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Combined Experimental and Theoretical Study of the Protonation of Polyfluorobenzenes $[C_6H_{6-n}F_n]$ ($n = 0$–6)

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In a recent high-pressure mass spectrometric revision to the gas-phase basicity scale (J. E. Szulejko and T. B. McMahon, *J. Am. Chem. Soc.* 115, 7839 (1993)), it was observed that the proton affinity for hexafluorobenzene was 24 kcal mol^{-1} (1 kcal = 4.184 kJ) lower than the accepted National Institute of Science and Technology (NIST) database value of 177.7 kcal mol^{-1} (S. G. Lias *et al.*, *J. Phys. Chem. Ref. Data* 17, Suppl. 1 (1988)). Furthermore, the proton affinities for most other polyfluorobenzenes were also found to differ substantially from the NIST values. For many of the polyfluorobenzenes large protonation entropy changes were noted, which were substantially greater than then those expected from rotational symmetry number changes alone. In view of these observations, MP2/6–31G//HF/6–31G** *ab initio* calculations were undertaken to investigate further the proton affinity and entropy changes with respect to the degree of fluorine substitution. The present proton affinity variations found for the polyfluorobenzenes (hexaflorobenzene excepted) can be interpreted with the aid of the *ab initio* results in terms of a simple additivity scheme. Each fluorine substituent *para*, *meta*, *ortho* or *ipso* to the ring protonation site will induce an incremental proton affinity change with respect to benzene of 1.5, −7.0, −1.5 and −19.0 kcal mol^{-1}, respectively. This additivity scheme can also be used to rationalize the re-evaluated proton affinities for the polymethylbenzenes and *m*- and *o*-fluorotoluenes. The corresponding methyl increments are 7.5, 5.5, 2.5 and 1.0 kcal mol^{-1} for *para*, *meta*, *ortho* and *ipso* protonation respectively. From the present *ab initio* statistical thermodynamic analysis of the various protonation entropy components, it was concluded that the low-frequency vibrations are almost exclusively responsible for the large excess entropy changes observed experimentally. *Ab initio* calculated barriers for 1,2 proton shifts in arenium species available in the literature are concluded to be too large to allow the existence of a so-called dynamic proton. Large excess protonation entropies are noted from the literature for polymethylbenzenes, naphthalene and 1-methylnaphthalene. © 1997 by John Wiley & Sons, Ltd.**

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KEYWORDS: polyfluorobenzenes; proton affinities; additivity scheme; entropies; *ab initio*

INTRODUCTION

The initial impetus for our high-pressure mass spectrometric (HPMS) experiments, which led to the recently published revision to the gas-phase proton affinity scale,[1] was to re-examine the basicity scale of McMahon and Kebarle,[2] obtained at a single temperature (400 K), over an extended temperature range.[3] Such temperature-dependent measurements enable both the enthalpy and entropy for equilibrium proton transfer to be determined accurately. This is inherently more satisfactory than reliance on entropy estimation assumptions to convert a Gibbs free energy, ΔG°_{400}, scale into an absolute proton affinity (*PA*) scale which is anchored to a reference base of known absolute proton affinity. The absolute proton affinity for CO of 141.9 kcal mol^{-1} (1 kcal = 4.184 kJ) obtained from appearance energy measurements and supported by high-level *ab initio* calculations was used as the only absolute proton affinity standard in our work.

In our re-evaluation of the basicity regime from N_2 to H_2S[3], we concluded that it was necessary to revise the values of the proton affinities for H_2O and H_2S downward by ~1.5 kcal mol^{-1} from those given in the National Institute of Science and Technology (NIST) database.[4] It was decided, in the light of this observation, to extend the study to include another absolute proton affinity standard, propene, as an additional anchor to confirm the new proton affinities for H_2O and H_2S found in that work. Examination of the NIST

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databases[4,5] suggested that hexafluorobenzene would have been an excellent intermediate base to bridge the basicity span between H_2S and C_6H_6. However, when equilibrium proton transfer experiments were attempted between benzene and hexafluorobenzene, little or no protonated hexafluorobenzene could be observed, except possibly during the initial 3 keV electron beam ionization pulse. Three bases of decreasing proton affinity were tried: H_2S, CS_2 and SO_2. Only with SO_2 could equilibrium proton transfer be observed. This led to the surprising conclusion that the proton affinity of hexafluorobenzene must be ~24 kcal mol^{-1} lower than the NIST[4] entry. In view of this observation, the study was expanded to ascertain whether the proton affinities for the other polyfluorobenzenes might also differ substantially from the NIST[4] values. Subsequently, the polyfluorobenzenes[1] proved extremely valuable in establishing the relative basicities of H_2S, C_3H_6 and C_6H_6 through the use of multiple overlap proton transfer equilibria.

When proton transfer experiments were carried out between a polyfluorobenzene (in large excess) and a base of substantially higher basicity, for example between 1,2,4 trifluorobenzene and benzene, a substantial long-lived molecular cation of the polyfluorobenzene was observed. A finite ^{13}C isotope correction due to the molecular cation therefore had to be subtracted from the signal occurring at the mass corresponding to the protonated polyfluorobenzene of interest. As shown, for example, in Fig. 1, under our HPMS conditions this ^{13}C isotope correction term never became a major concern. The NIST[4] proton affinities for the polyfluorobenzenes had been based on data derived mainly from variable-temperature, low-resolution ion cyclotron resonance (ICR) experiments by Hartman and Lias[6] in 1978. Subsequent reassessment[7] of these data has shown that under the ICR conditions the intensity of the peak corresponding to the mass of the protonated polyfluorobenzene of interest was almost entirely composed of ^{13}C carryover from the molecular cation. Another complication evident from our HPMS work was the slow proton transfer kinetics, even in the exothermic direction, especially between polyfluorobenzenes. For example, proton transfer from hexafluorobenzene to pentafluorobenzene occurs with a rate constant of 6.5×10^{-11} cm^3 s^{-1} at 500 K. This could then have been another contributing factor affecting the reliability of the ICR data in which only a non-equilibrium steady state would have been observed on the ICR time-scale. In view of the relatively slow kinetics, equilibrium constants for proton transfer between pairs of polyfluorobenzenes of differing fluorine content were not measured, as equilibrium could be not established within our HPMS time-scale (5–25 ms) before the ion count rate decayed to zero, due to either diffusional losses or reactive losses with impurities.

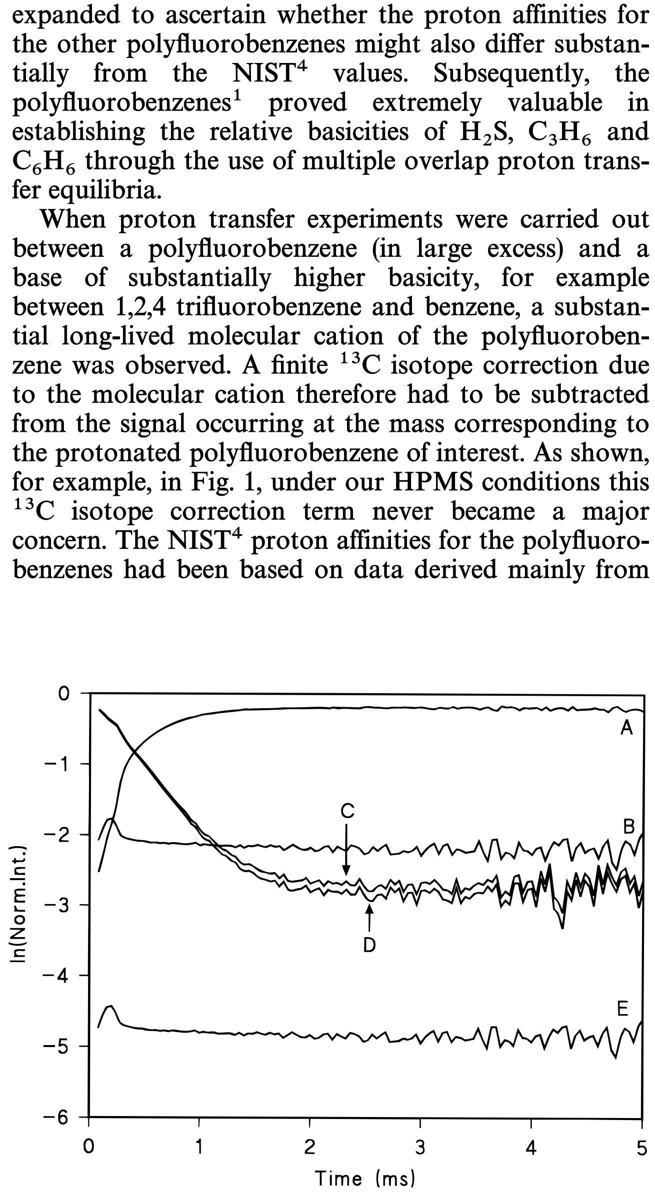


Figure 1. Normalized time–intensity profiles of ions observed in a mixture of benzene and 1,2,4-trifluorobenzene in methane showing the minor ^{13}C contamination due the radical molecular cation of 1,2,4-trifluorobenzene at the mass corresponding to protonated 1,2,4-trifluorobenzene (A) *m/z* 79, protonated benzene; (B) *m/z* 132, 1,2,4-$^{12}C_6H_3F_3^{+\cdot}$; (C) signal at *m/z* 133 due to 1,2,4-$^{12}C_5{}^{13}CH_3F_3^{+\cdot}$ and $(1,2,4\text{-}^{12}C_6H_3F_3)^+$; (D) pure $(1,2,4\text{-}^{12}C_6H_3F_3)H^+$ signal; (E) signal due to the 1,2,4-$^{12}C_5{}^{13}CH_3F_3^{+\cdot}$ component. Ion source conditions: total pressure = 7.4 Torr (1 Torr = 133.3 Pa), benzene partial pressure = 0.70 mTorr, 1,2,4-trifluorobenzene partial pressure = 76 mTorr and temperature = 500 K.

