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

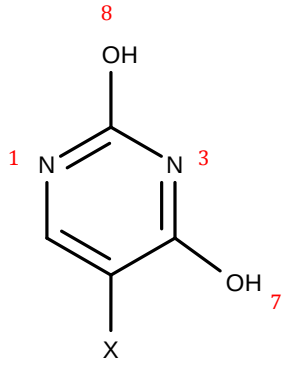
Supplementary Information : An experimental and theoretical investigation of the XPS and NEXAFS of the 5-halouracils

M.C. Castrovilli, P. Bolognesi, E. Bodo, G. Mattioli, A. Cartoni and L. Avaldi

SI.1 Calculations of the binding energies of the N and O 1s in the enolic forms using the ADF method

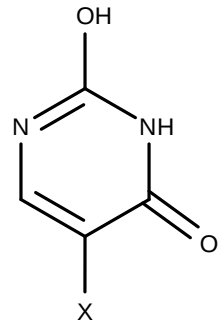
Enolic form (37-18)

	Expt		Theor
Cl-U	537.28	O7	540.31
	537.79	O8	540.04
	406.88	N1	405.13
	406.63	N3	405.35
Br-U	537.17	O7	540.27
	537.74	O8	540.01
	406.95	N1	405.07
	406.45	N3	405.29



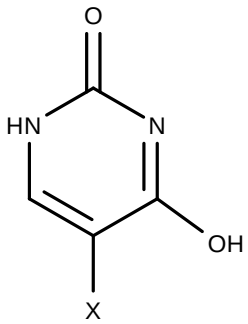
Enolic form (18)

	Expt		Theor
Cl-U	537.28	O7	537.45
	537.79	O8	540.82
	406.88	N1	405.34
	406.63	N3	407.281
Br-U	537.17	O7	537.41
	537.74	O8	540.79
	406.95	N1	405.28
	406.45	N3	407.22



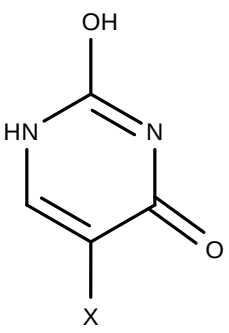
Enolic form (37)

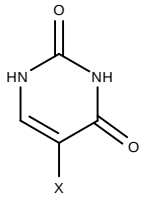
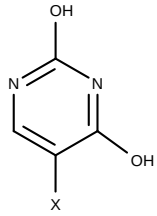
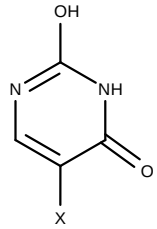
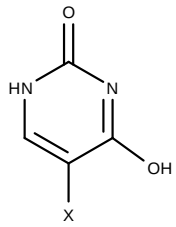
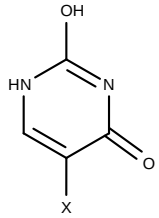
	Expt	Num std	Theor
Cl-U	537.28	O7	540.36
	537.79	O8	537.13
	406.88	N1	407.01
	406.63	N3	405.01



Enolic form (18)

	Expt	Num std	Theor
Cl-U	537.28	O7	536.89
	537.79	O8	540.710
	406.88	N1	407.591
	406.63	N3	404.95



Structure		DE (kcal/mol)	Alogen
	KETO	0.0	
	ENOL 18-37	11.5 11.7 11.7 12.6	Br Cl F I
	ENOL 18	9.5 9.7 9.3 10.5	Br Cl F I
	ENOL 37	11.7 12.1 12.4 12.6	Br Cl F I
	ENOL 38	17.5 17.7 16.9 18.5	Br Cl F I

Relative energies (kcal/mol). Method: all electron, ZORA B3LYP/ZORA-def2-TZVP(-f)

