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

Supplementary information for: Ionization and Fragmentation of Uracil upon Microhydration

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The present Supplementary information file includes data corresponding to the calculation of equilibrium structural parameters, as well as the computed adiabatic (AIE) and vertical (VIE) ionization energies of the uracil molecule using 8 functionals belonging to density functional theory

Equilibrium Structural parameters obtained at the B3LYP/6-311++G(d,p) are compared to previous experimental and theoretical results and reported in Table S1, while the computed AIEs and VIEs are gathered in Table S2 and Table S3 respectively.

We also report comparison of the top three functionals with only a limited subset of large basis set that gave results close to the experimental AIEs and VIEs ionization energies.

Several supplementary references are also reported mainly full reference of the Gaussian software[1].

Table S1. Structural parameters of the gas phase uracil compared to theoretical and experimental results

	Present work	B3LYP[a]	MP2[b]	PBE[c]	Exp1[d]	Exp2[e]
N_1-C_2	1.393	1.394	1.390	1.400	1.406	1.371
C_2-N_3	1.383	1.385	1.385	1.388	1.393	1.377
N_3-C_4	1.412	1.412	1.408	1.419	1.371	1.399
C_4-C_5	1.458	1.459	1.460	1.459	1.430	1.462
C_5-C_6	1.347	1.352	1.353	1.355	1.340	1.462
C_6-N_1	1.375	1.377	1.375	1.375	1.359	1.399
C_2-O_7	1.212	1.220	1.214	1.226	1.215	1.212
C_4-O_8	1.215	1.223	1.218	1.229	1.245	1.212

[a] B3LYP/6-31+G* from Ref [2]

[b] MP2/6-311G* from Ref [3]

[c] PBE/TZVP from Ref [4]

[d] X-ray diffraction experiments from Ref [5]

[e] Electron diffraction experiments from Ref [6]

Table S2 calculated adiabatic ionization energies (eV) at different levels of theory

	B3LYP	PBE	CAM-B3LYP	LC-BLYP	M062X	wB97XD	mPW2PLYP	B2PLYP
6-31g	9.131	8.977	9.204	9.329	9.38	9.246	9.052	9.021
6-31g(d)	8.944	8.805	9.016	9.142	9.165	9.052	8.922	8.9
6-31g(d.p)	8.953	8.811	9.024	9.149	9.167	9.063	8.941	8.921
6-31+g(d)	9.244	9.11	9.321	9.458	9.391	9.288	9.22	9.195
6-31+g(d.p)	9.253	9.12	9.329	9.465	9.394	9.299	9.239	9.215
6-31++g(d)	9.243	9.11	9.32	9.458	9.39	9.287	9.22	9.194
6-31++g(d.p)	9.252	9.12	9.329	9.465	9.393	9.298	9.238	9.215

6-311g	9.307	9.145	9.386	9.538	9.531	9.377	9.211	9.183
6-311g(d)	9.114	8.971	9.19	9.339	9.314	9.178	9.066	9.047
6-311g(d.p)	9.134	8.992	9.209	9.357	9.329	9.198	9.1	9.082
6-311+g(d)	9.268	9.133	9.347	9.495	9.429	9.294	9.234	9.211
6-311+g(d.p)	9.289	9.155	9.367	9.514	9.445	9.315	9.268	9.246
6-311++g(d)	9.267	9.132	9.346	9.494	9.428	9.293	9.233	9.21
6-311++g(d.p)	9.288	9.154	9.366	9.513	9.444	9.314	9.267	9.245
Tzv	9.361	9.204	9.442	9.593	9.558	9.368	9.278	9.248
Tzvp	9.26	9.12	9.338	9.488	9.432	9.27	9.231	9.212

Table S3 calculated vertical ionization energies (eV) at different levels of theory

	B3LYP	PBE	CAM-B3LYP	LC-BLYP	M062X	wB97XD	mPW2PLYP	B2PLYP
6-31g	9.275	9.004	9.386	9.55	9.578	9.427	9.228	9.191
6-31g(d)	9.154	8.883	9.27	9.55	9.448	9.305	9.161	9.132
6-31g(d.p)	9.161	8.888	9.276	9.448	9.448	9.314	9.178	9.15
6-31+g(d)	9.452	9.208	9.572	9.754	9.672	9.539	9.455	9.422
6-31+g(d.p)	9.459	9.214	9.578	9.76	9.673	9.549	9.471	9.439
6-31++g(d)	9.452	9.208	9.571	9.753	9.671	9.538	9.455	9.421
6-31++g(d.p)	9.459	9.214	9.578	9.76	9.673	9.548	9.471	9.439
6-311g	9.444	9.167	9.56	9.752	9.719	9.55	9.377	9.344
6-311g(d)	9.332	9.064	9.452	9.647	9.606	9.439	9.317	9.29
6-311g(d.p)	9.353	9.08	9.472	9.666	9.622	9.46	9.352	9.327
6-311+g(d)	9.484	9.237	9.606	9.799	9.719	9.553	9.48	9.45
6-311+g(d.p)	9.505	9.253	9.626	9.819	9.735	9.575	9.515	9.486
6-311++g(d)	9.483	9.236	9.605	9.798	9.717	9.552	9.479	9.449
6-311++g(d.p)	9.504	9.252	9.625	9.818	9.734	9.573	9.514	9.485
Tzv	9.496	9.24	9.614	9.805	9.744	9.541	9.441	9.406
tzvp	9.473	9.216	9.594	9.79	9.716	9.528	9.473	9.446

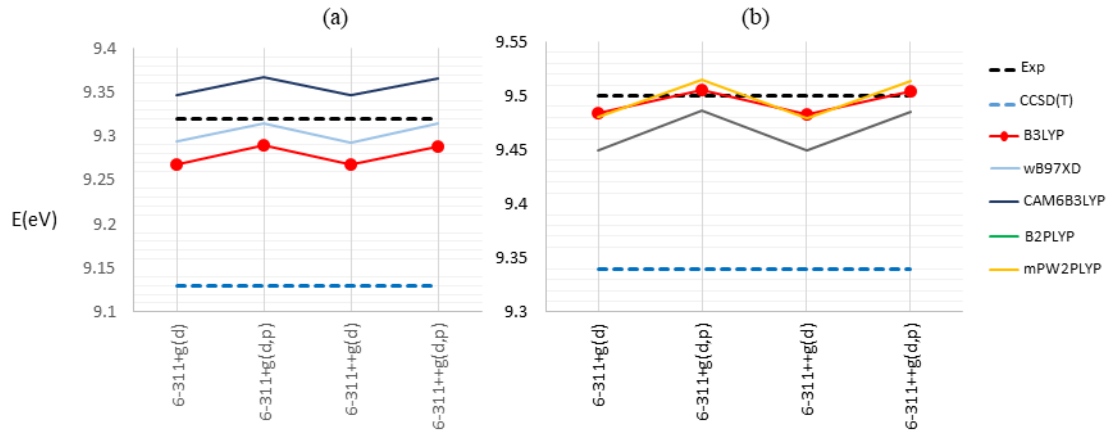

Figure S1 Adiabatic (a) and vertical (b) ionization energies of top three functionals

Figure S2 shows that B3LYP gave good results for both AIEs and VIEs in agreement with the experimental result and thus retained for this study with the pople 6-311++G(d,p), all computed data for adiabatic and vertical ionization energies are reported in Table S2 and Table S3 respectively.

Supplementary references

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