pKa Prediction of Per- and Polyfluoroalkyl Acids in Water Using *in silico* Gas Phase Stretching Vibrational Frequencies and Infrared Intensities

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Supporting Information I

Summary (33 Pages, 16 Tables, 9 Figures)

Table S1. pKa, COO^- antisymmetric stretching vibrational frequency of the carboxylate anion ($\boldsymbol{\nu_{COO^-}}$), OH stretching vibrational frequency ($\boldsymbol{\nu_{OH}}$), and corresponding infrared intensities (IR_{Int}) of the carboxylic acids in the training and validation sets. Experimental pKa taken from refs.[1–5]

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	$IR_{Int,\ COO^-}$	ν_{OH} (cm^{-1})	$IR_{Int,\ OH}$
1	4-Methoxybenzoic acid	100-09-4	4.49	1725.540	535.207	3825.220	125.920
2	Butanoic acid	107-92-6	4.82	1698.870	677.088	3816.470	85.466
3	4-Mercaptobenzoic acid	1074-36-8	4.06	1731.060	523.864	3821.760	135.108
4	Pentanoic acid	109-52-4	4.70	1700.975	675.924	3814.880	86.504
5	2-Formylbenzoic acid	119-67-5	4.50	1727.260	509.019	3818.750	136.419
6	3-Nitrobenzoic acid	121-92-6	3.50	1746.420	543.677	3813.280	139.378
7	4-Sulfamoylbenzoic acid	138-41-0	3.63	1743.100	505.714	3816.740	140.795
8	4-Aminobenzoic acid	150-13-0	4.78	1723.290	529.236	3826.260	123.626
9	4-(Methoxycarbonyl)benzoic acid	1679-64-7	3.74	1734.710	527.406	3819.280	135.401
10	3-Cyanobenzoic acid	1877-72-1	3.59	1743.890	511.953	3813.317	139.267
11	2-(Methylsulfinyl)benzoic acid	19093-34-6	3.10	1733.750	620.913	3818.018	139.417
12	4-(Methylsulfinyl)benzoic acid	33963-58-5	3.66	1737.560	511.256	3820.499	137.879
13	Cyanoacetic acid	372-09-8	2.46	1764.450	669.177	3812.438	116.332
14	3-Phenoxybenzoic acid	3739-38-6	3.95	1735.480	482.105	3825.839	134.917
15	2-Cyanobenzoic acid	3839-22-3	3.10	1750.110	518.735	3818.643	137.633
16	2,6-Difluorobenzoic acid	385-00-2	2.24	1762.520	684.898	3808.246	119.980
17	4-(Methylsulfonyl)benzoic acid	4052-30-6	3.48	1742.530	505.246	3817.414	142.488
18	3-Trifluoromethylbenzoic acid	454-92-2	3.75	1739.150	526.043	3821.812	132.801
19	3-Fluorobenzoic acid	455-38-9	3.88	1734.250	478.415	3816.155	126.967
20	4-Fluorobenzoic acid	456-22-4	4.16	1731.500	531.588	3819.982	125.734
21	3-Mercaptobenzoic acid	4869-59-4	3.96	1733.790	477.348	3823.832	129.319
22	3,5-Dimethylbenzoic acid	499-06-9	4.30	1726.920	431.772	3822.139	121.807
23	2,6-Dichlorobenzoic acid	50-30-6	1.59	1762.240	582.985	3793.861	114.113
24	3,4-Dichlorobenzoic acid	51-44-5	3.64	1741.390	491.734	3822.266	141.768
25	3-(Methylsulfonyl)benzoic acid	5345-27-7	3.53	1743.310	502.950	3817.838	137.758
26	3-Chlorobenzoic acid	535-80-8	3.84	1736.220	482.623	3820.363	131.418
27	2-Nitrobenzoic acid	552-16-9	2.17	1759.530	557.358	3806.788	129.746

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	IR$_{Int, COO^-}$	ν_{OH} (cm^{-1})	IR$_{Int, OH}$
28	4-Acetamidobenzoic acid	556-08-1	4.30	1729.460	520.875	3825.082	133.365
29	2-Acetylbenzoic acid	577-56-0	4.13	1728.150	608.074	3820.802	132.355
30	3-Bromobenzoic acid	585-76-2	3.86	1737.310	476.151	3822.121	133.182
31	3-Methoxybenzoic acid	586-38-9	4.12	1729.530	458.468	3825.448	124.279
32	3-Acetylbenzoic acid	586-42-5	3.86	1739.640	495.870	3818.959	130.933
33	4-Bromobenzoic acid	586-76-5	3.99	1734.840	522.175	3819.100	136.863
34	4-Acetylbenzoic acid	586-89-0	3.74	1735.490	531.834	3818.934	134.735
35	3-Acetamidobenzoic acid	587-48-4	4.06	1734.660	405.374	3822.249	125.350
36	2,3-Dibromopropanoic acid	600-05-5	2.36	1764.700	552.026	3808.293	118.791
37	2,6-Dibromobenzoic acid	601-84-3	1.51	1764.200	536.927	3793.810	116.142
38	2,6-Dinitrobenzoic acid	603-12-3	1.14	1794.620	522.324	3798.416	148.067
39	3,4-Dimethylbenzoic acid	619-04-5	4.40	1725.570	485.165	3826.697	124.725
40	4-Cyanobenzoic acid	619-65-8	3.50	1741.330	517.545	3816.336	142.534
41	4-Formylbenzoic acid	619-66-9	3.72	1736.440	518.745	3818.820	135.908
42	4-Nitrobenzoic acid	62-23-7	3.40	1743.060	458.221	3815.353	141.284
43	3-Sulfamoylbenzoic acid	636-76-0	3.68	1744.060	502.666	3821.600	137.287
44	Acetic acid	64-19-7	4.75	1693.520	715.286	3810.595	83.581
45	Benzoic acid	65-85-0	4.21	1727.660	511.177	3823.486	121.396
46	4-Chlorobenzoic acid	74-11-3	4.00	1733.840	524.553	3819.461	133.740
47	Propanoic acid	79-09-4	4.88	1698.459	672.894	3817.262	84.442
48	Chloroacetic acid	79-11-8	2.85	1751.140	590.810	3800.521	105.541
49	Hydroxyacetic acid	79-14-1	3.85	1729.140	568.972	3805.455	95.899
50	Isobutanoic acid	79-31-2	4.88	1698.180	620.268	3814.507	86.463
51	Dichloroacetic acid	79-43-6	1.34	1783.480	571.417	3815.883	127.043
52	2,6-Diisopropoxybenzoic acid	92035-95-5	3.60	1723.890	756.310	3805.215	86.268
53	2,6-Dipropoxybenzoic acid	82560-07-4	3.55	1720.950	806.837	3806.423	96.080
54	2,6-Diethoxybenzoic acid	82935-36-2	3.50	1739.210	647.939	3802.388	91.667
55	3-Nitro-4-chlorobenzoic acid	96-99-1	3.29	1749.790	549.630	3821.319	149.880
56	4-*tert*Butylbenzoic acid	98-73-7	4.36	1727.500	515.998	3822.643	129.293
57	3-Methylbenzoic acid	99-04-7	4.27	1727.510	470.673	3820.823	122.338
58	3,5-Dinitrobenzoic acid	99-34-3	2.67	1761.910	551.318	3809.704	156.852

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	$IR_{Int,\ COO^-}$	ν_{OH} (cm^{-1})	$IR_{Int,\ OH}$
59	4-Methylbenzoic acid	99-94-5	4.35	1726.040	517.723	3821.769	124.255
60	2-(Methylsulfonyl)benzoic acid	33963-55-2	2.53	1747.130	601.045		
61	2-(Methoxycarbonyl)benzoic acid	4376-18-5	3.18	1732.670	613.529		
62	3-Hydroxybenzoic acid	99-06-9	4.09	1730.200	455.846		
63	4-Hydroxybenzoic acid	99-96-7	4.59	1726.410	527.111		
64	Fluoroacetic acid	144-49-0	2.70	1740.495	716.395		
65	Difluoroacetic acid	381-73-7	1.20	1767.563	691.577		
66	Trifluoroacetic acid	76-05-1	0.30	1797.866	724.337		
67	Trifluoropropanoic acid	2516-99-6	3.00	1749.642	736.452		
68	Trifluorobutanoic acid	406-93-9	4.20	1716.672	681.725		
69	Chlorodifluoroacetic acid	76-04-0	0.46	1812.904	666.725		
70	Tribromoacetic acid	75-96-7	-0.15	1845.749	423.285		
71	Trichloroacetic acid	76-03-9	0.52	1834.880	505.802		
72	Nitroacetic acid	625-75-2	1.68	1785.875	659.415		
73	2-Propynoic acid	471-25-0	1.89	1746.140	732.528		
74	Trichloroacrylic acid	2257-35-4	1.15	1786.313	586.936		
75	Trifluoroacrylic acid	433-68-1	1.79	1767.024	654.667		
76	2,2-Dichloropropanoic acid	75-99-0	2.06	1784.726	543.734		
77	2,3-Dichloropropanoic acid	565-64-0	2.85	1755.213	637.526		
78	Acetoacetic acid (18°C)	541-50-4	3.58	1733.803	717.853		
79	2-Propenoic acid	79-10-7	4.26	1724.980	302.868		
80	Hexanoic acid	142-62-1	4.80	1701.293	677.185		
81	Heptanoic acid	111-14-8	4.89	1701.766	678.849		
82	Octanoic acid	124-07-2	4.89	1701.616	679.257		
83	Formic acid	64-18-6	3.75	1711.065	887.385		
84	Oxoacetic acid	298-12-4	3.30	1758.054	517.175		
85	Nonanoic acid	112-05-0	4.95	1704.944	672.147		
86	4,4,5,5,6,6,6-Heptafluorohexanoic acid	356-02-5	4.18	1725.355	667.823		
87	4,4,5,5,6,6,6-Heptafluoro-2-hexenoic acid	356-03-6	3.23	1749.117	247.818		
88	Chloropropynoic acid	6795-92-2	1.85	1759.419	712.839		
89	2-Cyano-2-methylpropanoic acid	22426-30-8	2.42	1755.172	577.561		

