Differences between the HOMO and LUMO orbitals:

Energy-Donating Groups:

- Electron-donating groups increase the energy level of the HOMO of the benzene ring and slightly increase the energy levels of the LUMO as well.
- The overall effect on the HOMO-LUMO gap (the energy difference between the two orbitals) depends on the specific substituents and their position

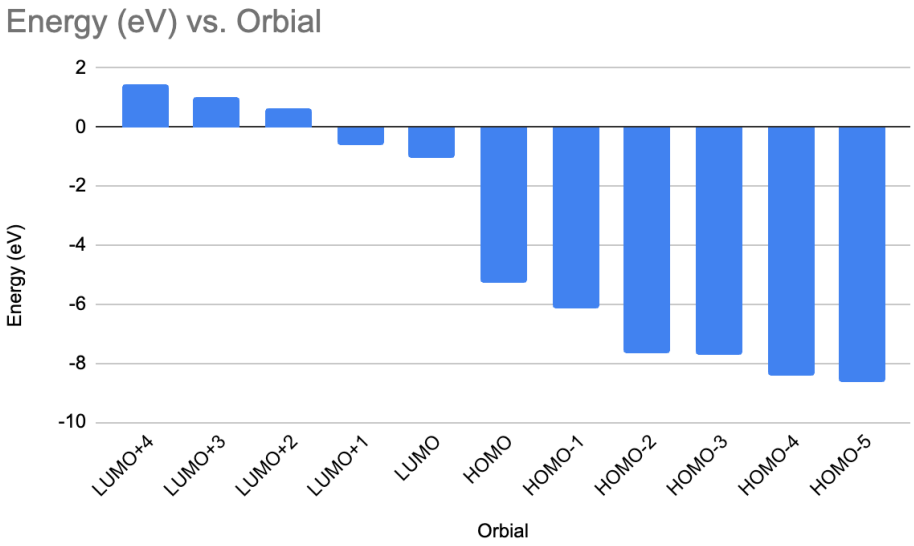
Electron-Withdrawing Groups:

- Decrease the energy level of the LUMO and slightly decrease the energy of the HOMO.
- Decrease in the HOMO-LUMO gap

Electron-Donating Groups:

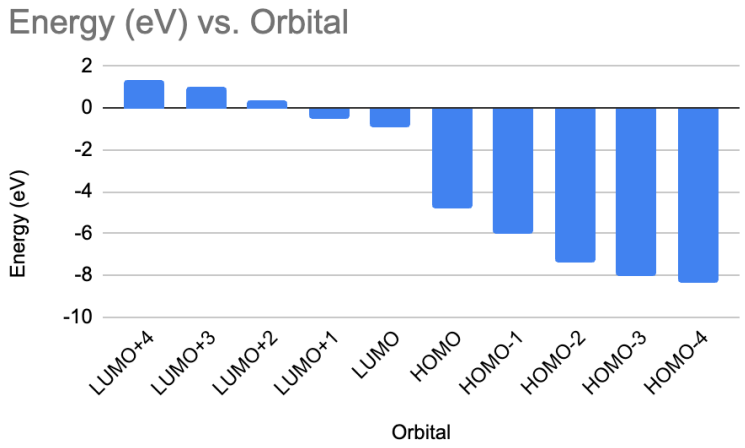
1) Anisole
    a) HOMO-LUMO energy information:

Orbial	Status	Energy (eV)
LUMO+4	100%	1.478
LUMO+3	100%	1.001
LUMO+2	100%	0.626
LUMO+1	100%	-0.593
LUMO	100%	-1.028
HOMO	100%	-5.299
HOMO-1	100%	-6.144
HOMO-2	100%	-7.664
HOMO-3	100%	-7.734
HOMO-4	100%	-8.435
HOMO-5	100%	-8.650



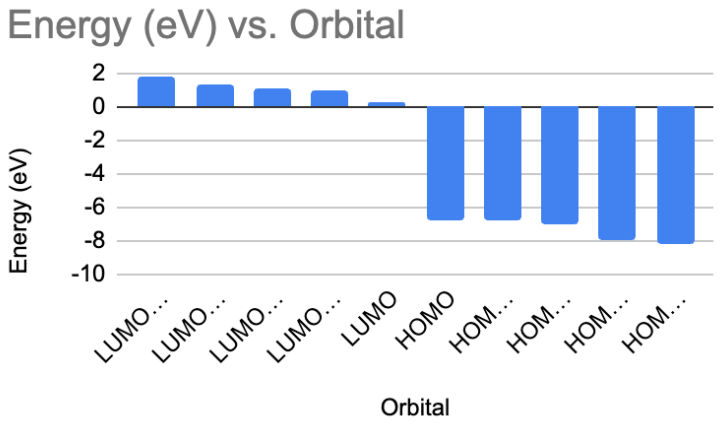
2) Aniline

Orbital	Energy (eV)	Status
LUMO+4	1.331	100%
LUMO+3	1.027	100%
LUMO+2	0.385	100%
LUMO+1	-0.481	100%
LUMO	-0.923	100%
HOMO	-4.81	100%
HOMO-1	-5.998	100%
HOMO-2	-7.425	100%
HOMO-3	-8.018	100%
HOMO-4	-8.324	100%



