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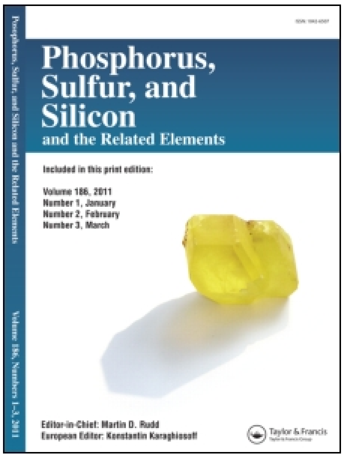

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Further Adventures in Germanium NMR

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The acoustic ring signal that dominates NMR spectra of low gyromagnetic ratio nuclei has always been a problem when trying to observe signals from weak samples. This work looks at some ways of improving the observability of ^{73}Ge – one such nucleus.

Keywords: Germanium; NMR; Baseline Roll

INTRODUCTION

During the 1980's the earlier pioneering observations on ^{73}Ge NMR were followed up[1] by the groups of Takeuchi, Lukevics and ourselves largely using an observing frequency of 3.1 MHz. Compounds observed included hydrides, alkylgermanes, alkylpolygermanes, silicon-germanium hydrides and alkyl derivatives, tetraalkyl germanes, carbofunctional alkyls, tetraalkoxides, and tetrahalides.

The work highlighted the problems of working with high spin, low resonance frequency nuclei. The baseline roll resulting from 'acoustic ringing' creates difficulties in trying to observe the expected broader line

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signals from non-symmetric species within wide spectral windows.

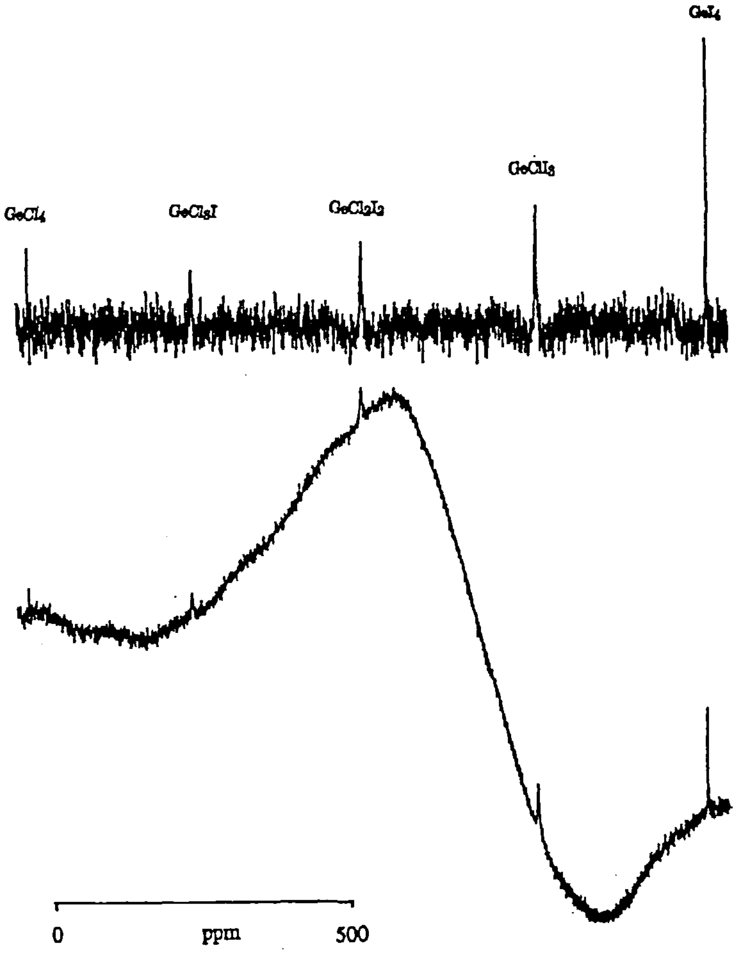

FIGURE 1 ^{73}Ge spectra, at 10.5 MHz, of a mixture of Me_2GeCl_2 and GeI_4 (in excess). See text for spectral details

The common approach is to zero the first few data points of the FID. For example Figure 1 shows spectra resulting from the mixing of Me_2GeCl_2 and GeI_4. The lower trace is a standard one pulse experiment, while the upper trace shows the reasonably smooth baselines

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obtained by zeroing 32 data points. However, any broad-line, fast relaxing species would be lost. The spectra show only the mixed tetrahalide species, with no ^{73}Ge signals from Me_2GeCl_2, Me_2GeClI or Me_2GeI_2 although ^{13}C and ^{1}H NMR showed that these species were present.

To observe broadline species a number of pulse sequences have been used, including RIDE and EXSPEC[2].

In recent times only occasional observations of germanium have been reported[3]. The studies to date have shown that there are straight-line ^{73}Ge, ^{29}Si, and ^{73}Ge, ^{119}Sn chemical shift correlations between equivalent germanium, silicon, and tin, compounds[1].

Observations made to date raise some questions. While mixed tetra-alkyl and mixed tetra-halide species have been observed no mixed R_nGeX_{4-n} species have been observed (see Figure 1). As mixed halide species such as $GeCl_2I_2$ are expected to have greater field gradients than some of the mixed alkyl halide species, why are the former, but not the latter observed?

