Journal of Fluorine Chemistry 130 (2009) 389–393

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Vicinal fluorine–fluorine coupling constants in perfluoropropyl groups

Richard A. Newmark [*]

Newmark Consulting, 810 Woodduck Drive, Woodbury, MN 55125, United States

ARTICLE INFO

Article history:
Received 17 December 2008
Received in revised form 15 January 2009
Accepted 19 January 2009
Available online 30 January 2009

Keywords:
^{19}F NMR
Vicinal coupling constants
1,1,2,2,3,3,3-Heptafluoro-1-methoxypropane
Perfluorobutyric acid
2,2,3,3,4,4,4-Heptafluorobutanol

ABSTRACT

The geminal fluorines in $XCF_2–CF_2Y$ groups are magnetically inequivalent. The fluorines comprise an AA′XX′ spin which should show non-first-order NMR spectra, but usually appear deceptively simple with little indication of vicinal coupling. Detailed analysis of the spectra of perfluorobutyric acid (**1**) and 2,2,3,3,4,4,4-heptafluorobutanol (**2**) are reported. The $^3J(AX)$ and $^3J(AX')$ range between 4 and 9 Hz and are of opposite sign.

1. Introduction

It is generally observed that $^3J_{FF}$ is small (under 2 Hz) in $–CF_2CF_2–$ or $CF_3CF_2–$ groups in a perfluorinated chain, although $^4J_{FF}$ (typically >8 Hz) are always observed and used for assignments along the chain [1]. Vicinal $^3J_{FF}$ are very dependent on electronegativity [2] and range from +3.5 Hz in $CF_3–CF_3$ [3] to −15.4 Hz in $CF_3–CFH_2$ [4] and −22.9 in $CF_2Cl–CFClI$ [5]. It was concluded that the electronegativity of CF_2 or CF_3 groups is such that the averaged value of $^3J_{FF} \sim 0$ in perfluorinated chains [3,5]. However, Harris and Woodman [6] in 1968 determined the vicinal $–CF_2CF_2–$ coupling constants, $^3J(AX) = +12.2$ Hz and $^3J(AX') = -5.4$ Hz in perfluorobutane by analyzing the naturally abundant ^{13}C isomer $CF_3{}^{13}CF_2CF_2CF_3$ that renders the two CF_2 groups chemically inequivalent. Further, Brunelle et al. have shown that the gauche and trans $^3J_{FF}$ in CF_3CFCl_2 are + 15 and −18 Hz by freezing out the two distinct rotamers at low temperature [7]. Similarly, they observed very different gauche and trans $^3J_{FF}$ in CF_3CF_2Cl and CF_3CF_2Br.

Non-first-order spectra have been observed between CF_2's in perfluoropropyl groups such as $CF_3CF_2CF_2CO_2H$ [8] or $CF_3CF_2CF_2–$ substituents on 1,3,5-triazines [9], but the spectra have not been analyzed for the individual coupling constants. Complex higher order spectra are also observed in the middle $–CF_2CF_2–$ of $HCF_2CF_2CF_2CF_2CH_2OH$ [10]. Non-first-order spectra are expected on account of the intrinsic magnetic inequivalence of the geminal fluorines in the CF_2 group, but good resolution and sensitivity are required to observe the splittings and minor resonances. We discuss the complete analysis of the NMR spectra of perfluorobutyric acid (**1**) and 2,2,3,3,4,4,4-heptafluoro butanol (**2**) to determine true values of the two fluorine–fluorine coupling constants in these $AA'XX'M_3$ spin systems.

