Application of Proton Polarization Transfer to a High-spin Nucleus, Germanium-73

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The application of proton polarization transfer (p.t.) *via* insensitive nuclear enhancement by p.t. pulse sequences to germanium-73 n.m.r. is investigated for a variety of compounds. Despite the relatively short ^{73}Ge relaxation times of this quadrupolar nucleus, and long, inhomogeneous radio frequency pulses, this method gives significant p.t. enhancements from compounds with hydrogen, methyl, or ethyl groups bonded to germanium. Signal enhancements range from 2- to 6-fold for proton-decoupled spectra and up to 20-fold for coupled spectra. Reductions in the time required to obtain a ^{73}Ge spectrum range from 3- to 10-fold for a decoupled spectrum to 100-fold for a coupled spectrum. Applications of the technique are illustrated.

Modern techniques have rendered most of the Group 4 elements readily accessible to n.m.r. studies, and work on ^{13}C, ^{29}Si, ^{117,119}Sn, and ^{207}Pb is highly feasible. The exception is germanium, whose one magnetic isotope, ^{73}Ge with spin $\frac{9}{2}$, presents a combination of properties unfavourable to magnetic resonance studies: the natural abundance is 7.76%, the gyromagnetic ratio [1] is very small ($\gamma = -0.9332 \times 10^7$ rad T^{-1} s^{-1}), and the nuclear quadrupole moment is moderately large. The sensitivity relative to ^{1}H at natural abundance and constant field is only 1.08×10^{-4} and, since quadrupolar relaxation dominates, dipole–dipole relaxation and nuclear Overhauser effects (n.O.e.) are unimportant. For example, we have measured a n.O.e. factor of approximately -0.3 for GeMe$_4$. Unsymmetric compounds often give broad ^{73}Ge signals. As a result, only a limited number of ^{73}Ge n.m.r. studies have been reported: signals have been observed from halides [2] (GeX$_4$), mixed halides [3] (*e.g.* GeCl$_3$Br), and from alkyls [2] (GeR$_4$), but not from mixed halide–alkyls [2] (*e.g.* GeCl$_3$Me). Before these, and other apparent limits, can be fully investigated it is advantageous to explore methods of signal enhancement appropriate to ^{73}Ge observation.

In addition to the intrinsic value of ^{73}Ge studies (*e.g.*, in characterisation or to examine trends in Group 4), this nucleus also represents a useful limiting case which can be suggestive for studies of other difficult nuclei. For example, the nuclear spin of $\frac{9}{2}$ is the highest value encountered for nuclei of general chemical interest. Where higher values are known, such as 6 for ^{50}V or 7 for ^{176}Lu, other isotopes of the elements have lower spins and higher sensitivities. However, ^{87}Sr, ^{93}Nb, ^{115}In, or ^{209}Bi which all have spins of $\frac{9}{2}$ together with a substantial number of isotopes with spins $\frac{7}{2}$, are the most accessible species available. Of these, ^{73}Ge shows the lowest sensitivity at natural abundance and constant field with the sole exception of ^{43}Ca. Thus it represents an excellent probe of the limits of feasible observation.

In this paper, we report the extension of the methods of signal enhancement by polarization transfer (p.t.) to ^{73}Ge and indicate applications in analysis. Such methods have been developed mainly for spin $\frac{1}{2}$ nuclei and have scarcely been tested on nuclei with larger spin quantum numbers.

Spin–spin coupling between a nucleus of small gyromagnetic ratio, γ, and one of high γ (usually ^{1}H) allows transfer [4] of nuclear spin polarisation to the former. Since germanium compounds containing hydrogen are numerous,[5] and resolvable scalar spin–spin coupling, $J(^{73}\text{Ge}-^{1}\text{H})$ exists,[2,6,7] proton p.t. *via J* coupling is a good means of sensitivity enhancement. One method of p.t. consists of a class of multipulse sequences that Morris and Freeman [8] have termed ' insensitive nuclei enhancement by p.t.' (i.n.e.p.t.). This method is employed here, since it is relatively accessible experimentally.

I.n.e.p.t. sequences have become well established for ^{13}C studies,[9] and widely extended to other spin $\frac{1}{2}$ nuclei [10–15] including ^{15}N, ^{29}Si, ^{57}Fe, ^{103}Rh, ^{109}Ag, ^{119}Sn, and ^{183}W, but studies of nuclei with spins greater than $\frac{1}{2}$ are limited to the work of Doddrell and co-workers on ^{14}N (spin = 1),[16] and ^{11}B (spin = $\frac{3}{2}$) or ^{10}B (spin = 3).[17] The ^{73}Ge quadrupole moment [18] is moderate in size (-0.18×10^{-28} m^2) but the quadrupole line broadening is attenuated by the large spin quantum number. Since the resonance frequency is low,[19] acoustic ringing is significant and radio frequency pulse widths are long and inhomogenous. Application of i.n.e.p.t. to ^{73}Ge is thus a significant extension and test of the method.

Results

I.N.E.P.T. applied to Spin $\frac{9}{2}$.—The general theories presented by Pegg *et al.*[17] on proton p.t. enhancements and timing, using an i.n.e.p.t. pulse sequence need to be applied here to the case of spin quantum number $\frac{9}{2}$. Coupled enhancement varies as equation (1), where E is the coupled p.t. enhancement, M_H the total proton spin, τ the preparation time in the pulse sequence, γ_I the gyromagnetic ratio of the I multiplet, and J the scalar coupling constant. Following the example of Pegg

$$E(M_H,I,\tau) = M_H\gamma_H\gamma_I^{-1}[\sum_{m_I} m_I \sin(4\pi J m_I\tau)]/\sum_{m_I} m_I^2 \quad (1)$$

et al., equation (1) is re-expressed as $E(M_H,I) = kE(\alpha)$ [where $k = 2(M_H\gamma_H)/(\gamma_I \sum_{m_I} m_I^2)$ and $\alpha = 4\pi J\tau$]. For the present example, the ^{73}Ge resonances in GeH$_4$, $E(\alpha) = \sum_{m_I=\frac{1}{2}}^{\frac{9}{2}} m_I\sin(m_I\alpha)$ and $k = -0.6949M_H$, where $M_H = \pm2$, ±1, or 0. In Figure 1, a plot of this trigonometric function is shown for the $M_H = 1$ and 2 transitions, together with the experimental variation of coupled enhancement with timing. Taking relaxation effects into account, there is very good agreement between the form of the experimental and theoretical curves, thus confirming the validity of equation (1) for this spin value.

