

Spectral separation of gaseous fluorocarbon mixtures and measurement of diffusion constants by ^{19}F gas phase DOSY NMR

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ABSTRACT

Diffusion-ordered (DOSY) NMR techniques have for the first time been applied to the spectral separation of mixtures of fluorinated gases by diffusion rates. A mixture of linear perfluoroalkanes from methane to hexane was readily separated at 25 °C in an ordinary experimental setup with standard DOSY pulse sequences. Partial separation of variously fluorinated ethanes was also achieved. The constants of self-diffusion of a set of pure perfluoroalkanes were obtained at pressures from 0.25 to 1.34 atm and temperatures from 20 to 122 °C. Under all conditions there was agreement within 20% of experimental self-diffusion constant D and values calculated by the semiempirical Fuller method.

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1. Introduction

Diffusion-based NMR techniques based on pulsed field gradients have enjoyed increasing popularity and scope of application in recent years. Such techniques can be broadly divided into two classes: those that effect spectral separation of a mixture of analyte species (Diffusion Ordered Spectroscopy, or DOSY [1]), and those that aim to determine accurately the diffusion rates of the analytes. Both have been widely applied to solution phase systems [2–6]. In gaseous systems, there has been significant interest in the determination of diffusion rates, both as surface probes in materials science [7–10] and as an experimental datum in pulmonary MRI studies. This last application most often uses hyperpolarized ^3He [11–13] and ^{129}Xe [7,11] (and even ^{83}Kr [14]), though the use of fluorinated gases has been reported as well [12,15].

NMR acquisition in the gas phase (or, more simply, gas phase NMR) has been applied by our laboratories to the study of the kinetics of fluorocarbon chemistry, often at $T > 300\text{ °C}$ [16–17], mimicking the conditions of industrial fluorine chemistry. Such chemistry is often rather unselective, creating a complex mixture of volatile by-products which are often either highly reactive (and thus not suitable for solution phase analysis), or insoluble in common NMR solvents. The application of DOSY techniques for spectral simplification and elucidation directly upon the gaseous mixture is therefore of industrial relevance. However, to the best

of our knowledge, the spectral separation of gaseous mixtures by DOSY NMR has not yet been reported. The purpose of this study was to explore the application of DOSY NMR techniques to gas phase acquisition with the primary aim of spectral separation of components by diffusion rate. In addition, the derivation of accurate rates of self-diffusion of gases under various conditions may be an important tool in large-scale reaction modeling. To validate the use of gas phase NMR to obtain that data, the self-diffusion rates of single-component systems at various temperatures and pressures were obtained and compared with expected values.

2. Results and discussion

While gas phase NMR experiments remain relatively uncommon, they are substantially similar to solution phase experiments in principle and in experimental practice. The primary spectroscopic difference with gas phase NMR is the great efficiency of the spin-rotation relaxation process, and consequently short T_1 and T_2 times. For ^{19}F gas phase NMR, these are generally 10–50 ms at pressures near 1 atm [18]. As a consequence, linewidths are generally no narrower than *ca.* 30 Hz. However, the efficient longitudinal relaxation permits rapid signal averaging, with an effective improvement in sensitivity.

With DOSY NMR, another important difference between the gas phase and solution phase is in the rate of diffusion of the analytes, typically 10^3 – 10^4 higher for small molecules in a gaseous system at pressures less than e.g., 5 atm. The experimental implications of this fast diffusion are clear from the Stejskal–Tanner equation [19] governing the loss of signal intensity in DOSY experiments:

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$$I/I_0 = \exp(-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)) \quad (1)$$

where I/I_0 is the fraction of intensity retained after diffusive loss, γ is the magnetogyric ratio of the observed nucleus, g is the applied field gradient strength, D is the constant of diffusion in m^2s^{-1} , δ is the duration of the applied field gradient pulse, and Δ is the length of the diffusion period. In order to retain an observable fraction of the signal intensity, g , Δ , and/or δ must be reduced relative to standard solution phase experimental parameters. This is not without its advantages; since a strong pulsed gradient field is not needed, gas phase DOSY NMR experiments can be performed on NMR probes systems with ordinary gradient coils and amplifiers (*vide infra*), and specialized high power gradient probes and amplifiers are not required.