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	IR$_{Int, COO^-}$	ν_{OH} (cm^{-1})	IR$_{Int, OH}$
90	Bromoacetic acid	79-08-3	2.90	1755.679	563.604		
91	2-Chlorobutanoic acid	4170-24-5	2.83	1749.363	545.276		
92	3-Chlorobutanoic acid	1951-12-8	3.98	1728.453	650.992		
93	4-Chlorobutanoic acid	627-00-9	4.52	1715.011	662.694		
94	3-Butenoic acid	625-38-7	4.35	1723.107	651.853		
95	2,2-Dimethylpropanoic acid	75-98-9	5.03	1707.704	583.468		
96	3-Methylbutanoic acid	503-74-2	4.77	1707.210	655.495		
97	2-Methylbutanoic acid	116-53-0	4.80	1704.913	594.637		
98	2-Butynoic acid	590-93-2	2.62	1739.104	721.221		
99	2-Chloropropanoic acid	598-78-7	2.83	1748.586	550.720		
100	3-Bromopropanoic acid	590-92-1	4.00	1723.134	698.802		
101	3-Chloropropionic acid	107-94-8	3.98	1719.481	699.982		
102	*trans*-Crotonic acid	107-93-7	4.69	1753.046	89.929		
103	Oxalic acid	144-62-7	1.25	1791.131	455.327		
104	Nitroacetic acid	625-75-2	1.48	1792.765	652.040		
105	Malonic acid	141-82-2	2.87	1752.899	688.948		
106	Methoxyacetic acid	625-45-6	3.57	1737.465	674.446		
107	2-Hydroxypropanoic acid	79-33-4	3.83	1730.063	513.749		
108	3-Hydroxypropanoic acid	503-66-2	4.49	1711.763	563.296		
109	Bromopropiolic acid	16900-53-1	1.86	1762.080	706.187		
110	*trans*-3-Chloroacrylic acid	2345-61-1	3.79	1733.670	593.196		
111	*cis*-3-Chloroacrylic acid	1609-93-4	3.45	1736.145	641.959		
112	*cis*-3-bromoacrylic acid	1609-92-3	3.32	1739.600	629.070		
113	*trans*-3-bromoacrylic acid	6213-89-4	3.71	1735.813	599.966		
114	2-bromopropanoic acid	598-72-1	3.01	1753.867	513.501		
115	Oxaloacetic acid	328-42-7	2.22	1780.898	470.621		
116	Methylthioacetic acid	2444-37-3	3.66	1729.370	613.226		
117	2-Mercaptopropanoic acid	79-42-5	3.65	1729.940	560.032		
118	3-Mercaptopropanoic acid	107-96-0	4.38	1716.115	674.655		
119	2,3-dimercaptopropanoic acid	6220-25-3	3.45	1731.643	487.477		
120	Trifluoromethylthioacetic acid	2408-17-5	2.95	1742.855	629.925		

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	$IR_{Int,\ COO^-}$	ν_{OH} (cm^{-1})	$IR_{Int,\ OH}$
121	3-Butynoic acid	2345-51-9	3.32	1750.665	644.851		
122	2-Methyl-2-propenoic acid	79-41-4	4.65	1703.830	493.825		
123	Tartaric acid	526-83-0	3.03	1763.088	491.548		
124	Ethoxyacetic acid	627-03-2	3.84	1733.715	665.231		
125	3-Chloro-2-Butenoic acid	55831-56-6	4.10	1747.616	334.901		
126	2-Chloro-3-butenoic acid	24253-33-6	2.55	1758.853	596.694		
127	4-Sulfobutanoic acid	62605-67-8	4.91	1681.934	652.773		
128	2-Furoic acid	88-14-2	3.20	1747.162	600.836		
129	2-Pentynoic acid	5963-77-9	2.61	1744.361	701.637		
130	3-Pentynoic acid	36781-65-4	3.59	1739.857	651.530		
131	4-Pentynoic acid	6089-09-4	4.20	1714.745	668.745		
132	*trans*-2-pentenoic acid	13991-37-2	4.74	1699.769	493.728		
133	Glutaric acid	110-94-1	4.35	1715.687	654.432		
134	2-Thiophenecarboxylic acid	527-72-0	3.50	1736.430	530.917		
135	4,4-Dinitropentanoic acid	5029-31-2	3.98	1729.220	697.332		
136	4-Chloropentanoic acid	32607-54-8	4.40	1714.401	653.831		
137	5-Sulfopentanoic acid	89211-38-1	5.04	1683.948	667.169		
138	2,5-Furandicarboxylic acid	3238-40-2	2.60	1765.141	456.593		
139	2-Hexen-4-ynoic acid		4.20	1727.700	520.262		
140	4-Hexen-2-ynoic acid	129223-16-1	2.67	1750.981	684.596		
141	5-Hexen-3-ynoic acid		3.39	1750.383	626.125		
142	5-Hexynoic acid	53293-00-8	4.59	1710.695	658.957		
143	*trans*-2-hexenoic acid	13419-69-7	4.75	1703.657	511.575		
144	*cis*-2-hexenoic acid	1577-28-2	4.63	1691.416	518.553		
145	5-oxohexanoic acid	3128-06-1	4.80	1709.688	709.158		
146	2,2-dimethylbutanoic acid	595-37-9	4.93	1708.425	549.167		
147	2-Methylpentanoic acid	97-61-0	4.78	1705.227	607.889		
148	3-methylpentanoic acid	105-43-1	4.77	1706.375	661.032		
149	2-Cyano-3-methylbutanoic acid	22426-27-3	2.40	1759.268	589.135		
150	5-Chlorohexanoic acid	112176-22-4	4.60	1714.228	668.984		
151	2-Heptynoic acid	1483-67-6	2.60	1744.669	697.465		

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	$IR_{Int,\ COO^-}$	ν_{OH} (cm^{-1})	$IR_{Int,\ OH}$
152	6-Heptynoic acid	30964-00-2	4.57	1709.924	667.616		
153	*trans*-2-heptenoic acid	18999-28-5	4.88	1704.368	491.707		
154	*cis*-2-methyl-2-hexenoic acid		4.44	1700.290	634.148		
155	*trans*-2-methyl-2-hexenoic acid	28897-58-7	5.13	1706.415	543.982		
156	Heptanedioic acid	111-16-0	4.50	1707.787	668.014		
157	3,3-dimethylpentanedioic acid	4839-46-7	3.73	1707.905	620.097		
158	2,2-dimethylpentanoic acid	1185-39-3	4.97	1706.820	544.086		
159	4,4-dinitroheptanedioic acid	5029-40-3	3.52	1734.428	529.004		
160	Phenylacetic acid	103-82-2	4.30	1734.241	632.535		
161	Phenoxyacetic acid	122-59-8	3.16	1750.823	647.301		
162	Octanedioic acid	505-48-6	4.52	1706.316	669.994		
163	3-propylpentanedioic acid	4165-98-4	4.32	1709.515	701.716		
164	2,4-Dichlorophenoxyacetic acid	94-75-7	2.90	1763.669	643.113		
165	2,6-Dichlorophenoxyacetic acid	575-90-6	3.30	1759.749	640.642		
166	4-nitrophenoxyacetic acid	1798-11-4	2.81	1763.285	645.227		
167	Phenylsulfonylacetic acid	3959-23-7	2.51	1779.272	601.620		
168	3-Phenylpropynoic acid	637-44-5	2.23	1760.779	656.143		
169	2,4-Nonadiynoic acid	80220-96-8	1.89	1763.555	672.215		

Table S2. Individual QSARs developed for $\boldsymbol{v_{OH}}$ and $\boldsymbol{v_{COO^-}}$

