Electronic Supplementary Information for "Simulation of the Resonance Raman Spectra For 5-Halogenated (F, Cl, and Br) Uracils"

Shuai Sun, Alex Brown*

Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2

E-mail: alex.brown@ualberta.ca

Phone: +01 (780) 492-1854. Fax: +01 (780) 492-8231

*To whom correspondence should be addressed

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Table S1: Cartesian Coordinates of 5-Halogenated Uracils Optimized in H_2O (C-PCM) at the PBE0/aug-cc-pVTZ Level of Theory.

	5-fluorouracil		
C	1.19914	0.33679	0.00000
C	1.13808	-1.00145	0.00000
N	-0.06709	-1.63969	0.00000
C	-1.27164	-0.98792	0.00000
N	-1.15726	0.38364	0.00000
C	0.00000	1.14616	0.00000
O	-2.34244	-1.56269	0.00000
O	-0.03403	2.36245	0.00000
H	2.02226	-1.62275	0.00000
H	-0.10265	-2.64640	0.00000
H	-2.02929	0.89401	0.00000
F	2.36650	0.97866	0.00000
	5-chlorouracil		
C	0.00000	0.89771	0.00000
C	-1.29321	0.52604	0.00000
N	-1.65321	-0.78398	0.00000
C	-0.75298	-1.81980	0.00000
N	0.55642	-1.40571	0.00000
C	1.04753	-0.10791	0.00000
O	-1.08261	-2.98836	0.00000
O	2.24425	0.10519	0.00000
H	-2.10297	1.24183	0.00000
H	-2.62868	-1.03764	0.00000
H	1.24794	-2.14239	0.00000
Cl	0.46236	2.55031	0.00000
	5-bromouracil		
C	0.00000	0.35821	0.00000
C	1.34587	0.37934	0.00000
N	2.07257	-0.76806	0.00000
C	1.51364	-2.02199	0.00000
N	0.14106	-2.00796	0.00000
C	-0.70780	-0.90923	0.00000
O	2.17078	-3.04281	0.00000
O	-1.91406	-1.05997	0.00000
H	1.91506	1.29811	0.00000
H	3.07961	-0.72720	0.00000
H	-0.30552	-2.91435	0.00000
Br	-1.00425	1.93599	0.00000

Table S2: Equilibrium Geometries of 5-Halogenated Uracils as Determined in H_2O (C-PCM) at the PBE0/aug-cc-pVTZ Level of Theory.

bond length /Å	5-fluorouracil	experiment[d]	5-chlorouracil	experiment[e]	5-bromouracil	experiment[f]	$\|\Delta r\|$[b]	$\|\Delta r\|$[c]
$r(C_5\text{-}C_6)$	1.3396	1.35	1.3456	1.370	1.3460	1.355	0.0060	0.0064
$r(C_5\text{-}C_4)$	1.4467	1.46	1.4521	1.432	1.4517	1.443	0.0054	0.0050
$r(C_5\text{-}X_{11})$[a]	1.3322	1.36	1.7161	1.715	1.8703	1.867	0.3839	0.5381
$r(C_6\text{-}N_1)$	1.3637	1.39	1.3586	1.374	1.3582	1.372	0.0051	0.0055
$r(C_6\text{-}H_{12})$	1.0806		1.0808	0.96	1.0808	0.96	0.0002	0.0002
$r(N_1\text{-}C_2)$	1.3696	1.40	1.3723	1.363	1.3729	1.358	0.0027	0.0033
$r(N_1\text{-}H_7)$	1.0073		1.0079	1.03	1.0079	0.81	0.0006	0.0006
$r(C_2\text{-}N_3)$	1.3763	1.40	1.3733	1.359	1.3726	1.372	0.0030	0.0037
$r(C_2\text{-}O_8)$	1.2153	1.20	1.2142	1.227	1.214	1.224	0.0011	0.0013
$r(N_3\text{-}C_4)$	1.3859	1.39	1.3876	1.386	1.3884	1.389	0.0017	0.0025
$r(N_3\text{-}H_9)$	1.0104		1.0104	0.85	1.0104	0.94	0.0000	0.0000
$r(C_4\text{-}O_{10})$	1.2168	1.24	1.2155	1.238	1.2156	1.231	0.0013	0.0012
RMSD		0.01		0.02		0.003		

bond angle /°	5-fluorouracil	experiment[d]	5-chlorouracil	experiment[e]	5-bromouracil	experiment[f]	$\|\Delta\theta\|$[b]	$\|\Delta\theta\|$[c]
$\theta(C_6\text{-}C_5\text{-}C_4)$	121.4057	125	120.1343	120.6	120.0803	120.4	1.2714	1.3254
$\theta(C_6\text{-}C_5\text{-}X_{11})$[a]	121.4162	122	121.6652	120.6	121.5771	120.4	0.2490	0.1609
$\theta(C_4\text{-}C_5\text{-}X_{11})$[a]	117.1781	113	118.2005	118.8	118.3426	119.2	1.0224	1.1645
$\theta(C_5\text{-}C_6\text{-}N_1)$	120.5172	118	121.4007	119.3	121.4485	120.4	0.8835	0.9313
$\theta(C_5\text{-}C_6\text{-}H_{12})$	122.4832		122.4897		122.6778		0.0065	0.1946
$\theta(N_1\text{-}C_6\text{-}H_{12})$	116.9996		116.1096		115.8737		0.8900	1.1259

$\theta(C_6\text{-}N_1\text{-}C_2)$	123.6777	122	123.6403	123.4	123.6275	123.3	0.0374	0.0502
$\theta(C_6\text{-}N_1\text{-}H_7)$	119.9282		119.9418		120.0245		0.0136	0.0963
$\theta(C_2\text{-}N_1\text{-}H_7)$	116.3941		116.4179		116.348		0.0238	0.0461
$\theta(N_1\text{-}C_2\text{-}N_3)$	113.6501	116	113.4447	115.4	113.4389	115.2	0.2054	0.2112
$\theta(N_1\text{-}C_2\text{-}O_8)$	123.3571	121	123.2533	122.2	123.2038	122.8	0.1038	0.1533
$\theta(N_3\text{-}C_2\text{-}O_8)$	122.9928	123	123.302	122.5	123.3573	122.0	0.3092	0.3645
$\theta(C_2\text{-}N_3\text{-}C_4)$	128.1482	127	128.2766	126.4	128.2746	126.6	0.1284	0.1264
$\theta(C_2\text{-}N_3\text{-}H_9)$	115.5719		115.6395		115.6436		0.0676	0.0717
$\theta(C_4\text{-}N_3\text{-}H_9)$	116.2799		116.0839		116.0818		0.1960	0.1981
$\theta(C_5\text{-}C_4\text{-}N_3)$	112.6011	112	113.1034	114.9	113.1302	114.1	0.5023	0.5291
$\theta(C_5\text{-}C_4\text{-}O_{10})$	125.6207	126	126.0723	125.7	126.3039	125.8	0.4516	0.6832
$\theta(N_3\text{-}C_4\text{-}O_{10})$	121.7781	122	120.8243	119.4	120.5659	120.1	0.9538	1.2122
RMSD		3.59		1.06		0.86		

dihedral angle /°	5-fluorouracil	5-chlorouracil	5-bromouracil	$\lvert\Delta\phi\rvert^b$	$\lvert\Delta\phi\rvert^c$
$\phi(C_4\text{-}C_5\text{-}C_6\text{-}N_1)$	0.0	0.0	0.0	0	0
$\phi(C_4\text{-}C_5\text{-}C_6\text{-}H_{12})$	180.0	180.0	180.0	0	0
$\phi(X_{11}\text{-}C_5\text{-}C_6\text{-}N_1)^a$	180.0	180.0	180.0	0	0
$\phi(X_{11}\text{-}C_5\text{-}C_6\text{-}H_{12})^a$	0.0	0.0	0.0	0	0
$\phi(C_6\text{-}C_5\text{-}C_4\text{-}N_3)$	0.0	0.0	0.0	0	0
$\phi(C_6\text{-}C_5\text{-}C_4\text{-}O_{10})$	180.0	180.0	180.0	0	0
$\phi(X_{11}\text{-}C_5\text{-}C_4\text{-}N_3)^a$	180.0	180.0	180.0	0	0
$\phi(X_{11}\text{-}C_5\text{-}C_4\text{-}O_{10})^a$	0.0	0.0	0.0	0	0
$\phi(C_5\text{-}C_6\text{-}N_1\text{-}C_2)$	0.0	0.0	0.0	0	0