2.1. DOSY for spectral separation

A simple proof-of-concept experiment was devised in which the homologous series of linear perfluoroalkanes (methane to hexane) were sealed in a 5 mm NMR tube at ca. 0.25 atm partial pressure of each. In a 700 MHz 5 mm ^1H , ^{19}F $\{^{13}\text{C}\}$ NMR probe at 23 °C, a gradient compensated stimulated echo (GCSTE) pulse sequence [20] was run with $\Delta = 10$ ms, $\delta = 500$ μs , and $g < 0.18$ T m^{-1} . The result is given in Fig. 1. The spectral separation of the perfluoroalkanes from one another (and from the adventitious impurities) is readily apparent. The CF_3 moieties of perfluoropentane and perfluorohexane are not resolved in the gas phase at this field (658 MHz), hence the apparent absence of the CF_3 resonance in perfluoropentane.

The GCSTE sequence described above was chosen for most of the experiments in this study after comparison with a set of other common sequences (Fig. 2): the basic stimulated echo sequence (PFGSTE) [20], bipolar pulse pair simulated echo (BPPSTE) [21], bipolar pulse pair with longitudinal eddy delay (BPPLLED) [22], with and without adiabatic 180° pulses, and the GCSTE sequence with spin lock (GCSTESL) [20]. All of these sequences succeeded in achieving spectral separation of the perfluoroalkane sample, but the sensitivity of the CF_4 was reduced in most cases relative to GCSTE. Table 1 compares the signal to noise ratio of the CF_4 and

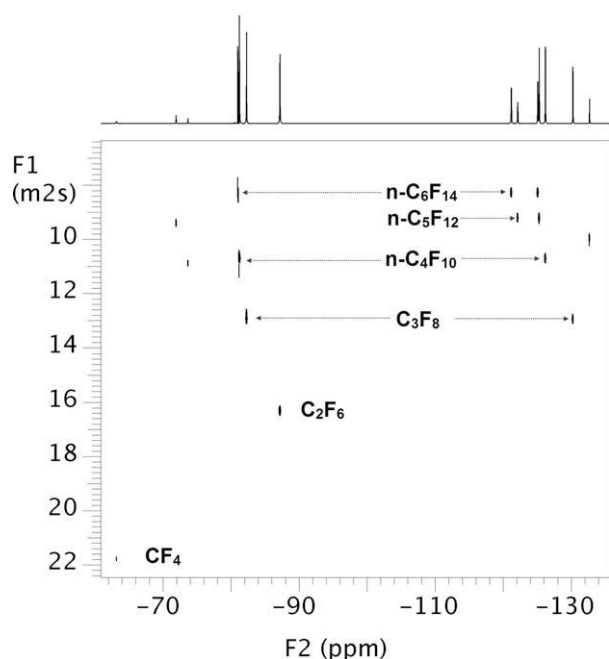


Fig. 1. ^{19}F GCSTE spectrum of mixed perfluoroalkanes in the gas phase. Ordinate axis in units of $10^{-7} \text{m}^2 \text{s}^{-1}$.

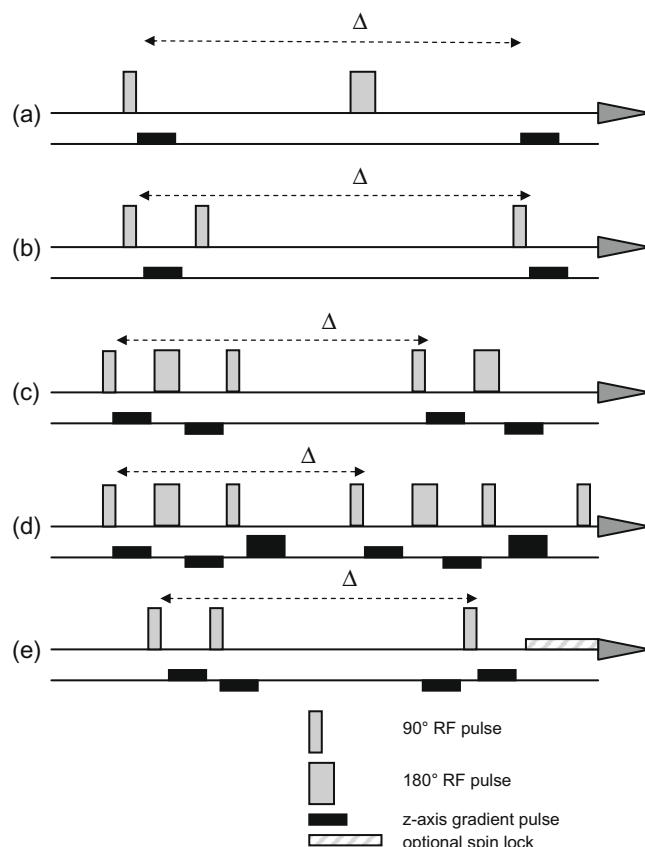


Fig. 2. Diagram of pulse sequences used in this study. (a) Spin echo sequence. (b) PFGSTE. (c) BPPSTE. (d) BPPLLED. (e) GCSTE. Diffusion period indicated by Δ .

