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10. Application of ^{19}F Detected PFG Inverse NMR Technique

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^{19}F detected PFG inverse NMR method is applied to determine the structure of fluorinated organic compounds, which show AB-type signals on the ^{19}F NMR spectra. It is shown that the application of this method can lead to the signal assignment of ^{19}F and ^{13}C NMR spectra for fluorinated materials. We have also tried to remove the pseudo correlation signals in inverse 2D NMR spectra by applying the composite pulses and phase cycling. The long-range coupling correlation could be observed easily with ^{19}F detected inverse NMR experiments for the low concentration sample.

1. Introduction

Novel perfluorinated monomers have been developed for the use in the fields, such as polymer electrolyte fuel cell and optical materials[1]~[3]. NMR spectroscopy is one of the most powerful techniques to confirm the novel products, and to identify the impurities. ^{19}F NMR spectroscopy is especially important to determine the structure of fluorinated materials, because of the high sensitivity and wide range of chemical shifts. In ^{19}F NMR spectra, AB-type signals make the signal assignment complicated, whereas they can supply much information for ^{19}F NMR analysis. On the other hand, the signal assignment is easier for ^{13}C NMR spectra by applying 2D NMR techniques[4]. Usually, ^{13}C-^{19}F shift correlation spectroscopy methods are useful to assign the ^{19}F NMR spectra. However, ^{13}C detected experiments need the long time accumulation for ^{13}C NMR and ^{13}C-^{19}F 2D correlation spectroscopy, because of low sensitivity due to the low natural absorbance of ^{13}C. The detection of long-range coupling correlation is much difficult for ^{13}C-^{19}F shift correlation spectroscopy.

^{19}F detected PFG inverse NMR method is useful to assign ^{19}F NMR spectra[5]~[9]. The sensitivity is much higher for ^{19}F detection than ^{13}C detection from the difference in the natural abundance and gyromagnetic ratio. Therefore, the long-range coupling correlation might be detected for the low concentration sample by ^{19}F detected inverse NMR experiments. Berger[6] applied the ^{19}F detected PFG inverse NMR method to analyze the perfluoro-n-octyl bromide and the fluorinated pyridine. Riberiro[7] has reported the ^{19}F detected PFG inverse NMR method analysis of perfluoroheptanoic acid. Recently, Cheatham[8] has reported ^{19}F multiple selected 2D NMR correlation experiments to obtain better correlation. Newmark[9] has assigned the ^{19}F NMR and ^{13}C NMR spectra of perfluoro-1,3-and 1,4-dimethylcyclohexane using ^{19}F multiple selected 2D NMR correlation experiments. Although their applications were successful, only the simple fluorinated materials were examined, for which the signal assignment is not difficult for ^{19}F NMR spectra without inverse 2D NMR. In our best knowledge, there is no such application for the complicated spectra with AB-type signals.

In this paper, we have investigated a ^{19}F detected PFG inverse NMR method to determine the structure of fluorinated organic compounds, which show AB-type signals in the ^{19}F NMR spectra. We have also tried to remove the pseudo correlation signals in inverse 2D NMR spectra by applying the composite pulses and phase cycling.

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2. Experimental details

2.1 Samples

Two kinds of monomer samples were obtained from Asahi Glass Co., LTD. 2,2,3,3,4,4-Hexafluoro-4-trifluorovinyloxy-butyric acid methyl ester (M1), 2-Difluoromethylene-4,4,5-trifluoro-5-trifluoromethyl-[1,3] dioxolane (M2) were used for NMR measurements. The structures of these monomers are shown in **Fig. 1**.

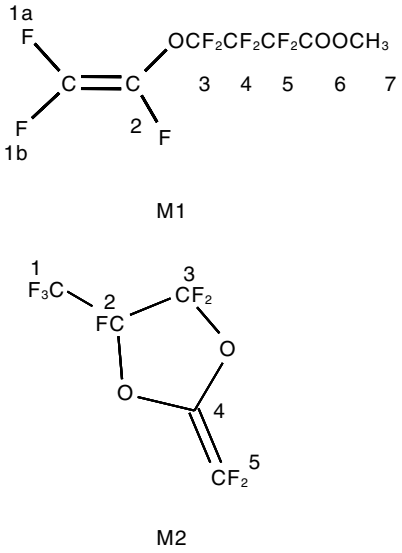

Fig. 1 Chemical structure of fluorinated monomers.