3) Toluene

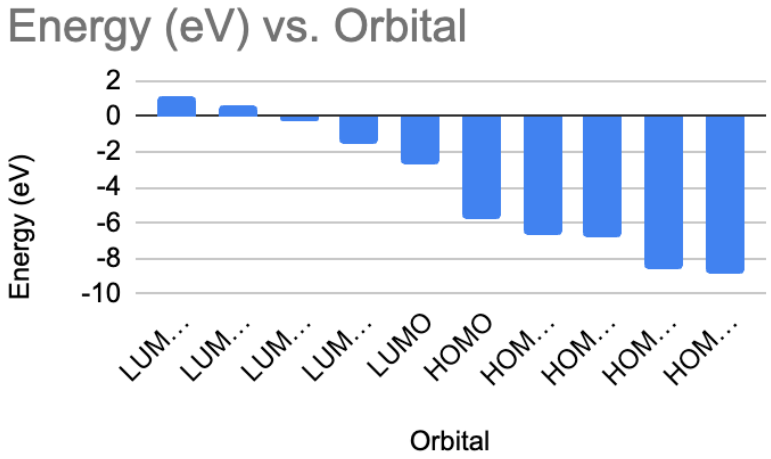
Orbital	Energy (eV)	Status
LUMO+4	1.81	100%
LUMO+3	1.365	100%
LUMO+2	1.111	100%
LUMO+1	0.931	100%
LUMO	0.293	100%
HOMO	-6.754	100%
HOMO-1	-6.796	100%
HOMO-2	-7.068	100%
HOMO-3	-7.902	100%
HOMO-4	-8.136	100%



Electron-Withdrawing Groups

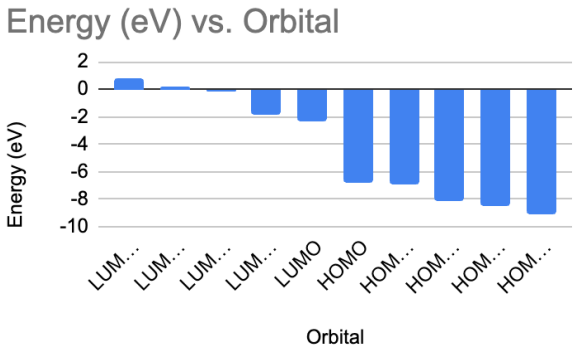
1) Benzaldehyde

Orbital	Energy (eV)	Status
LUMO+4	1.163	100%
LUMO+3	0.621	100%
LUMO+2	-0.285	100%
LUMO+1	-1.539	100%
LUMO	-2.763	100%
HOMO	-5.79	100%
HOMO-1	-6.654	100%
HOMO-2	-6.753	100%
HOMO-3	-8.581	100%
HOMO-4	-8.841	100%



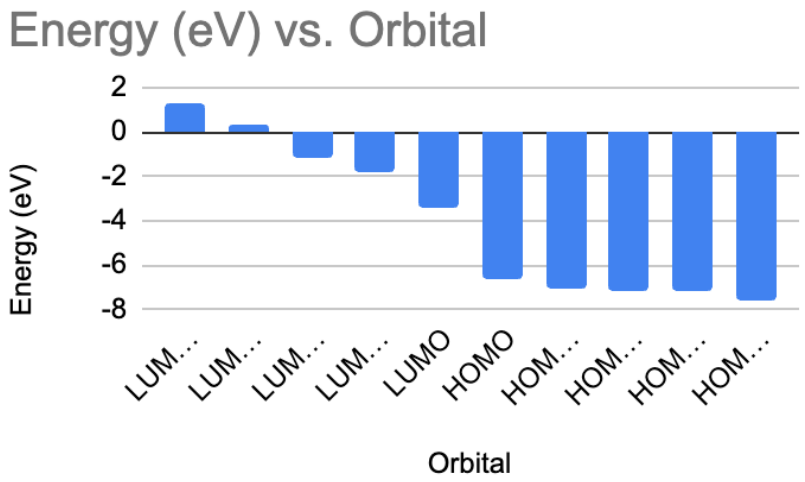
2) Benzonitrile

Orbital	Energy (eV)	Status
LUMO+4	0.749	100%
LUMO+3	0.257	100%
LUMO+2	-0.167	100%
LUMO+1	-1.809	100%
LUMO	-2.386	100%
HOMO	-6.758	100%
HOMO-1	-6.965	100%
HOMO-2	-8.114	100%
HOMO-3	-8.443	100%
HOMO-4	-9.065	100%