C_2F_6 resonances of the same sample obtained under analogous conditions of g , Δ , and δ (see Experimental section) in PFGSTE, GCSTE, BPPLLED with adiabatic 180° pulses, and simple 90° -grad- 180° -grad spin-echo experiments, using only a single value of g . The BPPLLED, GCSTE, and spin-echo sequences yielded comparable signal intensity for the C_2F_6 resonances (and indeed those of the larger perfluoroalkanes). However, the BPPLLED and particularly the spin-echo sequence yielded less signal intensity for CF_4 . This can be attributed to T_2 effects; CF_4 has the shortest T_2^* of any of the compounds in this mixture (5.0 ms under these conditions). In the spin echo sequence, magnetization resides in the x, y plane during the entire sequence, rendering it particularly sensitive to T_2 losses. The BPPLLED is not as extreme, but does keep the magnetization in the transverse plane longer than either GCSTE or PFGSTE. The greater number of pulses in the BPPLLED sequence may also come into play, exacerbating the effects of imperfect 90° and 180° pulses. (The adiabatic version of this sequence has not been thoroughly tested; further optimization may be possible.) The

Table 1
Comparison of sensitivities of spin-echo, PFGSTE, GCSTE, and BPPLLED (with adiabatic inversion pulses) sequences under analogous conditions.

Sequence	S/N (CF_4)	S/N (C_2F_6)	Duration of transverse magnetization in pulse sequence (ms)	Duration of longitudinal magnetization in pulse sequence (ms)
Spin-echo	17 ± 2	632 ± 78	11.2	0.0
PFGSTE	101 ± 10	1134 ± 114	1.8	9.5
GCSTE	70 ± 9	713 ± 76	1.8	9.1
BPPLLED	46 ± 7	673 ± 98	4.3	8.8

most sensitive sequence was the simple PFGSTE. However, in the wide spectral window needed for ^{19}F acquisition, a large first order phase correction was required on the PFGSTE spectra, imposing a roll on the baseline. (This problem was later corrected by modification of the timing between the last gradient pulse and the start of the acquisition period.) In order to avoid this problem at the time, the slightly less sensitive GCSTE sequence, which did not experience this phasing problem, was chosen for the rest of this study.

More stringent tests of the separatory power of this technique were then attempted. In the first of these, a mixture of linear perfluorobutane and cycloperfluorobutane at 1 atm partial pressure each was tested, with the aim of gauging the success of this technique at separating species of similar molecular weights but different geometries. The GCSTE spectrum acquired at 25 °C is shown in Fig. 3; again, spectral separation is observed. A mixture of variously fluorinated ethanes was then created ($\text{C}_2\text{F}_n\text{H}_{6-n}$, $n = 1-6$, 0.25 atm partial pressure of each, eight species in all) with the object being to test analytes of similar molecular geometry but different molecular weights. The GCSTE spectrum acquired is shown in Fig. 4. This experiment was not successful in effecting spectral separation between the analytes other than CFH_2CH_3 , CF_2HCH_3 , and CF_3CH_3 .

2.2. Derivation of diffusion constants

The second aim of this study was to validate the diffusion constants derived from gas phase diffusion NMR against predicted values under the experimental conditions. For this purpose we employed the Fuller method [23–24], a semiempirical method that calculates D as a function of temperature, pressure, molecular weight of the analyte, and an empirically-derived atomic volume diffusion parameter. Pure samples of each perfluoroalkane from methane to hexane at 0.25 atm pressure at 23 °C and from methane to butane at 1.00 atm pressure at 23 °C were created in sealed NMR tubes. The diffusion constants were obtained in GCSTE experiments, again using $\Delta = 10$ ms and $\delta = 500$ μs . g was adjusted per the diffusion rate of each species, varying from a maximum of $9.0 \times 10^{-3} \text{ T m}^{-1}$ for 0.25 atm CF_4 to $1.4 \times 10^{-1} \text{ T m}^{-1}$ for 1.00 atm C_4F_{10} . The diffusion constants D were calculated by a linear