SI.2 NEXAFS Calculations

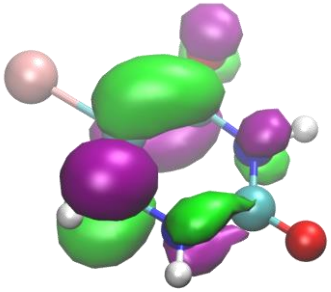
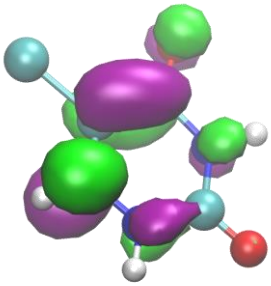
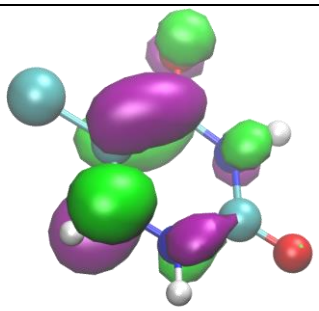
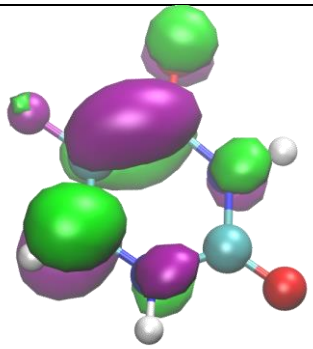
SI.2.1 C 1s excitation

Table 1: Selected excitation energies and oscillator strengths as obtained with CAM-B3LYP. The calculated values have been shifted by 10.2 eV to match the experimental values. The corresponding single excitations with values of the square modulus of the CI coefficient larger than 0.1 are also reported.

Molecule	Band	Energy (eV)	osc. str.	Composition ($\|C\|^2$>0.1)
5F-Uracil	a2	286.037	0.046	C6(1s)→33 (LUMO) c=1
	a1	286.706	0.020	C5(1s)→33 c=0.9
	a3	287.340	0.045	C4(1s)→33 c=0.8
		288.513	0.010	C6(1s)→34 c=0.8
		288.923	0.064	C2(1s)→37 c=0.2 C2(1s)→38 c=0.6
		289.312	0.008	C6(1s)→37 c=0.1 C6(1s)→38 c=0.4
		289.349	0.012	C5(1s)→37 c=0.1 C5(1s)→38 c=0.4
5Cl-Uracil	a1+a2	285.906	0.024	C5(1s)→37 (LUMO) c=1
	a1+a2	285.993	0.042	C6(1s)→37 c=0.9
	a3	287.389	0.043	C4(1s)→37 c=0.1
		287.912	0.033	C5(1s)→43 c=0.2 C5(1s)→48 c=0.2
		288.463	0.016	C5(1s)→41 c=0.3 C5(1s)→42 c=0.5
		288.506	0.010	C6(1s)→38 c=0.7
	a4	288.857	0.060	C2(1s)→37 c=0.2 C2(1s)→41 c=0.2 C2(1s)→42 c=0.5
5Br-Uracil	a1+a2	285.745	0.024	C5(1s)→46 (LUMO) c=1
	a1+a2	286.002	0.045	C6(1s)→46 c=0.1
		287.068	0.037	C5(1s)→47 c=0.2 C5(1s)→48 c=0.4 C5(1s)→51 c=0.1
	a3	287.396	0.045	C4(1s)→46 c=0.8
		288.303	0.016	C5(1s)→50 c=0.3 C5(1s)→52 c=0.5
		288.325	0.010	C6(1s)→47 c=0.7
	a4	288.850	0.062	C2(1s)→52 c=0.5 C2(1s)→46 c=0.2
5I-Uracil	a1	285.548	0.020	C5(1s)→55 (LUMO) c=1
	a2	286.045	0.036	C6(1s)→55 c=0.9
		286.310	0.046	C5(1s)→56 c=0.7 C5(1s)→57 c=0.3

a3	287.528	0.046	C4(1s)→55 c=0.8
	288.042	0.009	C6(1s)→56 c=0.9
	288.099	0.073	C5(1s)→59 c=0.7
	288.673	0.001	C5(1s)→56 c=0.2 C5(1s)→57 c=0.7

Table 2: KS (CAM-B3LYP) molecular orbitals involved in the transitions reported in Table 1.

