Chemical Applications of Oxygen-17 Nuclear and Electron Spin Resonance

By Brian L. Silver and Zeev Luz
ISOTOPE DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL

1 Introduction

Of the three stable isotopes of oxygen, ^{16}O, ^{17}O, and ^{18}O, only ^{17}O has a magnetic nucleus. It has a spin quantum number of $\frac{5}{2}$ and a gyromagnetic ratio of 577 c./sec. per gauss. Unfortunately the natural abundance of ^{17}O is only 0·037% and for this reason, despite the chemical importance of oxygen, relatively little work has been reported on the effect of ^{17}O on nuclear and electron spin resonance (n.m.r. and e.s.r.). Recent progress in the large-scale separation of oxygen isotopes has resulted in an increased availability of materials enriched in ^{17}O. During the last six years ^{17}O n.m.r. and to a less extent e.s.r., have been used to study a number of fundamental problems in chemistry and this is a Review of the achievements of these studies. The coverage of the literature is essentially complete up to the beginning of 1966, and we have discussed only a part of the articles published during 1966.

^{17}O n.m.r. signals were first observed by Alder and Yu[1] in water, and a number of organic liquids, both in isotopically normal and slightly enriched material. The list of compounds was extended by Weaver *et al.*[2] and Dharmatti *et al.*,[3] both groups using isotopically normal compounds. Christ[4] and subsequently Christ, Diehl, Schneider, and Dahn[5] examined over a 100 compounds, most of them organic. Shifts for inorganic compounds have been published by Figgis *et al.*[6] and Bramley *et al.*[7] and more recently by Jackson and Taube.[8]

Very few cases have been reported of the effect of ^{17}O on e.s.r. spectra. Baird[9] in 1961 observed ^{17}O hyperfine splitting in di-s-butylnitric oxide, and subsequently such splitting has been reported for several other free radicals.[10–15]

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[1] F. Alder and F. C. Yu, *Phys. Rev.*, 1951, **81**, 1967.
[2] H. E. Weaver, B. M. Tolbert, and R. C. LaForce, *J. Chem. Phys.*, 1955, **23**, 1956.
[3] S. S. Dharmatti, J. K. Sundara Rao, and R. Vijayoraghan, *Nuovo cim.*, 1959, **11**, 656.
[4] H. A. Christ, *Helv. Phys. Acta*, 1960, **33**, 572.
[5] H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn, *Helv. Chim. Acta*, 1961, **44**, 865.
[6] B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc.*, 1962, *A*, **269**, 469.
[7] R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893.
[8] J. A. Jackson and H. Taube, *J. Phys. Chem.*, 1965, **69**, 1844.
[9] J. C. Baird, *J. Chem. Phys.*, 1962, **37**, 1879.
[10] A. Reiker and K. Scheffler, *Tetrahedron Letters*, 1965, **19**, 1337.
[11] K. Dimroth, F. Bar, and A. Berndt, *Angew. Chem.*, 1965, **77**, 217.
[12] W. M. Gulick and D. H. Geske, *J. Amer. Chem. Soc.*, 1965, **87**, 4049.
[13] (*a*) B. L. Silver, Z. Luz, and C. Eden, *J. Chem. Phys.*, 1966, **44**, 4258; (*b*) W. M. Gulick, jun. and D. H. Geske, *J. Amer. Chem. Soc.*, 1966, **88**, 4119.
[14] Z. Luz, B. L. Silver, and C. Eden, *J. Chem. Phys.*, 1966, **44**, 4421.
[15] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **44**, 434.

Most of this Review will be concerned with ^{17}O n.m.r. in solutions. The effect of ^{17}O on e.s.r. spectra will be dealt with in Section 3.

^{17}O n.m.r. measurements in dilute solutions, accurate line-width studies, and the detection of ^{17}O hyperfine splitting in e.s.r. require compounds isotopically enriched in ^{17}O. Water containing up to about 10 atoms % of ^{17}O has been commercially available for several years and recently ^{17}O isotope has been enriched up to 65 atoms % by thermal diffusion of oxygen gas.[16] Since ^{17}O is normally supplied in the form of water, the most convenient method for synthesising ^{17}O-labelled compounds is often an isotopic exchange reaction between the normal compound and solvent $H_2{}^{17}O$, or a mixed solvent containing $H_2{}^{17}O$. The exchange of isotopic oxygen with organic compounds and methods of isotopic synthesis have been reviewed.[17]

2 Nuclear Magnetic Resonance

A. Line-widths.—Studies of line-widths in n.m.r. have provided much insight into details of nuclear relaxation processes. In subsequent sections we will discuss the effect on n.m.r. line-widths of chemical exchange and interactions with paramagnetic ions. In the absence of these factors the dominant effect on the ^{17}O line-width in solution is quadrupole relaxation, which depends on the electric field gradient at the ^{17}O nucleus, and the tumbling time of the molecule.[18] The field gradient necessarily vanishes if the symmetry around the oxygen atom is cubic or higher, or it could vanish owing to a suitable electron distribution in the orbitals closely associated with the oxygen atom. A case in which oxygen is at a site of cubic symmetry is not expected in molecules and is not known, though it often occurs in crystalline lattices. In fact an n.m.r. signal has been detected in solid $Mg^{17}O$ in which the oxygen is located at a site with cubic symmetry.[19] In molecules the field gradient at a nucleus is determined largely by the population of the p orbitals.[20] A zero contribution to the field gradient at the ^{17}O nucleus occurs when the total population of the p orbitals in the bonds surrounding the oxygen nucleus is six (O^{2-}), zero (O^{6+}), or (in the case of sp^3 hybridisation) four (O^{2+}). Large formal positive charges on oxygen are very unlikely, but an oxygen bonded to a highly electropositive atom may carry close to two electronic charges, and have a very small field gradient.

