



### Theoretical Study On Intermolecular Interactions Of Uracil With H<sub>2</sub>O, H<sub>2</sub>S And H<sub>2</sub>Se


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#### ABSTRACT

Twelve fully optimized geometries of uracil-H<sub>2</sub>O, uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes have been obtained with density function theory (DFT) method at the B3LYP/6-311++G\*\* level. The intermolecular interaction energy is calculated with zero point energy (ZPE) correction and basis set superposition error (BSSE) correction. The greatest corrected intermolecular interaction of the uracil-water complexes is -31.503KJ/mol, -12.750KJ/mol and -10.997KJ/mol, respectively, indicating that the intensity of interaction between uracil and H<sub>2</sub>O is stronger than that of uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se. Natural bond orbital (NBO) analysis is performed to reveal the origin of the interaction. Frequency calculations are carried out on each optimized structure, and their IR spectra are discussed. Vibrational analysis show that there are large red-shifts for H-X (X= C, N, O, S and Se) stretching vibrational frequencies in the uracil's complexes. The changes of thermodynamic properties from the monomer to complexes with the temperature ranging from 200K to 800K have been obtained using the statistical thermodynamic method. It is found that the uracil-H<sub>2</sub>O complexes can be produced spontaneously from uracil and H<sub>2</sub>O at low temperature, while the uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes are produced difficultly.

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#### KEYWORDS

Uracil;  
Uracil-H<sub>2</sub>O complex;  
Uracil-H<sub>2</sub>S complex;  
Uracil-H<sub>2</sub>Se complex;  
Density functional theory;  
Intermolecular interaction;  
Geometry optimization;  
Natural bond  
orbital analysis;  
IR spectra;  
Thermodynamic property.

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### INTRODUCTION

Many attentions are paid to the intermolecular interactions in the past decades because they are important in a wide range of physical, chemical and biological fields<sup>[1-19]</sup>. It has been found that a lot of physical and chemical phenomena are closely related to the intermolecular weak interaction or the formation of various complexes, which are combined with charge transference, hydrogen bond, various Van der Waals forces. Among them, charge transference interaction is one of the most important styles of interaction and the most important methods of energy transference in the biology systems. In these systems there exist various kinds of weak interactions and such systems are often called supermolecular systems.

The studies about the intermolecular interaction of biological molecules are basis to learn the special functions and the mechanism of recognition processes. Bases of nucleotides are the most important portions to build up the DNA or RNA molecules. Weak interactions exist around these bases widely and they are important to life phenomenon. Uracil is one of the most important nucleic acid bases (NAB) occurring in RNA<sup>[20-24]</sup>. In DNA, it is replaced by thymine, its 5-methyl derivative. It also belongs to a group of the most important pyrimidines that play a fundamental role in the structure and function of enzymes and drugs. Generally, the keto form of uracil exists as the main form in the double helix. Water, the most abundant substance in living systems, can profoundly influence the structure, self-assembly, and properties of all cellular components, including proteins, nucleic acids, and lipids. Moreover, both sulfur and selenium is important element in living systems. Therefore, we investigated theoretically the intermolecular interactions of uracil with water, hydrogen sulfide and hydrogen selenide in this paper.

#### Computational methods

The geometries of isolated uracil and their corresponding complexes obtained from Chem 3D software were fully optimized at the DFT-B3LYP<sup>[25,26]</sup> level by the Berny method<sup>[27,28]</sup> with 6-311++G\*\* basis set. Natural bond orbital analyses and frequency calculations were performed on each optimized

structure. Frequency calculations are carried out on each optimized structure, and their IR spectra are discussed. Thermodynamic data and their changes upon compounding were derived from statistical thermodynamics based on the frequencies.

The interaction energy of the complex is evaluated as the energy difference of the subsystem and complex. The basis sets commonly used to calculate the energies are far from being saturated. As a result, each subsystem in any complex will tend to lower its energy due to the use of the basis functions of the other subsystem. The energies obtained at the equilibrium geometry of the complex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This energy difference is the so-called basis set superposition error (BSSE) that can be checked by the Boys and Bernardi's counterpoise procedure (CP)<sup>[29-31]</sup>. All calculations were performed with Gaussian03W program<sup>[32]</sup>.

### RESULTS AND DISCUSSION

#### Optimized geometries

Twelve stable structures of the uracil-H<sub>2</sub>O, uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes were obtained (Figure 1). After stationary points were located, vibrational frequencies were calculated in order to ascertain that each structure found corresponds to a minimum on the potential energy surfaces (no imaginary frequencies) for all structures in figure 1.

Some geometrical parameters are collected in TABLE 1. Compared to the monomer, the bond lengths of the uracil-H<sub>2</sub>O complexes change largely. The lengths of N1-H9, C2-O7 and O13-H14 of complex **(I)** increase by 1.2 pm, 1.2 pm and 1.3 pm, respectively, while the N1-C2 length decrease by 1.0 pm. The lengths of complex **(II)**'s C2-O7, N3-H10 and O13-H14 increase by 1.2 pm, 1.1 pm and 1.0 pm, respectively, while the C2-N3 length decrease by 0.9 pm. The lengths of **(III)**'s N3-H10, C4-O8 and O13-H14 increase by 1.0 pm, 1.1 pm and 1.3 pm, respectively, while the N3-C4 length decrease by 1.2 pm. The lengths of **(IV)**'s C4-O8 and O13-H14 increase by 0.9 pm and 1.1 pm, respectively.

The uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes are

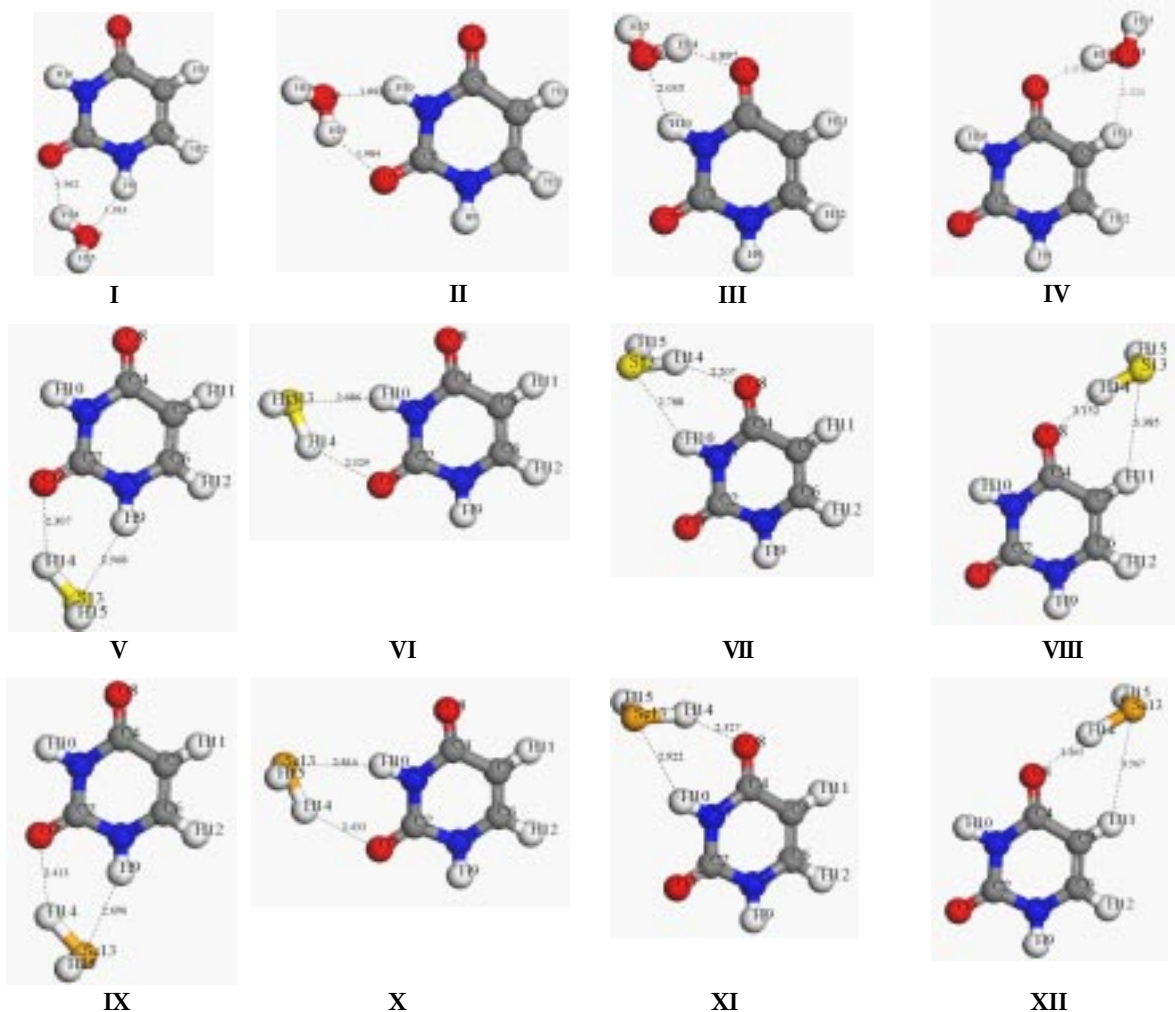


Figure 1: Atomic number, optimized geometries and intermolecular distance (Å) of uracil's complexes

analogous to the uracil-H<sub>2</sub>O complexes. The changes of other bond lengths of the uracil's complexes become smaller. As a whole, intermolecular H-bonds elongate the C-O and X-H (X=C, N, O, S, Se) bonds.

The bond angles and the dihedral angles of all twelve uracil's complexes change slightly from its monomer, which implies that the influence of interaction on bond bending or internal rotation is small.

Figure 1 shows that there are two H-bonds in the uracil complexes. According to the intermolecular distances, there are both two strong in complexes (I), (II), (III), (V), (VI), (VII), (IX), (X) and (XI) in their six-numbered rings, and there are a strong and a weak H-bond in complexes (IV)'s, (VIII)'s and XII's six-numbered ring. The H-bonding lengths usually determine the binding energies when the intermolecular contacts are the same. Judged by the in-

termolecular distances, it can be speculated that the intensities of interactions may be in the order: (I) > (II) ≈ (III) > (IV), (V) > (VI) ≈ (VII) > (VIII), (IX) > (X) ≈ (XI) > (XII).