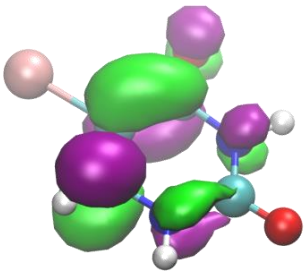
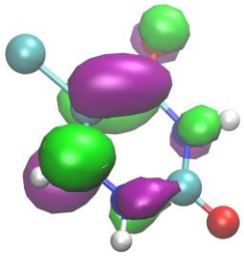
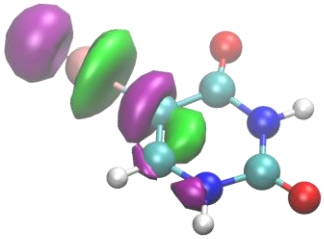
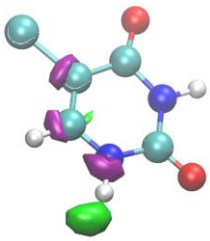
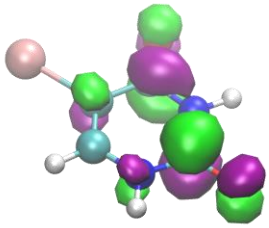
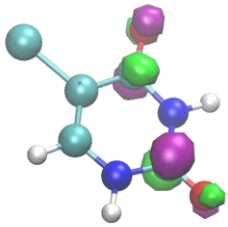
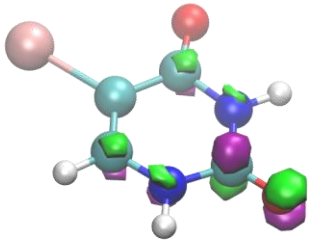
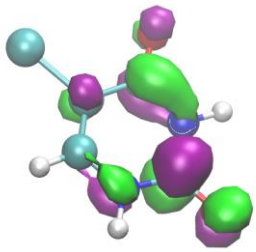
I	Br
 LUMO (55)	 LUMO (46)
Cl	F
 LUMO (37)	 LUMO (33)

SI.2.2 N1s excitation

Table 3: Selected excitation energies and oscillator strengths as obtained with CAM-B3LYP. The calculated values have been shifted by 13.4 eV to match the experimental values. The corresponding single excitations with values of the square modulus of the CI coefficient larger than 0.1 are also reported.

Element	Band	Energy (eV)	Osc. Str.	Composition ($\|C\|^2$ >0.1)
5F-Uracil	b1	402.571	0.012	N3 1s→33 (LUMO) c=1
	b1	402.972	0.008	N1 1s →33 c=1
	b2	403.726	0.004	N3 1s →37 c=0.1 N3 1s →38 c=0.8
	b2	404.157	0.009	N1 1s →34 c=0.8
	b2	404.176	0.010	N1 1s →38 c=0.7 N1 1s →37 c=0.1
	b2	404.527	0.007	N3 1s →34 c=0.2 N3 1s →35 c=0.5
5Cl-Uracil	b1	402.573	0.012	N3 1s →37 (LUMO) c=1
	b1	402.858	0.008	N1 1s →37 c=1
	b2	403.634	0.002	N3 1s →41 c=0.3 N3 1s →42 c=0.7
	b2	404.159	0.008	N1 1s →38 c=0.8
	b2	404.206	0.010	N1 1s →41 c=0.3 N1 1s →42 c=0.6
	b2	404.490	0.007	N3 1s →38 c=0.2 N3 1s →39 c=0.3 N3 1s →40 c=0.2
5Br-Uracil	b1	402.569	0.012	N3 1s →46 (LUMO) c=1
	b1	402.844	0.008	N1 1s →46 c=1
	b2	403.624	0.003	N3 1s →50 c=0.3 N3 1s →52 c=0.7
	b2	404.129	0.008	N1 1s →47 c=0.8
	b2	404.209	0.011	N1 1s →50 c=0.3 N1 1s →52 c=0.6
	b2	404.449	0.006	N3 1s →47 c=0.3 N3 1s →49 c=0.4
5I-Uracil	b1	402.649	0.012	N3 1s →55 (LUMO) c=0.9
	b1	402.909	0.009	N1 1s →55 c=1.0
	b2	403.690	0.003	N3 1s →59 c=0.8 N3 1s →61 c=0.1
	b2	404.148	0.007	N1 1s →56 c=0.7
	b2	404.290	0.011	N1 1s →59 c=0.8 N1 1s →61 c=0.1
	b2	404.379	0.003	N3 1s →56 c=0.6 N3 1s →58 c=0.2

Table 4: KS (CAM-B3LYP) molecular orbitals involved in the transitions reported in Table 3.

