

GENERAL DISCUSSION

At one point during the Discussion, **Prof. E. L. Hahn** (*Berkeley*) raised the general question of the potential value to chemists of multipulse line-narrowing techniques and cross-polarization, double resonance techniques. It is convenient to separate the replies to Prof. Hahn's query from the main body of the Discussion, so they are printed first.

Dr. P. Mansfield (*Nottingham*) said: The question as to whether multiple pulse techniques will ever gain the popularity and acceptance of chemists as a tool for "high resolution" studies of spin systems seems to me to depend on several factors.

The first is that the heyday of multipulse development was undoubtedly the period from 1968–1973. In this five year period sophisticated schemes were developed for homonuclear line narrowing which culminated in some very efficient fully compensated cycles which, for reasons about which we can only speculate, have not yet been properly exploited by physical chemists interested in pure application. But in any case, it seems that new ideas, especially complicated ones, usually take about 5 years to emerge and be adopted, so one must be patient.

During the last 5 years, one or two groups have sprung up and are using multiple pulse sequences both in Europe and America. But often they are using the simplest, and therefore the least efficient, cycles. I can only assume that the apparent complexities of the 16 pulse cycles (and longer) frighten off the prospective user.

However, I would like to urge interested researchers into trying some of the more sophisticated pulse sequences. With the possibility which now exists of fully compensating cycles for various pulse imperfections, the sequences are relatively easy to set up and once set up remain stable for days.

The second point is that originators of the multipulse schemes have, without exception, all been apparatus designers and builders as well. Whilst commercial firms offered the necessary number of r.f. channels and pulse programmers to enable some of the first multiple pulse sequences to be performed at an early stage in their development, it would seem that few, if any, people were able to obtain results with the commercial equipment. In this respect, it must be pointed out that we had found r.f. stability and phase coherence rather important instrumental factors. However, as far as I know, modern commercial machines are now capable of performing multiple pulse experiments in solids. Indeed, one can now buy a computer controlled programmer with sufficient flexibility to perform some of the more sophisticated cycles referred to earlier.

I can only assume that the lack of success with those early commercial machines dulled the appetite of the more adventurous chemists and physicists who by and large have now moved on to other things.

The third point concerns the value of experimental results obtained by multiple pulse experiments. The popularity of ^{13}C double resonance experiments and the wealth of information coming from them should kill the old myth, still put about by some chemists, that interest lies only in the isotropic chemical shielding tensor. The full shift tensor contains valuable information on the bonding and structure of molecules and would, I feel sure, be the normal expectation if it were not considered too

difficult to measure. My feeling is that, as with ^{13}C experiments, there is a wealth of information to be obtained from combined multipulse and sample spinning experiments and this approach has only just begun to be tried and investigated by a few groups.

I do not see multipulse experiments as in some way competing with low abundance double resonance experiments. It is simply a matter of which nucleus is of interest. Undoubtedly ^1H and ^{19}F (in solids) must always be studied by multipulse methods. However, although 100 % isotopically abundant, ^{31}P is a good candidate for double resonance experiments. But I am bound to say that in our own ^{31}P - ^1H double resonance work (unpublished), results were somewhat disappointing, invariably because of the very short rotating frame spin-lattice relaxation times of the protons.

In some of the materials we studied, the ^{31}P - ^{31}P dipolar interaction also seemed to be important so that some combined form of multipulse and double resonance experiment was indicated.

Dr. A. N. Garroway (*Washington*) said: Cross-polarization techniques are many times combined with magic angle spinning, so that both dipolar and chemical shift anisotropy broadenings are suppressed. Multiple pulse methods are generally applied in single crystals or when the spectrum is sufficiently simple that anisotropy effects are not a severe complication. Most chemists, with backgrounds in proton or ^{13}C liquid state spectroscopy, are reluctant to embrace single crystal studies, especially of complex molecules. Cross-polarization and magic angle spinning, on the other hand, give spectra not too different than in the liquid state. I think that the popularity of cross-polarization techniques, at least in the newest commercial spectrometers, reflects more the ease of its marriage to magic angle spinning, rather than the inherent difficulties of each technique.

Dr. R. K. Harris (*Norwich*) said: One very good measure of the immediate potential of techniques such as these is the involvement of commercial companies, since they respond to what they see as the market demand from chemists interested in applications. Several companies are already offering equipment for the cross-polarisation, magic angle spinning experiment and others are developing such equipment. There is much less commercial activity on multiple-pulse experiments. In my view this implies that, at least in the medium term, the cross-polarisation technique is going to be more utilised than multiple pulse experiments.

Dr. K. J. Packer (*Norwich*) said: It is a fact that the single-resonance multiple pulse-cycle techniques for suppression of homonuclear dipolar interactions are complementary to the dipolar-decoupling, cross-polarisation, magic angle spinning techniques in that they are not applicable to the same systems. The former generally are applicable to abundant spin-species such as ^1H and ^{19}F whereas the second group of techniques require the dilute spin/abundant spin combination. It is generally believed by chemists, however, that the multiple pulse techniques are rather more demanding on apparatus and experimenter than the double resonance methods and as such have not yet proved particularly popular as a tool for the chemist. On the other hand there is every evidence that the double-resonance methods are in the process of being adopted and developed in a large number of chemistry laboratories and commercial manufacturers of n.m.r. spectrometers are already offering equipment for this type of work. Time will tell whether this is the correct choice for large scale applications work but it is my opinion that it is.

Dr. P. Mansfield (*Nottingham*) said: I would like to comment on Dr. Erofeev's paper, as follows:

Most of the early work on multipulse experiments was performed at or close to resonance and the theories developed were based on the projection of magnetization loss at the second solid echo. This procedure gives an exponential decay of successive echo peaks with an effective decay time constant $T_{2e} \propto \tau^{-5}$. This rather simple approach seemed to be confirmed by the experimental behaviour of the ^{19}F resonance in single crystals of CaF_2 . Indeed, the τ^{-5} dependence appeared to be confirmed over three and a half decades of T_{2e} variation in these experiments.

Further unpublished work on ^{31}P in powdered Zn_3P_2 performed by Dr. K. Richards in 1969 and now shown in fig. 1, also strongly suggests that T_{2e} is proportional to

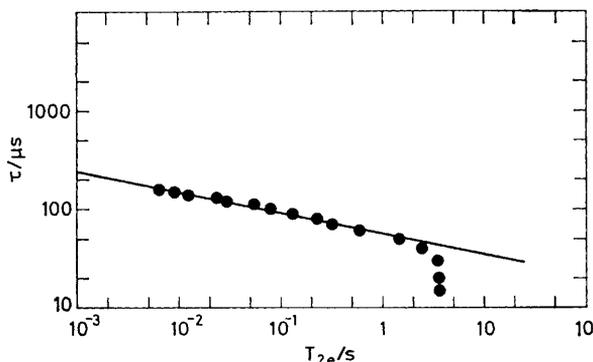


FIG. 1.—Plot of τ against T_{2e} for ^{31}P in powdered Zn_3P_2 . Slope of solid line is -5 .

τ^{-5} over about three decades. The 90° r.f. pulse lengths used in these experiments were approximately $2.0 \mu\text{s}$. The solid line in fig. 1 is drawn with a slope of -5 . The plateau in T_{2e} above 2.0 s is caused by rundown of the power supply with consequent degradation of the r.f. pulses from 90° to a smaller angle. In spite of this fact, however, the magnitude of T_{2e} is observed to vary exponentially from about 50 ms to a value in excess of 1.0 s before equipment limitations are manifest.

The shortest value of the pulse spacing, τ , which still gives a good fit on the solid line, is about $50 \mu\text{s}$. The relatively longer T_2 of the phosphorus resonance allows a larger pulse spacing than could be used for ^{19}F in CaF_2 , but still produces a greater effective line narrowing. In this sense, the experiment corresponds much more to the ideal case where delta function 90° r.f. pulses are used.

A difference between CaF_2 and Zn_3P_2 , which might play a significant role in producing the τ^{-5} dependence, is that ^{31}P exhibits some chemical shift anisotropy. This means that unlike ^{19}F in CaF_2 , there is a built-in offset effect. On the other hand, as I recall, for relatively small offsets, there were no significant changes in T_{2e} .

More recent work on line narrowing sequences like the MREV 8 cycle, for example, which is specifically designed to work off resonance, shows a comfortable consistency with the τ^{-5} results on resonance, in that theoretically the line width W slightly off resonance varies as $W \propto \tau^4 / \Delta\omega$ where $\Delta\omega$ is the offset angular frequency. This behaviour seems to be confirmed experimentally. Dr. Erofeev's paper raises several questions: (1) How are the different quantal absorption processes referred to in fig. 4 of his paper measured experimentally? In particular, how is the process characterized by the operator $\hat{R}_3(t)$ isolated? (2) For τ less than $6.0 \mu\text{s}$, there is a decrease in T_{2e} indicated. Is this a pulse degradation effect similar to the one described above? (3) It is difficult to tell from the data corresponding to the $\hat{R}_4(t)$ process how good a fit

it is to a slope of -4 . In view of the roll-off for $\tau < 6.0 \mu\text{s}$, and the fact that T_{2e} is observed over less than two decades could it be that the observed slope is itself a manifestation of pulse droop?

Prof. T. C. Waddington (*Durham*) (*communicated*): Could Dr. Haeberlen comment on the sensitivity of his final values for the difference tensor, $\sigma_{\text{exptl}}^1 - \sigma_{\text{calc}}^1$, to his chosen values of $\chi(\text{Pb}^{2+})$ and $\chi(\text{Ca}^{2+})$? The reason I ask is that the value chosen in the paper for $\chi(\text{Ca}^{2+})$, -27×10^{-6} , is nearly twice the value of $\chi(\text{K}^+)$ selected by Trew and Husain,¹ and also supported by my own analysis² of the theoretical calculations and magnetic susceptibility data, $\chi(\text{K}^+) = -14.5 \times 10^{-6}$. The tighter nuclear binding of the electrons in the isoelectronic Ca^{2+} ion would lead one to expect a lower value for $\chi(\text{Ca}^{2+})$ than for $\chi(\text{K}^+)$.

It is very difficult to establish an accurate value for $\chi(\text{Ca}^{2+})$ but two separate calculations, using the range of values of $\chi(\text{Mg}^{2+})$ given by Trew, Husain and Siddiqi³ and then (a) assuming $\chi(\text{Mg}^{2+})/\chi(\text{Ca}^{2+}) = \chi(\text{Na}^+)/\chi(\text{K}^+)$ or (b) taking the difference between the measured values of $\chi(\text{CaO})$ and $\chi(\text{MgO})$, give a value for $\chi(\text{Ca}^{2+})$ of between -6×10^{-6} and -8×10^{-6} .

Dr. U. Haeberlen (*Heidelberg*) (*communicated*): As a matter of fact the value chosen for $\chi(\text{Ca}^{2+})$ was not -27×10^{-6} , as given in the paper, but -22×10^{-6} c.g.s. units. I am grateful to Prof. Waddington for drawing my attention to this error. In order to bring internal consistency into his numbers, I must assume that the number quoted for $\chi(\text{Mg}^{2+})$, $(-6 - -8) \times 10^{-6}$ c.g.s. units, is actually meant to be the value for Ca^{2+} . If we insert a number in this range in the formula for σ_{inter} , eqn (1) of my paper, it is not possible to obtain for the two proton sites in Ca-formate proton shielding tensors which have the same characteristics, *i.e.*, which have their most, intermediate and least shielded directions along the *same* molecular directions. The value we have chosen for $\chi(\text{Ca}^{2+})$ was obtained by comparing experimental susceptibilities of Pb— and Ca salts, and by assuming $\chi(\text{Pb}^{2+}) = -47 \times 10^{-6}$ c.g.s. units. We are well aware that this procedure may introduce some uncertainties, indeed, the need of molecular and ionic susceptibilities, which are not themselves experimentally definable quantities, is one of the critical points in our analysis of intermolecular shielding contribution.

Dr. P. Mansfield (*Nottingham*) said: In spite of the remarkably fine data presented on amongst other compounds, calcium formate, where ^1H line widths of 34 Hz are quoted, Haeberlen refers to the general difficulty of performing such line narrowing experiments except in well chosen single crystals. All the work reported has been achieved using the phase compensated MREV 8 multipulse sequence. In this cycle, it is necessary to perform the experiments off resonance, in order to achieve additional offset line narrowing or second averaging. It is well known, however, that too much offset, either introduced experimentally or caused by intrinsic chemical shifts, results in a broadening of the line. (A shift of 5 p.p.m. at 240 MHz is after all nearly 1.0 kHz!)

For comparison with other line narrowing sequences, the unscaled line width for ideal 90° r.f. pulses should be multiplied by $3/\sqrt{2}$ resulting in a true line width of about 72 Hz for the protons in $\text{Ca}(\text{HCOO})_2$.

There are a few multipulse cycles which although somewhat more complicated

¹ V. C. G. Trew and S. F. A. Husain, *Trans. Faraday Soc.*, 1961, **57**, 223.

² T. C. Waddington, *Trans. Faraday Soc.*, 1966, **62**, 1482.

³ V. C. G. Trew, S. F. A. Husain and A. J. Siddiqi, *Trans. Faraday Soc.*, 1965, **61**, 1086.

than the MREV 8 cycle, are slightly better at line narrowing, especially near to resonance. The PP 16 pulse sequence (see my paper) is one such cycle which has a scaling factor of $\sqrt{6}$ for ideal pulses. Nevertheless for a single crystal of CaF_2 the ^{19}F resonance with \mathbf{B}_0 along the [111] direction yields a true scaled line width of 70 Hz. with $\tau = 6.4 \mu\text{s}$. It would be interesting to see how well the PP 16 cycle performs for ^1H on Dr. Haeberlen's spectrometer.

Dr. U. Haeberlen (Heidelberg) said: We have not tried the PP 16 cycle on our spectrometer. I am hesitant of using cycles with ever smaller scaling factors. There are good reasons to believe that the minimum linewidths which we have seen both from Ca-formate and CaF_2 were not limited by any property of the multiple pulse sequence used but rather by such seemingly trivial things such as applied field homogeneity. Remember we cannot shim using the actual crystal samples, the values of T_1 are simply too long. When "true" linewidths are down to ≈ 100 Hz or so the shape of the samples and details of their mountings have a strong influence on the ultimate resolution. This may not be so at 9 MHz, but it is certainly true for spectrometer frequencies of 90, and, *a fortiori*, 270 MHz. In spite of using spherical crystal samples and a "shim sample" of doped water matching in its geometry closely the crystal samples, we have not mastered fully the applied field homogeneity problem. I would like to stress that, although we are never satisfied with the resolution achieved, we feel that meaningful applications of the multiple pulse techniques, see, *e.g.*, your paper, and interpretation of actual data obtained at some limited resolution are what is called for now and not so much the hunt for new records in terms of linewidths.