2. Results

2.1. AA′XX′ analysis

Fig. 1 shows the three rotamers of **1**, $R = CO_2H$. The two CF_2 groups represent a typical example of an AA′XX′ spin system in which nuclei are chemically equivalent but magnetically inequivalent. The most common example in organic chemistry is a *para*-substituted aromatic compound with two different substituents. The three possible rotamers are shown in Fig. 1, one trans (**I**) and two equivalent gauche (**IIa** and **IIb**) rotamers with equal energies and populations. Rotational averaging is fast on the NMR time scale at ambient temperature and the NMR spectrum is averaged over the chemical shifts and coupling constants in the three rotamers weighted by their populations [11]. Note F_A and F'_A have identical chemical shifts; F'_A is trans to the CO_2H in **IIa**, but F_A is trans to the CO_2H in **IIb**. However J(AX) is not the same as J(AX′) since the coupling constants do not average to the same value. The AA′XX′ analysis is discussed in detail in the early NMR literature and in numerous textbooks [5,12,13]. The spectrum is determined by four coupling constants, $^2J(AA')$, $^2J(XX')$, $^3J(AX) = {}^3J(A'X')$ and $^3J(AX') = {}^3J(A'X)$. The calculated AA′ portion of a typical AA′XX′ spectrum with coupling constants typical of a $–CF_2CF_2–$ group is in

---

[*] Tel.: +1 651 270 9345.
E-mail address: ranewmark@gmail.com.

0022-1139/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2009.01.005

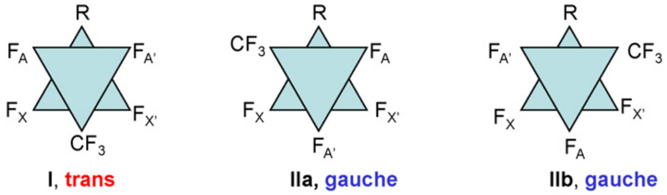

Fig. 1. The three rotamers of a heptafluoro propyl group with a $–CF_2CF_2–$ substructure. R = CO_2H in perfluorobutyric acid (**1**).

Fig. 2. The AA′ and XX′ subspectra are identical, and each is symmetrical about its midpoint. Each portion consists of two major resonances (resonances labeled 1–2 and 3–4 in Fig. 2), each with 25% of the total intensity, separated by the sum of $^3J(AX) + {}^3J(A'X)$. There should be two typical AB type multiplets. The first (resonances labeled 9–12 in Fig. 2) is readily observed and the splittings are a function of the difference between the geminal coupling constants, $^2J(AA') - {}^2J(XX')$, and the difference between the two vicinal coupling constants, $^3J(AX) - {}^3J(A'X)$. The second AB multiplet is observed as a nearly degenerate singlet (resonances labeled 6 and 7 in Fig. 2) in $–CF_2CF_2–$ groups since the splittings are a function of the sum of the geminal coupling constants, $^2J(AA') + {}^2J(XX')$, and $^3J(AX) - {}^3J(A'X)$. Since the sum is very large (about 550 Hz) and the difference no more than 10–20 Hz, the outside lines (resonances 5 and 8, not shown in Fig. 2) are at ~±550 Hz with intensity under 0.01% relative to the major resonances 6 and 7. The splitting of resonances 6 and 7 is under 0.12 Hz and probably not resolvable; it is observed in the calculated spectrum in Fig. 2 in which the line widths are set to 0.05 Hz. Coupling constants for the molecules analyzed in this paper were calculated using the equations in the references [5,12,13]. Since resonances 6 and 7 are not resolved, it is not possible to determine the values of the $^2J_{FF}$ geminal coupling constants, but the spectra are very sensitive to the difference between the two geminal coupling constants. Since all published $^2J_{FF}$ in perfluorinated non-cyclic $R–CF_2–CF_2–R$ groups, where R = F or C, range between 260 and 290 Hz [14], it was assumed that $^2J(AA') = 285$ Hz.