Christ and Diehl[18] measured the ^{17}O line-widths, and calculated the quadrupole interaction constants, for a number of diamagnetic organic compounds. The line-widths ranged from 100 to 1000 c./sec. and the quadrupole coupling constant varied from 3 to 10 Mc./sec. Measurements on a series of alcohols showed that the ^{17}O line-widths varied linearly with the calculated tumbling time of the molecule, which indicates that the field gradient in the hydroxyl group of different

[16] I. Dostrovsky and F. S. Klein, personal communication.

[17] (*a*) D. Samuel and B. L. Silver, in 'Advances in Physical Organic Chemistry', vol. 3, Academic Press, New York, 1965, p. 123; (*b*) I. Dostrovsky and D. Samuel, in 'Inorganic Isotopic Syntheses', W. A. Benjamin, New York, 1962, ch. 5.

[18] H. A. Christ and P. Diehl, 11th Colloque Ampere, Eindhoven, 1962, p. 224.

[19] J. A. Jackson, *J. Phys. Chem. Solids*, 1963, **24**, 591.

[20] W. J. Orville-Thomas, *Quart. Rev.*, 1957, **11**, 162.

alcohols is very nearly constant. It is generally observed that ^{17}O line-widths decrease with increasing temperature[21] as would be expected from the corresponding decrease in tumbling times.

B. Chemical Shifts in Diamagnetic Molecules.—An extensive survey of the ^{17}O chemical shifts of organic compounds was carried out by Christ, Diehl, Schneider and Dahn.[5] Most of the measurements were made on isotopically unenriched materials. This work has provided the basic data for the systemisation of ^{17}O chemical shifts. The shifts covered a range of up to 1000 p.p.m., and almost all compounds exhibited a low-field shift compared with $H_2{}^{17}O$. The most striking feature of the results is the marked division between the shifts of doubly bonded oxygen which usually fall below -250 p.p.m. relative to $H_2{}^{17}O$ and oxygen involved in single bonds (singly bonded oxygen) which usually fall above -250 p.p.m. A finer classification of the shifts is provided by the fact that they are grouped into small ranges characteristic of each functional group.

Chemical shifts are conveniently considered as being the sum of two contributions: $\delta = \delta_A + \delta_L$, where δ_A is the diamagnetic and δ_L the paramagnetic contribution. Order-of-magnitude considerations and substituent effects indicate that the dominant contribution to the ^{17}O chemical shift is due to paramagnetic shielding. That this is so, at least for doubly bonded oxygen, was convincingly demonstrated by Figgis, Kidd, and Nyholm.[6] The paramagnetic shift arises from the creation of electronic angular momentum about the nucleus, *via* the mixing into the ground state of excited states having angular momentum. Mixing results from the perturbation due to the external magnetic field, and is inversely proportional to the energy difference, ΔE, between the ground and excited states. In the case of doubly bonded oxygen, *e.g.*, the carbonyl group, the dominant contribution most probably arises from mixing into the ground state of a state resulting from the excitation of a single electron from the non-bonding orbital, *n*, localised on the oxygen atom, to the π^* antibonding orbital of the carbonyl bond. This results in the creation of electronic angular momentum about the oxygen nucleus. The paramagnetic shift is then proportional to:[6]

$$\frac{< | 0 | L^2 | \pi^* >}{\Delta E_{0,\pi*}}$$

where $< 0 | L^2 | \pi^* >$ is the matrix element of the square of the angular momentum operator between the ground state and the antibonding n^* state, and $\Delta E_{0,\pi*}$ is the $n \rightarrow \pi^*$ transition energy. Figgis *et al.*[6] showed that there is a linear correlation between the chemical shift of doubly bonded oxygen and the reciprocal of $\Delta E_{0,\pi*}$ (Figure 1). Thus the diamagnetic shift of ^{17}O, δ_A, appears to vary little between the different compounds.

Figgis *et al.*[6] measured the ^{17}O shifts in a number of diamagnetic transition-metal oxyanions of general formula $MO_4{}^{n-}$. The shifts again give a very good linear correlation with the inverse of the energy of the lowest observed electronic

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[21] S. W. Rabideau and J. A. Jackson, *J. Chem. Phys.*, 1965, 41, 3405.

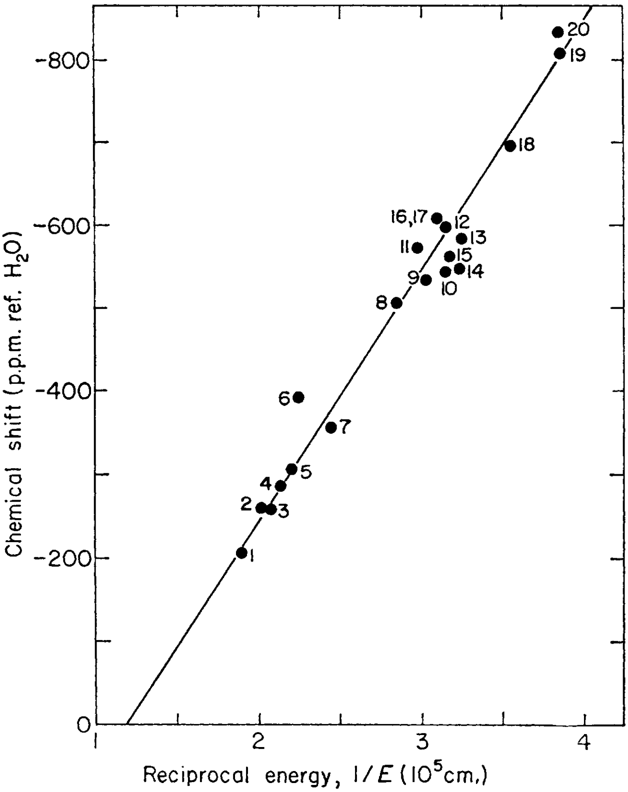


Fig. 1 *Correlation between the chemical shift of doubly bonded oxygen and* $n \rightarrow \pi^*$ *transition energy* [From B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc.*, 1962, *A*, **269**, 469]

1. $(NH_2)_2CO$
2. $CH_3CO.OH$
3. $HCO.OH$
4. $CH_3CO.NH_3$
5. $HCO.NH_2$
6. $(CH_3CO)_2O$
7. $CH_3CO.OC_2H_5$
8. $CH_3CO.Cl$
9. Furfural
10. $Cl_3C\ CH.O$
11. $(CH_3)_2CO$
12. $CH_3CH_2CH.O$
13. $CH_3CH.O$
14. Cyclohexanone
15. Cyclopentanone
16. CH_3NO_2
17. $C_3H_7NO_2$
18. $(C_2H_5)_2N.NO$
19. C_3H_7ONO
20. C_4H_9ONO

transition. However, a calculation on permanganate ion showed that the main contribution to the paramagnetic shift does not come from the lowest excited state, and the correlation must therefore, as the authors pointed out, be regarded as somewhat fortuitous. Nevertheless, the dominant contribution of the paramagnetic shift is clearly demonstrated.