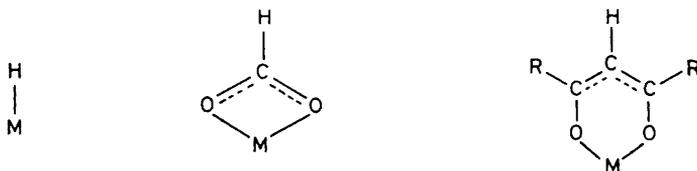
Dr. Joan Mason (Open University) (communicated): Measurements such as those reported by Dr. Haeberlen, given that they require great expertise and resourcefulness, offer a unique opportunity to test and improve the theory of "distant" contributions to nuclear magnetic shielding. Because of well-known difficulties of shielding theory, many or most theoretical treatments are restricted to the local term (arising from electrons on the resonant atom only). The "distant" contribution, therefore, includes even those from next (bonded) neighbours, although the local term cannot of course be observed separately from these. Recourse to neighbour anisotropy approximations for the distant terms raises intractable problems: of the extension of the neighbouring dipoles (since point dipoles give poor results) and their positioning (whether on atoms or bonds), as well as the distance at which the approximation is expected to be valid (discussed by Dr. Haeberlen). Flygare has remarked that group anisotropies derived from n.m.r. shift measurements are usually too small, and sometimes not even of the right sign (adding "The fact that magnetic susceptibility anisotropies derived from chemical shifts agree so poorly with direct measurements would seem to indicate that some other contribution to the chemical shift has not been properly evaluated.")¹

Dr. Haeberlen's experiments with metal formates have important advantages for a study in which the shielding contributions from the resonant atom and the near neighbours are held effectively constant, so that the variation in the distant contribution from different cations can be measured. Advantages are the high sensitivity of the proton, the small local shielding and the relatively large metal ion contribution. Furthermore, with isostructural M^{II} formates, the variation in the shielding tensor should correlate with the increase in magnetic susceptibility of the cation down the

¹ T. G. Schmalz, C. L. Norris and W. H. Flygare, *J. Amer. Chem. Soc.*, 1973, **95**, 7961; W. H. Flygare, *Chem. Rev.* 1974, **74**, 653; *cf.* also W. Haberditzl, *Angew. Chem. (Int. Edn)*, 1966, **5**, 288.

group of the periodic table, and the tendency (with the usual periodic irregularities) to decrease across the row.¹

If the technical difficulties can be surmounted, the variation in the shielding contribution with distance from the metal ion and also with its electron configuration, might be observed by comparison (for example) of the proton shielding in the metal hydride, formate and a suitable acetylacetonate, with appropriate metal ions.



In the acetylacetonates the (isotropic) shielding of the 3-proton tends to increase down the group of the metal, and decrease across the row.²

As an improvement on the dipole approximation, simplified versions of the Ramsey theory have been used to calculate the shielding tensor for ^{19}F in crystalline MgF_2 ³ and for the proton in d^6 and d^8 metal hydrides⁴ and have been given also for d^{10} and $d^{10}s^2$ ions such as Hg^{II} and Pb^{II} .^{5,6} Information on the shielding tensor of a proton attached to a transition metal is eagerly awaited by inorganic chemists.

Dr. A. M. Achlama (*Rehovot*) said: Dr. Y. Zur and I have measured the e.f.g. tensors at the carboxylic and olefinic deuterons in potassium hydrogen maleate. As has been pointed out by Prof. J. A. S. Smith, the orientation of the e.f.g. tensor of the carboxylic deuterons was the same as that of the chemical shift tensor of these protons.⁷ In the case of the olefinic fragment, however, the *least* shielded component was in the direction of the C–H bond,⁸ but this also was the direction of the *largest* component of the (nearly axially symmetric) e.f.g. tensor. This component was in the molecular plane, building an angle of $117.3 \pm 0.3^\circ$ with the C=C bond, whereas the crystallographic value for the C–H bond direction was $115.8 \pm 1.5^\circ$.⁹

Intermolecular interactions have been invoked for the interpretation of spectra of potassium hydrogen maleate, where only olefinic protons have been substituted by deuterons. Pake doublets have been observed in the spectra of these deuterons, originating in the dipolar interaction with the carboxylic proton of a neighbouring molecule.

Dr. J. W. Emsley (*Southampton*) (*partly communicated*): The paper by Morris *et al.* is ambiguous about the presence of internal motion in the perfluoroalkyl chain. It is claimed that X-ray data and the S values show the impossibility of an all-*trans* configuration for the chain. But, if rotational isomerism occurs the CF_2 groups will have S values which vary along the chain, a conclusion rejected on the basis that the

¹ P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1956); G. Malli and S. Fraga, *Theor. Chim. Acta*, 1966, **5**, 284.

² J. Mason, unpublished observations.

³ R. W. Vaughan, D. D. Elleman, W. K. Rhim and L. M. Stacey, *J. Chem. Phys.*, 1972, **57**, 5383.

⁴ A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747 and 4583.

⁵ L. E. Orgel, *Mol. Phys.*, 1958, **1**, 322.

⁶ W. G. Schneider and A. D. Buckingham, *Disc. Faraday Soc.*, 1962, **34**, 137.

⁷ A. M. Achlama, U. Kohlschütter and U. Haeberlen, *Chem. Phys.*, 1975, **7**, 287.

⁸ A. M. Achlama, H. Post and U. Haeberlen, *Chem. Phys.*, 1978, **31**, 203.

⁹ S. F. Darlow, *Acta Cryst.*, 1961, **14**, 1257.

^{19}F spectra can be reproduced by a model which uses a constant S_{CF} value for each part of the alkyl chain, excepting the end CF_3 . This contradiction may be a consequence of the assumptions made in analysing the data, which for convenience I will discuss in separate parts.

(1) The experiments measure $\bar{\sigma}_{\parallel}^i$ the partially-averaged component of σ^i along the director (or perpendicular in the case of the hexagonal phase, but $\sigma_{\perp}^i = -\frac{1}{2}\sigma_{\parallel}^i$). This quantity $\bar{\sigma}_{\parallel}^i$ is related to components of σ^i in a molecule-fixed frame xyz , with z along a CF bond, by

$$\begin{aligned} \sigma_{\parallel}^i = & \sigma_{\text{iso}}^i + S_{zz}^i \sigma_{zz}^i + \frac{1}{3}(\sigma_{xx}^i - \sigma_{yy}^i)(S_{xx}^i - S_{yy}^i) \\ & + \frac{4}{3}S_{xy}^i \sigma_{xy}^i + \frac{4}{3}S_{xz}^i \sigma_{xz}^i + \frac{4}{3}S_{yz}^i \sigma_{yz}^i. \end{aligned}$$

The superscript i refers to the seven CF_2 groups.

In their work Morris *et al.* assume xyz to be principal axes for σ , in which case the terms involving off-diagonal elements of S are zero. But symmetry does not restrict the principal axes to lie in these directions, and hence all the terms may be significant in magnitude.

(2) If xyz is assumed to be a principal set of axes then $\bar{\sigma}_{\parallel}^i$ is $\sigma_{\parallel}^i = \sigma_{\text{iso}}^i + S_{zz}^i \sigma_{zz}^i + \frac{1}{3}(\sigma_{xx}^i - \sigma_{yy}^i)(S_{xx}^i - S_{yy}^i)$.

Even if values of σ_{zz}^i , $(\sigma_{xx}^i - \sigma_{yy}^i)$ are assumed from experiments on solids, and σ_{iso}^i from isotropic solutions, then there are still two unknowns on the RHS of the equation. It is doubtful that the lineshape for the CF_2 resonances cannot be reproduced by a model which assumes constant values of the matrix elements of σ^i as i varies, but varying values of S_{zz}^i and $(S_{xx}^i - S_{yy}^i)$.

(3) If the chain is rigid then it is possible to relate the individual $\bar{\sigma}_{\parallel}^i$ to one molecule-fixed set of axes, as suggested by Morris *et al.* However, it is not possible to choose these axes on symmetry grounds to be principal axes for S , because even in the all-*trans* shape there is at most only a molecular mirror plane. Rotation of the whole molecule does not affect this conclusion for a liquid crystal phase and thus the analogy with rotation of molecules in solids is misleading.

(4) For hydrocarbon chains in lyotropic mesogens it is usually assumed that internal motion does take place and also that it is possible to describe the partial averaging of second-rank quantities in terms of one ordering matrix which is diagonal and axially symmetric when one axis is chosen to lie along "the long axis of the molecule". However, the assumption of a single S matrix depends upon the relative rates of internal motion, v_{int} , and motion of the whole molecule relative to the director, v_{mol} . If $v_{\text{int}} \gg v_{\text{mol}}$ the averaging can be done with one S matrix, but which is not necessarily axially symmetric. If $v_{\text{int}} \ll v_{\text{mol}}$ the averaging process cannot be done with one S matrix, but must invoke a matrix S^n for all n configurations adopted by the chain, and each S^n has a differently orientated set of principal axes.

(5) I conclude with the observation that liquid crystal solutions are complex! The presence of internal motion in a mesogen introduces several additional unknown quantities and it is not possible to reach precise conclusions on conformational mobility unless there is a wealth of experimental data. I doubt that the present experiment can yield enough information to decide between rigid and flexible chains.

Dr. P. Morris (*Nottingham*) (*communicated*): For perfluoro-octanoate groups in liquid crystal phases, the ^{19}F chemical shift tensor is unquestionably axially symmetric with σ_{\parallel} oriented parallel to the long molecular axis. [See our ref. (2), fig. 4.] Our experiment measures the shift components σ_{\parallel}^i , σ_{\perp}^i ($\sigma_{\perp}^i \neq -\frac{1}{2}\sigma_{\parallel}^i$) which depend on the motional averaging in a complex manner. However, this dependence manifests itself in terms of a simple scaling S^i of the shift anisotropy $\Delta\sigma^i = \sigma_{\parallel}^i - \sigma_{\perp}^i$. Whilst

it is just conceivable that the same scaling factors S^i could arise from averaging processes which vary down the chain, the strong implication is that, within experimental error, the motion is independent of position.

To estimate "absolute" order parameters, the known shift tensor for low temperature PTFE (whose principal axis system does not correspond to the usual molecular frame) is averaged by rapid rotation about the long molecular axis. The result is an axially symmetric tensor with anisotropy $\Delta\sigma \approx 104$ p.p.m. Any reduction from this value is attributed to motion about the normal to the surfactant water interface, which can be described by a single order parameter S owing to the axial symmetry imposed by the rapid rotation. That it is not unreasonable to average over the rotation first is indicated by the good agreement obtained between the shift anisotropy of a rotating PTFE molecule calculated from the static shift tensor and that observed experimentally at room temperature.

Finally, we make the comment that higher frequency measurements would allow separation of the inequivalent ^{19}F resonances allowing accurate measurements of the shift anisotropy as a function of chain position. This would be a rather more sensitive test of the degree to which S remains constant.

Dr. G. J. T. Tiddy (*Port Sunlight*) (*communicated*): In answer to Dr. Emsley's comments, I would like to make the following observations.

Concerning his second point; it is of course possible to use more parameters (S_{zz}^i etc., dependent on i) to fit the spectrum. But we thought it generally undesirable to introduce more parameters than necessary to explain the results.

Concerning his third point; the chain is not "rigid".

Concerning point (4); for hydrocarbons, the liquid-like nature of the chains is deduced from the magnitude of transition heats for the l.c./gel phase transition (almost the same as for melting hydrocarbons), the rapid self-diffusion of surfactant ($\approx 10^{-6} - 10^{-8}$ cm² s⁻¹), the n.m.r. proton second moment (too small for rigid solids), the ^2H order parameters (also too small for rigid solids) and the absence of sharp high angle X-ray lines. However, order parameters are *similar* for the part of the chain adjacent to the head group, and only decrease for the last 3 or 4 carbons. For fluorocarbons we can say:

- (i) Transition heats for solid + H₂O \rightarrow l.c.
or solid \rightarrow liquid } have similar magnitude.
- (ii) The ^{19}F second moment is smaller than for PTFE.
- (iii) The self-diffusion coefficient $\simeq 3 \times 10^{-8}$ cm² s⁻¹ for Li PFO.
- (iv) No high-angle X-ray spacing (as might indicate ordered rigid chains).
- (v) The order parameters are too small for no molecular motion.

Thus we conclude that we have disordered chains with motion.

Now let us consider the arrangement of chains. We have data from X-rays that the fluorocarbon layer thickness is about 17 Å in our samples, and we expect ≈ 22.5 Å for a bilayer with all-*trans* chains at right angles. This is clearly inconsistent.

The three models (fig. 2) could account for the reduced bilayer thickness.

Case (a): the order parameters exclude this model with ordered packing because the tilt angle required is too large. If chains have no regular packing then they will undergo exchange between different directions and conformations and will look like (c).

Case (b): if we consider the cross-sectional area of each segment of chain the order parameter will relate (in part) to the fraction of "all-*trans*" molecules present.

Chain segments near the head group have a large surface area and so a small order parameter. Segments near the tail have *half* the surface area and so are nearly "all-*trans*". From X-ray data we estimate the surface area/mol to be 45–50 Å². Half of this is close to the area required for close-packed "all-*trans*" groups. Thus for interpenetration or interdigitation we expect very high order parameters for the terminal CF₂ and CF₃ groups (>0.6) and *low* order parameters for groups near the head group. (A rough calculation from X-rays shows that half the chain in "all-*trans*" is interdigitated.) If the first part of the chain is extended one may ask what occupies the residual space.

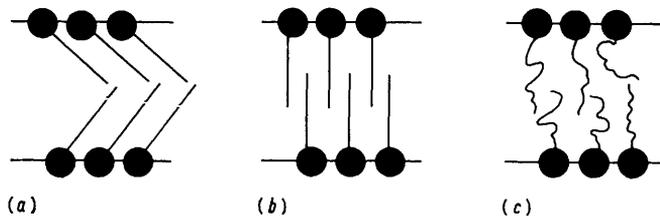


FIG. 2.—Models explaining reduced bilayer thickness: (a) tilted chains, (b) interpenetration and (c) disorder.

The solubility of fluorocarbons is less than hydrocarbons. If we suppose that H₂O is there, then the dimensions calculated from X-ray studies would be incorrect, because they involve the assumption of separate alkyl and water regions and there would be much less need to postulate any interdigitation.

Again we get higher *S* values with the hexagonal rather than the lamellar phase, in agreement with the X-ray dimensions. If the lamellar phase is interdigitated the question which naturally arises is why the hexagonal phase occurs. It is unlikely to have the same interdigitation, yet the order parameters are higher. This would suggest that our model for LiPFO is the most plausible one.

Dr. P. Mansfield (*Nottingham*) (*communicated*): In reply to Dr. Emsley's comments I would like to take each point in turn. First let me say that we do not claim that all alkyl groups along the LiPFO chain have the same order parameter *S*, only that we cannot distinguish experimentally between them. Indeed, had we the facility to work at frequencies higher than 9.0 MHz, it would be possible to separate each alkyl group, known on the basis of their high resolution isotropic shifts to be chemically slightly different. The changes in *S* along the chain, due to rotational isomerism could if present then be studied directly.