ϕ(C_5-C_6-N_1-H_7)	180.0	180.0	180.0	0	0
ϕ(H_{12}-C_6-N_1-C_2)	180.0	180.0	180.0	0	0
ϕ(H_{12}-C_6-N_1-H_7)	0.0	0.0	0.0	0	0
ϕ(C_6-N_1-C_2-N_3)	0.0	0.0	0.0	0	0
ϕ(C_6-N_1-C_2-O_8)	180.0	180.0	180.0	0	0
ϕ(H_7-N_1-C_2-N_3)	180.0	180.0	180.0	0	0
ϕ(H_7-N_1-C_2-O_8)	0.0	0.0	0.0	0	0
ϕ(N_1-C_2-N_3-C_4)	0.0	0.0	0.0	0	0
ϕ(N_1-C_2-N_3-H_9)	180.0	180.0	180.0	0	0
ϕ(O_8-C_2-N_3-C_4)	180.0	180.0	180.0	0	0
ϕ(O_8-C_2-N_3-H_9)	0.0	0.0	0.0	0	0
ϕ(C_2-N_3-C_4-C_5)	0.0	0.0	0.0	0	0
ϕ(C_2-N_3-C_4-O_{10})	180.0	180.0	180.0	0	0
ϕ(H_9-N_3-C_4-C_5)	180.0	180.0	180.0	0	0
ϕ(H_9-N_3-C_4-O_{10})	0.0	0.0	0.0	0	0

[a] X=F, Cl, Br.

[b] Difference between 5-chlorouracil and 5-fluorouracil.

[c] Difference between 5-bromouracil and 5-fluorouracil.

[d] Crystal structure of 5-fluorouracil in Ref. 1.

[e] Crystal structure of 5-chlorouracil in Ref. 2.

[f] Crystal structure of 5-bromouracil in Ref. 2.

Table S3: Potential Energy Distribution Analysis and Vibrational Frequencies (ω/cm^{-1}) of Ground State Normal Modes of 5-Fluorouracil at the PBE0/aug-cc-pVTZ level of theory in H_2O (C-PCM).

mode	ω	PED
8	545	+stretch(O_8C_2)[2%]+stretch($O_{10}C_4$)[1%]+stretch(C_5C_6)[2%]+stretch(N_1C_6)[1%]
		+stretch(N_3C_2)[7%]+stretch(N_3C_4)[13%]+stretch($F_{11}C_5$)[1%]+bend($C_4N_3C_2$)[1%]
		-bend($H_9N_3C_4$)[1%]-bend($H_{12}C_6C_5$)[1%]-bend($O_8C_2N_3$)[1%]+bend($O_{10}C_4N_3$)[25%]
		+bend($C_5C_6N_1$)[5%]-bend($C_6N_1C_2$)[16%]-bend($N_3C_2N_1$)[22%]+bend($F_{11}C_5C_4$)[1%]
9	585	+torsion($H_7N_1C_6C_5$)[94%]+torsion($H_9N_3C_4C_5$)[4%]-out-of-plane($O_{10}N_3C_5C_4$)[2%]
10	637	-stretch($O_{10}C_4$)[1%]-stretch(C_5C_6)[5%]+stretch(N_1C_2)[4%]-stretch(N_3C_2)[1%]
		-bend($C_4N_3C_2$)[12%]-bend($H_7N_1C_6$)[1%]+bend($H_9N_3C_4$)[2%]-bend($O_8C_2N_3$)[27%]
		+bend($O_{10}C_4N_3$)[15%]-bend($C_5C_6N_1$)[1%]+bend($C_6N_1C_2$)[1%]-bend($N_3C_2N_1$)[1%]
		+bend($F_{11}C_5C_4$)[28%]
11	662	-torsion($H_7N_1C_6C_5$)[4%]+torsion($H_9N_3C_4C_5$)[90%]+torsion($H_{12}C_6C_5C_4$)[2%]
		-torsion($C_5C_6N_1C_2$)[1%]+torsion($N_3C_2N_1C_6$)[2%]-out-of-plane($O_8N_1N_3C_2$)[1%]
		-out-of-plane($F_{11}C_6C_4C_5$)[1%]
12	762	+stretch($O_{10}C_4$)[2%]+stretch(C_5C_6)[1%]+stretch(N_1C_6)[8%]+stretch(N_1C_2)[17%]
		+stretch(N_3C_2)[9%]+stretch(N_3C_4)[2%]+stretch($F_{11}C_5$)[7%]-bend($C_4N_3C_2$)[12%]
		+bend($H_9N_3C_4$)[1%]-bend($O_8C_2N_3$)[2%]-bend($C_5C_6N_1$)[10%]+bend($C_6N_1C_2$)[5%]
		+bend($N_3C_2N_1$)[22%]-bend($F_{11}C_5C_4$)[1%]
13	772	+torsion($H_9N_3C_4C_5$)[1%]+torsion($C_5C_6N_1C_2$)[3%]-torsion($N_3C_2N_1C_6$)[5%]
		+torsion($C_4N_3C_2N_1$)[3%]+out-of-plane($O_8N_1N_3C_2$)[90%]