### Binding energies

TABLE 2 gives both the uncorrected and corrected binding energies. There are no imaginary frequencies for any of the structures in TABLE 2, indicating that the structures in figure 1 are indeed the minima on their potential energy surfaces.

TABLE 2 shows that the ZPE corrected values of twelve uracil's complexes are almost equivalent to the BSSE corrected values, both sum of them account for 39.19%, 50.41%, 43.25%, 47.24%, 36.01%, 45.36%, 38.99%, 44.86%, 41.37%, 43.64%, 39.51% and 45.11% of corrected binding energies,

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TABLE 1: Part of fully optimized geometries of uracil and uracil's complexes at B3LYP/6-311++G\*\* level<sup>a</sup>

Geometry	uracil	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
N1-C2	1.393	1.383	1.388	1.397	1.391	1.388	1.391	1.395	1.393	1.388	1.391	1.395	1.393
N1-C6	1.375	1.372	1.376	1.371	1.375	1.374	1.376	1.373	1.374	1.374	1.375	1.373	1.374
N1-H9	1.009	1.021	1.009	1.009	1.009	1.017	1.009	1.009	1.009	1.017	1.009	1.009	1.009
C2-N3	1.383	1.377	1.374	1.385	1.386	1.38	1.379	1.385	1.385	1.381	1.38	1.385	1.385
C2-O7	1.212	1.224	1.224	1.211	1.212	1.219	1.218	1.211	1.211	1.218	1.217	1.211	1.211
N3-C4	1.413	1.415	1.412	1.401	1.403	1.414	1.414	1.407	1.406	1.414	1.413	1.408	1.407
N3-H10	1.013	1.013	1.024	1.023	1.013	1.013	1.019	1.018	1.013	1.013	1.019	1.018	1.013
C4-C5	1.458	1.456	1.46	1.453	1.454	1.456	1.459	1.455	1.455	1.457	1.459	1.456	1.455
C4-O8	1.215	1.215	1.214	1.226	1.224	1.215	1.214	1.221	1.22	1.215	1.214	1.22	1.219
C5-C6	1.347	1.349	1.346	1.348	1.348	1.348	1.346	1.348	1.348	1.348	1.346	1.348	1.348
C5-H11	1.079	1.079	1.079	1.079	1.08	1.079	1.079	1.079	1.08	1.079	1.079	1.079	1.08
C6-H12	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083
O13-H14	(0.962)	0.975	0.972	0.975	0.973								
O13-H15	(0.962)	0.961	0.961	0.961	0.961								
S13-H14	(1.348)					1.354	1.352	1.354	1.354				
S13-H15	(1.348)					1.348	1.348	1.348	1.348				
Se13-H14	(1.472)									1.476	1.474	1.475	1.474
Se13-H15	(1.472)									1.471	1.471	1.472	1.471

<sup>a</sup>Bond lengths are in Å and values in parentheses are data of H<sub>2</sub>O, H<sub>2</sub>S and H<sub>2</sub>Se

TABLE 2: Total energy, zero-point energy and interaction energy(kJ/mol) at B3LYP/6-311++G\*\* level

Energy	H <sub>2</sub> O	Uracil	I	II	III	IV
E	-200741.872	-1089441.095	-1290227.195	-1290218.016	-1290220.101	-1290212.644
ΔE			-44.227	-35.048	-37.133	-29.676
ZPEC			9.015	8.362	8.221	7.548
BSSE			3.332	3.268	2.887	1.872
ΔE <sub>C,ZPEC</sub>			-31.503	-23.068	-25.681	-19.941
	H <sub>2</sub> S	Uracil	V	VI	VII	VIII
E	-1048684.062	-1089441.095	-2138145.427	-2138139.277	-2138140.044	-2138138.413
ΔE			-20.269	-14.120	-14.886	-13.255
ZPEC			5.240	4.337	4.410	4.365
BSSE			2.060	2.068	1.395	1.582
ΔE <sub>C,ZPEC</sub>			-12.750	-7.533	-8.896	-7.125
	H <sub>2</sub> Se	Uracil	IX	X	XI	XII
E	-6308427.310	-1089441.095	-7397885.011	-7397879.321	-7397879.558	-7397877.547
ΔE			-16.605	-10.916	-11.153	-9.141
ZPEC			4.013	3.322	3.554	3.687
BSSE			1.429	1.442	0.853	0.437
ΔE <sub>C,ZPEC</sub>			-10.997	-6.013	-6.598	-4.863

respectively, which illustrates that it is necessary to and corrected binding energies indicate that the sta-  
correct ZPE and BSSE values. Both the uncorrected bility of the complexes is in the order of

TABLE 3: The calculated natural atomic charges of uracil and uracil's complexes<sup>a</sup>