2.2. *Perfluorobutyric acid (1)*

The CF_3 resonance of $CF_3CF_2CF_2CO_2H$, **1**, is a first order triplet of triplets with $^4J_{FF} = 8.6$ Hz and $^3J_{FF} = 0.7$ Hz. The ^{19}F NMR spectra of the CF_2 groups are in Figs. 3 and 4 and show AA′XX′ patterns in addition to the quartets from coupling to the CF_3. Thus, the expected resonances of the CF_2 α to the CO_2H comprise an 8.6 Hz 1:3:3:1 quartet of the XX′ patterns described above (Fig. 3). Resonances of the left major peak in the quartet are assigned following the scheme from Fig. 2; resonances of the right major quartet are listed with primes. Note minor resonances 12 and 9′ are not observed due to overlap with resonances from the minor quartets. Also, resonances 1–4 and 6–7 are not resolved. The overlap of all of the major AA′ resonances is also observed for the CF_2 β to the CO_2H, but now each of these

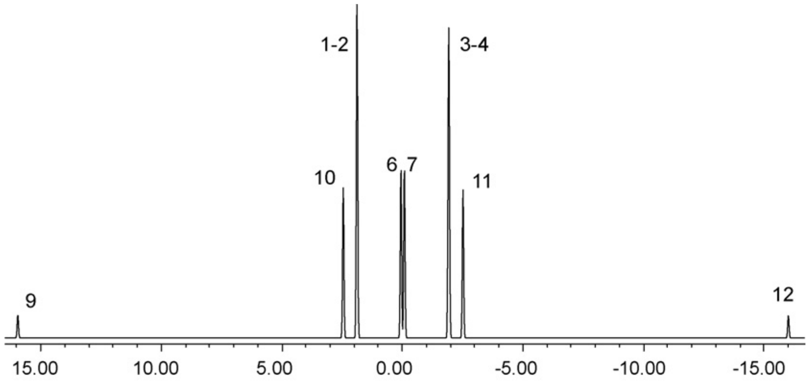

Fig. 2. Calculated AA′ subspectrum of an AA′XX′ spin system with a linewidth of 0.05 Hz for $\nu(AA') = 0$; $\nu(XX') = 2000$ Hz; $J(AA') = -285$, $J(XX') = -271.5$, $J(AX) = 8.2$, $J(A'X) = -4.4$ Hz. Scale is in Hz.

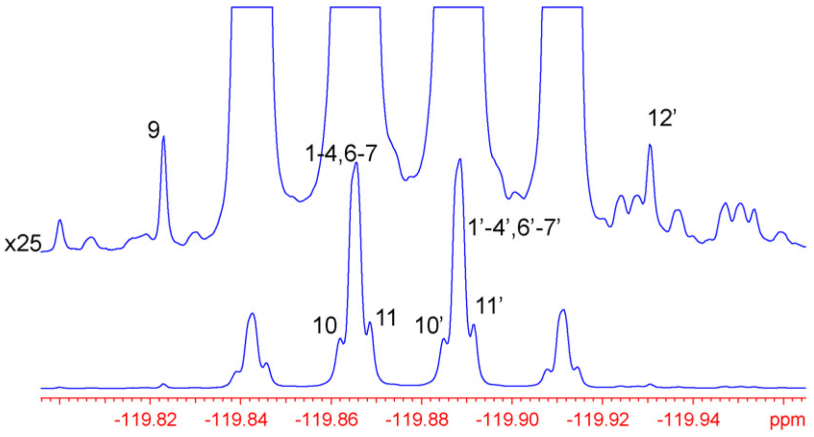

Fig. 3. ^{19}F NMR spectrum of the α CF_2 of $CF_3–CF_2–CF_2–CO_2H$. The 8.6 Hz 1:3:3:1quartet is from the $^4J_{FF}$; the splittings on each of the quartet resonances are from the XX′ pattern. Resonances are labeled in the two major quartets from the $^4J_{FF}$ according to the scheme in Fig. 2 as 1–11 and 1′–12′. Resonance 12 is symmetric with respect to 9, 10, and 11 and is under the upfield major quartet. Similarly, 9′ is under the lowfield major quartet. Resonances 6–7 are in the center of the 1.0 Hz (half width) center peak; resonances 1–2 and 3–4 are assumed separated by 0.5 Hz in this center peak.

