Solvation Enhances the Distinction between Carboxylated Armchair and Zigzag Single-wall Carbon Nanotubes (SWNT-COOH)

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Figure S1 - Optimized structures of (4,4)-COOH , (8,0)-COOH and (9,0)-COOH in gas, CS2, THF and water. Distances are in Å.

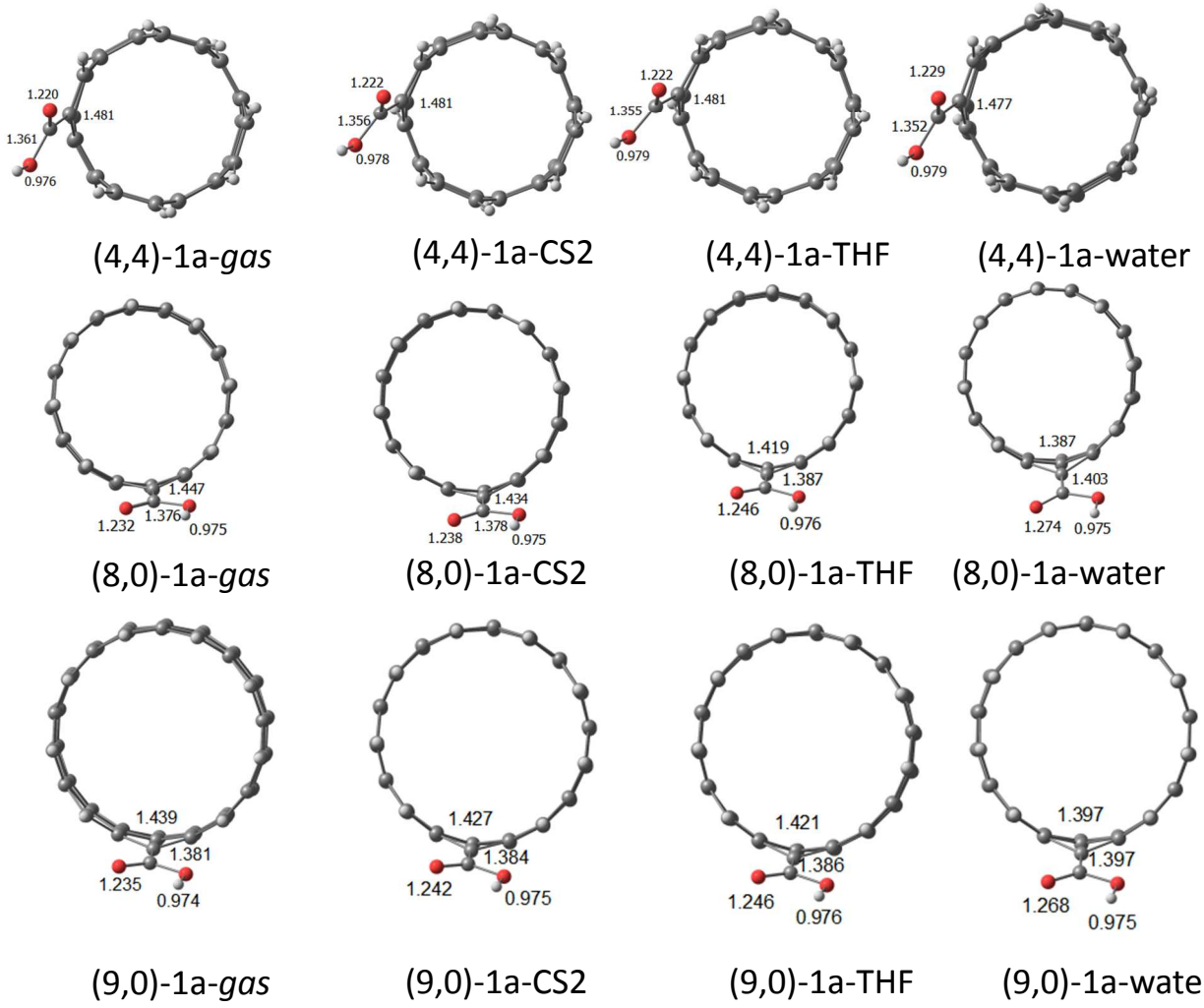
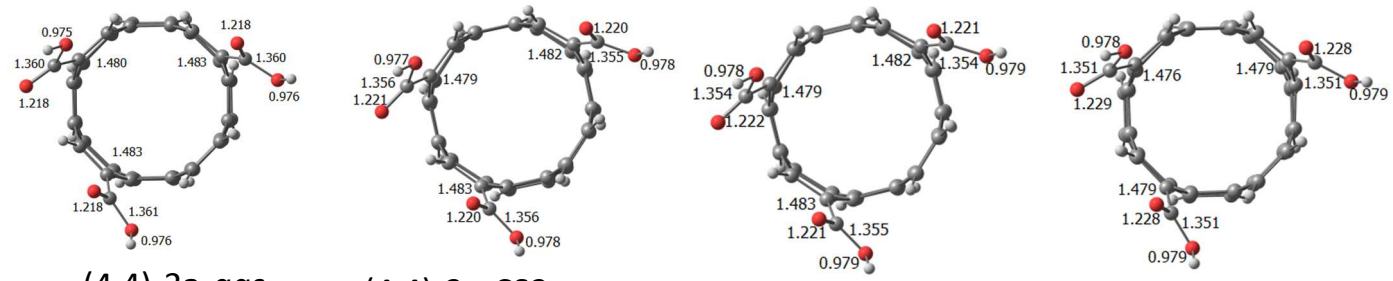
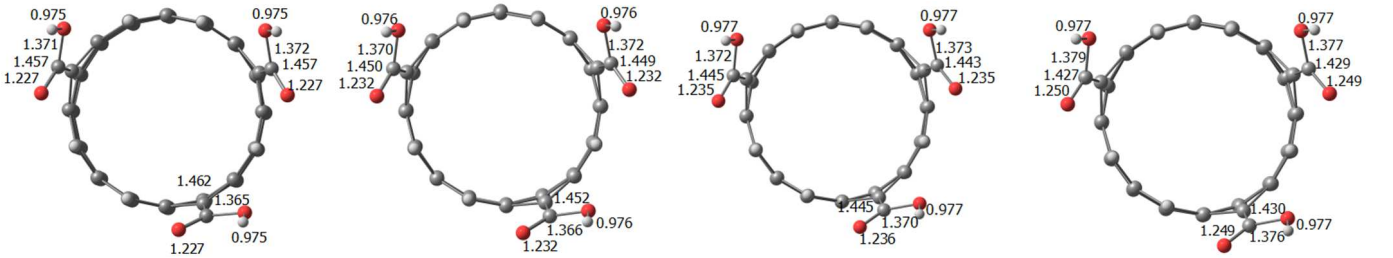