The fact that different functional groups are each characterised by a comparatively narrow range of chemical shifts can sometimes be used in determining the chemical nature of the group in which the oxygen atom finds itself. For example, acetone in water gives a single ^{17}O resonance at -520 p.p.m. which falls in the range characteristic for carbonyl oxygen. On the other hand, formaldehyde in aqueous solution has a single resonance at −50 p.p.m., characteristic of the hydroxyl group. This indicates that formaldehyde is completely hydrated as has also been shown by other methods. Consistently, acetaldehyde, which is known to be about 50% hydrated in aqueous solution at room temperature, gives two signals: one at −560 p.p.m. due to the unhydrated acetaldehyde and another at −70 p.p.m. from the hydrated molecules[22a] (Figure 2).

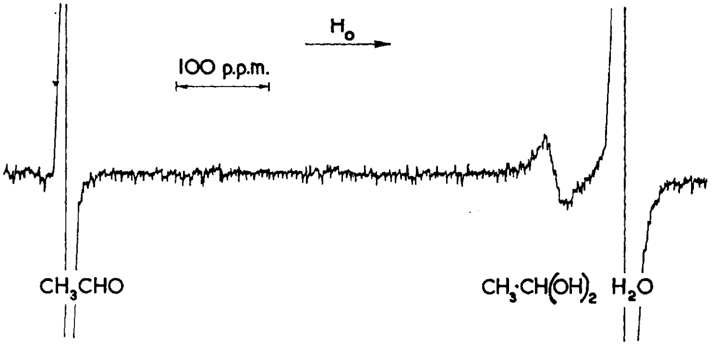
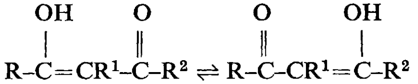


Fig. 2 *The ^{17}O nuclear magnetic resonance spectrum of a concentrated solution of acetaldehyde in water enriched in ^{17}O. The smaller height of the line due to the hydrate is due to its much greater width* [From P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, 1967, **89**, 749]

An interesting application of ^{17}O n.m.r. shifts is in the study of the equilibria between the two enol forms in asymmetric β-diketones.[23] β-Diketones are known to exist as mixtures of tautomeric forms. In asymmetric β-diketones, R·C(:O)·CHR^1·C(:O)R^2, there are one keto and two rapidly interconverting enol forms (I and II) possible



$$\mathrm{R{-}\overset{\overset{\textstyle OH}{|}}{C}{=}CR^1{-}\overset{\overset{\textstyle O}{\|}}{C}{-}R^2 \rightleftharpoons R{-}\overset{\overset{\textstyle O}{\|}}{C}{-}CR^1{=}\overset{\overset{\textstyle OH}{|}}{C}{-}R^2}$$

(I) (II)

A given oxygen atom in the enol form can exist in two different environments; either as a carbonyl oxygen with a chemical shift δ^{CO}, or as a hydroxyl oxygen with shift δ^{COH}. Owing to fast intramolecular proton transfer the actual spectrum of the enol forms will consist of two lines due to the two nonequivalent oxygens, the observed shift of a given oxygen being the weighted average of its shifts in the two forms. Thus the observed chemical shift of the oxygen adjacent to R is given by: $\delta^{\mathrm{R}} = \delta^{\mathrm{COH}} \times$ fraction of (I) $+ \delta^{\mathrm{CO}} \times$ fraction of (II). A similar equation holds for the oxygen adjacent to R^2. By using the tabulated[5] chemical

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[22] (*a*) P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, 1967, **89**, 749; (*b*) P. Greenzaid, unpublished work.

[23] M. Gorodetzky and Z. Luz, and Y. Mazur, *J. Amer. Chem. Soc.*, 1967, **89**, 1183.

shifts for the keto and hydroxyl oxygen it is possible from the observed chemical shifts, to determine the position of equilibrium between forms (I) and (II). Specific isotopic labelling of one of the two oxygens in the asymmetric β-diketone enables the ^{17}O peaks to be assigned. The equilibrium constants for a number of asymmetric β-diketones, have been determined in this way.[23]

The shift of the $H_2{}^{17}O$ line was measured[24] in solutions containing a large range of 1 : 1 diamagnetic electrolytes. Both positive and negative shifts occur and it was possible to show that the observed shifts can be broken down into ionic contributions due separately to the cations and anions. The results were interpreted in terms of a direct interaction between anions and water molecules.

C. Contact Shifts.—A special kind of chemical shift is that due to the scalar interaction between the nucleus and the magnetic moment of unpaired electrons in paramagnetic molecules. Often these shifts fall far outside the range of shifts covered by diamagnetic compounds. The contribution of this so-called contact shift to the total shift is

$$\frac{\Delta H}{H} = -\frac{S(S+1)g\,|\,\beta\,|\,A}{3kT\gamma_I}$$

where A is the isotropic hyperfine interaction constant which is a measure of the energy of the interaction between a nucleus and the unpaired spin in the *s* shells surrounding the nucleus. The hyperfine interaction also contributes to the n.m.r. line-width and often this broadening is so extreme as to prevent observation of an n.m.r. resonance. Nevertheless, if the electron spin relaxation time, or some other characteristic exchange time, is short compared with A^{-1}, it is sometimes possible to observe n.m.r. signals in paramagnetic molecules, and such signals have been directly observed from the solvation shell of Ni^{2+} and Co^{2+} in aqueous solutions and Co^{2+} in methanol.[25,26] Consistently, for these ions the electron spin relaxation time is very short, and at low temperatures the exchange of solvent molecules in and out of the solvation shell is sufficiently slow to allow separate resonances to be observed for the solvation shell and bulk molecules. A ^{17}O resonance was also found for manganese(III)–trisacetylacetone in benzene solution,[27] for which the electron spin relaxation time is known to be very short. In the solid state a ^{17}O n.m.r. signal has been reported for MnO and CoO powder.[28] In all these cases a shift of the order of 1% to low field was observed, indicating a positive spin polarisation at the oxygen nucleus.