For decoupled p.t. enhancement, E_d, Pegg *et al.*[17] derived the general equation (2), where Δ is the final delay time in the pulse sequence, n is the number of scalar coupled protons, and

$$E_d(n,I,\Delta) = \tfrac{1}{2}nf(I)\gamma_H\gamma_I^{-1}\cos^{n-1}(\pi J\Delta)\sin(\pi J\Delta) \quad (2)$$

where $f(I) = E_{(opt)}M_H^{-1}\gamma_H^{-1}\gamma_I$ [(opt) indicates the optimum value of the first maximum in the enhancement or the associated timing]. As for equation (1), we can re-express equation (2) as equation (3). Here, $k' = \frac{1}{2}E_{(opt)}M_H^{-1}$, $\beta = \pi J\Delta$, and

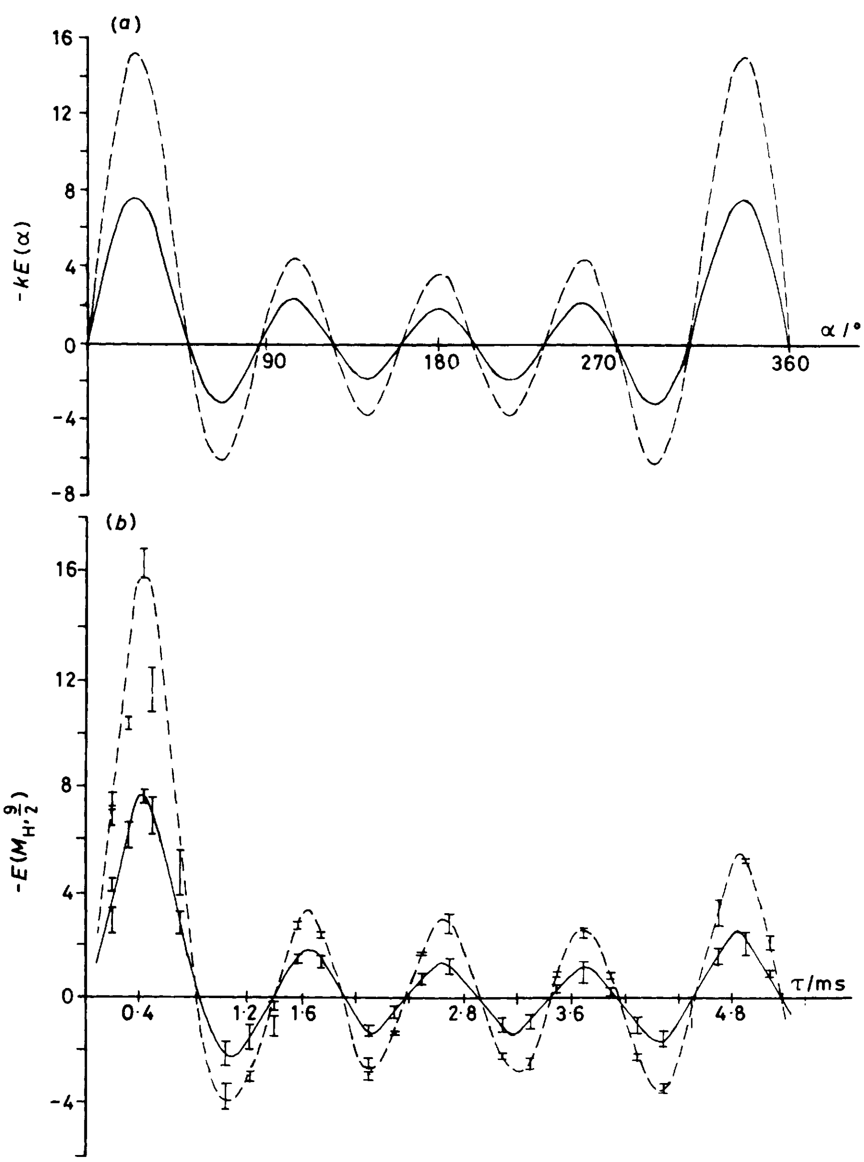

Figure 1. (*a*) Plots of the trigonometric function, $E(\alpha) = \sum_{m_I = \frac{1}{2}}^{\frac{9}{2}} m_I \sin(m_I \alpha)$ for $0 \leqslant \alpha \leqslant 360°$ and $M_H = 1$ (——) and 2 (— — —). (*b*) Experimental variation of $E(M_H, \frac{9}{2})$; $M_H = 1$ (——) and 2 (— — —), with respect to τ, where $\alpha = 70.3\tau + 9.9$, as procured from the coupled ^{73}Ge resonances in GeH_4

$E_d(\beta) = n \cos^{n-1}\beta \sin \beta$. This equation has received only limited testing for higher values of *n* although the first

$$E_d(n,l) = k'E_d(\beta) \qquad (3)$$

maximum was examined [15] for $SnMe_4$ ($n = 12$). In Figure 2, the full functional form of equation (2) is examined for $GeMe_4$. A plot of $E_d(\beta) = 12\cos^{11}\beta \sin\beta$ for $0 \leqslant \beta \leqslant 360°$ is compared with the experimentally observed variation of the decoupled enhancement as a function of Δ. The good agreement between the forms of the experimental and calculated curves gives further positive support to the theories [17] applied to E_d.