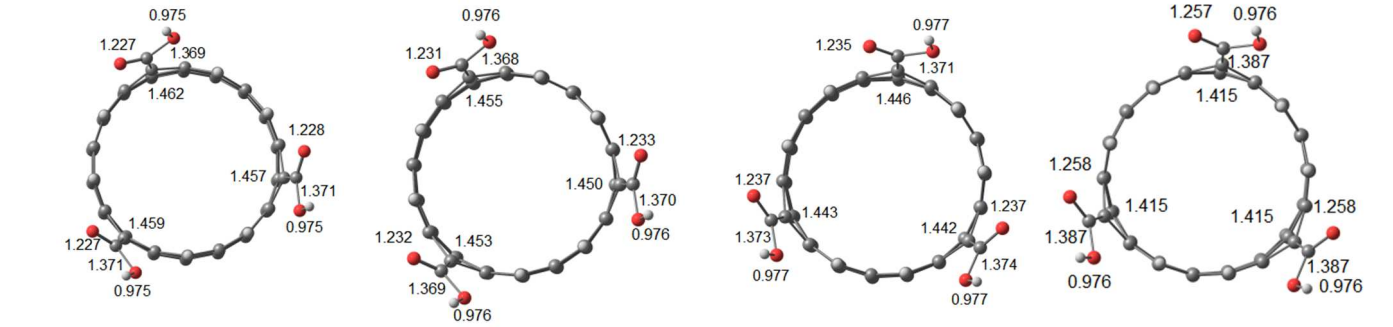
Figure S2 - Optimized structures of (4,4)-$(COOH)_3$ and (8,0)-$(COOH)_3$ in gas, CS2, THF and water. Distances are in Å.



(4,4)-3a-*gas* (4,4)-3a-CS2 (4,4)-3a-THF (4,4)-3a-water

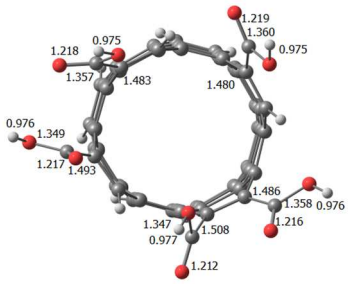


(8,0)-3a-*gas* (8,0)-3a-CS2 (8,0)-3a-THF (8,0)-3a-water

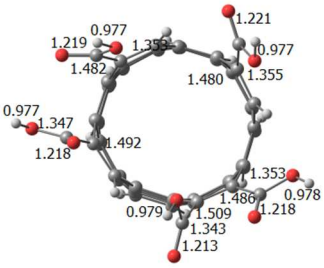


(9,0)-3a-*gas* (9,0)-3a-CS2 (9,0)-3a-THF (9,0)-3a-water

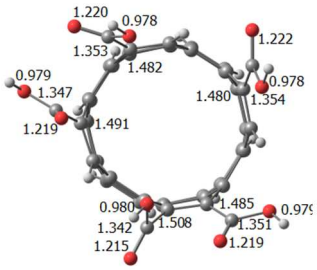
Figure S3 - Optimized structures of (4,4)-$(COOH)_5$ and (8,0)-$(COOH)_5$ in gas, CS2, THF and water. Distances are in Å.