It is of course appreciated that the principal axes system for the chemical shift tensor in ¹⁹F may not quite coincide with the *z* axis lying along the C–F bond, but it seems a plausible and good approximation.

As stated above, a single value of *S* does allow quite good fits to the observed experimental data. Small changes in *S* of the order of ±0.02 give marked deviation from the best fit of our data. Such small changes in *S*, although applied to all alkyl groups along the chain, would seem to suggest that a significant spread in *S* values along the chain would result in a worse fit than we obtain.

In the rigid chain, the individual C–F bond directions are tilted (as in PTFE for example) and presumably form part of a helix. However, we assume implicitly that the C–F bonds are all normal to the chain axis. [See ref. (20) in our paper to our earlier work on PTFE.] In this case it is possible to define one transformation from

the PAX system to the MOL system. The rotational transformations about the molecular axis then follow.

It is not intended to suggest that the motion and conformation of the alkyl chain is in reality simple. However, the model of LiPFO which we have analysed does seem to give remarkably good agreement with the experimental results. Some of the agreement could well be fortuitous in the sense that higher resolution data may well indicate interesting deviations from our model. But with our present experimental limitations this must remain in the realm of speculation.

Dr. N. Boden (*Leeds*) said: The partially averaged values obtained for the principal components of the ^{19}F chemical shift tensor are seen to be essentially the same for all CF_2 groups in the perfluoro-octanoate chain in the lamellar phase. This is an interesting result which could be interpreted as implying that either (i) the amphiphile reorients as a "rigid" molecule, or (ii) all CF_2 segments are similarly affected by internal rotation. The latter behaviour would be in marked contrast to that observed for hydrocarbon amphiphiles. Nevertheless, on the basis of the consistency between the chain length calculated from

$$\langle L \rangle = 1.25 \left(\frac{n}{2} + \sum_i s_{\text{CD}} \right)$$

and that obtained from X-ray data, Morris *et al.* conclude that this is the correct explanation for their measurements. I would like to ask whether this agreement is a coincidence? The reasons why I think it might be are as follows. (a) Using the molecular dimensions given in the paper, the numerical coefficient in the above formula comes out as 1.54. (b) The table below compares values of bilayer thicknesses similarly obtained for the lamellar phase in a 45% w/w mixture of caesium perfluoro-octanoate and water.¹

temp/°C	23	25	30	35	40	45	50
$d_0/\text{Å}$ (neutron diffraction)	17.5	16.9	16.0	15.5	15.2	15.1	15.0
$d_0/\text{Å}$ (order parameter)	17.3	17.2	17.1	16.9	16.8	16.5	16.0

Note how the two sets of values cross at low temperatures, but diverge at higher temperatures, particularly in the mid-temperature range.

Dr. G. J. T. Tiddy (*Port Sunlight*) (*communicated*): If the amphiphiles are rigid and in the "all-*trans*" conformation then our order parameters would not be consistent with the bilayer dimensions. Alternative bilayer models are set out in answers to Dr. Emsley's question.

Since the equation for $\langle L \rangle$ is derived for CH_2 groups it is perhaps surprising that it fits our results, and the agreement with our results is possibly a coincidence, but, of course, the chains are *not* stiff rods.

Dr. Boden's data are for a CsPFO sample in the "nematic-lamellar phase" which has a viscosity that is sufficiently low for the sample to align in a magnetic field. Such low viscosities are unlikely with stiff chain molecules.

For example, the "gel" phases prepared from hydrocarbon surfactants, which are known to have rigid chains, have high viscosities.

The calculations of aggregate dimensions using X-ray or neutron diffraction involve an assumption about the density of the fluorocarbon layer (assumed to be independent of water thickness, *i.e.* independent of surfactant surface area). In my opinion this may not be valid and so the dimensions quoted by Dr. Boden may not be correct.

¹ N. Boden, M. C. Holmes, K. J. McMullen and P. J. Jackson, unpublished results.

I think that a correct model for the chains is one with chains having rapid motion about a long axis ($\tau_c^{\parallel} \approx 10^{-10}$ s say), and (possibly) "slow" interconversion between different conformations $\tau_c \geq 10 \tau_c^{\parallel}$. This must mean that the "free" space in the fluorocarbon layer is more than in a liquid hydrocarbon, *i.e.*, that the chains do not pack together all that well. I note that P. J. Flory, in his book *Statistical Mechanics of Chain Molecules* (J. Wiley N.Y., 1969) says on p. 157 "... a chain molecule must be endowed with a minimum tortuosity as a requisite for packing to high density in the random-coiled form ..."

Dr. J. W. Emsley (*Southampton*) said: The case of the multiple quantum spectrum of the protons in the liquid crystal 5-CB raises additional points to those mentioned for benzene. First, the interacting spins are eight protons and eleven deuterons. At least one ^2H - ^1H dipolar coupling is large (≈ 60 Hz, depending on the reduced temperature), and might be expected to affect the spectra. However, does the use of a spin-echo to improve line widths complicate the interpretation of a spectrum from strongly coupled protons which are interacting with strongly coupled deuteriums?

Secondly, the eight protons give rise to a spectrum which depends on fifteen independent parameters, twelve dipolar couplings and three shifts. Is it practicable to deduce all these quantities with high precision from the $q = 7$ and 6 spectra?

Third, computer resolution is a major problem for complex, single-quantum, proton spectra of liquid crystals. In the TPPI echo spectra it seems to be necessary to record all orders of q simultaneously, which would seem to impose even greater demands on computer storage than when only the $q = 1$ spectrum is obtained. How much computer storage is required to define the TPPI echo spectrum of 5-CB?

Mr. D. P. Weitekamp (*Berkeley*) said: The use of a single echo pulse will lead to complications in the spectrum of the proton spins to the extent that the proton deuterium interactions do not commute with the interactions between like spins. This will necessitate deuterium decoupling which could be achieved by double quantum decoupling,¹ irradiation of the quadrupole satellites of the offending deuterons,² or perhaps more simply by a train of proton π pulses during the evolution period t_1 .

The latter means of decoupling has the additional recommendation that it will simultaneously remove chemical shifts. This not only reduces the number of independent parameters, but removes those parameters most difficult to estimate and of least interest for a structural determination. Further reduction in the number of parameters is possible to the extent that one is willing to incorporate chemical intuition and literature values of certain bond distances into a model which relates the various dipolar couplings. Ultimate precision will, of course, depend on the sensitivity of resolved transitions to variations in the parameter set. A confirmation of a parameter set derived by the relatively simple analysis of the higher order spectra would be the successful calculation with this set of lower orders.

The computer storage requirements needed do indeed grow large. The time increment in the t_1 dimension needs to be sufficient for a Nyquist frequency of $N\Delta\omega$ and $\Delta\omega$ needs to be as great as the width of a single order. For $N = 8$, $\Delta\omega = 40$ kHz and a spectral resolution of 10 Hz per point, storage of 64 kwords is needed.

Dr. D. T. Edmonds (*Oxford*) said: The interpretation of a multiple quantum spectrum is tractable only if the N spin flips occur within a single system and not partially

¹ A. Pines, S. Vega and M. Mehring, *Phys. Rev. B*, 1978, **18**, 112.

² J. W. Emsley, G. R. Luckhurst, G. W. Gray and A. Mosley, *Mol. Phys.*, 1978, **35**, 1499.

within the system and partially within near-neighbour systems. Taking a single molecule as the system this means that intramolecular spin-spin interactions must be much stronger than any intermolecular spin-spin interaction.

(i) In general how do you envisage that the molecule under study be isolated from its environment and how can the efficacy of such isolation be tested experimentally?

(ii) Will the necessity for such isolation prove a serious limitation of the applicability of the technique?

Mr. D. P. Weitekamp (*Berkeley*) said: In the liquid crystal systems with which we are currently concerned, molecular diffusion reduces the intermolecular couplings and allows a treatment in terms of intramolecular terms alone. Of course, the dipole Hamiltonian does not formally distinguish between intermolecular and intramolecular terms and, in general, one would need to dilute a molecule in an isotopically distinct background to be certain that only intramolecular terms were effective.

One may prevent certain lines from developing by keeping τ much shorter than the inverse of some small dipolar couplings. This will reduce the magnitude of those transitions which depended on this coupling for their intensity and thus give some measure of control over intermolecular transitions if intermolecular couplings are the smallest ones. This control will allow work at practical isotopic or chemical dilutions in systems where diffusion does not provide sufficient isolation.

One experimental test of isolation is spectral simulation, including the simplest test of checking that the only significant contribution to the N order spectrum of a presumed N spin $\frac{1}{2}$ system is a single line at $N\Delta\omega$. Another test would be further dilution to the point of diminishing change in the spectrum.

Prof. E. L. Hahn (*Berkeley*) said: I would like to hear a discussion of the significance of RF pulse amplitude for the various pulses of the TPPI echo experiment.

Mr. D. P. Weitekamp (*Berkeley*) said: The amplitude requirement for the preparation pulses is not at all stringent. The derivation of eqn (11) of our paper holds equally well for a preparation sequence of arbitrary amplitude, frequency, and phase, so long as the high field approximation holds. It merely states the manner in which any coherences, which may be produced, are altered when this arbitrary sequence is repeated with all radiation phase shifted by φ . If one hopes substantially to excite all or most of the multiple quantum coherences then the preparation sequence should supply irradiation over a substantial part of the spectral width and should extend in time for a period of at least the inverse of some dipolar couplings. Many such schemes can be imagined.

The echo pulse should be much shorter than the inverse couplings if we are to neglect the internal Hamiltonian during the pulse. This requires that the nutation frequency ω_1 be greater than the dipolar couplings. This is technically less difficult to achieve than it is in a multiple pulse line narrowing experiment in which the probe Q must be suppressed. Of course, the echo is unnecessary if magnet homogeneity is sufficient.

The requirements of a detection pulse or sequence are similar to those of the preparation sequences and a variety of schemes deserve consideration.

Dr. P. Mansfield (*Nottingham*) said: The multiple quantum transitions are observed in an effective rotating frame so that the truncated dipolar interaction is responsible for the observed multi-line spectra. If this is the case, then presumably all quantum transitions have the same spectral density coupling to the lattice. However,

it would be valuable if laboratory frame multiple quantum transitions could be observed in small molecules with such clarity. Such experiments if possible, might yield useful spectral density information over a wider frequency range.

(1) Have you any comment on this aspect of multiple quantum transitions?

(2) Even in the rotating frame, inequivalent nuclei in small molecules may relax differently. Can such differential spin lattice relaxation effects be observed in the TPPI echo spectra?

Mr. D. P. Weitekamp (*Berkeley*) said: Within the range of validity of the Bloch–Wangsness–Redfield type of relaxation theory, spectral densities at frequencies higher than twice the Larmor frequency do not appear. This is because the effects of random time dependent terms in the Hamiltonian are accounted for only up to the first non-vanishing order in the perturbation theory. This involves correlation functions of first and second rank tensor operators. For the relevant case of dipolar relaxation and a dipolar spectrum this approach is certainly valid when $\omega_D \tau \ll 1$, where ω_D indicates a typical eigenfrequency of the average dipolar Hamiltonian and τ a correlation time for the motion. The high field approximation, which leads to the use of the truncated dipolar Hamiltonian, enforces the conditions that the eigenoperators of H_D are also eigenoperators of I_z with eigenvalue q and that the relaxation matrix does not connect eigenoperators with different q . One might relax these conditions by following the relaxation in low field, but then one has reduced the range of the spectral densities involved by reducing the Larmor frequency. The possibility of observing a truly multiple phonon relaxation mechanism is an intriguing one. Such a phenomenon must be sought in a situation where the lower order terms are not sufficient and a treatment including multiple time correlation functions is warranted.

Thus in neither high nor low field is the frequency range of spectral densities substantially different for the single and multiple quantum experiments. The familiar relaxation matrices suffice, and it is the initial conditions and the observables which increase in variety. This makes it possible to measure many more linear combinations of spectral densities and thus to sort out individual spectral densities. These constitute the information available from the different relaxation times of the spin system.

The TPPI echo experiment is a convenient way to separate the orders and eliminate inhomogeneous broadening. It will be valuable for measurement of both line widths and spin lattice relaxation rates with a variety of initial conditions. Work in progress in our laboratory has demonstrated its usefulness in studies of relaxation by paramagnetic impurities and by conformational exchange.

Dr. K. J. Packer (*East Anglia*) said: I would like to support Mr. Weitekamp's answer to this question by mentioning some work we have recently carried out.¹ We have calculated the response to a $90_x - \tau - \theta_y - T - \theta_y \rightarrow t$ pulse sequence of a spin-1 subject to the Hamiltonian

$$H = H_z + h_Q + H_Q(t)$$

where H_z is the Zeeman interaction, h_Q a secular quadrupole interaction. h_Q produces a doublet splitting in the spectrum, $2\Omega_Q$, whilst $H_Q(t)$ determines the relaxation properties *via* its spectral densities, $j_Q(\omega)$. The $90_x - \tau - \theta_y$ pulse pair distributes the entropy associated with the equilibrium magnetisation M_0 amongst the diagonal (zero quantum) single and double quantum elements of the spin density matrix in a manner determined by the product $\Omega_Q \tau$ and the value of θ . For example, if $\Omega_Q \tau = n\pi/2$ (n odd) and $\theta = 45^\circ$ then three quarters of the order is placed into the zero

¹ S. B. Ahmad and K. J. Packer, *Mol. Phys.*, 1979, 37, 47.

quantum states and the remaining quarter in the double quantum states. The third pulse produces a signal, $S_y(t)$, which can be analysed to give the relaxation properties of the various density matrix elements in the interval T . All density matrix elements relax by combinations of the spectral densities $j_Q(0)$, $j_Q(\omega_0)$ and $j_Q(2\omega_0)$. For example, the double quantum elements relax according to a rate given by $6j_Q(\omega_0) + 12j_Q(2\omega_0)$. Thus it is the mechanism of relaxation (quadrupolar in this example) which determines which frequencies are involved in the spectral densities not the quantum multiplicity of the states relaxing. What this means, as Mr. Weitekamp has already pointed out, is that by studying the relaxation of the various multiple quantum states one may determine the values of the individual spectral densities.

Mr. D. P. Weitekamp (Berkeley) (communicated): In response to comments made informally by Dr. Haeberlen, I would like to remark that the frequency of the highest order transition of an isolated molecule is determined by the sum of the chemical shifts of the spins involved and is unaffected by the dipolar couplings. The powder pattern or rotation pattern of this transition will reflect the sum of the chemical shift tensors, which is itself some new second rank tensor. The principal components of the sum tensor depend on the relative orientations of the individual spin tensors and their principal components. If these individual principal components are known from a multiple pulse powder spectrum then the principal components of the sum tensor, obtained from a multiple quantum powder spectrum, provide information on the relative orientation of the individual spin tensors. In favourable cases, this would provide the tensor orientations in the molecular frame without a need for a single crystal.

This approach would have the additional advantage of insensitivity to pulse imperfections. This would make its use over a wide temperature range much simpler.

