

Measured vs. Estimated Vapor Pressure of Fluorotelomer Alcohols: Reconsideration of an Important Property Used to Predict Long-Range Transport Potential.

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Vapor pressure and aqueous solubility are important parameters used to estimate the potential for transport of chemical substances in the atmosphere. For fluorotelomer alcohols that are sparingly soluble in water, vapor pressure is the more significant factor. Vapor pressure is an essential physical property widely used to quantify the "volatility" of a chemical and is a key input parameter used to predict and understand environmental partitioning behavior. We have measured the vapor pressures of a homologous series of fluorotelomer alcohols (FTOHs), $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2,3,4,5$), in the temperature range 21 – 250 °C by three independent methods, including a novel method based on gas-phase NMR, a technique largely unfamiliar to

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chemists and holding promise for studies of relevance to environmental chemistry. The values obtained indicate that recently published vapor pressure data overestimate, in one case by as much as approximately 100 times, the vapor pressure, and thereby the volatility, at ambient temperature of this class of compounds. Substantial -O-H...F- intramolecular hydrogen bonding between the hydroxylic H atom (-OH) and the two fluorines next to the ethanol moiety was proposed to be responsible for the putatively exceptional volatility of FTOHs. Gas-phase NMR, gas-phase FTIR, 2D NMR heteronuclear Overhauser effect measurements, and high-level *ab initio* computations unequivocally show that intramolecular hydrogen bonding is not significant. Fluorotelomer alcohols are currently under scrutiny by environmental scientists as potential precursors of persistent perfluorocarboxylates (PFCAs). The reported high volatility of FTOHs based upon estimated vapor pressures at ambient temperatures has been central to a proposed atmospheric transport and degradation pathway. Our results indicate that the importance of this proposed pathway should be reconsidered based upon measured lower FTOH vapor pressures.

Introduction

Perfluorinated compounds such as perfluorosulfonates (*e.g.*, perfluorooctane sulfonate, PFOS) and perfluorocarboxylates (*e.g.*, perfluorooctanoic acid, PFOA) have gained attention recently since they have been found in trace amounts in human sera in North America and Europe (1,2,3). Other studies have reported that PFOS, and to a lesser extent PFOA, are found in wildlife and the environment (4, 5, 6). In addition to substantial direct-release sources of perfluorocarboxylates (7,8,9,10) in the environment, questions have been raised regarding to what extent fluorotelomer alcohols (FTOHs) may represent an indirect source of PFOA and other perfluorocarboxylates in the environment.

In order for a molecule to be widely present in the environment, long-range transport via water or air is usually required, unless direct local sources are identified. In the case of fluorotelomer alcohols, solubility in water is minimal (11). Recent publications disagree, in one case by two orders of magnitude, on the ambient temperature vapor pressure of these FTOHs (11, 12, 13). Also, it has been postulated that intramolecular hydrogen bonding (forming a cyclic structure) is responsible for estimated higher than expected vapor pressures for fluorotelomer alcohols. In this paper we report fluorotelomer alcohol vapor pressure determinations by three independent

experimental methods, and we compare the results with the values obtained by extrapolation to ambient temperature from experimental data obtained at higher temperatures. We also present *ab initio* computations and experimental data that unequivocally rule out significant intermolecular hydrogen bonding within these molecules.

Fluorotelomer alcohols (FTOHs), $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2,3,4,5,6$), are linear molecules of six to fourteen carbons, comprised of an even-number perfluoroalkyl segment attached to an ethanol moiety. The nomenclature n-2 FTOH specifies the number of fluorinated and hydrogenated carbons in the molecule (*e.g.*, 8-2 FTOH for $CF_3-(CF_2)_7-CH_2-CH_2-OH$). Alternatively, the fluorinated alcohols are also termed Telomer B Alcohols (*e.g.*, 8-2 TBA). Fluorotelomer alcohols are intermediates in the production of a variety of surface-active fluorotelomer-based polymeric and surfactant products where the low surface energy of the perfluoroalkyl chain produces useful surface properties including water and oil repellency (14,15).

Fluorotelomer alcohols, especially 8-2 FTOH, have been the subject of several recent studies to understand their relevance and potential contribution *via* degradation chemistry to trace amounts of perfluorocarboxylates (PFCAs), including perfluorooctanoic acid (PFOA), detected in the environment. Studies concerned with the occurrence of some fluorotelomer alcohols in the North American troposphere (6,16), with their atmospheric chemistry (17,18,19), as well as with their microbial biodegradation (20, 21) have been reported. An earlier study, as well as very recent work, describe the mammalian metabolism of 8-2 FTOH in rats (22, 23). As the environmental and toxicological significance of fluorotelomer alcohols is being investigated and informed by new studies, there is a critical need for reliable analytical methodologies to assay these compounds and their degradation products in biological and environmental matrices (24,25,26). Similarly, it is critically important to know accurately their physicochemical properties and to understand the effects of their chemical structure on their physical, chemical and transport behavior.

A physicochemical property that is central to the potential for atmospheric transport and partitioning of fluorotelomer alcohols is their vapor pressure at ambient temperature. Conventional boiling point and controlled pressure measurements for high-boiling substances can generally be carried out accurately only at fairly elevated temperatures. The estimation of the vapor pressure at ambient temperature from such data, therefore, requires an extrapolation well outside the range of

direct measurements of a quantity that behaves exponentially with temperature. Methods exist that are suitable for very low vapor pressures and that can be used for high-boiling substances directly at room temperature providing a check of the extrapolated values from measurements performed at higher temperatures. In a preliminary communication, we have reported vapor pressure measurements for the 8-2 fluorotelomer alcohol (8-2 FTOH) carried out by two such methods as well as by a novel method based on gas-phase NMR, a technique largely unfamiliar to chemists holding promise for studies of relevance to environmental chemistry (11).

The vapor pressures of fluorotelomer alcohols n -2 FTOH ($n = 4, 6, 8, 10$) were the subject of a very recent study (12,13), reporting *inter alia* an extrapolated vapor pressure for 8-2 FTOH at 25 °C about 50 times higher than our concordant values obtained by three different techniques. Vapor pressure values extrapolated to ambient temperature, incorrectly labeled as “experimental” values, were used as the yardsticks to judge the reliability of environmental models used to predict vapor pressures. The observation that the four models used consistently yielded lower vapor pressures at ambient temperature than the “experimental” values was taken as an indication that the models did not account for a putatively significant $\text{-O-H}\cdots\text{F-}$ intramolecular hydrogen bonding between the hydroxyl (-OH) hydrogen atom and the two fluorines next to the ethanol moiety. Such hydrogen bonding, inferred from fragmentation patterns in mass spectrometric studies (27) and ^{17}O NMR data (28), was proposed to impart to fluorotelomer alcohols higher than expected volatility by “masking” the -OH functional group from other molecules.

We report vapor pressure determinations for the same series of fluorotelomer alcohols in the temperature range from 21 – 250 °C by three methods, including an improved gas-phase NMR method. The pitfalls encountered in extrapolating vapor pressure data obtained at elevated temperatures to ambient temperatures are discussed. We also show that the recently published vapor pressure data (12) seriously overestimate the volatility at ambient temperature, important to considerations of the potential for atmospheric transport. Furthermore, we show that the $\text{-O-H}\cdots\text{F-}$ intramolecular hydrogen bonding postulated to be the cause for the putatively exceptional volatility of these compounds, is not significant as demonstrated by gas-phase NMR, gas-phase FTIR, and 2D NMR Overhauser effect measurements in solution. High-level *ab initio* computational chemistry for

the 2-2 and 4-2 fluorotelomer alcohols do predict a very weak intramolecular hydrogen bonding interaction of the order of 1 kcal/mol, in agreement with several related molecular systems reported in the literature. Such weak hydrogen bonding cannot have material consequences on vapor pressure at ambient and higher temperatures.

