ABSORPTION SPECTRA OF NUCLEIC ACID BASES STUDIED BY THE SYMMETRY-ADAPTED-CLUSTER CONFIGURATION-INTERACTION (SAC-CI) METHOD

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This study is sincerely dedicated to Dr. Zdeněk Havlas to celebrate his 60th birthday and his high, long-standing science activities in his Institute, Czech Republic, and international scientific communities.

The ground and excited states of five nucleic acid bases (adenine, guanine, cytosine, uracil and thymine) were calculated by employing the SAC/SAC-CI (symmetry adapted cluster/SAC configuration-interaction) method. The absorption spectra with the SAC-CI method were compared with the experimental spectra. The spectra obtained with the SAC-CI method were in good agreement with the experimental spectra in gas phase. Comparisons with the calculations with other methods were made.
Keywords: SAC-CI method; Nucleobases; Absorption spectroscopy; Excited states; Ab initio calculations; Quantum chemistry.

Five nucleic acid bases, adenine, guanine, cytosine, uracil and thymine, are the component elements of DNA and RNA [1]. DNA is composed of four kinds of deoxyribonucleotides, which are deoxyadenosine monophosphate (dAMP), deoxyguanosine monophosphate (dGMP), deoxycytidine monophosphate (dCMP) and deoxythymidine monophosphate (dTMP). dTMP is also called thymidine monophosphate (TMP), since TMP exists only as a deoxyribonucleotide, while guanine, adenine and cytosine can exist also as ribonucleotide. The ribonucleotide of TMP exists as uridine monophosphate (UMP), where a hydrogen in uridine is replaced by a methyl group in thymidine (Fig. 1). Thymine is not present in RNA, while uracil is not present in DNA. In the experimental absorption spectra of dXMP, where X

denotes a special nucleic acid base, the main peak comes from the $\pi \rightarrow \pi^*$ transition of nucleic acid base X, which is supported by the similarity of the experimental absorption spectra between X and dXMP [2].

The excited states of nucleic acid bases were studied by many theoretical methods [3–12]. The symmetry-adapted-cluster configuration-interaction (SAC-CI) theory [13–15] is a useful established correlation theory published in 1978 for studying ground, excited, ionized, and electron attached states of molecules. It is included in Gaussian suit of programs [16] and its 09 version now available includes some new useful features like direct SAC/SAC-CI [17] and circular dichroism [18] codes.
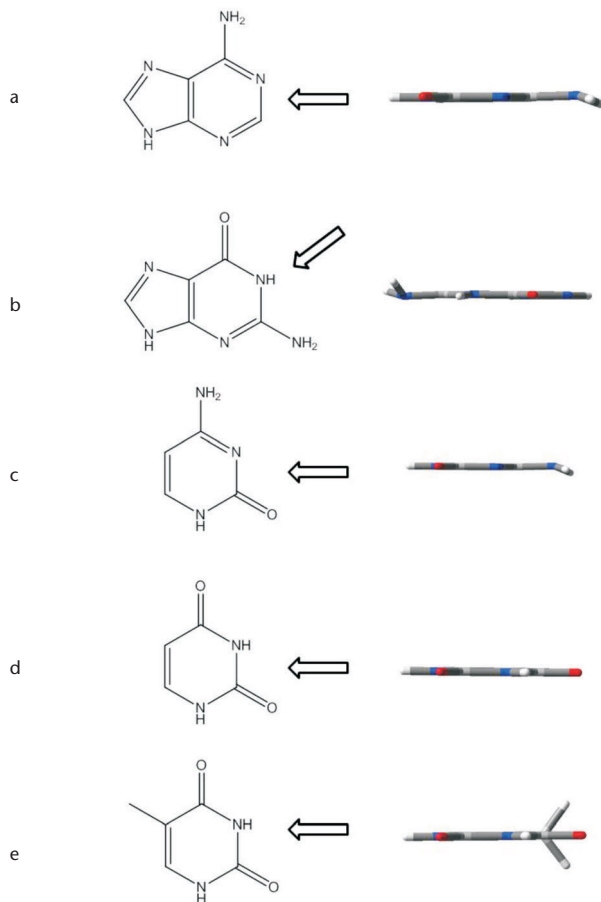

