

# Electronic Supplementary Information

## Impact of Solvation on the Electronic Resonances in Uracil

Divya Tripathi,<sup>†</sup> Maneesh Pyla,<sup>†</sup> Achintya Kumar Dutta,<sup>‡</sup> and Spiridoula

Matsika<sup>\*,†</sup>

<sup>†</sup>*Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States*

<sup>‡</sup>*Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, 400076, India*

E-mail: smatsika@temple.edu

This file contains: 1) Coordinates of uracil used in this work; 2) additional CASSCF details and results; 3) additional details on charge stabilization; 4) orbital stabilization plots; 5) additional results for the comparison between microsolvation and bulk solvation; 6) comparison of EOM-EA-CCSD results for the 1p resonance using a singlet or triplet reference; 7) resonance parameters at different levels of solvation.

## 1 Coordinates of isolated uracil

The uracil geometry was optimized at the second order perturbation (MP2)/6-31G\* level of theory. The cartesian coordinates are given in [Table S1](#).

**Table S1: Cartesian Coordinates of Isolated Uracil in Å**

Element	x	y	z
N	1.1610	0.6570	0.0000
H	2.0480	1.1550	0.0000
C	0.0050	1.4610	0.0000
O	0.0970	2.6850	0.0000
C	-1.2310	0.6900	0.0000
H	-2.1710	1.2240	0.0000
C	-1.1820	-0.6610	0.0000
H	-2.0730	-1.2820	0.0000
N	0.0130	-1.3430	0.0000
H	0.0410	-2.3560	0.0000
C	1.2580	-0.7250	0.0000
O	2.3140	-1.3440	0.0000

## 2 Details of CASSCF calculations

The active orbitals used in the CASSCF calculations are shown in [Figure S1](#). Since we are interested in  $\pi$  resonances, we have included all the 8 valence  $\pi$  orbitals in our active space. We have also added an extra diffuse  $\pi$  orbital, resulting in an active space CAS(11,9). Stabilization plots are generated at the CAS(11,9)/cc-pVDZ+1p level of theory and are presented in [Figure S2](#) and [Figure S3](#) for gas phase uracil and solvated uracil, respectively.

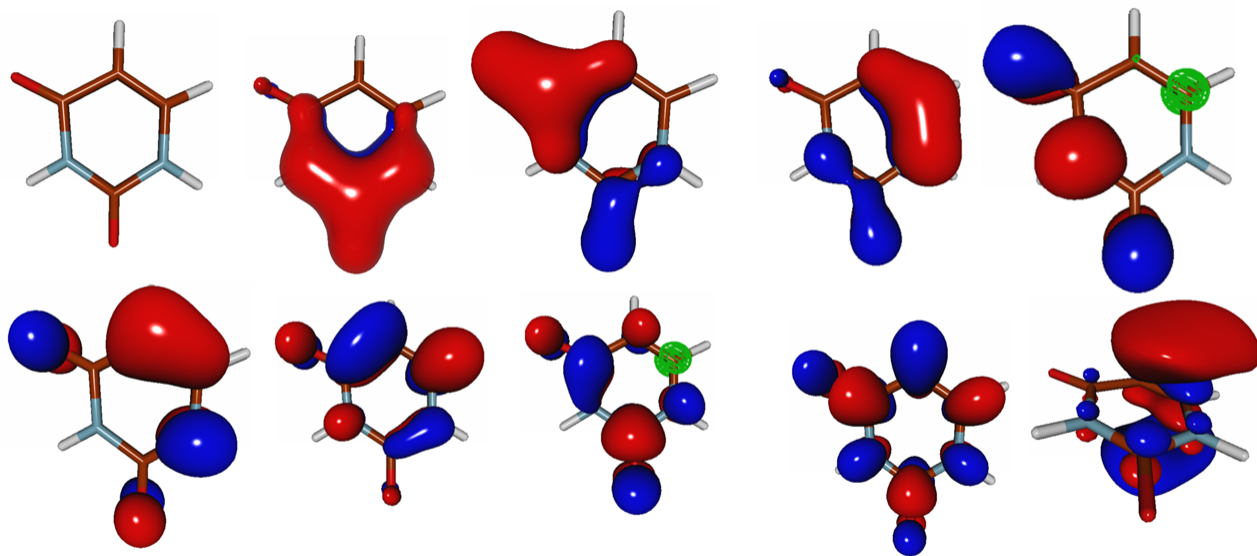


Figure S1: Active space orbitals in CAS(11,9)/cc-pVDZ+1p calculation of isolated uracil.

When using CASSCF for stabilization plots, the number of electronic states to be used in the average can affect the results and lead to discontinuities in the plots. So, the calculations are much more challenging than the EOM-EA-CCSD stabilization calculations. We demonstrate this by comparing results using 5 and 15 states in the average CASSCF for one snapshot of solvated uracil. The stabilization plots are shown in [Figure S3](#). When 15 states are used, one can see small jumps in the energies at the values of  $\alpha$  where higher states change character. This happens since the continuum-like states are affected by  $\alpha$  much more than the resonances, so the higher energy ones become higher than the 15th state as  $\alpha$  increases. This can be very challenging to fix. In this case, we were able to obtain smooth curves when only 5 states were included. These states are the 4 resonances and only one continuum-like state. Results for the 15 averaged states can be obtained nevertheless if the jumps are not near the avoided crossings, although one should be very careful using such results. In [Table S2](#) we are comparing the values using 5 and 15 states, and we can see that the energies differ by 0.03 – 0.18 eV while the widths are even more sensitive.