Experimental Section

Materials. Fluorotelomer alcohols. 4-2 FTOH was obtained from Sigma-Aldrich Inc. (97%). 6-2 FTOH was a DuPont product obtained by distillation of a mixture of fluorotelomer alcohols (>96%). 8-2 FTOH (CAS number 678-39-7) was obtained from Clariant, GmbH (Germany) and was shown to be 99.2% pure via gas chromatography (m.p. 48-50 °C, Clariant). The major impurity (0.8% by area) was tentatively identified as $C_7F_{15}CF=CHCH_2OH$ based on the mass spectral fragmentation pattern. 10-2 FTOH was obtained from Lancaster Synthesis (97%, m.p. 94 °C). The fluorotelomer alcohols were kept and manipulated in a nitrogen glove box (Vacuum Atmospheres Inc.). Cyclopropane was purchased from Matheson Tri-Gas Company (>99%).

Vapor Pressure by Conventional Techniques. Two conventional techniques were used to determine vapor pressure. The first method is based on a dynamic measurement procedure developed by Scott wherein the equilibrium temperature is measured at a controlled pressure (29). It was used to determine the vapor pressures of the 6-2 and 8-2 fluorotelomer alcohols. Approximately 30 g of the fluorotelomer alcohol was placed in a round bottom flask boiler. The pressure was held constant to 0.01% (0.01 kPa) and measured to an accuracy of 0.01 %. The apparatus consisted of a Mensor PCS400 pressure controller (San Marcos, TX), a Paroscientific 740 pressure transducer (Redmond, WA), and a Hart Scientific stack base unit for temperature measurement (American Fork, UT). The temperature varied from 60 to 200 °C.

The second procedure was based on the EPA OPPTS gas saturation method in which the quantity of a substance transported by a known volume of a carrier gas is determined (30). This method is particularly suited for low vapor pressures and was used to determine the vapor pressure of the 6-2, 8-2 and 10-2 fluorotelomer alcohols at 21 °C, 35°C and 35°C, respectively. The alcohol

sample was placed in a glass thermostatted tube. Gas-chromatographic grade helium (99.999%) was flowed over the solid. The flow was controlled by a flow controller on a Hewlett Packard (now Agilent, Little Falls, DE) model 5890 gas chromatograph. Due to the adsorptive properties of the alcohol, the vapor pressure was calculated from weight loss rather than from the weight of trapped material downstream. The vapor pressure is calculated from the vapor density, W/V , by means of the equation $P / \text{Pa} = W/V \times RT/M_r$ where P is the vapor pressure in Pascals, W is the mass of transported substance in grams, V is the volume of saturated gas in cubic meters, R is the universal molar gas constant, T is the temperature in K, and M_r is the relative molecular mass.

Vapor Pressure by Gas-Phase NMR. The third method is novel and is based on gas-phase NMR that has been recently employed (with proton and fluorine detection) to study the kinetics of a variety of reactions of organic and fluoroorganic compounds in the vapor phase at temperatures up to 400 °C (31, 32, 33, 34, 35). The details of the new methodology are presented in the Supporting Information and only an overview is given here. Briefly, a small amount of substance (~200 μmol) is sealed in a 10 mm o.d. glass ampule of about 4 mL internal volume (with a 5 mm o.d. extension to facilitate sealing and attachment to a vacuum system) together with ~ 1 mol % of accurately metered volatile mass standard. Tetramethylsilane and cyclopropane have been used as mass standards for proton detection and hexafluoroethane for fluorine detection. The high volatility of the mass standard and its small amount ensures that most mass standard molecules are in the headspace of the ampule at the temperatures of interest. Corrections are made when this is not the case. The ampule is placed in the NMR probe so that the spectrometer probes only the molecules in the vapor phase. Spectra are then acquired at appropriate increments of temperature from the lowest temperature giving sufficient vapor pressure for detection up to the temperature of complete vaporization. Comparison of the integrated intensities of the signals relative to the mass standard affords the number of micromoles of substance in the vapor phase at each temperature. Since the internal volume of the ampule is known, the vapor pressure is calculated by the ideal gas law.

2D HOESY NMR. The 4-2 and 8-2 fluorotelomer alcohols were studied by 2D heteronuclear Overhauser effect spectroscopy (HOESY) (36). In each case 0.10 M solutions in CD_2Cl_2 dried over 4 Å molecular sieves and containing traces of TMS and fluorotrichloromethane (Freon®-11) were used. The 2D ^{19}F - ^1H HOESY spectra (^{19}F observed) were acquired on a 500 MHz Bruker Avance

DRX spectrometer with a ^{19}F frequency of 470.712 MHz. The pulse sequence used was Hoesyph, found in the Bruker pulse sequence library. A quad probe was used for this experiment with a ^{19}F 90° pulse of 12 μsec (using 100 W amplifier) and with a ^1H 90° pulse of 40 μsec (using a 10 W amplifier). The spectra were obtained at 30 $^\circ\text{C}$ using 300 and 600 msec mixing times, 10 s recycle time (due to the long relaxation times of the fluorines in solution), 1024 t_2 points, 256 scan averages, and 110 t_1 with a 30441.4 Hz t_2 and a 3369.59 Hz t_1 spectral width and with ^1H decoupling during the acquisition time. The spectrum was processed using a Gaussian function in t_2 with 1024 points and a Gaussian function in t_1 with 1024 points. The spectra were displayed in phase-sensitive mode and linear prediction was used, backward in the t_2 and forward in the t_1 dimensions.

Gas-phase FTIR. The IR spectrum of 4-2 FTOH in the vapor phase in equilibrium with its liquid phase at room temperature was acquired using a 10 cm gas IR cell with NaCl windows and with a well containing approximately 1 mL of the liquid alcohol. Prior to the IR measurement, the cell was attached to a vacuum system and the 4-2 FTOH in the well was degassed by freeze-pump-thaw cycling. The IR spectrum of the equilibrated vapor at room temperature was obtained with a Nicolet Magna 760 FTIR spectrometer equipped with a cooled MCTB detector. 4 cm^{-1} resolution and 64 scans were employed.

Results and Discussion

Vapor pressure. The vapor pressures determined by the Scott method at various temperatures up to the normal boiling point for the 6-2 and 8-2 fluorotelomer alcohols and by the gas saturation method at close to ambient temperatures for the 6-2 (35 $^\circ\text{C}$), 8-2 (21 $^\circ\text{C}$), and 10-2 (35 $^\circ\text{C}$) fluorotelomer alcohols are tabulated in Table 1 and are shown graphically on a logarithmic scale in Figure 1 (white crosses and filled squares, respectively).