2.2 Measurement

JEOL α-600 nuclear magnetic resonance spectrometer was used with TH5FG probe for NMR measurements. A 90 ° pulse width is 11.0 μs for ^{13}C and 15.4 μs for ^{19}F. The resonance frequency is 150.80 MHz for ^{13}C and 564.55 MHz for ^{19}F. Samples were dissolved in $CDCl_3$ for NMR measurements. Some drops of fluorotrichloromethane were added as an internal standard. The geminal coupling and the long-range correlation are observed using HMQC technique. In this paper, we have estimated the pseudo correlation in details. We have made comparison of the pulse sequences with phase cycling and without phase cycling. And also, we have examined the uniformity of 180 ° pulse over the widen frequency region using composite pulses {90 °(X) 180 °(Y) 90 °(X)}.

3. Results and discussion

3.1 Application for M1 monomer

^{19}F detected PFG inverse NMR spectra are shown in **Fig. 2** and **3** for the M1 monomers. The geminal coupling is mainly observed in the HMQC spectra for which the coupling constant is set in J = 280 Hz (**Fig. 2**). The long-range correlation is observed in the HMQC spectra for which the coupling constant is set in J = 10 Hz (**Fig. 3**). The sensitivity of these signals is quite good because the

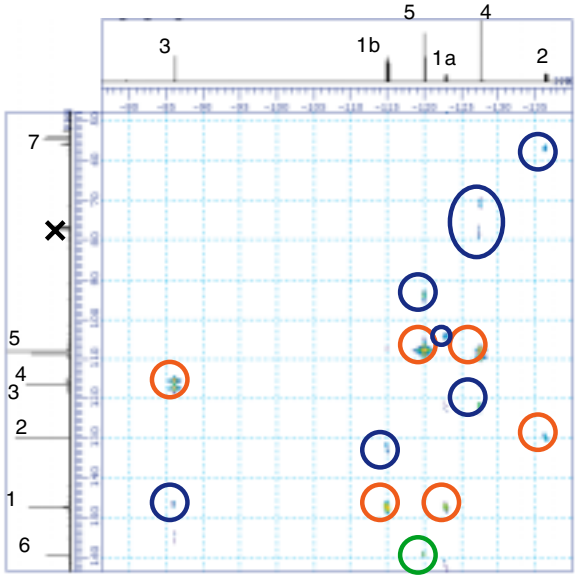

Fig. 2 ^{19}F detected PFG inverse 2D NMR spectrum of M1 HMQC, J = 280 Hz, without phase cycling, without composite pulses {90 °(X) 180 °(Y) 90 °(X)}. The circles in the figure indicate the signals for (Red) geminal (Green) vicinal and (Blue) pseudo correlations.

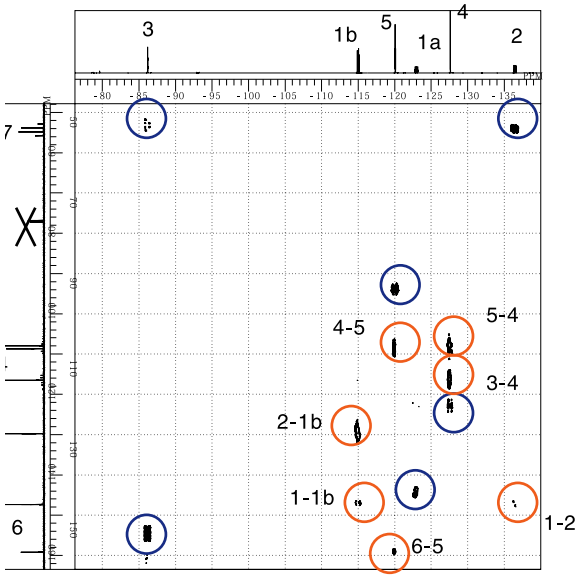

Fig. 3 ^{19}F detected PFG inverse 2D NMR spectrum of M1 HMQC, J = 10 Hz, without phase cycling, without composite pulses {90 °(X) 180 °(Y) 90 °(X)}. The circles in the figure indicate the signals for (Red) vicinal and (Blue) pseudo correlations.