Atom	uracil	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
N1	-0.612	-0.621	-0.607	-0.609	-0.609	-0.625	-0.610	-0.610	-0.609	-0.625	-0.611	-0.611	-0.610
C2	0.809	0.817	0.817	0.810	0.809	0.813	0.813	0.810	0.809	0.813	0.813	0.810	0.809
N3	-0.648	-0.640	-0.656	-0.654	-0.639	-0.644	-0.658	-0.655	-0.642	-0.645	-0.658	-0.655	-0.644
C4	0.644	0.644	0.644	0.653	0.654	0.644	0.644	0.650	0.650	0.644	0.645	0.649	0.650
C5	-0.357	-0.359	-0.349	-0.357	-0.361	-0.357	-0.352	-0.357	-0.361	-0.358	-0.354	-0.358	-0.361
C6	0.078	0.086	0.073	0.085	0.085	0.083	0.075	0.083	0.085	0.083	0.076	0.082	0.084
O7	-0.616	-0.665	-0.665	-0.609	-0.613	-0.643	-0.642	-0.609	-0.611	-0.638	-0.637	-0.611	-0.612
O8	-0.590	-0.592	-0.585	-0.638	-0.632	-0.591	-0.584	-0.615	-0.614	-0.592	-0.586	-0.610	-0.608
H9	0.419	0.456	0.418	0.419	0.420	0.431	0.419	0.419	0.420	0.430	0.419	0.419	0.420
H10	0.423	0.423	0.459	0.459	0.425	0.423	0.435	0.435	0.425	0.423	0.434	0.434	0.425
H11	0.238	0.237	0.237	0.238	0.264	0.238	0.238	0.238	0.246	0.238	0.238	0.239	0.246
H12	0.211	0.212	0.211	0.211	0.213	0.212	0.211	0.212	0.213	0.212	0.211	0.212	0.213
O13	(-0.916)	-0.967	-0.959	-0.968	-0.961								
H14	(0.458)	0.497	0.492	0.491	0.485								
H15	(0.458)	0.472	0.468	0.467	0.458								
S13	(-0.260)					-0.298	-0.292	-0.304	-0.311				
H14	(0.130)					0.174	0.166	0.169	0.168				
H15	(0.130)					0.138	0.134	0.134	0.130				
Se13	(-0.166)									-0.199	-0.193	-0.204	-0.214
H14	(0.083)									0.124	0.117	0.119	0.118
H15	(0.083)									0.091	0.086	0.087	0.084

<sup>a</sup> Values in parentheses are data of H<sub>2</sub>O, H<sub>2</sub>S and H<sub>2</sub>Se.

(I) < (II) < (III) < (IV) > (V) < (VI) < (VII) < (VIII) < (X) < (XI) > (XII), so the stability of the optimized complexes is (I) > (II) < (III) > (IV) > (V) > (IX) > (VI) < (VII) > (VIII) > (X) < (XI) > (XII), indicating that the intensity of interaction between uracil and H<sub>2</sub>O is stronger than that of uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se.

### Atomic charges and charge transfer

TABLE 3 lists the atomic NBO charges of uracil and its complexes.

Compared to subsystem, charges on the H14 and H15 of (I)'s H<sub>2</sub>O subsystem increase by 0.039e and 0.014 e, respectively, while charges on O13 decrease by 0.051e, net charge of water molecule increases by 0.002e, charges on the C2 and H10 of (I)'s uracil subsystem increase by 0.008e and 0.037e, while charges on N1 and O7 decrease by 0.008 e and 0.048 e, respectively, indicating an effect of charge transfer through molecular contacting. Charges on the C2, H10, H14 and H15 of complex (II) increase by 0.008 e, 0.036e, 0.034e and 0.010e, respectively, while

charges on N3, O7 and O13 decrease by 0.008e, 0.048e and 0.042e, respectively, net charge of water molecule increases by 0.002e. Similarly, charges on the C4, H10, H14 and H15 of complex (III) increase by 0.008e, 0.035e, 0.035e and 0.009e, respectively, while charges on O8 and O13 decrease by 0.008e, 0.047e and 0.052e, respectively. Charges on the H11 and H14 of complex (IV) increase by 0.026e and 0.027e, respectively, while charges on O8 and O13 decrease by 0.008e, 0.042e and 0.044e, respectively.

The uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes are similar to uracil-H<sub>2</sub>O complexes. As a whole, the atoms whose charges change more are primarily these atoms of the vicinity of subsystem.

The dipole moments of the uracil, water, hydrogen sulfide, hydrogen selenide and twelve complexes are 4.5774, 2.1592, 1.3491, 0.8675, 4.0668, 4.9899, 4.5311, 2.9809, 3.8788, 5.1747, 5.3471, 4.5065, 4.0189, 4.9533, 5.0601, 4.5590 Debye.

