Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information:

A theoretical analysis of atomic charge fluxes in chlorofluoromethanes and relations with bonding character descriptors

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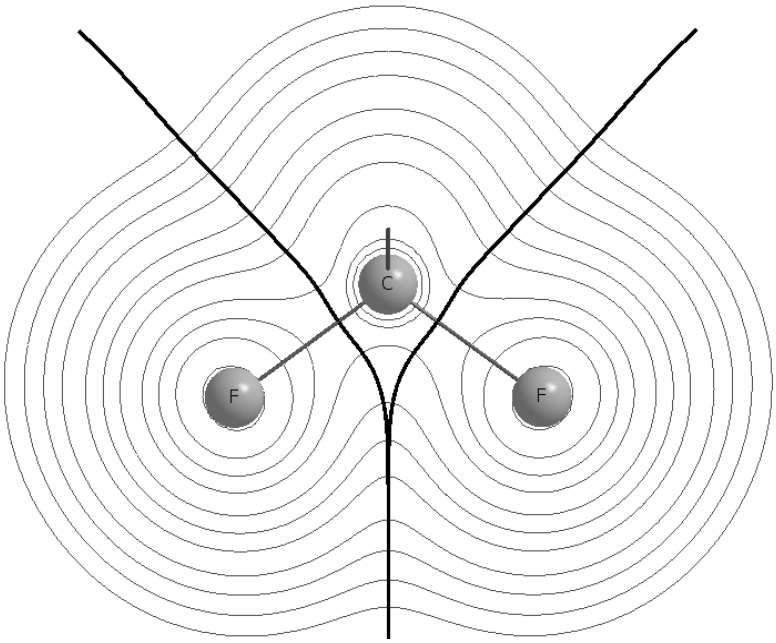

Figure S1 – Contour diagram of the electron density over the FCF plane in the CH_2F_2 molecule. The bifurcated bold line shows the interatomic surface intersection.

Table S1 – QTAIM atomic charges (*e*) in chlorofluoromethanes obtained at the CCSD/cc-pVQZ level.

Molecules	C	H	Cl	F
CH_4	0.109	-0.027	-	-
CH_3Cl	0.229	0.022	-0.295	-
CH_2Cl_2	0.336	0.067	-0.235	-
$CHCl_3$	0.431	0.108	-0.180	-
CCl_4	0.516	-	-0.129	-
CH_3F	0.718	-0.004	-	-0.705
CH_2F_2	1.363	0.028	-	-0.709
CHF_3	2.057	0.074	-	-0.710
CF_4	2.813	-	-	-0.703
$CClF_3$	2.244	-	-0.144	-0.700
CCl_2F_2	1.676	-	-0.141	-0.696
CCl_3F	1.098	-	-0.135	-0.692
CH_2ClF	0.859	0.049	-0.257	-0.701
$CHCl_2F$	0.987	0.096	-0.193	-0.697
$CHClF_2$	1.534	0.084	-0.210	-0.704

Table S2 – Geometry data obtained after optimization at the CCSD/cc-pVQZ level.

Molecules	Bond length (Å)						Bond angles (degree)							
CH_4	C-H	1.0864					∟HCH	109.47						
CH_3F	C-H	1.0872	C-F	1.3770			∟HCF	108.95	∟HCH	109.99				
CH_2F_2	C-H	1.0867	C-F	1.3489			∟HCF	108.80	∟HCH	113.07	∟FCF	108.47		
CHF_3	C-H	1.0849	C-F	1.3267			∟HCF	110.43			∟FCF	108.50		
CH_3Cl	C-H	1.0833	C-Cl	1.7802			∟HCCl	108.47	∟HCH	110.45				
CH_2Cl_2	C-H	1.0809	C-Cl	1.7666			∟HCCl	108.22	∟HCH	111.57	∟ClCCl	112.42		
CH_2ClF	C-H	1.0836	C-Cl	1.7670	C-F	1.3543	∟HCCl	107.91	∟HCH	112.30	∟ClCF	110.22	∟HCF	109.23
$CHClF_2$	C-H	1.0837	C-Cl	1.7598	C-F	1.3318	∟HCCl	109.28	∟FCF	108.17	∟ClCF	109.70	∟HCF	109.99
$CHFCl_2$	C-H	1.0817	C-Cl	1.7592	C-F	1.3397	∟HCCl	108.51	∟ClCCl	111.49	∟ClCF	109.34	∟HCF	109.61
$CHCl_3$	C-H	1.0796	C-Cl	1.7615			∟HCCl	107.89			∟ClCCl	111.01		
$CFCl_3$	C-Cl	1.7600	C-F	1.3312			∟ClCCl	110.44			∟ClCF	108.48		
$CClF_3$	C-F	1.3174	C-Cl	1.7516			∟FCF	108.66			∟ClCF	110.27		
CF_4	C-F	1.3122					∟FCF	109.47						
CCl_4	C-Cl	1.7645					∟ClCCl	109.47						

Table S3 – Atomic dipole moment components (e Å) of the A atoms in chloro- and fluoromethane molecules from CCSD/cc-pVQZ calculations.

