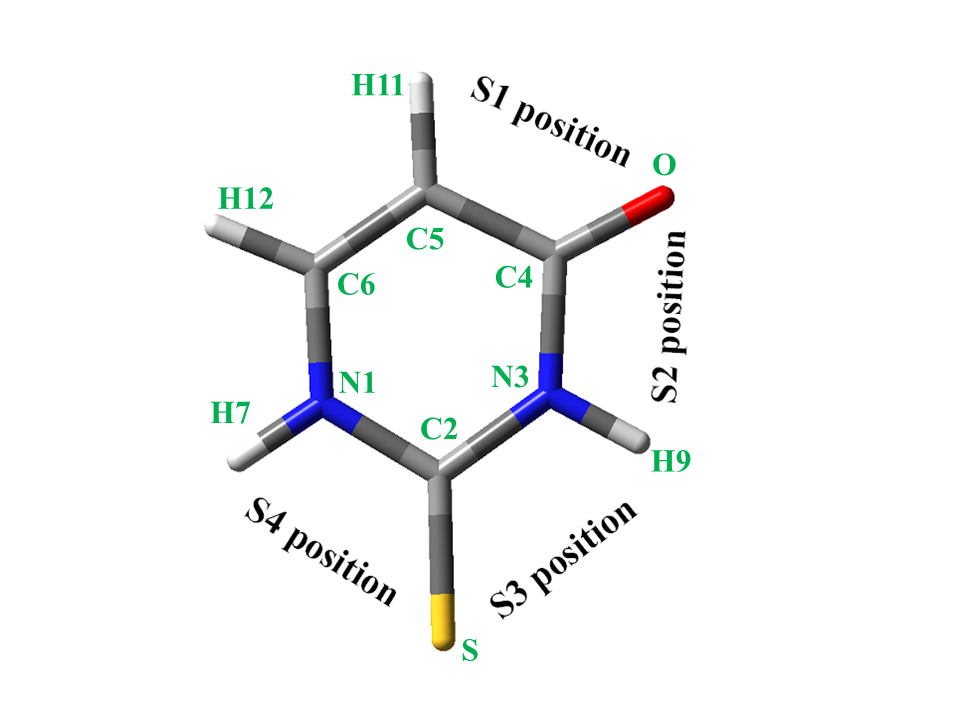
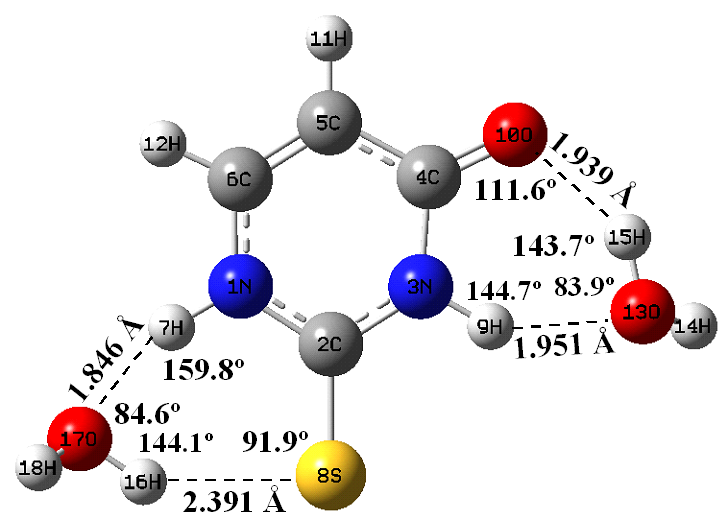
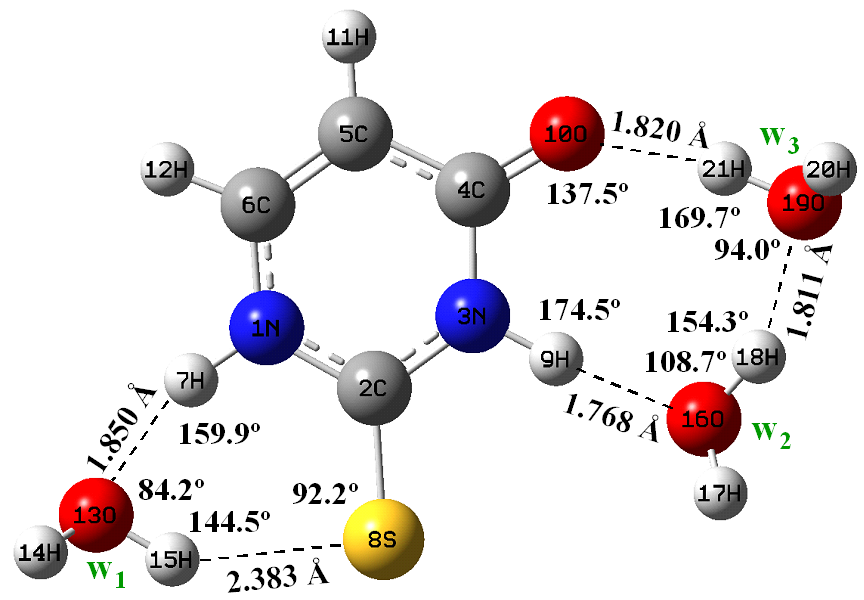
**SUPPLEMENTARY MATERIAL**

****

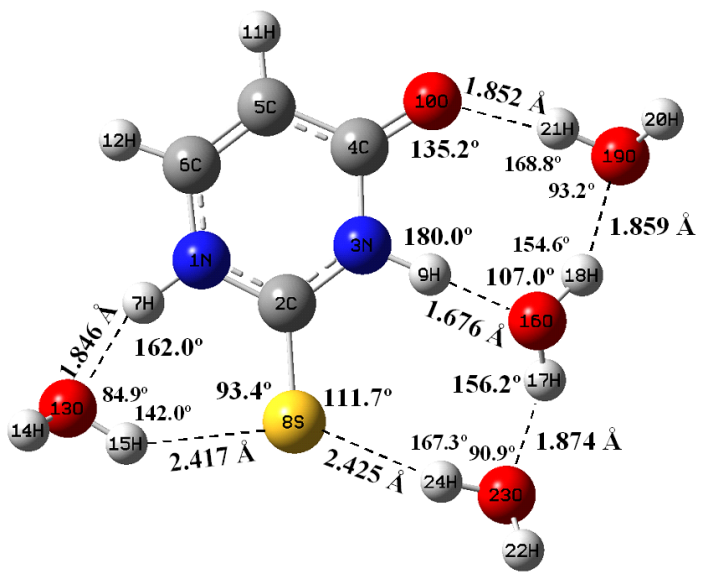
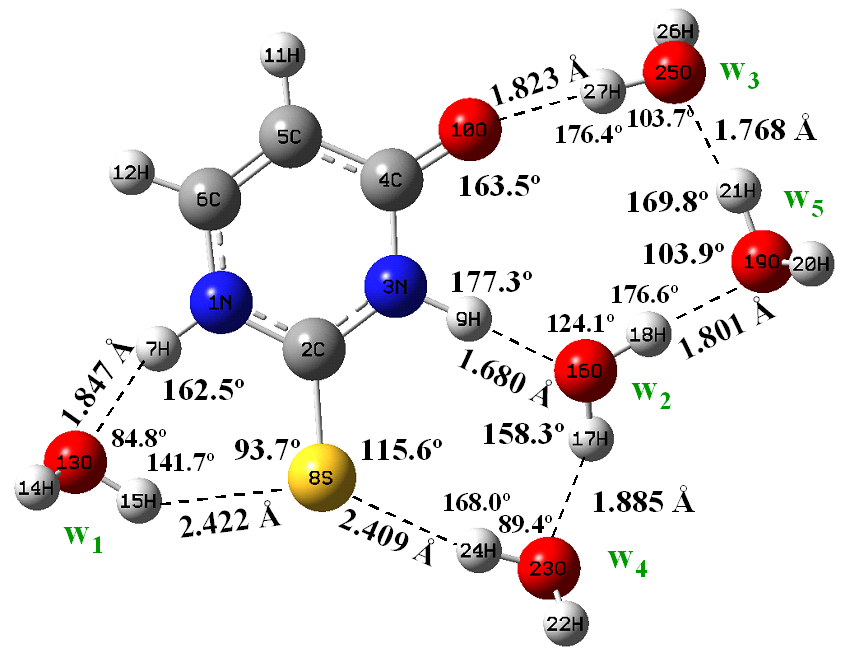
**Scheme 1-SUP.** Labeling of the atoms in 2TU. S1 to S4 are the four regions of H-bond formation with water molecules.