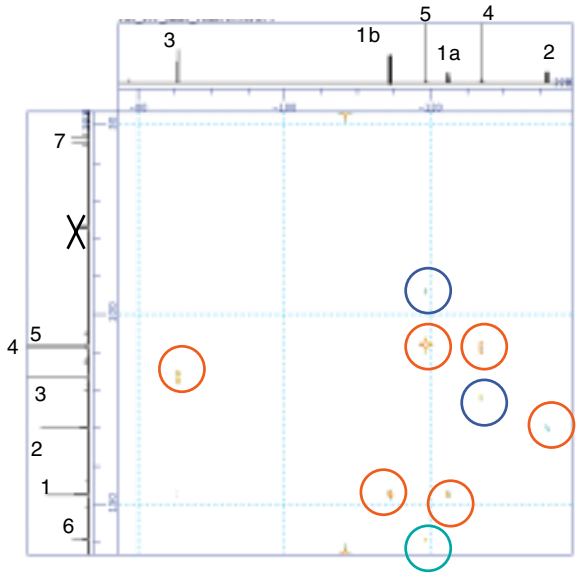

Fig. 4 ^{19}F detected PFG inverse 2D NMR spectrum of M1 HMQC, J = 280 Hz, with phase cycling, with composite pulses {90 ℡(X) 180 ℡(Y) 90 ℡(X)}. The circles in the figure indicate the signals for (Red) geminal (Green) vicinal and (Blue) pseudo correlations.

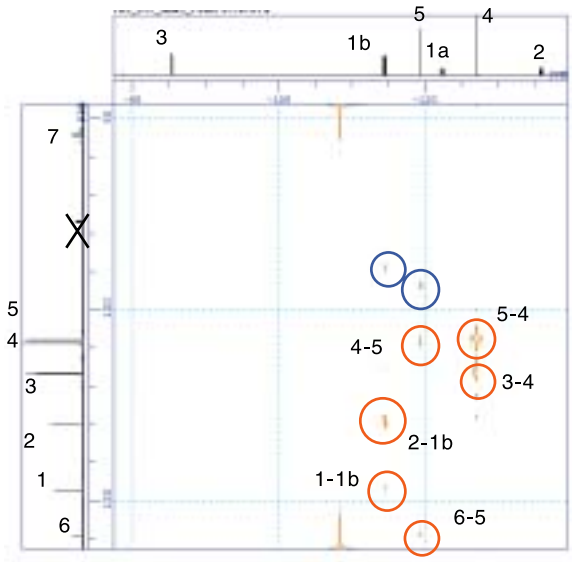

Fig. 5 ^{19}F detected PFG inverse 2D NMR spectrum of M1 HMQC, *J* = 10 Hz, with phase cycling, with composite pulses {90 ℡(X) 180 ℡(Y) 90 ℡(X)}. The circles in the figure indicate the signals for (Red) vicinal and (Blue) pseudo correlations.

inverse 2D spectra are observed from ^{19}F nuclei. As a result, the assignment is obvious for all signals. However, the pseudo correlation signals are also detected as artifacts in these spectra (**Fig. 2** and **3**).

Next, We have estimated the pseudo correlation in details. In order to remove the pseudo correlation signals, we have applied the pulse sequence with phase cycling. And also, we have examined the uniformity of 180 ° pulse over the widen frequency region using composite pulses to remove the pseudo correlation signals. As shown in **Fig. 4** and **5**, some pseudo correlation signals are removed from the HMQC spectra.

Here, we confirm the effect of the composite 180 ° pulses, in addition that the pseudo correlation signals are less for the inverse 2D NMR spectra with the phase cycling than those without phase cycling. As a result, the reduction of the pseudo correlation is achieved by improving the perfectness of the 180 ° pulse using composite pulse and the sequence with phase cycling. This fact implies that the pseudo correlation is due to the imperfectness of 180 ° pulse[8]. Since the chemical shift range is wide for ^{19}F NMR spectroscopy, it is difficult to make uniformity excitation for the required frequency range with a single 180 ° pulse, that is difficult to remove the pseudo correlation signals completely. In order to remove the pseudo correlation signal more completely, we should apply the inverse probe. For example, the inverse probe, which Riberiro[7] used (90 ° pulses width is 10.0 μs for ^{13}C and 8.0 μs for ^{19}F) can cover the wider range of ^{19}F chemical shifts than our results. Recently, it is reported that the use of selective adiabatic pulses can cover the entire fluorine chemical shift range, leading to better correlation[8], [9].