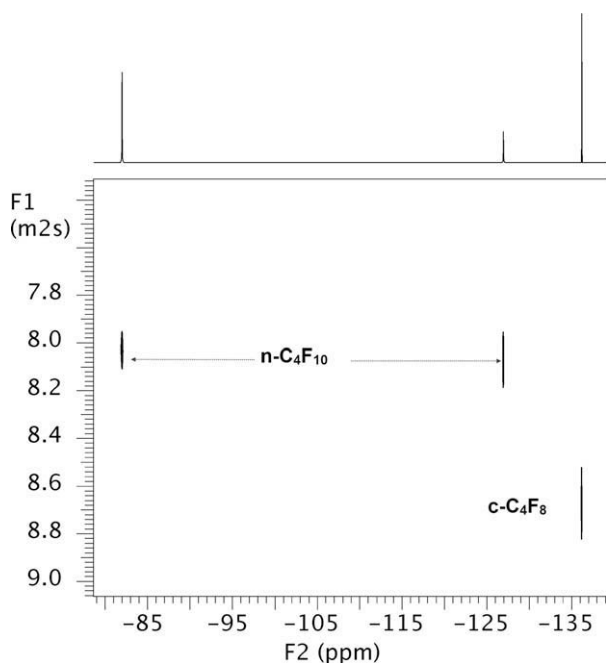


Fig. 3. ^{19}F GCSTE spectrum of a mixture of *n*-perfluorobutane and *c*-perfluorobutane in the gas phase. Ordinate axis in units of $10^{-7} \text{ m}^2 \text{ s}^{-1}$.

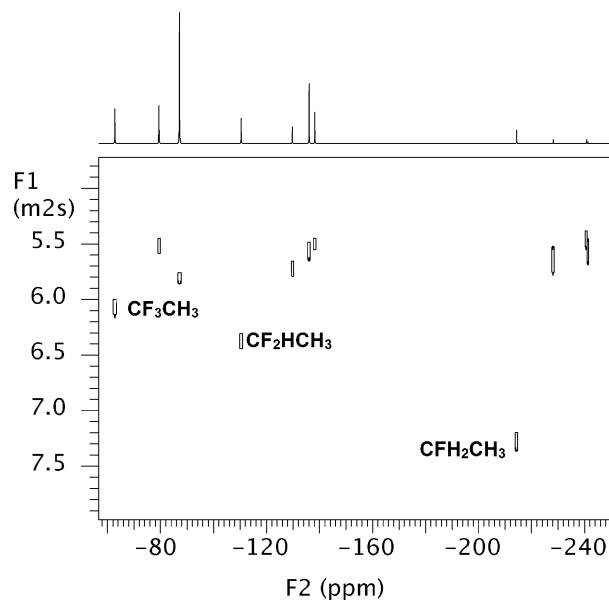


Fig. 4. ^{19}F GCSTE spectrum of a mixture of variously fluorinated ethanes in the gas phase. Ordinate axis in units of $10^{-7} \text{ m}^2 \text{ s}^{-1}$.

regression of the plot of $\ln(I/I_0) v g^2$, per Eq. 1. Table 2 lists all of the experimentally derived diffusion constants and the values predicted by the Fuller method.

The fastest diffusing sample in this study was that containing only 0.25 atm partial pressure of CF_4 at 23 °C ($D = 2.07 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$). With this sample, g was varied from 9.0×10^{-3} to $2.2 \times 10^{-2} \text{ T m}^{-1}$. At gradient strengths below $9.0 \times 10^{-3} \text{ T m}^{-1}$, the fit of integrated signal intensity $v g^2$ was poor. This may reflect a nonlinearity in the pulsed field gradient amplifier at very low power levels. A superior approach for fast-diffusing analytes may be to reduce δ . With the spectrometer and probe used in this study, reducing δ from 500 to 250 μs did not affect the obtained diffusion rates. Furthermore, in a series of experiments with 1 atm of *n*- C_4F_{10} , the obtained diffusion rates were constant within 1% upon reducing the gradient stabilization delay to as little as 10 μs . Standard gradient recover calibrations for this system indicated that, at the higher gradient powers used in this study, 40 μs were required for amplitude recovery and 70 μs were required for full phase recovery. The GCSTE experiments are thus rather insensitive to imperfect gradient recovery under these conditions. Therefore, though the upper limit of D that can be accurately obtained was not rigorously determined in this study, we believe it to be higher than the $2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ observed with the 0.25 atm CF_4 sample, as a further reduction of δ is possible before experimental accuracy is sacrificed.