** **

**+ 2 H2O**

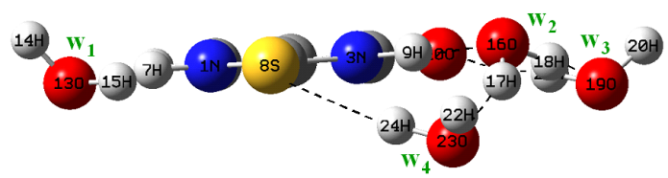
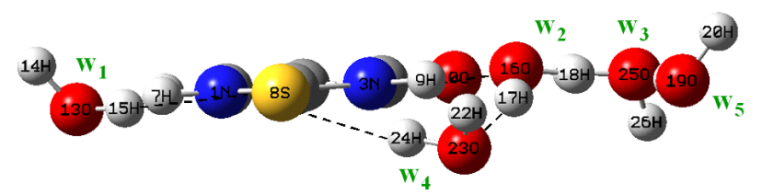
**+ 3 H2O**

*E* = -890.724588 (*G* = -890.763584), µ = 3.638 D-967.175637 (-967.218911), µ = 4.775 D

**** 

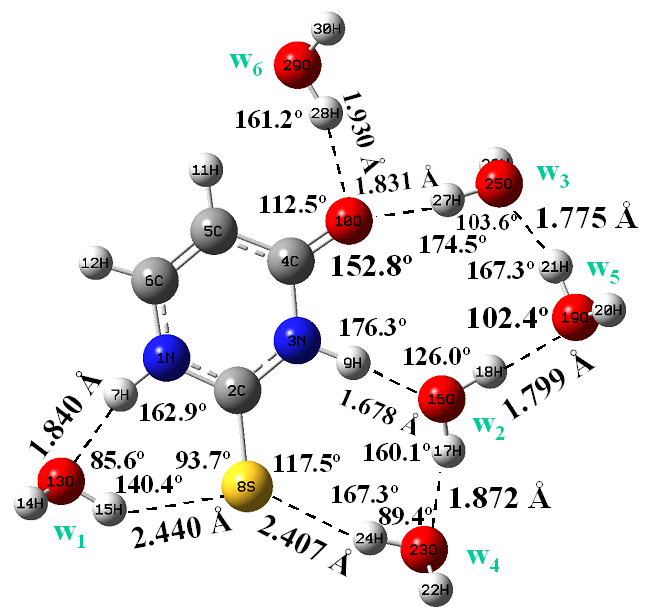
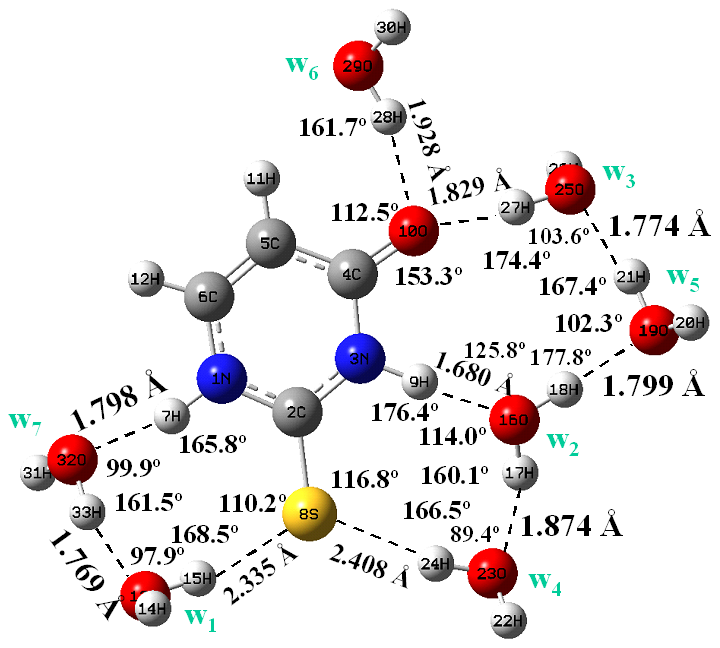
**+ 4 H2O**

**+ 5 H2O**

**** 

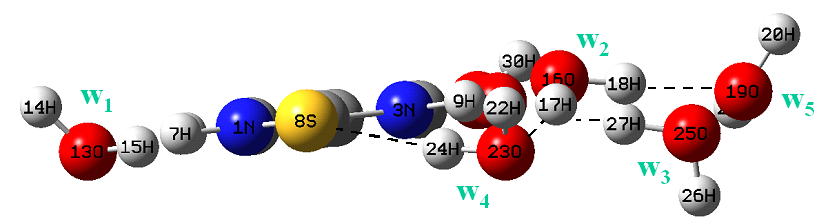
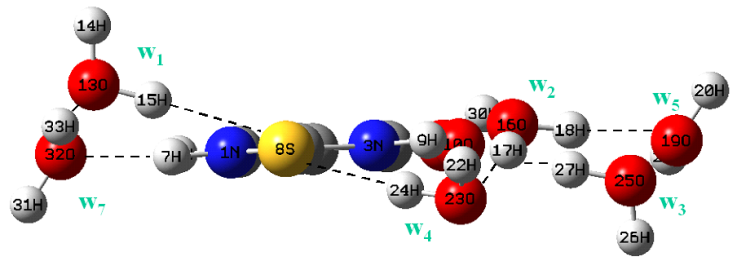
-1043.623837 (-1043.670705), µ= 5.025 D-1120.072089 (-1120.124651), µ= 5.064 D

**(Fig. 1-SUP)** Optimized most stable hydration clusters of 2TU from two up to 5 water molecules at the B3LYP/6-311+G(2d,p) level. Two views of each cluster are plotted in several cases. The total energy+ZPE and the Free energy G (in parentheses) are in atomic units. The dipole moment (µ) is in Debyes.