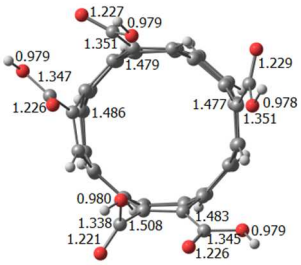
(4,4)-5a-gas



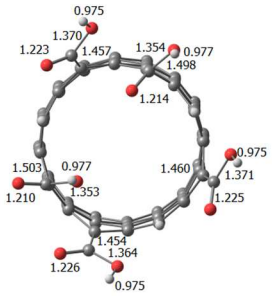
(4,4)-5a-CS2



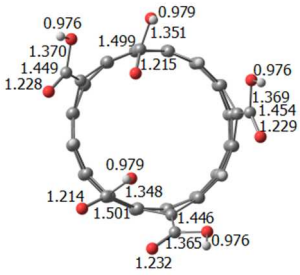
(4,4)-5a-THF



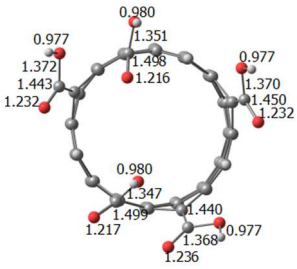
(4,4)-5a-water



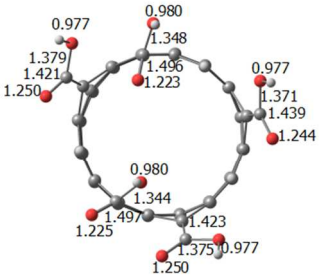
(8,0)-5a-gas



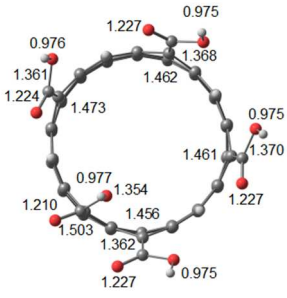
(8,0)-5a-CS2



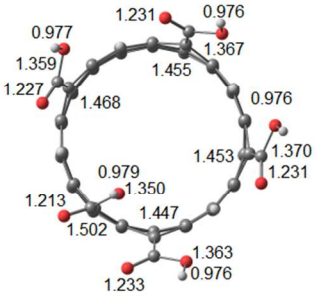
(8,0)-5a-THF



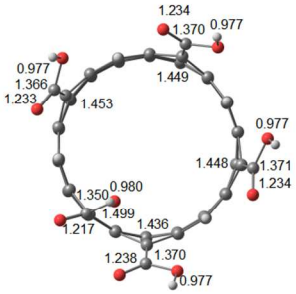
(8,0)-5a-water



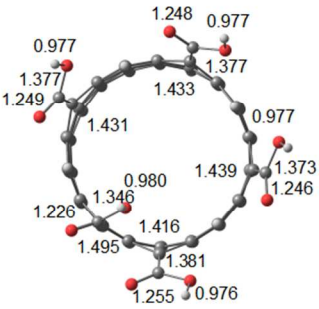
(9,0)-5a-gas



(9,0)-5a-CS2

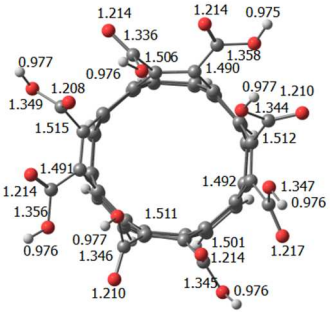


(9,0)-5a-THF

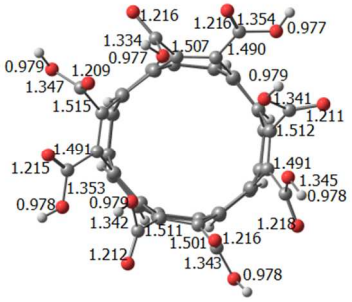


(9,0)-5a-water

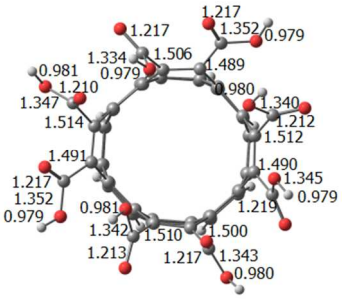
Figure S4 - Optimized structures of (4,4)-$(COOH)_5$ and (8,0)-$(COOH)_5$ in gas, CS2, THF and water. Distances are in Å.



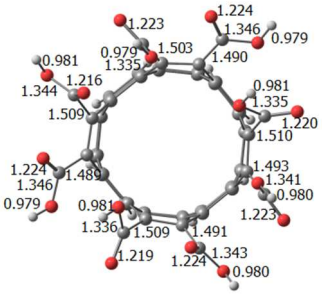
(4,4)-(COOH)8-Gas



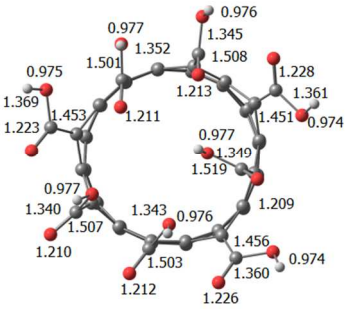
(4,4)-(COOH)8-CS2



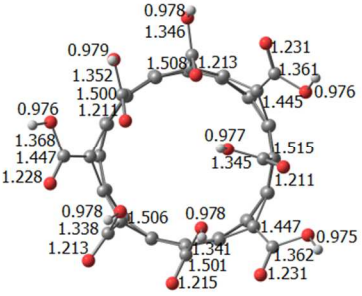
(4,4)-(COOH)8-THF



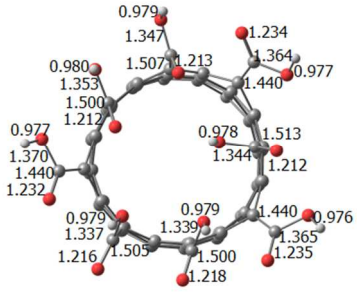
(4,4)-(COOH)8-Water



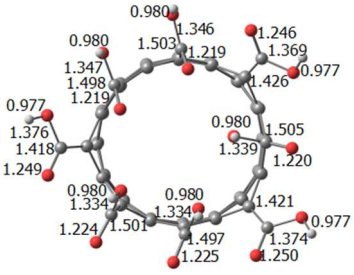
(8,0)-(COOH)8-Gas



(8,0)-(COOH)8-CS2



(8,0)-(COOH)8-THF



(8,0)-(COOH)8-Water

Figure S5 - Variation of C=O distance in different medium. Onsager function $F_o = (\varepsilon - 1)/(\varepsilon + 2)$, where ε refers to the dielectric constant of the medium. Ben, Anth and Phen stand for benzene, anthracene and phenanthrene, respectively.