The hyperfine shift of the hydration-shell molecules of paramagnetic ions can be deduced from the observed ^{17}O shift of solvent water, provided the chemical exchange of the hydration-shell molecules is fast compared with the frequency shift (see Section 2F). In this case only a single ^{17}O signal is observed, the shift of which is the weighted average shift of the bulk and solvation-shell molecules.

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[24] Z. Luz and G. Yagil, *J. Phys. Chem.*, 1966, **70**, 554.
[25] R. E. Connick and D. Fiat, *J. Chem. Phys.*, 1966, **44**, 4103.
[26] D. Fiat, B. L. Silver, Z. Luz, unpublished work.
[27] Z. Luz, B. L. Silver, and D. Fiat, *J. Chem. Phys.*, 1967, **46**, 469.
[28] D. E. O'Reilly and T. Tsang, *J. Chem. Phys.*, 1964, **40**, 734.

Knowing the concentration of the paramagnetic ions and their solvation number, one can deduce the contact shift of the ^{17}O in the solvation shell. The hyperfine interaction constants between co-ordinated water and bivalent cations of the first transition series and the tervalent rare-earth series have been obtained in this way.[29–32] In all these hydrates the source of the unpaired electron is a paramagnetic metal ion.

That contact shifts of ^{17}O occur at all is because unpaired spin is delocalised from the metal on to the ligand. More specifically, it is necessary that unpaired spin resides in an *s* orbital of the ^{17}O atom. For the first series of transition-metal ions all ^{17}O contact shifts reported have been paramagnetic,[29] *i.e.*, the external field at the ^{17}O nucleus is augmented by the field due to the magnetic moment of the unpaired electrons. The mechanism by which spin is delocalised in these complexes is *via* the bonds formed by the overlap of the cation 3*d* orbitals with the oxygen orbitals, resulting in the transfer of spin from the metal to the ^{17}O 2*s* orbitals. An estimate of the covalency of the metal–oxygen bond can be obtained from the magnitude of the contact shift.[27] In the complexes of the transition-metal ions of the first series the orbital angular momentum is largely quenched so that the electron spin on the metal is aligned essentially parallel with the external magnetic field, and therefore the ^{17}O contact shift is paramagnetic.

Lewis, Jackson, Lemons, and Taube[30] have reported the ^{17}O shift in aqueous solution of all the rare-earth ions except promethium. The elements from Ce to Sm gave paramagnetic, *i.e.*, low-field shifts and the rest diamagnetic, *i.e.*, high-field shifts. These results are the opposite of those expected if spin delocalisation occurs *via* overlap of metal 4*f* and oxygen *sp* hybrid orbitals. The observed shifts are only consistent with a spin polarisation on the ligand opposed to that on the cation. The following model has been suggested[30] to account for the experimental findings. There is a slight overlap of the *sp* hybrid orbitals of the oxygen and the 6*s* orbital of the rare-earth ion, giving bonding and antibonding orbitals. Configuration interaction promotes a bonding electron, with spin parallel with the spin on the cation, into the empty antibonding orbital, thus leaving a spin of opposite polarisation on the oxygen atom. For the rare earths the crystal field of the ligands is too small to interfere significantly with the orbital angular momenta of the electrons, and strong spin–orbit coupling tends to align the unpaired spins antiparallel to the external magnetic field for the first half of the series, and parallel with the magnetic field in the second half of the series. It follows that for the first half of the rare-earth series the spin left on the oxygen will be parallel to the external field and paramagnetic shifts are expected. The opposite situation applies to the second half of the series and will result in diamagnetic shifts as observed experimentally. In dealing with Eu^{3+} second-order effects become important and produce a small diamagnetic shift.

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[29] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; 1964, **41**, 2553.

[30] W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 1962, **36**, 695.

[31] R. G. Shulman and B. J. Wyluda, *J. Chem. Phys.*, 1959, **30**, 335.

[32] L. E. Orgel, *J. Chem. Phys.*, 1959, **30**, 1617.

In addition to the magnitude of contact shifts interesting information can also be obtained from the line-widths of the n.m.r. signals of paramagnetic molecules. Thus measurements of the line-width can be used to give values for electron spin relaxation times, in particular for metal ions for which an e.s.r. signal is not observable. From the temperature-dependence of the ^{17}O line-widths in aqueous solutions of the first series of transition-metal ions, Swift and Connick[29] were able to derive values, or upper limits, for the electron spin relaxation times of these ions.

An interesting observation has been made by Jackson, Lemons, and Taube[33] on the shift of ^{17}O in aqueous solutions of Cr^{2+} containing various anions. They found that the shift of the $H_2{}^{17}O$ resonance becomes less paramagnetic upon addition of certain anions, in particular ClO_4^-. They interpreted this phenomenon in terms of a complexing mechanism in which the axial water molecules of the Cr^{2+} hydrate are substituted by the anions. In agreement with this model was the observation that the resonance of $Cl^{17}O_4^-$ is strongly dependent on the concentration of Cr^{2+} in the solution, which indicates direct bonding between the anion and the metal. A similar but stronger effect of Co^{2+} on the ^{17}O resonance of MnO_4^- ion has also been observed and explained in terms of direct bonding between the two species.[8]

D. Spin–Spin Couplings.—The comparatively large line-widths of ^{17}O n.m.r. resonances often preclude the observation of splitting due to spin–spin coupling with other magnetic nuclei. Even when coupling might be expected to be strong, the splitting can be averaged out by chemical exchange or quadrupole relaxation of the neighbouring nucleus. A few spin–spin couplings have however been reported. Several organophosphorus and inorganic phosphorus compounds have been studied by Christ and Diehl[34] and oxygen–phosphorus coupling constants were found to range from 100 to 200 c./sec. The ^{17}O resonance of water diluted in acetone is a 1 : 2 : 1 triplet as would be expected from spin–spin coupling with 2 equivalent protons under conditions of slow proton exchange[35] (Figure 3).

