

# Theoretical Study of the Electronic Spectra of Uracil and Thymine

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**Abstract:** The complete active space (CAS) SCF method combined with multiconfigurational second-order perturbation theory has been used to study the electronic spectra—*i.e.*, vertical excitation energies, oscillator strengths, and transition moment directions—of the nucleic acid base monomers uracil and thymine. The wave functions and the transition properties are computed at the CASSCF level, while dynamic correlation contributions to the excitations energies are obtained through the perturbation treatment. The method yields energies, which are in agreement with experiment, while the determination of transition moment directions is more uncertain since they depend strongly on solvent effects. For uracil the following energies are obtained for  $\pi \rightarrow \pi^*$  transitions (experimental data in parentheses): 5.0 (4.6–4.9), 5.8 (5.8–6.1), 6.5 (6.3–6.6), and 7.0 (6.8–7.0) eV. Corresponding data for the four lowest  $n \rightarrow \pi^*$  transitions are 4.5, 6.0, 6.4, and 7.0 eV, respectively (no experimental data available). Computed (and experimental)  $\pi \rightarrow \pi^*$  transition energies for thymine are 4.9 (4.5–4.7), 5.9 (5.8–6.0), 6.1 (6.3–6.6), and 7.1 (7.0) eV.  $n \rightarrow \pi^*$  energies are 4.9, 5.9, 6.1, and 7.1 eV, respectively. It is proposed that the bands found around 5 eV in uracil and thymine are due to an  $n \rightarrow \pi^*$  transition. The error limit of computed energies is  $\pm 0.3$  eV.

## Introduction

The elucidation of the structure and function relationships in nucleic acids and complexes thereof remains an important and difficult problem in biomolecular sciences. Various spectroscopic techniques are used to monitor the conformation of the polynucleotides and/or the changes in their environment. For this purpose, reliable data concerning the excitation energies, oscillator strengths, and transition moment directions in a molecule-fixed reference frame are needed. However, the spectra of the nucleic acids consist of rather broad, strongly overlapping bands. Moreover, the transition moment directions are difficult to assess unambiguously from experiment. For these reasons, we have undertaken a project aiming at the determination of the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  excitation energies and transition moments of the nucleic acids.

In this paper we report on the gas phase spectra. Such spectra may not be of direct experimental interest because environmental effects can be considerable, especially for the transition moments and their directions.<sup>1</sup> From a theoretical standpoint it is, however, important to solve first all problems related to the description of the excited states in the free molecule before invoking the interaction with a surrounding solvent or crystal. This will be done in the second stage of the project and forthcoming publication. It should also be emphasized that even if gas phase transition moment directions are sensitive to the surroundings, this is less so for the energies and total intensities of the transitions. Therefore, gas phase studies can provide information, which is of interest for all types of experimental studies. The difficulties that have to be overcome in these studies were illustrated in earlier calculations on the base monomers, which were carried out using the complete active space (CAS) SCF model.<sup>2,3</sup> Computed excitation energies were very sensitive to the choice of active orbitals, and differences between theoretical and experimental data were too large to

allow a conclusive assignment. It was clear from these studies that it is imperative to include a large fraction of the dynamic correlation energy in order to obtain quantitative results. It is only when these problems have been solved that it becomes meaningful to start a discussion of the environmental effects on the spectral properties in these systems.

In a previous publication we have presented results from such a study of the excited states in cytosine.<sup>4</sup> The final results were obtained by CASSCF calculations supplemented with estimates of the remaining electron correlation effects using second-order perturbation theory. The calculations were able to account, qualitatively and quantitatively, for the experimentally observed electronic spectra of cytosine in the range of 4–7 eV and predicted four  $\pi \rightarrow \pi^*$  transitions located at 4.4, 5.4, 6.1, and 6.7 eV.

The present paper reports the results of a similar study on the pyrimidine bases uracil and thymine. The  $\pi \rightarrow \pi^*$  transitions lowest in energy are predicted to be located at 5.0, 5.8, 6.5, and 7.0 eV for uracil and at 4.9, 5.9, 6.1, and 7.1 eV for thymine. Combining the present results with our earlier study on cytosine, we are capable to provide a single, consistent picture for the pyrimidine nucleotides. Specifically, we predict four  $\pi \rightarrow \pi^*$  singlet excited states with transition energies smaller than 7.0 eV. In addition, we locate four  $n \rightarrow \pi^*$  transitions and find the first one to be close in energy to the lowest  $\pi \rightarrow \pi^*$  transition.

## Details of the Calculations

The geometry used in the present calculations are the averaged experimental heavy atom bond distances and angles reported by Taylor and Kennard.<sup>5</sup> The molecules were placed in the *xy* plane. The NH and CH distances were assumed to be 1.01

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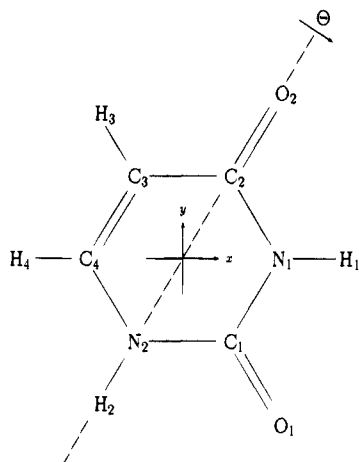
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**Figure 1.** Molecular structure and atom numbering in uracil and thymine. The angle  $\Theta$  gives the orientation of dipole and transition moments.

and 1.08 Å, respectively, and we used Hug and Tinoco's<sup>6</sup> conventions to label atoms and define angles throughout (cf. Figure 1).

Generally contracted basis sets of atomic natural orbital (ANO) type<sup>7,8</sup> are used and contracted to the following structure: C,N,O/[4s,3p,1d] and H/[2s]. In addition, the basis sets were supplemented with basis functions designed to describe Rydberg states and positioned at the center of nuclear charge. These are constructed in the following way: A CASSCF wave function for the  $^2A'$  cation was computed using the ANO basis set contracted to a minimal basis and augmented with an uncontracted set of eight primitives of s-, p-, and d-type of which the exponents are selected according to ref 9. The diffuse, virtual orbitals of each angular type were used to determine the ANO contraction coefficients using the method of density averaging.<sup>8</sup> A set of 1s-, 1p-, and 1d-contracted, Rydberg-type functions are then included in the final basis set. This approach has proven to yield well-described Rydberg states which interact only very weakly with other states. It should be emphasized that the Rydberg functions are essential, not because there is a specific interest in Rydberg excited states but to minimize spurious interaction between them and the valence excited states. Once the Rydberg orbitals have been determined (see below), they will actually be deleted from the one-electron MO basis. For a detailed discussion of these aspects, the interested reader is referred to refs 10 and 4.