Maximum Enhancements and Optimum Timing.—The value of Δ for which E_d is an optimum is given by equation (4) with

$$\Delta_{(opt)} = (\pi J)^{-1} \arcsin n^{-\frac{1}{2}} \qquad (4)$$

a corresponding value of E_d given by equation (5).

$$E_{d(opt)} = (\tfrac{1}{2}) f(l) \gamma_H \gamma_I^{-1} n^{\frac{1}{2}} (1 - 1/n)^{(n-1)/2} \qquad (5)$$

In summary, the theories of Pegg *et al.*, applied to ^{73}Ge-{^{1}H} i.n.e.p.t. predict that: $\tau_{(opt)} = (29.9J)^{-1}$, $E_{(opt)} = -7.583M_H$, and $E_{d(opt)} = -3.791\, n^{\frac{1}{2}}\, (1 - 1/n)^{(n-1)/2}$.

Depicted in Figures 3 and 4 are samples of ^{73}Ge n.m.r., with and without i.n.e.p.t., on a variety of germanium compounds. Maximum experimental enhancements, and the timing are compared with theoretical values in the Table. The experimental enhancement factors are the signal-to-noise ratio of decoupled i.n.e.p.t. spectra relative to that found in the spectra from 90° ^{73}Ge pulses with reverse gated decoupling. Coupled i.n.e.p.t. signal-to-noise values are compared with 90° pulse values without n.O.e. The minimum recycle times needed for a maximum i.n.e.p.t. signal were employed.

Significant enhancement factors were attained experimentally. Values found were between 3 and 20 for coupled spectra and 2 and 6 for decoupled ones. Enhancements very close to theory were obtained for GeH_4 which, having germanium in a site of tetrahedral symmetry, is expected to have a relatively long quadrupolar relaxation time, and exhibit short precession times, as it has a large coupling constant. As relaxation times decrease, or precession times increase, there is more opportunity for the loss of the p.t. signal, and the observed enhancements are reduced from the theoretical values. Adding the relatively long free precession times concomitant with decoupling yields spectra with lower $E\%$ values (percentage fraction of the theoretical enhancement actually attained) than coupled spectra. Spectra from p.t. *via* ^2J(Ge–H) on $GeMeH_3$ yield smaller values of $E\%$ than spectra from p.t. *via* ^1J(Ge–H) on the same compound. Since ^2J is about 30 times smaller than ^1J, and p.t. occurs for the same number of protons, i.n.e.p.t. *via* the former coupling has about 30-fold longer free precession times than the latter. However, the ^2J enhancement would become advantageous in species like $GeMe_2H_2$ or $GeMe_3H$. Even though Ge_2H_6 has short ^{73}Ge relaxation times, with an apparent spin–spin relaxation time of 25 ± 5 ms, p.t. enhancements are still attained, albeit somewhat reduced from the theoretical values.

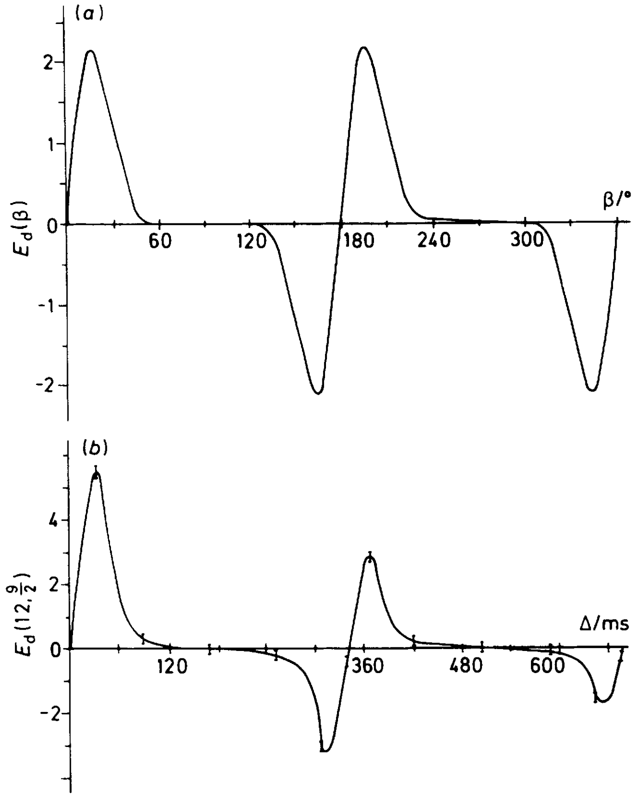

Figure 2. (*a*) Plot of trigonometric function, $E_d(\beta) = 12\cos^{11}\beta\sin\beta$ for $0 \leqslant \beta \leqslant 360°$. (*b*) Experimental variation of $E_d(12, \frac{9}{2})$ with Δ, where $\beta = 0.53\Delta + 0.6$, as obtained from the decoupled ^{73}Ge resonance in $GeMe_4$

There is a large error in $T\%$, the percentage deviation of experimental timing from the theoretical, arising from random error in J, and from an uncertainty in the exact measurement points of the timing in the pulse sequences. Bearing in mind this error, and that $T\%$ is both positive and negative, the experimental timing compares favourably with the theoretical timing. For example, the experimental timing of τ and Δ for $GeMe_4$ is $(30J)^{-1}$ and $(11J)^{-1}$, respectively, while the theoretical timing is $(29.9J)^{-1}$ and $(10.7J)^{-1}$.

Relative multiplet intensity ratios from coupled i.n.e.p.t. using a differential p.t. ($\Delta = 0$) are obtained theoretically by multiplying the binomial intensity ratios for a particular compound by the corresponding values of M_H. I.n.e.p.t. multiplet intensity ratios are generally as predicted. Differences between experimental and theoretical intensity ratios are similar for both coupled i.n.e.p.t. and coupled Fourier-transform spectra, with the exception of i.n.e.p.t. *via* the longer range coupling ^2J in $GeMeH_3$. In this case, four ' quartets ' are expected, adjacent quartets being separated by ^1J and each one in the i.n.e.p.t. intensity ratio −1 : −1 : 1 : 1, with coupling ^2J.