Even with such pulse sequences the broadest signal observed to date is 500 Hz, considerably narrower than signals observed in other multinuclear NMR experiments of quadrapolar nuclei. Why is it that broader lined species are not observed?

CURRENT WORK

We are presently looking at what improvement higher field (300 MHz), and a dedicated germanium probe gives to the observation of this low resonance frequency nucleus. Higher field NMR improves the observation frequency and the sensitivity, but to maintain reasonable observation windows more powerful pulses are needed, and this aggravates the ‘acoustic ring’. The current generation of spectrometers allow for greater use of composite pulses, and greater phase cycling. This assists in providing better suppression of rolling baselines using the

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various pulse sequences available. Figure 2 shows what can be achieved using the more detailed pulse sequences.

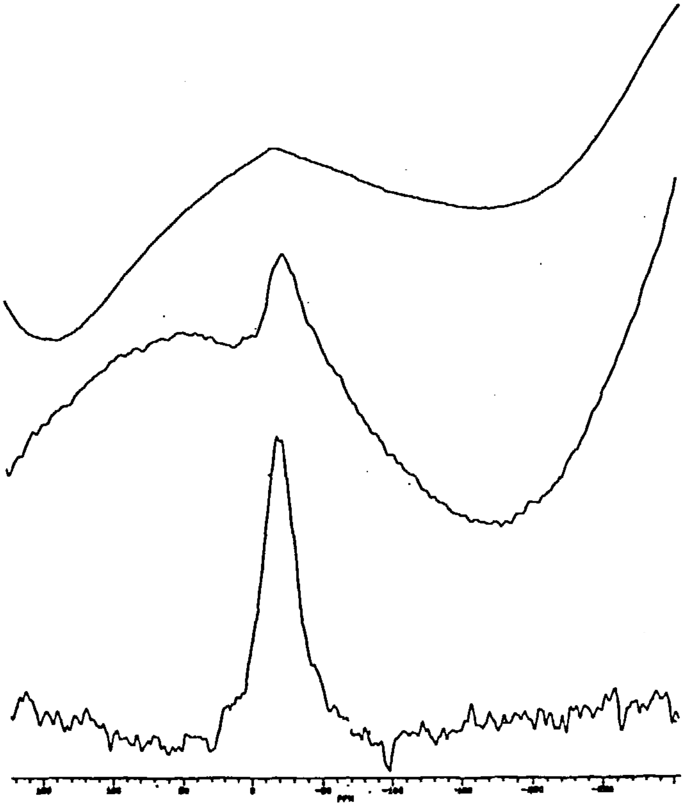

FIGURE 2 ^{73}Ge NMR spectrum of EtGe(Ph)$_3$. The upper trace is a standard one pulse experiment and shows no obvious signal. The middle trace was obtained using the RIDE sequence and while showing a signal from the sample still contains considerable baseline roll. The lower trace was obtained using the EXSPEC sequence and shows very good removal of the rolling baseline. Each spectrum was acquired over 8 hrs.

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Table 1 shows recent, previously unpublished observations, including those made at higher field.

TABLE 1 Recent Germanium-73 Chemical Shift Observations.

Compound	Chemical Shift (ppm)(a)	Linewidth (Hz)
Observations made at 3.1 MHz.		
GeH_3GeMe_2Cl	-280.5 (only GeH_3 observed)	39
$GeH_3GeH_2Mn(CO)_5$	-291.8 (only GeH_3 observed)	68
$GeH_3GeH(Me)Mn(CO)_5$	-277.9 (only GeH_3 observed)	17
GeH_3D	-293.3	1.95
GeD_4	-299.1	3.1
Ge_2D_6	-318.0	63
Observations made at 10.5 MHz.		
Ge_2Ph_6	-67	90
Ge_2Me_6	-59	
$MeGePh_3$	-22.9	43
$EtGePh_3$	-19.7	
$(Ph_3Ge)_3GeH$	-314	200
$(Ph_3Ge)_3SiH$	-53.2	40
$(Ph_3Sn)_4Ge$	-480.4	24

(a) w.r.t. Me_4Ge at 0 ppm.

The availability of computer programs for testing the theoretical efficiency of pulse sequences, and composite pulses, allow the non-mathematical among us to more easily carry out tests on likely sequences without tying up too much spectrometer time. Work is continuing on efforts to improve the observation windows.

Germanium NMR is a useful tool in looking at exchange reactions such as those shown in Figure 1. Proton or carbon NMR, for other than simple R groups, may contain far too much overlap to obtain useful kinetic data from this type of reaction. We are working on a number of halide exchange reactions.

To better understand the effect substituents have on the field gradient, and therefore the line widths, there is a need to look at a greater range of germanium compounds.

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Experimental

A sample of Me_2GeCl_2 (^1H 0.8 ppm/^{13}C 11.1 ppm), containing 8% of $MeGeCl_3$ (^1H 1.3 ppm/^{13}C 16.4 ppm), was dissolved in CS_2 and an excess of GeI_4 added. At equilibrium a signal for Me_2GeClI (^1H 1.2 ppm/^{13}C 14.4 ppm) containing approx 5% of the total Cl was observed. Peaks for the other species in solution totalled less than 1%.

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