14	789	+torsion($H_7N_1C_6C_5$)[1%]-torsion($H_9N_3C_4C_5$)[1%]-torsion($H_{12}C_6C_5C_4$)[3%]
		+torsion($C_5C_6N_1C_2$)[1%]+out-of-plane($O_{10}N_3C_5C_4$)[80%]+out-of-plane($F_{11}C_6C_4C_5$)[15%]
15	826	-stretch(O_8C_2)[8%]-stretch($O_{10}C_4$)[2%]+stretch(C_5C_6)[3%]-stretch(N_1C_6)[1%]
		-stretch(N_1C_2)[8%]-stretch(N_3C_2)[6%]-stretch(N_3C_4)[2%]+stretch($F_{11}C_5$)[19%]
		-bend($C_4N_3C_2$)[11%]+bend($H_7N_1C_6$)[2%]+bend($H_9N_3C_4$)[2%]-bend($H_{12}C_6C_5$)[1%]
		-bend($O_8C_2N_3$)[1%]+bend($O_{10}C_4N_3$)[2%]+bend($C_5C_6N_1$)[25%]-bend($C_6N_1C_2$)[1%]
		+bend($N_3C_2N_1$)[6%]+bend($F_{11}C_5C_4$)[1%]
16	942	+torsion($H_{12}C_6C_5C_4$)[75%]+torsion($C_5C_6N_1C_2$)[11%]-torsion($N_3C_2N_1C_6$)[4%]
		-torsion($C_4N_3C_2N_1$)[1%]+out-of-plane($F_{11}C_6C_4C_5$)[8%]
17	995	-stretch($O_{10}C_4$)[2%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[21%]+stretch(N_3C_2)[12%]
		-stretch(N_3C_4)[1%]-bend($C_4N_3C_2$)[12%]+bend($H_7N_1C_6$)[1%]-bend($H_9N_3C_4$)[6%]
		-bend($H_{12}C_6C_5$)[10%]+bend($O_8C_2N_3$)[1%]-bend($O_{10}C_4N_3$)[6%]+bend($C_5C_6N_1$)[5%]
		-bend($C_6N_1C_2$)[17%]+bend($N_3C_2N_1$)[4%]
18	1185	-stretch(C_5C_6)[1%]-stretch(N_1C_6)[26%]+stretch(N_1C_2)[3%]+stretch(N_3C_2)[3%]
		+stretch(N_3C_4)[6%]-stretch($F_{11}C_5$)[5%]-bend($H_7N_1C_6$)[23%]+bend($H_{12}C_6C_5$)[13%]
		-bend($O_8C_2N_3$)[3%]-bend($O_{10}C_4N_3$)[4%]+bend($C_5C_6N_1$)[10%]-bend($F_{11}C_5C_4$)[2%]
19	1227	+stretch(N_1C_2)[1%]-stretch(N_3C_2)[18%]+stretch(N_3C_4)[34%]-stretch($F_{11}C_5$)[4%]
		-bend($C_4N_3C_2$)[1%]+bend($H_7N_1C_6$)[3%]+bend($H_9N_3C_4$)[11%]-bend($H_{12}C_6C_5$)[18%]
		-bend($O_{10}C_4N_3$)[4%]+bend($C_5C_6N_1$)[1%]-bend($C_6N_1C_2$)[1%]+bend($N_3C_2N_1$)[2%]
		-bend($F_{11}C_5C_4$)[2%]
20	1278	+stretch(C_5C_6)[1%]-stretch(N_1C_6)[27%]+stretch(N_1C_2)[3%]-stretch(N_3C_2)[8%]
		+stretch(N_3C_4)[1%]+stretch($F_{11}C_5$)[39%]+bend($C_4N_3C_2$)[2%]-bend($H_7N_1C_6$)[2%]

		-bend($C_5C_6N_1$)[8%]+bend($C_6N_1C_2$)[3%]-bend($N_3C_2N_1$)[5%]
21	1370	+stretch(C_5C_6)[16%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[2%]-stretch(N_3C_2)[9%] +stretch(N_3C_4)[4%]-stretch($F_{11}C_5$)[3%]+bend($C_4N_3C_2$)[1%]+bend($H_7N_1C_6$)[8%] -bend($H_9N_3C_4$)[2%]+bend($H_{12}C_6C_5$)[39%]+bend($O_8C_2N_3$)[1%]-bend($C_5C_6N_1$)[1%] -bend($C_6N_1C_2$)[6%]+bend($N_3C_2N_1$)[3%]+bend($F_{11}C_5C_4$)[5%]
22	1415	+stretch(O_8C_2)[6%]-stretch($O_{10}C_4$)[8%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[2%] +stretch(N_3C_2)[1%]-stretch(N_3C_4)[7%]+bend($C_4N_3C_2$)[2%]-bend($H_7N_1C_6$)[4%] +bend($H_9N_3C_4$)[59%]+bend($H_{12}C_6C_5$)[3%]+bend($O_8C_2N_3$)[5%]-bend($C_6N_1C_2$)[1%]
23	1454	+stretch(O_8C_2)[5%]-stretch($O_{10}C_4$)[3%]-stretch(N_1C_6)[5%]-stretch(N_1C_2)[12%] +stretch(N_3C_2)[10%]+stretch(N_3C_4)[4%]+stretch($F_{11}C_5$)[4%]-bend($C_4N_3C_2$)[8%] +bend($H_7N_1C_6$)[25%]+bend($H_9N_3C_4$)[3%]+bend($H_{12}C_6C_5$)[1%]-bend($O_8C_2N_3$)[7%] -bend($O_{10}C_4N_3$)[5%]-bend($C_5C_6N_1$)[3%]+bend($C_6N_1C_2$)[4%]+bend($N_3C_2N_1$)[1%]
24	1533	-stretch(O_8C_2)[7%]-stretch($O_{10}C_4$)[2%]+stretch(C_5C_6)[1%]+stretch(N_1C_6)[8%] -stretch(N_1C_2)[18%]+stretch(N_3C_4)[10%]+stretch($F_{11}C_5$)[2%]-bend($C_4N_3C_2$)[3%] -bend($H_7N_1C_6$)[23%]+bend($H_{12}C_6C_5$)[1%]-bend($O_{10}C_4N_3$)[2%]-bend($C_5C_6N_1$)[15%] +bend($C_6N_1C_2$)[5%]+bend($N_3C_2N_1$)[2%]
25	1730	-stretch(O_8C_2)[4%]+stretch($O_{10}C_4$)[15%]+stretch(C_5C_6)[47%]-stretch(N_1C_6)[3%] -stretch(N_3C_4)[2%]-stretch($F_{11}C_5$)[3%]-bend($C_4N_3C_2$)[2%]-bend($H_7N_1C_6$)[1%] +bend($H_9N_3C_4$)[4%]-bend($H_{12}C_6C_5$)[6%]-bend($C_5C_6N_1$)[1%]+bend($C_6N_1C_2$)[3%] -bend($N_3C_2N_1$)[4%]+bend($F_{11}C_5C_4$)[3%]
26	1740	-stretch(O_8C_2)[16%]+stretch($O_{10}C_4$)[40%]-stretch(C_5C_6)[18%]+stretch(N_1C_6)[2%] -stretch(N_3C_4)[1%]+stretch($F_{11}C_5$)[3%]+bend($H_7N_1C_6$)[4%]+bend($H_9N_3C_4$)[6%]

		+bend($H_{12}C_6C_5$)[4%]+bend($O_8C_2N_3$)[1%]-bend($O_{10}C_4N_3$)[2%]-bend($C_6N_1C_2$)[1%] -bend($N_3C_2N_1$)[3%]
27	1782	+stretch(O_8C_2)[49%]+stretch($O_{10}C_4$)[22%]-stretch(N_1C_2)[7%]-stretch(N_3C_2)[3%] -bend($C_4N_3C_2$)[6%]-bend($H_7N_1C_6$)[3%]-bend($C_6N_1C_2$)[3%]+bend($N_3C_2N_1$)[5%]

Table S4: Potential Energy Distribution Analysis and Vibrational Frequencies (ω/cm^{-1}) of Ground State Normal Modes of 5-Chlorouracil at the PBE0/aug-cc-pVTZ level of theory in H_2O (C-PCM).