The sample containing 1.00 atm C_4F_{10} at 23 °C was also subject to spectral acquisition at elevated temperature (up to 122 °C). In this case, the convection-compensated version of the GCSTE sequence was used [25] to eliminate the effects of lamellar convective flow in the NMR tube. The sample was also tested at 60 °C without the convection compensation; surprisingly, the disagreement was only 6%. Seeking to explore this further, the sample was tested at 122 °C with convection correction and $\Delta = 10$, 20, and 30 ms. If convection were a major contributor to the observed loss of signal intensity with increased g , then one would expect the values of D obtained from these experiments to differ greatly. Instead, the difference is subtle; $D = 1.75 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ was obtained with convection correction, $D = 1.88 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, $1.93 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, and $1.97 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ were obtained without con-

Table 2
Obtained diffusion constants D for pure perfluoroalkanes.

Compound	Pressure (atm)	T (°C)	Experimental D ($10^{-6} \text{ m}^2 \text{ s}^{-1}$)	Predicted D ($10^{-6} \text{ m}^2 \text{ s}^{-1}$)	Error (%)
CF ₄	0.253	25.0	20.7	18.1	12.3
CF ₄	1.01	25.0	5.21	4.54	12.9
C ₂ F ₆	0.253	25.0	10.4	10.6	-1.6
C ₂ F ₆	1.01	25.0	2.68	2.64	1.5
C ₃ F ₈	0.253	25.0	6.87	7.31	-6.4
C ₃ F ₈	1.01	25.0	1.75	1.83	-4.4
C ₃ F ₈	1.12	60.7	1.91	1.99	-4.0
<i>n</i> -C ₄ F ₁₀	0.253	25.0	4.89	5.53	-13.1
<i>n</i> -C ₄ F ₁₀	1.01	25.0	1.26	1.38	-9.7
<i>n</i> -C ₄ F ₁₀	1.12	60.7	1.43	1.50	-5.0
<i>n</i> -C ₄ F ₁₀	1.00	20.0	1.20 ^a	1.36	-13.7
<i>n</i> -C ₄ F ₁₀	1.01	25.0	1.26 ^a	1.38	-9.7
<i>n</i> -C ₄ F ₁₀	1.06	40.3	1.36 ^a	1.44	-5.5
<i>n</i> -C ₄ F ₁₀	1.13	60.7	1.42 ^a	1.50	-6.0
<i>n</i> -C ₄ F ₁₀	1.20	81.1	1.56 ^a	1.57	-0.8
<i>n</i> -C ₄ F ₁₀	1.27	101.5	1.67 ^a	1.64	1.8
<i>n</i> -C ₄ F ₁₀	1.34	122.0	1.75 ^a	1.71	2.4
<i>n</i> -C ₅ F ₁₂	0.253	25.0	3.70	4.41	-19.3
<i>n</i> -C ₆ F ₁₄	0.253	25.0	3.22	3.65	-13.5

^a Convection-corrected version of the GCSTE sequence used to determine D .

vection correction and $\Delta = 10$ ms, 20 ms, and 30 ms, respectively. These results support the conclusion that lamellar convective flow is a minor contributor to the apparent diffusivity signal loss. Note that turbulent convective flow is not compensated for by the convection correction sequence. However, the good agreement between the predicted values of D and the experimental NMR results suggests that turbulent convection is also a minor process under these conditions.

As a check on the validity of these results, a comparison was made between values of D derived from ¹⁹F detected experiments and those obtained from ¹H detected experiments on the same system. A sample was prepared with 2 atm partial pressure each of CF₃CH₃ and CF₂HCF₂H. A GCSTE experiment was run on each sample at 25 °C, first with ¹⁹F detection, then with ¹H, on the same probe. By ¹⁹F, the obtained values of D were $8.96 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $8.28 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ for CF₃CH₃ and CF₂HCF₂H, respectively; by ¹H, the values were $9.00 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $8.26 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, giving agreement within 0.5%.

The simplicity of the experimental approach in this study should be noted; the analytes were simply condensed into an evacuated 5 mm NMR tube, which was flame-sealed at a normal height (ca. 20 cm). No attempt was made to restrict the gas to the thermostatted region of the tube, yet even at elevated temperatures the agreement with predicted values of D was good. We expect that greater accuracy will be realized with future improvements of the experimental protocols, but the apparent robustness of the method under ordinary conditions is encouraging.