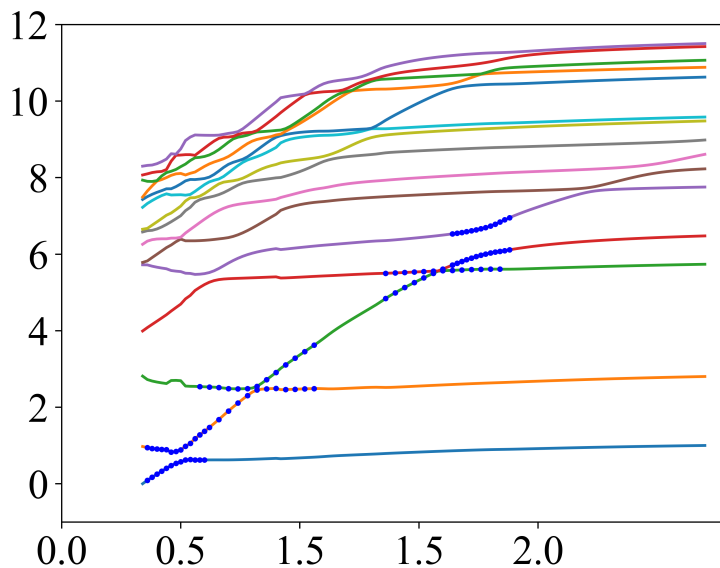


Figure S2: Orbital stabilization plot of isolated uracil at CASSCF(11,9)/cc-pVDZ+1p level of theory averaged over 15 states. Blue points indicate the avoided crossings that were used in GPA calculations.

**Table S2: EA energies (and widths in parenthesis) in eV for the four  $A''$  resonances in solvated uracil using MM for snapshot 8 using CASSCF(11,9) averaged over different number of states. Values for isolated uracil are also shown. All calculations used the cc-pVDZ+1p basis set.**

Method	$1^2 A''$ ( $1\pi^*$ ) <sup>1</sup>	$2^2 A''$ ( $2\pi^*$ ) <sup>1</sup>	$3^2 A''$ ( $3\pi^*$ ) <sup>1</sup>	$4^2 A''$ ( $\pi$ ) <sup>1</sup> ( $\pi^*$ ) <sup>2</sup>
CASSCF/MM(5 states)	2.37(0)	3.75(0)	6.80 (0.11)	8.20(0.36)
CASSCF/MM(15 states)	2.30(0)	3.57(0.02)	6.77(0.28)	8.05(0.07)
CASSCF(15 states)	2.12 (0.03)	4.05 (0.03)	7.17 (0.15)	8.01 (0.29)