The ground and excited states of uracil and thymine are described by wave functions derived from second-order perturbation theory (CASPT2) based on multiconfigurational reference functions. In particular we used the CASSCF/CASPT2 method. The CASSCF method is, by now, a standard *ab initio* quantum chemistry tool to evaluate multiconfigurational wave functions. The occupied orbitals are divided into inactive orbitals, which are always double occupied, and active orbitals, with variable occupancy. The CASSCF wave function includes all configurations with appropriate symmetry and spin that can

be formed by distributing the electrons in the active space among all active orbitals (for further details, see ref 11).

The CASPT2 method<sup>12,13</sup> computes the first-order wave function and the second-order energy in the full CI space without any further approximation, with a CASSCF wave function constituting the reference function. The zeroth-order Hamiltonian is defined as a Fock-type one-electron operator and is constructed such that a Möller–Plesset-type perturbation theory is obtained in the closed shell single-determinant case. Here we shall present the results obtained by using the zeroth-order Hamiltonian derived from only the diagonal part of the Fock matrix. The CASPT2 program also calculates the weight,  $\omega$ , of the CASSCF reference in the first-order wave function. This weight is a measure of how large a fraction of the wave function is treated variationally. Thus the relative weight  $\omega$  in different states allows to inspect the result to ensure that the CASSCF wave function includes all chemically important correlation effects and represents the state of interest. The ability of the CASSCF/CASPT2 approach in computing accurate excitation energies and transition moments has been shown in a large number of applications in organic chemistry. For a recent review, see ref 14.

The selection of the proper active space is the crucial step of a whole calculation. In general, the active space should include all orbitals with occupation numbers appreciably different from two or zero in any of the excited states under consideration. All near-degeneracy effects are then included in the CASSCF reference function, and consequently there will be no large terms in the perturbation expansion. This is a necessary prerequisite for a low-order perturbation treatment to work. In practice it means, as shown by Roos *et al.*,<sup>15</sup> that the active space should include at least all valence  $\pi$ -orbitals in conjugated systems. When Rydberg states are interfering with valence excited state additional orbitals, the Rydberg orbitals have to be included. One also may want to include the lone pair orbitals to allow for  $n \rightarrow \pi^*$  excitations. For the present systems such a calculation is not feasible (12 electrons in two  $\sigma$ -orbitals, eight  $\pi$ -orbitals, and nine Rydberg orbitals). Out of the nine Rydberg orbitals, six have  $\sigma$  symmetry and need not be further considered, since no mixing between valence excited and Rydberg states are expected, which involves these orbitals. But even 12 electrons in 13 orbitals is too large a calculation to be feasible. Instead, the Rydberg states were considered first. An average CASSCF calculation was performed with the eight  $\pi$ -electrons in 11 active orbitals. The average calculation was performed over 12 electronic states of  $^1A'$  symmetry, such that all pertinent Rydberg states are included. The natural orbitals emerging from this calculation contained well-defined Rydberg orbitals. They were deleted from the MO basis together with the Rydberg orbitals of  $\sigma$ -type, which could be identified directly from the virtual MO space since there is only little interaction with valence orbitals in this case.

Having in this way eliminated the Rydberg states, the next set of calculations was designed to determine the  $\pi \rightarrow \pi^*$  valence excited states. A series of CASSCF/CASPT2 calcula-

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**Table 1.** Population Analysis for Uracil in Its Ground State<sup>a</sup> (Atoms are labeled according to Figure 1)

	atom											
	O <sub>1</sub>	O <sub>2</sub>	N <sub>1</sub>	N <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>
	Gross Atomic Populations											
s-type	1.78	1.80	1.62	1.51	1.04	1.14	1.19	1.08	0.38	0.42	0.62	0.63
p-type	4.62	4.58	4.01	4.06	2.01	2.01	3.13	2.85				
d-type	0.04	0.04	0.07	0.08	0.40	0.35	0.12	0.19				
	$\pi$ Populations											
	1.44	1.38	1.65	1.68	0.88	0.86	1.10	0.99				
	Total Charges											
	-0.44	-0.42	-0.71	-0.66	+0.54	+0.40	-0.45	-0.12	+0.62	+0.58	+0.38	+0.37

<sup>a</sup> 0.1 electrons are located in Rydberg-type orbitals and are not included.

tions were performed with all 10  $\pi$ -electrons active and with an increasing number of active  $\pi$ -orbitals. This procedure was followed in order to study the convergence in computed properties with an increasing active space. For uracil, the final results are obtained with an active space including 12 orbitals. For thymine, two more diffuse orbitals of  $\sigma^*$ -type appear with large occupation numbers in the CASPT2 wave function. They have also been deleted in order to avoid intruder state problems. The alternative, to include them in the active space, is not feasible.

The four lowest  $n \rightarrow \pi^*$  transitions (<sup>1</sup>A'') were computed with an active space including the eight  $\pi$ -orbitals and the two oxygen  $\sigma$  lone pair orbitals with 12 active electrons (eight  $\pi$  and four  $\sigma$ , leaving two  $\pi$ -electrons inactive). All Rydberg orbitals were again deleted.

It is only the energy which is computed at the CASPT2 level. All other properties, including the transition moments, have been calculated using CASSCF wave functions. The CAS state interaction (CASSI) method has been used to compute transition properties.<sup>16</sup> Intensities were obtained by combining the CASSCF transition moments with CASPT2-evaluated excitation energies, a method which in a number of previous applications has proven to give accurate results.<sup>14</sup> However, even if the size of the transition moment vector is not much affected by dynamical correlation effects, the direction is more sensitive, in particular for weak transitions where two or more configurations interact strongly in the excited state. A small change in the relative energy of the two configurations may in such cases lead to appreciable changes in the directions. The study of the transition moments as a function of the size of the active space is therefore important, since this gives an indication of how sensitive the direction is to the level of treatment for a given excitation. All calculations have been performed with the MOLCAS-2<sup>17</sup> quantum chemistry software on IBM RS/6000 workstations.