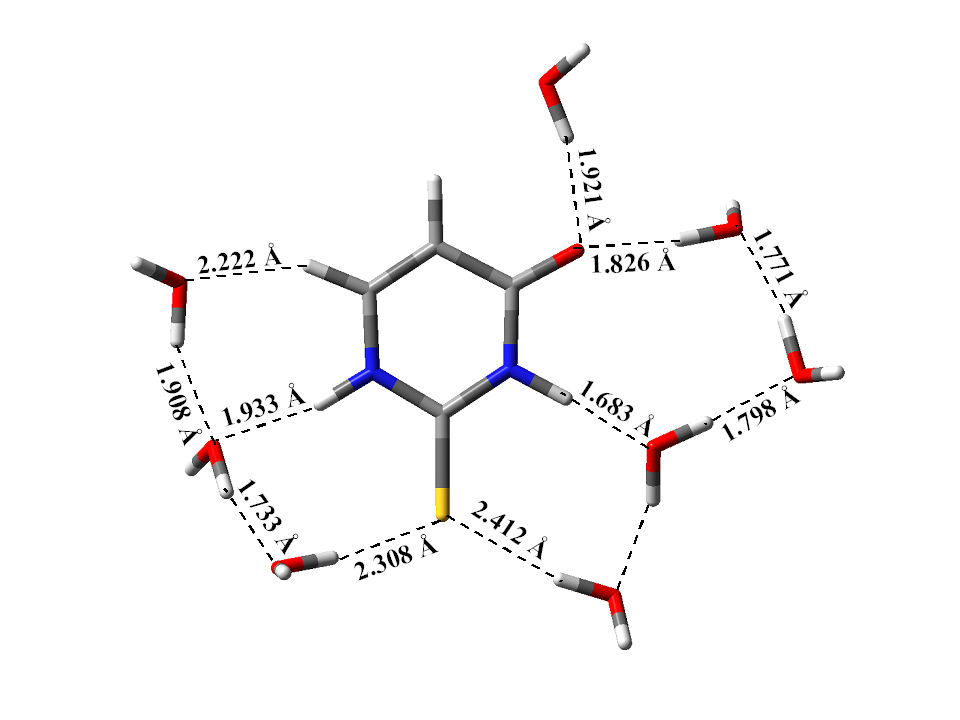
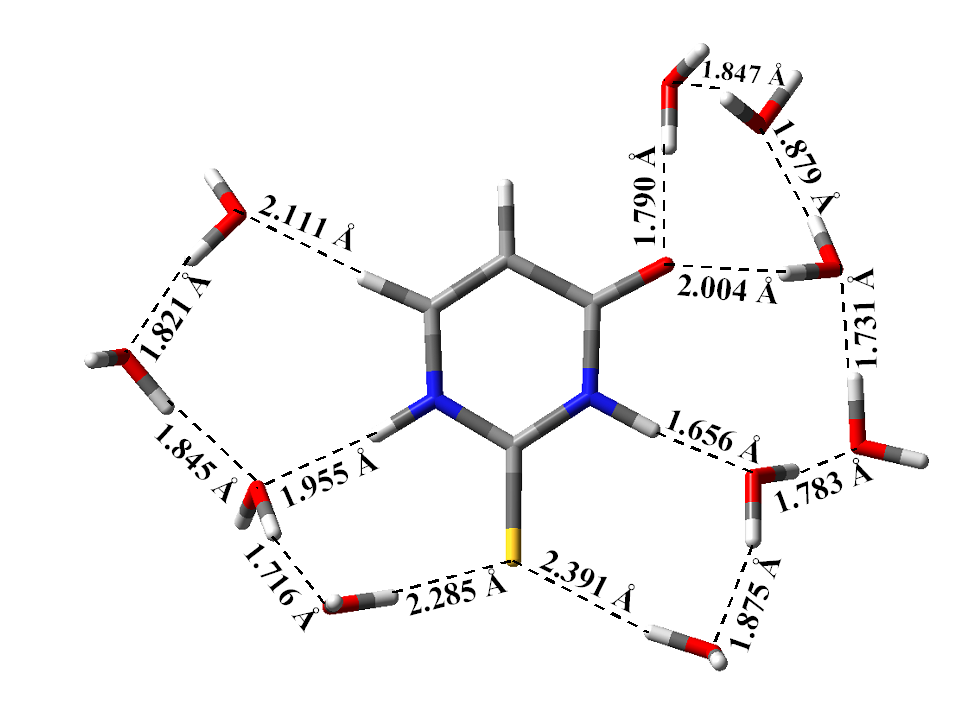
**+ 7 H2O**

**+ 6 H2O**

-1196.517128 (-1196.574563 AU), µ= 4.293 D -1272.967966 (-1273.029865 AU), µ= 2.572 D

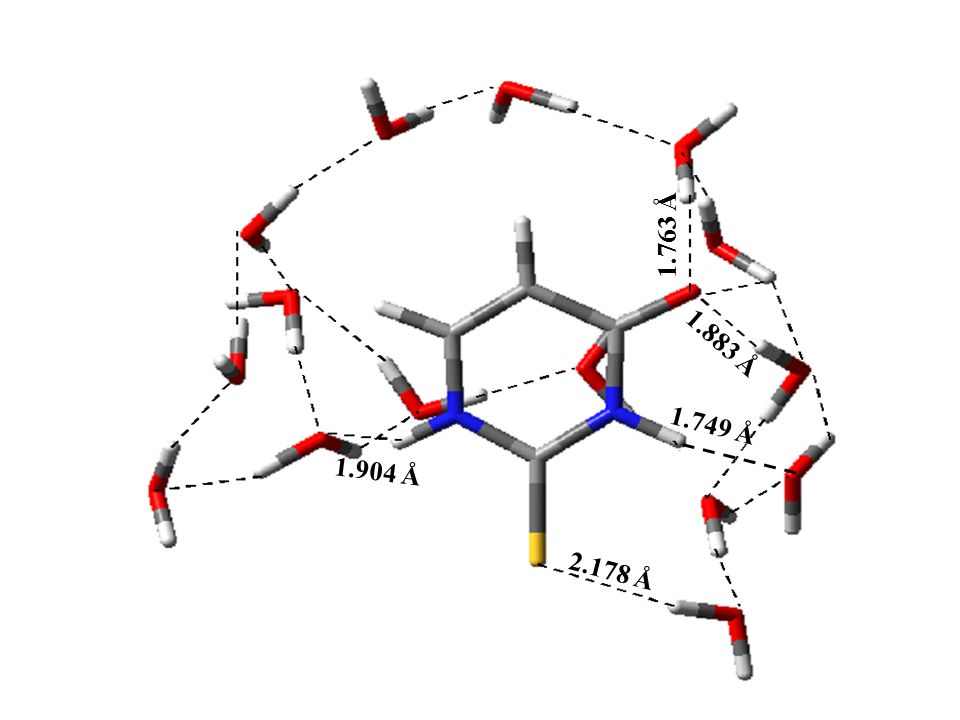
**+ 8 H2O**

**+ 10 H2O**

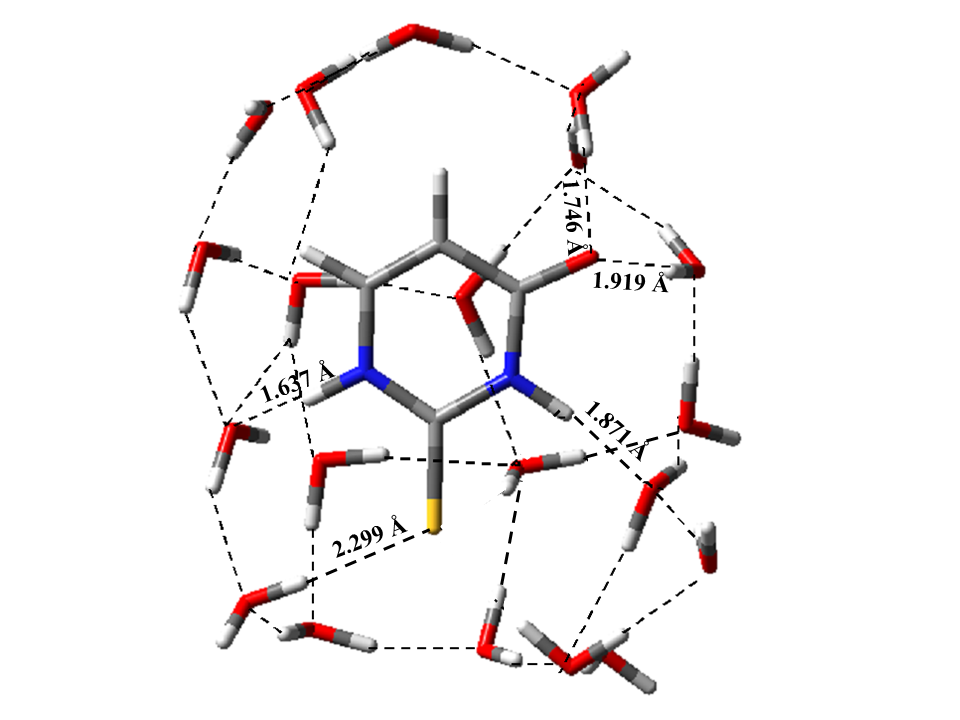
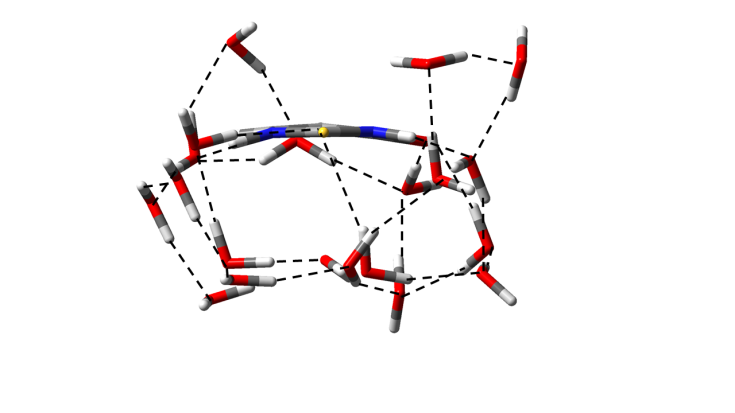
-1349.414376 (-1349.480530 AU), µ= 5.211 D-1502.313201 (-1502.385980 AU), µ= 6.788 D

**(Fig. 2-SUP)** Optimized most stable hydration clusters at the B3LYP/6-311+G(2d,p) level of 2TU from 6 to 10 water molecules. Two views of the clusters with 6 and 7 water molecules are shown. The total energy+ZPE and the Free energy G (in parentheses) are in atomic units. The dipole moment (µ) is in Debyes.