Mol.	A	x	y	z	$\|m\|$	Mol.	A	x	y	z	$\|m\|$
CH_3Cl	C	0.108	-0.000	-0.036	0.114	CH_3F	C	0.334	0.000	-0.114	0.353
	H*	0.010	0.000	-0.065	0.066		H*	0.006	0.000	-0.064	0.065
	Cl	-0.058	0.000	0.019	0.061		F	0.140	0.000	-0.048	0.148
	H	0.038	-0.050	0.018	0.066		H	0.034	-0.051	0.019	0.065
	H	0.038	0.050	0.018	0.066		H	0.034	0.051	0.019	0.065
CH_2Cl_2	C	0.054	0.096	-0.075	0.133	CH_2F_2	C	0.190	0.317	-0.244	0.443
	H*	0.005	0.008	-0.064	0.065		H*	0.003	0.005	-0.063	0.063
	Cl	-0.058	0.020	0.007	0.061		F	0.165	0.008	-0.061	0.176
	Cl	0.048	-0.038	0.007	0.061		F	-0.070	0.150	-0.061	0.176
	H	0.031	0.055	0.014	0.065		H	0.031	0.051	0.019	0.063
$CHCl_3$	C	-0.000	-0.001	-0.113	0.113	CHF_3	C	-0.000	-0.000	-0.428	0.428
	H*	0.000	0.000	-0.065	0.065		H*	0.000	0.000	-0.062	0.062
	Cl	-0.067	0.000	-0.001	0.067		F	0.185	0.000	-0.079	0.201
	Cl	0.034	-0.058	-0.001	0.067		F	-0.092	0.160	-0.079	0.201
	Cl	0.034	0.058	-0.001	0.067		F	-0.092	-0.160	-0.079	0.201

* The asterisk indicates the atom that is placed at the positive end of the z axis.

Table S4 - Atomic dipole moment components (e Å) of the *A* atoms in chlorofluoromethane molecules from CCSD/cc-pVQZ calculations.

Mol.	*A*	*x*	*y*	*z*	|*m*|	Mol.	*A*	*x*	*y*	*z*	|*m*|
CCl_4	C	-0.001	0.000	-0.001	0.002	CH_4	C	0.000	0.000	0.000	0.000
	Cl*	0.000	0.000	-0.077	0.077		H*	0.000	0.000	-0.068	0.068
	Cl	-0.073	0.000	0.026	0.077		H	-0.064	0.000	0.023	0.068
	Cl	0.036	-0.063	0.026	0.077		H	0.032	-0.056	0.023	0.068
	Cl	0.036	0.063	0.026	0.077		H	0.032	0.056	0.023	0.068
CCl_3F	C	0.000	-0.001	0.343	0.343	CH_2ClF	C	-0.068	0.323	-0.168	0.371
	F*	0.000	0.000	0.207	0.207		H*	0.007	0.005	-0.064	0.064
	Cl	-0.062	0.000	0.019	0.065		Cl	-0.042	0.020	0.002	0.046
	Cl	0.031	-0.054	0.019	0.065		F	-0.080	0.143	-0.058	0.174
	Cl	0.031	0.054	0.019	0.065		H	0.033	0.052	0.017	0.064
CCl_2F_2	C	-0.150	-0.273	0.228	0.386	$CHClF_2$	C	-0.276	0.000	-0.332	0.432
	F*	-0.004	-0.007	0.212	0.212		H*	0.004	0.000	-0.064	0.064
	Cl	-0.051	0.002	0.017	0.054		Cl	-0.038	0.000	-0.010	0.040
	Cl	0.029	-0.042	0.017	0.054		F	-0.010	0.156	-0.073	0.199
	F	-0.098	-0.179	-0.058	0.212		F	-0.010	-0.156	-0.073	0.199
$CClF_3$	C	0.000	0.000	-0.324	0.324	$CHCl_2$ F	C	0.289	0.000	-0226	0.367
	Cl*	0.000	0.000	-0.044	0.044		H*	-0.004	0.000	-0.065	0.065
	F	0.200	0.000	-0.082	0.222		F	0.181	0.000	-0.066	0.193
	F	-0.010	0.173	-0.082	0.222		Cl	0.024	-0.47	-0.006	0.053
	F	-0.010	-0.173	-0.082	0.222		Cl	0.024	0.047	-0.006	0.053
CF_4	C	0.000	0.000	0.000	0.001						
	F*	0.000	0.000	0.219	0.219						
	F	0.206	0.000	-0.073	0.219						
	F	-0.103	0.179	-0.073	0.219						
	F	-0.103	-0.179	-0.073	0.219						

* The asterisk indicates the atom that is placed at the positive end of the z axis.