Analysis of the lower order powder spectra would involve consideration of both dipolar and chemical shift terms and could in principle provide additional information on the tensor orientations, since the dipolar terms have an obvious relation to the molecular frame.

If a multiple pulse line narrowing sequence were applied during the evolution period, the spectra of all orders would be free of dipolar terms, but would be sensitive to a variety of linear combinations of individual spin tensors, providing a wealth of information on the relative orientations of these tensors. This approach would have the additional advantage of removing intermolecular dipolar broadening.

Dr. A. N. Garroway (Washington) (communicated): For the three glassy polymers studied, Dr. Stejskal finds that the spin-lattice contribution to the average carbon rotating frame relaxation rate $\langle T_{1\rho}(C) \rangle^{-1}$ is relatively constant, ranging from 81 to 85 % (his table 1). Yet the local fields are quite different, due to motional averaging. What is the origin of this clustering near 80 % spin-lattice contribution?

Dr. E. O. Stejskal (St. Louis) (communicated): The local fields are determined primarily by the strength of the proton interactions and only secondarily by motional averaging. On the other hand, $T_{\rho L}$ is directly determined by molecular motion. Thus the two quantities are free to vary independently, and the apparent clustering is fortuitous. Furthermore, no particular importance should be placed on the fact that these numbers are so close together. The data analysis was not intended to be more than semi-quantitative.

Mr. E. M. Menger (Nijmegen) said: As a comment to Dr. Stejskal's paper we

would like to report ^{13}C $T_{1\rho}$ measurements on polyoxymethylene (Delrin), performed at 45 MHz, using a ^{13}C r.f. field of 25 kHz.

For samples, rotating at the magic angle, a clear double-exponential decay of the ^{13}C magnetization, prepared by $500\ \mu\text{s}$ ^1H - ^{13}C cross-polarization, as a function of the hold time τ was observed. A typical $T_{1\rho}$ measurement, at a sample rotation frequency of 2.1 kHz, is shown in fig. 3(a). The ^{13}C spectrum of a stationary sample, consisting of a motionally narrowed line (≈ 800 Hz) with a short $T_{1\rho}$ (≈ 3.0 ms), superimposed on a broad chemical shift powder pattern with a much longer $T_{1\rho}$ (≈ 17.5 ms) convinced us that the polymer was partly amorphous and partly crystalline,

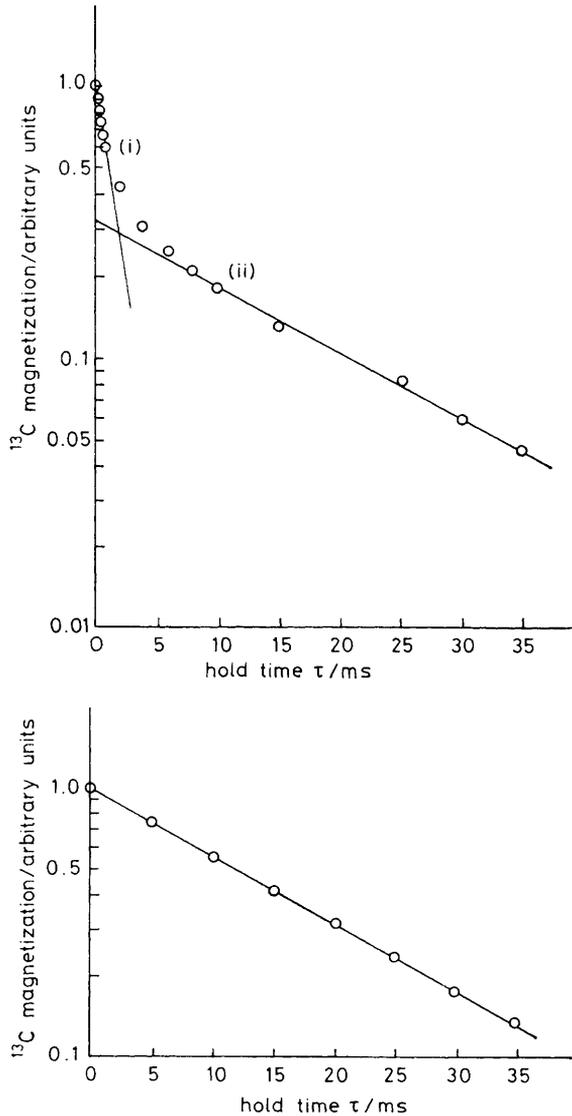


FIG. 3.— ^{13}C $T_{1\rho}$ measurements on Delrin, see text. (a) ^{13}C magnetization prepared by ^1H - ^{13}C cross-polarization: (i) $T_{1\rho} \approx 1.5$ ms (amorphous part); (ii) $T_{1\rho} \approx 17.5$ ms (crystalline part). (b) ^{13}C magnetization prepared by a ^{13}C 90° pulse, $T_{1\rho} \approx 17.5$ ms (crystalline part).

the amorphous part having the short $T_{1\rho}$ and the crystalline part the relatively long $T_{1\rho}$. A noticeable dispersion of relaxation rates due to anisotropy was not observed for stationary samples, neither for the crystalline part, nor for the amorphous part.

$T_{1\rho}$ experiments on samples, rotating at the magic angle, where the ^{13}C magnetization is prepared by a ^{13}C 90° pulse, rather than cross-polarization, reveal a single-exponential decay of the ^{13}C spin locked magnetization as a function of the hold time τ , if the repolarization time is short (1 s), the $T_{1\rho}$ being ≈ 17.5 ms. A double exponential decay is observed if the repolarization time is long (30 s) indicating a short T_1 for the crystalline part and a relatively long T_1 for the amorphous part. A typical experiment, using a repolarization time of 1 s is shown in fig. 3(b).

Experiments at various magic angle spinning frequencies showed that the $T_{1\rho}$ of the crystalline part, which is thought to be dominated by spin-spin contributions, as suggested by Stejskal *et al.*, as well as the dipolar relaxation time T_{1D} , are virtually independent of the spinning frequency. The $T_{1\rho}$ of the amorphous part, however, thought to be dominated by spin lattice relaxation, showed a marked dependence on the spinning frequency, as shown in fig. 4.

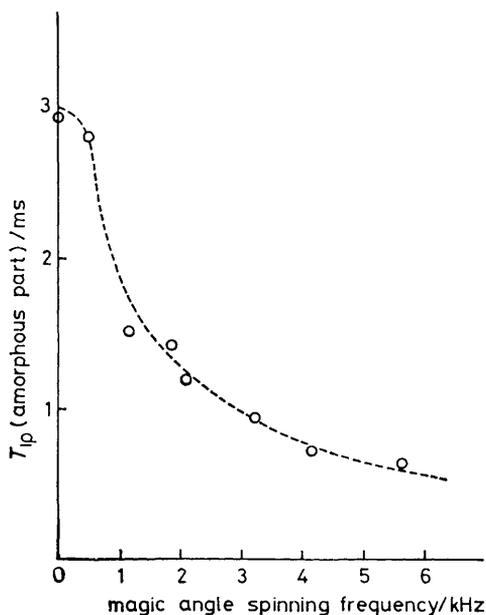


FIG. 4.—Variation of the $T_{1\rho}$ of the amorphous part of Delrin with the magic angle spinning frequency.

Another interesting observation can be made by studying the width of the ^{13}C n.m.r. line as a function of the spinning frequency. Since the crystalline and amorphous parts have quite different relaxation times T_1 and $T_{1\rho}$ we were able to record spectra, where both the crystalline and amorphous parts contribute to the linewidth, for example by performing a standard cross-polarization experiment, and spectra where the linewidth is completely determined by the crystalline part, for example by performing a standard cross-polarization experiment, followed by a long spin lock pulse τ ($\tau \gg T_{1\rho}$ of the amorphous part) or by preparing the ^{13}C magnetization by a 90° pulse, using a repolarization time, which is much shorter than the T_1 of the amorphous part.

At relatively low spinning frequencies (say 2 kHz) the composite linewidth is

somewhat larger than the linewidth, determined by the crystalline material alone. At the highest spinning frequencies we could reach (≈ 5.5 kHz) a considerable line broadening of the composite line was observed, while the linewidth of the crystalline material remained the same.

This seems real evidence that at high spinning frequencies stress in the material increases the chemical shift dispersion in the amorphous part, while this has no effect on the chemical shift dispersion of the crystalline material.

Dr. E. O. Stejskal (*St. Louis*) said: We have made a few cross-polarization measurements on polyoxymethylene with a ^{13}C r.f. field of 25 kHz. In particular, our $T_{1\rho}$ data at that r.f. field are quite similar to those shown in fig. 3(a) of the previous remark. However, we feel that a ^1H r.f. field of 25 kHz is marginal for both spin locking and dipolar decoupling in the more rigid regions of polyoxymethylene and may distort their representation in the ^{13}C spectrum. For materials with such strong proton interactions, we prefer r.f. fields of at least 30 kHz.

We disagree with a few aspects of the interpretation of the data in this comment: namely, the assignment of the short- T_1 , long- $T_{1\rho}$ phase as the crystalline part. To test this assignment, Dr. M. D. Sefcik of our group has obtained non-spinning spectra of polyoxymethylene (f.t. at 15 MHz, with 36 kHz pulsed dipolar decoupling during data acquisition, and without c.w. proton saturation for n.o.e. at other times) for 1 and 30 s repolarization times. The spectrum with the shorter repolarization time has a smaller (but not negligible) contribution from the more rigid component. Furthermore, the $T_{1\rho}$ associated with the short- T_1 phase is too long for an r.f. field so close to the local field.

Since the basis for assigning this phase is the behaviour of the line shape in a non-spinning $T_{1\rho}$ experiment, we must question that behaviour. In our spectra, we can clearly see the amorphous phase as distinct from the central maximum in the well defined chemical shift anisotropy pattern of the crystalline phase [fig. 17 in our ref. (15)]. It is much too narrow (5–10 p.p.m.) to correspond to the portion of the spectrum referred to in this comment (≈ 800 Hz or ≈ 18 p.p.m.) which suggests that far too much of the spectrum has been interpreted as due to the amorphous phase. Perhaps we are looking at samples with different thermal histories (we have seen a line-shape dependence on thermal history) or perhaps the marginal decoupling has reduced the resolution.

Incidentally, fig. 3(a) would seem to suggest that the initial slope of this decay curve has been assigned to a particular phase. In fact, in a multiple-phase system, the initial slope yields a relaxation rate corresponding to a weighted average of all the relaxation rates of all the phases present.

The spinning dependence of $T_{1\rho}$ shown in fig. 4 of the previous remark is not unexpected. There are many ways that spinning may modulate the interactions responsible for relaxation, as we note in the discussion section of our paper. Stress effects are also possible although we have looked for and have been unable to detect their existence in other polymers. Probably the sharp initial drop in $T_{1\rho}$ is due to the collapse of the dispersion of relaxation rates due to orientation relative to the laboratory field.

In summary, polyoxymethylene is a complex system involving at least two phases, each of which is far from homogeneous in its relaxation behaviour. It does not enjoy the advantage of clearly defined chemical shift differences to aid in its interpretation.

Dr. A. N. Garroway (*Washington*) said: An r.f. field of 25 kHz is very low for

rather rigid materials and I would expect to see a substantial spin-spin contribution to rotating frame relaxation with a time constant of the order of 1 ms.

The observed drop by a factor of two to three in the reported $T_{1\rho}$ on spinning could possibly reflect an averaging over different orientations. This averaging would occur for both spin-spin and spin-lattice contributions. Dr. Stejskal may be able to comment further on that aspect.

The increase in linewidth at the high spinning rate of 5.5 kHz may indicate molecular motions at the spinning frequency which are subverting the averaging of the anisotropy pattern by magic angle rotation. Further, as the spinning also removes the dipolar interactions, one effect of high speed spinning is to put 5.5 kHz sidebands on the decoupler frequency of 25 kHz. Hence, the spinning may reduce the efficiency of the carbon-proton dipolar decoupling and lead to increased broadening. Varying the r.f. field strength would be useful.

Dr. P. Mansfield (*Nottingham*) said: All the double resonance studies of ^{13}C have been performed by what is now known as the direct method. In assisting in the extrication and separation of $T_{1\rho}$ and cross-coupling relaxation effects, would not observation of the proton spins be of value?

An intriguing possibility might also be to remove the I-S dipolar interaction during the ^{13}C hold period in the $T_{1\rho}(\text{C})$ measurements. This can be achieved by a large spin stirring pulse H_{1x} which severely violates the Hahn condition. A string of short 90° pulses will also achieve the same end so long as the mean r.f. field again violates the Hahn condition.

Dr. E. O. Stejskal (*St. Louis*) said: No doubt there are cases where changes in the proton polarization could be used to estimate the magnitude of the spin-spin coupling to the ^{13}C spins in the $T_{1\rho}(\text{C})$ experiment. For instance, after a $T_{1\rho}(\text{C})$ experiment in which the spin-locked carbon polarization is not achieved by cross-polarization but rather by a conventional spin-locking procedure, following thermal equilibration (without any irradiation of the protons), there should be order in the proton dipolar field, observable by means of adiabatic remagnetization into the rotating frame, as a consequence of any spin-spin relaxation mechanism. (Alternation of the carbon spin temperature will facilitate detection of this polarization.) However, since most of the systems we have studied are dominated by spin-lattice relaxation with T_{1D} , $T_{1\rho}(\text{H})$, and $T_{1\rho}(\text{C})$ much shorter than $T_{1S}(\text{ADRF})$, this experiment will not necessarily be an improvement over the direct method. Furthermore, since there is no spin diffusion among the carbons, the direct method permits relaxation of chemically distinguishable carbons to be studied independently. Spin diffusion among the protons would tend to average the various relaxation rates even if some kind of proton line-narrowing technique were able to identify the protons attached to different carbons. Indeed, in those systems where spin diffusion among the protons does not average $T_{1\rho}(\text{H})$ to a single value, we prefer to determine that relaxation parameter by means of the carbon signal in a cross-polarization experiment, *via* eqn (7) of our paper, because of the clearer connection between relaxation and chemical structure.

Dr. K. J. Packer (*East Anglia*) said: Both Dr. Garroway and Dr. Stejskal are concerned with distinguishing spin-spin from spin-lattice processes when measuring $T_{1\rho}$ for a magnetically dilute spin system (*e.g.*, ^{13}C) in the presence of an abundant spin system (*e.g.*, ^1H). This complication arises because, in the absence of a decoupling field at the proton frequency, there is the possibility that the cold, rotating frame Zeeman reservoir of the ^{13}C spins may be heated by cross-relaxation to the

proton dipolar reservoir and thence coupled to the lattice. I would like to ask what I suspect is a naive question which relates to the method of measurement. Would it not be possible to carry out the $T_{1\rho}$ measurement for the ^{13}C spins in the presence of a proton decoupling field but one that is severely mis-matched with respect to the Hartmann-Hahn condition. In principle it would seem that this might allow an isolation of the pure ^{13}C spin-lattice processes from the spin-spin processes.