I	Br
 LUMO (55)	 LUMO (46)
 56	 47
 59	 50
 61	 52

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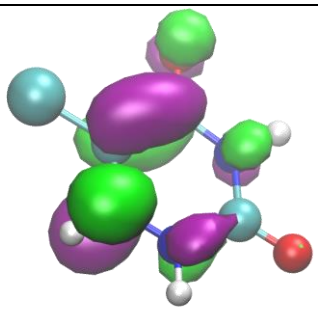
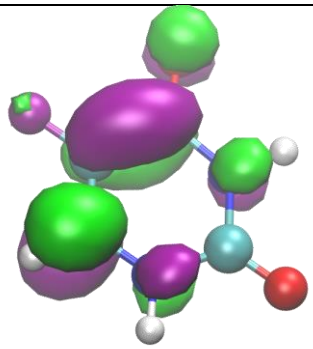
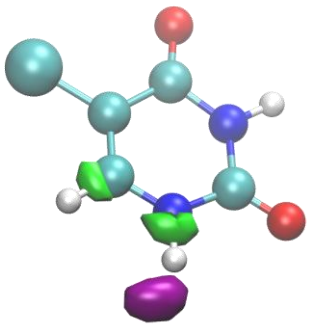
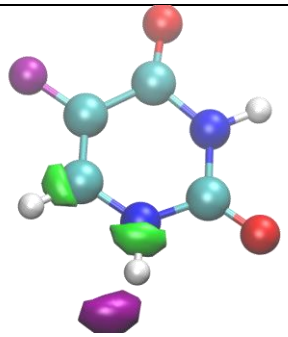
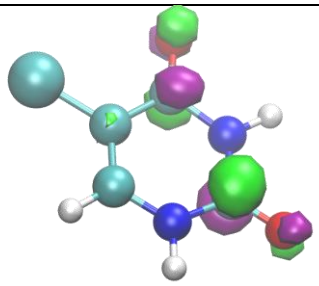
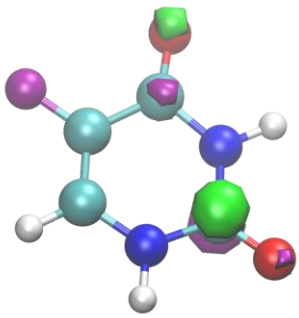
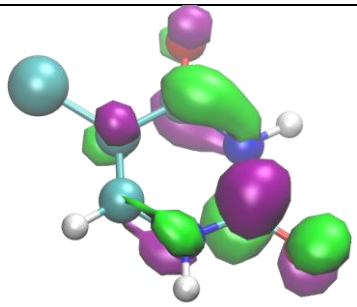
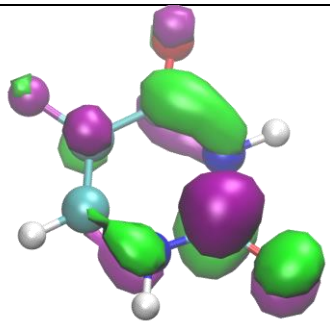
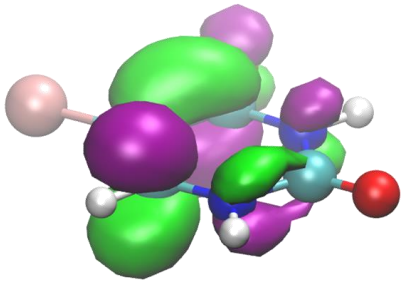
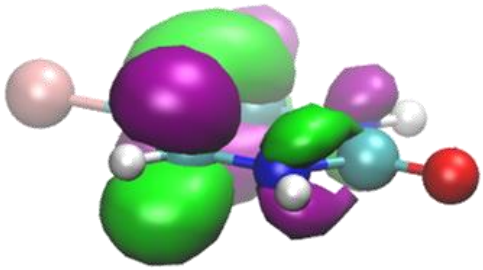
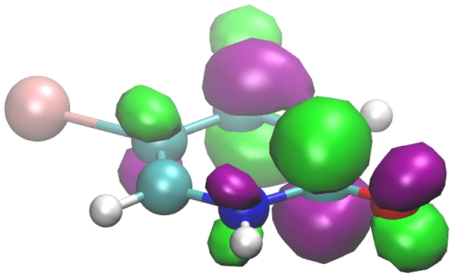
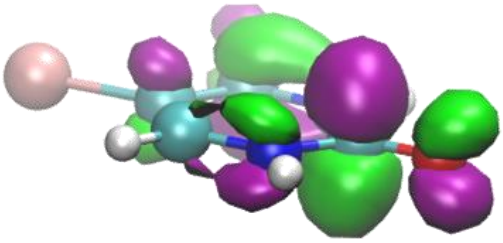
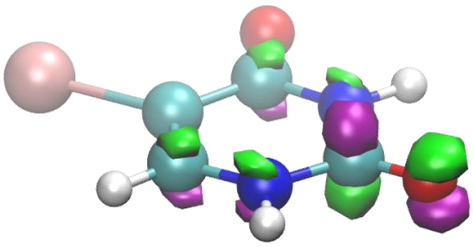
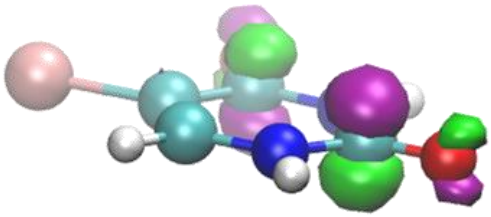
 LUMO (37)	 LUMO (33)
 38	 34
 41	 37
 42	 38

