate of data acquisition or of 'dead time' in the electronics following the pulse.

Oxygen and Sulphur.—These two elements are important chemically, in the same group of the Periodic Table, and are similar in their properties in that: there is only one magnetic isotope for each element (^{17}O and ^{33}S); these isotopes are both quadrupolar, $I = \frac{5}{2}$ and $\frac{3}{2}$, respectively; they are both in low natural abundance, 0.04% and 0.7% respectively.

The ^{17}O nucleus is the more important of the two: it has been studied in the past mostly using enriched material.[51] With the advent of FT spectroscopy there are hopes that natural-abundance ^{17}O n.m.r. will prove a useful tool, and

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[78] P. C. Lauterbur, in 'Determination of Organic Structures by Physical Methods', ed. F. C. Nachod and W. D. Phillips, Academic Press, New York, 1962, Vol. 2, Chap. 7.

Table 3 *A Partial list of quadrupolar nuclei of potential n.m.r. importance*[a]

Isotope	*Spin*	*Natural abundance* $N\%$	*Magnetic moment* μ/μ_N	*Magnetogyric ratio* $\gamma/10^7$ rad T^{-1} s^{-1}	*Quadrupole moment* $Q/10^{-28}$ m^2	*N.m.r. frequency* Ξ/MHz	*Relative receptivity*	*References*
^{2}H[b]	1	0.015	1.2125	4.1064	2.73×10^{-3}	15.351	1.45×10^{-6}	44—46
^{7}Li	3/2	92.6	4.2035	10.3964	-3×10^{-2}	38.864	0.272	49
^{9}Be	3/2	100	−1.5200	3.7594	5.2×10^{-2}	14.053	1.39×10^{-2}	50
^{11}B[c]	3/2	80.42	3.4702	8.5828	3.55×10^{-2}	32.084	0.133	1
^{14}N[b]	1	99.63	0.5706	1.9324	1.6×10^{-2}	7.224	1.00×10^{-3}	4, 48
^{17}O	5/2	0.037	−2.2398	3.6266	-2.6×10^{-2}	13.557	1.08×10^{-5}	51, 52
^{23}Na	3/2	100	2.8610	7.0760	0.14—0.15	26.451	9.25×10^{-2}	49, 53
^{25}Mg	5/2	10.1	−1.0110	1.6370	—[d]	6.1195	2.71×10^{-4}	54
^{27}Al	5/2	100	4.3051	6.9706	0.149	26.057	0.206	55, 56
^{33}S	3/2	0.76	0.8296	2.0517	-6.4×10^{-2}	7.670	1.71×10^{-5}	57, 58
^{35}Cl[c]	3/2	75.5	1.0598	2.6212	-7.89×10^{-2}	9.798	3.55×10^{-3}	59, 60
^{39}K	3/2	93.1	0.5047	1.2484	0.11	4.666	4.73×10^{-4}	49
^{43}Ca	7/2	0.145	−1.4914	1.7999	—[d]	6.728	9.27×10^{-6}	61
^{45}Sc	7/2	100	5.3851	6.4989	−0.22	24.294	0.301	62

Table 3 (*continued*)