### Natural bond orbital analysis

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TABLE 4: Part of calculated results of uracil-H<sub>2</sub>O, uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes at the B3LYP/6-311++G\*\* level by NBO analysis<sup>a</sup>

Structure	Donor NBO(i)	Acceptor NBO(j)	E(kJ mol <sup>-1</sup> )
I	BD(1)N1-H9	BD*(1)O13-H15	1.34
	LP(1)O7	BD*(1)O13-H14	5.64
	LP(2)O7	BD*(1)O13-H14	23.05
	BD(1)O13-H14	BD*(1)N1-H9	2.09
	LP(2)O13	BD*(1)N1-H9	36.10
II	BD(1)N3-H10	BD*(1)O13-H15	1.00
	LP(1)O7	BD*(1)O13-H14	4.97
	LP(2)O7	BD*(1)O13-H14	19.91
	BD(1)O13-H14	BD*(1)N3-H10	1.71
	LP(2)O13	BD*(1)N3-H10	30.96
III	BD(1)N3-H10	BD*(1)O13-H15	1.25
	LP(1)O8	BD*(1)O13-H14	8.40
	LP(2)O8	BD*(1)O13-H14	28.99
	BD(1)O13-H14	BD*(1)N3-H10	1.63
	LP(2)O13	BD*(1)N3-H10	22.80
IV	LP(1)O8	BD*(1)O13-H14	7.11
	LP(2)O8	BD*(1)O13-H14	27.82
	LP(2)O13	BD*(1)C5-H12	3.47
V	LP(1)O7	BD*(1)S13-H14	2.67
	LP(2)O7	BD*(1)S13-H14	9.03
	BD(1)S13-H14	BD*(1)N1-H9	1.33
	LP(2)S13	BD*(1)N1-H9	23.51
VI	LP(1)O7	BD*(1)S13-H14	2.46
	LP(2)O7	BD*(1)S13-H14	7.69
	LP(2)S13	BD*(1)N3-H10	16.15
VII	LP(1)O8	BD*(1)S13-H14	4.72
	LP(2)O8	BD*(1)S13-H14	11.75
	LP(2)S13	BD*(1)N3-H10	10.87
VIII	LP(1)O8	BD*(1)S13-H14	5.94
	LP(2)O8	BD*(1)S13-H14	14.10
	LP(2)S13	BD*(1)C6-H12	1.12
IX	LP(1)O7	BD*(1)Se13-H14	2.008
	LP(2)O7	BD*(1)Se13-H14	7.029
	BD(1)Se13-H15	BD*(1)N1-H9	1.339
	LP(2)Se13	BD*(1)N1-H9	22.301
X	LP(1)O7	BD*(1)Se13-H14	1.966
	LP(2)O7	BD*(1)Se13-H14	6.067
	LP(2)Se13	BD*(1)N3-H10	15.648

TABLE 4 Continued

Structure	Donor NBO(i)	Acceptor NBO(j)	E(kJ mol <sup>-1</sup> )
XI	LP (1)O8	BD*(1)Se13-H14	3.305
	LP (2)O8	BD*(1)Se13-H14	8.117
	LP (2)Se13	BD*(1) N 3-H10	10.753
XII	BD(2)C4-O8	BD*(1)Se13- H14	1.004
	LP(1)O8	BD*(1)Se13- H14	5.356
	LP(2)O8	BD*(1)Se13- H14	11.757

<sup>a</sup> E denotes the stabilization energy, BD denotes bonding orbital, BD\* denotes antibonding orbital, LP denotes lone-pair. For BD and BD\*: (1) and (2) denote  $\sigma$  orbital and  $\pi$  orbital respectively. For LP: (1) and (2) denote the first and the second lone pair electron respectively. Only the stable energies over 1.00 kJ/mol are listed.

TABLE 4 summarizes the second-order perturbative estimates of ‘donor-acceptor’ (bond-antibond) interactions in the NBO basis for all the complexes. This is carried out by examining all possible interactions between ‘filled’ (donor) Lewis-type NBOs and ‘empty’ (acceptor) non-Lewis NBOs, and estimating their stabilization energy by second order perturbation theory<sup>[33-35]</sup>. The stabilization energies E(2) are proportional to the NBO interacting intensities. When the donor and the acceptor belong to different submolecules in a complex, we call it intermolecular NBO interaction. It is the intermolecular NBO interaction that reveals the origin of intermolecular interactions.

As can be seen from the intermolecular NBO interaction in TABLE 4, the main NBO interacting in the four uracil-H<sub>2</sub>O complexes are that the lone pairs on oxygen atom of H<sub>2</sub>O and uracil submolecule act as donor and that the N-H antibond of uracil submolecule and O13-H14 antibond of water submolecule as acceptor. Two lone pairs of each oxygen interact with N-H or O-H antibonds in the uracil-H<sub>2</sub>O complexes. Similarly, the main NBO interacting in the four uracil-H<sub>2</sub>S complexes are that the lone pairs on oxygen atom of uracil and sulfur atom of H<sub>2</sub>S submolecule act as donor and that the N-H antibond of uracil submolecule and S13-H14 antibond of sulfureted hydrogen submolecule as acceptor. Lone pairs of oxygen and sulfur atoms interact with N-H or S-H antibonds in the four uracil-H<sub>2</sub>S complexes. The main NBO interacting in the uracil-H<sub>2</sub>Se complexes are that the lone pairs on selenide atom of H<sub>2</sub>Se and oxygen atom uracil submolecule act as donor and that the N-H antibond

TABLE 5: The thermodynamic properties of H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, uracil, and twelve complexes at different temperatures<sup>a</sup>