mode	ω	PED
8	549	+stretch(O_8C_2)[1%]+stretch($O_{10}C_4$)[2%]+stretch(C_5C_6)[2%]+stretch(N_3C_2)[12%]
		+stretch(N_3C_4)[14%]+stretch($Cl_{11}C_5$)[2%]+bend($C_4N_3C_2$)[9%]-bend($H_{12}C_6C_5$)[1%]
		-bend($O_8C_2N_3$)[2%]+bend($O_{10}C_4N_3$)[28%]+bend($C_5C_6N_1$)[1%]-bend($C_6N_1C_2$)[17%]
		-bend($N_3C_2N_1$)[7%]
9	611	+torsion($H_7N_1C_6C_5$)[89%]+torsion($H_9N_3C_4C_5$)[7%]-out-of-plane($O_{10}N_3C_5C_4$)[3%]
10	613	+stretch($O_{10}C_4$)[1%]+stretch(C_5C_6)[2%]-stretch(N_1C_6)[1%]-stretch(N_1C_2)[2%]
		+stretch(N_3C_2)[2%]+stretch($Cl_{11}C_5$)[1%]+bend($C_4N_3C_2$)[13%]+bend($H_7N_1C_6$)[2%]
		-bend($H_9N_3C_4$)[1%]+bend($O_8C_2N_3$)[27%]-bend($O_{10}C_4N_3$)[17%]+bend($C_5C_6N_1$)[2%]
		-bend($C_6N_1C_2$)[4%]+bend($N_3C_2N_1$)[8%]-bend($Cl_{11}C_5C_4$)[16%]
11	675	-torsion($H_7N_1C_6C_5$)[7%]+torsion($H_9N_3C_4C_5$)[87%]+torsion($H_{12}C_6C_5C_4$)[1%]
		-torsion($C_5C_6N_1C_2$)[1%]+torsion($N_3C_2N_1C_6$)[2%]-out-of-plane($O_8N_1N_3C_2$)[1%]
12	676	-stretch(O_8C_2)[1%]+stretch(C_5C_6)[1%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[3%]
		+stretch(N_3C_2)[1%]+stretch($Cl_{11}C_5$)[27%]-bend($C_4N_3C_2$)[10%]+bend($H_9N_3C_4$)[2%]
		-bend($O_8C_2N_3$)[4%]+bend($O_{10}C_4N_3$)[3%]-bend($C_5C_6N_1$)[6%]-bend($C_6N_1C_2$)[7%]
		+bend($N_3C_2N_1$)[33%]
13	773	-torsion($H_7N_1C_6C_5$)[1%]+torsion($H_9N_3C_4C_5$)[1%]+torsion($C_5C_6N_1C_2$)[2%]
		-torsion($N_3C_2N_1C_6$)[4%]+torsion($C_4N_3C_2N_1$)[2%]+out-of-plane($O_8N_1N_3C_2$)[88%]
		-out-of-plane($O_{10}N_3C_5C_4$)[3%]-out-of-plane($Cl_{11}C_6C_4C_5$)[1%]

14	787	+torsion($H_7N_1C_6C_5$)[1%]-torsion($H_{12}C_6C_5C_4$)[2%]+torsion($C_5C_6N_1C_2$)[3%] -torsion($N_3C_2N_1C_6$)[1%]+torsion($C_4N_3C_2N_1$)[2%]+out-of-plane($O_8N_1N_3C_2$)[3%] +out-of-plane($O_{10}N_3C_5C_4$)[79%]+out-of-plane($Cl_{11}C_6C_4C_5$)[9%]
15	797	+stretch(O_8C_2)[5%]+stretch($O_{10}C_4$)[3%]+stretch(C_5C_6)[1%]+stretch(N_1C_6)[4%] +stretch(N_1C_2)[24%]+stretch(N_3C_2)[12%]+stretch(N_3C_4)[5%]-stretch($Cl_{11}C_5$)[3%] +bend($C_4N_3C_2$)[5%]-bend($H_7N_1C_6$)[1%]-bend($O_{10}C_4N_3$)[1%] -bend($C_5C_6N_1$)[2%]+bend($C_6N_1C_2$)[19%]-bend($N_3C_2N_1$)[14%]
16	958	+torsion($H_{12}C_6C_5C_4$)[78%]+torsion($C_5C_6N_1C_2$)[12%]-torsion($N_3C_2N_1C_6$)[5%] -torsion($C_4N_3C_2N_1$)[1%]+out-of-plane($Cl_{11}C_6C_4C_5$)[5%]
17	999	+stretch($O_{10}C_4$)[1%]-stretch(N_1C_6)[1%]-stretch(N_1C_2)[21%]-stretch(N_3C_2)[12%] +stretch(N_3C_4)[1%]+bend($C_4N_3C_2$)[12%]-bend($H_7N_1C_6$)[1%]+bend($H_9N_3C_4$)[6%] +bend($H_{12}C_6C_5$)[9%]-bend($O_8C_2N_3$)[1%]+bend($O_{10}C_4N_3$)[6%]-bend($C_5C_6N_1$)[7%] +bend($C_6N_1C_2$)[17%]-bend($N_3C_2N_1$)[4%]
18	1102	-stretch(O_8C_2)[1%]+stretch(N_1C_6)[2%]-stretch(N_1C_2)[1%]+stretch(N_3C_4)[5%] -stretch($Cl_{11}C_5$)[23%]-bend($C_4N_3C_2$)[4%]+bend($H_9N_3C_4$)[4%]-bend($O_8C_2N_3$)[1%] -bend($O_{10}C_4N_3$)[1%]+bend($C_5C_6N_1$)[38%]-bend($C_6N_1C_2$)[8%]+bend($N_3C_2N_1$)[11%]
19	1207	+stretch(C_5C_6)[2%]+stretch(N_1C_6)[51%]-stretch(N_1C_2)[2%]-stretch(N_3C_2)[1%] -stretch(N_3C_4)[4%]-stretch($Cl_{11}C_5$)[3%]+bend($C_4N_3C_2$)[1%]+bend($H_7N_1C_6$)[24%] -bend($H_{12}C_6C_5$)[6%]+bend($O_8C_2N_3$)[1%]+bend($O_{10}C_4N_3$)[2%]-bend($C_6N_1C_2$)[1%] +bend($N_3C_2N_1$)[1%]+bend($Cl_{11}C_5C_4$)[2%]
20	1233	-stretch(N_1C_6)[1%]-stretch(N_3C_2)[25%]+stretch(N_3C_4)[35%]+bend($H_7N_1C_6$)[3%] +bend($H_9N_3C_4$)[8%]-bend($H_{12}C_6C_5$)[19%]-bend($O_{10}C_4N_3$)[2%]-bend($C_5C_6N_1$)[1%]

		-bend($C_6N_1C_2$)[2%]+bend($N_3C_2N_1$)[2%]-bend($Cl_{11}C_5C_4$)[1%]
21	1360	+stretch(C_5C_6)[23%]+stretch(N_1C_2)[2%]-stretch(N_3C_2)[10%]+stretch(N_3C_4)[2%] +bend($C_4N_3C_2$)[2%]+bend($H_7N_1C_6$)[4%]-bend($H_9N_3C_4$)[2%]+bend($H_{12}C_6C_5$)[44%] +bend($O_8C_2N_3$)[1%]-bend($C_5C_6N_1$)[2%]-bend($C_6N_1C_2$)[4%]+bend($N_3C_2N_1$)[1%] +bend($Cl_{11}C_5C_4$)[2%]
22	1419	+stretch(O_8C_2)[6%]-stretch($O_{10}C_4$)[7%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[1%] +stretch(N_3C_2)[1%]-stretch(N_3C_4)[8%]+bend($C_4N_3C_2$)[1%]-bend($H_7N_1C_6$)[5%] +bend($H_9N_3C_4$)[62%]+bend($H_{12}C_6C_5$)[2%]+bend($O_8C_2N_3$)[5%]-bend($C_6N_1C_2$)[1%]
23	1442	-stretch(O_8C_2)[3%]+stretch($O_{10}C_4$)[3%]+stretch(N_1C_2)[19%]-stretch(N_3C_2)[12%] -stretch(N_3C_4)[7%]-stretch($Cl_{11}C_5$)[1%]+bend($C_4N_3C_2$)[9%]-bend($H_7N_1C_6$)[15%] -bend($H_9N_3C_4$)[3%]-bend($H_{12}C_6C_5$)[4%]+bend($O_8C_2N_3$)[7%]+bend($O_{10}C_4N_3$)[7%] +bend($C_5C_6N_1$)[5%]-bend($C_6N_1C_2$)[3%]-bend($N_3C_2N_1$)[3%]
24	1522	+stretch(O_8C_2)[9%]-stretch(N_1C_6)[15%]+stretch(N_1C_2)[12%]-stretch(N_3C_4)[8%] +bend($C_4N_3C_2$)[1%]+bend($H_7N_1C_6$)[36%]+bend($O_{10}C_4N_3$)[1%]+bend($C_5C_6N_1$)[13%] -bend($C_6N_1C_2$)[2%]-bend($N_3C_2N_1$)[2%]
25	1688	+stretch(C_5C_6)[64%]-stretch(N_1C_6)[7%]-stretch(N_1C_2)[2%]+stretch(N_3C_2)[1%] -stretch(N_3C_4)[1%]-stretch($Cl_{11}C_5$)[2%]-bend($C_4N_3C_2$)[1%]-bend($H_7N_1C_6$)[3%] +bend($H_9N_3C_4$)[1%]-bend($H_{12}C_6C_5$)[13%]-bend($C_5C_6N_1$)[2%]+bend($C_6N_1C_2$)[1%] -bend($N_3C_2N_1$)[1%]+bend($Cl_{11}C_5C_4$)[1%]
26	1738	-stretch(O_8C_2)[13%]+stretch($O_{10}C_4$)[65%]+stretch(N_1C_2)[1%]+stretch(N_3C_2)[1%] -stretch(N_3C_4)[1%]-bend($C_4N_3C_2$)[2%]+bend($H_7N_1C_6$)[1%]+bend($H_9N_3C_4$)[9%] -bend($O_{10}C_4N_3$)[1%]+bend($C_6N_1C_2$)[1%]-bend($N_3C_2N_1$)[4%]