The thermodynamic basis for interpreting the temperature dependence of the vapor pressures of liquids is the Clapeyron equation expressing a relationship between the temperature coefficient of the vapor pressure, the absolute temperature T , the molar heat of vaporization ΔH , and the volume change per mol transferred from the liquid to the vapor phase (37). The assumptions that a) the molar volume of the vapor is much greater than that of the liquid, b) the vapor behaves as an ideal

gas, and c) ΔH is constant lead to the Clausius-Clapeyron equation $\log(P) = A - B/T$ where A and $B = -\Delta H / (2.3026 R)$ are constants. It has long been known, however, that the temperature dependence of $\log(P)$ is linear only in a narrow temperature range, and a whole series of semiempirical equations have been proposed (37). Of these, the Antoine equation (38), $\log(P) = A - B/(t + C)$, has been used extensively since it represents well the vapor pressures of most substances over large temperature intervals. Indeed, an excellent fit of the data, including the low temperature determinations by the gas saturation method, was obtained using this equation (Figure 1). The resulting values of the Antoine parameters are collected in Table 2 together with the extrapolated values of the vapor pressures of the fluorotelomer alcohols at ambient temperatures. The normal boiling points (vapor pressure at 101.325 kPa) of 171.5 °C and 201.3 °C were extracted for 6-2 FTOH and 8-2 FTOH. Excluding the gas saturation values from the data to be fitted had no effect on the resulting Antoine parameters, as expected by the fact that these values are several orders of magnitude smaller than the vapor pressures at higher temperatures measured by the Scott method. It is reassuring, therefore, keeping in mind the difficulties in extrapolating exponential behavior far from the range of the measurements and that the extrapolation for a substance that is a solid at room temperature (8-2 FTOH) strictly refers to a supercooled liquid phase, that the gas saturation points for 6-2 FTOH (35 °C) and 8-2 FTOH (21 °C) fall so close to the respective extrapolated values based on the Antoine equation (Table 2, Figure 1).

Since the vapor pressures of fluorotelomer alcohols at ambient temperatures are important for understanding their potential for atmospheric transport, the extrapolation of the vapor pressure data to these temperatures based on the Clausius-Clapeyron equation, used in ref. 12, was also considered. Careful scrutiny of the $\ln(P)$ vs. $1/T$ plot of Figure 2 shows a slight downward curvature of all the data, indicating that the data cannot be adequately represented by a straight line. Accordingly, the extrapolated values at ambient temperature based on the Clausius-Clapeyron equation will be higher than those based on the Antoine equation. For example, the extrapolated value of the vapor pressure for 8-2 FTOH at 21 °C based on the on the Clausius-Clapeyron equation is 16 Pa compared to 4 Pa obtained by the Antoine fit.

Figure 3A shows the proton NMR spectrum of the vapor phase in equilibrium with a small pool of liquid 8-2 FTOH at 148 °C in an ampoule charged with 73 mg (155 μ mol) of the

fluorotelomer alcohol and 1.5 μmol of cyclopropane. There are three absorptions for the $-\text{CH}_2\text{CH}_2\text{OH}$ protons with their spin-spin interaction structures (*cf.*, Supporting Information) as well as a single absorption for the six equivalent protons of cyclopropane. No spin-spin interaction of the hydroxylic proton with any fluorine spin is discernible. As the temperature is raised, the intensities of the 8-2 fluorotelomer alcohol resonances increase relative to that of cyclopropane as more of the fluorotelomer alcohol vaporizes (Figure 3B).

The fluorine resonances of 8-2 FTOH behave similarly with temperature as shown in Figure 3C and 3D: they also grow in intensity as the temperature is increased until all 8-2 FTOH has entered the vapor phase. The broader lines characteristic for fluorines in the vapor phase mask any spin-spin structure and reduce the accuracy of integration compared to proton detection. Accordingly, the quantitative treatment to yield vapor pressure was carried out using proton detection.

The number of micromoles of 8-2 FTOH in the vapor phase at each temperature can be easily determined by comparing the average integrated NMR intensity for the three protons with the $1/T$ corrected integrated intensity (*cf.*, Supporting Information) for the cyclopropane mass standard present in known micromolar amounts ($\sim 1 \text{ mol } \%$). The integrated intensities must, of course, be normalized for the number of equivalent protons giving rise to each resonance (2 for the CH_2 protons, 1 for the OH proton, and 6 for the cyclopropane protons). Since the internal volume of the ampoule is known, the vapor pressure at each temperature can be calculated using the ideal gas law. The same procedure was followed for the 4-2, 6-2, and 10-2 fluorotelomer alcohols whose ^1H gas-phase NMR spectra are almost indistinguishable from that of 8-2 FTOH save for the temperature dependence of the NMR intensities. The vapor pressures determined by proton gas-phase NMR for these compounds are tabulated in Table 1 and are plotted on a logarithmic scale as a function of temperature in Figure 1 together with the Scott-method and gas-saturation-method determinations for 6-2 FTOH and 8-2 FTOH. Figure 1 also shows the curves obtained by least-squares fits of the data to the Antoine equation extended to ambient temperatures. For 8-2 FTOH the calculated vapor pressure at 21 $^\circ\text{C}$ is 2 Pa to be compared with 4 Pa derived from the fit of the Scott-method data (experimental value = 3 Pa), while for the 6-2 FTOH the calculated value at 35 $^\circ\text{C}$ is 50 Pa to be compared with 107 Pa derived from the Scott-method data (experimental value = 108 Pa) (Table

2). The least squares fit for the 10-2 FTOH is less straightforward than for the lower analogs as a result of the reduced curvature of the data, and the corresponding Antoine parameters (Table 2) depend somewhat on the starting values chosen for the least squares process. As with the lower homologs, the extrapolated vapor pressure at 35 °C for 10-2 FTOH is somewhat lower than the value obtained by the gas saturation measurement at the same temperature (1.4 Pa). As mentioned above, the inadequate linear fits of the $\ln(P)$ vs. $1/T$ plot (Figure 2) yield higher extrapolated values compared to the Antoine-equation fits and will not be discussed further. Inspection of Figure 1 indicates that the NMR-derived vapor pressures are systematically somewhat lower than the Scott-method measurements, resulting also in somewhat lower extrapolated values at ambient temperatures, although the agreement for the 8-2 FTOH, the purest of the samples, is quite impressive.

In view of the foregoing, we were surprised by the results in a very recent publication (12) reporting vapor pressure measurements by the boiling-point method for the same series of fluorotelomer alcohols and their extrapolation to 25 °C using the Clausius-Clapeyron equation in that a) these values were stated as ‘experimental’ values and b) they were much higher than our extrapolated values and our measured values by the gas-saturation method at ambient temperatures. These reported ‘experimental’ values were used to judge the reliability of four environmental models to predict vapor pressures. The observation that these models consistently yielded lower vapor pressures at ambient temperature than the ‘experimental’ values was taken as an indication that the models did not account for a putatively significant -O-H...F- intramolecular hydrogen bonding between the hydroxylic H atom and the two fluorines next to the ethanol moiety. A direct comparison of these “experimental” values at 25 °C with our gas-saturation determinations is made difficult by the different temperatures used in our experiments (21 °C and 35 °C). Table 3 compares these literature values with the extrapolated values at 25 °C from our data using the Antoine parameters of Table 2. It is quite apparent that the reported literature values are seriously overestimated.

Intramolecular hydrogen bonding in fluorotelomer alcohols? The temperature dependence of NMR chemical shifts, particularly for hydroxylic protons if unaffected by intermolecular hydrogen bonding (high dilution limit), can provide information about intramolecular hydrogen bonding (39).