Structure	TEMP.	C <sup>0</sup> p	S <sup>0</sup> m	H <sup>0</sup> m	ΔS <sub>T</sub>	ΔH <sub>T</sub>	ΔG <sub>T</sub>
	(K)	(J·mol <sup>-1</sup> K <sup>-1</sup> )	(J·mol <sup>-1</sup> K <sup>-1</sup> )	(kJ/mol)	(J·mol <sup>-1</sup> K <sup>-1</sup> )	(kJ/mol)	(kJ/mol)
Uracil	200.00	78.03	297.39	10.10			
	298.15	110.41	334.65	19.37			
	400.00	139.65	371.32	32.15			
	600.00	180.88	436.39	64.53			
	800.00	206.87	492.25	103.49			
H <sub>2</sub> O	200.00	33.27	181.04	6.65			
	298.15	33.53	194.36	9.93			
	400.00	34.28	204.30	13.38			
	600.00	36.41	218.59	20.44			
	800.00	38.75	229.38	27.95			
I	200.00	112.82	345.63	14.35	-132.80	-37.61	-11.05
	298.15	150.56	397.86	27.31	-131.15	-37.20	1.90
	400.00	183.67	446.89	44.39	-128.73	-36.35	15.13
	600.00	230.27	530.90	86.14	-124.08	-34.04	40.40
	800.00	260.25	601.53	135.39	-120.10	-31.26	64.81
II	200.00	114.42	347.02	14.51	-131.41	-37.45	-11.17
	298.15	151.91	399.85	27.62	-129.16	-36.89	1.61
	400.00	184.67	449.24	44.82	-126.38	-35.92	14.62
	600.00	230.84	533.56	86.73	-121.42	-33.45	39.39
	800.00	260.58	604.32	136.07	-117.31	-30.58	63.26
III	200.00	114.12	349.10	14.62	-129.33	-28.95	-3.09
	298.15	151.6	401.80	27.70	-127.21	-28.42	9.50
	400.00	184.46	451.10	44.87	-124.52	-27.48	22.31
	600.00	230.73	535.36	86.75	-119.62	-25.04	46.72
	800.00	260.52	606.10	136.07	-115.53	-22.19	70.22
IV	200.00	116.09	359.42	15.20	-119.01	-23.68	0.11
	298.15	153.26	412.86	28.46	-116.15	-22.97	11.65
	400.00	185.73	462.59	45.78	-113.03	-21.88	23.32
	600.00	231.44	547.26	87.85	-107.72	-19.25	45.37
	800.00	260.87	618.15	137.28	-103.48	-16.29	66.48
H <sub>2</sub> S	200.00	33.40	197.97	6.66			
	298.15	34.24	211.43	9.97			
	400.00	35.70	221.68	13.53			
	600.00	39.11	236.79	21.00			
	800.00	42.65	248.52	29.18			
V	200.00	120.89	374.74	16.04	-120.62	-15.74	8.37
	298.15	156.86	429.82	29.70	-116.26	-14.66	19.99

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TABLE 5 Continued

	400.00	189.02	480.56	47.37	-112.44	-13.33	31.63
	600.00	235.15	566.6	90.12	-106.58	-10.43	53.50
	800.00	265.43	638.68	140.38	-102.09	-7.31	74.35
VI	200.00	122.87	382.66	16.55	-112.70	-9.99	12.54
	298.15	158.14	438.4	30.36	-107.68	-8.76	23.34
	400.00	189.87	489.44	48.14	-103.56	-7.32	34.10
	600.00	235.57	575.74	91.01	-97.44	-4.30	54.16
	800.00	265.65	647.91	141.33	-92.86	-1.12	73.16
VII	200.00	122.43	384.07	16.48	-111.29	-10.75	11.50
	298.15	157.95	439.68	30.27	-106.40	-9.54	22.18
	400.00	189.79	490.69	48.03	-102.31	-8.126	32.79
	600.00	235.58	576.97	90.90	-96.21	-5.10	52.61
	800.00	265.68	649.14	141.22	-91.63	-1.92	71.37
VIII	200.00	122.80	395.45	16.76	-99.91	-8.89	11.09
	298.15	158.33	451.21	30.58	-94.87	-7.65	20.63
	400.00	190.10	502.32	48.38	-90.68	-6.19	30.08
	600.00	235.75	588.70	91.30	-84.48	-3.12	47.56
	800.00	265.73	660.91	141.64	-79.86	0.07	63.96
H <sub>2</sub> Se	200.00	33.54	211.38	6.66			
	298.15	34.74	224.96	10.00			
	400.00	36.52	235.41	13.63			
	600.00	40.47	250.95	21.32			
	800.00	44.30	263.12	29.81			
IX	200.00	122.91	397.32	16.79	-111.45	-12.56	9.72
	298.15	158.46	453.11	30.62	-106.5	-11.34	20.41
	400.00	190.55	504.30	48.45	-102.43	-9.92	31.04
	600.00	236.88	591.00	91.53	-96.34	-6.91	50.89
	800.00	267.28	663.59	142.14	-91.78	-3.75	69.67
X	200.00	124.56	403.78	17.18	-104.99	-7.17	13.82
	298.15	159.56	460.12	31.15	-99.49	-5.81	23.85
	400.00	191.29	511.58	49.06	-95.15	-4.31	33.74
	800.00	267.46	671.17	142.92	-84.20	2.02	69.38
XI	200.00	124.07	403.53	17.09	-105.24	-7.26	13.77
	298.15	159.31	459.73	31.02	-99.88	-5.94	23.83
	400.00	191.16	511.14	48.92	-95.59	-4.45	33.77
	600.00	237.20	598.02	92.09	-89.32	-1.35	52.23
	800.00	267.45	670.68	142.75	-84.69	1.85	69.60
XII	200.00	124.16	422.4	17.24	-86.37	-4.97	12.30
	298.15	159.57	478.67	31.19	-80.94	-3.63	20.50
	400.00	191.42	530.16	49.12	-76.57	-2.11	28.51
	600.00	237.35	617.13	92.33	-70.21	1.026	43.15
	800.00	267.49	689.82	143.01	-65.55	4.25	56.69
	600.00	237.24	598.5	92.25	-88.84	-1.19	52.11