FIG. 1
The optimized geometries of adenine (a), guanine (b), cytosine (c), uracil (d) and thymine (e)

In the present paper, we calculate the absorption spectra of the above five nucleic acid bases using the SAC-CI method, compare the results with the experimental absorption spectra in solution[2] and in gas phase[19,20], together with other theoretical results[3–12], and discuss the assignments of the absorpion spectra. The present SAC-CI results correspond to the experimental spectra in gas phase but we compare them with the experimental spectra in water, because the experimental spectra in water were published for all nucleic acid bases but the gas phase experimental data are available only for guanine and cytosine. Further, the solvent effects that cause the difference in the spectra are very interesting and will be a topic of the succeeding paper.

COMPUTATIONAL DETAILS

The ground state geometries of the five nucleic acid bases were optimized with Gaussian 09[16] using the density-functional theory (DFT)[21–24] with B3LYP functional[25,26] for the 6-31G(d,p) basis set[27,28]. The geometries of five nucleic acid bases were optimized without symmetry, since there is a possibility that even the main ring may not be planer. For the SAC/SAC-CI calculations, the basis functions employed were cc-pVTZ[29] for all atoms. The core orbitals of C, O and N atoms were treated as frozen orbitals, and all singles and selected doubles were included as linked terms. Perturbation selection[30] was carried out with the threshold sets of 1×10^{-6} and 1×10^{-7} hartree for the SAC and SAC-CI calculations, respectively (level 3 in Gaussian/SAC-CI).

RESULTS AND DISCUSSIONS

Ground State Geometries

Figure 1 shows the optimized geometries of five nucleic acid bases. The optimized geometries were not on the plane for adenine, guanine and cytosine. On the other hand, all atoms were almost on the plane for uracil and thymine except for the methyl group of thymine. Therefore, we may use Cs symmetry for thymine and uracil. However, since we should use the same computational conditions for all nucleic acid bases, the excited states were calculated without symmetry for all nucleic acid bases.

Excited States

Figure 2 shows the SAC-CI spectra of the five compounds compared with the experimental spectra in solution[2] instead of gas phase, because we could not find the absorption spectra of all nucleic acid bases in gas phase. At the bottom, we gave eV scale and at the top, nm scale. The excited states
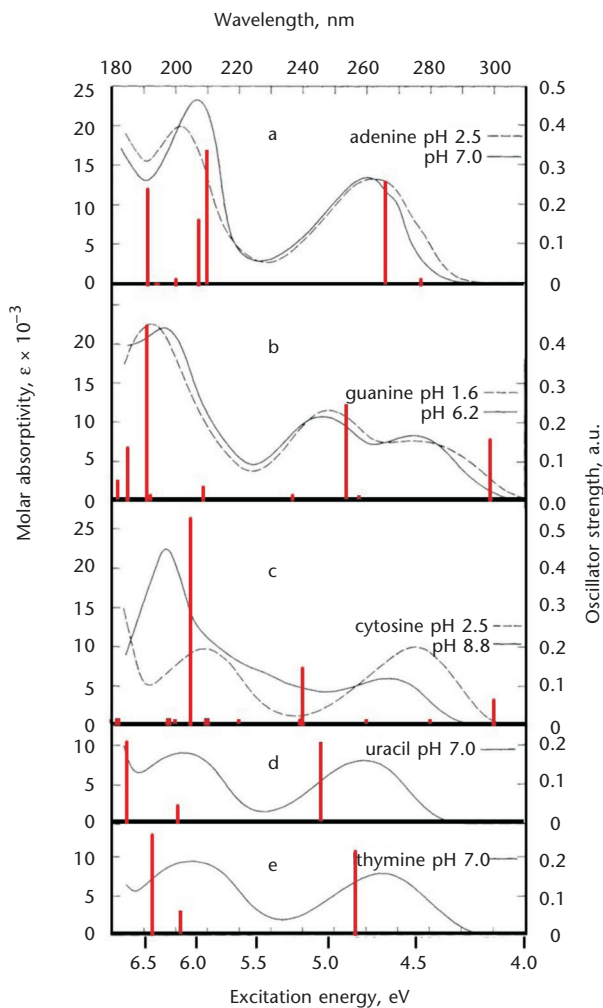