3.2 Application for M2 monomer

^{19}F detected PFG inverse NMR spectra are shown in **Fig. 6**～**9** for the M2 monomer. The assignment is not obvious only from the ^{19}F NMR spectrum. The geminal coupling is mainly observed in the HMQC spectra for which the coupling constant is set in J = 280 Hz (**Fig. 6** and **8**). The long-range correlation is observed in the HMQC for which the coupling constant is set in J = 10 Hz (**Fig. 7** and **9**). From the application of ^{19}F detected PFG inverse NMR technique, we could assign all signals.

For an easier assignment, it is necessary to remove the pseudo correlation signals for ^{19}F detected PFG inverse NMR method. When the composite 180 ° pulses and the pulse sequence with phase cycling are introduced, the pseudo signals and t_1 noises are suppressed from the HMQC spectra (**Fig. 6,** and **7**). The suppression of t_1 noises is also achieved by improving the perfectness of the 180 ° pulse (**Fig. 7**). But the pseudo signals still remain. It is obvious that the characteristic pseudo

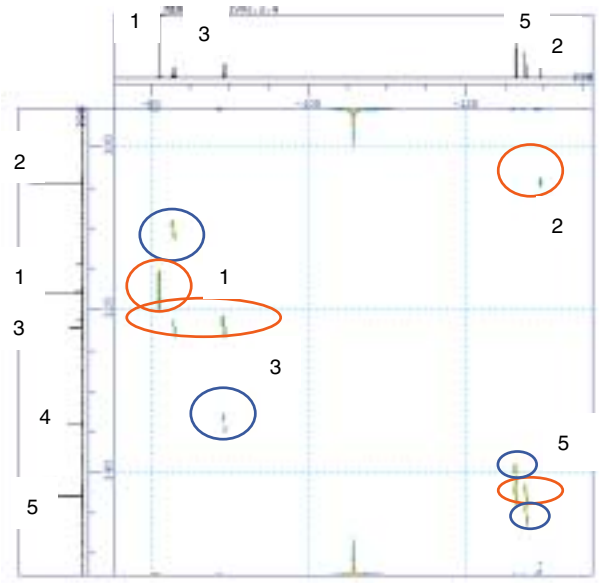

Fig. 6 ^{19}F detected PFG inverse 2D NMR spectrum of M2 HMQC, J = 280 Hz, with phase cycling, with composite pulses {90 ϕ(X) 180 ϕ(Y) 90 ϕ(X)}. The circles in the figure indicate the signals for (Red) geminal and (Blue) pseudo correlations.

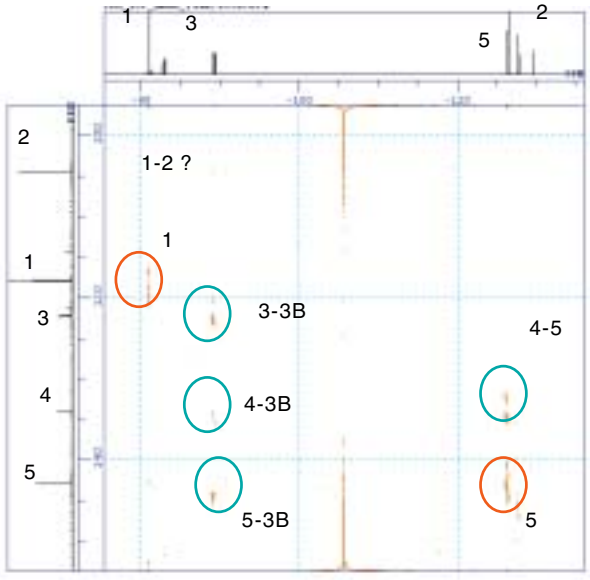

Fig. 7 ^{19}F detected PFG inverse 2D NMR spectrum of M2 HMQC, J = 10 Hz, with phase cycling, with composite pulses {90 ϕ(X) 180 ϕ(Y) 90 ϕ(X)}. The circles in the figure indicate the signals for (Red) geminal (Green) vicinal correlations.