<sup>a</sup> $\Delta S_T = (S_T^0)I - (S_T^0)_{Uracil} \cdot (S_T^0)ii$ ,  $\Delta H_T = (H_T^0 + E(HF) + ZPE)i - (H_T^0 + E(HF) + ZPE)_{Uracil} \cdot (H_T^0 + E(HF) + ZPE)ii$ ,  $\Delta G_T = \Delta H_T - T\Delta S_T$ , (i=I,II, III and IV, ii=H<sub>2</sub>O, i=V, VI, VII and VIII, ii=H<sub>2</sub>S, i=IX, X, XI and XII, ii=H<sub>2</sub>Se).



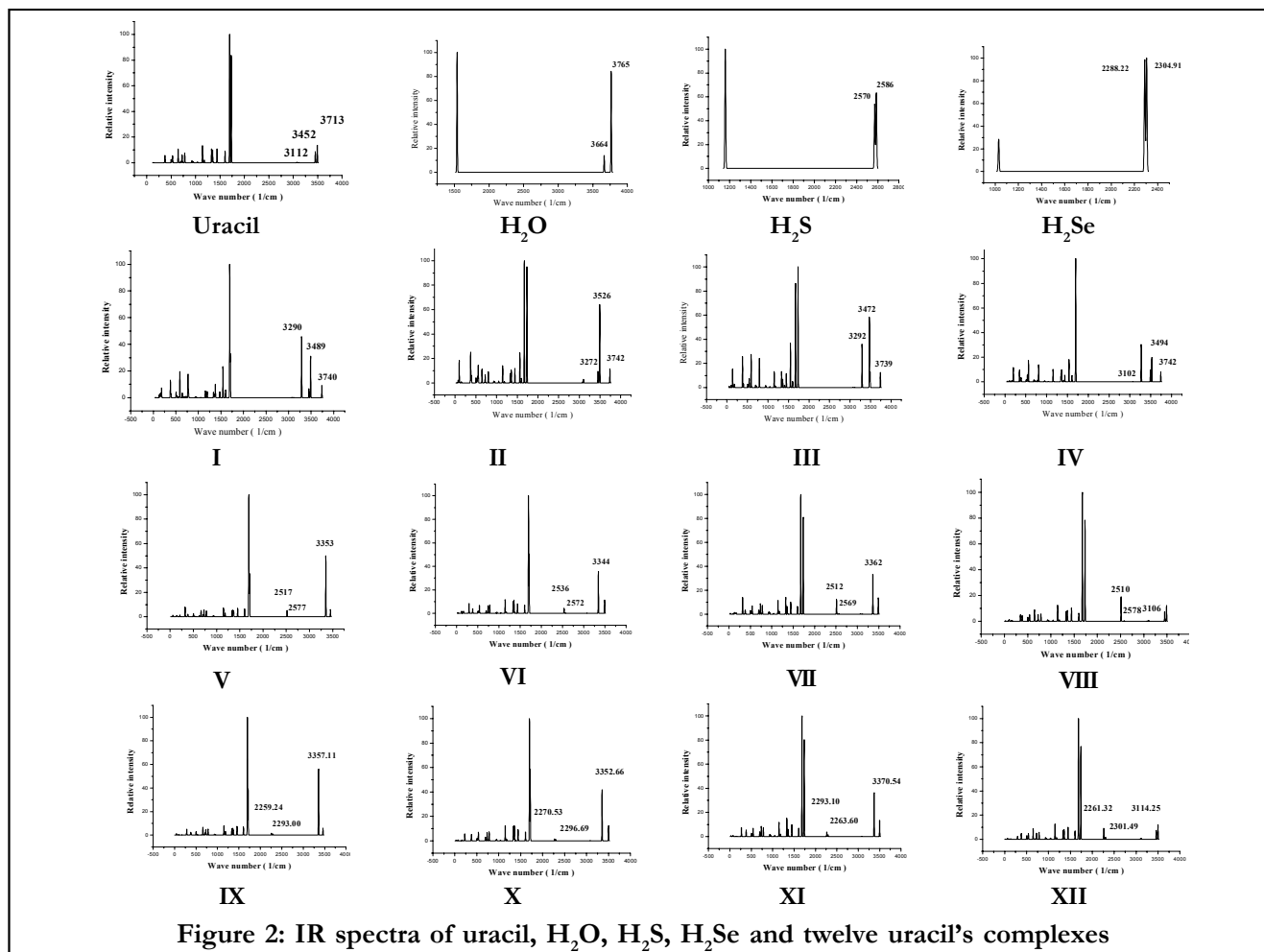


Figure 2: IR spectra of uracil,  $H_2O$ ,  $H_2S$ ,  $H_2Se$  and twelve uracil's complexes

of uracil submolecule and Se-H antibond of  $H_2Se$  submolecule as acceptor. Two lone pairs of e selenide or oxygen atoms interact with N-H or Se-H antibonds in the uracil- $H_2Se$  complexes.