SI.2.3 O 1s excitation

Table 5: Selected excitation energies and oscillator strengths as obtained with CAM-B3LYP. The calculated values have been shifted by 13.4 eV to match the experimental values. The corresponding single excitations with absolute values of their CI coefficients larger than 0.1 are also reported.

Element	Energy (eV)	Osc. Str.	Composition (|CI| >0.1)
5F-Uracil	531.282	0.028	O7 1s→33 (LUMO) c=0.8
	532.201	0.027	O8 1s →38 c=0.7
			O8 1s →37 c=0.1
	533.426	0.0007	O8 1s →33 c=0.9
5Cl-Uracil	531.315	0.028	O7 1s →37 (LUMO) c=0.7
	532.126	0.027	O8 1s →42 c=0.5
			O8 1s →41 c=0.2
			O8 1s →37 c=0.1
	533.443	0.001	O8 1s →37 c=0.8
5Br-Uracil	531.329	0.028	O7 1s →46 (LUMO) c=0.7
	532.106	0.027	O8 1s →52 c=0.5
			O8 1s →50 c=0.1
			O8 1s →46 c=0.2
	533.434	0.001	O8 1s →46 c=0.8
5I-Uracil	531.452	0.028	O7 1s →55 (LUMO) c=0.7
	532.192	0.027	O8 1s →59 c=0.6
			O8 1s →55 c=0.1
			O8 1s →61 c=0.1
	533.542	0.001	O8 1s →55 c=0.8

Table 6: KS (CAM-B3LYP) molecular orbitals involved in the transitions reported in Table 5.

I	Br
 LUMO	 LUMO
 59	 50
 61	 52

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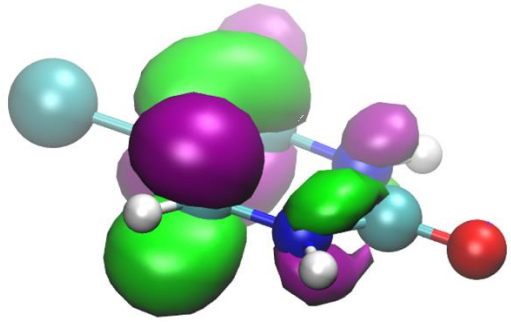
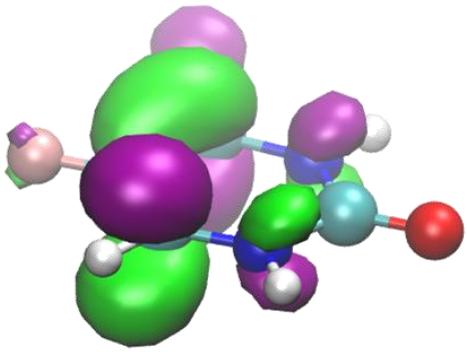
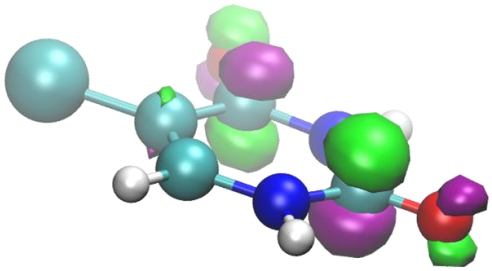
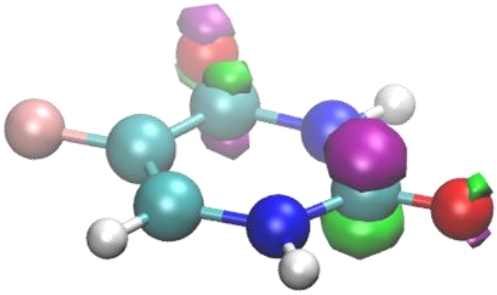
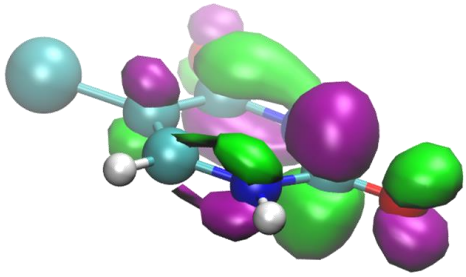
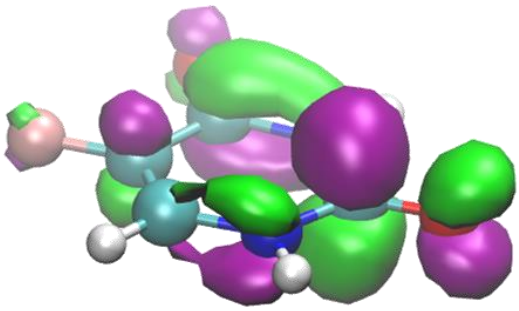
 LUMO	 LUMO
 41	 37
 42	 38