## Results and Discussion

Before discussing the different excited states for uracil and thymine, we would like to present some data for the ground state. The population analysis for uracil is presented in Table 1. We should remind the reader that such data are somewhat arbitrary and depend strongly on the basis sets used. Not much significance should, for example, be attached to the partitioning of charge between a hydrogen and its neighboring atom. However, a few features are worth noting. One is the large 3d population in the carboxyl carbon atoms. Similar populations have also been found in other CO bonds, like formaldehyde

**Table 2.** Singlet  $\pi \rightarrow \pi^*$  Excited States of Uracil: Excitation Energies/Transition Moment Angles ( $\Delta E/\Theta$ ) with Different Active Spaces<sup>a</sup>

state	active orbitals			
	0,8	0,10	0,11	0,12
2 <sup>1</sup> A'	4.96/-2 (0.69)	4.91/-8 (0.69)	4.97/-7 (0.69)	5.00/-7 (0.69)
3 <sup>1</sup> A'	5.52/-69 (0.67)	5.77/-31 (0.70)	5.78/-31 (0.71)	5.81/-29 (0.71)
4 <sup>1</sup> A'	5.79/79 (0.12)	6.06/32 (0.15)	6.56/11 (0.69)	6.46/24 (0.68)
5 <sup>1</sup> A'	6.94/-27 (0.31)	6.98/-39 (0.69)	6.92/-46 (0.70)	7.01/-42 (0.70)

<sup>a</sup> CASPT2 excitation energies in eV. CASSCF reference weights in parentheses.

and acetone, and seem to be a consequence of the large positive charge on the carbon atom. The calculated dipole moments for uracil and thymine are 4.4 and 5.0 D, respectively. Values for the quadrupole moments are given in Tables 5 and 6.

The strong polarity of the CO bonds makes it possible to think of the  $\pi$ -system as consisting of two oxygen lone pairs and an aromatic pyrimidine ring with six  $\pi$ -electrons. This picture is certainly oversimplified, since the population analysis shows that the effective number of  $\pi$ -electrons in the ring is seven rather than six. Some of the spectroscopic properties are, however, surprisingly similar to those of the pyrimidine molecule (*vide infra*).

**The  $\pi \rightarrow \pi^*$  States.** The results obtained for the singlet states of A' symmetry in uracil are presented in Table 2. The calculations were performed with 8, 10, 11 and 12 active  $\pi$ -orbitals. These calculations make it possible to study how the computed properties vary with the active space. The larger the CAS space, the smaller the fraction of the correlation energy which is computed using perturbation theory. The CAS orbitals are optimized and define the most important natural orbitals in the system. Increasing the number of such natural orbitals makes the second-order approximation for the remaining correlation energy less severe.

Inspection of the excitation energies given in Table 2 shows that the first, second, and fourth excited states are stable with respect to the variation of the active space. The variation is less than 0.1 eV (except for 2<sup>1</sup>A' in the smallest active space). We conclude that these three transition energies are well determined by the present perturbative approach. The large number of previous studies performed on similar compounds with the CASPT2 method and basis sets of the same quality gives strong evidence that the computed energies are accurate to at least 0.3 eV. The situation is somewhat more uncertain for the third state. The results obtained with the two smaller active spaces are unreliable, due to the appearance of intruder states in the first-order wave function. The weight of the reference state is only 12% and 15%, respectively. This problem disappears with the larger active spaces. However, the energy changes by 0.1 eV when the active space is increased from 11 to 12 orbitals, which is a little bit much. Neither has the direction of the transition moment vector stabilized. The change

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**Table 3.** Singlet  $\pi \rightarrow \pi^*$  Excited States of Thymine: Excitation Energies/Transition Moment Angles ( $\Delta E/\Theta$ ) with Different Active Spaces and Delete Options<sup>a</sup>

state	active/deleted orbitals							
	0,8/6,3	0,10/6,3	0,11/6,3	0,8/7,3	0,10/7,3	0,11/7,3	0,11/8,3	0,12/8,3
2 <sup>1</sup> A'	4.63/8 (0.66)	4.80/16 (0.66)	4.80/16 (0.65)	4.63/8 (0.66)	4.80/16 (0.66)	4.84/16 (0.65)	4.88/16 (0.66)	4.85/15 (0.66)
3 <sup>1</sup> A'	5.70/-25 (0.49)	5.81/-19 (0.68)	5.82/-19 (0.68)	5.70/-25 (0.45)	5.84/-19 (0.68)	5.85/-19 (0.68)	5.88/-19 (0.68)	5.85/-19 (0.69)
4 <sup>1</sup> A'	5.86/76 (0.43)	5.91/74 (0.35)	6.02/64 (0.39)	5.86/76 (0.43)	5.93/74 (0.35)	6.16/64 (0.13)	6.10/64 (0.60)	6.09/67 (0.60)
5 <sup>1</sup> A'	7.02/-30 (0.28)	6.97/-33 (0.23)	6.94/-35 (0.06)	7.02/-30 (0.29)	6.97/-33 (0.67)	7.04/35 (0.67)	7.13/-35 (0.67)	7.10/-35 (0.67)

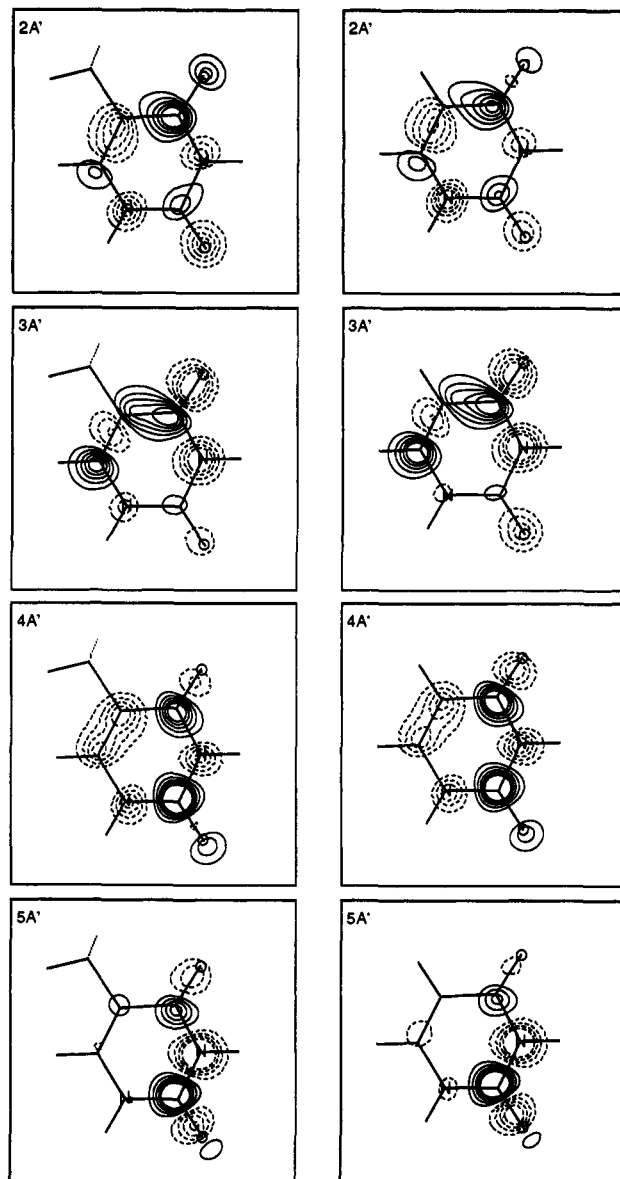
<sup>a</sup> CASPT2 excitation energies in eV. CASSCF reference weights in parentheses.