A previous HPMS study by Yamdagni and Kebarle[8] at 600 K provided data for fluorobenzene, 1,3-difluorobenzene and 1,3,5-trifluorobenzene, all having basicities close to that of benzene. Unfortunately, that study did not include any other polyfluorobenzenes. On the other hand, thermochemical data for proton transfer between benzene and fluorobenzene have been obtained in a number of laboratories[1,6,8–12] and are generally in excellent agreement with one another (Table 1). These data notwithstanding, there is a general paucity of experimental basicity data for the polyfluorobenzenes.

Hartree–Fock,[13–16] MNDO,[17,18] MP2,[19,20] AM1[21] and G2[22] calculations have been reported for many protomers of toluene,[13,19] xylenes,[13] benzene,[13,14,19,22] fluorobenzene,[13–16,19] aniline,[20a] pyridine,[20a] phenol,[20b] difluorobenzenes,[19,21] fluorotoluenes,[19] polyfluorobenzenes,[21a] trifluorobenzenes[17,18,21a] and polychlorophenols.[21b] The preferred sites for protonation (ring or fluorine substituent) have also been studied experimentally in detail by several laboratories either by examination of the mass spectra[23,24] or by low-energy collisional activation[25,26] spectra of the protonated polyfluorobenzenes, produced by Brønsted acid protonation reagent ions (HN_2^+, CO_2H^+, CH_5^+, N_2OH^+,

Table 1. Summary of thermochemical data[a] for proton transfer between benzene and fluorobenzene

$\Delta H°$	$\Delta S°$	$\Delta G°_{300}$	$\Delta G°_{600}$	Ref.	Method
−0.8	−2.7	0.0	0.8	6	ICR
−1.3	−3.4	−0.3	0.7	1	HPMS
			0.9	8	HPMS
−1.3	−3.5	−0.3	0.8	9	HPMS
−1.4	−3.6	−0.3	0.8	10	HPMS
−1.2	−3.7	−0.2	1.0	11	HPMS
−1.4	−3.6	−0.3	0.8	12	HPMS

[a] $\Delta H°$ and $\Delta G°$ in kcal mol^{-1}, $\Delta S°$ in cal mol^{-1} K^{-1}.

Table 2. Thermochemical data analysis of molecules studied in the present work

PS[a]	Molecule	PA[b]	PA[c]	PA[d]	PA[e]	$\Delta S^\circ_{1/2}$[b]	$\Delta S^\circ_{\sigma 1/2}$[f]	$\Delta S^\circ_{1/2xs}$[g]	$\Delta S^\circ_{1/2}$[h]
4	Toluene	187.7	189.8	187.3		3.0	0.0	3.0	0.0
4	Fluorobenzene	181.3	182.6	181.6		1.5	0.0	1.5	0.0
1	Benzene	180.0	181.3	179.9	178.8[i]	5.5	3.6	2.0	3.5
4	1,3-Difluorobenzene	180.0	181.9	181.0		3.0	1.4	1.5	1.0
2	1,3,5-Trifluorobenzene	178.4	181.0	180.0		2.5	2.2	0.5	1.5
4	1,2-Difluorobenzene	175.7	181.8	175.0		2.0	1.4	0.5	1.5
5	1,2,4-Trifluorobenzene	174.7	181.4	174.7		1.0	0.0	1.0	0.0
4	1,2,3-Trifluorobenzene	173.0		174.0		5.0	1.4	3.6	
2	1,4-Difluorobenzene	171.5	181.2	172.4		6.0	2.8	3.0	1.5
4	1,2,3,5-Tetrafluorobenzene	170.0	180.6			7.5	1.4	6.0	1.5
5	1,2,3,4-Tetrafluorobenzene	165.8	181.1	168.2		7.0	1.4	5.5	0.0
3	1,2,4,5-Tetrafluorobenzene	161.0	179.7	164.2		10.0	2.8	7.0	3.5
6	Pentafluorobenzene	164.3	179.9	166.8	166.0[j]	6.0	0.0	6.0	1.5
1	Hexafluorobenzene	153.8	177.7	153.8	153.8[k]	9.5	5.0	4.5	4.5

[a] PS = protonation site; see also Table 6 for proton affinity *vs*. protonation site by additivity scheme estimation.

[b] Taken from Ref. 1 except for 1,2,3,5-tetrafluorobenzene from Ref. 35.

[c] Ref. 4.

[d] 0 K PA, Ref. 19.

[e] G2 or combined G2–HPMS determined PA.

[f] $\Delta S^\circ_{\sigma 1/2} = R\ln(\sigma_B/\sigma_{BH^+})$ due to rotational symmetry (see text).

[g] Eqn (10).

[h] $\Delta S^\circ_{1/2}$ is calculated from the LLL 298 K basicity and proton affinity compilation (Ref. 5) as follows: $\Delta S^\circ_{1/2} = 26.0 - (PA - \text{basicity})/0.298$ cal mol^{-1} K^{-1}.

[i] 298 K G2 result, Ref. 22.

[j] From combined G2 *ab initio* calculations on CH_3I, $PA = 165.2$ kcal mol^{-1} (Ref. 33); CS_2, $PA = 163.0$ kcal mol^{-1} (Ref. 32) and HPMS H^+ exchange between CH_3I and C_6HF_5 ($\Delta H^\circ = -1.1$ kcal mol^{-1}, $\Delta S^\circ = -3.8$ cal mol^{-1} K^{-1} (Ref. 31)); or CS_2 and C_6HF_5 ($\Delta H^\circ = -2.8$ kcal mol^{-1}, $\Delta S^\circ = -4.6$ cal mol^{-1} K^{-1}, HPMS study (Ref. 1).

[k] From combined G2 *ab initio* calculations on CH_3Cl, $PA = 155.3$ kcal mol^{-1}; CH_3Br, $PA = 158.4$ kcal mol^{-1}; and HPMS H^+ exchange between C_6F_6 and CH_3Cl ($\Delta H^\circ = -1.7$ kcal mol^{-1}, $\Delta S^\circ = -5.2$ cal mol^{-1} K^{-1}) or C_6F_6 and CH_3Br ($\Delta H^\circ = -4.5$ kcal mol^{-1}, $\Delta S^\circ = -3.5$ cal mol^{-1} K^{-1}) (Ref. 33).

HCO^+, $C_2H_5{}^+$ and H_3O^+). Apart from ring or substituent protonation sites, the possibility of a face-centred π complex isomer of the benzenium ion has been postulated by Mason *et al.*[27] In order to explore the relative energetics of possible protonation sites in the polyfluorobenzenes, an extensive *ab initio* study of fluorobenzene *o*-, *m*- and *p*-difluorobenzenes and hexafluorobenzene has also been undertaken. The results of this combined experimental and *ab initio* study are described herein.

EXPERIMENTAL

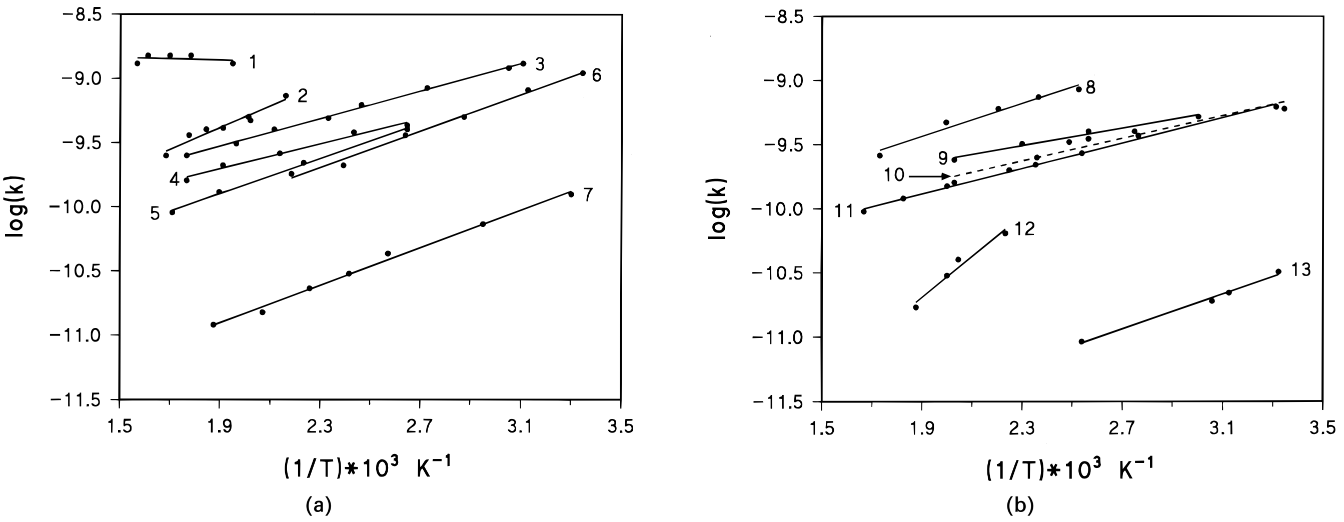
All experiments were performed on a pulsed ionization high-pressure mass spectrometer constructed at the University of Waterloo configured around a VG 70-70 mass spectrometer whose geometry has been reversed to provide a B–E instrument. The experimental conditions employed, the apparatus and its capabilities have all been described in detail previously.[28] Polyfluorobenzenes and other chemicals were obtained from commercial sources and were used as supplied. Gaseous mixtures for the proton transfer experiments were prepared as described previously. Occasionally, higher mass resolution than the normal setting (~500) was sometimes used (⩽2000) to remove or separate isobaric H,C,O background interferences from the sometimes weak protonated polyfluorobenzene signals of interest.