3) Nitrobenzene

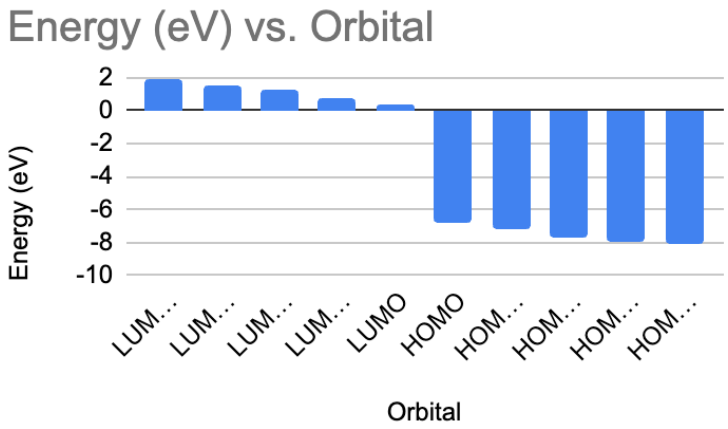
Orbital	Energy (eV)	Status
LUMO+4	1.278	100%
LUMO+3	0.309	100%
LUMO+2	-1.196	100%
LUMO+1	-1.847	100%
LUMO	-3.45	100%
HOMO	-6.607	100%
HOMO-1	-7.009	100%
HOMO-2	-7.139	100%
HOMO-3	-7.154	100%
HOMO-4	-7.567	100%



Halogens

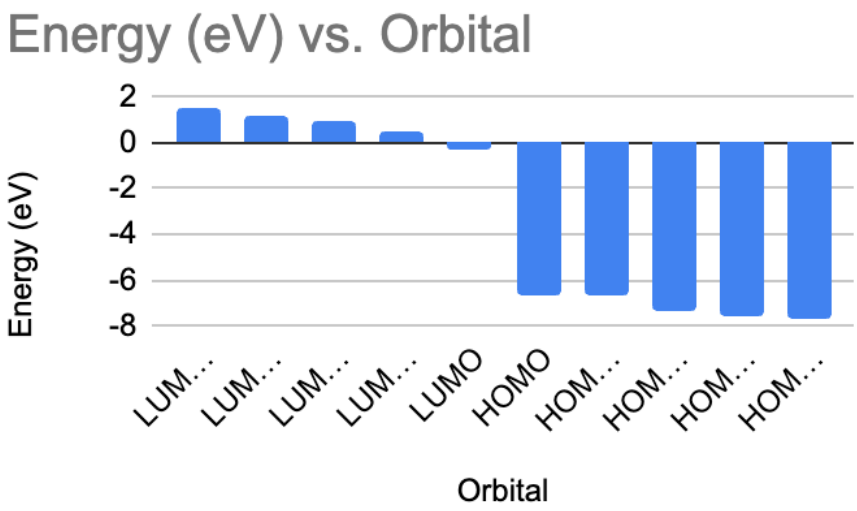
1) Fluorine

Orbital	Energy (eV)	Status
LUMO+4	1.912	100%
LUMO+3	1.481	100%
LUMO+2	1.209	100%
LUMO+1	0.786	100%
LUMO	0.334	100%
HOMO	-6.863	100%
HOMO-1	-7.178	100%
HOMO-2	-7.772	100%
HOMO-3	-7.985	100%
HOMO-4	-8.151	100%



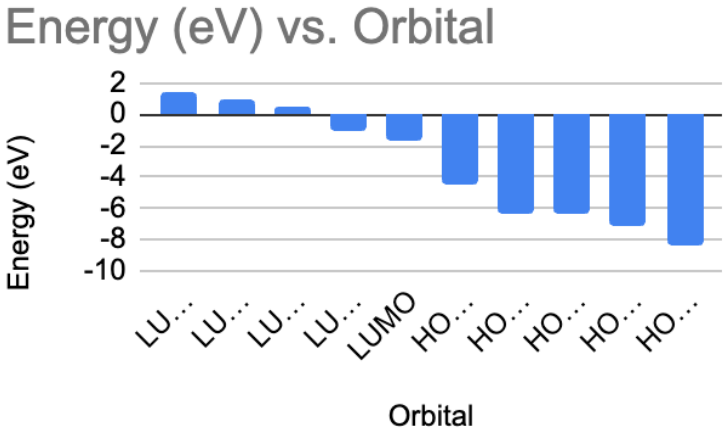
2) Chlorine

Orbital	Energy (eV)	Status
LUMO+4	1.51	100%
LUMO+3	1.147	100%
LUMO+2	0.905	100%
LUMO+1	0.538	100%
LUMO	-0.268	100%
HOMO	-6.619	100%
HOMO-1	-6.664	100%
HOMO-2	-7.374	100%
HOMO-3	-7.524	100%
HOMO-4	-7.702	100%