QSAR	$\boldsymbol{a}$	$\boldsymbol{c}$
$\boldsymbol{pKa = av_{OH} + c}$	(7.47 ± 1.10) x 10^{-2}	(-2.81 ± 0.41) x 10^{2}
$\boldsymbol{pKa = av_{COO^-} + c}$	(-4.25 ± 0.25) x 10^{-2}	(7.74 ± 0.44) x 10^{1}

Table S3. QSARs developed with $\boldsymbol{v_{OH}}$ and $\boldsymbol{v_{COO^-}}$ and their corresponding IR_{Int}

QSAR	$\boldsymbol{a}$	$\boldsymbol{b}$	$\boldsymbol{c}$
$\boldsymbol{pKa = av_{OH} + bIR_{Int} + c}$	(9.72 ± 0.82) x 10^{-2}	(-2.77 ± 0.36) x 10^{-2}	(-3.64 ± 0.31) x 10^{2}
$\boldsymbol{pKa = av_{COO^-} + bIR_{Int} + c}$	(-4.58 ± 0.18) x 10^{-2}	(-3.34 ± 0.43) x 10^{-3}	(8.50 ± 0.32) x 10^{1}

Table S4. Symmetric ($\boldsymbol{\nu_{COO^-,sym}}$) and antisymmetric ($\boldsymbol{\nu_{COO^-}}$) COO^- stretching vibrational frequencies and corresponding infrared intensities calculated using different functionals and basis sets for the first 59 carboxylic acids listed in Table S1.

	M06-2X/ aug-cc-pVDZ		***M06-2X/6-311++G(2d,2p)***		***B3LYP/Def2TZVP***		***ωB97X-D/cc-pVTZ***	
#	**$\nu_{COO^-,\,sym}$ (cm^{-1})**	**$IR_{Int,\,COO^-\,sym}$**	**ν_{COO^-} (cm^{-1})**	**$IR_{Int,\,COO^-}$**	**ν_{COO^-} (cm^{-1})**	**$IR_{Int,\,COO^-}$**	**ν_{COO^-} (cm^{-1})**	**$IR_{Int,\,COO^-}$**
1	1390.104	400.286	1726.794	549.625	1683.187	416.262	1752.585	437.960
2	1400.906	311.025	1700.538	682.634	1671.421	520.312	1737.220	527.284
3	1387.364	427.904	–	–	1685.879	404.586	1755.331	423.989
4	–	–	1702.254	681.959	1672.167	518.600	1737.922	528.852
5	1380.306	225.070	1725.755	507.475	1678.427	358.089	1752.100	362.414
6	1381.362	380.406	1747.072	545.552	1699.492	402.036	1768.508	425.214
7	1382.275	378.576	1740.700	514.788	1694.343	390.434	1765.829	412.455
8	1390.386	424.258	1723.548	534.557	1680.647	408.551	1749.020	433.008
9	1384.853	336.233	1733.178	538.376	1687.917	407.630	1760.352	433.333
10	1382.695	377.772	1742.416	518.891	1699.241	395.324	1768.152	415.958
11	1389.743	273.884	1729.962	618.032	1683.106	505.849	1750.683	524.405
12	1384.671	404.114	1740.856	528.136	1692.190	395.175	1761.956	415.118
13	1354.800	375.713	1766.761	679.697	1743.225	534.372	1803.630	538.553
14	1383.535	391.753	1735.079	488.936	1692.291	372.749	1761.121	395.283
15	1379.122	317.468	1748.660	524.262	1701.592	400.327	1774.696	424.536
16	1374.405	445.256	1767.013	691.621	1723.768	521.021	1795.639	536.184
17	1381.910	380.816	1742.049	515.167	1694.689	389.264	1765.944	411.090
18	1389.360	221.555	1739.169	533.205	1695.815	404.633	1764.383	426.132
19	1384.149	380.380	1731.132	483.868	1690.804	370.011	1759.828	395.391
20	1388.179	373.860	1730.559	538.267	1687.804	414.733	1754.964	438.111
21	1383.909	411.975	1734.527	491.209	1690.650	364.475	1759.827	393.561
22	1397.556	211.700	1726.427	437.760	1683.082	331.638	1751.932	376.207
23	1374.234	321.208	1763.190	592.840	1720.705	449.851	1795.020	468.533
24	1379.517	428.350	1746.703	505.309	1696.759	380.488	1765.785	400.848
25	1381.503	377.048	1743.165	518.955	1698.276	390.292	1768.852	409.477
26	1381.243	408.037	1735.512	488.371	1693.537	369.773	1762.013	394.669
27	1372.498	335.938	1761.192	548.767	1709.232	452.331	1780.917	457.090
28	1386.660	498.172	1731.879	534.413	1686.837	409.542	1756.330	420.099

	M06-2X/ aug-cc-pVDZ		*M06-2X/6-311++G(2d,2p)*		*B3LYP/Def2TZVP*		*ωB97X-D/cc-pVTZ*	
#	$\nu_{COO^-,\,sym}$ (cm^{-1})	$IR_{Int,\,COO^-\,sym}$	ν_{COO^-} (cm^{-1})	$IR_{Int,\,COO^-}$	ν_{COO^-} (cm^{-1})	$IR_{Int,\,COO^-}$	ν_{COO^-} (cm^{-1})	$IR_{Int,\,COO^-}$
29	1392.388	300.448	1725.713	604.216	1677.225	562.397	1745.062	598.914
30	1379.296	425.063	1736.595	482.099	1695.088	361.159	1764.112	387.467
31	1386.346	414.806	1727.896	464.095	1686.499	352.922	1756.555	384.669
32	1383.975	373.168	1740.877	506.490	1695.514	380.881	1763.675	378.306
33	1385.761	401.446	1733.335	529.412	1689.567	404.600	1758.885	424.026
34	1384.654	321.429	1732.286	540.715	1687.752	419.741	1759.405	447.429
35	1383.398	353.600	1734.289	445.622	1691.734	311.002	–	–
36	1370.446	218.121	1766.102	558.652	1726.694	434.430	1794.669	455.667
37	1370.903	287.080	1762.515	544.098	1724.399	416.871	1794.974	440.066
38	1346.885	284.190	1792.383	543.553	1740.250	394.756	1813.973	435.317
39	1387.260	302.627	1730.771	506.043	1682.408	378.082	1750.661	404.771
40	1381.567	401.371	1739.273	526.083	1694.034	396.172	1765.380	417.428
41	1381.698	402.789	1733.915	530.906	1688.767	401.336	1761.852	424.959
42	1379.550	486.933	1740.957	463.651	1690.356	365.526	1765.741	400.184
43	1380.867	379.104	1742.290	517.448	1698.008	389.046	1768.858	409.931
44	1398.880	323.405	1697.195	716.079	1674.439	530.819	1739.797	527.425
45	1389.782	369.448	1727.142	518.093	1685.257	391.857	1753.038	417.402
46	1386.236	394.416	1732.329	532.171	1689.897	407.513	1758.064	426.376
47	–	–	1699.644	677.143	1671.257	521.086	1737.021	522.783
48	1383.253	270.097	1755.586	600.378	1722.406	453.167	1789.626	460.727
49	1411.063	267.031	1727.692	576.760	1698.838	421.370	1761.903	440.243
50	1413.046	212.052	1698.216	627.356	1669.660	476.296	1733.708	478.895
51	1364.857	279.883	1789.490	578.966	1746.575	446.956	1815.130	461.805
52	1403.596	238.034	1718.654	742.438	1672.570	538.408	1746.743	568.969
53	1404.439	344.910	1706.946	437.670	1675.957	586.302	–	–
54	1389.046	375.979	1734.886	652.582	1701.309	487.511	1773.118	498.623
55	1378.283	392.854	1752.252	555.002	1703.534	409.530	1774.616	430.423
56	1389.692	435.973	1726.455	526.003	1684.129	398.577	1752.763	418.182
57	1391.101	297.726	1726.138	477.441	1684.979	361.222	1753.055	395.829
58	1371.909	390.711	–	–	1712.018	398.070	1782.940	425.367
59	1389.894	391.544	1725.370	525.791	1683.040	398.721	1751.328	420.821

Table S5. QSARs developed with $\boldsymbol{\nu_{COO^-}}$ and their corresponding IR_{Int} using different functionals and basis sets.