FIG. 2
The absorption spectra of adenine (a), guanine (b), cytosine (c), uracil (d) and thymine (e). The SAC-CI spectra (red lines) compared with the experimental absorption spectra[2] (black lines)

of adenine, guanine, cytosine, uracil and thymine are summarized in Tables I–V in comparison with the experimental data in gas phase[19,20] and solutions[2]. Tables VI–X show the comparisons with the several published results for the $\pi \rightarrow \pi^*$ excitations.

Adenine

For adenine, we refer to Table I and the top of Fig. 2. There are two bands in the absorption spectrum in both gas phase and water. The first band was observed at 4.92 eV in gas phase but 4.72 and 4.76 eV in water of pH 2.5 and 7.0, respectively. The second band was observed at 5.99 eV in gas phase and 6.18 and 5.99 eV in water of pH 2.5 and 7.0, respectively. The third band seems to exist in the shorter wavelength region than 180 nm (6.89 eV), as seen from the experimental spectrum.

TABLE I
Excited states of adenine

	SAC-CI				Experimental, eV (nm)		
State	Nature	EE, eV	EE, nm	Osc	Gas phase[a]	Water (pH 2.5)[b]	Water (pH 7.0)[b]
1^1A	$n \rightarrow \pi^*$	4.38	283	0.00			
2^1A	$\pi \rightarrow \pi^*$	4.48	277	0.01			
3^1A	$\pi \rightarrow \pi^*$	4.66	266	0.26	4.92 (252)	4.72 (262.5)	4.76 (260.5)
4^1A	$n \rightarrow \pi^*$	4.99	249	0.00			
5^1A	$n \rightarrow \pi^*$	5.47	227	0.00			
6^1A	$\pi \rightarrow \pi^*$	5.92	210	0.34	5.99 (207)	6.18 (200.5)	5.99 (207)
7^1A	$\pi \rightarrow \pi^*, \sigma^*$	5.98	207	0.16			
8^1A	$n \rightarrow \pi^*$	6.20	200	0.01			
9^1A	$\pi \rightarrow \sigma^*, \pi^*$	6.29	197	0.00			
10^1A	$\pi \rightarrow \sigma^*, \pi^*$	6.30	197	0.00			
11^1A	$n \rightarrow \pi^*$	6.40	194	0.00			
12^1A	$\pi \rightarrow \pi^*$	6.50	191	0.24			
13^1A	$\pi \rightarrow \sigma^*$	7.17	173	0.00			

[a] Ref.[19]; [b] ref.[2]

The 3^1A state calculated at 4.66 eV, which is the excitation from the HOMO (π) to the LUMO (π^*), is assigned to the first observed band because of its large oscillator strength. The calculated excitation energy is closer, however, to the experimental value in water, rather than that in gas phase. The second observed band is considered to be composed of the 6 and 7^1A state (5.92 and 5.98 eV). The 6^1A state is the mixed excitation from the next-HOMO (π) to the LUMO (π^*) and from the HOMO (π) to the second lowest π^* orbital. The 7^1A state is the excitation from the HOMO (π) to the π^* of the purine base + the σ^* orbital of the amino group and its intensity is smaller than that of the 6^1A state. The 12^1A state of a π–π^* nature with a strong intensity of 0.24 is calculated at 6.50 eV and is considered to correspond to the third band.