27	1782	+stretch(O_8C_2)[60%]+stretch($O_{10}C_4$)[16%]-stretch(N_1C_2)[6%]-stretch(N_3C_2)[4%] -bend($C_4N_3C_2$)[5%]-bend($H_7N_1C_6$)[4%]-bend($C_6N_1C_2$)[2%]+bend($N_3C_2N_1$)[3%]

Table S5: Potential Energy Distribution Analysis and Vibrational Frequencies (ω/cm^{-1}) of Ground State Normal Modes of 5-Bromouracil at the PBE0/aug-cc-pVTZ level of theory in H_2O (C-PCM).

mode	ω	PED
8	547	+stretch(O_8C_2)[1%]+stretch($O_{10}C_4$)[2%]+stretch(C_5C_6)[2%]+stretch(N_3C_2)[13%]
		+stretch(N_3C_4)[11%]+stretch($Br_{11}C_5$)[3%]+bend($C_4N_3C_2$)[13%]-bend($H_{12}C_6C_5$)[1%]
		-bend($O_8C_2N_3$)[2%]+bend($O_{10}C_4N_3$)[28%]+bend($C_5C_6N_1$)[3%]-bend($C_6N_1C_2$)[17%]
		-bend($N_3C_2N_1$)[2%]-bend($Br_{11}C_5C_4$)[1%]
9	605	+stretch(O_8C_2)[1%]-stretch($O_{10}C_4$)[2%]-stretch(C_5C_6)[1%]+stretch(N_1C_6)[2%]
		+stretch(N_1C_2)[1%]-stretch(N_3C_2)[2%]-stretch($Br_{11}C_5$)[2%]-bend($C_4N_3C_2$)[9%]
		-bend($H_7N_1C_6$)[2%]+bend($H_9N_3C_4$)[1%]-bend($O_8C_2N_3$)[25%]+bend($O_{10}C_4N_3$)[16%]
		+bend($C_6N_1C_2$)[5%]-bend($N_3C_2N_1$)[18%]+bend($Br_{11}C_5C_4$)[13%]
10	609	+torsion($H_7N_1C_6C_5$)[90%]+torsion($H_9N_3C_4C_5$)[6%]-out-of-plane($O_{10}N_3C_5C_4$)[3%]
11	639	-stretch(O_8C_2)[2%]+stretch(N_1C_2)[2%]-stretch(N_3C_4)[1%]+stretch($Br_{11}C_5$)[24%]
		-bend($C_4N_3C_2$)[8%]+bend($H_9N_3C_4$)[3%]-bend($O_8C_2N_3$)[10%]+bend($O_{10}C_4N_3$)[7%]
		-bend($C_5C_6N_1$)[4%]-bend($C_6N_1C_2$)[6%]+bend($N_3C_2N_1$)[31%]-bend($Br_{11}C_5C_4$)[1%]
12	676	-torsion($H_7N_1C_6C_5$)[6%]+torsion($H_9N_3C_4C_5$)[88%]+torsion($H_{12}C_6C_5C_4$)[1%]
		-torsion($C_5C_6N_1C_2$)[1%]+torsion($N_3C_2N_1C_6$)[2%]-out-of-plane($O_8N_1N_3C_2$)[1%]
13	774	-torsion($H_7N_1C_6C_5$)[1%]+torsion($H_9N_3C_4C_5$)[1%]+torsion($C_5C_6N_1C_2$)[2%]
		-torsion($N_3C_2N_1C_6$)[4%]+torsion($C_4N_3C_2N_1$)[2%]+out-of-plane($O_8N_1N_3C_2$)[87%]
		-out-of-plane($O_{10}N_3C_5C_4$)[5%]-out-of-plane($Br_{11}C_6C_4C_5$)[1%]
14	787	+torsion($H_7N_1C_6C_5$)[1%]-torsion($H_{12}C_6C_5C_4$)[1%]+torsion($C_5C_6N_1C_2$)[4%]

		-torsion($N_3C_2N_1C_6$)[2%]+torsion($C_4N_3C_2N_1$)[3%]+out-of-plane($O_8N_1N_3C_2$)[6%]
		+out-of-plane($O_{10}N_3C_5C_4$)[77%]+out-of-plane($Br_{11}C_6C_4C_5$)[7%]
15	794	+stretch(O_8C_2)[4%]+stretch($O_{10}C_4$)[3%]+stretch(C_5C_6)[1%]+stretch(N_1C_6)[5%]
		+stretch(N_1C_2)[25%]+stretch(N_3C_2)[12%]+stretch(N_3C_4)[5%]-stretch($Br_{11}C_5$)[2%]
		+bend($C_4N_3C_2$)[4%]-bend($C_5C_6N_1$)[5%]+bend($C_6N_1C_2$)[21%]-bend($N_3C_2N_1$)[12%]
16	961	+torsion($H_{12}C_6C_5C_4$)[78%]+torsion($C_5C_6N_1C_2$)[12%]-torsion($N_3C_2N_1C_6$)[5%]
		-torsion($C_4N_3C_2N_1$)[1%]+out-of-plane($Br_{11}C_6C_4C_5$)[3%]
17	1001	-stretch($O_{10}C_4$)[1%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[21%]+stretch(N_3C_2)[12%]
		-stretch(N_3C_4)[1%]-bend($C_4N_3C_2$)[13%]+bend($H_7N_1C_6$)[1%]-bend($H_9N_3C_4$)[6%]
		-bend($H_{12}C_6C_5$)[8%]+bend($O_8C_2N_3$)[1%]-bend($O_{10}C_4N_3$)[6%]+bend($C_5C_6N_1$)[6%]
		-bend($C_6N_1C_2$)[17%]+bend($N_3C_2N_1$)[3%]
18	1074	-stretch(O_8C_2)[1%]+stretch(N_1C_6)[3%]-stretch(N_1C_2)[2%]+stretch(N_3C_4)[3%]
		-stretch($Br_{11}C_5$)[16%]-bend($C_4N_3C_2$)[4%]+bend($H_9N_3C_4$)[4%]-bend($H_{12}C_6C_5$)[1%]
		-bend($O_8C_2N_3$)[1%]-bend($O_{10}C_4N_3$)[1%]+bend($C_5C_6N_1$)[40%]-bend($C_6N_1C_2$)[10%]
		+bend($N_3C_2N_1$)[13%]
19	1204	+stretch(C_5C_6)[2%]+stretch(N_1C_6)[51%]-stretch(N_1C_2)[3%]-stretch(N_3C_4)[10%]
		-stretch($Br_{11}C_5$)[2%]+bend($C_4N_3C_2$)[1%]+bend($H_7N_1C_6$)[21%]-bend($H_9N_3C_4$)[1%]
		-bend($H_{12}C_6C_5$)[2%]+bend($O_8C_2N_3$)[1%]+bend($O_{10}C_4N_3$)[3%]-bend($C_5C_6N_1$)[1%]
		-bend($C_6N_1C_2$)[1%]+bend($N_3C_2N_1$)[1%]+bend($Br_{11}C_5C_4$)[2%]
20	1235	+stretch(N_1C_2)[1%]-stretch(N_3C_2)[26%]+stretch(N_3C_4)[29%]+bend($H_7N_1C_6$)[7%]
		+bend($H_9N_3C_4$)[7%]-bend($H_{12}C_6C_5$)[20%]-bend($O_{10}C_4N_3$)[1%]-bend($C_5C_6N_1$)[2%]
		-bend($C_6N_1C_2$)[2%]+bend($N_3C_2N_1$)[3%]