Fig. 3 *The* ^{17}O *spectrum of* $H_2{}^{17}O$ *dissolved in acetone. The structure is due to spin–spin coupling with the two equivalent protons of the water molecule* [From J. Reuben, A. Tzalmona, and D. Samuel, *Proc. Chem. Soc.*, 1962, 353]

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[33] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 1963, **38**, 836.

[34] H. A. Christ and P. Diehl, *Helv. Phys. Acta*, 1963, **63**, 170.

[35] J. Reuben, A. Tzalmona, and D. Samuel, *Proc. Chem. Soc.*, 1962, 353.

A nice example of spin–spin coupling between oxygen and a nucleus having a spin higher than $\frac{1}{2}$ is provided by the spectrum of ^{17}O-enriched perchlorate ion.[36] The spectrum of this ion has four lines of equal intensity with a splitting of 86 c./sec. due to spin–spin interaction with ^{35}Cl. In the ClO_4^- ion the chlorine nucleus is at a centre of cubic symmetry and consequently has a long spin–lattice relaxation time. In contrast the ^{17}O-labelled chlorate ion, ClO_3^- shows only one resonance line because the expected splitting is cancelled by quadrupole relaxation of the chlorine.

The ^{17}O spectrum of $Xe^{17}OF_4$ shows a triplet with a strong central peak and two symmetrically disposed satellites.[37] The two satellites are due to spin–spin interaction with ^{129}Xe which has a spin of $\frac{1}{2}$ and a natural abundance of 26·2%. The central peak is from those molecules containing other xenon isotopes. The splitting due to spin–spin interaction with ^{131}Xe (spin $\frac{3}{2}$; natural abundance 21·2%) is washed out because of fast quadrupole relaxation of ^{131}Xe. No spin–spin coupling between Xe and ^{17}O was seen in xenic acid.[38]

E. Kinetic Measurements.—The n.m.r. method can be employed in two ways in the study of kinetics. (i) For reactions having half-lives of longer than about one minute it is possible to follow changes in the intensity of different resonances as the reaction proceeds; (ii) n.m.r. can also be used to study fast reactions at equilibrium. This method is based upon the fact that in general reactions proceeding at a rate comparable with the chemical shift or line-width of the chemical species involved will affect the shape of the resonance lines. The method has been used extensively to study proton exchange reactions but is of more limited use in the case of ^{17}O, since processes involving the transfer of oxygen are not usually fast enough to fall in the range of rates which can affect the n.m.r. line-shapes. Several types of reaction can however be studied by the line-broadening method (ii), some of which will be discussed in this and the subsequent two sections.

Considerations of price and availability favour ^{18}O as the isotope of choice in studies of oxygen exchange. In general the use of ^{18}O necessitates the separation and purification of the reacting species before their conversion into a gas suitable for mass-spectroscopic analysis. Often the time taken to separate the reaction components would be of the same order as the exchange half-life. In such cases ^{17}O n.m.r. provides an advantage over conventional tracer methods. An example is the exchange of oxygen between acetone and water. Upon dissolving acetone in $H_2{}^{17}O$ oxygen exchange occurs and the intensity of the ^{17}O resonance due to the carbonyl group increases with time. The reaction was found to be both general acid and general base catalysed, and catalysis constants for several catalysts were obtained.[22b] In a similar way it has been possible to study oxygen exchange between telluric acid and water.[39]

When a molecule has two functional groups containing oxygen, the study of

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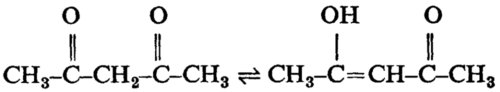
[36] M. Alei, jun., *J. Chem. Phys.*, 1965, **43**, 2904.
[37] J. Shamir, H. Selig, D. Samuel, and J. Reuben, *J. Amer. Chem. Soc.*, 1965, **87**, 2359.
[38] J. Reuben, D. Samuel, H. Selig, and J. Shamir, *Proc. Chem. Soc.*, 1963, 270.
[39] Z. Luz and I. Pecht, *J. Amer. Chem. Soc.*, 1966, **88**, 1152.

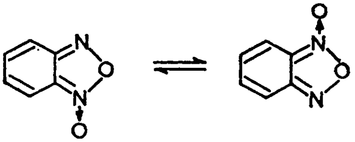
oxygen exchange would normally require tedious degradation procedures. ^{17}O n.m.r. provides a straightforward technique to deal with such cases. A simple example is levulinic acid which has both a carbonyl and a carboxyl group, the latter having been found to exchange much more slowly than the former.[40] Another example is acetylacetone in water, where there are two tautomeric forms in equilibrium:



$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \rightleftharpoons CH_3\text{-}\overset{OH}{\overset{|}{C}}=CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

Each tautomer gives one ^{17}O resonance, the keto-form at *ca.* -560 p.p.m. and the enol form at *ca.* -270 p.p.m. Using ^{17}O labelled water one can follow independently the exchange of the keto and enol forms.[41]

The use of ^{17}O line-broadening to study fast organic reactions has hardly begun. An interesting example of a fast intramolecular reaction is the rearrangement of benzofurazan oxide:[42]



At room temperature this molecule shows two ^{17}O peaks from the two nonequivalent oxygen atoms. As the temperature is raised the two peaks broaden and eventually collapse into a single peak. From the temperature at which the peaks coalesce, and by comparison with proton magnetic resonance results, the rate and activation parameters of the rearrangement reaction could be determined.[42]