Considering just the idealized equilibrium between the unbound gauche (u) and the H-bonded (b) conformations shown below, that disregards other rotational degrees of freedom, the chemical shift of the hydroxylic proton in the two conformers will most likely have different values, $\delta(b)$ and $\delta(u)$. If the equilibration is sufficiently rapid, the observed chemical shift $\delta(\text{obs})$ will be the average of $\delta(b)$ and $\delta(u)$ weighted by the populations of the b and u conformers, $\delta(\text{obs}) = P(b) \delta(b) + P(u) \delta(u)$. The varying populations at different temperatures will produce changes in the observed chemical shift until, at sufficiently elevated temperatures, an isotropic average is observed. The temperature dependence of the proton and fluorine chemical shifts in the gas-phase for 8-2 FTOH, a by-product of the vapor pressure measurements, are shown in Figure 4. The chemical shift of the hydroxylic proton hardly shows any change with temperature over more than a 250 °C temperature range providing no evidence for hydrogen bonding at these temperatures. However, a $\delta(\text{obs})$ independent of temperature can also result if $\delta(u)$ and $\delta(b)$ should be accidentally very similar (*vide infra*), leading to an inconclusive result. The chemical shifts of the fluorines adjacent to the CH_2 group have the largest temperature coefficient probably because the $-\text{CH}_2-\text{CF}_2-$ bond has torsional vibrations of greater amplitude than those of the $-\text{CF}_2-\text{CF}_2-$ bonds of the stiffer fluoroalkyl chain (40).

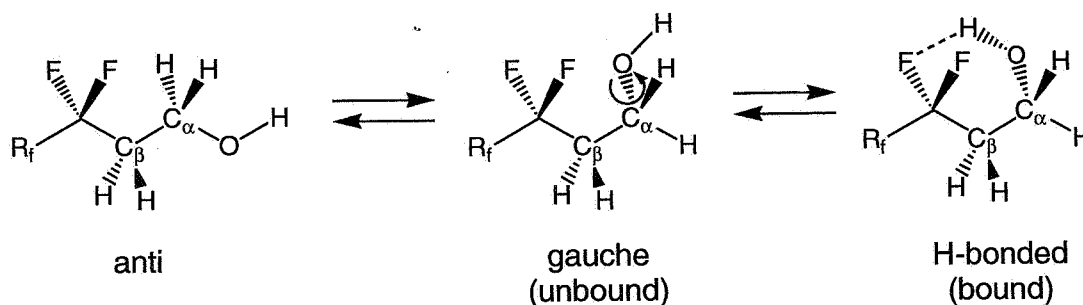
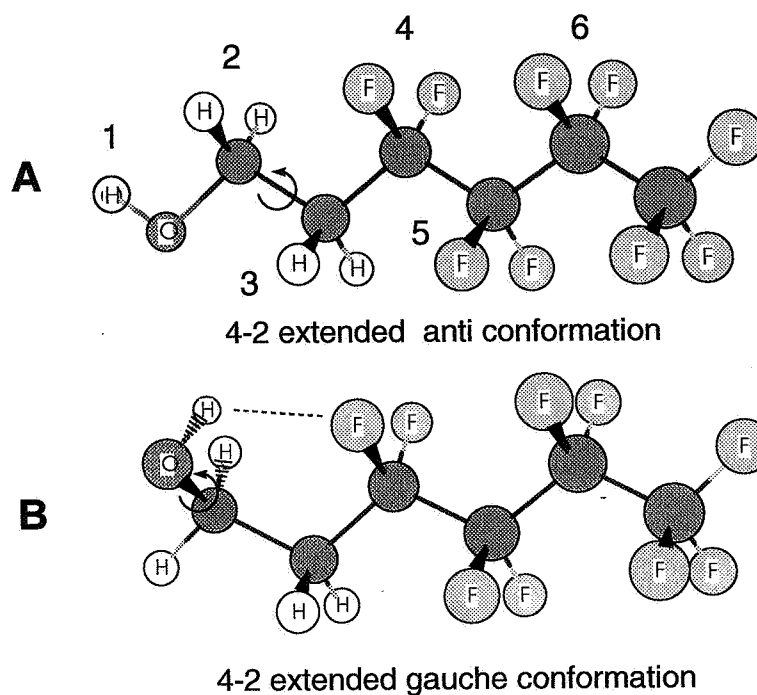


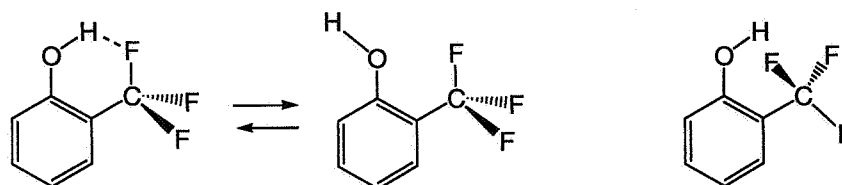
Figure 5 shows the contour plots obtained by heteronuclear 2D Overhauser effect experiments (HOESY) on 4-2 FTOH and 8-2 FTOH in dilute methylene chloride solutions at 30 °C. The nuclear Overhauser effect provides valuable information regarding molecular dynamics and structure (36). Since NOE is related to $(r_{AB})^{-6}$, the average through-space distance between two dipolar interacting spins A and B can be estimated. It is apparent from Figure 5 that the smallest

NOE is that labeled 1,4 (see arrows in Figure 5) between the hydroxylic proton and the fluorines of the $-\text{CF}_2-$ group attached to the ethanol moiety. Stronger and almost equal NOEs are observed for the pairs 3,4, 2,4 and 3,5 arguing in favor of an extended anti equilibrium conformation **A**. Consistent with this conformation, there are about equal NOEs between the pairs 2,5 and 3,6. Thus, the heteronuclear 2D NOE experiments for both 4-2 FTOH and 8-2 FTOH fluorotelomer alcohols provide no support for appreciable contribution of a hydrogen bonded structure such as **B** below.



The IR $-\text{O}-\text{H}$ stretch vibration mode is a very sensitive indicator of hydrogen bonding. Thus, for ortho-trifluoromethylphenol, one of a relatively small number of known $-\text{O}-\text{H}\cdots\text{F}-$ weakly hydrogen bonded systems, in isooctane solutions dilute enough so that no intermolecular association could be detected, two overlapping IR bands were observed whose relative intensities changed in

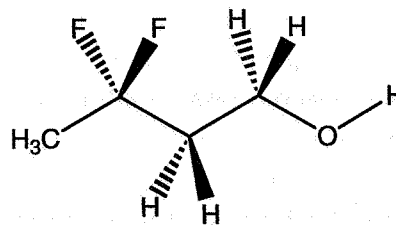
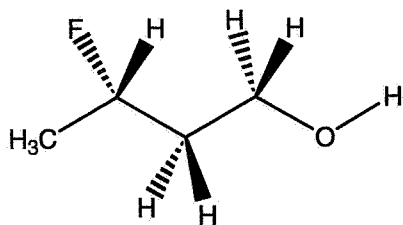
the temperature range from -30 to $25\text{ }^{\circ}\text{C}$ (41). This behavior was the manifestation of the equilibrium, idealized below, between a hydrogen-unbonded and a hydrogen-bonded structure. The latter is appreciably populated only at sub-ambient temperatures. The resulting $\Delta H = 1.4\text{ kcal/mol}$ for this equilibrium is a measure of the strength of this hydrogen bond. More recent theoretical studies indicated a preference of the same magnitude for a bifurcated cyclic structure idealized below (42).



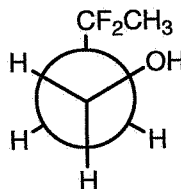
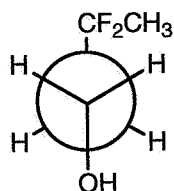
In contrast with the above, the IR spectrum of the vapor phase of 8-2 FTOH in equilibrium with its liquid phase at ambient temperature, 25°C , (Figure 6) showed no indication of a second O-H stretch vibrational band that might result from an appreciable population of a similarly hydrogen bonded structure as idealized in structure **B** above.