*E* = -1883.944172 AU (*G* = -1884.021061 AU), μ=2.289 D

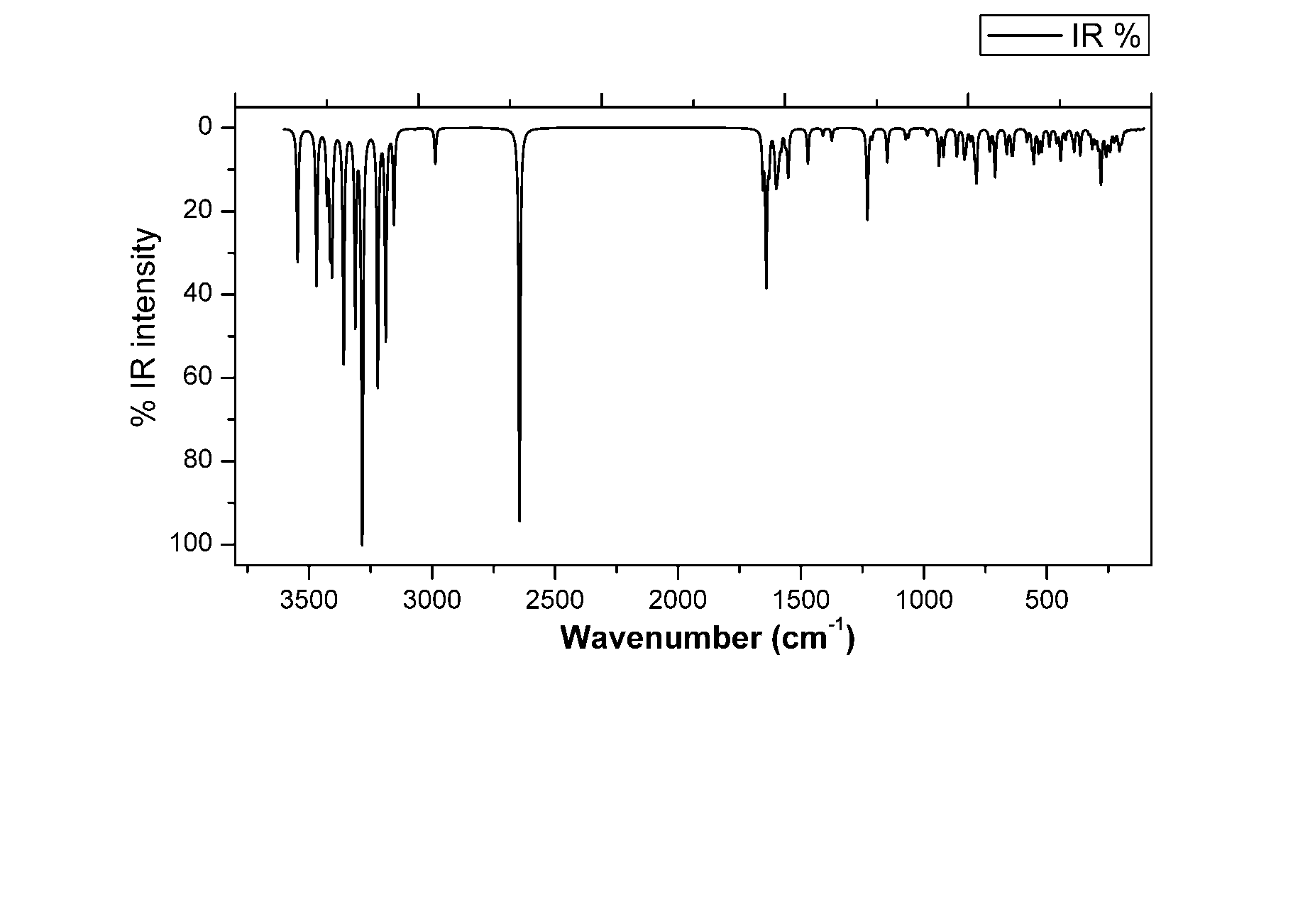
**+ 15 H2O**

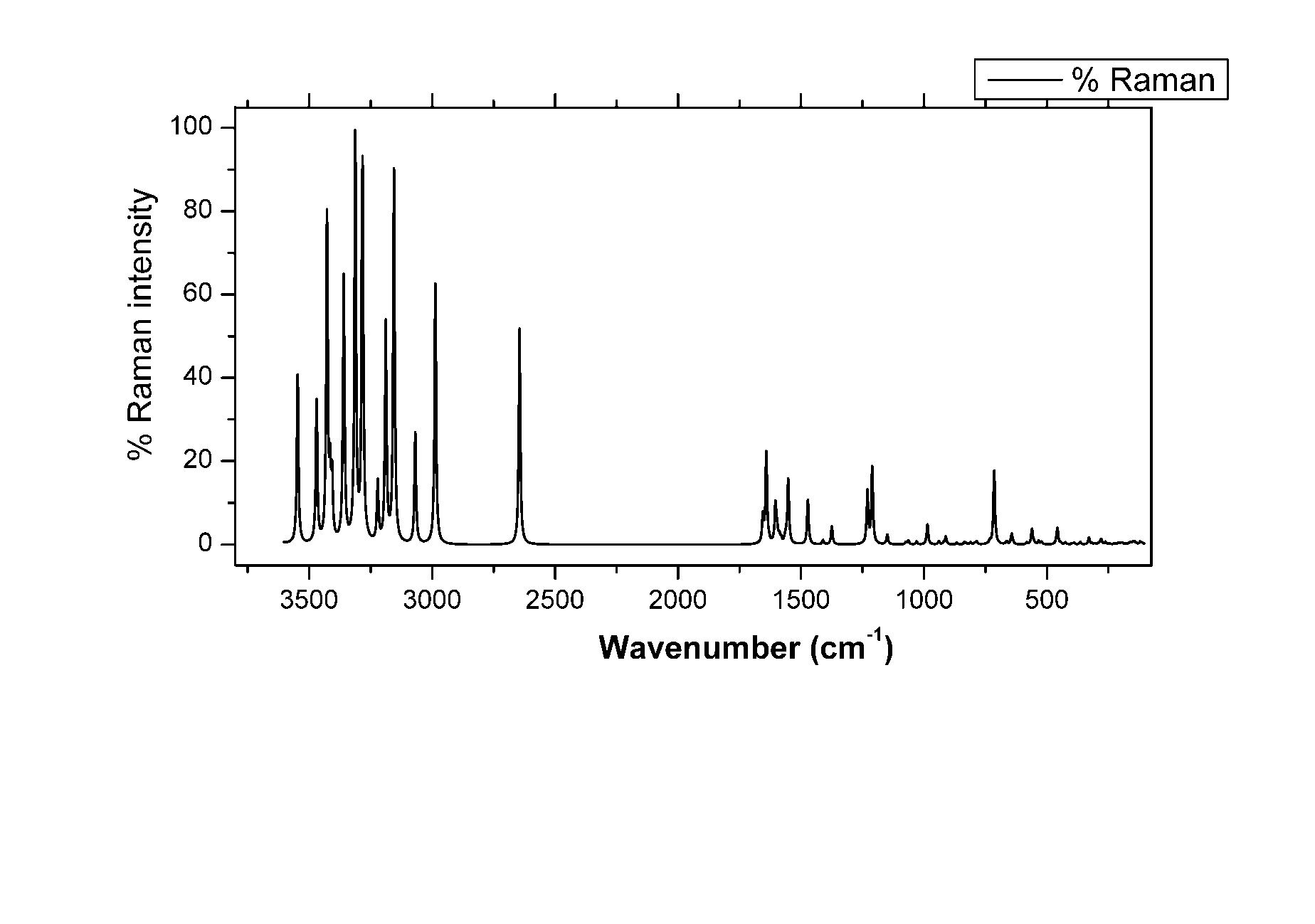
 

**+ 20 H2O**

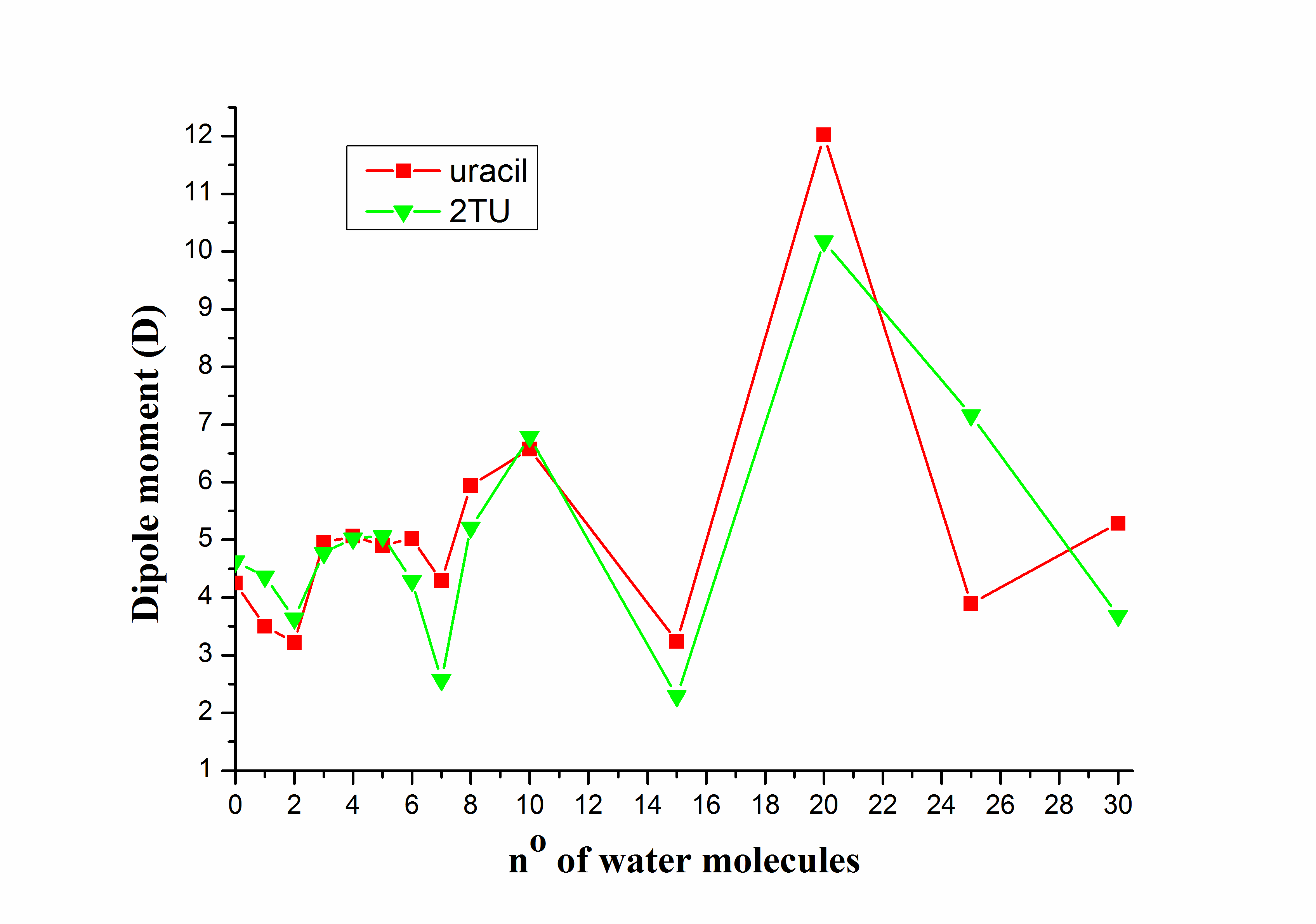
*E* = -2266.024165 AU (*G* = -2266.116386 AU), μ = 10.173 D

**(Fig. 3-SUP)** Optimized most stable hydration clusters at the B3LYP/6-31G(d,p) level of 2TU with 15 and 20 water molecules. Two views of each cluster are plotted. The total energy+ZPE and the Free energy G (in parentheses) are in atomic units.. The dipole moment (µ) is in Debyes.