AB INITIO CALCULATIONS

Molecular orbital calculations for a number of neutral and protonated fluorobenzenes were carried out at the MP2/6–31G**//HF/6–31G** level using the Gaussian 92 program suite.[29] The HF/6–31G** calculated vibrational frequencies and zero point energies were scaled[30] by 0.89 in the calculation of gas phase thermochemical quantities, such as entropies at the HF/6–31G** level and the 0 K proton affinities from MP2/6–31G** total energies. The HF/6–31G** level vibrational thermochemical quantities were calculated using the harmonic approximation in the statistical thermodynamic formulae. Smith and Radom[31] have recently dealt with the performance of various theoretical methods in calculating proton affinities and have demonstrated that proton affinities calculated at the MP2 level with relatively small basis sets can predict accurate proton affinities for many systems.

RESULTS

The gas-phase basicities for most of the protonated polyfluorobenzenes studied here have been tabulated previously[1] and were obtained from the temperature dependence of proton transfer equilibrium constants for ~80 pairs of bases ranging in proton affinity from N_2



(a) (b)

Figure 2. Proton transfer kinetics: Arrhenius plots [Eqn (7)] between pairs of bases [$B_1 \rightarrow B_2$, Eqn (5)]. (1) $H_2S \rightarrow C_6H_6$; (2) 1,4-$C_6H_4F_2 \rightarrow C_6H_6$; (3) $C_6H_6 \rightarrow C_6H_5CH_3$; (4) $CS_2 \rightarrow$ 1,2,3,5-$C_6H_2F_4$; (5) 1,2,3-$C_6H_3F_3 \rightarrow C_6H_6$; (6) $C_6H_5F \rightarrow C_6H_5CH_3$; (7) 1,2,3-$C_6H_3F_3 \rightarrow C_6H_6$; (8) $CS_2 \rightarrow$ 1,2,3-$C_6H_3F_3$; (9) 1,2-$C_6H_4F_2 \rightarrow C_6H_6$; (10) $C_6F_6 \rightarrow CS_2$; (11) 1,2,4-$C_6H_3F_3 \rightarrow C_6H_6$; (12) $C_6F_6 \rightarrow CF_3CN$; (13) $CS_2 \rightarrow C_6HF_5$.

Table 3. Summary of proton transfer kinetic data

B_1	B_2	ΔH^* [a]	ΔS^* [a]	k_{600} [b]	k_{300} [b]	ΔH^* [c]	ΔS^* [c]	ΔH° [d]	ΔS° [d]
C_6H_5F	$C_6H_5CH_3$	-3.2	-22.6	7.2×10^{-11}	1.1×10^{-9}	-4.7	-26.5	-6.1	1.8
C_6H_6	$C_6H_5CH_3$	-2.5	-19.6	2.2×10^{-10}	1.8×10^{-9}	-4.1	-23.4	-8.0	-2.1
1,3,5-$C_6H_3F_3$	C_6H_6	-3.4	-27.4	8.4×10^{-12}	1.4×10^{-10}	-4.9	-31.2	-1.5	2.1
1,2-$C_6H_4F_2$	C_6H_6	-1.6	-18.0	1.9×10^{-10}	7.0×10^{-10}	-3.1	-22.1	-4.2	3.1
1,2,4-$C_6H_3F_3$	C_6H_6	-2.3	-21.1	9.5×10^{-11}	6.7×10^{-10}	-4.0	-24.8	-5.2	4.1
1,2,3-$C_6H_3F_3$	C_6H_6	-3.1	-22.3	8.8×10^{-11}	1.2×10^{-9}	-5.0	-26.8	-7.0	-0.3
1,4-$C_6H_4F_2$	C_6H_6	-3.7	-21.8	2.5×10^{-10}	5.5×10^{-9}	-5.7	-26.0	-8.6	-1.5
H_2S	C_6H_6	0.2	-12.5	1.5×10^{-9}	1.2×10^{-9}	-2.0	-16.5	-10.7	3.0
CS_2	1,2,3-$C_6H_3F_3$	-2.9	-20.5	2.6×10^{-10}	3.0×10^{-9}	-4.8	-24.4	-11.4	-6.5
CS_2	1,2,3,5-$C_6H_2F_4$	-2.2	-20.1	2.5×10^{-10}	9.8×10^{-10}	-3.9	-24.0	-8.7[e]	-3.5[e]
CS_2	C_6HF_5	-3.1	-28.8	2.3×10^{-12}	3.1×10^{-11}	-4.5	-32.8	-2.8	-4.6
C_6F_6	CS_2	-2.0	-19.5	1.3×10^{-10}	6.6×10^{-10}	-3.5	-23.5	~-8.0[f]	~1.2[f]
C_6F_6	CF_3CN	-7.3	-34.6	8.5×10^{-12}	4.5×10^{-9}	-9.3	-34.0	N.M.[g]	N.M.[g]

[a] Arrhenius plot, ln k *vs.* $1/T$ [Eqn (7)] (ΔH^* in kcal mol^{-1}; ΔS^* in cal mol^{-1} K^{-1}).
[b] Extrapolated Arrhenius 300 and 600 K rate constants (in cm^3 s^{-1}).
[c] Modified Arrhenius plot, ln(k/T^2) *vs.* $1/T$ [Eqn (8)].
[d] Equilibrium data [Eqn (1)] taken from Ref. 1 unless noted otherwise (ΔH° in kcal mol^{-1} and ΔS° in cal mol^{-1} K^{-1}).
[e] This work.
[f] Not originally included in Ref. 1.
[g] Not measurable, equilibrium was not established within the HPMS time-scale.

to *tert*-butylamine. Equilibrium proton transfer between two neutral bases, B_1 and B_2 [Eqn (1)] was examined and the corresponding equilibrium constant at each temperature determined from the ion intensity ratio of the two protonated bases at equilibrium $(I_{B_2H^+})/(I_{B_1H^+})$, and the partial pressure ratios (P_{B_1}/P_{B_2}) of the two neutral bases [Eqn (2)] (see Fig. 1 for representative normalized time intensity profiles).

Table 4. Summary of single-temperature proton transfer kinetic data

B_1	B_2	Temperature (°C)	k (cm^3 s^{-1})
C_6HF_5	C_6H_6	191	7.5×10^{-10}
C_6F_6	C_6HF_5	69	4.2×10^{-11}
C_6F_6	C_6HF_5	226	6.7×10^{-12}
C_6F_6	C_6H_6	255	1.1×10^{-9}
SO_2	C_6F_6	175	1.0×10^{-10}
SO_2	C_6F_6	270	6.5×10^{-11}
1,4-$C_6H_4F_2$	1,2,4-$C_6H_3F_3$	58	1.0×10^{-12}
1,3-$C_6H_4Cl_2$	C_6H_6	97	8.0×10^{-13}
H_2S	1,2,3-$C_6H_3F_3$	80	1.0×10^{-9}

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \tag{1}$$

$$K_{eq} = (I_{B_2H^+} \cdot P_{B_1})/(I_{B_1H^+} \cdot P_{B_2}) \tag{2}$$

The variation of ln K_{eq} *vs.* reciprocal temperature (van't Hoff plot) [Eqn (3)]

$$\ln K_{eq} = -\Delta H^\circ/RT + \Delta S^\circ/R \tag{3}$$

was used to derive the new experimental proton affinities and protonation entropies, $\Delta S^\circ_{1/2}$, presented in Table 2 for the protonated polyfluorobenzenes. Also shown for comparison are the NIST database[4,5] values. Carbon monoxide was chosen as the only primary standard. A 300 K absolute proton affinity of 141.9 kcal mol^{-1} and a 500 K half-reaction protonation entropy change, $\Delta S^\circ_{1/2}$, of 3.0 cal mol^{-1} K^{-1} have been assigned to carbon monoxide.[1] The half-reaction entropy change, $\Delta S^\circ_{1/2}$, for a protonation reaction [Eqn (4)] is defined as the difference in entropy between the protonated base, BH^+, and the neutral base, B. The entropy of the protonated base can be approximated to that of a known isoelectronic analog (e.g. H_3O^+ as NH_3). If the entropies of B and the isoelectronic neutral analogue of BH^+ are known from the literature, then an estimate can be made for $\Delta S^\circ_{1/2}$. The temperature of 500 K has been assigned to the $\Delta S^\circ_{1/2}$ scale based on the following: (i) the average temperature of the ~80 van't Hoff plots and (ii) the estimated $\Delta S^\circ_{1/2}$ [Eqn (4)] for N_2, CO, H_2O, H_2S and NH_3. In this way, the estimated $\Delta S^\circ_{1/2}$ for N_2, CO, H_2O, H_2S and NH_3 are most consistent with the experimental results in the Szulejko–McMahon study.[1]