	$\boldsymbol{pKa = a\nu_{COO^-} + bIR_{Int} + c}$		
Functional/Basis Set	$\boldsymbol{a}$	$\boldsymbol{b}$	$\boldsymbol{c}$
M06-2X/6-311++G(2d,2p)	(-4.14 ± 0.25) x 10^{-2}	(-2.37 ± 0.70) x 10^{-3}	(7.69 ± 0.44) x 10^{1}
B3LYP/Def2TZVP	(-4.51 ± 0.28) x 10^{-2}	(-1.80 ± 0.82) x 10^{-3}	(8.09 ± 0.48) x 10^{1}
ωB97X-D/cc-pVTZ	(-4.62 ± 0.21) x 10^{-2}	(-2.35 ± 0.75) x 10^{-3}	(8.61 ± 0.38) x 10^{1}

Table S6. Experimental pKa of perfluoroalkyl carboxylic acids.

pKa	SD[a]	PFAS[b]	Reference
0.54	0.06	TFA	Moroi et al., 2000 - Titration [6]
0.62		TFA	Moroi et al., 2000 - Conductivity [6]
0.25	0.03	TFA	Henne et al., 1951 [7]
0.44	0.03	PFPrA	Moroi et al., 2000 - Titration [6]
0.54		PFPrA	Moroi et al., 2000 - Conductivity [6]
-0.42		PFPrA	Hershfield et al., 1973 [8]
0.38	0.09	PFBA	Moroi et al., 2000 - Titration [6]
0.42		PFBA	Moroi et al., 2000 - Conductivity [6]
0.19	0.03	PFBA	Henne et al., 1951[7]
< 1.60		PFBA	Vierke et al., 2013[9]
0.64		PFPeA	Moroi et al., 2000 - Titration [6]
0.43		PFPeA	Moroi et al., 2000 - Conductivity [6]
0.89	0.05	PFHxA	Moroi et al., 2000 - Titration [6]
0.75		PFHxA	Moroi et al., 2000 - Conductivity [6]
< 1.60		PFHxA	Vierke et al., 2013 [9]
< 1.60		PFHpA	Vierke et al., 2013 [9]
3.80	0.10	PFOA	Burns et al., 2008 [10]
2.80	0.03	PFOA	Brace, 1962 [11]
0.50		PFOA	Vierke et al., 2013 [9]
1.31	0.07	PFOA	Lopez-Fontan et al., 2005 [12]
1.01		PFOA	Igarashi et al., 1992 [13]
< 0.42		PFOA	Feehan et al., 2019 [14]
< 1.00		PFOA	Cheng et al., 2009 [15]
< 1.60		PFNA	Vierke et al., 2013 [9]
2.58		PFDA	Moroi et al., 2000 - Solubility [6]
< 1.60		PFDA	Vierke et al., 2013 [9]

a Standard deviation (SD) calculated with *n* values as reported in the corresponding source. ***b*** Name of the perfluorinated compound.

Table S7. pKa, COO^- antisymmetric stretching vibrational frequencies of the carboxylate anions (ν_{COO^-}), and corresponding infrared intensities (IR_{Int}) of selected betaines.

#	Chemical	CAS #	Exp. pKa	ν_{COO^-} (cm^{-1})	IR_{Int}	Est. pKa[a]	Source
1	1-1Betaine (1-1)	6915-17-9	2.03	1802.119	624.781	0.61	[16]
2	5-1Betaine	68409-45-0	4.25	1737.031	675.441	3.20	[16]
3	10-1Betaine		4.61	1716.916	677.872	4.05	[16]
4	1-12Betaine	66455-29-6	1.80	1795.901	699.228	0.65	[16]
5	2-12Betaine		3.25	1739.601	557.664	3.44	[16]
6	3-12Betaine		3.96	1738.824	774.940	2.84	[16]
7	1-Methyl-3-aceticacidimidazole		2.00	1802.882	693.027	0.37	[17]
8	1-Methyl-3-butanoicacidimidazole		3.83	1743.256	879.335	2.34	[17]
9	1,3-diaceticacidimidazole		1.33	1799.756	696.799	0.49	[17]

[a] Estimated with the "All" QSAR developed for CAs (Table 1).

Table S8. pKa and SO_3^- antisymmetric stretching vibrational frequencies ($\nu_{SO_3^-}$) of selected sulfonic acids.

#	Chemical	CAS #	Exp. pKa	$\nu_{SO_3^-}$ (cm^{-1})	Source
1	1-Aminoethanesulfonic acid	1636-31-3	-0.33	1168.235	[2]
2	Methanesulfonic acid	75-75-2	-1.92	1181.601	[18]
3	Ethanesulfonic acid	594-45-6	-1.68	1169.817	[18]
4	Propanesulfonic acid	5284-66-2	-1.53	1172.773	[18]
5	Benzenesulfonic acid	98-11-3	-2.80	1203.927	[19]
6	4-Bromobenzenesulfonic acid	138-36-3	-3.10	1208.881	[19]
7	4-Nitrobenzenesulfonic acid	138-42-1	-4.00	1216.146	[19]
8	Methoxysulfonic acid	75-93-4	-3.40	1205.629	[19]
9	Chlorosulfonic acid	7790-94-5	-6.00	1269.302	[19]
10	Fluorosulfonic acid	7789-21-1	-6.40	1264.687	[19]
11	Trifluoromethanesulfonic acid (PFMS)	1493-13-6	-5.90	1250.669	[19]
12	4-Hydroxybenzenesulfonic acid	98-67-9	-2.19	1190.983	[20]
13	1,2-Ethanedisulfonic acid	110-04-3	-2.06	1183.473	[21]
14	2-Naphthalenesulfonic acid	120-18-3	-2.00	1193.097	[22]

Table S9. pKa, HPO_3^- antisymmetric stretching vibrational frequencies ($\boldsymbol{\nu_{HPO_3^-}}$), and corresponding infrared intensities (IR_{Int}) of selected phosphonic acids. Experimental pKa taken from refs.[23,24]

#	Chemical	CAS #	Exp. pKa	$\boldsymbol{\nu_{HPO_3^-}}$ (cm^{-1})	IR_{Int}
1	Methylphosphonic acid	993-13-5	2.38	1259.911	346.244
2	Ethylphosphonic acid	6779-09-5	2.43	1265.300	250.245
3	Propylphosphonic acid	4672-38-2	2.49	1254.214	274.565
4	Isopropylphosphonic acid	4721-37-3	2.66	1244.634	173.165
5	Butylphosphonic acid	3321-64-0	2.59	1257.099	285.363
6	2-Butylphosphonic acid	6778-87-6	2.74	1252.448	204.311
7	2-Methylpropylphosphonic acid	4721-34-0	2.70	1258.839	289.701
8	*tert*-butylphosphonic acid	4923-84-6	2.79	1256.695	280.344
9	*tert*-pentylphosphonic acid		2.84	1254.027	158.348
10	*neo*-pentylphosphonic acid		2.88	1252.783	285.286
11	Trifluoromethylphosphonic acid (PFMP)	374-09-4	1.16	1314.145	355.786
12	Chloromethylphosphonic acid	2565-58-4	1.40	1289.460	307.029
13	Dichloromethylphosphonic acid	13113-88-7	1.14	1301.224	271.063
14	Trichloromethylphosphonic acid	5994-41-2	0.78	1316.437	242.286
15	Bromomethylphosphonic acid	7582-40-3	1.15	1292.066	298.898
16	2-Bromoethylphosphonic acid	999-82-6	1.62	1277.544	261.942
17	Hydroxymethylphosphonic acid	2617-47-2	1.91	1274.333	300.096
18	3-Chloro-4-methoxyphenylphosphonic acid		2.25	1278.672	223.349
19	2-Chloro-4-nitrophenylphosphonic acid	114792-24-4	1.12	1292.216	263.788
20	2-Fluorophenylphosphonic acid		1.64	1285.402	299.877
21	Hexylphosphonic acid	4721-24-8	2.60	1257.069	203.635
22	Phenylphosphonic acid	1571-33-1	1.83	1272.743	259.552
23	4-Methylphenylphosphonic acid	3366-72-1	1.84	1270.894	249.490

Table S10. pKa, SO_2^- stretching vibrational frequencies ($\nu_{SO_2^-}$), and corresponding infrared intensities (IR_{Int}) of selected sulfonamides.

#	Chemical	CAS #	Exp. pKa	$\nu_{SO_2^-}$ (cm^{-1})	$IR_{Int,}$	Source
1	Trifluoromethanesulfonamide (PFMSA)	421-85-2	6.33	1257.478	327.454	[25]
2	1,1,1-Trifluoro-N-phenylmethanesulfonamide	456-64-4	4.45	1254.350	364.183	[25]
3	4-Fluorobenzenesulfonamide	402-46-0	10.02	1226.372	176.554	[26]
4	3-Trifluoromethylbenzenesulfonamide	672-58-2	9.69	1230.237	194.076	[26]
5	4-Trifluoromethylbenzenesulfonamide	830-43-3	9.64	1232.273	172.371	[26]
6	2,3,4,5,6-Pentafluorobenzenesulfonamide	778-36-9	8.30	1269.719	142.198	[26]
7	4-Aminobenzenesulfonamide	63-74-1	10.22	1223.224	162.755	[27]
8	Methanesulfonamide	3144-09-0	10.80	1221.006	196.636	[25]
9	N-phenylmethanesulfonamide	1197-22-4	8.85	1215.339	249.499	[25]
10	N-4-Chlorophenyl-1,1,1-trifluoromethanesulfonamide	23384-04-5	3.90	1270.475	367.961	[25]
11	N-3-methylphenyl-1,1,1-trifluoromethanesulfonamide		3.75	1269.316	326.808	[25]
12	1,1,1-Trifluoro-N-3-trifluoromethylphenylmethanesulfonamide	23384-11-4	3.50	1267.736	339.758	[25]
13	N-4-[Methylsulfonylphenyl]trifluoromethanesulfonamide		2.84	1276.533	383.118	[25]
14	Difluoromethanesulfonamide	50585-74-5	8.06	1246.962	248.053	[25]
15	Fluoromethanesulfonamide	50585-72-3	9.32	1250.945	165.537	[25]
16	Fluoromethanesulfonanilide	2070-61-3	7.57	1253.383	147.387	[25]
17	Difluoromethanesulfonanilide	658-43-5	6.19	1260.756	317.998	[25]
18	N-Benzyltriflamide	36457-58-6	6.82	1264.859	218.913	[25]

Table S11. pKa, OH stretching vibrational frequencies ($\boldsymbol{\nu_{FTOH}}$), CO^- stretching vibrational frequencies ($\boldsymbol{\nu_{CO^-}}$), and corresponding infrared intensities (IR_{Int}) of selected alcohols.