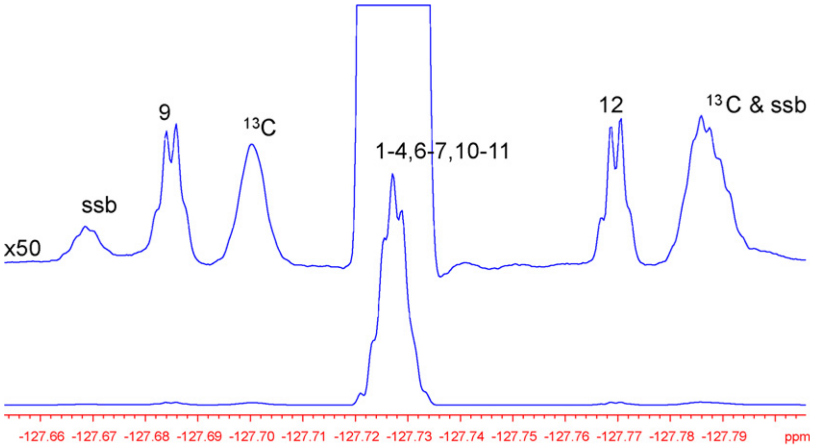

Fig. 4. ^{19}F NMR spectrum of the β CF_2 of CF_3–*CF_2*–CF_2–CO_2H. This resonance is a 0.70 Hz quartet, from the $^3J_{FF}$ to the CF_3, of AA′ subspectra. The 0.7-Hz quartets are most clearly seen in the weak outside resonances of the AA′ multiplet labeled peaks 9 and 12. Spinning sidebands (ssb) and ^{13}C satellites ($^2J_{CF}$ = 33.5 Hz) are labeled.

AA′ resonances is a 0.7 Hz quartet (Fig. 4). The minor resonance lines 9 and 12 are clearly observed with intensities comparable to the ^{13}C satellite (from the $^2J_{CF}$ = 33.5 Hz coupling with an isotope shift of −0.017 ppm). The coupling constants from the AA′XX′ analysis are given in Table 1.

*2.3. 2,2,3,3,4,4,4-Heptafluorobutyl alcohol (**2**)*

The ^{19}F NMR spectrum of the lowfield half of the α CF_2 group of $CF_3CF_2CF_2CH_2OH$, **2**, is in Fig. 5. The spectrum is similar to that of **1**, but the α CF_2 XX′ multiplet is split by 9.0 Hz quartets ($^4J_{FF}$) of 15.0 Hz triplets ($^3J_{HF}$); these splittings were first determined from first order analyses of the CF_3 and CH_2 resonances. Since $^3J(AX) + {}^3J(AX') = 4.3$ Hz, the AA′XX′ multiplets overlap except for the two most lowfield or upfield patterns in the α CF_2 resonances. Resonances are assigned to the two lowfield XX′ multiplets in Fig. 5. The CF_2 β to the CF_3 is not interpretable because the AA′ multiplets are split by the 1.6 Hz $^4J_{HF}$ and 0.6 Hz $^3J_{FF}$ which are comparable to the splittings in the AA′ multiplet.

*2.4. 1,1,1,2,2,3,3-Heptafluoro-3-methoxy propane (**3**)*

Unlike the acid and alcohol described above, the spectra of $CF_3CF_2CF_2OCH_3$, **3**, are first order and show no AA′XX′ character. Spectra were obtained in chloroform and a mixture of DMSO and acetonitrile. Spectra in both solvents were first order although the electronegativity differences should have been sufficient to change the relative populations of the gauche and trans rotamers.