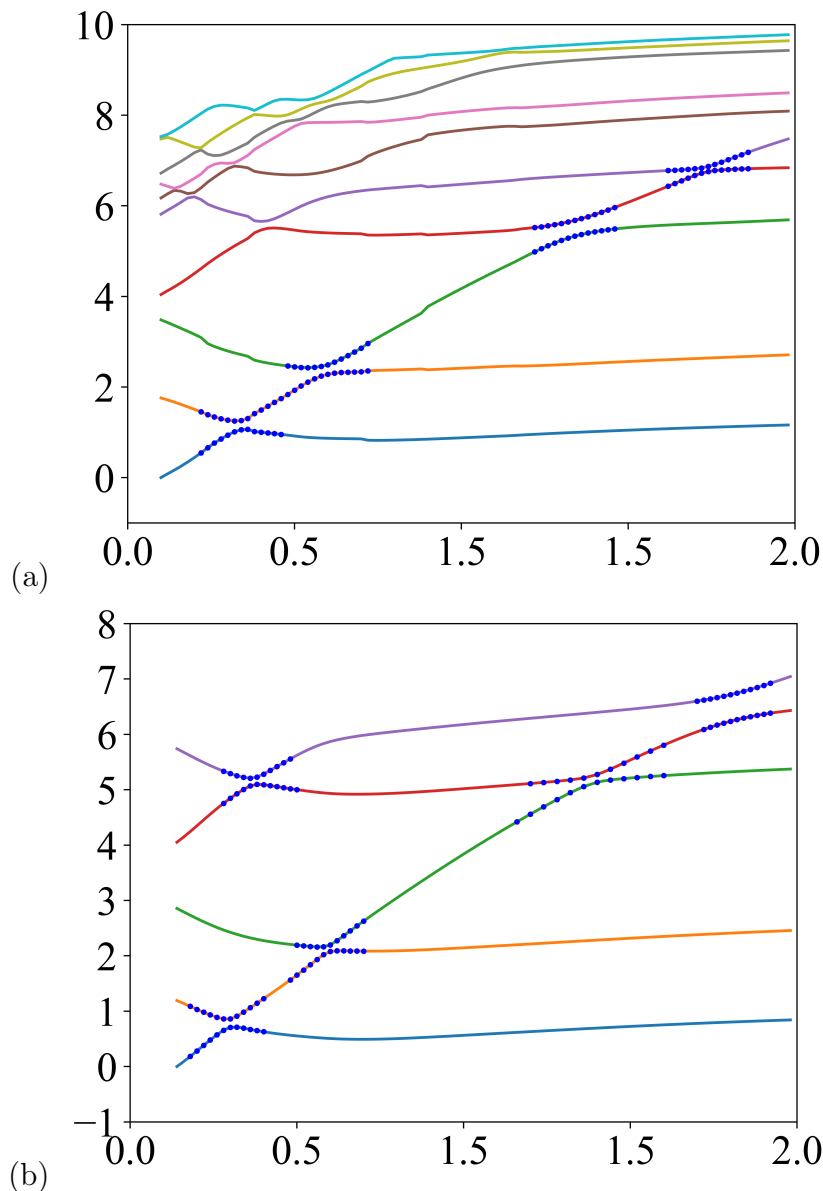


Figure S3: (a) Orbital stabilization plot of uracil with water as point charges obtained using CASSCF(11,9)/cc-pVDZ+1p level of theory averaged over 15 states. (b) Orbital stabilization plot of uracil with water as point charges obtained using CASSCF(11,9)/cc-pVDZ+1p level of theory averaged over 5 states. Blue points indicate the avoided crossings that were used in GPA calculations.

Figure S4 shows how the EA values obtained at the CASSCF/MM level for 5 snapshots are correlated to the EA values obtained using EOM-EA-CCSD/EFP for the same snapshots. The data are taken from Table 4 in the main paper. It is clear that there is a strong correlation between them. Values for both 1p and 2p1h resonances are included. This strong correlation

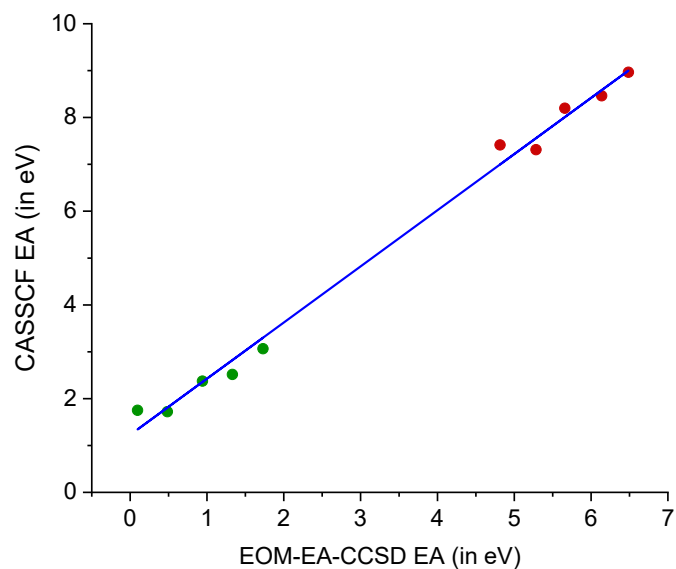


Figure S4: Correlation between EA values obtained using EOM-EA-CCSD/EFP vs EA values from CASSCF/MM. EA for both 1p (green dots) and 2p1h (red dots) resonances are included.

indicates that, regardless the shortcomings of each approach, they predict similar trends.

### 3 Details of charge stabilization plots

In order to find the optimum range of charge  $z$  to use in the charge stabilization plots, we plotted the energies for charges between 0.5 to 0.9 for 25 snapshots. These are shown in [Figure S5](#). Using smaller charges did not lead to stabilization of the resonance, so they could not be used. It is also obvious from the plots that a smaller range of charges would suffice, so for the remaining snapshots we only used three charges, between 0.6 and 0.8. [Table S3](#) compares results using three or five charges, and it shows that the results are not affected by the smaller number of charges.

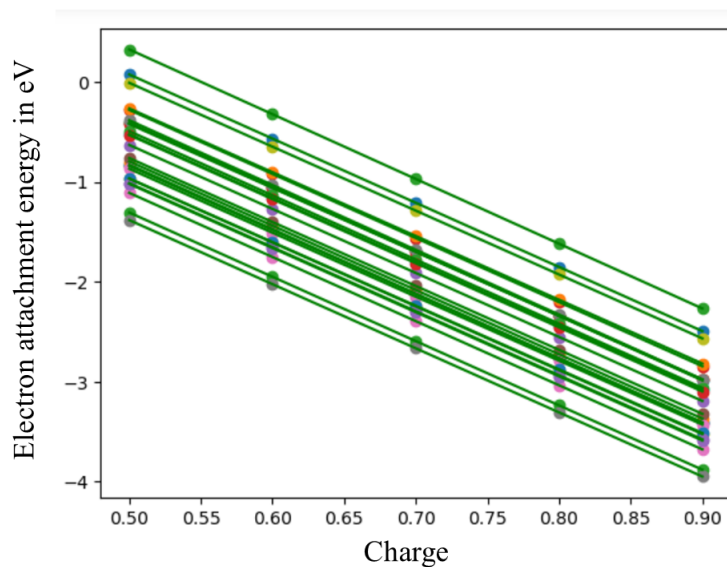


Figure S5: Electron attachment energies plotted against charge in charge stabilization method. Extrapolation to zero provides the resonance position

**Table S3:** Comparison of EA- $D_N(\text{T})$  for 25 snapshots obtained by varying charges from 0.5 to 0.9 with EA- $D_N(\text{T})$  obtained by varying charges from 0.6 to 0.8 with a difference of 0.1 in the charge stabilization method at the EOM-EA-CCSD(cc-pVDZ)/EFP level. Snapshot numbers correspond to the time steps in the MD simulations.