#	Chemical	CAS #	Exp. pKa	ν_{CO^-} (cm^{-1})	$IR_{Int, CO-}$	ν_{FTOH} (cm^{-1})	$IR_{Int, OH}$	Source
1	Methanol	67-56-1	15.54	1180.297	399.641	3900.051	42.539	[28]
2	Ethanol	64-17-5	15.50	1220.375	268.189	3880.029	32.165	[28]
3	1-Propanol	71-23-8	16.10	1218.517	329.893	3886.329	32.988	[28]
4	Isopropanol	67-63-0	16.50	1229.196	172.417	3861.374	24.439	[29]
5	*tert*-butanol	75-65-0	16.00	1251.417	200.576	3870.975	23.005	[28]
6	2-Buten-1-ol	4088-60-2	15.52	1185.866	257.214	3885.237	32.981	[28]
7	1,3-Propanediol	504-63-2	15.10	1224.836	271.550	3880.724	34.855	[28]
8	1,4-Butanediol	110-63-4	15.10	1233.507	316.422	3890.623	34.120	[28]
9	1,3-Butanediol	107-88-0	14.90	1238.069	68.936	3883.840	35.163	[28]
10	2-Methoxyethanol	109-86-4	14.80	1212.711	240.375	3891.958	37.958	[28]
11	2-Propynol	107-19-7	13.55	1200.278	305.768	3882.202	47.151	[28]
12	Trifluoroethanol (1:1FTOH)	75-89-8	11.40; 12.37; 12.50; 12.80	1250.246	306.619	3863.723	62.859	[29]
13	Trichloroethanol	115-20-8	12.02	1296.482	249.362	3860.144	50.410	[28]
14	2-Trifluoromethyl-2-propanol	507-52-8	11.60	1279.509	233.081	3898.058	44.813	[28]
15	Benzylalcohol	100-51-6	15.40	1183.016	132.539	3866.361	35.341	[28]
16	Cyclohexanol	108-93-0	16.84	1223.803	90.715	3885.775	30.118	[28]
17	3-Amino-1,1,1-trifluoropropanol	431-38-9	12.29	1246.635	227.779	3847.077	54.495	[30]
18	Hexafluoro-2-methylisopropanol	1515-14-6	9.60	1294.952	211.274	3862.603	71.173	[31]
19	Hexafluoroisopropanol	920-66-1	9.30	1279.124	250.349	3867.115	91.578	[31]
20	Perfluorotertbutanol	2378-02-1	5.20	1355.065	212.430	3839.789	103.032	[31]
21	1,1-Bistrifluoromethyl-2,2,2-trichloroethanol	7594-49-2	5.10	1397.959	229.161	3814.020	82.778	[31]
22	1,1,1-Trifluoro-2-propanol	374-01-6	11.80	1250.678	145.136	3864.845	60.251	[32]
23	2-Propenol	107-18-6	15.52	1193.635	239.786	3874.678	36.535	[32]
24	1,2,3,4-Butanetetrol	149-32-6	13.90	1213.811	34.661	3874.077	47.250	[29]
25	Butanol	71-36-3	16.10	1214.823	186.036	3887.177	32.315	[29]
26	2,2,3,3,3-Pentafluoro-1-propanol (2:1FTOH)	422-05-9	11.35	1259.863	180.539	3861.983	63.331	[29]
27	1-Chloro-1,1,3,3-tetrafluoropropane		7.90	1460.701	148.329	3834.932	90.088	[29]
28	Hexafluoropropane-2,2-diol	677-71-4	6.58	1475.555	220.339	3857.304	131.099	[29]
29	1,1,3-Trichloro-1,3,3-trifluoropropane-2,2-diol		6.48	1465.232	262.386	3837.372	84.677	[29]
30	1,1,3,3-Tetrachloro-1,3-difluoropropane-2,2-diol	677-70-3	6.42	1466.674	226.130	3849.099	89.497	[29]
31	1,1,3,3-Tetrafluoropropane-2,2-diol		8.79	1480.390	190.339	3817.332	70.890	[29]
32	1,1,3,3-Tetrafluoro-1.3-dichloropropane-2,2-diol		6.67	1461.649	255.259	3837.017	86.904	[29]

#	Chemical	CAS #	Exp. pKa	ν_{CO^-} (cm^{-1})	$IR_{Int, CO-}$	ν_{FTOH} (cm^{-1})	$IR_{Int, OH}$	Source
33	1,1,1-Trifluoro-3,3-dibromopropane-2,2-diol		7.69	1476.616	247.082	3837.667	100.375	[29]
34	2,2,3,3-tetrafluoro-1-propanol	76-37-9	12.74	1255.800	243.845	3909.715	72.949	[29]
35	2,2-Dichloroethanol	598-38-9	12.89	1303.953	141.462	3919.200	72.511	[29]
36	2,2-Difluoroethanol	359-13-7	12.00	1264.557	247.230	3924.976	62.452	[29]
37	1,2-Ethanediol	107-21-1	15.10	1183.034	93.090	3875.570	39.130	[29]
38	Glycerol	56-81-5	14.15	1181.428	99.468	3907.875	62.876	[29]
39	Propyleneglycol	57-55-6	14.90	1179.325	214.178	3893.756	34.942	[29]

Table S12. Estimated pKa of fluorinated betaines compiled from different models/sources and calculated using the Betaines QSAR (Table 3).

Chemical	CAS Number	v_{COO^-}	IR_{Int}	Estimated pKa			
				VF Model	NN – Pan et al., 2021	SPARC	Chemicalize
1-1[a]		1802.119	624.781	1.73	1.90	2.32	3.26
1-1PF		1817.098	626.669	1.23	1.60	1.82	2.31
1-2PF		1823.193	615.837	1.02	1.70	1.67	2.22
1-3PF		1822.711	576.099	1.04	1.70	1.60	1.78
1-4PF		1823.105	574.738	1.03	1.70	1.57	0.98
1-2Trifluoroethyl		1807.744	613.088	1.54	1.70	2.14	2.73
1-2Pentafluoropropyl		1806.646	657.809	1.58	1.70	2.07	2.51
1-2Heptafluorobutyl		1807.967	668.631	1.53	1.70	2.04	2.02

[a] Non-fluorinated betaine; used to compare models with the experimental pKa.

Table S13. Estimated pKa of per- and polyfluoroalkyl sulfonic acids compiled from different models/sources and calculated using the Sulfonic Acids QSAR (Table 3).

Chemical	CAS Number	$v_{SO_3^-}$	Estimated pKa					
			VF Model	NN – Pan et al., 2021	QC -Rayne & Forest, 2010	SPARC	Chemicalize	OPERA
PFMS	1493-13-6	1250.669	-5.51	-3.40	-5.80	0.98	-3.43	0.03
PFES	354-88-1	1242.154	-5.05	-3.00	-5.80	0.14	-3.31	-0.13
PFPrS	423-41-6	1261.901	-6.11	-2.80	-5.50	0.14	-3.31	-0.49
PFBS	375-73-5	1266.474	-6.36	-2.90	-5.50	0.14	-3.31	-1.61
PFPeS	2706-91-4	1240.307	-4.95	-2.90	-5.50	0.14	-3.32	-1.77
PFHxS	355-46-4	1261.594	-6.10	-2.90	-5.50	0.14	-3.32	-1.64
PFHpS	375-92-8	1256.465	-5.82	-2.90	-5.50	0.14	-3.32	-1.81
PFOS	1763-23-1	1256.743	-5.84	-2.90	-5.50	0.14	-3.32	-1.64
PFNS	68259-12-1	1255.673	-5.78	-2.80		0.14	-3.24	-1.68
4:2FTS	757124-72-4	1176.173	-1.51	1.40		0.36	-2.64	0.93
6:2FTS	27619-97-2	1172.621	-1.32	1.40		0.36	-2.72	1.23

Table S14. Estimated pKa of PFPA compiled from different models/sources and calculated using the Phosphonic Acids QSAR (Table 3).