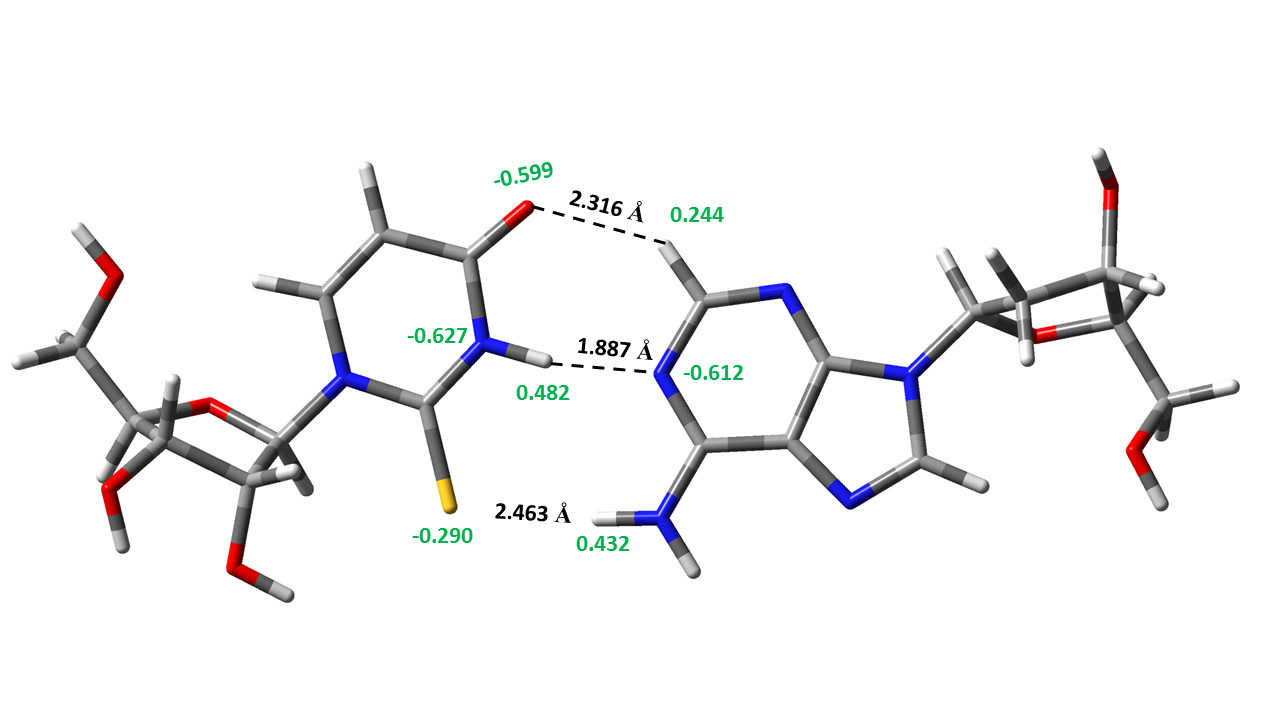




**(Fig. 4-SUP)** Theoretical scaled IR and Raman spectra at the B3LYP/6-31G(d,p) level in the cluster 2TU(H2O)15.



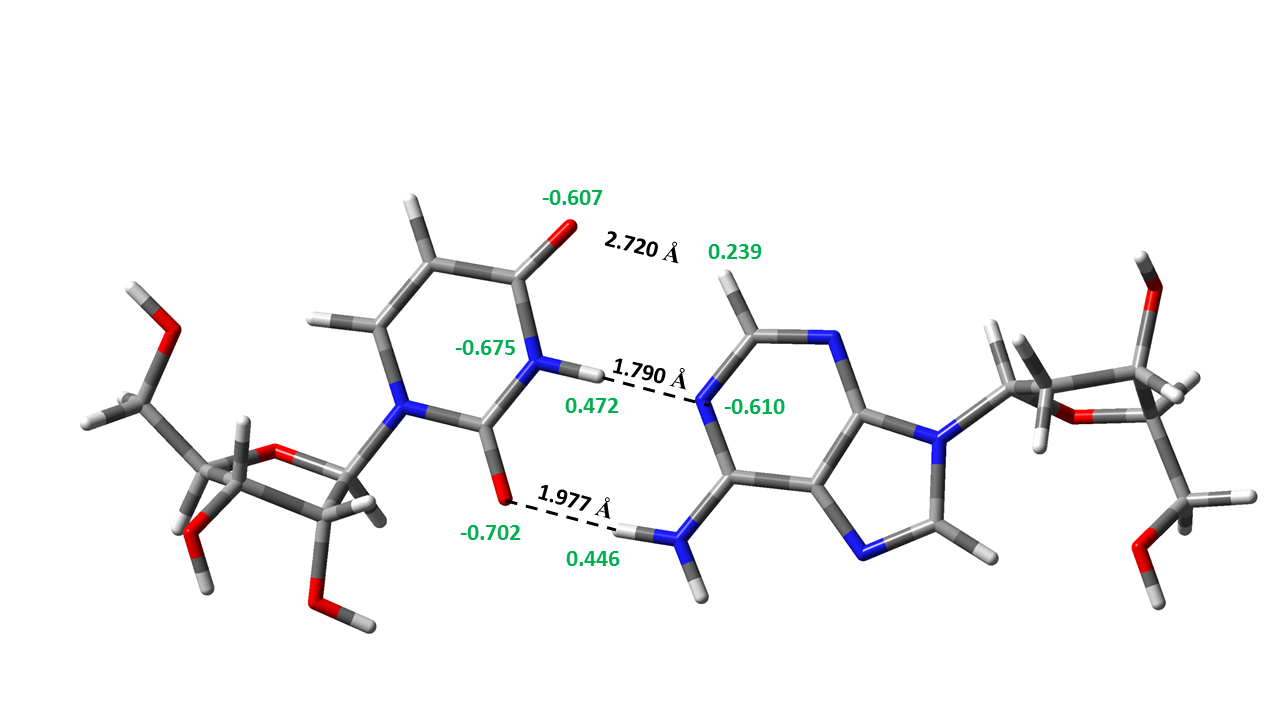
**(Fig. 5-SUP)** Changes obtained in the dipole moment of 2TU with the increase of the number of water molecules. The calculated values were at the B3LYP/6-31G(d,p) level.



**2-thiouridine**

**2'-deoxyadenosine**

*E* = -2121.891632 AU (*G* = -2121.960542 AU), μ = 1.419 D



**uridine**

**2'-deoxyadenosine**

*E* = -1798.938590 AU (*G* = -1799.008241 AU), μ = 4.090 D

**(Fig. 6-SUP)** Optimum pairs at the B3LYP/6-31G(d,p) level + ZPE of the reverse Watson-Crick 2-thiouridine···2′-deoxyadenosine (dA), and the natural one uridine···dA. The NBO atomic charges are plotted in green colour, the energy in AU and the dipole moment (μ) in Debye.

**Table 1-SUP.** xyz coordinates of several base pairs optimized structures

2'deoxy-adenosine + 2-thiouridine

N -4.22980800 0.16775600 -0.43660400

C -2.87010400 -0.11328300 -0.36718200

N -2.05654600 0.97811900 -0.21537300

C -2.44915100 2.31629000 -0.10345300

C -3.87865700 2.51896800 -0.16907300

C -4.70104000 1.45965000 -0.33859500

C -5.18876500 -0.96060500 -0.64776300

C -5.56852300 -1.68186700 0.65959700

C -6.89483000 -0.98936300 1.03760500

C -7.50879400 -0.73455500 -0.34328800

O -6.38756100 -0.44740500 -1.19559000

O -1.61710000 3.21475300 0.03892300

H -5.77667600 1.56237300 -0.41009100

H -4.70876700 -1.65486300 -1.33800100

H -7.99637300 -1.65948200 -0.68002400

C -8.51891000 0.39303300 -0.42211800

O -7.95890800 1.56634500 0.16162500

H -9.42362400 0.07214500 0.11498200

H -8.78247400 0.55594500 -1.47593500

H -8.55094300 2.30812600 -0.01242900

C 1.72364200 1.65021100 0.02378800

C 3.11019400 1.36743300 0.04255700

C 3.47260700 0.02448500 -0.05511100

N 0.86894600 0.60367700 -0.08759100

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N 4.85403600 0.01839500 -0.01856900

N 2.64751500 -1.02741900 -0.16721500

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C 5.23431600 1.34704200 0.10192700

H 6.27570800 1.62826700 0.17737500

C 5.68888800 -1.17506900 -0.09569800

C 6.54701100 -1.26659700 -1.37020500

C 7.92588000 -0.78483100 -0.92016600

C 7.95989700 -1.26767900 0.54119500

C 8.82044800 -0.44184100 1.49075000

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H 6.12252900 -0.69935700 -2.19999000

H 7.98706100 0.31121900 -0.94182500

H 8.30161500 -2.31423400 0.54473900

H 8.85750900 -0.93006000 2.47509300

H 9.84629100 -0.39956800 1.10688800

H 7.46854400 0.83563500 1.97547400

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H 0.62204000 -1.42848300 -0.25948000

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H -4.26332500 3.52651400 -0.09200400

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O -5.82542200 -3.03404900 0.34505700

H -6.54869000 -3.30824600 0.93281700

2'-deoxy-adenosine + Uridine

N -4.25560700 0.23007500 -0.49993000

C -2.86917600 0.01307400 -0.49771700

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C -2.56313800 2.43858300 -0.08163200

C -4.00635000 2.57146900 -0.09490100

C -4.78593200 1.48396200 -0.30509100

C -5.09523900 -0.96536000 -0.76637900

C -5.29710700 -1.84711100 0.47842000

C -6.64472900 -1.33047400 1.02144100

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O -6.38081400 -0.54822100 -1.18547200

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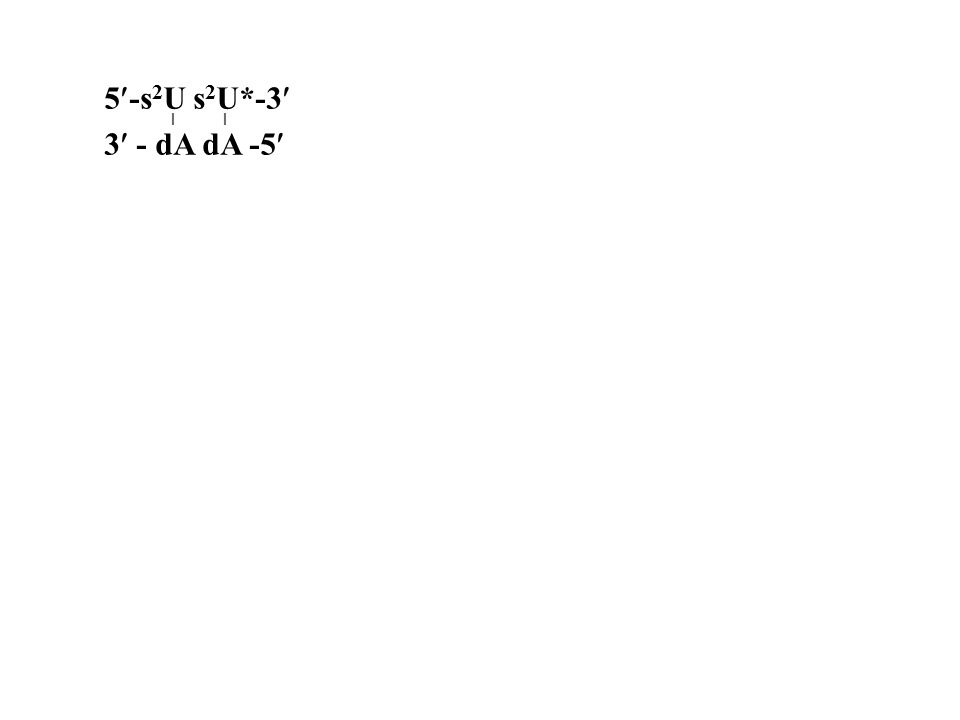
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H 7.05883300 -3.83359200 4.10401100

