Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

The conformational landscape of 2-(4-fluoro-phenyl)-ethylamine: Consequences of fluorine substitution at the *para*-position

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Table S1. The numbering of the normal vibrations, their transition frequencies (cm^{-1}) and intensities (arb. units) as obtained from the measured ionization-loss stimulated Raman and from the scaled harmonic Raman spectra, computed at the M06-2X/6-311++G(d,p) level of theory, for the G1, G2 and A2 conformers of 2-(4-fluoro-phenyl)-ethylamine.

	G1					G2					A2			
	Calculated		Measured			Calculated		Measured			Calculated		Measured	
	Freq.	Int.	Freq.	Int.		Freq.	Int.	Freq.	Int.		Freq.	Int.	Freq.	Int.
ν_1	3427.9	0.31	3416.2	0.44	ν_1	3421.4	0.24	3408.5	0.50	ν_{31} (A")	3427.6	0.29	3418.4	0.39
ν_2	3347.3	0.88	3347.6	0.77	ν_2	3341.5	0.69	3344.1	1.07	ν_1(A')	3347.4	0.80	3351.1	1.01
			3230.5	0.16	ν_3	3080.4	1.18	3083.0	1.46	ν_2(A')	3079.1	1.92	3084.5	1.00
			3207.9	0.13	ν_4	3078.6	1.13			ν_{32} (A")	3079.1	1.92		
ν_3	3081.2	1.01	3085.0	1.00	ν_5	3047.5	0.40	3054.3	0.40	ν_3 (A')	3044.1	0.57	3051.6	0.38
ν_4	3079.0	0.99			ν_6	3044.4	0.42	3049.6	0.39	ν_{33} (A")	3043.8	0.57		
ν_5	3053.1	0.31	3059.7	0.35				3027.0	0.48				3024.7	0.32
ν_6	3043.2	0.39	3051.4	0.30				3014.1	0.26	ν_{34} (A")	2970.0	0.01		
			3027.2	0.38				2976.8	0.36	ν_{35} (A")	2933.1	0.45	2943.9	0.33
			3016.4	0.24	ν_7	2966.7	0.43	2948.2	1.15	ν_4 (A')	2911.0	0.19	2925.6	0.33
ν_7	2977.6	0.28	2961.1	0.77				2944.1	0.10	ν_5 (A')	2897.2	1.56	2909.9	0.70
ν_8	2941.1	1.43	2936.2	0.67	ν_8	2943.2	0.92	2926.6	0.92				2885.4	0.34
ν_9	2915.7	0.85	2920.5	0.45				2902.6	0.46				2876.3	0.37
			2871.5	0.30	ν_9	2908.6	1.47	2882.2	0.68				2866.9	0.41
			2862.4	0.32	ν_{10}	2901.2	1.22	2862.1	0.61				2853.9	0.22
ν_{10}	2844.6	0.88	2849.6	0.46				2788.0	0.35	ν_6 (A')	1642.7	0.38		
			2747.4	0.26				2769.0	0.34	ν_{36} (A")	1627.4	0.09		
ν_{11}	1642.1	0.29	1633.6	0.23	ν_{11}	1641.6	0.35	1636.8	0.45	ν_7 (A')	1622.2	0.07		
ν_{17}	1422.7	0.01	1416.8	0.13	ν_{17}	1421.6	<0.01			ν_{38} (A")	1351.0	0.10		
ν_{18}	1383.1	0.06	1396.1	0.20	ν_{18}	1356.7	0.24	1363.0	0.62	ν_{39} (A")	1306.7	0.04	1310.6	0.23
ν_{19}	1331.2	0.48	1336.4	0.41	ν_{19}	1352.6	0.02			ν_{40} (A")	1283.0	0.05		
ν_{20}	1311.0	0.13	1316.1	0.14	ν_{20}	1320.8	0.36	1327.6	0.78	ν_{12} (A')	1280.8	0.40	1283.6	0.80
ν_{21}	1296.8	0.04	1304.0	0.14	ν_{21}	1296.0	0.11	1305.0	0.39	ν_{41} (A")	1262.1	0.03		
ν_{22}	1282.6	0.03	1288.7	0.09	ν_{22}	1282.2	0.03			ν_{13} (A')	1251.2	0.68		