21	1361	+stretch(C_5C_6)[24%]+stretch(N_1C_2)[2%]-stretch(N_3C_2)[10%]+stretch(N_3C_4)[2%] +bend($C_4N_3C_2$)[2%]+bend($H_7N_1C_6$)[3%]-bend($H_9N_3C_4$)[2%]+bend($H_{12}C_6C_5$)[47%] +bend($O_8C_2N_3$)[1%]-bend($C_5C_6N_1$)[1%]-bend($C_6N_1C_2$)[3%]+bend($N_3C_2N_1$)[1%] +bend($Br_{11}C_5C_4$)[2%]
22	1418	+stretch(O_8C_2)[5%]-stretch($O_{10}C_4$)[7%]+stretch(N_1C_6)[1%]+stretch(N_1C_2)[2%] +stretch(N_3C_2)[1%]-stretch(N_3C_4)[8%]+bend($C_4N_3C_2$)[2%]-bend($H_7N_1C_6$)[6%] +bend($H_9N_3C_4$)[61%]+bend($H_{12}C_6C_5$)[2%]+bend($O_8C_2N_3$)[5%]-bend($C_6N_1C_2$)[1%]
23	1438	+stretch(O_8C_2)[3%]-stretch($O_{10}C_4$)[3%]+stretch(N_1C_6)[1%]-stretch(N_1C_2)[19%] +stretch(N_3C_2)[12%]+stretch(N_3C_4)[7%]-bend($C_4N_3C_2$)[10%]+bend($H_7N_1C_6$)[14%] +bend($H_9N_3C_4$)[4%]+bend($H_{12}C_6C_5$)[4%]-bend($O_8C_2N_3$)[7%]-bend($O_{10}C_4N_3$)[7%] -bend($C_5C_6N_1$)[4%]+bend($C_6N_1C_2$)[3%]+bend($N_3C_2N_1$)[3%]
24	1518	+stretch(O_8C_2)[9%]-stretch(N_1C_6)[16%]+stretch(N_1C_2)[12%]-stretch(N_3C_4)[8%] +bend($C_4N_3C_2$)[1%]+bend($H_7N_1C_6$)[37%]-bend($H_{12}C_6C_5$)[1%]+bend($O_{10}C_4N_3$)[1%] +bend($C_5C_6N_1$)[11%]-bend($C_6N_1C_2$)[2%]-bend($N_3C_2N_1$)[1%]
25	1681	+stretch(C_5C_6)[63%]-stretch(N_1C_6)[7%]-stretch(N_1C_2)[2%]+stretch(N_3C_2)[1%] -stretch(N_3C_4)[1%]-stretch($Br_{11}C_5$)[1%]-bend($C_4N_3C_2$)[1%]-bend($H_7N_1C_6$)[3%] +bend($H_9N_3C_4$)[1%]-bend($H_{12}C_6C_5$)[13%]-bend($O_8C_2N_3$)[1%]-bend($C_5C_6N_1$)[2%] +bend($C_6N_1C_2$)[2%]-bend($N_3C_2N_1$)[1%]+bend($Br_{11}C_5C_4$)[1%]
26	1736	-stretch(O_8C_2)[10%]+stretch($O_{10}C_4$)[68%]+stretch(N_1C_2)[1%]+stretch(N_3C_2)[1%] -stretch(N_3C_4)[1%]-bend($C_4N_3C_2$)[3%]+bend($H_7N_1C_6$)[1%]+bend($H_9N_3C_4$)[9%] -bend($O_{10}C_4N_3$)[1%]+bend($C_6N_1C_2$)[1%]-bend($N_3C_2N_1$)[4%]
27	1782	+stretch(O_8C_2)[62%]+stretch($O_{10}C_4$)[14%]-stretch(N_1C_2)[6%]-stretch(N_3C_2)[4%]

-bend($C_4N_3C_2$)[5%]-bend($H_7N_1C_6$)[4%]-bend($C_6N_1C_2$)[2%]+bend($N_3C_2N_1$)[2%]

Table S6: Vibrational Frequencies (ω/cm^{-1}) and Dimensionless Displacements ($|\Delta|$) for the S_1 Excited State of 5-Halogenated Uracils at the CAMB3LYP/aug-cc-pVTZ level of theory with the ground state equilibrium geometry determined using PBE0/aug-cc-pVTZ in H_2O (C-PCM).

5-fluorouracil	modes	8	9	10	11	12	13	14	15	16	17	18	19
	ω	545	585	637	662	762	772	789	826	942	995	1185	1227
	$\|\Delta\|$	0.7051	0.0000	0.3025	0.0000	0.6311	0.0000	0.0000	0.5241	0.0000	0.0457	0.0253	0.5852
	modes	20	21	22	23	24	25	26	27				
	ω	1278	1370	1415	1454	1533	1730	1740	1782				
	$\|\Delta\|$	0.5348	0.9796	0.2126	0.0775	0.3863	1.1035	0.1935	0.2688				
5-chlorouracil	modes	8	9	10	11	12	13	14	15	16	17	18	19
	ω	549	611	613	675	676	773	787	797	958	999	1102	1207
	$\|\Delta\|$	0.5591	0.0000	0.4572	0.0000	0.2412	0.0000	0.0000	0.8020	0.0000	0.0733	0.0312	0.0216
	modes	20	21	22	23	24	25	26	27				
	ω	1233	1360	1419	1442	1522	1688	1738	1782				
	$\|\Delta\|$	0.6093	0.9867	0.2054	0.1840	0.3436	1.0617	0.2603	0.2945				
5-bromouracil	modes	8	9	10	11	12	13	14	15	16	17	18	19
	ω	547	605	609	639	676	774	787	794	961	1001	1074	1204
	$\|\Delta\|$	0.4571	0.4802	0.0000	0.1282	0.0000	0.0000	0.0000	0.8029	0.0000	0.1084	0.0243	0.0202
	modes	20	21	22	23	24	25	26	27				
	ω	1235	1361	1418	1438	1518	1681	1736	1782				
	$\|\Delta\|$	0.6261	0.9782	0.1603	0.1928	0.3367	1.0354	0.2775	0.2893				

Table S7: Relative Peak Intensities of Resonance Raman Spectra for 5-Fluorouracil Simulated with Different Incident Light Energies (ω_{in}) and Vertical Excitation Energies (ω_{ge}).