Dr. E. O. Stejskal (*St. Louis*) said: Because ^{13}C is a rare spin, $T_{\rho\text{L}}$ is determined by fluctuating magnetic fields arising from the motion of nearby protons, the abundant spin. The $T_{1\rho}(\text{C})$ experiment, as defined, is performed in the absence of irradiation of the protons. To irradiate the protons strongly will modulate the magnetic field giving rise to $T_{\rho\text{L}}$ and hence change it. In fact, it is necessary to replace $T_{\rho\text{L}}$ in eqn (7) and (8) of our paper with $T_{\rho\text{L}}'$ to take the presence of the proton r.f. field into account. The $T_{\rho\text{L}}$ measured in the severely mis-matched experiment would not be the one desired.

Dr. A. N. Garroway (*Washington*) said: Under proton irradiation, proton dipolar order is still present but in the rotating frame dipolar reservoir, and spin fluctuations still persist in general. What may well prove useful is to suppress proton spin fluctuations by off-resonant proton irradiation so that the effective proton field is at the magic angle as in the Lee and Goldberg experiment. Because of the exponential dependence of the carbon-proton spin-spin processes on proton fluctuation time τ_{D} , the magic angle need not be well set.

Dr. W. S. Veeman (*Nijmegen*) said: Preliminary results of $T_{1\text{D}}$ measurements on polyoxymethylene (Delrin) via the r.f. pulse sequence $90_x^\circ - \tau - 45_y^\circ - t - 45_y^\circ$ on the proton spins with magic angle spinning of the sample are shown in fig. 5 (p. 180) for three different spinning rates. Although these results are somewhat complicated by the fact that both the amorphous and crystalline part of the sample contribute to the signal, we find for the FID amplitude as a function of t an oscillation with frequency equal to the spinning frequency superimposed on a more or less exponential decay. The amplitude of this oscillation seems to decrease at the highest spinning frequency of 5450 Hz.

Does not this imply that spinning the sample at a few kHz still should be considered as an adiabatic variation of the local field¹ and how does this agree with $T_{1\text{D}}$ measurements at lower spinning frequencies?

Dr. A. N. Garroway (*Washington*) said: These are very intriguing results. I have not looked in detail at the fate of dipolar order under high speed magic angle spinning; for the purpose at hand I only wish to establish that dipolar order decays due to spinning. As pointed out by Pourquie [ref. (27) of our paper], the decay of dipolar order under slow perpendicular spinning does indeed contradict the supposition that the dipolar system follows slow motions perfectly adiabatically.

The $T_{1\text{D}}$ experiment under high speed magic angle spinning poses some conceptual problems. The dipolar hamiltonian is modulated at Ω and 2Ω and there is no time independent dipolar hamiltonian to define clearly the dipolar reservoir. Similarly spin diffusion is reduced, slowing internal thermalization and complicating the establishment of dipolar order by the two pulse method. I think the oscillation in dipolar order that you observe represents the substantially non-adiabatic nature of the evolu-

¹ M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon Press, Oxford, 1970).

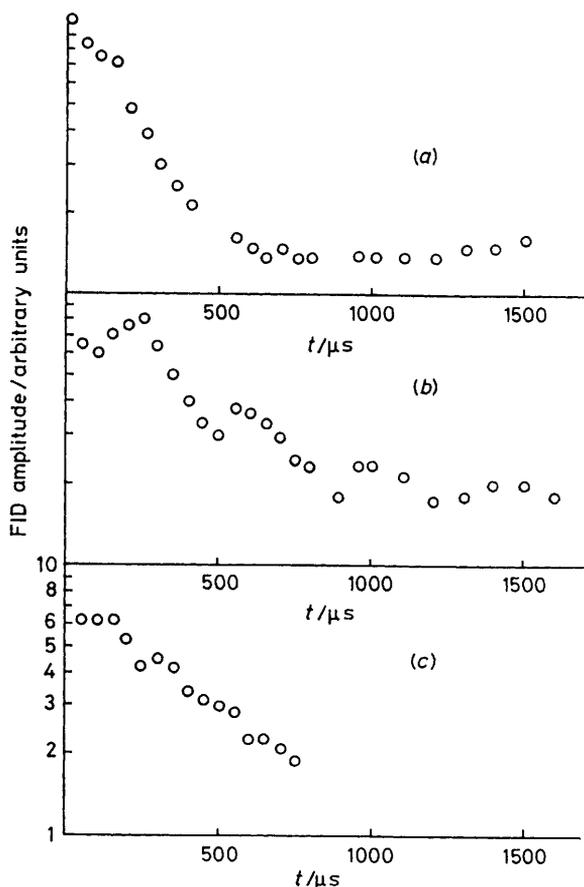


FIG. 5.— T_{1D} measurements on Delrin at various magic angle spinning frequencies, see text: (a) 550, (b) 2800 and (c) 5450 Hz.

tion: the short correlation time limit of $\Omega\tau_D \ll 1$ is no longer valid. The “sudden” approximation may be more suited at high speed.

Indeed this behaviour may be analogous to the experiment discussed by Jenner *et al.* [ref. (19) of our paper], in which a dipolar ordered state is irradiated with a large r.f. field. After the field is turned off, the spins thermalize with the new dipolar hamiltonian and so the oscillation of the observed magnetization reflects oscillation of the local field; in that case the oscillation is at $2\omega_1$ where $\omega_1 = \gamma B_1$.

Dr. R. K. Harris (*Norwich*) said: The observed peak widths of the spectra in fig. 3 of Dr. Garroway’s paper vary widely, presumably partly due to heterogeneity of the local environment (both intra- and inter-molecular) and partly due to lifetime broadening. The former effect is of considerable chemical interest. What qualitative or quantitative conclusions can be drawn from the data regarding this heterogeneity? The sharpness of the signal for the central quaternary carbon of DGEBA has its parallel for the similar carbon of amorphous polycarbonate, as confirmed by observations in our own laboratory.

Dr. A. N. Garroway (*Washington*) said: The lifetime broadening in the spectra

arises from molecular motion at the decoupler frequency ω_{1H} , for which decoupling is inefficient. Hence, the motional contribution to the carbon $T_{1\rho}$ provides an estimate of this broadening because in general the proton decoupling and carbon spin locking frequencies are comparable, $\omega_{1H} \simeq \omega_{1C}$. At room temperature for this epoxy I find that the lifetime broadenings, inferred from $T_{1\rho}$, range for the various lines from about 10 to 35% of the measured widths, at a carbon frequency of 15 MHz and decoupler field of 55 kHz.

The carbon methyl line broadens and indeed disappears around 150 K. This is qualitatively consistent with the extrapolated temperature dependence of the methyl carbon $T_{1\rho}$. Near the glass temperature I have some indication that all the lines broaden. For highest resolution one should work at as high a temperature as possible, up to the point of $T_{1\rho}$ lifetime broadening. High temperature also can average out some chemical shift broadening due to conformational interconversion. For polymers, distribution of chemical shifts appears to be the dominant broadening mechanism. The quaternary carbon is well buried in the molecule and so rather oblivious to other conformations and hence yields the narrowest line in the polymer.

Dr. E. O. Stejskal (*St. Louis*) said: Is it necessary to wait as long as 500 μ s before the beginning of data acquisition in a ^{13}C $T_{1\rho}$ experiment?

Dr. A. N. Garroway (*Washington*) said: A delay of 500 μ s is rather conservative. In the first 50 or 100 μ s any transient oscillation certainly vanishes. To ignore possible complications of dipolar ordering created during the spin lock process, I allow more time for the dipolar order to decay; an additional few hundred μ s is probably adequate.

Dr. K. J. Packer (*Norwich*) said: Eqn (9a) of the paper by Garroway *et al.* describes the contribution of macroscopic sample spinning to the dipolar spin-lattice relaxation rate $(T_{1D})^{-1}$. It appears to have the form of a typical "secular" $(T_2)^{-1}$ contribution under motional averaging conditions in which the angular spinning rate plays the role of the modulated second moment with τ_D being the correlation time. Is this apparent similarity coincidence and if not, is it possible to see simply how the spinning rate acts as the effective second moment for this relaxation process?

Dr. A. N. Garroway (*Washington*) said: Recall the simple BPP picture. A local field jumps between the values $\pm B_L$ with correlation time τ . The magnetization perpendicular to B_L rotates with instantaneous frequency γB_L , but as the process is phase-interrupted at τ , the relaxation rate involves the random walk step length $\omega_L \tau$. Hence, $T_2^{-1} \propto \omega_L^2 \tau \propto M^{(2)} \tau$ where $M^{(2)}$ is a second moment. Here the fast correlation time approximation has been assumed, $\omega_L \tau \ll 1$. Similarly for slow perpendicular mechanical spinning at Ω , the time dependent dipolar hamiltonian oscillates at Ω . Dipolar spin fluctuations change the instantaneous local field with a correlation time τ_D . The local field then executes a random walk with step length $\Omega \tau_D$ which is superposed on the coherent precession at Ω . The local field then loses phase coherence at the rate $T_{1D}^{-1} \propto \Omega(\Omega \tau_D) = \Omega^2 \tau_D$. There is a parallel to the self-decoupling of an I-S dipolar interaction by rapid I-I spin flips; in the spinning case, spin flips "decouple" the dipolar system from the mechanical motion. It is no coincidence that Ω^2 plays the role of the second moment $M^{(2)}$.

Another way to see this, which is incorrect but helpful, is to suppose that all the spins with instantaneous local field smaller than $\pm \Omega$ cannot follow the motion adiabatically while those seeing larger local fields can. The fraction which cannot follow adiabatically is $\propto \Omega T_2 \propto \Omega \tau_D$ and that fraction dephases over about one period of

revolution. By spin diffusion, this "hole" diffuses outward and other fresh spins move in. Hence the dipolar reservoir is fractionally reduced by $\Omega\tau_D$ every Ω^{-1} seconds and so the net relaxation is $T_{1D}^{-1} \propto \Omega^2\tau_D$.

Dr. J. H. Strange (*Canterbury*) said: Have measurements of the proton relaxation times been made as a function of temperature in this cured resin? Such measurements could probably help to check the interpretation of the ^{13}C data and confirm values obtained for the activation energy of methyl group motion and for segmental mobility. For example, measurements of proton relaxation times, in DGEBA cured with methylene dianiline¹ gave T_1 and $T_{1\rho}$ minima attributed to methyl group motion at ≈ 190 and 150 K, respectively. An activation energy of 23 kJ mol^{-1} was obtained from the position of these minima which is much higher than found in these experiments. It would seem possible that too low a value of activation energy might have been obtained here as the temperature dependence of $T_{1\rho}$ in these high resolution measurements would be reduced if there were a wide distribution of correlation times for the motion.

The proton relaxation measurements² also provided an insight into the curing kinetics. Is it likely that these elegant ^{13}C high resolution measurements would provide significantly more information?

Dr. A. N. Garroway (*Washington*) said: Analysis of the temperature dependence of the proton relaxation times would certainly complement the ^{13}C data. As you observe and your proton data show for a similar epoxy system, the activation energy inferred from the slope of the $T_{1\rho}$ against temperature data will undervalue the activation energy determined from the frequency dependence of the relaxation minima if there is a distribution of relaxation times. I did not follow the methyl relaxation to the $T_{1\rho}$ minimum.

The advantages of ^{13}C $T_{1\rho}$ seem to lie in the determination of very particular kinds of motion without the complications of spin diffusion. While proton relaxation measurements are far more straightforward than their ^{13}C analogues, it requires very good data and perhaps a model to peel off the methyl rotation contribution in order to look at, say, details of the backbone motion. This is especially true for motions with low activation energies and when the glass point T_g is not sufficiently remote from the methyl relaxation minimum. I hasten to add that these interesting details are certainly not obvious in the very limited range of data presented here.

Furthermore, the ^{13}C $T_{1\rho}$ measurement may become impractical near very sharp $T_{1\rho}$ minima. As mentioned in the paper and also in ref. (26), $T_{1\rho}$ estimates the lifetime broadening of the line. The ^{13}C resonance lines broaden and may disappear when there is substantial molecular motion at the decoupling frequency.

Prof. W. M. Ritchey has already found high resolution ^{13}C spectra very useful in suggesting the cure chemistry in a polyimide system. The ^{13}C relaxation data should test further the possible models of curing. However, to the extent that average proton properties faithfully reflect the kinetics of the cure, the proton relaxation will be very attractive.

Mr. S. Brosnan (*Oxford*) said: I direct my comment to Prof. Brown. We are interested in the size of the r.f. field H_1 used in your experiments because of the line broadening effects of high power irradiation. We have recently calculated that dipolar coupling between oxygen-17 nuclei and neighbouring protons will give a com-

¹ D. W. Larsen and J. H. Strange, *J. Polymer Sci.*, 1973, **11**, 449.

D. W. Larsen and J. H. Strange, *J. Polymer Sci.*, 1973, **11**, 1453.

posite line due to the O-H system. Several transitions are possible and these may be split by up to 60 kHz, the exact splitting depending on the particular quadrupole transition, the field gradient parameters, the bond lengths, and bond angles with the field gradient axes. Have you considered the possibility of using smaller r.f. fields to try to resolve such splitting?

Prof. T. L. Brown (Urbana) said: The optimal cross-relaxation rate at resonance in the zero-field spin mixing experiment is attained when $\gamma_S \sigma H_{1S} \simeq \gamma_H H_L$. There is, in effect, a resonance interaction in the rotating frame when $\omega_0 - \omega$, the offset from the pure quadrupole resonance, is zero.

In principle it should be possible to observe a doublet structure in the ^{17}O spectra, with lines at offsets from ω_0 given by $[(\omega_0 - \omega)^2 + (\gamma_S \sigma H_{1S})^2]^{\frac{1}{2}} \simeq \gamma_H H_L$, by using sufficiently low level H_{1S} .¹ In practice, the cross-relaxation rates are too low under these conditions. We normally employ an H_{1S} in the ^{17}O work on the order of 20 G, based on 0.5 of the peak-to-peak applied r.f. voltage.

Dr. C. P. Cheng has noted that in certain cases (e.g., 2,5-dichlorobenzoquinone), application of a static magnetic field H' of 4 to 6×10^{-4} T produces a doublet splitting in the ^{17}O line. The maxima in cross-relaxation rates in this case occur at $[(\omega_0 - \omega)^2 + (\gamma_S \sigma H_{1S})^2]^{\frac{1}{2}} \simeq \gamma_H [H_L^2 + H'^2]^{\frac{1}{2}}$. Because H' is large relative to H_L , the splitting varies approximately as $\gamma_H H'$. For $H' > \approx 7 \times 10^{-4}$ T, the lines are broadened due to the effects of H' on the ^{17}O spin levels.

Dr. W. S. Veeman (Nijmegen) said: In relation to one of the previous comments about the possibility of doing quadrupole-proton double resonance in a magnetic field, I would like to mention a technique to transfer polarization between a quadrupolar nucleus and the dipolar reservoir.²

By sweeping through a quadrupole resonance line of a powder in a magnetic field the dipolar reservoir is polarized and this polarization can be transferred to the proton Zeeman reservoir by adiabatically applying a r.f. field to the protons.