TABLE II
Excited states of guanine

| State | Nature | SAC-CI | | | Experimental, eV (nm) | | |
		EE, eV	EE, nm	Osc	Gas phase[a]	Water (pH 1.6)[b]	Water (pH 6.2)[b]
1^1A	$\pi\rightarrow\pi^*$	4.15	299	0.15	4.23 (293) 4.37 (284)	4.54 (273)	4.51 (275)
2^1A	$n\rightarrow\pi^*$	4.80	258	0.01			
3^1A	$\pi\rightarrow\pi^*$	4.87	254	0.24		4.99 (248.5)	5.04 (246)
4^1A	$\pi\rightarrow\sigma^*$	5.23	237	0.01			
5^1A	$n\rightarrow\pi^*$	5.50	225	0.00			
6^1A	$\pi\rightarrow\sigma^*$	5.72	217	0.00			
7^1A	$\pi\rightarrow\sigma^*$	5.73	216	0.00			
8^1A	$\pi\rightarrow\pi^*$	5.92	209	0.03			
9^1A	$\pi\rightarrow\sigma^*$	6.45	192	0.01			
10^1A	$\pi\rightarrow\pi^*$	6.50	191	0.44		6.44 (192.5)	6.33 (196)
11^1A	$\pi\rightarrow\pi^*$	6.69	185	0.13			
12^1A	$\pi\rightarrow\sigma^*$	6.81	182	0.05			
13^1A	$\pi\rightarrow\sigma^*$	7.09	175	0.00			
14^1A	$\pi\rightarrow\sigma^*$	7.14	174	0.01			

[a] Ref.[19]; [b] ref.[2]

TABLE III
Excited states of cytosine

	SAC-CI				Experimental, eV (nm)		
State	Nature	EE, eV	EE, nm	Osc	Gas phase[a]	Water (pH 2.5)[b]	Water (pH 8.8)[b]
1^1A	$\pi \rightarrow \pi^*$	4.13	300	0.06	4.28 (290)	4.49 (276)	4.64 (267)
2^1A	$n \rightarrow \pi^*$	4.38	283	0.00			
3^1A	$\pi \rightarrow \pi^*$	5.16	240	0.14			5.39 (230)
4^1A	$n \rightarrow \pi^*$	5.19	239	0.01			
5^1A	$n \rightarrow \pi^*$	5.46	227	0.00			
6^1A	$\pi \rightarrow \sigma^*$	5.90	210	0.01			
7^1A	$\pi \rightarrow \pi^*$	6.04	205	0.52		5.93 (209)	6.31 (196.5)
8^1A	$n \rightarrow \pi^*$	6.27	198	0.01			
9^1A	$\pi \rightarrow \sigma^*$	6.80	182	0.01			

[a] Ref.[19]; [b] ref.[2]

TABLE IV
Excited states of uracil

	SAC-CI				Experimental, eV (nm)	
State	Nature	EE, eV	EE, nm	Osc	Gas phase[a]	Water (pH 7.0)[b]
1^1A	$n \rightarrow \pi^*$	4.38	283	0.00		
2^1A	$\pi \rightarrow \pi^*$	5.04	246	0.20	5.08 (244)	4.78 (259.5)
3^1A	$n \rightarrow \pi^*$	5.87	211	0.00		
4^1A	$\pi \rightarrow \pi^*$	6.17	201	0.04	6.05 (205)	
5^1A	$\pi \rightarrow \sigma^*$	6.41	193	0.00		
6^1A	$\pi \rightarrow \pi^*$	6.70	185	0.20	6.63 (187)	6.12 (202.5)
7^1A	$n \rightarrow \pi^*$	6.88	180	0.00		
8^1A	$\pi \rightarrow \pi^*$	7.37	168	0.49		
9^1A	$\pi \rightarrow \sigma^*$	7.76	160	0.01		

[a] Ref.[19]; [b] ref.[2]

Next we refer to Table VI to compare the present result with the other theoretical results. The first and second bands were calculated at 5.30 and 6.35 eV by the CASPT2 method and at 5.42 and 6.58 eV by the CC2 method[7]. The SAC-CI values are lower than the other values but are in better agreement with the experimental values. The 2^1A state, 4.48 eV by the SAC-CI method was calculated at 5.67 and 4.98 eV by the EOM-CCSD and CR-EOM-CCSD(T) methods using cc-pVDZ basis sets[9]. This indicates that the basis sets are more important than the triple excitation for adenine.