SI.2.4 O 1s excitation with functional B2-PLYP.

For sake of comparison in the case of the O 1s excitation in uracil the two main transitions of the absorption spectrum have been calculated with different functionals. The results are reported in Table 7

Table 7: Excitation energies (eV) of the two main transitions of the absorption spectrum in Uracil calculated with different functionals

Functional	ωB97x	M062X	CAM-B3LYP	B2PLYP	EXP
d1	517.98	527.79	517.88	531.10	531.37
d2	518.86	528.69	518.76	532.08	532.35

The mismatch between the DFT and the measured transition energies in the core excitation spectra depends mainly on the percentage of exact exchange in the DFT functional. B3LYP has a relatively small fraction of exact exchange and the correction turns out to be around 10-12 eV. Functional rich in exact exchange as the B2PLYP (50%) require a much smaller shift of only few hundreds of meV.

For sake of comparison the main transitions of the absorption spectrum of all the studied samples have been calculated also with the B2-PLYP functional using the same basis set as for CAM-B3LYP, but without the TDA approximation. Double corrections were not included.

Table 8: Selected excitation energies and oscillator strengths as obtained with B2-PLYP. The calculated values have been shifted by **0.024 eV** to match the experimental values. The corresponding single excitations with absolute values of their CI coefficients larger than 0.1 are also reported.

Element	Energy (eV)	Osc. Str	Composition (|CI| >0.1)
5F-Uracil	531.053	0.043	O7 1s →33 (LUMO) c=0.6
	532.109	0.041	O8 1s →40 c=0.5 O8 1s →43 c=0.2
	535.107	0.0002	O8 1s →33 c=0.9
5Cl-Uracil	531.079	0.043	O7 1s →37 (LUMO) c=0.6 O7 1s →45 c=0.2
	532.050	0.041	O8 1s →45 c=0.6
	535.060	0.0004	O8 1s →37 c=0.9
5Br-Uracil	531.098	0.043	O7 1s →46 (LUMO) c=0.6 O7 1s →54 c=0.2
	532.029	0.041	O8 1s →54 c=0.6
	535.051	0.0005	O8 1s →46 c=0.9
5I-Uracil	531.204	0.042	O7 1s →55 (LUMO) c=0.6 O7 1s →61 c=0.2
	532.091	0.041	O8 1s →61 c=0.7
	535.135	0.0005	O8 1s →55 c=0.9

The results are not very different from the ones obtained with the CAM-B3LYP functional. For example the third transition due to 1s(O8 in *para* position)→LUMO remains weak due the poor orbital overlap. A significant contribution of the diffuse orbital in the second transition is noticeable only for the 5F-uracil molecule (orbital 43). This diffuse orbital does not make an appreciable contribution in all other halogenate molecules. The transition pattern is the following: the first excited state is dominated by 1s (O7 in *ortho)*→LUMO excitation with minor contribution from another π^* that is located slightly higher in energy and that is delocalized over both C=O bonds. The latter orbital is the one that is populated during the transition giving rise to the second peak which originates from the hole in the *para* position.