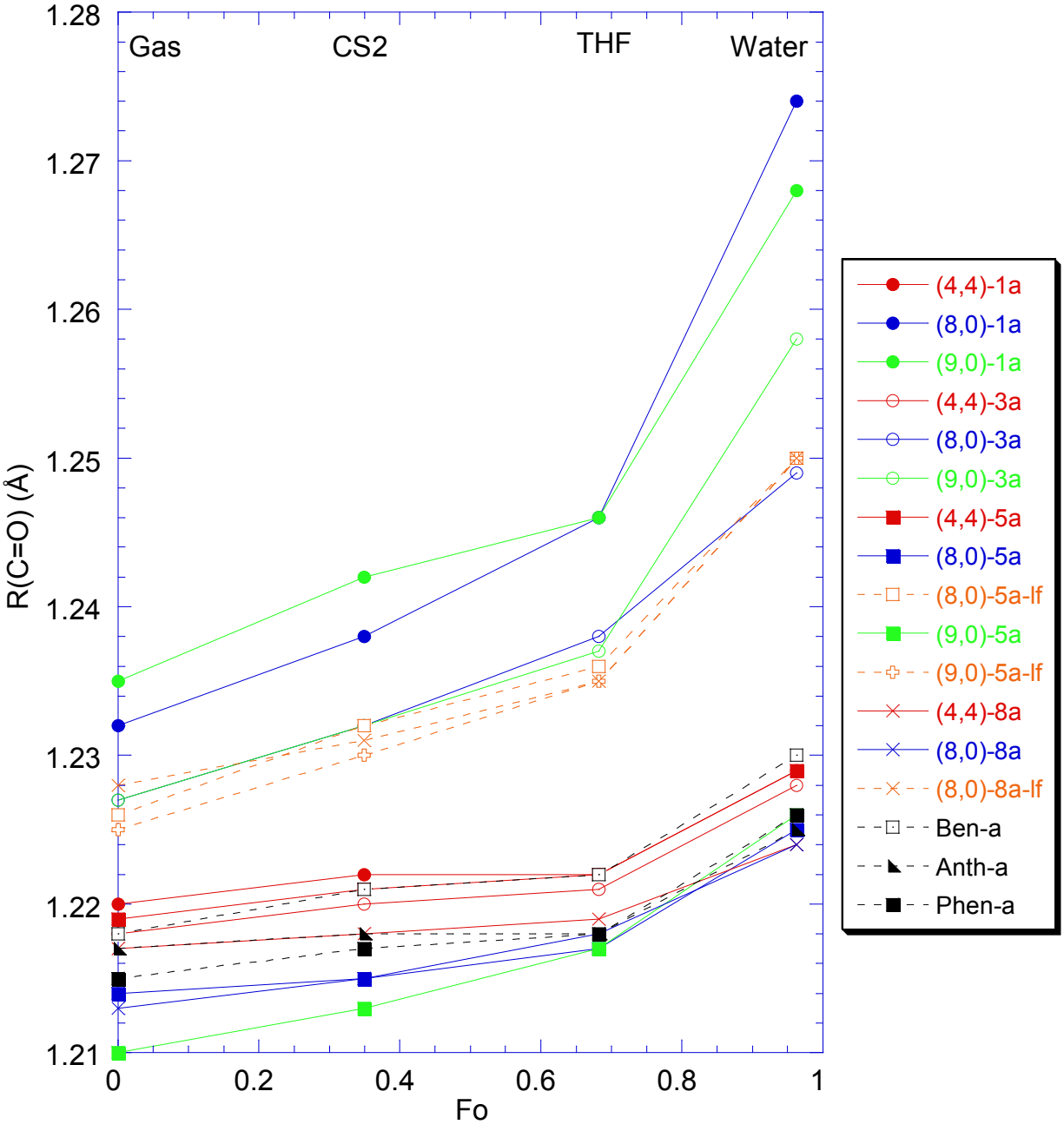
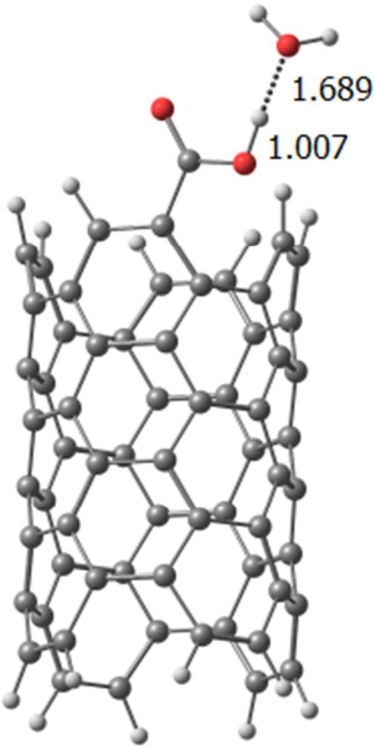
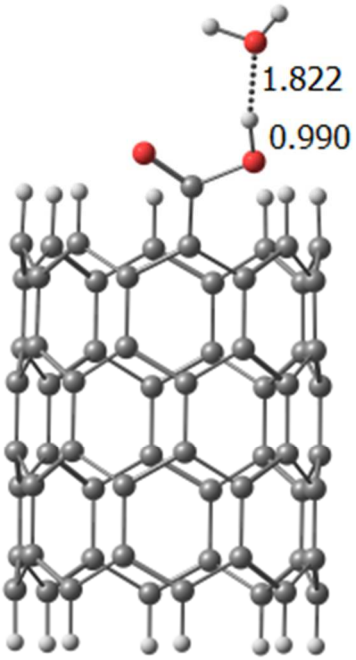


Figure S6. Optimized structures of (4,4)-COOH-H_2O and (8,0)-COOH-H_2O in water as solvent. Distances in Angstrom. H-bond energies are corrected for basis set superposition errors (BSSE energy is from gas-phase calculation).



(4,4)-COOH-H_2O
E(H-bond) = 3.62 kcal/mol



(8,0)-COOH-H_2O
E(H-bond) = 1.75 kcal/mol

Figure S7 - B3LYP IR spectra of (4,4)-COOH and (8,0)-COOH in different medium. FWHF is considered at 20 cm^{-1}. Theoretical frequencies are scaled by 0.96.