in the last step is 13°. The angle is more stable for the other states. We conclude that the third state has been determined somewhat less precisely, with an estimated maximum error in the transition energy of  $\pm 0.4$  eV. The uncertainty in the angle is more difficult to estimate. It is strikingly different from thymine (24° compared to 67°). In order to investigate this in more detail, we performed CASSI calculations, where 12 different CASSCF wave functions were allowed to mix, which had been obtained in different state average calculations. The energies obtained were very similar to the CASSCF results reported in Table 2. The transition moment angles for the four lowest states were -2°, -24°, 62°, and -32°. These values are again similar to the five state average results, except for the third state. The CASSI results are based on a more exact density and should be more accurate. It is also more similar to the thymine value as one would expect. However, these calculations show that the energy for the third state and to a larger extent the transition moment angle strongly depend on the level of theory used, and the present results cannot be considered as converged.

The results obtained for thymine (cf. Table 3) are very similar. Here it was, however, necessary to delete two more virtual orbitals (of  $\sigma^*$ -type) in order to avoid all intruder state problems. These intruder states appear for the third and fourth states and give rise to low reference weights. The effect on the transition energies is, however, small, and we estimate the maximum error to be  $\pm 0.3$  eV for all four states in thymine. Here too, the third state is somewhat less stable and exhibits larger variations in the transition angle.

The similarity between the transition in uracil and thymine is illustrated in Figure 2, which shows plots of the electron density difference between the ground state and the excited state ( $\rho_0 - \rho_i$  for the  $i$ th state). The plot is made 1.0 au above the molecular plane. The first transition takes place in the pyrimidine ring. The corresponding state in pyrimidine itself (<sup>1</sup>B<sub>2</sub>) appears 5.1 eV above the ground state. The computed CASPT2 value is 4.93 eV.<sup>18</sup> The intensity is low, and the direction of the transition moment is perpendicular to the C<sub>2v</sub> axis, corresponding to an angle of about +30°. This is different from uracil and thymine, where the angle is -7° and +15°, respectively. It is also clear from the figure that the charge migration in these molecules is not entirely symmetric with respect to the two nitrogen atoms.

The next transition involves more of the CO  $\pi$ -bond with charge transfer into the ring and is therefore unique to uracil and thymine. The third excited state is again almost completely localized to the ring. The computed energy is 6.46 eV. Experimentally, the transition in pyrimidine to the 2<sup>1</sup>A<sub>1</sub> state occurs at 6.7 eV with an intensity of about 0.1. The corresponding CASSCF/CASPT2 results are 6.72 eV and 0.05.<sup>18</sup> The transition moment angle in pyrimidine is -60°, which is different from the angles found in uracil and thymine. It is



**Figure 2.** Electron density differences between the ground state and each of the four  $\pi \rightarrow \pi^*$  excited states. The plot is made 1.0 au above the molecular plane, uracil to the left, thymine to the right. Dotted lines: large density in the ground state. Solid lines: larger density in the excited state.

clear that the moment directions are more perturbed than other properties.

The fourth and last of the studied  $\pi \rightarrow \pi^*$  excited states involves charge migration in the region of the two CO units and the connecting nitrogen. Here, the excitation is best characterized as CO  $\pi \rightarrow \pi^*$  combined with charge transfer from the nitrogen atom to the carbon atom of the CO units. This is the most intense transition. The moment is directed approximately along the line connecting the two oxygen atoms.

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**Table 4.** Singlet  $n \rightarrow \pi^*$  Excited States of Uracil and Thymine: Excitation Energies ( $\Delta E$ ) with Different Active Spaces<sup>a</sup>

state	active orbitals		
	2,8	2,9	2,10
	Uracil		
1 <sup>1</sup> A''	4.80 (0.73)	4.54 (0.73)	4.54 (0.73)
2 <sup>1</sup> A''	6.20 (0.72)	6.01 (0.73)	6.00 (0.70)
3 <sup>1</sup> A''	6.70 (0.04)	6.38 (0.68)	6.37 (0.61)
4 <sup>1</sup> A''	6.29 (0.47)	7.27 (0.17)	6.95 (0.71)
	Thymine		
1 <sup>1</sup> A''	4.41 (0.70)		4.39 (0.71)
2 <sup>1</sup> A''	5.87 (0.70)		5.91 (0.71)
3 <sup>1</sup> A''	6.01 (0.61)		6.15 (0.66)
4 <sup>1</sup> A''	6.78 (0.61)		6.70 (0.63)

<sup>a</sup> CASPT2 excitation energies in eV. CASSCF reference weights in parentheses.