ν_{23}	1250.7	0.74	1241.4	0.61	ν_{23}	1251.2	0.9	1228.9	0.63				1227.4	0.53
			1231.1	0.49	ν_{24}	1209.5	0.21	1208.3	0.99	ν_{14} (A')	1202.1	0.53	1205.2	0.49
ν_{24}	1202.8	0.34	1209.5	0.77	ν_{25}	1200.3	0.61	1202.6	0.95	ν_{15} (A')	1148.9	0.14	1150.0	0.20
ν_{25}	1183.7	0.06	1185.9	0.18	ν_{26}	1149.0	0.16	1151.3	0.20	ν_{42} (A")	1105.0	<0.01		
ν_{26}	1149.1	0.16	1161.1	0.45	ν_{27}	1127.9	0.09	1137.5	0.44	ν_{16} (A')	1092.6	0.13		
ν_{27}	1138.6	0.10	1141.5	0.52	ν_{28}	1095.4	0.03	1097.7	0.20	ν_{43} (A")	1074.2	0.05		
ν_{28}	1093.8	0.05	1099.2	0.18	ν_{29}	1073.2	0.09	1073.2	0.23	ν_{17} (A')	1023.7	0.59	1020.1	0.84
ν_{29}	1087.6	0.12	1084.3	0.20				1033.1	0.26	ν_{18} (A')	1009.0	0.01		
ν_{30}	1028.3	0.09	1024.6	0.38	ν_{30}	1009.3	0.01			ν_{44} (A")	964.9	<0.01		
ν_{31}	1009.5	0.01			ν_{31}	988.7	0.17	992.0	0.84	ν_{45} (A")	945.5	<0.01		
ν_{32}	966.8	<0.01			ν_{32}	965.5	<0.01			ν_{19} (A')	939.7	0.06	941.7	0.47
ν_{33}	942.5	<0.01			ν_{33}	943.8	<0.01						857.3	0.63
ν_{34}	908.6	0.19	913.1	0.23	ν_{34}	903.4	0.24	911.9	0.76	ν_{20} (A')	854.8	1.15	851.7	1.00
ν_{35}	872.0	0.20	876.0	0.47				888.9	0.3	ν_{21} (A')	838.1	0.59	832.5	0.49
			845.2	0.50	ν_{35}	865.1	0.07	864.5	0.65	ν_{46} (A")	824.9	0.01		
ν_{36}	835.0	1.83	839.7	1.00	ν_{36}	838.5	3.81	841.2	0.51	ν_{22} (A')	815.9	0.20	810.8	0.49
ν_{37}	834.1	0.24			ν_{37}	826.6	0.17	823.5	0.55				781.1	0.74
ν_{38}	826.7	0.01	823.5	0.92	ν_{38}	822.2	0.22	819.7	0.44	ν_{23} (A')	762.9	0.09	755.2	0.67
ν_{39}	819.7	0.03	816.3	0.37	ν_{39}	814.8	0.03			ν_{47} (A")	743.6	<0.01		
			794.6	0.37	ν_{40}	714.6	0.03			ν_{24} (A')	706.5	0.07	687.4	0.69
ν_{40}	721.6	0.05	727.4	0.36	ν_{41}	701.9	0.12	707.2	0.55	ν_{48} (A")	633.0	0.27	628.2	0.52
ν_{41}	703.2	0.10	709.3	0.45				666.2	0.45				603.3	0.72
			693.0	0.17	ν_{42}	632.6	0.3	624.2	0.53	ν_{25} (A')	544.2	0.06		
ν_{42}	632.6	0.27	640.5	0.87	ν_{43}	550.6	<0.01	529.2	0.48	ν_{26} (A')	496.5	0.09		
ν_{43}	551.0	0.01			ν_{44}	478.7	0.19			ν_{49} (A")	420.4	<0.01		
ν_{44}	478.4	0.12	481.1	0.43	ν_{45}	423.3	0.08			ν_{50} (A")	413.0	<0.01		
ν_{45}	428.3	0.17	432.1	0.42	ν_{46}	419.1	0.32	425.7	0.41					
ν_{46}	418.3	0.19	423.1	0.50	ν_{47}	413.6	<0.01							
ν_{47}	413.9	0.03	406.8	0.19										

[a] Also given are the symmetry species (A' and A") of the different modes.

Table S2. Atomic charges, obtained from natural bond orbital analysis at the M06-2X/6-311++G(d,p) level of theory for the G1, G2, A1 and A2 conformers of 2-(4-fluoro-phenyl)-ethylamine (4-FPEA) and 2-phenylethylamine (PEA).

	4-FPEA				PEA			
	G1	G2	A1	A2	G1	G2	A1	A2
C1	-0.058210	-0.056740	-0.050620	-0.053480	-0.040480	-0.039160	-0.032930	-0.035900
C2	-0.193670	-0.196960	-0.187200	-0.188240	-0.214970	-0.217460	-0.208040	-0.209040
C3	-0.269210	-0.268480	-0.267410	-0.266680	-0.202740	-0.201890	-0.201430	-0.200670
C4	0.410020	0.410680	0.410290	0.410660	-0.217030	-0.216190	-0.216640	-0.216170
C5	-0.267980	-0.265250	-0.268030	-0.266680	-0.202000	-0.199770	-0.201910	-0.200670
C6	-0.190760	-0.189530	-0.188940	-0.188240	-0.211650	-0.210570	-0.209780	-0.209040
H14	0.210390	0.211320	0.209670	0.210180	0.206570	0.207450	0.205760	0.206270
H15	0.227700	0.228630	0.227550	0.228090	0.208930	0.209840	0.208680	0.209220
F(H)16	-0.358520	-0.357430	-0.358520	-0.357940	0.209660	0.210480	0.209520	0.209960
H17	0.228450	0.228630	0.227850	0.228090	0.209690	0.209800	0.208990	0.209220
H18	0.220660	0.210960	0.212050	0.210180	0.216380	0.207050	0.208170	0.206270
sum	-0.041130	-0.044170	-0.033310	-0.034060	-0.037640	-0.040420	-0.029610	-0.030550
C7	-0.410980	-0.421250	-0.411360	-0.420130	-0.412740	-0.422740	-0.41263	-0.421360
C8	-0.174540	-0.178320	-0.173360	-0.177370	-0.173890	-0.177790	-0.1731	-0.177050
H9	0.188690	0.188740	0.162460	0.187140	0.187520	0.187670	0.16263	0.187250
H10	0.160240	0.185100	0.186690	0.187140	0.160170	0.185210	0.18676	0.187260
H12	0.211750	0.213940	0.201460	0.203460	0.211570	0.213590	0.20071	0.202770
H13	0.215970	0.202500	0.218790	0.203460	0.215290	0.201600	0.21808	0.202770
N11	-0.863320	-0.847900	-0.855100	-0.845170	-0.863170	-0.848450	-0.85507	-0.845430
H19	0.356880	0.345440	0.347310	0.347770	0.357860	0.344750	0.35548	0.347170
H20	0.356450	0.355910	0.356410	0.347770	0.355060	0.356580	0.34675	0.347170
sum	0.041140	0.044160	0.033300	0.034070	0.037670	0.040420	0.029610	0.030550