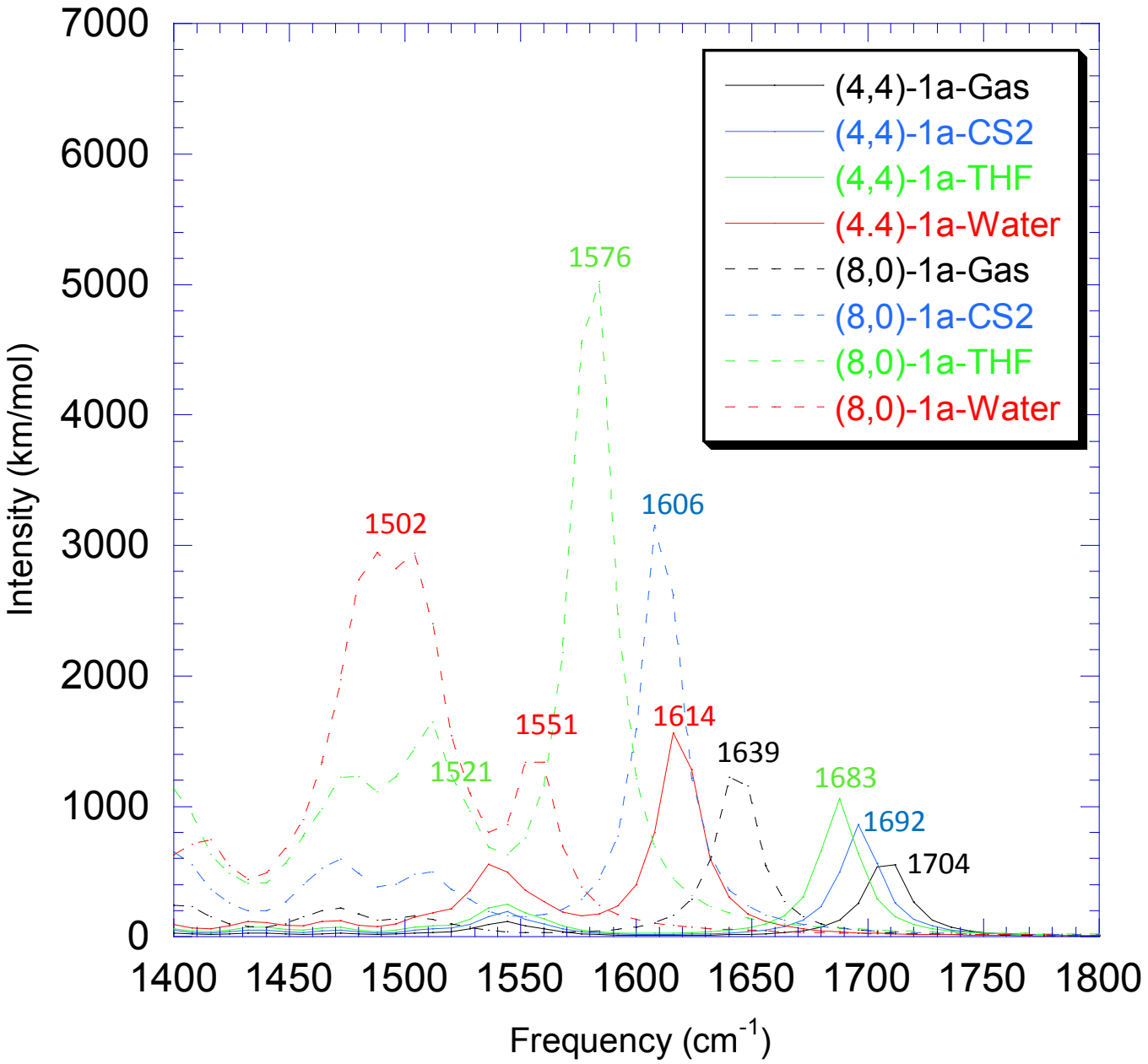


Figure S8 - B3LYP IR spectra of (8,0)-COOH and (9,0)-COOH in different medium. FWHF is considered at 20 cm^{-1}. Theoretical frequencies are scaled by 0.96.

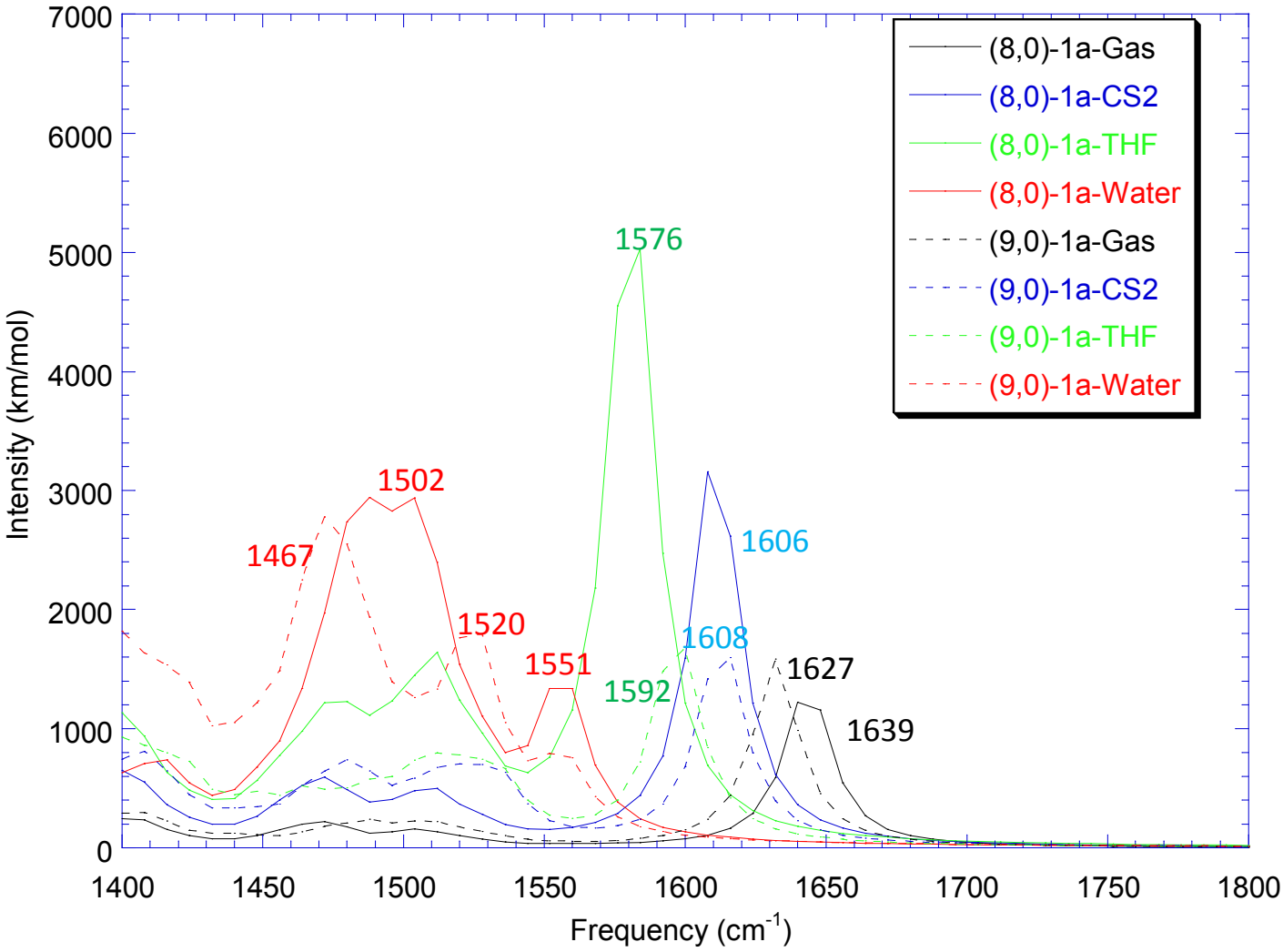


Figure S9 - B3LYP IR spectra of (4,4)-$(COOH)_3$ and (8,0)-$(COOH)_3$ in different medium. FWHF is considered at 20 cm^{-1}. Theoretical frequencies are scaled by 0.96.