Snapshot	0.5 to 0.9 EA- $D_N(\text{T})$	0.6 to 0.8 EA- $D_N(\text{T})$
350	3.287	3.288
351	2.803	2.804
352	1.911	1.912
353	2.928	2.929
354	2.573	2.574
355	2.369	2.369
356	2.099	2.100
357	1.826	1.827
358	2.227	2.227
359	2.810	2.811
360	2.400	2.401
361	2.424	2.425
362	3.566	3.567
363	2.778	2.779
364	2.191	2.191
365	2.439	2.439
366	2.331	2.332
367	2.860	2.860
368	3.189	3.189
369	2.674	2.675
370	2.220	2.221
371	2.927	2.928
372	2.721	2.721
373	2.677	2.678
374	2.193	2.194



## 4 EOM-EA-CCSD orbital stabilization curves

Table S4 shows results for avoided crossings for which GPA (7,7,7) did not work, so we used a smaller GPA, as shown in the table.

**Table S4: List of calculations for which different GPAs were used other than GPA (7,7,7). All are from EOM-EA-CCSD/cc-pVDZ+1p stabilization curves.**

Snapshot	Method	GPA
5	uracil(QM) + 3 $H_2O$ (QM)	(5,5,5)
7	uracil(QM) + 3 $H_2O$ (QM)	(4,4,4)
7	uracil(QM) + 3 $H_2O$ (EFP)	(5,5,5)
8	uracil(QM) + 3 $H_2O$ (EFP)	(4,4,4)
8	uracil(QM) + PCM	(4,4,4)
8	uracil(QM) + Point Charges	(4,4,4)
8	uracil(QM) + 1a $H_2O$ (QM)	(4,4,4)
8	uracil(QM) + 1b $H_2O$ (QM)	(4,4,4)
8	uracil(QM) + 2 $H_2O$ (QM)	(4,4,4)
8	uracil(QM) + 3 $H_2O$ (QM)	(4,4,4)
8	uracil(QM) + 7 $H_2O$ (QM)	(4,4,4)
9	uracil(QM) + 3 $H_2O$ (EFP)	(4,4,4)
13	uracil(QM) + 6 $H_2O$ (EFP)	(5,5,5)

The stabilization curves from Figure S6 to Figure S18 were generated at the EOM-EA-CCSD level, with corresponding GPA results presented in Table 1 of the main paper.

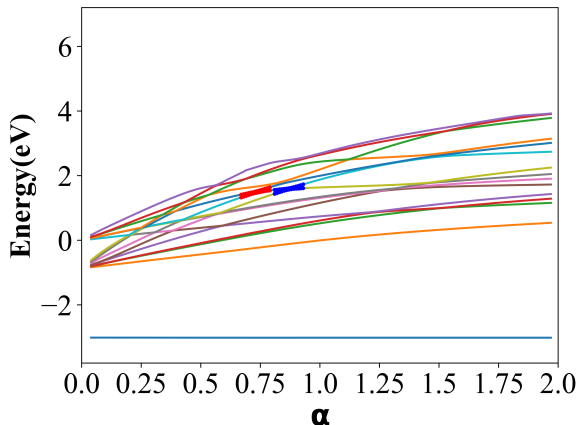


Figure S6: Orbital stabilization plot of isolated uracil obtained at the EOM-EA-CCSD/aug-cc-pVDZ+1p level of theory. Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

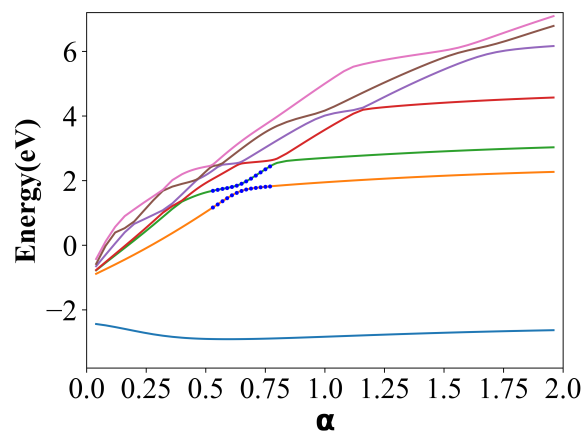


Figure S7: Orbital stabilization plot of isolated uracil obtained at the EOM-EA-CCSD/cc-pVDZ+1p level of theory. Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