The SAC-CI spectrum is in good agreement with the experimental spectrum in water of pH 7.0 as shown in Fig. 2a. Therefore, the geometry of the present calculation may also reflect the one of adenine in water of pH 7.0. However, the excitation energy of the 1^1A state is lower than the data in gas phase. This tendency is similar to the SAC-CI result of guanine as shown later. These results indicate that the first excitation energies of adenine and guanine of purine base are slightly lower than the experimental values in this computational condition.

Guanine

For guanine, there are three bands in the absorption spectrum in water (Fig. 2), but we could find the data of only the first band (4.23 and 4.37 eV) in gas phase (Table II). The first band is observed at 4.23 and 4.37 eV in gas phase and at 4.54 and 4.51 eV in water of pH 1.6 and 6.2, respectively. We think that the two peaks (4.23 and 4.37 eV) in gas phase reflect the vibrational structures of the first band. The second band is observed at 4.99 and 5.04 eV in water of pH 1.6 and 6.2, respectively. The third band is observed at 6.44 and 6.33 eV in water of pH 1.6 and 6.2, respectively. The absorption spectra of guanine depend slightly on the pH.

The first band is assigned to the 1^1A state calculated at 4.15 eV, which is the excitation from the HOMO (π) to the lowest π^* orbital. This value is close to the value in gas phase. The second band is assigned to the 3^1A state (4.87 eV) having the strong oscillator strength, which is the excitation from the HOMO (π) to the second lowest π^* orbital. The third band is assigned mainly to the 10^1A state (6.50 eV), which is the excitation from the next-HOMO (π) to the lowest π^* orbital. The contribution from the 11^1A state (6.69 eV) is also considered due to its oscillator strength of 0.13.

Referring to Table VII, these three bands were calculated at 4.76, 5.09 and 6.65 eV by the CASPT2 method[8] and the lowest two bands were calculated at 4.98 and 5.47 eV by the CC2 method[4]. Their excitation energies, corre-

Excited states of thymine

		SAC-CI			Experimental, eV (nm)	
State	Nature	EE, eV	EE, nm	Osc	Gas phase[a]	Water (pH 7.0)[b]
1^1A	n→π*	4.28	289	0.00		
2^1A	π→π*	4.83	257	0.21	4.95	4.69 (264.5)
3^1A	n→π*	5.86	212	0.00		
4^1A	π→σ*	6.10	203	0.00		
5^1A	π→π*	6.12	202	0.06		
6^1A	π→π*	6.41	193	0.25	6.2	6.05 (205)
7^1A	n→π*	6.85	181	0.00		
8^1A	π→σ*	7.26	171	0.00		
9^1A	π→π*	7.35	169	0.44	7.4	

[a] Ref.[20]; [b] ref.[2]

Table VI
Excitation energies (eV) of π→π* for adenine, compared with the several published results

	Theoretical				Experimental		
State	SAC-CI[a]	CASPT2[b]	CC2[c]	EOM-CC	Gas phase[f]	Water (pH 2.5)[g]	Water (pH 7.0)[g]
2^1A	4.48	5.20	5.28	5.67[d] 4.98[e]			
3^1A	4.66	5.30	5.42		4.92	4.72	4.76
6^1A	5.92	6.35	6.58		5.99	6.18	5.99
7^1A	5.98	6.64	6.93				
12^1A	6.50	6.88	7.49				

[a] This work. [b] CASPT2/TZVP (see ref.[7]). [c] CC2/TZVP (see ref.[7]). [d] EOM-CCSD/cc-pVDZ (see ref.[9]). [e] CR-EOM-CCSD(T)/cc-pVDZ (see ref.[9]). [f] Ref.[19]. [g] Ref.[2]

sponding to the first band, are much higher for the first band, comparing with the SAC-CI method.