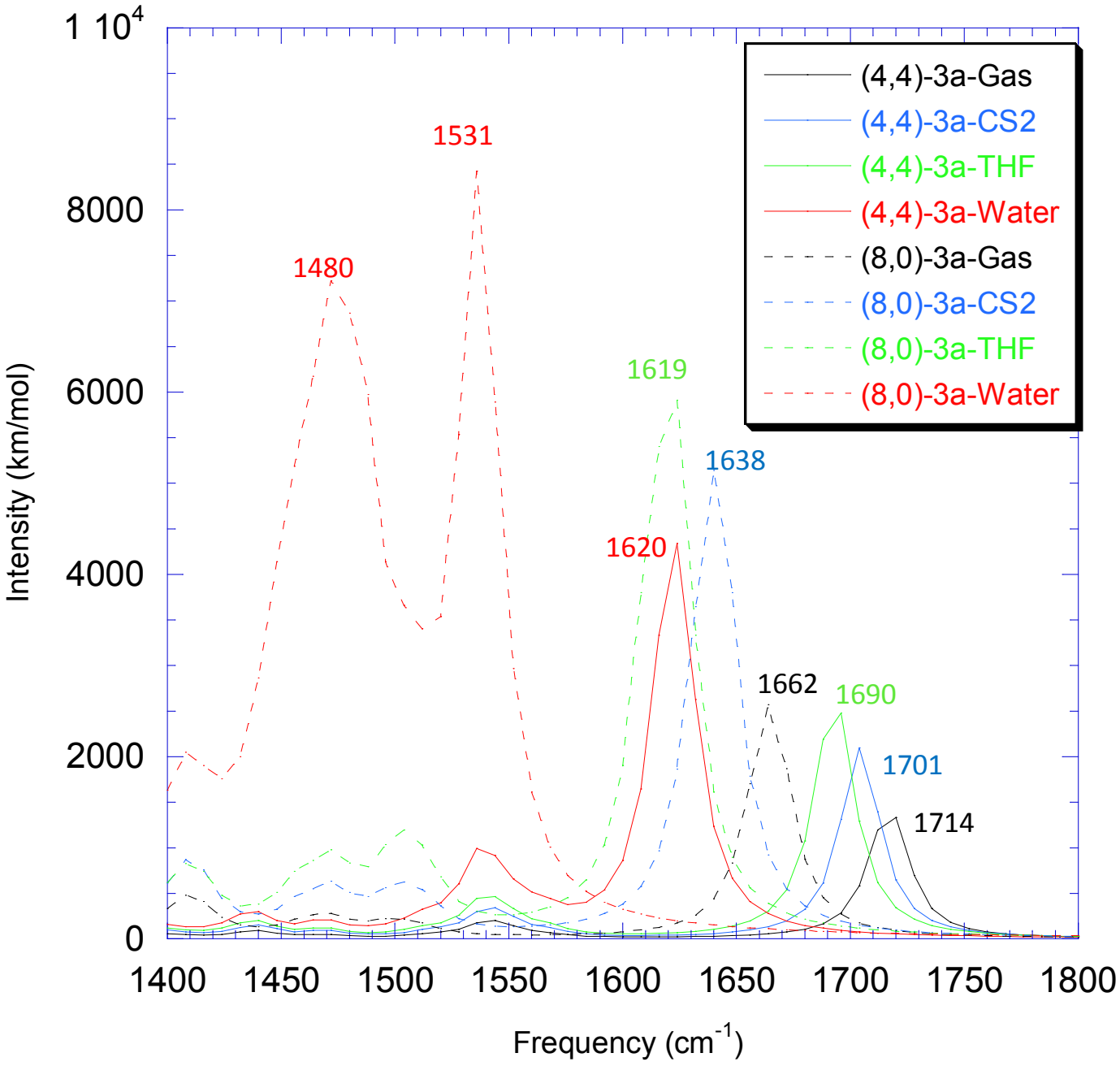


Figure S10 - B3LYP IR spectra of (8,0)-$(COOH)_3$ and (9,0)-$(COOH)_3$ in different medium. FWHF is considered at 20 cm^{-1}. Theoretical frequencies are scaled by 0.96.