I wonder if this technique can be used for double resonance in a magnetic field.

Prof. T. L. Brown (Urbana) (communicated): I wish to make a considered response to two remarks made informally by Prof. Hahn and Dr. Haebleren.

Prof. Hahn asked about our experience with T_1 behaviour in various prospective samples.

In the field-cycling double resonance methods, there is potentially a problem with relaxation of the abundant nuclear spins at either extreme in the range of T_1 values. Long T_1 values result in slow acquisition of the spectra, because time must be allowed for sufficient remagnetization following each cycle in the experiment. In samples with very long T_1 values for which the ^{14}N n.q.r. spectrum is desired, we have irradiated samples with γ rays from a ^{139}Cs source to generate a very low concentration of paramagnetic damage centres. Reductions in T_1 on the order of 100-fold are readily achieved. The samples must be maintained at 77 K to prevent the damage from annealing out.

The level-crossing experiment is not feasible if T_1 of the abundant spin is too short in high field. In our experience, this is invariably the situation at 77 K with samples containing unpaired spins, e.g., transition metal complexes. In addition, we have noted short T_1 values in many low spin complexes of Co^{III} , in which there may be a contribution to T_1 from the temperature-independent paramagnetism. T_1 may also

¹ S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, 1962, **128**, 2042.

² W. S. Veeman and C. S. Yannoni, *Chem. Phys. Letters*, 1975, **32**, 499.

be short as a result of motional effects, as in methyl or η^5 -cyclopentadienyl group rotation, or low frequency modes in polymer chains. It is occasionally possible to replace a CH_3 group responsible for short T_1 by a CD_3 group. In addition, the T_1 values for hydrated samples may be increased by use of D_2O .

Dr. Haerberlen commented that the field gradient tensor contains five not two pieces of information, and he asked whether one can be confident regarding the orientation of the e.f.g. tensor in the molecular axis system from powder n.q.r. data alone.

Whether one regards the orientation of the e.f.g. tensor in the crystallographic axis system as a property of the tensor itself is a matter of semantics. In any event, Dr. Haerberlen is certainly correct in arguing that the study of oriented single crystals can provide information in addition to that obtained from powders. In some cases, the additional information is essential in defining the orientation of the tensor axes in the molecular axis system, or in identifying the direction of the principal tensor component. At the same time, it is also true that for very many quadrupole resonance data, the orientation of the e.f.g. tensor is well defined by the molecular symmetry or even the lattice site symmetry.

It should be kept in mind that the components of the field gradient tensor are the expectation values of one-electron operators, with a r^{-3} dependence on distance from the nuclear quadrupole to the element of charge distribution of interest. It is thus reasonable to expect that in molecular crystals, the non-specific intermolecular interactions make only small contributions to the e.f.g. tensor. We thus expect that the e.f.g. tensor at, let us say, ^{17}O in an organic ketone, is dependent almost entirely on the intramolecular charge distribution. However, more energetic intermolecular effects such as hydrogen bonding or Lewis acid-base adduct formation do produce noticeable effects; indeed, the n.q.r. technique serves well in the study of such interactions, as exemplified by several ^{14}N n.q.r. studies of coordinated nitrogen.¹

The point at issue is, in my opinion, of considerable importance. If n.q.r. spectroscopy of light elements such as ^{14}N , ^{17}O , and ^2H is to develop as a technique generally useful to the chemist, the sample requirements must not be too restrictive. I believe that much of the work already accomplished demonstrates that the n.q.r. data obtained at lower temperatures on samples that are polycrystalline or liquid at room temperature can reveal important new information regarding charge distribution and bonding.

Dr. P. Mansfield (*Nottingham*) said: The point was emphasised by Dr. Edmonds that pure quadrupole double resonance field cycling experiments were relatively cheap to perform and often used "off the shelf" powdered samples. However, double resonance experiments in high magnetic fields allow (at least in principle) the determination of the full quadrupolar splitting tensor. Furthermore, identification and assignment of the principal tensor components with respect to the crystalline axes is much simplified, even with non-equivalent quadrupolar split nuclei. It is accepted that pure quadrupole resonance may be the only way to proceed in cases where single crystals just cannot be grown, as in the case of many biological molecules. But many of the organic and inorganic compounds being studied by various research groups could, one suspects, be grown into single crystals. I wonder, therefore, why so few groups are pursuing what amounts to Hahn and Hartmann's original high field double resonance experiment.

Dr. D. T. Edmonds (*Oxford*) said: There are several facets to this comment and I will attempt to reply to them in turn.

¹ e.g., see Y.-N. Hsieh, G. V. Rubenacker, C. P. Cheng and T. L. Brown, *J. Amer. Chem. Soc.*, 1977, **99**, 1384; C. I. H. Ashby, C. P. Cheng and T. L. Brown, *J. Amer. Chem. Soc.*, 1978, **100**, 6057.

(1) If n.q.r. is to become a widely used analytical and structural technique in chemistry and biology then it seems to me essential that high resolution spectra be obtainable from frozen liquid and powdered solid specimens, and not solely from single crystals. This essentially means that the n.q.r. must be detected in zero or small applied magnetic field. This in turn leads to the use of field cycling techniques to obtain the desired high sensitivity especially at low (< 5 MHz) frequencies.

(2) If a single crystal specimen is available then it is certainly possible to extract extra information consisting of the directions of the principal axes of the electric field gradient. However this information is easy to obtain with a single crystal, using field cycling techniques, by applying small steady magnetic fields during the irradiation phase. In fact all the Zeeman techniques developed for conventional, continuous wave n.q.r., can be used with field cycling provided a single crystal specimen is employed.

(3) If n.q.r. is to mature as has n.m.r. then much of the structural information extracted will not reside simply in the quadrupole line centre frequencies but in the shifts and fine structure of the n.q.r. lines due to the interaction of the quadrupolar nucleus with neighbouring nuclei. We have already reported fine structure due to deuterium–deuterium and deuterium–proton interaction in ^2D n.q.r.¹ and also due to nitrogen–proton² and nitrogen–deuterium³ interaction in ^{14}N n.q.r. Recently⁴ we have detected fine structure in the n.q.r. spectra of naturally abundant ^{17}O spectra due to oxygen–proton and oxygen–deuterium interaction in OH groups. Such fine structure would not be observed in the presence of a large applied magnetic field.

For all these reasons I believe the future of n.q.r. lies in field cycling techniques in which the n.q.r. is detected in zero or small applied magnetic fields.

Prof. T. C. Waddington (*Durham*) said: Dr. Edmonds used specimens enriched with ^{17}O while Prof. Brown detects the n.q.r. of ^{17}O in natural abundance. Could the differences between the two techniques be explained please?

Dr. D. T. Edmonds (*Oxford*) said: In our experiments we used the technique of double resonance with spin mixing by level crossing (d.r.l.c.) whilst Prof. Brown used double resonance in the laboratory frame (d.r.l.f.). D.r.l.f. is much more sensitive than d.r.l.c. but does require the application of radio-frequency fields of large amplitude to attain its high sensitivity. We have always tried to avoid the application of large amplitude radio-frequency fields in the hope of obtaining narrow lines so that any fine structure on the line is made more easily discernible.

Recently Mr. Brosnan and I have developed a technique⁴ which has a sensitivity comparable to d.r.l.f. for the detection of the n.q.r. of naturally abundant ^{17}O but which does not require large amplitude radio-frequency fields. Using this technique we do detect fine structure on the ^{17}O lines due to oxygen–proton and oxygen–deuteron interaction in OH groups of several compounds. An understanding of such fine structure should enhance n.q.r. as a structure-determining tool.

Prof. T. L. Brown (*Urbana*) said: Dr. Edmonds and his co-workers report the ^{14}N n.q.r. data for pyridine hydrogen-bonded to a water molecule. We have developed a model that accounts for the e.f.g. tensor parameters in “coordinated” nitrogen, in terms of the extent of electron withdrawal from the nitrogen.⁵ The

¹ D. T. Edmonds and J. P. G. Mailer, *J. Magnetic Resonance*, 1978, **29**, 213.

² D. T. Edmonds, M. J. Hunt and A. L. MacKay, *J. Magnetic Resonance*, 1973, **9**, 66.

³ M. J. Hunt and A. L. MacKay, *J. Magnetic Resonance*, 1974, **15**, 404.

⁴ S. G. P. Brosnan and D. T. Edmonds, *J. Magnetic Resonance*, 1979, to be published.

⁵ Y.-N. Hsieh, G. V. Rubenacker, C. P. Cheng and T. L. Brown, *J. Amer. Chem. Soc.*, 1977, **99**, 1384.

extent of charge withdrawal is reflected in the donor orbital occupancy, which is 2.0 in the free base. The decrease from this value in the acid-base adduct is a measure of the Lewis acidity of the group to which the pyridine is bound. For L-histidine and imidazole, in which there is N-H . . . N hydrogen bonding, the donor orbital occupancies are 1.93 and 1.92, respectively.¹ Application of the ¹⁴N data of Davidson, Edmonds and White to our previously published correlation for pyridine yields a nitrogen donor orbital occupancy in the pyridine water complex of 1.93. It will be of interest to search for regularities in the derived orbital occupancies in a given nitrogen base as the hydrogen donor is varied, but on the basis of the limited results in hand, ¹⁴N n.q.r. looks like a promising tool for probing hydrogen bonding interactions.

Dr. P. Mansfield (*Nottingham*) said: The spectra shown by Dr. Boden are all obtained from quadrupolar echoes produced on resonance. In the Fourier transformation, therefore, only half the spectrum is obtained about the origin and it is valid to reflect the frequency data about the origin only if the quadrupolar line shape is indeed symmetric.

My concern is that in general this may not be so, even for spin $I = 1$ systems, especially when $\eta \neq 0$. I would therefore make the comment that it would in general be better to make measurements either off resonance or preferably on resonance but using quadrature detection.

The second order quadrupolar shift is of the order of v_Q^2/v_0 , where v_Q is the first order quadrupolar shift and v_0 the Larmor frequency. For first order shifts of up to 100 kHz and a Larmor frequency of 10 MHz, second order effects can give resonance shift asymmetries of up to 100 p.p.m. in half integer spins, for example, thus vitiating any proposal to measure chemical shifts in such systems.

Could this be an important factor in the present experiments where only $I = 1$ spins are studied?

Dr. N. Boden (*Leeds*) said: Dr. Mansfield's question raises a very fundamental point. I will try to answer it. We have followed the normal practice and assumed that first order theory gives a valid description of deuterium n.m.r. spectra in organic solids. The effects of the second order quadrupole term for $\eta = 0$ have been discussed by Cohen and Reif² and Abragam.³ For $I = 1$, the first order quadrupole splitting is unaffected but the centre of the spectrum is shifted by an amount proportional to $(e^2qQ/h)^2/v_0$. Let us consider how this affects, say, the "rigid lattice" powder spectrum of [²H₆]benzene* measured at 77 K and 10 MHz: the singularities are shifted by 233 Hz with respect to the wings of the spectrum which are unaffected. Thus, the spectrum will be distorted, but by an amount small compared with the dipolar broadening (6.5 kHz) and less than the resolution of our transformed spectra (600 Hz). We do not, therefore, expect the deuterium frequency spectra obtained from resonant spin echo responses to be measurably distorted. This conclusion is confirmed by the agreement between data obtained in this way and that determined by c.w. methods. Nevertheless, quadrature detection would be preferable, as you suggest, and we are currently constructing equipment for this purpose.

Turning to the second question. The second order frequency shift will, as you point out, make a substantial contribution to the "apparent" chemical shift. For

¹ C. I. H. Ashby, C. P. Cheng and T. L. Brown, *J. Amer. Chem. Soc.*, 1978, **100**, 6057.

² M. H. Cohen and F. Reif, *Solid State Phys.*, 1957, **5**, 321.

³ A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961), p. 233.

* For [²H₆]benzene $\eta \neq 0$, but the corresponding powder pattern has not hitherto been calculated. However, η is very small for organic solids and its inclusion should not seriously affect the conclusions reached herein.

a homogeneously oriented principal axis system, such as may be found in single crystal studies, this shift may, at least in principle, be calculated enabling the chemical shift to be unambiguously obtained. It is not possible to say without further calculation how these second order shifts affect the frequency dependence of the echo maxima for either single crystals or powders. We will have to check this.

Mr. D. P. Weitekamp (*Berkeley*) said: I would like to comment on the issue of the second order quadrupole term raised by Dr. Mansfield. For a spin one nucleus in an axially symmetric electric-field gradient this term in the energy is an odd function of the Zeeman quantum number and its angular dependence is non-negative.¹ The effect on the single quantum spectrum will be to shift all components of the powder pattern in the same direction by varying amounts and thus give an angle-dependent artifactual chemical shift. The double quantum powder patterns show the effect clearly as these contain frequencies unaffected by the much larger first order quadrupole term.²

I have two questions for Dr. Boden. The first is whether it is accurate to calculate the quadrupole echo dynamics as if the quadrupole Hamiltonian did not act at all on the time scale of the pulses. The second is whether one can ignore the possibility of a change in the static bulk susceptibility during a phase change when determining chemical shift differences between solids and liquids without an internal reference.

Dr. N. Boden (*Leeds*) said: The quadrupole echo response obtained with pulses of finite width are identical to those predicted assuming δ -function pulses corresponding to the mid-points of the actual pulses provided the r.f. amplitude is sufficient. The question is what do we mean by sufficient? We might expect $1/\pi t_p \gg$ width of spectrum would be necessary. However, we find the $90^\circ\text{-}\tau\text{-}90^\circ_{90^\circ}$ echo response is undistorted for much longer pulses. A similar result obtains in the measurement of FID signal and is well understood.³

There will indeed be a small change in the bulk susceptibility associated with the change in density on going from liquid to solid which I suppose we should calculate.

Dr. J. W. Emsley (*Southampton*) said: It is interesting to compare the results obtained for e^2qQ/\hbar and η for deuterobenzene by the study of polycrystalline samples and by deuterium n.m.r. of C_6D_6 dissolved in a liquid crystal solvent. In the case of a liquid crystal sample the spectrum shows a doublet with a splitting $\Delta\nu$ given by,

$$\Delta\nu = -\frac{3}{4} \frac{e^2qQ}{\hbar} S(1 \pm \eta).$$

The +ve sign before η applies when the 2-axis for V is perpendicular to the molecular plane, and -ve sign when it lies in this plane. The S is the order parameter of the 6-fold rotation axis, and is obtained from dipolar coupling. To obtain e^2qQ/\hbar it is necessary to know η and the location of the 2-axis. Taking η to be 0.041 and the 2-axis perpendicular to the plane, as found by Boden *et al.*, and using the liquid crystal data of Caspary *et al.*,⁴ then e^2qQ/\hbar is determined as 186.0 ± 4.0 kHz. Choosing the 2-axis to lie in the benzene plane gives 202.0 ± 4.0 kHz. Clearly one is tempted to assume that the principal axes for V do not change on going from the solid to liquid crystal solution. There is, however, a discrepancy in the magnitude of either or both

¹ A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961), p. 233.