Chemical	CAS Number	$\nu_{HPO_3^-}$	Estimated pKa				
			VF Model	NN – Pan et al., 2021	SPARC	Chemicalize	OPERA
PFMP	374-09-4	1314.145	0.75	0.70	0.34	-0.06	0.55
PFEP	103305-01-7	1312.900	0.79	0.90	-0.03	0.41	0.27
PFPrP		1320.583	0.55	0.90	-0.07	0.46	-0.67
PFBP	52299-24-8	1320.382	0.56	0.90	-0.16	0.46	-1.71
PFPeP		1318.774	0.61	0.90	-0.20	0.46	-2.74
PFHxP	40143-76-8	1318.924	0.60	0.90	-0.22	0.46	-2.52
PFHpP		1318.317	0.62	0.90	-0.23	0.46	-2.63

Table S15. Estimated pKa of sulfonamides compiled from different models/sources and calculated using the Sulfonamides QSAR (Table 3).

Chemical	CAS Number	$\nu_{SO_2^-}$	IR_{Int}	Estimated pKa				
				VF Model	NN – Pan et al., 2021	SPARC	Chemicalize	OPERA
PFMSA	421-85-2	1257.478	327.4538	5.29	6.50	6.10	6.19	7.04
PFESA	78491-70-0	1284.859	492.9215	0.45	6.50	6.57	2.63	7.72
PFPrSA		1265.561	265.3803	5.90	6.60	6.59	3.06	7.72
PFBSA	30334-69-1	1265.680	237.5232	6.40	6.60	6.59	3.34	6.97
PFPeSA		1275.231	253.3838	5.49	6.60	6.58	3.37	6.66
PFHxSA	41997-13-1	1258.773	253.2143	6.57	6.60	6.57	3.37	7.05
PFHpSA		1270.055	262.1327	5.67	6.60	6.57	3.37	6.54
PFOSA	754-91-6	1271.171	170.3701	7.28	6.60	6.56	3.37	6.78

Table S16. Estimated pKa of FTOH compiled from different models/sources and calculated using the v_{FTOH} QSAR (Table 3).

				Estimated pKa				
Chemical	**CAS Number**	v_{FTOH}	**IR$_{Int}$**	**VF Model**	**NN – Pan et al., 2021**	**SPARC**	**Chemicalize**	**OPERA**
1:1FTOH	75-89-8	3863.723	62.859	11.40	12.30	12.45	11.49	9.22
2:1 FTOH	422-05-9	3861.983	63.331	11.28	12.60	12.36	12.52	9.44
2:2 FTOH	54949-74-5	3888.438	45.978	14.23	13.80	14.43	15.76	10.02
3:2 FTOH	755-40-8	3888.035	44.848	14.33	13.80	14.29	15.76	9.08
4:2 FTOH	2043-47-2	3878.906	43.976	14.04	13.80	14.23	15.76	9.75
5:2 FTOH	185689-57-0	3888.107	48.060	14.00	13.80	14.21	15.76	9.78
6:2 FTOH	647-42-7	3886.248	48.076	13.92	13.80	14.20	15.76	9.74
7:2 FTOH	755-02-2	3881.977	43.069	14.26	13.80	14.19	15.76	9.58
2:3 FTOH	148043-73-6	3905.514	54.399	14.07	13.80	15.26	15.96	
2:4 FTOH	58556-45-9	3885.746	38.296	14.93	13.80	15.58		
2:6 FTOH	161981-34-6	3903.573	48.821	14.57	13.80	15.73		

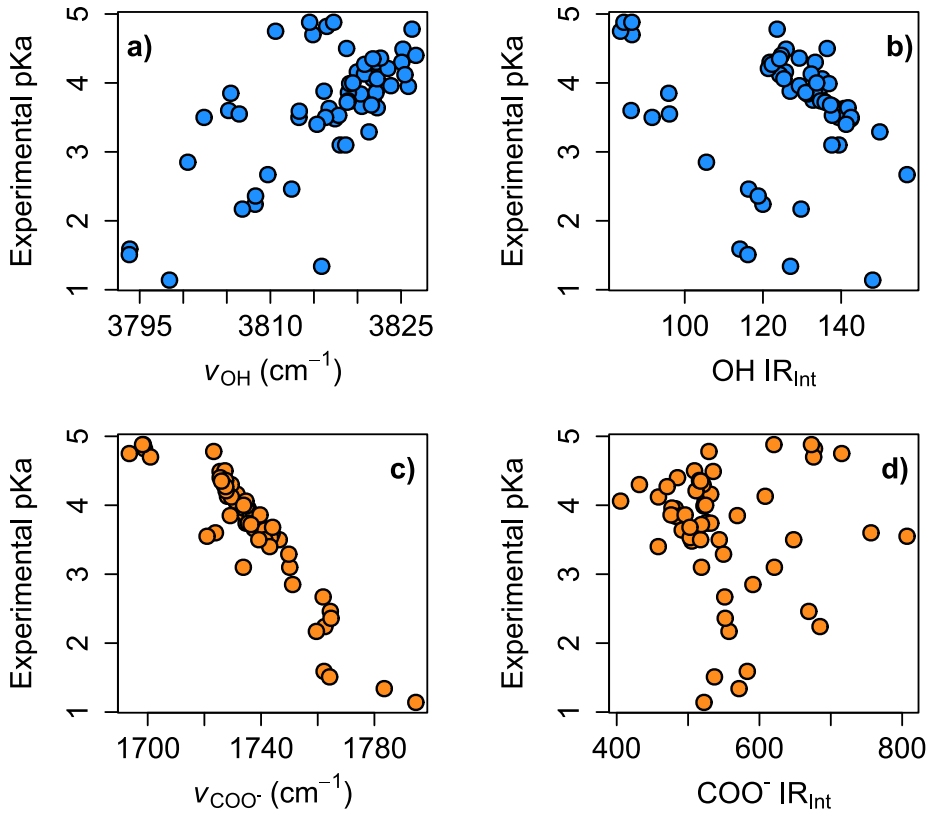

Figure S1. Linear correlations between the pKa of a subset of carboxylic acids (#1-59; Table S1) and **a)** the stretching OH vibrational frequency (ν_{OH}), **b)** the infrared intensity (IR_{Int}) of the corresponding ν_{OH}, **c)** the antisymmetric stretching COO^- vibrational frequency (ν_{COO^-}), and **d)** the IR_{Int} of the corresponding ν_{COO^-}.

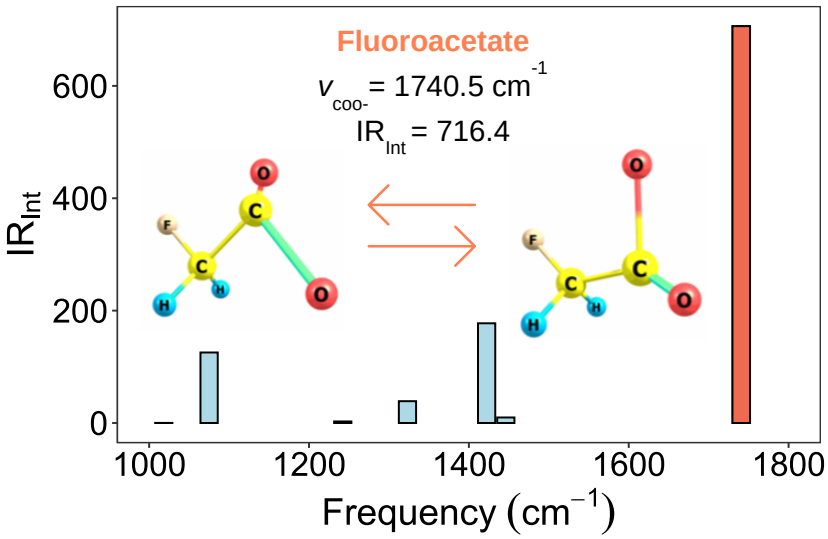

Figure S2. Vibrational frequency and IR_{Int} for the antisymmetric COO^- stretch of fluoroacetate (in orange) obtained computationally. A graphical representation of this frequency mode is shown in the inset with its corresponding value and IR_{Int}.