3. Discussion

The $^3J(AX)$ and $^3J(AX')$ coupling constants observed *are not* gauche and trans coupling constants, but are the sums of the different gauche and trans coupling constants in the two inequivalent trans, **I**, and gauche, **II**, rotamers. These coupling constants are weighted according to the populations of **I**, p^T and **II**, p^G, with coupling constants J_g^T and J_t^T in the trans rotamer **I** and J_g^G, $J_{g'}^G$, $J_{g''}^G$ and J_t^G in the gauche rotamer **II**.

$$^3J(AX) = p^T \times J_g^T + p^G[J_g^G + J_t^G]$$

$$^3J(AX') = p^T \times J_t^T + p^G[J_{g'}^G + J_{g''}^G]$$

Attempts to determine the several J_t and J_g by observing J vs. temperature in other fluorinated ethanes have failed due to the large changes in $^3J_{FF}$ with temperature [15]. It has been proposed that the values of the several different gauche and trans coupling constants can be unambiguously determined by obtaining spectra of a sample in solvents of varying electronegativity and/or dielectric constant which change the relative populations of the three possible rotamers. Abraham et al. describe the unambiguous determination of the several values of the gauche and trans $^3J_{HH}$ and $^3J_{HF}$ coupling constants from the observed solvent dependence of the vicinal coupling constants in CF_2HCFH_2 [16]. However, this technique did not work for $^3J_{FF}$ in which correlation coefficients for the $^3J_{HF}$ couplings vs. the $^3J_{HH}$ couplings exceed 0.99, whereas the correlation coefficient for the $^3J_{FF}$ couplings vs. the $^3J_{HH}$ couplings is only 0.93. Thus other factors apart from the conformational equilibrium influence the solvent dependence of the couplings

Table 1
Chemical shifts (ppm) and coupling constants (Hz) in $CF_3CF_2CF_2R$ for R = CO_2H, CH_2OH, and OMe. Signs of $^3J(AX)$ and $^3J(AX')$ are opposite, but may be interchanged.

Compound	Solvent	δ CF_3	δ CF_2	δ CF_2R	2J(AA′) − 2J(XX′)[a]	3J(AX)	3J(AX′)	4J(FF)	3J(FF)[b]
1[c]	DMSO	−80.6	−126.9	−119.0	15.0	−4.6	+4.1	+8.6	0.7
2[d]	DMSO	−81.4	−128.0	−122.3	14.5	−4.9	+8.2	+9.2	0.6
2[e]	Acetone	−81.9	−128.4	−123.3	15.3	−4.3	+8.7	+9.4	[f]
3[g]	$CDCl_3$	−82.2	−130.1	−90.0	n.a.			+7.1	0.6
3[h]	DMSO/MeCN	−82.2	−130.1	−89.2	n.a.			+7.2	0.6

[a] $^2J(AA')$ and $^2J(XX')$ range between 260 and 290 Hz in halogenated ethanes [14], but individual values cannot be determined from these spectra (see text). The difference may be positive or negative.

[b] $^3J_{FF}$ from CF_3 to CF_2, sign not determined.

[c] δ 10.5 (s, CO_2H).

[d] ^{1}H, δ 3.96 (2H, CH_2, t, 15.0; d, 6.3, t, 1.5); 2.08 (1H, OH, t, 6.4).

[e] ^{1}H δ 4.09 (2H, CH_2, t, 14.6, t, 1.6); 5.17 (1H, OH, s).

[f] Not resolved.

[g] ^{1}H δ 3.73 (OCH_3, t, 0.60, t, 0.28).

[h] ^{1}H δ 3.94 (OCH_3, t, 0.60).