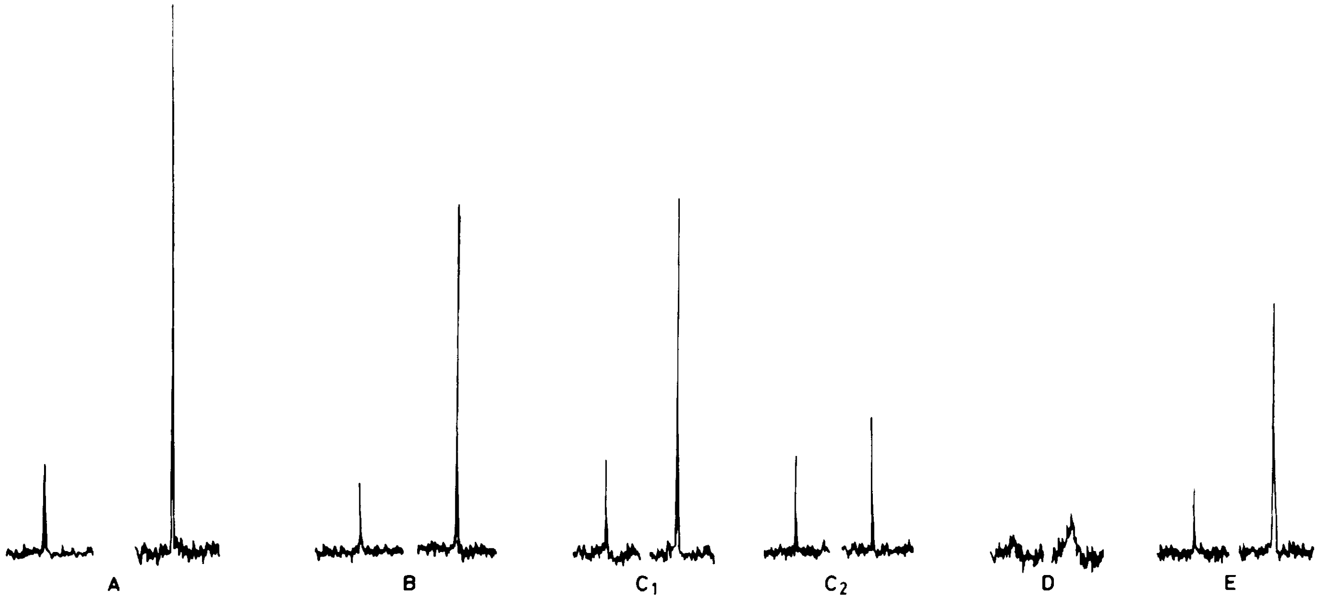

Figure 3. Single-pulse decoupled ^{73}Ge n.m.r. and decoupled ^{73}Ge i.n.e.p.t. spectra for the compounds GeH_4 (A), $GeMe_4$ (B), $GeMeH_3$ using ^1J (C_1), $GeMeH_3$ using ^2J (C_2), Ge_2H_6 (D), and $GeEt_4$ (E). For each, the larger signal of the pair was obtained by using i.n.e.p.t. Spectra are the average of 10 scans for A, B, and C, 40 scans for D, and 4 scans for E. Windows were 500—2 000 Hz with 4 096 or 8 192 data points. All linewidths were *ca.* 1 Hz, except for that of 13 Hz for Ge_2H_6