$$\Delta S^\circ_{1/2} = S^\circ_{500}(BH^+) - S^\circ_{500}(B) \qquad (4)$$

Bimolecular proton transfer kinetics for a number of pairs of \bases [Eqn (5)] were studied as a function of temperature. The variation of ln k *vs.* $1/T$ (Arrhenius plot) for each of the systems studied is shown in Fig. 2. The pre-exponential temperature term in the transition state bimolecular rate equation (Eqn (6), standard state 1 atm) has been treated as a pseudo-constant, T_m, the mid-temperature of the temperature range studied. The term c is the conversion factor to convert from concentrations expressed in atm to molecules cm^{-3}. The Arrhenius parameters[34] [the enthalpy, ΔH^*, and entropy, ΔS^*, of activation, Eqn (7)] derived from transition state theory are presented in Table 3, together with the extrapolated 300 and 600 K rate constants. The mathematically rigorous treatment would be to perform linear regression on $\ln(k/T^2)$ *vs.* $1/T$ [Eqn (8)]. The data thus derived are also shown in Table 3. Other determinations for other proton transfer kinetic experiments carried out at a few temperatures are summarized in Table 4

$$B_1H^+ + B_2 \rightarrow B_2H^+ + B_1 \qquad (5)$$

$$k = c(kT/h)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT)\ \text{cm}^3\ \text{s}^{-1}$$
$$(k \text{ in units of molecules}^{-1}\ \text{cm}^3\ \text{s}^{-1}) \qquad (6)$$

$$k = AT_m^2 \exp(\Delta S^*/R)\exp(-\Delta H^*/RT)\ \text{cm}^3\ \text{s}^{-1} \qquad (7)$$

$$(k/T^2) = A \exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (8)$$

where $c = (22\,400T)/(273L)$ molecules^{-1} cm^3, $A = c(k/hT)$, $L = 6.02 \times 10^{23}$ molecules.

DISCUSSION

Polyfluorobenzene protonation sites

The *ab initio* proton affinities at various levels of theory (Table 5) for possible sites for protonation in fluorobenzene[14–16,19,21a] have predicted the site order of decreasing proton affinity to be protonation *para*, *ortho*, *meta*, *ipso* to the fluorine substituent and on fluorine. At a much lower level of theory, MNDO[17] calculations on all three isomers of trifluorobenzene and AM1[21a] calculations on polyfluorobenzenes have yielded similar conclusions and qualitatively reproduced relative proton affinities found in the present work. The MNDO calculations of Hrušák[17] have shown that the proton affinity is substantially reduced if a carbon atom that possesses a formal positive charge is *ortho* to a carbon bearing a fluorine substituent. The carbon atom in the highly polar $C^{\delta+}$—$F^{\delta-}$ bond carries a large partial positive charge and, being *ortho* to a formal positive charge site, is very unfavourable energetically. Protonation on fluorine is also very unfavourable. A pair of neighbouring fluorine substituents increase the proton affinity by ~1.0 kcal mol^{-1}. With these general rules in mind, the observed variation of proton affinities on fluorine content and substitution patterns can now be fully rationalized in terms of an additivity scheme (see below) partly based on *ab initio* calculations and the experimentally observed proton affinity trends.

Tkaczyk and Harrison[26] have studied the low-energy CID of protonated polyfluorobenzenes as a function of Brønsted acid protonation chemical ionization reagents of decreasing acidity, such as CO_2D^+, $CD_5{}^+$ DCO^+, $C_2D_5{}^+$ and D_3O^+, by monitoring the loss of DF. Deuteronation on fluorine can only occur if the proton affinity of the Brønsted base is lower than that of the fluorine site. The fluorine is preferentially protonated by Brønsted acids due to long-range ion–dipole interactions of the highly polar ${}^{\delta+}C$—$F^{\delta-}$ bond and the Brønsted acid. The proton affinity for fluorine protonation would be bracketed by monitoring the occurrence or non-occurrence of DF loss as a function of Brønsted acid acidity. However, in that study, no data for hexafluorobenzene were presented. Under CI conditions, very little protonated hexafluorobenzene

Table 5. Comparison of fluorobenzene proton affinities (kcal mol^{-1}) *vs.* protonation sites

	Fluorobenzene protonation site					
Method used	F	*ipso*	*meta*	*ortho*	*para*	Comments
4–31G[a]	138.5	170.0	178.5	184.5	186.4	
MP2/6–31G** [b]	150.3	160.8	172.9	179.7	182.0	
	6.6	3.7	4.1	4.0	2.5	(300 K $\Delta S^\circ_{1/2}$)[c]
MP2(fc)/6–31G**//HF/6–31G* [d]		160.4	172.5	179.4	181.6	
Experimental					181.3	(500 K *PA*)[e]
					2.0	(500 K $\Delta S^\circ_{1/2}$)[e]

[a] Electronic *PA*, Ref. 15.
[b] This work, 0 K *PA*, Z_{pe} scaled by 0.89; see also Ref. 16.
[c] This work, in units of cal mol^{-1} K^{-1} [Eqn (4)].
[d] 0 K *PA*, Z_{pe} scaled by 0.89, Ref. 19.
[e] Ref. 1.

Table 6. Additivity estimated and present MP2/6–31G//HF/6–31G** calculated proton affinities *vs*. ring protonation sites for polyfluorobenzenes[a]**

		Ring protonation site, C-1 to C-6								
F[b]	Substitution[c]	C-1	C-2	C-3	C-4	C-5	C-6	F[d]	*Pa*$_{expt}$[e]	Method used
1	1	161.0	178.5	173.0	**181.5**[e]	—	—	—	181.3	Additivity scheme, Eqn (9)
1	1	160.8	179.7	172.9	**182.0**	—	—	150.3	181.3	0 K MP2/6–31G**, this work
1	1	160.4	179.4	172.5	**181.6**	—	—	—	181.3	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19a, 19c
2	1,3	154.0	177.0	—	**180.0**	166.0			180.0	Additivity scheme, Eqn (9)
2	1,3	153.1	178.3	—	**181.1**	165.8	—	—	180.0	0 K MP2/6–31G**, this work
2	1,3	152.8	178.3	—	**181.1**	165.6	—	—	180.0	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19a, 19c
2	1,2	160.5	—	172.5	**175.5**				175.7	Additivity scheme, Eqn (9)
2	1,2	159.7	—	172.2	**175.1**	—	—	—	175.7	0 K MP2/6–31G**, this work
2	1,2	162.4	—	172.2	**175.0**	—	—	—	175.7	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19a, 19c
2	1,4	162.5	**171.5**	—	—	—	—	—	171.5	Additivity scheme, Eqn (9)
2	1,4	163.5	**172.5**	—	—	—	—	—	171.5	0 K MP2/6–31G**, this work
2	1,4	163.4	**172.4**	—	—	—	—	—	171.5	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19a, 19c
3	1,3,5	147.0	**178.5**	—	—	—	—	—	178.4	Additivity scheme, Eqn (9)
3	1,3,5	145.7	**180.0**	—	—	—	—	—	178.4	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19b, 19c
3	1,2,4	162.0	153.5	171.0	156.5	**174.0**	165.5	—	174.5	Additivity scheme, Eqn (9)
3	1,2,4	165.6	155.3	171.0	156.6	**174.7**	165.1	—	174.5	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19b
3	1,2,3	152.5	158.0	—	**173.0**	167.5	—	—	173.0	Additivity scheme, Eqn (9)
3	1,2,3	155.0	164.0	—	**174.0**	168.6	—	—	173.0	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19b, 19c
4	1,2,3,5	145.5	159.5	—	**171.5**	148.5	—	—	170.0	Additivity scheme, Eqn (9)
4	1,2,3,4	154.0	151.0	—	—	**166.0**	—	—	165.8	Additivity scheme, Eqn (9)
4	1,2,3,4	158.2	156.6	—	—	**168.2**	—	—	165.8	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19b, 19c
4	1,2,4,5	154.0	—	**163.0**	—	—	—	—	161.0	Additivity scheme, Eqn (9)
5	Pentafluoro	147.0	152.5	144.0	—	—	**164.5**	—	164.3	Additivity scheme, Eqn (9)
5	Pentafluoro	152.5	160.4	149.6	—	—	**166.8**	—	164.3	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19b, 19c
6	Hexafluoro	**145.5**	—	—	—	—	—	—	153.8	Additivity scheme, Eqn (9)
6	Hexafluoro	**153.9**	—	—	—	—	—	123.4	153.8	0 K MP2/6–31G**, this work
6	Hexafluoro	**153.8**	—	—	—	—	—	—	153.8	0 K MP2(fc)/6–31G**//HF/6–31G*, Ref. 19b, 19c

[a] Symmetry redundant values are not shown. *PA* in kcal mol^{-1}.
[b] Number of fluorine atoms.
[c] Fluorine substitution pattern.
[d] Protonation on a fluorine substituent.
[e] Data from Ref. 1.
[e] Values in bold denote the most favourable protonation sites.

could have been produced by the H_3O^+ and $C_2H_5{}^+$ reagent ions, even though the Lias *et al.* basicity scale[5] would have suggested otherwise. The present work now places the proton affinity for hexafluorobenzene below that of water and ethene, contrary to the Lias *et al.*[5] and NIST[4] values. A few other studies have been reported on the Brønsted acid CI mass spectra[23,24] of polyfluorobenzenes in order to gain a qualitative insight into sites for protonation, e.g. fluorine *vs.* ring protonation.