² J. Murdoch, personal communication.

³ D. Barnaal and I. J. Lowe, *Phys. Rev. Letters*, 1963, **11**, 258.

⁴ W. J. Caspary, F. Millett, M. Reichbach and B. P. Dailey, *J. Chem. Phys.*, 1969, **51**, 623.

η and e^2qQ/h between the two phases but this may reflect the error in measuring S for the case of C_6D_6 . A similar comparison has been made for pyridine

	e^2qQ/h	η
polycrystalline C_5ND_5 ¹	178.0 ± 1.2	0.039
liquid crystal solution of 4-[² H]pyridine ²	181.9 ± 1.0	0.039

Comparing data obtained in two different phases has two interesting aspects. First, if changes in e^2qQ/h and η are small, then it is possible to determine the orientation of the principal axes. This method will work when molecular rotation does not take place in the solid, and depends only on the magnitude of η compared with possible changes in the magnitude of e^2qQ/h and η on changing phase. Secondly, as more precise data on both phases becomes available it should be possible to detect changes in V on changing phase.

Dr. N. Boden (Leeds) said: We wanted to show in the paper how the quadrupole coupling tensor for deuterium in an organic molecule could be obtained from a comparison of the "rigid lattice" and rotationally averaged* powder spectra. In applying the technique to solid C_6D_6 we used the values 180.7 ± 1.5 kHz and 0.041 ± 0.007 for, respectively, e^2qQ/h and η as obtained by Barnes and Bloom from c.w. measurements at liquid nitrogen temperature. At this temperature T_1 is inconveniently very long; however, by temperature-cycling we have measured the spectrum by the spin echo technique and obtained the values 182.3 ± 1.3 kHz and 0.048 ± 0.007 which are in excellent agreement with those of Barnes and Bloom. Using our value for η , the liquid crystal measurements on C_6D_6 yield 184.8 kHz for e^2qQ/h . The discrepancy between the two values is interesting as it reflects differences in the averaging of the quadrupole splitting by the atomic vibrations. The liquid crystal value is averaged by intramolecular vibrations (the reorientational averaging is contained in S), whilst the molecular crystal value is averaged by intermolecular vibrations (librations), too. The latter are larger in amplitude than the former and we may, to a first approximation, assume the molecule vibrates as a rigid body in the crystal and include the averaging by the intramolecular vibrations in the "molecular" quadrupole tensor. The liquid crystal value of e^2qQ/h may, on this basis, be taken as representing the static molecule value. The observed temperature dependence of the quadrupole splitting may then be considered to be entirely due to the averaging of e^2qQ/h by the librational motion of the molecule, since contributions from changes in the small value of η will be negligible. The change in e^2qQ/h , thus obtained, is from 184.8 to 171.0 kHz between 0 and 280 K and ought to be calculable from lattice dynamics.

Dr. A. M. Achlana (Rehovot) said: The chemical shift tensor of deuterium in single crystals may be detected using straightforward FTNMR at high field. Fig. 6 shows a ²D spectrum of a fully deuterated single crystal of potassium hydrogen maleate. There are two magnetically distinguishable molecules in the unit cell, each containing one carboxylic and two olefinic deuterons. Consequently the spectrum contains six pairs of lines. The line at the centre is due to free water molecules trapped in the crystal while growing and may serve as an internal reference. Note that the midpoints of the different pairs of lines do not coincide, due to the different chemical shifts of the corresponding nuclei.

¹ R. G. Barnes and J. W. Bloom, *J. Chem. Phys.*, 1972, **57**, 3082.

² J. W. Emsley, J. C. Lindon and J. Tabony, *J.C.S. Faraday II*, 1975, **71**, 579.

* Alternatively, the reorientationally averaged quadrupole splitting measured for the molecule in a nematic solvent could be used as suggested by Emsley.

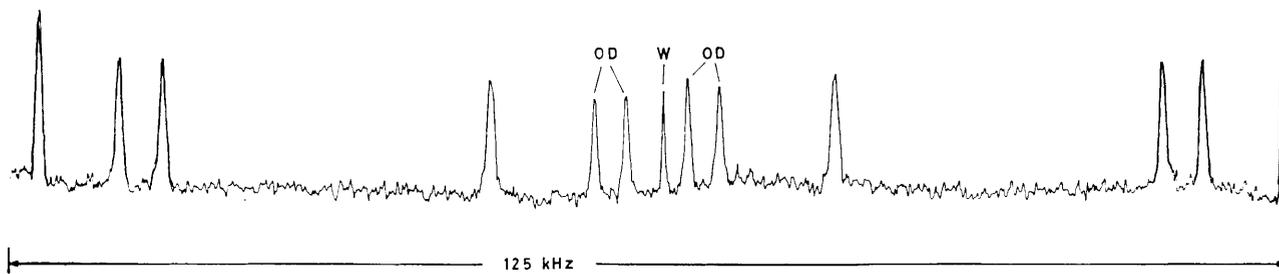


FIG. 6.— ^2D f.t.n.m.r. spectrum of a single crystal of deuterated potassium hydrogen maleate at 41.45 MHz. The magnetic field was in a general position. The spectral width was 125 kHz, pulse width $4 \mu\text{s}$, 400 scans with 100 s between consecutive pulses. The quadrature detection mode was employed.

Dr. N. Boden (*Leeds*) said: Deuterium chemical shifts may indeed be extracted from measurements of the mid-point frequencies of quadrupole doublets provided the corresponding second order quadrupole shift can be calculated. Whilst this is possible in principle, it is not so easy in practice when $\eta \neq 0$.

Dr. J. R. Brookeman (*Gainesville*) said: I would like to ask Dr. van der Klink if in their study of the $K_2 Pt Cl_6$ type mixed crystals, they saw any evidence for relaxation of the host lattice around the point defect sites. In our n.q.r. study of mixed isotopic crystals of $^{14}N_2$ and $^{15}N_2$ some years ago, we found clear evidence of this lattice relaxation, and this enabled us to explain the difference between the calculated temperature independent shift of the n.q.r. frequencies and the smaller experimentally observed shift.

Dr. J. J. van der Klink (*Lausanne*) said: I certainly think that effects of the kind you refer to do exist in our mixed crystals. In your analysis¹ you consider the case of a ^{14}N - ^{14}N molecule placed in a pure ^{15}N host, and you observe the ^{14}N n.q.r. signal. The analogous experiment in our rhenate crystals would be to observe the ^{79}Br signal from the impurity. Unfortunately we are not equipped at the moment to observe this resonance, that occurs around 200 MHz. In the case of our stannate crystals the situation is different: we attribute the additional lines in the cubic phase to NH_4 —impurity nearest-neighbour chlorine atoms. That these signals are visible at all indicates that local volume defects are less important here, as one would expect from the small relative difference (0.6 %) in lattice parameter between the pure ammonium and the pure potassium salt.

Dr. J. H. Strange (*Canterbury*) (*communicated*): It seems probable that the reduction that we observed in $T_{1\rho}$ and also in T_1 was due to $SnCl_6^{2-}$ reorientation, although the dipolar interaction between the chlorine and proton nuclei is surprisingly strong, presumably because the minimum separating distance becomes small when reorientation occurs. The motion may well be rather complex, however, as the ω^2 dependence for $T_{1\rho}$ and the ratio for $T_{1\rho}$ to T_1 were not those predicted for a simple rotational model. It is reassuring to see this other evidence for $SnCl_6^{2-}$ reorientation in $(NH_4)_2SnCl_6$.

Dr. R. K. Harris (*Norwich*) said: Although the intramolecular barrier to internal rotation in the anilinium ions is sixfold and, therefore, very low, that for the ethylenediammonium ions is of lower symmetry and presumably much higher in magnitude. Are the observed barriers (table 4 Prof. Dunell's paper) for the bromides and iodides of these two systems therefore of different origin? If so, is their remarkable similarity purely coincidental?

Dr. C. I. Ratcliffe and Prof. B. A. Dunell (*Vancouver*) said: The internal barrier to reorientation of $-NH_3^+$ in the ethylenediammonium ion should indeed be much larger than that in the anilinium ion. Inelastic neutron scattering measurement on the methylammonium ion² have indicated an internal barrier of $\approx 9.0 \text{ kJ mol}^{-1}$ (750 cm^{-1}), and the internal barrier in the ethylenediammonium ion should not be greatly different. The internal barrier thus appears to account for almost all of the barrier

¹ J. R. Brookeman, M. M. McEnnan and T. A. Scott, *Phys. Rev. B*, 1971, **4**, 3661.

² C. J. Ludman, C. I. Ratcliffe and T. C. Waddington, *J.C.S. Faraday II*, 1976, **72**, 1759.

to reorientation of $-\text{NH}_3^+$ in ethylenediammonium bromide and iodide and both of Harris' questions should apparently be answered in the affirmative. If the external barriers to $-\text{NH}_3^+$ reorientation in ethylenediammonium bromide and iodide are close to zero despite the possibility of hydrogen bonding between the NH_3^+ group and the halide ions, we would rationalize that condition by suggesting that the halide ion environment of the $-\text{NH}_3^+$ rotor in these two compounds is probably a regular n -fold arrangement about the direction of the C-N axis with $n \neq 3$. An answer to the question raised by Dr. Harris as to why the total barriers for the ethylenediammonium bromide and iodide should parallel so closely the total barriers for the anilinium salts when their origins are different requires structural information on the ethylenediammonium salts and possibly further experimental work that would separate the internal and external barriers.

Prof. T. C. Waddington (*Durham*) said: I would like to make some comments on the comparison of energies of activation E_{ACT} , measured from n.m.r. T_1 data and energies of activation obtained by calculation from measured torsional frequencies of the $-\text{NH}_3^+$ group.

As the authors point out, in order to compare the two types of measurement we have to make an assumption about the form of the potential well

$$V(a) = \frac{3V_3}{2} (1 - \cos 3a) + \dots \quad (1)$$

and indeed unless we ignore terms above V_3 we have a two or more parameter problem and cannot compare the two measurements.

What I want to suggest is that the agreement between the two measurements for anilinium chloride is very good, even better than the authors indicate, but that a fair sized discrepancy remains for the bromide and also exists for the iodide, for which we have recently measured the $-\text{NH}_3^+$ torsional frequency. An explanation for this probably lies in the mismatch of the symmetries of the $-\text{NH}_3^+$ rotor and the external environment of the $-\text{NH}_3^+$ group.

(1) The torsional frequencies are temperature dependent. We do not at the moment have a comparison of the frequencies of the $-\text{NH}_3^+$ group in the anilinium salts at differing temperatures, but some recent results for the ethylammonium halides, where the $-\text{NH}_3^+$ torsional frequencies are higher, indicate that the torsional frequencies decrease by $\approx 3\%$ in going from liquid nitrogen to room temperature and this would produce a lowering of the calculated barrier by $\approx 5-6\%$ over the same temperature range. Percentage shifts in torsional frequencies and therefore in barrier heights appear to increase with lower torsional frequencies. The values of the $-\text{NH}_3^+$ torsions reported in the paper are at 77 K.

(2) The barrier heights calculated by the authors assume a moment of inertia appropriate to a tetrahedral $-\text{NH}_3^+$ group. In fact the C-N . . . (X = Cl^- , Br^-) bond angle is rather less than the tetrahedral bond angle, and even though the assumption that the H atoms of the $-\text{NH}_3^+$ group lie along the N . . . Cl directions may be an extremum, some distortion of the C-N-H bond angle to values lower than tetrahedral is to be expected.

Roughly re-working the calculations in the paper, including corrections for (1) and (2) and including a recent i.n.s. determination of the $-\text{NH}_3^+$ torsion in anilinium iodide we find:

	C ₆ H ₅ NH ₃ Cl	C ₆ H ₅ NH ₃ Br	C ₆ H ₅ NH ₃ I
$\nu_{\text{NH}_3^+}/\text{cm}^{-1}$	442	294	230
$E_{\text{ACT}}(\text{i.n.s.})$ corrected for (1) and (2)	39.4	19.3	13.3
$E_{\text{ACT}}(\text{n.m.r.})$	37.1	11.2	8.5
$\Delta E/\%$	5.8	42.0	36.1

Since the iodide is thought to be isostructural with the bromide these rough results do seem to confirm the authors' conclusions. It would be of considerable interest to use the n.m.r. and the i.n.s. results together to calculate the ratio of V_3 and the next term for each case.

Prof. A. Weiss (Darmstadt) said: From X-ray diffraction it is proved that the room temperature phase of anilinium iodide is isotypic to the high temperature phase I of anilinium bromide. The space group of C₆H₅NH₃⁺I⁻(I) is $D_{2h}^{10}(\text{Pnaa})$ with $a = 1.738$ nm, $b = 0.636$ nm, $c = 0.704$ nm, $Z = 4$ at room temperature.¹ The transformation temperature of the anilinium iodide is $T_{\text{II,I}} = 241$ K.²

Preliminary results of a neutron diffraction study³ on C₆H₅NH₃⁺Br⁻(I) at 343 K show that the Debye-Waller factor of the proton in the *para*-position is higher than those of the protons in the *meta*- and *ortho*-positions. It can therefore be concluded that the vibrations around the axis normal to the benzene ring and the axis in the ring plane and normal to C₍₄₎ . . . C₍₁₎⁻N are of importance in the dynamical behaviour of both the anilinium bromide and the anilinium iodide.

Dr. E. M. Cashell (Nottingham) said: (1) The inference drawn from Prof. Dunell's fig. 3 that τ_c° is constant for all the samples is inconsistent with the Eyring⁴ interpretation for this factor [$\tau_c^\circ = \frac{h}{ekT} \exp(-\Delta S/R)$]. A useful elaboration of their experiments therefore would be achieved by making measurements at different frequencies: this would gain more data points for their plot of activation energy (E) against the temperature at the T_1 minimum. The linearity of this plot and the significance of the Eyring interpretation for τ_c° in the context of these activated processes could then be stated more categorically.

(2) A factor of some importance in the Eyring formula is the entropy of activation which is indicative of the differing degrees of order required of the excited state for motion to take place. Taking their values for τ° (Prof. Dunell's table 2) I have estimated the entropies associated with the activated rotor process for each sample. These are presented below, along with the corresponding activation energies:

sample	ΔS /kJ K ⁻¹ × 10 ³	E /kJ mol ⁻¹
chloride	-4.24	37.1
bromide	10.39	11.2
iodide	10.88	8.5
sulphate	4.06	11.2

¹ G. Fecher and A. Weiss, unpublished results.

² W. Pies and A. Weiss, *J. Magn. Res.*, 1978, **30**, 469; W. Pies, M. Schahbazi and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 594.

³ G. Fecher, H. Fuess and A. Weiss, unpublished results.

⁴ S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill N.Y., 1941).

One point of significance is the negative entropy change and large activation energy associated with the chloride, especially because it is clear when one compares columns two and three that a larger activation energy does not necessarily imply a larger entropy change.