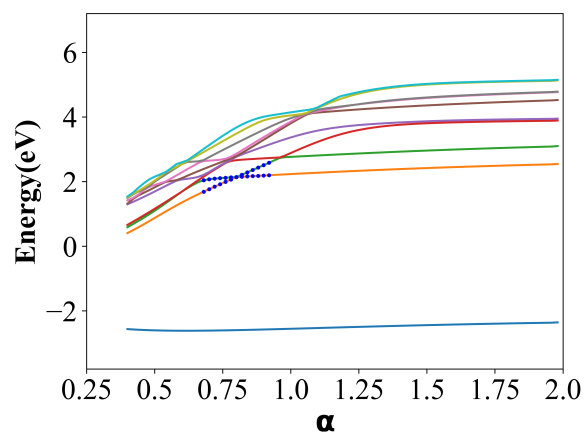


Figure S8: Orbital stabilization plot of uracil with PCM at the EOM-EA-CCSD/cc-pVDZ+1p level of theory. Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

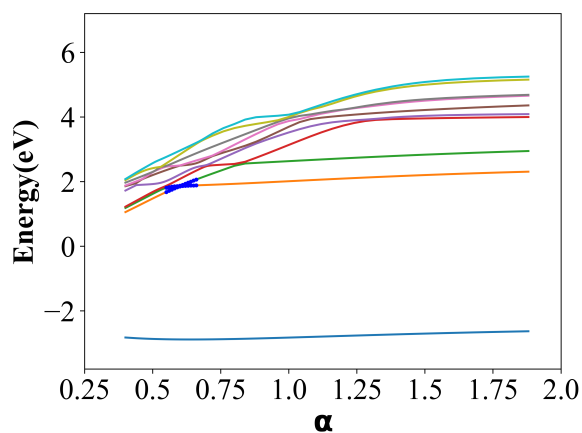


Figure S9: Orbital stabilization plot of uracil with water as point charges at the EOM-EA-CCSD/cc-pVDZ+1p level of theory. Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

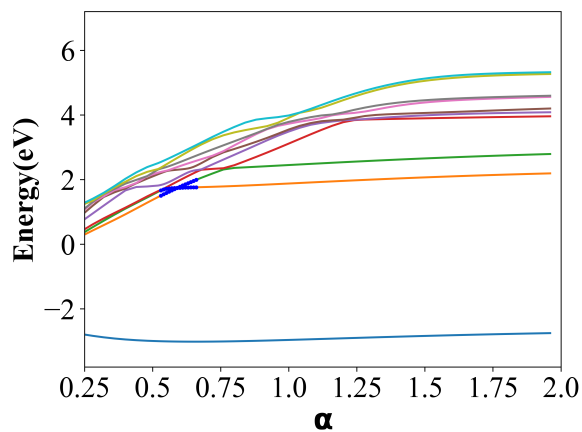


Figure S10: Orbital stabilization plot obtained at the EOM-EA-CCSD/EFP level using cc-pVDZ+1p basis set where uracil treated at QM level and 2460 water molecules at the EFP level. Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

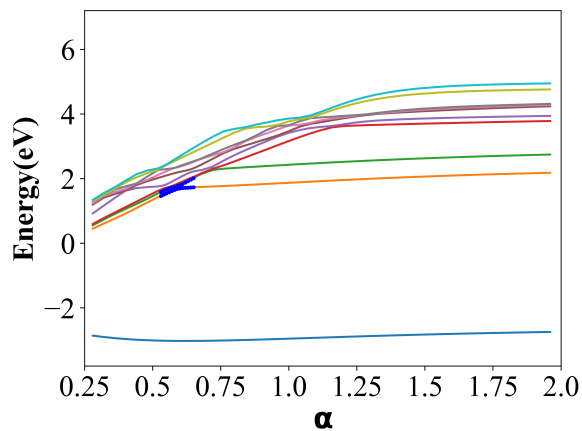


Figure S11: Orbital stabilization plot obtained at the EOM-EA-CCSD/EFP level using the cc-pVDZ+1p basis set, where uracil and 3 water molecules were treated at the QM level and 2457 water molecules were treated at the EFP level. Blue points indicate the avoided crossings that were used in GPA calculations. The results are presented in Table 1 of the main paper.

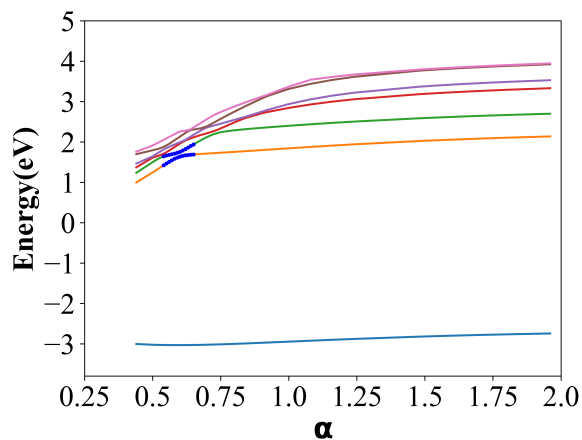


Figure S12: Orbital stabilization plot obtained at the EOM-EA-CCSD/EFP level using cc-pVDZ+1p basis set where uracil and 7 water molecules were treated at QM level and 2453 water molecules were treated at EFP level. Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