A face-protonated π complex of benzene had been postulated to be the most stable isomer of benzenium in the gas phase, as inferred from a collision activation study[27] of labelled H,D benzenium as a function of ion source temperature. Calculations performed at the G2 level[22] on isomeric benzenium species have demonstrated conclusively that the C_{2v} σ-bonded benzenium species is the global minimum. The C_{6v} π complex of benzenium, in contrast, was found to be a second-order saddle point, 47.5 kcal mol^{-1} higher in energy. Face protonation of a polyfluorobenzene can therefore be discounted with a very high level of confidence and certainty.

Polyfluorobenzene proton affinity substitution pattern

An additivity scheme can be constructed to predict an experimental proton affinity to within 1.0 kcal mol^{-1} for most polyfluorobenzenes. The following incremental parameters (I_{pX}) were defined [for Eqn (9)]: I_{pF} (1.5 kcal mol^{-1}), I_{oF} (-1.5 kcal mol^{-1}), I_{mF} (-7.0 kcal mol^{-1}) and I_{iF} (-19.4 kcal mol^{-1}) as the proton affinity changes relative to benzene for protonation *para*, *ortho*, *meta* or *ipso* to a fluorine substituent, respectively. For two neighbouring fluorine substituents an I_{nF} of 1.4 kcal mol^{-1} in 1,2-difluorobenzene and 1,2,4-trifluorobenzene is also defined. The experimental values derived for the five parameters used (I_{pF}, I_{oF}, I_{mF}, I_{iF}, I_{nF}) were estimated initially from the *ab initio* calculations performed on fluorobenzene and subsequently were adjusted to give the best fit to the experimental proton affinities (excluding C_6F_6). The parameter I_{iF} (*ipso* protonation) was estimated from the 0 K MP2/6–31G** proton affinity values. The 0 K MP2/6–31G** values for the parameters are $I_{pF} = 2.1$, $I_{oF} = -0.9$ and $I_{mF} = -7.2$ kcal mol^{-1} (C_6F_6 excepted).

$$PA = 180.0 + pI_{\mathrm{pF}} + oI_{\mathrm{oF}} + mI_{\mathrm{mF}} + iI_{\mathrm{iF}} + nI_{\mathrm{nF}} \quad (9)$$

where p, m and o are the number of fluorine substituents *para*, *meta* or *ortho* to the protonation site, respectively, and i and $n = 0$ except for $i = 1$ for *ipso* protonation and $n = 1$ only for 1,2-difluorobenzene or 1,2,4-trifluorobenzene. (Note: if p, m, o, i and n are set to zero, Eqn (9) simply yields the proton affinity for benzene.) The results predicted by additivity are presented in Table 6 for the most favourable ring protonation site (in bold) and other ring protonation sites together with the MP2/6–31G**//HF/6–31G** calculated values. Recent proton affinity calculations[19] at the MP2(fc)6–31G**//HF6–31G* level on fluorobenzene and all three isomers of difluorobenzene are in excellent agreement with our MP2/6–31G**//HF/6–31G** calculated values. It is readily apparent that the agreement is excellent throughout except for hexafluorobenzene, for which the additivity-calculated proton affinity is ~10 kcal mol^{-1} lower than either the HPMS experimental or the MP2/6–31G**//HF/6–31G** results. This may be due to the fact that the value of the parameter I_{pF} may differ if the protonation site is both *ipso* to one fluorine substituent and *para* to another fluorine substituent. It is observed experimentally that the proton affinity for the polyfluorobenzenes generally decreases with increasing fluorine substitution.

A similar additivity scheme can also be constructed for the polymethylbenzenes to fit the revaluated proton affinities[35,37,38,40] presented in Table 7, with $I_{\mathrm{pMe}} = 7.6$, $I_{\mathrm{oMe}} = 5.3$, $I_{\mathrm{mMe}} = 2.1$ and $I_{\mathrm{iMe}} = 1.7$ kcal mol^{-1} for protonation *para*, *ortho*, *meta* or *ipso* to a methyl substituent, respectively. This scheme is in good agreement with the low-level *ab initio* isodesmic calculations of Attinà *et al.*[13] Recent calculations[19] at the MP2(fc)6–31G**//HF6–31G* level on toluene[19a] and xylenes[19b] also support the additivity assignments for the I_{pMe}, I_{oMe}, I_{mMe} and I_{iMe} parameters. The two separate proton affinity additivity schemes presented here for the polyfluorobenzenes and for the polymethylbenzenes can be combined to predict the proton affinities for the *meta* and *ortho* fluorotoluenes to within 0.5 kcal mol^{-1} of the revised experimental proton affinities,[36,37] shown in Table 7, and are also in good agreement with calculations[19] performed at the MP2(fc)6–31G**//HF6–31G* level. The proton affinity of *p*-fluorotoluene

Table 7. HPMS-determined proton affinities and protonation entropies for aromatics[a]

Reference (R)[b]	Molecule (M)	*PA* (M)[c]	*PA* (M)[d]	*PA* (M)[e]	$\Delta S^\circ_{1/2}$[f]	$\Delta S^\circ_{1/2}$[g]	M[h]
i-C_4H_8	*m*-Xylene	192.2	195.9	193.3	7.5	0.0	35
$CH_3CO_2C_2H_5$	*m*-Xylene	192.5	195.9	193.3	7.5	0.0	35
$(CH_3)_2O$	*m*-Xylene	193.7	195.9	193.3	5.0	0.0	37, 38
$(CH_3)_2O$	*o*-Xylene	190.0	193.3	189.7	9.5	2.0	37, 38
$(CH_3)_2O$	*p*-Xylene	189.2	192.0	189.1	11.0	1.5	37, 38
c-$C_3H_5COCH_3$	1,3,5-Trimethylbenzene	198.7	200.7		6.5	0.0	35
$CH_3CO_2C_2H_5$	1,3,5-Trimethylbenzene	198.5	200.7		6.5	0.0	40
$CH_3CO_2C_2H_5$	1,2,3,5-Tetramethylbenzene	200.7			5.5		40
$CH_3CO_2C_2H_5$	Pentamethylbenzene	201.9			6.5		40
$CH_3CO_2C_2H_5$	Hexamethylbenzene	204.1	207.3		8.5	1.5	40
$C_6H_5CH_3$	*m*-Fluorotoluene	187.4	189.5	188.0	2.0		36, 37
$C_6H_5CH_3$	*m*-Chlorotoluene	186.7	188.9		3.5		36, 37
$C_6H_5CH_3$	*o*-Fluorotoluene	184.6	187.0	185.1	3.5		36, 37
$C_6H_5CH_3$	*o*-Chlorotoluene	181.9	184.3		10.0		36, 37
C_6H_6	Fluorobenzene	181.3	182.6	181.6	2.0	0.0	1
C_6H_6	Fluorobenzene	181.3	182.6	181.6	2.0	0.0	9
C_6H_6	Fluorobenzene	181.3	182.6	181.6	2.0	0.0	12
C_6H_6	Fluorobenzene	181.4	182.6	181.6	2.0	0.0	10
C_6H_6	Fluorobenzene	181.2	182.6	181.6	1.5	0.0	11
C_6H_6	Chlorobenzene	181.1	181.7		2.0	1.5	9
C_6H_6	Chlorobenzene	180.7	181.7		3.0	1.5	10
$(CH_3)_2CO$	1-Methylnapthalene	196.9	200.7		6.0	0.0	11
$(C_2H_5)_2CO$	1-Methylnapthalene						11
$(CH_3)_2CO$	Naphthalene	189.7	194.7		9.5	3.0	11
$(C_2H_5)_2CO$	Indene	202.6			3.5		11
$(C_2H_5)_2CO$	Styrene	199.7	202.0		4.0	0.0	11
i-C_4H_8	Styrene	199.6	202.0		4.0	0.0	39

[a] *PA* in kcal mol^{-1} and $\Delta S^\circ_{1/2}$ in cal mol^{-1} K^{-1}.

[b] The proton affinities for the reference bases, R, have been re-evaluated according to the *PA* scale in Ref. 1.

[c] *PA* of M calculated from literature proton transfer thermochemistry between R and M and the re-evaluated data for R.

[d] Ref. 4.

[e] 0 K *PA*, Ref. 19.

[f] $\Delta S^\circ_{1/2}$ for M calculated from literature proton transfer thermochemistry between R and M and the re-evaluated data for R.

[g] Ref. 5.

[h] Proton transfer thermochemistry literature reference.

can be estimated by additivity to be 183.2 kcal mol^{-1} with protonation *ipso* to the methyl group. The 0 K proton affinity of *p*-fluorotoluene (protonated *ortho* to the fluorine substituent) has been calculated at the MP2(fc)6–31G**//HF6–31G* level[19] to be 182.5 kcal mol^{-1}. However, no calculated proton affinity was presented for protonation *ipso* to methyl in *p*-fluorotoluene.[19] This quantity is experimentally difficult or impossible to measure by HPMS.[12]

The available experimental and MP2 *ab initio*[19,20] proton affinity increments (I_{pX}) relative to benzene for substituents (X = F, CH_3, OH and NH_2) and position (p = *para*, *ortho*, *meta* and *ipso*) to the site for protonation are summarized in Table 8. In principle, the proton affinity for ring protonation on any arbitrary F, CH_3, OH or NH_2 substituted benzene can be estimated with reasonable confidence by summing all I_{pX} contributions [to Eqn (9)] from the data presented in Table 8.