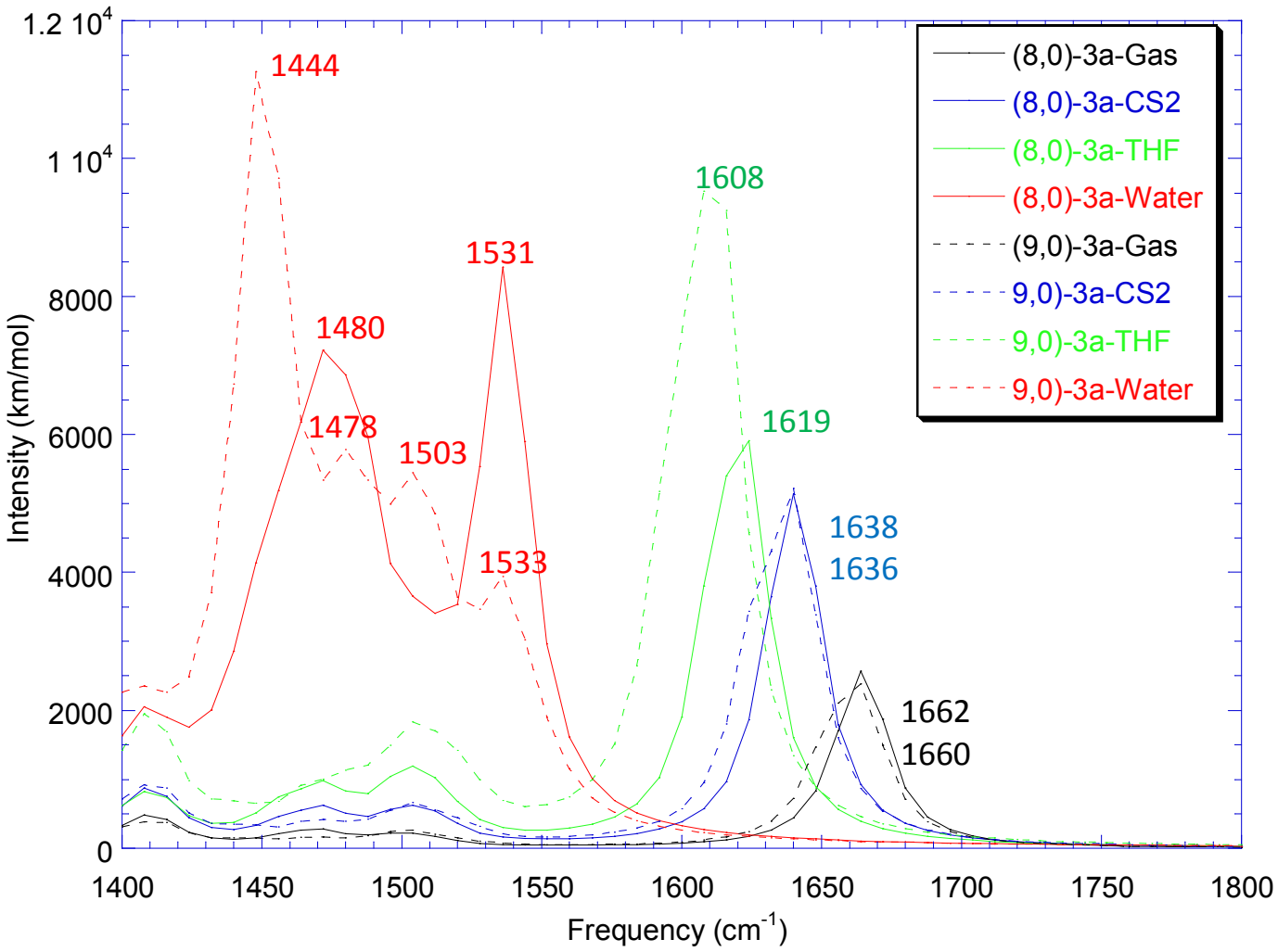
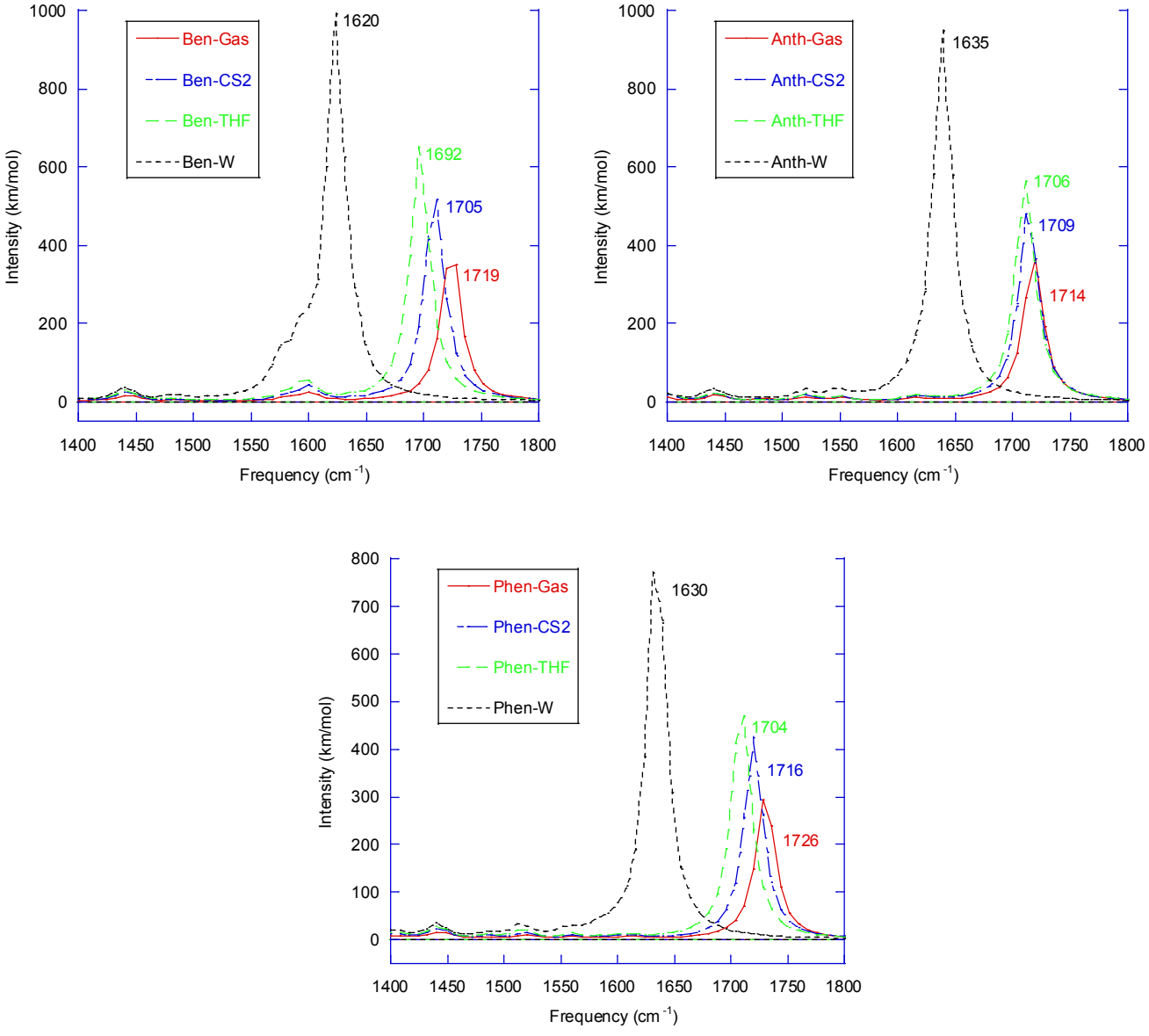
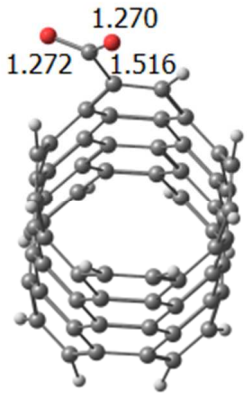


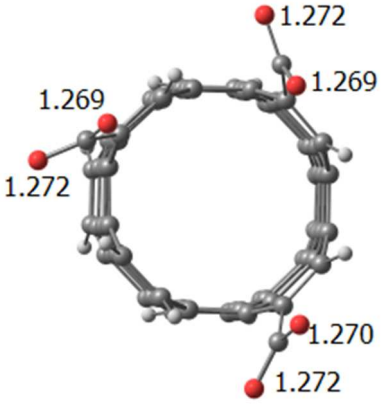
Figure S11 - B3LYP IR spectra of Benzene-COOH (Ben), Anthracene-COOH (Anth) and Phenanthrene-COOH (Phen) in different medium. FWHF is considered at 20 cm^{-1}. Theoretical frequencies are scaled by 0.96.