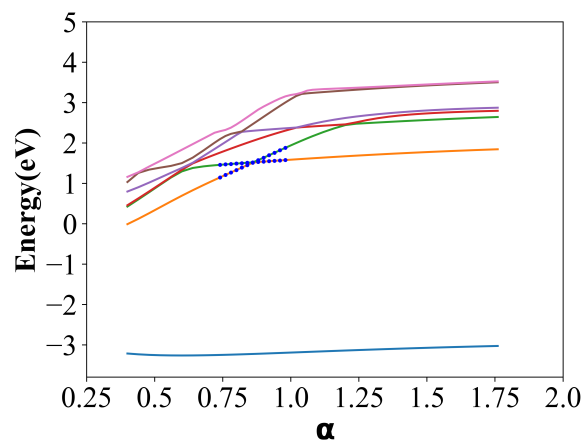


Figure S13: Orbital stabilization plot of uracil+1a  $H_2O$  cluster obtained at the QM level (EOM-EA-CCSD/cc-pVDZ+1p). Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

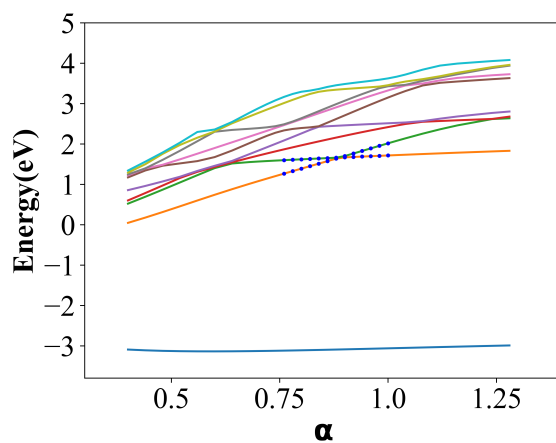


Figure S14: Orbital stabilization plot of uracil+1b  $H_2O$  cluster obtained at the QM level (EOM-EA-CCSD/cc-pVDZ+1p). Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

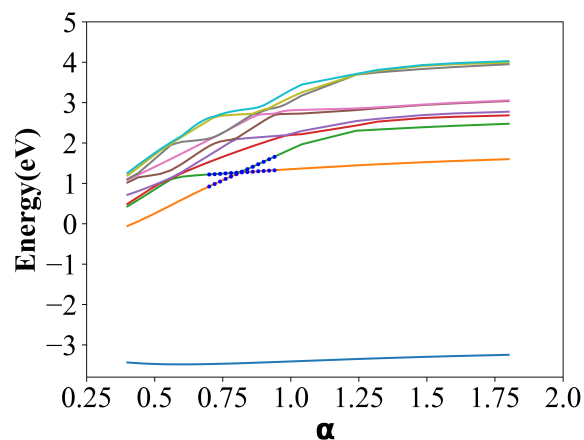


Figure S15: Orbital stabilization plot of uracil water cluster with 2 water molecule at the QM level (EOM-EA-CCSD/cc-pVDZ+1p). Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

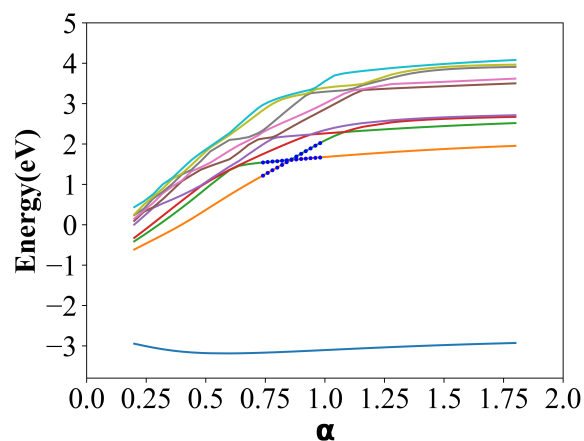


Figure S16: Orbital stabilization plot of uracil water cluster with 3 water molecule at the QM level (EOM-EA-CCSD/cc-pVDZ+1p). Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

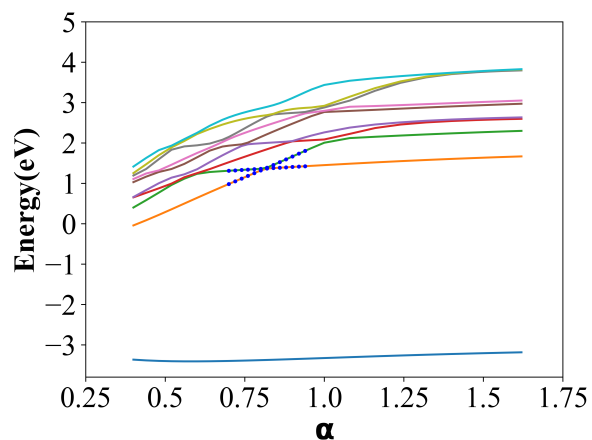


Figure S17: Orbital stabilization plot of uracil water cluster with 4 water molecule at the QM level (EOM-EA-CCSD/cc-pVDZ+1p). Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