Ab-initio computation of intramolecular hydrogen bonding in fluorotelomer alcohols. To further elucidate the potential role of intramolecular hydrogen bonding in fluorotelomer alcohols, we performed an extensive series of *ab-initio* quantum chemical calculations. Hydrogen bonding is ubiquitous in the chemistry of solvated and condensed-phase systems and plays a critical role in determining the structure of biological molecules (43). For this study we used density functional theory (DFT) as described in the Supporting Information.

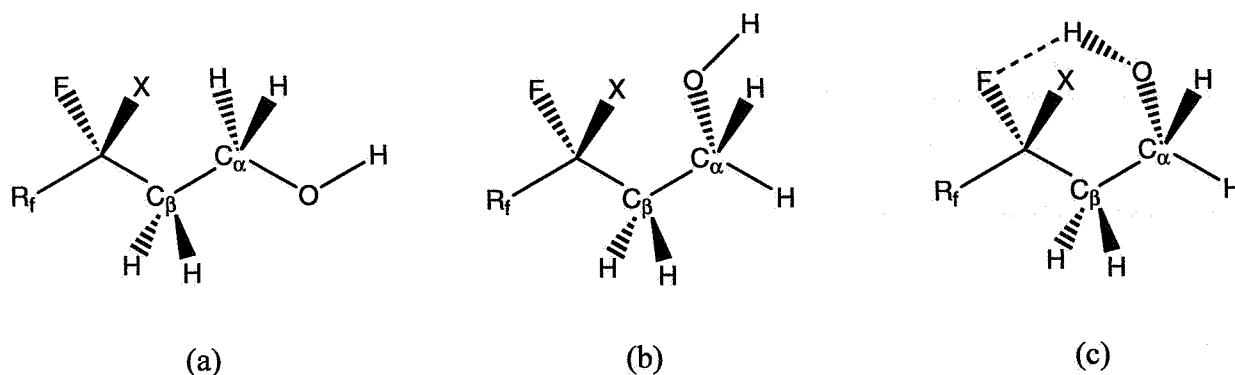
Before performing calculations on larger, highly fluorinated systems, we studied two small sparsely fluorinated molecules to see if any evidence of a $-\text{C}-\text{F}\cdots\text{H}-\text{O}-$ hydrogen-bonding exists. The prototype species studied were 3-fluorobutan-1-ol and 3,3-difluorobutan-1-ol sketched in anti-conformation below.



Each of these structures, and all other linear fluoroalcohols, exist in a variety of rotational conformations. Of critical concern for the current problem are the anti and gauche conformations, corresponding to rotation about the C_{α} - C_{β} single bond, illustrated below by Newman projections. The gauche conformation brings a fluorine atom and the hydroxyl group into close proximity and affords the best chance of forming an intramolecular $-C-F \cdots H-O-$ hydrogen bond.



Below are sketched the three important molecular conformations for linear fluorotelomer alcohols in which X is either H or F. Structure (a) shows the extended anti form which *a priori* is expected to be the lowest energy conformation. Structure (b) shows the gauche conformation related to the anti form by a 120° rotation around the C_{α} - C_{β} single bond. Finally, structure (c) shows the likely conformation of the proposed hydrogen-bonded 6-membered ring structure. In the rest of this discussion, we will refer to these conformations as “anti”, “gauche” and “bonded”, respectively.



In Table 4 are listed the calculated relative enthalpies of these three conformations of 3-fluorobutan-1-ol and 3,3-difluorobutan-1-ol. For both molecules, and in all subsequent tables, the reported enthalpies are relative to the anti conformation. The quoted values are ideal gas enthalpy differences at 298.15 K and 1 atmosphere corrected for zero-point energy differences.

As Table 4 shows, the hydrogen-bonded conformation (bonded) is the lowest energy state, that is a hydrogen bond is predicted to exist, and, as expected, the gauche form is the least stable conformation. The $-C-F \cdots H-O-$ hydrogen bonds are weak. A sensible definition of the bond strength is the calculated enthalpy of the bonded conformation relative to that of the gauche form. On this measure, the calculated bond strength of the singly fluorinated system is 3.57 kcal/mol and in the doubly fluorinated system it is 2.45 kcal/mol.

Our calculations on prototype systems encouraged us to examine more representative systems. Ideally, we would perform calculations for the molecules of particular interest to atmospheric scientists, such as 8-2 FTOH, but calculations on such large systems are computationally tedious due to the large number of molecular electrons. In any case, such calculations are unnecessary. As the perfluorinated tail lengthens, the hydrogen bond strength in the 6-membered ring structure will quickly stabilize to a value that is independent of the length of the tail.

We performed calculations for two fluorotelomer alcohols: 2-2 FTOH and 4-2 FTOH. Table 5 shows the calculated relative enthalpies for the three critical conformations. The trends we

observed for the prototype systems remain unaltered. The hydrogen-bonded conformation is the lowest energy state and the gauche form is the least stable conformation. The $\text{-C-F}\cdots\text{H-O-}$ hydrogen bonds are now very weak. For 2-2 FTOH the bond strength is 1.32 kcal/mol and for 4-2 FTOH it is 1.42 kcal/mol consistent with the claim that the bond strength quickly becomes independent of chain length. Armed with these results, we confidently predict that the higher FTOHs will have very weak hydrogen bonds of the order of ~ 1 kcal/mol.

Proton NMR Chemical Shifts. We also calculated ^1H NMR chemical shifts for all four species studied in the previous section. For comparison with the experimental results for 8-2 FTOH reported in the section on gas-phase NMR, we will discuss the calculated values obtained for 4-2 FTOH, although we note that the results obtained for 2-2 FTOH are essentially identical. The NMR shielding tensors and absolute chemical shifts were calculated using the Gauge-Independent Atomic Orbitals (GIAO) method (44). The calculations were performed with B3LYP/6-311++G(3df,2p)// B3LYP/6-31+G(d,p), and the details are summarized in the Supporting Information.

Tables S1-S3 of the Supporting Information contain the calculated proton shifts for the bonded, anti and gauche conformations, respectively (*cf.*, structures c, a, and b above, $\text{X} = \text{F}$, $\text{R}_f = \text{C}_3\text{F}_7$). Examination of these Tables shows that the agreement between theory and experiment is exceptionally good and that the calculated proton shifts vary little among the three conformations. The average proton shifts for the $\text{-CH}_2\text{O-}$ group vary from a minimum of 4.08 ppm in the bonded state to a maximum of 4.22 ppm in the gauche conformation (~ 4.0 ppm experimentally, Figure 4). For the $\text{-CF}_2\text{CH}_2\text{-}$ protons, the average computed shifts vary from 2.30 ppm in the bonded state to 2.44 ppm in the anti conformer (~ 2.4 ppm experimentally, Figure 4). The largest change is for the hydroxyl proton H that varies from 0.38 ppm to 1.35 ppm (~ 1.0 ppm experimentally, Figure 4). The variation is very modest and rules out the use of temperature dependence of the observed proton shifts to quantify the relative occupation of each state.

High level *ab initio* calculations do show a very weak intramolecular hydrogen bonding interaction in fluorotelomer alcohols of the order of 1 kcal/mol. With such small enthalpy differences, the hydrogen bonded conformations cannot be preferentially populated by any appreciable extent relative to unbound conformations at ambient temperatures to be of any

consequence as regards vapor pressure and atmospheric transport.