H -1.33671400 -2.87446900 -0.77105200

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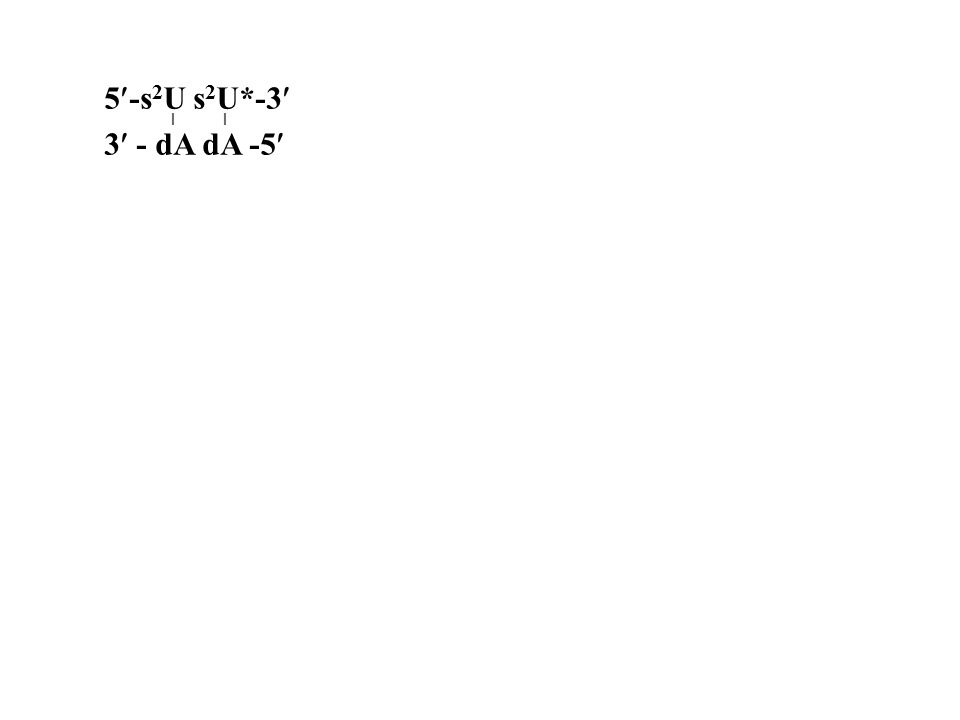
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S -2.38882100 3.62852200 1.18200100

S -1.63892500 -1.88405000 -3.33862600

 (stable structure not included in the manuscript)