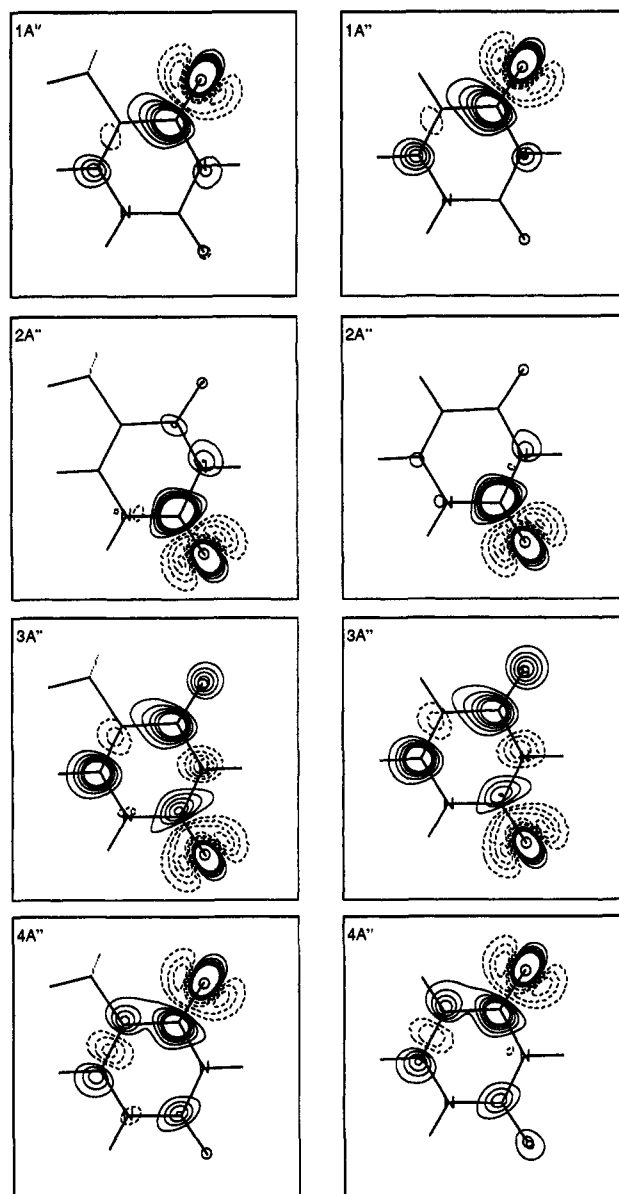
Inspection of the molecular orbitals also show that the main orbital occupied by the excitation is an out of phase combination of the CO  $\pi^*$ -orbitals.

It might be argued that the comparison made above between the excited states of the uracil thymine pair and pyrimidine is not valid since pyrimidine is an aromatic system with six  $\pi$ -electrons while uracil has 10. This is certainly a valid argument. However, as pointed out above, the difference between the two systems may not be as large as one might expect. The population analysis shows that the CO bonds are strongly polarized toward oxygen. One interpretation would then be that the CO  $\pi$ -electrons are localized on the oxygen atoms, leaving six electrons on the ring. The parallel to pyrimidine is then clear. See, however, the discussion in ref 19.

**The  $n \rightarrow \pi^*$  States.** The four lowest  $n \rightarrow \pi^*$  states have also been computed. They correspond to excitations out of the two oxygen lone pair orbitals (in plane  $\pi$ ) to the two lowest empty  $\pi$ -orbitals. Here too, the convergence of the results was studied as a function of the number of active  $\pi$ -orbitals. The results for uracil and thymine are presented in Table 4. For uracil, the calculation with eight active  $\pi$ -orbitals leads to intruder state problems for the two upper states. Increasing the active space with one orbital stabilizes the three first states, and their energies remain the same when the active space is further increased to 10  $\pi$ -orbitals. However, the fourth state is still affected to some extent by intruder states as can be seen from the relative low weight of the reference configuration. For economical reasons, the calculations on thymine were only performed with the 8 and 10 active spaces. No intruder states appear with the eight active spaces, and the excitation energies are stable.

A plot of the electron density difference between the ground and  $n \rightarrow \pi^*$  excited states is shown in Figure 3. The plot is made 1 au above the molecular plane in order to show the effect in both the  $\sigma$ - and  $\pi$ -orbital spaces. The two lowest excited states are almost entirely localized to the CO groups. The excitation is from the in-plane oxygen lone pair orbital to the antibonding CO  $\pi$ -orbital. None of the  $\pi \rightarrow \pi^*$  excitations are so localized, which shows that the  $\pi^*$ -orbitals that describe the  $n \rightarrow \pi^*$  excitations are different from those describing the  $\pi \rightarrow \pi^*$  excited states. The two higher  $n \rightarrow \pi^*$  states have the excited electron more delocalized. The difference in energy between the two lowest excited states (4.5 and 6.0 eV, respectively, in uracil) shows that the two CO bonds are not equivalent.

**Comparison between Uracil and Thymine.** The final results are presented in Tables 5 and 6, which give the excitation



**Figure 3.** Electron density differences between the ground state and each of the four  $n \rightarrow \pi^*$  excited states. The plot is made 1.0 au above the molecular plane, uracil to the left, thymine to the right. Dotted lines: large density in the ground state. Solid lines: larger density in the excited state.

energies, the transition moment directions, the oscillator strengths, and the dipole moments of the ground and excited states. The differential dynamic correlation contribution to the excitation energies is large, 1.2–2.2 eV, for the  $\pi \rightarrow \pi^*$  excited states. The weights,  $\omega$ , of the reference function in the first-order perturbed wave function ranges from 0.68 to 0.71 for uracil and from 0.60 to 0.68 for thymine. Thus, the calculations are well balanced (with some uncertainty for the 4<sup>1</sup>A' state). Somewhat lower weights are obtained for thymine, since more electrons are correlated. The effect of dynamic correlation on the  $n \rightarrow \pi^*$  excitation energies is somewhat smaller, especially for the two first transitions.

By comparing the results presented in Tables 5 and 6, we note that the transition energies are similar for both molecules. There is not a unique shift in all  $\pi \rightarrow \pi^*$  excitation energies between uracil and thymine. Two of the states undergo a red shift while the other two are slightly blue-shifted. There is a complete correlation between these energy shifts and the shift of the dipole moment between the ground and excited states. A