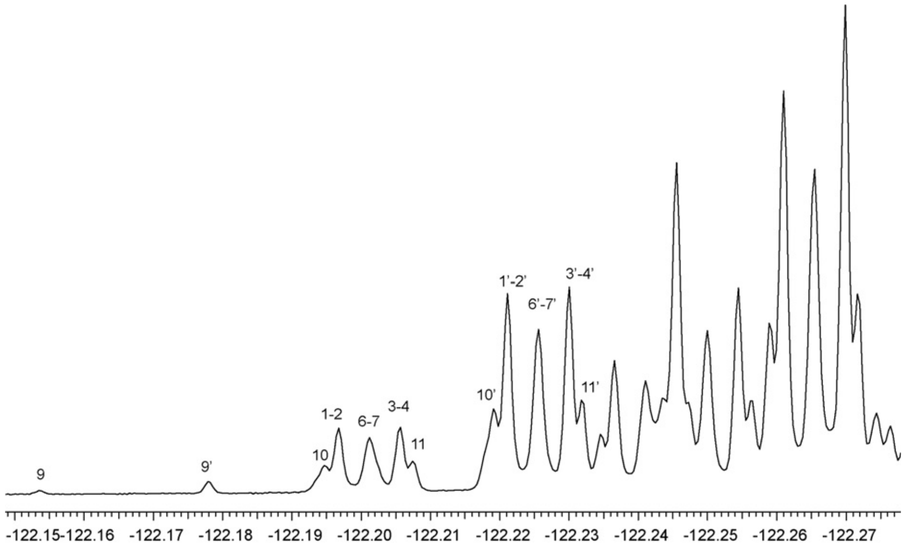

Fig. 5. ^{19}F NMR spectrum of the α CF_2 of CF_3–CF_2–*CF_2*–CH_2OH. The spectrum is a 9.0-Hz quartet ($^4J_{FF}$) of 15.0 Hz triplets ($^3J_{HF}$) of AA′XX′ multiplets and is symmetrical about its midpoint; only the lowfield half is shown. Resonances 1–11 and 1′–11′ of the lowest field AA′ patterns, separated by 9.0 Hz, are labeled, resonances 12 and 12′ are under more intense upfield resonances and resonances 5, 8, 5′, and 8′ are too weak to observe.

[16]. It has also been long recognized that $^3J_{FF}$ does not show a Karplus dependence on dihedral angle [17]. Thus, it does not appear possible to determine the individual values of the several J_g and J_t.

Although few examples of relative energies of individual conformations of halogenated ethanes are available, conformer energies have been reported for $CF_2BrCFBr_2$ [18]. The unique conformer with the three bromines all in gauche orientations is 760 cal/mol (2.2 kJ/mol) higher in energy than the conformation with two bromines in a gauche orientation. The energy difference between the gauche and trans forms of CF_2Br–CF_2Br is 945 cal/mol [19]. If the energy difference between **IIa** and **IIb** relative to **I** were similar to these examples for **1** and **2**, only 12–18% of the molecules would be in the 2 equivalent high energy conformations. Neglecting this minor gauche contribution would give $p^G \sim 0$, $p^T \sim 1$ and the difference between the vicinal coupling constants is simply:

$$[{}^3J(AX) - {}^3J(AX')] = J_g^T - J_t^T$$

The populations of the three rotamers **I**, **IIa**, and **IIb**, could be similar in **3** on account of dipolar and electronegativity effects [20] and, perhaps, hydrogen bonding between the OCH_3 and one of the CF_2's [21]. Then if the gauche and trans coupling constants do not depend on the orientation of the CF_3 and R (OMe) substituents $[{}^3J(AX) - {}^3J(AX')] \sim 0$ and the two vicinal coupling constants are equal.

4. Conclusion

Although it is generally assumed that $^3J_{FF}$ is very small in perfluorinated groups, the results in this study and the low temperature analysis of CF_3CFCl_2 [7] indicate that the actual values are much larger. Magnetic inequivalence should be observed for geminal fluorines in CF_2 groups and determination of the vicinal coupling constants then requires a non-first-order analysis. At present there is no way to observe the individual gauche and trans $^3J_{FF}$ between CF_2 groups except from very low temperature (∼100 K) spectra at which rotation between the three rotamers is slow [7]. But if steric effects are important in the relative populations of the rotamers such that the population of the gauche rotamer is nil, then the difference between the observed $^3J(AX)$ and $^3J(AX')$ coupling constants equals the difference between the gauche and trans coupling constants in the trans rotamer **I**.