C 1.59534400 -0.48495000 2.04367200

C 2.79760000 0.28781500 2.01301600

C 2.63230600 1.69003000 1.81607200

N 0.41209900 0.17995400 2.00169100

N 4.09640900 -0.04386000 2.11262600

N 3.92339900 2.19906100 1.79070900

N 1.48805900 2.32951200 1.70548300

C 0.41311000 1.50089800 1.84221800

C 4.74951200 1.12335100 1.95310600

H 5.83833400 1.17645000 1.95025400

C 4.24504700 3.57954200 1.29512800

C 5.40505900 4.27141100 2.01891200

C 6.61440400 3.83324300 1.18629000

C 6.01562200 3.75688100 -0.23631400

C 6.63805000 2.70723200 -1.14786400

O 4.60261300 3.48926000 -0.05830800

O 6.79909700 1.44282800 -0.49536500

H 3.29273500 4.10600800 1.38857900

H 5.47902100 4.01352800 3.07734700

H 6.90496000 2.83612500 1.52003600

H 6.11912900 4.74213400 -0.71122700

H 5.98262200 2.54151600 -2.00777500

H 7.60617400 3.07724400 -1.49566300

N 1.59177000 -1.81351400 2.08955200

H 2.47403600 -2.30156100 2.15762400

H 0.69662200 -2.32690300 1.97849200

H -0.55748500 1.98454600 1.86144400

H 5.26877200 5.35464000 1.93453600

P 8.21397800 1.12066500 0.33793200

O 9.17081600 2.25853100 0.12178000

O 7.78975100 0.70239200 1.73043200

O 8.70697300 -0.20552000 -0.50542800

C 8.32616400 -1.52618000 -0.10785100

C 8.53127100 -2.44575200 -1.32748100

H 8.91615900 -1.83320000 0.76207700

C 6.82027900 -1.68696200 0.13365600

H 9.28079700 -2.03138200 -2.00651400

O 7.26624900 -2.45279900 -2.03612300

C 6.29578500 -1.74173700 -1.29958900

H 6.63368600 -2.64597500 0.62939500

H 6.38598200 -0.89624700 0.73803400

H 6.12757600 -0.73746400 -1.70121700

N 5.02032400 -2.46167100 -1.43007800

C 4.84160400 -3.80705900 -1.58170800

C 3.75505600 -1.90886800 -1.37502600

H 5.68970900 -4.46561000 -1.70723200

N 3.56172700 -4.18141000 -1.60695300

C 2.87824800 -3.01265700 -1.47865600

N 3.40741200 -0.63144500 -1.27568700

C 1.48466700 -2.71358100 -1.46254900

C 2.06880900 -0.46560400 -1.30940200

N 1.11904500 -1.40405000 -1.38335500

N -4.43788200 -1.40455300 2.48906700

C -3.28791400 -0.68664800 2.72578400

N -2.12435200 -1.30329500 2.35277600

C -1.98055000 -2.57716500 1.79682500

C -3.22996500 -3.23195400 1.51688200

C -4.39762100 -2.63164400 1.86523600

C -5.76709400 -0.83907900 2.95251400

C -6.31012400 0.27011100 2.00849300

C -7.15015000 -0.59512600 1.07270700

C -7.77117000 -1.62736600 2.01170100

O -6.71064100 -1.86827200 2.98182200

O -0.85197000 -3.03831800 1.57317000

H -5.36420800 -3.07793200 1.65197000

H -5.57988000 -0.45305200 3.95714700

H -8.63188200 -1.19712700 2.53673200

H -1.26162800 -0.74042600 2.41930700

O -8.11724100 0.07110200 0.29336700

H -6.44664900 -1.12637600 0.42556400

H -5.51013700 0.80047300 1.48344900

N -3.36064900 1.03733500 -1.47984800

C -2.02183500 0.74686100 -1.38267600

N -1.69065200 -0.57121600 -1.46402100

C -2.56685100 -1.65625400 -1.65003300

C -3.94934300 -1.27113100 -1.78181500

C -4.28924900 0.03708900 -1.68841300

C -3.84222800 2.45996800 -1.35538400

C -3.97429000 3.16835200 -2.71803000

C -5.48656500 3.03460400 -3.01803600

C -6.10630400 3.05877300 -1.61433000

O -5.10946000 2.45367500 -0.75634600

H -5.32336700 0.35718700 -1.75292100

H -3.10844900 2.97051200 -0.73083900

H -6.24910900 4.10433400 -1.31293500

C -7.42138000 2.31513200 -1.46631400

O -7.23487700 0.97654100 -1.92208000

H -8.18287600 2.82263500 -2.07122000

H -7.73671500 2.32542600 -0.41846700

H -5.71712500 2.08634600 -3.51338000

H -3.33402400 2.70238900 -3.48066900

P -8.17773200 -0.26572400 -1.33487500

O -9.58986700 -0.11370700 -1.79165500

O -7.34932200 -1.51064200 -1.59796300

H -4.71745800 -2.01492600 -1.94916500

H -3.22133500 -4.18975300 1.01618600

O -5.97059700 4.14339000 -3.76661300

H -6.02609700 3.89394500 -4.69766100

O 7.71868700 4.69584100 1.27664900

H 8.48521700 4.15691100 1.00239500

C -8.17431900 -2.93208100 1.32681300

H -8.35537000 -3.69477400 2.09160800

H -9.12352900 -2.75231400 0.80357900

O -7.18203100 -3.42897100 0.44674300

H -7.25116300 -2.90703800 -0.38518300

O -3.64917900 4.52498100 -2.52573900

H -4.26767700 5.02419300 -3.08675900

O -7.13791700 1.15706100 2.72821500

H -6.55978600 1.75380200 3.22376300

C 8.91913900 -3.86693000 -0.92909400

H 9.94786200 -3.83578800 -0.53800400

H 8.26745700 -4.21967100 -0.11211500

O 8.80820700 -4.70218100 -2.06966900

H 9.20447700 -5.55564900 -1.85391000

H -0.67939600 -0.81354000 -1.41060600

O -2.12937400 -2.80767200 -1.69110100

H 1.70955200 0.55959800 -1.28670200