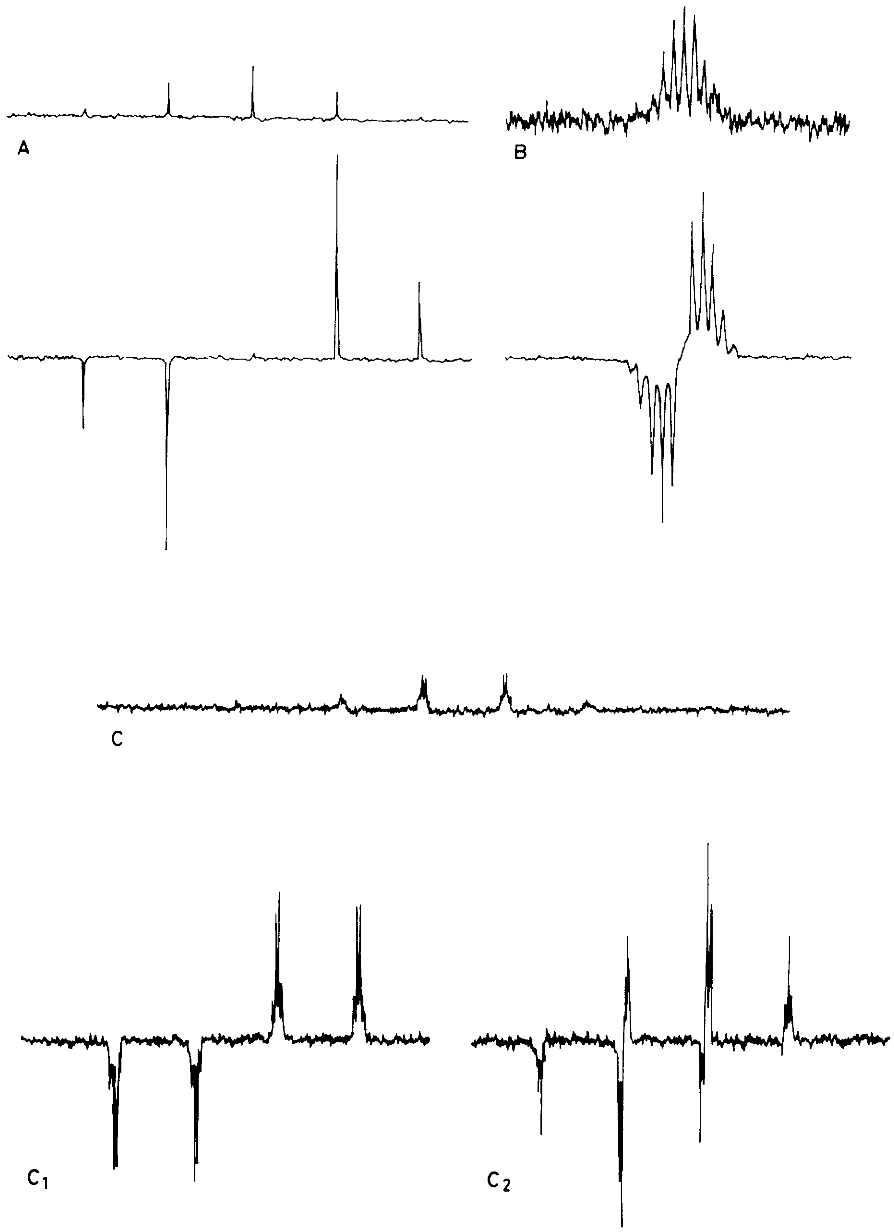

Figure 4. Normal 90° pulse coupled ^{73}Ge and coupled ^{73}Ge i.n.e.p.t. n.m.r. spectra of the compounds GeH_4 (A), $GeMe_4$ (B), and $GeMeH_3$ (C). The following conditions were used for the i.n.e.p.t. spectra: A, 100 scans, 2 000 Hz window, 4 096 data points; B, 304 scans, 500 Hz, 8 192; C_1, ^1J(Ge–H) 482 scans, 1 000 Hz, 8 192; C_2 ^2J(Ge–H), 482 scans, 1 000 Hz, 4 096. *J* Values are as given in the Table

Table. Maximum experimental enhancements and associated timing of ^{73}Ge i.n.e.p.t. compared to theory

	Maximum enhancement		Average *E*%		Average *T*%		
Compound	coupled [a]	decoupled	coupled	decoupled	τ	Δ	Coupling *J*(Ge–H)/Hz
GeH_4 [b]	7.2, 16	4.8	100	98	14	5	97.6 ± 0.3
$GeMe_4$ [c]	5.8, 20	5.8	75	72	−0.3	−3	2.95 ± 0.03
$GeMeH_3$ [b,d]	3.4, 9	3.3	85	75	18	8	94.3 ± 0.3
$GeMeH_3$	3.6, 6	1.7	75	40	14	13	3.5 ± 0.1
Ge_2H_6 [b]	4, 10	2	85	40	13	8	95.5 ± 0.5
$GeEt_4$ [e]	—	4.3	—	64	−35	−30 [f]	3 ± 0.6

[a] The smallest non-zero enhancement from the innermost multiplets is reported, together with the largest enhancement from the outermost multiplets, respectively. [b] In solution in $Bu^n{}_2O$. [c] Neat with traces of $Bu^n{}_2O$. [d] Same sample. [e] Neat. [f] For the purposes of calculation, the resolved coupling is assumed to be ^2J(Ge–H) rather than ^3J(Ge–H).

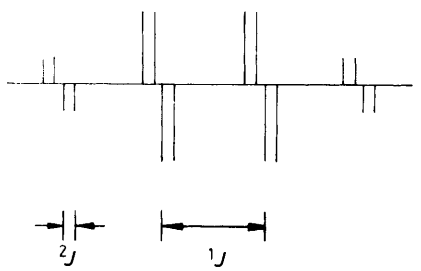

Figure 5. Expected intensity ratios when using ^{73}Ge i.n.e.p.t. *via* ^2J(Ge–H) on $GeMeH_3$ (C_2)

However, each quartet is modulated by the binomial intensity ratio 1 : 3 : 3 : 1 (see Figure 5). It is found that the outer quartets do not have a one-to-one correspondence between the observed and the expected signs. Intensity distortions have been reported [20] in coupled p.t. spectra when using long range $J(I–S)$. If I is coupled to two or more S spins, which, in turn have homonuclear couplings, $J(S–S)$, then intensity modulation may occur for the I multiplet when $J(I–S) \simeq J(S–S)$. In the present case $GeMeH_3$, this form of distortion can occur, *i.e.* since $^2J(Ge–H) = 3.5$ Hz $\simeq$ $^3J(H–H) = 4.1$ Hz. Radio frequency inhomogeneity and pulse missetting can also contribute to intensity distortions.

Instrument Time-saving.—While enhancements, E or E_d, of ^{73}Ge signal-to-noise by using i.n.e.p.t. have been demonstrated above, these will only lead to more effective instrument use if they are not offset by large increases in recycle time. If r is the ratio of the i.n.e.p.t. recycle time r_1 to the single pulse time r_0, then the instrument time-saving factor is E^2/r. Thus, i.n.e.p.t. is advantageous only if $E^2 > r$.

For the decoupled spectra of GeH_4 and $GeMe_4$, there is significant signal loss if $r_1 < 30$ s but r_0 must be less than several seconds for a large signal loss to occur. The single 90° pulse sequences have recycle times largely governed by the ^{73}Ge spin-lattice relaxation time (T_1). It has been suggested [19] that accurate intensity measurements for single 90° pulse sequences require a minimum r_0 of $5T_1$, thus at least 2—$4T_1$ is needed to avoid large signal loss. For $GeMe_4$ and GeH_4, T_1 is of the order of one second, thus r_0 would be around 2—4 s as observed. Thus E^2/r is at least 2 for GeH_4 or $GeMe_4$.

I.n.e.p.t. recycle times are governed [8] by the proton T_1 (T_1^H). Measurements yielded T_1 values of 16 ± 5 s for GeH_4 and 9 ± 1 s for $GeMe_4$, on the same samples as used for the i.n.e.p.t. experiment. Thus the experimental i.n.e.p.t. recycle time when signal loss occurs is 2—$3T_1^H$. When $<10^{-3}$ mol dm^{-3} of the paramagnetic relaxant [19] [Cr(acac)$_3$] (acac = acetylacetonate) was added to $GeMe_4$ in Bu^n_2O, r_1 was reduced, giving a time-saving factor of 13 compared with 3 for neat $GeMe_4$, and this factor was similar when 10^{-2} mol dm^{-3} [Cr(acac)$_3$] was used in C_6H_6. Thus, the addition of very small amounts ($<10^{-3}$ mol dm^{-3}) of [Cr(acac)$_3$] will greatly improve the instrument time-saving factor in the study of the decoupled ^{73}Ge resonances of the germanium hydrides and, even if reaction takes place with Ge–H, loss of sample will be minor at this concentration.