ω_{in}	ω_{ge}	mode	8	9	10	11	12	13	14	15	16	17
		ω/cm^{-1}	545.10	585.46	636.95	662.36	762.31	771.98	788.83	826.33	941.63	994.51
4.7 eV	4.7 eV	intensity	0.04	0.00	0.01	0.00	0.06	0.00	0.00	0.05	0.00	0.00
4.5 eV	4.7 eV	intensity	0.11	0.00	0.03	0.00	0.13	0.00	0.00	0.10	0.00	0.00
4.5 eV	4.9 eV	intensity	0.19	0.00	0.04	0.00	0.20	0.00	0.00	0.15	0.00	0.00
ω_{in}	ω_{ge}	mode	18	19	20	21	22	23	24	25	26	27
		ω/cm^{-1}	1184.77	1227.33	1277.98	1370.01	1414.68	1454.08	1533.47	1729.60	1740.35	1782.21
4.7 eV	4.7 eV	intensity	0.00	0.14	0.13	0.50	0.03	0.00	0.10	1.00	0.03	0.06
4.5 eV	4.7 eV	intensity	0.00	0.16	0.14	0.51	0.03	0.00	0.10	1.00	0.03	0.06
4.5 eV	4.9 eV	intensity	0.00	0.24	0.20	0.71	0.03	0.00	0.12	1.00	0.03	0.06

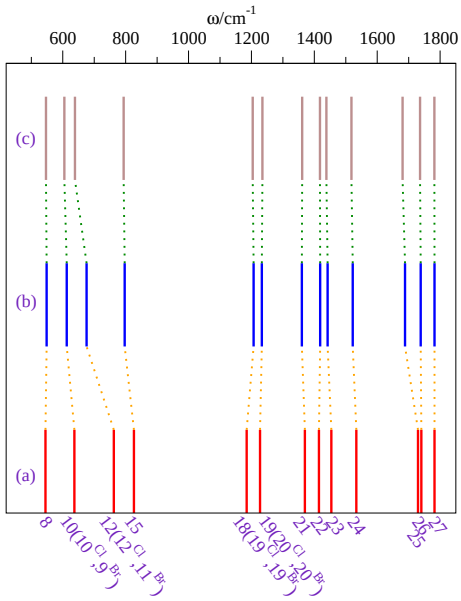

Figure S1: Comparison between the ground state vibrational frequencies of (a) 5-fluorouracil (b) 5-chlorouracil and (c) 5-bromouracil. x-axis is vibrational mode numbered according to 5-fluorouracil, unless indicated otherwise, i.e., N^{Cl}, N^{Br}.

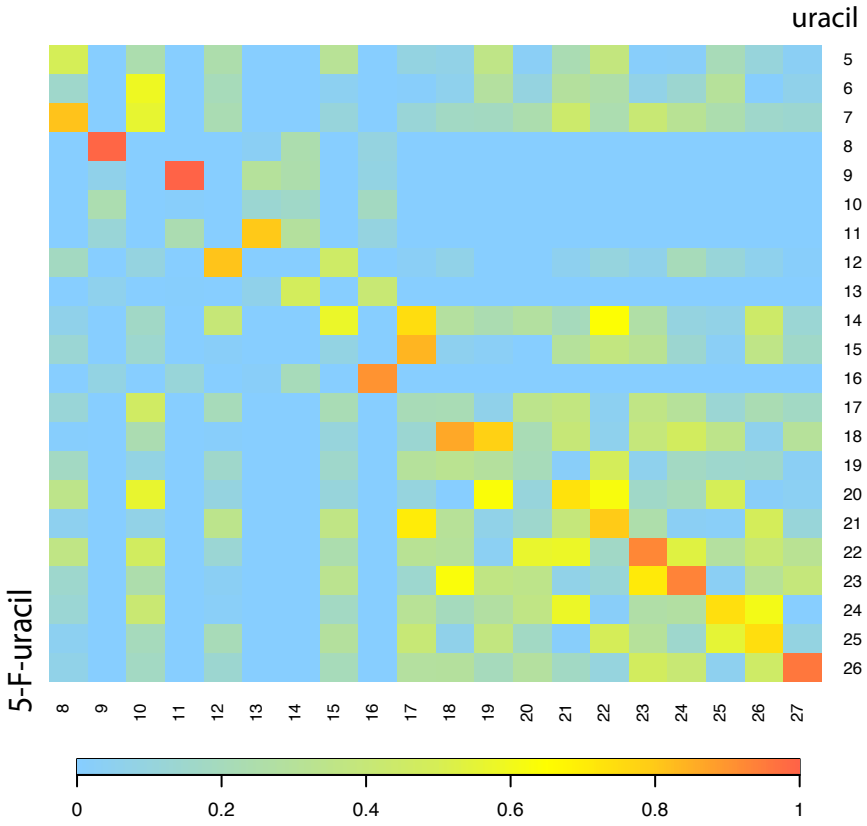

Figure S2: The cosine similarity for the normal modes of 5-fluorouracil vs. uracil. x- and y-axes are corresponding vibrational mode numbering.

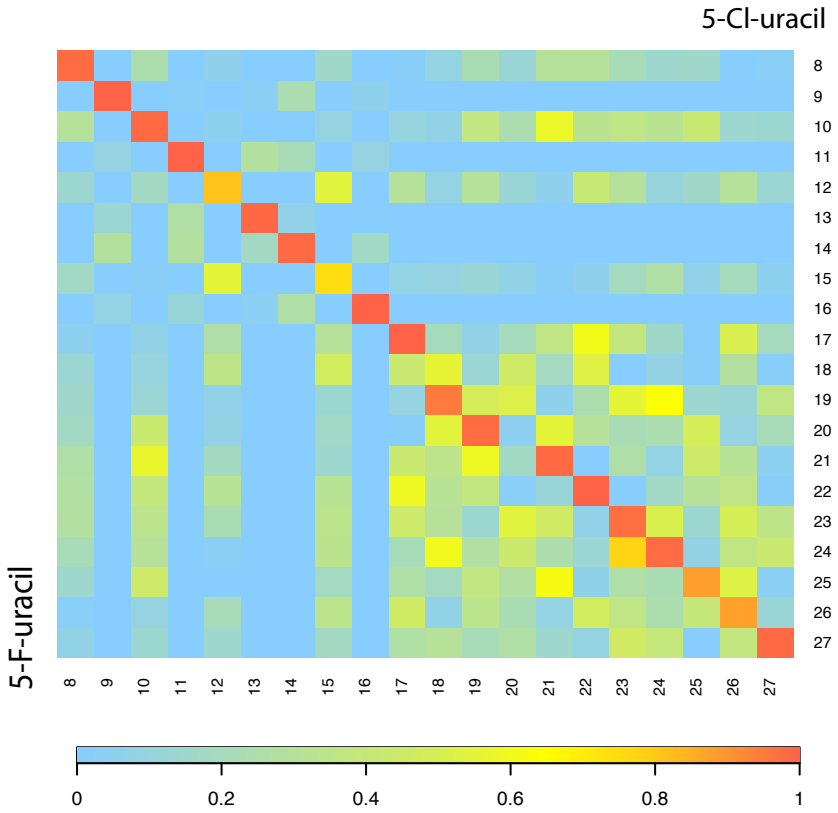

Figure S3: The cosine similarity for the normal modes of 5-fluorouracil vs. 5-chlorouracil. x- and y-axes are corresponding vibrational mode numbering.