In conclusion, experimental and computational studies demonstrate that the vapor pressures of fluorotelomer alcohols at ambient temperature are in fact significantly lower than previously reported and that intramolecular hydrogen bonding is very weak and does not affect the vapor pressure of fluorotelomer alcohols. These results, as well as the highly sorptive nature of fluorotelomer alcohol (45), suggest that the potential atmospheric transport pathway for these compounds should be reconsidered.

Supporting Information. Details of the gas-phase NMR methodology and of the *ab-initio* computations are provided in the Supporting Information.

Table 1. Measured Vapor Pressure Data of Fluorotelomer Alcohols ^a

<u>4-2 FTOH</u>		<u>6-2 FTOH</u>		<u>8-2 FTOH</u>		<u>10-2 FTOH</u>	
T (°C)	Vapor Pressure (kPa)	T (°C)	Vapor Pressure (kPa)	T (°C)	Vapor Pressure (kPa)	T (°C)	Vapor Pressure (kPa)
50.0	1.2	35.0	0.108 ^c	21	0.003 ^c	35.0	0.0014 ^c
74.8	6.5	60.8	0.640 ^b	84	0.71 ^b	123.5	1.6
99.2	22	72.5	1.40 ^b	96	1.5 ^b	147.6	6.0
108.9	33	74.8	1.19	99.2	1.7	171.6	16
118.6	51	85.2	2.99 ^b	107	2.8 ^b	185.8	28
128.3	72	97.8	5.81 ^b	119	4.9 ^b	195.3	33
133.2	88	99.2	5.04	123.5	5.7	204.8	52
138.0	100	109.9	10.43 ^b	130	8.3 ^b	214.3	60
142.8	120	121.3	17.24 ^b	142	14 ^b	223.7	92
147.6	140	123.5	15.91	147.6	17	233.1	117
		136.0	31.03 ^b	155	23 ^b	237.8	130
		146.2	44.80 ^b	166	34 ^b		
		147.6	38.81	171.6	40		
		157.2	59.58	179	52 ^b		
		158.1	66.85 ^b	185.9	62.05		
		166.8	81.26	190	72 ^b		
		171.3	100.62 ^b	195.3	82		
		176.3	109.23	201	100 ^b		
				204.8	110		
				209.5	126		

^a Determined by gas-phase NMR unless noted otherwise.

^b Obtained by the Scott method.

^c Obtained by the gas-saturation method.

Table 2. Antoine Parameters and Extrapolated Vapor Pressures of Fluorotelomer Alcohols

$$\log_{10} P/\text{kPa} = A - B / (t/^{\circ}\text{C} + C)$$

FTOH	Method	A	B	C	Calcd.	Exp. ^a
					v.p. (Pa)	v.p. (Pa)
4-2	NMR	6.681	1448	172	489 ^b	
6-2	NMR	6.566	1506	156	50 ^b	
6-2	Scott	6.419	1497	168	107 ^b	
8-2	NMR	6.412	1555	151	2 ^c	
8-2	Scott	6.458	1623	163	4 ^c	
10-2	NMR	6.386	1570	130	0.7 ^b	1.4 ^b

^a Gas saturation method.

^b At 35 °C.

^c At 21 °C.

Table 3. Extrapolated Vapor Pressures at 25 °C of Select Fluorotelomer Alcohols

FTOH	Literature ^a (Clausius- Clapeyron) (Pa)	Scott Method (Antoine) (Pa)	Gas-phase NMR (Antoine) (Pa)	Normal Boiling Point (°C)
4-2	992		216	137.5 ^b
6-2	713	44	18	173.8 ^b
8-2	254	7	4	171.5 ^c 202.0 ^b
10-2	144		0.2 ^d	201.3 ^c 228.4 ^b

^a From ref. 12.

^b Gas phase NMR using Antoine fit.

^c Scott method using Antoine fit.

^d Compare with experimental value of 1.4 Pa at 35 °C.

Table 4. Relative enthalpies ^a (kcal/mol) of the three critical conformations of 3-fluorobutan-1-ol and 3,3-difluorobutan-1-ol

Species	anti	gauche	bonded
3-fluorobutan-1-ol	0	+2.65	-0.92
3,3-difluorobutan-1-ol	0	+1.74	-0.71

^a Computational method used B3LYP/6-311++G(3df,2p)// B3LYP/6-31+G(d,p). Enthalpies reported at 298.15 K and 1 atmosphere.

Table 5. Relative enthalpies ^a (kcal/mol) of the three critical conformations of 2-2 FTOH and 4-2 FTOH

Species	anti	gauche	bonded
2-2 FTOH	0	+1.03	-0.29
4-2 FTOH	0	+1.08	-0.34

^a Computational method used B3LYP/6-311++G(3df,2p)// B3LYP/6-31+G(d,p). Enthalpies reported at 298.15 K and 1 atmosphere.

Captions to Figures

Figure 1 Plot of vapor pressure of fluorotelomer alcohols vs. temperature as determined by three methods: gas-phase ^1H NMR, Scott method, gas-saturation method (filled squares). Data are fit by the Antoine equation.

Figure 2 Plot of $\ln$ (vapor pressure) vs. $1/T$ of the fluorotelomer alcohols. Data fit by Clausius-Clapeyron equation.

Figure 3 ^1H -Proton (A, B) and ^{19}F -fluorine (C, D) gas-phase NMR spectra of 8-2 FTOH at different temperatures (*cf.*, Supporting Information).

Figure 4 Plots of chemical shifts (^1H and ^{19}F) of 8-2 FTOH vs. temperature.

Figure 5 2D (^1H , ^{19}F) HOESY NMR spectra of 4-2 and 8-2 FTOH. Arrows designate the NOE corresponding to interactions between the hydroxyl proton and the CF_2 group adjacent to the ethanol moiety.

Figure 6 Gas-phase FTIR spectrum of 4-2 FTOH in equilibrium with its liquid phase at 25 °C. The inset is an expansion of the region of absorbance for O-H stretches.

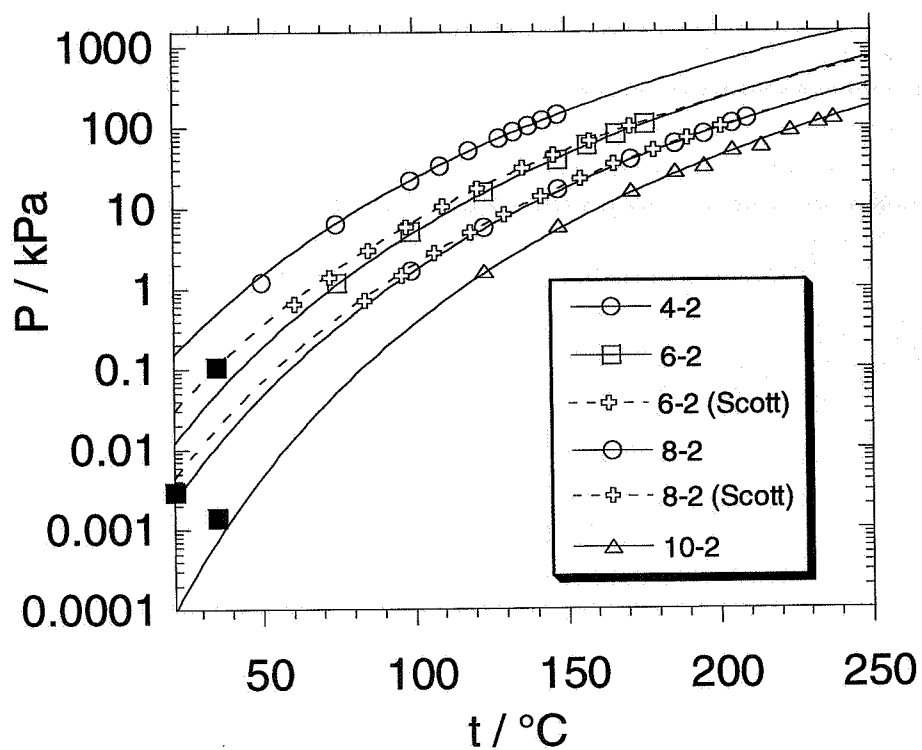


Figure 1 Plot of vapor pressure of fluorotelomer alcohols vs. temperature as determined by three methods: gas-phase ^1H NMR, Scott method, gas-saturation method (filled squares). Data are fit by the Antoine equation.