3. Conclusions

Standard DOSY pulse sequences such as GCSTE applied to gas phase samples were shown to effect good spectral separation of fluorocarbons of different chain lengths, and modest separation of analytes of different geometry (linear v. cycloperfluorobutane) and molecular weight (variously fluorinated ethanes). The rapidity of diffusion in the gas phase, relative to solution, can be compensated for by reducing the pulsed field gradient strength and duration and the diffusion period appropriately. The maximum value of D consistent with the experimental hardware used in this study (a standard commercial 5 mm NMR probe and console) is likely greater than $2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Diffusion constants obtained for a variety of perfluoroalkane samples at various temperatures and

pressures agree with semiempirical predictions within 20%, and greater accuracy can probably be obtained with improvements in the experimental protocols. With gaseous samples at temperatures between 20 and 122 °C and pressures between 0.25 and 1.34 atm in a standard 5 mm tube, convection processes are minor relative to diffusion.

4. Experimental

The fluorinated gases used in this study were obtained from Synquest Laboratories, Inc. Purity was >98% by ¹⁹F NMR. Perfluorohexane (>99% purity) was obtained from PCR Inc. Samples were prepared by vacuum transfer of the gases into an evacuated 5 mm medium-walled (wall thickness 0.77 mm) NMR tube through a manostatted manifold (manifold $T = 23$ °C). The tube was then flame-sealed at a specified height. The internal volume of the sealed tubes vary within ca. 2%, the volume of the manifold is known, therefore, the partial pressures of the analyte in the tube are calculated by Boyle's law ($P_1V_1 = P_2V_2$ at constant T). The nonideality of small fluorocarbon and hydrofluorocarbon gases would account for much less than 1% error at these temperatures and pressures.

Experiments were performed on a 700 MHz Varian VNMR5 spectrometer equipped with a 5 mm inverse detection probe (inner coil doubly tuned to ¹H and ¹⁹F, outer coil tuned to ¹³C). The system was equipped with a Performa IV gradient amplifier capable of generating 0.60 T m^{-1} gradient field in the NMR probe. Calibration of the pulsed field gradient strength was performed with a sample of 1% H₂O in D₂O at 25.0 °C per a known correction (M. Nilsson, personal communication) and with a sample containing H₂O in a confined 5.0 mm space in a 5 mm NMR tube (a "phantom"). These techniques agreed within 0.7%. Temperature calibration of the probe was performed with an ethylene glycol standard.

The conditions for the experimental comparison given in Table 1 are as follows: $\Delta = 10$ ms, $\delta = 0.50$ ms, $g = 1.81 \times 10^{-2} \text{ T m}^{-1}$, 16 averaged transients, 0.10 s acquisition time, 1.4 s recycle delay, and 10 Hz exponential line broadening. The BPPLIED sequence was run with a 1 ms eddy delay. The signal-to-noise ratios reported for the for the two peaks were calculated from the mean of ten randomly chosen noise regions, and the reported error represents the standard deviation of these measurements.

In a typical ^{19}F GCSTE experiment, $\Delta = 10$ ms and $\delta = 0.50$ ms, with 0.40 ms permitted for stabilization after a gradient pulse. Gradient strength g was set appropriately for each sample, and was arrayed such that g^2 was spaced in constant increments. 16–64 increments of g were typically employed. The number of transients averaged in each increment varied by the signal intensity of the sample; 16–512 were typical. A recycle delay of 1.0 s ($>10 T_1$) and an acquisition period of 0.10–0.20 s were used, yielding a typical experiment time of 4 min to 10 h, depending on the sample. For experiments conducted at elevated temperature, a period of 1 h was allowed for thermal equilibration of the sample before the experiment was started. Experiments with pulse sequences other than GCSTE were also conducted with $\Delta = 10$ ms and $\delta = 0.50$ ms, with the gradient strength and number of transients set appropriately for each sample.

The ^1H GCSTE experiment was conducted with a recycle delay of 15.0 s, 16 increments of g , and 32 averaged transients per increment.

The 2D DOSY spectra (Figs. 1, 2 and 4) were generated with standard Varian software. The upper limit of D preset in the software was appropriate for solution phase samples, and had to be modified. Values of D given in Table 2 were obtained by integration of the resonances in each increment of the DOSY experiment and applying a linear regression to the plot of $\ln(I/I_0) \nu g^2$ in Microsoft Excel[®]. The square of the Pearson coefficient R was greater than 0.997 in all cases except for 0.25 atm CF_4 , with which the signal intensity was weakest.

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