**Table 5.** Singlet Excited States of Uracil: Excitation Energies ( $\Delta E$ , eV), Oscillator Strengths ( $f$ ), Transition Directions ( $\Theta$ ), and Dipole Moments ( $\mu$ , D) Computed at the CASSCF/CASPT2 Level of Approximation

state	$\Delta E$		$f$	$\Theta$	$\mu$
	CASSCF	CASPT2			
$\pi \rightarrow \pi^*$ Transitions					
1 <sup>1</sup> A'					4.4 <sup>a</sup>
2 <sup>1</sup> A'	6.88	5.00 (0.69)	0.19	-7 (-2) <sup>b</sup>	6.3
3 <sup>1</sup> A'	7.03	5.82 (0.71)	0.08	-29 (-24) <sup>b</sup>	2.4
4 <sup>1</sup> A'	8.35	6.46 (0.68)	0.29	23 (62) <sup>b</sup>	6.9
5 <sup>1</sup> A'	8.47	7.00 (0.70)	0.76	-42 (-32) <sup>b</sup>	3.7
$n \rightarrow \pi^*$ Transitions					
1 <sup>1</sup> A''	4.78	4.54 (0.73)	$0.18 \times 10^{-3}$		3.4
2 <sup>1</sup> A''	6.31	6.00 (0.73)	$0.38 \times 10^{-6}$		4.8
3 <sup>1</sup> A''	7.80	6.37 (0.67)	$0.71 \times 10^{-4}$		8.7
4 <sup>1</sup> A''	7.88	6.95 (0.55)	$0.81 \times 10^{-4}$		3.6

<sup>a</sup> Ground state quadrupole moment:  $Q_{xx} = 14.8$ ,  $Q_{yy} = -15.2$ , and  $Q_{zz} = 0.4 \times 10^{-26}$  esu cm<sup>2</sup>. <sup>b</sup> Values in parentheses have been obtained with the CASSI method (see text for further explanation).

**Table 6.** Singlet Excited States of Thymine: Excitation Energies ( $\Delta E$ , eV), Oscillator Strengths ( $f$ ), Transition Directions ( $\Theta$ ), and Dipole Moments ( $\mu$ , D) Computed at the CASSCF/CASPT2 Level of Approximation

state	$\Delta E$		$f$	$\Theta$	$\mu$
	CASSCF	CASPT2			
$\pi \rightarrow \pi^*$ Transitions					
1 <sup>1</sup> A'					5.0 <sup>a</sup>
2 <sup>1</sup> A'	6.75	4.88 (0.66)	0.17	15	6.5
3 <sup>1</sup> A'	7.15	5.88 (0.68)	0.17	-19	1.5
4 <sup>1</sup> A'	8.33	6.10 (0.60)	0.15	67	7.8
5 <sup>1</sup> A'	8.62	7.13 (0.67)	0.85	-35	3.1
$n \rightarrow \pi^*$ Transitions					
1 <sup>1</sup> A''	5.22	4.39 (0.71)	$0.19 \times 10^{-3}$		3.2
2 <sup>1</sup> A''	6.77	5.91 (0.71)	$0.13 \times 10^{-4}$		4.6
3 <sup>1</sup> A''	8.14	6.15 (0.66)	$0.84 \times 10^{-4}$		8.6
4 <sup>1</sup> A''	8.41	6.70 (0.63)	$0.91 \times 10^{-3}$		4.1

<sup>a</sup> Ground state quadrupole moment:  $Q_{xx} = 11.6$ ,  $Q_{yy} = -13.6$ ,  $Q_{zz} = 2.1 \times 10^{-26}$  esu cm<sup>2</sup>.

larger dipole moment in the excited states yields a red shift and vice versa. The dipole of the ring interacts with the polarizable methyl group, and it is the relative strength of this interaction that determines the shift. In this sense, the energy shift between thymine and uracil will mimic the solvent shifts of the corresponding transitions.

The computed oscillator strengths show the existence, in both molecules, of three weak transitions followed by one strong transition. The transition directions in thymine are rotated by 5–20° relative to those in uracil in accord with the experimental estimate of 20°. It should be noted, however, that the transition direction for the 4<sup>1</sup>A' state in uracil is very sensitive to the level of theory. The result reported in Table 5 was obtained using the CASSI method together with several CASSCF wave functions. It is thus not directly comparable to the other results. The large fluctuation of the angle may be explained, as pointed out in the previous paragraph, by the convergence problems encountered for this state in uracil. The cause of the problem is most probably the near degeneracy effects between roots 4<sup>1</sup>A' and 5<sup>1</sup>A', which in uracil are separated by only 0.12 eV at the CASSCF level of approximation.

The  $n \rightarrow \pi^*$  transitions are all weak with oscillator strengths in the range  $10^{-6}$ – $10^{-3}$ . They appear at almost the same energies in both molecules. There is not such a direct relation

with the change in dipole moment and energy shift as was found for the  $\pi \rightarrow \pi^*$  states. Partly, this is due to rather small variations in the dipole moments, which make higher order corrections more important. An exception is the state 3<sup>1</sup>A'', which has a very large dipole moment. There is also a red shift of 0.22 eV for this transition.

**Comparison with Experiment.** The results obtained in the present study are for an isolated molecule. The most direct way to compare with experiment would therefore be to use gas phase absorption spectroscopy. Vapor spectra for some purine and pyrimidine bases were recorded by Clark *et al.* in 1965.<sup>21</sup> Experimental results obtained for uracil and thymine (in some cases 1-methyluracil and 1-methylthymine or uridine and thymidine where the sugar backbone is present) are presented in Tables 7 and 8. The spectrum for uracil shows two maxima and one shoulder in the energy range below 6.7 eV. The location corresponds closely to the three lowest  $\pi \rightarrow \pi^*$  excited states studied here. For thymine there are actually two shoulders in the region between the two maxima. A possible interpretation is then that two of the states are located in this region and that the spectrum exhibits four excited states. Such an interpretation would confirm the large red shift obtained between uracil and thymine for transition III. The red shift in transition I is also confirmed.

The absorption spectra in solution show three broad and unstructured maxima in the energy range up to 7.0 eV (177 nm).<sup>21–23</sup> It is generally believed that the second band contains two  $\pi \rightarrow \pi^*$  transitions, and this is confirmed by the present results and the circular dichroism (CD) spectra (*vide infra*). The first band is red-shifted in solution. The composite nature of the second band makes a corresponding analysis impossible. The solvent shift of the fourth band seems to be small. Sublimed film measurements give similar results.<sup>24</sup> We conclude that the absorption spectroscopy of uracil and thymine is in agreement with the theoretical results both qualitatively and quantitatively. The deviations from experimental transition energies are *ca.* 0.2 eV. So far, there is no evidence of any  $n \rightarrow \pi^*$  transitions.

The CD and MCD spectra have a more complicated structure and actually show that the first and second bands are composite. Both are resolved into two electronic transitions. The individual transitions in the second band occur at *ca.* 6.0 and 6.5 eV in both molecules (for details, see Tables 7 and 8). The energy shifts between uracil and thymine discussed above are thus not resolved in the CD spectra, but the occurrence of four  $\pi \rightarrow \pi^*$  transitions is confirmed.