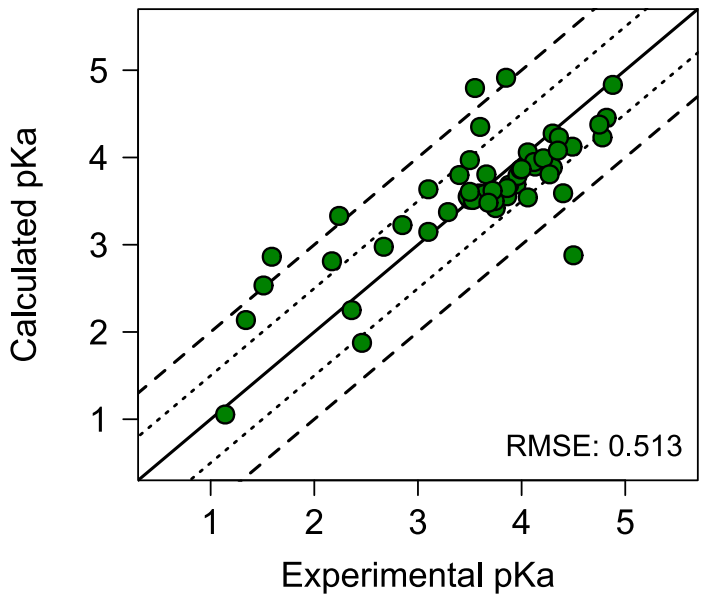

Figure S3. Correlation between the experimental and calculated pKa of a subset of carboxylic acids (Table S4) using as predictors symmetric COO^- stretching vibrational frequencies ($\nu_{COO^-,\,sym}$) and corresponding IR_{Int}. $a, b, and\ c$ in $pKa = a\nu_{COO^-,sym} + bIR_{Int} + c$ are (6.11 ± 0.63) x 10^{-2}, (3.69 ± 1.04) x 10^{-3}, and (-8.23 ± 0.89) x 10^{1}. The solid black line shows the 1:1 line, the dotted lines the 0.5 pKa units bounds, and the dashed lines the 1 pKa unit bounds.

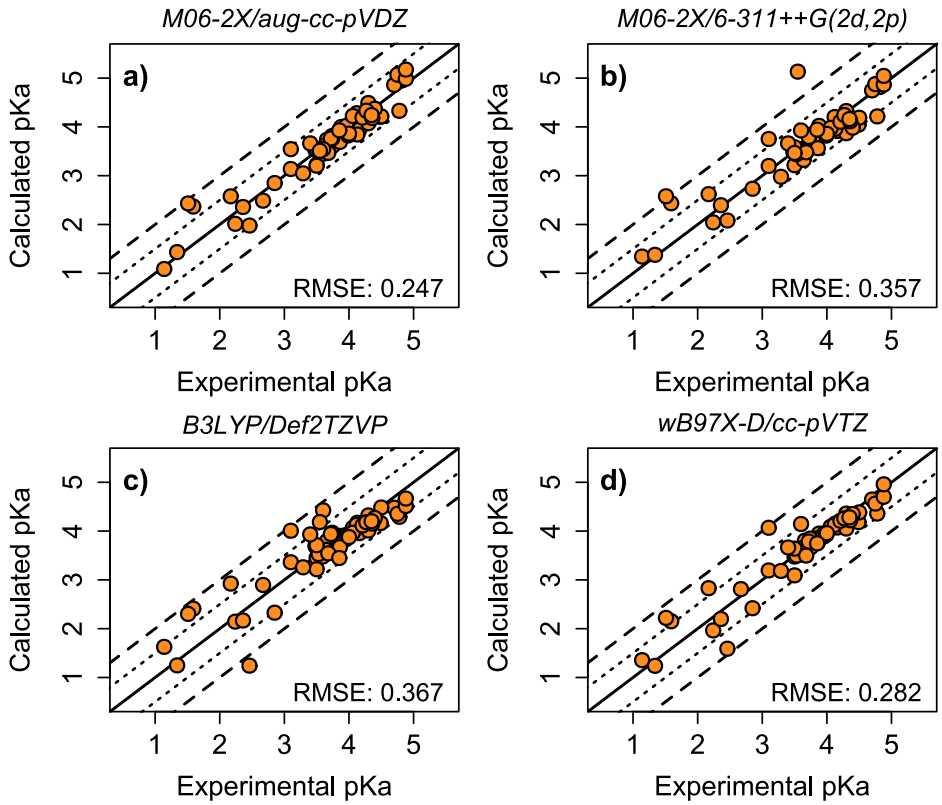

Figure S4. Correlations between calculated and experimental pKa of a subset of carboxylic acids (#1-59, Table S1) using different functionals and basis sets. COO^- vibrational frequencies (ν_{COO^-}) and corresponding infrared intensities (IR_{Int}) were used as predictors (Table S4) – see QSARs in Table S5. The values for M06-2X/aug-cc-pVDZ are presented in Tables S1 and S3.

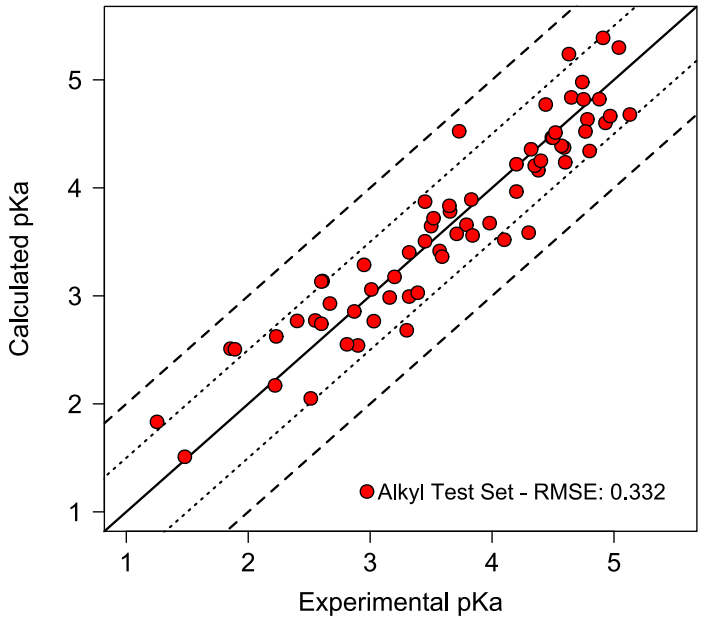

Figure S5. Correlation between experimental and calculated pKa of the alkyl carboxylic acids in the validation set (n = 67) using its own QSAR where $a, b, and\ c$ in $pKa = av_{COO^-} + bIR_{Int} + c$ are (-3.50 ± 0.16) x 10^{-2}, (-1.35 ± 0.53) x 10^{-3}, and (6.52 ± 0.29) x 10^{1}. The solid black line shows the 1:1 line, the dotted lines the 0.5 pKa units bounds, and the dashed lines the 1 pKa unit bounds. The experimental pKa are listed in Table S1.

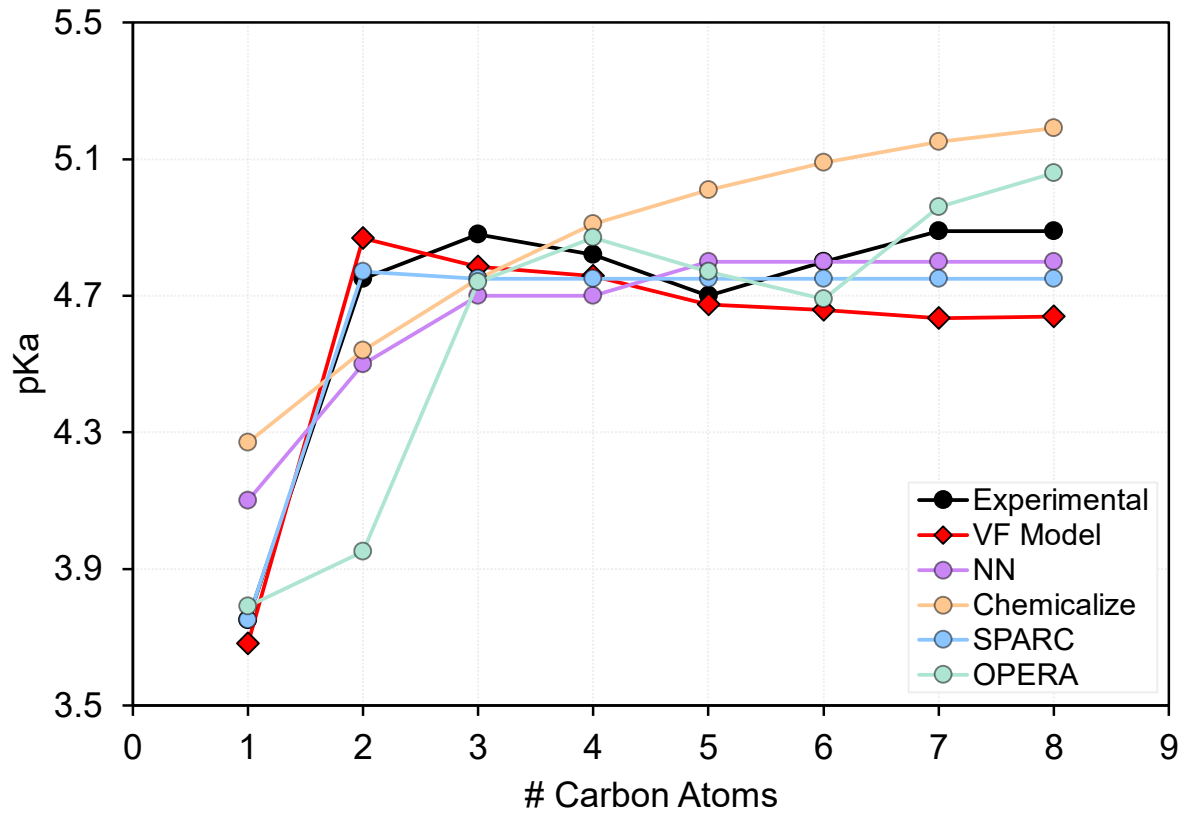

Figure S6. Experimental and calculated pKa of non-fluorinated alkyl carboxylic acids with chain lengths of one (formic acid) to eight (octanoic acid) carbons. The experimental pKa can be found in Table S1. The calculated pKa were obtained using the "Alkyl" QSAR of the VF Model, the Neural Network (NN) approach by Pan et al., 2021 (https://xundrug.cn/molgpka),[33] Chemicalize by ChemAxon (https://chemicalize.com),[34] SPARC calculator by ARChem (http://archemcalc.com/), and the OPERA App (accessed through the Chemical Transformation Simulator - https://qed.epa.gov/cts/).[35]