Table 9: KS (B2-PLYP) molecular orbitals involved in the transitions reported in Table 7.

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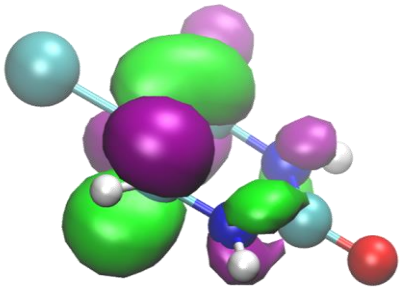
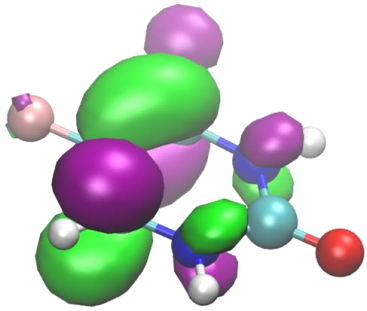
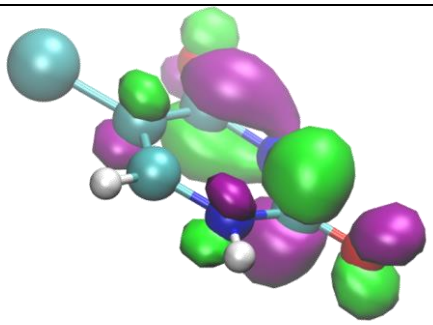
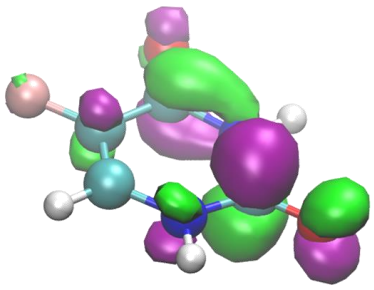
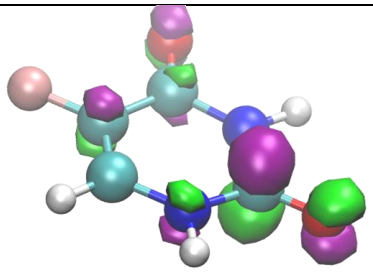
 LUMO	 LUMO
 45	 40
	 43

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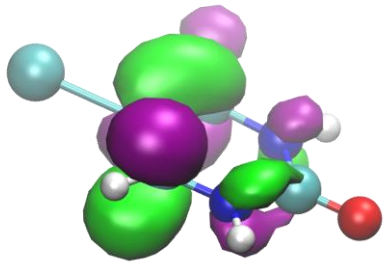
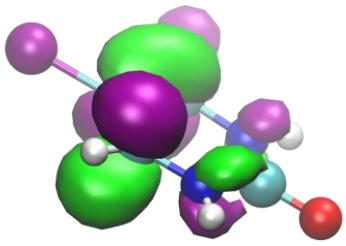
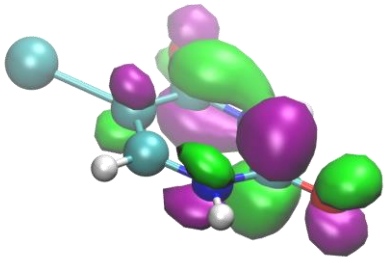
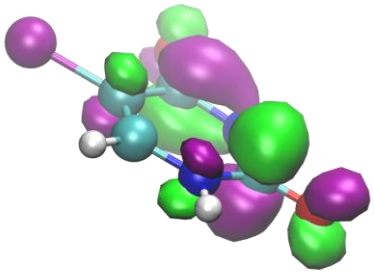
 LUMO	 LUMO
 61	 54