^{47}Ti^{c}	5/2	7.28	−0.9313	1.5079	—^{d}	5.637	1.52×10^{-4}	63
^{51}V	7/2	99.8	5.827	7.032	-4×10^{-2}	26.29	0.381	64
^{55}Mn	5/2	100	4.0749	6.5980	0.55	24.665	0.175	65
^{59}Co	7/2	100	5.2344	6.3170	0.40	23.614	0.277	66, 67
^{63}Cu^{c}	3/2	69.1	2.8668	7.0904	−0.16	26.505	6.43×10^{-2}	68
^{67}Zn	5/2	4.11	1.0333	1.6731	0.15	6.254	1.17×10^{-4}	69
^{71}Ga^{c}	3/2	39.6	3.2984	8.1578	0.112	30.495	5.62×10^{-2}	55, 70
^{73}Ge	9/2	7.8	−0.9693	0.9332	−0.2	3.488	1.09×10^{-4}	71
^{79}Br^{c}	3/2	50.5	2.7098	6.7021	0.33	25.054	3.97×10^{-2}	59, 60
^{85}Rb^{c}	5/2	72.8	1.5952	2.5829	0.27	9.655	7.58×10^{-3}	49
^{87}Sr	9/2	7.02	−1.2042	−1.1594	0.2	4.334	1.89×10^{-4}	19
^{93}Nb	9/2	100	6.7919	6.5387	−0.2	24.443	0.482	72
^{115}In^{c,e}	9/2	95.7	6.0892	5.8622	1.16	21.914	0.332	73
^{121}Sb^{c}	5/2	57.25	3.9537	6.4016	−0.5	23.930	9.15×10^{-2}	74
^{127}I	5/2	100	3.3055	5.3521	−0.69	20.007	9.34×10^{-2}	59, 60
^{133}Cs	7/2	100	2.9076	3.5089	-3×10^{-3}	13.117	4.74×10^{-2}	49
^{181}Ta	7/2	99.99	2.6533	3.2021	3	11.970	3.60×10^{-2}	75
^{187}Re^{c,e}	5/2	62.93	3.7578	6.0843	2.6	22.744	8.64×10^{-2}	76

[a] See also the relevant footnotes to Table 1. [b] A useful isotope of $I = \frac{1}{2}$ exists. [c] Other stable quadrupolar isotopes exist. [d] Not reported. [e] Radioactive, with a long half-life ($> 10^{10}$ years).

some research is being carried out in this direction. Some tentative conclusions[79] are that natural-abundance work is feasible for non-viscous liquids with high concentrations of the compounds of interest. Obviously it is expected that aqueous systems will be of importance, but situations with large linewidths are best avoided, and these include cases where hydrogen-bonding and/or chemical exchange are complicating factors. Possibly, therefore, the best results will be secured from non-aqueous systems. Figure 8 shows the sort of signal-to-noise ratio and linewidths which may be achieved[79] in a short time (*ca.* 16 min) in a relatively favourable case. References 57 and 58 report work on ^{33}S.

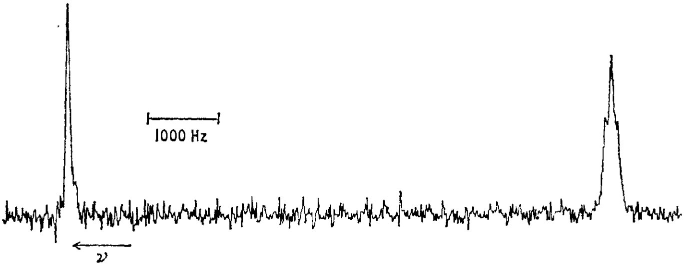

Figure 8 13.5 HMz ^{17}O *FT n.m.r. spectrum of an acetone-water solution,*[79] *derived from* 11 000 *pulses of acquisition time* 0.1 s (*total time* ca. 16 min). *The signal at the left is due to* Me_2CO (*linewidth* 60 Hz). *That on the right is due to* H_2O *and shows a triplet splitting due to* $|J_{OH}| = 82$ Hz

The Halogens and Alkali Metals.—As stated earlier, the only element in these categories with $I = \frac{1}{2}$ is fluorine; all the others have reasonably useful quadrupolar nuclei, and a number of reviews have been published.[53,59,77] For studies of aqueous solutions these elements are extremely important, particularly[53] the ^{23}Na and ^{35}Cl nuclei for biochemical work. One reason for their importance is the sensitivity of both chemical shifts and linewidths (relaxation times) to environment. Thus n.m.r. is provided with sensitive probes to study solvation, interionic interactions, binding to biomolecules, *etc.* The effects can be very large—*e.g.*, the ^{81}Br chemical shift for aqueous CsBr changes[80] by over 60 p.p.m. in the concentration range 0—5 mol l^{-1}. These variations are reportedly[80] due to cation–anion binary interactions (repulsive overlap of closed-shell ion orbitals).