However, the long acquisition times, which are common when observing coupled spectra, will increase r_0 even though the acquisition time itself may be longer than the waiting time necessary to avoid signal loss by ' saturation effects '. Doping with [Cr(acac)$_3$] may be unnecessary in this case. A good example of this effect is found when running overnight accumulations of the same instrumental time, on neat $GeMe_4$, yielding 8 000 scans from the unenhanced coupled sequence, and 900 scans from coupled i.n.e.p.t. The i.n.e.p.t. sequence gives signal-to-noise gains of 3—13, representing potential time-saving factors of *ca.* 10—150. In addition, all 12 out of the 12 possible multiplets are observed using p.t., while only 10 out of the 13 possible multiplets are observed using conventional Fourier-transform n.m.r. In a similar fashion potential time-saving factors of 2—20 using coupled i.n.e.p.t. are attainable with GeH_4.

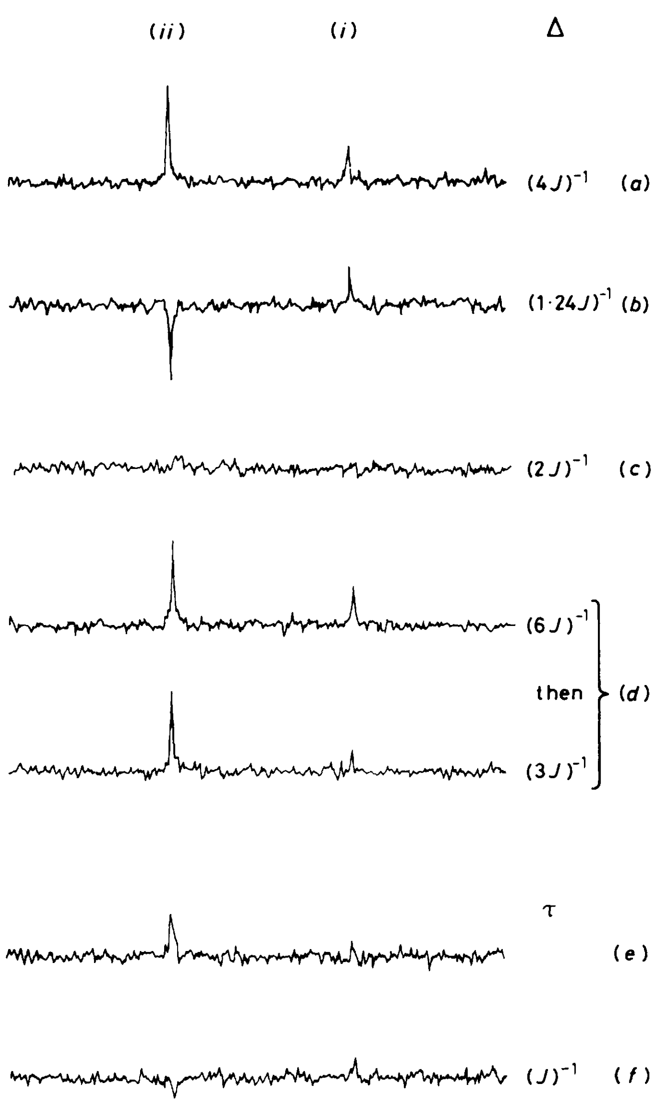

Figure 6. Demonstration of ^{73}Ge i.n.e.p.t. as an assignment aid. Decoupled spectra of the products of the self reaction of [Fe(CO)$_4$(GeMe$_2$H)(GeMeH$_2$)] in C_6H_6. (*a*) Phasing reference, $n \neq 0$ (↑) (positive); (*b*) n = 1 and 3 (↑), n = 2 and 4 (↓); (*c*) n = 1 (↑), $n \neq 1$ (zero). Thus signal (*i*) has n = 3 and arises from $GeMeH_3$; (*d*) n = 2 has same intensity in the two experiments, while n = 4 has intensity reduced by a factor of three for $\Delta = (3J)^{-1}$. Thus signal (*ii*) has n = 2 and arises from $GeMe_2H_2$. For comparison, (*e*) is a standard 90° pulse sequence with reverse gated decoupling sequence and (*f*) a spin-echo J-modulated sequence with the same number of scans as i.n.e.p.t.

Some Illustrations of ^{73}*Ge Observations.*—(*a*) *Methylgermanes.* It has been shown for $GeMe_mH_{4-m}$ (m = 0, 1, or 4) that the experimental values of $\Delta_{(opt)}$ are reasonably close to the theoretical values of $\Delta_{(opt)}$. Using $\Delta_{(opt)} = [D_{(opt)}J]^{-1}$, then $D_{(opt)}$ is essentially a function of the number of protons, n, used in p.t. Thus, decoupled i.n.e.p.t. can be used as an assignment aid for ^{73}Ge n.m.r. in a similar manner to its current use[9,21] in ^{13}C n.m.r. The values of $D_{(opt)}$ used to identify n are the same for any nucleus. We have found[22] that $[Fe(CO)_4(GeMe_xH_{3-x})(GeMe_yH_{3-y})]$ species eliminate a methylgermane $GeMe_mH_{4-m}$ and form an Fe_2Ge_2 species. While this reaction can be followed by ^{1}H or ^{13}C n.m.r., signals from the free germanes and the Ge–Fe species all occur close together and may be quite complex when $x \neq y$. In contrast, ^{73}Ge signals are observed only from the methylgermanes, presumably being too broad for detection in the Ge–Fe species, and the value of m may readily be identified by varying Δ. Thus, when the species with $x = 2$ and $y = 1$ was allowed to react in C_6H_6 at room temperature, the series of ^{73}Ge spectra shown in Figure 6 was observed using i.n.e.p.t. *via* ^1J(Ge–H) taken as 95 Hz. The reasoning given in the caption shows that the weaker signal (*i*) arises from $GeMeH_3$, while (*ii*) results from $GeMe_2H_2$. The instrumental time for this i.n.e.p.t. experiment is similar to the proton-decoupled spin-echo J-modulated experiment, despite the faster recycle time of the latter.