Protonation entropy $\Delta S^\circ_{1/2}$

The protonation entropies, $\Delta S^\circ_{1/2}$, for the compounds studied by Szulejko and McMahon[1] are presented in Table 2. Additional data[9–12,35–40] from the literature are presented in Table 7. It is readily apparent that the protonation entropy, $\Delta S^\circ_{1/2}$, for many of the aromatics is very large and well above that expected from changes in symmetry numbers alone in the protonation process. In order to account for this phenomenon, Mason and co-workers[36,37] had introduced the concept of a dynamic proton in the protonated base for which the barrier for proton migration around the benzene ring is very low. Such a mobile proton was believed to have an appreciable internal translational entropy as the proton circulates around the ring. In earlier publications,[36,37] Mason and co-workers had suggested that $\Delta S^\circ_{1/2}$ for benzene was as large as 12–13 cal mol^{-1} K^{-1}. Evidence in support of a dynamic proton conjecture came from low-level *ab initio* calculations and super acid solution-phase NMR studies. The protonation entropy for benzene was later revised to ~4 cal mol^{-1} K^{-1} based on additional experiments[12] and thus no unusually large entropy due to dynamic proton was evident at least for benzene. The early Mason and co-workers,[36,37] $\Delta S^\circ_{1/2}$ entropy ladder is therefore questionable in view of the fact that *p*-chlorotoluene and *p*-fluorotoluene were the only compounds used to connect toluene to benzene in its construction. In addition, upon protonation, the *p*-halotoluenes are believed to isomerize[12] to the *meta* isomers. Therefore, no true proton transfer equilibrium data could have been obtained in that work. Mason and co-workers[12] therefore later recanted the dynamic proton concept.

The $\Delta S^\circ_{1/2}$ expected from rotational symmetry changes for benzene upon protonation is $R\ln 6$ (3.6 cal mol^{-1} K^{-1}) compared with a 500 K experimental value of 5.5 cal mol^{-1} K^{-1}. Almost all of the additional entropy, ~2.0 cal mol^{-1} K^{-1}, can be reasonably ascribed to a larger number of lower frequency vibrational modes being present in the protonated species over that of the neutral benzene. *Ab initio* calculations on a number of protonated aromatic species have estimated vibrational frequencies of the order of 200 cm^{-1} for a CH_2 group wagging motion.[14,16,22] Upon protonation, three additional vibrational modes are created and may have vibrational frequencies low enough to contribute significantly to the $\Delta S^\circ_{1/2}$ found experimentally. *Ab initio* vibrational frequencies are not available in the literature for the more highly substituted polyfluorobenzenes.

The puckering mode in neutral hexafluorobenzene (the lowest frequency mode present) has been calculated to be quite harmonic[41,42] up to least 3 kcal mol^{-1} above the well bottom. The theoretical vibrational frequencies, scaled by 0.89, are in excellent agreement with the experimentally determined vibrational frequencies[43–45] in the literature for neutral fluorobenzenes such as fluorobenzene,[43] difluorobenzenes[44] and hexafluorobenzene.[45] However, no experimentally determined vibrational frequencies have been obtained for the protonated fluorobenzenes. The vibrational modes can be assumed to be reasonably harmonic for both the neutral and protonated polyfluorobenzenes. Torsional modes or internal rotors are absent for both the neutral and ring protonated bases. In Table 9 are

Table 8. Experimental and MP2 *ab initio* proton affinity increments I_{pX} [a] (kcal mol^{-1}) relative to benzene for substituent type (X) and position (p) with respect to the ring protonation site

X →	F			CH_3		OH	NH_2
p[b]	Expt.[c]	MP2[d]	MP2[e]	Expt.[f]	MP2[e]	MP2[g]	MP2[h]
Para	1.5	2.0	1.5	7.5	7.5	15.5	22.5
Ortho	−1.5	−1.0	−0.5	5.5	6.0	13.0	18.0
Meta	−7.0	−7.0	−7.5	2.5	3.0	0.0	−2.5
Ipso	−9.5	−19.5	−23.0	1.0	0.0	−18.0	−17.0

[a] To the nearest 0.5 kcal mol^{-1}.

[b] Substituent position relative to the ring protonation site.

[c] Based on analysis of data presented in Table 2.

[d] Present MP2/6–31G**//HF/6–31G** calculations on fluorobenzene and *p*-, *m*- and *o*-difluorobenzenes (hexafluorobenzene excepted).

[e] MP2(fc)/6–311 + G**//HF/6–31G* calculations on toluene and *o*-, *m*- and *p*-fluorotoluenes; Ref. 19.

[f] Based on the re-evaluated experimental HPMS data presented in Table 7.

[g] MP2(fc)/6–311 + G**//HF/6–31G* calculations on phenol only; Ref. 20b.

[h] MP2(fc)/6–311 + G**//HF/6–31G* calculations on aniline and 4-methylaniline; Ref. 20a.

Table 9. Comparison of HF/6–31G and MP2/6–31G** calculated thermochemical data with experimental quantities for the polyfluorobenzenes[a]**

Species	PS[b]	Z_{pe} [c,d] HF/6–31G**	E_{MP2} [c,d] MP2/6–31G**	PA[d,e] 0 K MP2	PA[d,e] 298 K MP2	PA[f] 0 K MP2	ΔPA[e,g] 0 K MP2	ΔPA[f,g] 0 K MP2	ΔPA[h] HPMS	S°_{298} [i] 298 K HF/6–31G**	S°_{298} [j] Expt.	$\Delta S^\circ_{1/2}$ [i] 298 K HF/6–31G**	$\Delta S^\circ_{1/2}$ [k] HPMS
C_6H_5F	U	0.098 881 4	−330.514 433 9							72.4	72.3		
	1	0.110 499 7	−330.781 128 6	160.8	162.0	156.7	21.2	24.9		76.1		3.7	
	2	0.110 264 5	−330.811 054 7	179.7	180.8	179.4	2.3	2.2		76.4		4.0	
	3	0.109 384 2	−330.799 395 2	172.9	174.0	172.5	9.1	9.1		76.5		4.1	
	4	0.110 284 9	−330.814 649 2	182.0	183.1	181.6	0.0	0.0	0.0	74.9		2.5	1.5
	F	0.107 746 0	−330.761 889 8	150.3	150.9		31.7			79.0		6.6	
1,3-$C_6H_4F_2$	U	0.090 341 2	−429.523 748 0							76.4	76.6		
	1	0.101 686 5	−429.777 884 0	153.1	154.2	148.9	28.9	32.7		78.7		2.3	
	2	0.102 140 5	−429.818 568 6	178.3	179.5	178.3	3.7	3.3					
	4	0.102 218 7	−429.823 039 2	181.1	182.2	181.1	0.9	0.5	1.3	78.7		2.3	3.0
	5	0.100 525 3	−429.797 064 9	165.8	166.9	165.6	16.2	16.0		79.0		2.6	
1,2-$C_6H_4F_2$	U	0.090 386 1	−429.517 413 9							76.9	76.5		
	1	0.102 653 8	−429.787 648 0	159.7	160.9	160.0	22.3	21.6		80.8		3.9	
	3	0.101 499 8	−429.801 949 0	172.2	173.3	172.2	9.8	9.4		81.0		4.1	
	4	0.101 683 7	−429.806 624 0	175.1	176.2	175.0	6.9	6.6	5.6	80.7		3.8	2.0
1,4-$C_6H_4F_2$	U	0.090 292 7	−429.522 908 0							76.1	75.4		
	1	0.102 638 6	−429.794 632 6	163.5	164.7	160.8	18.5	20.8		80.7		4.6	
	2	0.101 519 9	−429.807 893 8	172.5	173.6	172.4	9.5	9.2	9.8	80.9		4.8	6.0
C_6F_6	U	0.056 158 8	−825.509 776 4							91.7	91.6		
	1	0.069 186 2	−825.766 810 2	153.9	155.2	153.8	28.1	27.8	27.5	99.7		8.0	9.5
	F	0.066 193 1	−825.715 586 5	123.5	124.3		58.5			99.6		7.9	

[a] PA and ΔPA in kcal mol^{-1}, ΔS° and $\Delta S^\circ_{1/2}$ in cal mol^{-1} K^{-1}.

[b] PS = protonation site: U = unprotonated base, 1, 2, 3, ... = ring protonation site and F = protonation on F.

[c] In hartree.

[d] This work.

[e] Present HF/6–31G** frequencies scaled by 0.89 in the calculation of 0 and 298 K proton affinities.

[f] Ref. 19, MP2(fc)6–31G**//HF/6–31G*, HF/6–31G* frequencies scaled by 0.89.

[g] ΔPA relative to fluorobenzene, protonated at the most favourable site (*para*).

[h] Experimental ΔPA relative to fluorobenzene, data taken from Ref. 1.

[i] Present HF/6–31G** geometries and frequencies scaled by 0.89.

[j] Ref. 44. Gas phase data.