The SAC-CI spectrum is in rather good agreement with the experimental spectrum of pH 6.2 for the second and third bands as shown in Fig. 2b. However, the first peak is in good agreement with the experimental value

TABLE VII
Excitation energies (eV) of $\pi \rightarrow \pi^\star$ for guanine, compared with the several published results

	Theoretical				Experimental		
	SAC-CI[a]		CASPT2[b]	CC2[c]	Gas phase[d]	Water (pH 1.6)[e]	Water (pH 6.2)[e]
State	C_1	C_s					
1^1A	4.15	4.35	4.76	4.98	4.23 4.37	4.54	4.51
3^1A	4.87	4.92	5.09	5.47		4.99	5.04
8^1A	5.92		5.96				
10^1A	6.50	6.67	6.55			6.44	6.33

[a] This work using C_1 symmetry (Table II) and C_s symmetry. [b] CASPT2/double-ζ quality (see ref.[8]). [c] CC2/aug-cc-pVTZ (see ref.[4]). [d] Ref.[19]; [e] Ref.[2]

TABLE VIII
Excitation energies (eV) of $\pi \rightarrow \pi^\star$ for cytosine, compared with the several published results

	Theoretical				Experimental		
State	SAC-CI[a]	CASPT2[b]	CC2[c]	EOM-CC	Gas phase[g]	Water (pH 2.5)[h]	Water (pH 8.8)[h]
1^1A	4.13	4.68	4.80	5.11[d] 5.06[e] 4.87[f]	4.28	4.49	4.64
3^1A	5.16	5.54	5.71	6.11[d] 6.06[e] 5.76[f]			5.39
7^1A	6.04	6.40	6.65			5.93	6.31

[a] This work. [b] CASPT2/TZVP (see ref.[7]). [c] CC2/TZVP (see ref.[7]). [d] EOM-CCSD/cc-pCVDZ (see ref.[10]). [e] EOM-CCSD/cc-pCVTZ (see ref.[10]). [f] EOM-CC3/cc-pVDZ (see ref.[10]). [g] Ref.[19]. [h] Ref.[2]

in gas phase and the solvent makes the first band shifted by about 0.3 eV. The first and second bands are calculated at 4.35 and 4.92 eV by the SAC-CI/cc-pVTZ calculation with C_S symmetry. This result indicates that the amino group must be on the plane in solution. Guanine may form hydrogen bonds to water in solution, as guanine forms hydrogen bonds with cytosine in DNA.

Cytosine

For cytosine, three bands are observed in the absorption spectrum in water, but for gas phase, we could find the data of only the first band (Table III). The first band is observed at 4.28 eV in gas phase and at 4.49 and 4.64 eV in water of pH 2.5 and 8.8, respectively. The solvent effect is large. The second band is observed at 5.39 eV only in water of pH 8.8 as a broad band but it is hidden in the water of pH 2.5. The third band is observed at 5.93 and 6.31 eV in water of pH 2.5 and 8.8, respectively. The absorption spectra depend largely on the pH of water for cytosine.

The first band is assigned to the 1^1A state (4.13 eV), which is the HOMO (π)–LUMO (π^*) excitation (Table III). The calculated value is in good agreement with the data (4.28 eV) in gas phase, but is much lower than the data in water. This is probably due to large interactions between cytosine and water in water solutions of pH 2.5 and 8.8. The second band is assigned to the 3^1A (5.16 eV) state, which is the excitation from next-HOMO (π) to LUMO. This state seems to exist in the spectrum (Fig. 2c) in water of pH 8.8, but not in water of pH 2.5. The third band is assigned to the 7^1A state, which is the excitation from the HOMO to the second lowest π^* orbital. The second and third band are calculated at lower energy than those in water of pH 8.8.