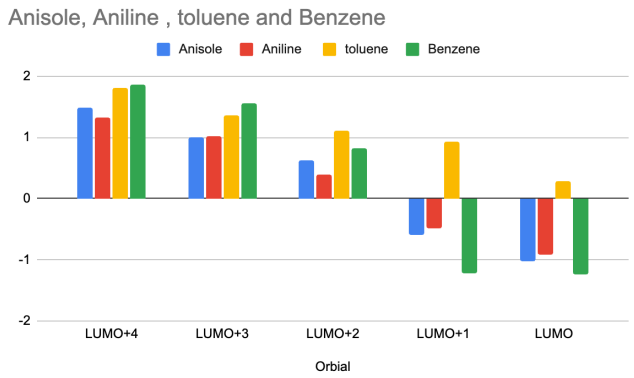


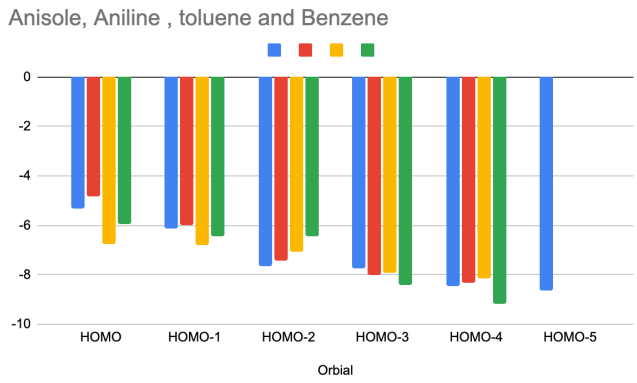
3) Bromine

Orbital	Energy (eV)	Status
LUMO+4	1.422	100%
LUMO+3	0.961	100%
LUMO+2	0.437	100%
LUMO+1	-1.133	100%
LUMO	-1.684	100%
HOMO	-4.539	100%
HOMO-1	-6.375	100%
HOMO-2	-6.414	100%
HOMO-3	-7.061	100%
HOMO-4	-8.336	100%

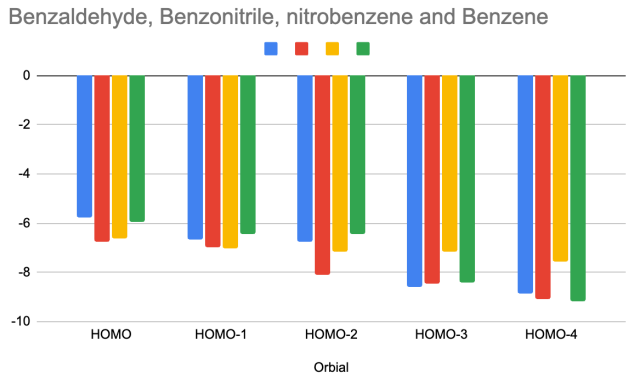


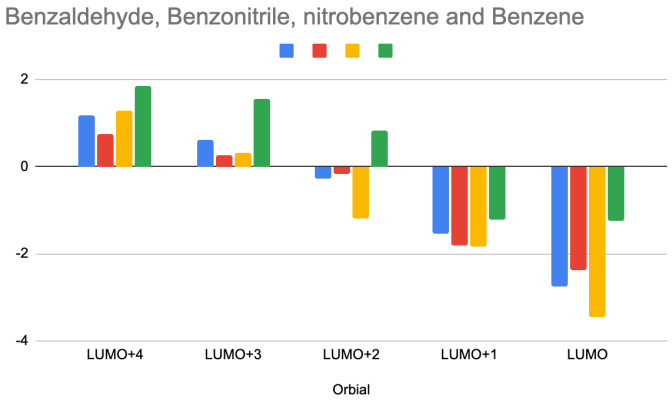
Comparison:
Electron Donating Groups:
Electron-donating groups are expected to significantly increase the energy level of the HOMO of the Benzene ring and have lighter, similar effects on the LUMO. As expected, LUMO+2, LUMO+1, and LUMO show a small increase in energy while LUMO+4 and LUMO+3 show slight decreases.





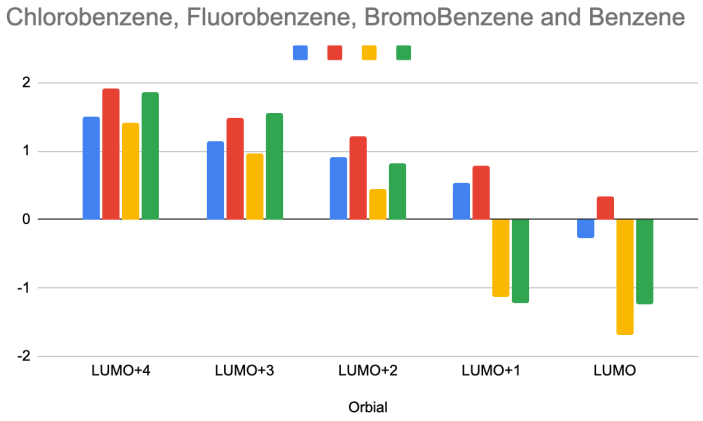
Electron-Withdrawing Groups:
electron -withdrawing groups are expected to decrease the energy levels of the LUMO and slightly decrease the energy of the HOMO. This pattern is, on average, supported by the graph below, although there are still some inconsistencies.