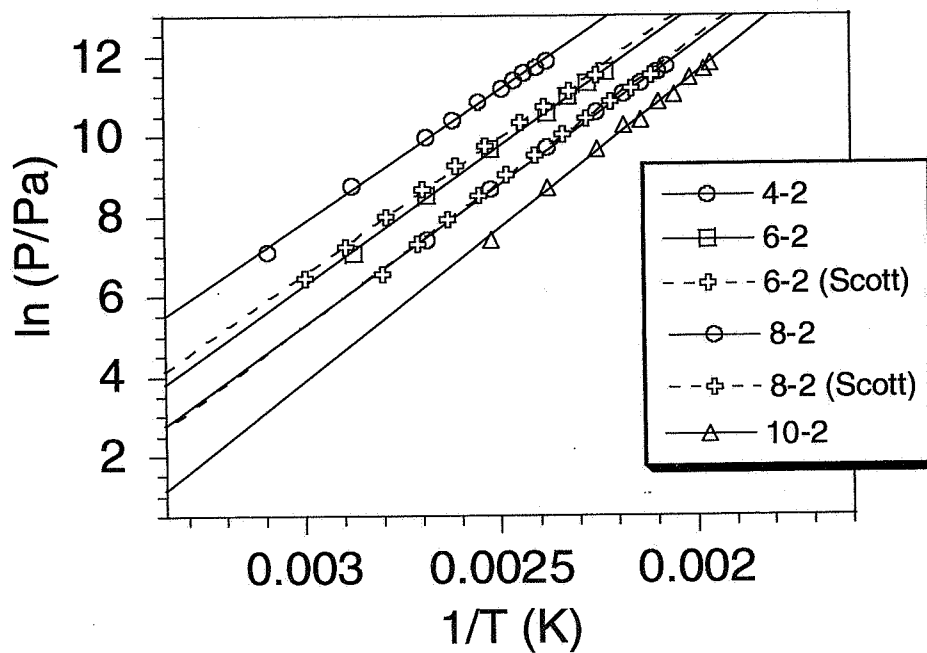


Figure 2 Plot of $\ln$ (vapor pressure) vs. $1/T$ of the fluorotelomer alcohols. Data fit by Clausius-Clapeyron equation.

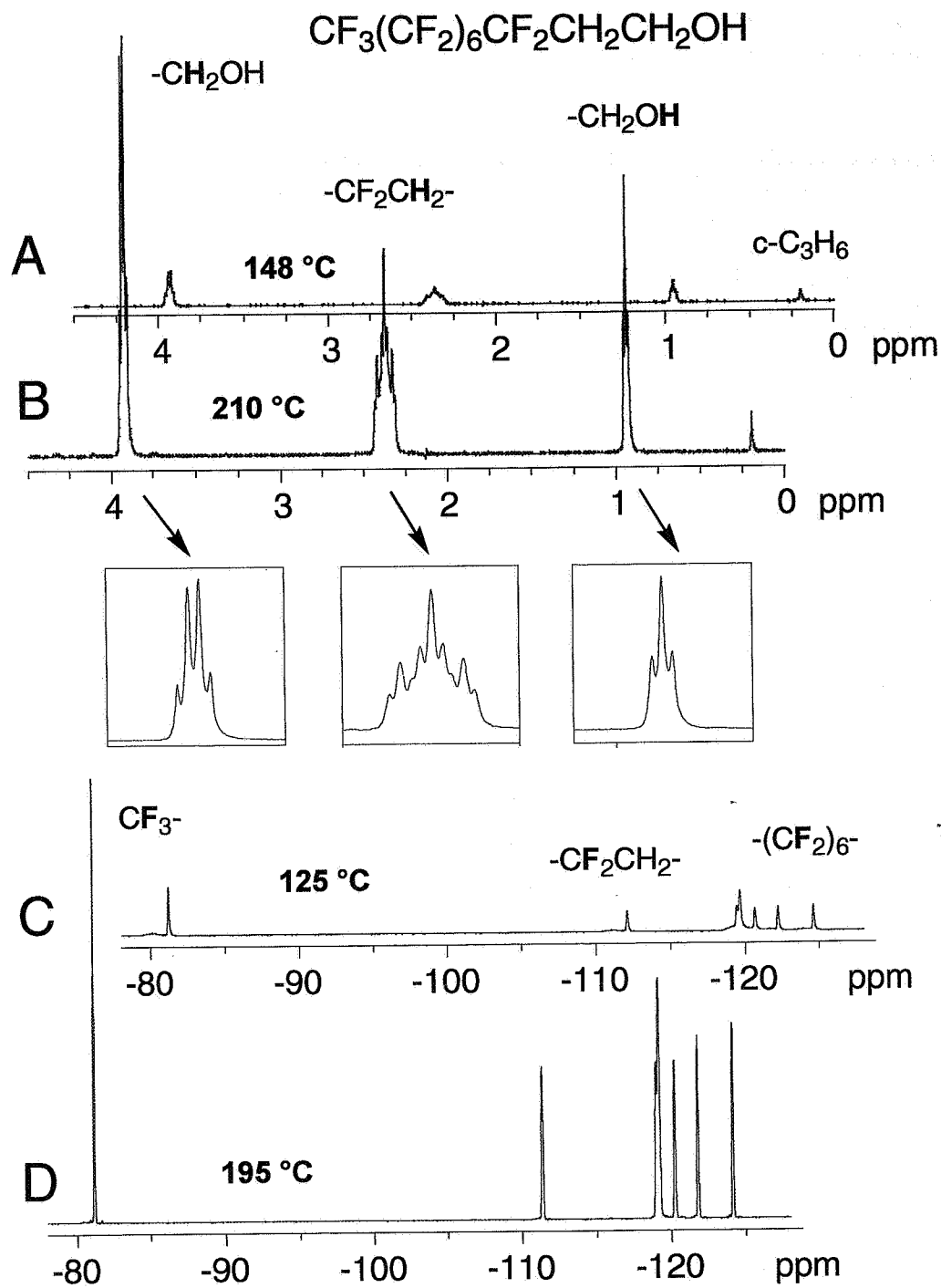
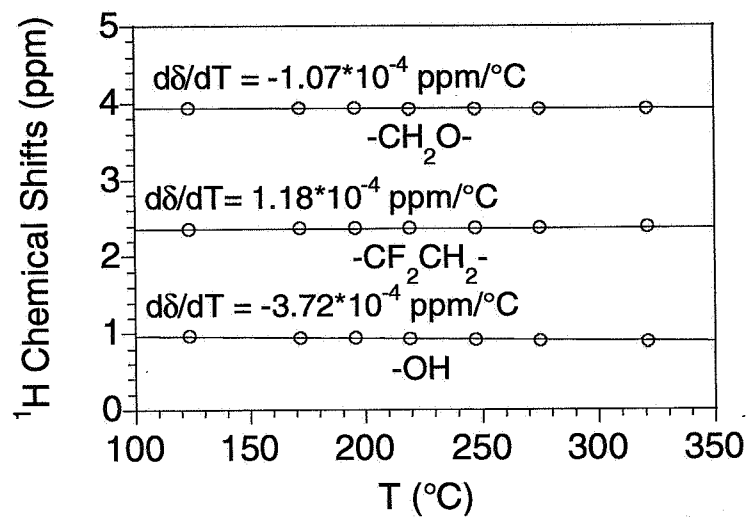


Figure 3 ^1H -Proton (A, B) and ^{19}F -fluorine (C, D) gas-phase NMR spectra of 8-2 FTOH at different temperatures (*cf.*, Supporting Information).