The linewidth variations may be traced to the influences of electric-field gradient and molecular tumbling rate mentioned earlier for ^{14}N. In the case of the halogens it is clear that for covalent compounds the electric-field gradient may be very large, whereas for the ions it will be very small (being due to medium influences only). Thus for ^{35}Cl the linewidth for CCl_4 is *ca.* 10 kHz but for dilute aqueous NaCl it is only *ca.* 10 Hz. Linewidths for the ions will give information about the structure of the solution around the ion and the dynamics of changes in each structure.

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[79] C. Rodger and N. Sheppard, unpublished work.
[80] C. Deverell and R. E. Richards, *Mol. Phys.*, 1969, **16**, 421.

One type of use for linewidth studies is the 'halide probe' technique,[81] which relies on the great change in linewidth when chloride ion, say, binds to a site in a biomolecule (both τ_q and χ increase markedly). Exchange between bound and free Cl^- species is normally sufficient to give a single signal with a weighted average linewidth. The change from the free Cl^- linewidth can be detected for very low concentrations (*ca.* 5×10^{-6} mol l^{-1}), corresponding to those of natural biomolecules. In fact Br^- and I^- are even better in this respect. The binding sites are often metal ions such as Hg^{2+} or Pb^{2+}, which are readily incorporated in many biomolecules as a label. In such a case the linewidth effect is only seen when *both* the halide ion and the metal ion are present with the biomolecule. The technique may be used to study the biomolecule concentration and structure.

Vanadium, Manganese, and Cobalt.—In the first transition series of metals there is only one case of a spin-$\frac{1}{2}$ nucleus, ^{57}Fe; this is very unfavourable for n.m.r. study because of its low natural abundance and very low magnetic moment. On the other hand the quadrupolar nuclei ^{51}V, ^{55}Mn, and ^{59}Co have high magnetic moments and *ca.* 100% natural abundances (^{45}Sc also falls into this category but is likely to be less used for n.m.r., mainly for chemical reasons). Moreover all three have relatively high magnetic moments, so that relative receptivities are high (0.381, 0.175, and 0.277 respectively). Cobalt-59 has been the most studied of these three nuclei, and so far chemical interest has largely been directed to octahedral cobalt(III) complexes, generally in aqueous solution (see, *e.g.*, ref. 67). The chemical shift range for these compounds is very large, *ca.* 14 000 p.p.m., and shifts have been related to second-order paramagnetism, and hence to the influence of ligand-field strength on the optical absorption maxima. For ^{55}Mn, on the other hand, it is derivatives of manganese carbonyls that have received most attention,[65] with the emphasis on how electronic effects control the linewidths (which may be up to 3000 Hz owing to quadrupolar relaxation). Vanadium-51 has not been widely studied as yet, but is of potential importance.[64] It seems clear that for all three nuclei the areas of application have been somewhat at random so far. Of course, for these and for other metals it is important to remember that only diamagnetic compounds can be readily studied (the problems for paramagnetic systems are rather different, and relatively sharp spectra are not to be expected); this consideration will dominate the choice of chemical species to be investigated. Indeed this is the reason for the predominance of work on Co^{III} rather than Co^{II} species in aqueous solution. However, it is clear that n.m.r. will become of major importance for transition metals, both for ionic systems and for organometallic compounds.

5 Conclusion

N.m.r. is rapidly moving away from the era when proton work dominated the field. Some nuclei (^{11}B, ^{13}C, ^{19}F, ^{31}P) are already well-established for n.m.r. purposes, but studies with a much wider variety of nuclei should soon become

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[81] T. R. Stengle and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, 1967, **89**, 3945.

commonplace. There are suitable nuclei in every group of the Periodic Table. However, some further instrumental advances are probably necessary before truly versatile multinuclear n.m.r. spectrometers become available at reasonable cost.

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