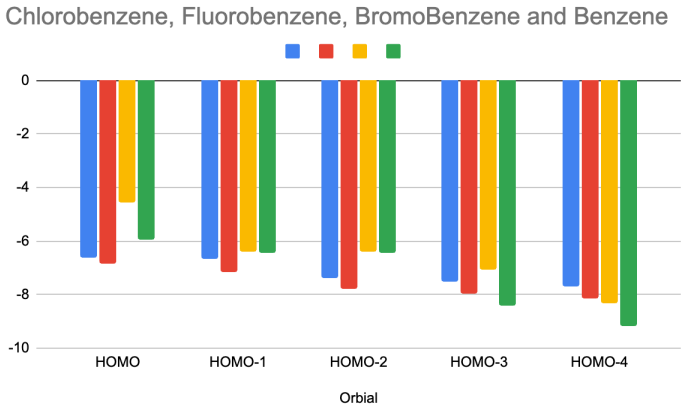




Halogens:

While Halogens are known to have both inductive and resonance properties, adding to both withdrawing and donating groups, they are known to have electron-donating properties all around. While there are slight inconsistent increases in the LUMO orbitals, this idea is more supported by the HOMO orbitals which show a more consistent increase.

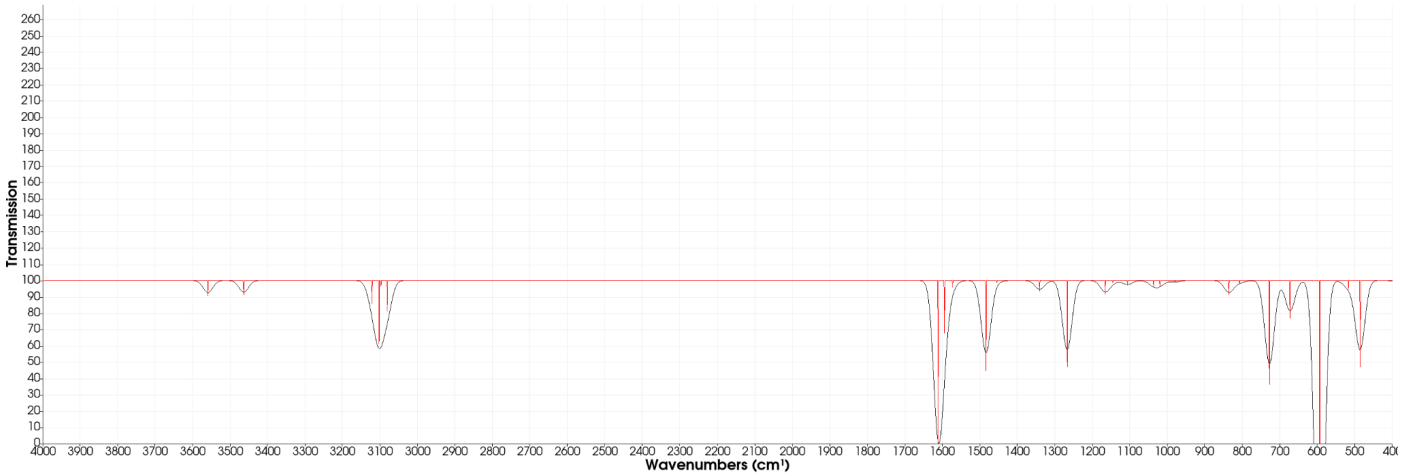




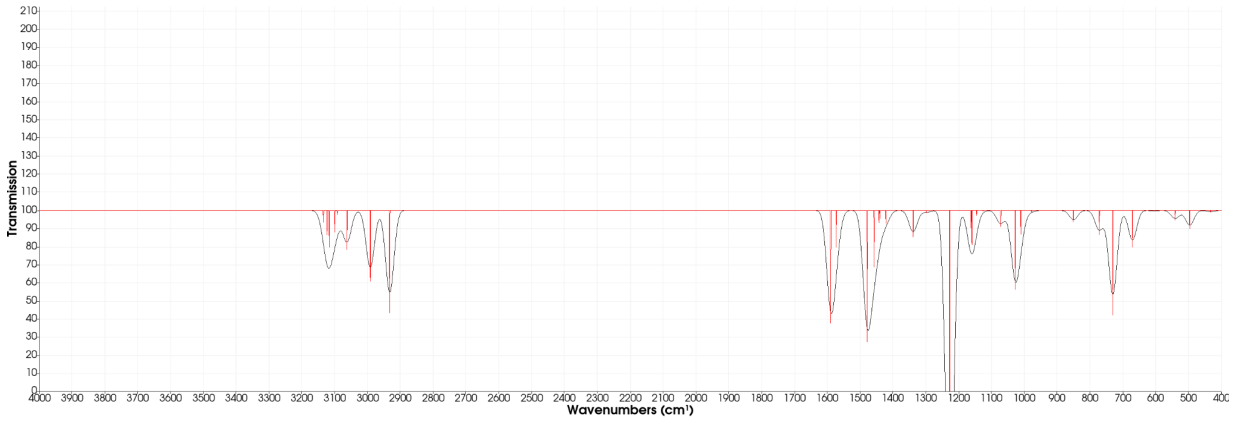
Frequency Results:

Electron Donating Groups:

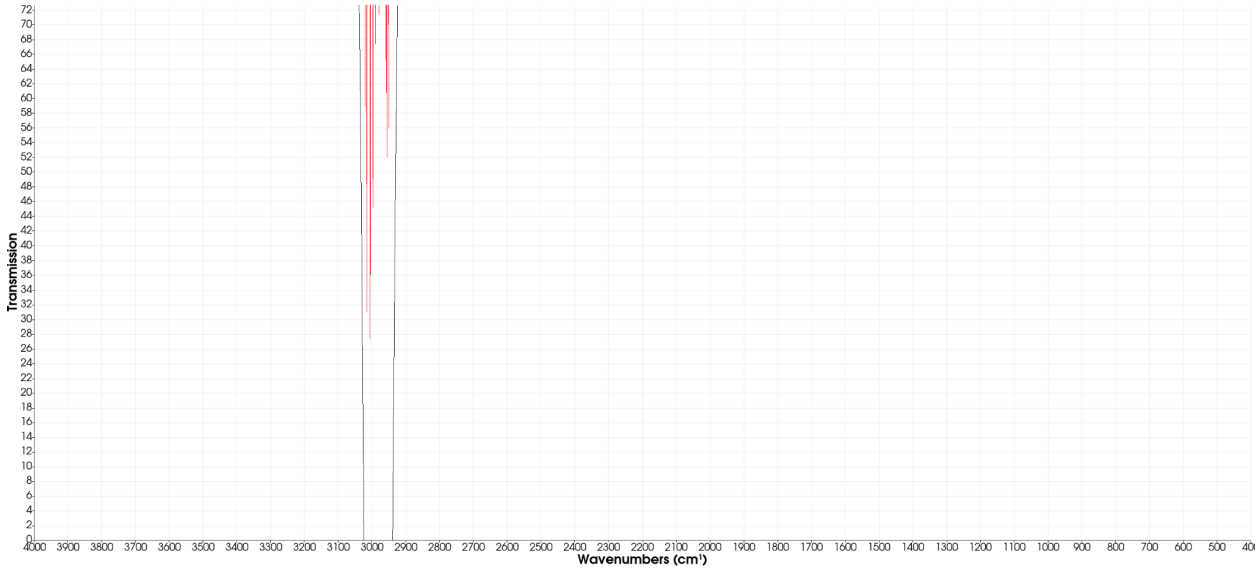
1) Aniline:



2) Anisole:

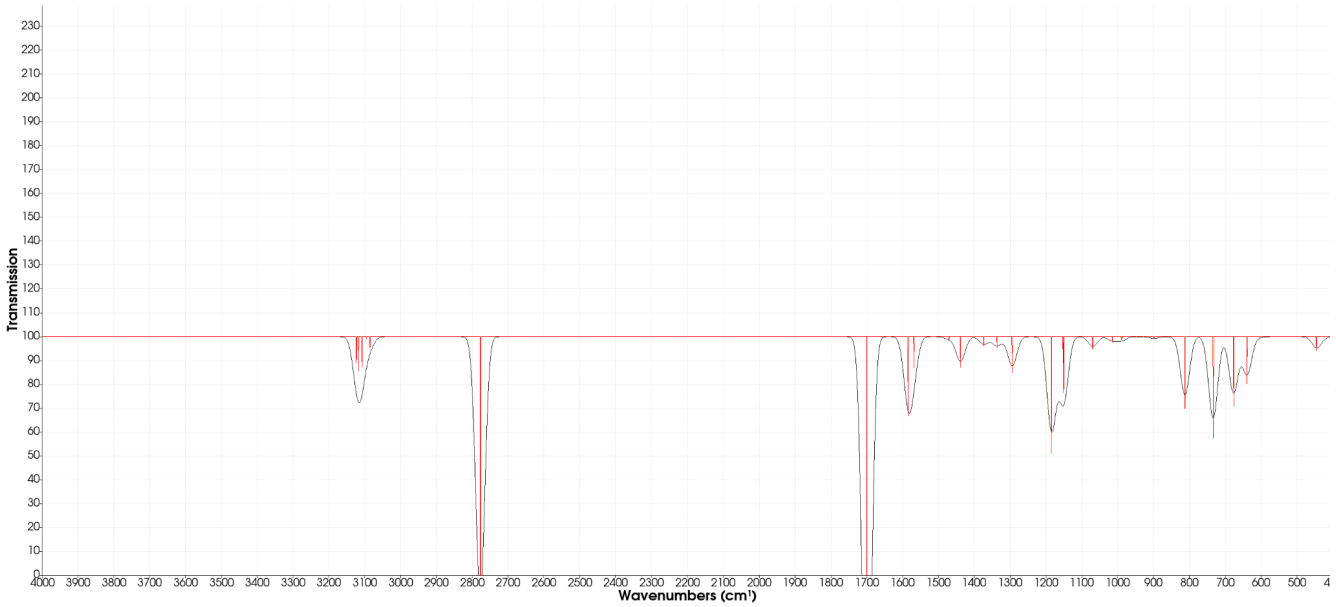


3) Toluene

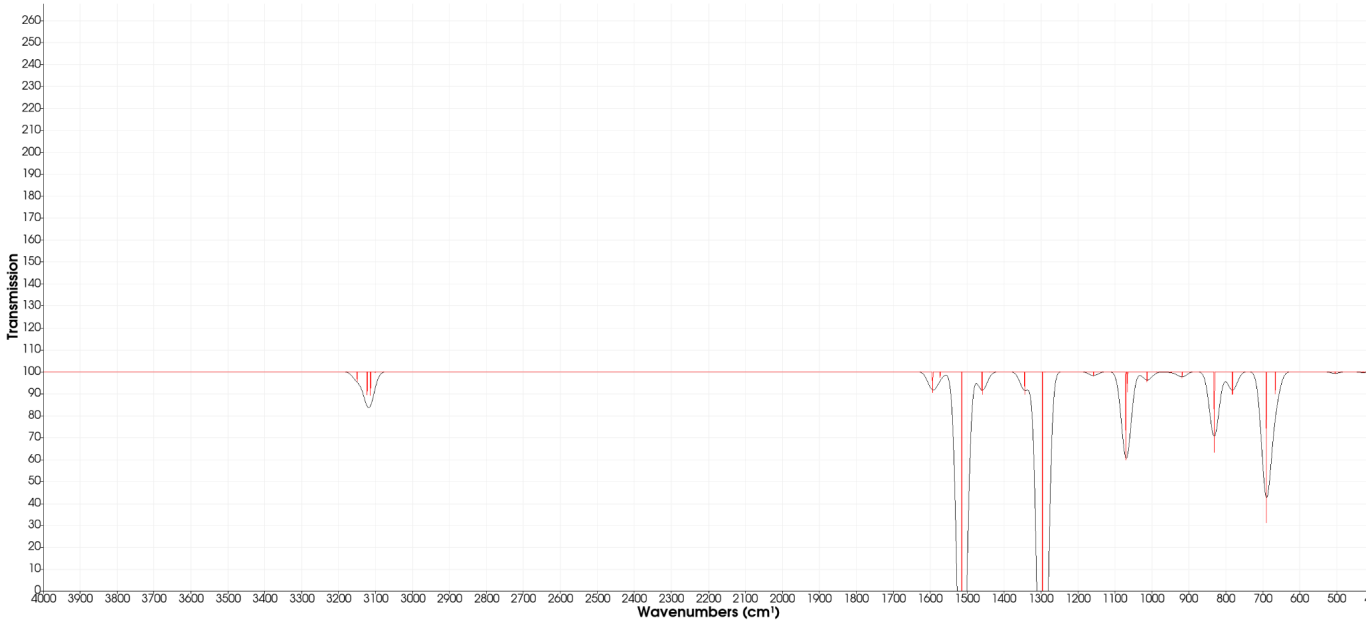


Electron-withdrawing Groups:

1) Benzaldehyde

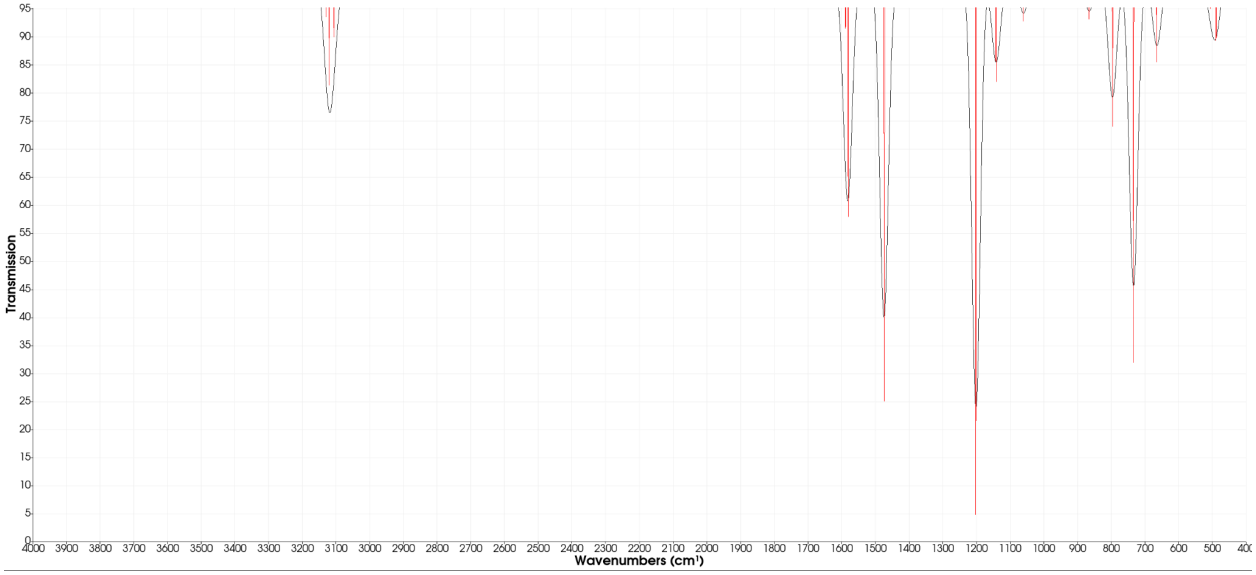


2) Benzonitrile
3) Nitrobenzene

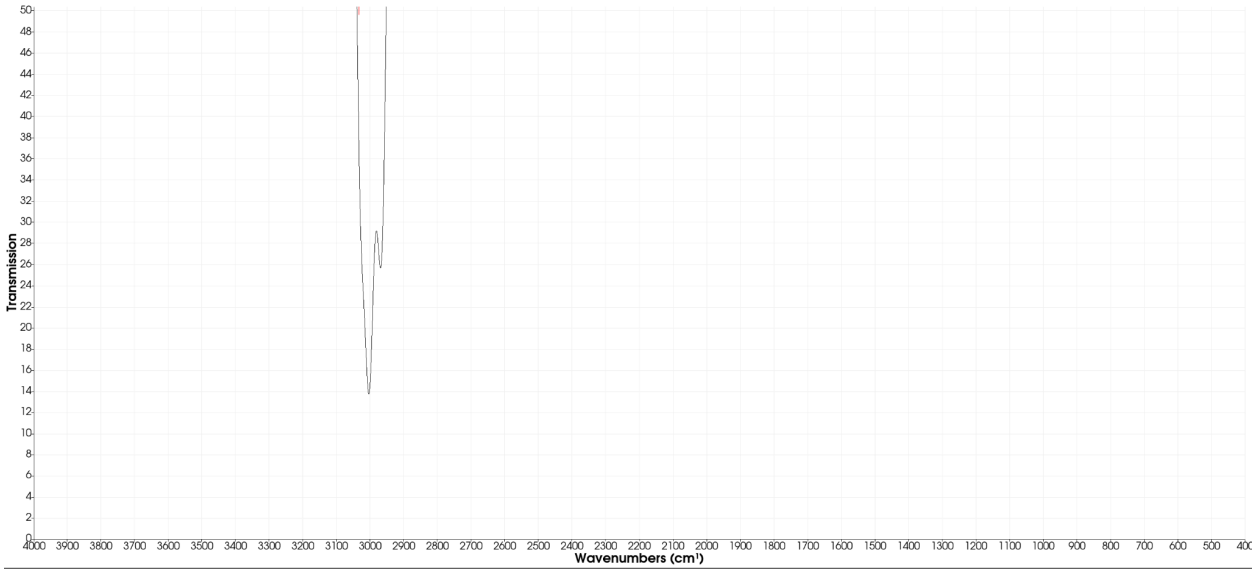


Halogens

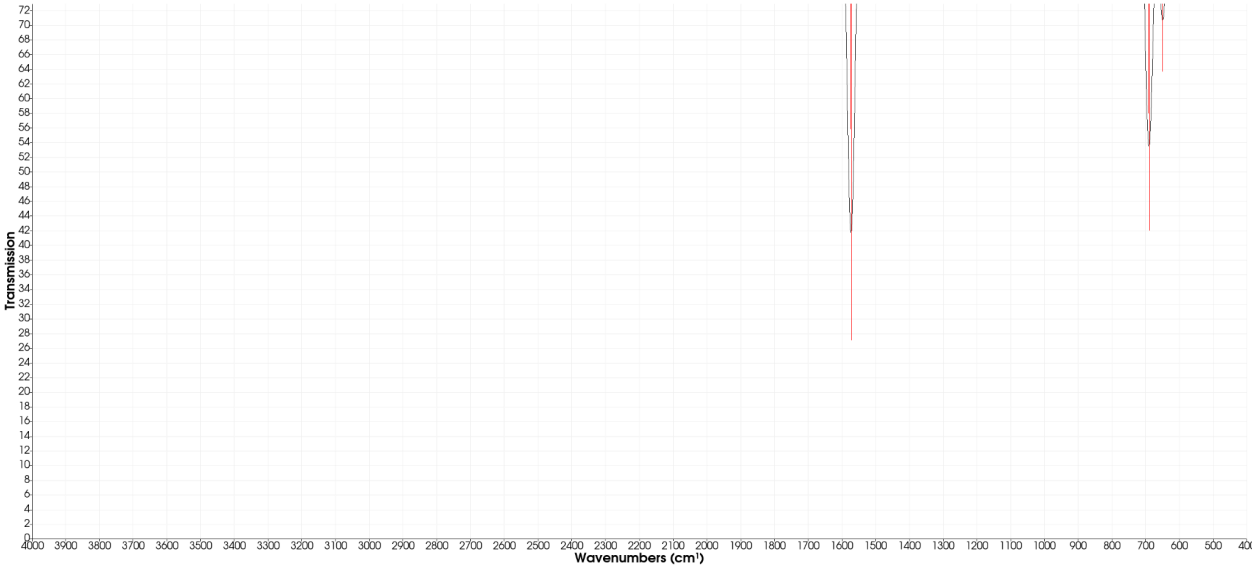
1) Fluorobenzene



2) Chlorobenzene



3) Bromobenzene



Their vibrational frequencies, as well as the IR spectra, are as expected and similar to literature values.