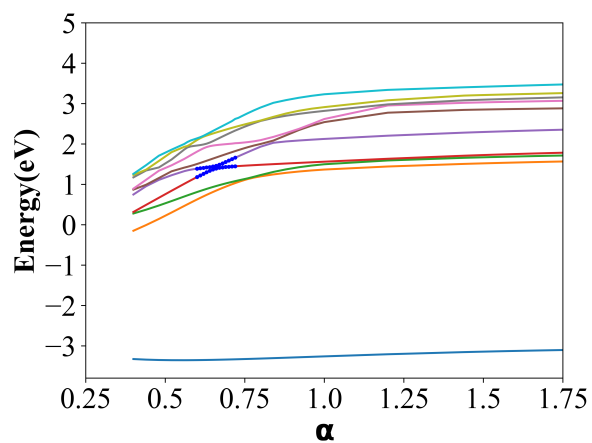


Figure S18: Orbital stabilization plot of uracil water cluster with 7 water molecule at the QM level (EOM-EA-CCSD/cc-pVDZ+1p). Blue points indicate the avoided crossings that were used in GPA calculations and the results are presented in Table 1 of the main paper.

## 5 Comparison between microsolvation and bulk solvation

Figure S19 shows the comparison between the microsolvation and bulk solvation for the 1p resonance and the results are tabulated in Table S5. Similar comparison is made for the 2p1h resonance for the 13 snapshots which is presented in Figure 10 and Table 3 of the main paper. Similar to 2p1h resonance, the values for 1p resonance also increases from left to right in the case of bulk. But the EA values for the clusters show no such trend.

**Table S5: Comparison of electron attachment energies EA- $D_0$  between clusters with a small number of water molecules and bulk solvation where all the water molecules are included at the EFP level. 13 different configurations were chosen from the normal distribution as shown in Figure 2 in the main paper by picking them using the average and standard deviation. All values are shown in eV and are calculated at the EOM-EA-CCSD/EFP/cc-pVDZ+1p level. "Water" indicates the number of water molecules in the cluster.**

Snapshot	# Water	Clusters E	Bulk E
1 (Average - 2.0 SD)	10	0.277	0.097
2 (Average - 1.5 SD)	12	0.971	0.312
3 (Average - 1.0 SD)	10	0.252	0.484
4 (Average - 0.5 SD)	9	0.074	0.734
5 (Average)	8	0.534	0.940
6 (Average)	9	1.008	0.992
7 (Average)	10	0.377	0.973
8 (Average)	7	0.657	0.942
9 (Average)	10	0.245	0.956
10 (Average + 0.5 SD)	10	0.759	1.094
11 (Average + 1.0 SD)	10	0.853	1.331
12 (Average + 1.5 SD)	10	1.289	1.532
13 (Average + 2.0 SD)	6	0.593	1.729

Figure S20 shows a correlation plot between EA- $D_N(S)$  and EA- $D_0$  for the cluster including only waters around the first solvation of uracil. An equivalent plot for bulk solvation is shown in the main text, Figure 9. In both of these plots, a strong correlation is shown between the EA of the two types of resonances. This indicates that the solvation effects are similar for both resonances, and thus the electron density of the particular state does not play a big role in the solvation effects.

Figure S21 shows the correlation between the EA of the 1p resonance and the 2p1h



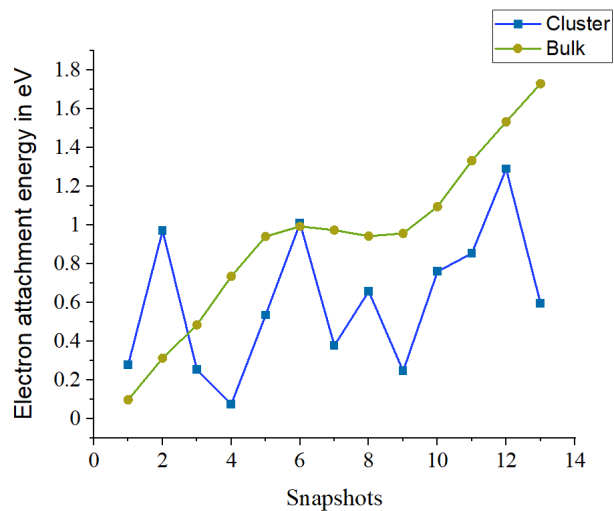


Figure S19: Comparison of EA- $D_0$  between a cluster including only waters around the first solvation of uracil and bulk solvation for the 1p resonance.

resonance at the EOM-EA-CCSD/EFP level using only 5 snapshots. The values are also depicted in Table 4 in the main paper. This plot is equivalent to Figure 9a in the main paper, which was done using EOM-EA-CCSD values for 300 snapshots. Comparison between the two plots shows that similar linear correlation is obtained even with only 5 snapshots.