5. Experimental

All NMR spectra were obtained on a Varian INOVA 400 spectrometer operating at 400 MHz for ^1H. Chemical shifts are reported relative to internal TMS or $CFCl_3$. The AA′XX′ subspectra were analyzed using an Xcel spreadsheet. Calculated spectra including the CF_3 and CH_2 groups were performed using Varian software; these calculations confirmed that errors in the coupling constants assuming a AA′XX′ spin system instead of an AA′BB′ were under 0.01 Hz. Spectra were obtained in DMSO for **1**, in DMSO and acetone for **2** and in $CDCl_3$ and a 50:50 mixture of DMSO and acetonitrile for **3**. Acquisition times were 6.0 s for the ^{19}F spectra in order to maximize the resolution. At least 1000 transients were time-averaged to observe the very weak resonances.

Acknowledgments

I thank Peter Rinaldi and Elizabeth McCord for helpful discussions and 3M for the use of the NMR facilities in their Corporate Research Analytical Laboratory.

References

[1] S. Berger, S. Braun, H.-O. Kalinowski, NMR Spectroscopy of the Non-Metallic Elements, Wiley, New York, 1997, pp. 398–698.
[2] R.R. Dean, J. Lee, Trans. Faraday Soc. 64 (1968) 1409–1417.
[3] R.E. Graves, R.A. Newmark, J. Chem. Phys. 47 (1967) 3681.
[4] D.D. Elleman, C. Brown, D. Williams, J. Mol. Spectrosc. 7 (1961) 307–321.
[5] L. Cavalli, J. Magn. Reson. 6 (1972) 298–315.
[6] R.K. Harris, C.M. Woodman, J. Mol. Spectrosc. 26 (1968) 432–443.
[7] J.A. Brunelle, L.J. Letendre, E.E. Weltin, J.H. Brown, C.H. Bushweller, J. Phys. Chem. 96 (1992) 9225–9231.
[8] D.A. Ellis, K.A. Denkenberger, T.E. Burrow, S.A. Mabury, J. Phys. Chem. A 108 (2004) 10099–10106.
[9] W.S. Brey, D.W. Richardson, J. West, J. Fluorine Chem. 125 (2004) 755–761.
[10] R.A. Newmark, unpublished results.
[11] H.S. Gutowsky, G.G. Belford, P.E. McMahon, J. Chem. Phys. 36 (1962) 3353–3368.
[12] J.W. Emsley, J. Feeney, L.H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, vol. 1, Pergamon Press, London, 1965, pp. 392–399.
[13] F.A. Bovey, Nuclear Magnetic Resonance Spectroscopy, Academic Press, San Diego, 1988, pp. 179–182.
[14] A. Foris, Magn. Reson. Chem. 39 (2001) 386–398.
[15] R.J. Abraham, L. Cavalli, Mol. Phys. 9 (1965) 67–75.

[16] R.J. Abraham, P. Leonard, T.A.D. Smith, W.A. Thomas, Magn. Reson. Chem. 34 (1996) 71–77.
[17] S. Kurtkaya, V. Barone, J.E. Peralta, R.H. Contreras, J.P. Snyder, J. Amer. Chem. Soc. 124 (2002) 9702–9703.
[18] R.A. Newmark, C.H. Sederholm, J. Chem. Phys. 43 (1965) 602–623.
[19] G. Serboli, B. Minasso, Spectrochim. Acta 27A (1971) 1175–1183.
[20] S. Ng, J. Chem. Soc., Faraday Trans. 2 (71) (1975) 1839–1843.
[21] B.E. Smart, J. Fluorine Chem. 109 (2001) 3–11.