Of course, a complicating factor is that the activation energy itself possibly changes with temperature¹ and valid comparison with the associated entropy change should allow for this. Measurement of the T_1 minimum at different frequencies would facilitate the determination of this effect since the temperature at which the minimum occurs and hence the activation energy (if temperature dependent) shift with frequency.

Dr. K. J. Packer (*Norwich*) said: I would like to comment on the use of the pulsed field gradient spin echo technique used by Drs. Gordon and Strange. First I would like to say that anyone who has worked with those techniques will appreciate the considerable achievement represented by the direct n.m.r. measurement of these self-diffusion coefficients at the very high temperatures involved. Secondly I would like to ask the authors whether they used the stimulated spin echo sequence and if not, whether this might have significantly extended the range over which they were able to make their measurements.

Dr. J. H. Strange (*Canterbury*) said: The simple spin-echo sequence of $90^\circ-\tau-180^\circ$ pulses was used. We had investigated the possibility of using the $90^\circ-\tau_1-90^\circ-\tau_2-90^\circ$ sequence which can have advantages when T_1 is significantly longer than T_2 . In our case we calculated that the increase in range to slower diffusion rates was very limited because the T_1 to T_2 ratio is not enough at 10 MHz to exploit fully the advantages of the stimulated echo sequence.

In response to Dr. Pope's informal inquiry, the following information should be added to my paper. "The pulsed magnetic field gradient was achieved using a quadrupolar coil. Since these coils were mounted outside the furnace they were necessarily large, and with 100 A being switched through them, produced 100 G cm^{-1} at the sample."

Mr. W. H. M. Alsem (*Groningen*) said: A mass transport phenomenon which can also be investigated suitably by means of the nuclear spin relaxation technique is the motion of dislocations in crystalline solids.^{2,3} Dislocations are line defects characterized by their Burgersvector b and the vector ξ along the dislocation line, together determining the glide plane (fig. 7).

Stresses applied on crystals may cause dislocations to move on their glide planes, opposed by lattice friction. This motion is assisted by thermal activation; the friction is caused by lattice periodicity [Peierls-Nabarro (PN) force] and strong obstacles, *viz.* other dislocations and impurities. If the obstacles exert a much larger counterforce than the PN force, the dislocation motion will be stepwise, *i.e.*, the dislocation (or dislocation segment) waits at an obstacle during an average time interval τ which is much larger than the time τ_s it actually moves. Consequently the mean velocity of a dislocation is determined by τ and the distance L covered in one "jump".

Dislocation motion has been studied by means of the spin-locking technique, because the atomic motions involved are in the ultra-slow region. The strong colli-

¹ C. Brot., *Chem. Phys. Letters*, 1969, 3, 319.

² G. Hut, A. W. Sleeswyk, H. J. Hackelöer, H. Selbach and O. Kanert, *Phys. Rev. B*, 1976, 14, 921.

³ H. J. Hackelöer, H. Selbach, O. Kanert, A. W. Sleeswyk and G. Hut, *Phys. Stat. Sol. (b)*, 1977, 80, 235.

sion approximation, which can be derived from the general theory of Wolf¹ applies here. From this follows the dependence of $1/T_{1\rho}$, the spin-lattice relaxation rate in the rotating frame, on τ . The quadrupolar fluctuations caused by the lattice distortions around moving dislocations dominate the dipolar effects on the relaxation rate.

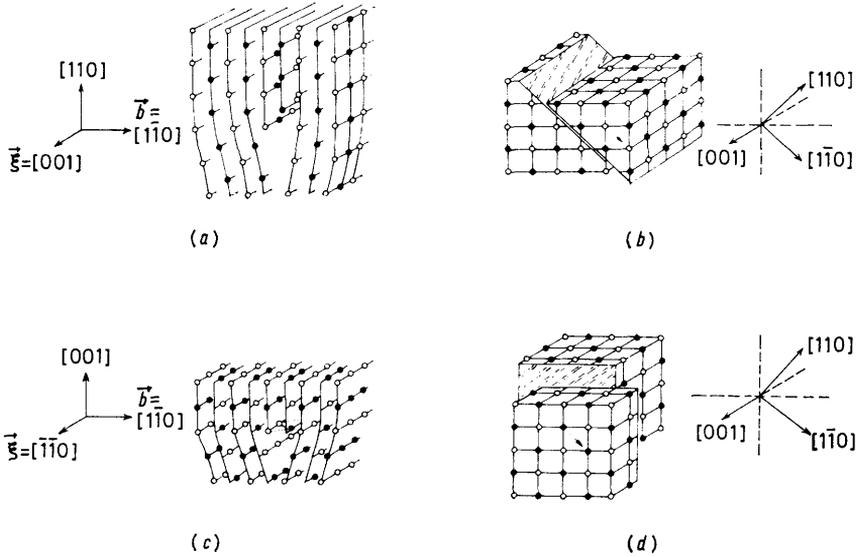


FIG. 7.—Examples of dislocations on $\{110\}$ and $\{100\}$ glide planes in crystals with the NaCl structure and the shear caused by their motion.

Using the relation between the plastic deformation rate $\dot{\epsilon}$ and the dislocation velocity:

$$\dot{\epsilon} = \varphi \rho_m b \bar{v}, \quad (1)$$

the relaxation rate can be expressed in the form:

$$R_D^B \equiv \frac{1}{T_{1\rho}} = \frac{H_D^2}{H_1^2 + H_D^2 + H_Q^2} \times \frac{1}{\rho_t} \times \frac{1}{\varphi b L} \times \dot{\epsilon}, \quad (2)$$

where ρ_m is the mobile dislocation density, ρ_t the total dislocation density (including ρ_m), φ a factor dependent on the angles between the deformation direction and the slip direction and b the magnitude of the Burgers vector of the moving dislocations.

In our experiments, the change in the relaxation rate due to dislocation motion has been measured in alkali halide single crystals, plastically compressed uniaxially, as a function of the strain rate $\dot{\epsilon}$ (fig. 8) and the magnitude of the locking field, confirming relation (2).

In the $R_D^B(\dot{\epsilon})$ curve of pure ²³NaCl single crystals, compressed in the $\langle 100 \rangle$ direction, a maximum occurs which is an indication of the transition from the strong collision to the weak collision region. The position of this maximum, at $\dot{\epsilon} = 20 \text{ s}^{-1}$, represents a mean waiting time $\tau_m = 2.8 \times 10^{-5} \text{ s}$ and from the height of the maximum a mobile fraction of dislocations of $\rho_m/\rho_t = 0.22$ is derived. From the R_D^B values in the strong collision region a mean distance between strong obstacles $L = 1.6 \times 10^{-6} \text{ m}$ could be deduced. Assuming that the dislocations are homogeneously distributed in the crystal this value corresponds to a total dislocation density of $\rho_t =$

¹ D. Wolf, *Phys. Rev. B*, 1976, **14**, 932.

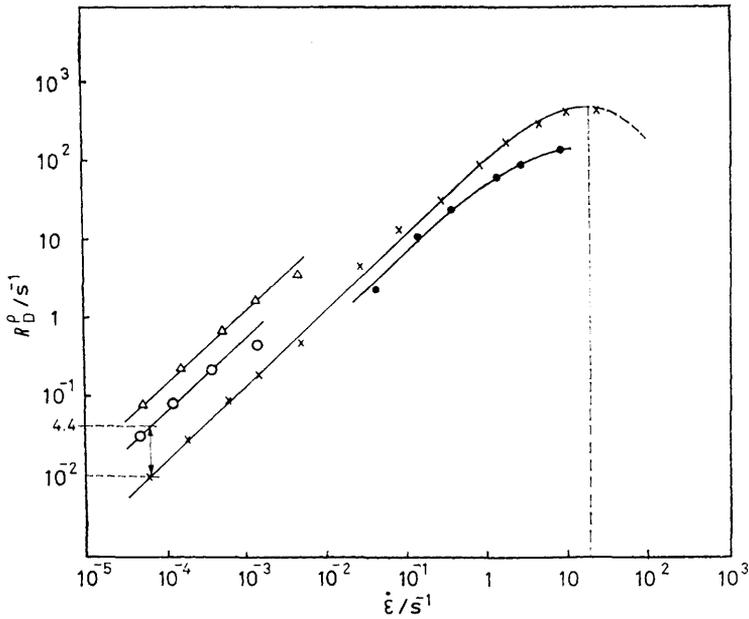


FIG. 8.—Dislocation induced part of the relaxation rate R_D^ρ as a function of the strain rate $\dot{\epsilon}$ measured on different nuclei in alkali halide single crystals, deformed in the $\langle 100 \rangle$ direction. $T = 293$ K, $\langle \epsilon \rangle \approx 3\%$, $H_0 \parallel \langle 110 \rangle$. \times , $^{23}\text{NaCl}$, $H_1 = 2.2$ G; \bullet , ^{23}NaF , $H_1 = 5.5$ G; Δ , $^{87}\text{RbCl}$, $H_1 = 2.0$ G; \circ , $\text{Na } ^{35}\text{Cl}$, $H_1 = 2.2$ G.

$4 \times 10^{11} \text{ m}^{-2}$, which is approximately the same as the values found in pure crystals using other methods. This confirms that for a moving dislocation in a pure crystal the main strong obstacles are the dislocations it intersects.

The impurity content of the NaCl single crystals has been varied (fig. 9). The impurities consist of Ca^{2+} ions, which are bound to cation vacancies, constituting

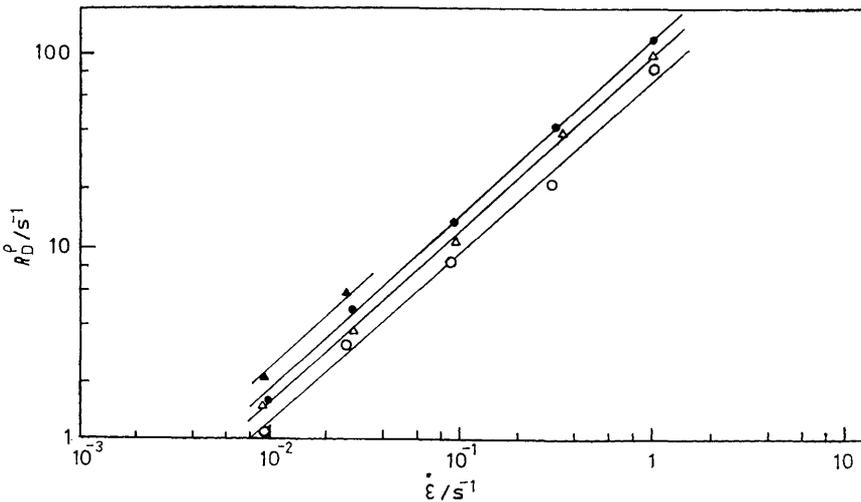


FIG. 9.—Dislocation induced part of the relaxation rate R_D^ρ as a function of $\dot{\epsilon}$ in $^{23}\text{NaCl}$ single crystals doped with different amounts of impurities. $T = 295$ K; $1 < \epsilon/\% < 5$; $H_0 \parallel \langle 110 \rangle$, $H_1 = 2.2$ G. \circ , 0.0007; Δ , 0.0017; \bullet , 0.0080; \blacktriangle , 0.0340 mol % Ca^{2+} .

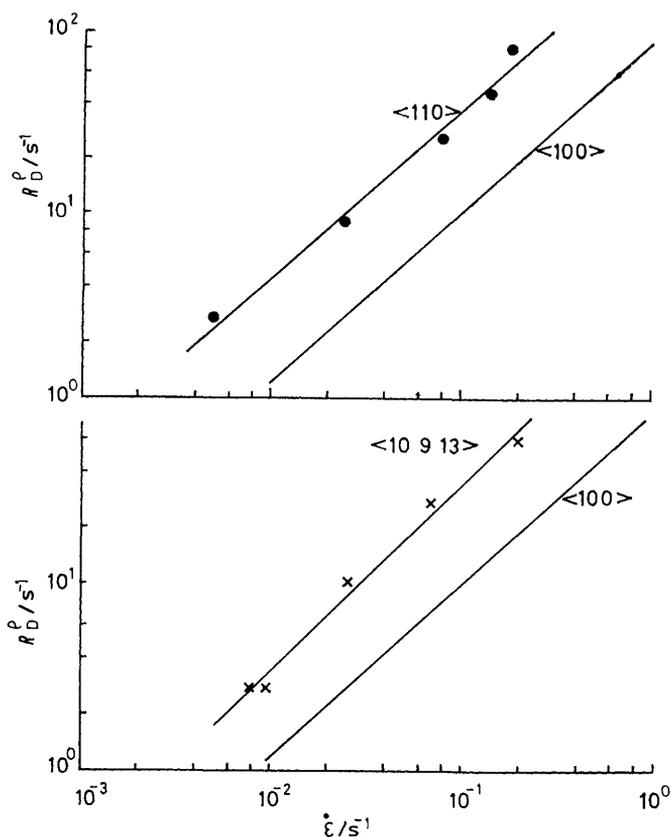


FIG. 10.—Dislocation induced part of the relaxation rate R_D^ρ as a function of $\dot{\epsilon}$ in $^{23}\text{NaCl}$ single crystals for different crystal orientations with respect to the deformation axis. $T = 295\text{ K}$, $H_1 = 2.2\text{ G}$. Upper: $\langle 110 \rangle$, $\langle \epsilon \rangle = 4\%$, $\sigma = 80\text{ MPa}$; $\langle 100 \rangle$, $\langle \epsilon \rangle = 3\%$, $\sigma = 10\text{ MPa}$; lower: $\langle 10\ 9\ 13 \rangle$, $\langle \epsilon \rangle = 4\%$, $\sigma = 80\text{ MPa}$; $\langle 100 \rangle$, $\langle \epsilon \rangle = 3\%$, $\sigma = 10\text{ MPa}$.

additional local obstacles for dislocation motion. The mean distance L covered during one dislocation “jump” consequently diminishes and, therefore, the relaxation rate increases with increasing doping concentration. From the position of the lines in fig. 9 however, an impurity concentration is derived which is much smaller than the actual Ca^{2+} content. This indicates that aggregates of Ca^{2+} -ions have grown in the crystals during their slow furnace-cooling.

The orientation of $^{23}\text{NaCl}$ crystals with respect to the deformation direction has been varied as well. For crystals with the $\langle 110 \rangle$ orientation and crystals orientated near the $\langle 111 \rangle$ direction (*i.e.*, $\langle 10\ 9\ 13 \rangle$) the relaxation rates have been compared with the measurements in fig. 8 on $\langle 100 \rangle$ orientated crystals; in each case the orientation is parallel to the deformation direction (fig. 10).

To understand these relaxation-rate changes one should realise that dislocations can move on different glide-planes. Which one is chosen depends on the orientation of the crystal relative to the compression axis accounted for by the factor φ in eqn (1), on the PN force of the glide-planes, and on the dislocation density on other planes. Therefore in eqn (2) H_Q , ρ , φ and L change with changing orientation.

In conclusion one can say that the experimental results supply extensive quantitative information on dislocation motion.