Referring to Table VIII, these three bands were calculated at 4.68, 5.54 and 6.40 eV by the CASPT2 method and at 4.80, 5.71 and 6.65 eV by the CC2 method[7]. The first and second bands were calculated at 5.06 and 6.06 eV by the EOM-CCSD method using cc-pCVTZ and at 4.87 and 5.76 eV by the EOM-CC3 method using cc-pVDZ[10]. The excitation energies are underestimated for the SAC-CI method and overestimated for the other method, comparing with the experimental values in water of pH 8.8. However, the 1^1A state calculated at 4.13 eV by the SAC-CI method is close to the experimental value (4.28 eV) in gas phase.

Although the excitation energies are lower than the experimental values in water of pH 8.8, the shape of the SAC-CI spectrum is closer to the experimental spectrum of pH 8.8 than that of pH 2.5, because the SAC-CI spec-

trum in gas phase has three strong peaks. Theoretical study of the solvent effect is very interesting for cytosine, because it is very large. Such study is now in progress in our laboratory.

Uracil

For uracil, there are three bands in the absorption spectrum (Fig. 2d and Table IV). The first band is observed at 5.08 eV in gas phase and at 4.78 eV in water of pH 7.0. The second band is observed at 6.05 eV only in gas phase and is hidden in water of pH 7.0. The third band is observed at 6.63 eV in gas phase and at 6.12 eV in water of pH 7.0. In water, the first and third bands are shifted lower by 0.3 and 0.5 eV, respectively: the solvent effects are very large.

The first band is assigned to the π–π* excitation to the 2^1A state (5.04 eV), which is the HOMO (π)–LUMO (π*) excitation. The second band is assigned to the 4^1A state (6.17 eV) which is the next-HOMO (π) to LUMO (π*) excitation, but the calculated oscillator strength is small. The third band is assigned to the 6^1A state (6.70 eV), which is the excitation from the HOMO (π) to the second lowest π* orbital. The SAC-CI calculation shows that the fourth band due to the 8^1A state exists at around 7.37 eV with a strong oscillator strength of 0.49. The calculated three n–π* states of 1, 3 and 7^1A and one π–σ* state of 5^1A are weak and would be hidden by the strong bands of the four π–π* states.

Referring to Table IX, these three bands were calculated at 5.23, 6.15 and 6.75 eV by the CASPT2 method and at 5.52, 6.43 and 6.96 eV by the CC2

TABLE IX
Excitation energies (eV) of $\pi \rightarrow \pi$* for uracil, compared with the several published results

	Theoretical				Experimental	
State	SAC-CI[a]	CASPT2[b]	CC2[c]	EOM-CC[d]	Gas phase[e]	Water (pH 7.0)[f]
2^1A	5.04	5.23	5.52	6.29	5.08	4.78
4^1A	6.17	6.15	6.43		6.05	
6^1A	6.70	6.75	6.96		6.63	6.12
8^1A	7.37	7.42	7.66			

[a] This work. [b] CASPT2/TZVP (see ref.[7]). [c] CC2/TZVP (see ref.[7]). [d] CR-EOM-CCSD(T)/double-ζ quality (see ref.[11]). [e] Ref.[19]; [f] Ref.[2]

method[7]. The first band was calculated at 6.29 eV by the CR-EOM-CCSD(T) method[11]. The SAC-CI results are similar to the CASPT2 results except for the first excited state.

The SAC-CI peaks are in good agreement with the experimental ones in gas phase. The solvent effects in water of pH 7.0 are large and cause red shift for both of the first and third states. The nature of the solvent effects is interesting and is under study in our laboratory.