Recently the line-broadening technique has been applied to the reactions of oxyanions. In a solution of periodic acid in water, no signal due to periodate ion can be detected. However, the water resonance is appreciably broader than that in pure water. This was explained by the existence of a fast oxygen exchange between periodate ion and solvent water. From the temperature-dependence of the line-width, rate constants and activation parameters for this reaction could be determined.[43]

In an aqueous solution of dichromate ion separate resonances are observed for the bridging and terminal oxygen atoms. Upon the addition of strong acid or base, the resonances broaden owing to breaking and re-forming of the chromium–oxygen bond. The reaction was studied in acidic solutions by Jackson and Taube,[8] and interpreted in terms of the acid-catalysed hydrolysis of the dichromate ion. Figgis, Kidd, and Nyholm[44] examined aqueous solutions of

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[40] H. Dahn, Proc. Conf. Prep. and Storing Marked Molecules, Brussels, 1963, Euratom, 1964, p. 1303.

[41] Z. Luz and B. L. Silver, *J. Phys. Chem.*, 1966, **70**, 1328.

[42] P. Diehl, H. A. Christ, and F. B. Mallory, *Helv. Chim. Acta*, 1962, **45**, 504.

[43] I. Pecht and Z. Luz, *J. Amer. Chem. Soc.*, 1965, **87**, 4068.

[44] B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Canad. J. Chem.*, 1965, **43**, 145.

sodium dichromate to which varying amounts of NaOH were added. In these solutions both chromate and dichromate ions exist and the results were interpreted in terms of the nucleophilic attack of CrO_4^- on $Cr_2O_7^{2-}$.

F. Proton Transfer in Water.—The process of proton transfer in aqueous solutions is of fundamental importance in the chemistry of electrolyte solutions. Meiboom[45] has shown that the kinetics of these reactions can be studied from the effect of ^{17}O on the proton magnetic resonance of water. In normal water only one proton line is observed and since there is only one distinct magnetic environment no broadening of this line is expected due to proton exchange between different water molecules. If the water contains a certain amount of ^{17}O atoms, they will provide additional magnetic environments through spin–spin interaction between protons and ^{17}O nuclei. In practice even in highly enriched water the proton magnetic resonance spectrum does not display the expected six satellites because the splitting is partially averaged out by the oxygen quadrupole relaxation and by proton exchange.[45] However, in pure water and neutral aqueous solutions exchange is still not fast enough completely to average out these lines, and the excess of width of the proton line over the corresponding width in water unenriched in ^{17}O provides a measure of the rate of proton exchange between water molecules. Addition of acid or base increases the rate of proton exchange *via* the reactions

$$H_2O + H_3O^+ \xrightarrow{k_1} H_3O^+ + H_2O$$

$$H_2O + OH^- \xrightarrow{k_2} OH^- + H_2O$$

which results in a narrowing of the proton line. From the pH-dependence of the proton line-width Meiboom[45] derived values for k_1 and k_2 of $10{\cdot}6 \times 10^9$ l.mole^{-1}sec.$^{-1}$ and $3{\cdot}8 \times 10^9$ l.mole^{-1}sec.$^{-1}$ respectively. The activation parameters for k_1 and k_2 have also been determined by the same method.[46,47]

The technique of using ^{17}O-enriched water has been applied to studies of proton transfers between solvent water and solute molecules (trimethylammonium ion).[48] It is particularly useful in cases where proton exchange is too fast to give separate proton signals for water and solute and has been used to study proton exchange in aqueous solutions of acetate, phosphate, and phenolate buffers.[49]

Proton exchange is also expected to affect the ^{17}O n.m.r. line-shape.[45] At low rates of proton exchange the ^{17}O resonance of water should be a triplet owing to spin–spin interaction with the two protons. However, proton exchange partially averages this splitting and in pure water only one broad ^{17}O line is observed,

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[45] S. Meiboom, *J. Chem. Phys.*, 1961, **34**, 375.

[46] A. Loewenstein and A. Szoke, *J. Amer. Chem. Soc.*, 1962, **84**, 1151.

[47] Z. Luz and S. Meiboom, *J. Amer. Chem. Soc.*, 1964, **86**, 4768.

[48] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1963, **39**, 366.

[49] Z. Luz and S. Meiboom, *J. Amer. Chem. Soc.*, 1963, **85**, 3923; 1964, **86**, 4764; 1964, **86**, 4766.

although at low temperature the line-shape indicates the presence of some structure.[50] This line narrows upon addition of acids or bases owing to the proton exchange reactions discussed above. In principle the changes in the ^{17}O line-width could be used to derive values for proton transfer reactions. Direct measurements on the ^{17}O resonance do not however have an advantage over proton resonance studies, since the range of broadening of the oxygen resonance is limited. On the other hand, the broadening of the proton resonance can, within limits, be fixed by the ^{17}O concentration used, and accurate line-width measurements can be done especially by the spin echo technique.

G. Hydration of Metal Ions.—The ^{17}O nucleus provides a unique chemical probe for studying the hydration of ions in aqueous solution, in particular solvation numbers and the lifetime of water molecules in the solvation shell. In some cases the solvation number of the ion can be determined directly. The interpretation of the nuclear magnetic resonance results differ for paramagnetic and diamagnetic ions. In paramagnetic ions the interaction with the electron spin often results in large shifts and line-broadening. In contrast with the situation for paramagnetic ions the ^{17}O resonance due to the solvation shell of diamagnetic ions is not appreciably broadened and is almost unshifted from the position of the resonance of the bulk solvent. Paramagnetic ions will be considered first.