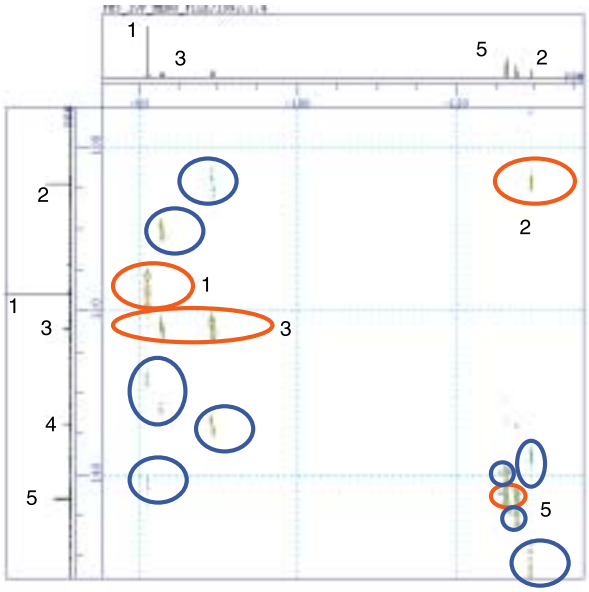

Fig. 8 ^{19}F detected PFG inverse 2D NMR spectrum of M2 HMQC, J = 280 Hz, without phase cycling, with composite {90 ϕ(X) 180 ϕ(Y) 90 ϕ(X)}. The circles in the figure indicate the signals for (Red) geminal and (Blue) pseudo correlations.

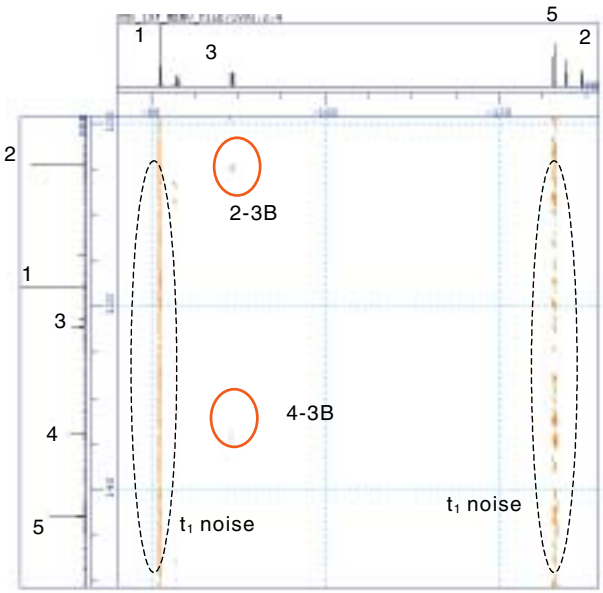

Fig. 9 ^{19}F detected PFG inverse 2D NMR spectrum of M2 HMQC, J = 10 Hz, without phase cycling, with composite pulses {90 ϕ(X) 180 ϕ(Y) 90 ϕ(X)}. The circles in the figure indicate the signals for (Red) vicinal correlations.

correlation signals are appeared when ^{19}F NMR spectrum includes AB-type signals. However, those pseudo correlation signals can supply the information about AB-type signals.

4. Conclusions

In this paper, we have investigated a ^{19}F detected PFG inverse NMR method to determine the structure of fluorinated organic compounds, which show AB-type signals in the ^{19}F NMR spectra. The pseudo correlation signals are also detected as artifacts in HMQC spectra, and are due to both the imperfectness of pulses and AB-type signals. We have succeeded to suppress the pseudo correlation signals by improving the perfectness of pulses using composite pulse. However, AB-type characteristic signals could not be removed from HMQC spectra, whereas those pseudo correlation signals can supply the information about AB-type signals. It is concluded that ^{19}F detected PFG inverse NMR technique can help the signal assignment of ^{19}F and ^{13}C NMR spectra and the determination of the intricate structure for fluorinated compounds.

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