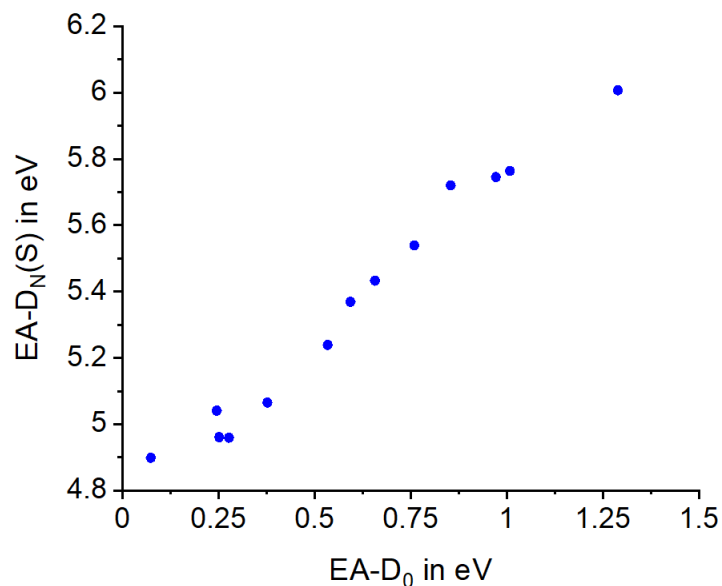


Figure S20: Correlation plot between EA- $D_N(S)$  and EA- $D_0$  for the cluster including only waters around the first solvation of uracil. Values are obtained from EOM-EA-CCSD/cc-pVDZ+1p stabilization graph. An equivalent plot for bulk solvation is shown in Figure 9 of the main paper.

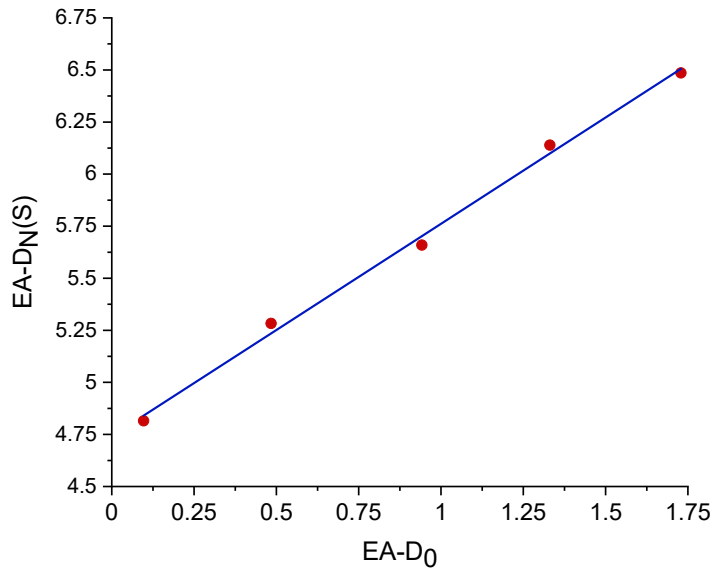


Figure S21: Correlation plot between EA- $D_N(S)$  and EA- $D_0$  using EOM-EA-CCSD results for the 5 solvated configurations shown in Table 4 in the main paper. Values are obtained from the orbital stabilization method. Linear fitting on these points gives the equation  $y = 0.9766x - 4.6269$  with  $R^2 = 0.9962$ .

## 6 Comparison of EOM-EA-CCSD results for the 1p resonance using a singlet or triplet reference

In order to examine the sensitivity of the EA results for the first 1p resonance on the reference state used in CCSD, we carried out the calculations using either the ground singlet state or the lowest triplet state. The standard way to get this resonance is by using the ground singlet state, but in this work we can also get it as a byproduct when we use the triplet neutral state as reference. The energy for the first 1p resonance using the two different references was calculated for three configurations: minimum, average and maximum energy from the normal distribution, using the charge stabilization/cc-pVDZ+1p method. The results are shown in [Table S6](#), and they confirm that the results do not depend strongly on the reference. Furthermore, both results show the same trends on how the EA changes for the three snapshots. This comparison confirms that the correlation between the two resonances (1p and 2p1h) discussed in detail in the main paper (Section 3.4) is not because of how we carried out the calculations, but rather it is physical.

**Table S6: Resonance energies in eV for configurations at the minimum, average, and maximum energy from a normal energy distribution shown in Figure 5 of the main paper obtained using charge stabilization method**

Snapshots	EA- $D_0$ with singlet as reference	EA- $D_0$ with triplet as reference
Minimum	0.327	0.379
Average	1.417	1.456
Maximum	2.100	2.468

## 7 Resonance parameters at different levels of solvation

The positions and widths of the first 2p1h resonance of uracil were calculated for five solvation configurations around average of the normal distribution using (7, 7, 7) GPA, as shown in [Table S7](#). Stabilization curves were generated for each representative snapshot using EOM-EA-CCSD/cc-pVDZ+1p theory. These results are used in Figure 11 of the main paper,

where they are subtracted from values for isolated uracil.

**Table S7: Positions(Widths) of the First Core-Excited Shape Resonance of Uracil at Different Solvation Levels (in eV)**

Snapshots	Uracil+2460 $H_2O$ (EFP)	Uracil+3 $H_2O$ (QM)+2457 $H_2O$ (EFP)	Uracil+3 $H_2O$ (QM)
5	1.709 (0.038)	1.672 (0.059)	1.656 (0.017)
6	1.716 (0.034)	1.796 (0.040)	1.260 (0.014)
7	1.749 (0.038)	1.771 (0.024)	1.443 (0.025)
8	1.759 (0.027)	1.749 (0.053)	1.612 (0.017)
9	1.778 (0.025)	1.792 (0.034)	1.348 (0.024)