### Vibrational frequencies and their shifts

Figure 2 shows the simulated infrared (IR) spectra for the uracil and its complexes, where the intensity is plotted against the harmonic vibrational frequencies (the scale factor is 0.9624).

For the complexity of vibrational modes, it is difficult to attribute all bands, so we have only analyzed some H-X (X=C, N, O, S and Se) vibrational frequencies in the uracil and its complexes. For the water and uracil, it is found that the  $H_2O$  symmetry and anti-symmetry stretching vibrations appear at 3765  $cm^{-1}$  and 3664  $cm^{-1}$ , respectively, uracil's N1-H9, N3-H10 and C5-H11 stretching vibrations appear at 3501  $cm^{-1}$ , 3450  $cm^{-1}$ , and 3120  $cm^{-1}$ , respectively. Compared to water and uracil monomer, the  $H_2O$  symme-

try and anti-symmetry stretching vibrations and N1-H9 stretching vibration of complex (I) appear at 3740  $cm^{-1}$ , 3489  $cm^{-1}$  and 3290  $cm^{-1}$ , respectively, indicating red-shifts. The  $H_2O$  and N3-H10 stretching vibrations of complex II appear at 3742  $cm^{-1}$ , 3526  $cm^{-1}$  and 3272  $cm^{-1}$ , respectively. Those of complex III appear at 3739  $cm^{-1}$ , 3472  $cm^{-1}$  and 3292  $cm^{-1}$ , respectively. The  $H_2O$  and C5-H11 stretching vibration of complex IV appear at 3742  $cm^{-1}$ , 3494  $cm^{-1}$  and 3102  $cm^{-1}$ , respectively.

The uracil- $H_2S$  and uracil- $H_2Se$  complexes have an analogy with uracil- $H_2O$  complexes. All calculation show that there are strong interactions in the O-H-X (X=C, N, O, S and Se) hydrogen bond and there are large red-shifts for H-X stretching vibrational frequencies in the uracil's complexes.

### Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamic, the standard thermodynamic func-

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tions, heat capacities ( $C_p^0$ ), entropies ( $S_m^0$ ) and enthalpies ( $H_m^0$ ), were obtained and listed in TABLE 5.

It can be seen that the values of the calculated functions of all structures increase with the increasing temperature. The magnitudes of  $C_p^0$  of twelve complexes are approximately the same at each temperature, In the course of monomer to complexes, both the entropy and the enthalpy decrease at any temperature from 200K to 800 K. The intermolecular interaction is therefore an exothermic process accompanied by a decrease in the probability, and the interactions weaken as temperature increases.

From the  $\Delta G = \Delta H - T\Delta S$  equation, the changes of Gibbs free energies ( $\Delta G$ ) in the processes from the monomer to the complexes are all negative for the uracil-H<sub>2</sub>O complexes under 200 K. Four uracil-H<sub>2</sub>O complexes can be spontaneously produced from the isolated monomer under 200 K. The  $\Delta G_T$  value increases as temperature increases for each complex, thus the interactions weaken as temperature increases. While the changes of  $\Delta G$  in the processes from the monomer to the complexes are all positive for uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes under 200 K, indicating the uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes being produced from uracil and H<sub>2</sub>S or H<sub>2</sub>Se difficultly. Obviously, these results are only applicable to systems in the gas phase at low pressure.

### CONCLUSIONS

From the DFT-B3LYP calculations reported in the paper, the following conclusions can be drawn:

1. Intermolecular H-bonds elongate the C=O and X-H (X=C, N, O, S and Se) bonds and influence slightly the bond angles and the dihedral angles of twelve uracil complexes.
2. It is necessary to correct ZPE and BSSE values. The greatest corrected intermolecular interactions of the uracil-H<sub>2</sub>O, uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes are -31.503KJ/mol -12.750KJ/mol and -10.997KJ/mol, respectively.
3. Vibrational analysis show that there are strong interactions in the O-H-X (X= C, N, O, S and Se) hydrogen bonds and there are large red-shifts for H-X stretching vibrational frequencies in the uracil-H<sub>2</sub>O, uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes.
4. The interaction is an exothermic process along with the decreases of entropies. The differences of free energy between the monomer and the complex decrease as temperature decreases. The process of forming uracil-H<sub>2</sub>O complexes from uracil and H<sub>2</sub>O is spontaneous at low temperature, while the process of forming uracil-H<sub>2</sub>S and uracil-H<sub>2</sub>Se complexes from uracil and H<sub>2</sub>S or H<sub>2</sub>Se is very difficult.

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