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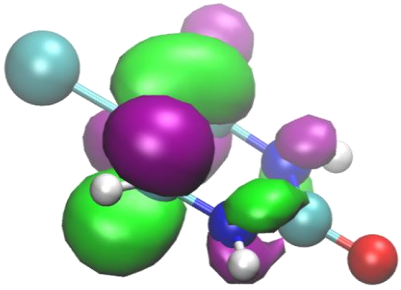
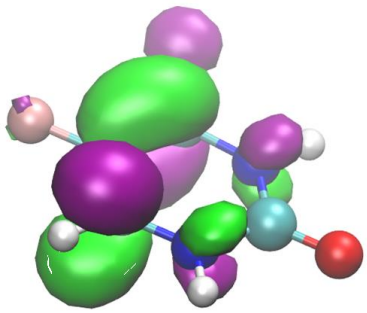
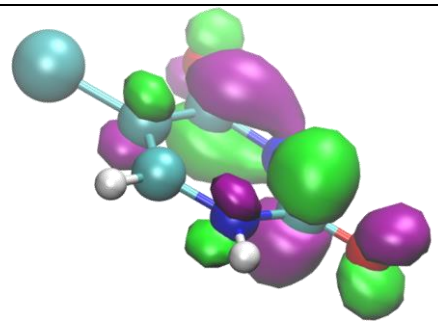
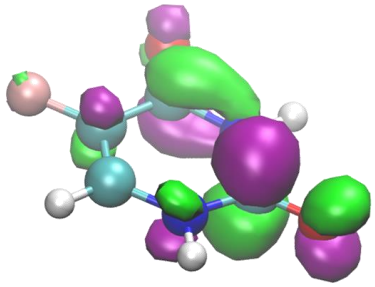
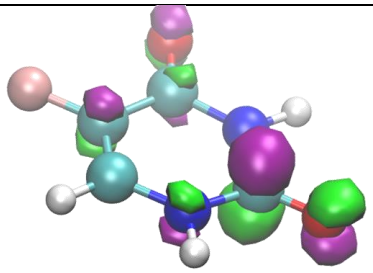
 LUMO	 LUMO

 45	 40
	 43

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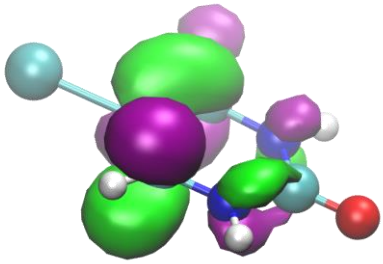
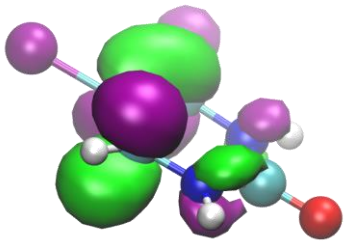
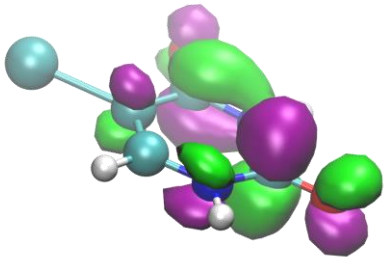
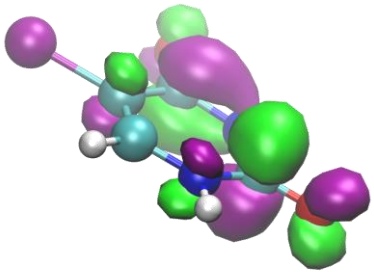
 LUMO	 LUMO
 61	 54

SI.3 Screening of the C_2 1s hole

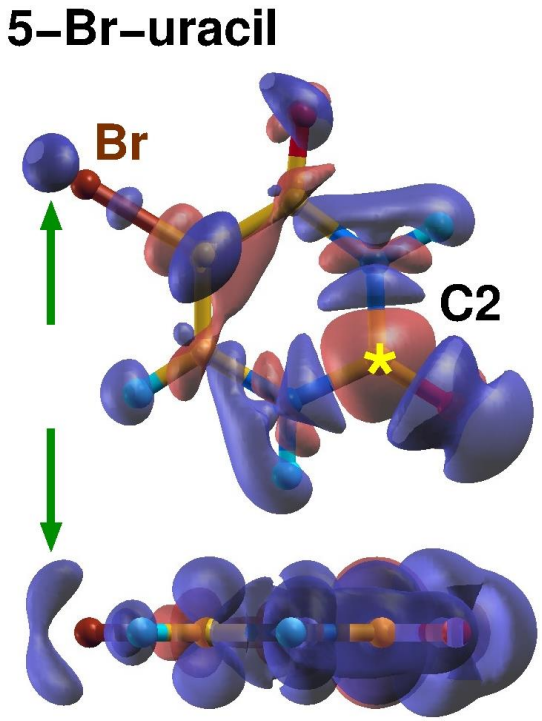


Figure 1 : Difference charge density map plotted with a 0.003 e/au^2 step of the isosurface sampling to better show the contribution of the Br atom to the screening of the C2 1s hole (top and side view)