[k] Data taken from Ref. 1 [Eqn (4)].

presented the MP2/6–31G** electronic energies, the HF/6–31G** unscaled zero point energies, the HF/6–31G** 298 K entropies and available experimental data.[46] It is readily apparent that the 298 K HF/6–31G** entropies for the neutral fluorobenzenes are in almost perfect agreement with the experimentally determined values. The theoretical $\Delta S^\circ_{1/2}$ values are in very good agreement with the HPMS results. This gives additional confidence in the HF/6–31G** results. From the available *ab initio* data, it is proposed that most of the excess protonation entropy, $\Delta S^\circ_{1/2\mathrm{xs}}$, over and above that expected from symmetry number changes for the most stable protonated species (see Tables 2 and 7) [Eqn (10)]:

$$\Delta S^\circ_{1/2\mathrm{xs}} = \Delta S^\circ_{1/2} - R\ \ln(\sigma_\mathrm{B}/\sigma_{\mathrm{BH}^+}) \qquad (10)$$

is in fact readily accounted for by the presence of additional lower frequency vibrational modes in the protonated substituted benzenes. The degree of fluxionality (or floppiness) for a protonated polysubstituted aromatic probably increases with increasing $\Delta S^\circ_{1/2\mathrm{xs}}$ (see Tables 2 and 7). Low-level calculations have estimated the barrier for H^+ migration in protonated fluorobenzene[16] to be 25 kcal mol^{-1} and that in protonated 1,2,3-trifluorobenzene[17] to be 36 kcal mol^{-1}. Calculations at the AM1 level[21a] on benzene and the polyfluorobenzenes have also estimated the barrier for proton migration to be of the order of 25–32 kcal mol^{-1} for the most stable protonated species. A G2(MP2)[22] study on benzenium has calculated a 1,2 activation barrier of 8.2 kcal mol^{-1}. These data therefore do not support the concept of a mobile proton at the temperatures and time-scales prevailing in our HPMS experiments.

It has been observed that a crude correlation exists which links an increase in the protonation entropy, $\Delta S^\circ_{1/2}$, found in the present work with an increase in the number of lower vibrational frequencies,[42–49] which in turn increases with increasing fluorine content. This argument can also be extended to correlate, qualitatively, the protonation entropy, $\Delta S^\circ_{1/2}$ (see Table 7) with the vibrational frequencies[50] for the polymethylbenzenes.

Protonation on fluorine will create one internal free rotor, analogous to the OH group in a phenol. This internal rotor can contribute up to 4.5 cal mol^{-1} K^{-1} additional entropy. However, protonation on the fluorine substituent can be entirely discounted in view of the fact that the HPMS experimentally determined proton affinities are all substantially larger than the

125–150 kcal mol^{-1} estimated for fluorine protonation from *ab initio* calculations.

It was noted at the HF/6–31G** level of theory that centre of mass rotational entropy contributed less than 0.1 cal mol^{-1} K^{-1} to $\Delta S^\circ_{1/2}$. Owing to the very small mass difference in the protonation reaction, the translational entropy contribution to $\Delta S^\circ_{1/2}$ is almost identically zero. Hence the only major contributions to the experimental $\Delta S^\circ_{1/2}$ arise from vibrational effects and symmetry considerations.

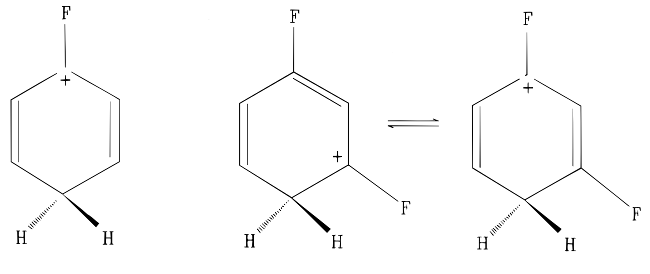
Geometry changes upon protonation

The bond lengths for the fluorobenzenes and their most stable protonated forms calculated in the present work at the HF/6–31G** level are presented in Table 10. The MNDO results for the trifluorobenzenes taken from the literature[17] are also presented. The gas-phase geometries obtained experimentally for the all neutral fluorobenzenes have been ascertained either by electron diffraction[51–54] or by microwave spectroscopy[55,56] in numerous studies. The gas-phase experimental bond lengths for fluorobenzene,[52,55,56] 1,3-difluorobenzene,[53,56] 1,2-difluorobenzene,[56] 1,4-difluorobenzene[54,56] and hexafluorobenzene[51,51] are in excellent agreement with our HF/6–31G** values. The difference between experimental[51–56] and HF/6–31G** bond lengths lies in the ranges 0.000–0.015 Å for C—C bonds, 0.004–0.009 Å for C—H bonds and 0.002–0.032 Å for C—F bonds. The experimental bond lengths are all consistently larger than the HF/6–31G** values. The MNDO bond lengths for the trifluorobenzenes[17] are in good agreement with the experimental literature, where the variation is larger at 0.02–0.05 Å for C—C and C—F bonds. Our HF/6–31G** bond lengths are in good accord with the best available experimental gas-phase data, thus increasing our confidence in the HF/6–31G** level of theory to reproduce experimentally determined parameters. The HF/6–31G** calculated bond lengths and scaled vibrational frequencies for 1,4-difluorobenzene are also in excellent agreement with a recent MP2 calculation.[57]

The present HF/6–31G** calculations have shown that, upon protonation, the polyfluorobenzenes undergo considerable geometry changes e.g. in bond lengths (see Table 10). At the HF/6–31G** level, the lowest energy structure of a protonated polyfluorobenzene has almost all the atoms remain planar except for the two substituents now present at the protonation site which lie out of the plane.

If the formal positive charge can be delocalized at carbon atoms bearing a fluorine substituent (supported by Mulliken analysis of electron density), the C—F bond length is reduced significantly, ~0.05–0.1 Å. The methylene carbon (the protonation site) bond distances to its neighbouring carbons are lengthened substantially to an essentially alkane C—C single bond length.

The protonated polyfluorobenzenes will try to adopt either of two possible HF/6–31G** calculated geometries. The most favourable (structure **I**, Fig. 3) resembles that of a generic cyclohexa-1,4-diene-3H$^+$-6F structure in which the formal positive charge can be located on C-6 bearing an F substituent and with two hydrogen substituents on C-3. If that is not possible, the other candidate (structure **II**, Fig. 3) is a tautomerization between cyclohexa-1,3-diene-6H$^+$-3,5F$_2$ and cyclohexa-1,4-diene-6H$^+$-3,5F$_2$ in which the formal positive change can be delocalized either on C-3 or C-5 that might bear a fluorine substituent and with two hydrogen substituents on C-6. The C-3—C-4 and C-4—C-5 bonds show allylic character while the C-5—C-6, C-6—C-1 and C-2—C-3 bonds are simple C—C alkane-type single bonds and the C-1—C-2 bond is essentially a alkene-type double bond. The available theoretical results have shown that for any ring protonated polyfluorobenzene, the geometry can be assigned uniquely either to structure **I** or **II**.



I II

Figure 3. Bond orders and charge site(s) in protonated polyfluorobenzenes species inferred from present Hartree–Fock calculations.

Proton transfer kinetics

The kinetic data obtained in the present study are presented in Tables 3 and 4. The proton transfer kinetics were mainly studied in detail for systems for which the equilibrium constant was large, the proton acceptor base is mainly an aromatic and the normalized pseudo-first-order decay rate constant of protonated weaker base could be monitored for 0.5 ms or more before equilibrium was established. Typical kinetic data for proton exchange behaviour for 1,2,4-trifluorobenzene and benzene are shown in Fig. 1. A few proton transfer reactions were attempted between pairs of polyfluorobenzenes of differing fluorine content in order to have additional, smaller steps in the Szulejko–McMahon proton affinity ladder.[1] It was observed, on an empirical level, that the proton transfer rate constant for reaction in the exothermic direction decreases substantially when the proton affinity difference is decreased. For example, at 600 K: (i) 1,4-$C_6H_4F_2$ and C_6H_6, $\Delta PA = 8.6$ kcal mol^{-1}, $k_f = 2.5 \times 10^{-10}$ cm^3 s^{-1}; (ii) 1,2,4-$C_6H_3F_3$ and C_6H_6, $\Delta PA = 5.2$ kcal mol^{-1}, $k_f = 9.5 \times 10^{-11}$ cm^3 s^{-1}; and (iii) 1,3,5-$C_6H_3F_3$ and C_6H_6, $\Delta PA = 1.5$ kcal mol^{-1}, $k_f = 8.4 \times 10^{-12}$ cm^3 s^{-1}. When proton transfer experiments were attempted between fluorobenzenes of differing fluorine content, very slow proton transfer kinetics were observed, for example between 1,4-$C_6H_4F_2$ and 1,2,4-$C_6H_3F_3$. In view of this observation and the general inverse temperature dependence, equilibrium proton transfer experiments of this type were not pursued further.