(*b*) *A methyldigermane.* Multiplicity assignment aided by decoupled i.n.e.p.t. will be a very useful tool in the assignment of more complex germanium hydrides. In general, chemical shift comparisons will yield little or no information about multiplicity in polygermanes. As an example, the compound $GeMe_2HGeH_3$ was studied by ^{73}Ge i.n.e.p.t. *via* ^1J. In a convenient instrument time, one ^{73}Ge resonance is observed. Using $D = 2$, no signal was observed, from which it was deduced that the signal is not from a GeH group. Following this, $D = 1.2$ was employed to differentiate $n = 3$ from even multiplicities. The positive intensity signal indicates the expected multiplicity of 3. Thus, the single resonance in $GeMe_2HGeH_3$ is from the GeH_3 group. With difficulty, the GeH and GeH_3 groups could be distinguished using a spin-echo J-modulated pulse sequence.[23] Finally, an overnight accumulation using coupled i.n.e.p.t. revealed a $-1 : -1 : 1 : 1$ ' quartet ', confirming the GeH_3 assignment.

(*c*) *Germanium hydride mixtures.* Ge_2H_6, Ge_3H_8, or the higher hydrides are difficult to free completely from traces of their homologues and also form GeH_4 on thermal decomposition. The ^{73}Ge chemical shifts of all the germanes are likely to be very similar. However, use may be made of the ' up-down ' appearance of coupled i.n.e.p.t. ($\Delta = 0$), and the null signal, $M_H = 0$, to separate overlapping proton-coupled ^{73}Ge resonances. The example illustrated, Figure 7, is a mixture of GeH_4 and Ge_2H_6 in $Bu^n{}_2O$. The two ^{73}Ge signals overlap [Figure 7(*a*)] in the simple spectrum, making accurate determination of ^1J(Ge–H) in digermane impossible (and ^{73}Ge satellites were not found in the ^{1}H spectrum of Ge_2H_6). Coupled ^{73}Ge i.n.e.p.t., with a factor of 1.4 less in instrumental time, and a factor of 21 less in the number of scans, gives the spectrum in Figure 7(*b*). The signal-to-noise ratio of the spectrum from i.n.e.p.t. is still greater than in the ordinary coupled spectrum. The expected i.n.e.p.t. intensity ratios are obtained, being close to $-1 : -2 : 0 : 2 : 1$ for GeH_4, and $-1 : -1 : 1 : 1$ for Ge_2H_6. Now the Ge_2H_6 multiplet in the same position as the null $M_H = 0$ GeH_4 multiplet is readily observed. In addition, the remaining Ge_2H_6 multiplets are more readily distinguishable from the GeH_4 ones in the i.n.e.p.t. spectrum than in the Fourier-transform one. This allows the coupling constant of digermane from the i.n.e.p.t. spectrum to be measured (95.5 ± 0.5 Hz) with much lower random error than from the Fourier-transform spectrum (95 ± 10 Hz).