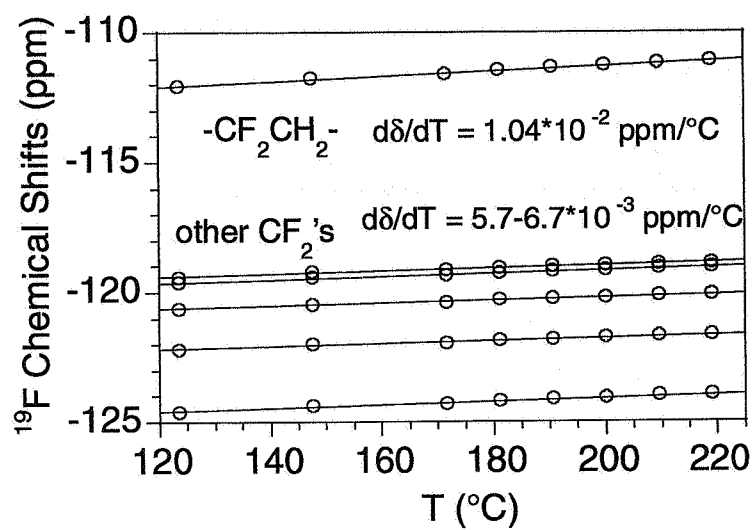


Figure 4 Plots of chemical shift (^1H and ^{19}F) of 8-2 FTOH vs. temperature.

^1H

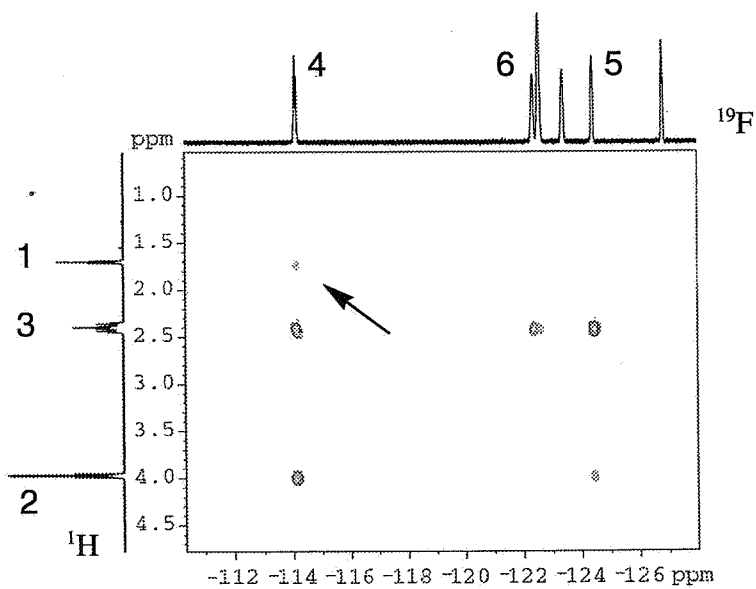
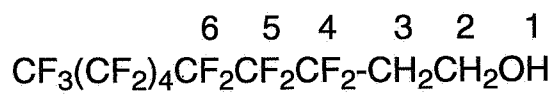
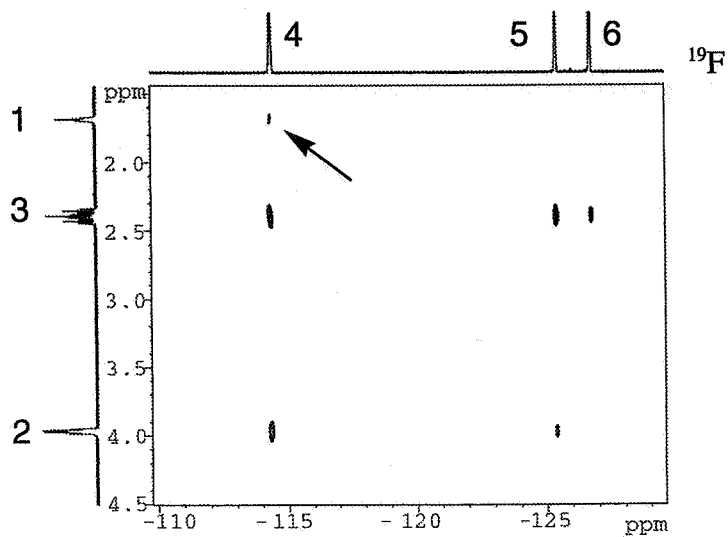
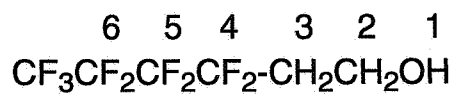


Figure 5 2D (^1H , ^{19}F) HOESY NMR spectra of 4-2 and 8-2 FTOH. Arrows designate the NOE corresponding to interactions between the hydroxyl proton and the CF_2 group adjacent to the ethanol moiety.

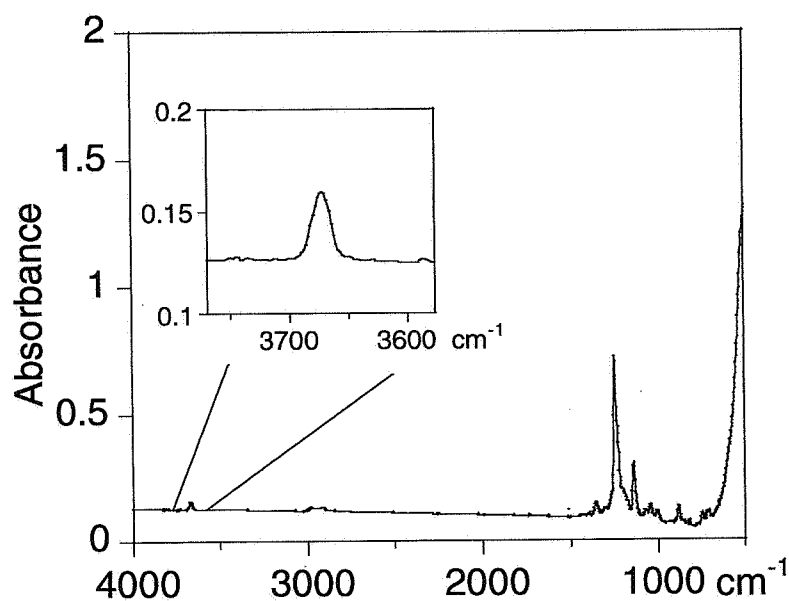


Figure 6 Gas-phase FTIR spectrum of 4-2 FTOH in equilibrium with its liquid phase at 25 $^{\circ}\text{C}$. The inset is an expansion of the region of absorbance for O-H stretches.

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