Table S5 – Delocalization index (%) in terminal atoms (H, Cl and F) of chlorofluoromethanes given by CCSD/cc-pVQZ calculations.

Molecules	H	Cl	F
CH_4	46.5	-	-
CH_3Cl	47.9	30.5	-
CH_2Cl_2	49.6	32.5	-
$CHCl_3$	51.3	34.5	-
CCl_4	-	36.3	-
CH_3F	46.2	-	44.2
CH_2F_2	46.7	-	45.7
CHF_3	48.4	-	46.4
CF_4	-	-	46.9
$CClF_3$	-	32.9	49.0
CCl_2F_2	-	34.0	50.9
CCl_3F	-	35.1	52.8
CH_2ClF	48.2	31.4	47.1
$CHCl_2F$	50.3	33.3	50.0
$CHClF_2$	49.2	32.1	48.2

Table S6 – Total absolute atomic dipole flux (*e*) of the *A* atoms in chloro- and fluoromethane molecules during the stretching of C-X bond, X=(Cl, F, H), from CCSD/cc-pVQZ calculations.

Mol.		X		Mol.		X	
	A	Cl	H		*A*	F	H
CH_3Cl	C	-0.306	0.201	CH_3F	C	-0.528	0.246
	H*	-0.007	-0.051		H*	-0.013	-0.048
	Cl*	-0.326	0.012		F*	-0.176	0.048
	H	-0.007	0.004		H	-0.013	0.004
	H	-0.007	0.004		H	-0.013	0.004
CH_2Cl_2	C	-0.156	0.327	CH_2F_2	C	-0.166	0.379
	H*	-0.003	-0.058		H*	-0.009	-0.057
	Cl	-0.018	0.013		F	0.101	0.052
	Cl*	-0.274	0.013		F*	-0.223	0.052
	H	-0.003	0.004		H	-0.009	0.004
$CHCl_3$	C	-0.066	0.520	CHF_3	C	0.012	0.496
	H*	-0.001	-0.070		H	-0.005	-0.068
	Cl	-0.016	0.016		F	0.108	0.043
	Cl	-0.016	0.016		F	0.108	0.044
	Cl*	-0.268	0.016		F*	-0.266	0.043

* The asterisk indicates the X atoms displaced to obtain the dipole flux values.

Table S7 - Absolute atomic dipole flux (*e*) of the *A* atoms in chloro- and fluoromethane molecules during the stretching of C-X bond, X=(Cl, F, H), from CCSD/cc-pVQZ calculations.

Mol.	*A*	X		Mol.	*A*	X		
		Cl	F			Cl	F	H
CCl_4	C	0.084	-	CH_4	C	-	-	-0.011
	Cl*	-0.282	-		H*	-	-	-0.049
	Cl	-0.015	-		H	-	-	0.003
	Cl	-0.015	-		H	-	-	0.003
	Cl	-0.015	-		H	-	-	0.003
CCl_3F	C	0.149	-0.681	CH_2ClF	C	0.086	-0.530	0.302
	F*	0.074	-0.455		H*	-0.006	-0.008	-0.056
	Cl*	-0.287	0.028		Cl*	-0.258	0.036	0.011
	Cl	-0.014	0.028		F*	0.084	-0.259	0.046
	Cl	-0.014	0.029		H	-0.006	-0.008	0.003
CCl_2F_2	C	0.178	-0.221	$CHClF_2$	C	0.181	-0.186	0.426
	F*	0.074	-0.415		H*	-0.005	-0.006	-0.066
	Cl*	-0.296	0.027		Cl*	-0.244	0.034	0.009
	Cl	-0.009	0.027		F	0.083	0.098	0.044
	F	0.074	0.095		F*	0.083	-0.310	0.044
$CClF_3$	C	0.156	0.019	$CHCl_2F$	C	0.123	-0.558	0.359
	Cl*	-0.311	0.031		H*	-0.003	-0.005	-0.066
	F*	0.072	-0.368		F*	0.079	-0.349	0.043
	F	0.072	0.100		Cl	-0.016	0.032	0.014
	F	0.072	0.100		Cl*	-0.259	0.032	0.014
CF_4	C	-	-0.011					
	F*	-	0.321					
	F	-	0.102					
	F	-	0.102					
	F	-	0.102					

* The asterisk indicates the X atoms displaced to obtain the dipole flux values.