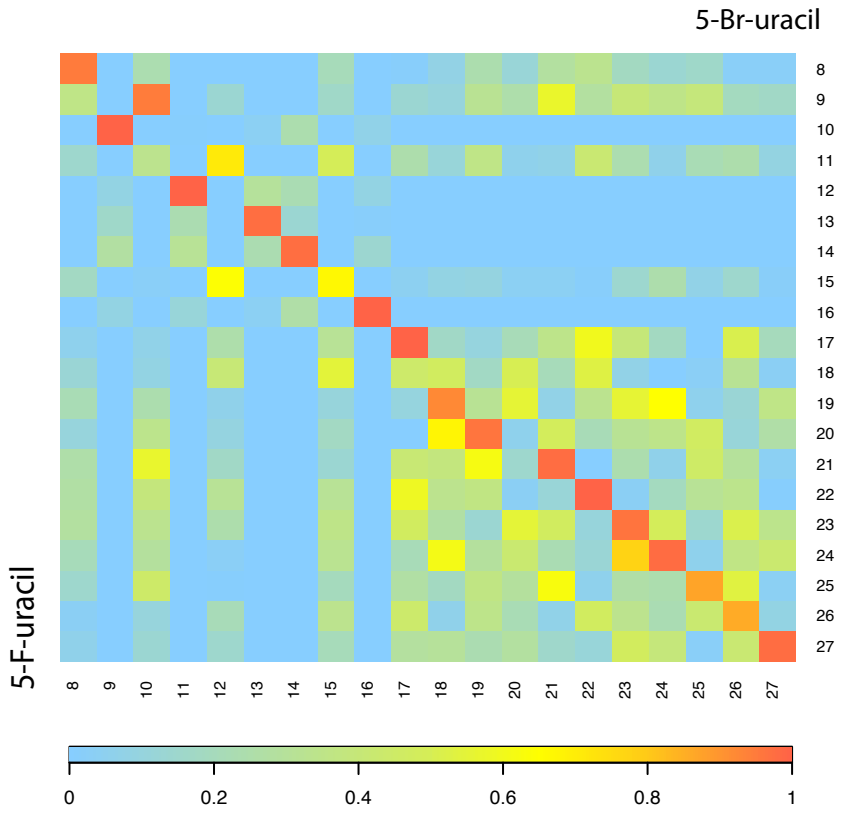

Figure S4: The cosine similarity for the normal modes of 5-fluorouracil vs. 5-bromouracil. x- and y-axes are corresponding vibrational mode numbering.

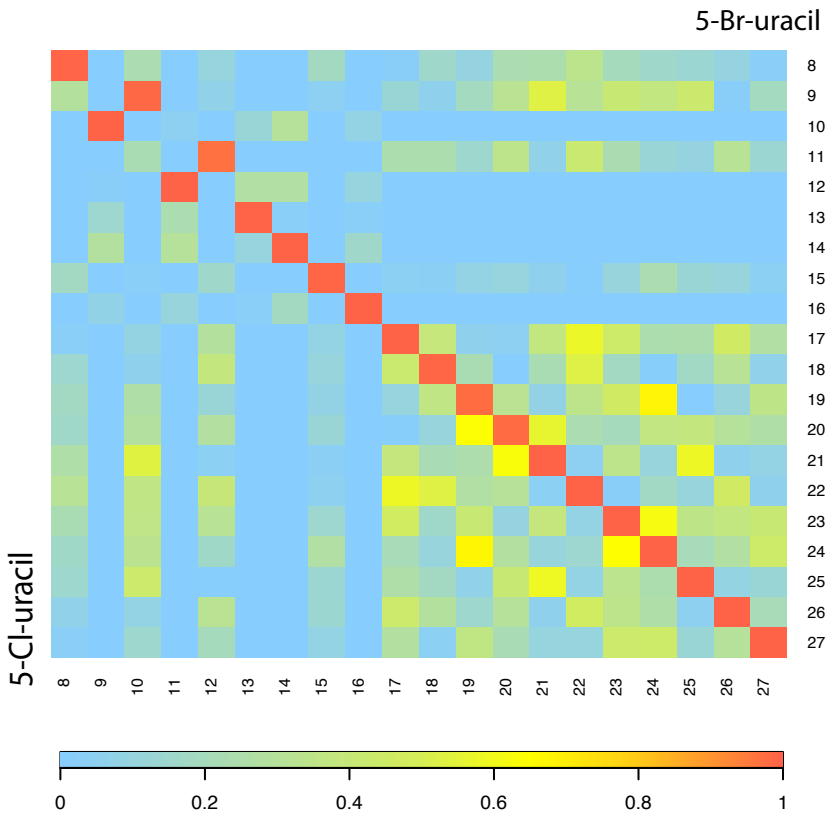

Figure S5: The cosine similarity for the normal modes of 5-chlorouracil vs. 5-bromouracil. x- and y-axes are corresponding vibrational mode numbering.

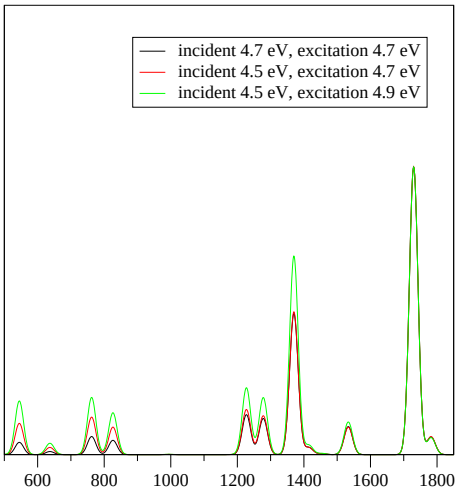

Figure S6: Resonance Raman spectra for 5-fluorouracil simulated with (a) $\omega_{\text{in}} = \omega_{ge}$, (b) $\omega_{\text{in}} = 4.5$ eV (experiment) and $\omega_{ge} = 4.7$ eV (experiment), and (c) $\omega_{\text{in}} = 4.5$ eV (experiment) and $\omega_{ge} = 4.9$ eV (computation).

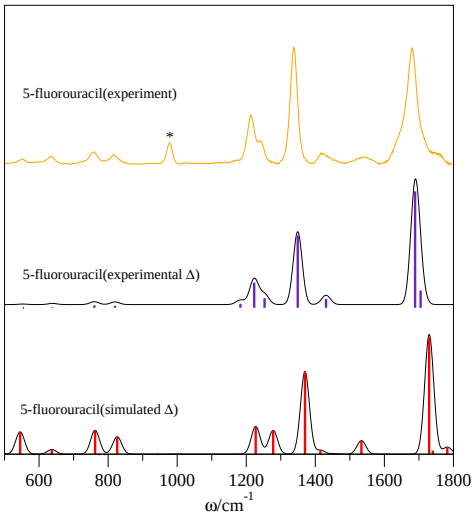

Figure S7: Resonance Raman spectra for 5-fluorouracil simulated with the experimentally-fit and TD-DFT computed $|\Delta|$s.

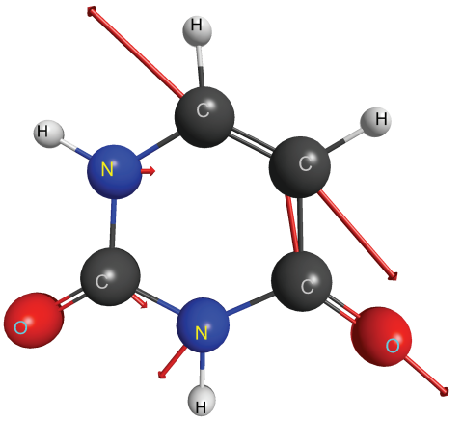

Figure S8: Vectors illustrating the Cartesian gradients for each atom of uracil using TD-CAMB3LYP/aug-cc-pVTZ in H_2O (C-PCM) for the S_1 excited state.

References

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(2) Sternglanz, H.; Bugg, C. E. Relationship Between the Mutagenic and Base-stacking Properties of Halogenated Uracil Derivatives. The Crystal Structures of 5–chloro– and 5–bromouracil. *Biochim. Biophys. Acta, Nucleic Acids Protein Synth.* **1975**, *378*, 1–11.