The ^{17}O resonance of water in dilute solutions of the bivalent ions of the first transition-metal series is broadened and shifted relative to the resonance of pure water.[51] This effect can be understood[29,52] by considering a model in which there are two magnetic environments possible for the solvent molecules: (i) free solvent, and (ii) the co-ordination shell of the paramagnetic ion. In the latter environment the scalar and dipolar interactions between the ^{17}O nucleus and the unpaired spin of the ion cause rapid relaxation and large contact shifts of the ^{17}O resonance. In principle it would be expected that two separate ^{17}O peaks would be observed, but chemical exchange of solvent between the two environments broadens the peaks. Swift and Connick[29] have treated the case in which the number of nuclei in the bulk far exceeds the number in the co-ordination shell (dilute solutions), and derived expressions relating the line-width and shifts of the bulk resonance to the exchange rate. From the temperature-dependence of the ^{17}O resonance in aqueous solutions of the ions Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} they were able to derive values for the lifetime of water molecules in the first co-ordination sphere of the cations and the activation energy for the hydration–dehydration reaction.[29,53] From the rate constants found[29] for the hydration of Ni^{2+} and Co^{2+}, it could be predicted that separate peaks for the bulk and solvation shell molecules would be observable below room tempera-

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[50] J. A. Glasel, *Proc. Nat. Acad. Sci.*, 1966, **55**, 479.

[51] (*a*) R. E. Connick and R. E. Poulson, *J. Chem. Phys.*, 1959, **30**, 759; (*b*) R. E. Connick and E. D. Stover, *J. Phys. Chem.*, 1961, **65**, 2075.

[52] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 2686.

[53] See also W. B. Lewis, M. Alie, and L. O. Morgan, *J. Chem. Phys.*, 1966, **44**, 2409.

ture, and it was indeed possible to observe two separate ^{17}O peaks in both cases.[25,26]

In aqueous solutions of diamagnetic salts one would expect to observe separate ^{17}O resonances due to the bulk solvent and the hydration shell of the cations, provided the exchange rate between the two sites is small compared with the chemical shift between the two resonances and, of course, provided the two lines do not overlap. In fact in the spectrum of an aqueous solution of the ion $[(NH_3)_5CoOH_2]^{3+}$ a separate ^{17}O signal appears owing to water bonded in the complex.[54] A number of other salts fail to show a separate signal from the hydration shell in aqueous solution, although it is known that for some of them the hydration shell does not exchange rapidly with the bulk solvent. Jackson, Lemons, and Taube[54] speculated that the signal of the cation hydration shell falls below that of the bulk solvent, and had the ingenious idea of shifting the latter signal by the addition of a small amount of Co^{2+} ion. This ion, as explained above, will shift the resonance line of free bulk water towards low field, but will not affect the position of the hydration shell signal provided this shell does not exchange water molecules rapidly with the bulk. By use of this technique it was possible to observe separate resonances at room temperature for the solvation shells of Al^{3+}, Be^{2+}, and Ga^{3+}. No separate signal was found for H^+, Li^+, Mg^{2+}, Ba^{2+}, Sn^{2+}, Hg^{2+}, or Bi^{3+} indicating that the solvation shells of these ions exchange quickly with the solvent. Where a comparison can be made, these findings are consistent with other evidence on the exchange rates of the solvation shell.

If highly enriched water is used the study of the solvation shell can be put on a more quantitative basis, *i.e.*, hydration number, and the rate of exchange of the hydration shell, can be determined. One method is to determine the relative amounts of bound and free water from the integrated intensities of the n.m.r. signals corresponding to the two types of water. From the known concentration of electrolyte, the hydration number of the cation can be calculated. This method has been applied to Al^{3+} and Be^{2+} by Connick and Fiat,[55] using water enriched to 11·48% in $H_2{}^{17}O$. Average values were found of 5·9 and 4·2 respectively for the hydration number of these ions. Recently these authors have also determined the hydration number of Ga^{3+}, which was found to be six.[55b]

The shift caused by a paramagnetic ion having a labile solvation shell is inversely proportional to the amount of free water in the solution. Thus if the solution also contains a cation that ties up water in its solvation shell, the amount of free water decreases and its shift for a given amount of paramagnetic ion will accordingly increase.[54] This fact has been exploited by Alei and Jackson[56] to study the hydration number of Al^{3+}, Be^{2+}, and Cr^{3+}. These authors used Dy^{3+} to shift the water line and the values obtained for the hydration numbers were

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[54] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 1960, **32**, 553.

[55] (*a*) R. E. Connick and D. Fiat, *J. Chem. Phys.*, 1963, **39**, 1349; (*b*) D. Fiat and R. E. Connick *J. Amer. Chem. Soc.*, 1966, **88**, 4754; T. J. Swift, O. G. Fritz, and T. A. Stephenson, *J. Chem. Phys.*, 1967, **46**, 406.

[56] M. Alei, jun. and J. A. Jackson, *J. Chem. Phys.*, 1964, **41**, 3402.

5·9, 3·8, and 6·8 respectively. Considering the experimental error in the measurements the last figure does not agree with the value of 6·0 found by the isotopic dilution method.[57] Alei and Jackson suggested that the discrepancy can be explained by the existence of a second solvation shell which does not exchange very quickly with the bulk.

The technique of shifting the water line is generally applicable to the case of a signal suspected of lying beneath the solvent water line. For example, in aqueous solution chloral is completely hydrated, but fails to give a ^{17}O signal. Addition of Dy^{3+} to the solution shifts the water line and reveals the resonance due to the *gem*-diol oxygen atoms of chloral hydrate.[22a]

3 Electron Spin Resonance

A. Hyperfine Splitting.—Electron spin resonance spectra of free radicals exhibit hyperfine structure caused by the Fermi contact interaction. The ^{17}O nucleus has a spin quantum number of $\frac{5}{2}$ and will therefore split each e.s.r. resonance line into six components. A very simple example shown in Figure 4 is the spectrum