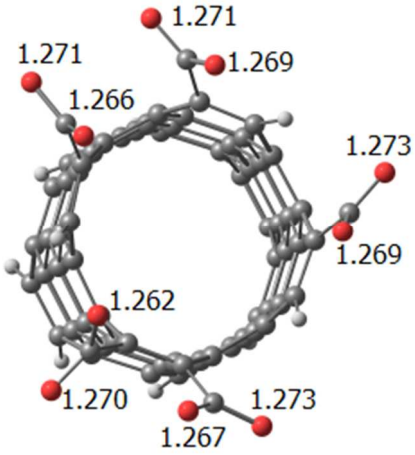
S12. Optimized structures of (4,4)-$(COO)_n^{-n}$ and (8,0)-$(COO)_n^{-n}$, n = 1, 3 and 5. Bond distances are in Angstrom.



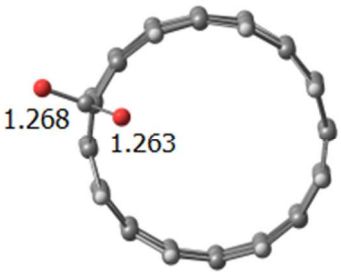
(4,4)-COO^{-1}



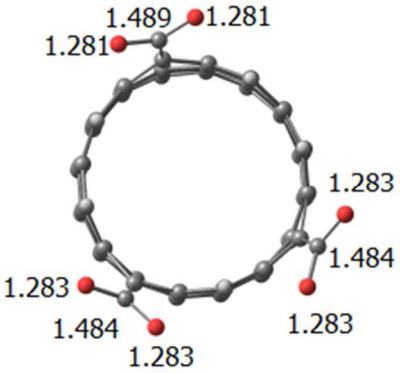
(4,4)-$(COO)_3^{-3}$



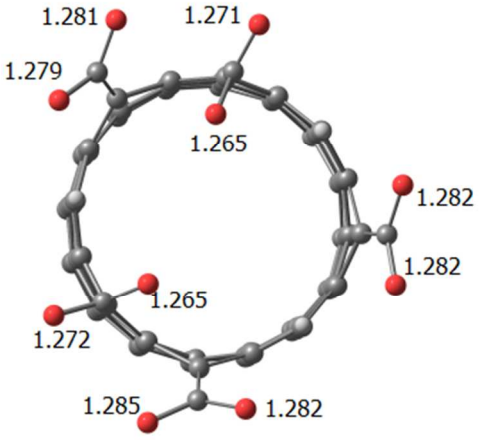
(4,4)-$(COO)_5^{-5}$



(8,0)-COO^{-1}



(8,0)-$(COO)_3^{-3}$



(8,0)-$(COO)_5^{-5}$

Table S1. Key geometric parameters[a] of SWNT-$(COOH)_8$. Bond lengths are in Å

	R(C=O)	R(C-O)	R(O-H)	R(C-COOH)
(4,4)-$(COOH)_8$				
Gas	1.208-1.217	1.336-1.358	0.974-0.977	1.490-1.515
CS2	1.209-1.218	1.334-1.356	0.977-0.979	1.490-1.515
THF	1.210-1.219	1.334-1.352	0.979-0.981	1.489-1.514
Water	1.216-1.224	1.335-1.346	0.979-0.981	1.489-1.510
(8.0)-$(COOH)_8$[b]				
Gas	1.209-1.213 1.223-1.228	1.340-1.352 1.360-1.369	0.976-0.977 0.974-0.975	1.501-1.519 1.451-1.456
CS2	1.211-1.215 1.228-1.231	1.338-1.352 1.346-1.368	0.977-0.978 0.975-0.976	1.500-1.515 1.445-1.447
THF	1.212-1.218 1.232-1.235	1.337-1.353 1.364-1.370	0.978-0.980 0.976-0.977	1.500-1.513 1.440
Water	1.219-1.224 1.246-1.250	1.334-1.347 1.374-1.369	0.980 0.977	1.497-1.505 1.418-1.426

[a] Range of bond distances, [b] The first set of bond lengths correspond to regular COOH groups and the second set of values are for low-frequency (lf) COOH group. See figure S4 for the position of different COOH groups. Single distance is given when such bond lengths are same for all -COOH of the same kind of group.

Table S2. NPA group charges (in me) of COOH groups. Negative numbers indicate charge flow from SWNT to COOH, otherwise from COOH to SWNT.

	(4,4)-COOH	(8,0)-COOH	(9,0)-COOH
Gas	-22	-125	-154
CS2	-26	-177	-209
THF	-25	-245	-240
Water	-35	-420	-163
	(4,4)-$(COOH)_3$	(8,0)-$(COOH)_3$	(9,0)-$(COOH)_3$
Gas	-31	-243	-253
CS2	-43	-340	-335
THF	-47	-418	-443
Water	-80	-628	-842
	(4,4)-$(COOH)_5$	(8,0)-$(COOH)_5$[a]	(9,0)-$(COOH)_5$ [a]
Gas	+89	-110 (-192, +82)	-194 (-241, +47)
CS2	+69	-226 (-290,+64)	-323 (-361, +38)
THF	+58	-315 (-366, +51)	-491 (-514, +23)
Water	+8	-565 (-588, +23)	-829 (-832, +3)

[a] Group charge of lf and r in parenthesis, negative numbers from lf-COOH and positive values from regular COOH groups.