Thymine

The spectra of thymine are similar to those of uracil, because thymine is produced from uracil by the methylation (see Fig. 1). For thymine, there are four bands in the absorption spectrum. The first band is observed at 4.95 eV in gas phase and at 4.69 eV in water of pH 7.0, which is lower than that of uracil by about 0.1 eV. The second band is hidden between two strong bands. The third band is observed at 6.20 eV in gas phase and at 6.05 eV in water of pH 7.0, which correspond to the third band of uracil. The fourth band is observed at 7.40 eV in gas phase and in the shorter wavelength region than 180 nm (6.89 eV) in water of pH 7.0. In water, the first and third bands are shifted higher by 0.26 and 0.15 eV, respectively: large solvent effects. In water, two bands of thymine are lower than those of uracil by about 0.1 eV. This is the so-called hyper-conjugation effect of the methyl group.

TABLE X
Excitation energies (eV) of $\pi \rightarrow \pi^*$ for thymine, compared with the several published results

	Theoretical				Experimental	
State	SAC-CI[a]	CASPT2[b]	CC2[c]	EOM-CC[d]	Gas phase[e]	Water (pH 7.0)[f]
2^1A	4.83	5.06	5.39	5.76	4.95	4.69
5^1A	6.12	6.15	6.46			
6^1A	6.41	6.52	6.80		6.2	6.05
9^1A	7.35	7.43	7.71		7.4	

[a] This work. [b] CASPT2/TZVP (see ref.[7]). [c] CC2/TZVP (see ref.[7]). [d] EOM-CCSD/6-31G(d) (see ref.[12]). [e] Ref.[20]; [f] Ref.[2]

The first and third bands are assigned to the 2 and 6^1A states which are the excitation from the HOMO and correspond to the 2 and 6^1A states of uracil. The second and fourth bands are assigned to the 5 and 9^1A states which are the excitation from the next-HOMO and correspond also to the 4 and 8^1A states of uracil. The methyl group of thymine makes the HOMO orbital energy higher, comparing with the other orbitals. Therefore, the excitation energy from HOMO in thymine is lower than in uracil by 0.21 eV for the 2^1A state and by 0.29 eV for the 6^1A states. However, the excitation energy from the next-HOMO is similar between thymine and uracil.

Referring to Table X, these three bands were calculated at 5.06, 6.52 and 7.43 eV by the CASPT2 method and at 5.39, 6.80 and 7.71 eV by the CC2 method[7]. The SAC-CI spectrum is similar to the CASPT2 spectrum except for the first excited state. This is similar to the case of Uracil, as expected. The 2^1A (4.83 eV) state by the SAC-CI method was calculated at 5.76 eV by the EOM-CCSD method[12]. The difference between SAC-CI and EOM-CCSD methods are attributed to the difference in the basis sets, because, as is well known, EOMCC is essentially an imitation of SAC-CI.

CONCLUSION

For the pyrimidine bases studied here, when we have the experimental spectra in gas phase, the SAC-CI theoretical results agree well with the experimental peaks, as should be so. For example, the SAC-CI absorption spectrum of uracil is in good agreement with the experimental spectrum in gas phase. Thymine, which is the methylation product of uracil, is also in good agreement with the experimental spectrum in gas phase. The same is true for the cytosine first peak.

For the purine base, the first band of guanine is in good agreement between the experimental data in gas phase and the SAC-CI value. The second and third bands are similar to the experimental spectra in water. However, the SAC-CI spectrum of adenine is in good agreement with the experimental spectrum in water of pH 7.0 instead of that in gas phase. The first excited state is underestimated, similar to the first excited state of guanine.

Although the peak positions are red or blue shifted in water, all bands of the experimental absorption spectra are assigned to the $\pi-\pi^*$ excitations of the nucleic acid bases from the SAC-CI method as well as all published results. Therefore, we can guess that all the spectra in DNA and RNA are assigned mainly to the excited states originating from the nucleic acid bases. The SAC-CI excitation energies are generally lower than the other published results, and are in good agreement with the experimental values in gas phase.

The origins of the solvent effects observed in the experimental spectra in water are interesting subject and are now under study in our laboratory.

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