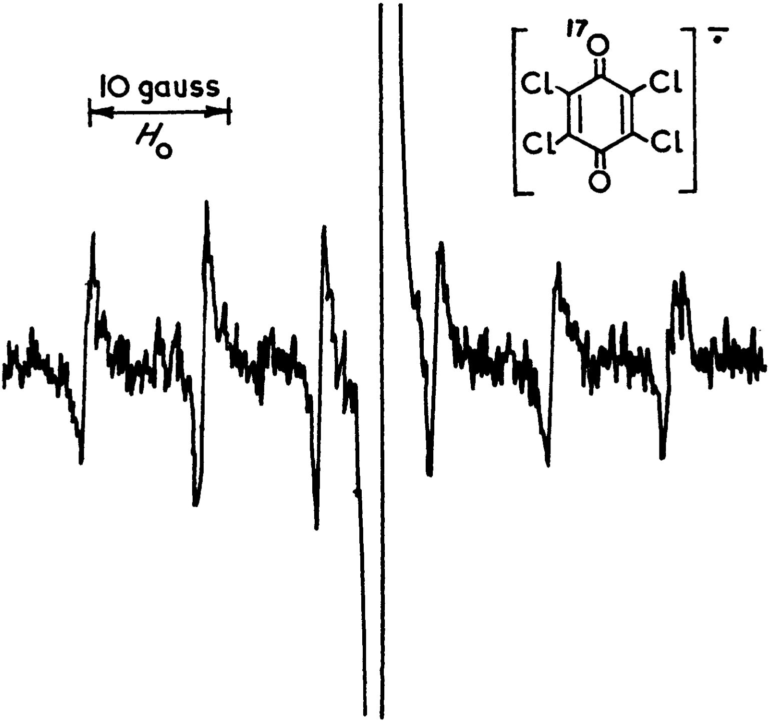

Fig. 4 *The e.s.r. spectrum of chloranil anion enriched in ^{17}O. The strong central line is due to the unlabelled compound and the six satellites to the chloranil anion containing one ^{17}O atom* [From M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, 1967, **46**, 4891]

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[57] J. P. Hunt and H. Taube, *J. Chem. Phys.*, 1951, **19**, 603.

of ^{17}O-labelled chloranil anion. A collection of splitting constants due to ^{17}O in some free radicals is given in the Table.

^{17}O *Hyperfine coupling constants*, a_O, *in free radicals*

Radical	*Solvent**	$\lvert a_O \rvert$ (G)	*Spin density on oxygen*
1,4-Benzosemiquinone[a]	DMF	9·53	0·2477[g]
1,4-Naphthasemiquinone[a]	DMF	8·58	0·2224[g]
9,10-Anthrasemiquinone[a]	DMF	7·54	0·1964[g]
2,5-Dichloro-1,4-benzosemiquinone[a]	DMF	9·28	0·2356[g]
Chloranil anion[a]	DMF	8·98	0·2244[g]
2,5-Diphenyl-1,4-benzosemiquinone[a]	DMF	9·07	—
2,5-Dioxo-1,4-benzosemiquinone[a]	H_2O	4·57	0·1515[g]
3,6-Dichloro-2,5-dioxo-1,4-benzosemiquinone[a]	H_2O	4·79	0·1516[g]
2,4,6-Triphenylphenoxyl[b]	N.S.	9·7	—
2,4,6-Tri-t-butylphenoxyl[c]	N.S.	10·23	0·174[c]
Nitrobenzene anion[d]	CH_3CN	8·66	0·195[h]
Di-s-butylnitric oxide[e]	C_6H_6	19·71	0·651[i]
Fremy's salt	H_2O	20·6	0·651[i]
FOO[f]	CF_4(liq)	22·17	—
		14·50	—

*DMF = Dimethylformamide; N.S. = Not specified.
[a] Ref. 58; [b] Ref. 11; [c] Ref. 10; [d] Ref. 12; [e] Ref. 9; [f] Ref. 15; [g] Calculated[59] by Hückel molecular orbital method using $a_O = \alpha + 0{\cdot}40\beta$ $\beta_{CO} = 1{\cdot}38\beta$; [h] Ref. 59*b*; [i] G. Bertier, H. Lemaire, A. Rassat, and A. Veillard, *Theoret. Chim. Acta*, 1965, **3**, 17.

Hyperfine structure has proved to be a rich source of information on the electronic structure of free radicals. The basis for this information is the well-established correlation that has been shown to exist[59] between spin densities and hyperfine interaction constants of ^1H, ^{14}N, and ^{13}C. A similar correlation between spin-density distribution and a_O has been shown to hold for a_O in *p*-semiquinones:[58]

$$a_O = -40{\cdot}5\rho_O + 6{\cdot}4\rho_C$$

where ρ_O and ρ_C are the $p\pi$ spin densities on the oxygen and neighbouring carbon atom respectively (as calculated by the Hückel molecular orbital method with the parameters given in footnote *g* of the Table). Although the value of the coefficient of ρ_C is not very certain, there can be no doubt that in this case the major contribution to a_O arises from the spin density on the oxygen atom itself.

The signs of hyperfine coupling constants are of great theoretical importance. From the analysis of the line-widths of the e.s.r. spectra, it was possible to show

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[58] M. Broza, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, 1967, **46**, 4891.

[59] (*a*) H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764; (*b*) P. H. Reiger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609; (*c*) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

that the sign of a_O is the same as the (negative) sign of γ_O, the gyromagnetic ratio of oxygen, in both benzosemiquinone[13a] and Fremy's salt.[14] In most other cases there are line-width variations which indicate a similar sign for a_O.[12,15,59] The physical significance of this is that the net spin polarisation at the ^{17}O nucleus is parallel with the total spin of the radical.

B. Electron Spin Resonance Line-widths.—E.s.r. spectra often show variation in line-width between different hyperfine components, as seen for example for chloranil anion in Figure 4. The general theory for e.s.r. line-widths[60] predicts marked effects on the line-widths of hyperfine components due to nuclei having a high spin density and high magnetic moment. Since ^{17}O has a relatively high spin quantum number and often carries high spin densities, it furnishes an excellent probe with which to test the theory. Good agreement with the theory of line-widths was in fact found for the ^{17}O satellites of *p*-benzosemiquinone[13a] and Fremy's salt,[14] in the spectra of which large line-width variations are seen.

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[60] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 326.