N 0.54830700 -3.65330600 -1.53862900

H 0.83312500 -4.61942100 -1.61029400

H -0.44906600 -3.39600800 -1.53341300

S -3.26062100 0.84934500 3.42119800

S -0.82428600 1.93688900 -1.18381800

**Table 2-SUP**. Interatomic angles (in degrees) in the simulated base pairs with 2-thiouridine or uridine (A) and 2´-deoxiadenosine (B).

|  |  |  |  |
| --- | --- | --- | --- |
| Base pair | Interaction A···(H)B  or H···B | modified base pair with 2-thiouridine | standard base pair with uridine |
| WC | O4···(H)N6  N3(H)···N  N3-H···N-C(B) | 175.2  175.7  -172.4 | 175.3  178.7  115.5 |
| Reverse WC | O4···H-C(B)  N3-H···N(B)  N3-H···N-C(B) | 140.7  170.5  -178.4 | 134.1  179.5  155.3 |

**Table 3-SUP.** Several selected optimized geometric parameters of the uracil ring calculated at the B3LYP/6-31G(d,p) level. Bond lengths in Å

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | **Bond lengths (Å)** | | | | | Bond angles (º) | | Torsional angles (º) | | | NBO atomic charges | | | | |
| **Structure** | | **N1-C2** | **C2=O** | **C2-N3** | **N3-C4** | **C4=O** | **N1-C2-N3** | **C2-N3-C4** | **N1-C-N3-C** | **C2-N3-C-C** | **C-N1-C-N3** | **N1** | **O2/S2** | **N3** | **O4** | **N1A** |
| **Nucleobasis** | **U\*···A** | 1.398 | 1.220 | 1.379 | 1.393 | 1.234 | 113.7 | 127.0 | 0.0 | 0.0 | 0.0 | -0.639 | -0.630 | -0.685 | -0.640 | -0.610 |
| **2TU\*···A** | 1.381 | 1.670 | 1.367 | 1.403 | 1.230 | 114.3 | 126.3 | 0.0 | 0.0 | 0.0 | -0.589 | -0.193 | -0.634 | -0.628 | -0.614 |
| **Nucleosides** | **U\*···dA** | 1.403 | 1.225 | 1.376 | 1.393 | 1.236 | 114.9 | 127.1 | 0.7 | -0.5 | -0.2 | -0.482 | -0.642 | -0.678 | -0.650 | -0.609 |
| **U\* ···dA rev** | 1.397 | 1.235 | 1.366 | 1.406 | 1.225 | 115.6 | 127.2 | 0.8 | -0.6 | -0.3 | -0.481 | -0.681 | -0.679 | -0.610 | -0.610 |
| **s2U\*···dA** | 1.390 | 1.677 | 1.370 | 1.399 | 1.233 | 115.2 | 127.2 | 1.1 | -0.4 | -0.8 | -0.437 | -0.198 | -0.630 | -0.640 | -0.610 |
| **s2U\* ···dA rev** | 1.387 | 1.688 | 1.361 | 1.412 | 1.224 | 115.7 | 127.2 | 0.7 | 0.0 | -0.7 | -0.439 | -0.241 | -0.630 | -0.604 | -0.611 |
| **Nucleotides pair** | Notation 2-base pair dA | 1.400 | 1.231 | 1.374 | 1.401 | 1.236 | 115.0 | 126.8 | 3.3 | -1.4 | -3.5 | -0.484 | -0.669 | -0.677 | -0.653 | -0.610 |
| Notation 2-base pair with S | 1.387 | 1.681 | 1.370 | 1.400 | 1.235 | 115.1 | 127.1 | 4.8 | -0.9 | -5.1 | -0.436 | -0.221 | -0.630 | -0.650 | -0.609 |

\*Indicate the nucleobase/nucleoside on which the values are shown. a O2···H

**Table 4-SUP.** Backbone parameters and furanose ring torsional anglesa calculated in the nucleoside pointed with a “\*” in the optimum stable structures of the microhelix at the B3LYP/6-31G(d,p) level. Endocyclic and exocyclic torsional angles in degrees, pseudorotational angle P in degrees, total energy *E* (+ZPE) in AU, and dipole moments (μ) in Debyes.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Structure** | | **χ** | **ζ** | **α** | **β** | **γ** | **δ** | **ε** | **ε´** | **ν0** | **ν1** | **ν2** | **ν3** | **ν4** | **P** | **νmax** | ***E*** | **μ** |
| **Nucleosides** | **U\*···dA** | -160.3 | - | - | 172.8 | 51.2 | 85.0 | -158.0 | -34.0 | 3.47 | -25.02 | 35.43 | -34.47 | 19.94 | 13.4 | 36.4 | -1798.937324 | 4.937 |
| **U\* ···dA rev** | -157.6 | - | - | 170.3 | 50.5 | 85.1 | -157.0 | -33.4 | 2.39 | -24.06 | 34.93 | -34.58 | 20.68 | 15.0 | 36.2 | -1798.934894 | 4.967 |
| **s2U\*···dA** | -157.4 | - | - | 171.5 | 51.1 | 84.7 | -157.8 | -34.4 | 1.72 | -23.7 | 34.98 | -34.98 | 21.38 | 16.0 | 36.4 | -2121.889313 | 6.005 |
| **s2U\*···dA rev** | -157.6 | - | - | -170.9 | 50.7 | 84.6 | -157.8 | -34.3 | 1.90 | -23.90 | 35.14 | -35.0 | 21.29 | 15.7 | 36.5 | -2121.885202 | 4.707 |
| **Nucleotides pair** | Notation 2-base pair dA | -156.0 | -103.0 | -50.4 | 155.0 | 58.6 | 87.9 | -141.1b | -93.1c | 3.81 | -22.54 | 31.40 | -29.65 | 16.60 | 11.6 | 32.1 | -4579.427968 | 3.315 |
| Notation 2-base pair with S | -147.1 | -78.3 | -63.3 | 178.4 | 50.9 | 88.7 | -118.9 | -177.4 | 2.23 | -22.2 | 32.4 | -31.9 | 18.99 | 14.9 | 33.5 | -5225.326782 | 7.074 |

\*Indicate the nucleoside on which the values are shown. aχ(O4′-C1′-N1-C2), ζ(C3′0-O3′0-P-O5′), α(O3′0-P-O5′-C5′), β(P-O5′-C5′-C4′), γ(O5′-C5′-C4′-C3′), δ(C5′-C4′-C3′-O3′), ε(C4′-C3′-O3′-P-1), ε´(H2′-O2′-C2′-C3′), ν0(C4′-O4′-C1′-C2′), ν1(O4′-C1′-C2′-C3′), ν2(C1′-C2′-C3′-C4′), ν3(C2′-C3′-C4′-O4′), ν4(C3′-C4′-O4′-C1′). b On O3′0. c On O2′0