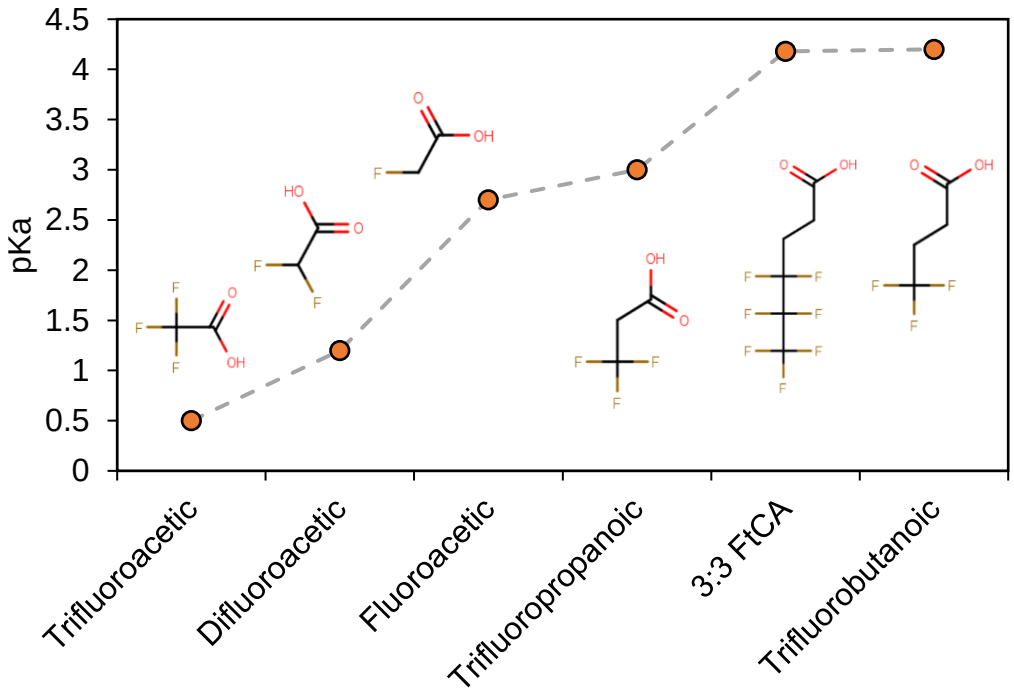

Figure S7. Experimental pKa of selected fluorinated carboxylic acids found in Table S1.

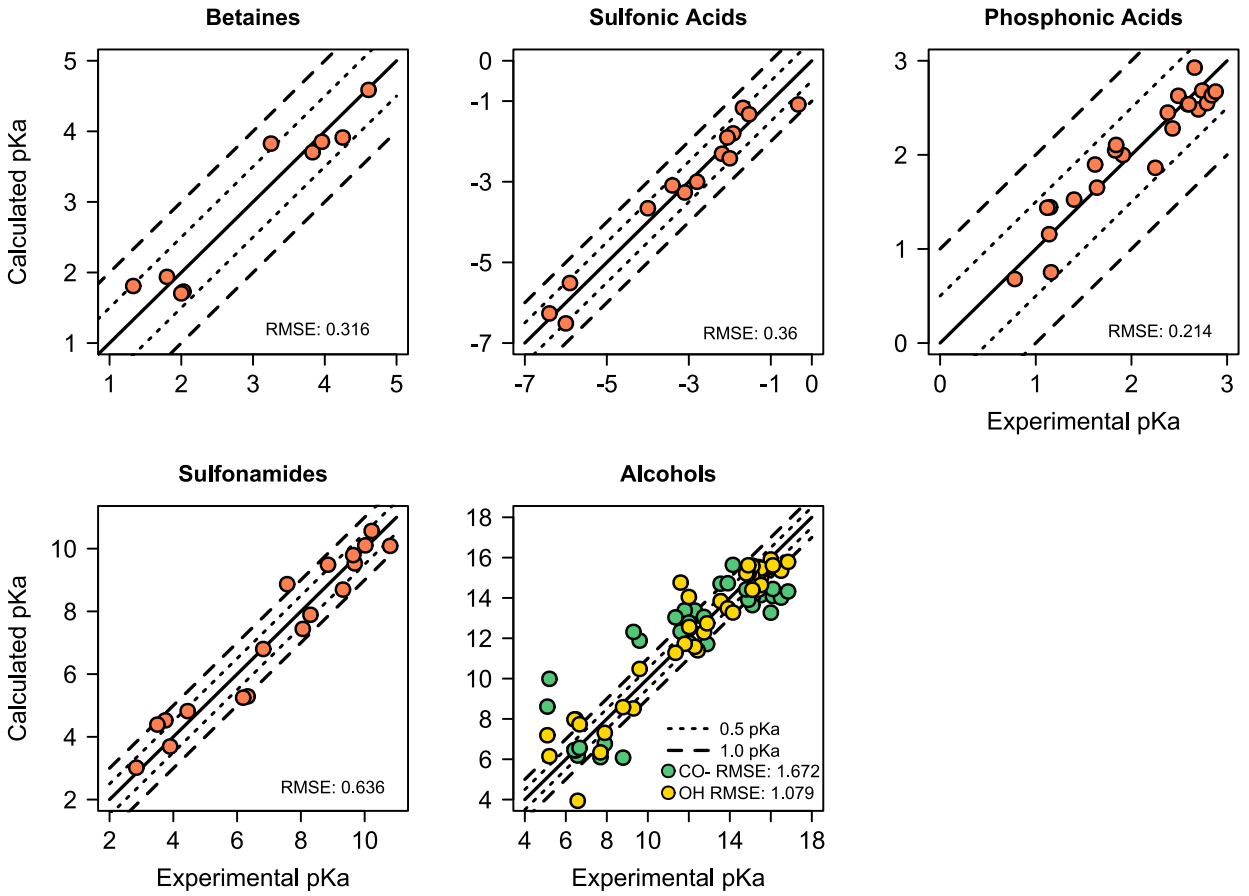

Figure S8. Correlations between calculated and experimental pKa of different acids. The QSARs utilized to estimate the pKa are listed in Table 3 of the main text. The experimental pKa, vibrational frequencies and IR_{Int} are presented in Tables S7 – S11.

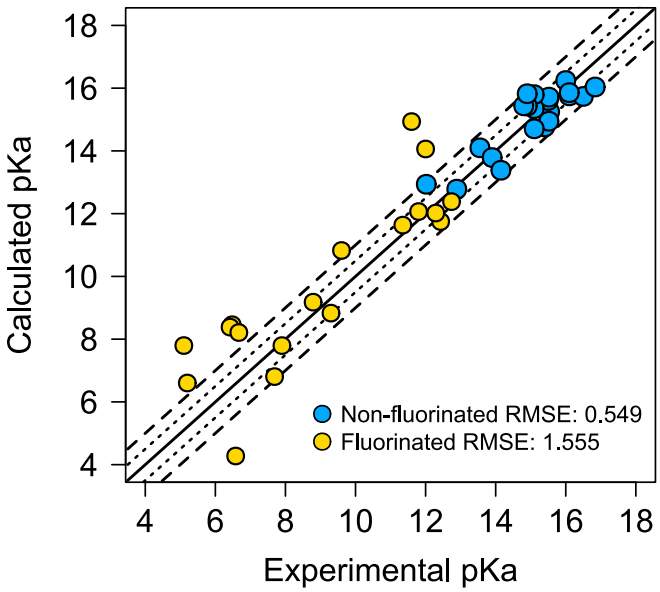

Figure S9. Correlation between calculated and experimental pKa of the 39 alcohols listed in Table S11. The QSAR was developed with non-fluorinated alcohols (n: 21) and used to predict the pKa of fluorinated alcohols (n: 18). $a, b, and\ c$ in $pKa = av_{FTOH} + bIR_{Int} + c$ are (3.70 ± 1.13) x 10^{-2}, (-1.06 ± 0.14) x 10^{-1}, and (-1.24 ± 0.44) x 10^{2}.

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