The experimental bimolecular rate constants were analysed using transition state theory[32] appropriate to

Table 10. Bond lengths in neutral polyfluorobenzenes and the most stable protonated polyfluorobenzene species[a]

	Bond description[b]												
Species	C-1–C-2	C-2–C-3	C-3–C-4	C-4–C-5	C-5–C-6	C-6–C-1	C-1–X	C-2–X	C-3–X	C-4–X	C-5–X	C-6–X	Comment, reference
1-C_6H_5F	1.383	1.395	1.397	—	—	—	1.354	1.081	1.083	1.080	—	—	Expt., Refs 50, 53, 54
1-C_6H_5F	1.372	1.384	1.389	—	—	—	1.329	1.075	1.075	1.075	—	—	HF, this work
1-C_6H_5F-4-H^+	1.412	1.345	1.482	—	—	—	1.277	1.073	1.076	1.093[c]	—	—	HF, this work
1,3-$C_6H_4F_2$	1.389	1.389	1.383	1.396	1.396	1.383	1.354	1.082	1.354	1.080	1.082	1.080	Expt., Refs 51, 54
1,3-$C_6H_4F_2$	1.379	1.379	1.379	1.385	1.385	1.379	1.327	1.073	1.327	1.073	1.075	1.073	HF, this work
1,3-$C_6H_4F_2$-4-H^+	1.401	1.351	1.487	1.486	1.339	1.424	1.274	1.072	1.283	1.089[c]	1.075	1.073	HF, this work
1,2-$C_6H_4F_2$	1.378	1.381	1.392	1.400	1.400	1.381	1.352	1.352	1.080	1.084	1.084	1.080	Expt., Ref. 54
1,2-$C_6H_4F_2$	1.379	1.377	1.387	1.384	1.387	1.376	1.325	1.325	1.074	1.074	1.075	1.074	HF, this work
1,2-$C_6H_4F_2$-4-H^+	1.421	1.336	1.482	1.479	1.350	1.406	1.270	1.308	1.076	1.093[c]	1.076	1.073	HF, this work
1,4-$C_6H_4F_2$	1.388	1.400	1.388	1.388	1.400	1.388	1.354	1.088	1.088	1.354	1.088	1.088	Expt., Refs 52, 54
1,4-$C_6H_4F_2$	1.390	1.396	1.390	1.390	1.396	1.390	1.357	1.085	1.085	1.357	1.085	1.085	MP2, Ref. 55
1,4-$C_6H_4F_2$	1.378	1.385	1.378	1.378	1.385	1.378	1.331	1.074	1.074	1.331	1.074	1.074	HF, this work
1,4-$C_6H_4F_2$-2-H^+	1.474	1.483	1.334	1.425	1.383	1.368	1.279	1.093[c]	1.074	1.312	1.077	1.073	HF, this work
1,3,5-$C_6H_3F_3$	1.402	1.402	1.402	1.402	1.401	1.402	1.305	1.090	1.305	1.090	1.305	1.090	Expt., Refs 50, 54
1,3,5-$C_6H_3F_3$	1.420	1.420	1.420	1.420	1.420	1.420	1.322	1.090	1.322	1.090	1.322	1.090	MNDO, Ref. 17
1,3,5-$C_6H_3F_3$-2-H^+	1.526	1.526	1.395	1.442	1.442	1.395	1.304	—[c]	1.304	—	1.298	—	MNDO, Ref. 17
1,2,4-$C_6H_3F_3$	1.375	1.381	1.383	1.383	1.397	1.381	1.354	1.354	1.083	1.354	1.085	1.083	Expt., Ref. 54
1,2,4-$C_6H_3F_3$	1.420	1.420	1.420	1.420	1.420	1.420	1.322	1.322	1.090	1.322	1.090	1.090	MNDO, Ref. 17
1,2,4-$C_6H_3F_3$-5-H^+	1.482	1.425	1.412	1.525	1.498	1.382	1.317	1.297	—	1.299	—[c]	—	MNDO, Ref. 17
1,2,4-$C_6H_3F_3$	1.375	1.381	1.383	1.383	1.397	1.381	1.354	1.354	1.083	1.354	1.085	1.083	Expt., Ref. 54
1,2,4-$C_6H_3F_3$	1.420	1.420	1.420	1.420	1.420	1.420	1.322	1.322	—	1.322	—	—	MNDO, Ref. 17
1,2,4-$C_6H_3F_3$-3-H^+	1.418	1.519	1.522	1.407	1.410	1.441	1.317	1.302	—[c]	1.301	—	—	MNDO, Ref. 17
1,2,3-$C_6H_3F_3$	1.372	1.372	1.381	1.391	1.391	1.381	1.354	1.354	1.354	1.082	1.082	1.082	Expt., Ref. 54
1,2,3-$C_6H_3F_3$	1.420	1.420	1.420	1.420	1.420	1.420	1.322	1.322	1.322	—	—	—	MNDO, Ref. 17
1,2,3-$C_6H_3F_3$-4-H^+	1.458	1.419	1.520	1.499	1.372	1.450	1.296	1.317	1.300	—[c]	—	—	MNDO, Ref. 17
C_6F_6	1.394	—	—	—	—	—	1.327	—	—	—	—	—	Expt., Refs 49, 50
C_6F_6	1.392	1.392	1.392	—	—	—	1.325	1.325	1.325	1.325	—	—	HF, this work; see also Ref. 40
C_6F_6-1-H^+	1.504	1.339	1.418	—	—	—	1.336[c]	1.275	1.301	1.260	—	—	HF. this work

[a] Symmetry redundant values are not shown.
[b] Bond lengths in Å.
[c] Two substituents, protonation site.

the fully thermalized conditions of an HPMS, to obtain both the enthalpy and entropy of activation. Two sets of derived kinetic data (from ln k *vs.* $1/T$, Eqn (7), or $\ln(k/T^2)$ *vs.* $1/T$, Eqn (8), plots) are presented in Table 3. Most of the systems studied shown an inverse temperature dependence for the rate constant in the exothermic direction and $-\Delta H^*$ is of the order of 3 kcal mol^{-1}. The exothermic proton transfer rate constants tend to approach the Langevin collision rate constant for an ion–dipole interaction ($\sim 2.0 \times 10^{-9}$ $\text{cm}^3\ \text{s}^{-1}$) at temperatures approaching 300 K at pressures of 3–10 Torr prevailing in our HPMS apparatus. No proton transfer kinetic data for any of the polyfluorobenzenes are available from low-pressure ICR ($\sim 10^{-6}$ Torr) studies. The entropy of activation, ΔS^*, is generally small (20–25 eu), in keeping with a loose association transition complex, probably a long-range ion–dipole orbiting complex which is bound by ~ 3 kcal mol^{-1}, the value of ΔH^* found experimentally (see Table 3). In a few examples, ΔS^* is larger (e.g. hexafluorobenzene and trifluoroacetonitrile, $\Delta S^* = 35$ cal mol^{-1} K^{-1}), suggesting a more ordered or rigid transition complex on the lines of a weakly proton-bound complex of the two bases.

In Table 3, the 300 and 600 K rate constants, interpolated from the Arrhenius plots, are displayed. For most systems for which data are available, the rate constant generally varies by an order of magnitude from 300 to 600 K. For the hexafluorobenzene–trifluoroacetonitrile pair, the proton transfer rates varied by three orders of magnitude, in contrast to the H_2S–benzene pair, in which no significant change in the essentially Langevin collision rate constant of 1.5×10^{-9} $\text{cm}^3\ \text{s}^{-1}$ is experimentally observable.

CONCLUSIONS

With the aid of *ab initio* MP2/6–31G**//HF/6–31G** calculations, the variation of the HPMS experimental proton affinities with the degree of fluorine substitution and relative positions in fluorobenzenes can be rationalized in terms of a simple additivity scheme. For most polyfluorobenzenes, the agreement between the HPMS experimental proton affinities and those predicted by additivity is excellent, to within 1 kcal mol^{-1}. A similar additivity scheme can also be constructed for the re-evaluated proton affinities for the polymethylbenzenes, accurate to within 1 kcal mol^{-1}. An almost identical additivity scheme is also presented in Ref. 19b, in excellent agreement with the present analysis.

These two additivity schemes can be combined to estimate proton affinities for the *o*- and *m*-fluorotoluenes again, to within 1 kcal mol^{-1} of the revised literature values presented here. The agreement between the revised experimental and additivity calculated proton affinities with other recent *ab initio*[19,20] MP2 calculations in the literature (for benzene, toluene, xylenes, fluorobenzene, polyfluorobenzenes and fluorotoluenes) is excellent throughout. The additivity schemes presented here can be used to estimate proton affinity for *p*-fluorotoluene, which is impossible to measure by HPMS. Protonated *p*-fluorotoluene is believed to isomerize to protonated *m*-fluorotoluene by a facile 1,2-methyl shift.[12]

Recent *ab initio* MP2 calculations[19,20] in the literature on phenol, aniline and pyridine have calculated the proton affinity for substituent and ring sites available for protonation. It should be possible, in principle, to estimate a ring site proton affinity for any combination of methyl, fluoro, hydroxy and amino substitution in benzene to within 1 kcal mol^{-1} of an experimental value. This may be an area for further HPMS experimental and *ab initio* studies to explore the nuances in greater detail.

Many of the polyfluorobenzenes upon protonation exhibit large $\Delta S^\circ_{1/2}$ values, well in excess of those expected from symmetry number changes alone. For example, hexafluorobenzene has an experimental $\Delta S^\circ_{1/2}$ of 9.5 cal mol^{-1} K^{-1}, compared with 5.0 cal mol^{-1} K^{-1} due to symmetry alone. From our *ab initio* study on the hexafluorobenzene system with the aid of statistical thermodynamics, almost all of the excess entropy is in fact readily ascribed to vibrational entropy. Protonation leads to a greater number of lower vibrational frequencies in the range which contribute significantly to the entropy. The theoretically calculated barriers[16,17,21a,22] for a 1,2 proton shift from the thermodynamically most favourable protonation site in benzene and the polyfluorobenzenes are of the order of 8–30 kcal mol^{-1}. It can therefore be concluded from theoretical considerations that the concept of a dynamic proton can be discounted with relative certainty at least for protonated polyfluorobenzenes in thermal equilibrium up to 650 K. From examination of the available literature on aromatic protonations, large protonation entropies ($\Delta S^\circ_{1/2}$) appear to be a fairly general phenomenon.

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