The resolution of the first absorption band into two CD bands is more problematic, and different interpretations are available in the literature. The two transition energies obtained in the CD spectra are 4.6–4.8 and 4.9–5.2 eV for uridine and 4.5–4.6 and 5.0–5.1 eV for thymidine. Up to now all theoretical calculations, including the present, predict a large gap,  $\approx 0.8$  eV, between the first and second  $\pi \rightarrow \pi^*$  transitions, and one does not expect to find two such states in the region around 5 eV. Most spectra have been recorded for uridine and thymidine, but the effect of the sugar backbone on the transition energies seems to be small.<sup>25</sup> We shall therefore assume that the spectra recorded will reflect the situation for the bare compounds. The

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**Table 7.** Singlet  $\pi \rightarrow \pi^*$  Excited States of Uracil: Excitation Energies (eV), Oscillator Strengths or Extinction Coefficients (in parentheses), and Transition Moment Directions (deg)

	transition				ref
	I	II	III	IV	
$\Delta E$	5.0 (0.19)	Theory 5.8 (0.08)	6.5 (0.29)	7.0 (0.76)	this work
		Absorption Spectra			
Gas Phase	5.1	6.0	6.6		21
in TMP	4.8 (7800)	6.1 (8200)		6.9 (11 800)	21, 22
in H <sub>2</sub> O	4.8 (8100)	6.1 (8800)		6.9 (15 500)	21, 23
sublimed film	4.7	6.1		7.0	24
	Polarized Reflection Spectra of Single Crystals of 1-Methyluracil				
	4.5	5.8			20, 32
	Circular Dichroism Spectra of Uridine <sup>a</sup>				
	4.6	5.9	6.5		26
	4.8	6.1			25
	4.6	5.8	6.3		33
	4.7	5.8	6.3		34
	4.6	5.8	6.4	7.0	27
	Transition Moment Angles <sup>c</sup>				
theory <sup>d</sup>	-2	-24	+62	-32	this work
	0 or +7				32 <sup>e</sup>
	-11 or +7				35 <sup>b</sup>
	-9 or +16	-53 or +59			20 <sup>e</sup>

<sup>a</sup> The band occurring at 4.9–5.2 eV is classified as  $n \rightarrow \pi^*$  and is not included. <sup>b</sup> Uracil. <sup>c</sup> For the definition of the angle, see Figure 1. <sup>d</sup> From the extended CASSI calculations. <sup>e</sup> 1-Methyluracil.

**Table 8.** Singlet  $\pi \rightarrow \pi^*$  Excited States of Thymine: Excitation Energies (eV), Oscillator Strengths or Extinction Coefficients (in parentheses), and Transition Moment Directions (deg)

	transition				ref
	I	II	III	IV	
$\Delta E$	4.9 (0.17)	Theory 5.9 (0.17)	6.1 (0.15)	7.1 (0.85)	this work
		Absorption Spectra			
gas phase	4.8	5.7	6.2	> 6.7	21 <sup>a</sup>
in TMP	4.7 (7000)	6.1 (6500)		6.8 (14 100)	21, 22
in H <sub>2</sub> O	4.7	6.1		6.6	21, 23
sublimed film	4.6	5.9		7.0	24
	Polarized Reflection Spectra of Single Crystals of Thymine				
	4.5	5.8			20, 36
	Circular Dichroism Spectra of Thymidine <sup>b</sup>				
	4.6	5.9	6.5		26
	4.6	6.1			25 <sup>c</sup>
	4.6	5.8	6.3		33
	4.6	5.9	6.4		34
	4.5	5.8	6.5	7.0	27
	Transition Moment Angles				
theory	+15	-19	+67	-35	this work
	-19				32 <sup>d</sup>
	-31 or +51				35 <sup>c</sup>
	-12 or +70	-31 or +91			20 <sup>e</sup>
	-20				20 <sup>d</sup>

<sup>a</sup> 1,3-Dimethyluracil. <sup>b</sup> The band occurring at 4.9–5.2 eV is classified as  $n \rightarrow \pi^*$  and is not included. <sup>c</sup> Thymine. <sup>d</sup> 1-Methylthymine.

first CD spectrum was recorded by Miles *et al.*<sup>26</sup> who interpreted the four first transitions in uridine and thymidine as  $\pi \rightarrow \pi^*$  and related them to the benzene spectrum. This analogy has also been used in later work. As was discussed in a previous section of this work, such an analogy is not valid, due to the strong involvement of the CO  $\pi$ -electrons in some of the excited states.

It is generally agreed that the first band corresponds to a  $\pi \rightarrow \pi^*$  transition. Considering the solvent shift, such an assignment is in agreement with the present results. Most authors agree with Miles *et al.*<sup>26</sup> that the second state has the

same character. Sprecher and Johnson<sup>27</sup> suggest, however, that an  $n \rightarrow \pi^*$  transition might be responsible for this feature in the spectrum. Novros and Clark<sup>20</sup> observed a small out-of-plane component in the polarized absorption spectrum of 1-methyluracil crystals at 4.7 eV, which might point in the same direction. Such an assignment would locate the  $n \rightarrow \pi^*$  transition at *ca.* 5 eV, which is 0.5 eV above the energy predicted here (cf. Tables 5 and 6). The present study suggests that the first excited state is  $n \rightarrow \pi^*$  and the second  $\pi \rightarrow \pi^*$ . However, that is a gas phase result. For the  $\pi \rightarrow \pi^*$  state, we expect a red shift in solution, but for the  $n \rightarrow \pi^*$  state, we expect a considerable blue shift, since the excitation will break the hydrogen bonds

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around the oxygen atom. A recent theoretical study of the  $n \rightarrow \pi^*$  transitions in hydrogen-bonded formaldehyde complexes shows that with two bonded water molecules a blue shift of 0.3 eV is obtained.<sup>28</sup> Thus we expect to find this transition around 4.8 eV in uracil and 4.7 eV in thymine. The experimental CD energies vary between 4.9 and 5.1 eV for uracil and are close to 5.0 eV for thymine. This is in good agreement as we can expect. If we assume that the higher  $n \rightarrow \pi^*$  states are also blue-shifted, they will fall under the intense  $\pi \rightarrow \pi^*$  transitions in the second and third absorption band and will therefore not be seen in the spectrum.