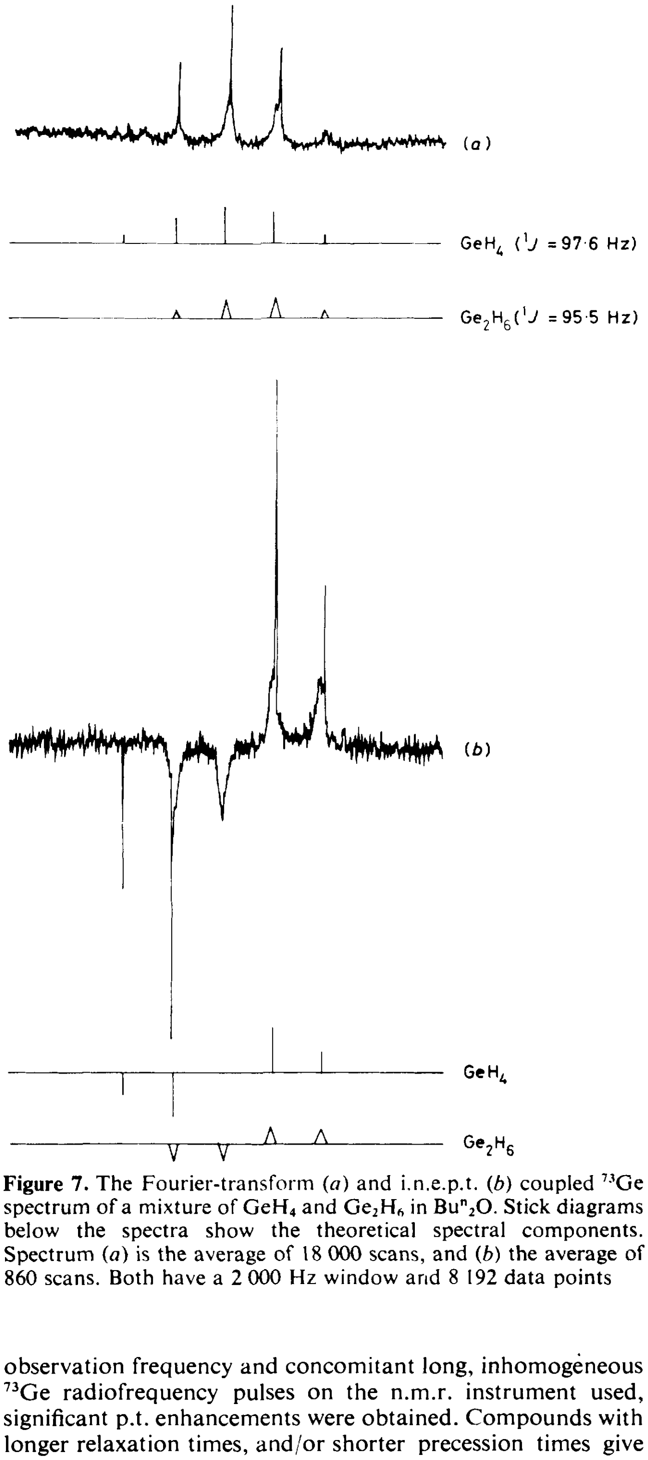

Figure 7. The Fourier-transform (*a*) and i.n.e.p.t. (*b*) coupled ^{73}Ge spectrum of a mixture of GeH_4 and Ge_2H_6 in $Bu^n{}_2O$. Stick diagrams below the spectra show the theoretical spectral components. Spectrum (*a*) is the average of 18 000 scans, and (*b*) the average of 860 scans. Both have a 2 000 Hz window and 8 192 data points

Discussion

It has been demonstrated that the general theories, used to obtain the p.t. enhancement as a function of timing parameters, are applicable to this high-spin case of $I = \frac{9}{2}$. Despite the low observation frequency and concomitant long, inhomogeneous ^{73}Ge radiofrequency pulses on the n.m.r. instrument used, significant p.t. enhancements were obtained. Compounds with longer relaxation times, and/or shorter precession times give enhancements close to the theoretical.

The long i.n.e.p.t. cycle times required by long proton spin–lattice relaxation times limited significant instrument time-saving to compounds with a large ^{73}Ge T_1 to ^{1}H T_1 ratio, or to accumulations with long acquisition times. However, the addition of very small amounts of $[Cr(acac)_3]$ considerably reduced i.n.e.p.t. recycle times. Decoupled i.n.e.p.t. as an aid in multiplicity assignment, applied *via* ^1J(Ge–H) coupling, was useful in a number of experiments. Thus, proton p.t. to ^{73}Ge using i.n.e.p.t. is a useful tool in ^{73}Ge n.m.r., remembering that the range of compounds containing both germanium and hydrogen is extensive. Since proton p.t. *via* i.n.e.p.t. works on a ' high-spin ' nucleus of significant quadrupole moment and low observation frequency, this result may be an incentive for the application of p.t. *via* i.n.e.p.t. to other quadrupolar nuclei.

There will be reported elsewhere work currently in progress on ^{73}Ge chemical shifts, coupling constants, and relaxation time measurements. Preliminary work on the use of the pulse sequence ' distortionless enhancement by p.t.'[24] in ^{73}Ge n.m.r. has yielded smaller enhancements with GeH_4 to that obtained by proton decoupled ^{73}Ge i.n.e.p.t.

Experimental

Compounds.—The germanium compounds were prepared by standard methods.[25] The gases GeH_4, Ge_2H_6, and $GeMeH_3$ were sealed in dry, degassed, $Bu^n{}_2O$ with approximately 1 atm pressure above the solution. $GeMe_4$ was sealed with a small amount of $Bu^n{}_2O$. All the samples were run in sealed 5-mm o.d. tubes held concentrically in 10-mm tubes containing fresh D_2O for the lock. Purities were checked spectroscopically (^{1}H and ^{13}C n.m.r. and i.r.).

Instrumentation.—Measurements were made on a JEOL FX 90Q spectrometer equipped with the NM-IT 10LF low-frequency insert and the PG200 programmable pulse generator. The instrument is modified to allow the application of phase controlled ^{1}H radiofrequency pulses on the irradiation channel. The observing frequency was 3.125 MHz, the probe temperature was 27 °C, the 90° pulses had widths of 130 ± 3 μs for ^{73}Ge observation and 48 ± 3 μs for ^{1}H on the irradiation channel.

A typical pulse sequence for obtaining ^{1}H coupled n.m.r. spectra for a nucleus I is as follows: $90°[H,y]\text{-}\tau\text{-}180°[H,x]$, $180°[I,x]\text{-}\tau\text{-}90°[H,x],90°[I,y]$ (acquire). Proton decoupled I n.m.r. spectra are procured by the inclusion of the following pulses, and decoupling, to the sequence- $\frac{\Delta}{2}\text{-}180°[H,x],180°\text{-}[I,x]\text{-}\frac{\Delta}{2}$-(decouple), (acquire); where $90°[H,x]$ represents a pulse along the x axis to rotate the ^{1}H magnetization 90° from its original parallel to the z axis. The final pair of 90° pulses are applied sequentially, the I pulse being applied last. Phase alternation is employed on this pair of pulses.

The J-modulated sequence used is as follows: (decouple), $90°[I,x]\text{-}\tau\text{-}180°[I,x]$, (decouple)-τ-(acquire), (decouple); where τ represents the interval between the given events, and the proton decoupler is off only between the two radiofrequency pulses.

Chemical Shifts.—The ^{73}Ge chemical shifts of the compounds discussed are (p.p.m.) $GeMe_4 = 0$; $GeEt_4 = 17.8$; $GeH_4 = -298.9$; $Ge_2H_6 = -311.8$; $GeMeH_3 = -209.2$; $GeMe_2H_2 = -127.6$; $Ge_2MeH_5 = -306.2$ (GeH_3); and -211.0 ($GeMeH_2$). Values were measured w.r.t. neat $GeCl_4$ and converted by $\delta(GeMe_4) = \delta(GeCl_4) + 30.9$; negative values are to high field of $GeMe_4$. Absolute frequencies, relative to the ^{1}H signal of $SiMe_4$ = 100 000 000 Hz, were 3 488 423 ± 10 Hz for $GeCl_4$ (lit.,[2] 3 488 423 ± 10 Hz) and 3 488 318 ± 20 Hz for $GeMe_4$ (lit.,[2] 3 488 315 ± 10 Hz).

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