Polarized absorption and reflection experiments on uracil and its derivatives found the polarization angle for the first transition to be close to zero (parallel to the  $C_4-N_1$  axis, cf. Figure 1). The computed value  $-2^\circ$  is in accord with the experimental data at hand. Since the error in the computed polarization angles is typically *ca.*  $15^\circ$ , we cannot draw firm conclusions about the sign of the angle. Novros and Clark<sup>20</sup> also succeeded in measuring the polarization angle of the second  $\pi \rightarrow \pi^*$  transition,  $-53^\circ$  or  $+59^\circ$ , in crystals of 1-methyluracil. The computed angle  $-24^\circ$  clearly favors the first choice. Novros and Clark suggest, however, the large positive angle, since choice is more consistent with the results obtained by Matsuoka and Nordén. It might be noted that Anex *et al.* in an earlier study gave the angle  $-31^\circ$ , which is close to the present value. Substitution effects may affect the angle somewhat, but as we have already pointed out, there is a large uncertainty in the computed values, since we have not included the effects of the crystal field.

There seems to be general agreement that the angle for the first transition in thymine is negative with a value varying between  $-12^\circ$  and  $-31^\circ$ . This is not in agreement with the present result, which gives  $+15^\circ$ . We have no explanation for this discrepancy. Novros and Clark give arguments that suggest that the angle for the second transition in thymine is  $-31^\circ$  or  $+47^\circ$ . The computed value is  $-19^\circ$ , which would favor the first choice. It is generally accepted knowledge that the polarization direction of the energetically lowest electronic transitions in thymine is rotated by  $\approx 20^\circ$  relative to uracil. The computed change,  $17^\circ$ , is in accord with experiment, and also the absolute direction,  $15^\circ$ , is in agreement with the angles reported by Steward and Davidson<sup>29</sup> and Fucaloro and Forster.<sup>30</sup>

**Comparison with Earlier Calculations.** The comparison will be focused on the works of Fülischer *et al.*<sup>3</sup> and Petke *et al.*<sup>31</sup> The reason is that these calculations give a good picture of the behavior of *ab initio* calculations. For more details about earlier semiempirical work, we refer to the review of Callis.<sup>19</sup> The general feature of the previous studies is the lack of  $\sigma-\pi^*$  correlation effects in the wave functions, which leads to errors of 1–2 eV even at the MRCI level with only  $\pi$ -orbitals in the active space.

The spectra obtained at the CASSCF level correlates well with corresponding results obtained by Fülischer *et al.* The only mismatches are in the properties of the fourth state of uracil, which has proven to be problematic to describe properly at the CASSCF level due to near-degeneracies. If one makes averages with different weights and roots and then allows all these wave functions to mix in a RASSI calculation, the properties will be in agreement with those obtained for thymine.

The need for a proper treatment of the Rydberg states is clear from previous studies using the CASPT2 method. The lack of

adequate basis functions to describe the Rydberg states will lead to an artificial mixing with valence excited states and also give rise to a number of intruder states arising from excitations of a quasi-Rydberg character. Petke *et al.* have performed multi-reference (MR) CI and random phase (RPA) calculations for uracil and cytosine, with a basis set of DZP quality with added diffuse  $\pi$ -type basis functions.<sup>31</sup> Their MRCI results yield 10  $^1A'$  states in the energy range 6–10 eV. However, only two of them can be characterized as true valence excitations (at 6.28 and 7.27 eV). The remaining states are Rydberg-like or mixtures of Rydberg and valence excited states. This behavior is certainly more a result of the chosen basis set and correlation treatment than a correct description of the interaction between the valence and Rydberg excited states. The large errors in computed energies (1–2 eV) made a comparison with the experimental spectrum difficult. However, by using the computed intensities in the assignment and scaling down the energies by 1–3 eV, it was possible to identify four  $\pi \rightarrow \pi^*$  excitations in the energy interval below 7.0 eV. The RPA method gives results of similar quality as the MRCI approach.

**Comparison with Cytosine.** The substitution of one carbonyl group with an amino group can be expected to have a profound effect on the electronic structure both in the ground state and in the excited state. There are also considerable differences in the spectroscopic properties. The excited states of cytosine have recently been studied by using the same approach as has been used in the present study.<sup>4</sup> Four excited  $\pi \rightarrow \pi^*$  states were found in the region below 7.0 eV, but here the third state was the most intense. The transition energy was found to be 6.2 eV, which is about 1 eV less than the energy for the most intense transition in uracil and thymine. Also the other transition energies are lower in cytosine. The first transition occurs at 4.4 eV, which is 0.6 eV lower than in uracil. In uracil and thymine, the first and third transitions were found to involve mainly electrons in the pyrimidine ring systems. They should therefore not be so much affected by the substitution of one of the carbonyl groups. In cytosine the corresponding transitions are I and IV. Transition IV in cytosine is shifted 0.3 eV up compared to the third transition in uracil. The intensities are similar. The first  $n \rightarrow \pi^*$  transition in cytosine is found at 5.0 eV, which is 0.5 eV higher than in uracil.

## Summary

Theoretical studies have been performed for the properties of the lower valence excited states in the free molecules uracil and thymine. The CASSCF/CASPT2 method was used in combination with high-quality basis sets which were extended to describe Rydberg orbitals. Computed excitation energies have errors which are not larger than 0.3 eV (with the possible exception of the third excited  $\pi \rightarrow \pi^*$  state in uracil).

Combining the present results with those reported previously for cytosine leads to a single consistent picture for the spectroscopy of the pyrimidine nucleotides. Specifically, we predict four  $\pi \rightarrow \pi^*$  singlet excited states with transition energies smaller than 7.0 eV. The calculated transition energies are in agreement with measured energies, taking into account expected solvent shifts. The comparison of the computed transition moment directions with experiment is less straightforward. Partly, this is due to large environmental effects and

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partly to difficulties in the theoretical treatment, especially for the third excited state. Comparing uracil and thymine shows that the effect of the methyl group is to act as a polarizability, which interacts with the dipole of the ring system. The computed energy shift is directly proportional to the change in the dipole moment between the ground and excited states.

The  $n \rightarrow \pi^*$  transition lowest in energy is found to be close in energy to the first  $\pi \rightarrow \pi^*$  transition at energies near to 4.5 eV. As a consequence, the low-energy features observed in

CD spectroscopy at  $\approx 5.0$  eV can be attributed to such a transition. The difference to the computed value is due to a solvent blue shift.

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